

ABSTRACT

“Synthesis and Coordination Studies of [(diphenylphosphino)methyl]pyridine Coordination Compounds”

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The coordination properties of the bifunctional ligand 2-[(diphenylphosphino)methyl]pyridine, its two corresponding oxides, and the ligand 4-[(diphenylphosphino)methyl]pyridine towards different transition metal salts are described. The ligand 2-[(diphenylphosphino)methyl]pyridine and both of its oxide derivatives, *P* oxide and *N,P* dioxide, showed preference to behave in a chelating mode, although bridging behavior was also observed in a few cases such as when silver was the metal center involved. Unusual polymeric structures were obtained demonstrating the functionality of these ligands in the multidimensional network construction. Due to opposite positioning of its donor centers, the ligand 4-[(diphenylphosphino)methyl]pyridine showed an inclination to behave as a bridge, usually in a head-to-tail fashion, rather than as a chelate. The crystal structures were determined by single-crystal X-ray crystallography. With the use of this technique several supramolecular interactions were identified. It was demonstrated that, even though these interactions are rather weak, they play an important role in the control of the overall

structure of the molecular array. The anion present and the solvent system used to grow the crystals studied herein were variables with heavy influence in the resulting molecular structures. The synthesized novel complexes were fully characterized by elemental analysis, UV-visible spectroscopy, FT-IR spectroscopy and multinuclear NMR spectroscopy, where the technique was appropriate.

Synthesis and Characterization of (diphenylphosphino)methylpyridine
Coordination Compounds

by

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A Dissertation

Approved by the Department of Chemistry and Biochemistry

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Submitted to the Graduate Faculty of
Baylor University in Partial Fulfillment of the
Requirements for the Degree
of
Doctor of Philosophy

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May 2013

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LIST OF ABBREVIATIONS

General Abbreviations and Symbols

M	Metal
L	Ligand
R	H, alkyl, aryl
JT	Jahn Teller
Hg(Tfa) ₂	Mercury trifluoroacetate
Hg(OTf) ₂	Mercury trifluoromethanesulfonate
Hg(SCN) ₂	Mercury thiocyanate
Hg(CN) ₂	Mercury cyanate
Hg(Cl) ₂	Mercury chloride
AgTfa	Silver trifluoroacetate
AgOTf	Silver trifluoromethanesulfonate
AgBF ₄	Silver tetrafluoroborate
Co(BF ₄) ₂ x 6H ₂ O	Cobalt tetrafluoroborate hexahydrate
Ni(BF ₄) ₂ x 6H ₂ O	Nickel tetrafluoroborate hexahydrate
Cu(BF ₄) ₂ x 6H ₂ O	Copper tetrafluoroborate hexahydrate
Zn(BF ₄) ₂ x 6H ₂ O	Zinc tetrafluoroborate hexahydrate
Py	Pyridine
THF	Tetrahydrofuran

Crystallography

$K\alpha$	maxima in the X-ray emission spectrum ($\text{MoK}\alpha 1 = 0.71073 \text{ \AA}$)
λ	monochromated X-ray wavelength taken as weighted average of $K\alpha$ emission.
$\theta, \chi, \varphi, \omega$	angles variable on the X-ray diffraction experiment.
h, k, l	Miller indices: reciprocals of the fractional intercepts which a particular plane makes with a crystallographic axis.
a, b, c	lattice parameter defining unit cell dimensions.
α, β, δ	lattice parameter defining unit cell angles.
D_{calcd}	calculated density.
$F(000)$	total number of electrons per unit cell.
GooF	Goodness-of-fit: error in the weighting scheme that provides an indication of the agreement between observed and calculated structure factors.
$R1$	conventional agreement factor based on refinement of F data.
$wR2$	weighted agreement factor based on refinement of F^2 data.
R_{int}	agreement factor between observed and average intensities.
M	linear absorption coefficient.
V	volume of the unit cell.
Z	number of molecules per unit cell.
$2\theta_{\text{max}}$	maximum value of 2θ collected in a crystallographic experiment.
e.s.d.	estimated standard deviation.

Spectroscopy

NMR	Nuclear Magnetic Resonance
δ	Chemical shift
ppm	Parts per million
J	Coupling constant
Hz	Hertz
MHz	Megahertz
s	Singlet
d	Doublet
dd	Doublet of doublet
t	Triplet
q	Quartet
m	Multiplet
IR-FT	Fourier Transform Infrared

CHAPTER ONE

Introduction

There has been an increased interest in the development of new ligands that can selectively chelate transition metal ions. Their capacity to produce enhanced stability to coordination complexes has attracted a great deal of attention due to the variety of application that this feature offers, these applications being of both industrial and social interest, *e.g.* in the production of chelates of metallic radioisotopes for applications in nuclear medicine^{1,2} as contrast agents for magnetic resonance imaging (MRI),³⁻⁵ catalysts in RNA hydrolysis,⁶ as active agents in radiotherapy,⁷ in the treatment of human diseases related to heavy metal overload,⁸⁻¹³ production of new materials with enhanced physical and chemical properties,¹⁴⁻¹⁸ in homogeneous catalysis,¹⁹⁻²¹ extraction of lanthanide and actinide cations,^{22,23,24} among others.²⁵⁻²⁸

Each application demands chelating agents with very specific characteristics, which can be tuned by changing the electronic and steric properties of these compounds. Although the modification of these two important properties can be carefully planned in order to tailor a ligand with desired characteristics, the prediction of the final product is often difficult due to several factors such as the transition metals involved, the counter-anion present, the solvent where the reaction takes place, etc. Therefore, the design of new chelating ligands and the fundamental study of their coordination behavior toward transition metals are of extreme importance, and despite the efforts many research groups around the world have put into this matter as well as the advances achieved during these past decades, much is still to be done.

Chelating ligands possessing both hard and soft donors are of special interest due to their dynamic ability that provides a potential site for reversible binding of analytes to a transition metal center. This characteristic was first described as hemilabile by Jeffery and Rauchfuss in 1979, while studying ruthenium chelates derived from o-(diphenylphosphino)anisole (Figure 1.1).²⁹

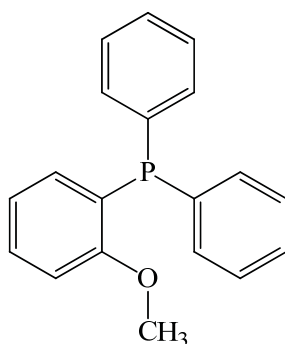
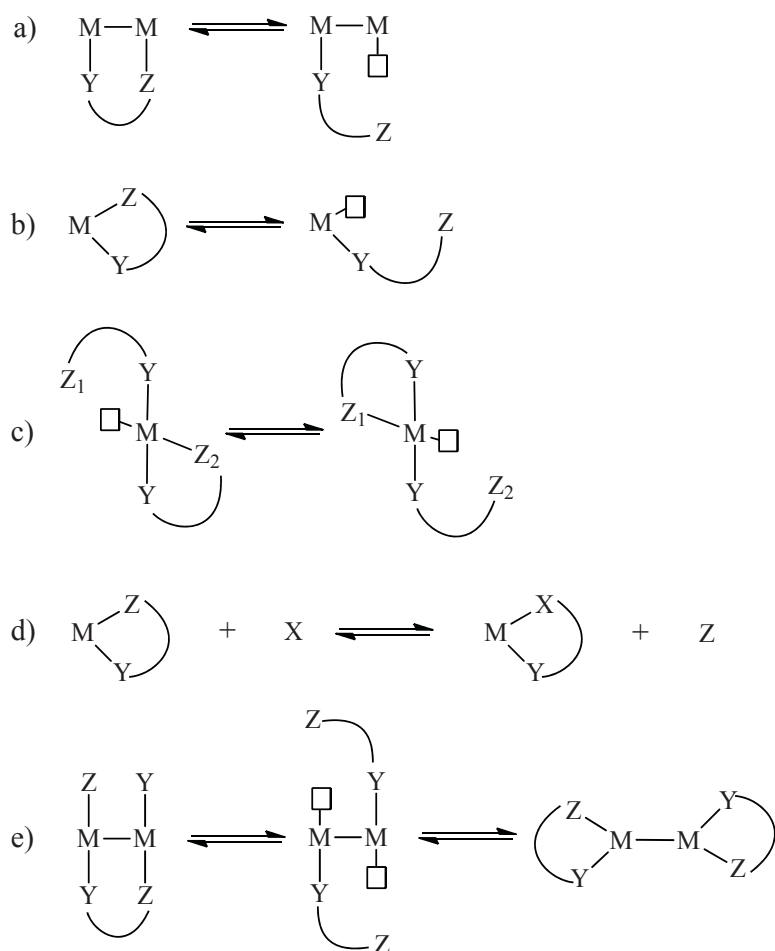


Figure 1.1. First ligand to be termed hemilabile, (investigated by Jeffery and Rauchfuss): o-(diphenylphosphino)anisole, PO.

For a ligand to be considered hemilabile at least one of the donor functionalities, Z, must be labile while the other, Y, must remain inertly bound to the metal center (Scheme 1.1). This concept can be extrapolated to dinuclear complexes and clusters. In these cases, the labile donor Z is not necessarily coordinated to the same metal center as the stronger donor Y is. Instead, it can be coordinated to an adjacent metal center. Thus, the selective breaking of the $Z \rightarrow M$ interaction can take place in different ways depending on several factors such as the introduction of an external ligand or a different metal center, the presence of another ligand coordinated to the metal center, a combination of these, etc. Braunstein suggested the reversibility of the formation/displacement of the $Z \rightarrow \text{metal}$ interaction should also be considered as a criterion before classifying a ligand as hemilabile.³⁰ Some cases of hemilability are illustrated in scheme 1.1.



Scheme1.1. Examples of hemilabile situations ($\square$ represents a vacant coordination site on the metal center).

Inspired by all the possible applications in which hemilabile ligands can be used, many of these compounds have been reported and their coordination properties investigated. A particular example is represented by phosphorus-oxygen based ligands. This group of hybrid ligands includes ether-phosphines, keto-phosphines and ester-phosphines.³¹⁻³³ The presence of soft phosphorus donors and hard oxygen donors makes them potential candidates in catalysis. For example, they have been used in the carbonylation of methanol,³⁴ methyl-oxygen bond cleavage,³⁵ hydroformylation of 1-hexene³⁶, hydrogenation of the α,β -unsaturated ketones and in other catalytic reactions.³⁷

All these reactions have employed a variety of transition metals, including palladium,^{38,39} rhodium⁴⁰⁻⁴² and ruthenium.⁴³ Another common type of P/O ligands are those bearing ketone-carbonyl functionalities.⁴⁴ Complexes of ruthenium containing the ligand Ph₂PCH₂C(O)Ph have shown catalytic activity in the hydrogenation and isomerization of 1-hexene at atmospheric hydrogen pressure (Figure 1.2).³³ Complexes of Ni, Pd and Pt with this ligand have shown to lead to acetophenone and chelating Ph₂PCH=C(Ph)OPPh₂ by thermal cleavage of the P-CH₂ bond.⁴⁵

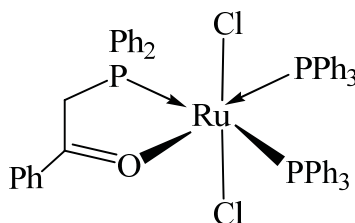


Figure 1.2. *trans,mer*-[RuCl₂{Ph₂PCH₂C(O)Ph}(PPh₃)₂] used by Braunstein in the hydrogenation and isomerization of hex-1-ene at atmospheric hydrogen pressure.

Ligands containing nitrogen and phosphorus donor centers, *N,P* ligands, have been widely studied during the past decades due to their hemilabile character. These mixed ligands have exhibited a high performance in a large array of catalytic transformations. They have been used in hydrogenation reactions yielding great turnover efficiency and selectivity. Chiral iridium complexes of pyridine-aminophosphine ligands have been efficiently used in the asymmetric hydrogenation of β -aryl β -ketoesters with high enantioselectivity and turnover number under mild reaction conditions.⁴⁶ In 2007, Wang synthesized new unsymmetrical hybrid phosphine-aminophosphine ligands which displayed good enantioselectivities in the Rh-catalyzed asymmetric hydrogenation of various α -enol ester phosphonates and α -enamido phosphonates (Figure 1.3).⁴⁷ In 2010,

this same research group further attempted to optimize the electronic properties of these ligands by placing either donor or withdrawing groups on the phenyl rings (Figure 1.4).

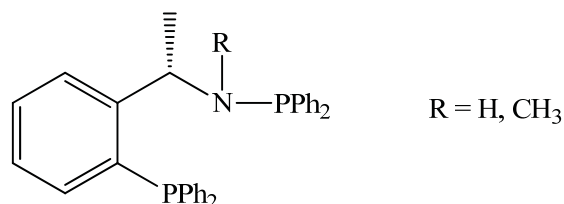


Figure 1.3. Chiral 1-phenylethylamine-derived phosphine-aminophosphine ligands prepared by Wang and co-workers.

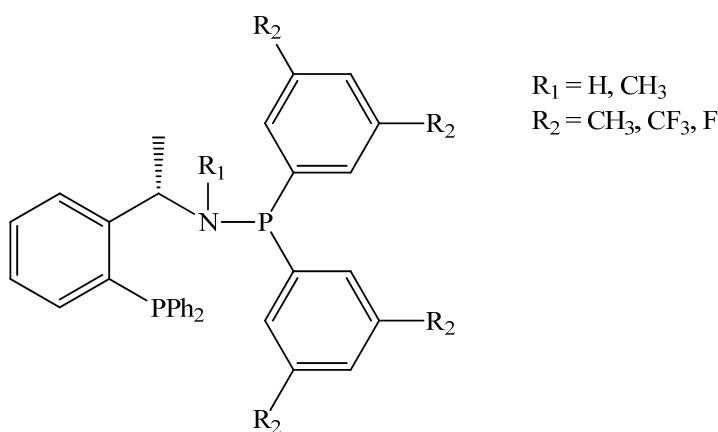


Figure 1.4. Chiral 1-phenylethylamine-derived phosphine-aminophosphine ligands.

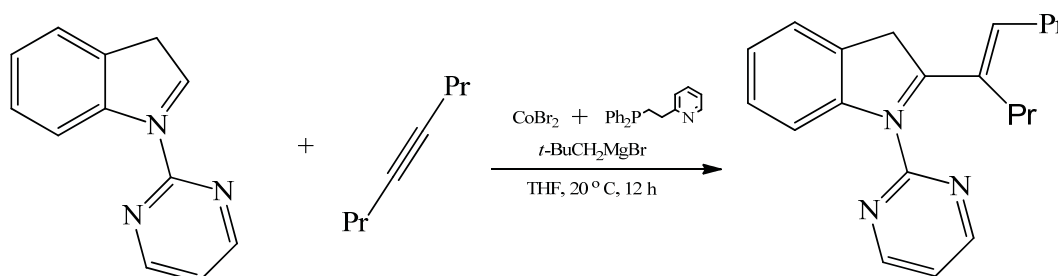
This new family of ligands was then used in the Rh-catalyzed asymmetric hydrogenation of some functionalized olefins including enamides, β -dehydroamino acid esters, dimethyl itaconate, and α -dehydroamino acid ester.⁴⁸

Phosphinopyridine ligands are an interesting variation of *N,P* ligands. The simultaneous presence of the borderline pyridine and soft phosphine donor groups confers the potential for static or dynamic (hemilabile) *P,N*-chelation.³⁰ Depending on the position of the nitrogen donor with respect to the methyl group, these compounds can either bridge or chelate metal centers. Furthermore, their electronic and steric properties

can be fine-tuned, making them useful in a wide range of applications in coordination chemistry of transition metals and in homogeneous catalysis.⁴⁸⁻⁵³

The incorporation of a pyridyl moiety enhances the ligand geometrical flexibility. The free rotation of the P-C_{ipso} bond favors a proper orientation of the nitrogen donor to effectively coordinate to a wide range of transition metals, being mostly soft and borderline acids, including Fe²⁺, Co²⁺, Ni²⁺, Cu⁺, Ag⁺, Au⁺, Hg²⁺, Ru²⁺, Ir⁺ and Pd²⁺.⁵³⁻⁶¹

Complexes of pyridylphosphine ligands have been used in the stereoselective C₂-alkenylation reaction of indoles with alkynes (Scheme 1.2),⁵⁵ reductive amination of aromatic aldehydes⁵⁴ and cross-coupling of cyclic anhydrides with diorganozinc compounds.⁵³ They also present luminescent properties and have been employed to produce electroluminescent devices.^{56,57,59,62,63}



Scheme 1.2. C₂-alkenylation of indoles by a cobalt complex of the ligand Ph₂P(CH₂)₂Py.

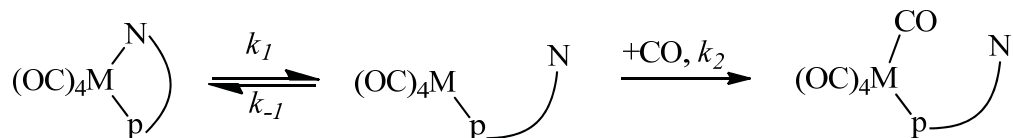
Modification of pyridylphosphine ligands by oxidizing the *P,N* centers can be performed in order to improve their coordination affinity towards hard acceptors. The resulting bifunctional ligands containing both P=O and N-O donors can potentially act as chelating and/or bridging agents through the two pairs of electrons on the oxygen atoms. It has been demonstrated that these chelating reagents produce stable complexes not only with 3*d* metal ions but with *f*-elements as well. Such a coordination property can be

taken advantage of for important applications such as in the recovery of lanthanide and actinide ions and production of new luminescent materials. In the past decades, Rapko, Pain and co-workers have investigated the coordination behavior of several mixed ligands containing P=O and N-O towards different lanthanide ions. Their work showed that these bifunctional ligands produce stable complexes with U^{3+} and Ln^{3+} and that modest effectiveness can be achieved in liquid-liquid extractions of Eu^{3+} , Ce^{3+} , Yb^{3+} and Am^{3+} from acidic aqueous solutions^{23,24,64}. In 1994 they published a study done on the coordination properties of the two tridentate mixed ligands 2,6-($Ph_2P(=O)-CH_2$)₂ C_5H_3NO and 2,6-[(EtO)₂ $P(=O)-CH_2$]₂ C_5H_3NO towards the oxophilic Bi^{3+} , which is found in a number of nuclear waste streams.²²

The size of the resulting chelate ring plays an important part in the stability of the complex. Hancock and co-workers have confirmed through analysis of formation constants that the number of members in a chelate ring is an important factor that allows controlling the selectivity for metal ions based on their size.⁶⁵⁻⁶⁷

In general, it is expected that complexes exhibiting chelates with five or six-membered rings will be more stable than those with four or more than six-membered rings.⁶⁵ Kinetic studies performed by Knebel and Angelici using a series of $(C_6H_5)_2PCH_2CH_2NHR_2$ ligands, ($R = H, CH_3$ or Ph), support the increased stability of complexes containing five-membered chelate rings *versus* the six-membered chelate ring complexes.⁶⁸ They found that the overall rates of reaction are primarily determined by the rates of N-donor dissociation, k_I , and explained the mechanistic insights in terms of a reversible dissociation of the N donor of the *N,P* ligand followed by attack of the CO on a penta-coordinate intermediate (Scheme 1.3). Nevertheless, superior stability of

complexes with seven-membered rings of chelating ligands containing N-O and P=O groups have been also reported.^{69,70}



Scheme 1.3. Chelate ring opening mechanism in metal carbonyl complexes of *N,P* ligands proposed by Knebel and Angelici (M = Cr, Mo or W).

In this work, the coordination behavior of the ligand 2-(diphenylphosphinomethyl)pyridine, 2-(diphenylphosphinomethyl)pyridine oxide and 2-(diphenylphosphinomethyl)pyridine *N,P*-dioxide and has been investigated. Several transition metal ions were used in combination with different counter-anions in order to evaluate their influence in the final molecular structures of the complexes obtained. In Chapter Two complexes based on Hg^{2+} and the ligands 2-(diphenylphosphinomethyl)pyridine and 2-(diphenylphosphinomethyl)pyridine oxide were studied. In order to evaluate the effect that the counter-anion had on the resulting structure, different counter-anions were employed. Chapter Three presents different complexes of Ag^+ with the ligand 2-(diphenylphosphinomethyl)pyridine *N,P*-dioxide. The reactions were performed under similar conditions, where the only variable used was the counter-anion. Chapter Four deals with several complexes based on the ligand 2-(diphenylphosphinomethyl)pyridine *N,P*-dioxide and the first row transition metal ions Co^{2+} , Ni^{2+} , Cu^{2+} and Zn^{2+} . In Chapter Five the coordination behavior of the ligand 4-(diphenylphosphinomethyl)pyridine towards different mercury salts was investigated. All new compounds were structurally characterized by single crystal X-ray diffraction and different spectroscopic techniques in addition to elemental analysis.

CHAPTER TWO

Syntheses and Coordination Studies of 2-[(diphenylphosphino)methyl]pyridine and its Oxide Towards Mercury(II)

Introduction

Hemilabile ligands have become the focus of intense research in the past few decades due to their possible application in catalytic reactions.^{71–75} Our group has put considerable effort into the study of the coordination chemistry of pyridyl containing phosphines, phosphinites, and phosphonites where the pyridyl ring is substituted in various positions by the attendant phosphorus moiety. This has resulted in a number of both discrete and polymeric structures formed by the reaction of the ligand with various Ag^+ salts. A part of these studies has been an examination of the influence of the coordinating ability of the anion present in the salt, which effects a large influence on the solid state structure adopted by the complex or polymer.^{76–82}

The bidentate ligand 2-[(diphenylphosphino)methyl]pyridine (**L1**, Figure 2.1, left) possesses a combination of a softer phosphine moiety and a harder pyridine nitrogen functionality for which it can be included in the hemilabile ligand category.^{6,83} The chelating ability of this bifunctional ligand is well documented as it easily conforms to the formation of a 5-membered ring.^{84–91} The bridging mode of this ligand has only been seen when reacted with Ag^+ as geometric constraints are overcome by the ability of Ag^+ to form Ag–Ag interactions.⁷⁶ Only two instances of monodentate binding have been seen thus far, once with Fe complexes, and once with Ag in both of these cases the softer P binds to the metal with pyridyl functionality dangling.^{76,92}

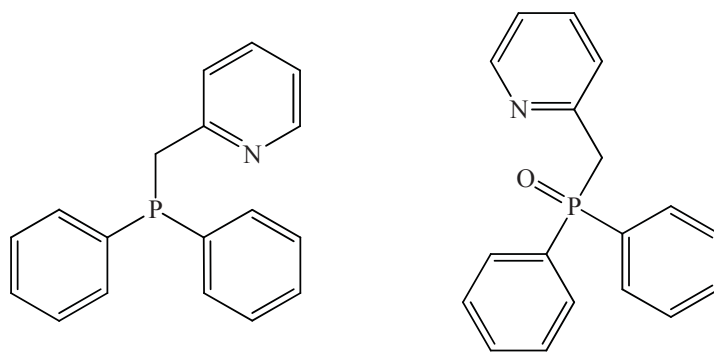


Figure 2.1. Structure of 2-[(diphenylphosphino)methyl]pyridine (**L1**), (left), and 2-[(diphenylphosphoryl)methyl]pyridine oxide (**L2**), (right).

The oxidized form, (**L2**, Figure 2.1, right), modifies the softer phosphorus to a phosphoryl (P=O) group in which the oxygen moiety can act as a hard donor. In this way the coordination mode of **L1** and **L2** can depend on the “hardness” or “softness” of the transition metal ion interacting with the ligand. As with **L1** the expected normal binding mode is to chelate the metal center to form a 6-membered ring.^{78,89} An example is also known where only the N moiety is bound with the P=O group dangling, in this example with PdCl₂, the P=O moiety is pointed away from the metal center.⁹³

Mercury(II) salts possess a soft metal center known to react with tertiary phosphines to yield complexes with a range of ligand-to-metal ratios, the most common being 1:1 and 2:1. The 2:1 complexes are tetra-coordinated and usually display monomeric tetrahedral structures in which the degree of distortion depends on the electronic and steric properties of the phosphine. On the other hand, 1:1 complexes exhibit a variety of molecular structures ranging from discrete dimers to supramolecular networking assemblies.^{94–97}

In this research we describe the synthesis of several mercury(II) complexes of 2-[(diphenylphosphino)methyl]pyridine and its corresponding oxide. The synthesized

compounds have been characterized by single crystal X-ray diffraction, multinuclear NMR spectroscopy and elemental analysis.

Result and Discussion

Synthesis

The ligands **L1** and **L2** were synthesized according to a previously reported procedure.^{76,98} Complexes **2.1** – **2.5** were synthesized at room temperature and atmospheric pressure and were obtained as white solids. The reaction of Hg(SCN)₂ with an equimolar quantity of **L2** gave rise to the dimeric compound [Hg(μ -SCN)₂(**L2**)]₂ (**2.1**). In contrast, the reaction of 2 equiv. of **L1** with 1 equiv. of Hg(SCN)₂ produced the monomeric complex Hg(SCN)₂(**L1**)₂ (**2.2**). The complex [HgCl₂(**L2**)]₂ (**2.3**) was obtained by the reaction of HgCl₂ with an equimolar quantity of **L2**, producing a dimeric structure, as in the case of complex **2.1**. The reaction of 2 equiv. of **L1** with 1 equiv. of Hg(OTf)₂ produced the complex Hg(OTf)₂(**L1**)₂ (**2.4**) while the reaction of 2 equiv. of **L2** with 1 equiv. of Hg(OTf)₂ yielded the compound Hg(OTf)₂(**L2**)₂ (**2.5**). Compounds **2.1** – **2.5** were purified by washing the solid with THF, since the products were sparingly soluble in this solvent. The presented compounds were very stable under normal conditions, showing no signs of decomposition while exposed to light or air at room temperature.

Description of the Crystal Structures

Complex **2.1**, shown in Figure 2.2, was obtained by the reaction of Hg(SCN)₂ and **L2** in a 1:1 ligand to metal ratio. The structure consists of a centrosymmetric thiocyanate-bridged dimer with two mercury centers.

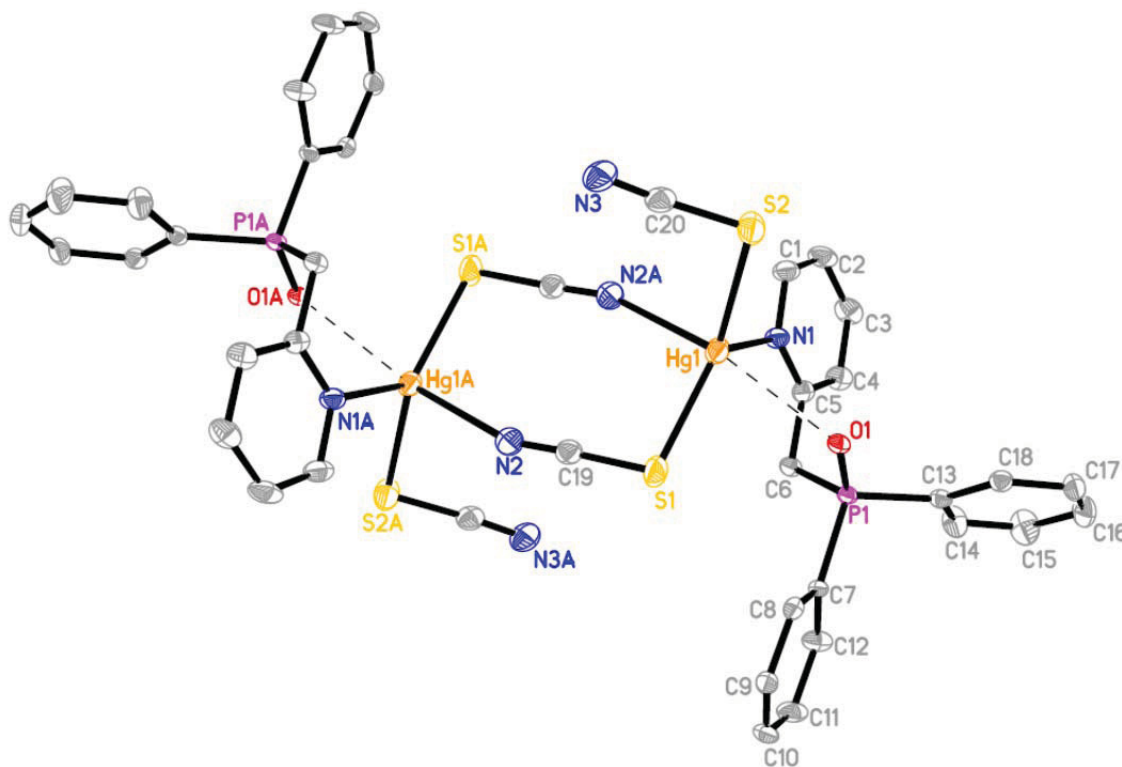


Figure 2.2. Thermal ellipsoid of **2.1** with an atomic numbering scheme. Ellipsoids are shown at the 50% level. Hydrogen atoms have been removed for clarity.

This nonplanar eight-membered ring is formed by two bridging thiocyanate anions coordinated in a head-to-tail fashion, $\text{Hg1}-(\mu_{1,3}\text{-SCN})_2\text{-Hg1A}$, with a Hg1-Hg1A distance of 5.945 Å. The geometry around the mercury centers can be described as distorted trigonal-bipyramidal. The equatorial plane is defined by a nitrogen donor from the **L2** and two sulfur atoms from two thiocyanate ions, where the O1-Hg1-N2A , N1-Hg1-S1 and S1-Hg1-S2 angles are 119.2° , 139.7° and 100.6° (average = 119.8°), respectively. The axial positions are occupied by one nitrogen atom from a bridging counter-anion and an oxygen atom from the ligand where the O1-Hg1-N2A angle is 154.4° . The distortions from a regular trigonal-bipyramidal geometry may be attributed to the formation of the mercury(II) thiocyanate metallacycle with rigid NCS-Hg-NCS

bond angles, and to the long range interaction between the soft Hg²⁺ metal center and the hard oxygen donor, with a Hg–O distance of 2.721 Å. Selected bond lengths and angles for compound **2.1** are listed in Table 2.1.

Table 2.1. Selected bond lengths (Å) and angles (°) for compound **2.1**.*

Hg(1)-N(1)	2.361(3)	N(1)-Hg(1)-S(1)	119.20(7)
Hg(1)-N(2A)	2.560(3)	N(1)-Hg(1)-S(2)	100.64(7)
Hg(1)-S(1)	2.4484(10)	S(1)-Hg(1)-S(2)	139.71(4)
Hg(1)-S(2)	2.4537(9)	N(1)-Hg(1)-N(2A)	83.66(9)
Hg(1)-O(1)	2.7214(19)	S(1)-Hg(1)-N(2A)	96.42(7)
		S(2)-Hg(1)-N(2A)	93.45(7)
O(1)-Hg(1)-S(2)	106.71(0.05)	O(1)-Hg(1)-N(1)	77.28(0.07)
O(1)-Hg(1)-N(2A)	154.36(0.08)	O(1)-Hg(1)-S(1)	78.54(0.05)

*Symmetry transformations used to generate equivalent atoms: -x+2, -y, -z+1.

The crystal structure of complex **2.2**, displayed in Figure 2.3, was obtained by the reaction of Hg(SCN)₂ with **L1** in a 2:1 ligand to metal ratio. This compound is monomeric possessing a crystallographic C₂ axis passing through the four-coordinate mercury center. The geometry around the mercury atom consists of a distorted tetrahedron with two **L1** ligands coordinated through the phosphorus atoms, and two monodentate thiocyanate anions bound *via* the sulfurs to complete the coordination sphere of the metal center. The steric hindrance caused by the bulky substituents on the phosphine ligands makes the P–Hg–P (127.7°) angle much wider than the angle S–Hg–S (93.9°), which is formed by the sulfur atoms on the smaller counter-anions and the mercury center. The Hg–P (2.4688 Å) and Hg–S (2.6460 Å) distances fall in the range of values previously reported in literature.^{96–98}

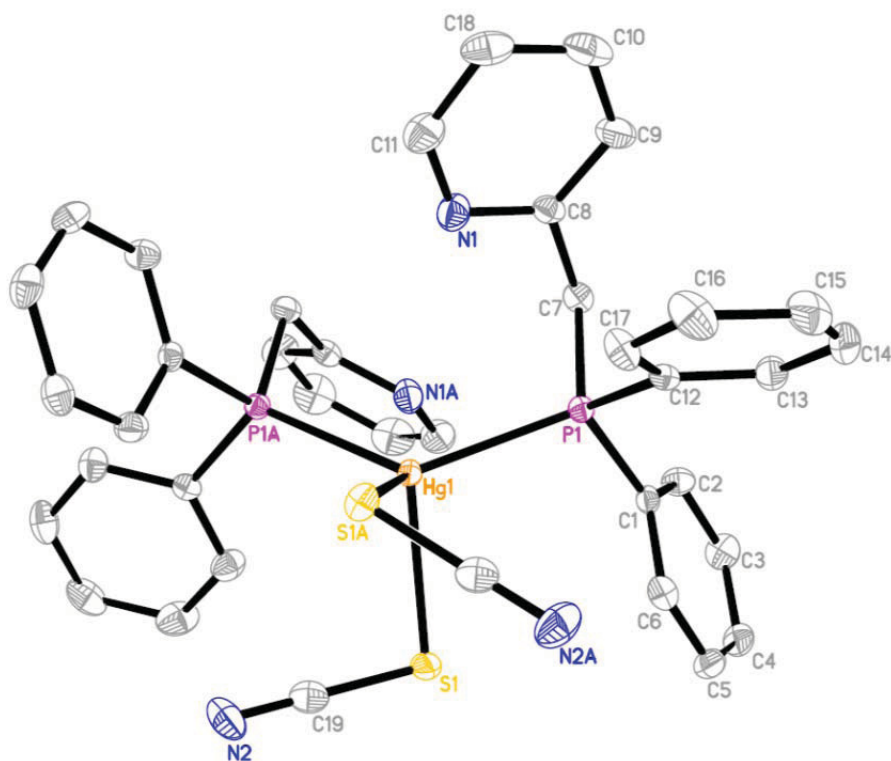


Figure 2.3. Thermal ellipsoid of **2** with an atomic numbering scheme. Ellipsoids are shown at the 50% level. Hydrogen atoms have been removed for clarity.

In contrast to complex **2.1** above, the unoxidized ligand in complex **2.2** features a soft phosphorus moiety and forms a 2:1 complex with the harder pyridyl nitrogen being unbound. In this case, complex **2.2** features two bulky units of the ligand bound to one metal center. This sterically constrained environment prevents the thiocyanate ions from adopting the sterically demanding bridging coordination mode, limiting the counter-anions in the coordination sphere of **2.2** to act as terminal ligands. Regardless of initial reaction stoichiometry, the 2:1 complex always results. Selected bond lengths and angles for compound **2.2** can be found in Table 2.2.

Table 2.2. Selected bond lengths (Å) and angles (°) for compound **2.2**.*

Hg(1)-P(1)	2.4707(12)	P(1)-Hg(1)-P(1A)	127.57(10)
Hg(1)-S(1)	2.6439(17)	P(1)-Hg(1)-S(1)	104.05(3)
N(2)-C(19)	1.154(5)	P(1A)-Hg(1)-S(1)	111.10(3)
S(1)-C(19)	1.676(4)	S(1A)-Hg(1)-S(1)	93.98(8)

*Symmetry transformations used to generate equivalent atoms for compound **2.2**: -x+1, -y+1, z.

The reaction of HgCl₂ with **L2** in a 1:1 stoichiometry afforded the complex with a halo-bridged dimeric structure **2.3** as shown in Figure 2.4.

The geometry around the mercury atom presents a heavily distorted trigonal-bipyramid that is defined by the nitrogen and oxygen donors from the bidentate **L2** and three chloride anions. Two of the chloride atoms act as bridging connectors and one as a simple terminal ligand. The axial positions are occupied by the hard oxygen donor and one of the bridging chloride anions with Cl2A-Hg1-O1 angle of 164.2°, while the equatorial plane is formed by the nitrogen donor and two chloride anions coordinated to the mercury center with Cl2-Hg1-Cl1, Cl1-Hg1-N1 and Cl2-Hg1-N1 angles of 130.8°, 116.4° and 113.3°, respectively (an average angle of 120.16°).

The bridging region shows a high degree of asymmetry with bond distances of 2.974 and 2.417 Å for the bridging Hg-Cl and 2.388 Å for the terminal Hg-Cl. The two bridged Hg-Cl bond lengths are typical for mercury structures containing chloro-bridging moieties.^{99,100} The terminal Hg-Cl bond length, 2.388 Å, is comparable to 2.401 Å, observed in the case of [HgCl(Ph₃P)(μ-Cl)]₂, and 2.375 Å, reported for the complex [HgCl(Ph₂Ppym)(μ-Cl)]₂ as well as other previous works.⁹⁹⁻¹⁰³ Selected bond lengths and angles for compound **2.3** can be found in Table 2.3.

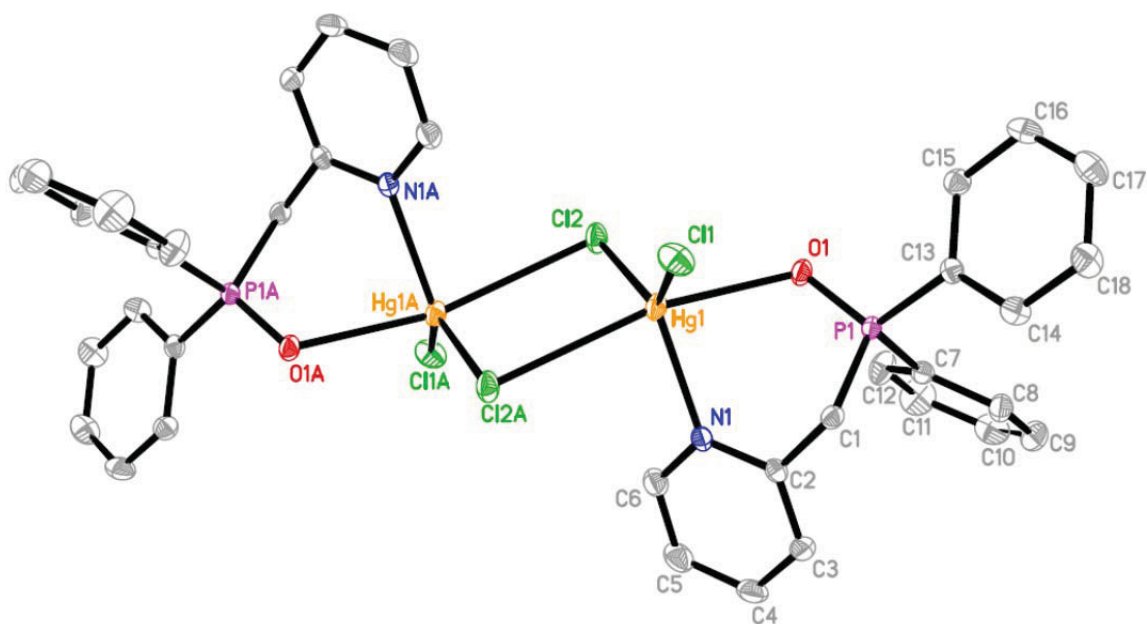


Figure 2.4. Thermal ellipsoid of **2.3** with an atomic numbering scheme. Ellipsoids are shown at the 50% level. Hydrogen atoms and one molecule of THF have been removed for clarity.

Table 2.3. Selected bond lengths (Å) and angles (°) for compound **2.3**.*

Hg(1)-N(1)	2.309(2)	Cl(1)-Hg(1)-Cl(2)	130.30(3)
Hg(1)-Cl(1)	2.3887(8)	N(1)-Hg(1)-O(1)	81.00(8)
Hg(1)-Cl(2)	2.4172(7)	Cl(1)-Hg(1)-O(1)	94.44(5)
Hg(1)-O(1)	2.510(2)	Cl(2)-Hg(1)-O(1)	94.00(5)
Hg(1)-Cl(2A)	2.9738(7)	N(1)-Hg(1)-Cl(2A)	85.15(6)
Cl(2)-Hg(1A)	2.9738(7)	Cl(1)-Hg(1)-Cl(2A)	98.57(3)
		Cl(2)-Hg(1)-Cl(2A)	84.45(2)
N(1)-Hg(1)-Cl(1)	116.36(7)	O(1)-Hg(1)-Cl(2A)	164.17(5)
N(1)-Hg(1)-Cl(2)	113.33(7)	Hg(1)-Cl(2)-Hg(1A)	95.55(2)

*Symmetry transformations used to generate equivalent atoms for compound **2.3**:- x+1, -y+1, -z.

Complex **2.4**, the product from the reaction of $\text{Hg}(\text{OTf})_2$ with **L1** in a 2:1 ligand to metal ratio, is shown in Figure 2.5. The crystal structure exhibits a distorted octahedral geometry with a linear P–Hg–P angle of 179.55° and an N–Hg–N angle of 76.85° . The

bite angle of the ligand (74.58°) featured in this complex constrains the environment around the metal center which pushes the geometry away from ideal octahedral.

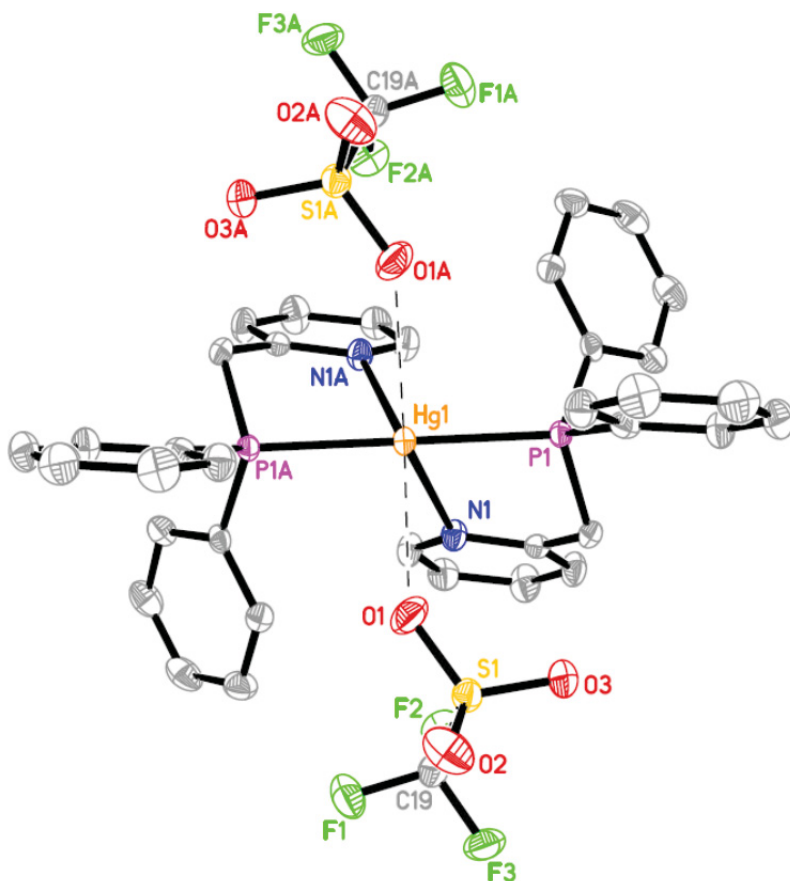


Figure 2.5. Thermal ellipsoid of **2.4** with an atomic numbering scheme. Ellipsoids are shown at the 50% level. Hydrogen atoms have been removed for clarity.

Contrary to complex **2.2**, in which the strongly coordinated thiocyanate anions deny the access of a second ligand unit due to steric congestion, complex **2.4** features weakly coordinated triflate oxygen atoms to the soft mercury(II). This allows the coordination of two ligand moieties *via* the soft phosphorus and nitrogen atoms in a five-membered chelated ring fashion ($\text{Hg1-S1} = 2.6460 \text{ \AA}$ for complex **2.2** and $\text{Hg1-O1} =$

3.102 Å for complex **2.4**). Selected bond lengths and angles for compound **2.4** are listed in Table 2.4.

Table 2.4. Selected bond lengths (Å) and angles (°) for compound **2.4**.*

Hg(1)-P(1)1	2.3854(7)	P(1)-Hg(1)-N(1)	74.58(5)
Hg(1)-N(1)	2.631(2)	N(1A)-Hg(1)-N(1)	76.85(11)
Hg(1)-O(1)	3.1024(0.0024)	O(1)-Hg(1)-N(1)	87.61(0.07)
		O(1)-Hg(1)-P(1)	90.21(0.05)
P(1A)-Hg(1)-P(1)	179.55(4)	O(1)-Hg(1)-N(1A)	154.14(0.07)
P(1A)-Hg(1)-N(1)	105.06(5)	O(1)-Hg(1)-P(1A)	90.04(0.05)
		O(1)-Hg(1)-O(1A)	113.58(0.08)

*Symmetry transformations used to generate equivalent atoms for compound **2.4**: -x+1, y, -z+1/2.

Complex **2.5** was obtained from the reaction of 1 equiv. of Hg(OTf)₂ with 2 equiv. of **L2**. The product displays a 2:1 ligand to metal ratio as shown in Figure 2.6. Two independent molecules are present in the asymmetric unit with only slight differences in the bond lengths around the Hg centers.

As in the case of complex **2.4**, the geometry around the metal center in complex **2.5** can be described as a distorted octahedron supported by two six-membered chelating rings and the weak interaction between the triflate oxygen atoms and the mercury(II). In contrast to complex **2.4**, the six-membered ring in complex **2.5** allows a more flexible structure which more closely approximates the geometry of an ideal octahedron. The angles N1–Hg1–N2 and O1–Hg1–O2 are 177.34° and 175.82°, respectively, and the angles N1–Hg1–O1 and N2–Hg1–O2 are 88.26° and 87.22°, respectively. Furthermore, the flexibility in structure **2.5**, given by the six-membered rings, makes the bite angle of the ligand more obtuse than in complex **2.4**, which bears a five-membered chelate ring. Selected bond lengths and angles for compound **2.5** are listed in Table 2.5.

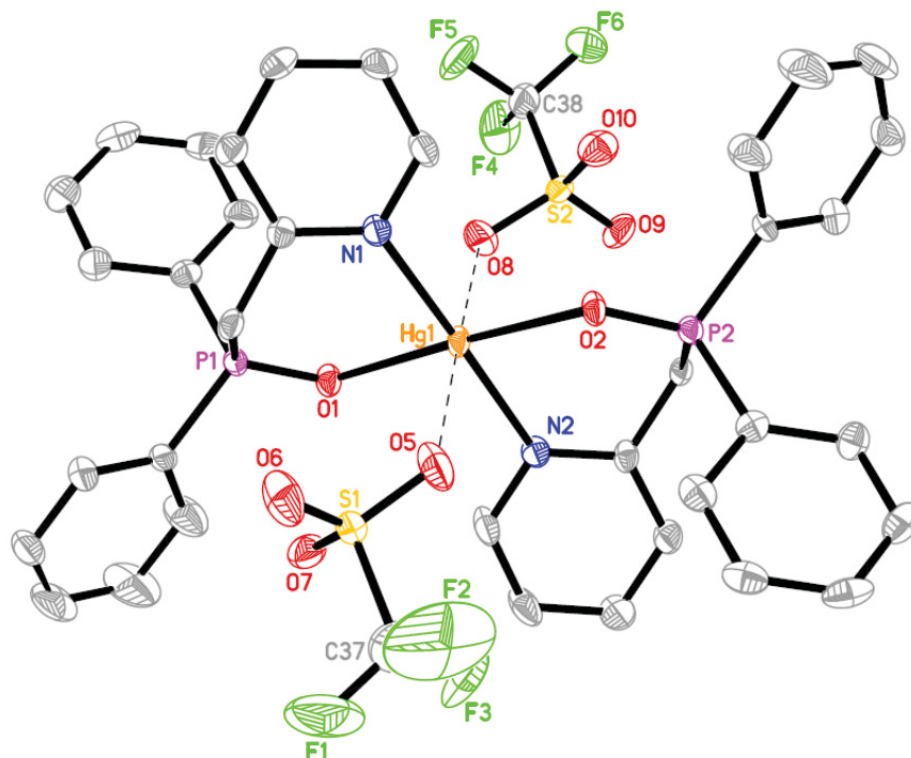


Figure 2.6. Thermal ellipsoid of **2.5** with an atomic numbering scheme. Ellipsoids are shown at the 50% level. Hydrogen atoms have been removed for clarity.

Table 2.5. Selected bond lengths (Å) and angles (°) for compound **2.5**.*

Hg(1)-N(2)	2.120(3)	N(1)-Hg(1)-O(2)	92.03(9)
Hg(1)-N(1)	2.122(3)	N(2)-Hg(1)-O(1)	92.31(9)
Hg(1)-O(2)	2.520(2)	N(1)-Hg(1)-O(1)	88.26(9)
Hg(1)-O(1)	2.541(2)	O(2)-Hg(1)-O(1)	175.82(7)
Hg(2)-N(4)	2.126(3)	N(4)-Hg(2)-N(3)	176.43(11)
Hg(2)-N(3)	2.135(3)	N(4)-Hg(2)-O(4)	88.09(9)
Hg(2)-O(4)	2.511(2)	N(3)-Hg(2)-O(4)	92.97(9)
Hg(2)-O(3)	2.520(2)	N(4)-Hg(2)-O(3)	90.44(9)
Hg(2)-O(11)	2.631(3)	N(3)-Hg(2)-O(3)	88.41(9)
Hg(2)-O(14)	2.7154 (0.0027)	O(4)-Hg(2)-O(3)	177.80(9)
Hg(1)-O(8)	2.6744 (0.0029)	N(4)-Hg(2)-O(11)	103.46(9)
Hg(1)-O(5)	2.7452 (0.0031)	N(3)-Hg(2)-O(11)	80.02(10)
		O(4)-Hg(2)-O(11)	85.92(8)
N(2)-Hg(1)-N(1)	177.34(12)	O(3)-Hg(2)-O(11)	96.01(8)
N(2)-Hg(1)-O(2)	87.22(9)	O(2)-Hg(1)-O(5)	73.00(0.08)
		O(2)-Hg(1)-O(8)	107.45(0.08)

*Symmetry transformations used to generate equivalent atoms for **2.5**: -x, y, -z+1/2.

Complex **2.6**, the product from the reaction between $\text{Hg}(\text{CN})_2$ and **L2**, has a ligand to metal ratio of 1:1 (Figure 2.7). The metal center adopts a severely distorted trigonal bipyramidal geometry. The oxidized ligand, **L2**, adopts a chelating mode of coordination in which the oxygen atom on the phosphoryl group and the nitrogen atom on the pyridyl group bind to the Hg^{2+} ion to form a six-membered ring with a O1-Hg-N3 bite angle of 74.2° . The Hg1-O1 and Hg1-N3 bond lengths are 2.572 Å and 2.645 Å respectively.

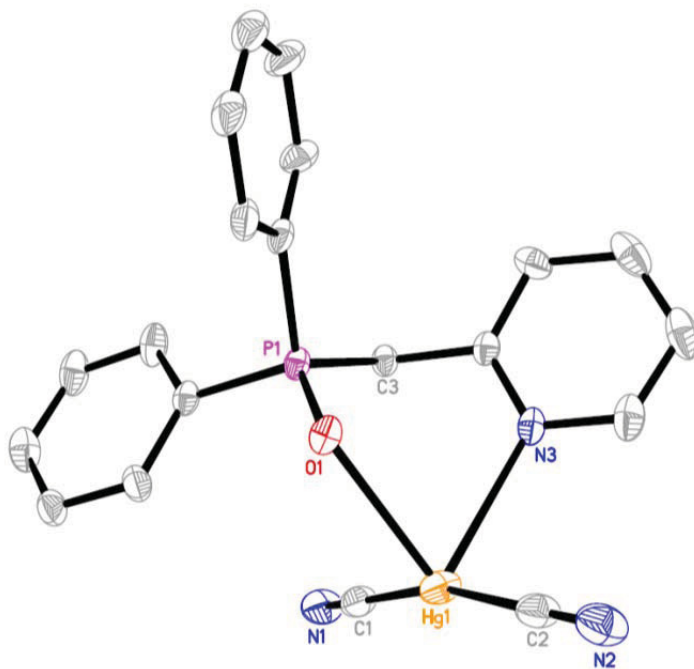


Figure 2.7. Thermal ellipsoid of **2.6** with an atomic numbering scheme. Ellipsoids are shown at the 50% level. Hydrogen atoms have been removed for clarity.

The cyanide anions act as terminally bonded monodentate ligand to complete the tetrahedral geometry around the metal center. The Hg-C bond lengths are $\text{Hg-C1} = 2.051$ Å and $\text{Hg-C2} = 2.040$ Å, with a C1-Hg-C2 angle of 166.1° . The bond angles O1-Hg-C1, O1-Hg-C2, N3-Hg-C1 and N3-Hg-C2 are 89.8° , 102.4° , 96.0° and 93.2° , respectively.

All bond distances and bond angles for complex **2.6** are in the expected range of values. The bite angle O1-Hg1-N3 was 74.58°. Selected bond lengths and angles for compound **2.6** are listed in Table 2.6.

Table 2.6. Selected bond lengths (Å) and angles (°) for compound **2.6**.

Hg(1)-C(2)	2.044(4)	C(2)-Hg(1)-C(1)	166.27(17)
Hg(1)-C(1)	2.048(4)	C(2)-Hg(1)-O(1)	102.39(14)
Hg(1)-O(1)	2.577(3)	C(1)-Hg(1)-O(1)	89.55(13)
Hg(1)-N(3)	2.639(3)	C(2)-Hg(1)-N(3)	93.76(14)
Hg(2)-C(21)	2.042(4)	C(1)-Hg(1)-N(3)	96.04(14)
Hg(2)-C(22)	2.049(4)	O(1)-Hg(1)-N(3)	74.14(9)
Hg(2)-O(2)	2.557(3)	C(21)-Hg(2)-C(22)	165.58(15)
Hg(2)-N(6)	2.629(3)	C(21)-Hg(2)-O(2)	101.31(13)
P(1)-O(1)	1.496(3)	C(22)-Hg(2)-O(2)	89.50(13)
P(2)-O(2)	1.497(3)	C(21)-Hg(2)-N(6)	94.88(14)
		C(22)-Hg(2)-N(6)	97.21(13)
		O(2)-Hg(2)-N(6)	74.58(9)

The reaction between Hg(Tfa)₂ and **L1** yields complex **2.7** (Figure 2.8). This compound displays a tetracoordinate mercury center with a 2:1 ligand to metal ratio and two trifluoroacetate counter anions. The resulting tetrahedral coordination sphere around the mercury is described by the angles P(1)-Hg(1)-P(2), 159.1°, and O(1)-Hg(1)-O(3), 98.1°. Even though **L1** can act as a chelating agent *via* the soft phosphorus and the hard nitrogen atoms, the soft mercury shows preference to coordinate to the soft phosphorus atoms from two different ligand units, leaving uncoordinated the flexible pyridyl group with the nitrogen atoms oriented to the metal center due weak electrostatic interactions. The Hg(1)-N(1) and Hg(1)-N(2) distances are 3.107 Å and 2.938 Å, respectively, with a N(1)-Hg(1)-N(2) angle of 67.1°. The bulky phenyl substituents on the ligand are disposed in a way that the steric interactions are minimized. The stability of the crystal lattice is further stabilized by supramolecular forces of the type π - π between parallel displaced

phenyl moieties of consecutive molecular units (Figure 2.9). Selected bond lengths and angles for compound **2.7** are listed in Table 2.7.

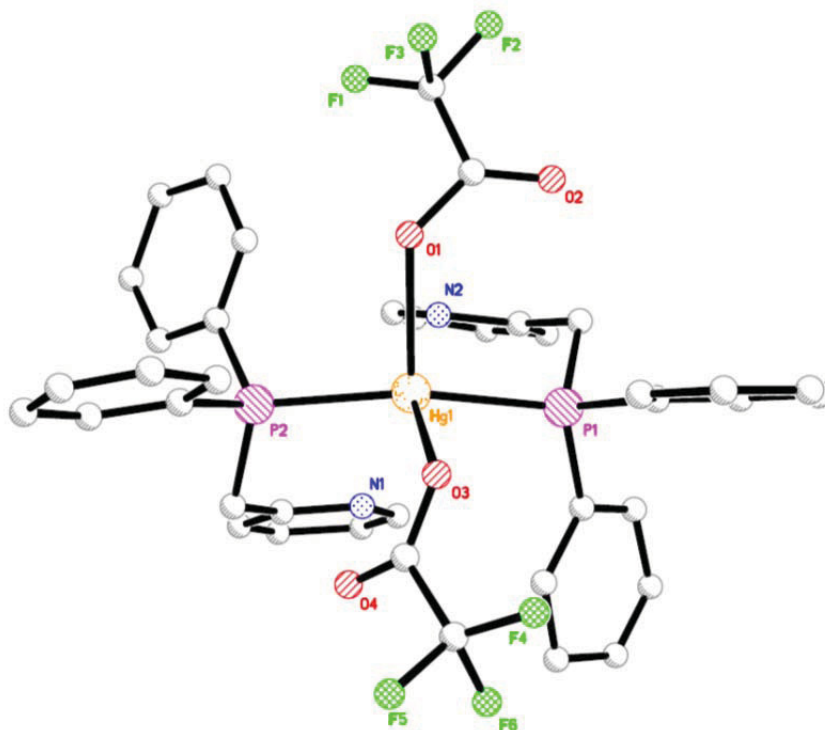


Figure 2.8. Thermal ellipsoid of **2.7** with an atomic numbering scheme. Ellipsoids are shown at the 50% level. Hydrogen atoms have been removed for clarity.

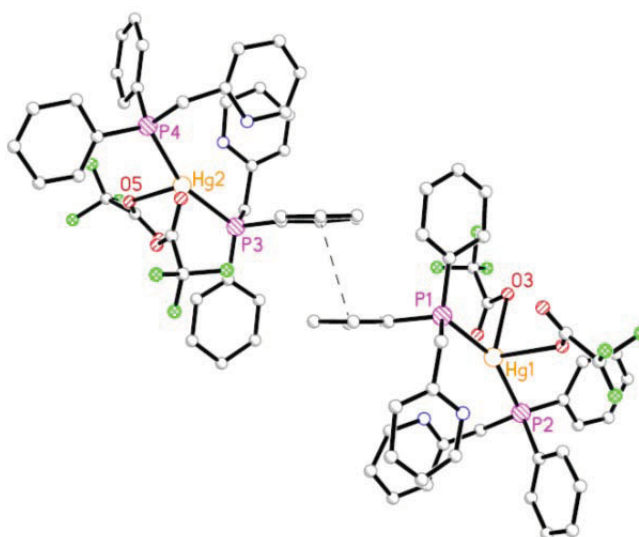
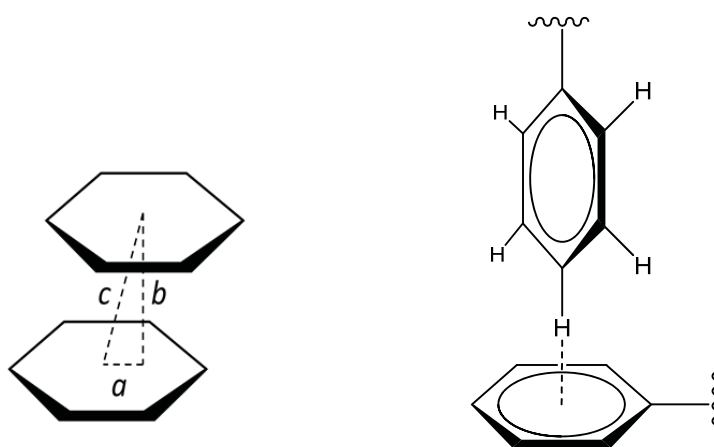


Figure 2.9. View of the π - π stacking observed in the X-ray structure of **2.7**.

Table 2.7. Selected bond lengths (Å) and angles (°) for compound **2.7**.

Hg(1)-P(1)	2.4108(6)	P(1)-Hg(1)-P(2)	159.04(2)
Hg(1)-P(2)	2.4180(6)	P(1)-Hg(1)-O(3)	96.31(5)
Hg(1)-O(3)	2.5296(18)	P(2)-Hg(1)-O(3)	99.72(5)
P(1)-C(13)	1.807(3)	C(13)-P(1)-C(7)	106.32(11)
P(1)-C(7)	1.811(3)	C(13)-P(1)-C(1)	107.53(12)
P(1)-C(1)	1.823(3)	C(7)-P(1)-C(1)	106.94(12)
P(2)-C(31)	1.809(3)	C(13)-P(1)-Hg(1)	112.15(8)
P(2)-C(25)	1.811(3)	C(7)-P(1)-Hg(1)	115.67(9)
P(2)-C(19)	1.818(3)	C(1)-P(1)-Hg(1)	107.85(8)
N(1)-C(2)	1.340(3)	C(31)-P(2)-C(25)	105.82(12)
N(1)-C(6)	1.344(4)	C(31)-P(2)-C(19)	107.64(12)
N(2)-C(24)	1.340(4)	C(25)-P(2)-C(19)	104.97(12)
N(2)-C(20)	1.341(3)	C(31)-P(2)-Hg(1)	111.10(8)

The centroid – centroid distance, c , is 3.710 Å, the plane to plane separation, b , is 3.454 Å and the offset distance of centroids, a , is 1.353 Å (Scheme 2.1, left). Weak electrostatic interactions are also observed between the π -cloud of the phenyl rings and the hydrogen atom of another phenyl substituent in the adjacent molecular unit. The distance observed between the face ring hydrogen and the center of the other phenyl group is 2.898 Å with a T-shaped orientation (Scheme 2.1, right).



Scheme 2.1. Geometric characteristics for two stacked aromatic rings for compound **2.7** (left). T-shaped aromatic-aromatic orientation in compound **2.7** (right).

Complex **2.8** was obtained by reaction $\text{Hg}(\text{Tfa})_2$ with **L2** in a 1:1 ratio. The molecular structure consists of one central eight-membered ring with two five-membered rings on each side (Figure 10). Interestingly, the trimetallacycle structure displays two C-Hg bonds product of the abstraction two of the hydrogen atoms from the methylene groups of two **L2** units and the loss of one counter-anion from the metal centers. The molecular structure of the carbanionic ligand **HL2** is shown in Figure 2.11.

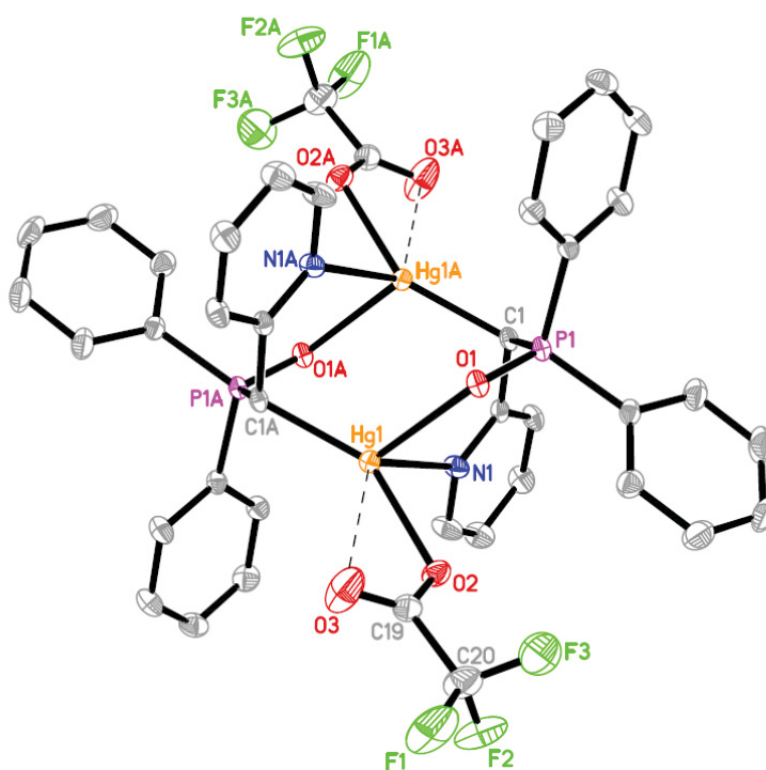


Figure 2.10. Thermal ellipsoid of **2.8** with an atomic numbering scheme. Ellipsoids are shown at the 50% level. Hydrogen atoms have been removed for clarity.

Each of the penta-coordinate Hg^{2+} centers interact with the oxygen and nitrogen donors of one deprotonated **L2** unit, **HL2**, a deprotonated carbon atom of a second **HL2** and two oxygen atoms of one counter-anion.

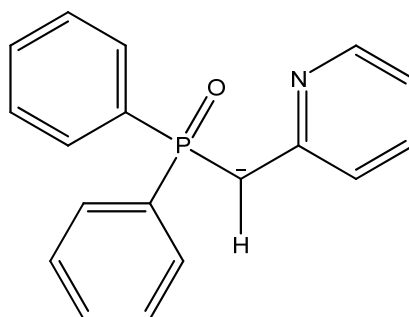


Figure 2.11. Molecular structure of HL2.

The Hg1-C1A, Hg1-O_{P1=O1} and Hg-N distances, are 2.133 Å, 2.421 Å and 2.405 Å, respectively. One of the Hg-O_{Tfa-} interactions presents a relatively short distance of 2.221 Å, while the other is rather long (3.050 Å). The C1A-Hg1-O_{P1=O1} angle of 145.9° represents the wider angle in the metallacycle, while the angle form by the Hg²⁺ and the Tfa⁻ oxygen atoms is the narrower (O2-Hg1-O3 = 47.1°). In between these values are found the C1A-Hg1-N1, O3_{Tfa-}-Hg1-O_{P1=O1} and O2_{Tfa-}-Hg1-O_{P1=O1} angles (101.3°, 96.6° and 87.8°, respectively). The angle N1-Hg1-O1 was found to be 84.8°. The P=O bond is virtually the same than that reported for complexes **2.2**, **2.3** and **2.5**, which bear the same ligand. Selected bond lengths and angles for compound **2.8** are listed in Table 2.8.

Table 2.8. Selected bond lengths (Å) and angles (°) for compound **2.8**.

Hg(1)-C(1)#1	2.133(3)	C(1)#1-Hg(1)-O(2)	145.87(9)
Hg(1)-O(2)	2.2214(19)	C(1)#1-Hg(1)-N(1)	125.55(9)
Hg(1)-N(1)	2.405(2)	O(2)-Hg(1)-N(1)	82.16(8)
Hg(1)-O(1)	2.4213(19)	C(1)#1-Hg(1)-O(1)	111.94(8)
Hg(2)-C(21)#2	2.129(3)	O(2)-Hg(1)-O(1)	87.78(7)
Hg(2)-O(5)	2.176(2)	N(1)-Hg(1)-O(1)	84.76(7)
Hg(2)-O(4)	2.3925(19)	O(5)-Hg(2)-O(4)	87.54(7)
Hg(2)-N(2)	2.485(3)	O(5)-Hg(2)-N(2)	80.21(8)
P(1)-O(1)	1.503(2)	O(4)-Hg(2)-N(2)	81.85(8)
P(2)-O(4)	1.501(2)	O(1)-P(1)-C(1)	113.74(12)
C(21)-Hg(2)#2	2.129(3)	O(1)-P(1)-C(7)	110.86(12)
C(1)-Hg(1)#1	2.133(3)	C(1)-P(1)-C(7)	104.03(13)

Motivated by the formation of the carbanionic HL2 ligand in complex **2.8**, attempts were performed to produce similar results with a different Hg²⁺ salt by stoichiometrically adding a base after ligand complexation. Unsatisfactory results were obtained by using either NH₃ or NaOH. Also, it was attempted to directly deprotonate the ligand in a step prior to complexation using solutions of these same bases, but no favorable results were obtained. Later on, taking advantage of the uncoordinated oxygen atoms on complex **2.1**, a reaction between 1 equivalent of complex **2.1** and 2 equivalents of AgTfa was run in order to obtain a heterometallic complex of Hg²⁺ and Ag⁺. After a month, a single crystal suitable for x-ray diffraction was obtained. Surprisingly, the crystallographic data showed a structure analogous to complex **2.8**, where two of the L2 units were deprotonated to form the anionic HL2. No Ag⁺ was observed in the crystal structure. Upon coordination of two HL2 to the metal centers the metallacycle shown in Figure 2.12 was generated.

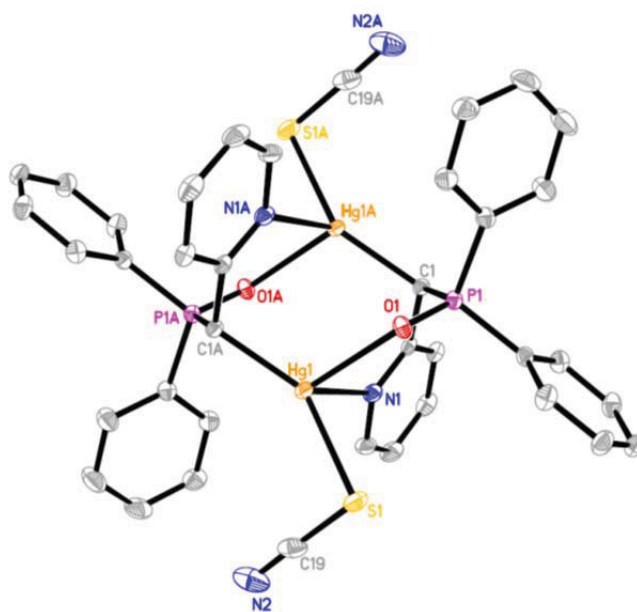


Figure 2.12. Thermal ellipsoid of **2.9** with an atomic numbering scheme. Ellipsoids are shown at the 50% level. Hydrogen atoms have been removed for clarity.

All the bond angles and bond distances around this Hg^{2+} are similar to those in complex **2.8**. Selected bond lengths and angles for compound **2.9** are listed in Table 2.9.

Table 2.9. Selected bond lengths (Å) and angles (°) for compound **2.9**.*

Hg(1)-C(1)#1	2.150(2)	O(1)-Hg(1)-S(1)	91.11(4)
Hg(1)-O(1).	2.4127(14)	C(1)#1-Hg(1)-N(1)	121.48(7)
Hg(1)-S(1)	2.4633(6)	O(1)-Hg(1)-N(1)	82.51(5)
Hg(1)-N(1)	2.5225(18)	S(1)-Hg(1)-N(1)	89.39(4)
S(1)-C(19)	1.680(3)	C(19)-S(1)-Hg(1)	94.79(9)
P(1)-O(1)	1.5033(15)	O(1)-P(1)-C(1)	114.18(9)
P(1)-C(1)	1.797(2)	O(1)-P(1)-C(13)	109.95(9)
C(1)-Hg(1)#1	2.150(2)	C(1)-P(1)-C(13)	105.04(10)
		O(1)-P(1)-C(7)	110.98(9)
C(1)#1-Hg(1)-O(1)	110.03(6)	C(1)-P(1)-C(7)	108.09(10)
C(1)#1-Hg(1)-S(1)	143.74(6)	C(13)-P(1)-C(7)	108.29(10)
O(1)-Hg(1)-S(1)	91.11(4)	P(1)-O(1)-Hg(1)	122.18(8)
C(1)#1-Hg(1)-O(1).	110.03(6)	P(1)-C(1)-Hg(1)#1	108.13(10)
C(1)#1-Hg(1)-S(1).	143.74(6)	N(2)-C(19)-S(1)	178.7(3)

*Symmetry transformations used to generate equivalent atoms: #1 -x+1,-y,-z.

In contrast to complex **2.8**, complex **2.9** presents intermolecular interactions between the nitrogen atoms on the anions and hydrogen atoms on phenyl rings of two neighboring molecular units, with a $\text{N}\cdots\text{H}-\text{C}$ distance of 2.732 Å (Figure 2.13). This kind of interactions also exist between the anions and the hydrogen atom left on the methylene group ($\text{N}\cdots\text{H}-\text{C} = 2.755$ Å).

NMR Spectra

All the products were characterized by multinuclear NMR spectroscopy techniques. The TMS (internal) reference was used for ^1H NMR and H_3PO_4 (external) for ^{31}P NMR. The spectra were recorded as acetonitrile- d_3 , methanol- d_4 or THF- d_8 solution, depending on the solubility of the compounds.

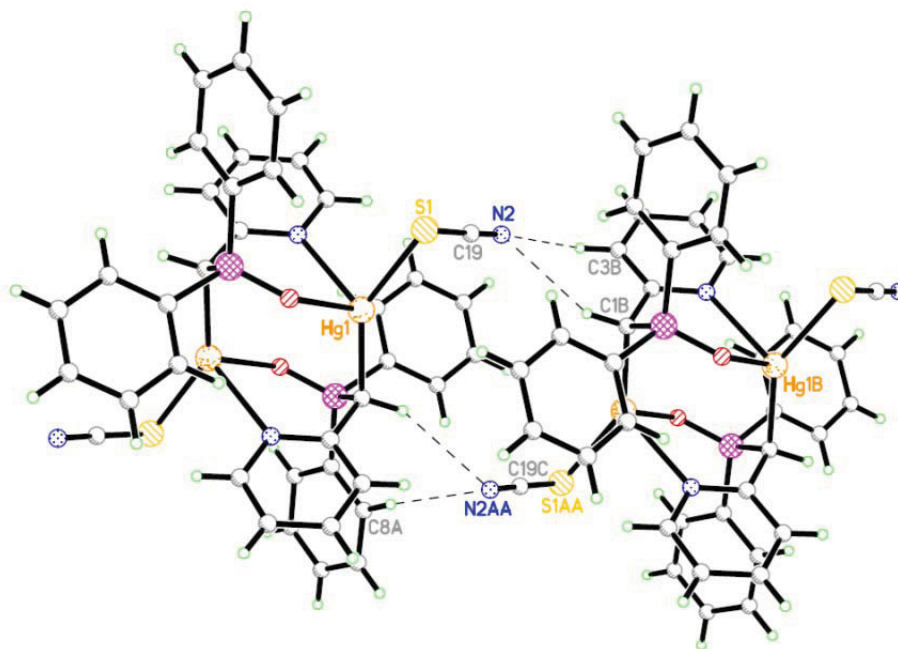


Figure 2.13. Intermolecular hydrogen bonding ($\text{N}\cdots\text{H}-\text{C}$) in compound **2.9**.

The ^1H NMR spectra of compounds **2.1** – **2.7** are similar with small variations in the chemical shift compared to the free ligand spectrum. In complex **2.4**, a chemical shift upfield was observed, causing overlapping of the signals corresponding to the hydrogen adjacent to the nitrogen in the pyridyl substituent and the rest of the aromatic hydrogen atoms in the ligand. This chemical shift suggests that the pyridyl moiety may not be coordinated to the mercury center while in solution; although the coordination is observed in solid state. For complex **2.5** we observe $^3J(^1\text{H}-^{199}\text{Hg})$ coupling to the bound pyridyl which supports that the pyridyl is bound in solution.^{104–106}

The ^{31}P NMR spectra of these complexes show the presence of only one phosphorus-containing species in solution. For **2.2** and **2.4** the shift from free ligand is from -13.7 to 35.0 and 34.9 ppm, respectively, the magnitude of this shift to lower field is consistent with previous work with other phosphines and mercury.^{104,107,108} In complex **2.4**, where the phosphorus atom is directly coordinated to the Hg atom, the spectrum

showed the expected satellites due to $^1J(^{31}\text{P}-^{199}\text{Hg})$ coupling (^{199}Hg , 16.84% natural abundance, nuclear spin $I = 1/2$). Similarly, complex **2.6** showed two sets of weak satellite signals at 0.15ppm and 0.25ppm from the main peak, which was found to be 32.91ppm.

The solubility of complex **2.2** was very poor in common organic solvents, and were unable to detect the corresponding satellite peaks. For complexes **2.1**, **2.3** and **2.5**, which have the oxidized ligand **L2**, only a slight shift is observed from the free ligand resonance. This is likely due the weaker interaction of the P=O group with the metal as compared to the much softer P moiety of **L1**. Chemical shift and proton integration values are provided in the experimental section.

Conclusions

Several complexes of Hg^{2+} and 2-[(diphenylphosphino)methyl]pyridine, **L1**, and its oxide, **L2**, have been synthesized and their structures determined by single-crystal X-ray crystallography. The ligand has shown the capability to coordinate to the mercury center in a monodentate or chelating fashion, dependent on both the sterically demanding phosphine substituents and the coordination properties of the counterion. Due to the soft nature of mercury, the coordination of **L1** and **L2** through the softer donor atoms (phosphorus and nitrogen, respectively), was preferred when the ligands acted in a monodentate fashion. This coordination behavior of the ligand suggests that the harder moiety of the ligand, either nitrogen in **L1** or phosphoryl (P=O) in **L2**, could reversibly bind the soft mercury center when in the presence of a harder Lewis acid. Different geometries were observed around the metal center, including distorted tetrahedral and distorted trigonal–pyramidal, with the degree of distortion depending on the steric effects

and the chelating capability of the ligand. In the cases where a direct comparison was possible, it was observed that the weaker the coordination of the mercury center with the anion, the stronger the coordination of the ligand with the metal center. Also, the distance between the mercury centers and the anion increases when the metal is coordinated to the non oxidized ligand, **L1**, when compared to the same distance in the complexes obtained with **L2**. This observation is due to the stronger coordination of the soft Hg^{2+} to the softer P atoms in the **L1**. We are continuing to study the coordination properties of this versatile phosphine ligand and its two possible oxidized products (one bearing a P=O and a nitrogen moieties and the other fully oxidized, bearing a P=O and N–O moieties) toward mercury salts and other transition metals.

Experimental

General Remarks

Caution! Mercury compounds are highly toxic. Appropriate engineering control measures and personal protection equipment must be used at all time while handling these compounds. Consult the corresponding Material Safety Data Sheets (MSDS) for further safety information before attempting to work with these compounds. All experiments were performed under nitrogen atmosphere were stored and handled in an inert atmosphere glovebox and used as received. All solvents were reagent grade and distilled under inert atmosphere from the appropriate drying agent prior to use. ^1H and ^{31}P NMR spectra were recorded at 499.78 and 202.31 MHz, respectively, at 25.0 °C/298.1 K, using a Varian VNMRs 500 MHz Spectrometer. Elemental analyses were

performed by Atlantic Microlabs Inc. in Norcross, Georgia. Yields for compounds **2.1** – **2.9** were calculated with respect to HgX_2 ($\text{X} = \text{SCN}^-$, OTf^- , Tfa^- , Cl^- , CN^-).

Preparation

*Synthesis of $[\text{Hg}(\text{SCN})_2(\text{L2})]_2$ (**2.1**).* A solution of **L2** (0.116 g, 0.394 mmol) in THF (5 mL) was added to a solution of $\text{Hg}(\text{SCN})_2$ (0.480 g, 0.394 mmol) in THF (5 mL). The resulting solution was allowed to stir for 15 min and then dried under vacuum to leave an off-white powder. Colorless blocks were obtained by slow diffusion of ether into a DMF solution of **2.1** at 5 °C. Yield 59% (0.284 g, 0.231 mmol). ^1H NMR (CD_3CN , 298.1 K): δ 4.21 (d, 2H), 7.53 (m, 13H), 8.53 (d, 1H). ^{31}P NMR (CD_3CN , 298.1 K) δ 36.2, (s) ppm. Anal. Calc. for $\text{C}_{40}\text{H}_{32}\text{Hg}_2\text{N}_6\text{O}_2\text{P}_2\text{S}_4 \cdot 2.5\text{THF}$ (1220.124): C, 42.88; H, 3.74; N, 6.00. Found: C, 42.97; H, 3.30; N, 6.16%.

*Synthesis of $\text{Hg}(\text{SCN})_2(\text{L1})_2$ (**2.2**).* A solution of **L1** (0.107 g, 0.386 mmol) in THF (5 mL) was added to a solution of $\text{Hg}(\text{SCN})_2$ (0.0611 g, 0.193 mmol) in THF (5 mL). The resulting solution was allowed to stir for 20 min and then dried in vacuum to leave an off-white powder. This was then dissolved in a small amount of CH_3CN and precipitated with ether. Colorless blocks were obtained by slow diffusion of ether into a DMF solution of **2.2** at 5 °C. Yield 78% (0.132 g, 0.151 mmol). ^1H NMR (THF-d_8 , 298.1 K): δ 4.53 (d, 2H), 7.54 (m, 13H), 8.62 (d, 1H). ^{31}P NMR (CD_3OD , 298.1 K) δ 35.0. Anal. Calc. for $\text{C}_{38}\text{H}_{32}\text{HgN}_4\text{P}_2\text{S}_2$ (871.36): C, 52.38; H, 3.370; N, 6.43. Found: C, 52.09; H, 3.78; N, 6.45%.

Synthesis of $[HgCl_2(L2)]_2$ (2.3). A solution of **L2** (0.059 g, 0.200 mmol) in THF (5 mL) was added to a solution of $HgCl_2$ (0.054 g, 0.200 mmol) in THF (5 mL). The resulting solution was allowed to stir for 15 min and then dried in vacuum to leave an off-white powder. This was then dissolved in a small amount of CH_3CN and precipitated with ether. Colorless blocks were obtained by slow diffusion of ether into a THF solution of **2.3** at 5 °C. Yield 80% (0.180 g, 0.160 mmol). 1H NMR (CD_3CN , 298.1 K): δ 4.24 (d, 2H), 7.52 (m, 13H), 8.49 (d, 1H). ^{31}P NMR (CD_3CN , 298.1 K): δ 35.3, (s) ppm. Anal. Calc. For $C_{36}H_{32}Cl_4Hg_2N_2O_2P_2 \cdot H_2O$ (1129.6): C, 37.67; H, 2.98; N, 2.44. Found: C, 37.74; H, 2.71; N, 2.41%.

Synthesis of $Hg(OTf)_2(L1)_2$ (2.4). A stirred solution of **L1** (0.112 g, 0.405 mmol) in THF (5 mL) was added to a stirred solution of $Hg(OTf)_2$ (0.100 g, 0.201 mmol) in THF (5 mL). A white precipitate was formed and washes with THF (2 x 30 ml) were performed. The solvent was dried in vacuum to leave an off-white powder. Colorless blocks were obtained by slow diffusion of ether into a CH_3CN solution of **2.4** at 5 °C. Yield 92% (0.197 g, 0.187 mmol). 1H NMR (CD_3OD , 298.1 K): δ 4.85 (d, 2H), 7.00 (m, 1H), 7.11 (m, 1H), 7.65 (m, 4H), 7.76 (m, 3H), 7.95 (m, 5H). ^{31}P NMR (CD_3CN , 298.1 K): δ 34.9, (s) ppm, $^1J(^{31}P-^{199}Hg)$: 5981.29 Hz. Anal. Calc. for $C_{38}H_{32}HgN_2P_2F_6S_2O_6 \cdot H_2O$ (1053.34): C, 42.602; H, 3.19; N, 2.615. Found: C, 42.45; H, 3.02; N, 2.60%.

Synthesis of $Hg(OTf)_2(L2)_2$ (2.5). A stirred solution of **L2** (0.118 g, 0.402 mmol) in THF (5 mL) was added to a solution of $Hg(OTf)_2$ (0.100 g, 0.200 mmol) in THF (5 mL). The resulting solution was allowed to stir for 5 min. A white precipitate was

formed and washes with THF (2 x 30 mL) were performed. The solvent was dried under vacuum to leave an off-white powder. Colorless blocks were obtained by slow diffusion of ether into a CH₃CN solution of **2.5** at 5 °C. Yield 89% (0.193 g, 0.178 mmol). ¹H NMR (CD₃CN, 298.1 K): δ 4.56 (d, 2H), 7.50 (m, 13H), 8.94 (d, 1H), ³*J*(¹H–¹⁹⁹Hg): 53.21 Hz. ³¹P NMR (CD₃CN, 298.1 K): δ 38.5, (s) ppm. Anal. Calc. for C₃₈H₃₂HgN₂P₂F₆S₂O₈·2H₂O (1085.34): C, 40.70; H, 3.23; N, 2.49. Found: C, 40.43; H, 2.85; N, 2.39%.

Synthesis of Hg(CN)₂(L2) (2.6). A stirred solution of **L2** (0.055 g, 0.200 mmol) in THF (5 mL) was added to a solution of Hg(OTf)₂ (0.085 g, 0.200 mmol) in THF (5 mL). The resulting solution was allowed to stir for 10 min. No precipitate was observed upon mixing the reactants. The solvent was dried under vacuum to leave an off-white powder. Colorless blocks were obtained by slow diffusion of hexanes into a THF solution of **2.6** at -5 °C. Yield 82% (0.087 g, 0.164 mmol). ¹H NMR (CD₃CN, 298.1 K): δ 4.10 (d, 2H), 7.18 (d, 1H), 7.27 (t, 1H), 7.53 (m, 7H), 7.77 (m, 4H), 8.47 (d, 1H). ³¹P NMR (CD₃CN, 298.1 K): δ 32.85, (s) ppm.

Synthesis of Hg(Tfa)₂(L1)₂ (2.7). A stirred solution of **L1** (0.110 g, 0.400 mmol) in THF (5 mL) was added to a solution of Hg(OTf)₂ (0.085 g, 0.200 mmol) in THF (5 mL). The resulting solution was allowed to stir for 10 min. No precipitate was observed upon mixing the reactants. The solvent was dried under vacuum to leave an off-white powder. Colorless blocks were obtained by slow diffusion of hexanes into a THF solution of **2.7** at -5 °C. Yield 73% (0.147 g, 0.148 mmol). ¹H NMR (CD₃CN, 298.1 K): δ 4.62 (s, 2H), 7.03 (m, 1H), 7.52 (m, 6H), 7.63 (t, 2H), 7.43 (td, 1), 7.81 (s, 4). ³¹P NMR

(CD₃CN, 298.1 K): δ 35.9, (s) ppm. $^1J(^{31}\text{P}-^{199}\text{Hg})$: 3981.66 Hz. Anal. Calc. for C₄₀H₃₂F₆HgN₂O₄P₂ (891.22): C, 48.96; H, 3.28; N, 2.85. Found: C, 48.31; H, 3.10; N, 2.81%.

Synthesis of Hg(Tfa)₂(HL2) (2.8). A stirred solution of **L2** (0.058 g, 0.200 mmol) in THF (5 mL) was added to a solution of Hg(OTf)₂ (0.085 g, 0.200 mmol) in THF (5 mL). The resulting solution was allowed to stir for 15 min. No precipitate was observed upon mixing the reactants. The solvent was dried under vacuum to leave an off-white powder. Colorless blocks were obtained by slow diffusion of hexanes into a THF solution of **2.6** at -5 °C. Yield 90% (0.267 g, 0.220 mmol). ¹H NMR (CD₂Cl₂, 298.1 K): δ 4.31 (d, 1H), 7.48 (m, 13H), 8.83 (d, 1H). ³¹P NMR (CD₂Cl₂, 298.1 K): δ 36.12, (s) ppm.

X-ray Crystallography

Crystallographic data were collected on crystals with dimensions 0.108 x 0.119 x 0.178 mm for **2.1**, 0.231 x 0.156 x 0.142 mm for **2.2**, 0.108 x 0.178 x 0.221 mm for **2.3**, 0.256 x 0.133 x 0.103 mm for **2.4**, 0.105 x 0.115 x 0.147 mm for **2.5**, 0.291 x 0.127 x 0.165 mm for **2.6**, 0.147 x 0.141 x 0.191 mm for **2.7**, 0.220 x 0.141 x 0.095 mm for **2.8** and 0.291 x 0.248 x 0.287 mm for **2.9**. Data were collected at 110 K on a Bruker X8 Apex using Mo K α radiation (λ = 0.71073 Å). All structures were solved by direct methods after correction of the data using SADABS.^{109,110} Crystal data are presented in Tables 2.10, 2.11 and 2.12. All the data were processed using the Bruker AXS SHELXTL software, version 6.10.¹¹¹ Unless otherwise noted, all non-hydrogen atoms were refined anisotropically and hydrogen atoms were placed in calculated positions.

Table 2.10. Crystallographic data for compounds **2.1** through **2.3**.

	2.1	2.2	2.3
Empirical formula	C ₄₀ H ₃₂ Hg ₂ N ₆ O ₂ P ₂ S ₄	C ₃₈ H ₃₂ HgN ₄ P ₂ S ₂	C ₃₆ H ₃₂ Cl ₄ Hg ₂ N ₂ O ₂ P ₂
Formula mass	610.06	871.33	1273.76
<i>a</i> (Å)	8.4467(6)	12.5734(10)	12.5791(7)
<i>b</i> (Å)	9.7171(7)	19.6504(15)	8.6549(4)
<i>c</i> (Å)	13.9400(10)	14.2674(15)	20.9536(10)
α (°)	76.694(3)	90.00	90°
β (°)	89.100(3)	90.00	96.738(2)
γ (°)	71.610(4)	90.00	90
<i>V</i> (Å ³)	1054.57(13)	3525.1(5)	2265.5(2)
<i>Z</i>	2	4	2
Crystal System	Triclinic	Orthorhombic	Monoclinic
Space Group	P-1	Aba2	P2(1)/n
T(K)	110(2)	110(2)	110(2)
D _{calcd.} (g/cm ⁻³)	1.921	1.642	1.867
μ (mm ⁻¹)	7.587	4.609	7.119
2 θ_{max} (°)	28.28°	28.24	28.28°
Reflections measured	16424	19700	36763
Reflections used	5164	9974	5635
Data / restraints / parameters	5164 / 0 / 253	2268 / 1 / 214	5635 / 0 / 262
R ₁ [<i>I</i> > 2 σ (<i>I</i>)]	0.0229	0.0165	0.0220
wR ₂ [<i>I</i> > 2 σ (<i>I</i>)]	0.0512	0.0438	0.0550
R(<i>F</i> ² _o) (all data)	0.0256	0.0189	0.0250
<i>R</i> _w (<i>F</i> ² _o) (all data)	0.0524	0.0451	0.0566
GOF on <i>F</i> ²	1.056	1.099	1.046

Table 2.11. Crystallographic data for compounds **2.4** through **2.6**.

	2.4	2.5	2.6
Empirical formula	C ₃₈ H ₃₂ HgN ₂ P ₂ F ₆ S ₂ O ₆	C ₃₈ H ₃₂ HgN ₂ P ₂ F ₆ S ₂ O ₈	C ₄₄ H ₄₀ Hg ₂ N ₆ O ₃ P ₂
Formula mass	1053.31	1085.31	1163.94
<i>a</i> (Å)	20.289(2)	30.2478(14)	9.8660(4)
<i>b</i> (Å)	9.8162(12)	25.6146(12)	14.0244(6)
<i>c</i> (Å)	19.468(2)	20.7312(9)	16.3177(7)
α (°)	90°	90	109.198(2)
β (°)	90°	93.707(2)	90.244(2)
γ (°)	90°	90	99.757(2)
<i>V</i> (Å ³)	3877.3(8)	16028.6(13)	2097.02(15)
<i>Z</i>	4	16	2
Crystal System	Orthorhombic	Monoclinic	Triclinic
Space Group	Pbcn	C2/c	P-1
T(K)	110(2)	110(2)	110(2)
D _{calcd.} (g/cm ⁻³)	1.804	1.799	1.843
μ (mm ⁻¹)	4.238	4.108	7.436
$2\theta_{max}$ (°)	28.29	28.33	28.26
Reflections measured	39442	71806	32544
Reflections used	4801	19917	10257
Data / restraints / parameters	4801 / 0 / 258	19917 / 0 / 1063	10257 / 10 / 530
R ₁ [<i>I</i> > 2σ(<i>I</i>)]	0.0227	0.0329	0.0288
wR ₂ [<i>I</i> > 2σ(<i>I</i>)]	0.0428	0.0670	0.0629
R(<i>F</i> ² _o) (all data)	0.0444	0.0544	0.0357
<i>R_w</i> (<i>F</i> ² _o) (all data)	0.0508	0.0749	0.0659
GOF on <i>F</i> ²	1.011	1.006	1.073

Table 2.12. Crystallographic data for compounds **2.7** through **2.9**.

	2.7	2.8	2.9
Empirical formula	C ₄₀ H ₃₂ F ₆ HgN ₂ O ₄ P ₂	C ₄₄ H ₃₈ F ₆ Hg ₂ N ₂ O ₇ P ₂	C ₃₈ H ₃₀ Hg ₂ N ₄ O ₂ P ₂ S ₂
Formula mass	981.21	1283.88	1101.90
<i>a</i> (Å)	10.6023(5)	9.6970(7)	9.9674(5)
<i>b</i> (Å)	12.5809(6)	10.7458(7)	9.2381(4)
<i>c</i> (Å)	15.4969(11)	21.5698(15)	20.0667(9)
α (°)	100.797(2)	83.9650(10)	90
β (°)	91.140(2)	89.9890(10)	98.738(2)
γ (°)	114.392(2)	83.808(2)	90
<i>V</i> (Å ³)	1838.28(18)	2222.0(3)	1826.29(15)
<i>Z</i>	2	2	2
Crystal System	Triclinic	Triclinic	Monoclinic
Space Group	P-1	P-1	P2(1)/c
T(K)	110(2)	110(2)	110(2)
D _{calcd.} (g/cm ⁻³)	1.773	1.919	2.004
μ (mm ⁻¹)	4.350	7.050	8.639
$2\theta_{max}$ (°)	28.32	28.27	28.31
Reflections measured	24590	31336	24348
Reflections used	9039	10889	4545
Data / restraints / parameters	9039 / 0 / 496	10889 / 0 / 568	4545 / 0 / 226
R ₁ [<i>I</i> > 2 σ (<i>I</i>)]	0.0222	0.0217	0.0158
wR ₂ [<i>I</i> > 2 σ (<i>I</i>)]	0.0550	0.0474	0.0338
R(<i>F</i> ² _o) (all data)	0.0249	0.0281	0.0176
<i>R_w</i> (<i>F</i> ² _o) (all data)	0.0561	0.0499	0.0343
GOF on <i>F</i> ²	1.058	1.024	1.083

CHAPTER THREE

Syntheses and Coordination Studies of 2-[(diphenylphosphino)methyl]pyridine *N,P*-Dioxide Towards Silver(I)

Introduction

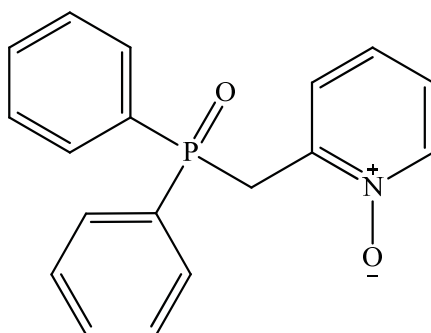
The design of new metallo-polymeric materials has become an important field of research in recent years. Much of the current interest stems from their usefulness in a variety of applications such as molecular sensing, separations, and storage, as well as catalysis and other functions.¹¹²⁻¹¹⁹ The ligand of choice for the building of these extended structures often incorporates the strongly binding carboxylate functionality as this provides exceptional stability. A variety of the other types of ligands are also being studied for the construction of these materials, among them are those containing phosphorus and or nitrogen. Nitrogen ligands particularly in the form of N-heterocyclics have become ubiquitous.¹¹⁹ The oxides of tertiary phosphines and pyridines also provide a possible entry into the arena of coordination polymers especially should the two functionalities be combined into a single ligand.

The capability of Ag^+ ions to coordinate in a wide range of coordination numbers and adopt different geometries, is known to give rise to materials with interesting structural motifs, functional properties and potential applications.^{118,120} The solid state packing has been shown to be strongly dependant on the ligand functionality, interacting ability of the anion, metal-metal interactions and supramolecular forces,^{118,121-129} variables that can be used to predict the molecular structure of the resulting product.

Regardless the soft nature of the Ag^+ , there are a number of reported examples of pyridine N-O moieties complexed to this metal ion,¹³⁰⁻¹³⁴ many of which form cluster

compounds due to the additional presence of bridging carboxylate groups. On the other hand, there are a limited number of examples of P=O bound to silver¹³⁵⁻¹³⁷ and only one previous example where the phosphoryl oxygen bridges two Ag centers.¹³⁵

The 2-[(diphenylphosphino)methyl]pyridine ligand, **L1**, has proven to have great versatility for the construction of new compounds, from discrete molecules to polymeric arrays, depending on its coordination mode.^{138,139} The fully oxidized counterpart of this ligand, **L3**, shown in scheme 3.1, bears a P=O and an N-O function, formally has five lone pairs of electrons located on the two oxide groups, a feature which we demonstrate greatly enhances its coordination ability. It can act as a bridge between to metal centers, as a chelating agent or it could even display both coordination modes simultaneously, as it can be seen in the following pages.



Scheme 3.1. Structure of 2-[(diphenylphosphino)methyl]pyridine *N,P*-dioxide (**L3**).

In this work we report the synthesis and characterization of three new coordination complexes of silver, as a contribution to the understanding of the systematic control on the coordination framework topology of these important materials. These complexes take advantage of the increased number of available lone pairs from the oxidized ligand to create novel coordination structures.

Results and Discussion

Synthesis

The ligand **L3** was synthesized according to a previously reported procedure.^{23,76,78} Crystals of **L3** were obtained by slow evaporation of a saturated methanol solution of the ligand. Pure **L3** is stable at room temperature and while expose to light, and can be stored for over a year with no sign of decomposition. Crystals of compounds **3.1** – **3.3** were obtained by layering or vapor diffusion recrystallization techniques using an appropriate solvent mixture, as noted in the experimental section. Complexes **3.1** – **3.3** were isolated as crystalline products regardless of initial reaction stoichiometry. These compounds were stable under normal conditions, showing no signs of decomposition at room temperature while exposed to light or air during short periods of time.

Description of the Crystal Structures

The crystal structure of ligand **L3** displays a nearly tetrahedral geometry about the phosphorus (Figure 3.1). The C-P-C angles are slightly smaller than 109.5° while the C-P-O angles are slightly greater than 109.5°. The P=O distance is 1.484 Å while the N-O distance is 1.315 Å. The oxygen atoms are oriented away from each other with a distance of 5.189 Å between them. Both oxygen atoms interact with hydrogen atoms on adjacent phenyl rings, being the shortest O···H distance 2.341 Å and the longest 2.851 Å. The C8-H8···O1, C14-H14···O1 and C18-H18···O2 angles are 102.1°, 99.9° and 165.0°, respectively. The oxygen atom O1 also interacts with one of the methylene hydrogen

atoms ($\text{O}\cdots\text{H}$ distance = 2.249 Å; $\text{C-H}\cdots\text{O}$ angle 110.5°). Selected angles and interatomic distances for compound **L3** are given in Table 3.1.

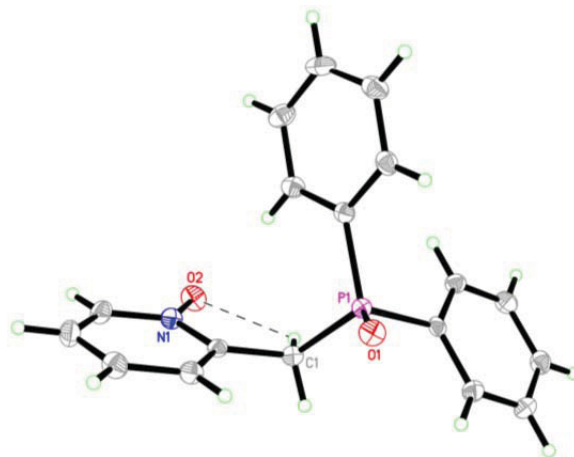


Figure 3.1. Thermal ellipsoid of **L3** with an atomic numbering scheme. Ellipsoids are shown at the 50% level.

Table 3.1. Selected bond lengths and angles for 2-[(diphenylphosphino)methyl]pyridine *N,P*-dioxide (**L3**).

P(1)-O(1)	1.4843(12)	O(1)-P(1)-C(7)	113.15(7)
P(1)-C(13)	1.8005(17)	O(1)-P(1)-C(1)	113.59(7)
P(1)-C(7)	1.8043(17)	C(13)-P(1)-C(1)	108.68(8)
P(1)-C(1)	1.8148(17)	C(7)-P(1)-C(1)	101.46(8)
O(2)-N(1)	1.3152(18)	O(2)-N(1)-C(6)	118.99(14)
N(1)-C(6)	1.360(2)	O(2)-N(1)-C(2)	120.79(14)
N(1)-C(2)	1.369(2)	C(6)-N(1)-C(2)	120.21(14)
C(16)-C(17)	1.383(3)	C(2)-C(1)-P(1)	115.43(12)
C(17)-C(18)	1.389(3)	N(1)-C(2)-C(3)	119.02(15)
		N(1)-C(2)-C(1)	117.69(14)

Complex **3.1** was obtained by the reaction of one equiv. of **L3** and three equiv. of AgTfa. The structure consists of a polynuclear silver complex in a 1:3 ligand-to-metal ratio.

The unique portion of the molecule is formed by the three silver atoms Ag1, Ag2 and Ag3, three Tfa⁻ counter-anions and one **L3** ligand unit.

The complete structure, shown in Figure 3.2, displays a hexa-nuclear metal core supported by two ligands and six Tfa⁻ counter-anions.

This complex possesses an inversion center which passes through the Ag2-Ag2A axis.

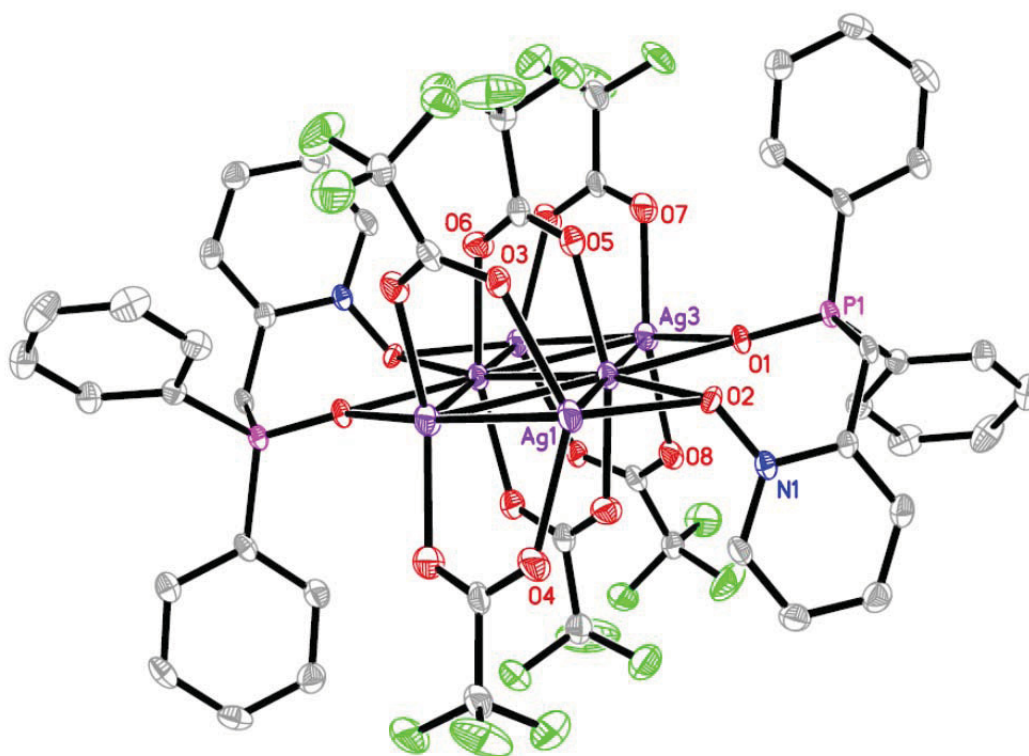


Figure 3.2. Thermal ellipsoid of **3.1** with an atomic numbering scheme. Ellipsoids are shown at the 50% level. Hydrogen atoms have been removed for clarity.

The metal core displays a planar framework of interacting silver centers in a parallelogram form and contains four nearly ideal equilateral triangles, as illustrated in Figure 3.3. All the Ag $\cdots$ Ag distances are in the range 2.871–3.074 Å, being much shorter than the sum of the van der Waals radii for silver (3.44 Å).

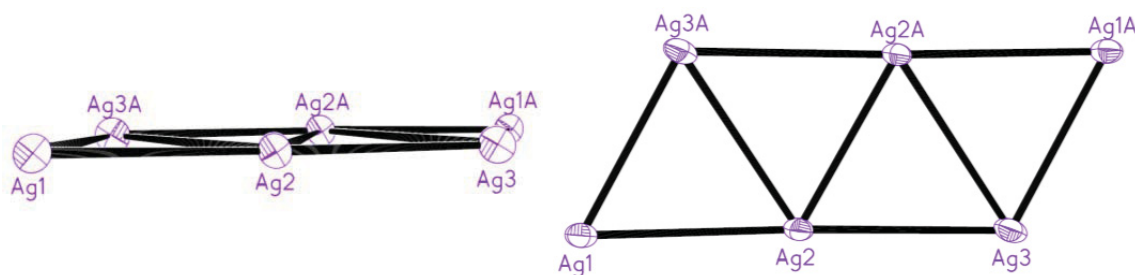


Figure 3.3. Geometric arrangement of the metal core of complex **3.1**.

The silver center Ag1 is penta-coordinate and interacts with the oxygen atom from the pyridyl group of one ligand (Ag1-O2 distance = 2.377 Å), and two oxygen atoms from two different anions (Ag1-O3 and Ag1-O4 = 2.246 Å and 2.252 Å, respectively). The coordination number of five is completed by the argentophilic interaction of Ag1 with two other Ag atoms (average Ag-Ag distance = 2.945 Å). The coordination sphere around Ag2 is eight-coordinate.

The Ag ion interacts with two oxygen donors from two different anions (Ag2-O5; Ag2-O6A distances = 2.194 Å; 2.202 Å) and the two oxygen atoms from the P=O and N-O groups of one ligand (Ag-O distances: Ag2-O1 = 2.457 Å and Ag1-O2 = 2.462 Å, respectively). The coordination number is completed by the argentophilic interaction of Ag2 with Ag1, Ag3, Ag2A and Ag3A, with an average Ag $\cdots$ Ag contact of 3.01 ± 0.09 Å (Ag $\cdots$ Ag contact distances: Ag2-Ag1 = 3.064 Å; Ag2-Ag3 = 3.073 Å; Ag2-Ag2A = 2.871 Å; Ag2-Ag3A = 3.034 Å). A search based on the Cambridge Structural Database (CSD) reported that from 3,319 crystal structures containing silver ions coordinated to non-metal atoms, only 0.3% are eight-coordinate making it the least common coordination number for this metal ion.¹³⁸ The silver center Ag3 coordinates to two oxygen donors from two different Tfa⁻ anions (Ag-O7 and Ag-O8 distances = 2.187 Å and 2.195 Å, respectively), the oxygen atom from the ligand P=O function (Ag3-O1

distance = 2.406 Å) and three other silver atoms (average Ag $\cdots$ Ag distance = 3.018 $\pm$ 0.063 Å), completing a coordination number of six.

The supramolecular interactions are reinforced by F $\cdots$ H-C bonding with H $\cdots$ F distance range of 2.609-2.979 Å and F $\cdots$ H-C angle range of 145.1-153.2°. Interactions of this kind are illustrated in Figure 3.4, between F4B and H3, with H $\cdots$ F distance of 2.609 Å and F $\cdots$ H-C angle of 153.2°. Selected angles and interatomic distances for compound **3.1** are given in Table 3.2.

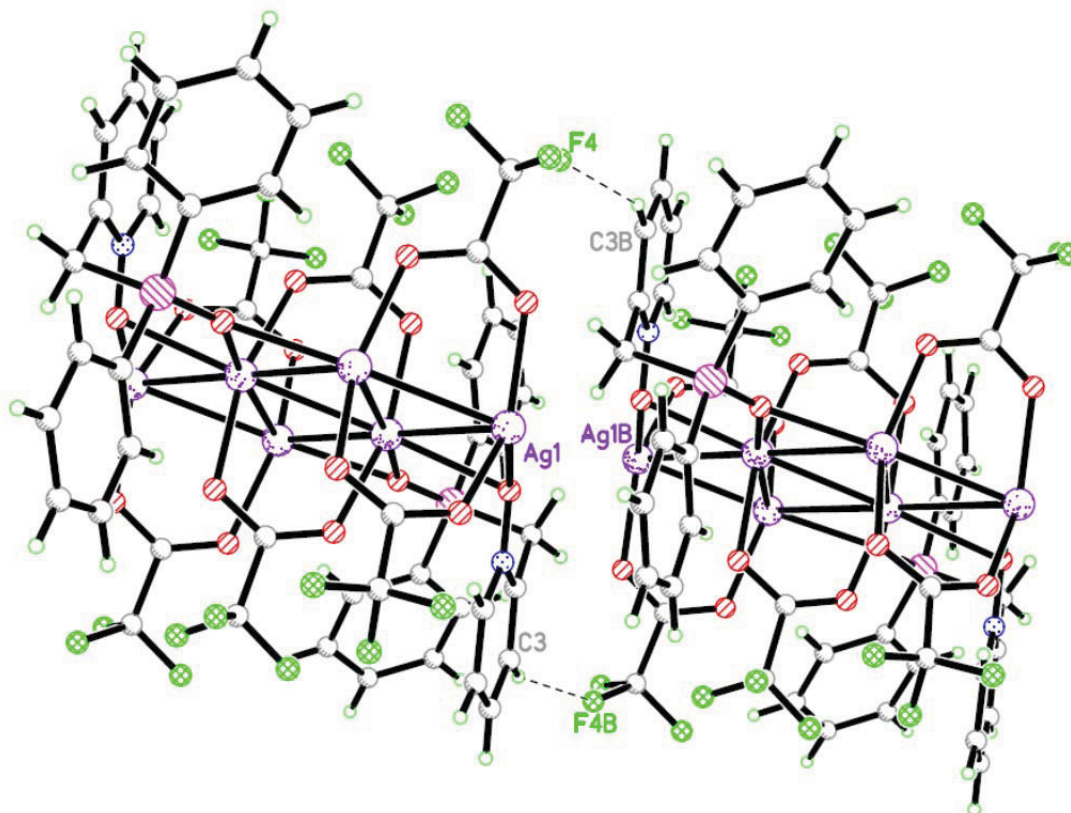


Figure 3.4. Intermolecular hydrogen bonding (F $\cdots$ H-C) in compound **3.1**.

There is a subtle N-O or P=O bond elongation in the complex compared to the free ligand **L3**. The P1-O1-Ag2 and P1-O1-Ag3 angles are nearly equal (140.6° and

139.7°, respectively) while the N1-O2-Ag1 and N1-O2-Ag2 are 126.1° and 109.1°, respectively.

Table 3.2. Selected bond lengths (Å) and angles (°) for compound **3.1**.^{*}

Ag(1)-O(3)	2.246(2)	Ag(2)-O(2)	2.467(2)
Ag(1)-O(4)	2.252(2)	Ag(2)-Ag(2)#1	2.8715(5)
Ag(1)-O(2)	2.377(2)	Ag(2)-Ag(3)#1	3.0337(4)
Ag(1)-Ag(3)#1	2.9492(4)	Ag(2)-Ag(3)	3.0734(4)
Ag(1)-Ag(2)	3.0641(4)	Ag(3)-O(7)	2.187(2)
Ag(2)-O(5)	2.194(2)	Ag(3)-O(8)	2.195(2)
Ag(2)-O(6)#1	2.202(2)	Ag(3)-O(1)	2.406(2)
Ag(2)-O(1)	2.457(2)	N(1)-O(2)	1.335(3)
P(1)-O(1)	1.496(2)		
O(3)-Ag(1)-O(4)	138.19(8)	O(6)#1-Ag(2)-Ag(1)	91.76(6)
O(3)-Ag(1)-O(2)	113.86(7)	O(1)-Ag(2)-Ag(1)	128.16(5)
O(4)-Ag(1)-O(2)	105.83(8)	O(2)-Ag(2)-Ag(1)	49.46(5)
O(3)-Ag(1)-Ag(3)#	77.99(5)	Ag(2)#1-Ag(2)-Ag(1)	120.488(13)
O(4)-Ag(1)-Ag(3)#1	75.46(6)	Ag(3)#1-Ag(2)-Ag(1)	57.846(9)
O(2)-Ag(1)-Ag(3)#1	111.98(5)	O(5)-Ag(2)-Ag(3)	86.91(6)
O(3)-Ag(1)-Ag(2)	94.78(6)	O(6)#1-Ag(2)-Ag(3)	89.67(6)
O(4)-Ag(1)-Ag(2)	99.51(6)	O(1)-Ag(2)-Ag(3)	50.07(5)
O(2)-Ag(1)-Ag(2)	52.07(5)	O(2)-Ag(2)-Ag(3)	128.98(5)
Ag(3)#1-Ag(1)-Ag(2)	60.561(9)	Ag(2)#1-Ag(2)-Ag(3)	61.257(10)
O(5)-Ag(2)-O(6)#1	163.03(8)	Ag(3)#1-Ag(2)-Ag(3)	123.912(10)
O(5)-Ag(2)-O(1)	92.14(8)	Ag(1)-Ag(2)-Ag(3)	177.923(10)
O(6)#1-Ag(2)-O(1)	98.38(8)	O(7)-Ag(3)-O(8)	150.87(9)
O(5)-Ag(2)-O(2)	102.74(8)	O(7)-Ag(3)-O(1)	97.61(8)
O(6)#1-Ag(2)-O(2)	92.32(8)	O(8)-Ag(3)-O(1)	96.63(7)
O(1)-Ag(2)-O(2)	79.29(7)	O(7)-Ag(3)-Ag(1)#1	86.63(6)
O(5)-Ag(2)-Ag(2)#1	83.49(6)	O(8)-Ag(3)-Ag(1)#1	84.04(6)
O(6)#1-Ag(2)-Ag(2)#1	80.30(6)	O(1)-Ag(3)-Ag(1)#1	169.18(5)
O(1)-Ag(2)-Ag(2)#1	111.33(5)	O(7)-Ag(3)-Ag(2)#1	104.23(6)
O(2)-Ag(2)-Ag(2)#1	167.73(5)	O(8)-Ag(3)-Ag(2)#1	95.41(6)
O(5)-Ag(2)-Ag(3)#1	86.98(6)	O(1)-Ag(3)-Ag(2)#1	107.63(5)
O(6)#1-Ag(2)-Ag(3)#1	81.16(6)	Ag(1)#1-Ag(3)-Ag(2)#1	61.593(9)
O(1)-Ag(2)-Ag(3)#1	173.98(5)	O(7)-Ag(3)-Ag(2)	108.73(7)
O(2)-Ag(2)-Ag(3)#1	106.72(5)	O(8)-Ag(3)-Ag(2)	100.03(6)
Ag(2)#1-Ag(2)-Ag(3)#1	62.655(10)	O(1)-Ag(3)-Ag(2)	51.54(5)
O(5)-Ag(2)-Ag(1)	92.15(6)	Ag(1)#1-Ag(3)-Ag(2)	117.669(11)

^{*}Symmetry transformations used to generate equivalent atoms: #1 -x,-y+2,-z+1.

The reaction of two equiv. of **L3** with 3 equiv. of AgOTf yields the polymeric compound **3.2**. The one dimensional (1-D) polymeric chain, shown in Figure 3.5, consists of consecutive triads of silver atoms interconnected by a bridging $\text{Ag}(\text{OTf})_2^-$ unit. The $\text{Ag}\cdots\text{Ag}$ contact distance within a triad is 3.252 Å and the Ag-Ag-Ag angle is 180.0°. The argentophilic interactions are assisted by two ligand units, coordinated on either side of the trinuclear axis, and by two bidentate OTf⁻ anions, coordinated on each side of this same axis.

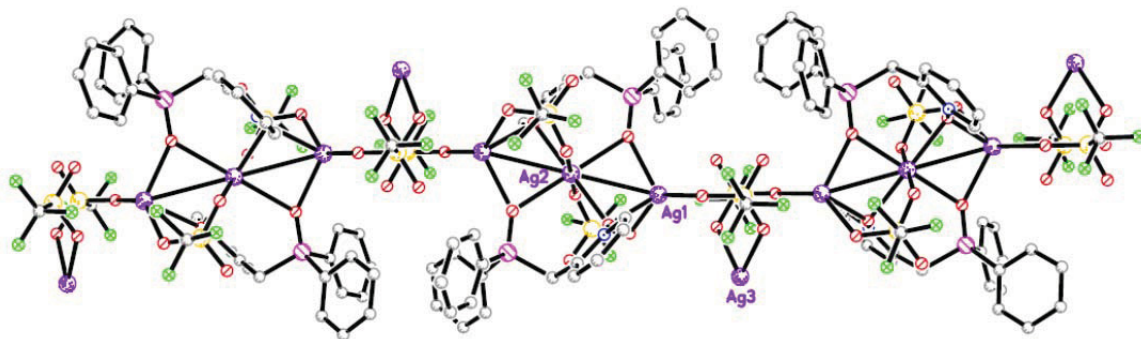


Figure 3.5. Perspective view of the one-dimensional (1D) polymeric structure of **3.2**.

The silver center Ag1 is five-coordinate, being bonded by two OTf⁻ anions through the oxygen atoms O6 and O4A (bond lengths: Ag1-O6 = 2.546 Å; Ag1-O4A = 2.411 Å), and the two oxygen atoms of the P1=O2 and N1-O1 functions from two different ligand units (bond lengths: Ag-O_{P1=O2} = 2.353 Å; Ag-O_{N1-O1} = 2.431 Å). The Ag1 $\cdots$ Ag2 interaction completes the penta-coordinate sphere of Ag1 (Figure 3.6).

As in complex **3.1**, the N-O and P=O bond lengths are very similar compared to those in the free ligand. The Ag-O average bond distance for complex **3.2** (2.412 ± 0.192 Å) is similar to that found for complex **3.1** (2.426 ± 0.042 Å).

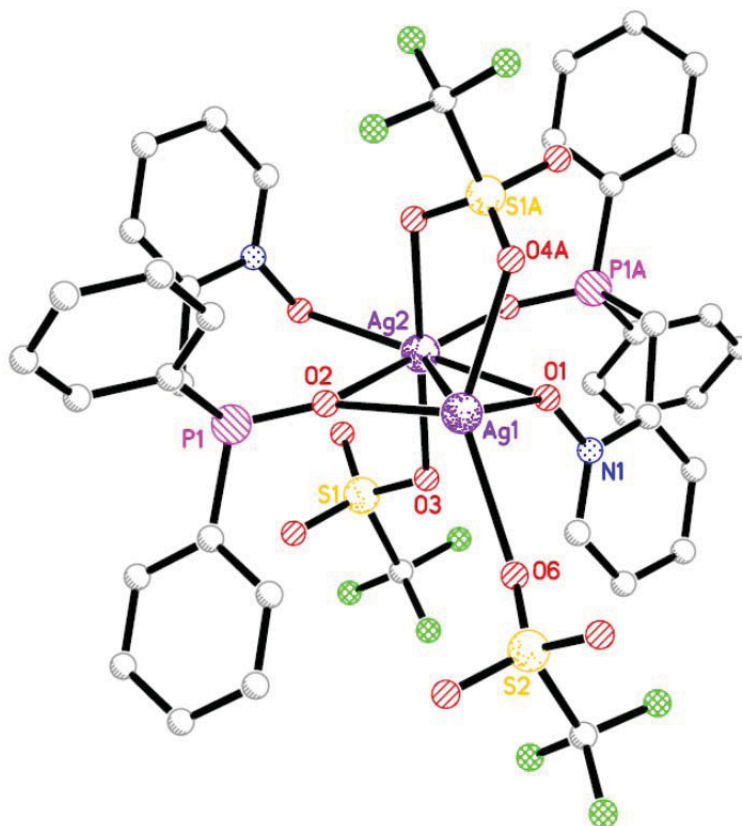


Figure 3.6. Perspective view of the penta-coordinate silver center Ag1 in complex **3.2**.

The uncommon eight-coordinate inner sphere environment around this metal center includes two oxygen donors, O3 and O3A, from two different OTf anions, (Ag-O distance = 2.502 Å), four oxygen donors from the bridging P=O and N-O functions of two bidentate ligand units (bond lengths: Ag2-O_{P=O} = 2.569 Å; Ag2-O_{N-O} = 2.356 Å), and two silver atoms, Ag1 and Ag1A, on each side (Ag $\cdots$ Ag distance = 3.252 Å).

The silver center Ag1 is five-coordinate, being bonded by two OTf anions through the oxygen atoms O6 and O4A (bond lengths: Ag1-O6 = 2.546 Å; Ag1-O4A = 2.411 Å), and the two oxygen atoms of the P1=O2 and N1-O1 functions from two different ligand units (bond lengths: Ag-O_{P1=O2} = 2.353 Å; Ag-O_{N1-O1} = 2.431 Å). The Ag1 $\cdots$ Ag2 interaction completes the penta-coordinate sphere of Ag1. As in complex **3.1**,

the N-O and P=O bond lengths are very similar compared to those in the free ligand. The Ag-O average bond distance for complex **3.2** (2.412 ± 0.192 Å) is similar to that found for complex **3.1** (2.426 ± 0.042 Å).

The central silver atom, Ag2, shown in Figure 3.7, is octa-coordinate and lies on a crystallographic inversion center.

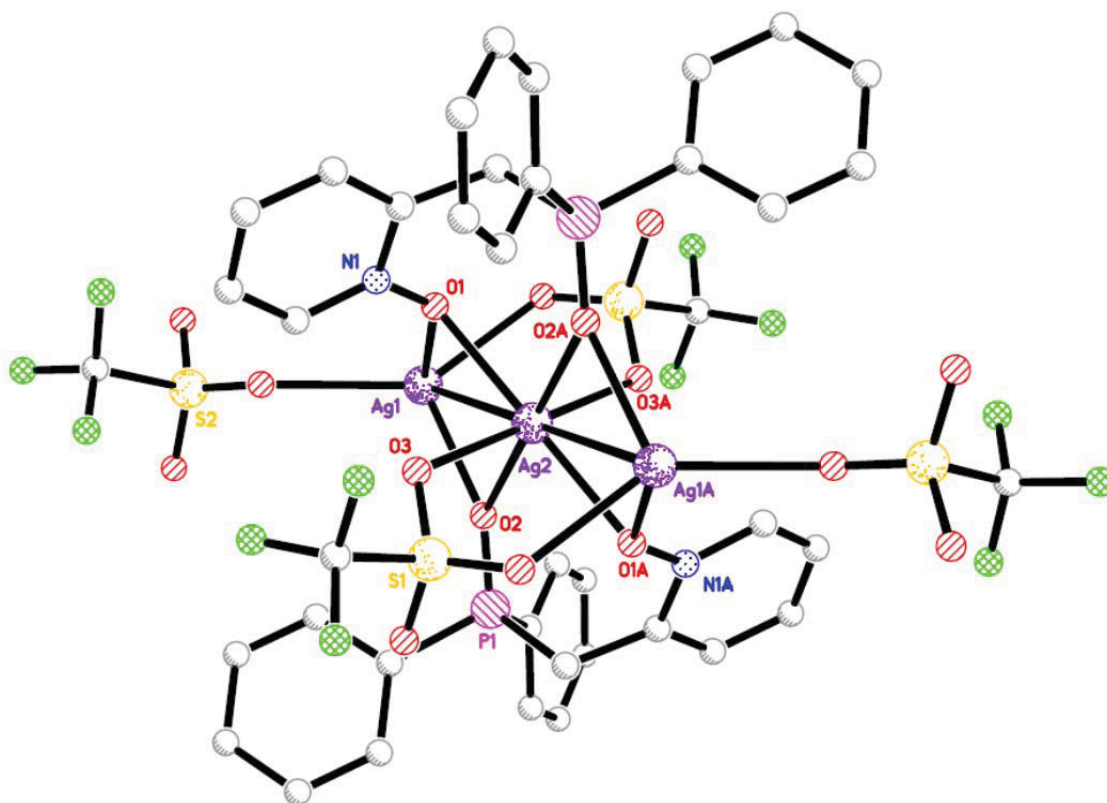


Figure 3.7. Perspective view of the octa-coordinate silver center Ag2 in complex **3.2**.

The uncommon eight-coordinate inner sphere environment around this metal center includes two oxygen donors, O3 and O3A, from two different OTf anions, (Ag-O distance = 2.502 Å), four oxygen donors from the bridging P=O and N-O functions of two bidentate ligand units (bond lengths: $\text{Ag2-O}_{\text{P=O}} = 2.569$ Å; $\text{Ag2-O}_{\text{N-O}} = 2.356$ Å), and two silver atoms, Ag1 and Ag1A, on each side ($\text{Ag}\cdots\text{Ag}$ distance = 3.252 Å).

The resulting linear macromolecule is propagated to a two-dimensional (2-D) network, shown in Figure 3.8, through the coordination of the distorted tetrahedral silver center Ag3 *via* a bis- η^2 interaction with two phenyl moieties in the adjacent polymeric chain.

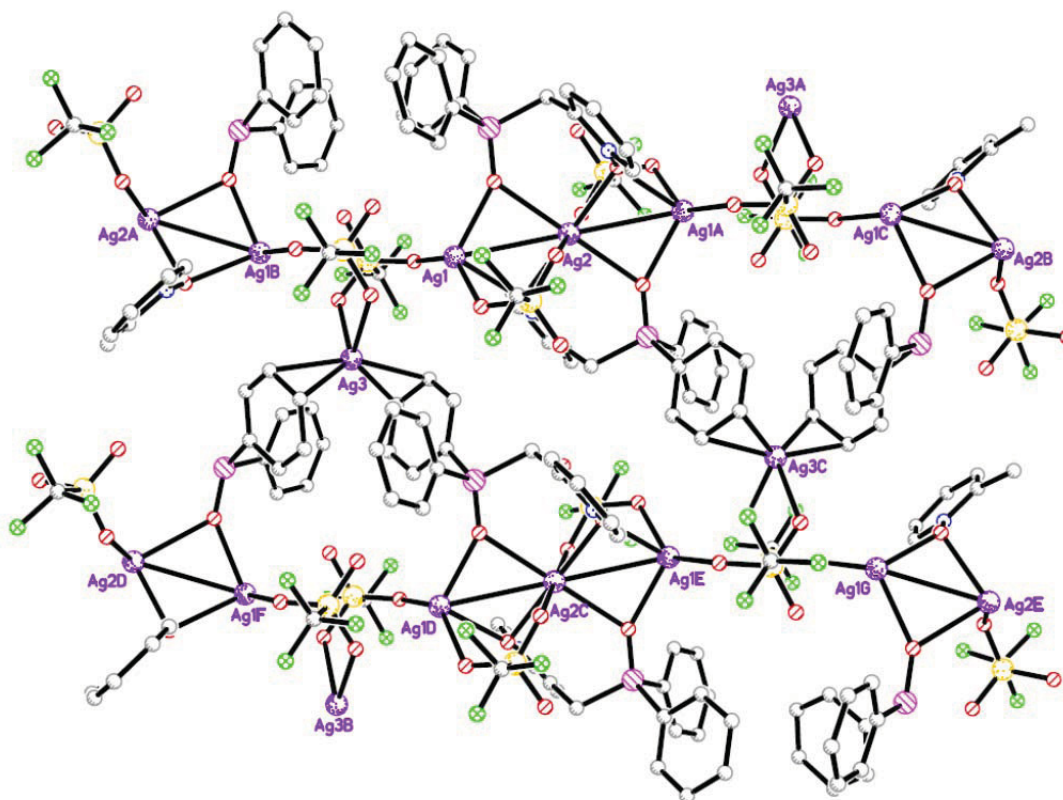


Figure 3.8. Perspective view of the two-dimensional (2D) silver(I) polymer sheet of **3.2**.

The tetrahedral geometry around Ag3, displayed in Figure 3.9, is completed by the interaction of this silver center with oxygen atoms from two bridging triflate groups (Ag3-O7 distance = 2.398 Å), with O7-Ag3-O7A angle of 88.4°. The Ag3-C16 and Ag3-C17 distances are 2.532 Å and 2.472 Å, respectively, with C16-Ag3-C17 angle of 32.4°. The distance from the Ag3 ion center to the center of the C16=C17 bond, C_{C1}, is 2.402 Å, with a C_{C1}-Ag3-C_{C2} angle of 140.1°, where C_{C2} represents the center of the C16A=C17A

bond. The angles O7A-Ag3-C_{C1} and O7A-Ag3-C_{C2} are 89.8° and 119.5°, respectively. The C16=C17 bond length (1.399 Å) shows a slight elongation, compared to the same C=C bond in the free ligand (1.382 Å).

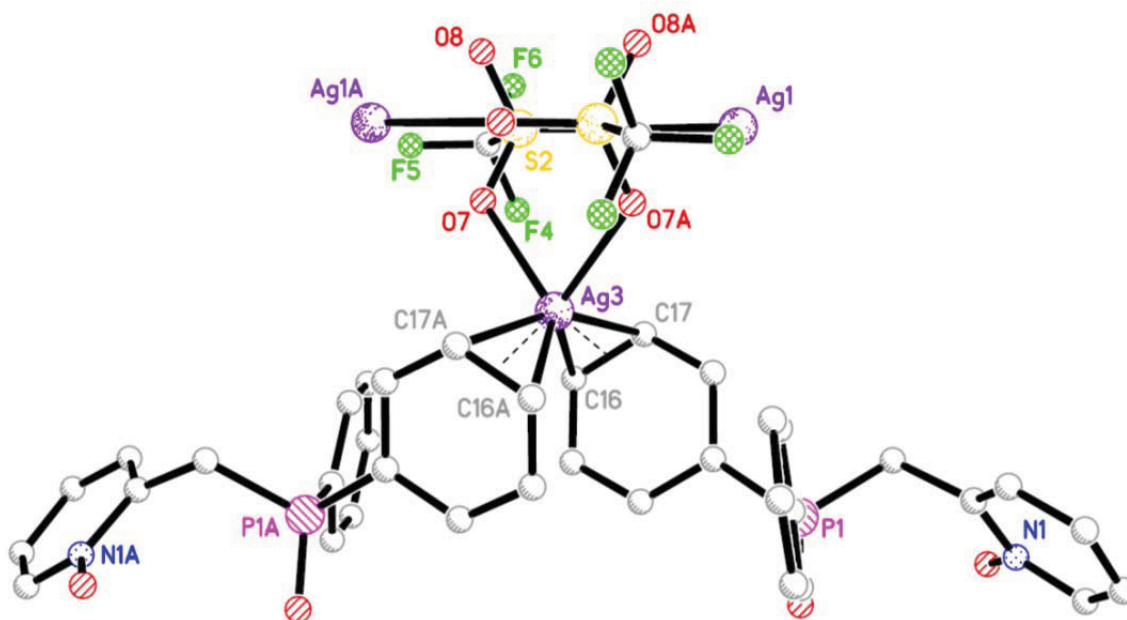


Figure 3.9. Perspective view of the pseudo-tetrahedral geometry around Ag3 in complex 3.2.

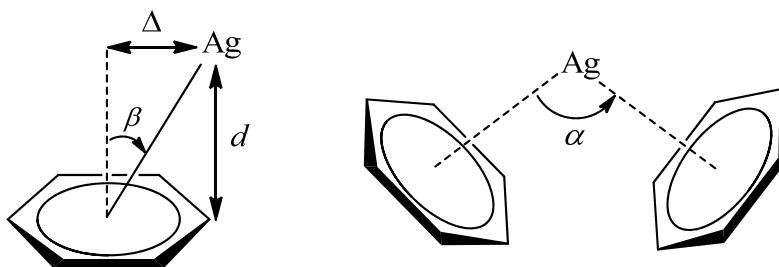
This observation suggests that the interaction between the silver center Ag3 and the π -faces of the phenyl moieties is mainly electrostatic (charge-induced dipole) in nature, with small back-donation of electronic density from the 4d orbitals of the silver ion into the π^* -²*p* orbitals of the C16=C17 bond. Also, this C16=C17 bond distance is shorter than that found by other research groups (1.405 Å) and those predicted by different computational approaches, including Density Functional Theory B3LYP (1.430 Å) and Hartree-Fock (1.403 Å), reported in other work.^{139,140}

Table 3.3. Selected bond lengths (Å) and angles (°) for compound **3.2**.*

Ag(1)-O(2)	2.346(4)	Ag(2)-O(2)	2.558(4)
Ag(1)-O(4)#1	2.416(6)	Ag(2)-Ag(1)#1	3.2523(5)
Ag(1)-O(1)	2.427(4)	Ag(3)-O(7)	2.392(5)
Ag(1)-O(6)	2.542(5)	Ag(3)-C(17)#3	2.459(6)
Ag(1)-Ag(2)	3.2523(5)	Ag(3)-C(16)#3	2.513(8)
Ag(2)-O(1)	2.345(5)	Ag(2)-O(3)	2.498(6)
P(1)-O(2)	1.492(4)	N(1)-O(1)	1.343(7)
O(2)-Ag(1)-O(4)#1	104.52(18)	O(3)#1-Ag(2)-Ag(1)	73.04(13)
O(2)-Ag(1)-O(1)	95.76(15)	O(3)-Ag(2)-Ag(1)	106.96(13)
O(4)#1-Ag(1)-O(1)	78.73(18)	O(2)-Ag(2)-Ag(1)	45.71(9)
O(2)-Ag(1)-O(6)	111.53(16)	O(2)#1-Ag(2)-Ag(1)	134.29(9)
O(4)#1-Ag(1)-O(6)	142.96(18)	O(1)-Ag(2)-Ag(1)#1	131.89(10)
O(1)-Ag(1)-O(6)	89.30(15)	O(1)#1-Ag(2)-Ag(1)#1	48.11(11)
O(2)-Ag(1)-Ag(2)	51.32(10)	O(2)-Ag(2)-Ag(1)#1	134.29(9)
O(4)#1-Ag(1)-Ag(2)	82.12(13)	Ag(1)-Ag(2)-Ag(1)#1	180.000(1)
O(1)-Ag(1)-Ag(2)	45.98(11)	O(7)-Ag(3)-O(7)#2	88.3(2)
O(6)-Ag(1)-Ag(2)	114.06(11)	O(7)-Ag(3)-C(17)#3	103.0(2)
O(1)-Ag(2)-O(1)#1	180.0(2)	O(7)#2-Ag(3)-C(17)#3	91.77(19)
O(1)-Ag(2)-O(3)#1	91.18(16)	O(7)#2-Ag(3)-C(17)#4	103.0(2)
O(1)-Ag(2)-O(3)	88.82(16)	C(17)#3-Ag(3)-C(17)#4	159.4(3)
O(3)#1-Ag(2)-O(3)	180.00(14)	O(7)-Ag(3)-C(16)#3	135.3(2)
O(1)-Ag(2)-O(2)	92.37(14)	O(7)#2-Ag(3)-C(16)#3	88.6(2)
O(1)#1-Ag(2)-O(2)	87.63(14)	C(17)#3-Ag(3)-C(16)#3	32.6(2)
O(3)-Ag(2)-O(2)	101.68(18)	C(17)#4-Ag(3)-C(16)#3	132.2(2)
O(3)-Ag(2)-O(2)#1	78.32(18)	O(1)-Ag(2)-Ag(1)	48.11(11)
O(2)-Ag(2)-O(2)#1	180.00(13)		

*Symmetry transformations used to generate equivalent atoms: #1 -x+2,-y+2,-z+1; #2 -x+2,y,-z+1/2; #3 -x+2,y+1,-z+1/2; #4 x,y+1,z; #5 x,y-1,z.

The distance between Ag3 and the main plane of the coordinated phenyl group, d , is 2.47 Å, with a deviation from the centroid axis, Δ , of 1.33 Å. The angular parameter β is 30.9° (Scheme 3.2), while the angle between the planes of the coordinated phenyl groups, α , is 100.8°. The structural parameters d , Δ and β found for Ag3 in complex **3.2** are consistent with those reported by Kochi as optimal (bonding) values ($d = 2.41 \pm 0.05$ Å; $\Delta = 1.53 \pm 0.2$ Å; $\beta = 32^\circ \pm 3^\circ$).¹⁴¹



Scheme 3.2. Structural features of Ag₃-arene in complex **3.2**.

The reaction between AgBF₄ and **L3** yields the one-dimensional polymeric compound **3.3**, with a 1:2 ligand-to-metal ratio. Similar to **3.2**, consecutive Ag-Ag-Ag triads are observed in complex **3.3**, resulting in a zigzag chain-like arrangement of silver atoms extended along the x axis, as illustrated in Figure 3.10. Within a triad, the Ag-Ag-Ag angle is 180° and the Ag⋯Ag contact distance is 3.199 Å, while between triads, the Ag-Ag-Ag angle is 162.5° and the Ag⋯Ag distance 3.224 Å. The metallophilic interactions are supported by the bridging P=O and N-O ligand functions and by two fluorine donors from one dual bridging BF₄[−] unit, which generates the loss of linearity along the polymeric structure, as shown in Figure 3.10 (right). The BF₄[−] anion also acts in a chelating fashion on Ag1 through F1 and F2, presenting the shortest Ag⋯F distances (Ag1⋯F1 = 2.807 Å and Ag1⋯F2 = 2.798 Å) in this complex. The Ag⋯F interactions distance range is 2.807-3.071 Å, with an average distance of 2.902 ± 0.128 Å. A search in the Cambridge Structural Database (CSD, version 5.32) showed 4 different crystal structures containing interactions between silver ions and BF₄[−] anions. All these structures were reported to act in a chelating fashion towards the silver centers.¹⁴²⁻¹⁴⁵ To the best of our knowledge, complex **3.3** is the first reported solid-state coordination compound where the BF₄[−] anion simultaneously acts in a chelating and a dual-bridging mode.

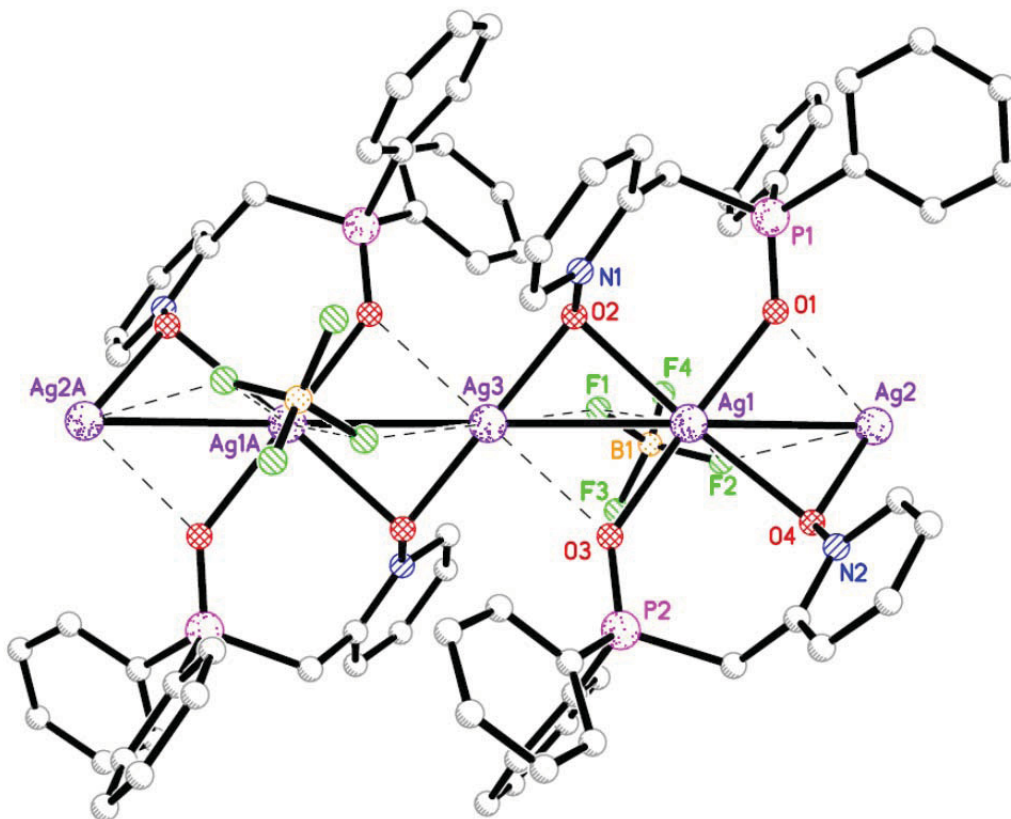


Figure 3.10. Perspective view of the one-dimensional (1D) polymeric structure of **3.3**.

The Ag-O_{P=O} distances range from 2.270 Å (Ag1-O3) to 2.680 Å (Ag3-O3), with an Ag-O_{P=O} average distance of 2.530 ± 0.226 Å, while the Ag-O_{N-O} distances range from 2.199 Å (Ag3-O2) to 2.512 Å (Ag1-O2), with an Ag-O_{N-O} average distance of 2.316 ± 0.170 Å. As in complexes **3.1** and **3.2**, the N-O and P=O bond distances in complex **3.3** present a small elongation when comparing to the free ligand. Nevertheless, these differences in bond distance fall within the experimental error. The Ag-O average bond distance for complex **3.3** (2.423 ± 0.214 Å) is also similar to that obtained for complexes **3.1** (2.426 ± 0.042 Å) and **3.2** (2.412 ± 0.192 Å).

The silver center Ag1, illustrated in Figure 3.11 (left), possesses an octa-coordinate environment, interacting with two silver centers (Ag-Ag-Ag angle = 162.5°;

Ag $\cdots$ Ag distances: Ag1-Ag2 = 3.224 Å; Ag1-Ag3 = 3.199 Å), two fluorine donors from one BF $_4^-$ unit (F1-Ag1-F2 angle = 47.8°; distances: Ag1-F1 = 2.807 Å, Ag1-F2 = 2.798 Å) and four oxygen atoms from the P=O and N-O functions of two ligand units.

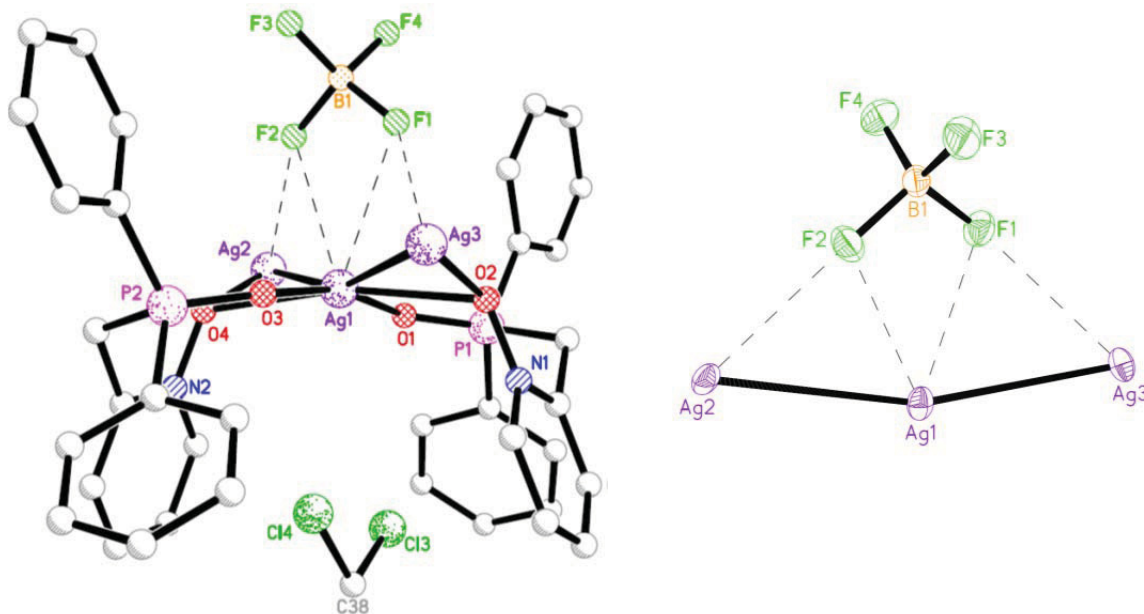


Figure 3.11. Coordination environment around the silver center Ag1 in complex **3.3** (left). Perspective view of the dual bridging mode of the BF $_4^-$ anion in complex **3.3** (right).

The Ag1-O_{P1=O1} and Ag1-O_{P2=O3} distances (2.265 Å and 2.270 Å, respectively) are shorter than the corresponding Ag1-O_{N1-O2} and Ag1-O_{N2-O4} (2.512 Å and 2.499 Å, respectively). The angles formed by the interaction of Ag1 with two oxygen atoms in the same ligand unit (O1-Ag1-O2 = 85.4° and O3-Ag1-O4 = 85.7°) are smaller than those formed by this same silver center and two oxygen atoms from two different ligand units (O2-Ag1-O3 = 94.7° and O4-Ag1-O1 = 91.5°). These angle differences can be attributed to the steric hindrance between the two ligand units generated by the bulky phenyl substituents.

A molecule of CH₂Cl₂ solvent is sitting in the pocket formed by the phenyl groups, with the chloride atoms oriented toward the electron deficient Ag¹ ion.

The metal center Ag₂, shown in Figure 3.12, displays a heavily distorted octahedral geometry, defined by the angles F2A-Ag₂-O4 (104.6°), F2A-Ag₂-O4A (75.4°) and the symmetry-forced straight angles Ag1A-Ag₂-Ag1, O4-Ag₂-O4A, F2B-Ag₂-F2A (180°).

The hexa-coordinate environment around Ag₂ is formed by the interaction of this silver ion with the two silver ions Ag1 and Ag1A (Ag···Ag distance: 3.224 Å), two fluorine donor from two BF₄⁻ anion units (Ag₂-F2 distance = 2.807 Å) and the N-O groups of two ligand units (bond length: Ag₂-O_{N2-O4} = 2.237 Å).

The bond length Ag₂-O_{N2-O4} is significantly shorter than the Ag-O_{N-O} distances in complexes **3.1** and **3.2**, where the Ag-O_{N-O} distance range is 2.35-2.43 Å. This contraction is also observed in the Ag-O_{P=O} bond lengths. In complex **3.1**, the Ag-O_{P=O} distance is 2.265 Å, while in **3.2** and **3.3** it is in the range of 2.35-2.57 Å. This suggests that the silver centers in **3.3** are more deficient in electron density than in complexes **3.1** and **3.2**, likely due to the poorer coordinating ability of the BF₄⁻ (Ag-F distance range = 2.935-3.071 Å) compared to the Tfa⁻ and OTf⁻, which can partially neutralize the charge on the silver ions more efficiently (Ag-O_{Tfa} and Ag-O_{OTf} distance range = 2.187-2.252 Å and 2.398-2.546 Å, respectively). As a result of this, in addition to the steric effects imposed by the bulky ligands, coulombic repulsions between inter-chain Ag⁺ centers contribute to the separation of adjacent macromolecules in **3.3**, with chain-chain distances of 10.784 Å.

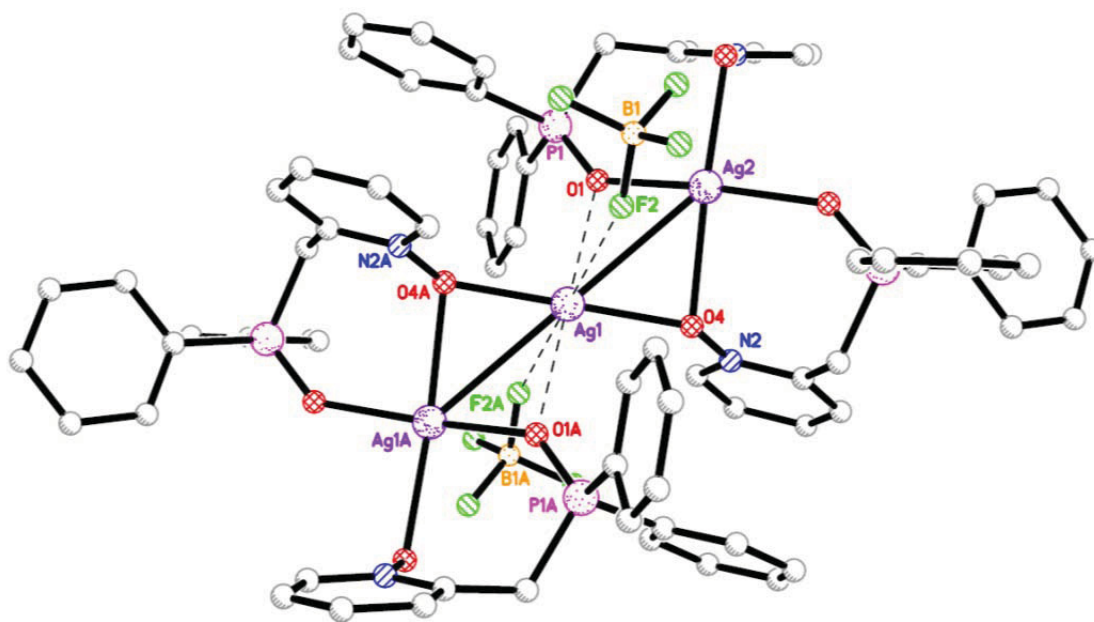


Figure 3.12. Coordination environment around the silver center Ag2 in complex **3.3**.

The silver center Ag3 presents an octa-coordinate environment, as shown in Figure 3.13. The geometry around this silver center is formed by its interaction with the two silver ions Ag1 and Ag1A ($\text{Ag}\cdots\text{Ag}$ distance: 3.199 Å), two fluorine donor from two BF_4^- anion units (bond length: $\text{Ag2-F2} = 3.071$ Å) and the N-O groups of two ligand units (bond length: $\text{Ag2-O}_{\text{N1-O2}} = 2.199$ Å).

The angles F1-Ag3-F1A , Ag1-Ag3-Ag1B and O2-Ag3-O2B are forced to 180° by symmetry, while the angles F1-Ag3-Ag1 , F1-Ag3-O2 and Ag1-Ag3-O2 are 53.1° , 71.1° and 51.5° , respectively. Table 3.4 lists selected bond lengths and angles for compound **3.3**.

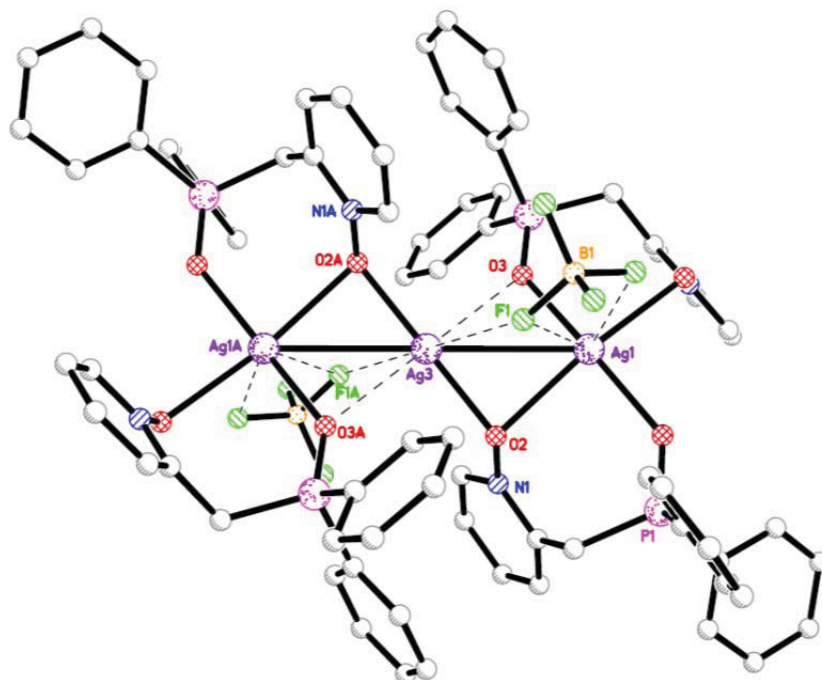


Figure 13. Coordination environment around the silver center Ag3 in complex 4.

Table 3.4. Selected bond lengths (Å) and angles (°) for compound **3.3**.*

Ag(1)-O(1)	2.265(2)	Ag(2)-O(4)	2.237(2)
Ag(1)-O(3)	2.270(2)	Ag(3)-O(2)	2.199(2)
Ag(1)-O(4)	2.499(3)	Ag(1)-Ag(2)	3.2244(3)
Ag(1)-O(2)	2.512(3)	P(1)-O(1)	1.503(3)
Ag(1)-Ag(3)	3.1990(3)	P(2)-O(3)	1.498(3)
O(2)-N(2)	1.348(4)	O(4)-N(2)	1.348(4)
O(1)-Ag(1)-O(3)	166.68(9)	O(2)-Ag(1)-Ag(2)	137.79(6)
O(1)-Ag(1)-O(4)	91.46(8)	Ag(3)-Ag(1)-Ag(2)	162.463(10)
O(3)-Ag(1)-O(4)	85.67(8)	O(4)-Ag(2)-O(4)#1	180.000(1)
O(1)-Ag(1)-O(2)	85.39(8)	O(4)-Ag(2)-Ag(1)#1	129.39(6)
O(3)-Ag(1)-O(2)	94.72(8)	O(4)-Ag(2)-Ag(1)	50.61(6)
O(4)-Ag(1)-O(2)	167.87(8)	O(4)#1-Ag(2)-Ag(1)	129.39(6)
O(1)-Ag(1)-Ag(3)	127.81(6)	Ag(1)#1-Ag(2)-Ag(1)	180.0
O(3)-Ag(1)-Ag(3)	55.60(6)	O(2)#2-Ag(3)-O(2)	180.00(10)
O(4)-Ag(1)-Ag(3)	140.65(6)	O(2)#2-Ag(3)-Ag(1)	128.50(7)
O(2)-Ag(1)-Ag(3)	43.24(5)	O(2)-Ag(3)-Ag(1)	51.50(7)
O(1)-Ag(1)-Ag(2)	54.15(6)	Ag(1)-Ag(3)-Ag(1)#2	180.0
O(3)-Ag(1)-Ag(2)	127.46(6)		

*Symmetry transformations used to generate equivalent atoms: #1 -x+2,-y,-z+1; #2 -x+2,-y+1,-z+1.

NMR Spectroscopy

Complexes **3.1** – **3.3** were characterized by multinuclear NMR spectroscopy. The internal reference TMS and the external H_3PO_4 were used for ^1H NMR and ^{31}P NMR, respectively. The NMR spectra for **3.1**, **3.2** and **3.3** were recorded in acetonitrile- d_3 , methanol- d_4 and CD_2Cl_2 solutions, respectively. These spectra did not show significant variations in the ^{31}P NMR chemical shift compared to the free ligand **L3**. Chemical shift and proton integration values are provided in the experimental section.

Conclusions

Three novel silver(I)-2-[(diphenylphosphino)methyl]pyridine *N,P*-dioxide complexes have been synthesized and characterized by elemental analysis, multinuclear NMR spectroscopy techniques and single-crystal X-ray crystallography. The molecular structure of the complexes showed a strong dependence on the counter-anion coordination properties, steric hindrance imposed by the bulkiness of the ligand substituents, and weak supramolecular forces, such as π -metal interactions and coulombic interactions between the silver centers. The counter-anions and ligand's ability to act in a polydentate manner gave support to the molecular structures to yield the hexa-nuclear Ag^+ cluster **3.1** and the polymeric complexes **3.2** and **3.3**. The linearity of **3.2** was severely affected by the interaction of the OTf^- counter-anions with the metal centers. On the other hand, complex **3.3** showed a zigzag chain-like arrangement of silver atoms extended along the polymeric backbone, a product of the weak interactions of the BF_4^- counter-anions with the silver ions. The structural parameters d , Δ and β found for the Ag-arene interactions in complex **3.2** showed consistency with those previously reported in other work as optimal bonding values.

Experimental Section

General Remarks

All experiments were performed under nitrogen atmosphere using Schlenk techniques. All air and light sensitive compounds were stored and handled in an inert atmosphere glovebox and used as received. All solvents were reagent-grade and distilled under inert atmosphere from the appropriate drying agent right before use. ^1H NMR and ^{31}P NMR spectra were recorded at 499.78 and 202.31 MHz respectively, at 25.0 °C / 298.1 K MHz, using a Varian VNMRs 500 MHz Spectrometer. Elemental analyses were performed by Atlantic Microlabs Inc. in Norcross, Georgia. Yields for compounds **3.1** – **3.3** were calculated with respect to **L3**.

Preparation

Synthesis of AgTfa(L3) (3.1). A solution of **L3** (0.061 g, 0.200 mmol) in CH_2Cl_2 (5 mL) was added to a solution of Ag(Tfa), (0.132 g, 0.600 mmol), in CH_2Cl_2 (5 mL). The resulting solution was allowed to stir for 5 min and then dried under vacuum to leave an off-white powder. This was then dissolved in a small amount of CH_2Cl_2 and precipitated with ether (30 mL). Colourless blocks were obtained by slow diffusion of ether into a CH_2Cl_2 solution of **3.1** at 5°C. Yield 68.5 % (0.133 g). ^1H NMR (CD_3OD , 298.1 K): δ = 4.42 (d, 2H), 7.54 (m, 13H), 8.28 (d, 1H). ^{31}P NMR (CD_3OD , 298.1 K): δ = 34.59, (s) ppm. Anal. Calc. for $\text{C}_{24}\text{H}_{16}\text{Ag}_3\text{F}_9\text{NO}_8\text{P}\cdot 2\text{CH}_2\text{Cl}_2$ (971.95): C, 27.35; H, 1.76; N, 1.22. Found: C, 27.04; H, 1.34; N, 1.20 %.

Synthesis of AgOTf(L3) (3.2). A solution of **L3** (0.0635 g, 0.205 mmol) in CH_2Cl_2 (5 mL) was added to a solution of AgOTf (0.112 g, 0.410 mmol) in CH_2Cl_2 (5

mL). The resulting solution was allowed to stir for 10 min and then dried under vacuum to leave an off-white powder. This was then dissolved in a small amount of CH₂Cl₂ and precipitated with ether (30 mL). Colorless blocks were obtained by layering ether into a CH₂Cl₂ solution of **3.2** at 5°C. Yield 84.1 % (0.142 g). ¹H NMR (CD₃CN, 298.1 K): δ = 4.24 (d, 2H), 7.49 (m, 13H), 8.07 (d, 1H). ³¹P NMR (CD₃CN, 298.1 K): δ = 29.82, (s) ppm. Anal. Calc. for C₂₀H₁₆Ag₂F₆NO₈PS₂•2CH₂Cl₂ (823.18): C, 26.60; H, 2.03; N, 1.41. Found: C, 26.20; H, 1.92; N, 1.54%.

Synthesis of AgBF₄(L3) (3.3). A solution of **L3** (0.068 g, 0.220 mmol) in CH₂Cl₂ (5 mL) was added to a solution of AgBF₄ (0.086 g, 0.440 mmol) in CH₂Cl₂ (5 mL). The resulting solution was allowed to stir for 10 min and then dried under vacuum to leave an off-white powder. This was then dissolved in a small amount of CH₂Cl₂ and precipitated with ether (30 mL). Colorless blocks were obtained by layering ether into a CH₂Cl₂ solution of **3.3** at 5°C. Yield 74.5 % (0.163 g). ¹H NMR (CD₂Cl₂, 298.1 K): δ = 4.22 (d, 2H), 7.48 (m, 13H), 8.06 (d, 1H). ³¹P NMR (CD₂Cl₂, 298.1 K): δ = 41.99, (s) ppm. Anal. Calc. for C₃₆H₃₂Ag₂B₂F₈N₂O₄P₂•CH₂Cl₂xH₂O (1007.95): C, 40.00; H, 3.26; N, 2.52. Found: C, 39.79; H, 3.37; N, 2.53%.

X-ray Crystallographic Analysis

Crystallographic data was collected on crystals with dimensions 0.297 x 0.130 x 0.118 mm for **L3**, 0.243 x 0.083 x 0.081 mm for **3.1**, 0.067 x 0.193 x 0.100 mm for **3.2** and 0.050 x 0.136 x 0.140 mm for **3.3**. Summary of the crystallographic data is shown in tables **3.5** and **3.6**. Full tables of bond lengths and angles can be found in Appendix B. Data was collected at 110 K on a Bruker X8 Apex using Mo-K radiation (λ = 0.71073 Å).

Table 3.5. Crystallographic data for compounds **L3** and **3.1**.

	L3	3.1
Empirical formula	C ₁₈ H ₁₆ NO ₂ P	C ₄₈ H ₃₂ Ag ₆ F ₁₈ N ₂ O ₁₆ P ₂
Formula mass	309.29	1943.92
<i>a</i> (Å)	10.6764(4)	10.4423(9)
<i>b</i> (Å)	7.8602(3)	11.7176(9)
<i>c</i> (Å)	35.7789(12)	13.0240(11)
α (°)	90	84.704(4)
β (°)	90	66.423(3)
γ (°)	90	81.360(4)
<i>V</i> (Å ³)	3002.52(19)	1443.1(2)
<i>Z</i>	8	1
Crystal System	Orthorhombic	Triclinic
Space Group	Pbca	P-1
T(K)	110(2)	110(2)
D _{calcd.} (g/cm ⁻³)	1.368	2.237
μ (mm ⁻¹)	0.190	2.179
$2\theta_{max}$ (°)	26.72	25.35
Reflections measured	26503	30768
Reflections used	3173	5218
Data / restraints / parameters	3173/0/199	5218/0/415
R ₁ [<i>I</i> > 2σ(<i>I</i>)]	0.0383	0.0238
wR ₂ [<i>I</i> > 2σ(<i>I</i>)]	0.0835	0.0526
R(<i>F</i> ² _o) (all data)	0.0523	0.0360
<i>R_w</i> (<i>F</i> ² _o) (all data)	0.0901	0.0579
GOF on <i>F</i> ²	1.054	1.021

Table 3.6. Crystallographic data for compounds **3.2** and **3.3**.

	3.2	3.3
Empirical formula	C ₂₁ H ₁₈ Ag ₂ Cl ₂ F ₆ NO ₈ PS ₂	C ₃₈ H ₃₆ Ag ₂ B ₂ Cl ₄ F ₈ N ₂ O ₄ P ₂
Formula mass	908.09	1177.79
<i>a</i> (Å)	26.8758(13)	11.5012(7)
<i>b</i> (Å)	9.6622(5)	12.6965(8)
<i>c</i> (Å)	23.8190(12)	15.0632(10)
α (°)	90	85.727(4)
β (°)	114.924(2)	81.373(4)
γ (°)	90	77.937(3)
<i>V</i> (Å ³)	5609.2(5)	2124.6(2)
<i>Z</i>	8	2
Crystal System	Monoclinic	Triclinic
Space Group	C2/c	P-1
T(K)	110(2)	110(2)
D _{calcd.} (g/cm ⁻³)	2.151	1.841
μ (mm ⁻¹)	1.881	1.328
2 θ_{max} (°)	26.36	26.66
Reflections measured	39988	27334
Reflections used	5703	8748
Data / restraints / parameters	5703/0/390	8748/0/562
R ₁ [<i>I</i> > 2 σ (<i>I</i>)]	0.0531	0.0370
wR ₂ [<i>I</i> > 2 σ (<i>I</i>)]	0.1560	0.0723
R(<i>F</i> ² _o) (all data)	0.0685	0.0598
R _w (<i>F</i> ² _o) (all data)	0.1692	0.0816
GOF on <i>F</i> ²	1.071	1.016

All structures were solved by direct methods after correction of the data using SADABS.^{109,110} All the data were processed using the Bruker AXS SHELXTL software, version 6.10.¹¹¹ Unless otherwise noted, all non-hydrogen atoms were refined anisotropically and hydrogen atoms were placed in calculated positions.

CHAPTER FOUR

Syntheses and Coordination Studies of 2-[(diphenylphosphino)methyl]pyridine *N,P* Dioxide towards Tetrafluoroborate Salts of Co^{2+} , Ni^{2+} , Cu^{2+} and Zn^{2+}

Introduction

Chelating ligands and their coordination behavior have been studied for a long time. They have received great attention due to their ability to coordinate to transition metals, an important characteristic in many biological processes and industrial applications, such as metal ion extraction,¹⁴⁶⁻¹⁵⁰ synthesis of new luminescent and polymeric materials and homogeneous catalysis, treatment of human diseases related to metal overload (e.g. hemochromatosis,¹⁵¹⁻¹⁵³ saturnism,^{154,155} aluminum overload,^{156,157} among others.¹⁵⁸⁻¹⁶⁵

It is known that anionic or neutral ligands with strong oxygen donor centers form stable coordination complexes with hard acids. Due to this important characteristic, monofunctional ligands containing phosphoryl or nitrosyl groups have been used to study fundamental coordination chemistry in order to explore and ultimately improve those properties that make these coordination complexes so attractive for the applications mentioned above. For example, chelating phosphine oxides have been used in the synthesis of new luminescent materials due to their ability of stabilizing metal centers with higher oxidation state.¹⁶⁶ Also, they possess an enhanced capacity to improve both photoluminescent and electroluminescent properties of these complexes through the reduction of solvent-induced quenching and improvement of intramolecular electron transfer.¹⁶⁷ These ligands have also shown to be good extractants for lanthanide and actinide ions under specific conditions.^{168,169} Recently, Rosario-Amorin described the

synthesis of monofunctional P=O-containing ligands and their coordination properties towards several *f*-block metal cations. In this study they showed that these ligands could be used for liquid-liquid solvent extraction of hard acceptor ions.¹⁷⁰

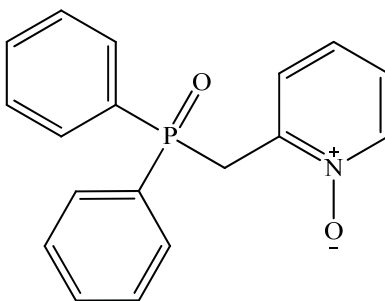
The design of compounds based on *N*-oxides has been of interest due to their dual application in both metal-free catalytic transformations, mostly organosilicon-based chemistry, and as ligands in metal-based catalysis.¹⁷¹ Liang synthesized different monofunctional ligands containing N-O groups and investigated their role in the Cu-catalyzed *N*-arylation of imidazoles using water as a solvent. They found that ligands based on pyridine *N*-oxides were more beneficial to the catalytic process than their pyridine analogues. The higher catalytic activities obtained were partly attributed to their excellent solubility in water, and out of three different N-O-containing ligands employed, the bidentate more flexible one gave the highest yield.¹⁷² In 2009, Zhang developed a novel chiral indium complex, based on (*S*)-pipecolic acid-derived *N,N'*-dioxide ligands, for the enantioselective allylation of ketones. Their results showed that the novel chiral indium complex could be an efficient catalyst for this reaction yielding good enantioselectivity. In a more recent work, Liu synthesized a new family of *C*₂-symmetric *N,N'*-dioxide amide ligands and demonstrated that these compounds could participate in a wide range of chiral ligand-metal-catalyzed and organocatalyzed asymmetric reactions under mild reaction conditions obtaining excellent enantioselectivity and activity.¹⁷³

Sidall suggested that bifunctional carbamoylmethylphosphonate ligands with the ability to adopt bidentate chelate structures in solution could be used as improved chelating agents for the recovery of lanthanide and actinide ions, when compared to the monofunctional organophosphoryl and organoamide ligands.¹⁷⁴ Several studies on the

coordination chemistry of bifunctional ligands that contain both P=O and N-O donors have demonstrated that these chelating reagents produce stable complexes with *3d* metal ions as well as with *f*-elements.¹⁷⁵⁻¹⁷⁸ Rapko and his group have studied the coordination ability of several mixed ligands containing P=O and N-O towards different lanthanide ions. Their work revealed that these bifunctional ligands produce stable complexes with U^{3+} and Ln^{3+} and that modest effectiveness can be achieved in liquid-liquid extractions of Eu^{3+} , Ce^{3+} , Yb^{3+} and Am^{3+} under certain conditions.²²⁻²⁴ It has been observed that complexes displaying seven-membered rings, product of the coordination of metal ions to flexible chelating ligands containing N-O and P=O groups, have superior stability compared to the analogues with five and six-membered chelating rings.^{179,180}

Our group has put considerable effort to study the coordination behavior of different *N,P* chelating ligands towards several transition metal ions. This work has shown the versatility of these ligands to stabilize metal ions in different oxidation states. Furthermore, we have studied several coordination complexes based on bifunctional ligands of phosphines oxides containing one or two pyridyl groups. These studies showed that the hard oxygen donor in these ligands would coordinate to borderline acids like Cu^{2+} and even to soft acids like Hg^{2+} yielding stable structures, probably due to large entropic contributions.^{181,58} In order to expand our understanding in the coordination behavior of these mixed ligands, we have turned our attention to their oxidized counterparts, which contain the harder N-O and P=O functions. In a recent work, we studied the coordination properties of the tridentate ligand phenylphosphino-bis-2-methylpyridine *N,N',P*-trioxide towards Cu^{2+} ,⁵⁸ and more recently, the coordination behavior of the bifunctional ligand 2-[(diphenylphosphino)methyl]pyridine *N,P*-dioxide,

L3, (Scheme 4.1), towards the soft Ag^+ ion.¹⁸² This last study showed the expanded coordination ability of this ligand compared to its non-oxidized counterpart, and how the resulting molecular structures have a strong dependence on the counter-anion interacting with the silver centers. In the present study we focus our attention on the coordination mode of this versatile ligand towards the borderline acids Co^{2+} , Ni^{2+} , Cu^{2+} and Zn^{2+} .



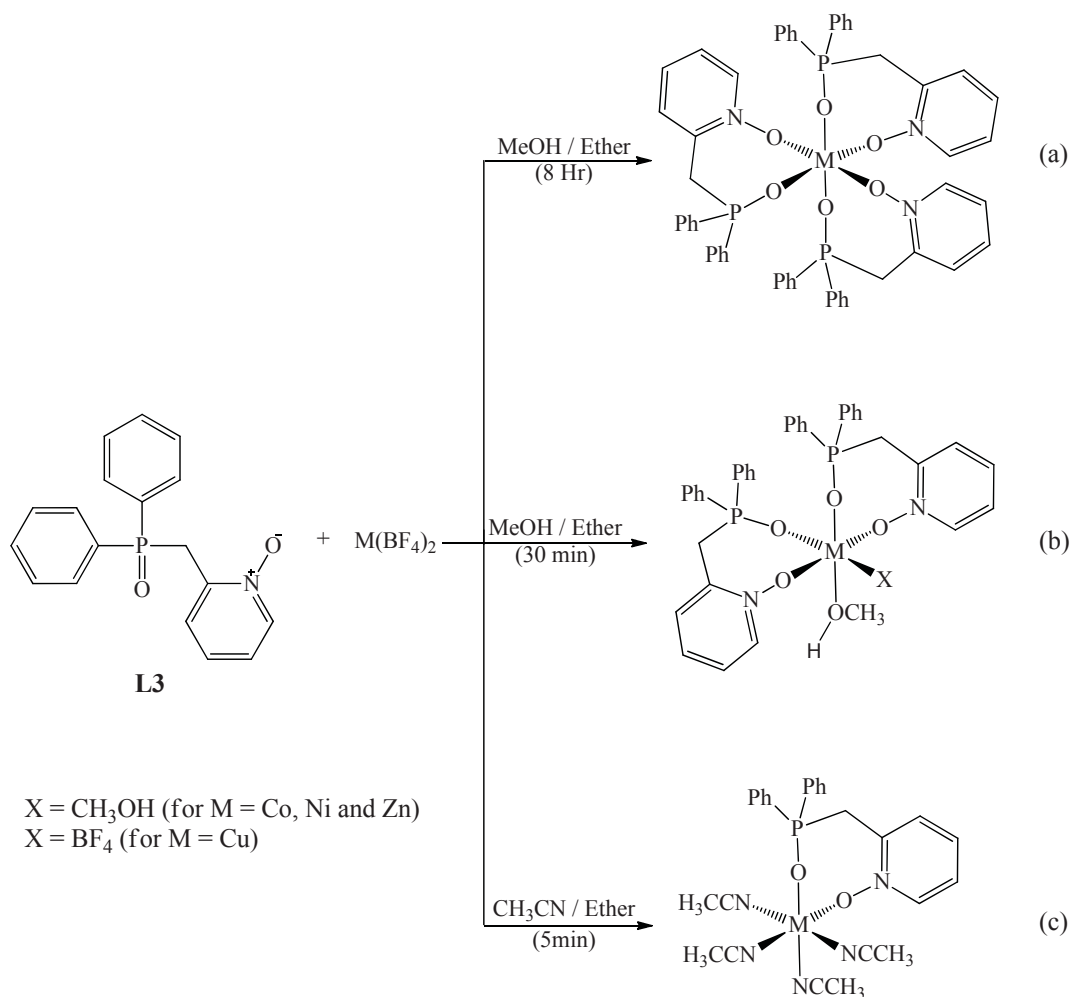
Scheme 4.1. Structure of 2-[(diphenylphosphino)methyl]pyridine *N,P* dioxide (**L3**).

Results and Discussion

Synthesis

The ligand **L3** was synthesized according to a previously reported procedure.^{23,76,78} Compounds **4.1** – **4.4** were synthesized by the direct reaction of **L3** with $\text{M}(\text{BF}_4)_2 \cdot 6\text{H}_2\text{O}$ in a 3:1 ligand-to-metal ratio. This mixture was allowed to stir for 8 hours. The resulting complexes were isolable as a pink solid for **4.1** (Co^{2+}), green solid for **4.2** (Ni^{2+}), blue-green solid for **4.3** (Cu^{2+}) and white solid for **4.4** (Zn^{2+}). Single crystals of **4.1** – **4.4** were obtained from diffusion of ether into a methanolic solution of the corresponding product at room temperature (Scheme 4.2, a), as noted in the experimental section. These compounds were stable under normal conditions, in solid state or in solution, showing no signs of decomposition at room temperature while

exposed to light or air during long periods of time. Multinuclear NMR was performed only on complex **4.4**, since the other three are paramagnetic species. TMS was used as internal reference for ^1H NMR and H_3PO_4 (25%) as external reference for ^{31}P NMR. As expected, the ^1H NMR for complex **4.4** looks very similar to the free ligand spectrum showing small variations only in the chemical shifts. On the other hand, a single signal was observed in the ^{31}P NMR, which presented a chemical shift downfield of 7.28 ppm with respect to the free ligand, indicating that **L3** remains coordinated to the Zn^{2+} ion in the acetonitrile- d_3 solution. Complexes **4.5** – **4.8** were obtained by reacting 2 equiv. of **L3** with 1 equiv. of the appropriate $\text{M}(\text{BF}_4)_2$ salt. The mixture was allowed to stir for 30 minutes. Single crystals for all these complexes were obtained at $-5\text{ }^\circ\text{C}$, using a CH_3CN /Ether solvent system for **1** and MeOH /Ether solvent system for **4.2**, **4.3** and **4.4** (Scheme 4.2, b). The products showed crystal structures with an octahedral environment around the metal centers in a 2:1 ligand-to-metal ratio. The hexa-coordinate geometry is completed by the coordination of two CH_3CN units for **4.5**, two MeOH units for **4.6** and **4.8**, and one molecule of MeOH and one counter-anion for complex **4.7**. The complex **4.9** was obtained in a 1:1 ligand-to-metal ratio by reacting 1 equiv. of $\text{Ni}(\text{BF}_4)_2 \cdot 6\text{H}_2\text{O}$ with 1 equiv. of **L3**. The mixture was allowed to stir for 5 minutes. Single crystals were obtained by slow diffusion of ether into a solution of **4.9** in acetonitrile at $-5\text{ }^\circ\text{C}$. These crystals were re-dissolved in 3ml of MeOH and the resulting solution turned immediately a green color. Ether was allowed to slowly diffuse into this solution at room temperature and crystals with a 2:1 ligand-to-metal ratio were obtained after 5 days. Attempts to obtain complexes of Co^{2+} , Cu^{2+} or Zn^{2+} in a 1:1 ligand-to-metal ratio were not successful (Scheme 4.2, c).



Scheme 4.2. Schematic representation of the conditions used to obtain single crystal of complexes **4.1 – 4.4** (a), **4.5 – 4.8** (b) and **4.9** (c).

The resulting ligand to metal ratio for the complexes presented in this work showed dependence with the reaction time. When the starting materials $M(\text{BF}_4)_2$ and **L3** are allowed to react in methanol for 8 hours the resulting complexes are 3:1 in a ligand-to-metal ratio. In order to obtain single crystals the products were re-dissolved in acetonitrile (since they were no longer soluble in methanol) and ether was slowly diffused in the resulting solutions at room temperature. The isolated products show the 3:1 ligand-to metal-ratio independent of the ratio of the starting materials (1:1, 2:1 or 3:1). On the other hand, when the reaction time was cut down to 30 minutes and the

crystals were allowed to grow at -5 °C, the resulting complexes showed a 2:1 ligand-to-metal ratio. Finally, if the starting materials are allowed to stir for 5 minutes and the crystals are set to grow at -5 °C, the complex obtained (only for complex **4.9**) displays a 1:1 ligand-to-metal ratio. In contrast to complexes with a ligand-to-metal ratio 3:1 and 2:1, obtaining of complexes with a 1:1 ratio depends on the ratio of the starting materials. This observation was supported by running reactions at 1:1 and 2:1 starting material ratios, *vide infra*. When 2 equiv. of **L3** is added to 1 equiv. of Ni(BF₄)₂ the color of the solution turns immediately from light blue to green. Instead, when 1 equiv. of **L3** is added to 1 equiv. of Ni(BF₄)₂ the color of the resulting solution changes from light blue to a more intense blue. All reactions were run in 10 ml of methanol at room temperature. Single crystals of the 3:1 complexes can also be obtained at room temperature by slow diffusion of ether in a methanolic solution of the products, regardless of the initial reaction stoichiometries, if the time at which the starting materials are allowed to stir is short (if the reaction is allowed to stir for several hours the product become insoluble in methanol). Further characterization of complexes **4.5** – **4.9** was not performed due to the uncertainty on the presence of products with 2:1 and/or 3:1 ligand-to-metal ratio.

Description of the Crystal Structures

Crystallographic analyses of complexes **4.1** – **4.4** evidenced crystal structures with a 3:1 ligand-to-metal ratio. Only *mer-trans* isomers were observed. These coordination complexes display an octahedral geometry, where three units of bidentate **L3** are coordinated in a chelating fashion to the M²⁺ center through the oxygen atoms of the phosphoryl and nitrosyl groups, forming three seven-membered rings. The molecular structure of these compounds is shown in Figures. **4.1** – **4.4**.

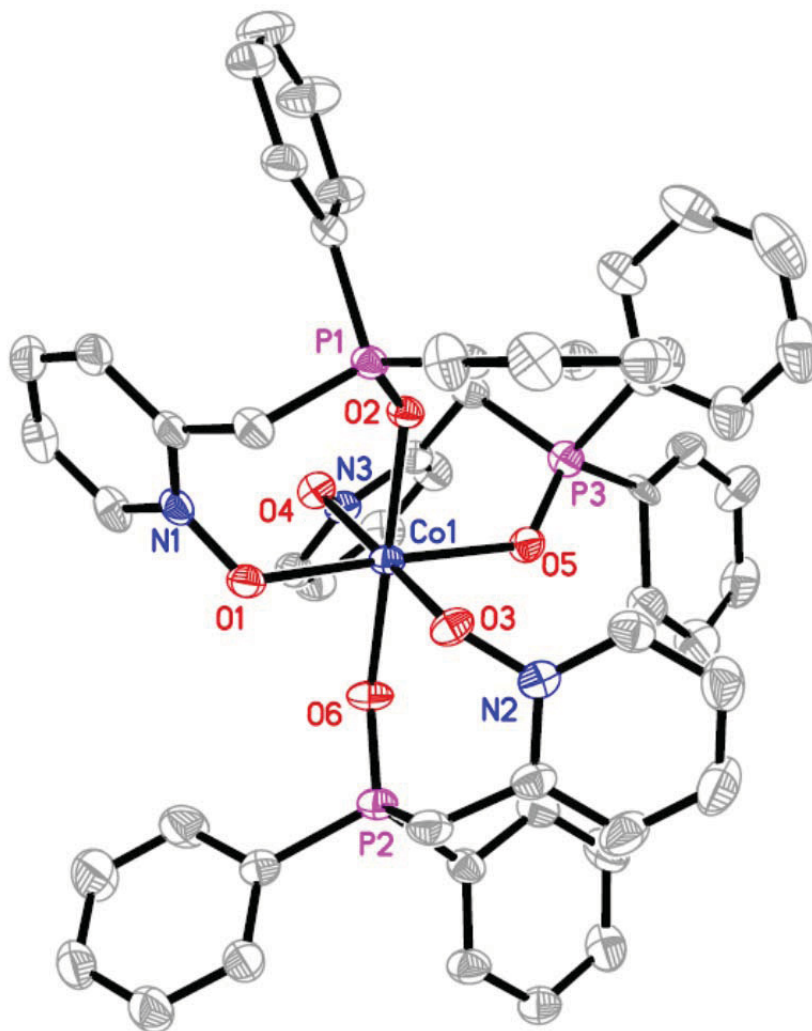


Figure 4.1. Thermal ellipsoid of **4.1** with an atomic numbering scheme. Ellipsoids are shown at the 50% level. Hydrogen atoms have been removed for clarity.

The axial positions are occupied by the two oxygen atoms of two P=O groups, with M-O_{P=O} distance range of 2.133 Å – 2.116 Å. The O_{P=O}-M-O_{P=O} axial angle was found to be nearly linear for all 4 complexes: 175.0° for **1**, 174.3° for **4.2**, 171.0 for **4.3** and 173.8° for **4.4**.

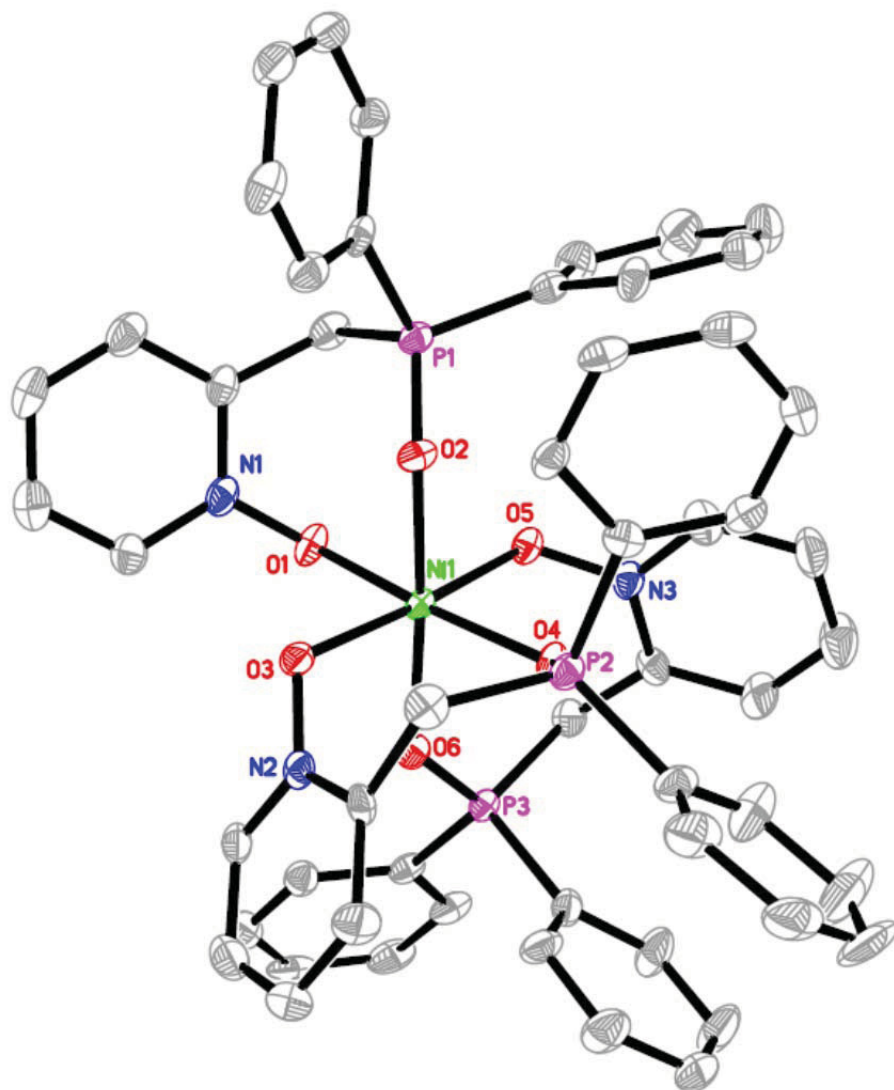


Figure 4.2. Thermal ellipsoid of **4.2** with an atomic numbering scheme. Ellipsoids are shown at the 50% level. Hydrogen atoms have been removed for clarity.

The equatorial positions are occupied by three other oxygen atoms corresponding to three N-O groups ($M-O_{N-O}$ distance range: 1.973 Å – 2.090 Å) and one P=O group ($M-O_{P=O}$ distance range: 1.986 Å – 2.103 Å). The shortest equatorial bond lengths and the longest axial bond lengths were observed in complex **4.3**, $Cu(BF_4)_2L_3$. This elongation is due to the presence of Jahn-Teller distortion in this d^9 complex.

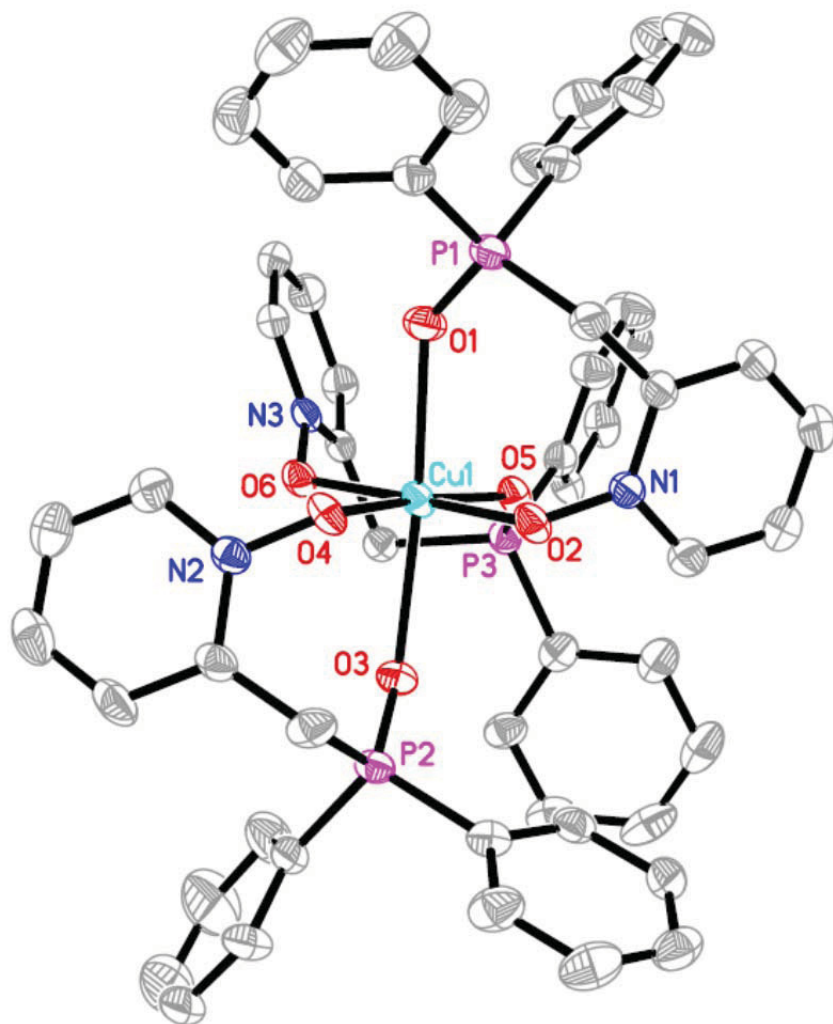


Figure 4.3. Thermal ellipsoid of **4.3** with an atomic numbering scheme. Ellipsoids are shown at the 50% level. Hydrogen atoms have been removed for clarity.

In complex **4.1**, $\text{Co}(\text{BF}_4)_2\text{L}_3$, no appreciable distortion in the Z axis is observed suggesting that this d^7 octahedral complex possesses a high-spin system, which agrees with the ligand **L3** being a rather weak field ligand. The angles O-M-O in the equatorial plane are all close to 90° with an average angle of $90.0^\circ \pm 4.38^\circ$. The bite angles for all three chelating ligand units of **L3** in complex **4.1** to **4.4** range from 91.23° to 93.53° , with an average bite angle of $92.65^\circ \pm 1.57^\circ$.

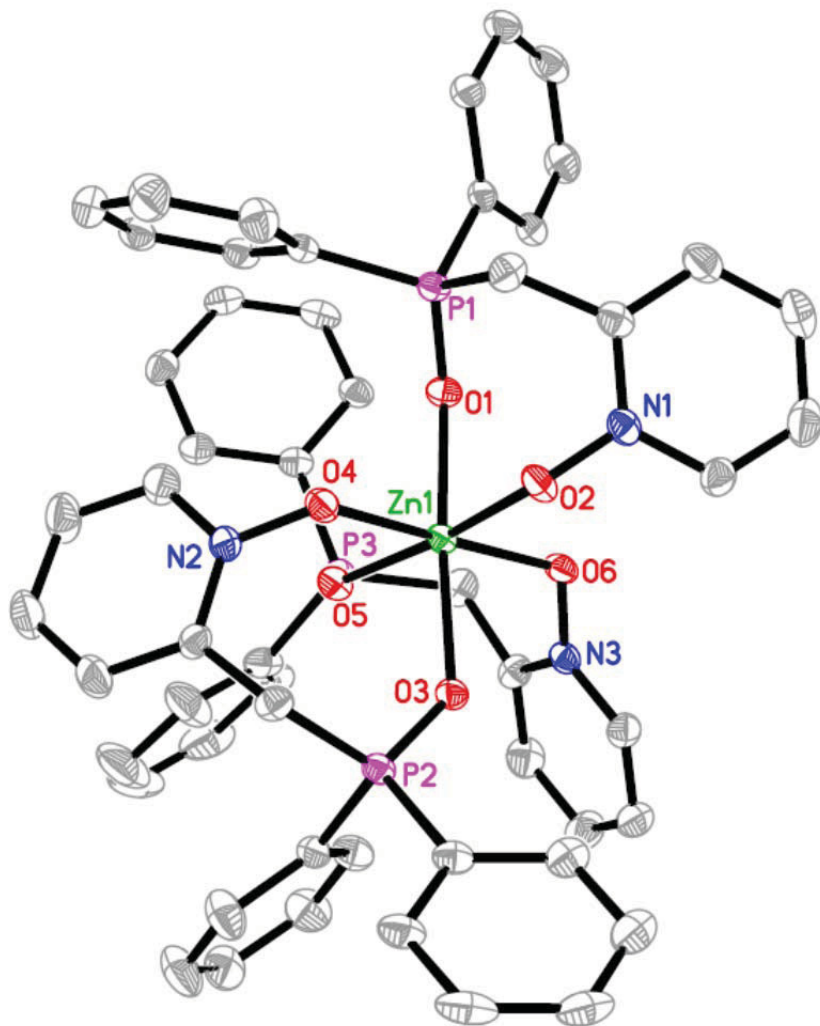


Figure 4.4. Thermal ellipsoid of **4.4** with an atomic numbering scheme. Ellipsoids are shown at the 50% level. Hydrogen atoms have been removed for clarity.

Several hydrogen bonding of the type $F \cdots H-C$ were observed between the BF_4^- fluorine atoms and hydrogen atoms on the phenyl rings and solvent molecules, with $H \cdots F$ distance range of 2.120 – 2.941 Å. The distances between the metal centers and the boron atoms in the counter-anions range between 6.357 Å and 12.201 Å. A summary of selected bond lengths, angles, and interatomic distances for compounds **4.1** and **4.2** are given in Table 4.1 and for compounds **4.3** and **4.4** in Table 4.2.

Table 4.1. Selected bond lengths (Å) and angles (°) for compound **4.1** and **4.2**.

4.1			
Co(1)-O(4)	2.0441(13)	O(3)-Co(1)-O(5)	91.12(5)
Co(1)-O(3)	2.0603(13)	O(1)-Co(1)-O(5)	177.33(5)
Co(1)-O(1)	2.0790(13)	O(4)-Co(1)-O(6)	89.96(5)
Co(1)-O(5)	2.1053(12)	O(3)-Co(1)-O(6)	94.07(5)
Co(1)-O(6)	2.1187(12)	O(1)-Co(1)-O(6)	90.08(5)
Co(1)-O(2)	2.1289(12)	O(5)-Co(1)-O(6)	88.99(5)
P(1)-O(2)	1.4975(13)	O(4)-Co(1)-O(2)	85.94(5)
P(2)-O(6)	1.5016(13)	O(3)-Co(1)-O(2)	90.23(5)
P(3)-O(5)	1.4989(13)	O(1)-Co(1)-O(2)	92.27(5)
O(1)-N(1)	1.3326(19)	O(5)-Co(1)-O(2)	88.85(5)
O(3)-N(2)	1.334(2)	O(6)-Co(1)-O(2)	175.23(5)
O(4)-N(3)	1.3253(19)	N(1)-O(1)-Co(1)	119.00(10)
N(1)-C(6)	1.359(6)	P(1)-O(2)-Co(1)	131.78(7)
N(1)-C(2)	1.376(6)	N(2)-O(3)-Co(1)	116.79(10)
N(2)-C(24)	1.337(6)	N(3)-O(4)-Co(1)	120.58(10)
O(4)-Co(1)-O(3)	173.61(5)	P(3)-O(5)-Co(1)	128.51(8)
O(4)-Co(1)-O(1)	88.60(5)	P(2)-O(6)-Co(1)	134.10(8)
O(3)-Co(1)-O(1)	86.45(5)	O(1)-N(1)-C(6)	119.33(16)
O(4)-Co(1)-O(5)	93.91(5)	O(1)-N(1)-C(2)	119.41(15)
4.2			
Ni(1)-O(3)	2.052(3)	O(1)-Ni(1)-O(4)	172.86(13)
Ni(1)-O(1)	2.052(3)	O(5)-Ni(1)-O(4)	90.51(12)
Ni(1)-O(5)	2.053(3)	O(3)-Ni(1)-O(6)	89.21(14)
Ni(1)-O(4)	2.063(3)	O(1)-Ni(1)-O(6)	89.33(13)
Ni(1)-O(6)	2.064(3)	O(5)-Ni(1)-O(6)	91.71(13)
Ni(1)-O(2)	2.072(3)	O(4)-Ni(1)-O(6)	89.85(12)
P(1)-O(2)	1.502(3)	O(3)-Ni(1)-O(2)	85.16(14)
P(2)-O(4)	1.502(3)	O(1)-Ni(1)-O(2)	91.71(12)
P(3)-O(6)	1.489(3)	O(5)-Ni(1)-O(2)	93.96(13)
O(1)-N(1)	1.325(5)	O(4)-Ni(1)-O(2)	89.81(13)
O(3)-N(2)	1.341(5)	O(6)-Ni(1)-O(2)	174.32(13)
O(5)-N(3)	1.339(4)	N(1)-O(1)-Ni(1)	118.7(3)
N(1)-C(6)	N(1)-C(6)	P(1)-O(2)-Ni(1)	129.63(19)
N(1)-C(2)	N(1)-C(2)	N(2)-O(3)-Ni(1)	117.8(2)
		P(2)-O(4)-Ni(1)	129.68(18)
O(3)-Ni(1)-O(1)	93.20(13)	N(3)-O(5)-Ni(1)	118.5(2)
O(3)-Ni(1)-O(5)	175.52(12)	P(3)-O(6)-Ni(1)	134.3(2)
O(1)-Ni(1)-O(5)	82.43(13)	O(1)-N(1)-C(6)	119.4(4)
O(3)-Ni(1)-O(4)	93.88(12)	O(1)-N(1)-C(2)	120.0(4)

Table 4.2. Selected bond lengths (Å) and angles (°) for compound **4.3** and **4.4**.

4.3			
Cu(1)-O(6)	1.9675(18)	O(2)-Cu(1)-O(5)	91.45(8)
Cu(1)-O(4)	1.973(2)	O(6)-Cu(1)-O(1)	86.60(7)
Cu(1)-O(2)	1.9778(19)	O(4)-Cu(1)-O(1)	92.01(8)
Cu(1)-O(5)	1.9864(19)	O(2)-Cu(1)-O(1)	93.29(7)
Cu(1)-O(1)	2.2961(18)	O(5)-Cu(1)-O(1)	91.19(8)
Cu(1)-O(3)	2.4339(18)	O(6)-Cu(1)-O(3)	85.27(7)
P(1)-O(1)	1.488(2)	O(4)-Cu(1)-O(3)	91.85(7)
P(2)-O(3)	1.4864(19)	O(2)-Cu(1)-O(3)	95.25(7)
P(3)-O(5)	1.506(2)	O(5)-Cu(1)-O(3)	85.79(7)
O(2)-N(1)	1.340(3)	O(1)-Cu(1)-O(3)	171.01(7)
O(4)-N(2)	1.335(3)	P(1)-O(1)-Cu(1)	131.12(11)
O(6)-N(3)	1.334(3)	N(1)-O(2)-Cu(1)	116.25(15)
O(6)-Cu(1)-O(4)	90.19(8)	P(2)-O(3)-Cu(1)	125.91(11)
O(6)-Cu(1)-O(2)	173.04(8)	N(2)-O(4)-Cu(1)	118.43(15)
O(4)-Cu(1)-O(2)	82.86(8)	P(3)-O(5)-Cu(1)	130.23(11)
O(6)-Cu(1)-O(5)	95.50(8)	N(3)-O(6)-Cu(1)	118.91(14)
O(4)-Cu(1)-O(5)	173.63(8)		
4.4			
Zn(1)-O(6)	2.0680(18)	O(2)-Zn(1)-O(5)	172.43(8)
Zn(1)-O(4)	2.0726(18)	O(6)-Zn(1)-O(3)	88.79(9)
Zn(1)-O(2)	2.090(2)	O(4)-Zn(1)-O(3)	90.65(9)
Zn(1)-O(5)	2.091(2)	O(2)-Zn(1)-O(3)	91.45(8)
Zn(1)-O(3)	2.102(2)	O(5)-Zn(1)-O(3)	89.77(8)
Zn(1)-O(1)	2.118(2)	O(6)-Zn(1)-O(1)	85.12(9)
P(1)-O(1)	1.495(2)	O(4)-Zn(1)-O(1)	95.48(9)
P(2)-O(3)	1.489(2)	O(2)-Zn(1)-O(1)	89.94(8)
P(3)-O(5)	1.503(2)	O(5)-Zn(1)-O(1)	89.63(8)
O(2)-N(1)	1.329(3)	O(3)-Zn(1)-O(1)	173.84(8)
O(4)-N(2)	1.343(3)	P(1)-O(1)-Zn(1)	129.73(12)
O(6)-N(3)	1.333(3)	N(1)-O(2)-Zn(1)	118.44(17)
O(6)-Zn(1)-O(4)	176.45(9)	P(2)-O(3)-Zn(1)	134.56(12)
O(6)-Zn(1)-O(2)	94.43(8)	N(2)-O(4)-Zn(1)	118.63(16)
O(4)-Zn(1)-O(2)	82.08(8)	P(3)-O(5)-Zn(1)	130.20(13)
O(6)-Zn(1)-O(5)	93.06(8)	N(3)-O(6)-Zn(1)	118.30(15)
O(4)-Zn(1)-O(5)	90.44(8)		

Complexes **4.5** – **4.8**, with molecular formula $M(\text{BF}_4)_2\text{L}_2\text{S}_2$ ($M = \text{Co}^{2+}$, Ni^{2+} , Cu^{2+} and Zn^{2+} , respectively, and $S = \text{MeOH}$ or CH_3CN), are product of the reaction between 1

equiv. of the corresponding metal salt of $M(\text{BF}_4)_2$, ($M = \text{Co}^{2+}$, Ni^{2+} , Cu^{2+} or Zn^{2+}), and 2 equiv. of **L3**. The molecular structure of these compounds is displayed in Figures 4.5 – 4.8.

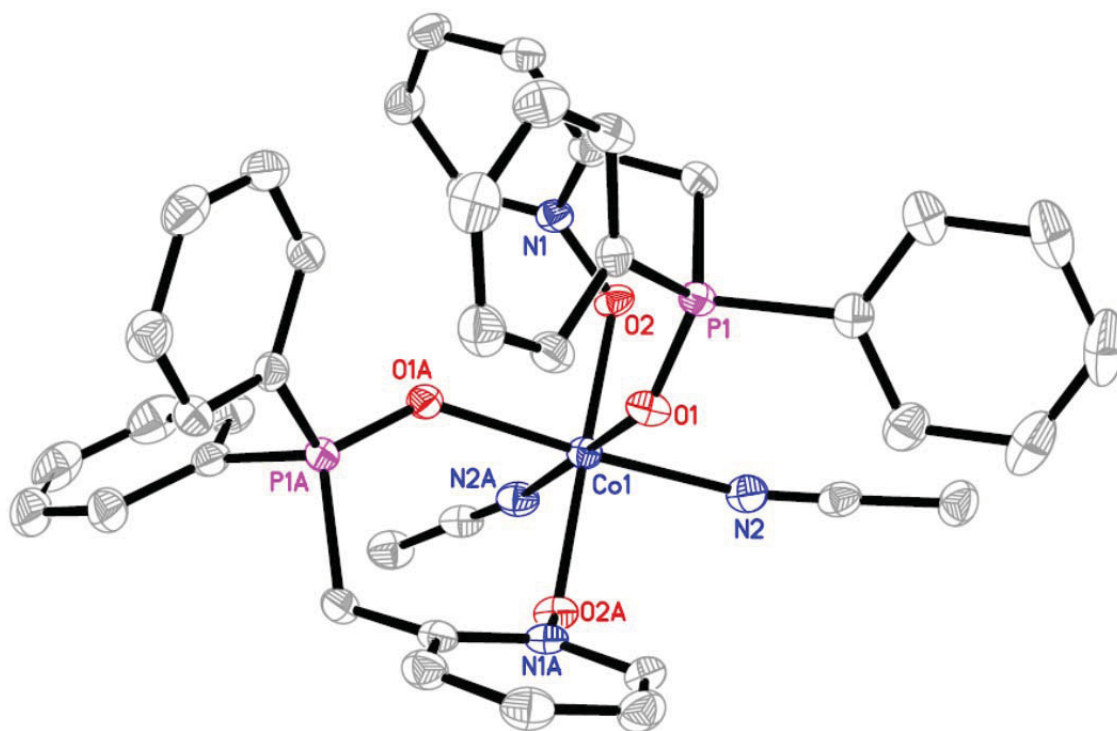


Figure 4.5. Thermal ellipsoid of **4.5** with an atomic numbering scheme. Ellipsoids are shown at the 50% level. Hydrogen atoms have been removed for clarity.

Complexes **4.5** – **4.8** also present an octahedral geometry around the metal center M , with two **L3** units coordinated in a chelating fashion generating two seven-membered rings. The other two coordination sites are occupied by two solvent molecules, in the case of **4.5**, **4.6** and **4.8**, and one solvent molecule and one counter anion in the case of **4.7**. The axial positions in complex **4.7** are occupied by one $\text{O}_{\text{P}=\text{O}}$ and one of the BF_4^- fluorine atoms, which is positioned towards the Cu^{2+} center.

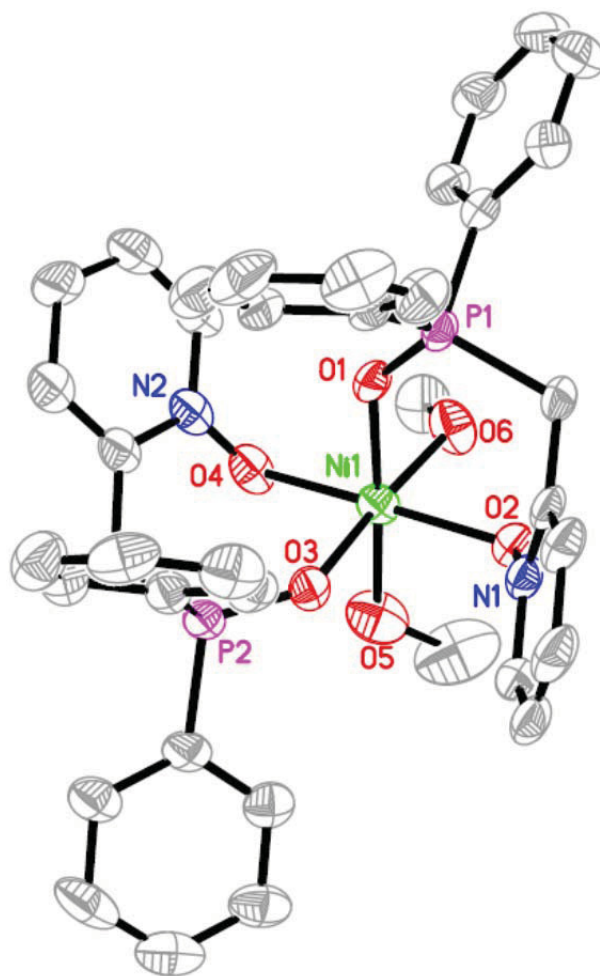


Figure 4.6. Thermal ellipsoid of **4.6** with an atomic numbering scheme. Ellipsoids are shown at the 50% level. Hydrogen atoms have been removed for clarity.

The crystal structure analysis showed evidence of an intramolecular electrostatic interaction between the Cu^{2+} center and the hydrogen atom in the coordinated methanol unit, with a $\text{M}\cdots\text{H}$ distance of 2.417 Å, and $\text{M}\cdots\text{H}-\text{O}$ angle of 47.9° . A long range hydrogen interaction is also observed between the Cu^{2+} center and one of the hydrogen atoms in the methanol $-\text{CH}_3$ group ($\text{M}\cdots\text{H}$ distance = 2.985 Å and $\text{M}\cdots\text{H}-\text{C}$ angle = 83.6°). Complexes **4.5**, **4.6** and **4.8** presented $\text{M}-\text{O}_{\text{P}=\text{O}}$ and $\text{M}-\text{O}_{\text{N}-\text{O}}$ average bond distances of 2.062 ± 0.021 Å and 2.047 ± 0.014 Å, respectively, which are within the range of those found for complexes **4.1** – **4.4**.

The average bite angle $O_{P=O}-M-O_{N-O}$ was also in the range of that found for complexes **4.1** – **4.4**. Similarly to complex **4.3**, complex **4.7** was found to experience an elongation of bonds on the z-axis (Z-out distortion) with Cu- $O_{P2=O3}$ and Cu-F1 bond lengths of 2.2577(15) Å and 2.5289(14) Å, respectively.

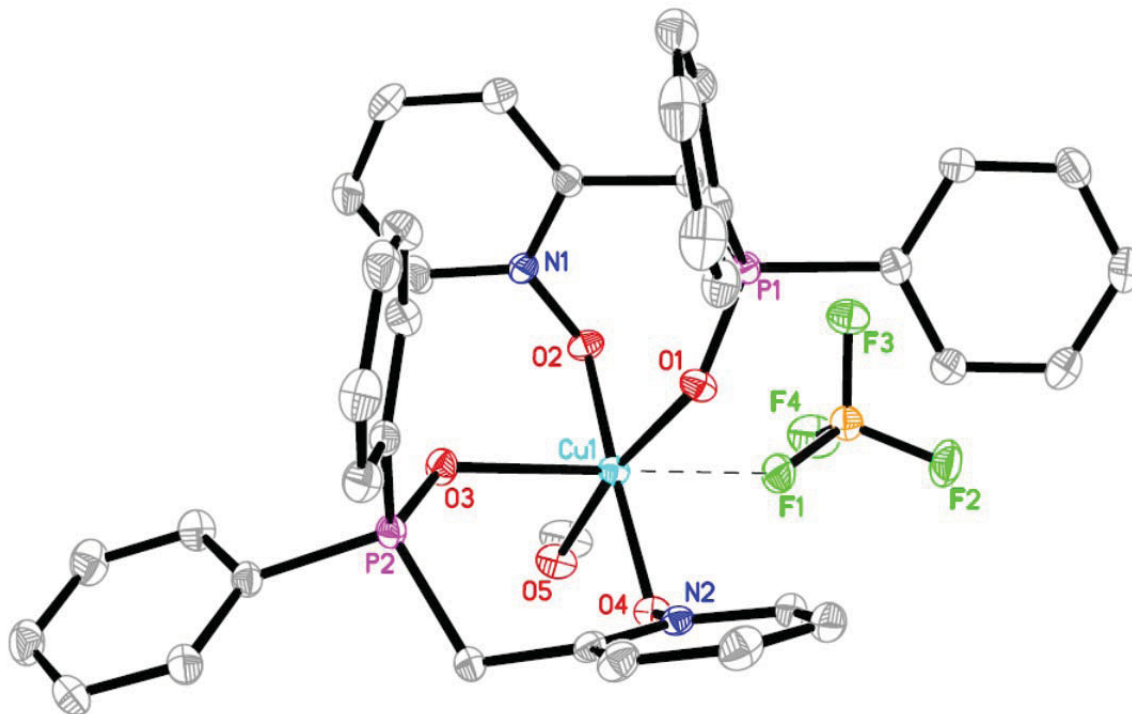


Figure 4.7. Thermal ellipsoid of **4.7** with an atomic numbering scheme. Ellipsoids are shown at the 50% level. Hydrogen atoms have been removed for clarity.

The O3-Cu-F1 angle was found to be 170.2°. The equatorial plane is formed by the interaction of the Cu center with the $O_{P1=O1}$ and O_{N1-O2} atoms of one **L3** unit, the O_{N2-O4} atom of the other ligand and the oxygen atom, O5, of one methanol molecule.

The bond lengths for these interactions presented the following values: 1.9464(15) Å for Cu-O1, 1.9532(16) Å for Cu-O2, 1.9524(16) Å for Cu-O4 and 1.9747(17) Å for Cu-O5. The longest value was observed for the interaction Cu-O5, possibly due to the steric hindrance imposed by the methanolic -CH₃ group.

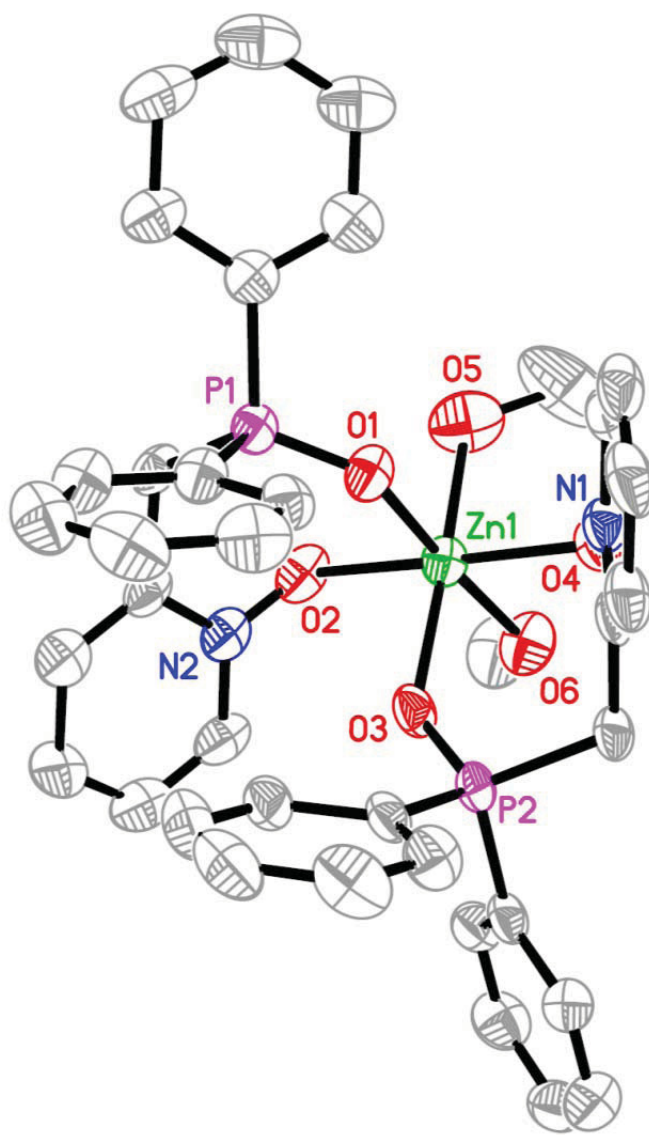


Figure 4.8. Thermal ellipsoid of **4.8** with an atomic numbering scheme. Ellipsoids are shown at the 50% level. Hydrogen atoms have been removed for clarity.

A summary of selected bond lengths, angles, and interatomic distances for compounds **4.5** and **4.6** are given in Table 4.3 and for compounds **4.7** and **4.8** in Table 4.4.

Complex **4.9** is product of the reaction between 1 equiv. of $\text{Ni}(\text{BF}_4)_2 \cdot 6\text{H}_2\text{O}$ and 1 equiv. of **L3**. The crystallographic analysis showed a hexa-coordinate environment

around the nickel center where one **L3** unit acts in a bidentate fashion and four CH₃CN molecules complete the octahedral geometry (Figure 4.9).

Table 4.3. Selected bond lengths (Å) and angles (°) for compound **4.5** and **4.6**.*

4.5			
Co(1)-O(2)	2.0470(18)	O(2)#1-Co(1)-N(2)	91.10(8)
Co(1)-O(1)	2.0890(19)	O(2)-Co(1)-N(2)	87.54(8)
Co(1)-N(2)	2.131(2)	O(1)#1-Co(1)-N(2)	176.24(8)
P(1)-O(1)	1.4945(19)	O(1)-Co(1)-N(2)	87.85(9)
O(2)-N(1)	1.336(3)	N(2)-Co(1)-N(2)#1	94.77(13)
B(1)-F(4)	1.325(4)	P(1)-O(1)-Co(1)	136.12(11)
B(1)-F(1)	1.341(4)	N(1)-O(2)-Co(1)	119.05(14)
B(1)-F(3)	1.345(4)	O(1)-P(1)-C(13)	110.20(12)
B(1)-F(2)	1.364(4)	O(1)-P(1)-C(7)	111.40(12)
		C(13)-P(1)-C(7)	108.06(12)
O(2)#1-Co(1)-O(2)	177.99(10)	O(1)-P(1)-C(1)	113.96(12)
O(2)-Co(1)-O(1)	91.71(7)	C(13)-P(1)-C(1)	109.80(13)
O(2)-Co(1)-O(1)#1	89.71(7)	C(7)-P(1)-C(1)	103.08(12)
O(1)#1-Co(1)-O(1)	89.67(11)	C(6)-N(1)-C(2)	122.0(2)
4.6			
Ni(1)-O(2)	2.032(3)	O(4)-Ni(1)-O(6)	92.24(16)
Ni(1)-O(4)	2.034(4)	O(3)-Ni(1)-O(6)	175.57(15)
Ni(1)-O(3)	2.035(3)	O(2)-Ni(1)-O(1)	92.68(14)
Ni(1)-O(6)	2.046(4)	O(4)-Ni(1)-O(1)	91.24(15)
Ni(1)-O(1)	2.046(4)	O(3)-Ni(1)-O(1)	90.38(15)
Ni(1)-O(5)	2.064(5)	O(6)-Ni(1)-O(1)	89.26(16)
P(1)-O(1)	1.485(4)	O(2)-Ni(1)-O(5)	90.93(18)
P(2)-O(3)	1.486(3)	O(4)-Ni(1)-O(5)	85.1(2)
O(2)-N(1)	1.341(5)	O(3)-Ni(1)-O(5)	90.97(17)
O(4)-N(2)	1.327(6)	O(6)-Ni(1)-O(5)	89.67(18)
B(1)-F(3)	1.378(8)	O(1)-Ni(1)-O(5)	176.13(17)
B(1)-F(4)	1.380(8)	P(1)-O(1)-Ni(1)	136.2(2)
B(1)-F(2)	1.381(7)	N(1)-O(2)-Ni(1)	118.1(3)
B(1)-F(1)	1.389(8)	P(2)-O(3)-Ni(1)	137.0(2)
		N(2)-O(4)-Ni(1)	116.8(3)
O(2)-Ni(1)-O(4)	175.12(15)	C(37)-O(5)-Ni(1)	124.4(5)
O(2)-Ni(1)-O(3)	90.70(13)	C(38)-O(6)-Ni(1)	127.5(4)
O(4)-Ni(1)-O(3)	92.18(14)	O(2)-N(1)-C(6)	118.6(4)
O(2)-Ni(1)-O(6)	84.91(15)	O(2)-N(1)-C(2)	119.4(4)

*Symmetry transformations used to generate equivalent atoms: For **4.5**: #1 -x+1,y,-z+3/2.

Table 4.4. Selected bond lengths (Å) and angles (°) for compound **4.5** and **4.6**.

4.7			
Cu(1)-O(1)	1.9464(15)	O(2)-Cu(1)-O(5)	90.09(7)
Cu(1)-O(4)	1.9524(16)	O(1)-Cu(1)-O(3)	99.97(7)
Cu(1)-O(2)	1.9532(16)	O(4)-Cu(1)-O(3)	92.96(7)
Cu(1)-O(5)	1.9747(17)	O(2)-Cu(1)-O(3)	92.90(6)
Cu(1)-O(3)	2.2577(15)	O(5)-Cu(1)-O(3)	88.43(7)
P(1)-O(1)	1.4986(17)	F(1)-Cu(1)-O(1)	88.28 (6)
P(2)-O(3)	1.4885(16)	F(1)-Cu(1)-O(2)	81.21 (6)
O(2)-N(1)	1.332(2)	F(1)-Cu(1)-O(3)	170.19 (5)
O(4)-N(2)	1.340(2)	F(1)-Cu(1)-O(4)	92.11 (6)
Cu(1)-F(1)	2.5289 (14)	F(1)-Cu(1)-O(5)	83.76 (6)
O(1)-Cu(1)-O(4)	91.52(7)	P(1)-O(1)-Cu(1)	137.48(9)
O(1)-Cu(1)-O(2)	93.49(7)	N(1)-O(2)-Cu(1)	116.59(12)
O(4)-Cu(1)-O(2)	171.52(6)	P(2)-O(3)-Cu(1)	129.44(9)
O(1)-Cu(1)-O(5)	170.67(7)	N(2)-O(4)-Cu(1)	119.64(13)
O(4)-Cu(1)-O(5)	83.96(7)	C(37)-O(5)-Cu(1)	125.44(16)
4.8			
Zn(1)-O(4)	2.061(4)	O(1)-Zn(1)-O(3)	90.85(18)
Zn(1)-O(2)	2.063(4)	O(4)-Zn(1)-O(6)	84.62(19)
Zn(1)-O(1)	2.067(4)	O(2)-Zn(1)-O(6)	93.06(19)
Zn(1)-O(3)	2.076(4)	O(1)-Zn(1)-O(6)	175.13(18)
Zn(1)-O(6)	2.087(5)	O(3)-Zn(1)-O(6)	89.0(2)
Zn(1)-O(5)	2.104(6)	O(4)-Zn(1)-O(5)	91.9(2)
P(1)-O(1)	1.479(4)	O(2)-Zn(1)-O(5)	85.0(2)
P(2)-O(3)	1.490(4)	O(1)-Zn(1)-O(5)	92.2(2)
O(2)-N(2)	1.322(7)	O(3)-Zn(1)-O(5)	174.9(2)
O(4)-N(1)	1.335(6)	O(6)-Zn(1)-O(5)	88.4(2)
O(4)-Zn(1)-O(2)	176.22(18)	P(1)-O(1)-Zn(1)	136.8(2)
O(4)-Zn(1)-O(1)	90.53(17)	N(2)-O(2)-Zn(1)	116.8(3)
O(2)-Zn(1)-O(1)	91.81(17)	P(2)-O(3)-Zn(1)	136.0(2)
O(4)-Zn(1)-O(3)	92.15(17)	N(1)-O(4)-Zn(1)	117.8(3)
O(2)-Zn(1)-O(3)	90.77(18)		

The Ni-O_{P=O} and Ni-O_{N-O} distances are 2.048 Å and 2.029 Å, respectively, with a P=O bond length of 1.506 Å and N-O bond length of 1.336 Å. The O-Ni-O bite distance is 2.933 Å with a bite angle of 92.0°. The average Ni-N distance was found to be 2.071 ± 0.010 Å.

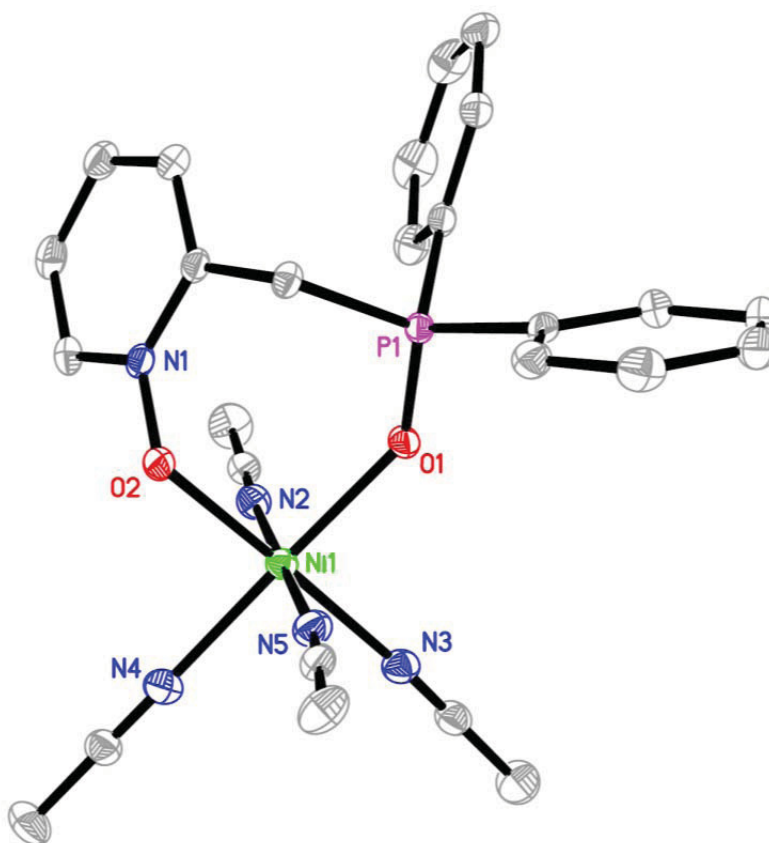


Figure 4.9. Thermal ellipsoid of **4.9** with an atomic numbering scheme. Ellipsoids are shown at the 50% level. Hydrogen atoms have been removed for clarity.

All the N-Ni-N angles between the CH₃CN molecules positioned *cis* to each other are nearly 90° (average = $90.2 \pm 2.30^\circ$). The N5-Ni-N2 angle (*trans* CH₃CN groups) is 178.3°. Interactions are observed between the hydrogen atoms in one of the phenyl rings and an oxygen atom on the phosphoryl group ($\text{H}\cdots\text{O}_{\text{P=O}} = 2.625 \text{ \AA}$; $\text{C-H}\cdots\text{O}_{\text{P=O}} = 106.0^\circ$). Similarly, one hydrogen atom on the **L3** methylene group interacts with the nitrosyl oxygen atom with a $\text{H}\cdots\text{O}_{\text{N=O}}$ distance of 2.412 Å and a $\text{C-H}\cdots\text{O}_{\text{N=O}}$ angle of 97.0°. Interactions of this type are also present in the crystal structure of the ligand **L3** and all the other complexes presented in this work. Selected bond lengths and angles for compound **4.9** are listed in Table 4.5.

Table 4.5. Selected bond lengths (Å) and angles (°) for compound **4.9**.

4.9			
Ni(1)-O(2)	2.0293(12)	N(2)-Ni(1)-N(4)	88.77(6)
Ni(1)-O(1)	2.0483(12)	O(2)-Ni(1)-N(5)	85.02(5)
Ni(1)-N(2)	2.0584(15)	O(1)-Ni(1)-N(5)	90.17(5)
Ni(1)-N(4)	2.0679(15)	N(2)-Ni(1)-N(5)	178.28(6)
Ni(1)-N(5)	2.0739(15)	N(4)-Ni(1)-N(5)	92.33(6)
Ni(1)-N(3)	2.0840(15)	O(2)-Ni(1)-N(3)	177.85(5)
P(1)-O(1)	1.5057(12)	O(1)-Ni(1)-N(3)	89.04(5)
N(1)-O(2)	1.3363(18)	N(2)-Ni(1)-N(3)	88.24(6)
O(2)-Ni(1)-O(1)	92.00(5)	N(4)-Ni(1)-N(3)	88.63(6)
O(2)-Ni(1)-N(2)	93.66(5)	N(5)-Ni(1)-N(3)	93.11(6)
O(1)-Ni(1)-N(2)	88.78(5)	P(1)-O(1)-Ni(1)	137.09(7)
O(2)-Ni(1)-N(4)	90.40(5)	N(1)-O(2)-Ni(1)	119.09(9)
O(1)-Ni(1)-N(4)	176.67(5)		

It is interesting to note that in complexes 2:1 (**4.1** – **4.4**) only isomers with P=O groups in *cis* position and N-O groups in *trans* positions are formed. Similarly, for complexes with a ratio 3:1 (**4.5** – **4.8**) only the *mer-trans* isomer are formed. The Second ligand unit coordinates preferentially with N-O groups *trans* to each other and P=O groups *cis* to each other, even though a *trans* positioning between the two P=O would be sterically less demanding.

FT-IR Spectra

The FT-IR spectra of complexes **4.1** – **4.4** showed redshift of the N-O stretching bands relative to the free ligand **L3** (Table 4.6). Complex **4.3** presents the lowest energy N-O stretching band, 1202 cm⁻¹, which is consistent with a contraction in the equatorial plane due to the Jahn-Teller distortion, leading to a weakening of the N-O bonds. All the other complexes showed nearly the same stretching frequencies, with a shift to lower energies of approximately 50 cm⁻¹ with respect to **L3**. A broad band, characteristic for the

B-F bond in the BF_4^- counter-anion, was observed at 1036, 1037, 1033 and 1035 cm^{-1} for complexes **4.1** – **4.4**, respectively. These bands are shift 25 – 30 cm^{-1} to lower energies compared to the $\text{M}(\text{BF}_4)_2$ starting materials. This wavelength differences can be attributed to the increase in the B-F vibration energy due to the weaker interaction of the BF_4^- counter-anions with the M centers after coordination of the **L3** units. The P=O bands were not assigned due to overlapping with the much broader BF_4^- bands.

Table 4.6. FT-IR data for compounds **4.1** – **4.4**.

Compound	$\nu(\text{B-F}) (\text{cm}^{-1})$	$\nu(\text{N-O}) (\text{cm}^{-1})$
L3	-	1266 (s)
4.1	1061 (s)	1211 (s)
4.2	1062 (s)	1213 (s)
4.3	1067 (s)	1202 (s)
4.4	1060 (s)	1212 (s)

UV-Visible Spectra

The UV-Vis spectra for compounds **4.1** – **4.3** were obtained at room temperature from solutions with concentration 4×10^{-4} M in CH_3CN . A comparison with the parent starting materials $\text{M}(\text{BF}_4)_2 \cdot \text{H}_2\text{O}$ is shown in Table 7. All three complexes showed a red-shift relative to the $\text{M}(\text{BF}_4)_2$ starting materials. Complex **4.1** showed one absorption band at 386 nm, with a small shoulder at 490 nm, corresponding to the *d-d* electronic transitions $^4T_{1g}(\text{F}) \rightarrow ^4T_{1g}(\text{P})$ and $^4T_{1g}(\text{F}) \rightarrow ^4A_{2g}$, and another band at 593 nm corresponding to the transition $^4T_{1g}(\text{F}) \rightarrow ^4T_{2g}$. Complex **4.2** showed one absorption band at 393 nm, assigned to the electronic transition $^3A_{2g} \rightarrow ^3T_{1g}(\text{P})$. Complex **4.3** showed a band at 858 nm which corresponds to a $^2E_g \rightarrow ^2T_{2g}$ transition. None of the compounds discussed here show any fluorescence even at liquid nitrogen temperatures.

Table 4.7. UV–Vis data for compounds **4.1** – **4.3** at room temperature and 4×10^{-4} M in CH₃CN.

Compound	λ_{max} (nm)	M(BF ₄) ₂
4.1	386, 593	491
4.2	393	366, 585, 967
4.3	858	759

Conclusions

Several new octahedral coordination complexes of Co²⁺, Ni²⁺, Cu²⁺ and Zn²⁺ were synthesized by the reaction of their corresponding tetrafluoroborate salts with 2-[(diphenylphosphino)methyl]pyridine *N,P* dioxide, **L3**. All crystal structures showed an octahedral geometry around the metal centers. The ligand **L3** coordinates in a chelating fashion to the M²⁺ centers through the oxygen atoms of the phosphoryl and nitrosyl groups, forming three seven-membered rings. As expected, a strong Jahn-Teller distortion is observed in complexes **4.3** and **4.7** where the central atom, Cu²⁺, is a *d*⁹ ion. In the case of complex Co(BF₄)₂L₃ (**4.1**), a *d*⁷ high-spin system, this distortion is not observed. The *d-d* electronic transitions displayed in the UV-visible spectra were in the expected range of energies. The FT-IR spectra also showed stretching bands in the range reported in other work. The formation of the isomer *mer-trans* is probably driven by both kinetic and entropic effects.

Experimental

General Remarks

Caution! All the M(BF₄)₂•6H₂O used in this work are potentially dangerous. Please consult the Material Safety Data Sheet (MSDS) for additional information

regarding appropriate storage/handling and engineering control/personal protective equipment before working with these materials. All experiments were performed under nitrogen atmosphere using Schlenk techniques. All air and light sensitive compounds were stored and handled in an inert atmosphere glovebox and used as received. All solvents were reagent-grade and distilled under inert atmosphere from the appropriate drying agent right before use. Infrared spectra were recorded on a Thermo Nicolet Nexus 870 (FT-IR *E.S.P.* System) spectrometer. ^1H and ^{31}P NMR spectra were recorded at 499.78 and 202.31 MHz respectively, at 25.0 °C / 298.1 K MHz, using a Varian VNMRS 500 MHz Spectrometer. UV–Vis absorption data were acquired on a Varian Cary Bio spectrophotometer. Solutions were prepared in CH_3CN and charged into quartz cuvettes. Elemental analyses were performed by Atlantic Microlabs Inc. in Norcross, Georgia. Yields for compounds **4.1** – **4.4** were calculated with respect to $\text{M}(\text{BF}_4)_2 \cdot 6\text{H}_2\text{O}$.

Preparation

Synthesis of $\text{M}(\text{BF}_4)_2\text{L}_3$. A solution of **L3** (0.0927 g, 0.300 mmol) in MeOH (5 mL) was added to a solution of $\text{M}(\text{BF}_4)_2 \cdot 6\text{H}_2\text{O}$, ($\text{M} = \text{Co}^{2+}$ for **4.1**, Ni^{2+} for **4.2**, Cu^{2+} for **4.3** and Zn^{2+} for **4.4**), (0.100 mmol), in MeOH (5 mL). The resulting solution was allowed to stir for 8 hours and then dried under vacuum to leave a powder. This was then dissolved in a small amount of MeOH and precipitated with ether (30 mL). Crystals were obtained by slow diffusion of ether into a MeOH solution of the corresponding product at room temperature. (**4.1**) Yield 79 % (0.092 g). Anal. Calc. for $\text{C}_{54}\text{H}_{48}\text{B}_2\text{CoF}_8\text{N}_3\text{O}_6\text{P}_3 \cdot \text{H}_2\text{O}$ (1178.46): C, 55.03; H, 4.27; N, 3.56. Found: C, 54.82; H, 4.28; N, 3.58 %. IR (KBr, cm^{-1}): 1211 (ν_{NO}), 1061 (ν_{PO} , br). (**4.2**) Yield 91 % (0.106 g). Anal. Calc. for $\text{C}_{54}\text{H}_{48}\text{B}_2\text{F}_8\text{N}_3\text{NiO}_6\text{P}_3 \cdot \text{H}_2\text{O}$ (1178.22): C, 55.04; H, 4.27; N, 3.56. Found: C, 54.68; H,

4.24; N, 3.55%. IR (KBr, cm^{-1}): 1213 (ν_{NO}), 1062 (ν_{PO} , br). **(4.3)** Yield 76 % (0.089 g). Anal. Calc. for $\text{C}_{54}\text{H}_{48}\text{B}_2\text{CuF}_8\text{N}_3\text{O}_6\text{P}_3\cdot\text{H}_2\text{O}$ (1183.08): C, 54.82; H, 4.26; N, 3.55. Found: C, 54.49; H, 3.95; N, 3.42%. IR (KBr, cm^{-1}): 1202 (ν_{NO}), 1067 (ν_{PO} , br). **(4.4)** Yield 87 % (0.101 g). Anal. Calc. for $\text{C}_{54}\text{H}_{48}\text{B}_2\text{F}_8\text{N}_3\text{O}_6\text{P}_3\text{Zn}$ (1166.91): C, 55.58; H, 4.15; N, 3.60. Found: C, 55.43; H, 4.12; N, 3.53%. ^1H NMR (CD_3CN , 298.1 K): δ = 4.50 (d, 2H), 7.05 (d, 12H), 7.44 (m, 1H), 8.09 (d, 1H). ^{31}P NMR (CD_3CN , 298.1 K): δ = 41.43, (s) ppm. IR (KBr, cm^{-1}): 1212 (ν_{NO}), 1060 (ν_{PO} , br).

X-ray Crystallography

Crystallographic data was collected on crystals with dimensions 0.304 x 0.112 x 0.137 mm for **4.1**, 0.158 x 0.150 x 0.143 mm for **4.2**, 0.131 x 0.150 x 0.084 mm for **4.3** and 0.241 x 0.273 x 0.285 mm for **4.4**, 0.164 x 0.186 x 0.126 mm for **4.5**, 0.199 x 0.180 x 0.170 mm for **4.6**, 0.206 x 0.206 x 0.108 mm for **4.7**, 0.322 x 0.175 x 0.150 mm for **4.8** and 0.176 x 0.108 x 0.355 for **4.9**. Data was collected at 110 K on a Bruker X8 Apex using Mo-K radiation (λ = 0.71073 Å). All structures were solved by direct methods after correction of the data using *SADABS*.^{109,110} Details of the crystal parameters, data collection, and refinement are summarized in Tables 4.8, for compounds **4.1** – **4.3**, Table 4.9 for compounds **4.4** - **4.6** and Table 4.10 for compounds **4.7** – **4.9**. All the data were processed using the Bruker AXS *SHELXTL* software, version 6.10.¹¹¹ Unless otherwise noted, all non-hydrogen atoms were refined anisotropically and hydrogen atoms were placed in calculated positions.

Table 4.8. Crystallographic data for compounds **4.1** – **4.3**.

	4.1	4.2	4.3
Empirical formula	C ₅₄ H ₄₈ B ₂ CoF ₈ N ₃ O ₆ P ₃	C ₅₄ H ₄₈ B ₂ F ₈ N ₃ NiO ₆ P ₃	C ₅₄ H ₄₈ B ₂ CuF ₈ N ₃ O ₆ P ₃
Formula mass	1160.41	1192.24	1202.38
<i>a</i> (Å)	13.9051(9)	10.5814(19)	14.1007(10)
<i>b</i> (Å)	23.1098(16)	15.021(2)	22.6498(17)
<i>c</i> (Å)	17.9489(11)	17.249(3)	17.5725(12)
α (°)	90	90	90
β (°)	95.906(3)	91.786(6)	98.585(4)
γ (°)	90	90	90
<i>V</i> (Å ³)	5737.2(6)	2740.3(7)	5549.4(7)
<i>Z</i>	4	2	4
Crystal System	Monoclinic	Monoclinic	Monoclinic
Space Group	P2(1)/c	P2(1)	P2(1)/c
T(K)	110(2)	110(2)	110(2)
D _{calcd.} (g/cm ³)	1.343	1.445	1.439
μ (mm ⁻¹)	0.458	0.524	0.562
2 θ_{max} (°)	28.31	26.75	28.35
Reflections measured	103376	27498	50561
Reflections used	14240	10845	13836
Data / restraints / parameters	14240 / 0 / 732	10845 / 1 / 714	13836 / 4 / 738
R ₁ [<i>I</i> > 2 σ (<i>I</i>)]	0.0444	0.0582	0.0539
wR ₂ [<i>I</i> > 2 σ (<i>I</i>)]	0.1029	0.1392	0.1163
R(<i>F</i> ² _o) (all data)	0.0611	0.0701	0.1020
R _w (<i>F</i> ² _o) (all data)	0.1104	0.1460	0.1419
GOF on <i>F</i> ²	1.078	1.043	1.008

Table 4.9. Crystallographic data for compounds **4.4** – **4.6**.

	4.4	4.5	4.6
Empirical formula	C ₅₄ H ₄₈ B ₂ F ₈ N ₃ O ₆ P ₃ Zn	C ₄₄ H ₄₄ B ₂ CoF ₈ N ₆ O ₄ P ₂	C ₃₉ H ₄₄ BF ₄ N ₂ NiO ₇ P ₂
Formula mass	1198.90	1015.34	860.22
<i>a</i> (Å)	10.5390(5)	17.7024(19)	13.175(5)
<i>b</i> (Å)	15.0341(7)	18.9467(17)	13.669(5)
<i>c</i> (Å)	17.2991(8)	14.0724(15)	14.543(4)
α (°)	90	90	67.989(7)
β (°)	92.116(2)	90	69.059(11)
γ (°)	90	90	77.423(7)
<i>V</i> (Å ³)	2739.1(2)	4719.9(8)	2257.1(13)
<i>Z</i>	2	4	2
Crystal System	Monoclinic	Orthorhombic	Triclinic
Space Group	P2(1)	Pbcn	P-1
T(K)	110(2)	110(2)	110(2)
D _{calcd.} (g/cm ³)	1.454	1.429	1.266
μ (mm ⁻¹)	0.618	0.512	0.562
2 θ_{max} (°)	27.72	26.44	25.74
Reflections measured	41116	37923	41663
Reflections used	12760	4857	8273
Data / restraints / parameters	12760 / 1 / 714	4857 / 0 / 305	8273 / 0 / 514
R ₁ [<i>I</i> > 2 σ (<i>I</i>)]	0.0438	0.0515	0.0756
wR ₂ [<i>I</i> > 2 σ (<i>I</i>)]	0.1041	0.1218	0.1977
R(<i>F</i> ² _o) (all data)	0.0535	0.0643	0.0916
R _w (<i>F</i> ² _o) (all data)	0.1108	0.1316	0.2059
GOF on <i>F</i> ²	1.023	1.033	1.041

Table 4.10. Crystallographic data for compounds **4.7** – **4.9**.

	4.7	4.8	4.9
Empirical formula	C ₃₇ H ₃₆ B ₂ CuF ₈ N ₂ O ₅ P ₂	C ₃₉ H ₄₄ BF ₄ N ₂ O ₇ P ₂ Zn	C ₂₈ H ₃₁ B ₂ F ₈ N ₆ NiO ₂ P
Formula mass	887.78	866.88	746.89
<i>a</i> (Å)	10.844(3)	13.245(9)	11.0974(5)
<i>b</i> (Å)	12.839(4)	13.670(10)	25.2713(11)
<i>c</i> (Å)	15.666(5)	14.573(10)	12.0411(6)
α (°)	90.874(4)	67.655(13)	90
β (°)	107.544(4)	68.811(11)	97.489(2)
γ (°)	113.885(4)	77.101(14)	90
<i>V</i> (Å ³)	1877.9(10)	2264(3)	3348.1(3)
<i>Z</i>	2	2	4
Crystal System	Triclinic	Triclinic	Monoclinic
Space Group	P-1	P-1	P 21/n
T(K)	110(2)	110(2)	110(2)
D _{calcd.} (g/cm ³)	1.570	1.272	1.482
μ (mm ⁻¹)	0.753	0.674	0.708
$2\theta_{max}$ (°)	28.42	25.00	29.57
Reflections measured	18227	17372	37197
Reflections used	8720	7792	9298
Data /restraints/parameters	8720 / 0 / 519	7792 / 1 / 517	9298 / 0 / 438
R ₁ [<i>I</i> > 2σ(<i>I</i>)]	0.0399	0.0805	0.0384
wR ₂ [<i>I</i> > 2σ(<i>I</i>)]	0.0938	0.2193	0.0881
R(<i>F</i> ² _o) (all data)	0.0515	0.0974	0.0543
R _w (<i>F</i> ² _o) (all data)	0.1023	0.2286	0.0966
GOF on <i>F</i> ²	1.034	1.048	1.023

CHAPTER FIVE

Syntheses and Coordination Studies of 4-[(diphenylphosphino)methyl]pyridine Towards Mercury(II)

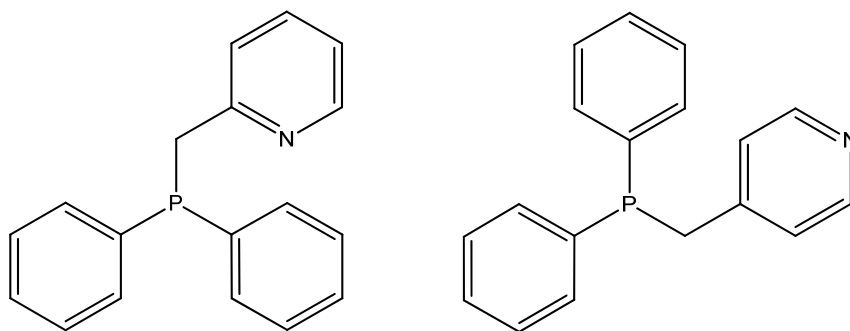
Introduction

In the past three chapters of this work several complexes of different transition metal ions based on the ligand 2-[(diphenylphosphino)methyl]pyridine and its P=O and N-O/P=O variations have been thoroughly studied. These ligands demonstrated their coordination capacity to act in both bridging and chelating mode, depending on several factors including the metal present, counter-anion associated with the metal, solvents used for the reaction and to grow the crystals, etc. This situation makes the coordination mode of these ligands rather difficult to predict. On the other hand, a small variation on the structure of **L1** can induce the ligand to preferentially act as a bridge moiety between two metal centers. This can be accomplished by placing the nitrogen donor on **L1** in the fourth position with respect to the methyl group, thus generating the ligand 4-[(diphenylphosphino)methyl]pyridine, **L4** (Scheme 5.1). Even though this feature gives to **L4** the advantage to act as a bridging moiety between two metal centers, it also introduces spatial restrictions to act as a chelating agent. The ability to form bridges between metal centers represents an interesting feature that can be exploited for the production of organometallic polymers.

The ligand **L4** was first reported as a bidentate ligand in 2009 by Hung.¹⁸³ In his work several coordination compounds of Ag^+ , including discrete molecules and complex coordination polymers, were studied. In all the complexes reported, **L4** bridged two Ag^+ centers in a head-to-tail fashion.

The cationic ligand methyldiphenyl-4-pyridylphosphonium bromide, structurally similar to **L4**, was reported by Weiner in 1974.¹⁸⁴ Three decades after Weiner's study, Angurell reported bimetallic complexes of Ru/Rh, Ru/Pd and Ru/Au where the ligand diphenyl-4-pyridylphosphine bridged the two metal centers.¹⁸⁵ This ligand was also employed by Carson and Lippard in the synthesis of diiron complexes, although the one ligand unit was terminally bound to each of the iron centers through the harder nitrogen donors, leaving the diphenylphosphine as a pendant group.¹⁸⁶

Another example where the 4-pyridyldiphenylphosphane ligand was utilized to bridge two tungsten centers was published by Hirsivaara and co-workers.¹⁸⁷ No other study on the coordination behavior of **L4** has yet been reported in literature.



Scheme 5.1. Structure of 2-[(diphenylphosphino)methyl]pyridine (**L1**), (left), and 4-[(diphenylphosphino)methyl]pyridine (**L4**), (right).

In the present chapter, the molecular structure of different Hg^{2+} complexes of the 4-[(diphenylphosphino)methyl]pyridine ligand are studied with the help of single crystal X-ray diffraction.

Results and Discussion

Synthesis

The ligand 4-[(diphenylphosphino)methyl]pyridine, **L4**, was synthesized according to a previously reported procedure.¹⁸³ Crystals of compounds **5.1** – **5.3** were obtained by layering or vapor diffusion recrystallization techniques using an appropriate solvent mixture, as noted in the experimental section. Complexes **5.1** – **5.3** were isolated as crystalline products regardless of initial reaction stoichiometry. These compounds were stable under normal conditions and showed no signs of decomposition at room temperature while exposed to light or air during long periods of time.

Description of the Crystal Structures

Complex **5.1** is the product of the reaction between $\text{Hg}(\text{SCN})_2$ and **L4**, in a 1:1 ratio. The resulting structure is a centrosymmetric dimer, where two ligand units act in a bridging mode connecting two mercury(II) centers which are separated by a distance of 7.746 Å (Figure 5.1). The metal centers can be described as a heavily distorted tetrahedron conformed by the interaction of the metal center with a phosphorus atom of one ligand unit, the nitrogen atom of the other ligand unit and two SCN^- anions. In contrast to complex $[\text{Hg}(\mu\text{-SCN})_2(\text{L1})]_2$, **2.1**, where the counter-anions act as bridging moieties, in complex $[\text{Hg}(\text{SCN})_2(\mu\text{-L1})]_2$, **5.1**, the pyridyl substituent in the ligand plays this role. This coordination mode difference between the ligands 4-[(diphenylphosphino)methyl]pyridine, **L4**, and 2-[(diphenylphosphino)methyl]pyridine, **L1**, towards $\text{Hg}(\text{SCN})_2$ can be attributed to the minimized steric hindrance obtained when the ligand acts in a bridging mode.

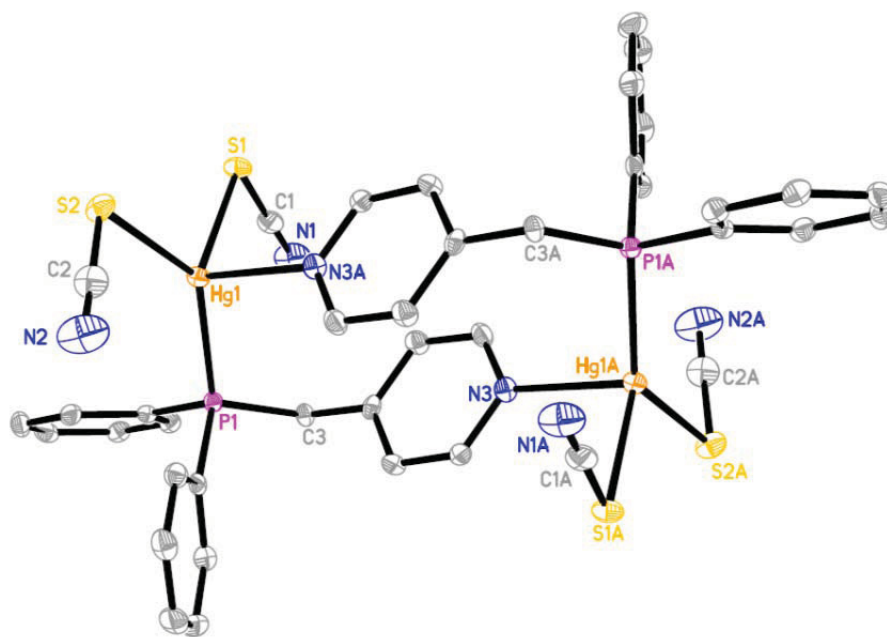


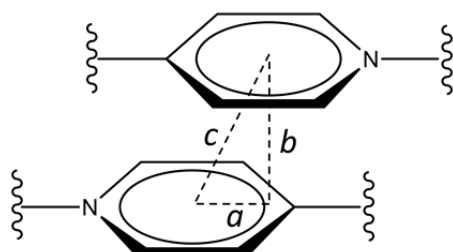
Figure 5.1. Thermal ellipsoid of **5.1** with an atomic numbering scheme. Ellipsoids are shown at the 50% level. Hydrogen atoms have been removed for clarity.

The angle formed by the *ipso*-carbon in the pyridyl group, the methyl carbon and the phosphorus atom in the ligand unit in complex **1**, C_{ipso} -C-P, is 113.5° , very similar to its counterpart in complex **2.1**, where this angle was found to be 112.9° . The bond distances P-Hg and N-Hg are $2.432 \text{ \AA}$ and $2.495 \text{ \AA}$, respectively, with a P-Hg-N angle of 70.3° .

The Hg- S_{SCN^-} distances are $2.565 \text{ \AA}$ and $2.472 \text{ \AA}$, with a S_{SCN^-} -Hg- S_{SCN^-} angle of 101.2° . The nitrogen atoms in the counter-anions are directed towards the metal center, although the distance of $4.047 \text{ \AA}$ is not close enough to be considered an interaction. The P1-Hg1-S1 and P1-Hg1-S2 are 113.9° and 137.4° , respectively.

Additional structural stability of **5.1** is obtained by intramolecular van der Waals attractions of the type dipole-dipole between the electron-poor pyridyl moieties. The interplane angle between the pyridyl rings is nearly zero. The centroid – centroid

distance, c , is 3.584 Å with a plane-to-plane separation, b , of 3.4553 Å and offset distance of centroids, a , of 0.9517 Å (Scheme 5.2). These parameters are within the range of values previously reported in other work.



Scheme 5.2. Geometric characteristics for two interacting pyridyl rings.

The supramolecular extended structure of **5.1** is built up by edge-to-face phenyl-phenyl interactions between molecular units. The distances between the two hydrogen atoms and the centroid of the phenyl ring are 3.349 Å and 2.790 Å (Figure 5.2).

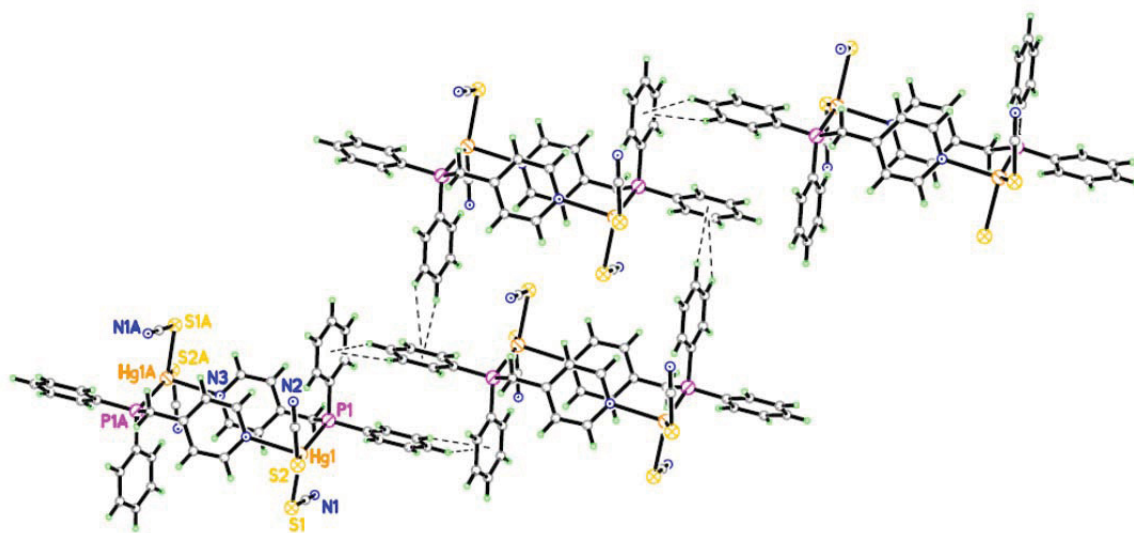


Figure 5.2. Perspective view of the edge-to-face phenyl-phenyl interactions in structure **5.1**.

Selected bond lengths and angles for compound **5.1** are listed in Table 5.1.

Table 5.1. Selected bond lengths (Å) and angles (°) for compound **5.1**.

Hg(1)-P(1)	2.4340(9)	P(1)-Hg(1)-S(2)	137.44(3)
Hg(1)-S(2)	2.4718(10)	P(1)-Hg(1)-N(3)#1	104.35(8)
Hg(1)-N(3)#1	2.495(3)	S(2)-Hg(1)-N(3)#1	94.39(7)
Hg(1)-S(1)	2.5655(9)	P(1)-Hg(1)-S(1)	113.89(3)
S(1)-C(1)	1.671(4)	S(2)-Hg(1)-S(1)	101.16(3)
S(2)-C(2)	1.676(4)	N(3)#1-Hg(1)-S(1)	96.55(7)
P(1)-C(15)	1.805(4)	C(1)-S(1)-Hg(1)	96.87(13)
P(1)-C(9)	1.807(4)	C(2)-S(2)-Hg(1)	97.58(15)
P(1)-C(3)	1.826(4)	C(15)-P(1)-Hg(1)	112.34(12)
N(1)-C(1)	1.153(5)	C(9)-P(1)-Hg(1)	112.40(12)
N(2)-C(2)	1.150(5)	C(3)-P(1)-Hg(1)	113.66(12)
N(3)-C(7)	1.339(4)	C(7)-N(3)-Hg(1)#1	118.0(2)
N(3)-C(6)	1.339(5)	C(6)-N(3)-Hg(1)#1	124.8(2)
N(3)-Hg(1)#1	2.495(3)		

The reaction between $\text{Hg}(\text{Tfa})_2$ and **L4** in a 1:1 ligand-to-metal ratio yielded complex **5.2**. The crystal structure, displayed in Figure 5.3, consists of a centrosymmetric dimer in which two **L4** ligand units are coordinated to the two mercury centers through the nitrogen and phosphorus atoms, generating a 14-membered metallacycle structure. Similar to complex **5.1**, intramolecular van der Waals attractions of the type dipole-dipole between the pyridyl moieties is observed. Complex **5.2** displays a more distorted metallacycle compared to complex **5.1**. The planes where the pyridyl group lie are parallel with respect to each other, with a centroid – centroid distance, c , of 3.822 Å, a plane-to-plane separation, b , of 3.461 Å and an offset distance of centroids, a , of 1.621 Å (Scheme 5.1). The geometrical parameter a in complex **5.2** is 0.67 Å shorter than in complex **5.1**, probably due to the stronger interaction between the metal centers and the bridging ligands in complex **5.2**, product of the weaker $\text{Hg-O}_{\text{Tfa}^-}$ interactions for this complex when compared to the $\text{Hg-S}_{\text{SCN}^-}$ interactions complex **5.1**. Each mercury center is arranged in a distorted tetrahedral environment with two Tfa^- counter-anions, the

phosphorus atoms of one ligand unit and the nitrogen of the other ligand unit coordinated to the metal. The tetrahedral angles range from 87.7° to 131.6°, with an average angle of $115.5^\circ \pm 22.4^\circ$.

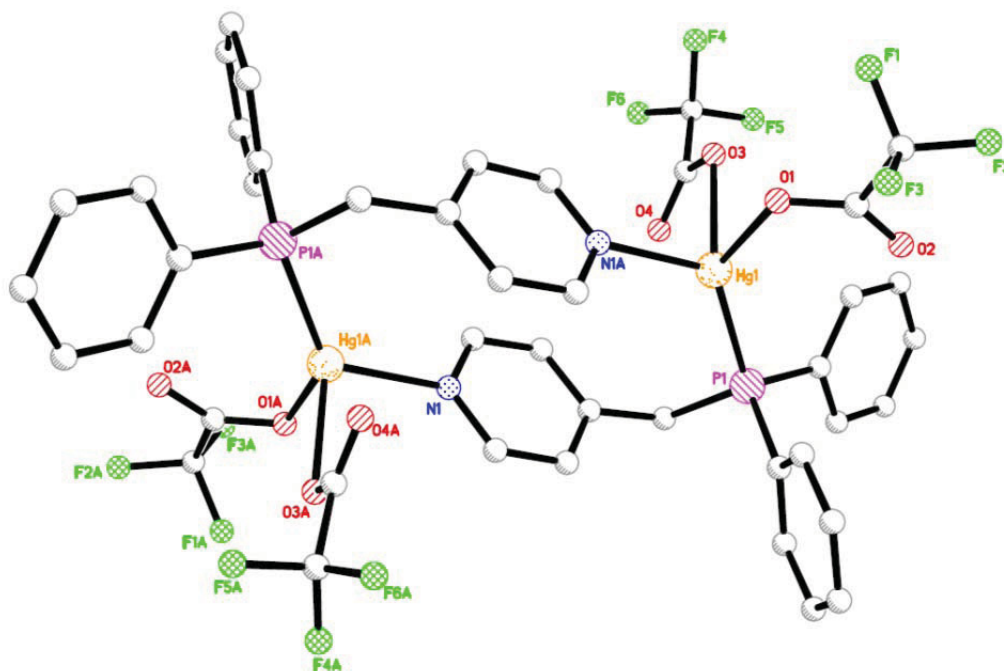


Figure 5.3. Perspective view of compound **5.2**.

The angle between the metal center and the Tfa⁻ oxygen atoms, O1-Hg-O3, is 87.7° smaller than the angle P1-Hg-N1A, which is 128.2°. This difference can be attributed to the greater steric effects generated by the bulky phenyl groups bonded to the phosphorus atom, compared to the smaller Tfa⁻ anions, and to the spatial constraints imposed by the metallacycle structure.

Each of the counter-anions are directly coordinated to the metal center through one of their oxygen atoms, while the other two oxygen atoms are weakly interacting with the metal center, with Hg-O2 and Hg-O4 distances of 3.196 Å and 2.940 Å, respectively.

The distances between the closest Tfa⁻ oxygen atoms to the mercury center fall within normal range (Hg-O1 = 2.271 Å; Hg-O3 = 2.285 Å). The CCOO groups of the trifluoroacetate ions are planar; O1 and O2 of one of these anions are coplanar with Hg and N1A while the plane the CCOO group of the other trifluoroacetate lies on is orthogonal to this plane. The supramolecular structure is further supported by H⁺⋯F and π - π intermolecular interactions (Figure 5.4).

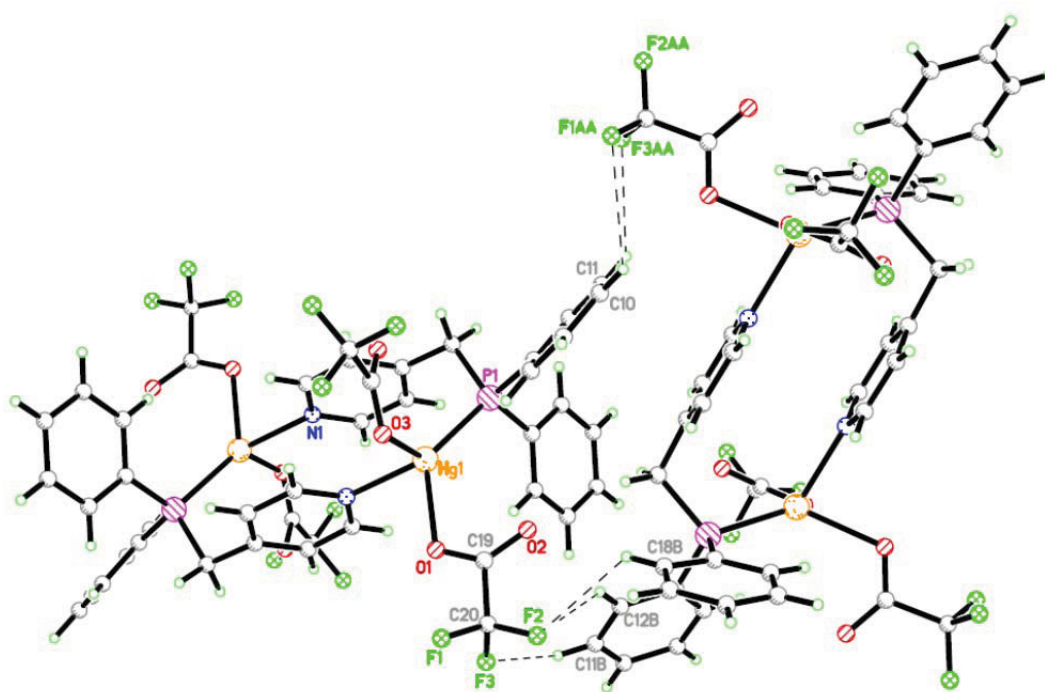
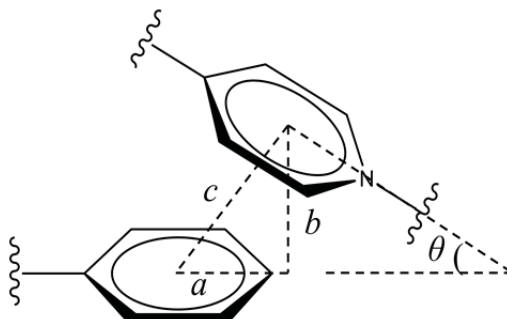


Figure 5.4. Perspective view of the C-H⁺⋯F interactions in structure 5.2.

The F⁺⋯H bonding range from 2.698 Å to 2.935 Å with a F-H-C angle range of 118.4° - 134.7°. These values are within range of those reported in other work.

The interactions of the type π - π are observed between one phenyl ring and one pyridyl ring of two adjacent molecular units. The interplane angle θ is 11.3°, with a centroid – centroid distance, c , of 3.651 Å, plane-to-plane separation, b , of 3.284 Å and

offset distance of centroids, a , of 1.595 Å (Scheme 5.3). Selected bond lengths and angles for compound **5.2** are listed in Table 5.2.



Scheme 5.3. Geometric characteristics for two interacting aromatic rings.

Table 5.2. Selected bond lengths (Å) and angles (°) for compound **5.2**.*

Hg(1)-O(1)	2.271(3)	O(1)-Hg(1)-P(1)	131.56(8)
Hg(1)-N(1)#	2.272(3)	N(1)#1-Hg(1)-P(1)	128.17(8)
Hg(1)-O(3)	2.285(3)	O(3)-Hg(1)-P(1)	119.51(8)
Hg(1)-P(1)	2.3656(9)	C(13)-P(1)-C(7)	110.12(17)
P(1)-C(13)	1.809(4)	C(13)-P(1)-C(1)	107.64(19)
P(1)-C(7)	1.810(4)	C(7)-P(1)-C(1)	104.85(17)
P(1)-C(1)	1.839(4)	C(13)-P(1)-Hg(1)	112.04(13)
O(1)-C(19)	1.246(5)	C(7)-P(1)-Hg(1)	111.84(13)
O(2)-C(19)	1.225(4)	C(1)-P(1)-Hg(1)	110.02(12)
O(3)-C(21)	1.255(6)	F(1)-C(20)-F(2)	107.8(4)
O(4)-C(21)	1.207(6)	F(1)-C(20)-F(3)	105.7(3)
		F(2)-C(20)-F(3)	106.6(4)
O(1)-Hg(1)-N(1)#1	82.68(10)	F(1)-C(20)-C(19)	112.2(4)
O(1)-Hg(1)-O(3)	87.65(13)	F(2)-C(20)-C(19)	113.4(3)
N(1)#1-Hg(1)-O(3)	95.20(12)	F(3)-C(20)-C(19)	110.6(3)

*Symmetry transformations used to generate equivalent atoms: #1 -x+1/2,-y+1/2,-z.

Complex **5.3** results from the reaction of Hg(OTf)₂ with PMP-41 in a 1:1 ratio. The crystal structure consists of a cyclic trimer, where three **L4** units act in a bidentate fashion, serving as bridges between three mercury centers, as shown in Figure 5.5. One

triflate anion is interacting with the three mercury centers through its three oxygen atoms, giving additional stability to the overall structure.

The geometry around the mercury center Hg1, shown in Figure 5.6, is a heavily distorted octahedron which is formed by the coordination of two ligand units, three OTf counter-anions and one acetonitrile molecule.

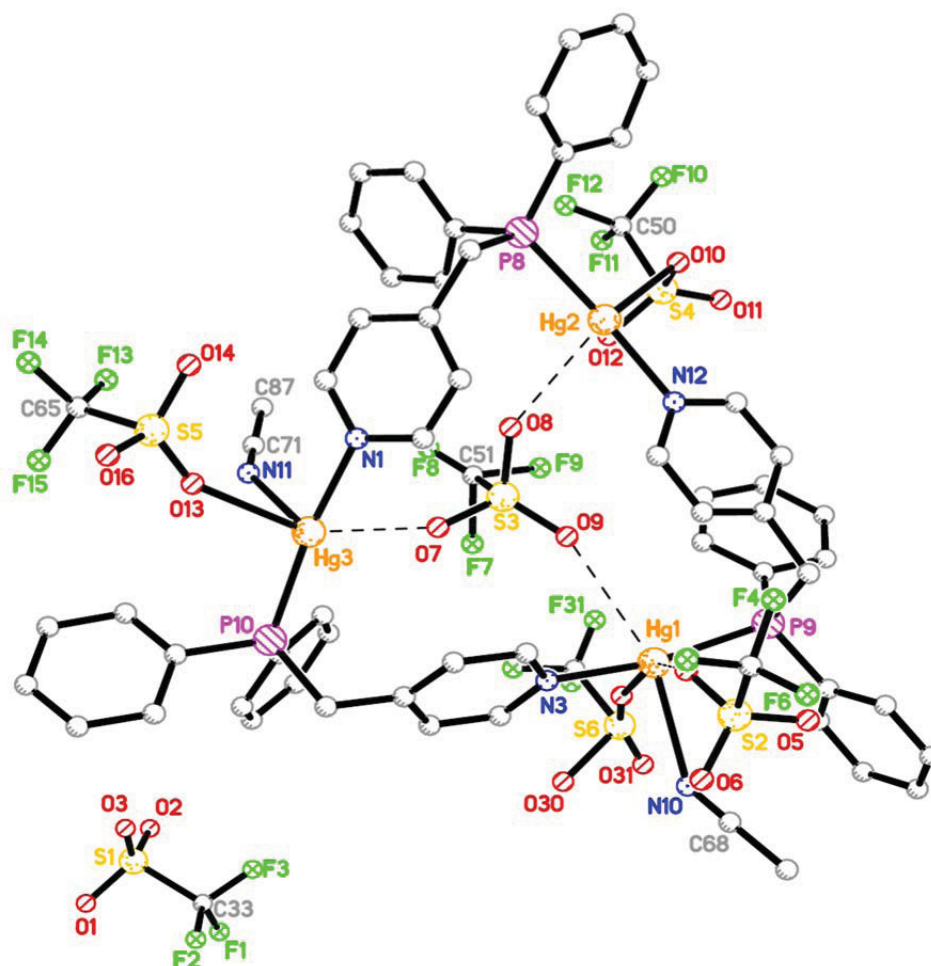


Figure 5.5. Perspective view of complex 5.3.

The coordinated nitrogen atom of one **L4** unit is in *trans* position with respect to the coordinated phosphorus atom of the other **L4** unit. The Hg-N and Hg-P bond lengths are 2.125 Å and 2.6362 Å, respectively, with a N-Hg-P angle of 168.8°.

The average angle between atoms *cis* to each other is 89.7°. For atoms *trans* to each other the average angle is 163.8° (N4-Hg1-O9 = 161.6°; O3-Hg1-O15 = 161.0°; N3-Hg1-P10 = 168.8°).

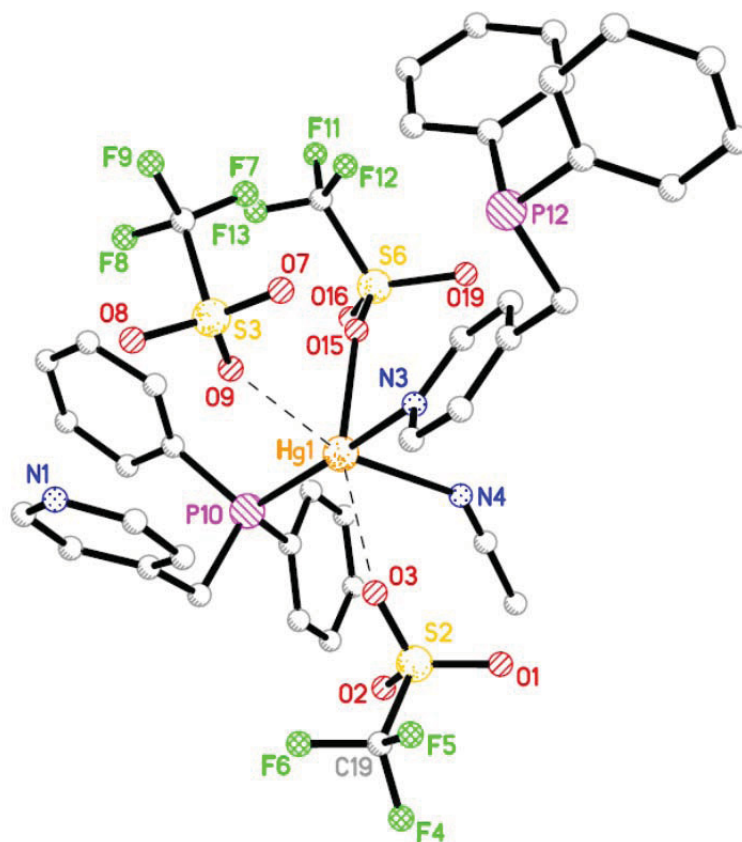


Figure 5.6. Perspective view of the hexa-coordinate environment around Hg1.

On the other hand, the mercury center Hg2 is tetra-coordinated and is interacting with two OTf⁻ anions through two of their oxygen atoms, with a O8-Hg2-O11 angle of 121.1° and Hg2-O8 and Hg2-O11 bond lengths of 2.880 Å and 2.570 Å, respectively (Figure 5.7). The tetra-coordinate environment is completed by the interaction of an **L4** nitrogen atom which is at 2.106 Å from the Hg2 center and *trans* to a coordinated phosphorus atom of another **L4** unit with a Hg2-P bond length of 2.357 Å.

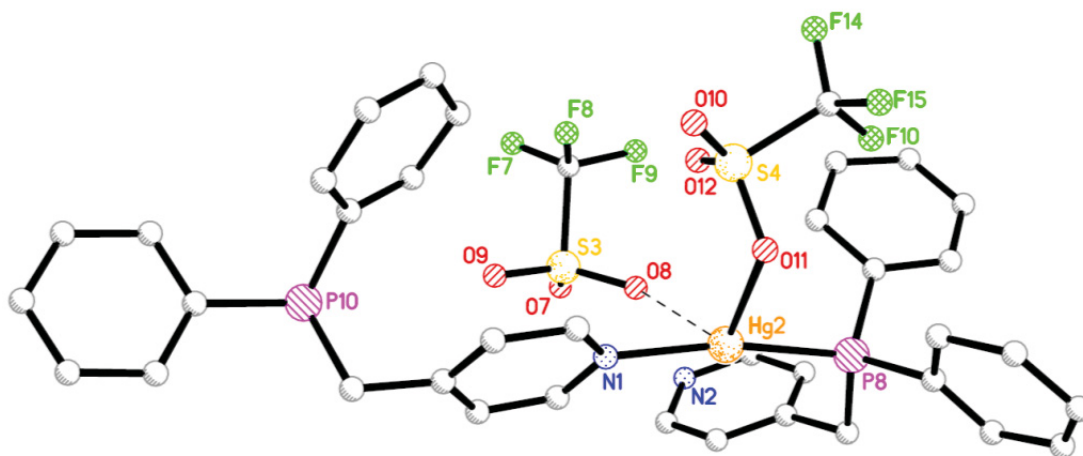


Figure 5.7. Perspective view of the tetra-coordinate geometry around Hg2.

Lastly, the mercury center Hg3, displayed in Figure 5.8, possesses a distorted square planar geometry which consists of the interaction of two ligand units, through the N atom of one and the P atom of the other, and two oxygen atoms of two different OTf anions.

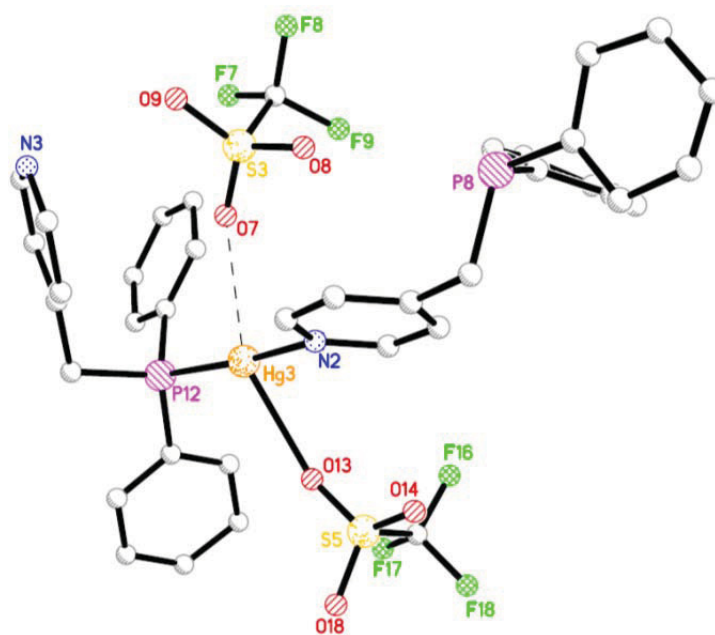


Figure 5.8. Perspective view of the distorted square planar geometry around Hg3.

The O-Hg3-O angle was found to be 155.3° and the Hg-O distances 2.572 Å and 2.788 Å, being the longest Hg3-O distance the one corresponding to the OTf anion centered within the crystal structure.

Table 4.3. Selected bond lengths (Å) and angles (°) for compound **5.3**.

		P(1)-Hg(1)-N(3)	168.97 (17)
		N(3)-Hg(1)-O(7)#	91.63 (17)
Hg(1)-N(3)	2.1203 (58)	N(3)-Hg(1)-N(4)	91.46 (15)
Hg(1)-P(1)	2.3626 (17)	P(1)-Hg(1)-O(7)#	95.28 (5)
Hg(1)-O(7)#1	2.4687	P(1)-Hg(1)-N(4)	97.87 (5)
Hg(1)-N(4)	2.5857	N(4)-Hg(1)-O(7)#	83.39
Hg(2)-N(1)	2.1036 (57)	P(2)-Hg(2)-N(1)	169.00 (17)
Hg(2)-P(2)	2.3570 (18)	N(1)-Hg(2)-O(10)	91.71 (16)
Hg(2)-O(10)	2.5797	P(2)-Hg(2)-O(10)	98.22 (5)
Hg(3)-N(2)	2.1068 (65)	P(3)-Hg(3)-N(2)	173.09 (17)
Hg(3)-P(3)	2.3590 (24)	O(13)-Hg(3)-N(2)	83.55 (16)
Hg(3)-O(13)	2.5612	N(5)-Hg(3)-N(2)	88.72 (16)
Hg(1)-N(5)	2.6815	O(13)-Hg(1)-P(3)	102.11 (6)
		N(5)-Hg(1)-P(3)	96.01 (6)
		N(5)-Hg(1)-O(13)	81.33

Conclusions

Three new coordination compounds of mercury(II) and the ligand 4-[(diphenylphosphino)methyl]pyridine, **L4**, were synthesized and their structures determined by single-crystal X-ray crystallography. Similar to the results obtained in Chapter II with the ligand 2-[(diphenylphosphino)methyl]pyridine, **L1**, the ligand-to-metal ratio observed in complexes **5.1** - **5.3** was 1:1, expected for complexes of mercury(II). Even though dimeric structures similar to those displayed by complexes **5-1** and **5.2** have been observed in previous works, the interesting structure of complex **5.3** consists in a trimer with a molecular arrangement that has not been reported to the date. The structural variation observed in complex **5.3** shows that the resulting structure has

certain degree of dependence with the counter-anion present. The ligand **L4**, proved to have inferior coordination versatility with respect to its relative **L1**. On the other hand, an increased predictability can be achieved with **L4**. As expected, its coordination behavior showed preference to bridge two metal centers, in head-to-tail fashion, rather than to chelate them. Intramolecular interaction of the type π - π were observed, contributing to the overall stability of complexes **5-1** and **5.2**. The extended molecular assembly of complex **5.2** was possible with the assistance of weak C-H $\cdots$ F bonding between neighboring molecular units.

Experimental

General Remarks

Caution! Mercury compounds are highly toxic. Appropriate engineering control measures and personal protection equipment must be used at all time while handling these compounds. Consult the corresponding Material Safety Data Sheets (MSDS) for further safety information before attempting to work with these compounds.

All experiments were performed under nitrogen atmosphere, were stored and handled in an inert atmosphere glovebox and used as received. All solvents were reagent grade and distilled under inert atmosphere from the appropriate drying agent prior to use. ^1H and ^{31}P NMR spectra were recorded at 499.78 and 202.31 MHz, respectively, at 25.0 °C/298.1 K, using a Varian VNMRs 500 MHz Spectrometer. Elemental analyses were performed by Atlantic Microlabs Inc. in Norcross, Georgia. Yields for compounds **5.1** – **5.3** were calculated with respect to HgX_2 (X = SCN^- , OTf^- and Tfa^-).

Preparation

Synthesis of $[Hg(SCN)_2(\mu-L4)]_2$ (5.1). A solution of **L4** (0.083 g, 0.300 mmol) in THF (5 mL) was added to a solution of $Hg(SCN)_2$ (0.095 g, 0.300 mmol) in THF (5 mL). The resulting solution was allowed to stir for 10 min and then dried under vacuum to leave an off-white powder. Colorless blocks were obtained by slow diffusion of ether into a DMF solution of **5.1** at -5 °C. Yield 88% (0.313 g, 0.264 mmol). 1H NMR (DMF, 298.1 K): δ 4.66 (d, 2H), 7.26 (m, 2H), 7.67 (m, 4H), 7.76 (m, 2), 7.93 (m, 4H), 8.46 (2H). ^{31}P NMR (DMF, 298.1 K) δ 44.20, (s) ppm. Anal. Calc. for $C_{20}H_{15}HgN_3PS_2$ (1186.1): C, 40.44; H, 2.71; N, 7.07. Found: C, 40.33; H, 2.44; N, 7.06%.

Synthesis of $[Hg(Tfa)_2(\mu-L4)]_2$ (5.2). A solution of **L4** (0.055 g, 0.200 mmol) in CH_3CN (5 mL) was added to a solution of $Hg(Tfa)_2$ (0.085 g, 0.200 mmol) in CH_3CN (5 mL). The resulting solution was allowed to stir for 15 min and then dried in vacuum to leave an off-white powder. This was then dissolved in a small amount of CH_3CN and precipitated with ether. Colorless blocks were obtained by slow diffusion of ether into a DMF solution of **5.2** at -5 °C. Yield 78% (0.219 g, 0.156 mmol).

Synthesis of $[Hg(OTf)_2(\mu-L4)]_3$ (5.3). A solution of **L4** (0.178 g, 0.357 mmol) in THF (5 mL) was added to a solution of $Hg(OTf)_2$ (0.099 g, 0.357 mmol) in THF (5 mL). The resulting solution was allowed to stir for 20 min and then dried in vacuum to leave an off-white powder. The remaining product was then dissolved in a small amount of CH_3CN and precipitated with ether. Colorless blocks were obtained by slow diffusion of ether into a CH_3CN solution of **5.3** at -5 °C. Yield 92% (0.763 g, 0.328 mmol). 1H NMR (CD_3CN , 298.1 K): δ 4.62 (d, 2H), 7.50 (m, 2H), 7.67 (m, 10H) 8.66 (d, 2H). ^{31}P NMR

(CD₃CN, 298.1 K): δ 43.39, (s) ppm. $^1J(^{31}\text{P}-^{199}\text{Hg})$: 4268.95 Hz. Anal. Calc. For C₂₀H₁₅F₆HgNO₆PS₂ (2325.06): C, 30.95; H, 2.07; N, 1.80. Found: C, 30.62; H, 2.07; N, 1.88%.

X-ray crystallography

Crystallographic data were collected on crystals with dimensions 0.127 x 0.150 x 0.87 mm for **5.1**, 0.334 x 0.324 x 0.224 mm for **5.2**, and 0.180 x 0.200 x 0.096 mm for **5.3**. Data were collected at 110 K on a Bruker X8 Apex using Mo K α radiation (λ = 0.71073 Å). All structures were solved by direct methods after correction of the data using SADABS.¹⁰⁹⁻¹¹⁰ Crystal data are presented in Table 5.4. All the data were processed using the Bruker AXS SHELXTL software, version 6.10.¹¹¹ Unless otherwise noted, all non-hydrogen atoms were refined anisotropically and hydrogen atoms were placed in calculated positions.

Table 5.4. Crystallographic data for compounds **5.1** and **5.2**.

	5.1	5.2
Empirical formula	C ₄₀ H ₃₂ Hg ₂ N ₆ P ₂ S ₄	C ₅₂ H ₅₂ F ₁₂ Hg ₂ N ₂ O ₁₀ P ₂
Formula mass	1188.08	1556.08
<i>a</i> (Å)	8.8219(6)	23.783(3)
<i>b</i> (Å)	8.9937(7)	11.7416(12)
<i>c</i> (Å)	13.6100(10)	20.191(2)
α (°)	72.400(4)	90
β (°)	88.895(4)	94.233(2)
γ (°)	76.924(4)	90
<i>V</i> (Å ³)	1001.20(13)	5623.1(11)
<i>Z</i>	1	4
Crystal System	Triclinic	Monoclinic
Space Group	P-1	C2/c
T(K)	110(2)	110(2)
D _{calcd.} (g/cm ⁻³)	1.970	1.838
μ (mm ⁻¹)	7.985	5.608
$2\theta_{max}$ (°)	28.48	28.33
Reflections measured	11675	31033
Reflections used	4931	6943
Data / restraints / parameters	4931 / 0 / 244	6943 / 2 / 371
R ₁ [<i>I</i> > 2 σ (<i>I</i>)]	0.0251	0.0315
wR ₂ [<i>I</i> > 2 σ (<i>I</i>)]	0.0551	0.0668
R(<i>F</i> ² _o) (all data)	0.0303	0.0414
R _w (<i>F</i> ² _o) (all data)	0.0565	0.0711
GOF on <i>F</i> ²	1.060	1.075

CHAPTER SIX

Summary

This work reports the synthesis and characterization of several complexes of silver, mercury, and divalent first row transition metals based on methylpyridylphosphine ligands and their corresponding *P* and *N,P* oxides. The resulting structures showed strong dependence with the counter-anion present, metal center, and solvent molecules. The molecular structure of the complexes of Co^{2+} , Ni^{2+} , Cu^{2+} , and Zn^{2+} , discussed in Chapter IV, also proved to be dependent on the temperature at which the crystals were grown. Several inter and intramolecular interactions were identified with the help of X-ray crystal structure analysis. These interactions seem to support the extended molecular structures and might play a role in the stability of the crystals formed. Interactions of the type $\text{X}\cdots\text{H-C}$, ($\text{X} = \text{N}, \text{O}$ or F), were observed in several of the coordination compounds obtained. The great versatility of the coordination number of the Ag^+ was evidenced in the compounds presented in Chapter III. Several of these silver(I) centers even showed the unusual hepta- and octa-coordinate environment around the metal centers. The weak supramolecular $\pi\text{-Ag}$ and argentophilic interactions aided in the formation of a variety of macromolecular arrays, including one-dimensional and two-dimensional polymers. Instead, the mercury complexes were restricted to the formation of discrete molecules with a 1:1 and 2:1 ligand-to-metal ratios. Also, the mercury centers reported herein presented a variety of geometries, including tetrahedral and trigonal-bipyramidal, which are common in the literature for this cation. All complexes of the divalent first-row transition metals studied in Chapter IV presented octahedral geometry. As expected, a

strong Jahn-Teller distortion was observed in the d^9 complexes of Cu^{2+} . In regard to the ligands, the compound 2-[(diphenylphosphino)methyl]pyridine showed preference to coordinate in a monodentate or chelating mode, depending on the strength of the interaction between the metal center and the anion, whilst the 4-[(diphenylphosphino)methyl]pyridine compound coordinates in a bridging mode. The ligand 2-[(diphenylphosphino)methyl]pyridine *N,P*-dioxide takes advantage of the extra lone pairs of electrons on the oxygen atoms to chelate and bridge metal centers at the same time, as demonstrated in Chapter III. On the other hand, the generation of the monoanionic 2-[(diphenylphosphino)methyl]pyridine oxide species represents an interesting opportunity for the synthesis and catalytic studies of novel methylpyridylphosphine-based organometallic compounds. This study describes the fundamental bonding studies of several transition metal ions with hemilabile methylpyridylphosphine ligands and with their harder donor relatives bearing phosphoryl and nitrosyl moieties.

APPENDICES

APPENDIX A

Procedures for X-ray Crystal Structure Determinations

General Considerations

Quality crystals suitable for X-ray diffraction were isolated on a binocular polarized microscope in chemically inert Paratone-N[®] oil. The ideal crystals were perfectly single, optically transparent and with dimensions of 0.15 to 0.30 mm³. After identification and isolation, the ideal crystal was immobilized on a polymer-fiber cryoloop in a nitrogen cold stream. This setup was then mounted on the goniometer magnetic base and centered in the X-ray beam with the help of a magnifying digital camera.

Data Collection and Reduction

Data was collected at 110(2) K on a Bruker X8 Apex using Mo-K radiation ($\lambda = 0.71073$ Å). All structures were solved by direct methods after correction of the data using SADABS. All the data were processed using the Bruker AXS SHELXTL software, version 6.10. Unless otherwise noted, all non-hydrogen atoms were refined anisotropically and hydrogen atoms were placed in calculated positions.

APPENDIX B

Crystallographic Data

The tables to follow are provided to supplement the selected crystallographic parameters presented in the text. Included are statistical data, full bond lengths, full bond angles, torsion angles and hydrogen bonding distances.

Table B.1 Experimental and statistical crystal data for **2.1**.*

Empirical formula	$\text{C}_{20}\text{H}_{16}\text{Hg N}_3\text{OPS}_2$	
Formula weight	610.06	
Temperature	110(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P-1	
Unit cell dimensions	$a = 8.4467(6)$ Å	$\alpha = 76.694(3)^\circ$
	$b = 9.7171(7)$ Å	$\beta = 89.100(3)^\circ$
	$c = 13.9400(10)$ Å	$\delta = 71.610(4)^\circ$
Volume	$1054.57(13)$ Å ³	
Z	2	
Density (calculated)	1.921 Mg/m ³	
Absorption coefficient	7.587 mm ⁻¹	
F(000)	584	
Crystal size	$0.178 \times 0.119 \times 0.108$ mm ³	
Theta range for data collection	2.27 to 28.28°	
Index ranges	$-11 \leq h \leq 11$, $-12 \leq k \leq 12$, $-16 \leq l \leq 18$	
Reflections collected	16424	
Independent reflections	5164 [R(int) = 0.0291]	
Completeness to $\theta = 28.28^\circ$	98.8 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.442 and 0.350	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	5164 / 0 / 253	
Goodness-of-fit on F^2	1.056	
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0229$, $wR_2 = 0.0512$	
R indices (all data)	$R_1 = 0.0256$, $wR_2 = 0.0524$	
Largest diff. peak and hole	2.314 and -0.867 e.Å ⁻³	

Table B.1. (continued)

Bond Lengths (Å)

Hg(1)-N(1)	2.361(3)	C(6)-H(6A)	0.9900
Hg(1)-S(1)	2.4484(10)	C(6)-H(6B)	0.9900
Hg(1)-S(2)	2.4537(9)	C(7)-C(8)	1.392(4)
Hg(1)-N(2)#1	2.560(3)	C(7)-C(12)	1.400(4)
S(1)-C(19)	1.671(3)	C(8)-C(9)	1.387(4)
S(2)-C(20)	1.687(3)	C(8)-H(8)	0.9500
P(1)-O(1)	1.499(2)	C(9)-C(10)	1.385(5)
P(1)-C(7)	1.799(3)	C(9)-H(9)	0.9500
P(1)-C(13)	1.804(3)	C(10)-C(11)	1.382(5)
P(1)-C(6)	1.825(3)	C(10)-H(10)	0.9500
N(1)-C(1)	1.345(4)	C(11)-C(12)	1.388(4)
N(1)-C(5)	1.349(4)	C(11)-H(11)	0.9500
N(2)-C(19)	1.143(4)	C(12)-H(12)	0.9500
N(2)-Hg(1)#1	2.560(3)	C(13)-C(18)	1.390(4)
N(3)-C(20)	1.148(4)	C(13)-C(14)	1.397(4)
C(1)-C(2)	1.380(5)	C(14)-C(15)	1.385(5)
C(1)-H(1)	0.9500	C(14)-H(14)	0.9500
C(2)-C(3)	1.376(5)	C(15)-C(16)	1.385(5)
C(2)-H(2)	0.9500	C(15)-H(15)	0.9500
C(3)-C(4)	1.385(5)	C(16)-C(17)	1.388(5)
C(3)-H(3)	0.9500	C(16)-H(16)	0.9500
C(4)-C(5)	1.387(4)	C(17)-C(18)	1.386(4)
C(4)-H(4)	0.9500	C(17)-H(17)	0.9500
C(5)-C(6)	1.503(4)	C(18)-H(18)	0.9500

Bond Angles (°)

N(1)-Hg(1)-S(1)	119.20(7)	C(8)-C(7)-C(12)	119.7(3)
N(1)-Hg(1)-S(2)	100.64(7)	C(8)-C(7)-P(1)	118.2(2)
S(1)-Hg(1)-S(2)	139.71(4)	C(12)-C(7)-P(1)	122.0(2)
N(1)-Hg(1)-N(2)#1	83.66(9)	C(9)-C(8)-C(7)	120.1(3)
S(1)-Hg(1)-N(2)#1	96.42(7)	C(9)-C(8)-H(8)	119.9
S(2)-Hg(1)-N(2)#1	93.45(7)	C(7)-C(8)-H(8)	119.9
C(19)-S(1)-Hg(1)	100.82(11)	C(10)-C(9)-C(8)	119.7(3)
C(20)-S(2)-Hg(1)	97.53(12)	C(10)-C(9)-H(9)	120.1
O(1)-P(1)-C(7)	111.81(13)	C(8)-C(9)-H(9)	120.1
O(1)-P(1)-C(13)	112.44(12)	C(11)-C(10)-C(9)	120.7(3)
C(7)-P(1)-C(13)	107.95(13)	C(11)-C(10)-H(10)	119.6
O(1)-P(1)-C(6)	112.11(12)	C(9)-C(10)-H(10)	119.6
C(7)-P(1)-C(6)	104.69(13)	C(10)-C(11)-C(12)	119.9(3)
C(13)-P(1)-C(6)	107.42(13)	C(10)-C(11)-H(11)	120.0

Table B.1. (continued)

C(1)-N(1)-C(5)	119.0(3)		
C(1)-N(1)-Hg(1)	115.7(2)	C(12)-C(11)-H(11)	120.0
C(5)-N(1)-Hg(1)	125.2(2)	C(11)-C(12)-C(7)	119.7(3)
C(19)-N(2)-Hg(1)#1	157.2(3)	C(11)-C(12)-H(12)	120.1
N(1)-C(1)-C(2)	122.6(3)	C(7)-C(12)-H(12)	120.1
N(1)-C(1)-H(1)	118.7	C(18)-C(13)-C(14)	118.9(3)
C(2)-C(1)-H(1)	118.7	C(18)-C(13)-P(1)	118.9(2)
C(3)-C(2)-C(1)	118.7(3)	C(14)-C(13)-P(1)	122.1(2)
C(3)-C(2)-H(2)	120.7	C(15)-C(14)-C(13)	120.3(3)
C(1)-C(2)-H(2)	120.7	C(15)-C(14)-H(14)	119.9
C(2)-C(3)-C(4)	119.3(3)	C(13)-C(14)-H(14)	119.9
C(2)-C(3)-H(3)	120.4	C(14)-C(15)-C(16)	120.2(3)
C(4)-C(3)-H(3)	120.4	C(14)-C(15)-H(15)	119.9
C(3)-C(4)-C(5)	119.5(3)	C(16)-C(15)-H(15)	119.9
C(3)-C(4)-H(4)	120.2	C(15)-C(16)-C(17)	120.1(3)
C(5)-C(4)-H(4)	120.2	C(15)-C(16)-H(16)	120.0
N(1)-C(5)-C(4)	121.0(3)	C(17)-C(16)-H(16)	120.0
N(1)-C(5)-C(6)	117.8(3)	C(18)-C(17)-C(16)	119.6(3)
C(4)-C(5)-C(6)	121.3(3)	C(18)-C(17)-H(17)	120.2
C(5)-C(6)-P(1)	112.9(2)	C(16)-C(17)-H(17)	120.2
C(5)-C(6)-H(6A)	109.0	C(17)-C(18)-C(13)	120.9(3)
P(1)-C(6)-H(6A)	109.0	C(17)-C(18)-H(18)	119.5
C(5)-C(6)-H(6B)	109.0	C(13)-C(18)-H(18)	119.5
P(1)-C(6)-H(6B)	109.0	N(2)-C(19)-S(1)	176.6(3)
H(6A)-C(6)-H(6B)	107.8	N(3)-C(20)-S(2)	175.7(3)

*Symmetry transformations used to generate equivalent atoms: #1 -x+2,-y,-z+1

Table B.2 Experimental and statistical crystal data for **2.2**.*

Empirical formula	C ₃₈ H ₃₂ HgN ₄ P ₂ S ₂	
Formula weight	871.33	
Temperature	110(2) K	
Wavelength	0.71073 Å	
Crystal system	Orthorhombic	
Space group	Aba2	
Unit cell dimensions	a = 12.5734(10) Å	$\alpha = 90^\circ$.
	b = 19.6504(15) Å	$\beta = 90^\circ$.
	c = 14.2674(15) Å	$\delta = 90^\circ$.
Volume	3525.1(5) Å ³	
Z	4	
Density (calculated)	1.642 Mg/m ³	
Absorption coefficient	4.609 mm ⁻¹	

Table B.2. (continued)

F(000)	1720
Crystal size	0.23 x 0.16 x 0.14 mm ³
Theta range for data collection	2.07 to 28.25°
Index ranges	-16<=h<=16, -23<=k<=26, -18<=l<=17
Reflections collected	19700
Independent reflections	2268 [R(int) = 0.0507]
Completeness to theta = 28.25°	99.9 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.5606 and 0.4157
Refinement method	Full-matrix least-squares on F ²
Data / restraints / parameters	2268 / 1 / 214
Goodness-of-fit on F ²	1.099
Final R indices [I>2sigma(I)]	R1 = 0.0165, wR2 = 0.0438
R indices (all data)	R1 = 0.0189, wR2 = 0.0451
Absolute structure parameter	0.47(2)
Largest diff. peak and hole	0.725 and -0.399 e. Å ⁻³

Bond Lengths (Å)

Hg(1)-P(1)	2.4707(12)	C(3)-C(4)	1.382(5)
Hg(1)-P(1)#1	2.4707(12)	C(4)-C(5)	1.382(5)
Hg(1)-S(1)#1	2.6439(17)	C(5)-C(6)	1.371(8)
Hg(1)-S(1)	2.6439(17)	C(7)-C(8)	1.513(5)
S(1)-C(19)	1.676(4)	C(8)-C(9)	1.380(5)
P(1)-C(1)	1.814(5)	C(9)-C(10)	1.388(6)
P(1)-C(12)	1.814(3)	C(10)-C(18)	1.397(7)
P(1)-C(7)	1.830(3)	C(11)-C(18)	1.393(6)
N(1)-C(11)	1.338(5)	C(12)-C(13)	1.383(4)
N(1)-C(8)	1.360(5)	C(12)-C(17)	1.389(4)
N(2)-C(19)	1.154(5)	C(13)-C(14)	1.392(5)
C(1)-C(2)	1.388(8)	C(14)-C(15)	1.371(5)
C(1)-C(6)	1.395(7)	C(15)-C(16)	1.391(5)
C(2)-C(3)	1.401(4)	C(16)-C(17)	1.385(5)

Bond Angles (°)

P(1)-Hg(1)-P(1)#1	127.57(10)	C(6)-C(5)-C(4)	120.0(5)
P(1)-Hg(1)-S(1)#1	111.10(3)	C(5)-C(6)-C(1)	120.4(5)
P(1)#1-Hg(1)-S(1)#1	104.05(3)	C(8)-C(7)-P(1)	108.3(2)
P(1)-Hg(1)-S(1)	104.05(3)	N(1)-C(8)-C(9)	123.2(3)

Table B.2. (continued)

P(1)#1-Hg(1)-S(1)	111.10(3)	N(1)-C(8)-C(7)	115.5(3)
S(1)#1-Hg(1)-S(1)	93.98(8)	C(9)-C(8)-C(7)	121.2(3)
C(19)-S(1)-Hg(1)	94.19(14)	C(8)-C(9)-C(10)	119.0(4)
C(1)-P(1)-C(12)	105.59(18)	C(9)-C(10)-C(18)	119.1(4)
C(1)-P(1)-C(7)	107.9(3)	N(1)-C(11)-C(18)	124.4(4)
C(12)-P(1)-C(7)	104.15(15)	C(13)-C(12)-C(17)	120.0(3)
C(1)-P(1)-Hg(1)	108.7(2)	C(13)-C(12)-P(1)	119.5(2)
C(12)-P(1)-Hg(1)	118.14(11)	C(17)-C(12)-P(1)	120.4(2)
C(7)-P(1)-Hg(1)	111.75(12)	C(12)-C(13)-C(14)	119.8(3)
C(11)-N(1)-C(8)	116.7(3)	C(15)-C(14)-C(13)	120.2(3)
C(2)-C(1)-C(6)	120.1(5)	C(14)-C(15)-C(16)	120.2(4)
C(2)-C(1)-P(1)	123.2(5)	C(17)-C(16)-C(15)	119.8(4)
C(6)-C(1)-P(1)	116.7(5)	C(16)-C(17)-C(12)	120.0(3)
C(1)-C(2)-C(3)	118.9(4)	C(11)-C(18)-C(10)	117.6(3)
C(4)-C(3)-C(2)	120.3(3)	N(2)-C(19)-S(1)	179.4(4)
C(5)-C(4)-C(3)	120.3(3)		

*Symmetry transformations used to generate equivalent atoms: #1 -x+1,-y+1,z

Table B.3 Experimental and statistical crystal data for **2.3**.*

Empirical formula	$C_{44}H_{48}Cl_4Hg_2N_2O_4P_2$	
Formula weight	1273.76	
Temperature	110(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P2(1)/n	
Unit cell dimensions	a = 12.5791(7) Å	$\alpha = 90^\circ$.
	b = 8.6549(4) Å	$\beta = 96.738(2)^\circ$.
	c = 20.9536(10) Å	$\delta = 90^\circ$.
Volume	2265.5(2) Å ³	
Z	2	
Density (calculated)	1.867 Mg/m ³	
Absorption coefficient	7.119 mm ⁻¹	
F(000)	1232	
Crystal size	0.22 x 0.18 x 0.11 mm ³	
Theta range for data collection	2.55 to 28.28°.	
Index ranges	-15 ≤ h ≤ 16, -11 ≤ k ≤ 11, -27 ≤ l ≤ 27	
Reflections collected	36763	
Independent reflections	5635 [R(int) = 0.0339]	
Completeness to theta = 28.28°	99.9 %	
Absorption correction	Semi-empirical from equivalents	

Table B.3. (continued)

Max. and min. transmission	0.5136 and 0.3022
Refinement method	Full-matrix least-squares on F ²
Data / restraints / parameters	5635 / 0 / 262
Goodness-of-fit on F ²	1.046
Final R indices [I>2sigma(I)]	R1 = 0.0220, wR2 = 0.0550
R indices (all data)	R1 = 0.0250, wR2 = 0.0566
Largest diff. peak and hole	1.812 and -1.485 e. Å ³

Bond Lengths (Å)

Hg(1)-N(1)	2.309(2)	C(7)-C(12)	1.389(4)
Hg(1)-Cl(1)	2.3887(8)	C(7)-C(8)	1.395(4)
Hg(1)-Cl(2)	2.4172(7)	C(8)-C(9)	1.389(5)
Hg(1)-O(1)	2.510(2)	C(9)-C(10)	1.378(5)
Hg(1)-Cl(2)#1	2.9738(7)	C(10)-C(11)	1.386(5)
Cl(2)-Hg(1)#1	2.9738(7)	C(11)-C(12)	1.390(5)
P(1)-O(1)	1.501(2)	C(13)-C(14)	1.397(4)
P(1)-C(13)	1.793(3)	C(13)-C(15)	1.401(4)
P(1)-C(7)	1.797(3)	C(14)-C(18)	1.393(4)
P(1)-C(1)	1.823(3)	C(15)-C(16)	1.385(4)
N(1)-C(6)	1.345(4)	C(16)-C(17)	1.386(5)
N(1)-C(2)	1.348(4)	C(17)-C(18)	1.385(5)
C(1)-C(2)	1.505(4)	C(19)-C(20)	1.399(5)
C(2)-C(3)	1.395(4)	C(19)-O(2)	1.421(6)
C(3)-C(4)	1.381(5)	C(20)-C(21)	1.529(6)
C(4)-C(5)	1.383(5)	C(21)-C(22)	1.526(7)
C(5)-C(6)	1.381(5)	C(22)-O(2)	1.494(7)

Bond Angles (°)

N(1)-Hg(1)-Cl(1)	116.36(7)	C(4)-C(3)-C(2)	119.6(3)
N(1)-Hg(1)-Cl(2)	113.33(7)	C(3)-C(4)-C(5)	119.1(3)
Cl(1)-Hg(1)-Cl(2)	130.30(3)	C(6)-C(5)-C(4)	118.9(3)
N(1)-Hg(1)-O(1)	81.00(8)	N(1)-C(6)-C(5)	122.4(3)
Cl(1)-Hg(1)-O(1)	94.44(5)	C(12)-C(7)-C(8)	119.9(3)
Cl(2)-Hg(1)-O(1)	94.00(5)	C(12)-C(7)-P(1)	117.8(2)
N(1)-Hg(1)-Cl(2)#1	85.15(6)	C(8)-C(7)-P(1)	122.2(2)
Cl(1)-Hg(1)-Cl(2)#1	98.57(3)	C(9)-C(8)-C(7)	119.3(3)
Cl(2)-Hg(1)-Cl(2)#1	84.45(2)	C(10)-C(9)-C(8)	120.8(3)
O(1)-Hg(1)-Cl(2)#1	164.17(5)	C(9)-C(10)-C(11)	119.9(3)
Hg(1)-Cl(2)-Hg(1)#1	95.55(2)	C(10)-C(11)-C(12)	120.0(3)
O(1)-P(1)-C(13)	112.04(13)	C(7)-C(12)-C(11)	120.1(3)

Table B.3. (continued)

O(1)-P(1)-C(7)	111.08(13)	C(14)-C(13)-C(15)	119.4(3)
C(13)-P(1)-C(7)	107.46(13)	C(14)-C(13)-P(1)	123.4(2)
O(1)-P(1)-C(1)	111.64(13)	C(15)-C(13)-P(1)	117.0(2)
C(13)-P(1)-C(1)	107.98(14)	C(18)-C(14)-C(13)	119.9(3)
C(7)-P(1)-C(1)	106.37(14)	C(16)-C(15)-C(13)	120.2(3)
P(1)-O(1)-Hg(1)	116.31(11)	C(15)-C(16)-C(17)	120.0(3)
C(6)-N(1)-C(2)	119.1(3)	C(18)-C(17)-C(16)	120.4(3)
C(6)-N(1)-Hg(1)	118.8(2)	C(17)-C(18)-C(14)	120.1(3)
C(2)-N(1)-Hg(1)	122.05(19)	C(20)-C(19)-O(2)	110.7(3)
C(2)-C(1)-P(1)	110.2(2)	C(19)-C(20)-C(21)	107.1(4)
N(1)-C(2)-C(3)	121.0(3)	C(22)-C(21)-C(20)	103.4(4)
N(1)-C(2)-C(1)	117.8(3)	O(2)-C(22)-C(21)	103.4(4)
C(3)-C(2)-C(1)	121.2(3)	C(19)-O(2)-C(22)	104.9(5)

*Symmetry transformations used to generate equivalent atoms: #1 -x+1,-y+1,-z.

Table B.4. Experimental and statistical crystal data for **2.4**.*

Empirical formula	C ₃₈ H ₃₂ F ₆ HgN ₂ O ₆ P ₂ S ₂	
Formula weight	1053.31	
Temperature	110(2) K	
Wavelength	0.71073 Å	
Crystal system	Orthorhombic	
Space group	Pbcn	
Unit cell dimensions	a = 20.289(2) Å	a = 90°.
	b = 9.8162(12) Å	b = 90°.
	c = 19.468(2) Å	g = 90°.
Volume	3877.3(8) Å ³	
Z	4	
Density (calculated)	1.804 Mg/m ³	
Absorption coefficient	4.238 mm ⁻¹	
F(000)	2072	
Crystal size	0.26 x 0.13 x 0.10 mm ³	
Theta range for data collection	2.09 to 28.29°.	
Index ranges	-27 ≤ h ≤ 27, -12 ≤ k ≤ 13, -25 ≤ l ≤ 25	
Reflections collected	39442	
Independent reflections	4801 [R(int) = 0.0392]	
Completeness to theta = 28.29°	99.9 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.6693 and 0.4100	
Refinement method	Full-matrix least-squares on F ²	
Data / restraints / parameters	4801 / 0 / 258	

Table B.4. (continued)

Goodness-of-fit on F^2	1.011
Final R indices [$I > 2\sigma(I)$]	$R1 = 0.0227$, $wR2 = 0.0428$
R indices (all data)	$R1 = 0.0444$, $wR2 = 0.0508$
Largest diff. peak and hole	0.702 and -0.638 e.Å ⁻³

Bond Lengths (Å)

Hg(1)-P(1)#1	2.3854(7)	F(3)-C(19)-S(1)	111.4(2)
Hg(1)-P(1)	2.3854(7)	C(2)-C(3)	1.381(4)
Hg(1)-N(1)#1	2.631(2)	C(3)-C(4)	1.384(4)
Hg(1)-N(1)	2.631(2)	C(4)-C(5)	1.383(5)
S(1)-O(2)	1.436(2)	C(5)-C(6)	1.379(4)
S(1)-O(3)	1.443(2)	C(7)-C(8)	1.394(4)
S(1)-O(1)	1.445(2)	C(7)-C(12)	1.394(4)
S(1)-C(19)	1.823(3)	C(8)-C(9)	1.387(4)
P(1)-C(13)	1.799(3)	C(9)-C(10)	1.384(5)
P(1)-C(7)	1.806(3)	C(10)-C(11)	1.372(4)
P(1)-C(1)	1.814(3)	C(11)-C(12)	1.390(4)
F(1)-C(19)	1.331(3)	C(13)-C(18)	1.388(4)
F(2)-C(19)	1.342(4)	C(13)-C(14)	1.397(4)
F(3)-C(19)	1.336(3)	C(14)-C(15)	1.384(4)
N(1)-C(6)	1.340(4)	C(15)-C(16)	1.380(5)
N(1)-C(2)	1.346(4)	C(16)-C(17)	1.372(5)
C(1)-C(2)	1.514(4)	C(17)-C(18)	1.389(4)

Bond Angles (°)

P(1)#1-Hg(1)-P(1)	179.55(4)	F(2)-C(19)-S(1)	110.9(2)
P(1)#1-Hg(1)-N(1)#1	74.58(5)	C(3)-C(2)-C(1)	121.2(3)
P(1)-Hg(1)-N(1)#1	105.06(5)	C(2)-C(3)-C(4)	119.0(3)
P(1)#1-Hg(1)-N(1)	105.06(5)	C(5)-C(4)-C(3)	119.4(3)
P(1)-Hg(1)-N(1)	74.58(5)	C(6)-C(5)-C(4)	118.0(3)
N(1)#1-Hg(1)-N(1)	76.85(11)	N(1)-C(6)-C(5)	123.4(3)
O(2)-S(1)-O(3)	115.11(15)	C(8)-C(7)-C(12)	120.2(3)
O(2)-S(1)-O(1)	115.11(16)	C(8)-C(7)-P(1)	122.1(2)
O(3)-S(1)-O(1)	114.03(14)	C(12)-C(7)-P(1)	117.7(2)
O(2)-S(1)-C(19)	103.18(14)	C(9)-C(8)-C(7)	119.0(3)
O(3)-S(1)-C(19)	103.39(14)	C(10)-C(9)-C(8)	120.4(3)
O(1)-S(1)-C(19)	103.82(14)	C(11)-C(10)-C(9)	120.9(3)
C(13)-P(1)-C(7)	108.37(12)	C(10)-C(11)-C(12)	119.5(3)
C(13)-P(1)-C(1)	108.33(13)	C(11)-C(12)-C(7)	120.0(3)
C(7)-P(1)-C(1)	108.15(13)	C(18)-C(13)-C(14)	119.9(3)

Table B.4. (continued)

C(13)-P(1)-Hg(1)	118.94(10)	C(18)-C(13)-P(1)	121.4(2)
C(7)-P(1)-Hg(1)	109.11(9)	C(14)-C(13)-P(1)	118.6(2)
C(1)-P(1)-Hg(1)	103.46(9)	C(15)-C(14)-C(13)	120.1(3)
C(6)-N(1)-C(2)	118.0(3)	C(16)-C(15)-C(14)	119.5(3)
C(6)-N(1)-Hg(1)	125.95(19)	C(17)-C(16)-C(15)	120.7(3)
C(2)-N(1)-Hg(1)	113.50(18)	C(16)-C(17)-C(18)	120.6(3)
C(2)-C(1)-P(1)	111.50(19)	C(13)-C(18)-C(17)	119.1(3)
N(1)-C(2)-C(3)	122.1(3)	F(1)-C(19)-F(3)	108.2(2)
N(1)-C(2)-C(1)	116.7(2)	F(1)-C(19)-F(2)	107.5(3)
F(1)-C(19)-S(1)	111.4(2)	F(3)-C(19)-F(2)	107.2(2)

*Symmetry transformations used to generate equivalent atoms: #1 -x+1,y,-z+1/2

Table B.5. Experimental and statistical crystal data for **2.5**.

Empirical formula	$\text{C}_{38}\text{H}_{32}\text{F}_6\text{HgN}_2\text{O}_8\text{P}_2\text{S}_2$	
Formula weight	1085.31	
Temperature	110(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	C2/c	
Unit cell dimensions	$a = 30.2478(14)$ Å	$\alpha = 90^\circ$.
	$b = 25.6146(12)$ Å	$\beta = 93.707(2)^\circ$.
	$c = 20.7312(9)$ Å	$\delta = 90^\circ$.
Volume	$16028.6(13)$ Å ³	
Z	16	
Density (calculated)	1.799 Mg/m ³	
Absorption coefficient	4.108 mm ⁻¹	
F(000)	8544	
Crystal size	$0.168 \times 0.157 \times 0.136$ mm ³	
Theta range for data collection	2.09 to 28.33° .	
Index ranges	$-39 \leq h \leq 40$, $-33 \leq k \leq 34$, $-26 \leq l \leq 27$	
Reflections collected	71806	
Independent reflections	19917 [R(int) = 0.0470]	
Completeness to $\theta = 28.33^\circ$	99.6 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.572 and 0.506	
Refinement method	Full-matrix least-squares on F ²	
Data / restraints / parameters	19917 / 0 / 1063	
Goodness-of-fit on F ²	1.006	
Final R indices [I > 2sigma(I)]	R1 = 0.0329, wR2 = 0.0670	
R indices (all data)	R1 = 0.0544, wR2 = 0.0749	
Largest diff. peak and hole	2.193 and -1.109 e. Å ⁻³	

Table B.5. (continued)

Bond Lengths (Å)

Hg(1)-N(2)	2.120(3)	C(20)-C(21)	1.382(5)
Hg(1)-N(1)	2.122(3)	C(21)-C(22)	1.378(5)
Hg(1)-O(2)	2.520(2)	C(21)-H(21)	0.9500
Hg(1)-O(1)	2.541(2)	C(22)-C(23)	1.385(6)
Hg(2)-N(4)	2.126(3)	C(22)-H(22)	0.9500
Hg(2)-N(3)	2.135(3)	C(23)-C(24)	1.361(6)
Hg(2)-O(4)	2.511(2)	C(23)-H(23)	0.9500
Hg(2)-O(3)	2.520(2)	C(24)-H(24)	0.9500
Hg(2)-O(11)	2.631(3)	C(25)-C(26)	1.390(5)
S(1)-O(6)	1.427(3)	C(25)-C(30)	1.397(5)
S(1)-O(7)	1.431(3)	C(26)-C(27)	1.394(5)
S(1)-O(5)	1.434(3)	C(26)-H(26)	0.9500
S(1)-C(37)	1.810(5)	C(27)-C(28)	1.370(6)
S(2)-O(9)	1.434(3)	C(27)-H(27)	0.9500
S(2)-O(10)	1.435(3)	C(28)-C(29)	1.387(5)
S(2)-O(8)	1.442(3)	C(28)-H(28)	0.9500
S(2)-C(38)	1.807(4)	C(29)-C(30)	1.391(5)
S(3)-O(13)	1.428(3)	C(29)-H(29)	0.9500
S(3)-O(12)	1.431(3)	C(30)-H(30)	0.9500
S(3)-O(11)	1.444(3)	C(31)-C(32)	1.382(5)
S(3)-C(75)	1.819(4)	C(31)-C(36)	1.389(5)
S(4)-O(16)	1.428(3)	C(32)-C(33)	1.386(5)
S(4)-O(15)	1.434(3)	C(32)-H(32)	0.9500
S(4)-O(14)	1.441(3)	C(33)-C(34)	1.379(6)
S(4)-C(76)	1.807(4)	C(33)-H(33)	0.9500
P(1)-O(1)	1.496(2)	C(34)-C(35)	1.384(7)
P(1)-C(7)	1.797(4)	C(34)-H(34)	0.9500
P(1)-C(13)	1.800(4)	C(35)-C(36)	1.375(6)
P(1)-C(1)	1.814(3)	C(35)-H(35)	0.9500
P(2)-O(2)	1.492(2)	C(36)-H(36)	0.9500
P(2)-C(31)	1.790(3)	C(39)-C(40)	1.494(5)
P(2)-C(25)	1.799(4)	C(39)-H(39A)	0.9900
P(2)-C(19)	1.821(3)	C(39)-H(39B)	0.9900
P(3)-O(3)	1.499(3)	C(40)-C(41)	1.381(5)
P(3)-C(45)	1.795(4)	C(41)-C(42)	1.388(5)
P(3)-C(51)	1.795(4)	C(41)-H(41A)	0.9500
P(3)-C(39)	1.823(3)	C(42)-C(43)	1.380(5)
P(4)-O(4)	1.502(3)	C(42)-H(42A)	0.9500
P(4)-C(69)	1.790(4)	C(43)-C(44)	1.371(5)
P(4)-C(63)	1.795(4)	C(43)-H(43A)	0.9500
P(4)-C(57)	1.820(3)	C(44)-H(44A)	0.9500

Table B.5. (continued)

F(1)-C(37)	1.340(6)	C(45)-C(50)	1.397(5)
F(2)-C(37)	1.289(7)	C(45)-C(46)	1.397(5)
F(3)-C(37)	1.318(8)	C(46)-C(47)	1.396(5)
F(4)-C(38)	1.322(5)	C(46)-H(46A)	0.9500
F(5)-C(38)	1.338(5)	C(47)-C(48)	1.370(6)
F(6)-C(38)	1.335(5)	C(47)-H(47A)	0.9500
F(7)-C(75)	1.329(4)	C(48)-C(49)	1.382(5)
F(8)-C(75)	1.327(4)	C(48)-H(48A)	0.9500
F(9)-C(75)	1.335(4)	C(49)-C(50)	1.389(5)
F(10)-C(76)	1.312(4)	C(49)-H(49A)	0.9500
F(11)-C(76)	1.338(5)	C(50)-H(50A)	0.9500
F(12)-C(76)	1.330(5)	C(51)-C(52)	1.386(5)
N(1)-C(6)	1.347(4)	C(51)-C(56)	1.394(5)
N(1)-C(2)	1.356(4)	C(52)-C(53)	1.374(5)
N(2)-C(24)	1.345(5)	C(52)-H(52A)	0.9500
N(2)-C(20)	1.349(4)	C(53)-C(54)	1.378(6)
N(3)-C(44)	1.344(4)	C(53)-H(53A)	0.9500
N(3)-C(40)	1.352(4)	C(54)-C(55)	1.380(5)
N(4)-C(58)	1.346(4)	C(54)-H(54A)	0.9500
N(4)-C(62)	1.346(4)	C(55)-C(56)	1.378(5)
C(1)-C(2)	1.505(5)	C(55)-H(55A)	0.9500
C(1)-H(1A)	0.9900	C(56)-H(56A)	0.9500
C(1)-H(1B)	0.9900	C(57)-C(58)	1.496(5)
C(2)-C(3)	1.382(5)	C(57)-H(57A)	0.9900
C(3)-C(4)	1.379(5)	C(57)-H(57B)	0.9900
C(3)-H(3)	0.9500	C(58)-C(59)	1.383(5)
C(4)-C(5)	1.396(5)	C(59)-C(60)	1.378(5)
C(4)-H(4)	0.9500	C(59)-H(59A)	0.9500
C(5)-C(6)	1.366(5)	C(60)-C(61)	1.383(5)
C(5)-H(5)	0.9500	C(60)-H(60A)	0.9500
C(6)-H(6)	0.9500	C(61)-C(62)	1.362(5)
C(7)-C(12)	1.389(5)	C(61)-H(61A)	0.9500
C(7)-C(8)	1.393(5)	C(62)-H(62A)	0.9500
C(8)-C(9)	1.389(5)	C(63)-C(64)	1.392(5)
C(8)-H(8)	0.9500	C(63)-C(68)	1.395(5)
C(9)-C(10)	1.380(6)	C(64)-C(65)	1.376(5)
C(9)-H(9)	0.9500	C(64)-H(64A)	0.9500
C(10)-C(11)	1.379(6)	C(65)-C(66)	1.378(5)
C(10)-H(10)	0.9500	C(65)-H(65A)	0.9500
C(11)-C(12)	1.392(5)	C(66)-C(67)	1.389(6)
C(11)-H(11)	0.9500	C(66)-H(66A)	0.9500
C(12)-H(12)	0.9500	C(67)-C(68)	1.377(5)
C(13)-C(14)	1.385(5)	C(67)-H(67A)	0.9500
C(13)-C(18)	1.390(5)	C(68)-H(68A)	0.9500

Table B.5. (continued)

C(14)-C(15)	1.383(5)	C(69)-C(70)	1.391(5)
C(14)-H(14)	0.9500	C(69)-C(74)	1.397(5)
C(15)-C(16)	1.368(7)	C(70)-C(71)	1.381(5)
C(15)-H(15)	0.9500	C(70)-H(70A)	0.9500
C(16)-C(17)	1.379(7)	C(71)-C(72)	1.375(6)
C(16)-H(16)	0.9500	C(71)-H(71A)	0.9500
C(17)-C(18)	1.375(6)	C(72)-C(73)	1.391(5)
C(17)-H(17)	0.9500	C(72)-H(72A)	0.9500
C(18)-H(18)	0.9500	C(73)-C(74)	1.385(5)
C(19)-C(20)	1.506(5)	C(73)-H(73A)	0.9500
C(19)-H(19A)	0.9900	C(74)-H(74A)	0.9500
C(19)-H(19B)	0.9900		

Bond Angles (°)

N(2)-Hg(1)-N(1)	177.34(12)	C(29)-C(30)-C(25)	119.8(4)
N(2)-Hg(1)-O(2)	87.22(9)	C(29)-C(30)-H(30)	120.1
N(1)-Hg(1)-O(2)	92.03(9)	C(25)-C(30)-H(30)	120.1
N(2)-Hg(1)-O(1)	92.31(9)	C(32)-C(31)-C(36)	119.1(3)
N(1)-Hg(1)-O(1)	88.26(9)	C(32)-C(31)-P(2)	124.1(3)
O(2)-Hg(1)-O(1)	175.82(7)	C(36)-C(31)-P(2)	116.8(3)
N(4)-Hg(2)-N(3)	176.43(11)	C(31)-C(32)-C(33)	120.6(4)
N(4)-Hg(2)-O(4)	88.09(9)	C(31)-C(32)-H(32)	119.7
N(3)-Hg(2)-O(4)	92.97(9)	C(33)-C(32)-H(32)	119.7
N(4)-Hg(2)-O(3)	90.44(9)	C(34)-C(33)-C(32)	120.0(4)
N(3)-Hg(2)-O(3)	88.41(9)	C(34)-C(33)-H(33)	120.0
O(4)-Hg(2)-O(3)	177.80(9)	C(32)-C(33)-H(33)	120.0
N(4)-Hg(2)-O(11)	103.46(9)	C(33)-C(34)-C(35)	119.5(4)
N(3)-Hg(2)-O(11)	80.02(10)	C(33)-C(34)-H(34)	120.2
O(4)-Hg(2)-O(11)	85.92(8)	C(35)-C(34)-H(34)	120.2
O(3)-Hg(2)-O(11)	96.01(8)	C(36)-C(35)-C(34)	120.6(4)
O(6)-S(1)-O(7)	114.88(18)	C(36)-C(35)-H(35)	119.7
O(6)-S(1)-O(5)	114.17(18)	C(34)-C(35)-H(35)	119.7
O(7)-S(1)-O(5)	114.64(18)	C(35)-C(36)-C(31)	120.3(4)
O(6)-S(1)-C(37)	102.5(3)	C(35)-C(36)-H(36)	119.9
O(7)-S(1)-C(37)	103.5(2)	C(31)-C(36)-H(36)	119.9
O(5)-S(1)-C(37)	105.2(2)	F(2)-C(37)-F(3)	107.5(6)
O(9)-S(2)-O(10)	114.96(17)	F(2)-C(37)-F(1)	109.2(6)
O(9)-S(2)-O(8)	114.61(17)	F(3)-C(37)-F(1)	107.1(5)
O(10)-S(2)-O(8)	114.24(18)	F(2)-C(37)-S(1)	110.7(5)
O(9)-S(2)-C(38)	102.77(18)	F(3)-C(37)-S(1)	111.5(5)
O(10)-S(2)-C(38)	104.51(19)	F(1)-C(37)-S(1)	110.8(4)
O(8)-S(2)-C(38)	103.69(18)	F(4)-C(38)-F(6)	107.5(4)

Table B.5. (continued)

O(13)-S(3)-O(12)	115.43(18)	F(4)-C(38)-F(5)	108.2(3)
O(13)-S(3)-O(11)	115.88(18)	F(6)-C(38)-F(5)	107.0(4)
O(12)-S(3)-O(11)	113.06(17)	F(4)-C(38)-S(2)	111.9(3)
O(13)-S(3)-C(75)	104.63(17)	F(6)-C(38)-S(2)	110.9(3)
O(12)-S(3)-C(75)	103.00(17)	F(5)-C(38)-S(2)	111.2(3)
O(11)-S(3)-C(75)	102.57(17)	C(40)-C(39)-P(3)	114.2(2)
O(16)-S(4)-O(15)	115.1(2)	C(40)-C(39)-H(39A)	108.7
O(16)-S(4)-O(14)	114.46(19)	P(3)-C(39)-H(39A)	108.7
O(15)-S(4)-O(14)	114.74(17)	C(40)-C(39)-H(39B)	108.7
O(16)-S(4)-C(76)	102.5(2)	P(3)-C(39)-H(39B)	108.7
O(15)-S(4)-C(76)	104.08(18)	H(39A)-C(39)-H(39B)	107.6
O(14)-S(4)-C(76)	103.73(18)	N(3)-C(40)-C(41)	119.6(3)
O(1)-P(1)-C(7)	112.64(16)	N(3)-C(40)-C(39)	119.4(3)
O(1)-P(1)-C(13)	112.95(16)	C(41)-C(40)-C(39)	121.0(3)
C(7)-P(1)-C(13)	107.70(16)	C(40)-C(41)-C(42)	120.3(3)
O(1)-P(1)-C(1)	111.24(15)	C(40)-C(41)-H(41A)	119.9
C(7)-P(1)-C(1)	104.93(16)	C(42)-C(41)-H(41A)	119.9
C(13)-P(1)-C(1)	106.90(16)	C(43)-C(42)-C(41)	119.0(4)
O(2)-P(2)-C(31)	111.92(16)	C(43)-C(42)-H(42A)	120.5
O(2)-P(2)-C(25)	112.65(16)	C(41)-C(42)-H(42A)	120.5
C(31)-P(2)-C(25)	109.31(16)	C(44)-C(43)-C(42)	118.9(4)
O(2)-P(2)-C(19)	111.30(14)	C(44)-C(43)-H(43A)	120.6
C(31)-P(2)-C(19)	106.76(16)	C(42)-C(43)-H(43A)	120.6
C(25)-P(2)-C(19)	104.48(16)	N(3)-C(44)-C(43)	121.9(3)
O(3)-P(3)-C(45)	111.72(16)	N(3)-C(44)-H(44A)	119.1
O(3)-P(3)-C(51)	112.09(16)	C(43)-C(44)-H(44A)	119.1
C(45)-P(3)-C(51)	109.60(16)	C(50)-C(45)-C(46)	119.5(3)
O(3)-P(3)-C(39)	111.23(15)	C(50)-C(45)-P(3)	121.7(3)
C(45)-P(3)-C(39)	106.68(16)	C(46)-C(45)-P(3)	118.8(3)
C(51)-P(3)-C(39)	105.18(16)	C(47)-C(46)-C(45)	119.4(4)
O(4)-P(4)-C(69)	112.01(16)	C(47)-C(46)-H(46A)	120.3
O(4)-P(4)-C(63)	111.74(16)	C(45)-C(46)-H(46A)	120.3
C(69)-P(4)-C(63)	109.37(16)	C(48)-C(47)-C(46)	120.6(4)
O(4)-P(4)-C(57)	111.31(14)	C(48)-C(47)-H(47A)	119.7
C(69)-P(4)-C(57)	105.08(16)	C(46)-C(47)-H(47A)	119.7
C(63)-P(4)-C(57)	107.00(16)	C(47)-C(48)-C(49)	120.4(4)
P(1)-O(1)-Hg(1)	116.36(13)	C(47)-C(48)-H(48A)	119.8
P(2)-O(2)-Hg(1)	117.72(13)	C(49)-C(48)-H(48A)	119.8
P(3)-O(3)-Hg(2)	115.95(13)	C(48)-C(49)-C(50)	120.0(4)
P(4)-O(4)-Hg(2)	116.16(13)	C(48)-C(49)-H(49A)	120.0
S(3)-O(11)-Hg(2)	130.80(16)	C(50)-C(49)-H(49A)	120.0
C(6)-N(1)-C(2)	120.0(3)	C(49)-C(50)-C(45)	120.1(3)
C(6)-N(1)-Hg(1)	114.9(2)	C(49)-C(50)-H(50A)	120.0
C(2)-N(1)-Hg(1)	124.7(2)	C(45)-C(50)-H(50A)	120.0

Table B.5. (continued)

C(24)-N(2)-C(20)	119.5(3)	C(52)-C(51)-C(56)	118.6(3)
C(62)-N(4)-Hg(2)	114.3(2)	C(52)-C(51)-P(3)	117.3(3)
C(2)-C(1)-P(1)	113.5(2)	C(56)-C(51)-P(3)	124.1(3)
C(2)-C(1)-H(1A)	108.9	C(53)-C(52)-C(51)	120.6(4)
P(1)-C(1)-H(1A)	108.9	C(53)-C(52)-H(52A)	119.7
C(2)-C(1)-H(1B)	108.9	C(51)-C(52)-H(52A)	119.7
P(1)-C(1)-H(1B)	108.9	C(52)-C(53)-C(54)	120.5(4)
H(1A)-C(1)-H(1B)	107.7	C(52)-C(53)-H(53A)	119.7
N(1)-C(2)-C(3)	119.7(3)	C(54)-C(53)-H(53A)	119.7
N(1)-C(2)-C(1)	119.3(3)	C(53)-C(54)-C(55)	119.6(4)
C(3)-C(2)-C(1)	121.0(3)	C(53)-C(54)-H(54A)	120.2
C(4)-C(3)-C(2)	120.7(4)	C(55)-C(54)-H(54A)	120.2
C(4)-C(3)-H(3)	119.7	C(56)-C(55)-C(54)	120.2(4)
C(2)-C(3)-H(3)	119.7	C(56)-C(55)-H(55A)	119.9
C(3)-C(4)-C(5)	118.7(4)	C(54)-C(55)-H(55A)	119.9
C(3)-C(4)-H(4)	120.7	C(55)-C(56)-C(51)	120.5(4)
C(5)-C(4)-H(4)	120.7	C(55)-C(56)-H(56A)	119.8
C(6)-C(5)-C(4)	118.7(4)	C(51)-C(56)-H(56A)	119.8
C(6)-C(5)-H(5)	120.7	C(58)-C(57)-P(4)	111.6(2)
C(4)-C(5)-H(5)	120.7	C(58)-C(57)-H(57A)	109.3
N(1)-C(6)-C(5)	122.3(4)	P(4)-C(57)-H(57A)	109.3
N(1)-C(6)-H(6)	118.8	C(58)-C(57)-H(57B)	109.3
C(5)-C(6)-H(6)	118.8	P(4)-C(57)-H(57B)	109.3
C(12)-C(7)-C(8)	119.9(3)	H(57A)-C(57)-H(57B)	108.0
C(12)-C(7)-P(1)	121.7(3)	N(4)-C(58)-C(59)	120.0(3)
C(8)-C(7)-P(1)	118.3(3)	N(4)-C(58)-C(57)	119.0(3)
C(9)-C(8)-C(7)	119.5(4)	C(24)-N(2)-Hg(1)	113.3(2)
C(9)-C(8)-H(8)	120.3	C(20)-N(2)-Hg(1)	125.9(2)
C(7)-C(8)-H(8)	120.3	C(44)-N(3)-C(40)	120.4(3)
C(10)-C(9)-C(8)	120.7(4)	C(44)-N(3)-Hg(2)	115.7(2)
C(10)-C(9)-H(9)	119.7	C(40)-N(3)-Hg(2)	123.6(2)
C(8)-C(9)-H(9)	119.7	C(58)-N(4)-C(62)	119.8(3)
C(11)-C(10)-C(9)	119.9(4)	C(58)-N(4)-Hg(2)	124.8(2)
C(11)-C(10)-H(10)	120.0	C(59)-C(58)-C(57)	121.0(3)
C(9)-C(10)-H(10)	120.0	C(60)-C(59)-C(58)	120.3(4)
C(10)-C(11)-C(12)	120.3(4)	C(60)-C(59)-H(59A)	119.9
C(10)-C(11)-H(11)	119.9	C(58)-C(59)-H(59A)	119.9
C(12)-C(11)-H(11)	119.9	C(59)-C(60)-C(61)	118.8(4)
C(7)-C(12)-C(11)	119.8(4)	C(59)-C(60)-H(60A)	120.6
C(7)-C(12)-H(12)	120.1	C(61)-C(60)-H(60A)	120.6
C(11)-C(12)-H(12)	120.1	C(62)-C(61)-C(60)	118.9(4)
C(14)-C(13)-C(18)	118.8(4)	C(62)-C(61)-H(61A)	120.5
C(14)-C(13)-P(1)	124.5(3)	C(60)-C(61)-H(61A)	120.5
C(18)-C(13)-P(1)	116.7(3)	N(4)-C(62)-C(61)	122.2(4)

Table B.5. (continued)

C(15)-C(14)-C(13)	120.7(4)	N(4)-C(62)-H(62A)	118.9
C(15)-C(14)-H(14)	119.6	C(61)-C(62)-H(62A)	118.9
C(13)-C(14)-H(14)	119.6	C(64)-C(63)-C(68)	119.2(3)
C(16)-C(15)-C(14)	119.9(4)	C(64)-C(63)-P(4)	124.2(3)
C(16)-C(15)-H(15)	120.1	C(68)-C(63)-P(4)	116.5(3)
C(14)-C(15)-H(15)	120.1	C(65)-C(64)-C(63)	120.4(4)
C(15)-C(16)-C(17)	120.0(4)	C(65)-C(64)-H(64A)	119.8
C(15)-C(16)-H(16)	120.0	C(63)-C(64)-H(64A)	119.8
C(17)-C(16)-H(16)	120.0	C(64)-C(65)-C(66)	120.5(4)
C(18)-C(17)-C(16)	120.6(5)	C(64)-C(65)-H(65A)	119.8
C(18)-C(17)-H(17)	119.7	C(66)-C(65)-H(65A)	119.8
C(16)-C(17)-H(17)	119.7	C(65)-C(66)-C(67)	119.5(4)
C(17)-C(18)-C(13)	120.0(4)	C(65)-C(66)-H(66A)	120.3
C(17)-C(18)-H(18)	120.0	C(67)-C(66)-H(66A)	120.3
C(13)-C(18)-H(18)	120.0	C(68)-C(67)-C(66)	120.7(4)
C(20)-C(19)-P(2)	112.5(2)	C(68)-C(67)-H(67A)	119.7
C(20)-C(19)-H(19A)	109.1	C(66)-C(67)-H(67A)	119.7
P(2)-C(19)-H(19A)	109.1	C(67)-C(68)-C(63)	119.8(4)
C(20)-C(19)-H(19B)	109.1	C(67)-C(68)-H(68A)	120.1
P(2)-C(19)-H(19B)	109.1	C(63)-C(68)-H(68A)	120.1
H(19A)-C(19)-H(19B)	107.8	C(70)-C(69)-C(74)	119.4(3)
N(2)-C(20)-C(21)	120.6(3)	C(70)-C(69)-P(4)	118.3(3)
N(2)-C(20)-C(19)	119.0(3)	C(74)-C(69)-P(4)	122.1(3)
C(21)-C(20)-C(19)	120.4(3)	C(71)-C(70)-C(69)	119.6(4)
C(22)-C(21)-C(20)	119.8(4)	C(71)-C(70)-H(70A)	120.2
C(22)-C(21)-H(21)	120.1	C(69)-C(70)-H(70A)	120.2
C(20)-C(21)-H(21)	120.1	C(72)-C(71)-C(70)	121.2(4)
C(21)-C(22)-C(23)	118.8(4)	C(72)-C(71)-H(71A)	119.4
C(21)-C(22)-H(22)	120.6	C(70)-C(71)-H(71A)	119.4
C(23)-C(22)-H(22)	120.6	C(71)-C(72)-C(73)	119.7(4)
C(24)-C(23)-C(22)	119.3(4)	C(71)-C(72)-H(72A)	120.2
C(24)-C(23)-H(23)	120.4	C(73)-C(72)-H(72A)	120.2
C(22)-C(23)-H(23)	120.4	C(74)-C(73)-C(72)	119.7(4)
N(2)-C(24)-C(23)	122.0(4)	C(74)-C(73)-H(73A)	120.2
N(2)-C(24)-H(24)	119.0	C(72)-C(73)-H(73A)	120.2
C(23)-C(24)-H(24)	119.0	C(73)-C(74)-C(69)	120.4(4)
C(26)-C(25)-C(30)	119.9(3)	C(73)-C(74)-H(74A)	119.8
C(26)-C(25)-P(2)	118.4(3)	C(69)-C(74)-H(74A)	119.8
C(30)-C(25)-P(2)	121.5(3)	F(8)-C(75)-F(7)	108.0(3)
C(25)-C(26)-C(27)	119.3(4)	F(8)-C(75)-F(9)	106.9(3)
C(25)-C(26)-H(26)	120.3	F(7)-C(75)-F(9)	107.3(3)
C(27)-C(26)-H(26)	120.3	F(8)-C(75)-S(3)	111.6(2)
C(28)-C(27)-C(26)	120.8(4)	F(7)-C(75)-S(3)	111.0(3)
C(28)-C(27)-H(27)	119.6	F(9)-C(75)-S(3)	111.8(3)

Table B.5. (continued)

C(26)-C(27)-H(27)	119.6	F(10)-C(76)-F(12)	108.0(4)
C(27)-C(28)-C(29)	120.2(4)	F(10)-C(76)-F(11)	108.3(3)
C(27)-C(28)-H(28)	119.9	F(12)-C(76)-F(11)	106.7(4)
C(29)-C(28)-H(28)	119.9	F(10)-C(76)-S(4)	112.1(3)
C(28)-C(29)-C(30)	120.0(4)	F(12)-C(76)-S(4)	111.4(3)
C(28)-C(29)-H(29)	120.0	F(11)-C(76)-S(4)	110.3(3)
C(30)-C(29)-H(29)	120.0		

Table B.6. Experimental and statistical crystal data for **2.6**.

Empirical formula	$C_{44}H_{40}Hg_2N_6O_3P_2$	
Formula weight	1163.94	
Temperature	110(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P-1	
Unit cell dimensions	$a = 9.8660(4)$ Å	$\alpha = 109.198(2)^\circ$.
	$b = 14.0244(6)$ Å	$\beta = 90.244(2)^\circ$.
	$c = 16.3177(7)$ Å	$\delta = 99.757(2)^\circ$.
Volume	$2097.02(15)$ Å ³	
Z	2	
Density (calculated)	1.843 Mg/m ³	
Absorption coefficient	7.436 mm ⁻¹	
F(000)	1120	
Crystal size	0.29 x 0.17 x 0.13 mm ³	
Theta range for data collection	2.10 to 28.26°.	
Index ranges	-13 ≤ h ≤ 13, -18 ≤ k ≤ 18, -21 ≤ l ≤ 21	
Reflections collected	32544	
Independent reflections	10257 [R(int) = 0.0290]	
Completeness to theta = 28.26°	98.6 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.4519 and 0.2209	
Refinement method	Full-matrix least-squares on F ²	
Data / restraints / parameters	10257 / 10 / 530	
Goodness-of-fit on F ²	1.073	
Final R indices [I > 2σ(I)]	R1 = 0.0288, wR2 = 0.0629	
R indices (all data)	R1 = 0.0357, wR2 = 0.0659	
Largest diff. peak and hole	4.182 and -4.066 e. Å ⁻³	

Table B.6. (continued)

Bond Lengths (Å)

Hg(1)-C(2)	2.044(4)	C(13)-C(14)	1.402(6)
Hg(1)-C(1)	2.048(4)	C(15)-C(16)	1.394(6)
Hg(1)-O(1)	2.577(3)	C(15)-C(20)	1.400(6)
Hg(1)-N(3)	2.639(3)	C(16)-C(17)	1.390(6)
Hg(2)-C(21)	2.042(4)	C(17)-C(18)	1.389(6)
Hg(2)-C(22)	2.049(4)	C(18)-C(19)	1.380(7)
Hg(2)-O(2)	2.557(3)	C(19)-C(20)	1.387(6)
Hg(2)-N(6)	2.629(3)	C(23)-C(24)	1.503(5)
P(1)-O(1)	1.496(3)	C(24)-C(25)	1.392(5)
P(1)-C(9)	1.802(4)	C(25)-C(26)	1.387(6)
P(1)-C(15)	1.804(4)	C(26)-C(27)	1.378(6)
P(1)-C(3)	1.822(4)	C(27)-C(28)	1.381(6)
P(2)-O(2)	1.497(3)	C(29)-C(30)	1.390(5)
P(2)-C(29)	1.798(4)	C(29)-C(34)	1.394(5)
P(2)-C(35)	1.801(4)	C(30)-C(31)	1.392(6)
P(2)-C(23)	1.820(4)	C(31)-C(32)	1.386(6)
N(1)-C(1)	1.149(5)	C(32)-C(33)	1.383(6)
N(2)-C(2)	1.139(6)	C(33)-C(34)	1.385(6)
N(3)-C(4)	1.346(5)	C(35)-C(40)	1.395(6)
N(3)-C(8)	1.346(5)	C(35)-C(36)	1.394(5)
N(4)-C(21)	1.141(5)	C(36)-C(37)	1.392(6)
N(5)-C(22)	1.143(5)	C(37)-C(38)	1.390(6)
N(6)-C(24)	1.347(5)	C(38)-C(39)	1.380(6)
N(6)-C(28)	1.346(5)	C(39)-C(40)	1.395(6)
C(3)-C(4)	1.508(5)	O(3)-C(41)	1.33(2)
C(4)-C(5)	1.390(6)	O(3)-C(44)	1.57(2)
C(5)-C(6)	1.393(6)	C(41)-C(42)	1.340(11)
C(6)-C(7)	1.377(7)	C(42)-C(43)	1.447(10)
C(7)-C(8)	1.372(7)	C(43)-C(44)	1.398(15)
C(9)-C(14)	1.388(6)	O(4)-C(45)	1.33(2)
C(9)-C(10)	1.390(6)	O(4)-C(48)	1.57(2)
C(10)-C(11)	1.386(6)	C(45)-C(46)	1.341(11)
C(11)-C(12)	1.380(7)	C(46)-C(47)	1.447(10)
C(12)-C(13)	1.381(7)	C(47)-C(48)	1.398(14)

Bond Angles (°)

C(2)-Hg(1)-C(1)	166.27(17)	C(13)-C(12)-C(11)	120.9(4)
C(2)-Hg(1)-O(1)	102.39(14)	C(12)-C(13)-C(14)	119.4(4)
C(1)-Hg(1)-O(1)	89.55(13)	C(9)-C(14)-C(13)	119.7(4)
C(2)-Hg(1)-N(3)	93.76(14)	C(16)-C(15)-C(20)	

Table B.6. (continued)

C(1)-Hg(1)-N(3)	96.04(14)	C(16)-C(15)-P(1)	124.0(3)
O(1)-Hg(1)-N(3)	74.14(9)	C(20)-C(15)-P(1)	116.9(3)
C(21)-Hg(2)-C(22)	165.58(15)	C(17)-C(16)-C(15)	120.4(4)
C(21)-Hg(2)-O(2)	101.31(13)	C(18)-C(17)-C(16)	119.8(5)
C(22)-Hg(2)-O(2)	89.50(13)	C(19)-C(18)-C(17)	120.3(4)
C(21)-Hg(2)-N(6)	94.88(14)	C(18)-C(19)-C(20)	120.2(4)
C(22)-Hg(2)-N(6)	97.21(13)	C(19)-C(20)-C(15)	120.1(4)
O(2)-Hg(2)-N(6)	74.58(9)	N(4)-C(21)-Hg(2)	178.1(4)
O(1)-P(1)-C(9)	112.18(18)	N(5)-C(22)-Hg(2)	175.7(4)
O(1)-P(1)-C(15)	110.93(18)	C(24)-C(23)-P(2)	114.0(3)
C(9)-P(1)-C(15)	107.22(18)	N(6)-C(24)-C(25)	121.6(4)
O(1)-P(1)-C(3)	113.41(17)	N(6)-C(24)-C(23)	117.5(3)
C(9)-P(1)-C(3)	105.01(17)	C(25)-C(24)-C(23)	120.8(3)
C(15)-P(1)-C(3)	107.69(18)	C(26)-C(25)-C(24)	119.4(4)
O(2)-P(2)-C(29)	111.88(17)	C(27)-C(26)-C(25)	119.3(4)
O(2)-P(2)-C(35)	111.41(17)	C(26)-C(27)-C(28)	118.1(4)
C(29)-P(2)-C(35)	106.57(17)	N(6)-C(28)-C(27)	123.7(4)
O(2)-P(2)-C(23)	113.30(17)	C(30)-C(29)-C(34)	119.8(4)
C(29)-P(2)-C(23)	104.75(17)	C(30)-C(29)-P(2)	119.3(3)
C(35)-P(2)-C(23)	108.50(18)	C(34)-C(29)-P(2)	121.0(3)
P(1)-O(1)-Hg(1)	120.22(15)	C(29)-C(30)-C(31)	119.6(4)
P(2)-O(2)-Hg(2)	122.63(15)	C(32)-C(31)-C(30)	120.2(4)
C(4)-N(3)-C(8)	117.7(4)	C(33)-C(32)-C(31)	120.2(4)
C(4)-N(3)-Hg(1)	125.2(2)	C(32)-C(33)-C(34)	119.9(4)
C(8)-N(3)-Hg(1)	115.0(3)	C(33)-C(34)-C(29)	120.2(4)
C(24)-N(6)-C(28)	117.9(3)	C(40)-C(35)-C(36)	119.6(4)
C(24)-N(6)-Hg(2)	125.8(2)	C(40)-C(35)-P(2)	116.2(3)
C(28)-N(6)-Hg(2)	115.9(3)	C(36)-C(35)-P(2)	124.2(3)
N(1)-C(1)-Hg(1)	175.2(4)	C(37)-C(36)-C(35)	119.8(4)
N(2)-C(2)-Hg(1)	176.9(4)	C(38)-C(37)-C(36)	120.4(4)
C(4)-C(3)-P(1)	112.9(3)	C(39)-C(38)-C(37)	120.1(4)
N(3)-C(4)-C(5)	122.1(4)	C(38)-C(39)-C(40)	119.9(4)
N(3)-C(4)-C(3)	116.7(3)	C(35)-C(40)-C(39)	120.3(4)
C(5)-C(4)-C(3)	121.1(4)	C(41)-O(3)-C(44)	106.9(15)
C(4)-C(5)-C(6)	118.6(4)	C(42)-C(41)-O(3)	107.7(11)
C(7)-C(6)-C(5)	119.5(4)	C(41)-C(42)-C(43)	111.3(7)
C(8)-C(7)-C(6)	118.2(4)	C(44)-C(43)-C(42)	106.3(8)
N(3)-C(8)-C(7)	123.9(4)	C(43)-C(44)-O(3)	102.5(10)
C(14)-C(9)-C(10)	120.1(4)	C(45)-O(4)-C(48)	106.8(15)
C(14)-C(9)-P(1)	118.6(3)	C(46)-C(45)-O(4)	107.6(11)
C(10)-C(9)-P(1)	121.2(3)	C(45)-C(46)-C(47)	111.2(7)
C(11)-C(10)-C(9)	120.0(4)	C(48)-C(47)-C(46)	106.3(8)
C(12)-C(11)-C(10)	119.9(4)	C(47)-C(48)-O(4)	102.5(10)

Table B.7. Experimental and statistical crystal data for **2.7**.

Empirical formula	C ₄₀ H ₃₂ F ₆ HgN ₂ O ₄ P ₂		
Formula weight	981.21		
Temperature	110(2) K		
Wavelength	0.71073 Å		
Crystal system	Triclinic		
Space group	P-1		
Unit cell dimensions	a = 10.6023(5) Å	α = 100.797(2)°.	
	b = 12.5809(6) Å	β = 91.140(2)°.	
	c = 15.4969(11) Å	δ = 114.392(2)°.	
Volume	1838.28(18) Å ³		
Z	2		
Density (calculated)	1.773 Mg/ m ³		
Absorption coefficient	4.350 mm ⁻¹		
F(000)	964		
Crystal size	0.19 x 0.15 x 0.14 mm ³		
Theta range for data collection	2.02 to 28.32°.		
Index ranges	-14<= <i>h</i> <=14, -16<= <i>k</i> <=16, -20<= <i>l</i> <=20		
Reflections collected	24590		
Independent reflections	9039 [R(int) = 0.0255]		
Completeness to theta = 28.32°	98.8 %		
Absorption correction	Semi-empirical from equivalents		
Max. and min. transmission	0.5791 and 0.4905		
Refinement method	Full-matrix least-squares on F ²		
Data / restraints / parameters	9039 / 0 / 496		
Goodness-of-fit on F ²	1.058		
Final R indices [I>2σ(I)]	R1 = 0.0222, wR2 = 0.0550		
R indices (all data)	R1 = 0.0249, wR2 = 0.0561		
Largest diff. peak and hole	2.040 and -0.818 e. Å ⁻³		
Bond Lengths (Å)			
Hg(1)-P(1)	2.4108(6)	C(19)-C(20)	1.507(4)
Hg(1)-P(2)	2.4180(6)	C(20)-C(21)	1.390(4)
Hg(1)-O(3)	2.5296(18)	C(21)-C(22)	1.377(4)

Table B.7. (continued)

P(1)-C(13)	1.807(3)	C(22)-C(23)	1.382(5)
P(1)-C(7)	1.811(3)	C(23)-C(24)	1.385(4)
P(1)-C(1)	1.823(3)	C(25)-C(26)	1.390(4)
P(2)-C(31)	1.809(3)	C(25)-C(30)	1.398(4)
P(2)-C(25)	1.811(3)	C(26)-C(27)	1.396(4)
P(2)-C(19)	1.818(3)	C(27)-C(28)	1.379(5)
N(1)-C(2)	1.340(3)	C(28)-C(29)	1.387(5)
N(1)-C(6)	1.344(4)	C(29)-C(30)	1.391(4)
N(2)-C(24)	1.340(4)	C(31)-C(36)	1.396(4)
N(2)-C(20)	1.341(3)	C(31)-C(32)	1.398(4)
C(1)-C(2)	1.512(4)	C(32)-C(33)	1.387(4)
C(2)-C(3)	1.389(4)	C(33)-C(34)	1.388(4)
C(3)-C(4)	1.387(4)	C(34)-C(35)	1.388(4)
C(4)-C(5)	1.381(4)	C(35)-C(36)	1.385(4)
C(5)-C(6)	1.383(4)	O(3)-C(39)	1.248(3)
C(7)-C(8)	1.398(4)	O(4)-C(39)	1.231(3)
C(7)-C(12)	1.398(4)	C(39)-C(40)	1.550(4)
C(8)-C(9)	1.395(4)	C(40)-F(5)	1.292(4)
C(9)-C(10)	1.385(4)	C(40)-F(6)	1.298(4)
C(10)-C(11)	1.380(4)	C(40)-F(4)	1.400(4)
C(11)-C(12)	1.391(4)	O(1)-C(37)	1.238(3)
C(13)-C(18)	1.393(4)	O(2)-C(37)	1.239(3)
C(13)-C(14)	1.397(4)	C(37)-C(38)	1.546(4)
C(14)-C(15)	1.393(4)	C(38)-F(1)	1.311(3)
C(15)-C(16)	1.385(4)	C(38)-F(3)	1.324(4)
C(16)-C(17)	1.381(4)	C(38)-F(2)	1.326(3)
C(17)-C(18)	1.390(4)		

Bond Angles (°)

P(1)-Hg(1)-P(2)	159.04(2)	N(2)-C(20)-C(21)	122.9(3)
P(1)-Hg(1)-O(3)	96.31(5)	N(2)-C(20)-C(19)	116.7(2)
P(2)-Hg(1)-O(3)	99.72(5)	C(21)-C(20)-C(19)	120.3(2)
C(13)-P(1)-C(7)	106.32(11)	C(22)-C(21)-C(20)	118.7(3)
C(13)-P(1)-C(1)	107.53(12)	C(21)-C(22)-C(23)	119.2(3)
C(7)-P(1)-C(1)	106.94(12)	C(22)-C(23)-C(24)	118.5(3)
C(13)-P(1)-Hg(1)	112.15(8)	N(2)-C(24)-C(23)	123.2(3)
C(7)-P(1)-Hg(1)	115.67(9)	C(26)-C(25)-C(30)	119.8(2)
C(1)-P(1)-Hg(1)	107.85(8)	C(26)-C(25)-P(2)	121.7(2)
C(31)-P(2)-C(25)	105.82(12)	C(30)-C(25)-P(2)	118.5(2)
C(31)-P(2)-C(19)	107.64(12)	C(25)-C(26)-C(27)	119.6(3)
C(25)-P(2)-C(19)	104.97(12)	C(28)-C(27)-C(26)	120.3(3)
C(31)-P(2)-Hg(1)	111.10(8)	C(27)-C(28)-C(29)	120.5(3)

Table B.7. (continued)

C(25)-P(2)-Hg(1)	120.17(9)	C(28)-C(29)-C(30)	119.6(3)
C(19)-P(2)-Hg(1)	106.44(9)	C(29)-C(30)-C(25)	120.2(3)
C(2)-N(1)-C(6)	117.1(2)	C(36)-C(31)-C(32)	119.4(2)
C(24)-N(2)-C(20)	117.4(3)	C(36)-C(31)-P(2)	121.05(19)
C(2)-C(1)-P(1)	113.23(17)	C(32)-C(31)-P(2)	119.4(2)
N(1)-C(2)-C(3)	122.8(2)	C(33)-C(32)-C(31)	120.0(3)
N(1)-C(2)-C(1)	115.9(2)	C(32)-C(33)-C(34)	120.2(3)
C(3)-C(2)-C(1)	121.2(2)	C(33)-C(34)-C(35)	119.9(3)
C(4)-C(3)-C(2)	119.2(3)	C(36)-C(35)-C(34)	120.2(3)
C(5)-C(4)-C(3)	118.6(3)	C(35)-C(36)-C(31)	120.2(3)
C(4)-C(5)-C(6)	118.5(3)	C(39)-O(3)-Hg(1)	126.22(17)
N(1)-C(6)-C(5)	123.8(3)	O(4)-C(39)-O(3)	131.3(3)
C(8)-C(7)-C(12)	119.7(2)	O(4)-C(39)-C(40)	115.1(3)
C(8)-C(7)-P(1)	119.4(2)	O(3)-C(39)-C(40)	113.6(2)
C(12)-C(7)-P(1)	120.86(19)	F(5)-C(40)-F(6)	113.0(3)
C(9)-C(8)-C(7)	119.8(3)	F(5)-C(40)-F(4)	101.8(3)
C(10)-C(9)-C(8)	120.0(3)	F(6)-C(40)-F(4)	101.3(3)
C(11)-C(10)-C(9)	120.2(3)	F(5)-C(40)-C(39)	116.0(3)
C(10)-C(11)-C(12)	120.6(3)	F(6)-C(40)-C(39)	114.7(3)
C(11)-C(12)-C(7)	119.6(2)	F(4)-C(40)-C(39)	107.9(3)
C(18)-C(13)-C(14)	120.1(2)	O(1)-C(37)-O(2)	129.6(3)
C(18)-C(13)-P(1)	122.0(2)	O(1)-C(37)-C(38)	116.3(2)
C(14)-C(13)-P(1)	117.9(2)	O(2)-C(37)-C(38)	114.2(2)
C(15)-C(14)-C(13)	119.6(3)	F(1)-C(38)-F(3)	106.9(3)
C(16)-C(15)-C(14)	119.9(3)	F(1)-C(38)-F(2)	106.3(3)
C(17)-C(16)-C(15)	120.4(3)	F(3)-C(38)-F(2)	105.9(3)
C(16)-C(17)-C(18)	120.4(3)	F(1)-C(38)-C(37)	114.6(2)
C(17)-C(18)-C(13)	119.5(2)	F(3)-C(38)-C(37)	111.5(2)
C(20)-C(19)-P(2)	112.97(17)	F(2)-C(38)-C(37)	111.1(2)

Table B.8. Experimental and statistical crystal data for **2.8**.*

Empirical formula	C ₄₄ H ₃₈ F ₆ Hg ₂ N ₂ O ₇ P ₂		
Formula weight	1283.88		
Temperature	110(2) K		
Wavelength	0.71073 Å		
Crystal system	Triclinic		
Space group	P-1		
Unit cell dimensions	a = 9.6970(7) Å	$\alpha = 83.9650(10)^\circ$.	
	b = 10.7458(7) Å	$\beta = 89.9890(10)^\circ$.	
	c = 21.5698(15) Å	$\delta = 83.808(2)^\circ$.	
Volume	2222.0(3) Å ³		

Table B.8. (continued)

Z	2
Density (calculated)	1.919 Mg/m ³
Absorption coefficient	7.050 mm ⁻¹
F(000)	1232
Crystal size	0.22 x 0.14 x 0.10 mm ³
Theta range for data collection	2.05 to 28.27°.
Index ranges	-12<=h<=12, -14<=k<=14, -28<=l<=28
Reflections collected	31336
Independent reflections	10889 [R(int) = 0.0304]
Completeness to theta = 28.27°	98.7 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.5540 and 0.3061
Refinement method	Full-matrix least-squares on F ²
Data / restraints / parameters	10889 / 0 / 568
Goodness-of-fit on F ²	1.024
Final R indices [I>2sigma(I)]	R1 = 0.0217, wR2 = 0.0474
R indices (all data)	R1 = 0.0281, wR2 = 0.0499
Largest diff. peak and hole	1.017 and -0.802 e. Å ⁻³

Bond Lengths (Å)

Hg(1)-C(1)#1	2.133(3)	C(7)-C(8)	1.399(4)
Hg(1)-O(2)	2.2214(19)	C(8)-C(9)	1.390(4)
Hg(1)-N(1)	2.405(2)	C(9)-C(10)	1.385(4)
Hg(1)-O(1)	2.4213(19)	C(10)-C(11)	1.384(4)
Hg(2)-C(21)#2	2.129(3)	C(11)-C(12)	1.390(4)
Hg(2)-O(5)	2.176(2)	C(13)-C(14)	1.392(4)
Hg(2)-O(4)	2.3925(19)	C(13)-C(18)	1.396(4)
Hg(2)-N(2)	2.485(3)	C(14)-C(15)	1.386(4)
P(1)-O(1)	1.503(2)	C(15)-C(16)	1.373(5)
P(1)-C(1)	1.795(3)	C(16)-C(17)	1.382(5)
P(1)-C(7)	1.803(3)	C(17)-C(18)	1.385(4)
P(1)-C(13)	1.810(3)	C(19)-C(20)	1.537(4)
P(2)-O(4)	1.501(2)	C(21)-C(22)	1.503(4)
P(2)-C(21)	1.797(3)	C(21)-Hg(2)#2	2.129(3)
P(2)-C(33)	1.803(3)	C(22)-C(23)	1.386(4)
P(2)-C(27)	1.808(3)	C(23)-C(24)	1.392(4)
F(1)-C(20)	1.298(4)	C(24)-C(25)	1.384(5)
F(2)-C(20)	1.330(4)	C(25)-C(26)	1.373(5)
F(3)-C(20)	1.349(4)	C(27)-C(32)	1.387(4)
F(4)-C(40)	1.339(4)	C(27)-C(28)	1.392(4)
F(5)-C(40)	1.330(4)	C(28)-C(29)	1.391(5)
F(6)-C(40)	1.336(4)	C(29)-C(30)	1.379(5)

Table B.8. (continued)

O(2)-C(19)	1.256(4)	C(30)-C(31)	1.390(5)
O(3)-C(19)	1.218(4)	C(31)-C(32)	1.382(5)
O(5)-C(39)	1.277(3)	C(33)-C(34)	1.385(4)
O(6)-C(39)	1.209(4)	C(33)-C(38)	1.396(4)
N(1)-C(6)	1.338(4)	C(34)-C(35)	1.389(4)
N(1)-C(2)	1.346(3)	C(35)-C(36)	1.377(5)
N(2)-C(26)	1.337(4)	C(36)-C(37)	1.383(5)
N(2)-C(22)	1.353(4)	C(37)-C(38)	1.387(4)
C(1)-C(2)	1.498(4)	C(39)-C(40)	1.543(4)
C(1)-Hg(1)#1	2.133(3)	O(7)-C(44)	1.437(4)
C(2)-C(3)	1.386(4)	O(7)-C(41)	1.441(4)
C(3)-C(4)	1.387(4)	C(41)-C(42)	1.510(5)
C(4)-C(5)	1.375(4)	C(42)-C(43)	1.510(5)
C(5)-C(6)	1.377(4)	C(43)-C(44)	1.500(5)
C(7)-C(12)	1.390(4)		

Bond Angles (°)

C(1)#1-Hg(1)-O(2)	145.87(9)	C(15)-C(14)-C(13)	119.8(3)
C(1)#1-Hg(1)-N(1)	125.55(9)	C(16)-C(15)-C(14)	120.6(3)
O(2)-Hg(1)-N(1)	82.16(8)	C(15)-C(16)-C(17)	120.0(3)
C(1)#1-Hg(1)-O(1)	111.94(8)	C(16)-C(17)-C(18)	120.4(3)
O(2)-Hg(1)-O(1)	87.78(7)	C(17)-C(18)-C(13)	119.7(3)
N(1)-Hg(1)-O(1)	84.76(7)	O(3)-C(19)-O(2)	129.4(3)
C(21)#2-Hg(2)-O(5)	157.46(9)	O(3)-C(19)-C(20)	118.4(3)
C(21)#2-Hg(2)-O(4)	108.77(9)	O(2)-C(19)-C(20)	112.1(3)
O(5)-Hg(2)-O(4)	87.54(7)	F(1)-C(20)-F(2)	108.6(3)
C(21)#2-Hg(2)-N(2)	116.63(9)	F(1)-C(20)-F(3)	105.7(3)
O(5)-Hg(2)-N(2)	80.21(8)	F(2)-C(20)-F(3)	104.7(3)
O(4)-Hg(2)-N(2)	81.85(8)	F(1)-C(20)-C(19)	114.6(3)
O(1)-P(1)-C(1)	113.74(12)	F(2)-C(20)-C(19)	112.5(3)
O(1)-P(1)-C(7)	110.86(12)	F(3)-C(20)-C(19)	110.1(3)
C(1)-P(1)-C(7)	104.03(13)	C(22)-C(21)-P(2)	116.31(19)
O(1)-P(1)-C(13)	109.91(12)	C(22)-C(21)-Hg(2)#2	111.86(18)
C(1)-P(1)-C(13)	108.20(13)	P(2)-C(21)-Hg(2)#2	105.37(14)
C(7)-P(1)-C(13)	109.93(13)	N(2)-C(22)-C(23)	121.4(3)
O(4)-P(2)-C(21)	114.64(12)	N(2)-C(22)-C(21)	119.1(3)
O(4)-P(2)-C(33)	109.14(13)	C(23)-C(22)-C(21)	119.4(3)
C(21)-P(2)-C(33)	108.06(13)	C(22)-C(23)-C(24)	119.5(3)
O(4)-P(2)-C(27)	110.32(13)	C(25)-C(24)-C(23)	118.6(3)
C(21)-P(2)-C(27)	106.15(13)	C(26)-C(25)-C(24)	118.6(3)
C(33)-P(2)-C(27)	108.33(13)	N(2)-C(26)-C(25)	123.6(3)
P(1)-O(1)-Hg(1)	120.08(10)	C(32)-C(27)-C(28)	119.8(3)

Table B.8. (continued)

C(19)-O(2)-Hg(1)	111.09(19)	C(32)-C(27)-P(2)	116.3(2)
P(2)-O(4)-Hg(2)	126.66(11)	C(28)-C(27)-P(2)	123.7(2)
C(39)-O(5)-Hg(2)	115.56(19)	C(29)-C(28)-C(27)	119.8(3)
C(6)-N(1)-C(2)	118.3(2)	C(30)-C(29)-C(28)	120.0(3)
C(6)-N(1)-Hg(1)	114.24(19)	C(29)-C(30)-C(31)	120.1(3)
C(2)-N(1)-Hg(1)	126.75(18)	C(32)-C(31)-C(30)	120.0(3)
C(26)-N(2)-C(22)	118.2(3)	C(31)-C(32)-C(27)	120.1(3)
C(26)-N(2)-Hg(2)	112.2(2)	C(34)-C(33)-C(38)	120.1(3)
C(22)-N(2)-Hg(2)	129.6(2)	C(34)-C(33)-P(2)	122.0(2)
C(2)-C(1)-P(1)	116.27(19)	C(38)-C(33)-P(2)	117.9(2)
C(2)-C(1)-Hg(1)#1	109.99(17)	C(33)-C(34)-C(35)	119.8(3)
P(1)-C(1)-Hg(1)#1	105.49(13)	C(36)-C(35)-C(34)	120.2(3)
N(1)-C(2)-C(3)	121.1(3)	C(35)-C(36)-C(37)	120.4(3)
N(1)-C(2)-C(1)	117.7(2)	C(36)-C(37)-C(38)	120.0(3)
C(3)-C(2)-C(1)	121.1(2)	C(37)-C(38)-C(33)	119.6(3)
C(2)-C(3)-C(4)	119.8(3)	O(6)-C(39)-O(5)	129.5(3)
C(5)-C(4)-C(3)	118.7(3)	O(6)-C(39)-C(40)	119.4(3)
C(4)-C(5)-C(6)	118.3(3)	O(5)-C(39)-C(40)	111.1(3)
N(1)-C(6)-C(5)	123.6(3)	F(5)-C(40)-F(6)	107.0(3)
C(12)-C(7)-C(8)	119.2(3)	F(5)-C(40)-F(4)	107.1(3)
C(12)-C(7)-P(1)	118.2(2)	F(6)-C(40)-F(4)	107.1(3)
C(8)-C(7)-P(1)	122.5(2)	F(5)-C(40)-C(39)	112.6(3)
C(9)-C(8)-C(7)	120.2(3)	F(6)-C(40)-C(39)	111.3(3)
C(10)-C(9)-C(8)	119.9(3)	F(4)-C(40)-C(39)	111.5(3)
C(11)-C(10)-C(9)	120.4(3)	C(44)-O(7)-C(41)	109.2(2)
C(10)-C(11)-C(12)	119.9(3)	O(7)-C(41)-C(42)	106.4(3)
C(11)-C(12)-C(7)	120.5(3)	C(41)-C(42)-C(43)	101.6(3)
C(14)-C(13)-C(18)	119.5(3)	C(44)-C(43)-C(42)	102.6(3)
C(14)-C(13)-P(1)	122.8(2)	O(7)-C(44)-C(43)	105.0(3)
C(18)-C(13)-P(1)	117.7(2)		

*Symmetry transformations used to generate equivalent atoms: #1 -x+1,-y+1,-z #2 -x,-y+1,-z+1.

Table B.9. Experimental and statistical crystal data for **2.9**.*

Empirical formula	C ₃₈ H ₃₀ Hg ₂ N ₄ O ₂ P ₂ S ₂	
Formula weight	1101.90	
Temperature	110(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P2(1)/c	
Unit cell dimensions	a = 9.9674(5) Å	$\alpha = 90^\circ$.

Table B.9. (continued)

	$b = 9.2381(4) \text{ \AA}$	$\beta = 98.738(2)^\circ$
	$c = 20.0667(9) \text{ \AA}$	$\delta = 90^\circ$
Volume	$1826.29(15) \text{ \AA}^3$	
Z	2	
Density (calculated)	2.004 Mg/m^3	
Absorption coefficient	8.639 mm^{-1}	
F(000)	1048	
Crystal size	$0.291 \times 0.287 \times 0.248 \text{ mm}^3$	
Theta range for data collection	$2.05 \text{ to } 28.31^\circ$	
Index ranges	$-13 \leq h \leq 13, -12 \leq k \leq 12, -26 \leq l \leq 26$	
Reflections collected	24348	
Independent reflections	4545 [R(int) = 0.0259]	
Completeness to $\theta = 28.31^\circ$	99.8 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.107 and 0.102	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	4545 / 0 / 226	
Goodness-of-fit on F^2	1.083	
Final R indices [$I > 2\sigma(I)$]	$R1 = 0.0158, wR2 = 0.0338$	
R indices (all data)	$R1 = 0.0176, wR2 = 0.0343$	
Largest diff. peak and hole	$0.623 \text{ and } -0.635 \text{ e. \AA}^{-3}$	

Bond Lengths ($\text{\AA}$)

Hg(1)-C(1)#1	2.150(2)	C(3)-C(4)	1.379(3)
Hg(1)-O(1)	2.4127(14)	C(4)-C(5)	1.389(3)
Hg(1)-S(1)	2.4633(6)	C(5)-C(6)	1.376(3)
Hg(1)-N(1)	2.5225(18)	C(7)-C(8)	1.392(3)
S(1)-C(19)	1.680(3)	C(7)-C(12)	1.397(3)
P(1)-O(1)	1.5033(15)	C(8)-C(9)	1.386(3)
P(1)-C(1)	1.797(2)	C(9)-C(10)	1.382(3)
P(1)-C(13)	1.797(2)	C(10)-C(11)	1.383(3)
P(1)-C(7)	1.802(2)	C(11)-C(12)	1.384(3)
N(1)-C(2)	1.346(3)	C(13)-C(18)	1.389(3)
N(1)-C(6)	1.347(3)	C(13)-C(14)	1.394(3)
N(2)-C(19)	1.154(3)	C(14)-C(15)	1.393(3)
C(1)-C(2)	1.491(3)	C(15)-C(16)	1.379(4)
C(1)-Hg(1)#1	2.150(2)	C(16)-C(17)	1.381(4)
C(2)-C(3)	1.397(3)	C(17)-C(18)	1.386(3)

Table B.9. (continued)

Bond Angles (°)

C(1)#1-Hg(1)-O(1)	110.03(6)	C(3)-C(2)-C(1)	120.19(19)
C(1)#1-Hg(1)-S(1)	143.74(6)	C(4)-C(3)-C(2)	119.5(2)
O(1)-Hg(1)-S(1)	91.11(4)	C(3)-C(4)-C(5)	119.0(2)
C(1)#1-Hg(1)-N(1)	121.48(7)	C(6)-C(5)-C(4)	118.5(2)
O(1)-Hg(1)-N(1)	82.51(5)	N(1)-C(6)-C(5)	123.1(2)
S(1)-Hg(1)-N(1)	89.39(4)	C(8)-C(7)-C(12)	119.4(2)
C(19)-S(1)-Hg(1)	94.79(9)	C(8)-C(7)-P(1)	123.16(17)
O(1)-P(1)-C(1)	114.18(9)	C(12)-C(7)-P(1)	117.45(16)
O(1)-P(1)-C(13)	109.95(9)	C(9)-C(8)-C(7)	120.3(2)
C(1)-P(1)-C(13)	105.04(10)	C(10)-C(9)-C(8)	119.9(2)
O(1)-P(1)-C(7)	110.98(9)	C(9)-C(10)-C(11)	120.3(2)
C(1)-P(1)-C(7)	108.09(10)	C(10)-C(11)-C(12)	120.1(2)
C(13)-P(1)-C(7)	108.29(10)	C(11)-C(12)-C(7)	120.0(2)
P(1)-O(1)-Hg(1)	122.18(8)	C(18)-C(13)-C(14)	119.8(2)
C(2)-N(1)-C(6)	118.50(19)	C(18)-C(13)-P(1)	117.26(16)
C(2)-N(1)-Hg(1)	126.62(14)	C(14)-C(13)-P(1)	122.90(17)
C(6)-N(1)-Hg(1)	114.75(14)	C(15)-C(14)-C(13)	119.4(2)
C(2)-C(1)-P(1)	114.92(15)	C(16)-C(15)-C(14)	120.2(2)
C(2)-C(1)-Hg(1)#1	111.65(14)	C(15)-C(16)-C(17)	120.5(2)
P(1)-C(1)-Hg(1)#1	108.13(10)	C(16)-C(17)-C(18)	119.7(2)
N(1)-C(2)-C(3)	121.34(19)	C(17)-C(18)-C(13)	120.3(2)
N(1)-C(2)-C(1)	118.43(18)	N(2)-C(19)-S(1)	178.7(3)

*Symmetry transformations used to generate equivalent atoms: #1 -x+1,-y,-z.

Table B.10. Experimental and statistical crystal data for **L3**.

Empirical formula	C ₁₈ H ₁₆ NO ₂ P	
Formula weight	309.29	
Temperature	110(2) K	
Wavelength	0.71073 Å	
Crystal system	Orthorhombic	
Space group	Pbca	
Unit cell dimensions	a = 10.6764(4) Å	$\alpha = 90^\circ$.
	b = 7.8602(3) Å	$\beta = 90^\circ$.
	c = 35.7789(12) Å	$\delta = 90^\circ$.
Volume	3002.52(19) Å ³	
Z	8	
Density (calculated)	1.368 Mg/m ³	

Table B.10. (continued)

Absorption coefficient	0.190 mm ⁻¹
F(000)	1296
Crystal size	0.297 x 0.13 x 0.118 mm ³
Theta range for data collection	2.28 to 26.72°
Index ranges	-13 ≤ h ≤ 12, -9 ≤ k ≤ 8, -41 ≤ l ≤ 45
Reflections collected	26503
Independent reflections	3173 [R(int) = 0.0498]
Completeness to theta = 26.72°	99.9 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.977 and 0.970
Refinement method	Full-matrix least-squares on F ²
Data / restraints / parameters	3173 / 0 / 199
Goodness-of-fit on F ²	1.054
Final R indices [I > 2sigma(I)]	R1 = 0.0383, wR2 = 0.0835
R indices (all data)	R1 = 0.0523, wR2 = 0.0901
Largest diff. peak and hole	0.317 and -0.380 e.Å ³

Bond Lengths (Å)

P(1)-O(1)	1.4843(12)	C(7)-C(12)	1.392(2)
P(1)-C(13)	1.8005(17)	C(7)-C(8)	1.394(2)
P(1)-C(7)	1.8043(17)	C(8)-C(9)	1.385(2)
P(1)-C(1)	1.8148(17)	C(9)-C(10)	1.386(2)
O(2)-N(1)	1.3152(18)	C(10)-C(11)	1.387(2)
N(1)-C(6)	1.360(2)	C(11)-C(12)	1.390(2)
N(1)-C(2)	1.369(2)	C(13)-C(18)	1.394(2)
C(1)-C(2)	1.493(2)	C(13)-C(14)	1.399(2)
C(2)-C(3)	1.381(2)	C(14)-C(15)	1.383(3)
C(3)-C(4)	1.381(2)	C(15)-C(16)	1.391(3)
C(4)-C(5)	1.384(2)	C(16)-C(17)	1.383(3)
C(5)-C(6)	1.369(3)	C(17)-C(18)	1.389(3)

Bond Angles (°)

O(1)-P(1)-C(13)	112.42(8)	C(12)-C(7)-C(8)	119.48(16)
O(1)-P(1)-C(7)	113.15(7)	C(12)-C(7)-P(1)	123.08(13)
C(13)-P(1)-C(7)	106.79(8)	C(8)-C(7)-P(1)	117.32(13)
O(1)-P(1)-C(1)	113.59(7)	C(9)-C(8)-C(7)	120.05(16)
C(13)-P(1)-C(1)	108.68(8)	C(8)-C(9)-C(10)	120.48(17)
C(7)-P(1)-C(1)	101.46(8)	C(9)-C(10)-C(11)	119.66(17)
O(2)-N(1)-C(6)	118.99(14)	C(10)-C(11)-C(12)	120.24(16)

Table B.10. (continued)

O(2)-N(1)-C(2)	120.79(14)	C(11)-C(12)-C(7)	120.08(16)
C(6)-N(1)-C(2)	120.21(14)	C(18)-C(13)-C(14)	119.56(16)
C(2)-C(1)-P(1)	115.43(12)	C(18)-C(13)-P(1)	123.70(13)
N(1)-C(2)-C(3)	119.02(15)	C(14)-C(13)-P(1)	116.72(13)
N(1)-C(2)-C(1)	117.69(14)	C(15)-C(14)-C(13)	120.19(17)
C(3)-C(2)-C(1)	123.28(15)	C(14)-C(15)-C(16)	119.84(17)
C(2)-C(3)-C(4)	121.25(16)	C(17)-C(16)-C(15)	120.34(17)
C(3)-C(4)-C(5)	118.51(16)	C(16)-C(17)-C(18)	120.16(17)
C(6)-C(5)-C(4)	119.77(16)	C(17)-C(18)-C(13)	119.90(17)
N(1)-C(6)-C(5)	119.77(16)		

Table B.11. Experimental and statistical crystal data for **3.1**.*

Empirical formula	$C_{48}H_{32}Ag_6F_{18}N_2O_{16}P_2$		
Formula weight	1943.92		
Temperature	110(2) K		
Wavelength	0.71073 Å		
Crystal system	Triclinic		
Space group	P-1		
Unit cell dimensions	$a = 10.4423(9)$ Å	$\alpha = 84.704(4)^\circ$	
	$b = 11.7176(9)$ Å	$\beta = 66.423(3)^\circ$	
	$c = 13.0240(11)$ Å	$\delta = 81.360(4)^\circ$	
Volume	$1443.1(2)$ Å ³		
Z	1		
Density (calculated)	2.237 Mg/m ³		
Absorption coefficient	2.179 mm ⁻¹		
F(000)	936		
Crystal size	$0.24 \times 0.08 \times 0.08$ mm ³		
Theta range for data collection	2.57 to 25.35°		
Index ranges	$-12 \leq h \leq 12$, $-14 \leq k \leq 13$, $-15 \leq l \leq 15$		
Reflections collected	30768		
Independent reflections	5218 [R(int) = 0.0400]		
Completeness to theta = 25.35°	98.5 %		
Absorption correction	Semi-empirical from equivalents		
Max. and min. transmission	0.8433 and 0.6196		
Refinement method	Full-matrix least-squares on F ²		
Data / restraints / parameters	5218 / 0 / 415		
Goodness-of-fit on F ²	1.021		
Final R indices [I > 2sigma(I)]	R1 = 0.0238, wR2 = 0.0526		
R indices (all data)	R1 = 0.0360, wR2 = 0.0579		
Largest diff. peak and hole	0.707 and -0.736 e. Å ⁻³		

Table B.11. (continued)

Bond Lengths (Å)

Ag(1)-O(3)	2.246(2)	C(1)-C(2)	1.496(4)
Ag(1)-O(4)	2.252(2)	C(2)-C(3)	1.383(4)
Ag(1)-O(2)	2.377(2)	C(3)-C(4)	1.380(4)
Ag(1)-Ag(3)#1	2.9492(4)	C(4)-C(5)	1.379(5)
Ag(1)-Ag(2)	3.0641(4)	C(5)-C(6)	1.370(4)
Ag(2)-O(5)	2.194(2)	C(7)-C(8)	1.394(4)
Ag(2)-O(6)#1	2.202(2)	C(7)-C(12)	1.396(4)
Ag(2)-O(1)	2.457(2)	C(8)-C(9)	1.383(5)
Ag(2)-O(2)	2.467(2)	C(9)-C(10)	1.379(5)
Ag(2)-Ag(2)#1	2.8715(5)	C(10)-C(11)	1.390(5)
Ag(2)-Ag(3)#1	3.0337(4)	C(11)-C(12)	1.376(5)
Ag(2)-Ag(3)	3.0734(4)	C(13)-C(14)	1.389(4)
Ag(3)-O(7)	2.187(2)	C(13)-C(18)	1.404(4)
Ag(3)-O(8)	2.195(2)	C(14)-C(15)	1.387(4)
Ag(3)-O(1)	2.406(2)	C(15)-C(16)	1.389(5)
Ag(3)-Ag(1)#1	2.9492(4)	C(16)-C(17)	1.385(5)
Ag(3)-Ag(2)#1	3.0337(4)	C(17)-C(18)	1.390(4)
P(1)-O(1)	1.496(2)	C(19)-O(8)#1	1.247(4)
P(1)-C(13)	1.798(3)	C(19)-C(20)	1.539(5)
P(1)-C(7)	1.803(3)	C(20)-F(6)	1.330(4)
P(1)-C(1)	1.819(3)	C(20)-F(4)	1.333(4)
N(1)-O(2)	1.335(3)	C(20)-F(5)	1.335(4)
N(1)-C(6)	1.354(4)	C(21)-C(22)	1.540(5)
N(1)-C(2)	1.373(4)	C(22)-F(3)	1.320(4)
O(3)-C(19)	1.244(4)	C(22)-F(1)	1.320(4)
O(4)-C(23)#1	1.245(4)	C(22)-F(10)	1.326(4)
O(5)-C(21)	1.244(4)	C(23)-O(4)#1	1.245(4)
O(6)-C(21)	1.242(4)	C(23)-C(24)	1.536(5)
O(6)-Ag(2)#1	2.202(2)	C(24)-F(8)	1.322(4)
O(7)-C(23)	1.238(4)	C(24)-F(7)	1.328(4)
O(8)-C(19)#1	1.247(4)	C(24)-F(9)	1.330(4)

Bond Angles (°)

O(3)-Ag(1)-O(4)	138.19(8)	P(1)-O(1)-Ag(2)	140.59(12)
O(3)-Ag(1)-O(2)	113.86(7)	Ag(3)-O(1)-Ag(2)	78.39(6)
O(4)-Ag(1)-O(2)	105.83(8)	N(1)-O(2)-Ag(1)	126.08(16)
O(3)-Ag(1)-Ag(3)#1	77.99(5)	N(1)-O(2)-Ag(2)	109.07(15)
O(4)-Ag(1)-Ag(3)#1	75.46(6)	Ag(1)-O(2)-Ag(2)	78.47(6)
O(2)-Ag(1)-Ag(3)#1	111.98(5)	C(19)-O(3)-Ag(1)	126.3(2)
O(3)-Ag(1)-Ag(2)	94.78(6)	C(23)#1-O(4)-Ag(1)	129.2(2)

Table B.11. (continued)

O(4)-Ag(1)-Ag(2)	99.51(6)	C(21)-O(5)-Ag(2)	120.6(2)
O(2)-Ag(1)-Ag(2)	52.07(5)	C(21)-O(6)-Ag(2)#1	124.2(2)
Ag(3)#1-Ag(1)-Ag(2)	60.561(9)	C(23)-O(7)-Ag(3)	118.0(2)
O(5)-Ag(2)-O(6)#1	163.03(8)	C(19)#1-O(8)-Ag(3)	120.5(2)
O(5)-Ag(2)-O(1)	92.14(8)	C(2)-C(1)-P(1)	110.6(2)
O(6)#1-Ag(2)-O(1)	98.38(8)	N(1)-C(2)-C(3)	118.4(3)
O(5)-Ag(2)-O(2)	102.74(8)	N(1)-C(2)-C(1)	117.7(3)
O(6)#1-Ag(2)-O(2)	92.32(8)	C(3)-C(2)-C(1)	123.9(3)
O(1)-Ag(2)-O(2)	79.29(7)	C(4)-C(3)-C(2)	121.1(3)
O(5)-Ag(2)-Ag(2)#1	83.49(6)	C(5)-C(4)-C(3)	119.1(3)
O(6)#1-Ag(2)-Ag(2)#1	80.30(6)	C(6)-C(5)-C(4)	119.6(3)
O(1)-Ag(2)-Ag(2)#1	111.33(5)	N(1)-C(6)-C(5)	120.9(3)
O(2)-Ag(2)-Ag(2)#1	167.73(5)	C(8)-C(7)-C(12)	120.0(3)
O(5)-Ag(2)-Ag(3)#1	86.98(6)	C(8)-C(7)-P(1)	117.1(2)
O(6)#1-Ag(2)-Ag(3)#1	81.16(6)	C(12)-C(7)-P(1)	122.9(2)
O(1)-Ag(2)-Ag(3)#1	173.98(5)	C(9)-C(8)-C(7)	119.4(3)
O(2)-Ag(2)-Ag(3)#1	106.72(5)	C(10)-C(9)-C(8)	120.5(3)
Ag(2)#1-Ag(2)-Ag(3)#1	62.655(10)	C(9)-C(10)-C(11)	120.3(3)
O(5)-Ag(2)-Ag(1)	92.15(6)	C(12)-C(11)-C(10)	119.8(3)
O(6)#1-Ag(2)-Ag(1)	91.76(6)	C(11)-C(12)-C(7)	120.0(3)
O(1)-Ag(2)-Ag(1)	128.16(5)	C(14)-C(13)-C(18)	119.3(3)
O(2)-Ag(2)-Ag(1)	49.46(5)	C(14)-C(13)-P(1)	117.5(2)
Ag(2)#1-Ag(2)-Ag(1)	120.488(13)	C(18)-C(13)-P(1)	123.3(2)
Ag(3)#1-Ag(2)-Ag(1)	57.846(9)	C(15)-C(14)-C(13)	120.3(3)
O(5)-Ag(2)-Ag(3)	86.91(6)	C(14)-C(15)-C(16)	120.4(3)
O(6)#1-Ag(2)-Ag(3)	89.67(6)	C(17)-C(16)-C(15)	119.8(3)
O(1)-Ag(2)-Ag(3)	50.07(5)	C(16)-C(17)-C(18)	120.2(3)
O(2)-Ag(2)-Ag(3)	128.98(5)	C(17)-C(18)-C(13)	120.0(3)
Ag(2)#1-Ag(2)-Ag(3)	61.257(10)	O(3)-C(19)-O(8)#1	130.0(3)
Ag(3)#1-Ag(2)-Ag(3)	123.912(10)	O(3)-C(19)-C(20)	114.4(3)
Ag(1)-Ag(2)-Ag(3)	177.923(10)	O(8)#1-C(19)-C(20)	115.6(3)
O(7)-Ag(3)-O(8)	150.87(9)	F(6)-C(20)-F(4)	107.1(3)
O(7)-Ag(3)-O(1)	97.61(8)	F(6)-C(20)-F(5)	107.4(3)
O(8)-Ag(3)-O(1)	96.63(7)	F(4)-C(20)-F(5)	106.2(3)
O(7)-Ag(3)-Ag(1)#1	86.63(6)	F(6)-C(20)-C(19)	113.7(3)
O(8)-Ag(3)-Ag(1)#1	84.04(6)	F(4)-C(20)-C(19)	112.3(3)
O(1)-Ag(3)-Ag(1)#1	169.18(5)	F(5)-C(20)-C(19)	109.8(3)
O(7)-Ag(3)-Ag(2)#1	104.23(6)	O(6)-C(21)-O(5)	130.7(3)
O(8)-Ag(3)-Ag(2)#1	95.41(6)	O(6)-C(21)-C(22)	115.6(3)
O(1)-Ag(3)-Ag(2)#1	107.63(5)	O(5)-C(21)-C(22)	113.7(3)
Ag(1)#1-Ag(3)-Ag(2)#1	61.593(9)	F(3)-C(22)-F(1)	107.2(3)
O(7)-Ag(3)-Ag(2)	108.73(7)	F(3)-C(22)-F(10)	106.4(3)
O(8)-Ag(3)-Ag(2)	100.03(6)	F(1)-C(22)-F(10)	106.9(3)
O(1)-Ag(3)-Ag(2)	51.54(5)	F(3)-C(22)-C(21)	111.6(3)

Table B.11. (continued)

Ag(1)#1-Ag(3)-Ag(2)	117.669(11)	F(1)-C(22)-C(21)	113.5(3)
Ag(2)#1-Ag(3)-Ag(2)	56.088(10)	F(10)-C(22)-C(21)	110.8(3)
O(1)-P(1)-C(13)	111.81(13)	O(7)-C(23)-O(4)#1	130.6(3)
O(1)-P(1)-C(7)	110.67(13)	O(7)-C(23)-C(24)	116.5(3)
C(13)-P(1)-C(7)	110.20(15)	O(4)#1-C(23)-C(24)	112.9(3)
O(1)-P(1)-C(1)	111.77(13)	F(8)-C(24)-F(7)	107.1(3)
C(13)-P(1)-C(1)	105.98(14)	F(8)-C(24)-F(9)	108.0(3)
C(7)-P(1)-C(1)	106.18(14)	F(7)-C(24)-F(9)	106.1(3)
O(2)-N(1)-C(6)	120.3(2)	F(8)-C(24)-C(23)	113.6(3)
O(2)-N(1)-C(2)	118.7(2)	F(7)-C(24)-C(23)	110.0(3)
C(6)-N(1)-C(2)	121.0(3)	F(9)-C(24)-C(23)	111.8(3)
P(1)-O(1)-Ag(3)	139.74(12)		

*Symmetry transformations used to generate equivalent atoms: #1 -x,-y+2,-z+1

Table B.12. Experimental and statistical crystal data for **3.2**.

Empirical formula	C ₂₁ H ₁₈ Ag ₂ Cl ₂ F ₆ NO ₈ PS ₂	
Formula weight	908.09	
Temperature	110(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	C2/c	
Unit cell dimensions	a = 26.8758(13) Å	$\alpha = 90^\circ$.
	b = 9.6622(5) Å	$\beta = 114.924(2)^\circ$.
	c = 23.8190(12) Å	$\delta = 90^\circ$.
Volume	5609.2(5) Å ³	
Z	8	
Density (calculated)	2.151 Mg/m ³	
Absorption coefficient	1.881 mm ⁻¹	
F(000)	3552	
Crystal size	0.193 x 0.10 x 0.067 mm ³	
Theta range for data collection	2.27 to 26.36°.	
Index ranges	-33 ≤ h ≤ 33, -12 ≤ k ≤ 12, -29 ≤ l ≤ 29	
Reflections collected	39988	
Independent reflections	5703 [R(int) = 0.0442]	
Completeness to theta = 26.36°	99.7 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.882 and 0.799	
Refinement method	Full-matrix least-squares on F ²	
Data / restraints / parameters	5703 / 0 / 390	
Goodness-of-fit on F ²	1.071	
Final R indices [I > 2σ(I)]	R1 = 0.0531, wR2 = 0.1560	

Table B.12. (continued)

R indices (all data)
Largest diff. peak and hole

R1 = 0.0685, wR2 = 0.1692
1.206 and -2.467 e. Å⁻³

Bond Lengths (Å)

Ag(1)-O(2)	2.346(4)	F(2)-C(19)	1.324(11)
Ag(1)-O(4)#1	2.416(6)	F(3)-C(19)	1.350(12)
Ag(1)-O(1)	2.427(4)	F(4)-C(20)	1.328(8)
Ag(1)-O(6)	2.542(5)	F(5)-C(20)	1.309(9)
Ag(1)-Ag(2)	3.2523(5)	F(6)-C(20)	1.337(9)
Ag(2)-O(1)	2.345(5)	O(1)-N(1)	1.343(7)
Ag(2)-O(1)#1	2.345(5)	O(4)-Ag(1)#1	2.416(6)
Ag(2)-O(3)#1	2.498(6)	N(1)-C(6)	1.345(9)
Ag(2)-O(3)	2.498(6)	N(1)-C(2)	1.369(8)
Ag(2)-O(2)	2.558(4)	C(1)-C(2)	1.501(10)
Ag(2)-O(2)#1	2.558(4)	C(1)-P(1)#1	1.817(6)
Ag(2)-Ag(1)#1	3.2523(5)	C(2)-C(3)	1.377(10)
Ag(3)-O(7)	2.392(5)	C(3)-C(4)	1.378(11)
Ag(3)-O(7)#2	2.392(5)	C(4)-C(5)	1.391(11)
Ag(3)-C(17)#3	2.459(6)	C(5)-C(6)	1.353(10)
Ag(3)-C(17)#4	2.459(6)	C(7)-C(12)	1.370(9)
Ag(3)-C(16)#3	2.513(8)	C(7)-C(8)	1.401(9)
Ag(3)-C(16)#4	2.513(8)	C(8)-C(9)	1.393(10)
S(1)-O(5)	1.428(6)	C(9)-C(10)	1.379(11)
S(1)-O(3)	1.432(5)	C(10)-C(11)	1.385(12)
S(1)-O(4)	1.443(6)	C(11)-C(12)	1.390(10)
S(1)-C(19)	1.830(9)	C(13)-C(18)	1.401(9)
S(2)-O(6)	1.442(5)	C(13)-C(14)	1.403(9)
S(2)-O(8)	1.442(5)	C(14)-C(15)	1.374(10)
S(2)-O(7)	1.453(5)	C(15)-C(16)	1.397(10)
S(2)-C(20)	1.831(8)	C(16)-C(17)	1.396(10)
P(1)-O(2)	1.492(4)	C(16)-Ag(3)#5	2.513(8)
P(1)-C(7)	1.801(6)	C(17)-C(18)	1.383(9)
P(1)-C(13)	1.801(6)	C(17)-Ag(3)#5	2.459(6)
P(1)-C(1)#1	1.817(6)	C(21)-Cl(1)	1.755(16)
F(1)-C(19)	1.276(12)	C(21)-Cl(2)	1.789(16)

Bond Angles (°)

O(2)-Ag(1)-O(4)#1	104.52(18)	O(8)-S(2)-C(20)	105.6(3)
O(2)-Ag(1)-O(1)	95.76(15)	O(7)-S(2)-C(20)	101.8(3)
O(4)#1-Ag(1)-O(1)	78.73(18)	O(2)-P(1)-C(7)	112.6(3)

Table B.12. (continued)

O(2)-Ag(1)-O(6)	111.53(16)	O(2)-P(1)-C(13)	112.5(3)
O(4)#1-Ag(1)-O(6)	142.96(18)	C(7)-P(1)-C(13)	106.0(3)
O(1)-Ag(1)-O(6)	89.30(15)	O(2)-P(1)-C(1)#1	112.7(3)
O(2)-Ag(1)-Ag(2)	51.32(10)	C(7)-P(1)-C(1)#1	105.6(3)
O(4)#1-Ag(1)-Ag(2)	82.12(13)	C(13)-P(1)-C(1)#1	106.9(3)
O(1)-Ag(1)-Ag(2)	45.98(11)	N(1)-O(1)-Ag(2)	113.2(3)
O(6)-Ag(1)-Ag(2)	114.06(11)	N(1)-O(1)-Ag(1)	134.9(4)
O(1)-Ag(2)-O(1)#1	180.0(2)	Ag(2)-O(1)-Ag(1)	85.91(15)
O(1)-Ag(2)-O(3)#1	91.18(16)	P(1)-O(2)-Ag(1)	146.3(3)
O(1)#1-Ag(2)-O(3)#1	88.82(16)	P(1)-O(2)-Ag(2)	130.1(2)
O(1)-Ag(2)-O(3)	88.82(16)	Ag(1)-O(2)-Ag(2)	82.97(13)
O(1)#1-Ag(2)-O(3)	91.18(16)	S(1)-O(3)-Ag(2)	119.9(3)
O(3)#1-Ag(2)-O(3)	180.00(14)	S(1)-O(4)-Ag(1)#1	122.3(3)
O(1)-Ag(2)-O(2)	92.37(14)	S(2)-O(6)-Ag(1)	139.8(3)
O(1)#1-Ag(2)-O(2)	87.63(14)	S(2)-O(7)-Ag(3)	127.9(3)
O(3)#1-Ag(2)-O(2)	78.32(18)	O(1)-N(1)-C(6)	119.7(5)
O(3)-Ag(2)-O(2)	101.68(18)	O(1)-N(1)-C(2)	118.3(5)
O(1)-Ag(2)-O(2)#1	87.63(14)	C(6)-N(1)-C(2)	122.0(6)
O(1)#1-Ag(2)-O(2)#1	92.37(14)	C(2)-C(1)-P(1)#1	110.4(4)
O(3)#1-Ag(2)-O(2)#1	101.68(18)	N(1)-C(2)-C(3)	118.1(6)
O(3)-Ag(2)-O(2)#1	78.32(18)	N(1)-C(2)-C(1)	117.7(6)
O(2)-Ag(2)-O(2)#1	180.00(13)	C(3)-C(2)-C(1)	124.2(6)
O(1)-Ag(2)-Ag(1)	48.11(11)	C(2)-C(3)-C(4)	121.0(7)
O(1)#1-Ag(2)-Ag(1)	131.89(11)	C(3)-C(4)-C(5)	118.4(7)
O(3)#1-Ag(2)-Ag(1)	73.04(13)	C(6)-C(5)-C(4)	120.5(7)
O(3)-Ag(2)-Ag(1)	106.96(13)	N(1)-C(6)-C(5)	120.0(7)
O(2)-Ag(2)-Ag(1)	45.71(9)	C(12)-C(7)-C(8)	120.2(6)
O(2)#1-Ag(2)-Ag(1)	134.29(9)	C(12)-C(7)-P(1)	119.4(5)
O(1)-Ag(2)-Ag(1)#1	131.89(10)	C(8)-C(7)-P(1)	120.4(5)
O(1)#1-Ag(2)-Ag(1)#1	48.11(11)	C(9)-C(8)-C(7)	119.7(7)
O(3)#1-Ag(2)-Ag(1)#1	106.96(13)	C(10)-C(9)-C(8)	119.9(7)
O(3)-Ag(2)-Ag(1)#1	73.04(13)	C(9)-C(10)-C(11)	120.0(7)
O(2)-Ag(2)-Ag(1)#1	134.29(9)	C(10)-C(11)-C(12)	120.4(7)
O(2)#1-Ag(2)-Ag(1)#1	45.71(9)	C(7)-C(12)-C(11)	119.9(7)
Ag(1)-Ag(2)-Ag(1)#1	180.000(1)	C(18)-C(13)-C(14)	119.9(6)
O(7)-Ag(3)-O(7)#2	88.3(2)	C(18)-C(13)-P(1)	123.2(5)
O(7)-Ag(3)-C(17)#3	103.0(2)	C(14)-C(13)-P(1)	116.7(5)
O(7)#2-Ag(3)-C(17)#3	91.77(19)	C(15)-C(14)-C(13)	119.8(6)
O(7)-Ag(3)-C(17)#4	91.77(19)	C(14)-C(15)-C(16)	120.5(6)
O(7)#2-Ag(3)-C(17)#4	103.0(2)	C(17)-C(16)-C(15)	119.9(7)
C(17)#3-Ag(3)-C(17)#4	159.4(3)	C(17)-C(16)-Ag(3)#5	71.6(4)
O(7)-Ag(3)-C(16)#3	135.3(2)	C(15)-C(16)-Ag(3)#5	105.3(5)
O(7)#2-Ag(3)-C(16)#3	88.6(2)	C(18)-C(17)-C(16)	120.0(6)
C(17)#3-Ag(3)-C(16)#3	32.6(2)	C(18)-C(17)-Ag(3)#5	102.4(4)

Table B.12. (continued)

C(17)#4-Ag(3)-C(16)#3	132.2(2)	C(16)-C(17)-Ag(3)#5	75.8(4)
O(7)-Ag(3)-C(16)#4	88.6(2)	C(17)-C(18)-C(13)	119.9(6)
O(7)#2-Ag(3)-C(16)#4	135.3(2)	F(1)-C(19)-F(2)	107.5(8)
C(17)#3-Ag(3)-C(16)#4	132.2(2)	F(1)-C(19)-F(3)	108.0(8)
C(17)#4-Ag(3)-C(16)#4	32.6(2)	F(2)-C(19)-F(3)	107.0(9)
C(16)#3-Ag(3)-C(16)#4	122.9(3)	F(1)-C(19)-S(1)	113.0(8)
O(5)-S(1)-O(3)	115.1(4)	F(2)-C(19)-S(1)	110.9(6)
O(5)-S(1)-O(4)	113.9(4)	F(3)-C(19)-S(1)	110.2(6)
O(3)-S(1)-O(4)	115.9(4)	F(5)-C(20)-F(4)	108.8(6)
O(5)-S(1)-C(19)	103.9(4)	F(5)-C(20)-F(6)	107.9(6)
O(3)-S(1)-C(19)	103.6(4)	F(4)-C(20)-F(6)	107.6(6)
O(4)-S(1)-C(19)	102.0(4)	F(5)-C(20)-S(2)	111.7(5)
O(6)-S(2)-O(8)	115.7(3)	F(4)-C(20)-S(2)	110.4(5)
O(6)-S(2)-O(7)	114.4(3)	F(6)-C(20)-S(2)	110.3(5)
O(8)-S(2)-O(7)	113.3(3)	Cl(1)-C(21)-Cl(2)	110.4(8)
O(6)-S(2)-C(20)	104.1(3)		

Table B.13. Experimental and statistical crystal data for **3.3**.

Empirical formula	$\text{C}_{38}\text{H}_{36}\text{Ag}_2\text{B}_2\text{Cl}_4\text{F}_8\text{N}_2\text{O}_4\text{P}_2$	
Formula weight	1177.79	
Temperature	110(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P-1	
Unit cell dimensions	$a = 11.5012(7)$ Å	$\alpha = 85.727(4)^\circ$.
	$b = 12.6965(8)$ Å	$\beta = 81.373(4)^\circ$.
	$c = 15.0632(10)$ Å	$\delta = 77.937(3)^\circ$.
Volume	$2124.6(2)$ Å ³	
Z	2	
Density (calculated)	1.841 Mg/m ³	
Absorption coefficient	1.328 mm^{-1}	
F(000)	1168	
Crystal size	$0.14 \times 0.14 \times 0.05 \text{ mm}^3$	
Theta range for data collection	1.64 to 26.66° .	
Index ranges	$-14 \leq h \leq 11$, $-15 \leq k \leq 15$, $-18 \leq l \leq 18$	
Reflections collected	27334	
Independent reflections	8748 [$R(\text{int}) = 0.0432$]	
Completeness to $\theta = 26.66^\circ$	97.8 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.9366 and 0.8359	

Table B.13. (continued)

Refinement method	Full-matrix least-squares on F ²
Data / restraints / parameters	8748 / 0 / 562
Goodness-of-fit on F ²	1.016
Final R indices [I>2sigma(I)]	R1 = 0.0370, wR2 = 0.0723
R indices (all data)	R1 = 0.0598, wR2 = 0.0816
Largest diff. peak and hole	0.588 and -0.528 e.Å ⁻³

Bond Lengths (Å)

Ag(1)-O(1)	2.265(2)	C(11)-C(12)	1.383(5)
Ag(1)-O(3)	2.270(2)	C(13)-C(18)	1.389(5)
Ag(1)-O(4)	2.499(3)	C(13)-C(14)	1.397(5)
Ag(1)-O(2)	2.512(3)	C(14)-C(15)	1.385(5)
Ag(1)-Ag(3)	3.1990(3)	C(15)-C(16)	1.383(5)
Ag(1)-Ag(2)	3.2244(3)	C(16)-C(17)	1.378(5)
Ag(2)-O(4)	2.237(2)	C(17)-C(18)	1.383(5)
Ag(2)-O(4)#1	2.237(2)	C(19)-C(20)	1.494(5)
Ag(2)-Ag(1)#1	3.2244(3)	C(20)-C(21)	1.382(5)
Ag(3)-O(2)#2	2.199(2)	C(21)-C(22)	1.375(5)
Ag(3)-O(2)	2.199(2)	C(22)-C(23)	1.385(5)
Ag(3)-Ag(1)#2	3.1990(3)	C(23)-C(24)	1.376(5)
P(1)-O(1)	1.503(3)	C(25)-C(30)	1.393(5)
P(1)-C(13)	1.795(3)	C(25)-C(26)	1.395(5)
P(1)-C(7)	1.796(4)	C(26)-C(27)	1.388(5)
P(1)-C(1)	1.824(3)	C(27)-C(28)	1.384(6)
P(2)-O(3)	1.498(3)	C(28)-C(29)	1.382(5)
P(2)-C(25)	1.798(3)	C(29)-C(30)	1.388(5)
P(2)-C(31)	1.800(4)	C(31)-C(36)	1.398(5)
P(2)-C(19)	1.827(4)	C(31)-C(32)	1.402(5)
O(2)-N(1)	1.346(4)	C(32)-C(33)	1.385(6)
O(4)-N(2)	1.348(4)	C(33)-C(34)	1.377(6)
N(1)-C(6)	1.354(4)	C(34)-C(35)	1.376(5)
N(1)-C(2)	1.357(4)	C(35)-C(36)	1.385(5)
N(2)-C(24)	1.352(4)	C(37)-Cl(1)	1.754(4)
N(2)-C(20)	1.356(4)	C(37)-Cl(2)	1.759(4)
C(1)-C(2)	1.495(4)	C(38)-Cl(3)	1.760(4)
C(2)-C(3)	1.376(5)	C(38)-Cl(4)	1.778(4)
C(3)-C(4)	1.380(5)	F(5)-B(2)	1.380(5)
C(4)-C(5)	1.369(5)	F(6)-B(2)	1.375(5)
C(5)-C(6)	1.364(5)	F(7)-B(2)	1.390(5)
C(7)-C(12)	1.392(5)	F(8)-B(2)	1.384(5)
C(7)-C(8)	1.394(5)	F(1)-B(1)	1.411(4)
C(8)-C(9)	1.401(5)	F(2)-B(1)	1.395(5)

Table B.13. (continued)

C(9)-C(10)	1.382(6)	B(1)-F(4)	1.378(5)
C(10)-C(11)	1.376(6)	B(1)-F(3)	1.381(5)

Bond Angles (°)

O(1)-Ag(1)-O(3)	166.68(9)	C(5)-C(4)-C(3)	119.1(4)
O(1)-Ag(1)-O(4)	91.46(8)	C(6)-C(5)-C(4)	120.0(3)
O(3)-Ag(1)-O(4)	85.67(8)	N(1)-C(6)-C(5)	120.1(4)
O(1)-Ag(1)-O(2)	85.39(8)	C(12)-C(7)-C(8)	119.6(4)
O(3)-Ag(1)-O(2)	94.72(8)	C(12)-C(7)-P(1)	117.2(3)
O(4)-Ag(1)-O(2)	167.87(8)	C(8)-C(7)-P(1)	123.2(3)
O(1)-Ag(1)-Ag(3)	127.81(6)	C(7)-C(8)-C(9)	119.6(4)
O(3)-Ag(1)-Ag(3)	55.60(6)	C(10)-C(9)-C(8)	120.0(4)
O(4)-Ag(1)-Ag(3)	140.65(6)	C(11)-C(10)-C(9)	120.3(4)
O(2)-Ag(1)-Ag(3)	43.24(5)	C(10)-C(11)-C(12)	120.4(4)
O(1)-Ag(1)-Ag(2)	54.15(6)	C(11)-C(12)-C(7)	120.1(4)
O(3)-Ag(1)-Ag(2)	127.46(6)	C(18)-C(13)-C(14)	119.7(3)
O(4)-Ag(1)-Ag(2)	43.77(5)	C(18)-C(13)-P(1)	122.9(3)
O(2)-Ag(1)-Ag(2)	137.79(6)	C(14)-C(13)-P(1)	117.3(3)
Ag(3)-Ag(1)-Ag(2)	162.463(10)	C(15)-C(14)-C(13)	119.8(4)
O(4)-Ag(2)-O(4)#1	180.000(1)	C(16)-C(15)-C(14)	119.8(4)
O(4)-Ag(2)-Ag(1)#1	129.39(6)	C(17)-C(16)-C(15)	120.6(3)
O(4)#1-Ag(2)-Ag(1)#1	50.61(6)	C(16)-C(17)-C(18)	120.0(4)
O(4)-Ag(2)-Ag(1)	50.61(6)	C(17)-C(18)-C(13)	120.0(3)
O(4)#1-Ag(2)-Ag(1)	129.39(6)	C(20)-C(19)-P(2)	116.6(3)
Ag(1)#1-Ag(2)-Ag(1)	180.0	N(2)-C(20)-C(21)	118.3(3)
O(2)#2-Ag(3)-O(2)	180.00(10)	N(2)-C(20)-C(19)	118.1(3)
O(2)#2-Ag(3)-Ag(1)	128.50(7)	C(21)-C(20)-C(19)	123.5(3)
O(2)-Ag(3)-Ag(1)	51.50(7)	C(22)-C(21)-C(20)	121.2(3)
O(2)#2-Ag(3)-Ag(1)#2	51.50(7)	C(21)-C(22)-C(23)	118.8(3)
O(2)-Ag(3)-Ag(1)#2	128.50(7)	C(24)-C(23)-C(22)	119.7(4)
Ag(1)-Ag(3)-Ag(1)#2	180.0	N(2)-C(24)-C(23)	119.9(3)
O(1)-P(1)-C(13)	112.42(15)	C(30)-C(25)-C(26)	119.7(3)
O(1)-P(1)-C(7)	111.19(16)	C(30)-C(25)-P(2)	123.2(3)
C(13)-P(1)-C(7)	108.54(16)	C(26)-C(25)-P(2)	117.0(3)
O(1)-P(1)-C(1)	113.89(15)	C(27)-C(26)-C(25)	120.0(4)
C(13)-P(1)-C(1)	101.82(16)	C(28)-C(27)-C(26)	120.2(4)
C(7)-P(1)-C(1)	108.47(17)	C(29)-C(28)-C(27)	119.9(3)
O(3)-P(2)-C(25)	111.16(16)	C(28)-C(29)-C(30)	120.6(4)
O(3)-P(2)-C(31)	113.02(16)	C(29)-C(30)-C(25)	119.7(4)
C(25)-P(2)-C(31)	106.86(16)	C(36)-C(31)-C(32)	119.3(3)
O(3)-P(2)-C(19)	113.32(15)	C(36)-C(31)-P(2)	122.6(3)
C(25)-P(2)-C(19)	108.91(16)	C(32)-C(31)-P(2)	118.1(3)

Table B.13. (continued)

C(31)-P(2)-C(19)	103.07(16)	C(33)-C(32)-C(31)	119.7(4)
P(1)-O(1)-Ag(1)	138.97(15)	C(34)-C(33)-C(32)	120.3(3)
N(1)-O(2)-Ag(3)	120.98(18)	C(35)-C(34)-C(33)	120.7(4)
N(1)-O(2)-Ag(1)	113.35(19)	C(34)-C(35)-C(36)	120.1(4)
Ag(3)-O(2)-Ag(1)	85.26(8)	C(35)-C(36)-C(31)	120.0(3)
P(2)-O(3)-Ag(1)	139.57(15)	Cl(1)-C(37)-Cl(2)	112.8(2)
N(2)-O(4)-Ag(2)	125.56(19)	Cl(3)-C(38)-Cl(4)	111.5(2)
N(2)-O(4)-Ag(1)	110.97(18)	F(6)-B(2)-F(5)	108.9(4)
Ag(2)-O(4)-Ag(1)	85.62(8)	F(6)-B(2)-F(8)	109.2(3)
O(2)-N(1)-C(6)	119.8(3)	F(5)-B(2)-F(8)	109.8(3)
O(2)-N(1)-C(2)	118.7(3)	F(6)-B(2)-F(7)	109.5(3)
C(6)-N(1)-C(2)	121.5(3)	F(5)-B(2)-F(7)	109.4(3)
O(4)-N(2)-C(24)	119.7(3)	F(8)-B(2)-F(7)	110.0(3)
O(4)-N(2)-C(20)	118.3(3)	F(4)-B(1)-F(3)	110.1(3)
C(24)-N(2)-C(20)	122.0(3)	F(4)-B(1)-F(2)	110.0(3)
C(2)-C(1)-P(1)	118.6(3)	F(3)-B(1)-F(2)	110.5(3)
N(1)-C(2)-C(3)	118.6(3)	F(4)-B(1)-F(1)	109.5(3)
N(1)-C(2)-C(1)	117.2(3)	F(3)-B(1)-F(1)	108.8(3)
C(3)-C(2)-C(1)	124.1(3)	F(2)-B(1)-F(1)	107.9(3)
C(2)-C(3)-C(4)	120.7(4)		

*Symmetry transformations used to generate equivalent atoms: #1 -x,-y+2,-z+1

Table B.14. Experimental and statistical crystal data for **4.1**.

Empirical formula	$\text{C}_{54}\text{H}_{48}\text{B}_2\text{CoF}_8\text{N}_3\text{O}_6\text{P}_3$	
Formula weight	1160.41	
Temperature	110(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P2(1)/c	
Unit cell dimensions	a = 13.9051(9) Å	$\alpha = 90^\circ$.
	b = 23.1098(16) Å	$\beta = 95.906(3)^\circ$.
	c = 17.9489(11) Å	$\delta = 90^\circ$.
Volume	5737.2(6) Å ³	
Z	4	
Density (calculated)	1.343 Mg/m ³	
Absorption coefficient	0.458 mm ⁻¹	
F(000)	2380	
Crystal size	0.30 x 0.14 x 0.11 mm ³	
Theta range for data collection	1.44 to 28.31°.	
Index ranges	-18 ≤ h ≤ 18, -30 ≤ k ≤ 30, -23 ≤ l ≤ 23	

Table B.14. (continued)

Reflections collected	103376
Independent reflections	14240 [R(int) = 0.0665]
Completeness to theta = 28.31°	99.8 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.9505 and 0.8733
Refinement method	Full-matrix least-squares on F ²
Data / restraints / parameters	14240 / 0 / 732
Goodness-of-fit on F ²	1.078
Final R indices [I>2sigma(I)]	R1 = 0.0444, wR2 = 0.1029
R indices (all data)	R1 = 0.0611, wR2 = 0.1104
Largest diff. peak and hole	0.615 and -0.463 e.Å ⁻³

Bond Lengths (Å)

Co(1)-O(4)	2.0441(13)	C(23)-C(24)	1.372(3)
Co(1)-O(3)	2.0603(13)	C(25)-C(26)	1.380(3)
Co(1)-O(1)	2.0790(13)	C(25)-C(30)	1.395(3)
Co(1)-O(5)	2.1053(12)	C(26)-C(27)	1.387(3)
Co(1)-O(6)	2.1187(12)	C(27)-C(28)	1.371(3)
Co(1)-O(2)	2.1289(12)	C(28)-C(29)	1.381(3)
P(1)-O(2)	1.4975(13)	C(29)-C(30)	1.382(3)
P(1)-C(7)	1.798(2)	C(37)-C(38)	1.491(3)
P(1)-C(13)	1.8006(19)	C(38)-C(39)	1.387(3)
P(1)-C(1)	1.8170(19)	C(39)-C(40)	1.381(3)
P(2)-O(6)	1.5016(13)	C(40)-C(41)	1.379(3)
P(2)-C(31A)	1.777(18)	C(41)-C(42)	1.376(3)
P(2)-C(25)	1.802(2)	C(43)-C(48)	1.387(3)
P(2)-C(19)	1.811(2)	C(43)-C(44)	1.398(3)
P(2)-C(31)	1.86(2)	C(48)-C(47)	1.400(3)
P(3)-O(5)	1.4989(13)	C(46)-C(47)	1.372(4)
P(3)-C(49)	1.79(3)	C(46)-C(45)	1.381(4)
P(3)-C(43)	1.796(2)	C(45)-C(44)	1.391(3)
P(3)-C(37)	1.818(2)	B(1)-F(1)	1.384(3)
P(3)-C(49A)	1.83(3)	B(1)-F(2)	1.390(3)
O(1)-N(1)	1.3326(19)	B(1)-F(3)	1.392(3)
O(3)-N(2)	1.334(2)	B(1)-F(4)	1.395(3)
O(4)-N(3)	1.3253(19)	B(2)-F(6)	1.343(3)
N(1)-C(6)	1.351(3)	B(2)-F(7)	1.374(3)
N(1)-C(2)	1.363(2)	B(2)-F(8)	1.383(3)
N(2)-C(24)	1.349(3)	B(2)-F(5)	1.386(3)
N(2)-C(20)	1.361(2)	C(31)-C(36)	1.35(3)
N(3)-C(42)	1.350(2)	C(31)-C(32)	1.49(3)
N(3)-C(38)	1.360(2)	C(32)-C(33)	1.44(4)

Table B.14. (continued)

C(1)-C(2)	1.491(3)	C(33)-C(34)	1.29(4)
C(2)-C(3)	1.385(3)	C(34)-C(35)	1.393(9)
C(3)-C(4)	1.380(3)	C(35)-C(36)	1.391(7)
C(4)-C(5)	1.387(3)	C(31A)-C(32A)	1.28(3)
C(5)-C(6)	1.373(3)	C(31A)-C(36A)	1.608(12)
C(7)-C(12)	1.393(3)	C(32A)-C(33A)	1.41(3)
C(7)-C(8)	1.395(3)	C(33A)-C(34A)	1.37(2)
C(8)-C(9)	1.387(3)	C(34A)-C(35A)	1.389(7)
C(9)-C(10)	1.381(3)	C(35A)-C(36A)	1.401(5)
C(10)-C(11)	1.376(3)	C(49)-C(50)	1.18(3)
C(11)-C(12)	1.387(3)	C(49)-C(54)	1.659(18)
C(13)-C(14)	1.386(3)	C(50)-C(51)	1.41(2)
C(13)-C(18)	1.399(3)	C(51)-C(52)	1.389(9)
C(14)-C(15)	1.396(3)	C(52)-C(53)	1.390(9)
C(15)-C(16)	1.380(3)	C(53)-C(54)	1.399(8)
C(16)-C(17)	1.387(4)	C(49A)-C(54A)	1.14(2)
C(17)-C(18)	1.387(3)	C(49A)-C(50A)	1.66(3)
C(19)-C(20)	1.484(3)	C(50A)-C(51A)	1.36(2)
C(20)-C(21)	1.387(3)	C(51A)-C(52A)	1.360(10)
C(21)-C(22)	1.373(4)	C(52A)-C(53A)	1.359(10)
C(22)-C(23)	1.382(4)	C(53A)-C(54A)	1.412(8)

Bond Angles (°)

O(4)-Co(1)-O(3)	173.61(5)	C(18)-C(17)-C(16)	119.8(2)
O(4)-Co(1)-O(1)	88.60(5)	C(17)-C(18)-C(13)	119.8(2)
O(3)-Co(1)-O(1)	86.45(5)	C(20)-C(19)-P(2)	112.08(14)
O(4)-Co(1)-O(5)	93.91(5)	N(2)-C(20)-C(21)	118.08(19)
O(3)-Co(1)-O(5)	91.12(5)	N(2)-C(20)-C(19)	117.52(18)
O(1)-Co(1)-O(5)	177.33(5)	C(21)-C(20)-C(19)	124.40(19)
O(4)-Co(1)-O(6)	89.96(5)	C(22)-C(21)-C(20)	121.0(2)
O(3)-Co(1)-O(6)	94.07(5)	C(21)-C(22)-C(23)	119.2(2)
O(1)-Co(1)-O(6)	90.08(5)	C(24)-C(23)-C(22)	119.4(2)
O(5)-Co(1)-O(6)	88.99(5)	N(2)-C(24)-C(23)	120.5(2)
O(4)-Co(1)-O(2)	85.94(5)	C(26)-C(25)-C(30)	118.77(19)
O(3)-Co(1)-O(2)	90.23(5)	C(26)-C(25)-P(2)	119.48(15)
O(1)-Co(1)-O(2)	92.27(5)	C(30)-C(25)-P(2)	121.74(15)
O(5)-Co(1)-O(2)	88.85(5)	C(25)-C(26)-C(27)	120.0(2)
O(6)-Co(1)-O(2)	175.23(5)	C(28)-C(27)-C(26)	121.1(2)
O(2)-P(1)-C(7)	113.48(8)	C(27)-C(28)-C(29)	119.3(2)
O(2)-P(1)-C(13)	109.84(8)	C(28)-C(29)-C(30)	120.1(2)
C(7)-P(1)-C(13)	109.16(9)	C(29)-C(30)-C(25)	120.7(2)
O(2)-P(1)-C(1)	112.72(8)	C(38)-C(37)-P(3)	108.79(13)

Table B.14. (continued)

C(7)-P(1)-C(1)	105.67(9)	N(3)-C(38)-C(39)	118.11(17)
C(13)-P(1)-C(1)	105.58(9)	N(3)-C(38)-C(37)	117.52(16)
O(6)-P(2)-C(31A)	113.7(5)	C(39)-C(38)-C(37)	124.37(18)
O(6)-P(2)-C(25)	113.74(9)	C(40)-C(39)-C(38)	120.82(19)
C(31A)-P(2)-C(25)	110.6(6)	C(41)-C(40)-C(39)	119.42(19)
O(6)-P(2)-C(19)	112.44(8)	C(42)-C(41)-C(40)	119.09(19)
C(31A)-P(2)-C(19)	100.0(3)	N(3)-C(42)-C(41)	120.68(19)
C(25)-P(2)-C(19)	105.27(9)	C(48)-C(43)-C(44)	119.6(2)
O(6)-P(2)-C(31)	106.5(7)	C(48)-C(43)-P(3)	123.70(16)
C(31A)-P(2)-C(31)	11.0(8)	C(44)-C(43)-P(3)	116.68(16)
C(25)-P(2)-C(31)	108.1(8)	C(43)-C(48)-C(47)	119.6(2)
C(19)-P(2)-C(31)	110.8(5)	C(47)-C(46)-C(45)	120.5(2)
O(5)-P(3)-C(49)	114.8(5)	C(46)-C(45)-C(44)	119.8(2)
O(5)-P(3)-C(43)	115.21(8)	C(45)-C(44)-C(43)	120.1(2)
C(49)-P(3)-C(43)	101.2(6)	C(46)-C(47)-C(48)	120.4(2)
O(5)-P(3)-C(37)	111.31(8)	F(1)-B(1)-F(2)	109.57(17)
C(49)-P(3)-C(37)	105.1(10)	F(1)-B(1)-F(3)	109.05(17)
C(43)-P(3)-C(37)	108.33(9)	F(2)-B(1)-F(3)	109.51(17)
O(5)-P(3)-C(49A)	105.0(6)	F(1)-B(1)-F(4)	109.27(17)
C(49)-P(3)-C(49A)	10.5(8)	F(2)-B(1)-F(4)	109.44(17)
C(43)-P(3)-C(49A)	109.6(7)	F(3)-B(1)-F(4)	109.98(17)
C(37)-P(3)-C(49A)	107.1(10)	F(6)-B(2)-F(7)	114.0(2)
N(1)-O(1)-Co(1)	119.00(10)	F(6)-B(2)-F(8)	109.2(2)
P(1)-O(2)-Co(1)	131.78(7)	F(7)-B(2)-F(8)	105.49(19)
N(2)-O(3)-Co(1)	116.79(10)	F(6)-B(2)-F(5)	110.29(18)
N(3)-O(4)-Co(1)	120.58(10)	F(7)-B(2)-F(5)	109.40(19)
P(3)-O(5)-Co(1)	128.51(8)	F(8)-B(2)-F(5)	108.2(2)
P(2)-O(6)-Co(1)	134.10(8)	C(36)-C(31)-C(32)	114(2)
O(1)-N(1)-C(6)	119.33(16)	C(36)-C(31)-P(2)	113.6(16)
O(1)-N(1)-C(2)	119.41(15)	C(32)-C(31)-P(2)	116.1(16)
C(6)-N(1)-C(2)	121.23(17)	C(33)-C(32)-C(31)	120(3)
O(3)-N(2)-C(24)	118.79(16)	C(34)-C(33)-C(32)	116(2)
O(3)-N(2)-C(20)	119.38(16)	C(33)-C(34)-C(35)	123.3(14)
C(24)-N(2)-C(20)	121.74(17)	C(36)-C(35)-C(34)	119.0(5)
O(4)-N(3)-C(42)	118.75(15)	C(31)-C(36)-C(35)	119.0(12)
O(4)-N(3)-C(38)	119.36(15)	C(32A)-C(31A)-C(36A)	115.7(14)
C(42)-N(3)-C(38)	121.82(16)	C(32A)-C(31A)-P(2)	128.9(15)
C(2)-C(1)-P(1)	109.20(13)	C(36A)-C(31A)-P(2)	111.5(9)
N(1)-C(2)-C(3)	118.91(18)	C(31A)-C(32A)-C(33A)	121.2(19)
N(1)-C(2)-C(1)	117.48(17)	C(34A)-C(33A)-C(32A)	124.7(17)
C(3)-C(2)-C(1)	123.57(17)	C(33A)-C(34A)-C(35A)	117.8(9)
C(4)-C(3)-C(2)	120.75(19)	C(34A)-C(35A)-C(36A)	119.9(4)
C(3)-C(4)-C(5)	118.7(2)	C(35A)-C(36A)-C(31A)	117.8(8)
C(6)-C(5)-C(4)	119.8(2)	C(50)-C(49)-C(54)	115(2)

Table B.14. (continued)

N(1)-C(6)-C(5)	120.54(19)	C(50)-C(49)-P(3)	137.8(16)
C(12)-C(7)-C(8)	119.25(18)	C(54)-C(49)-P(3)	107.5(12)
C(12)-C(7)-P(1)	123.15(15)	C(49)-C(50)-C(51)	128.7(14)
C(8)-C(7)-P(1)	117.61(14)	C(52)-C(51)-C(50)	119.5(11)
C(9)-C(8)-C(7)	120.26(19)	C(51)-C(52)-C(53)	120.3(8)
C(10)-C(9)-C(8)	119.81(19)	C(52)-C(53)-C(54)	120.0(5)
C(11)-C(10)-C(9)	120.4(2)	C(53)-C(54)-C(49)	116.6(11)
C(10)-C(11)-C(12)	120.3(2)	C(54A)-C(49A)-C(50A)	120(3)
C(11)-C(12)-C(7)	120.0(2)	C(54A)-C(49A)-P(3)	132.5(18)
C(14)-C(13)-C(18)	119.89(18)	C(50A)-C(49A)-P(3)	106.4(12)
C(14)-C(13)-P(1)	119.20(15)	C(51A)-C(50A)-C(49A)	112.8(13)
C(18)-C(13)-P(1)	120.90(15)	C(52A)-C(51A)-C(50A)	120.4(11)
C(13)-C(14)-C(15)	120.1(2)	C(53A)-C(52A)-C(51A)	123.6(9)
C(16)-C(15)-C(14)	119.5(2)	C(52A)-C(53A)-C(54A)	117.7(6)
C(15)-C(16)-C(17)	120.8(2)	C(49A)-C(54A)-C(53A)	125.0(15)

Table B.15. Experimental and statistical crystal data for **4.2**.

Empirical formula	$\text{C}_{55}\text{H}_{52}\text{B}_2\text{F}_8\text{N}_3\text{NiO}_7\text{P}_3$	
Formula weight	1192.24	
Temperature	110(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P2(1)	
Unit cell dimensions	$a = 10.5814(19)$ Å	$\alpha = 90^\circ$.
	$b = 15.021(2)$ Å	$\beta = 91.786(6)^\circ$.
	$c = 17.249(3)$ Å	$\delta = 90^\circ$.
Volume	$2740.3(7)$ Å ³	
Z	2	
Density (calculated)	1.445 Mg/m ³	
Absorption coefficient	0.524 mm ⁻¹	
F(000)	1228	
Crystal size	0.16 x 0.15 x 0.14 mm ³	
Theta range for data collection	1.80 to 26.75°.	
Index ranges	-13 ≤ h ≤ 13, -19 ≤ k ≤ 19, -21 ≤ l ≤ 21	
Reflections collected	27498	
Independent reflections	10845 [R(int) = 0.0597]	
Completeness to theta = 26.75°	99.5 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.9289 and 0.9218	
Refinement method	Full-matrix least-squares on F ²	

Table B.15. (continued)

Data / restraints / parameters	10845 / 1 / 714
Goodness-of-fit on F^2	1.043
Final R indices [$I > 2\sigma(I)$]	$R1 = 0.0582$, $wR2 = 0.1392$
R indices (all data)	$R1 = 0.0701$, $wR2 = 0.1460$
Absolute structure parameter	0.023(14)
Largest diff. peak and hole	1.049 and -0.459 e. $\text{\AA}^{-3}$

Bond Lengths ($\text{\AA}$)

Ni(1)-O(3)	2.052(3)	C(24)-H(24)	0.9500
Ni(1)-O(1)	2.052(3)	C(25)-C(30)	1.373(8)
Ni(1)-O(5)	2.053(3)	C(25)-C(26)	1.382(7)
Ni(1)-O(4)	2.063(3)	C(26)-C(27)	1.413(8)
Ni(1)-O(6)	2.064(3)	C(26)-H(26)	0.9500
Ni(1)-O(2)	2.072(3)	C(27)-C(28)	1.365(10)
P(1)-O(2)	1.502(3)	C(27)-H(27)	0.9500
P(1)-C(7)	1.790(5)	C(28)-C(29)	1.344(10)
P(1)-C(13)	1.790(5)	C(28)-H(28)	0.9500
P(1)-C(1)	1.813(5)	C(29)-C(30)	1.407(8)
P(2)-O(4)	1.502(3)	C(29)-H(29)	0.9500
P(2)-C(31)	1.798(5)	C(30)-H(30)	0.9500
P(2)-C(25)	1.800(5)	C(31)-C(36)	1.400(6)
P(2)-C(19)	1.827(5)	C(31)-C(32)	1.402(7)
P(3)-O(6)	1.489(3)	C(32)-C(33)	1.389(7)
P(3)-C(43)	1.800(5)	C(32)-H(32)	0.9500
P(3)-C(49)	1.812(5)	C(33)-C(34)	1.375(7)
P(3)-C(37)	1.820(5)	C(33)-H(33)	0.9500
O(1)-N(1)	1.325(5)	C(34)-C(35)	1.393(7)
O(3)-N(2)	1.341(5)	C(34)-H(34)	0.9500
O(5)-N(3)	1.339(4)	C(35)-C(36)	1.388(7)
N(1)-C(6)	1.359(6)	C(35)-H(35)	0.9500
N(1)-C(2)	1.376(6)	C(36)-H(36)	0.9500
N(2)-C(24)	1.337(6)	C(37)-C(38)	1.478(7)
N(2)-C(20)	1.357(6)	C(37)-H(37A)	0.9900
N(3)-C(42)	1.347(6)	C(37)-H(37B)	0.9900
N(3)-C(38)	1.356(6)	C(38)-C(39)	1.398(7)
C(1)-C(2)	1.503(7)	C(39)-C(40)	1.377(8)
C(1)-H(1A)	0.9900	C(39)-H(39)	0.9500
C(1)-H(1B)	0.9900	C(40)-C(41)	1.387(8)
C(2)-C(3)	1.378(7)	C(40)-H(40)	0.9500
C(3)-C(4)	1.371(8)	C(41)-C(42)	1.376(7)
C(3)-H(3)	0.9500	C(41)-H(41)	0.9500
C(4)-C(5)	1.386(8)	C(42)-H(42)	0.9500

Table B.15. (continued)

C(4)-H(4)	0.9500	C(43)-C(44)	1.382(7)
C(5)-C(6)	1.367(7)	C(43)-C(48)	1.407(7)
C(5)-H(5)	0.9500	C(44)-C(45)	1.382(7)
C(6)-H(6)	0.9500	C(44)-H(44)	0.9500
C(7)-C(8)	1.401(7)	C(45)-C(46)	1.376(7)
C(7)-C(12)	1.405(7)	C(45)-H(45)	0.9500
C(8)-C(9)	1.382(7)	C(46)-C(47)	1.377(8)
C(8)-H(8)	0.9500	C(46)-H(46)	0.9500
C(9)-C(10)	1.406(8)	C(47)-C(48)	1.369(8)
C(9)-H(9)	0.9500	C(47)-H(47)	0.9500
C(10)-C(11)	1.389(8)	C(48)-H(48)	0.9500
C(10)-H(10)	0.9500	C(49)-C(50)	1.388(7)
C(11)-C(12)	1.370(7)	C(49)-C(54)	1.394(6)
C(11)-H(11)	0.9500	C(50)-C(51)	1.384(7)
C(12)-H(12)	0.9500	C(50)-H(50)	0.9500
C(13)-C(14)	1.398(7)	C(51)-C(52)	1.375(8)
C(13)-C(18)	1.405(7)	C(51)-H(51)	0.9500
C(14)-C(15)	1.377(8)	C(52)-C(53)	1.383(7)
C(14)-H(14)	0.9500	C(52)-H(52)	0.9500
C(15)-C(16)	1.407(8)	C(53)-C(54)	1.389(7)
C(15)-H(15)	0.9500	C(53)-H(53)	0.9500
C(16)-C(17)	1.386(8)	C(54)-H(54)	0.9500
C(16)-H(16)	0.9500	B(1)-F(4)	1.350(7)
C(17)-C(18)	1.382(7)	B(1)-F(3)	1.356(8)
C(17)-H(17)	0.9500	B(1)-F(1)	1.381(9)
C(18)-H(18)	0.9500	B(1)-F(2)	1.403(7)
C(19)-C(20)	1.516(7)	B(2)-F(8)	1.330(8)
C(19)-H(19A)	0.9900	B(2)-F(5)	1.352(7)
C(19)-H(19B)	0.9900	B(2)-F(6)	1.372(8)
C(20)-C(21)	1.382(7)	B(2)-F(7)	1.441(9)
C(21)-C(22)	1.381(8)	C(55)-O(7)	1.388(10)
C(21)-H(21)	0.9500	C(55)-H(55A)	0.9800
C(22)-C(23)	1.401(8)	C(55)-H(55B)	0.9800
C(22)-H(22)	0.9500	C(55)-H(55C)	0.9800
C(23)-C(24)	1.369(7)	O(7)-H(7)	0.8400
C(23)-H(23)	0.9500		

Bond Angles (°)

O(3)-Ni(1)-O(1)	93.20(13)	C(33)-C(32)-H(32)	120.5
O(3)-Ni(1)-O(5)	175.52(12)	C(31)-C(32)-H(32)	120.5
O(1)-Ni(1)-O(5)	82.43(13)	C(34)-C(33)-C(32)	121.5(5)
O(3)-Ni(1)-O(4)	93.88(12)	C(29)-C(30)-H(30)	119.8

Table B.15. (continued)

O(1)-Ni(1)-O(4)	172.86(13)	C(30)-C(29)-H(29)	119.9
O(5)-Ni(1)-O(4)	90.51(12)	C(25)-C(30)-C(29)	120.4(6)
O(3)-Ni(1)-O(6)	89.21(14)	C(26)-C(27)-H(27)	119.6
O(1)-Ni(1)-O(6)	89.33(13)	C(29)-C(28)-C(27)	120.3(6)
O(5)-Ni(1)-O(6)	91.71(13)	C(29)-C(28)-H(28)	119.8
O(4)-Ni(1)-O(6)	89.85(12)	C(27)-C(28)-H(28)	119.8
O(3)-Ni(1)-O(2)	85.16(14)	N(2)-C(24)-H(24)	119.1
O(1)-Ni(1)-O(2)	91.71(12)	C(23)-C(24)-H(24)	119.1
O(5)-Ni(1)-O(2)	93.96(13)	C(30)-C(25)-C(26)	119.6(5)
O(4)-Ni(1)-O(2)	89.81(13)	C(30)-C(25)-P(2)	118.6(4)
O(6)-Ni(1)-O(2)	174.32(13)	C(26)-C(25)-P(2)	121.5(4)
O(2)-P(1)-C(7)	111.4(2)	C(25)-C(26)-C(27)	118.8(6)
O(2)-P(1)-C(13)	113.9(2)	C(25)-C(26)-H(26)	120.6
C(7)-P(1)-C(13)	105.6(2)	C(16)-C(17)-H(17)	119.8
O(2)-P(1)-C(1)	111.2(2)	C(17)-C(18)-C(13)	120.4(5)
C(7)-P(1)-C(1)	106.7(2)	C(17)-C(18)-H(18)	119.8
C(13)-P(1)-C(1)	107.7(2)	C(13)-C(18)-H(18)	119.8
O(4)-P(2)-C(31)	115.4(2)	C(20)-C(19)-P(2)	112.5(3)
O(4)-P(2)-C(25)	109.7(2)	C(20)-C(19)-H(19A)	109.1
C(31)-P(2)-C(25)	104.0(2)	P(2)-C(19)-H(19A)	109.1
O(4)-P(2)-C(19)	112.3(2)	C(20)-C(19)-H(19B)	109.1
C(31)-P(2)-C(19)	105.7(2)	P(2)-C(19)-H(19B)	109.1
C(25)-P(2)-C(19)	109.4(2)	H(19A)-C(19)-H(19B)	107.8
O(6)-P(3)-C(43)	111.5(2)	N(2)-C(20)-C(21)	119.0(4)
O(6)-P(3)-C(49)	110.3(2)	N(2)-C(20)-C(19)	116.3(4)
C(43)-P(3)-C(49)	107.2(2)	C(21)-C(20)-C(19)	124.5(4)
O(6)-P(3)-C(37)	114.4(2)	C(22)-C(21)-C(20)	120.7(5)
C(43)-P(3)-C(37)	107.6(2)	C(22)-C(21)-H(21)	119.7
C(49)-P(3)-C(37)	105.4(2)	C(34)-C(33)-H(33)	119.2
N(1)-O(1)-Ni(1)	118.7(3)	C(32)-C(33)-H(33)	119.2
P(1)-O(2)-Ni(1)	129.63(19)	C(33)-C(34)-C(35)	119.6(5)
N(2)-O(3)-Ni(1)	117.8(2)	C(33)-C(34)-H(34)	120.2
P(2)-O(4)-Ni(1)	129.68(18)	C(35)-C(34)-H(34)	120.2
N(3)-O(5)-Ni(1)	118.5(2)	C(36)-C(35)-C(34)	120.1(5)
P(3)-O(6)-Ni(1)	134.3(2)	C(36)-C(35)-H(35)	120.0
O(1)-N(1)-C(6)	119.4(4)	C(34)-C(35)-H(35)	120.0
O(1)-N(1)-C(2)	120.0(4)	C(35)-C(36)-C(31)	120.1(4)
C(6)-N(1)-C(2)	120.6(4)	C(35)-C(36)-H(36)	119.9
C(24)-N(2)-O(3)	119.3(4)	C(31)-C(36)-H(36)	119.9
C(24)-N(2)-C(20)	121.2(4)	C(38)-C(37)-P(3)	115.0(3)
O(3)-N(2)-C(20)	119.4(4)	C(38)-C(37)-H(37A)	108.5
O(5)-N(3)-C(42)	118.2(4)	P(3)-C(37)-H(37A)	108.5
O(5)-N(3)-C(38)	119.1(4)	C(38)-C(37)-H(37B)	108.5
C(42)-N(3)-C(38)	122.7(4)	P(3)-C(37)-H(37B)	108.5

Table B.15. (continued)

C(2)-C(1)-P(1)	109.5(3)	H(37A)-C(37)-H(37B)	107.5
C(2)-C(1)-H(1A)	109.8	N(3)-C(38)-C(39)	117.4(5)
P(1)-C(1)-H(1A)	109.8	N(3)-C(38)-C(37)	118.4(4)
C(2)-C(1)-H(1B)	109.8	C(39)-C(38)-C(37)	124.1(5)
P(1)-C(1)-H(1B)	109.8	C(40)-C(39)-C(38)	121.0(5)
H(1A)-C(1)-H(1B)	108.2	C(40)-C(39)-H(39)	119.5
N(1)-C(2)-C(3)	118.8(4)	C(38)-C(39)-H(39)	119.5
N(1)-C(2)-C(1)	115.8(4)	C(39)-C(40)-C(41)	119.3(5)
C(3)-C(2)-C(1)	125.4(5)	C(39)-C(40)-H(40)	120.3
C(4)-C(3)-C(2)	121.0(5)	C(41)-C(40)-H(40)	120.3
C(4)-C(3)-H(3)	119.5	C(42)-C(41)-C(40)	119.1(5)
C(2)-C(3)-H(3)	119.5	C(42)-C(41)-H(41)	120.5
C(3)-C(4)-C(5)	119.2(5)	C(40)-C(41)-H(41)	120.5
C(3)-C(4)-H(4)	120.4	N(3)-C(42)-C(41)	120.4(5)
C(5)-C(4)-H(4)	120.4	N(3)-C(42)-H(42)	119.8
C(6)-C(5)-C(4)	119.7(5)	C(41)-C(42)-H(42)	119.8
C(6)-C(5)-H(5)	120.1	C(44)-C(43)-C(48)	119.0(5)
C(4)-C(5)-H(5)	120.1	C(44)-C(43)-P(3)	117.8(3)
N(1)-C(6)-C(5)	120.7(5)	C(48)-C(43)-P(3)	123.1(4)
N(1)-C(6)-H(6)	119.7	C(43)-C(44)-C(45)	120.4(5)
C(5)-C(6)-H(6)	119.7	C(43)-C(44)-H(44)	119.8
C(8)-C(7)-C(12)	119.8(4)	C(45)-C(44)-H(44)	119.8
C(8)-C(7)-P(1)	120.2(4)	C(46)-C(45)-C(44)	120.0(5)
C(12)-C(7)-P(1)	120.0(4)	C(46)-C(45)-H(45)	120.0
C(9)-C(8)-C(7)	119.7(5)	C(44)-C(45)-H(45)	120.0
C(9)-C(8)-H(8)	120.1	C(45)-C(46)-C(47)	120.2(5)
C(7)-C(8)-H(8)	120.1	C(45)-C(46)-H(46)	119.9
C(8)-C(9)-C(10)	120.3(5)	C(47)-C(46)-H(46)	119.9
C(8)-C(9)-H(9)	119.9	C(48)-C(47)-C(46)	120.5(5)
C(10)-C(9)-H(9)	119.9	C(48)-C(47)-H(47)	119.7
C(11)-C(10)-C(9)	119.3(5)	C(46)-C(47)-H(47)	119.7
C(11)-C(10)-H(10)	120.4	C(47)-C(48)-C(43)	119.9(5)
C(9)-C(10)-H(10)	120.4	C(47)-C(48)-H(48)	120.1
C(12)-C(11)-C(10)	121.1(5)	C(43)-C(48)-H(48)	120.1
C(12)-C(11)-H(11)	119.5	C(50)-C(49)-C(54)	120.3(4)
C(10)-C(11)-H(11)	119.5	C(50)-C(49)-P(3)	122.5(4)
C(11)-C(12)-C(7)	119.8(5)	C(54)-C(49)-P(3)	117.1(3)
C(11)-C(12)-H(12)	120.1	C(51)-C(50)-C(49)	119.5(5)
C(7)-C(12)-H(12)	120.1	C(51)-C(50)-H(50)	120.2
C(14)-C(13)-C(18)	119.2(5)	C(49)-C(50)-H(50)	120.2
C(14)-C(13)-P(1)	124.5(4)	C(52)-C(51)-C(50)	120.4(5)
C(18)-C(13)-P(1)	116.2(4)	C(52)-C(51)-H(51)	119.8
C(15)-C(14)-C(13)	120.0(5)	C(50)-C(51)-H(51)	119.8
C(15)-C(14)-H(14)	120.0	C(51)-C(52)-C(53)	120.5(5)

Table B.15. (continued)

C(13)-C(14)-H(14)	120.0	C(51)-C(52)-H(52)	119.8
C(14)-C(15)-C(16)	120.8(5)	C(53)-C(52)-H(52)	119.8
C(14)-C(15)-H(15)	119.6	C(52)-C(53)-C(54)	119.9(5)
C(16)-C(15)-H(15)	119.6	C(52)-C(53)-H(53)	120.0
C(17)-C(16)-C(15)	119.2(5)	C(54)-C(53)-H(53)	120.0
C(17)-C(16)-H(16)	120.4	C(53)-C(54)-C(49)	119.4(5)
C(15)-C(16)-H(16)	120.4	C(53)-C(54)-H(54)	120.3
C(18)-C(17)-C(16)	120.4(5)	C(49)-C(54)-H(54)	120.3
C(18)-C(17)-H(17)	119.8	F(4)-B(1)-F(3)	109.6(5)
C(20)-C(21)-H(21)	119.7	F(4)-B(1)-F(1)	109.4(6)
C(21)-C(22)-C(23)	118.8(5)	F(3)-B(1)-F(1)	111.0(6)
C(21)-C(22)-H(22)	120.6	F(4)-B(1)-F(2)	110.3(5)
C(23)-C(22)-H(22)	120.6	F(3)-B(1)-F(2)	109.1(5)
C(24)-C(23)-C(22)	118.6(5)	F(1)-B(1)-F(2)	107.3(5)
C(24)-C(23)-H(23)	120.7	F(8)-B(2)-F(5)	111.8(6)
C(22)-C(23)-H(23)	120.7	F(8)-B(2)-F(6)	116.3(6)
N(2)-C(24)-C(23)	121.7(5)	F(5)-B(2)-F(6)	110.4(5)
C(27)-C(26)-H(26)	120.6	F(8)-B(2)-F(7)	105.5(6)
C(28)-C(27)-C(26)	120.8(6)	F(5)-B(2)-F(7)	105.1(6)
C(28)-C(27)-H(27)	119.6	F(6)-B(2)-F(7)	106.9(5)
C(28)-C(29)-C(30)	120.1(7)	O(7)-C(55)-H(55A)	109.5
C(28)-C(29)-H(29)	119.9	O(7)-C(55)-H(55B)	109.5
C(25)-C(30)-H(30)	119.8	H(55A)-C(55)-H(55B)	109.5
C(36)-C(31)-C(32)	119.6(4)	O(7)-C(55)-H(55C)	109.5
C(36)-C(31)-P(2)	118.0(4)	H(55A)-C(55)-H(55C)	109.5
C(32)-C(31)-P(2)	122.4(4)	H(55B)-C(55)-H(55C)	109.5
C(33)-C(32)-C(31)	119.0(4)	C(55)-O(7)-H(7)	109.5

Table B.16. Experimental and statistical crystal data for **4.3**.

Empirical formula	$\text{C}_{55}\text{H}_{48}\text{B}_2\text{CuF}_8\text{N}_3\text{O}_6\text{P}_3$		
Formula weight	1202.38		
Temperature	110(2) K		
Wavelength	0.71073 Å		
Crystal system	Monoclinic		
Space group	P2(1)/c		
Unit cell dimensions	a = 14.1007(10) Å	$\alpha = 90^\circ$.	
	b = 22.6498(17) Å	$\beta = 98.585(4)^\circ$.	
	c = 17.5725(12) Å	$\delta = 90^\circ$.	
Volume	5549.4(7) Å ³		
Z	4		
Density (calculated)	1.439 Mg/m ³		

Table B.16. (continued)

Absorption coefficient	0.562 mm ⁻¹
F(000)	2472
Crystal size	0.15 x 0.13 x 0.08 mm ³
Theta range for data collection	2.72 to 28.35°
Index ranges	-18 ≤ h ≤ 18, -26 ≤ k ≤ 30, -23 ≤ l ≤ 23
Reflections collected	50561
Independent reflections	13836 [R(int) = 0.0753]
Completeness to theta = 25.00°	99.8 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.9543 and 0.9204
Refinement method	Full-matrix least-squares on F ²
Data / restraints / parameters	13836 / 4 / 738
Goodness-of-fit on F ²	1.008
Final R indices [I > 2sigma(I)]	R1 = 0.0539, wR2 = 0.1163
R indices (all data)	R1 = 0.1020, wR2 = 0.1419
Largest diff. peak and hole	0.778 and -0.587 e.Å ⁻³

Bond Lengths (Å)

Cu(1)-O(6)	1.9675(18)	C(21)-H(21)	0.9500
Cu(1)-O(4)	1.973(2)	C(22)-C(23)	1.380(5)
Cu(1)-O(2)	1.9778(19)	C(22)-H(22)	0.9500
Cu(1)-O(5)	1.9864(19)	C(23)-C(24)	1.377(4)
Cu(1)-O(1)	2.2961(18)	C(23)-H(23)	0.9500
Cu(1)-O(3)	2.4339(18)	C(24)-H(24)	0.9500
P(1)-O(1)	1.488(2)	C(25)-C(26)	1.370(5)
P(1)-C(7)	1.794(3)	C(25)-C(30)	1.394(4)
P(1)-C(13)	1.800(3)	C(26)-C(27)	1.388(5)
P(1)-C(1)	1.815(3)	C(26)-H(26)	0.9500
P(2)-O(3)	1.4864(19)	C(27)-C(28)	1.375(7)
P(2)-C(31)	1.800(3)	C(27)-H(27)	0.9500
P(2)-C(25)	1.803(3)	C(28)-C(29)	1.364(7)
P(2)-C(19)	1.811(3)	C(28)-H(28)	0.9500
P(3)-O(5)	1.506(2)	C(29)-C(30)	1.395(5)
P(3)-C(43)	1.786(3)	C(29)-H(29)	0.9500
P(3)-C(49)	1.796(3)	C(30)-H(30)	0.9500
P(3)-C(37)	1.813(3)	C(31)-C(32)	1.389(4)
O(2)-N(1)	1.340(3)	C(31)-C(36)	1.391(4)
O(4)-N(2)	1.335(3)	C(32)-C(33)	1.386(4)
O(6)-N(3)	1.334(3)	C(32)-H(32)	0.9500
N(1)-C(6)	1.348(3)	C(33)-C(34)	1.384(5)

Table B.16. (continued)

N(1)-C(2)	1.364(3)	C(33)-H(33)	0.9500
N(2)-C(24)	1.349(3)	C(34)-C(35)	1.380(5)
N(2)-C(20)	1.363(3)	C(34)-H(34)	0.9500
N(3)-C(38)	1.354(4)	C(35)-C(36)	1.380(5)
N(3)-C(42)	1.360(3)	C(35)-H(35)	0.9500
B(1)-F(4)	1.361(5)	C(36)-H(36)	0.9500
B(1)-F(1)	1.370(5)	C(37)-C(38)	1.499(4)
B(1)-F(3)	1.380(5)	C(37)-H(37A)	0.9900
B(1)-F(2)	1.381(5)	C(37)-H(37B)	0.9900
B(2)-F(7)	1.360(4)	C(38)-C(39)	1.379(4)
B(2)-F(6)	1.376(4)	C(39)-C(40)	1.387(4)
B(2)-F(5)	1.379(4)	C(39)-H(39)	0.9500
B(2)-F(8)	1.390(4)	C(40)-C(41)	1.382(4)
C(1)-C(2)	1.489(4)	C(40)-H(40)	0.9500
C(1)-H(1A)	0.9900	C(41)-C(42)	1.366(4)
C(1)-H(1B)	0.9900	C(41)-H(41)	0.9500
C(2)-C(3)	1.379(4)	C(42)-H(42)	0.9500
C(3)-C(4)	1.376(4)	C(43)-C(48)	1.397(4)
C(3)-H(3)	0.9500	C(43)-C(44)	1.397(4)
C(4)-C(5)	1.388(4)	C(44)-C(45)	1.388(4)
C(4)-H(4)	0.9500	C(44)-H(44)	0.9500
C(5)-C(6)	1.366(4)	C(45)-C(46)	1.382(5)
C(5)-H(5)	0.9500	C(45)-H(45)	0.9500
C(6)-H(6)	0.9500	C(46)-C(47)	1.376(5)
C(7)-C(12)	1.394(4)	C(46)-H(46)	0.9500
C(7)-C(8)	1.398(4)	C(47)-C(48)	1.389(4)
C(8)-C(9)	1.383(4)	C(47)-H(47)	0.9500
C(8)-H(8)	0.9500	C(48)-H(48)	0.9500
C(9)-C(10)	1.378(5)	C(49)-C(50)	1.385(4)
C(9)-H(9)	0.9500	C(49)-C(54)	1.390(4)
C(10)-C(11)	1.370(5)	C(50)-C(51)	1.382(4)
C(10)-H(10)	0.9500	C(50)-H(50)	0.9500
C(11)-C(12)	1.384(5)	C(51)-C(52)	1.382(5)
C(11)-H(11)	0.9500	C(51)-H(51)	0.9500
C(12)-H(12)	0.9500	C(52)-C(53)	1.380(5)
C(13)-C(14)	1.383(4)	C(52)-H(52)	0.9500
C(13)-C(18)	1.391(4)	C(53)-C(54)	1.389(4)
C(14)-C(15)	1.389(5)	C(53)-H(53)	0.9500
C(14)-H(14)	0.9500	C(54)-H(54)	0.9500
C(15)-C(16)	1.385(5)	O(7)-C(55)	1.431(13)
C(15)-H(15)	0.9500	O(7)-H(7)	0.8400
C(16)-C(17)	1.370(5)	C(55)-H(55A)	0.9800
C(16)-H(16)	0.9500	C(55)-H(55B)	0.9800
C(17)-C(18)	1.387(5)	C(55)-H(55C)	0.9800

Table B.16. (continued)

C(17)-H(17)	0.9500	O(7A)-C(55A)	1.433(14)
C(18)-H(18)	0.9500	O(7A)-H(7A)	0.8400
C(19)-C(20)	1.486(4)	C(55A)-H(55D)	0.9800
C(19)-H(19A)	0.9900	C(55A)-H(55E)	0.9800
C(19)-H(19B)	0.9900	C(55A)-H(55F)	0.9800
C(20)-C(21)	1.384(4)	O(8)-H(8A)	0.851(10)
C(21)-C(22)	1.375(5)	O(8)-H(8B)	0.857(10)

Bond Angles (°)

O(6)-Cu(1)-O(4)	90.19(8)	C(20)-C(19)-H(19B)	109.4
O(6)-Cu(1)-O(2)	173.04(8)	P(2)-C(19)-H(19B)	109.4
O(4)-Cu(1)-O(2)	82.86(8)	H(19A)-C(19)-H(19B)	108.0
O(6)-Cu(1)-O(5)	95.50(8)	N(2)-C(20)-C(21)	118.1(3)
O(4)-Cu(1)-O(5)	173.63(8)	N(2)-C(20)-C(19)	117.3(2)
O(2)-Cu(1)-O(5)	91.45(8)	C(21)-C(20)-C(19)	124.7(3)
O(6)-Cu(1)-O(1)	86.60(7)	C(22)-C(21)-C(20)	121.1(3)
O(4)-Cu(1)-O(1)	92.01(8)	C(22)-C(21)-H(21)	119.4
O(2)-Cu(1)-O(1)	93.29(7)	C(20)-C(21)-H(21)	119.4
O(5)-Cu(1)-O(1)	91.19(8)	C(21)-C(22)-C(23)	119.0(3)
O(6)-Cu(1)-O(3)	85.27(7)	C(21)-C(22)-H(22)	120.5
O(4)-Cu(1)-O(3)	91.85(7)	C(23)-C(22)-H(22)	120.5
O(2)-Cu(1)-O(3)	95.25(7)	C(24)-C(23)-C(22)	119.9(3)
O(5)-Cu(1)-O(3)	85.79(7)	C(24)-C(23)-H(23)	120.0
O(1)-Cu(1)-O(3)	171.01(7)	C(22)-C(23)-H(23)	120.0
O(1)-P(1)-C(7)	113.09(13)	N(2)-C(24)-C(23)	119.8(3)
O(1)-P(1)-C(13)	111.40(14)	N(2)-C(24)-H(24)	120.1
C(7)-P(1)-C(13)	109.04(13)	C(23)-C(24)-H(24)	120.1
O(1)-P(1)-C(1)	113.09(12)	C(26)-C(25)-C(30)	119.2(3)
C(7)-P(1)-C(1)	103.46(14)	C(26)-C(25)-P(2)	118.7(2)
C(13)-P(1)-C(1)	106.25(14)	C(30)-C(25)-P(2)	122.1(3)
O(3)-P(2)-C(31)	113.31(12)	C(25)-C(26)-C(27)	120.9(4)
O(3)-P(2)-C(25)	111.64(14)	C(25)-C(26)-H(26)	119.5
C(31)-P(2)-C(25)	107.35(13)	C(27)-C(26)-H(26)	119.5
O(3)-P(2)-C(19)	112.43(12)	C(28)-C(27)-C(26)	119.8(5)
C(31)-P(2)-C(19)	104.87(14)	C(28)-C(27)-H(27)	120.1
C(25)-P(2)-C(19)	106.75(15)	C(26)-C(27)-H(27)	120.1
O(5)-P(3)-C(43)	115.31(13)	C(29)-C(28)-C(27)	119.9(4)
O(5)-P(3)-C(49)	109.29(12)	C(29)-C(28)-H(28)	120.0
C(43)-P(3)-C(49)	106.21(13)	C(27)-C(28)-H(28)	120.0
O(5)-P(3)-C(37)	110.81(12)	C(28)-C(29)-C(30)	120.7(4)
C(43)-P(3)-C(37)	108.44(13)	C(28)-C(29)-H(29)	119.6
C(49)-P(3)-C(37)	106.31(13)	C(30)-C(29)-H(29)	119.6

Table B.16. (continued)

P(1)-O(1)-Cu(1)	131.12(11)	C(25)-C(30)-C(29)	119.3(4)
N(1)-O(2)-Cu(1)	116.25(15)	C(25)-C(30)-H(30)	120.3
P(2)-O(3)-Cu(1)	125.91(11)	C(29)-C(30)-H(30)	120.3
N(2)-O(4)-Cu(1)	118.43(15)	C(32)-C(31)-C(36)	119.3(3)
P(3)-O(5)-Cu(1)	130.23(11)	C(32)-C(31)-P(2)	117.3(2)
N(3)-O(6)-Cu(1)	118.91(14)	C(36)-C(31)-P(2)	123.4(2)
O(2)-N(1)-C(6)	118.7(2)	C(33)-C(32)-C(31)	120.1(3)
O(2)-N(1)-C(2)	119.5(2)	C(33)-C(32)-H(32)	119.9
C(6)-N(1)-C(2)	121.7(2)	C(31)-C(32)-H(32)	119.9
O(4)-N(2)-C(24)	118.8(2)	C(34)-C(33)-C(32)	120.2(3)
O(4)-N(2)-C(20)	119.0(2)	C(34)-C(33)-H(33)	119.9
C(24)-N(2)-C(20)	122.1(2)	C(32)-C(33)-H(33)	119.9
O(6)-N(3)-C(38)	120.0(2)	C(35)-C(34)-C(33)	119.8(3)
O(6)-N(3)-C(42)	119.1(2)	C(35)-C(34)-H(34)	120.1
C(38)-N(3)-C(42)	120.8(2)	C(33)-C(34)-H(34)	120.1
F(4)-B(1)-F(1)	108.4(3)	C(36)-C(35)-C(34)	120.3(3)
F(4)-B(1)-F(3)	111.9(4)	C(36)-C(35)-H(35)	119.8
F(1)-B(1)-F(3)	108.1(3)	C(34)-C(35)-H(35)	119.8
F(4)-B(1)-F(2)	108.2(3)	C(35)-C(36)-C(31)	120.3(3)
F(1)-B(1)-F(2)	110.1(4)	C(35)-C(36)-H(36)	119.9
F(3)-B(1)-F(2)	110.2(3)	C(31)-C(36)-H(36)	119.9
F(7)-B(2)-F(6)	110.7(3)	C(38)-C(37)-P(3)	106.72(18)
F(7)-B(2)-F(5)	110.9(3)	C(38)-C(37)-H(37A)	110.4
F(6)-B(2)-F(5)	108.6(3)	P(3)-C(37)-H(37A)	110.4
F(7)-B(2)-F(8)	108.8(3)	C(38)-C(37)-H(37B)	110.4
F(6)-B(2)-F(8)	109.0(3)	P(3)-C(37)-H(37B)	110.4
F(5)-B(2)-F(8)	108.7(3)	H(37A)-C(37)-H(37B)	108.6
C(2)-C(1)-P(1)	114.5(2)	N(3)-C(38)-C(39)	119.4(2)
C(2)-C(1)-H(1A)	108.6	N(3)-C(38)-C(37)	116.6(2)
P(1)-C(1)-H(1A)	108.6	C(39)-C(38)-C(37)	123.9(3)
C(2)-C(1)-H(1B)	108.6	C(38)-C(39)-C(40)	120.7(3)
P(1)-C(1)-H(1B)	108.6	C(38)-C(39)-H(39)	119.7
H(1A)-C(1)-H(1B)	107.6	C(40)-C(39)-H(39)	119.7
N(1)-C(2)-C(3)	117.7(3)	C(41)-C(40)-C(39)	118.6(3)
N(1)-C(2)-C(1)	117.5(2)	C(41)-C(40)-H(40)	120.7
C(3)-C(2)-C(1)	124.7(3)	C(39)-C(40)-H(40)	120.7
C(4)-C(3)-C(2)	121.7(3)	C(42)-C(41)-C(40)	119.9(3)
C(4)-C(3)-H(3)	119.2	C(42)-C(41)-H(41)	120.1
C(2)-C(3)-H(3)	119.2	C(40)-C(41)-H(41)	120.1
C(3)-C(4)-C(5)	118.8(3)	N(3)-C(42)-C(41)	120.7(3)
C(3)-C(4)-H(4)	120.6	N(3)-C(42)-H(42)	119.6
C(5)-C(4)-H(4)	120.6	C(41)-C(42)-H(42)	119.6
C(6)-C(5)-C(4)	119.0(3)	C(48)-C(43)-C(44)	119.6(3)
C(6)-C(5)-H(5)	120.5	C(48)-C(43)-P(3)	122.5(2)

Table B.16. (continued)

C(4)-C(5)-H(5)	120.5	C(44)-C(43)-P(3)	117.9(2)
N(1)-C(6)-C(5)	121.1(3)	C(45)-C(44)-C(43)	119.8(3)
N(1)-C(6)-H(6)	119.5	C(45)-C(44)-H(44)	120.1
C(5)-C(6)-H(6)	119.5	C(43)-C(44)-H(44)	120.1
C(12)-C(7)-C(8)	118.8(3)	C(46)-C(45)-C(44)	120.1(3)
C(12)-C(7)-P(1)	119.5(2)	C(46)-C(45)-H(45)	120.0
C(8)-C(7)-P(1)	121.8(2)	C(44)-C(45)-H(45)	120.0
C(9)-C(8)-C(7)	120.5(3)	C(47)-C(46)-C(45)	120.6(3)
C(9)-C(8)-H(8)	119.8	C(47)-C(46)-H(46)	119.7
C(7)-C(8)-H(8)	119.8	C(45)-C(46)-H(46)	119.7
C(10)-C(9)-C(8)	119.9(3)	C(46)-C(47)-C(48)	120.2(3)
C(10)-C(9)-H(9)	120.1	C(46)-C(47)-H(47)	119.9
C(8)-C(9)-H(9)	120.1	C(48)-C(47)-H(47)	119.9
C(11)-C(10)-C(9)	120.3(3)	C(47)-C(48)-C(43)	119.8(3)
C(11)-C(10)-H(10)	119.8	C(47)-C(48)-H(48)	120.1
C(9)-C(10)-H(10)	119.8	C(43)-C(48)-H(48)	120.1
C(10)-C(11)-C(12)	120.6(3)	C(50)-C(49)-C(54)	120.0(3)
C(10)-C(11)-H(11)	119.7	C(50)-C(49)-P(3)	119.1(2)
C(12)-C(11)-H(11)	119.7	C(54)-C(49)-P(3)	120.8(2)
C(11)-C(12)-C(7)	120.0(3)	C(51)-C(50)-C(49)	119.8(3)
C(11)-C(12)-H(12)	120.0	C(51)-C(50)-H(50)	120.1
C(7)-C(12)-H(12)	120.0	C(49)-C(50)-H(50)	120.1
C(14)-C(13)-C(18)	119.7(3)	C(50)-C(51)-C(52)	120.2(3)
C(14)-C(13)-P(1)	117.8(2)	C(50)-C(51)-H(51)	119.9
C(18)-C(13)-P(1)	122.5(3)	C(52)-C(51)-H(51)	119.9
C(13)-C(14)-C(15)	120.2(3)	C(53)-C(52)-C(51)	120.3(3)
C(13)-C(14)-H(14)	119.9	C(53)-C(52)-H(52)	119.8
C(15)-C(14)-H(14)	119.9	C(51)-C(52)-H(52)	119.8
C(16)-C(15)-C(14)	119.3(4)	C(52)-C(53)-C(54)	119.8(3)
C(16)-C(15)-H(15)	120.4	C(52)-C(53)-H(53)	120.1
C(14)-C(15)-H(15)	120.4	C(54)-C(53)-H(53)	120.1
C(17)-C(16)-C(15)	121.0(3)	C(53)-C(54)-C(49)	119.8(3)
C(17)-C(16)-H(16)	119.5	C(53)-C(54)-H(54)	120.1
C(15)-C(16)-H(16)	119.5	C(49)-C(54)-H(54)	120.1
C(16)-C(17)-C(18)	119.7(3)	C(55A)-O(7A)-H(7A)	109.5
C(16)-C(17)-H(17)	120.2	O(7A)-C(55A)-H(55D)	109.5
C(18)-C(17)-H(17)	120.2	O(7A)-C(55A)-H(55E)	109.5
C(17)-C(18)-C(13)	120.0(3)	H(55D)-C(55A)-H(55E)	109.5
C(17)-C(18)-H(18)	120.0	O(7A)-C(55A)-H(55F)	109.5
C(13)-C(18)-H(18)	120.0	H(55D)-C(55A)-H(55F)	109.5
C(20)-C(19)-P(2)	111.1(2)	H(55E)-C(55A)-H(55F)	109.5
C(20)-C(19)-H(19A)	109.4	H(8A)-O(8)-H(8B)	103.4(16)
P(2)-C(19)-H(19A)	109.4		

Table B.17. Experimental and statistical crystal data for **4.4**.

Empirical formula	C ₅₅ H ₅₂ B ₂ F ₈ N ₃ O ₇ P ₃ Zn		
Formula weight	1198.90		
Temperature	110(2) K		
Wavelength	0.71073 Å		
Crystal system	Monoclinic		
Space group	P2(1)		
Unit cell dimensions	a = 10.5390(5) Å	α = 90°.	
	b = 15.0341(7) Å	β = 92.116(2)°.	
	c = 17.2991(8) Å	δ = 90°.	
Volume	2739.1(2) Å ³		
Z	2		
Density (calculated)	1.454 Mg/m ³		
Absorption coefficient	0.618 mm ⁻¹		
F(000)	1232		
Crystal size	0.24 x 0.16 x 0.14 mm ³		
Theta range for data collection	1.80 to 27.72°.		
Index ranges	-13<=h<=13, -19<=k<=19, -22<=l<=22		
Reflections collected	41116		
Independent reflections	12760 [R(int) = 0.0667]		
Completeness to theta = 27.72°	99.8 %		
Absorption correction	Semi-empirical from equivalents		
Max. and min. transmission	0.9184 and 0.8663		
Refinement method	Full-matrix least-squares on F ²		
Data / restraints / parameters	12760 / 1 / 714		
Goodness-of-fit on F ²	1.023		
Final R indices [I>2sigma(I)]	R1 = 0.0438, wR2 = 0.1041		
R indices (all data)	R1 = 0.0535, wR2 = 0.1108		
Absolute structure parameter	-0.020(7)		
Largest diff. peak and hole	0.958 and -0.541 e.Å ⁻³		
Bond Lengths (Å)			
Zn(1)-O(6)	2.0680(18)	C(10)-C(11)	1.379(5)
Zn(1)-O(4)	2.0726(18)	C(11)-C(12)	1.390(4)
Zn(1)-O(2)	2.090(2)	C(13)-C(14)	1.390(4)
Zn(1)-O(5)	2.091(2)	C(13)-C(18)	1.396(4)
Zn(1)-O(3)	2.102(2)	C(14)-C(15)	1.394(5)
Zn(1)-O(1)	2.118(2)	C(15)-C(16)	1.385(5)
P(1)-O(1)	1.495(2)	C(16)-C(17)	1.391(5)
P(1)-C(7)	1.790(3)	C(17)-C(18)	1.386(4)
P(1)-C(13)	1.796(3)	C(19)-C(20)	1.499(4)

Table B.17. (continued)

P(1)-C(1)	1.814(3)	C(20)-C(21)	1.370(5)
P(2)-O(3)	1.489(2)	C(21)-C(22)	1.392(5)
P(2)-C(31)	1.791(3)	C(22)-C(23)	1.391(5)
P(2)-C(25)	1.808(3)	C(23)-C(24)	1.370(5)
P(2)-C(19)	1.816(3)	C(25)-C(30)	1.391(4)
P(3)-O(5)	1.503(2)	C(25)-C(26)	1.393(4)
P(3)-C(49)	1.799(3)	C(26)-C(27)	1.379(5)
P(3)-C(43)	1.808(3)	C(27)-C(28)	1.391(5)
P(3)-C(37)	1.822(3)	C(28)-C(29)	1.378(5)
F(1)-B(1)	1.368(5)	C(29)-C(30)	1.389(5)
F(2)-B(1)	1.369(5)	C(31)-C(32)	1.387(4)
F(3)-B(1)	1.385(5)	C(31)-C(36)	1.400(4)
F(4)-B(1)	1.367(5)	C(32)-C(33)	1.390(5)
F(5)-B(2)	1.359(5)	C(33)-C(34)	1.380(5)
F(6)-B(2)	1.326(6)	C(34)-C(35)	1.375(5)
F(7)-B(2)	1.362(5)	C(35)-C(36)	1.379(5)
F(8)-B(2)	1.466(6)	C(37)-C(38)	1.501(5)
O(2)-N(1)	1.329(3)	C(38)-C(39)	1.379(5)
O(4)-N(2)	1.343(3)	C(39)-C(40)	1.382(5)
O(6)-N(3)	1.333(3)	C(40)-C(41)	1.383(5)
N(1)-C(6)	1.356(4)	C(41)-C(42)	1.378(5)
N(1)-C(2)	1.364(4)	C(43)-C(44)	1.383(5)
N(2)-C(24)	1.347(4)	C(43)-C(48)	1.388(5)
N(2)-C(20)	1.356(4)	C(44)-C(45)	1.407(6)
N(3)-C(42)	1.344(4)	C(45)-C(46)	1.361(7)
N(3)-C(38)	1.366(4)	C(46)-C(47)	1.364(7)
C(1)-C(2)	1.502(4)	C(47)-C(48)	1.412(6)
C(2)-C(3)	1.379(4)	C(49)-C(50)	1.396(4)
C(3)-C(4)	1.395(5)	C(49)-C(54)	1.396(4)
C(4)-C(5)	1.392(5)	C(50)-C(51)	1.370(5)
C(5)-C(6)	1.357(5)	C(51)-C(52)	1.384(5)
C(7)-C(8)	1.398(4)	C(52)-C(53)	1.398(5)
C(7)-C(12)	1.404(4)	C(53)-C(54)	1.389(5)
C(8)-C(9)	1.376(5)	O(7)-C(55)	1.387(6)
C(9)-C(10)	1.376(5)		

Bond Angles (°)

O(6)-Zn(1)-O(4)	176.45(9)	C(18)-C(13)-P(1)	115.8(2)
O(6)-Zn(1)-O(2)	94.43(8)	C(13)-C(14)-C(15)	119.6(3)
O(4)-Zn(1)-O(2)	82.08(8)	C(16)-C(15)-C(14)	120.2(3)
O(6)-Zn(1)-O(5)	93.06(8)	C(15)-C(16)-C(17)	120.4(3)
O(4)-Zn(1)-O(5)	90.44(8)	C(18)-C(17)-C(16)	119.5(3)

Table B.17. (continued)

O(2)-Zn(1)-O(5)	172.43(8)	C(17)-C(18)-C(13)	120.3(3)
O(6)-Zn(1)-O(3)	88.79(9)	C(20)-C(19)-P(2)	114.6(2)
O(4)-Zn(1)-O(3)	90.65(9)	N(2)-C(20)-C(21)	118.2(3)
O(2)-Zn(1)-O(3)	91.45(8)	N(2)-C(20)-C(19)	117.6(3)
O(5)-Zn(1)-O(3)	89.77(8)	C(21)-C(20)-C(19)	124.1(3)
O(6)-Zn(1)-O(1)	85.12(9)	C(20)-C(21)-C(22)	121.2(3)
O(4)-Zn(1)-O(1)	95.48(9)	C(23)-C(22)-C(21)	118.7(3)
O(2)-Zn(1)-O(1)	89.94(8)	C(24)-C(23)-C(22)	118.9(3)
O(5)-Zn(1)-O(1)	89.63(8)	N(2)-C(24)-C(23)	120.8(3)
O(3)-Zn(1)-O(1)	173.84(8)	C(30)-C(25)-C(26)	119.8(3)
O(1)-P(1)-C(7)	111.09(13)	C(30)-C(25)-P(2)	122.7(2)
O(1)-P(1)-C(13)	113.62(13)	C(26)-C(25)-P(2)	117.4(2)
C(7)-P(1)-C(13)	105.52(14)	C(27)-C(26)-C(25)	120.1(3)
O(1)-P(1)-C(1)	111.19(14)	C(26)-C(27)-C(28)	119.9(3)
C(7)-P(1)-C(1)	107.39(15)	C(29)-C(28)-C(27)	120.3(3)
C(13)-P(1)-C(1)	107.69(14)	C(28)-C(29)-C(30)	120.0(3)
O(3)-P(2)-C(31)	111.55(13)	C(29)-C(30)-C(25)	119.8(3)
O(3)-P(2)-C(25)	110.51(13)	C(32)-C(31)-C(36)	118.6(3)
C(31)-P(2)-C(25)	107.28(15)	C(32)-C(31)-P(2)	118.1(2)
O(3)-P(2)-C(19)	114.45(14)	C(36)-C(31)-P(2)	123.2(3)
C(31)-P(2)-C(19)	107.67(14)	C(31)-C(32)-C(33)	121.1(3)
C(25)-P(2)-C(19)	104.94(14)	C(34)-C(33)-C(32)	119.2(3)
O(5)-P(3)-C(49)	114.95(14)	C(35)-C(34)-C(33)	120.5(3)
O(5)-P(3)-C(43)	110.04(14)	C(34)-C(35)-C(36)	120.6(3)
C(49)-P(3)-C(43)	104.25(14)	C(35)-C(36)-C(31)	120.0(3)
O(5)-P(3)-C(37)	112.49(14)	C(38)-C(37)-P(3)	113.0(2)
C(49)-P(3)-C(37)	105.93(14)	N(3)-C(38)-C(39)	118.7(3)
C(43)-P(3)-C(37)	108.68(16)	N(3)-C(38)-C(37)	116.8(3)
P(1)-O(1)-Zn(1)	129.73(12)	C(39)-C(38)-C(37)	124.3(3)
N(1)-O(2)-Zn(1)	118.44(17)	C(38)-C(39)-C(40)	120.5(3)
P(2)-O(3)-Zn(1)	134.56(12)	C(39)-C(40)-C(41)	119.7(3)
N(2)-O(4)-Zn(1)	118.63(16)	C(42)-C(41)-C(40)	118.6(3)
P(3)-O(5)-Zn(1)	130.20(13)	N(3)-C(42)-C(41)	121.1(3)
N(3)-O(6)-Zn(1)	118.30(15)	C(44)-C(43)-C(48)	120.4(3)
O(2)-N(1)-C(6)	119.0(3)	C(44)-C(43)-P(3)	121.5(3)
O(2)-N(1)-C(2)	119.9(2)	C(48)-C(43)-P(3)	117.7(3)
C(6)-N(1)-C(2)	121.0(3)	C(43)-C(44)-C(45)	118.8(4)
O(4)-N(2)-C(24)	118.4(3)	C(46)-C(45)-C(44)	121.1(4)
O(4)-N(2)-C(20)	119.5(3)	C(45)-C(46)-C(47)	120.3(4)
C(24)-N(2)-C(20)	122.1(3)	C(46)-C(47)-C(48)	120.3(5)
O(6)-N(3)-C(42)	119.0(3)	C(43)-C(48)-C(47)	119.1(4)
O(6)-N(3)-C(38)	119.6(3)	C(50)-C(49)-C(54)	119.2(3)
C(42)-N(3)-C(38)	121.3(3)	C(50)-C(49)-P(3)	122.9(2)
C(2)-C(1)-P(1)	109.2(2)	C(54)-C(49)-P(3)	117.9(2)

Table B.17. (continued)

N(1)-C(2)-C(3)	119.4(3)	C(51)-C(50)-C(49)	120.4(3)
N(1)-C(2)-C(1)	115.9(3)	C(50)-C(51)-C(52)	121.1(3)
C(3)-C(2)-C(1)	124.6(3)	C(51)-C(52)-C(53)	119.0(3)
C(2)-C(3)-C(4)	120.0(3)	C(54)-C(53)-C(52)	120.4(3)
C(5)-C(4)-C(3)	118.7(3)	C(53)-C(54)-C(49)	119.9(3)
C(6)-C(5)-C(4)	119.9(3)	F(4)-B(1)-F(1)	108.4(3)
N(1)-C(6)-C(5)	120.9(3)	F(4)-B(1)-F(2)	111.6(4)
C(8)-C(7)-C(12)	119.9(3)	F(1)-B(1)-F(2)	108.6(4)
C(8)-C(7)-P(1)	119.8(2)	F(4)-B(1)-F(3)	108.9(4)
C(12)-C(7)-P(1)	120.3(2)	F(1)-B(1)-F(3)	110.4(4)
C(9)-C(8)-C(7)	119.3(3)	F(2)-B(1)-F(3)	109.0(3)
C(8)-C(9)-C(10)	121.2(3)	F(6)-B(2)-F(5)	112.1(4)
C(9)-C(10)-C(11)	120.1(3)	F(6)-B(2)-F(7)	117.8(5)
C(10)-C(11)-C(12)	120.3(3)	F(5)-B(2)-F(7)	111.2(4)
C(11)-C(12)-C(7)	119.2(3)	F(6)-B(2)-F(8)	104.3(4)
C(14)-C(13)-C(18)	119.9(3)	F(5)-B(2)-F(8)	103.8(4)
C(14)-C(13)-P(1)	124.2(3)	F(7)-B(2)-F(8)	106.2(3)

Table B.18. Experimental and statistical crystal data for **4.5**.*

Empirical formula	$\text{C}_{44}\text{H}_{44}\text{B}_2\text{CoF}_8\text{N}_6\text{O}_4\text{P}_2$		
Formula weight	1015.34		
Temperature	110(2) K		
Wavelength	0.71073 Å		
Crystal system	Orthorhombic		
Space group	Pbcn		
Unit cell dimensions	$a = 17.7024(19)$ Å	$\alpha = 90^\circ$.	
	$b = 18.9467(17)$ Å	$\beta = 90^\circ$.	
	$c = 14.0724(15)$ Å	$\delta = 90^\circ$.	
Volume	$4719.9(8)$ Å ³		
Z	4		
Density (calculated)	1.429 Mg/m ³		
Absorption coefficient	0.512 mm ⁻¹		
F(000)	2084		
Crystal size	0.19 x 0.16 x 0.13 mm ³		
Theta range for data collection	1.57 to 26.44°.		
Index ranges	-22 ≤ h ≤ 21, -23 ≤ k ≤ 18, -17 ≤ l ≤ 17		
Reflections collected	37923		
Independent reflections	4857 [R(int) = 0.0558]		
Completeness to theta = 26.44°	99.7 %		

Table B.18. (continued)

Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.9383 and 0.9109
Refinement method	Full-matrix least-squares on F ²
Data / restraints / parameters	4857 / 0 / 305
Goodness-of-fit on F ²	1.033
Final R indices [I>2sigma(I)]	R1 = 0.0515, wR2 = 0.1218
R indices (all data)	R1 = 0.0643, wR2 = 0.1316
Largest diff. peak and hole	1.017 and -0.935 e.Å ⁻³

Bond Lengths (Å)

Co(1)-O(2)#1	2.0470(18)	C(5)-C(6)	1.373(4)
Co(1)-O(2)	2.0470(18)	C(7)-C(8)	1.396(4)
Co(1)-O(1)#1	2.0890(19)	C(7)-C(12)	1.396(4)
Co(1)-O(1)	2.0890(19)	C(8)-C(9)	1.384(4)
Co(1)-N(2)	2.131(2)	C(9)-C(10)	1.383(6)
Co(1)-N(2)#1	2.131(2)	C(10)-C(11)	1.386(6)
P(1)-O(1)	1.4945(19)	C(11)-C(12)	1.393(4)
P(1)-C(13)	1.797(3)	C(13)-C(14)	1.394(4)
P(1)-C(7)	1.799(3)	C(13)-C(18)	1.397(4)
P(1)-C(1)	1.818(3)	C(14)-C(15)	1.389(4)
O(2)-N(1)	1.336(3)	C(15)-C(16)	1.384(4)
N(1)-C(6)	1.353(4)	C(16)-C(17)	1.387(4)
N(1)-C(2)	1.358(3)	C(17)-C(18)	1.384(4)
N(2)-C(19)	1.138(4)	C(19)-C(20)	1.456(4)
N(3)-C(21)	1.140(4)	C(21)-C(22)	1.455(4)
C(1)-C(2)	1.490(4)	B(1)-F(4)	1.325(4)
C(2)-C(3)	1.392(4)	B(1)-F(1)	1.341(4)
C(3)-C(4)	1.381(4)	B(1)-F(3)	1.345(4)
C(4)-C(5)	1.385(4)	B(1)-F(2)	1.364(4)

Bond Angles (°)

O(2)#1-Co(1)-O(2)	177.99(10)	N(1)-C(2)-C(1)	117.1(2)
O(2)#1-Co(1)-O(1)#1	91.71(7)	C(3)-C(2)-C(1)	124.6(2)
O(2)-Co(1)-O(1)#1	89.71(7)	C(4)-C(3)-C(2)	120.9(3)
O(2)#1-Co(1)-O(1)	89.71(7)	C(3)-C(4)-C(5)	118.8(3)
O(2)-Co(1)-O(1)	91.71(7)	C(6)-C(5)-C(4)	120.0(3)
O(1)#1-Co(1)-O(1)	89.67(11)	N(1)-C(6)-C(5)	120.1(3)
O(2)#1-Co(1)-N(2)	91.10(8)	C(8)-C(7)-C(12)	119.9(3)
O(2)-Co(1)-N(2)	87.54(8)	C(8)-C(7)-P(1)	121.5(2)
O(1)#1-Co(1)-N(2)	176.24(8)	C(12)-C(7)-P(1)	118.6(2)

Table B.18. (continued)

O(1)-Co(1)-N(2)	87.85(9)	C(9)-C(8)-C(7)	119.6(3)
O(2)#1-Co(1)-N(2)#1	87.54(8)	C(10)-C(9)-C(8)	120.7(3)
O(2)-Co(1)-N(2)#1	91.10(8)	C(9)-C(10)-C(11)	120.0(3)
O(1)#1-Co(1)-N(2)#1	87.85(9)	C(10)-C(11)-C(12)	120.0(3)
O(1)-Co(1)-N(2)#1	176.24(8)	C(11)-C(12)-C(7)	119.8(3)
N(2)-Co(1)-N(2)#1	94.77(13)	C(14)-C(13)-C(18)	119.6(3)
O(1)-P(1)-C(13)	110.20(12)	C(14)-C(13)-P(1)	124.3(2)
O(1)-P(1)-C(7)	111.40(12)	C(18)-C(13)-P(1)	116.0(2)
C(13)-P(1)-C(7)	108.06(12)	C(15)-C(14)-C(13)	119.6(3)
O(1)-P(1)-C(1)	113.96(12)	C(16)-C(15)-C(14)	120.3(3)
C(13)-P(1)-C(1)	109.80(13)	C(15)-C(16)-C(17)	120.3(3)
C(7)-P(1)-C(1)	103.08(12)	C(18)-C(17)-C(16)	119.7(3)
P(1)-O(1)-Co(1)	136.12(11)	C(17)-C(18)-C(13)	120.4(3)
N(1)-O(2)-Co(1)	119.05(14)	N(2)-C(19)-C(20)	178.4(3)
O(2)-N(1)-C(6)	118.3(2)	N(3)-C(21)-C(22)	178.5(3)
O(2)-N(1)-C(2)	119.6(2)	F(4)-B(1)-F(1)	112.2(4)
C(6)-N(1)-C(2)	122.0(2)	F(4)-B(1)-F(3)	110.7(4)
C(19)-N(2)-Co(1)	162.2(2)	F(1)-B(1)-F(3)	105.6(3)
C(2)-C(1)-P(1)	116.24(19)	F(4)-B(1)-F(2)	106.2(3)
N(1)-C(2)-C(3)	118.2(2)	F(1)-B(1)-F(2)	113.7(4)
		F(3)-B(1)-F(2)	108.4(3)

*Symmetry transformations used to generate equivalent atoms: #1 -x+1,y,-z+3/2.

Table B.19. Experimental and statistical crystal data for **4.6**.

Empirical formula	$\text{C}_{39}\text{H}_{44}\text{BF}_4\text{N}_2\text{NiO}_7\text{P}_2$	
Formula weight	860.22	
Temperature	110(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P-1	
Unit cell dimensions	a = 13.175(5) Å	$\alpha = 67.989(7)^\circ$.
	b = 13.669(5) Å	$\beta = 69.059(11)^\circ$.
	c = 14.543(4) Å	$\delta = 77.423(7)^\circ$.
Volume	2257.1(13) Å ³	
Z	2	
Density (calculated)	1.266 Mg/m ³	
Absorption coefficient	0.562 mm ⁻¹	
F(000)	894	
Crystal size	0.20 x 0.18 x 0.17 mm ³	
Theta range for data collection	1.59 to 25.74°.	

Table B.19. (continued)

Index ranges	-15<=h<=16, -16<=k<=16, -17<=l<=16
Reflections collected	41663
Independent reflections	8273 [R(int) = 0.0755]
Completeness to theta = 25.74°	95.8 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.9105 and 0.8963
Refinement method	Full-matrix least-squares on F ²
Data / restraints / parameters	8273 / 0 / 514
Goodness-of-fit on F ²	1.041
Final R indices [I>2sigma(I)]	R1 = 0.0756, wR2 = 0.1977
R indices (all data)	R1 = 0.0916, wR2 = 0.2059
Largest diff. peak and hole	1.465 and -0.602 e.Å ⁻³

Bond Lengths (Å)

Ni(1)-O(2)	2.032(3)	C(10)-C(11)	1.388(9)
Ni(1)-O(4)	2.034(4)	C(11)-C(12)	1.373(9)
Ni(1)-O(3)	2.035(3)	C(13)-C(14)	1.388(7)
Ni(1)-O(6)	2.046(4)	C(13)-C(18)	1.396(7)
Ni(1)-O(1)	2.046(4)	C(14)-C(15)	1.377(8)
Ni(1)-O(5)	2.064(5)	C(15)-C(16)	1.380(9)
P(1)-O(1)	1.485(4)	C(16)-C(17)	1.369(9)
P(1)-C(13)	1.792(5)	C(17)-C(18)	1.371(8)
P(1)-C(7)	1.803(5)	C(19)-C(20)	1.492(8)
P(1)-C(1)	1.809(5)	C(20)-C(21)	1.379(9)
P(2)-O(3)	1.486(3)	C(21)-C(22)	1.397(8)
P(2)-C(25)	1.783(6)	C(22)-C(23)	1.376(9)
P(2)-C(31)	1.798(5)	C(23)-C(24)	1.354(9)
P(2)-C(19)	1.819(5)	C(25)-C(30)	1.383(8)
O(2)-N(1)	1.341(5)	C(25)-C(26)	1.402(8)
O(4)-N(2)	1.327(6)	C(26)-C(27)	1.385(8)
O(5)-C(37)	1.412(10)	C(27)-C(28)	1.378(9)
O(6)-C(38)	1.406(7)	C(28)-C(29)	1.380(11)
N(1)-C(6)	1.350(7)	C(29)-C(30)	1.408(9)
N(1)-C(2)	1.367(7)	C(31)-C(32)	1.379(7)
N(2)-C(20)	1.356(7)	C(31)-C(36)	1.402(7)
N(2)-C(24)	1.362(7)	C(32)-C(33)	1.408(8)
C(1)-C(2)	1.481(7)	C(33)-C(34)	1.372(9)
C(2)-C(3)	1.379(7)	C(34)-C(35)	1.364(9)
C(3)-C(4)	1.378(8)	C(35)-C(36)	1.383(8)
C(4)-C(5)	1.378(9)	O(7)-C(39)	1.388(8)
C(5)-C(6)	1.372(8)	B(1)-F(3)	1.378(8)
C(7)-C(8)	1.379(7)	B(1)-F(4)	1.380(8)

Table B.19. (continued)

C(7)-C(12)	1.400(7)	B(1)-F(2)	1.381(7)
C(8)-C(9)	1.393(8)	B(1)-F(1)	1.389(8)
C(9)-C(10)	1.369(9)		

Bond Angles (°)

O(2)-Ni(1)-O(4)	175.12(15)	C(8)-C(7)-C(12)	120.5(5)
O(2)-Ni(1)-O(3)	90.70(13)	C(8)-C(7)-P(1)	118.6(4)
O(4)-Ni(1)-O(3)	92.18(14)	C(12)-C(7)-P(1)	120.9(4)
O(2)-Ni(1)-O(6)	84.91(15)	C(7)-C(8)-C(9)	119.6(5)
O(4)-Ni(1)-O(6)	92.24(16)	C(10)-C(9)-C(8)	120.0(6)
O(3)-Ni(1)-O(6)	175.57(15)	C(9)-C(10)-C(11)	120.2(6)
O(2)-Ni(1)-O(1)	92.68(14)	C(12)-C(11)-C(10)	120.7(6)
O(4)-Ni(1)-O(1)	91.24(15)	C(11)-C(12)-C(7)	118.9(6)
O(3)-Ni(1)-O(1)	90.38(15)	C(14)-C(13)-C(18)	119.3(5)
O(6)-Ni(1)-O(1)	89.26(16)	C(14)-C(13)-P(1)	124.1(4)
O(2)-Ni(1)-O(5)	90.93(18)	C(18)-C(13)-P(1)	116.6(4)
O(4)-Ni(1)-O(5)	85.1(2)	C(15)-C(14)-C(13)	119.9(6)
O(3)-Ni(1)-O(5)	90.97(17)	C(14)-C(15)-C(16)	120.2(6)
O(6)-Ni(1)-O(5)	89.67(18)	C(17)-C(16)-C(15)	120.0(6)
O(1)-Ni(1)-O(5)	176.13(17)	C(16)-C(17)-C(18)	120.7(6)
O(1)-P(1)-C(13)	109.7(2)	C(17)-C(18)-C(13)	119.8(5)
O(1)-P(1)-C(7)	111.1(2)	C(20)-C(19)-P(2)	114.5(3)
C(13)-P(1)-C(7)	108.7(2)	N(2)-C(20)-C(21)	118.8(5)
O(1)-P(1)-C(1)	114.1(2)	N(2)-C(20)-C(19)	117.0(5)
C(13)-P(1)-C(1)	109.0(2)	C(21)-C(20)-C(19)	124.2(5)
C(7)-P(1)-C(1)	104.0(2)	C(20)-C(21)-C(22)	121.2(6)
O(3)-P(2)-C(25)	111.6(2)	C(23)-C(22)-C(21)	117.6(6)
O(3)-P(2)-C(31)	110.2(2)	C(24)-C(23)-C(22)	120.9(6)
C(25)-P(2)-C(31)	108.2(2)	C(23)-C(24)-N(2)	120.6(6)
O(3)-P(2)-C(19)	113.9(2)	C(30)-C(25)-C(26)	120.3(5)
C(25)-P(2)-C(19)	104.5(2)	C(30)-C(25)-P(2)	121.6(5)
C(31)-P(2)-C(19)	108.2(3)	C(26)-C(25)-P(2)	118.1(4)
P(1)-O(1)-Ni(1)	136.2(2)	C(27)-C(26)-C(25)	120.5(6)
N(1)-O(2)-Ni(1)	118.1(3)	C(28)-C(27)-C(26)	119.0(6)
P(2)-O(3)-Ni(1)	137.0(2)	C(27)-C(28)-C(29)	121.4(6)
N(2)-O(4)-Ni(1)	116.8(3)	C(28)-C(29)-C(30)	120.1(6)
C(37)-O(5)-Ni(1)	124.4(5)	C(25)-C(30)-C(29)	118.8(6)
C(38)-O(6)-Ni(1)	127.5(4)	C(32)-C(31)-C(36)	119.8(5)
O(2)-N(1)-C(6)	118.6(4)	C(32)-C(31)-P(2)	124.1(4)
O(2)-N(1)-C(2)	119.4(4)	C(36)-C(31)-P(2)	115.9(4)
C(6)-N(1)-C(2)	121.9(4)	C(31)-C(32)-C(33)	119.4(5)
O(4)-N(2)-C(20)	119.9(5)	C(34)-C(33)-C(32)	119.7(6)

Table B.19. (continued)

O(4)-N(2)-C(24)	119.1(5)	C(35)-C(34)-C(33)	121.1(5)
C(20)-N(2)-C(24)	120.9(5)	C(34)-C(35)-C(36)	120.2(5)
C(2)-C(1)-P(1)	115.1(3)	C(35)-C(36)-C(31)	119.8(5)
N(1)-C(2)-C(3)	117.7(5)	F(3)-B(1)-F(4)	110.9(5)
N(1)-C(2)-C(1)	116.8(4)	F(3)-B(1)-F(2)	110.9(5)
C(3)-C(2)-C(1)	125.5(5)	F(4)-B(1)-F(2)	109.1(5)
C(4)-C(3)-C(2)	121.9(6)	F(3)-B(1)-F(1)	108.6(5)
C(5)-C(4)-C(3)	118.2(5)	F(4)-B(1)-F(1)	109.0(5)
C(6)-C(5)-C(4)	120.4(6)	F(2)-B(1)-F(1)	108.2(5)
N(1)-C(6)-C(5)	119.9(5)		

Table B.20. Experimental and statistical crystal data for **4.7**.

Empirical formula	$\text{C}_{37}\text{H}_{36}\text{B}_2\text{CuF}_8\text{N}_2\text{O}_5\text{P}_2$		
Formula weight	887.78		
Temperature	110(2) K		
Wavelength	0.71073 Å		
Crystal system	Triclinic		
Space group	P-1		
Unit cell dimensions	$a = 10.844(3)$ Å	$\alpha = 90.874(4)^\circ$.	
	$b = 12.839(4)$ Å	$\beta = 107.544(4)^\circ$.	
	$c = 15.666(5)$ Å	$\delta = 113.885(4)^\circ$.	
Volume	$1877.9(10)$ Å ³		
Z	2		
Density (calculated)	1.570 Mg/m ³		
Absorption coefficient	0.753 mm ⁻¹		
F(000)	906		
Crystal size	$0.21 \times 0.21 \times 0.11$ mm ³		
Theta range for data collection	1.38 to 28.42° .		
Index ranges	$-11 \leq h \leq 14$, $-17 \leq k \leq 17$, $-20 \leq l \leq 20$		
Reflections collected	18227		
Independent reflections	8720 [$R(\text{int}) = 0.0426$]		
Completeness to $\theta = 25.00^\circ$	96.2 %		
Absorption correction	Semi-empirical from equivalents		
Max. and min. transmission	0.9230 and 0.8602		
Refinement method	Full-matrix least-squares on F^2		
Data / restraints / parameters	8720 / 0 / 519		
Goodness-of-fit on F^2	1.034		
Final R indices [$I > 2\sigma(I)$]	$R1 = 0.0399$, $wR2 = 0.0938$		
R indices (all data)	$R1 = 0.0515$, $wR2 = 0.1023$		
Largest diff. peak and hole	0.449 and -0.559 e.Å ⁻³		

Table B.20. (continued)

Bond Lengths (Å)

Cu(1)-O(1)	1.9464(15)	C(11)-H(11)	0.9500
Cu(1)-O(4)	1.9524(16)	C(12)-H(12)	0.9500
Cu(1)-O(2)	1.9532(16)	C(13)-C(14)	1.384(3)
Cu(1)-O(5)	1.9747(17)	C(13)-C(18)	1.397(3)
Cu(1)-O(3)	2.2577(15)	C(14)-C(15)	1.386(3)
P(1)-O(1)	1.4986(17)	C(14)-H(14)	0.9500
P(1)-C(13)	1.782(2)	C(15)-C(16)	1.379(4)
P(1)-C(7)	1.792(2)	C(15)-H(15)	0.9500
P(1)-C(1)	1.816(2)	C(16)-C(17)	1.380(4)
P(2)-O(3)	1.4885(16)	C(16)-H(16)	0.9500
P(2)-C(31)	1.794(2)	C(17)-C(18)	1.375(3)
P(2)-C(25)	1.799(2)	C(17)-H(17)	0.9500
P(2)-C(19)	1.814(2)	C(18)-H(18)	0.9500
F(1)-B(1)	1.397(3)	C(19)-C(20)	1.490(3)
F(2)-B(1)	1.382(3)	C(19)-H(19A)	0.9900
F(3)-B(1)	1.401(3)	C(19)-H(19B)	0.9900
F(4)-B(1)	1.375(3)	C(20)-C(21)	1.386(3)
F(5)-B(2)	1.387(3)	C(21)-C(22)	1.383(3)
F(6)-B(2)	1.399(3)	C(21)-H(21)	0.9500
F(7)-B(2)	1.383(3)	C(22)-C(23)	1.383(3)
F(8)-B(2)	1.368(3)	C(22)-H(22)	0.9500
O(2)-N(1)	1.332(2)	C(23)-C(24)	1.371(3)
O(4)-N(2)	1.340(2)	C(23)-H(23)	0.9500
O(5)-C(37)	1.430(3)	C(24)-H(24)	0.9500
O(5)-H(1)	0.79(4)	C(25)-C(30)	1.384(3)
N(1)-C(2)	1.355(3)	C(25)-C(26)	1.394(3)
N(1)-C(6)	1.355(3)	C(26)-C(27)	1.389(3)
N(2)-C(24)	1.346(3)	C(26)-H(26)	0.9500
N(2)-C(20)	1.353(3)	C(27)-C(28)	1.378(4)
C(1)-C(2)	1.488(3)	C(27)-H(27)	0.9500
C(1)-H(1A)	0.9900	C(28)-C(29)	1.375(4)
C(1)-H(1B)	0.9900	C(28)-H(28)	0.9500
C(2)-C(3)	1.379(3)	C(29)-C(30)	1.393(3)
C(3)-C(4)	1.383(3)	C(29)-H(29)	0.9500
C(3)-H(3)	0.9500	C(30)-H(30)	0.9500
C(4)-C(5)	1.374(4)	C(31)-C(36)	1.391(3)
C(4)-H(4)	0.9500	C(31)-C(32)	1.392(3)
C(5)-C(6)	1.365(4)	C(32)-C(33)	1.378(3)
C(5)-H(5)	0.9500	C(32)-H(32)	0.9500
C(6)-H(6)	0.9500	C(33)-C(34)	1.385(4)
C(7)-C(12)	1.382(3)	C(33)-H(33)	0.9500
C(7)-C(8)	1.394(3)	C(34)-C(35)	1.376(4)

Table B.20. (continued)

C(8)-C(9)	1.391(3)	C(34)-H(34)	0.9500
C(8)-H(8)	0.9500	C(35)-C(36)	1.386(3)
C(9)-C(10)	1.383(4)	C(35)-H(35)	0.9500
C(9)-H(9)	0.9500	C(36)-H(36)	0.9500
C(10)-C(11)	1.378(3)	C(37)-H(37A)	0.9800
C(10)-H(10)	0.9500	C(37)-H(37B)	0.9800
C(11)-C(12)	1.388(3)	C(37)-H(37C)	0.9800

Bond Angles (°)

O(1)-Cu(1)-O(4)	91.52(7)	C(15)-C(16)-H(16)	119.8
O(1)-Cu(1)-O(2)	93.49(7)	C(17)-C(16)-H(16)	119.8
O(4)-Cu(1)-O(2)	171.52(6)	C(18)-C(17)-C(16)	120.3(3)
O(1)-Cu(1)-O(5)	170.67(7)	C(18)-C(17)-H(17)	119.9
O(4)-Cu(1)-O(5)	83.96(7)	C(16)-C(17)-H(17)	119.9
O(2)-Cu(1)-O(5)	90.09(7)	C(17)-C(18)-C(13)	119.8(3)
O(1)-Cu(1)-O(3)	99.97(7)	C(17)-C(18)-H(18)	120.1
O(4)-Cu(1)-O(3)	92.96(7)	C(13)-C(18)-H(18)	120.1
O(2)-Cu(1)-O(3)	92.90(6)	C(20)-C(19)-P(2)	115.12(16)
O(5)-Cu(1)-O(3)	88.43(7)	C(20)-C(19)-H(19A)	108.5
O(1)-P(1)-C(13)	108.94(10)	P(2)-C(19)-H(19A)	108.5
O(1)-P(1)-C(7)	111.82(10)	C(20)-C(19)-H(19B)	108.5
C(13)-P(1)-C(7)	108.29(10)	P(2)-C(19)-H(19B)	108.5
O(1)-P(1)-C(1)	112.70(9)	H(19A)-C(19)-H(19B)	107.5
C(13)-P(1)-C(1)	109.95(11)	N(2)-C(20)-C(21)	118.23(19)
C(7)-P(1)-C(1)	105.02(10)	N(2)-C(20)-C(19)	118.36(19)
O(3)-P(2)-C(31)	109.93(10)	C(21)-C(20)-C(19)	123.4(2)
O(3)-P(2)-C(25)	112.41(9)	C(22)-C(21)-C(20)	120.8(2)
C(31)-P(2)-C(25)	107.92(10)	C(22)-C(21)-H(21)	119.6
O(3)-P(2)-C(19)	114.10(10)	C(20)-C(21)-H(21)	119.6
C(31)-P(2)-C(19)	107.55(10)	C(23)-C(22)-C(21)	118.9(2)
C(25)-P(2)-C(19)	104.57(11)	C(23)-C(22)-H(22)	120.6
P(1)-O(1)-Cu(1)	137.48(9)	C(21)-C(22)-H(22)	120.6
N(1)-O(2)-Cu(1)	116.59(12)	C(24)-C(23)-C(22)	119.5(2)
P(2)-O(3)-Cu(1)	129.44(9)	C(24)-C(23)-H(23)	120.3
N(2)-O(4)-Cu(1)	119.64(13)	C(22)-C(23)-H(23)	120.3
C(37)-O(5)-Cu(1)	125.44(16)	N(2)-C(24)-C(23)	120.5(2)
C(37)-O(5)-H(1)	106(3)	N(2)-C(24)-H(24)	119.8
Cu(1)-O(5)-H(1)	115(3)	C(23)-C(24)-H(24)	119.8
O(2)-N(1)-C(2)	119.59(17)	C(30)-C(25)-C(26)	119.4(2)
O(2)-N(1)-C(6)	118.59(19)	C(30)-C(25)-P(2)	118.04(18)
C(2)-N(1)-C(6)	121.7(2)	C(26)-C(25)-P(2)	122.49(16)
O(4)-N(2)-C(24)	118.17(18)	C(27)-C(26)-C(25)	119.7(2)

Table B.20. (continued)

O(4)-N(2)-C(20)	119.57(17)	C(27)-C(26)-H(26)	120.1
C(24)-N(2)-C(20)	122.11(19)	C(25)-C(26)-H(26)	120.1
C(2)-C(1)-P(1)	113.60(15)	C(28)-C(27)-C(26)	120.4(2)
C(2)-C(1)-H(1A)	108.8	C(28)-C(27)-H(27)	119.8
P(1)-C(1)-H(1A)	108.8	C(26)-C(27)-H(27)	119.8
C(2)-C(1)-H(1B)	108.8	C(29)-C(28)-C(27)	120.1(2)
P(1)-C(1)-H(1B)	108.8	C(29)-C(28)-H(28)	119.9
H(1A)-C(1)-H(1B)	107.7	C(27)-C(28)-H(28)	119.9
N(1)-C(2)-C(3)	118.55(19)	C(28)-C(29)-C(30)	120.0(2)
N(1)-C(2)-C(1)	117.0(2)	C(28)-C(29)-H(29)	120.0
C(3)-C(2)-C(1)	124.5(2)	C(30)-C(29)-H(29)	120.0
C(2)-C(3)-C(4)	120.6(2)	C(25)-C(30)-C(29)	120.3(2)
C(2)-C(3)-H(3)	119.7	C(25)-C(30)-H(30)	119.9
C(4)-C(3)-H(3)	119.7	C(29)-C(30)-H(30)	119.9
C(5)-C(4)-C(3)	119.0(2)	C(36)-C(31)-C(32)	119.0(2)
C(5)-C(4)-H(4)	120.5	C(36)-C(31)-P(2)	124.08(18)
C(3)-C(4)-H(4)	120.5	C(32)-C(31)-P(2)	116.96(17)
C(6)-C(5)-C(4)	120.1(2)	C(33)-C(32)-C(31)	120.6(2)
C(6)-C(5)-H(5)	120.0	C(33)-C(32)-H(32)	119.7
C(4)-C(5)-H(5)	120.0	C(31)-C(32)-H(32)	119.7
N(1)-C(6)-C(5)	120.0(2)	C(32)-C(33)-C(34)	119.9(2)
N(1)-C(6)-H(6)	120.0	C(32)-C(33)-H(33)	120.0
C(5)-C(6)-H(6)	120.0	C(34)-C(33)-H(33)	120.0
C(12)-C(7)-C(8)	120.2(2)	C(35)-C(34)-C(33)	120.1(2)
C(12)-C(7)-P(1)	118.88(17)	C(35)-C(34)-H(34)	120.0
C(8)-C(7)-P(1)	120.90(18)	C(33)-C(34)-H(34)	120.0
C(9)-C(8)-C(7)	119.1(2)	C(34)-C(35)-C(36)	120.2(2)
C(9)-C(8)-H(8)	120.5	C(34)-C(35)-H(35)	119.9
C(7)-C(8)-H(8)	120.5	C(36)-C(35)-H(35)	119.9
C(10)-C(9)-C(8)	120.4(2)	C(35)-C(36)-C(31)	120.2(2)
C(10)-C(9)-H(9)	119.8	C(35)-C(36)-H(36)	119.9
C(8)-C(9)-H(9)	119.8	C(31)-C(36)-H(36)	119.9
C(11)-C(10)-C(9)	120.3(2)	O(5)-C(37)-H(37A)	109.5
C(11)-C(10)-H(10)	119.8	O(5)-C(37)-H(37B)	109.5
C(9)-C(10)-H(10)	119.8	H(37A)-C(37)-H(37B)	109.5
C(10)-C(11)-C(12)	119.7(2)	O(5)-C(37)-H(37C)	109.5
C(10)-C(11)-H(11)	120.1	H(37A)-C(37)-H(37C)	109.5
C(12)-C(11)-H(11)	120.1	H(37B)-C(37)-H(37C)	109.5
C(7)-C(12)-C(11)	120.2(2)	F(4)-B(1)-F(2)	110.0(2)
C(7)-C(12)-H(12)	119.9	F(4)-B(1)-F(1)	110.16(19)
C(11)-C(12)-H(12)	119.9	F(2)-B(1)-F(1)	109.21(19)
C(14)-C(13)-C(18)	119.6(2)	F(4)-B(1)-F(3)	109.7(2)
C(14)-C(13)-P(1)	124.05(18)	F(2)-B(1)-F(3)	109.23(19)
C(18)-C(13)-P(1)	116.30(19)	F(1)-B(1)-F(3)	108.5(2)

Table B.20. (continued)

C(13)-C(14)-C(15)	120.2(2)	F(8)-B(2)-F(7)	110.7(2)
C(13)-C(14)-H(14)	119.9	F(8)-B(2)-F(5)	109.4(2)
C(15)-C(14)-H(14)	119.9	F(7)-B(2)-F(5)	109.0(2)
C(16)-C(15)-C(14)	119.7(3)	F(8)-B(2)-F(6)	110.6(2)
C(16)-C(15)-H(15)	120.1	F(7)-B(2)-F(6)	109.0(2)
C(14)-C(15)-H(15)	120.1	F(5)-B(2)-F(6)	108.2(2)
C(15)-C(16)-C(17)	120.4(2)		

Table B.21. Experimental and statistical crystal data for **4.8**.

Empirical formula	$\text{C}_{39}\text{H}_{44}\text{BF}_4\text{N}_2\text{O}_7\text{P}_2\text{Zn}$	
Formula weight	866.88	
Temperature	110(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P-1	
Unit cell dimensions	$a = 13.245(9)$ Å	$\alpha = 67.655(13)^\circ$
	$b = 13.670(10)$ Å	$\beta = 68.811(11)^\circ$
	$c = 14.573(10)$ Å	$\delta = 77.101(14)^\circ$
Volume	$2264(3)$ Å ³	
Z	2	
Density (calculated)	1.272 Mg/m ³	
Absorption coefficient	0.674 mm ⁻¹	
F(000)	898	
Crystal size	$0.32 \times 0.16 \times 0.15$ mm ³	
Theta range for data collection	1.59 to 25.00°	
Index ranges	$-15 \leq h \leq 15$, $-16 \leq k \leq 16$, $-17 \leq l \leq 17$	
Reflections collected	17372	
Independent reflections	7792 [R(int) = 0.0451]	
Completeness to $\theta = 25.00^\circ$	97.7 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.9056 and 0.8121	
Refinement method	Full-matrix least-squares on F ²	
Data / restraints / parameters	7792 / 1 / 517	
Goodness-of-fit on F ²	1.048	
Final R indices [I > 2σ(I)]	R1 = 0.0805, wR2 = 0.2193	
R indices (all data)	R1 = 0.0974, wR2 = 0.2286	
Largest diff. peak and hole	2.004 and -0.887 e.Å ⁻³	

Table B.21. (continued)

Bond Lengths (Å)

Zn(1)-O(4)	2.061(4)	C(10)-C(11)	1.390(12)
Zn(1)-O(2)	2.063(4)	C(11)-C(12)	1.389(10)
Zn(1)-O(1)	2.067(4)	C(13)-C(18)	1.375(9)
Zn(1)-O(3)	2.076(4)	C(13)-C(14)	1.386(9)
Zn(1)-O(6)	2.087(5)	C(14)-C(15)	1.387(9)
Zn(1)-O(5)	2.104(6)	C(15)-C(16)	1.371(11)
P(1)-O(1)	1.479(4)	C(16)-C(17)	1.382(11)
P(1)-C(7)	1.783(7)	C(17)-C(18)	1.404(10)
P(1)-C(13)	1.805(6)	C(19)-C(20)	1.493(8)
P(1)-C(1)	1.816(6)	C(20)-C(21)	1.372(9)
P(2)-O(3)	1.490(4)	C(21)-C(22)	1.388(10)
P(2)-C(31)	1.790(6)	C(22)-C(23)	1.376(11)
P(2)-C(19)	1.798(6)	C(23)-C(24)	1.379(10)
P(2)-C(25)	1.804(6)	C(25)-C(26)	1.385(9)
O(2)-N(2)	1.322(7)	C(25)-C(30)	1.389(9)
O(4)-N(1)	1.335(6)	C(26)-C(27)	1.398(10)
O(5)-C(37)	1.407(12)	C(27)-C(28)	1.373(11)
O(6)-C(38)	1.411(9)	C(28)-C(29)	1.381(11)
N(1)-C(24)	1.354(8)	C(29)-C(30)	1.391(9)
N(1)-C(20)	1.369(8)	C(31)-C(32)	1.383(9)
N(2)-C(2)	1.353(8)	C(31)-C(36)	1.398(8)
N(2)-C(6)	1.367(8)	C(32)-C(33)	1.378(10)
C(1)-C(2)	1.500(9)	C(33)-C(34)	1.368(11)
C(2)-C(3)	1.376(10)	C(34)-C(35)	1.366(11)
C(3)-C(4)	1.405(9)	C(35)-C(36)	1.368(10)
C(4)-C(5)	1.376(11)	B(1)-F(1)	1.363(8)
C(5)-C(6)	1.353(11)	B(1)-F(2)	1.374(9)
C(7)-C(8)	1.377(9)	B(1)-F(3)	1.392(9)
C(7)-C(12)	1.393(10)	B(1)-F(4)	1.395(10)
C(8)-C(9)	1.420(10)	O(7)-C(39)	1.408(9)
C(9)-C(10)	1.348(12)		

Bond Angles (°)

O(4)-Zn(1)-O(2)	176.22(18)	C(8)-C(7)-C(12)	119.9(6)
O(4)-Zn(1)-O(1)	90.53(17)	C(8)-C(7)-P(1)	122.2(5)
O(2)-Zn(1)-O(1)	91.81(17)	C(12)-C(7)-P(1)	117.9(5)
O(4)-Zn(1)-O(3)	92.15(17)	C(7)-C(8)-C(9)	118.8(7)
O(2)-Zn(1)-O(3)	90.77(18)	C(10)-C(9)-C(8)	120.6(8)
O(1)-Zn(1)-O(3)	90.85(18)	C(9)-C(10)-C(11)	121.2(7)
O(4)-Zn(1)-O(6)	84.62(19)	C(12)-C(11)-C(10)	118.7(8)

Table B.21. (continued)

O(2)-Zn(1)-O(6)	93.06(19)	C(11)-C(12)-C(7)	120.8(7)
O(1)-Zn(1)-O(6)	175.13(18)	C(18)-C(13)-C(14)	120.7(6)
O(3)-Zn(1)-O(6)	89.0(2)	C(18)-C(13)-P(1)	123.3(5)
O(4)-Zn(1)-O(5)	91.9(2)	C(14)-C(13)-P(1)	115.8(5)
O(2)-Zn(1)-O(5)	85.0(2)	C(13)-C(14)-C(15)	120.1(6)
O(1)-Zn(1)-O(5)	92.2(2)	C(16)-C(15)-C(14)	119.7(6)
O(3)-Zn(1)-O(5)	174.9(2)	C(15)-C(16)-C(17)	120.5(6)
O(6)-Zn(1)-O(5)	88.4(2)	C(16)-C(17)-C(18)	120.1(7)
O(1)-P(1)-C(7)	111.8(3)	C(13)-C(18)-C(17)	118.8(7)
O(1)-P(1)-C(13)	109.8(3)	C(20)-C(19)-P(2)	115.4(4)
C(7)-P(1)-C(13)	108.1(3)	N(1)-C(20)-C(21)	118.2(6)
O(1)-P(1)-C(1)	113.9(3)	N(1)-C(20)-C(19)	116.3(5)
C(7)-P(1)-C(1)	104.4(3)	C(21)-C(20)-C(19)	125.5(6)
C(13)-P(1)-C(1)	108.6(3)	C(20)-C(21)-C(22)	122.1(7)
O(3)-P(2)-C(31)	109.9(3)	C(23)-C(22)-C(21)	118.0(6)
O(3)-P(2)-C(19)	113.9(3)	C(22)-C(23)-C(24)	120.1(7)
C(31)-P(2)-C(19)	109.1(3)	N(1)-C(24)-C(23)	120.4(7)
O(3)-P(2)-C(25)	111.0(3)	C(26)-C(25)-C(30)	120.9(6)
C(31)-P(2)-C(25)	108.5(3)	C(26)-C(25)-P(2)	120.9(5)
C(19)-P(2)-C(25)	104.1(3)	C(30)-C(25)-P(2)	118.1(5)
P(1)-O(1)-Zn(1)	136.8(2)	C(25)-C(26)-C(27)	118.8(7)
N(2)-O(2)-Zn(1)	116.8(3)	C(28)-C(27)-C(26)	120.5(7)
P(2)-O(3)-Zn(1)	136.0(2)	C(27)-C(28)-C(29)	120.4(7)
N(1)-O(4)-Zn(1)	117.8(3)	C(28)-C(29)-C(30)	120.2(7)
C(37)-O(5)-Zn(1)	123.6(6)	C(25)-C(30)-C(29)	119.2(6)
C(38)-O(6)-Zn(1)	126.9(5)	C(32)-C(31)-C(36)	119.3(6)
O(4)-N(1)-C(24)	119.2(5)	C(32)-C(31)-P(2)	124.0(5)
O(4)-N(1)-C(20)	119.5(5)	C(36)-C(31)-P(2)	116.7(5)
C(24)-N(1)-C(20)	121.2(5)	C(33)-C(32)-C(31)	119.5(7)
O(2)-N(2)-C(2)	120.0(5)	C(34)-C(33)-C(32)	120.7(7)
O(2)-N(2)-C(6)	118.4(5)	C(35)-C(34)-C(33)	120.2(7)
C(2)-N(2)-C(6)	121.5(6)	C(34)-C(35)-C(36)	120.3(7)
C(2)-C(1)-P(1)	114.8(4)	C(35)-C(36)-C(31)	120.0(7)
N(2)-C(2)-C(3)	118.3(6)	F(1)-B(1)-F(2)	111.9(6)
N(2)-C(2)-C(1)	116.8(6)	F(1)-B(1)-F(3)	109.5(6)
C(3)-C(2)-C(1)	124.9(6)	F(2)-B(1)-F(3)	108.4(7)
C(2)-C(3)-C(4)	122.0(7)	F(1)-B(1)-F(4)	107.8(6)
C(5)-C(4)-C(3)	116.5(7)	F(2)-B(1)-F(4)	110.7(6)
C(6)-C(5)-C(4)	121.9(7)	F(3)-B(1)-F(4)	108.4(6)
C(5)-C(6)-N(2)	119.9(7)		

Table B.22. Experimental and statistical crystal data for **4.9**.

Empirical formula	C ₂₈ H ₃₁ B ₂ F ₈ N ₆ NiO ₂ P		
Formula weight	746.89		
Temperature	110(2) K		
Wavelength	0.71073 Å		
Crystal system	Monoclinic		
Space group	P 21/n		
Unit cell dimensions	a = 11.0974(5) Å	α = 90°.	
	b = 25.2713(11) Å	β = 97.489(2)°.	
	c = 12.0411(6) Å	δ = 90°.	
Volume	3348.1(3) Å ³		
Z	4		
Density (calculated)	1.482 Mg/m ³		
Absorption coefficient	0.708 mm ⁻¹		
F(000)	1528		
Crystal size	0.35 x 0.17 x 0.11 mm ³		
Theta range for data collection	1.89 to 29.57°.		
Index ranges	-15<=h<=15, -34<=k<=33, -16<=l<=16		
Reflections collected	37197		
Independent reflections	9298 [R(int) = 0.0567]		
Completeness to theta = 29.57°	99.1 %		
Absorption correction	Semi-empirical from equivalents		
Max. and min. transmission	0.9274 and 0.7881		
Refinement method	Full-matrix least-squares on F ²		
Data / restraints / parameters	9298 / 0 / 438		
Goodness-of-fit on F ²	1.023		
Final R indices [I>2sigma(I)]	R1 = 0.0384, wR2 = 0.0881		
R indices (all data)	R1 = 0.0543, wR2 = 0.0966		
Largest diff. peak and hole	0.578 and -0.668 e.Å ⁻³		
Bond Lengths (Å)			
Ni(1)-O(2)	2.0293(12)	C(4)-C(5)	1.386(3)
Ni(1)-O(1)	2.0483(12)	C(5)-C(6)	1.374(3)
Ni(1)-N(2)	2.0584(15)	C(7)-C(8)	1.396(2)
Ni(1)-N(4)	2.0679(15)	C(7)-C(12)	1.399(2)
Ni(1)-N(5)	2.0739(15)	C(8)-C(9)	1.394(2)
Ni(1)-N(3)	2.0840(15)	C(9)-C(10)	1.380(3)
P(1)-O(1)	1.5057(12)	C(10)-C(11)	1.386(3)
P(1)-C(13)	1.7889(17)	C(11)-C(12)	1.391(2)
P(1)-C(7)	1.7904(17)	C(13)-C(18)	1.395(2)
P(1)-C(1)	1.8240(16)	C(13)-C(14)	1.397(2)

Table B.22. (continued)

O(2)-N(1)	1.3363(18)	C(14)-C(15)	1.386(3)
N(1)-C(6)	1.354(2)	C(15)-C(16)	1.380(3)
N(1)-C(2)	1.360(2)	C(16)-C(17)	1.384(3)
N(2)-C(19)	1.138(2)	C(17)-C(18)	1.385(3)
C(19)-C(20)	1.449(3)	N(6)-C(27)	1.135(3)
N(3)-C(21)	1.135(2)	C(27)-C(28)	1.457(3)
C(21)-C(22)	1.458(3)	B(2)-F(6)	1.348(3)
N(4)-C(23)	1.138(2)	B(2)-F(5)	1.383(3)
C(23)-C(24)	1.454(3)	B(2)-F(7)	1.386(3)
N(5)-C(25)	1.135(2)	B(2)-F(8)	1.386(2)
C(25)-C(26)	1.454(2)	B(1)-F(4)	1.383(3)
C(1)-C(2)	1.497(2)	B(1)-F(1)	1.385(3)
C(2)-C(3)	1.389(2)	B(1)-F(3)	1.389(3)
C(3)-C(4)	1.388(2)	B(1)-F(2)	1.394(3)

Bond Angles (°)

O(2)-Ni(1)-O(1)	92.00(5)	N(1)-C(2)-C(1)	117.60(14)
O(2)-Ni(1)-N(2)	93.66(5)	C(3)-C(2)-C(1)	123.30(15)
O(1)-Ni(1)-N(2)	88.78(5)	C(4)-C(3)-C(2)	120.24(17)
O(2)-Ni(1)-N(4)	90.40(5)	C(5)-C(4)-C(3)	118.82(17)
O(1)-Ni(1)-N(4)	176.67(5)	C(6)-C(5)-C(4)	120.23(17)
N(2)-Ni(1)-N(4)	88.77(6)	N(1)-C(6)-C(5)	119.87(16)
O(2)-Ni(1)-N(5)	85.02(5)	C(8)-C(7)-C(12)	119.72(15)
O(1)-Ni(1)-N(5)	90.17(5)	C(8)-C(7)-P(1)	120.89(13)
N(2)-Ni(1)-N(5)	178.28(6)	C(12)-C(7)-P(1)	119.10(13)
N(4)-Ni(1)-N(5)	92.33(6)	C(9)-C(8)-C(7)	119.63(17)
O(2)-Ni(1)-N(3)	177.85(5)	C(10)-C(9)-C(8)	120.25(18)
O(1)-Ni(1)-N(3)	89.04(5)	C(9)-C(10)-C(11)	120.62(17)
N(2)-Ni(1)-N(3)	88.24(6)	C(10)-C(11)-C(12)	119.73(18)
N(4)-Ni(1)-N(3)	88.63(6)	C(11)-C(12)-C(7)	120.05(17)
N(5)-Ni(1)-N(3)	93.11(6)	C(18)-C(13)-C(14)	120.17(17)
O(1)-P(1)-C(13)	110.93(8)	C(18)-C(13)-P(1)	118.56(14)
O(1)-P(1)-C(7)	111.98(7)	C(14)-C(13)-P(1)	120.78(13)
C(13)-P(1)-C(7)	108.45(8)	C(15)-C(14)-C(13)	119.55(18)
O(1)-P(1)-C(1)	112.65(7)	C(16)-C(15)-C(14)	120.05(19)
C(13)-P(1)-C(1)	104.33(8)	C(15)-C(16)-C(17)	120.57(18)
C(7)-P(1)-C(1)	108.13(8)	C(16)-C(17)-C(18)	120.21(19)
P(1)-O(1)-Ni(1)	137.09(7)	C(17)-C(18)-C(13)	119.41(18)
N(1)-O(2)-Ni(1)	119.09(9)	N(6)-C(27)-C(28)	179.4(2)
O(2)-N(1)-C(6)	118.76(14)	F(6)-B(2)-F(5)	109.84(19)
O(2)-N(1)-C(2)	119.41(13)	F(6)-B(2)-F(7)	111.60(19)
C(6)-N(1)-C(2)	121.83(15)	F(5)-B(2)-F(7)	108.79(17)

Table B.22. (continued)

C(19)-N(2)-Ni(1)	176.78(15)	F(6)-B(2)-F(8)	110.64(19)
N(2)-C(19)-C(20)	178.5(2)	F(5)-B(2)-F(8)	108.59(18)
C(21)-N(3)-Ni(1)	169.30(15)	F(7)-B(2)-F(8)	107.29(17)
N(3)-C(21)-C(22)	179.6(2)	F(4)-B(1)-F(1)	109.44(19)
C(23)-N(4)-Ni(1)	167.78(15)	F(4)-B(1)-F(3)	109.73(18)
N(4)-C(23)-C(24)	179.3(2)	F(1)-B(1)-F(3)	108.88(18)
C(25)-N(5)-Ni(1)	172.15(14)	F(4)-B(1)-F(2)	109.03(18)
N(5)-C(25)-C(26)	179.2(2)	F(1)-B(1)-F(2)	109.65(17)
C(2)-C(1)-P(1)	108.03(11)	F(3)-B(1)-F(2)	110.09(19)
N(1)-C(2)-C(3)	118.96(15)		

Table B.23. Experimental and statistical crystal data for **5.1**.*

Empirical formula	$C_{40}H_{32}Hg_2N_6P_2S_4$		
Formula weight	1188.08		
Temperature	110(2) K		
Wavelength	0.71073 Å		
Crystal system	Triclinic		
Space group	P-1		
Unit cell dimensions	$a = 8.8219(6)$ Å	$\alpha = 72.400(4)^\circ$	
	$b = 8.9937(7)$ Å	$\beta = 88.895(4)^\circ$	
	$c = 13.6100(10)$ Å	$\delta = 76.924(4)^\circ$	
Volume	$1001.20(13)$ Å ³		
Z	1		
Density (calculated)	1.970 Mg/m ³		
Absorption coefficient	7.985 mm ⁻¹		
F(000)	568		
Crystal size	$0.15 \times 0.13 \times 0.09$ mm ³		
Theta range for data collection	2.37 to 28.48°		
Index ranges	$-11 \leq h \leq 11$, $-12 \leq k \leq 12$, $-18 \leq l \leq 15$		
Reflections collected	11675		
Independent reflections	4931 [$R(\text{int}) = 0.0271$]		
Completeness to $\theta = 25.00^\circ$	98.4 %		
Absorption correction	Semi-empirical from equivalents		
Max. and min. transmission	0.5434 and 0.3805		
Refinement method	Full-matrix least-squares on F^2		
Data / restraints / parameters	4931 / 0 / 244		
Goodness-of-fit on F^2	1.060		
Final R indices [$I > 2\sigma(I)$]	$R1 = 0.0251$, $wR2 = 0.0551$		
R indices (all data)	$R1 = 0.0303$, $wR2 = 0.0565$		
Largest diff. peak and hole	1.761 and -0.977 e.Å ⁻³		

Table B.23. (continued)

Bond Lengths (Å)

Hg(1)-P(1)	2.4340(9)	C(4)-C(8)	1.392(5)
Hg(1)-S(2)	2.4718(10)	C(5)-C(6)	1.386(5)
Hg(1)-N(3)#1	2.495(3)	C(7)-C(8)	1.380(5)
Hg(1)-S(1)	2.5655(9)	C(9)-C(14)	1.390(5)
S(1)-C(1)	1.671(4)	C(9)-C(10)	1.400(5)
S(2)-C(2)	1.676(4)	C(10)-C(11)	1.379(5)
P(1)-C(15)	1.805(4)	C(11)-C(12)	1.389(6)
P(1)-C(9)	1.807(4)	C(12)-C(13)	1.368(6)
P(1)-C(3)	1.826(4)	C(13)-C(14)	1.387(5)
N(1)-C(1)	1.153(5)	C(15)-C(16)	1.393(5)
N(2)-C(2)	1.150(5)	C(15)-C(20)	1.397(5)
N(3)-C(7)	1.339(4)	C(16)-C(17)	1.382(5)
N(3)-C(6)	1.339(5)	C(17)-C(18)	1.391(5)
N(3)-Hg(1)#1	2.495(3)	C(18)-C(19)	1.385(5)
C(3)-C(4)	1.502(5)	C(19)-C(20)	1.391(5)
C(4)-C(5)	1.392(5)		

Bond Angles (°)

P(1)-Hg(1)-S(2)	137.44(3)	C(8)-C(4)-C(3)	122.6(3)
P(1)-Hg(1)-N(3)#1	104.35(8)	C(6)-C(5)-C(4)	119.4(3)
S(2)-Hg(1)-N(3)#1	94.39(7)	N(3)-C(6)-C(5)	123.3(3)
P(1)-Hg(1)-S(1)	113.89(3)	N(3)-C(7)-C(8)	123.3(3)
S(2)-Hg(1)-S(1)	101.16(3)	C(7)-C(8)-C(4)	119.8(3)
N(3)#1-Hg(1)-S(1)	96.55(7)	C(14)-C(9)-C(10)	120.0(3)
C(1)-S(1)-Hg(1)	96.87(13)	C(14)-C(9)-P(1)	121.2(3)
C(2)-S(2)-Hg(1)	97.58(15)	C(10)-C(9)-P(1)	118.8(3)
C(15)-P(1)-C(9)	105.59(16)	C(11)-C(10)-C(9)	119.3(4)
C(15)-P(1)-C(3)	105.71(16)	C(10)-C(11)-C(12)	120.1(4)
C(9)-P(1)-C(3)	106.52(17)	C(13)-C(12)-C(11)	120.8(4)
C(15)-P(1)-Hg(1)	112.34(12)	C(12)-C(13)-C(14)	119.9(4)
C(9)-P(1)-Hg(1)	112.40(12)	C(13)-C(14)-C(9)	119.8(4)
C(3)-P(1)-Hg(1)	113.66(12)	C(16)-C(15)-C(20)	120.0(3)
C(7)-N(3)-C(6)	117.1(3)	C(16)-C(15)-P(1)	117.2(3)
C(7)-N(3)-Hg(1)#1	118.0(2)	C(20)-C(15)-P(1)	122.7(3)
C(6)-N(3)-Hg(1)#1	124.8(2)	C(17)-C(16)-C(15)	120.4(3)
N(1)-C(1)-S(1)	179.0(4)	C(16)-C(17)-C(18)	119.8(4)
N(2)-C(2)-S(2)	178.7(4)	C(19)-C(18)-C(17)	119.9(3)
C(4)-C(3)-P(1)	113.5(2)	C(18)-C(19)-C(20)	120.8(3)
C(5)-C(4)-C(8)	117.1(3)	C(19)-C(20)-C(15)	119.0(3)

*Symmetry transformations used to generate equivalent atoms: #1 -x+2,-y,-z.

Table B.24. Experimental and statistical crystal data for **5.2**.*

Empirical formula	C ₅₂ H ₅₂ F ₁₂ Hg ₂ N ₂ O ₁₀ P ₂		
Formula weight	1556.08		
Temperature	110(2) K		
Wavelength	0.71073 Å		
Crystal system	Monoclinic		
Space group	C2/c		
Unit cell dimensions	a = 23.783(3) Å	α = 90°.	
	b = 11.7416(12) Å	β = 94.233(2)°.	
	c = 20.191(2) Å	δ = 90°.	
Volume	5623.1(11) Å ³		
Z	4		
Density (calculated)	1.838 Mg/m ³		
Absorption coefficient	5.608 mm ⁻¹		
F(000)	3024		
Crystal size	0.20 x 0.18 x 0.10 mm ³		
Theta range for data collection	1.94 to 28.33°.		
Index ranges	-31<=h<=31, -15<=k<=15, -26<=l<=26		
Reflections collected	31033		
Independent reflections	6943 [R(int) = 0.0504]		
Completeness to theta = 28.33°	98.8 %		
Absorption correction	Semi-empirical from equivalents		
Max. and min. transmission	0.6151 and 0.4001		
Refinement method	Full-matrix least-squares on F ²		
Data / restraints / parameters	6943 / 2 / 371		
Goodness-of-fit on F ²	1.075		
Final R indices [I>2sigma(I)]	R1 = 0.0315, wR2 = 0.0668		
R indices (all data)	R1 = 0.0414, wR2 = 0.0711		
Largest diff. peak and hole	2.125 and -1.495 e.Å ⁻³		
Bond Lengths (Å)			
Hg(1)-O(1)	2.271(3)	C(3)-C(4)	1.384(5)
Hg(1)-N(1)#1	2.272(3)	C(5)-C(6)	1.380(5)
Hg(1)-O(3)	2.285(3)	C(7)-C(8)	1.381(6)
Hg(1)-P(1)	2.3656(9)	C(7)-C(12)	1.394(5)
P(1)-C(13)	1.809(4)	C(8)-C(9)	1.385(6)
P(1)-C(7)	1.810(4)	C(9)-C(10)	1.390(6)
P(1)-C(1)	1.839(4)	C(10)-C(11)	1.375(6)
F(1)-C(20)	1.326(5)	C(11)-C(12)	1.382(5)
F(2)-C(20)	1.332(5)	C(13)-C(14)	1.390(6)
F(3)-C(20)	1.342(5)	C(13)-C(18)	1.392(6)

Table B.24. (continued)

F(4)-C(22)	1.324(7)	C(14)-C(15)	1.387(6)
F(5)-C(22)	1.328(6)	C(15)-C(16)	1.378(6)
F(6)-C(22)	1.315(7)	C(16)-C(17)	1.381(7)
O(1)-C(19)	1.246(5)	C(17)-C(18)	1.383(7)
O(2)-C(19)	1.225(4)	C(19)-C(20)	1.548(6)
O(3)-C(21)	1.255(6)	C(21)-C(22)	1.538(7)
O(4)-C(21)	1.207(6)	O(5)-C(23)	1.382(8)
N(1)-C(4)	1.340(5)	O(5)-C(25A)	1.451(9)
N(1)-C(6)	1.347(5)	O(5)-C(25)	1.451(8)
N(1)-Hg(1)#1	2.272(3)	C(23)-C(24)	1.480(9)
C(1)-C(2)	1.511(5)	C(25)-C(26)	1.497(12)
C(2)-C(5)	1.386(5)	C(25A)-C(26A)	1.497(12)
C(2)-C(3)	1.392(5)		

Bond Angles (°)

O(1)-Hg(1)-N(1)#1	82.68(10)	C(11)-C(12)-C(7)	120.1(4)
O(1)-Hg(1)-O(3)	87.65(13)	C(14)-C(13)-C(18)	119.4(4)
N(1)#1-Hg(1)-O(3)	95.20(12)	C(14)-C(13)-P(1)	119.6(3)
O(1)-Hg(1)-P(1)	131.56(8)	C(18)-C(13)-P(1)	121.0(3)
N(1)#1-Hg(1)-P(1)	128.17(8)	C(15)-C(14)-C(13)	120.2(4)
O(3)-Hg(1)-P(1)	119.51(8)	C(16)-C(15)-C(14)	120.2(4)
C(13)-P(1)-C(7)	110.12(17)	C(15)-C(16)-C(17)	119.7(4)
C(13)-P(1)-C(1)	107.64(19)	C(16)-C(17)-C(18)	120.8(4)
C(7)-P(1)-C(1)	104.85(17)	C(17)-C(18)-C(13)	119.7(4)
C(13)-P(1)-Hg(1)	112.04(13)	O(2)-C(19)-O(1)	129.9(4)
C(7)-P(1)-Hg(1)	111.84(13)	O(2)-C(19)-C(20)	118.2(4)
C(1)-P(1)-Hg(1)	110.02(12)	O(1)-C(19)-C(20)	111.9(3)
C(19)-O(1)-Hg(1)	115.1(2)	F(1)-C(20)-F(2)	107.8(4)
C(21)-O(3)-Hg(1)	106.9(3)	F(1)-C(20)-F(3)	105.7(3)
C(4)-N(1)-C(6)	118.6(3)	F(2)-C(20)-F(3)	106.6(4)
C(4)-N(1)-Hg(1)#1	122.6(3)	F(1)-C(20)-C(19)	112.2(4)
C(6)-N(1)-Hg(1)#1	118.8(2)	F(2)-C(20)-C(19)	113.4(3)
C(2)-C(1)-P(1)	110.9(3)	F(3)-C(20)-C(19)	110.6(3)
C(5)-C(2)-C(3)	117.7(3)	O(4)-C(21)-O(3)	128.1(5)
C(5)-C(2)-C(1)	120.3(3)	O(4)-C(21)-C(22)	116.3(5)
C(3)-C(2)-C(1)	122.0(3)	O(3)-C(21)-C(22)	115.5(5)
C(4)-C(3)-C(2)	119.9(4)	F(6)-C(22)-F(4)	107.9(5)
N(1)-C(4)-C(3)	121.9(4)	F(6)-C(22)-F(5)	106.3(5)
C(6)-C(5)-C(2)	119.7(4)	F(4)-C(22)-F(5)	106.0(5)
N(1)-C(6)-C(5)	122.3(4)	F(6)-C(22)-C(21)	112.9(5)
C(8)-C(7)-C(12)	119.8(4)	F(4)-C(22)-C(21)	113.5(5)
C(8)-C(7)-P(1)	120.3(3)	F(5)-C(22)-C(21)	109.8(4)

Table B.24. (continued)

C(12)-C(7)-P(1)	119.8(3)	C(23)-O(5)-C(25A)	98.6(8)
C(7)-C(8)-C(9)	119.8(4)	C(23)-O(5)-C(25)	125.3(7)
C(8)-C(9)-C(10)	120.3(4)	O(5)-C(23)-C(24)	111.5(5)
C(11)-C(10)-C(9)	119.8(4)	O(5)-C(25)-C(26)	112.1(9)
C(10)-C(11)-C(12)	120.2(4)	O(5)-C(25A)-C(26A)	96.1(10)

*Symmetry transformations used to generate equivalent atoms: #1 -x+1/2,-y+1/2,-z.

APPENDIX C

General Considerations

All experiments were performed under nitrogen atmosphere using Schlenk techniques. All air and light sensitive compounds were stored and handled in an inert atmosphere glovebox and used as received. All solvents were reagent-grade and distilled under inert atmosphere from the appropriate drying agent right before use. More specific details have been indicated on the experimental section of the appropriate chapter.

Synthetic Procedures

All experiments were performed under nitrogen atmosphere using Schlenk techniques. All air and light sensitive compounds were stored and handled in an inert atmosphere glovebox and used as received. All solvents were reagent-grade and distilled under inert atmosphere from the appropriate drying agent right before use.

Spectroscopic Characterization

Infrared spectra for compound **4.1** – **4.4** and for the corresponding starting materials were recorded in KBr pellets on a Thermo Nicolet Nexus 870 instrument (FT-IR *E.S.P.* System). The spectra are found in APPEDIX D. ^1H and ^{31}P NMR spectra were recorded at 499.78 and 202.31 MHz respectively, at 25.0 °C / 298.1 K MHz, using a Varian VNMRs 500 MHz Spectrometer. UV–Vis absorption data were acquired on a Varian Cary Bio spectrophotometer. Details for the samples preparation are indicated on the experimental section of the appropriate chapter.

APPENDIX D

FT-IR Spectra

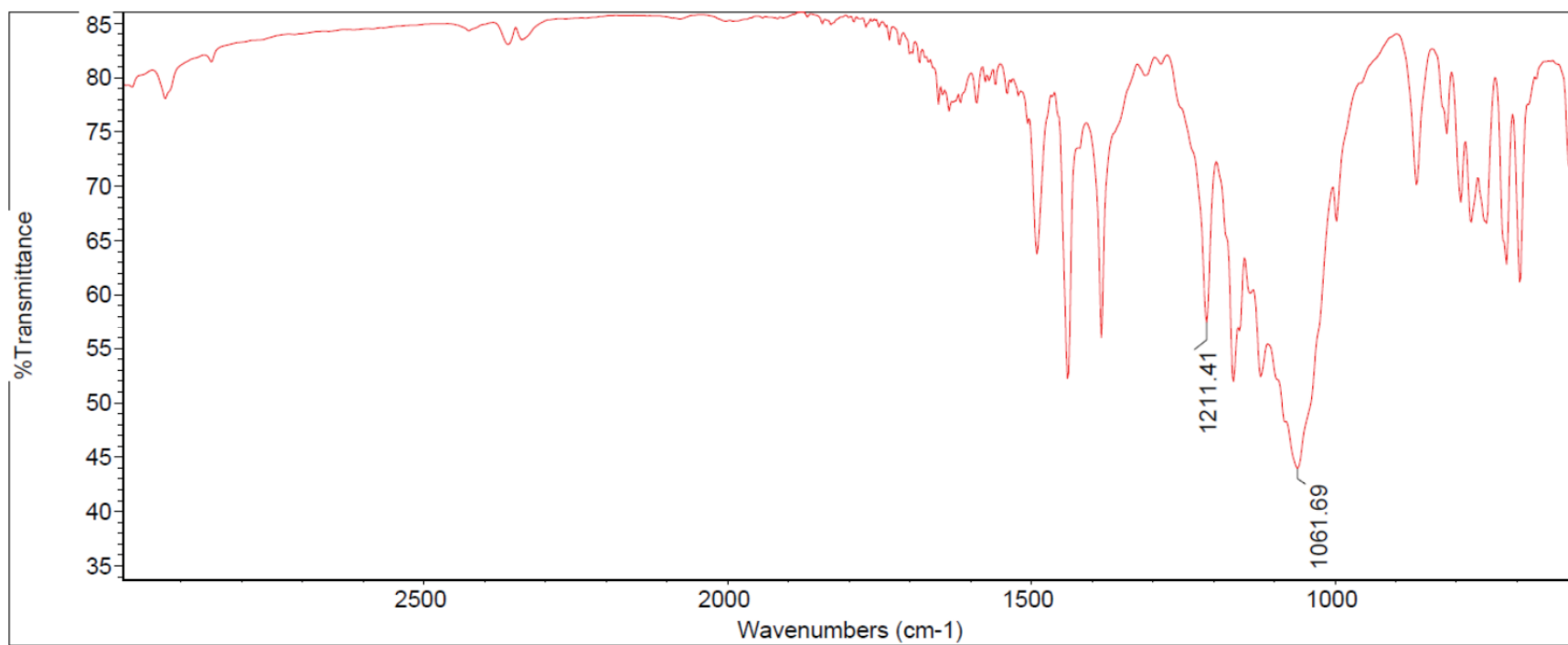


Figure D1. FT-IR spectrum of compound **4.1**.

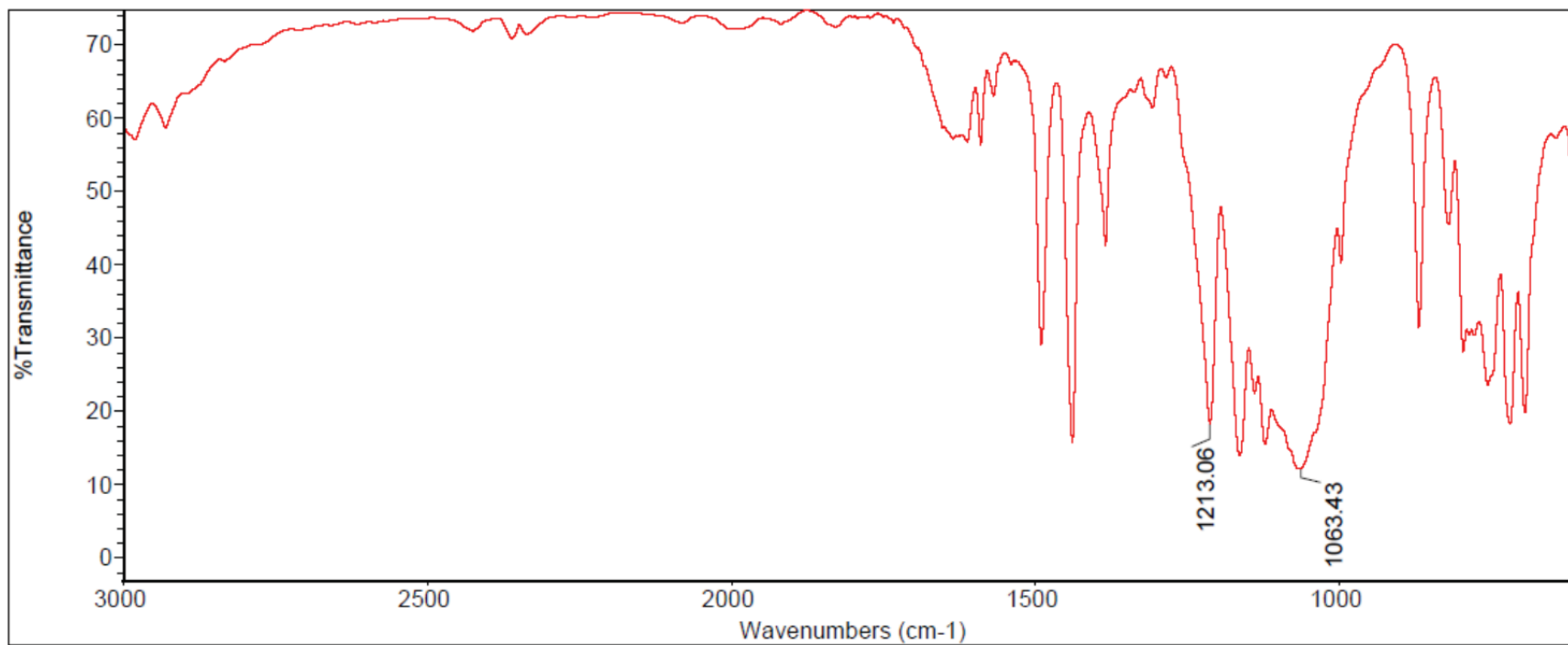


Figure D2. FT-IR spectrum of compound **4.2**.

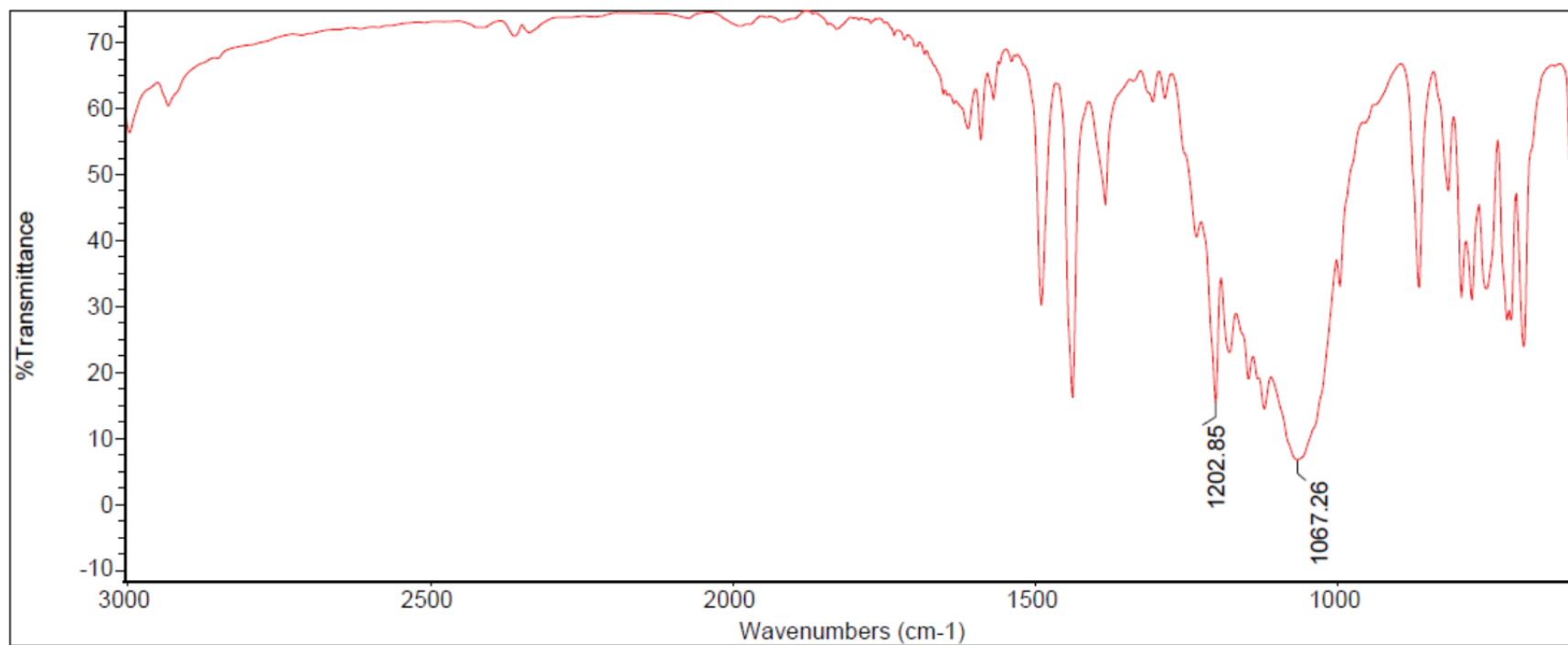


Figure D3. FT-IR spectrum of compound **4.3**.

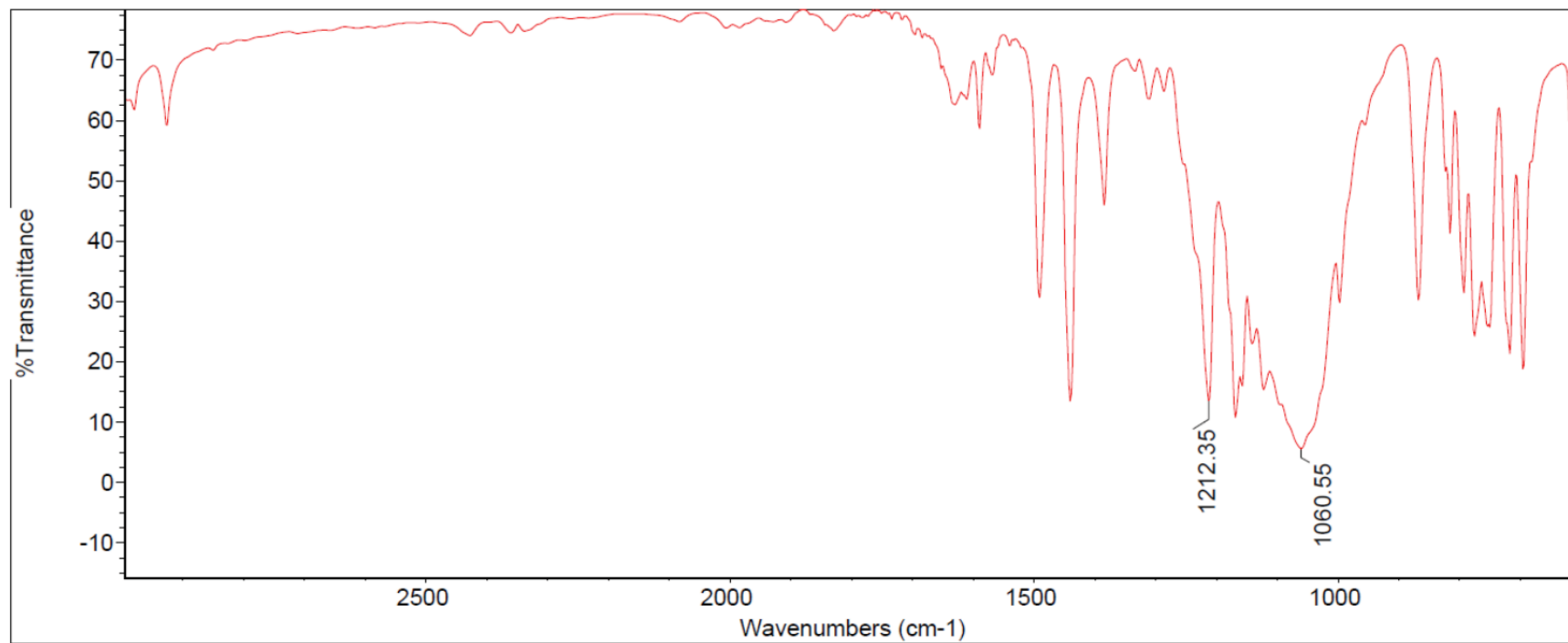


Figure D4. FT-IR spectrum of compound **4.4**.

UV-Vis Spectra

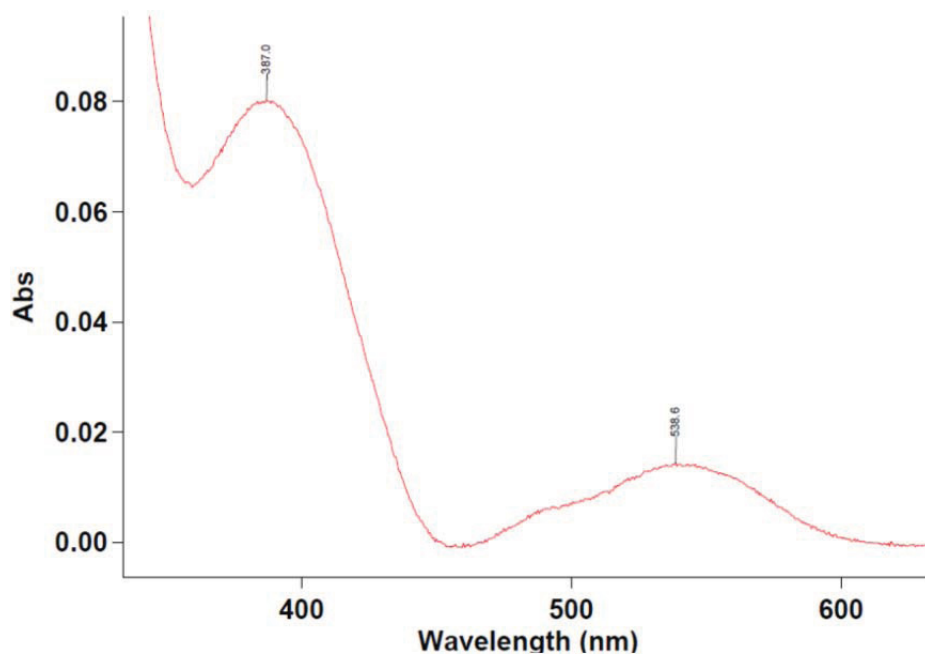


Figure D5. UV-Vis spectrum of compound **4.1** at room temperature and 4×10^{-4} M in CH_3CN .

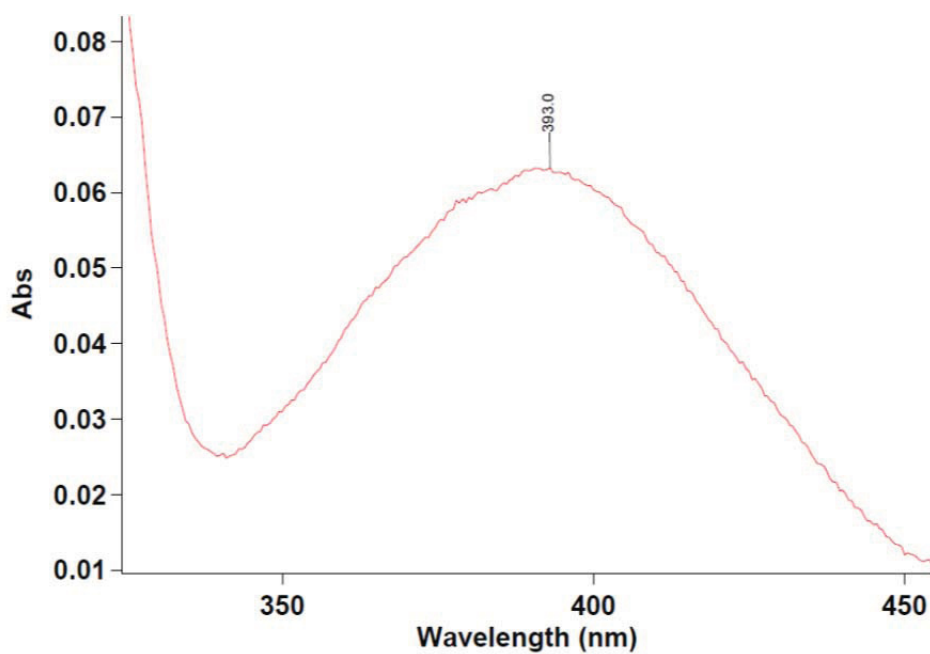


Figure D6. UV-Vis spectrum of compound **4.2** at room temperature and 4×10^{-4} M in CH_3CN .

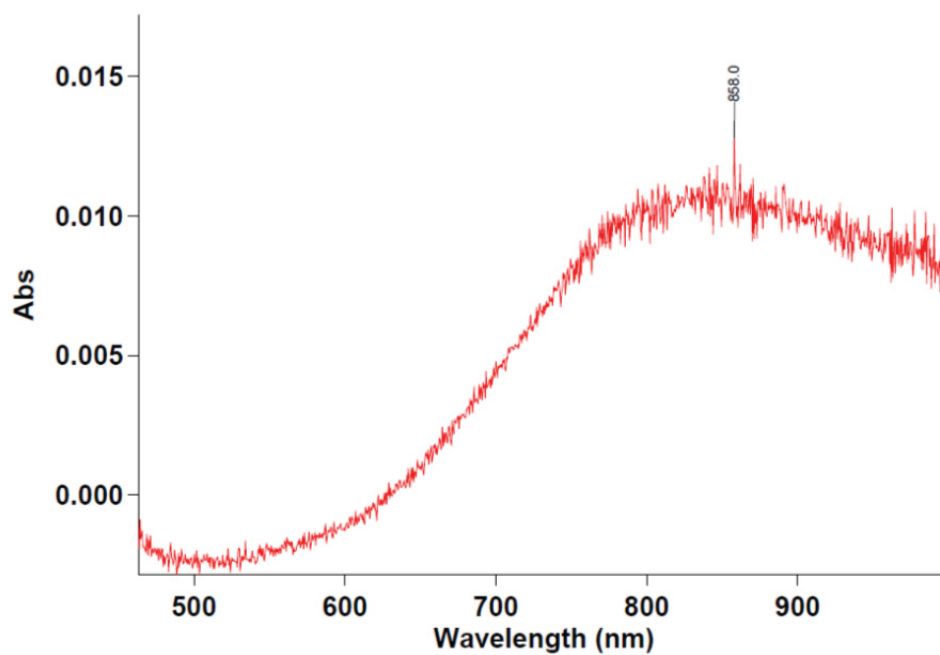


Figure D7. UV-Vis spectrum of compound **4.3** at room temperature and 4×10^{-4} M in CH_3CN .

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