

# Synthesis and structural characterization of Zn<sup>2+</sup>, Cd<sup>2+</sup> and Hg<sup>2+</sup> complexes with tripyrrolidinophosphine chalcogenides

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## Abstract

Six new complexes of zinc(II), cadmium(II) and mercury(II) chlorides with tripyrrolidinophosphine chalcogenides of the types  $[MCl_2(Pyrr_3PE)_2]$  ( $M = Zn, E = S$  (**1**) or  $E = Se$  (**2**);  $M = Cd, E = S$  (**3**) or  $E = Se$  (**4**)) and  $[\{HgCl(Pyrr_3PE)\}_2(\mu-Cl)_2]$  ( $E = S$  (**5**) or  $Se$  (**6**)) have been prepared in yields of 66-92% by reaction of the ligands with metal chloride in ethanol and characterized by <sup>1</sup>H and <sup>31</sup>P NMR, IR, elemental analysis, conductivity, and single crystal X-ray diffraction analysis. The results show that the complexes are pseudo tetrahedral containing coordinated chloride atoms. Interestingly, the X-ray studies reveal that whilst the title ligands produce dinuclear complexes with mercury, their Cd and Zn complexes are mononuclear. The tetrahedral bond angles vary from 85.69(5)° to 126.25(4)° in the dinuclear complexes **5** and **6** and from 93.51(3)° to 117.38(3)° in mononuclear species **2-4**. The P=E bond lengths are in the range 1.999(9)-2.198(2) Å. The coordination properties of the title ligands are discussed and compared to those obtained for their bulkier counterparts.

**Keywords:** Phosphine chalcogenides, Pyrrolidine, metal complexes, NMR spectroscopy.

## 1. Introduction

Phosphine chalcogenides of the types R<sub>3</sub>PE (E= O, S, Se) have attracted much attention owing to their easy preparation [1-5], high solubility [6,7] and good reactivity toward different metal ions in many organic solvents [6-8]. The stability of these compounds depends

largely on the nature of substituents on the phosphorus [9-11]. Furthermore, renewed interest in the coordination chemistry of such compounds stems from their increasing use as suitable single source precursors for the preparation of metal chalcogenide thin films ME (M= Hg<sup>2+</sup>, Cd<sup>2+</sup> or Zn<sup>2+</sup>; E = S, Se or Te) as well as ME quantum dots [12-15]. However, the coordination chemistry of cyclic amino analogues of the type (R<sub>2</sub>N)<sub>3</sub>PE (R<sub>2</sub>N = piperidine, pyrrolidine, morpholine, etc.) is still much less studied [16-19].

We have previously shown that whilst piperidine containing bidentate ligands MeN(Pip<sub>2</sub>PE)<sub>2</sub> (Pip = piperidiny, E= S or Se) [20] form mononuclear complexes, analogous monodentate ligands, Pip<sub>3</sub>PE (Pip = piperidiny, E = S or Se), produce dinuclear complexes [21]. More recently, we investigated the generality of this observation using the oxide analogue, Pip<sub>3</sub>PO, and showed that it forms mononuclear complexes [22], in contrast to dinuclear adducts obtained with its above mentioned sulfide and selenide counterparts, Pip<sub>3</sub>PE [21].

For the purpose of comparison with mercury, cadmium and zinc chloride chemistry with Pip<sub>3</sub>PE, we have investigated the chemistry of the same metal chlorides towards two pyrrolidine (Pyrr) containing ligands, Pyrr<sub>3</sub>PS and Pyrr<sub>3</sub>PSe, which would also allow studying the effect of such smaller ligands on the nuclearity of the resulting complexes. This paper reports the synthesis, characterization and structural features of mercury(II), cadmium(II) and zinc(II) chloride complexes with tripyrrolinophosphine chalcogenides.

## 2- Experimental

### 2.1 General experimental procedures

PCl<sub>3</sub> (Fluka), pyrrolidine (Fluka), ZnCl<sub>2</sub> (Merck), CdCl<sub>2</sub> (Merck) and HgCl<sub>2</sub> (Merck) were used as received. All reactions were carried out under a nitrogen atmosphere in solvents dried by standard techniques and stored over molecular sieves [23]. The ligands Pyrr<sub>3</sub>PE (E= S [24] or Se [25]) were prepared and purified according to literature methods.

### 2.2 Instrumentation

NMR spectra were recorded on a Bruker AC-300 spectrometer in CDCl<sub>3</sub>, <sup>31</sup>P{<sup>1</sup>H} at 121 MHz (85% H<sub>3</sub>PO<sub>4</sub>), and <sup>1</sup>H at 300 MHz. IR spectra were obtained using a YL 2000 FT-

IR spectrometer in  $\text{CHCl}_3$  solutions. The conductivity measurements were carried out for  $10^{-3}$  M solutions of the complexes dissolved in dichloromethane (dried over molecular sieves).

### **2.3 General procedure for the preparation of complexes 1-6**

To a stirred solution of metal chloride (1 mmol for Zn (0.14 g) or Cd (0.23 g) and 2 mmol for Hg (0.54 g)) in ethanol (20 mL) was added the ligand 2 mmol (0.55 g for  $\text{Pyrr}_3\text{P}=\text{S}$  or 0.64 g for  $\text{Pyrr}_3\text{P}=\text{Se}$ ) in anhydrous dichloromethane (5 mL). The reaction mixture was stirred at room temperature for 12 h and concentrated *in vacuo* to give an oil residue. The oil was washed with dry diethyl ether (3x30 mL) to give more viscous oil. A solid was obtained upon addition of dry hexane or petroleum ether to this oil and cooling in the fridge overnight led to further precipitation of the complex. This was filtered, washed with hexane and dried under vacuum for several hours to give brown to yellow solids, which upon recrystallization in a DCM-hexane mixture gave colourless solids.

Suitable crystals for X-ray analysis were obtained by slow evaporation from DCM for **2** and **5**, whilst **3**, **4**, and **6** were grown by solvent diffusion (DCM and hexane).

#### **2.3.1 Dichlorobis(tripyrrolidinophosphine sulfide)zinc(II) (1)**

Yield = 0.39 g (57%),  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ):  $\delta$  (ppm) 1.87 (m, 4H, N- $\text{CH}_2\text{-CH}_2$ ), 3.24 (m, 4H, N- $\text{CH}_2\text{-CH}_2$ ).  $^{31}\text{P}$  NMR (121 MHz,  $\text{CDCl}_3$ ):  $\delta$  (ppm) 60.81. IR ( $\text{CHCl}_3$ ):  $\nu$  2964, 2870, 1456, 1207, 1085, 1010, 916, 747, 633 (P=S), 545  $\text{cm}^{-1}$ .  $\Lambda_{\text{M}} = 19.0 \text{ } \Omega^{-1} \cdot \text{m}^2 \cdot \text{mol}^{-1}$ . Anal calcd. for  $\text{C}_{24}\text{H}_{48}\text{Cl}_2\text{N}_6\text{P}_2\text{S}_2\text{Zn}$ , C, 42.20; H, 7.08; N, 12.30. Found; C, 42.83; H, 7.20; N, 12.

#### **2.3.2 Dichlorobis(tripyrrolidinophosphine selenide)zinc(II) (2)**

Yield = 0.60 g (77%), m.p = 97 °C,  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ):  $\delta$  (ppm) 1.90 (m, 4H, N- $\text{CH}_2\text{-CH}_2$ ), 3.25 (m, 4H, N- $\text{CH}_2\text{-CH}_2$ ).  $^{31}\text{P}$  NMR (121 MHz,  $\text{CDCl}_3$ ):  $\delta$  (ppm) 55.58. IR ( $\text{CHCl}_3$ ):  $\nu$  2972, 2866, 1446, 1206, 1070, 1013, 913, 740, 585 (P=Se), 537  $\text{cm}^{-1}$ .  $\Lambda_{\text{M}} = 14.0 \text{ } \Omega^{-1} \cdot \text{m}^2 \cdot \text{mol}^{-1}$ . Anal calcd. For  $\text{C}_{24}\text{H}_{48}\text{Cl}_2\text{N}_6\text{P}_2\text{Se}_2\text{Zn}$ , C, 37.11; H, 6.23; N, 10.82. Found; C, 36.90; H, 6.34; N, 10.97.

#### **2.3.3 Dichlorobis(tripyrrolidinophosphine sulfide)cadmium(II) (3)**

Yield = 0.51 g (66%), m.p = 101 °C,  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ):  $\delta$  (ppm) 1.80 (m, 4H, N- $\text{CH}_2\text{-CH}_2$ ), 3.15 (m, 4H, N- $\text{CH}_2\text{-CH}_2$ ).  $^{31}\text{P}$  NMR (121 MHz,  $\text{CDCl}_3$ ):  $\delta$  (ppm) 63.24. IR ( $\text{CHCl}_3$ ):  $\nu$  2965, 2863, 1450, 1200, 1085, 1010, 910, 747, 619 (P=S), 544

$\text{cm}^{-1}$ .  $\Lambda_M = 1.03 \text{ } \Omega^{-1} \cdot \text{m}^2 \cdot \text{mol}^{-1}$ . Anal calcd. for  $\text{C}_{24}\text{H}_{48}\text{CdCl}_2\text{N}_6\text{P}_2\text{S}_2$ : C, 39.48; H, 6.63; N, 11.51. Found; C, 40.02; H, 6.71; N, 11.88.

#### **2.3.4 Dichlorobis(tripyrrolidinophosphine selenide)cadmium(II) (4)**

Yield = 0.68 g (79%), m.p = 120 °C,  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ):  $\delta$  (ppm) 1.83 (m, 4H, N- $\text{CH}_2\text{-CH}_2$ ), 3.20 (m, 4H, N- $\text{CH}_2\text{-CH}_2$ ).  $^{31}\text{P}$  NMR (121 MHz,  $\text{CDCl}_3$ ):  $\delta$  (ppm) 56.68; IR ( $\text{CHCl}_3$ );  $\nu$  2964, 2863, 1457, 1200, 1078, 909, 855, 734, 578 (P=Se),  $531 \text{ cm}^{-1}$ .  $\Lambda_M = 4.37 \text{ } \Omega^{-1} \cdot \text{m}^2 \cdot \text{mol}^{-1}$ . Anal calcd. for  $\text{C}_{24}\text{H}_{48}\text{CdCl}_2\text{N}_6\text{P}_2\text{S}_2$ , C, 34.99; H, 5.87; N, 10.20. Found; C, 35.34; H, 5.96; N, 9.89.

#### **2.3.5 Di- $\mu$ -chlorido-bis-[chlorido-(tripyrrolidinophosphine sulfide)mercury(II)] (5)**

Brown solid, yield = 2.0 g (92%), m.p = 94 °C,  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ):  $\delta$  (ppm) 1.93 (m, 4H, N- $\text{CH}_2\text{-CH}_2$ ), 3.35 (m, 4H, N- $\text{CH}_2\text{-CH}_2$ ).  $^{31}\text{P}$  NMR (121 MHz,  $\text{CDCl}_3$ ):  $\delta$  (ppm) 60.02. IR ( $\text{CHCl}_3$ );  $\nu$  2968, 2861, 1444, 1201, 1083, 1010, 909, 740, 612 (P=S),  $542 \text{ cm}^{-1}$ .  $\Lambda_M = 27.4 \text{ } \Omega^{-1} \cdot \text{m}^2 \cdot \text{mol}^{-1}$ . Anal calcd. for  $\text{C}_{24}\text{H}_{48}\text{Cl}_4\text{Hg}_2\text{N}_6\text{P}_2\text{S}_2$ , C, 26.45; H, 4.44; N, 7.71. Found; C, 26.21; H, 4.53; N, 7.46.

#### **2.3.6 Di- $\mu$ -chlorido-bis-[chlorido-(tripyrrolidinophosphine selenide)mercury(II)] (6)**

White solid, yield = 2.06 g (87%), m.p = 129 °C,  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ):  $\delta$  (ppm) 1.85(m, 4H, N- $\text{CH}_2\text{-CH}_2$ ), 3.20(m, 4H, N- $\text{CH}_2\text{-CH}_2$ ).  $^{31}\text{P}$  NMR (121 MHz,  $\text{CDCl}_3$ ):  $\delta$  (ppm) 53.18. IR ( $\text{CHCl}_3$ );  $\nu$  2958, 2863, 1450, 1207, 1085, 1010, 909, 855, 734, 558 (P=Se)  $\text{cm}^{-1}$ .  $\Lambda_M = 10.3 \text{ } \Omega^{-1} \cdot \text{m}^2 \cdot \text{mol}^{-1}$ . Anal calcd. for  $\text{C}_{24}\text{H}_{48}\text{Cl}_4\text{Hg}_2\text{N}_6\text{P}_2\text{Se}_2$ , C, 24.36; H, 4.09; N, 7.10. Found; C, 24.11; H, 4.16; N, 6.95.

### **2.4 Crystal structure determinations**

X-ray analyses for **4** and **6** were performed at 173 K using a Rigaku SCX-Mini diffractometer and for **2**, **3** and **5** using a Rigaku FRX (dual port) rotating anode / confocal optic high brilliance generator with Dectris P200 detector at 173 K. Intensity data were collected using  $\omega$  steps accumulating area detector images spanning at least a hemisphere of reciprocal space. All data were collected with Mo- $\text{K}\alpha$  radiation ( $\lambda = 0.71075 \text{ \AA}$ ) and corrected for Lorenz and polarization effects. The data for all compounds were collected and processed using CrystalClear (Rigaku) [26]. The structures were solved using dual space methods (SHELXT) [27] and refined using full matrix least square techniques (SHELXL) [28]. All non-hydrogen atoms were refined anisotropically and hydrogen atoms were placed geometrically using the riding model. All calculations for structures **2-4** were performed using Olex 2 [29] and CrystalStructure [30] was used for structures **5** and **6** (Table 1). The structures show high thermal motion potential disorder in the periphery of one of the pyrrolidine rings, this is

particularly obvious for **5** and **6**. No attempt was made to model this disorder. The structures allow the gross geometry at the metal centres to be determined and only that aspect is discussed below. **5**  $P2_1/n$ ,  $a = 10.5885(13)$ ,  $b = 10.0546(12)$ ,  $c = 16.986(2)$  Å,  $\beta = 99.464(4)$  U= 1783.8(4) Å<sup>3</sup>,  $R_1 = 0.0368$ . **6**  $P2_1/n$ ,  $a = 10.1806(7)$ ,  $b = 18.1187(12)$ ,  $c = 10.1697(7)$  Å,  $\beta = 99.464(4)$  U= 105.391(5) Å<sup>3</sup>,  $R_1 = 0.0323$

**Table 1**

### **3 Results and discussion**

#### **3.1 Synthesis**

1:2 (Metal:ligand) adducts of the type  $[MCl_2(Pyrr_3PE)_2]$  for M = Zn or Cd (**1-4**) and 1:1 adducts  $[MCl_2(Pyrr_3PE)]_2$  for M = Hg (**5** and **6**) were obtained by reaction of metal chloride in ethanol with Pyrr<sub>3</sub>PE in dichloromethane (Schemes 1 and 2). It is worth noting that the 1:1 adducts  $[MCl_2(Pyrr_3PE)]_2$  (**5** and **6**) are constantly obtained even when 1:3 (metal:ligand) molar ratios were used. These complexes were initially purified by addition of dry diethyl ether followed by addition of hexane or petroleum ether, which led to precipitation of the complexes as brown to yellow solids. These were further recrystallized in hexane-DCM mixture to give colourless solids. They are partially soluble in dichloromethane and chloroform. The non-electrolytic nature of these complexes was confirmed by conductivity measurements (see experimental). The relatively higher values observed for zinc (**1** and **2**) and mercury (**5** and **6**) complexes are presumably due to better solubility of these complexes in dichloromethane and/or extensive dissociation in this solvent compared to cadmium complexes **3** and **4**, consistent with our previous results on closely related complexes [21].

#### **Scheme 1**

#### **Scheme 2**

#### **3.2 Spectroscopic characterization**

The metal complexes **1-6** were characterized by NMR and IR spectroscopic techniques (Figs.S1-24: see Supplementary Information); the corresponding data are shown in Table 2. For instance, the  $\nu(P=S)$  and  $\nu(P=Se)$  infrared absorption bands observed for ligands are, as expected, shifted towards lower wave numbers, on coordination to the metal ion. The

coordination shift ( $\Delta\nu_{(P=E)}$ ) is attributed to a lowering of the P=E bond order in the complexes. This shift decreases with decreasing metal softness from Hg to Cd to Zn and is in line with the soft nature of the title ligands, suggesting as expected weaker interaction down the series (see table 2). The smaller shifts of the selenides as compared to sulfides are consistent with the difference observed between P=O and P=S absorption upon coordination in related complexes [22,31] and are reasonable since the vibrations involving the relatively heavy sulfur or selenium atom would be less sensitive to coordination than those with the lighter oxygen atom. In contrast, the increase in the frequency of the P-N vibration range (909-1087 vs. 850-1080  $\text{cm}^{-1}$  in the free ligands) suggests that the nitrogen atoms are not involved in coordination, in agreement with previously results observed in related systems [21].

The complexes were characterized in solution with NMR spectroscopy. In particular, the  $^{31}\text{P}$  NMR spectra display resonances of bound ligands that are shifted to lower frequencies compared with those of the free ligand. This suggests that the phosphorus nucleus in the complex is placed in a higher electron density environment due to compensation from nitrogen atoms upon coordination through the P=E group, thus providing further evidence that the bonding occurs through the chalcogen atom. Furthermore, the magnitude of the coupling constant  $^1J_{\text{P-Se}}$  for the free ligand is larger than that of the bound one (Table 2). This can be ascribed to the expected weakening of the P=Se bond upon coordination to the metal centre through the selenium atom [33], in fair agreement with the IR data mentioned above. The  $^{31}\text{P}$  NMR coordination shift ( $\Delta\delta^{31}\text{P}$ ) is much more important for the selenide derivatives **6**, **4** and **2** than the sulfide complexes (**5**, **3** and **1**) (Table 2). Such a difference could indicate that the selenide ligands interact in solution more strongly with these ions, as expected for the softer character of selenium compared to sulfur atoms.

It should be noted that the room temperature  $^{31}\text{P}$  NMR spectra of complexes display relatively broad signals (13.36-101 Hz vs. 1.21-2.43 Hz for free ligands) (see Table 2) and no  $^2J(^{31}\text{P-M})$  couplings could be detected for the cadmium and mercury complexes **3-6**. This may be explained by ligand exchange due presumably to complex dissociation in solution at room temperature.

## Table 2

### 3.3 X-ray structures

In order to investigate the constitution of complexes **1-6** and see the effect of switching the ligand structure from Pip<sub>3</sub>PE [21] to the smaller Pyrr<sub>3</sub>PE on the stereochemistry

of these complexes, the solid state structures of complexes **2-6** were analyzed. Unfortunately, attempts to obtain good quality crystals of complex **1** were unsuccessful. Structures of these complexes were thus determined and revealed that Zn and Cd complexes **2, 3 and 4** are mononuclear, whilst those of the partially resolved Hg complexes **5** and **6** are dinuclear species with two bridging chloride ions. Figures 1-5 show the structures of the compounds and the system of numbering of the atoms. Selected bond lengths and angles for **2-4** and cell constants for **5** and **6** are given in Table 3. The geometries of complexes **2-4** are similar, the only difference being the nature of the chalcogen and metal atoms.

**Fig 1**

**Fig 2**

**Fig 3**

**Fig 4**

**Fig 5**

**Table 3**

In the mercury complexes **5** and **6**, one chalcogenide atom of the Pyrr<sub>3</sub>PE ligand, one terminal and two bridging chloride ions coordinate to each metal and the geometry around the mercury center is distorted tetrahedral in a dinuclear form (Figs. 1 and 2), in agreement with the structure observed for mercury chloride complexes with tripiperinophosphine chalcogenides (Pip<sub>3</sub>PE; E = S or Se) [21] and other related mercury chloride and iodide adducts of Ph<sub>3</sub>PSe [34]. In contrast, cadmium and zinc complexes **3, 4** and **2**, are mononuclear species containing two ligands and two chloride ions coordinated to the metal centre (Figs 3-5), similar to the complexes containing the ligands n-Bu<sub>3</sub>PE [14], (Me<sub>2</sub>N)<sub>3</sub>PSe [35], MeN[(Me<sub>2</sub>N)<sub>2</sub>PE]<sub>2</sub> [36] and even the corresponding piperidinyll bidentate ligands MeN(Pip<sub>2</sub>PE)<sub>2</sub> [20], which all exist as mononuclear species. This is, however, in contrast to cadmium and even zinc complexes with Pip<sub>3</sub>PE (E = S or Se), which are all dinuclear species [21]. The difference in nuclearity between cadmium and zinc complexes of Pip<sub>3</sub>PE and Pyrr<sub>3</sub>PE could be interpreted in terms of bulkier piperidinyll groups in the former as compared to pyrrolidinyll ones in the latter ligands. The P-E bond lengths 1.999(9)-2.034(3) Å for P=S and 2.152(16)-2.198(2) Å for P=Se in **4** and **6** are characteristic for P=E double bonds and consistent with values described for related mercury complexes [34]. The P=Se bond in the mercury dinuclear **6** (2.198(2) Å) is slightly longer than that in the mononuclear cadmium complex **4** (2.162 Å). The P=E bond lengths in

complexes **1-6** are longer than that observed for the free ligands. For example, the P=Se bond is significantly lengthened upon complexation when compared to that in the free ligand (2.105(2) Å) [32]. This suggests that the P=E bond is weakened upon complex formation with the singly bonded structure becoming more pronounced down the period [37] with an increasing dipole moment along the series  $P^+—S^- < P^+—Se^-$  [21,38,39]. In addition, the average P-E-M angle varies from 104.37(5)° for Hg-Se-P in **2** to 109.72(4)° for Cd-S-P in **3**. Recently, we have shown that the Cd-O-P angle in the oxide analog of complex **3**, [CdCl<sub>2</sub>(Pyrr<sub>3</sub>PO)<sub>2</sub>], was closer to a linear arrangement (more axial) (156.9(3)°) [22]. This further indicates that the ligands Pyrr<sub>3</sub>PS and Pyrr<sub>3</sub>PSe behave similarly as Pip<sub>3</sub>PE analogues [21] and could be thus classified as  $\pi$ -donors, employing P-E  $\pi$ -bonding electrons for donation, rather than  $\sigma$ -non-bonding electrons (lone pairs) used for coordination in the oxide derivative, in fair agreement with our previous works [14, 21, 22] and with the bonding model proposed by Burford *et al.* [40]. The trends in M-E, P-N and M-Cl bond distances as well as Cl-M-Cl bond angles (Table 3) for complexes **2-6** are all consistent with those observed in our previous work [21] and with literature data on related systems [41-44]. Examination of the solid state packing of the structures reveals no significant intermolecular interactions.

#### 4- Conclusion

New complexes of mercury(II), cadmium(II) and zinc(II) with tripyrrolidinophosphine chalcogenide ligands (Pyrr<sub>3</sub>PE) were synthesized. These complexes were characterized in solution by <sup>1</sup>H and <sup>31</sup>P NMR spectroscopy, and IR and in the solid state by single crystal X-ray analyses. We have shown that whilst analogous Hg, Cd and Zn dinuclear complexes were formed with corresponding piperidinyl counterparts Pip<sub>3</sub>PE, the title ligands Pyrr<sub>3</sub>PE produced dinuclear species only with HgCl<sub>2</sub> and monomeric complexes with CdCl<sub>2</sub> and ZnCl<sub>2</sub>. The dinuclear Hg complexes **5** and **6** are the only species formed even when in a 1:3 (metal:ligand) ratio was used. This was explained in terms of the difference in the bulkiness of the piperidinyl derivatives as compared to pyrrolidinyl ligands. The coordination chemistry of these ligands with other metal ions as well as the use of their complexes **1-6** as single source precursors for the preparation of metal chalcogenide nanoparticles are ongoing.

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## Appendix

CCDC numbers 2076157, 2067378, 2067376, 2067377 and 2076158 contain the supplementary crystallographic data for complexes **5**, **6**, **3**, **4** and **2**, respectively. These data can be obtained free of charge via <http://www.ccdc.cam.ac.uk/conts/retrieving.html>, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax : (+44) 1223-336-033 ; or e-mail : [deposit@ccdc.cam.ac.uk](mailto:deposit@ccdc.cam.ac.uk).

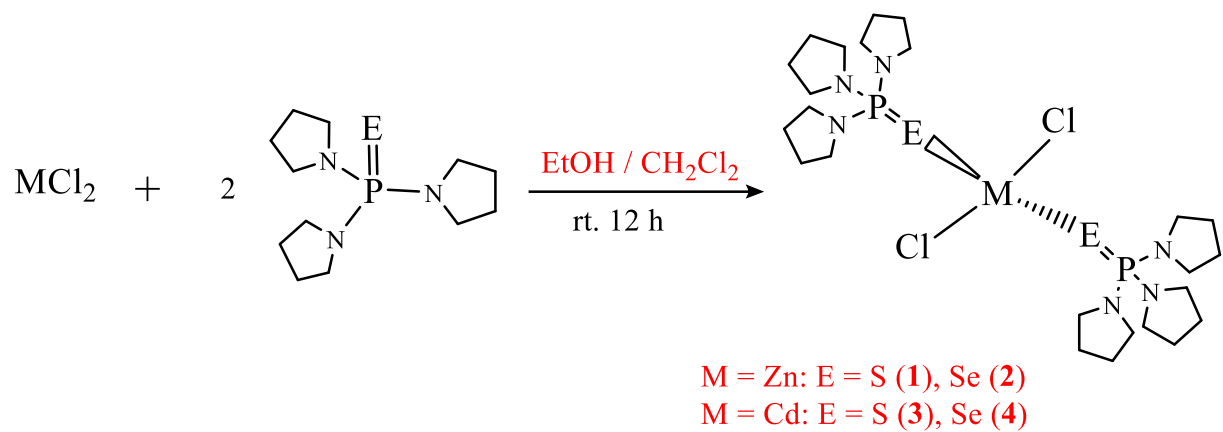
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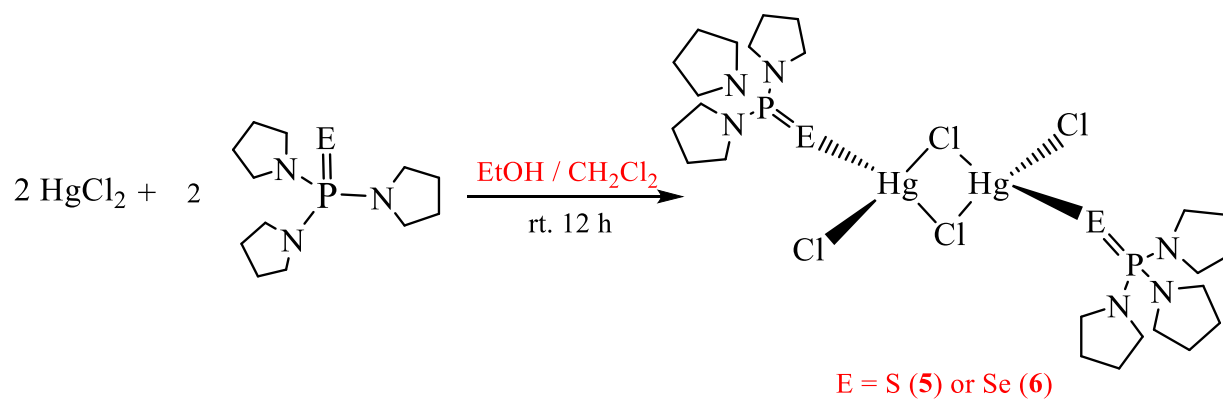
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**Scheme 1**



**Scheme 2**

**Table 1.**Crystallographic data for complexes **2-4**.

Complex data	<b>2</b>	<b>3</b>	<b>4</b>
Temperature (K)	173	173	173
Empirical formula	C <sub>24</sub> H <sub>48</sub> Cl <sub>2</sub> ZnN <sub>6</sub> P <sub>2</sub> Se <sub>2</sub>	C <sub>24</sub> H <sub>48</sub> CdCl <sub>2</sub> N <sub>6</sub> P <sub>2</sub> S <sub>2</sub>	C <sub>24</sub> H <sub>48</sub> CdCl <sub>2</sub> N <sub>6</sub> P <sub>2</sub> Se <sub>2</sub>
Formula weight	776.84	730.07	823.87
Crystal color, Habit	Colorless prism	Colorless prism	Colorless prism
Crystal dimensions (mm)	0.130X0.110X 0.09	0.06x0.06x0.06	0.40x0.21x0.12
Crystal system	monoclinic	monoclinic	monoclinic
a (Å)	15.3828(10)	15.2993(17)	15.5294(6)
b (Å)	11.8225(8)	11.8087(11)	11.8162(5)
c (Å)	18.7594(13)	18.777(2)	19.0264(7)
β (°)	108.742(9)	108.184(3)	108.984(4)
V(Å <sup>3</sup> )	3230.7(4)	3222.9(6)	3301.4(2)
Space group	<i>P2<sub>1</sub>/n</i>	<i>P2<sub>1</sub>/n</i>	<i>P2<sub>1</sub>/n</i>
Z	4	4	4
D <sub>calc</sub> (g/cm <sup>-3</sup> )	1.597	1.504	1.657
F (000)	1584	1512	1656
μ(Mo Kα) (cm <sup>-1</sup> )	3.3034	1.098	3.151
Measured Reflections	32627	43929	40284
R <sub>int</sub>	0.1501	0.0505	0.0286
Observed Reflections	7401	5185	8226
Residuals: R <sub>1</sub> (I >2.0σ(I))	0.0535	0.0312	0.0350
Residuals: wR (All reflections)	0.1295	0.0364	0.0572
Max/Min peak in final difference map (e Å <sup>-3</sup> )	0.94/-0.63	0.82/-0.91	1.09/-0.98

**Table 2.**NMR ( $\delta$ /ppm and J/Hz)<sup>a</sup> and IR ( $\nu$ /cm<sup>-1</sup>) data for complexes **1-6** and their ligands.

Complex	NMR			IR		
	$\delta^{31}\text{P}$	(hw) <sup>b</sup>	( $\Delta\delta^{31}\text{P}$ ) <sup>c</sup>	<sup>1</sup> J <sub>P-Se</sub>	$\nu_{(\text{P}=\text{E})}$	( $\Delta\nu_{(\text{P}=\text{E})}$ ) <sup>d</sup>
Pyrr <sub>3</sub> PS	64.72	(1.22)	-	-	672	-
Pyrr <sub>3</sub> PSe	62.59	(2.43)	-	760	608	-
[ZnCl <sub>2</sub> (Pyrr <sub>3</sub> PS) <sub>2</sub> ] ( <b>1</b> )	60.81	(-)	3.91	-	626	46
[ZnCl <sub>2</sub> (Pyrr <sub>3</sub> PSe) <sub>2</sub> ] ( <b>2</b> )	55.58	(32.80)	7.01	624	567	41
[CdCl <sub>2</sub> (Pyrr <sub>3</sub> PS) <sub>2</sub> ] ( <b>3</b> )	63.24	(53.46)	1.48	-	619	53
[CdCl <sub>2</sub> (Pyrr <sub>3</sub> PSe) <sub>2</sub> ] ( <b>4</b> )	56.68	(101)	5.91	-	578	30
[HgCl <sub>2</sub> (Pyrr <sub>3</sub> PS) <sub>2</sub> ] ( <b>5</b> )	60.02	(-)	4.70	-	612	60
[HgCl <sub>2</sub> (Pyrr <sub>3</sub> PSe) <sub>2</sub> ] ( <b>6</b> )	53.18	(13.36)	9.41	648	558	50

<sup>a</sup> At room temperature in CDCl<sub>3</sub>.<sup>b</sup> hw: half width of the signal in Hz.<sup>c</sup>  $\Delta\delta^{31}\text{P} = [\delta^{31}\text{P}(\text{ligand}) - \delta^{31}\text{P}(\text{complex})]$ .<sup>d</sup>  $\Delta\nu_{(\text{P}=\text{E})} = [\nu_{(\text{P}=\text{E})}(\text{ligand}) - \nu_{(\text{P}=\text{E})}(\text{complex})]$ .**Table 3.**Selected bond lengths (Å) and angles (°) for mononuclear complexes **2-4** and cell constants for dinuclear complexes (**5** and **6**)<sup>a</sup>.

<b>2</b>		<b>3</b>		<b>4</b>	
[ZnCl <sub>2</sub> (Pyrr <sub>3</sub> PSe) <sub>2</sub> ]		[CdCl <sub>2</sub> (Pyrr <sub>3</sub> PS) <sub>2</sub> ]		[CdCl <sub>2</sub> (Pyrr <sub>3</sub> PSe) <sub>2</sub> ]	
Zn(1)-Se(1)	2.514(10)	Cd(1)-S(33)	2.562(7)	Cd(1)-Se(4)	2.653(4)
Zn(1)-Se(2)	2.492(9)	Cd(1)-S(34)	2.575(8)	Cd(1)-Se(5)	2.679(5)
Zn(1)-Cl(1)	2.232(2)	Cd(1)-Cl(4)	2.425(1)	Cd(1)-Cl(2)	2.448(1)
Zn(1)-Cl(2)	2.245(2)	Cd(1)-Cl(5)	2.438(1)	Cd(1)-Cl(3)	2.433(1)
Se(1)-P(1)	2.152(16)	S(33)-P(35)	2.005(1)	Se(4)-P(6)	2.163(8)
Se(2)-P(2)	2.163(18)	S(34)-P(2)	1.999(9)	Se(5)-P(7)	2.160(7)
P-N	1.6318	P-N	1.6328	P-N	1.6346
Se(1)-Zn(1)-Se(2)	93.51(3)	Cl(4)-Cd(1)-Cl(5)	115.30(4)	Se(4)-Cd(1)-Se(5)	93.62(1)
Cl(1)-Zn(1)-Se(1)	115.81(7)	Cl(4)-Cd(1)-S(33)	108.46(4)	Cl(2)-Cd(1)-Se(4)	108.46(3)
Cl(1)-Zn(1)-Se(2)	110.36(6)	Cl(4)-Cd(1)-S(34)	115.06(3)	Cl(3)-Cd(1)-Se(4)	117.38(3)
Cl(2)-Zn(1)-Se(2)	116.05(7)	Cl(5)-Cd(1)-S(33)	115.59(3)	Cl(2)-Cd(1)-Se(5)	115.97(3)
Cl(2)-Zn(1)-Se(1)	105.74(7)	Cl(5)-Cd(1)-S(34)	104.66(3)	Cl(3)-Cd(1)-Se(5)	105.40(3)
Cl(1)-Zn(1)-Cl(2)	113.82(8)	S(33)-Cd(1)-S(34)	96.38(2)	Cl(2)-Cd(1)-Cl(3)	114.47(4)
Zn(1)-Se(1)-P(1)	104.59(5)	Cd(1)-S(33)-P(35)	109.72(4)	Cd(1)-Se(4)-P(6)	107.59(2)
Zn(1)-Se(2)-P(2)	108.36(4)	Cd(1)-S(34)-P(2)	104.98(3)	Cd(1)-Se(5)-P(7)	102.45(2)
N-P-Se	111.396	N-P-S	111.393	N-P-Se	111.203

<sup>a</sup> **5**: .....; **6**: .....

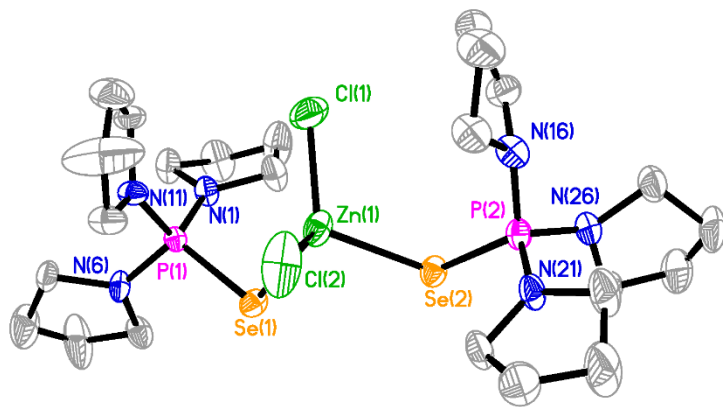


Fig 1.

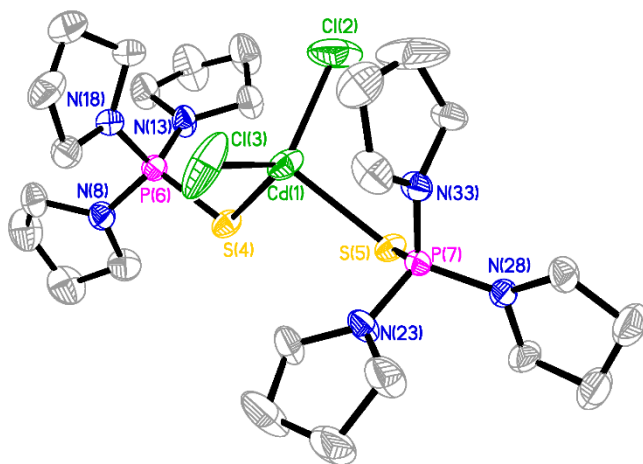


Fig 2.



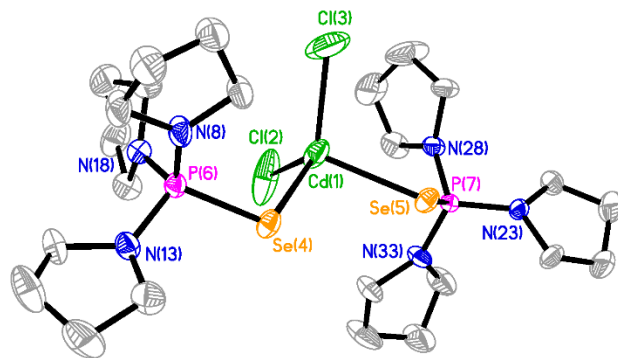


Fig 3.

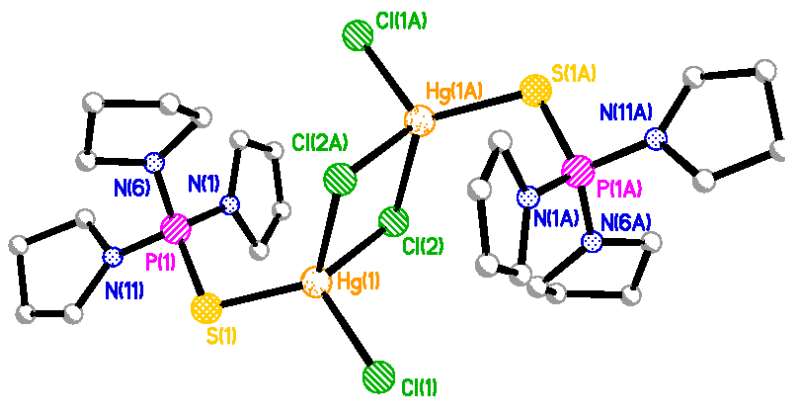


Fig 4.

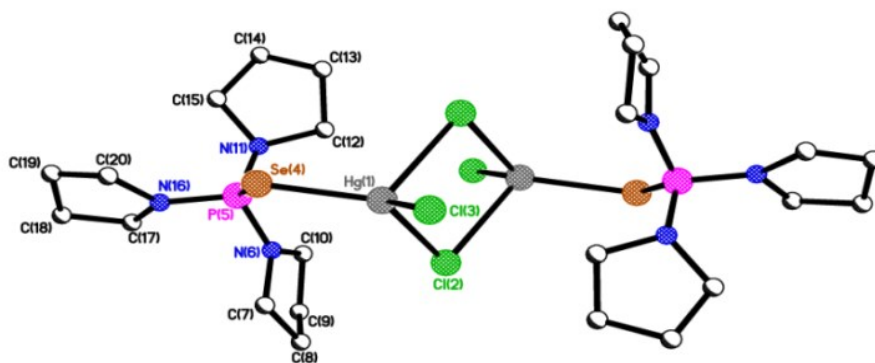


Fig 5.

## Figure captions

**Scheme 1:** Preparation of complexes **1-4**.

**Scheme 2:** Preparation of complexes **5** and **6**.

**Fig 1:** The X-ray crystal structure of  $[\text{ZnCl}_2(\text{Pyrr}_3\text{PSe})_2]$  (**2**), Hydrogens bonded to carbon atoms are omitted for clarity.

**Fig 3:** The X-ray crystal structure of  $[\text{CdCl}_2(\text{Pyrr}_3\text{PS})_2]$  (**3**), Hydrogens bonded to carbon atoms are omitted for clarity.

**Fig 3:** The X-ray crystal structure of  $[\text{CdCl}_2(\text{Pyrr}_3\text{PSe})_2]$  (**4**), Hydrogens bonded to carbon atoms are omitted for clarity.

**Fig 4:** The X-ray crystal structure of  $[\text{HgCl}_2(\text{Pyrr}_3\text{PS})]_2$  (**5**). Hydrogen atoms are omitted for clarity.

**Fig 5:** The X-ray crystal structure of  $[\text{HgCl}_2(\text{Pyrr}_3\text{PSe})]_2$  (**6**), Hydrogen atoms are omitted for clarity.