

Synthesis, characterization, and structural properties of mercury(II), cadmium(II) and zinc(II) tripiperidinophosphine chalcogenide complexes

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Abstract

Reaction of metal chlorides (MCl_2) with tripiperidinophosphine chalcogenides (Pip_3PE) produces new dimer species (**1-6**) of the formula $[MCl_2(Pip_3PE)]_2$ (Pip = piperidinyl; E = S or Se; M = Hg, Cd or Zn). These coordination complexes were characterized by elemental analysis, IR, multinuclear (^{31}P , ^{113}Cd and ^{199}Hg) NMR spectroscopy and single crystal X-ray analysis. Compounds **1-6** exist as centrosymmetric homobimetallic dimers, $[M(\mu-Cl)Cl(Pip_3PE)]_2$. Each dimer incorporates two μ_2 -chloro atoms and two terminal $M-Cl$ bonds. The E atom of Pip_3PE forms terminal $M-E$ bonds {S: 2.305(11); Se: 2.412(6)-2.589(15) Å} and thus the geometry about each metal centre is distorted tetrahedral and the range of tetrahedral bond angles is 102.83(3) to 113.32(3)°. The $P=Se$ bond lengths of 2.183(9)-2.205(2) Å in the selenide complexes are slightly elongated compared to those in the free ligands [2.1090(4) Å]. The results are discussed and compared with those obtained for related analogues.

Keywords: Cadmium, mercury, zinc complex, tripiperidinophosphine chalcogenide, ^{31}P , ^{77}Se and ^{113}Cd NMR .

1. Introduction

Studies into the coordination chemistry of phosphine chalcogenides R_3PE ($E=O, S, Se$) and related compounds have attracted much attention due to their easy preparation, high solubility, and good reactivity toward different metal ions in many organic solvents [1–9]. In

addition, there has been a renewed interest in the coordination chemistry of this class of compounds in view of their increasing use as suitable single-source precursors for the production of binary metal chalcogenide thin films ME (M = Zn, Cd or Hg; E = S, Se or Te) as well as ME quantum dots [10, 11]. There is rather less work on the coordination chemistry of dialkylamino analogues of the type (R₂N)₃PE (R = alkyl), especially those containing cyclic amino moieties such as piperidinyl groups [12, 13]. In this context, we have recently described the synthesis and characterization of tetrahedral metal complexes derived from the bidentate piperidine containing ligands MeN(Pip₂PE)₂ (Pip = piperidinyl, E = S or Se) [14] as well as from the monodentate phosphine chalcogenides n-Bu₃PE (E = O, S or Se) [15]. In both cases, a common feature was that the complexes exist as monomeric species. Here, we report on studies to investigate the generality of this observation by extension of the chemistry to include two monodentate piperidine-containing ligands, Pip₃PS and Pip₃PSe. This paper describes the synthesis, characterization and structural properties of mercury(II) cadmium(II) and zinc(II) chloride complexes with tripiperidinophosphine chalcogenides.

2. Experimental

2.1. General experimental procedures

All preparations were carried out under a nitrogen atmosphere in solvents dried by standard techniques [16] and stored over molecular sieves. PCl₃ (Fluka), piperidine (Fluka), CdCl₂ (Merck) and HgCl₂ (Merck) were used as received.

2.2. Instrumentation

The NMR spectra were recorded on Bruker AC-300 instrument, equipped with a variable temperature unit B-VT-2000 and two probes, CD₂Cl₂ was used as the solvent; ³¹P at 121 MHz (85% H₃PO₄-D₂O), ¹¹³Cd at 66.5 MHz (aq. Cd(NO₃)₂, 2M) and ¹⁹⁹Hg at 53.7 (HgMe₂). The IR spectra were recorded on a Thermo Scientific Nicolet IR200 spectrometer. The conductivity measurements were carried out using 10⁻³ M solutions of the complexes dissolved in acetonitrile (dried on molecular sieves).

2.3. General procedure for the preparation of complexes 1-6

The ligand (Pip₃P(E)) (1 mmol) dissolved in dichloromethane (5 mL) was added dropwise to a stirred solution of the metal chloride (1 mmol) in ethanol (20 mL). The reaction mixture was stirred for 2 h. After solvent evaporation, the solid obtained was washed with anhydrous diethyl ether, dried *in vacuo* and recrystallized from a mixture of hexane-

dichloromethane to give the complexes as white solids which become yellow to orange on storing.

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

2.3.1. $[\text{HgCl}_2(\text{Pip}_3\text{PS})]_2$ (**1**)

Beige solid, yield = 0.60 g (51%). *m.p.* = 180.5 °C. *Anal. Calcd for* $[\text{C}_{30}\text{H}_{60}\text{N}_6\text{P}_2\text{S}_2\text{Hg}_2\text{Cl}_4]$: C, 30.70; H, 5.15; N, 7.16% *found*: C, 30.24; H, 5.46; N, 6.66%. IR: 2947, 2864, 1450, 1071, 583 ($\nu(\text{P}=\text{S})$), 459 cm^{-1} . $\Lambda_{\text{M}}(\Omega^{-1}\cdot\text{cm}^2\cdot\text{mol}^{-1}) = 17.5$.

2.3.2. $[\text{HgCl}_2(\text{Pip}_3\text{PSe})]_2$ (**2**)

Beige solid, yield = 0.63 g (50%). *m.p.* = 203.7 °C. *Anal. Calcd for* $[\text{C}_{30}\text{H}_{60}\text{N}_6\text{P}_2\text{Se}_2\text{Hg}_2\text{Cl}_4]$: C, 28.42; H, 4.77; N, 6.63% *found*: C, 27.85; H, 5.20; N, 6.33%. IR: 2945, 2863, 1450, 1069, 555 ($\nu(\text{P}=\text{Se})$), 450 cm^{-1} . $\Lambda_{\text{M}}(\Omega^{-1}\cdot\text{cm}^2\cdot\text{mol}^{-1}) = 16.7$.

2.3.3. $[\text{CdCl}_2(\text{Pip}_3\text{PS})]_2$ (**3**)

White solid, yield = 0.26 g (26%). *m.p.* = 136.8 °C. *Anal. Calcd for* $[\text{C}_{30}\text{H}_{60}\text{N}_6\text{P}_2\text{S}_2\text{Cd}_2\text{Cl}_4]$: C, 36.12; H, 6.06; N, 8.42% *found*: C, 35.81; H, 6.46; N, 7.91%. IR: 2950, 2869, 1448, 575 ($\nu(\text{P}=\text{S})$), 492 cm^{-1} . $\Lambda_{\text{M}}(\Omega^{-1}\cdot\text{cm}^2\cdot\text{mol}^{-1}) = 4.5$.

2.3.4. $[\text{CdCl}_2(\text{Pip}_3\text{PSe})]_2$ (**4**)

White solid, yield = 0.63 g (58%). *m.p.* = 196.2 °C. *Anal. Calcd for* $[\text{C}_{30}\text{H}_{60}\text{N}_6\text{P}_2\text{Se}_2\text{Cd}_2\text{Cl}_4]$: C, 33.02; H, 5.54; N, 7.70% *found*: C, 3.51; H, 5.57; N, 7.22%. IR: 2948, 2864, 1450, 558 ($\nu(\text{P}=\text{Se})$), 492 cm^{-1} . $\Lambda_{\text{M}}(\Omega^{-1}\cdot\text{cm}^2\cdot\text{mol}^{-1}) = 2.6$.

2.3.5. $[\text{ZnCl}_2(\text{Pip}_3\text{PS})]_2$ (**5**)

Beige solid, yield = 0.63 g (70%). *m.p.* = 168.2 °C. *Anal. Calcd for* $[\text{C}_{30}\text{H}_{60}\text{N}_6\text{P}_2\text{S}_2\text{Zn}_2\text{Cl}_4]$: C, 39.88; H, 6.69; N, 9.30% *found*: C, 39.47; H, 7.03; N, 8.95%. IR: 2944, 2863, 1642, 1075, 569 ($\nu(\text{P}=\text{S})$), 476 cm^{-1} . $\Lambda_{\text{M}}(\Omega^{-1}\cdot\text{cm}^2\cdot\text{mol}^{-1}) = 8.6$.

2.3.6. $[\text{ZnCl}_2(\text{Pip}_3\text{PSe})]_2$ (**6**)

Grey solid, yield = 0.36 g (37%). *m.p.* = 125.5 °C. *Anal. Calcd for* $[\text{C}_{30}\text{H}_{60}\text{N}_6\text{P}_2\text{Se}_2\text{Zn}_2\text{Cl}_4]$: C, 39.24; H, 6.59; N, 9.15% *found*: C, 39.14; H, 6.95; N, 8.58%. IR: 2997, 2946, 2861, 1638, 1067, 558 ($\nu(\text{P}=\text{Se})$), 496 cm^{-1} . $\Lambda_{\text{M}}(\Omega^{-1}\cdot\text{cm}^2\cdot\text{mol}^{-1}) = 16.34$.

2.4. Crystal structure determinations

X-ray analyses for **5** was performed using a Rigaku sealed tube generator and a Saturn 724 detector at 173 K and for **2**, **4** and **6** using a Rigaku FRX (dual port) rotating anode/confocal optic high brilliance generator with Dectris P200 detectors at 93 K for **2** and

4, but 173 k for **6** for. Intensity data for all experiments were collected using ω steps accumulating area detector images spanning at least a hemisphere of reciprocal space. All data were collected with Mo-K α radiation ($\lambda = 0.71075 \text{ \AA}$) and corrected for Lorentz and polarization effects. The data for all compounds were collected and processed using CrystalClear (Rigaku) [17]. The crystal structures were all solved using dual space methods (SHELXT) [18] and refined using full matrix least square techniques (SHELEXT) [19]. All non-hydrogen atoms were refined anisotropically and hydrogen atoms were placed geometrically using the riding model. All calculations for structures **2** and **4** were performed using Olex 2 [20] and CrystalStructure [21] was used for structures **5** and **6** (Table 1). As well as being isomorphous, the four structures even exhibited very similar disorder. One of the rings in each asymmetric unit exhibits significant dynamic disorder, elongating the thermal ellipsoids, whereas another exhibits clear static disorder – which has been successfully modelled by parts in each case.

Table 1. Crystallographic data for complexes **2** and **4-6**.

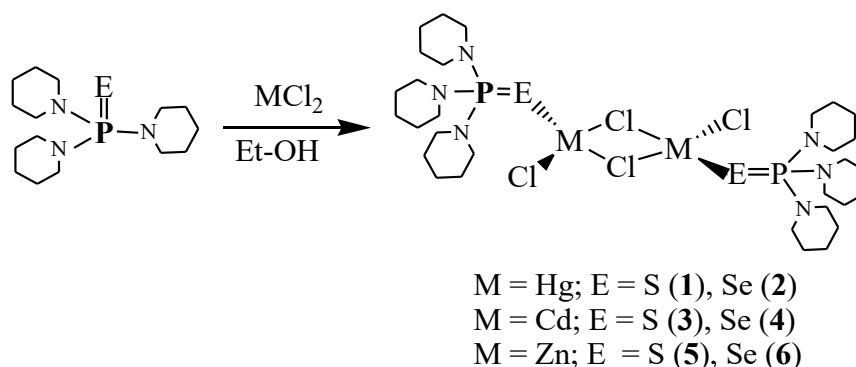
	2	4	5	6
Empirical Formula	C ₃₀ H ₆₀ N ₆ P ₂ Se ₂ Hg ₂ Cl ₄	C ₃₀ H ₆₀ N ₆ P ₂ Se ₂ Cd ₂ Cl ₄	C ₃₀ H ₆₀ N ₆ P ₂ S ₂ Zn ₂ Cl ₄	C ₃₀ H ₆₀ N ₆ P ₂ Se ₂ Zn ₂ Cl ₄
Formula Weight	1267.68	1091.30	903.48	997.28
Crystal Color, Habit	Colorless, prism	Colorless, prism	Orange prism	Colorless prism
Crystal Dimensions (mm)	0.12 X 0.03 X 0.03	0.05 X 0.05 X 0.03	0.24 x 0.04 x 0.04	0.06 x 0.06 x 0.03
Crystal System	triclinic	triclinic	triclinic	triclinic
Lattice Parameters				
a (Å)	9.454(3)	9.513(5)	9.331(6)	9.3698(15)
b (Å)	10.662(3)	10.767(5)	10.713(7)	10.7866(17)
c (Å)	10.960(3)	11.131(5)	10.856(7)	10.9381(18)
α (°)	99.197(4)	99.292(9)	97.505(10)	98.175(4)
β (° γ (°))	104.424(4)	104.351(8)	102.206(9)	102.875(4)
γ (°)	98.360(5)	97.883(10)	98.254(10)	98.635(3)
V(Å ³)	1036.2	1071.2(9)	1035.11	1047.6(3)
Space Group	P-1	P-1	P-1	P-1
Z value	1	1	1	1
Dcalc (g/cm ³)	2.032	1.692	1.449	1.581
F ₀₀₀	608	544	472	508
μ (MoK α) (cm ⁻¹)	9.521	3.045	16.245	32.431
No. of Reflections Measured	14997	3932	8983	30975
R _{int}	0.0483	0.0884	0.0498	0.1067
No. Observations	3807	3932	3773	3827
Residuals: R1 (I>2.00 σ (I))	0.0336	0.0465	0.0365	0.0334
Residuals:wR (All reflections)	0.0784	0.1347	0.0926	0.0950
Maximum peak in Final Diff. Map (e ⁻ /Å ³)	1.82	1.02	0.54	0.68
Minimum peak in Final Diff. Map (e ⁻ /Å ³)	-3.55	-1.93	-0.59	-0.88

3. Results and discussion

3.1. Synthesis

The tripiperidinophosphine chalcogenides (Pip₃PE) were prepared using previously reported methods [22, 23].

The reaction of cadmium, mercury or zinc chlorides in ethanol with Pip₃PE gives the 1:1 molar adducts (Pip₃PE)₂M₂Cl₄ (E = S or Se and M= Hg, Cd or Zn), even when 3:1 (ligand: M) reaction ratios are used (Scheme 1). These compounds were purified by recrystallization in a mixture of dry hexane-dichloromethane to give the pure complexes as white or grey solids that are partially soluble in dichloromethane and chloroform. Conductivity measurements show the complexes to be nonelectrolytes. The relatively higher values measured for Hg complexes **1** and **2** are probably due to their better solubility in dichloromethane and/or extensive dissociation in this solvent compared to Cd complexes **3** and **4**. and **4**.



Scheme 1.

3.2. Spectroscopic characterization

The spectroscopic data obtained for the metal complexes **1–6** are shown in Table 2.

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 with the effect being more pronounced for sulfide as compared to selenide derivatives (Table 2). The coordination shift is attributed to a lowering of the P=E bond order in the complexes. The smaller shifts of the selenides compared to that in the sulfides are consistent with the difference observed between P=O and P=S absorptions upon coordination [24] in related complexes and are reasonable since the vibrations involving the relatively heavy selenium atom would be less sensitive to

coordination than those with the lighter oxygen or sulfur atoms. There is an increase in the frequency of the P-N vibration upon complexation (960–980 vs. 900–955 cm⁻¹ in the free ligands) as observed in related systems [22], indicating that the nitrogen atoms are not involved in coordination.

The ³¹P NMR spectra show that the resonances of bound ligands are shifted to lower frequencies compared with those of the free ligand. It is evident that the phosphorus nucleus in the complex is placed in a lower electron-density environment, thus providing further evidence that the bonding occurs through the chalcogenophosphoryl atom. In addition, the coupling constant ¹J_{P-Se} of the free ligand is larger than that of the bound one (Table 2). Such changes are attributed to the expected weakening of the P=Se bond upon coordination to the metal center through the selenium atom [25].

Table 2. NMR (δ/ppm and J/Hz)^a and IR data for complexes **1–6**.

Complex	NMR				IR	
	δ ³¹ P	(Δδ ³¹ P) ^b	δM	¹ J(P-Se)	ν(P=E)	(Δν(P=E)) ^c
[HgCl ₂ (Pip ₃ PS)] ₂ (1)	66.0	8.80	-1003	-	583	44
[HgCl ₂ (Pip ₃ PSe)] ₂ (2)	61.5	13.7	-1137	582	555	27
[CdCl ₂ (Pip ₃ PS)] ₂ (3)	75.7	0.90	538 ^d	-	575	51
[CdCl ₂ (Pip ₃ PSe)] ₂ (4)	73.7	1.50	506 ^d	665 ^d	558	23
[ZnCl ₂ (Pip ₃ PS)] ₂ (5)	73.4	1.45	-	-	569	58
[ZnCl ₂ (Pip ₃ PSe)] ₂ (6)	74.3	0.90	-	678 ^d	558	23

a) At room temperature in CD₂Cl₂.

b) Δδ³¹P = |δ³¹P_L - δ³¹P_{Complex}|.

c) Δν(P=E) = |ν(P=E)_L - ν(P=E)_{Complex}|.

d) Measured at 238 K.

As can also be seen from Table 2, the ³¹P NMR coordination shift (Δ³¹P) is much more important for the mercury complexes **1** and **2** than in cadmium (**3** and **4**) and zinc (**5** and **6**) complexes (8-14 vs. 1-1.5 ppm, respectively). This could suggest that the ligand interact in solution more strongly with mercury than with cadmium or zinc ions, as expected for the softer character of mercury compared to the latter cations. Such an effect is consistent with the very small coordination shift in ³¹P NMR and in P=Se stretching frequency observed for the zinc selenide complex **6**, presumably indicating a substantial dissociation of this complex in solution (Table 2).

It is worth noting that no ²J(³¹P–M) couplings could be detected for the cadmium and mercury complexes **1-4** nor in their ³¹P, ¹⁹⁹Hg or ¹¹³Cd NMR spectra, even at the lowest

temperature attainable. This is in contrast to analogous monomer complexes with $(\text{Me}_2\text{N})_3\text{PSe}$ [26] or corresponding bidentate ligands [14, 27] where metal satellites in the ^{31}P NMR and the expected triplets in corresponding metal NMR spectra were observed. Such a difference could be explained by the dimeric nature of complexes 1-6. This is further supported by their x-ray solid state structure analyses detailed in the following section.

3.3. X-ray structures

To elucidate the constitution of the complexes formed, as well as to provide a clear understanding of the effect of ligand structure on the stereochemistry of these complexes, we examined the solid state structure of these complexes. The X-ray structures of complexes 2, and 4-5 reveal that they are dimers with two bridging chloride ions. The structures of the compounds and the system of numbering of the atoms are shown in Figures 1-4. Important bond lengths and angles are given in Table 3. The X-ray structures are isomorphous and the geometries of complexes are similar, the only difference being the nature of the chalcogen and metal atoms. One chalcogenide atom of the Pip_3PE ligand, one terminal and two bridging chloride ions coordinate to each metal and the geometry around each metal center is distorted tetrahedral in a dimeric form (Figures 1-4), consistent with the structure observed for the related mercury chloride and iodide complexes of Ph_3PSe [28]. This is in contrast to homologous complexes containing the ligands $n\text{-Bu}_3\text{PE}$ [15], $(\text{Me}_2\text{N})_3\text{PSe}$ [26], $\text{MeN}[(\text{Me}_2\text{N})_2\text{PE}]_2$ [27] and even the corresponding piperidiny l bidentate ligands $\text{MeN}(\text{Pip}_2\text{PE})_2$ [14], which all exist as monomer species. The difference could be explained by the presence of both the bulky chalcogen atoms and the three piperidiny l groups in the monodentate ligands described here. The P-E bond lengths 2.0259(13) Å for P=S and 2.205(2)-2.1833(9) for P=Se are typical for P=E double bonds and consistent with values reported for related mercury complexes [28]. The average P=E bond distances are all shorter than the sum of the representative covalent radii of P and E atoms, implying some retention of π bonding in the complex. However, these P=E bond lengths are longer than that observed for the free ligands. For example, the P=Se distances in the selenide complexes are approximately 0.1 Å longer than in the free ligand Pip_3PSe (2.111 Å) [29]. This indicates that the P=E bond is weakened upon complex formation with the singly bonded structure becoming more pronounced down the period [30] with an increasing dipole moment along the series $+\text{P-S-} < +\text{P-Se-}$ [31, 32]. Moreover, the structures of these complexes reveal that the average P-E-M angle varies from 98.93(5)° for P-Se-Hg to 107.40(5)° for P-S-Zn. This suggests that the title

ligands could be classified as π -donors, employing P-E π -bonding electrons for donation, rather than σ -non-bonding electrons (lone pairs) used for coordination in the oxide derivative, in fair agreement with our previous work [15] and with the bonding model proposed by Burford *et al.* [33]. The M–E bonds have distances of 2.3057(11) Å for sulfide and 2.4122(6)-2.5896(5) Å for selenide derivatives (Table 3). These are longer than the sum of covalent radii for representative single P–E bonds but much shorter than the sum of van der Waals radii [34]. The effect is more important down the series, in agreement with the order obtained from our IR and NMR data for the magnitude of metal-ligand interaction. The average P–N distances in the complexes are 1.629(3)-1.73(2) Å and 1.618(5)-1.663(6) Å for sulfide and selenide derivatives, respectively, which are shorter than in corresponding ligands [30, 35, 36]. Finally, M–Cl bond distances (2.2009(1)-2.5691(3) Å), particularly that of mercury, are almost midway between regular tetrahedral and linear values [37]. The acute Cl(2)–Hg–Cl(2)' angle (87.8°) and the length of the Hg–Cl bridge bonds indicate that these bonds, when regarded as covalent in character, must involve mercury orbitals of predominant *p*-character ; the reduction of the bond angle to less than 90° is presumably the result of an Hg–Hg' repulsion, in nice agreement with previous results reported by Dent Glasser *et al.* for related mercury chloride complexes [28a].

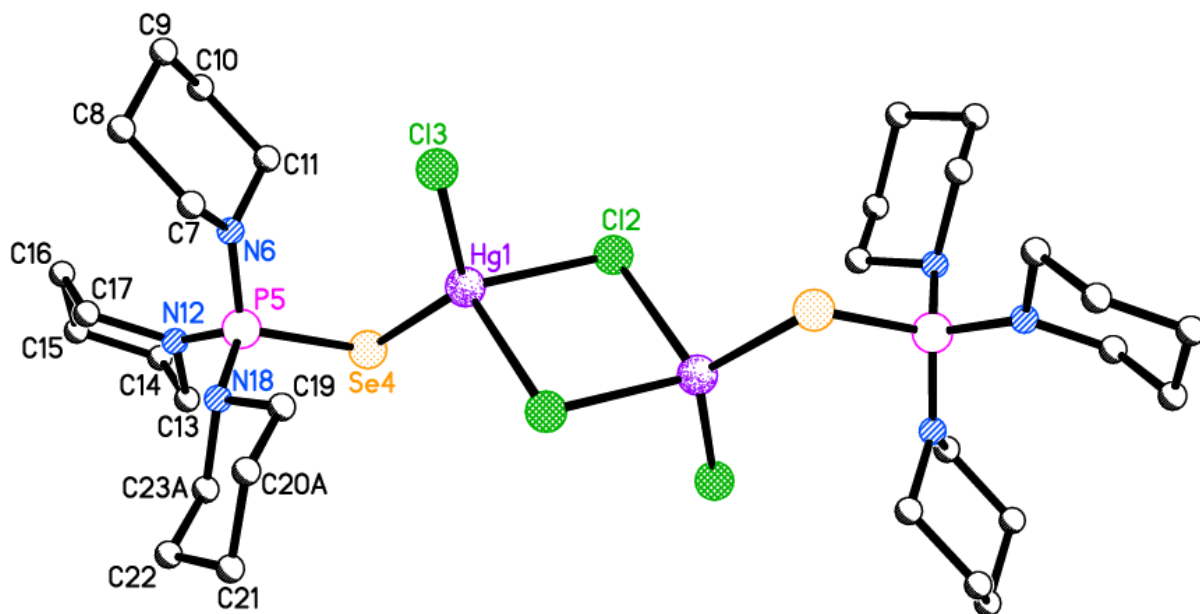


Figure 1.

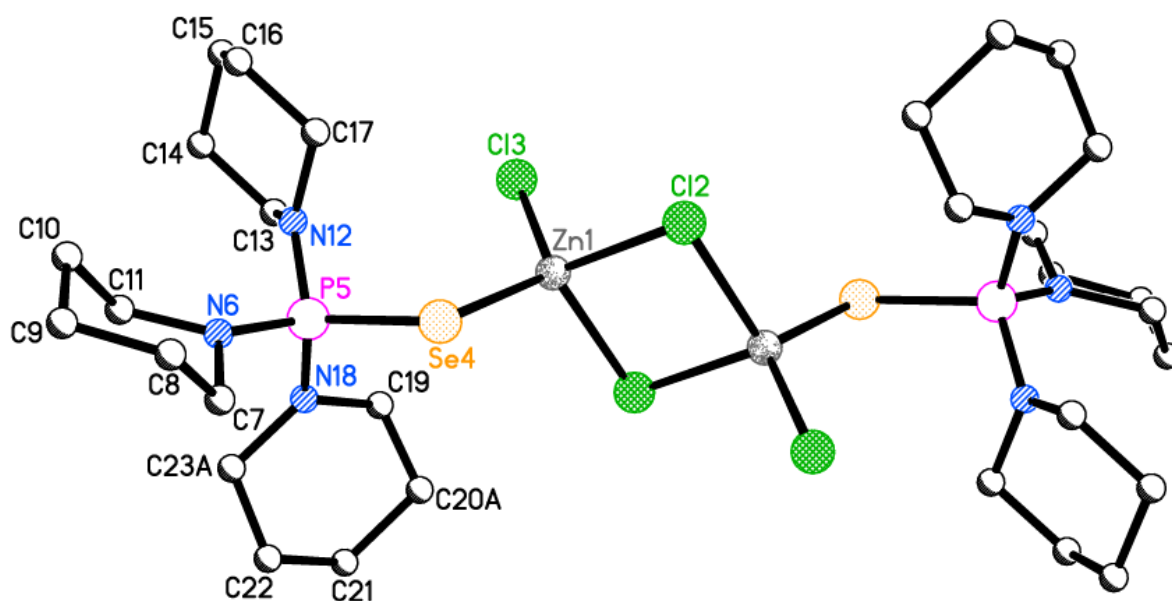


Figure 4.

Table 3. Selected bond lengths (Å) and angles (°) for the complexes 2 and 4-6.

	2	4	5	6
M(1)-E(4)	2.5025(10)	2.5896(15)	2.3057(11)	2.4122(6)
M(1)-Cl(2)	2.5691(16)	2.5596(18)	2.3500(10)	2.3528(8)
M(1)-Cl(3)	2.4168(16)	2.4197(18)	2.2009(10)	2.2044(8)
P(5)-E(4)	2.2005(19)	2.205(2)	2.0259(13)	2.1833(9)
P(5)-N(6)	1.618(5)	1.624(5)	1.629(3)	1.629(2)
P(5)-N(12)	1.628(5)	1.645(6)	1.634(3)	1.636(2)
P(5)-N(18)	1.636(6)	1.663(6)	1.73(2)	1.642(3)
N(6)-C(7)	1.466(7)	1.478(8)	1.469(5)	1.471(4)
Cl(2)-M(1)-Cl(3)	106.16(6)	109.88(7)	113.08(4)	113.32(3)
Cl(2)-M(1)-E(4)	111.99(5)	107.37(5)	102.84(4)	102.83(3)
M(1)-E(4)-P(5)	98.93(5)	100.53(5)	107.40(5)	103.90(2)
E(4)-P(5)-N(6)	112.53(19)	112.1(2)	112.54(11)	112.80(9)
E(4)-P(5)-N(12)	105.18(19)	106.3(2)	105.75(12)	105.87(10)
E(4)-P(5)-N(18)	113.2(3)	113.5(3)	118.1(7)	113.51(11)
M(1)-Cl(2)-M(1)	92.22(5)	89.50(5)	87.29(4)	87.56(3)

4. Conclusions

We have synthesized six new coordination complexes of cadmium(II), mercury(II) and zinc(II) with neutral monodentate chalcogenide ligands containing piperidiny groups

(Pip₃PE). Unlike analogous monomer adducts formed with corresponding bidentate ligands MeN(Pip₂PE)₂, these complexes were found to exist as dimer species. The complexes were characterized in solution by multinuclear (³¹P, ¹¹³Cd and ¹⁹⁹Hg) spectroscopy and in the solid state by single crystal X-ray analyses. The results show that the dimeric nature of these complexes could be interpreted in terms of the presence of both the bulkier chalcogen atoms and the three piperidinyl groups in the monodentate ligand. The reactions of the title ligands with other metal ions as well as the use of complexes **1-6** as single source precursors for the preparation of metal chalcogenide nanoparticles are already under investigation.

Acknowledgements

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Supplementary material

CCDC numbers 1864112, 1864113, 1864114 and 1864115 contain the supplementary crystallographic data for complexes **4**, **5**, **2** and **6**, 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 Center, 12 Union Road, Cambridge CB2 1EZ, UK; Fax: (+44) 1223-336-033; or E-mail: deposit@ccdc.cam.ac.uk.

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Figure captions

Scheme 1: Preparation of complexes (1-6).

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

Figure 2: The X-ray crystal structure of $[\text{CdCl}_2(\text{Pip}_3\text{PSe})]_2$ (**4**). Hydrogens bonded to carbon atoms are omitted for clarity.

Figure 3: The X-ray crystal structure of $[\text{ZnCl}_2(\text{Pip}_3\text{PS})]_2$ (**5**). Hydrogens bonded to carbon atoms are omitted for clarity.

Figure 4: The X-ray crystal structure of $[\text{ZnCl}_2(\text{Pip}_3\text{PSe})]_2$ (**6**). Hydrogens bonded to carbon atoms are omitted for clarity.