

Synthesis, characterization and structures of cadmium(II) and mercury(II) complexes with bis(dipiperidinylphosphino)methylamine dichalcogenides

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ABSTRACT

Two new bidentate phosphine dichalcogenide ligands of the type $\text{MeN}(\text{Pip}_2\text{PE})_2$ [(Pip = piperidinyl; E = S (**1**) or Se (**2**)] and their cadmium(II) and mercury(II) chloride complexes $\text{MCl}_2\{\text{MeN}(\text{Pip}_2\text{PE})_2\}$ [M = Cd; E = S (**3**); Se (**4**) or M = Hg; L = S (**5**); Se (**6**)] were prepared and characterized by elemental analysis, IR, multinuclear (^{31}P , ^{77}Se and ^{113}Cd) NMR spectroscopy and single crystal X-ray analyses. Ligands **1** and **2** were found to adopt anti conformation structures in the solid state in which both P=E groups are trans to each other. Complexes **3-6** are comprised of one ligand coordinated in a bidentate fashion to the metal centre in a distorted tetrahedral arrangement [98.46(3)-121.24(4)°]. The P=S bond lengths of 1.999(15)-2.003(14) Å in the complex (**3**) are slightly elongated compared to those in free ligand [1.933(15)-1.950(14) Å]. The results are discussed and compared with closely related analogues.

Keywords: Cadmium, mercury complex, bis(dichlorophosphino)methylamine, ^{31}P , ^{77}Se and ^{113}Cd NMR .

1. Introduction

Studies into the coordination chemistry of dichalcogenoimidodiphosphinates $\text{HN}(\text{R}_2\text{PE})_2$ (E=O, S, Se) and related compounds have attracted much attention due to their easy preparation and analogy to β -diketonates [1-9]. There have been a renewed interest in the metal complexes 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 alkyl analogues of the type $\text{R}'\text{N}(\text{R}_2\text{PE})_2$ (R' = alkyl), especially those containing R as terminal dialkylamino groups (R_2N) [12-14]. For instance, the nonamethylimidodiphosphoramidate, $\text{MeN}[\text{P}(\text{O})(\text{NMe}_2)_2]_2$ (NIPA), has been shown to be an excellent extracting ligand of metal ions and the corresponding complexes with Al, Be and Cd have been reported [13]. In related

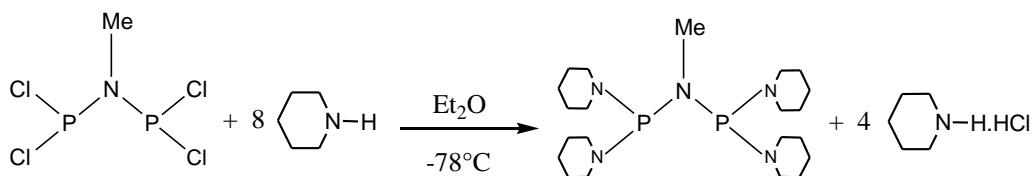
work, the preparation and kinetic studies of Cd and Zn complexes with the thio analogue, MeN[P(S)(NMe₂)₂]₂ (SNIPA) were also investigated [14]. More recently, complexes of cadmium and zinc with the selenide analogue, MeN[P(Se)(NMe₂)₂]₂ (SeNIPA), have been reported though their characterisation was limited to spectroscopic techniques [15].

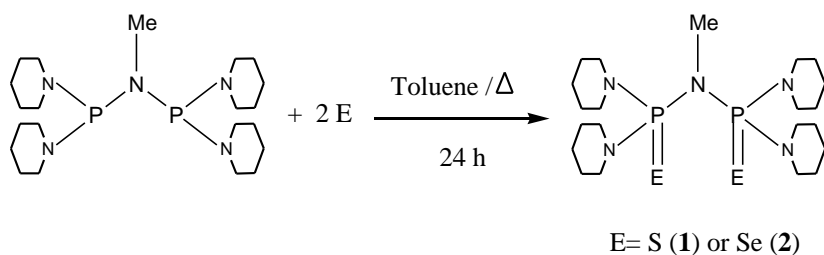
We have previously reported on the coordination complexes of neutral monodentate phosphine chalcogenides of the type (R₂N)₃PE (E = S, Se or Te) with cadmium(II) and mercury(II) and showed that these complexes could be used as precursors for the production of metal chalcogenide nanoparticles [16,17]. As a continuation of this work, we describe herein the synthesis, characterisation and structural investigation of corresponding bidentate phosphine dichalcogenide ligands, the piperidinyl derivatives of SNIPA and SeNIPA, as well as their cadmium(II) and mercury(II) chloride complexes. The new compounds were characterized in solution by multinuclear (³¹P, ⁷⁷Se, ¹¹³Cd and ¹⁹⁹Hg) NMR spectroscopy and in the solid state by single crystal X-ray crystallography.

2. Results and discussion

2.1. Synthesis

The compound bis(dipiperidinylphosphino)methylamine, MeN(PPip)₂, was prepared in a 68% yield using a method previously reported for MeN[P(NMe)₂]₂ [18] and was oxidised by sulfur or selenium in refluxing toluene to produce the two new bidentate ligands **1** and **2** as shown in Scheme 1.

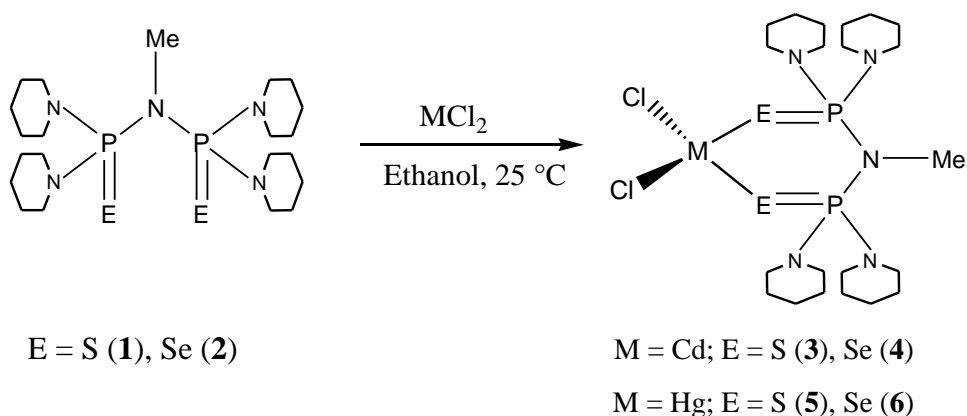




Scheme 1:

The IR spectra of **1** and **2** show characteristic stretching vibrations at 623 and 580 cm^{-1} attributed to P=S and P=Se bonds, respectively.

Reaction of cadmium or mercury chlorides in ethanol solution with the ligand **1** or **2** produces the complexes CdCl_2L (L = **1** (**3**); **2** (**4**)) and HgCl_2L (L = **1** (**5**); **2** (**6**)). These were purified by recrystallisation in a mixture of dichloromethane and hexane to give the pure complexes as white or yellow solids that are soluble in dichloromethane and chloroform. Conductivity measurements show the complexes to be nonelectrolytes and the relatively higher values measured for Cd complexes **3** and **4** are probably due to their better solubility in acetonitrile and/or extensive dissociation in this solvent compared to Hg complexes **5** and **6**. All complexes **3-6** and their ligands **1** and **2** are stable in air and to oxidation, but some times precipitate elemental chalcogen if left for a long time in chlorinated solvents.



Scheme 2:

The $\nu_{\text{P=S}}$ and $\nu_{\text{P=Se}}$ infrared absorption bands observed for ligands **1** and **2** are, as expected, shifted by 50 and 30 cm^{-1} , respectively towards lower wave numbers for the sulfide and selenide complexes, on coordination to the metal ion. 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 sulfides are consistent with that observed between P=O and P=S absorptions [19] 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. In addition, there is an increase in the frequency of the $\nu(\text{PNP})$ vibration upon complexation (1050-1120 vs 840-960 cm^{-1} in the free ligands) as observed in related systems [2].

2.2. NMR Studies

The NMR data on ligands **1** and **2** and their metal complexes **3-6** are shown in Table 1. For example, the ^1H NMR spectra of **1** and **2** show in addition to the piperidinyl protons a triplet at 3.04 ppm for the protons of the bridging methylamino group due to coupling to the two equivalent phosphorus nuclei ($^3J_{\text{H-P}} = 15.0$ and 13.5 Hz for **1** and **2**, respectively) (Fig. 1). The ^{31}P NMR resonances of bound ligand are shifted to lower frequency compared with those of the free ligand, whereas the ^{77}Se NMR resonances show a higher frequency shift on complexation. The difference in the ^{77}Se chemical shift between free and bound ligands is more important than that observed in ^{31}P NMR spectra. Furthermore, the coupling constant $^1J_{\text{P-Se}}$ of the free ligand is larger than that of the bound one. Such changes are attributed to a weakening of the P=Se bond upon coordination to the metal atom through selenium [20].

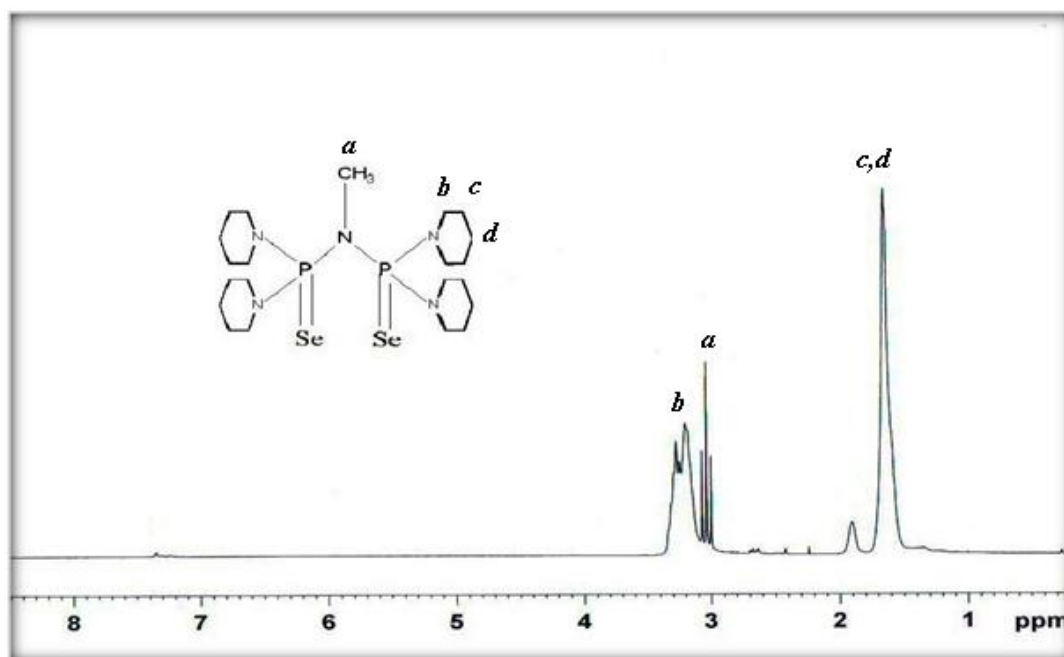


Fig. 1.

Table 1

NMR Data (δ /ppm and J /Hz) for ligands **1** and **2** and their complexes **3-6** in CD_2Cl_2 .

Compound	$\delta^{31}\text{P}$	$\delta^{77}\text{Se}$	δM	$^1J_{\text{P-Se}}$	$^2J_{\text{P-M}}$
$\text{MeN}(\text{Pip}_2\text{PS})_2$ (1)	73.1	-	-	-	-
$\text{MeN}(\text{Pip}_2\text{PSe})_2$ (2)	70.5	-230	-	816	-
$[\text{CdCl}_2(\mathbf{1})]$ (3)	70.3	-	620	-	a
$[\text{CdCl}_2(\mathbf{2})]$ (4)	63.2	-160	525	682	a
$[\text{HgCl}_2(\mathbf{1})]$ (5)	68.1	-	-804	-	75.5
$[\text{HgCl}_2(\mathbf{2})]$ (6)	61.9	-82.7	-934	686	119

a) Not observed even at 178 K.

The $^{31}\text{P}\{^1\text{H}\}$ NMR spectra for each of the mercury complexes **5** and **6** show at 238 K singlet resonances flanked by two satellites of equal intensities arising from the two-bond mercury-phosphorus coupling, $^2J(^{31}\text{P}-^{199}\text{Hg})$, with weak selenium satellites (Fig. 2). However, no $^2J(^{31}\text{P}-^{113/111}\text{Cd})$ couplings could be detected for cadmium analogues **3** and **4** even at the lowest temperature attainable. This could suggest that the bidentate ligands **1** and **2** interact in solution more strongly with mercury than with cadmium.

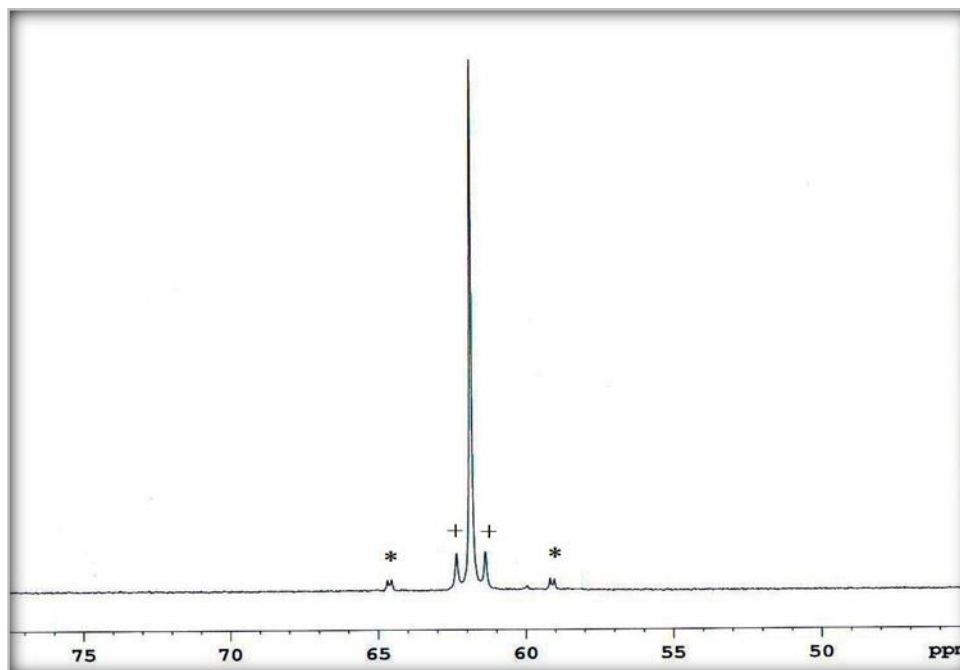


Fig. 2

Although ${}^2J({}^{31}\text{P-M})$ couplings were observed at 238 K in the ${}^{31}\text{P}$ NMR spectra of complexes **5** and **6**, no such couplings were detected in the corresponding ${}^{113}\text{Cd}$ or ${}^{199}\text{Hg}$ NMR spectra of all the complexes **3-6** which show relatively broad signals even at 188 K, instead of the expected triplet observed previously for the cadmium complex with the dimethylamino analogue, SeNIPA [15]. This difference is likely due to steric hindrance in the piperidinyll derivatives **1** and **2**.

If ligands **1** and **2** adopt the *anti* conformation in solution, as is the case in the X-ray solid state structure, two doublets should be observed in their ${}^{31}\text{P}$ NMR spectra as previously reported for ${}^i\text{PrN}(\text{R}_2\text{PO})_2$ [12c]. However the relatively broad ${}^{31}\text{P}$ NMR signal displayed at room temperature is retained even at 178 K. This could be attributed to a rapid P-N bond rotation even at the lowest temperature attainable, presumably due to the less sterically hindered group (Me) present on the bridging nitrogen atom.

2.3. X-ray structures

The geometries of ligands **1** (Fig. 3) and **2** (Fig. 4) are similar; the only difference being the nature of the chalcogen. These were obtained after recrystallisation from n-hexane at -40 °C. The P-E bond lengths in **1** and **2** (Table 2) are consistent with those in HN(R₂PE)₂ [2a, 2b] and SeNIPA analogues. The P-S [1.940(2)-1.959(3) Å] and P-Se [2.106(14)-2.113(14) Å] bond lengths typical for P=S and P=Se double bonds and the P-N [1.631(3)-1.708(4) Å] are single.

There are, in principle, two possible conformations for **1** and **2**. The X-ray structures reveal that they have similar structures, adopting *anti* conformations (Figs. 3 and 4) with P=E groups rotated with respect to the P-N-P plane, the E(4)-P(2)...E(5)-P(3) torsion angles being 79 and 80° for **1** and **2**, respectively: E(4)-P(2) and E(5)-P(3) are rotated by 36° and 43° (in opposite direction) with respect to the P-N-P plane, in agreement with structures observed for analogous HN(ⁱPr₂PE)₂ [2a, 2b].

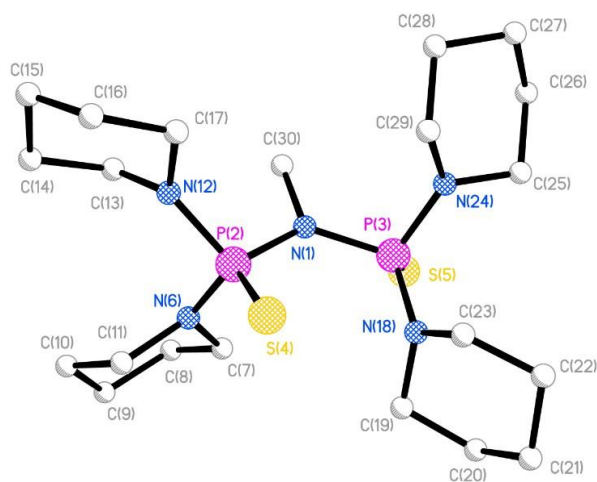


Fig. 3

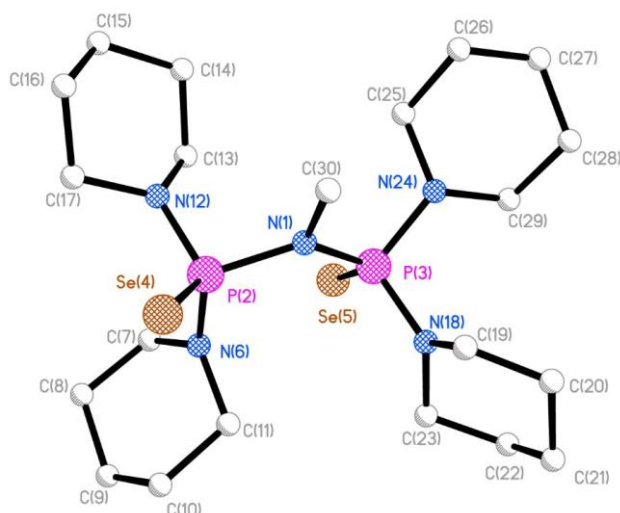


Fig. 4

Table 2
Selected bond lengths (Å) and angles (°) for MeN(Pip₂PE)₂ (E = S (**1**), Se (**2**))

	1	2		1	2
E(4)-P(2)	1.933(15)	2.113(14)	E(4)-P(2)-N(1)	114.42(12)	110.98(13)
E(5)-P(3)	1.950(14)	2.106(14)	E(4)-P(2)-N(6)	116.66(12)	112.86(14)
P(2)-N(1)	1.689(3)	1.708(4)	E(4)-P(2)-N(12)	110.72(12)	112.25(14)
P(2)-N(6)	1.643(3)	1.648(4)	N(1)-P(2)-N(6)	104.49(15)	107.5(2)
P(2)-N(12)	1.651(3)	1.651(4)	N(1)-P(2)-N(12)	106.76(16)	103.5(2)
P(3)-N(1)	1.694(3)	1.701(4)	N(6)-P(2)-N(12)	102.71(17)	109.31(19)
P(3)-N(18)	1.631(3)	1.640(4)	N(1)-P(3)-N(18)	110.55(16)	109.95(19)
P(3)-N(24)	1.639(3)	1.670(4)	P(2)-N(1)-P(3)	131.48(19)	128.5(2)
N(1)-C(30)	1.488(5)	1.505(6)	P(2)-N(1)-C(30)	115.1(3)	111.2(3)
N(6)-C(7)	1.463(5)	1.456(6)	P(3)-N(1)-C(30)	113.0(2)	120.0(3)

The crystal structure of complexes **3** was elucidated after recrystallisation in n-hexane at -40 °C. As illustrated in Fig. 5, the complex is comprised of one ligand, which is *E,E'*-coordinated to the metal (II) chloride. The structure of **3** is isostructural with the analogous Cd and Hg complexes of HN(R₂PE)₂ [2, 8], revealing a distorted metal centre with S-Cd-S angle of 98.46(3)°. Shortening of P-N bonds and subsequently extended P=E in related complexes with anionic ligands M[N(R₂PE)₂]₂ due to delocalisation within the

dichalcogenoimidodiphosphinate architecture [2] is also observed in complex **3** (Table 3), but the effect being less pronounced owing to the absence of such delocalisation (neutral ligands being complexed).

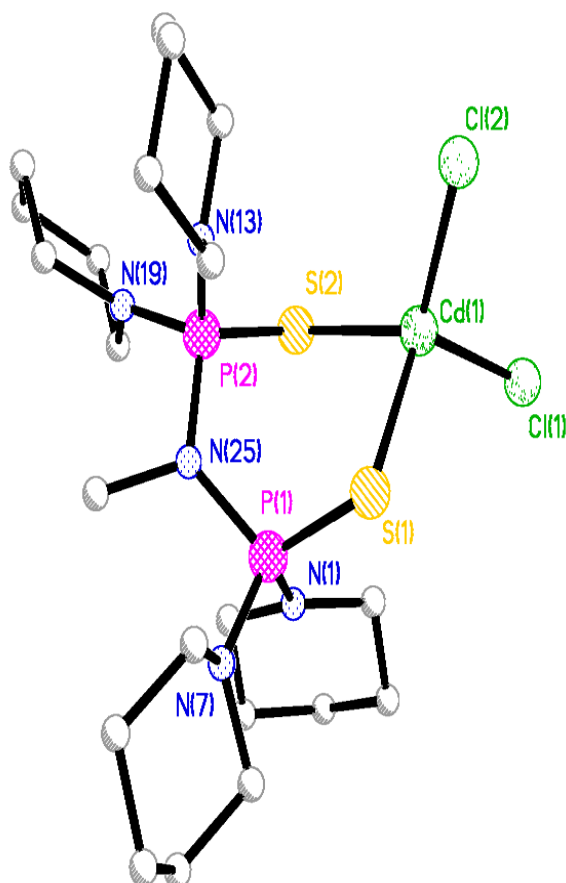


Fig. 5

Table 3Selected bond lengths (Å) and angles (°) for the complexes [CdCl₂{MeN(Pip₂PS)₂}] (**3**).

Bond length		Bond angle	
Cd(1)-S(1)	2.578(10)	Cl(1)-Cd(1)-Cl(2)	112.99(4)
Cd(1)-S(2)	2.558(10)	Cl(1)-Cd(1)-S(1)	115.17(4)
Cd(1)-Cl(1)	2.442(13)	Cl(1)-Cd(1)-S(2)	100.66(4)
Cd(1)-Cl(2)	2.417(12)	Cl(2)-Cd(1)-S(1)	107.82(4)
S(1)-P(1)	2.003(14)	Cl(2)-Cd(1)-S(2)	121.24(4)
S(2)-P(2)	1.999(15)	S(1)-Cd(1)-S(2)	98.46(3)
P(1)-N(1)	1.634(4)	Cd(1)-S(1)-P(1)	104.88(5)
P(1)-N(7)	1.656(3)	Cd(1)-S(2)-P(2)	99.82(5)
P(2)-N(19)	1.649(3)	S(1)-P(1)-N(1)	113.40(13)
N(1)-C(2)	1.464(6)	S(1)-P(1)-N(7)	110.06(13)

3. Conclusions

We have synthesised two new neutral bidentate dichalcogenide ligands containing piperidinyl groups. The reactions of these ligands with CdCl₂ or HgCl₂ produced novel cadmium(II) and mercury(II) chloride complexes. The ligands and their complexes were characterised in solution by multinuclear (³¹P, ⁷⁷Se, ¹¹³Cd and ¹⁹⁹Hg) spectroscopy and in the solid state by single crystal X-ray analyses. The two ligands **1** and **2** were shown to adopt *anti* conformation structures in the solid state with the two P=E groups rotating in the opposite direction with respect to the P-N-P plane. In addition, the X-ray structure of the complex **3** shows that it contains one ligand S,S'-coordinated to the metal centre in a distorted tetrahedral arrangement. The reactions of ligands **1** and **2** with other metal ions as well as the use of complexes **3-6** as single source precursors for the preparation of metal chalcogenide nanoparticles is already underway in our laboratory.

4. Experimental section

4.1. Reagents and general procedures

All preparations were carried out under a nitrogen atmosphere in solvents dried by standard techniques [21] and stored over molecular sieves. PCl_3 (Fluka), piperidine (Fluka), CdCl_2 (Merck) and HgCl_2 (Merck) were used as received.

4.2. Instrumentation

The NMR spectra were recorded on Bruker AC-300 instrument, equipped with a variable temperature unit B-VT-2000 and two probes, CD_2Cl_2 were used as solvent; ^{31}P at 121 MHz (85% $\text{H}_3\text{PO}_4\text{-D}_2\text{O}$), ^{77}Se at 57.2 MHz (Me_2Se) and ^{113}Cd at 66.5MHz (aq. $\text{Cd}(\text{NO}_3)_2$, 2M).

The IR spectra were recorded on a Thermo Scientific Nicolet IR200 spectrometer. The conductivity measurements were carried out for 10^{-3} M solutions of the complexes dissolved in acetonitrile (dried on molecular sieves).

4.3. Preparation of $\text{MeN}(\text{Pip}_2\text{P})_2$ (Pip: piperidinyl group)

To a stirred solution of $(\text{Cl}_2\text{P})_2\text{NMe}$ [22-24] (4 g, 17.2 mmol) in anhydrous diethyl ether (200 mL) cooled to -78 °C, piperidine (11.7 g, 137.6 mmol) was added dropwise in the same solvent (20 mL). The reaction mixture was kept at -78 °C for 12 h. After removal of the piperidinium salt and evaporation of solvent, the oil obtained was redissolved in petroleum ether ($40\text{-}60$ °C) to remove any residual salt. The solvent was evaporated *in vacuo* to give the product $(\text{Pip}_2\text{P})_2\text{NMe}$ as an oil which solidified on cooling. This was found to be pure as shown by its ^{31}P and ^1H NMR spectra and was used in the next step without further purification. Yield = 68%. M.P. = 39.2 °C. ^{31}P NMR (300 MHz, CDCl_3): δ [ppm] = 113.4.

4.4. Preparation of the ligands 1 and 2

(0.02 mol) of sulfur or selenium was added to a solution of $\text{MeN}(\text{Pip}_2\text{P})_2$ (4.27 g, 0.01 mol) in toluene (50 mL). The reaction mixture was stirred at reflux for 24 h. After filtration to

remove excess S or Se, the solvent was evaporated *in vacuo* to leave a deep orange solid which was crystallised from petroleum ether (40-60 °C), giving MeN(Pip₂PE)₂ as white solids.

MeN(Pip₂PS)₂ (1)

Yield = 60%, M.P. = 128.9 °C. Elemental analysis (%) calcd for C₂₁H₄₃N₅P₂S₂: C 51.30 H 8.82 N 14.24 found: C 51.55 H 8.60 N 14.11. FT-IR (KBr)/cm⁻¹: 623 (ν(P=S)); 958, 870 (ν(PNP)).

MeN(Pip₂PSe)₂ (2)

Yield = 49%, M.P. = 146.2 °C. Elemental analysis (%) calcd for C₂₁H₄₃N₅P₂Se₂: C 43.08 H 7.40 N 11.96 found: C 42.82 H 7.57 N 11.81. FT-IR (KBr)/cm⁻¹: 580 (ν(P=Se)); 955, 871 (ν(PNP)).

4.5. General procedure for the preparation of complexes 3-6

To a stirred solution of the metal chloride (1 mmol) in ethanol (20 mL), the ligand (**1** or **2**) (1 mmol) dissolved in dichloromethane (5 mL) was added dropwise. The reaction mixture was stirred for 2 h. After solvent evaporation, the solid obtained was washed with anhydrous diethyl ether, dried *in vacuo* and recrystallised from a mixture of hexane-dichloromethane to give the complexes as white solids which become yellow to orange on storing.

[CdCl₂{MeN(Pip₂PS)₂}] (3)

Yield = 85%. M.P. = 181.6 °C. Elemental analysis (%) calcd for C₂₁H₄₃CdCl₂N₅P₂S₂: C 37.37 H 6.42 N 10.38 found: C 37.49 H 6.68 N 10.55. FT-IR (KBr)/cm⁻¹: 560 (ν(P=S)); 1116, 782 (ν(PNP)). Λ_M (cm² Ω⁻¹ mol⁻¹) = 85.

[CdCl₂{MeN(Pip₂PSe)₂}] (4)

Yield = 88%. M.P. = 187.2 °C. Elemental analysis (%) calcd for C₂₁H₄₃CdCl₂N₅P₂Se₂: C 32.81 H 5.64 N 9.11 found: C 32.98 H 5.90 N 9.36. FT-IR (KBr)/cm⁻¹: 551 (ν(P=Se)); 1105, 792 (ν(PNP)). Λ_M (cm² Ω⁻¹ mol⁻¹) = 79.

[HgCl₂{MeN(Pip₂PS)₂}] (5)

Yield = 87%. M.P. = 185.6 °C. Elemental analysis (%) calcd for C₂₁H₄₃Cl₂HgN₅P₂S₂: C 33.05 H 5.68 N 9.18 found: C 33.13 H 5.61 N 9.10. FT-IR (KBr)/cm⁻¹: 569 (ν(P=S)); 1066, 768 (ν(PNP)). Λ_M (cm² Ω⁻¹ mol⁻¹) = 44.

[HgCl₂{MeN(Pip₂PSe)₂}] (6)

Yield = 82%. M.P. = 166.5 °C. Elemental analysis (%) calcd for C₂₁H₄₃Cl₂HgN₅P₂Se₂: C 29.43 H 5.06 N 8.17 found: C 29.45 H 5.01 N 8.12. FT-IR (KBr)/cm⁻¹: 549 (ν(P=Se)); 1064, 778 (ν(PNP)). Λ_M (cm² Ω⁻¹ mol⁻¹) = 35.

4.6. Crystal structure determinations

X-ray analyses for **1** and **2** were performed using a Rigaku Sealed tube generator and Saturn 724 detector at 125 K and for **3** using a Rigaku FRX (dual port) rotating anode/confocal optic high brilliance generator with Dectris P200 detectors, and Oxford Cryostream Cobra accessory at -180(1) °C. All data were collected with Mo-Kα radiation (λ = 0.71073 Å) and corrected for Lorentz and polarisation effects. The data for all of the compounds were collected and processed using CrystalClear (Rigaku) [25]. The crystal structures were solved using direct methods [26] or heavyatom Patterson methods [27] and expanded using Fourier techniques [28]. The non-hydrogen atoms were refined anisotropically, hydrogen atoms were refined using the riding model. All calculations were performed using CrystalStructure [29] crystallographic software package and SHELXL-97 (Table 4) [30].

Table 4Crystallographic data for ligands **1** and **2** and complexes **3**, **5** and **6**.

	1	2	3
Empirical Formula	C ₂₁ H ₄₃ N ₅ P ₂ S ₂	C ₂₁ H ₄₃ N ₅ P ₂ Se ₂	C ₂₁ H ₄₄ CdCl ₂ N ₅ O _{0.50} P ₂ S ₂
Formula Weight	491.67	585.47	684.00
Crystal Color, Habit	colorless, prism	colorless, prism	colorless, prism
Crystal Dimensions (mm)	0.09 X 0.06 X 0.03	0.09 X 0.06 X 0.03	0.06 X 0.03 X 0.03
Crystal System	monoclinic	triclinic	monoclinic
Lattice Parameters			
a (Å)	16.282(7)	10.080(3)	17.198(2)
b (Å)	12.401(4)	11.877(3)	18.480(2)
c (Å)	13.602(7)	22.936(8)	19.242(3)
α(°)	90	82.63(3)	90
β(°)	107.566(10)	85.71(3)	98.566(2)
γ(°)	90	73.49(2)	90
V(Å ³)	2618(2)	2608(14)	6047(13)
Space Group	P121/c1 (#14)	P-1 (#2)	P21/c (#14)
Z value	4	4	8
D _{calc} (g/cm ³)	1.247	1.491	1.502
F ₀₀₀	1064.00	1208.00	2824.00
μ(MoKα) (mm ⁻¹)	0.344	2.976	11.654
No. of Reflections Measured	4600	9094	10959
R _{int}	0.1213	0.0590	0.0617
No. Observations	2697	5859	8619
Residuals: R1 (I > 2.00σ(I))	0.0559	0.0442	0.0472
Residuals: R (All reflections)	0.1267	0.0957	0.0630
Maximum peak in Final Diff. Map (e ⁻ /Å ³)	0.35	0.71	0.86
Minimum peak in Final Diff. Map (e ⁻ /Å ³)	-0.34	-0.69	-1.20

Supplementary data

CCDC numbers 1483438, 1483439 and 1483440 contain the supplementary crystallographic data for ligands **1** and **2** and complex **3**, respectively. These data can be obtained free of

charge from the Cambridge Crystallographic Data Centre via <http://www.ccdc.cam.ac.uk/Community/Requestastructure>.

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Figure captions

Scheme 1: Preparation of MeN(Pip₂PE)₂ (**1** and **2**).

Scheme 2: Preparation of complexes MCl₂L (**3-6**).

Fig. 1 ¹H NMR spectrum of ligand **2** in CDCl₃ at 298 K.

Fig. 2 ³¹P-¹H NMR spectrum of complex **6** in CDCl₃ at 238 K (* and +: signals related to Se and Cd satellites, respectively).

Fig. 3 The X-ray crystal structure of ligand **1**. Hydrogens bonded to carbon atoms are omitted for clarity.

Fig. 4 The X-ray crystal structure of ligand **2**. Hydrogens bonded to carbon atoms are omitted for clarity.

Fig. 5 The X-ray crystal structure of [CdCl₂{MeN(Pip₂PS)₂}] (**3**). Hydrogens bonded to carbon atoms are omitted for clarity.