

Structural diversity of four-co-ordinate metal(II) compounds with the bidentate bis(diphenylselenophosphoryl)amide ligand, $[M\{N(PPh_2Se)_2-Se,Se'\}_2]$ (M = Sn, Pb, Zn, Cd or Hg)

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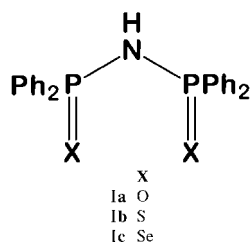
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The $[N(PPh_2Se)_2]^-$ ion formed stable bis-chelates with M^{II} (M = Sn, Pb, Zn, Cd or Hg), $[M\{N(PPh_2Se)_2-Se,Se'\}_2]$, which exhibit a large diversity of structural arrangements around the metal, as shown by X-ray crystallography. The tin(II) complex crystallises dimorphically, as yellow triclinic prisms (**1**) and red tetragonal octahedrons (**1'**). The yellow isomer is square planar, representing the first example of a true square-planar tin(II) spiro-compound. The red isomer and the lead(II) compound (**2**) exhibit a distorted ψ -trigonal-bipyramidal co-ordination geometry with a vacant equatorial position, which suggests the presence of a stereoactive electron lone pair. The cadmium(II) and mercury(II) complexes (**3** and **4**) are tetrahedral.

Most tin(II) compounds display distorted geometries around the tin atom. In fact there are only a few examples of derivatives having a regular co-ordination geometry.^{1,2} This is often explained by the presence of a non-stereochemically active lone pair. Recently, we reported the first example of a square-planar tin(II) compound with $N(PPh_2Se)_2$.² This selenium-based ligand belongs to the group I which are ideally suited to study the presence of a stereochemically active lone pair on account of their chelating ability and their great flexibility. These proportions are demonstrated by the variation observed in the ring angles (P–N–P, M–X–P, X–P–N) and in the ring bite (X...X) range for complexes containing these ligands,^{3,4} and in the occurrence of unusual structures of some of them.^{2,5} This and the feature that the lead(II) materials show a major tendency to exhibit a symmetrical environment around the lead atom prompted us to synthesize the analogous four-co-ordinate lead(II) compound, as well as a range of derivatives with $[N(PPh_2Se)_2]^-$, thus allowing the comparison of oxygen and sulfur *versus* selenium as the donor set in a series of bis-chelates, with six-membered rings containing tin(II),² lead(II), zinc(II), cadmium(II) and mercury(II). The new compounds have been characterised by microanalysis, multielement NMR, IR, positive-ion FAB mass spectroscopy, and four of them (**1–4**) by X-ray diffraction.



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Experimental

The ³¹P (121), ⁷⁷Se (51.2) and ¹¹⁹Sn (111.8 MHz) NMR spectra were recorded in CDCl₃ on a Varian VXR 300s spectrometer using as external reference 85% H₃PO₄, Ph₂Se and SnMe₄, respectively. FAB mass spectra in 3-nitrobenzyl alcohol in the positive-ion mode on a JEOL JMS-SX102A instrument and infrared spectra (as KBr discs) on a Perkin-Elmer 282B spectrometer. Microanalyses were performed by Galbraith Laboratories. The amine $NH(PPh_2Se)_2$ and its potassium salt were prepared by literature methods.^{3b}

Syntheses

[Sn{N(PPh₂Se)₂-Se,Se'}₂] 1. The syntheses and characterisation of both isomers of this compound, **1** and **1'**, have been previously reported.²

[Pb{N(PPh₂Se)₂-Se,Se'}₂] 2. A solution of $K[N(PPh_2Se)_2]$ (0.141 g, 0.3 mmol) in methanol (10 cm³) was added to a solution of $Pb(O_2CMe)_2 \cdot 3H_2O$ (0.07 g, 0.15 mmol) in water, with stirring. The resulting precipitate was filtered off, washed with water and dried *in vacuo*. Yield 0.132 g (81%), m.p. 204–206 °C (Found: C, 44.5; H, 3.05. Calc. for $C_{48}H_{40}N_2P_4PbSe_4$: C, 44.65; H, 3.1%). ³¹P-¹H NMR (CDCl₃): δ 30.2 (s). $\tilde{\nu}_{max}/cm^{-1}$ (KBr) 1188s [ν(PN)], 1176vs [ν(PN)/δ(CH)], 743m [ν(PN)], 540vs [γ(PNP)/ν(PSe)] and 439wm [ν(PSe)]. Positive-ion FAB mass spectrum: *m/z* 1293 [⁸⁰Se₄(PPh₂)₄N₂Pb⁺], 750 [⁸⁰Se₂(PPh₂)₂-NPb⁺], 544 [⁸⁰Se₂(PPh₂)₂N⁺], 464 [⁸⁰Se(PPh₂)₂N⁺], 384 [(PPh₂)₄-N⁺] and 154 [PhP₂N⁺].

[Cd{N(PPh₂Se)₂-Se,Se'}₂] 3. A solution of CdCl₂ (0.046 g, 0.25 mmol) in water (10 cm³) was added to a methanolic solution of $K[N(PPh_2Se)_2]$ (0.29 g, 0.5 mmol) in methanol (15 cm³). The white solid precipitated was filtered off, washed with water and methanol, and dried *in vacuo*. Yield 0.254 g, 85% (Found: C, 48.1; H, 3.35. Calc. for $C_{48}H_{40}CdN_2P_4Se_4$: C, 48.15; H, 3.35%). ³¹P-¹H NMR (CDCl₃): δ 31.7 (s). $\tilde{\nu}/cm^{-1}$ (KBr) 1203s (br) [ν(PN)], 1177s [ν(PN)/δ(CH)], 743m [ν(PN)], 527vs [γ(PNP)/

Table 1 Crystallographic data for the complexes **1–4**^a

	1	1'	2	3	4
Empirical formula	C ₄₈ H ₄₀ N ₂ P ₄ Se ₄ Sn	C ₄₈ H ₄₀ N ₂ P ₄ Se ₄ Sn	C ₄₈ H ₄₀ N ₂ P ₄ PbSe ₄	C ₄₈ H ₄₀ CdN ₂ P ₄ Se ₄	C ₄₈ H ₄₀ HgN ₂ P ₄ Se ₄
Colour, habit	Yellow, prism	Red, octahedron	Yellow, prism	Clear, block	Amber, prism
<i>M</i>	1203.2	1203.2	1291.7	1197.00	1285.1
Diffractionmeter	Siemens P4	Siemens P4	Siemens P4	Rigaku AFC7S	Siemens P4
Radiation (λ/Å)	Mo-Kα (0.710 73)	Mo-Kα (0.710 73)	Mo-Kα (0.710 73)	Cu-Kα (1.541 78)	Mo-Kα (0.710 73)
Crystal size/mm	0.36 × 0.28 × 0.18	0.48 × 0.32 × 0.28	0.40 × 0.22 × 0.22	0.10 × 0.10 × 0.23	0.24 × 0.20 × 0.20
Space group	<i>P</i> $\bar{1}$ (no. 2)	<i>P</i> 4 ₁ 2 ₁ 2 (no. 92)	<i>P</i> 4 ₁ 2 ₁ 2 (no. 92)	<i>P</i> $\bar{1}$ (no. 2)	<i>P</i> $\bar{1}$ (no. 2)
Crystal system	Triclinic	Tetragonal	Tetragonal	Triclinic	Triclinic
<i>a</i> /Å	10.124(5)	10.250(2)	10.234(2)	14.005(3)	13.776(2)
<i>b</i> /Å	13.085(4)			14.349(3)	13.9620(10)
<i>c</i> /Å	18.260(4)	43.882(6)	43.858(6)	13.764(2)	14.361(2)
α /°	89.42(2)			97.48(2)	65.750(0)
β /°	82.75(2)			109.72(2)	82.610(0)
γ /°	77.62(2)			65.63(1)	70.230(0)
<i>U</i> /Å ³	2343.3(17)	4610.8(14)	4593.3(14)	2371.5(8)	2369.7(6)
<i>Z</i>	2 ^{b,c}	4 ^b	4 ^b	2	2
<i>D</i> _c /g cm ⁻³	1.705	1.733	1.868	1.676	1.801
μ /mm ⁻¹	3.824	3.667	7.019	8.99	6.490
<i>F</i> (000)	1176	2352	2480	1172	1236
2 θ Range/°	3.0–50.0	3.0–50.0	3.0–60.0	3.0–50.0	3.0–50.0
Scan type	ω	ω	ω	ω -2 θ	ω
Minimum, maximum transmission	0.3240, 0.4703	0.1426, 0.1901	0.5935, 0.7180	0.2601, 0.3783	0.3589, 0.4397
Independent reflections	8145	6498	5435	7053	8082
Observed reflections	3743 [<i>F</i> > 4.0 σ (<i>F</i>)]	2466 [<i>F</i> > 4.0 σ (<i>F</i>)]	2202 [<i>F</i> > 4.0 σ (<i>F</i>)]	5955 [<i>I</i> > 3.0 σ (<i>I</i>)]	3834 [<i>F</i> > 4.0 σ (<i>F</i>)]
Parameters refined	536	267	218	532	533
<i>R</i> (<i>F</i> _o), <i>R'</i> (<i>F</i> _o) ^d	0.085, 0.098	0.780, 0.076	0.067, 0.040	0.038, 0.044	0.060, 0.057
Largest and mean Δ / σ	0.039, 0.004	0.406, 0.002	0.002, 0.0		0.290, 0.027
Maximum, minimum peaks in final difference map/e Å ⁻³	1.20, -2.44	1.57, -1.52	2.51, -2.29	0.84, -0.77	0.94, -0.97
Goodness of fit	1.69	1.31	1.24	3.22	1.16

^a Temperature (data collection) 293 K. ^b Complexes have crystallographic *C*_i symmetry. ^c Two crystallographically independent molecules. ^d $R = \sum |F_o - F_c| / \sum |F_o|$, $R' = [\sum w(F_o^2 - F_c^2)^2 / \sum w(F_o^2)^2]^{1/2}$.

v(PSe)] and 437 cm⁻¹ [v(PSe)]. Positive-ion FAB mass spectrum: *m/z* 1196 [⁸⁰Se₄(PPh₂)₄N₂Cd⁺], 652 [⁸⁰Se₂(PPh₂)₂NCd⁺], 544 [⁸⁰Se₂(PPh₂)₂N⁺], 464 [⁸⁰Se(PPh₂)₂N⁺], 384 [(PPh₂)₄N⁺] and 154 [PhP₂N⁺].

[Hg{N(PPh₂Se)₂-Se,Se'}₂] 4. A solution of Hg(O₂CMe)₂ (0.054 g, 0.172 mmol) in methanol (10 cm³) was added to a solution of K[N(PPh₂Se)₂] (0.199 g, 0.344 mmol) in methanol (15 cm³). The precipitated solid was filtered off, washed with methanol and dried *in vacuo*. Yield 0.1 g, 41% (Found: C, 44.75; H, 3.2. Calc. for C₄₈H₄₀HgN₂P₄Se₄: C, 44.85; H, 3.15%). ³¹P-¹H NMR (CDCl₃): δ 30.2 (s), $\tilde{\nu}_{\max}$ /cm⁻¹ (KBr) 1217s [v(P=N)], 1174m [v(PN)/ δ (CH)], 777m [v(PN)], 532s and 519sm [γ (PNP)/v(P=Se)].

[Zn{N(PPh₂Se)₂-Se,Se'}₂] 5. A solution of Zn(O₂CMe)₂ (0.031 g, 0.172 mmol) in methanol (10 cm³) was added to a solution of K[N(PPh₂Se)₂] (0.199 g, 0.344 mmol) in methanol (15 cm³). The product precipitated as a light yellow solid and was filtered off and washed with methanol *in vacuo*. Yield 0.097 g, 49.4%, m.p. 303–305 °C (Found: C, 49.9; H, 3.45. Calc. for C₄₈H₄₀N₂P₄Se₄Zn: C, 50.15; H, 3.5%). ³¹P-¹H NMR (CDCl₃): δ 30.3 (s), $\tilde{\nu}_{\max}$ /cm⁻¹ (KBr) 1202m [v(P=N)], 1175m [v(PNP)/ δ (CH)], 791w [v(PN)], 534vs and 520m [γ (PNP)/v(P=Se)]. Positive-ion FAB mass spectrum: *m/z* 1150 [⁸⁰Se₄(PPh₂)₄N₂⁶⁴Zn⁺], 613 [⁸⁰Se₂(PPh₂)₂N⁶⁴Zn⁺], 544 [⁸⁰Se₂(PPh₂)₂N⁺], 464 [⁸⁰Se(PPh₂)₂N⁺], 384 [(PPh₂)₄N⁺] and 154 [PhP₂N⁺].

Crystallography

Crystals suitable for X-ray analysis were obtained by slow diffusion of hexane into chloroform solutions of the appropriate compound. Details of the data collections and refinements are summarised in Table 1. In all cases data were corrected for background and Lorentz-polarisation effects, and a semiempiri-

cal (ψ -scan) absorption correction was applied. The structures of complexes **1**, **2** and **4** were solved by direct methods, with full-matrix least-squares refinement,⁶ whilst that of **3** was solved by the Patterson method using DIRDIF 92, also with full-matrix least-squares refinement.⁷ All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were calculated as a riding model with fixed isotropic *U*. Selected bond distances and angles for structures **1–4** are summarised in Table 2.

Atomic coordinates, thermal parameters, and bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1997, Issue 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 186/382.

Results and Discussion

The crystalline metal compounds **1–5** were easily obtained from the corresponding metal(II) salts and the K[N(PPh₂Se)₂]. All are air stable and soluble in organic solvents such as CHCl₃ and benzene, but insoluble in ethanol and hexane. The ³¹P-¹H NMR spectra at room temperature consist of a singlet [δ 31.7 (**1**), 30.2 (**2**), 31.7 (**3**), 30.2 (**4**) and 30.3 (**5**)], in the case of both tin(II) isomers,² with selenium and tin satellites [d, *J*(⁷⁷Se-³¹P) 560.7 Hz and qnt, *J*(¹¹⁹Sn-³¹P) 95 Hz]. The solution ³¹P, ⁷⁷Se and ¹¹⁹Sn NMR spectra are the same for both isolated tin(II) isomers. By using donor solvents as CD₃CN or Me₂SO, or raising the temperature, multiple signals appear, including that corresponding to the free NH(PPh₂Se)₂. This indicates decomposition.

In the IR spectra the assignments of the phosphazene bands were relatively easy after identifying the usual phenyl group bands common to (XPPH₂)₂N⁻ ligands.^{3–5} The individual assignments of the v(P=Se) bands are only partially possible because of the overlap with the corresponding γ (PNP) vi-

Table 2 Selected bond lengths (Å) and angles (°) for complexes **1–4**

	1	1'	2	3	4
M(1)–Se(1)	2.643(3)	2.943(2)	2.997(2)	2.6170(8)	2.637(3)
M(1)–Se(2)	2.662(2)	2.803(2)	2.874(3)	2.6357(8)	2.612(2)
M(2)–Se(3)	2.634(3)			2.6407(8)	2.657(2)
M(2)–Se(4)	2.681(3)			2.6415(8)	2.640(3)
N(1)–P(1)	1.564(17)	1.582(15)	1.594(15)	1.600(4)	1.599(12)
N(1)–P(2)	1.597(20)	1.623(15)	1.596(15)	1.581(4)	1.557(17)
N(2)–P(3)	1.623(20)			1.592(4)	1.576(16)
N(2)–P(4a)	1.531(17)			1.585(4)	1.583(16)
P(1)–Se(1)	2.173(6)	2.161(5)	2.151(6)	2.167(2)	2.184(5)
P(2)–Se(2)	2.177(6)	2.188(5)	2.186(6)	2.173(2)	2.175(6)
P(3)–Se(3)	2.170(7)			2.166(2)	2.170(7)
P(4)–Se(4)	2.170(6)			2.163(2)	2.170(4)
Se(1)–M(1)–Se(2)	91.6(1)	71.4(1)	71.1(1)	112.98(3)	114.1(1)
Se(1)–M(1)–Se(2a)	88.4(1)	88.5(1)	87.9(1)		
Se(1)–M(1)–Se(1a)	180.0(1)	143.6(1)	141.8(1)		
Se(2)–M(1)–Se(2a)		112.7(1)	113.0(1)		
Se(1)–M(1)–Se(3)				104.51(3)	105.6(1)
Se(1)–M(1)–Se(4)				106.42(3)	113.0(1)
Se(2)–M(1)–Se(3)				113.64(3)	105.8(1)
Se(2)–M(1)–Se(4)				107.11(3)	105.6(1)
Se(3)–M(1)–Se(4)				112.04(3)	112.6(1)
Se(3)–M(2)–Se(4)	92.0(1)				
Se(3)–M(2)–Se(3a)	180.0(1)				
Se(3)–M(2)–Se(4a)	88.0(1)				
P(1)–N(1)–P(2)	136.2(13)	129.3(10)	130.1(10)	137.2(3)	139.2(12)
P(3)–N(2)–P(4)	138.7(12)		96.0(2)	133.7(3)	135.5(12)
M(1)–Se(1)–P(1)	97.0(2)	97.2(1)	98.9(1)	100.96(5)	93.0(2)
M(1)–Se(2)–P(2)	96.8(2)	99.6(1)		93.53(5)	99.6(1)
M(1)–Se(3)–P(3)				92.39(5)	95.3(1)
M(1)–Se(4)–P(4)				96.22(5)	92.2(2)
M(2)–Se(3)–P(3)	96.4(2)				
M(2)–Se(4)–P(4)	88.5(2)		117.4(6)		
N(1)–P(1)–Se(1)	118.5(8)	116.9(6)	116.2(6)	119.9(2)	119.2(7)
N(1)–P(2)–Se(2)	118.4(7)	116.3(6)		119.9(2)	119.4(6)
N(2)–P(3)–Se(3)	118.3(7)			117.5(2)	119.2(8)
N(2)–P(4)–Se(4)	119.1(8)			119.9(2)	116.7(5)

brations (ν 525–575 cm^{-1}).⁸ The positive-ion FAB mass spectra exhibit low-intensity signals for the molecular ion, but rather intense fragments containing metal centres. There are relatively intense peaks corresponding to ligand fragments, *i.e.* $[\text{Se}_2(\text{PPh}_2)_2\text{N}^+]$ (m/z 544), $[\text{Se}(\text{PPh}_2)_2\text{N}^+]$ (m/z 464), $[(\text{PPh}_2)_4\text{N}^+]$ (m/z 384) and $[\text{PhP}_2\text{N}^+]$ (m/z 154). All of the observed signals exhibit the expected, characteristic, isotopic distribution patterns.

Crystal structures

The structures of compounds **1–4** are built up of discrete $[\text{M}\{\text{N}(\text{PPh}_2\text{Se})_2\}_2]$ molecules (M = Sn, Pb, Cd or Hg). Every metal centre is co-ordinated to the selenium atoms by two bidentate ligands, forming six-membered chelate rings. The ligands display an asymmetrical co-ordination to the tin(II) and lead(II) cations, resulting in a substantially increased bonding between the metal and one of the selenium atoms in the chelate ring. This behaviour is consistent with some localisation of the bonding (Table 2). In the case of cadmium(II) and mercury(II) the co-ordination is symmetric. The average M–Se bond distances are 2.622(11) and 2.626(18) Å for **3** and **4**, respectively. The average P–N [1.589(8) **3** and 1.57(1) Å **4**] and P–Se bond lengths [2.167(4) **3** and 2.174(6) Å **4**] are consistent with a π -delocalised structure involving the five ligand atoms in the chelate ring, as has been noted in cyclic phosphazenes.⁹

Comparison with the structure of the free **1c**^{3c} reveals that the P–Se bond lengths in these bis-chelates are considerably increased [**1c**, average P–Se 2.092(8) Å], whilst the P–N bond distances are shortened [**1c**, average P–N 1.682(4) Å] (Table 2). This has also been noted in previous analogous structures³ as a consequence of deprotonation and co-ordination. The Se–P–N angles are only marginally enhanced [**1c**, average Se–P–N

115.4(9)°], while the P–N–P angles are increased in complexes **1**, **3** and **4** [**1c**, average P–N–P 122.2(2)°] but are contracted in the distorted ψ -trigonal-bipyramidal compounds **1'** and **2** (Table 2). Along the series of derivatives described here, the great variation observed in the chelate rings angles (P–N–P, M–Se–P and Se–P–N) and the distinct ring conformations adopted reflect the stereochemical freedom of the $\text{MSe}_2\text{P}_2\text{N}$ rings. These differences are accounted for by the variation in size of the central atom and overall structure and demonstrate the high flexibility of this ligand.

The tin(II) compound crystallises dimorphically, as yellow triclinic prisms (**1**) and red tetragonal octahedra (**1'**).² Isomer **1** contains two crystallographically independent molecules. In both the geometry at tin(II) is square planar but the chelate rings are quite different, as demonstrated by the values of the Sn–Se–P angles [average 96.9(1) and 92.4(5.5)°], as well as those of the torsion angles (Table 3). They reveal a distorted chair conformation, just like that in the square-planar tellurium(II) and selenium(II) complexes with **1b**.^{5d,e} In addition, there seem to be important intermolecular contacts between the selenium and hydrogen atoms belonging to the phenyl rings from a neighbouring molecule, which lead to a polymeric structure. Preliminary theoretical studies show that the presence of these hydrogen bridges is fundamental for the stabilisation of the square-planar structure of this yellow isomer (**1**) over the square-pyramidal structure of the red isomer **1'**. Fig. 1 shows the packing of both independent molecules of the square-planar isomer. By contrast, the red isomer **1'** exhibits a completely different geometry. The arrangement around the central atoms in this and the lead(II) derivative **2** can best be described as a ψ -trigonal bipyramid distorted towards a square pyramid (Fig. 2).

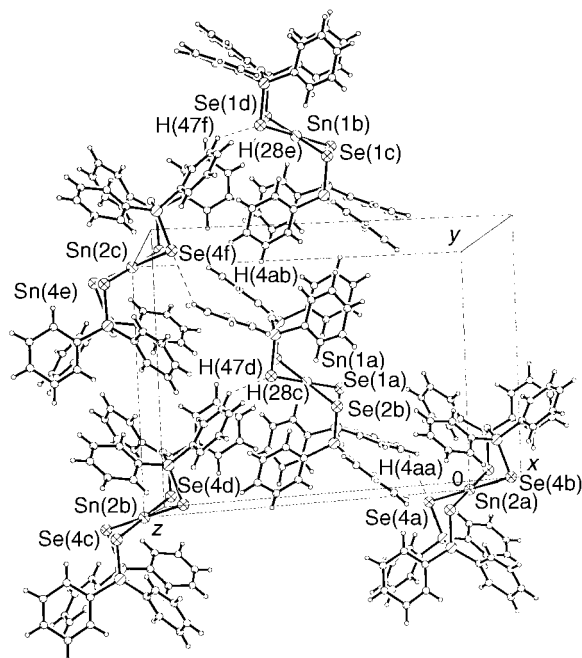


Fig. 1 Packing of the tin(II) square-planar isomer **1**, showing some of the hydrogen bridges

Table 3 Torsion angles ($^{\circ}$) of the SnSeP₂N chelate rings for both independent molecules of isomer **1**

Atom 1	Atom 2	Atom 3	Atom 4	Angle
Chelate ring: molecule containing Sn(1)				
Sn(1)	Se(1)	P(1)	N(1)	-56.2(8)
Se(1)	Sn(1)	Se(2)	P(2a)	111.6(2)
Se(1a)	Sn(1)	Se(2)	P(2a)	68.4(2)
Se(1)	P(1)	N(1)	P(2)	35.9(1.8)
Se(2)	Sn(1)	Se(1)	P(1)	-111.1(2)
Se(2a)	Sn(1)	Se(1)	P(1)	68.9(2)
Chelate ring: molecule containing Sn(2)				
Sn(2)	Se(3)	P(3)	N(2)	24.5(8)
Sn(2)	Se(4)	P(4)	N(2a)	50.9(8)
Se(3)	Sn(2)	Se(4)	P(4)	101.8(2)
Se(3a)	Sn(2)	Se(4)	P(4)	-78.2(2)
Se(3)	P(3)	N(2)	P(4a)	27.7(2.1)

All the angles at the metal centres are reduced by the influence of the stereochemically active lone pair of electrons situated at the vacant equatorial position. Four of the Se-M-Se bond angles are less than 90° , while the other two are $112.7(1)$ and $143.6(1)^{\circ}$ for **1'**, and $113.0(1)$ and $141.8(1)^{\circ}$ for **2**. The last bond angles correspond to the equatorial and axial angles. The two respective M-Se bonds, which are axial in the ψ -trigonal bipyramid, are 0.14 (**1'**) and 0.12 Å (**2**) longer than the two equatorial M-Se bonds (Table 2). Both Sn-Se bond lengths are longer than those in the yellow isomer **1**.² The MSe₂P₂N chelate rings are arranged in a distorted boat conformation with the metal and nitrogen atoms at the apices, as is common in most structures of derivatives involving **1a** and **1b**.⁴

A comparison with the structures of lead(II) and tin(II) complexes containing analogous ligands, [Sn{N(PPh₂X)₂-X,X'}₂] (X = O or S),¹⁰ [Pb{N(PPh₂S)₂-S,S'}₂]¹¹ and [Pb{N(PPh₂)₂SO-S,O'}₂],¹² reveals a similar geometry around the central atoms and also the same asymmetrical co-ordination pattern. It is interesting that the selenium-based lead(II) compound does not display any intermolecular interactions as it was observed in both analogous lead(II) complexes.^{11,12}

In complexes **3** and **4** the co-ordination geometry around the metal centres exhibits a distorted tetrahedral arrangement (Fig. 3). The Se-M-Se bond angles suffer only minor deviations from

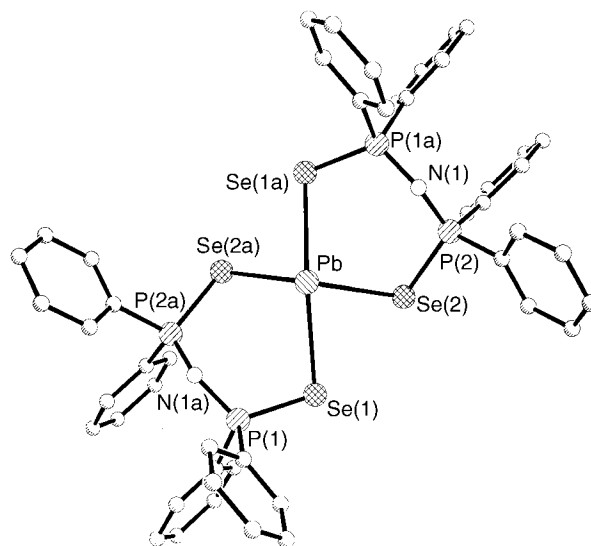


Fig. 2 Molecular structure of the lead(II) compound **2**; the structure of isomer **1'** is very similar² (hydrogen atoms omitted for clarity)

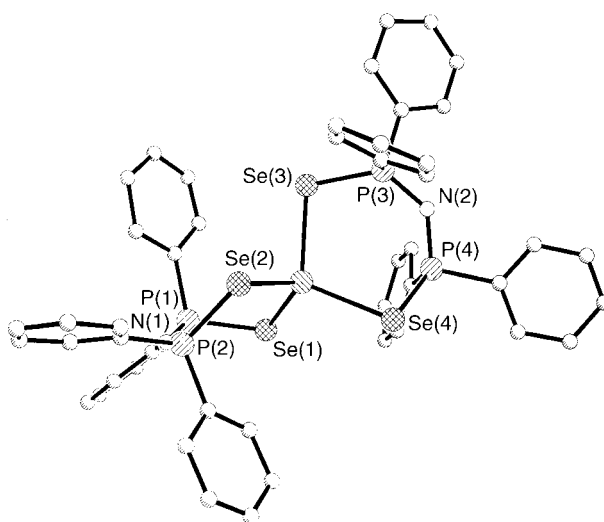


Fig. 3 Molecular structure of [Hg{N(PPh₂)₂-Se,Se'}₂] **4**; the structure complex of **3** is quite similar (hydrogen atoms omitted for clarity)

the ideal tetrahedral value of 109.5° (ca. 4° above and below the ideal value). The average Se...Se interatomic distances are $3.73(8)$ and $4.30(10)$ Å for **3** and **4**, respectively. The cadmium(II) derivative of **1b**, [Cd{N(PPh₂S)₂-S,S'}₂], exhibits the same co-ordination geometry.¹³

The MSe₂P₂N chelate rings (M = Cd or Hg) are arranged in a distorted boat conformation with selenium and phosphorus atoms at the apices. This conformation was previously observed in the MSe₂P₂N chelate rings in the platinum(II), palladium(II),^{3b} antimony(III), bismuth(III) and indium(III)^{3d} chelate compounds.

The observed structural diversity of [M{N(PPh₂Se)₂-Se,Se'}₂] complexes demonstrates the ability of the selenium-based ligand to fulfil the requirements imposed by the central atom. This is due to its great flexibility and notable chelating ability as well as the employment of soft donor atoms.

Acknowledgements

This work was supported by UNAM-DGAPA project grant IN100395. V. G.-M. acknowledges the Mexican National Council of Science and Technology, CONACYT, for generous support. P. K. thanks Soros Foundation Open Society Funds and Hlavkouch Foundation for travel support. We also thank

L. Velasco-Ibarra and R. L. Gaviño-Ramírez for recording the FAB mass and NMR spectra, respectively.

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Received 15th July 1996; Paper 6/04961C