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Synthesis, crystal structures and spectra of Hg(II)-1,2-bis(diphenylphosphino)ethane monoxide complexes: Monomer and polymer formation

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Abstract

The reaction of mercury(II) halides with 1,2-bis(diphenylphosphino)ethane monoxide (dppeO) in 1:1 molar ratio yielded P,O-coordinated polymers having the empirical formula $[HgX_2(dppeO)]_n$ [X = Cl (**1**), Br (**2**), I (**3**)]. In contrast, the reaction between the same reactants in a 1:2 molar ratio yielded the P, P-coordinated monomeric complexes, $HgX_2(dppeO)_2$[X = Cl (**4**), Br (**5**), I (**6**)]. The structures of **2**, **3**, **4** and **5** have been characterized crystallographically. The results indicate that the geometry around the mercury atom in each of these molecules is tetrahedral with considerable distortion. The ^{31}P NMR spectra of the 1:1 complexes indicate the dissociation of the Hg–O bond in solution.

Keywords: Bisphosphine monoxide; Mercury(II) complexes; Coordination polymer

1. Introduction

Mercury(II) phosphine complexes are well known [1,2], and bisphosphine monoxides (BPMOs) are an important class of hemilabile ligands containing both soft (P) and hard (O) nucleophilic centers [3]. Transition metal complexes of these ligands have attracted much attention due to their versatile coordination chemistry and their application in catalysis [3–5]. Grim et al. [6] have reported complexes of $Ph_2PCH_2P(O)Ph_2$ and $Ph_2P(O)CH(Pr)PPh_2$ (Pr = *n*-propyl) with HgX_2 (X = Cl, Br). The complexes have been formulated as P,O-chelates although no appreciable change in $\nu(P=O)$ has been observed in the IR spectra in some cases. In the crystal structure of a P,O-chelate complex, *trans*-$[Hg\{Ph_2PNP(O)Ph_2–P,O\}_2]$, the Hg atom was found to have a square planar geometry [7]. The complexes of mercury(II) with other unsymmetrical phosphines containing P, N [8] and P, S [9] donors have also been studied. The crystal structures of $[Cl_2(Ph_2PCH_2CH_2NEt_2)Hg]$ [8] and $[\{Ph_2PCH_2P(S)\}HgI_2]$ [10] revealed a chelate mode of coordination with the mercury atom having a distorted tetrahedral geometry. It is apparent that the presence of different donor atoms in the same ligand induces different geometries and structures in the Hg(II) complexes. Furthermore, coordination of ligands towards Hg(II) has assumed importance since, in the natural mercury detoxification process, the initial Hg–C bond cleavage involves the increase in the coordination numbers around Hg [11]. In addition, evidence for new classes of metal-binding motifs in enzymes, transcription factors and regulatory proteins emphasize the need for structural insights about local Hg(II) coordination environments [12]. Herein, we report the synthesis, spectral and structural characterization of

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Hg(II) halide complexes of a BPMO ligand 1,2-bis(diphenylphosphino)ethane monoxide (dppeO).

2. Experimental

All reactions were carried out under an atmosphere of dry nitrogen. Reactants and reagents were obtained from Aldrich Chemical Company and used without further purification. The solvents were dried and distilled using standard methods [13].

2.1. Instrumentation

The ^{1}H and ^{31}P–{^{1}H}NMR spectra were recorded in $CDCl_3$ solution on a Bruker DPX400 spectrometer at 400.13 and 161.98 MHz, referenced relative to residual $CHCl_3$ and external 85% H_3PO_4, respectively. The IR spectra in the interval of 4000–400 cm^{-1} were recorded on a Perkin–Elmer 1720X FT-IR spectrometer using KBr pellets. Elemental analyses were performed at the Ecole d'ingénieurs de Fribourg, Switzerland.

2.2. Synthesis of compounds

2.2.1. 1,2-Bis(diphenylphosphino)ethane monoxide (dppeO)

The phosphonium salt obtained by the reaction of 1,2-bis(diphenylphosphino)ethane (dppe) with benzyl bromide in dry toluene, was hydrolysed with aqueous sodium hydroxide to yield the ligand, as reported previously [14]. IR (cm^{-1}): 3052, 1937, 2903, 1588, 1480, 1435, 1182, 1122, 1106, 1069, 1025, 997, 881, 783, 727, 692, 712, 536, 513, 504, 474. ^{1}H NMR : 2.28 (br, 4H), 7.29–7.71 (m, 20H). ^{31}P NMR : −11.68 (d, $^{3}J_{P–P} = 48.4$), 33.18 (d, $^{3}J_{P–P} = 48.4$).

*2.2.2. [HgCl$_2$(dppeO)]$_n$ (**1**)*

To a methanolic solution of mercury(II) chloride (0.13 g, 0.48 mmol), solid dppeO (0.2 g, 0.48 mmol) was added in portions and allowed to stir overnight. The white precipitate obtained was filtered, washed with cold methanol and recrystallized from acetonitrile. Yield: 0.27 g, 83%; m.p.: 253–255 °C. *Anal.* Calc. for $C_{26}H_{24}Cl_2HgOP_2$: C, 45.53; H, 3.53. Found. C, 45.93; H, 3.51%. IR (cm^{-1}): 3054, 2913, 1589, 1436, 1160, 1121, 1103, 997, 741, 725, 690, 540, 516, 506, 476. ^{1}H NMR : 2.87–2.97 (m, 2H), 3.08–3.13 (m, 2H), 7.40–7.91 (m, 20H). ^{31}P NMR : 33.40 (d, $^{3}J_{P–P} = 58.9$), 37.12 (d, $^{3}J_{P–P} = 58.9$, $^{1}J_{Hg–P} = 7449$).

*2.2.3. [HgBr$_2$(dppeO)]$_n$ (**2**)*

The reaction was carried out as for **1** using mercury(II) bromide (0.17 g, 0.48 mmol). The product obtained was recrystallized by slow evaporation of a chloroform solution. Yield: 0.32 g, 87%; m.p.: 225–227 °C. *Anal.* Calc. for $C_{26}H_{24}Br_2HgOP_2$: C, 40.30; H, 3.12. Found. C, 40.21; H, 3.08%. IR (cm^{-1}): 3054, 2907, 1589, 1483, 1435, 1409, 1164, 1121, 1101, 1069, 1026, 997, 739, 726, 690, 540, 515, 476. ^{1}H NMR : 2.89 (br, 2H), 3.06 (br, 2H), 7.42–7.89 (m, 20H). ^{31}P NMR : 29.46 (d, $^{3}J_{P–P} = 57.5$), 33.38 (d, $^{3}J_{P–P} = 57.5$, $^{1}J_{Hg–P} = 6422$).

*2.2.4. [HgI$_2$(dppeO)]$_n$ (**3**)*

Complex **3** was obtained in the same way as **1** using mercury(II) iodide (0.22 g, 0.48 mmol) and dppeO (0.2 g, 0.48 mmol). The product obtained was recrystallized by slow evaporation of a chloroform solution. Yield: 0.35 g, 83%; m.p.: 212–214 °C. *Anal.* Calc. for $C_{26}H_{24}Hg\ I_2OP_2$: C, 35.94; H, 2.78. Found. C, 35.87; H, 2.75%. IR (cm^{-1}): 3053, 2906, 1588, 1484, 1436, 1411, 1156, 1120, 1098, 998, 739, 726, 691, 538, 507, 494, 474. ^{1}H NMR: 2.75 (br, 2H), 2.92 (br, 2H), 7.45–7.86 (m, 20H). ^{31}P NMR: 6.34 (br, $^{1}J_{Hg–P} = 4366$), 32.93 (d, $^{3}J_{P–P} = 54.9$).

*2.2.5. [HgCl$_2$(dppeO)$_2$] (**4**)*

A solution of mercury(II) chloride (0.098 g, 0.36 mmol) in methanol was added dropwise to a solution of dppeO (0.3 g, 0.72 mmol) in dichloromethane. The mixture was stirred for 3 h. White feathery crystals obtained after slow evaporation of the solvent were washed with cold methanol and dried *in vacuo*. Yield: 0.29 g, 75%; m.p.: 250 °C. *Anal.* Calc. for $C_{52}H_{48}Cl_2HgO_2P_4$: C, 56.76; H, 4.40. Found. C, 56.47; H, 4.35%. IR (cm^{-1}): 3051, 2912, 1573, 1484, 1436, 1188, 1121, 1104, 997, 738, 728, 693, 540, 517, 506, 479. ^{1}H NMR: 2.90 (br, 8H), 7.27–7.91 (m, 40H). ^{31}P NMR: 28.75 (br, $^{1}J_{Hg–P} = 4654$), 34.08 (br).

*2.2.6. [HgBr$_2$(dppeO)$_2$] (**5**)*

Complex **5** was prepared in the same way as for **4** using mercury(II) bromide (0.13 g, 0.36 mmol). Yield: 0.29 g, 70%. m.p.: 216–218 °C. *Anal.* Calc. for $C_{52}H_{48}Br_2HgO_2P_4$: C, 52.52; H, 4.07. Found. C, 51.92; H, 4.06%. IR (cm^{-1}): 3429, 3051, 2910, 1573, 1484, 1436, 1190, 1121, 1103, 996, 737, 727, 693, 539, 516, 507, 478. ^{1}H NMR: 2.88 (br, 8H), 7.45–7.93 (m, 40H). ^{31}P NMR: 21.19 (br, $^{1}J_{Hg–P} = 3874$), 33.21 (br).

*2.2.7. [HgI$_2$(dppeO)$_2$] (**6**) · CHCl$_3$*

Complex **6** was prepared in the same way as for **4** using mercury(II) iodide (0.16 g, 0.36 mmol). The product was crystallized in chloroform. Yield: 0.35 g, 75%; m.p.: 196–198 °C. *Anal.* Calc. for $C_{53}H_{49}Cl_3HgI_2O_2P_4$: C, 45.38; H, 3.52. Found. C, 45.82; H, 3.53%. IR (cm^{-1}): 3052, 2942, 1589, 1483, 1436, 1184, 1120, 1103, 997, 736, 692, 538, 508, 478. ^{1}H NMR: 2.70–2.83 (m, 8H), 7.27–7.88 (m, 40H). ^{31}P NMR: 4.32 (br, $^{1}J_{Hg–P} = 3042$), 33.14 (br).

2.3. X-ray crystallography

Single crystals of **2** and **3** were obtained by slow evaporation of a chloroform solution. Well formed crystals of **4** were obtained as a DMSO solvate by mixing two equivalents of dppeO, 1 equiv. of $HgCl_2$ and one equivalent of dimethyltin dichloride, in DMSO and allowed to stand. Crystals of **5** were grown from a dichloromethane solution by vapour diffusion of hexane. The intensity data were collected at 173 K (−100 °C) on a Stoe Mark II-Image Plate Diffraction System [15] equipped with a two-circle goniometer using Mo Kα graphite monochromated radiation. The structures were solved by Direct methods using the programme SHELXS-97 [16]. The refinement and all further calculations were carried out using SHELXL-97 [17]. The H-atoms were included in calculated positions and treated as riding atoms using SHELXL default parameters. The non-H atoms were refined anisotropically, using weighted full-matrix least-squares on F^2. In complex **2**, disorder was noted in one of the ligand molecules in the atoms C53, C54, P6, O3 and the phenyl rings C67–C72 and C73–C78; two sets of positions were refined for the above atoms (occupancies 0.47(A) and 0.53(B)). The phenyl ring atoms C42, C43, C45 and C46 were also found to be disordered over two positions and refined with occupancies 0.5 for both the positions (A and B). In the co-crystallised chloroform molecule, the chlorine atoms were found to be disordered over two positions (occupancies 0.566 (A) and 0.434 (B)), the C–Cl distances were constrained to their theoretical values and the thermal parameters made equal. All the phenyl rings, except ring C21–C26, have been constrained to have thermal parameters equal to that of their respective *ipso* carbon atom. Complex **3** crystallized in the non-centrosymmetric triclinic space group $P\bar{1}$ and was refined as an inversion twin (final BASF value =0.418(13)). In complexes **3** and **4**, the phenyl rings were constrained to have thermal parameters equal to that of their respective *ipso* carbon atom. Disorder was also found in the phenyl rings and in atoms P2 and O1 of complex **5**. Two sets of positions (A and B) were refined with occupancies of 0.5,

Table 2
Selected bond lengths (Å) and bond angles (°)

Complex **2**			
Hg(1)–P(1)	2.395(2)	Hg(1)–O(3A^i)	2.56(2)
Hg(2)–P(3)	2.404(2)	Hg(2)–O(1)	2.526(6)
Hg(3)–P(5)	2.411(2)	Hg(3)–O(2)	2.566(6)
Br(1)–Hg(1)	2.491(1)	Br(4)–Hg(2)	2.590(1)
Br(2)–Hg(1)	2.609(1)	Br(5)–Hg(3)	2.521(1)
Br(3)–Hg(2)	2.510(1)	Br(6)–Hg(3)	2.557(1)
O(1)–P(2)	1.489(6)	O(2)–P(4)	1.497(7)
O(3A)–P(6A)	1.51(2)		
P(1)–Hg(1)–O(3A^i)	88.2(5)	P(3)–Hg(2)–O(1)	81.42(14)
P(1)–Hg(1)–Br(1)	134.95(6)	P(3)–Hg(2)–Br(3)	134.13(6)
P(1)–Hg(1)–Br(2)	114.17(5)	P(3)–Hg(2)–Br(4)	118.62(6)
Br(1)–Hg(1)–Br(2)	107.87(4)	Br(3)–Hg(2)–Br(4)	104.51(4)
O(3A^i)–Hg(1)–Br(2)	92.7(4)	Br(3)–Hg(2)–O(1)	107.91(14)
Br(1)–Hg(1)–O(3A^i)	105.5(5)	O(1)–Hg(2)–Br(4)	98.78(14)
P(5)–Hg(3)–O(2)	86.67(16)	Br(5)–Hg(3)–Br(6)	107.92(6)
P(5)–Hg(3)–Br(5)	127.60(7)	Br(5)–Hg(3)–O(2)	102.45(15)
P(5)–Hg(3)–Br(6)	121.91(7)	Br(6)–Hg(3)–O(2)	97.94(14)
Symmetry operation, i = $x, y-1, z$.			
Complex **3**			
Hg(1)–P(1)	2.468(8)	Hg(1)–I(2)	2.699(2)
Hg(2)–P(3^i)	2.477(7)	Hg(1)–I(1)	2.732(3)
Hg(1)–O(2)	2.480(19)	Hg(2)–I(3)	2.700(3)
Hg(2)–O(1)	2.49(2)	Hg(2)–I(4)	2.709(3)
O(1)–P(2)	1.531(19)	O(2)–P(4)	1.467(17)
P(1)–Hg(1)–O(2)	90.8(5)	P(3^i)–Hg(2)–O(1)	91.7(4)
P(1)–Hg(1)–I(2)	124.4(2)	P(3^i)–Hg(2)–I(3)	122.2(2)
P(1)–Hg(1)–I(1)	118.1(2)	P(3^i)–Hg(2)–I(4)	117.7(2)
I(2)–Hg(1)–I(1)	110.29(9)	I(3)–Hg(2)–I(4)	114.31(9)
O(2)–Hg(1)–I(1)	106.6(5)	O(1)–Hg(2)–I(4)	102.8(5)
O(2)–Hg(1)–I(2)	100.4(5)	O(1)–Hg(2)–I(3)	100.0(5)
Symmetry operation, i = $x, y, z-1$			

Table 1
Crystal data and refinement details for complexes **2**–**5**

	2	**3**	**4**	**5**
Empirical formula	$C_{78}H_{72}Br_6Hg_3O_3P_6$, $CHCl_3$	$C_{52}H_{48}Hg_2I_4O_2P_4$	$C_{52}H_{48}Cl_2HgO_2P_4$, $(CH_3)_2SO$	$C_{52}H_{48}Br_2HgO_2P_4$
Formula weight	2443.77	1737.56	1178.40	1189.19
Crystal system	triclinic	triclinic	orthorhombic	orthorhombic
Space group	$P\bar{1}$ (No. 2)	$P\bar{1}$ (No. 1)	*Pbcm* (No. 57)	*Pbcm* (No. 57)
Unit cell dimensions				
a (Å)	11.9992(9)	9.282(2)	8.8571(5)	8.8042(5)
b (Å)	17.8071(12)	10.667(2)	23.6279(17)	23.320(2)
c (Å)	21.2026(14)	15.108(3)	24.4130(12)	24.2351(16)
α (°)	71.616(5)	108.594(15)	90	90
β (°)	81.423(6)	90.358(17)	90	90
γ (°)	78.554(6)	102.191(17)	90	90
V (Å^3)	4195.4(5)	1381.4(5)	5109.0(5)	4975.7(6)
Z	2	1	4	4
Absorption coefficient (mm^{-1})	8.588	7.938	3.326	4.866
Collected reflections	57012	11767	45912	20451
Independent reflections	22579	8184	4687	4540
R_{int}	0.0845	0.1151	0.0899	0.1174
Observed reflections [$I > 2\sigma(I)$]	12462	4892	3675	3157
R_1 (observed data)	0.0587	0.0782	0.0536	0.0544
WR_2 (all data)	0.1369	0.2078	0.1273	0.1228

Table 3
Selected bond lengths (Å) and bond angles (°)

Complex **4**			
Hg(1)–P(2)	2.453(2)	Cl(2)–Hg(1)	2.587(3)
Cl(1)–Hg(1)	2.594(3)	O(1)–P(1)	1.481(5)
P(2)–Hg(1)–P(2^{i})	143.93(8)	P(2)–Hg(1)–Cl(1)	106.09(4)
P(2)–Hg(1)–Cl(2)	95.59(5)	Cl(2)–Hg(1)–Cl(1)	98.16(10)
Symmetry operation, $i = x, y, -z - 1/2$			
Complex **5**			
Hg(1)–P(1)	2.456(2)	Br(2)–Hg(1)	2.664(1)
Br(1)–Hg(1)	2.725(1)	O(1)–P(2)	1.483(13)
P(1)–Hg(1)–P(1^{i})	142.34(10)	P(1)–Hg(1)–Br(1)	92.92(6)
P(1)–Hg(1)–Br(2)	107.11(6)	Br(2)–Hg(1)–Br(1)	105.19(5)
Symmetry operation, $i = x, y, -z + 3/2$			

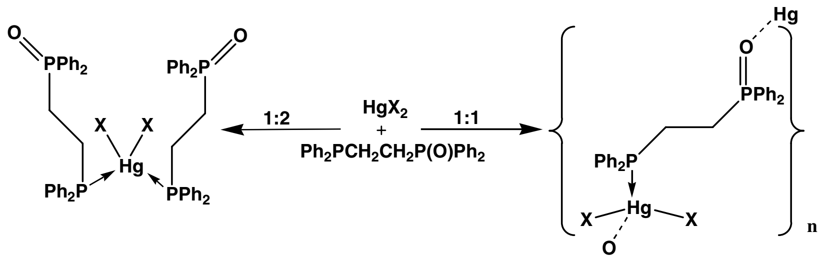
and the bond distances have been constrained to their theoretical values. Semi-empirical absorption corrections were applied using MULscanABS (PLATON) for **2** ($T_{min}/T_{max} = 0.080/0.178$) and **5** ($T_{min}/T_{max} = 0.621/0.895$). Empirical absorption corrections were applied using DELrefABS (PLATON) for **3** ($T_{min}/T_{max} = 0.167/0.639$) and **4** ($T_{min}/T_{max} = 0.401/0.796$). Further crystallographic data are given in Table 1 and selected bond distances and angles are given in Tables 2 and 3. The molecular structure and crystallographic numbering schemes are illustrated in ORTEP III [18] and PLATON [19] drawings, Figs. 1–5.

3. Results and discussion

The reaction of 1,2-bis(diphenylphosphino)ethane monoxide (dppeO) with various mercury(II) halides has been carried out. Different coordination modes have been observed with different metal to ligand stoichiometry. The reactions are represented in Scheme 1.

3.1. Hg(II)–dppeO 1:1 complexes

The reaction of HgX_2 (X = Cl, Br, I) and dppeO in equimolar ratio in methanol yielded white precipitates immediately. The IR spectra of the products show strong



Scheme 1. Reaction of dppeO with Hg(II) halides.

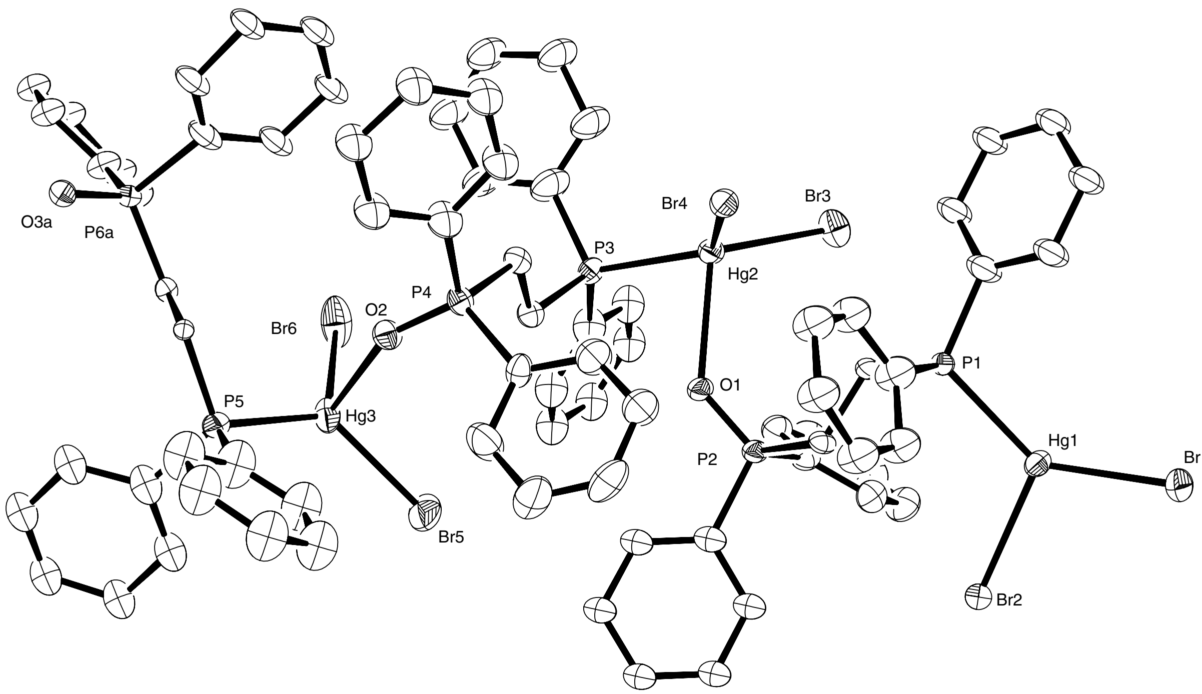


Fig. 1. Asymmetric unit of **2** at 30% probability ellipsoids. The hydrogen atoms, the disordered components and the solvent molecule of $CHCl_3$ have been omitted for clarity.

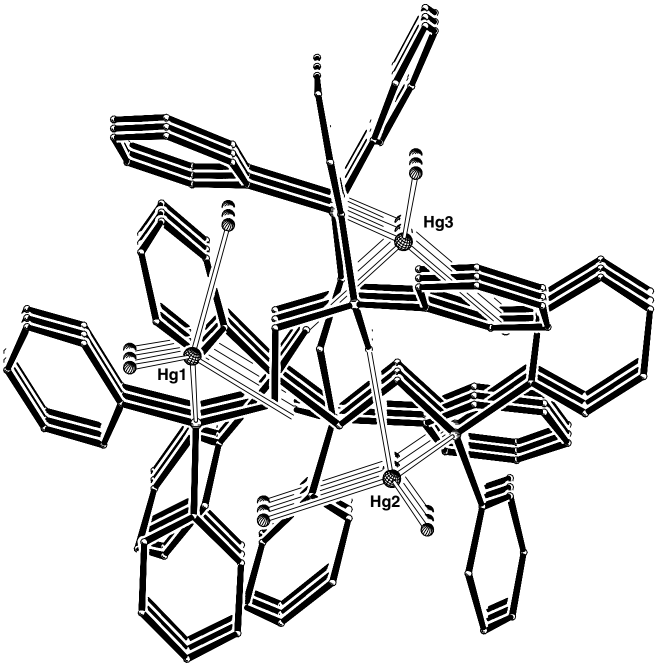


Fig. 2. A view of complex **2** along crystallographic *b*-axis. The figure shows the pseudo three-fold screw axis leading to an helical arrangement.

bands at 1160, 1164 and 1156 cm^{-1} for **1**, **2** and **3**, respectively, attributed to the coordinated (P = O) group. The ^{1}H NMR spectra exhibit two broad multiplets for two magnetically non-equivalent methylene protons in the ligand. Of the two signals in the ^{31}P NMR spectra, the ones exhibiting satellite signals due to ^{199}Hg (16.4% natural abundance, $I = 1/2$), are assigned to the coordinated 'PPh$_2$'. The chemical shifts and the coupling constants decrease going from chloride to iodide (see Table 4) as observed previously for [HgX$_2$(PPh$_3$)$_n$] (X = Cl, Br,I) ($n = 1$, 2) [20,21]. The ^{31}P NMR signals due to 'Ph$_2$P = O' are not shifted much from the corresponding free ligand resonance (+33.18 ppm), suggesting the dissociation of the Hg–O bond in solution.

3.2. Hg(II)–dppeO 1:2 complexes

When 1 equiv. of HgX$_2$ (X = Cl, Br, I) was added dropwise to two equivalents of dppeO, the 1:2 complexes were obtained in which the ligand coordinates exclusively with the phosphine moiety. The IR and ^{31}P NMR spectra are in accordance with the observed coordination mode. Interestingly, the coordination chemical shifts ($\Delta\delta = \delta_{\text{complex}} - \delta_{\text{ligand}}$) and the Hg–P coupling constants are lower for the 1:2 complexes (Table 4). The difference in the spectral parameters for the 1:1 and 1:2 complexes is most probably dominated by the steric interactions [20] due to the proximity of bulky phenyl groups to the metal center in the latter. Indeed, complex **6** with bulky iodide ligands appears very labile in solution. Repeated attempts to obtain single crystals of complex **6** lead to the formation

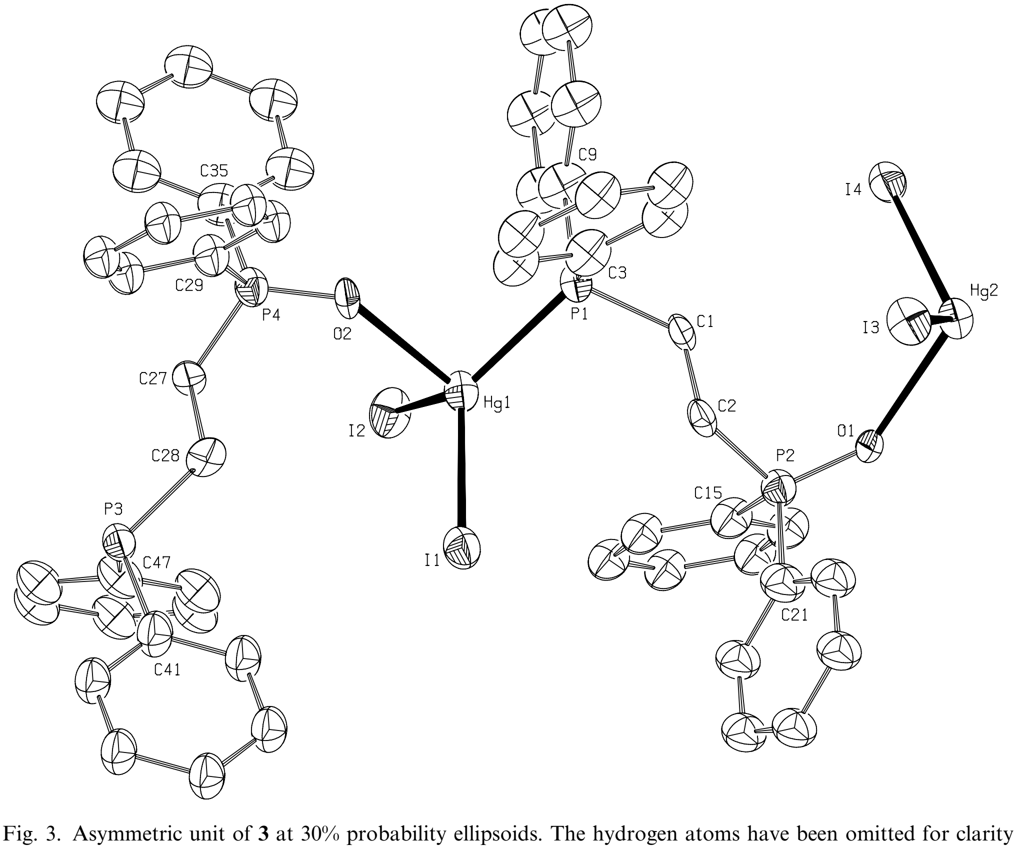


Fig. 3. Asymmetric unit of **3** at 30% probability ellipsoids. The hydrogen atoms have been omitted for clarity.

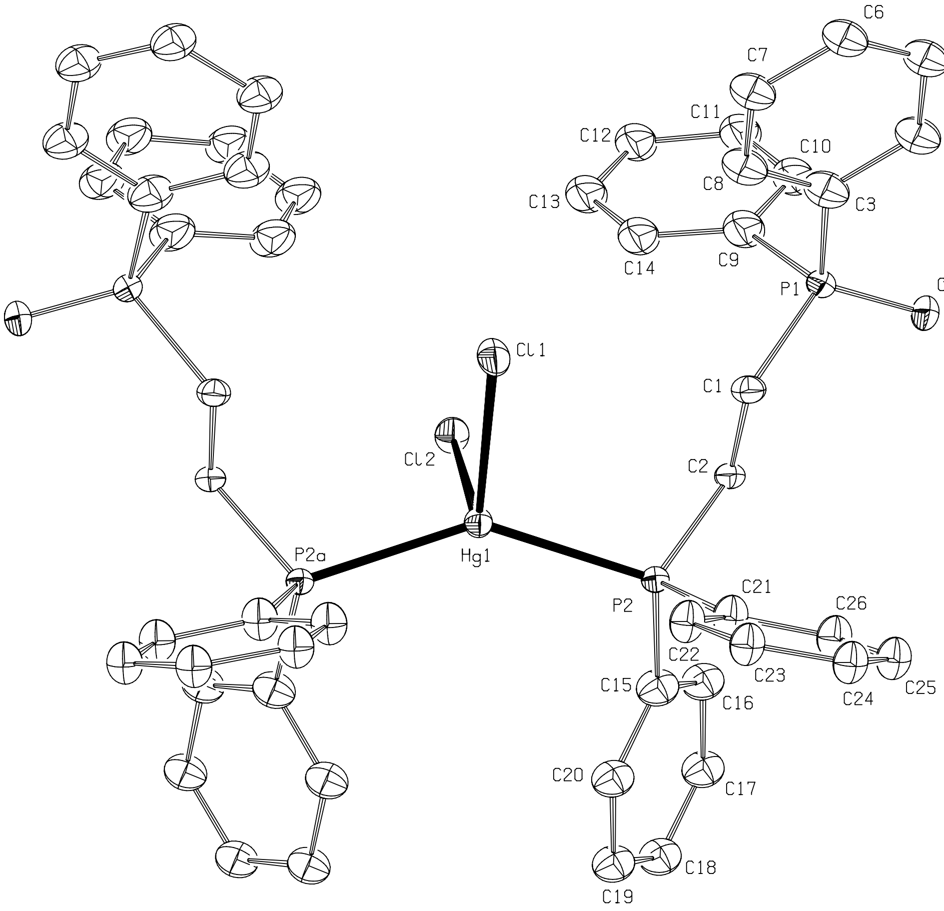


Fig. 4. Molecular structure of **4** at 30% probability ellipsoids. Atoms Hg1, Cl1 and Cl2 lie in the mirror plane. The hydrogen atoms and the DMSO solvent molecule have been omitted for clarity.

of complex **3**, as confirmed by the unit cell parameters derived from the preliminary X-ray diffraction data. In the ^{1}H NMR spectra, the methylene protons of the dppeO framework appear as a single peak for complexes **4** and **5**, while the same protons show two broad resonances for complex **6**.

A noteworthy feature of the ^{31}P NMR spectra is the increased intensity of the phosphine oxide signal which seems to have merged peaks. This may be attributed to the presence of $Ph_2P(O)CH_2CH_2P(O)Ph_2$ (dppeO$_2$) in solution, formed due to the oxidation of dissociated dppeO by Hg^{2+}. Catalytic oxidation of bis(diphenylphosphino)methane (dppm) by Hg^{2+} to dppmO and dppmO$_2$ has been noted previously [22].

3.3. Molecular structures of the 1:1 complexes 2 and 3

The molecular structures of complexes **2** and **3** are shown in Figs. 1 and 3, respectively, and selected bond distances and angles are given in Table 2. The asymmetric unit of **2** is composed of three $HgBr_2$ units bridged by three dppeO ligands and a molecule of chloroform solvent. The X-ray analysis reveals the coordination of both ‘P’ and ‘O’ atoms of the ligand to mercury thereby forming an infinite one dimensional polymeric chain. The chain contains a pseudo three-fold screw axis which propagates along the crystallographic *b*-axis, thus exhibiting a pseudo-helical arrangement (Fig. 2).

The geometries around the three Hg centers are highly distorted tetrahedral. The bond angles range from 88.2(5)° to 134.95(6)°, 81.42(14)° to 134.13(6)° and 86.67(16)° to 127.62(7)° for Hg(1), Hg(2) and Hg(3), respectively. Similar range has been observed in $[Hg\{Ph_2P(S)CH_2PPh_2\}I_2]$ [10]. The geometry around Hg in the above complex was considered as flattened tetrahedral, since the metal deviates by only 0.3823(8) Å from the least-squares plane defined by the two I atoms and one P atom in the direction of the capping S atom. In the present case the Hg atom deviations from the best least-squares plane defined by the two Br atoms and one P atom are 0.244, 0.234, 0.229 Å for Hg(1), Hg(2) and Hg(3), respectively, from the direction of the capping O atom. Such type of flattening from the tetrahedral geometry could be the result of several factors including the steric interactions. While the Hg–P distances (2.395(2)–2.411(2) Å) are comparable to the same distance in the P,O-chelate complex *trans*-$[Hg\{Ph_2PNP(O)Ph_2–P,O\}_2]$ [7], the Hg–O bonds (mean distance 2.55(9) Å) are longer than the *normal*

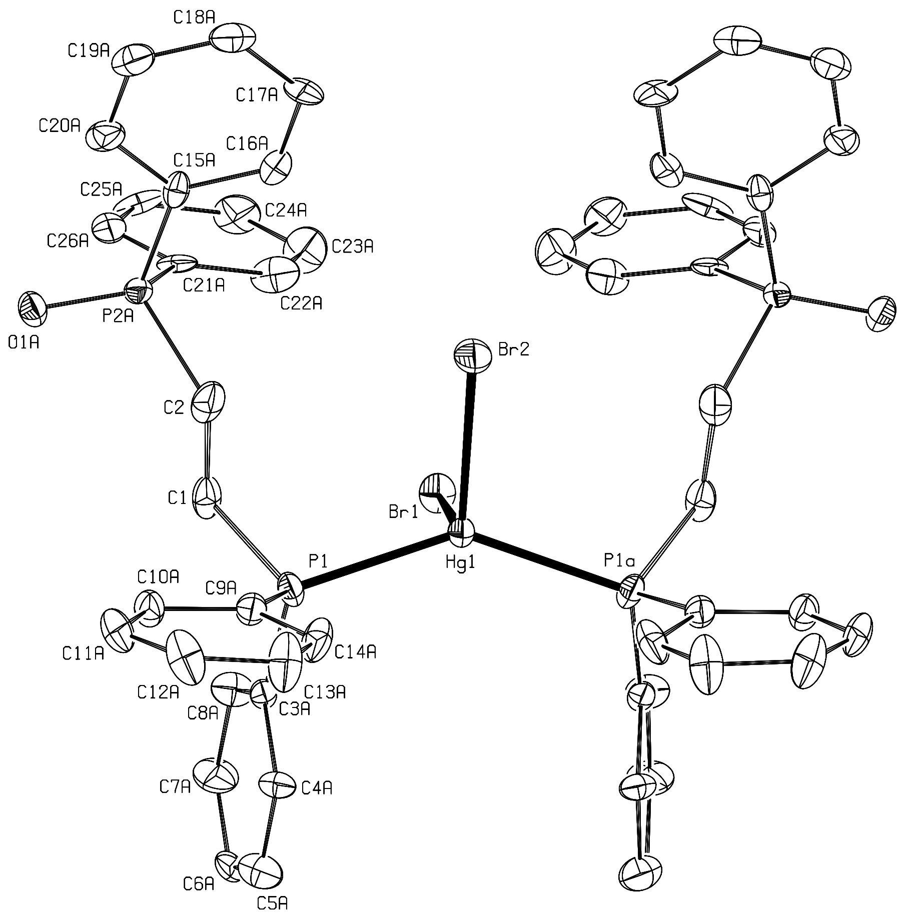


Fig. 5. Molecular structure of complex **5** at 30% probability ellipsoids. Atoms Hg1, Br1 and Br2 lie in the mirror plane. The hydrogen atoms and the disordered components have been omitted for clarity.

Hg–O covalent bond (ca. 2.1 Å), thus accounting for its dissociation in solution as noted in the ^{31}P NMR spectra.

Complex **3** crystallizes in the non-centrosymmetric triclinic space group $P\bar{1}$. The asymmetric unit consists of two HgI_2 units bridged by two dppeO molecules, resulting in the formation of a linear zig-zag polymeric chain. A similar distorted arrangement is observed as that of **2**. However, compared to **2,** the deviations of the Hg(1) and Hg(2) atoms from the least-squares plane described by two I atoms and one P atom are high being equal to 0.406 and 0.367 Å, respectively. The average Hg–P distance of 2.472(7) Å is longer than the values observed in **2**, while the average Hg–O distance of 2.485(2) Å is shorter.

It is interesting to note that although the precursor ligand, dppe and its fully oxidized form $dppeO_2$ have the pronounced tendency to act as a bridging ligands, the bridging tendency of dppeO has not been, to the best of our knowledge, previously confirmed [23] crystallographically with any metal. Hence, complexes **2** and **3** represent the first examples of structurally characterized polymeric complexes where dppeO acts as a bridging bidentate ligand.

Table 4
IR and ^{31}P NMR spectral parameters [ν (cm^{-1}), δ (ppm), J (Hz)]

	$\nu(P=O)$	δ PPh_2	δ $Ph_2P=O$	$^3J_{(P-P)}$	$^1J_{(Hg-P)}$	$\Delta\delta^a$ (PPh_2)
dppeO	1182	−11.68	33.18	48.4		
1	1160	37.12	33.40	58.9	7449	48.7
2	1164	29.46	33.38	57.5	6422	41.1
3	1156	6.34	32.93	54.9	4366	18.0
4	1188	28.75	34.08		4654	40.4
5	1190	21.19	33.21		3874	32.9
6	1184	4.32	33.14		3042	16.0

[a] ($\Delta\delta = \delta_{complex} - \delta_{ligand}$).

3.4. *Molecular structures of 1:2 complexes* **4** *and* **5**

The molecular structures of the 1:2 complexes **4** and **5** are shown in Figs. 4 and 5, respectively. Table 3 contains selected bond distances and angles. The mercury atom is coordinated to two halogens and two phosphorus atoms. The P = O groups in both complexes remain free and no significant interaction with the metal has been observed. The mercury and the two halogen atoms lie in the mirror plane. Complex **4** crystallizes as a DMSO solvate. The geometry around mercury is distorted tetrahedral. The Hg–P distances of 2.453(2) and 2.456(2) Å in **4** and **5**, respectively, are in the range of 2.39(1)–2.574(3) Å reported previously for 1:2 mercuric halide–phosphine complexes [24,25]. The P–Hg–P angles 143.93(8)° and 142.34(10)° in **4** and **5**, respectively, are significantly higher than the tetrahedral angle. Such a trend was observed in the complexes [$HgCl_2(PPh_3)_2$] [24] and [$HgCl_2(PEt_3)_2$] [26], where the P–Hg–P angles are 134° and 158°, respectively. These were interpreted in terms of strong Hg–P bonding and weaker Hg–Cl interactions. It seems reasonable to include steric effects as well as the tendency of Hg(II) to acquire primary coordination of valency of two, to account for the higher P–Hg–P angles.

In summary, we have prepared and characterized mercury(II)–dppeO complexes with different molecular structures and geometries. The P, O-coordinated infinite one- dimensional polymers were obtained when 1:1 molar ratio of metal to ligand was used. Complexes **2** and **3** represent the first crystallographically characterized examples containing dppeO ligand in bridging bidentate coordination mode. The Hg(II) center is located in a highly distorted tetrahedral environment. The change in the halogen from bromide to iodide has a marked influence in the structure of the polymeric chain from pseudo helical to a zig-zag arrangement. On the other hand exclusively P, P-coordinated complexes were obtained when two equivalents of ligand were added to one equivalent of the metal salt . The complexes were discretely monomeric containing uncoordinated phosphine oxide group. The results suggest that the interaction of Hg(II) with different phosphines remain an active field of research leading to complexes with unusual structures.

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Appendix A. Supplementary material

CCDC 617574, 617575, 617576 and 617577 contain the supplementary crystallographic data for **2**, **3**, **4** and **5**. 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. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.poly.2006.10.030.

References

[1] K. Brodersen, H.-U. Hummel, in: G. Wilkinson (Ed.), Comprehensive Coordination Chemistry, vol. 5, Pergamon Press, Oxford, 1987, pp. 1047–1097.

[2] D.J. Eisler, R.J. Puddephatt, Dalton Trans. (2003) 3567, and references therein.

[3] V.V. Grushin, Chem. Rev. 104 (2004) 1629.

[4] C. Abu-Gnim, I. Amer, J. Organomet. Chem. 516 (1996) 235.

[5] R.W. Wegman, A.G. Abatjoglou, A.M. Harrison, J. Chem. Soc., Chem. Commun. (1987) 1891.

[6] S.O. Grim, L.C. Satek, C.A. Tolman, J.P. Jesson, Inorg. Chem. 14 (1975) 655.

[7] R. Haid, R. Gutmann, G. Czermak, C. Langes, W. Oberhauser, H. Kopacka, K.-H. Ongania, P. Bruggeller, Inorg. Chem. Commun. 6 (2003) 61.

[8] P.K.S. Gupta, L.W. Houk, D. van der Helm, M.B. Hossain, Inorg. Chim. Acta 44 (1980) L235.

[9] T.S. Lobana, P.K. Sharma, Ind. J. Chem. 27A (1988) 732.

[10] T.S. Lobana, M.K. Sandhu, M.J. Liddell, E.R.T. Tiekink, J. Chem. Soc., Dalton Trans. (1990) 691.

[11] P. Barbaro, F. Cecconi, C.A. Ghilardi, S. Midollini, A. Orlandini, A. Vacca, Inorg. Chem. 33 (1994) 6163.

[12] D.C. Bebout, A.E. DeLanoy, D.E. Ehmann, M.E. Kastner, D.A. Parrish, R.J. Butcher, Inorg. Chem. 37 (1998) 2952.

[13] W.L.F. Armarego, D.D. Perrin, Purification of Laboratory Chemicals, 4th ed., Butterworth Heinemann, Oxford, 1996.

[14] D.S. Amenta, B.R. Ayras, J. Jurica, J.W. Gilje, Inorg. Chim. Acta 336 (2002) 115.

[15] Stoe, X-AREA V1.17 & X-RED32 V1.04 Software, Stoe & Cie GmbH, Darmstadt, Germany, 2002.

[16] G.M. Sheldrick, Acta Crystallogr. A46 (1990) 467.

[17] G.M. Sheldrick, SHELXL-97, Universität Göttingen, Göttingen, Germany, 1999.

[18] L.J. Farrugia, J. Appl. Crystallogr. 30 (1997) 565.

[19] A.L. Spek, J. Appl. Crystallogr. 36 (2003) 7.

[20] E.C. Alyea, S.A. Dias, R.G. Goel, W.O. Ogini, P. Pilon, D.W. Meek, Inorg. Chem. 17 (1978) 1697.

[21] H.B. Buergi, R.W. Kunz, P.S. Pregosin, Inorg. Chem. 19 (1980) 3707.

[22] W. Oberhauser, T. Stampfl, R. Haid, G. Langes, C. Bachmann, H. Kopacka, K.-H. Ongania, P. Bruggeller, Polyhedron 20 (2001) 727.

[23] The complex [(μ-dppeO)Eu(acac-F_6)$_3$(μ-dppeO)PdCl_2]$_n$ has been formulated as a polymer based on spectroscopic studies V.A. Petrov, W.J. Marshall, V.V. Grushin, Chem. Commun. (2002) 520.

[24] N.A. Bell, T.D. Dee, M. Goldstein, P.J. McKenna, I.W. Nowell, Inorg. Chim. Acta 71 (1983) 135.

[25] M. Kubicki, S.K. Hadjikakou, M.N. Xanthopoulou, Polyhedron 20 (2001) 2179.

[26] N.A. Bell, T.D. Dee, P.L. Goggin, M. Goldstein, R.J. Goodfellow, T. Jones, K. Kessler, D.M. McEwan, I.W. Nowell, J. Chem. Res. (S)2 (M) (1981) 201.