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# First true square-planar Hg(II) compound: synthesis and full characterization of *trans*-[Hg{Ph<sub>2</sub>PNP(O)Ph<sub>2</sub>-P, O}<sub>2</sub>]

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#### Abstract

The reaction of  $Hg(O_3SCF_3)_2$  with bis(diphenylphosphino)amine, Ph<sub>2</sub>PNHPPh<sub>2</sub> (dppam), produces the novel, rare face-to-face complex  $[Hg_2(O_3SCF_3)_4(dppam)_2]$  (1). Treatment of 1 with Na<sub>2</sub>N<sub>2</sub>O<sub>3</sub> leads to *trans*- $[Hg\{Ph_2PNP(O)Ph_2-P, O\}_2]$  (2) via regiose-lective oxidation and simultaneous deprotonation of dppam. 2 is the first true square-planar Hg(II) compound. In 2 the coordination plane and the five-membered rings of the HgNOP<sub>2</sub> moieties are completely coplanar indicating strong  $\pi$ -bonding interactions. Both 1 and 2 have been fully characterized by X-ray structure analyses, NMR spectroscopy (<sup>199</sup>Hg{<sup>1</sup>H}, <sup>31</sup>P{<sup>1</sup>H}, <sup>13</sup>C{<sup>1</sup>H}, <sup>1</sup>H), ESI and FAB mass spectrometry, IR spectroscopy, elemental analyses, and melting points. Since in Hg(II) compounds relativistic effects favour linear coordination and Hg(II) donor atom preferences play a significant role, the Hg–P bond length of 2.4042(7) Å in 2 is short, whereas the Hg–O bond length of 2.7138(15) Å is long. In view of the X-ray structures of 1 and 2, it is shown that the delocalized charge in [Ph<sub>2</sub>PNP(O)Ph<sub>2</sub>]<sup>-</sup> is responsible for the achievement of the square-planar coordination in a Hg(II) compound. A similar  $\pi$ -bonding effect has been observed in several square-planar complexes of Pt(II), Pd(II), and Ni(II) containing *cis*-1,2-bis(diphenylphosphino)ethene (*cis*-dppen).

Keywords: Crystal structures; Mercury complexes; Square-planar mercury; Face-to-face complexes; Diphosphine complexes; Heterodifunctional ligands

## 1. Introduction

The tolerance for many different coordination numbers and coordination geometries is typical of the coordination chemistry of Hg(II) [1]. However, to the best of our knowledge including a careful search of the Cambridge Structural Database, no true square-planar Hg(II) compound is known. [Hg(BMPA)NCCH<sub>3</sub>] (ClO<sub>4</sub>)<sub>2</sub>, where BMPA is bis[(2-pyridyl)methyl]amine, could be regarded as distorted square-planar complex, but the four nitrogen atoms are displaced as much as 0.5 Å from their mean plane [2]. Furthermore, close association to two axial perchlorates with Hg–O distances of 2.707(7) and 2.90(2) Å are indicative of a five- or six-coordinate species. By contrast, linear twocoordination is more predominant in the chemistry of mercury than for any other element, where relativistic effects strongly reduce intermolecular interactions between HgX<sub>2</sub> (X = F, Cl, Br, I, H) molecules [3]. In the case of phosphines the thoroughly investigated complexes containing the core HgL<sub>2</sub>P<sub>2</sub> (P, triorganophosphine; L, anionic ligand) prefer tetrahedral coordination [4]. Also phosphorus podal ligands increase the coordination number of Hg(II) and force a tetrahedral geometry around the mercury ion [5]. The same preference for T<sub>d</sub> is found in the virtual symmetry of the first structurally characterized homoleptic phosphine complex of Hg(II),  $[Hg(PMe_2Ph)_4]^{2+}$  [6]. Bulky phosphides reduce the coordination number of Hg(II) again and the central Hg atoms have a two-coordinate

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linear geometry in  $[Hg(t-Bu_2P)_2]$  and  $\{Hg[P(SiMe_3)_2]_2\}_2$ [7,8].

Only recently it has been shown that bis(diphenvlphosphino)amine, Ph<sub>2</sub>PNHPPh<sub>2</sub> (dppam), favours face-to-face complexes in the case of Hg(II) [9] and the first fully characterized Hg(II) compound containing dppam,  $[Hg_2(HN_2O_3)_2(NO_3)_2(dppam)_2]$ , has been presented. In this work the second fully characterized complex of Hg(II) and dppam,  $[Hg_2(O_3SCF_3)_4]$  $(dppam)_2$  (1), is given. 1 reacts with Na<sub>2</sub>N<sub>2</sub>O<sub>3</sub> to produce the first true square-planar Hg(II) compound, trans-[Hg{Ph<sub>2</sub>PNP(O)Ph<sub>2</sub>-P, O]<sub>2</sub>] (2), where 2 is also fully characterized. Although trioxodinitrate was first described as a component of Angeli's salt, Na<sub>2</sub>N<sub>2</sub>O<sub>3</sub>, in 1896 [10], it remains the least familiar of the isolable oxynitrogen anions [11–13] and the regioselective oxidation and simultaneous deprotonation of dppam leading from 1 to 2 via extrusion of mercury are unique. The coordination chemistry of phosphorus containing ligands with inorganic backbones as in 1 and 2 has been the topic of much interest [14–18]. In 2  $\pi$ -bonding caused by the  $\pi$ -delocalized nature of chelating  $[Ph_2PNP(O)Ph_2]^-$  leads to complete coplanar fivemembered rings of the HgNOP<sub>2</sub> moieties and hence to the first square-planar Hg(II) coordination. It is well known, that the unsaturated backbone of the chelating diphosphine *cis*-1,2-bis(diphenylphosphino)ethene (*cis*dppen) produces a comparable effect [19–24].

## 2. Experimental

 $Na_2N_2O_3$  was synthesized according to literature methods [25] and dried in vacuo at 120 °C for several hours. All other reagents were obtained commercially. Dry solvents of purissimum grade quality were used for the syntheses, NMR measurements, and crystallization purposes. A Schlenk apparatus and oxygen-free, dry Ar were used in the syntheses of 1 and 2. Solvents were degassed by several freeze–pump–thaw cycles prior to use. Positive chemical shifts are downfield from the standards: aqueous Hg(ClO<sub>4</sub>)<sub>2</sub> (2 mmol of HgO per cm<sup>3</sup> of 60% HClO<sub>4</sub>) for the <sup>199</sup>Hg{<sup>1</sup>H}, 85% H<sub>3</sub>PO<sub>4</sub> for the <sup>31</sup>P{<sup>1</sup>H}, and TMS for the <sup>13</sup>C{<sup>1</sup>H} and <sup>1</sup>H resonances.

## 2.1. Synthesis of $[Hg_2(O_3SCF_3)_4 (dppam)_2]$ (1)

Dppam (0.195 mmol, 0.075 g) was dissolved in 8 ml of  $CH_2Cl_2$  and  $Hg(O_3SCF_3)_2$  (0.195 mmol, 0.097 g) was added with vigorous stirring. The reaction mixture was stirred at ambient temperature for 3 days. A yellowish solution and a white precipitate were obtained. Forty ml of *n*-hexane was added and the slurry was stirred for 12 h. The slurry was filtered, and the white residue was washed with toluene and dried in vacuo. A white powder was recrystallized from  $CH_2Cl_2$ : yield 0.0955 g

(55.4%); m.p. = 105 to 108 °C. IR (KBr, cm<sup>-1</sup>) v(N–H): 3170. ESI mass spectrum (MeOH): m/z 1385.1 (1 – 3CF<sub>3</sub>SO<sub>3</sub> + 2MeOH)<sup>+</sup>, 1204.0 (1 – 4CF<sub>3</sub>SO<sub>3</sub> + MeOH)<sup>+</sup>. <sup>199</sup>Hg{<sup>1</sup>H} NMR(CH<sub>2</sub>Cl<sub>2</sub>):  $\delta$  1159.4 (t, <sup>1</sup>J(Hg, P) = 3528 Hz). <sup>31</sup>P{<sup>1</sup>H} NMR (CH<sub>2</sub>Cl<sub>2</sub>):  $\delta$  71.2 (s). <sup>13</sup>C{<sup>1</sup>H} NMR (CH<sub>2</sub>Cl<sub>2</sub>–d<sup>2</sup>):  $\delta$  129.35–132.35 (m, Ph). <sup>1</sup>H NMR (CH<sub>2</sub>Cl<sub>2</sub>–d<sup>2</sup>):  $\delta$  7.25–7.97 (m, Ph). Anal. Calcd for C<sub>52</sub>H<sub>42</sub>F<sub>12</sub>Hg<sub>2</sub>N<sub>2</sub>O<sub>12</sub>P<sub>4</sub>S<sub>4</sub>: C, 35.3; H, 2.39; N, 1.58; S, 7.25. Found: C, 35.1; H, 2.48; N, 1.54; S, 7.10. Single crystals suitable for an X-ray structure analysis with the composition [Hg<sub>2</sub>(O<sub>3</sub>SCF<sub>3</sub>)<sub>4</sub>(dppam)<sub>2</sub>] were obtained from a CH<sub>2</sub>Cl<sub>2</sub> solution of 1 at ambient temperature.

## 2.2. Synthesis of trans- $[Hg\{Ph_2PNP(O)Ph_2-P,O\}_2]$ (2)

1 (0.113 mmol, 0.200 g) was dissolved in 12 ml of  $CH_2Cl_2$  and  $Na_2N_2O_3$  (0.452 mmol, 0.055 g) was added with vigorous stirring and prevention of light. The reaction mixture was stirred at ambient temperature for several days. The slurry was filtered and the solvent was evaporated completely. The residue was dissolved in CH<sub>2</sub>Cl<sub>2</sub> and a white powder was recrystallized from  $CH_2Cl_2$ : yield 0.0401 g (35.4%); m.p. > 310 °C. IR (KBr, cm<sup>-1</sup>) v(PNP): 1272, 1123, 1084. FAB mass spectrum: m/z 1001.3 **2**<sup>+</sup>. <sup>31</sup>P{<sup>1</sup>H} NMR (CH<sub>2</sub>Cl<sub>2</sub>):  $\delta$ 69.8 (s,  ${}^{1}J(Hg, P) = 4076 \text{ Hz}, Ph_2P$ ), 57.1 (s,  ${}^{2}J(Hg, P) +$  ${}^{3}J(Hg, P) = 560 \text{ Hz}, Ph_2PO)$ . Anal. Calcd for C<sub>48</sub>H<sub>40</sub>Hg N<sub>2</sub>O<sub>2</sub>P<sub>4</sub>: C, 57.6; H, 4.03; N, 2.80. Found: C, 57.4; H, 4.15; N, 2.73. Single crystals suitable for an X-ray structure analysis with the composition trans- $[Hg{Ph_2PNP(O)Ph_2-P, O}_2]$  were obtained by gas-phase diffusion of *n*-hexane into a  $CH_2Cl_2$  solution of 2 at ambient temperature.

## 2.3. Structure determination

Details of the crystals and data collections are summarized in Table 1. In the case of 1, all data were collected on a Siemens P4 diffractometer using omegascans. Cell refinement and data reduction were done by the software of the Siemens P4 diffractometer [26], and the empirical absorption corrections were based on  $\psi$ scans of nine reflections, respectively ( $\chi = 78$  to 102°, 360° scans in 10° steps in  $\psi$ ) [27]. In the case of 2, the data collection was performed on a Nonius Kappa CCD diffractometer using combined  $\phi$ - $\omega$ -scans. Cell refinement, data reduction, and the empirical absorption correction were done by Denzo and Scalepack programs [28].

All structure determination calculations were carried out using SHELXTL NT 5.10 including SHELXS-97 [29] and SHELXL-97 [30]. Final refinements on  $F^2$  were carried out with anisotropic thermal parameters for all non-hydrogen atoms. In the case of 1, the N–H protons were located and isotropically refined with fixed U. The

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Table 1

Structure determination	data for [Hg <sub>2</sub>	$(O_3SCF_3)_4(dppam)_2$	(1) and trans-	$[Hg{Ph_2PNP(O)Ph_2$	-P,	$O_{2}^{2}$	(2)
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	1	2
Formula	$C_{52}H_{42}F_{12}Hg_2N_2O_{12}P_4S_4$	$C_{48}H_{40}HgN_2O_2P_4$
Formula weight	1768.21	1001.33
Colour; habit	Colourless; prismatic	Colourless; prismatic
Crystal system	Monoclinic	Triclinic
Space group	$P2_1/n$	ΡĪ
a (Å)	13.420(4)	8.2073(1)
b (Å)	16.302(3)	11.0828(2)
c (Å)	14.071(3)	11.6938(2)
α (°)		87.437(1)
β (°)	99.43(1)	81.638(1)
γ(°),		86.887(1)
$V(\mathbf{A}^{2})$	3036.8(12)	1050.08(3)
<i>T</i> (K)	178	213
Ζ	2	1
Crystal dimensions (mm)	0.70 imes 0.70 imes 0.20	0.40  imes 0.30  imes 0.20
$D_{calc} (Mg m^{-3})$	1.933	1.584
$\mu \text{ (mm}^{-1})$	5.393	7.497
Diffractometer (Mo-Ka radiation)	Siemens P4	Nonius Kappa CCD
$2\theta$ Range (°)	4.6–55.0	3.5-55.0
No. observed $(I > 3\sigma(I) (1), > 2\sigma(I) (2))$ reflections		
	3958	4818
No. parameters refined	400	340
$R_1$ (on $F$ )	0.0331	0.0152
$wR_2$ (on $F^2$ )	0.0790	0.0385
GOF	0.978	1.06
Largest difference peak (e $Å^{-3}$ )	1.81	0.37
R <sub>int</sub>	0.026	0.021
Transmission	0.278 - 1.000	0.882-1.000

aromatic hydrogen atoms were included using a riding model with isotropic U values depending on  $U_{eq}$  of the adjacent carbon atoms. For 2 all protons were located and isotropically refined. This means that due to the low *R*-values for both X-ray structures, the deprotonation at nitrogen during the reaction leading from 1 to 2 can be directly seen in their X-ray structures. Parallel refinements with all hydrogen atoms in idealized positions show no beneficial effects on the *R*-values or statistical significance of both structures. In 1 the largest difference peak of 1.81 e Å<sup>-3</sup> is located only 0.95 Å away from Hg, which can be typical for a 5d metal.

#### 3. Results and discussion

Hg is unique among the transition metals in that it readily forms two-, three-, and four-coordinate compounds with the same ligand type [31]. Furthermore, regioselective oxidation and simultaneous deprotonation of dppam completely changes the coordination behaviour of this ligand type with respect to Hg(II). This reaction sequence leading from 1 to 2 is achieved by the unique properties of the dibasic anion  $N_2O_3^{2-}$ , which is destabilized upon protonation to the monobasic form  $HN_2O_3^-$  [12]. The deprotonation of 1 (Eq. (1)) initiates the following reaction sequence:

 $HN_2O_3^- \to HNO + NO_2^- \tag{2}$ 

$$[Hg_2(O_3SCF_3)_2(Ph_2PNPPh_2)_2] + 4HNO$$
  

$$\rightarrow \mathbf{2} + 2N_2 + 2H_2O + Hg(O_3SCF_3)_2$$
(3)

Also the decomposition reaction of  $HN_2O_3^-$  (Eq. (2)) leading to nitroxyl (HNO) and nitrite is well-known [13]. It has been shown, that the reduction of HNO (Eq. (3)) produces  $N_2$  [13] and the regioselective oxidation product  $[Ph_2PNP(O)Ph_2]^-$  forms **2** by five-membered chelate ring closure and extrusion of  $Hg(O_3SCF_3)_2$ .

Since 1 belongs to the class of rare face-to-face complexes of Hg(II) containing dppam [9] and in order to confirm the above reaction sequence, the solid state structure of 1 was determined by X-ray crystallography. The crystal structure of 1 consists of two discrete  $[Hg_2(O_3SCF_3)_4(dppam)_2]$  molecules per unit cell.  $[Hg_2(O_3SCF_3)_4(dppam)_2]$  is located on a centre of symmetry. Views of 1 are given in Fig. 1. Table 2 contains selected bond distances and bond angles.

Fig. 1 clearly reveals the face-to-face coordination of dppam in 1. The Hg  $\cdots$  Hg distance of 3.2805(7) Å in 1 is comparable to the corresponding parameter of 3.2213(9) Å in [Hg<sub>2</sub>(HN<sub>2</sub>O<sub>3</sub>)<sub>2</sub>(NO<sub>3</sub>)<sub>2</sub>(dppam)<sub>2</sub>] [9] and



Fig. 1. (a) View of  $[Hg_2(O_3SCF_3)_4(dppam)_2]$  (1), showing the atomic numbering. (b) View of  $[Hg_2(O_3SCF_3)_4(dppam)_2]$  (1), with the plane through Hg(1), P(1), Hg(1A) and P(1A) perpendicular to the projection plane. The  $O_3SCF_3^-$  groups have been omitted for clarity.

Table 2 Selected bond distances (Å) and bond angles (°) for  $[Hg_2 (O_3SCF_3)_4(dppam)_2]$  (1) and *trans*- $[Hg\{Ph_2PNP(O)Ph_2-P, O_{1/2}]$  (2)

2.4213(13)			
2.4257(13)			
2.746(4)			
2.893(5)			
2.814(4)			
2.679(4)			
3.2805(7)			
1.679(4)			
1.681(5)			
169 78(5)			
94 35(11)			
95 49(11)			
86 35(10)			
80.35(10) 07.85(10)			
97.83(10) 01.08(10)			
91.08(10) 02.58(10)			
50 12(12)			
50.15(12) 84.71(14)			
$124 \ 27(12)$			
134.27(13) 112.75(16)			
112.73(10) 112.20(16)			
113.30(10) 124.0(2)			
134.0(3)			
/0.15(10)			
2.4042(7)			
2.7138(15)			
1.5963(15)			
1.6152(16)			
1.5035(15)			
76.83(4)			
180.00(2)			
103.17(4)			
112.37(6)			
117.42(8)			
109.63(7)			
123.35(10)			

<sup>a</sup> Symmetry transformations used to generate equivalent atoms: -x, -y, -z.

indicates that there is no bonding interaction between the Hg(II) centres. The Hg-P bond lengths of 2.4213(13) and 2.4257(13) Å in 1 are located within the typical range of 2.36–2.91 Å [32–35]. This wide range of values confirms the easy deformability of the coordination sphere of a d<sup>10</sup> metal ion [36] and is reflected in the Hg–O bond lengths of 1. The Hg(1)–O(1) and Hg(1)-O(6) distances of 2.746(4) and 2.679(4) Å, respectively, are relatively short and the Hg-O distances of the bridging oxygen O(2) (see Fig. 1(a)) of 2.893(5) and 2.814(4) Å are relatively long indicating strong and weak contacts of the  $O_3SCF_3^-$  groups to mercury. Comparable Hg-O bond lengths of 2.526(5), 2.621(5), and 2.864(5) Å have been found in  $[Hg_2(HN_2O_3)_2]$  $(NO_3)_2(dppam)_2$  [9] and for the bidentate coordination of the nitrate groups in  $[Hg(NO_3)_2(PPh_3)_2]$  [35] with corresponding Hg-O distances of 2.507(4) and 2.790(4) Å. In line with these results, the range of the Hg–O bond lengths in  $[Hg_2(\mu-dpma)_2(O_3SCF_3)_2]$  $(CH_3OH)_3$  (PF<sub>6</sub>)<sub>2</sub> is 2.46–2.79 Å, where dpma is bis((diphenylphosphino)methyl)phenylarsine [37]. Furthermore, a particularly strong interaction between the central mercury atom and the oxygen atom of a methoxy group of 2.672(4) A is present in [HgI<sub>2</sub>] (DMPP)], where DMPP is tris(2,6-dimethoxyphenyl)phosphine [38]. Since all these Hg–O contacts are within the sum of the van der Waals radii for the interacting atoms of 3.1 Å, the geometry around the mercury ion in 1 should be regarded as six-coordinate and distorted octahedral (Fig. 1(a)). In 1 the N-H protons of dppam have been found in its X-ray structure and in the IR spectrum they are responsible for v(N-H) at 3170 cm<sup>-1</sup> in the typical range [16]. The eight-membered ring of 1 is folded resulting in a flat chair conformation, where the dihedral angle between the planes through Hg(1), P(1), Hg(1A), P(1A), and P(1A), N(1), P(2), respectively, is 18.8° (see Fig. 1(b)).

In order to confirm the regioselective oxidation and deprotonation of dppam during the reaction sequence of Eqs. (1)–(3) and to characterize **2** definitely, also the solid state structure of **2** was determined by X-ray crystallography. The crystal structure of **2** consists of one discrete *trans*-[Hg{Ph<sub>2</sub>PNP(O)Ph<sub>2</sub>-*P*, *O*}<sub>2</sub>] molecule per unit cell. *Trans*-[Hg{Ph<sub>2</sub>PNP(O)Ph<sub>2</sub>-*P*, *O*}<sub>2</sub>] is located on a centre of symmetry. Views of **2** are given in Fig. 2. Table 2 contains selected bond distances and bond angles.

Fig. 2 clearly reveals the first true square-planar coordination of a Hg(II) compound. The Hg-P bond length of 2.4042(7) A in 2 is significantly shorter than the Hg–P distances of 2.4213(13) and 2.4257(13) Å in 1, but again located within the typical range of 2.36–2.91 Å [32–35]. The Hg–O bond length of 2.7138(15) Å in 2 is comparable to the relatively short and strong Hg-O contacts of the  $O_3SCF_3^-$  groups to mercury in 1. Therefore, the coordination number of Hg(II) in 2 clearly is four (Fig. 2(a)). Furthermore, Fig. 2(b) shows the nearly complete planarity of the five-membered HgNOP<sub>2</sub> rings. Due to crystallographic constraints produced by the centre of symmetry this means, that both five-membered chelate rings of 2 are also coplanar. The largest deviation from a least-squares plane through Hg(1), P(1), N(1), P(2), and O(1) is only 0.045 A for N(1). Of course, the coordination plane itself consisting of the atoms Hg(1), P(1), O(1), P(1A), and O(1A) is completely planar again due to crystallographic constraints.

The observed coplanarity of the coordination plane with the backbone atoms in 2 is indicative of  $\pi$ -bonding effects [19–24]. It is well-known, that short M-P bonds as in 2 compared with 1 result from an enhancement of M-to-P  $\pi$ -bonding caused by the unsaturated nature of a chelating ligand [19]. This means, that in 2 a degree of delocalization of the negative charge formally attached to the deprotonated nitrogen atoms over the two fivemembered spiro-rings is present. In [PtH(PPh<sub>3</sub>) (NPP-H)], where NPP-H is deprotonated 2-pyridylbis(diphenylphosphino)methane, a comparable delocalization of the negative charge formally attached to the deprotonated methine carbon over the four-membered ring and some degree of  $\pi$ -interaction between the pyridyl group and this delocalized charge have been found [39]. Furthermore, there is evidence for  $\pi$ -delocalization within the E-P-N-P-O and P-N-P-O backbones of the E-ligating or O, E-chelating ligand  $[Ph_2P(O)NP(E)]$  $Ph_2$ <sup>-</sup> (E=S or Se) [14]. In the case of  $Ph_2PNP(O)$ Ph<sub>2</sub>]<sup>-</sup>, short P-N bond lengths as in [Pd{Ph<sub>2</sub>PNP(O)  $Ph_2-P_2(en)$  ranging from 1.593(2) to 1.604(2) A [14] indicate some degree of delocalization within the P-N-P backbone. This effect is clearly visible in the significant reduction of the P–N distances of 1.679(4) and 1.681(5) Å in 1 compared with 1.5963(15) and 1.6152(16) Å in 2. By contrast, the P–O bond length of 1.5035(15) A for the coordinated phosphinoyl moieties in 2 is significantly longer than the corresponding parameters of 1.465(5) and 1.478(4) A for P-unidentate Ph<sub>2</sub>PNHP (O)Ph<sub>2</sub> in *trans*-[Pt(CH<sub>3</sub>)Cl{Ph<sub>2</sub>PNHP(O)Ph<sub>2</sub>-P}] [16].



Fig. 2. (a) View of *trans*-[Hg{Ph<sub>2</sub>PNP(O)Ph<sub>2</sub>-P, O}<sub>2</sub>] (2), showing the atomic numbering. (b) View of *trans*-[Hg{Ph<sub>2</sub>PNP(O)Ph<sub>2</sub>-P, O}<sub>2</sub>] (2), with the least-squares plane through Hg(1), P(1), N(1), P(2) and O(1) perpendicular to the projection plane.

Thus, in agreement with previous results [14-18,40] the deprotonation and chelation of Ph<sub>2</sub>PNHP(O)Ph<sub>2</sub> lengthens the P–O bond length and electronic delocalization shortens the P–N bond length. In this context a comparison of Figs. 1(b) and 2(b) is particularly helpful demonstrating the onset of this electronic delocalization, since the eight-membered ring of **1** is folded and the two five-membered rings of **2** are planar.

Furthermore, Fig. 2(a) clearly reveals the mutual *trans* arrangement of the  $[Ph_2PNP(O)Ph_2]^-$  ligands in 2. This is in contrast to  $cis-[Pt{Ph_2PNP(O)Ph_2-P, O}_2]$ [16], where the beneficial combination of an atom with high trans influence like phosphorus and an atom with low trans influence like oxygen in mutual trans position dominates. Obviously, square-planar Hg(II) prefers a symbiotic *trans* arrangement of identical atoms, which is common in octahedral complexes containing comparable heterodifunctional ligands like *trans*- $[NiCl_2(Ph_2P(O))]$ CH<sub>2</sub>py)<sub>2</sub>] with trans arrangements O-Ni-O and N-Ni-N [39]. Also the small P(1)-Hg(1)-O(1) chelate angle in **2** of only  $76.83(4)^{\circ}$  is unique, where the corresponding parameters in cis-[Pt{Ph<sub>2</sub>PNP(O)Ph<sub>2</sub>-P, O}] are 86.1(2)° and 86.0(2)° [16].

The uncertainties introduced by motional averaging in solution and structural perturbations imposed by packing constraints in the solid require that correlations between solid-state structures and solution-state NMR properties always be made cautiously [2]. In the case of 1, the occurrence of the <sup>199</sup>Hg{<sup>1</sup>H} NMR signal as a triplet and the single <sup>31</sup>P{<sup>1</sup>H} NMR peak are in accordance with its solid state structure. The  ${}^{1}J(Hg, P)$  value of 3528 Hz in 1 is comparable to the same parameter of 4430 Hz in  $[Hg_2(HN_2O_3)_2(NO_3)_2(dppam)_2]$  [9] and located within the range of 1417-6300 Hz found for pseudotetrahedral  $[Hg(PR_3)_nX_{4-n}]$  complexes, where X is an anionic ligand [4,36]. Also in the case of 2, the single <sup>31</sup>P{<sup>1</sup>H} NMR resonances at 69.8 and 57.1 correspond to its solid state structure. The downfield signal is attributed to the Ph<sub>2</sub>P groups, since its  ${}^{1}J(Hg, P)$ coupling of 4076 Hz is again in the typical range [4,9,36]. The highfield signal showing a  ${}^{2}J(Hg,P) + {}^{3}J(Hg,P)$ coupling of 560 Hz stems from the Ph<sub>2</sub>PO groups. Though the value of this coupling is large, variations in  ${}^{3}J(Hg, P)$  coupling [41] and limited experimental examples of long range coupling to Hg(II) make the assessment of this value difficult. Unfortunately, due to the low solubility of **2** no reasonable  ${}^{13}C{}^{1}H$  NMR spectrum of **2** showing only a broad peak at about  $\delta$  of 130 typical of the phenyl groups was obtained. However, the large shift of the  $\delta(^{31}P)$  of 57.1 for the P=O group in 2 upon chelation, where  $\delta(^{31}P)$  for the P=O group in the free ligand Ph<sub>2</sub>PNHP(O)Ph<sub>2</sub> is 21.4 [16], is due to the chelate ring effect, a feature that has been well studied with other phosphorus-based ligands like cis-dppen forming five-membered rings [19–24]. This chelate ring effect in 2 clearly indicates coordinated P=O groups,

where in  $[Hg\{2-C_6H_4P(O)Ph_2\}_2]$  the corresponding  $\delta(^{31}P)$  value for the free P=O groups is 31.7 [41]. By contrast,  $\delta(^{31}P)$  for the coordinated P=O groups in *cis*-[Pt{Ph\_2PNP(O)Ph\_2 - P, O}\_2] is 62.3 [16]. Thus, compelling evidence for formation of 1 and 2 in solution is provided by a combination of symmetry, shielding, and heteronuclear coupling arguments. This means, that as a first approximation the forces on 1 and 2 in solution are of the same order as those in the solid [42].

It seems likely, that the formation of the two very stable five-membered rings in **2** is the thermodynamic driving force leading from **1** to **2**. Therefore, a comparison with the well-known  $\pi$ -bonding effect in square-planar complexes containing *cis*-dppen is interesting [43]. [Ph<sub>2</sub>PNP(O)Ph<sub>2</sub>]<sup>-</sup> belongs to the class of valuable hemilabile ligands that have proven usefulness in several important applications [45,46]. In this work the hetero-difunctional properties of these ligands have lead to the achievement of a unique square-planar coordination of Hg(II).

## Supplementary material

An X-ray crystallographic file, in CIF format, for  $[Hg_2(O_3SCF_3)_4(dppam)_2]$  (1), *trans*- $[Hg\{Ph_2PNP(O) Ph_2-P, O\}_2]$  (2), and  $[PdCl_2 (cis-dppen)]$  (3) is available from the authors on request. Further details on the structure determination are also obtainable at the Cambridge Structural Database.

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