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# Copper(I) and mercury(II) halide complexes of 1,2-bis(diphenylthioylphosphino)hydrazine

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### Abstract

The reaction of 1,2-bis(diphenylthioylphosphino)hydrazine (L) with copper(I) and mercury(II) halides affords the complexes,  $[{CuLX}_2] (X = I, Br \text{ or } Cl), [HgLX_2] (X = Cl \text{ or } Br)$  and the tetrametallic complex,  $[{L(HgI_2)_2}_2]$ . Single crystal X-ray structures have been performed on the uncoordinated ligand, L, as well as the complexes  $[{CuLX}_2] (X = I, Br \text{ and } Cl), [HgLBr_2] \text{ and } [{L(HgI_2)_2}_2]$ . The molecules of L exist as dimers as a result of pairs of N-H···S hydrogen bonds. The copper(I) complexes are centrosymmetric dimetallic species, the two copper atoms being bridged by L and the X atoms. In all cases the coordination sphere around the Cu atoms is approximately trigonal pyramidal with an 'S<sub>2</sub>X<sub>2</sub>' donor set. The complex, [HgLBr\_2], is a distorted tetrahedral monomer with an 'S<sub>2</sub>Br<sub>2</sub>' donor set and L acting as a bidentate thus forming a seven-membered chelate ring. The tetramercury iodo complex, [{L(HgI\_2)\_2}\_2], contains two 'L(HgI\_2)\_2' units linked centrosymmetrically via an I atom from each moiety. The geometry around the Hg atoms is distorted tetrahedral. The influence of hydrogen bonding between the hydrazine backbone hydrogens of L and the coordinated halide ions in for the structures of the metal complexes is discussed.

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## 1. Introduction

The coordination chemistry of phosphine chalcogenide ligands is well established and their metal complexes have been the subjects of various structure and reactivity studies [1,2]. Of continuing interest are diphosphine chalcogenide ligands of the general type  $Ph_2P(E)(CH_2)_nP(E)Ph_2$  (E = O or S) [3–13]. Also extensively studied are ligands of the type  $Ph_2P(E)NH(E)PPh_2$  (E = O or S) which, after deprotonation, behave as monoanionic ligands, i.e., inorganic analogues of acetylacetone (acac). However, comparatively

few reports exist on the hydrazine derivatives where the backbone is  $(NH)_2$ .

The compound  $Ph_2P(NH)_2PPh_2$  was reported by Nielsden and Sisler, being prepared from the reaction between  $Ph_2PCl$  and anhydrous hydrazine [14]. Bock and Rudolph prepared the chalcogen derivatives from analogous reactions of  $Ph_2P(E)Cl$  (E = O, S) [15]. The only coordination compounds reported for these ligands are platinum and palladium dichloride and molybdenum tetracarbonyl complexes of  $Ph_2P(S)(NH)_2P(S)Ph_2$  (L), the title compound, which were characterised by IR and <sup>31</sup>P NMR [16,17].

Given the scarcity of information on the (1,2-diphenylphosphino)hydrazine derivatives and the absence of any X-ray structural data, we have undertaken a study to examine further the coordination chemistry of L. This report comprises the first structural data for a (1,2-diphenylphosphino)hydrazine type ligand and five of its metal

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complexes with copper(I) and mercury(II) halides, including an unusual tetrametallic complex,  $[{L(HgI_2)_2}_2]$ . A common feature for all the complexes is the occurrence of hydrogen bonding between the hydrazine backbone hydrogens of L and the coordinated halide ions.

# 2. Experimental

## 2.1. Materials and instrumentation

All reactions were carried out under an atmosphere of dry dinitrogen. Analytical grade solvents were purchased from standard chemical suppliers and were used without further purification. HgI<sub>2</sub> (M&B), HgBr<sub>2</sub> (BDH) and HgCl<sub>2</sub> (M&B) were used as received. CuCl, CuBr, CuI and (1,2-diphenylphosphino)hydrazine were prepared according to the literature [18,19,14]. <sup>1</sup>H and <sup>31</sup>P NMR spectra were recorded on a Bruker Avance 400 spectrometer. IR spectra were run as KBr discs on a Perkin–Elmer FT-IR Paragon 1000 spectrometer. Microanalyses were performed by the Campbell Microanalytical Laboratory, University of Otago.

## 2.2. Syntheses

#### 2.2.1. 1,2-Bis(diphenylthioylphosphino)hydrazine (L)

To a solution of 1,2-bis(diphenylphosphino)hydrazine (2.585 g, 6.436 mmol) in toluene (20 mL) was added sulfur (0.42 g, 13.1 mmol) and the mixture was heated at reflux over 2 h. The toluene was removed on a rotary evaporator to give a cream coloured solid that was washed with cold acetone ( $2 \times 5$  mL). The solid was dissolved in hot acetone (60 mL) and slow evaporation of the solution produced a crop of white crystalline material. Yield 1.15 g (38%). <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  7.81–7.76 (m, 8H, PPh<sub>2</sub>), 7.46 (m, 4H, PPh<sub>2</sub>), 7.34–7.30 (m, 8H, PPh<sub>2</sub>), 4.62 (m, 2H, NH). <sup>31</sup>P NMR (CDCl<sub>3</sub>):  $\delta$  66.0 (s, 2P, P=S).  $v_{PS}$ /cm<sup>-1</sup>: 633, 615.  $v_{NH}$ /cm<sup>-1</sup>: 3222, 3158. *Anal.* Calc. for C<sub>24</sub>H<sub>22</sub>N<sub>2</sub>P<sub>2</sub>S<sub>2</sub>: C, 62.05; H, 4.99; N, 6.03. Found: C, 62.18; H, 4.73; N, 6.07%. m.p. 201–204 °C (*lit.* 204 °C).

# 2.2.2. $[{CuLCl}_2]$

A mixture of L (0.100 g, 0.215 mmol) and CuCl (0.022 g, 0.222 mmol) in MeCN (70 mL) was heated at reflux over 7 h. The reaction mixture was filtered while hot and a white microcrystalline precipitate formed on cooling. Yield 0.105 g. An analytically pure sample and X-ray quality crystals of [{CuLCl}<sub>2</sub>] · 4MeCN were obtained after a second recrystallisation of a portion of the material from hot MeCN. *Anal.* Calc. for C<sub>48</sub>H<sub>44</sub>Cl<sub>2</sub>Cu<sub>2</sub>N<sub>4</sub>P<sub>4</sub>S<sub>4</sub>: C, 51.15; H, 3.94; N, 4.97. Found: C, 51.10; H, 4.02; N, 5.01%.  $\nu_{PS}/$  cm<sup>-1</sup>: 620, 599.  $\nu_{NH}/$ cm<sup>-1</sup>: 3070. m.p. 246–250 °C (dec.).

# 2.2.3. $[{CuLBr}_2]$

A mixture of L (0.100 g, 0.215 mmol) and CuBr (0.032 g, 0.222 mmol) in MeCN (90 mL) was heated at reflux over 4 h. The reaction mixture was filtered while hot and a white

microcrystalline precipitate formed on cooling. Yield 0.097 g. An analytically pure sample and X-ray quality crystals of  $[CuLBr]_2 \cdot 2MeCN$  were obtained after a second recrystallisation of a portion of the material from hot MeCN. *Anal.* Calc. for C<sub>48</sub>H<sub>44</sub>Br<sub>2</sub>Cu<sub>2</sub>N<sub>4</sub>P<sub>4</sub>S<sub>4</sub>: C, 47.41; H, 3.65; N, 4.61. Found: C,47.64; H, 3.55; N, 5.19%. v<sub>PS</sub>/cm<sup>-1</sup>: 620, 601. v<sub>NH</sub>/cm<sup>-1</sup>: 3075. m.p. 255–270 °C (dec.).

#### 2.2.4. $[{CuLI}_2] \cdot CH_3CN$

A mixture of L (0.100 g, 0.215 mmol) and CuI (0.041 g, 0.215 mmol) in CHCl<sub>3</sub> (5 mL) was heated at reflux over 1 h. The mixture was allowed to cool and a white precipitate was collected by filtration. Yield 0.075 g. X-ray quality crystals of [{CuLI}<sub>2</sub>] · 2MeCN and an analytically pure crop of the monosolvated complex were obtained by recrystallisation from hot MeCN (20 mL). *Anal.* Calc. for  $C_{50}H_{47}Cu_2I_2N_5P_4S_4$ : C, 44.45; H, 3.51; N, 5.18. Found: 44.11; H, 3.24; N, 5.62%.  $\nu_{PS}/cm^{-1}$ : 613, 602.  $\nu_{NH}/cm^{-1}$ : 3085. m.p. 255–261 °C (dec.).

#### 2.2.5. $[{L(HgI_2)_2}_2]$

A mixture of L (0.100 g, 0.215 mmol) and HgI<sub>2</sub> (0.196 g, 0.431 mmol) in MeCN (20 mL) was heated at reflux over 1.5 h. The reaction mixture was filtered while hot and a pale yellow crystalline solid formed on cooling. Yield 0.217 g. *Anal.* Calc. for C<sub>48</sub>H<sub>44</sub>Hg<sub>4</sub>I<sub>8</sub>N<sub>4</sub>P<sub>4</sub>S<sub>4</sub>: C, 20.99; H, 1.61; N, 2.04. Found: C, 21.06; H, 1.60; N, 2.09%.  $v_{PS}/cm^{-1}$ : 620, 595.  $v_{NH}/cm^{-1}$ : 3154, 3052. m.p. 168–200 °C (dec.).

## 2.2.6. [HgLCl<sub>2</sub>]

A mixture of L (0.100 g, 0.215 mmol) and HgCl<sub>2</sub> (0.059 g, 0.217 mmol) in MeCN (35 mL) was heated at reflux over 5 h. The reaction mixture was allowed to cool and a white precipitate was collected by filtration. Yield 0.123 g. A small amount of material was recrystallised from hot nitromethane. *Anal.* Calc. for C<sub>24</sub>H<sub>22</sub>Cl<sub>2</sub>HgN<sub>2</sub>P<sub>2</sub>S<sub>2</sub>: C, 39.16; H, 3.01; N, 3.81. Found: C, 38.92; H, 3.04; N, 3.92%.  $v_{PS}/cm^{-1}$ : 619, 594.  $v_{NH}/cm^{-1}$ : 3057. m.p. 215–230 °C (dec.).

#### 2.2.7. $[HgLBr_2]$

A mixture of L (0.100 g, 0.215 mmol) and HgCl<sub>2</sub> (0.078 g, 0.216 mmol) in MeCN (10 mL) was heated at reflux over 2 h. The reaction mixture was allowed to cool and a white precipitate was collected by filtration, washed with cold acetonitrile and air dried. Yield 0.140 g. A sample of the material was recrystallised from hot nitromethane and crystals suitable for X-ray analysis were also obtained from this solvent. *Anal.* Calc. for C<sub>24</sub>H<sub>22</sub>Br<sub>2</sub>HgN<sub>2</sub>P<sub>2</sub>S<sub>2</sub>: C, 34.94; H, 2.69; N, 3.40. Found: C, 34.88; H, 2.66; N, 3.41%.  $v_{PS}$ /cm<sup>-1</sup>: 620, 593.  $v_{NH}$ /cm<sup>-1</sup>: 3075. m.p. 210–225 °C (dec.).

## 2.3. Crystallography

The X-ray data were collected on a Siemens P4 four circle diffractometer, using a Siemens SMART 1K CCD area

detector. The crystals were mounted in an inert oil, transferred into the cold gas stream of the detector and irradiated with graphite monochromated Mo-K $\alpha$  ( $\lambda = 0.71073$  Å) X-rays. The data were collected by the SMART program and processed with SAINT to apply Lorentz and polarisation corrections to the diffraction spots (integrated 3 dimensionally). The structures were solved by direct methods and refined using the SHELXTL [20] program. The hydrogen atoms bound to the nitrogen atoms on the hydrazine backbone were located from the electron difference map and refined using a riding model. All other hydrogen atoms were calculated at ideal positions. Refinement, collection and crystal data are given on Table 1.

# 3. Results and discussion

## 3.1. Syntheses of the compounds

The free ligand L was prepared from the sulfuration of the parent phosphine, (1,2-diphenylphosphino)hydrazine in toluene. This differs from the previously reported method where it was prepared from the reaction between Ph<sub>2</sub>P(S)Cl and anhydrous hydrazine [15]. The <sup>31</sup>P NMR chemical shift of L is 66 ppm in CDCl<sub>3</sub> and downfield of phosphorus signal in (1,2-diphenylphosphino)ethane (L<sup>1</sup>) which occurs at 44 ppm. The ligand exhibits IR bands at 3222 and 3158 cm<sup>-1</sup>, (assigned to NH) and 633 and 615 cm<sup>-1</sup>, (assigned to P=S) stretching frequencies, respectively.

Table 1 Crystal and refinement data Pure samples of copper halide complexes of stoichiometry [{CuLX}<sub>2</sub>] (X = I, Br or Cl) were obtained from the reactions between the ligand and the appropriate copper(I) halide followed by crystallisation from hot acetonitrile solutions. Satisfactory elemental analyses were obtained in each case. The complexes have poor solubility in common organic solvents at room temperature which precluded characterisation by NMR. In the IR spectra, both the NH and PS stretching bands are shifted to lower wave numbers when compared with the free ligand. Thus the v(NH) stretching frequencies are observed at 3084, 3070 and 3074 cm<sup>-1</sup> and the pairs of v(PS) bands at 612 and 601, 619 and 599 and 620 and 600, respectively, for the series X = I, Cl, Br.

Similarly 1:1 mercury(II) chloride and bromide complexes, [HgLX<sub>2</sub>] (X = Cl or Br) were obtained from the reaction of equimolar ligand and mercury(II) halide in MeCN. Initially we attempted to prepare a 1:1 mercury(II) iodide complex in the same way but it was apparent that we were obtaining mixtures, with one of the components being the [{L(HgI<sub>2</sub>)<sub>2</sub>}<sub>2</sub>] species reported here. This latter complex was obtained in good yield from the reaction of the metal salt and the ligand in a 2:1 molar ration. The IR spectra for the mercury bromide and chloride complexes are similar with NH stretching frequencies at 3074 and 3056 cm<sup>-1</sup> and pairs of PS stretching frequencies at 618 and 593 and 619 and 593 cm<sup>-1</sup>. The tetrametallic mercury iodide complex has a different spectrum with two stretching

| Compound                                     | L                       | [{CuLI}2] · 2MeCN              | [{CuLBr} <sub>2</sub> ] · MeCN  | $[{CuLCl}]_2 \cdot 4MeCN]$ | $[{L(HgI_2)_2}_2]$ | [HgLBr <sub>2</sub> ]  |
|--|-------------------------|--------------------------------|---------------------------------|----------------------------|--------------------|--|
| Molecular formula                            | $C_{24}H_{22}N_2P_2S_2$ | $C_{52}H_{50}Cu_2I_2N_6P_4S_4$ | $C_{50}H_{47}Br_2Cu_2N_5P_4S_4$ | C56H56Cl2Cu2N8P4S4         | C48H44Hg4I8N3P4S4  | C <sub>24</sub> H <sub>22</sub> Br <sub>2</sub> HgN <sub>2</sub> P <sub>2</sub> S <sub>2</sub> |
| Molecular weight $(M)$                       | 464.50                  | 1391.98                        | 1256.95                         | 1291.19                    | 2746.56            | 1649.81  |
| $T(\mathbf{K})$                              | 200(2)                  | 200(2)                         | 200(2)                          | 200(2)                     | 83(2)              | 83(2)  |
| Crystal system                               | monoclinic              | monoclinic                     | monoclinic                      | triclinic                  | triclinic          | monoclinic   |
| Space group                                  | P2(1)                   | P2(1)/n                        | P2(1)/n                         | $P\bar{1}$                 | $P\bar{1}$         | P2(1)/n  |
| a (Å)  | 10.5252(2)              | 12.0932(2)                     | 12.019(2)                       | 10.5608(1)                 | 10.5535(3)         | 8.0292(1)  |
| b (Å)  | 18.2405(3)              | 15.4958(2)                     | 15.559(3)                       | 11.1659(1)                 | 11/8678(3)         | 17.4989(2)   |
| <i>c</i> (Å)                                 | 24.7358(1)              | 15.0715(3)                     | 15.181(3)                       | 15.1527(1)                 | 14.8929(4)         | 18.9981(2)   |
| α (°)  |                         |                                |                                 | 70.607(1)                  | 78.697(1)          |  |
| β (°)  | 102.253(1)              | 94.648(1)                      | 91.82(3)                        | 72.411(1)                  | 74.292(1)          | 92.535(1)  |
| γ (°)  |                         |                                |                                 | 65.012(1)                  | 68.929(1)          |  |
| $V(\text{\AA}^3)$                            | 4640.72(12)             | 2815.02(8)                     | 2837.3(10)                      | 1500.03(2)                 | 1665.43(8)         | 2666.66(5)   |
| Ζ  | 8                       | 4                              | 4                               | 2                          | 2                  | 4  |
| $\mu$ (MoK $\alpha$ ) (mm <sup>-1</sup> )    | 0.381                   | 2.155                          | 2.455                           | 1.088                      | 13.154             | 9.062  |
| $\rho_{\rm calc} ({\rm g}{\rm cm}^{-3})$     | 1.330                   | 1.642                          | 1.471                           | 1.429                      | 2.738              | 2.055  |
| 2θ Maximum (°)                               | 50.78                   | 51.36                          | 53.26                           | 54.20                      | 51.36              | 54.26  |
| Number of unique reflections                 | 15697                   | 5329                           | 5737                            | 6468                       | 6289               | 5862   |
| Data/restraints/<br>parameters               | 15697/1/1081            | 5329/0/317                     | 5737/0/317                      | 6468/0/347                 | 6289/0/325         | 5862/0/298   |
| Final <i>R</i> indices<br>$[I > 2\sigma(I)]$ | $R_1 = 0.0279$          | $R_1 = 0.0198$                 | $R_1 = 0.0434$                  | $R_1 = 0.0259$             | $R_1 = 0.0224$     | $R_1 = 0.0235$   |
|  | $wR_2 = 0.0642$         | $wR_2 = 0.0496$                | $wR_2 = 0.1275$                 | $wR_2 = 0.0730$            | $wR_2 = 0.0523$    | $wR_2 = 0.0506$  |
| <i>R</i> indices (all data)                  | $R_1 = 0.0315$          | $R_1 = 0.0220$                 | $R_1 = 0.0575$                  | $R_1 = 0.0304$             | $R_1 = 0.0238$     | $R_1 = 0.0306$   |
| ()   | $wR_2 = 0.0667$         | $wR_2 = 0.0504$                | $wR_2 = 0.1360$                 | $\dot{wR_2} = 0.0757$      | $wR_2 = 0.0530$    | $wR_2 = 0.0542$  |
| Goodness of fit on $F^2$                     | 1.098                   | 1.112                          | 1.130                           | 1.048                      | 1.107              | 1.087  |

frequencies assignable to NH at 3153 and  $3051 \text{ cm}^{-1}$  and a pair of PS stretching frequencies at 617 and 595 cm<sup>-1</sup>. The solubilities of the mercury complexes in common organic solvents were also low.

The two P=S stretching frequencies for L at 632 and 614 cm<sup>-1</sup> are both lowered by about 12–21 cm<sup>-1</sup> for the complexes, consistent with metal coordination of the sulfur atoms [16]. Similarly, the two N–H stretching frequencies at 3222 and 3158 cm<sup>-1</sup> for L are replaced with one band at about 3056–3084 cm<sup>-1</sup> for all the complexes, apart from [ $\{L(HgI_2)_2\}_2$ ], which displays two bands at 3052 cm<sup>-1</sup> and 3153 cm<sup>-1</sup>. The lowering of these frequencies is consistent with the presence of N–H···X hydrogen bonds in the structure, rather than coordination by N–H groups in a strained four-membered ring. Moreover, the trend of the v(NH) frequencies to lower energies increases along the series  $I^- < Br^- < CI^-$ , which parallels the hydrogen-bonding ability of the anions [21].

All of the copper complexes with L remained unchanged upon recrystallization from hot CH<sub>3</sub>CN. However, the CuCl complex of 1,2-bis(diphenylphosphino)hydrazine, after initial recrystallization from hot toluene and then left to crystallize for several months, was hydrolytically unstable with cleavage of the P–N bonds [22], and one of the products isolated was diphenylphosphinic acid. Similar reactivity has been observed for aminobis(phosphines) [23]. The polarity of the P–N bond favours attack on the phosphorus atom by the water nucleophile, and this is followed by oxidation of the P atom. This reaction is slowed down when the ligand is already oxidized as in L and does not occur when P–C bonds are present. This is the first reported cleavage reaction for a coordinated hydrazinobis(phosphine).

## 3.2. Description of the structures

#### 3.2.1. 1,2-Bis(diphenylthioylphosphino)hydrazine (L)

The free ligand L crystallises from an acetone solution in the space group P2(1) with four molecules in the asymmetric unit. Every independent molecule has a similar conformation in which the PNNP backbone has a torsion angle of around 16° and both pairs of N-H and P=S bonds are directed towards the same side of the mean PNNP plane. This arrangement of the sulfur atoms is similar to that observed in the structure of  $Ph_2P(S)CH_2CH_2P(S)Ph_2$  (L<sup>1</sup>) although the PCCP backbone is slightly more twisted with a torsion angle of ca. 25° [24]. However, molecules of L exist as hydrogen bonded dimers in the solid state with both molecules in the dimer contributing one N-H<sup>--</sup>S bond to the array (Fig. 1), whereas the sulfur atoms in  $L^1$  are only involved in close contacts with aromatic hydrogen atoms on nearby diphenylphosphine groups. In this respect, the packing in L more resembles  $Ph_2P(O)CH_2CH_2$  $P(O)Ph_2$ , in which two adjacent molecules each supply a close contact between a hydrogen atom on the  $(CH_2)_2$ backbone and a P=O bond, although in this compound the P=O bonds on the same molecule are directed towards



Fig. 1. Diagram of the dimeric form of L in the solid state. Thermal ellipsoids drawn at 50% probability level and most hydrogen atoms removed for clarity.

opposite sides of the PCCP mean plane [25]. Selected bond lengths and angles are given in Table 2. Structural data on hydrazinobis(phosphine) adducts is scarce although the P– N and N–N bond lengths in L (average 1.695 and 1.441 Å) are comparable with those observed in a cyclic example, 3,6-dimethoxy-1,2,4,5-tetraaza-3,6-diphosphacyclohexanedisulfide (average 1.663 and 1.435 Å) and the P–S bond lengths (average 1.945 Å) are comparable to those in L<sup>1</sup> (1.941 Å) [26].

## 3.2.2. Copper(I) halide complexes of L

X-ray quality crystals of the copper(I) halide complexes of L were obtained in from MeCN solutions. In each case the overall structure is similar and comprises a dimetallic species of stoichiometry [{CuLX}<sub>2</sub>] in which L acts as a bridging ligand, bonding to separate copper centres through either sulfur atom (Fig. 2., X = I). Selected bond lengths and angles are given in Table 3.

The coordination spheres of the Cu(I) centres have  $S_2X_2$ ' donor sets with a somewhat unusual geometry, being best described as trigonal pyramidal. The copper bonds to X1, S1 and S2 (sulfur atoms from different ligands) and X1A. The halides link the two symmetry related Cu atoms with the Cu–X1A bond lengths being around 0.5–0.65 Å longer than the Cu–X1 bonds lengths (Table 3). The X1A ion forms the apex of the trigonal pyramid. The sum of the three angles in the coordination planes formed about the copper atom by X1 and the sulfur atoms are approximately 354.7, 357.1 and 356.9°, respectively, for X1 = I, Br and Cl hence approaching an ideal trigonal geometry. The copper atom is displaced from the trigonal plane towards X1A by 0.3210, 0.2318 and 0.2360 Å, respectively, for X = I, Br and Cl.

The overall structures are comparable to the arrangement observed in  $[{CuL^1Cl}_2][27]$  but with some subtle dif-

| Table 2  |      |         |       |     |        |           |  |
|----------|------|---------|-------|-----|--------|-----------|--|
| Selected | bond | lengths | (Å) a | and | angles | (°) for L |  |

|              | Molecule A | Molecule B | Molecule C | Molecule D |
|--------------|------------|------------|------------|------------|
| P1-N1        | 1.693(2)   | 1.701(2)   | 1.6968(19) | 1.701(2)   |
| P2-N2        | 1.707(2)   | 1.6859(19) | 1.695(2)   | 1.683(2)   |
| N1-N2        | 1.446(3)   | 1.435(3)   | 1.439(3)   | 1.443(3)   |
| P1-S1        | 1.9507(9)  | 1.9397(9)  | 1.9399(9)  | 1.9415(9)  |
| P2-S2        | 1.9401(9)  | 1.9504(9)  | 1.9516(9)  | 1.9485(9)  |
| S1-P1-N1     | 116.77(7)  | 116.39(8)  | 117.05(7)  | 115.76(8)  |
| S1-P1-C11    | 114.26(8)  | 114.60(8)  | 114.58(8)  | 114.55(8)  |
| S1-P1-C21    | 113.68(9)  | 112.90(9)  | 113.37(9)  | 113.07(9)  |
| S2-P2-N2     | 115.77(8)  | 116.81(8)  | 116.54(8)  | 117.31(8)  |
| S2-P2-C31    | 113.15(10) | 112.76(9)  | 112.28(9)  | 112.57(9)  |
| S2-P2-P2-C41 | 115.02(9)  | 114.73(8)  | 113.93(9)  | 115.27(9)  |
| P1-N1-N2     | 111.55(14) | 110.70(14) | 113.05(14) | 110.59(14) |
| P2-N2-N1     | 112.66(14) | 113.04(15) | 111.17(14) | 113.12(15) |



Fig. 2. Diagram of the dimetallic complex [{CuLI}2]. Thermal ellipsoids drawn at 50% probability level and most hydrogen atoms removed for clarity.

Table 3 Selected bond lengths (Å) and angles (°) for the copper(I) complexes

|             | [{CuLI}2] · 2MeCN | [{CuLBr}2] · MeCN | [{CuLCl}2] · 4MeCN |
|-------------|-------------------|-------------------|--------------------|
| Cu1–S1      | 2.3045(5)         | 2.888(12)         | 2.2822(4)          |
| Cu1–S2      | 2.2951(5)         | 2.2927(12)        | 2.2851(4)          |
| Cu1–X1      | 2.5990(3)         | 2.4353(8)         | 2.3117(4)          |
| Cu1–X1A     | 3.0859(3)         | 3.0851(1)         | 2.8687(5)          |
| P1-S1       | 1.9769(6)         | 1.9865(14)        | 1.9864(5)          |
| P2-S2       | 1.9859(6)         | 1.9884(15)        | 1.9848(5)          |
| N1-N2       | 1.444(2)          | 1.450(4)          | 1.4448(16)         |
| S1-Cu1-S2   | 115.752(19)       | 115.15(4)         | 114.073(15)        |
| S1-Cu1-X1   | 118.448(15)       | 119.41(4)         | 120.657(15)        |
| S1-Cu1-X2   | 120.487(16)       | 122.53(4)         | 122.121(15)        |
| S1–Cu1–X1A  | 94.951(15)        | 95.76(4)          | 99.79(1)           |
| S2-Cu1-C1A  | 98.924(16)        | 98.03(4)          | 100.56(1)          |
| X1–Cu1–X1A  | 99.130(9)         | 93.36(3)          | 87.86(1)           |
| Cu1-X1-Cu1A | 80.870(10)        | 86.64(3)          | 92.14(1)           |
| P1-S1-Cu1   | 106.44(2)         | 105.38(5)         | 101.705(8)         |
| P2-S2-Cu1   | 104.66(2)         | 102.79(5)         | 100.396(19)        |

ferences. In the three L Cu(I) complexes there are four strong intramolecular hydrogen bonds (Table 4) of the type  $N-H \cdots X$  which have the effect of creating two pairs of fused 6-membered chelate rings. This assembly appears to have an increasing influence on the PNNP backbone as X becomes smaller and more electronegative (in each case the torsion angle for PNNP is 10, 13 and  $16^{\circ}$  for X = I, Br and Cl). In [{CuL<sup>1</sup>Cl}<sub>2</sub>] the PCCP torsion angle is  $4^{\circ}$  and the intramolecular contacts from the ligand backbone are long (the relevant C-H···Cl contacts are 2.708 and 2.581 Å) compared with [{CuLCl}<sub>2</sub>] where N-H···Cl are 2.410 and 2.351 Å. Hence the ligand backbones in the [{CuLX}<sub>2</sub>] complexes remain twisted in their compression towards the  $Cu_2X_2$  core whereas in [{ $CuL^1Cl$ }<sub>2</sub>] the ligand backbone is somewhat flattened. In [{CuLCl}<sub>2</sub>]the sulfur atoms on the same ligand are further apart (5.989 cf. 5.846 Å) even though the phosphorus atoms are closer (4.083 cf. 4.424 Å). The impact of this on the coordination spheres is that in  $[{CuL^1Cl}_2]$  the Cu···Cu separation in [{CuLCl}<sub>2</sub>] is longer (3.751 *cf.* 3.327 Å) and the bridging Cu-Cl distances (2.869 cf. 2.639 Å) are also increased.

3.2.3.  $[{L(HgI_2)_2}_2]$ 

The reaction of 2 equiv of  $HgI_2$  with L and subsequent recrystallisation from acetonitrile afforded the unusual tetrametallic complex [{L(HgI\_2)\_2}]. In this complex L is again acting as a bridging, ligand binding different Hg(II)

Table 4

Hydrogen-bond lengths (Å) and angles (°) in the  $[\{CuLX\}_2]$  complexes

|                          | D–H  | $H{\cdots}A$ | D···A      | ∠(DHA) |
|--------------------------|------|--------------|------------|--------|
| N1–H1 <sup>…</sup> I1    | 0.85 | 2.84         | 3.6506(15) | 160.7  |
| N2–H2 <sup>···</sup> I1A | 0.86 | 2.75         | 3.5480(14) | 156.4  |
| N2–H2 <sup>···</sup> Br1 | 0.92 | 2.62         | 3.502(3)   | 160.3  |
| N1–H1 <sup>···</sup> Br1 | 0.89 | 2.59         | 3.436(3)   | 158.5  |
| N1-H1 Cl1                | 0.93 | 2.35         | 3.2394(12) | 159.7  |
| N2-H2 <sup>···</sup> Cl1 | 0.89 | 2.41         | 3.2674(12) | 161.7  |

ions through each sulfur donor with each ligand creating a moiety of stoichiometry ' $L(HgI_2)_2$ '. Two such moieties are linked by iodide bridges which lie about a centre of inversion to give the tetrametallic complex (Fig. 3). Selected bond lengths and angles are given in Table 5.

Hence the molecule contains two different tetrahedral 'I<sub>3</sub>S' coordination spheres. Hg1 is bonded to I1 and I2 [2.6726(4) and 2.6919(3) Å] and is bridged to Hg2 through a slightly longer bond to I3 [3.1084(3) Å]. Hg2 is coordinated by three bridging iodine ligands I3, I4 and I4A; the bond lengths being 2.7244(4), 2.7323(3) and 3.1572(4) Å, respectively. The Hg2-S2 bond length of 2.5587(11) Å is significantly shorter than the Hg1-S1 bond length of 2.6150(11) Å although the P=S bond lengths are similar and longer than in the free ligand [1.9965(16) and 2.0012(16) Å compared to an average of 1.945 Å]. As with the dimetallic copper(I) halide structures, the NH-NH ligand backbones in  $[{L(HgI_2)_2}_2]$  participate in strong hydrogen bonding interactions with the iodide coligands; H1...I2 is 2.91 Å and H2...I3 is 2.90 Å and the PNNP torsion angle is 17.7°.

# 3.2.4. [HgLBr<sub>2</sub>]

From the reaction of 1 equiv of  $HgBr_2$  with L, crystals of  $[HgLBr_2]$  were obtained from nitromethane in which L acts as a bidentate ligand bonding through the two sulfur atoms to form a seven-membered chelate ring. The complex has a distorted tetrahedral geometry and selected bond lengths and angles are given in Table 6.

The complex (Fig. 4) is comparable with  $[HgL^{1}Br_{2}]$  which has a similar donor set and distorted tetrahedral coordination geometry [8]. The ligand bite angle of 119.52(3)° in  $[HgLBr_{2}]$  is close to that of 118.85(8)° in  $[HgL^{1}Br_{2}]$ . However the bond lengths in the coordination sphere of each complex are quite different. The two Hg–S bonds in  $[HgLBr_{2}]$  are shorter at 2.5312(9) and 2.5173(9) Å compared to 2.678(2) and 2.552(2) Å in  $[HgL^{1}Br_{2}]$  while the two Hg–Br



Fig. 3. Diagram of the tetrametallic complex  $[{L(HgI_2)_2}_2]$ . Thermal ellipsoids drawn at 50% probability level and most hydrogen atoms removed for clarity.

Table 5 Selected bond lengths (Å) and angles (°) for  $[{L(HgI_2)_2}_2]$ 

| Hg1–S1     | 2.6150(11)  | Hg2–S2      | 2.5587(11)  |
|------------|-------------|-------------|-------------|
| Hg1–I1     | 2.6726(4)   | Hg2–I3      | 2.7244(4)   |
| Hg1–I2     | 2.6919(3)   | Hg2–I4      | 2.7323(3)   |
| Hg1–I3     | 3.1084(3)   | Hg2–I4A     | 3.1752(4)   |
| P1-S1      | 1.9965(16)  | P2-S2       | 2.0012(16)  |
| N1-N2      | 1.441(5)    |             |             |
| S1–Hg1–I1  | 105.26(3)   | S2-Hg2-I3   | 115.50(3)   |
| S1-Hg1-I2  | 114.88(3)   | S2–Hg2–I4   | 111.85(3)   |
| I1-Hg1-I2  | 134.101(12) | I3-Hg2-I4   | 128.543(12) |
| S1–Hg1–I3  | 97.27(3)    | S2–Hg2–I4A  | 104.81(3)   |
| I1-Hg1-I3  | 102.885(11) | I3–Hg2–I4A  | 96.727(10)  |
| I2–Hg1–I3  | 93.488(10)  | I4–Hg2–I4A  | 89.626(10)  |
| Hg1–I3–Hg2 | 99.254(10)  | Hg2–I4–Hg2A | 90.374(10)  |
| P1-S1-Hg1  | 100.80(5)   | P2–S2–Hg2   | 103.50(6)   |

Table 6

Selected bond lengths (Å) and angles (°) for [HgLBr<sub>2</sub>]

| Hg1–S1     | 2.5173(9)  | Hg1–S2      | 2.5312(9)   |
|------------|------------|-------------|-------------|
| Hg1–Br1    | 2.6089(4)  | Hg1–Br2     | 2.6078(4)   |
| P1-S1      | 1.9878(12) | P2-S2       | 1.9979(12)  |
| N1-N2      | 1.419(4)   |             |             |
| S1–Hg1–S2  | 119.52(3)  | S2–Hg1–Br1  | 112.55(2)   |
| S1-Hg1-Br1 | 98.82(2)   | S2–Hg1–Br2  | 102.19(2)   |
| S1-Hg1-Br2 | 112.98(2)  | Br1-Hg1-Br2 | 111.107(12) |
| P1-S1-Hg1  | 107.43(4)  | P2–S2–Hg2   | 108.36(4)   |

bonds are considerably longer at 2.6089(4) and 2.6078(4) Å compared to 2.5592(11) and 2.5509(11) Å.

A possible reason for this presents itself from an examination of the packing in [HgLBr<sub>2</sub>]. Contrary to the conformation found in the bridging structures previously discussed, the N–H bonds on the ligand backbone of L are now directed towards the opposite side of the PNNP mean plane to the sulfur donor atoms. This allows adjacent molecules of  $[HgLBr_2]$  to engage in intermolecular hydrogen bonding in the crystalline state, with the distances H1...Br2A and H2...Br1A being 2.58 and 2.64 Å, respectively. It also results in a lengthening of the Hg–Br bonds along with any compensating effects due to short Hg–S bonds. The outcome is the formation of a second, seven-membered chelate-type ring *viz*. Hg1A–Br1A...H2– N2–N1–H1...Br2A in a bridging arrangement as columns of [LHgBr<sub>2</sub>] stack along the *a*-axis (Fig. 5). Further



Fig. 5. A diagram showing how  $[HgLBr_2]$  molecules pack in columns along the *a*-axis.



Fig. 4. Diagram of the complex [HgLBr<sub>2</sub>]. Thermal ellipsoids drawn at 50% probability level and most hydrogen atoms removed for clarity.

reinforcement of the columnar array is provided by the close contacts  $S1A\cdots H35$  and  $S2B\cdots H23$  on adjacent molecules (2.916 and 2.835 Å, respectively). Interestingly, the N–N bond is significantly shorter at 1.419(4) Å than in the other structures described here [1.435(3)-1.450(4) Å] and the PNNP torsion angle is significantly larger (37.8°).

# 4. Conclusion

The ligand, 1.2-bis(diphenylthioylphosphino)hydrazine (L), reacts with copper(I) and mercury(II) halides affording the complexes,  $[{CuLX}_2](X = I, Br \text{ or } Cl), [HgLX_2](X = I)$ Cl or Br) and the tetrametallic complex,  $[{L(HgI_2)_2}_2]$ . The complexes contain the metal in a four coordinate environment which approximates trigonal pyramidal for the copper complexes and distorted tetrahedral for the mercury complexes. In the dimetallic copper complexes L bridges the two metal atoms, with bridging halides completing the coordination sphere. The tetrametallic mercury complex,  $[{L(HgI_2)_2}_2]$ , also contains L bridging two Hg atoms but the two ' $L(HgI_2)_2$ ' moieties are linked by coordinated iodide ions. Hydrogen bonds between the hydrazine N-H hydrogens of L and the halide ligands are an important feature in the structures of the metal complexes. This is a much more dominant effect than is observed with similar complexes of L<sup>1</sup>, and is an interesting ligand design strategy.

## Appendix A. Supplementary material

CCDC 646490–646494 contains the supplementary crystallographic data for this paper. 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.2007.08.009.

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