

*Dedicated to Professor Ionel Haiduc  
on the occasion of his 80th anniversary*

## SYNTHESIS AND STRUCTURAL CHARACTERIZATION OF $\text{HgX}[(\text{SPPh}_2)_2\text{N-S,S}']$ ( $\text{X} = \text{Cl, Br, I}$ ) – MOLECULAR STRUCTURES AND SUPRAMOLECULAR ASPECTS\*\*

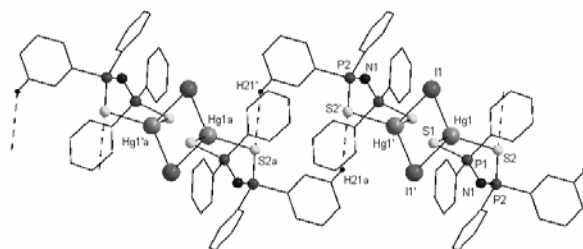
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The reactions between  $\text{HgX}_2$  with  $\text{K}[(\text{SPPh}_2)_2\text{N}]$  in 1:1 molar ratio afforded isolation of inorganic mercury(II) complexes with mixed halo / dithioimidodiphosphinato ligands,  $\text{HgX}[(\text{SPPh}_2)_2\text{N-S,S}']$  [ $\text{X} = \text{Cl}$  (**1**),  $\text{Br}$  (**2**),  $\text{I}$  (**3**)]. All compounds were characterized by multinuclear NMR ( $^1\text{H}$ ,  $^{13}\text{C}$ ,  $^{31}\text{P}$ ) and IR spectroscopy. Single-crystal X-ray diffraction studies revealed the symmetric chelating coordination of the dithio ligand to the metal centre. Regardless the nature of the halogen, the crystals contain dimer associations built through bridging  $\text{Hg-X-Hg}$ . This results in dimetallic units with a central planar  $\text{Hg}_2\text{X}_2$  ring and distorted tetrahedral  $\text{S}_2\text{HgX}_2$  cores. Moreover, while short  $\text{C-H}\cdots\text{X}$  ( $\text{X} = \text{Cl, Br}$ ) and  $\text{C-H}\cdots\text{S}$  contacts result in a 3D supramolecular architecture for **1** and **2**, in the crystal of the iodide **3** only a ribbon-like polymer based on intermolecular sulfur-hydrogen contacts between dimer associations of  $\lambda$ -**3** and  $\delta$ -**3** isomers is formed.



### INTRODUCTION

The tetraorganodichalcogenoimidodiphosphinato and -diphosphato ligands,  $[(\text{XPR}_2)(\text{YPR}'_2)\text{N}]^-$  ( $\text{X, Y} = \text{O, S, Se, Te}$ ;  $\text{R, R}' = \text{alkyl, aryl, alkoxy, aryloxy}$ ) were systematically investigated during last years both in relation to their coordination versatility<sup>1,2</sup> and the potential use of their metal complexes for catalysis,<sup>3</sup> materials science [e.g.

luminescent compounds,<sup>4</sup> single-source precursors for chemical vapor deposition (CVD) methods<sup>5</sup>], selective metal extraction,<sup>6</sup> NMR shift reagents<sup>7</sup> or as active biological agents.<sup>8</sup> Regarding the  $\text{Hg(II)}$  compounds containing such ligands, an early publication reported on the synthesis and IR spectra of  $\text{Hg}[(\text{SPPh}_2)_2\text{N}]_2$  and  $\text{HgCl}[(\text{SPPh}_2)_2\text{N}]$ , the latter being often contaminated with the complex  $\text{HgCl}_2[(\text{SPPh}_2)_2\text{NH}]$ .<sup>9</sup> Later, Fluck and co-workers reported on the synthesis and structure

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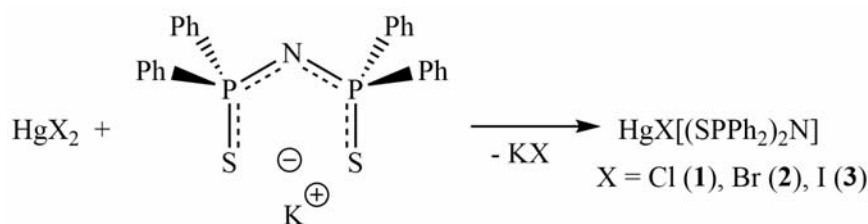
\*\* Supporting information on : <http://web.icf.ro/rch/> or <http://revroum.lew.ro>

of monomeric  $\text{PhHg}[\text{N}\{\text{P}(\text{O})(\text{OPh})_2\}_2\text{-N}]$ , a compound in which the tetraphenylimidodiphosphato ligand is attached to the metal through the nitrogen atom.<sup>10</sup> This contrasts with the dimeric, organometallic species  $[\text{PhHg}\{\mu\text{-(OPR}_2\text{)}_2(\text{SPPH}_2)\text{N}\}\text{-O,S}]_2$  ( $\text{R} = \text{Me, Ph}$ ) built through *S,O*-bridging organophosphorus ligands.<sup>11</sup> Several inorganic Hg(II) compounds with various tetraorganodichalcogenoimidodiphosphinato ligands, *i.e.*  $\text{Hg}[(\text{EPPH}_2)_2\text{N-E,E}]_2$  ( $\text{E} = \text{S},^{12\text{a}} \text{Se}^{12\text{b}}$ ),  $\text{Hg}[(\text{EPPr}_2)_2\text{N-E,E}]_2$  ( $\text{E} = \text{Se},^{12\text{c}} \text{Te}^{12\text{d}}$ ) and  $\text{Hg}[(\text{EPMe}_2)(\text{SPPH}_2)\text{N-E,S}]_2$  ( $\text{E} = \text{O, S}$ ),<sup>12\text{e}} were reported previously and for all these compounds the crystals contain monomeric species, with chelating tetraorganodichalcogenoimidodiphosphinato ligand coordinated to the metal through both chalcogens. The complex  $[\text{HgI}_2\{(\text{SPPH}_2)_2\text{NH}\}]$  was reported in the context of studies regarding the oxidation of liquid mercury with the adduct  $(\text{SPPH}_2)_2\text{NH}\cdot\text{I}_2$ , a process which might be useful in the recovery of the metal from waste materials.<sup>12\text{a}}</sup> Some Hg(II) compounds with selenium- or tellurium containing ligands, *e.g.* inorganic  $\text{Hg}[(\text{EPR}_2)_2\text{N-E,E}]_2$  ( $\text{E} = \text{Se},^{12\text{c}} \text{Te}^{12\text{d}}$ ) as well as organometallic  $\text{RHg}[(\text{SePPr}_2)_2\text{N}]$ <sup>12\text{c}}</sup> derivatives, were investigated as single-source precursors of metal chalcogenide thin films.</sup>

We report here on the synthesis, the spectroscopic characterization in solution as well as the molecular structure of new inorganic mercury(II) complexes with mixed halo / dithioimidodiphosphinato ligands,  $\text{HgX}[(\text{SPPH}_2)_2\text{N}]$  [ $\text{X} = \text{Cl}$  (**1**),  $\text{Br}$  (**2**),  $\text{I}$  (**3**)], useful as starting materials for the preparation of novel mixed-ligand inorganic or organomercury(II) species.

## RESULTS

The mixed halo / tetraphenyldithioimidodiphosphinato mercury(II) compounds were obtained by reacting  $\text{HgX}_2$  ( $\text{X} = \text{Cl, Br, I}$ ) with  $\text{K}[(\text{SPPH}_2)_2\text{N}]$ , in 1:1 molar ratio, in dichloromethane (Scheme 1).



Scheme 1

Details of the methods of synthesis are given in the Experimental section. The new Hg(II) compounds were isolated as white (the chloride **1** and the bromide **2**) or yellowish (the iodide **3**) crystalline solids readily soluble in chlorinated solvents ( $\text{CH}_2\text{Cl}_2$ ,  $\text{CHCl}_3$ ). The elemental analysis supported the stoichiometry of the title compounds.

All three compounds were characterized in solid state by IR spectroscopy and in solution by  $^1\text{H}$ ,  $^{13}\text{C}$  and  $^{31}\text{P}$  NMR spectroscopy. The NMR spectra were recorded in  $\text{CDCl}_3$  at room temperature. Attempts to record  $^{199}\text{Hg}$  NMR spectra failed, no resonance being observed.

The IR spectra confirmed the presence of the deprotonated dithioimidodiphosphinato ligand for compounds **1–3**, medium to very strong bands being assigned to  $\nu_{\text{as}}(\text{P}_2\text{N})$  and  $\nu(\text{PS})$  stretching vibrations.

The  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra exhibit in the aromatic region one set of resonances for the phenyl groups attached to the phosphorus atoms. The multiplicity of the resonances corresponds to the phosphorus-hydrogen and phosphorus-carbon couplings. The  $^{31}\text{P}$  NMR spectra for compounds **1–3** show one resonance with a chemical shift consistent with the presence of a deprotonated dithioimidodiphosphinato ligand.

Single crystals of enough good quality were obtained by diffusion of *n*-hexane into the methylene dichloride solution of each of the three inorganic Hg(II) species described here. The crystal and molecular structures were established by X-ray diffraction studies. Regardless the nature of the halide it was found that the crystals contain discrete dimer associations built through halogen bridges; no unusual intermolecular distances, shorter than the sum of the van der Waals radii of the corresponding heavy atoms, were observed. As an example of structure for this type of compound, Figure 1 shows the ORTEP-like representation, with the atom numbering scheme, for the molecule of the iodide **3**. Selected bond distances and angles are listed in Table 1.

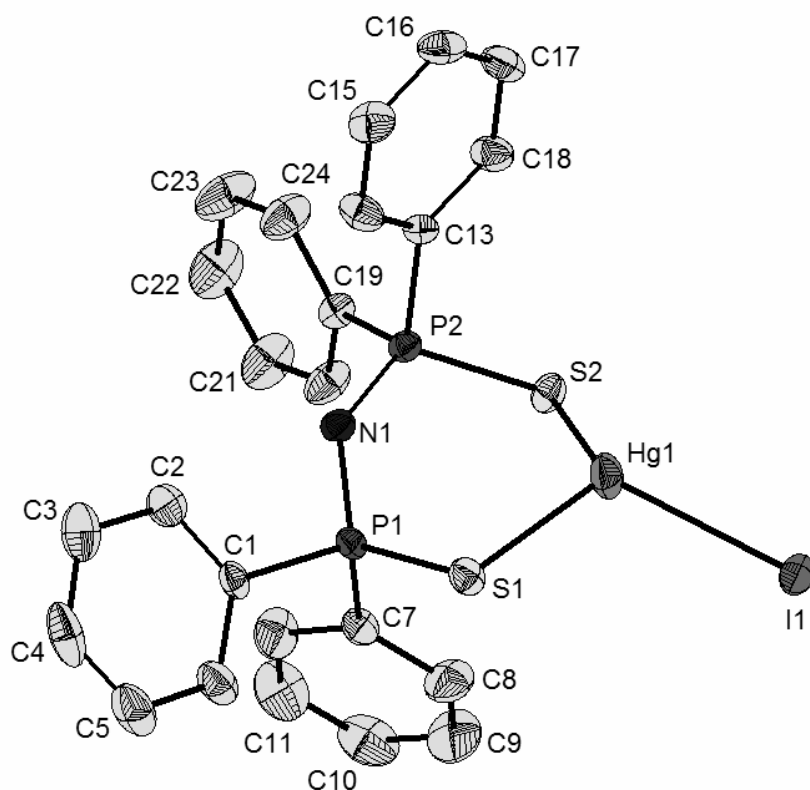


Fig. 1 – ORTEP representation and atom numbering scheme for  $\delta$ -isomer of  $\text{HgI}[(\text{SPPPh}_2)_2\text{N}]$  (**3**). The atoms are drawn with 30% probability ellipsoids. Hydrogen atoms are omitted for clarity.

Table 1

Selected interatomic distances ( $\text{\AA}$ ) and angles (deg) in  $\text{Hg}[(\text{SPPPh}_2)_2\text{N}]\text{X}$  [X = Cl (**1**), Br (**2**), I (**3**)]<sup>a</sup>

	<b>1</b>	<b>2</b>	<b>3</b>
Hg(1)–S(1)	2.4476(14)	2.453(2)	2.483(2)
Hg(1)–S(2)	2.4491(12)	2.452(3)	2.460(2)
Hg(1)–X(1)	2.5776(12)	2.7054(11)	2.7496(6)
Hg(1)–X(1') <sup>b</sup>	2.6154(13)	2.7004(11)	3.0734(7)
P(1)–S(1)	2.0374(18)	2.032(3)	2.024(3)
P(2)–S(2)	2.0382(16)	2.027(3)	2.036(3)
P(1)–N(1)	1.578(4)	1.578(7)	1.588(7)
P(2)–N(1)	1.580(3)	1.564(7)	1.583(7)
P(1)–C(1)	1.87(2) [1.764(8)] <sup>c</sup>	1.792(8)	1.801(7)
P(1)–C(7)	1.800(5)	1.791(12) [1.84(2)] <sup>c</sup>	1.801(8)
P(2)–C(13)	1.787(6) [1.867(18)] <sup>d</sup>	1.803(9)	1.796(8)
P(2)–C(19)	1.796(4)	1.728(12) [1.861(16)] <sup>f</sup>	1.803(7)
Hg(1)–X(1)–Hg(1') <sup>b</sup>	94.15(4)	91.11(3)	85.15(2)
S(1)–Hg(1)–S(2)	117.25(4)	116.94(9)	113.60(6)
S(1)–Hg(1)–X(1)	107.10(5)	117.33(6)	111.50(5)
S(2)–Hg(1)–X(1)	119.02(4)	105.53(8)	122.00(4)
S(1)–Hg(1)–X(1') <sup>b</sup>	117.95(5)	106.65(6)	101.89(5)
S(2)–Hg(1)–X(1') <sup>b</sup>	106.06(4)	118.65(9)	109.25(5)
X(1)–Hg(1)–X(1') <sup>b</sup>	85.85(4)	88.88(3)	94.85(2)
P(1)–N(1)–P(2)	136.6(2)	137.8(5)	134.5(4)
N(1)–P(1)–S(1)	116.41(14)	118.8(3)	116.8(3)

Table 1 (continued)

N(1)–P(1)–C(1)	104.9(8) [115.8(4)] <sup>c</sup>	109.7(4)	107.0(3)
N(1)–P(1)–C(7)	107.7(2)	108.7(5) [105.2(8)] <sup>e</sup>	111.1(4)
S(1)–P(1)–C(1)	117.9(9) [104.1(4)] <sup>c</sup>	109.1(3)	104.3(2)
S(1)–P(1)–C(7)	104.40(17)	105.2(4) [108.3(14)] <sup>e</sup>	110.2(3)
C(1)–P(1)–C(7)	104.6(9) [107.6(4)] <sup>c</sup>	104.2(5) [104.7(17)] <sup>e</sup>	106.6(4)
N(1)–P(2)–S(2)	119.50(15)	116.3(3)	118.4(3)
N(1)–P(2)–C(13)	107.6(2) [106.0(6)] <sup>d</sup>	107.9(4)	108.1(3)
N(1)–P(2)–C(19)	109.92(18)	115.8(7) [106.0(8)] <sup>f</sup>	110.0(3)
S(2)–P(2)–C(13)	105.2(2) [106.3(9)] <sup>d</sup>	105.0(3)	108.6(2)
S(2)–P(2)–C(19)	109.14(12)	104.7(6) [115.2(7)] <sup>f</sup>	104.3(2)
C(13)–P(2)–C(19)	104.4(3) [104.9(11)] <sup>d</sup>	106.2(7) [105.8(8)] <sup>f</sup>	107.1(3)
Hg(1)–S(1)–P(1)	95.78(6)	95.45(11)	97.07(9)
Hg(1)–S(2)–P(2)	95.60(5)	95.86(13)	97.49(9)

<sup>a</sup> X is Cl for **1**, Br for **2**, and I for **3**; <sup>b</sup> Symmetry equivalent atoms ( $l-x, y, 0.5-z$ ) for **1** and **2**, and ( $l-x, l-y, 2-z$ ) for **3**, are given by “prime”; <sup>c</sup> For C(1B); <sup>d</sup> For C(13B); <sup>e</sup> For C(7B); <sup>f</sup> For C(19B).

## DISCUSSION

### Solution behavior

The <sup>1</sup>H and <sup>13</sup>C NMR spectra of all three title compounds are very similar regardless the nature of the halogen atom attached to mercury. They show only one set of resonances in the aromatic region, thus being consistent with equivalent phenyl groups attached to the phosphorus atoms in a ligand unit, in solution, at the NMR time scale. The resonance for the *ipso* carbon appears as a doublet of doublets (<sup>1</sup>J<sub>PC</sub> range 111.9 – 112.6 Hz; <sup>3</sup>J<sub>PC</sub> range 3.4 – 3.9 Hz), a pattern resulted from its coupling with both phosphorus atoms from the ligand moiety. However, in the <sup>31</sup>P NMR spectra of **1–3** only one sharp resonance was observed, suggesting either an isobidentate *S,S'*-monometallic biconnective coordination pattern of the dithioimidodiphosphinato ligand in solution (as observed in solid state, *vide infra*) or a fast dynamic process at the NMR time scale.

### Solid state structure

In the IR spectra of compounds **1–3** the assignment of the  $\nu_{\text{as}}(\text{P}_2\text{N})$  and  $\nu(\text{PS})$  stretching vibrations was made by comparison with the IR spectra of the free (SPPH<sub>2</sub>)<sub>2</sub>NH acid and its potassium salt, K[(SPPH<sub>2</sub>)<sub>2</sub>N], used as starting material.<sup>13</sup> The presence of strong bands at about 1215, 1175 cm<sup>-1</sup> and very strong bands at about 555 cm<sup>-1</sup> are indicative for characteristic  $\nu_{\text{as}}(\text{P}_2\text{N})$

and  $\nu(\text{PS})$  stretching vibrations, respectively, and thus consistent with the deprotonated dithioimidodiphosphinato ligand [c.f.<sup>13e</sup> (SPPH<sub>2</sub>)<sub>2</sub>NH:  $\nu_{\text{as}}(\text{P}_2\text{NH})$  920vs,  $\nu(\text{PS})$  645vs cm<sup>-1</sup>; K[(SPPH<sub>2</sub>)<sub>2</sub>N]:  $\nu_{\text{as}}(\text{P}_2\text{N})$  1195vs, 1170,  $\nu(\text{PS})$  600vs, 580s cm<sup>-1</sup>].

The molecular structure of compounds **1–3** are very similar, regardless the nature of the halogen atom attached to mercury. Thus, in a molecule of HgX[(SPPH<sub>2</sub>)<sub>2</sub>N-*S,S'*] the dithio ligand acts as an isobidentate, monometallic biconnective moiety (Fig. 1), being coordinated to the metal centre through both sulfur atoms [Hg(1)–S(1) / Hg(1)–S(2) 2.4476(14) / 2.4491(12) Å (**1**); 2.453(2) / 2.452(3) Å (**2**); 2.483(2) / 2.460(2) Å (**3**); *cf.* the sum of the covalent radii of mercury and sulfur,  $\Sigma r_{\text{cov}}(\text{Hg},\text{S})$  2.48 Å<sup>14</sup>]. Within the SPNPS skeleton the interatomic distances correspond to single P–S bonds, while the phosphorus-nitrogen bonds are intermediate between single P–N and double P=N bonds (see Table 1; *cf.* [2-(Me<sub>2</sub>NCH<sub>2</sub>)C<sub>6</sub>H<sub>4</sub>]Te–S–PPh<sub>2</sub>=N–PPh<sub>2</sub>=S:<sup>15a</sup> P–S 2.057(1), P=S 1.945(1), P–N 1.612(3), P=N 1.557(3) Å; Ph<sub>2</sub>P(=S)–N=P(–SMe)Ph<sub>2</sub>:<sup>15b</sup> P–S 2.071(1), P=S 1.954(1), P–N 1.610(2), P=N 1.562(2) Å].

The coordination geometry of the HgXS<sub>2</sub> core in a molecule of HgX[(SPPH<sub>2</sub>)<sub>2</sub>N-*S,S'*] is distorted trigonal pyramidal as reflected by the bond angles at mercury (see Table 1), with the trigonal base described by the sulfur atoms and by the halogen atom and the metal atom in the apex, out from the best XS<sub>2</sub> plane by 0.59 Å (**1**), 0.67 Å (**2**) and 0.54 Å (**3**), respectively.

The resulting six-membered HgS<sub>2</sub>P<sub>2</sub>N ring is not planar, but folded along the P(1)⋯S(2) axis.

This induces chirality and the crystals of compounds **1–3** contain both  $\lambda$  and  $\delta$  isomers.<sup>16</sup> The halogen atom is bridging two metal atoms in all three compounds. For the chloride **1** and the iodide **3** asymmetric Hg–X $\cdots$ Hg bridges are formed [Hg(1)–X(1) / Hg(1)–X(1') 2.5776(12) / 2.6154(13) Å for **1** and 2.7496(6) / 3.0734(7) Å for **3**; *cf.* sum of the covalent and van der Waals radii, respectively, of mercury and halogen:  $\Sigma r_{\text{cov}}(\text{Hg,Cl})$  2.43 Å and  $\Sigma r_{\text{vdW}}(\text{Hg,Cl})$  3.31 Å;  $\Sigma r_{\text{cov}}(\text{Hg,I})$  2.77 Å and  $\Sigma r_{\text{vdW}}(\text{Hg,I})$  3.65 Å<sup>14</sup>]. By contrast, in the crystal of the bromide **2** symmetric Hg–Br–Hg bridges are formed [Hg(1)–Br(1) / Hg(1)–Br(1') 2.7054(11) / 2.7004(11) Å; *cf.*  $\Sigma r_{\text{cov}}(\text{Hg,Br})$  2.58 Å and  $\Sigma r_{\text{vdW}}(\text{Hg,Br})$  3.45 Å<sup>14</sup>]. As result dimer associations with double, bent halogen bridges [Hg(1)–X(1)–Hg(1') 94.15(4)°, 91.11(3)° and 85.15(2)° for **1**, **2**; and **3**, respectively] and with planar Hg<sub>2</sub>X<sub>2</sub> rings are formed in the crystals, *i.e.* pairs of  $\lambda$  isomers, ( $\lambda$ -**1**)<sub>2</sub> and ( $\lambda$ -**2**)<sub>2</sub> [and pairs of  $\delta$  isomers, ( $\delta$ -**1**)<sub>2</sub> and ( $\delta$ -**2**)<sub>2</sub>, respectively] for the chloride and the bromide, while for the iodide the dimer is formed by one  $\lambda$  isomer and one  $\delta$  isomer, *i.e.* ( $\lambda$ -**3** /  $\delta$ -**3**) (Fig. 2). The metal centers in a dimer association Hg<sub>2</sub>( $\mu$ -X)<sub>2</sub>[(SPPPh<sub>2</sub>)<sub>2</sub>N-*S,S'*]<sub>2</sub> exhibit a distorted tetrahedral HgX<sub>2</sub>S<sub>2</sub> core with bond angles at mercury in the range 85.85(4)–119.02(4)° for **1**, 88.88(3)–118.65(9)° for **2**, and 94.85(2)–122.00(4)° for **3**, respectively (Table 1), the

smallest, acute bond angle being always the X(1)–Hg(1)–X(1') angle.

Another remarkable difference observed in the crystals of compounds **1–3** is reflected by the supramolecular association of the Hg<sub>2</sub>( $\mu$ -X)<sub>2</sub>[(SPPPh<sub>2</sub>)<sub>2</sub>N-*S,S'*]<sub>2</sub> dimers through intermolecular C–H $\cdots$ halogen and C–H $\cdots$ S interactions. For the chloride **1** and the bromide **2** similar ribbon-like polymer are formed in the crystal, based on intermolecular C–H $\cdots$ halogen contacts between alternating ( $\lambda$ -**1**)<sub>2</sub> and ( $\delta$ -**1**)<sub>2</sub> (Figs. 3a and 3b) or ( $\lambda$ -**2**)<sub>2</sub> and ( $\delta$ -**2**)<sub>2</sub> dimers, respectively [inter-dimer distance: Cl(1) $\cdots$ H(11'a)<sub>aryl</sub> 2.92 Å for **1**, and Br(1) $\cdots$ H(15'a)<sub>aryl</sub> 2.96 Å for **2**; *cf.*  $\Sigma r_{\text{vdW}}(\text{Cl,H})$  3.01 Å and  $\Sigma r_{\text{vdW}}(\text{Br,H})$  3.15 Å<sup>14</sup>]. For both compounds further C–H $\cdots$ S interactions between such parallel ribbon-like chain polymers result in a 3D architecture (Fig. 3c, for **1**) [inter-chain distance: S(2) $\cdots$ H(22'')<sub>aryl</sub> 2.92 Å for **1**, and S(2) $\cdots$ H(4'')<sub>aryl</sub> 3.02 Å for **2**; *cf.*  $\Sigma r_{\text{vdW}}(\text{S,H})$  3.05 Å<sup>14</sup>] (see also the Supplementary material).

By contrast, the crystal of the iodide **3** contains ribbon-like polymers based on intermolecular C–H $\cdots$ sulfur contacts between ( $\lambda$ -**3** /  $\delta$ -**3**) dimer associations (Fig. 4) [inter-dimer distance: S(2) $\cdots$ H(21'b)<sub>aryl</sub> 3.00 Å; *cf.*  $\Sigma r_{\text{vdW}}(\text{S,H})$  3.05 Å<sup>14</sup>]. No further contacts are established between the chains in the case of the iodide **3**.

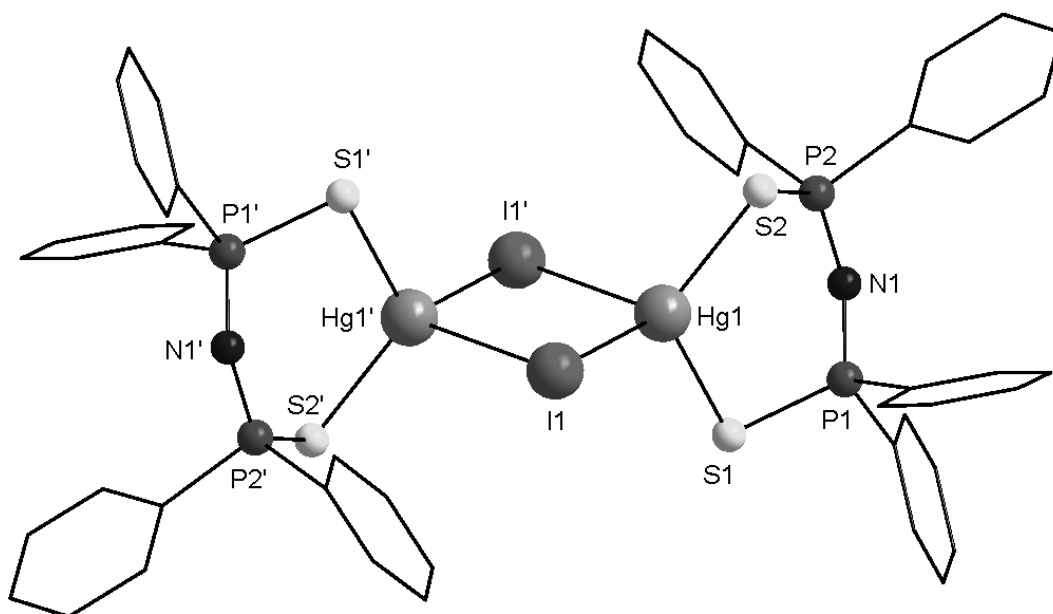


Fig. 2 – View of a dimer association of  $\lambda$ - and  $\delta$ -**3** isomers based on intermolecular iodine-mercury bonds in the crystal of **3** [symmetry equivalent atoms (*l*-*x*, *l*-*y*, 2-*z*) are given by “prime”]. Hydrogen atoms are omitted for clarity.

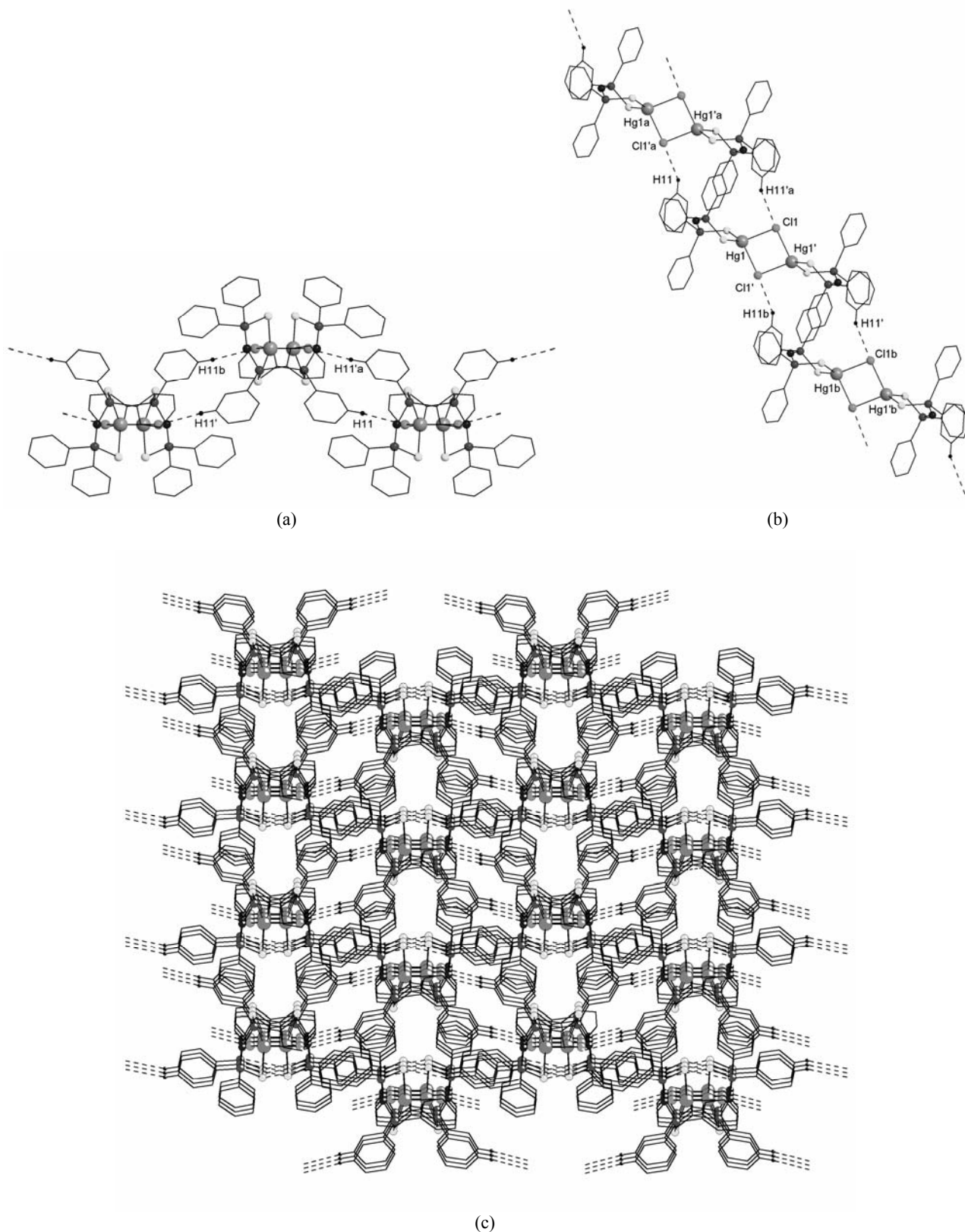


Fig. 3 – View along *a* axis (a) and *b* axis (b) of a ribbon-like polymer based on intermolecular Cl $\cdots$ H interactions between alternating ( $\lambda$ -1) $_2$  and ( $\delta$ -1) $_2$  dimer associations, respectively; (c) view along *a* axis of the 3D architecture based on intermolecular S $\cdots$ H contacts between ribbon-like polymers in the crystal of **1** (only hydrogen atoms involved in C–H $\cdots$ Cl and C–H $\cdots$ S contacts are shown) [symmetry equivalent atoms ( $1-x, y, 0.5-z$ ), ( $-0.5+x, 0.5-y, -0.5+z$ ), ( $0.5-x, 0.5-y, -z$ ), ( $0.5+x, 0.5-y, 0.5+z$ ), ( $1.5-x, 0.5-y, 1-z$ ) and ( $x, 1-y, 0.5+z$ ) are given by “prime”, “a”, “prime a”, “b”, “prime b” and “double prime”, respectively].

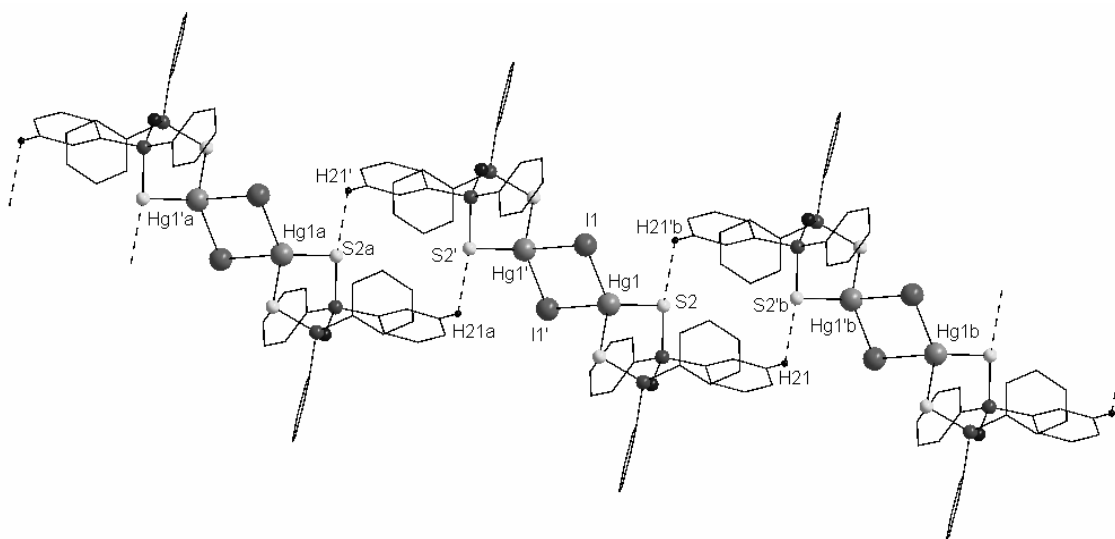


Fig. 4 – View along  $a$  axis of a ribbon-like polymer based on intermolecular sulfur-hydrogen contacts between ( $\lambda$ -**3** /  $\delta$ -**3**) dimer associations, in the crystal of **3** (only hydrogen atoms involved in C–H $\cdots$ S contacts are shown) [symmetry equivalent atoms ( $l-x$ ,  $l-y$ ,  $2-z$ ), ( $x$ ,  $y$ ,  $l+z$ ), ( $l-x$ ,  $l-y$ ,  $3-z$ ), ( $x$ ,  $y$ ,  $-l+z$ ) and ( $l-x$ ,  $l-y$ ,  $l-z$ ) are given by “prime”, “a”, “prime a”, “b” and “prime b”, respectively].

## EXPERIMENTAL

K[(SPPPh<sub>2</sub>)<sub>2</sub>N] was obtained as reported previously.<sup>17</sup> Mercury(II) dihalides, used as starting materials, were commercial products and were used as received. When appropriate, the solvents were dried and freshly distilled under argon prior to use. Elemental analyses were performed on a VarioEL analyser at the Faculty of Pharmacy, “Iuliu Hațieganu” University of Medicine and Pharmacy, Cluj-Napoca (Romania). Melting points were measured on an Electrothermal 9200 apparatus and they are not corrected. The FT-IR spectra were recorded in the range 4000–500 cm<sup>-1</sup> on a JASCO FTIR-610 spectrometer equipped with an ATR attachment with a horizontal ZnSe crystal (JASCO PRO400S). Room-temperature <sup>1</sup>H and <sup>13</sup>C NMR spectra, including 2D experiments, were recorded on a BRUKER AVANCE DRX 400 instrument, while <sup>31</sup>P NMR spectra were recorded at room temperature on a VARIAN GEMINI 300S instrument. The chemical shifts are reported in  $\delta$  units (ppm) relative to TMS (<sup>1</sup>H and <sup>13</sup>C) and H<sub>3</sub>PO<sub>4</sub> 85% (<sup>31</sup>P). The assignment of the <sup>1</sup>H and <sup>13</sup>C resonances was made using 2D NMR experiments (COSY, HSQC, HMBC). The NMR spectra were processed using the *MestReC* and *MestReNova* software.<sup>18</sup>

### Synthesis of (tetraphenyldithioimidodiphosphinato-*S,S'*)(chloro)mercury(II), HgCl[(SPPPh<sub>2</sub>)<sub>2</sub>N-*S,S'*] (**1**)

Stoichiometric amounts of HgCl<sub>2</sub> (0.318 g, 1.17 mmol) and K[(SPPPh<sub>2</sub>)<sub>2</sub>N] (0.570 g, 1.17 mmol) were stirred, in dichloromethane (40 mL), at reflux, for 24 h. The reaction mixture was filtered to remove the resulted KCl and the filtrate was evaporated under reduced pressure to give an oily product. This oily residue was stirred for 10 min. with 20 mL n-hexane, when a white solid deposited. The solid was separated by filtration, washed with n-hexane and dried under vacuum. Recrystallization from CH<sub>2</sub>Cl<sub>2</sub>/n-hexane (1:5, v/v) gave **1** as a white crystalline solid. Yield: 0.58 g (73%). M.p. = 175 °C (lit.<sup>9</sup> -). Anal. Calcd. for C<sub>24</sub>H<sub>20</sub>ClHgNP<sub>2</sub>S<sub>2</sub> (MW 684.54): C, 42.11; H, 2.94; N, 2.05%. Found: C, 41.88; H, 3.07; N, 2.14%. FT-IR (ATR, cm<sup>-1</sup>): 1215s, 1176m [ $\nu_{as}(\text{P}_2\text{N})$ ],

718m, 682vs [ $\nu(\text{PC})$ ], 553s [ $\nu(\text{PS})$ ]. <sup>1</sup>H NMR (400.16 MHz, CDCl<sub>3</sub>, 300 K):  $\delta$  7.43 (8H, m, C<sub>6</sub>H<sub>5</sub>-meta), 7.49 (4H, m, C<sub>6</sub>H<sub>5</sub>-para), 7.90 (8H, ddd, C<sub>6</sub>H<sub>5</sub>-ortho, <sup>3</sup>J<sub>PH</sub> = 13.7, <sup>3</sup>J<sub>HH</sub> 7.2, <sup>4</sup>J<sub>HH</sub> 1.4 Hz). <sup>13</sup>C NMR (100.62 MHz, CDCl<sub>3</sub>, 300 K):  $\delta$  128.77 (m, C<sub>m</sub>, <sup>3</sup>J<sub>PC</sub> = 13.9 Hz), 130.90 (m, C<sub>o</sub>, <sup>2</sup>J<sub>PC</sub> = 12.0 Hz), 131.93 (s, C<sub>p</sub>), 136.90 (dd, C<sub>i</sub>, <sup>1</sup>J<sub>PC</sub> 112.6, <sup>3</sup>J<sub>PC</sub> 3.4 Hz). <sup>31</sup>P NMR (121.48 MHz, CDCl<sub>3</sub>, 300 K):  $\delta$  38.4 (s).

Compounds **2** and **3** were prepared similarly:

**(Tetraphenyldithioimidodiphosphinato-*S,S'*)(bromo)mercury(II), HgBr[(SPPPh<sub>2</sub>)<sub>2</sub>N-*S,S'*] (**2**)**, from HgBr<sub>2</sub> (0.396 g, 1.1 mmol) and K[(SPPPh<sub>2</sub>)<sub>2</sub>N] (0.536 g, 1.1 mmol) in 40 mL dichloromethane. After recrystallization from CH<sub>2</sub>Cl<sub>2</sub>/n-hexane (1:5, v/v) compound **2** was isolated as a white crystalline solid. Yield: 0.39 g (49%). M.p. = 240 °C. Anal. Calcd. for C<sub>24</sub>H<sub>20</sub>BrHgNP<sub>2</sub>S<sub>2</sub> (MW 728.99): C, 39.54; H, 2.77; N, 1.92%. Found: C, 39.23; H, 2.67; N, 2.04%. FT-IR (ATR, cm<sup>-1</sup>): 1215s, 1176m [ $\nu_{as}(\text{P}_2\text{N})$ ], 717m, 685vs [ $\nu(\text{PC})$ ], 553vs [ $\nu(\text{PS})$ ]. <sup>1</sup>H NMR (400.16 MHz, CDCl<sub>3</sub>, 300 K):  $\delta$  7.43 (8H, m, C<sub>6</sub>H<sub>5</sub>-meta), 7.49 (4H, m, C<sub>6</sub>H<sub>5</sub>-para), 7.90 (8H, ddd, C<sub>6</sub>H<sub>5</sub>-ortho, <sup>3</sup>J<sub>PH</sub> = 14.0, <sup>3</sup>J<sub>HH</sub> 7.6, <sup>4</sup>J<sub>HH</sub> 1.4 Hz). <sup>13</sup>C NMR (100.62 MHz, CDCl<sub>3</sub>, 300 K):  $\delta$  128.76 (m, C<sub>m</sub>, <sup>3</sup>J<sub>PC</sub> = 14.0 Hz), 130.90 (m, C<sub>o</sub>, <sup>2</sup>J<sub>PC</sub> = 12.1 Hz), 131.90 (s, C<sub>p</sub>), 136.97 (dd, C<sub>i</sub>, <sup>1</sup>J<sub>PC</sub> 112.4, <sup>3</sup>J<sub>PC</sub> 3.6 Hz). <sup>31</sup>P NMR (121.48 MHz, CDCl<sub>3</sub>, 300 K):  $\delta$  38.3 (s).

**(Tetraphenyldithioimidodiphosphinato-*S,S'*)(iodo)mercury(II), HgI[(SPPPh<sub>2</sub>)<sub>2</sub>N-*S,S'*] (**3**)**, from HgI<sub>2</sub> (0.495 g, 1.1 mmol) and K[(SPPPh<sub>2</sub>)<sub>2</sub>N] (0.536 g, 1.1 mmol), in 40 mL dichloromethane. Recrystallization from CH<sub>2</sub>Cl<sub>2</sub>/n-hexane (1:5, v/v) gave **3** as a yellowish crystalline solid. Yield: 0.49 g (58%). M.p. = 252 °C. Anal. Calcd. for C<sub>24</sub>H<sub>20</sub>IHgNP<sub>2</sub>S<sub>2</sub> (MW 775.99): C, 37.15; H, 2.60; N, 1.81%. Found: C, 36.92; H, 2.47; N, 1.74%. FT-IR (ATR, cm<sup>-1</sup>): 1211s, 1174m [ $\nu_{as}(\text{P}_2\text{N})$ ], 717m, 686vs [ $\nu(\text{PC})$ ], 557vs [ $\nu(\text{PS})$ ]. <sup>1</sup>H NMR (400.16 MHz, CDCl<sub>3</sub>, 300 K):  $\delta$  7.45 (12H, m, C<sub>6</sub>H<sub>5</sub>-meta+para), 7.91 (8H, dd, C<sub>6</sub>H<sub>5</sub>-ortho, <sup>3</sup>J<sub>PH</sub> = 13.6, <sup>3</sup>J<sub>HH</sub> 7.2 Hz). <sup>13</sup>C NMR (100.62 MHz, CDCl<sub>3</sub>, 300 K):  $\delta$  128.68 (m, C<sub>m</sub>, <sup>3</sup>J<sub>PC</sub> = 13.9 Hz), 130.93 (m, C<sub>o</sub>, <sup>2</sup>J<sub>PC</sub> = 12.1 Hz), 131.72 (s, C<sub>p</sub>), 137.39 (dd, C<sub>i</sub>, <sup>1</sup>J<sub>PC</sub> 111.9, <sup>3</sup>J<sub>PC</sub> 3.9 Hz). <sup>31</sup>P NMR (121.48 MHz, CDCl<sub>3</sub>, 300 K):  $\delta$  38.4 (s).

Table 2  
Crystallographic data for HgX[(SPPPh<sub>2</sub>)<sub>2</sub>N] [X = Cl (**1**), Br (**2**), I (**3**)]

	<b>1</b>	<b>2</b>	<b>3</b>
Empirical formula	C <sub>48</sub> H <sub>40</sub> Cl <sub>2</sub> Hg <sub>2</sub> N <sub>2</sub> P <sub>4</sub> S <sub>4</sub>	C <sub>48</sub> H <sub>40</sub> Br <sub>2</sub> Hg <sub>2</sub> N <sub>2</sub> P <sub>4</sub> S <sub>4</sub>	C <sub>48</sub> H <sub>40</sub> Hg <sub>2</sub> I <sub>2</sub> N <sub>2</sub> P <sub>4</sub> S <sub>4</sub>
<i>M</i>	1369.02	1457.94	1551.92
Crystal system	Monoclinic	Monoclinic	Triclinic
Space group	<i>C2/c</i>	<i>C2/c</i>	<i>P-1</i>
Temperature (K)	297(2)	297(2)	297(2)
<i>a</i> /Å	16.1370(13)	16.1110(14)	10.4340(8)
<i>b</i> /Å	16.5418(13)	16.7497(15)	10.6944(8)
<i>c</i> /Å	18.7731(15)	18.9202(17)	12.7762(10)
$\alpha^\circ$	90	90	81.613(1)
$\beta^\circ$	98.371(1)	98.357(2)	88.655(1)
$\gamma^\circ$	90	90	65.147(1)
<i>V</i> /Å <sup>3</sup>	4957.8(7)	5051.5(8)	1278.64(17)
<i>Z</i>	4	4	1
<i>D</i> <sub>calc</sub> /gcm <sup>-3</sup>	1.834	1.917	2.016
<i>F</i> (000)	2640	2784	732
$\mu$ (Mo-K $\alpha$ )/mm <sup>-1</sup>	6.627	7.981	7.527
Crystal size (mm <sup>3</sup> )	0.33 x 0.29 x 0.28	0.32 x 0.26 x 0.19	0.21 x 0.19 x 0.12
$\theta$ range for data collection (°)	1.77 to 25.00	1.76 to 25.00	1.61 to 25.00
Reflections collected	12859	17988	12387
Independent reflections	4369 [ <i>R</i> <sub>int</sub> = 0.0303]	4453 [ <i>R</i> <sub>int</sub> = 0.0502]	4504 [ <i>R</i> <sub>int</sub> = 0.0326]
Absorption correction	Multi-Scan <sup>21</sup>	Multi-Scan <sup>21</sup>	Multi-Scan <sup>21</sup>
Data / restraints / parameters	4369 / 222 / 336	4453 / 216 / 258	4504 / 0 / 280
Goodness-of-fit on <i>F</i> <sup>2</sup>	1.056	1.193	1.197
Final <i>R</i> indices [ <i>I</i> > 2 $\sigma$ ( <i>I</i> )]	<i>R</i> <sub>1</sub> = 0.0321 <i>wR</i> <sub>2</sub> = 0.0666	<i>R</i> <sub>1</sub> = 0.0598 <i>wR</i> <sub>2</sub> = 0.1149	<i>R</i> <sub>1</sub> = 0.0451 <i>wR</i> <sub>2</sub> = 0.0877
<i>R</i> indices (all data)	<i>R</i> <sub>1</sub> = 0.0455 <i>wR</i> <sub>2</sub> = 0.0702	<i>R</i> <sub>1</sub> = 0.0739 <i>wR</i> <sub>2</sub> = 0.1203	<i>R</i> <sub>1</sub> = 0.0499 <i>wR</i> <sub>2</sub> = 0.0895
Largest difference peak and hole (e Å <sup>-3</sup> )	0.670 and -0.608	1.028 and -0.956	1.380 and -1.353

### Crystal structure determination

Crystals of compounds **1**, **2** and **3** were grown from a mixture of CH<sub>2</sub>Cl<sub>2</sub>/n-hexane (1/5, v/v). Block crystals of **1** (white), **2** (white) and **3** (yellow) were mounted on cryoloops. Data collection and processing was carried on a Bruker SMART APEX system (Babes-Bolyai University, Cluj-Napoca), using graphite-monochromated Mo-K $\alpha$  radiation ( $\lambda = 0.71073$  Å). Cell constants are given in Table 2, along with details of the crystal structure determination and refinement.

The structures were refined with anisotropic thermal parameters. The hydrogen atoms were refined with a riding model and a mutual isotropic thermal parameter. For structure refinement the software package SHELX-2014 was used.<sup>19</sup> Two phenyl groups of **2** and **3** were found disordered over two positions and were refined using free variables. In **2** the ratio between site occupancies of the two components were 0.37 : 0.63 and 0.80 : 0.20, whereas in **3** the values found were 0.72 : 0.28 and 0.57 : 0.43. In the refinement of **2** and **3**, the *U*<sub>ij</sub> components of the carbon atoms of the disordered rings C1 > C6, C1B > C6B, C13B > C18B and C7 > C12, C19 > C24, C19B > C24B, respectively, were restrained *via* SIMU. The anisotropic displacement parameters were constrained *via* EADP for the carbon atoms of group C13B > C18B in **2**, and for the carbon atoms of groups C7B > C12B, C19 > C24 and C19B > C24B in **3**. The drawings were created with the Diamond program.<sup>20</sup>

### CONCLUSIONS

Three new mercury(II) derivatives, HgX[(SPPPh<sub>2</sub>)<sub>2</sub>N-S,S'] (X = Cl, Br, I), are reported.

These compounds might be useful starting materials for the synthesis of further mixed-ligand mercury(II) species by substitution of the halogen atom. Dimerization of all three compounds occurs through halogen bridges between metal atoms. However, different supramolecular architectures based on C-H...halogen and C-H...S interactions were observed in the crystal of these mixed-ligand mercury(II) compounds, depending on the nature of the halogen atom.

### Supplementary material

Electronic Supplementary Information (ESI) available from the corresponding author: figures representing ORTEP representation of compounds **1** and **2**, the optical isomers as well as the supramolecular architectures in the crystals of compounds **1–3**. Crystallographic data for the structural analyses have been deposited with the Cambridge Crystallographic Data Centre, CCDC Nos. 215785, 299492 and 299491 for **1**, **2** and **3**, respectively. Copies of the information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).



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