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Solvent dependent crystallization of a few Hg(II) thiocarboxylates

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ABSTRACT

During the process of crystallization of newly synthesized heterobimetallic complexes $[(Ph_3P)_2Cu(\mu\text{-}SCOR)_2Hg(SCOR)]$ [R = Ph (**1**), th (thiophene) (**2**)] Hg(II) thiocarboxylate complexes were isolated. In chloroform/diethyl ether a phosphine migration led to the formation of $Hg(Ph_3P)(SCOPh)_2$ (**3**) and $Hg(Ph_3P)(SCOth)_2$ (**4**) while in chloroform/*n*-hexane the binary Hg(II) complexes, $Hg(SCOPh)_2$ (**5**) and $Hg(SCOth)_2$ (**6**) were isolated. In another reaction a heterobimetallic complex, $Hg(SCOPh)_2TiCl_4$ (**7**) was obtained as the end product. Molecular structures of **3**, 4 and **6** were studied by single crystal X-ray diffraction. The crystals of **4** provided an interesting example of polytopal isomerism. Structures and electronic transitions have been explained on the basis of DFT calculations.

1. Introduction

Ligands containing both O and S donor sites exhibit interesting coordination properties. Earlier studies on complexes of monothiocarbamates [1] revealed the bonding features of the ligands which can be explained on the bases of Pearson's acid base theory [2]. Though a bidentate bonding mode of a thiocarboxylate is less favorable [3], yet thiocarboxylate ligands have been found to exhibit rich coordination chemistry. Anionic thiocarboxylate complexes [4] have been exploited as metalloligands and a good number of bimetallic complexes have been prepared during recent years which have also been used as precursors for ternary chalcogenides [5].

A few thiocarboxylate complexes of group 12 metals have been prepared and structurally characterized by Vittal et al. [6–8]. Besides the neutral binary compounds $[M(SCOR)_2]$ {M = Zn, Cd, Hg} [9] these metals form mono- and dianionic complexes $[M(SCOR)_n]^{m-}$ {$n = 3$; $m = 1$ and $n = 4$; $m = 2$} [6–8] also. In addition Hg(II) has been reported to form unusual anionic complexes, $[MCl_4Hg(SCOPh)_2]^{2-}$ {M = Cd(II)/Hg(II)} [10]. Very recently, we have reported synthesis and structures of Pb/Cu and Pb/Ag heterobimetallic complexes of thiobenzoate ligands which could be used to prepare ternary oxides [11]. In view of these we have now taken up the synthesis and characterization of thiocarboxylate complexes containing Zn/Cu, Zn/Ag [12], Cd/Cu, Cd/Ag [13] and Hg/Cu. Here, we report the results of our studies on the Hg(II) complexes.

2. Experimental

2.1. Reagents and general procedures

All the solvents were dried according to standard procedures and distilled before use. *Bis*(triphenylphosphine)copper(I) nitrate [14] and thiophene-2-thiocarboxylic acid was synthesised by a method we have reported recently [15]. Sodium salt of thiophene-2-thiocarboxylic acid was obtained by reacting the acid with sodium methoxide in stoichiometric ratio. Thiobenzoic acid, triphenylphosphine and mercuric nitrate were purchased from Sigma–Aldrich and used as received.

2.2. Instrumentation

IR Spectra was recorded using Varian-3100 FTIR instruments. NMR spectra were obtained using a JEOL AL300 FT NMR spectrometer. Electronic absorption spectra were recorded using a Shimadzu UV-1700 PharmaSpec Spectrometer. The electronic absorption spectra of the **1**–**4** were recorded in chloroform solutions while of **5** and **6** were recorded in DMSO solutions. Since **1** and **2** dissociate in solution we refrain from analyzing the solution spectral data of these two. Solid state absorption spectra of **1**–**4** and **6** were also recorded. Elemental analyses were performed by the EAT Exeter Analytical Inc. CE-440, elemental analyzer.

Single crystal X-ray data of all complexes were collected on a Xcalibur Eos, Oxford diffractometer using graphite monochromated Mo Kα radiation ($\lambda = 0.7107$ Å). Data collections were carried out at room temperature (293 K) using hemisphere mode. Structures were solved by the direct method and then refined on F^2 by

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Table 1
Crystal data and structure refinement of **3**, **4** and **6**.

	3	**4**	**6**
Empirical formula	$C_{64}H_{50}O_4S_4P_2Hg_2$	$C_{84}H_{63}O_6S_{12}P_3Hg_3$	$C_{10}H_6O_2S_4Hg$
T (K)	293	293	293
Crystal system	Monoclinic	triclinic	triclinic
Space group	$P2_1/n$	$P\bar{1}$	$P\bar{1}$
a (Å)	12.732(5)	12.7085(8)	6.6482(6)
b (Å)	17.069(5)	14.0629(9)	14.1942(11)
c (Å)	13.512(5)	15.3760(11)	14.7473(9)
α (°)	90	85.449(6)	73.609(6)
β (°)	109.324(5)	82.363(6)	79.430(6)
γ (°)	90	78.704(5)	86.273(7)
V (Å^3)	2771.0(17)	2666.8(3)	1312.30(18)
Z	2	1	4
μ(Mo Kα) (mm^{-1})	5.792	6.170	12.348
Final R indices [$I > 2\sigma(I)$]	0.0295	0.0727	0.0952
R indices (all data)	0.0428	0.0913	0.1431
Goodness-of-fit (GOF) on F^2	0.982	1.089	1.000

the full matrix least square technique with SHELX-97 set of software [16] using the WINGX program package. [17] Crystal data of complexes **3**, **4** and **6** are given in Table 1.

2.3. Theoretical calculations

The atomic coordinates were obtained from X-ray crystallographic results for TDDFT calculations [18] and NBO calculation. The calculations were performed at B3LYP level using 6-31G** basis set for C, H, O, P and S atoms while the CEP-121G basis set was used for Hg. All the calculations were carried out using GAUSSIAN 03 program package [19].

2.4. Syntheses

2.4.1. Synthesis of $[(Ph_3P)_2Cu(\mu\text{-}SCOPh)_2Hg(SCOPh)]$ **1**

To a solution of sodium thiobenzoate (0.414 g, 3.0 mmol) (generated *in situ* by a reaction of thiobenzoic acid and sodium metal in methanol) in 10.0 ml of methanol was added a solution of $Hg(NO_3)_2\cdot H_2O$ (0.342 g, 1.0 mmol) in methanol (5.0 ml) drop wise with stirring in an ice bath. The reaction mixture was stirred for 15–20 min. then added a solution of $(PPh_3)_2CuNO_3$ (0.650 g, 1.0 mmol) in 5.0 ml of dichloromethane. Then reaction mixture was stirred for an hour and dried under reduced pressure. The light yellow colored residue was dissolved in chloroform and filtered off the insoluble $NaNO_3$ formed. Solvent from filtrate was evaporated under reduced pressure and then dried under vacuum. Yield: 1.092 g (91%). *Anal.* Calc. for $C_{57}H_{45}O_3S_3P_2HgCu$: C, 57.04; H, 3.78. Found: C, 57.45; H, 3.77%. IR spectra (KBr, cm^{-1}): 1625, 1575 ν(CO), 1201 ν(Ph–C), 905 ν(C–S). NMR ($CDCl_3$, δ ppm): ^{1}H NMR 7.12–7.92 (Ph). ^{13}C NMR 128.46–137.93 (Ph), 197.28 (COS). ^{31}P NMR 1.82.

2.4.2. Synthesis of $[(Ph_3P)_2Cu(\mu\text{-}SCOth)_2Hg(SCOth)]$ **2**

A procedure similar to that described for the synthesis of **1** was followed using sodium thiophene-2-thiocarboxylate (0.498 g, 3.0 mmol) in place of sodium thiobenzoate. Yield: 0.523 g (70%). *Anal.* Calc. for $C_{51}H_{39}O_3S_6P_2Hg$: C, 50.28; H, 3.23. Found: C, 50.43; H, 3.20%. IR spectra (KBr, cm^{-1}): 1590, 1560 ν(CO), 1194 ν(th–C), 890 ν(C–S). NMR ($CDCl_3$, δ ppm): ^{1}H NMR 7.02–7.74 (Ph and th). ^{13}C NMR 127.58–145.56 (Ph and th), 190.61 (COS). ^{31}P NMR 3.43.

2.4.3. Attempt to crystallize **1**: synthesis of $Hg(PPh_3)(SCOPh)_2$ **3**

The complex **1** (1.198 g, 1.0 mmol) was dissolved in chloroform, layered with diethyl ether and kept for crystallization. Single crystals of **3** were obtained after two days. Yield: 0.508 g (69%). *Anal.* Calc. for $C_{64}H_{50}O_4S_4P_2Hg_2$: C, 52.13; H, 3.42. Found: C, 52.09; H, 3.40%. IR spectra (KBr, cm^{-1}): 1613, 1572 ν(CO), 1197 ν(Ph–C), 906 ν(C–S). NMR ($CDCl_3$, δ ppm): ^{1}H NMR 7.11–7.91 (Ph). ^{13}C NMR 128.19–138.83 (Ph), 198.39 (COS). ^{31}P NMR 4.45, 11.94.

2.4.4. Attempt to crystallize **2**: synthesis of $Hg(PPh_3)(SCOth)_2$ **4**

The complex **2** (1.217 g, 1.0 mmol) was dissolved in chloroform, layered with diethyl ether and kept for crystallization. Single crystals of **4** were obtained on the next day. Yield: 0.539 g (72%). *Anal.* Calc. for $C_{84}H_{63}O_6S_{12}P_3Hg_3$: C, 44.88; H, 2.82. Found: C, 44.45; H, 2.81%. IR spectra (KBr, cm^{-1}): 1606, 1570 ν(CO), 1198 ν(th–C), 893 ν(C–S). NMR ($CDCl_3$, δ ppm): ^{1}H NMR 7.00–7.74 (Ph and th). ^{13}C NMR 127.59–145.42 (Ph and th), 190.43 (COS). ^{31}P NMR 2.62, 24.00.

2.4.5. Attempt to crystallize **1**: synthesis of $Hg(SCOPh)_2$ **5**

The complex **1** was dissolved in chloroform, layered with *n*-hexane and kept for crystallization. Crystals of **5** settled down within 30 min. Yield: 0.421 g (89%). *Anal.* Calc. for $C_{10}H_6O_2S_4Hg$: C, 24.66; H, 1.24. Found: C, 24.62; H, 1.23%. IR spectra (KBr, cm^{-1}): 1624 ν(CO), 1201 ν(th–C), 1047 ν(C–S). NMR (DMSO, δ ppm): ^{1}H NMR 7.41, 7.81 and 7.92 (th). ^{13}C NMR 128.59, 133.38, 134.36 and 143.85 (th), 187.34 (COS).

2.4.6. Attempt to crystallize **2**: synthesis of $Hg(SCOth)_2$ **6**

The complex **2** was dissolved in chloroform, layered with *n*-hexane and kept for crystallization. Well formed single crystals of **6** were obtained within 1 h. Yield: 0.418 g (86%). *Anal.* Calc. for $C_{14}H_{10}O_2S_2Hg$: C, 35.40; H, 2.12. Found: C, 35.37; H, 2.12%. IR spectra (KBr, cm^{-1}): 1624 ν(CO), 1201 ν(Ph–C), 906 ν(C–S). NMR (DMSO, δ ppm): ^{1}H NMR 7.48–7.98 (Ph). ^{13}C NMR 128.13–138.52 (Ph), 196.03 (COS).

2.4.7. Synthesis of $[TiCl_4.Hg(SCOPh)_2]$ **7**

To a stirred solution of NaSCOPh prepared *in situ* by reacting thiobenzoic acid (0.414 g, 3.0 mmol) and sodium metal (0.069 g, 3.0 mmol) in MeOH (15 mL) was added a methanolic solution (5 mL) of $HgCl_2$ (0.271 g, 1.0 mmol) to get a yellow colored solution of $Na[Hg(SCOPh)_3]$. A solution of $TiCl_4$ (0.047 g, 0.25 mmol) in methanol (10 mL) was then added to the reaction mixture with vigorous stirring at 10 °C. Stirring was continued for 1 h maintaining the temperature below 10 °C. The solvent was then evaporated under reduced pressure and the residue was extracted with $CHCl_3$ (20 mL). The insoluble particles were filtered off and solvent from the filtrate was evaporated under reduced pressure. The product was apparently a mixture of two compounds. Washed the mixture with ethanol and diethyl ether to remove the colorless product. The red colored crystalline compound was dried under vacuum for 1 h. Yield (based on $TiCl_4$): 0.158 g (95%). M^+/e, 663. *Anal.* Calc. for $C_{14}H_{10}O_2S_2Hg_1Ti_1Cl_4$: C, 25.31; H, 1.52. Found: C, 24.80; H, 1.65%. IR spectra (KBr, cm^{-1}): 1625 ν(CO), 1215 ν(Ph–C), 908 ν (C–S). ^{1}H NMR ($CDCl_3$, δ ppm): 7.3–7.8 (Ph). ^{13}C NMR; 126–137 (Ph), 197.3 (COS).

3. Results and discussion

3.1. Syntheses and characterization

The anionic complexes, $[Hg(SCOR)_3]^-$ were generated *in situ* by reacting sodium salt of the thiocarboxylate with mercuric nitrate in methanol. Reaction of the anion with *bis*(triphenylphosphine)copper(I) was carried out to isolate the heterobimetallic complexes, $[(Ph_3P)_2Cu(\mu\text{-}SCOR)_2Hg(SCOR)]$ [R = Ph (**1**), th (**2**)]. In the IR spectra of the compounds two CO stretching bands are clearly observable in both the cases of **1** and **2**. The peak at higher frequency indicates a monodentate (through S) bonding mode while the other band is indicative of a bidentate bonding mode of the thiocarboxylate ligand. In absence of crystal structures it is not possible to comment on the geometries of the molecules of **1** and **2**. However, in view of the structures of analogous bimetallic complexes such as $[(Ph_3P)_2Cu(\mu\text{-}SCOPh)_2Pb(SCOPh)]$ [11], $[(Ph_3P)_2Cu(\mu\text{-}SCOPh)_2Cd(SCOPh)]$ and $[(Ph_3P)_2Cu(\mu\text{-}SCOth)_2Cd(SCOth)]$ [13] one may tentatively propose a similar structure for **1** and **2** in which Cu atom is bonded to the sulfur atoms of the bridging thiocarboxylate groups. In contrast to the analogous highly stable complexes of Cu/Zn and Cu/Cd, **1** and **2** dissociated in solution giving a variety (depending on the solvents) of Hg(II) thiocarboxylates (see Scheme 1). In chloroform/diethyl ether a triphenylphosphine migrated from Cu(I) to Hg(II) center and the products obtained were $Hg(Ph_3P)(SCOR)_2$ [R = Ph (**3**) and th (**4**)] while in chloroform/*n*-hexane **1** and **2** dissociated completely into $Hg(SCOR)_2$ [R = Ph (**5**), th (**6**)] and $Cu(PPh_3)_2(SCOR)$.

Though quite a few triphenylphosphine complexes of Hg(II) have been synthesized [20] yet this is the first example containing a thiocarboxylate ligand. Triphenylphosphine migration has been known from one metal to another in some cases and we have recently studied one such example where the ligand migrates from Cu(I) to Zn(II) [12], however, to the best of our knowledge no report on phosphine migration to a Hg(II) center is available. Phosphine migration can be understood in view of the fact that metal triphenylphosphine complexes are in general, known to dissociate in solution. As a result various species exist in dynamic equilibrium [21]. ^{31}P NMR spectra of **3** and **4** showed two peaks at room temperature indicating the existence of two different phosphine containing species in solution. The spectra of other compounds showed one peak which is possibly due to fast scrambling process at room temperature [21].

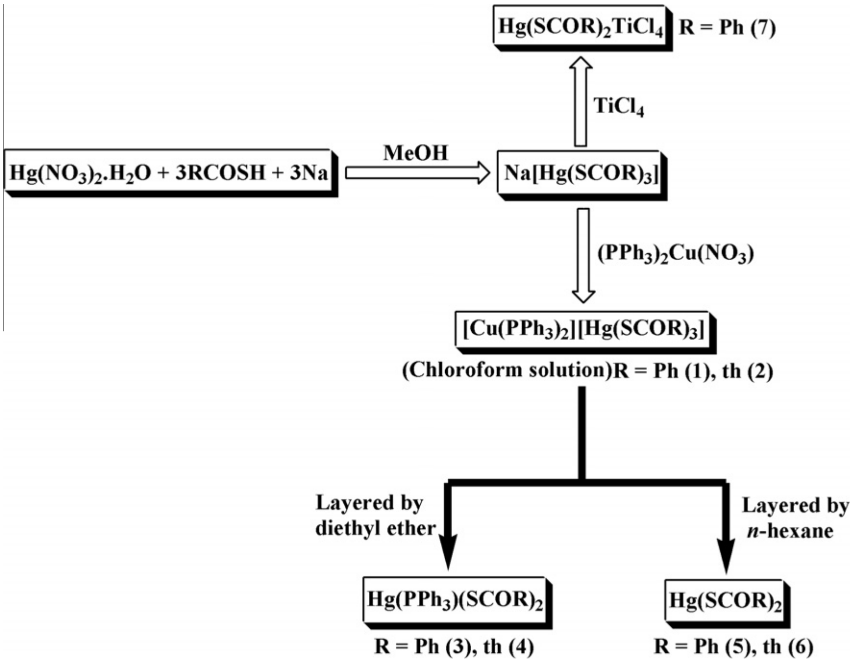
Notably, a direct reaction of mercuric salt with sodium thiobenzoate in presence of triphenylphosphine, however, did not yield **3**, instead an insoluble product was isolated which is possibly a mixture and could not be characterized. Although binary Hg(II) thiocarboxylates can be prepared by a direct reaction of the ligand's sodium salt and Hg^{2+} in aqueous medium, yet it is rather difficult to crystallize the product owing to its insolubility in suitable solvents. Notably, **5** and **6** were obtained as single crystals from chloroform/*n*-hexane solutions of **1** and **2** respectively. The crystals once formed were, however, insoluble in chloroform. Since the Cu/Hg complexes dissociate in solution we thought it worthwhile to prepare a heterobimetallic complex in which an early transition metal in higher oxidation state (hard metal) is present along with Hg(II). One may expect the oxygen atom to bind with the hard metal ion leaving the sulfur atom available for Hg(II). Interestingly, when the anionic complex $[Hg(SCOPh)_3]^-$ was treated with $TiCl_4$ a complex, $HgTiCl_4(SCOPh)_2$ was isolated (see Scheme 1).

Electronic absorption bands of **3** were observed at 298 and 261 nm where as in solid state observed at 327, 300, 265, and 231 nm. Electronic absorption bands of **6** were observed at 318 and 276 nm whereas in solid state it showed at 315, 299, 283 and 247 nm. These peaks may be assigned as intra/interligand and ligand to metal charge transfer transitions (in a dithiocarbamate complex the LMCT transitions have been reported at 253 and 259 nm [22]) Absorption bands of the compounds are given in supplementary file (Figs. S1–S6).

For unambiguous assignment of the spectral bands TDDFT calculations have been carried out. Orbitals involved in selected transitions in the cases of **3** and **6** are shown in Figs. 1 and 2, respectively. From TDDFT its clear that lower energy band in case of **3** due to mixed transitions of ligand to metal and interligand charge transfer transition where as higher energy bands are due to inter/intraligand charge transfer transitions. But in case of **6** all the absorption bands are due to inter and intraligand charge transfer transitions.

3.2. Crystal and molecular structures

Complex **3** crystallized in monoclinic system with $P2_1/n$ space group. The asymmetric unit consists of a Hg(II) center coordinated by two sulfur atoms of thiobenzoate ligands and a phosphorous of triphenylphosphine. In the lattice the molecules are packed in such



Scheme 1. Synthesis of complexes.

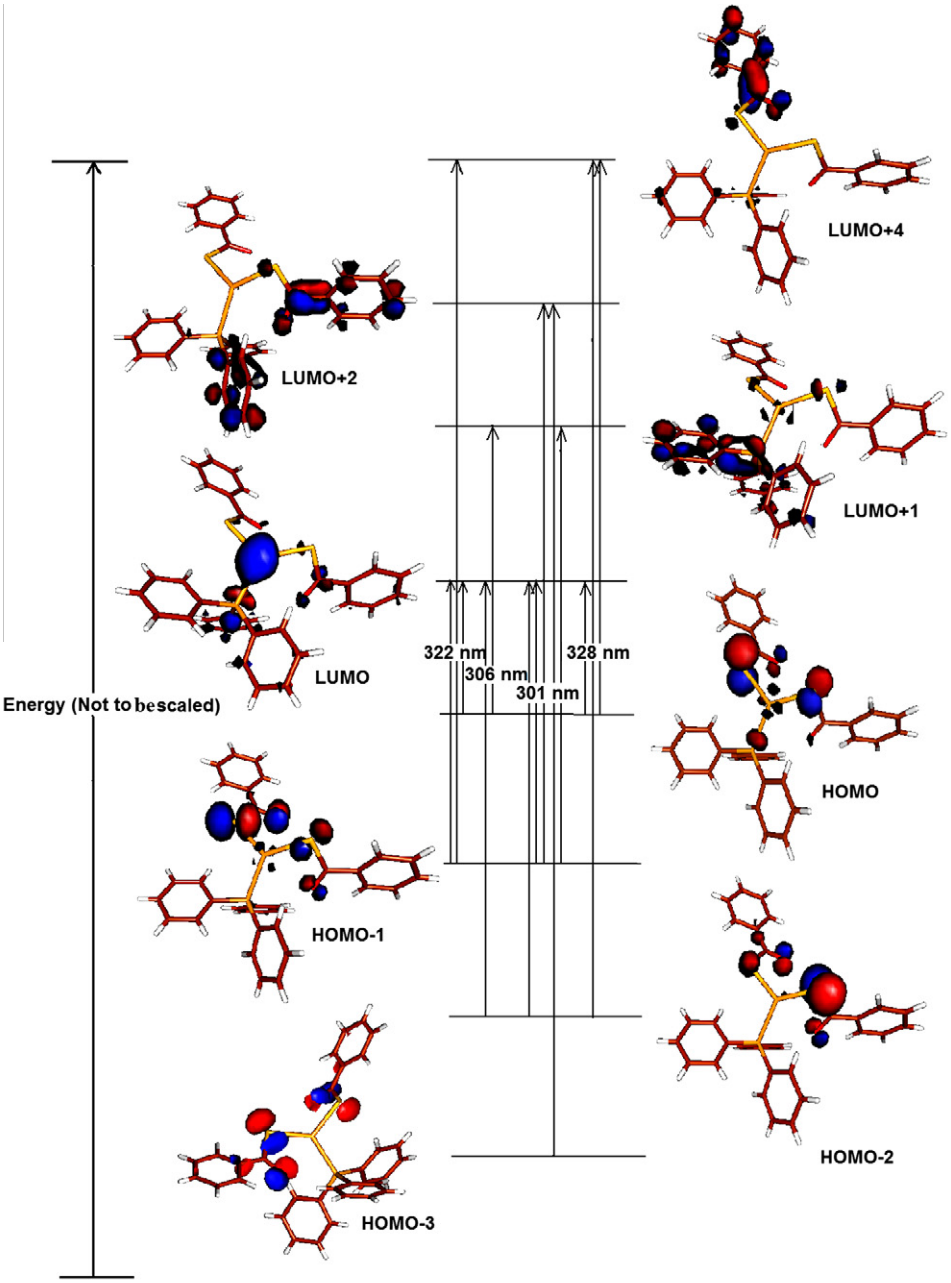


Fig. 1. Selected molecular orbitals for **3** (orbital contour value 0.05).

a way that two molecules join with each other by a pair of μ-S bridges as shown in Fig. 3. A closer look into the structure, however, reveals that the Hg–S and Hg···S distances are unequal and one of them is too long (3.130 Å) to be considered as a covalent bond. This is, however, shorter than the sum of the van der Waals' radii of S and Hg atoms (3.35 Å) and is indicative of a weak interaction. To understand the nature of the Hg–S interaction we have carried out DFT calculations. From the natural bond orbital (NBO) analysis it became clear that there is no primary bonding between the Hg–S atoms (with longer internuclear distance), however, second order perturbation effect due to Lp(s) → σ^*(Hg) electron transfer plays an important role and leads to a stabilization of 21.4 kcal/mol.

The thermal ellipsoid plot of a single molecule is depicted in Fig. 4 and selected bond length and bond angles are given in Table 2.

Mercury is bonded to two sulfur atoms of thiobenzoate and one phosphorus atom of triphenylphosphine ligand. The two Hg–S bond lengths are almost equal and are comparable to those observed in the anionic mercury thiocarboxylates (2.402–2.533 Å) and marginally longer than the sum of the covalent radii of S and Hg atoms (2.37 Å). The oxygen atoms are quite away from the Hg1 and the HgO distances (3.053 and 3.102 Å) are equal to the sum of the van der Waals radii of the two atoms.

The three donor atoms subtend 359.70° at Hg1 thus resulting in a trigonal planar coordination environment. Trigonal planar coordination of Hg(II) have been reported in anionic thiolate [23], phenolate [24] and thiocarboxylate complexes [5–7,25] and the deviation from planarity is usually less than 0.07 Å. In the case of **3** also Hg1 is tipped above the S1S2P1 plane by 0.065 Å.

Complex **4** crystallized in $P\bar{1}$ space group with triclinic system. The arrangement of two different structures in the same lattice

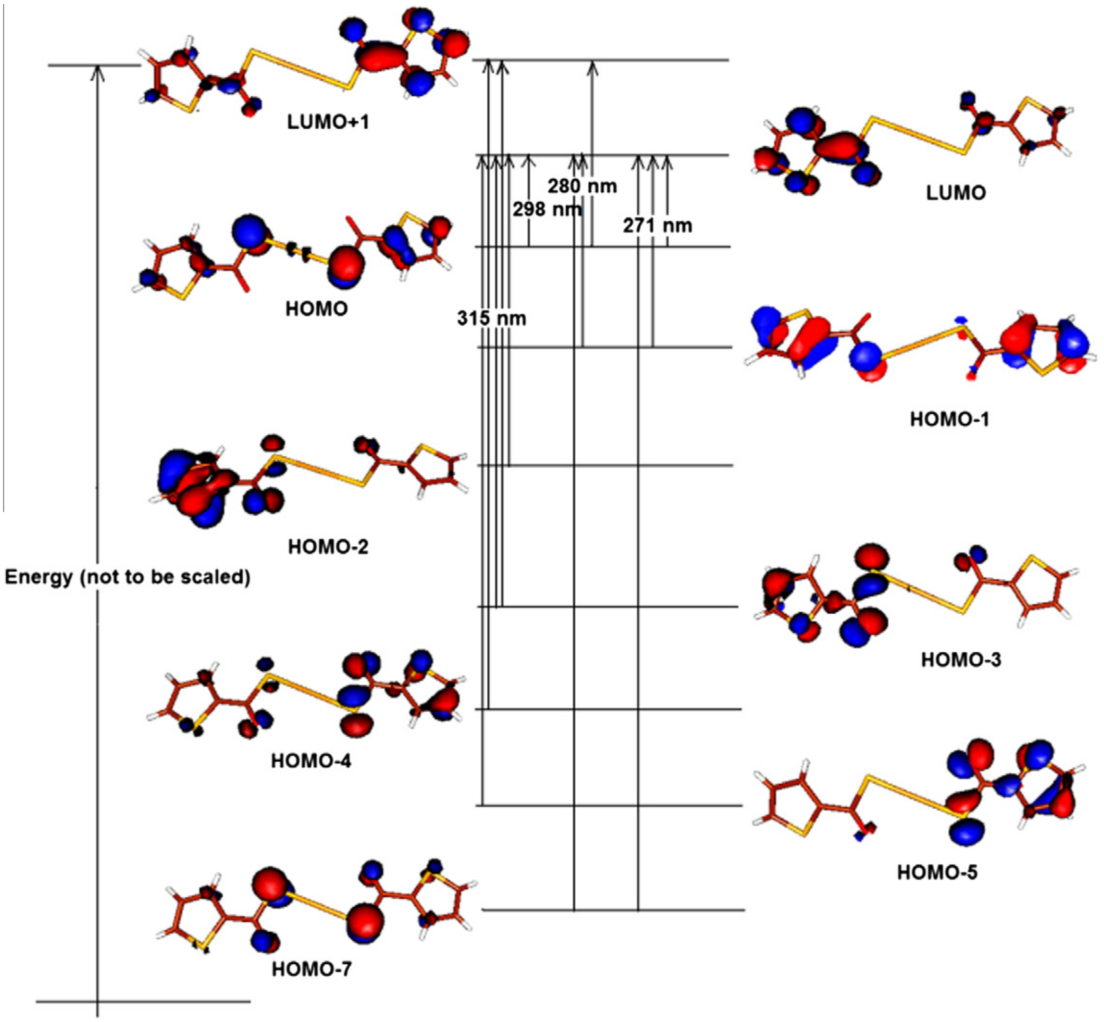


Fig. 2. Selected molecular orbitals for **6** (orbital contour value = 0.05).

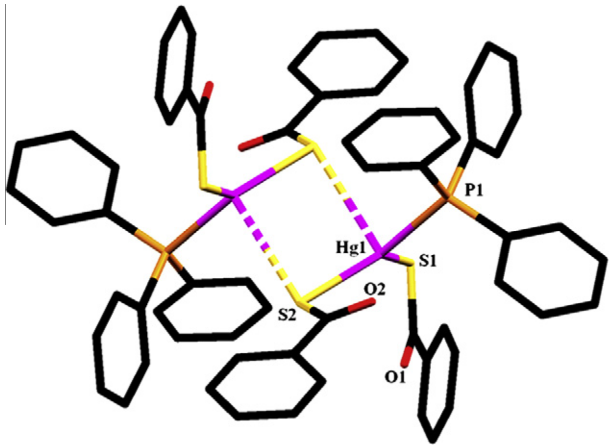


Fig. 3. A pair of molecules of **3** showing centrosymmetric $P_2S_4Hg_2$ core.

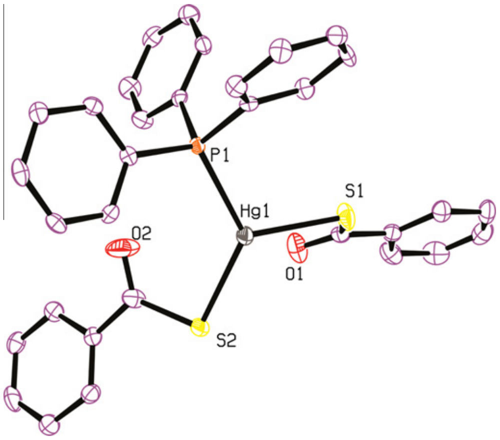


Fig. 4. Molecular structure of **3** at 50% probability level (hydrogen atoms are omitted for clarity).

offers an interesting example of polytopal isomerism. Molecular structures are depicted in Fig. 5. Selected bond lengths and bond angles are given in Table 2. Two types of isomers crystallized together in the same unit cell. Two discrete molecules are present in the asymmetric unit. In one case the molecule is mononuclear and Hg1 is bonded to one triphenylphosphine and two thiophene-2-thiocarboxylates through their sulfur atoms. Though a weak interaction between Hg1 and O2 is evinced by the distance between the two (2.875 Å) yet the sum of angles subtended by P, S1 and S3 is 359.33° which render a trigonal planar geometry around the metal center. Though two molecules are arranged in

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

Complex				
Selected bond lengths (Å)				
3	$Hg_1–S_1$	2.461(1)	$Hg_1–S_2$	2.464(1)
	$Hg_1–P_1$	2.501(1)		
4	$Hg_1–S_1$	2.427(3)	$Hg_1–S_3$	2.567(3)
	$Hg_1–O_2$	2.875	$Hg_1–P_1$	2.431(3)
	$Hg_2–S_5$	2.445(3)	$Hg_2–S_7$	2.541(3)
	$Hg_2–P_2$	2.435(3)	$Hg_2–S–_7$	3.073
6	$Hg_1–S_1$	2.353(4)	$Hg_1–S_3$	2.357(4)
	$Hg_1–O_1$	2.994	$Hg_1–O_2$	3.002
Selected bond angles (°)				
3	$S_1–Hg_1–S_2$	121.50(4)	$S_1–Hg_1–P_1$	110.29(4)
	$S_2–Hg_1–P_1$	128.00(4)		
4	$S_1–Hg_1–S_3$	97.51(11)	$S_1–Hg_1–P_1$	138.75(11)
	$S_3–Hg_1–P_1$	123.07(11)	$O_1–Hg_1–S_1$	57.07
	$O_1–Hg_1–S_3$	91.80	$O_1–Hg_1–P_1$	103.57
	$S_5–Hg_2–S_7$	97.78(10)	$S_5–Hg_2–P_2$	134.33(10)
	$S_7–Hg_2–P_2$	125.86(10)	$Hg_2–S_7–Hg_2$	100.74
6	$S_1–Hg_1–S_3$	178.89(16)		

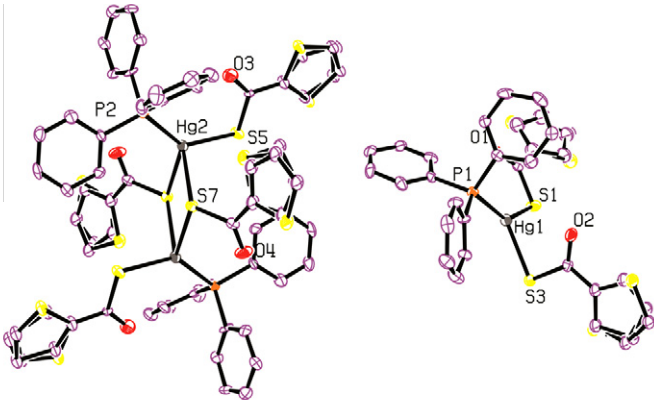


Fig. 5. Molecular structure of **4** at 50% probability level (hydrogen atoms are omitted for clarity).

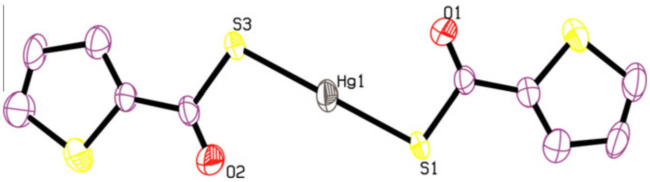


Fig. 6. Molecular structure of **6** at 50% probability level (hydrogen atoms are omitted for clarity).

the lattice giving a dimeric look, yet the intermolecular Hg···S distances (3.259 Å) are quite long and are comparable to the sum of the van der Waals radii of the two atoms (3.35 Å). The other molecule is a centro-symmetric dimer; a mercury atom (Hg2) is bonded with one triphenylphosphine and two thiophene-2-thiocarboxylates out of which one is terminal and other forms a bridge with the second mercury atom via a weak interaction (Hg···S = 3.073 Å). The molecular core is isostructural to that of **3**.

Though $Hg(SCOPh)_2$ is known for a long time [6], to the best of our knowledge no neutral binary mercury thiocarboxylate has yet been structurally characterized. Crystals of both **5** and **6** could be isolated from the solution of **1**, and **2**, respectively, however, those of **6** were suitable for X-ray crystallography. Molecular structure of **6** is shown in Fig. 6 and selected bond lengths and bond angles are given in Table 2. There are two molecules in the asymmetric unit. There is no significant intermolecular interaction between the two molecules and the internuclear distance between two Hg atoms of the two molecules is 4.426 Å. Both have similar structures except for the fact that the interplanar planar angles between the two SCO units in each molecule are quite different. (31.58° and 5.13°). In both the cases, however, mercury atom is bonded to two sulfurs of two thiophene-2-thiocarboxylate ligands and there is no interaction between oxygen atoms and mercury. Thus the geometry around Hg(II) is linear with slight distortion. This is in sharp contrast to the case of Hg(II) monothiocarbamate complex where the ligands bind to the metal through covalent Hg–S bonds and weak intramolecular Hg···O interactions leading to the formation of a hexameric cluster and the coordination polyhedron around each Hg atom is highly distorted octahedron [26].

The molecules (containing Hg2) with higher inter-SCO torsional angles form pairs due to intermolecular hydrogen bonding (between oxygen of thiocarboxylate and hydrogen of thiophene ring) in the lattice leaving a slit along the *a*-axis (intermolecular hydrogen bonding [27] is evinced by short H···O distance of 2.641 Å and C–H···O angle of 129.86°).

The chain formed by the other molecules (containing Hg1) goes parallel but does not have any interaction with the molecules containing Hg2 (Fig. S7: Supplementary information).

FAB mass spectrum of **7** (Fig. 7) showed a molecular ion peak at 663 which corresponds to $Hg(SCOPh)_2TiCl_4$. In spite of our best efforts single crystals of **7** could not be grown. One may expect the thiobenzoate ligand to bridge (μ-O,S) the Ti(IV) and Hg(II) centers. It may be noted that there are two reported complexes of mercury, $[Ph_4As]_2[Hg_2Cl_4(SCOPh)_2]$ and $[Ph_4As]_2[CdCl_4Hg(SCOPh)_2]$ in which the thiobenzoate ligands are bonded to the Hg atom in a monodentate manner through their sulfur atoms constructing a linear HgS_2 skeleton [10]. The Hg(II) center is further connected to the two Cl atoms forming a $MCl_4^{2-}\cdots Hg(SCOPh)_2$ donor acceptor complex. Such a structure forming a $Ti(Cl)_2(\mu\text{-}Cl)_2\cdots Hg(SCOPh)_2$ type complex is also possible. Both the possible structures (Fig. 8) have been simulated using MM2 [28] force field.

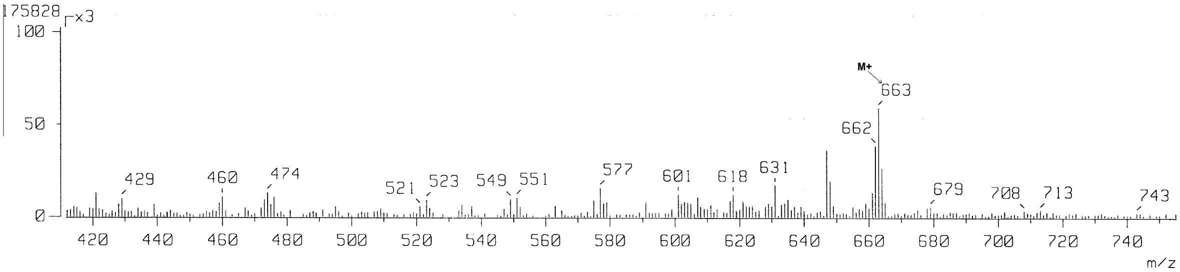


Fig. 7. FAB mass spectrum of **7**.

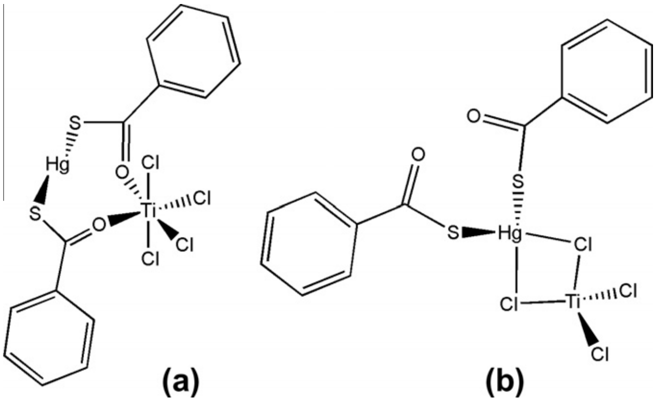


Fig. 8. Probable structures of **7**.

Structure **b** (Fig. 8) is found to be more stable as its steric energy is lower by 101.2 kcal/mol than that of **a**.

4. Conclusions

Three heterobimetallic complexes, [(Ph$_3$P)$_2$Cu(μ-SCOR)$_2$Hg(SCOR)] [R = Ph (**1**), th (thiophene) (**2**)] and Hg(SCOPh)$_2$TiCl$_4$ (**7**) were prepared and characterized by different spectroscopic techniques. During crystallization of **1** and **2** in chloroform/diethyl ether mixture the complexes disproportionated resulting in complexes, Hg(Ph$_3$P)(SCOPh)$_2$ and Hg(Ph$_3$P)(SCOth)$_2$ respectively, whereas in chloroform/*n*-hexane mixture they were dissociated resulting in binary compounds Hg(SCOPh)$_2$ and Hg(SCOth)$_2$, respectively. Structural investigations on representative molecules revealed bonding of the thiocarboxylate ligands through the S atoms only.

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Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.ica.2012.01.039.

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