

# Versatile coordination environment and interplay of metal assisted secondary interactions in the organization of supramolecular motifs in new Hg(II)/PhHg(II) dithiolates

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## ABSTRACT

New mercury(II) complexes of the form [PhHg(L)] ( $L = L_1$  (1),  $L_2$  (2),  $L_3'$  (3),  $L_4 =$  (4));  $[Hg(L)_2]$  ( $L = L_5$  (5),  $L_4$  (7)) and  $[Hg_2(L_6)_4]$  (6) have been synthesized and characterized by micro analysis and X-ray crystallography. Both 1 and 2 are linear; complex 2 revealed intramolecular  $Hg \cdots O$  bonding interactions. Complex 3 possesses T-shaped geometry in a linear polymeric chain motif. Although serendipitously formed, 3 is the first example of a metal trithioxanthate complex. 4 is a typical dimer and in 5, a helical chain motif is generated via  $Hg \cdots S$  contacts. 6 is a dinuclear complex with distorted square pyramidal geometry. 7 is mononuclear with a tetrahedrally coordinated mercury(II) ion. All complexes are luminescent in solution and solid state. In 2 the nature of  $Hg \cdots O$  interactions have been assessed by DFT calculations and the electronic transitions in 3 have been corroborated by TDDFT calculations.

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## 1. Introduction

Transition metal 1,1 dithiolates including those of group 12 metals (Zn, Cd, Hg) have been extensively studied because of their structural versatility [1–4], molecular electrical conducting and optical properties, utility as precursors in metal organic chemical vapour deposition (MOCVD) for the preparation of metal sulphides as semiconducting materials with useful optical properties and widespread industrial applications as rubber vulcanization accelerators, oil lubricants and fungicides and pesticides [1–2,5]. The strong affinity of mercury(II) and organomercurials towards distinctly soft sulphur donor atoms makes them useful for the detoxification of mercury in biological processes and as scavengers from globally distributed waste products [6]. Mercury(II) chemistry has been dominated by the sulphur based ligands including those of the ubiquitous dithiocarbamates and even xanthates. These ligands have been found extremely versatile for metal-directed self assembly forming supramolecular architectures [2,7]. The Lewis acidity, high polarizability of mercury(II) ion, satiation of maximum coordination numbers, steric bulk on the pendant groups of the ligands and the crystal packing effects have demonstrated the crucial role of sulphur ligands as supramolecular synthons in homo- and heteroleptic mercury(II) complexes [8], often with a wide range of

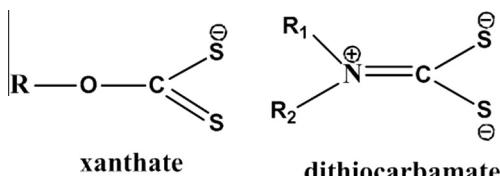
bond lengths. Albeit, the preferred coordination geometry of mercury(II) is linear however higher coordination numbers up to six are also exhibited [8]. The luminescent transition metal complexes including those with closed shell,  $d^{10}$  cations are of growing importance because of their potential applications as luminescent materials, LEDs, biological probes and sensors [9].

The dithiocarbamate and xanthate ligands despite some obvious resemblances differ significantly with regard to their dominant canonical structures Fig. 1 which contribute significantly to the overall description of structure and electronic properties of their complexes.

Many mercury(II) dithiocarbamates and even xanthates are known [2,7f]. Until recently the analogous organomercury(II) dithio compounds have not been well established [2e,10,11a]. In general the dithiocarbamate and xanthate ligands exhibit S,S chelating behaviour. Recently the bonding features and the luminescent properties of the novel pyridyl functionalized dithiocarbamate ligand complexes exhibiting interesting intermolecular  $Hg \cdots N$  bonding interactions have been explored [11]. Given this versatility and lack of exploration of pyridyl functionalized dithiocarbamate ligand, in order to gain more insight into the fascinating coordination patterns and properties, in this work we present the synthesis, crystal structures and luminescent properties of new mercury(II) and phenylmercury(II) compounds of the xanthate and dithiocarbamate ligands with varying pendant groups such as naphthyl, *N*-methyl-pyrrole and 3-pyridyl on the  $CS_2$  backbone

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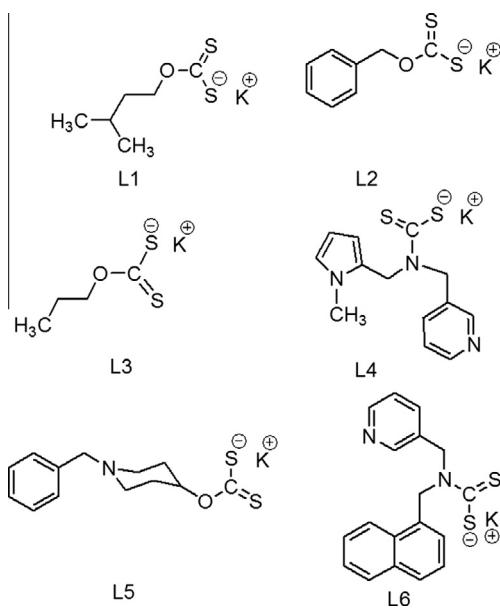
**Fig. 1.** Dominant canonical form of xanthate and dithiocarbamate ligands.

of these ligands. The most important aspect of this work was to investigate the implications of various functional groups on the dithio backbone in deciding the mercury(II) coordination sphere, non-covalent interactions including those involving the metal centre in the construction of varied supramolecular architectures owing to the fact that the field of sulphur donor coordination polymers is less explored [10e]. Furthermore, by contrast to the well known trithiocarboxylate [12a–c] complexes and rarely reported trithiocarbamates [12d,e] that play an important role in the rubber vulcanization process [12f], for the first time the trithioxanthate complex of PhHg(II) has been isolated and structurally characterized. The luminescent characteristics of the compounds have been correlated with their structures. In order to assess the nature of Hg···O bonding interactions DFT calculations on **1** and **2** have been performed. TDDFT calculations were performed on **3** to support the electronic transitions observed in this complex. The results of these investigations are described here.

## 2. Experimental

### 2.1. Materials and methods

All reactions were carried out in the open at ambient temperature and pressure. The metal salts  $\text{Hg}(\text{CO}_2\text{CH}_3)_2$  and  $\text{C}_6\text{H}_5\text{Hg}(\text{CO}_2\text{CH}_3)$  and chemicals such as carbon disulfide, 1-naphthaldehyde,  $\text{C}_6\text{H}_5\text{CH}_2\text{OH}$ ,  $(\text{CH}_3)_2\text{CHCH}_2\text{CH}_2\text{OH}$ ,  $\text{CH}_3\text{CH}_2\text{CH}_2\text{OH}$ ; 1-benzyl-4-hydroxy piperidine, 3-picolyamine and *N*-methyl-2-pyrrolecarboxaldehyde were purchased from SD Fine Chemicals, India and Sigma Aldrich respectively and used without further purification. The solvents were distilled according to standard procedures. Potassium salts of the xanthate and dithiocarbamate ligands Fig. 2 i.e.



**Fig. 2.** Structure of the ligands used in present study.

iso-amylxanthate (**KL1**), benzylxanthate (**KL2**), n-propylxanthate (**KL3**), *N*-(*N*-methyl-2-pyrrole)-*N*-(methyl-3-pyridyl)dithiocarbamate (**KL4**), 1-benzyl-4-hydroxypiperidinexanthate (**KL5**) and *N*-methylnaphthyl-*N*-(methyl-3-pyridyl)dithiocarbamate (**KL6**) were prepared according to literature procedures [11] by the reaction of the appropriate alcohol or secondary amine with  $\text{CS}_2$  and KOH.

The experimental details pertaining to elemental analyses (C, H, N, S) and recording of IR(KBr),  $^1\text{H}$  and  $^{13}\text{C}\{^1\text{H}\}$  NMR and UV-Vis. spectra in  $\text{CH}_2\text{Cl}_2$  and as Nujol mull are the same as described earlier [11]. The photoluminescent spectra in  $\text{CH}_2\text{Cl}_2$  solution and solid state and the quantum yield measurements were performed at room temperature using a Fluorolog Horiba Jobin Yvon spectrophotometer. Sodium salicylate was used as the standard phosphor for the quantum yield determinations. The overall quantum yields ( $\Phi_{\text{overall}}$ ) were measured following the protocol described by Bril and co-workers [13] and calculations were done according to the following expression:

$$\Phi_{\text{overall}} = \{\Phi_{\text{st}}(1 - R_{\text{st}})(A_c)\}/\{(1 - R_c)(A_{\text{st}})\}$$

where  $R_c$  and  $R_{\text{st}}$  represent the diffuse reflectance of the coordination complex and of the standard phosphor respectively at a fixed wavelength.  $\Phi_{\text{st}}$  represents the quantum yield of the standard phosphor. The terms  $A_c$  and  $A_{\text{st}}$  represent the area under the complex and the standard phosphor emission spectra respectively.

### 2.2. Synthesis of the compounds

The compounds were prepared adopting similar procedures as given below.

### 2.3. [PhHg(L1)] (**1**)

To a (10 mL) stirred methanolic solution of the ligand **KL1** (0.101 g, 0.5 mmol) was added slowly a 10 mL solution of PhHg( $\text{CO}_2\text{CH}_3$ ) (0.168 g, 0.5 mmol) in the same solvent. The reaction mixture was then stirred for about 3 h at room temperature. The greenish yellow solid thus formed was filtered off and washed with methanol followed by diethylether. The crude product was dissolved in acetone and filtered to discard any undissolved residue and the clear solution was kept for crystallization. Thin plate-like colourless crystals were obtained within 2–3 weeks.

Yield: (0.154 g, 70%). *Anal.* Calc. for  $\text{C}_{12}\text{H}_{16}\text{HgOS}_2$  (440.98): C, 32.65; H, 3.66; S, 14.50. Found: C, 32.42; H, 3.75; S, 14.18%. IR (KBr,  $\text{cm}^{-1}$ ): 1234 ( $\nu_{\text{C}-\text{O}}$ ), 1027 ( $\nu_{\text{C}-\text{S}}$ ).  $^1\text{H}$  NMR (300.40 MHz,  $\text{CDCl}_3$ , ppm):  $\delta$  0.98, 0.96 (d,  $J = 6$ , 6H,  $(\text{CH}_3)_2$ ), 1.55–1.75 (m, 1H,  $-\text{CH}-$ ), 1.75, 1.73, 1.71, 1.70 (q,  $J = 6.00$  Hz, 2H,  $-\text{CH}_2-$ ), 4.55, 4.53, 4.51 (t,  $J = 6.00$  Hz, 2H,  $-\text{O}-\text{CH}_2-$ ), 7.39–7.25 (m, 5H,  $\text{C}_6\text{H}_5$ ).  $^{13}\text{C}\{^1\text{H}\}$  NMR (75.45 MHz,  $\text{CDCl}_3$ , ppm)  $\delta$  22.43 (Me), 25.06 ( $-\text{CH}-$ ), 36.85 ( $-\text{CH}_2-$ ), 74.63 ( $-\text{CH}_2-\text{O}-$ ), 128.93, 129.02, 136.86, 154.56 ( $\text{C}_6\text{H}_5$ ), 223.88 ( $-\text{OCS}_2$ ). UV-Vis. ( $\text{CH}_2\text{Cl}_2$ ,  $\lambda_{\text{max}}$  (nm),  $\epsilon$  ( $\text{M}^{-1} \text{cm}^{-1}$ )): 297 ( $1.8 \times 10^4$ ).

### 2.4. [PhHg(L2)] (**2**)

Colourless crystals of compound **2** were prepared and isolated following the procedure similar to **1** but using **KL2** (0.117 g, 0.5 mmol). Yield: (0.166 g, 72%). *Anal.* Calc. for  $\text{C}_{14}\text{H}_{12}\text{HgOS}_2$  (460.97): C, 36.48; H, 2.62; S, 13.91. Found: C, 36.22; H, 2.70; S, 13.56%. IR (KBr,  $\text{cm}^{-1}$ ): 1262 ( $\nu_{\text{C}-\text{O}}$ ), 1041 ( $\nu_{\text{C}-\text{S}}$ ).  $^1\text{H}$  NMR (300.40 MHz,  $\text{CDCl}_3$ , ppm):  $\delta$  5.50 (s, 2H,  $-\text{CH}_2-\text{O}-$ ), 7.44–7.21 (m, 10H, Ar-CH).  $^{13}\text{C}\{^1\text{H}\}$  NMR (75.45 MHz,  $\text{CDCl}_3$ , ppm)  $\delta$  75.76 ( $-\text{CH}_2-\text{O}-$ ), 156.60–126.43 (Ar-C), 221.72 ( $-\text{OCS}_2$ ). UV-Vis. ( $\text{CH}_2\text{Cl}_2$ ,  $\lambda_{\text{max}}$  (nm),  $\epsilon$  ( $\text{M}^{-1} \text{cm}^{-1}$ )): 297 ( $1.67 \times 10^4$ ).

## 2.5. [PhHg(L3)] (**3**)

Colourless crystals of compound **3** were prepared and isolated following the procedure similar to **1** but using KL3 (0.093 g, 0.5 mmol). Yield: (0.160 g, 72%). *Anal.* Calc. for  $C_{10}H_{12}HgOS_3$  (445.00): C, 26.99; H, 2.72; S, 21.62. Found: C, 26.59; H, 2.83; S, 21.47%. IR (KBr,  $\text{cm}^{-1}$ ): 1262 ( $\nu_{\text{C}-\text{O}}$ ), 1044 ( $\nu_{\text{C}-\text{S}}$ ).  $^1\text{H}$  NMR (300.40 MHz,  $\text{CDCl}_3$ , ppm):  $\delta$  1.04, 1.01, 0.99 (t,  $J = 9.01$  Hz, 3H,  $\text{CH}_3$ –), 1.88–1.55 (m, 2H,  $-\text{CH}_2-$ ), 4.47, 4.45, 4.43 (t,  $J = 6.00$  Hz, 2H,  $-\text{CH}_2-\text{O}$ –), 7.44–7.25 (m, 5H,  $\text{C}_6\text{H}_5$ ).  $^{13}\text{C}\{\text{H}\}$ NMR (75.45 MHz,  $\text{CDCl}_3$ )  $\delta$  10.39 ( $\text{CH}_3$ ), 21.67 ( $-\text{CH}_2-$ ), 77.42–76.57 (merged with  $\text{CDCl}_3$  peaks,  $-\text{CH}_2-\text{O}$ –), 154.54, 136.85, 129.01, 128.92 ( $\text{C}_6\text{H}_5$ ), 223.98 ( $-\text{OCS}_2$ ). UV–Vis. ( $\text{CH}_2\text{Cl}_2$ ,  $\lambda_{\text{max}}$  (nm),  $\varepsilon$  ( $\text{M}^{-1} \text{cm}^{-1}$ )): 298 (0.68  $\times 10^4$ ).

## 2.6. [PhHg(L4)] (**4**)

Pale yellow crystals of **4** were obtained and isolated following the procedure similar to **1** but using KL4 (0.156 g, 0.5 mmol). The crystals were grown in  $\text{CH}_2\text{Cl}_2$ . Yield: (0.216 g, 78%). *Anal.* Calc. for  $C_{38}H_{38}\text{Hg}_2\text{N}_6\text{S}_4$  (1108.16): C, 41.18; H, 3.42; N, 7.58; S, 11.55. Found: C, 41.03; H, 3.35; N, 7.59; S, 11.224%. IR (KBr,  $\text{cm}^{-1}$ ): 1280 ( $\nu_{\text{C}-\text{O}}$ ), 1040 ( $\nu_{\text{C}-\text{S}}$ ).  $^1\text{H}$  NMR (300.40 MHz,  $\text{CDCl}_3$ , ppm):  $\delta$  3.58 (s, 3H,  $-\text{CH}_3$ ), 5.01 (s, 2H,  $-\text{CH}_2-\text{C}_4\text{H}_3\text{N}-\text{CH}_3$ ), 5.10 (s, 2H,  $-\text{CH}_2-\text{C}_6\text{H}_4\text{N}$ ), 7.25, 6.60, 6.08 (s, 3H,  $-\text{C}_4\text{H}_3\text{N}-\text{CH}_3$ ), 8.54–7.26 (m, 4H,  $\text{C}_5\text{H}_4\text{N}$ ).  $^{13}\text{C}\{\text{H}\}$ NMR (75.45 MHz,  $\text{CDCl}_3$ , ppm)  $\delta$  34.38 ( $\text{CH}_3-\text{NC}_4\text{H}_3$ ), 49.90 ( $-\text{CH}_2-\text{C}_4\text{H}_3\text{N}-\text{CH}_3$ ), 52.61 ( $-\text{CH}_2-\text{C}_5\text{H}_4\text{N}$ ), 154.01–107.50 (Ar-C), 205.13 ( $-\text{NCS}_2$ ). UV–Vis. ( $\text{CH}_2\text{Cl}_2$ ,  $\lambda_{\text{max}}$  (nm),  $\varepsilon$  ( $\text{M}^{-1} \text{cm}^{-1}$ )): 255 (2.8  $\times 10^4$ ), 303 (1.00  $\times 10^4$ ).

## 2.7. [ $\text{Hg}(L5)_2$ ] (**5**)

Pale yellow crystals of compound **5** were obtained and isolated following the procedure similar to **1** but using KL5 (0.160 g, 0.5 mmol) and  $\text{HgCl}_2$  (0.070 g, 0.25 mmol). Yield: (0.138 g, 75%). *Anal.* Calc. for  $C_{26}H_{32}\text{HgN}_2\text{O}_2\text{S}_4$  (733.41): C, 42.57; H, 4.36; N, 3.82; S, 17.45. Found: C, 42.27; H, 4.39; N, 3.64; S, 17.15%. IR (KBr,  $\text{cm}^{-1}$ ): 1405 ( $\nu_{\text{C}-\text{N}}$ ), 1023 ( $\nu_{\text{C}-\text{S}}$ ).  $^1\text{H}$  NMR (300.40 MHz,  $\text{CDCl}_3$ , ppm):  $\delta$  1.62–2.69 (m, 8H,  $\text{NC}_4\text{H}_8\text{CH}-\text{O}$ ), 3.52 (s, 2H,  $\text{CH}_2-\text{NC}_5\text{H}_9$ ), 5.20, 5.18, 5.17 (t,  $J = 6.00$  Hz, 1H,  $-\text{O}-\text{CH}-\text{C}_4\text{H}_8\text{N}$ ), 7.32–7.24 (m, 5H,  $\text{C}_6\text{H}_5$ ).  $^{13}\text{C}\{\text{H}\}$ NMR (75.45 MHz,  $\text{CDCl}_3$ , ppm)  $\delta$  50.00, 30.16 ( $\text{C}_5\text{H}_9\text{N}$ ), 62.86 ( $-\text{CH}_2-\text{NC}_5\text{H}_9$ ), 84.42 ( $-\text{O}-\text{CH}-\text{C}_4\text{H}_8\text{N}$ ), 138.19–127.11 ( $\text{C}_6\text{H}_5$ ), 221.44 ( $-\text{OCS}_2$ ). UV–Vis. ( $\text{CH}_2\text{Cl}_2$ ,  $\lambda_{\text{max}}$  (nm),  $\varepsilon$  ( $\text{M}^{-1} \text{cm}^{-1}$ )): 276 (2.30  $\times 10^4$ ).

## 2.8. [ $\text{Hg}_2(L6)_4$ ] (**6**)

Yellow crystals of compound **6** were obtained and isolated following the procedure similar to **4** but using KL6 (0.187 g, 0.5 mmol) and  $\text{Hg(OAc)}_2$  (0.080 g, 0.25 mmol). Yield: (0.172 g, 80%). *Anal.* Calc. for  $C_{73}H_{64}\text{Hg}_2\text{N}_8\text{O}_8$  (1727.06): C, 50.76; H, 3.71; N, 6.48; S, 14.82. Found: C, 50.58; H, 3.68; N, 6.22; S, 14.48%. IR (KBr,  $\text{cm}^{-1}$ ): 1412 ( $\nu_{\text{C}-\text{N}}$ ), 1089 ( $\nu_{\text{C}-\text{S}}$ ).  $^1\text{H}$  NMR (300.40 MHz,  $\text{CDCl}_3$ , ppm):  $\delta$  5.50 (s, 2H,  $-\text{CH}_2-\text{C}_{10}\text{H}_7$ ), 5.00 (s, 2H,  $-\text{CH}_2-\text{C}_5\text{H}_4\text{N}$ ), 7.25–8.54 (m, 11H, Ar-H).  $^{13}\text{C}\{\text{H}\}$ NMR (75.45 MHz,  $\text{CDCl}_3$ , ppm)  $\delta$  55.60 ( $-\text{CH}_2-\text{C}_{10}\text{H}_7$ ), 57.27 ( $-\text{CH}_2-\text{C}_5\text{H}_4\text{N}$ ), 149.46–122.90 (Ar-C), 207.80 ( $-\text{NCS}_2$ ). UV–Vis. ( $\text{CH}_2\text{Cl}_2$ ,  $\lambda_{\text{max}}$  (nm),  $\varepsilon$  ( $\text{M}^{-1} \text{cm}^{-1}$ )): 243 (6.5  $\times 10^4$ ), 282 (7.70  $\times 10^4$ ).

## 2.9. [ $\text{Hg}(L4)_2$ ] (**7**)

Yellow crystals of compound **7** were obtained and isolated following the procedure similar to **6** but using KL4 (0.156 g, 0.5 mmol). Yield: (0.146 g, 78%). *Anal.* Calc. for  $C_{26}H_{28}\text{HgN}_6\text{S}_4$  (753.41): C, 41.44; H, 3.71; N, 11.15; S, 16.99. Found: C, 41.26; H, 3.80; N, 10.84; S, 16.62%. IR (KBr,  $\text{cm}^{-1}$ ): 1418 ( $\nu_{\text{C}-\text{N}}$ ), 1024 ( $\nu_{\text{C}-\text{S}}$ ).

$^1\text{H}$  NMR (300.40 MHz,  $\text{CDCl}_3$ , ppm):  $\delta$  3.60 (s, 3H,  $-\text{CH}_3$ ), 4.97 (s, 2H,  $-\text{CH}_2-\text{C}_4\text{H}_3\text{N}-\text{CH}_3$ ), 5.05 (s, 2H,  $-\text{CH}_2-\text{C}_6\text{H}_4\text{N}$ ), 7.26, 6.60, 6.08 (s, 3H,  $-\text{C}_4\text{H}_3\text{N}-\text{CH}_3$ ), 8.55–7.28 (m, 4H,  $\text{C}_5\text{H}_4\text{N}$ ).  $^{13}\text{C}\{\text{H}\}$ NMR (75.45 MHz,  $\text{CDCl}_3$ , ppm)  $\delta$  34.61 ( $\text{CH}_3-\text{NC}_4\text{H}_3$ ), 51.43 ( $-\text{CH}_2-\text{C}_4\text{H}_3\text{N}-\text{CH}_3$ ), 53.80 ( $-\text{CH}_2-\text{C}_5\text{H}_4\text{N}$ ), 149.48–107.74 (Ar-C), 206.46 ( $-\text{NCS}_2$ ). UV–Vis. ( $\text{CH}_2\text{Cl}_2$ ,  $\lambda_{\text{max}}$  (nm),  $\varepsilon$  ( $\text{M}^{-1} \text{cm}^{-1}$ )): 275 (6.3  $\times 10^4$ ).

## 2.10. Crystallization and X-ray crystal structure determinations

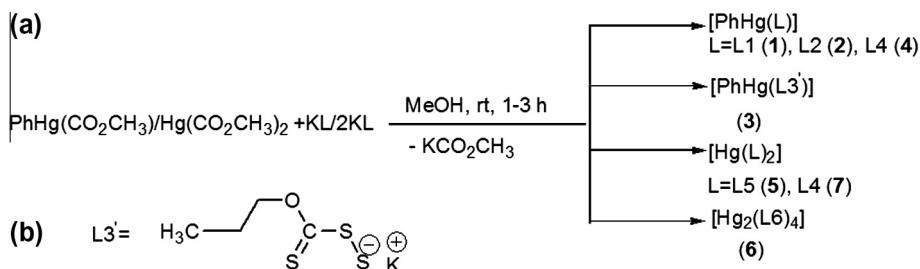
Single crystals were obtained by slow evaporation of solutions of the products **1–3** and **5** in acetone and **4**, **6** and **7** in  $\text{CH}_2\text{Cl}_2$  solution. Apart from a little black residue of mercuric sulphide no other crystalline by-product was found within the crystalline sample of **3**. Single crystal X-ray diffraction data for **1–7** were collected on an Oxford X-calibur CCD diffractometer at 293 K using Mo  $\text{K}\alpha$  radiation. Data reduction for **1–7** was carried out using the CrysAlis program [14]. The structures were solved by direct methods using SHELXS-97 [15] and refined on  $F^2$  by full matrix least squares method using SHELXL-97 [16]. Non-hydrogen atoms were refined anisotropically and hydrogen atoms were geometrically fixed with thermal parameters equivalent to 1.2 times that of the atom to which they were bonded. Diagrams for all complexes were prepared using ORTEP [17], Diamond and Mercury software.

## 2.11. Computational methods

All calculations were performed by the density functional theory (DFT) methodology using the GAUSSIAN 09 software suite [18]. The ground state energy calculations for complexes **1–3** were performed using the Truhlar's M06–2X Global-hybrid-meta-GGA functional. A mixed basis set approach was followed in all the calculations. The Hg atom is treated with LANL2DZ (Los Alamos National Laboratory 2 Double-Zeta), a ECP type basis set, the aug-cc-pVDZ basis set for S, O, N and the cc-pVDZ basis set were used for C and H-atoms. Input geometries used in the calculations were obtained from X-ray diffraction data. The neutron normalized H-atom coordinates were used for complexes **1** and **2**. Electronic excited state calculations on **3** were performed using the Time-Dependent Density Functional Theory (TDDFT) in solution (solvent = dichloromethane) using the PCM model and five different functionals at the mixed basis set described above.

## 3. Results and discussion

The homo- and heteroleptic Hg(II)/PhHg(II) complexes have been isolated by the treatment of a methanolic solution of Hg ( $\text{CO}_2\text{CH}_3$ )<sub>2</sub> or PhHg( $\text{CO}_2\text{CH}_3$ ) with the potassium salt of the ligands (KL1–KL6) in required molar ratios Scheme 1. Notably the reaction of PhHg( $\text{CO}_2\text{CH}_3$ ) with *n*-propylxanthate (L3) serendipitously yielded a trithioxanthate complex **3** in good yield by self-assembly with a phenylmercury acetate salt, to the best of our knowledge not reported earlier. The complexes are air-stable and are soluble in common organic solvents such as  $\text{CH}_2\text{Cl}_2$  and  $\text{CHCl}_3$ . They have been characterized by elemental analysis, IR, NMR, UV–Vis. spectra and single crystal X-ray diffraction. An investigation of their X-ray structures revealed varied coordination geometries and diverse structural patterns due to bonding interactions involving the metal ions. The significance of secondary interactions involved in the construction of supramolecular structures has been supported by theoretical calculations on **1** and **2**. The pertinent electronic transitions in **3** have been corroborated by TDDFT calculations. The luminescent properties of the complexes have been correlated with their solid state structures.



**Scheme 1.** (a) General methodology for the synthesis of complexes (1–7); (b) *In situ* generated n-propyltrithioxanthate ligand L3'.

All the complexes show  $\nu_{(\text{C}-\text{N})}$ ,  $\nu_{(\text{C}-\text{O})}$  and  $\nu_{(\text{C}-\text{S})}$  vibrations diagnostic of coordinated dithiocarbamate and xanthate ligands. Particularly a significant enhancement in the  $\nu_{(\text{C}-\text{N})}$  frequency of the complexes in comparison to the free dithiocarbamate ligands indicates the dominant contribution of the canonical form Fig. 1 in the overall description of the structures of dithiocarbamate and xanthate complexes.  $^1\text{H}$  NMR of all the complexes exhibit resonances characteristic of the functional groups of the ligands. All the complexes show a single downfield resonance in the  $\delta$  210–223 ppm range characteristic of  $\text{CS}_2$  unit of the dithioligands.

### 3.1. Crystal structures



within this category were in clearly defined coordination sites [2a,10e,20].

结构 1 是一个典型的 2-配位单体复合物，汞(II)与 ipso-碳原子（2.066(17) Å）和 xanthate 肋道 L1 的 S11 原子（2.366(4) Å）成键，C31-Hg1-S11 角度为 178.40(4) $^\circ$  表明线性几何（Fig. 3a）。S13 原子位于 Hg(II) 金属原子处（3.114(4) Å），笨重的异丙基链有利于通过分子间 C-H... $\pi$  作用力（3.24 Å）而不是通过 Hg...S 作用力（2a,e）实现超分子稳定化。

汞(II) 在 2 中的配位几何与 1 中观察到的相似，具有线性几何，汞(II) 与 ipso-碳原子 C31（2.042(9) Å）和 L2 的 S11 原子（2.386(2) Å）成键。C31-Hg1-S11 角度为 175.5(3) $^\circ$ 。该结构的一个新特征是配体的构象使得 O14 原子（而不是 S13）更靠近金属，由 Hg1-S11-C12-O14 键角为 12.4(4) $^\circ$  表明。然而，Hg1...O14 距离为 2.894(8) Å 可能仅表示弱相互作用，尽管它远小于汞(II)（1.71 Å）和氧（1.52 Å）的范德瓦尔斯半径 [2a,19]。图 4a 显示了这些 Hg...O 作用力，尽管它们不如 Hg...S 作用力普遍，但根据 HSAB 概念，汞(II) 作为硬酸而 O 作为硬供体，因此不那么有利。

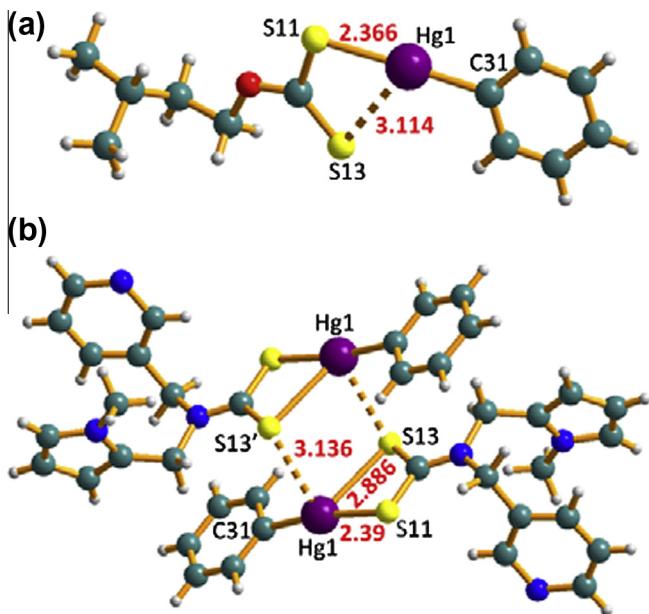
**Table 1**  
Crystal data and refinement parameters for complexes 1–7.

Compound	1	2	3	4	5	6	7
Chemical formula	$\text{C}_{12}\text{H}_{16}\text{HgOS}_2$	$\text{C}_{14}\text{H}_{12}\text{HgOS}_2$	$\text{C}_{10}\text{H}_{12}\text{HgOS}_3$	$\text{C}_{38}\text{H}_{38}\text{Hg}_2\text{N}_6\text{S}_4$	$\text{C}_{26}\text{H}_{32}\text{Hg N}_2\text{O}_2\text{S}_4$	$\text{C}_{73}\text{H}_{64}\text{Hg}_2\text{N}_8\text{O S}_8$	$\text{C}_{26}\text{H}_{28}\text{HgN}_6\text{S}_4$
Formula weight	440.96	460.97	444.97	1108.20	733.37	1727.06	753.37
Crystal system	monoclinic	monoclinic	monoclinic	triclinic	monoclinic	triclinic	triclinic
Space group	$P21/c$	$P21/c$	$P21/c$	$\bar{P}1$	$C2/c$	$\bar{P}1$	$\bar{P}1$
a (Å)	15.020(5)	15.1541(6)	13.6902(16)	8.709(2)	39.384(3)	11.2835(7)	7.8970(6)
b (Å)	5.6389(2)	8.1463(3)	8.1303(12)	10.615(2)	6.3017(3)	11.8933(7)	10.7825(10)
c (Å)	17.888(6)	11.6168(5)	10.9444(17)	11.133(3)	24.8682(16)	13.8094(9)	16.9660(13)
$\alpha$ ( $^\circ$ )	(90)	(90)	(90)	69.48(2)	(90)	74.797(5)	96.704(7)
$\beta$ ( $^\circ$ )	104.28(4)	97.454(3)	96.096(12)	85.255(19)	110.488(8)	79.823(5)	92.145(6)
$\gamma$ ( $^\circ$ )	(90)	(90)	(90)	80.711(19)	(90)	85.869(5)	95.664(7)
V (Å $^3$ )	1468.2(9)	1421.97(10)	1211.3(3)	950.9(4)	5781.6(7)	1759.56(19)	1426.0(2)
Z	4	4	4	1	8	1	2
$D_{\text{calc}}$ (g cm $^{-3}$ )	1.995	2.097	2.440	1.932	1.685	1.630	1.755
T (K)	293(2)	293(2)	293(2)	293(2)	293(2)	293(2)	293(2)
$\mu$ (Mo K $\alpha$ ) (mm $^{-1}$ )	10.746	11.098	13.193	8.318	5.639	4.645	5.717
F(000)	832	840	832	532	2896	854	740
Reflections collected	6070	12,920	5151	6705	12,370	13,010	10,814
Independent reflections	3217	3220	2736	4106	6325	7713	6195
Reflections with $I > 2\sigma(I)$	1806	2414	1803	2846	3458	4253	3691
Final indices [ $I > 2\sigma(I)$ ] $R_1$ <sup>a</sup> , $wR_2$ <sup>b</sup>	0.0689, 0.1449	0.0406, 0.0811	0.1003, 0.2572	0.0583, 0.1157	0.0466, 0.0692	0.0571, 0.1036	0.0823, 0.2041
$R_{1[\text{a}]}, wR_{2[\text{b}]}$ [all data]	0.1178, 0.1751	0.0623, 0.0905	0.1359, 0.2992	0.0915, 0.1373	0.1020, 0.0835	0.1288, 0.1273	0.1365, 0.2390
Goodness-of-fit (GOF) on $F^2$ <sup>c</sup>	0.956	1.026	1.039	0.983	0.879	0.942	1.045

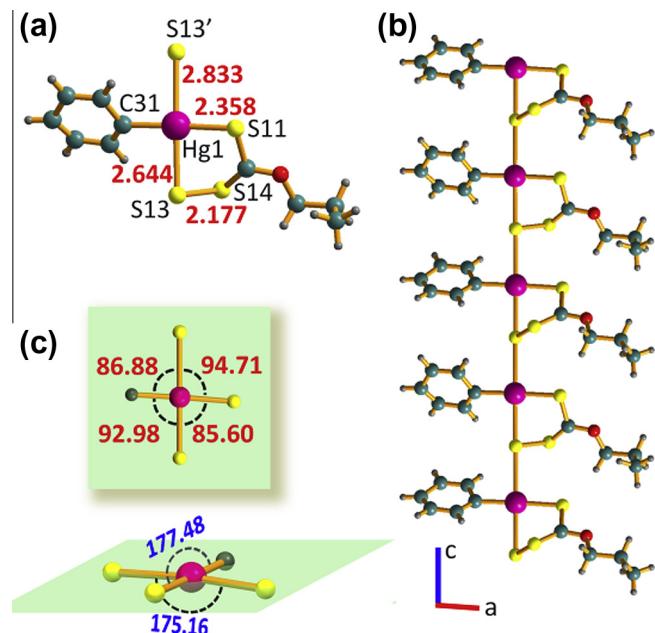
<sup>a</sup>  $R_1 = \sum(|F_0| - |F|)/\sum|F|$ .

<sup>b</sup>  $wR_2 = [(w(\sum(|F_0|^2 - |F_c|^2)^2)/\sum(w|F_0|^4))]^{1/2}$ .

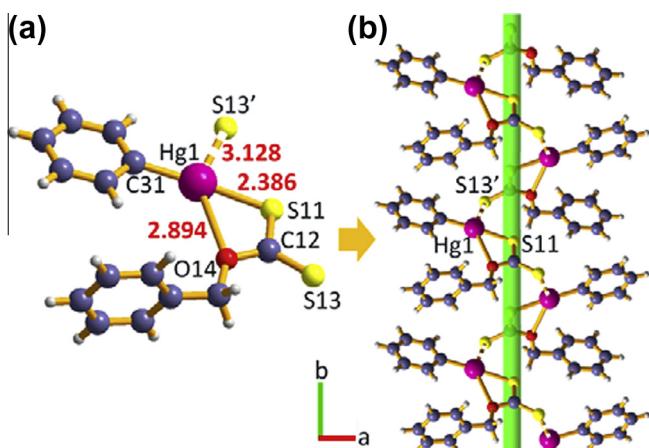
<sup>c</sup> Goodness of fit =  $[(w(\sum(|F_0| - |F_c|^2)^2)/(n-p))^{1/2}$ , where n is the number of reflections, and p is the number of refined parameters.



**Fig. 3.** (a) Molecular structure and Hg–S bond distances in compounds (a) **1** and (b) **4**.



**Fig. 5.** (a) Molecular structure of **3**. (b) 1-D linear polymeric chain view of **3** projected down the *c*-axis; (c) Bond angles about mercury atom for effective square planar coordination.



**Fig. 4.** (a) Molecular structure and intramolecular Hg···O (2.890(8) Å) interactions and intermolecular Hg···S (3.127(2) Å) interactions in **2**. (b) Helical chain motif in **2** along the crystallographic 2<sub>1</sub> screw axis.

has been observed sporadically in methylmercury xanthate  $\text{Hg}(\text{S}_2\text{CO})_2$  and carbamoylbenzenethiol mercury(II) complexes with  $\text{Hg}\cdots\text{O}$  distances [19b] in the range 2.65–3.06 Å. The overall supramolecular structure of **2** is constructed on  $\text{Hg}_1\cdots\text{S}_13'$  interactions at (3.128(2) Å) ( $' = 2 - x, 1/2 + y, 1/2 - z$ ) presenting a helical chain **Fig. 4b** around a twofold screw axis. The helical motif bends at  $\text{S}_{13}'$  at an angle of 84.6(2)° between the planes defined by  $\text{S}_{13}', \text{Hg}_1, \text{S}_{11}, \text{C}_{31}$  and  $\text{C}_{12}, \text{Hg}_1, \text{S}_{11}, \text{O}_{14}$  atoms. Also the structure is stabilized by non-covalent  $\text{C}-\text{H}\cdots\text{S}$  (2.98 Å) interactions.

In the crystal structure of **3** the Hg atom is three coordinate with a T-shaped geometry being bonded to the *ipso*-carbon C31 of a phenyl ring, S11 and S13 atoms of a bidentate trithioxanthate ligand **Fig. 5a**. The metal centre is also weakly coordinated to a fourth  $\text{S}_{13}'$  atom ( $' = x, 1/2 - y, 1/2 + z$ ) on an adjacent ligand leading to a unique linear 1-D polymeric chain and an effective coordination number of four in a distorted square planar coordination environment; unusual for a  $d^{10}$  metal centre **Fig. 5b,c**. The  $\text{Hg}_1-\text{S}_{11}$  and  $\text{Hg}_1-\text{S}_{13}$  distances of 2.358(7) and 2.644(8), respectively

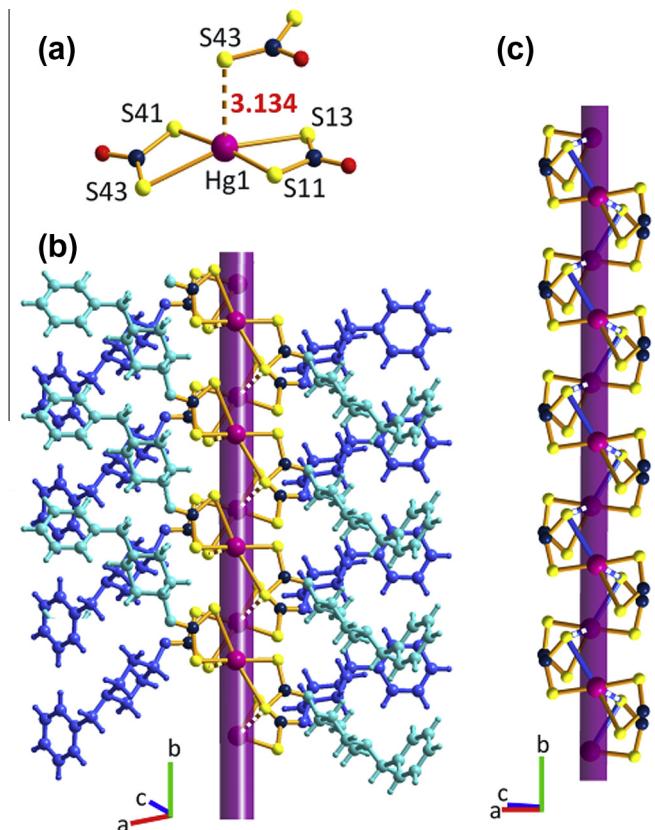
are well within the range and although longer, the  $\text{Hg}_1-\text{S}_{13}'$  distance of 2.833(8) Å is at the borderline value reported for Hg–S distances in bonding range [2a,20]. The four atoms in the equatorial plane show an r.m.s. deviation of 0.265 Å with the metal atom 0.300(6) Å from the plane. Angles in the plane are shown in **Fig. 5c**. In order to adjust the steric modularities and attain symmetry, the  $\text{S}_{14}$  atom orients back and forth along the  $\text{Hg}_1\cdots\text{S}_{13}\cdots\text{Hg}_1$  backbone. The 1-D polymeric chain is constructed due to the perforce orientation of trithioxanthate and phenyl ligands on the mercury atom in the crystal lattice. To the best of our knowledge **3** is the first example of a polymeric metal trithioxanthate complex. The conformation of the five-membered chelate ring containing  $\text{Hg}_1, \text{S}_{11}, \text{C}_{12}, \text{S}_{13}, \text{S}_{14}$  shows that the first four atoms are approximately coplanar with an r.m.s. deviation of 0.035 Å while  $\text{S}_{14}$  is 1.62(1) Å from the plane. Also the supramolecular structure is sustained through  $\text{C}-\text{H}\cdots\text{S}$  (2.73 Å) non-covalent interactions and remarkably short  $\text{S}_{13}\cdots\text{S}_{14}$  ( $1 - x, y - 1/2, 1/2 - z$ ) intermolecular interactions at 2.536(9) Å which connect the adjacent chains.

The coordination geometry about the Hg atom in **4** is defined by the *ipso*-carbon C31 of the phenyl ring and the S11 atom of the dithiocarbamate ligand L4 with bond lengths 2.100(9) and 2.391(3) Å respectively and a C31–Hg1–S11 angle of 171.6(3)° in addition there is a weaker  $\text{Hg}_1-\text{S}_{13}$  bond of 2.886(3) Å **Fig. 3b**. The crystal structure of **4** depicts a typical but considerably stronger head to tail centrosymmetric dimer via  $\text{Hg}_1\cdots\text{S}_{13}'$  ( $' = 2 - x, 1 - y, 2 - z$ ) contacts (3.136(4) Å), a distance that can be compared to that found in previously reported PhHg(II)dithiocarbamate complexes, 3.117(13)–3.133(3) Å and mercury(II) dithiocarbamate complexes 3.147(7) Å showing essentially linear geometry [2a]. It is to be noted that in comparison to  $\text{Hg}\cdots\text{N}(\text{Py})$  interactions observed in the reported pyridyl functionalized PhHg(II)dithiocarbamate complexes [11a] no such interactions occur in this compound probably due to the steric restrictions of the methyl group on the N of the pyrrole ring. The molecular association in the crystal structure of **4** is stabilized via  $\text{C}-\text{H}\cdots\pi$  interactions.

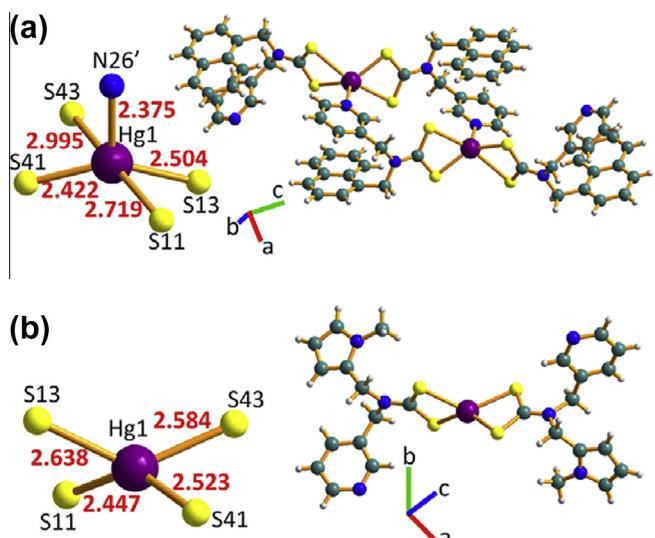
Complexes **5**, **6** and **7** contain mercury(II) with various dithio ligands. In **5** the linear, mercury(II) ion is unsymmetrically coordinated by two xanthate ligands (L5). Each ligand forms a strong

bond and a weak bond, thus Hg1–S11 and Hg1–S41 distances are 2.381(16) and 2.370(17) Å, respectively with a S11–Hg1–S41 angle of 172.9(7)° while Hg1–S13, Hg1–S43 are 2.953(17), 3.032(17) Å, respectively are within the range [20] Fig. 6a. A close look into the structure of this compound reveals a remarkable molecular aggregation through intermolecular Hg1···S43' (3.134(18) Å) ( $' = 1/2 - x, y - 1/2, 1.5 - z$ ) interactions leading to generation of a helical chain motif via a twofold screw axis Fig. 6 b,c. Thus the effective coordination number of the metal atom is five with distorted square pyramidal geometry which can be contrasted with the prevalent tetrahedral geometry noticed in the majority of analogous xanthate complexes [2a]; the only complex  $\text{Hg}(\text{S}_2\text{COMe}_2)_2$  complex [19a] containing small methyl substituents showed the Hg atom in a T-shaped environment in a polymeric chain. Two adjacent molecules in the helical chain network are with the appended orthogonally at Hg1–S43–Hg1 angle of 91.89(5)° which adjusts the steric requirements of the bulky appendages on the  $\text{OCS}_2$  core of the ligand. The packing diagram of 5 presents an attractive ‘butterfly shaped’ structure along the  $c$ -axis Fig. S2, ESI. The supramolecular architecture is stabilised through substantial S···S (3.51 Å), C–H···S (2.98 Å) and C–H···O (2.71 Å) intermolecular interactions Fig. S3, ESI.

Complex **6** is a unique centrosymmetric dinuclear mercury(II) complex with a 3-pyridyl functionalized ligand (L6) in which each Hg atom is unsymmetrically chelated through S11, S13 and S41, S43 of two bidentate dithiocarbamate ligands. A fifth coordination site on each mercury(II) ion is occupied by a N atom of a bridging-chelating dithiocarbamate ligand L6 in a  $\mu_2,\kappa^2\text{N},\text{S},\text{S}$  fashion establishing a distorted square pyramidal geometry Fig. 7a, thus each ligand exhibits one short and one long bond distance. The Hg–S bonds occupy the equatorial plane with distances for Hg1–S11,



**Fig. 6.** (a) Strong Hg1···S13 intermolecular interactions of 3.134(18) Å in **5**. (b) The helical chain network built on Hg···S scaffold. (c) Simplified depiction of helical chain motif in **5**.



**Fig. 7.** (a) Molecular structure of the dinuclear mercury complex **6** and selected bond distances. (b) Molecular diagram and Hg–S bond lengths observed in **7**.

Hg1–S41, Hg1–S13 and weaker Hg1–S43; 2.504(19), 2.422(17), 2.719(2) and 2.995(2) Å, respectively Fig. 7a. The axial position is occupied by N26' ( $2 - x, 2 - y, -z$ ) at 2.375(5) Å. The angles subtended at the metal from the axial N26' atom and a sulphur atom in the equatorial plane are 109.94(14), 99.69(15), 107.22(14), 91.47(15) for S11, S13, S41 and S43 respectively. The two trans angles in the equatorial plane S11–Hg1–S41 and S13–Hg1–S43 are 140.15(8) and 166.03(6)° respectively. This is a unique example of a dinuclear mercury(II) dithiocarbamate complex. The  $\tau$  value of 0.431 is slightly closer to a square pyramid [21] ( $=0$ ) than a trigonal bipyramidal [21] ( $=1$ ) at 0.43. The Hg1 atom lies 0.539(1) Å above the plane of the four sulphur atoms in the equatorial plane (r.m.s deviation = 0.262 Å) in the direction of the transannular N26' atom. This distortion in the square pyramidal geometry may be attributed to the longer Hg1–S43 distance (2.995(2) Å) for the terminally chelated ligand than for the normal Hg–S bond distances and the smaller bite angle of 65.64(6)° about the metal atom. Intramolecular O–H···N hydrogen bonds are formed between the N(Py) and methanolic proton of the solvent molecule in this compound. Intermolecular C–H···S and C–H···π non-covalent interactions play an important role in stabilising the supramolecular structure of the molecule.

The mercury atom in **7** is bonded to two bidentate ligands L4 with dimensions 2.447(2), 2.638(2) Å for S11 and S13 and 2.523(2), 2.584(2) Å for S41 and S43 in an approximate tetrahedral geometry Fig. 7b. The two chelate rings intersect at an angle of 82.78(2)°. The steric obstructions exerted by the orientation of the *N*-methylpyrrole substituents prohibit the involvement of the Py(N) atom in Hg–N bonding (as in **6**) or the Hg···N interactions in this complex [11a]. In the structure of **7** there are no significant interactions between the metal and sulphur atoms from adjacent molecules with the closest contact Hg1···S41' (3.842 Å ( $' = 1 - x, 1 - y, -z$ )). The intermolecular S···S contacts (3.28 Å, less than sum of van der Waals radii) between the adjacent molecules indicates substantial intermolecular interactions between the aggregates in the solid state. Additionally the supramolecular structure is sustained via C–H···π, S···S and C–H···S weak intermolecular interactions Fig. S3, ESI.

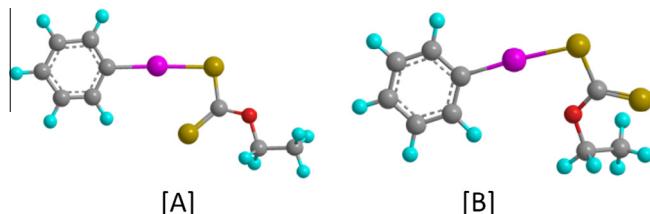
In the dithiocarbamate structures, the C12–N14 bond lengths are in the range 1.31–1.33 Å intermediate between the C–N (1.47 Å) and C=N (1.28 Å) in accordance with the dominant contribution of resonance form Fig. 1 of the ligand. In xanthate

complexes the C12–O14 distances of 1.30–1.34 Å are somewhat longer than the C=O distance indicating C–O character of this bond **Fig. 1**. The C–S bond lengths in the range 1.655(6)–1.741(10) Å are significantly shorter than the C–S single bond (ca. 1.81 Å) due to  $\pi$  electron delocalisation over the X–CS<sub>2</sub> (X = O, N) unit. The C–S distances are also influenced by the participation of corresponding S atoms in intra- and intermolecular Hg···S interactions leading to supramolecular organization. The disulfide S13–S14 distance of 2.176(9) Å in the trithioxanthate complex **3** is well within the range of disulfide linkage [12f].

A thorough inspection of crystal structures of the complexes reveals that apart from the non-covalent and hydrogen bonding interactions, the interesting Hg···O and Hg···S bonding interactions and Hg–N bonding are imperative in bringing out vividly the various coordination modes about the mercury(II) ion in the self assembly of the molecules providing variety of structural motifs.

### 3.2. Theoretical calculations

To assess the role of intramolecular Hg···O bonding interactions in the stabilization of the molecular structure in **2** as opposed to **1**



**Fig. 8.** [A–B] Structure of model compounds employed for assessing the role of Hg···O interactions in **2** as against **1**. (Magenta-mercury, blue-hydrogen, grey-carbon, dirty yellow-sulphur, red-oxygen). (Color online.)

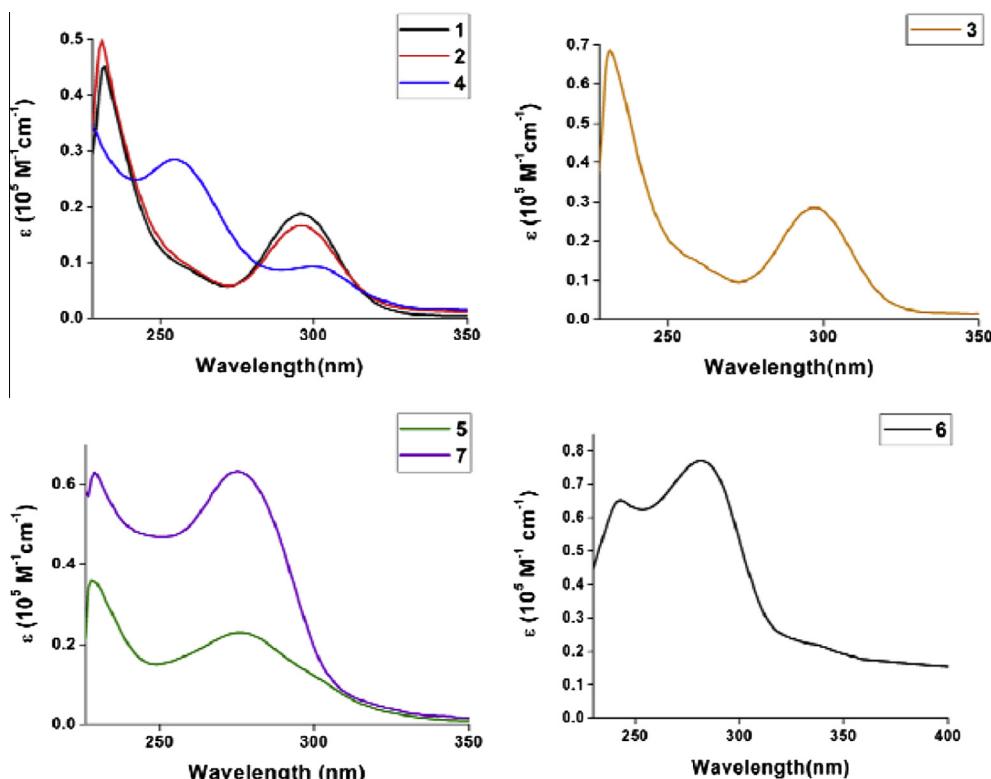
theoretical calculations were carried out taking some model complexes as shown in **Fig. 8**. The iso-amyl and benzyl groups were replaced by the putative derivative CH<sub>3</sub>CH<sub>2</sub> on the O-atom of the xanthate ligand in **1** (model A) and **2** (model B) thus differing only in the core interactions present in each model complex.

The ground state energy difference between model A and B (i.e.  $E_A - E_B$ ) was calculated to be –5.02 kcal/mol which can be attributed to the extra stabilization provided by the intramolecular Hg···O bonding interactions. These results support the fact that the stabilization due to Hg···O interactions favour the orientation of benzyl group towards phenyl ring on Hg atom on the xanthate ligand.

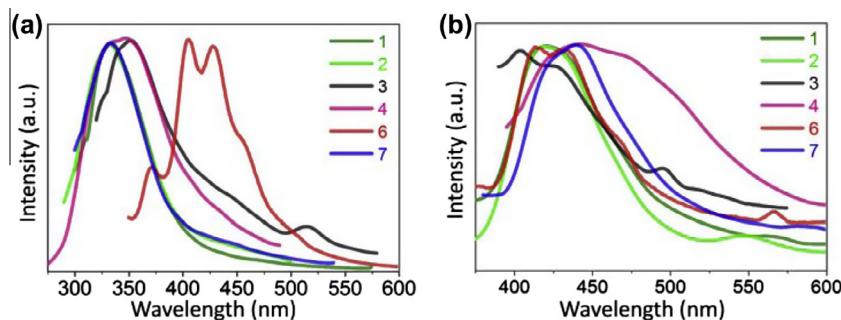
### 3.3. Electronic absorption and emission spectra

The electronic absorption spectra of the complexes **1–7** were recorded in CH<sub>2</sub>Cl<sub>2</sub> solution **Fig. 9** and as solid in Nujol mull **Fig. S5, ESI**. The complexes **1–7** feature one high energy absorption at 240–260 nm and a low energy absorption at 275–300 nm which are assigned to  $\pi-\pi^*$  intra ligand charge transfer (ILCT) transitions of the dithiocarbamate and xanthate ligands [7a,22]. In Nujol mull additional absorptions at 330–360 nm may be assigned to metal perturbed ILCT charge transfer character [7f,22].

TDDFT calculations with various DFT functionals were performed for **3**. The results reveal that a low energy absorption at 297 nm (calculated value) with oscillator strength 0.59143 arises mainly due to HOMO → LUMO transition and may be attributed to the electron transfer from CS<sub>3</sub> core to OCS<sub>2</sub> backbone in the trithioxanthate ligand L' in **3** **Fig. S4, ESI**. Five different functionals (M062X [23a], LC- $\omega$ PBE [23b], CAM-B3LYP [23c], B3LYP [23d], and  $\omega$ B97X [23e]) were used to corroborate prominent theoretical and experimental absorption energies. It is found that CAM-B3LYP functional gives best results for the molecular system as in **3** and



**Fig. 9.** Electronic absorption spectra of complexes in CH<sub>2</sub>Cl<sub>2</sub> solution.



**Fig. 10.** Solution (a) and solid (b) phase emission spectra of complexes **1–7**.

the high energy absorptions in the 235–269 nm region are also well supported [Table S4, ESI](#).

In comparison to other metal ions the luminescent properties of mercury or organomercury compounds are less explored [7f,11a,24]. The luminescent spectra of all the complexes were recorded in  $\text{CH}_2\text{Cl}_2$  solution and solid state at 298 K. When excited at 270–300 nm in solution the **1–4** and **7** show an unstructured emission near 350 nm [Fig. 10a](#). Complex **5** does not luminesce. The luminescence observed in these complexes is associated with the ligand centred transitions. The small Stokes' shift between the absorption and emission bands is indicative of fluorescence emission between the singlet states. Upon excitation at 330 nm, **6** exhibits a structured emission at 370, 406 and 428 nm in solution; the significant red shifted emission in this compound may be ascribed to enhanced delocalisation due to the naphthalene and electron donating pyridine substituents on the  $\text{NCS}_2$  backbone of the dithiocarbamate ligand L6 [Fig. 10a, Table S6-ESI](#).

In the solid state upon excitation at 330–370 nm **1–4** and **7** exhibit unstructured emissions at 400–500 nm however **6** retains the structured feature of the emission bands observed in the solution almost in the same region [Fig. 10b, Table S5-ESI](#). Virtually equivalent solution and solid state emission spectra of **6** suggests that the dinuclear structure is retained in solution as well.

#### 4. Conclusions

Seven new PhHg(II) and mercury(II) dithiocarbamate and xanthate compounds have been synthesized and fully characterized. Their X-ray structures revealed varied coordination patterns involving the intermolecular  $\text{Hg}\cdots\text{S}$  and less common intramolecular  $\text{Hg}\cdots\text{O}$  bonding interactions that have demonstrated unique structural motifs in the organization of supramolecular structures in **2** and **5** respectively. The pyridyl functionalized ligand (L6) formed a  $\mu_2,\kappa^2$  N,S,S bridged dinuclear complex **6** while the analogous pyridyl functionalized ligand, L4 gave a dimer **4** via  $\text{Hg}\cdots\text{S}$  aggregation and a mononuclear dithiocarbamate complex **7**. Notably, **4** and **7** do not form polymeric chains via additional  $\text{Hg}\cdots\text{N}$  interactions as has been established to occur in the analogous dithiocarbamate complexes [11a] presumably because the bulkier naphthyl and N-methyl pyrrole groups involved in the  $\text{C}-\text{H}\cdots\pi$  interactions prevent the formation of close  $\text{Hg}\cdots\text{N}$  interactions. To the best of our knowledge the serendipitously formed **3** is the first example of a PhHg(II) trithioxanthate complex organizing into a 1-D polymeric chain. Compounds **2** and **5** present attractive helical chain motifs built on  $\text{Hg}\cdots\text{S}$  bonding interactions. In the majority of compounds the supramolecular structures have been stabilized through  $\text{C}-\text{H}\cdots\pi$ ,  $\text{C}-\text{H}\cdots\text{S}$ ,  $\text{S}\cdots\text{S}$  and  $\text{C}-\text{H}\cdots\text{O}$  secondary interactions. Except **5**, all the complexes are luminescent in both solution and solid state. The nature of the  $\text{Hg}\cdots\text{O}$  bonding interactions in **2** have been assessed by DFT calculations. This study

demonstrates that the steric bulk and the type of functionality on the N or O atom of the dithiocarbamate and xanthate ligands and the presence or absence of a co-ligand are the key factors that control the adoption of various coordination patterns and their properties. The architecture of supramolecular framework is also governed by various covalent and non covalent interactions including those involving the metal atom. This study widens the scope of the pyridyl functionalized ligands in conjunction with steric bulk of the substituents on the dithio moiety for the design and synthesis of molecular frameworks which may display novel structural organization and material properties.

#### Acknowledgements

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#### Appendix A. Supplementary data

CCDC CCDC 957325, 795905, 915319, 869392, 874505, 928155 and 869393 contain the supplementary crystallographic data for compounds **1–7**, respectively. 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 <http://dx.doi.org/10.1016/j.poly.2013.12.005>.

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