



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 = L1 (**1**), L2 (**2**), L3' (**3**), L4 = (**4**)); [Hg(L)₂] (L = L5 (**5**), L4 (**7**) and [Hg₂(L6)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···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···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···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, d¹⁰ 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···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 CS₂ backbone

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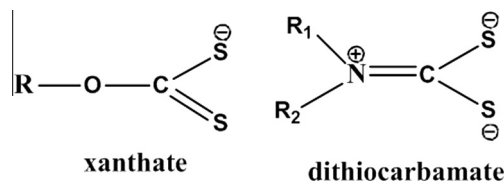


Fig. 1. Dominant canonical form of xanthate and dithiocarbamate ligands.

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 Hg(CO₂CH₃)₂ and C₆H₅Hg(CO₂CH₃) and chemicals such as carbon disulfide, 1-naphthaldehyde, C₆H₅CH₂OH, (CH₃)₂CHCH₂CH₂OH, CH₃CH₂CH₂OH; 1-benzyl-4-hydroxy piperidine, 3-picolylamine and *N*-methyl-2-pyrrolicarboxaldehyde 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.

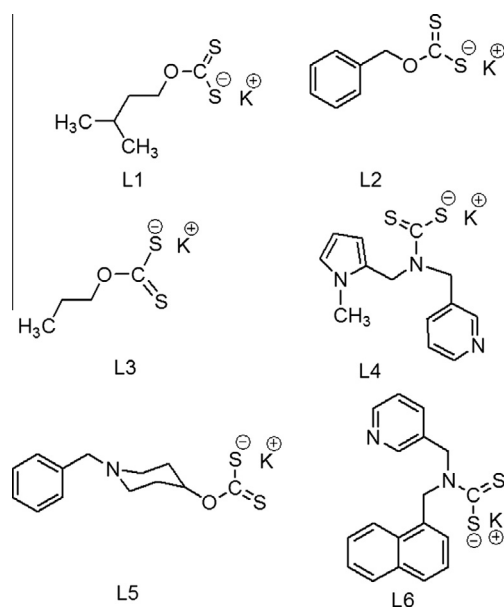


Fig. 2. Structure of the ligands used in present study.

iso-amylxanthate (**KL1**), benzylxanthate (**KL2**), *n*-propylxanthate (**KL3**), *N*-(*N*-methyl-2-pyrrolicarboxaldehyde)-*N*-(methyl-3-pyridyl)dithiocarbamate (**KL4**), 1-benzyl-4-hydroxypiperidine xanthate (**KL5**) and *N*-methyl-1-naphthyl-*N*-(methyl-3-pyridyl)dithiocarbamate (**KL6**) were prepared according to literature procedures [11] by the reaction of the appropriate alcohol or secondary amine with CS₂ and KOH.

The experimental details pertaining to elemental analyses (C, H, N, S) and recording of IR(KBr), ¹H and ¹³C{¹H} NMR and UV–Vis. spectra in CH₂Cl₂ and as Nujol mull are the same as described earlier [11]. The photoluminescent spectra in CH₂Cl₂ 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 (Φ_{overall}) were measured following the protocol described by Brill and co-workers [13] and calculations were done according to the following expression:

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

where R_{c} and R_{st} represent the diffuse reflectance of the coordination complex and of the standard phosphor respectively at a fixed wavelength. Φ_{st} represents the quantum yield of the standard phosphor. The terms A_{c} and A_{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(CO₂CH₃) (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 C₁₂H₁₆HgOS₂ (440.98): C, 32.65; H, 3.66; S, 14.50. Found: C, 32.42; H, 3.75; S, 14.18%. IR (KBr, cm⁻¹): 1234 ($\nu_{\text{C-O}}$), 1027 ($\nu_{\text{C-S}}$). ¹H NMR (300.40 MHz, CDCl₃, ppm): δ 0.98, 0.96 (d, $J = 6$, 6H, (CH₃)₂), 1.55–1.75 (m, 1H, –CH–), 1.75, 1.73, 1.71, 1.70 (q, $J = 6.00$ Hz, 2H, –CH₂–), 4.55, 4.53, 4.51 (t, $J = 6.00$ Hz, 2H, –O–CH₂–), 7.39–7.25 (m, 5H, C₆H₅). ¹³C {¹H}NMR (75.45 MHz, CDCl₃, ppm) δ 22.43 (Me), 25.06 (–CH–), 36.85 (–CH₂–), 74.63 (–CH₂–O–), 128.93, 129.02, 136.86, 154.56 (C₆H₅), 223.88 (–OCS₂). UV–Vis. (CH₂Cl₂, λ_{max} (nm), ϵ (M⁻¹ cm⁻¹)): 297 (1.8 × 10⁴).

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 C₁₄H₁₂HgOS₂ (460.97): C, 36.48; H, 2.62; S, 13.91. Found: C, 36.22; H, 2.70; S, 13.56%. IR (KBr, cm⁻¹): 1262 ($\nu_{\text{C-O}}$), 1041 ($\nu_{\text{C-S}}$). ¹H NMR (300.40 MHz, CDCl₃, ppm): δ 5.50 (s, 2H, –CH₂–O–), 7.44–7.21 (m, 10H, Ar–CH). ¹³C {¹H}NMR (75.45 MHz, CDCl₃, ppm) δ 75.76 (–CH₂–O–), 156.60–126.43 (Ar–C), 221.72 (–OCS₂). UV–Vis. (CH₂Cl₂, λ_{max} (nm), ϵ (M⁻¹ cm⁻¹)): 297 (1.67 × 10⁴).

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