Syntheses, crystal and molecular structures, and properties of some new phenylmercury(II) dithiolate complexes[†]

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A series of new phenylmercury(II) dithio complexes [PhHg(Bu^n_2dtc)] (1; $Bu^n_2dtc^- =$ di-n-butyldithiocarbamate), [PhHg(morphdtc)] (2; morphdtc⁻ = morpholinedithiocarbamate), $[PhHg(Bz_3dtc)]$ (3; Bz_3dtc⁻ = dibenzyldithiocarbamate), [PhHg(methoxethxant)] (4; methoxethxant⁻ = 2-methoxyethylxanthate) [(PhHg)₂NED] (5; NED²⁻ = 1-nitroethylene-2,2-dithiolate) and $[(PhHg)_2CDC]$ (6; CDC²⁻ = cyanodithioimidocarbonate) have been prepared and characterized by elemental analysis, UV-Vis, IR, ¹H and ¹³C NMR spectra and mass spectrometry. The crystal structures of 1, 2 and 3 showed a linear Hg(II) core at the center of the molecules. The weak intra- and intermolecular $Hg \cdots S$ interactions provide a molecular chain framework. The reaction of PhHgO₂CCH₃ with Buⁿ₂dtcH gave the known dimeric complex Hg(Buⁿ₂dtc)₂ while the Ni(O₂CCH₃)₂ mediated reaction gave 1 instead of the expected heterobimetallic complex [PhHgNi(Buⁿ, CS₂)₂]O₂CCH₃ which has been corroborated by natural charges at each atom obtained at the density functional level (DFT) of theory. Upon excitation at 358 nm 3 exhibited a medium strong photoluminescence emission at 420 nm as a consequence of intraligand $\pi \rightarrow \pi^*$ transitions. The electronic absorption bands of **3** were assigned from time dependent density functional theory (TD-DFT) calculations. Geometrical configurations of 4, 5 and 6 have been optimized using the DFT method. All of the complexes are weakly conducting ($\sigma_{rr} \sim 10^{-12} \text{ S cm}^{-1}$). However 2 and 6 exhibited semiconductivity with band gaps of 0.39 and 0.94 eV respectively.

Introduction

Organomercury(II) compounds of the type R_2Hg and RHgX (R = alkyl or aryl; $X = halide or acetate)^1$ have received considerable attention over the last three decades mainly related to the search for biologically active compounds and versatile reagents in controlled transmetallation reactions.² These compounds have been used for many years as intermediates in organic chemistry³ and in the preparation of other organometallics.⁴ Their convenience lies in the ease with which they transfer their organic groups to other atoms, usually replacing a halide or other anionic group. In this way, many new cyclometallated complexes otherwise inaccessible by classical Grignard or lithiation reactions have been prepared.^{4a,i,5} Recent studies have indicated that the coordination of organomercury(II) ions by the donors so as to increase the metal coordination from the usual linear dicoordination to a higher coordination number is quite important in the activation of the Hg–C bond, both in the enzymatic degradation processes and laboratory chemical reactions.6 Symmetrization is a general reaction of the organomercurials which allows the simultaneous formation of symmetric diorganomercurials HgR_2 and Hg(II) complexes.⁷ Such reactions, involving the cleavage of an Hg–C bond, are promoted by strong complexing agents such as sulfur donors.⁷

The xanthate and dithiocarbamate ligands have been found to be extremely versatile moieties for metal directed self assembly leading to supramolecular arrays.⁸ In recent years some organomercury dithiocarbamates, xanthates and dithiophosphates have been prepared and their structures investigated.⁸⁻¹⁰ These possess a linear geometry with significant intra- and intermolecular Hg...S interactions.¹¹ Organomercury(II) compounds provide Lewis acidic metal centers having greater propensity for soft sulfur donors, which can provide intra- and intermolecular Hg...S secondary or hypervalent interactions¹²⁻¹⁴ with diverse and fascinating structural motifs required for crystal engineering.

Mono anionic 1,1-dithioligands such as dithiocarbamate and xanthate as well as dianionic 1,1-dithioligands *e.g.* cyanodithioimidocarbonate $(CDC^{2-})^{15}$ and 1-nitroethylene-2,2dithiolate (NED^{2-}) , where thio functions are on the same carbon, differ appreciably in behaviour.¹⁶⁻¹⁸ The dinegative CDC^{2-} and NED^{2-} may exhibit greater electron delocalization in their complexes through C–S, C=N and N–C=N bonds in CDC^{2-} and C–S, C=C and NO₂ bonds in NED^{2-} , while no such dominant delocalizations are envisaged in the case of xanthate and dithiocarbamate ligands (Chart 1).

Further, the ligand dithiocarbamates and xanthate discussed herein differ from those reported with regards to differing bulky functionalities.¹⁹ This difference in behaviour may provide varying degrees of strain thereby influencing inter- and intra-ligand $S \cdots S$

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 $[\]S$ For crystallographic correspondence.



and $Hg \cdots S$ and other weaker interactions such as hydrogen bonding affecting the overall geometry and molecular stacking in the solid phase.

Despite their synthetic versatility¹⁶⁻¹⁸ and wide range of applications, to the best of our knowledge no work is reported on the organomercury complexes with the dinegative ligands CDC²⁻ and NED²⁻. Bearing in mind the above facts and our interest in the solid state structure and properties of the organomercury(II) dithio complexes, we herein report the synthesis, characterization, solid state conductivity and photoluminescent properties of a series of complexes formed with PhHg(II) and the ligands Buⁿ₂dtc⁻, morphdtc⁻, Bz₂dtc⁻, methoxethxant⁻, NED²⁻ and CDC²⁻. Density functional theory (DFT) and time dependent density functional theory (TD-DFT) calculations have been performed in order to obtain insights into the reaction mechanisms and electronic spectral properties respectively.

Results and discussion

General aspects

Excepting **1**, all the other phenylmercury(II) dithio complexes were synthesized by reacting a methanolic solution of phenylmercuric acetate and the dithio ligands in methanol–water in appropriate stoichiometric ratios as shown in eqn 1 and 2.

PhHgO₂CCH₃ + HL or ML
$$\xrightarrow{\text{MeOH}, \text{H}_2\text{O}}$$

PhHgL + CH₃COOH or CH₃COOM
HL = C₄H₈ONCS₂H; ML = KS₂CO(CH₂)₂CH₃ and NaS₂CNBz₂
(1)

$$2PhHgO_2CCH_3 + K_2L \xrightarrow{MeOH, H_2O} (PhHg)_2L + 2KO_2CCH_3$$
(2)

$$K_2L = K_2CDC \text{ and } K_2NED$$

The synthetic procedure for **1** was entirely different in comparison to the other above mentioned compounds. An attempt was made to prepare **1** by reacting Buⁿ₂NCS₂H and PhHgO₂CCH₃ in stoichiometric ratio but it resulted in the formation of the dimeric Hg(Buⁿ₂NCS₂)₂ complex²⁰ which we have also characterized crystallographically. However, in an attempt to isolate the heterobimetallic complex [PhHgNi(Buⁿ₂NCS₂)₂]O₂CCH₃ by the reaction of Ni(Buⁿ₂NCS₂)₂ and PhHgO₂CCH₃, the crystals of **1** were obtained leaving a black precipitate of nickel sulfide.

The natural charges over various atoms of interest are displayed in Scheme 1. In the case of the nickel complex, the coordinated sulfur and nitrogen atoms of the dithiocarbamate ligand possess



negative charges while the nickel possesses the positive charge as expected, whereas in the phenyl mercuric acetate the mercury atom and the carboxylic carbon bear the positive charge and the two oxygen atoms possess negative charges, which indicates that the ionic interaction is dominating between the Hg and the acetate O atom.

Due to the positive charge on the mercury(II), the coordinated sulfur atom of the nickel complex attacks the thiophilic mercury center to form the preferred linear organomercury(II) dithio complex. The remaining unstable part of the nickel complex gives nickel sulfide. From the calculated natural charges on various atoms, we propose the expected reaction pathway for the formation of **1** (Scheme 1).

All of the compounds are air stable. Crystals of 2 suitable for X-ray analysis were obtained by slow evaporation of acetone–acetonitrile solution while that of 3 was obtained by slow diffusion of methanol in chloroform solution. While the crystals of 1 were obtained directly from the reaction mixture.

Spectroscopy

The IR spectra of all the complexes show distinct vibrational bands at 1003–1029 and 973–991 cm⁻¹ that can be assigned to $v(CS_2)$ vibration. The observed splitting of the $v(CS_2)$, especially in **1**, **2**, **3** and **4**, may be attributed to monodentate coordination of the sulfur atom of the ligand to the PhHg moiety. In **5** and **6**, the presence of only one strong absorption suggests symmetrical bidentate behaviour of the dithiolate groups. The bands in the 1315–1425 cm⁻¹ region in **1**, **2**, **3** and **6** are associated primarily with the thioureide vibration and is assigned to v(C=N), which is appreciably higher than the free ligand and indicates a significant increase in the partial double bond character in the C–N bond. In the case of **4** the v(C=O) frequency also noticeably increases because of the greater electron delocalization over the O–CS₂ group. The bands at 422–460 cm⁻¹ are assigned to the stretching vibration of Hg–C.

The purity and composition of the compounds were checked by NMR spectroscopy. All of the compounds display well-resolved ¹H NMR signals which integrate to the corresponding hydrogens. A perceptible shift of ~10 ppm in the ¹³C spectrum for the C–S₂ carbon in all the complexes as compared to the free dithio ligands indicates the M–S bonding in the complexes. The ES-MS spectra of **1**, **2** and **3** are summarized in the Experimental section.

Crystal structure

The immediate coordination geometry about the Hg atom in **1** and **2** is defined by the *ipso*-C atom of the phenyl group and the atom

S(1) of the dithiocarbamate ligand (Fig. 1 and 2). The Hg–S(1)bond lengths for 1 and 2 are 2.402(2) and 2.3979(12) Å respectively. These are significantly shorter than the $Hg \cdots S(2)$ distances of 2.9465(19) and 2.9725(13) Å for 1 and 2 respectively, thereby reflecting the propensity of Hg to exist in linear coordination geometry. The proximity of atom S(2) is partly responsible for the deviation from the ideal linear geometry, as seen in the C(1)-Hg-S(1) bond angle of 170.60(19)° and 169.97(14)° for 1 and 2 respectively. The deviations from planarity of atoms Hg, S(1), S(2)and C(7), defining the chelate ring are 0.03, 0.06, 0.05 and 0.08 Å respectively for 1, while for 2 these are 0.02, 0.03, 0.03 and 0.04 Å respectively. For 1, the angle between the least-squares plane, *i.e.* Hg, S(1), S(2) and C(7), and that through the Hg-bound phenyl ring is 23.2°, and for 2 it is 23.1°, thereby indicating a certain degree of coplanarity. The C(7)-N bond length in 1 and 2 are 1.322(9) and 1.332(6) Å respectively. These values are intermediate to that of C-N (1.47 Å) and C=N (1.28 Å), thereby indicating the partial double bond character between the C(7)-N bond of the ligand moiety. In 2 the morpholine ring adopts a normal ⁴C chair conformation. Selected bond lengths and bond angles are given in Table 1.



Fig. 1 ORTEP diagram of a molecule of **1** with 50% probability, together with the atom numbering scheme; H atoms are omitted for clarity.



Fig. 2 ORTEP diagram of a molecule of **2** at 50% probability with the atom numbering scheme; H atoms are omitted for clarity.

Like 1 and 2, the crystal structure of 3 has two molecules in the asymmetric unit (Fig. 3 and Table 1) and a mercury core at the center of the linear coordination sphere. The Hg(1)–S(2) and Hg(2)–S(3) bond lengths are 2.395(2) and 2.392(2) Å respectively which are shorter than Hg(1) \cdots S(1) and Hg(2) \cdots S(4) distances having dimensions 2.905(3) and 2.924(3) Å respectively. There is considerable difference between the two C–S bond distances of the ligand, which is the possible cause for the slight deviation from ideal linear geometry as seen in the C(1)–Hg(1)–S(2) and C(22)–Hg(2)–S(3) bond angles 176.1° and 174.0° respectively. The deviation from planarity of atoms Hg(1), S(1), S(2) and



Fig. 3 ORTEP diagram of a molecule of **3** at 50% probability with the atom numbering scheme; H atoms are omitted for clarity. The asymmetric unit comprises two independent molecules.

C(7), which defines the chelate ring, are 0.02, 0.03, 0.04 and 0.05 Å respectively. For Hg(2), S(3), S(4) and C(28) these are 0.02, 0.03, 0.03 and 0.04 Å respectively. The angle between these least-squares planes and those through the Hg-bound phenyl rings are 37.9° and 35.0° respectively, thereby indicating a certain degree of coplanarity in the two molecules present in the asymmetric unit.

The intermolecular $S(2) \cdots Hg'$ interactions in **1** and **2** have distances of 3.22 and 3.17 Å respectively (sym. op: 1 - x, -y, 1 - z) and join the molecules into dimers (Fig. 4 and 5). These Hg \cdots S contacts are comparable to the sum of the van der Waals radii of the respective elements ($r_{vdw}(Hg) = 1.73-2.00$ Å and $r_{vdw}(S) =$ 1.80 Å) and are in the range for organomercury dithiocarbamates.⁸ These dimers are almost orthogonal to each other so there are also weak Hg["] \cdots S(1) interactions in both **1** and **2**, having distances of 3.87 and 3.61 Å respectively (sym. op.: x - 1/2, 1/2 - y, z), joining the dimers together and thus give rise to chains of dimers in both **1** and **2**.



Fig. 4 Molecular chain for 1 showing weak intra- and intermolecular Hg \cdots S interactions. Symmetry operation: Hg' = 1 - x, -y, 1 - z; Hg" = x - 1/2, 1/2 - y, z.

Unlike 1 and 2, in 3 there are only chains of molecules, not chains of dimers, (Fig. 6) due to weak bonds between $S(3)' \cdots Hg(1)$ (3.42 Å) and $S(2) \cdots Hg'$ (3.41 Å) (sym. op: 1 + x, y, z). Also in 3, each Hg atom has two short interactions with the neighboring

Table 1Selected bond lengths and angles for complexes 1, 2 and 3

Bond lengths/Å						
1		2		3		
Hg-C(1) Hg-S(1) Hg-S(2) S(1)-C(7) S(2)-C(7) N-C(7)	2.085(8) 2.402(2) 2.9465(19) 1.754(7) 1.712(7) 1.322(9)	Hg-C(1) Hg-S(1) Hg-S(2) S(1)-C(7) S(2)-C(7) N-C(7)	2.078(5) 2.3979(12) 2.9725(13) 1.750(5) 1.699(5) 1.332(6)	$\begin{array}{c} Hg(1)-C(1)\\ Hg(1)-S(2)\\ Hg(1)-S(1)\\ Hg(2)-C(22)\\ Hg(2)-S(3)\\ Hg(2)-S(3)\\ Hg(2)-S(4)\\ S(1)-C(7)\\ S(2)-C(7)\\ S(3)-C(28)\\ S(4)-C(28)\\ N(1)-C(7)\\ N(2)-C(28)\\ \end{array}$	$\begin{array}{c} 2.079(10)\\ 2.395(2)\\ 2.905(3)\\ 2.098(9)\\ 2.392(2)\\ 2.924(3)\\ 1.665(9)\\ 1.726(10)\\ 1.789(12)\\ 1.699(11)\\ 1.399(14)\\ 1.296(13) \end{array}$	
Bond angles/°						
1		2		3		
C(1)-Hg-S(1) C(1)-Hg-S(2) S(1)-Hg-S(2) C(7)-S(1)-Hg C(7)-S(2)-Hg C(7)-N-C(8) C(7)-N-C(12) C(12)-N-C(8)	170.60(19) $118.6(2)$ $67.17(5)$ $94.5(2)$ $77.9(2)$ $122.5(6)$ $122.5(6)$ $114.9(6)$	C(1)-Hg-S(1) C(1)-Hg-S(2) S(1)-Hg-S(2) C(7)-S(1)-Hg C(7)-S(2)-Hg C(9)-O-C(10) C(7)-N-C(8) C(7)-N-C(11) C(11)-N-C(8)	169.97(14) 114.32(14) 66.66(4) 95.19(16) 77.70(16) 108.9(3) 123.9(4) 121.8(4) 113.4(4)	$\begin{array}{c} C(1)-Hg(1)-S(2)\\ C(1)-Hg(1)-S(1)\\ S(2)-Hg(1)-S(1)\\ C(22)-Hg(2)-S(3)\\ C(22)-Hg(2)-S(4)\\ S(3)-Hg(2)-S(4)\\ C(7)-S(1)-Hg(1)\\ C(7)-S(2)-Hg(1)\\ C(28)-S(3)-Hg(2)\\ C(28)-S(4)-Hg(2)\\ C(7)-N(1)-C(8)\\ C(7)-N(1)-C(15)\\ C(8)-N(1)-C(15)\\ C(8)-N(1)-C(15)\\ C(28)-N(2)-C(29)\\ C(29)-N(2)-C(36)\\ C(29)-N(2)-C(36)\\ C(29)-N(2)-C(36)\\ \end{array}$	$\begin{array}{c} 176.1(3)\\ 116.5(3)\\ 67.26(7)\\ 174.0(3)\\ 117.4(3)\\ 67.40(8)\\ 77.6(4)\\ 92.9(4)\\ 95.0(3)\\ 79.8(4)\\ 121.8(7)\\ 123.8(8)\\ 114.4(7)\\ 125.0(9)\\ 120.7(9)\\ 114.2(8)\end{array}$	



Fig. 5 Molecular chain for 2 showing weak intra- and intermolecular Hg \cdots S interactions. Symmetry operation: Hg' = 1 - x, -y, 1 - z; Hg" = x - 1/2, 1/2 - y, z.

phenyl ring. Hg(1) · · · C(23) (3.36 Å), Hg(1) · · · C(24) (3.55 Å); Hg(2) · · · C(5) (3.51 Å), Hg(2) · · · C(6) (3.37 Å) which are absent in the case of 1 and 2. These distances fall within the sum of the van der Waals radii of the element (r_{vdw} (Hg) = 1.73–2.00 Å and r_{vdw} (C) = 1.70 Å) and are comparable to those found in several mercurials that features Hg · · · C(π) interactions.²¹

Despite our best efforts we could not grow single crystals of 4, 5 and 6. The optimized structure of all these are shown in Fig. 7. In all the three optimized structures, the mercury core lies at the



Fig. 6 Molecular chain for 3 showing weak intra- and intermolecular Hg \cdots S and intermolecular Hg \cdots C interactions. Symmetry operation: 1 + x, y, z.



Fig. 7 Optimised molecular structures for 4, 5 and 6.

center of the almost linear coordination sphere. In 4, the Hg lying at the center of the linear coordination sphere exhibits

Table 2	Selected	bond	lengths	and	angles	for	complexes 4	4, 5	and	6
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Bond lengths/Å						
4		5		6		
Hg-S(1) Hg-S(2) C(2)-S(1) C(3)-S(2) Hg-C(1)	2.501 2.935 1.921 1.875 2.058	$\begin{array}{c} Hg(1)-S(1) \\ Hg(2)-S(2) \\ C(3)-S(1) \\ C(3)-S(2) \\ Hg(1)-C(1) \\ Hg(2)-C(2) \end{array}$	2.465 2.435 1.743 1.795 2.112 2.113	$\begin{array}{c} Hg(1)-S(1)\\ Hg(2)-S(2)\\ C(3)-S(1)\\ C(3)-S(2)\\ Hg(1)-C(1)\\ Hg(2)-C(2)\\ \end{array}$	2.503 2.508 1.903 1.900 2.056 2.048	
Bond angles/°						
4		5		6		
S(1)-Hg-C(1) S(2)-Hg-C(1) S(1)-C(2)-S(2)	171.99 112.36 123.98	S(2)-Hg(2)-C(2) S(1)-Hg(1)-C(1) S(1)-C(3)-S(2)	177.83 174.22 109.27	S(2)-Hg(2)-C(2) S(1)-Hg(1)-C(1) S(1)-C(3)-S(2) C(4)-N-C(3)	175.11 160.11 120.32 114.95	

intramolecular Hg...S interactions. In the case of **5**, only one Hg is involved in an Hg...O interaction with the nitro group while the other remains free. In **6**, one Hg is showing an intramolecular Hg...N interaction with the nitrile group, while the other Hg displays an intramolecular Hg...N interaction with the imido nitrogen of the CDC²⁻ ligand. The selected bond lengths and bond angles for **4**, **5** and **6** are given in Table 2.

Electronic absorption spectra and photoluminescent properties

As compared to other metal ions, studies on the photoluminescent properties of mercury(II) compounds are scarce.^{22–25} Compounds 1, 2 and 3 display very similar electronic absorption spectra in chloroform and exhibit bands near 250, 300 and 350 nm which may be assigned to intraligand transitions.

In CHCl₃ solution, **3** exhibits three bands at 358, 300 and 260 nm in the ultraviolet region (Fig. 8). The TD-DFT calculation indicates that the low energy band (calculated at 356 nm with oscillator strength of 0.0014) is due to the HOMO \rightarrow LUMO electron excitation and attributed to the electron transfer from the uncoordinated sulfur atom of the ligand to the imido nitrogen (Fig. 9). The next two bands (calculated at 288 and 263 nm with oscillator strengths of 0.0547 and 0.2137 respectively) are assigned to the charge transfer transitions from the coordinated and uncoordinated sulfur atoms to the imido group of the ligand dibenzyldithiocarbamate and to the aromatic ring of the organomercury (Fig. 9). Additionally, the absorptions calculated at 259 and 253 nm with oscillator strengths of 0.0466 and 0.0261 respectively are ascribed to ligand-to-metal charge



Fig. 8 Electronic absorption (---) and fluorescence spectra (---) of 3.



Fig. 9 Selected molecular orbitals for 3 (orbital contour values are 0.05).

transfer (LMCT) transitions (Fig. 9). The absorption wavelength values, oscillator strengths and major contributions are listed in Table 3.

When excited at its maximum wavelength for absorption, *i.e.* at 358 nm, only **3** shows a medium-strong photoluminescence emission at 420 nm (Fig. 8). These bands are mainly associated with the intraligand $(\pi \rightarrow \pi^*)^{25}$ transitions, possibly with some admixture of the metal orbitals.

Table 3 Computed absorption wavelength (λ/nm) , oscillator strengths (f), and transition nature of **3**

λ	Energy/eV	Oscillator strength	Major contribution
356	3.4821	0.0014	$n \rightarrow \pi^*$
288	4.2982	0.0547	$n \to \pi^*$
272	4.5614	0.0024	$n ightarrow \pi^*$
263	4.7156	0.2137	$n \rightarrow \pi^*$ (ILCT)
259	4.7809	0.0466	LMCT
254	4.8849	0.0261	LMCT
253	4.9093	0.0014	$\pi ightarrow \pi^*$
252	4.9140	0.0221	$n ightarrow \pi^*$
252	4.9162	0.0106	$\pi ightarrow \pi^*$
249	4.9735	0.0039	$n \to \pi^*$

Pressed pellet conductivity

All the compounds are very weakly conducting with $\sigma_{rt} = 10^{-12}$ S cm⁻¹. Nevertheless **2** and **6** exhibit semiconductivity with band gaps of 0.39 and 0.94 eV respectively (Fig. 10). The solid-state electronic absorption spectra of **2** and **6** display bands between 230–500 nm region which indicates intramolecular delocalisation.† However, the absence of bands in the visible region is indicative of the fact that there is no intermolecular conjugation between the molecules in the solid state. The absence of intermolecular conjugation, along with the irregular stacked structures, is the probable cause of the extremely weak conducting behaviour of the compounds. Also, with an increase in temperature the enhancement in σ may be attributed to the thermal activation of electrons.



Fig. 10 Temperature dependence pressed pellet conductivity for 2 and 6.

Conclusions

In summary, we have synthesized and characterized six phenylmercury(II) complexes with some mono- and di-negative 1,1dithioligands. The weak Hg...S interactions exhibited by the complexes 1, 2 and 3 lead to supramolecular aggregation. Unlike other phenylmercury(II) dithiocarbamates, 3 exhibited only one Hg...S interaction because of bulkiness of the ligand and, exclusively, also shows Hg...C(π) interactions. Addition of nickel(II) promoted the synthesis of 1 which was not isolated otherwise by conventional reaction of the reactants. The complexes **2** and **6** exhibited semiconductivity, whereas **3** showed photoluminescent properties because of the significant intraligand $\pi \rightarrow \pi^*$ transitions. The TD-DFT calculations show that the electronic absorption spectrum of **3** exhibits charge transfer transitions mainly from the coordinated and uncoordinated sulfur atoms to the imido group of the ligand dibenzyldithiocarbamate. The unsuccessful synthesis of **1** by the reaction of $Bu_2^nNCS_2H$ and PhHgO₂CCH₃, which led to the formation of known dimeric [Hg(Bu₂ⁿCS₂)₂]₂, confirms the group transferring property of the organomercury compounds.

Experimental

General considerations

All manipulations were conducted under open atmosphere. Solvents were dried in accordance with the literature procedures. IR as KBr pellets and ¹H and ¹³C NMR spectra were recorded on Varian 3100 FTIR and JEOL AL300 FTNMR spectrophotometers respectively. Chemical shifts were reported in parts per million using TMS as internal standard. Electronic absorption and fluorescence spectra were collected on Shimadzu UV-1700 PharmaSpec UV-Vis Spectrophotometer and Perkin Elmer LS-45 fluorescence spectrometer respectively. Elemental analyses and ESI-MS were performed by Sophisticated Analytical Instrumentation Facility, Central Drug Research Institute, Lucknow. The pressed pellet conductivity of the complexes was recorded on a Keithley 236 Source Measure Unit by employing a conventional two probe technique. Cyanamide, potassium hydroxide, phenylmercuric acetate (Aldrich), carbon disulfide (Merck), di-n-butylamine, dibenzylamine (BDH), morpholine (Qualigens), nitromethane (Spectrochem) and methoxyglycol (Riedel) were used as received. Dipotassium cyanodithioimidocarbonato²⁶ and dipotassium 1nitroethylene-2,2-dithiolate27 were synthesized according to the literature procedure. The dithioxanthate CH₃OCH₂CH₂OCS₂K was prepared by reacting the methoxyglycol, carbon disulfide and KOH in equimolar ratio.

Synthesis of [PhHg(Buⁿ₂dtc)] (1). Di-n-butylamine (0.34 ml, 2 mmol) in water (4 ml) was added gradually to CS_2 (0.12 ml, 2 mmol) at 0 °C with continuous stirring. This was additionally stirred at room temperature for 1 h. Ni(O₂CCH₃)₂·6H₂O (0.249 g, 1 mmol) dissolved in water (4 ml) was added to this reaction mixture slowly and was continually stirred for 4 h at room temperature. To this diethyl ether (20 ml) was added to separate the organic phase which was washed thrice with water. The dark green coloured ethereal solution was filtered and to this was added a methanolic solution (30 ml) of PhHgO₂CCH₃ (0.336 g, 1 mmol) and stirred for another 2 h. The resulting solution was filtered to obtain a clear light green solution which was kept for evaporation. After 24 h the colour of the solution changed to black and thereafter keeping it for 3 d colourless crystals of 1 (0.130 g, 27%) (instead of anticipated heterobimetallic complex) were separated along with the black precipitate presumably of nickel sulfide. Found: C, 37.14; H, 4.78; N, 2.87; S, 13.30%. C₁₅H₂₃NS₂Hg requires: C, 37.26; H, 4.80; N, 2.90; S, 13.24%. $v_{\rm max}$ (KBr)/cm⁻¹ 1420 cm⁻¹ (C=N), 1018 and 973 (C-S), 453 (Hg-C). λ_{max} (CHCl₃)/nm 299 and 349. δ_{H} (300 MHz; CDCl₃; Me₄Si) 0.97 (t, 6H, -CH₃), 1.38 (q, 4H, -CH₂-), 1.79 (t, 4H, -CH₂-), 3.76

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(t, 4H, -CH₂-N), 7.38 (m, 5H, -C₆H₅). $\delta_{\rm C}$ (75.45 MHz; CDCl₃; Me₄Si) 12.8 (-CH₃), 19.1 (-CH₂-), 28.0 (-CH₂-), 54.6 (-CH₂-N), 126.4, 127.1, 128.8, 135.5, 136.2, 153.7 (-C₆H₅), 200.9 (C-S). *m/z* (EI) 172.0 (40%), 412.3 (42), 452.6 (100), 483.1 (8). $\sigma_{\rm rt}$ 9.24 × 10⁻¹² S cm⁻¹.

Synthesis of [PhHg(morphdtc)] (2). To a stirring aqueous solution (4 ml) of morpholine (0.87 ml, 1 mmol) was added CS₂ (0.06 ml, 1 mmol) at 0 °C and then stirred for 1 h at room temperature. To this was added a methanolic solution (15 ml) of PhHgO₂CCH₃ (0.338 g, 1 mmol) which yielded white precipitate 2 (0.343 g, 78%) immediately. This was stirred for another 30 min and the compound formed was suction filtered, washed 5 times with methanol, followed by diethyl ether and dried in vacuo over anhydrous calcium chloride. Found: C, 29.89; H, 2.96; N, 3.16; S, 14.48%. C₁₁H₁₃NOS₂Hg requires: C, 29.93; H, 2.97; N, 3.18; S, 14.50%. v_{max} (KBr)/cm⁻¹ 1425 (C=N), 1024 and 991 (C-S), 1425 (C–O), 450 (C–Hg). λ_{max} (CHCl₃)/nm 296 and 354. δ_{H} (300 MHz; DMSO-d₆; Me₄Si) 3.66 (t, 4H, -CH₂O-), 4.04 (t, 4H, -CH₂N-), 7.20 (t, 1H, $-C_6H_5$), 7.31 (t, 2H, $-C_6H_5$), 7.38 (t, 2H, $-C_6H_5$). $\delta_{\rm C}(75.45 \,{\rm MHz};{\rm DMSO-d_6};{\rm Me_4Si})\,51.6(-{\rm O-CH_2}),65.5(-{\rm N-CH_2}),$ 127.2, 128.3, 137.1, 138.2, 155.6 (-C₆H₅), 201.0 (C-S). m/z (EI) 88.1 (6%), 130.1(12), 279.4 (11), 370.3 (28), 410.7 (100), 439.0 (4). $\sigma_{\rm rt} \ 12.01 \times 10^{-12} \ {\rm S \ cm^{-1}}.$

Synthesis of [PhHg(Bz₂dtc)] (3). To a stirring methanolic solution (30 ml) of PhHgO₂CCH₃ (0.337 g, 1 mmol) was added a methanolic solution (20 ml) of Na(C₆H₅CH₂)₂NCS₂ (0.297 g, 1 mmol). The white precipitate **3** (0.479 g, 87%) formed was additionally stirred for 30 min. This was filtered and treated as for **2**. Found: C, 45.84; H, 3.45; N, 2.58; S, 11.67%. C₂₁H₁₉NS₂Hg requires: C, 45.87; H, 3.47; N, 2.56; S, 11.70%. v_{max} (KBr)/cm⁻¹ 1416 (C=N), 1029 and 1078 (C–S), 460 (C–Hg). λ_{max} (CHCl₃)/nm 260, 300 and 358. $\delta_{\rm H}$ (300 MHz; CDCl₃; Me₄Si) 5.06 (s, 4H,–CH₂–), 7.38 (m, 15H, –C₆H₃). $\delta_{\rm C}$ (75.45 MHz, CDCl₃, Me₄Si) 56.8 (–CH₂–), 127.8, 128.4, 128.8, 134.8, 137.1, 154.1 (–C₆H₅), 205.5 (–C–S). *m*/*z* (EI) 181.2 (8%), 240.1 (100), 411.5 (12), 443.3 (6), 550.0 (2), 600.3 (16). $\sigma_{\rm rt}$ 8.47 × 10⁻¹² S cm⁻¹.

Synthesis of [PhHg(methoxethxant)] (4). A methanolic solution (20 ml) of PhHgO₂CCH₃ (0.337 g, 1 mmol) was added dropwise to a methanolic solution (20 ml) of KCH₃O–CH₂CH₂OCS₂ (0.189 g, 1 mmol) with continuous stirring. Yellow compound **4** (0.339 g,79%) was immediately precipitated. This was stirred for an additional 30 min and isolated in a similar fashion to **2**. Found: C, 27.87; H, 2.80; S, 14.89%. C₁₀H₁₂O₂S₂Hg requires: C, 27.91; H, 2.81; S, 14.87%. ν_{max} (KBr)/cm⁻¹ 1137 (C–O), 1022 and 1055 (C–S), 443 (C–Hg). λ_{max} (CHCl₃)/nm 425, 350 and 265. $\delta_{\rm H}$ (300 MHz; CDCl₃; Me₄Si) 3.42 (s, 3H, –OCH₃), 3.77 (t, 2H, O–CH₂), 4.65 (t, 2H,–CH₂–N), 7.39 (m, 5H, –C₆H₅). $\delta_{\rm C}$ (75.45 MHz; CDCl₃; Me₄Si) 59.1 (CH₃–O), 69.7 (–OCH₂–), 74.2 (–CH₂–O), 128.7, 129.0, 129.1, 136.8, 137.6 (–C₆H₅). 223.8 (C–S). $\sigma_{\rm rt}$ insulating.

Synthesis of [(PhHg)₂NED] (5). To a methanolic solution (30 ml) of PhHgO₂CCH₃ (0.676 g, 2 mmol), was added dropwise a K_2 NED (0.213 g, 1 mmol) solution (30 ml) in 90:10 v/v CH₃OH:H₂O mixture over a period of 15 min with vigorous stirring. Brown yellow compound 5 (0.540 g, 80%) immediately precipitated. This was stirred for another 3 h and thereafter isolated in the same manner as **2**. Found: C, 24.83; H, 1.62; N, 4.12; S, 9.45%. C₁₄H₁₁NO₂S₂Hg₂ requires: C, 24.89; H, 1.64; N,

4.15; S, 9.47%. ν_{max} (KBr)/cm⁻¹ 1591 (C=C), 1291 and 1508 (N–O), 905 (C–N), 1021 (C–S), 422 (C–Hg). λ_{max} (DMSO)/nm 286 and 410. δ_{H} (300 MHz; DMSO-d₆; Me₄Si) 4.22 (s, 1H, –C=C–H), 7.35 (m, 10H, –C₆H₅). δ_{C} (75.45 MHz; DMSO-d₆; Me₄Si) 127.1 (H–C=C), 127.9, 128.4, 136.7, 138.2 (–C₆H₅), 171.0 (C–S). σ_{rt} 11.09 × 10⁻¹² S cm⁻¹.

Synthesis of [(PhHg)₂CDC] (6). To a methanolic solution (30 ml) of PhHgO₂CCH₃ (0.676 g, 2 mmol) was added dropwise a methanolic solution (45 ml) of K₂C₂N₂S₂ (0.194 g, 1 mmol) with vigorous stirring. This was additionally stirred for another 1 h to obtain the yellow product **6** (0.559 g, 83%). This was filtered and treated in accordance with **2**. Found: C, 24.82; H, 1.45; N, 4.18; S, 9.52%. C₁₄H₁₀N₂S₂Hg₂ requires: C, 24.93; H, 1.50; N, 4.16; S, 9.49%. ν_{max} (KBr)/cm⁻¹ 2167 (C≡N), 1313 (C=N), 1020 (C–S), 447 (Hg–C). λ_{max} (DMSO)/nm 220, 360 and 460. $\delta_{\rm H}$ (300 MHz; DMSO-d₆, Me₄Si) 7.35 (m, -C₆H₅). $\delta_{\rm C}$ (75.45 MHz; DMSO-d₆; Me₄Si) 118.4 (-C≡N), 127.8, 128.3, 136.8, 138.2 (-C₆H₅), 210.2 (-C–S). $\sigma_{\rm rt}$ 2.04 × 10⁻¹² S cm⁻¹.

Crystallography

Details about data collection and solution refinement are given in Table 4. Intensity data for the colourless crystals **1**, **2** and **3** were collected at 150(2) K on a Nonius Kappa CCD diffractometer system equipped with graphite monochromated Mo K α radiation $\lambda = 0.71073$ Å. The final unit cell determination, scaling of the data, and corrections for Lorentz and polarization effects were performed with Denzo-SMN.²⁸ The structures were solved by direct methods (SIR97²⁹) and refined by a full-matrix leastsquares procedure based on F^2 .³⁰ All non-hydrogen atoms were refined anisotropically; hydrogen atoms were located at calculated positions and refined using a riding model with isotropic thermal parameters fixed at 1.2 times the U_{eq} value of the appropriate carrier atom. Figures for **1**, **2** and **3** were prepared using ORTEP.³¹

The asymmetric unit in **3** consists of 2 molecules. While the final residuals are acceptable, they are somewhat larger than desirable, a reflection of crystal twinning. Modelling of this pseudo-merohedral twinning (47% for a 100° rotation about the 0 4 1 reciprocal lattice direction) which led to a reduction of *R*1 [based on data for which $I > 2\sigma(I)$] from 15% to the value reported here (7.11%). Concomitant with the convergence of the refinement factor was a reduction in size of the largest peak/hole in the difference map from 28 and -5.06 e Å⁻³, respectively, to the values reported in Table 4. Residual electron density, while chemically non-significant, remains larger than desirable. Overall however, the structure is unambiguous and is being presented on this basis.

Computational details

Geometry optimizations were carried out at the level of density functional theory (DFT) using B3LYP³² functional. Natural charges at each atom have been computed using Kohn–Sham³³ orbitals obtained from DFT calculations. The electronic absorption energies and oscillator strengths for **3** were computed using time dependent density functional theory (TD-DFT) methods using its single crystal X-ray geometry. The 6-31G* basis set was used for C, H, N, O and S atoms. The CEP³⁴ basis set was used for Hg. All calculations were performed using the Gaussian 03³⁵ program.

Table 4 Crystallographic data and structure refinements for 1, 2 and 3

	1	2	3
Empirical formula	$C_{15}H_{23}HgNS_2$	$C_{11}H_{13}HgNOS_2$	$C_{21}H_{19}HgNS_2$
Formula weight/g mol ⁻¹	482.05	439.93	550.08
Temperature/K	150(2)	150(2)	150(2)
Crystal system	Monoclinic	Orthorhombic	Triclinic
Space group	$P2_1/a^a$	$Pcab^{b}$	$P\overline{1}$
a/Å	9.4107(5)	9.4300(10)	8.8490(3)
b/Å	12.8145(6)	12.031(2)	11.6810(5)
c/Å	14.1706(8)	21.6724(3)	18.5340(7)
$a/^{\circ}$			80.935(2)
β/°	95.681(2)		85.358(2)
y/°			90.025(2)
$V/Å^3$	1700.49(15)	2458.78(6)	1885.47(13)
Ζ	4	8	4
$D_{\rm calc}/{ m g~cm^{-3}}$	1.883	2.377	1.938
Absorption coefficient/mm ⁻¹	9.285	12.836	8.388
F(000)	928	1648	1056
Crystal size/mm	$0.25 \times 0.20 \times 0.10$	$0.35 \times 0.35 \times 0.35$	$0.25 \times 0.23 \times 0.10$
θ (minmax.)/°	3.2–27.4	3.3–27.5	5.2-27.4
Reflections collected	23 174	31 979	23 996
Independent reflections	$3847 [R_{int} = 0.118]$	$2817 [R_{int} = 0.095]$	23 996
Data/restraints/parameters	3847/0/174	2817/0/145	23 996/0/453
Final R indices $[\hat{I} > 2\sigma(I)]$	$R_1 = 0.043, wR_2 = 0.091$	$R_1 = 0.031, wR_2 = 0.076$	$R_1 = 0.071, wR_2 = 0.183$
R indices (all data)	$R_1 = 0.078, wR_2 = 0.104$	$R_1 = 0.041, WR_2 = 0.081$	$R_1 = 0.101, wR_2 = 0.202$
Goodness-of-fit on F^2	1.02	1.01	1.05
Largest difference peak and hole/e $Å^{-3}$	1.862 and -2.030	0.968 and -1.013	3.594 and -3.044
$R_1 = \sum F_0 - F_c / \sum F_0 \cdot R_2 = \{ \sum w(F_0) \}$	$(2^{2} - F_{c}^{2}) / \sum w(F_{o}^{2})^{2}]^{1/2}, w = 1 / [\sigma^{2}(F_{o}^{2})^{2}]^{1/2}$	$(xP)^2$, where $P = (F_0^2 + 2F_c^2)/3.^a$	Non-standard setting of $P2_1$

no. 14. ^b Non-standard setting of *Pbca*, no. 61.

Molecular orbital diagrams were constructed with the MOLDEN program.³⁶

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