

Synthesis, structural aspects and ligation behaviour of phenylmercury(II) dithio complexes having Hg-S bonds

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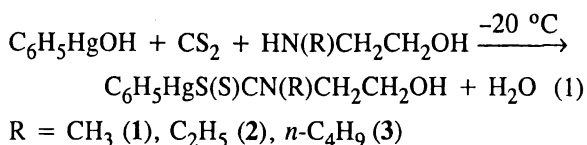
Abstract : Reactions of C_6H_5HgOH with CS_2 and 2-alkyl amino ethanol at $-20^\circ C$ yield neutral two coordinate unsymmetrically substituted phenylmercury(II) *N*-alkyl, *N*-hydroxyethyl dithiocarbamate complexes, $[C_6H_5HgS(S)CN(R)CH_2CH_2OH]$ [$R = CH_3$ (1), C_2H_5 (2), $n-C_4H_9$ (3)]. Few bimetallic derivatives of compound 1 and 2 with Hg^{II} , Cd^{II} and Ag^I salts have also been prepared. The products have been characterised using analytical and spectroscopic (IR, UV, 1H and ^{13}C NMR) data. The bimetallic adducts 4-13 are formed through the coordination of the sulfur atom of phenylmercury(II) *N*-alkyl, *N*-hydroxyethyl dithiocarbamate to the soft metal acceptors.

Keywords : Phenyl mercury, bimetallic adducts, Hg-S bond.

Although the chemistry of metal dithio complexes has been widely studied in bonding mode¹, catalyst², redox-active enzymes³, cubane like cluster⁴ and reactivity⁵ but synthesis and characterisation of bimetallic adducts of metal dithiocarbamates are scarce, and few such compounds have been reported⁶⁻⁸. In view of the above and our interest in studies of the chemistry of sulfur bearing ligands⁹, we report herein the synthesis, spectral characterization and ligation behaviour of some phenylmercury(II) *N*-alkyl, *N*-hydroxyethyl dithiocarbamates.

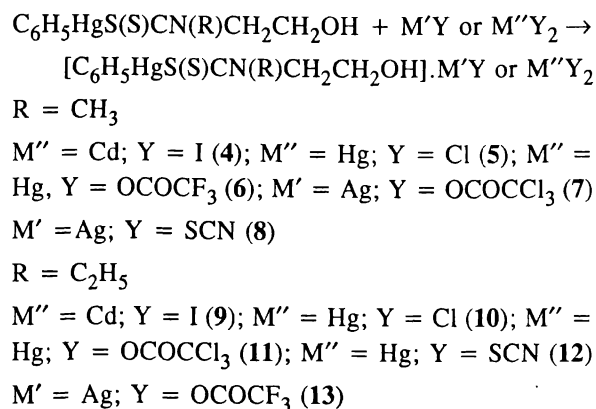
Results and discussion

The interaction of CS_2 with phenyl mercury hydroxide and 2-alkyl amino ethanol at $-20^\circ C$ using tetrahydrofuran as solvent yields the desired products.



In case of *N*-ethyl, *N*-hydroxyethyl dithiocarbamate, 2,2'-dimethoxy propane is used as solvent.

The 1 : 1 bimetallic adducts of compounds 1 and 2 with soft metal acceptors, such as Hg^{II} , Cd^{II} and Ag^I , have been obtained by stirring a mixture of the two components in absolute methanol at room temperature.



The analytical data of the newly synthesized compounds 1-3 are given in Table 1, which indicate 1 : 1 [C_6H_5Hg : dtc] stoichiometry. The products are green solids and are insensitive to atmospheric moisture and oxygen. They are partially soluble in methanol but soluble in DMF and DMSO.

The analytical data for the bimetallic adducts 4-13 are given in Table 2, correspond to 1 : 1 (donor : acceptor) stoichiometry. They are solid and stable at room temperature. They are insoluble in common organic solvents but soluble in DMF and DMSO.

The molar conductance data ($2.63-3.53 \Omega^{-1} cm^2 mol^{-1}$) of compounds 1-3 and bimetallic adducts 4-13 point towards non-electrolytic nature in DMF.

Table 1. Analytical data of 1-3

Sl. no.	Compds.	Colour	Decomp. temp. (°C)	Yield (%)	Elemental analysis (%) : Found (Calcd.)		
					C	H	N
1.	1	Green	194	86	28.14 (28.06)	3.11 (3.06)	3.38 (3.27)
2.	2	Light green	172	88	29.78 (29.89)	3.37 (3.42)	3.08 (3.17)
3.	3	Green	180	82	33.29 (33.22)	4.12 (4.07)	2.91 (2.98)

Table 2. Analytical data of compounds 1-13

Sl. no.	Compds.	Colour	Decomp. temp. (°C)	Yield (%)	Elemental analysis (%) : Found (Calcd.)		
					C	H	N
1.	4	Cream	190	85	15.02 (15.12)	1.71 (1.65)	1.81 (1.76)
2.	5	Off white	210	80	17.15 (17.17)	1.81 (1.87)	2.06 (2.00)
3.	6	Cream	110	92	19.74 (19.67)	1.48 (1.53)	1.73 (1.64)
4.	7	White	165	82	20.57 (20.64)	1.81 (1.88)	2.07 (2.00)
5.	8	White	128	87	20.13 (20.22)	2.29 (2.21)	4.64 (4.72)
6.	9	Cream	125	81	16.25 (16.34)	1.85 (1.87)	1.76 (1.73)
7.	10	Off white	100	90	18.56 (18.52)	2.07 (2.12)	1.89 (1.96)
8.	11	Cream	115	88	11.24 (11.18)	1.35 (1.35)	1.46 (1.44)
9.	12	Cream	186	91	20.55 (20.58)	2.06 (1.99)	5.56 (5.54)
10.	13	White	118	82	23.57 (23.56)	2.21 (2.28)	2.16 (2.11)

UV spectra : UV spectra of compounds 1-3 exhibit a strong absorption band at 263 ± 6 nm, which is attributed to $\pi \rightarrow \pi^*$ transition of $\text{N}=\text{C}=\text{S}$. Another medium band at 291 ± 1 nm belongs to $\pi-\pi^*$ transition of $\text{S}=\text{C}=\text{S}$ moiety. A weak absorption at 315 ± 2 nm is attributed to metal \rightarrow ligand charge transfer. These data supports the presence of CS_2 group in the dithiocarbamate moiety.

IR spectra : The FTIR spectra of these new compounds have been examined in the range $4000-450$ cm^{-1} in KBr. Tentative assignments have been made on the basis of earlier reports¹⁰. The monodentate or bidentate character of the dithiocarbamate group can be distinguished

on the basis of the $(\text{C}=\text{S})$ stretching mode of vibration. The presence of a doublet at 1050 ± 11 and 1019 ± 1 cm^{-1} in the compounds 1-3 invariably indicates the presence of the unidentate dithiocarbamate group bonded to a phenylmercury moiety¹¹.

The absorption at 1470 ± 1 cm^{-1} assigned to $\nu\text{C}=\text{N}$ is characteristic of thiuride bond having partial double bond character¹¹. The $\nu(\text{Hg}-\text{Ph})$ stretching mode of vibration appears in the range 455 ± 2 cm^{-1} (Ref. 12).

In the IR spectra of the bimetallic adducts 4-13, absorption due to $\nu(\text{C}=\text{S})$ are shifted to lower frequency and appear at 1037 ± 7 cm^{-1} . Absorption due to $\nu(\text{C}-\text{S})$ at 1019 ± 1 cm^{-1} , remains almost unaffected indicating

the presence of the unidentate *N*-alkyl, *N*-hydroxyethyl dithiocarbamate group. The $\nu(\text{Hg-S})$ stretching mode of vibration could not be identified as they lie beyond the recorded range of the spectra.

The considerable lowering of the $\nu(\text{C}=\text{S})$ frequency indicates coordination of the sulfur atom of the ligand to the mercury and soft metal acceptors. There is a shift of electron density from nitrogen through carbon and sulfur to the soft metal acceptors. Absorption associated with $\nu\text{C}\cdots\text{N}$ shifts to higher wave number and appears at $1501 \pm 9 \text{ cm}^{-1}$. It is evident that on coordination from the sulfur to soft metal acceptors, a considerable shift of electron density increases the bond order of the $\text{C}\cdots\text{N}$ bond.

The trifluoroacetate groups are unidentate¹³ since $\nu_{\text{asy}}(\text{OCO})$ and $\nu_{\text{sym}}(\text{OCO})$ appear at $1636 \pm 3 \text{ cm}^{-1}$ and $1380 \pm 3 \text{ cm}^{-1}$ respectively with $-\Delta\nu = 256 \pm 6 \text{ cm}^{-1}$. The trichloroacetate group is also unidentately coordinated^{13,14} as $\nu_{\text{asy}}(\text{OCO})$ and $\nu_{\text{sym}}(\text{OCO})$ are located at $1637 \pm 3 \text{ cm}^{-1}$ and $1318 \pm 2 \text{ cm}^{-1}$ respectively with $-\Delta\nu = 319 \pm 6 \text{ cm}^{-1}$. The thiocyanate group is S-bonded since $\nu(\text{NCS})$, $\nu(\text{C}=\text{S})$ and $\delta(\text{SCN})$ appear at 2078 ± 8 , 725 ± 3 and 470 cm^{-1} respectively¹⁵. Absorption due to Hg-Cl and Cd-I stretching modes could not be identified as they lie beyond the recorded range of the spectra.

It is concluded that one of the sulfur atoms of the

unidentate dithiocarbamate group is now attached to phenylmercury and the other is coordinated to the soft metal, giving rise to *N*-alkyl, *N*-hydroxyethyl dithiocarbamate bridged bimetallic adducts.

¹H NMR spectra :

The ¹H NMR spectral data of four representative compounds **1**, **2**, **5** and **9** are presented in Table 3. In the ¹H NMR spectra of all the compounds, the signals of ArH from phenyl protons (*ortho*-, *meta*- and *para*- to Hg) are as expected and appeared at δ 7.18–7.45 ppm as multiplets.

In the ¹H NMR spectra of compound **1**, a multiplet and a triplet appearing at δ 3.85–3.87 ppm and δ 3.70–3.74 ppm are assigned to OCH_2 and NCH_2 respectively. A singlet appears at δ 2.25 ppm for NCH_3 and a triplet at δ 4.92–4.95 ppm is due to OH whereas in the ¹H NMR spectra of compound **2**, a multiplet and a triplet appearing at δ 3.90–4.01 ppm and δ 1.33–1.37 ppm are assigned to $\text{NCH}_2 + \text{OCH}_2$ and CH_3 respectively. A triplet at δ 4.90–4.96 ppm is due to OH.

In the ¹H NMR spectra of bimetallic adduct **5**, a multiplet and a triplet appearing at δ 3.89–3.94 ppm and δ 3.52–3.56 ppm are assigned to OCH_2 and NCH_2 respectively. A singlet appears at δ 2.56 ppm for NCH_3 and a triplet at δ 4.96–5.02 ppm is due to OH. The NCH_2 and

Table 3. ¹H NMR spectral data of compounds **1**, **2**, **5** and **9**

Sl. no.	Compds.	Aryl protons (δ , ppm)	Alkyl protons (δ , ppm)
1.	1	7.18–7.39 (5H, m, $\text{C}_6\text{H}_5\text{-Hg}$)	3.85–3.87 (2H, m, OCH_2 , $^3J(\text{H-H})$ 5.4 Hz), 3.70–3.74 (2H, t, NCH_2), 2.25 (3H, s, NCH_3), 4.92–4.95 (H, t, OH, $^3J(\text{H-H})$ 5.1 Hz)
2.	2	7.25–7.44 (5H, m, $\text{C}_6\text{H}_5\text{-Hg}$)	3.90–4.01 (6H, m, $\text{NCH}_2 + \text{OCH}_2$), 1.31–1.33 (3H, t, CH_3 , $^3J(\text{H-H})$ 7.2 Hz), 4.90–4.96 (H, t, OH, $^3J(\text{H-H})$ 6.6 Hz)
3.	5	7.27–7.45 (5H, m, $\text{C}_6\text{H}_5\text{-Hg}$)	3.89–3.94 (2H, m, OCH_2 , $^3J(\text{H-H})$ 5.4 Hz), 3.52–3.56 (2H, t, NCH_2), 2.56 (3H, s, NCH_3), 4.96–5.02 (H, t, OH, $^3J(\text{H-H})$ 5.1 Hz)
4.	9	7.26–7.41 (5H, m, $\text{C}_6\text{H}_5\text{-Hg}$)	3.94–4.04 (6H, m, $\text{NCH}_2 + \text{OCH}_2$), 1.35–1.40 (3H, t, CH_3 , $^3J(\text{H-H})$ 7.2 Hz), 4.96–5.02 (H, t, OH, $^3J(\text{H-H})$ 6.6 Hz)

NCH_3 signals are deshielded with respect to that of the parent compound **1**.

In the ^1H NMR spectra of bimetallic adduct **9**, a multiplet and a triplet appearing at δ 3.94–4.04 ppm and δ 1.35–1.40 ppm are assigned to $\text{NCH}_2 + \text{OCH}_2$ and CH_3 respectively. A triplet appears at δ 4.96–5.02 ppm is due to OH. The $\text{NCH}_2 + \text{OCH}_2$ and CH_3 signals are deshielded with respect to that of the parent compound **2**. The deshielding of the alkyl protons viz. NCH_2 , NCH_3 , $\text{NCH}_2 + \text{OCH}_2$ and CH_3 in the bimetallic adducts indicates considerable shift of electron density from alkyl group of the dithiocarbamate moiety to the soft metal atom through carbon and sulfur. These results support the findings of infrared spectral data.

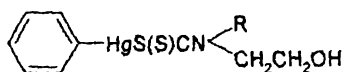
$^{13}\text{C}\{^1\text{H}\}$ NMR spectra :

The $^{13}\text{C}\{^1\text{H}\}$ NMR spectra of two representative compounds **1** and **9** were recorded in DMSO. Assignments for various signals in compound **1** has been made as δ 44.1 ppm (NCH_3), 58.0 ppm (NCH_2), 59.0 ppm (OCH_2), 152.6 ppm (ArC, linked to Hg), 135.9 ppm (ArC, *o* to Hg), 128.8 ppm (ArC, *m* to Hg), 127.3 ppm (ArC, *p* to Hg), 201.5 ppm (NCS_2).

In $^{13}\text{C}\{^1\text{H}\}$ NMR spectra of bimetallic adduct **9**, assignments for various signals are as δ 45.0 ppm (NCH_3), 58.1 ppm (NCH_2), 59.7 ppm (OCH_2), 152.3 ppm (ArC, linked to Hg), 137.0 ppm (ArC, *o* to Hg), 128.3 ppm (ArC, *m* to Hg), 127.9 ppm (ArC, *p* to Hg), 201.6 ppm (NCS_2).

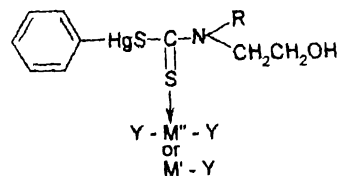
The deshielding of the alkyl carbon viz. OCH_2 , NCH_2 and NCH_3 indicates considerable shift of electron density from alkyl group of the dithiocarbamate moiety to the soft metal atom through carbon and sulfur, which authenticate the results obtained from IR and ^1H NMR spectral data.

On the basis of preceding discussion mainly based on analytical and spectral (UV, IR, ^1H and ^{13}C NMR) evidences and support from previous work^{12,16}, a linear structure containing a unidentate dithiocarbamate group and a two coordinated mercury atom is assigned to compounds **1-3**.



In case of bimetallic adducts **4-13** it may be concluded that the two molecules of metal acceptors are binded to

two different sulfur atoms. The dithiocarbamate group thus acts as a bridge between phenylmercury and soft metal. The following structure may be proposed for $[\text{C}_6\text{H}_5\text{HgS}(\text{S})\text{CN}(\text{R})\text{CH}_2\text{CH}_2\text{OH}]\cdot\text{M}'\text{Y}$ or $\text{M}''\text{Y}_2$.



In these bimetallic adducts, Hg^{II} and Cd^{II} are tri-coordinated¹⁷⁻²⁰ and Ag^{I} possess a coordination number of two²¹.

Experimental

Phenylmercury acetate (Aldrich) was used as such. Solvents were dried and purified by standard procedures²². Phenylmercury hydroxide was freshly prepared by the interaction of 5–10% solution of sodium hydroxide with phenylmercury acetate. The molar conductance of the compounds was measured using a dip-type conductivity cell on a Decible conductivity meter model DC 610 in anhydrous DMF. Microanalysis was carried out on Elementar Vario EL III analyzer.

UV spectra were recorded on a Systronics 2101 double beam spectrophotometer (DMSO, 200–400 nm). FTIR spectra were recorded on a Bruker IFS66V spectrometer (KBr, 4000–450 cm^{-1}). ^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR spectra were recorded at 300 MHz and 75.47 MHz on a Bruker DRX 300FT NMR spectrometer using TMS (as an internal standard) respectively in DMSO (d_6).

Synthesis of phenylmercury(II) N-ethyl, N-hydroxyethyl dithiocarbamate (**2**) :

In a representative experiment, to a mixture of freshly prepared phenylmercury hydroxide (2.94 g, 10 mmol) and carbon disulphide (0.60 mL, 10 mmol) in 2,2'-dimethoxypropane (10 mL), a solution of 2-ethyl amino ethanol (0.98 mL, 10 mmol) in same solvent (10 mL) was added dropwise at -20°C . The mixture was stirred for 3–4 h. The compound was precipitated by the addition of a mixture of diethyl ether and pet ether. It was filtered and washed with diethyl ether. It was dried over P_2O_5 under *vacuo*.

Similarly, the reactions of $\text{C}_6\text{H}_5\text{OH}$, CS_2 with 2-methyl amino ethanol and 2-butyl amino ethanol were carried out.

Reaction of phenylmercury(II) N-alkyl, N-hydroxyethyl dithiocarbamates and soft metal acceptors :

In a typical experiment, a solution of $\text{Hg}(\text{SCN})_2$ (0.316 g, 1 mmol) in absolute methanol (5 mL) was added to a solution of **2** in absolute methanol (5 mL) (0.442 g, 1 mmol) and mixture was stirred at room temperature for 4 h. The precipitated product was filtered, washed several times with methanol to produce analytically pure product and dried under *vacuo*.

Similar bimetallic adducts **4-11,13** were prepared using Hg^{II} , Cd^{II} and Ag^{I} salts as acceptors with compounds **1** and **2**.

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