Phenylmercury Dithio Complexes as Ligands: Preparation and Spectroscopic Characterization of Heterobimetallic Complexes Obtained from Bisdithio Complexes of Ni(II), Pd(II), and Pt(II) as Lewis Acids

Nanhai SINGH,* Nand Kishore SINGH, and Chetna KAW
Chemistry Department, Banaras Hindu University, Varanasi 221005, India

(Received August 28, 1989)

Reaction of PhHgX [X=ethylxanthate (xant) or *N*,*N*′-diethyldithiocarbamate (dtc)] with MX_2 [M=Ni(II), Pd(II) or Pt(II)] occurs, to afford a new class of golden green to yellowish brown organo heterobimetallic complexes, $PhHgXMX_2$ with MS_4 coordination geometry. The precursor PhHgX, have also been characterized. All the complexes are quite stable in solid and solution and are non-conducting species. In PhHgX, IR and NMR spectral studies suggest that dithio ligands are bound to phenylmercury in a linear fashion with additional Hg····S linkage in monodentate manner. Diamagnetism and electronic spectra indicate square planar geometry around M(II) in all the heterobimetallic complexes. IR and NMR spectral studies suggest the presence of monodentate and symmetrical bidentate dithio groups in heterobimetallic complexes.

The chemistry associated with neighboring electronically different metals in bi- and polynuclear clusters is a topic of current interest.1) The interest in heterobinuclear transition metal complexes has risen sharply in recent years2–4) for several reasons such as, models for the active sites of many enzyme systems,5) evaluating the factors that contribute to magnetic exchange6) and formation of heterobinuclear complexes as precursor complex with bridging ligands in electron transfer reactions.7,8) Heterobimetallic complexes are of interest as models of various catalytic processes9) such as the Fischer Tropsch synthesis.10) Organomercury cations are known to react extensively with living organism. Interest in the interaction of mercurials with sulfur containing ligands is high because of the topical problems of mercury poisoning.11) One of the most important applications of organo mercury compounds in organic synthesis is related to their potential for generating radical intermediates.12)

Recently13) several planar bis dithiocomplexes of Ni, Pd, and Pt have attracted much interest because of their high conductivities. Of particular interest is $[Ni(dmit)_2]^{2-}$ which becomes a superconductor at low temperatures and under high pressure.

Binary and ternary complexes of xanthate, dithiocarbamate and dithiophosphate have been extensively studied.14) It is now well established14–18) that when reaction occurs between MX_2 [M=Ni(II), Pd(II), Pt(II)] and most nitrogen or phosphorus donor ligands either 5/6 coordinate or 4 coordinate complexes with structural rearrangement of the bonding sites of ligands are formed. Spectroscopic and X-ray crystallographic studies of MeHgdtc is reported.19) Formation of PhHgxant, with lack of physicochemical studies, is also reported,20) but to our dismay other phenylmercury dithio complexes such as PhHgdtc or PhHgdtp are not known so far.

By Coucouvanis and Cafferry,21) and in the recent years from our laboratory a few papers22,23) have been published on heterobimetallic complexes of *i*-MNT, xanthate, and dithiocarbamate. In view of these wide range of applications and as a part of our on going research we wish to report our investigations on preparation and spectroscopic characterization of organo heterobimetallic complexes by treating phenylmercury dithio complexes as Lewis bases and bis(dithio) complexes of Ni(II) , Pd(II), or Pt(II) as Lewis acids.

Experimental

Materials and Methods: Potassium tetrachloroplatinate(II) and potassium tetrachloropalladate(II) (Johnson-Matthey), phenylmercury acetate (Aldrich), and ammonium diethyldithiophosphate (EGA-CHEMIE) were used as such. Potassium ethylxanthate, sodium diethyldithiocarbamate trihydrate and the simple MX_2 [M=Ni(II), Pd(II), Pt(II); X=dtp, dtc or xant] were prepared according to literature procedures.14,16,24) All other chemicals were BDH (AR) or equivalent grade. The solvents were freshly distilled and dried, if necessary, before use.

Preparation of the Complexes. (i) PhHgX [X=dtp, dtc or xant]: The precursor phenylmercury dithio complexes were synthesized by the reaction of (3.36 g, 10 mmol) 100 cm^3 ethanolic solution of phenylmercury acetate and (1.6 g, 10 mmol) 50 cm^3 aqueous methanolic solution (80 : 20, v/v) of potassium ethylxanthate; (2.25 g, 10 mmol) of diethyldithiocarbamate or (2.03 g, 10 mmol) of ammonium diethyldithiophosphate. The complexes which precipitated immediately as fine crystalline solids were filtered, washed with ethanol, followed by diethyl ether and dried in vacuo.

Heterobimetallic Complexes. (ii) $PhHgXMX_2$ [M=Ni(II), Pd(II), or Pt(II); X=dtc, xant]: Heterobimetallic complexes $PhHgxantNi(xant)_2$ and $PhHgdtcNi(xant)_2$ were prepared by reacting methanol/acetone solution or suspension of (0.40 g, 1 mmol) 10 cm^3 phenylmercury xanthate (0.42 g, 1 mmol) 15 cm^3 phenylmercury dithiocarbamate and 10 cm^3 (0.30 g, 1 mmol) acetone solution of nickel ethylxanthate. The reaction mixture was digested on a water bath at ca. 60 °C. A clear solution is formed which on cooling yielded golden green crystals of the compounds.

Table 1. Color, Melting Point, and Selected Infrared Bands (cm^{-1}) of the Complexes

Complex	Color	Mp/d °C	ν(C-O)	ν(C$\doteq$S)	ν(Hg-C)	ν(M-S)/ν(Hg-S)
PhHgdtc	White	109	—	980(s) 1010(m)	455(m)	— 245(m)
PhHgxant	Light lemon	126	1220(s)	1000$^{a)}$(m)	455(m)	— 250(w)
PhHgxantNi(xant)$_2$	Golden green	102—104	1260(vs)	1000$^{a)}$(s) 1035(s, b)	450(m)	290(m), 250(w)
PhHgdtcNi(xant)$_2$	Golden green	104—106	1250(s)	1000$^{a)}$(s) 1030(s,b)	460(m)	290(m), 240(w)
PhHgxantPd(xant)$_2$	Orange	110(d)	1265(m)	1000$^{a)}$ 1030(s,b)	455(m)	270(w), 255(w)
PhHgxantPd(dtc)$_2$	Yellow	110	1265	1000$^{a)}$	450(m)	275(m), 255(w)
PhHgdtcPd(xant)$_2$	Yellow	75	1270(s)	1000$^{a)}$(s) 1035(s)	455(m)	275(w), 250(m)
PhHgxantPt(xant)$_2$	Dark brown	>300$^{b)}$	1270(w)	1000$^{a)}$(s) 1030(s,b)	450(m)	270(w), 250(w)
PhHgdtcPt(xant)$_2$	Dark brown	>300$^{b)}$	1270(w)	1000$^{a)}$(s) 1025(s,b)	450(m)	270(m), 250(w)
PhHgxantPt(dtc)$_2$	Yellow	160(d)	1260	1000$^{a)}$(s)	450(m)	270(w), 250(w)
			ν(PO$_2$)	ν(P=S)	ν(P-S)	ν(P-O-C) ν(Hg-S)
PhHgdtp	White	74—75	730	660	550	375 250(w)

a) Split band. b) Sharp melting point is not observed due to the dark brown color.

Table 2a. ^{1}H NMR Chemical Shift Data for the Complexes (δ/ppm)

Complex	xant		dtc	
	-C$\underline{H}_3$	-OC$\underline{H}_2$	-C$\underline{H}_3$	-NC$\underline{H}_2$
PhHgdtc	—	—	1.33(t)	3.81(q)
PhHgxant	1.40(t)	4.48(t)	—	—
PhHgxantNi(xant)$_2$	1.47(t)	4.57(q)	—	—
PhHgdtcNi(xant)$_2$	1.48(t)	4.58(q)	1.26(t)	3.61(q)
PhHgxantPd(xant)$_2$	1.47(t)	4.62(q)	—	—
PhHgxantPd(dtc)$_2$	1.35(s)	4.56(q)	1.35(5)	3.71(q)
PhHgxantPt(xant)$_2$	1.43(q)	4.54(5)	—	—
PhHgdtcPt(xant)$_2$	1.40(6)	4.54(6)	1.40(6)	3.56(q)
PhHgxantPt(dtc)$_2$	1.40(6)	4.57(q)	1.40(6)	3.58(q)

Table 2b. ^{13}C NMR Chemical Shift Data for the Complexes (δ/ppm)

Complex	xant		dtc	
	-$\underline{C}$H$_3$	-O$\underline{C}$H$_2$	-$\underline{C}$H$_3$	-N$\underline{C}$H$_2$
PhHgdtc	—	—	12.27	50.18
PhHgxant	13.80	72.21	—	—
PhHgxantNi(xant)$_2$	14.85	68.96	—	—
PhHgdtcNi(xant)$_2$	13.77	68.91	12.48	43.94(d)
PhHgxantPd(xant)$_2$	13.81	68.20 71.62	—	—
PhHgxantPd(dtc)$_2$	13.90	71.70	12.46	44.13
PhHgxantPt(xant)$_2$	13.83	70.25	—	—
PhHgdtcPt(xant)$_2$	13.83	67.5 68.0(d)	12.53	44.39 49.13(d)
PhHgxantPt(dtc)$_2$	13.83	71.64	12.34	44.06

d=doublet.

PhHgXMX$_2$ [M=Pd(II) or Pt(II)] were prepared exactly in the same way in chloroform or 1,2-dichloroethane. The reaction mixture was stirred for ca. 4 hours at room temperature. The light yellowish to yellowish brown crystals of the complexes were formed on keeping the solution for a few days.

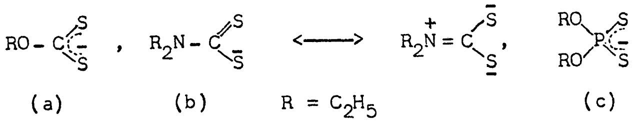
Alternatively PhHgxantM(xant)$_2$ [M=Ni(II) or Pt(II)] were prepared by the reaction of [M(xant)$_3$]$^-$ prepared in situ[25,26] in acetone or CH$_2$Cl$_2$/CHCl$_3$ and phenylmercury acetate in acetone.

The complexes as prepared above were filtered, washed with solvent mixture followed by diethyl ether and dried in vacuo.

Analysis and Physical Measurements: The nickel complexes were analyzed for their metal and sulfur contents following the standard procedures. Carbon, hydrogen, and nitrogen were estimated on a Perkin-Elmer 240 C model microanalyzer. The molecular weight of the complexes was determined cryoscopically in benzene. Magnetic susceptibility measurements were made at room temperature on a Cahn-Faraday electrobalance using Hg[Co(NCS)$_4$] as calibrant. Molar conductivity measurements of the complexes were done in nitrobenzene on a WTW conductivity meter. The infrared spectra were recorded in the region 4000—200 cm^{-1} on Perkin-Elmer 783 in Nujol using KBr discs. Selected IR bands together with color and mp of the complexes are given in Table 1. Electronic spectra were recorded on a Cary-14 spectrophotometer as Nujol-mulls following the procedure of Lee. NMR spectra were obtained in CDCl$_3$ on a JEOL FX-90 Q multinuclear spectrophotometer using TMS as internal reference for ^{1}H and ^{13}C, and H$_3$PO$_4$ as external reference for ^{31}P. The chemical shifts are given in Tables 2a and 2b. Mass spectra of some representative complexes were measured on a JEOL JMS-D 300 mass spectrometer from CDRI, Lucknow.

Results and Discussion

The precursor, phenylmercury dithio complexes, PhHgX melt in 74—126 °C temperature range and are nonconducting in nitrobenzene. Their molecular weights indicate monomeric nature.



There is much evidence that canonical forms of the type (a), (b), and (c) play an important role in the description of the structures of xanthate, dithiophosphate, and dithiocarbamate complexes. For dithiocarbamate, resonance form (b) also contributes considerably. Xanthate, dithiocarbamate or dithiophosphate group can act as a mono, bidentate or bridging ligands and this different behavior can be inferred from IR spectra. However, the assignment of structures of metal xanthates, dithiocarbamates, and dithiophosphates from IR spectra has not always been reliable.

The spectra of these complexes are being dominated by bands characteristics of mono-substituted benzene ring which are known to be relatively insensitive to the nature of the substituents. The occurrence of bands in 1420—1580 cm^{-1} in the infrared spectra of PhHgdtc, is associated primarily, with the thioureide vibration[14a] and is attributed to the ν(C-N) vibration of the S$_2$C-NC$_2$H$_5$ bond. A number of phenyl ring vibrations also occur in this region, so the bands observed in this region cannot be unequivocally assigned either for ν(C-N) or phenyl ring vibrations.

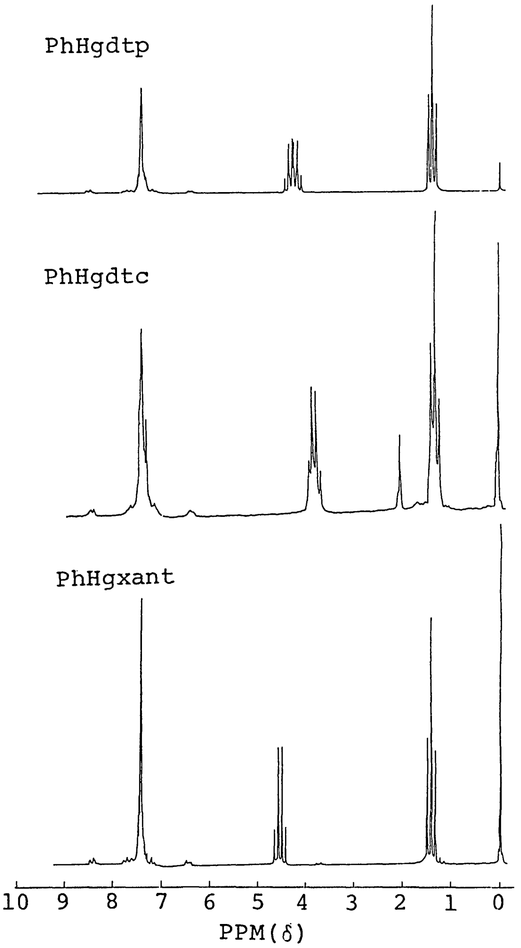


Fig. 1a. ^{1}H NMR spectra.

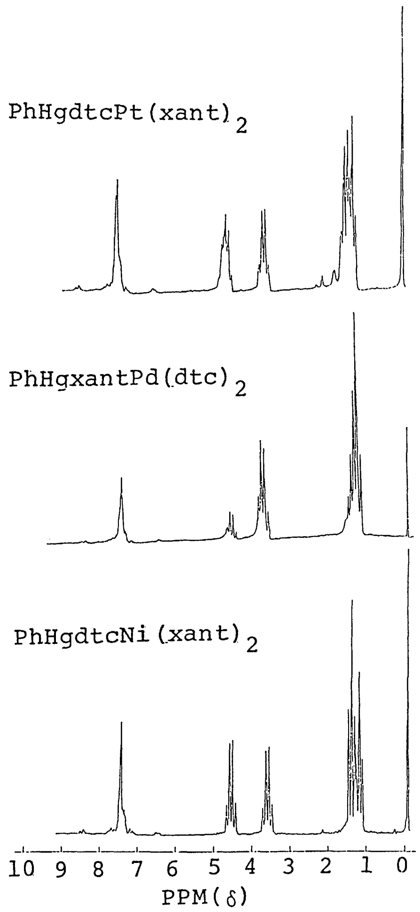


Fig. 1b. ^{1}H NMR spectra.

The second important region between 950—1050 cm^{-1} is associated with the C=S stretching vibrations and has been used effectively in differentiating between bidentate (symmetrical) and monodentate (unsymmetrical) dithiocarbamate ligands. In the former case only one ν(C-S) vibration occurs[28] in the region 950—1050 cm^{-1}, however, if two stretching vibrations are observed in this region with a separation of ca. 20 cm^{-1} [29] monodentate or unsymmetrical bidentate coordination of the ligand may be deduced. Phenylmercury dithiocarbamate exhibits two stretching modes at 980 and 1000 cm^{-1}. These bands may be assigned to ν(C=S) vibrations showing monodentate behavior of dithiocarbamate similar to MeHgdtc.[19]

^{1}H NMR spectra (Fig. 1) of PhHgdtc exhibit a triplet at δ=1.33 and a quartet at δ=3.81 due to -CH$_3$ and -NCH$_2$ protons. The position of -NCH$_2$ proton is near that reported for monodentate dithiocarbamate.[16,20] The ^{13}C NMR spectra (Fig. 2) shows two signals at δ=12.27 and 50.18 due to methyl and methylene carbon atoms. The chemical shift for -NCH$_2$- carbon atom is higher as compared to bidentate (δ=44) dithiocarbamate.

The complexes where xanthate group is bidentate

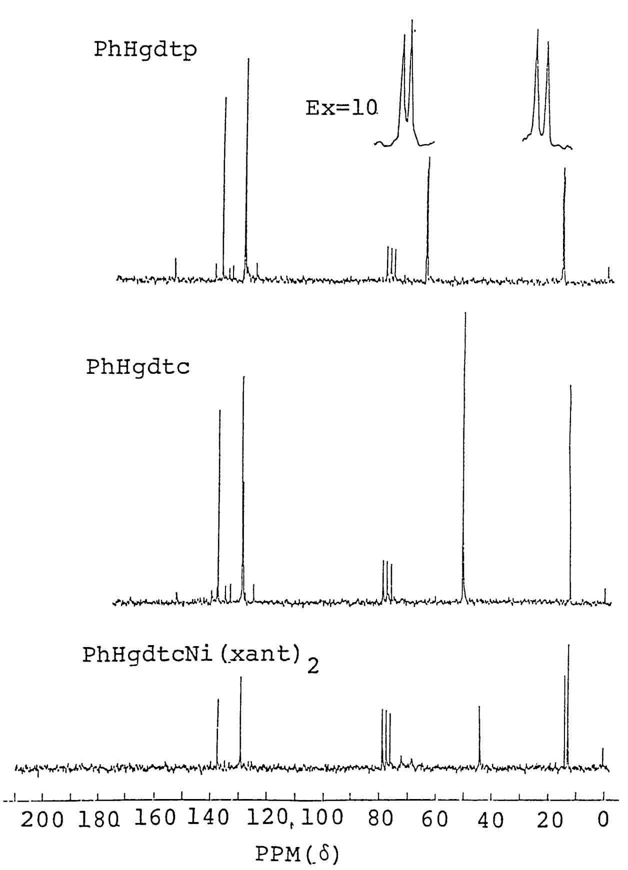


Fig. 2. ^{13}C NMR spectra.

are very common but comparatively very few are known showing monodentate behavior of the ligand.[31,32] The bands observed in the infrared spectra of PhHgxant at 1220 cm^{-1} and a doublet at 1000 cm^{-1} may be assigned to ν(C-O) and ν(C$\dot{=}$S) modes respectively, which may be indicative[24a] of monodentate or asymmetric bidentate behavior of xanthate group.

^{1}H NMR spectra (Fig. 1a) of PhHgxant shows a triplet at δ 1.40 and a quartet at δ 4.48 due to -CH$_3$ and -OCH$_2$ protons. This shows a marked upfield shift as compared to bidentate xanthate in Ni(xant)$_2$ [$\delta_{\mathrm{CH_3}}$=1.62 (t) and $\delta_{\mathrm{OCH_2}}$=4.81 (q)] and is well in the range of monodentate xanthate group reported for CpNiPPh$_3$xant.[32] The ^{13}C NMR spectra of this complex shows two signals at δ=14.19 and 72.21 for -CH$_3$ and -OCH$_2$ carbons respectively. The downfield shift in these carbon atoms as compared to Ni(xant)$_2$ further supports the above nature of xanthate group.

Dithiophosphate group may act in a monodentate, bidentate, bridging or bridging as well as bidentate or mixed bidentate and monodentate fashion[33] with metal ions. In general bidentate or bridging dithiophosphate groups are common but relatively monodentate is rare. On the basis of infrared spectral studies, it is very difficult to distinguish between bidentate and monodentate behavior[33] of dithiophosphate, however, the occurrence of bands in the infrared spectra of PhHgdtp at 730, 660, 550, and 375 cm^{-1} may be assigned to ν(PO$_2$), ν(P=S), ν(P-S), and ν(P-O-C) stretching modes, indicating monodentate or asymmetrical bidentate behavior of dithiophosphate.[33]

^{1}H NMR spectra (Fig. 1a) of PhHgdtp exhibits a triplet at δ=1.42 and a multiplet between δ=4.19—4.55 comprising 8 peaks due to -CH$_3$ and -OCH$_2$ protons respectively. The protons attached to the carbon atoms of P-O-C group show additional coupling with ^{31}P nuclei. The chemical shift observed for -OCH$_2$ proton of PhHgdtp is slightly higher as compared to bidentate dithiophosphate[14a,16] but occurrence of doublet in the ^{13}C NMR spectrum at δ=15.97 and 64.30 due to -CH$_3$ and -OCH$_2$ carbon atoms are well in the range of bidentate dithiophosphate. In the ^{13}C NMR spectra the ^{13}C- ^{31}P NMR coupling has been observed upto three bond lengths. The two lines observed for -CH$_3$ and -OCH$_2$ carbons are due to the coupling of ^{13}C to ^{31}P[33] with a coupling constant of 8 and 9 Hz and may be correlated with ^{2}J(^{13}C- ^{31}P) and ^{3}J(^{13}C- ^{31}P). The ^{31}P spectrum of this complex displays five peaks at δ=98.2 with a coupling constant of 11 Hz corresponding to ^{3}J(P-H), which shows that dtp is covalently bound to Hg(II).[14,33,34]

All the complexes exhibit signals characteristic for phenyl protons and carbons in the expected δ=7.3—7.4 and 129—137 region respectively.[33,35] On the basis of these studies and close similarity of PhHgdtc with MeHgdtc[19] and also to those of PhHgxant and PhHgdtp it may be suggested that these compounds are isostructural where phenylmercury is bonded to one sulfur atom of the dithioligands covalently in a linear manner while second sulfur atom has some additional Hg....S contact (Fig. 3) because of the propensity of mercury toward sulfur donors and also the availability of lone pairs on the coordinated sulfur.

The scope of these interactions in the synthesis of heteronuclear complexes have been explored and accordingly they have been treated as Lewis bases. The Ni(II) (borderline) and Pd(II) or Pt(II) (soft metal)xanthates, dithiocarbamates and dithiophosphate can either raise their coordination number beyond four or may undergo fascile ligand substitution/rearrangement reactions and accordingly they have been treated as Lewis acids.

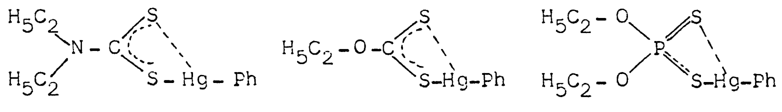


Fig. 3.

Heterobimetallic Complexes. The heterobimetallic complexes $PhHgXMX_2$ are soluble in acetone, methanol, chloroform, benzene, and nitrobenzene. They are non-conducting and melt or decompose in 75—160 °C temperature range. The diamagnetic nature and electronic spectral bands of these complexes are well in the range of square planar geometry around Ni(II), Pd(II), or Pt(II) reported for their bis dithio complexes. Very small change observed in the position of bands as compared to MX_2 suggests that MS_4 coordination around M(II) is retained on heterobimetallic complex formation with some rearrangements in the bonding modes of the dithio ligands covering two metal centers.

Heterobimetallic complexes $PhHgxantM(xant)_2$ invariably show strong IR absorption bands in 1250—1270 cm^{-1}, 1020—1040 cm^{-1} and a split band ca. 1000 cm^{-1} due to ν(C-O) and ν(C$\doteq$S) stretching modes, indicating presence of bidentate and monodentate behavior of xanthate group. In all the complexes, the bands occurring below 500 cm^{-1} have been assigned to ν(Hg-C), ν(P-O-C), and ν(M-S) stretching vibrations.

The ^1H NMR spectra of these complexes (Table 2a) show the characteristic resonances due to presence of $-CH_3$ and $-OCH_2$ protons. The appearance of a sharp quartet (Fig. 1b) at δ=4.58 and a triplet at δ=1.47 due to $-OCH_2$ and $-CH_3$ protons are in between monodentate and bidentate xanthate groups showing intermediate behavior. On bimetallic complex formation two types of xanthate groups viz. bridging and symmetrical bidentate are expected but probably due to rapid rotation of xanthate moiety and additional linkage of one of the free sulfur end of xanthate group to Hg(II), they are not detectable.

In case of $PhHgxantM(dtc)_2$ [M=Pd(II), Pt(II)] the IR absorption bands (Table 1) are characteristic of monodentate as well as bidentate behavior of the ligands. The position of $-OCH_2$ proton δ=4.56 shows an upfield shift (Table 2a) as compared to PhHgxant, indicating monodentate character of xanthate moiety while no appreciable change is observed for methyl proton except increased number of peaks due to mixing of $-CH_3$ protons of dithiocarbamate. The position of $-NCH_2$ proton shows a downfield shift as compared to PhHgdtc, indicating intermediate behavior of dithiocarbamate due to presence of both bidentate as well as monodentate dithiocarbamate.

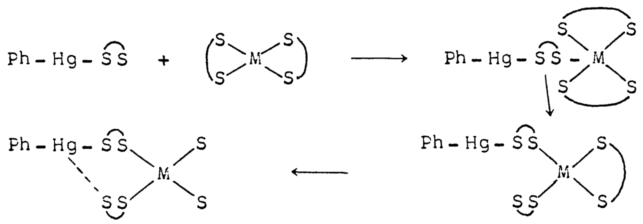
The IR spectra of $PhHgdtcM(xant)_2$ exhibit a split band at 1000 cm^{-1} due to ν(C$\doteq$S) stretching mode. This band may be related to the mixed monodentate and bidentate nature of xant and dtc which is not clearly distinguishable.

The ^1H NMR spectra of these complexes give rise to signals in δ=1.26—1.48 region where the $-CH_3$ protons of xanthate or dtc are mixed (Fig. 1b), giving increased number of peaks. A marked upfield shift is observed for $-NCH_2$ protons of dtc as compared to PhHgdtc on bimetallic complex formation with MX_2 and occurs very near to that known for bidentate dithiocarbamates. This may be caused as a result of monodentate nature of dtc. On the other hand the signals due to $-OCH_2$ protons of xanthates are intermediate, those reported for $M(xant)_2$ and PhHgxant showing monodentate as well as bidentate behavior of xanthate group.

In case of ^1H NMR spectra of $PhHgXPtX_2$ generally each resonance is accompained by weaker doublet signals arising from coupling of ^{195}Pt (I=1/2, natural abundance 34%) and methyl protons of the ligands due to ^5J(Pt-H) giving coupling constant ca. 25 Hz.

In general ^{13}C NMR spectra of the complexes (Table 2b) show the resonances characteristic of $-CH_3$, $-OCH_2$, or $-NCH_2$ carbons of the dithio ligands with no appreciable change in heterobimetallic complex formation; but their position is well in the range reported for covalently bonded xanthate, dithiocarbamate or dithiophosphate group. However, in case of $PhHgdtcMX_2$ and $PhHgXM(dtc)_2$, there is a marked change in the position of $-NCH_2$ carbon of dithiocarbamate (Table 2b). The $-NCH_2$ carbon observed (Fig. 2) at δ=50.18 in PhHgdtc is invariably observed ca. δ=44 in heterobimetallic complexes. This upfield shift observed in ^{13}C NMR spectra may be related to a change in the coordination mode of dithiocarbamate on bimetallic complex formation.

The plausible mechanism for the formation of heterobimetallic complexes $PhHgXMX_2$ is suggested by the following scheme:



M=Ni(II), Pd(II), or Pt(II); $\overset{\frown}{SS}$=xant, dtc

The five coordinate intermediate is expected to arise from PhHgX coordination to metal centers in MX_2. This intermediate could revert to a four coordinate complex around M(II) by displacement of one of the sulfur atoms of dithio group. The four coordinate complex would then contain one chelating and one dangling dithio moiety. The well-known affinity of mercury for sulfur donor and the availability of lone pair on the sulfur atom of dangling dithio group provides additional Hg....S linkage, yielding stable heterobimetallic complexes.

Mass Spectra: The fragmentation pattern of PhHgdtc, $PhHgdtcNi(xant)_2$, and $PhHgxantNi(xant)_2$ exhibit some obvious similarities. Except PhHgdtc, neither of the compounds gives the molecular ion peak. The fragmentation patterns differ in the relative intensities. In PhHgdtcNi(xant)$_2$ the highest observed molecular ion is the one apparently arising from its splitting into PhHgxant and Ni(xant) (dtc). In compound PhHgxantNi(xant)$_2$, the highest observed molecular ion is the one arising from the loss of one xanthate ion at 578. Relatively, this peak is very weak. In this compound the dominating peaks are observed mainly from its splitting into PhHgxant and Ni(xant)$_2$. In general the fragments containing the metal atom were readily identified by their characteristic isotopic patterns.

Authors gratefully acknowledge the free gift of palladium and platinum salts from Dr. R. N. Singh and Dr. S. P. Singh, Banaras Hindu University. One of the authors (Chetna Kaw) is also thankful to CSIR (Scheme) for financial assistance in the form of JRF.

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