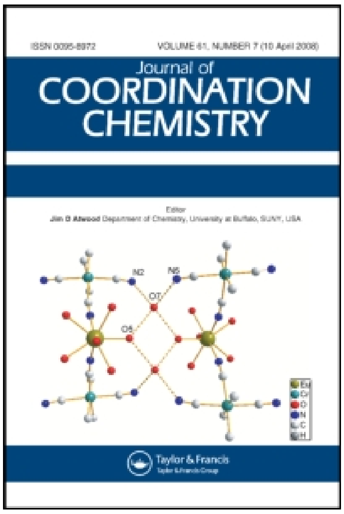

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SYNTHESIS AND STRUCTURAL STUDIES OF A NEW CLASS OF ORGANOBIMETALLIC COMPOUNDS

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SYNTHESIS AND STRUCTURAL STUDIES OF A NEW CLASS OF ORGANOBIMETALLIC COMPOUNDS

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A new class of organobimetallic compounds of general formula $(SCN)_2Zn(NCSHgR)_2$ and $(SCN)_2Co(NCSHgR)_2$ ($R = CH_3$, C_2H_5, n-C_4H_9 and *iso*-C_4H_9) have been synthesized. The cobalt analogs have been found to act as Lewis acids hence their complexes with pyridine, nicotinamide and 2,2′-bipyridyl have also been prepared. The corresponding zinc compounds decompose on reaction with these bases. These compounds have been characterized by elemental analyses, molar conductance, molecular weight determination, infrared spectral (4000–50 cm^{-1}), electronic spectral and magnetic moment studies. These studies indicate that the Lewis acids are monomers and the cobalt or zinc and mercury atoms are connected through bridging thiocyanate groups. The cobalt or zinc atoms acquire a tetrahedral coordination geometry, whereas mercury retains its linearity.

INTRODUCTION

Organometallic compounds having two different metal ions are rare in the literature. In our recent communication[1] we have reported for the first time studies on two new organobimetallic compounds and their complexes. A more systematic study on a few more new compounds is presented in this paper.

EXPERIMENTAL

Materials and Manipulations

Reagent grade (BDH) chemicals were purified and dried before use. C_2H_5HgCl, n-C_4H_9HgCl and *iso*-C_4H_9HgCl were prepared from the Grignard reagent by adopting the procedure described elsewhere.[2] These chlorides were converted into thiocyanates by stirring them with KSCN in acetone in a 1 : 1 molar ratio. The precipitated KCl was filtered off and the filtrate was concentrated by evaporation under reduced pressure. On addition of water to the concentrate, the thiocyanates were precipitated, filtered, washed with water, recrystallised from ethanol and dried over P_2O_5 in vacuum. C_2H_5HgSCN m.p. 131°C, n-C_4H_9HgSCN m.p. 80°C, *iso*-C_4H_9HgSCN m.p. 40°C. CH_3HgSCN could not be prepared from CH_3HgCl hence for its preparation $(CH_3)_2Hg$ was first prepared from the Grignard reagent[3] and the thiocyanate was obtained by the metathetical reaction of $(CH_3)_2Hg$ and $Hg(SCN)_2$ in acetone. The CH_3HgSCN was recrystallised from ethanol, m.p. 110°C. The RHgSCN complexes were characterized by elemental analyses and infrared spectra.

Preparation of Lewis-acids $(SCN)_2M(NCSHgR)_2$ ($R = CH_3$, C_2H_5, n-C_4H_9 and iso-C_4H_9, M = Co(ii), Zn(II)

(1) 1.75 gm of $Co(NCS)_2$ (1 mmol) and 5.6 gm of CH_3HgSCN (2 mmol) were dissolved in 25 cm^3 of ethanol and 100 cm^3 of ethyl acetate in two separate flasks. Both solutions were

mixed and stirred for 24 hours. A blue precipitate appeared, which was filtered, washed with ethyl acetate and dried in vacuum. Ethyl, *n*-butyl and *iso*-butyl analogs were similarly prepared from their respective thiocyanates. These compounds melt with decomposition in the range 165–180°C. The zinc analogs were similarly prepared from $Zn(NCS)_2$ and RHgSCN.

(2) 3.32 gm of $Co(NCS)_2.2py$ (1 mmol) and 5.6 gm of CH_3HgSCN (2 mmol) were separately dissolved in 100 cm^3 of ethanol. The two solutions were mixed and stirred for 24 hours. A pink precipitate appeared which was filtered, washed with solvent, recrystallised from acetone and dried in vacuum. The analytical results and molecular weight determination show that it has a molecular formula $Py_2Co(NCS)_2(NCSHgR)_2$. On heating this compound in vacuum $(NCS)_2Co(NCSHgCH_3)_2$ was obtained. Ethyl, *n*-butyl and *iso*-butyl analogs were similarly prepared.

Preparation of complexes $L_2Co(NCS)_2(NCSHgR)_2$ and $[Co(L-L)_3][(SCN)_2HgR]_2$ L = py, nia, $L-L$ = 22'-bipyridyl

$Co(NCS)_2$ 2nia was prepared by reaction of $Co(NCS)_2$ with nicotinamide in a 1:2 molar ratio. This compound was crystallized and characterized. 4.18 gm of $Co(NCS)_2.2$ nia (1 m mol) was dissolved in 100 cm^3 of ethanol. To this solution 100 cm^3 of an ethanolic solution containing 5.6 gm of CH_3HgSCN (2 mmol) was added. The mixture was stirred until a pink compound was formed. This was filtered, washed with solvent, recrystallised from acetone and dried in vacuum. The pyridine complexes were prepared in a similar manner.

Alternatively these compounds can be prepared by mixing a suspension of the Lewis acid in ethanol with the solution of the ligand in the same solvent in the suitable molar ratio and completing the process as above. Bipyridyl derivatives were prepared by mixing a suspension of the Lewis acid in ethanol with an ethanolic solution of bipyridyl in a 1 : 3 molar ratio and stirring for 24 hours. A pink solid appeared which was filtered, washed with solvent, recrystallized from a DMSO and methanol mixture and dried in vacuum. The ethyl, *n*-butyl and *iso*-butyl derivatives were prepared similarly from their respective thiocyanates.

Analyses

Sulphur was estimated as barium sulphate, mercury as mercury sulphide, cobalt as cobalt anthranilate and zinc as zinc ammonium phosphate. Nitrogen was estimated by a semi-micro Kjeldahl method. All complexes gave satisfactory elemental analyses and the results are given in Table I.

Physical Measurements

Molecular weights were determined in DMSO by the cryoscopic method. Infrared spectra of the complexes were recorded in nujol mulls or in KBr pellets on a Perkin Elmer spectrophotometer model 621 in the range 4000–400 cm^{-1} and in polyethylene discs in the range 500–50 cm^{-1} on a polytech F.I.R. 30 fourier spectrophotometer. Important spectral bands and their assignments are given in Table II. Electronic spectra were recorded in nujol mulls using a Cary-14 spectrophotometer. Magnetic susceptibility measurements were made at room temperature on a Cahn-Faraday electro balance using $CoHg(SCN)_4$ as calibrant. The μ_{eff} values, position of d-d transition bands, their assignments and various ligand field parameters are presented in Table III. The conductance of the complexes were determined in DMF using a Philips conductivity bridge model PR-9500.

TABLE I
Analytical data for the complexes

Complexes	Colour	M.P.(°)	% Cobalt Zinc		% Mercury		% Sulphur		% Nitrogen	
			cal	found	cal	found	cal	found	cal	found
$(SCN)_2Co(NCSHgCH_3)_2$	Blue	185[a]	8.0	7.5	55.5	54.9	17.7	17.6	7.7	7.4
$py_2Co(NCS)_2(NCSHgCH_3)_2$	Red	180	6.6	6.2	45.5	44.5	14.5	14.4	9.5	9.2
$(nia)_2Co(NCS)_2(NCSHgCH_3)_2$	pink	165[a]	6.0	5.7	41.5	40.4	13.3	13.1	11.6	11.3
$[Co(bipy)_3][(NCS)_2HgCH_3]_2$	Red	195[a]	4.9	4.5	33.7	32.8	10.8	10.3	11.8	11.6
$(SCN)_2Co(NCSHgC_2H_5)_2$	Blue	180[a]	7.7	7.2	53.5	52.4	17.1	17.0	7.5	7.2
$py_2Co(NCS)_2(NCSHgC_2H_5)_2$	Red	182	6.4	5.9	44.1	43.2	14.1	14.0	9.3	9.1
$(nia)_2Co(NCS)_2(NCSHgC_2H_5)_2$	Pink	165[a]	5.8	5.3	40.3	39.2	12.9	12.7	11.3	10.9
$[Co(bipy)_3][(NCS)_2HgC_2H_5]_2$	Red	190[a]	4.7	4.2	32.9	32.0	10.5	10.4	11.5	11.0
$(SCN)_2Co(NCSHg\ n\text{-}C_4H_9)_2$	Blue	165[a]	7.2	6.8	49.7	48.9	15.9	15.7	6.9	6.7
$py_2Co(NCS)_2(NCSHg\ n\text{-}C_4H_9)_2$	Pink	163	6.0	5.4	41.6	41.0	13.3	13.0	8.7	8.4
$(nia)_2Co(NCS)_2(NCSHg\ n\text{-}C_4H_9)_2$	Pink	160[a]	5.5	5.0	38.2	37.4	12.2	11.9	10.7	10.4
$[Co(bipy)_3][(NCS)_2Hg\ n\text{-}C_4H_9]_2$	Red	175[a]	4.6	4.3	31.4	30.8	10.0	9.7	11.0	10.6
$(SCN)_2Co(NCSHg\ n\text{-}C_4H_9)_2$	Blue	165[a]	7.2	6.8	49.7	48.9	15.9	15.6	6.9	6.7
$py_2Co(NCS)_2(NCSHg\ iso\text{-}C_4H_9)_2$	Pink	163	6.0	5.7	41.6	40.7	13.3	13.0	8.7	8.3
$(nia)_2Co(NCS)_2(NCSHg\ iso\text{-}C_4H_9)_2$	Pink	165[a]	5.5	5.1	38.2	37.8	12.2	11.7	10.7	10.2
$[Co(bipy)_3][(NCS)_2Hg\ iso\text{-}C_4H_9]_2$	Red	175[a]	4.6	4.3	31.4	30.5	10.0	9.7	11.0	10.5
$(SCN)_2Zn(NCSHgCH_3)_2$	White	172[a]	8.9	8.4	55.1	54.2	17.6	17.1	7.7	7.2
$(SCN)_2Zn(NCSHgC_2H_5)_2$	White	165[a]	8.6	8.1	52.0	51.5	16.9	16.2	7.4	7.0
$(SCN)_2Zn(NCSHg\ n\text{-}C_4H_9)_2$	White	165[a]	7.9	7.2	48.8	47.1	15.6	15.1	6.8	6.5
$(SCN)_2Zn(NCSHg\ iso\text{-}C_4H_9)_2$	White	160[a]	7.9	7.1	48.8	47.4	15.6	15.2	6.8	6.3

[a] Melt with decomposition.

TABLE II
Infrared spectral band assignments for the complexes

Complexes	νHg-C	νHg-SCN	νM-NCS	νM-L	δL-M-L	δN-M-N	δS-Hg-C
$(SCN)_2Co(NCSHgCH_3)_2$	530(s)	220(s)	300(vs)	—	—	177(s)	77(s)
$(Py)_2Co(NCS)_2(NCSHgCH_3)_2$	525(m)	230(s)	257(s)	277(sh)	155(m)	177(sh)	75(m)
$(nia)_2Co(NCS)_2(NCSHgCH_3)_2$	530(s)	225(m)	258(sh)	270(m)	157(sh)	165(m)	79(w)
$[Co(bipy)_3][(NCS)_2HgCH_3]_2$	543(s)	230(s)	—	245(s)	160(m)	—	77(s)
$(SCN)_2Co(NCSHgC_2H_5)_2$	520(s)	205(s)	290(vs)	—	—	180(m)	80(m)
$(Py)_2Co(NCS)_2(NCSHgC_2H_5)_2$	530(s)	220(w)	273(s)	260(m)	177(s)	188(sh)	80(m)
$(nia)_2Co(NCS)_2(NCSHgC_2H_5)_2$	535(m)	230(m)	265(s)	270(sh)	155(sh)	170(m)	75(w)
$[Co(bipy)_3][(NCS)_2HgC_2H_5]_2$	540(s)	225(s)	—	250(s)	165(m)	—	77(m)
$(SCN)_2Co(NCSHg\ n\text{-}C_4H_9)_2$	525(s)	220(s)	300(vs)	—	—	178(s)	80(m)
$(Py)_2Co(NCS)_2(NCSHg\ n\text{-}C_4H_9)_2$	510(m)	230(m)	250(m)	260(s)	165(m)	172(w)	80(sh)
$(nia)_2Co(NCS)_2(NCSHg\ n\text{-}C_4H_9)_2$	530(s)	235(s)	260(s)	270(m)	150(w)	170(m)	77(w)
$[Co(bipy)_3][(NCS)_2Hg\ n\text{-}C_4H_9]_2$	525(m)	230(s)	—	255(s)	155(m)	—	75(m)
$(SCN)_2Zn(NCSHgCH_3)$	530(s)	220(m)	305(s)			178(m)	80(m)
$(SCN)_2Zn(NCSHgC_2H_5)_2$	520(s)	230(m)	300(s)	—	—	180(m)	77(s)
$(SCN)_2Zn(NCSHg\ n\text{-}C_4H_9)_2$	525(s)	225(s)	305(s)	—	—	188(m)	75(m)

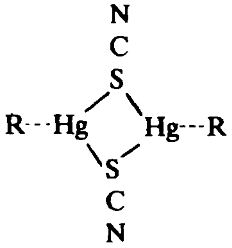
TABLE III
Selected electronic bands and their spectral parameters, molar conductance and mol. wts.

Complexes	μ_{eff} (B.M)	ν_3 cm^{-1}	ν_2 cm^{-1}	ν_1 cm^{-1}	Dq cm^{-1}	B′	β	Λ cm^2 mhos/mol		Mol. wt.	
								M/512	M/1024	cal.	found
$(SCN)_2Co(NCSHgCH_3)_2$	4.60	16390	7840	—	425	897	0.92	51.6	59.1		
$py_2Co(NCS)_2(NCSHgCH_3)_2$	5.15	20830	16666	9000	891	948	0.97	55.7	60.2	878	953
$(nia)_2Co(NCS)_2(NCSHgCH_3)_2$	5.10	21050	17210	9000	920	944	0.97	60.1	61.9	964	1070
$[Co(bipy)_3][(NCS)_2HgCH_3]_2$	4.99	21050	16530	8950	884	967	0.99	124.2	138.8		
$(SCN)_2Co(NCSHgC_2H_5)_2$	4.42	16530	7905	—	429	905	0.93	52.5	60.4		
$py_2Co(NCS)_2(NCSHgC_2H_5)_2$	5.06	20620	16530	8850	883	963	0.96	53.4	59.5	906	1001
$(nia)_2Co(NCS)_2(NCSHgC_2H_5)_2$	5.10	20930	16955	9100	906	945	0.97	56.8	60.7	992	895
$[Co(bipy)_3][(NCS)_2HgC_2H_5]_2$	5.00	21460	16530	9020	885	946	0.97	130.1	138.2		
$(SCN)_2Co(NCSHg\ n\text{-}C_4H_9)_2$	4.41	16450	7815	—	424	902	0.92	49.2	55.5		
$py_2Co(NCS)_2(NCSHg\ n\text{-}C_4H_9)_2$	4.95	21050	17210	9010	920	944	0.97	52.7	58.7	962	840
$(nia)_2Co(NCS)_2(NCSHg\ n\text{-}C_4H_9)_2$	5.02	20920	16950	9100	905	944	0.97	50.9	56.5	1048	918
$[Co(bipy)_3][(NCS)_2Hg\ n\text{-}C_4H_9]_2$	4.90	21400	16390	8750	877	943	0.96	130.8	135.5		
$(SCN)_2Co(NCSHg\ iso\text{-}C_4H_9)_2$	4.30	16660	8000	—	415	875	0.90	60.1	64.5		
$py_2Co(NCS)_2(NCSHg\ iso\text{-}C_4H_9)_2$	5.10	21740	17830	9000	890	910	0.93	50.5	55.7		
$(nia)_2Co(NCS)_2(NCSHg\ iso\text{-}C_4H_9)_2$	4.95	21270	17000	8860	870	925	0.95	55.1	60.2		
$[Co(bipy)_3][(NCS)_2Hg\ iso\text{-}C_4H_9]_2$	5.19	21470	16535	9025	887	945	0.97	130.8	138.5		

RESULTS AND DISCUSSION

Lewis acids

$(SCN)_2M(NCSHgR)_2$ (M = Co, Zn). These are non conducting in polar solvents and are formed by direct addition of RHgSCN to $M(NCS)_2$. The molecular weights of their derivatives, solubility and low melting point indicate that they are monomeric adducts. In these compounds $M(NCS)_2$ probably act as Lewis acids and RHgSCN as Lewis bases. The acid base behaviour of the two components can be demonstrated by the changes observed in the infrared spectral bands of RHgSCN on adduct formation. The structure of RHgSCN may be dimeric centrosymmetric where a four membered Hg_2S_2 rings is formed.[4] The solid phase ir spectra of



this compound show the presence of C-N (st) bands at 2181, C-S (st) at 738, Hg-S (st) at 238, SCN bending at 440 and Hg-C (st) at 543 cm^{-1}. The position of these bands is considerably changed when the spectrum is recorded in solution. The C-N (st) is observed at 2136 and Hg-S (st) at 283.[4] This indicates that bridging through the sulphur of thiocyanate is broken in solution. On comparison of the various bands of RHgSCN with the corresponding bands of the adducts, changes are observed in the C-N (st), C-S (st), Hg-S (st) and Hg-C (st) bands (Table II). These changes indicate that the thiocyanate of RHgSCN, becomes bridging and coordinates to M through its N-end. A band in C-N (st) region at 2080 cm^{-1} is also observed in all the Lewis acids. This can be attributed to N-bonded thiocyanate arising from M-NCS, and can be supported by its analogy to the reported band in $M(NCS)_2.2L$.[5,6] The positions of M-N (st) and C-N (st) bands in $M(NCS)_2$ are not altered on adduct formation. The electronic spectra of the Lewis-acids show the presence of two intense bands due to d-d transitions in the region 16500 cm^{-1} and 8000 cm^{-1}. The positions of these bands in solid and solution phase spectra remain the same which shows that there is no solvolysis. The bands in the region 16500 cm^{-1} are assigned to $^4A_2 \rightarrow {}^4T_2(F)$ (ν_3) and in the region 8000 cm^{-1} to $^4A_2 \rightarrow {}^4T_1(F)$ (ν_2). The Dq values as calculated from ν_3 and ν_2 band positions are in the range 420–425. Magnetic moment are 4.2–4.6 B.M. These results show that cobalt has tetrahedral geometry. (Figure 1). This symmetry will yield one ir active band for M-N, which is consistent with the observations.

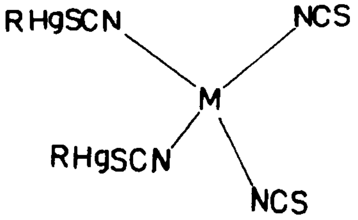


FIGURE 1

In order to establish the position of various RHgSCN ligands in the spectrochemical series, the Dq values were compared with the Dq values of known tetrahedral complexes of Co(II), Table III, and suggests the following order for RHgSCN in the spectrochemical series.

$$NCO^- < iso\text{-}C_4H_9HgSCN < n\text{-}C_4H_9HgSCN < CH_3HgSCN < C_2H_5HgSCN < SCN^-$$

A reference to Table III shows that β values for all of the complexes studied by us are lower than the free ion value (971 cm^{-1}) of cobalt, which suggests that there is orbital overlap. The nephelauxetic parameter β shows a decrease in the order $C_2H_5HgSCN > n\text{-}C_4H_9HgSCN > CH_3HgSCN > iso\text{-}C_4H_9HgSCN$. The lowest value of β for *iso*-C_4H_9HgSCN suggest that it has the highest covalency. RHgSCN can be placed in nephelauxetic series in order of their decreasing β values as follows

$$C_2H_5HgSCN > n\text{-}C_4H_9HgSCN > CH_3HgSCN > iso\text{-}C_4H_9HgSCN$$

It is interesting to note that the ligands have different sequences in the spectrochemical and nephelauxetic series. This is in conformity with the observations of Schaffer[7,8] who has given a different sequence for ligands in the two series.

From the Dq and β values it is evident that C_2H_5HgSCN is the strongest ligand of the series. If the shift in Hg-SCN (st) frequency on coordination is considered as the measure of bond strength, the shift in the case of C_2H_5HgSCN is maximum.

On treatment with Lewis bases such as pyridine, nicotinamide, and bipyridyl the cobalt Lewis acid forms well defined complexes whereas zinc analogs decompose on reaction with these bases. This difference in behavior shows that the thiocyanate bridge in between zinc and mercury is weak as compared with the thiocyanate bridge between cobalt and mercury.

Complexes

$(SCN)_2Co(NCSHgR)_2$ can be treated as Lewis-acids, as the coordination number of cobalt (II) is four compared with a maximum of six. Accordingly they have been treated with certain Lewis bases. The zinc analogs decompose on reaction with the same Lewis bases.

I-*Dinuclear bridged complexes* $L_2Co(NCS)_2(NCSHgR)_2$ (L = py, nia): Pyridine and nicotinamide react with the cobalt Lewis acids, and form pink complexes which melt at about 180°C, and are soluble in organic solvents. They are non conducting in dimethylformamide[9] and are monomeric. On heating in vacuum pyridine is given off and the parent blue Lewis acid $(SCN)_2Co(NCSHgR)_2$ is obtained. This shows that pyridine coordinates to the cobalt of the Lewis acid, and changes its tetrahedral geometry to octahedral. Electronic spectra in the solid phase give three distinct d-d transition bands in the range 20830–21740 cm^{-1}, 16390–17730 cm^{-1} and 8750–9100 cm^{-1} assignable to ${}^4T_{1g} \rightarrow {}^4T_{1g}(P)$ (ν_3), ${}^4T_{1g} \rightarrow {}^4A_{2g}$ (ν_2) and ${}^4T_{1g} \rightarrow {}^4T_{2g}$ (ν_1) transitions respectively. The μ_{eff} values are in the range 4.99–5.2 B.M. The infrared spectra of the complexes show a negative shift of the magnitude of 30–50 cm^{-1}, in the Co-NCS stretching frequency on complex formation. These observations also support octahedral coordination geometry around cobalt.[10,11]

A comparison of the spectra of the Lewis acids and that of the pyridine or nicotinamide complexes as presented in Table II shows the appearance of new bands assigned to Co-L (st) and L-Co-L. The position of C-N (st), C-S (st) and NCS bending bands, however, remain unaltered. This indicates that the parent structure of the Lewis-acids is not disturbed and only the coordination geometry around cobalt changes on account of the linkage of pyridine to cobalt. This linkage can be either at *trans* or at *cis* positions. The local symmetry around cobalt has been determined for both *cis* (C_{2v}) (Figure 2b) and *trans* (D_{4h}) (Figure 2a)

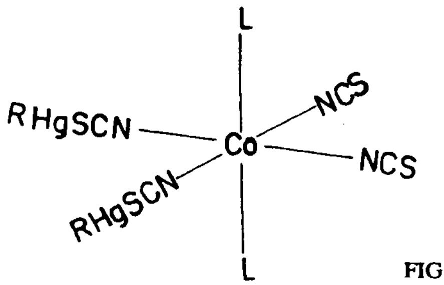


FIGURE 2a

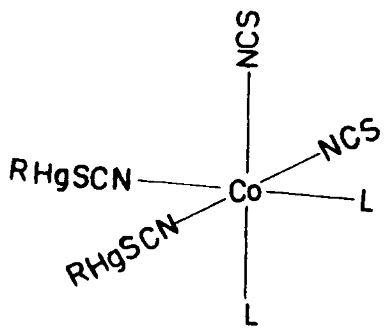


FIGURE 2b

configurations. While C_{2v} symmetry yields two bands due to Co-L, the D_{4h} symmetry gives only one band. Only one strong band is observed corresponding to Co-L (st) which supports *trans*-octahedral geometry for these complexes. Though the final structure can be established only by single crystal X-ray analysis, on the basis of the above results the structure shown in Figure (2a) can be proposed for the complexes. The proposed structure can be further supported by the following:

1) The organomercury compounds, in general, show little tendency to increase their coordination number.[12,13] Thus pyridine linkage to cobalt is more probable. Far ir spectra of our complexes do not show any absorption due to Hg-L (st).

2) Quantitative softness values of metal ion, NCS^-, SCN^- and various ligands have been calculated by the method reported elsewhere[14,15] and are presented in Table IV as $E_n^\ddagger$ for the metal ion and $E_m^\ddagger$ for the thiocyanate ions and ligands. A higher value for the difference ($\Delta E_{nm}^\ddagger$) between the metal ion and the base indicates a better match.[16] Based on this assumption the ligand would prefer to coordinate to cobalt. Similarly the N-end of thiocyanate shows a better match with cobalt and the S-end with mercury. Various linkages shown in the proposed structure are consistent with the HSAB principle.[17]

II. *Cationic-anionic complexes* $[Co(bipy)_3][(SCN)_2HgR]_2$: The molar conductance values of the bipyridyl complexes (132–140 cm^{-1} mhos/mol) indicate that they are 1:2 electrolytes. The electronic spectra are consistent with an octahedral stereochemistry and show the presence of three bands in the 21050–21670 cm^{-1}, 16530–16590 cm^{-1} and 8750–9020 cm^{-1} regions, assigned to ${}^4T_{1g} \rightarrow {}^4T_{1g}(P)$ (ν_3), ${}^4T_{1g} \rightarrow {}^4A_{2g}$ (ν_2) and ${}^4T_{1g} \rightarrow {}^4T_{2g}$ (ν_1) transitions respectively. The μ_{eff} values (4.99 to 5.2 B.M.) also support an octahedral environment. The presence of νC-N, νC-S and δNCS bands at about 2100 cm^{-1}, 700 cm^{-1} and 435 cm^{-1} respec-

TABLE IV
Softness values of metal ions, ligands and their matching[a]

Ligand	$E^{\ddagger}_{m}$	$E^{\ddagger}_{nm}$(Co-L)	$E^{\ddagger}_{nm}$(Hg-L)
Py	−11.74	11.00	5.22
nia	−13.86	13.12	7.34
Bipy	−12.04	11.30	5.52
NCS^-(N-end)	−11.61	11.87	6.09
NCS^-(S-end)	−8.29	7.55	1.34

The $E^{\ddagger}_{n}$ values of Co^{2+} and Hg^{2+} are −0.74 and −6.52 respectively.
[a] Softness values in ethyl acetate.

tively indicate the linkage of thiocyanate through S-end, and the absence of bridging thiocyanate. The presence of a strong band in the region of 225 cm^{-1} indicates the presence of a Co—N bond similar to reported Co—N bonds in bipyridyl complexes.[18] On the basis of these observations a cationic-anionic formula as shown in Figure 3 can be proposed.

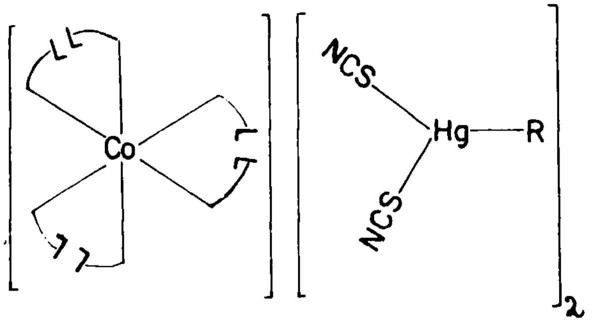


FIGURE 3

The coordination number of mercury in the anion is three which is not uncommon since previous workers[19,20] have also reported mercury in a tricoordinated state. The cation $[Co(bipy)_3]^{2+}$ and anion $[RHg(SCN)_2]^-$ will have O_h and C_{2v} local symmetry around the metal respectively. These symmetries will give one ir active band for Co—N and one for Hg-S, which are consistent with the observations.

Softness Out of the two sets of Lewis acids of the present series the thiocyanate bridge in $(SCN)_2(NCSHgR)_2$ appears more stable than in $(SCN)_2Zn(NCSHgR)_2$ since the former forms complexes with pyridine, nicotinamide and bipyridine, whereas the latter decomposes when reacted with these bases. This difference in behavior can be related to the difference in total softness values between cobalt and mercury and zinc and mercury which have been evaluated as given below. The results are presented in Table V.

$$
\begin{aligned}
TE^{\ddagger}_{n}(M) &= E^{\ddagger}_{n}(M) + 4E^{\ddagger}_{m}(NCS) \quad (M = Co, Zn)\\
TE^{\ddagger}_{n}(Hg) &= 2E^{\ddagger}_{n}(Hg) + 2E^{\ddagger}_{m}(SCN) + 2E^{\ddagger}_{m}(R)\\
\Delta TE^{\ddagger}_{n}(M\text{-}Hg) &= TE^{\ddagger}_{n}(M) - TE^{\ddagger}_{n}(Hg)
\end{aligned}
$$

TABLE V
Calculated differences in total softness values

	$\Delta TE_n^{\ddagger}$(Co-Hg)	$\Delta TE_n^{\ddagger}$(Zn-Hg)
$(NCS)_2M(NCSHgCH_3)_2$	14.48	13.10
$(NCS)_2M(NCSHgC_2H_5)_2$	14.34	12.97
$(NCS)_2M(NCSHgC_4H_9)_2$	14.24	12.87

Reference to Table V indicates that $\Delta TE_n^{\ddagger}$(Co-Hg) values are higher than $\Delta TE_n^{\ddagger}$(Zn-Hg). This shows that the thiocyanate bridge in the former is more stable, which is consistent with the experimental results. A similar sequence in the stability of the thiocyanate bridge between different metal ions has been shown earlier.[21]

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