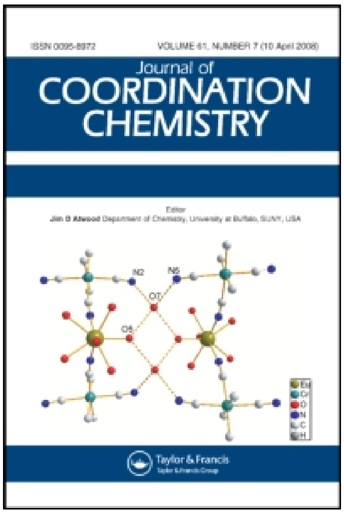

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LEAD DIISOTHIOCYANATO BIS-μ-THIOCYANATO DITHIOCYANATO COBALTATE(II) MERCURATE(II) AND ITS COMPLEXES

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LEAD DIISOTHIOCYANATO BIS-μ-THIOCYANATO DITHIOCYANATO COBALTATE(II) MERCURATE(II) AND ITS COMPLEXES

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Trimetallic hexathiocyanate of general formula $Pb[MHg(SCN)_6]$ [M = Co(II) and Ni(II)] have been synthesized by reaction with the three respective dithiocyanates. These hexathiocyanates have been reacted with a number of Lewis bases and the products obtained have been studied. Evidence based on infrared, electronic spectra, magnetic moment values, and molar conductance values indicate that out of the six thiocyanates two are N-bonded to cobalt or nickel, two S-bonded to mercury and the remaining two are bridged between cobalt and mercury. The lead is in the form of a cation, and hexathiocyanate is formulated as: $Pb[(SCN)_2M(NCS)_2Hg(SCN)_2]$. The Lewis bases get attached to cobalt or nickel as their first preference and to lead as second preference. Proposed structures of the complexes have also been supported by quantitative values of softness.

INTRODUCTION

Cobalt(II) thiocyanate and mercury(II) thiocyanate react to form $CoHg(SCN)_4$. It was thought of interest to react three thiocyanates viz. $Co(NCS)_2$, $Hg(SCN)_2$ and $M(SCN)_2$ [M = Pb(II), Zn(II), Cd(II)], together and prepare a trimetallic hexathiocyanate. Review of literature show that Scaife[1] made an attempt to synthesize trimetallic thiocyanate and was successful in synthesizing $Hg[M_{(x)}Zn_{(1-x)}](NCS)_4$ [M = Mn(II), Fe(II), Co(II), Ni(II) and Cu(II)]. Our attempts to synthesize the stipulated trimetallic hexathiocyanate $M[CoHg(SCN)_6]$ were ultimately successful and we obtained $Pb[CoHg(SCN)_6]$. The method of synthesis, the structure of compound and its reaction with various Lewis bases are presented in this paper.

EXPERIMENTAL SECTION

Materials and Manipulations

Reagent grade cobalt(II), nickel(II), mercury(II) and lead(II) nitrates (BDH) were used from fresh bottles. Potassium thiocyanate (BDH) was used after drying in vacuum at room temperature. Ligands were purified either by recrystallization or by distillation. Solvents were dried before use.

Synthesis of $Pb[CoHg(SCN)_6]$

$Pb[CoHg(SCN)_6]$ was synthesized by two different methods:

i) $Pb(SCN)_2$, $Hg(SCN)_2$ and $Co(NCS)_2$ were prepared by the reaction of respective nitrates and potassium thiocyanates as reported earlier.[2,7] $Pb(SCN)_2$ and $Hg(SCN)_2$ were stirred in equimolar ratio in ethanol for 8 hrs. To this mixture $Co(NCS)_2$ was added in the same ratio. The blue colour of $Co(NCS)_2$ spontaneously changed to pink and within minutes to green blue. The whole mixture was stirred for 6 hrs., and then filtered. The residue was washed with the solvent and dried in vacuum.

The compound has also been prepared by first stirring an equimolar mixture of $Pb(NCS)_2$ and $Co(NCS)_2$ for 8 hrs. in ethanol, followed by an addition of equimolar quantity of $Hg(SCN)_2$ and continuing the stirring for 6 hrs.

A similar procedure was adopted for preparing the nickel analogue, but in this case the compound crystallized with two molecules of ethanol.

ii) KSCN and $Hg(SCN)_2$ were taken in 2:1 molar ratio in water and stirred till the latter dissolved. To the solution $Pb(SCN)_2$ was added in 1:1 molar ratio and stirred for 8 hrs., followed by an addition of equimolar quantity of hydrated cobalt(II) nitrate. The colour of the mixture immediately changed from deep pink to greenish blue. The mixture was stirred for 6 hrs. and thereafter filtered, washed with water and finally with alcohol. The compound was dried in vacuum.

iii) We carried out similar reactions by substituting $Pb(SCN)_2$ with $Zn(NCS)_2$ and $Cd(SCN)_2$. The stipulated complexes Zn[CoHg$(SCN)_6$] and Cd[CoHg$(SCN)_6$] could not be isolated.

iv) Our attempt to synthesize the complex by stirring CoHg$(SCN)_4$ with Pb$(SCN)_2$ in equimolar ratio in ethanol failed.

Reaction of Pb[MHg(SCN)$_6$] [M = Co(II), Ni(II)] with certain Lewis bases and isolation of the products

A known quantity of Pb[MHg$(SCN)_6$] was added in 50 ml of ethanol in a number of 100 ml flasks and a homogeneous suspension in each case was prepared by stirring. To each suspension different bases in the same solvent in suitable molar ratio were added and the stirring continued for 24 hrs. Solid compounds were formed in each case, which were filtered, washed with the solvent and dried in vacuum.

Analysis of the Complexes†

The complexes were analysed for sulphur as sulphate, mercury as mercury sulphide, cobalt as cobalt anthranilate and nickel as dimethylglyoximate. Lead was estimated as lead sulphate. Nitrogen was estimated by Kjeldahl method.

Physical Measurements

Molar conductance values of soluble complexes were measured in dimethylformamide using a Phillips-PR 9500 conductivity bridge.

Magnetic susceptibility measurements were made at room temperature by Guoy method using CoHg(SCN) as standard. The diamagnetic corrections were also made by using Pascals constants.

The infrared spectra in the region 4000–400 cm^{-1} were recorded on a Perkin-Elmer 621 spectrophotometer. Samples were run either as nujol mull or as KBr pellets. Far infrared spectra in the region 500–50 cm^{-1} were recorded on Polytech FIR-30 spectrophotometer as polyethylene pellets.*

Electronic spectra in the range 250–2500 nm were recorded on Carl Zeiss DMR-21 spectrophotometer. Soluble complexes were run as solution in dimethylformamide and insoluble as nujol mull by adopting the procedure of Lee.[2]

RESULTS AND DISCUSSION

We could not determine the molecular weight of these complexes on account of their insolubility in suitable solvent. On account of the same difficulty we could not grow a single crystal for X-ray analysis. Therefore, the structures of the complexes have been proposed on the basis of information obtained from the infrared spectral, electronic spectral, magnetic moment value, molar conductance value and chemical studies only. The proposed structures are accordingly tentative.

Lewis acids: Pb[CoHg(SCN)$_6$] and Pb[NiHg(SCN)$_6$·2C$_2$H$_5$OH]

The analytical results indicate that the molecular formula of the Lewis acid is Pb[CoHg$(SCN)_6$]. The molar conductance value of this complex in dimethylformamide[3] is 84.6 cm^2mhos/mol which suggests that it is an 1:1 electrolyte. On reaction with KCl in water, $PbCl_2$ is precipitated, probably by double decomposition. Other simple chemical reactions also prove the presence of Pb^{+2}. This indicates that Pb^{+2} is the cation and $[CoHg(SCN)_6]^{-2}$ is the anion. On the basis of these results it can be assumed that the compound has a cationic-anionic structure of the type Pb^{+2} $[CoHg(SCN)_6]^{-2}$.

i) The infrared spectral data of the complex show three well defined strong bands and a shoulder in the CN stretching region, which indicate the presence of both bridged and terminal thiocyanate groups.[4-8] The bands assigned to terminal thiocyanates are in the range 2020–2120 cm^{-1} and those assigned to bridged thiocyanate are in the range 2130–2160 cm^{-1}. The position and number of absorption bands in CS stretching and NCS bending region also support the presence of both terminal and bridged thiocyanates.[9-13] On the basis of these results the following structure can be suggested to the anion.

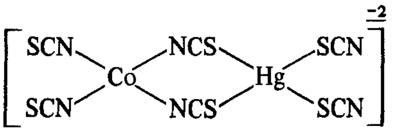

FIGURE 1

ii) It has been shown that the greater is the difference in softness value $\Delta E_n^{\ddagger}$(M–M′) of M/M′ the greater is the stability of thiocyanate bridge.[14]

A reference to Table I indicates that the thiocyanate bridge will be more stable in-between cobalt and mercury or nickel and mercury. This also supports the presence of thiocyanate bridge as shown in the structure.

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†The analytical data and infrared frequencies are on file in our office and will be provided on request.

TABLE I

M/M′	Softness of M $E_n^{\ddagger}(M)$ in ethanol	Softness of M′ $E_n^{\ddagger}(M')$ in ethanol	Difference of softness $\Delta E_n^{\ddagger}(M-M')$
Ni/Hg	−0.16	−4.99	4.83
Co/Hg	−0.38	−4.99	4.61
Pb/Hg	−2.17	−4.99	2.82
Ni/Pb	−0.16	−2.17	2.01
Co/Pb	−0.38	−2.17	1.79

The cobalt as shown in the structure has a tetrahedral coordination geometry. This geometry is supported by the electronic spectral band positions as presented in Table III and by the magnetic moment value.

The corresponding nickel compound always crystallizes with two molecules of C_2H_5OH, which is probably linked to nickel, because the electronic spectral band positions and magnetic moment value indicate the presence of an octahedral geometry for nickel in this complex. The following structure in Figure 2 can accordingly be proposed for the nickel analogue.

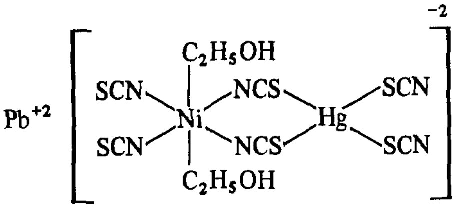


FIGURE 2

A close look to Figures 1 and 2 shows that the compounds can be treated as Lewis acid similar to $CoHg(SCN)_4$ as Pb(II), Hg(II) and Co(II) can raise their coordination number to six by reacting with Lewis bases. The $Pb[CoHg(SCN)_6]$ and $Pb[NiHg(SCN)_6 \cdot 2\ C_2H_5OH]$ have accordingly been reacted with number of Lewis bases and the results are presented below.

Reaction with: triphenylphosphine (PPh_3), tetrahydrofuran (THF), and Dimethyl sulfoxide (DMSO)

On reaction, a blue complex with triphenylphosphine and pink complexes with rest of the bases are formed with $Pb[CoHg(SCN)_6]$.

i) The number and positions of infrared bands in CN(st), CS(st) and NCS(bending) and the molar conductance values in dimethylformamide, of these complexes are in the range of their parent Lewis acid. This indicates that the basic structures of the two are similar.

ii) In case of triphenylphosphine complexes, the electronic spectral band positions and magnetic moment values indicate that cobalt and nickel have tetrahedral and square planar coordination geometry respectively in their complexes. On the basis of these observations two structures can be proposed.

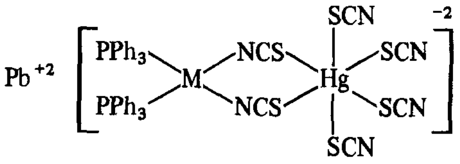


FIGURE 3

M = Co(II), Ni(II)

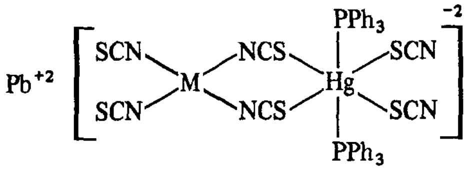


FIGURE 4

Structure in Figure 3 is more probable on the following grounds:

i) The far infrared spectra as discussed later show the presence of νCo–P and νNi–P bands and absence of νHg–P band.

ii) The low spin nature of the nickel complex indicate that triphenylphosphine is attached to nickel because the reported compound $(PPh_3)_2Ni(NCS)_2$ is low spin.[15]

iii) In case of the reported complex $(PPh_3)_2$-$CoHg(SCN)_4$, the triphenylphosphine has been shown linked to cobalt.[4] This also indicates that PPh_3 prefers linkage to cobalt.

iv) The difference in total softness values of cobalt and mercury as discussed later also support the structure in Figure 3.

The electronic spectral band positions and magnetic moment values of cobalt and nickel in rest of the complexes indicate the presence of octahedral coordination geometries around these metals. The probable structure of these complexes will therefore be similar to the structure proposed in Figure 2 where ethanol can be substituted by THF and DMSO.

TABLE II

Softness of metal ion	Ni(II)	Co(II)	Pb(II)	Hg(II)		
$E_n^{\ddagger}$ in ethanol in ev	−0.16	−0.38	−2.17	−4.99		
Softness of ligand	N(−NCS)	phen.	bipy.	4-ampy	nia.	
$E_m^{\ddagger}$ in ethanol in ev	−12.65	−11.81	−11.44	−11.76	−13.75	
	py.	THF	DMSO	ethanol	S(−SCN)	PPh_3
	−11.49	−11.42	−11.04	−10.94	−8.16	−6.85

Reaction with: pyridine(py), nicotinamide(nia), 4-aminopyridine(4-ampy), bipyridine(bipy) and phenanthroline(phen)

The analytical data show that six molecules of pyridine, nicotinamide, 4-aminopyridine and four molecules of bipyridine and phenanthroline (bidentate) get attached to the Lewis acid. The possible site of their coordination to the metal atoms has been drawn on the basis of H.S.A.B. principle.[16] The quantitative values of softness of the various bases and of the metal atoms as calculated from Klopman equation[17] are presented below.

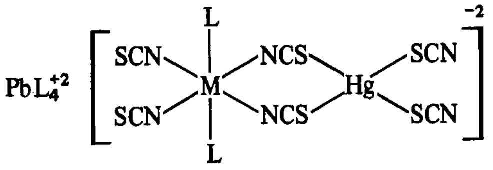
A reference to Table II shows that these ligands will have their first preference for cobalt(II) and nickel(II), second for lead(II) and third for mercury(II). Since cobalt and nickel acquire octahedral coordination geometries in all these complexes, it is evident that the ligands are attached to these metals It is after the saturation of coordination number of these metals, the ligands get attached to lead(II) as their second preference. It is only in case of bipyridine and phenanthroline, where ligands get attached to mercury(II) after saturating the coordination numbers of cobalt and lead. Since the molar conductance values and position of various bands in infrared spectra of these complexes remain in the range of the Lewis acid, the basic structure is believed to be similar to the Lewis acid, and the structures to various complexes are accordingly proposed as below.

Electronic Spectra

Electronic spectra of certain typical complexes have been recorded to support the proposed coordination geometries of cobalt and nickel in various complexes. The assignments of various bands and the parameters derived[18] from them are presented in Table III. The position of bands and the parameters derived from them indicate that cobalt and nickel are in octahedral configuration in all these complexes, except in the triphenylphosphine complex, where the cobalt is in tetrahedral configuration. The magnetic moment values also support the same configuration.

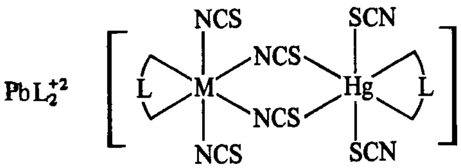
Far Infrared Spectra

In order to extend support to the proposed structures, we have also recorded far infrared spectra of certain complexes in the range 500–50 cm^{-1}. The assignments of various bands have been made on the basis of earlier workers.



L = py, nia and 4-ampy
M = Co(II), Ni(II)

FIGURE 5



L = bipy and phen(bidentate)
M = Co(II), Ni(II)

FIGURE 6

TABLE III

Electronic spectral bands, parameters and magnetic moment values.

Complexes	Assignments (cm^{-1})			Dq (cm^{-1})	B′ (cm^{-1})	β	μ_{eff} (B.M.)
	$^4A_{2g} \rightarrow {}^4T_{1g}(P)$	$^4A_{2g} \rightarrow {}^4T_{1g}(F)$					
$Pb[(SCN)_2Co(NCS)_2Hg(SCN)_2]$	16000	7692		450	680	0.70	4.22
$Pb[(PPh_3)_2Co(NCS)_2Hg(SCN)_4]$	16666	7545		438	738	0.76	4.18
	$^4T_{1g} \rightarrow {}^4T_{1g}(P)$	$^4T_{1g} \rightarrow {}^4A_{2g}(F)$	$^4T_{1g} \rightarrow {}^4T_{2g}(F)$				
$Pb[(THF)_2(SCN)_2Co(NCS)_2Hg(SCN)_2]$	21052	16666	8000	891	963	0.98	5.05
$Pb(py)_4[(py)_2(SCN)_2Co(NCS)_2Hg(SCN)_2]$	20000	16120	–	862	907	0.93	4.99
$Pb(bipy)_2[(bipy)(SCN)_2Co(NCS)_2Hg(SCN)_2(bipy)]$	19230	–	7200	720	–	–	5.15
	$^3A_{2g} \rightarrow {}^3T_{1g}(P)$	$^3A_{2g} \rightarrow {}^3T_{1g}(F)$	$^3A_{2g} \rightarrow {}^3T_{2g}(F)$				
$Pb[(ethan)_2(SCN)_2Ni(NCS)_2Hg(SCN)_2]$	26316	14285	8695	852	1003	0.97	3.16
$Pb[(DMSO)_2(SCN)_2Ni(NCS)_2Hg(SCN)_2]$	26666	15384	8695	933	937	0.91	3.08
$Pb[(THF)_2(SCN)_2Ni(NCS)_2Hg(SCN)_2]$	27029	16000	–	1043	827	0.82	3.12
$Pb(nia)_4[(nia)_2(SCN)_2Ni(NCS)_2Hg(SCN)_2]$	27035	16666	9090	979	910	0.88	2.98

The bands in the region 158–180 cm^{-1} have been assigned to νCo–P and νNi–P[4,22] and at about 137 cm^{-1} to νHg–P.[20] In our triphenylphosphine complexes we observe that bands are present in the range prescribed for νCo–P and νNi–P bands and there is no band in the range given for νHg–P. This shows that triphenylphosphine is linked to cobalt or nickel and not to mercury as shown in Figure 3.

The bands assigned to νM–py[4,8,21], νM–bipy[4,21], νM–DMSO[23,28-30] and νM–ethanol[23,28-30] are in the range 205–233 cm^{-1}, 260–280 cm^{-1} and 350–395 cm^{-1} respectively. Bands corresponding to these assignments are present in the respective complexes which supports the linkages proposed by us in various structures. Clark and Williams[8] have reported that a negative shift of the order of 65 cm^{-1} is observed when tetrahedral Co–NCS changes to octahedral Co–NCS. In the Lewis acid the band assigned to νCo–NCS appears at about 300 cm^{-1} [19,4] whereas in the corresponding complexes this band shows a negative shift of the order of about 60 cm^{-1} This change in position also shows that the geometry of cobalt is changed on complexation, which further goes to support that the ligands are coordinated to cobalt. The bands in the region 198–230 cm^{-1} have been assigned to Hg–SCN stretching mode.[8,19,24] This band in the Lewis acid has been assigned at 224 cm^{-1}. On complex formation the position of this band remains unaltered, which goes to show that the ligands are not linked to mercury. In case of bipyridine complex where coordination also takes place at mercury, the position of νHg–SCN band changes to a lower region.

In some of our complexes the lead is in the form of Pb^{+2} ion, whereas in case of pyridine and bipyridine it is in the form of $[PbL_4]^{+2}$ ion. In the latter cases a band appears at about 155 cm^{-1} which on the basis of previous assignments,[25,26] has been assigned to Pb–N stretching.

Usually the bending vibrations have frequencies not greater than half of the associated stretching vibrations.[31] On this basis we have given tentative assignments to various bending modes.

Quantitative Values of Softness

i) The difference of total softness of M and M′ as shown in the following equation has been related with the stability of the thiocyanate bridge[32] in bimetallic tetrathiocyanate.

$$\Delta[(M'\text{–}S_4) - (M\text{–}N_4)] = [E^{\ddagger}(M'\text{–}S_4) - E^{\ddagger}(M\text{–}N_4)] \qquad \text{(i)}$$

where,

$$E^{\ddagger}(M'\text{–}S_4) = E^{\ddagger}_{n}(M') + 4\,E^{\ddagger}_{m}(SCN)$$
$$E^{\ddagger}(M\text{–}N_4) = E^{\ddagger}_{n}(M) + 4\,E^{\ddagger}_{m}(NCS)$$

The total softness of M and M′ have been calculated in respect of the complexes of present series by adding the softness of the ligands, and the thiocyanate to the $E^{\ddagger}_{n}$ of M and M′ and the difference evaluated by adopting the following relation.

$$\Delta TE^{\ddagger}_{n}(M\text{–}M') = [E^{\ddagger}_{n}(M) + \Sigma E^{\ddagger}_{m}(M_L) + \Sigma E^{\ddagger}_{m}(M\text{–}NCS)] - [E^{\ddagger}_{n}(M') + \Sigma E^{\ddagger}_{m}(M'_L) + \Sigma E^{\ddagger}_{m}(M'\text{–}SCN)] \qquad \text{(ii)}$$

where,

$E^{\ddagger}_{n}(M)$ and $E^{\ddagger}_{n}(M')$ are softness values of M and M′ respectively.
$\Sigma E^{\ddagger}_{m}(M_L)$ is sum of softness values of ligands attached to M.
$\Sigma E^{\ddagger}_{m}(M'_L)$ is sum of softness values of ligands attached to M′.
$\Sigma E^{\ddagger}_{m}(M\text{–}NCS)$ is sum of softness values of NCS (–N end) attached to M.
$\Sigma^{\ddagger}_{m}(M'\text{–}SCN)$ is sum of softness values of SCN (S–end) attached to M′.
$\Delta TE^{\ddagger}_{n}(M\text{–}M')$ is total softness difference between M and M′.

The $\Delta TE^{\ddagger}_{n}(M\text{–}M')$ are higher in respect of the proposed structures. If the site of the coordination of the ligand is changed the value of $\Delta TE^{\ddagger}_{n}(M\text{–}M')$ gets lower. The higher value of $\Delta TE^{\ddagger}_{n}(M\text{–}M')$ is indicative of a more stable bridge hence supports the proposed structures. An instance here is quoted to make the situation more clear. In case of triphenylphosphine complex two structures have been proposed as shown in Figures 3 and 4 and the $\Delta TE^{\ddagger}_{n}(M\text{–}M')$ value for these two structures are 19.06 and 4.84 respectively. In case of Figure 3 the value is higher, hence this structure is more probable. Similar derivations support the other structures. The $\Delta TE^{\ddagger}_{n}(M\text{–}M')$ [M = Co(II), Ni(II) and M′ = Hg(II)] values of all the complexes are presented in Table IV.

ii) Bipyridine and phenanthroline, rupture the thiocyanate bridge in $CoHg(SCN)_4$ and form cationic–anionic complexes of the type $[CoL_3]^{+2}[Hg(SCN)_4]^{-2}$ The thiocyanate bridge in $[CoHg(SCN)_6]^{-2}$ is however, retained on reaction with these ligands. The extra-stability of the bridge in the anion has also been explained on the basis of $\Delta TE^{\ddagger}_{n}(M\text{–}M')$ value. The

TABLE IV
Total softness difference values of the complexes

Complexes	$TE_{\text{n}}^{\ddagger}(\text{M})$	$TE_{\text{n}}^{\ddagger}(\text{M}')$	$\Delta TE_{\text{n}}^{\ddagger}(\text{M}-\text{M}')$
$\text{Pb}[(\text{SCN})_2\text{Co}(\text{NCS})_2\text{Hg}(\text{SCN})_2]$	38.33	29.47	8.86
$\text{Pb}[(\text{PPh}_3)_2\text{Co}(\text{NCS})_2\text{Hg}(\text{SCN})_4]$	26.73	45.79	19.06
$\text{Pb}[(\text{DMSO})_2(\text{SCN})_2\text{Co}(\text{NCS})_2\text{Hg}(\text{SCN})_2]$	60.41	29.47	30.94
$\text{Pb}[(\text{THF})_2(\text{SCN})_2\text{Co}(\text{NCS})_2\text{Hg}(\text{SCN})_2]$	61.21	29.47	31.74
$\text{Pb}(\text{py})_4[(\text{py})_2(\text{SCN})_2\text{Co}(\text{NCS})_2\text{Hg}(\text{SCN})_2]$	61.31	29.47	31.84
$\text{Pb}(\text{nia})_4[(\text{nia})_2(\text{SCN})_2\text{Co}(\text{NCS})_2\text{Hg}(\text{SCN})_2]$	65.83	29.47	36.36
$\text{Pb}(4\text{-ampy})_4[(4\text{-ampy})_2(\text{SCN})_2\text{Co}(\text{NCS})_2\text{Hg}(\text{SCN})_2]$	61.85	29.47	32.38
$\text{Pb}(\text{bipy})_2[(\text{bipy})(\text{SCN})_2\text{Co}(\text{NCS})_2\text{Hg}(\text{SCN})_2(\text{bipy})]$	49.77	40.91	8.86
$\text{Pb}(\text{phen})_2[(\text{phen})(\text{SCN})_2\text{Co}(\text{NCS})_2\text{Hg}(\text{SCN})_2(\text{phen})]$	50.44	41.28	8.86
$\text{Pb}[(\text{ethan})_2(\text{SCN})_2\text{Ni}(\text{NCS})_2\text{Hg}(\text{SCN})_2]$	59.99	29.47	30.52
$\text{Pb}[(\text{PPh}_3)_2\text{Ni}(\text{NCS})_2\text{Hg}(\text{SCN})_4]$	26.51	45.79	18.84
$\text{Pb}[(\text{DMSO})_2(\text{SCN})_2\text{Ni}(\text{NCS})_2\text{Hg}(\text{SCN})_2]$	60.19	29.47	30.72
$\text{Pb}[(\text{THF})_2(\text{SCN})_2\text{Ni}(\text{NCS})_2\text{Hg}(\text{SCN})_2]$	60.99	29.47	31.52
$\text{Pb}(\text{py})_4[(\text{py})_2(\text{SCN})_2\text{Ni}(\text{NCS})_2\text{Hg}(\text{SCN})_2]$	61.09	29.47	31.62
$\text{Pb}(\text{nia})_4[(\text{nia})_2(\text{SCN})_2\text{Ni}(\text{NCS})_2\text{Hg}(\text{SCN})]$	65.61	29.47	36.14
$\text{Pb}(4\text{-ampy})_4[(4\text{-ampy})_2(\text{SCN})_2\text{Ni}(\text{NCS})_2\text{Hg}(\text{SCN})_2]$	61.63	29.47	32.16
$\text{Pb}(\text{bipy})_2[(\text{bipy})(\text{SCN})_2\text{Ni}(\text{NCS})_2\text{Hg}(\text{SCN})_2(\text{bipy})]$	49.55	40.91	8.64
$\text{Pb}(\text{phen})_2[(\text{phen})(\text{SCN})_2\text{Ni}(\text{NCS})_2\text{Hg}(\text{SCN})_2(\text{phen})]$	49.92	41.28	8.64

M = Co(II), Ni(II) and M′ = Hg(II)

$\Delta TE_{\text{n}}^{\ddagger}(\text{M}-\text{M}')$ value in these cases have been calculated by adopting the following procedure.

In case of $[\text{CoHg}(\text{SCN})_6]^{-2}$ the total softness value of cobalt and mercury have been calculated in combination of three N-bonded and three S-bonded thiocyanates respectively. Similarly in case of $\text{CoHg}(\text{SCN})_4$ the total softness of cobalt and mercury have been derived in combination of two N-bonded and two S-bonded thiocyanate respectively. The details of derivation are presented below.

i) For $[\text{CoHg}(\text{SCN})_6]^{-2}$.

$$TE_{\text{n}}^{\ddagger}(\text{Co}) = E_{\text{n}}^{\ddagger}(\text{Co}) + 3\,E_{\text{m}}^{\ddagger}(\text{NCS}) \qquad (1)$$

$$TE_{\text{n}}^{\ddagger}(\text{Co}) = (0.38) + (37.95)$$

$$TE_{\text{n}}^{\ddagger}(\text{Hg}) = E_{\text{n}}^{\ddagger}(\text{Hg}) + 3\,E_{\text{m}}^{\ddagger}(\text{SCN}) \qquad (2)$$

$$TE_{\text{n}}^{\ddagger}(\text{Hg}) = (4.99) + (24.48)$$

where,

$TE_{\text{n}}^{\ddagger}(\text{Co})$ and $TE_{\text{n}}^{\ddagger}(\text{Hg})$ are total softness of cobalt and mercury respectively.

$$TE_{\text{n}}^{\ddagger}(\text{Co–Hg}) = TE_{\text{n}}^{\ddagger}(\text{Co}) - TE_{\text{n}}^{\ddagger}(\text{Hg}) \qquad (3)$$

$$\Delta TE_{\text{n}}^{\ddagger}(\text{Co–Hg}) = 8.86$$

ii) Similarly for $\text{CoHg}(\text{SCN})_4$:

$$TE_{\text{n}}^{\ddagger}(\text{Co}) = E_{\text{n}}^{\ddagger}(\text{Co}) + 2\,E_{\text{m}}^{\ddagger}(\text{NCS}) \qquad (4)$$

$$TE_{\text{n}}^{\ddagger}(\text{Co}) = (0.38) + (25.30)$$

$$TE_{\text{n}}^{\ddagger}(\text{Hg}) = E_{\text{n}}^{\ddagger}(\text{Hg}) + 2\,E_{\text{m}}^{\ddagger}(\text{SCN}) \qquad (5)$$

$$TE_{\text{n}}^{\ddagger}(\text{Hg}) = (4.99) + (16.32)$$

$$TE_{\text{n}}^{\ddagger}(\text{Co–Hg}) = TE_{\text{n}}^{\ddagger}(\text{Co}) - TE_{\text{n}}^{\ddagger}(\text{Hg}) \qquad (6)$$

$$\Delta TE_{\text{n}}^{\ddagger}(\text{Co–Hg}) = 4.37$$

It is perhaps the higher value of total softness difference $\Delta TE_{\text{n}}^{\ddagger}(\text{Co–Hg})$ that provides greater stability to the thiocyanate bridge in case of $[\text{CoHg}(\text{SCN})_6]^{-2}$.

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