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Quantitative Values of Softness and Structure of Bimetallic Tetrathiocyanate Complexes

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Bimetallic tetrathiocyanate complexes of the type $MM'(SCN)_4 \cdot xL$ [M = Ni(II), Co(II), Zn(II); M' = Cd(II), Hg(II) and L = thiazolidinethione (tzt), thiohydantoin (thn), ethylenethiourea (etu); x = 2, 4, 6] have been prepared and their structures have been proposed by elemental analysis, molar conductance, magnetic moment, infrared spectral, electronic spectral studies and quantitative values of softness. These studies indicate that the complexes are of two types: cationic–anionic, viz. *$[ML_x]^{++}[Cd(SCN)_4]^{--}$ [M = Co(II), Ni(II); L = tzt, thn, etu; x = 4, 6] and monomeric thiocyanate bridged,* viz. *$L_2M(NCS)_2Hg(SCN)_2$ [M = Zn, Co, Ni; L = tzt, etu, thn] and $L_4'Ni(NCS)_2$-$Hg(SCN)_2$ (L' = etu, thn). Thiocarbonyl sulphur is the donor site in cationic–anionic complexes and imino nitrogen in bridged thiocyanate complexes in all three ligands. The relative strength of thiocyanate bridges have been correlated with the total softness difference $\Delta TE_n^{\ddagger}(M–M')$ which was calculated using Klopman's equation. Symmetry and group theoretical calculations have also been made to support the proposed structures.*

Introduction

In this paper we are presenting a new approach for elucidating the structure of bimetallic tetrathiocyanate complexes. This new method is based upon the quantitative values of softness of different ligands and metals which have been calculated by adopting the Klopman equation [1]. The structures of the complexes proposed by infrared, electronic, magnetic moment, and conductance studies, have been correlated with the quantitative softness values of the ligands and the Lewis acids.

Experimental

Synthesis of the Complexes

$M(NCS)_2$ [M = Co, Ni, Zn] and $M'(SCN)_2$ [M' = Cd, Hg] were mixed in 100 ml of ethanol in equimolar ratio and stirred for 24 h. To the resulting solution or suspension, ligands were added in suitable molar ratio and stirred for 36 h. Solid complexes were formed, which were filtered, washed with solvent and dried under vacuum.

Analysis of the Complexes

Sulphur was estimated as sulphate, nickel as dimethylglyoximate, mercury as sulphide, zinc, cobalt and cadmium as their anthranilates gravimetrically. Nitrogen was estimated by semimicro Kjeldahl's method. The results are recorded in Table I.

Physical Measurements

The infrared spectra of the ligand in chloroform solution and of complexes as nujol mulls were recorded on a Perkin Elmer model 621 spectrophotometer. The electronic spectra were recorded on a Cary-14 spectrophotometer. Magnetic susceptibility measurements were made at room temperature by Gouy's method using cobalt–mercury tetrathiocyanate as standard. The diamagnetic corrections were made according to Figgis [2]. Molar conductances were measured in acetone and N,N'-dimethylformamide by a Philips PR-9500 conductivity bridge.

Results and Discussion

The complexes are not soluble in solvents suitable for molecular weight determination or for obtaining a single crystal, hence the structures of the complexes have been proposed on the basis of infrared, electronic spectral, molar conductance and magnetic susceptibility studies only. On the basis of these studies the complexes have been classified into two groups.

(A) Cationic–Anionic Complexes viz. *$[CoL_4]^{++}$-$[Cd(SCN)_4]^{--}$ and $[NiL_6]^{++}[Cd(SCN)_4]^{--}$ (L = thn, etu, tzt)*

(i) The analytical results (Table I) of these complexes indicate that four molecules of ligands are coordinated to $CoCd(SCN)_4$ and six molecules to $NiCd(SCN)_4$.

TABLE I. Analytical Results, Molar Conductance and Magnetic Moment Data.

Complexes	Colour	M.P.[a] (°C)	% Sulphur		% Nitrogen		% M (Ni,Co,Zn)		% M′(Cd,Hg)		Molar Conductance (mhos cm^2 mol^{-1})	Ionic nature	μ_{eff} (B.M.) at room temperature
			calc.	obs.	calc.	obs.	calc.	obs.	calc.	obs.			
$(etu)_2Co(NCS)_2Hg(SCN)_2$	Blue	120	27.6	27.0	16.1	15.5	8.5	9.0	28.8	29.5	31.2	Non-electrolyte	4.42
$[Co(etu)_4][Cd(SCN)_4]$	Light blue	131	31.6	32.0	20.7	19.9	7.2	6.9	13.8	13.3	98.1	1:1	4.44
$(etu)_4Ni(NCS)_2Hg(SCN)_2$	Green	142(d)	28.5	27.8	18.7	17.9	6.6	7.0	22.2	23.1	32.9	Non-electrolyte	3.12
$[Ni(etu)_6][Cd(SCN)_4]$	Green	188	31.5	32.0	22.0	21.9	5.8	6.0	11.0	11.4	28.8	Non-electrolyte	3.11
$(etu)_2Zn(NCS)_2Hg(SCN)_2$	White	133	27.5	28.0	15.9	15.2	9.3	10.0	28.5	29.2	27.8	Non-electrolyte	–
$(thn)_2Co(NCS)_2Hg(SCN)_2$	Blue	205	27.4	26.6	16.0	16.5	8.2	8.6	28.7	28.4	28.2	Non-electrolyte	4.41
$[Co(thn)_4][Cd(SCN)_4]$	Blue	160(d)	29.5	30.2	19.3	18.7	6.9	6.5	12.9	12.4	100.2	1:1	4.5
$(thn)_4Ni(NCS)_2Hg(SCN)_2$	Green	172(d)	26.8	26.0	17.6	16.9	6.2	6.9	20.9	19.8	32.0	Non-electrolyte	3.05
$[Ni(thn)_6][Cd(SCN)_4]$	Violet	109	29.1	29.6	20.3	19.9	5.3	5.7	10.1	10.4	105.2	1:1	3.2
$(thn)_2Zn(NCS)_2Hg(SCN)_2$	Brown	194	29.2	28.5	15.4	14.9	8.9	9.0	27.4	26.9	33.2	Non-electrolyte	–
$(tzt)_2Co(NCS)_2Hg(SCN)_2$	Blue	197(d)	35.1	35.9	11.5	11.0	8.1	8.7	27.4	27.0	34.1	Non-electrolyte	4.41
$[Co(tzt)_4][Cd(SCN)_4]$	Blue	110	43.7	43.1	12.1	12.8	6.7	6.3	12.7	12.3	104.6	1:1	4.4
$(tzt)_4Ni(NCS)_2Hg(SCN)_2$	Blue	195(d)	39.7	40.3	11.5	10.9	8.1	7.8	11.5	12.1	25.4	Non-electrolyte	3.15
$[Ni(tzt)_6][Cd(SCN)_4]$	Green	188(d)	45.8	45.0	12.5	12.9	5.3	5.6	10.0	11.2	109.5	1:1	3.1
$(tzt)_2Zn(NCS)_2Hg(SCN)_2$	Greyish	112	34.8	35.4	11.4	12.0	8.9	8.4	27.2	28.0	25.8	Non-electrolyte	–

[a](d) = decomposes.

(ii) The molar conductance values (Table I) of these complexes in acetone indicate that they are 1:1 electrolytes.

(iii) The positions of infrared spectral bands due to νC–N, νC–S and δNCS modes of thiocyanate vibrations are indicative of S-bonded thiocyanates [3–5].

(iv) The electronic spectra and magnetic moment values as discussed later show very clearly that cobalt and nickel in these complexes are in tetrahedral and octahedral coordination geometry, respectively.

On the basis of the above results, the following structures are possible for the complexes of cobalt:

$$\underset{\text{I}}{[CoL_4]^{++}[Cd(SCN)_4]^{--}},\quad \underset{\text{II}}{[Co(NCS)_4]^{--}[CdL_4]^{++}},$$

$$\underset{\text{III}}{[Co(NCS)L_3]^{+}[CdL(SCN)_3]^{-}}$$

and the following for the complexes of nickel:

$$\underset{\text{IV}}{[NiL_6]^{++}[Cd(SCN)_4]^{--}},\quad \underset{\text{V}}{[NiL_2(NCS)_4]^{--}[CdL_4]^{++}},$$

$$\underset{\text{VI}}{[NiL_3(NCS)_3]^{-}[CdL_3(SCN)_3]^{+}}$$

(L = tzt, thn, etu)

The data enumerated below suggest that the most plausible structure for cobalt complexes is $[CoL_4]^{++}$-$[Cd(SCN)_4]^{--}$ and for nickel complexes is $[NiL_6]^{++}$-$[Cd(SCN)_4]^{--}$.

(i) The reported Dq values of the ions $[CoL_4]^{++}$ and $[Co(NCS)_4]^{--}$ are 338–378 cm^{-1} and 455 cm^{-1} respectively [6–8]. The Dq values of our cobalt complexes are close to those of $[CoL_4]^{++}$ (Table IV). This shows that cobalt is surrounded by four ligands as $[CoL_4]^{++}$. The Dq values of $[NiL_6]^{++}$ obtained by us (Table IV) are close to the reported Dq values of $[NiL_6]^{++}$ [8, 9]. Hence it favours the existence of $[NiL_6]^{++}$ cation and the possible anion will be $[Cd(SCN)_4]^{--}$.

(ii) The positions of the bands due to νC–N, νC–S and δNCS modes are indicative of S-bonded thiocyanates, which support the existence of $[Cd(SCN)_4]^{--}$ anion. Hence the structures II, III, V and VI are ruled out.

(iii) Structure III is ruled out on the basis of group theoretical calculations. The number of infrared active bands for the cation $[CoL_4]^{++}$ and anion $[Cd(SCN)_4]^{--}$ have been calculated by assuming a T_d point group for both the ions. The number of calculated bands along with the symmetry species for νCo–L, νC–N, νC–S, δNCS and νCd–NCS modes as presented in the following table are in conformity with the observed number of bands. This provides an additional support to the structure I. If the structure III is correct, the number of bands will be higher.

TABLE II(a). Number of I.R. Active Thiocyanate Bands along with Symmetry Species in Cationic–Anionic Complexes.

Complexes	Point group		Thiocyanate modes with sym. species					
	Cation	Anion	νC–N	νC–S	δNCS	νM–L	δLML	νCd–SCN
$[CoL_4][Cd(SCN)_4]$	T_d	T_d	T_2	T_2	T_2	T_2	T_2	T_2
$[Co(tzt)_4][Cd(SCN)_4]$	T_d	T_d	2070s	750m	465m	256m	–	234s
$[Co(thn)_4][Cd(SCN)_4]$	T_d	T_d	2075s	805m	450s	262m	–	230m
$[Co(etu)_4][Cd(SCN)_4]$	T_d	T_d	2100s	740m	465m	258s	–	232m
$[NiL_6]^{++}[Cd(SCN)_4]^{--}$	O_h	T_d	T_2	T_2	T_2	T_{1u}	T_{1u}	T_2
$[Ni(tzt)_6][Cd(SCN)_4]$	O_h	T_d	2065s	755m	425s	222s	–	236m
$[Ni(thn)_6][Cd(SCN)_4]$	O_h	T_d	2075s	750s	430m	220m	–	230s
$[Ni(etu)_6][Cd(SCN)_4]$	O_h	T_d	2100s	770m	450s	224m	–	234m

TABLE II(b). Number of I.R. Active Thiocyanate Bands along with the Symmetry Species in Monomeric Bridged Complexes.

Complexes	Point group	Thiocyanate modes with symmetry species				
		νC–N(bri.) νC–N(ter.)	νC–S(bri.) νC–S(ter.)	δNCS(bri.) δNCS(ter.)	νM–NCS νM–L	νHg–SCN
$L_2M(NCS)_2Hg(SCN)_2$	C_{2v}	$A_1 + B_1$ $A_1 + B_2$	$A_1 + B_1$ $A_1 + B_2$	$A_1 + B_1$ $A_1 + B_2$	$A_1 + B_1$ $A_1 + B_2$	$A_1 + B_1$
$(etu)_2Co(NCS)_2Hg(SCN)_2$	C_{2v}	2140m 2090s	790s 710s	485m, 470w 415sh	270m 234w	215w
$(thn)_2Co(NCS)_2Hg(SCN)_2$	C_{2v}	2125s 2094s	770s 735m	465m 445s	272m 234s	212w
$(tzt)_2Co(NCS)_2Hg(SCN)_2$	C_{2v}	2170m 2090s	810m, 760m 740s	475s, 460s 425m	270m 235w	210w
$(etu)_2Zn(NCS)_2Hg(SCN)_2$	C_{2v}	2135s 2086s	800w 715m	485m, 470m 420sh	275m 230w	210w
$(thn)_2Zn(NCS)_2Hg(SCN)_2$	C_{2v}	2145s 2060sh	775s 745m	460m 445m	270m 233s	214w
$(tzt)_2Zn(NCS)_2Hg(SCN)_2$	C_{2v}	2155s 2095s	760sb 725m	478m 465m	274m 230m	215w
$L_4Ni(NCS)_2Hg(SCN)_2$	C_{2v}	$A_1 + B_1$ $A_1 + B_2$	$A_1 + B_1$ $A_1 + B_2$	$A_1 + B_1$ $A_1 + B_2$	$A_1 + B_1$ $2A_1 + B_1 + B_2$	$A_1 + B_1$ –
$(etu)_4Ni(NCS)_2Hg(SCN)_2$	C_{2v}	2150s,2125s 2090s	775s 740w	475m 435m	275m 230w	215w
$(thn)_4Ni(NCS)_2Hg(SCN)_2$	C_{2v}	2130s 2090sh	780sh 750s	465s 430m	270m 232s	210w
$(tzt)_4Ni(NCS)_2Hg(SCN)_2$	C_{2v}	2145s 2105s	750m 725m	450s 430w	272s 234m	215w

Similarly in the case of nickel complexes the number of infrared active bands have been calculated by assuming O_h point group for cation and T_d for anion. The number of calculated and observed bands along with the symmetry species as presented in Table II(a) are in good agreement [10].

'tzt', 'thn' and 'etu' possess multidonor sites of bonding in their molecules. To decide the actual site of bonding, the infrared spectrum of the ligand has been compared with those of complexes. Intermolecular hydrogen bonding between hydrogen of N–H and the sulphur of C=S is present in these ligands. This hydrogen bonding has a marked effect on the positions of the νN–H and νC=S bands [6, 11, 12]. To eliminate this effect, we have taken the spectrum of the ligand in dilute chloroform solution for the purpose of comparison. On comparing the infrared spectra (Table III) of 'etu', 'tzt' and 'thn' with the spectra of the complexes, it is observed that there is no negative shift in the positions of the νN–H bands and no positive shift in δN–H modes. On the other hand there is negative shift of about 40 cm^{-1} in the positions of the bands assigned to thiocarbonyl group [13]. This indicates that 'tzt', 'thn' and 'etu' are coordinated through their thiocarbonyl sulphur instead of the imino nitrogen. This observation is also supported by the earlier reported results in such cases [7]. A positive shift in the bands at 653 cm^{-1}

TABLE III. Assignments of Infrared Spectral Bands of Ligand Vibrations (cm^{-1}).[a]

Ligand/Complexes	ν(N–H)	δ(N–H)	Ring ν(C–S)	Thiocarbonyl sulphur (stretch)	ν(C=O)
'etu' (Nujol)	3245s	1470m	–	1250s	–
'etu' (Chloroform)	3425s	1490s	–	1265	–
$(Etu)_2Co(NCS)_2Hg(SCN)_2$	3250s	1510s	–	1272s	–
$[Co(etu)_4][Cd(SCN)_4]$	3380s	1490sh	–	1255s	–
$(etu)_4Ni(NCS)_2Hg(SCN)_2$	3275s	1525s	–	1285s	–
$[Ni(etu)_6][Cd(SCN)_4]$	3390sb	1495sh	–	1250s	–
$(etu)_2Zn(NCS)_2Hg(SCN)_2]$	3270sb	1505s	–	1270s	–
'thn' (Nujol)	3270m	1710s	–	1535s	1770s
'thn' (Chloroform)	3400s	–	–	–	–
$(thn)_2Co(NCS)_2Hg(SCN)_2$	3295s	1710s	–	1540s	1775s
$[Co(thn)_4][Cd(SCN)_4]$	3410sb	1705m	–	1500m	1770s
$(thn)_4Ni(NCS)_2Hg(SCN)_2$	3225sb	1710s	–	1545s	1765s
$[Ni(thn)_6][Cd(SCN)_4]$	3405sb	1700s	–	1505s	1768m
$(thn)_2Zn(NCS)_2Hg(SCN)_2$	3220s	1720s	–	1535s	1770s
'tzt' (Nujol)	3120s	1512s	652s	1294s	–
'tzt' (Chloroform)	3425s	1490s	652s	1295s	–
$(tzt)_2Co(NCS)_2Hg(SCN)_2$	3250s	1540s	670s	1310s	–
$[Co(tzt)_4][Cd(SCN)_4]$	3405sb	1495w	660m	1245b	–
$(tzt)_4Ni(NCS)_2Hg(SCN)_2$	3225sb	1515s	670s	1310s	–
$[Ni(tzt)_6][Cd(SCN)_4]$	3420sb	1490s	655w	1255b	–
$(tzt)_2Zn(NCS)_2Hg(SCN)_2$	3245sb	1510s	665s	1318s	–

[a]s = strong, sh = shoulder, m = medium, b = broad, w = weak.

assigned to C–S ring vibrations also rules out the possibility of coordination through the ring sulphur in case of 'tzt'. In case of 'thn', there is a positive shift in the position of the band at 1770 cm^{-1} assigned to carbonyl oxygen. This observation rules out the possibility of coordination of 'thn' through its carbonyl oxygen.

(B) Monomeric Thiocyanate Bridged Complexes viz. *$L_2M(NCS)_2Hg(SCN)_2$ and $L_4Ni(NCS)_2Hg(SCN)_2$ (L = tzt, thn, etu; M = Co(II), Zn(II))*

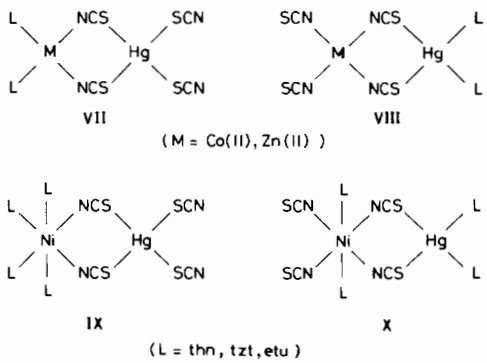
(i) The analytical results indicate that two molecules of ligands are coordinated to $MHg(SCN)_4$ (M = Co, Zn) and four molecules to $NiHg(SCN)_4$.

(ii) The molar conductance of these complexes in acetone and N,N′-dimethylformamide indicate that they are non-electrolytes.

(iii) In the infrared spectrum (Table II(b)), the presence of three absorption bands in νC–N stretching region show the presence of both terminal and bridged thiocyanates [3, 4, 5, 10]. The position and number of absorption bands due to νC–S and δNCS modes also support the presence of both types of thiocyanates. The band at higher frequency is due to bridged thiocyanate and that at lower frequency to the terminal one.

(iv) The electronic spectra and magnetic moment values, as discussed later, show that cobalt and nickel in these complexes are in tetrahedral and octahedral coordination geometry respectively.

On the basis of the above facts the following structures are possible:



The data enumerated below suggest that the most probable structures are VII and IX.

(i) Softness data and symbiosis theory as discussed later favour the structures VII and IX.

(ii) Comparison of calculated Dq values (Table IV) of these complexes with reported Dq values of similar complexes indicate that cobalt is surrounded by two ligands and two thiocyanate groups while nickel is surrounded by four ligands and two thiocyanate groups as shown in formulae VII and IX [4, 8, 14].

(iii) Group theoretical calculations have also been made assuming a C_{2v} point group for this class of compounds. The calculated bands along with their

TABLE IV. Selected Electronic Bands and Spectral Parameters.

Complexes	ν_2 (cm^{-1})	ν_3 (cm^{-1})	Dq (cm^{-1})	B' (cm^{-1})	β	λ' (cm^{-1})
$[Co(thn)_4][Cd(SCN)_4]$	6540	15090	375	692	0.71	147
$[Co(tzt)_4][Cd(SCN)_4]$	6500	16030	364	774	0.79	120
$[Co(etu)_4][Cd(SCN)_4]$	6520	14285	372	643	0.66	132
$(thn)_2Co(NCS)_2Hg(SCN)_2$	7620	16380	434	910	0.96	145
$(etu)_2Co(NCS)_2Hg(SCN)_2$	7200	16400	408	757	0.78	139
$(tzt)_2Co(NCS)_2Hg(SCN)_2$	6700	17000	385	810	0.83	129
$[Ni(tzt)_6][Cd(SCN)_4]$	15005	28150	991	895	0.84	236
$(thn)_4Ni(NCS)_2Hg(SCN)_2$	16500	27600	1015	910	0.87	198
$[Ni(etu)_6][Cd(SCN)_4]$	16950	25400	1045	913	0.88	249
$(tzt)_4Ni(NCS)_2Hg(SCN)_2$	16100	28500	978	985	0.94	276

symmetry species (Table II(b)) are in good agreement with the observed number of bands [10]. This provides an additional support to these structures.

(iv) On comparing the infrared spectra (Table III) of 'tzt', 'thn' and 'etu' with those of complexes of this group, it is observed that there is a negative shift in the positions of the bands due to νN–H and a positive shift due to δN–H modes. These observations indicate that coordination has taken place through the imino nitrogen. This assumption is also supported by the positive shift in the bands due to thiocarbonyl group which rules out the coordination through sulphur. In case of 'tzt' there is also a positive shift in the band at 652 cm^{-1} assigned to C–S ring vibration. This rules out the possibility of coordination through the ring sulphur. In the case of 'thn' complexes there is no change in the position of the bands due to νC=O which indicates that coordination has not taken place through its carbonyl oxygen.

Far I.R. Spectral Discussion

In cationic–anionic complexes of cobalt and nickel, we observe bands at about 260 cm^{-1} and 220 cm^{-1} which could be assigned to νM–S modes respectively [15, 16]. We tentatively assigned the bands at about 230 cm^{-1} to Cd–SCN stretching frequency in all cationic–anionic complexes [17].

In monomeric bridged complexes we observe two bands in the region 210–275 cm^{-1} which may be due to νM–NCS, νM'–SCN and νM–L (N-donor) modes. The region of these modes are very close, hence it is difficult to assign them separately. However, we assign the band at 275 cm^{-1} to νM–NCS mode and the bands at lower region due to νM–SCN or νM–L modes. The bands in the far i.r. spectra indirectly favour our proposed structure.

Electronic Spectra

The electronic spectra of the complexes have been recorded as nujol mulls. The position of bands, their assignment and spectral parameters derived from them are presented in Table IV.

All the cobalt complexes show the presence of two intense bands, one in the region 14,285–17,000 cm^{-1} which is assigned to $^4A_2 \rightarrow {}^4T_1(P)$ transition (ν_3) and the other in the region 6,500–7,620 cm^{-1} assigned to $^4A_2 \rightarrow {}^4T_1(F)$ transition (ν_2). Using the values of these bands we have derived the spectral parameters Dq, B' and β [18]. The band position and the values of spectral parameters indicate that the cobalt is in tetrahedral coordination geometry. These results support the proposed structures.

Similarly the position of the bands of nickel complexes are in the range prescribed for octahedral nickel. The bands assigned to the transitions $^3A_{2g} \rightarrow {}^3T_{1g}(F)$ (ν_2) and $^3A_{2g} \rightarrow {}^3T_{1g}(P)$ (ν_3) are observed at 15,000–16,950 cm^{-1} and 25,400–28,500 cm^{-1} respectively. The position of electronic absorption bands and the values of spectral parameters (Table IV) calculated from ν_2 and ν_3 clearly indicate the presence of octahedral environment around nickel [19]. The magnetic moment values also support octahedral coordination geometry around nickel.

A correlation between spectral and magnetic studies has been obtained by calculating effective values of spin–orbit coupling constant (λ') for the Co(II) and Ni(II) complexes [19, 20] (Table IV). The values in complexes appear generally lower than the values of 178 cm^{-1} of the free ions of Co(II) and Ni(II) respectively. It is due to orbital overlap resulting in delocalization of the d-electrons.

Conclusions

(i) 'etu', 'thn' and 'tzt' coordinate through their thiocarbonyl sulphur to cobalt and nickel ions in cationic–anionic complexes. The linkage of these ligands through their thiocarbonyl sulphur is in accordance with the linkages proposed by Nardelli and coworkers [21], who have shown such a linkage on the basis of X-ray crystallographic technique. Other workers [7] have also shown that thiocarbonyl sulphur is the donor site in such complexes. On the

contrary, these ligands coordinate through the imino nitrogen in case of monomeric bridged complexes. Such a change in donor site on changing the nature of complexes needs explanation. The only explanation that we can afford at the moment is based on the difference in softness values of cobalt and nickel ions in the two types of complexes. The softness values of free cobalt and nickel ions in ethanol are –0.38 and –0.16 eV respectively, whereas in the case of monomeric bridged complexes the softness values of cobalt and nickel are affected on account of their linkage with thiocyanate group. Jørgensen [22] noted that metal ions prefer bonding to ligands of the same kind, whether they are hard or soft. Hard–Soft mixed bonding results in an unstable species. In monomeric bridged complexes, the cobalt or nickel has to link with nitrogen atom of the ligand, since they are already attached with N-end of thiocyanates according to the *Symbiosis principle*. Thus we can say that the cobalt ion in case of cationic–anionic complexes is softer than the cobalt in monomeric bridged complexes. In ligands, their imino nitrogen is harder than thiocarbonyl sulphur, hence the ligands prefer coordination through thiocarbonyl sulphur to softer cobalt and imino nitrogen to harder cobalt.

(ii) $CoCd(SCN)_4$ and $NiCd(SCN)_4$ form cationic–anionic type of complexes with all the three ligands, whereas the same ligands form monomeric bridged complexes with $CoHg(SCN)_4$ and $NiHg(SCN)_4$. The change in the nature of the complexes is evidently caused by the replacement of cadmium by mercury in the latter case. This can be explained as follows:

Recently [14] it has been shown that the stability of the bridge depends upon the difference in softness values of the two metals of the tetrathiocyanates. The stability of the bridge has been related to the nature of the complexes as shown in Table V. Since $\Delta E_n^{\ddagger}$ (M–M′) is lower in the case of $MCd(SCN)_4$ and higher in the case of $MHg(SCN)_4$ (M = Co, Ni), the thiocyanate bridge breaks in the case of the former and forms cationic–anionic type of complexes and does not break in the case of the latter and forms monomeric bridged complexes.

TABLE V. Softness Values of Metals and Their Differences in ev.

M/M′	$E_n^{\ddagger}(M)$	$E_n^{\ddagger}(M')$	$\Delta E_n^{\ddagger}(M-M')$
Co/Hg	–0.38	–4.99	4.61
Ni/Hg	–0.16	–4.99	4.83
Co/Cd	–0.38	–2.42	2.04
Ni/Cd	–0.16	–2.42	2.26

(iii) Cobalt prefers a tetrahedral coordination geometry with 'etu', 'thn' and 'tzt' similar to its preference with thiazolidinethione, dimethyl acetamide and N-allyl urea [6, 23]. The preference of tetrahedral geometry with these ligands indicates that they have a weak base strength.

(iv) The relative stability of thiocyanate bridge with respect to different ligands in case of monomeric bridged complexes of $MHg(SCN)_4$ (M = Co, Ni, Zn) has also been evolved as follows.

Recently [24] the difference in the total softness values [$\Delta TE_n^{\ddagger}(M-M')$] of M and M′ in a series of complexes of the type $\rangle L_xM(NCS)_2M'(SCN)_2\langle$ have been used to support the site of coordination of the ligand to M or M′. It has been shown that out of various possible structures, the one which gives the higher $\Delta TE_n^{\ddagger}(M-M')$ value is supposed to be the possible structure. For instance in case of $CoHg(SCN)_4 \cdot 2tpp$, the $\Delta TE_n^{\ddagger}(M-M')$ values were derived in respect of the two possible structures: (i) $(tpp)_2Co(NCS)_2Hg(SCN)_2$ (17.67) and (ii) $(SCN)_2Co(NCS)_2Hg(tpp)_2$ (8.93). The $\Delta TE_n^{\ddagger}(M-M')$ value for the first structure has been found to be higher, hence this structure has been proposed. Experimental results also support this structure.

The total softness values of M and M′ and their difference in respect of the complexes $MM'(SCN)_4 \cdot xL$ can be calculated by adopting the following equations:

$$\Delta TE_n^{\ddagger}(M-M') = TE_n^{\ddagger}(M) - TE_n^{\ddagger}(M') \quad \text{(i)}$$

$$= [E_n^{\ddagger}(M) + \Sigma E_m^{\ddagger}(M_L) + \Sigma E_m^{\ddagger}(M - NCS)] - [E_n^{\ddagger}(M') + \Sigma E_m^{\ddagger}(M'_L) + \Sigma E_m^{\ddagger}(M'-SCN)] \quad \text{(ii)}$$

where $E_n^{\ddagger}(M)$, $E_n^{\ddagger}(M')$ are the softness values of M and M′ respectively. $\Sigma E_m^{\ddagger}(M_L)$ and $\Sigma E_m^{\ddagger}(M-NCS)$ are the sum of the softness values of ligands and N-end of thiocyanates attached to M respectively. $\Sigma E_m^{\ddagger}(M'_L)$ and $\Sigma E_m^{\ddagger}(M'-SCN)$ are the sum of softness values of ligands and S-end of thiocyanates attached to M′ respectively. $TE_n^{\ddagger}(M)$ and $TE_n^{\ddagger}(M')$ are the total softness of M and M′ respectively. Using the above relations we have calculated the total softness values for the proposed as well as for alternative structures of the complexes of the present series. The results of these calculations are presented in Table VI. The details of the calculation of the total softness difference in two cases are presented below:

(I) *$CoHg(SCN)_4 \cdot 2etu$*

For proposed structure $(etu)_2Co(NCS)_2Hg(SCN)_2$ (VII)

$$TE_n^{\ddagger}(Co) = E_n^{\ddagger}(Co) + 2E_m^{\ddagger}(etu) + 2E_m^{\ddagger}(NCS) = 0.38 + 23.24 + 25.30 = 48.92$$

$$TE_n^{\ddagger}(Hg) = E_n^{\ddagger}(Hg) + 4E_m^{\ddagger}(SCN) = 4.99 + 32.64 = 37.63$$

$$\Delta TE_n^{\ddagger}(Co-Hg) = 11.29$$

TABLE VI. Total Softness Difference for Various Structures of Monomeric Bridged Complexes.

Complexes	Proposed structure $L_2Co(NCS)_2Hg(SCN)_2$	Alternative structure $(SCN)_2Co(NCS)_2HgL_2$
$CoHg(SCN)_4 \cdot 2etu$	11.29	6.43
$CoHg(SCN)_4 \cdot 2thn$	10.95	6.77
$CoHg(SCN)_4 \cdot 2tzt$	11.31	6.41
$ZnHg(SCN)_4 \cdot 2etu$	13.75	6.99
$ZnHg(SCN)_4 \cdot 2thn$	13.41	7.33
$ZnHg(SCN)_4 \cdot 2tzt$	13.77	6.97
	$L_4Ni(NCS)_2Hg(SCN)_2$	$L_2(SCN)_2Ni(NCS)_2HgL_2$
$NiHg(SCN)_4 \cdot 4etu$	34.31	29.45
$NiHg(SCN)_4 \cdot 4thn$	33.63	29.45
$NiHg(SCN)_4 \cdot 4tzt$	34.35	29.45

For alternative structure $(SCN)_2Co(NCS)_2Hg(etu)_2$ (VIII)

$$TE_n^{\ddagger}(Co) = E_n^{\ddagger}(Co) + 4E_m^{\ddagger}(NCS) = 0.38 + 50.60 = 50.98$$

$$TE_n^{\ddagger}(Hg) = E_n^{\ddagger}(Hg) + 2E_m^{\ddagger}(SCN) + 2E_m^{\ddagger}(etu) = 4.99 + 16.32 + 23.24 = 44.55$$

$$\Delta TE_n^{\ddagger}(Co\text{–}Hg) = 6.43$$

$NiHg(SCN)_4 \cdot 4tzt$

For proposed structure $(tzt)_4Ni(NCS)_2Hg(SCN)_2$ (IX)

$$TE_n^{\ddagger}(Ni) = E_n^{\ddagger}(Ni) + 4E_m^{\ddagger}(tzt) + 2E_m^{\ddagger}(NCS) = 0.16 + 46.52 + 25.30 = 71.98$$

$$TE_n^{\ddagger}(Hg) = E_n^{\ddagger}(Hg) + 4E_m^{\ddagger}(SCN) = 4.99 + 32.64 = 37.63$$

$$\Delta TE_n^{\ddagger}(Ni\text{–}Hg) = 34.35$$

For alternative structure $(tzt)_2(SCN)_2Ni(NCS)_2$-$Hg(tzt)_2$ (X)

$$TE_n^{\ddagger}(Ni) = E_n^{\ddagger}(Ni) + 2E_m^{\ddagger}(tzt) + 4E_m^{\ddagger}(NCS) = 0.16 + 23.26 + 50.60 = 74.02$$

$$TE_n^{\ddagger}(Hg) = E_n^{\ddagger}(Hg) + 2E_m^{\ddagger}(SCN) + 2E_m^{\ddagger}(tzt) = 4.99 + 16.32 + 23.26 = 44.57$$

$$\Delta TE_n^{\ddagger}(Ni\text{–}Hg) = 29.45$$

From the above calculations it is clear that the total softness difference is higher in respect of the proposed structure. If the site of coordination of the ligand is changed, the value of $\Delta TE_n^{\ddagger}(M\text{–}M')$ becomes lower. The higher value of $\Delta TE_n^{\ddagger}(M\text{–}M')$ is indicative of more stable bridge in bridged complexes [24].

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References

1 G. Klopman, *J. Am. Chem. Soc., 90,* 223 (1968).
2 B. N. Figgis and R. S. Nyholm, *J. Chem. Soc.,* 4190 (1958).
3 P. P. Singh and S. A. Khan, *Inorg. Chim. Acta, 14,* 143 (1975).
4 P. P. Singh, L. P. Pathak and S. A. Khan, *J. Inorg. Nucl. Chem., 38,* 475 (1976).
5 I. S. Ahuja and A. Garg, *J. Inorg. Nucl. Chem., 34,* 1929 (1972).
6 P. P. Singh and R. Rivest, *Can. J. Chem., 46,* 2361 (1968).
7 L. Corlin Richard and L. H. Smith Jr., *Inorg. Chem., 2,* 849 (1963).
8 A. B. P. Lever, "Inorganic Electronic Spectroscopy", Elsevier, London, pp. 324, 328, 336 (1968).
9 D. E. Billing and A. E. Underhill, *J. Chem. Soc. A,* 29 (1968).
10 P. P. Singh and S. A. Khan, *Z. Anorg. Allgem. Chem., 423,* 173 (1976).
11 P. P. Singh and I. M. Pande, *J. Inorg. Nucl. Chem., 34,* 591 (1972).
12 P. P. Singh, O. P. Agrawal and A. K. Gupta, *Inorg. Chim. Acta, 18,* 19 (1976).
13 D. T. Elmore, *J. Chem. Soc.,* 3489 (1958).
14 P. P. Singh and S. B. Sharma, *J. Coord. Chem., 6,* 65 (1976).
15 C. D. Flint and M. Goodgame, *J. Chem. Soc. A,* 744 (1966).
16 D. M. Adams and J. B. Cornell, *J. Chem. Soc. A,* 2178 (1968).
17 D. Forster and D. M. L. Goodgame, *Inorg. Chem., 4,* 715 (1965).

18 Y. Tanabe and S. Sugano, *J. Phys. Soc. Japan, 9,* 753 (1954).
19 R. A. Baily and T. R. Peterson, *Can. J. Chem., 46,* 3119 (1968).
20 J. T. Donoghue and R. S. Drago, *Inorg. Chem., 1,* 866 (1962).
21 M. Nardelli, I. Chierici and A. Braibanti, *Gazz. Chim. Ital., 88,* 37 (1958).
22 C. K. Jørgensen, *Inorg. Chem., 3,* 1201 (1964).
23 P. P. Singh and I. M. Pande, *Can. J. Chem., 50,* 2603 (1972).
24 P. P. Singh and A. K. Gupta, *Inorg. Chem., 17,* 1 (1978).