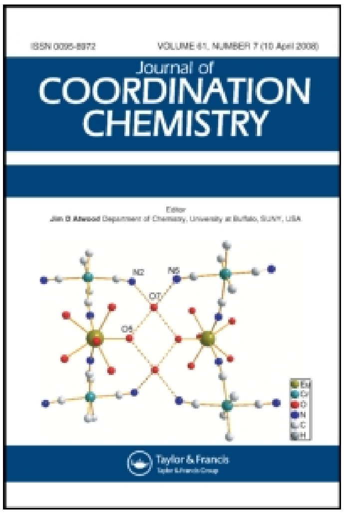

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NATURE OF SELENOCYANATE BONDING IN THE COMPLEXES OF [MM^1(NCSe)$_4$] (M=Co, Ni AND M^1=Zn, Cd, Hg) WITH CERTAIN PYPIDINE DERIVATIVES

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Complexes of [MM′(NCSe)$_4$] (M = Co, Ni and M′ = Zn, Cd, Hg) with certain ligands(L) viz. 3-cyanopyridine, 3-aminopyridine, nicotinamide and isonicotinic acid hydrazide have been synthesized and characterized. Their molar conductance, magnetic moment, infrared and electronic spectral studies indicate that these complexes are of three types: cationic-anionic viz. [ML$_6$] [Zn(NCSe)$_4$], monomeric bridged viz. [(L$_4$)M(NCSe)$_2$Cd(SeCN)$_2$] and polymeric bridged viz. >(SeCN)$_2$L$_2$M(NCSe)$_2$Hg(SeCN)$_2$<. The softness and hardness of M, M′, –N–(NCSe$^-$) and –Se–(SeCN$^-$) have also been calculated to derive certain conclusions.

INTRODUCTION

[MM′(NCS)$_4$] (M = Co, Ni and M′ = Zn, Cd, Hg), have recently been used as Lewis acids and their complexes with number of Lewis bases have been synthesized and studied.[1–5] The effect of change of M and M′, and of bases, on the bonding nature of thiocyanates in these tetrathiocyanates have also been discussed.[2–5] There, however, appear only few references[6–10,23] on the study of the complexes of corresponding tetraselenocyanates. In this communication we, therefore, report the synthesis and study of certain new complexes of tetraselenocyanates, with two main interests: Firstly to see the effect of change of M and M′ on the nature of tetraselenocyanate bonding and secondly to compare their bonding nature with corresponding tetrathiocyanate complexes.

EXPERIMENTAL SECTION

Materials and Manipulations

Hydrated Metal nitrates (B.D.H.) (Metal=Co, Ni, Zn, Cd, Hg) were used as such from fresh bottles. Potassium selenocyanate was prepared and doubly recrystallized by the method described elsewhere.[11] 3-Cyanopyridine (cpy) and 3-aminopyridine (apy) were synthesized by known methods,[12] and purified by distillation under reduced pressure. Nicotinamide (nia) (B.D.H.), isonicotinic acid hydrazide (inh) (Aldrich Chemicals) and pyridine (py) (B.D.H.), were used as such. All solvents were strictly dried before use.

Synthesis of the Complexes

Metal diselenocyanates were first prepared by direct reaction of metal(II) nitrates and potassium selenocyanate in methanol. KNO$_3$ was removed by filtration and the solutions of selenocyanates were preserved. For the preparation of [CoHg(SeCN)$_4$], the solution of Co(NCSe)$_2$ and Hg(SeCN)$_2$ were mixed in 1:1 ratio and stirred for 8 h. Similarly, other tetraselenocyanates [NiHg(SeCN)$_4$], [ZnHg(SeCN)$_4$], [CoCd(SeCN)$_4$], [NiCd(SeCN)$_4$] and [CdHg(SeCN)$_4$] were prepared by mixing the two corresponding diselenocyanates. In case of [CoZn(NCSe)$_4$] and [NiZn(NCSe)$_4$] the stirring time was only 30 minutes.

To the suspensions or solutions of these tetraselenocyanates, the solution of ligands (py,nia,cpy,apy and inh) in methanol were added in suitable molar ratio and stirred for 6 h. In case of [CoZn(NCSe)$_4$] and [NiZn(NCSe)$_4$] complexes, the stirring was done only for 1 h. In each case solid complexes were formed which were filtered, washed with the solvent and dried in vacuum. All complexes were recrystallized from methanol except [NiHg(SeCN)$_4$] and [CoHg(SeCN)$_4$] complexes, which were insoluble in this solvent.

Analysis of the Complexes

Selenium was estimated as selenium metal, mercury as mercury sulphide and cobalt as cobalt anthranilate. In case of $[\mathrm{CoCd(SeCN)_4}]$ and $[\mathrm{CoZn(NCSe)_4}]$ complexes, zinc and cadmium were estimated as mixed anthranilate of cobalt. Nitrogen was estimated by Kjeldahl method. Analytical data are presented in Table 1.

Physical Measurements

The molar conductance of the complexes were measured in methanol or dimethylformamide by Philips conductivity bridge model PR-9500. These data are included in the Table I.

The infrared spectra of ligands and complexes were recorded on a Perkin–Elmer 621 spectrophotometer in the range 4000–200 cm^{-1}. Samples were run as Nujol mulls using CsI plates. Spectra of the ligands were also recorded in solution.

Electronic spectra were obtained on Cary-14 spectrophotometer between 1500–300 mμ. Samples were run as their dimethylformamide or methanol solutions.

Magnetic susceptibility measurements were made by Gouy's method using $[\mathrm{CoHg(SCN)_4}]$ as standard.[22]

RESULTS AND DISCUSSION

On the basis of structure of the complexes we have divided our study in three groups:

Cationic–anionic Complexes

Viz. $[\mathrm{CoL_6}][\mathrm{Zn(NCSe)_4}]$, $[\mathrm{NiL_6}][\mathrm{Zn(NCSe)_4}]$, $[\mathrm{CdL_4}][\mathrm{Hg(SeCN)_4}]$ [L = nia, inh, cpy;]

Molar conductance values of these complexes in methanol indicate that they are 1:1 cationic–anionic. The colour, B.M. values and positions of peaks in electronic spectra of the complexes show that cobalt(II) and nickel(II) are in an octahedral environment. The possible cation, therefore, will be $[\mathrm{CoL_6}]^{2+}$ and $[\mathrm{NiL_6}]^{2+}$ because the ligands(L) which show features of coordination through ring nitrogen, will coordinate to Co(II) or Ni(II) according to H.S.A.B. theory.[13] The Dq values also favour the existence of such a cation as they are in the range of previously reported Dq values of $[\mathrm{Ni(py)_6}]^{2+}$.[14,15] The possible anion will be $[\mathrm{Zn(NCSe)_4}]^{2-}$. The positions of γCN, γCSe and δNCSe bands in infrared spectra (Table II) indicate that selenocyanates are N-bonded[16–20,24]. In case of $[\mathrm{CdL_4}][\mathrm{Hg(SeCN)_4}]$, the positions of γCN, γCSe and δNCSe bands show the presence of Se-bonded selenocyanates.[16–19,22] The selenocyanate is shown linked to mercury(II), as it is more soft than cadmium(II), the ligand will, therefore, coordinate to cadmium(II). Thus the anion will be $[\mathrm{Hg(SeCN)_4}]^{2-}$ and cation $[\mathrm{CdL_4}]^{2+}$.

If the proposed formula is correct, the anions will belong to Td point group. Assuming this point group, we have calculated the number of normal modes, the results of which indicate the presence of only one band in γCN, γCSe and δNCSe regions. The observed

TABLE I
Analytical Results and Molar Conductance Data

Complexes	Colour	M.P. °C	% Nitrogen		% Selenium		% Zinc, Cadmium or mercury		% Cobalt+Zinc or Cobalt+Cadmium		% Cobalt or nickel		Molar Conductance (λm) mhos cm^{-2} mol	
			calc.	obs.	calc.	obs.	calc.	obs.	calc.	obs.	calc.	obs.	M/512	M/1024
$[\mathrm{Co(nia)_6}][\mathrm{Zn(NCSe)_4}]$	Pink	145(d)	17.5	16.9	24.8	25.3	–	–	13.9	14.2	–	–	124	140
$[\mathrm{Co(cpy)_6}][\mathrm{Zn(NCSe)_4}]$	Pink	115(d)	19.2	18.6	27.0	27.5	–	–	15.1	14.8	–	–	126	155
$[\mathrm{Co(inh)_6}][\mathrm{Zn(NCSe)_4}]$	Light pink	165(d)	22.5	21.9	23.1	22.7	–	–	12.9	13.4	–	–	110	130
$[\mathrm{Ni(nia)_6}][\mathrm{Zn(NCSe)_4}]$	Violet	170(d)	17.5	16.9	24.8	23.9	5.1	4.9	–	–	4.6	5.0	145	160
$[\mathrm{Ni(cpy)_6}][\mathrm{Zn(NCSe)_4}]$	Violet	165(d)	19.2	18.4	27.1	26.4	5.6	7.0	–	–	5.0	4.9	135	142
$[\mathrm{Ni(inh)_6}][\mathrm{Zn(NCSe)_4}]$	Violet	170(d)	22.5	21.9	23.1	22.7	4.7	5.0	–	–	4.3	3.9	110	127
$[\mathrm{Cd(cpy)_4}][\mathrm{Hg(SeCN)_4}]$	White	190(d)	14.5	14.1	27.5	28.1	17.4	16.8*	–	–	–	–	150	165
$[\mathrm{Cd(nia)_4}][\mathrm{Hg(SeCN)_4}]$	White	180(d)	14.0	13.6	26.4	26.9	17.1	16.4*	–	–	–	–	140	155
$[\mathrm{(cpy)_4Co(NCSe)_2Cd(SeCN)_2}]$	Light pink	175(d)	16.7	16.4	31.4	31.6	–	–	17.0	16.7	–	–	71	80
$[\mathrm{(nia)_4Ni(NCSe)_2Cd(SeCN)_2}]$	Violet	180(d)	15.5	15.2	29.2	28.2	10.4	9.9	–	–	5.5	5.2	65	78
$[\mathrm{(cpy)_4Ni(NCSe)_2Cd(SeCN)_2}]$	Violet	165(d)	16.7	17.1	31.4	30.8	11.1	10.8	–	–	5.8	6.1	75	84
$[\mathrm{(apy)_4Ni(NCSe)_2Cd(SeCN)_2}]$	Violet	185(d)	17.4	16.9	32.7	33.0	11.6	11.3	–	–	6.1	5.9	57	68
$[\mathrm{(py)_4Zn(NCSe)_2Hg(SeCN)_2}]$.	White	200(d)	10.0	9.8	36.9	37.5	24.1	23.7*	–	–	–	–	64	72
$[\mathrm{(cpy)_4Zn(NCSe)_2Hg(SeCN)_2}]$	White	190(d)	12.5	12.7	35.4	36.1	22.4	21.9*	–	–	–	–	60	68
$[\mathrm{(nia)_4Zn(NCSe)_2Hg(SeCN)_2}]$	White	180(d)	12.0	11.8	34.2	33.9	21.5	22.0*	–	–	–	–	68	76
$>\mathrm{(SeCN)_2(cpy)_2Co(NCSe)_2Hg(SeCN)_2}<$	Light pink	185(d)	12.0	11.6	35.5	34.8	22.5	22.9	–	–	6.6	6.4	45	65
$>\mathrm{(SeCN)_2(apy)_2Co(NCSe)_2Hg(SeCN)_2}<$	Yellowish pink	220(d)	12.9	12.6	36.4	35.8	23.1	22.8	–	–	6.8	7.1	40	48
$>\mathrm{(SeCN)_2(nia)_2Co(NCSe)_2Hg(SeCN)_2}<$	Pink	195(d)	14.4	13.8	27.0	27.5	18.0	19.1	–	–	5.0	4.8	50	66
$>\mathrm{(SeCN)_2(inh)_2Co(NCSe)_2Hg(SeCN)_2}<$	Pink	180(d)	18.2	17.9	25.7	26.1	16.3	17.0	–	–	4.8	5.2	58	72
$>\mathrm{(SeCN)_2(cpy)_2Ni(NCSe)_2Hg(SeCN)_2}<$	Violet	225(d)	12.6	11.9	35.6	34.9	22.5	21.9	–	–	6.6	7.1	55	67
$>\mathrm{(SeCN)_2(apy)_2Ni(NCSe)_2Hg(SeCN)_2}<$	Violet	190(d)	12.9	12.4	36.7	37.5	23.1	22.8	–	–	6.8	7.2	65	75
$>\mathrm{(SeCN)_2(inh)_2Ni(NCSe)_2Hg(SeCN)_2}<$	Violet	185(d)	14.7	15.2	33.2	32.3	21.0	19.8	–	–	6.2	5.9	63	70

(d) = decomposes * = % mercury

TABLE II
Infrared Spectral Band Assignments (4000–200 cm^{-1})

Complexes	γCN	2δNCSe	γCSe	δNCSe	γM–L	γM–NCSe
$[Co(nia)_6][Zn(NCSe)_4]$	2077s	850w	650sh	420w,410sh	278w	250w,235w
$[Co(cpy)_6][Zn(NCSe)_4]$	2075s	865w	645m	403wb	280w,260w	240w
$[Co(inh)_6][Zn(NCSe)_4]$	2073s	870w,820sh	650sh	435w,410sh	265w,250w	230w
$[Ni(nia)_6][Zn(NCSe)_4]$	2070s	860w	637m	425w	–	–
$[Ni(cpy)_6][Zn(NCSe)_4]$	2065s	845w	630w	420wb	–	–
$[Ni(inh)_6][Zn(NCSe)_4]$	2067s	835sh	635sh	425m	–	–
$[Cd(cpy)_4][Hg(SeCN)_4]$	2105s	790m	585m	–	–	–
$[Cd(nia)_4][Hg(SeCN)_4]$	2100s	750mb	570mb	–	–	–
$[(cpy)_4Co(NCSe)_2Cd(SeCN)_2]$	2135s,2120sh,2090s	790w,770w,750sh	615w,600m,580m	397sh,385w,375w	275wb	250w,230w
$[(nia)_4Ni(NCSe)_2Cd(SeCN)_2]$	2122s,2090sh,2050s	825w,790sh,760w	605m,590w,665sh	410sh,405w	–	–
$[(cpy)_4Ni(NCSe)_2Cd(SeCN)_2]$	2125s,2090sh,2083s	795w,765w	600m,585m,570sh	410w,407m	–	–
$[(apy)_4Ni(NCSe)_2Cd(SeCN)_2]$	2130s,2110sh,2090s	810sh,780w,770sh	615m,585sh,575w	415w,405sh	–	–
$[(py)_4Zn(NCSe)_2Hg(SeCN)_2]$	2125s,2105sh,2085s	828w,795w,755sh	630m,600w,570w	412m,407w	–	–
$[(cpy)_4Zn(NCSe)_2Hg(SeCN)_2]$	2140sh,2100sh,2085sh	830w,790w,760sh	624m,590sh,560w	415w,405m	–	–
$[(nia)_4Zn(NCSe)_2Hg(SeCN)_2]$	2135s,2100sh,2090s	825w,795sh,775w	625m,600sh,580w	410m,405sh	–	–
$>(SeCN)_2(cpy)_2Co(NCSe)_2Hg(SeCN)_2<$	2135s,2095sh	800sh,785w	600m,590sh	402m,390sh	270w	224w,210w
$>(SeCN)_2(apy)_2Co(NCSe)_2Hg(SeCN)_2<$	2130s,2095sh	810sh,775w	585wb,570m	400m,390sh	285m,270sh	245w,225w,205sh
$>(SeCN)_2(nia)_2Co(NCSe)_2Hg(SeCN)_2<$	2135s,2115sh	785w,775w	597m,590sh	403sh,395m	280sh,270w	250w,205w
$>(SeCN)_2(inh)_2Co(NCSe)_2Hg(SeCN)_2<$	2125sh,2105sh	810w,785w	593w,610sh	450wb,385sh	285w	260w,225sh
$>(SeCN)_2(cpy)_2Ni(NCSe)_2Hg(SeCN)_2<$	2125s,2100sh	805w,790w	600m,590sh	410w,405sh	–	–
$>(SeCN)_2(apy)_2Ni(NCSe)_2Hg(SeCN)_2<$	2130s,2105sh	810w,785sh	630m,596w	415w,407m	–	–
$>(SeCN)_2(inh)_2Ni(NCSe)_2Hg(SeCN)_2<$	2125s,2110sh	815sh,790w	625m,600sh	410w,405w	–	–

s = strong, m = medium, sh = shoulder, w = weak, b = broad

number of bands are in agreement with the calculated number. This also favours the proposed formula.

Monomeric Bridged complexes

Viz. $[(cpy)_4Co(NCSe)_2Cd(SeCN)_2]$, $[(L)_4Ni(NCSe)_2Cd(SeCN)_2]$ and $[(L)_4Zn(NCSe)_2Hg(SeCN)_2]$ (L = cpy, nia, apy and py)

The molar conductance values of these complexes in methanol, indicate that they are non-conducting in nature. The colour, B.M. values and electronic spectra show that Co(II) and Ni(II) are in octahedral environment. All these complexes show the presence of three bands in γCN, γCSe and δNCSe regions in infrared spectra. This indicates the presence of two types of selenocyanates. In γCN region two bands are observed in the range 2110–2135 cm^{-1} indicating the presence of bridged selenocyanates.[16–21] The third band is observed in cadmium complexes at 2095 cm^{-1} and in zinc complexes at 2075 cm^{-1} indicating the presence of Se-bonded and N-bonded terminal selenocyanates, respectively. On the basis of these results, the structure at the foot of the previous column is proposed for this class of complexes.

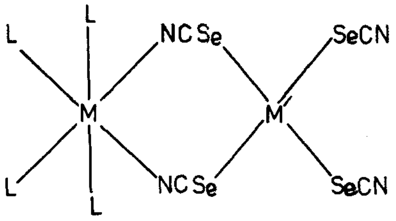

FIGURE 1 When M = Co(II), Ni(II); M′ = Cd(II). and when M = Zn, M′ = Hg(II). L = py, apy, cpy, nia and inh.

The ligands which show coordination through ring nitrogen, and the N-end of selenocyanates, have been shown linked to cobalt(II) and nickel(II) and the selenium end, to cadmium(II) or mercury(II) according to H.S.A.B. theory.[13]

Assuming C_{2v} point group, for the proposed structure, the number of normal modes for γCN, γCSe and δNCSe have been calculated. The calculated and observed number of bands in these regions is three. This also supports the proposed structure.

Polymeric Bridged Complexes

Viz. $>(SeCN)_2L_2M(NCSe)_2Hg(SeCN)_2<$ (M = Co,Ni; L = cpy, nia, inh;)

All these complexes are non-conducting in dimethylformamide. The colour, B.M. values and electronic spectral band positions (Table III), show that Co(II) and Ni(II) in these complexes are in octahedral configuration. In infrared spectra, two bands are present in γCN region in the range 2100–2155 cm^{-1}. In γCSe and δNCSe regions also two bands are present in the range 585–600 cm^{-1} and 385–405 cm^{-1}, respectively. The positions of these bands clearly show the presence of only bridged selenocyanates.[16,18,20] The N-end of bridging selenocyanates will link to Co(II) or Ni(II) and Se-end to Hg(II). The ligands (L) which show features of coordination through ring nitrogen, are borderline base on softness scale,[13] hence will link to borderline metal ion Co(II) or Ni(II). Hg(II) is softer hence will have less preference for these bases. On the basis of these observations we can propose the following structure to these complexes:

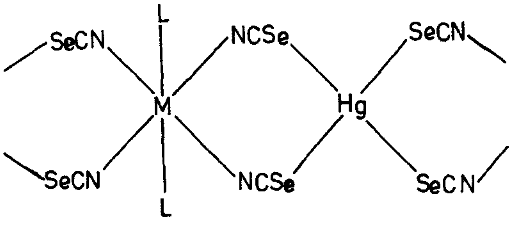

FIGURE 2 M = Co(II), Ni(II); L = cpy, apy, nia and inh.

These complexes also belong to C_{2v} point group but the normal mode calculations show the presence of only two bands in γCN, γCSe and δNCSe regions. The observed number of bands in these regions is also two, hence lend a strong support to the proposed structure.

Electronic Spectral Discussion

To confirm the proposed configuration of Co(II) and Ni(II) we have recorded electronic spectra in the range 3500–1200 cm^{-1}. The assignment of bands[15] and the spectral parameters[33] derived from them are presented in Table III.

In case of Co(II) complexes γ_2 band is weak. The electronic spectral band position and Bohr magneton values very clearly indicate that all nickel(II) and cobalt(II) complexes have octahedral configuration.[14–15] The Dq values of the ions $[NiL_6]^{2+}$ are in the range of the previously reported Dq values of octahedral complexes having $[NiN_6]^{2+}$ skeleton.[24]

Electronic spectral data have been very useful in finding the site of bonding in selenocyanates. When the linkage takes place through nitrogen, the reported values of 10Dq in case of $[Ni(NCSe)_6]^{4-}$ are about 10000 cm^{-1}.[24] The 10Dq values of the nickel(II) complexes in the present series are in the range 9600–10600 cm^{-1}. This shows that nickel is bonded through nitrogen end of selenocyanate in these complexes.

DIFFERENCES WITH TETRATHIOCYANATE COMPLEXES

The nature of bonding in tetraselenocyanate complexes[6, 25, 30] is basically similar to that of the corresponding tetrathiocyanate complexes. Few differences are, however, notable:

i) The nia and inh complexes of $[MHg(SeCN)_4]$[25] are polymeric in nature, while that of $[MHg(SCN)_4]$[29] are monomeric, where M = Co, Ni;

TABLE III
Electronic Spectral Band Assignments, Spectral Parameters and B.M. Values

Complexes	$^3A_{2g} \xrightarrow{\gamma_3} {}^3T_{1g}(P)$	$^3A_{2g} \xrightarrow{\gamma_2} {}^3T_{1g}(F)$	10 Dq	B′	β	μ_{eff} B.M.
$[Ni(nia)_6][Zn(NCSe)_4]$	25400	16000	10200	722	.69	3.1
$[Ni(cpy)_6][Zn(NCSe)_4]$	27900	17500	10400	948	.91	3.0
$[Ni(inh)_6][Zn(NCSe)_4]$	27700	17200	10800	833	.80	3.2
$[(nia)_4Ni(NCSe)_2Cd(SeCN)_2]$	25000	16600	10100	753	.72	3.0
$[(cpy)_4Ni(NCSe)_2Cd(SeCN)_2]$	24690	15800	9600	780	.75	3.1
$[(apy)_4Ni(NCSe)_2Cd(SeCN)_2]$	28570	17000	10450	948	.91	3.0
$>(SeCN)_2(cpy)_2Ni(NCSe)_2Hg(SeCN)_2<$	24690	15800	9600	780	.75	3.1
$>(SeCN)_2(apy)_2Ni(NCSe)_2Hg(SeCN)_2<$	25000	15380	9600	767	.77	3.0
$>(SeCN)_2(inh)_2Ni(NCSe)_2Hg(SeCN)_2<$	26000	16500	10600	714	.69	3.1
	$^4T_{1g} \rightarrow {}^4T_{1g}(P)$	$^4T_{1g} \rightarrow {}^4A_{2g}$				
$[Co(nia)_6][Zn(NCSe)_4]$	21200	18500	–	–	–	4.9
$[Co(cpy)_6][Zn(NCSe)_4]$	20400	18100	–	–	–	5.0
$[Co(inh)_6][Zn(NCSe)_4]$	21800	18900	–	–	–	4.9
$[(cpy)_4Co(NCSe)_2Cd(SeCN)_2]$	20400	17800	–	–	–	5.0
$>(SeCN)_2(cpy)_2Co(NCSe)_2Hg(SeCN)_2<$	20000	17850	–	–	–	5.0
$>(SeCN)_2(apy)_2Co(NCSe)_2Hg(SeCN)_2<$	20800	18100	–	–	–	5.1
$>(SeCN)_2(nia)_2Co(NCSe)_2Hg(SeCN)_2<$	20600	18000	–	–	–	5.1
$>(SeCN)_2(inh)_2Co(NCSe)_2Hg(SeCN)_2<$	21700	18500	–	–	–	4.9

ii) When $[CoCd(NCS)_4]$ is reacted with py, bipy or cpy, cationic anionic complexes of the type $[CoL_6][Cd(NCS)_4]$ are formed[2–3], whereas the corresponding tetraselenocyanate complexes are monomeric bridged.[6, 29] These differences indicate that selenocyanate bridged in between M′ and M is more stable as compared to the thiocyanate bridge in $[MM'(NCX)_4]$ (M = Co, Ni; M′ = Cd, Hg; X = S or Se).

iii) In $[Cd(NCS)_4]^{2-}$ [2, 3] the cadmium is N-bonded, but in $[Cd(SeCN)_4]^{2-}$ [30] it is selenium bonded. The preference of Se-end by Cd(II) is perhaps due to easy formation of $d_\pi - d_\pi$ bonding between their d orbitals which are on the same energy level (4d).[27]

CALCULATION OF SOFTNESS AND HARDNESS AND THEIR DISCUSSION

Drago and Wayland[31] have given a two parameter equation for quantitative evaluation of acid base interaction

$$-\Delta H = E_A E_B + C_A C_B$$

where E is the measure of hardness and C of softness of Lewis acid or base. They have so far used this equation only for some organic acid and base interactions. E_A and C_A parameters for the metal ions are not available.

Misono[32] has evaluated quantitative values of softness in terms of Y parameter by using the following equation:

$$pK = -\log K = \alpha X + \beta Y + \gamma$$

The α, β and X values of this equation are based on high degree of incorrectness[32] hence can not be very profitably used.

Klopman[28] has calculated the softness values by using the equations (I) and (II). These equations too involve number of standards hence the values derived are crude. We have, however, used these equations by using fixed standards for a series of metal ions and have calculated softness values. These values have been found useful for deriving certain conclusions in respect of the stability of thiocyanate and selenocyanate bridge in their corresponding tetrathiocyanates and tetraselenocyanates. The softness values of –N– end and –S–end of thiocyanate, and –N–end and –Se–end of selenocyanate have also been calculated by using the equation (I).

$$E_m^{\ddagger} = IP_m - a^2(IP_m - EA_m) - \frac{x_r(c_r^m)^2}{R_r}\left(1 - \frac{1}{e}\right)\left[q_r + 2b^2x_r(c_r^m)^2\right] \qquad (I)$$

$$E_n^{\ddagger} = IP_n - b^2(IP_n - EA_n) - \frac{x_s(c_s^n)^2}{R_s}\left(1 - \frac{1}{e}\right)\left[q_s - 2b^2x_s(c_s^n)^2\right] \qquad (II)$$

where $E_n^{\ddagger}$ and $E_m^{\ddagger}$ are the softness of Lewis acid and base, respectively,

$$R_s = r + .82$$

r = ionic radii of Lewis acid (Pauling's radii)

$$b^2 = \tfrac{1}{4} \quad a^2 = \tfrac{3}{4} \quad (c_s^n)^2 = (c_r^m)^2 = 1$$

$$x_s = q_s - (q_s - 1)\sqrt{k} \quad k = .75$$

q_s and q_r is the charge on the Lewis acid or base, IP_n and IP_m the ionization potentials and EA_n and EA_m, the electron affinities, respectively. R_r = Pauling's covalent radii of Lewis base.

The calculations refer to the medium of methanol for which e = 32.6. Sulphur, nitrogen and selenium have been treated as atoms and their atomic radii have been used in place of R_r. The values of charge (q_r) have been taken from Wagner's Table.[26]

The results of the calculations are presented in the following Table:

TABLE IV

	Cation	$E_n^{\ddagger}$	Anion	$E_m^{\ddagger}$
SOFTNESS ↓	Co^{2+}	−0.22	N($-NCSe^-$)	−8.93
	Ni^{2+}	−0.28	N($-NCS^-$)	−8.10
	Zn^{2+}	−1.29	S($-SCN^-$)	−5.20
	Cd^{2+}	−2.27	Se($-SeCN^-$)	−4.41
	Hg^{2+}	−4.86		

The values of softness very clearly show that the N-end of selenocyanate will coordinate to cobalt(II) or nickel(II) and Se-end to cadmium(II) or mercury(II). We were unable to calculate the exact values of softness of pyridine and its derivatives for want of certain data. These bases have, therefore, been considered as borderline bases,[13] hence are shown coordinated to the borderline metals viz. nickel(II) or cobalt(II). These calculations support our preceding discussion, in which we have shown cobalt(II) and nickel(II), N-bonded and zinc, cadmium and mercury, Se-bonded in selenocyanates.

CONCLUSIONS

i) In $[MM'(NCX)_4]$ (M = Co, Ni; M' = Zn, Cd, Hg; X = S or Se) the selenocyanate bridge is more stable than the thiocyanate bridge.

ii) $[CoZn(NCSe)_4]$ and $[NiZn(NCSe)_4]$ have the weakest selenocyanate bridge, because it breaks in presence of ligands(L) and form cationic–anionic complexes. $[CoHg(SeCN)_4]$ and $[NiHg(SeCN)_4]$ are the most stable, as the polymeric nature of selenocyanate bridge is retained on complex formation. $ZnHg(SeCN)_4$, $CoCd(SeCN)_4$, and $NiCd(SeCN)_4$ have intermediate stability and form monomeric bridged complexes. The sequence of stability of selenocyanate bridge will, therefore, be in the following order:

$$[CoHg(SeCN)_4] \sim [NiHg(SeCN)_4] > [ZnHg(SeCN)_4] > [CoCd(SeCN)_4] \sim [NiCd(SeCN)_4] > [CoZn(NCSe)_4] \sim [NiZn(NCSe)_4].$$

The stability of tetrathiocyanate bridge has also the same sequence.[3,4] We have derived the values of softness differences ($\Delta E_n^{\ddagger}(MM')$) between $E_n^{\ddagger}$ values of M and M' in $[MM'(NCSe)_4]$ (M = Co, Ni; M' = Zn, Cd, Hg;), which are presented in Table V. The sequence of $\Delta E_n^{\ddagger}$ values and the stability of selenocyanate bridge have the same order. $\Delta E_n^{\ddagger}$ values can, therefore, be useful in predicting the nature of selenocyanate bonding in their complexes.

TABLE V

M/M'	$E_n^{\ddagger}(M)$	$E_n^{\ddagger}(M')$	$\Delta E_n^{\ddagger}(M-M')$	Possible nature of the complex
Co/Hg	−0.22	−4.86	4.64	Polymeric bridged
Ni/Hg	−0.28	−4.86	4.58	
Zn/Hg	−1.29	−4.86	3.57	
Co/Cd	−0.22	−2.27	2.05	Monomeric bridged
Ni/Cd	−0.28	−2.27	1.99	
Co/Zn	−0.22	−1.29	1.07	Cationic–anionic
Ni/Zn	−0.28	−1.29	1.01	

This sequence appears applicable only when M are the metals of Ist transition series, because $[CdHg(SeCN)_4]$ forms cationic–anionic complexes though the value of $\Delta E_n^{\ddagger}(Cd-Hg)$ is 2.59.

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REFERENCES

1. R. Makhija, L. Pazdernik and R. Rivest, *Can. J. Chem.*, 51, 438, 2987 (1973).
2. P. P. Singh, U. P. Shukla, R. Makhija and R. Rivest, *J. Inorg. Nucl. Chem.*, **37**, 679 (1975).
3. P. P. Singh and S. A. Khan, *Inorg. Chim. Acta*, **14**, 143 (1975).
4. P. P. Singh and J. N. Seth, *Inorg. Chim. Acta*, **16**, 227 (1975).
5. P. P. Singh, L. P. Pathak and S. A. Khan, *J. Inorg. Nucl. Chem.*, **38**, 475 (1976)
6. P. P. Singh, A. K. Srivastava and R. Rivest, *J. Inorg. Nucl. Chem.*, **38**, 439 (1976).
7. S. M. Nelson, *Proc. Chem. Soc.* 372 (1961).
8. I. I. Kharitanov and V. V. Skopenko, *Zh. Neorg. Khim.*, **10**, 1803 (1965).
9. R. M. Alasaniya, V. V. Skopenko and G. V. Tsintsadze, *Tr. Gruz. Politekh. Inst.*, 28 (1968); *Tr. Gruz. Politekh. Inst.*, **1**, 29 (1967); *Tr. Gruz. Politekh. Inst.*, **4**, 53 (1967).
10. M. Czakis-Sulikowska, *Chem. Anal. (Bucharect)*, **10**, 1189 (1965).
11. G. R. Waitkins and R. Shutt "Inorganic Synthesis" Vol. II McGraw-Hill Book Company, Inc. 186 (1946).
12. A. I. Vogel "Practical Organic Chemistry" Longman publ. London, Third Ed., 849, (1965).
13. R. G. Pearson, *J. Chem. Ed.*, 45, 581, 643 (1968).
14. D. E. Billing and A. E. Underhill, *J. Chem. Soc., (A)*, 29 (1968).
15. A. B. P. Lever, "Inorganic Electronic Spectroscopy" Elsevier publ. Company, New York, 328 (1968).
16. R. A. Bailey, S. L. Kozak, T. W. Michelsen and W. N. Mills, *Coord. Chem. Rev.*, **6**, 407 (1971).
17. A. Turco, C. Pecile and M. Nicolini, *Proc. Chem. Soc.*, 213 (1961).
18. A. Turco, C. Pecile and M. Nicolini, *J. Chem. Soc.*, 3006 (1962).
19. A. Sabatini and I. Bertini, *Inorg. Chem.*, **4**, 959 (1965).
20. Ya. Ya. Kharitonov and G. V. Tsintsadze, *Zh. Neorg. Khim.*, **10**, 1191 (1965).
21. H. W. Morgen, *J. Inorg. Nucl. Chem.*, **10**, 367 (1961).
22. B. N. Figgis and R. S. Nyholm. *J. Chem. Soc.*, 12 (1954).
23. J. L. Burmeister and L. E. Williams, *Inorg. Chem.*, **5**, 113 (1966).
24. D. Forster and D. M. L. Goodgame, *Inorg. Chem.*, **4**, 1712 (1965).
25. This work.
26. E. L. Wagner, *J. Chem. Phys.*, **43**, 2728 (1965).
27. A. H. Norbury and A. I. P. Sinha, *J. Chem. Soc. (A)*, 1958 (1968).
28. G. Kopman. *J. Amer. Chem. Soc.*, **90**, 223 (1968).
29. P. P. Singh and S. A. Khan, *Z. anorg. u. allgem. Chem.*, (In press).
30. P. P. Singh, A. K. Srivastava and S. B. Sharma, *Ind. J. Chem.* (In press).
31. R. S. Drago and B. B. Wayland, *J. Amer. Chem. Soc.*, **87**, 3571 (1965).
32. J. E. Huheey 'Inorganic Chemistry' Harper & Row publishers, New York, Evanston, London pp. 231, 1972.
33. Y. Tanabe and S. Sugano, *J. Phys. Soc. Japan* **9**, 753 (1954).