Monatshefte für Chemie 116, 177—187 (1985)

Monatshefte für Chemie
Chemical Monthly

Study of Comparative *Lewis*-Base Behaviour of *p*-Tolyl Mercury Selenocyanate and α-Naphthylmercury Selenocyanate

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(Received 21 February 1984. Accepted 13 April 1984)

p-Tolylmercury selenocyanate and α-naphthylmercury selenocyanate act as *Lewis*-bases towards $Co(NCS)_2 \cdot 2\,C_2H_5N$ and form a pink compound of the formula $(CH_5N)_2(SCN)_2Co(NCSeHg\mathit{R})_2$ (R = *p*-tolyl or α-naphthyl). On heating this compounds in vacuum, a blue compound $(SCN)_2Co(NCSeHg\mathit{R})_2$ was formed, *R*HgSeCN gives a similar compound on reaction with $Ni(NCS)_2$. The compounds $(SCN)_2\mathit{M}(NCSeHg\mathit{R})_2$; M = Co(II), Ni(II) again act as *Lewis*-acids. In these *Lewis*-acids Co(II) has a tetrahedral geometry whereas nickel(II) has an octahedral environment through elongated axial bondings of *X*CN-groups (X = S or Se). The selenocyanate bridging of the type $R-Hg-SeCN-M$ is present in these monomer compounds which were characterized by elemental analyses, molar conductance, molecular weight, magnetic moment, stability constant ($\log K$) infrared and electronic spectral studies. These physico-chemical studies indicate that the *p*-tolylmercury selenocyanate is a better donor than the α-naphthylmercury selenocyanate and $Ni(NC\mathit{X})_2$ is a better acceptor than $Co(NC\mathit{X})_2$. It has also been observed that *R*HgSCN is a better donor than *R*HgSeCN. These results are supported by the derivations made from softness parameters.

(Keywords: Lewis base behaviour; Aryl mercury selenocyanates)

Untersuchungen zum Lewis-basischen Verhalten von p-Tolyl-quecksilber-selenocyanaten und α-Naphthyl-quecksilber-selenocyanaten

p-Tolyl-quecksilber-selenocyanat und α-Naphthyl-quecksilber-selenocyanat verhalten sich gegenüber $Co(NCS)_2 \cdot 2\,C_5H_5N$ als *Lewis*-Basen, wobei rosagefärbte Verbindungen der Formel $(C_5H_5N)_2(SCN)_2Co(NCSeHg\mathit{R})_2$ (R = *p*-Tolyl oder α-Naphthyl) entstehen. Beim Erhitzen dieser Verbindungen im Vakuum entstehen die blauen Komplexe $(SCN)_2Co(NCSeHg\mathit{R})_2$, *R*HgSeCN gibt eine ähnliche Verbindung mit $Ni(NCS)_2$. Die Verbindungen $(SCN)_2\mathit{M}(NCSeHg\mathit{R})_2$ mit M = Co(II) oder Ni(II) agieren wieder als *Lewis*-Säuren. In diesen *Lewis*-Säuren besitzt das Co(II) eine tetraedrische Geometrie, währenddessen Ni(II) wegen der gedehnten axialen Bindungen der *X*CN-Gruppen ($X = S$ oder Se) eine oktaedrische Umgebung aufweist. In den monomeren Verbindungen, die mittels Elementaranalyse, molarer Leitfähigkeit, Molekulargewichtsbestimmungen, magnetischem Moment, Stabilitätskonstanten (log *K*), IR und Elektronenspektren charakterisiert wurden, ist eine Selenocyanat-Brücke des Typs $R-Hg-SeCN-M$ vorhanden. Die physikalisch-chemischen Daten zeigen an, daß *p*-Tolyl-quecksilber-selenocyanat der bessere Donor als α-Naphthyl-quecksilber-selenocyanat und $Ni(NCX)_2$ der bessere Acceptor als $Co(NCX)_2$ ist. Ebenso wurde beobachtet, daß *R*HgSCN der bessere Donor als *R*HgSeCN ist. Diese Resultate werden mittels HSAB-Parameter unterstützt.

Introduction

*R*Hg*X*CN (R = alkyl or aryl group; X = Cl, Br, I, SCN) have been reported to act as poor acceptors[1]. Due to the availability of lone pair electrons on organomercury pseudohalides, they can also function as *Lewis*-bases[2,3]. In view of the above, in this paper, *p*-tolyl mercury selenocyanate and α-naphthylmercury selenocyanate have been used as *Lewis*-bases towards cobalt and nickelthiocyanate as *Lewis*-acids to form a new class of organometallic compounds. The relative donor ability of *R*Hg*X*CN and the acceptor ability of $M(NCX)_2$ has also been studied.

Experimental

Reagent grade (BDH) solvents were used after purification. *p*-Tolylmercury(II) chloride and α-naphthylmercury(II) chloride were prepared by the diazotization method[4]. They were converted into their corresponding selenocyanates by reacting them with potassium selenocyanate in 1 : 1 molar ratio in acetone. KCl was filtered off, and from the filtrate the organomercury selenocyanates were precipitated by the addition of petroleum ether, dried in vacuum and recrystallized from acetone. Both the organomercury selenocyanates are unstable, and within hours of their isolation they start to decompose, giving free selenium metal. It is better if they are kept in solution. They were characterized by elemental analyses and infrared spectra.

Anal. Calcd. for *p*-tolylmercury selenocyanate (*p-TMS*) Se 19.9%, N 3.5%. Found Se 19.8%, N 3.4%. M.p. 126° (d).

IR (nujol): $2100\,\mathrm{cm}^{-1}$ ν (C−N), 740 ν (C−S), 440 δ (NCSe).

Anal. Calcd. for α-naphthylmercury selenocyanate (α-*NMS*) Se 18.2%, N 3.3%. Found: Se 18.1%, N 3.2%. M.p. 87° (d).

IR (nujol): 2085, $2135\,\mathrm{cm}^{-1}$ ν (C−N), 545 ν (C−Se), 390 δ (NCSe).

Preparation of the Complexes

1. $(SCN)_2Co(NCSeHgR)_2$ and $(py)_2(SCN)_2Co(NCSeHgR)_2$; R = *p*-Tolyl, α-naphthyl; *py* = pyridine

p-Tolylmercury selenocyanate (7.92 g, 2 mmol) and α-naphthylmercury selenocyanate (8.64 g, 2 mmol) were separately dissolved in 100 ml of acetone. To each solution an acetone solution of $Co(NCS)_2(py)_2$ (3.33 g, 1 mmol) was added and stirred for 5 h. A pink precipitate appeared in each case which was filtered, washed with acetone and dried in vacuum. The *Lewis*-acid $(SCN)_2Co(NCSeHg\mathit{R})_2$ was prepared by heating the pyridine adducts $(\mathit{py})_2Co(NCS)_2(NCSeHg\mathit{R})_2$. When acetone solutions of *R*HgSeCN and $Co(NCS)_2$ were directly reacted $(SCN)_2Co(NCSHg\mathit{R})_2$ was not formed. The dimethylsulphoxide (*DMSO*) adducts can be prepared by stirring $(SCN)_2Co(NCSeHg\mathit{R})_2$ in *DMSO*.

2. $[Co(\mathit{bipy})_3]\,[RHg(SeCN)\,(SCN)]_2$; *bipy* = 2,2'bipyridyl

$(SCN)_2Co(NCSeHg\cdot\mathit{p}\text{-tolyl})_2$ (0.967 g, 1 mmol) and $(SCN)_2Co(NCSeHg\text{-}\alpha\text{-naphthyl})_2$ (1.0 g, 1 mmol) were separately dissolved in 50 ml of ethanol. To each solution an ethanolic solution of 2,2'bipyridyl (0.47 g, 5 mmol) was added and stirred for 6 h. Brownish precipitate in each case appeared, which was filtered, washed with ethanol and dried in vacuum.

3. $(SCN)_2Ni(NCSeHg\mathit{R})_2$

p-Tolylmercury selenocyanate (7.92 g, 2 mmol) and α-naphthylmercury selenocyanate (8.64 g, 1 mmol) were separately dissolved in acetone. To each solution a methanolic solution of $Ni(NCS)_2$ (1.75 g, 1 mmol) was added. A grey precipitate appeared at once in each case, which was filtered after stirring for 1 h. The residue was washed with methanol and dried in a vacuum.

4. $(\mathit{py})_2Ni(NCS)_2(NCSeHg\mathit{R})_2$ and $[Ni(\mathit{bipy})_3]\,[\mathit{R}HgSeCN\cdot SCN)]_2$

$(SCN)_2Ni(NCSeHg\text{-}\mathit{p}\text{-tolyl})_2$ (0.967 g, 1 mmol) and $(SCN)_2Ni(NCSeHg\text{-}\alpha\text{-naphthyl})_2$ (1.09 g, 1 mmol) were separately dissolved in 60 ml of ethanol. To each solution an ethanolic solution of pyridine (0.2 ml, 2 mmol) was added and stirred for 6 h. A grey precipitate appeared in each case, which was filtered, washed with ethanol and dried in a vacuum.

Alternatively these complexes were prepared by the reaction of $Ni(NCS)_2(\mathit{py})_2$ and *R*HgSeCN in 1 : 2 molar ratio in acetone. $Ni(\mathit{bipy})_3(\mathit{R}HgSeCN\cdot SCN)_2$ were similarly prepared by reacting separately an ethanolic solution of 2,2'bipyridyl (0.468 g, 3 mol) with an ethanolic solution of $(SCN)_2Ni(NCSeHg\text{-}\mathit{p}\text{-tolyl})_2$ (0.967 g, 1 mmol) and $(SCN)_2Ni(NCSeHg\text{-}\alpha\text{-naphthyl})_2$ (1.09 g, 1 mmol).

5. $(SeCN)_2Co(NCSeHg\mathit{R})_2$ and $(SeCN)_2Ni(NCSeHg\mathit{R})_2$

p-Tolylmercury selenocyanate (7.9 g, 2 mmol) and α-naphthylmercury selenocyanate (8.64 g, 2 mmol) were separately dissolved in acetone. To each solution an acetone solution of $Co(NCSe)_2$ was added, immediately a red mass of selenium metal was separated and the desired *Lewis*-acid could not be formed. The nickel and zinc analogues could also not be isolated on account of similar difficulties.

6. $(\mathit{py})_2(SeCN)_2Co(NCSeHg\mathit{R})_2$ and $(\mathit{py})_2(SeCN)_2Ni(NCSeHg\mathit{R})_2$

p-Tolylmercury selenocyanate (7.92 g, 2 mmol) and α-naphthylmercury selenocyanate (0.64 g, 2 mmol) were separately dissolved in acetone. To each solution an acetone solution of $Co(NCSe)_2(\mathit{py})_2$ (4.27 g, 1 mmol) was added and stirred for 3 h. A pink precipitate appeared in each case, which was filtered, washed with acetone and dried in a vacuum.

Similarly, $(\mathit{py})_2(SeCN)_2Ni(NCSeHg\mathit{R})_2$ was also prepared by replacing $Co(NCSe)_2(\mathit{py})_2$ with $Ni(NCSe)_2(\mathit{py})_2$.

Table 1. *Analytical data and molar*

No.	Complexes	Colour	M.p. °C	Molar conductance (λm)
1.	$(\mathrm{SCN})_2\mathrm{Co}(p\text{-}TMS)_2$	bluish green	212 (d)	59.8
2.	$(\mathrm{SCN})_2\mathrm{Co}(\alpha\text{-}NMS)_2$	bluish green	180 (d)	57.6
3.	$(py)_2(\mathrm{SCN})_2\mathrm{Co}(p\text{-}TMS)_2$	pink	212 (d)	58.7
4.	$(py)_2(\mathrm{SCN})_2\mathrm{Co}(\alpha\text{-}NMS)_2$	pink	180 (d)	61.2
5.	$[\mathrm{Co}(bipy)_3]\,[p\text{-}TMS\cdot\mathrm{SCN})]_2$	brownish	150 (d)	140.4
6.	$[\mathrm{Co}(bipy)_3]\,[p\text{-}NMS\cdot\mathrm{SCN}]_2$	brown	182 (d)	142.2
7.	$(\mathrm{SCN})_2\mathrm{Ni}(p\text{-}TMS)_2$	grey	225 (d)	62.1
8.	$(\mathrm{SCN})_2\mathrm{Ni}(\alpha\text{-}NMS)_2$	grey	230 (d)	64.3
9.	$(py)_2(\mathrm{SCN})_2\mathrm{Ni}(p\text{-}TMS)_2$	grey	200 (d)	53.9
10.	$(py)_2(\mathrm{SCN})_2\mathrm{Ni}(\alpha\text{-}NMS)_2$	grey	205 (d)	64.2
11.	$[\mathrm{Ni}(bipy)_3]\,[(p\text{-}TMS)]_2$	pink	140	139.6
12.	$[\mathrm{Ni}(bipy)_3]\,[\alpha\text{-}NMS\cdot\mathrm{SCN}]_2$	pink	135	146.2
13.	$(py)_2(\mathrm{SeCN})_2\mathrm{Co}(p\text{-}TMS)_2$	pink	178 (d)	58.98
14.	$(py)_2(\mathrm{SeCN})_2\mathrm{Co}(\alpha\text{-}NMS)_2$	pink	162 (d)	59.1
15.	$(py)_2(\mathrm{SeCN})_2\mathrm{Ni}(p\text{-}TMS)_2$	sky blue	158 (d)	54.4
16.	$(py)_2(\mathrm{SeCN})_2\mathrm{Ni}(\alpha\text{-}NMS)_2$	grey	170 (d)	56.2

d = decomposed; *p*-Tolylmercury selenocyanate (*p-TMS*); α-naphthylmercury selenocyanate (α-*NMS*).

Analysis of the Complexes

The complexes were analysed for cobalt as anthranilate, nickel as dimethylglyoximate, sulphur as sulphate, selenium as selenium metal and mercury as sulphide gravimetrically. Nitrogen was estimated by the semimicre *Kjedahl* method. Analytical results along with melting points are presented in Table 1.

Physical Measurements

Infrared spectra of the complexes were recorded as nujol mulls or as KBr pellets on a Perkin-Elmer Spektrophotometer 621 and on a Pye Unicam sp 3-300 in the range of 4 000–200 cm^{-1}. Electronic spectra were recorded as nujol mulls or as solutions on Cary-14 and Pye-Unicam sp 5-500 Spectrophotometer. Molecular weights of the complexes were determined in dimethylsulphoxide cryoscopically. Magnetic moments were determined by *Gouy*'s method at room temperature using $\mathrm{HgCo(NCS)_4}$ as standard. Molar conductances of the complexes were determined in dimethyl-formamide using a Philips conductivity bridge model PR-9 500.

Results and Discussions

Lewis-Acids $(X\mathrm{CN})_2M(\mathrm{NCSeHg}R)_2$ *and Adducts* $(py)_2(X\mathrm{CN})_2M(\mathrm{NCSeHg}R)_2$

These complexes are soluble in common solvents like ethanol, methanol, acetone, dimethylformamide and dimethylsulphoxide. They *conductance values of the complexes*

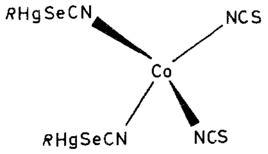
% Sulphur		% Selenium		% Mercury		% Co/Ni		% Nitrogen	
calc.	obs.	calc.	obs.	calc.	obs.	calc.	obs.	calc.	obs.
6.6	6.5	16.3	16.2	41.4	41.3	6.1	5.9	5.6	5.8
6.1	6.00	14.9	14.8	38.2	38.1	5.6	5.5	5.1	5.3
5.7	5.8	13.8	13.7	35.5	35.4	5.3	5.2	7.4	7.5
5.3	5.2	13.0	12.8	33.2	33.1	4.9	4.0	6.92	7.0
4.5	4.4	10.9	10.9	27.9	27.8	4.1	3.9	9.7	9.8
4.3	4.2	10.4	10.3	26.6	26.3	3.9	3.8	9.2	9.3
6.6	6.6	16.3	16.3	41.4	41.3	6.1	6.0	5.7	5.8
6.1	6.1	14.9	14.8	38.2	38.1	5.6	5.5	5.2	5.3
5.7	5.6	13.8	13.7	35.5	35.4	5.3	5.2	7.4	7.5
5.3	5.2	12.7	12.9	33.2	33.0	4.9	4.8	6.9	7.0
4.5	4.4	16.9	16.8	27.9	27.8	4.1	4.0	9.7	9.8
4.3	4.2	10.4	10.2	26.6	26.5	3.9	3.8	9.2	9.3
–	–	12.9	12.8	32.8	32.7	4.8	4.7	6.8	6.9
–	–	12.2	12.1	31.0	30.9	4.6	4.5	6.4	6.5
–	–	13.0	12.9	32.8	32.7	4.9	4.7	6.8	6.9
–	–	12.2	12.1	31.0	30.9	4.6	4.5	6.4	6.5

decompose on standing, giving free selenium metal even in solutions and hence could not be recrystallized. Cryoscopic molecular weight determination of $(py)_2(\mathrm{SCN})_2M(\mathrm{NCSeHg}R)_2$ and $(py)_2(\mathrm{SeCN})_2\mathrm{M}(\mathrm{NCSeHg}R)_2$ in dimethylsulphoxide show them to be monomeric in nature. They are non-conducting in dimethylformamide (Table 1). The solid phase IR spectra of RHgSeCN show the presence of ν(C–N), ν(C–Se), δ(NCSe) and ν(Hg–Se) bonds at 2 130, 2 085, 545, 390 and 245 cm^{-1}, respectively. The positions of these bands remain the same in solution except the band observed at 2 085 cm^{-1} which disappears. The presence of this band in solid phase was attributed to crystal field interaction. On formation of $(\mathrm{SCN})_2M(\mathrm{NCSeHg}R)_2$ changes are observed in the positions of various bands (Table 2). The positions of ν(C–N) band shifts from 2 130 to 2 170 cm^{-1} indicating that selenocyanate has become bridging[5,6]. This is possible only by coordination through N-end to M. The shifts in ν(C–Se) and δ(NCSe) also support the presence of bridging selenocyanate[6]. A band at about 2 080 cm^{-1} is also observed, which is assigned to N-bonded terminal thiocyanate arising from $M(\mathrm{NCS})_2$[7]. The infrared spectra of the adducts show the presence of several bands in the ν(C–N), ν(C–X) and δ(NCX) regions similar to that of their *Lewis*-acids with slight changes in positions. These changes

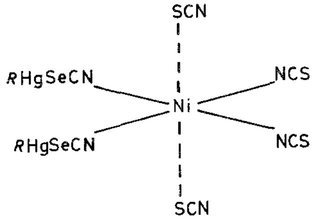
Table 2. *Assignments of infrared spectral bands (4000–200 cm^{-1})*

No.	ν(C–N)	ν(CX)	δ(NCX)	(Hg–C)	ν(M–NCX)/ ν(M–L)
1.	2165 s, 2110 w, 2075 sh	810 m, 535 m	440 w, 405 s	465 s	310 s, 295 w
2.	2170 s, 2115 s, 2080 m	800 m, 540 m	435 sh, 395 w	450 s	305 s, 290 w
3.	2175 s, 2120 s, 2090 sh	795 s, 535 s	430 sh, 405 s	455 s	250 s, 240 sh
4.	2170 s, 2115 sh, 2085 sh	800 w, 620 s, 545 sh	435 sh, 400 s	465 s	255 s, 245 sh
5.	2120 s, 2100 sh	730 m, 640 sh, 530 s	430 s, 410 sh	460 s	265 s
6.	2125 s, 1110 sh	720 s, 640 w, 510 sh	430 m, 415 w	465 s	270 s
7.	2170 s, 2105 m, 2085 sh	820 m, 620 s, 530 sh	430 sh, 405 m	450 s	255 s, 235 sh
8.	2180 s, 2110 sh, 2080 sh	805 w, 505 sh, 540 s	435 sh, 395 sh	460 s	265 s, 238 m
9.	2185 s, 2130 s, 2085 sh	800 s, 535 sh	435 sh, 410 sh	450 s	260 s, 235 b
10.	2175 s, 2110 w, 2090 sh	780 w, 630 s, 525 w	430 sh, 410 s	465 s	250 s, 230 sh
11.	2100 s, 2095 sh	740 s, 540 m, 525 sh	430 w, 405 sh	455 s	270 s
12.	2100 s, 2095 sh	740 s, 540 m, 525 sh	430 w, 400 sh	460 s	265 s
13.	2170 s, 2090 sh	690 s, 625 w	395 s	468 s	265 m
14.	2175 sh, 2085 s	680 s, 630 w	405 s	450 s	240 m
15.	2165 s, 2090 sh	675 s, 650 sh	400 s	455 s	235 sh
16.	2170 s, 2085 sh	655 s, 620 w	415 s	470 s	255 w

may be due to change in stereochemistry around M[8]. The electronic spectra and magnetic moment values as discussed later show that the cobalt in the *Lewis*-acids has a tetrahedral configuration but nickel has an octahedral configuration, which is achieved by axial coordination through sulphur or selenium of the NCX group of an adjacent layer[9]. In *Lewis*-acids the far infrared region shows the presence of bands at about 300 cm^{-1} assignable to ν(Co–NCS) and at about 270 cm^{-1} assigned to ν(Ni–NCS). A lower band in case of nickel is indicative of the presence of an octahedral geometry around nickel whereas in cobalt the configuration is tetrahedral. The Co–NCX band in cobalt *Lewis*-acids shifts to 250 cm^{-1} on adduct formation. Such a negative shift is indicative for a change of the tetrahedral geometry around cobalt in *Lewis*-acids to an octahedral in adducts[7]. In case of nickel derivatives an octahedral configuration geometry is indicated both in *Lewis*-acids and adducts. From these observations and their close similarities with earlier reported compounds[3] structures **1**, **2**, and **3** may be proposed for these complexes.



1



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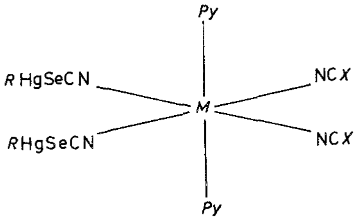

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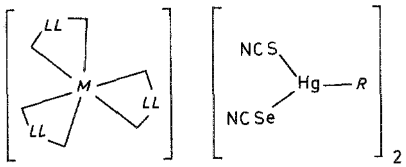

4

LL = bipyridil $R = p$-tolyl, α-naphthyl M = Co(II), Ni(II); X = S, Se

Ionic Complexes $[M(bipy)_3]\,[R\text{HgSCN}\cdot\text{SeCN}]_2$

These compounds are more stable than the pyridine adducts and their decomposition into free selenium is very slow. The molar conductance values of these complexes indicate that they are 1 : 2 electrolytes[10]. The infrared spectra of the complexes show the absence of bands assigned to bridging selenocyanates and N-bonded thiocyanate[3,5]. In the $\nu(\text{C}-\text{N})$ region two bands are observed in the range 2 095–2 125 cm^{-1}, which can be assigned to S-bonded thiocyanate and Se-bonded selenocyanate[11]. The position of bands in the $\nu(\text{C}-N)$, $\nu(\text{C}-X)$ and $\delta(\text{NC}X)$ regions also support bonding through S-end and Se-end. A band at about 270 cm^{-1} is present in all the complexes which is assigned to $\nu(M-\text{N})$[5]. The electronic spectral band positions, spectral parameters, and magnetic moment values (Table 3) indicate the presence of an octahedral configuration around cobalt and nickel.

On the basis of these observations we can suggest that the cation has cobalt or nickel duly coordinated with three molecules of bipyridyl. The anion possibly has a tricoordinated mercury linked with one S-bonded thiocyanate, one Se-bonded selenocyanate and one aryl group. Tricoordinated mercury compounds have been reported by earlier workers also[12,13]. The preference of bipyridyl for cobalt or nickel in comparision to mercury and S- and Se-end of *X*CN (S or Se) to mercury in comparision to N-end is in conformity with the HSAB principle[14] and $\Delta E^{+}_{\mathrm{nm}}$ requirements[5]. The far IR spectra show the presence of νHg−SCN at 210 cm^{-1}, νHg−SeCN at 235 cm^{-1} and absence of νM−NCX bands[15].

On the basis of these results the structure **4** is proposed to cationic-anionic complexes.

Table 3. *Selected electronic bands, their spectral parameters and magnetic moment values*

No.	ν_3 (cm^{-1})	ν_2 (cm^{-1})	ν_1 (cm^{-1})	Dq	B'	β	μ_{eff} ($B.M.$)
1.	16 000	8 170	–	482	647	166	4.18
2.	16 200	8 230	–	485	658	168	4.14
3.	20 700	18 300	9 620	978	873	0.89	5.16
4.	20 400	18 500	9 680	988	810	0.88	5.09
5.	20 800	9 560	18 000	989	874	0.92	5.08
6.	26 300	16 200	10 200	990	857	0.82	3.12
7.	26 600	16 400	10 350	1 012	803	0.84	3.05
8.	28 490	17 160	10 350	1 060	925	0.89	3.14
9.	29 050	17 300	10 580	1 062	966	0.93	3.19
10.	28 100	17 200	11 600	1075	873	0.84	3.32
11.	26 660	18 180	11 000	1 180	629	0.60	3.09
12.	21 590	19 000	10 440	1 020	950	0.97	5.1
13.	26 665	16 660	10 520	1 054	880	0.85	3.12
14.	24 390	17 550	10 310	1 098	600	0.58	3.30

Electronic Spectra

The assignments of the electronic spectral bands, their positions and spectral parameters derived from ν_2 and ν_3 bands are included in Table 3. The values of Dq, B' and β have been calculated from the values of ν_3 and ν_2 bands using the equations of *Underhill* and *Billing*[16]. In case of $(SCN)_2Co(NCSeHgR)_2$ the position of electronic spectral bands, their spectral parameters, and magnetic moment values indicate the presence of a tetrahedral geometry around cobalt[5]. Similarly, in case of $L_2(X\mathrm{CN})_2M(\mathrm{NCSeHg}R)_2$, the positions of electronic spectral bands and spectral parameters suggest an octahedral configuration around Co(II) and Ni(II)[5,7]. Magnetic moment values as presented in Table 3 also support these geometries. The cation-anionic complexes of both cobalt and nickel series show three distinct bands in the ν_3 ν_2 and ν_1 regions (Table 3). The positions of these bands and *Dq* values are in the typical range of metals in octahedral geometry[5,17].

Calculation of Softness Parameters

The effective softness of an atom in neutral *Lewis*-acids $E^{\ddagger}_{n(eff)}$ and in neutral *Lewis*-bases $E^{\ddagger}_{m(eff)}$ can be derive by known methods[18,19]. The matching between an acid and base has been derived by the following equation[19]:

$$\text{Matching } (\Delta E^{\ddagger}_{nm}) = |E^{\ddagger}_{n(eff)} - E^{\ddagger}_{m(eff)}|$$

Table 4. *Matching* ($\Delta E^{\ddagger}_{nm}$) *derived from* $E^{\ddagger}_{n(eff)}$ *of M and* $E^{\ddagger}_{m(eff)}$ *of* N-end *of* *R*HgXCN

*R*Hg*X*CN	$E^{\ddagger}_{m(eff)}$ of N-end of *R*Hg*X*CN	$\Delta E^{\ddagger}_{nm}$ with Co(II)	$\Delta E^{\ddagger}_{nm}$ with Ni(II)
$C_2H_5COOC_6H_4HgSCN$	−12.70	9.18	9.72
$C_4H_9COOC_6H_4HgSCN$	−11.54	8.02	8.56
p-$CH_3C_6H_4HgSCN$	−11.42	7.90	8.44
α-naphthylHgSCN	−11.31	7.79	8.33
I-C_6H_4HgSCN	−10.98	7.46	8.00
$CH_3OC_6H_4HgSCN$	−10.96	7.44	7.98
Cl−C_6H_4HgSCN	−10.86	7.34	7.88
NO_2−C_6H_4HgSCN	−10.69	7.17	7.71
p-$CH_3C_6H_4HgSeCN$	−11.35	7.83	8.37
α-naphthyl HgSeCN	−11.26	7.74	8.28

$E^{\ddagger}_{n(eff)}$ of Co(II) = −3.52, $E^{\ddagger}_{n(eff)}$ of Ni(II) = −2.98.

A higher value of $\Delta E^{\ddagger}_{nm}$ indicates a better match[19]. The matching constant is expressed in the following way[19]:

$$\text{Matching constant} = \Delta E^{\ddagger}_{nm} + CFSE$$

The following conclusions have been drawn with the help of softness parameters and physio-chemical studies.

(i) A higher negative value in case of *Lewis*-acid and a lower negative value in case of Lewis-base indicate a soft character while the opposite indicates a hard character[18,19]. The softness values of N-end in *R*Hg*X*CN (Table 4) indicate that the N-ends in the *p*-tolyl series are more hard than in the corresponding α-naphthyl series. In corresponding selenocyanates the hardness at N-end decrease. The $\Delta E^{\ddagger}_{nm}$ values (Table 4) indicate that *p*-tolyl mercury thiocyanate and selenocyanate show better match with $M(NCX)_2$ (X = S or Se) than the α-naphthylmercury thiocyanate or selenocyanate. The $\Delta E^{\ddagger}_{nm}$ values also indicate that RHgXCN have better matching with Ni(NCX)$_2$ than Co(NCX)$_2$ (Table 4).

(ii) The formation of $(X\mathrm{CN})_2M(\mathrm{NCSHg}R)_2$ can be attributed to the reaction between $M(\mathrm{NC}X)_2$ and RHgXCN, the former acting as a *Lewis*-acid and the latter as a base. Metal ligand bond strengths have recently been represented in terms of matching constants[19]. The matching constant values of this acid-base system have been derived in Table 5. Table 5 shows that the matching constant values are higher in case of the complexes of the tolyl series than of naphthyl series. The matching constant values in case of RHgSCN are higher than the corresponding complexes of RHgSeCN. The matching constant values also indicate that the complexes were M = Ni(II) are more stable than the corresponding Co(II) complexes. The sequence of stability is in agreement with the *Irving Williams* stability sequence[20]. The above theoretical conclusions are supported by the experimental values of log K which have been determined spectrophotometrically using acetone as solvent. The nickel complexes have comparatively low values of log K which may be due to the octahedral environment around Ni(II).

Table 5. *Matching constants and stability constants* (log K) *of some complexes*

Complexes	Dq (cm^{-1})	*CFSE* (eV)	$\Delta E^{\ddagger}_{nm}$	Matching constant	log K
$(\mathrm{SCN})_2\mathrm{Co}(\mathrm{NCSHg}\ p\text{-tolyl})_2$	480	4.94	7.90	12.84	6.24
$(\mathrm{SCN})_2\mathrm{Co}(\mathrm{NCSeHg}\ p\text{-tolyl})_2$	482	4.92	7.83	12.75	5.74
$(\mathrm{SCN})_2\mathrm{Co}(\mathrm{NCSHg}\ \alpha\text{-naphthyl})_2$	475	4.95	7.79	12.74	5.84
$(\mathrm{SCN})_2\mathrm{Co}(\mathrm{NCSeHg}\ \alpha\text{-naphthyl})_2$	485	4.89	7.74	12.63	4.84
$(\mathrm{SCN})_2\mathrm{Ni}(\mathrm{NCSHg}\ p\text{-tolyl})_2$	990	6.87	8.44	15.31	5.62
$(\mathrm{SCN})_2\mathrm{Ni}(\mathrm{NCSeHg}\ p\text{-tolyl})_2$	1 020	6.67	8.28	14.95	4.12
$(\mathrm{SCN})_2\mathrm{Ni}(\mathrm{NCSHg}\ \alpha\text{-naphthyl})_2$	1 006	6.76	8.44	15.20	4.24
$(\mathrm{SCN})_2\mathrm{Ni}(\mathrm{NCSeHg}\ \alpha\text{-naphthyl})_2$	1 012	6.72	8.28	15.00	3.94
$(\mathrm{SeCN})_2\mathrm{Co}(\mathrm{NCSHg}\ p\text{-tolyl})_2$	489	4.85	7.90	12.75	6.11
$(\mathrm{SeCN})_2\mathrm{Co}(\mathrm{NCSHg}\ \alpha\text{-naphthyl})_2$	485	4.89	7.83	12.72	5.97

Acknowledgement

The authors gratefully acknowledge the financial support from CSIR, New Delhi.

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