

Quantitative Softness Parameters & Their Relationship with Physicochemical Data of Organobimetallic Complexes

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Softness parameters of a series of new organobimetallic compounds of general formula $(SCN)_2M(RHgXCN)_2$ [$M = Mn(II), Co(II), Ni(II), Cu(II), Zn(II)$; $R = C_6H_4CH_3, C_6H_4NO_2$, $X = S, Se$] have been derived. These compounds have been studied by various physicochemical techniques also. Correlation of the softness parameters with various physicochemical data e.g. infrared spectral, electronic spectral and stability constant data indicate that $CH_3C_6H_4HgSCN$ is a better donor than $NO_2C_6H_4HgSCN$ and $Co(NCS)_2$ is a better acceptor than $Mn(NCS)_2$ and $Zn(NCS)_2$. Also $RHgSCN$ are better donors than the corresponding selenocyanates.

Recently, the effective softness values of some lewis acids and bases have been calculated and their applications to various chemical phenomena described¹⁻⁴. We have developed some new relationships between softness values and the physicochemical data of the compounds and these are being reported here. These correlations have been applied to a new series of organobimetallic systems. The experimental results relate well to the softness parameters.

Materials and Methods

Reagent grade (BDH) solvents were purified before use. Pyridine was used from fresh bottles.

$M(NCS)_2 \cdot 2py$ was prepared by reacting pyridine with $M(NCS)_2$ in acetone [$M = Co(II), Cu(II), Mn(II)$]. *m*-Tolylmercury(II) chloride and *m*-nitrophenylmercury(II) chloride were prepared by the diazotisation method⁵. Organomercury(II) chlorides were converted into thiocyanates by reacting them with potassium thiocyanate in acetone in 1:1 molar ratio and filtering off the precipitated potassium chloride. The filtrate was concentrated by evaporating under reduced pressure. On adding water to the concentrates, organomercury(II) thiocyanate separated out. It was filtered, washed with water, recrystallized from ethanol and dried *in vacuo*. The corresponding organomercury(II) selenocyanates were prepared by reacting the organomercury(II) chlorides with potassium selenocyanates in acetone. After removing the potassium chloride the filtrate was concentrated *in vacuo* and petroleum ether was added when the selenocyanates separated out. These were washed with petroleum ether and dried *in vacuo*. The organomercury(II) selenocyanates are unstable and start decomposing into free selenium. It is better to keep

them in solution. These were characterized by elemental analyses and infrared spectra.

Preparation of the complexes

(i) $(SCN)_2M(NCSHgR)_2$: $M = Co(II), Cu(II), Mn(II)$; $X = S, Se$; $R = m$ -tolyl, *m*-nitrophenyl

The complexes were prepared by reacting $M(NCS)_2 \cdot 2py$ (1 *m* mol) with $RHgSCN$ (2 *m* mol) using suitable solvents. Ethanol, DMSO and ethyl acetate were used for making solutions of $Co(NCS)_2 \cdot 2py$, $Cu(NCS)_2 \cdot 2py$ and $Mn(NCS)_2 \cdot 2py$ respectively. $RHgSCN$ were dissolved in the same solvents. The reaction mixtures were stirred for 48 hr. A precipitate was obtained in all the cases except for $Cu(II)$ complexes. The $Cu(II)$ complexes were prepared by the addition of ethanol to the reaction mixture. The complexes were filtered, washed with proper solvent and dried *in vacuo*. Except the $Mn(II)$ complexes, which were recrystallized from ethanol-ethyl acetate mixtures, all the complexes were recrystallized from ethanol-acetone mixture. The corresponding selenocyanate complexes of cobalt were prepared by stirring solutions of $Co(NCS)_2 \cdot 2py$ and $RHgSeCN$ (1:2) in acetone for 4 hr as described above. When $Mn(NCS)_2 \cdot 2py$ and $Cu(NCS)_2 \cdot 2py$ were treated with $RHgSeCN$ in acetone or ethanol, free selenium was liberated, so the complexes could not be isolated.

On heating the pyridine complexes of thio and selenocyanate series *in vacuo* at 50-60°C, pyridine was given off and the complexes of empirical formula $(NCS)_2M(RHgXCN)_2$ [$X = S, Se$] were obtained.

(ii) $(SCN)_2M(NCSHgR)_2$ $M = Ni(II), Zn(II)$

Solutions of $Ni(SCN)_2$ (1.7 g, 1 *m* mol) in methanol and $Zn(NCS)_2$ (1.8 g, 1 *m* mol) in ethanol were

prepared. These were separately mixed with an ethanolic solution (2m mol) of RHgSCN and stirred for 36 hr. The precipitates obtained were filtered, washed with ethanol and dried *in vacuo*. The nickel(II) complexes were recrystallized from DMSO-acetone mixture while the Zn(II) complexes were recrystallized from acetone. The corresponding selenocyanate complexes of nickel were similarly prepared but the stirring time was 4 hr. The zinc analogue of selenocyanate could not be isolated due to its rapid decomposition into selenium metal.

Sulphur was estimated as barium sulphate and selenium as selenium metal. Cobalt, nickel, zinc, manganese and mercury were estimated gravimetrically by known methods. Nitrogen was estimated by semi-micro Kjeldahl's method. The analytical results are included in Table 1.

Infrared spectra of the complexes were recorded in nujol or KBr on Perkin-Elmer spectrophotometer-621 and Pye Unicam SP-3-300 spectrophotometer in the range $4000\text{--}200\text{ cm}^{-1}$. Electronic spectra were recorded in nujol or in solution on Cary-14 and Pye Unicam SP-5-500 spectrophotometers. Magnetic

moments were determined by Gouy's method using $\text{HgCo}(\text{NCS})_4$ as standard. Molar conductances of the complexes were determined in DMF using a Philips conductivity bridge model PR-9500. The stability constants ($\log K$) were determined on a Pye Unicam SP 5-500 spectrophotometer using ethanol as the solvent.

Calculation of softness parameters

The softness of metal ions is expressed by E_n^+ and that of base ions by E_m^+ . The softness of an atom in neutral lewis-acids and neutral lewis-bases is termed as effective softness; these values are expressed by $E_{n(\text{eff})}^+$ and $E_{m(\text{eff})}^+$ respectively. The E_n^+ or E_m^+ value can be derived using the Klopman equation⁶ and $E_{n(\text{eff})}^+$ or $E_{m(\text{eff})}^+$ value by a modified equation described elsewhere³. High negative values in case of lewis acid and low negative values in case of lewis base indicate soft character while the reverse of that indicates hard character. The matching between acid and base is given by the following equation:

$$\text{Matching} = \Delta E_{nm}^+ = \left| E_{n(\text{eff})}^+ - E_{m(\text{eff})}^+ \right|$$

Table 1—Analytical Data of the Complexes

Complexes	Colour	m.p. (°C)	Found (Calc.), %					Λ_M (ohm ⁻¹ cm ² mol ⁻¹)	Magnetic moment (B.M.)
			S	Hg	M	N	Se		
$(\text{SCN})_2\text{Co}(\text{NCSHgC}_6\text{H}_4\text{CH}_3)_2$	Blue	180	14.64 (14.52)	45.14 (44.52)	45.88 (45.99)	6.40 (6.50)	—	41.70	4.42
$(\text{SCN})_2\text{Ni}(\text{NCSHgC}_6\text{H}_4\text{CH}_3)_2$	Grey	150(d)	14.63 (14.32)	45.80 (44.10)	6.62 (6.58)	6.40 (6.35)	—	40.71	2.99
$(\text{SCN})_2\text{Cu}(\text{NCSHgC}_6\text{H}_4\text{CH}_3)_2$	Yellow	210(d)	10.22 (11.18)	40.89 (38.87)	6.49 (6.27)	5.72 (4.70)	—	32.60	1.61
$(\text{SCN})_2\text{Mn}(\text{NCSHgC}_6\text{H}_4\text{CH}_3)_2$	White	280	14.39 (13.37)	41.19 (40.17)	6.18 (6.05)	6.29 (6.25)	—	42.06	5.9
$(\text{SCN})_2\text{Zn}(\text{NCSHgC}_6\text{H}_4\text{CH}_3)_2$	White	225(d)	14.38 (14.30)	45.05 (45.01)	7.50 (7.29)	6.29 (6.78)	—	—	—
$(\text{SCN})_2\text{Co}(\text{NCSeHgC}_6\text{H}_4\text{CH}_3)_2$	Blue	224(d)	6.60 (6.50)	41.27 (11.20)	5.88 (5.80)	5.77 (5.70)	8.15 (8.52)	51.69	4.50
$(\text{SCN})_2\text{Ni}(\text{NCSeHgC}_6\text{H}_4\text{CH}_3)_2$	Sky blue	220(d)	6.59 (6.54)	41.26 (40.25)	5.80 (5.78)	5.75 (5.69)	8.14 (8.42)	55.89	3.02
$(\text{SCN})_2\text{Co}(\text{NCSHgC}_6\text{H}_4\text{NO}_2)_2$	Blue	210(d)	13.70 (13.82)	42.93 (41.06)	6.20 (6.18)	5.99 (5.80)	—	42.90	4.28
$(\text{SCN})_2\text{Ni}(\text{NCSHgC}_6\text{H}_4\text{NO}_2)_2$	Grey	214	13.68 (13.02)	42.91 (40.80)	6.19 (6.20)	5.18 (5.76)	—	41.05	2.98
$(\text{SCN})_2\text{Cu}(\text{NCSHgC}_6\text{H}_4\text{NO}_2)_2$	Yellow	110(d)	13.63 (12.60)	42.59 (39.59)	6.70 (5.70)	8.79 (7.99)	—	34.80	1.98
$(\text{SCN})_2\text{Mn}(\text{NCSHgC}_6\text{H}_4\text{NO}_2)_2$	White	260	13.40 (12.20)	41.88 (39.88)	7.69 (7.68)	5.75 (4.65)	—	40.87	5.90
$(\text{SCN})_2\text{Zn}(\text{NCSHgC}_6\text{H}_4\text{NO}_2)_2$	White	230	13.19 (12.10)	41.23 (39.22)	6.90 (5.69)	8.65 (7.65)	—	—	—
$(\text{SCN})_2\text{Co}(\text{NCSHgC}_6\text{H}_4\text{NO}_2)_2$	Blue	258	6.23 (6.20)	38.98 (38.90)	5.55 (5.50)	8.18 (8.10)	7.69 (8.20)	52.90	4.40
$(\text{SCN})_2\text{Ni}(\text{NCSeHgC}_6\text{H}_4\text{NO}_2)_2$	Sky blue	250(d)	6.22 (6.18)	38.95 (38.89)	5.54 (5.49)	8.17 (8.15)	7.68 (7.42)	51.49	3.01

d = decomposed

A high value of $\Delta E_{nm}^\dagger$ indicates better match. Matching constant is derived by adding CFSE (eV) to $\Delta E_{nm}^\dagger$.

$$\text{Matching constant} = \Delta E_{nm}^\dagger + \text{CFSE (eV)}$$

Results and Discussion

Softness parameters

- (i) In the present study the lewis acids with R = *m*-tolyl constitute the tolyl series and those with R = *m*-nitrophenyl constitute the nitro series. The softness values of N in RHgXCN (Table 2) indicate that the N-ends in RHgXCN are hard. The N-end in tolyl series is more hard than that in the corresponding nitro series. In the corresponding selenocyanate the hardness of N-end decreases.
- (ii) The $\Delta E_{nm}^\dagger$ values (Table 2) indicate that tolylmercury thiocyanate and selenocyanate show better match with various M(NCS)₂ than the nitrophenylmercury thiocyanate or selenocyanates. This observation is consistent with inductive effects of methyl and nitro groups. The change of R with different groups produces the following matching order towards M(NCS)₂: NCSHgC₆H₅COOC₂H₅ > NCSHgC₆H₅COOC₄H₉ > NCSHgC₆H₄CH₃ > NCSHgC₆H₅I > NCSHgC₆H₅OCH₃ > NCSHgC₆H₅Cl > NCSHgC₆H₅NO₂.
- (iii) The $\Delta E_{nm}^\dagger$ values indicate that RHgSCN has a better match with the hard Mn²⁺, than that with the soft Zn²⁺.
- (iv) These values have been related to the positions of $\nu(\text{CN})$, $\nu(\text{CS})$, $\delta(\text{NCS})$ and $\nu(\text{M}-\text{NCS})$ bands in the spectra of the complexes having similar geometry around M, i.e. for cobalt, zinc and manganese complexes in which M is in tetrahedral configuration. The $\Delta E_{nm}^\dagger$ value and the spectral band positions are presented in Table 3. The $\nu(\text{C}-\text{N})$ bands in the bridging thiocyanate occur at the highest wave numbers in Zn(II) and at the lowest in Mn(II) complexes showing a reverse relation with $\Delta E_{nm}^\dagger$ values. The $\delta(\text{NCS})$ and $\nu(\text{M}-\text{NCS})$ band positions increase from manganese to zinc complexes exhibiting the same trend as the $\Delta E_{nm}^\dagger$ values. $\nu(\text{C}-\text{S})$ bands do not show any definite relation with $\Delta E_{nm}^\dagger$.
- (v) The strength of the thiocyanate bridge between M and mercury has been related to the difference in softness values of the two metal ions. A higher difference indicates greater stability⁸. Such a difference is observed in the present complexes (Table 4). The difference is highest in manganese(II) complexes; hence, the thiocyanate bridge is expected to be most stable in this case. This stability is demonstrated by the fact that the thiocyanate bridge in these complexes is not ruptured on reaction with chelating bases like 2,2'-bipyridyl. The thiocyanate bridge in the rest of the complexes is ruptured on such a reaction. The $\Delta E_n^\dagger(\text{M}-\text{Hg})$ does not give any definite value on the basis of which cleavage of the bridge can be predicted. It simply indicates comparative stability of the thiocyanate bridge amongst the various complexes.
- (vi) The $\Delta E_{nm}^\dagger$ values derived from M(NCS)₂ and N-end of RHgSCN are higher as compared to the corresponding values derived from RHgSeCN.
- (vii) The formation of (SCN)₂N(NCXHgR)₂ can be attributed to reaction between M(NCS)₂ and RHgXCN, the former acting as an acid and the latter as a base. The matching constant values of this acid base system have been calculated

Table 2—The $\Delta E_{nm}^\dagger$ Values Derived from $E_{n(\text{eff})}^\dagger$ of M and $E_{m(\text{eff})}^\dagger$ of N-end of RHgSCN

RHgXCN	$E_{n(\text{eff})}^\dagger$ of N-end of RHgXCN	$E_{m(\text{eff})}^\dagger$ of Mn = 2.48	$E_{n(\text{eff})}^\dagger$ of Co = -3.52	$E_{n(\text{eff})}^\dagger$ of Ni = -2.98	$E_{n(\text{eff})}^\dagger$ of Cu (I I) = -7.31	$E_{n(\text{eff})}^\dagger$ of Zn = 5.20
	$E_{nm}^\dagger$	$\Delta E_{nm}^\dagger$	$\Delta E_{nm}^\dagger$	$\Delta E_{nm}^\dagger$	$\Delta E_{nm}^\dagger$	$\Delta E_{nm}^\dagger$
C ₂ H ₅ COOC ₆ H ₄ HgSCN	-12.70	10.22	9.18	9.72	5.39	7.50
C ₄ H ₉ COOC ₆ H ₄ HgSCN	-11.54	9.06	8.02	8.56	4.23	6.34
CH ₃ C ₆ H ₄ HgSCN	-11.16	8.68	7.64	8.18	3.85	5.96
IC ₆ H ₄ HgSCN	-10.96	8.49	7.45	7.99	3.66	5.77
CH ₃ OC ₆ H ₄ HgSCN	-10.94	8.46	7.42	7.96	3.63	5.74
ClC ₆ H ₄ HgSCN	-10.85	8.37	7.33	7.87	3.54	5.65
O ₂ NC ₆ H ₄ HgSCN	-10.69	8.21	7.17	7.71	3.38	5.49
CH ₃ C ₆ H ₄ HgSeCN	-11.10	8.62	7.58	8.10	3.79	5.90
NO ₂ C ₆ H ₄ HgSeCN	-10.59	8.11	7.07	7.61	3.28	5.30

Table 3—Infrared Spectral Data of Complexes and Relationship Between $\Delta E_{nm}^\ddagger$ and Some Infrared Spectral Band Positions (cm^{-1})

Complexes	$\Delta E_{nm}^\ddagger$	νCN	νCS	δNCS	$\nu\text{Hg-C}$	$\nu\text{M-NCS}$	$\nu\text{Hg-S}$
$(\text{SCN})_2\text{Mn}(\text{NCSHgC}_6\text{H}_4\text{NO}_2)_2$	8.21	2150 2070	775 710	445	464	300	226
$(\text{SCN})_2\text{Co}(\text{NCSHgC}_6\text{H}_4\text{NO}_2)_2$	7.17	2160	690	441	464	296	229
$(\text{SCN})_2\text{Zn}(\text{NCSHgC}_6\text{H}_4\text{NO}_2)_2$	5.49	2175 2060	765 697	432	458	290	225
$(\text{SCN})_2\text{Mn}(\text{NCSHgC}_6\text{H}_4\text{CH}_3)_2$	8.68	2155 2065	772 692	440	463	310	210
$(\text{SCN})_2\text{Co}(\text{NCSHgC}_6\text{H}_4\text{CH}_3)_2$	7.64	2175 2075	780 618	435	465	300	220
$(\text{SCN})_2\text{Zn}(\text{NCSHgC}_6\text{H}_4\text{CH}_3)_2$	5.96	2160 2074	710 690	441	496	296	228
$(\text{SCN})_2\text{Mn}(\text{NCSHgC}_6\text{H}_4\text{COOC}_2\text{H}_5)_2$	10.22	2150	755	445	—	308	—
$(\text{SCN})_2\text{Co}(\text{NCSHgC}_6\text{H}_4\text{COOC}_2\text{H}_5)_2$	9.18	2155	760	445	—	295	—
$(\text{SCN})_2\text{Zn}(\text{NCSHgC}_6\text{H}_4\text{COOC}_2\text{H}_5)_2$	7.50	2172	698	435	—	395	—
$(\text{SCN})_2\text{Mn}(\text{NCSHgC}_6\text{H}_4\text{COOC}_4\text{H}_9)_2$	9.06	2160	775	445	—	305	—
$(\text{SCN})_2\text{Co}(\text{NCSHgC}_6\text{H}_4\text{COOC}_4\text{H}_9)_2$	8.02	2160	772	442	—	298	—
$(\text{SCN})_2\text{Zn}(\text{NCSHgC}_6\text{H}_4\text{COOC}_4\text{H}_9)_2$	6.34	2175	698	432	—	295	—
$(\text{SCN})_2\text{Ni}(\text{NCSHgC}_6\text{H}_4\text{NO}_2)_2$	—	2170 2090	740 665	425	456	308	220
$(\text{SCN})_2\text{Cu}(\text{NCSHgC}_6\text{H}_4\text{NO}_2)_2$	—	2165 2062	778 693	430	460	305	227
$(\text{SCN})_2\text{Ni}(\text{NCSHgC}_6\text{H}_4\text{CH}_3)_2$	—	2145 2070	760 695	425	468	305	220
$(\text{SCN})_2\text{Cu}(\text{NCSHgC}_6\text{H}_4\text{CH}_3)_2$	—	2160 2070	750 695	418	464	298	227
$(\text{SCN})_2\text{Co}(\text{NCSeHgC}_6\text{H}_4\text{CH}_3)_2$	—	2165 2050	690 630	440 410	460	290	—
$(\text{SCN})_2\text{Ni}(\text{NCSeHgC}_6\text{H}_4\text{CH}_3)_2$	—	2172 2135	628 660	430 408	470	288	—
$(\text{SCN})_2\text{Co}(\text{NCSeHgC}_6\text{H}_4\text{NO}_2)_2$	—	2160 2145	650 670	445 410	465	485	—
$(\text{SCN})_2\text{Ni}(\text{NCSeHgC}_6\text{H}_4\text{NO}_2)_2$	—	2172 2125	660 680	435 425	468	280	—

(Table 5). Cobalt complexes have the highest value amongst the complexes with tetrahedral stereochemistry around M. The cobalt(II) is also expected to have higher stability constant according to the established order of stabilities⁹. The matching constant values are higher in the case of the complexes of the tolyl series than those of nitro series. On the basis of matching constant values the following order of stabilities is obtained in different cobalt thiocyanate complexes.

$\text{NCS}^- > \text{C}_6\text{H}_9\text{COOC}_6\text{H}_4\text{HgSCN}$

$> \text{C}_2\text{H}_5\text{COOC}_6\text{H}_4\text{HgSCN}$

$> \text{CH}_3\text{C}_6\text{H}_4\text{HgSCN} > \text{NO}_2\text{C}_6\text{H}_4\text{HgSCN}$

The above sequence indicates that the thiocyanate ion is a better donor towards cobalt(II) than RHgSCN . The matching constant values in the case of RHgSCN complexes are higher than those for the corresponding complexes of RHgSeCN .

(viii) The stability constants ($\log K$) of the complexes

Table 4—Difference in Effective Softness Values ($E_{n(\text{eff})}^\ddagger$) of M and Hg or $E_n^\ddagger$ (M-Hg)

$(\text{SCN})_2\text{M}(\text{NCSHgR})_2$	$E_{n(\text{eff})}^\ddagger$		$E_n^\ddagger$ (M-Hg)				
	Hg	Mn	Ni	Co	Zn	Cu	
$\text{R} = \text{C}_6\text{H}_4\text{CH}_3$	-6.28	3.8	3.3	2.76	1.08	1.03	
$\text{R} = \text{C}_6\text{H}_4\text{NO}_2$	-6.94	4.46	3.9	3.42	1.74	0.37	
$\text{R} = \text{C}_6\text{H}_4\text{COOC}_4\text{H}_9$	-6.50	4.02	3.52	2.98	1.30	0.81	
$\text{R} = \text{C}_6\text{H}_4\text{COOC}_2\text{H}_5$	-6.61	4.13	3.63	3.09	1.41	0.71	

$E_{n(\text{eff})}^\ddagger$ of M in $\text{M}(\text{NCS})_2$: $\text{Mn(II)} = -2.48$, $\text{Ni(II)} = -2.98$, $\text{Co(II)} = -3.52$, $\text{Zn(II)} = -5.20$, $\text{Cu(II)} = -7.31$.

have been experimentally determined (Table 5). The $\log K$ values of the complexes of tolyl series are higher than those for the complexes of nitro series. The $\log K$ values of the cobalt complexes are the highest and that of the zinc are the lowest. The complexes of thiocyanate series have higher $\log K$ values than the complexes of selenocyanate

Table 5—Matching Constant and Stability Constants of $(\text{SCN})_2\text{M}(\text{NCXHgR})_2$

Complexes	ΔE_{nm}	$10 Dq$ (cm^{-1})	CFSE (eV)	Matching constant	Stability constant (log K)
<i>M in tetrahedral environment</i>					
$(\text{SCN})_2\text{Mn}(\text{NCSHgC}_6\text{H}_4\text{COOC}_2\text{H}_5)_2$	10.22	0	0	10.22	—
$(\text{SCN})_2\text{Co}(\text{NCSHgC}_6\text{H}_4\text{COOC}_2\text{H}_5)_2$	9.18	4660	4.69	13.87	—
$(\text{SCN})_2\text{Zn}(\text{NCSHgC}_6\text{H}_4\text{COOC}_2\text{H}_5)_2$	7.50	0	0	7.50	—
$(\text{SCN})_2\text{Mn}(\text{NCSHgC}_6\text{H}_4\text{COOC}_4\text{H}_9)_2$	9.06	0	0	9.06	—
$(\text{SCN})_2\text{Co}(\text{NCSHgC}_6\text{H}_4\text{COOC}_4\text{H}_9)_2$	8.02	4720	4.68	12.70	—
$(\text{SCN})_2\text{Zn}(\text{NCSHgC}_6\text{H}_4\text{COOC}_4\text{H}_9)_2$	6.34	0	0	6.34	—
$(\text{SCN})_2\text{Mn}(\text{NCSHgC}_6\text{H}_4\text{CH}_3)_2$	8.68	0	0	8.68	4.11
$(\text{SCN})_2\text{Co}(\text{NCSHgC}_6\text{H}_4\text{CH}_3)_2$	7.64	5400	4.62	12.26	6.11
$(\text{SCN})_2\text{Zn}(\text{NCSHgC}_6\text{H}_4\text{CH}_3)_2$	5.96	0	0	5.96	3.73
$(\text{SCN})_2\text{Mn}(\text{NCSHgC}_6\text{H}_4\text{NO}_2)_2$	8.21	0	0	8.21	3.89
$(\text{SCN})_2\text{Co}(\text{NCSHgC}_6\text{H}_4\text{NO}_2)_2$	7.17	4700	4.69	11.86	5.97
$(\text{SCN})_2\text{Zn}(\text{NCSHgC}_6\text{H}_4\text{NO}_2)_2$	5.49	0	0	5.49	3.44
$\text{Co}(\text{NCS})_4^2$	11.96	4550	4.48	16.44	—
$(\text{SCN})_2\text{Co}(\text{NCSeHgC}_6\text{H}_4\text{CH}_3)_2$	7.58	5700	4.59	12.17	5.62
$(\text{SCN})_2\text{Co}(\text{NCSeHgC}_6\text{H}_4\text{NO}_2)_2$	7.07	4840	4.67	11.74	4.86
<i>M in octahedral environment</i>					
$(\text{SCN})_2\text{Ni}(\text{NCSHgC}_6\text{H}_4\text{CH}_3)_2$	8.17	10130	5.93	14.10	5.59
$(\text{SCN})_2\text{Ni}(\text{NCSHgC}_6\text{H}_4\text{NO}_2)_2$	7.71	9520	6.02	13.73	4.20
$(\text{SCN})_2\text{Ni}(\text{NCSeHgC}_6\text{H}_4\text{CH}_3)_2$	8.12	10400	5.88	14.00	4.08
$(\text{SCN})_2\text{Ni}(\text{NCSeHgC}_6\text{H}_4\text{NO}_2)_2$	7.61	10100	5.93	13.64	3.97

series. These observations are consistent with the trends in $\Delta E_{\text{nm}}^{\ddagger}$ and matching constant values.

Infrared spectral studies

The infrared spectral bands due to $\nu(\text{CN})$, $\nu(\text{CS})$, $\delta(\text{NCS})$, $\nu(\text{Hg}-\text{S})$ and $\nu(\text{Hg}-\text{C})$ modes of tolyl and nitrophenyl mercury thiocyanates and selenocyanates are almost in the same region (Table 3). The positions of these bands are considerably changed on complexation with $\text{M}(\text{NCS})_2$. Both the $\nu(\text{CN})$ and $\nu(\text{CS})$ bands show positive shifts while the δNCS shows a negative shift. These changes indicate bridging nature of RHgXCN . The $\nu(\text{Hg}-\text{S})$ and $\nu(\text{Hg}-\text{C})$ modes also show positive shifts. Two additional bands at 2070 and 300 cm^{-1} are observed, which are assigned to $\nu(\text{CN})$ and $\nu(\text{M}-\text{NCS})$, originating from $\text{M}(\text{NCS})_2$. The bands assigned to bridging $\nu(\text{CN})$, $\nu(\text{CS})$ and $\delta(\text{NCS})$ occur at different positions in the complexes of tolyl and nitro series. The $\nu(\text{CN})$ and $\nu(\text{CS})$ bands in tolyl series occur at higher wave numbers than the corresponding bands in the nitro series. These changes in band positions with change in R can be attributed to different inductive effects of the two groups. The terminal N-bonded $\nu(\text{CN})$ and $\nu(\text{M}-\text{NCS})$ bands originating from M-NCS moiety also occur at different positions in the tolyl and nitro series. The positions of $\nu(\text{CN})$ band show no definite sequence whereas the $\nu(\text{M}-\text{NCS})$ bands in the tolyl series occur at higher wave numbers. The position of $\nu(\text{M}-\text{NCS})$ changes with change in the metal. The $\nu(\text{Hg}-\text{S})$ and

$\nu(\text{Hg}-\text{C})$ bands in tolyl mercury thiocyanate and nitrophenylmercury thiocyanate, appear at 200 and 460 cm^{-1} respectively. These bands show a positive shift on complexation.

The corresponding complexes of RHgSeCN show a similar behaviour. The presence of four bands in the $\nu(\text{CN})$ region can be explained on the basis of change in local symmetry around cobalt from T_d in thiocyanate complexes to C_{2v} in selenocyanate complexes. Similarly there is a change in symmetry around nickel in both the cases. Based on these symmetries the numbers of bands have been calculated. The number of bands observed in case of $(\text{SCN})_2\text{Co}(\text{NCSHgR})_2$ is consistent with the calculated number whereas in case of thiocyanate analogues two bands are present against the expected one (T_2). This is on account of the splitting of T_2 mode, possibly because of the presence of bridged and terminal thiocyanates. Additional bands are also observed due to $\nu(\text{CSe})$ and $\nu(\text{NCSe})$.

The far infrared regions show bands at 300 cm^{-1} due to $\nu(\text{M}-\text{NCS})$ [$\text{M} = \text{Co}, \text{Mn}, \text{Zn}$] and at 270 cm^{-1} due to $\nu(\text{Ni}-\text{NCS})$. A lower value in case of $\nu(\text{Ni}-\text{NCS})$ is indicative of the presence of octahedral geometry around nickel¹⁰ whereas in other cases the configuration around the metal ion is tetrahedral.

Electronic spectral studies

The electronic spectra of cobalt complexes of tolyl series show the presence of two intense bands in the

Table 6—Electronic Spectral Band Parameters (in cm^{-1})

Complexes	ν_3	ν_2	ν_1	$10 Dq$	B'	β
$(\text{SCN})_2\text{Co}(\text{NCSHgC}_6\text{H}_4\text{CH}_3)_2$	13000	8300	—	5400	840	0.84
$(\text{SCN})_2\text{Ni}(\text{NCSHgC}_6\text{H}_4\text{CH}_3)_2$	28200	17750	10120	10130	573	0.83
$(\text{SCN})_2\text{Co}(\text{NCSeHgC}_6\text{H}_4\text{CH}_3)_2$	16050	9520	—	5700	590	0.86
$(\text{SCN})_2\text{Ni}(\text{NCSeHgC}_6\text{H}_4\text{CH}_3)_2$	27100	16690	10400	10400	917	0.98
$(\text{SCN})_2\text{Co}(\text{NCSHgC}_6\text{H}_4\text{NO}_2)_2$	16900	8010	—	4700	682	0.71
$(\text{SCN})_2\text{Ni}(\text{NCSHgC}_6\text{H}_4\text{NO}_2)_2$	26180	17030	9500	9520	732	0.72
$(\text{SCN})_2\text{Co}(\text{NCSeHgC}_6\text{H}_4\text{NO}_2)_2$	16210	8230	—	4840	748	0.67
$(\text{SCN})_2\text{Ni}(\text{NCSeHgC}_6\text{H}_4\text{NO}_2)_2$	26100	10100	10020	10100	883	0.85

regions 13000 cm^{-1} and 8300 cm^{-1} which are assigned to the transitions ${}^4A_2 \rightarrow {}^4T_1(P)$ (ν_3) and ${}^4A_2 \rightarrow {}^4T_1(F)$ (ν_2) respectively (Table 6). The corresponding bands in the complexes of nitrophenyl series appear at 16900 and 8010 cm^{-1} . The D_q , B' and β values derived from ν_2 and ν_3 also differ in the two series. The D_q values in the tolylmercury(II) thiocyanate and selenocyanate are higher showing better interaction with cobalt thiocyanate. This observation is consistent with the results obtained from infrared spectral data and softness parameter, $\Delta E_{\text{mm}}^\ddagger$. The magnetic moment values in these cases are also indicative of tetrahedral geometry around cobalt. The local symmetry around cobalt appears to be T_q because there is no splitting in the electronic spectral band¹¹. The selenocyanates show a similar behaviour but the D_q values are higher than those for the thiocyanate complexes.

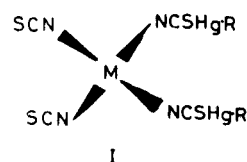
Presence of tetrahedral geometry in Mn(II) and Zn(II) complexes can be predicted on the basis of similarity in number of bands in $\nu(\text{M}-\text{NCS})$ region with that in Co(II) complexes. The analytical data and the preference for this geometry by these metal ions also support the presence of tetrahedral geometry. In case of manganese the magnetic moment values (5.9 B.M.) also favour tetrahedral geometry.

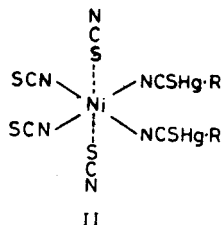
The electronic spectra of nickel complexes in solid and solution phases show some variation hence spectra have been recorded in mull. The mull spectra show the presence of three bands (Table 6) assigned to the transitions ${}^3A_{2g} \rightarrow {}^3T_{2g}$ (ν_1), ${}^3A_{1g} \rightarrow {}^3T_{1g}$ (ν_2) and ${}^3A_{2g} \rightarrow {}^3T_{1g}(P)$ (ν_3). These spectral band positions are indicative of the presence of octahedral geometry around nickel. The positions of spectral bands and the parameters derived from them in tolyl and nitrophenyl series are different. The D_q values in the case of tolyl series are higher than those in the nitro series in agreement with conclusions drawn from softness parameter values. The β values, however, show greater delocalization in nitro series. The D_q values of selenocyanate complexes are higher than those of their thiocyanate analogs. The magnetic moment values also support octahedral configuration around nickel which can be explained on the basis of axial

coordination from the sulphur end of thiocyanates from adjacent layer in solid phase¹².

In solution phase, the axial coordination through S-end is perhaps disrupted by the solvent, as a result of which the positions of the electronic spectral bands are changed. The split nature of ν_2 band also indicates that there is departure from O_h symmetry around nickel and possible presence of D_{4h} (ref. 13, 14). The magnetic moment values are very close to spin only value, which also support departure from O_h symmetry. The complexes are non-conducting in nature. The copper complexes in general give rise to orbitally non-degenerate ground states involving a static form of distortion resulting in elongated tetragonal octahedron having D_{4h} symmetry. Such complexes exhibit one absorption band in visible region near 16000 cm^{-1} which can often be resolved into three components assignable to transitions from d_{xy} , d_{z^2} and d_{yz} levels to antibonding and half filled $d_{x^2-y^2}$ (ref. 15, 16) levels. In the complexes of tolyl series bands at 10300 and 14700 cm^{-1} are observed which may be due to the splitting of the band expected to appear at 16000 cm^{-1} . The magnetic moment values (1.98 B.M.) also indicate the presence of octahedral configuration with extensive distortion. The octahedral configuration by copper is perhaps achieved by elongated axial coordination through the free sulphur end of adjacent layer as in the case of nickel, hence, a similar structure having an elongated axial band can be proposed. Since the axial coordination is weak, it is readily replaced by polar solvent on account of which the positions of peaks in solid and solution phase electronic spectra differ.

On the basis of these studies the structures I and II are proposed for various complexes.





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