1,1′-Bis(selenocyanatomercurio)ferrocene as Ligand towards $M(NCS)_2$ [M=Co(II), Ni(II), and Zn(II)]

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A comparative study of the behaviors of 1,1′-bis(selenocyanatomercurio)ferrocene (FBMS) with those of its thiocyanate analog (FBMT), has been made. Various physicochemical studies indicate that the Lewis acids and the adducts formed by FBMS are less stable than those of FBMT. The D_q values of FBMS adducts are higher, but the β values are lower. The matching constant values of FBMT complexes are higher than their corresponding FBMS complexes. The structures of Lewis acids and the adducts are similar in both the cases.

In our recent communication we have reported on the complexes of 1,1′-bis(thiocyanatomercurio)ferrocene (FBMT).[1] Since selenocyanate derivatives differ in their mode of bonding in certain cases,[2] a comparative study of the complexes of 1,1′-bis(selenocyanatomercurio)ferrocene (FBMS) was done.

Experimental

Material and Manipulation. Reagent grade solvents were purified before use. KSeCN was prepared and recrystallized by the method described elsewhere.[3] Nicotinamide (nia) and 2,2′-bipyridyl (bpy) were used from fresh bottle. 1,1′-Bis(selenocyanatomercurio)ferrocene (FBMS) was prepared as given below.

Preparation of FBMS. 11.5 g of ferrocene was dissolved in 65 ml of benzene. A suspension of 20 g of $Hg(OAc)_2$ in 250 ml of methanol was very slowly added to the solution of ferrocene through a dropping funnel with vigorous stirring. A clear dark brown solution was obtained. To this a solution of 6.5 g KSeCN in 10 ml of water was added with continuous stirring. A yellow precipitate was obtained, which was filtered on a Buchner funnel and washed with petroleum ether. This yellow compound was a mixture of (selenocyanatomercurio)ferrocene and FBMS. The former was removed by repeated extraction with hot 1,2-dichloroethane. FBMS left as insoluble yellow solid was dissolved in DMSO. To the solution a few drops of water were added, and it was left for a few days. Crystals of FBMS formed, were filtered, washed with the solvent and dried in vacuum.

Analytical Data. Mp 115 °C (decomp); Found: N, 6.74; Hg, 50.00; Se, 19.12%; Calcd for $C_{12}N_2H_8Se_2Hg_2Fe$: N, 7.04; Hg, 50.37; Se, 19.89%. IR (Nujol); ν(C–N) 2180(s), 2130(s), 2080 (sh); ν(C–Se) 765(s), 730(s), 680(m); δ(NCSe) 440(s), 420(s). IR(acetone): ν(C–N) 2130(s), 2070(s); ν(C–Se) 760(s), 740(s), 680(s), 660(m); δ(NCSe) 440(s), 510(s).

Preparation of Lewis Acids, $Fe(C_5H_4HgSeCN)_2M(NCS)_2$ [M=Ni(II), Co(II), and Zn(II)]. A calculated amount of FBMS was dissolved in a small quantity of DMSO and diluted to 200 ml of acetone. $M(NCS)_2$ was dissolved either in acetone or DMSO-acetone mixture. The solutions were mixed in 1 : 1 molar ratio and stirred for 24 h or until precipitate appeared. When the quantity of DMSO was too much, the precipitate was obtained by the addition of ethanol. The precipitate was filtered, washed with ethanol and dried in vacuum. The compounds thus obtained were recrystallized from acetone–ethanol mixture.

Preparation of Adducts, $Fe(C_5H_4HgSeCN)_2M(NCS)_2 \cdot L_x$ [M=Ni(II), Co(II), and Zn(II); x=2 when L is nia and one when bpy]. The adducts were prepared by two methods:

1. A suspension or solution of the Lewis acids was prepared in acetone–ethanol mixture and mixed with an ethanol solution of nicotinamide in 1 : 2 molar ratio or with bpy in 1 : 1 molar ratio and stirred for 24 h. In each case precipitate was formed, filtered, washed with ethonal, and dried in vacuum. The compounds were recrystallized from acetone–ethanol mixture.

2. $M(NCS)_2(nia)_2$ were first prepared by reaction of $M(NCS)_2$ with nicotinamide in 1 : 2 molar ratio in ethanol. Precipitate appeared in each case which was filtered, washed with ethanol and dried in vacuum. The complexes were recrystallized from acetone–ethanol mixture. $M(NCS)_2(nia)_2$ was dissolved in acetone and FBMS was dissolved in DMSO-acetone mixture. The solutions of $M(NCS)_2(nia)_2$ and FBMS were mixed in 1 : 1 molar ratio and stirred for 24 h. The precipitate formed was filtered, washed with ethanol and dried in vacuum. The compounds were recrystallized from acetone–ethanol mixture.

Analysis of the Complexes. Selenium was estimated as selenium metal, the other elements (Co, Ni, S, Hg) were analyzed as described.[1]

Physical Measurements. The molar conductance of the complexes were measured in DMSO using a Philips conductivity bridge model PR 9500. The magnetic susceptibility measurements were made at room temperature by Gouy's method using $CoHg(SCN)_4$ as standard. The diamagnetic corrections were made using Pascal's constants. Infrared spectra of the complexes were recorded as Nujol mulls on a Pye Unicam SP3-300 infrared spectrophotometer in the range 4000—200 cm^{-1}. The electronic spectra in DMSO (except $FBMS \cdot Co(NCS)_2$) were recorded on a Cary-14 spectrophotometer. The spectra of $FBMS \cdot Co(NCS)_2$ was recorded in solid phase adopting the procedure of Lee.[10]

Results and Discussion

Lewis Acids, $Fe(C_5H_4HgSeCN)_2M(NCS)_2$ [M=Ni(II), Co(II), and Zn(II)]. Like their SCN analogs[1] these Lewis acids are prepared by direct reaction of FBMS and $M(NCS)_2$. The positions of IR bands in the region of ν(CN), ν(CSe), and δ(NCSe) in $FBMS \cdot Co(NCS)_2$ are basically similar to those of $FBMT \cdot Co(NCS)_2$ except in the number of bands in the ν(CN), ν(CX), and δ(NCX) (X=S or Se) regions (cf. Table 2). This difference is due to the different local symmetries around Co(II), i.e. Td in the former C_{2v} in the latter.

Table 1. Analytical Data of the Complexes

Complex	Colour	Mp	% Sulfur		% Mercury		% Metal		% Nitrogen		% Selenium		Mole conductance
		θ_m/°C	Calcd	Found	Calcd	Found	Calcd	Found	Calcd	Found	Calcd	Found	cm^2 mho mol^{-1}
$Fe(C_5H_4HgSeCN)_2$-$Ni(NCS)_2$	Brown	173(d)	6.61	6.12	41.32	40.20	6.09	5.99	5.78	5.61	16.42	16.14	61.71
$Fe(C_5H_4HgSeCN)_2$-$Co(NCS)_2$	Blue	168(d)	6.61	6.23	41.32	40.12	6.09	5.85	5.78	5.55	16.42	16.23	42.75
$Fe(C_5H_4HgSeCN)_2$-$Zn(NCS)_2$	Grey	140(d)	6.56	6.25	41.02	40.89	6.66	6.32	5.74	5.53	16.30	16.35	58.81
$Fe(C_5H_4HgSeCN)_2$-$Ni(NCS)_2(bpy)$	Brown	190(d)	5.69	5.52	35.58	34.91	5.16	4.98	4.98	4.73	14.05	13.95	60.11
$Fe(C_5H_4HgSeCN)_2$-$Ni(NCS)_2(nia)_2$	Brown	185(d)	5.28	5.19	33.00	32.59	4.78	4.15	4.62	4.42	13.03	12.99	63.23
$Fe(C_5H_4HgSeCN)_2$-$Co(NCS)_2(bpy)$	Brown	180(d)	5.69	5.49	35.58	35.13	5.16	5.01	4.92	4.71	14.05	13.92	41.15
$Fe(C_5H_4HgSeCN)_2$-$Co(NCS)_2(nia)_2$	Brown	170(d)	5.28	5.12	33.00	33.10	4.78	4.32	4.62	4.33	13.03	12.95	43.01
$Fe(C_5H_4HgSeCN)_2$-$Zn(NCS)_2(bpy)$	Dirty white	175(d)	5.65	5.53	35.36	34.93	5.74	5.54	4.95	4.66	13.97	13.82	66.18
$Fe(C_5H_4HgSeCN)_2$-$Zn(NCS)_2(nia)_2$	Dirty white	155(d)	5.24	5.15	32.81	32.13	5.33	5.03	4.59	4.41	12.96	12.82	59.12

d = decomposes.

Table 2. Infrared Spectral and Electronic Spectral Bands with Spectral Parameters

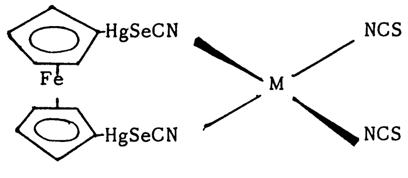
Complex	ν(C-N)	ν(C-X)	δ(NCX)	ν(M-NCX/M-L)	ν_1	ν_2	ν_3	D_q	B'	β	μ_{eff}
	cm^{-1}	cm^{-1}	cm^{-1}	cm^{-1}	cm^{-1}	cm^{-1}	cm^{-1}	cm^{-1}	cm^{-1}		BM
Lewis acid											
$Fe(C_5H_4HgSeCN)_2$-$Ni(NCS)_2$	2180s, 2120m, 2050sh	780s, 750s, 680w, 660s	460s, 410s	250s, 230sh	10010	16800	28200	1031	938	0.96	3.01
$Fe(C_5H_4HgSeCN)_2$-$Co(NCS)_2$	2180m, 2130s, 2090sh	775s, 740sh, 670w, 650m	460s, 410s	310s, 280sh	—	6000	15500	356	721	0.74	4.25
$Fe(C_5H_4HgSeCN)_2$-$Zn(NCS)_2$	2160m, 2120s, 2070sh	730s, 710s, 650w, 630s	400s, 400w	315s, 270sh	—	—	—	—	—	—	—
Adduct											
$Fe(C_5H_4HgSeCN)_2$-$Ni(NCS)_2(nia)_2$	2170s, 2090s, 2050sh	760s, 745w, 695s, 660w	470m, 415s	295s, 230sh	9100	16950	27850	1052	882	0.85	2.99
$Fe(C_5H_4HgSeCN)_2$-$Ni(NCS)_2(bpy)$	2160s, 2100s, 2060sh	760s, 740s, 690s, 665m	470s, 420w	275s, 225sh	9500	16700	28000	1025	930	0.90	3.02
$Fe(C_5H_4HgSeCN)_2$-$Co(NCS)_2(nia)_2$	2160w, 2090s, 2050s	660s, 750m, 690s,660s	460s, 410w	280s, 215sh	10450	17700	20800	944	914	0.94	5.14
$Fe(C_5H_4HgSeCN)_2$-$Co(NCS)_2(bpy)$	2155s, 2090b, 2040s	760s, 735sh, 680s, 650s	466w, 420s	270s, 210sh	10500	15870	19230	866	898	0.92	5.06
$Fe(C_5H_4HgSeCN)_2$-$Zn(NCS)_2(nia)_2$	2160s, 2110w, 2040sh	740s, 720sh, 670s, 730m	450m, 400s	275s, 210sh	—	—	—	—	—	—	—
$Fe(C_5H_4HgSeCN)_2$-$Zn(NCS)_2(bpy)$	2140s, 2110w, 2030sh	730m, 715s, 670s, 635w	445s, 425s	270s, 220sh	—	—	—	—	—	—	—

s=strong, sh=shoulder, b=broad, m=medium, w=weak; X=S or Se.

This increase of number of bands is due to the presence of ν(CN), ν(CS), ν(CSe), δ(NCS), and δ(NCSe) bands. The IR spectra show the presence of both bridged and terminal NCX groups (Table 1).

The magnetic moment values show close resemblance with the SCN analogs. The electronic spectral bands positions and the spectral parameters of FBMS·$Co(NCS)_2$ are presented in Table 2. Two intense bands (Fig. 5) observed in the region 15500 and 6000 cm^{-1} are assigned to $^4A_2 \rightarrow {}^4T_2(F)$ (ν_3) and $^4A_2 \rightarrow {}^4T_1(P)$ (ν2). These bands, D_q and magnetic moment values show that cobalt is in tetrahedral geometry. The compound is non-conducting but is dissociated significantly. The following structure (Fig. 1) can thus be proposed for the Lewis acids where M is Co(II), and also for Zn(II) which is very similar.

The electronic spectra of Lewis acid with Ni(II) show three bands in the region 28200, 16800, and 10010 cm^{-1} which are assigned to $^3A_{2g} \rightarrow {}^3T_{1g}$ (P) (ν_3), $^3A_{2g} \rightarrow {}^3T_{1g}$ (F) (ν_2), and $^3A_{2g} \rightarrow {}^3T_{2g}$ (F) (ν_1), respectively. Various spectral parameters have been calculated with the help of ν_2 and ν_3 bands using the secular equation



M = Co(II) and Zn(II)

Fig. 1.

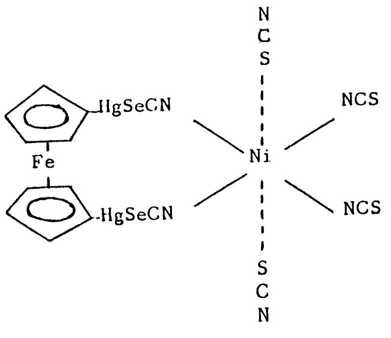
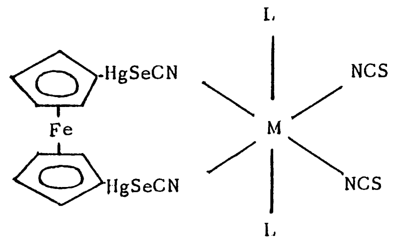
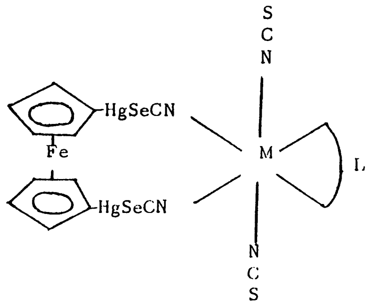


Fig. 2.



[M= Co(II), Ni(II) and Zn (II); L= nicotinamide (nia)]

Fig. 3.



[M= Co(II), Ni(II) and Zn (II); L= 2,2′-bipyridyl (bpy)]

Fig. 4.

of Tanabe and Sugano[4] and the results are included in Table 2. The electronic spectra and magnetic moment values for FBMS·Ni(NCS)$_2$ are indicative of octahedral coordination geometry around Ni(II), which is achieved by axial coordination from adjacent layer. On the basis of these results the structure in Fig. 2 can be proposed for it.

The D_q values of the FBMT Lewis acids are lower than those of FBMS Lewis acids. This indicates that FBMS exerts stronger ligand field than FBMT.[5] The B' value shows a decrease on changing from FBMT to FBMS indicating greater orbital overlap. The D_q, B', and β values of different series are presented in Table 2.

Adducts. Fe(C$_5$H$_4$HgSeCN)$_2$M(NCS)$_2$L$_x$ [M= Co(II), Ni(II), Zn(II); x=2 when L is nia and one when bpy]. In FBMS-M(NCS)$_2$ the coordination number of Co(II) and Zn(II) is four, against the maximum of six, hence they can be treated as Lewis acids. In case of the Ni(II) analogs the weak axial NCS ligands can easily be replaced by any strong base. Accordingly, when all the Lewis acids were treated with nicotinamide and 2,2′-bipyridyl, adducts of general formula FBMS·M(NCS)$_2$·L$_x$ were formed. The molar conductance values of these complexes in DMSO are in the range 40 to 63 cm^2 mho mol^{-1} (Table 1) showing that they are dissociated significantly.

IR spectra show that the positions of ν(CN), ν(CS), ν(CSe), δ(NCS), and δ(NCSe) bands of the Lewis acids are not significantly changed on adduct formation. The slight changes observed are due to, the change in stereochemistry around M. This reveals that the original structure of the Lewis acids is retained and only the coordination geometry of M changes on account of linkage of ligands. On adduct formation there is a slight change in ν(M-NCS) band in the case of Co and Zn. While, there is almost no change in ν(M-NCS) band in the case of Ni. The negative shifts in the case of Co and Zn are due to the change from tetrahedral geometry around M in the Lewis acids to octahedral in the adducts.[6,7] Such a change is not observed in Ni adduct because of the presence of octahedral configuration in the Lewis acids and the adducts as well. The electronic spectra of FBMS·Co(SCN)$_2$L$_x$ show the presence of three bands in the regions 19230—20800, 15870—17700, and 10450—10500 cm^{-1} which are assigned to $^4T_{1g}\rightarrow{}^4T_{1g}(P)$ (ν_3), $^4T_{1g}\rightarrow{}^4A_{2g}$ (ν_2), and $^4T_{1g}\rightarrow{}^4T_{2g}$ (ν_1) transitions respectively. The electronic spectra of Ni complexes show the presence of three bands in the regions 27850—28000, 16700—16950, and 9100—9500 cm^{-1} which are assigned just as in the case of the parent Lewis acid. The D_q values calculated from ν_2 and ν_3 are presented in Table 2. The structure as in Figs. 3 and 4 can be proposed for the adducts. Though a trans structure has been shown in Fig. 3, yet the possibility of cis structure is not ruled out.

Comparison with the Complexes of FBMT.

1. The Lewis acids and the adducts formed by FBMS are less stable than those formed by FBMT. The former complexes start decomposing after a month giving selenium metal.
2. Molar conductance values of FBMS complexes are slightly lower than those of FBMT analog, indicating that their dissociation in solution is less.
3. Complexes of FBMS are less soluble in DMSO than those of FBMT.

4. Three bands are present in ν(CN) region in the Lewis acids and adducts of FBMS series against two in FBMT analog. This is due to the difference in local symmetry around M.

5. The ν(M-NCSe) bands in the Lewis acid appear at lower frequency as compared with ν(M-NCS) band.

6. The D_q values of FBMS adducts are higher than their FBMT analogs. The β values show a decrease on changing from the latter to the former, indicating greater orbital overlap.

Quantitative Softness. The softness value of a metal ion has been denoted by $E^{\ddagger}_{n}$ and that of a base ion by $E^{\ddagger}_{m}$ and the difference between the two by $\Delta E^{\ddagger}_{nm}$.[8] The softness value of any metal in different compounds has been expressed by effective softness and denoted by $E^{\ddagger}_{n(eff)}$, similarly the softness of any atom in a neutral base such as nitrogen in nicotinamide and 2,2′-bipyridyl has been denoted by $E^{\ddagger}_{m(eff)}$ the difference between the two is denoted by $\Delta E^{\ddagger}_{nm(eff)}$. This is described as matching. A higher value of $\Delta E^{\ddagger}_{nm}$ indicates better matching. This can be represented by the following equation. The detail description of estimation of various softness parameters is given in Ref. 9.

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

The $\Delta E^{\ddagger}_{nm}$ values in the Table 3 indicate that FBMT show better match with various $M(NCS)_2$ than FBMS. The effective softness of ligands and of M in the Lewis acids have also been calculated. The matching between the two has been derived and is presented in Table 4. A reference to Table 4 shows that 2,2′-

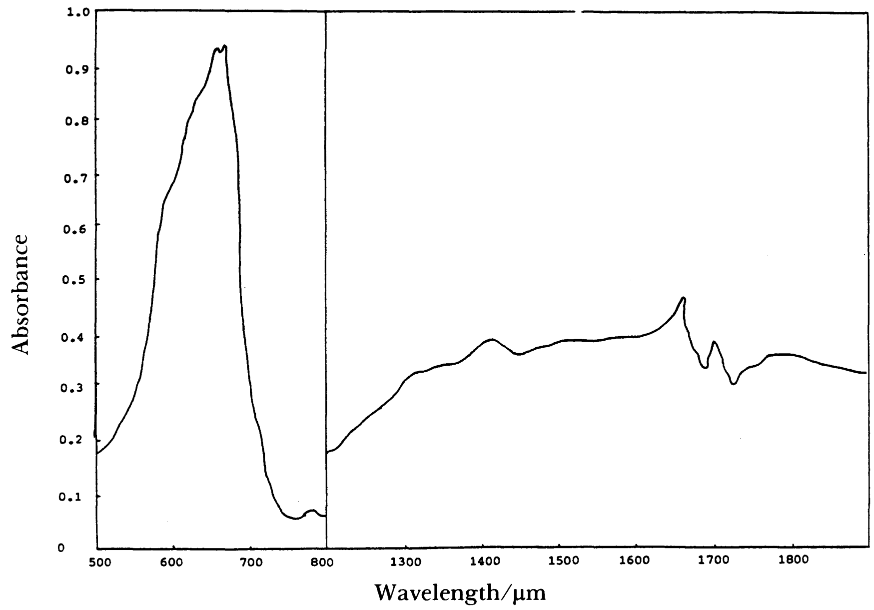


Fig. 5. Electronic spectra of FBMS·$Co(NCS)_2$.

Table 3. $\Delta E^{\ddagger}_{nm}$ Derived from $E^{\ddagger}_{n(eff)}$ of M in $M(NCS)_2$ and $E^{\ddagger}_{m(eff)}$ of FBMS in the Formation of Lewis Acids

Lewis acid	$E^{\ddagger}_{n(eff)}$ of M in $M(NCS)_2$	$E^{\ddagger}_{m(eff)}$ of FBMS	$\Delta E^{\ddagger}_{nm}$	CFSE	Matching constant $\Delta E^{\ddagger}_{nm}$+CFSE
$Fe(C_5H_4HgSeCN)_2Ni(NCS)_2$	−3.10	−11.14	8.04	6.41	14.45
$Fe(C_5H_4HgSeCN)_2Co(NCS)_2$	−3.56	−11.14	7.58	4.68	12.19
$Fe(C_5H_4HgSeCN)_2Zn(NCS)_2$	−4.92	−11.14	6.22	—	6.22

Table 4. $\Delta E^{\ddagger}_{nm}$ Derived from $E^{\ddagger}_{n(eff)}$ of M in FBMS·$M(NCS)_2$ and $E^{\ddagger}_{m(eff)}$ of the Ligand in the Formation of Adducts

Complex	$E^{\ddagger}_{n(eff)}$ of M in Lewis acids	$E^{\ddagger}_{m(eff)}$	$\Delta E^{\ddagger}_{nm}$	CFSE	Matching constant
$Fe(C_5H_4HgSeCN)_2Ni(NCS)_2(nia)_2$	−2.29	13.86	11.57	6.39	17.96
$Fe(C_5H_4HgSeCN)_2Ni(NCS)_2(bpy)$	−2.29	24.08	19.14	6.42	25.56
$Fe(C_5H_4HgSeCN)_2Co(NCS)_2(nia)_2$	−2.85	13.86	11.01	4.22	15.23
$Fe(C_5H_4HgSeCN)_2Co(NCS)_2(bpy)$	−2.85	24.08	18.38	4.29	22.67
$Fe(C_5H_4HgSeCN)_2Zn(NCS)_2(nia)_2$	−4.13	13.86	9.73	—	9.73
$Fe(C_5H_4HgSeCN)_2Zn(NCS)_2(bpy)$	−4.13	24.08	15.82	—	15.82

bipyridyl forms more stable M–L bond than nicotinamide agreeing with the established fact. $\Delta E^{\ddagger}_{\mathrm{nm(eff)}}$ values are highest when M=Ni(II) and lowest when M=Zn(II). The sequence with other M is as follows:

$$\text{Nickel} > \text{Cobalt} > \text{Zinc}.$$

On changing organomercury thiocyanate part of the Lewis acid with organomercury selenocyanate, the M becomes slightly more soft and accordingly $\Delta E^{\ddagger}_{\mathrm{nm}}$ values also become lower. Thus the complexes of FBMT are more stable than those of FBMS.

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