Volume 17
Number 1
January 1978

Inorganic Chemistry

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Synthesis and Structural Studies of Bimetallic Dithiocyanate Diselenocyanate and Related Complexes

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Received December 13, 1976

>M(NCS)(NCSe)M′(SeCN)(SCN)< [M = Co(II), Ni(II); M′ = Hg(II), Cd(II), Zn(II)] have been synthesized and studied by elemental analysis, magnetic moment, and electronic and infrared spectral measurements. These studies indicate that the structure of these compounds is basically similar to >M(NCS)$_2$M′(SCN)$_2$< and >M(NCSe)$_2$M′(SeCN)$_2$<; however, their properties are intermediate to these two compounds. On reaction with pyridine, polymeric bridged complexes of the type >(py)$_2$M(NCS)(NCSe)M′(SeCN)(SCN)< are formed when M = Co(II) or Ni(II) and M′ = Hg(II) and cationic–anionic type complexes are formed when M = Co(II) or Ni(II) and M′ = Cd(II) or Zn(II). With 2,2′-bipyridine, monomeric bridged complexes are formed when M′ = Hg(II), and cationic–anionic complexes are formed when M′ = Cd(II) or Zn(II). All the complexes of triphenylphosphine are monomeric bridged. The total softness values of (M–N$_4$) and (M′–X$_4$) units (X = S, Se) for different M and M′ in >M(NCS)$_2$M′(SCN)$_2$<, >M(NCSe)$_2$M′(SeCN)$_2$<, and >M(NCS)(NCSe)-M′(SeCN)(SCN)< have been calculated, viz., in the case of >M(NCS)(NCSe)M′(SeCN)(SCN)<: E^*(M–N$_4$) = E_n^*(M) + 2E_m^*(NCS) + 2E_m^*(NCSe) and E^*(M′–X$_4$) = E_n^*(M′) + 2E_m^*(SCN) + 2E_m^*(SeCN), where E_n^*(M) is the softness value of metal ion and E_m^* is the softness value of anion. The difference of total softness of the (M–N$_4$) and (M′–X$_4$) unit has been derived and designated by Δ[(M′–X$_4$) – (M–N$_4$)]. On relating Δ[(M′–X$_4$) – (M–N$_4$)] with the stability of the thio or selenocyanate bridge, we get the following order: >M(NCSe)$_2$M′(SeCN)$_2$< > >M(NCS)(NCSe)M′-(SeCN)(SCN)< > >M(NCS)$_2$M′(SCN)$_2$<.

Introduction

Recently >M(NCS)$_2$M′(SCN)$_2$< and >M(NCSe)$_2$M′-(SeCN)$_2$< [M = Co(II), Ni(II); M′ = Hg(II), Cd(II), Zn(II)] have been used as Lewis acids and their complexes with a number of Lewis bases have been synthesized and studied.[1–12] In this paper we report the synthesis and study of >M-(NCS)(NCSe)M′(SCN)(SeCN)< and their complexes.

Experimental Section

Material and Manipulations. All chemicals were of reagent grade and purified by known methods. Potassium selenocyanate was prepared and recrystallized by the method described elsewhere.[13]

Selenocyanates [M(NCSe)$_2$], M = Co(II) or Ni(II), were prepared by reacting 2 mmol of potassium selenocyanate with 1 mmol of the respective metal(II) nitrate in methanol. The residue KNO_3 was rejected, and, from the filtrate, selenocyanates were obtained by evaporating the solvent under vacuum. Thiocyanates [M′(SCN)$_2$], M′ = Hg(II), Cd(II), and Zn(II), were similarly prepared by reacting 2 mmol of potassium thiocyanate with 1 mmol of the respective metal(II) nitrate. In the case of Hg(SCN)$_2$ water was used in place of methanol.

All the thiocyanates and selenocyanates were dried for 24 h under vacuum before use.

Preparation of Lewis Acids, viz., >M(NCS)(NCSe)M′(SeCN)-(SCN)< [M = Co(II), Ni(II); M′ = Hg(II), Cd(II), Zn(II)]. >Co(NCS)(NCSe)Hg(SeCN)(SCN)< and >Ni(NCS)(NCSe)-Hg(SeCN)(SCN)< were prepared by stirring 1 mmol of thiocyanates and 1 mmol of selenocyanates in methanol for 6 h and filtering. The residue was washed with the solvent and dried under vacuum. The rest of the Lewis acids were similarly prepared but remained dissolved in the solvent. The solvent was evaporated under vacuum and the compound isolated. Finally the compounds were washed with ether and dried under vacuum over phosphorus pentoxide.

Preparation of Pyridine and 2,2′-Bipyridine Complexes viz., >(py)$_2$M(NCS)(NCSe)Hg(SeCN)(SCN)<, (bpy)$_2$M(NCS)-(NCSe)Hg(SeCN)(SCN), [M(py)$_6$][M″(NCS)$_2$(NCSe)$_2$], [M-(bpy)$_3$][M″(NCS)$_2$(NCSe)$_2$] (M = Co(II), Ni(II); M″ = Cd(II), Zn(II)). These complexes were prepared by stirring 1 mmol of Lewis acid and 6 mmol of pyridine or 3 mmol of 2,2′-bipyridine in ethanol for 6 h. The ligands were always kept in slight excess. The reaction mixtures were filtered and the complexes were obtained, which were washed with the solvent and dried under vacuum.

Preparation of Triphenylphosphine Complexes, viz., (Ph$_3$P)$_2$M-(NCS)(NCSe)M′(SeCN)(SCN) [M = Co(II), Ni(II); M′ = Hg(II), Cd(II), Zn(II)]. These complexes were similarly prepared, but the stirring time was 24 h.

Analysis of the Complexes. The complexes were analyzed for nitrogen by the Kjeldahl method. Selenium was estimated as selenium, nickel as nickel dimethylglyoxime, mercury as mercury sulfide and cobalt, cadmium and zinc as anthranilates. The analytical data, along with melting point and color of the complexes are presented in Table I.[14]

Physical Measurements. Infrared spectra in the range 4000–400 cm^{-1} were recorded using a Perkin–Elmer Model 521 spectrophotometer. Electronic spectra as methanol solution or as mulled solids were recorded on a Carl Zeiss DMR–21 spectrophotometer between 1800 and 300 mμ. Molar conductance values were determined in methanol, acetone, or dimethylformamide using a Philips conductivity bridge Model PR 9500. The magnetic susceptibility measurements were made at room temperature by the Gouy method using cobalt mercury tetrathiocyanate as standard. The diamagnetic corrections were also made by using Pascal's constants.

Results and Discussion

All the complexes are insoluble in solvents suitable for molecular weight determination and hence their molecular weight could not be determined. We could not obtain single crystals for x-ray analysis. Hence, the studies of these complexes have been confined to electronic spectral, magnetic moment, infrared spectral, and conductance measurements. On the basis of the results of these studies the complexes have been divided into four groups.

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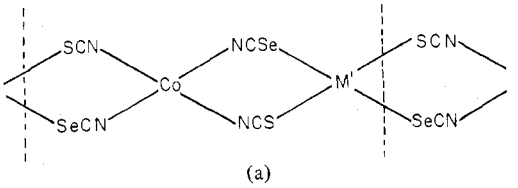
Table II

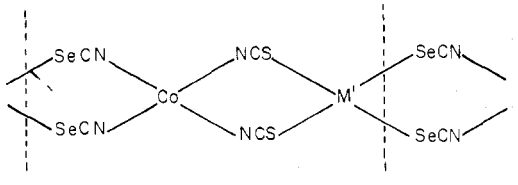
Compd	γ(C–N)	γ(C–X)	δ(NCX)	Ref
>Co(NCS)$_2$Hg(SCN)$_2$<	2142, 2130	790	465, 442	1, 2
>Co(NCSe)$_2$Hg(SeCN)$_2$<	2146, 2135	639	417, 403	8, 10, 15
>Co(NCS)(NCSe)Hg(SeCN)(SCN)<	2145, 2137	780, 640	473, 457 420, 410	

(1) Lewis Acids, e.g., >M(NCS)(NCSe)M′(SeCN)(SCN)< [M = Co(II), Ni(II); M′ = Hg(II), Cd(II), Zn(II)]. The positions of IR spectral bands in the region of C–N stretch, C–S stretch, and C–Se stretch and δ(NCS) and δ(NCSe) in >Co(NCS)(NCSe)Hg(SeCN)(SCN)< are basically similar to >Co(NCS)$_2$Hg(SCN)$_2$< and >Co(NCSe)$_2$Hg(SeCN)$_2$< (Table II) except in the number of bands in γ(C–X) and δ(NCX) regions (X = S, Se).

This difference in number of bands is probably due to the difference in symmetry species and point group of >Co(NCS)(NCSe)Hg(SeCN)(SCN)< with corresponding tetrathiocyanate and selenocyanate. In >Co(NCS)$_2$Hg(SCN)$_2$< and >Co(NCSe)$_2$Hg(SeCN)$_2$< the symmetry species combination for the stretching frequencies, viz., γ(C–N) and γ(C–X), is $2A_1 + B_1 + B_2$ whereas in >Co(NCS)(NCSe)Hg(SeCN)(SCN)< it is 2A. In >Co(NCS)$_2$Hg(SCN)$_2$< and >Co(NCSe)$_2$Hg(SeCN)$_2$< the cobalt is surrounded by four nitrogen atoms of thiocyanates and selenocyanates, respectively. Similarly, the mercury is surrounded by either four –S– of thiocyanates or four –Se– of selenocyanates. As a result of the surrounding symmetry both the atoms possess T_d point groups. In >Co(NCS)(NCSe)Hg(SeCN)(SCN)< the cobalt is surrounded by two –N– ends of thiocyanates and two of selenocyanates and similarly mercury is surrounded by two –Se– and two –S–, hence each of them belongs to C_{2v} point groups. It is on this account that increased number of bands are observed. These bands are due to γ(C–N) (NCS), γ(C–N) (NCSe), γ(C–S), γ(C–Se), δ(NCS), and δ(NCSe). All of them possess symmetry species 2A. It should, however, be noted that the whole molecule of the Lewis acid will belong to C_1 point group. This observation indicates that cobalt is surrounded by two NCS and two NCSe groups and similarly mercury by two SCN and two SeCN groups. The complex has therefore the possibility of having either of the two or a mixture of the two structures proposed in structure I (a and b).



(a)



(b)

I, M′ = Hg(II), Cd(II), Zn(II)

We can propose more structures to these complexes by interchanging the positions of Co and M′ or by changing the site of N, S, and Se bonding. But all such structures have not been considered because the available data and the reported literature[3–5,11,12] favor one out of the two structures proposed in structure I (a and b).

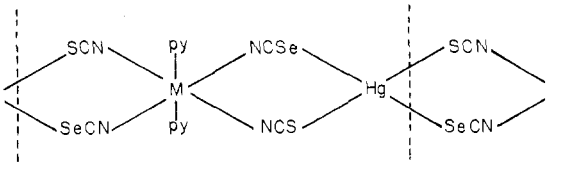
Similar to >Co(NCS)$_2$Hg(SCN)$_2$< and >Ni(NCS)$_2$Hg(SCN)$_2$< the electronic spectral band positions and magnetic moments are indicative of the presence of cobalt and nickel in tetrahedral and tetragonal (six-coordinated) configuration in >Co(NCS)(NCSe)Hg(SeCN)(SCN)< and >Ni(NCS)(NCSe)Hg(SeCN)(SCN)<, respectively.[8,15–18] However, the *Dq* and magnetic moment of >Co(NCS)(NCSe)Hg(SeCN)(SCN)< as presented in Table III have intermediate values, which also indicates that cobalt is in the surrounding of two NCS and two NCSe groups as shown in structure I (a and b).

Table III

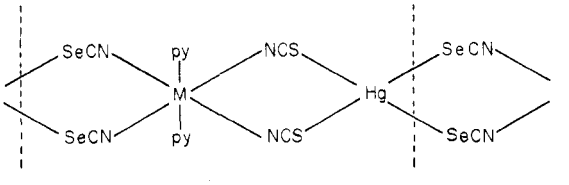
Complexes	*Dq*, cm^{-1}	μ_{eff}, μ_B	Ref
>Co(NCS)$_2$Hg(SCN)$_2$<	488	4.33	8, 17
>Co(NCSe)$_2$Hg(SeCN)$_2$<	498	4.36	8, 15
>Co(NCS)(NCSe)Hg(SeCN)(SCN)<	493	4.34	

(2) Polymeric Bridged Complexes, e.g., >(py)$_2$M(NCS)(NCSe)Hg(SeCN)(SCN)< [M = Co(II), Ni(II)]. On reaction with pyridine the blue Lewis acid >Co(NCS)(NCSe)Hg(SeCN)(SCN)< changes to pink and a solid complex is isolated. This shows that the pyridine has linked to cobalt and its geometry has changed from tetrahedral to octahedral. This coordination geometry of cobalt is also established by electronic spectra and magnetic moments. Similarly the electronic spectra and magnetic moments of nickel also support octahedral coordination geometry for nickel in its complexes. Since cobalt and nickel have almost similar softness, it can be presumed that pyridine has linked to nickel.

The γ(C–N), γ(C–X), and δ(NCX) bands (Table IV)[14] of the complexes and that of the Lewis acids are almost at the same positions. This indicates that possibly these complexes have polymeric structure, II (a and b), similar to their parent



(a)



(b)

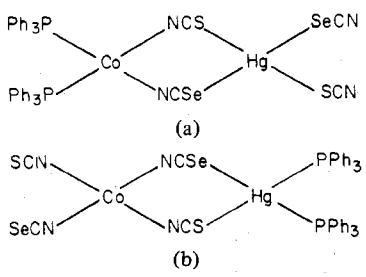
II

Lewis acids, except that cobalt and nickel acquire octahedral geometry, by way of coordination to ligands. These two structures show geometrical isomerism. One cannot say definitely whether the complexes are one form of the isomers or a mixture of the two isomers because we have not been able to separate the two.

All these complexes belong to a C_1 point group like the Lewis acids and have a similar number of bands in γ(C–N), γ(C–X), and δ(NCX) regions. Details of symmetry species of these bands are also presented in Table IV. The characteristic pyridine bands at 1602 (s), 1591 (m), 1218 (s), 1151 (s), 1070 (s), 1042 (s), and 1017 (s) cm^{-1} show features of coordination.[19,20]

(3) Monomeric Bridged Complexes, e.g., $(Ph_3P)_2M(NCS)(NCSe)M'(SeCN)(SCN)$ and $(bpy)_2M(NCS)(NCSe)Hg(SeCN)(SCN)$ [M = Co(II), Ni(II); M′ = Hg(II), Cd(II), Zn(II); and Ph_3P = Triphenylphosphine, bpy = 2,2′-Bipyridine]. The molar conductance values in *N,N′*-dimethylformamide show that these complexes are nonconducting in nature.[21] The color, magnetic moments, and electronic spectra reveal that cobalt is in tetrahedral and nickel is in octahedral coordination geometry in their triphenylphosphine complexes. The octahedral geometry by nickel is perhaps achieved by coordination of thiocyanate ions in adjacent layers in solid state. In bipyridine complexes, both cobalt and nickel acquire octahedral geometry by coordination to two molecules of bpy. All these complexes show the presence of one or two bands in the S– or Se–bonded region and two in the bridging C–N range. The former bands are at about 2090 cm^{-1} and the latter at 2180 cm^{-1}. Similarly, the number of bands in the δ(NCS), δ(NCSe), γ(C–S), and γ(C–Se) region also support the presence of both bridging and terminal thio- and selenocyanates. The bands in the range 510–770 cm^{-1} have not been assigned with certainty as ligand bands also appear in this region.[22] On the basis of the above results we can propose a monomeric bridged structure to these complexes.

The characteristic X-sensitive q, r, t, and y (Whiffin's bands) of triphenylphosphine are shifted to higher frequencies which indicate that the ligand is coordinated.[23,24] Triphenylphosphine has equal chances to link either to cobalt or to mercury in >Co(NCS)(NCSe)Hg(SeCN)(SCN)<; hence two different structures, III (a and b), are possible.



III

Structures on the basis of Ib can also be proposed. It is our practical observation that whenever cobalt acquires four-coordination geometry by linkage to triphenylphosphine, it does not further react with pyridine or any other such base. In order to establish one out of the two structures we have taken the help of this observation and have reacted the triphenylphosphine complex with pyridine. Since, there is no reaction we believe that triphenylphosphine is linked to cobalt. Had triphenylphosphine been linked to mercury the pyridine would have attached at the cobalt and the green complex should have changed to a pink complex of the type shown in eq i.

$$(SeCN)(SCN)Co(NCS)(NCSe)Hg(PPh_3)_2 + 2py \rightarrow (py)_2(SeCN)(SCN)Co(NCS)(NCSe)Hg(PPh_3)_2 \quad \text{(i)}$$

$$(Ph_3P)_2Co(NCS)(NCSe)Hg(SeCN)(SCN) + 2py \rightarrow \text{no reaction} \quad \text{(ii)}$$

The reported literature[23] and presence of Co–P and Ni–P bands at 160 and at 235 cm^{-1} in the far-IR region also indicate the linkage of triphenylphosphine to cobalt or nickel.

Assuming C_1 point group for the proposed structures, the number of normal modes for γ(C–N), γ(C–S), γ(C–Se), δ(NCS), and δ(NCSe) have been calculated. The calculated and observed number of bands (Table IV)[14] in these regions are in good agreement. This also supports the proposed structure, i.e., $(Ph_3P)_2M(NCS)(NCSe)M'(SeCN)(SCN)$.

(4) Cationic–Anionic Complexes, e.g., $[M(py)_6][M''(NCS)_2(SeCN)_2]$ and $[M(bpy)_3][M''(NCS)_2(SeCN)_2]$ (M = Co(II), Ni(II); M″ = Cd(II), Zn(II)). The molar conductance values of these complexes in methanol, acetone, and dimethylformamide are equivalent to a 1:1 electrolyte. The color, magnetic moments, and electronic spectra indicate that cobalt and nickel are in octahedral coordination geometry. The ligands which show features of coordination through their ring nitrogens are believed to be linked to cobalt because the tetrahedral nature of cobalt changes to octahedral on reaction with the ligands. The possible cation will therefore be $[Co(py)_6]^{2+}$ or $[Co(bpy)_3]^{2+}$. Similarly in the case of nickel complexes the cation will be $[Ni(py)_6]^{2+}$ or $[Ni(bpy)_3]^{2+}$. The positions of infrared bands assigned to γ(C–N), γ(C–S), γ(C–Se), δ(NCS), and δ(NCSe) (Table IV)[14] indicate the presence of terminal thio- and selenocyanates, which may be N bonded, S bonded, or Se bonded. Hence, the anion will be $[M''(NCSe)_2(NCS)_2]^{2-}$ or $[M''(SeCN)_2(NCS)_2]^{2-}$ or $[M''(NCSe)_2(SCN)_2]^{2-}$ or $[M''(SeCN)_2(SCN)_2]^{2-}$.

Assuming a C_{2v} point group for the tetrahedral anions, we have calculated the number of normal modes. The observed number of bands are in good agreement with the calculated number of modes. This also favors either of the proposed structures.

Electronic Spectral Discussion. To confirm the proposed coordination geometry of cobalt and nickel, we have recorded electronic spectra and magnetic moment values of all the complexes, the results of which are included in Table V.

In the case of pink complexes of cobalt, bands are observed in the region 9400–9900, 17 900–18 500, and 20 700–21 700 cm^{-1}, which are assigned to transitions $^4T_{2g} \leftarrow {}^4T_{1g}(\nu_1)$, $^4A_{2g} \leftarrow {}^4T_{1g}(\nu_2)$, and $^4T_{1g}(P) \leftarrow {}^4T_{1g}(\nu_3)$, respectively. The ν_1 is generally broad and ν_3 is a multiple which may be due to the mixing of a spin-forbidden transition. The ν_2 band is very weak. Similarly, in all nickel complexes bands are observed in the regions 9900–11 000, 16 000–17 200, and 26 300–28 100 cm^{-1}, which are assigned to transitions $^3T_{2g} \leftarrow {}^3A_{2g}(\nu_1)$, $^3T_{1g} \leftarrow {}^3A_{2g}(\nu_2)$, and $^3T_{1g}(P) \leftarrow {}^3A_{2g}(\nu_3)$, respectively.

We have calculated Dq, B', and β values of nickel(II) complexes with the help of matrices of Tanabe and Sugano,[25] using the values of ν_2 and ν_3. The electronic spectral band positions, spectral parameters, and magnetic moments very clearly indicate that all nickel complexes and the pink complexes of cobalt(II) have octahedral coordination geometry.[26]

In all blue complexes of cobalt two intense bands assigned to transitions $^4T_1(P) \leftarrow {}^4A_2(\nu_3)$ and $^4T_1(F) \leftarrow {}^4A_2(\nu_2)$ are observed in the regions 16 500–17 500 and 7800–8500 cm^{-1}, respectively. The ν_2 band splits into triplets which are characteristic of cobalt(II) in tetrahedral environment having C_{2v} symmetry.[27] With the help of the positions of ν_2 and ν_3 bands, the Dq, B', and β values have been calculated. Electronic spectral results, thus, support the structures that we have proposed for the complexes.

Calculation of Quantitative Values of Softness and Their Discussion. We have calculated the quantitative values of softness of metal ions and of –X– and –N– ends of NCX^- using the Klopman equation.[28] The results presented in Table VI indicate that Co^{2+}, Ni^{2+}, and Zn^{2+} have compatibility with nitrogen ends and Cd^{2+} and Hg^{2+} with sulfur or selenium ends. In >M(NCS)(NCSe)M′(SeCN)(SCN)< each M is linked to two N ends of NCS and two N ends of NCSe. The softness values of M and all the four N ends have been added, i.e., $E_n^{\ddagger}$ (M) + $2E_m^{\ddagger}$ (NCS) + $2E_m^{\ddagger}$ (NCSe). When M is cobalt(II) the total softness values of the $(M–N_4)$ unit will be

$$-0.22 + 2(-8.10) + 2(-8.93) = -34.28$$

Similarly, the total softness value of the $(Hg–S_2Se_2)$ unit will be

$$-4.87 + 2(-5.20) + 2(-4.41) = -24.09$$

Table V. Electronic Spectral Band Position and Their Assignments in cm^{-1}, Spectral Parameters, and Magnetic Moments

Complexes	γ_3	γ_2	γ_1	Dq	B'	β	μ_{eff}
	$^4T_{1g}(P) \leftarrow {}^4T_{1g}(F)$	$^4A_{2g} \leftarrow {}^4T_{1g}(F)$	$^4T_{2g}(F) \leftarrow {}^4T_{1g}(F)$				
$[Co(py)_6][Cd(SeCN)_2(NCS)_2]$	21 000	18 200	9 800	995	913	0.94	4.94
$[Co(py)_6][Zn(NCSe)_2(NCS)_2]$	21 700	18 500	9 900	1006	896	0.92	5.08
$[Co(bpy)_3][Cd(SeCN)_2(NCS)_2]$	21 300	17 900	9 600	990	930	0.96	5.17
$[Co(bpy)_3][Zn(NCSe)_2(NCS)_2]$	21 100	18 100	9 500	998	910	0.94	4.90
$(bpy)_2Co(NCS)(NCSe)Hg(SeCN)(SCN)$	20 800	18 000	9 600	989	894	0.92	5.20
$>(py)_2Co(NCS)(NCSe)Hg(SeCN)(SCN)<$	20 700	18 300	9 400	978	873	0.90	5.14
	$^4T_1(P) \leftarrow {}^4A_2$	$^4T_1(F) \leftarrow {}^4A_2$	$^4T_2(F) \leftarrow {}^4A_2$				
$>Co(NCS)(NCSe)Hg(SeCN)(SCN)<$	16 600	8 400	-	494	679	0.70	4.34
$>Co(NCS)(NCSe)Cd(SeCN)(SCN)<$	16 900	8 200	-	490	693	0.72	4.32
$>Co(NCS)(NCSe)Zn(SeCN)(SCN)<$	16 800	8 000	-	473	707	0.73	4.36
$(Ph_3P)_2Co(NCS)(NCSe)Hg(SeCN)(SCN)$	17 000	8 500	-	498	704	0.73	4.44
$(Ph_3P)_2Co(NCS)(NCSe)Cd(SeCN)(SCN)$	16 700	7 900	-	467	706	0.73	4.42
$(Ph_3P)_2Co(NCS)(NCSe)Zn(SeCN)(SCN)$	16 500	7 800	-	461	698	0.72	4.38
	$^3T_{1g}(P) \leftarrow {}^3A_{2g}$	$^3T_{1g}(F) \leftarrow {}^3A_{2g}$	$^3T_{2g}(F) \leftarrow {}^3A_{2g}$				
$[Ni(py)_6][Cd(SeCN)_2(NCS)_2]$	26 300	16 200	10 200	990	857	0.82	3.28
$[Ni(py)_6][Zn(NCSe)_2(NCS)_2]$	27 000	16 700	10 400	1041	835	0.80	3.22
$[Ni(bpy)_3][Cd(SeCN)_2(NCS)_2]$	27 300	16 500	10 100	1021	881	0.85	3.26
$[Ni(bpy)_3][Zn(NCSe)_2(NCS)_2]$	28 100	17 200	11 000	1075	873	0.84	3.24
$(bpy)_2Ni(NCS)(NCSe)Hg(SeCN)(SCN)$	27 800	16 900	10 100	1043	893	0.80	3.30
$(Ph_3P)_2Ni(NCS)(NCSe)Hg(SeCN)(SCN)$	26 000	16 400	10 300	1012	803	0.77	3.00
$(Ph_3P)_2Ni(NCS)(NCSe)Cd(SeCN)(SCN)$	27 700	16 800	10 400	1052	976	0.94	2.97
$(Ph_3P)_2Ni(NCS)(NCSe)Zn(SeCN)(SCN)$	29 000	17 200	10 500	1057	966	0.93	2.94
$>(py)_2Ni(NCS)(NCSe)Hg(SeCN)(SCN)<$	26 800	16 100	9 900	993	873	0.84	3.12
$>Ni(NCS)(NCSe)Hg(SeCN)(SCN)<$	27 600	17 100	10 400	1073	833	0.80	3.20
$>Ni(NCS)(NCSe)Cd(SeCN)(SCN)<$	28 200	17 000	10 300	1021	971	0.93	3.16
$>Ni(NCS)(NCSe)Zn(SeCN)(SCN)<$	28 600	17 000	10 400	1043	954	0.91	3.14

Table VI

Metal ions	$E_n^{\ddagger}$	Anion	$E_m^{\ddagger}$
Ni^{2+}	−0.52	$N(-NCSe^-)$	−8.93
Co^{2+}	−0.22	$N(-NCS^-)$	−8.10
Zn^{2+}	−1.24	$S(-SCN^-)$	−5.20
Cd^{2+}	−2.26	$Se(-SeCN^-)$	−4.41
Hg^{2+}	−4.87		

Adopting this procedure the total softness values of M and M′ have been calculated in $>M(NCS)_2M'(SCN)_2<$, $>M(NCSe)_2M'(SeCN)_2<$, and $>M(NCS)(NCSe)M'(SeCN)(SCN)<$, and the results are presented in Table VII. The difference of total softness of M and M′ has also been derived and designated by $\Delta[(M'-X_4) - (M-N_4)]$. This value is highest in the case of $>M(NCSe)_2M'(SeCN)_2<$ and lowest in the case of $>M(NCS)_2M'(SCN)_2<$. If we relate $\Delta[(M'-X_4) - (M-N_4)]$ values with the stability of the thio- or selenocyanate bridge, we get the following order: $>M(NCSe)_2M'(SeCN)_2< > >M(NCS)(NCSe)M'(SeCN)(SCN)< > >M(NCS)_2M'(SCN)_2<$.

This order of stability of the bridge is consistent with their reaction with pyridine. The selenocyanate bridge in $>Co(NCSe)_2Cd(SeCN)_2<$ and $>Ni(NCSe)_2Cd(SeCN)_2<$ is not ruptured on reaction with pyridine, and monomeric bridged types of complexes are formed, whereas in the case of $>M(NCS)_2Cd(SCN)_2<$ and $>M(NCS)(NCSe)Cd(SeCN)(SCN)<$ the bridges are ruptured and cationic–anionic types of complexes are formed. The maximum stability of $>M(NCSe)_2M'(SeCN)_2<$ is further established when reacted with bipyridine; $>Co(NCSe)_2Hg(SeCN)_2<$, $>Ni(NCSe)_2Hg$-

Table VII

Complexes	$E_n^{\ddagger} + E_m^{\ddagger}$ (M-N_4)	$E_n^{\ddagger} + E_m^{\ddagger}$ (M′-X_4)	$\Delta[(M'-X_4) - (M-N_4)]$	Nature of complexes[a] Pyridine	2,2′-Bipyridine	Triphenylphosphine
$>Co(NCSe)_2Hg(SeCN)_2<$	−35.94	−22.51	13.43	P.B.	M.B.	M.B.
$>Co(NCS)(NCSe)Hg(SeCN)(SCN)<$	−34.28	−24.09	10.19	P.B.	M.B.	M.B.
$>Co(NCS)_2Hg(SCN)_2<$	−32.62	−25.67	6.95	P.B.	C.A.	M.B.
$>Ni(NCSe)_2Hg(SeCN)_2<$	−36.24	−22.51	13.73	P.B.	M.B.	M.B.
$>Ni(NCS)(NCSe)Hg(SeCN)(SCN)<$	−34.58	−24.09	10.49	P.B.	M.B.	M.B.
$>Ni(NCS)_2Hg(SCN)_2<$	−32.92	−25.67	7.25	P.B.	C.A.	M.B.
$>Co(NCSe)_2Cd(SeCN)_2<$	−35.94	−19.90	16.04	M.B.	M.B.	M.B.
$>Co(NCS)(NCSe)Cd(SeCN)(SCN)<$	−34.28	−21.48	12.80	C.A.	C.A.	M.B.
$>Co(NCS)_2Cd(SCN)_2<$	−32.62	−23.06	9.56	C.A.	C.A.	M.B.
$>Ni(NCSe)_2Cd(SeCN)_2<$	−36.24	−19.90	16.34	M.B.	M.B.	M.B.
$>Ni(NCS)(NCSe)Cd(SeCN)(SCN)<$	−34.58	−21.48	13.10	C.A.	C.A.	M.B.
$>Ni(NCS)_2Cd(SCN)_2<$	−32.92	−23.06	9.86	C.A.	C.A.	M.B.
$>Co(NCSe)_2Zn(SeCN)_2<$	−35.94	−18.88	17.06	C.A.	C.A.	M.B.
$>Co(NCS)(NCSe)Zn(SeCN)(SCN)<$	−34.28	−20.46	13.82	C.A.	C.A.	M.B.
$>Co(NCS)_2Zn(SCN)_2<$	−32.62	−22.04	10.58	C.A.	C.A.	M.B.
$>Ni(NCSe)_2Zn(SeCN)_2<$	−36.24	−18.88	17.36	C.A.	C.A.	M.B.
$>Ni(NCS)(NCSe)Zn(SeCN)(SCN)<$	−34.58	−20.46	14.12	C.A.	C.A.	M.B.
$>Ni(NCS)_2Zn(SCN)_2<$	−32.92	−22.04	10.88	C.A.	C.A.	C.A.

[a] Key: P.B. = polymeric bridged, M.B. = monomeric bridged, C.A. = cationic-anionic.

$(SeCN)_2<$, and $>Co(NCSe)_2Cd(SeCN)_2<$ retain a selenocyanate bridge on reaction with bpy, whereas in the thiocyanate analogues they are always ruptured and cationic–anionic types of complexes are formed. $>M(NCS)(NCSe)Hg(SeCN)(SCN)<$ show intermediate behavior and monomeric bridged complexes are formed. The relation of $\Delta[(M'-X_4) - (M-N_4)]$ with the nature of the complexes is presented in Table VII.

It should, however, be noted that stability of the thio- and selenocyanate bridge also depends upon the nature of ligands, besides depending upon $\Delta[(M'-X_4) - (M-N_4)]$.[5,12,29] The complexes of triphenylphosphine are always monomeric bridged,[23,30,31] whereas pyridine forms all three types of complexes, i.e., polymeric bridged, monomeric bridged, and cationic–anionic, and 2,2′-bipyridine forms mostly the cationic–anionic type of complexes and occasionally monomeric bridged complexes. The ligands having weak base strength are unable to rupture the thiocyanate or selenocyanate bridge[5,12,29] and those having strong base strength mostly rupture the bridge.[4,11]

Comparison of the Complexes of $>M(NCS)(NCSe)M'(SeCN)(SCN)<$, $>M(NCS)_2M'(SCN)_2<$, and $>M(NCSe)_2M'(SeCN)_2<$. (1) The 2,2′-bipyridine and pyridine complexes of (i) $>M(NCSe)_2Cd(SeCN)_2<$ are monomeric bridged in which the Se end of selenocyanates is linked with cadmium.[11] (ii) $>M(NCS)_2Cd(SCN)_2<$ are cationic–anionic in which thiocyanate is N bonded with cadmium.[4] (iii) $>M(NCS)(NCSe)Cd(SeCN)(SCN)<$ are also cationic–anionic, where the cation is $[M(bpy)_3]^{2+}$ or $[M(py)_6]^{2+}$ and anion is $[Cd(SeCN)_2(NCS)_2]^{2-}$ or $[Cd(NCSe)_2(SCN)_2]^{2-}$. This indicates that the bridge in $>M(NCS)(NCSe)Cd(SeCN)(SCN)<$ is weaker as compared to $>M(NCSe)_2Cd(SeCN)_2<$.

(2) The 2,2′-bipyridine complexes of (i) $>M(NCSe)_2Hg(SeCN)_2<$ are monomeric bridged. (ii) $>M(NCS)_2Hg(SCN)_2<$ are cationic–anionic, and (iii) $>M(NCS)(NCSe)Hg(SeCN)(SCN)<$ are also monomeric bridged. (3) Nickel(II) acquires an octahedral geometry in its triphenylphosphine complexes of $>Ni(NCS)(NCSe)M'(SeCN)(SCN)<$ and square-planar configurations in the corresponding complexes of tetrathiocyanates and tetraselenocyanates in solid state.

Acknowledgment. Authors gratefully acknowledge the financial support from CSIR, New Delhi, and thank the RSIC, IIT, Madras, for providing instrumentation facilities.

Registry No. $[Co(py)_6][Cd(SeCN)_2(NCS)_2]$, 64200-53-9; $[Cd(py)_6][Zn(NCSe)_2(NCS)_2]$, 64200-71-1; $[Co(bpy)_3][Cd(SeCN)_2(NCS)_2]$, 64200-70-0; $[Co(bpy)_3][Zn(NCSe)_2(NCS)_2]$, 64200-69-7; $(bpy)_2Co(NCS)(NCSe)Hg(SeCN)(SCN)$, 64200-68-6; $>(py)_2Co(NCS)(NCSe)Hg(SeCN)(SCN)<$, 64294-64-0; $>Co(NCS)(NCSe)Hg(SeCN)(SCN)<$, 64294-59-3; $>Co(NCS)(NCSe)Cd(SeCN)(SCN)<$, 64294-57-1; $>Co(NCS)(NCSe)Zn(SeCN)(SCN)<$, 64294-58-2; $(Ph_3P)_2Co(NCS)(NCSe)Hg(SeCN)(SCN)$, 64200-67-5; $(Ph_3P)_2Co(NCS)(NCSe)Cd(SeCN)(SCN)$, 64200-66-4; $(Ph_3P)_2Co(NCS)(NCSe)Zn(SeCN)(SCN)$, 64200-65-3; $[Ni(py)_6][Cd(SeCN)_2(NCS)_2]$, 64200-64-2; $[Ni(py)_6][Zn(NCSe)_2(NCS)_2]$, 64200-63-1; $[Ni(bpy)_3][Cd(SeCN)_2(NCS)_2]$, 64200-62-0; $[Ni(bpy)_3][Zn(NCSe)_2(NCS)_2]$, 64200-61-9; $(bpy)_2Ni(NCS)(NCSe)Hg(SeCN)(SCN)$, 64200-59-5; $(Ph_3P)_2Ni(NCS)(NCSe)Hg(SeCN)(SCN)$, 64200-58-4; $(Ph_3P)_2Ni(NCS)(NCSe)Cd(SeCN)(SCN)$, 64200-57-3; $(Ph_3P)_2Ni(NCS)(NCSe)Zn(SeCN)(SCN)$, 64200-56-2; $>(py)_2Ni(NCS)(NCSe)Hg(SeCN)(SCN)<$, 64294-65-1; $>Ni(NCS)(NCSe)Hg(SeCN)(SCN)<$, 39292-29-0; $>Ni(NCS)(NCSe)Cd(SeCN)(SCN)<$, 64294-56-0; $>Ni(NCS)(NCSe)Zn(SeCN)(SCN)<$, 64294-63-9; $Co(NCSe)_2$, 64188-71-2; $Ni(NCSe)_2$, 64188-70-1; $Hg(SCN)_2$, 592-85-8; $Cd(SCN)_2$, 865-38-3; $Zn(SCN)_2$, 557-42-6; $>Co(NCSe)_2Hg(SeCN)_2<$, 60646-76-6; $>Co(NCS)_2Hg(SCN)_2<$, 12072-82-1; $>Ni(NCSe)_2Hg(SeCN)_2<$, 64567-39-1; $>Ni(NCS)_2Hg(SCN)_2<$, 64294-60-6; $>Co(NCSe)_2Cd(SeCN)_2<$, 64294-52-6; $>Co(NCS)_2Cd(SCN)_2<$, 12543-83-8; $>Ni(NCSe)_2Cd(SeCN)_2<$, 64294-53-7; $>Ni(NCS)_2Cd(SCN)_2<$, 12543-85-0; $>Co(NCSe)_2Zn(SeCN)_2<$, 64294-55-9; $>Co(NCS)_2Zn(SCN)_2<$, 64294-54-8; $>Ni(NCSe)_2Zn(SeCN)_2<$, 64294-62-8; $>Ni(NCS)_2Zn(SCN)_2<$, 64294-61-7; pyridine, 110-86-1; 2,2′-bipyridine, 37275-48-2; triphenylphosphine, 603-35-0.

Supplementary Material Available: A listing of analytical data and molar conductance values (Table I) and infrared spectral assignments (Table II) (4 pages). Ordering information is given on any current masthead page.

References and Notes

(1) A. Tramer, *J. Chim. Phys.*, **59**, 232 (1962).
(2) R. A. Bailey, S. L. Kozak, T. W. Michelsen, and W. N. Mills, *Coord. Chem. Rev.*, **6**, 407 (1971).
(3) R. Makhija, L. Pazdernik, and R. Rivest, *Can. J. Chem.*, **51**, 438, 2987 (1973).
(4) P. P. Singh, U. P. Shukla, R. Makhija, and R. Rivest, *J. Inorg. Nucl. Chem.*, **37**, 679 (1975).
(5) P. P. Singh and S. A. Khan, *Inorg. Chim. Acta*, **14**, 143 (1975).
(6) P. P. Singh and J. N. Seth, *Inorg. Chim. Acta*, **15**, 227 (1975).
(7) A. Turco and C. Pecile, *Nature (London)*, **196**, 66 (1961).
(8) A. Turco, C. Pecile, and M.Nicolini, *J. Chem. Soc.*, 3008 (1962).
(9) Yu. Ya. Kharitonov and G. V. Tsintsadze, *Zh. Neorg. Khim.*, **10**, 1191 (1965); *Russ. J. Inorg. Chem.*, **10**, 645 (1965).
(10) Yu. Ya. Kharitonov and V. V. Skopenko, *Zh. Neorg. Khim.*, **10**, 1803 (1965); *Russ. J. Inorg. Chem.*, **10**, 984 (1965).
(11) P. P. Singh, A. K. Srivastava, and R. Rivest, *J. Inorg. Nucl. Chem.*, **38**, 439 (1976).
(12) P. P. Singh and S. B. Sharma, *J. Coord. Chem.*, **6**, 65 (1976).
(13) G. R. Waitkins and R. Shutt, "Inorganic Synthesis", Vol. II, McGraw-Hill, New York, N.Y., 1946, p 186.
(14) Supplementary material.
(15) F. A. Cotton, D. M. L. Goodgame, M. Goodgame, and T. E. Haas, *Inorg. Chem.*, **1**, 565 (1962).
(16) D. Forster and D. M. L. Goodgame, *Inorg. Chem.*, **4**, 715 (1965).
(17) F. A. Cotton, D. M. L. Goodgame, M. Goodgame, and A. Sacco, *J. Am. Chem. Soc.*, **83**, 4157 (1961).
(18) D. Forster and D. M. L. Goodgame, *Inorg. Chem.*, **4**, 823 (1965).
(19) J. K. Wilmhurst and H. J. Bernstein, *Can. J. Chem.*, **35**, 1185 (1957).
(20) A. R. Katritzky, *Q. Rev. Chem. Soc.*, **4**, 353 (1959).
(21) K. H. Shaw and G. J. Sutton, *Aust. J. Chem.*, **22**, 1841 (1969).
(22) A. I. Brusilovets, V. V. Skopenko, and G. V. Tsintsadze, *Zh. Neorg. Khim.*, **14**, 467 (1967); *Russ. J. Inorg. Chem.*, **14**, 2 (1969).
(23) R. C. Makhija and R. Rivest, *Spectrochim. Acta. Part A*, **30A**, 977 (1974).
(24) G. B. Deacon and J. H. S. Green, *Chem. Ind. (London)*, 1031 (1965).
(25) Y. Tanabe and S. Sugano, *J. Phys. Soc. Jpn.*, **9**, 753 (1954).
(26) A. B. P. Lever, "Inorganic Electronic Spectroscopy", Elsevier, Amsterdam, 1968, Chapter 9.
(27) M. J. M. Champbell, D. W. Cardand, and G. Grzeskowiak, *Inorg. Nucl. Chem. Lett.*, **5**, 39 (1969).
(28) G. Klopman, *J. Am. Chem. Soc.*, **90**, 223 (1968).
(29) P. P. Singh, L. P. Pathak, and S. A. Khan, *J. Inorg. Nucl. Chem.*, **38**, 475 (1976).
(30) P. P. Singh, S. P. Yadav, and S. B. Sharma, *Aust. J. Chem.*, in press.
(31) P. P. Singh, S. A. Khan, and R. B. Pal, *Inorg. Nucl. Chem. Lett.*, **11**, 807 (1975).