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BIMETALLIC TETRATHIOCYANATES AND SELENOCYANATES AS LEWIS ACIDS

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CONTENTS

ABBREVIATIONS

bipy = 2,2-bipyridine
phen = 1, 10-phenanthroline
nia = nicotinamide
cpy = cyanopyridine
ent = ethylnicotinate
inh = isonicotinic acid hydrazide
bit = 4-benzylisothiazole
mit = 4-methylisothiazole
ist = isothiazole
dmt = 2,4-dimethyl thiazole
abt = 2-aminobenzothiazole
pza = pyrazine-2-carboxamide

tzt = thiazolidine-2-thione
thn = thiohydantoin
etu = ethylenethiourea
PPh_3 = triphenylphosphine
py = pyridine
en = ethylenediamine
trien = triethylenetetramine
dmu = dimethylurea
dmtu = dimethylthiourea
nit = 4-nitroisothiazole
pzd = pyrazine-2,3-dicarboxamide
eu = ethyleneurea
thf = tetrahydrofuran
diox = dioxane
anl and anil = aniline
EtOH = ethanol
MeOH = methanol
apy, amp and ampy = aminopyridine
tzd = thiazolidine-2-dione
pic = L-picoline
acet = acetone
dmf = *N,N*-dimethylformamide
dmso = dimethylsulphoxide
ampyd and ampn = aminopyrimidine

A. INTRODUCTION

Complexes of metal thiocyanates and selenocyanates have been the subject of interest, and different workers have studied their different aspects. Porai-Koshits and Tsintsadze [1] reviewed the structure of thiocyanate complexes, and also included some selenocyanate complexes. Burmeister [2,3] described the effect of a large number of ligands on the change of M—SCN bonding to M—NCS, and also reviewed linkage isomerism [4] which included thiocyanate ions. Norbury and Sinha [5] discussed in detail the problem associated with these effects. Balahura and Lewis [6] described the factors important in linkage isomerism, and gave a detailed account of these factors, which covered HSAB principle, steric, electronic, solvent and kinetic effects. In another review Burmeister [7] emphasised the factors which were bonding mode determinants for coordinated thiocyanate ions. He described physical methods, diffraction studies, infrared spectroscopy, Raman spectroscopy, electron spectroscopy, nuclear magnetic resonance spectroscopy and photoelectron spectroscopy (ESCA); useful for determining thiocyanate bonding modes. Norbury [8] compiled work on chalcogenocyanates of different metal ions and described the basic knowledge of chalcogenocyanate ions including their preparation, molecular geometry, molecular vibrations and spectroscopic studies etc. Bailey et al. [9] discussed the infrared spectra of bimetallic tetrathiocyanates and selenocyanates and described the effect of change of metal on the infrared active bands associated with the thiocyanate or selenocyanate ions. This review describes the Lewis-acid character of bimetallic tetrathiocyanate and selenocyanate of $CoHg(XCN)_4$ (X = S, Se) type, which have hitherto not been discussed in any of the reviews and are of recent origin.

The structure of $CoHg(SCN)_4$ has been crystallographically established by Jeffery [10,11]. The cobalt and mercury atoms are surrounded by four nitrogen and four sulphur atoms, respectively, in approximately tetrahedral arrangements, and the thiocyanate is bridged in between cobalt and mercury in the form of a polymeric chain. $NiHg(SCN)_4 \cdot 2\ H_2O$ is the only such compound where nickel is octahedral due to coordination with two molecules of water [12]. Forster and Goodgame [13—16] have been actively involved in infrared, magnetic and electronic spectral studies of bimetallic tetrathiocyanates.

The corresponding selenocyanates have also been studied, but comparatively less is reported in the literature. Complexes of simple selenocyanates were first reported by Nelson [17] and their bonding modes were discussed by Pecile and co-workers [18,19] and Burmeister and Janaki [20]. The crystal structure of $CoHg(SeCN)_4$ was reported by Turco and co-workers [21] who showed that selenocyanate ion is bridged between cobalt and mercury similar to its thiocyanate analog. Burmeister [22—24] et al. studied linkage isomerism in the complexes of various selenocyanates. Goodgame and co-workers [25,26] have described electronic spectral and magnetic properties of $[Co(NCSe)_4]^{2-}$.

Both bimetallic tetrathiocyanates and selenocyanates of general formula $MM'(XCN)_4$ M = Mn(II), Fe(II), Co(II), Ni(II), Cu(II); M' = Zn(II), Cd(II), Hg(II), Pd(II); X = S, Se can be used as Lewis acids because the coordination numbers of M and M' in $MM'(XCN)_4$ are four rather than their maximum of six. An attempt could therefore be made to raise their coordination numbers to six, by reacting them with Lewis bases. In other words they could behave as bi acceptors having two acceptor sites, one at M and the other at M'.

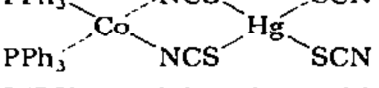
Rivest and co-workers [27] first reacted $CoHg(SCN)_4$ with Lewis bases and studied the products. They reported three types of complexes:

(i) Cationic—anionic

$[Co(LL)_3][Hg(SCN)_4]$

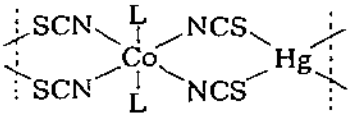
(LL = ethylenediamine, 2,2'-bipyridine, 1,10-phenanthroline)

(ii) Monomeric bridged



I (PPh_3 = triphenylphosphine)

(iii) Polymeric bridged

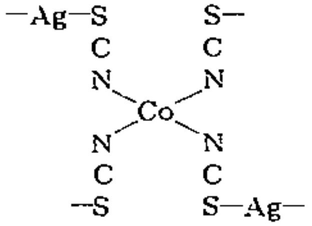


II (L = tetrahydrofuran, pyridine, aniline)

In the cationic—anionic type of complexes the thiocyanate bridge between M and M′ breaks and a cation and anion of general formula $[ML_6]^{2+}$ and $[M'(SCN)_4]^{2-}$ respectively, are formed. In the monomeric bridged type, which may also be called a dinuclear bridged complex, the polymeric chain of thiocyanate bridges is broken and only a dinuclear compound having a thiocyanate bridge is formed. In the polymeric bridged complexes the ligands are attached to cobalt, but the polymeric structure of the parent Lewis acid $CoHg(SCN)_4$ is retained.

Singh et al. extended the work to other bimetallic tetrathiocyanates, viz. $MM'(SCN)_4$ M = Mn(II), Fe(II), Co(II), Ni(II), Cu(II), Zn(II); M′ = Zn(II), Cd(II), Hg(II), Pd(II) and also studied the corresponding tetraselenocyanates [28—46]. They observed that the nature of these tetrathiocyanates or selenocyanates depends mainly upon the nature of M and M′ in $MM'(NCX)_4$ (X = S, Se), and also upon the base strength of the ligands. In the last five years much work has been completed on this new class of bi acceptor. This article describes the various studies that have been made in this field.

In $MM'(SCN)_4$, both M and M′ are in their preferred tetrahedral coordination geometry, and the compound is energetically quite stable. Formation of bimetallic compounds in which one metal prefers a tetrahedral geometry and the other a linear geometry e.g. Ag(I), has been reported by Tramer [47], and recently developed by us [48—52]. These compounds have been shown to have a zig-zag structure (III).

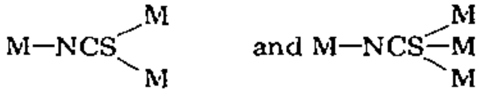


III

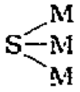
The Lewis-acid character of this class of bi acceptor, e.g. $Co[Ag(SCN)_2]_2$ has also been studied, as they are interestingly comparable with $MM'(SCN)_4$. We include coverage of such work here.

B. INFRARED SPECTRAL STUDIES

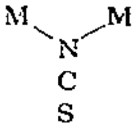
There are three ways in which a thiocyanate or selenocyanate ion can link to a metal ion; (a) through nitrogen, M—NCX (X = S, Se), (b) through sulphur or selenium, M—XCN and (c) through both nitrogen and X simultaneously, M—NCX—M′. Further bonding modes of thiocyanate ions have also recently been described. Gazo and co-workers [53,54] have shown by X-ray analysis that the sulphur donor of the thiocyanate ion can link to more than one metal ion (IV).


IV

On the basis of ^{13}C NMR, and infrared studies sulphur can coordinate to more than one metal ion at a time [55] (V).


V

The nitrogen end of the thiocyanate ion can also link to more than one metal ion [56] (VI).


VI

Infrared spectroscopy has been a versatile tool in distinguishing the type of bonding. Diagnosis of bonding is characterized by the number and position of C—N stretching, C—X stretching and NCX bending vibrations of NCX ion in the infrared spectra. Because of some overlap of certain of these ranges, other criteria such as the integrated intensities of the ν_{CN} modes should be employed [7]. These data are summarised in Table 1.

Far infrared spectra in the region 450—200 cm^{-1} can also indicate the type of bonding in thiocyanates or selenocyanates. The strong band at 280—300

TABLE 1

Diagnostic regions for various types of thiocyanate and selenocyanate bonding (cm^{-1}) [57—75]

Type of bonding	C—N(st)	C—X(st)	NCX(bend)	M—NCX(st)
Free NCS ion	2049—2066	746—748	471—484	—
N-bonded NCS	2040—2080	780—860	460—490	290—310
S-bonded NCS	2090—2110	690—720	410—440	210—230
—SCN bridged	2110—2175	790—795	—	—
Free NCSe ion	2071—2083	559	417	—
N-bonded NCSe	2040—2090	650—690	430—480	240—260
Se-bonded NCSe	2100—2120	520—580	400—425	180—195
—SeCN— bridged	2125—2190	635—640	—	—

TABLE 2

Infrared active thio or selenocyanate fundamental vibrations in different types of complexes

Complexes	Point group	ν_{CN}	ν_{CS}	ν_{CSe}	δ_{NCS}	δ_{NCSe}	ν_{M-NCX}	ν_{M-L}
Cationic—anionic								
$[ML_6]^{2+}$	O_h	—	—	—	—	—	—	T_{1u}
$[ML_4]^{2+}$	T_d	—	—	—	—	—	—	T_2
$[M'(NCS)_4]^{2-}$	T_d	T_2	T_2	—	T_2	—	T_2	—
$[M'(NCS)_2(NCSe)_2]^{2-}$	C_{2v}	$2A_1 + B_1 + B_2$	$A_1 + B_1$	$A_1 + B_2$	$A_1 + B_1$	$A_1 + B_2$	$2A_1 + B_1 + B_2$	—
Monomeric bridged								
$L_2M(NCS)_2M'(SCN)_2$	C_{2v}	$(A_1 + B_1)$[a]	$(A_1 + B_1)$[a]	—	$(A_1 + B_1)$[a]	—	$(A_1 + B_1)$[a]	$A_1 + B_2$
		$(A_1 + B_2)$[a]	$(A_1 + B_2)$[a]	—	$(A_1 + B_2)$[a]	—	$(A_1 + B_2)$[a]	
$L_2M(NCS)(NCSe)M'$-(SeCN)(SCN)	C_1	$(2A) + (2A)$[a]	$2A$		$2A$	$2A$	$2A + 2A$	$2A$
Polymeric bridged								
$>L_2M(NCS)_2M'(SCN)_2<$	C_{2v}	$2A_1 + B_1 + B_2$	$2A_1 + B_1 + B_2$	—	$2A_1 + B_1 + B_2$	—	$A_1 + B_1$	$A_1 + B_2$
$>L_2M(NCS)(NCSe)M'$-(SeCN)(SCN)$<$	C_1	$4A$	$2A$	$2A$	$2A$	$2A$	$2A + 2A$	$2A$

[a] Symmetry species in the two parentheses refer to the bridging and terminal NCX, respectively.

cm^{-1} was assigned to M—NCS, M = Mn(II), Fe(II), Co(II), Ni(II), Zn(II), Cu(II) in $[M(NCS)_4]^{2-}$ and at 200—230 cm^{-1} to M—SCN in $[M(SCN)_4]^{2-}$. In changing from T_d symmetry in $[M(NCS)_4]^{2-}$ to O_h in $[M(NCS)_6]^{4-}$ the band assigned to ν_{M-NCS} shows a negative shift and becomes weaker in intensity [16]. If both ν_{M-N} and ν_{M-S} are present a bridging thiocyanate certainly exists. In the case of selenocyanate complexes, these bands appear 30—40 cm^{-1} lower than the corresponding thiocyanate bands.

$MM'(SCN)_4$ forms three types of complexes and each of these can be distinguished on the basis of their infrared spectra. The number of characteristic

TABLE 3

Cationic—anionic complexes of $MM'(SCN)_4$ and their spectral data

(i) M in octahedral coordination geometry

The complexes of this series are $[Co(bipy)_3][Hg(SCN)_4]$ [27], $[Co(phen)_3][Hg(SCN)_4]$ [27], $[Co(phen)_3][Cd(SCN)_4 \cdot phen]$ [28], $[Co(bipy)_3][Cd(SCN)_4]$ [28], $[Co(nia)_6][Cd(NCS)_4]$ [29], $[Co(3\text{-}cpy)_6][Cd(NCS)_4]$ [29], $Co(3\text{-}cpy)_6][Cd(NCS)_4]$ [29], $Co(bipy)_3][Pd(SCN)_4]$ [35], $[Co(phen)_3][Pd(SCN)_4]$ [35], $[Co(3\text{-}cpy)_6][Zn(NCS)_4]$ [29], $[Co(4\text{-}cpy)_6][Zn(NCS)_4]$ [29], $[Co(nia)_6][Zn(NCS)_4]$ [29], $[Co(ent)_6][Zn(NCS)_4]$ [29], $[Co(inh)_6][Zn(NCS)_4]$ [29], $[Co(py)_6][Zn(NCS)_4]$ [28], $[Co(phen)_3][Zn(NCS)_4 \cdot phen]$ [28], $[Co(bipy)_3][Zn(NCS)_4]$ [28], $[Ni(bit)_6][Zn(NCS)_4]$ [45], $[Ni(mit)_6][Zn(NCS)_4]$ [45], $[Ni(nit)_6][Zn(NCS)_4]$ [45], $[Ni(ist)_6][Zn(NCS)_4]$ [25], $[Ni(dmt)_6][Zn(NCS)_4]$ [45], $[Ni(abt)_6][Zn(NCS)_4]$ [45], $[Ni(pza)_6][Zn(NCS)_4]$ [30], $[Ni(tzt)_6][Cd(SCN)_4]$ [46], $[Ni(thn)_6][Cd(SCN)_4]$ [46], $[Ni(etu)_6][Cd(SCN)_4]$ [46], $[Ni(phen)_3][Pd(SCN)_4]$ [35], $[Ni(bipy)_3][Pd(SCN)_4]$ [35], $[Cu(bipy)_3][Hg(SCN)_4]$ [99], $[Cu(phen)_3][Hg(SCN)_4]$ [99], $[Zn(bipy)_3][Pd(SCN)_4]$ [35], $[Ni(PPh_3)_4][Zn(NCS)_4]$ [34].

In all these complexes, one or two absorption bands are generally observed corresponding to CN stretching mode in the range 2020—2110 cm^{-1}, two bands due to CS stretching mode in the range 720—860 cm^{-1} and two bands due to NCS bending mode in the range 410—490 cm^{-1}. *Dq* values in case of cobalt complexes are in the range 880—990 cm^{-1}, and in case of nickel complexes the range is 1010—1200 cm^{-1}. The μ_{eff} values of cobalt complexes are around 5.00 B.M. and of nickel complexes around 3.00 B.M.

(ii) M in tetrahedral coordination geometry

These complexes are $[Co(etu)_4][Cd(SCN)_4]$ [46], $[Co(thn)_4][Cd(SCN)_3]$ [46], $[Co(tzt)_4][Cd(SCN)_4]$ [46], $[Co(amp)_2][Cd(NCS)_4]$ [30], $[Co(2\text{-}apy)_2][Zn(NCS)_4]$ [29], $[Co(ampy)_2][Zn(NCS)_4]$ [30], $[Cd(py)_4][Pd(SCN)_4]$ [35], $[Cd(bipy)_2][Pd(SCN)_4]$ [35], $[Pd(py)_4][Hg(SCN)_4]$ [35], $[Pd(bipy)_2][Hg(SCN)_4]$ [35].

In these complexes one or two bands appear in CN stretching region in the range 2040 cm^{-1}, two in CS stretching region in the range 740—860 cm^{-1} and two in NCS bending region in the range 440—480 cm^{-1}. *Dq* values of these complexes are in the range 400—500 cm^{-1}. The μ_{eff} values of cobalt complexes are in the range 4.00—4.60 B.M.

(iii) M in square planar coordination geometry

These complexes are $[Co(en)_2][Cd(SCN)_4(en)]$ [28], $[Co(trien)_2][Cd(NCS)_4]$ [28], $[Co(trien)_2][Zn(NCS)_4]$ [28].

In these complexes one band is observed in the range 2010—2050 cm^{-1} (CN stretching mode), two bands in the range 750—860 cm^{-1} (CS stretching mode) and two bands in the range 400—500 cm^{-1} (NCS bending mode). The μ_{eff} values of these complexes are in the range 2.00—2.80 B.M.

bands for each type of thiocyanate or selenocyanate bonding has been derived by group theoretical calculations and the results are shown in Table 2.

In cationic—anionic complexes, the cation has either T_d symmetry $[\mathrm{M(L)_4}]^{2+}$ or O_h symmetry $[\mathrm{M(L)_6}]^{2+}$ and the anion usually T_d symmetry $[\mathrm{M'(XCN)_4}]^{2-}$. In the case of monomeric and polymeric bridged complexes, the symmetry of the molecules is C_{2v}, however, the number of bands in each case differs. In some cases different symmetries have also been proposed [40].

In the case of cationic—anionic complexes, the thiocyanate ions are coordinated to M′ through sulphur and in case of selenocyanate through selenium, hence the M′—XCN bands are always in the region of X-bonded thiocyanate or selenocyanate. When M′ is Zn or Cd, the bonding is through nitrogen of thiocyanate. In the case of selenocyanates, the selenium is bonded to Cd and nitrogen to Zn. The numbers of bands in the ν_{CN}, ν_{CX}, δ_{NCX} and $\nu_{\mathrm{M-XCN}}$ regions are presented in Tables 3 and 4. The position of $\nu_{\mathrm{M-SCN}}$ remains in the 200—230 cm^{-1} region and there is no band corresponding to $\nu_{\mathrm{M-NCS}}$.

Monomeric bridged complexes and their infrared spectral data are given in Tables 5 and 6. These complexes are of two types, one in which M acquires a tetrahedral coordination geometry and the other in which it is octahedral as shown in (VII) and (VIII). In the case of these complexes both bridged and terminal NCX are present. The terminal NCX is generally X-bonded, the

TABLE 4

Cationic—anionic complexes of $\mathrm{MM'(NCSe)_4}$ and their spectral data

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(i) M in octahedral coordination geometry

These complexes are $[\mathrm{Co(py)_6}][\mathrm{Zn(NCSe)_4}]$ [36], $[\mathrm{Co(bipy)_3}][\mathrm{Zn(NCSe)_4\cdot bipy}]$ [36], $[\mathrm{Co(nia)_6}][\mathrm{Zn(NCSe)_4}]$ [37], $[\mathrm{Co(inh)_6}][\mathrm{Zn(NCSe)_4}]$ [37], $[\mathrm{Co(cpy)_6}][\mathrm{Zn(NCSe)_4}]$ [37], $[\mathrm{Ni(en)_3}][\mathrm{Zn(NCSe)_4\cdot en}]$ [38], $[\mathrm{Ni(trien)_2}][\mathrm{Zn(NCSe)_4}]$ [38], $[\mathrm{Ni(en)_3}][\mathrm{Hg(SeCN)_4}]$ [38], $[\mathrm{Ni(en)_3}][\mathrm{Cd(NCSe)_4(en)}]$ [38].

(ii) M in tetrahedral coordination geometry

These complexes are $[\mathrm{Co(py)_4}][\mathrm{Zn(NCSe)_4}]$ [36], $[\mathrm{Cd(nia)_4}][\mathrm{Hg(SeCN)_4}]$ [37], $[\mathrm{Cd(cpy)_4}][\mathrm{Hg(SeCN)_4}]$ [37].

(iii) M in square planar coordination geometry

$[\mathrm{Co(en)_2}][\mathrm{Hg(SeCN)_4\cdot en}]$ [38].

In these complexes, one to two bands are generally observed each in CN stretching, CSe stretching and NCSe bending regions in the ranges 2070—2015 cm^{-1}, 540—660 cm^{-1} and 390—440 cm^{-1}, respectively. *Dq* values of octahedral cobalt complexes are in the range 1020—1050 cm^{-1} and octahedral nickel in the range 1140—1170 cm^{-1}. *Dq* value of the tetrahedral cobalt complex is 489 cm^{-1}. The μ_{eff} values of octahedral cobalt and nickel complexes are around 5.20 B.M. and 3.00 B.M., respectively. μ_{eff} value of the tetrahedral cobalt complex is 4.48 B.M. and that of square planar cobalt complex is 2.0 B.M. Cd/Hg complexes are diamagnetic.

TABLE 5

Monomeric bridged complexes of $MM'(SCN)_4$ and their complexes

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(i) M in octahedral coordination geometry

These complexes are $(nia)_4Co(NCS)_2Hg(PPh_3)_2(SCN)_2$ [44], $(py)_2(SCN)_2Co(NCS)_2Hg(PPh_3)_2$ [44], $(nit)_2Co(NCS)_2Cd(SCN)_2$ [33], $(4\text{-cpy})_4Co(NCS)_2Hg(SCN)_2$ [29], $(nia)_4Ni(NCS)_2Hg(SCN)_2$ [32], $(4\text{-cpy})_4Ni(NCS)_2Hg(SCN)_2$ [32], $(etu)_4Ni(NCS)_2Hg(SCN)_2$ [46], $(thn)_4Ni(NCS)_2Hg(SCN)_2$ [46], $(tzt)_4Ni(NCS)_2Hg(SCN)_2$ [46], $(eu)_4Ni(NCS)_2Hg(SCN)_2$ [39], $(dmu)_4Ni(NCS)_2Hg(SCN)_2$ [39], $(dmtu)_4Ni(NCS)_2Hg(SCN)_2$ [39], $(py)_2(SCN)_2Ni(NCS)_2Hg(PPh_3)_2$ [44], $(nia)_2(SCN)_2Ni(NCS)_2Hg(PPh_3)_2$ [44], $(ist)_4Ni(NCS)_2Cd(SCN)_2$ [45], $(nit)_4Ni(NCS)_2Cd(SCN)_2$ [45], $(mit)_4Ni(NCS)_2Cd(SCN)_2$ [45], $(dmt)_4Ni(NCS)_2Cd(SCN)_2$ [45], $(abt)_4Ni(NCS)_2Cd(SCN)_2$ [45], $(bit)_4Ni(NCS)_2Cd(SCN)_2$ [45], $(py)_2(SCN)_2Cu(NCS)_2Hg(PPh_3)_2$ [44], $(nia)_2(SCN)_2Cu(NCS)_2Hg(PPh_3)_2$ [44].

(ii) M in tetrahedral coordination geometry

These complexes are $(abt)_2Co(NCS)_2Cd(SCN)_2$ [33], $(Ph_3P)_2Co(NCS)_2Cd(SCN)_2$ [34], $(3\text{-apy})_2Co(NCS)_2Zn(SCN)_2$ [29], $(4\text{-apy})_2Co(NCS)_2Zn(SCN)_2$ [29], $(PPh_3)_2Co(NCS)_2Zn(SCN)_2$ [34], $(PPh_3)_2Co(NCS)_2Hg(SCN)_2$ [27], $(dmu)_2Co(NCS)_2Hg(SCN)_2$ [39], $(pzd)_2Co(NCS)_2Hg(SCN)_2$ [39], $(etu)_2Co(NCS)_2Hg(SCN)_2$ [46], $(tzt)_2Co(NCS)_2Hg(SCN)_2$ [46], $(thn)_2Co(NCS)_2Hg(SCN)_2$ [46], $(eu)_2Co(NCS)_2Hg(SCN)_2$ [39], $(tzt)_2Zn(NCS)_2Hg(SCN)_2$ [46], $(thn)_2Zn(NCS)_2Hg(SCN)_2$ [46], $(etu)_2Zn(NCS)_2Hg(SCN)_2$ [46], $(pzd)_2Zn(NCS)_2Hg(SCN)_2$ [30], $(py)_2(SCN)_2Zn(NCS)_2Hg(PPh_3)_2$ [43], $(nia)_2(SCN)_2Zn(NCS)_2Hg(PPh_3)_2$ [43].

(iii) M in square planar coordination geometry

$(Ph_3P)_2Ni(NCS)_2Cd(SCN)_2$ [34], $(Ph_3P)_2Ni(NCS)_2Hg(SCN)_2$ [27].

In these complexes, four bands are generally observed each due to CN stretching mode in the region 2020—2170 cm^{-1}, CS stretching mode in the region 720—860 cm^{-1} and NCS bending mode in the region 400—480 cm^{-1}. Dq values of octahedral cobalt complexes are in the range 1000—1050 cm^{-1} and those of nickel complexes in the range 1020—1080 cm^{-1}. μ_{eff} values of octahedral cobalt, nickel and copper complexes are in the range 5.0—5.2, 3.0—3.3 and 1.7—1.9 B.M., respectively. All Zn/Hg complexes are diamagnetic. Dq values of tetrahedral cobalt complexes are in the range 360—460 cm^{-1} and μ_{eff} values in the range 4.0—4.6 B.M. All the nickel square planar complexes are diamagnetic.

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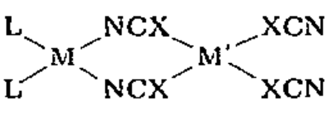
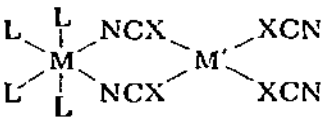
ligand is attached to M, and NCX to M′ through X.



(VII)



(VIII)

Because of the presence of both bridged and terminal bonded NCX, the number of bands corresponding to the various modes of NCX, e.g. CN(st), CX(st) and NCX(bend) is increased. The position of the M—SCN band remains unaltered. The bands corresponding to ν_{M-NCS} show a negative shift in those complexes where M changes its coordination geometry from tetrahedral to octahedral [71] as shown in (VIII). In those complexes where the coordination geometry remains tetrahedral such as shown in (VII) the position of

TABLE 6

Monomeric bridged complexes of $MM'(SeCN)_4$ and their spectral data

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(i) M in octahedral coordination geometry

These complexes are $(bipy)_2Co(NCSe)_2Cd(SeCN)_2$ [36], $(py)_4Co(NCSe)_2Cd(SeCN)_2$ [36], $(3\text{-}cpy)_4Co(NCSe)_2Cd(SeCN)_2$ [37], $(py)_2(SeCN)_2Co(NCSe)_2Hg(PPh_3)_2$ [44], $(nia)_2(SeCN)_2Co(NCSe)_2Hg(PPh_3)_2$ [44], $(mit)_2Ni(NCSe)_2Hg(SeCN)_2$ [42], $(py)_2(SeCN)_2Ni(NCSe)_2Hg(PPh_3)_2$ [44], $(nia)_2(SeCN)_2Ni(NCSe)_2Hg(PPh_3)_2$ [44], $(py)_4Ni(NCSe)_2Cd(SeCN)_2$ [36], $(3\text{-}cpy)_4Ni(NCSe)_2Cd(SeCN)_2$ [37], $(nia)_4Ni(NCSe)_2Cd(SeCN)_2$ [37], $(3\text{-}apy)_4Ni(NCSe)_2Cd(SeCN)_2$ [37], $(bipy)_2Cu(NCSe)_2Hg(SeCN)_2$ [99], $(phen)_2Cu(NCSe)_2Hg(SeCN)_2$ [99], $(nia)_4Zn(NCSe)_2Hg(SeCN)_2$ [37], $(py)_4Zn(NCSe)_2Hg(SeCN)_2$ [37], $(3\text{-}cpy)_4Zn(NCSe)_2Hg(SeCN)_2$ [37], $(py)_2(SeCN)_2Zn(NCSe)_2Hg(PPh_3)_2$ [44], $(nia)_2(SeCN)_2Zn(NCSe)_2Hg(PPh_3)_2$ [44].

(ii) M in tetrahedral coordination geometry

These complexes are $(PPh_3)_2Co(NCSe)_2Hg(SeCN)_2$ [34], $(PPh_3)_2Co(NCSe)_2Cd(SeCN)_2$ [34], $(PPh_3)_2Co(NCSe)_2Zn(SeCN)_2$ [34].

(iii) M in square planar coordination geometry

$(PPh_3)_2Ni(NCSe)_2Hg(SeCN)_2$ [34], $(PPh_3)_2Ni(NCSe)_2Cd(SeCN)_2$ [34], $(PPh_3)_2Ni(NCSe)_2Zn(SeCN)_2$ [34].

In all the above listed complexes, three to four bands are generally observed due to CN stretching mode in the range 2020—2190 cm^{-1}, CSe stretching mode in the range 530—660 cm^{-1} and NCSe bending mode in the range 390—480 cm^{-1}. *Dq* values of octahedral cobalt complexes are in the range 1000—1050 cm^{-1} and those of nickel complexes in the range 1000—1100 cm^{-1}. μ_{eff} values of octahedral cobalt, nickel and copper complexes are around 5.00, 3.00 and 1.90 B.M., respectively. All Zn/Hg complexes are diamagnetic. The *Dq* values of tetrahedral cobalt complexes are in the range 450—500 cm^{-1}.

ν_{M-NCS} band remains almost unaltered. In the monomeric bridged complexes the $M(NCX)_4$ unit invariably changes to $L_2M(NCX)_2$ or $L_4M(NCX)_2$, hence there is always an increase in the number of M—NCX bands due to change in symmetry from T_d to C_{2v}.

Polymeric bridged complexes are included in Tables 7 and 8 along with their spectral data. In these complexes, only bridging NCX is present, hence the bands corresponding to ν_{CN}, ν_{CX} and δ_{NCX} modes are present in the range prescribed for bridging NCX group, and the number of bands is less, compared to monomeric bridged complexes. The bands corresponding to ν_{M-NCX} always show a negative shift because of the change of coordination geometry around M from tetrahedral in Lewis acid to octahedral in the complexes (IX). The position of the $\nu_{M'-SCN}$ bands are, however, not disturbed except in those cases where the ligands are also linked to M′(X). The number of bands due to ν_{M-NCS} modes always increases due to a change in symmetry. In the case of complexes where the ligands are also attached to M′, the number of

TABLE 7

Polymeric bridged complexes of $\mathrm{MM'(SCN)_4}$ and their spectral data

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M in octahedral coordination geometry

These complexes are $\mathrm{>(thf)_2Fe(NCS)_2Hg(SCN)_2<}$ [27], $\mathrm{>(py)_2Fe(NCS)_2Hg(SCN)_2<}$ [27], $\mathrm{>(nia)_2Fe(NCS)_2Hg(SCN)_2<}$ [32], $\mathrm{>(2\text{-}apm)_2Fe(NCS)_2Hg(SCN)_2<}$ [32], $\mathrm{>(thf)_2Co(NCS)_2Hg(SCN)_2<}$ [27], $\mathrm{>(diox)_2Co(NCS)_2Hg(SCN)_2<}$ [27], $\mathrm{>(py)_2Co(NCS)_2Hg(SCN)_2<}$ [27], $\mathrm{>(anil)_2Co(NCS)_2Hg(SCN)_2<}$ [27], $\mathrm{>(2\text{-}apy)_2Co(NCS)_2Hg(SCN)_2<}$ [29], $\mathrm{>(3\text{-}apm)_2Co(NCS)_2Hg(SCN)_2<}$ [29], $\mathrm{>(4\text{-}apy)_2Co(NCS)_2Hg(SCN)_2<}$ [29], $\mathrm{>(ent)_2Co(NCS)_2Hg(SCN)_2<}$ [29], $\mathrm{>(nia)_2Co(NCS)_2Hg(SCN)_2<}$ [29], $\mathrm{>(3\text{-}cpy)_2Co(NCS)_2Hg(SCN)_2<}$ [29], $\mathrm{>(ist)_2Co(NCS)_2Hg(SCN)_2<}$ [33], $\mathrm{>(bit)_2Co(NCS)_2Hg(SCN)_2(bit)_2<}$ [33], $\mathrm{>(pza)_2Co(NCS)_2Hg(pza)_2(SCN)_2<}$ [30], $\mathrm{>(2\text{-}amp)_2Co(NCS)_2Hg(SCN)_2<}$ [30], $\mathrm{>(EtOH)_2Co(NCS)_2Pd(SCN)_2<}$ [35], $\mathrm{>(3\text{-}cpy)_2Ni(NCS)_2Hg(3\text{-}cpy)_2(SCN)_2<}$ [32], $\mathrm{>(4\text{-}cpy)_2Ni(NCS)_2Hg(4\text{-}cpy)_2(SCN)_2<}$ [32], $\mathrm{>(inh)_2Ni(NCS)_2Hg(inh)_2(SCN)_2<}$ [32], $\mathrm{>(pza)_2Ni(NCS)_2Hg(pza)_2(SCN)_2<}$ [30], $\mathrm{>(ampy)_2Ni(NCS)_2Hg(SCN)_2<}$ [30], $\mathrm{>(ist)_2Ni(NCS)_2Hg(ist)_2(SCN)_2<}$ [45], $\mathrm{>(mit)_2Ni(NCS)_2Hg(SCN)_2<}$ [45], $\mathrm{>(bit)_2Ni(NCS)_2Hg(SCN)_2<}$ [45], $\mathrm{>(dmt)_2Ni(NCS)_2Hg(SCN)_2<}$ [45], $\mathrm{>(abt)_2Ni(NCS)_2Hg(SCN)_2<}$ [45], $\mathrm{>(thf)_2Ni(NCS)_2Hg(SCN)_2<}$ [27], $\mathrm{>(py)_2Ni(NCS)_2Hg(SCN)_2<}$ [27], $\mathrm{>(diox)_2Cu(NCS)_2Hg(SCN)_2<}$ [99], $\mathrm{>(2\text{-}apy)_2Cu(NCS)_2Hg(SCN)_2<}$ [99], $\mathrm{>(py)_2Zn(NCS)_2Hg(SCN)_2<}$ [27], $\mathrm{>(thf)_2Cd(NCS)_2Hg(SCN)_2<}$ [27], $\mathrm{>(py)_2Cd(NCS)_2Hg(SCN)_2<}$ [27], $\mathrm{>(MeOH)_2Zn(NCS)_2Pd(SCN)_2<}$ [35].

In these complexes, two absorption bands are generally observed due to CN stretching mode in the range 2060—2160 $\mathrm{cm^{-1}}$, two bands due to CS stretching mode in the range 720—790 $\mathrm{cm^{-1}}$ and two bands due to NCS bending mode in the range 420—480 $\mathrm{cm^{-1}}$. *Dq* values of octahedral cobalt complexes are in the range 890—1050 $\mathrm{cm^{-1}}$ and those of nickel complexes in the range 1000—1200 $\mathrm{cm^{-1}}$. μ_{eff} values of cobalt, nickel and copper complexes are around 5.00, 3.00 and 1.90 B.M., respectively. Zinc and cadmium complexes are diamagnetic.

TABLE 8

Polymeric bridged complexes of $\mathrm{MM'(SeCN)_4}$ and their spectral data

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M in octahedral coordination geometry

This series includes the complexes $\mathrm{>(py)_2Co(NCSe)_2Hg(SeCN)_2<}$ [36], $\mathrm{>(3\text{-}cpy)_2Co(NCSe)_2Hg(SeCN)_2<}$ [27], $\mathrm{>(3\text{-}apy)_2Co(NCSe)_2Hg(SeCN)_2<}$ [37], $\mathrm{>(nia)_2Co(NCSe)_2Hg(SeCN)_2<}$ [37], $\mathrm{>(inh)_2Co(NCSe)_2Hg(SeCN)_2<}$ [37], $\mathrm{>(ist)_2Co(NCSe)_2Hg(ist)_2(SeCN)_2<}$ [42], $\mathrm{>(mit)_2Co(NCSe)_2Hg(SeCN)_2<}$ [42], $\mathrm{>(bit)_2Co(NCSe)_2Hg(SeCN)_2<}$ [42], $\mathrm{>(ist)_2Co(NCSe)_2Cd(ist)_2(SeCN)_2<}$ [42], $\mathrm{>(bit)_2Co(NCSe)_2Cd(SeCN)_2<}$ [42], $\mathrm{>(py)_2Ni(NCSe)_2Hg(SeCN)_2<}$ [36], $\mathrm{>(3\text{-}cpy)_2Ni(NCSe)_2Hg(SeCN)_2<}$ [37], $\mathrm{>(3\text{-}apy)_2Ni(NCSe)_2Hg(SeCN)_2<}$ [37], $\mathrm{>(inh)_2Ni(NCSe)_2Hg(SeCN)_2<}$ [37], $\mathrm{>(ist)_2Ni(NCSe)_2Hg(ist)_2(SeCN)_2<}$ [42], $\mathrm{>(bit)_2Ni(NCSe)_2Hg(SeCN)_2<}$ [42], $\mathrm{>(ist)_2Ni(NCSe)_2Cd(ist)_2(SeCN)_2<}$ [42], $\mathrm{>(mit)_2Ni(NCSe)_2Cd(SeCN)_2<}$ [42], $\mathrm{>(bit)_2Ni(NCSe)_2Cd(SeCN)_2<}$ [42], $\mathrm{>Cu(NCSe)_2Hg(SeCN)_2<}$ [99], $\mathrm{>(thf)_2Cu(NCSe)_2Hg(SeCN)_2<}$ [99], $\mathrm{>(diox)_2Cu(NCSe)_2Hg(SeCN)_2<}$ [99], $\mathrm{>(py)_2Cu(NCSe)_2Hg(SeCN)_2<}$ [99], $\mathrm{>(nia)_2Cu(NCSe)_2Hg(SeCN)_2<}$ [99], $\mathrm{>(apy)_2Cu(NCSe)_2Hg(SeCN)_2<}$ [99].

In these complexes, two absorption bands are generally observed due to CN stretching mode in the range 2100—2170 $\mathrm{cm^{-1}}$, two bands due to CSe stretching mode in the range 560—690 $\mathrm{cm^{-1}}$ and two bands due to NCSe bending mode in the range 380—450 $\mathrm{cm^{-1}}$. *Dq* values of octahedral cobalt complexes are in the range 1000—1050 $\mathrm{cm^{-1}}$ and those of nickel complexes in the range 900—1100 $\mathrm{cm^{-1}}$. The μ_{eff} values of cobalt, nickel and copper complexes are around 5.00, 3.00 and 1.90 B.M., respectively.

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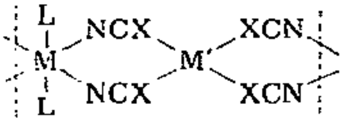
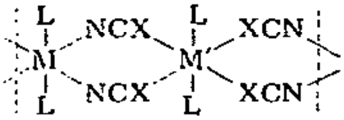
bands due to the M′—SCN mode also increases.



(IX)



(X)

In all three types of complexes, M—L stretching bands are observed in the range 160—285 cm^{-1}, however the positions of these bands cannot be used to distinguish different types of complexes, they can only indicate coordination of the ligands either to M or to M′.

Recently [40] a new class of mixed dithio-diselenocyanates of general formula $MM'(NCS)_2(NCSe)_2$, have been synthesized and their Lewis acid character studied. They also form all three types of complexes, and are included in Tables 9—11. Because of the presence of both thio- and selenocyanate groups, the point group of the complexes is changed (Table 2) and accordingly the number of bands in ν_{CN}, ν_{CX} and δ_{NCX} regions is also changed. The numbers and positions of characteristic infrared spectral bands are given in Tables 9—11.

C. ELECTRONIC SPECTRA AND MAGNETISM

Electronic spectra and various derived spectral parameters, e.g. *Dq* and *B′* have been found useful in establishing coordination geometries around M (M = Co, Ni, Cu) in the $MM'(XCN)_4$ complexes. Magnetic moments have similarly been useful.

TABLE 9

Cationic—anionic complexes of $MM'(SCN)_2(SeCN)_2$ and their spectral data [40]

M in octahedral coordination geometry

These complexes are $[Co(py)_6][Cd(SeCN)_2(SCN)_2]$, $[Co(py)_6][Zn(SeCN)_2(NCS)_2]$, $[Co(bipy)_3][Cd(SeCN)_2(SCN)_2]$, $[Co(bipy)_3][Zn(NCSe)_2(NCS)_2]$, $[Ni(py)_6][Cd(SeCN)_2(SCN)_2]$, $[Ni(py)_6][Zn(NCSe)_4(NCS)_2]$, $[Ni(bipy)_3][Cd(SeCN)_2(NCS)_2]$, $[Ni(bipy)_3][Zn(NCSe)_2(NCS)_2]$.

In these complexes two bands are generally observed each due to CN stretching, CSe stretching and CS stretching modes in the respective ranges 2050—2110 cm^{-1}, 580—670 cm^{-1} and 710—780 cm^{-1}, whereas three to four bands are observed due to NCX (X = S, Se) bending mode in the range 400—490 cm^{-1}. *Dq* values of octahedral cobalt and nickel complexes are in the ranges 900—1000 cm^{-1} and 990—1080 cm^{-1}, respectively. μ_{eff} values of octahedral cobalt and nickel complexes are around 5.00 B.M. and 3.20 B.M., respectively.

TABLE 10

Monomeric bridged complexes of $MM'(SCN)_2(SeCN)_2$ and their spectral data

(i) M in octahedral coordination geometry

These complexes are $(bipy)_2Co(NCS)(NCSe)Hg(SeCN)(SCN)$ [40], $(py)_4Co(NCS)(NCSe)Hg(SeCN)(SCN)(PPh_3)_2$ [43], $(bipy)_2Co(NCS)(NCSe)Hg(SeCN)(SCN)(PPh_3)_2$ [43], $(py)_4Co(NCS)(NCSe)Cd(SeCN)(SCN)(PPh_3)_2$ [43], $(bipy)_2Co(NCS)(NCSe)Cd(SeCN)(SCN)(PPh_3)_2$ [43], $(py)_4Co(NCS)(NCSe)Zn(SeCN)(SCN)(PPh_3)_2$ [43], $(bipy)_2Co(NCS)(NCSe)Zn(SeCN)(SCN)(PPh_3)_2$ [43], $(bipy)_2Ni(NCS)(NCSe)Hg(SeCN)(SCN)$ [40], $(py)_4Ni(NCS)(NCSe)Hg(SeCN)(SCN)(PPh_3)_2$ [43], $(bipy)_2Ni(NCS)(NCSe)Hg(SeCN)(SCN)(PPh_3)_2$ [43], $(py)_4Ni(NCS)(NCSe)Cd(SeCN)(SCN)(PPh_3)_2$ [43], $(bipy)_2Ni(NCS)(NCSe)Cd(SeCN)(SCN)(PPh_3)_2$ [43], $(py)_4Ni(NCS)(NCSe)Zn(SeCN)(SCN)(PPh_3)_2$ [43], $(bipy)_2Ni(NCS)(NCSe)Zn(SeCN)(SCN)(PPh_3)_2$ [43], $(bipy)_2Cu(NCS)(NCSe)Hg(SeCN)(SCN)$ [99].

(ii) M in tetrahedral coordination geometry [40]

These complexes are $(PPh_3)_2Co(NCS)(NCSe)Hg(SeCN)(SCN)$, $(PPh_3)_2Co(NCS)(NCSe)Cd(SeCN)(SCN)$, $(PPh_3)_2Co(NCS)(NCSe)Zn(SeCN)(SCN)$.

(iii) M in square planar coordination geometry

$(PPh_3)_2Ni(NCS)(NCSe)Hg(SeCN)(SCN)$ [40]

In these complexes, three to four bands are observed each due to CN stretching, CS stretching, CSe stretching and NCX bending modes in the ranges 2070—2180 cm^{-1}, 700—780 cm^{-1}, 510—680 cm^{-1} and 390—470 cm^{-1}, respectively. *Dq* values of octahedral cobalt and nickel complexes are in the ranges 990—1050 cm^{-1} and 1020—1080 cm^{-1}, respectively. μ_{eff} values of octahedral cobalt complexes are around 5.20 B.M. and those of octahedral nickel complexes around 3.10 B.M. *Dq* values of tetrahedral cobalt complexes are in the range 460—500 cm^{-1} and μ_{eff} values around 4.40 B.M.

TABLE 11

Polymeric bridged complexes of $MM'(SCN)_2(SeCN)_2$ and their spectral data

(i) M in octahedral coordination geometry

These complexes are $>(py)_2Co(NCS)(NCSe)Hg(SeCN)(SCN)<$ [40], $>Ni(NCS)(NCSe)Hg(SeCN)(SCN)<$ [40], $>Ni(NCS)(NCSe)Cd(SeCN)(SCN)<$ [40], $>Ni(NCS)(NCSe)Zn(SeCN)(SCN)<$ [40], $>(py)_2Ni(NCS)(NCSe)Hg(SeCN)(SCN)<$ [40], $>Cu(NCS)(NCSe)Hg(SeCN)(SCN)<$ [99], $>(thf)_2Cu(NCS)(NCSe)Hg(SeCN)(SCN)<$ [99], $>(diox)_2Cu(NCS)(NCSe)Hg(SeCN)(SCN)<$ [99], $>(py)_2Cu(NCS)(NCSe)Hg(SeCN)(SCN)$ [99], $>(nia)_2Cu(NCS)(NCSe)Hg(SeCN)(SCN)<$ [99], $>(apy)_2Cu(NCS)(NCSe)Hg(SeCN)(SCN)<$ [99].

(ii) M in tetrahedral coordination geometry

These complexes are $>Co(NCS)(NCSe)Hg(SeCN)(SCN)<$ [40], $>Co(NCS)(NCSe)Cd(SeCN)(SCN)<$ [40], $>Co(NCS)(NCSe)Zn(SeCN)(SCN)<$ [40].

In these complexes one to two bands are generally observed due to each CN stretching, CSe stretching and NCX bending modes in the ranges 2110—2160 cm^{-1}, 590—670 cm^{-1} and 390—490 cm^{-1}, respectively. Two to three bands are observed due to CS stretching mode in the range 700—790 cm^{-1}. Octahedral cobalt complex possesses *Dq* value of 978 cm^{-1}. *Dq* values of octahedral nickel and tetrahedral cobalt complexes are in the ranges 990—1070 cm^{-1} and 470—500 cm^{-1}, respectively. μ_{eff} value of octahedral cobalt complex is 5.14 B.M. μ_{eff} values of octahedral nickel and tetrahedral cobalt complexes are around 3.10 and 4.30 B.M., respectively. μ_{eff} values of octahedral copper complexes are around 1.90 B.M.

(i) Cobalt complexes

Octahedral

The electronic spectral parameters and magnetic moments of octahedral and tetrahedral complexes are listed in various Tables. In octahedral cobalt(II) complexes, three transitions namely $^4T_{1g} \rightarrow {}^4T_{2g}(F)(\nu_1)$, $^4T_{1g} \rightarrow {}^4A_{2g}(F)(\nu_2)$ and $^4T_{1g} \rightarrow {}^4T_{1g}(P)(\nu_3)$ are possible. Generally ν_1 and ν_3 are observed. ν_1 is broad and ν_3 is a multiple band and may be mixed with spin forbidden transitions. ν_2 is generally not observed, being formally a two electron transition [76]. The bands due to ν_1 are observed in the region 8400—12 000 cm^{-1} and those due to ν_3 in the region 20 000—23 000 cm^{-1}. Using the values of ν_1 and ν_3, values of the spectral parameters Dq, B' and β of the complexes have been calculated with the help of matrices of Tanabe and Sugano [77]. The values reported here are quite appropriate for octahedral cobalt (II) [78]. We have used these data only to establish the stereochemistry, not to distinguish the nature of the complexes. In the monomeric bridged type of complex the cobalt has generally been found to have a tetrahedral configuration whereas in polymeric and cationic—anionic complexes, it has an octahedral configuration. The magnetic moment values of octahedral complexes are in the range 4.9—5.2 B.M.

Since the cobalt has octahedral configuration in both cationic—anionic and polymeric bridged complexes, distinction between these two is more reliably made by molar conductance data.

Tetrahedral

Tetrahedral Co(II) complexes have magnetic moment values in the range 4.2—4.6 B.M. Their electronic spectra contain intense bands in the regions 14 000—19 000 cm^{-1} and 6400—8000 cm^{-1} which arise from the transitions $^4A_{2g} \rightarrow {}^4T_{1g}(P)(\nu_3)$ and $^4A_{2g} \rightarrow {}^4T_{1g}(F)(\nu_2)$ respectively. The ν_2 band splits into a triplet when the cobalt has C_{2v} symmetry [78]. Using ν_2 and ν_3 band energies Dq, B' and β values are calculated. The electronic spectra of the monomeric bridged complexes provide an important indication to distinguish them from polymeric complexes, because the cobalt in the latter case never has a tetrahedral configuration. In certain cationic—anionic complexes cobalt has a tetrahedral coordination geometry because of the presence of a $[\text{CoL}_4]^{2+}$ cation. A distinction between such cationic—anionic and monomeric bridged complexes is drawn on the basis of the number of bands appearing in the ν_2 region, though some times Co(II) in T_d symmetry also shows splitting of ν_2. In cationic—anionic complexes the cation $[\text{CoL}_4]^{2+}$ has T_d symmetry and frequently only one band is observed for the ν_2 transition. In the case of monomeric bridged type of complexes, the environment around cobalt changes to $\text{L}_2\text{Co(NCS)}_2$ which has C_{2v} symmetry, hence the ν_2 band is split into a triplet. The Dq values in the two cases are also different. The cationic—anionic and monomeric bridged complexes have accordingly been distinguished with the help of electronic spectral data. Distinction between the two may also be made on the basis of conductance data.

Square planar

Generally, the configuration of Co(II) complexes is determined by the nature of the ligand field [80]. However, Nishikawa and Yamada [81] have reported that in some cobalt(II) complexes the steric requirement of the ligand alone determines the configuration of the complex. Such a case has been observed in planar cobalt complexes. The magnetic moment of these complexes is generally in the range 1.9—2.26 B.M. Nyholm and co-workers [82,83] and Nishikawa and Yamada [81] have reported a low magnetic moment as one of the typical characteristics of cobalt(II) having a planar configuration. Relatively little is known about the electronic spectra of such complexes. In salcomine and related complexes [81] a sharp peak at 8333 cm^{-1} has been considered to be diagnostic of Co(II) complexes with a planar configuration. This peak has been ascribed to an electronic transition from $^2B_{2g}$ to $^2A_{2g}$ or ^2E_g. Nishida and Kida [84] have made a comparatively detailed study and have shown that in near infrared and visible region, these complexes show three bands, mainly due to the transitions $^2A_{1g} - {}^2B_{2g}$, $^2A_{1g} \to {}^2E'_g$ and $^2A_{1g} \to {}^2E'_{2g}$ appearing at about 4000, 7000 and 18 000 cm^{-1}, respectively. In our complexes [28], the bands at 5000, 7000 and 15 000 cm^{-1} have similarly been assigned to the transitions $^2A_{1g} \to {}^2E'_g$, $^2A_{1g} \to {}^2B_{2g}$ and $^2A_{1g} \to {}^2E'_{2g}$, respectively. These complexes have magnetic moments of about 2 B.M.

Close examination of square planar complexes of cobalt(II) in the literature reveals that the ethylenediamine unit is present in most of the cases. Perhaps it is this moiety which fulfills the stereochemical requirement of the square planar complexes of cobalt(II). In the present work, ligands which form square planar complexes are also ethylenediamine and triethylenetetramine. The low spin complexes of these ligands with CoHg(SCN)$_4$ were left unexplained by Rivest and co-workers [27], but the complexes can be considered to have a square planar configuration.

(ii) Nickel complexes

Nickel commonly prefers octahedral and square planar configurations. Electronic spectral bands and magnetic moment values are diagnostic of these configurations. In octahedral complexes three transitions are observed [85]. The bands in the region 23 500—31 340 cm^{-1} arise from the transition $^3A_{2g} \to {}^3T_{1g}(P)(\nu_3)$, near 14 500—16 000 cm^{-1} from $^3A_{2g} \to {}^3T_{1g}(F)(\nu_2)$ and near 10 700—9000 cm^{-1} from $^3A_{2g} \to {}^3T_{2g}(F)(\nu_1)$. The ν_2 bands are often split when there is departure from O$_h$ symmetry to a lower symmetry. Furlani [86] and Ballhausen and Liehr [87] first independently calculated the energy levels of nickel in a distorted octahedral environment, and showed that departure from cubic octahedral symmetry results in the splitting of orbital triplets $^3T_{1g}$ and $^3T_{2g}$, producing an increased number of electronic transitions. In cationic—anionic complexes, the cation [NiL$_6$]$^{2+}$ has O$_h$ symmetry, hence the ν_2 band is not split. In polymeric bridged and monomeric bridged complexes, the symmetry is often C_{2v} due to the presence of $(SCN)_2L_2Ni(NCS)_2$ and $L_4Ni(NCS)_2$ units, respectively. This change in symmetry may cause splitting of the ν_2 bands and demonstrates a possible point of distinction between cationic—anionic and bridged complexes. The splitting is, however, not observed when the ligand is nitrogen atom. The distinction between monomeric and polymeric bridged type is difficult on the basis of the nature of the electronic spectral bands, however, it can be made, though not very reliably, on the basis of Dq values which differ in the two cases.

Magnetic moments of the octahedral monomeric and polymeric bridged complexes span the range of effective magnetic moments observed for nickel(II). Distortions in these complexes result in departure from cubic O_h symmetry to lower symmetry, yielding magnetic moments closer to the spin-only value. In cationic—anionic complexes, where cubic symmetry is retained the magnetic moments are not so close to the spin-only value.

Square planar complexes

Most square planar complexes of nickel(II) exhibit a strong absorption band in the visible region between 15 000 and 25 000 cm^{-1}, and in many cases a second more intense band between 23 000 and 30 000 cm^{-1}. These are referred to as ν_2 and ν_3 bands [84,88—90]. Square planar complexes of nickel(II) with sulphur donor ligands [91] generally exhibit an additional well defined band of lower energy than ν_2, referred to as ν_1 [92—94]. In square planar amine complexes, the energy separation between the $d_{x^2-y^2}$ orbital and the next lowest orbital is invariably greater than 10 000 cm^{-1} [84b,95,96]. In the present study, the nickel has been found in square planar geometry only in monomeric bridged or cationic—anionic complexes. This geometry has not been observed in polymeric bridged complexes. Both in monomeric [34] and cationic—anionic complexes [34] the nickel acquires a square planar coordination geometry when the ligand is triphenylphosphine, but certain complexes of this ligand are also octahedral [40].

(iii) Copper(II) complexes

The majority of Cu(II) complexes give rise to orbitally non-degenerate ground states involving a static form of distortion, i.e., elongated tetragonal octahedral having D_{4h} symmetry. Such complexes exhibit one absorption band in the visible region near 16 000 cm^{-1} which can often be resolved into three components, assigned to transitions from d_{xy}, d_{z^2} and d_{xz}, d_{yz} to antibonding and half filled $d_{x^2-y^2}$ level [84b, 97].

In D_3 symmetry the ${}^2T_{2g}$ (in O_h) level is split into ${}^2E + {}^2A_1$, whilst the ${}^2E_g$ level is unaffected. Thus we expect two transitions corresponding to ${}^2E \rightarrow {}^2E$ and ${}^2E \rightarrow {}^2A_1$. Certain trigonally distorted copper derivatives such as tris-(dipyridyl) and tris(*o*-phenanthroline) copper(II) (D_3 symmetry) give rise to two well defined absorption bands near 6000 cm^{-1} and 15 000 cm^{-1} [98]. In our bridged complexes [99] a broad band at about 15 000 cm^{-1} is observed.

The broad band is not well resolved into its components. The presence of a single band at 15 000 cm^{-1} indicates that in our bridged complexes, the copper has tetragonal rather than trigonal octahedral configuration around Cu(II) [16].

In cationic—anionic complexes, however we observe bands near 6000 cm^{-1} and near 15 000 cm^{-1} indicating the presence of a trigonal octahedral structure for Cu(II) having D_3 symmetry [98]. Since the electronic spectra of only a few of these copper complexes have been studied [99], this cannot be used as a reliable guide to distinguish bridged from cationic—anionic complexes. However, on the basis of data available copper in bridged complexes has approximately D_{4h} symmetry and in cationic—anionic approximately D_3 symmetry. On the basis of this difference, the two can be differentiated by electronic spectra, but more reliably on the basis of conductance data.

D. QUANTITATIVE SOFTNESS AND STRUCTURE OF THE COMPLEXES

The application of quantitative softness values to the elucidation of structure of complexes of bimetallic tetrathiocyanates and selenocyanates is a new approach discussed here in detail.

(i) Formation of the three types of complexes depends upon the nature of M and M'. When both M and M' belong to class 'a' type metals, the thiocyanate bridge in the tetrathiocyanate is ruptured on reaction with pyridine or its derivatives, and cationic—anionic complexes are formed. When M belongs to 'a' type and M' to 'b' type metals, the thiocyanate bridge is

TABLE 12

Relation between $\Delta E_n^{\ddagger}$(M—M') and nature of the complexes of $MM'(XCN)_4$ with pyridine and its derivatives

M/M'	$E_n^{\ddagger}$(M)	$E_n^{\ddagger}$(M')	$\Delta E_n^{\ddagger}$(M—M')	Possible nature of the complexes
Co/Hg	−0.22	−4.86	4.64	P.B.
Ni/Hg	−0.28	−4.86	4.58	P.B.
Zn/Hg	−1.29	−4.86	3.57	P.B.
Co/Pd	−0.22	−3.17	2.95	M.B.
Ni/Pd	−0.28	−3.17	2.85	M.B.
Cd/Hg	−2.27	−4.86	2.59	M.B.
Co/Cd	−0.22	−2.27	2.05	M.B.
Ni/Cd	−0.28	−2.27	1.99	M.B.
Zn/Pd	−1.29	−3.17	1.88	M.B.
Pd/Hg	−3.17	−4.86	1.69	C.A.
Co/Zn	−0.22	−1.29	1.07	C.A.
Ni/Zn	−0.28	−1.29	1.01	C.A.
Cd/Zn	−2.27	−1.29	0.98	C.A.
Cd/Pd	−2.27	−3.17	0.90	C.A.

C.A. = Cationic—anionic; M.B. Monomeric bridged; P.B. = Polymeric bridged.

retained and polymeric bridged complexes are formed [29]. Since M and M′ have different softness the stability of the thiocyanate bridge is related to their quantitative softness value. The softness values $E_n^\ddagger$ of M and M′ were calculated by using Klopman's equation [100] and the difference evaluated. The difference was designated $\Delta E_n^\ddagger$ (M—M′) and related to the stability of thiocyanate bridge in MM′(SCN)$_4$ and subsequently to the nature of the complexes. These results, presented in Table 12, clearly indicate the relation between the nature of the complexes and $\Delta E_n^\ddagger$(M—M′) [41].

(ii) This relation holds equally well for the corresponding tetraselenocyanates in respect of their reaction with pyridine and its derivatives. However, it has been observed that the nature of the complexes formed by reaction with bipyridine is different in tetrathiocyanates and tetraselenocyanates. Tetrathiocyanates form cationic—anionic complexes [27], whereas the corresponding tetraselenocyanates form monomeric bridged complexes [36] with this ligand. This reveals a difference in the stabilities of thiocyanate and selenocyanate bridges. Similarly, different behaviour was shown by MM′(NCS)$_2$-(NCSe)$_2$ in respect of certain reactions [40]. To relate these experimental observations with the softness of M and M′ a new relation was developed [40]. The quantitative softness values of —NCX and —XCN were added to the softness values of M and M′, respectively. The softness values so derived were termed as total softness designated by the symbol $TE_n^\ddagger$. The difference in total softness $\Delta TE_n^\ddagger$ (M—M′) of M and M′ was evaluated and related to the stability of thiocyanate and selenocyanate bridges. The calculation of total softness and derivation of the difference was done by adopting the following procedure.

MM′(SCN)$_4$

$TE_n^\ddagger(\mathrm{M}) = E_n^\ddagger(\mathrm{M}) + 4E_m^\ddagger(\mathrm{NCS})$

$TE_n^\ddagger(\mathrm{M'}) = E_n^\ddagger(\mathrm{M'}) + 4E_m^\ddagger(\mathrm{SCN})$

$\Delta TE_n^\ddagger(\mathrm{M{-}M'}) = TE_n^\ddagger(\mathrm{M}) - TE_n^\ddagger(\mathrm{M'})$

MM′(SeCN)$_4$

$TE_n^\ddagger(\mathrm{M}) = E_n^\ddagger(\mathrm{M}) + 4E_m^\ddagger(\mathrm{NCSe})$

$TE_n^\ddagger(\mathrm{M'}) = E_n^\ddagger(\mathrm{M'}) + 4E_m^\ddagger(\mathrm{SeCN})$

$\Delta TE_n^\ddagger(\mathrm{M{-}M'}) = TE_n^\ddagger(\mathrm{M}) - TE_n^\ddagger(\mathrm{M'})$

MM′(NCS)$_2$(NCSe)$_2$

$TE_n^\ddagger(\mathrm{M}) = E_n^\ddagger(\mathrm{M}) + 2E_m^\ddagger(\mathrm{NCS}) + 2E_m^\ddagger(\mathrm{NCSe})$

$TE_n^\ddagger(\mathrm{M'}) = E_n^\ddagger(\mathrm{M'}) + 2E_m^\ddagger(\mathrm{SCN}) + 2E_m^\ddagger(\mathrm{SeCN})$

$\Delta TE_n^\ddagger(\mathrm{M{-}M'}) = TE_n^\ddagger(\mathrm{M}) - TE_n^\ddagger(\mathrm{M'})$

TABLE 13

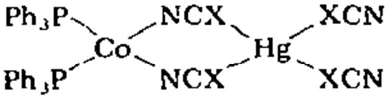
$TE_n^{\ddagger}$ values of M and M′ and their difference in Lewis acids

Complexes	$TE_n^{\ddagger}$(M)	$TE_n^{\ddagger}$(M′)	$\Delta TE_n^{\ddagger}$(M—M′)
$>\mathrm{Co(NCSe)_2Hg(SeCN)_2}<$	−35.94	−22.54	13.43
$>\mathrm{Co(NCS)(NCSe)Hg(SeCN)(SCN)}<$	−34.28	−24.09	10.19
$>\mathrm{Co(NCS)_2Hg(SCN)_2}<$	−32.62	−25.67	6.95
$>\mathrm{Ni(NCSe)_2Hg(SeCN)_2}<$	−36.24	−22.51	13.73
$>\mathrm{Ni(NCS)(NCSe)Hg(SeCN)(SCN)}<$	−34.58	−24.09	10.49
$>\mathrm{Ni(NCS)_2Hg(SCN)_2}<$	−32.92	−25.67	7.25
$>\mathrm{Co(NCSe)_2Cd(SeCN)_2}<$	−35.94	−19.90	16.04
$>\mathrm{Co(NCS)(NCSe)Cd(SeCN)(SCN)}<$	−34.28	−21.48	12.80
$>\mathrm{Co(NCS)_2Cd(SCN)_2}<$	−32.62	−23.06	9.56
$>\mathrm{Ni(NCSe)_2Cd(SeCN)_2}<$	−36.24	−19.90	16.24
$>\mathrm{Ni(NCS)(NCSe)Cd(SeCN)(SCN)}<$	−34.58	−21.48	13.10
$>\mathrm{Ni(NCS)_2Cd(SCN)_2}<$	−32.42	−23.06	9.86
$>\mathrm{Co(NCSe)_2Zn(SeCN)_2}<$	−35.94	−18.88	17.06
$>\mathrm{Co(NCS)(NCSe)Zn(SeCN)(SCN)}<$	−34.28	−20.46	14.12
$>\mathrm{Co(NCS)_2Zn(SCN)_2}<$	−32.62	−22.04	10.58
$>\mathrm{Ni(NCSe)_2Zn(SeCN)_2}<$	−36.24	−18.88	17.36
$>\mathrm{Ni(NCS)(NCSe)Zn(SeCN)(SCN)}<$	−34.56	−20.46	14.12
$>\mathrm{Ni(NCS)_2Zn(SCN)_2}<$	−32.92	−22.04	10.88

—NCS or —NCSe indicates N-bonded, —SCN or —SeCN indicates S- or Se-bonded. The quantitative softness values of the various ligands of NCS or NCSe have been calculated by using Klopman's equation.

The results of total softness $TE_n^{\ddagger}$ of M and M′ and $\Delta TE_n^{\ddagger}$(M—M′) derived from them in $\mathrm{MM'(SCN)_4}$, $\mathrm{MM'(SeCN)_4}$ and $\mathrm{MM'(SCN)_2(SeCN)_2}$ are presented in Table 13. The difference in total softness $\Delta TE_n^{\ddagger}$(M—M′) of M and M′ are highest for tetraselenocyanates and lowest in tetrathiocyanates. This indicates the following stability order for the —NCX—bridge [40]: $\mathrm{MM'(NCSe)_4} > \mathrm{MM'(NCSe)_2(SCN)_2} > \mathrm{MM'(NCS)_4}$. It is on account of this difference that bipyridine and certain other ligands form different types of complexes with these Lewis acids.

(iii) A difference has been reported between the structures of complexes of triphenylphosphine with $\mathrm{CoHg(XCN)_4}$ (X = S, Se) and the qualitative requirement of the H.S.A.B. principle [101]. Triphenylphosphine becomes attached to cobalt or nickel as shown in (XI). Whereas according to the soft—soft interaction [101] it should link to mercury as shown in (XII).



XI

XII

When pyridine and triphenylphosphine simultaneously react with CoHg-

$(NCS)_4$ the situation is different [44]. Pyridine is attached to cobalt and triphenylphosphine to mercury as shown in (XIII). These linkages are satisfactorily explained by $\Delta TE_n^{\ddagger}$(M—M′). The total softness of cobalt and mercury were calculated by adopting the following equations.

$$TE_n^{\ddagger}(\mathrm{Co}) = E_n^{\ddagger}(\mathrm{Co}) + 4E_m^{\ddagger}(\mathrm{py}) + 2E_m^{\ddagger}(\mathrm{NCS})$$

$$TE_n^{\ddagger}(\mathrm{Hg}) = E_n^{\ddagger}(\mathrm{Hg}) + 2E_m^{\ddagger}(\mathrm{PPh_3}) + 4E_m^{\ddagger}(\mathrm{SCN})$$

$$\Delta TE_n^{\ddagger}(\mathrm{Co{-}Hg}) = TE_n^{\ddagger}(\mathrm{Co}) - TE_n^{\ddagger}(\mathrm{Hg})$$

The values of $\Delta TE_n^{\ddagger}$(Co—Hg) in respect of alternative structure (XIV) was also derived by adopting a similar procedure. The difference in total softness

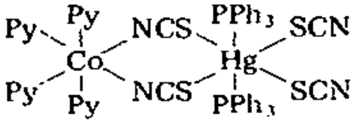
TABLE 14

$\Delta TE_n^{\ddagger}$(M—M′) values for probable and alternative structures of complexes

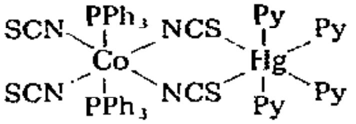
Complexes	Type	$TE_n^{\ddagger}$(M)	$TE_n^{\ddagger}$(M′)	$\Delta TE_n^{\ddagger}$-(M—M′)
$(Ph_3P)_2Co(NCS)_2Hg(SCN)_2$	A	−29.98	−25.66	4.32
$(SCN)_2Co(NCS)_2Hg(PPh_3)_2$	B	−32.62	−28.82	3.80
$(Ph_3P)_2Co(NCS)_2Cd(SCN)_2$	A	−29.98	−23.07	6.91
$(SCN)_2Co(NCS)_2Cd(PPh_3)_2$	B	−32.62	−26.23	6.39
$(Ph_3P)_2Co(NCS)_2Zn(SCN)_2$	A	−29.98	−22.09	7.89
$(SCN)_2Co(NCS)_2Zn(PPh_3)_2$	B	−32.62	−25.25	7.37
$(Ph_3P)_2Co(NCSe)_2Hg(SeCN)_2$	A	−31.64	−22.50	9.41
$(SeCN)_2Co(NCSe)_2Hg(PPh_3)_2$	B	−35.94	−27.24	8.70
$(Ph_3P)_2Ni(NCS)_2Hg(SCN)_2$	A	−30.04	−25.66	4.38
$(SCN)_2Ni(NCS)_2Hg(PPh_3)_2$	B	−32.68	−28.82	3.86
$(Ph_3P)_2Ni(NCSe)_2Hg(SeCN)_2$	A	−31.70	−22.50	9.20
$(SeCN)_2Ni(NCSe)_2Hg(PPh_3)_2$	B	−36.0	−27.24	8.76
$(Ph_3P)_2Co(NCS)(NCSe)Hg(SeCN)(SCN)$	A	−30.81	−24.09	6.72
$(SCN)(SeCN)Co(NCSe)(NCS)Hg(PPh_3)_2$	B	−34.28	−28.04	6.24
$(Ph_3P)_2Co(NCS)(NCSe)Cd(SeCN)(SCN)$	A	−30.88	−25.48	9.38
$(SCN)(SeCN)Co(NCSe)(NCS)Cd(PPh_3)_2$	B	−34.28	−25.44	8.84
$(Ph_3P)_2Co(NCS)(NCSe)Zn(SeCN)(SCN)$	A	−30.81	−20.51	10.30
$(SeCN)(SCN)Co(NCS)(SeCN)Zn(PPh_3)_2$	B	−34.28	−24.46	9.82
$(py)_2(SCN)_2Co(NCS)_2Hg(PPh_3)_2$	A	−55.50	−28.82	26.68
$(Ph_3P)_2(SCN)_2Co(NCS)_2Hg(py)_2$	B	−46.18	−38.14	8.04
$(SeCN)_2(nia)_2Co(NCSe)_2Hg(PPh_3)_2$	A	−63.18	−27.24	36.14
$(Ph_3P)_2(SeCN)_2Co(NCSe)_2Hg(nia)_2$	B	−49.50	−41.12	8.38
$(SCN)_2(nia)_2Ni(NCS)_2Hg(PPh_3)_2$	A	−60.12	−28.82	31.30
$(Ph_3P)_2(SCN)_2Ni(NCS)_2Hg(nia)_2$	B	−46.24	−42.70	3.54
$(py)_2(SCN)_2Cu(NCS)_2Hg(PPh_3)_2$	A	−56.0	−28.82	27.18
$(Ph_3P)_2(SCN)_2Cu(NCS)_2Hg(py)_2$	B	−46.68	−38.14	8.54
$(nia)_2(SeCN)_2Cu(NCSe)_2Hg(PPh_3)_2$	A	−63.88	−27.24	36.64
$(Ph_3P)_2(SeCN)_2Cu(NCSe)_2Hg(nia)_2$	B	−50.0	−41.12	8.88
$(py)_2(SeCN)_2Zn(NCSe)_2Hg(PPh_3)_2$	A	−59.89	−27.24	32.65
$(Ph_3P)_2(SeCN)_2Zn(NCSe)_2Hg(py)_2$	B	−50.57	−36.56	14.01

A = Probable structure; B = Alternative structure.

of cobalt and mercury in respect of (XII) was higher indicating a greater possibility for this structure, and supporting the observed results [44]. $\Delta TE_n^{\ddagger}$(M—M') values for a number of other complexes have also been calculated and the results are included in Table 14. Higher values of $\Delta TE_n^{\ddagger}$(M—M') have indeed been found in those structures established experimentally.



(XIII)



(XIV)

E. $Co[Ag(SCN)_2]_2$ AND ITS ANALOGS

$Co[Ag(SCN)_2]_2$ is also a bimetallic thiocyanate compound, but is structurally different from $MM'(XCN)_4$. In this compound, the cobalt prefers a tetrahedral and silver a linear [48] coordination geometry. Similarly, in other analogous compounds, e.g. $Co[Cu(SCN)_2]_2$ [50], $Ni[Ag(SCN)_2]_2$ [52], $Co[Ag(SeCN)_2]_2$ [49] and $[NiCu(SCN)_2]_2$ [51], the two metals have a preference for different geometries. This class of bimetallic thiocyanate or selenocyanate is energetically less stable then $CoHg(XCN)_4$, in which both the metals are in tetrahedral coordination geometries. In synthesizing these bimetallic thiocyanates or selenocyanates and their complexes, care was always taken about the choice of solvent. In water or other highly polar solvents, $Co[Ag(SCN)_2]_2$ or its analogs are not formed. Ethylacetate, ethylenedichloride or n-hexane are used to prepare these compounds. In a systematic study it was shown [48] that bases having donor numbers [102] and dielectric constants less than 17 and 36, respectively, do not have any effect on these compounds. Bases having donor numbers in the range 17—30 and dielectric constants below 36, form polymeric bridged complexes and retain the thiocyanate bridge. Bases having donor numbers higher than 30 and dielectric constants less than 36, rupture the thiocyanate bridge and form cationic—anionic complexes. The compounds decompose into AgSCN and $Co(NCS)_2$ in bases with dielectric constants above 36, irrespective of their donor numbers. Dimethylformamide and dimethylsulfoxide which have dielectric constants higher than 36, however, form polymeric bridged complexes when used as ligands in non-polar organic solvents. The Lewis bases which form coordination complexes with $Co[Ag(SCN)_2]_2$, have higher covalent parameters (C_B) than electrovalent (E_B) [103].

$Co[Ag(SCN)_2]_2$, $Co[Cu(SCN)_2]_2$, $Ni[Ag(SCN)_2]_2$ and $Co[Ag(SeCN)_2]_2$

TABLE 15

Cationic—anionic complexes of $M[M'(SCN)_2]_2$ and their spectral data M = Co(II), Ni(II); M′ = Ag(I), Cu(I)

(i) M in octahedral coordination geometry

These complexes are $[Co(anil)_6][Ag(SCN)_2]_2$ [48], $[Co(py)_6][Ag(SCN)_2]_2$ [48], $[Co(nia)_6][Ag(SCN)_2]_2$ [48], $[Co(bipy)_3][Ag(SCN)_2]_2$ [48], $[Co(phen)_3][Ag(SCN)_2]_2$ [48], $[Co(nia)_6][Cu(SCN)_2]_2$ [50], $[Co(py)_6][Cu(SCN)_2]_2$ [50], $[Co(phen)_3][Cu(SCN)_2]_2$ [50], $[Co(bipy)_3][Cu(SCN)_2]_2$ [50], $[Ni(bipy)_3][Ag(SCN)_2]_2$ [52], $[Ni(phen)_3][Ag(SCN)_2]_2$ [52], $[Ni(nia)_6][Ag(SCN)_2]_2$ [52], $[Ni(py)_6][Ag(SCN)_2]_2$ [52], $[Ni(apy)_6][Ag(SCN)_2]_2$ [52], $[Ni(anil)_6][Ag(SCN)_2]_2$ [52], $[Ni(tu)_6][Ag(SCN)_2]_2$ [52], $[Ni(etu)_6][Ag(SCN)_2]_2$ [52], $[Ni(pzd)_6][Ag(SCN)_2]_2$ [52], $[Ni(py)_6][Cu(SCN)_2]_2$ [51], $[Ni(nia)_6][Cu(SCN)_2]_2$ [51], $[Ni(2\text{-}apy)_6][Cu(SCN)_2]_2$ [51], $[Ni(3\text{-}apy)_6][Cu(SCN)_2]_2$ [51], $[Ni(4\text{-}apy)_6][Cu(SCN)_2]_2$ [51], $[Ni(pic)_6][Cu(SCN)_2]_2$ [51], $[Ni(apm)_6][Cu(SCN)_2]_2$ [51], $[Ni(bipy)_3][Cu(SCN)_2]_2$ [51], $[Ni(phen)_3][Cu(SCN)_2]_2$ [51].

(ii) M in tetrahedral coordination geometry

These complexes are $[Co(pic)_4][Cu(SCN)_2]_2$ [50], $[Co(3\text{-}amp)_4][Cu(SCN)_2]_2$ [50], $[Co(4\text{-}apm)_4][Cu(SCN)_2]_2$ [50], $[Co(2\text{-}amp)_2][Cu(SCN)_2]_2$ [50], $[Co(2\text{-}ampy)_2][Cu(SCN)_2]_2$ [50].

(iii) M in square planar coordination geometry

$[Ni(PPh_3)_4][Ag(SCN)_2]_2$ [52].

In these complexes one to two bands are observed due to CN stretching mode in the range 2080—2110 cm^{-1}, one to two bands (CS stretching mode) in the range 720—760 cm^{-1} and one to two bands (NCS bending mode) in the range 420—460 cm^{-1}. *Dq* values of octahedral cobalt complexes are found to be in the range 900—1000 cm^{-1} and those of octahedral nickel complexes in the range 1000—1100 cm^{-1}. μ_{eff} values of octahedral cobalt and nickel complexes are around 5.00 and 3.00 B.M., respectively. *Dq* values of tetrahedral cobalt complexes are in the range 400—500 cm^{-1} and the μ_{eff} values around 4.50 B.M.

TABLE 16

Cationic—anionic complexes of $Co[Ag(SeCN)_2]_2$ and their spectral data [49]

(i) M in octahedral coordination geometry

These complexes are $[Co(nia)_6][Ag(SeCN)_2]_2$, $[Co(py)_6][Ag(SeCN)_2]_2$, $[Co(bipy)_3][Ag(SeCN)_2]_2$, $[Co(phen)_3][Ag(SeCN)_2]_2$.

(ii) M in tetrahedral coordination geometry

These complexes are $[Co(4\text{-}ampy)_4][Ag(SeCN)_2]_2$, $[Co(pic)_4][Ag(SeCN)_2]_2$, $[Co(2\text{-}ampy)_2][Ag(SeCN)_2]_2$, $[Co(ampn)_2][Ag(SeCN)_2]_2$.

In these complexes one to two bands are observed in CN stretching region in the range 2070—2110 cm^{-1}, one band (CSe stretching) in the range 530—560 cm^{-1} and one band (NCSe bending) in the range 380—410 cm^{-1}. *Dq* values of octahedral cobalt complexes are in the range 890—940 cm^{-1} and those of tetrahedral complexes in the range 390—450 cm^{-1}. μ_{eff} values of octahedral and tetrahedral cobalt complexes are around 5.00 and 4.50 B.M., respectively.

TABLE 17

Monomeric bridged complexes of $M[M'(SCN)_2]_2$ and their spectral data

---

(i) M in tetrahedral coordination geometry

$[Ag(SCN)_2]_2 \cdot Co(PPh_3)_2$ [48].

(ii) M in square planar coordination geometry

$[Cu(SCN)_2]_2 \cdot Ni(PPh_3)_2$ [51].

In these complexes two bands are observed each due to CN stretching, CS stretching and NCS bending modes in the ranges 2080—2120 cm^{-1}, 720—760 cm^{-1} and 410—480 cm^{-1}, respectively. *Dq* and μ_{eff} values of cobalt complex are 468 cm^{-1} and 4.46 B.M., respectively.

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have been synthesized, and on the basis of their infrared, electronic spectral and magnetic properties, a zig-zag structure consisting of thiocyanate or selenocyanate bridge has been proposed [48]. This structure was mainly based upon its similarity with the crystal structure [104] of AgSCN.

$M[M'(XCN)_2]_2$ (M = Co(II), Ni(II); M' = Ag(I), Cu(I); X = S, Se) can also be used as Lewis acid similar to $CoHg(XCN)_4$, because the coordination numbers of cobalt or nickel can be raised from four to six. Accordingly a number of bases have been reacted with these Lewis acids and the complexes formed classified in three groups and listed in Tables 15—19 along with their spectral and magnetic moment data.

TABLE 18

Polymeric chain complexes of $M[M'(SCN)_2]_2$ and their spectral data

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(i) M in octahedral coordination geometry

These complexes are $[Ag(SCN)_2]_2 \cdot Co(acet)_2$ [48], $[Ag(SCN)_2]_2 \cdot Co(diox)_2$ [48], $[Ag(SCN)_2]_2 \cdot Co(dmf)_2$ [48], $[Ag(SCN)_2]_2 \cdot Co(dmso)_2$ [48], $[Ag(SCN)_2]_2 \cdot Co(thf)_2$ [48], $[Ag(SCN)_2]_2 \cdot Co(EtOH)_2$ [48], $[Cu(SCN)_2]_2 \cdot Co(diox)_2$ [48], $[Cu(SCN)_2]_2 \cdot Co(thf)_2$ [50], $[Cu(SCN)_2]_2 \cdot Co(dmf)_2$ [50], $[Cu(SCN)_2]_2 \cdot Co(dmso)_2$ [50], $[Cu(SCN)_2]_2 \cdot Co(anil)_2$ [50], $[Ag(SCN)_2]_2 \cdot Ni(diox)_2$ [52], $[Ag(SCN)_2]_2 \cdot Ni(acet)_2$ [52], $[Ag(SCN)_2]_2 \cdot Ni(dmf)_2$ [52], $[Cu(SCN)_2]_2 \cdot Ni(thf)_2$ [51], $[Cu(SCN)_2]_2 \cdot Ni(dmf)_2$ [51], $[Cu(SCN)_2]_2 \cdot Ni(dmso)_2$ [51], $[Cu(SCN)_2]_2 \cdot Ni(diox)_2$ [51].

(ii) M in tetrahedral coordination geometry

These complexes are $[Ag(SCN)_2]_2 \cdot Co$ [48], $[Cu(SCN)_2]_2 \cdot Co$ [50].

In these complexes, two bands are generally observed each due to CN stretching, CS stretching and NCS bending modes in the ranges 2120—2180 cm^{-1}, 720—780 cm^{-1} and 430—470 cm^{-1}, respectively. *Dq* values of octahedral cobalt and nickel complexes are in the ranges 960—980 cm^{-1} and 960—1050 cm^{-1}, respectively. *Dq* values of tetrahedral cobalt complexes are in the range 460—480 cm^{-1}. μ_{eff} values of octahedral cobalt, tetrahedral cobalt and octahedral nickel complexes are around 5.10, 4.40 and 3.00 B.M., respectively.

TABLE 19

Polymeric chain complexes of Co[Ag(SeCN)$_2$]$_2$ and their spectral data [49]

(i) M in octahedral coordination geometry

[Ag(SeCN)$_2$]$_2$ · Co(acet)$_2$, [Ag(SeCN)$_2$]$_2$ · Co(thf)$_2$, [Ag(SeCN)$_2$]$_2$ · Co(dmso)$_2$, [Ag(SeCN)$_2$]$_2$ · Co(anil)$_2$, [Ag(SeCN)$_2$]$_2$ · Co(dmf)$_2$.

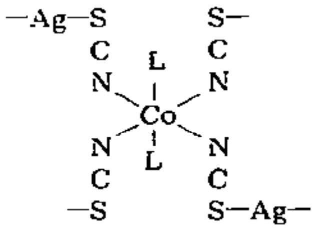
(ii) M in tetrahedral coordination geometry

[Ag(SeCN)$_2$]$_2$ · Co

In these complexes two bands are observed in each CN stretching, CSe stretching and NCSe bending regions in the ranges 2118–2155 cm^{-1}, 570–610 cm^{-1} and 385–420 cm^{-1}, respectively. *Dq* values of octahedral cobalt complexes are in the range 890–900 cm^{-1} and that of tetrahedral complex is 437 cm^{-1}. μ_{eff} values of octahedral cobalt complexes are around 5.00 B.M. Tetrahedral complex possesses the μ_{eff} value of 4.58 B.M.

(i) Polymeric chain complexes

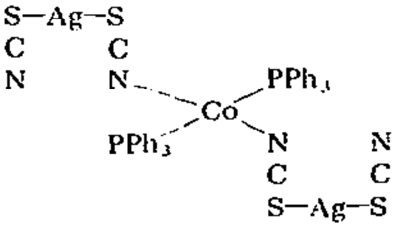
All five Lewis acids, viz., Co[Ag(SCN)$_2$]$_2$, Co[Cu(SCN)$_2$]$_2$, Co[Ag(SeCN)$_2$]$_2$, Ni[Ag(SCN)$_2$]$_2$ and Ni[Cu(SCN)$_2$]$_2$ so far reported, form polymeric chain complexes. Such complexes are formed by weak bases such as ethanol, acetone, tetrahydrofuran, dioxane, dimethylformamide and dimethylsulfoxide. Aniline forms polymeric chain compound with Co[Ag(SeCN)$_2$]$_2$ [49], but a cationic–anionic complex with Co[Ag(SCN)$_2$]$_2$ [48]. These ligands link to cobalt or nickel and raise their coordination number to six. The infrared spectra indicate the presence of only bridged thiocyanate or selenocyanate. The positions of the bands in the $\nu_{CN,\ CX}$, δ_{NCX} regions of these complexes and of the parent Lewis acids are in the same range. This indicates that the basic structure of the parent Lewis acids is not altered. A negative shift is however, observed in the ν_{Co-NCS} mode, due to a change of coordination number from four in the Lewis acid to six in the complexes [71]. The magnetic moments and electronic spectra also support a change in coordination geometry of cobalt or nickel from tetrahedral to octahedral. Various ligands which form these complexes show features of coordination through their donor atoms. On the basis of these results the structure (XV) has been proposed for the complexes.



(XV)

(ii) Dinuclear bridged complexes

These complexes have been reported only for $\mathrm{Co[Ag(SCN)_2]_2}$ [48] and $\mathrm{Ni[Cu(SCN)_2]_2}$ [51]. Triphenylphosphine is the sole ligand which forms such complexes with both Lewis acids. Perhaps the bulky ligand obstructs the formation of a polymeric chain complex, and subsequently dinuclear complexes are formed. The infrared spectra of these complexes indicate the presence of both bridging and S-bonded thiocyanates. The electronic spectra and magnetic moments demonstrate the presence of a tetrahedral coordination geometry for cobalt in $\mathrm{Co[Ag(SCN)_2]_2 \cdot 2\ PPh_3}$, and square planar geometry for nickel in $\mathrm{Ni[Cu(SCN)_2]_2 \cdot 2\ PPh_3}$. In the far infrared region the presence of Co—P and Ni—P is detected. On the basis of these results the structure (XVI) has been proposed.



(XVI)

(iii) Cationic—anionic complexes

These complexes are formed by all five Lewis acids reported so far. The Lewis bases which form such complexes generally have strong base strength. Pyridine and its derivatives, phenanthroline and bipyridine are such ligands. The infrared spectra demonstrate the presence of only S-bonded thiocyanate or selenium bonded selenocyanate. The far infrared region indicates the presence of Co—L or Ni—L bands. The electronic spectra and magnetic moments show that cobalt(II) or nickel(II) are octahedral. On the basis of these observations, a cationic—anionic formula consisting of the cation $[\mathrm{ML_6}]^{2+}$ (M = Co, Ni) and anion $[\mathrm{M'(XCN)_2}]_2{}^{2-}$(M = Ag(I), Cu(I); X = S, Se) has been suggested. In certain cases the cation has a tetrahedral configuration [50,52]. The ligands forming such cations are 4-aminopyridine, picoline and bidentate 2-aminopyridine and 2-aminopyrimidine.

F. COMPARATIVE STABILITY OF LEWIS ACIDS $\mathrm{M[M'(XCN)_2]_2}$ (M = Co, Ni; M' = Ag, Cu; X = S, Se)

The $\mathrm{Co[Ag(SeCN)_2]_2}$ appears more stable than $\mathrm{Co[Ag(SCN)_2]_2}$ in respect of its reaction with certain bases. For instance, aniline, pyridine, dimethylformamide and dimethylsulfoxide cause decomposition of $\mathrm{Co[Ag(SCN)_2]_2}$ into AgSCN and $\mathrm{Co(NCS)_2}$, when added directly in the absence of any non-polar solvent. These ligands, however, do not decompose $Co[Ag(SeCN)_2]_2$ but form well defined complexes. The former is also decomposed by water at room temperature, whereas the latter decomposes only after boiling in water. This indicates that the selenocyanate bridge between Co and Ag is more stable than the thiocyanate bridge. An approach based upon quantitative softness can explain this difference in stability. Adopting the same procedure as above the differences in total softness values of cobalt and silver in $Co[Ag(SCN)_2]_2$ and $Co[Ag(SeCN)_2]_2$ have been derived in the following manner.

$$TE_m^{\ddagger}(\text{Co}) = E_n^{\ddagger}(\text{Co}) + \Sigma E_m^{\ddagger}(\text{NCX}) + \Sigma E_m^{\ddagger}(\text{L})$$

$$TE_n^{\ddagger}(\text{Ag}) = E_n^{\ddagger}(\text{Ag}) + \Sigma E_m^{\ddagger}(\text{XCN})$$

$$\Delta TE_n^{\ddagger}(\text{Co—Ag}) = TE_n^{\ddagger}(\text{Ag}) - TE_n^{\ddagger}(\text{Co}) \ ... \ \text{I}$$

The $\Delta TE_n^{\ddagger}$(Co—Ag) values obtained equal 32.84 for $Co[Ag(SeCN)_2]_2$ and 31.82 for $Co[Ag(SCN)_2]_2$. A higher value for $Co[Ag(SeCN)_2]_2$ is consistent with the greater stability for the selenocyanate bridge, and explains the difference in behaviour of the two in respect of their reaction with various ligands.

The $\Delta TE_n^{\ddagger}$(Co—Ag) values for the complexes $L_2Co[Ag(SCN)_2]_2$ and $L_2Co[Ag(SeCN)_2]_2$ have also been derived and the values are included in Table 20. In each case the $\Delta TE_n^{\ddagger}$(Co—Ag) values are higher for the selenocyanate complexes than for their thiocyanate analogs.

Adopting the same procedure $\Delta TE_n^{\ddagger}$(M—M′) (M = Co(II), Ni(II); M′ = Ag(I), Cu(I)) has been calculated for all the Lewis acids, and tabulated in Table 21. The $\Delta TE_n^{\ddagger}$(M—M′), suggest the following order of stability for these Lewis acids in respect of their reaction with Lewis bases: $Co[Ag(SeCN)_2]_2 > Co[Cu(SCN)_2]_2 > Co[Ag(SCN)_2]_2 > Ni[Cu(SCN)_2]_2 > Ni[Ag(SCN)_2]_2$.

This order is in consonance with the observed results. Triphenylphosphine forms a bridging complex with $Ni[Cu(SCN)_2]_2$ [51] and a cationic—anionic complex with $Ni[Ag(SCN)_2]_2$ [52]. Since the bridge in $Ni[Cu(SCN)_2]_2$ is retained, it can be presumed that it has a more stable bridge compared with $Ni[Ag(SCN)_2]_2$.

TABLE 20

$\Delta TE_n^{\ddagger}$(Co—Ag) values in the complexes $Co[Ag(XCN)_2]_2 \cdot 2L$

Complexes	$\Delta TE_n^{\ddagger}$(Co—Ag) X = Se	$\Delta TE_n^{\ddagger}$(Co—Ag) X = S
$Co[Ag(XCN)_2]_2$	32.84	31.82
$(acet)_2Co[Ag(XCN)_2]_2$	53.94	53.12
$(thf)_2Co[Ag(XCN)_2]_2$	55.80	55.02
$(dmf)_2Co[Ag(XCN)_2]_2$	53.72	53.02
$(dmso)_2Co[Ag(XCN)_2]_2$	54.50	53.80

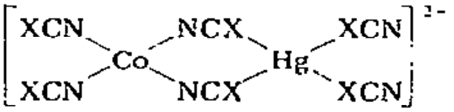
TABLE 21

$\Delta TE_n^{\ddagger}(M-M')$ values in the complexes $M[M'(XCN)_2]_2$

Lewis acids	$TE_n^{\ddagger}(M)$	$TE_n^{\ddagger}(M')$	$\Delta TE_n^{\ddagger}(M-M')$
$Co[Ag(SCN)_2]_2$	51.34	19.08	31.82
$Co[Cu(SCN)_2]_2$	51.34	18.97	32.37
$Co[Ag(SeCN)_2]_2$	51.10	18.26	32.84
$Ni[Ag(SCN)_2]_2$	50.48	19.08	31.40

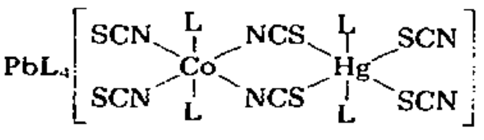
G. TRIMETALLIC THIOCYANATES $Pb[MHg(XCN)_6]$ (M = Co(II), Ni(II); X = S, Se)

Scaife [105] was successful in synthesizing $Hg[M_xZn_{(1-x)}(NCS)_4]$ M = Mn(II), Fe(II), Co(II), Ni(II) and Cu(II), but these were not further studied. We tried to synthesize $M[CoHg(XCN)_6]$ M = Zn(II), Cd(II), Pb(II); X = S, Se, but could only obtain $Pb[CoHg(NCX)_6]$ by direct reaction of three thiocyanates viz., $Hg(XCN)_2$, $Co(XCN)_2$ and $Pb(XCN)_2$ [106—108]. The structure of these Lewis acids has been proposed on the basis of infrared spectral, magnetic moment, electronic spectral and conductance studies. It has been established that lead is in the form of a cation Pb^{2+} and the other species form an anion $[CoHg(XCN)_6]^{2-}$. A bridged structure (XVII) has been proposed for the anion [106].



(XVII)

This compound has also been treated as a Lewis acid, because of the unsaturation in the coordination numbers of cobalt, mercury and lead. Upon reaction with different types of Lewis bases, various complexes have been formed, and are listed in Table 22. In all the complexes whether they are formed with weak bases like tetrahydrofuran, dimethylsulfoxide or strong bases like pyridine, bipyridine, phenanthroline, bridging between cobalt and mercury in the anion is retained and the structure of the Lewis acid and of the complexes remain very similar (XVIII).



(L = bipy, phen)

(XVIII)

Phenanthroline and bipyridine cause cleavage of the thiocyanate bridge in $CoHg(SCN)_4$ and lead to the formation of cationic—anionic complexes [27]. These ligands are, however, unable to cause cleavage of the thiocyanate bridge in $[CoHg(SCN)_6]^{2-}$. This extra stability in case of $[CoHg(SCN)_6]^{2-}$

TABLE 22

Complexes of Pb[MHg(XCN)$_6$] and their spectral data (M = Co, Ni; X = S, Se)

(i) M in octahedral coordination geometry

These complexes are Pb[(dmso)$_2$(SCN)$_2$Co(NCS)$_2$Hg(SCN)$_2$] [106], Pb[(thf)$_2$(SCN)$_2$Co(NCS)$_2$Hg(SCN)$_2$] [106], [Pb(py)$_4$][(py)$_2$(SCN)$_2$Co(NCS)$_2$Hg(SCN)$_2$] [106], [Pb(nia)$_4$][(nia)$_2$(SCN)$_2$Co(NCS)$_2$Hg(SCN)$_2$] [106], [Pb(4-ampy)$_4$][(4-ampy)$_2$(SCN)$_2$Co(NCS)$_2$Hg(SCN)$_2$] [106], [Pb(bipy)$_2$][(bipy)(SCN)$_2$Co(NCS)$_2$Hg(SCN)$_2$(bipy)] [106], [Pb(phen)$_2$][(phen)(SCN)$_2$Co(NCS)$_2$Hg(SCN)$_2$(phen)] [106], Pb[(dmso)$_2$(SeCN)$_2$Co(NCSe)$_2$Hg(SeCN)$_2$] [107], [Pb(py)$_4$][(py)$_2$(SeCN)$_2$Co(NCSe)$_2$Hg(SeCN)$_2$] [107], [Pb(nia)$_4$][(nia)$_2$(SeCN)$_2$Co(NCSe)$_2$Hg(SeCN)$_2$] [107], [Pb(3-ampy)$_4$][(3-ampy)$_2$(SeCN)$_2$Co(NCSe)$_2$Hg(SeCN)$_2$] [107], [Pb(4-ampy)$_4$][(4-ampy)$_2$(SeCN)$_2$Co(NCSe)$_2$Hg(SeCN)$_2$] [107], [Pb(2-ampyd)$_4$][(2-ampyd)$_2$(SeCN)$_2$Co(NCSe)$_2$Hg(SeCN)$_2$] [107], [Pb(bipy)$_2$][(bipy)(SeCN)$_2$Co(NCSe)$_2$Hg(SeCN)$_2$] [107], [Pb(phen)$_2$][(phen)(SeCN)$_2$Co(NCSe)$_2$Hg(SeCN)$_2$] [107], Pb[(dmso)$_2$(SCN)$_2$Co(NCSe)$_2$Hg(SCN)$_2$] [108], [Pb(py)$_4$][(py)$_2$(SCN)$_2$Co(NCSe)$_2$Hg(SCN)$_2$] [108], [Pb(nia)$_4$][(nia)$_2$(SCN)$_2$Co(NCSe)$_2$Hg(SCN)$_2$] [108], [Pb(3-ampy)$_4$][(3-ampy)$_2$(SCN)$_2$Co(NCSe)$_2$Hg(SCN)$_2$] [108], [Pb(4-ampy)$_4$][(4-ampy)$_2$(SCN)$_2$Co(NCSe)$_2$Hg(SCN)$_2$] [108], [Pb(2-ampyd)$_4$][(2-ampyd)$_2$(SCN)$_2$Co(NCSe)$_2$Hg(SCN)$_2$] [108], [Pb(bipy)$_2$][(bipy)(SCN)$_2$Co(NCSe)$_2$Hg(SCN)$_2$] [108], [Pb(phen)$_2$][(phen)(SCN)$_2$Co(NCSe)$_2$Hg(SCN)$_2$] [108], Pb[(dmso)$_2$(SeCN)$_2$Co(NCSe)$_2$Hg(SCN)$_2$] [108], [Pb(py)$_4$][(py)$_2$(SeCN)$_2$Co(NCSe)$_2$Hg(SCN)$_2$] [108], [Pb(nia)$_4$][(nia)$_2$(SeCN)$_2$Co(NCSe)$_2$Hg(SCN)$_2$] [108], [Pb(3-ampy)$_4$][(3-ampy)$_2$(SeCN)$_2$Co(NCSe)$_2$Hg(SCN)$_2$] [108], [Pb(2-ampyd)$_4$][(2-ampyd)$_2$(SeCN)$_2$Co(NCSe)$_2$Hg(SCN)$_2$] [108], [Pb(4-ampy)$_4$][(4-ampy)$_2$(SeCN)$_2$Co(NCSe)$_2$Hg(SCN)$_2$] [108], [Pb(bipy)$_2$][(bipy)(SeCN)$_2$Co(NCSe)$_2$Hg(SCN)$_2$] [108], [Pb(phen)$_2$][(phen)(SeCN)$_2$Co(NCSe)$_2$Hg(SCN)$_2$] [108], Pb[(EtOH)$_2$(SCN)$_2$Ni(NCS)$_2$Hg(SCN)$_2$] [106], Pb[(dmso)$_2$(SCN)$_2$Ni(NCS)$_2$Hg(SCN)$_2$] [106], Pb[(thf)$_2$(SCN)$_2$Ni(NCS)$_2$Hg(SCN)$_2$] [106], [Pb(py)$_4$][(py)$_2$(SCN)$_2$Ni(NCS)$_2$Hg(SCN)$_2$] [106], [Pb(nia)$_4$][(nia)$_2$(SCN)$_2$Ni(NCS)$_2$Hg(SCN)$_2$] [106], Pb[(4-ampy)$_4$][(4-ampy)$_2$(SCN)$_2$Ni(NCS)$_2$Hg(SCN)$_2$] [106], [Pb(bipy)$_2$][(bipy)(SCN)$_2$Ni(NCS)$_2$Hg(SCN)$_2$(bipy)] [106], [Pb(phen)$_2$][(phen)(SCN)$_2$Ni(NCS)$_2$Hg(SCN)$_2$(phen)] [106], Pb[(EtOH)$_2$(SeCN)$_2$Ni(NCSe)$_2$Hg(SeCN)$_2$] [107], Pb[(dmso)$_2$(SeCN)$_2$Ni(NCSe)$_2$Hg(SeCN)$_2$] [107], [Pb(py)$_4$][(py)$_2$(SeCN)$_2$Ni(NCSe)$_2$Hg(SeCN)$_2$] [107], [Pb(nia)$_4$][(nia)$_2$(SeCN)$_2$Ni(NCSe)$_2$Hg(SeCN)$_2$] [107], [Pb(3-ampy)$_4$][(3-ampy)$_2$(SeCN)$_2$Ni(NCSe)$_2$Hg(SeCN)$_2$] [107], [Pb(4-ampy)$_4$][(4-ampy)$_2$(SeCN)$_2$Ni(NCSe)$_2$Hg(SeCN)$_2$] [107], [Pb(2-ampyd)$_4$][(2-ampyd)$_2$(SeCN)$_2$Ni(NCSe)$_2$Hg(SeCN)$_2$] [107], [Pb(bipy)$_2$][(bipy)(SeCN)$_2$Ni(NCSe)$_2$Hg(SeCN)$_2$] [107], Pb(phen)$_2$[(phen)(SeCN)$_2$Ni(NCSe)$_2$Hg(SeCN)$_2$] [107].

(ii) M in tetrahedral coordination geometry

Pb[(SCN)$_2$Co(NCS)$_2$Hg(SCN)$_2$] [106], Pb[(Ph$_3$P)$_2$ Co(NCS)$_2$Hg(SCN)$_4$] [106], Pb[(SeCN)$_2$Co(NCSe)$_2$Hg(SeCN)$_2$] [107], Pb[(SCN)$_2$Co(NCSe)$_2$Hg(SCN)$_2$] [108], Pb[(Ph$_3$P)$_2$Co(NCSe)$_2$Hg(SCN)$_4$] [108], Pb[(SeCN)$_2$Co(NCSe)$_2$Hg(SCN)$_2$] [108].

(iii) M in square planar coordination geometry

Pb[(Ph$_3$P)$_2$Ni(NCS)$_2$Hg(SCN)$_4$] [106].

In all these complexes three to four absorption bands are observed due to CN stretching mode in the range 2030—2170 cm^{-1}. In case of thiocyanate complexes four bands appear in the IR spectra due to CS stretching mode (710—850 cm^{-1}), and for selenocyanate complexes (530—690 cm^{-1}) due to CSe stretching mode. In case of mixed thio-selenocyanate complexes four bands are observed in the range 600—850 cm^{-1} which covers both CS and CSe stretching regions. In all the complexes three to four bands are observed in the range 400—500 cm^{-1} due to CX stretching mode. *Dq* values of octahedral cobalt and nickel complexes are found to be in the ranges 850—1050 cm^{-1} and 860—1100 cm^{-1}, respectively. The μ_{eff} values of octahedral nickel and cobalt complexes are around 3.20 B.M. and 5.00 B.M., respectively. *Dq* values of tetrahedral cobalt complexes are found to be in the range 440—490 cm^{-1} and μ_{eff} values around 4.20 B.M.

has also been explained on the basis of total softness values. The total softness values of cobalt and mercury in $CoHg(SCN)_4$ and $[CoHg(SCN)_6]^{2-}$ have been calculated by adopting the procedure described in preceding paragraphs, and the difference in the total softness values of cobalt and mercury $\Delta TE_n^{\ddagger}$-(Co—Hg) has been derived in both cases. The $\Delta TE_n^{\ddagger}$(Co—Hg) values in case of $CoHg(SCN)_4$ and $[CoHg(SCN)_6]^{2-}$ are 4.43 and 8.84 respectively. The higher value indicates greater stability of the thiocyanate bridge in $[CoHg(SCN)_6]^{2-}$, and explains the difference in behaviour of the two in respect of their interaction with phenanthroline and bipyridine.

H. LIGAND EFFECT. COMPLEXES OF $MM'(XCN)_4$ M = Co(II), Ni(II); M' = Zn(II), Cd(II), Hg(II); X = S, Se

The effect of different ligands on various $MM'(XCN)_4$ has been divided into three groups as mentioned below.

(i) Strong ligands (ethylenediamine, phenanthroline, bipyridine)

Ethylenediamine always forms the cationic—anionic type of complex irrespective of the nature of M and M' in $MM'(XCN)_4$. Bipyridine and phenanthroline also form cationic—anionic type complexes with all types of tetrathiocyanates and selenocyanates with the exception of $MM'(SeCN)_4$ and $MM'(SCN)_2(SeCN)_2$ (M = Co, Ni; M' = Hg) where monomeric bridged complexes are formed.

(ii) Weak ligands (tetrahydrofuran, dioxane, dimethylformamide, dimethylsulfoxide)

They form polymeric bridged complexes with all types of tetrathiocyanates and selenocyanates. These ligands are quite weak and are unable to rupture the thio or selenocyanate bridge of $MM'(XCN)_4$.

(iii) Intermediate ligands (pyridine and their derivatives)

They form polymeric bridged complexes with $CoHg(XCN)_4$ and $NiHg(XCN)_4$—$CoCd(SCN)_4$ and $NiCd(SCN)_4$ form cationic—anionic complexes with these ligands, however, their selenocyanate analogs form monomeric bridged complexes. $CoZn(SCN_4)$ and $CoZn(SeCN)_4$ form cationic—anionic type complexes. $CoCd(SCN)_2(SeCN)_2$ and $NiCd(SCN)_2(SeCN)_2$ form monomeric bridged complexes. Isothiazole and its derivatives also act as bases of intermediate strength. These ligands form polymeric bridged complexes with $MM'(XCN)_4$ (M = Co, Ni; M' = Hg; X = S, Se). With $CoCd(SCN)_4$ and $NiCd(SCN)_4$ they form monomeric bridged complexes, but with their selenocyanate counterpart, polymeric bridged complexes are formed. However, $CoZn(SCN)_4$ and $NiCd(SCN)_4$ form cationic—anionic complexes with the same ligands.

TABLE 23

Relation between base strength of ligands and nature of complexes

Lewis acids	Strong ligands	Weak ligands	Intermediate ligands
$CoHg(SCN)_4$	C.A.	P.B.	P.B.
$CoHg(SeCN)_4$	M.B.	P.B.	P.B.
$CoHg(SeCN)_2(SCN)_2$	M.B.	P.B.	P.B.
$NiHg(SCN)_4$	C.A.	P.B.	P.B.
$NiHg(SeCN)_2(SCN)_2$	M.B.	—	P.B.
$ZnHg(SCN)_4$	—	P.B.	P.B.
$CoPd(SCN)_4$	C.A.	P.B.	M.B.
$NiPd(SCN)_4$	C.A.	P.B.	M.B.
$CdHg(SCN)_4$	—	P.B.	P.B.
$CoCd(SCN)_4$	C.A.	P.B.	C.A.
$CoCd(SeCN)_4$	C.A., M.B.	—	P.B., M.B.
$CoCd(SeCN)_2(SCN)_2$	C.A.	—	M.B.
$NiCd(SCN)_4$	C.A.	P.B.	C.A., M.B.
$NiCd(SeCN)_4$	C.A.	—	M.B., P.B.
$NiCd(SeCN)_2(SCN)_2$	C.A.	—	M.B.
$ZnPd(SCN)_4$	C.A.	P.B.	M.B.
$PdHg(SCN)_4$	C.A.	M.B.	C.A.
$CoZn(SCN)_4$	C.A.	P.B.	C.A.
$CoZn(SeCN)_4$	C.A.	—	C.A.
$CoZn(SeCN)_2(SCN)_2$	C.A.	—	C.A.
$NiZn(SCN)_4$	C.A.	P.B.	C.A.
$NiZn(SeCN)_4$	C.A.	P.B.	C.A.
$NiZn(SeCN)_2(SCN)_2$	C.A.	—	C.A.
$ZnCd(SCN)_4$	C.A.	P.B.	C.A.

C.A. = Cationic—anionic; M.B. = Monomeric bridged; P.B. = Polymeric bridged.

Triphenylphosphine always forms monomeric bridged complexes, probably, due to the presence of bulky phenyl groups which cause steric hindrance. In this case the base strength of the ligands plays a less important role than the steric hindrance factor.

The relation between the nature of the complexes and the nature of the ligands is shown in Table 23.

Double ligand complexes

Certain complexes have been reported [43,44] in which two different ligands are attached to M and M′, respectively. These complexes have been called ‘double ligand complexes’. In such cases the complexes are always of the monomeric bridged type. Bipyridine forms cationic—anionic complexes [40] with $CoM'(SCN)_2(SeCN)_2$ and $NiM'(SCN)_2(SeCN)_2$ (M = Zn, Cd) but when the same ligand reacts with these Lewis acids together with pyridine, monomeric bridged complexes are formed [43] in which bipyridine is coordinated to M and pyridine to M′. This shows that the stability of the —NCX— bridge is increased in such a situation.

Complexes of $M[M'(XCN)_2]_2$ (M = Co(II), Ni(II); M′ = Ag(I), Cu(I); X = S, Se)

These Lewis acids show a slightly different behaviour towards various ligands. Weak bases like dmf, diox, thf, dmso etc., form polymeric bridged complexes, whereas strong and intermediate bases like py, nia, bipy and phen always form cationic—anionic complexes with these Lewis acids. Aniline forms cationic—anionic complex with $Co[Ag(SCN)_2]_2$ and polymeric bridged complex with its selenocyanate analog. $Co[Cu(SCN)_2]_2$ also forms polymeric bridged complex with aniline. This shows that selenocyanate bridge is more stable than thiocyanate, and the bridge in $Co[Cu(SCN)_2]_2$ is more stable than in $Co[Ag(SCN)_2]_2$. Triphenylphosphine always forms monomeric bridged complexes with these Lewis acids. The single chain thiocyanate or selenocyanate bridging between M and M′ appears to be weak in these Lewis acids compared to the bridge in $MM'(XCN)_4$, because even the intermediate ligands cause cleavage of these bridges.

Complexes of $Pb[MHg(XCN)_6]$(M = Co(II), Ni(II); X = S, Se)

In the case of $[CoHg(XCN)_n]^{2-}$ the thio or selenocyanate bridge has extra stability because neither bipy nor phen cause their rupture.

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