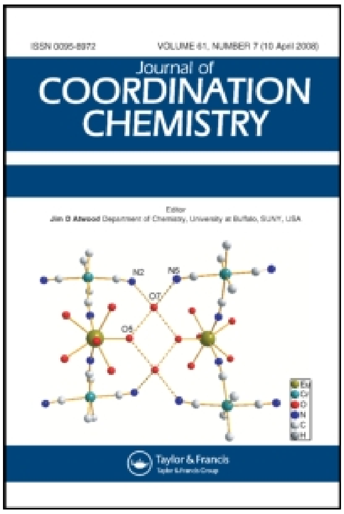

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STUDIES OF BIMETALLIC TETRASELENOCYANATE COMPLEXES OF COBALT, NICKEL, CADMIUM AND MERCURY WITH ISOTHIAZOLE AND ITS DERIVATIVES

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Complexes of the type $MM'(NCSe)_4.xL$ [M = Co(II), Ni(II), M' = Cd(II), Hg(II), L = isothiazole (ist), 4-methylisothiazole (mit), 4-benzylisothiazole (bit) and x = 2,4] have been prepared and characterised by elemental analysis i.r. spectra, electronic spectra and magnetic study. The nature of these complexes has been compared with corresponding tetrathiocyanato complexes. The donor sites of the ligands have been derived from the results of the infrared spectra and have been confirmed by the calculation of softness parameters $E_n^{\ddagger}$. Spectral parameters D_q and B′ are calculated to estimate the ligand field strength and metal–ligand covalency.

INTRODUCTION

In a previous paper, we have reported on the preparation and studies of some tetrathiocyanato complexes of cobalt, nickel, cadmium and mercury with heterocyclic ligands.[1] In this paper, we report the synthesis and study of corresponding tetraselenocyanato complexes.

Since the complexes are insoluble in appropriate solvents for molecular weight and molar conductance determination, the studies are mainly confined to physical properties, i.r. spectra, electronic spectra, magnetic moment values and softness parameters ($E_n^{\ddagger}$).

EXPERIMENTAL

Materials and Manipulation

Absolute ethanol was distilled over CaO to ensure the removal of moisture. Metal nitrates (BDH), isothiazole (ist), 4-methylisothiazole (mit), 4-benzylisothiazole (bit) (Aldrich Chemical Co.) were used as such from fresh bottles. Potassium selenocyanate (Aldrich Chemical Co.) was recrystallised from acetone. All the reactions were carried out in a dry box flushed with nitrogen.

Physical Measurements

Infrared spectra (4000–400 cm^{-1}) of ligands and complexes were recorded on a Perkin-Elmer model 521 recording spectrophotometer. The spectra of the ligands were taken as neat and those of the complexes as KBr discs.

Electronic spectra in solid phase were recorded on Cary-14 recording spectrophotometer in the range 28000–4000 cm^{-1}. The samples were run as Nujol mulls by the technique described by Lee *et al.*[2] Single value for broad and scattered peaks was obtained by the method of Cotton.[3]

Magnetic susceptibility measurements were carried out by the Gouy method using cobalt, mercury tetrathiocyanate as standard. Diamagnetic corrections were also made by using Pascal's constants.

Synthesis of the Complexes

Metal selenocyanates [Metal = Co(II), Ni(II), Cd(II), Hg(II)] were prepared by the reaction between ethanolic solutions of metal nitrates and potassium selenocyanate in 1:2 molar ratio. The reaction mixture was stirred for 15 minutes and the precipitated KNO_3 was filtered out. The filtrate containing metal selenocyanates was used for further reactions.

Ethanolic solutions of $M(NCSe)_2$ [M = Co, Ni] and $M'(NCSe)_2$ [M′ = Cd, Hg] were mixed in 1:1 molar ratio and stirred for 10 minutes. Ethanolic solutions of the ligand in suitable molar ratio were added to the reaction mixture and further stirred for 4 hours. A solid separated in each case, which was filtered, washed well with ethanol and dried in vacuum.

TABLE I
Analytical results

Complexes	Colour	m.p.	Co/Ni		Hg		Nitrogen		Selenium	
		°C	obs.	cal.	obs.	cal.	obs.	cal.	obs.	cal.
1. NiCd$(NCSe)_4$.4ist	Light pink	180 (d)	6.14	6.30	–	–	9.80	10.20	33.50	33.95
2. CoCd$(NCSe)_4$.4ist	Light pink	195 (d)	6.64	6.30	–	–	10.20	10.30	33.20	34.00
3. NiHg$(NCSe)_4$.4ist	Pink	148 (d)	5.28	5.75	18.80	19.60	9.10	9.41	30.12	30.91
4. CoHg$(NCSe)_4$.4ist	Buff	205 (d)	5.15	5.70	18.84	19.70	9.28	9.52	30.53	31.08
5. NiCd$(NCSe)_4$.2mit	Violet pink	145 (d)	7.05	7.71	–	–	8.86	9.02	32.90	33.40
6. CoCd$(NCSe)_4$.2mit	Light pink	148 (d)	7.22	7.70	–	–	9.30	9.10	33.10	33.50
7. NiHg$(NCSe)_4$.2mit	Buff	98 (d)	6.05	6.60	21.40	22.80	7.86	8.20	34.27	34.80
8. CoHg$(NCSe)_4$.2mit	Violet	165 (d)	6.23	6.55	21.90	22.80	7.94	8.31	34.56	34.90
9. NiCd$(NCSe)_4$.bit	Buff	127 (d)	6.03	6.48	–	–	7.48	7.62	32.95	33.38
10. CoCd$(NCSe)_4$.2bit	Light pink	175 (d)	5.98	6.40	–	–	7.16	7.70	33.13	33.50
11. NiHg$(NCSe)_4$.2bit	Buff	130 (d)	5.25	5.72	18.83	19.42	6.82	6.98	29.97	30.58
12. CoHg$(NCSe)_4$.2bit	Buff	172 (d)	5.18	5.80	18.94	19.50	6.94	7.05	30.28	30.69

(d) = decomposed.

Analysis of the Complexes

Complexes were analysed for cobalt, nickel, mercury and selenium by gravimetric methods. Nitrogen was estimated by the semi-micro Kjeldahl method. The analytical results, colour and melting points of all the complexes are presented in Table I.

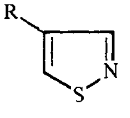
RESULTS AND DISCUSSION

Results have been discussed in following headings:

1) Donor sites in ligands
2) Structure of the complexes
3) Application of softness parameters to the nature of the bridge.

Donor Sites in Ligands

Isothiazole and its methyl and benzyl derivatives have two potential donor site, "nitrogen and sulphur" as shown below:



R = H = isothiazole
R = CH_3 = methyl isothiazole
R = $C_6H_5CH_2$ = benzyl isothiazole

In methyl isothiazole and benzylisothiazole, the γ(C–S) bands are assigned at 710 and 700 cm^{-1}, respectively. These bands show a positive shift of about 10 cm^{-1}, on complex formation. This rules out the possibility of coordination through sulphur end. The γ(N–S) band in case of these ligands is assigned at 605 and 588 cm^{-1} respectively. These bands show a negative shift of 10 cm^{-1} on coordination, which indicates that nitrogen is the donor site (4). In case of isothiazole the situation is slightly different. The γ(C–S) and γ(N–S) bands, which are present at 705 and 590 cm^{-1} respectively, show negative shift of about 10 cm^{-1} on coordination. The negative shift in both the bands indicate, that both sites are involved in coordination in isothiazole.

The involvement of both nitrogen and sulphur in coordination in isothiazole indicates two possibilities, one its behaviour as a bidentate ligand and other of coordination of the two different molecules to two different ions viz. cobalt and mercury in CoHg$(NCSe)_4$. To one of the metal ion it links through nitrogen and to the other metal ion, the second molecule through sulphur. The latter possibility is more likely on account of following reasons.

TABLE II
Softness parameters ($E_n^{\ddagger}$) in ethanol in ev

	Metal ions	$E_n^{\ddagger}$	Ligands	$E_m^{\ddagger}$ N-end	$E_m^{\ddagger}$ S-end
Increasing softness	Ni^{++}	−0.16	Isothiazole	−11.42	−8.32
	Co^{++}	−0.38	4-methylisothiazole	−11.45	−8.37
	Cd^{++}	−2.42	4-benzylisothiazole	−11.52	−8.39
	Hg^{++}	−4.99			

TABLE III
Electronic spectral bands, parameters and magnetic moment values

Complexes	Assignment (cm^{-1})			Dq (cm^{-1})	B′ (cm^{-1})	β	μ_{eff} (B.M.)
	$^4T_{1g} \longrightarrow ^4T_{1g}(P)$	$^4T_{1g} \longrightarrow ^4A_{2g}(F)$	$^4T_{1g} \longrightarrow ^4T_{2g}(F)$				
1. $CoCd(NCSe)_4$.4ist	22280	18800	9800	1000	912	0.93	4.99
2. $CoHg(NCSe)_4$.4ist	21780	19430	10150	1034	929	0.94	4.96
3. $CoCd(NCSe)_4$.2mit	21300	19100	9960	1015	903	0.92	5.06
4. $CoHg(NCSe)_4$.2mit	21940	19250	10260	1029	954	0.97	5.00
5. $CoCd(NCS)_4$.2bit	20900	18860	9680	1003	884	0.90	5.21
6. $CoHg(NCS)_4$.2bit	21100	19040	10100	1016	900	0.91	5.01
	$^3A_{2g} \longrightarrow ^3T_{1g}(P)$	$^3A_{2g} \longrightarrow ^3T_{1g}(F)$	$^3A_{2g} \longrightarrow ^3T_{2g}(F)$				
7. $NiCd(NCSe)_4$.4ist	24120	15000	9120	945	718	0.68	3.16
8. $NiHg(NCSe)_4$.4ist	24400	14940	9020	934	754	0.71	3.12
9. $NiCd(NCSe)_4$.2mit	23680	15100	9460	981	623	0.59	3.01
10. $NiHg(NCSe)_4$.2mit	25000	16600	–	1010	753	0.72	3.00
11. $NiCd(NCSe)_4$.2bit	24500	14860	8940	924	776	0.73	3.04
12. $NiHg(NCSe)_4$.2bit	24800	14800	8880	911	818	0.77	2.98

1) A highly unstable three membered chelate ring will be formed if ligand acts as bidentate ligand.

2) The bidentate behaviour of the ligand will cause both the metal ions to acquire 8 coordination number.

Therefore, the only possibility is of coordination of two molecules of isothiazole through nitrogen to cobalt/nickel and of the remaining two to Cd/Hg through sulphur. Such a possibility is also supported by H.S.A.B. theory[5] Nitrogen being the hard centre of isothiazole will link to comparatively harder metal ions viz. cobalt and nickel and sulphur end being soft will link to soft cadmium or mercury ion. The numerical values of softness of donor centres and metal ions as derived from Klopman's equation[6] are presented in Table II. These values also indicate that N end of isothiazole will have matching with cobalt or nickel and the sulphur end with cadmium or mercury.

Structure of the Complexes

The assignment of the electronic spectral bands, their positions and spectral parameters are presented in Table III. The values of Dq, and B′ have been calculated from ν_3 and ν_2 bands using the matrices of Tanabe and Sugano.[7]

All the complexes are octahedral around cobalt and nickel as is evidenced by the positions of spectral peaks. The weak intensity of ν_2 band may be attributed to the fact that it arises from two electron transition.[8]

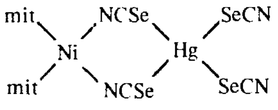
Dq values of these complexes are in the range of octahedral cobalt and nickel. These values are higher than corresponding tetrathiocynate complexes[1] showing that the ligand field strength of the ligands increases in tetraselenocynates. B′ values suggest that metal–ligand bond in tetraselenocynate is more covalent than M–L bond in tetrathiocynates.[1]

Magnetic moment values of these complexes, as presented in Table IV, suggest an octahedral environment around cobalt and nickel which supports the conclusion drawn from electronic spectra. Co(II) complexes have μ_{eff} values higher than the spin only value of cobalt ion suggesting an appreciable contribution of orbital moment towards the magnetic properties of these complexes.

The number and position of i.r. bands in νCN, νCSe and δNCSe region, indicate that there are two types of complexes viz. monomeric bridged and polymeric bridged.[9]

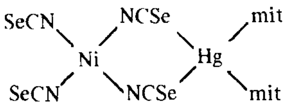
Monomeric Bridged Complex

In NiHg(NCSe)$_4$.2mit, there are three bands in νCN, νCSe and δNCSe region. The number and position of these bands indicate that this particular complex is monomeric bridged in nature and two following structures can be proposed.



STRUCTURE I

mit = 4-methylisothiazole



STRUCTURE II

It is difficult to distinguish between the two structures unless single crystal analysis is made and our attempts to find a conclusive proof could not be materialised as single crystal could not be grown. We have, therefore, been able to extend supports to either of the two structures only by H.S.A.B. theory,

TABLE IV

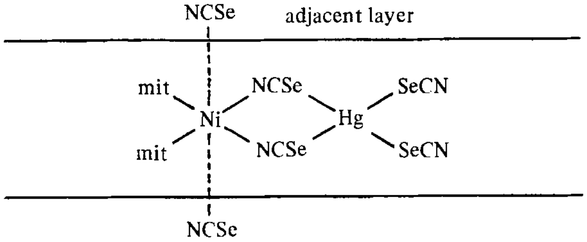
M/M′	$E^{\ddagger}_n(M)$	$E^{\ddagger}_n(M')$	$\Delta E^{\ddagger}_n(M-M')$	Possible nature of the complex
Co/Hg	−0.22	−4.86	4.64	Polymeric
Ni/Hg	−0.28	−4.86	4.58	Bridged
Zn/Hg	−1.29	−4.86	3.57	
Co/Cd	−0.22	−2.27	2.05	Monomeric
Ni/Cd	−0.28	−2.27	1.99	Bridged
Co/Zn	−0.22	−1.29	1.07	Cationic–anionic
Ni/Zn	−0.28	−1.29	1.01	

Structure I has been considered more likely as:

1) mit coordinates through its N end which has more compatibility with nickel as compared to mercury.

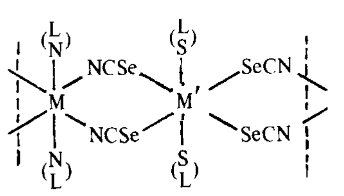
2) It has earlier been shown that the ligand first prefer to coordinate the harder metal ion.[10]

Nickel in this complex is in octahedral environment as is evidenced by the magnetic moment value and electronic spectral bands. Such a geometry is perhaps achieved by axial coordination through the free selenocyanate ends of adjacent layers in solid state as shown in following figure.



Polymeric Bridged Complexes

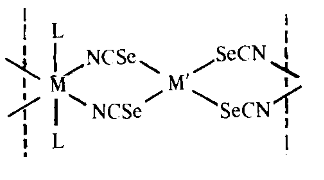
All other complexes are polymeric bridged. The position of νCN, νCSe and δNCSe are in the range of polymeric bridged complexes. Based upon previous observations [11–14] the following structures have been proposed for these complexes.



M = Co, Ni; M' = Cd, Hg

$\binom{L}{N}$ = isothiazole coordinated through nitrogen

$\binom{L}{S}$ = isothiazole coordinated through sulphur.



1. M = Co, M' = Cd, Hg; L = mit, bit
2. M = Ni, M' = Cd; L = mit
3. M = Ni, M' = Cd, Hg; L = bit

Application of the Softness Parameters to the Nature of the Bridge

Selenocyanates and thiocyanates of the type MM'$(NCX)_4$ (X = S,Se) form different type of complexes depending upon the nature of M, M' and ligands. The complexes generally reported are of three types viz. polymeric bridged, monomeric bridged and cationic–anionic. The nature of these complexes was related with the difference in quantitative values of softness of M and M'. These values were derived by adopting quantum mechanical procedure given by Klopman.[6] The difference in softness value "$\Delta E_n^{\ddagger}$(M–M')" as presented in Table IV gave a nice correlation with the nature of the complexes.[15]

The Table IV is applicable only when the reacting base is pyridine or its derivatives. To overcome this limitation, we have developed a new method of calculation which is applicable in general. This method is as follows.

Total softness values of M and M' have been derived by adding the softness values of ligands to them to the reported values of M and M'. The total softness values of M and M' can be given as "$E_n^{\ddagger}$(M) total" and "$E_n^{\ddagger}$(M') total". The difference between total softness value is designated as "$\Delta E_n^{\ddagger}$ total (M'–M)" and is given by the following equation.

$$\Delta E_n^{\ddagger}\ \text{total}\,(M'-M) = [E_n^{\ddagger}M' + \Sigma E_n^{\ddagger}M'_L] - [E_n^{\ddagger}M_L + \Sigma E_n^{\ddagger}M_L]\,\text{ev}$$

where,

$E_n^{\ddagger}M$ and $E_n^{\ddagger}M'$ are softness values of M and M' respectively.

$\Sigma E_n^{\ddagger}M_L$ is the sum of softness values of ligands attached to M.

$\Sigma E_n^{\ddagger}M'_L$ is the sum of softness values of ligand attached to M'.

"$\Delta E_n^{\ddagger}$ total (M'–M)" values and predictions obtained from them are presented in Table V. These values clearly differentiate between cationic–anionic, and bridged complexes. In our complexes, these values come in the range of bridged complexes. It has been found that for octahedral configuration the complex will be cationic–anionic if "$\Delta E_n^{\ddagger}$ total (M'–M)" values are higher than 40 and will be bridged if below 40. These values are very helpful in at least deciding the type of complex i.e. cationic–anionic or bridged in absence of molar conductance data.

Following conculsions are drawn on the basis of above studies:

1) Ligands cause greater ligand field splitting in

TABLE V
Total softness values of the complexes

Complexes	$E_n^{\ddagger}$ Tot.(M′−M)	Cationic–anionic/ Bridged	Ref.
1. $CoCd(NCSe)_4.2mit$	20.86	Bridged	a
2. $CoHg(NCSe)_4.2mit$	18.29	Bridged	a
3. $NiCd(NCSe)_4.2mit$	20.64	Bridged	a
4. $NiHg(NCSe)_4.2mit$	18.07	Bridged	a
5. $CoCd(NCSe)_4.2bit$	21.00	Bridged	a
6. $CoHg(NCSe)_4.2bit$	18.43	Bridged	a
7. $NiCd(NCSe)_4.2bit$	20.78	Bridged	a
8. $NiHg(NCSe)_4.2bit$	18.21	Bridged	a
9. $NiCd(NCSe)_4.4ist$	1.59	Bridged	a
10. $NiHg(NCSe)_4.4ist$	1.37	Bridged	a
11. $CoCd(NCSe)_4.ist$	4.16	Bridged	a
12. $CoHg(NCSe)_4.ist$	3.94	Bridged	a
13. $[Co(nia)_6][Zn(NCSe)_4]$	64.27	Cationic–anionic	15
14. $[Ni(nia)_6][Zn(NCSe)_4]$	64.33	Cationic–anionic	15
15. $[Co(py)_6][Zn(NCSe)_4]$	64.45	Cationic–anionic	15
16. $[Ni(py)_6][Zn(NCSe)_4]$	64.51	Cationic–anionic	15
17. $[Cd(Cpy)_4][Hg(SeCN)_4]$	41.09	Cationic–anionic	15
18. $[Cd(nia)_4][Hg(SeCN)_4]$	40.97	Cationic–anionic	15
19. $[Co(PPh)_{36}][Zn(NCSe)_4]$	64.03	Cationic–anionic	15
20. $[Ni(inh)_6][Zn(NCSe)_4]$	64.09	Cationic–anionic	15
21. $CoHg(NCSe)_4.2cpy$	17.20	Bridged	15
22. $CoHg(NCSe)_4.2nia$	16.52	Bridged	15

nia = Nicotinamide, Cpy = 3-cyanopyridine, inh = isonicotinic acid hydrazide, a = this work.

tetraselenocyanato complexes than in tetrathiocyanato complexes.

2) Metal–ligand bond in tetraselenocyanato compelxes is more covalent than in tetrathiocyanato complexes of corresponding ligands.

3) Steric hinderance of ligands is more prominent in tetraselenocyanate.

4) Ligands having more than one donor site can coordinate to a Lewis acid having more than one accepting centre, through its different donor sites on the principles of H.S.A.B. theory.

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