

Synthesis and Structural Studies of Some Tetrathiocyanate Complexes with Substituted Pyridines as Lewis Bases

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Tetrathiocyanate complexes of the type $CoM(NCS)_4 \cdot xL$ [$M = Zn(II)$, $Cd(II)$ or $Hg(II)$, $L = 2, 3$ and 4 -cyanopyridine (2, 3 and 4-cpy), 2, 3 and 4-aminopyridine (2, 3 and 4-apy), nicotinamide (nia), ethyl nicotinate (ent), or isonicotinic acid hydrazide' (inh) and $x = 2, 4$ or 6] have been prepared and characterized by elemental analysis, molar conductance, magnetic measurements, infrared and electronic spectral studies. The infrared spectral studies and molar conductance data show that the complexes of the type $(CoM(NCS)_4 \cdot 6L$ [$M = Zn(II)$ or $Cd(II)$ and $L = 2, 3$ and 4-cpy, nia, ent, or inh] and $CoZn(NCS)_4 \cdot 2(2-apy)$ are ionic and thiocyanate groups are bonded to zinc or cadmium through nitrogen end. The infrared spectral studies of the complexes of the type $CoHg(SCN)_4 \cdot xL$ [$L = 2, 3$ and 4-apy, 3-cpy, nia or ent and $x = 2$ or 4], show that the thiocyanate groups are bridged. In the complexes $CoHg(SCN)_4 \cdot 4(4-cpy)$ and $CoZn(NCS)_4 \cdot 2L$ ($L = 3$ and 4-apy) both bridging and terminal thiocyanates are present. The colour, magnetic moment data and electronic spectral studies show that in all the complexes cobalt is in octahedral environment except in the complexes of 2, 3 and 4-apy with $CoZn(NCS)_4$ in which it is in tetrahedral environment.

Introduction

In this communication we are presenting the effect of change of metal (M) and ligand on the structure of $CoM(NCS)_4 \cdot xL$ ($M = Zn(II)$, $Cd(II)$, $Hg(II)$ and $L = 2, 3$ and 4-cyanopyridine, ethyl nicotinate, 2, 3 and 4-aminopyridine, nicotinamide, and isonicotinic acid hydrazide). The metal has been varied from a typical class 'b' type of metal (Hg) to class 'a' type of metal (Zn). Cadmium which is at borderline has also been used. Various derivatives of pyridine have been tried as ligands, to see the effect of ligands.

Experimental

Materials and Manipulation

Anhydrous nickel(II) and cobalt(II) halides and nickel(II), cobalt(II), mercury(II), zinc(II) and cad-

mium(II) thiocyanates (Alfa Inorganics) were used after vacuum drying at room temperature. Ethyl nicotinate (ent), 3-cyanopyridine (3-cpy) and 2-cyanopyridine (2-cpy) (Aldrich Chemicals) were purified by distilling under reduced pressure. Nicotinamide (nia), 4-cyanopyridine (4-cpy), 2-aminopyridine (2-apy), 3-aminopyridine (3-apy), 4-aminopyridine (4-apy) and isonicotinic acid hydrazide (inh) (Aldrich Chemicals) were used after recrystallisation from ethanol. All the solvents were strictly dried before use.

Synthesis of the Complexes

$CoZn(NCS)_4 \cdot 4THF$

5 mmol of anhydrous cobalt(II) chloride and 10 mmol of zinc(II) thiocyanate were separately dissolved in 20 ml and 40 ml of freshly distilled tetrahydrofuran respectively. The above solutions were mixed together and stirred for 12 hr. A pink solid was formed, which was filtered quickly, washed with solvents several times and dried in vacuum.

$CoZn(NCS)_4 \cdot 2L$ ($L = 2-apy, 3-apy$ or $4-apy$)

5 mmol of $CoZn(NCS)_4 \cdot 4THF$ was dissolved in 70 ml of dry ethanol and 10 mmol of ligand was added slowly. A violet complex with 4-apy and blue complexes with 2 and 3-apy were formed after overnight stirring. The complexes were filtered, washed with dry ether and finally dried in vacuum at room temperature. The complexes were recrystallised from ethanol.

$CoZn(NCS)_4 \cdot 6L$ ($L = nia, ent, inh, 2-cpy, 3-cpy$ or $4-cpy$)

18 mmol of $CoZn(NCS)_4 \cdot 4THF$ was dissolved in 150 ml dry ethanol. This solution was divided into six parts and kept in six different flasks. To each flask, a 25 ml solution or suspension of ligand (18 mmol) was added separately. In the case of 'nia', pink complex was separated after 2 hours' stirring whereas in the case of 2-cpy, 3-cpy and 'inh', the complexes were formed after overnight stirring. In the case of 4-cpy and 'ent', red solutions were obtained after 2 hr and overnight stirring respectively. The solutions were concentrated and left for 8 hr when bright red crystals separated in the case of 4-cpy and a pink complex was

TABLE I. Analytical and Molar Conductance Data.

Complexes	Colour	M.P. (°C)	% Cobalt		% Cobalt and Zinc		% Mercury		% Thiocyanate		% Sulphur		Molar Conductance (cm ² mhos/mol) M/512 M/1024	Ionic Nature
			calc.	obs.	calc.	obs.	calc.	obs.	calc.	obs.	calc.	obs.		
CoZn(NCS) ₄ ·6(2cpy)	Pink	185	—	—	12.6	12.2	—	—	23.6	23.0	—	—	—	—
CoZn(NCS) ₄ ·6(3cpy)	Pink	180	—	—	12.6	12.1	—	—	23.6	23.0	69.2	104.2	69.2	1:1
CoZn(NCS) ₄ ·6(4cpy)	Pink	177(d) ^a	—	—	12.6	12.1	—	—	23.6	23.1	57.6	89.0	57.6	1:1
CoZn(NCS) ₄ ·6(nia)	Pink	133(d)	—	—	11.4	11.0	—	—	21.3	21.2	54.6	88.9	54.6	1:1
CoZn(NCS) ₄ ·6(ent)	Pink	80	—	—	9.8	9.7	—	—	18.9	18.2	58.9	93.9	58.9	1:1
CoZn(NCS) ₄ ·6(inh)	Pink	110(d)	—	—	10.5	10.2	—	—	19.7	19.1	59.3	85.8	59.3	1:1
CoZn(NCS) ₄ ·2(2apy)	Blue	135	—	—	22.8	22.1	—	—	42.6	42.1	54.2	95.3	54.2	1:1
CoZn(NCS) ₄ ·2(3apy)	Blue	182	—	—	22.8	22.2	—	—	42.6	42.0	18.8	22.7	18.8	—
CoZn(NCS) ₄ ·2(4apy)	Violet	140(d)	—	—	22.8	22.0	—	—	42.6	42.1	17.8	21.5	17.8	—
CoHg(SCN) ₄ ·2(3cpy)	Pink	192(d)	8.4	8.1	—	—	28.6	28.0	—	—	18.3	18.0	—	—
CoHg(SCN) ₄ ·4(4cpy)	Pink	180(d)	6.5	6.2	—	—	22.0	22.0	—	—	14.1	13.9	16.7	—
CoHg(SCN) ₄ ·2(2apy)	Pink	250(d)	8.7	8.5	—	—	29.4	29.0	—	—	18.8	18.1	—	—
CoHg(SCN) ₄ ·2(3apy)	Pink	220(d)	8.7	8.5	—	—	29.4	29.1	—	—	18.8	18.2	—	—
CoHg(SCN) ₄ ·2(4apy)	Pink	142(d)	8.7	8.4	—	—	29.4	28.9	—	—	18.8	18.0	14.6	—
CoHg(SCN) ₄ ·2(ent)	Pink	165(d)	7.7	7.2	—	—	25.2	24.9	—	—	16.1	15.9	—	—
CoHg(SCN) ₄ ·4(nia)	Pink	270	6.0	6.0	—	—	20.4	19.9	—	—	13.1	12.9	—	—
CoCd(NCS) ₄ ·6(nia)	Pink	185	5.2	5.0	—	—	—	—	—	—	11.3	11.0	70.2	98.3
CoCd(NCS) ₄ ·6(3cpy)	Pink	160	5.7	5.1	—	—	—	—	—	—	12.5	12.0	59.7	89.8

^a d = decomposes.

isolated in the case of 'ent' after adding n-hexane. 'nia', 4-cpy, and 'ent' complexes were recrystallised from ethanol. 2-cpy complex was insoluble in common organic solvents hence it could not be recrystallised.

CoHg(SCN)₄·xL (L = 3 and 4-cpy, nia, ent, 2,3 and 4-apy and x = 2 or 4)

Seven suspensions of 3 mmol of CoHg(SCN)₄·2THF¹ in 60 ml dry ethanol were made separately, and to each of them ligands (18 mmol) were added slowly. The reaction mixtures were stirred for 12–14 hr. A pink solid was obtained in each case. All the complexes were filtered, washed with solvents and finally with dry ether and dried in vacuum at room temperature. The complexes of 4-cpy, 4-apy and 'nia', were soluble in acetone and ethanol, and were recrystallised from these solvents. The complexes of the remaining ligands were insoluble in common organic solvents hence they could not be recrystallised.

CoCd(NCS)₄·6L (L = nia or 3-cpy)

15 mmol of anhydrous cobalt(II) thiocyanate and 15 mmol of cadmium(II) thiocyanate were separately dissolved in 20 ml and 30 ml dry ethanol respectively and mixed together. The whole reaction mixture was stirred at room temperature for 8 hr. A blue solution of CoCd(NCS)₄ was obtained which was divided into two parts. To the two solutions, 45 mmol of each ligand in 25 ml dry ethanol, was separately added and the reaction mixtures were stirred at room temperature for 12–16 hr. when pink complexes were formed. The complexes were filtered, washed with dry ether and dried in vacuum. The complexes of 'nia' and 3-cpy were recrystallised with acetone and ethanol respectively.

Analysis of the Complexes

The complexes were analysed for thiocyanate by Volhard's method² using ferric alum as an indicator. Sulphur was analysed as sulphate, cobalt and zinc as mixed anthranilate² and mercury as sulphide. The analytical data are presented in Table I.

Molar Conductance Measurements

The molar conductance of the complexes were measured in ethanol and acetone by a Philips-PR 9500 conductivity bridge. These data are given in Table I.

Infrared Spectra

The infrared spectra in the region 4000–200 cm⁻¹ were recorded on a Perkin-Elmer 621 spectrophotometer equipped with CsI optics. The spectra of the complexes were recorded as nujol mulls and that of ligand in solution as well.

Visible and Near Infrared Absorption Spectra

The spectra of the complexes were recorded in the region 1700–330 mμ on a Cary-14 spectrophoto-

meter using alcohol or acetone as solvent in cells of 1 cm light path. The single values for broad and scattered peaks were obtained by the centre of gravity method.

Magnetic Susceptibility Measurements

The measurements were made at room temperature by Gouy's method using cobalt mercury tetrathiocyanate as standard. The diamagnetic corrections were also made by using Pascal's constants.

Results and Discussions

On the basis of the structure of the complexes, we have divided our infrared discussions in three groups but all the infrared spectral band assignments are contained in Table II.

Cationic-Anionic Complexes

The examples of this group of complexes are: CoM(NCS)₄·6L, where M = Zn(II) or Cd(II), and L = 2, 3 and 4-cpy, nia, ent or inh.

Thiocyanate ion has three fundamental vibrational modes, which are C–N stretching, C–S stretching and NCS bending. The nature of thiocyanate bonding in a complex can be established with the help of the position of the bands due to these three modes.

The position of C–N stretching frequency in nitrogen bonded thiocyanate (M–NCS) falls in the region 2040–2080 cm⁻¹ and in sulphur bonded (M–SCN) in the region 2080–2120 cm⁻¹. For bridging thiocyanate groups (M–SCN–M'), the C–N stretching frequency falls generally in the region 2120–2180 cm⁻¹.^{3–5} The infrared results of our complexes show the presence of the bands due to C–N stretching mode, in the region 2010–2075 cm⁻¹, which is indicative of N-bonded thiocyanate groups⁶.

The second mode which is useful in establishing the bonding nature of thiocyanate, is the C–S stretching. Lewis and co-workers⁷ reported the band near 700 cm⁻¹ as indicative of S-bonding while those near 800–830 cm⁻¹ of N-bonding. On the other hand Turco and Pecile⁸ have suggested the range 690–720 cm⁻¹ for S-bonding and 780–860 cm⁻¹ for N-bonding. In our complexes, we observe C–S stretching bands in the region 750–878 cm⁻¹, which also indicates that the thiocyanate groups are nitrogen bonded.

The third important region which is useful for diagnosis of the type of bonding is NCS bending. Sabatini *et al.*^{9,10} and Lewis and co-workers⁷ have suggested the range 460–490 cm⁻¹ for isothiocyanate bonding (M–NCS) and the range 410–440 cm⁻¹ for thiocyanate bonding (M–SCN). In our complexes, these bands are observed in the region 445–490 cm⁻¹, which finally shows that thiocyanates are nitrogen bonded.

TABLE II. Infrared Spectral Assignments of Thiocyanate Vibrations.^a

Complexes	C–N (st)	C–S (st)	NCS (bend)	M–NCS (st)	M–L (st)	Hg–S (st)
CoZn(NCS) ₄ ·6(2cpy)	2065(b), 2040(sh)	878(s), 805(s) 750(s)	480(s), 465(s)	–	265(s)	–
CoZn(NCS) ₄ ·6(3cpy)	2075(s), 2040(sh)	810(s), 790(m)	490(s), 480(s)	–	270(sh)	–
CoZn(NCS) ₄ ·6(4cpy)	2055(s), 2010(sh)	865(sh), 790(m)	480(s), 460(s)	–	270(b)	–
CoCd(NCS) ₄ ·6(3cpy)	2055(s), 2010(sh)	880(sh), 800(s) 785(m)	480(m), 470(m)	–	280(sh)	–
CoZn(NCS) ₄ ·6(ent)	2050(b), 2010(sh)	870(sh), 850(sh) 830(m)	490(b), –	–	265(w)	–
CoZn(NCS) ₄ ·6(inh)	2065(s)	845(m)	472(s), –	285(sh)	308(s) 270(m)	–
CoZn(NCS) ₄ ·2(2apy)	2060(s), 2010(sh)	865(w), 773(s)	485(s), 445(m)	–	275(m)	–
CoZn(NCS) ₄ ·6(nia)	2060(s), 2010(sh)	870(s), 820(sh) 790(s)	475(s), 465(sh)	–	280(sh)	–
CoHg(SCN) ₄ ·2(3cpy)	2130(s), 2010(sh)	788(w), 718(s)	465(m), 450(s)	–	260(w)	230(w)
CoHg(SCN) ₄ ·4(4cpy)	2150(s), 2122(s) 2010(sh)	790(w), 720(s)	470(s), 450(s)	–	265(w)	230(sh)
CoHg(SCN) ₄ ·2(ent)	2130(s)	720(sh)	470(s), 448(s)	–	275(w)	230(w)
CoHg(SCN) ₄ ·4(nia)	2130(s), 2010(sh)	795(sh), 750(w)	465(m), 450(m)	–	280(sh) 260(sh)	220(sh)
CoZn(NCS) ₄ ·2(3apy)	2100(s), 2080(sh) 2020(sh)	845(sh), 800(sh) 725(m)	485(s), 445(s)	–	285(sh)	–
CoZn(NCS) ₄ ·2(4apy)	2110(sh), 2080(s) 2020(sh)	845(s), 810(s) 725(s)	490(s), 452(b)	–	275(sh)	–
CoHg(SCN) ₄ ·2(2apy)	2125(s)	788(s), 760(sh) 715(s)	470(s), 448(s)	–	270(sh)	210(w)
CoHg(SCN) ₄ ·2(3apy)	2120(s), 2010(sh)	748(sh), 715(s)	468(s), 445(s)	–	270(w)	210(sh)
CoHg(SCN) ₄ ·2(4apy)	2120(s), 2020(sh)	770(b), 720(s)	470(sh), 455(s)	–	270(m)	220(w)

^a s = strong, sh = shoulder, m = medium, b = broad, w = weak

On comparing the spectrum of the ligands with that of the complexes, we observe positive shifts in the bands of ring vibrations, which clearly shows the involvement of ring nitrogen in coordination^{11–15}. All the other possible donor sites remain unaffected. Isonicotinic acid hydrazide is the only exception, where we observe a negative shift of 37 cm⁻¹ in the carbonyl

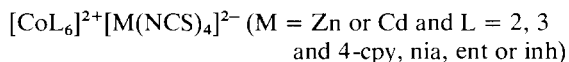
stretching frequency indicating the involvement of carbonyl oxygen in coordination. The bands of ring vibrations and NH stretching frequency are undisturbed.

The molar conductance data as presented in the Table I, show that these complexes are 1 : 1 electrolytes. The electronic spectra as discussed latter, the pink colour and the magnetic moment values (Table III)

TABLE III. Selected Electronic Bands, Spectral Parameters and Magnetic Moment Data.

Complexes	ν_3 (cm ⁻¹)	ν_2 (cm ⁻¹)	ν_1 (cm ⁻¹)	Dq (cm ⁻¹)	B' (cm ⁻¹)	β	μ_{eff} (B.M.)
CoZn(NCS) ₄ ·6(2cpy)	22100	–	9610	961	–	–	4.98
CoZn(NCS) ₄ ·6(4cpy)	20700	16800	9000	897	935	0.95	5.03
CoZn(NCS) ₄ ·6(nia)	20190	–	8880	888	–	–	4.99
CoZn(NCS) ₄ ·6(ent)	20490	16800	9009	903	932	0.94	5.00
CoHg(SCN) ₄ ·2(ent)	21730	–	9910	991	–	–	5.12
CoHg(SCN) ₄ ·2(3cpy)	21800	–	8930	893	–	–	5.08
CoHg(SCN) ₄ ·4(4cpy)	21500	–	9860	986	–	–	5.06
CoHg(SCN) ₄ ·2(4apy)	20490	–	8920	892	–	–	5.11
CoCd(NCS) ₄ ·6(3cpy)	20360	–	8840	884	–	–	5.04
CoCd(NCS) ₄ ·6(nia)	21740	–	9970	997	–	–	5.07
CoZn(NCS) ₄ ·2(2apy)	16200	7540	–	439	704	0.67	4.63
CoZn(NCS) ₄ ·2(3apy)	16600	6450	–	370	794	0.75	4.65
CoZn(NCS) ₄ ·2(4apy)	16800	6710	–	386	795	0.75	4.66

show that cobalt in these complexes is in octahedral field. On the basis of these results, we suggest that the complexes are cationic-anionic type in which cobalt with six ligands forms the cation and the zinc or cadmium with four thiocyanates, forms the anion:



Octahedral Bridged Complexes

The examples of this class of compounds are $\text{CoHg}(\text{SCN})_4 \cdot 2\text{L}$, ($\text{L} = 2, 3$ and $4\text{-apy, } 3\text{-cpy}$ or ent); $\text{CoHg}(\text{SCN})_4 \cdot 4\text{L}$, ($\text{L} = \text{nia}$ or 4-cpy).

In this class of compounds the bands due to C–N stretching, C–S stretching and NCS bending modes are present in the region 2120–2150, 715–795 and 445–470 cm^{-1} respectively, which show the presence of only bridging thiocyanates^{16,17}. Since only bridging thiocyanates are present a polymeric structure as shown in Figure 1 can be suggested. The two ligands have been attached to cobalt in order to bring it in octahedral configuration. The analytical data of nicotinamide complex show the presence of four nicotinamide per $\text{CoHg}(\text{SCN})_4$. The two extra ligands in this complex have been attached to mercury as shown in Figure 3. In this complex, therefore, both mercury and cobalt acquire an octahedral configuration.

The complex of 4-cyanopyridine is the only exception of this class, where three bands at 2150, 2122 and 2010 cm^{-1} are present in the C–N stretching region. The number and position of these bands show the presence of both terminal and bridged thiocyanates^{1,16,17,18}. Since terminal thiocyanates are also pres-

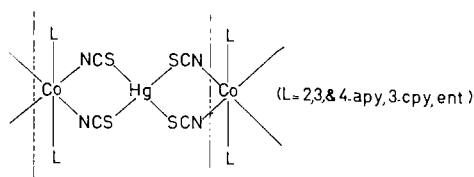


Figure 1

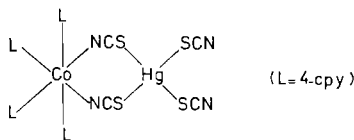


Figure 2

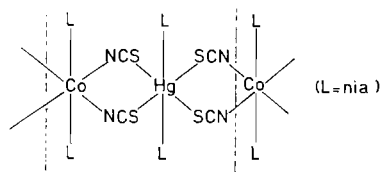


Figure 3

ent in this compound, a non-polymeric structure similar to the Figure 2 can be suggested. In this case all the four ligands have been attached to cobalt to bring it in octahedral configuration. All the ligands show features of coordination through ring nitrogen.

Tetrahedral Bridged and Cationic-Anionic Complexes

The examples of this group of complexes are $\text{CoZn}(\text{NCS})_4 \cdot 2\text{L}$, ($\text{L} = 2, 3$ and 4-apy).

The infrared spectra of the complexes of 3- and 4-apy with $\text{CoZn}(\text{NCS})_4$ show two bands around 2100 cm^{-1} and a shoulder band at 2020 cm^{-1} , due to C–N stretching mode. The presence of these bands clearly indicated the presence of two types of thiocyanate groups in these complexes. The C–N stretching band appearing at higher wavenumber is due to the bridging SCN group and the other at lower wavenumber is due to the terminal SCN group^{17,19}. The C–S stretching and NCS bending modes are also well in the range of the complexes having bridged and terminal thiocyanate groups. The non-conducting nature of these complexes also supports a bridged structure. The ligands show features of coordination through pyridyl nitrogen. The electronic spectra, Bohr magneton values and blue or violet colours of the complexes show that cobalt is in tetrahedral configuration. On the basis of these results, we can suggest that these complexes have two bridging and two terminal thiocyanate groups. The two ligands have been attached to cobalt to bring it in tetrahedral configuration as shown in figure 4.

2-aminopyridine shows a different behaviour. It acts as a bidentate ligand, as the ligand shows features of coordination through pyridyl nitrogen and the nitrogen of the amino group. This complex has a molar conductance value equivalent to a 1:1 electrolyte. The position of the bands due to C–N stretching, C–S stretching and NCS bending modes show the presence of only nitrogen bonded thiocyanates. On the basis of these results, a cationic-anionic structure, in which cobalt with two bidentate ligands will form the cation and zinc with four thiocyanate groups will form anion, can be suggested:



Cobalt in this case is also in tetrahedral configuration. Tetrahedral complexes of cobalt with bidentate ligands are uncommon²⁰.

M–L and M–NCS (or M–SCN) Vibrations

A band at 300–310 cm^{-1} has been assigned to Co–NCS stretching mode in tetrahedral environment by

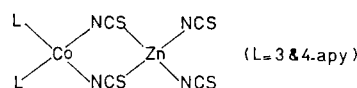


Figure 4

Forster and Goodgame²¹. This band is absent and a new band at about 260–275 cm^{-1} is present in all our complexes. This band could be due to the Co–NCS stretching mode or to the Co–N(ring) stretching mode in octahedral environment. Recently Nakamoto and co-workers²² have assigned Co–N(ring) stretching mode at 266 cm^{-1} and at 228 cm^{-1} in octahedral pyridine complex whereas Rivest *et al.*¹ and Strukl²³ have assigned this mode at 260 cm^{-1} and at 270 cm^{-1} in their bipyridine complexes. Likewise, we assign this band to Co–N(ring). This band is probably overlapped with the bands due to M–NCS stretching mode as it also appears in the same region.

In the isonicotinic acid hydrazide complex with $\text{CoZn}(\text{NCS})_4$ the band at 285 cm^{-1} is assigned to the Zn–NCS stretching mode and shoulder bands at 308 and at 270 cm^{-1} to the Co–O stretching mode²⁴. The bands in the region 210–230 cm^{-1} are assigned to the Hg–S stretching mode similar to the assignments given by Rivest *et al.*¹

Discussion of Electronic Spectra

While suggesting a structure to the complexes on the basis of infrared spectral results, we have assumed tetrahedral configuration to all aminopyridine complexes of $\text{CoZn}(\text{NCS})_4$ and octahedral to the rest of them. To confirm these configurations, we have studied electronic spectra of these two types of complexes.

In octahedral cobalt(II) complexes, three transitions, namely ${}^4\text{T}_{1g} \rightarrow {}^4\text{T}_{2g}$ (ν_1), ${}^4\text{T}_{1g} \rightarrow {}^4\text{A}_{2g}$ (ν_2) and ${}^4\text{T}_{1g} \rightarrow {}^4\text{T}_{1g}(\text{P})$ (ν_3) are possible. Out of which, absorption bands due to ν_1 and ν_3 are generally observed. The ν_1 is generally broad and ν_3 is a multiple band and may be mixed with spin forbidden transition. The ν_2 is normally not observed, being formally a two electron transition.

Out of ten octahedral complexes, we observe all the three bands in $\text{CoZn}(\text{NCS})_4 \cdot 6(4\text{-cpy})$ and $\text{CoZn}(\text{NCS})_4 \cdot 6(\text{ent})$. The bands due to ν_1 is observed in the region 9000–9009 cm^{-1} , the one due to ν_2 at about 16800 cm^{-1} and that due to ν_3 in the region 20490–21500 cm^{-1} . The ν_1 is broad, ν_2 is weak and ν_3 a multiplet. Using the values of ν_2 and ν_3 , we have calculated Dq, B' and β values of these complexes with the help of matrices of Tanabe and Sugano. The 10 Dq value so obtained is equal to the position of ν_1 , which shows that our assignment of ν_2 is correct.

In all other complexes ν_2 is not observed; but ν_3 with multiplet and a weak band due to ν_1 are observed. The Dq values of these complexes have been derived from the position of ν_1 .

The values of various spectral parameters are well in the range of cobalt(II) in octahedral field. The magnetic moment values and colours of the complexes are typical of cobalt(II) in octahedral configuration.

All aminopyridine complexes with $\text{CoZn}(\text{NCS})_4$ are blue or violet in colour and have magnetic moment values of about 4.6 B.M. Their electronic spectra show

the presence of intense bands in the regions 16200–16800 and 6450–6710 cm^{-1} which arise from the transitions ${}^4\text{A}_{2g} \rightarrow {}^4\text{T}_{1g}(\text{P})$ (ν_3) and ${}^4\text{A}_{2g} \rightarrow {}^4\text{T}_{1g}(\text{F})$ (ν_2) respectively. The absorption band ν_2 splits into triplets which are characteristic of cobalt(II) in tetrahedral environment having C_{2v} symmetry²⁵. With the help of the positions of ν_2 and ν_3 bands, the Dq, B' and β values have been calculated. The position of bands and the values of spectral parameters are typical of cobalt(II) in tetrahedral environment²⁶.

The electronic spectral results support the various structures that we have proposed for the complexes. On the basis of infrared and electronic spectral results, we have derived certain conclusions which are presented below in the form of postulates.

Postulates

(i) In tetrathiocyanates of the type $\text{MM}'(\text{NCS})_4$ the thiocyanates are bridged between M and M'. When both M and M' belong to class 'a' type of metal, the bridging is weak and when one of the two changes to class 'b' type, the bridging becomes strong. To the former type of tetrathiocyanates we shall refer to as 'aa' type and to the latter as 'ab' type. $\text{CoZn}(\text{NCS})_4$ will, therefore, belong to 'aa' type and $\text{CoHg}(\text{SCN})_4$ to 'ab' type.

On reaction with a Lewis base, which coordinates with cobalt, the thiocyanate bridging breaks up more easily in 'aa' type than in the 'ab' type tetrathiocyanates, e.g. pyridine, nicotinamide, ethyl nicotinate, 3- and 4-cyanopyridine break the bridging in $\text{CoZn}(\text{NCS})_4$ and form cationic–anionic complexes of the type $[\text{CoL}_6]^{2+}[\text{Zn}(\text{NCS})_4]^{2-}$ (L = py, nia, 3 and 4-cpy)^{6,27}. The same ligands, however, are unable to break the bridging in $\text{CoHg}(\text{SCN})_4$ and form bridging complexes as shown in figures 1, 2 and 3. The examples are $\text{CoHg}(\text{SCN})_4 \cdot 2\text{L}$ (L = py, ent, 3-cpy)^{1,27}; $\text{CoHg}(\text{SCN})_4 \cdot 4\text{L}$ (L = nia, 4-cpy)^{1,27}.

(ii) The 'ab' type tetrathiocyanates generally have the tendency to form a long stable chain, whereas the chain of 'aa' type of tetrathiocyanates is weak. When two ligands coordinate to cobalt in 'ab' type, the chain does not break up and cobalt acquires an octahedral configuration (Figure 1). In the 'aa' type of tetrathiocyanates the chain breaks up when the ligands get attached to cobalt. Thus cobalt acquires a tetrahedral configuration with the same number of ligands (Figure 4). 3- and 4-aminopyridine form octahedral bridged complexes with $\text{CoHg}(\text{SCN})_4$ which belong to the 'ab' type and tetrahedral bridged complexes with $\text{CoZn}(\text{NCS})_4$, which is the 'aa' type tetrathiocyanate.

(iii) The nature of bonding in tetrathiocyanate also depends very much upon the basicity of ligands. When the ligand is weak, the bridging in tetrathiocyanates of both types is preserved. Tetrahydrofuran is a weak ligand, hence the reported complexes of tetrahydrofuran are bridging, e.g., $\text{CoHg}(\text{SCN})_4 \cdot 2\text{THF}$ ¹, CoZn

(NCS)₄·4THF, NiZn(NCS)₄·4THF and NiCd(NCS)₄·4THF⁶.

In the case of strong ligands like phenanthroline, bipyridine and ethylenediamine, the thiocyanate bridging in both types is destroyed and cationic-anionic type of complexes are formed, e.g., [Co(LL)]²⁺[M(NCS)₄]²⁻ (LL = bipy, phen, en and M = Zn(II) or Hg(II))^{1,6}.

It is very difficult to comment about the ligands which are of intermediate strength. The 'ab' type of tetrathiocyanates will generally form octahedral bridged complexes with them, whereas 'aa' type will form tetrahedral bridged or cationic-anionic types of complexes.

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