

Synthesis and Structural Studies of Some Tetrathiocyanate Complexes with Pyrazine Derivatives as Lewis Bases

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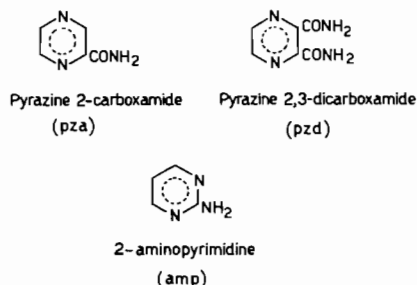
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Complexes of $\text{CoM}(\text{NCS})_4$ and $\text{NiM}(\text{NCS})_4$ ($M = \text{Zn, Cd, Hg}$) with pyrazine 2-carboxamide (pza), pyrazine 2,3-dicarboxamide (pzd) and 2-aminopyrimidine (amp), have been prepared and characterized by elemental analysis, molar conductance, magnetic measurements, infrared and electronic spectral studies. On the basis of these studies the complexes have been divided into three groups, viz. (i) cationic–anionic type, (ii) polymeric bridging type, and (iii) monomeric bridging type.

Introduction

In our recent communication¹ we have studied the structure of certain complexes of $\text{CoM}(\text{NCS})_4$ ($M = \text{Zn, Hg}$) with pyridine derivatives. To see the effect of change of ligands on the bonding mode of tetrathiocyanate we now present the structural discussion of the complexes of $\text{CoM}(\text{NCS})_4$ and $\text{NiM}(\text{NCS})_4$ with the following ligands:



Experimental

Synthesis of the Complexes

Tetrathiocyanates of general formula $\text{MM}'(\text{NCS})_4$, ($M = \text{Co, Ni}$ and $M' = \text{Zn, Cd, Hg}$) were first prepared by mixing and stirring equimolar quantities of M and M' thiocyanates in alcohol for 2 hours. To the solutions or suspensions of these different tetrathiocyanates in 50 ml of ethanol, 50 ml of ethanolic solutions of the

ligands were slowly added in suitable molar ratio and stirred for about 10 hours. Pink, blue or green complexes were formed, which were filtered, washed with solvent and dried under vacuum. A list of these complexes along with their melting points and colours are included in Table I.

Analyses and Physical Measurements

Analyses of the complexes, and all other physical measurements were made as reported earlier¹.

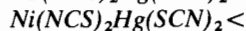
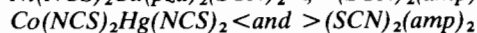
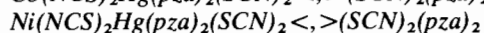
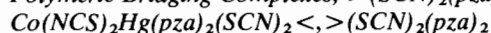
Results and Discussion

Cationic–Anionic Complexes, $[\text{Ni}(\text{pza})_6][\text{Zn}(\text{NCS})_4]$, $[\text{Co}(\text{amp})_2][\text{Cd}(\text{NCS})_4]$ and $[\text{Co}(\text{amp})_2][\text{Zn}(\text{NCS})_4]$

The molar conductance data (Table I) in acetone show that these complexes are 1:1 electrolytes. The Bohr magneton values, colours of the complexes and electronic spectra show that cobalt is in tetrahedral and nickel in octahedral configuration in these complexes. The infrared spectra show the presence of ν C–N, ν C–S and δ NCS bands in the regions which are typical of N-bonded thiocyanates^{3–6}. On the basis of these results we can propose a cationic–anionic formula to these complexes. The ligands pza, amp have been shown to be linked to nickel or cobalt to form the cation and the thiocyanate to zinc or cadmium to form the anion.

pza acts as a monodentate ligand and shows features of coordination through the ring nitrogen only, whereas amp acts as a bidentate ligand and coordinates through both the ring and the amino nitrogens.

Polymeric Bridging Complexes, $>(\text{SCN})_2(\text{pza})_2$



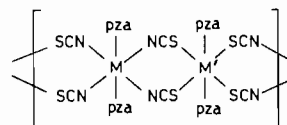
All these complexes are insoluble and do not melt. This shows that they have a polymeric thiocyanate bridging similar to the bridging in $\text{CoHg}(\text{NCS})_4$ and

TABLE I. Analytical Data.

Complexes	Colour	M.P. °C	% M ^a		% M ^a		% Sulphur		% Nitrogen		Molar Cond.	
			calc.	obs.	calc.	obs.	calc.	obs.	calc.	obs.	M/512	M/1024
[Ni(pza) ₆][Zn(NCS) ₄]	Light Green	241(d) ^c	5.0	5.7	6.0	-	11.7	11.2	28.2	28.1	46.3	80.5
[Co(amp) ₂][Cd(NCS) ₄]	Pink	270(d) ^c	9.9	10.2	18.9	-	21.6	21.7	23.6	23.3	-	-
[Co(amp) ₂][Zn(NCS) ₄]	Blue	172	10.8	10.4	11.9	-	23.4	23.7	25.6	25.8	82.1	100.1
>(SCN) ₂ (pza) ₂ Co(NCS) ₂ Hg(pza) ₂ (SCN) ₂ <	Pink	215(d) ^c	6.0	5.9	20.3	20.4	13.0	12.9	22.8	22.5	-	-
>(SCN) ₂ (pza) ₂ Ni(NCS) ₂ Hg(pza) ₂ (SCN) ₂ <	Green	280(d) ^c	5.6	6.3	20.4	20.7	13.1	12.8	22.9	22.3	-	-
>(SCN) ₂ (pza) ₂ Ni(NCS) ₂ Cd(pza) ₂ (SCN) ₂ <	Green	^b	6.2	7.0	12.6	-	14.4	14.7	25.1	24.9	-	-
>(SCN) ₂ (amp) ₂ Co(NCS) ₂ Hg(SCN) ₂ <	Pink	^b	8.6	8.4	29.4	29.4	18.8	18.4	20.6	20.3	-	-
>(SCN) ₂ (amp) ₂ Ni(NCS) ₂ Hg(SCN) ₂ <	Light Green	265(d) ^c	8.1	8.3	29.3	29.8	18.9	19.1	20.7	20.1	-	-
(pzd) ₂ Co(NCS) ₂ Hg(SCN) ₂	Blue	240	7.2	7.0	24.3	24.3	15.5	15.2	20.4	20.0	1.0	1.8
(pza) ₂ Zn(NCS) ₂ Hg(SCN) ₂	White	277	8.7	-	26.9	26.3	17.2	16.7	18.8	18.6	-	-

^aM = Co or Ni, M' = Zn, Cd or Hg. ^bDo not melt up to 300°C. ^cd = decomposed.

in the complexes reported earlier^{1,2}. The presence of only two bands at about 2135 cm⁻¹ in the spectra of all these complexes also shows that only one type of bridging thiocyanates⁷⁻⁹ is present. The number and position of ν C-S and δ NCS bands also support the presence of only bridging thiocyanates^{8,9}. The electronic spectral results and Bohr magneton values indicate that cobalt and nickel are in octahedral configuration. On the basis of these results the following structure can be proposed.

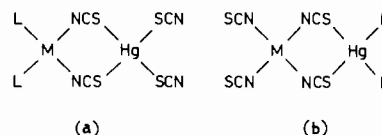


In pza complexes both the metals (M and M') have acquired octahedral configuration by coordination to four thiocyanates and two ligands (pza). In case of amp complexes only M acquires octahedral configuration and M' remains tetraordinated. The bridging thiocyanates have been shown to be linked through their nitrogen end to M and through the sulphur end to M' according to HSAB theory¹⁰.

pza and amp are coordinated through their ring nitrogen only and act as monodentate ligands.

Monomeric Bridging Complexes, (pzd)₂Co(NCS)₂Hg(SCN)₂ and (pza)₂Zn(NCS)₂Hg(SCN)₂

The infrared spectra of these two complexes show the presence of four bands in the CN stretching region, two of which are in the bridging range and two in the range of terminally N-bonded thiocyanate^{8,9,17}. The number and position of ν C-S and δ NCS bands also support the presence of both types of thiocyanates. These complexes are sharp melting and soluble in polar organic solvents. Their molar conductance data (Table I) in acetone show that they are non-conducting. The electronic spectra, colours and Bohr magneton values suggest tetrahedral configuration to cobalt in (pzd)₂Co(NCS)₂Hg(SCN)₂. Similarly the zinc is also expected to have tetrahedral configuration in (pza)₂Zn(NCS)₂Hg(SCN)₂. On the basis of these results we can propose either of the two following structures for these complexes.



(L is pzd when M is Co and pza when M is Zn)

The structure *b* has little probability as the ligands are nitrogen donors and will prefer cobalt and zinc

more than mercury according to HSAB theory¹⁰. These complexes are not sufficiently soluble, hence we were unable to determine their molecular weight.

pza and pzd are coordinated through their ring nitrogen only and act as monodentate ligands.

M–NCS, M–SCN and M–L Absorption Bands

In our complexes two bands in the region 200–320 cm^{-1} are present. It is difficult to say which one is the M–SCN or M–L stretching band. However on the basis of previous assignments^{11–13}, the bands in the lower frequency range can tentatively be assigned to

M–L or M–SCN and those in the higher frequency range to M–NCS vibrations. These assignments are included in Table II.

Electronic Spectral Discussion

To confirm the proposed configurations of cobalt and nickel we have recorded the electronic spectra and magnetic moment values of certain complexes, the results of which are included in Table III.

In the case of pink complexes of cobalt three bands are observed, which are assigned to transitions ${}^4T_{1g} \rightarrow {}^4T_{2g}(\nu_1)$, ${}^4T_{1g} \rightarrow {}^4A_{2g}(\nu_2)$ and ${}^4T_{1g} \rightarrow {}^4T_{1g}(P)(\nu_3)$.

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

Complexes	ν C–N	ν C–S ^b	δ NCS	ν M–NCS or ν M–L	ν M'–SCN or ν M–L
[Ni(pza) ₆][Zn(NCS) ₄]	2070s	860sh	485s	320m	–
[Co(amp) ₂][Cd(NCS) ₄]	2095s	790m	470sh	290w	240sh
[Co(amp) ₂][Zn(NCS) ₄]	2040s, 2060s	830sh	465s	310s, 295m	270w
>(SCN) ₂ (pza) ₂ Co(NCS) ₂ Hg(pza) ₂ (SCN) ₂ <	2120s, 2110s	770m, 805sh	460s, 485sh	305sh, 260sh	220w
>(SCN) ₂ (pza) ₂ Ni(NCS) ₂ Hg(pza) ₂ (SCN) ₂ <	2135s, 2105s	720m, 775sh	465w, 496m	320m	215w
>(SCN) ₂ (pza) ₂ Ni(NCS) ₂ Cd(pza) ₂ (SCN) ₂ <	2130s, 2100s	785mb	445s, 485s	280s	–
>(SCN) ₂ (amp) ₂ Co(NCS) ₂ Hg(SCN) ₂ <	2125s, 2140sh	715m, 785m	450s, 470m	290w	240sh
>(SCN) ₂ (amp) ₂ Ni(NCS) ₂ Hg(SCN) ₂ <	2135s	715m, 790m	450s	295w	–
(pzd) ₂ Co(NCS) ₂ Hg(SCN) ₂	2120s, 2140s, 2090sh	715m, 730sh, 775sh, 820sh	445m, 470m	305w, 290sh	240sh
(pza) ₂ Zn(NCS) ₂ Hg(SCN) ₂	2155s, 2130s, 2080s, 2060sh	710sh, 775m	445sh, 470s, 485sh	280w, 290w	240sh

^as = strong, sh = shoulder, m = medium, b = broad, w = weak.

^bThese assignments are tentative due to possible confusion with the ligand vibrations.

TABLE III. Selected Electronic Bands and Magnetic Moment Data.

Complexes	ν_3 (cm^{-1})	ν_2 (cm^{-1})	ν_1 (cm^{-1})	μ_{eff} (B.M.)
>(SCN) ₂ (pza) ₂ Co(NCS) ₂ Hg(pza) ₂ (SCN) ₂ <	20200	15650	7500	5.1
>(SCN) ₂ (amp) ₂ Co(NCS) ₂ Hg(SCN) ₂ <	20000	14800	7800	5.1
[Ni(pza) ₆][Zn(NCS) ₄]	–	–	–	3.2
>(SCN) ₂ (pza) ₂ Ni(NCS) ₂ Hg(pza) ₂ (SCN) ₂ <	–	–	–	3.2
>(SCN) ₂ (pza) ₂ Ni(NCS) ₂ Cd(pza) ₂ (SCN) ₂ <	22000	12900	8000	3.4
>(SCN) ₂ (amp) ₂ Ni(NCS) ₂ Hg(SCN) ₂ <	22700	13300	8000	3.5
[Co(amp) ₂][Cd(NCS) ₄]	–	–	–	4.4
[Co(amp) ₂][Zn(NCS) ₄]	16600	7200	–	4.1
(pzd) ₂ Co(NCS) ₂ Hg(SCN) ₂	15390	6940	–	4.0

Similarly in all nickel complexes three bands are observed which are assigned to transitions ${}^3A_{2g} \rightarrow {}^3T_{2g}(\nu_1)$, ${}^3A_{2g} \rightarrow {}^3T_{1g}(F)(\nu_2)$ and ${}^3A_{2g} \rightarrow {}^3T_{1g}(P)(\nu_3)$. The ν_1 bands in both cases are broad, the ν_2 band in case of cobalt is very weak. The electronic spectral band position and Bohr magneton values very clearly indicate that all nickel complexes and pink complexes of cobalt have octahedral configuration¹⁴.

In all blue complexes of cobalt only two intense bands (assigned transitions ${}^4A_{2g} \rightarrow {}^4T_{1g}(P)(\nu_3)$ and ${}^4A_{2g} \rightarrow {}^4T_{1g}(F)(\nu_2)$) are observed, which are typical of cobalt(II) in tetrahedral configuration¹⁵. The ν_2 band is split because of lower symmetry of the complexes. Electronic spectral results thus support our proposed structures. On the basis of the above observations and the reported results we have drawn certain conclusions which are presented below in the form of postulates.

Postulates

(i) Chelating ligands generally form cationic-anionic type $[CoL_x][Zn(NCS)_4]$ of complexes with $CoZn(NCS)_4$. However, the configuration of cobalt in the cation $[CoL_x]^{+2}$ depends upon the nature of the ligand. When L is ethylenediamine or triethylenetetramine, it is in square planar configuration, when L is phenanthroline or bipyridine it is in octahedral configuration¹⁸, and when L is aminopyrimidine¹⁹ and aminopyridine¹ it is in tetrahedral configuration.

(ii) Bulky ligands obstruct the formation of polymeric complexes even in 'ab' type of tetrathiocyanates. This can be exemplified by the triphenylphosphine complex of $CoHg(NCS)_4$ ², $ZnHg(NCS)_4$ and $NiHg(NCS)_4$ ¹⁶ and the pzd complex of this work.

(iii) amp is a chelating ligand, and breaks the thiocyanate bridging in $CoZn(NCS)_4$ which is 'aa' type tetrathiocyanate and is unable to break the bridging of 'ab' type of tetrathiocyanate $[CoHg(NCS)_4]$. The bridging in borderline tetrathiocyanate $[CoCd(NCS)_4]$ is also broken by this ligand.

Acknowledgements

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