

Complexes of Lewis Bases with Zn(II), Cd(II), Hg(II), Fe(II), Pd(II), Co(II), Ni(II) & Cu(II) Thiocyanates & Cyanates

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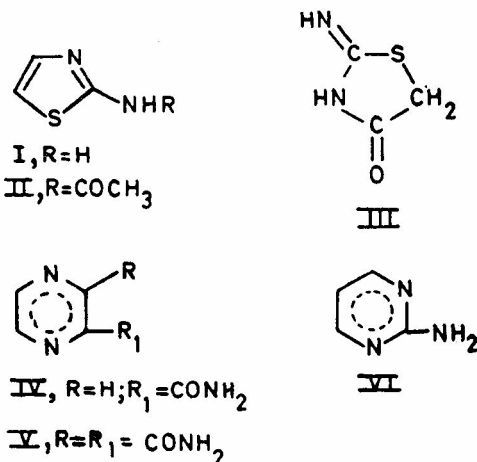
Thiocyanato and cyanato complexes of Zn(II), Cd(II), Hg(II), Fe(II), Pd(II), Co(II), Ni(II) and Cu(II) with 2-aminothiazole (atz), 2-(N-acetyl)aminothiazole (aatz), pseudothiohydantoin (pthn), 2-aminopyrimidine (amp), pyrazine-2-carboxamide (pza) and pyrazine-2,3-dicarboxamide (pzd) have been prepared and characterized on the basis of molar conductance, magnetic moment, infrared and electronic spectral studies. aatz and amp act as bidentate, and atz, pthn, pza and pzd as monodentate ligands. Thiocyanate unit is N-bonded in Zn(II), Co(II) and Fe(II) complexes, S-bonded in Hg(II) and Pd(II) complexes, N-bonded or bridged in Ni(II) complexes and S-bonded or bridged in Cd(II) complexes. Cyanate groups in Co(II) and Ni(II) complexes are bridged.

RECENTLY we have studied the mode of bonding of some heterocyclic ligands, viz. 2-aminothiazole (I, atz), 2-(N-acetyl)aminothiazole (II, atz), pseudothiohydantoin (III, pthn), 2-aminopyrimidine (IV, amp), pyrazine-2-carboxamide (V, pzo) and pyrazine-2,3-dicarboxamide (VI, pzd) towards certain metal halides¹⁻³. In this paper we report the donor behaviour of these ligands towards some bivalent metal thiocyanates and cyanates.

Materials and Methods

Reagent grade anhydrous Zn(II), Cd(II), Hg(II), Co(II), Ni(II), Cu(II), Pd(II) and Fe(II) thiocyanates (Alfa Inorganics) were used as such. Co(II) and Ni(II) cyanates were prepared by the reaction of cobalt and nickel nitrates with potassium cyanate (Alfa Inorganics). pza, pzd and amp (Aldrich Chemical Co.) were used as such while atz (Aldrich Chemical Co.) was used after recrystallization from dichloromethane. aatz was prepared by acetylation of atz and pthn by the method described by Horning⁴. Solvents were dried by standard methods and stored on molecular sieves.

Preparation of the complexes—The complexes were prepared by direct reaction of the metal thiocyanates or cyanates with the excess ligand. Dichloromethane was used as solvent in the preparation of complexes with atz, aatz and pthn while ethanol was used in the case of pza and amp complexes. Cyanate complexes were prepared using water as the solvent. The reaction mixtures were stirred for 12-48 hr and the complexes formed filtered. Excess ligand was removed by washing with the solvent of the reaction medium. Complexes were dried *in vacuo* at room temperature. atz, aatz and pthn complexes were recrystallized either from nitromethane or acetone. Rest could not be recrystallized. Analytical data of the complexes are given in Table 1.



Physical measurements—Infrared and electronic spectra (mull and solution) were recorded on Perkin-Elmer 621 and Cary-14 spectrophotometers respectively. Magnetic susceptibility measurements were carried out using Gouy's method employing Co[Hg(SCN₄)] as the standard.

Results and Discussion

atz and aatz complexes—The distinction between the ν C-S of the ligand and the thiocyanate group* was made by comparing the IR spectra with those of the corresponding halide complexes^{2,3}. In atz and aatz complexes, the band at 650 cm⁻¹ which is assigned to asymmetric ν C-S of the ligand is shifted to lower frequency while that at 690 cm⁻¹ which is assigned to symmetric ν C-S of the ligand either disappears or is reduced in intensity. It indicates that ring sulphur is involved in coordination in both atz and aatz complexes². ν N-H bands do not show features of coordination.

*Detailed IR spectra are available with the authors.

TABLE 1 — ANALYTICAL AND MELTING POINT DATA

Complexes	Found (Calc.) (%)					m.p.	
	C	H	N	S	Metal		NCS
Zn(atz) ₂ (NCS) ₂	25.17 (25.46)	2.09 (2.33)	22.02 (21.63)	33.56 (33.09)	17.14 (17.44)	—	155
Co(aatz) ₄ (NCS) ₂	29.21 (29.81)	2.78 (2.79)	24.34 (23.92)	33.39 (33.06)	10.26 (10.69)	—	160
Ni(atz) ₄ (NCS) ₂	29.23 (29.07)	2.78 (3.03)	24.36 (24.63)	33.40 (32.91)	10.21 (9.83)	—	215
Zn(aatz)(NCS) ₂	30.94 (31.26)	2.57 (2.49)	18.05 (18.33)	27.50 (27.31)	14.04 (14.26)	—	170
Co(aatz) ₂ (NCS) ₂	31.37 (31.04)	2.61 (2.36)	18.30 (18.02)	27.88 (27.40)	12.85 (12.36)	—	195
Ni(aatz) ₂ (NCS) ₂	31.44 (31.01)	2.62 (2.80)	18.34 (18.71)	27.94 (27.31)	12.66 (12.18)	—	200
Cd(aatz)(SCN) ₂	22.67 (22.36)	1.61 (2.00)	15.11 (15.62)	25.91 (25.64)	30.34 (30.07)	—	150
Zn(pthn) ₂ (NCS) ₂	23.20 (23.40)	2.39 (2.39)	20.30 (20.12)	30.93 (30.43)	15.79 (15.31)	—	180
Co(pthn) ₂ (NCS) ₂	17.69 (17.46)	1.96 (2.13)	20.63 (20.33)	31.44 (31.03)	14.49 (14.82)	—	225
Ni(pthn) ₃ (NCS) ₂	25.25 (25.67)	2.29 (2.60)	21.42 (21.06)	30.60 (30.41)	11.23 (10.79)	—	210
Cd(pthn) ₂ (SCN) ₂	20.80 (21.20)	1.73 (2.03)	18.24 (18.63)	27.80 (27.44)	24.41 (24.11)	—	135
Hg(pthn) ₂ (SCN) ₂	17.49 (17.63)	1.45 (1.26)	15.31 (15.02)	23.33 (23.04)	36.56 (36.74)	—	140
Cd(atz) ₂ (SCN) ₂	22.40 (22.74)	1.86 (1.47)	19.60 (20.03)	29.8 (30.02)	26.23 (26.02)	—	100
Hg(amp) ₂ (SCN) ₂	—	—	—	—	39.6 (39.1)	22.0 (22.2)	168
Co(amp) ₂ (SCN) ₂	—	—	—	—	16.2 (15.8)	31.8 (32.5)	177
Fe(amp) ₂ (NCS) ₂	—	—	—	—	15.5 (15.0)	32.0 (31.8)	(d)
Zn(amp) ₂ (NCS) ₂	—	—	—	—	17.5 (17.0)	31.2 (30.9)	185
Cu(amp)(NCS) ₂	—	—	—	—	33.1 (33.3)	42.2 (41.8)	140 (d)
Ni(amp)(NCS) ₂	—	—	—	—	21.8 (22.2)	43.0 (42.5)	250 (d)
Hg(pza)(SCN) ₂	—	—	—	—	45.7 (44.2)	26.4 (27.0)	210
Co(pza) ₂ (NCS) ₂	—	—	—	—	14.0 (13.8)	27.5 (26.9)	> 300
Cd(pza) ₂ (NCS) ₂	—	—	—	—	23.6 (22.9)	24.5 (23.8)	> 300
Ni(pza) ₂ (NCS) ₂	—	—	—	—	14.0 (14.2)	27.5 (27.3)	> 300
Co(pza) ₂ (NCO) ₂	—	—	28.8 (28.1)	—	15.2 (14.8)	—	200
Ni(pza) ₂ (NCO) ₂	—	—	28.8 (29.4)	—	15.2 (14.9)	—	240
Co(pzd) ₂ (NCS) ₂	—	—	—	—	11.6 (11.9)	22.9 (23.6)	244
Hg(pzd) ₂ (SCN) ₂	—	—	—	—	30.9 (30.5)	17.9 (17.8)	180 (d)
Ni(pzd) ₂ (NCS) ₂	—	—	—	—	11.6 (11.8)	22.9 (23.1)	250

In aatz complexes, in addition to negative shift observed in the ν C-S band, a negative shift of the order of 30 cm^{-1} is observed in ν C=O. This indicates that carbonyl oxygen is also involved in coordination and the ligand is bidentate⁶. The involvement of carbonyl oxygen in coordination is also shown by the appearance of an additional band in the region 375-390 cm^{-1} which could be assigned to ν M-O⁷. Bands appearing in the range 210-235 cm^{-1} are assigned to ν M-S in atz and aatz complexes⁸.

The positions and the nature of ν CN, ν C-S and δ NCS bands indicate that the thiocyanate unit is N-bonded in Zn(II), Co(II) and Ni(II) complexes,

and S-bonded in Cd(II) complexes⁹. The bands in the region 270-330 cm^{-1} in Zn(II), Co(II) and Ni(II) complexes and in the region 235-308 cm^{-1} in Cd(II) complexes may tentatively be assigned to ν M-N(NCS) and ν M-S(SCN) vibrations respectively. These bands have been assigned similarly in isothiocyanato and thiocyanato complexes by previous workers¹⁰⁻¹². Cd(II) and Hg(II) complexes melt at lower temperatures and dissolve readily in non-polar solvents, whereas the reverse is true for Co(II), Zn(II) and Ni(II) complexes. This observation further suggests that Cd(II) and Hg(II) complexes are more covalent in nature and probably S-bonded while

TABLE 2 — ELECTRONIC SPECTRAL AND MAGNETIC MOMENT DATA OF Co(II) AND Ni(II) COMPLEXES

Complexes	ν_2 (cm^{-1})	ν_3 (cm^{-1})	D_q (cm^{-1})	B' (cm^{-1})	β (cm^{-1})	μ_{eff} (BM)
Co(atz) ₄ (NCS) ₂ *	19230	21276	1022.00	656.4	0.67	5.2
Ni(atz) ₄ (NCS) ₂ †	19280	27027	847.59	1058.6	1.00	3.16
Co(aatz) ₂ (NCS) ₂ *	18867	21739	1005.0	697.0	0.71	5.0
Ni(aatz) ₂ (NCS) ₂ †	13888	24096	911.6	708.94	0.67	3.41
Co(pthn) ₂ (NCS) ₂ *	—	—	—	—	—	4.2
Ni(pthn) ₄ (NCS) ₂ †	15150	25000	937.0	802.66	0.76	3.28
Co(amp) ₂ (NCS) ₂ *	16000	20800	879.0	970.0	0.98	5.1
Ni(amp) ₂ (NCS) ₂ †	12200	22000	728.0	840.0	0.80	3.97

* $\nu_2 = {}^4T_{1g}(F) \rightarrow {}^4T_{1g}(P)$; $\nu_3 = {}^4T_{1g}(F) \rightarrow {}^4A_{2g}(F)$.

† $\nu_2 = {}^3A_{2g} \rightarrow {}^3T_{1g}(F)$; $\nu_3 = {}^3A_{2g} \rightarrow {}^3T_{1g}(P)$.

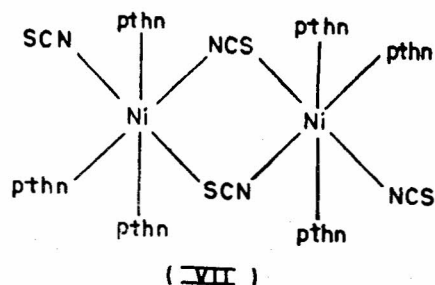
Ni(II), Zn(II) and Co(II) complexes are less covalent and N-bonded.

Co(II) and Ni(II) complexes are octahedral as shown by their colour, magnetic moment values and electronic spectral data (Table 2). Higher D_q values of Co(II) and Ni(II) complexes indicate that these complexes exert greater ligand field usually associated with complexes having N-bonded thiocyanate groups. Zn(II) and Cd(II) complexes are probably tetrahedral.

pthn complexes — pthn has four centres of coordination, viz. carbonyl oxygen, ring nitrogen, ring sulphur and exocyclic nitrogen. On coordination, $\nu\text{C}=\text{O}$ shows a negative shift of the order of 100 cm^{-1} , which indicates that coordination takes place through carbonyl oxygen⁸. $\nu\text{N-H}$ and $\nu\text{C-S}$ bands remain undisturbed. The presence of a band at about 370 cm^{-1} , which could be assigned to $\nu\text{M-O}$, also supports bonding through carbonyl oxygen.

The positions of thiocyanate vibrations, νCN , νCS and δNCS , indicate that thiocyanate is linked through nitrogen to Co(II) and Zn(II) and through sulphur to Cd(II) and Hg(II)^{6,9}. The colour and the magnetic moment values (Table 2) suggest that Co(II) is in tetrahedral configuration in the Co(pthn)₂(NCS)₂ complex. Zn(II), Cd(II) and Hg(II) are also expected to be tetrahedral.

The stoichiometry of Ni(II) thiocyanate complex is 1:3 and the positions of bands due to νCN , νCS and δNCS modes indicate bridging type of thiocyanate^{13,14}. The bands in the far IR region (~ 350 cm^{-1}) also indicate the presence of bridged thiocyanate group¹⁰. This complex is non-conducting. The colour, magnetic moment and electronic spectral data (Table 2) indicate that Ni(II) in this complex is octahedral. On the basis of these results we can suggest structure VII for this complex.



amp complexes — Comparison of the spectra of the ligand and the complexes shows a negative shift (~ 100 cm^{-1}) in $\nu\text{N-H}$ and a positive shift in $\nu\text{C-N}$ and $\nu\text{C-C}$ (ring vibrations) on complexation. These shifts clearly indicate that both amino nitrogen and ring nitrogen are involved in coordination and amp acts as a bidentate ligand.

The positions of the νCN , νCS and δNCS bands of thiocyanate group indicate that thiocyanate is N-bonded in the complexes of Zn(II), Co(II) and Fe(II), S-bonded in the complexes of Hg(II) and Cu(II) and bridged in the complexes of Cu(II) and Ni(II)^{6,9-12}.

The complexes are non-conducting. Thiocyanato-bridged complexes are insoluble and do not melt indicating their polymeric nature⁷. Co(II), Ni(II) and Cu(II) complexes have octahedral configuration as shown by their colour, magnetic moment values and electronic spectral data (Table 2). Hg(II) complex is also in octahedral configuration.

pza complexes — The $\nu\text{C-N}$, and $\nu\text{C-C}$ bands of pza show a positive shift on complex formation. This indicates that ring nitrogen of pyrazine nucleus is involved in coordination. It is difficult to identify definitely which of the two ring nitrogens is involved in coordination, but the nitrogen in the *meta* position to the amide group has a higher probability of bonding. The amide group remains unaffected on coordination.

The thiocyanate group shows features of coordination through its sulphur end to Pd(II) and Hg(II), and through both nitrogen and sulphur to Cd(II) and Ni(II). The Ni(II) and Cd(II) thiocyanate complexes are insoluble and do not melt, hence a polymeric bridged structure can be suggested for these complexes. Mercury thiocyanate forms 1:1 complex with pza. This complex may be assigned a trigonal-bipyramidal structure in which Hg(II) is penta-coordinated¹⁵.

In the case of cyanate complexes the positions of $\nu\text{C-N}$, $\nu\text{C-O}$ and δNCO bands indicate that cyanate group in both Co(II) and Ni(II) complexes are bridged¹⁶. The magnetic moment values and the colour of the complexes indicate that these have octahedral configuration.

pzd complexes — The infrared spectra of the complexes show that pzd coordinates through its ring nitrogen while the amide groups remain unaffected. The positions of thiocyanate bands, νCN , νCS and

δ NCS, indicate that it is bonded through sulphur in Hg(II) complex and through both sulphur and nitrogen in the Ni(II) complex. The colour and magnetic moment values show that Ni(II) is in octahedral configuration in its complex and perhaps has a polymeric structure as the complex neither melts nor dissolves in common solvents. Hg(II) is in tetrahedral configuration.

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