

## Hexamethylenetetramine complexes with manganese(II), cobalt(II), nickel(II), copper(II), zinc(II) and cadmium(II) thiocyanates

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**Abstract**—Coordination compounds formed by the interaction of hexamethylenetetramine (Hmta), a potentially tetradentate ligand, with Mn(II), Co(II), Ni(II), Cu(II), Zn(II) and Cd(II) thiocyanates have been prepared and characterized from their elemental analyses, magnetic susceptibilities, electronic and IR spectral studies down to  $200\text{ cm}^{-1}$  as well as X-ray powder diffraction patterns in the solid state. The compounds isolated are  $\text{Mn}(\text{NCS})_2(\text{Hmta})_2(\text{EtOH})_2$ ,  $\text{Mn}(\text{NCS})_2(\text{Hmta})_2$ ,  $\text{Co}(\text{NCS})_2(\text{Hmta})_2(\text{EtOH})_2$ ,  $\text{Co}(\text{NCS})_2(\text{Hmta})_2$ ,  $\text{Ni}(\text{NCS})_2(\text{Hmta})_2(\text{EtOH})_2$ ,  $\text{Ni}(\text{NCS})_2(\text{Hmta})_2$ ,  $\text{Cu}(\text{NCS})_2(\text{Hmta})_2$ ,  $\text{Zn}(\text{NCS})_2(\text{Hmta})_2$  and  $\text{Cd}(\text{NCS})_2(\text{Hmta})_2$ . It is shown that Hmta, though a potentially tetradentate ligand, acts only as a terminally bonded monodentate ligand or a bidentate ligand bridging between two metal atoms retaining the chair configuration of the uncoordinated molecule in all these complexes. The tentative stereochemistries of the complexes are discussed. The ligand field parameters  $10 Dq$ ,  $B$ ,  $\beta$ ,  $\lambda$  and  $\nu_2/\nu_1$  calculated for the cobalt, nickel and copper complexes are consistent with their proposed stereochemistries.

Hexamethylenetetramine (Hmta), a heterocyclic system having three fused rings in the chair configuration with four bridge-head nitrogen atoms, is known to form complexes with metal(II) halides [1-3] as well as with halogens [4, 5]. However, few spectroscopic studies have been made on these complexes [3, 5]. The replacement of halides by potentially multidentate thiocyanate groups offer interesting bonding possibilities. The present study on the preparation, magnetic susceptibilities, electronic and IR spectral features down to  $200\text{ cm}^{-1}$  as well as X-ray powder patterns of the coordination compounds formed by the interaction of manganese(II), cobalt(II), nickel(II), copper(II), zinc(II) and cadmium(II) thiocyanates with Hmta has been undertaken to elucidate the mode of bonding of Hmta, of the thiocyanate groups and the tentative stereochemistries of the complexes. It is shown that Hmta, though a potentially tetradentate ligand, acts only as a terminally bonded monodentate ligand, acts only as a terminally bonded monodentate ligand or a bidentate ligand bridging between two metal atoms retaining the chair configuration of the uncoordinated molecule in all the complexes. The complexes are tentatively assigned monomeric tetrahedral or octahedral structures or polymeric chain structures involving four- or six-coordinate environments around the metal atoms. Further, the ligand field parameters  $10 Dq$ ,  $B$ ,  $\beta$ ,  $\lambda$  and  $\nu_2/\nu_1$  calculated for the cobalt, nickel and copper complexes are consistent with their proposed stereochemistries.

### EXPERIMENTAL

Hexamethylenetetramine (Hmta) was obtained from Dr Theodor Schuchardt GmbH & Co Munich and used as such. The divalent manganese, cobalt, nickel, zinc and

cadmium thiocyanate complexes were synthesized by adding an excess of Hmta to an ethanolic solution of the respective metal(II) thiocyanate. The crystalline products obtained were suction-filtered, washed with ethanol and dried *in vacuo*. Manganese(II), cobalt(II) and nickel(II) thiocyanates gave complexes of the type  $\text{M}(\text{NCS})_2(\text{Hmta})_2(\text{EtOH})_2$ . These compounds on heating in an air oven at  $140^\circ\text{C}$  lost ethanol and gave the complexes  $\text{M}(\text{NCS})_2(\text{Hmta})_2$ . Copper(II) thiocyanate complex with Hmta was prepared by boiling a suspension of copper(II) thiocyanate in ethanol with an excess of the ligand. The complex obtained was suction-filtered, washed with ethanol and dried. Stoichiometries of the solid complexes isolated were checked by metal and thiocyanate estimations gravimetrically.

$\text{Mn}(\text{NCS})_2(\text{Hmta})_2(\text{EtOH})_2$  Found Mn = 10.0, NCS = 21.6. Calc Mn = 10.1, NCS = 21.4%.  
 $\text{Mn}(\text{NCS})_2(\text{Hmta})_2$  Found Mn = 12.3, NCS = 26.0. Calc Mn = 12.2, NCS = 25.7%.  
 $\text{Co}(\text{NCS})_2(\text{Hmta})_2(\text{EtOH})_2$  Found Co = 11.0, NCS = 21.2. Calc Co = 10.8, NCS = 21.2%.  
 $\text{Co}(\text{NCS})_2(\text{Hmta})_2$  Found Co = 13.1, NCS = 25.7. Calc Co = 13.0, NCS = 25.5%.  
 $\text{Ni}(\text{NCS})_2(\text{Hmta})_2(\text{EtOH})_2$  Found Ni = 10.8, NCS = 21.4. Calc Ni = 10.7, NCS = 21.2%.  
 $\text{Ni}(\text{NCS})_2(\text{Hmta})_2$  Found Ni = 13.0, NCS = 25.4. Calc Ni = 12.9, NCS = 25.5%.  
 $\text{Cu}(\text{NCS})_2(\text{Hmta})_2$  Found Cu = 13.8, NCS = 25.5. Calc Cu = 13.7, NCS = 25.3%.  
 $\text{Zn}(\text{NCS})_2(\text{Hmta})_2$  Found Zn = 14.0%, NCS = 25.1. Calc Zn = 14.1, NCS = 25.2%.  
 $\text{Cd}(\text{NCS})_2(\text{Hmta})_2$  Found Cd = 30.5, NCS = 31.4. Calc Cd = 30.4, NCS = 31.5%.

Electronic spectra of the manganese(II), cobalt(II), nickel(II) and copper(II) complexes were recorded as nujol

mulls in the range 33,000–6000  $\text{cm}^{-1}$  on a Cary 14 recording spectrophotometer. The mulls were smeared on filter paper and run against a reference consisting of a similar piece of filter paper soaked in nujol. Infrared spectra of the uncoordinated Hmta and of the metal thiocyanate complexes studied were recorded as nujol mulls on a Perkin-Elmer 621 spectrophotometer. The mulls were supported between sodium chloride plates (rock salt region) and thin polythene sheets (650–200  $\text{cm}^{-1}$ ). Magnetic susceptibilities were measured at room temperature by the Faradays' method with a Cahn R G Electro-balance Model 7550 using  $\text{HgCo}(\text{NCS})_4$  as the magnetic susceptibility standard. Pascals' constants were used for diamagnetic corrections and the magnetic moments were calculated using the equation

$$\mu_{\text{eff}} = 2.84 \sqrt{\chi_M^{\text{corr}} T}$$

X-ray diffraction powder patterns for the complexes were obtained with a 11.46 cm Debye-Scherrer camera using filtered  $\text{CuK}$  radiation. The samples were prepared by mounting the powder on a fine glass fibre using Quickfix.

### RESULTS AND DISCUSSION

The complexes isolated in the present study, their room temperature magnetic moments, observed bands in the electronic spectra and the

ligand field parameters are recorded in Table 1. Characteristic IR bands due to Hmta and the thiocyanate groups are listed in Table 2.

Hexamethylenetetramine (Hmta), a heterocyclic system having three fused rings in the chair configuration, possesses four bridge-head nitrogen atoms. The chemical and steric equivalence of the four nitrogen atoms has been demonstrated by various physico-chemical methods [6, 7]. It may thus act as a mono-, bi-, tri- or tetra-dentate ligand. Framework molecular models show that it is more likely to bond to different metal ions and thus act as bridging rather than a chelating ligand. The 1300–200  $\text{cm}^{-1}$  region IR spectrum of the uncoordinated Hmta shows absorption bands at 1225s, 1180w, 1040m, 1000s, 823w, 803s, 714w, 664s, 610m and 508s. Of these, the two strong absorption bands at 1225 and 1000  $\text{cm}^{-1}$  are assigned to the fundamentals of the C–N stretching vibrations [8]. Both these bands are split up into two well-defined and well separated bands in complexes in which Hmta acts as a bidentate bridging ligand [5]. However, complexes in which the Hmta

Table 1 Magnetic moments (B M), electronic bands and ligand field parameters ( $\text{cm}^{-1}$ )

Compound	$\mu_{\text{eff}}$	$\nu_1$	$\nu_2$	$\nu_3$	10Dq	B	$\beta$	$-\lambda$	$\nu_2/\nu_1$	Dq/B
$\text{Co}(\text{NCS})_2(\text{Hmta})_2(\text{EtOH})_2$	4.74	8334		19,530	10,548	894.5	0.912			1.179
$\text{Co}(\text{NCS})_2(\text{Hmta})_2$	4.18	6800		16,393	3230	986.5	1.015	111.9		0.327
$\text{Ni}(\text{NCS})_2(\text{Hmta})_2(\text{EtOH})_2$	3.15	8928	14,925	26,315	8928	963.7	0.925	212.9	1.67	0.926
$\text{Ni}(\text{NCS})_2(\text{Hmta})_2$	3.20	8547	14,285	25,316	8547	930.6	0.894	279.3	1.67	0.918
$\text{Cu}(\text{NCS})_2(\text{Hmta})_2$	1.35	14,705								

$\beta = B/B_0$ ,  $B_0 \pm 971 \text{ cm}^{-1}$  for cobalt(II) and  $1041 \text{ cm}^{-1}$  for nickel(II)

Table 2 Infrared bands ( $\text{cm}^{-1}$ ) due to coordinated Hmta and thiocyanate groups

Compound	Hmta modes		Coordinated thiocyanate modes				
	$\nu_{\text{CN}}$	$\nu_{\text{CN}}$	$\nu_{\text{CN}}$	$\nu_{\text{CS}}$	$\delta_{\text{NCS}}$	$\nu_{\text{M-NCS}}$	$\nu_{\text{M-O(EtOH)}}$
Hmta	1225s	1000s					
$\text{Mn}(\text{NCS})_2(\text{Hmta})_2(\text{EtOH})_2$	1230s	1000s	2056s	806m	472m	315m	470ssh
$\text{Mn}(\text{NCS})_2(\text{Hmta})_2$	1230s	1003s	2056s	803m	470m	290m	
	1216s	990s					
		983s					
$\text{Co}(\text{NCS})_2(\text{Hmta})_2(\text{EtOH})_2$	1228s	1000s	2062s	816m	472m	295m	460ssh
			2083s				
$\text{Co}(\text{NCS})_2(\text{Hmta})_2$	1245s	1015s	2080s	820m	476m	320m	
	1222s*	1000s†	2060s		470m	300m	
		990s					
$\text{Ni}(\text{NCS})_2(\text{Hmta})_2(\text{EtOH})_2$	1240s	1016s	2090s	814m	486m	290m	465m
	1222s*	1000s†					
		990s					
$\text{Ni}(\text{NCS})_2(\text{Hmta})_2$	1245s	1014s	2095s	820m	480m	300m	
	1220s	970s			470m		
$\text{Cu}(\text{NCS})_2(\text{Hmta})_2$	1245s	1014s	2118s	810m	483m	320m	
	1220s	970s	2060s				
$\text{Zn}(\text{NCS})_2(\text{Hmta})_2$	1245s	1015s	2085s	835m	485m	300m	
	1221s	985s	2065s		480m		
$\text{Cd}(\text{NCS})_2(\text{Hmta})_2$	1238s	1015s	2080s	780m	465m		
	1210s	980s			450m		

\* Minor split—doublet

† Minor split—triplet

molecule(s) act as monodentate ligand(s) bonding through only one of the four nitrogen atoms, both the C–N stretching bands suffer only a very minor splitting resulting in closely spaced doublets or triplets [9]. In addition to the splitting (well-defined or only very minor) of the C–N stretching bands the intensities of some more bands of Hmta undergo slight changes in the IR spectra of the metal thiocyanate complexes. Furthermore, apart from these intensity changes and the splitting of the C–N stretching bands, the IR spectra due to coordinated Hmta in all the complexes reported here are almost superimposable on the IR spectrum of the uncoordinated ligand. This may be attributed to the fact that the chair configuration of the uncoordinated Hmta [10] is retained in all the complexes. Although a potentially tetradentate ligand, stereochemically Hmta seems to act only as a terminally bonded monodentate or a bidentate bridging ligand thus retaining its chair configuration in all the metal thiocyanate–Hmta complexes studied herein. If chelated the coordinated Hmta must have a boat or *cis* configuration and IR spectra of such complexes would be anticipated to exhibit multiplicity of band owing to the increased number of IR-active fundamentals (cf. chelated 1,4-dioxane) [11].

#### Manganese (II) complexes

Both the complexes  $\text{Mn}(\text{NCS})_2(\text{Hmta})_2(\text{EtOH})_2$  and  $\text{Mn}(\text{NCS})_2(\text{Hmta})_2$  are high-spin and have room temperature magnetic moments of 5.91 and 5.45 B.M., respectively, consistent with high-spin manganese (II) irrespective of whether the arrangement of ligands around the Mn(II) ions is tetrahedral or octahedral [12]. The electronic spectra of these complexes do not show any absorption in the range 1700–300 nm. This is not surprising in manganese(II) complexes in centrosymmetric environments since all the transitions are both spin and symmetry forbidden [13]. The X-ray diffraction patterns, mode of metal–Hmta bonding, the fundamental vibrations due to thiocyanate groups and the overall similarity in the IR spectra of  $\text{Mn}(\text{NCS})_2(\text{Hmta})_2(\text{EtOH})_2$  and  $\text{Mn}(\text{NCS})_2(\text{Hmta})_2$  with those of  $\text{Ni}(\text{NCS})_2(\text{Hmta})_2(\text{EtOH})_2$  and  $\text{Ni}(\text{NCS})_2(\text{Hmta})_2$ , respectively, (*vide infra*) suggest that the manganese(II) complexes are isostructural with the corresponding nickel(II) complexes. The  $\text{Ni}(\text{NCS})_2(\text{Hmta})_2(\text{EtOH})_2$  and  $\text{Ni}(\text{NCS})_2(\text{Hmta})_2$  are shown from magnetic moments, electronic and IR spectral studies to be monomeric octahedral and polymeric octahedral structures, respectively (*vide infra*).

#### Cobalt (II) complexes

The compound  $\text{Co}(\text{NCS})_2(\text{Hmta})_2(\text{EtOH})_2$  is pink, crystalline and has a room temperature magnetic moment of 4.74 B.M. which is well within the range for octahedral divalent cobalt [12]. Its

electronic spectrum shows absorption bands at 8334 and  $19,530 \text{ cm}^{-1}$  which are assigned as  ${}^4T_{1g}(F) \rightarrow {}^4T_{2g}(F)$   $8334 \text{ cm}^{-1} \nu_1$  and  ${}^4T_{1g}(F) \rightarrow {}^4T_{1g}(P)$   $19,530 \text{ cm}^{-1} \nu_3$ . These magnetic and electronic spectral features are characteristic of divalent cobalt in a weak octahedral field and rule out a tetrahedral geometry which would show much stronger absorption in the range  $14,000\text{--}16,000 \text{ cm}^{-1}$ . Using these two assignments the transition  ${}^4T_{1g}(F) \rightarrow {}^4A_{2g} \nu_2$  is anticipated to occur at slightly higher energies than the  ${}^4T_{1g}(F) \rightarrow {}^4T_{1g}(P)$  band. However, since the  ${}^4A_{2g}$  state is derived from  $t_{2g}^3e_g^4$  configuration while  ${}^4T_{1g}(F)$  from  $t_{2g}^2e_g^4$  configuration, the  ${}^4T_{1g}(F) \rightarrow {}^4A_{2g}$  transition is essentially a two-electron process and hence should be of weaker intensity than the other transitions. This weakness combined with the proximity of  ${}^4T_{1g}(F) \rightarrow {}^4T_{1g}(P)$  transition results in the  ${}^4T_{1g}(F) \rightarrow {}^4A_{2g} \nu_2$  transition being unobserved. Moreover, the  $Dq/B$  value 1.179 also indicates the absence of this band as suggested by TANABE and SUGANO [14]. The following relationships [15] were used for calculating  $10 Dq$  and  $B$  the Racah parameter

$$10 Dq = 2\nu_1 - \nu_3 + 15B = 10,548.0 \text{ cm}^{-1}$$

$$B = \frac{1}{30} [-(2\nu_1 - \nu_3) \pm \{-\nu_1^2 + \nu_3^2 + \nu_1\nu_3\}^{1/2}]$$

$$= 894.5 \text{ cm}^{-1}$$

$$Dq/B = \frac{1054.8}{894.5} = 1.179$$

The  $B$  value of  $894.5 \text{ cm}^{-1}$ , which is less than the free ion value ( $971 \text{ cm}^{-1}$ ) is indicative of orbital overlap and delocalization of the  $d$ -orbitals. The fundamental frequencies due to coordinated thiocyanate groups are consistent with terminally N-bonded NCS groups. Moreover, the ethanol molecules are also coordinated to the metal ion as indicated [16] by the presence of Co–O (EtOH) bond at  $460 \text{ cm}^{-1}$ . Thus on the basis of colour, room temperature magnetic moment, electronic and IR spectral data the  $\text{Co}(\text{NCS})_2(\text{Hmta})_2(\text{EtOH})_2$  is tentatively assigned a monomeric, six-coordinated, octahedral environment of four nitrogen atoms (two from the terminally bonded mono-dentate Hmta molecules and two from terminally N-bonded NCS groups) and two oxygen atoms (from the two-coordinated ethanol molecules) around the metal atoms in the solid state. Each of the two Hmta molecules, NCS groups and EtOH molecules must be *trans* to each other as the unsymmetrical *cis* disposition of these groups would lead to multiplicity of bands due to their fundamental modes.

On heating the  $\text{Co}(\text{NCS})_2(\text{Hmta})_2(\text{EtOH})_2$  complex at  $140^\circ\text{C}$  for 30 min in an air oven resulted in the loss of two molecules of ethanol (and disappearance of the band at  $460 \text{ cm}^{-1}$  due to  $\nu\text{Co-O}$  mode) and a blue crystalline complex of the

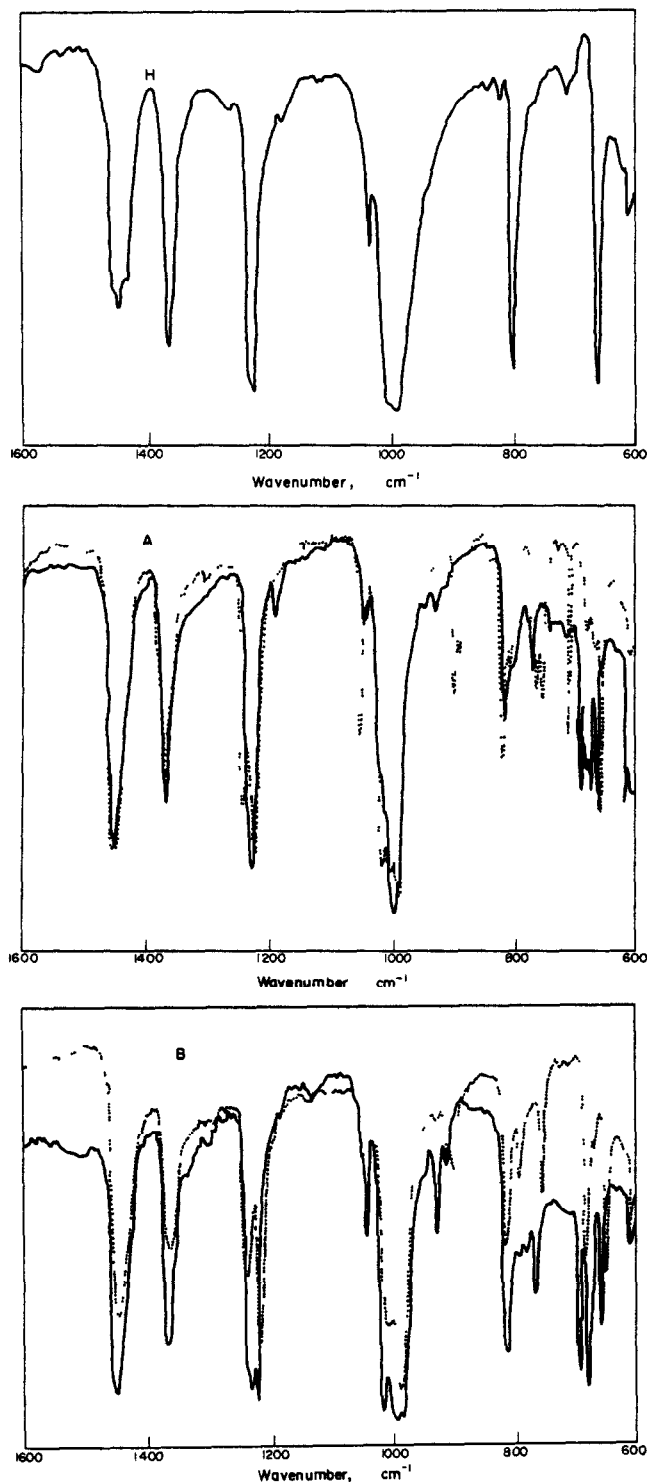


Fig 1 Infrared spectra H = Uncoordinated Hmta, (A) Solid line  $\text{Co}(\text{NCS})_2(\text{Hmta})_2(\text{EtOH})_2$ , dotted line  $\text{Co}(\text{NCS})_2(\text{Hmta})_2$  (B) Solid line  $\text{Ni}(\text{NCS})_2(\text{Hmta})_2(\text{EtOH})_2$ , dotted line  $\text{Ni}(\text{NCS})_2(\text{Hmta})_2$

stoichiometry  $\text{Co}(\text{NCS})_2(\text{Hmta})_2$  was obtained. The room temperature magnetic moment value, 4.18 B.M., suggests that the complex is tetrahedral [12] and the bands in the electronic spectrum confirm this [17]. The  ${}^4A_2 \rightarrow {}^4T_1$  transition is observed

as a broad absorption centred at  $6800 \text{ cm}^{-1}$  and the main component of  ${}^4A_2 \rightarrow {}^4T_1(P)$  transition  $16,393 \text{ cm}^{-1}$  with additional absorptions appearing as shoulders on both sides of this band. These data were used [18] to calculate  $10Dq$  and  $B$  the Racah

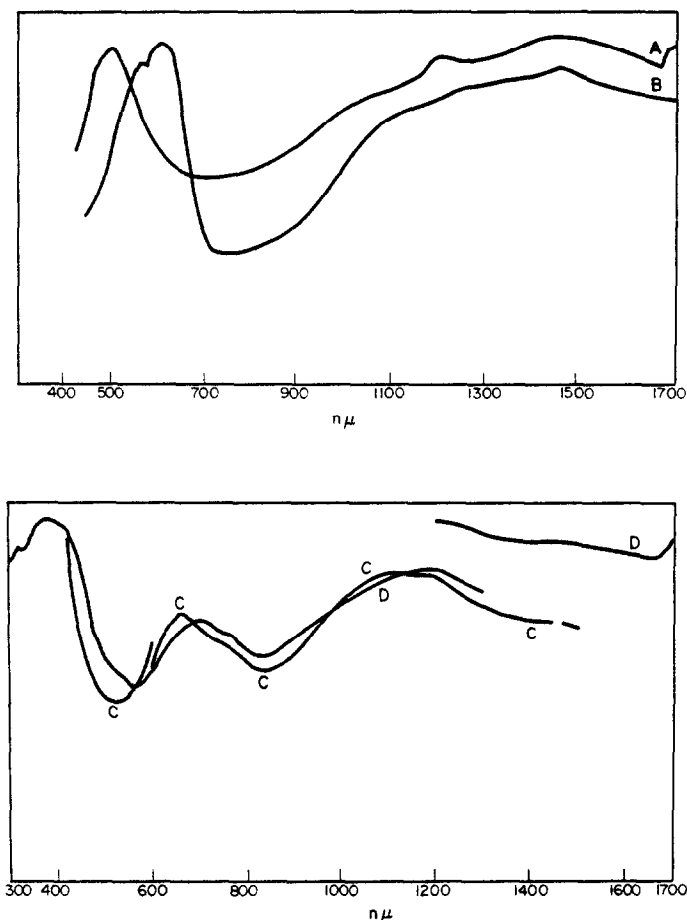


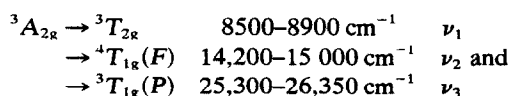
Fig. 2 Electronic spectra (A)  $\text{Co}(\text{NCS})_2(\text{Hmta})_2(\text{EtOH})_2$ , (B)  $\text{Co}(\text{NCS})_2(\text{Hmta})_2$ , (C)  $\text{Ni}(\text{NCS})_2(\text{Hmta})_2(\text{EtOH})_2$ , (D)  $\text{Ni}(\text{NCS})_2(\text{Hmta})_2$

parameter for tetrahedral cobalt(II)— $3230.6$  and  $986.5 \text{ cm}^{-1}$ , respectively. The spin-orbit coupling constant ( $\lambda$ ) obtained by using the procedure of BALLHAUSEN [13] indicate considerable overlap and delocalization of the  $d$ -orbitals of cobalt(II). Infrared spectrum due to coordinated Hmta does not show any significant splitting of the C–N stretching bands and except for the shifting of some bands and some intensity changes is almost superimposable on the i.r. spectrum of uncoordinated Hmta. These features clearly indicate the presence of terminally bonded mono-dentate Hmta molecules [9] retaining the chair configuration of the uncoordinated Hmta [10]. In addition to the ligand bands i.r. spectrum of this complex shows absorption bands at  $2080$ ,  $2060$ ,  $820$ ,  $476$ ,  $470$ ,  $320$  and  $300 \text{ cm}^{-1}$  due to coordinated thiocyanate groups. These bands are assigned as  $\nu_{\text{CN}}$  ( $2080$ ,  $2060 \text{ cm}^{-1}$ ),  $\nu_{\text{CS}}$  ( $820 \text{ cm}^{-1}$ ),  $\delta_{\text{NCS}}$  ( $476$ ,  $470 \text{ cm}^{-1}$ ) and  $\nu_{\text{Co-NCS}}$  ( $320$ ,  $300 \text{ cm}^{-1}$ ) modes and their frequencies are consistent with terminally N-bonded NCS groups [19]. From a consideration of its colour, room temperature magnetic moment, electronic bands, the presence of terminally bonded

mono-dentate Hmta molecules retaining the chair configuration and terminally N-bonded NCS groups the complex  $\text{Co}(\text{NCS})_2(\text{Hmta})_2$  is tentatively assigned to have a monomeric, four-coordinated structure with a tetrahedral environment of four nitrogen atoms (two from Hmta molecules and two from NCS groups) around the metal atoms in the solid state. The X-ray powder patterns of  $\text{Co}(\text{NCS})_2(\text{Hmta})_2(\text{EtOH})_2$  and  $\text{Co}(\text{NCS})_2(\text{Hmta})_2$  show significant differences in  $d$  ( $\text{\AA}$ ) values and intensities thereby clearly indicating that the two complexes have essentially different structures.

Both the nickel (II) thiocyanate complexes,  $\text{Ni}(\text{NCS})_2(\text{Hmta})_2(\text{EtOH})_2$  and  $\text{Ni}(\text{NCS})_2(\text{Hmta})_2$  (the latter was obtained on heating the former at  $140^\circ\text{C}$  for 30 min in an air oven) possess room temperature magnetic moments between 3.0 and 3.2 B.M. which definitely rule out the presence of square planar nickel (II) [12]. The electronic spectra of both these complexes exhibit absorption bands at  $\sim 8500$ – $8900$ ,  $14,200$ – $15,000$  and  $25,300$ – $26,350 \text{ cm}^{-1}$ . The nickel (II) ion has a  $d^8$  configuration which gives rise to  ${}^3A_{2g}$  ground state in a regular octahedral field and absorption bands at

~8500, 13,500 and 25,000  $\text{cm}^{-1}$  corresponding to transitions to the excited states  ${}^3T_{2g}$ ,  ${}^3T_{1g}(F)$  and  ${}^3T_{1g}(P)$ , respectively, are considered characteristic of nickel (II) in such an environment [18] The observed bands in the electronic spectra of the two nickel (II) complexes are assigned as



The frequencies of these bands agree well with those predicted from the LIEHR and BALLHAUSEN energy level diagram for nickel (II) in an octahedral field [20] From the observed absorption bands the value of  $10 Dq$  ( $8500\text{--}8900 \text{ cm}^{-1}$ ) is taken as the lowest energy transition  ${}^3A_{2g} \rightarrow {}^3T_{2g}$  and  $B$  the Racah parameter is calculated from the relationship [12]  $B = (\nu_2 + \nu_3 - 30 Dq)/15$  The observed values of the magnetic moments ( $\sim 3.2 \text{ B.M.}$ ) for both these complexes are somewhat higher than the spin-only value,  $2.84 \text{ B.M.}$ , for nickel (II) The reason for this deviation may be that the spin-orbit coupling causes an orbital contribution in the quenched  ${}^3A_{2g}$  ground state of the nickel (II) ion The influence on  $\mu$  is of second order perturbation and is given by the relation  $\mu_{\text{obs}} = \mu_{\text{so}}(1 - 4\lambda/10 Dq)$ ,  $\lambda$  being the spin-orbit coupling constant Substituting the values of  $10 Dq$  we obtain values for ( $\lambda$ ) of  $212$  and  $279 \text{ cm}^{-1}$  for  $\text{Ni}(\text{NCS})_2(\text{Hmta})_2(\text{EtOH})_2$  and  $\text{Ni}(\text{NCS})_2(\text{Hmta})_2$ , respectively Compared with the free ion value [17] of  $324 \text{ cm}^{-1}$  we have a significant reduction ( $\sim 30\text{--}15\%$ ) which indicates the high orbital contribution and covalent character The ratio  $\nu_2/\nu_1$ ,  $1.67$ , for both these complexes is lower than the value  $1.8$  for the octahedral species  $\text{Ni}(\text{H}_2\text{O})_6^{2+}$  and may be attributed to the asymmetric environment around nickel (II) and some distortion from the regular  $O_h$  symmetry The  $B$  values,  $963.7$  and  $930.6 \text{ cm}^{-1}$  (Table 1) for these complexes are also less than the free ion value of  $1041 \text{ cm}^{-1}$  which again is an indication of orbital overlap and delocalization of the  $d$ -orbitals. Thus the room temperature magnetic moment values and electronic spectral data of both these nickel complexes are consistent with pseudo-octahedral environments around nickel (II)

The C-N stretching bands at  $1225$  and  $1000 \text{ cm}^{-1}$  in uncoordinated Hmta do not suffer splittings in the IR spectrum of the light blue complex  $\text{Ni}(\text{NCS})_2(\text{Hmta})_2(\text{EtOH})_2$  In addition to the slight shifting of some IR bands, indicating the presence of terminally bonded Hmta molecules [9], IR spectrum due to Hmta in this complex is almost superimposable on that of uncoordinated Hmta indicating thereby that the chair configuration of the uncoordinated Hmta is retained in this complex Additional bands observed at  $2090$ ,  $814$ ,  $486$  and  $290 \text{ cm}^{-1}$  are assigned as  $\nu\text{CN}$ ,  $\nu\text{CS}$ ,  $\delta\text{NCS}$  and  $\nu\text{Ni-NCS}$  modes, respectively, consistent with the presence of terminally N-bonded NCS groups in

the complex [19] Furthermore, a band at  $465 \text{ cm}^{-1}$  in this complex is assigned to  $\nu\text{Ni-O}(\text{EtOH})$  mode Based on the considerations of magnetic moment value, electronic and IR spectral studies the  $\text{Ni}(\text{NCS})_2(\text{Hmta})_2(\text{EtOH})_2$  complex is tentatively assigned a monomeric, six-coordinated structure with an octahedral environment of four nitrogen atoms (two from two terminally bonded Hmta molecules retaining the chair configuration of the uncoordinated molecules, and two from terminally N-bonded NCS groups) and two oxygen atoms (from two coordinated EtOH molecules) around the metal ions in the solid state Moreover, the X-ray diffraction powder patterns of  $\text{Co}(\text{NCS})_2(\text{Hmta})_2(\text{EtOH})_2$  and  $\text{Ni}(\text{NCS})_2(\text{Hmta})_2(\text{EtOH})_2$  are almost identical in their  $d$  ( $\text{\AA}$ ) values and intensities thereby suggesting that the two complexes are isostructural

Infrared spectrum due to coordinated Hmta in the greenish-yellow complex  $\text{Ni}(\text{NCS})_2(\text{Hmta})_2$  is consistent with the presence of bidentate Hmta molecules bridged between metal atoms retaining the chair configuration of the uncoordinated Hmta Infrared bands due to NCS groups— $\nu\text{CN}$   $2095 \text{ cm}^{-1}$ ,  $\nu\text{CS}$   $820 \text{ cm}^{-1}$ ,  $\nu\text{NCS}$   $480$ ,  $470 \text{ cm}^{-1}$  and  $\nu\text{Ni-NCS}$   $300 \text{ cm}^{-1}$ —are consistent with terminally N-bonded NCS groups in the complex [19] From a consideration of magnetic moment value, electronic and IR spectral bands the  $\text{Ni}(\text{NCS})_2(\text{Hmta})_2$  complex is tentatively assigned to have a six-coordinated polymeric chain structure with an octahedral environment of six nitrogen atoms (four from bidentate bridging Hmta molecules, retaining the chair configuration, and two from terminally N-bonded NCS groups) around the metal ions in the solid state

#### Copper (II) complex

The copper (II) complex,  $\text{Cu}(\text{NCS})_2(\text{Hmta})_2$  is khaki in colour The  $\mu_{\text{eff}}$  value of  $1.35 \text{ B.M.}$  is, however, lower than the expected value ( $1.93 \text{ B.M.}$ ) suggesting an antiferromagnetic interaction presumably through the bridging groups Electronic spectrum of this complex shows a strong broad band at  $14,705 \text{ cm}^{-1}$  which certainly rules out tetrahedral geometry [21] for which no band is observed in the range  $10,000\text{--}12,000 \text{ cm}^{-1}$  The observed band at  $14,705 \text{ cm}^{-1}$  is characteristic of distorted octahedral geometry with a  $C_{4v}$  point symmetry [22]. Three bands are expected with this point group [22] The broad high energy main band may be assigned to the superimposed transitions  ${}^2B_1 \rightarrow {}^2B_2$  and  ${}^2B_1 \rightarrow {}^2E$  and the other band/shoulder to a  ${}^2B_1 \rightarrow {}^2A_1$  transition Thus the magnetic moment value and electronic spectral data suggest a pseudo-octahedral stereochemistry with weak Cu-Cu interactions Infrared bands due to coordinated Hmta molecules indicate the presence of bi-dentate-bridged Hmta molecules retaining the chair configuration of the uncoordinated

molecule in this complex. Moreover, the fundamental bands due to NCS groups suggest the exclusive presence of terminally N-bonded NCS groups [19]. The complex  $\text{Cu}(\text{NCS})_2(\text{Hmta})_2$  is thus tentatively assigned a polymeric chain six-coordinate structure with a distorted octahedral environment of six nitrogen atoms (four from bidentate bridging Hmta molecules and two from terminally N-bonded NCS groups) around the metal atoms in the solid state.

#### Zinc (II) and cadmium (II) complexes

Zinc thiocyanate gave a 1:2 complex with Hmta while cadmium thiocyanate a 1:1 complex. The techniques of electronic absorption spectroscopy and magnetic susceptibility measurements yield unambiguous structural information for transition metal compounds. However, these could not be studied for zinc (II) and cadmium (II) thiocyanate complexes as both these metal ions have closed shells of valence electrons. Information on the tentative stereochemistries of their complexes in the present study has been derived from a comparison of their metal-Hmta and metal-thiocyanate bondings with similar modes in complexes whose structures have been established by X-ray crystallography and/or magnetic susceptibility, electronic and IR spectral studies. Thiocyanates of group IIB metals offer interesting examples of the mode of metal-thiocyanate bonding. Whereas zinc (II) and mercury (II) generally form M-NCS and M-SCN complexes, respectively, cadmium (II) is intermediate in that both Cd-NCS and Cd-SCN species have been observed [23]. In fact, cadmium (II) halide and pseudohalide complexes  $\text{CdL}_2\text{X}_2$  and  $\text{CdLX}_2$ , where L = a monodentate ligand and X = Cl, Br, I or NCS, are mostly six-coordinated polymeric structures built up from chains of octahedra with halogen/pseudohalogen bridges [24]. A few monomeric four- and six-coordinated cadmium (II) thiocyanate complexes with terminally S-bonded thiocyanate groups have recently been reported [25].

Infrared spectra of  $\text{Zn}(\text{NCS})_2(\text{Hmta})_2$  and  $\text{Cd}(\text{NCS})_2(\text{Hmta})_2$  complex show splitting of bands at 1225 and 1000  $\text{cm}^{-1}$  due to CN stretching modes of Hmta, thereby, clearly indicating the presence of bi-dentate-bridged Hmta molecules retaining the chair configuration of the uncoordinated Hmta in both these complexes. In addition to the bands due to coordinated Hmta molecules, IR spectrum of the zinc complex shows absorption bands at 2085, 2065, 835, 485 and 300  $\text{cm}^{-1}$ . These bands are identified (Table 2) due to coordinated thiocyanate groups and their frequencies are consistent [19] with terminally N-bonded NCS groups. Moreover, the IR spectrum and the X-ray powder pattern of this complex are almost identical to those of  $\text{Mn}(\text{NCS})_2(\text{Hmta})_2$  and  $\text{Ni}(\text{NCS})_2(\text{Hmta})_2$ . This close similarity in the IR spectrum as well as the

X-ray powder pattern strongly suggest that the 1:2 zinc(II) thiocyanate-Hmta complex has a six-coordinate polymeric chain structure with an octahedral environment of six nitrogen atoms (four from bidentate bridging Hmta molecules retaining the chair configuration and two from terminally N-bonded NCS groups) around the zinc (II) ions in the solid state.

The fundamental frequencies due to coordinated thiocyanate groups (Table 2) in the 1:1 cadmium (II) thiocyanate-Hmta complex are consistent with terminally N-bonded NCS groups. With bi-dentate bridging Hmta molecules retaining the chair configuration (*vide supra*) and terminally N-bonded NCS groups, this compound is tentatively assigned to have a four-coordinated polymeric chain structure with a tetrahedral environment of four nitrogen atoms (two from bridging Hmta molecules and two from terminally N-bonded NCS groups) around the metal ions in the solid state.

The tentative stereochemistries of the compounds reported herein have been derived from a comparison of their magnetic moments, electronic and IR spectral features with those of compounds of established structures. However, unambiguous characterization of these compounds should be based on complete crystal structure determinations.

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