

## Infrared spectral evidence for mono-, bi- and tetra-dentate behaviour of hexamethylenetetramine

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**Abstract.** Infrared spectral features to distinguish the different modes of hexamethylenetetramine in metal complexes have been presented. The tentative mode of metal-hexamethylenetetramine bonding has been arrived at from the pattern of the two  $\nu_{\text{CN}}$  bands at 1225 and 1000  $\text{cm}^{-1}$ . It is shown that in complexes with terminal monodentate, bidentate and tetradentate the bands show differing behaviour. Except for the splitting of  $\nu_{\text{CN}}$  bands the IR spectra are superimposable on that of the uncoordinated molecule supporting the theory that chair configuration of the uncoordinated hexamethylenetetramine is retained in all the complexes.

**Keywords.** Infrared spectra; hexamethylenetetramine; monodentate; bidentate; tetradentate.

### 1. Introduction

Hexamethylenetetramine (HMTA), a potentially tetradentate ligand, has until recently been known to act only as bidentate ligand bridging between two metal ions (Negita *et al* 1965). A number of complexes of metal salts have been prepared with this ligand (Ahuja *et al* 1979, 1980, 1981a,b; 1982) and in this paper the IR spectral features to distinguish the different modes of metal HMTA bondings are reported.

### 2. Experimental, results and discussion

The complexes studied are listed in table 1.

HMTA is a heterocyclic system with three fused rings in the chair configuration and four bridge-head nitrogen atoms. The chemical and steric equivalence of the four nitrogen atoms (donor sites) has been demonstrated by various physicochemical methods (Andersen 1957). It is considered to act as a mono-, bi-, tri- or tetra-dentate ligand. Framework molecular models suggest that the lone pair of electrons on each of the four nitrogen atoms point outwards and the simultaneous coordination of more than one site to the same metal ion is ruled out. It can, however, act as a bidentate-bridging ligand resulting in polymeric structures or that all the bonding sites may coordinate simultaneously to four metal ions resulting in tetranuclear structures.

The 1300-200  $\text{cm}^{-1}$  region IR spectrum of uncoordinated HMTA (nujol mull) shows absorption bands at 1225s, 1180w, 1040m, 1000s, 813w, 803s, 714w, 664s, 610m and 508s  $\text{cm}^{-1}$ . Of these the two strong bands at 1225 and 1000  $\text{cm}^{-1}$  are assigned to the fundamentals of the CN stretching modes (Mecke and Spiescke 1955). Negita *et al* (1965) pointed out that both these  $\nu_{\text{CN}}$  bands are split into two well-defined and well-separated bands in complexes in which the HMTA was considered as bidentate-

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Table 1. Hexamethylenetetramine complexes with metal salts.

Complex	Tentative stereochemistry	Mode of Metal-HMTA bonding
UO <sub>2</sub> (HMTA) <sub>2</sub> SO <sub>4</sub>	Polymeric 8-coordinate	BB
UO <sub>2</sub> (HMTA)(NO <sub>3</sub> ) <sub>2</sub>	Polymeric 8-coordinate	BB
UO <sub>2</sub> (HMTA)(NCS) <sub>2</sub>	Polymeric 8-coordinate	BB
Hg(HMTA)Cl <sub>2</sub>	Polymeric tetrahedral	BB
Hg(HMTA)Br <sub>2</sub>	Polymeric tetrahedral	BB
Hg(HMTA)(CN) <sub>2</sub>	Polymeric tetrahedral	BB
Hg <sub>4</sub> (HMTA)(NCS) <sub>8</sub>	Monomeric tetranuclear three-coordinate	T
Co(HMTA)(NO <sub>3</sub> ) <sub>2</sub>	Polymeric octahedral	BB
Ni(HMTA)(NO <sub>3</sub> ) <sub>2</sub>	Polymeric octahedral	BB
Cu(HMTA) <sub>2</sub> (NO <sub>3</sub> ) <sub>2</sub>	Polymeric octahedral	BB
Zn(HMTA)(NO <sub>3</sub> ) <sub>2</sub>	Polymeric tetrahedral	BB
Ag(HMTA)(NO <sub>3</sub> ) <sub>2</sub>	Polymeric two-coordinate	BB
Cd(HMTA) <sub>2</sub> (NO <sub>3</sub> ) <sub>2</sub>	Polymeric octahedral	BB
Mn(HMTA) <sub>2</sub> (NCS) <sub>2</sub> (EtOH) <sub>2</sub>	Monomeric octahedral	TM
Mn(HMTA) <sub>2</sub> (NCS) <sub>2</sub>	Polymeric octahedral	BB
Co(HMTA) <sub>2</sub> (NCS) <sub>2</sub> (EtOH) <sub>2</sub>	Monomeric octahedral	TM
Co(HMTA) <sub>2</sub> (NCS) <sub>2</sub>	Monomeric tetrahedral	TM
Ni(HMTA) <sub>2</sub> (NCS) <sub>2</sub> (EtOH) <sub>2</sub>	Monomeric octahedral	TM
Ni(HMTA) <sub>2</sub> (NCS) <sub>2</sub>	Polymeric octahedral	BB
Cu(HMTA) <sub>2</sub> (NCS) <sub>2</sub>	Polymeric octahedral	BB
Zn(HMTA) <sub>2</sub> (NCS) <sub>2</sub>	Polymeric octahedral	BB
Cd(HMTA)(NCS) <sub>2</sub>	Polymeric tetrahedral	BB
Ni(HMTA) <sub>2</sub> (OAc) <sub>2</sub>	Monomeric octahedral	TM
Zn(HMTA) <sub>2</sub> (OAc) <sub>2</sub>	Monomeric tetrahedral	TM
Mn(HMTA)SO <sub>4</sub>	Polymeric octahedral	BB
Co(HMTA)SO <sub>4</sub>	Polymeric octahedral	BB
Ni(HMTA)SO <sub>4</sub>	Polymeric octahedral	BB
Zn(HMTA)SO <sub>4</sub>	Polymeric octahedral	BB
Cd(HMTA)SO <sub>4</sub>	Polymeric octahedral	BB

BB = Bidentate bridging; T = Tetradentate; TM = Terminal monodentate

bridging ligand. We find, however, that most of the complexes exhibit bidentate bridging nature of HMTA (figure 1). (Evidence of stereochemical environments deduced from their room temperature magnetic moment values, electronic spectral bands and ligand field parameters being considered is consistent with the bidentate-bridging behaviour of HMTA). Apart from some intensity changes and splitting of  $\nu_{CN}$  bands the IR spectra due to coordinated HMTA in all these complexes are almost superimposable on that of the uncoordinated ligand. This may be because the chair configuration of the uncoordinated HMTA is retained in the complexes irrespective of the mode of metal-HMTA bonding. The 1225 cm<sup>-1</sup> band splits into ~1215 and 1235 cm<sup>-1</sup> and the 1000 cm<sup>-1</sup> into ~1010 and 970 cm<sup>-1</sup> providing a means to distinguish the bidentate-bridging behaviour of HMTA (Negita *et al* 1965; Ahuja *et al* 1979, 1980, 1981, 1982). It may be pointed out that the geometry of HMTA rules out the possibility of it acting as a bidentate-chelating ligand.

The room temperature magnetic moment values, electronic spectral bands and ligand field parameters of the complexes Mn(HMTA)<sub>2</sub>(NCS)<sub>2</sub>(EtOH)<sub>2</sub>, Co(HMTA)<sub>2</sub>(NCS)<sub>2</sub>(EtOH)<sub>2</sub>, Co(HMTA)<sub>2</sub>(NCS)<sub>2</sub>, Ni(HMTA)<sub>2</sub>(NCS)<sub>2</sub>(EtOH)<sub>2</sub> and Ni(HMTA)<sub>2</sub>(OAc)<sub>2</sub> are consistent with octahedral environments (tetrahedral)

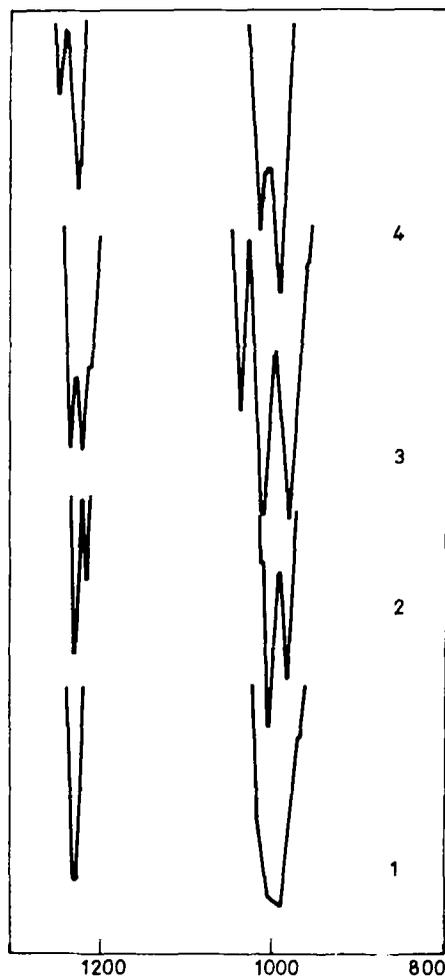


Figure 1. 1. Uncoordinated HMTA; 2.  $\text{Hg(HMTA)(CN)}_2$ ; 3.  $\text{Hg(HMTA)Br}_2$ ; 4.  $\text{Co(HMTA)Cl}_2$ .

(Ahuja *et al* (1982) in the case of  $\text{Co(HMTA)}_2(\text{NCS})_2$  around the respective metal ion (Ahuja *et al* 1981). Moreover, the fundamental frequencies due to the thiocyanate groups are consistent with the presence of terminally N-bonded NCS groups (Ahuja *et al* 1981). IR frequencies due to the acetate groups are consistent with bidentate chelating (acetato) ligands in the  $\text{Ni(HMTA)}_2(\text{OAc})_2$  complex (Ahuja *et al* 1981). These considerations lead one to conclude that HMTA molecules must be terminally-bonded monodentate ligands in all these complexes. The two  $\nu_{\text{CN}}$  bands at 1225 and 1000  $\text{cm}^{-1}$  in these complexes suffer only very minor splitting resulting in closely-spaced doublets or triplets (Ahuja *et al* 1982). Moreover, except for intensity changes of some absorption bands the IR spectra due to coordinated HMTA in these complexes are almost superimposable on that of the uncoordinated HMTA supporting the theory that the chair configuration of the uncoordinated HMTA is retained. It is thus evident that complexes in which HMTA is terminally-bonded monodentate ligand, only very minor splitting of the two  $\nu_{\text{CN}}$  bands at 1225 and 1000  $\text{cm}^{-1}$  occurs resulting in closely-spaced doublets or triplets (figure 2).

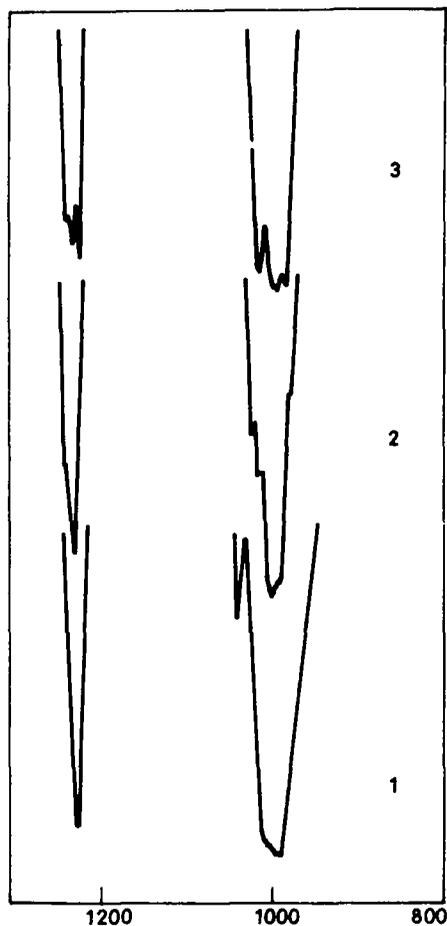


Figure 2. 1. Uncoordinated HMTA; 2.  $\text{Co}(\text{HMTA})_2(\text{NCS})_2(\text{EtOH})_2$ ; 3.  $\text{Ni}(\text{HMTA})_2(\text{NCS})_2(\text{EtOH})_2$ .

Although HMTA is a potentially tetradentate ligand not more than one donor site can coordinate to the same metal ion. These donor sites can, however, coordinate to four metal ions resulting in tetranuclear structures. Tetradentate HMTA would have the same symmetry as the uncoordinated molecule. With all the four donor atoms equivalent, *i.e.* coordinated (tetradentate HMTA), the IR spectrum due to tetradentate HMTA would not be expected to suffer any splitting of  $\nu_{\text{CN}}$  bands and would indeed be superimposable on that of the uncoordinated HMTA.

Except for some intensity changes and the slightly lower frequencies of some absorption bands (which provides good evidence for the absence of free ligand), cf. coordinated 1,4-dioxane (Mikawa *et al* 1966) the IR spectrum due to coordinated HMTA in 4:1 mercury (II) thiocyanate-HMTA complex is superimposable on that of the uncoordinated HMTA. The two  $\nu_{\text{CN}}$  bands at 1225 and 1000  $\text{cm}^{-1}$  do not suffer any splitting at all (figure 3) (Ahuja *et al* 1982). This close similarity in the IR spectra of uncoordinated HMTA and the coordinated HMTA and the non-splitting of the  $\nu_{\text{CN}}$  bands in this complex may be attributed to the fact that the overall symmetry and the chair configuration of uncoordinated HMTA is retained, or in other words, all the four donor sites are equivalent, that is coordinated in this compound.

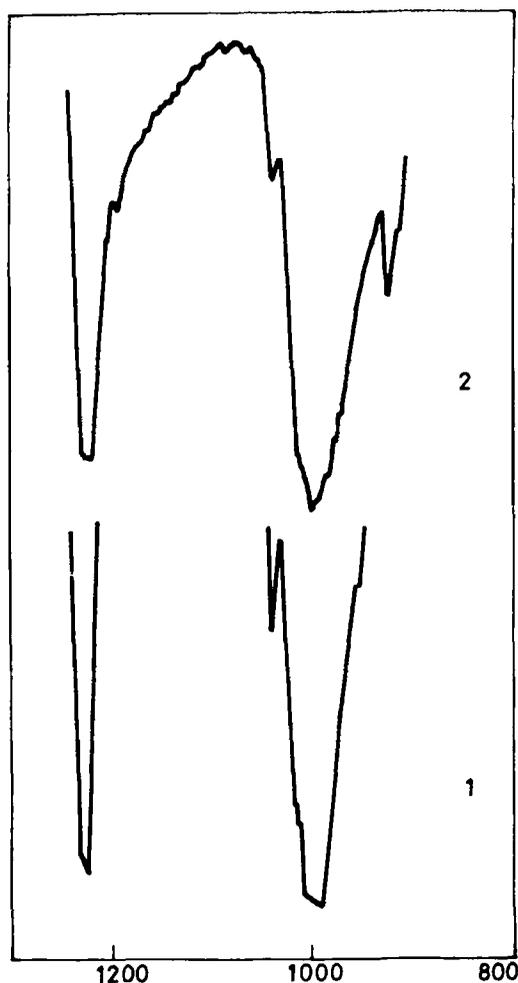


Figure 3. 1. Uncoordinated HMTA; 2.  $\text{Hg}_2(\text{HMTA}) (\text{NCS})_6$ .

It is thus concluded that the comparison of IR spectra of the coordinated HMTA with that of its uncoordinated spectrum in the  $\nu_{\text{CN}}$  region lends considerable support for distinguishing the mode of metal-HMTA bonding in metal complexes with this potentially tetradentate ligand. However, x-ray and Raman studies would lead to more conclusive support for the mode of metal-HMTA bonding.

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