

## PHYSICO-CHEMICAL STUDIES OF SOME HEXAMETHYLENETETRAMINE METAL(II) COMPLEXES

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**ABSTRACT.** Divalent metal (Mn, Co, Ni) complexes of the ligand hexamethylenetetramine (HMTA,  $C_6H_{12}N_4$ ) with sulfate, nitrate and fluoroborate as counter ions have been synthesized in ethanolic media. Whereas the complexes with  $BF_4^-$  and  $NO_3^-$  as counter ions have two molecules of hexamethylenetetramine, those with  $SO_4^{2-}$  as counter ion contain just one molecule of hexamethylenetetramine. The complexes have been characterized by elemental analyses, infrared and visible spectroscopy and room temperature magnetic susceptibility measurements. The results suggest octahedral coordination in which the central metal ion is bonded to hexamethylenetetramine and water molecules.

**KEY WORDS:** Divalent metal (Mn, Co, Ni) complexes, Hexamethylenetetramine, Sulfate as counter ion, Nitrate as counter ion, Fluoroborate as counter ion

### INTRODUCTION

The coordination chemistry of multi-dentate nitrogen-donor ligands has received much attention recently due to the enhanced thermodynamic and kinetic stability of the resulting complexes [1, 2], and their applications as chelating agents with potential applications as models to describe the active sites in metallo-proteins and other biological systems [3]. Some of these multi-dentate ligands have induced the formation of one- and two-dimensional framework structures as a result of constraints induced by coordination [1-3].

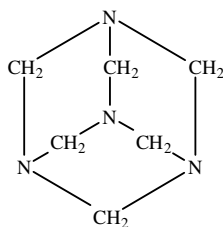


Figure 1. The structure of hexamethylenetetramine.

Among the multi-dentate N-donor ligands whose coordination behaviour has been studied is hexamethylenetetramine (HMTA,  $C_6H_{12}N_4$ ) which is a fairly strong organic base and possesses four potential nitrogen donor atoms (Figure 1). Hexamethylenetetramine reacts with many hydrated salts forming molecular complexes [4-7]. Frenkel and Panchenko [7] reported the synthesis of  $Zn(HMTA)X_2$ , X = halide, which was used as a catalyst in the vulcanisation of unsaturated rubbers. Similar work was reported by Allan *et al.* [8] who synthesised HMTA

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complexes of divalent metal ions with halide counter ions. The nature of these complexes depends on the inter-play between the metal ion, the counter ion and HMTA. In our previous paper [9], we reported the synthesis and characterisation of some hexamethylenetetramine complexes of some divalent metal acetates.

This paper reports our investigation on the effects of the counter ion (sulfate, nitrate, fluoroborate) on the physico-chemical properties of hexamethylenetetramine complexes of some divalent metal ions ( $\text{Mn}^{2+}$ ,  $\text{Co}^{2+}$ ,  $\text{Ni}^{2+}$ ). Our compounds have been characterised by elemental analyses, infrared and electronic spectroscopy and room temperature magnetic susceptibility measurements.

## EXPERIMENTAL

### *Synthesis of the complexes*

Samples of divalent metal salts (0.025 mol) and hexamethylenetetramine (0.025 mol) were separately dissolved in 50 mL of 95% ethanol. The hexamethylenetetramine solution was then added drop-wise to the stirred metal salt solution at room temperature and the mixture stirred for 4 h. The resulting crystals were filtered off, washed with ether and dried over silica gel in a desiccator under vacuum.

Complexometric titrations [10, 11] were carried out to determine manganese, cobalt and nickel. Elemental analyses for carbon, nitrogen and hydrogen were carried out in the Micro-analytical services of the Universities of Leeds and Ibadan. The physical and analytical data of the complexes are presented in Table 1.

Table 1. Physical and analytical data of divalent-HMTA complexes.

Compound	Colour	M.p. (°C)	Yield (%)	Elemental analyses							
				% Found				% Calculated			
				Metal	C	H	N	Metal	C	H	N
$\text{Mn}(\text{HMTA})(\text{H}_2\text{O})_8\text{SO}_4$	White	212	64	12.7	16.4	6.4	12.6	12.6	16.5	6.6	12.9
$\text{Mn}(\text{HMTA})_2(\text{H}_2\text{O})_2(\text{BF}_4)_2$	White	163	60	11.4	26.1	4.9	19.6	10.4	26.4	5.1	20.5
$\text{Mn}(\text{HMTA})_2(\text{H}_2\text{O})_8(\text{NO}_3)_2$	White	164	62	9.9	23.7	6.4	25.1	10.0	23.9	6.6	25.5
$\text{Co}(\text{HMTA})_2(\text{H}_2\text{O})_8\text{SO}_4$	Violet	106	66	13.4	16.1	6.6	12.8	13.5	16.4	6.4	12.7
$\text{Co}(\text{HMTA})_2(\text{H}_2\text{O})_5(\text{BF}_4)_2$	Violet	181	64	9.8	23.6	5.3	18.4	10.1	23.8	5.6	18.5
$\text{Co}(\text{HMTA})_2(\text{H}_2\text{O})_{10}(\text{NO}_3)_2$	Violet	92	71	9.0	22.1	6.5	21.9	9.2	22.4	6.8	21.7
$\text{Ni}(\text{HMTA})(\text{H}_2\text{O})_8\text{SO}_4$	Green	117	70	13.4	16.1	6.2	12.8	13.5	16.4	6.4	12.4
$\text{Ni}(\text{HMTA})_2(\text{H}_2\text{O})_4(\text{BF}_4)_2$	Green	186	67	10.4	26.0	6.0	19.0	10.1	26.2	5.8	19.2
$\text{Ni}(\text{HMTA})_2(\text{H}_2\text{O})_{10}(\text{NO}_3)_2$	Green	160	68	9.1	22.0	6.6	21.9	9.1	22.2	6.8	21.8

### *Infrared and electronic spectroscopy*

The infrared spectra of hexamethylenetetramine and the complexes were recorded in the region  $4000\text{--}200\text{ cm}^{-1}$  by use of a Perkin-Elmer 457 spectrophotometer and a pressed KBr disc. The instrument was calibrated with a polystyrene film. The electronic spectra of the complexes in methanol were recorded on an SP800 spectrophotometer.

### *Magnetic susceptibility measurements*

The magnetic susceptibilities of the powdered complexes were measured at room temperature using the Gouy method, with mercury tetrathiocyanato-cobaltate(II) as calibrant [12]. The effective magnetic moments,  $\mu_{\text{eff}}$  were calculated from the expression:

$$\mu_{\text{eff}} = 2.83 \sqrt{\chi_A T}$$

where  $\chi_A$  is the magnetic susceptibility per gram-atom after correction for diamagnetic contributions and T the temperature.

## RESULTS AND DISCUSSION

All the complexes showed sharp melting points, an indication that they are pure substances. The yields range between 60% and 71%. The metal salts from which the complexes are derived are more hygroscopic and more intense in colour than the corresponding complexes. Elemental analysis indicates that the complexes with sulfate ( $\text{SO}_4^{2-}$ ) as counter ion have only one molecule of HMTA in each case, for example,  $\text{M}(\text{HMTA})(\text{H}_2\text{O})_8\text{SO}_4$ . Aktanova *et al.* [13] obtained similar results with chloride as counter ion for Co(II) and Ni(II). On the other hand, complexes with fluoroborate and nitrate as counter ions have two molecules of HMTA in each case, i.e.  $\text{M}(\text{HMTA})_2(\text{H}_2\text{O})_x(\text{NO}_3)_2$  (with  $x = 8$  or  $10$ ) and  $\text{M}(\text{HMTA})_2(\text{H}_2\text{O})_x(\text{BF}_4)_2$ , (with  $x = 2, 4, 5$ ). Balicheva and Pologikh [6] and Allan *et al.* [8] who worked on complexes of transition metal perchlorates and halides with HMTA as ligand, also found that each molecular complex contains two HMTA molecules. In our case, the difference, between sulfate on the one hand, and nitrate or fluoroborate on the other, may reflect different charges on the counter ions but X-ray structural data are necessary to confirm this hypothesis.

### Infrared Spectra

The relevant vibrational frequencies of hexamethylenetetramine and the complexes are presented in Table 2. The infrared bands observed at  $1160\text{-}1090\text{ cm}^{-1}$  assigned to  $\nu(\text{SO}_4^{2-})$  are similar to those reported by Giuseppetti [14] and the bands at  $1400\text{-}1375\text{ cm}^{-1}$  have been assigned to uncoordinated  $\text{NO}_3^-$  ion [15]. The infrared band at  $535\text{ cm}^{-1}$  assigned to  $\nu(\text{BF}_4^-)$  def is similar to those reported for potassium [16] and copper or silver [17] perfluoroborates in which the  $\text{BF}_4^-$  anions are not (or very weakly) coordinated to the metal.

The coordinated bond between the water molecule and the cations results in the appearance of a vibrational band at  $682\text{-}750\text{ cm}^{-1}$  [ $\nu(\text{M-OH}_2)$ ] [6]. A single band at  $1600\text{-}1610\text{ cm}^{-1}$  for the fluoroborate complexes indicates the equivalence of all the water molecules. Their analogues,  $\text{SO}_4^{2-}$  and  $\text{NO}_3^-$  have two bands at  $1675$  and  $1610\text{ cm}^{-1}$  indicating two types of bonding of water molecules, i.e. coordinated and uncoordinated [18]. The very broad band at  $3395\text{-}3400\text{ cm}^{-1}$  observed in all the complexes has been assigned to  $\nu(\text{O-H})$  and is characteristic of coordinated water molecules.

The bands at  $1452, 1360$  and  $1230\text{ cm}^{-1}$ , which have been assigned respectively to  $\nu_{\text{as}}(\text{CH}_2)$ ,  $\nu_{\text{s}}(\text{CH}_2)$ , and  $\nu(\text{C-N})$  in the free HMTA, are similar to those reported by Baker [19] and Ennan [20].

These bands show significant differences in positions and intensities from those of the complexed HMTA (Table 2). These differences may be regarded as evidence that the ligand is coordinated to the metal ion.

Table 2. Selected IR bands ( $\text{cm}^{-1}$ ) of divalent metal-HMTA complexes.

Compound	$\nu(\text{O-H})$	$\nu(\text{H}_2\text{O})$	$\nu_s(\text{CH}_2)$	$\nu(\text{C-N})$	$\nu(\text{M-OH}_2)$	$\nu(\text{BF}_4^-)$	$\nu(\text{SO}_4^{2-})$	$\nu_s(\text{CH}_2)$	$\nu(\text{NO}_3^-)$
$\text{Mn}(\text{HMTA})(\text{H}_2\text{O})_8\text{SO}_4$	3400vbr	1635w 1610w	1370w	1235s	682m		1160w 1080br	1455m	
$\text{Mn}(\text{HMTA})_2(\text{H}_2\text{O})_2(\text{BF}_4)_2$	3400br	1600m	1372s	1234s	740br	535s		1458s	
$\text{Mn}(\text{HMTA})_2(\text{H}_2\text{O})_8(\text{NO}_3)_2$	3395br	1658m 1630w	1375s	1232s	682s			1458m	1375s
$\text{Co}(\text{HMTA})(\text{H}_2\text{O})_8\text{SO}_4$	3400vbr	1675m 1625w	1370s	1240s	690w		1100br	1468s	
$\text{Co}(\text{HMTA})_2(\text{H}_2\text{O})_5(\text{BF}_4)_2$	3395br	1605	1390s 1370m	1230w	750w	534w		1450m	
$\text{Co}(\text{HMTA})_2(\text{H}_2\text{O})_{10}(\text{NO}_3)_2$	3300vbr	1660br 1625w	1400br	1240m	685w			1470w	1400br
$\text{Ni}(\text{HMTA})(\text{H}_2\text{O})_8\text{SO}_4$	3400vbr	1655m 1610w	1375s	1235s	685w		1135w 1090br	1460s	
$\text{Ni}(\text{HMTA})_2(\text{H}_2\text{O})_4(\text{BF}_4)_2$	3400br	1615m	1370s	1232s	740w	534s		1455m	
$\text{Ni}(\text{HMTA})_2(\text{H}_2\text{O})_{10}(\text{NO}_3)_2$	3400br	1655m 1630br	1378s	1232s	685m			1458br	1378s
HMTA			1360m	1230s				1452m	

#### Room temperature magnetic moments

The room temperature magnetic moments for the complexes are presented in Table 3. Those for the manganese complexes:  $\text{Mn}(\text{HMTA})(\text{H}_2\text{O})_8\text{SO}_4$ ,  $\text{Mn}(\text{HMTA})_2(\text{H}_2\text{O})_8(\text{NO}_3)_2$  and  $\text{Mn}(\text{HMTA})_2(\text{H}_2\text{O})_2(\text{BF}_4)_2$  are 5.26, 6.10 and 6.21 B.M., respectively. Manganese(II), with an  $A_1$  ground term and in the absence of higher T-terms of sextuplet spin multiplicity, has a magnetic moment of 5.92 B.M. which is independent of temperature [21]. The values obtained for the complexes are slightly higher perhaps due to some distortion of the octahedral environment [8] or weak magnetic interactions [22].

At room temperature magnetic moment obtained for the cobalt complexes:  $\text{Co}(\text{HMTA})(\text{H}_2\text{O})_8\text{SO}_4$ ,  $\text{Co}(\text{HMTA})_2(\text{H}_2\text{O})_{10}(\text{NO}_3)_2$  and  $\text{Co}(\text{HMTA})_2(\text{H}_2\text{O})_5(\text{BF}_4)_2$  are 4.81, 4.74 and 5.08 B.M., respectively. These values are higher than the spin-only moment of 3.87 B.M. due to the large orbital contribution for an octahedral cobalt(II) ion with a  ${}^4T_{1g}$  ground state.

The room temperature magnetic moments for the nickel complexes  $\text{Ni}(\text{HMTA})(\text{H}_2\text{O})_8\text{SO}_4$ ,  $\text{Ni}(\text{HMTA})_2(\text{H}_2\text{O})_4(\text{BF}_4)_2$  and  $\text{Ni}(\text{HMTA})_2(\text{H}_2\text{O})_{10}(\text{NO}_3)_2$  are 3.76, 3.49 and 3.29 B.M., respectively. Usually, octahedral nickel(II) complexes have magnetic moments of 2.9-3.4 B.M. [23]. Our values are consistent with those reported for octahedral structures [8].

#### Visible spectroscopy

The solution electronic spectral data in methanol for the complexes are presented in Table 3. The visible spectra for the manganese(II) complexes could not be obtained.

The solution spectra for the cobalt complexes revealed two bands at  $(20620-20410) \text{ cm}^{-1}$  and  $19230 \text{ cm}^{-1}$  which have been assigned to  ${}^4T_{1g}(\text{F}) \rightarrow {}^4T_{2g}$  and  ${}^4T_{1g}(\text{F}) \rightarrow {}^4A_{2g}$  respectively. The third band  ${}^4T_{1g}(\text{F}) \rightarrow {}^4T_{1g}(\text{P})$  was not observed due to limitation of the instrument; its range could not permit the reading of this band.

Solution spectra for the nickel(II) complexes revealed weak bands at  $25000 \text{ cm}^{-1}$  and  $(14930-13700) \text{ cm}^{-1}$  and these have been assigned to  ${}^3A_{2g}(\text{F}) \rightarrow {}^3T_{1g}(\text{P})$  and  ${}^3A_{2g}(\text{F}) \rightarrow {}^3T_{1g}(\text{P})$  transitions, respectively.

The splitting of the second band is due to spin-orbit coupling which mixes the  ${}^3T_{1g}(F)$  and  ${}^1E_g$  states because they are very close in energy [24]. Sutton [25] reported that for octahedral nickel complexes the ratio of the first to the second band should be 1.8 whereas for tetrahedral complexes it should be close to 2.2. The ratios obtained for the three nickel complexes lie between 1.47 and 1.72 which suggests that the complexes assume the octahedral geometry.

Table 3. Room temperature magnetic moments and electronic spectral data for divalent metal-HMTA complexes in methanol.

Compound	$\mu_{\text{eff}}$ (B.M.)	Band maxima; $\text{cm}^{-1}$ ; ( $\epsilon$ , $\text{L mol}^{-1} \text{cm}^{-1}$ )	Assignment
Mn(HMTA)(H <sub>2</sub> O) <sub>8</sub> SO <sub>4</sub>	5.26		
Mn(HMTA) <sub>2</sub> (H <sub>2</sub> O) <sub>2</sub> (BF <sub>4</sub> ) <sub>2</sub>	6.21		
Mn(HMTA) <sub>2</sub> (H <sub>2</sub> O) <sub>8</sub> (NO <sub>3</sub> ) <sub>2</sub>	6.10		
Co(HMTA)(H <sub>2</sub> O) <sub>8</sub> SO <sub>4</sub>	4.81	20,620; (5.6) 19,230; (7.8)	${}^4T_{1g}(F) \rightarrow {}^4T_{1g}(P)$ ${}^4T_{1g}(F) \rightarrow {}^4A_{2g}$
Co(HMTA) <sub>2</sub> (H <sub>2</sub> O) <sub>5</sub> (BF <sub>4</sub> ) <sub>2</sub>	5.08	20,410; (7.0) 19,230; (6.6)	${}^4T_{1g}(F) \rightarrow {}^4T_{1g}(P)$ ${}^4T_{1g}(F) \rightarrow {}^4A_{2g}$
Co(HMTA) <sub>2</sub> (H <sub>2</sub> O) <sub>10</sub> (NO <sub>3</sub> ) <sub>2</sub>	4.74	20,410; (7.0) 19,230; (8.4)	${}^4T_{1g}(F) \rightarrow {}^4T_{1g}(P)$ ${}^4T_{1g}(F) \rightarrow {}^4A_{2g}$
Ni(HMTA)(H <sub>2</sub> O) <sub>8</sub> SO <sub>4</sub>	3.76	25,000; (8.2) 14,500; (3.0) 13,700; (3.1)	${}^3A_{2g} \rightarrow {}^3T_{1g}(P)$ ${}^3A_{2g} \rightarrow {}^3T_{1g}(F)$
Ni(HMTA) <sub>2</sub> (H <sub>2</sub> O) <sub>4</sub> (BF <sub>4</sub> ) <sub>2</sub>	3.49	25,130; (11.2) 14,930; (4.6) 13,700; (5.0)	${}^3A_{2g} \rightarrow {}^3T_{1g}(P)$ ${}^3A_{2g} \rightarrow {}^3T_{1g}(F)$
Ni(HMTA) <sub>2</sub> (H <sub>2</sub> O) <sub>10</sub> (NO <sub>3</sub> ) <sub>2</sub>	3.29	25,000; (11.8) 14,710; (4.0) 13,700; (4.1)	${}^3A_{2g} \rightarrow {}^3T_{1g}(P)$ ${}^3A_{2g} \rightarrow {}^3T_{1g}(F)$

## CONCLUSION

From our results, divalent metal complexes of HMTA with sulfate as counter ion have one HMTA molecule while those with nitrate and fluoroborate as counter ion have two HMTA molecules. The observed IR bands between 1230-1360  $\text{cm}^{-1}$  for HMTA molecules and the 682-750  $\text{cm}^{-1}$  for the complexes suggest the coordination of HMTA and H<sub>2</sub>O to the metal centres. The bands observed in the electronic spectra of the compounds do suggest octahedral coordination at the metal centres. These results shall be subsequently confirmed by TGA and X-ray analyses.

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