



SYNTHESIS, CHARACTERISATION AND CRYSTAL STRUCTURE OF A THREE-DIMENSIONAL NETWORK OF AN H-BONDED Ni (II) HEXAMETHYLENETETRAMINE COMPLEX

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ABSTRACT

A three-dimensional network of H-bonding nickel (II)-hexamethylenetetramine complex has been synthesized and characterised and its structure determined by single crystal X-ray diffraction studies which show that $[\text{Ni}(\text{H}_2\text{O})_6](\text{HMTA})_2\text{Cl}_{32}\cdot 4\text{H}_2\text{O}$ crystallizes in the triclinic crystal system with space group $P\bar{1}$, $a = 9.2955(4)$, $b = 9.3187(2)$, $c = 9.3996 \text{ \AA}$, $\alpha = 119.4160(10)$, $\beta = 94.4940(10)$, $\gamma = 100.8680(10)^\circ$, $V = 682.47(4) \text{ \AA}^3$ and $z = 1$. The nickel atoms are each bonded to six aquo ligands giving an octahedral geometry. The ligand hexamethylenetetramine (HMTA) and chloride ions are bonded to water molecules through hydrogen bonding. Thermal studies show a decomposition pattern corresponding to the loss of the coordinated and uncoordinated water molecules, chloride ions and HMTA ligand in the form of a mixture of gases.

Key words: Nickel, hexamethylenetetramine, chloride, complexes, X-ray, structure, thermal, spectroscopy studies.

INTRODUCTION

There has been some considerable and renewed interest in the synthesis and characterisation of metal complexes of hexamethylenetetramine, a heterocyclic ligand having three fused rings in the chair configuration with four nitrogen atoms that can each donate a pair of electrons¹⁻⁵. This is as a result of the varied coordination patterns which this ligand displays ranging from monodentate⁶, bridging⁷⁻¹⁰ non-chelating and the hydrogen-bonded frameworks^{5,11-14}. Chain polymers for example, $[\text{Co}(\text{NO}_3)_2(\text{H}_2\text{O})_2(\text{HMTA})_2]$ has also been reported¹⁵ in which HMTA is covalently bonded to cobalt. The combination of covalent and hydrogen bonding in some of these metal-organic species gives rise to the observed three dimensional framework structures which easily decompose on thermal treatment to give thin films of the metal oxide. These complexes could therefore serve as precursors for metal oxide dispersions¹⁶⁻¹⁷.

In our recent paper¹⁸, we reported on the synthesis of some metal(II)-HMTA-aquo complexes and showed by infrared studies that water molecules in these compounds are both coordinating and non-coordinating. Molar conductance studies of $\text{Ni}(\text{H}_2\text{O})_6\text{-HMTA-Cl}_2\cdot 4\text{H}_2\text{O}$ revealed a 1:2 electrolyte type with the chloride acting as counter ions, thus non-coordinating.

In this paper, we report on the synthesis, characterisation, thermal analysis and the crystal structure of a three-dimensional network of H-bonded nickel (II)-hexamethylenetetramine complex.

EXPERIMENTAL

All chemicals were used as supplied without further purification. The solvents were purified by standard methods. Elemental analyses for C, H, N were carried out on a Fisons Instrument 1108 CHNS-O, while quantitative estimation of Nickel (II) was done by complexometric titrations. Infrared spectra were recorded between pressed KBr discs on a Perkin – Elmer model IR-457 spectrometer and a Spectrum 100 FT-IR Perkin- Elmer Spectrometer, while electronic spectra were recorded on a Hitachi U-2000 spectrophotometer. Conductivity measurements were carried out in methanol using the Tacussel conductimeter, model CD810 at room temperature. Room temperature magnetic susceptibility measurements were determined using the Gouy method with mercury tetrathiocyanocobaltate (II) as calibrant. Thermogravimetric analyses were performed on a TGA Perkin – Elmer STA 6000 simultaneous Thermal Analyser Instrument under nitrogen atmosphere.

Synthesis of $[\text{Ni}(\text{H}_2\text{O})_6](\text{HMTA})_2\text{Cl}_2 \cdot 4\text{H}_2\text{O}$

A solution of hexamethylenetetramine (2.80 g; 2.0 mmol) in 20 mL methanol was added dropwise to an aqueous solution of $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ (4.75; 2.0 mmol) in 15 mL water with stirring. The mixture was further stirred for two hours and stored for four days during which crystallisation occurred giving green crystals. They were filtered, washed with diethylether and dried over silica gel in a dessicator, Mpt 215– 217°C.

Analyses: Calc. for $\text{C}_{12}\text{H}_{44}\text{N}_8\text{O}_{10}\text{Cl}_2\text{Ni}$ (590.262): C: 24.42; H: 7.51; N: 19.02; Ni: 9.95%. Found C: 24.58; H: 7.74; N: 18.87; Ni: 10.15. Characteristic IR absorptions (KBr): 1 666, 1 623, 1 240, 813, 752 cm^{-1} . Electronic: 24 938, 14 903 – 13 569 cm^{-1} . Room temperature magnetic moment, $\mu = 3.32$ B.M. molar conductance, $197\Omega^{-1}\text{cm}^{-1}\text{mol}^{-1}$.

X-ray Crystal Structure Determination

Suitable single crystals (green prism) of $[\text{Ni}(\text{H}_2\text{O})_6](\text{HMTA})_2\text{Cl}_2 \cdot 4\text{H}_2\text{O}$ (0.70 x 0.60 x 0.55 mm^3) coated with dry perfluoropolyether were mounted on glass fibres and fixed to the goniometer head in cold nitrogen stream (T =173 K). Data collection was performed on a Bruker-Nonius X8APEX-II CCD diffractometer using monochromatic radiation, $\lambda(\text{Mo-K}_{\alpha 1}) = 0.71073\text{Å}$.

Out of the 33648 measured reflections, the final cell parameters were obtained by full matrix least squares techniques¹⁹ on 4140 observed unique reflections ($R_{\text{int}}=0.0233$) and 181 refined parameters with final $R_1=0.0229$ for reflections with $I > 2\sigma(I)$ and $\omega R_2 = 0.0644$ for all data for the compound.

All non-hydrogen atoms were refined with anisotropic displacement parameters. The data were reduced and corrected for Lorentz polarisation effects and absorption by multiscan method²⁰. The structure was solved by direct methods²¹.

The hydrogen atoms were included from calculated positions and refined riding on their respective carbon atoms with isotropic displacement parameters.

Supplementary crystallographic data have been deposited at the Cambridge crystallographic data centre with deposition number CCDC 719425

RESULTS AND DISCUSSIONS

The nickel (II)-Hexmethylenetetramine complex melted sharply at 215-217°C. It has a molar conductance values of $197\Omega^{-1}\text{cm}^{-1}\text{mol}^{-1}$, suggesting that it is a 1:2 electrolyte type²². The counter ion, Cl^- is therefore not coordinated to the nickel ion in the compound. The IR absorption bands observed at 1240cm^{-1} and assigned to N-C stretch and the bands observed at 813cm^{-1} and assigned to CH_2 rock are in the range of 1240 and 813cm^{-1} observed for the free hexamethylenetetramine ligand²³. This observation suggests that hexamethylenetetramine is not strongly coordinated to the nickel ion. The IR bands at $1666, 1623\text{cm}^{-1}$ assigned to $\nu_{\text{H}_2\text{O}}$, are an indication of two types of crystallographically non-equivalent water molecules, (coordinated and non-coordinated water molecules)²⁴. The coordinate bond between water molecules and nickel ions results in the IR vibrational band observed at 752cm^{-1} . Hexamethylenetetramine is most probably bonded to the water molecules and the chloride anions by hydrogen bonds²⁴.

The compound has a room temperature magnetic moment of 3.32 B.M. which is slightly higher than the spin-only value of 2.87 B.M. though within the 2.9 – 3.4 B.M. range for octahedral nickel (II) complexes²⁵. The visible absorption spectrum of the compound reveals a band at 24950cm^{-1} and another

broad and split band at 14800-13570 cm^{-1} . These bands have been assigned to ${}^3A_{2g} \rightarrow {}^3T_{1g}(\text{P})$ and ${}^3A_{2g} \rightarrow {}^3T_{1g}(\text{F})$ transitions respectively²⁵. The splitting of the second band is probably due to spin-orbit coupling which mixes the ${}^3T_{1g}(\text{F})$ and 1E_g states. The ratio of 1.84 of the height of the first to that of the second band is indicative of an octahedral geometry about the nickel ion²⁶.

Thermal studies

Thermogravimetric, analysis (TGA) performed on powdered samples of the compound shows that it undergoes gradual mass loss from about 35°C to 246°C (Fig. 1). The TGA curve shows a decomposition pattern which corresponds to the loss of ca. 12%, 18% and 42% mass consistent with the departure of four uncoordinated water molecules at 35 – 65°C, six coordinated water molecules at 85-110°C and the chloride ion and HMTA in the form of a mixture of various gases at 130-246°C.

The differential thermal analysis curves revealed endothermic peaks at ca. 50-190°C corresponding to the loss of water molecules and exothermic peaks at 205-246°C corresponding to the loss of the anions and HMTA molecules and the formation of nickel oxide.

X-ray Crystal Structures of compounds 1 and 2

The ORTEP view of the crystal structure of the compound is shown in Fig. 2, together with the atom numbering scheme used in the corresponding tables. The crystallographic and refinement data for this compound are shown on Table 1 while selected bond parameters are shown in Tables 2-4. The complex was found to crystallise in the triclinic crystal system, with space group $P\bar{1}$ and $Z=1$.

Our results of elemental analysis, infrared, visible spectra, conductance and magnetic susceptibility measurements suggest that the nickel (II) ion in hexaaqua nickel (II)bis(hexamethylenetetramine) chloride tetrahydrate assumes an octahedral geometry with six water molecules covalently bonded to it. These results have been confirmed by X-ray structural analysis (Fig. 2) and TGA studies (Fig. 1). The Ni-O bond length of 2.0223(8) Å is consistent for nickel-oxygen covalently bonded species in an octahedral geometry²⁷. The chloride ions, hexamethylenetetramine ligands and the four uncoordinated water molecules are linked to each other through hydrogen bonding in which the chloride ions are hydrogen-bonded to free water molecules, which in turn form H-bonds with each other and with N-atoms of hexamethylenetetramine ligands, thus forming an overall three dimensional network structure.

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Table-1: Summary of crystallographic and structure refinement data for $[\text{Ni}(\text{H}_2\text{O})_6](\text{HMTA})_2(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$

Formula	$\text{C}_{12}\text{H}_{44}\text{Cl}_2\text{N}_8\text{NiO}_{10}$ $[2(\text{C}_6\text{H}_{12}\text{N}_4), \text{H}_{12}\text{NiO}_6, 4(\text{H}_2\text{O}), 2(\text{Cl})]$
Formula mass, g mol^{-1}	590.16
Collection T, K	173(2)
λ (Mo $K\alpha$), Å	0.71073
crystal system	triclinic
space group	$P\bar{1}$
a, Å	9.2955(4)
b, Å	9.3187(2)
c, Å	9.3996(2)
α , deg	119.4160(10)
β , deg	94.4940(10)
γ , deg	100.8680(10)

V, Å ³	682.47(4)
Z	1
ρ(calcd), Mg m ⁻³	1.436
F(000)	314
μ, mm ⁻¹	0.963
Crystal dimensions,	0.70 x 0.60 x 0.55mm
θ range, deg	2.53–30.50
No. of collected reflections	33648
No. of independent reflections/parameters	4140 / 181
R _{int}	0.0233
R ₁ (F) [F ² >2σ(F ²)] ^[a]	0.0229
wR ₂ (F ²) ^[b] (all data)	0.0658
S ^[c] (all data)	1.065
max./min. residual electron density, e Å ⁻³	+0.527 / -0.286

^[a] $R_1(F) = \sum(|F_o| - |F_c|) / \sum|F_o|$ for the observed reflections [F²>2σ(F²)]. ^[b] $wR_2(F^2) = \{\sum [w(F_o^2 - F_c^2)^2] / \sum w(F_o^2)^2\}^{1/2}$. ^[c] $S = \{\sum [w(F_o^2 - F_c^2)^2] / (n-p)\}^{1/2}$; (n = number of reflections, p = number of parameters).

Table-2: Selected Bond lengths [Å] and Bond angles [°] for [Ni(H₂O)₆](HMTA)₂(NO₃)₂·4H₂O

Ni(1)-O(2)	2.0223(8)
Ni(1)-O(1)	2.0434(7)
Ni(1)-O(3)	2.0562(8)
O(1)-H(1AO)	0.860(13)
O(1)-H(1BO)	0.849(13)
O(3)-H(3BO)	0.842(13)
O(4)-H(4AO)	0.840(14)
O(4)-H(4BO)	0.869(13)
O(5)-H(5AO)	0.875(15)
O(5)-H(5BO)	0.858(15)
N(1)-C(3)	1.4731(13)
N(1)-C(1)	1.4751(13)
N(1)-C(2)	1.4753(14)
N(2)-C(5)	1.4706(14)
O(2)-Ni(1)-O(2)	180.0
O(2)-Ni(1)-O(1)	86.94(3)
O(2)-Ni(1)-O(1)	93.06(3)
O(2)-Ni(1)-O(3)	90.01(4)
O(1)-Ni(1)-O(3)	86.30(3)
O(3)-Ni(1)-O(3)	180.0
Ni(1)-O(1)-H(1AO)	118.7(10)
Ni(1)-O(1)-H(1BO)	127.0(11)
H(1AO)-O(1)-H(1BO)	106.4(15)
Ni(1)-O(2)-H(2AO)	126.7(12)
Ni(1)-O(2)-H(2BO)	126.2(12)
H(2AO)-O(2)-H(2BO)	106.6(16)
Ni(1)-O(3)-H(3AO)	118.7(11)
Ni(1)-O(3)-H(3BO)	125.9(12)
C(3)-N(1)-C(2)	108.44(8)
C(1)-N(1)-C(2)	108.54(8)

Symmetry transformations used to generate equivalent atoms: #1 -x+1, -y, y, -z+2

Table-3: Hydrogen bonds for $[\text{Ni}(\text{H}_2\text{O})_6](\text{HMTA})_2(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ [\AA and $^\circ$].

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
O(1)-H(1AO)...N(1)#2	0.860(13)	1.954(13)	2.8069(11)	171.3(14)
O(1)-H(1BO)...O(5)#3	0.849(13)	1.891(13)	2.7268(12)	167.8(15)
O(2)-H(2AO)...O(4)#2	0.846(14)	1.867(14)	2.6997(12)	167.6(17)
O(2)-H(2BO)...N(4)#4	0.840(14)	1.955(14)	2.7818(12)	167.8(16)
O(3)-H(3AO)...N(2)#3	0.846(13)	1.971(14)	2.7999(11)	166.0(16)
O(3)-H(3BO)...Cl(1)#5	0.842(13)	2.412(14)	3.1897(9)	153.8(15)
O(4)-H(4AO)...Cl(1)	0.840(14)	2.325(14)	3.1603(9)	173.2(15)
O(4)-H(4BO)...N(3)#6	0.869(13)	1.952(14)	2.8154(13)	172.6(15)
O(5)-H(5AO)...Cl(1)	0.875(15)	2.354(15)	3.2290(12)	178.6(6)
O(5)-H(5BO)...Cl(1)#7	0.858(15)	2.341(16)	3.1896(11)	170(2)

Symmetry transformations used to generate equivalent atoms:

#1 -x+1,-y,-z+2 #2 x,y,z+1 #3 -x+1,-y+1,-z+1

#4 -x+1,-y+1,-z+2 #5 x,y-1,z #6 x+1,y,z #7 -x+2,-y+2,-z+1

Table-4: Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for $[\text{Ni}(\text{H}_2\text{O})_6](\text{HMTA})_2(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Ni(1)	5000	0	10000	16(1)
O(1)	3866(1)	1353(1)	9375(1)	25(1)
O(2)	6169(1)	2265(1)	12002(1)	31(1)
O(3)	6473(1)	295(1)	8583(1)	30(1)
Cl(1)	8093(1)	8230(1)	5630(1)	34(1)
O(4)	8054(1)	4966(1)	2190(1)	30(1)
O(5)	8522(1)	9526(2)	3036(2)	48(1)
N(1)	3441(1)	4516(1)	1708(1)	22(1)
N(2)	3358(1)	7429(1)	2565(1)	23(1)
N(3)	1162(1)	5408(1)	2424(1)	23(1)
N(4)	3385(1)	6526(1)	4597(1)	23(1)
C(1)	3941(1)	5975(1)	1479(1)	24(1)
C(2)	1792(1)	4000(1)	1342(1)	25(1)
C(3)	3970(1)	5092(1)	3469(1)	23(1)
C(4)	1708(1)	6848(1)	2180(1)	25(1)
C(5)	3883(1)	7943(1)	4307(1)	24(1)
C(6)	1740(1)	5963(1)	4171(1)	25(1)

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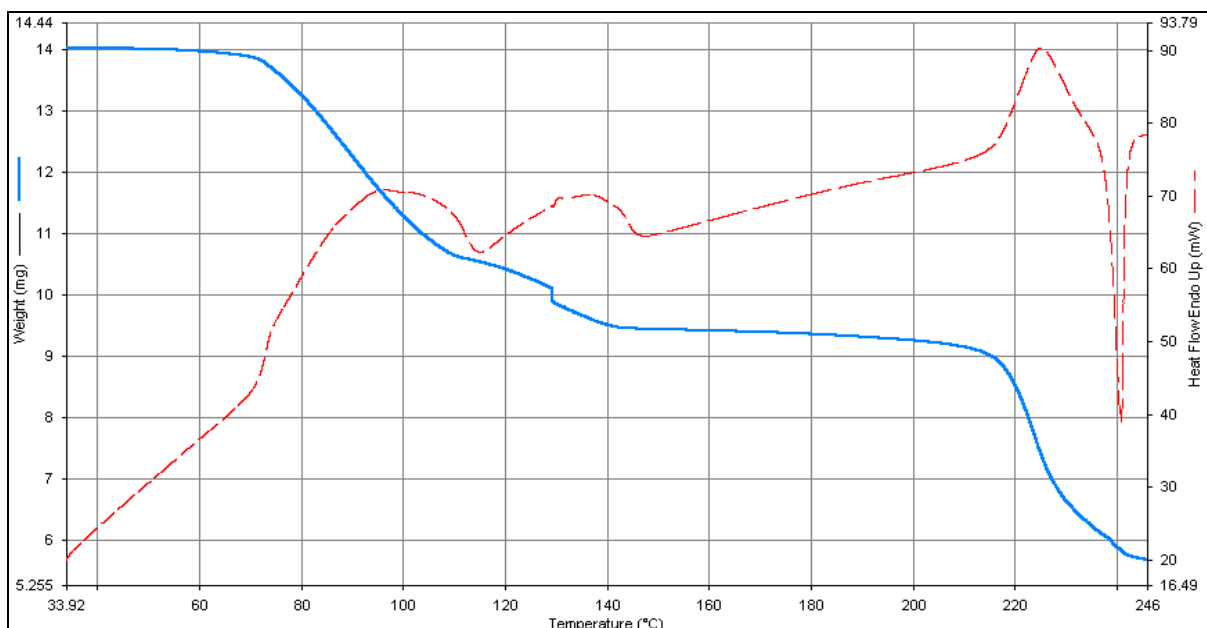


Fig.-1: TGA and DTA curves for Compound 1 ($[\text{Ni}(\text{H}_2\text{O})_6](\text{HMTA})_2(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$)

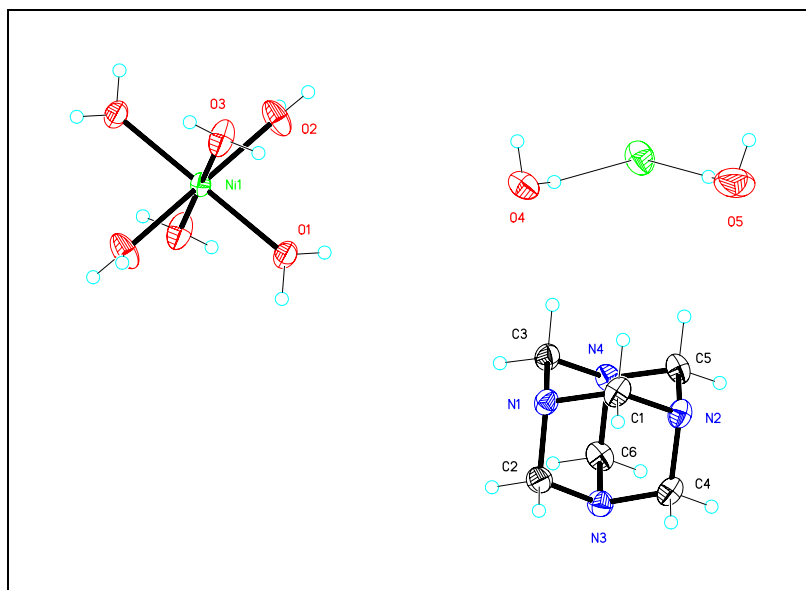


Fig.-2: Ortep Drawing and Numbering scheme used for $[\text{Ni}(\text{H}_2\text{O})_6](\text{HMTA})_2\text{Cl}_2 \cdot 4\text{H}_2\text{O}$

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