

# Coordination Compounds of Hexamethylenetetramine with Metal Salts: A Review

## Properties and applications of a versatile model ligand

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Hexamethylenetetramine (hmta) was chosen as a model ligand. Each of the four nitrogen atoms has a pair of unshared electrons and behaves like an amine base, undergoing protonation and *N*-alkylation and being able to form coordination compounds with many inorganic elements. The ligand can be used as an outer coordination sphere modulator of the inner coordination sphere and as a crosslinking agent in dinuclear and multinuclear coordination compounds. It can also be used as a model for bioactive molecules to form a great number of complexes with different inorganic salts containing other molecules. Studies of hmta coordination compounds with different metal salts have therefore attracted much attention. The present review summarises the synthesis, preparation, structure analysis and applications of coordination compounds of hmta with different metal salts.

### Introduction

Hexamethylenetetramine as a reagent has been used as a source of  $-\text{CH}=\text{N}-$  and  $-\text{CH}=\text{N}-$  functions. It has a cage-like structure and is considered to be a crucial basic material for the

chemical industry. It has been used in many fields including as a curing agent for phenolic resins (1), as an accelerant in vulcanisation (2), in food preservatives (3) and explosives (4) because of its useful properties including high solubility in water and polar organic solvents (5). In addition, hmta can act as a multifunctional ligand, using its N atom to form coordination complexes with many transition metals (6–10). It has been employed to prepare complexes with metals, and has been increasingly applied in chemical synthesis where it has received increasing attention due to its simple operation, mild conditions and environmental friendliness (11, 12).

### 1. Coordination with Metal Salts

A large number of complexes of hmta and metal salts have been studied and reports on their synthesis, preparation, structure analysis and applications in medicine and military are summarised below.

#### 1.1 Coordination with Metal Salts of Main Group Elements

The magnesium dichromate hmta complex was first crystallised by Debucquet and Velluz with  $5\text{H}_2\text{O}$  in 1933 (13), but subsequent analysis showed the presence of six water molecules instead of five and on the basis of former study, Dahan put forward the topic of “the crystal structure of the magnesium dichromate hmta hexahydrate complex” in 1973 (14). In Dahan’s study, the

structure of the Mg dichromate hmta hexahydrate complex can be regarded as composed of two  $\text{CrO}_4$  tetrahedra joined through a shared oxygen atom, a slightly distorted octahedron around Mg and two hmta molecules. There were no coordination bonds between these groups. They are linked by hydrogen bonds, thus determining the packing and controlling the stability.

Sieranski and Kruszynski (15) studied complexes of Mg and hmta in 2011. Sieranski chose hmta and 1,10-phenanthroline as ligands complexed with Mg sulfate. Coordination compounds  $[\text{Mg}(\text{H}_2\text{O})_6]^{2+} \cdot 2(\text{hmta}) \cdot \text{SO}_4^{2-} \cdot 5(\text{H}_2\text{O})$  and  $\text{Mg}(\text{C}_{12}\text{H}_8\text{N}_2)(\text{H}_2\text{O})_3\text{SO}_4$  were synthesised and characterised by elemental and thermal analysis, infrared (IR) spectroscopy, ultraviolet-visible (UV-vis) spectroscopy, fluorescence spectroscopy and X-ray crystallography. The compounds were found to be air stable and well soluble in water.

Mg and calcium have been most studied but heavier alkaline earth metals have also been investigated. For instance, after the development of the strontium-based drug, strontium ranelate, which reduces the incidence of fractures in osteoporotic patients, there has been an increasing awareness of this metal's role in humans.

Khandolkar *et al.* (16) studied the synthesis, crystal structure, redox characteristics and photochemistry of a new heptamolybdate supported coordination compound  $(\text{hmta})_2[\{\text{Mg}(\text{H}_2\text{O})_5\}_2\{\text{Mo}_7\text{O}_{24}\}] \cdot 3\text{H}_2\text{O}$  in 2015. In their study, the synthesis, characterisation and photochemistry of a new heptamolybdate supported Mg-aqua coordination complex using hmta as structure directing agent was reported.

Tanco Salas (17) studied a complex of aluminium and hmta ('Al-hmta') in 2004. The Al-hmta complex was found to have deodorant and therapeutic properties with potential applications in cosmetic and pharmaceutical compositions. Furthermore, the Al-hmta complex had the capacity to trap substances which could subsequently be released, therefore being useful as a carrier of those substances.

## 1.2 Coordination with Salts of Main Group Elements and Subgroup B Elements

Different metal salts have different coordination abilities and properties. Usually, the complex is made up of the main group element as the central atom, and the subgroup elements appear in the ligands. The combination of two metals may

lead to new materials such as polyoxometalates (POMs) with different properties and more stable structures.

Chen *et al.* synthesised two new extended frameworks based on two different sandwich-type polytungstoarsenates under routine conditions in 2009. They found an advance on the sandwich-type POMs, which had larger volumes and more negative charges than commonly used POMs, allowing the formation of higher coordination numbers with metal cations. Thus, sandwich-type POMs should be excellent building blocks for constructing extended networks (28).

## 1.3 Coordination with Different Metal Salts of Subgroup B Elements

Allan *et al.* (30) studied transition metal halide complexes of hmta in 1970. Complexes of hmta have been prepared with the halides of manganese(II), cobalt(II), nickel(II), zinc(II), cadmium(II), iron(II) and copper(II) and also with the thiocyanates of Co(II), Ni(II) and Zn(II). These complexes have been characterised by elemental analysis, vibrational and electronic spectra and magnetic moments.

Ahuja *et al.* (31) studied hmta complexes with Mn(II), Co(II), Ni(II), Cu(II), Zn(II) and Cd(II) thiocyanates. As a potentially tetradentate ligand, hmta complexes with Mn(II), Co(II), Ni(II), Cu(II), Zn(II) and Cd(II) thiocyanates were prepared and characterised by their elemental analyses, magnetic susceptibilities, electronic and IR spectral studies down to  $200\text{ cm}^{-1}$ ,  $611\text{ cm}^{-1}$  as well as X-ray powder diffraction patterns in the solid state. It was 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 were discussed.

Agwara *et al.* (32) studied the physicochemical properties of hmta complexes with Mn(II), Co(II) and Ni(II) in 2004, and in 2012 these complexes had been synthesised in water and ethanol (33). All the complexes were hydrogen-bonded, except the Co complex  $[\text{Co}(\text{hmta})_2(\text{NO}_3)_2(\text{H}_2\text{O})_2]$  which was polymeric. These complexes were characterised by elemental analysis, IR and visible spectroscopy as well as conductivity measurements. The results suggest octahedral coordination in which the central metal ion is bonded to aqua ligands and the hmta is bonded to the aqua ligands through

Table I Major Crystal Data and Refinement for Compounds of hmta Salts with Main Group Elements

Formula (M:hmta)	Serial No.	Crystal system, space group	Z, d, Mg m <sup>-3</sup>	R indices (all data)	F (000)	CCDC No.	Reference No.
[Li(H <sub>2</sub> O) <sub>4</sub> ] <sup>+</sup> •2(hmta)•ClO <sub>4</sub> <sup>-</sup> (1:2)	1a	Orthorhombic, Pna <sub>2</sub> 1 (No. 33)	4, 1.416	R <sub>1</sub> = 0.0384, wR <sub>2</sub> = 0.0964	976	1003176	(19)
[Na(ClO <sub>4</sub> )(H <sub>2</sub> O)(hmta)] <sub>n</sub> (1:1)	1b	Orthorhombic, Pnma (No. 62)	4, 1.625	R <sub>1</sub> = 0.0284, wR <sub>2</sub> = 0.0867	584	1003177	(19)
[Na(hmta)(H <sub>2</sub> O) <sub>4</sub> ] <sub>2</sub> <sup>2+</sup> •2SCN <sup>-</sup> (1:1)	2b	Monoclinic, P2 <sub>1</sub> /c (No. 14)	2, 1.366	R <sub>1</sub> = 0.0378, wR <sub>2</sub> = 0.0900	624	802360	(20)
[K <sub>2</sub> (hmta)(SCN) <sub>2</sub> ] <sub>n</sub> (2:1)	1c	Monoclinic, C2/c (No. 15)	4, 1.559	R <sub>1</sub> = 0.0339, wR <sub>2</sub> = 0.0877	688	833296	(20)
[NaNO <sub>3</sub> •(hmta)] <sub>n</sub> (1:1)	3b	Trigonal, R3c (No. 161)	6	R <sub>1</sub> = 0.0268, wR <sub>2</sub> = 0.0777	1212	266846	(8)
[Li(H <sub>2</sub> O) <sub>4</sub> ] <sup>+</sup> •(hmta)•Cl <sup>-</sup> (1:1)	2a	Trigonal, R32 (No. 155)	18, 1.289	R <sub>1</sub> = 0.0339, wR <sub>2</sub> = 0.0881	2448	859820	(21)
[Li(H <sub>2</sub> O) <sub>4</sub> ] <sup>+</sup> •(hmta)•I <sup>-</sup> (1:1)	3a	Monoclinic, P2 <sub>1</sub> /c (No. 14)	4, 1.629	R <sub>1</sub> = 0.0546, wR <sub>2</sub> = 0.1321	688	859821	(21)
[Na(H <sub>2</sub> O) <sub>4</sub> •(hmta)] <sub>2</sub> <sup>2+</sup> •2H <sub>2</sub> O•2Br <sup>-</sup> (1:1)	4b	Orthorhombic, Pbca (No. 61)	4, 1.522	R <sub>1</sub> = 0.0388, wR <sub>2</sub> = 0.0806	1376	859822	(21)
[Na(H <sub>2</sub> O) <sub>4</sub> •(hmta)] <sub>2</sub> <sup>2+</sup> •2H <sub>2</sub> O•2I <sup>-</sup> (1:2)	5b	Orthorhombic, Pbca (No. 61)	4, 1.649	R <sub>1</sub> = 0.0450, wR <sub>2</sub> = 0.1192	1520	859823	(21)
[K(H <sub>2</sub> O)(hmta)] <sub>n</sub> (1:1)	2c	Monoclinic, C2/m (No. 12)	4, 1.913	R <sub>1</sub> = 0.0308, wR <sub>2</sub> = 0.0716	632	859824	(21)
[Rb(H <sub>2</sub> O)(hmta)] <sub>n</sub> (1:1)	1d	Monoclinic, C2/m (No. 12)	4, 2.095	R <sub>1</sub> = 0.0234, wR <sub>2</sub> = 0.0639	704	859825	(21)
(hmta) <sub>2</sub> [Mg(H <sub>2</sub> O) <sub>5</sub> ] <sub>2</sub> {Mo <sub>7</sub> O <sub>24</sub> ] <sup>3-</sup> •3H <sub>2</sub> O (1:2)	1e	Monoclinic, C2/c (No. 15)	4, 2.493	R <sub>1</sub> = 0.0382, wR <sub>2</sub> = 0.0829	3152	1049780	(16)
MgCr <sub>2</sub> O <sub>7</sub> •2(hmta)•6H <sub>2</sub> O (1:2)	2e	Triclinic P1̄ (No. 2)	2, 1.595	-	654	-	(14)
[Mg(H <sub>2</sub> O) <sub>6</sub> ] <sup>2+</sup> •2(hmta)•SO <sub>4</sub> <sup>2-</sup> •5(H <sub>2</sub> O) (1:2)	3e	Triclinic, P1 (No. 1)	1, 1.446	R <sub>1</sub> = 0.0317, wR <sub>2</sub> = 0.0761	322	813464	(15)
[Mg(H <sub>2</sub> O) <sub>6</sub> ] <sup>2+</sup> •2(hmta)•2NO <sub>3</sub> <sup>2-</sup> •4H <sub>2</sub> O (1:2)	4e	Monoclinic, P2 <sub>1</sub> /c (No. 14)	4, 1.3782	R <sub>1</sub> = 1.0538, wR <sub>2</sub> = 0.1334	1304	865230	(18)
[Ca <sub>2</sub> (H <sub>2</sub> O) <sub>6</sub> (NO <sub>3</sub> ) <sub>4</sub> ] <sub>2</sub> •2(hmta) (1:1)	1f	Monoclinic, P2 <sub>1</sub> /c (No. 14)	2, 1.580	R <sub>1</sub> = 0.0401, wR <sub>2</sub> = 0.1214	752	865231	(18)
[Sr <sub>2</sub> (H <sub>2</sub> O) <sub>6</sub> (NO <sub>3</sub> ) <sub>4</sub> ] <sub>2</sub> •2(hmta) (1:1)	1g	Monoclinic, P2 <sub>1</sub> /c (No. 14)	2, 1.733	R <sub>1</sub> = 0.0304, wR <sub>2</sub> = 0.0735	864	865232	(18)

Table II Major Crystal Data and Refinement for Compounds of hmta with Different Metal Salts

Formula (M:hmta)	Crystal system, space group	Z, d, Mg m <sup>-3</sup>	R indices (all data)	F (000)	CCDC No.	Reference No.
Li <sub>3</sub> [Fe(CN) <sub>6</sub> ] <sub>2</sub> •2(hmta)•5H <sub>2</sub> O (3:1:2)	Orthorhombic, Immm2 (No. 44)	2, 1.43	-	-	-	(22)
Na <sub>3</sub> [Fe(CN) <sub>6</sub> ] <sub>2</sub> •2(hmta)•5H <sub>2</sub> O (3:1:2)	Orthorhombic, Pca2 <sub>1</sub> (No. 29)	4, 1.50	R <sub>1</sub> = 0.044, wR <sub>2</sub> = 0.043	-	-	(23)
K <sub>3</sub> [Fe(CN) <sub>6</sub> ] <sub>2</sub> •2(hmta)•4H <sub>2</sub> O (3:1:2)	Triclinic, P1 (No. 1)	4, 1.48	R <sub>1</sub> = 0.042, wR <sub>2</sub> = 0.045	-	-	(23)
Ca <sub>2</sub> [Fe(CN) <sub>6</sub> ] <sub>2</sub> •2(hmta)•6H <sub>2</sub> O (2:1:2)	Monoclinic, P2 <sub>1</sub> (No. 4)	4, 1.72	R <sub>1</sub> = 0.055, wR <sub>2</sub> = 0.055	-	-	(24)
Cr <sub>2</sub> O <sub>7</sub> Ca•2(hmta)•7H <sub>2</sub> O (1:2:2)	Monoclinic, C2/c (No. 15)	4, 1.676	R <sub>1</sub> = 0.038, wR <sub>2</sub> = 0.036	-	-	(25)
Sr <sub>3</sub> [Fe(CN) <sub>6</sub> ] <sub>2</sub> •3(hmta)•18H <sub>2</sub> O (3:2:3)	Tetragonal, P4 <sub>2</sub> /nmc (No. 137)	4, 1.83	R <sub>1</sub> = 0.066, wR <sub>2</sub> = 0.062	-	-	(26)
Ba <sub>3</sub> [Fe(CN) <sub>6</sub> ] <sub>2</sub> •2(hmta)•11H <sub>2</sub> O (3:2:2)	Monoclinic, P2 <sub>1</sub> /c (No. 14)	2, 1.76	R <sub>1</sub> = 0.057	-	-	(26)
[(hmta)-CH <sub>3</sub> ] <sub>2</sub> K <sub>3.5</sub> Na <sub>8.5</sub> [K<{FeCe(AsW <sub>10</sub> O <sub>38</sub> )(H <sub>2</sub> O) <sub>2</sub> } <sub>3</sub> ] <sub>3</sub> •~36H <sub>2</sub> O	Triclinic, P1 (No. 1)	2, 4.047	R <sub>1</sub> = 0.0591, wR <sub>2</sub> = 0.1743	8504	660692	(27)
[(hmta)-CH <sub>3</sub> ] <sub>2</sub> (hmta)K <sub>2</sub> Na <sub>7</sub> [Ce(AsVW <sub>11</sub> O <sub>39</sub> ) <sub>2</sub> ] <sub>2</sub> •19H <sub>2</sub> O	Monoclinic, P2 <sub>1</sub> /c (No. 14)	4, 3.681	R <sub>1</sub> = 0.0863, wR <sub>2</sub> = 0.2071	11708	705356	(28)
[(hmta)-H•H <sub>2</sub> O] [(hmta)-CH <sub>2</sub> OH] [H <sub>3</sub> V <sub>10</sub> O <sub>28</sub> {Na(H <sub>2</sub> O) <sub>4</sub> }] <sub>4</sub> •4H <sub>2</sub> O (10:1:2)	Triclinic, P1 (No. 1)	1, 2.329	R <sub>1</sub> = 0.0389, wR <sub>2</sub> = 0.1141	725	-	(29)

hydrogen-bonding. Antibacterial activities of the ligand and its complexes show that the ligand was active against one out of 10 tested bacteria species; the Co complexes  $[\text{Co}(\text{H}_2\text{O})_6](\text{hmta})_2(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$  and  $[\text{Co}(\text{hmta})_2(\text{NO}_3)_2(\text{H}_2\text{O})_2]$  were the most active, showing activity against all the microorganisms. These Co complexes also show greater activity than the reference antibiotic gentamycin against *Klebsiella pneumoniae*.

Kumar *et al.* (34) studied Cd hmta nitrate in 2012. The crystal structure analysis of the complex revealed a zig-zag polymeric network in which the Cd(II) ions are linked *via* the nitrogen atom of the hmta ligand. The complex has a network of hydrogen bonds. For isothermal thermogravimetry (TG) data, use of the isoconversional method was an effective means of unmasking complex kinetics.

Salem (35), of Tanta University, Egypt, studied the catalytic effect of some transition metal hmta complexes in hydrogen peroxide decomposition. The kinetics of the catalytic decomposition of  $\text{H}_2\text{O}_2$  with Wofatit KPS resin (4% divinylbenzene), (40–80  $\mu\text{m}$ ) in the form of 1: 1 Cu(II)-, Mn(II)-, Co(II)- and Ni(II)-hexamine complexes was studied in an aqueous medium. The decomposition reaction was first order with respect to  $[\text{H}_2\text{O}_2]$  and the rate constant,  $k$  (per gram of dry resin) increased in the following sequence: Mn(II) > Co(II) > Cu(II) > Ni(II). The active species, formed as an intermediate at the beginning of the reaction, had an inhibiting effect on the reaction rate. An anionic surfactant, sodium dodecyl sulfate (SDS), considerably inhibited the reaction rate. A probable mechanism for the decomposition process was suggested, which was consistent with the results obtained.

Paboudam *et al.* (36), reported the results of a study on the influence of solvent on the electronic and structural properties of metal-hmta complexes in aqueous and non-aqueous solvents. Their goal was to study the effect of aqueous and non-aqueous media on the coordination of hmta to metal ions. The protometric studies of the hmta ligand had confirmed that only one basic site was protonated in acidic medium and this ligand was decomposed in acidic medium. In aqueous medium, hmta ligand does not coordinate directly to the metal ions but rather through the H-bonded species. In non-aqueous solvents, hmta coordinates to metal ions displaying diversity in the resulting structures in which hmta can either be monodentate, bridged, tridentate or tetradentate.

Cai *et al.* (37) studied a Co(II)-hmta complex prepared using jet milling. An organic metal

complex may exhibit different structures when synthesised by different methods. For instance, the Co(II)-hmta complexes  $\text{Co}(\text{hmta})_2\text{Cl}_2 \cdot 10\text{H}_2\text{O}$  and  $\text{Co}(\text{hmta})_2\text{Cl}_2 \cdot 6\text{H}_2\text{O}$  could be obtained using solution synthesis and mechanical grinding, respectively. The thermogravimetric analysis (TGA) result further confirmed that the structure of the Co(II)-hmta complex obtained by grinding was  $\text{Co}(\text{hmta})_2\text{Cl}_2 \cdot 6\text{H}_2\text{O}$ . In addition, there were also studies on complexes of hmta with Cu and silver ion salts.

Stocker (38) studied the crystal structure of a novel Cu(I) cyanide complex with hmta,  $(\text{CuCN})_3(\text{hmta})_2$  in 1990. Grodzicki *et al.* (39) studied a complex of Cu(II) chloride with hmta in 1991. Their study included spectroscopic and magnetic investigations which indicated that, in the crystal structure of this compound, polymeric chains,  $3\text{CuCl} \cdot 2\text{hmta} \cdot 2\text{H}_2\text{O}$  and hmta•HCl groups occurred.

Hazra *et al.* (40) studied four new Cu(II)-hmta complexes synthesised and structurally characterised by X-ray crystallography in 2013. The unique feature of the study was that it had been possible to construct all probable architectures that can be assembled by utilising linear dinuclear Cu(II) carboxylate as a node and hmta as a spacer (angular, pyramidal and tetrahedral) varying only slightly the nonfunctional part of the aromatic carboxylic acids.

A thesis by Degagsa *et al.* (41) showed that  $[\text{Cu}(\text{hmta})_3(\text{H}_2\text{O})_3]\text{SO}_4$  had been synthesised by direct reaction of hmta and penta-hydrated Cu sulfate ( $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ ) and was characterised by magnetic susceptibility measurements, atomic absorption spectroscopy, IR and UV-vis spectroscopic analysis as well as conductivity measurements. Sulfate ion and hmta composition of the complex were also determined using gravimetric and volumetric analysis respectively. The structure of the complex was then proposed to be distorted octahedral in which a single Cu ion is bonded to three water and three hmta molecules. The antimicrobial activity of hmta was enhanced upon complexation due to the increase in lipo-solubility of the complex upon coordination with the ligands. It can also be concluded that the complexes show greater antibacterial activity than the reference antibiotic, gentamycin, towards *Staphylococcus aureus* and *Salmonella typhi*. Thus, with further investigation and exploitation this complex could be developed as an antibacterial drug for the treatment of infections caused by these bacteria.

Carlucci *et al.* (42) studied  $[\text{Ag}_6(\text{hmta})_6]^{6+}$  in 1997. When solutions of  $\text{AgPF}_6$  and hmta in

ethanol/dichloromethane were evaporated to dryness, a polymeric species was obtained,  $[\text{Ag}(\text{hmta})](\text{PF}_6)\cdot\text{H}_2\text{O}$ , containing a three-dimensional (3D) triconnected network topologically related to the prototypal  $\text{SrSi}_2$ .

Plotnikov *et al.* (43) studied antibacterial and immunomodulatory effects of hmta Ag nitrate in 2016. The antibacterial properties and influence on immune blood cells of the Ag-based compound with general formula  $[\text{Ag}(\text{hmta})]\text{NO}_3$  were investigated. A noticeable inhibitory effect of the drug was observed only at high concentration in phytohemagglutinin (PHA)-stimulated reaction of blast transformation of lymphocytes (RBTL). Based on this result, the tested Ag complex could be considered as a potential candidate for an antibacterial drug with low toxicity.

## 1.4 Coordination with Metal Salts of Lanthanide Elements

Zalewicz (82) carried out thermal analysis of complex salts of lanthanide chlorides with hmta in 1989. Thermal decomposition of lanthanide chloride complex salts with hmta of the general formula  $\text{LnCl}_3\cdot 2\text{hmta}\cdot n\text{H}_2\text{O}$  ( $\text{Ln}$  = lanthanum, praseodymium, neodymium, samarium, dysprosium, erbium;  $n$  = 8, 10, 12) was examined. Mechanisms of the thermal dehydration reaction of these salts were established and kinetic parameters of the first state of the dehydration reaction were determined. The following year, the same survey was carried out for lanthanide bromine salts (83).

Zalewicz *et al.* (84) carried out coupled thermogravimetry-mass spectrometry (TG-MS) investigations of lanthanide(III) nitrate complexes with hmta in 2004. New transition metal compounds of the general formula  $\text{Ln}(\text{NO}_3)_3\cdot 2[\text{hmta}]n\text{H}_2\text{O}$ , where  $\text{Ln}$  = La, Nd, Sm, gadolinium, terbium, Dy, Er, lutetium;  $n$  = 7–12, were obtained. The compounds and the gases evolved in the course of their thermal decomposition were characterised by TGA. The measurements were carried out in air and argon environments in order to compare the intermediate products, final products and the mechanism of the thermal decomposition. The combined TG-MS system was used to identify the main volatile products of thermal decomposition and fragmentation processes of the obtained compounds.

Singh *et al.* (85) studied the kinetics of thermolysis of La nitrate with hmta in 2014. The highlights were the confirmation of the crystal structure of this complex by X-ray crystallography, its thermal

analysis by TG and thermogravimetry coupled with differential scanning calorimetry (TG-DSC), the discovery that the complex is insensitive towards impact and friction and the evaluation of its kinetics by model fitting. The preparation, characterisation and thermolysis of the La nitrate complex with hmta were investigated.

Trzesowska *et al.* (86) studied the synthesis, crystal structure and thermal properties of a mixed ligand 1,10-phenanthroline and hmta complex of La nitrate, providing insight into the coordination sphere geometry changes of La(III) 1,10-phenanthroline complexes. Geometry optimisation was carried out using a density functional theory (DFT) method using the Becke, three-parameter, Lee-Yang-Parr (B3LYP) functional by means of the Gaussian 03 program package. The minimal basis set CEP-4G was used on La and 6-31G(d') on oxygen, nitrogen, carbon and hydrogen atoms.

## 1.5 Coordination with Metal Salts of Quaternary Nitrogen

In **Table IV**, the grey background compounds are made up of hmta coordinated with quaternary nitrogen, while those on a white background are formed by coordination of hmta molecules. In other words, the hmta molecule links to other small atoms or molecules directly, to form new molecules with different properties. This particular mode of coordination makes it easier for molecules in such complexes to be connected and form mesh structures (**Scheme I**).

Interestingly, it was found that when the hmta is changed into a  $[\text{hmta}-\text{CH}_3]^+$  cation during reaction, acid-catalysed decomposition of some hmta molecules resulted and led to a subsequent alkylation of hmta in solution (27).

## 2. Discussion of the Coordination Mode of hmta with Metal Salts

### 2.1 Effect of Different Metal Cations

The reaction of main group metal salts with hmta leads to the formation of coordination compounds, mononuclear in case of lithium compounds, dinuclear in other element compounds. The electronic properties of the cations strongly influence the coordination modes of both hmta molecules and anions. Li ions are four-coordinated, Na, potassium and rubidium ions are six-coordinated, and Mg, Ca, Sr and barium ions are six or more. Thus the

Table III Major Crystal Data and Refinement for Compounds of hmta with Metal Salts of Subgroup B Elements

Formula (M:hmta)	Crystal system, space group	Z, d, Mg m <sup>-3</sup>	R indices (all data)	F (000)	CCDC No.	Reference No.
[Fe(H <sub>2</sub> O) <sub>6</sub> ](NO <sub>3</sub> ) <sub>2</sub> •2(hmta)•4H <sub>2</sub> O (1:2)	Triclinic, P1 (No. 1)	1, 1.523	-	-	-	(44)
[Fe(H <sub>2</sub> O) <sub>4</sub> {H <sub>2</sub> O-(hmta)} <sub>2</sub> ](NO <sub>3</sub> )•4H <sub>2</sub> O (1:2)	Triclinic, P1̄ (No. 2)	1, 1.562	R <sub>1</sub> = 0.039, wR <sub>2</sub> = 0.088	976	-	(45)
H <sub>6</sub> V <sub>10</sub> O <sub>28</sub> •2(hmta)•8H <sub>2</sub> O (5:1)	Monoclinic, C2/m (No. 12)	2, 2.252	R <sub>1</sub> = 0.0396, wR <sub>2</sub> = 0.1068	1384	729399	(46)
H <sub>4</sub> V <sub>10</sub> O <sub>28</sub> •{(hmta)-CH <sub>2</sub> OH} <sub>2</sub> •6H <sub>2</sub> O (5:1)	Triclinic, P1 (No. 1)	1, 2.294	R <sub>1</sub> = 0.0295, wR <sub>2</sub> = 0.0792	704	685560	(47)
H <sub>4</sub> V <sub>10</sub> O <sub>28</sub> •{(hmta)-CH <sub>2</sub> OH} <sub>2</sub> •4H <sub>2</sub> O (5:1)	Monoclinic, P2 <sub>1</sub> /c (No. 14)	2, 2.275	R <sub>1</sub> = 0.0352, wR <sub>2</sub> = 0.0932	1368	746415	(47)
[(hmta)-CH <sub>3</sub> ] <sub>4</sub> [H <sub>2</sub> V <sub>10</sub> O <sub>28</sub> ] 5H <sub>2</sub> O (5:2)	Monoclinic, C2/m (No. 12)	2, 2.247	R <sub>1</sub> = 0.0358, wR <sub>2</sub> = 0.0896	1348	-	(48)
[(hmta)-H] [(hmta)-CH <sub>2</sub> OH] <sub>2</sub> [H <sub>5</sub> V <sub>10</sub> O <sub>28</sub> ]•6H <sub>2</sub> O (10:3)	Orthorhombic, Pna2 <sub>1</sub> (No. 33)	4, 2.077	R <sub>1</sub> = 0.0573, wR <sub>2</sub> = 0.1052	3112	-	(48)
Mn(hmta) <sub>2</sub> (H <sub>2</sub> O) <sub>6</sub> (NO <sub>3</sub> ) <sub>2</sub> •4H <sub>2</sub> O (1:2)	Monoclinic, P2 <sub>1</sub> /c (No. 14)	4, 1.42	R <sub>1</sub> = 0.046, wR <sub>2</sub> = 0.118	1355.7	211785	(49)
[Mn{H <sub>2</sub> O-(hmta)-H <sub>2</sub> O} <sub>2</sub> (H <sub>2</sub> O-ClO <sub>4</sub> ) <sub>2</sub> (H <sub>2</sub> O) <sub>2</sub> ] (1:1)	Triclinic, P1̄ (No. 2)	1, 1.583	R <sub>1</sub> = 0.056, wR <sub>2</sub> = 0.126	355	658325	(45)
[Mn(H <sub>2</sub> O) <sub>6</sub> ](NO <sub>3</sub> ) <sub>2</sub> •2(hmta)•4H <sub>2</sub> O (1:2)	Monoclinic, P2 <sub>1</sub> /c (No. 14)	4, 1.416	-	-	-	(50)
(hmta) <sub>2</sub> Mn(OH) <sub>2</sub> (Br) <sub>2</sub> (1:2)	Orthorhombic, Pna2 <sub>1</sub> (No. 33)	4, 1.865	R <sub>1</sub> = 0.0241	1068	293765	(51)
[Mn <sub>3</sub> O(O <sub>2</sub> CCMe <sub>3</sub> ) <sub>6</sub> (hmta) <sub>3</sub> ]•(n-C <sub>3</sub> H <sub>7</sub> OH) (1:1)	Hexagonal, P6 <sub>3</sub> /m (No. 176)	2, 1.224	R <sub>1</sub> = 0.0702, wR <sub>2</sub> = 0.1783	1350	837612	(52)
[Mn <sub>3</sub> O(O <sub>2</sub> CCMe <sub>3</sub> ) <sub>6</sub> (hmta) <sub>3</sub> ]•(C <sub>6</sub> H <sub>5</sub> CH <sub>3</sub> ) (1:1)	Monoclinic, P2 <sub>1</sub> /c (No. 14)	4, 1.349	R <sub>1</sub> = 0.0482, wR <sub>2</sub> = 0.0997	2764	837613	(52)
[MnFe <sub>2</sub> O(O <sub>2</sub> CCMe <sub>3</sub> ) <sub>6</sub> (hmta) <sub>2</sub> ] •0.5MeCN (1:2:2)	Orthorhombic, Aea2 (No. 41)	8, 1.300	R <sub>1</sub> = 0.0867, wR <sub>2</sub> = 0.15156	4624	837614	(52)
[MnFe <sub>2</sub> O(O <sub>2</sub> CCMe <sub>3</sub> ) <sub>6</sub> (hmta) <sub>2</sub> ]•Me <sub>3</sub> CCO <sub>2</sub> H•(n-C <sub>6</sub> H <sub>14</sub> ) (1:2:2)	Orthorhombic, Pbcn (No. 60)	8, 1.306	R <sub>1</sub> = 0.1273, wR <sub>2</sub> = 0.2047	5184	837615	(52)
[MnFe <sub>2</sub> O(O <sub>2</sub> CCMe <sub>3</sub> ) <sub>6</sub> (hmta) <sub>1.5</sub> ]•(C <sub>6</sub> H <sub>5</sub> CH <sub>3</sub> )	Monoclinic, P2 <sub>1</sub> /c (No. 14)	4, 1.342	R <sub>1</sub> = 0.0731, wR <sub>2</sub> = 0.1366	4632	837616	(52)

(Continued)

Formula (M:hmta)	Crystal system, space group	Z, d, Mg m <sup>-3</sup>	R indices (all data)	F (000)	CCDC No.	Reference No.
[Mn(H <sub>2</sub> O) <sub>6</sub> ](C <sub>4</sub> H <sub>4</sub> O <sub>4</sub> ) <sub>2</sub> •2(hmta)•4H <sub>2</sub> O (1:2)	Triclinic, P $\bar{1}$ (No. 2)	-	-	-	1267/1319	(53)
Mn <sub>2</sub> (hmta)(H <sub>2</sub> O) <sub>2</sub> (mal) <sub>2</sub> (2:1) (mal = malonate)	Orthorhombic, Immm2 (No. 44)	2, 1.862	R <sub>1</sub> = 0.0255, wR <sub>2</sub> = 0.0659	500	256349	(54)
Co(hmta) <sub>2</sub> (H <sub>2</sub> O) <sub>6</sub> (NO <sub>3</sub> ) <sub>2</sub> •4H <sub>2</sub> O (1:2)	Triclinic, P1 (No. 1)	1, 1.50	R <sub>1</sub> = 0.032, wR <sub>2</sub> = 0.086	328.9	211784	(49)
(NO <sub>3</sub> ) <sub>2</sub> Co(H <sub>2</sub> O) <sub>6</sub> (hmta) <sub>2</sub> •4H <sub>2</sub> O (1:2)	Triclinic, P $\bar{1}$ (No. 2)	1, 1.52	-	-	-	(55)
{[Co(hmta) <sub>2</sub> (tfbdc)(H <sub>2</sub> O) <sub>2</sub> ]•(H <sub>2</sub> tfbdc)•(C <sub>2</sub> H <sub>5</sub> OH) <sub>2</sub> } <sub>n</sub> (1:2) (H <sub>2</sub> tfbdc = 2,3,5,6-tetrafluoroterephthalic acid)	Triclinic, P $\bar{1}$ (No. 2)	1, 1.685	R <sub>1</sub> = 0.0622, wR <sub>2</sub> = 0.1550	485	905135	(52)
{[Co(hmta)(tfbdc)(H <sub>2</sub> O) <sub>2</sub> ]•(H <sub>2</sub> O) <sub>2</sub> } <sub>n</sub>	Triclinic, P $\bar{1}$ (No. 2)	2, 1.769	R <sub>1</sub> = 0.0751, wR <sub>2</sub> = 0.1484	518	905136	(52)
[Cu <sub>4</sub> (O <sub>2</sub> CCH <sub>2</sub> CO <sub>2</sub> ) <sub>4</sub> (hmta)]•7H <sub>2</sub> O (4:1)	Orthorhombic, Pmmn (No. 59)	4, 1.944	-	896	-	(56)
[Co(H <sub>2</sub> O) <sub>4</sub> {H <sub>2</sub> O-(hmta)} <sub>2</sub> ](NO <sub>3</sub> ) <sub>2</sub> •4H <sub>2</sub> O (1:2)	Triclinic, P $\bar{1}$ (No.2)	1, 1.546	R <sub>1</sub> = 0.044, wR <sub>2</sub> = 0.094	341	639634	(45)
[Co(H <sub>2</sub> O) <sub>6</sub> ](ClO <sub>4</sub> ) <sub>2</sub> •(hmta) <sub>2</sub> •2H <sub>2</sub> O (1:2)	Triclinic, P1 (No. 1)	1, 1.640	-	-	-	(57)
[Co(hmta) <sub>2</sub> (H <sub>2</sub> O) <sub>4</sub> {Co(H <sub>2</sub> O) <sub>6</sub> }] (SO <sub>4</sub> ) <sub>2</sub> •6H <sub>2</sub> O (1:1)	Triclinic, P1 (No. 1)	1.123	R <sub>1</sub> = 0.036, wR <sub>2</sub> = 0.062	924	-	(58)
(NO <sub>3</sub> ) <sub>2</sub> Ni(H <sub>2</sub> O) <sub>6</sub> (hmta) <sub>2</sub> •4H <sub>2</sub> O (1:2)	Triclinic, P $\bar{1}$ (No. 2)	1, 1.53	-	-	-	(55)
[Ni{H <sub>2</sub> O-(hmta)-H <sub>2</sub> O} <sub>2</sub> (H <sub>2</sub> O-ClO <sub>4</sub> ) <sub>2</sub> (H <sub>2</sub> O) <sub>2</sub> ] (1:2)	Triclinic, P $\bar{1}$ (No. 2)	1, 1.638	R <sub>1</sub> = 0.054, wR <sub>2</sub> = 0.131	358	658326	(45)
[Ni(H <sub>2</sub> O) <sub>4</sub> {H <sub>2</sub> O-(hmta)} <sub>2</sub> ](NO <sub>3</sub> ) <sub>2</sub> •4H <sub>2</sub> O (1:2)	Triclinic, P $\bar{1}$ (No.2)	1, 1.566	R <sub>1</sub> = 0.055, wR <sub>2</sub> = 0.127	342	639635	(45)
Ni(H <sub>2</sub> O) <sub>6</sub> (NO <sub>3</sub> ) <sub>2</sub> •(hmta) <sub>2</sub> •4H <sub>2</sub> O (1:2)	Triclinic P $\bar{1}$ (No. 2)	1	R <sub>1</sub> = 0.056, wR <sub>2</sub> = 0.147	-	1267/1129	(59)
Ni(hmta) <sub>2</sub> (C <sub>7</sub> H <sub>5</sub> O <sub>2</sub> ) <sub>2</sub> (H <sub>2</sub> O) <sub>2</sub> •2H <sub>2</sub> O (1:2)	Monoclinic C2/c (No. 15)	4	R <sub>1</sub> = 0.074, wR <sub>2</sub> = 0.156	-	1267/1142	(60)
[Ni(hmta) <sub>2</sub> (H <sub>2</sub> O) <sub>4</sub> {Ni(H <sub>2</sub> O) <sub>6</sub> }] (SO <sub>4</sub> ) <sub>2</sub> •6H <sub>2</sub> O (1:1)	P $\bar{1}$ (No. 2)	1	R <sub>1</sub> = 0.028, wR <sub>2</sub> = 0.076	-	-	(58)
[Ni(H <sub>2</sub> O) <sub>6</sub> ](ClO <sub>4</sub> ) <sub>2</sub> •2(hmta)•2H <sub>2</sub> O (1:2)	Triclinic P1 (No. 1)	1, 1.619	-	-	281949	(61)

(Continued)



Formula (M:hm <sub>2</sub> a)	Crystal system, space group	Z, d, Mg m <sup>-3</sup>	R indices (all data)	F (000)	CCDC No.	Reference No.
[Ni(H <sub>2</sub> O) <sub>6</sub> ] <sub>2</sub> [C <sub>12</sub> •2(hm <sub>2</sub> a)•4H <sub>2</sub> O] (1:2)	Triclinic P1 (No. 1)	1, 1.412	-	-	281950	(61)
[Ni(3-nbz) <sub>2</sub> (hm <sub>2</sub> a) <sub>2</sub> (H <sub>2</sub> O) <sub>2</sub> ]•2(3-nbzH) (1:2) (3-nbz = 3-nitrobenzoate)	Triclinic, P1 (No. 1)	1, 1.557	-	-	969623	(62)
Ni(H <sub>2</sub> btc) <sub>2</sub> (hm <sub>2</sub> a) <sub>2</sub> (H <sub>2</sub> O) (1:2) (btc = benzene-1,3,5-tricarboxylate)	Orthorhombic, Pccn (No. 56)	4, 1.579	-	1612	-	(63)
[Ni(2-nbz) <sub>2</sub> (μ <sub>2</sub> -hm <sub>2</sub> a)(H <sub>2</sub> O) <sub>2</sub> ] <sub>n</sub> (1:1) (2-nbz = 2-nitrobenzoate)	Triclinic, P1 (No. 1)	2, 1.639	-	-	969622	(62)
[Ni(4-nbz) <sub>2</sub> (μ <sub>2</sub> -hm <sub>2</sub> a)(H <sub>2</sub> O) <sub>2</sub> ] <sub>n</sub> (1:1) (4-nbz = 4-nitrobenzoate)	Triclinic, P1 (No. 1)	2, 1.709	-	-	969624	(62)
Cu(NCO) <sub>2</sub> (hm <sub>2</sub> a) <sub>2</sub> (1:2)	Triclinic, P1 (No. 1)	-	R <sub>1</sub> = 0.048, wR <sub>2</sub> = 0.062	-	-	(64)
(CuCN) <sub>3</sub> (hm <sub>2</sub> a) <sub>2</sub> (1:2)	Monoclinic, C2/c (No. 15)	4, 1.817	-	-	-	(38)
Cu <sub>2</sub> (hm <sub>2</sub> a)(H <sub>2</sub> O) <sub>2</sub> (mal) <sub>2</sub> (2:1) (mal = malonate)	Orthorhombic, Immm2 (No. 44)	2, 2.047	R <sub>1</sub> = 0.0572, wR <sub>2</sub> = 0.1577	516	256350	(54)
[Cu <sub>3</sub> (2-nbz) <sub>6</sub> (μ <sub>2</sub> -hm <sub>2</sub> a)] <sub>n</sub> (3:1)	Tetragonal, I4 <sub>2</sub> d (No. 122)	16, 1.624	-	-	942350	(40)
[Cu <sub>3</sub> (pa) <sub>6</sub> (μ <sub>3</sub> -hm <sub>2</sub> a)] <sub>n</sub> (3:1) (pa = phenylacetate)	Triclinic P1 (No. 1)	2, 1.491	-	-	942351	(40)
[Cu <sub>3</sub> (4-nbz) <sub>6</sub> (μ <sub>3</sub> -hm <sub>2</sub> a)] <sub>n</sub> (3:1)	Trigonal P3 (No. 143)	2, 1.581	-	-	942352	(40)
[Cu(3-nbz) <sub>2</sub> (μ <sub>4</sub> -hm <sub>2</sub> a)•H <sub>2</sub> O] <sub>n</sub> (1:1)	Tetragonal I4 <sub>1</sub> /a (No. 88)	8, 1.754	-	-	942353	(40)
[Zn{H <sub>2</sub> O-(hm <sub>2</sub> a)-H <sub>2</sub> O} <sub>2</sub> (H <sub>2</sub> O-ClO <sub>4</sub> ) <sub>2</sub> (H <sub>2</sub> O) <sub>2</sub> ] <sub>n</sub> (1:1)	Triclinic, P1 (No. 2)	1, 1.639	R <sub>1</sub> = 0.047, wR <sub>2</sub> = 0.120	360	658327	(45)
[Zn(hm <sub>2</sub> a) <sub>2</sub> (H <sub>2</sub> O) <sub>4</sub> ] <sub>n</sub> <sup>2+</sup> •[Zn(H <sub>2</sub> O) <sub>6</sub> ] <sub>n</sub> <sup>2+</sup> •2SO <sub>4</sub> <sup>2-</sup> •6H <sub>2</sub> O (1:1)	Triclinic P1 (No. 2)	2, 1.634	R <sub>1</sub> = 0.0792, wR <sub>2</sub> = 0.2011	936	963566	(65)
[Zn(H <sub>2</sub> O) <sub>6</sub> ] <sub>n</sub> <sup>2+</sup> •2(hm <sub>2</sub> a)•2NO <sub>3</sub> <sup>-</sup> •4H <sub>2</sub> O (1:2)	Triclinic P1 (No. 2)	1, 1.547	R <sub>1</sub> = 0.0324, wR <sub>2</sub> = 0.0888	344	963568	(65)
[Zn <sub>2</sub> (4-nbz) <sub>4</sub> (H <sub>2</sub> O)(hm <sub>2</sub> a) <sub>2</sub> ] <sub>n</sub> (1:1)	Triclinic P1 (No. 1)	2, 1.702	R <sub>1</sub> = 0.0714, wR <sub>2</sub> = 0.1165	-	849277	(66)

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Formula (M:hmta)	Crystal system, space group	Z, d, Mg m <sup>-3</sup>	R indices (all data)	F (000)	CCDC No.	Reference No.
[Zn <sub>2</sub> (2-nbz) <sub>4</sub> (hmta) <sub>2</sub> ] (1:1)	Triclinic P1 (No. 1)	2, 1.658	R <sub>1</sub> = 0.0759, wR <sub>2</sub> = 0.0839	-	849278	(66)
[Zn <sub>3</sub> (3-nbz) <sub>4</sub> (hmta)(OH) <sub>2</sub> ] (3:1)	Monoclinic P2 <sub>1</sub> /c (No. 14)	4, 1.782	R <sub>1</sub> = 0.1640, wR <sub>2</sub> = 0.2172	-	849279	(66)
[Cd(hmta)(H <sub>2</sub> O) <sub>4</sub> ] <sub>n</sub> <sup>2+</sup> nSO <sub>4</sub> <sup>2-</sup> • 2nH <sub>2</sub> O (1:1)	Triclinic P1̄ (No. 2)	4, 1.913	R <sub>1</sub> = 0.0514, wR <sub>2</sub> = 0.1506	928	963567	(65)
[Cd(hmta)(NO <sub>3</sub> ) <sub>2</sub> (H <sub>2</sub> O) <sub>2</sub> ] <sub>n</sub> (1:1)	Monoclinic C2/c (No.15)	4, 2.094	R <sub>1</sub> = 0.0162, wR <sub>2</sub> = 0.0391	824	963569	(65)
Cd <sub>3</sub> (CTO) <sub>2</sub> (μ <sub>2</sub> -hmta)(DMF)(C <sub>2</sub> H <sub>5</sub> OH)(H <sub>2</sub> O)•2H <sub>2</sub> O (3:1) (CTC = <i>cis,cis</i> -1,3,5-cyclohexanetricarboxylate)	Orthorhombic, Pna2 <sub>1</sub> (No. 33)	4, 1.816	R <sub>1</sub> = 0.0584, wR <sub>2</sub> = 0.0627	2192	232121	(67)
[Cd(SCN) <sub>2</sub> (hmta) <sub>0.5</sub> (H <sub>2</sub> O)] <sub>2</sub> •H <sub>2</sub> O (2:1)	Orthorhombic, Aea2 (No. 41)	4, 2.072	R <sub>1</sub> = 0.0362, wR <sub>2</sub> = 0.1003	-	684814	(68)
[{Cd(H <sub>2</sub> O) <sub>3</sub> } <sub>34</sub> (hmta) <sub>17</sub> ]Cl <sub>68</sub> •46H <sub>2</sub> O•68DMF (2:1)	Cubic, Fd3m (No. 227)	8, 1.185	-	40800	-	(69)
[Cd(cdpc)(hmta)(H <sub>2</sub> O)]•H <sub>2</sub> O (1:1) (cdpc = 1-carboxymethyl-3,5-dimethyl-1H-pyrazole-4-carboxylic)	Orthorhombic, Fdd2 (No. 43)	16, 1.727	-	3936	1025425	(70)
[Cd(2-nbz) <sub>2</sub> (μ <sub>2</sub> -hmta)(OH <sub>2</sub> )]•2H <sub>2</sub> O (1:1)	Monoclinic P2 <sub>1</sub> /c (No. 14)	4, 1.748	-	-	903838	(71)
[Cd(3-nbz) <sub>2</sub> (hmta) <sub>2</sub> (OH <sub>2</sub> ) <sub>2</sub> ]•2(3-nbzH) (1:2)	Triclinic P1 (No. 1)	1, 1.641	-	-	903839	(71)
[Cd(3-nbz) <sub>4</sub> (μ <sub>2</sub> -hmta)] (1:1)	Orthorhombic Cmm2 (No. 35)	2, 1.866	-	-	903840	(71)
{[Cd <sub>2</sub> (4-nbz) <sub>4</sub> (μ <sub>2</sub> -hmta) <sub>2</sub> (OH <sub>2</sub> ) <sub>2</sub> ]•H <sub>2</sub> O} (1:1)	Triclinic P1 (No. 1)	2, 1.785	-	-	903841	(71)
Cd(hmta)(NO <sub>3</sub> ) <sub>2</sub> (H <sub>2</sub> O) <sub>2</sub> (1:1)	Monoclinic, C2/c (No. 15)	4, 2.096	-	-	-	(34)
[Cd(H <sub>2</sub> O) <sub>4</sub> (hmta) <sub>2</sub> (ClO <sub>4</sub> ) <sub>2</sub> ]•2H <sub>2</sub> O (1:2)	Monoclinic, P2 <sub>1</sub> /c (No. 14)	2, 1.824	-	-	281951	(61)
Ag(L <sub>1</sub> )(hmta) (1:1) (L <sub>1</sub> = ligand)	Orthorhombic, Pbcn (No. 60)	-	-	-	782486	(72)
Ag(L <sub>2</sub> )(hmta)(H <sub>2</sub> O) (1:1) (L <sub>2</sub> = ligand 1)	Monoclinic, P2 <sub>1</sub> /c (No. 14)	-	-	-	782487	(72)

(Continued)

Formula (M:hmta)	Crystal system, space group	Z, d, Mg m <sup>-3</sup>	R indices (all data)	F (000)	CCDC No.	Reference No.
[Ag(L <sub>3</sub> )(hmta)]•(H <sub>2</sub> O) (1:1) (L <sub>3</sub> = ligand)	Orthorhombic, Pca2 <sub>1</sub> (No. 29)	-	-	-	782488	(72)
[Ag <sub>2</sub> (L <sub>4</sub> )(hmta) <sub>2</sub> ]•2(CH <sub>3</sub> OH) (1:1) (L <sub>4</sub> = ligand)	Monoclinic, P2 <sub>1</sub> /c (No. 14)	-	-	-	782489	(72)
[Ag <sub>6</sub> (L <sub>5</sub> ) <sub>6</sub> (hmta) <sub>6</sub> ]•18(H <sub>2</sub> O) (1:1) (L <sub>5</sub> = ligand)	Monoclinic, P2 <sub>1</sub> (No. 4)	-	-	-	782490	(72)
[Ag <sub>6</sub> (L <sub>6</sub> ) <sub>6</sub> (hmta) <sub>6</sub> ]•16(H <sub>2</sub> O) (1:1) (L <sub>6</sub> = ligand)	Monoclinic, P2 <sub>1</sub> (No. 4)	-	-	-	782491	(72)
[Ag(μ <sub>3</sub> -hmta)](abs) (1:1) (abs = 4-aminobenzenesulfonate)	Orthorhombic, Pmn2 <sub>1</sub> (No. 31)	2, 1.863	-	-	169729	(73)
[Ag(μ <sub>3</sub> -hmta)](ns)•0.5(C <sub>6</sub> H <sub>6</sub> )•2H <sub>2</sub> O (1:1) (ns = 2-naphthalenesulfonate)	Orthorhombic, Pmn2 <sub>1</sub> (No. 31)	4, 1.675	-	-	169730	(73)
[Ag(μ <sub>3</sub> -hmta)] <sub>2</sub> [Ag(NH <sub>3</sub> ) <sub>2</sub> ] <sub>2</sub> (pma)•3H <sub>2</sub> O (1:1) (pma = 1,2,4,5-benzenetetracarboxylate)	Orthorhombic, Pnmm (No. 58)	2, 2.248	-	-	169731	(73)
[Ag <sub>3</sub> (μ <sub>4</sub> -hmta) <sub>2</sub> (μ-ssa)(H <sub>2</sub> O)](NO <sub>3</sub> )•3H <sub>2</sub> O (1:1) (ssa = sulfosalicylate)	Orthorhombic, Pna2 <sub>1</sub> (No.33)	4, 2.170	R <sub>1</sub> = 0.0670, wR <sub>2</sub> = 0.1624	-	-	(74)
[Ag <sub>8</sub> (μ <sub>3</sub> -hmta) <sub>2</sub> (μ <sub>4</sub> -hmta) <sub>2</sub> (m-pma) <sub>2</sub> (m-H <sub>2</sub> O) <sub>3</sub> ]•18H <sub>2</sub> O (2:1) (pma = 1,2,4,5-benzenetetracarboxylate)	Monoclinic, C2/c (No. 15)	4, 2.148	R <sub>1</sub> = 0.0617, wR <sub>2</sub> = 0.2012	-	-	(74)
[Ag(μ <sub>3</sub> -hmta)(p-nba)]•2.5H <sub>2</sub> O (1:1) (p-nba = 4-nitrobenzoate)	Monoclinic, P2 <sub>1</sub> /c (No. 14)	4, 1.828	R <sub>1</sub> = 0.0478, wR <sub>2</sub> = 0.1263	-	-	(75)
[Ag(μ <sub>3</sub> -hmta)(m-nba)]•2.5H <sub>2</sub> O (1:1) (m-nba = 3-nitrobenzoate)	Monoclinic, P2 <sub>1</sub> /c (No. 14)	4, 1.885	R <sub>1</sub> = 0.0376, wR <sub>2</sub> = 0.0987	-	-	(75)
[Ag(μ <sub>3</sub> -hmta)(dnba)] (1:1) (dnba = 3,5-dinitrobenzoate)	Orthorhombic, Pnma (No. 62)	4, 1.939	R <sub>1</sub> = 0.0380, wR <sub>2</sub> = 0.0848	-	-	(75)
[Ag(μ <sub>3</sub> -hmta)(σ-hna)](C <sub>2</sub> H <sub>5</sub> OH) (1:1) (σ-hna = 1-hydroxy-2-naphthate)	Orthorhombic, Pca2 <sub>1</sub> (No. 29)	4, 1.577	R <sub>1</sub> = 0.0414, wR <sub>2</sub> = 0.1110	-	-	(75)

(Continued)

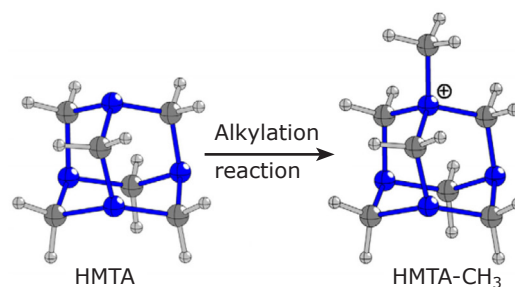
Formula (M:hmta)	Crystal system, space group	Z, d, Mg m <sup>-3</sup>	R indices (all data)	F (000)	CCDC No.	Reference No.
[Ag(μ <sub>3</sub> -hmta)(β-hna)](C <sub>2</sub> H <sub>5</sub> OH) (1:1) (β-hna = 3-hydroxy-2-naphthate)	Orthorhombic, Pca2 <sub>1</sub> (No. 29)	4, 1.576	R <sub>1</sub> = 0.0461, wR <sub>2</sub> = 0.1156	-	-	(75)
[Ag(μ <sub>3</sub> -hmta)(noa)](H <sub>2</sub> O)(C <sub>2</sub> H <sub>5</sub> OH) (1:1) (noa = 2-naphthoxyacetate)	Orthorhombic, Pbcn (No. 61)	8, 1.509	R <sub>1</sub> = 0.0579, wR <sub>2</sub> = 0.1490	-	-	(75)
[Ag <sub>2</sub> (μ <sub>3</sub> -hmta) <sub>2</sub> (fa)]•4H <sub>2</sub> O (1:1) (fa = fumarate)	Orthorhombic, Pbcn (No. 60)	4, 1.965	R <sub>1</sub> = 0.0499, wR <sub>2</sub> = 0.1362	-	-	(75)
[Ag <sub>2</sub> (μ <sub>3</sub> -hmta) <sub>2</sub> (adp)]•8H <sub>2</sub> O (1:1) (adp = adipate)	Orthorhombic, Pnnm (No. 58)	2, 1.814	R <sub>1</sub> = 0.0446, wR <sub>2</sub> = 0.1264	-	-	(75)
[Ag(hmta)(fma) <sub>0.5</sub> •2H <sub>2</sub> O] <sub>n</sub> (1:1) (fma = fumaric acid)	Orthorhombic, Pbcn (No. 60)	8, 1.970	R <sub>1</sub> = 0.0451, wR <sub>2</sub> = 0.1314	1376	-	(76)
[Ag <sub>5</sub> (hmta) <sub>6</sub> ](PF <sub>6</sub> ) <sub>3</sub> •3CH <sub>2</sub> Cl <sub>2</sub> (5:5)	Hexagonal, P6 <sub>3</sub> /m (No. 176)	2, 2.101	-	-	-	(76)
[Ag <sub>4</sub> (hmta) <sub>3</sub> (H <sub>2</sub> O)](PF <sub>6</sub> ) <sub>4</sub> •3C <sub>2</sub> H <sub>5</sub> OH (4:3)	Cubic, Pa3 (No. 205)	8, 2.022	-	-	-	(76)
[Ag <sub>2</sub> (μ <sub>4</sub> -hmta)(Tos) <sub>2</sub> ] (2:1) (Tos = <i>p</i> -toluenesulfonate)	Monoclinic C2/c (No. 15)	4, 2.014	R <sub>1</sub> = 0.1071, wR <sub>2</sub> = 0.0957	1392	-	(76)
[Ag <sub>2</sub> (μ <sub>3</sub> -hmta) <sub>2</sub> (CF <sub>3</sub> SO <sub>3</sub> )(H <sub>2</sub> O)](CF <sub>3</sub> SO <sub>3</sub> )•H <sub>2</sub> O (1:1)	Monoclinic C2/c (No.15)	4, 2.103	R <sub>1</sub> = 0.2275, wR <sub>2</sub> = 0.1439	1648	-	(77)
[Ag <sub>3</sub> (μ <sub>3</sub> -hmta) <sub>2</sub> (H <sub>2</sub> O) <sub>4</sub> ](PF <sub>6</sub> ) <sub>3</sub> (3:2)	Monoclinic P2 <sub>1</sub> /c (No. 14)	4, 2.321	R <sub>1</sub> = 0.0788, wR <sub>2</sub> = 0.1149	2160	-	(77)
[Ag(NO <sub>3</sub> )•(hmta)] (1:1)	Orthorhombic	-	-	-	-	(78)
[H-(hmta)]][HgCl <sub>3</sub> ] (1:1)	Orthorhombic, Cmc2 <sub>1</sub> (No. 36)	4, 2.33	R <sub>1</sub> = 0.045, wR <sub>2</sub> = 0.054	-	-	(79)
[Hg(hmta) <sub>0.5</sub> Br <sub>2</sub> ] (2:1)	Monoclinic, C2/c (No. 15)	8, 3.850	R <sub>1</sub> = 0.0676, wR <sub>2</sub> = 0.1894	-	-	(50)
(hmta)•2Hg(SCN) <sub>2</sub> (2:1)	Monoclinic, P2 <sub>1</sub> /m (No. 11)	2, 2.830	R <sub>1</sub> = 0.060, wR <sub>2</sub> = 0.073	-	-	(80)
(HgCl <sub>2</sub> ) <sub>2</sub> (hmta) (2:1)	Orthorhombic, Fddd (No. 70)	8, 3.548	-	-	-	(81)

Table IV Major Crystal Data and Refinement for Compounds of hmta with Metal Salts

Formula (M:hmta)	Crystal system, space group	Z, d, Mg m <sup>-3</sup>	R indices (all data)	F (000)	CCDC No.	Reference No.
[La(NO <sub>3</sub> ) <sub>2</sub> •C <sub>12</sub> H <sub>8</sub> N <sub>2</sub> •(H <sub>2</sub> O) <sub>4</sub> ] <sup>+</sup> •NO <sub>3</sub> <sup>-</sup> •(hmta)•2H <sub>2</sub> O (1:1)	Monoclinic, P2 <sub>1</sub> /n (No. 14)	4, 1.731	R <sub>1</sub> = 0.0504, wR <sub>2</sub> = 0.0396	1520	269659	(86)
[La(NO <sub>3</sub> ) <sub>2</sub> (H <sub>2</sub> O) <sub>6</sub> ] <sup>+</sup> •2(hmta)•NO <sub>3</sub> <sup>-</sup> •H <sub>2</sub> O (1:2)	Monoclinic, P2 <sub>1</sub> /c (No. 14)	4, 1.686	R <sub>1</sub> = 0.0697, wR <sub>2</sub> = 0.1239	-	993310	(85)
[Nd(H <sub>2</sub> O) <sub>9</sub> ][Cl <sup>-</sup> •2(hmta)•4H <sub>2</sub> O (1:2)	Triclinic, P1 (No. 1)	2, 1.638	-	-	-	(87)
La(NCS) <sub>3</sub> •2(hmta)•9H <sub>2</sub> O (1:2)	Orthorhombic, Pnma (No 62)	-	R <sub>1</sub> = 0.037, wR <sub>2</sub> = 0.071	-	1003/4553	(88)
[Ln(H <sub>2</sub> O) <sub>8</sub> ][M(CN) <sub>6</sub> ] <sup>-</sup> •(hmta)[FeDy] (1:2)	Cubic, Fm $\bar{3}$ m (No. 225)	4, 1.655	R <sub>1</sub> = 0.0261, wR <sub>2</sub> = 0.0623	1544	-	(89)
[La(NO <sub>3</sub> ) <sub>2</sub> (H <sub>2</sub> O) <sub>6</sub> ] <sup>+</sup> •NO <sub>3</sub> <sup>-</sup> •2(hmta)•2H <sub>2</sub> O (1:2)	Monoclinic, P2 <sub>1</sub> /c (No. 14)	4, 1.707	R <sub>1</sub> = 0.0307, wR <sub>2</sub> = 0.0634	1528	258316	(90)
[Ce(NO <sub>3</sub> ) <sub>2</sub> (H <sub>2</sub> O) <sub>6</sub> ] <sup>+</sup> •NO <sub>3</sub> <sup>-</sup> •2(hmta)•2H <sub>2</sub> O (1:2)	Monoclinic, P2 <sub>1</sub> /c (No. 14)	4, 1.712	-	1532	266394	(90)
[Pr(NO <sub>3</sub> ) <sub>2</sub> (H <sub>2</sub> O) <sub>6</sub> ] <sup>+</sup> •NO <sub>3</sub> <sup>-</sup> •2(hmta)•2H <sub>2</sub> O (1:2)	Monoclinic, P2 <sub>1</sub> /c (No. 14)	4, 1.721	-	1536	266395	(90)
[Nd(NO <sub>3</sub> ) <sub>2</sub> (H <sub>2</sub> O) <sub>6</sub> ] <sup>+</sup> •NO <sub>3</sub> <sup>-</sup> •2(hmta)•2H <sub>2</sub> O (1:2)	Monoclinic, P2 <sub>1</sub> /c (No. 14)	4, 1.793	-	1580	-	(90)
[Sm(NO <sub>3</sub> )(H <sub>2</sub> O) <sub>7</sub> ] <sup>+</sup> •2NO <sub>3</sub> <sup>-</sup> •2(hmta)•3H <sub>2</sub> O (1:2)	Monoclinic, P2 <sub>1</sub> /c (No. 14)	4, 1.730	-	1628	266396	(90)
[Eu(NO <sub>3</sub> )(H <sub>2</sub> O) <sub>7</sub> ] <sup>+</sup> •2NO <sub>3</sub> <sup>-</sup> •2(hmta)•3H <sub>2</sub> O (1:2)	Monoclinic, P2 <sub>1</sub> /c (No. 14)	4, 1.740	R <sub>1</sub> = 0.0333, wR <sub>2</sub> = 0.0879	1632	258317	(90)
[Gd(NO <sub>3</sub> )(H <sub>2</sub> O) <sub>7</sub> ] <sup>+</sup> •2NO <sub>3</sub> <sup>-</sup> •2(hmta)•3H <sub>2</sub> O (1:2)	Monoclinic, P2 <sub>1</sub> /c (No. 14)	4, 1.75	-	1636	266397	(90)
[Dy(H <sub>2</sub> O) <sub>8</sub> ] <sup>3+</sup> •3NO <sub>3</sub> <sup>-</sup> •2(hmta)•2H <sub>2</sub> O (1:2)	Triclinic, P1 (No. 1)	2, 1.756	R <sub>1</sub> = 0.0287, wR <sub>2</sub> = 0.0754	822	258318	(90)
[Ho(H <sub>2</sub> O) <sub>8</sub> ] <sup>3+</sup> •3NO <sub>3</sub> <sup>-</sup> •2(hmta)•2H <sub>2</sub> O (1:2)	Triclinic, P1 (No. 1)	2, 1.767	-	824	266389	(90)

(Continued)

Formula (M:hmta)	Crystal system, space group	Z, d, Mg m <sup>-3</sup>	R indices (all data)	F (000)	CCDC No.	Reference No.
[Tm(H <sub>2</sub> O) <sub>8</sub> ] <sup>3+</sup> •3NO <sub>3</sub> <sup>-</sup> •2(hmta)•2H <sub>2</sub> O (1:2)	Triclinic, P1 (No. 1)	2, 1.781	-	828	266391	(90)
[Yb(H <sub>2</sub> O) <sub>8</sub> ] <sup>3+</sup> •3NO <sub>3</sub> <sup>-</sup> •2(hmta)•2H <sub>2</sub> O (1:2)	Triclinic, P1 (No. 1)	2, 1.801	-	830	266392	(90)
[Lu(H <sub>2</sub> O) <sub>8</sub> ] <sup>3+</sup> •3NO <sub>3</sub> <sup>-</sup> •2(hmta)•2H <sub>2</sub> O (1:2)	Triclinic, P1 (No. 1)	2, 1.807	-	832	266393	(90)
{H-(hmta)} <sub>2</sub> (H <sub>3</sub> O)[Ce(H <sub>2</sub> O) <sub>5</sub> Mo <sub>7</sub> O <sub>24</sub> ] <sup>+</sup> •4H <sub>2</sub> O (1:1)	Orthorhombic, Pnma (No. 62)	4, 2.798	R <sub>1</sub> = 0.0659, wR <sub>2</sub> = 0.1256	3192	-	(91)
{H-(hmta)} <sub>2</sub> [(UO <sub>2</sub> ) <sub>2</sub> (C <sub>4</sub> H <sub>4</sub> O <sub>5</sub> ) <sub>2</sub> (OH) <sub>2</sub> ] <sup>+</sup> •2H <sub>2</sub> O (1:1)	Monoclinic, C2/m (No. 12)	4, 1.54178	-	-	-	(92)



Scheme I. Schematic diagram of alkylation reaction

ability to form multinuclear species depends on the type of metal and increases with increasing atomic number.

## 2.2 Effect of Different Anions

In the studied compounds, unshared electrons were not only provided by ligands, but also by anions such as Cl<sup>-</sup>, Br<sup>-</sup>, I<sup>-</sup>, NO<sub>3</sub><sup>-</sup>, ClO<sub>4</sub><sup>-</sup>, Cr<sub>2</sub>O<sub>7</sub><sup>2-</sup> and SCN<sup>-</sup>. Different anions are mainly used for regulating the electric charge and sometimes make the overall molecule slightly distorted. Among the inorganic anions serving as ligands the most popular is SCN<sup>-</sup> due to its great tendency to link metal ions.

## 2.3 Effect of Water Molecules

Among these compounds, water molecules also play a very important role, providing oxygen atoms or hydrogen bonds and making the overall structure more stable. Thermal analyses show that the water molecules in the investigated compounds were totally removed during thermal decomposition and further heating.

## 2.4 Coordination Positions and Crystal System

The hmta molecule is a tetrafunctional neutral organic ligand which can be used as an outer coordination sphere modulator of an inner coordination sphere or as a crosslinking agent building block in di- and multinuclear compounds. It has been used to assemble new supramolecular structures with metal ions, *via* various coordination modes, involving one to four N atoms of the hmta molecule.

The ions and molecules appear in different positions, called the inner and outer coordination spheres. For example, main group metal salts coordinate with hmta in the inner coordination

sphere in the case of Na, K and Rb compounds, and in the outer coordination sphere in the case of Li, Mg, Ca and Sr compounds. This phenomenon may be affected by many factors, the electronic properties of the cation being the most important.

Under the action of hmta, different ions and water molecules form different crystal systems: orthorhombic, monoclinic, triclinic, hexagonal, cubic or parallelepiped. Among them, monoclinic and triclinic crystal structures are the most common. There are also some rare 3D hybrid compounds, such as  $[\text{Na}(\text{ClO}_4)(\text{H}_2\text{O})(\text{hmta})]_n$ ,  $[\text{NaNO}_3 \cdot \text{hmta}]_n$ ,  $[\text{K}_2(\text{hmta})(\text{SCN})_2]_n$ ,  $[\text{K}(\text{H}_2\text{O})(\text{hmta})\text{I}]_n$  and  $[\text{Rb}(\text{H}_2\text{O})(\text{hmta})\text{I}]_n$ . It is thereby demonstrated that simple inorganic anions and organic molecules can be used to construct 3D networks possessing high complexity (multinodal nets with complicated stoichiometry) after proper selection of the molecular species for net self-assembly.

## 2.5 A Discussion on Synthetic Methods

As the ligands, salts and hmta are soluble in water almost all of the synthetic methods are similar: make the solution at a certain proportion and stir them together for a number of hours, followed by treatment for several days or weeks at either room temperature or a specific temperature. So far, most complexes were prepared by virtue of this method. When the molecules are larger or ligand types are more complex, the synthesis conditions should manipulate a number of variables such as pH, ligand and cation size and type.

## 2.6 The Similarities and Differences of Transition Metal Complexes

Compared to transition metal coordination compounds, those of alkaline earth metals have not been widely studied. Such materials should be environmentally friendly and their syntheses should be simple and economical. Thus, investigation of alkaline earth metal coordination chemistry is indispensable for obtaining new compounds and new materials.

There has been much research on transition metal complexes with hmta as well as comparison of their performance in a range of potential applications. Among the most studied are complexes with Ni, Mn, Cu or Zn. As a transition metal centre, Ni is well suited for the construction of various coordination polymers with N- and/or O-ligands on account of its variable oxidation states, different geometries,

spectral and magnetic features and ligand field effects.

Organometallic complexes of lanthanide metals are mainly used to catalyse organic reactions. Some other functional studies are still in progress.

## 3. Applications of hmta with Metal Salts

### 3.1 Military Applications

Complexes of hmta have been investigated for military applications as explosives. Singh *et al.* (45) characterised a complex of lanthanum nitrate with hmta by X-ray crystallography. Thermolysis of the complex was undertaken using TG and TG-DSC, a micro-destructive technique which does not require any pretreatment before analysis and can provide useful information about thermal and chemical reaction processes in a relatively short time. In order to establish safe handling procedures, sensitivity of explosives towards mechanical destructive stimuli such as impact and friction are measured. The development of highly energetic materials includes processability and the ability to attain insensitive munitions (IM). The paper investigated the preparation of a lanthanum nitrate complex of hmta in water at room temperature. The complex, of molecular formula  $[\text{La}(\text{NO}_3)_2(\text{H}_2\text{O})_6](2\text{hmta})(\text{NO}_3)(\text{H}_2\text{O})$ , was characterised by X-ray crystallography. Thermal decomposition was investigated using TG, TG-DSC and ignition delay measurements. Kinetic analysis of isothermal TG data was carried out using model fitting methods as well as model free iso-conversional methods. The complex was found to be insensitive towards mechanical destructive stimuli such as impact and friction.

In order to identify the end product of thermolysis, the X-ray diffraction (XRD) patterns were examined which proved the formation of  $\text{La}_2\text{O}_3$ . The crystal structure reveals that the lanthanum metal had a coordination number of 10. TG-DSC studies showed a three-step decomposition of the complex. The oxidation-reduction reaction between oxidiser ( $\text{NO}_3$ ) and fuel (hmta) led to ignition yielding  $\text{La}_2\text{O}_3$  and gaseous products. The oxide residue was confirmed by the XRD pattern. The impact and friction sensitivity measurements showed that this compound exhibited remarkably low sensitivity towards impact (>73 J) and friction (>360 N). This nitrogen-rich metal complex may be a good candidate as a 'green' metal energetic

material for potential applications in propellants, explosives and pyrotechnics.

#### 4. Conclusion

Through studies of the synthesis, preparation, structure analysis and applications of complexes of hmta with different metal salts, a rough understanding of these materials has been gained. From the earliest synthetic and structural analyses, the physical and chemical properties and a range of applications have been investigated. The understanding gained from this provides a basis for the study of other organic ligands. With the development of computer technology, future research can also be carried out by theoretical calculation to select better metal complexes.

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