

## Two different zinc(II)-aqua complexes held up by a metal-oxide based support: Synthesis, crystal structure and catalytic activity of $[\text{HMTAH}]_2[\{\text{Zn}(\text{H}_2\text{O})_5\}\{\text{Zn}(\text{H}_2\text{O})_4\}\{\text{Mo}_7\text{O}_{24}\}]\cdot 2\text{H}_2\text{O}$ (HMTAH = protonated hexamethylenetetramine)

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**Abstract.** An inorganic–organic hybrid material,  $[\text{HMTAH}]_2[\{\text{Zn}(\text{H}_2\text{O})_5\}\{\text{Zn}(\text{H}_2\text{O})_4\}\{\text{Mo}_7\text{O}_{24}\}]\cdot 2\text{H}_2\text{O}$  (**1**) (where HMTAH = protonated hexamethylenetetramine) has been synthesized and structurally characterized. The compound **1** crystallizes in a monoclinic space group  $C2/c$ . The crystal data of **1**:  $a = 43.12(3)$ ,  $b = 12.399(10)$ ,  $c = 16.285(13)$ ,  $\beta = 111.131(11)$ ,  $Z = 8$ . Its crystal structure shows that two different Zn(II)-aqua complexes,  $[\text{Zn}(\text{H}_2\text{O})_5]^{2+}$  and  $[\text{Zn}(\text{H}_2\text{O})_4]^{2+}$  are covalently coordinated to a heptamolybdate anion  $[\text{Mo}_7\text{O}_{24}]^{6-}$  resulting in an anionic species of polyoxometalate supported zinc-aqua complexes,  $[\{\text{Zn}(\text{H}_2\text{O})_5\}\{\text{Zn}(\text{H}_2\text{O})_4\}\{\text{Mo}_7\text{O}_{24}\}]^{2-}$ , that is stabilized with two protonated hexamethylenetetramine cations in the title compound **1**. In the crystal structure, both lattice water molecules are found to interact with the heptamolybdate cluster anion and the protonated hexamethylenetetramine cation resulting in an intricate three-dimensional hydrogen bonding network. Interestingly, compound **1** exhibits catalytic activity towards oxidation of some primary alcohols.

**Keywords.** Inorganic–organic hybrid material; polyoxometalate supported zinc complexes; crystal structure; supramolecular interactions; catalytic activity.

### 1. Introduction

Polyoxometalate (POM), a metal-oxide-based cluster, has attracted considerable research interest in recent years because of its applications in diverse areas, such as, biomedical chemistry, catalysis, magnetism, sorption properties, etc.<sup>1</sup> One of the recent advances in POM chemistry is to synthesize inorganic–organic hybrid materials having well-defined channels and cavities, that are important in terms of materials chemistry.<sup>2</sup> Such inorganic–organic hybrid materials are generally prepared by hydrothermal synthesis.<sup>3</sup> Rao and co-workers made significant contribution in this area.<sup>3a–g</sup> Another important progress in POM chemistry is the polyoxoanion-supported transition metal complexes.<sup>4</sup> These metal oxide-based inorganic complexes not only provide new and exciting functional materials with an interesting optical, electronic, and magnetic properties but also serve as structural models for understanding the functions of oxide-supported catalysts.<sup>5</sup> One possible route to synthesize POM supported transi-

tion metal complexes is to use organic amine cations (e.g. protonated amines) that stabilize the POM cluster anion with the assistance of supramolecular non-covalent interactions.<sup>6</sup> Previously, by using protonated hexamethylenetetramine ( $\text{HMTAH}^+$ ) as counter ions, Cronin and co-workers were able to stabilize and isolate a highly charged POM anion,  $[\text{H}_2\text{Mo}^{\text{V}}_4\text{Mo}^{\text{VI}}_{16}\text{O}_{52}]^{10-}$  ( $\{\text{Mo}16\}$  cluster), which represents a new structural type.<sup>7a</sup> They have also shown that this  $\{\text{Mo}16\}$  cluster anion decomposes in the presence of divalent transition metal cations ( $\text{Fe}^{2+}$  and  $\text{Mn}^{2+}$ ) in high concentrations, to produce the isostructural  $\{\text{Mo}_7\text{M}_2\}$ -type compounds  $(\text{HMTAH}^+)_2[\text{Fe}_2(\text{H}_2\text{O})_9\text{Mo}_7\text{O}_{24}]\cdot 2\text{H}_2\text{O}$  and  $(\text{HMTAH}^+)_2[\text{Mn}_2(\text{H}_2\text{O})_9\text{Mo}_7\text{O}_{24}]\cdot 2\text{H}_2\text{O}$  which are based on individual heptamolybdate fragments.<sup>7b</sup> In the present work, we have synthesized the zinc analogue of this system,  $[\text{HMTAH}]_2[\{\text{Zn}(\text{H}_2\text{O})_5\}\{\text{Zn}(\text{H}_2\text{O})_4\}\{\text{Mo}_7\text{O}_{24}\}]\cdot 2\text{H}_2\text{O}$  (**1**) in a simple one-pot wet synthesis. We have described the single crystal structure of compound **1** emphasizing two different modes of coordination of two different zinc–aqua coordination complexes to the same heptamolybdate anion. The supramolecular hydrogen bonding interactions ( $\text{C–H}\cdots\text{O}$ ,  $\text{N–H}\cdots\text{O/O–H}\cdots\text{N}$ ,

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O–H...O), that exist among the POM cluster anion, the organic amine cations and lattice water molecules resulting in an intricate three-dimensional network, have been discussed in details. Even though, in the recent past, numerous POM supported transition metal complexes have been prepared and structurally characterized,<sup>8</sup> the catalysis aspect of these POM supported metal coordination complexes is largely unexplored. We have demonstrated here that compound **1** catalyses the oxidation of benzyl alcohol to benzaldehyde at a moderate temperature in a heterogeneous reaction, in which the catalyst (compound **1**) is recyclable. We have also discussed the TG–MS studies of compound **1** giving stress on, how two different modes of coordination of two zinc-aqua complexes to a same POM anion influence their thermal stability. To our knowledge, this is one of the rare examples of POM supported transition metal complexes, for which catalytic activity has been explored.

## 2. Experimental

### 2.1 Materials and methods

All the chemicals that were of reagent grade were used without any further purification. The distilled water was used throughout the work. Benzyl alcohol is distilled before use and its purity has been checked by <sup>1</sup>H NMR spectral studies. 30% hydrogen peroxide is used for catalysis studies.

Infrared (with KBr pellets) spectra were recorded using a JASCO FT/IR-5300 FT–IR spectrophotometer. The elemental analysis data were obtained with Flash 1112 SERIES EA analyzer. Thermo gravimetric analysis was carried out on a STA 409 PC analyzer, and corresponding masses were analysed by QMS 403 C mass analyzer, under the flow of N<sub>2</sub> gas with a heating rate of 5°C min<sup>-1</sup>, in the temperature range of 30–1100°C. <sup>1</sup>H NMR spectra in CDCl<sub>3</sub> solution were recorded on a Bruker DRX-400 spectrometer using Si(CH<sub>3</sub>)<sub>4</sub> as an internal standard.

### 2.2 Synthesis of compound [HMTAH]<sub>2</sub> [Zn(H<sub>2</sub>O)<sub>5</sub>]{Zn(H<sub>2</sub>O)<sub>4</sub>Mo<sub>7</sub>O<sub>24</sub>}·2H<sub>2</sub>O (**1**)

Sodium molybdate (1 g, 4.13 mmol) was dissolved in 100 mL of water, and its pH was adjusted to 3.0 by adding conc. HCl. To this solution, a mixture of Zn(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O (0.5 g, 1.68 mmol) and hexamethylenetetramine (0.2 g, 1.42 mmol) dissolved in 20 mL

of water was added slowly. The resulting reaction mixture was stirred for 5 h and then it was filtered. The colourless filtrate was kept in an open beaker at room temperature. After three days, colourless crystals were filtered and washed thoroughly with water and then dried at room temperature. Yield 0.35 g (36% based on Mo).

Analysis: Calc. for C<sub>12</sub>H<sub>48</sub>Mo<sub>7</sub>N<sub>8</sub>O<sub>35</sub>Zn<sub>2</sub>: C, 8.65; H, 2.90; N, 6.72%. Found: C, 8.85; H, 3.04; N, 6.58%. FT–IR (KBr pellet): 3449 (*br*), 1655 (*m*), 1462 (*s*), 1369 (*s*), 1300 (*s*), 1253 (*s*), 1211 (*s*), 1024 (*s*), 979 (*s*), 893 (*s*), 671 (*s*) cm<sup>-1</sup>.

### 2.3 X-ray crystallography

The crystallographic data for compound **1** has been collected at 293 K on Bruker SMART APEX CCD, area detector system [ $\lambda(\text{Mo-K}\alpha) = 0.71073 \text{ \AA}$ ], graphite monochromator, 2400 frames were recorded with an  $\omega$  scan width of 0.3°, each for 10 s, crystal-detector distance 60 mm, collimator 0.5 mm. Data reduction was done by SAINTPLUS,<sup>9</sup> absorption correction by using an empirical method SADABS,<sup>10</sup> structure solution using SHELXS-97,<sup>11</sup> and refined using SHELXL-97.<sup>12</sup> All non-hydrogen atoms were refined anisotropically. Hydrogen atoms of the organic cations were introduced at calculated positions and included in the refinement riding on their respective parent atoms. Additional details of the data collection parameters and refinement are collected in table 1. The final Fourier difference synthesis showed minimum and maximum peaks of  $-1.357$  and  $+1.527 e\text{\AA}^{-3}$ . CCDC-671099 contains the supplementary crystallographic data for complex **1**. This can be obtained free of charge on application to the Director, CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: +44 1223 336 033; e-mail: deposit@ccdc.cam.ac.uk or www: <http://www.ccdc.cam.ac.uk>).

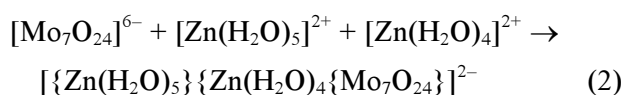
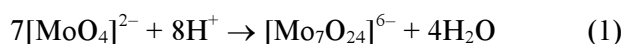
## 3. Results and discussion

The compound [HMTAH]<sub>2</sub>[Zn(H<sub>2</sub>O)<sub>5</sub>]{Zn(H<sub>2</sub>O)<sub>4</sub>Mo<sub>7</sub>O<sub>24</sub>}·2H<sub>2</sub>O (**1**) has been synthesized in an one-pot wet synthesis starting from sodium molybdate, zinc nitrate and hexamethylenetetramine from an aqueous medium of pH 3.0. We believe that aqueous molybdate solution results in the formation of heptamolybdate anion, [Mo<sub>7</sub>O<sub>24</sub>]<sup>6-</sup> at pH of 3.0. The formation of this cluster anion, [Mo<sub>7</sub>O<sub>24</sub>]<sup>6-</sup> can be explained by the protonation of molybdate anion at

**Table 1.** Crystal data and structure refinement for compound **1**.

Compound	<b>1</b>
Empirical formula	C <sub>12</sub> H <sub>48</sub> Mo <sub>7</sub> N <sub>8</sub> O <sub>35</sub> Zn <sub>2</sub>
Formula weight	1666.90
Temperature (K)	293(2)
Wavelength (Å)	0.71073
Crystal system	Monoclinic
Space group	C2/c
<i>a</i> (Å)	43.12(3)
<i>b</i> (Å)	12.399(10)
<i>c</i> (Å)	16.285(13)
<i>α</i> (deg)	90.00
<i>β</i> (deg)	111.131(11)
<i>γ</i> (deg)	90.00
Volume (Å <sup>3</sup> )	8122(11)
<i>Z</i>	8
<i>ρ</i> (g cm <sup>-3</sup> )	2.726
<i>μ</i> (mm <sup>-1</sup> )	3.367
<i>F</i> (000)	6480
Crystal size (mm)	0.25 × 0.15 × 0.08
Theta range for data collection (deg)	1.01 to 26.05
Reflections collected/unique	31611/7363 [ <i>R</i> (int) = 0.0539]
Data/restraints/parameters	7363/0/577
Goodness of fit on <i>F</i> <sup>2</sup>	1.110
Final <i>R</i> indices [ <i>I</i> > 2 sigma( <i>I</i> )]	<i>R</i> 1 = 0.0636, <i>wR</i> 2 = 0.1940
<i>R</i> indices (all data)	<i>R</i> 1 = 0.0867, <i>wR</i> 2 = 0.2238
Largest diff. Peak and hole (e.Å <sup>-3</sup> )	1.527 and -1.357

lower pH (3.0) followed by a series of condensation reactions. The overall reaction for this cluster formation is shown in (1). The zinc–aqua-complexes [Zn(H<sub>2</sub>O)<sub>5</sub>]<sup>2+</sup> and [Zn(H<sub>2</sub>O)<sub>4</sub>]<sup>2+</sup>, formed *in situ* from zinc nitrate and water, in this reaction are subsequently coordinated to the POM cluster anion [Mo<sub>7</sub>O<sub>24</sub>]<sup>6-</sup> resulting the POM supported zinc–aqua complexes, [Zn(H<sub>2</sub>O)<sub>5</sub>]{Zn(H<sub>2</sub>O)<sub>4</sub>{Mo<sub>7</sub>O<sub>24</sub>}}<sup>2-</sup> (2). Finally, the two negative charges of this anionic species is counter-balanced by two mono-protonated hexamethylenetetramine cations ([HMTAH]<sup>+</sup>) resulting in the isolation of the title compound **1**. It is important to note that, even though the cyclic amine (hexamethylenetetramine) is, in principle, capable of coordinating to Zn<sup>2+</sup> ion through its nitrogen donors, this did not happen in this synthesis. We argue that low pH (3.0) is not favourable for such metal–nitrogen bond, because the metal–nitrogen bond undergoes facile acid-hydrolysis reaction at a lower pH.

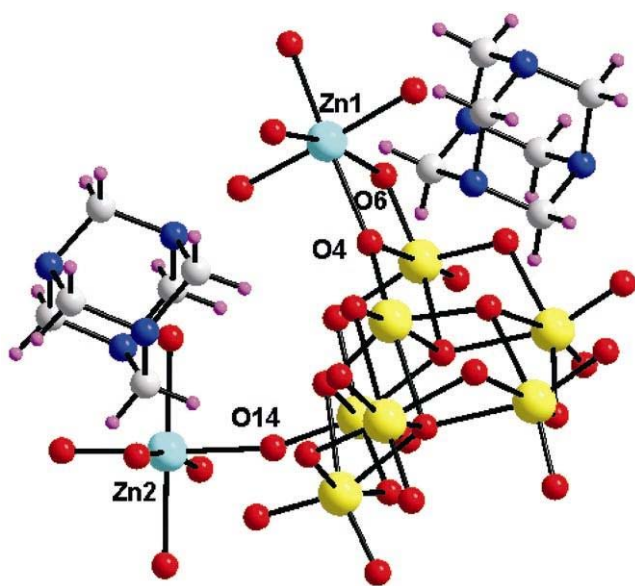


The infra red spectra of compound **1** show the characteristic strong peaks at 902 and 945 cm<sup>-1</sup>, that are attributed to the vibrations of Mo=O bonds. The sharp peaks at 1300 and 1253 cm<sup>-1</sup> are probably due to the C–H stretching. The zinc-coordinated water molecules along with lattice water molecules are reflected by a broad feature at around 3450 cm<sup>-1</sup> and a relatively sharp band at around 1650 cm<sup>-1</sup>.

The single crystal X-ray structure determination of compound **1** shows that, one heptamolybdate cluster anion, that is functionalized by two dissimilar zinc–aqua complexes [Zn(H<sub>2</sub>O)<sub>5</sub>]<sup>2+</sup> and [Zn(H<sub>2</sub>O)<sub>4</sub>]<sup>2+</sup>, two protonated hexamethylenetetramines as cations ([HMTAH]<sup>+</sup>) and two lattice water molecules are present in its asymmetric unit and hence compound **1** can be formulated as [HMTAH]<sub>2</sub>[Zn(H<sub>2</sub>O)<sub>5</sub>]{Zn(H<sub>2</sub>O)<sub>4</sub>{Mo<sub>7</sub>O<sub>24</sub>}}·2H<sub>2</sub>O. Thermal ellipsoidal representation of the anionic part of compound **1** is given in section of Supplementary materials and the molecular structure of compound **1** is shown in figure 1. The POM cluster anion [Mo<sub>7</sub>O<sub>24</sub>]<sup>6-</sup> acts as a ligand coordinating two different zinc–aqua complexes [Zn(H<sub>2</sub>O)<sub>5</sub>]<sup>2+</sup> and [Zn(H<sub>2</sub>O)<sub>4</sub>]<sup>2+</sup> in two different modes. In the case of penta-aqua complex [Zn(H<sub>2</sub>O)<sub>5</sub>]<sup>2+</sup>, the cluster anion is coordinated

**Table 2.** Selected bond lengths (Å) for compound 1.

C(1)–N(1)	1.471(18)	C(2)–N(3)	1.440(16)
C(2)–N(2)	1.496(16)	C(6)–N(4)	1.464(19)
C(8)–N(6)	1.489(17)	C(9)–N(7)	1.425(16)
C(9)–N(5)	1.520(17)	C(11)–N(8)	1.478(17)
C(12)–N(8)	1.464(18)	Mo(1)–O(1)	1.703(10)
Mo(1)–O(6)	1.753(9)	Mo(1)–O(4)	2.491(9)
Mo(2)–O(8)	1.705(9)	Mo(2)–O(2)	2.002(9)
Mo(2)–O(3)	2.167(8)	Mo(2)–O(10)	2.253(9)
Mo(3)–O(11)	1.691(9)	Mo(3)–O(5)	1.961(8)
Mo(4)–O(15)	1.718(9)	Mo(4)–O(10)	1.880(9)
Mo(4)–O(16)	2.237(7)	Mo(5)–O(17)	1.708(9)
Mo(5)–O(18)	1.712(8)	Mo(5)–O(16)	2.190(8)
Mo(6)–O(20)	1.705(9)	Mo(6)–O(21)	1.739(10)
Mo(6)–O(16)	2.142(9)	Mo(6)–O(15)	2.525(9)
Mo(7)–O(24)	1.715(9)	Mo(7)–O(22)	1.722(9)
Mo(7)–O(16)	2.158(8)	Mo(7)–O(13)	2.225(8)
O(4)–Zn(1)	2.138(8)	O(6)–Zn(1)	2.169(10)
O(26)–Zn(1)	2.050(11)	O(27)–Zn(1)	2.117(12)
O(29)–Zn(2)	2.078(9)	O(30)–Zn(2)	2.146(10)
O(31)–Zn(2)	2.077(10)	O(33)–Zn(2)	2.132(12)

**Figure 1.** The molecular structure of compound 1 in ball and stick model. Colour code: O, red; Mo, yellow; C, gray; H, purple; Zn, cyan; N, blue.

to  $\text{Zn}^{2+}$  ion via the terminal oxygen O(14) of heptamolybdate and the remaining coordination sites of zinc ion in the complex are occupied by five water molecules completing a distorted octahedral geometry around zinc ion (figure 1). In tetra-aqua complex  $[\text{Zn}(\text{H}_2\text{O})_4]^{2+}$ , the  $\text{Zn}^{2+}$  ion is chelated to the anionic cluster in bidentate fashion via  $\text{O}_t(6)$  and  $\text{O}_b(4)$  ( $\text{O}_t$  and  $\text{O}_b$  are terminal and bridging oxygen atoms of

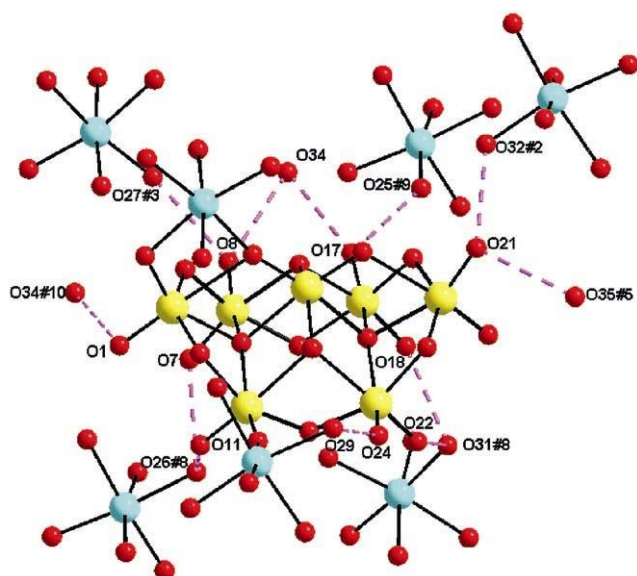
the cluster anion respectively). Four water molecules are additionally coordinated to  $\text{Zn}^{2+}$  ion leading to an octahedral geometry around zinc ion. The bond angles  $\text{Zn}(1)\text{--O}(6)\text{--Mo}(1)$  and  $\text{Zn}(1)\text{--O}(4)\text{--Mo}(1)$  in the tetra-aqua complex are  $91.23^\circ$  and  $115.00^\circ$  respectively. The selected bond lengths in the crystal structure of compound 1 are given in the table 2. This is one of rare examples of a POM supported metal coordination complex, in which a bridging oxygen atom of POM anion has extended its coordination to the metal ion (in the present case  $\text{Zn}^{2+}$  ion). The cyclic organic amine HMTA can be described as four nitrogen atoms interconnected by six methylene groups forming a bi-cyclic adamantane like structure with twelve C–N bonds, in which there are no C–C and N–N bonds. It is worth mentioning that, HMTA has been used as a versatile ligand in metallo-supramolecular chemistry via its possible coordination modes (one to four nitrogen atoms are involved in coordination) leading to novel topological architectures.<sup>13</sup> However, in the present study, we would not expect HMTA to coordinate to the zinc ion at the pH, maintained in the synthesis (vide supra).

In the crystal structure, four types of hydrogen bonding interactions are expected: N–H...O/O–H...N, O–H...O, C–H...O and N–H...N hydrogen bonds. Since the hydrogen atoms on nitrogen base and water oxygens could not be located, and only one nitrogen of each organic amine is protonated, it

**Table 3.** Geometrical parameters of the N–H...O/O–H...N and O–H...O hydrogen bonds (Å), represented as N...O and O...O distances respectively, involved in supra-molecular network in the crystal structure of compound 1.

O(34)–O(1)#4	2.888(17)	O(34)–O(8)	3.013(16)
O(34)–O(17)	2.810(16)	O(34)–N(4)	2.679(17)
O(35)–N(5)	2.740(18)	O(35)–O(35)#5	2.890(4)
O(35)–O(21)#5	2.842(18)	O(35)–O(31)#2	2.942(18)
O(31)–O(18)#6	2.735(15)	O(31)–O(22)#6	2.642(15)
O(31)–O(35)#7	2.942(18)	O(33)–O(9)#6	2.914(15)
O(32)–N(2)#7	2.730(16)	O(32)–O(21)#7	2.718(13)
O(29)–N(6)	2.882(14)	O(29)–O(24)	2.791(14)
O(14)–O(5)	2.709(13)	O(14)–O(13)	2.873(11)
O(14)–O(11)	2.707(13)	O(30)–N(7)#8	2.808(14)
O(14)–O(12)	2.778(13)	O(26)–O(11)#6	2.797(17)
O(26)–O(7)#6	2.836(15)	O(6)–O(5)	2.813(13)
O(6)–O(1)	2.767(14)	O(4)–O(13)	2.779(12)
O(4)–O(3)	2.713(11)	O(4)–O(2)	2.878(15)
O(4)–O(10)	2.807(12)	O(4)–O(15)	2.737(13)
O(28)–O(2)#3	2.955(14)	O(28)–N(1)	2.926(17)
O(25)–N(8)	2.806(15)	O(25)–O(17)#1	2.867(13)
O(27)–O(8)#3	2.841(17)	O(17)–O(25)#9	2.867(13)
O(7)–O(26)#8	2.836(15)	O(21)–O(32)#2	2.718(13)
O(11)–O(26)#8	2.797(17)	O(18)–O(31)#8	2.735(15)
O(1)–O(34)#10	2.888(17)	O(22)–O(31)#8	2.642(15)
N(2)–O(32)#2	2.730(16)	N(7)–O(30)#6	2.808(14)
O(21)–O(35)#5	2.842(18)		

Symmetric transformations used to generate equivalent atoms: #1  $x, 1 - y, 0.5 + z$ ; #2  $x, -1 + y, z$ ; #3  $0.5 - x, 1.5 - y, 1 - z$ ; #4  $0.5 - x, -0.5 + y, 0.5 - z$ ; #5  $-x, y, 0.5 - z$ ; #6  $x, 2 - y, 0.5 + z$ ; #7  $x, 1 + y, z$ ; #8  $x, 2 - y, -0.5 + z$ ; #9  $x, 1 - y, -0.5 + z$ ; #10  $0.5 - x, 0.5 + y, 0.5 - z$



**Figure 2.** The hydrogen bonding situation around the cluster anion  $[\text{Mo}_7\text{O}_{24}]^{6-}$ . Colour code: O, red; Mo, yellow; C, gray; Zn, cyan; purple dotted lines represent the O–H...O hydrogen bonding interaction.

would not be possible to distinguish between N–H...O, O–H...N hydrogen bonds around organic amine

cation. One of the organic amines (can be named as N1N2N3N4) undergoes three N–H...O/O–H...N hydrogen bonding interactions with two surrounding zinc–aqua complexes and one lattice water (O34) molecule (see figure S2(a) in Supplementary materials). Similarly the other organic amine (namely N5N6N7N8) interacts with three surrounding zinc–aqua complexes and one lattice water (O35) molecule by N–H...O/O–H...N hydrogen bonds (see figure S2(b) in Supplementary materials). The N–H...O/O–H...N and O–H...O hydrogen bonds are represented as N...O and O...O distances respectively in table 3.

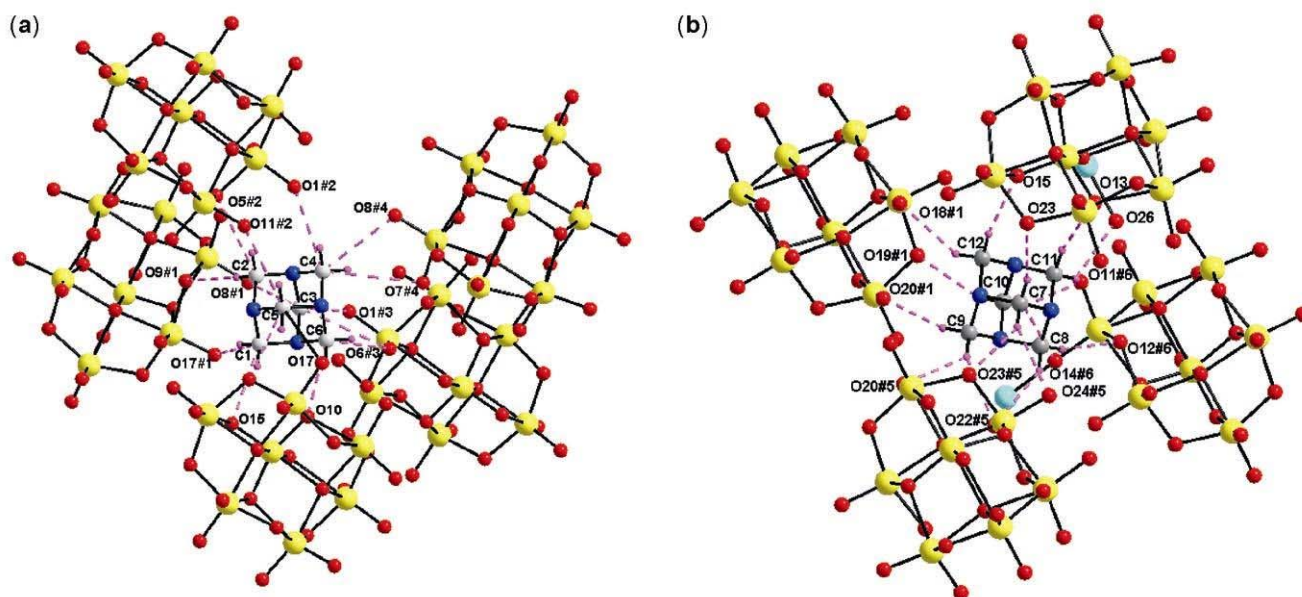
There are two lattice water molecules O34 and O35. The O34 water molecule is hydrogen bonded to one organic amine via N4 nitrogen atom (N–H...O/O–H...N hydrogen bond) and three terminal oxygen atoms (O1, O8 and O17) from two surrounding heptamolybdate anions (O–H...O hydrogen bonds). On the other hand, the O35 water molecule is hydrogen bonded to O35 itself (related by a symmetry operation) forming a water dimer (O–H...O hydrogen bond), a zinc-coordinated water molecule O31 (O–H...O hydrogen bond), a terminal oxygen atom O21 of a heptamolybdate anion (O–H...O hy-



**Table 4.** Geometrical parameters of the C–H...O hydrogen bonds (Å, °) involved in supramolecular network of compound 1. D = donor; A = acceptor.

D–H...A	<i>d</i> (D...H)	<i>d</i> (H...A)	<i>d</i> (D...A)	∠(DHA)
C1–H1A...O15	0.97	2.34	3.257(16)	158.2
C1–H1B...O17#1	0.97	2.51	3.411(19)	155.2
C2–H2A...O9#1	0.97	2.54	3.511(17)	179.3
C2–H2B...O5#2	0.97	2.46	3.361(16)	154.9
C3–H3A...O1#3	0.97	2.55	3.298(15)	133.5
C3–H3B...O8#1	0.97	2.55	3.444(18)	152.6
C4–H4A...O1#2	0.97	2.37	3.262(16)	153.0
C4–H4B...O7#4	0.97	2.73	3.541(15)	140.9
C5–H5B...O11#2	0.97	2.65	3.578(19)	159.8
C5–H5A...O17	0.97	2.59	3.379(17)	139.0
C5–H5A...O19	0.97	2.42	3.327(18)	155.1
C6–H6A...O6#3	0.97	2.65	3.492(18)	144.9
C6–H6B...O10	0.97	2.36	3.314(17)	166.9
C7–H7A...O23	0.97	2.38	3.328(16)	164.8
C7–H7B...O24#5	0.97	2.60	3.470(17)	148.7
C7–H7B...O23#5	0.97	2.51	3.354(16)	145.7
C8–H8A...O12#6	0.97	2.42	3.372(14)	165.9
C8–H8B...O22#5	0.97	2.50	3.349(17)	146.4
C9–H9A...O20#5	0.97	2.45	3.140(16)	127.5
C9–H9A...O22#5	0.97	2.50	3.355(17)	147.3
C9–H9B...O20#1	0.97	2.28	3.217(16)	163.1
C10–H10A...O11#6	0.97	2.45	3.331(15)	151.4
C10–H10A...O14#6	0.97	2.64	3.471(16)	144.4
C10–H10B...O19#1	0.97	2.56	3.473(16)	157.6
C11–H11A...O26	0.97	2.63	3.292(19)	125.8
C11–H11B...O13	0.97	2.54	3.482(17)	164.5
C12–H12A...O18#1	0.97	2.54	3.388(19)	146.6
C12–H12B...O15	0.97	2.21	3.153(19)	162.7

Symmetric codes are already specified in the footnote of table 3

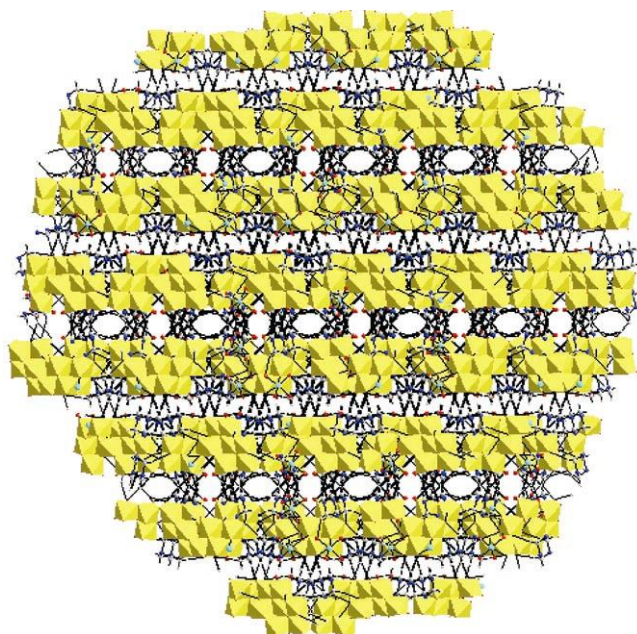


**Figure 3.** The C–H...O hydrogen bonding interactions of organic amine cations with surrounding cluster anion: (a) ‘N1N2N3N4’ and (b) ‘N5N6N7N8’. Colour code: O, red; Mo, yellow; C, gray; H, purple; Zn, cyan; N, blue; purple dotted lines represent the hydrogen bonding interactions.

drogen bond) and organic amine via N5 nitrogen atom (N–H...O/O–H...N hydrogen bond). See Supplementary materials for the hydrogen bonding situation of these lattice water molecules (figure S3).

The hydrogen bonding situation (O–H...O hydrogen bonds) around the cluster anion  $[\text{Mo}_7\text{O}_{24}]^{6-}$  is shown in figure 2. This shows that the heptamolybdate anion is hydrogen bonded to five surrounded zinc–aqua complexes besides two zinc–aqua complexes that are supported by the cluster anion through coordinate covalent bonds. Both zinc–aqua complexes undergo both O–H...O and N–H...O/O–H...N hydrogen bonding interactions with surrounding heptamolybdate anion and organic amine cations resulting in a complicated hydrogen bonding situation (see figure S4 in Supplementary materials).

The organic amine cations use their C–H bonds to form C–H...O hydrogen bonds with surrounding POM anions. As shown in figure 3, organic amines ‘N1N2N3N4’ and ‘N5N6N7N8’ are hydrogen bonded with five and four surrounding heptamolybdate anions respectively. Similarly, in the crystal structure, each isopolyanion is attached to six adjacent organic amine cations (see Supplementary materials, figure S5). This results in an intricate



**Figure 4.** Three-dimensional supramolecular network (formed by N–H...O/O–H...N, O–H...O, C–H...O and N–H...N hydrogen bonding interactions) having well-defined channels in a view looking down to the crystallographic *c* axis.

three-dimensional supramolecular network having well-defined channels in a view looking down to the crystallographic *c* axis, as shown in figure 4. The C–H...O hydrogen bonding parameters are presented in table 4. In compound **1**, Bond Valence Sum (BVS) calculation confirms that all the Mo and Zn atoms are in +6 and +2 respectively. The BVS results can be described as: Mo atoms are +6 ( $\Sigma s = 6.05\text{--}6.18$ ) and Zn atoms are +2 ( $\Sigma s = 1.88$ ).

### 3.1 Catalysis

The catalytic activity of compound  $[\text{HMTAH}]_2 [\{\text{Zn}(\text{H}_2\text{O})_5\} \{\text{Zn}(\text{H}_2\text{O})_4\} \{\text{Mo}_7\text{O}_{24}\}] \cdot 2\text{H}_2\text{O}$  (**1**) has been studied for the oxidation of a primary alcohol in the presence of hydrogen peroxide as an oxidant. We have selected benzyl alcohol (as a substrate) for the oxidation reaction. Compound **1** selectively oxidizes benzylalcohol to benzaldehyde with the moderate conversion percentage. The possible mechanism for the oxidation of alcohol in presence of hydrogen peroxide is discussed in the reported articles.<sup>14</sup> In a typical experiment, the mixture of benzyl alcohol (0.052 mL, 0.5 mmol), compound **1** (0.042 g, 0.025 mmol), 30% of hydrogen peroxide (0.460 mL) were taken in screwed vial and heated at 80°C for 9 h. The product was extracted by dichloromethane and analysis was done by <sup>1</sup>H NMR spectral studies. The result shows that, the conversion of benzyl alcohol to benzaldehyde occurs in 50%. The same reaction was checked without catalyst and without hydrogen peroxide separately that did not show any notable conversion. It clearly indicates the need of both catalyst and hydrogen peroxide for the successful oxidation. The <sup>1</sup>H NMR spectra of distilled benzyl alcohol and product mixture are given in Supplementary materials, figure S6.

Characterization data for benzyl alcohol: <sup>1</sup>H NMR ( $\text{CDCl}_3$ )  $\delta$ : 3.00 (*s*, 1H, OH), 4.51 (*s*, 2H,  $\text{CH}_2$ ), 7.16–7.26 (*m*, 5H, Ar-CH).

Characterization data for benzaldehyde: <sup>1</sup>H NMR ( $\text{CDCl}_3$ )  $\delta$ : 7.21–7.31 (*m*, 5H, Ar-CH), 10.03 (*s*, 1H, HC=O).

### 3.2 TG analysis

The thermo gravimetric analysis for compound **1** is performed in flowing nitrogen with a heating rate of 5° per minute in the temperature range from 30 to 1100°C. Compound **1** shows four weight losses. The first weight loss includes 7.51% in the temperature

range of 35–180°C that corresponds to the loss of seven water molecules (calculated mass loss for seven water molecules is 7.55%). These seven water molecules seem to be two lattice water molecules plus five water molecules from the penta-aqua-metal coordination site. The second weight loss of 4.63% in the temperature range of 180–250°C is due to the loss of four water molecules (calculated mass loss for four water molecules is 4.31%). The source of these four water molecules should be the tetra-aqua Zn-complex, supported on the POM anion by two coordinate covalent bonds (as if the heptamolybdate anion is a bidentate ligand towards this  $\text{Zn}(\text{H}_2\text{O})_4$  complex). The removal of these four water molecules at later stage and higher temperature is logical because this tetra-aqua-zinc complex is more strongly held by the POM anion support (two coordinate covalent bonds) compared to the penta-aqua-zinc complex (one coordinate covalent bond). Thus, two dissimilar zinc-aqua coordination complexes, supported on a same POM anion, can be realized by the TG plot. This also helps to understand, how stability of a metal-aqua complex increases with its number of coordination to the support (which is a metal oxide based cluster anion in the present case). The corresponding mass losses are given in the TGA/Mass graph (figure S7, Supplementary materials). The evolution of water molecules in these two stages have been evidenced by the mass loss curve. The third and fourth weight losses are 5.23% and 21.14% respectively, that are due to the structural decomposition including the organic amines, evidenced by the evolution of carbon dioxide gas as shown in violet color curve in the TG/Mass plot (figure S7, Supplementary materials).

#### 4. Conclusion

We have described two dissimilar Zn(II)-aqua complexes that are supported on a same polyoxometalate (POM) anion. The organic amine, hexamethylenetetramine (HMTA) has been used in its mono-protonated form to counter balance the negative charges of the POM supported Zn(II)-aqua complexes. Taking advantage of the ability of ring-N atoms and  $-\text{CH}_2$  groups on HMTA organic amine to form  $\text{N}-\text{H}\cdots\text{O}/\text{O}-\text{H}\cdots\text{N}$  hydrogen bonds and  $\text{C}-\text{H}\cdots\text{O}$  hydrogen bonds respectively, we are able to demonstrate, how an intricate three-dimensional supramolecular network is formed in the crystal structure of compound  $[\text{HMTAH}]_2[\{\text{Zn}(\text{H}_2\text{O})_5\}$

$\{\text{Zn}(\text{H}_2\text{O})_4\}\{\text{Mo}_7\text{O}_{24}\}]\cdot 2\text{H}_2\text{O}$  (**1**). The catalytic activity of compound **1** is studied for the selective oxidation of benzyl alcohol to benzaldehyde at a moderate temperature using  $\text{H}_2\text{O}_2$  as an oxidant. Catalysis work has been done in solvent free and ecological benign condition, where compound **1** (catalyst) is not soluble. Thus, we can utilize the used-catalyst in many cycles without losing its catalytic activity. We have, at least, done six catalysis experiments using same used-catalyst (compound **1**) just by filtering from the reaction mixture after each experiment is over. We are currently attempting the oxidation of other organic substrates with this and other similar POM based compounds in our laboratory, which will be published in near future. Thermo gravimetric studies are very common in POM chemistry, since very often the relevant crystalline compounds contain lattice water and metal coordinated water molecules. We have demonstrated here that thermal studies can be used to recognize different coordination modes of a metal coordination complex, held up by metal-oxide based support.

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