

Synthesis, characterization and photochemistry of a new heptamolybdate supported magnesium-aqua coordination complex

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Dedicated to Prof. Dr. S.K. Paknikar on the occasion of his 80th birthday

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Abstract. The synthesis, crystal structure, redox characteristics and photochemistry of a new heptamolybdate supported magnesium-aqua coordination complex viz. (hmtH)₂{[Mg(H₂O)₅]₂[Mo₇O₂₄]}·3H₂O **1** (hmt = hexamethylenetetramine) is reported. The cyclic voltammogram reveals quasireversible redox behaviour while the degradation of rhodamine B (RhB) by **1** under sunlight irradiation indicates its photocatalytic activity. In the crystal structure of **1**, two [Mg(H₂O)₅]²⁺ units are linked by a μ₂-bridging bidentate heptamolybdate ligand resulting in a heptamolybdate supported magnesium-aqua coordinated dianionic complex {[Mg(H₂O)₅]₂[Mo₇O₂₄]}²⁻ charge balanced by two (hmtH)⁺ cations. The cations, anions and the lattice water molecules are linked by several hydrogen bonding interactions.

Keywords. Heptamolybdate; Hexamethylenetetramine; μ₂-bridging bidentate ligand; Photocatalysis; Cyclic voltammogram.

1. Introduction

The study of polyoxometalates (POMs) is a frontier area of research in view of the rich structural diversity and interesting properties exhibited by the POMs.^{1–20} Among the POMs of the early transition metals, Mo-based POMs known as polyoxomolybdates represents diverse structures. Polyoxomolybdate synthesis is normally performed by acidification of an aqueous alkaline [MoO₄]²⁻ solution resulting in the condensation of the tetrahedral {MoO₄} units.²¹ The final product of the acidification is MoO₃, while the first product (~pH6), is the heptamolybdate [Mo₇O₂₄]⁶⁻ anion²² which has been isolated with a variety of counter cations.²³

The ability of [Mo₇O₂₄]⁶⁻ to function as a pure “inorganic ligand” has made it possible to use it as a building block²⁴ for the synthesis of new materials. A literature survey (table 1) reveals the rich coordination chemistry of the heptamolybdate ligand. The flexibility of heptamolybdate anion to exist in different structural environments and to adopt different binding modes depending upon the steric requirements of the heterometal leads to different heterometallic structural motifs.^{24–33}

Although many examples of heptamolybdate coordinating to *d* and *f*-block metal ions are known in the literature, the only known alkaline earth heptamolybdate is (ImH)₄[Ca(H₂O)₆(μ₂-Mo₇O₂₄)]·2(Im)·3H₂O.²⁹ In view of the preference of alkaline earths to bind to hard oxygen donor ligands, heptamolybdate can be expected to coordinate to alkaline earths under appropriate reaction conditions. Hence we have investigated the reaction of Mg(II) with [Mo₇O₂₄]⁶⁻ in the presence of hexamethylenetetramine (hmt). The result of this study describing the synthesis, structure characterization and properties of a new heptamolybdate supported magnesium-aqua coordination complex (hmtH)₂{[Mg(H₂O)₅]₂[Mo₇O₂₄]}·3H₂O **1** is reported herein.

2. Experimental

2.1 Materials and methods

All the chemicals employed in this work were used as received without any further purification. Infrared spectra of the samples diluted in KBr were recorded in the region 4000–400 cm⁻¹ using a Shimadzu (IR Prestige-21) FT-IR Spectrometer, at a resolution of 4 cm⁻¹. Raman spectra were recorded using Horiba Jobin-Yvon

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Table 1. Coordination geometry and different types of hetero-metallic unit of heptamolybdate compounds.

| Sr. No | Compound | Space Group | Hetero-metallic unit | Coordination geometry of heterometal 'M' | Ref |
|--------|--|------------------------------------|--|--|-----------|
| 1 | (2- <i>apH</i>) ₄ [Co(H ₂ O) ₅ Mo ₇ O ₂₄].9H ₂ O | <i>Pna</i> 2 ₁ | {MMo ₇ } | Octahedral | 24 |
| 2 | Na(NH ₄)[<i>bppH</i>] ₂ [Mo ₇ O ₂₄].8H ₂ O | <i>P</i> 2 ₁ / <i>m</i> | {MMo ₇ } | Octahedral | 25 |
| 3 | (NH ₄) ₄ [Ru(DMSO) ₃ Mo ₇ O ₂₄].6.5H ₂ O | <i>C</i> 2/ <i>c</i> | {MMo ₇ } | Trigonal | 26 |
| 4 | (NH ₄) ₄ [Os(DMSO) ₃ Mo ₇ O ₂₄].4.5H ₂ O | <i>C</i> 2/ <i>c</i> | {MMo ₇ } | Antiprismatic Trigonal | 26 |
| 5 | [2- <i>ampH</i>] ₄ {Zn(H ₂ O) ₅ }Mo ₇ O ₂₄ .9H ₂ O | <i>Pnma</i> | {MMo ₇ } | Octahedral | 27 |
| 6 | [3- <i>ampH</i>] ₄ {Zn(3- <i>ampy</i>)(H ₂ O) ₄ }Mo ₇ O ₂₄ .4H ₂ O | <i>Cc</i> | {MMo ₇ } | Distorted Octahedral | 27 |
| 7 | [3- <i>ampH</i>] ₄ {Co(3- <i>ampy</i>)(H ₂ O) ₄ }Mo ₇ O ₂₄ .4H ₂ O | <i>Cc</i> | {MMo ₇ } | Distorted Octahedral | 27 |
| 8 | (NH ₄) ₆ H ₂ [Cu(C ₂ O ₄) ₂ Mo ₇ O ₂₄].9H ₂ O | <i>P</i> 2 ₁ / <i>m</i> | {MMo ₇ } | Distorted Octahedral | 28 |
| 9 | (ImH) ₄ [Ca(H ₂ O) ₆ (μ ₂ -Mo ₇ O ₂₄)].2(Im).3H ₂ O | <i>C</i> 2/ <i>m</i> | {M(Mo ₇) ₂ } | Square Antiprismatic | 29 |
| 10 | (<i>hmtH</i>) ₂ [Mn ₂ (H ₂ O) ₉ Mo ₇ O ₂₄].2H ₂ O | <i>C</i> 2/ <i>c</i> | {M ₂ Mo ₇ } | Distorted Octahedral | 30 |
| 11 | (<i>hmtH</i>) ₂ [Fe ₂ (H ₂ O) ₉ Mo ₇ O ₂₄].2H ₂ O | <i>C</i> 2/ <i>c</i> | {M ₂ Mo ₇ } | Distorted Octahedral | 30 |
| 12 | (<i>hmtH</i>) ₂ _{1.5} (<i>ahmtH</i>) _{0.5} [Na ₂ (H ₂ O) ₅ Mo ₇ O ₂₄].4H ₂ O | <i>Pnma</i> | {M ₂ Mo ₇ } | Distorted Octahedral | 30 |
| 13 | (<i>hmtH</i>) ₂ {(Zn(H ₂ O) ₅ }{Zn(H ₂ O) ₄ }{Mo ₇ O ₂₄ }}.2H ₂ O | <i>C</i> 2/ <i>c</i> | {M ₂ Mo ₇ } | Distorted Octahedral | 31 |
| 14 | (<i>hmtH</i>) ₂ [Na ₂ (H ₂ O) ₅ (Mo ₇ O ₂₄)].4H ₂ O | <i>Pnma</i> | {M ₂ Mo ₇ } | Distorted Octahedral | 32 |
| 15 | (<i>hmtH</i>) ₂ {Mg(H ₂ O) ₅ } ₂ {Mo ₇ O ₂₄ }}.3H ₂ O | <i>C</i> 2/ <i>c</i> | {M ₂ Mo ₇ } | Distorted Octahedral | This work |
| 16 | (NH ₄) ₂₈ [Ce ₈ (MoO ₄) ₂ (H ₂ O) ₃₁ (Mo ₇ O ₂₄) ₈].74H ₂ O | <i>P</i> $\bar{1}$ | {M ₈ (Mo ₇) ₈ } | Trigonal prism | 33 |
| 17 | (NH ₄) ₂₆ [CoPr ₈ (MoO ₄) ₂ (H ₂ O) ₃₃ (Mo ₇ O ₂₄) ₈].54H ₂ O | <i>P</i> $\bar{1}$ | {M ₈ (Mo ₇) ₈ M} | Distorted Octahedral, Trigonal prism | 33 |
| 18 | (NH ₄) _{11.9} [Pr _{4.7} (MoO ₄)(H ₂ O) ₂₃ (Mo ₇ O ₂₄) ₄].34H ₂ O | <i>P</i> $\bar{1}$ | {M ₅ (Mo ₇)} | Trigonal prism, Tricapped trigonal prism | 33 |

Abbreviations used: *bpp* = 1,3-bis(4-pyridyl)propane; 2-*amp* = 2-aminopyridine; DMSO = dimethylsulfoxide; 3-*amp* = 3-aminopyridine; Im = imidazole; *hmt* = hexamethylenetetramine; *ahmt* = *N*-(aminomethylene)-hexamethylenetetramine

LabRAM HR Raman spectrometer in the range 3500–100 cm⁻¹ at a resolution of 4 cm⁻¹. The sample was finely powdered and pressed into a small depression on a metal disc and mounted on the sample compartment. The UV-Vis absorption spectra were recorded using UV-3600 Shimadzu UV-Vis spectrometer. Elemental analyses (C, H and N) were performed on a Variomicro cube CHNS analyser. X-ray powder patterns were measured on a Rigaku Miniflex II powder diffractometer using Cu-K α radiation with Ni filter. Simultaneous thermogravimetry (TG) and differential thermal analyses (DTA) of a powdered sample of **1** were performed in alumina crucible in the temperature range of 25°C to 800°C, using a Netzsch STA-409 PC thermal analyzer, at a heating rate of 10°C/min. Cyclic

voltammetry was performed in Electrochemical Workstation-CH Instrument (Inc. CHI6107), under inert atmosphere by using platinum as working electrode, platinum wire as counter electrode and saturated calomel electrode (SCE) as the reference with 0.2 M KCl solution as supporting electrolyte. ESR study was carried out on a Bruker EMx/micro-x instrument at room temperature.

2.2 Synthesis of (*hmtH*)₂{[Mg(H₂O)₅]₂{Mo₇O₂₄}}.3H₂O **1**

2.2a *Method 1*: Molybdic acid (1.134 g, 7 mmol) was taken in distilled water. To this basic magnesium carbonate (0.194 g, 0.4 mmol) was added. The

reaction mixture was then heated on a water bath to obtain a clear solution. To the clear solution obtained, hmt (0.280 g, 2 mmol) was added with continuous stirring. The final reaction mixture was then kept on water bath at 100°C for 40 min after adjusting its pH to 5.5 by adding few drops of dilute hydrochloric acid. Reaction mixture was cooled and filtered and the colourless filtrate was kept aside for crystallization. Fine, colourless crystals separated out after 1 h and when kept for further crystallization, **1** was obtained (1.23 g) in 75% yield.

2.2b Method 2: Ammonium heptamolybdate (1.236 g, 1 mmol) was dissolved in distilled water (~30 mL) by heating at 80°C followed by the addition of magnesium chloride hexahydrate (0.406 g, 2 mmol). To the resultant reaction mixture, hmt (0.280 g, 2 mmol) was added with continuous stirring. The final reaction mixture was then kept on water bath at 80°C for 30 min after adjusting its pH to 5.5, by adding few drops of dilute hydrochloric acid. Reaction mixture was allowed to cool and filtered, and the colourless filtrate was kept aside for crystallization. Fine, colourless, crystals separated out after 1 h and when kept for further crystallization, **1** (1.203 g) was obtained in 73% yield. Anal. Calcd for (**1**) (%): C, 8.89; H, 3.23; N, 6.91; O, 36.52; Mo, 41.44; Mg, 3.0%. Found % (**1**): C, 15.48; H, 5.25; N, 17.96%. IR data: 3447, 3186, 2963, 2891, 2405, 1834, 1658, 1466, 1440, 1377, 1300, 1259, 1236, 1149, 1061, 1010, 982, 917, 887, 832, 673, 574, 486 cm⁻¹. Raman data: 944, 894, 838, 363, 341, 279, 197, 145, 117 cm⁻¹. DTA (in °C): 184 (endo), 468(exo), 765 (endo).

2.3 Crystal structure determination

The intensity data were collected at room temperature using a Bruker Smart Apex CCD diffractometer with graphite monochromated Mo-K α radiation ($\lambda = 0.71073$ Å) by the ω -scan method. Integration and scaling of intensity data were accomplished using the program SAINT.³⁴ The structure was solved with direct methods using SHELXS-97³⁵ and refinement was done against F² using SHELXL-97.³⁵ All non-hydrogen atoms were refined anisotropically. H atom attached to the N atoms of (hmtH)⁺ cation was located in a difference Fourier density map and refined isotropically. The H atoms of the methylene groups were located in a difference electron density map but were positioned geometrically and included as riding atoms. The H atoms attached to the lattice water molecules OW1 and OW2 could not be located. Technical details of data

acquisition and selected refinement results are listed in table 2.

3. Results and Discussion

3.1 Description of the crystal structure of **1**

The compound (hmtH)₂[[Mg(H₂O)₅]₂{Mo₇O₂₄}]·3H₂O **1** is the first example of a structurally characterized Mg(II) complex containing a coordinated heptamolybdate. Compound **1** crystallizes in the centrosymmetric monoclinic space group *C2/c* and its crystal structure consists of an unique (hmtH)⁺ monocation with all atoms located in general position, an independent [[Mg(H₂O)₅]₂{Mo₇O₂₄}]²⁻ dianion with the Mo1 atom located on a two fold axis and two unique water molecules OW1 and OW2, one of which (OW1) is situated on a twofold axis (figure S1 in Supplementary Information). In view of the special position of the Mo1 and OW1 atoms, the asymmetric unit consists a half of the dianion, and a total of three lattice water molecules per formula unit. The metric parameters of the (hmtH)⁺ cation and the {Mo₇O₂₄} unit are in the normal range (table S1 in Supplementary Information). In the complex dianion, the [Mo₇O₂₄]⁶⁻ functions as a μ_2 -bridging bidentate ligand binding to two symmetry related [Mg(H₂O)₅]²⁺ units via O16 and O16ⁱ (for symmetry code see figure 1), completing an octahedral arrangement around Mg(II) (figure 1).

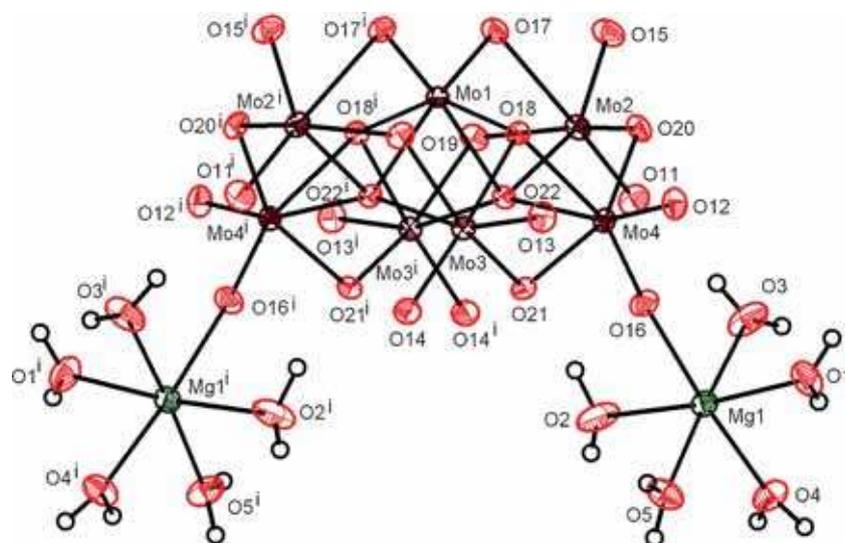
The cis O-Mg-O angles vary from 84.71(15) to 98.47(18)° while the trans O-Mg-O angles range from 173.82° to 176.74° indicating a distortion of the {MgO₆} octahedron. The Mg-O bond distances range from 2.027(4) to 2.089(4) Å (table 3).

It is well documented that Mg(II) tends to form compounds containing the octahedral [Mg(H₂O)₆]²⁺ unit when isolated from aqueous medium as evidenced by the structural characterization of several compounds containing the hexaaquamagnesium(II) cation. A search of the Cambridge database reveals several such compounds (table S2). A few examples containing less than six coordinated water molecules around Mg(II) are known.³⁶ The presence of {(H₂O)₅Mg} unit in the complex dianion can be attributed to the structure directing effect of the organic cation via H-bonding interactions with the O atoms of heptamolybdate and the O atoms of coordinated water. Hexacoordination around Mg(II) is achieved due to the bridging bidentate coordination of the centrosymmetric (μ_2 -Mo₇O₂₄)⁶⁻ ligand binding to two Mg(II) ions resulting in the formation of the complex dianion.

A scrutiny of the structure of **1** reveals a total of 15 weak hydrogen bonds comprising of seven O-H...O,

Table 2. Crystal data and structure refinement for compound **1**.

| | |
|--------------------------------------|---|
| Empirical formula | C ₁₂ H ₄₆ Mg ₂ Mo ₇ N ₈ O ₃₇ |
| Formula weight | 1614.77 |
| Temperature | 293(2) K |
| Wavelength | 0.71073 Å |
| Crystal system, space group | Monoclinic, <i>C</i> 2/ <i>c</i> |
| Unit cell dimensions | <i>a</i> = 23.947(12) Å, <i>b</i> = 8.758(4) Å <i>c</i> = 22.787(11) Å $\alpha = 90^\circ$, $\beta = 115.793(1)^\circ$, $\gamma = 90^\circ$ |
| Volume | 4303(4) Å ³ |
| Z, Calculated density | 4, 2.493 g/cm ³ |
| Absorption coefficient | 2.125 mm ⁻¹ |
| F(000) | 3152 |
| Crystal size | 0.30 × 0.12 × 0.25 mm ³ |
| θ range for data collection | 1.89° to 25.83° |
| Limiting indices | $-29 \leq h \leq 29$, $-10 \leq k \leq 10$, $-27 \leq l \leq 27$ |
| Reflections collected /unique | 17547/ 4043 [R(int) = 0.0415] |
| Completeness $\theta = 25.83^\circ$ | 97.2% |
| Absorption correction | Semi-empirical from equivalents |
| Refinement method | Full- matrix least-squares on F ² |
| Data / restraints / parameters | 4043 / 0 / 342 |
| Goodness of fit on F ² | 1.058 |
| Final R indices [I > 2 σ (I)] | R1 = 0.0337, wR2 = 0.0801 |
| R indices (all data) | R1 = 0.0382, wR2 = 0.0829 |
| Largest diff. peak and hole | 1.061 and -0.618 e.Å ⁻³ |

**Figure 1.** Representation of the anionic $[\{\text{Mg}(\text{H}_2\text{O})_5\}_2\{\text{Mo}_7\text{O}_{24}\}]^{2-}$ unit, showing atom labelling scheme. Thermal ellipsoids are drawn at the 30% probability level excepting for H atoms, which are shown as circles of arbitrary radius. Symmetry code: i) *x*, *y*, 0.5-*z*.

three O-H...N, one N-H...O and four C-H...O H-bonding interactions (table S3) which interlink the organic cations, the complex dianions and lattice water molecules into a supramolecular architecture (figure S2). In view of the inability to locate the H atoms attached to the lattice water a detailed description of the secondary interactions is not presented.

The ligational behaviour of $[\text{Mo}_7\text{O}_{24}]^{6-}$ towards other metals is well documented by the structural characterization of several compounds (table 1). It is interesting to note that in the closely related complexes $(\text{hmtH})_2[(\text{H}_2\text{O})_5\text{M}(\mu_2\text{-Mo}_7\text{O}_{24})\text{M}(\text{H}_2\text{O})_4] \cdot 2\text{H}_2\text{O}$ [*M* = Mn, Fe, Zn] all of which crystallize in the *C*2/*c* space group the $\{\text{Mo}_7\text{O}_{24}\}$ unit links

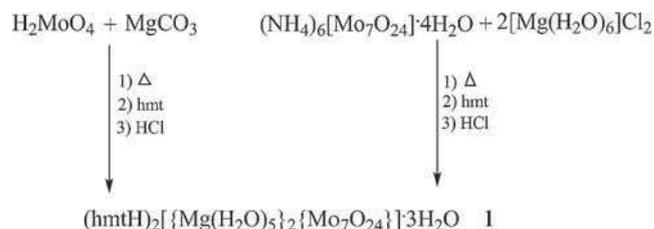
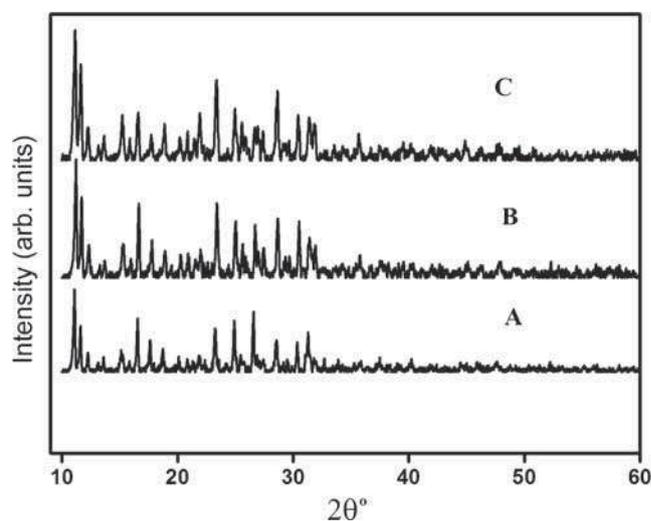
Table 3. Selected bond lengths (Å) and bond angles (°) for compound **1**.

| | | | |
|------------------|-----------|-------------------|------------|
| Bond lengths | | | |
| Mg(1)-O(1) | 2.027(4) | Mg(1)-O(4) | 2.076(4) |
| Mg(1)-O(2) | 2.055(5) | Mg(1)-O(16) | 2.078(3) |
| Mg(1)-O(3) | 2.059(4) | Mg(1)-O(5) | 2.089(4) |
| Bond angles | | | |
| O(1)-Mg(1)-O(2) | 174.5(2) | O(2)-Mg(1)-O(16) | 84.73(18) |
| O(1)-Mg(1)-O(3) | 87.0(2) | O(3)-Mg(1)-O(4) | 89.12(17) |
| O(1)-Mg(1)-O(4) | 88.83(18) | O(3)-Mg(1)-O(5) | 176.74(19) |
| O(1)-Mg(1)-O(5) | 92.18(19) | O(3)-Mg(1)-O(16) | 84.71(15) |
| O(1)-Mg(1)-O(16) | 90.48(17) | O(4)-Mg(1)-O(5) | 87.70(18) |
| O(2)-Mg(1)-O(3) | 89.9(2) | O(4)-Mg(1)-O(16) | 173.82(16) |
| O(2)-Mg(1)-O(4) | 95.6(2) | Mo(4)-O(16)-Mg(1) | 171.9(2) |
| O(2)-Mg(1)-O(5) | 91.1(2) | O(16)-Mg(1)-O(5) | 98.47(18) |

two $[M(H_2O)_x]^{2+}$ units but functions as a μ_2 -bridging tridentate ligand. The versatile coordination behaviour of the $[Mo_7O_{24}]^{6-}$ ligand can be evidenced by comparison of the structure of **1** with that of $(ImH)_4[Ca(H_2O)_6(\mu_2-Mo_7O_{24})\cdot 2(Im)\cdot 3H_2O]$ (entry No.29, table 1) in which the μ_2 -bridging bidentate coordination of the $\{Mo_7O_{24}\}$ unit results in a one-dimensional structure unlike a discrete complex for **1**. The extended structure is due to the fact that Ca(II) can adopt an eight coordination unlike hexacoordination around Mg(II) in **1**.

3.2 Synthetic aspects, spectral and thermal studies

For the synthesis of a Mg(II) heptamolybdate compound the reaction of H_2MoO_4 (acid) with $MgCO_3$ (base) was investigated (scheme 1). The insoluble molybdic acid starts dissolving in the presence of $MgCO_3$ when heated to $100^\circ C$ resulting in a clear solution. Addition of hmt at this stage to the reaction mixture, followed by crystallization at a pH of ~ 5.5 results in the formation of a crystalline compound. Analysis of the product reveals a stoichiometry of 2:2:7 for hmt:Mg:Mo. When the same mole ratio of reactants was employed by using alternate Mg source viz. $[Mg(H_2O)_6]Cl_2$ and a preformed heptamolybdate namely $(NH_4)_6[Mo_7O_{24}]\cdot 4H_2O$ and the reaction was performed in aqueous acid medium in the presence of hmt, the earlier mentioned phase **1** containing Mg:Mo in 2:7 ratio is obtained. This indicates the high formation tendency of **1** in aqueous acidic medium irrespective of the Mo and Mg sources. All our efforts to isolate a pure magnesium polyoxomolybdate viz. $[Mg(H_2O)_n]_3[Mo_7O_{24}]$ were not fruitful indicating the importance of the organic cation for product formation. An elemental analysis reveals that **1** contains two monoprotonated hexamethylenetetramine (hmtH)⁺ cations.

**Scheme 1.** Synthesis of a Mg(II) heptamolybdate compound **1**.**Figure 2.** X-ray powder patterns of products obtained in method 1 (A), method 2 (B) and at pH 3 (C).

In order to study the role of pH on the formation of **1**, the reaction was performed in a more acidic medium (pH 3) and the product thus obtained was studied by its powder pattern. The formation of the same compound is revealed by identical powder patterns (figure 2) showing that compound **1** can be isolated in a wide pH range.

Our results are in agreement with literature data³¹ reporting on the isolation of $[hmtH)_2[\{Zn(H_2O)_5\}]$

$\{Mo_7O_{24}\}\{Zn(H_2O)_4\}\cdot 2H_2O$ at pH 3.0. The identical infrared, Raman and optical spectra and satisfactory elemental analysis add credence to the formation of the same product material irrespective of the source of Mg or Mo employed for synthesis.

3.3 Spectroscopic and thermal characterization

A comparison of the infrared spectrum of **1** with that of ammonium heptamolybdate tetrahydrate (figure S3) reveals the presence of the heptamolybdate core as evidenced by bands assignable to the various Mo-O vibrations at 982, 887, 832 and 574 cm^{-1} as sharp peaks and weak bands in the region 917, 673 and 486 cm^{-1} . The appearance of a broad band centred at 3186 cm^{-1} and a sharp peak at 1658 cm^{-1} assignable for the stretching and bending O-H vibrations indicate the presence

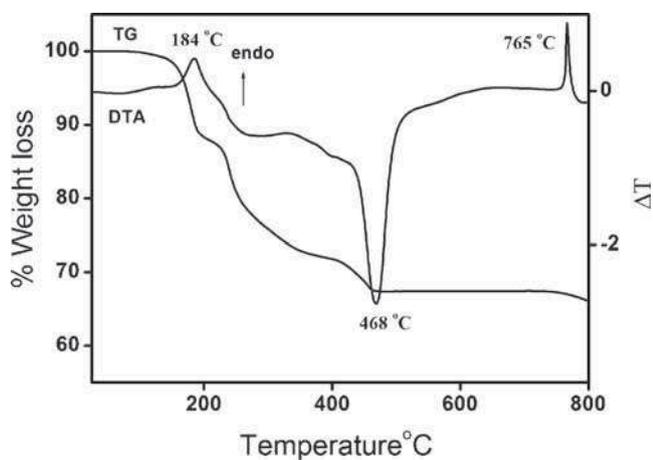


Figure 3. TG-DTA curves of **1**.

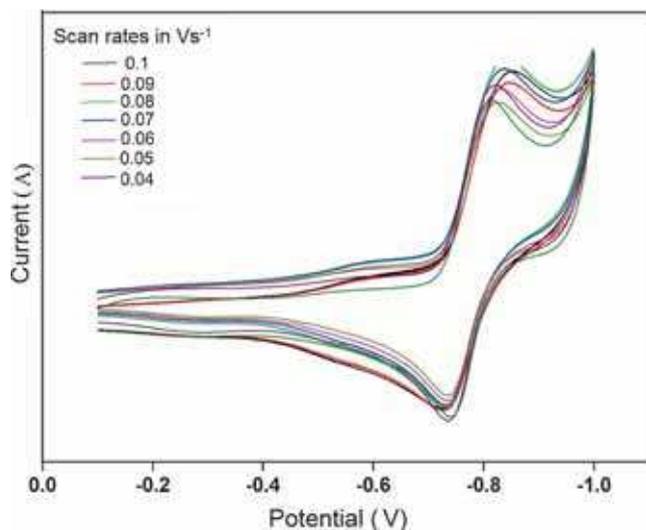


Figure 4. Cyclic voltammograms of **1** with scan rates of 0.1 to 0.04 Vs^{-1} in the potential range of $-0.1 V$ to $-1.0 V$ in 0.2 M KCl solution.

of water molecules. The Raman spectrum (figure S4) shows intense bands at 941, 891 and 691 cm^{-1} due to Mo-O vibrations. The optical spectrum indicates the presence of heptamolybdate core in **1** (figure S5). Thermal studies of **1** show that the compound is thermally stable upto 140 °C. In accordance with this no mass loss is observed when a powdered sample of **1** is heated on a water bath at 100 °C. The DTA curve exhibits thermal events at 184, 468 and 765 °C (figure 3).

The endothermic peak at 184 °C can be assigned for the loss of water molecules while the exothermic events can probably be assigned for the decomposition of organic moiety leaving residue of 67.30%. The theoretically calculated percentage for the complete loss of water and organics for a residual composition $\{Mo_7Mg_2O_{23}\}$ is found to be 67.39%. In accordance with this, heating of **1** in a furnace at 600 °C resulted in a residue (67.15%) which on acidification followed by addition of hmt results in formation of **1**.

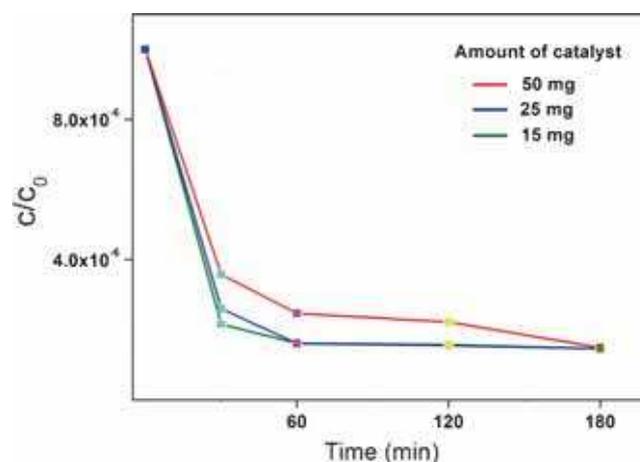


Figure 5. Time dependent decrease in the concentration of RhB.

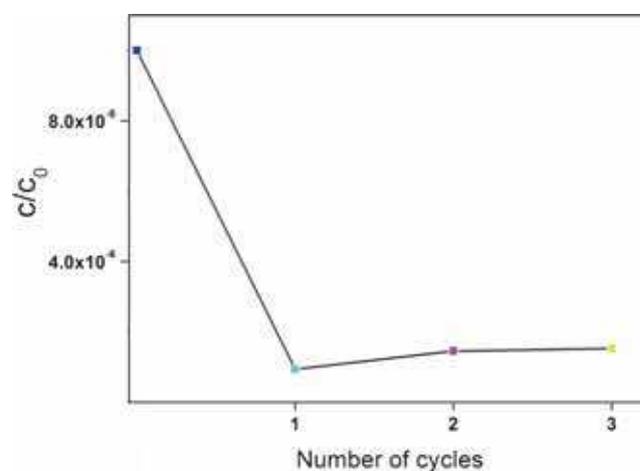


Figure 6. Recycling test of compound **1**.

Table 4. Degradation efficiency calculated for different amounts of **1**.

| Amount of catalyst used | Degradation Efficiency (%) = $c_0 - c/c_0 * 100\%$ | | | | |
|-------------------------|--|--------|--------|---------|---------|
| | 0 min | 30 min | 60 min | 120 min | 180 min |
| 15 mg | 0 | 78 | 83 | 84 | 86 |
| 25 mg | 0 | 74 | 84 | 85 | 88 |
| 50 mg | 0 | 64 | 75 | 78 | 85 |

3.4 Electrochemistry and photochemical investigations

The cyclic voltammogram of **1** recorded at different scan rates (figure 4) indicates its quasireversible redox behaviour. The mean peak potential ($E_{1/2} = (E_{pa} + E_{pc})/2$) of **1** calculated for a scan rate of 0.04 V s^{-1} is -0.780 V while the observed $E_{1/2}$ for the protonated salt of hmt namely hmtHCl is found to be -0.379 V (figure S6). Hence the electrochemical process occurring in **1** can be ascribed to one electron redox process of Mo. The photosensitive nature of alkylammonium polyoxomolybdates in solid as well as in solution is well documented in the literature.^{37–40} Upon irradiation with sunlight for 15 min, **1** turns into reddish brown **2**, and again reverts back to colourless compound slowly in the presence of oxygen. The solid state UV-Vis spectrum of **1** (figure S7) exhibits a band at 312 nm which is characteristic of $\text{O} \rightarrow \text{Mo}$ LMCT band. In the absorption spectrum of **2**, in addition to this band a shoulder is observed at 490 nm, which can be due to the photoreduction of Mo (VI) to Mo (V). The formation of Mo(V) is further confirmed by the ESR spectroscopy. The ESR spectrum of **2** (figure S8) exhibits characteristic Mo^{5+} signal, and the results are in accordance with literature data.³⁸

Thus, these investigations suggest its effectiveness as a photocatalyst. Hence the degradation of RhB in the presence of hydrogen peroxide as an oxidant under sunlight irradiation of **1** was investigated. The dye can be degraded to the extent of 88% after 3 h (figure 5) showing the good photocatalytic activity of **1**.

The recycling test showed that the efficiency and the stability of the photocatalyst is good over three cycles (figure 6). Photocatalytic experiments were performed by taking different amounts of photocatalyst (table 4), with 0.5 mL of 30% H_2O_2 for the degradation of 25 mL of 10^{-5} M concentration (c) of RhB dye solution.

At given solar irradiation time intervals, a series of aqueous solutions of a certain volume were collected and separated through a centrifuge to remove suspended catalyst particles and then subjected to UV-Vis spectroscopy. The absorption spectra (figures S9, S10 and S11) show a decrease in the absorption as the irradiation time increases indicating the degradation of

the dye. The degradation of organic dye was investigated three times and similar photocatalytic efficiencies were observed (figure 6). The high reproducibility of the results indicates the stability of **1** as photocatalyst, which is also evidenced by the nearly identical X-ray powder patterns (figure S12) of the recovered catalyst and the original compound **1**. To ensure that the effective photocatalysis is the combined result of activation of catalyst by sunlight irradiation and H_2O_2 as an oxidant, the absorption spectra were studied under various conditions (figure S13). These results reveal that for the effective photocatalysis, H_2O_2 is essential in the absence of which no degradation occurs.

4. Conclusion

In summary, the synthesis, characterization and photochemistry of a new heptamolybdate supported magnesium-aqua coordination complex, using hexamethylenetetramine as structure directing agent, is reported.

Supplementary Information

Crystallographic data (excluding structure factors) for the structure of (**1**) reported herein have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC 1049780. Copies of the data can be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK. (Fax: +44-(0)1223-336033; <http://www.ccdc.cam.ac.uk/conts/retrieving.html>; E-Mail: deposit@ccdc.cam.ac.uk).

Electronic supplementary information (for figures S1–S13, tables S1–S3 and checkcif file) is available at www.ias.ac.in/chemsci.

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