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Structural identification of two differently coordinated heptamolybdate ligands in a hexamagnesium compound

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Dissolution of freshly prepared molybdenum trioxide in hot aqueous magnesium carbonate followed by crystallization results in the formation of an all-inorganic heptamolybdate compound viz. $[Mg(H_2O)_6]_3[Mg(H_2O)_5(Mo_7O_{24})][(H_2O)_5Mg(\mu_2\text{-}Mo_7O_{24})Mg(H_2O)_5]\cdot 6H_2O$ (**1**). The crystal structure, spectral characteristics, thermal and electrochemical properties of **1** are reported. Compound **1**, which crystallizes in the acentric polar space group *Cc,* contains six unique Mg(II) ions. The two crystallographically independent heptamolybdate anions function as a monodentate (η^1) and μ_2-bridging bidentate ligand, respectively, forming the anionic $[Mg(H_2O)_5(Mo_7O_{24})]^{4-}$ and $[(H_2O)_5Mg(\mu_2\text{-}Mo_7O_{24})Mg(H_2O)_5]^{2-}$ species, which are charge balanced by three unique hexaaquamagnesium(II) cations. The electrochemical and conductivity studies of **1** reveal the presence of $[Mg(H_2O)_6]^{2+}$ cations and uncoordinated $(Mo_7O_{24})^{6-}$ anions in solution. Thermal decomposition of **1** leads to the formation of $Mg_2Mo_3O_{11}$ via $Mg_6Mo_{14}O_{48}$ and $3Mg_2Mo_3O_{11}\cdot 5MoO_3$.

Keywords: Heptamolybdate, Hexaaquamagnesium(II), Monodentate, μ_2-Bridging bidentate, Thermal decomposition

One of the earliest reports on the chemistry of molybdenum is a paper titled, '*Beitrag zur näheren Kenntniss des Molybdäns*[#]' by Berzelius[1]. In this work, Berzelius described the formation of a yellow product (ammonium phosphomolybdate) from the reaction of molybdate with phosphate. Since the publication of this paper in 1826, the chemistry of Mo and other early transition metals has been extensively investigated by several researchers. The oxoanions of Mo, W, V, Nb referred to by the general term polyoxometalate (POM) has been the subject of research reported in several papers* including review articles, monographs and books[2-9]. The reason for the continued study of POMs for more than a century and half as well as the scientific importance of these studies, can be evidenced from the following statement which is quoted verbatim from a review article of Pope and Müller[5], who have made seminal contributions in this area. "*Polyoxometalates form a class of inorganic compounds that is unmatched in terms of molecular and electronic structural versatility, reactivity, and relevance to analytical chemistry, catalysis, biology, medicine, geochemistry, materials science and topology.*"

A general method of synthesis of POM's described in all standard inorganic chemistry text books[10] is the condensation of anionic transition metal subunits (for example the tetrahedral $(MoO_4)^{2-}$ in the case of Mo) by an acidification reaction. The use of a suitable counter cation in the reaction medium or a cation generated *in situ* by diffusion of an appropriate volatile reagent[11] can facilitate the isolation of POMs. It is customary to name a POM based on the number of metal atoms, for example, hexamolybdate, heptamolybdate, decavanadate and so on. The structures of POMs charge balanced by organic or metal-organic cations are archived in the Cambridge Structural Database (CSD)[12], while the structures of POMs containing no carbon in the cation are available in the Inorganic Crystal Structure Database (ICSD)[13]. In the case of heptamolybdate $[Mo_7O_{24}]^{6-}$ which is the subject matter of this paper, more than seventy structurally characterized compounds containing a variety of counter cations are currently available demonstrating its structural flexibility to exist in many environments. Interestingly a majority of these structures were determined in the past two decades[14-29].

The name heptamolybdate indicates only seven Mo atoms and a negative species, but nothing is known about the number and type of oxygens; still heptamolybdate is the preferred terminology than the

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[#] Contribution to the knowledge of molybdenum

**Only few important works of the past more than 190 years are listed.*

very long IUPAC name[30] di-μ_4-oxo-di-μ_3-oxo-octa-μ-oxo-dodecaoxoheptamolybdate(6-) or the older name paramolybdate[31]. The IUPAC name reveals the presence of twelve terminal oxo ligands and three different types of bridging oxo ligands in heptamolybdate. Several instances of the terminal oxygens coordinating with metals are now known and hence heptamolybdate can be considered as a pure inorganic ligand[15].

As part of our research program, we are investigating the structure and synthetic chemistry aspects of heptamolybdates charge balanced by organic cations as well as *s*-block metal ions. In a recent paper, we performed a comparative study of the structural features of more than a dozen alkali metal heptamolybdates[32]. Based on this, we reported that the number of coordinated water molecules present in alkali metal heptamolybdates and their mode of binding could influence the denticity of the $[Mo_7O_{24}]^{6-}$ ligand. In addition to a base-promoted cation exchange methodology for the synthesis of mixed cationic lithium heptamolybdates using the commercially available $(NH_4)_6[Mo_7O_{24}]\cdot4H_2O$ as the Mo reagent, we have employed freshly prepared MoO_3 as Mo source for the synthesis of alkali metal heptamolybdates of Na, K and Rb[32,33]. The ready availability of the starting materials and the mild reaction conditions makes this method a good option for compound synthesis. For example, we synthesized $Na_6[Mo_7O_{24}]\cdot14H_2O$[33] by the reaction of MoO_3 with sodium carbonate instead of a hydrothermal method reported earlier for the same compound[34]. Later we applied the same methodology for the preparation of $[M'_6(H_2O)_4(Mo_7O_{24}]$ (M'=K or Rb). In the present study, we have extended this methodology for alkaline-earth metals. The use of $MgCO_3$ afforded a hexamagnesium compound viz. tris(hexaaquamagnesium(II)) pentaaqua(heptamolybdato)magnesium(II) μ_2-heptamolybdato-bis[(pentaaqua)magnesium(II)] hexahydrate having molecular formula $[Mg(H_2O)_6]_3[Mg(H_2O)_5(Mo_7O_{24})][(H_2O)_5Mg(\mu_2\text{-}Mo_7O_{24})Mg(H_2O)_5]\cdot6H_2O$ **1**. In this report, we describe the details of the synthesis, structure determination, spectral, thermal and electrochemical properties of the all-inorganic heptamolybdate **1**.

Materials and Methods

Experimental

All the chemicals used in this study were of reagent grade and were used without any further purification. Infrared (IR) spectra of the solid samples diluted with KBr were recorded on a Shimadzu (IR Prestige-21) FT-IR spectrometer from 4000−400 cm^{-1} at a resolution of 4 cm^{-1}. Raman spectra were recorded using 785 nm laser radiation for excitation with laser power set to 100 mW on an Agiltron PeakSeeker Pro Raman instrument. UV-visible spectra of aqueous solutions were recorded using Shimadzu UV-2450 double beam spectrophotometer (200–800 nm) using matched quartz cells. X-ray powder patterns were recorded 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 26 °C to 600 °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, a platinum wire as counter electrode and saturated calomel electrode (SCE) as the reference. The redox properties of the aqueous solution of **1** were studied using 0.1 M KNO_3 solution as supporting electrolyte at a scan rate of 0.03 Vs^{-1} in the potential region 1.0 to –1.0 V. Conductivity measurements of **1** were carried out at room temperature using a Digital conductivity meter (LT-16) from Labtronics equipped with a standard conductometric cell composed of two platinum black electrodes.

Synthesis of $[Mg(H_2O)_6]_3[Mg(H_2O)_5(Mo_7O_{24})][(H_2O)_5Mg(\mu_2\text{-}Mo_7O_{24})Mg(H_2O)_5]\cdot6H_2O$ (1)

Ammonium heptamolybdate tetrahydrate (6.17 g, 5 mmol) was taken in a silica crucible and heated to 650 °C in a furnace for 2 h to get molybdenum trioxide (MoO_3). After cooling in a desiccator, the freshly prepared MoO_3 was reacted with basic magnesium carbonate (1.47 g, 3 mmol) in distilled water (100 mL). The reaction mixture was heated to 100 °C. Slow effervescence was observed and a clear solution was obtained after half an hour. The pH of the clear reaction mixture was ~ 6.5. The reaction mixture was filtered and kept aside for product formation. A white solid mass was obtained from the filtrate after a week. Recrystallization of the solid from water yielded colorless rods in ~ 80 % yield calculated based on Mo. Alternatively, **1** can also be synthesized, by using commercial molybdic acid (H_2MoO_4) as Mo source and heating it to 200 °C to freshly obtain MoO_3 for reaction with basic magnesium carbonate maintaining a Mo:Mg ratio of 7:3.

IR data (cm^{-1}): 3546−3116, 1651, 933, 891, 837, 727, 562, 430; Raman data (cm^{-1}): 931, 894,720, 344; UV-Visible data: 208 nm; DTA (°C) : 94 (endo), 179 (endo) and 404 (exo).

X-ray crystal structure determination

Single crystal X-ray analysis of **1** was performed at the Sophisticated Analytical Instrument Facility (SAIF), Indian Institute of Technology Madras. X-ray intensity data were collected using Bruker AXS Kappa Apex II CCD Diffractometer equipped with graphite monochromated Mo (Kα) (λ = 0.7107 Å) radiation. The structure was solved by direct methods using SIR92[35] and refined by full-matrix least squares techniques using SHELXL-2014[36]. All non-hydrogen atoms were refined anisotropically. The H atoms attached to two of the water molecules, namely O82 and O87, could not be located. Technical details of data acquisition and selected refinement results are listed in Table 1.

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

Empirical formula	$H_{78}Mg_6Mo_{14}O_{87}$
Formula weight (g mol^{-1})	2959.64
Temperature (K)	296(2)
Wavelength (Å)	0.71073
Crystal system	Monoclinic
Space group	*Cc*
Unit cell dimensions	
a (Å)	16.576(5)
b (Å)	10.868(3)
c (Å)	40.814(12)
β (°)	97.257(6)
Volume (Å^3)	7294(4)
Z	4
D_{calc} (mg/m^3)	2.695
Absorption coefficient (mm^{-1})	2.515
F(000)	5736
Crystal size (mm^3)	0.30×0.30×0.20
θ range for data collection (°)	2.27 to 27.00
Limiting indices	$-21 \leq h \leq 21$, $-13 \leq k \leq 13$, $-52 \leq l \leq 52$
Reflections collected/ unique	80255 / 15573 [R(int) = 0.0281]
Completeness θ = 27.00°	99.9 %
Absorption correction	Multi-scan
Refinement method	Full- matrix least-squares on F^2
Data/ restraints/ parameters	15573 / 123 / 1215
Goodness of fit on F^2	1.123
Final R indices [I>2σ(I)]	R1 = 0.0180, wR2 = 0.0438
R indices (all data)	R1 = 0.0185, wR2 = 0.0440
Largest diff. peak and hole (e Å^{-3})	0.657 and −0.7987

Results and Discussion

Description of the crystal structure of hexamagnesium-bis(heptamolybdate) 1

The all-inorganic heptamolybdate **1** crystallizes in the acentric polar monoclinic space group *Cc* with all atoms situated in general positions. The crystal structure consists of a total of 107 non-hydrogen atoms out of which twenty are metal ions comprising of six magnesium (Mg1 to Mg6) and fourteen molybdenum (Mo1 to Mo14) atoms, while the rest eighty-seven are oxygen atoms. The oxygens can be classified into two groups namely the thirty-nine oxygen atoms of the water and the forty-eight oxygen atoms attached to Mo(VI) which constitute the two crystallographically independent $[Mo_7O_{24}]^{6-}$ ions. Of the thirty-nine water oxygens, thirty-three are bonded to the six unique Mg(II) ions and the rest six oxygens (O81 to O87) are those of the lattice water molecules. The asymmetric unit of **1** consists of three crystallographically unique $[Mg(H_2O)_6]^{2+}$ cations, which charge balance a crystallographically independent $[Mg(H_2O)_5(Mo_7O_{24})]^{4-}$ tetraanion, and an unique $[(H_2O)_5Mg(\mu_2\text{-}Mo_7O_{24})Mg(H_2O)_5]^{2-}$ dianion. In addition, six lattice water molecules are present in the crystal structure (Fig. 1).

All the six unique Mg(II) ions in **1** exhibit hexa coordination. Three Mg(II) ions viz. Mg4, Mg5 and Mg6 are bonded to six aqua ligands, while the other three Mg(II) ions namely (Mg1, Mg2 and Mg3) are bonded to five aqua ligands and the sixth ligand is a terminal oxygen from the crystallographically independent $[Mo_7O_{24}]^{6-}$ ions. The Mg-O bond distances in the three unique $[Mg(H_2O)_6]^{2+}$ dications vary from 2.028(3) to 2.129(3) Å (Table 2). The cis O-Mg-O angles varying from 86.43(13)° to 96.22(14)° and the trans angles ranging between 173.24(13)° to 179.70(17)° indicate a slight distortion of the $\{MgO_6\}$ octahedra.

The Mo-O bond distances and the O-Mo-O bond angles of the unique heptamolybdate anions (Supplementary Data, Table S1) are in agreement with the reported data[32,37]. In addition to functioning as charge balancing counter anions, the unique $[Mo_7O_{24}]^{6-}$ anions exhibit different binding modes in **1**. Unlike the octahedral $[Mg(H_2O)_6]^{2+}$ unit which is present in several structurally characterized Mg(II) compounds[38], fewer examples of hexacoordinate Mg(II) compounds containing the pentaaqua unit are known. The first unique heptamolybdate (Mo1 to Mo7) functions as a monodentate ligand binding to

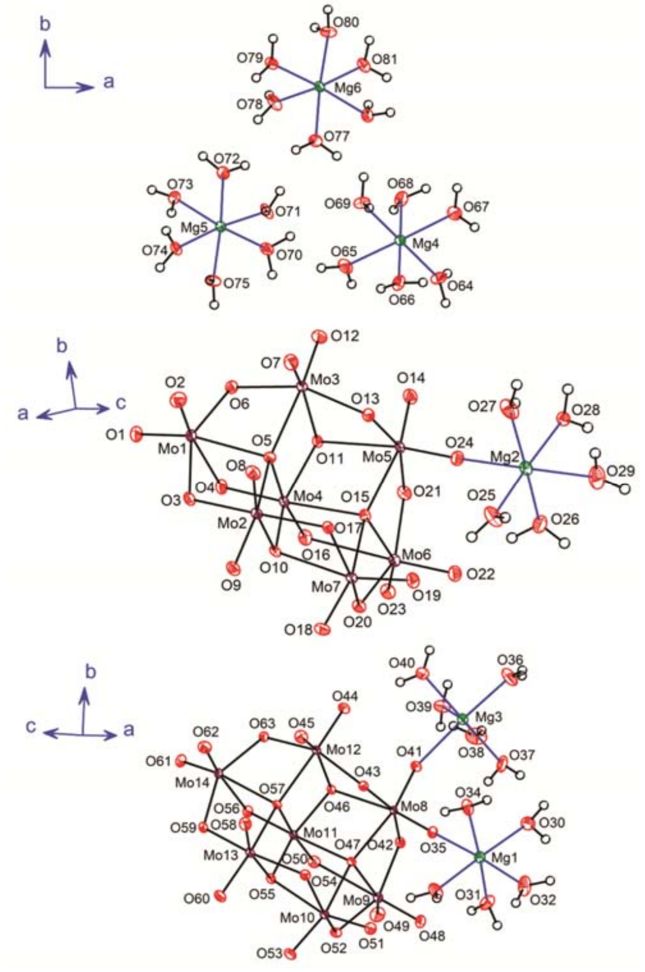


Fig. 1 — Atom labelling scheme for the three crystallographically unique $[Mg(H_2O)_6]^{2+}$ dications, (**top**), an independent $[Mg(H_2O)_5(\eta^1\text{-}Mo_7O_{24})]^{4-}$ tetraanion (**middle**) and the unique $[(H_2O)_5Mg(\mu_{2}\text{-}Mo_7O_{24})Mg(H_2O)_5]^{2-}$ dianion (**bottom**) in the crystal structure of **1**. The Mg-O bonds are displayed as blue lines. Displacement ellipsoids are drawn at 50% probability except for the H atoms, which are shown as spheres of arbitrary radii.

Mg2 of the $[Mg(H_2O)_5(Mo_7O_{24})]^{4-}$ tetraanion via O24 (Mg2-O24=2.125(3) Å) resulting in hexacoordination around Mg2 (Fig. 1). The Mg-O bond distances in $[Mg(H_2O)_5(Mo_7O_{24})]^{4-}$ vary between 2.029(3) and 2.125(3) Å (Table 2). The deviations of the *cis* O-Mg-O angles and the *trans* O-Mg-O angles from the ideal values of 90.0 and 180.0°, respectively, (Table 2) indicate distortion of the $\{MgO_6\}$ octahedron. The second unique heptamolybdate anion (Mo8 to Mo14) functions as a μ_2-η^1,η^1 bridging bidentate ligand and is bonded to Mg1 and Mg3 via O35 and O41 (Mg1-O35=2.169(3); Mg1-O41=2.124(3) Å), respectively resulting in octahedral geometry around these Mg (II) ions in the dianionic species $[(H_2O)_5Mg(\mu_{2}\text{-}Mo_7O_{24})Mg(H_2O)_5]^{2-}$ (Fig. 1). In this case, the observed Mg-O bond lengths range from 2.022(4) to 2.169(3) Å (Table 2). The distortions of the $\{MgO_6\}$ octahedra can be evidenced by the *cis* and *trans* O-Mg-O angles which vary from 85.29(14)° to 98.21(16)° and 172.56(14)° to 178.32(17)°, respectively. The μ_2-η^1, η^1 binding mode of heptamolybdate has also been observed earlier in a bis(magnesium)-heptamolybdate compound charge balanced by a pair of monoprotonated hexamethylenetetramine cations[37].

The presence of several H-donors in the coordinated and lattice water molecules and several H-acceptors in the crystal structure of **1** results in several intra and intermolecular O-H···O interactions, among the heptamolybdate anions, coordinated and lattice water molecules (Supplementary Data, Table S2, Figs S1 & S2). It has been reported that the self-assembly of lattice water molecules / cations and POMs result in the formation of water clusters[29]. The difficulty to locate the H-atoms of the lattice waters O82 and O87 in **1** precludes a detailed description of the secondary interactions in the title compound. The net result of the several H-bonding interactions is the organization of cations and anions into alternating layers with lattice water serving as links between the layers (Fig. 2).

Comparative structural chemistry of s-block metal heptamolybdates

The structural information of more than a dozen heptamolybdates charge balanced by *s*-block metal cations (Table 3) are available in the literature[15,19,22,32,34,37,39-44]. A perusal of this data reveals that all compounds excepting the title compound and $Na_6[Mo_7O_{24}]\cdot 14H_2O$ (Entry No. 14) crystallize in centrosymmetric space groups. All the compounds contain at least one water molecule coordinated to the *s*-block metal in addition to at least one lattice water molecule in all but three compounds. Although, the molecular formulae of some alkali-metal molybdates viz. $K_6[Mo_7O_{24}]\cdot 4H_2O$, $Cs_6[Mo_7O_{24}]\cdot 7H_2O$ indicate the presence of lattice water molecules, these compounds contain only coordinated water molecules and no lattice water[32]. In addition to its function as a charge balancing counter anion in all these compounds, the $[Mo_7O_{24}]^{6-}$ functions as an O-donor ligand. A perusal of the entries in Table 3 reveals the structural flexibility of the alkali-metals to exhibit variable coordination number and their oxophilic nature to bind to O-donors viz. H_2O or heptamolybdate. The versatile ligational

Table 2 — Mg-O bond distances (Å) and O-Mg-O bond angles (°)

Bond distances					
Mg1-O31	2.036(3)	Mg3-O36	2.022(4)	Mg5-O74	2.028(3)
Mg1-O33	2.046(3)	Mg3-O37	2.040(3)	Mg5-O70	2.064(3)
Mg1-O32	2.058(3)	Mg3-O40	2.061(3)	Mg5-O72	2.068(3)
Mg1-O30	2.066(3)	Mg3-O38	2.075(4)	Mg5-O75	2.069(3)
Mg1-O34	2.069(3)	Mg3-O39	2.095(3)	Mg5-O71	2.074(3)
Mg1-O35	2.169(3)	Mg3-O41	2.124(3)	Mg5-O73	2.111(3)
Mg2-O26	2.029(3)	Mg4-O66	2.029(3)	Mg6-O81	2.035(3)
Mg2-O25	2.044(3)	Mg4-O68	2.041(3)	Mg6-O77	2.056(3)
Mg2-O27	2.048(3)	Mg4-O69	2.049(3)	Mg6-O80	2.065(3)
Mg2-O28	2.102(3)	Mg4-O64	2.056(3)	Mg6-O78	2.071(3)
Mg2-O29	2.104(4)	Mg4-O65	2.077(3)	Mg6-O79	2.081(3)
Mg2-O24	2.125(3)	Mg4-O67	2.083(3)	Mg6-O76	2.129(3)
Bond Angles					
O31-Mg1-O33	92.04(15)	O36-Mg3-O37	90.56(16)	O74-Mg5-O70	89.25(13)
O31-Mg1-O32	89.15(15)	O36-Mg3-O40	89.27(15)	O74-Mg5-O72	88.73(13)
O33-Mg1-O32	87.05(14)	O37-Mg3-O40	178.32(17)	O70-Mg5-O72	86.11(13)
O31-Mg1-O30	90.65(14)	O36-Mg3-O38	94.09(16)	O74-Mg5-O75	86.97(12)
O33-Mg1-O30	174.29(15)	O37-Mg3-O38	90.71(16)	O70-Mg5-O75	95.79(13)
O32-Mg1-O30	87.95(15)	O40-Mg3-O38	90.96(16)	O72-Mg5-O75	175.27(14)
O31-Mg1-O34	172.56(14)	O36-Mg3-O39	92.99(15)	O74-Mg5-O71	173.24(13)
O33-Mg1-O34	89.46(14)	O37-Mg3-O39	90.57(14)	O70-Mg5-O71	89.40(14)
O32-Mg1-O34	98.21(16)	O40-Mg3-O39	87.78(14)	O72-Mg5-O71	97.79(13)
O30-Mg1-O34	88.52(13)	O38-Mg3-O39	172.78(15)	O75-Mg5-O71	86.57(12)
O31-Mg1-O35	85.43(12)	O36-Mg3-O41	176.56(15)	O74-Mg5-O73	91.59(13)
O33-Mg1-O35	92.09(12)	O37-Mg3-O41	86.07(13)	O70-Mg5-O73	174.04(13)
O32-Mg1-O35	174.48(15)	O40-Mg3-O41	94.13(12)	O72-Mg5-O73	88.01(12)
O30-Mg1-O35	93.15(13)	O38-Mg3-O41	85.29(14)	O75-Mg5-O73	90.15(12)
O34-Mg1-O35	87.23(12)	O39-Mg3-O41	87.71(11)	O71-Mg5-O73	90.44(13)
O26-Mg2-O25	90.49(15)	O66-Mg4-O68	178.16(18)	O81-Mg6-O77	89.64(14)
O26-Mg2-O27	176.36(17)	O66-Mg4-O69	89.12(14)	O81-Mg6-O80	86.43(13)
O25-Mg2-O27	91.32(15)	O68-Mg4-O69	92.15(14)	O77-Mg6-O80	175.52(15)
O26-Mg2-O28	89.31(14)	O66-Mg4-O64	90.62(14)	O81-Mg6-O78	174.05(14)
O25-Mg2-O28	177.01(14)	O68-Mg4-O64	88.11(14)	O77-Mg6-O78	96.22(14)
O27-Mg2-O28	89.04(14)	O69-Mg4-O64	179.70(17)	O80-Mg6-O78	87.75(13)
O26-Mg2-O29	92.29(15)	O66-Mg4-O65	88.72(15)	O81-Mg6-O79	90.46(14)
O25-Mg2-O29	90.65(15)	O68-Mg4-O65	90.02(15)	O77-Mg6-O79	87.63(14)
O27-Mg2-O29	90.84(17)	O69-Mg4-O65	86.72(16)	O80-Mg6-O79	94.55(13)
O28-Mg2-O29	86.37(14)	O64-Mg4-O65	93.13(16)	O78-Mg6-O79	88.75(14)
O26-Mg2-O24	85.37(12)	O66-Mg4-O67	91.80(15)	O81-Mg6-O76	90.71(13)
O25-Mg2-O24	92.74(13)	O68-Mg4-O67	89.48(15)	O77-Mg6-O76	87.82(13)
O27-Mg2-O24	91.39(14)	O69-Mg4-O67	92.24(15)	O80-Mg6-O76	90.06(13)
O28-Mg2-O24	90.22(11)	O64-Mg4-O67	87.91(15)	O78-Mg6-O76	90.55(14)
O29-Mg2-O24	175.90(15)	O65-Mg4-O67	178.83(17)	O79-Mg6-O76	175.30(13)

behavior of heptamolybdate to exhibit a variety of binding modes, especially multidentate bridging in some alkali metal compounds, can be evidenced from the entries in Table 3. However, in the case of alkaline-earth metal compounds, the denticity of heptamolybdate is limited to either monodentate or bidentate (Table 3 entry no. 11 to 13). This differing behavior can be explained due to the presence of

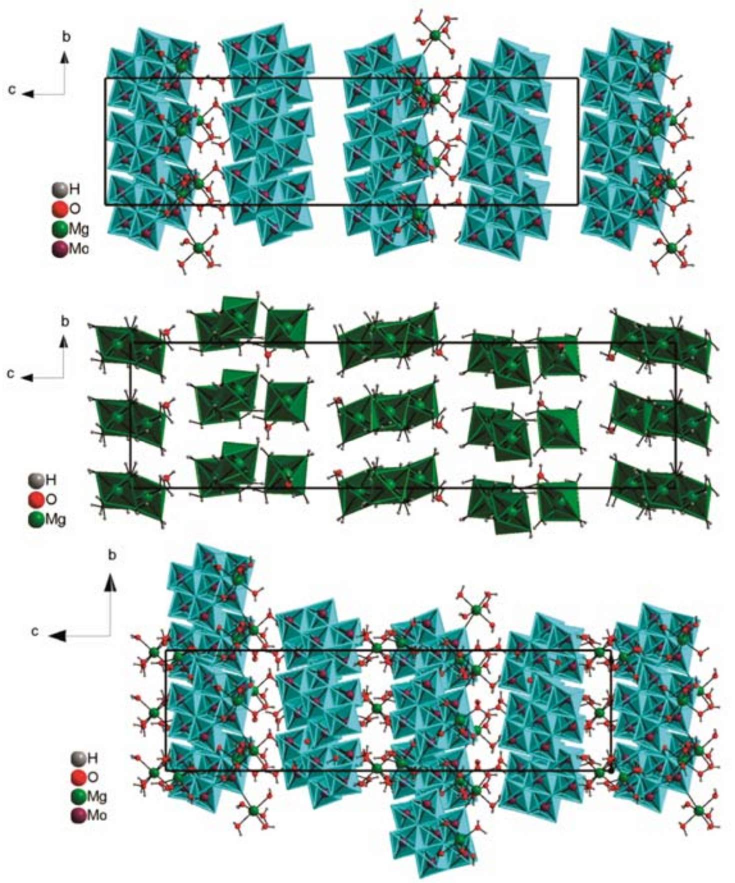


Fig. 2 — A view down the '*a*' axis of the unit cell packing of **1** showing the arrangement of the di and tetraanions (**top**); the unique $[Mg(H_2O)_6]^{2+}$ dications (**middle**); cations, anions & lattice water (**bottom**). For clarity, H-bonding interactions are not shown.

Table 3 — Structural analysis of *s*-block heptamolybdate compounds

No.	Compound	Space Group	s-block metal coord no.	Binding mode of $(Mo_7O_{24})^{6-}$
1	$Na_7[Mo_7O_{24}](OH)\cdot 21H_2O$[39]	*P2/n*	6, 6, 6, 6	μ_4-tetradentate
2	$[Na_2(H_2O)_5(hmtH_2)_2][Mo_7O_{24}]\cdot 4H_2O$[40]	*Pnma*	6, 6	μ_2-pentadentate
3	$(hmtH_2)_{1.5}(ahmtH_2)_{0.5}[Na_2(H_2O)_5Mo_7O_{24}]\cdot 4H_2O$[22]	*Pnma*	6, 6	μ_2-pentadentate
4	$(NH_4)_{16}(C_4H_{12}NO)_4[NaMo_7O_{24}]_4\cdot 4H_2O$[41]	*Pmmn*	6	μ_2-hexadentate
5	$Na(NH_4)[bppH_2]_2[Mo_7O_{24}]\cdot 8H_2O$[42]	$P2_1/m$	6	η^3-tridentate
6	$Cs_6[Mo_7O_{24}]\cdot 7H_2O$[43]	$P\bar{1}$	9, 10, 11, 11, 11, 11	μ_{18}-tritetracontadentate
7	$K_6[Mo_7O_{24}]\cdot 4H_2O$[44]	$P2_1/c$	8, 9, 9, 9, 9, 10	μ_{20}-tritetracontadentate
8	$[Rb_6(H_2O)_4Mo_7O_{24}]$[32]	$P2_1/n$	8, 9, 9, 9, 9, 10	μ_{20}-tritetracontadentate
9	$(NH_4)_3[Li_3(H_2O)_4(\mu_6\text{-}Mo_7O_{24})]\cdot 2H_2O$[15]	*Pnma*	3, 4, 5	μ_6-hexadentate
10	$(NH_4)_4[Li_2(H_2O)_7][Mo_7O_{24}]\cdot H_2O$[15]	$P2_1/n$	4, 4	Counterion
11	$(ImH)_4[Ca(H_2O)_6(\mu_2\text{-}Mo_7O_{24})]\cdot 2(Im)\cdot 3H_2O$[19]	*C2/m*	8	μ_2-bidentate
12	$(hmtH)_2[\{Mg(H_2O)_5\}_2\{Mo_7O_{24}\}]\cdot 3H_2O$[37]	*C2/c*	6, 6	μ_2-bidentate
13	$[Mg(H_2O)_6]_3[Mg(H_2O)_5(Mo_7O_{24})][(H_2O)_5Mg(\mu_2\text{-}Mo_7O_{24})Mg(H_2O)_5]\cdot 6H_2O$ **1**	*Cc*	6, 6, 6, 6, 6, 6	η^1-monodentate, μ_2-bidentate
14	$Na_6[Mo_7O_{24}]\cdot 14H_2O$[34]	$Pca2_1$	6, 6, 6, 6, 6, 6	μ_{11}-pentadecadentate

Abbreviations used: hmt= hexamethylenetetramine; ahmt =*N*-(aminomethylene)-hexamethylenetetramine; $(C_4H_{12}NO)$ = dimethyl(2-hydroxyethyl)ammonium; bpp = 1,3-bis(4-pyridyl)propane; Im = imidazole

several aqua ligands in these compounds. For example, the title compound **1** contains thirty-three aqua ligands for the six Mg(II) ions unlike only four or seven aqua ligands for the six potassium or six cesium ions in $K_6[Mo_7O_{24}]\cdot 4H_2O$ and $Cs_6[Mo_7O_{24}]\cdot 7H_2O$, respectively.

Synthetic aspects, spectral and thermal studies

The synthesis of the title compound **1** was performed in a two-step reaction. In the first step, molybdenum trioxide was freshly prepared by pyrolysis of $(NH_4)_6[Mo_7O_{24}]\cdot4H_2O$ or H_2MoO_4. In the second step, MoO_3 is reacted with basic magnesium carbonate in aqueous medium to obtain the title compound **1** in good yield. Although both reagents viz. MoO_3 and $MgCO_3$ are insoluble in water, they react with each other to give a clear solution. The dissolution is facilitated by heating the reaction mixture. The pH of the clear solution obtained at the end of the reaction was found to be slightly acidic (~6.5) and thus is suitable for the formation of heptamolybdate core. Slow evaporation of this solution resulted in the formation of a white solid mass, which when recrystallized from hot water yielded the crystalline product **1**. A comparison of the powder pattern of the bulk compound with the simulated powder pattern calculated from the single crystal data reveals the phase purity of **1** (Supplementary Data, Fig. S3). The product obtained is quite soluble in water and its optical spectrum is nearly identical to that of $(NH_4)_6[Mo_7O_{24}]\cdot4H_2O$ showing absorption maximum at 208 nm indicating the presence of heptamolybdate species (Supplementary Data, Fig. S4). The presence of water in **1** can be evidenced by the characteristic O–H stretching and bending vibrations of water in the IR spectrum (Supplementary Data, Fig. S5) which appear as a broad band at around 3546−3116 cm^{-1} and a strong signal in the region 1651 cm^{-1}, respectively. These peaks disappear completely when **1** is subjected to pyrolysis at 180 °C in a temperature controlled electric oven indicating loss of water (Supplementary Data, Fig. S5). Also, the formation of heptamolybdate core is indicated by the Raman spectrum of **1** (Supplementary Data, Fig. S6) which shows an intense band around 931 cm^{-1} assignable for the symmetric stretching vibration of the $\{MoO_6\}$ unit which builds up the $[Mo_7O_{24}]^{6-}$ core. This observation is further supported by the IR spectrum of **1**, which gives peaks attributable to various Mo-O stretching vibrations appearing at 837, 891, 727, 562, and 430 cm^{-1}.

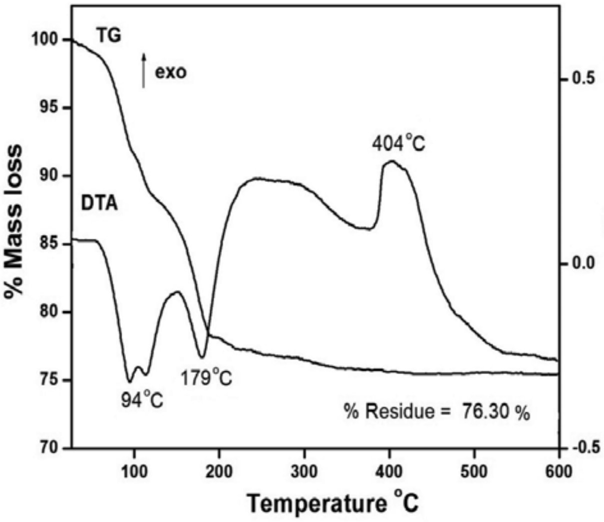
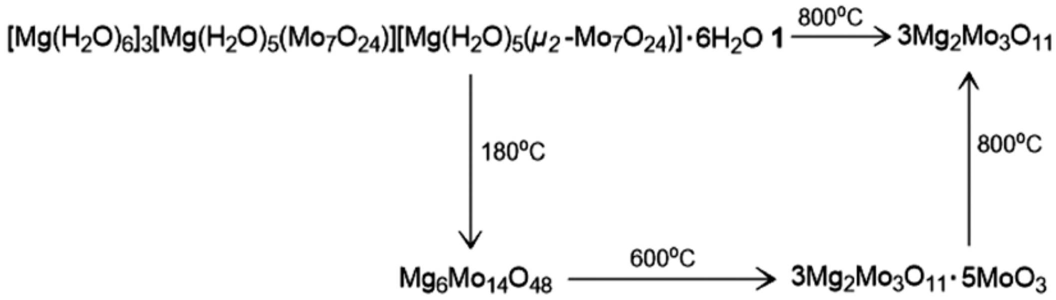


Fig. 3 — TG-DTA curves of **1**.

The thermal pattern of **1** (Fig. 3) shows an endothermic event at 94 °C in its DTA curve accompanied by a mass loss of 3.65% which can account for the loss of six lattice water molecules. Subsequently, two endothermic peaks are observed at 113 °C and 179 °C, which can explain the loss the rest of the water molecules. Above 20 °C, the DTA curve shows only exothermic peaks at 404 °C showing a residual mass of 76.30% which is in good agreement with the calculated residual mass (76.25 %) for a probable composition $Mg_6Mo_{14}O_{48}$. The pyrolysis study of **1** carried out at 600 °C in a furnace substantiates the above results. In order to identify the binary oxide phase the powder pattern of the pyrolyzed sample (600 °C) was compared with the powder patterns of reported possible oxide phases of Mo and Mg (Supplementary Data, Fig. S7). The X-ray powder pattern of the residue obtained reveals the formation of $Mg_2Mo_3O_{11}$. In addition, some peaks due to MoO_3 are also observed (Supplementary Data, Fig. S7).

This is also evidenced by the mass loss obtained (76.30%) accounting for the expected residual composition $3Mg_2Mo_3O_{11}\cdot5MoO_3$ (Scheme 1). Hence to get a pure oxide phase, **1** was heated at 800 °C for 2 h in a furnace. The powder pattern of the residue thus obtained (Fig. 4) is in good agreement with the reported $Mg_2Mo_3O_{11}$ phase (JCPDS No. 03-065-2421). These observations reveal that **1** can serve as an useful precursor to obtain a mixed metal oxide phase.

In recent reports from our laboratory[32,33] we have shown that dissolution of alkali-metal heptamolybdate compounds in water leads to their dissociation into hydrated ions resulting in high molar conductivity values with increasing dilution. Aqueous solutions containing different concentrations of **1** (Table 4) exhibit a similar trend of increasing molar conductivity with increasing dilution. This



Scheme 1 — Thermal decomposition of **1**.

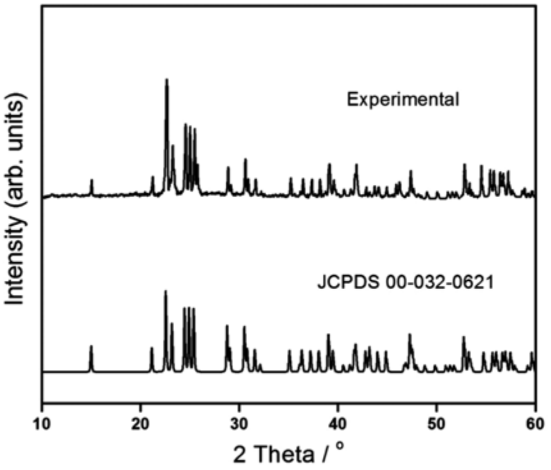


Fig. 4 — X-ray powder patterns of the residue obtained after pyrolysis of **1** at 800 °C and $Mg_2Mo_3O_{11}$ (JCPDS No. 00-032-0621).

Table 4 — Specific conductivity (Ꝁ) and molar conductivity (λ_m) data of **1**

Concentration (mole)	Specific conductivity (Ꝁ) (S cm^{-1})	Molar conductivity (λ_m) (S cm^2 mol^{-1})
0.1	0.0228	228
0.08	0.0235	235
0.06	0.0248	248
0.04	0.0309	309
0.02	0.0045	450

observation reveals that in solution the Mg(II) cations and the heptamolybdate anions are hydrated and are present as discrete ions and not as observed in the crystal structure of **1** wherein heptamolybdate is coordinated to Mg(II). The presence of hydrated $[Mo_7O_{24}]^{6-}$ species in an aqueous solution of **1** is further supported by a cyclic voltammetric study. The measured redox potential of **1** is referenced to a saturated calomel electrode (SCE). The cyclic voltammogram of **1** (Supplementary Data, Fig. S8) exhibits a single reversible redox event ($E_{1/2} = -0.551$ V) with a peak separation $\Delta E = 0.09$ V.

The redox potential of **1** is comparable with those of other known heptamolybdates $(NH_4)_6[Mo_7O_{24}]\cdot 4H_2O$[33] ($E_{1/2} = -0.538$ V), $(NH_4)_4[Li_2(H_2O)_7][Mo_7O_{24}]\cdot H_2O$ ($E_{1/2} = -0.579$ V)[15], $(NH_4)_3[Li_3(H_2O)_4(\mu_6\text{-}Mo_7O_{24})]\cdot 2H_2O$ ($E_{1/2} = -0.537$ V)[15], $[Rb_6(H_2O)_4(Mo_7O_{24})]$ ($E_{1/2} = -0.531$ V)[32] and $Na_6[Mo_7O_{24})]\cdot 14H_2O$ ($E_{1/2} = -0.605$ V)[33]. The nearly similar electrochemical behavior of all the above *s*-block metal heptamolybdates can be explained for the same redox event, proving the presence of free and not coordinated $(Mo_7O_{24})^{6-}$ anions in aqueous solution.

Conclusions

In this work, we have described a rational method for the synthesis of a hexamagnesium bis (heptamolybdate) containing coordinated and lattice water molecules. The all-inorganic compound **1** is a new example of an *s*-block metal compound which crystallizes in the acentric polar *Cc* space group and contains both hexaaqua and pentaaqua-magnesium(II) ions in addition to a monodentate and a μ_2-bridging bidentate heptamolybdate in the same compound. The electrochemical and ionic conductivity studies of **1** reveal the presence of discrete $[Mg(H_2O)_6]^{2+}$ dications and hydrated $[Mo_7O_{24}]^{6-}$ anions in solution. Thermal studies show that **1** is a useful precursor for the synthesis of the mixed metal oxide phase $Mg_2Mo_3O_{11}$.

Supplementary Data

Crystallographic data for the structure reported in this article have been deposited with FIZ-Karlsruhe as supplementary publication no. ICSD 432082 and can be obtained free of charge, on writing to FIZ, Hermann-von-Helmholtz-Platz 1, D-76344 Eggenstein -Leopoldshafen, Germany (Fax: 0049-7247-808-259), or Email: crysdata@fiz-karlsruhe.de. Supplementary Data associated with this article are available in the electronic form at: http://nopr.niscair.res.in/jinfo/ijca/IJCA_59A(04)517-525_SupplData.pdf.

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