

Synthesis, crystal structure and photochemistry of Hexakis(butan-1-aminium) heptamolybdate(VI) tetrahydrate

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Abstract. The synthesis, crystal structure, spectral characterization, photochemistry, electrochemical and thermal studies of the hexakis(butan-1-aminium) heptamolybdate(VI) tetrahydrate (**1**) are reported. Dissolution of a mixed mono-hepta compound $(\text{BuNH}_3)_8[(\text{Mo}_7\text{O}_{24})(\text{MoO}_4)] \cdot 3\text{H}_2\text{O}$ in water results in its transformation to the title compound *viz.*, $(\text{BuNH}_3)_6[\text{Mo}_7\text{O}_{24}] \cdot 4\text{H}_2\text{O}$ **1** (BuNH₃ = butan-1-aminium). The structure of the title compound consists of two crystallographically unique $[\text{Mo}_7\text{O}_{24}]^{6-}$ anions, twelve independent $(\text{BuNH}_3)^+$ cations and eight unique lattice water molecules, all of which are interlinked with the aid of three varieties of H-bonding interactions. Solar irradiation of **1** results in the formation of a bis(μ_2 -oxo) bridged diheptamolybdate product. Electrochemical studies reveal the role of **1** in the photodimerization process. Thermal decomposition of **1** results in the formation of crystalline α -MoO₃.

Keywords. Butan-1-aminium; heptamolybdate; H-bonding interactions; electrochemistry; photodimerization.

1. Introduction

Polyoxometalates (POMs) exhibit diverse structures and interesting properties and hence are studied by several researchers.^{1–9} Among the POM's of molybdenum, the structurally flexible heptamolybdate ion $[\text{Mo}_7\text{O}_{24}]^{6-}$ is known to exist in a variety of environments *viz.*, in combination with organic cations^{10–23} and/or metal complex cations.^{24–28} The heptamolybdates (Table 1) in which organic ammonium cations charge balance the $[\text{Mo}_7\text{O}_{24}]^{6-}$ ion exhibit interesting photochemistry.^{10,11,13,25,30,31} A survey of the reported synthetic protocols reveals that heptamolybdates are synthesized by a direct reaction of the commercially available $(\text{NH}_4)_6[\text{Mo}_7\text{O}_{24}] \cdot 4\text{H}_2\text{O}$ or MoO₃ with an organic amine or an appropriate metal containing reagent. Although some syntheses were performed under hydrothermal conditions¹² and in a few cases $\text{Na}_6[\text{Mo}_7\text{O}_{24}] \cdot 14\text{H}_2\text{O}$ or $\text{Na}_2\text{MoO}_4 \cdot 2\text{H}_2\text{O}$ were employed as a Mo source,^{21,22,29} it is interesting to note that except for the sodium rich $\text{Na}_7[\text{Mo}_7\text{O}_{24}]\text{OH} \cdot 21\text{H}_2\text{O}$ ²⁶ and the mixed monomolybdate-heptamolybdate compound¹⁰

$(\text{BuNH}_3)_8[(\text{Mo}_7\text{O}_{24})(\text{MoO}_4)] \cdot 3\text{H}_2\text{O}$ **1a** (BuNH₃ = butan-1-aminium), the final heptamolybdate product is always isolated from an acidic medium. Earlier, we reported¹⁰ the structural characterization of a heptamolybdate containing a cocrystallized $(\text{MoO}_4)^{2-}$ ion *viz.*, **1a**, which was isolated at a pH of ~ 8.0 by a room temperature reaction of MoO₃ with aqueous n-butylamine (BuNH₂). Prior to our work, Roman *et al.*,¹⁶ reported only the unit cell but not the atom coordinates of $(\text{BuNH}_3)_6[\text{Mo}_7\text{O}_{24}] \cdot 3\text{H}_2\text{O}$ isolated by a reaction of MoO₃ with aqueous BuNH₂ at 100°C. In order to determine the structure of a hexakis(butan-1-aminium) heptamolybdate devoid of any $(\text{MoO}_4)^{2-}$ ion, we have investigated the MoO₃/BuNH₂/water reaction system. During the course of these studies, we obtained the title compound $(\text{BuNH}_3)_6[\text{Mo}_7\text{O}_{24}] \cdot 4\text{H}_2\text{O}$ **1** serendipitously. The results of these investigations are described herein.

2. Experimental

2.1 Materials and methods

All the chemicals used in this study were of reagent grade and were used as received without any further purification. The known compound $(\text{BuNH}_3)_8[\text{Mo}_7\text{O}_{24}]$

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Dedicated to Prof. Parimal K Bharadwaj on the occasion of his 65th birthday

Table 1. List of structurally characterized heptamolybdate compounds containing organic counterions.

No	Compound	Space Group	Secondary Interactions	Ref
1	(H ₂ DABCO) ₃ [Mo ₇ O ₂₄]·4H ₂ O	<i>Cc</i>	O–H···O, N–H···O	11
2	(2-ampH) ₆ [Mo ₇ O ₂₄]·3H ₂ O	<i>P2₁/n</i>	O–H···O, N–H···O	12–14
3	(PyrNH ₂) ₆ [(Mo ₇ O ₂₄)·2H ₂ O	<i>P₁</i>	O–H···O, N–H···O, C–H···O	10
4	(PrNH ₃) ₆ [Mo ₇ O ₂₄]·3H ₂ O	<i>P₁</i>	O–H···O, N–H···O	10,15
5	(<i>i</i> PrNH ₃) ₆ [Mo ₇ O ₂₄]·3H ₂ O	<i>P2₁/n</i>	O–H···O, N–H···O	15
6	(PentNH ₃) ₆ [Mo ₇ O ₂₄]·3H ₂ O	<i>P2₁/n</i>	O–H···O, N–H···O	10,16
7	(HexNH ₃) ₆ [Mo ₇ O ₂₄]·3H ₂ O	<i>P2₁/n</i>	O–H···O, N–H···O	10,16
8	(BuNH ₃) ₆ [Mo ₇ O ₂₄]·3H ₂ O*	<i>P₁</i>	—	16
9	(<i>t</i> -BuNH ₃) ₆ [Mo ₇ O ₂₄]·7H ₂ O	<i>P2₁/n</i>	O–H···O, N–H···O, C–H···O	17
10	(TemedH ₂) ₃ [Mo ₇ O ₂₄]·4H ₂ O	<i>C2/c</i>	O–H···O, N–H···O	18
11	(4-apH) ₆ [Mo ₇ O ₂₄]·6H ₂ O	<i>P2₁/c</i>	O–H···O, N–H···O	19
12	(dienH ₃) ₂ [Mo ₇ O ₂₄]·4H ₂ O	<i>C2/c</i>	O–H···O, N–H···O, C–H···O	20
13	(dienH ₃) ₂ [Mo ₇ O ₂₄]·4H ₂ O	<i>P2₁/a</i>	O–H···O, N–H···O, C–H···O	20
14	(BuNH ₃) ₈ [(Mo ₇ O ₂₄)(MoO ₄)]·3H ₂ O	<i>P₁</i>	O–H···O, N–H···O, C–H···O	10
15	(BuNH ₃) ₆ [Mo ₇ O ₂₄]·4H ₂ O	<i>P2₁/c</i>	O–H···O, N–H···O, C–H···O	this work
16	(GuaNH ₂) ₆ [Mo ₇ O ₂₄]·H ₂ O	<i>C2/c</i>	O–H···O, N–H···O	21
17	(GuaNH ₂) ₆ [Mo ₇ O ₂₄]·H ₂ O	<i>P2₁/c</i>	O–H···O, N–H···O	22
18	[UreaH] ₃ (NH ₄) ₉ [Mo ₇ O ₂₄]·5[Urea]·4H ₂ O	<i>Fddd</i>	O–H···O, N–H···O	23
19	[2,3-diampH] ₄ [Co(H ₂ O) ₆][Mo ₇ O ₂₄]·6H ₂ O	<i>C2/c</i>	O–H···O, N–H···O, C–H···O	24
20	(hmtH) ₂ {[Mg(H ₂ O) ₅] ₂ {Mo ₇ O ₂₄ }}·3H ₂ O	<i>C2/c</i>	O–H···O, N–H···O, C–H···O	25

Abbreviations used: DABCO = 1,4-diazabicyclo[2.2.2]octane; 2-amp = 2-aminopyridine; (PyrNH₂)⁺ = pyrrolidinium; PrNH₂ = propan-1-amine; *i*PrNH₂ = isopropylamine; PentNH₂ = pentan-1-amine; HexNH₂ = hexan-1-amine; *t*BuNH₂ = *tert*-butylamine; Temed = *N, N, N, N*-tetramethylethylenediamine; (GuaNH₂)⁺ = guanidinium; 4-ap = 4-aminopyridine; dien = diethylentriamine.; 2,3-diamp = 2,3 diaminopyridine; BuNH₂ = butan-1-amine; * Atom coordinates are not reported.

[MoO₄]₃·3H₂O **1a** was prepared according to the literature report.¹⁰ 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 of compounds in solid state and in aqueous medium were recorded by using an Agiltron PeakSeeker Pro Raman instrument with 785 nm laser radiation for excitation and laser power set to 100 mW. The samples for Raman spectra were taken in a quartz cuvette. UV-Visible spectra were recorded using Shimadzu UV-2450 double beam spectrophotometer (200–800 nm) and (Agilent 8453) UV-Visible spectrophotometer (200–1100 nm) in water using quartz cells. Elemental analyses were performed on a Variomicro cube CHNS analyser. 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 32°C to 600°C, using a Netzsch STA- 409 PC thermal analyser, 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. The redox properties of the aqueous solutions of **1** and **1a** were studied using 0.1 M

KNO₃ 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 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.

2.2 Synthesis of hexakis(butan-1-aminium) heptamolybdate(VI) tetrahydrate **1**

The mono-hepta compound **1a** (2.0 g) was dissolved in distilled water (10 mL) and the solution was left aside for crystallization. Transparent crystals of **1** which formed after 2 days were isolated by filtration followed by washing with ice cold water. The crystals were air dried to obtain 1.70 g of **1** in ~88% yield with respect to **1a**. Anal. Calcd for (**1**) (%): C, 18.33; H, 5.13; N, 5.34; Found (%): C, 18.77; H, 4.78; N, 5.51; IR data (cm⁻¹): 3520, 2980, 2864, 2536, 2091, 1609, 1512, 1460, 1387, 1184, 1087, 1029, 904, 856, 663, 633, 547, 474; Raman data (cm⁻¹): 2967, 2933, 2918, 2879, 1441, 1079, 1049, 939, 904, 846, 363; UV- Vis data: 208 nm ($\epsilon = 24.7 \times 10^5 \text{ M}^{-1} \text{ cm}^{-1}$); Molar conductivity (λ_m) (0.02 M): 375 S cm² mol⁻¹; DTA (°C): 141 (endo), 271 (exo), 453 (exo).

2.3 X-ray crystal structure determination

The intensity data for **1** was collected with an Image Plate Diffraction System (IPDS-1) from STOE. The structure was solved with direct methods using SHELXS-97³² and refinement was done against F^2 using SHELXL-2014.³² All non-hydrogen atoms except some of the disordered C and N atoms were refined anisotropically. The C-H and N-H, H atoms were positioned with idealized geometry and refined using a riding model. The O-H, H atoms were located in difference map, their bond lengths were set to ideal values and afterwards they were refined using a riding model. Some of the organic cations are disordered and were refined using a split model using restraints (SAME). A numerical absorption correction was performed. Technical details of data acquisition and selected refinement results are listed in (Table 2).

3. Results and discussion

3.1 Crystal structure of $(\text{BuNH}_3)_6[\text{Mo}_7\text{O}_{24}]\cdot 4\text{H}_2\text{O}(\mathbf{1})$

The title compound **1** crystallises in the monoclinic space group $P2_1/c$ with all atoms situated in general positions. Its structure consists of two crystallographically

unique $[\text{Mo}_7\text{O}_{24}]^{6-}$ anions (Figure 1), eight independent lattice water molecule and twelve unique $(\text{BuNH}_3)^+$ cations five of which are disordered. The metric parameters of the $(\text{BuNH}_3)^+$ cations are in the normal range. The (Mo-O) bond lengths and (O-Mo-O) bond angles of the unique $[\text{Mo}_7\text{O}_{24}]^{6-}$ anions (Table S1 in Supplementary Information) agree well with reported data.^{10,25} Both the unique $[\text{Mo}_7\text{O}_{24}]^{6-}$ units are built up of seven edge sharing $\{\text{MoO}_6\}$ octahedra, and are very similar to the heptamolybdate first reported for the ammonium salt by Lindqvist.³³ It is interesting to note that the presence of lattice water in **1** is in accordance with our recent structure analysis of several heptamolybdates.³⁴ The lattice water can give rise to interesting water architecture for example in $(\text{BuNH}_3)_8[(\text{Mo}_7\text{O}_{24})(\text{MoO}_4)]\cdot 3\text{H}_2\text{O}$ ¹⁰ a water octamer was observed.

An analysis of the crystal structure of **1** reveals three varieties of H-bonding interactions namely N-H...O, O-H...O and C-H...O among $(\text{BuNH}_3)^+$ cations, lattice water and the heptamolybdate anions. The O atoms of the lattice water and the terminal O atoms of the unique $[\text{Mo}_7\text{O}_{24}]^{6-}$ anions function as H-acceptors. The H-atoms attached to the O of the lattice water, N and some C atoms of the organic cations act as H-donors. The O-H...O interactions among the lattice water molecules O61 and O62 result in a water dimer while

Table 2. Crystal data and structure refinement for $(\text{BuNH}_3)_6[\text{Mo}_7\text{O}_{24}]\cdot 4\text{H}_2\text{O} \mathbf{1}$.

Empirical formula	$\text{C}_{24}\text{H}_{80}\text{Mo}_7\text{N}_6\text{O}_{28} \mathbf{1}$
Formula weight	1572.52
Temperature	170(2) K
Wavelength	0.71073 Å
Crystal system, space group	Monoclinic, $P2_1/c$
Unit cell dimensions	$a = 21.2962(11)$ Å $b = 15.8321(9)$ Å $c = 32.0204(19)$ Å $\beta = 94.831(7)^\circ$
Volume	$10757.8(10)$ Å ³
Z, Calculated density	8, 1.942 mg/m ³
Absorption coefficient	1.662 mm^{-1}
F(000)	6272
Crystal size	$0.12 \times 0.08 \times 0.06 \text{ mm}^3$
θ range for data collection	1.76° to 24.97°
Limiting indices	$-25 < h \leq 22$, $-14 \leq k \leq 18$, $-37 \leq l \leq 37$
Reflections collected/unique	47199/18450 [R(int) = 0.0358]
Reflections with $[I > 2\sigma(I)]$	15276
Min/max transmission	Numerical
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	18450/11/1201
Goodness of fit on F^2	1.020
Final R indices $[I > 2\sigma(I)]$	R1 = 0.0338, wR2 = 0.0849
R indices (all data)	R1 = 0.0435, wR2 = 0.0893
Largest diff. peak and hole	0.779 and -0.818 e.Å^{-3}

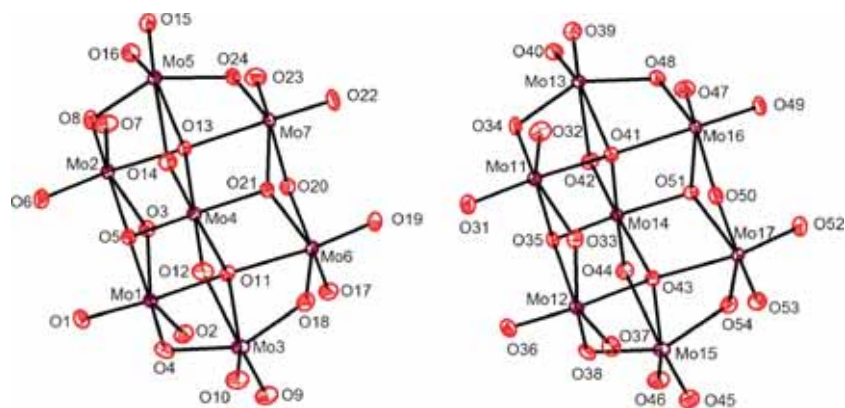


Figure 1. The atom-labelling scheme for the unique $[\text{Mo}_7\text{O}_{24}]^{6-}$ ions in **1**. Displacement ellipsoids are drawn at 30% probability level. For clarity, the butan-1-aminium cations and the lattice water molecules (Figure S1) in the crystal structure of **1** are not shown.

O63, O64, O65, O66 and O67 form a pentamer (Figure 2). In addition, all eight lattice water molecules *viz.* dimer, pentamer and O68 are involved in O-H...O interactions (Table 3) with four symmetry related heptamolybdate anions (Figure 2). The H-atoms attached to nitrogen and carbon of organic cations are linked to the heptamolybdate anions and six of the lattice water molecules (O61, O62, O64, O66, O67 and O68) with the aid of N-H...O and C-H...O interactions. In view of the disordered nature of five of the twelve unique $(\text{BuNH}_3)^+$ cations, a detailed description of the H-bonding situation around organic cations (Table S2) is not given. The net result of the H-bonding interaction is the organization of cations and anions in alternating layers with lattice water serving as links between the two layers (Figure S2).

In a very early study, Yamase^{30,31} explained the mechanism of photoredox process in alkylammonium heptamolybdates revealing the importance of H-bonding interactions. Like several other organic heptamolybdates, the title compound **1** also exhibits photochromism (*vide infra*). An analysis of the secondary interactions in organic heptamolybdates (Table 1) reveals that in many structurally characterized $[\text{Mo}_7\text{O}_{24}]^{6-}$ compounds, three varieties of H-bonds are present as in **1**.

3.2 Synthetic aspects, spectral characteristics and thermal studies

The mixed mono-hepta compound **1a**, was used as a precursor for the synthesis of the title heptamolybdate **1** (Scheme 1).

At room temperature MoO_3 dissolves in aqueous BuNH_2 to form a clear colourless solution (pH ~ 11.4). The Raman spectrum of the reaction mixture (Figure S3) reveals the presence of $(\text{MoO}_4)^{2-}$ ions in solution in the form of an intense band at 892 cm^{-1} assignable for

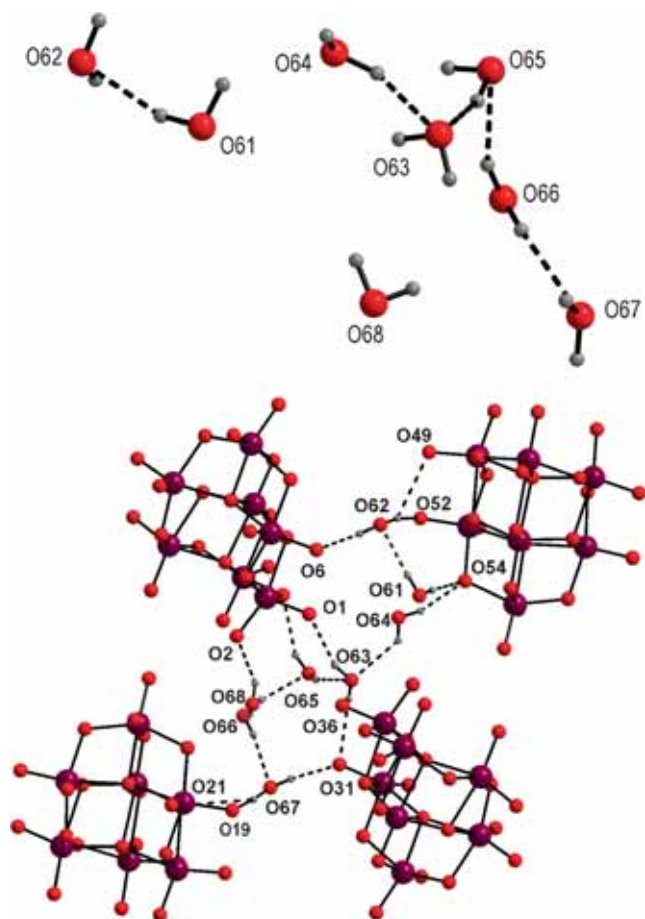
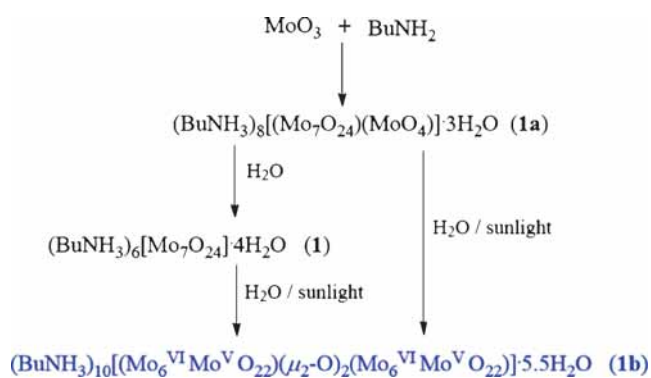


Figure 2. The H-bonding interactions among lattice water molecules in $(\text{BuNH}_3)_6[\text{Mo}_7\text{O}_{24}]\cdot 4\text{H}_2\text{O}$ **1**, showing the water dimer (O61 and O62) and water pentamer (O63, O64, O65, O66 and O67) (**top**). The lattice water molecules are linked to heptamolybdate anions via O-H...O bonding (**bottom**). (For symmetry relations, see Table 3).

the symmetric stretching vibration (ν_1) of the $(\text{MoO}_4)^{2-}$ tetrahedron.³⁶ Slow evaporation of the reaction mixture leads to the nucleation of crystals at pH ~ 8 . The

Table 3. Geometrical parameters (Å, °) of the O–H···O interactions in **1**.

D-H	d(D-H)	d(H···A)	<DHA	d(D···A)	A	Symmetry codes
O61-H1O	0.840	2.00	2.834(4)	2.834(4)	O54	-x+1, -y+1, -z+1
O61-H2O	0.840	2.04	2.853(4)	2.853(4)	O62	-x, -y+1, -z+1
O62-H3O	0.840	1.93	2.753(4)	2.753(4)	O6	
O62-H4O	0.840	2.02	2.793(4)	2.793(4)	O52	x-1, y, z
O62-H4O	0.840	2.59	3.110(4)	3.110(4)	O49	x-1, y, z
O63-H5O	0.840	2.05	2.841(4)	2.841(4)	O1	
O63-H6O	0.840	2.33	3.071(4)	3.071(4)	O31	-x+1, y-1/2, -z+3/2
O63-H6O	0.840	2.53	3.155(5)	3.155(5)	O36	-x+1, y-1/2, -z+3/2
O64-H7O	0.840	2.02	2.838(4)	2.838(4)	O54	-x+1, -y+1, -z+1
O64-H8O	0.840	2.27	2.914(5)	2.914(5)	O63	-x, -y+1, -z+1
O65-H9O	0.840	2.2	2.977(4)	2.977(4)	O4	
O65-H10O	0.840	2.08	2.866(6)	2.866(6)	O63	
O66-H11O	0.840	2.16	2.989(6)	2.989(6)	O67	
O66-H12O	0.840	2.02	2.813(7)	2.813(7)	O65	-x+1, y+1/2, -z+3/2
O67-H13O	0.840	1.98	2.816(5)	2.816(5)	O31	
O67-H14O	0.840	2.19	2.892(5)	2.892(5)	O19	
O67-H14O	0.840	2.55	3.214(4)	3.214(4)	O21	
O68-H15O	0.840	2.15	2.933(5)	2.933(5)	O2	-x+1, y+1/2, -z+3/2

**Scheme 1.** Synthesis and photochemistry of $(\text{BuNH}_3)_6[\text{Mo}_7\text{O}_{24}] \cdot 4\text{H}_2\text{O}$ **1**.

crystalline product, thus formed has been structurally characterized as a mixed mono-hepta compound namely **1a** and not the butan-1-aminium salt of $(\text{MoO}_4)^{2-}$ as reported earlier.¹⁰ In order to prepare a pure heptamolybdate devoid of $(\text{MoO}_4)^{2-}$, several experiments were performed with the $\text{MoO}_3/\text{BuNH}_2$ system by varying temperature and stoichiometry. However, all these attempts were not fruitful to obtain a heptamolybdate as well as the product reported by Roman *et al.*¹⁶ All reactions resulted in the formation of only the mixed mono-hepta compound **1a**. When crystals of **1a** were taken in water, the pH of the reaction medium was found to be acidic (pH~6). The Raman spectrum of the acidic reaction mixture (Figure S3) exhibits an intense signal at 939 cm^{-1} assignable for the symmetric stretching vibration of the $\{\text{MoO}_6\}$ unit, giving a definite clue for the presence of $(\text{Mo}_7\text{O}_{24})^{6-}$ ions in solution. Since heptamolybdates are generally isolated from acidic medium,³⁵ compound **1a** was dissolved in water

and the reaction mixture was left aside for slow evaporation to isolate the product. The powder pattern of the product was found to be different from the starting **1a** (Figure S4) indicating **1a** loses its identity in water leading to its transformation to a new product. The X-ray structure analysis (*vide supra*), revealed it to be the desired pure heptamolybdate **1** in view of the absence of $(\text{MoO}_4)^{2-}$ ion. The phase purity of the product was confirmed by a comparison of experimental X-ray powder pattern with that calculated from single crystal data (Figure S5).

The optical spectrum of **1** exhibits a strong absorption centred at around 208 nm (Figure S6) indicating the presence of heptamolybdate species. The IR spectrum of **1** shows several signals in the mid-IR region indicating the presence of organic moieties (Figure S7). The broad absorption seen around 3500 cm^{-1} in IR spectra of **1** can be attributed to the O–H stretching vibration of lattice water.³⁶ A signal appearing at around 3000 cm^{-1} can be assigned to the symmetric vibrations of the {N-H} moiety of organic ammonium cation. In **1** the symmetric stretching mode of the $\{\text{MoO}_6\}$ unit appears as an intense band in Raman spectrum at 939 cm^{-1} while the doubly degenerate asymmetric stretching mode occurs as a strong signal centred around 904 cm^{-1} in the IR spectrum.³⁷ A doublet centred around 663 and 633 cm^{-1} can be attributed to (Mo-O-Mo) vibrations.

Thermal analysis of **1** did not show any mass loss till $\sim 100^\circ\text{C}$. In the TG curve a decrease in mass of 4.60% accompanied by an endothermic event at 141°C in DTA curve (Figure 3) is observed. This can be attributed to the loss of four water molecules. Above 200°C , the

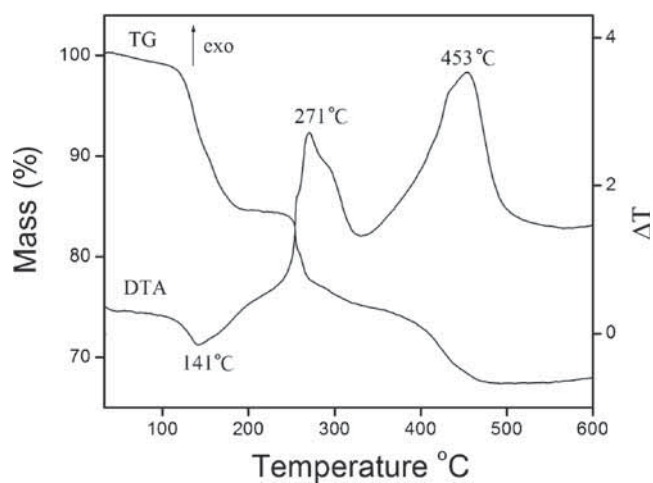


Figure 3. TG-DTA curves of $(\text{BuNH}_3)_6[\text{Mo}_7\text{O}_{24}]\cdot 4\text{H}_2\text{O}$ **1**.

DTA curve shows two exothermic peaks at 271 and 453°C, respectively, which can be assigned to the decomposition of the anhydrous organic heptamolybdate, leaving a residue of 64.23%. The residual mass obtained is in good agreement with the calculated residual mass (64.10%) for a probable residual composition of 7MoO_3 . The results obtained are in accordance with the pyrolysis study of **1** carried out at 600°C in a furnace. The percentage residual mass obtained and its matching powder pattern with the reported orthorhombic $\alpha\text{-MoO}_3$ (JCPDS No. 03-065-2421) presents good evidence for the formation of the phase pure $\alpha\text{-MoO}_3$ (Figure 4). Based on satisfactory elemental analysis, spectral data and thermal studies, the composition of **1** is found to be 6:1:4 for organic cation:heptamolybdate:water.

An aqueous solution of **1** or the pristine solid does not undergo any detectable changes when kept under diffused light in the laboratory for extended periods of time. In contrast, an aqueous solution of **1** turns to intense blue under solar irradiation for ~ 30 min. This photochemical behaviour is very similar to that of **1a**. A comparison of the optical spectra of the blue solution obtained by irradiation of **1** and **1a** reveals that both spectra are identical with absorption maxima at 610 and 734 nm (Figure S8 in Supplementary Information) indicating the presence of the same chromophore in both solutions. The blue product obtained by irradiation of **1a** has been structurally characterized and shown to be a bis(μ_2 -oxo)bridged diheptamolybdate $(\text{BuNH}_3)_{10}[(\text{Mo}_6^{\text{VI}}\text{Mo}^{\text{V}}\text{O}_{22})(\mu_2\text{-O})_2(\text{Mo}_6^{\text{VI}}\text{Mo}^{\text{V}}\text{O}_{22})]\cdot 5.5\text{H}_2\text{O}$ **1b** and a detailed photochemistry of **1a** has been described in our earlier report.¹⁰ Based on the synthetic protocol of **1** and the identical spectra of the irradiated products of **1** and **1a** the formation of the blue solution can be explained as follows: When the mono-hepta compound

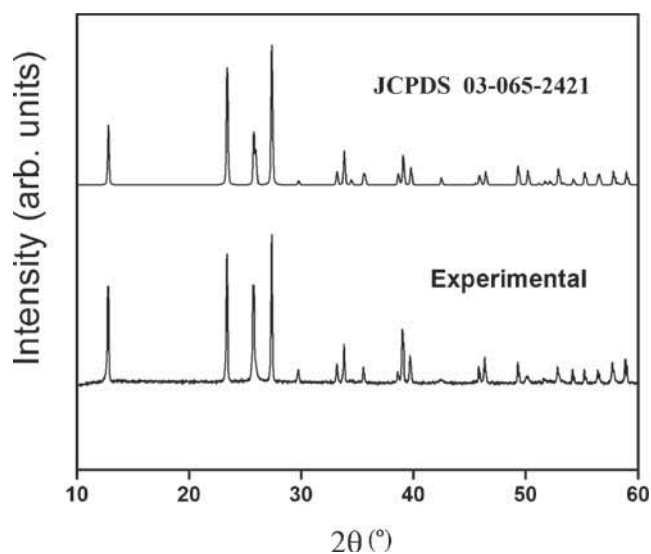


Figure 4. X-ray powder patterns of $\alpha\text{-MoO}_3$ (JCPDS-03-065-2421) and the residue obtained after pyrolysis of $(\text{BuNH}_3)_6[\text{Mo}_7\text{O}_{24}]\cdot 4\text{H}_2\text{O}$ **1** at 600°C.

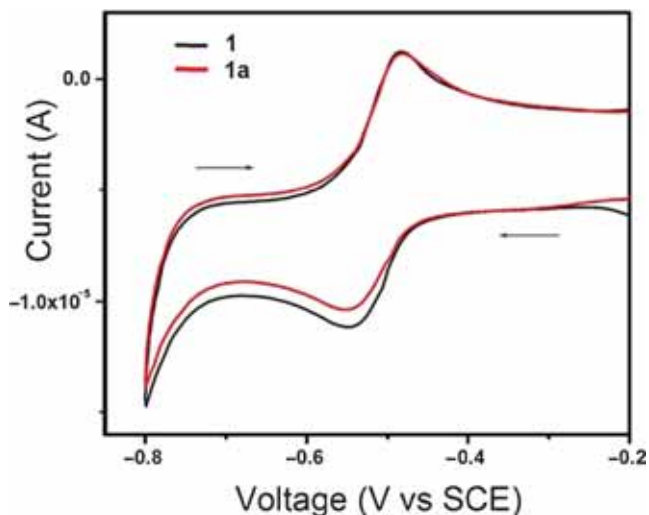
1a is dissolved in water it first transforms to a pure heptamolybdate devoid of $(\text{MoO}_4)^{2-}$ namely **1**, which then dimerizes to the blue bis(μ_2 -oxo) bridged diheptamolybdate **1b** (Scheme 1) under solar irradiation. Hence, we propose that compound **1** is an intermediate in the formation of the reduced bis(μ_2 -oxo) diheptamolybdate from **1a**. The above proposal gains more credence from the electrochemical investigations of **1** and **1a**.

3.3 Conductivity measurements and cyclic voltammetry

The specific and molar conductivity data of aqueous solutions containing different concentrations of **1** and **1a** (Table 4) exhibit a similar trend. The molar conductivity values show a steady increase with dilution indicating the facile dissociation of **1** and **1a** in dilute solution, which is in accordance with the crystal structure of **1** and **1a** showing discrete ions. The molar conductivity of **1** [(λ_m) (0.02 M): $375 \text{ S cm}^2 \text{ mol}^{-1}$] is slightly less than that of $(\text{NH}_4)_6[\text{Mo}_7\text{O}_{24}]\cdot 4\text{H}_2\text{O}$ [(λ_m) (0.02 M): $525 \text{ S cm}^2 \text{ mol}^{-1}$], but shows a pronounced decrease when compared with the λ_m of $(\text{NH}_4)_4[\text{Li}_2(\text{H}_2\text{O})_7][\text{Mo}_7\text{O}_{24}]\cdot \text{H}_2\text{O}$ [(λ_m) (0.02 M): $1119 \text{ S cm}^2 \text{ mol}^{-1}$]³⁴ and $(\text{NH}_4)_3[\text{Li}_3(\text{H}_2\text{O})_4(\mu_6\text{-Mo}_7\text{O}_{24})]\cdot 2\text{H}_2\text{O}$ [(λ_m) (0.02 M): $953 \text{ S cm}^2 \text{ mol}^{-1}$].³⁴ The conductivity data can be explained due to the different cations in these compounds. The observed data indicate that substitution of an ammonium ion by an organic ammonium cation does not affect the conductivity much unlike its substitution by a smaller Li^+ cation. It is interesting to note that an aqueous solution of **1** or **1a** exhibits nearly identical molar conductivity despite the presence of eight organic cations and an $(\text{MoO}_4)^{2-}$ ion

Table 4. Specific conductivity (κ) and molar conductivity (λ_m) data of **1** and **1a**.

Molar Concentration (M)	Specific conductivity (κ) (in S cm ⁻¹)		Molar conductivity (λ_m) (S cm ² mol ⁻¹)	
	1	1a	1	1a
0.1	0.0125	0.0127	125	127
0.08	0.0122	0.0123	152	153
0.06	0.0117	0.0119	195	198
0.04	0.0112	0.0113	280	282
0.02	0.0075	0.0077	375	385

**Figure 5.** Cyclic voltammograms of $(\text{BuNH}_3)_6[\text{Mo}_7\text{O}_{24}] \cdot 4\text{H}_2\text{O}$ **1** and $(\text{BuNH}_3)_8[(\text{Mo}_7\text{O}_{24})(\text{MoO}_4)] \cdot 3\text{H}_2\text{O}$ **1a** at a scan rate of 0.03 V s^{-1} .

in the formula of **1a** for each heptamolybdate unlike the six organic cations in **1** for each $[\text{Mo}_7\text{O}_{24}]^{6-}$. The similar conductivity data of aqueous solutions of **1** and **1a** not only reveal the absence of $(\text{MoO}_4)^{2-}$ in an aqueous solution of **1a** but also confirm that the ionic species present in solution in both cases is one and the same *viz.*, $(\text{BuNH}_3)^+$ and $[\text{Mo}_7\text{O}_{24}]^{6-}$.

The existence of only $[\text{Mo}_7\text{O}_{24}]^{6-}$ species in an aqueous solution of (**1** or **1a**) is further supported by the cyclic voltammetric study. All potentials in this work are referenced to the saturated calomel electrode (SCE). It is interesting to note that the current-voltage graphs of **1** and **1a** are nearly identical (Figure 5) and both exhibit a single reversible redox event ($E_{1/2} = -0.512 \text{ V}$) with a peak separation $\Delta E = 0.06 \text{ V}$. The redox potential of **1** (or **1a**) is quite comparable with those of other known heptamolybdates $(\text{NH}_4)_6[\text{Mo}_7\text{O}_{24}] \cdot 4\text{H}_2\text{O}$ ($E_{1/2} = -0.538 \text{ V}$),³⁴ $(\text{NH}_4)_4[\text{Li}_2(\text{H}_2\text{O})_7][\text{Mo}_7\text{O}_{24}] \cdot \text{H}_2\text{O}$ ($E_{1/2} = -0.579 \text{ V}$)³⁴ and $(\text{NH}_4)_3[\text{Li}_3(\text{H}_2\text{O})_4(\mu_6\text{-Mo}_7\text{O}_{24})] \cdot 2\text{H}_2\text{O}$ ($E_{1/2} = -0.537 \text{ V}$)³⁴ unlike the differing conductivity data. The observation of identical redox response in aqueous solutions of **1** and **1a** serves to confirm the

transformation of the mixed mono-hepta **1a** to a pure heptamolybdate **1**.

4. Conclusions

The investigations of the $\text{MoO}_3/\text{BuNH}_2/\text{water}$ reaction system reveal that MoO_3 dissolves in aqueous BuNH_2 . Although the clear reaction mixture contains $(\text{MoO}_4)^{2-}$ ions as evidenced by its Raman spectrum, slow evaporation results in the formation of a known mixed mono-hepta compound $(\text{BuNH}_3)_8[(\text{Mo}_7\text{O}_{24})(\text{MoO}_4)] \cdot 3\text{H}_2\text{O}$ **1a** and not the butan-1-aminium salt of $(\text{MoO}_4)^{2-}$. The title heptamolybdate charge balanced by $(\text{BuNH}_3)^+$ cations and devoid of any $(\text{MoO}_4)^{2-}$ can be crystallized as a tetrahydrate *viz.*, $(\text{BuNH}_3)_6[\text{Mo}_7\text{O}_{24}] \cdot 4\text{H}_2\text{O}$ **1** by dissolution of **1a** in water. The crystal structure, spectral and thermal characteristics of **1** is reported. The identical photochemical behaviour of **1** and **1a** to give a blue solution on irradiation and the identical conductivity and redox characteristics reveal that compound **1** is an intermediate in the formation of photodimerized bis(μ_2 -oxo) bridged diheptamolybdate **1b** from **1a**.

Supplementary Information (SI)

Electronic supplementary information (for Figures S1–S8, Tables S1–S2) is available at www.ias.ac.in/chemsci.

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