

# Synthesis and structural characterization of $(C_{14}H_{16}N_2)_3(C_{14}H_{17}N_2)_2[\beta-Mo_8O_{26}]$

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**Abstract.** A novel polyoxomolybdate  $(C_{14}H_{16}N_2)_3(C_{14}H_{17}N_2)_2[\beta-Mo_8O_{26}]$  (**1**) has been synthesized from hydrothermal reaction of tolidine and molybdenum trioxide in water and characterized by its IR and UV spectra, <sup>1</sup>H NMR, cyclic voltammetry and single crystal X-ray diffraction. Compound **1** crystallizes in the triclinic crystal system, space group *P* $\bar{1}$ , with the crystal cell parameters of  $a=11.5360$  Å,  $b=11.6080$  Å,  $c=15.2520$  Å,  $\alpha=72.50^\circ$ ,  $\beta=79.46^\circ$ ,  $\gamma=86.91^\circ$ ,  $V=1915.00$  Å<sup>3</sup> and  $Z=1$ . The asymmetric unit of the crystal structure of  $(C_{14}H_{16}N_2)_3(C_{14}H_{17}N_2)_2[\beta-Mo_8O_{26}]$  contains  $\beta$ -octamolybdate  $[\beta-Mo_8O_{26}]^{4-}$  anions, two tolidine molecules and shows the presence of monoprotonated tolidine cations. One tolidine molecule and a  $\beta-Mo_8O_{26}$  polyanions species lie across crystallographic inversion centres while the two tolidine molecules occupy general sites.

**Keywords.**  $\beta$ -Octamolybdate; Crystal structure; Electronic properties.

## 1. Introduction

Polyoxometalates (POMs) have attracted considerable attention due to potential applications in a variety of fields, including catalysis, analytic chemistry, medicine and materials science.<sup>1–5</sup> In particular, the chemistry of coordination compounds of polyoxomolybdates with organic ligands provides knowledge about the interactions of small organic molecules with polyoxometalates surfaces.<sup>6</sup> Furthermore, it is noteworthy that an important field in the polyoxomolybdates is the structural chemistry of the well-known polyoxomolybdate anion,  $[Mo_8O_{26}]^{4-}$ . An interesting aspect of octamolybdates is seen in varied structural patterns in the solid state and in their structural flexibility in solution.<sup>7</sup> Six isomeric forms of octamolybdate  $[Mo_8O_{26}]^{4-}$  have been prepared.<sup>8–13</sup> The  $\alpha$ - and  $\beta$ -forms have been crystallographically confirmed in several hybrid materials.<sup>14,15</sup> The  $\gamma$ -isomer has been found in  $[(CH_3)_3N(CH_2)_6N(CH_3)_3]_2[Mo_8O_{26}].2H_2O$ .<sup>12</sup> The  $\delta$ -isomer in  $[(RhcP^*)_2(\mu-SCH_3)_3]_4[Mo_8O_{26}].2CH_3CN$ ,<sup>7</sup>  $(2,4,6\text{-tripyridyl triazine})_2[Mo_8O_{26}].2H_2O$ <sup>16</sup> and  $[\{Cu(4,4\text{-bipy})\}_4(Mo_8O_{26})]^{13}$  has also been recently characterized. More recently, the  $\epsilon$  and  $\zeta$ -isomers have been characterized in the products of hydrothermal reactions.<sup>13,17</sup> The structures of the six octamolybdate isomers differ in the types of polyhedron that

fuse to form the cluster and in the linkage between polyhedral,<sup>7–18</sup> however, they are all composed of only two different molybdenum polyhedra. To the best of our knowledge, the octamolybdate isomers that contain Mo(VI) in three different types of coordination have not been observed hitherto.

These octamolybdate isomers are versatile inorganic building blocks for constructing new organic–inorganic hybrid materials with desirable properties.<sup>19</sup> In this paper, we report the hydrothermal synthesis and X-ray crystal structure determination of a new  $\beta$ -octamolybdate,  $(C_{14}H_{16}N_2)_3(C_{14}H_{17}N_2)_2 \beta-[Mo_8O_{26}]$  which has been characterized by IR and UV-Vis spectra, <sup>1</sup>H NMR, cyclic voltammetric data and electronic properties. The structure consists of alternating organic and inorganic layers; the inorganic layers are formed by  $[Mo_8O_{26}]^{4-}$  anions and the organic layers are built of  $(C_{14}H_{17}N_2)^+$  cations and  $(C_{14}H_{16}N_2)$  molecules.

## 2. Experimental

### 2.1 Materials and methods

Commercially available Molybdenum trioxide  $MoO_3$ , tolidine  $C_{14}H_{16}N_2$ , lithium perchlorate  $LiClO_4$ , dimethylformamide sulfoxide DMSO, were used without further purification. Hydrothermal synthesis has been carried out using a 23 mL Teflon-lined autoclave. IR

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spectra were obtained as KBr pellets on a FTIR-8201PC SHIMADZU spectrophotometer.  $^1\text{H}$  NMR spectra were recorded on a Bruker Avance DPX 250 (250Hz). UV-Vis spectra were recorded on a Jasco V-660 spectrophotometer. Cyclic voltammetry measurements were performed in a one-compartment cell with the use of a PGZ workstation at room temperature. The working and counter electrodes were platinum disk with a surface area of  $1\text{ mm}^2$  and platinum wire, respectively. All potentials were referred to a saturated calomel electrode (SCE). The typical solutions in DMSO were  $5.10^{-3}\text{ mol.L}^{-1}$  in  $\text{LiClO}_4$ , 0.1M. All solutions were deaerated by a dry nitrogen stream, maintained at a slight  $\text{N}_2$  overpressure during the experiments.

## 2.2 Hydrothermal synthesis

$(\text{C}_{14}\text{H}_{16}\text{N}_2)_3(\text{C}_{14}\text{H}_{17}\text{N}_2)_2[\text{Mo}_8\text{O}_{26}]$  (**1**) was synthesized from the reaction mixture of  $\text{C}_{14}\text{H}_{16}\text{N}_2$  (0.212 g, 2 mmol) and  $\text{MoO}_3$  (0.144 g, 1 mmol) in 6 mL of distilled water. The resulting solution was adjusted to about pH 5-7 with 6M HCl. After stirring for 30 min, the mixture was transferred to a 23 mL sealed Teflon-lined reactor and heated at  $140^\circ\text{C}$  for 24 h. After cooling the autoclave to room temperature for 48 h, yellow-green crystals obtained were filtered, washed several times with distilled water and dried in air.

## 2.3 X-ray crystallographic study

Single crystal of compound (**1**) with dimension  $0.22 \times 0.15 \times 0.09\text{ mm}$  was carefully selected for single crystal X-ray diffraction analysis. Data collection was performed on a APEXII, Bruker-AXS diffractometer with  $\text{MoK}\alpha$  monochromatic radiation ( $\lambda=0.71073\text{ \AA}$ ) at 150(2) K. Empirical absorption correction was applied. The structure was refined by the full matrix least-squares method on  $F^2$  using the SHELXL-97 crystallographic software package.<sup>20</sup> Anisotropic thermal parameters were used to refine all non-hydrogen atoms.

The methyl H atoms and ammonium H atoms were constrained to an ideal geometry ( $\text{C}-\text{H} = 0.96\text{ \AA}$ ,  $\text{N}-\text{H} = 0.91\text{ \AA}$ ) with  $U_{\text{iso}}(\text{H}) = 1.5 U_{\text{eq}}(\text{C})$  and  $U_{\text{iso}}(\text{H}) = 1.5 U_{\text{eq}}(\text{N})$ , but were allowed to rotate freely about the  $\text{C}-\text{C}$  and  $\text{C}-\text{N}$  bonds. H atoms of amino groups were constrained to an ideal geometry  $\text{N}-\text{H} = 0.88\text{ \AA}$  with  $U_{\text{iso}}(\text{H}) = 1.2 U_{\text{eq}}(\text{C})$ . All remaining H atoms were placed in geometrically idealized positions ( $\text{C}-\text{H} = 0.95\text{ \AA}$ ) and constrained to ride on their parent atoms with  $U_{\text{iso}}(\text{H})$  values of  $1.2 U_{\text{eq}}(\text{C})$ . Crystal data are listed in table 1.

**Table 1.** Crystal data and structure refinements for  $(\text{C}_{14}\text{H}_{16}\text{N}_2)_3(\text{C}_{14}\text{H}_{17}\text{N}_2)_2[\text{Mo}_8\text{O}_{26}]$ .

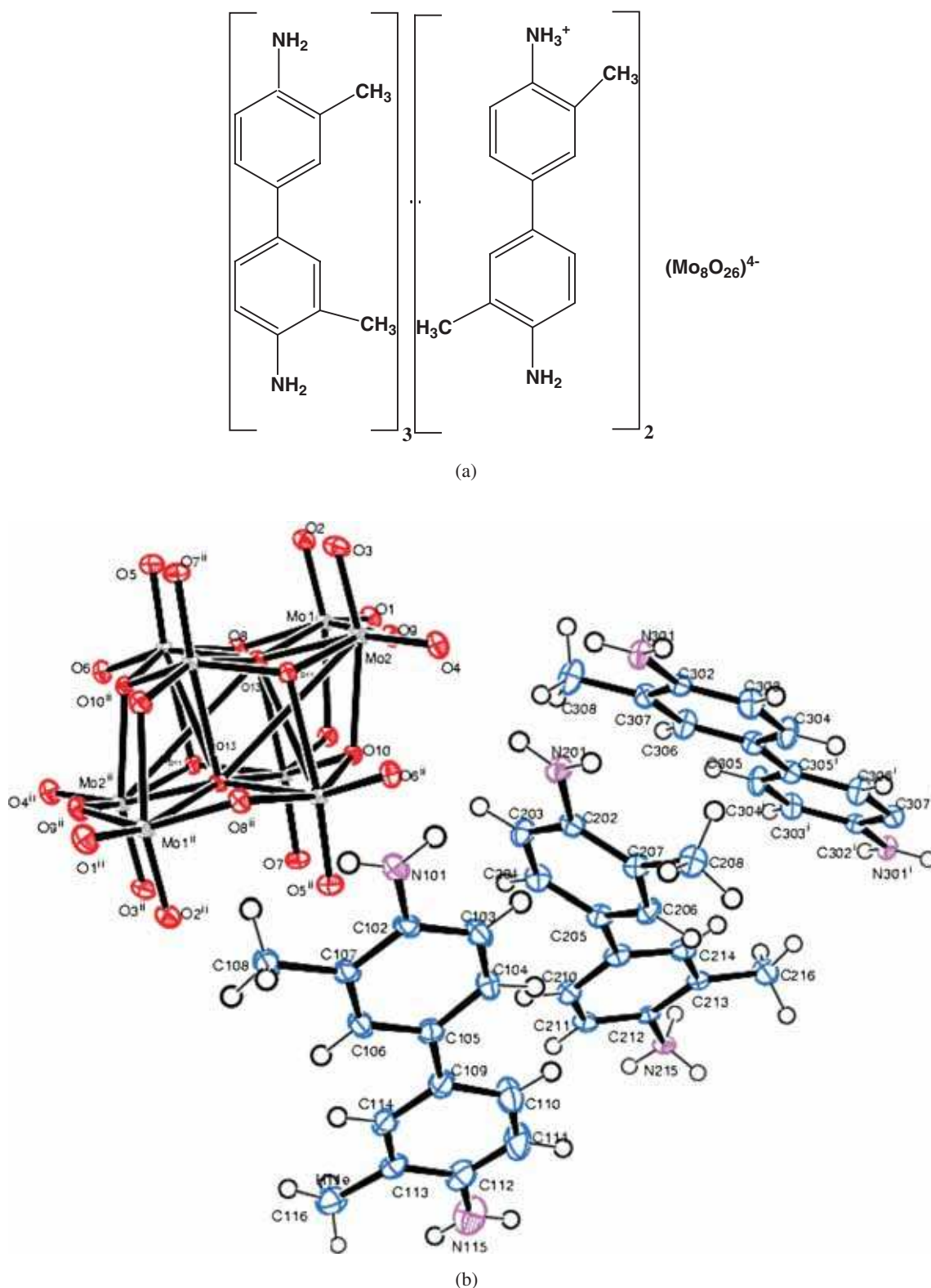
Molecule formula	$\text{C}_{70}\text{H}_{82}\text{Mo}_8\text{N}_{10}\text{O}_{26}$
Molecule weight	2246.98
Wavelength ( $\text{\AA}$ )	0.71073
Crystal system	Triclinic
Space group	P-1
a ( $\text{\AA}$ )	11.5453(15)
b ( $\text{\AA}$ )	11.6342(15)
c ( $\text{\AA}$ )	15.2755(19)
$\alpha$ (deg)	72.375(5)
$\beta$ (deg)	79.327(5)
$\gamma$ (deg)	86.852(6)
V ( $\text{\AA}^3$ )	1921.7(4)
Z	1
$\mu$ ( $\text{mm}^{-1}$ )	1.348
T (K)	150
Reflections measured	27416
Reflections independent	8736
Limiting indices	$-14 \leq h \leq 14$ , $-15 \leq k \leq 15$ , $-19 \leq l \leq 13$
Crystal size (mm)	$0.22 \times 0.15 \times 0.09$
Diffractometer	APEXII, Bruker-AXS

## 3. Results and Discussion

### 3.1 Crystal structure

In the present work, the synthesis by the hydrothermal method of  $\text{MoO}_3$  and 3,3'-dimethyl-4,4'-diaminobiphenyl resulted in the compound  $(\text{C}_{14}\text{H}_{16}\text{N}_2)_3(\text{C}_{14}\text{H}_{17}\text{N}_2)_2[\text{Mo}_8\text{O}_{26}]$ . As shown in figure 1, the compound contains six subunits (in a 3:2:1 ratio), *viz.*  $(\text{C}_{14}\text{H}_{16}\text{N}_2)$  molecules, a cationic group  $(\text{C}_{14}\text{H}_{17}\text{N}_2)^+$  and its anionic counterpart,  $\beta\text{-}[\text{Mo}_8\text{O}_{26}]^{4-}$  cluster. The octamolybdate anion and one tolidine molecule lie around an inversion center.

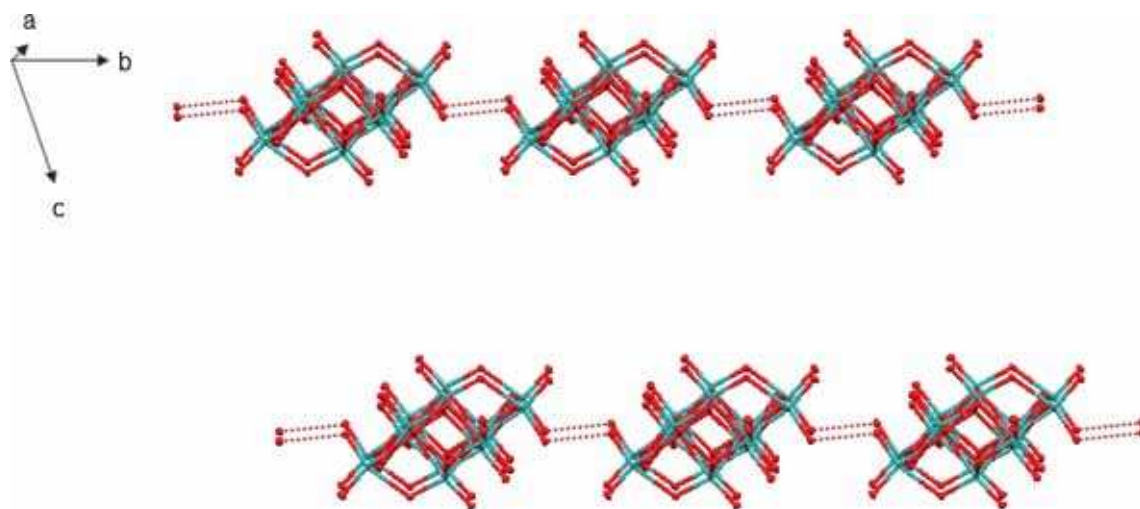
The structure of title compound **1** consists of  $\beta\text{-}\text{Mo}_8\text{O}_{26}$  polyanions and organic cations. These anions are constituted by eight  $\text{MoO}_6$  octahedra sharing edges and corners. The octahedra have different Mo-O bonds, which can be classified as short terminal [1.69019(9)–1.7219(9)  $\text{\AA}$ ], intermediate length lying in the range [1.7612(8)  $\text{\AA}$  - 1.9560(8)  $\text{\AA}$ ] binding Mo1 with O11 and Mo1 with O4 and long bonds [1.9986(8)–2.4754(8)  $\text{\AA}$ ]. In the octamolybdate anion, there are three different types of  $\text{MoO}_6$  octahedra: (i) octahedra formed by atoms Mo1 and Mo1a, which, being closest to the centroid of the polyanion, are the least distorted; (ii) octahedra formed by atoms Mo2 and Mo2a, which are the most distorted since they are farthest from the centroid; and (iii) octahedra formed by atoms Mo3, Mo3a, Mo4 and Mo4a, which have an intermediate degree of distortion.



**Figure 1.** (a) A split view of the molecular structure of **1**; (b) ORTEP drawing of compound **1** showing the labeling of atoms with thermal ellipsoids at 50% probability.

A striking structural feature is that the anions extend the linkage into a one-dimensional inorganic double

chain-like structure via weak interactions: O—O 2.926 Å along the direction of *b*-axis (figure 2).



**Figure 2.** A representation of the one-dimensional double chain running parallel to the crystallographic (*bc*) plane. Organic molecules are omitted for clarity.

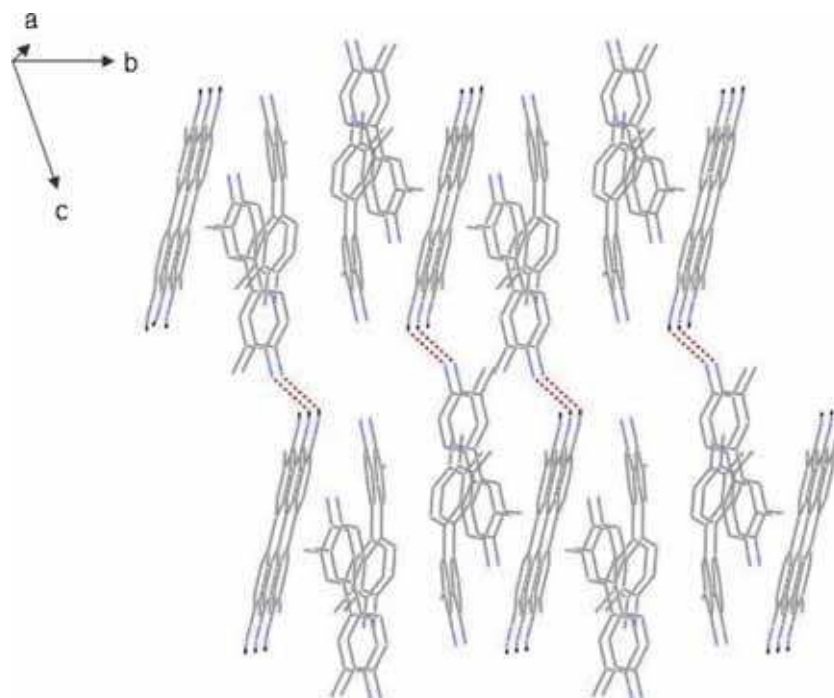
The organic moiety exhibits regular packing with face-to-face interactions between the monoprotonated cations and tolidine molecule, and between monoprotonated tolidine cations- tolidine molecule inter chain leading to a compact supramolecular framework structure to accommodate one-dimensional inorganic chains (figure 3).

The hydrogen bonding distances (table 2) between terminal  $O_t$  atoms of  $Mo_8O_{26}$  anion and hydrogen atoms are  $O_t(3)-H(21B)$  1.980 Å,  $O_t(5)-H(21A)$  2.030 Å,  $O_t(2)-H(21B)$  2.460 Å,  $O_t(4)-H(10A)$  2.220 Å

and  $O_t(6)-H(20A)$  2.400 Å. The  $H(30A)$  - tolidine molecules lie on the bridging oxygen  $O_\mu$  of  $Mo_8O_{26}$ , the hydrogen bonding distance is 2.000 Å for  $O_\mu(8)-H(30A)$  (figure 4).

### 3.2 IR spectral characterization

The IR spectrum of the title compound **1** in figure S1 (Supplementary Information) shows characteristic vibrational features similar to the known  $\beta-[Mo_8O_{26}]^{4-}$  anions.<sup>21</sup>

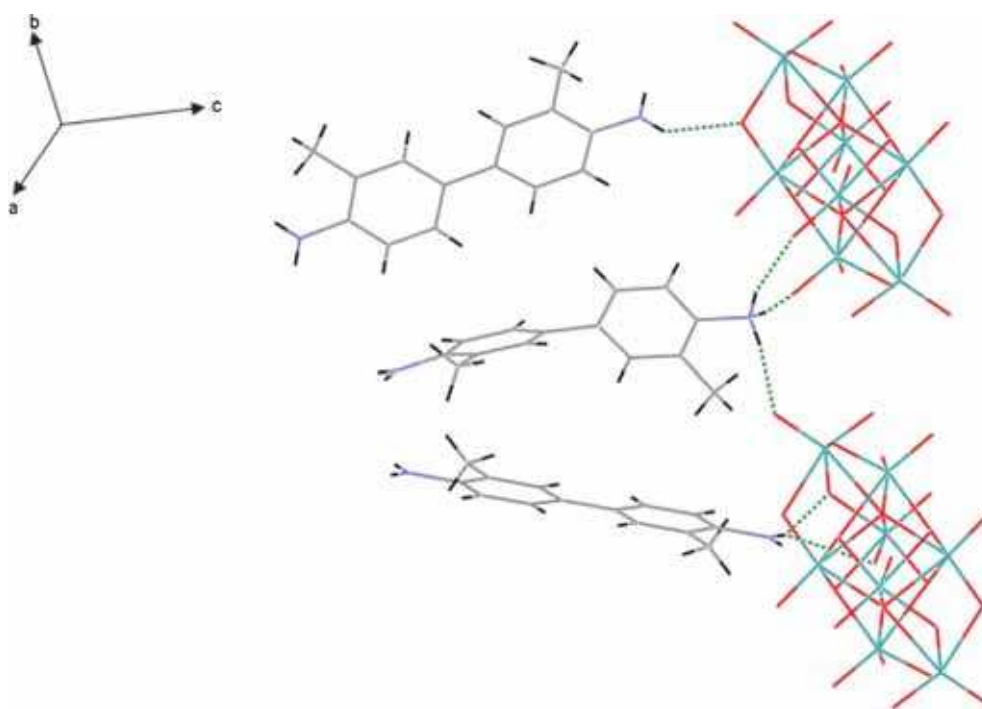


**Figure 3.** Packing map of organic molecules. Inorganic molecules are omitted for clarity.

**Table 2.** Hydrogen-bond geometry, distances and angles ( $\text{\AA}$ ,  $^\circ$ )

$D-H \cdots A$	$D-H$	$H \cdots A$	$D \cdots A$	$D-H \cdots A$
N101—H10A $\cdots$ O4 <sup>i</sup>	0.88	2.22	3.060 (3)	159
N101—H10B $\cdots$ N301 <sup>i</sup>	0.88	2.56	2.899 (3)	104
N115—H11A $\cdots$ O12 <sup>ii</sup>	0.88	2.55	3.327 (3)	147
N201—H20A $\cdots$ O6 <sup>iii</sup>	0.88	2.40	3.035 (3)	130
N201—H20B $\cdots$ O11 <sup>iv</sup>	0.88	2.53	3.388 (3)	166
N215—H21A $\cdots$ O5 <sup>v</sup>	0.91	2.03	2.888 (3)	158
N215—H21B $\cdots$ O2 <sup>v</sup>	0.91	2.46	2.785 (3)	101
N215—H21B $\cdots$ O3 <sup>v</sup>	0.91	1.98	2.878 (3)	171
N215—H21C $\cdots$ O1 <sup>vi</sup>	0.91	2.07	2.978 (3)	173
N301—H30A $\cdots$ O6 <sup>iv</sup>	0.88	2.59	3.024 (3)	112
N301—H30A $\cdots$ O8 <sup>iv</sup>	0.88	2.00	2.786 (3)	148
N301—H30B $\cdots$ N101 <sup>i</sup>	0.88	2.30	2.899 (3)	126
C108—H10D $\cdots$ O2 <sup>vii</sup>	0.98	2.45	3.382 (3)	158
C108—H10E $\cdots$ O8 <sup>iii</sup>	0.98	2.56	3.396 (3)	144

Symmetry codes: (i)  $-x+2, -y+1, -z$ ; (ii)  $-x+1, -y+1, -z+1$ ; (iii)  $-x+1, -y+1, -z$ ; (iv)  $x+1, y, z$ ; (v)  $x, y, z+1$ ; (vi)  $-x+1, -y, -z+1$ ; (vii)  $x, y+1, z$ .

**Figure 4.** A view showing the weak interaction of N-H—O occurring between organic cation and inorganic anion.

The stretching vibrations at  $954.1$  and  $713.6 \text{ cm}^{-1}$  are attributed to  $\nu_{\text{as}}(\text{Mo}-\text{O}_t)$  and  $\nu_{\text{as}}(\text{Mo}-\text{O}-\text{Mo})$ , respectively, and other peaks falling in the range of  $898.8$ – $759.9 \text{ cm}^{-1}$  are attributed to other  $\nu_{\text{as}}(\text{Mo}-\text{O})$ . Further, the presence of organic group is suggested by the occurrence of a series of vibrational bands at  $1624$ ,  $1492.8$  and  $1259.4 \text{ cm}^{-1}$  resulting from the tolidine ligand.

### 3.3 NMR spectroscopy

The spectrum (figure S2) showed three different signals assigned to aromatic protons, azote protons and methyl protons. A multiplet signal between  $7.25$ – $6.82$  ppm is assigned to aromatic protons. A broad peak at  $4.1$  ppm is due to  $\text{NH}_2$  and  $\text{NH}_3^+$  protons groups. A

singlet corresponding to methyl protons is observed at 2.15 ppm.

### 3.4 UV-Vis spectroscopy

Figure S3 shows the UV-Vis absorption spectrum of **1**. The electronic transition at 300 nm in  $\beta$ -[Mo<sub>8</sub>O<sub>26</sub>]<sup>4-</sup> was assigned to a L → M charge-transfer transition from the oxygen  $\pi$ -type HOMO to the molybdenum  $\pi$ -type LUMO. Detailed molecular orbital levels and representations for the hexamolybdate and other typical polyoxometalates have been described by Poblet *et al.*<sup>22</sup>

### 3.5 Cyclic voltammetric data

The voltammetric behaviour of compound **1** was carried out in LiClO<sub>4</sub> 0.1M/DMSO solution at different scan rates. As shown in figure S4, the cyclic voltammogram in a potential range of 800 mV to 200 mV exhibits two reversible redox peaks I and II and  $E_{1/2} = (E_{pa} + E_{pc})/2$  are +608.5 mV and +439.5 mV, respectively. They correspond to one-electron redox processes of Mo<sup>23</sup> and are ascribed to the redox reaction of the  $\beta$ -[Mo<sub>8</sub>O<sub>26</sub>]<sup>4-</sup> anions. The two reduction processes can be assigned to Mo<sup>VI</sup> → Mo<sup>V</sup> and Mo<sup>V</sup> → Mo<sup>IV</sup>.<sup>24</sup> With increasing of scan rates, the peak potential changes gradually with the scan rate from 20 mV/s to 400 mV/s: the cathodic peak potential shifts in the negative direction and the corresponding anodic peak potential shifts in the positive direction. Besides, the peak-to-peak separation between the corresponding peaks increases. The scan rate dependence of the anodic and cathodic peak current showed a linear increase in the peak currents as a function of the scan rate confirmed a non-diffusional surface-controlled redox process.

## 4. Conclusion

A new octamolybdate (C<sub>14</sub>H<sub>16</sub>N<sub>2</sub>)<sub>3</sub>(C<sub>14</sub>H<sub>17</sub>N<sub>2</sub>)<sub>2</sub>[Mo<sub>8</sub>O<sub>26</sub>] (**1**) has been synthesized by hydrothermal method and its crystallographic structure determined by X-ray single-crystal diffraction. This structure consists of  $\beta$ -octamolybdate [ $\beta$ -Mo<sub>8</sub>O<sub>26</sub>]<sup>4-</sup> anions, tolidine molecules, monoprotonated and diprotonated tolidine cations. One tolidine molecule and a  $\beta$ -Mo<sub>8</sub>O<sub>26</sub> polyanion species lie across crystallographic inversion centre while the two tolidine molecules occupy general sites. The cyclic voltammetry of compound **1** presents two reversible redox peaks which are assigned to redox reactions of molybdenum.

## Supplementary Information

IR, <sup>1</sup>H NMR, UV-Vis spectra and cyclic voltammetric data are available at [www.ias.ac.in/chemsci](http://www.ias.ac.in/chemsci).

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