



# A honeycomb network based on hybrid lanthanum complexes encircling a $[\beta\text{-Mo}_8\text{O}_{26}]^{4-}$ isomer: Synthesis, characterization and crystal structure of $[\text{La}(\eta^2\text{-NO}_3)(\text{dmsO})_7]_2[\beta\text{-Mo}_8\text{O}_{26}]$



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## ABSTRACT

A novel isopolymolybdates functionalized by rare earth complexes namely,  $[\text{La}(\eta^2\text{-NO}_3)(\text{dmsO})_7]_2[\beta\text{-Mo}_8\text{O}_{26}]$  (**1**) has been successfully synthesized and characterized by routine methods: IR, X-ray powder diffraction, UV–Visible absorption and single crystal X-ray diffraction. The title compound is crystallized in monoclinic space group  $P2_1/n$  with  $a = 11.566(2) \text{ \AA}$ ,  $b = 28.522(6) \text{ \AA}$ ,  $c = 12.644(3) \text{ \AA}$ ,  $\beta = 91.94(3)^\circ$ . The structural feature of **1** is that lanthanum complexes form a honeycomb network, in which resides the  $[\beta\text{-Mo}_8\text{O}_{26}]^{4-}$  isomer. The cohesion structure is ensured by non typical hydrogen bonding interactions causes a 3D supramolecular network. Absorption spectrum, optical band gap energies have been investigated.

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## 1. Introduction

Polyoxometalates (POMs) constitute a vast class of metal-oxygen clusters-based compounds which are important candidates for the design and the synthesis of new hybrid organic-inorganic frameworks. As a result of their structural features [1], their remarkable redox properties and their active physical and medical properties, POMs have a wide range of applications in a variety of fields, including catalysis [2], electronic semi-conductors [3], nonlinear optics, magnetic properties [4–6], especially single-molecule magnets [7], biological and medical properties [8–11], particularly their antitumor and antiretroviral activities. The Lindqvist anions,  $[\text{M}_6\text{O}_{19}]^{2-}$  ( $M = \text{Mo}, \text{W}$ ), are among the smallest members of the POMs family [12]. They exhibit high point group symmetry (Oh) and are highly stable in condensed phases and even in the gas phase [13]. Moreover, hexamolybdate cluster  $[\text{Mo}_6\text{O}_{19}]^{2-}$  can be easily converted to octamolybdate cluster  $[\text{Mo}_8\text{O}_{26}]^{4-}$ . The later isopolymolybdate has eight isomeric forms that have been already reported [14]. These isomers can be easily transformed into each other under mild reaction via intermediate modifications. In this context, some hybrid materials octamolybdate anions

$[\text{Mo}_8\text{O}_{26}]^{4-}$  containing lanthanides complexes, acting as building blocks, have been reported [15]. The incorporation of lanthanides ions in polyoxometalates is an important topic in the domain of supramolecular chemistry. It has been reported that lanthanide cations can link to POMs by terminal or bridging oxygen atoms to afford building blocks that can be interconnected by hydrogen bonds and van der Waals interactions to provide original hybrid frameworks [16]. One part of the challenging work in these fields is the preparation of novel organic–inorganic hybrid compounds containing polyoxoanions and lanthanide coordination cations. An intriguing area in this field is the construction of three-dimensional (3D) framework materials based on POM building blocks and lanthanide cations or lanthanide organic coordination complexes. In the present work, polyoxomolybdate anions have been used as building blocks and associated with La (III) ions complexes.

## 2. Experimental section

### 2.1. Materials

All chemicals of reagent grade were purchased from commercial sources and used without further purification.

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## 2.2. Synthesis of $[La(\eta^2\text{-NO}_3)(\text{dmsO})_7]_2[\beta\text{-Mo}_8\text{O}_{26}]$ (**1**)

The  $[(\text{C}_4\text{H}_9)_4\text{N}]_2[\text{Mo}_6\text{O}_{19}]$  salt was synthesized as described by Hur et al. [17].  $[La(\eta^2\text{-NO}_3)(\text{dmsO})_7]_2[\beta\text{-Mo}_8\text{O}_{26}]$  have been synthesized by mixing DMSO solutions of salts  $\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$  (1 mmol; 0.355 g) and  $[(\text{C}_4\text{H}_9)_4\text{N}]_2[\text{Mo}_6\text{O}_{19}]$  (0.2 mmol; 0.273 g) and heating under stirring at 333 K for about 2 h. After filtration of the solution, the solid material was dried under vacuum (yield 65%). The crystallization of **1** was done using 8 mm tubes by slow diffusion of 2-propanol in the DMSO solution and X-ray quality crystals were obtained after about two weeks. Elemental Anal. Calcd (%) for  $\text{C}_{28}\text{H}_{84}\text{La}_2\text{Mo}_8\text{N}_2\text{O}_{46}\text{S}_{14}$  (2679.20): C 12.46, H 3.07, N 0.98; found C, 12.55, H 3.16, N 1.05; O, 27.47 La, 10.37; Mo, 28.65; S, 16.76%. IR (KBr) ( $\text{cm}^{-1}$ ): 3422 (s), 3002 (ep), 2974 (ep), 1470 (s), 1641 (s), 1436 (ep), 1420 (ep), 1406 (ep), 1384 (s), 1318 (w), 1012 (s), 952 (s), 906 (w), 843 (w), 710 (s), 659 (ep), 555(w), 515 (w). UV–Vis [DMSO]:  $\lambda_{\text{max}}$  in nm (log): 286 (4.41), 326 (3.78) ( $[\text{Mo}_6\text{O}_{19}]$ ); 291 (4.48) ( $[\text{Mo}_8\text{O}_{26}]$ ); 284 (4.39) (compound (**1**)).

## 2.3. X-ray crystallographic study

Single crystal ( $0.20 \times 0.36 \times 0.59$ ) was selected for X-ray diffraction measurement. Intensity data was collected using an APEXII, Bruker-AXS single-crystal diffractometer equipped with graphite-monochromated Mo  $K\alpha$  radiation ( $\lambda = 0.71073 \text{ \AA}$ ) at 150 (2) K. Data reduction and cell refinement were performed with Denzo and Scalepack programs [18]. The structure was solved by direct method using SIR-2004 program [19] and refined by full-matrix least-squares on  $F_o$  using the SHELXL-97 program [20]. The non-hydrogen atoms were refined anisotropically. Crystal data collection and refinement parameter of the title compound are given in Table 1.

## 2.4. UV–vis absorption

The electronic absorption spectra were recorded with a Cary 300 UV/visible spectrophotometer.

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

	Complex <b>1</b>
Empirical formula	$\text{C}_{28} \text{H}_{84} \text{La}_2 \text{Mo}_8 \text{N}_2 \text{O}_{46} \text{S}_{14}$
Formula mass	2679.20
Temperature [K]	293 (2)
System	Monoclinic
Space group	$P2_1/n$
a [Å]	11.566 (2)
b [Å]	28.522 (6)
c [Å]	12.644 (3)
$\alpha$ [°]	90
$\beta$ [°]	91.94 (3)
$\gamma$ [°]	90
Volume [Å <sup>3</sup> ]	4168.5 (14)
Z	2
$\mu$ (MoK $\alpha$ ) (mm <sup>-1</sup> )	2.601
$\rho_{\text{calcd}}$ (g.cm <sup>-3</sup> )	2.178
$\theta$ range [°]	1.43–30.00
Index ranges	$-15 \leq h \leq 16$ $-40 \leq k \leq 38$ $-17 \leq l \leq 17$
Reflections collected/unique/observed	68581/12118/9815
$R_1$ [ $F_o > 4\sigma F_o$ ]	0.0243
$wR_2$	0.0675
G. O. F.	1.243
Residual density [e/Å <sup>3</sup> ]	–1.554/1.412
CCDC-reference	1403904

$$R_1 = \sum ||F_o| - |F_c|| / \sum |F_o|; wR_2 = [\sum w(F_o^2 - F_c^2)^2 / \sum w F_o^4]^{1/2}; S = [\sum w(F_o^2 - F_c^2)^2 / (n - p)]^{1/2}.$$

## 2.5. X-ray powder diffraction

Diffraction X-ray powder intensities have been collected using a Panalytical X'Pert Pro diffractometer with an X' Celerator detector (see supplementary; Figure S1). The typical recording conditions were 40 kV, 40 mA for Cu- $K\alpha$  ( $\lambda = 1.542 \text{ \AA}$ ), the diffractograms were recorded in  $\theta/\theta$  mode in 60 min between  $5^\circ$  and  $75^\circ$  (8378 measurements) with a step size of  $0.0084^\circ$  and a scan time of 3600 s. The calculated patterns were produced using the Powdercell and WinPLOTR software programs [21–23].

## 3. Results and discussion

### 3.1. Synthesis

The  $[\text{Mo}_6\text{O}_{19}]^{2-}$  undergoes a spontaneous conversion reaction, resulting in the formation of the  $[\text{Mo}_8\text{O}_{26}]^{4-}$  unit. It is interesting to note that the conversion between the hexamolybdate to the octamolybdate seems to be strongly dependent on the given reaction conditions such the intrinsic lability of the  $[\text{Mo}_6\text{O}_{19}]^{2-}$  unit in the chosen solvent DMSO and by heating the highly hygroscopic reaction mixture [24]. The reaction solution was overlaid with 2-propanol. Crystals of titled compound were obtained after two weeks after a slow diffusion of 2-propanol in the DMSO solution in tubes.(see Scheme 1).

### 3.2. Crystal structure of compound (**1**)

Compound **1** crystallized in monoclinic  $P2_1/n$  space group. Single crystal X-ray diffraction analysis of compound **2** was made of an organic-inorganic  $[La(\eta^2\text{-NO}_3)(\text{dmsO})_7]$  cation and a polyacid anion  $\beta\text{-}[\text{Mo}_8\text{O}_{26}]^{4-}$  lying about an inversion centre, as is shown in Fig. 1, (symmetry code: (i)  $2 - x, -y, 1 - z$ ). The  $\beta\text{-}[\text{Mo}_8\text{O}_{26}]^{4-}$  is built up from eight distorted edge-sharing  $[\text{MoO}_6]^{6-}$  octahedra. The  $\beta$ -isomer can be alternatively described as two cyclic  $[\text{Mo}_4\text{O}_{13}]$  subunits linked together by bridging oxygen atoms with an approximate  $C_{2h}$  symmetry. The Mo–O bonds can be divided into four categories, Mo–O( $t$ ), Mo–O( $\mu_2$ ), Mo–O( $\mu_3$ ), and Mo–O( $\mu_5$ ) whose bond lengths fall respectively in the ranges: 1.695 (2)Å–1.708 (2)Å; 1.902 (2)Å–1.9222 (19)Å; 1.9465 (18)Å–2.3720 (19)Å; 2.1439 (18)Å–2.511 (14)Å. These values are in good agreement with those reported for the  $[\beta\text{-Mo}_8\text{O}_{26}]$  isomer [25].

La1 is nonacoordinated by seven oxygen atoms from dimethylsulfoxide molecules and one nitrate molecule acting as a bidentate ligand through oxygen atoms. Calculations with SHAPE software [26] indicate that La1 coordination polyhedron is described by a distorted tricapped trigonal prism with  $D_{3h}$  symmetry group [27]. Two trigonal planes are composed by « P1 (O2, O19, O20) » and « P2 (O18, O15, O1A) » (Fig. 2a,b). The two basal planes are nearly parallel with a dihedral angle of  $28.15 (10)^\circ$ . The distances between  $\text{La}^{3+}$  and two trigonal planes are 1.74 (15) Å and 1.76 (15) Å, respectively. Coplanar « O18, O2, O19, O1A » form one square face (the average plane deviation is 0.035 Å) with O12 as a cap; coplanar « O18, O2, O20, O15 » form one square face (the average plane deviation is 0.054 Å) with O11 as a cap; and coplanar « O19, O1A, O15, O20 » form one square face (the average plane deviation is 0.087 Å) with O16 as a cap. The La–O bonds lengths are listed in Table 2 and are in the range 2.452(2)–2.693(2) Å.

The fact of the mean La–O (DMSO) bond distance, 2.508 Å is shorter than the La–O ( $\text{NO}_3$ )<sup>–</sup> bond distance, 2.676 Å, indicates that the La–O (DMSO) bonds are more stable than the La–O ( $\text{NO}_3$ )<sup>–</sup> bonds, that is probably because the charge density over the oxygen of S=O is bigger than that of the oxygen of  $\text{NO}_3$ <sup>–</sup> (see Table 2).

Supramolecular structure of compound **1** is shown in Fig. 3a. It

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