



# Crystal structure, physico-chemical and catalytic properties of two organic–inorganic hybrid polyoxometallate-based lanthanide complexes



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## ARTICLE INFO

### Article history:

Received 15 March 2016

Accepted 19 April 2016

Available online 4 May 2016

### Keywords:

Polyoxomolybdates

Organic–inorganic hybrid

Crystal structure

Electrochemical properties

Catalytic activity

## ABSTRACT

Two organic–inorganic compounds based on Keggin anions and lanthanide ions have been synthesized. Their chemical formulae are  $[\text{Eu}(\text{C}_2\text{H}_6\text{SO})_8][\text{PMo}_{12}\text{O}_{40}]$  (**1**) and  $[\text{Er}(\text{C}_2\text{H}_6\text{SO})_8][\text{PMo}_{12}\text{O}_{40}] \cdot 2(\text{C}_2\text{H}_6\text{SO}) \cdot 1/2\text{H}_2\text{O}$  (**2**), respectively. They have been structurally characterized by single-crystal X-ray diffraction, IR, thermal analyses and cyclic voltammetry measurements. **1** and **2** crystallize in the space groups  $P\bar{1}$  and  $P2_1/c$ , respectively. Their catalytic activity toward organic dyes is quite sizeable since the target removal after 120 min is about 78.6% in the presence of the system  $[\text{Eu}(\text{C}_2\text{H}_6\text{SO})_8][\text{PMo}_{12}\text{O}_{40}]/\text{H}_2\text{O}_2$  and 60.3% in the presence of the system  $[\text{Er}(\text{C}_2\text{H}_6\text{SO})_8][\text{PMo}_{12}\text{O}_{40}] \cdot 2(\text{C}_2\text{H}_6\text{SO}) \cdot 1/2\text{H}_2\text{O}/\text{H}_2\text{O}_2$ .

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## 1. Introduction

In recent decades polyoxometallates have attracted great interest because of their wide range of topological properties and great potential for application in catalysis, photochemistry, electrochromism, magnetism and photocatalysis [1–4]. Actually, polyoxometallates can constitute excellent anionic precursors due to their controllable shapes and sizes, as well as their potential interest for the design of new materials with abundant chemical combinations and multiple functionalities [5–7]. Polyoxometallate clusters constitute a class of inorganic compounds that show a great variety of molecular structures [8]. This is due to the great versatility of their primary building components that allows chemists to link them in many different ways. Using specific reaction routes, recent insights into molybdenum-oxide based chemistry enable us, for instance, to construct spherically shaped molecular systems [9]. The overwhelming structural diversity of polyoxometallates thus provides not only molecular systems with original functionalities, but also a truly aesthetic appeal resulting from their amazing spatial structures and symmetries.

Lanthanide elements are hard acids in the classification of Pearson [10] and, therefore, they are highly oxophilic [11,12] with a greater affinity for ligands that have hard donor atoms than for those that have soft donor atoms. Recently, the syntheses of lanthano-polyoxometallates (LnPOMs) has received strong interest and the incorporation of lanthanide ions ( $\text{Ln}^{3+}$ ) in polyoxometallates has become a focus in supramolecular chemistry because of their attractive physical properties, such as magnetic [13] and optical properties [14] which result from the synergy between the properties of the lanthanide ions and the POM clusters.

Here in, we describe the synthesis of two novel compounds:  $[\text{Eu}(\text{C}_2\text{H}_6\text{SO})_8][\text{PMo}_{12}\text{O}_{40}]$  (**1**) and  $[\text{Er}(\text{C}_2\text{H}_6\text{SO})_8][\text{PMo}_{12}\text{O}_{40}] \cdot 2(\text{C}_2\text{H}_6\text{SO}) \cdot 1/2\text{H}_2\text{O}$  (**2**). Their crystal structures were determined by single-crystal X-ray diffraction. They have also been analyzed by FT-IR spectroscopy, cyclic voltammetry and thermal analysis. Further, their ability for discoloration of solutions has been investigated. The effect of time was considered and the yield of color removal was calculated.

## 2. Experimental section

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

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## 2.1. Synthesis of compounds **1** and **2**

The  $[(C_4H_9)_4N]_4[H_3PMo_{11}O_{39}]$  starting material was prepared using the literature method (Combs-Walker et al., 1998) [15].

$[Eu(C_2H_6SO)_8][PMo_{12}O_{40}]$  (**1**) and  $[Er(C_2H_6SO)_8][PMo_{12}O_{40}] \cdot 2(C_2H_6SO) \cdot 1/2H_2O$  (**2**) were prepared according to the procedure described in the literature [16]. A dimethylsulfoxide solution of  $EuCl_3 \cdot 6H_2O$  ( $ErCl_3 \cdot 6H_2O$  respectively) and 2-hydroethylsalicylate ( $C_9H_{10}O_4$ ) (1:1 molar ratio) was added dropwise to a yellow dimethylsulfoxide solution of  $[(C_4H_9)_4N]_4[H_3PMo_{11}O_{39}]$  (0.33 mmol in 10 mL). The reaction mixture was then heated at 60 °C under stirring for 1 h. Single crystals suitable for X-ray crystallographic studies were obtained by diffusion of 2-propanol through the dimethylsulfoxide solution.

## 2.2. X-ray powder diffraction

X-ray powder diagrams have been recorded by using a Panalytical X'Pert Pro diffractometer with an X'Celerator detector. The typical recording conditions were 45 kV, 40 mA for Cu  $K\alpha$  ( $\lambda = 1.542 \text{ \AA}$ ), the diagrams were recorded in the  $\theta$ - $\theta$  mode over 60 min, between 5° and 70° with a step size of 0.0084° and a scan time of 50 s. The calculated patterns were produced using the Powdercell and Win PLOTR software programs [17,18].

Experimental and simulated powder X-ray diffraction diagrams for **1** and **2** are reported in Fig. S1. They support the mono phasic character of the samples.

## 2.3. Crystal structure determination

Single crystals of **1** and **2** were mounted on an APEXII AXS-Bruker diffractometer equipped with a CCD camera and a graphite-monochromated Mo  $K\alpha$  radiation source ( $\lambda = 0.71073 \text{ \AA}$ ). Data were collected at 150 K. Empirical absorption corrections were applied. Both crystal structures were solved by direct methods using the SIR-97 program [19] and refined with the full-matrix least-squares method on  $F^2$  via the SHELXL-97 program [20] and the WinGX interface [21]. All of non-hydrogen atoms were located in Fourier difference maps and were refined anisotropically. The

**Table 1**

Crystal and final structure refinement data for  $[Eu(C_2H_6SO)_8][PMo_{12}O_{40}]$  (**1**) and  $[Er(C_2H_6SO)_8][PMo_{12}O_{40}] \cdot 2(C_2H_6SO) \cdot 1/2H_2O$  (**2**).

|  |                                       |  |
|--|---------------------------------------|--|
| Empirical formula                          | $C_{16}H_{48}Eu_1Mo_{12}O_{48}P_1S_8$ | $C_{20}H_{60}Er_1Mo_{12}O_{50.5}P_1S_{10}$ |
| Formula weight<br>( $g \text{ mol}^{-1}$ ) | 2599.24                               | 2776.02                                    |
| Crystal system                             | triclinic                             | monoclinic                                 |
| Space group                                | $P\bar{1}$                            | $P2_1/c$                                   |
| $a$ (Å)                                    | 11.6800(13)                           | 12.667(6)                                  |
| $b$ (Å)                                    | 12.0590(3)                            | 19.659(7)                                  |
| $c$ (Å)                                    | 22.359(3)                             | 29.760(6)                                  |
| $\alpha$ (°)                               | 84.414(4)                             | 90   |
| $\beta$ (°)                                | 82.908(4)                             | 91.971(15)                                 |
| $\gamma$ (°)                               | 85.303(4)                             | 90   |
| $V$ (Å <sup>3</sup> )                      | 3127.5(6)                             | 7406.5(5)                                  |
| $T$ (K)                                    | 150                                   | 150  |
| $Z$  | 2                                     | 2  |
| $F(000)$                                   | 2476                                  | 5313                                       |
| $\mu$ ( $mm^{-1}$ )                        | 3.699                                 | 3.475                                      |
| Reflections collected                      | 41542                                 | 59643                                      |
| Independent reflections                    | 10339, $R_{int} = 0.05131$            | 4573, $R_{int} = 0.0834$                   |
| Goodness-of-fit (GOF)<br>on $F^2$ (S)      | 1.173                                 | 1.053                                      |
| $R_1 [I > 2\sigma(I)]$                     | 4.89%                                 | 6.49%                                      |
| $WR_2 [I > 2\sigma(I)]$                    | 10.05%                                | 16.70%                                     |
| CCDC Deposit number                        | 1057824                               | 1057913                                    |

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

crystal and final structure refinement data for **1** and **2** are listed in Table 1.

## 2.4. Thermal analyses

Thermal analyses were performed in platinum crucibles under a nitrogen atmosphere between room temperature and 800 °C with a heating rate of 10 °C  $min^{-1}$  using a Perkin-Elmer Pyris Diamond thermal analyzer.

## 2.5. FT-IR spectroscopy

FT-IR spectra were recorded in the range 400–4000  $cm^{-1}$  on a Nicolet 470 FT-IR spectrophotometer on pressed KBr pellets. IR spectra of **1** and **2** are very similar. Both present (Fig. S2) the characteristic peaks of the  $\alpha$ -Keggin anion  $[PMo_{12}O_{40}]^{3-}$ , namely  $\nu(P-Oa)$ ,  $\nu(Mo-Od)$ ,  $\nu(Mo-Ob-Mo)$  and  $\nu(Mo-Oc-Mo)$  at 1064, 960, 876 and 798  $cm^{-1}$  respectively [22]. The feature band at 1009  $cm^{-1}$  can be ascribed to the  $\nu(S=O)$  asymmetric stretching vibration of DMSO molecules. Compared with free DMSO, the  $\nu(S=O)$  shift from 1055 to 1009  $cm^{-1}$  supports that the DMSO ligands are coordinated to the metal ions by the oxygen atoms [23].

## 2.6. Electrochemical measurements

Cyclic voltammetry experiments on both complexes were carried out in 0.1 M  $Bu_4NPF_6/DMSO$  solutions under an argon atmosphere, with the potential ranging from –2000 to 1500 mV at a scan rate of 50  $mV s^{-1}$ . The electrochemical measurements were performed using a Potentiostat Galvanostat instrument (Voltalab 40). The electrochemical measurements were performed using three-electrode cell (volume 5 mL) containing a glassy carbon electrode (geometrical surface 0.07  $cm^2$ ) as the working electrode, a (Ag/AgCl) electrode as the reference electrode and a platinum wire as the counter electrode. All the electrochemical measurements were carried out in a Faraday cage at room temperature to avoid external interference which could perturb the impedance response.

## 2.7. Catalytic study

0.05 g of either  $[Eu(C_2H_6SO)_8][PMo_{12}O_{40}]$  or  $[Er(C_2H_6SO)_8][PMo_{12}O_{40}] \cdot 2(C_2H_6SO) \cdot 1/2H_2O$  were added to 50 mL of the organic dye solution, followed by the addition of a calculated dose of  $H_2O_2$ . The experiments were carried out in a batch system for 120 min and were uniformly agitated at a speed of 150 rpm. At the end of the chosen contact time, the content of the flasks were filtered using a Whatman No. 41 filter paper. The concentration of the dye in each filtrate was determined at the maximum wavelength (620 nm).

## 3. Results and discussion

The crystal structures of both compounds **1** and **2** are based on the centrosymmetric hetero-polyanion  $[PMo_{12}O_{40}]^{3-}$  and consist of a  $\alpha$ -Keggin structure in which a central tetrahedron of  $PO_4$  is surrounded by twelve  $MoO_6$  octahedrons, arranged in four groups of three edge-shared octahedral  $Mo_3O_{13}$  units. These groups are connected to one another by their vertices. Bond valence sum calculations (BVSC) [24] confirm that all the molybdenum atoms present a +VI oxidation state, the phosphorus atom presents a +V oxidation state and the erbium or europium atom presents a +III oxidation state.

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