

Short communication

## Synthesis and characterization of $[\text{NBu}_4][\text{La}(\text{CH}_3\text{OH})_2(\text{DCU})\text{NO}_3\{\text{Mo}_5\text{O}_{13}(\text{OMe})_4(\text{NO})\}]\cdot\text{CH}_3\text{OH}$ : A novel Lanthanide-substituted Lindqvist-type oxo-nitrosyl polymolybdate

Yunshen Zhang<sup>a,b,1</sup>, Hongli Jia<sup>b,1</sup>, Jiangwei Zhang<sup>b</sup>, Shijia Zhu<sup>b,c</sup>, Kun Chen<sup>b,\*</sup>, Yongge Wei<sup>b,\*</sup><sup>a</sup> Department of Petrochemical Engineering, Puyang Vocational and Technical College, Henan 457000, PR China<sup>b</sup> Department of Chemistry, Tsinghua University, Beijing 100084, PR China<sup>c</sup> Department of Chemistry, Imperial College London, England SW7 2AZ, UK

## ARTICLE INFO

## Article history:

Received 28 March 2016

Received in revised form 8 June 2016

Accepted 11 June 2016

Available online 13 June 2016

## Keywords:

Polyoxometalates

Lanthanide-substituted

One-pot

Coordination chemistry

Photoluminescence

## ABSTRACT

A 1:1 complex of Lanthanide-substituted Lindqvist-type oxo-nitrosyl polymolybdate  $[\text{NBu}_4][\text{La}(\text{CH}_3\text{OH})_2(\text{DCU})\text{NO}_3\{\text{Mo}_5\text{O}_{13}(\text{OMe})_4(\text{NO})\}]\cdot\text{CH}_3\text{OH}$  (**1**) has been successfully synthesized by a one-pot self-assembly process of hydroxylamine hydrochloride with octamolybdate, DCC and  $\text{La}(\text{NO}_3)_3$  in methanol under mild reaction conditions. The structure is determined by X-ray crystallography. It is notable that the compound is a Lindqvist-type POM with a capped lanthanum ion which is nine coordinated in a distorted square antiprism geometry. Interestingly,  $\text{NO}_3^-$  as the precursor, as well as the hydrated product DCU of DCC, are both coordinated with Lanthanum ion. The structure has also been characterized by IR, UV-vis and photoluminescence analysis. Photoluminescence analysis reveals that compound **1** emits weak green light in  $\text{CH}_3\text{CN}$ , with the maximum emission at 530 nm.

© 2016 Elsevier B.V. All rights reserved.

Polyoxometalates (POMs) are clusters of early transition metals in their highest oxidation states (typically group 5 or 6 metal) with variable structural features and extensive surface chemistry properties which make them suitable as models for probing the properties of non-molecular oxides, especially in the field of catalysis [1], as well as applied in molecular magnetism [2], electronics [3], material [4], and medicinal science [5]. Peculiarly, the functionalization of POM clusters not only enriches the structures but also brings about fine-tuned properties, which has been fully studied in recently years.

The Lindqvist-type POM  $[\text{M}_6\text{O}_{19}]^{n-}$  ( $\text{M} = \text{Mo}, \text{W}$  ( $n = 2$ );  $\text{Ta}, \text{Nb}$  ( $n = 8$ );  $\text{V}$  ( $n = 8$ )) [6] is one of the typical prototypes among POM structures. The chemical modification of the POM clusters surface mostly focuses on two areas: (1) Organically functionalized POMs with covalently grafted organic ligands [7], a sizable class of derivatives  $[\text{Mo}_6\text{O}_{18}(\text{L})]^{n-}$ , has been prepared based on the process in which one or more terminal oxo ligands within the parent structure is substituted by a nitrogen or an oxygen containing ligand, such as nitrosyl [8–13], phenyldiazenido [14–15], alcoholate [16] and organoimido [17–24], which makes the POMs, the physical and chemical properties more tunable. Among  $[\text{Mo}_6\text{O}_{18}(\text{L})]^{n-}$  species, organoimido hexamolybdates

$[\text{Mo}_6\text{O}_{18}(\text{NR})]^{2-}$  are well proceeded by Peng and Wei [18–24] with the so-called DCC protocol, which is faster, more efficient and the yields are higher. (2) Incorporation of various metal centers leads to the discovery of a range of heterometallic Lindqvist clusters  $[\text{M}'(\text{L})\text{M}_5\text{O}_{18}]^{n-}$  ( $\text{M} = \text{Mo}, \text{W}$ ;  $\text{M}' =$  transition metal, e.g. Co, V, Zr, Hf;  $\text{L} =$  ligand, e.g.  $\text{RO}^-$ ,  $\text{O}^{2-}$ , etc.) [25]. Among these structures, a derivatized defect Lindqvist-type  $[\text{Mo}_5\text{O}_{13}(\text{OMe})_4(\text{NO})]^{3-}$ , has been fully characterized by Anna Proust. In POM chemistry, monovacant anions can act as bidentate [11], tetradentate [8,10,13], or bisbidentate [11,12] ligands and have been considered as inorganic analogues of metalloporphyrins, and are convenient building blocks to accommodate transition metals or rare-earth metals, exhibiting a variable coordination chemistry [9–13], and boosting new species with different chemical stoichiometries, structural features and interesting properties.

In contrast, coordination chemistry derived from  $[\text{Mo}_5\text{O}_{13}(\text{OMe})_4(\text{NO})]^{3-}$  is still less common, and only a minority of these kinds of hybrids have been successfully reported by Anna Proust, which are mainly two types: (i) 1:1 complexes of the type  $[\text{X}\{\text{Mo}_5\text{O}_{13}(\text{OMe})_4(\text{NO})\}]^{n-}$  ( $\text{X} = \text{Na}^+$  [8],  $\text{Ni}^{2+}$  [9],  $\text{Ag}^+$  [12], and  $\text{Mn}^{2+}$  [13]). Among them, for  $\text{Ni}^{2+}$ , a central rhomb-like  $[\text{Ni}_2\text{Mo}_2]$  cluster is linked to two terminal  $[\text{Mo}_5\text{O}_{13}(\text{OMe})_4(\text{NO})]^{3-}$  units. As for  $\text{Ag}^+$ , each defect polyoxoanion bridging two  $\text{Ag}^+$  is in slightly distorted square-planar environment and significant  $\text{Ag}\cdots\text{Ag}$  bonding interaction exists in  $[\text{Ag}_2\{\text{Mo}_5\text{O}_{13}(\text{OMe})_4(\text{NO})\}_2]^{4-}$ . (ii) 2:1 complexes of  $[\text{X}\{\text{Mo}_5\text{O}_{13}(\text{OMe})_4(\text{NO})\}_2]^{n-}$  ( $\text{X} = \text{Ca}^{2+}$ ,  $\text{Sr}^{2+}$ ,  $\text{Ba}^{2+}$ ,  $\text{Ce}^{3+}$ ,  $\text{Eu}^{3+}$  and

\* Corresponding authors.

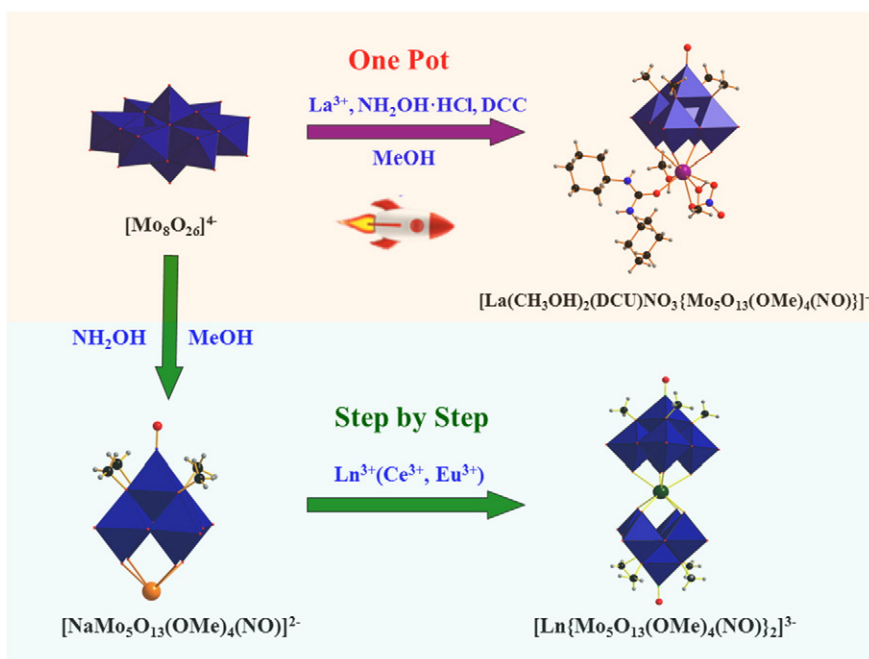
E-mail addresses: [ck1982@mail.tsinghua.edu.cn](mailto:ck1982@mail.tsinghua.edu.cn) (K. Chen),[yonggewei@mail.tsinghua.edu.cn](mailto:yonggewei@mail.tsinghua.edu.cn) (Y. Wei).<sup>1</sup> These authors contributed equally to this work.

$\text{Bi}^{3+}$  [10]). The environment is square prismatic for alkaline earth metal cations while it is square antiprismatic for rare earth metal cations and  $\text{Bi}^{3+}$ . Moreover, these compounds were obtained step-by-step by using  $[\text{NaMo}_5\text{O}_{13}(\text{OMe})_4(\text{NO})]^{2-}$  as precursor, since the sodium cation is easily displaced by metal cations to concrete diverse structures (see Scheme 1).

In view of the potential diversity of coordination chemistry for  $[\text{Mo}_5\text{O}_{13}(\text{OMe})_4(\text{NO})]^{3-}$ , one of the current investigations in our group is focusing on the structural characterization of novel 1:1 Lanthanide-substituted Lindqvist-type oxo-nitrosyl polymolybdate mainly based on following ideas: (i)  $[\text{Mo}_5\text{O}_{13}(\text{OMe})_4(\text{NO})]^{3-}$  is a convenient building block to coordinate with transition metals and rare-earth metals, thus it could well enrich the coordination chemistry. (ii)  $\text{Ln}^{3+}$  cations have the strong oxophilicity and could meet multiple coordination requirements [26], which is favorable to combine with lacunary POM precursors to create novel POM derivatives and may have potential applications in areas ranging from photochemistry, molecular magnetism, catalysis to gas adsorption [27], as well as lanthanide and actinide cations in connection with radioactive waste treatment [28]. What's more, Yagasaki's group [29] fabricated the 2:1 anion cluster  $[\text{Ln}(\text{Mo}_8\text{O}_{26})_2]^{5-}$  and 1:2  $\{[\text{Ln}(\text{NO}_3)_3]_2(\text{Mo}_8\text{O}_{26})\}^{4-}$  ( $\text{Ln} = \text{Y}, \text{La}, \text{Ce}, \text{Pr}, \text{Nd}, \text{Gd}, \text{Yb}$ ) with the highly oxophilic  $\text{Ln}^{3+}$  cations as well as the main building block  $[\beta\text{-Mo}_8\text{O}_{26}]^{4-}$  unit. (iii) 1:1 type of the species with  $\text{Ln}^{3+}$  cations are seldom focused on but could not be neglected. Lanthanide-substituted POMs can also serve as building blocks in further functionalization or fabrication to obtain more complicated and fascinating structures *via* post-modification or self-assembly procedures. Following the above consideration, we concentrated on the research of Lanthanide-substituted POMs and successfully obtained a novel 1:1 Lanthanide-substituted Lindqvist-type oxo-nitrosyl polymolybdate,  $[\text{NBu}_4][\text{La}(\text{CH}_3\text{OH})_2(\text{DCU})\text{NO}_3\{\text{Mo}_5\text{O}_{13}(\text{OMe})_4(\text{NO})\}] \cdot \text{CH}_3\text{OH}$  (**1**) by serendipity one-pot procedure through the DCC protocol developed in the organoimido chemistry of POMs. The result presented here maybe provides a protocol for the facile synthesis of Lanthanide-substituted Lindqvist-type oxo-nitrosyl polymolybdate.

Using DCC as the dehydrating agent, a one-pot refluxing reaction of  $(\text{Bu}_4\text{N})_4[\text{Mo}_8\text{O}_{26}]$ ,  $\text{La}(\text{NO}_3)_3$  and hydroxylamine chloride at

suitable ratios in hot  $\text{CH}_3\text{OH}$  solvent can afford the title compound **1** (see Scheme 1) in good yield of 60%. Single crystal X-ray diffraction analysis reveals that compound **1** is composed of one discrete  $n\text{-Bu}_4\text{N}^+$  cation, one  $[\text{La}(\text{CH}_3\text{OH})_2(\text{DCU})\text{NO}_3\{\text{Mo}_5\text{O}_{13}(\text{OMe})_4(\text{NO})\}]^-$  anion cluster and one  $\text{CH}_3\text{OH}$  solvent molecule, which crystallizes in triclinic system,  $P$  space group. Summaries of crystal data, data collection and refinement parameters of compound **1** are given in Table 1. As shown in Fig. 1, the molecular structure of the anion cluster of compound **1** is a monovacant nitrosyl-substituted Lindqvist-type POM capped with a lanthanum cation, obtained by formal removal of a  $\text{Mo} = \text{O}_t$  group. Due to the loss of a  $\text{Mo} = \text{O}_t$  group and the replacement of another  $\text{Mo} = \text{O}_t$  group by a  $\text{Mo}(\text{NO})^{3+}$  unit containing the nitrosyl group, the anion cluster is highly negatively-charged and is quadruply-methylated to balance the increased negative charges. Clearly, the site of methylation is located in the four Mo atoms adjacent to the  $\text{Mo}(\text{NO})^{3+}$  group. The central oxygen atom O1 has significantly shifted toward Mo1, the reduced Mo(II) center of the  $\text{Mo}(\text{NO})^{3+}$  group. In this respect, it is worthwhile to point out that the observed axial  $\text{Mo1-O1}$  bond length (2.117 Å) is significantly shorter than the average bond length value for the equatorial  $\text{Mo}_{\text{eq}}-\text{O}_1$  ( $\text{Mo}_{\text{eq}} = \text{Mo2}, \text{Mo3}, \text{Mo4}, \text{Mo5}$ ) bonds (2.336 Å), while the  $\text{Mo1}-\text{O}_b$  ( $\text{O}_b = \text{O15}, \text{O16}, \text{O17}, \text{O18}$ ) bond length (1.998 Å) is shorter than the average bond length value for  $\text{Mo}_{\text{eq}}-\text{O}_b$  (2.240 Å) either. In particular, the average Mo–O distances involving the coordinated axial oxygen atoms  $\text{O}_a$  (1.744 Å,  $\text{Mo2}-\text{O10}, \text{Mo3}-\text{O11}, \text{Mo4}-\text{O12}, \text{Mo5}-\text{O13}$ ), are comparable with those equatorial oxygen atoms  $\text{O}_e$  (1.699 Å,  $\text{Mo2}-\text{O7}, \text{Mo3}-\text{O8}, \text{Mo4}-\text{O9}, \text{Mo5}-\text{O6}$ ), indicating that the Lindqvist-type POM is greatly distorted. The  $\text{La}^{3+}$  ion occupies the vacant site and is nine coordinated in a distorted square antiprism geometry by four oxygen atoms from the  $\text{Mo}_5$  cluster, two oxygen atoms from  $\text{CH}_3\text{OH}$ , two oxygen atoms from  $\text{NO}_3^-$ , and one oxygen atom from DCU, the *N, N'*-dicyclohexylurea, a hydrated product of DCC. This is quite different with the coordination geometry in  $[\text{La}(\text{Mo}_8\text{O}_{26})_2]^{5-}$  and  $1:2 \{[\text{La}(\text{NO}_3)_3]_2(\text{Mo}_8\text{O}_{26})\}^{4-}$ , which the La atom in the former is sandwiched between two octamolybdate units and achieves 8-fold square-antiprismatic coordination, while in the latter structure the La atom achieves 10-fold coordination



Scheme 1. The synthesis of compound **1** and the comparison between one-pot and step-by-step method.

Download English Version:

<https://daneshyari.com/en/article/1305236>

Download Persian Version:

<https://daneshyari.com/article/1305236>

[Daneshyari.com](https://daneshyari.com)