

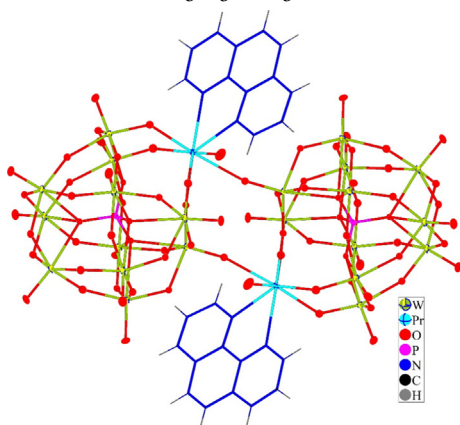
Short communication

Syntheses and characterizations of the first N-containing organic ligand functionalized mono-lanthanide-substituted polyoxometalates

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GRAPHICAL ABSTRACT

The first N-containing organic ligands functionalized mono-lanthanide-substituted polyoxometalates have been synthesized and characterized.



ARTICLE INFO

Keywords:

N-containing organic ligands
 Mono-lanthanide-substituted polyoxometalates
 Hydrothermal synthesis
 Crystal structure
 Catalysis

ABSTRACT

Four novel organic–inorganic hybrid compounds based on mono-lanthanide-substituted phosphotungstates, $[PW_{11}O_{39}Ln(phen)(H_2O)]_2(phen)_8 \cdot 8H_2O$ (1: Ln = Pr; 2: Ln = Gd; 3: Ln = Sm; 4: Ln = La; phen = 1,10-phenanthroline), have been synthesized under hydrothermal conditions and characterized by IR, UV–Vis spectrum, powder XRD, photoluminescence analysis, elemental analysis and X-ray diffraction analysis. Single crystal X-ray analysis reveals that compounds 1–4 are the first N-containing organic ligands functionalized mono-lanthanide-substituted polyoxometalates. The catalytic properties of these compounds were also investigated.

Polyoxometalates (POMs), as a distinctive class of metal-oxygen cluster compounds, are unique in their topological and electronic versatility and useful in fields as diverse as catalysis, analysis, biochemistry, materials science and medicine [1]. Lacunary POMs possessing vacant sites can function as inorganic ligands for constructing metal and lanthanide substituted POMs with potential applications in

catalysis, magnetism, medicine, photochemistry and materials science [2]. In 1914, Barbieri initiated the study of the combination of POMs and lanthanides with the discovery of $(NH_4)_2[H_6CeMo_{12}O_{42}] \cdot nH_2O$ [3], and after a long-standing sluggish period, in 1971 Peacock and Weakley firstly succeeded in preparing a series of 1:1- and 1:2-type lanthanide substituted POMs [4]. These preliminary discoveries shed light on the

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Received 21 May 2018; Received in revised form 9 July 2018; Accepted 10 July 2018

Available online 11 July 2018

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possibilities in introducing lanthanides to various POMs. Henceforth, a large number of lanthanide substituted POMs with fascinating structures and properties have been discovered [5].

Mono-lanthanide-substituted Keggin POMs have been carefully investigated by several groups, the family of this type compounds can be grouped into three categories: 1:1 type [4, 6], 1:2 type [2c, 4, 7] and 2:2 type [8]. Peacock and Weakley firstly verified the existence of 1:1- and 1:2-type mono-lanthanide substituted POMs in solution [4]. Tourné then reported a 1:2-type anion $[\text{U}(\text{GeW}_{11}\text{O}_{39})]^{12-}$ in 1980 [7d], Pope et al. reported 1:1-type lanthanide substituted POMs $[\text{Ln}(\text{SiW}_{11}\text{O}_{39})(\text{H}_2\text{O})_3]^{5-}$, which verified the structure of 1:1 type compounds [6a]. Subsequently, Mialane et al. isolated two 2:2-type dimers $\{(\text{R}-\text{SiW}_{11}\text{O}_{39})\text{Ln}(\text{COOCH}_3)(\text{H}_2\text{O})_2\}^{12-}$ ($\text{Ln} = \text{Gd}^{\text{III}}$ and Yb^{III}) [8d]. Recently, Kortz et al. prepared a family of 1:2 type compounds $[\text{Ln}(\beta\text{-SiW}_{11}\text{O}_{39})_2]^{13-}$ ($\text{Ln} = \text{La}^{\text{III}}$, Ce^{III} , Sm^{III} , Eu^{III} , Gd^{III} , Tb^{III} , Yb^{III} , Lu^{III}) [7e].

Organic-ligand-functionalized Ln-substituted POMs have also been investigated recently [5b, 6e, 8a, b, d–h, 9]. Notably, the research on the introduction of organic ligands to the Ln-POM system has aroused increasing interest in that organic linkers can somewhat facilitate the agglomeration of lanthanide centers to form polynuclear species [8f]. It should be noted that the organic ligands of all these reported organic-ligand-functionalized Ln-POM compounds are acetic acid [5b, 8a–e, 9a, j], 2,5-pyridinedicarboxylic acid [6e, 9f], pyridine-4-carboxylic acid [8g], oxalic acid [8h, 9d, j], picolinic acid [9b], glycine [8f], pyrazine-2,3-dicarboxylic acid [9c], citric acid [9e, h], and tartaric acid [9g, i]. It should be noted that the role of the organic ligand of An's compound which did not coordinate to the substituted lanthanides is different from those of ligands in other compounds [8g]. We concluded from the above-mentioned substituted POMs that all the involved organic ligands are aliphatic and aromatic carboxylic acid. To the best of our knowledge, still no N-containing organic ligands were introduced to these types of Ln-substituted POMs. Such a phenomenon is strange for that lanthanide ions are easy to be coordinated by many N-containing organic ligands. Therefore, we began the research of introducing N-containing organic ligands to the Ln-substituted POM compounds. And fortunately, in this paper, we reported four new organic-inorganic hybrid compounds based on organic-ligand-functionalized lanthanide-substituted phosphotungstates: $[\text{PW}_{11}\text{O}_{39}\text{Ln}(\text{phen})(\text{H}_2\text{O})]_2(\text{phen})_8\text{H}_3\text{O}$ (1: $\text{Ln} = \text{Pr}$; 2: $\text{Ln} = \text{Gd}$; 3: $\text{Ln} = \text{Sm}$; 4: $\text{Ln} = \text{La}$; phen = 1,10-phenanthroline). Compounds 1–4 all exhibit a 3-D supramolecular structure constructed from $[\text{PW}_{11}\text{O}_{39}\text{Ln}(\text{phen})(\text{H}_2\text{O})]_2^{8-}$, phen ligands and water molecules.

Compounds 1–4 were synthesized hydrothermally using similar procedures, there are only slight differences in the dosages of the starting materials used. In addition, (2,3-, 2,6- or 3,5-) pyridine-dicarboxylates were necessary for the preparations of compounds 1–4, though it is not incorporated into the final products. Single-crystal X-ray diffraction analyses show that compounds 1–4 are isomorphous and isostructural, belonging to the same monoclinic space group $\text{P}2(1)/n$. Compound 1 was detailedly described as below as an example.

The asymmetric unit of compound 1 is comprised of one $[\text{PW}_{11}\text{O}_{39}\text{Pr}]^{4-}$, one chelating phen (N(1) phen), four dissociated phen moieties (N(3), N(5), N(7) and N(9) phen), one coordinated water molecule and four free water molecules. $[\text{PW}_{11}\text{PrO}_{39}]^{4-}$ is derived from the well-known Keggin anion $[\text{PW}_{12}\text{O}_{40}]^{3-}$ with the substitution of Pr^{3+} for a $[\text{WO}]^{4+}$, inheriting the Keggin shell structure $\{\text{M}_{12}\text{O}_{36}\}$ encapsulating a PO_4^{3-} . one of the four oxygens of PO_4^{3-} is bonded to two tungstens of $\text{W}_2\text{PrO}_{12}$, the other three oxygens bind to three tungstens of W_3O_{13} , P–O distances are in the 1.522(6)–1.542(5) Å range. All the eleven tungstens of compound 1 exhibit an octahedral geometry with one terminal oxygen (W–O bond lengths: 1.705(6)–1.727(5) Å), four doubly bridging oxygens (W–O bond lengths: 1.759(5)–2.059(5) Å), and one μ_4 -O oxygen (W–O bond lengths: 2.376(5)–2.528(5) Å).

As shown in Fig. 1, $[\text{PW}_{11}\text{O}_{39}\text{Pr}(\text{phen})(\text{H}_2\text{O})]_2^{8-}$ in compound 1 is

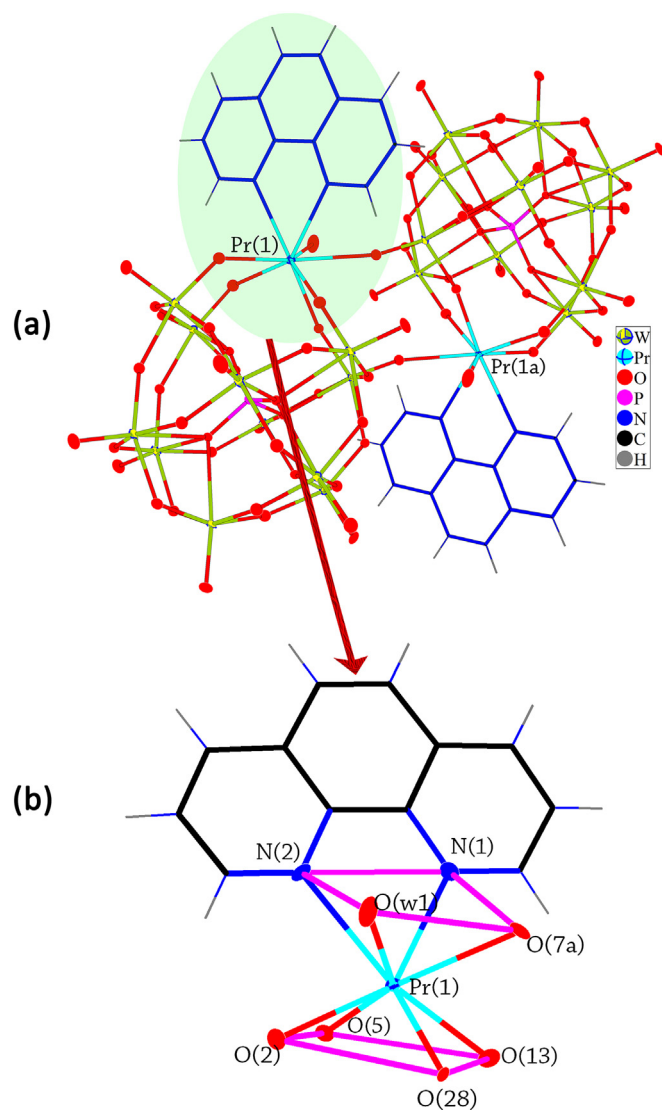


Fig. 1. (a) ellipsoid and wire representation of the 2:2 dimer in compound 1; (b) ellipsoid and wire representation of antiprismatic geometry around Pr(1). a: $1 - x, -y, 1 - z$.

formed from the assembly of two $[\text{PW}_{11}\text{PrO}_{39}]^{4-}$ through two covalent bond formations between the two substituted $\text{Pr}(1)^{3+}$ and two terminal oxygens O(7) of the two $[\text{PW}_{11}\text{PrO}_{39}]^{4-}$. $\text{Pr}(1)^{3+}$ is eight-coordinated in a distorted square antiprismatic geometry (pseudo- D_{4d}), which consists of two square planes constituted by O(2), O(5), O(13) and O(28) from the defect site of one $[\text{PW}_{11}\text{O}_{39}]^{7-}$ (Pr–O distances: 2.346(6)–2.421(5) Å) and by two nitrogens of a phen, one oxygen from O(1w) and one oxygen (O(7)) from the other $[\text{PW}_{11}\text{O}_{39}]^{7-}$ (Pr–O distances: 2.518(5)–2.571(6) Å; Pr–N distances: 2.636(7)–2.664(6) Å). The dihedral angle of the two square planes is 10.69°. The distances between $\text{Pr}(1)^{3+}$ and the two bottom planes are 1.143 and 1.590 Å, respectively. The above-mentioned data indicate that the square antiprism is distorted, which may be related to the different coordination atoms. $\text{Pr}(1)^{3+}$ is incorporated into the vacant site of $[\text{PW}_{11}\text{O}_{39}]^{7-}$, and is slightly positioned outward and away from the normal twelfth tungsten position of the Keggin framework. Compound 1 represents a 2:2-type mono-vacant Keggin polyoxotungstate dimers constituted by two $[\text{PW}_{11}\text{O}_{39}]^{7-}$ and two N-containing organic ligand functionalized praseodymium cations in POM chemistry.

Detailed analysis revealed that there are hydrogen bonds between oxygen atoms of $[\text{PW}_{11}\text{PrO}_{39}]^{4-}$ POMs and oxygen atoms of water molecules in compound 1 with O...O distances in the range of

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