

Short communication

A new dimeric polyoxometalate derivate assembled by divacant Dawson $\{P_2W_{16}\}$ units and isosceles triangle $\{Ce_3\}$ cluster

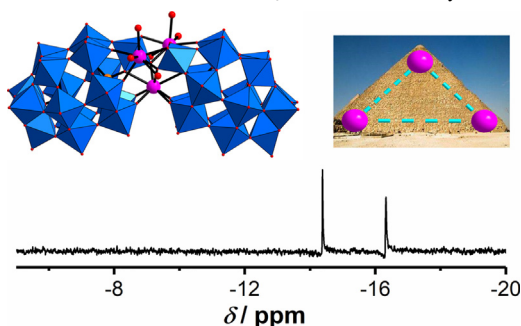


Hechen Wu, Xianrui Meng, Rong Wan, Pengtao Ma*, Jingping Wang, Jingyang Niu*

Henan Key Laboratory of Polyoxometalate Chemistry, College of Chemistry and Chemical Engineering, Henan University, Kaifeng, Henan 475004, PR China

GRAPHICAL ABSTRACT

A rare $[P_2W_{16}O_{59}]^{12-}$ ($\{P_2W_{16}\}$)-based polyoxometalate derivative $(TMA)_{10}H_5[Ce_3(H_2O)_6(P_2W_{16}O_{59})_2] \cdot 49H_2O$ (**1**) was successfully synthesized, and polyanion of **1** consists of two divacant $\{P_2W_{16}\}$ units connected by one standard isosceles triangle $\{Ce_3\}$ bridging cluster.



ARTICLE INFO

Keywords:

Polyoxometalates
Divacant Dawson
Isosceles triangle
Magnetic property

ABSTRACT

A new $[P_2W_{16}O_{59}]^{12-}$ ($\{P_2W_{16}\}$)-based polyoxometalate (POM) derivative $(TMA)_{10}H_5[Ce_3(H_2O)_6(P_2W_{16}O_{59})_2] \cdot 41H_2O$ (**1**) (TMA = tetramethyleamine) was successfully synthesized, which has been characterized by single crystal X-ray diffraction analysis, elemental analyses, cyclic voltammetry, thermogravimetric analyses (TGA), IR spectroscopy and ^{31}P NMR spectroscopy. The single crystal X-ray diffraction analyses indicate that polyanion of **1** consists of two divacant $\{P_2W_{16}\}$ units connected by one standard isosceles triangle $\{Ce_3\}$ bridging cluster via Ce–O–W and Ce–O–P linkages. The investigation of ^{31}P NMR spectroscopy shows the presence of two types of phosphorus in compound **1**. The study of magnetic susceptibility for **1** reveals the strong spin-orbital coupling and weak antiferromagnetic interactions exist in the three Ce^{3+} ions. The photoluminescence study indicates that the presence of $5d \rightarrow 4f$ electron transition of Ce^{3+} ion in **1**.

Polyoxometalates (POMs) are traditionally described as discrete anionic metal oxide clusters of early transition metals, which are generally constructed from connections of $\{MO_x\}$ polyhedra through edge-, corner- or face-sharing fashions, where early transition metal M is usually in its highest oxidation state (e.g., V^{5+} , Nd^{5+} , Mo^{6+} , Ta^{5+} and W^{6+}) [1,2]. POM clusters can exhibit the unmatched and tunable range of physical and chemical properties achieved by compositional variations on POM skeletons, leading to the potential applications in several

areas such as magnetic, optical, catalytic, biology and medicine, materials and surface sciences [3–6]. Furthermore, POMs also can be regarded as outstanding inorganic multidentate O-donor ligands, which coordinate to d- and/or f-metal ion to build functionalized POM derivatives [7,8].

Among the large family of POMs, the polyoxotungstates (POT), especially the Keggin- and Dawson-type derivatives, play a crucial role as they represent perfect candidates for the multi-step elaboration of

* Corresponding authors.

E-mail addresses: mpt@henu.edu.cn (P. Ma), jyniu@henu.edu.cn (J. Niu).

<https://doi.org/10.1016/j.inoche.2018.07.027>

Received 2 July 2018; Received in revised form 17 July 2018; Accepted 17 July 2018

Available online 19 July 2018

1387-7003/ © 2018 Elsevier B.V. All rights reserved.

POM-based materials [9]. According to the literature, a large variety of lacunary Keggin-type POT derivatives and their excellent properties have been investigated over the past several decades. However, the Dawson-type POT complexes are relatively less studied. In 1971, Peacock et al. firstly identified the 1:2-type Dawson-type POTs $[\text{Ce}^{3+}(\alpha\text{-P}_2\text{W}_{17}\text{O}_{61})_2]^{17-}$ and $[\text{Ce}^{4+}(\alpha\text{-P}_2\text{W}_{17}\text{O}_{61})_2]^{16-}$ by UV spectroscopy and elemental analyses [10]. Since then, a series of unexpected Dawson-type POT derivatives subsequently have been reported over the next three decades [11,12]. Among them, the monovacant $[\text{P}_2\text{W}_{17}\text{O}_{61}]^{10-}$ ($\{\text{P}_2\text{W}_{17}\}$) unit is the most frequent and stabilized building block, which usually take part in the combination of metal cations and lacunary POTs. Meanwhile, the study of $[\text{P}_2\text{W}_{16}\text{O}_{59}]^{12-}$ ($\{\text{P}_2\text{W}_{16}\}$)-based POT derivatives were relatively less addressed. In 2000, Pope and coworkers isolated the heteropolyanion $[\text{Ce}_4(\text{OH})_2(\text{H}_2\text{O})_9(\text{P}_2\text{W}_{16}\text{O}_{59})_2]^{14-}$ as a potassium salt by the reaction of $\text{K}_{12}\text{H}_2\text{P}_2\text{W}_{12}\text{O}_{48}\cdot 24\text{H}_2\text{O}$ with Na_2WO_4 and $\text{Ce}(\text{NO}_3)_3$, and the $\{\text{Ce}_4(\text{OH})_2(\text{H}_2\text{O})_9\}^{10+}$ cluster is sandwiched between two novel divacant Dawson $\{\text{P}_2\text{W}_{16}\}$ groups [13]. In 2003, Pope and coworkers synthesized another $[\text{Zr}_4(\mu_3\text{-O})_2(\mu_2\text{-OH})_2(\text{H}_2\text{O})_4(\text{P}_2\text{W}_{16}\text{O}_{59})]^{14-}$ by the method of $[\text{P}_2\text{W}_{15}\text{O}_{56}]^{12-}$ ($\{\text{P}_2\text{W}_{15}\}$) with solution of ZrCl_4 , and the structure of anion is comprised of an assembly of two $\{\text{P}_2\text{W}_{16}\}$ building blocks connected by a $\{\text{Zr}_4\text{O}_2(\text{OH})_2(\text{H}_2\text{O})_4\}^{10+}$ cluster [14]. In 2005, Hill and coworkers reported the synthesis of chiral, nonracemizing, enantiomerically POT derivatives $\{[\alpha\text{-P}_2\text{W}_{15}\text{O}_{55}(\text{H}_2\text{O})]\text{Zr}_3(\mu_3\text{-O})(\text{H}_2\text{O})(\text{L-tartH})[\alpha\text{-P}_2\text{W}_{16}\text{O}_{59}]\}^{15-}$ and $\{[\alpha\text{-P}_2\text{W}_{15}\text{O}_{55}(\text{H}_2\text{O})]\text{Zr}_3(\mu_3\text{-O})(\text{H}_2\text{O})(\text{D-tartH})[\alpha\text{-P}_2\text{W}_{16}\text{O}_{59}]\}^{15-}$, significant induced circular dichroism (CD) was observed in the absorption region of the POM chromophore [15]. In the same year, they found another stereoisomer $\{[\alpha\text{-P}_2\text{W}_{16}\text{O}_{59}]\text{Zr}_2(\mu_3\text{-O})(\text{C}_4\text{O}_5\text{H}_3)\}_2^{18-}$. The structure of Zr-substituted POTs ligating two malates of the same handedness consists of two divacant $\{\text{P}_2\text{W}_{16}\}$ anions connected by four Zr^{4+} cations [16]. In 2013, Kortz and coworkers successfully obtained the polyanion $[\text{Ti}_6(\text{C}_2\text{O}_4)_4\text{P}_4\text{W}_{32}\text{O}_{124}]^{20-}$, which comprises two $\{\text{P}_2\text{W}_{16}\}$ units containing each two titanium atoms, and the two $\{\text{P}_2\text{W}_{16}\}$ are connected by two oxalate group through titanium atoms [17]. In addition, our group also have reported an unprecedented $[\text{Ce}_4^{4+}\text{Ce}_3^{3+}\text{O}_6(\text{OH})_6(\text{CO}_3)(\text{H}_2\text{O})_{11}]^{17+}$ ($\{\text{Ce}_{10}\}$)-cluster-embedded POT $[\text{Ce}^{3+}(\text{H}_2\text{O})_6]\{[\text{Ce}_4^{4+}\text{Ce}_3^{3+}\text{O}_6(\text{OH})_6(\text{CO}_3)(\text{H}_2\text{O})_{11}][(\text{P}_2\text{W}_{16}\text{O}_{59})_3]\}^{16-}$ in 2016, where the $\{\text{Ce}_{10}\}$ cluster is surrounded by three $\{\text{P}_2\text{W}_{16}\}$ units, and each face-sharing $\{\text{Ce}_2\}$ unit from the $\{\text{Ce}_6(\text{Ce})\}$ hexagon occupies the vacant positions of divacant $\{\text{P}_2\text{W}_{16}\}$ units [18].

In this paper, we successfully synthesized a $\{\text{P}_2\text{W}_{16}\}$ -based POT (TMA) $_{10}\text{H}_5[\text{Ce}_3(\text{H}_2\text{O})_6(\text{P}_2\text{W}_{16}\text{O}_{59})_2]\cdot 49\text{H}_2\text{O}$ (**1**) (TMA = tetramethylethylenediamine), which has been characterized by single crystal X-ray diffraction analysis, elemental analyses, cyclic voltammetry (Fig. S1), thermogravimetric analyses (TGA), IR spectroscopy and ^{31}P NMR spectroscopy. The structural analyses reveal the polyanion of **1** is formed by two $\{\text{P}_2\text{W}_{16}\}$ building blocks connected through one isosceles triangle $[\text{Ce}_3(\text{H}_2\text{O})_6(\text{P}_2\text{W}_{16}\text{O}_{59})_2]^{15-}$ ($\{\text{Ce}_3\}$) cluster bridge. The temperature dependence magnetic susceptibility and photoluminescence property of **1** also have been investigated.

1 was synthesized by conventional aqueous solution method [19]. The compound **1** was obtained by reaction of CeCl_3 , isonicotinic acid and $\{\text{P}_2\text{W}_{15}\}$ precursor in a suitable molar ratio, and isolated as a tetramethyl-ammonium salt. The $\{\text{P}_2\text{W}_{16}\}$ building block was formed by the dissociation and recombination of the trivacant $\{\text{P}_2\text{W}_{15}\}$ precursor during the process of aqueous solution reaction and had been reported in the previous literature [18]. In detail, one $\{\text{WO}_6\}$ group derived from the dissociation of partial $\{\text{P}_2\text{W}_{15}\}$ precursor occupies cap position of $\{\text{P}_2\text{W}_{15}\}$ unit to construct the $\{\text{P}_2\text{W}_{16}\}$ building block in aqueous solution (Fig. S2). In addition, the organic carboxylic ligand plays a key role that the isonicotinic acid can effectively suppress the hydrolysis of Ce^{3+} ion during the process of reaction, hence the isonicotinic ligand is essential for synthesis of **1** in this system. The single crystal X-ray diffraction analysis exhibits that **1** crystallizes in the monoclinic space group $C2/c$ [20]. Compound **1** is comprised of one dimeric

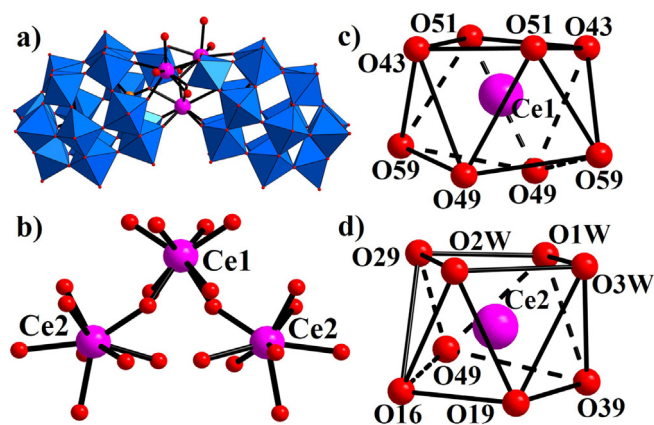


Fig. 1. (a) Combined polyhedral/ball-and-stick representation of polyanion $[\text{Ce}_3(\text{H}_2\text{O})_6(\text{P}_2\text{W}_{16}\text{O}_{59})_2]^{15-}$; (b) polyhedral/ball-and-stick representation of $\{\text{Ce}_3\}$; (c) the coordination environment of Ce1; (d) the coordination environment of Ce2.

$[\text{Ce}_3(\text{H}_2\text{O})_6(\text{P}_2\text{W}_{16}\text{O}_{59})_2]^{15-}$ polyanion, ten TMA counteranions and forty-nine lattice water molecules, and five protons was directly added for charge balance of the polyanion. As shown in Fig. 1a, the polyanion of **1** consists of two divacant $\{\text{P}_2\text{W}_{16}\}$ units connected by one $\{\text{Ce}_3\}$ bridging cluster via Ce–O–W and Ce–O–P linkages. The divacant $\{\text{P}_2\text{W}_{16}\}$ unit possesses two types of architecture: one can be regarded as the saturated Dawson-type POT $[\text{P}_2\text{W}_{18}\text{O}_{62}]^{6-}$ ($\{\text{P}_2\text{W}_{18}\}$) loses two edge-shared $\{\text{WO}_6\}$ polyhedrons at one polar position, and the other could be constructed by removing two adjacent $\{\text{WO}_6\}$ polyhedrons from the belt position of the parent $\{\text{P}_2\text{W}_{18}\}$ unit [18]. In **1**, the $\{\text{P}_2\text{W}_{16}\}$ units belong to the former architecture.

The $\{\text{Ce}_3\}$ cluster in **1** can be seen as a standard isosceles triangle architecture, in which the lengths of waist and bottom are 4.25(3) and 5.89(3) Å, respectively (Fig. 1b and Fig. S3). Furthermore, two kinds of crystallographically unique Ce^{3+} ions (Ce1 and Ce2) appear in this $\{\text{Ce}_3\}$ group. Both Ce1 and Ce2 centers adopt eight-coordinate configurations, which display distorted square antiprismatic geometries with the Ce–O distances ranging from 2.23(2) Å to 2.77(3) Å (Table S1). The Ce1 atom was shared by two $\{\text{P}_2\text{W}_{16}\}$ units in the polyanion; Ce1 and Ce2 atoms in the $\{\text{Ce}_3\}$ bridging cluster occupy the vacant sites of one $\{\text{P}_2\text{W}_{16}\}$ unit, and the shared Ce1 and the symmetrical Ce2 atoms take up the vacant positions of the other $\{\text{P}_2\text{W}_{16}\}$ unit to construct the polyanion of **1** (Fig. S4). The square antiprismatic geometry of Ce1 center is achieved by four oxygen atoms O43, O49, O51, and O59 from one $\{\text{P}_2\text{W}_{16}\}$ unit with the Ce–O distances in the range of 2.23(2)–2.77(3) Å, and another four oxygen atoms O43, O49, O51, and O59 from the other $\{\text{P}_2\text{W}_{16}\}$ unit (Fig. 1c and Table S1). The Ce2 center is surrounded by two oxygen atoms O19 and O39 from one $\{\text{P}_2\text{W}_{16}\}$ unit with the Ce–O distances of 2.40(3) Å and three oxygen atoms O16, O29, and O49 from the other $\{\text{P}_2\text{W}_{16}\}$ unit with the Ce–O distances ranging from 2.43(2) Å to 2.49(3) Å, three coordinated water molecules with the Ce–O distances in the range of 2.53(4)–2.61(3) Å (Fig. 1d and Table S1). The distorted square antiprismatic configuration of Ce centers may be assigned to different coordination environments of different coordination oxygen atoms from $\{\text{P}_2\text{W}_{16}\}$ unit and water molecules. Besides, the distances of the W–O bond range from 1.66(4) to 2.44(3) Å, and the angles of the O–W–O bond are in the region of 71.80(10)–173.10(12)° in **1** (Table S1 and Table S2). The packing arrangement of polyanion of **1** was shown in Fig. S5.

The IR spectra of **1** and TMA have been performed in KBr pellets on a Bruker VERTEX 70 IR spectrometer in the range of 400–4000 cm^{-1} . As shown in Fig. 2, the three peaks appeared at 1090, 1055 and 1010 cm^{-1} can be attributed to the stretching characteristic vibrations $\nu(\text{P}=\text{O})$. The four signals in different intensity in region of 1000–700 cm^{-1} are assigned to stretching vibrations $\nu(\text{W}=\text{O})$ and

Download English Version:

<https://daneshyari.com/en/article/7748386>

Download Persian Version:

<https://daneshyari.com/article/7748386>

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