Short communication

A new dimeric polyoxometalate derivate assembled by divacant Dawson {P2W16} units and isosceles triangle {Ce3} 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 [P2W16O59]12− (P2W16)-based polyoxometalate derivative (TMA)10H5[Ce3(H2O)6(P2W16O59)2]⋅49H2O (1) was successfully synthesized, and polyanion of 1 consists of two divacant (P2W16) units connected by one standard isosceles triangle (Ce3) bridging cluster.

ARTICLE INFO

Keywords:
Polyoxometalates
Divacant Dawson
Isosceles triangle
Magnetic property

ABSTRACT

A new [P2W16O59]12− (P2W16)-based polyoxometalate (POM) derivative (TMA)10H5[Ce3(H2O)6(P2W16O59)2]⋅41H2O (1) (TMA = tetramethyleneamine) was successfully synthesized, which has been characterized by single crystal X-ray diffraction analysis, elemental analyses, cyclic voltammetry, thermogravimetric analyses (TGA), IR spectroscopy and 31P NMR spectroscopy. The single crystal X-ray diffraction analyses indicate that polyanion of 1 consists of two divacant (P2W16) units connected by one standard isosceles triangle (Ce3) bridging cluster via Ce—O—W and Ce—O—P linkages. The investigation of 31P 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 Ce3+ ions. The photoluminescence study indicates that the presence of 5d → 4f electron transition of Ce3+ 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 (MOx) polyhedra through edge-, corner- or face-sharing fashions, where early transition metal M is usually in its highest oxidation state (e.g., V5+, Nd3+, Mo6+, Ta5+ and W6+) [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 derivate [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...
The temperature dependence magnetic susceptibility and photo-
emission property of the compound as shown in Fig. 2, the three peaks appeared at 1090, 1055 and 1020 cm−1 can be attributed to the stretching characteristic vibrations of Ce−O bond range from 1.66(4) to 1.96(4) Å, three oxygen atoms O16, O18, and O49 from the other {P2W16} unit with the CeO6 polyhedron. As shown in Fig. 1a, the polyanion of Ce3 units consists of two divacant {P2W16} units connected by one {Ce3} bridging cluster via Ce−O−W and Ce−O−P linkages. The divacant {P2W16} unit possesses two types of architecture: one can be regarded as the saturated Dawson-type POT [{P2W16O62}]6− (Fig. 1b) loses two edge-shared (WO4) polyhedrons at one polar position, and the other could be constructed by removing two adjacent (WO4) polyhedrons from the belt position of the parent {P2W16} unit [18]. In 1, the {P2W16} units belong to the former architecture.

The {Ce3} 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 Table S1). Furthermore, two kinds of crystallographically unique Ce3 ions (Ce1 and Ce2) appear in this {Ce3} group. Both Ce1 and Ce2 centers adopt eight-coordinate con-
figurations, which display distorted square antiprismatic geometries with different coordination oxygen atoms from {P2W16} unit and water molecules. The IR spectra of 1 were shown in Fig. S4. The square antiprismatic geometry of Ce1 center is achieved by four oxygen atoms O43, O49, O51, and O59 from one {P2W16} unit with the Ce−O−W distances ranging from 2.23(2) Å to 2.77(3) Å (Table S1). The Ce1 atom was shared by two {P2W16} units in the polyanion: Ce1 and Ce2 atoms in the {Ce3} bridging cluster occupy the vacant sites of one {P2W16} unit, and the shared Ce1 and the symmetrical Ce2 atoms take up the vacant positions of the other {P2W16} 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 {P2W16} unit with the Ce−O−W distances ranging from 2.23(2) Å to 2.77(3) Å, and another four oxygen atoms O43, O49, O51, and O59 from the other {P2W16} unit (Fig. 1c and Table S1). The Ce2 center is surrounded by two oxygen atoms O19 and O39 from one {P2W16} unit with the Ce−O−W distances of 2.40(3) Å and three oxygen atoms O16, O29, and O49 from the other {P2W16} unit with the Ce−O−W distances ranging from 2.43(2) Å to 2.49 (3) Å, three coordinated water molecules with the Ce−O−W 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 {P2W16} unit and water molecules. Besides, the distances of W−O bond range from 1.66(4) to 2.44(3) Å, 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 arrange-
ment of polyanion of 1 was shown in Fig. S5.

The IR spectra of 1 and 2 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 v(P−O). The four signals in different intensity in region of 1000−700 cm−1 are assigned to stretching vibrations v(W=O) and v(W−O)
The obvious peak at 1487 cm\(^{-1}\) in IR spectroscopy of 1 may be due to the stretching vibrations \(v(C-H)\) of organic TMA groups. It could be found that a high stretching vibrations \(v(C-H)\) at 1490 cm\(^{-1}\) and a weak stretching vibrations \(v(C-N)\) at 1405 cm\(^{-1}\) form the IR spectroscopy of TMA, indicating the presence of TMA groups in 1. The broad signal at 1625 cm\(^{-1}\) is attributed to bending vibration \(\delta(O-H)\) of lattice and/or coordinated water molecules in 1. All the results of IR spectroscopy can match well with the data of structural analyses of 1 collected from single-crystal X-ray diffraction.

\(^3\text{P}\) NMR spectroscopy is a common and sensitive measurement to assess the information of POM structural skeleton. The \(^3\text{P}\) NMR behavior of compound 1 has been investigated in solution (161.9 MHz, \(D_2O\)). The NMR spectroscopy of 1 display two obvious resonances located at \(-14.39\) and \(-16.33\) ppm (Fig. 3), in which the downfield resonance at \(-14.39\) ppm can be assigned to the phosphorus near the saturated side of Dawson skeleton, whereas the upfield resonance at \(-16.33\) ppm is attributed to the phosphorus on the other vacant site of the skeleton. The two different resonances in the NMR spectroscopy of 1 make clear that the presence of two types of phosphorus in compound 1, which also match well with the results of structural analyses containing two kinds of P atoms. In addition, the studies of \(^3\text{P}\) NMR spectroscopy of lacunary Dawson-type POTs have shown that the chemical shift of phosphorus near the saturated side is steady, meanwhile the chemical shift of phosphorus close to vacant site is sensitive to the chemical environment \([21]\). In our reported POT \([\text{Ce}^{3+}(H_2O)_{16}]([\text{Ce}^{3+}\text{W}_{16}O_{59}]_2^{14-}\) (Fig. 3) \([13]\), indicating the presence of two different \((P_2W_16)\) building blocks between 1 and 3. The analyses of crystal structure also confirmed the difference of phosphorus in 1 and 3.

Variable-temperature magnetic susceptibility for 1 at the temperature interval from 1.8 K to 300 K with an applied field of 1 kOe has been studied. As shown in Fig. 4, the room-temperature \(\chi_M T\) value of 2.44 emu K mol\(^{-1}\) is well close to the theoretical value of 2.41 emu K mol\(^{-1}\) expected for three non-interacting \(\text{Ce}^{3+}\) ions \((\text{Ce}^{3+} 2F_{5/2}, g = 6/7, J = 5/2)\). On lowering of the temperature, the \(\chi_M T\) value of 1 gradually decreases and reaches a minimum of 1.13 emu K mol\(^{-1}\) at 1.8 K. The relationship of 1/\(\chi_M\) versus \(T\) above 100 K can be fitted to the Curie-Weiss law, the fitting gives values of \(C = 3.64\) cm K mol\(^{-1}\) and \(\theta = -151.12\) K, characteristic of the evident antiferromagnetic exchange interactions (Fig. S7). Below 100 K, the relation of 1/\(\chi_M\) versus \(T\) for 1 does not follow the Curie-Weiss law, indicating the occurrence of strong spin-orbital coupling interactions and weak antiferromagnetic responses. The continuous decrease in \(\chi_M T\) upon cooling should be mainly attributed to the thermal depopulation effect of excited state around the \(\text{Ce}^{3+}\) ions.

The \(\text{Ce}^{3+}\)-based complexes commonly display a band emission as a result of the allowed 5d \(\rightarrow\) 4f electron transition under excitation \([22]\). The solid-state photoluminescence emission spectrum and excitation spectrum of 1 were measured at room temperature. The excitation spectrum consists of one broad band at 365 nm, which can be ascribed to the electron transition from 4f ground state to 5d level of \(\text{Ce}^{3+}\) ion (Fig. S8). The strong emission band located at 470 nm in the emission spectrum are attributed to the electron transition from lowest 5d energy level to 4f ground state of \(\text{Ce}^{3+}\) ion in 1 (Fig. S5).

In conclusion, one rare \((P_2W_{16})\)-based POT was obtained and further characterized by different methods. The single crystal X-ray diffraction analyses show that polyaniion of 1 is formed by two divacant \((P_2W_{16})\) units and one standard isosceles triangle \((\text{Ce}_2)\) bridging cluster via \(\text{O}–\text{O}–\text{W}\) and \(\text{Ce}–\text{O}–\text{P}\) linkages, where Ce1 and Ce2 atoms in the \((\text{Ce}_2)\) bridging cluster occupy the vacant positions of one \((P_2W_{16})\) unit and the shared Ce1 and another Ce2 atoms take up the vacant sites of the other \((P_2W_{16})\). The study of \(^3\text{P}\) NMR spectroscopy reveals compound 1 contains two kinds of P atoms. The investigation of magnetic susceptibility indicates the strong spin-orbital coupling and weak antiferromagnetic interactions exist in the three \(\text{Ce}^{3+}\) ions. The study of photoluminescence property shows that the allowed 5d \(\rightarrow\) 4f electron transition of \(\text{Ce}^{3+}\) ion appeared in the emission spectrum of 1.
**Acknowledgements**

This work was financially supported by the National Natural Science Foundation of China (21571050, 21573056, 21771053, 21771054), Natural Science Foundation of Henan Province (132300410144 and 162300410015) and Henan Province Science and Technology attack plan project (182102210237).

**Appendix A. Supplementary material**

Supplementary data to this article can be found online at https://doi.org/10.1016/j.inoche.2018.07.027.

**References**


**Fig. 5.** The emission spectrum of 1 at room temperature.