A novel organotriphosphoryl polyoxomolybdate: synthesis, crystal structure, and experimental and theoretical investigation of the absorption spectra

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20 ABSTRACT

A novel organotriphosphoryl polyoxomolybdate, namely, $[(CH_3)_4N][(CH_3)_3N][R(PO_3H)_2(PO_3)]PMo_9O_{28}$ (**1**), where $R = C_{12}H_{15}$, has been synthesized hydrothermally. The structure of **1** contains one trivacant $[PMo_9O_{34}]$ subunit on which is grafted one $R(POH)_2(PO)$ through three P-O-Mo bridges. Compound **1** is the first example of polyoxomolybdate decorated by three phosphonate groups from one organotriphosphonic acid. The structure of the compound was determined by single-crystal X-ray diffraction analysis and further characterized by infrared spectrum (IR) and elemental analysis. Moreover, the UV-vis absorption spectrum of the compound has been investigated experimentally and

theoretically.

Keywords: Polyoxomolybdate; organophosphoryl; theoretically; experimentally; absorption spectrum

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During the past few years, polyoxometalates (POMs) have attracted much interest due to their potential applications in the fields of magnetism [1-3], catalysis [4-6], sensing [7-9], and so on. It has long been recognized that the solubility and other physical properties of the POMs can be finely modified by introducing appropriate organic or organometallic groups onto the surface of POMs [10]. Therefore, the organic and organometallic derivatives of POMs have more selective applications [11-13]. So far, several kinds of organic derivatives of POMs have been explored, including organophosphoryl, organoarsenyl, organosilyl, organogermyl, organotin POMs derivatives, and so on [13].

15 In this regard, our attention mainly focused on the trivacant organophosphoryl POMs derivatives. Up to now, most of the reported trivacant organophosphoryl POMs were obtained by the directly reaction of organotriphosphonic acid ligands with trivacant POMs [10-13]. In this work, we report a new method to synthesize the trivacant organophosphoryl POMs. We use organotriphosphonic acid ligand and saturated Keggin type polyoxomolybdate as reactants to synthesize trivacant organophosphoryl polyoxomolybdate under the hydrothermal condition.

20 The target compound was synthesized by the reaction of the organotriphosphonic acid 2,4,6-trimethylbenzene-1,3,5-tris(methylenephosphonic acid) [14,15] (H_6L , chart 1), $H_3PMo_{12}O_{40} \cdot H_2O$, $CuCl_2 \cdot 2H_2O$ and tetramethylammonium hydroxide (TMAH) in water [16]. From the formula we can see that the $Cu(II)$ ions are not exist in the resultant compound. But if we remove $CuCl_2 \cdot 2H_2O$ from the reaction mixture, no crystal can be obtained after the hydrothermal reaction.

Chart 1. View of the H_6L ligand used in this work.

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The structure of compound **1** was determined by single-crystal X-ray diffraction analysis and further characterized by infrared spectrum (IR) and elemental analysis. In addition, the UV-vis spectrum of the compound has been investigated experimentally and theoretically. We hope that our work will be helpful for the further investigation of its potential applications.

Single-crystal X-ray diffraction analysis reveals that compound **1** crystallizes in the orthorhombic space group *Pbcm* [17]. The asymmetric unit of **1** consists of half a $R(POH)_2(PO)$, half a $[PMo_9O_{34}]$ subunit, half a trimethylamine molecule and half a tetramethyl ammonium (TMA) cation. The trimethylamine molecule presumably was generated by the decomposition of the TMAH [18]. The P-O bond lengths are in the range of 1.498(5)-1.583(4) Å, and the Mo-O bond distances are in the range of 1.658(5)-2.456(4) Å (Table S1). All these bond lengths are in the normal ranges as observed in other polyoxomolybdates [19-22]. The discrete structure of **1** contains one trivacant $[PMo_9O_{34}]$ subunit on which is grafted one $R(POH)_2(PO)$ through three P-O-Mo bridges (Fig. 1). The $[PMo_9O_{34}]$ subunit has a β -A-Keggin structure, which is formed by removing a M_3 cluster consists of corner shared octahedra from a saturated β -Keggin structure. Result from document indicates that a saturated Keggin type polyanion $[PM_{12}O_{40}]^{3-}$ can lose a $\{MO_{13}\}$ cluster to form a $[PM_9O_{34}]^{9-}$ unit under basic conditions [23]. To the best of our knowledge, compound **1** is the first example of polyoxomolybdate decorated by three phosphonate groups from one organotriphosphonic acid ligand. Moreover, there are intermolecular C-H...O hydrogen bonding interactions, which further extend the discrete structure into a 3D supramolecular framework (Table S2, Fig. 2).

Fig. 1. View of the discrete structure of **1**.

Fig. 2. View of the 3D supramolecular framework of **1**.

The UV-vis absorption spectrum of compound **1** has been studied in N, N'-

dimethyl formamide (DMF). As shown in Fig. 3, compound **1** shows a main absorption peak at 319 nm. In order to better understand the mechanism of the UV-vis absorption spectrum, we use the density functional theory (DFT) to get into the experimental data [24]. Based on the data of crystal structure, we use the Gaussian 09 software to carry out the electronic structure analysis [25]. We chose the hybrid B3LYP functional with basis set of LAN2DZ for Mo and 6-31G(d) for other elements to optimize the structure. The B3LYP functional is one of the most widely used functional to investigate the geometry of molecule with the balance of the amount of calculation and efficiency [26]. The cartesian coordinates of the molecule are listed in Table S3. The geometry calculated by theory corresponds well with the experimental data.

Fig. 3. The experimental (black dot) and computational (solid red line) patterns of the UV-Vis absorption spectra for the compound.

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Based on the optimized structure, we used the time-dependent density functional theory (TD-DFT) method to investigate the UV-Vis spectra of the molecule and compared the results with the experimental data [27]. The M06-2X hybrid functional was chosen since it is more suitable to describe the excited states for the transition elements [28]. As shown in Fig. 3, the predicted absorption peak is at 308 nm, which corresponds well with the experimental data (319 nm) with a slightly blue-shift. In the experiment, the measurement of the UV-Vis absorption spectrum of the compound was carried out in the DMF solution. So, in the theoretical simulation, the Polarizable Continuum Model (PCM) method was chosen to include the solvent reaction field. The main electronic transitions are from the organic ligand (occupied orbital) to the POM. For example, the absorption peak at 308 nm is mainly attributed to the electronic transitions from HOMO-1 to LUMO+5 and from HOMO-10 to LUMO with the large oscillator strength, and the main transitions assignments with the contributions are summarized in Table S4. As shown in Table S4, the transitions consist of two main wave lengths near 308 nm. The largest electron transitions

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contributions are from HOMO-1 to LUMO+5 (34.45%) and from HOMO-10 to LUMO (32.48%) as discussed above. Other transitions, for example, from HOMO-10 to LUMO, although the occupied electrons distributions (HOMO-10) are among the whole molecule, the organic fragment plays important part (see Fig.4). More molecular orbitals for the compound with the dominant electron transitions are shown in Fig. 4, from which it can be clearly seen that the absorption originates mainly from the electron transitions from the organic donor fragment to the POM part.

Fig. 4. Molecular orbital diagrams for the compound involved in the dominant electron transition.

In conclusion, a novel organotriphosphoryl polyoxomolybdate based on a trivacant $[\text{PMo}_9\text{O}_{34}]$ subunit has been synthesized under the hydrothermal condition. It should be pointed out that compound **1** is the first example of polyoxomolybdate decorated by three phosphonate groups from one organotriphosphonic acid. Moreover, the UV-vis absorption spectrum of the compound has been investigated experimentally and theoretically in detail, and the experimental spectrum of **1** corresponds well with the simulated result. The results indicate that the absorption spectrum of compound **1** can be approximately simulated by the theoretical calculation.

Acknowledgements

This work was supported by the National Science Foundation of China (21403081 and 21401063), the Jiangsu Province NSF (Grant Nos. BK20140453 and BK20140452). The authors thanks for the computational supported and discussion of Prof. Yongqing Qiu (NENU).

Appendix A. Supplementary material

CCDC 1482308 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data

Centre via www.ccdc.cam.ac.uk/data_request/cif. Supplementary data associated with this article can be found, in the online version, at doi:???

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[16] H_6L (0.04 g, 0.1 mmol), $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ (0.051 g, 0.3 mmol), $\text{H}_3\text{PMo}_{12}\text{O}_{40} \cdot \text{H}_2\text{O}$ (0.028 g, 0.015 mmol), TMAH (0.015 mL) and 8 mL water was sealed in a 15
30 mL Teflon reactor and heated at 180 °C for 3 days. After cooling to room

temperature at a rate of 10 °C/h, green crystals of compound **1** were collected in a 32% yield. Anal. Calcd for C₁₉H₃₈Mo₉N₂O₃₇P₄, (*M*_r = 1873.85): C, 12.18; H, 2.04; N, 1.50. Found: C, 12.09; H, 2.12; N, 1.61%. IR data (KBr, cm⁻¹): 3462 (s), 1620 (s), 1551 (w), 1489 (s), 1444 (w), 1416 (w), 1379 (w), 1214 (w), 1076 (s), 951 (s), 809 (s), 579 (s), 544 (s).

[17] Crystallographic data of the compound was recorded on an Oxford Diffraction Gemini R CCD with graphite-monochromated Mo K α radiation (λ = 0.71073 Å) at 293 K. Absorption correction was applied using multi-scan technique. The hydrogen atoms of H₂L were generate geometrically and refined as riding atoms with $d(\text{O-H}) = 0.82$ Å and $U_{\text{iso}} = 1.5U_{\text{eq}}(\text{O})$. Crystal data for **1**: C₁₉H₃₈Mo₉N₂O₃₇P₄, *M* = 1873.85, orthorhombic, space group *P b c m*, *T* = 293(2) K, *a* = 18.9514(5), *b* = 11.6892(3), *c* = 21.7443(6) Å, *V* = 4816.9(2) Å³, *Z* = 4, *D*_c = 2.584 g/cm³, a total of 17659 reflections were collected, of which 4293 were unique (*R*_{int} = 0.0454), final *R*₁ = 0.0313 for *I* > 2σ(*I*), *wR*₂ = 0.0698 for all data, GOOF = 0.989.

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Figure captions

5 **Chart 1.** View of the H₆L ligand used in this work.

Fig. 1. View of the discrete structure of **1**.

Fig. 2. View of the 3D supramolecular framework of **1**.

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Fig. 3. The experimental (black dot) and computational (solid red line) patterns of the UV–Vis absorption spectra for the compound.

Fig. 4. Molecular orbital diagrams for the compound involved in the dominant electron transition.

A novel organotriphosphoryl polyoxomolybdate has been prepared hydrothermally, where its absorption spectrum has been investigated experimentally and theoretically