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A Novel Organic–Inorganic Complex Based on Monosodium-substituted Keggin Phosphotungstate and Copper(II)–Ethylenediamine Groups

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A novel organic–inorganic complex $[Cu(en)_2]_3[\alpha\text{-}PW_{11}NaO_{39}]\cdot 2H_2O$ (**1**) was synthesized hydrothermally and characterized by elemental analyses, IR, UV, XPS, and X-ray single-crystal diffraction, constructed by monosodium-substituted Keggin phosphotungstates and copper(II)–ethylenediamine groups and formed a $6^5\cdot 8$ $CdSO_4$-like 3D framework.

Polyoxometalates (POMs) are discrete anionic clusters commonly based on molybdenum or tungsten oxides, which continue to attract interest as a result of their intriguing variety of architectures together with their potential applications in fields as disparate as catalysis,[1] materials science,[2] and medicine.[3] Among them, phosphotungstates are a classic subclass of POMs including multiplicate structural varieties, which can be constructed by saturated Keggin $[PW_{12}O_{40}]^{3-}$, monovacant $[PW_{11}O_{39}]^{7-}$, divacant $[PW_{10}O_{36}]^{7-}$, trivacant $[PW_9O_{34}]^{9-}$, or tetravacant $[PW_8O_{31}]^{9-}$ building units. For a long time, more investigations of phosphotungstates are focused on the reaction of saturated Keggin unit $[PW_{12}O_{40}]^{3-}$ or trivacant unit $[PW_9O_{34}]^{9-}$ with transition metal or lanthanide cations. Hitherto, however, the research on the monovacant $[PW_{11}O_{39}]^{7-}$ unit is comparatively limited. For example, in 1995, Galán-Mascarós et al. reported 1D chain-like manganese-monosubstituted Keggin phosphotungstates $(ET)_8[PW_{11}MnO_{39}]\cdot 2H_2O$.[4] Subsequently, Evans et al. and Yan et al. described respectively 1D chain-like monosubstituted phosphotungstate derivatives of cobalt $(Et_3NH)_5[PW_{11}CoO_{39}]\cdot 3H_2O$[5] and $[Co(dpa)_2(H_2O)_2]_2(Hdpa)[PW_{11}CoO_{39}]\cdot 3H_2O$.[6] In 2004 and 2005, Lisnard et al. extended the results of Evans and reported several phosphotungstates based on monosubstituted Keggin unit $[PW_{11}CuO_{39}]^{5-}$ with chain-like structure.[7] In 2006, Felices et al. discovered a 2D copper(II)-monosubstituted phosphotungstate $Na_2[Cu^I(4,4'\text{-bpy})]_3[PW_{11}CuO_{39}(H_2O)]\cdot 4H_2O$.[8] Synchronously, Nogueira et al. addressed a novel chain-like silver phosphotungstate $H_2Ag_{0.33}K_{3.67}[AgPW_{11}O_{39}]\cdot 8.25H_2O\cdot CH_3OH$.[9] In 2008, Zhao et al. reported several 1D copper(II)-monosubstituted phosphotungstates decorated by copper(II)–organoamine complexes.[10] To date, the 3D structural phosphotungstate framework constructed by monovacant $[PW_{11}O_{39}]^{7-}$ building units and transition-metal bridges has been not reported. Recently, our interest is focused on the assembly chemistry between lacunary Keggin phosphotungstates and lanthanide cations or transition metal in the presence of organic components, and we obtained two 2:2 types of monolanthanide-substituted polyoxometalates $[\{(\alpha\text{-}PW_{11}O_{39}H)Ln(H_2O)_3\}_2]^{6-}$ and $[\{(\alpha\text{-}PW_{11}O_{39})Ln(H_2O)(\eta^2,\mu\text{-}1,1)\text{-}CH_3COO\}_2]^{10-}$.[11] Herein, we report on a novel organic–inorganic complex $[Cu(en)_2]_3[\alpha\text{-}PW_{11}NaO_{39}]\cdot 2H_2O$ (**1**) (en = ethylenediamine),[12] which was constructed by monosodium-substituted Keggin phosphotungstates and copper(II)–ethylenediamine groups and formed $6^5\cdot 8$ $CdSO_4$-like 3D framework. In **1**, the reason of selecting en ligand is that it can adjust the reaction environment of solution and also coordinate to metal centers. To our knowledge, **1** represents the first 3D $6^5\cdot 8$ $CdSO_4$-like phosphotungstate derivative based on monovacant Keggin $[PW_{11}O_{39}]^{7-}$ subunits in POM chemistry.

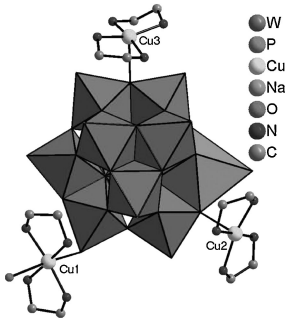

Figure 1. Polyhedral and ball-and-stick representation of polyoxo-anion of **1**. The hydrogen atoms are omitted for clarity.

The single-crystal X-ray diffraction analysis[13] of **1** revealed that the molecular structural unit of **1** (Figure 1) consists of a monosodium-substituted Keggin phosphotungstate unit $[\alpha\text{-}PW_{11}NaO_{39}]^{6-}$, three pendant crystallographic cations ($[Cu1(en)_2]^{2+}$, $[Cu2(en)_2]^{2+}$, and $[Cu3(en)_2]^{2+}$) and two lattice water molecules. In the crystal structure, the $[Cu1(en)_2]^{2+}$ cation adopts an octahedral geometry, which is coordinated by four nitrogen atoms from en ligands [Cu–N: 2.007(17)–2.029(16) Å] and two terminal oxygen atoms from two $[\alpha\text{-}PW_{11}NaO_{39}]^{6-}$ unit [Cu–O: 2.417(12)–2.624(13) Å], and bridges two "equatorial" WO_6 octahedra on two $[\alpha\text{-}PW_{11}NaO_{39}]^{6-}$ units through two terminal oxygen atoms. The pendant $[Cu2(en)_2]^{2+}$ cation is defined by four N atoms from two bidentate en ligands [Cu–N: 1.998(16)–2.035(17) Å] and one μ_3-O atom from the apical oxygen of the $\{W_2NaO_{13}\}$ triads [Cu–O: 2.440(11) Å], resulting in a five-coordinate square-pyramid geometry. Another five-coordinate $[Cu3(en)_2]^{2+}$ cation also displays a square pyramid where four N atoms from two en ligands [Cu–N: 1.938(19)–2.041(17) Å] build the basal plane and one μ_3-O atom from a W_3O_{13} triad stands on the apical position [Cu–O: 2.648(11) Å].

The remarkable feature of **1** is that the six-coordinate Na1 atom is incorporated into the lacunary site of the $[\alpha\text{-}PW_{11}O_{39}]^{7-}$ unit with Na–O bond lengths in the range of 2.244(13)–2.708(14) Å, and the adjacent $[\alpha\text{-}PW_{11}NaO_{39}]^{6-}$ units bridged by means of Na–O–W linkages generate 1D infinitely linear chain (Figure S1).[18] The mode of the 1D chains constituted by monosodium-substituted Keggin POM units is very rare,[14] although similar chain-like structures constructed from mono-transition-metal- or monolanthanide-substituted Keggin POM

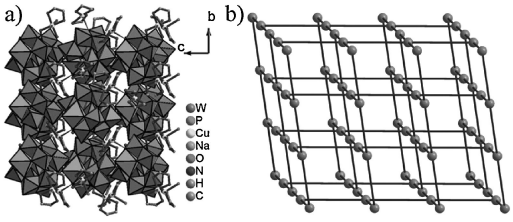

Figure 2. (a) The 3D structural framework of **1** viewed down the *a* axis. (b) The 3D $6^5 \cdot 8$ $CdSO_4$-like topological framework of **1**.

units have been reported frequently.[10,15]

Another feature of the polyoxoanion of **1** is three crystallographically independent $[Cu(en)_2]^{2+}$ complex cations anchoring to the $[\alpha\text{-}PW_{11}NaO_{39}]^{6-}$ unit, and the $[Cu1(en)_2]^{2+}$ bridged two adjacent $[\alpha\text{-}PW_{11}NaO_{39}]^{6-}$ units. Therefore, each $[\alpha\text{-}PW_{11}NaO_{39}]^{6-}$ unit connects four identical $[\alpha\text{-}PW_{11}NaO_{39}]^{6-}$ units by two Na1–O–W linkages and two W–O–Cu1–O–W linkages constructing a novel 3D extended network (Figure 2). From the topological point of view, the 3D framework of **1** is a four-connected network, belonging to the $6^5 \cdot 8$ $CdSO_4$ topology net, in which each $[\alpha\text{-}PW_{11}NaO_{39}]^{6-}$ unit acts as a four-connected node (Figure 2b). A topological analysis of this net was performed with OLEX.[16] The long topological (O'Keeffe) vertex symbol is $(6 \cdot 6 \cdot 6_2 \cdot 6 \cdot 6 \cdot \infty)$ for the $[\alpha\text{-}PW_{11}NaO_{39}]^{6-}$ node, which gives the short vertex (Schäfli) symbol $6^5 \cdot 8$.

IR spectrum shows that **1** displays characteristic vibration patterns of the Keggin-type structure (Figure S2).[18] The ν(P–O) vibration frequency appears at 1073 and 1042 cm^{-1}. Comparing with the saturated $[PW_{12}O_{40}]^{3-}$ anion,[17] the ν(P–O) asymmetric stretching vibration splits into two bands in monosubstituted $[\alpha\text{-}PW_{11}NaO_{39}]^{6-}$, resulting from the distortion of the PO_4 group encapsulated in the Keggin polyanion and the decline of polyanionic symmetry. In the low-wavenumber region ($\nu <$ 1000 cm^{-1}), several characteristic bands, appearing at 947; 883, 848, 801, 761; and 728 cm^{-1}, are attributed to $\nu(W\text{–}O_t)$, $\nu(W\text{–}O_b)$, and $\nu(W\text{–}O_c)$, respectively. The UV spectrum of **1** exhibits two obvious absorption bands (Figure S3).[18] The lower energy band at ca. 192 nm is attributed to the $p\pi\text{–}d\pi$ charge-transfer absorption band of $O_t \rightarrow W$ bonds, and the higher energy band at ca. 250 nm is attributed to the $p\pi\text{–}d\pi$ charge-transfer absorption band of $O_{c/b} \rightarrow W$ bonds.

In the XPS spectra for **1**, Figure 3a shows the spectrum of **1** in the W4f region with two peaks at 36.1 and 34.2 eV, corresponding to the $W4f_{7/2}$ and $W4f_{5/2}$ core-level, respectively, attributed to W^{6+}. XPS profiles of the Cu2p core-level spectra **1** are depicted in Figure 3b. The $Cu2p_{3/2}$ and $Cu2p_{1/2}$ core-level spectra show peaks appearing at 934.3 and 954.2 eV, respectively, ascribed to Cu^{2+}.

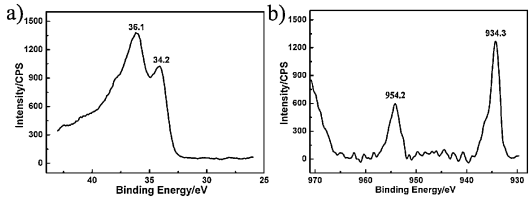

Figure 3. (a) XPS spectrum of $W4f_{7/2}$ and $W4f_{5/2}$ of **1** and (b) XPS spectrum of $Cu2p_{3/2}$ and $Cu2p_{1/2}$ of **1**.

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References and Notes

1 a) I. V. Kozhevnikov, *Chem. Rev.* **1998**, *98*, 171. b) C. L. Hill, *Angew. Chem., Int. Ed.* **2004**, *43*, 402.
2 T. Yamase, *Chem. Rev.* **1998**, *98*, 307.
3 D. A. Judd, J. H. Nettles, N. Nevins, J. P. Snyder, D. C. Liotta, J. Tang, J. Ermolieff, R. F. Schinazi, C. L. Hill, *J. Am. Chem. Soc.* **2001**, *123*, 886.
4 J. R. Galán-Mascarós, C. Giménez-Saiz, S. Triki, C. J. Gómez-García, E. Coronado, L. Ouahab, *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 1460.
5 H. T. Evans, T. J. R. Weakley, G. B. Jameson, *J. Chem. Soc., Dalton Trans.* **1996**, 2537.
6 B. Yan, Y. Xu, X. Bu, N. K. Goh, L. S. Chia, G. D. Stucky, *J. Chem. Soc., Dalton Trans.* **2001**, 2009.
7 a) L. Lisnard, A. Dolbecq, P. Mialane, J. Marrot, F. Sécheresse, *Inorg. Chim. Acta* **2004**, *357*, 845. b) L. Lisnard, A. Dolbecq, P. Mialane, J. Marrot, E. Codjovi, F. Sécheresse, *Dalton Trans.* **2005**, 3913.
8 L. S. Felices, P. Vitoria, J. M. Gutiérrez-Zorrilla, L. Lezama, S. Reinoso, *Inorg. Chem.* **2006**, *45*, 7748.
9 H. I. S. Nogueira, F. A. Almeida Paz, P. A. F. Teixeira, J. Klinowski, *Chem. Commun.* **2006**, 2953.
10 J.-W. Zhao, S.-T. Zheng, G.-Y. Yang, *J. Solid State Chem.* **2008**, *181*, 2205.
11 J. Niu, K. Wang, H. Chen, J. Zhao, P. Ma, J. Wang, M. Li, Y. Bai, D. Dang, *Cryst. Growth Des.* **2009**, *9*, 4362.
12 Preparation of **1**: $Na_8H[\beta\text{-}PW_9O_{34}] \cdot 26H_2O$ (0.395 g, 0.15 mmol), $CuCl_2 \cdot 2H_2O$ (0.256 g, 1.5 mmol), and en (0.15 mL) were dissolved into 10 mL of distilled water and then the pH value of the mixture was adjust to about 8.3 with hydrochloric acid (1 mol L^{-1}) solution; the solution was sealed in a 30-mL Teflon-lined autoclave and heated to 160 °C for 5 day. After slow cooling to room temperature, the black green crystals were obtained by filtering, washed with distilled water, and dried in air. Yield: 49% (based on W) Anal. Calcd for $C_{12}H_{52}Cu_3N_{12}NaO_{41}PW_{11}$ **1**: H, 1.59; C, 4.38; N, 5.11%. Found: H, 1.64; C, 4.42; N, 5.14%. IR (KBr pellets, ν/cm^{-1}): 3503(w), 3316(s), 3239(s), 2936(m), 2885(m), 1575(s), 1541(m), 1458(m), 1274(m), 1168(m), 1098(m), 1073(s), 1042(s), 947(s), 883(m), 848(s), 801(s), 762(m), and 728(m).
13 Crystal data for **1**: $C_{12}H_{52}Cu_3N_{12}NaO_{41}PW_{11}$, $M_r = 3287.59$, monoclinic, space group *Cc*, $a = 20.490(5)$, $b = 16.690(4)$, $c = 16.593(5)$ Å, $\beta = 104.582(4)°$, $V = 5492(2)$ $Å^3$, $T = 293(2)$ K, $Z = 4$, $\mu = 24.212$ mm^{-1}, 11611 reflections measured, 7768 independent ($R_{int} = 0.0343$). $R_1 = 0.0327$ ($I > 2\sigma(I)$), $wR_2 = 0.0855$ (all data). CCDC: 752862.
14 a) J. Zhao, Q. Han, P. Ma, L. Chen, J. Wang, J. Niu, *Inorg. Chem. Commun.* **2009**, *12*, 707. b) J.-Y. Niu, Z.-L. Wang, J.-P. Wang, *J. Solid State Chem.* **2004**, *177*, 3411.
15 J.-P. Wang, J.-W. Zhao, X.-Y. Duan, J.-Y. Niu, *Cryst. Growth Des.* **2006**, *6*, 507.
16 O. V. Dolomanov, A. J. Blake, N. R. Champness, M. Schröder, *J. Appl. Crystallogr.* **2003**, *36*, 1283.
17 L.-Z. Zhang, W. Gu, Z. Dong, X. Liu, B. Li, M.-L. Liu, *J. Solid State Chem.* **2009**, *182*, 1040.
18 Supporting Information is available electronically on the CSJ-Journal Web site, http://www.csj.jp/journals/chem-lett/index.html.

