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ScienceDirect
Chinese Chemical Letters 18 (2007) 81–84
CHINESE CHEMICAL LETTERS
www.elsevier.com/locate/cclet

A new chain-like heteropolytungstate formed by Keggin cluster units: Synthesis and structure of $[H_2bpy]_3[SiMnW_{11}O_{39}]\cdot 1.25H_2O$

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Received 15 May 2006

Abstract

A new heteropolytungstate, $[H_2bpy]_3[SiMnW_{11}O_{39}]\cdot 1.25H_2O$ (**1**), has been prepared under mild hydrothermal conditions and structurally characterized by single crystal X-ray diffraction. It is the first characterized compound containing 1D zigzag chain of transition metal substituted Keggin heteropolytungstate, which is connected through a common oxygen atom. The elemental analysis and IR of it are also described.

Keywords: Heteropolytungstate; Keggin clusters; Zigzag chain

As a rich and diverse class of organic–inorganic hybrid materials, transition metal substituted polyoxotungstates based on Keggin framework have received considerable attention for their fascinating structural, electrochemical, catalytic, magnetic and photophysical properties [1–4]. Although these transition metal substituted Keggin derivatives are generally reported as discrete entities, several literatures have shown that they are capable of acting as inorganic building blocks to form one-dimensional chain like self-assembly compounds, such as compounds $(ET)_8[PMnW_{11}O_{39}]\cdot 2H_2O$ (ET = bis (ethylenedithio) tetrathiofulvalene) [5], $[NEt_3H][XCoW_{11}O_{39}]\cdot 3H_2O$ (X = P, As) [6] and $[Co(dpa)_2(OH_2)_2]_2[Hdpa][PCoW_{11}O_{39}]$ (dpa = di-2-pyridylamine) [7] they all possess straight chain. In addition, Er^{III} mono-substituted $[\alpha\text{-}SiW_{11}O_{39}]^{8-}$ polyoxotungstate containing one-dimensional zigzag chainlike structure, which was connected by two common oxygen atoms, has been synthesized by Niu et al. [8].

On the basis of our previous works [9], here we report the synthesis and structure of the first characterized compound containing 1D zigzag chains of transition metal substituted Keggin heteropolytungstate **1**, which is connected through a common oxygen atom. It shows a new zigzag chain structure, which is different to the straight chain structure in the reported 1D transition metal substituted Keggin heteropolytungstate [5–7]. Furthermore, the zigzag chains of **1** form layers through short inter-species contact and these layers are stacked parallel and form a three-dimensional structure with dumbbell-like 1D channel.

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1001-8417/$ – see front matter
doi:10.1016/j.cclet.2006.11.020

1. Experimental

All organic solvents and materials used for synthesis were reagent grade and used without further purification. $K_8[\beta_2\text{-}SiW_{11}O_{39}]\cdot 14H_2O$ was prepared according to the literature method [10]. The identity was confirmed by IR spectrum.

Synthesis of the title compound: a mixture of $MnCl_2\cdot 4H_2O$ (0.25 g), 4,4′-bpy (0.032 g), $K_8[\beta_2\text{-}SiW_{11}O_{39}]\cdot 14H_2O$ (0.15 g) and H_2O (4 mL) was adjusted to pH (5–6) by adding HCl (1 mol/L), then the mixture was stirred for 20 min in air. The mixture was then transferred to a teflon-lined autoclave (20 mL) and kept at 130 °C for 5 days. After slow cooling to room temperature, red crystals were filtered, washed with distilled water and dried in a desiccator at room temperature to give a yield of 39% based on W. The elemental analysis (%) found: C, 11.20; H, 1.10; N, 2.55, calcd: C, 11.17; H, 1.02; N, 2.60. The ICP analysis (%) showed that **1** contained W, 62.50; Mn, 1.82; Si, 0.88, calcd: W, 62.68; Mn, 1.70; Si, 0.87. IR spectra: 3430, 1592, 1521, 1492, 1476, 1414, 1393, 1360, 1249, 1232, 1206, 1101, 1064, 1007, 961 and 914 cm^{-1}.

2. X-ray crystallography

A red single crystal of **1** was carefully selected under a polarizing microscope and glued at the tip of a thin glass fiber with cyanoacrylate (super glue) adhesive. Single crystal structure determination by X-ray diffraction was performed on a *R*-axis RAPID IP diffractometer equipped with a normal focus, 18 kW sealed tube X-ray source (Mo Kα radiation, λ = 0.71073 Å) operating at 50 kV and 200 mA. A total of 40,638 reflections were collected with 9320

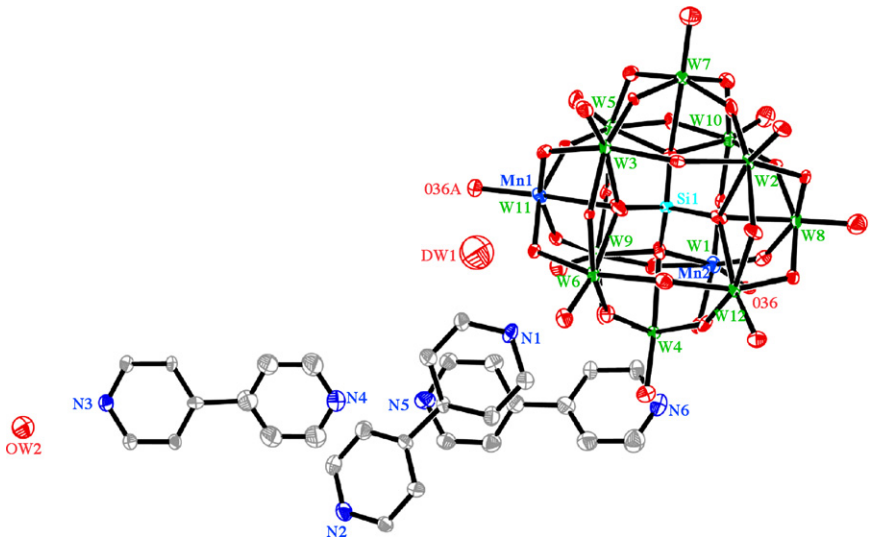

Fig. 1. ORTEP drawing of **1** showing the labeling of atoms with thermal ellipsoids at 50% probability. Hydrogen atoms are omitted for clarity.

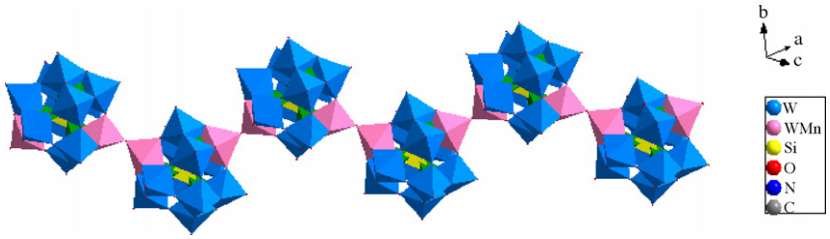

Fig. 2. A polyhedral view of the 1D chain in **1**. The pink octahedra are CuO_6, blue octahedra are WO_6 and yellow tetrahedra are SIO_4. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of the article.)

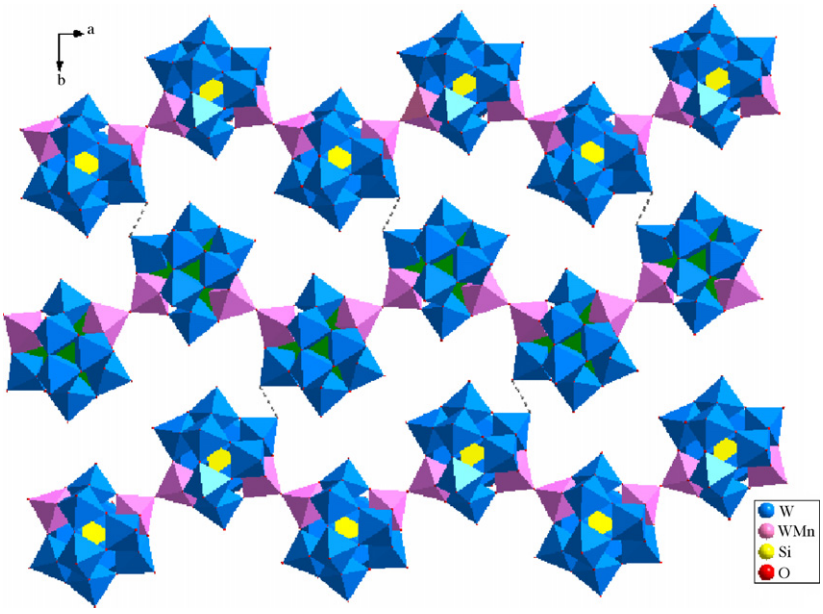

Fig. 3. View of the 2D layer in **1**.

($R_{int} = 0.1747$) independent reflections with $I > 2\sigma(I)$ ($3.05 < \theta < 25.00^{\circ}$, $-16 \leq h \leq 16$, $-30 \leq k \leq 31$, $-18 \leq l \leq 17$). The title compound is monoclinic, space group $P2(1)/n$ (no. 14) with $a = 13.577(3)$ Å, $b = 26.758(5)$ Å, $c = 15.142(3)$ Å, $\alpha = 90^{\circ}$, $\beta = 100.80(3)^{\circ}$, $\gamma = 90^{\circ}$, $V = 5403.4(19)$ Å [13], $Z = 4$, $R_1 = 0.0961$, $wR_2 = 0.1938$. Data processing was accomplished with the RAXWISH processing program. Empirical absorption correction was applied. The structure was solved by the direct method and refined by full-matrix least squares on F^2 using the SHELXL 97 software [11]. All of the non-hydrogen atoms were refined anisotropically.

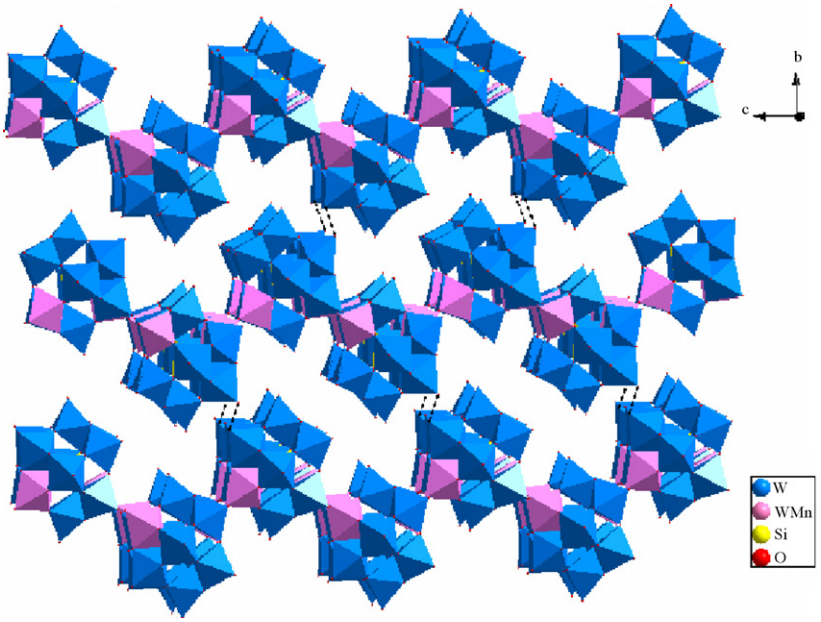

Fig. 4. Packing of the 2D layers showing the formation of 1D channel in **1**.

3. Results and discussion

The chemistry of Keggin polyoxotungstate has been studied for many years and is generally quite well known [12]. Though we have found similar zigzag chain structure in polyoxotungstates, but it is different in the connecting way [8]. The structure of **1** contains Keggin anions $SiMnW_{11}O_{39}^{6-}$, H_2bpy^{2+} cations and crystal water molecules (Fig. 1). These cations, polyanions and crystal water molecules are contacted with each other by N–H(bpy)···N(bpy), N–H(bpy)···O (polyanion), N–H(bpy)···O (crystal water) and O (crystal water)···O (polyanion) hydrogen bonds with distances of 2.60–3.00 Å. In **1**, W–O distances are ranged from 1.68(2) to 2.361(19) Å and the angles of O–W–O are varied between 71.5(7)° and 172.0(9)°. Si–O lengths are in the range of 1.64(2)–1.66(2) Å, the angles of O–Si–O are from 108.4(10)° to 110.9(11)°. The bond length of special O(36)–Mn(1)#2 is 1.83(2) Å. The Keggin anions are connected through a common oxygen atom to give a one-dimensional zigzag chain as shown in Fig. 2. This bridging oxygen atom connects two interval positions of the Keggin unit occupied by Mn(II) and W(VI). The zigzag chains in **1** form layers through short inter-species contact O15···O15 (at $1 - x$, $2 - y$, $-z$) 2.804 Å as shown in Fig. 3. Each $SiMnW_{11}O_{39}^{6-}$ unit joins with three adjacent $SiMnW_{11}O_{39}^{6-}$ units through covalent bonds and short inter-species contacts, respectively, thus resulting in dumbbell-liked voids circumscribed by six $SiMnW_{11}O_{39}^{6-}$ units. All such networks are piled in parallel to constitute a three-dimensional crystal structure. The voids left by stacking the layers form 1D channels in the direction perpendicular to the layers with dimensions of 21.496 × 3.765 Å [2] (Fig. 4). There are 4,4′-bipy cations and crystal water molecules situated in the dumbbell-like channels.

4. Conclusion

In summary, we have prepared a new chain-like heteropolytungstate formed by Keggin cluster units. The compound shows a zigzag chain structure, which is different from the straight chain structure formed in one-dimensional transition metal substituted Keggin heterotungstate. This work showed that the hydrothermal technique is a powerful method for the synthesis of new structural polyoxometalate compounds.

Acknowledgment

This work was supported by the National Natural Science Foundation of China (20371011).

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[13] Crystallographic data for structural analysis reported in this paper have been deposited in the Cambridge Crystallographic Data Center with the deposited number CCDC Number 612588 for **1**. Copy of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (e-mail: deposit@ccdc.cam.ac.uk; fax: +44 1223 336033).