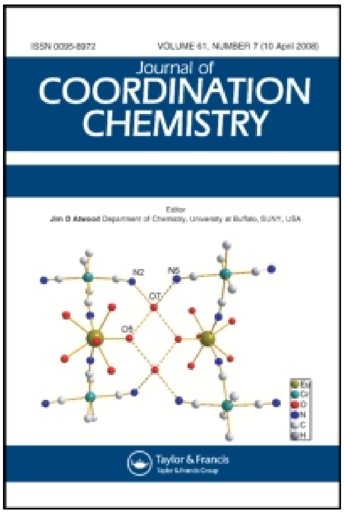

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Hydrothermal synthesis and crystal structure of a novel Metatungstate $[Cu(2,2'\text{-bipy})_3]_2H_2[H_2W_{12}O_{40}]\cdot4.5H_2O$

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HYDROTHERMAL SYNTHESIS AND CRYSTAL STRUCTURE OF A NOVEL METATUNGSTATE $[Cu(2,2'\text{-bipy})_3]_2H_2[H_2W_{12}O_{40}]\cdot 4.5H_2O$

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The title compound, $[Cu(2,2'\text{-bipy})_3]_2H_2[H_2W_{12}O_{40}]\cdot 4.5H_2O$, was synthesized by hydrothermal reaction and characterized by IR and single-crystal X-ray structural analysis. It belongs to the triclinic, space group $P\bar{1}$ with $a = 13.929(3)$ Å, $b = 17.493(4)$ Å, $c = 19.210(4)$ Å, $\alpha = 86.39(3)^\circ$, $\beta = 68.77(3)^\circ$, $\gamma = 74.21(3)^\circ$, $V = 4195.2(15)$ Å^3, $Z = 2$, $D_c = 3.158\,\mathrm{g\,cm^{-3}}$, $\mu = 16.970\,\mathrm{mm^{-1}}$, $F(000) = 3602$. This is the first hybrid material based on a metatungstate ion and transition metal coordination cations in which each copper atom is coordinated by six N atoms from three 2,2′-bipyridine molecules forming a distorted octahedron.

Keywords: Polyoxometalates; Hydrothermal synthesis; Crystal structure

INTRODUCTION

Polyoxometallates continue to be of interest because of their potential applications in sorption clathration, catalysis, electrical conductivity, magnetism and photochemistry [1–9]. Most polyoxometallates have discrete clusters of definite sizes and shapes constructed from closed and highly symmetrical networks of MO_6 octahedrons sharing corners, edges or faces [10]. Polyanions have acted as ligands coordinated to inorganic or organometallic complexes to form novel compounds with discrete units such as $[(CO)_3Mn(\textit{cis}\text{-}Nb_2W_4O_{19})]$ [11] and $[\{C_5Me_5\}Rh_2(Mo_{13}O_{40})]^{2+}$ [12], or with infinite extended structures as in $[\{Cu(2,2'\text{-bpy})\}_4(Mo_8O_{26})]$ [13] and $[Cu(en)_2(Mo_8O_{26})]$ [14].

The metatungstate ion $[H_2W_{12}O_{40}]^{6-}$ can be seen as a special Keggin polyanion in which two hydrogen atoms function as the heteroatom [15]. Since the reported preparation of $[(Bu_3NH)_5]H[H_2W_{12}O_{40}]$ [16], confirmed by only a structure analysis, a number of metatungstates such as $[N(CH_3)_4]_6[H_2W_{12}O_{40}]\cdot 2H_2O$ [17] and $Na_6[H_2W_{12}O_{40}]$ [18] have been prepared by various methods and characterized. However, to the best of our knowledge most of these are simple inorganic salts or organic ammonium salts

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without the participation of metal coordination cations. This paper deals with a novel hybrid material, $[Cu(2,2'\text{-bipy})_3]_2H_2[H_2W_{12}O_{40}]\cdot 4.5H_2O$, constructed from a metatungstate ion and copper-bipyridine cations.

EXPERIMENTAL

Materials and Methods

All chemicals were of reagent grade as received from commercial sources and used without further purification. C, H and N elemental analyses were performed on a Perkin-Elmer 240 C elemental analyzer. The infrared spectrum was recorded on a Nicolet 170SXFT-IR spectrometer with KBr pellets in the range 400–4000 cm^{-1}.

Synthesis of $[Cu(2,2'\text{-bipy})_3]_2H_2[H_2W_{12}O_{40}]\cdot 4.5\,H_2O$

A mixture of $Na_2WO_4\cdot 2H_2O$, $CuCl_2\cdot 2H_2O$, $CuSO_4\cdot 5H_2O$, 2,2′-bipyridine and H_2O in the mole ratio 1 : 0.2 : 0.2 : 0.2 : 260 was heated in a Teflon-lined acid digestion bomb for 96 h inside a programmable electric furnace at 160°C. After cooling the autoclave to room temperature for 48 h, the mixture gave slightly yellow crystals. The crystals were filtered, washed with distilled water and dried at ambient temperature. Yield: 20% based on W. Anal. Calc. for $[Cu(2,2'\text{-bipy})_3]_2H_2[H_2W_{12}O_{40}]\cdot 4.5H_2O$ (%): C, 18.02; H, 1.53; N, 4.20%; Found: C, 17.91; H, 1.20; N, 4.03%.

X-ray Crystallography of $[Cu(2,2'\text{-bipy})_3]_2H_2[H_2W_{12}O_{40}]\cdot 4.5H_2O$

A single crystal with dimensions $0.18\times 0.11\times 0.09$ mm was studied on a Rigaku RAXIS-IV image plate area detector using graphite monochromated Mo Kα diffraction ($\lambda = 0.71073$ Å) at room temperature. The data collection was in the range $4.48^\circ \leq 2\theta \leq 51.50^\circ$ with $-17 \leq h \leq +16$, $-21 \leq k \leq +21$ and $-23 \leq l \leq +21$. A total of 20 334 (14 346 independent reflections, $R_{\text{int}} = 0.1489$) reflections were measured. The data intensities were corrected by Lorentz polarization factors and empirical absorption. The structures were solved by direct methods and refined by the full-matrix least-squares method based on F^2 using SHELXTL-97 [19]. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were added according to theoretical models. The maximum and minimum peaks on the final difference Fourier map corresponded to 1.936 and -2.431 e Å^{-3}, respectively. A summary of the crystallographic data of the title compound is listed in Table I. Selected bond distances and bond angles are given in Table II.

RESULTS AND DISCUSSION

IR Spectra

The IR spectra of the title compound cations exhibited a series of characteristic bands from the 2,2′-bipyridine molecules at 1100–1600 cm^{-1}. Besides the complex cations, the title compound anion has four prominent peaks at 927, 871, 765 and 424 cm^{-1} attributed to $\nu(W{=}O_t)$, $\nu(W{-}O_b)$, $\nu(W{-}O_c)$ and $\nu(Cu{-}N)$, respectively. Comparing the IR

TABLE I Summary of crystallographic data of the title compound

Molecular formula	$C_{60}H_{61}Cu_2N_{12}O_{44.5}W_{12}$
Molecular weight	3995.44
Crystal system	triclinic
Space group	$P\bar{1}$
a	13.929(3) Å
b	17.493(4) Å
c	19.210(4) Å
α	86.39(3)°
β	68.77(4)°
γ	74.21(3)°
Z	2
V	4195.2(15) $Å^3$
Wavelength	$\lambda = 0.71073$ Å
D_{calcd}	3.158 gcm^{-3}
R_{int}	0.1489
Absorption coefficient	16.970 mm^{-1}
Goodness-of-fit on	0.664
Final R indices ($I > 2.0\sigma(I)$)	$R = 0.0785$, $Rw = 0.0972$
R indices (all data)	$R = 0.2476$, $Rw = 0.1215$

$w = 1/[\sigma^2(F_o^2) + (0.0147P)^2]$, $P = (F_o^2 + 2F_c^2)/3$.

TABLE II Selected bond distances (Å) and angles (°) of the title compound

Cu(1)–N(3′)	2.04(4)	Cu(1)–N(1′)	1.97(3)
Cu(1)–N(1)	2.09(3)	Cu(1)–N(2′)	2.05(4)
Cu(1)–N(3)	2.04(3)	Cu(1)–N(2)	2.09(3)
Cu(2)–N(6)	1.88(3)	Cu(2)–N(4)	2.03(3)
Cu(2)–N(6′)	1.90(3)	Cu(2)–N(5′)	1.90(3)
Cu(2)–N(4′)	2.00(3)	Cu(2)–N(5)	1.91(3)
W(1)–O(1)	1.75(2)	W(1)–O(37)	2.22(2)
W(2)–O(2)	1.80(2)	W(2)–O(37)	2.21(2)
W(3)–O(3)	1.64(3)	W(3)–O(37)	2.29(2)
W(4)–O(4)	1.79(2)	W(4)–O(40)	2.20(2)
W(5)–O(5)	1.77(2)	W(5)–O(40)	2.17(2)
W(6)–O(6)	1.57(3)	W(6)–O(40)	2.19(2)
W(7)–O(7)	1.770(19)	W(7)–O(38)	2.26(2)
W(8)–O(8)	1.63(2)	W(8)–O(38)	2.30(2)
W(9)–O(9)	1.67(2)	W(9)–O(38)	2.37(2)
W(10)–O(10)	1.73(3)	W(10)–O(39)	2.18(2)
W(11)–O(11)	1.58(3)	W(11)–O(39)	2.13(2)
W(12)–O(39)	2.180(18)	W(12)–O(12)	1.79(2)
W(10)–W(11)	3.219(3)	W(10)–W(12)	3.233(3)
W(11)–W(12)	3.208(3)	N(1)–Cu(1)–N(3)	178.4(13)
N(3′)–Cu(1)–N(3)	79.5(14)	N(1)–Cu(1)–N(1′)	80.5(12)
N(3′)–Cu(1)–N(1′)	89.3(13)	N(1)–Cu(1)–N(2′)	80.4(14)
N(3)–Cu(1)–N(1′)	98.3(14)	N(1′)–Cu(1)–N(2′)	98.8(16)
N(3′)–Cu(1)–N(2′)	171.9(17)	N(1)–Cu(1)–N(2)	97.8(11)
N(3)–Cu(1)–N(2′)	98.8(15)	N(1′)–Cu(1)–N(2)	177.7(11)
N(3′)–Cu(1)–N(2)	89.6(13)	N(2′)–Cu(1)–N(2)	82.3(15)
N(3′)–Cu(1)–N(1)	101.5(13)	N(6)–Cu(2)–N(6′)	81.5(13)
N(3)–Cu(1)–N(2)	83.5(12)	N(6)–Cu(2)–N(4′)	85.1(13)
N(6′)–Cu(2)–N(4′)	102.0(13)	N(6′)–Cu(2)–N(4)	175.6(14)
N(6)–Cu(2)–N(4)	96.5(13)	N(6)–Cu(2)–N(5′)	173.5(12)
N(4′)–Cu(2)–N(4)	81.6(12)	N(6)–Cu(2)–N(5)	90.0(13)
N(6′)–Cu(2)–N(5′)	95.9(12)	N(6′)–Cu(2)–N(5)	82.8(12)
N(4′)–Cu(2)–N(5′)	101.3(12)	N(4′)–Cu(2)–N(5)	172.6(14)
N(4)–Cu(2)–N(5′)	85.7(11)	N(5′)–Cu(2)–N(5)	83.7(11)
N(4)–Cu(2)–N(5)	93.4(12)	W(11)–W(10)–W(12)	59.64(6)
W(10)–W(11)–W(12)	60.39(7)	W(10)–W(12)–W(11)	59.97(6)

spectra of the title compound with the IR spectra of $[Bu_4N]_5H[H_2W_{12}O_{40}]$ [18], the vibration bands of $\nu(W{=}O_t)$, $\nu(W–O_b)$ and $\nu(W–O_c)$ have slight red shifts of about 17, 8 and $19\,cm^{-1}$. The results indicate that the $[H_2W_{12}O_{40}]^{6-}$ anion is affected weakly by surrounding metal coordination cations; the force constant and vibrational frequency of the W–O bonds are almost unchanged.

Structure Description

As shown in Fig. 1, the title compound is composed of one metatungstate anion, two copper-bipyridyl cations and 4.5 water molecules. The metatungstate anion $[H_2W_{12}O_{40}]^{6-}$ (Fig. 2) consists of two protons H^+ surrounded by a centrosymmetric $[W_{12}O_{40}]^{8-}$ cluster constructed from four W_3O_{13} groups that are linked together through sharing a corner. Each WO_6 octahedron is then linked to another by sharing an edge in every W_3O_{13} group in which three W atoms define an equilateral triangle with their angles 59.64, 59.97 and 60.39°, corresponding to bond lengths of 3.219, 3.223 and 3.208 Å, respectively. The oxygen atoms can be divided into four categories according to their different coordination environment in the heteropolyanions: O_t (terminal oxygen atoms connecting one W atom), O_b (atoms located in the shared corners between two W_3O_{13} units), O_c (oxygen atoms connecting edge-sharing WO_6 octahedra in the same W_3O_{13} unit) and O_a (oxygen atoms connecting the three W atoms). Relevant W–O bonds can be classified into three groups: W–O_t 1.57(3)–1.80(2) Å, W–$O_{b,c}$ 1.74(2)–2.09(2) Å, W–O_a 2.13(2)–2.37(2) Å. Their average distances are 1.71, 1.92 and 2.23 Å, respectively. Clearly, the average W–O distances increase with increasing coordination number of oxygen atoms. Comparing the W–O distances of the title compound with those of $TMA_6[H_2W_{12}O_{40}]\cdot 9H_2O$ [20], the W–O_t, W–$O_{b,c}$ and W–O_a lengths are shorter, which shows that $[H_2W_{12}O_{40}]^{6-}$ is little affected by the metal coordination cations $[Cu(2,2'\text{-bipy})_3]^{2+}$. The shortest bond distance is

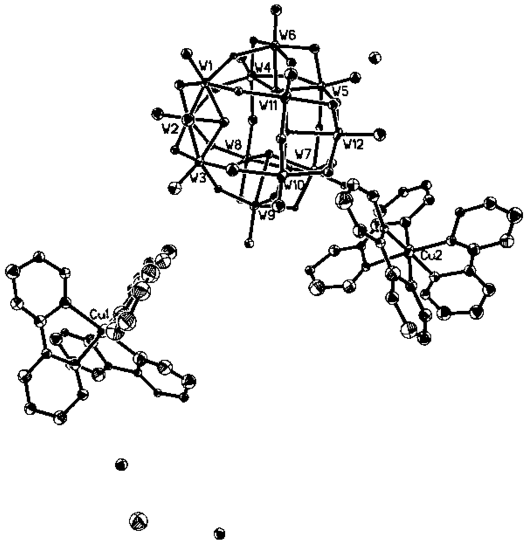

FIGURE 1 Molecular structure of $[Cu(2,2'\text{-bipy})_3]H_2[H_2W_{12}O_{40}]\cdot 4.5H_2O$ with partial atom labelling scheme. All hydrogen atoms are omitted for clarity.

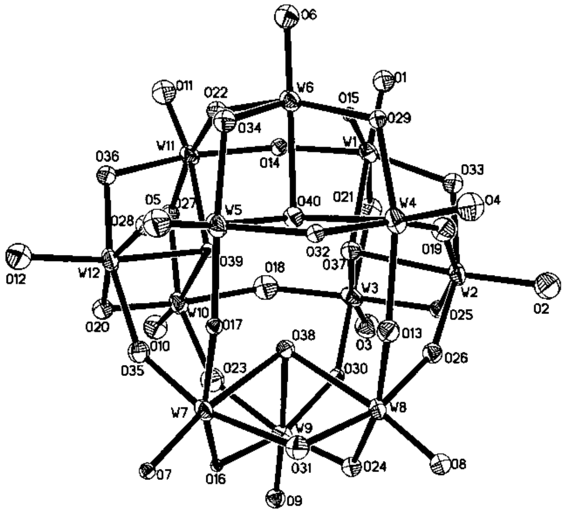

FIGURE 2 Structure of the metatungstate ion $[H_2W_{12}O_{40}]^{6-}$.

W(6)–O(6) 1.57(3) Å, while the longest bond length is W(9)–O(38) 2.37(2) Å. As can be seen from the bond distances, all the WO_6 octahedra were somewhat distorted in the metatungstate ion. The bond valences of O_a [O(37), O(38), O(39) and O(40)] calculated by means of the equation given in [21] are 1.258, 1.044, 1.54 and 1.447, respectively. Therefore, four oxygen (O_a) atoms are combined by two protons H^+, while two protons H^+ are near O_{37} and O_{39} atoms. Besides the metatungstate ion $[H_2W_{12}O_{40}]^{6-}$, there are two discrete $[Cu(2,2'\text{-bipy})_3]^{2+}$ cations acting as counterions. Each Cu atom is coordinated by six N atoms from three 2,2′-bipyridine molecules in a somewhat distorted CuN_6 octahedron. In $[Cu(1)(2,2'\text{-bipy})_3]^{2+}$, Cu(1)–N distances are in the range 1.97(3)–2.09(3) Å, corresponding to a mean value of 2.05 Å, while the average angle of N–Cu(1)–N is 90°. In the other $[Cu(2)(2,2'\text{-bipy})_3]^{2+}$ ion, Cu(2)–N distances are 1.88(3)–2.03(3) Å with an average value of 1.94 Å, and an average N–Cu(2)–N angle of 89.96°.

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