

一例夹心型含锰铋钨酸盐的合成、结构及磁学性质

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摘要: 在水相中合成了一例新的夹心型含锰铋钨酸盐 $\text{Na}_9\text{H}[(\text{Mn}(\text{H}_2\text{O})_3)_2(\text{Mn}(\text{H}_2\text{O})_2)(\text{WO}_2)(\text{BiW}_9\text{O}_{33})_2]\cdot 30\text{H}_2\text{O}$ (**1**)。通过元素分析、紫外光谱、红外光谱、粉末X射线衍射、单晶X射线衍射和热重分析对其进行了结构表征。单晶结构分析表明化合物**1**中的阴离子是由2个三缺位Keggin型 $\beta\text{-B}[\text{BiW}_9\text{O}_{33}]^{9-}$ 阴离子内、外连接2个 $[(\text{Mn}(\text{H}_2\text{O})_2)_{0.5}(\text{WO}_2)_{0.5}]^{2+}$ 配阳离子和2个 $[\text{Mn}(\text{H}_2\text{O})_3]^{2+}$ 亚单元组成。磁学性质研究表明在化合物**1**中锰离子之间存在反铁磁耦合作用。

关键词: 多金属氧酸盐; 夹心型; 晶体结构; 磁性

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Syntheses, Structures, and Magnetic Properties of Sandwich-Type Tungstobismuthate Containing Manganese

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Abstract: A new sandwich-type tungstobismuthate containing manganese (II), $\text{Na}_9\text{H}[(\text{Mn}(\text{H}_2\text{O})_3)_2(\text{Mn}(\text{H}_2\text{O})_2)(\text{WO}_2)(\text{BiW}_9\text{O}_{33})_2]\cdot 30\text{H}_2\text{O}$ (**1**), has been synthesized in the aqueous solutions and structurally characterized by elemental analyses, UV-Vis spectroscopy, IR spectroscopy, powder X-ray diffraction, single-crystal X-ray diffraction and thermogravimetric analysis. Single crystal X-ray analysis shows that the polyanion of **1** is composed of two trivacant $\beta\text{-B}[\text{BiW}_9\text{O}_{33}]^{9-}$ Keggin fragments joined together by two $[(\text{Mn}(\text{H}_2\text{O})_2)_{0.5}(\text{WO}_2)_{0.5}]^{2+}$ moieties and two $[\text{Mn}(\text{H}_2\text{O})_3]^{2+}$ subunits located in the inner and outer positions, respectively. Magnetic measurements indicate that **1** exhibits the antiferromagnetic couplings between Mn(II) centers. CCDC: 2141242.

Keywords: polyoxometalates; sandwich-type; crystal structure; magnetic property

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0 Introduction

Polyoxometalates (POMs) are a fascinating class of metal-oxygen cluster compounds, which exhibit compositional diversity and structural versatility as well as potential applications in a variety of fields, including catalysis, analytic chemistry, medicine, and materials science^[1-4]. In the development of POMs chemistry, lacunary polyoxoanions play an important role because they can serve as the nucleophilic inorganic multidentate ligands and coordinate to electrophiles of transition metal cations, organometallic or organic fragments to constitute a great quantity of novel transition metal substituted POMs (TMSPs) or organic-inorganic hybrid materials^[5-8]. Within the class of TMSPs, the sandwich-type polyoxoanions, accommodating lots of paramagnetic transition-metal cations between the two lacunary polyoxoanions, are an important subclass. Up to now, numerous sandwich-type polyoxoanions have been synthesized and mostly belong to the well-known Weakley- $[\text{M}_4(\text{H}_2\text{O})_2(\text{XW}_9\text{O}_{34})_2]^{n-}$ and $[\text{M}_4(\text{H}_2\text{O})_2(\text{X}_2\text{W}_{15}\text{O}_{56})_2]^{n-}$ ($\text{X}=\text{Si}^{\text{IV}}, \text{P}^{\text{V}}, \text{Ge}^{\text{IV}}, \text{As}^{\text{V}}$)^[9-11], Hervé- $[\text{M}_3(\text{H}_2\text{O})_3(\text{B}-\alpha-\text{XW}_9\text{O}_{33})_2]^{n-}$ ($\text{X}=\text{As}^{\text{III}}, \text{Sb}^{\text{III}}, \text{Se}^{\text{IV}}, \text{Te}^{\text{IV}}, \text{Bi}^{\text{III}}$)^[12-14], Krebs- $[(\text{WO}_2)_2\text{M}_2(\text{H}_2\text{O})_6(\beta-\text{XW}_9\text{O}_{33})_2]^{n-}$ ($\text{X}=\text{Sb}^{\text{III}}, \text{Bi}^{\text{III}}$) and $[\text{M}_4(\text{H}_2\text{O})_{10}(\beta-\text{XW}_9\text{O}_{33})_2]^{n-}$ ($\text{X}=\text{As}^{\text{III}}, \text{Sb}^{\text{III}}, \text{Te}^{\text{IV}}$)^[12,15-17] and Knoth-type $[\text{M}_3(\text{A}-\alpha-\text{XW}_9\text{O}_{34})_2]^{n-}$ ($\text{X}=\text{P}, \text{Si}$)^[18-19].

In contrast to the sandwich polyanions containing the $\text{Si}^{\text{IV}}, \text{P}^{\text{V}}$, and Ge^{IV} as heteroatoms, the analogues containing $\text{As}^{\text{III}}, \text{Sb}^{\text{III}}$, and Bi^{III} heteroatoms display peculiar crystal structures due to the stereochemical effect of the lone pair orbital electrons located on top of the trigonal pyramid^[15]. Besides, the ionic radius of Bi^{3+} (0.117 nm) is bigger than As^{3+} (0.072 nm) and Sb^{3+} (0.090 nm), which is also an important factor to induce the structural distinctiveness of polyoxotungstate clusters. In addition, it is well known that bismuth tungstate is a class of potential solid functional materials having excellent catalytic activity, ferroelectric, piezoelectric, and non-linear dielectric susceptibility^[20-22].

Therefore, the synthesis of polyoxotungstate clusters with heteroatom Bi^{3+} has aroused the wide attention of POMs researchers. Up to now, many dimeric tungstobismutates based on trivacant $\beta\text{-B}-(\text{BiW}_9\text{O}_{33})$ units have been reported, such as

$[(\text{WO}_2(\text{OH}))_2(\text{WO}_2)_2(\beta\text{-B}-\text{BiW}_9\text{O}_{33})_2]^{12-}$, and its transition/lanthanide metal-disubstituted complexes, $[(\text{M}(\text{H}_2\text{O})_3)_2(\text{WO}_2)_2(\beta\text{-B}-\text{BiW}_9\text{O}_{33})_2]^{(14-2n)-}$ ($\text{M}=\text{Fe}^{3+}, \text{Co}^{2+}, \text{Ni}^{2+}, \text{Cu}^{2+}, \text{Zn}^{2+}, \text{Mn}^{2+}$)^[9,15,23-26], $[(\text{M}(\text{H}_2\text{O})_3)_2(\text{WO}(\text{OH}))_2(\beta\text{-B}-\text{BiW}_9\text{O}_{33})_2]^{(14-2n)-}$ ($\text{M}=\text{Fe}^{3+}, \text{Cu}^{2+}$)^[27-28], $[\text{Sn}_{1.5}(\text{WO}_2(\text{OH}))_{0.5}(\text{WO}_2)_2(\beta\text{-B}-\text{BiW}_9\text{O}_{33})_2]^{10.5-}$ ^[29], $[(\text{M}(\text{H}_2\text{O})_2)_2(\text{WO}_2)_2(\beta\text{-B}-\text{BiW}_9\text{O}_{33})_2]^{(14-2n)-}$ ($\text{M}=\text{VO}^{2+}, \text{Co}^{2+}, \text{Ni}^{2+}, \text{Mn}^{2+}$)^[30-31], $[(\text{Pd}(\text{H}_2\text{O})_3)_3(\text{WO}_3)_2(\text{WO}_2)_2(\beta\text{-B}-\text{BiW}_9\text{O}_{33})_2]^{8-}$ ^[32], $[(\text{WO}(\text{dmsO}))_2(\text{Fe}(\text{dmsO})_3)_2(\beta\text{-B}-\text{BiW}_9\text{O}_{33})_2]^{4-}$ ^[33], $[\text{Fe}_4(\text{C}_2\text{O}_4)_4(\text{H}_2\text{O})_2(\beta\text{-B}-\text{BiW}_9\text{O}_{33})_2]^{14-}$ ^[34], $[(\text{RuC}_6\text{H}_6)_2(\text{WO}_2)_2(\beta\text{-B}-\text{BiW}_9\text{O}_{33})_2]^{10-}$ ^[35], $[(\text{W}(\text{OH}))_2(\text{Mn}(\text{H}_2\text{O})_3)_2(\beta\text{-B}-\text{BiW}_9\text{O}_{33})_2]^{6-}$ ^[36], $[(\text{M}(\text{H}_2\text{O})_3)_2(\text{Sn}(\text{CH}_2)_2\text{COO})_2(\beta\text{-B}-\text{BiW}_9\text{O}_{33})_2]^{10-}$ ($\text{M}=\text{Co}^{2+}, \text{Mn}^{2+}$)^[37], $[\text{Cu}_2(\text{WO}_2)_2(\beta\text{-B}-\text{BiW}_9\text{O}_{33})_2]^{12-}$ ^[38], $[(\text{M}(\text{H}_2\text{O})_2)_2(\text{M}_{0.5}(\text{W}_{0.5}\text{O}))_2(\beta\text{-B}-\text{BiW}_9\text{O}_{33})_2]^{10-}$ ($\text{M}=\text{Co}^{2+}, \text{Ni}^{2+}, \text{Mn}^{2+}$)^[39], and $[\text{Ln}_3(\text{H}_2\text{O})_{18}(\text{WO}_3)_2(\text{WO}_2)_2(\beta\text{-B}-\text{BiW}_9\text{O}_{33})_2]^{5-}$ ($\text{Ln}=\text{Ce}^{3+}, \text{Eu}^{3+}$)^[40-41]. Moreover, tungstobismuthates anions containing $\alpha\text{-B}-(\text{BiW}_9\text{O}_{33})$ units are also known as the Dawson-like polyanion $[\text{H}_3\text{BiW}_{18}\text{O}_{60}]^{6-}$ ^[42], dimeric polyanions $[\text{M}_x(\text{L})_y(\alpha\text{-B}-\text{BiW}_9\text{O}_{33})_2]^{(18-2n)-}$ ($\text{M}=\text{Co}^{2+}, \text{Mn}^{2+}, \text{L}=\text{imidazole}, 1\text{-methylimidazole}, \text{mim}, x=1, y=3; \text{M}=\text{Fe}^{3+}, \text{Co}^{2+}, \text{Ni}^{2+}, \text{Cu}^{2+}, \text{Cr}^{3+}, \text{Mn}^{2+}, \text{L}=\text{H}_2\text{O}, x=3, y=3; \text{M}=\text{Cu}^{2+}, \text{VO}^{2+}, x=3, y=0; \text{M}=\text{Cu}^{2+}, \text{L}=\text{H}_2\text{O}, x=1, y=3, x=4, y=2; \text{M}=\text{VO}^{2+}, x=2, y=0; \text{M}=\text{UO}_2^{2+}, \text{L}=\text{H}_2\text{O}, x=2, y=4$)^[43-53], $\{[\text{Cu}(\text{im})_4]\{\text{Na}(\text{H}_2\text{O})_2\}_3\{\text{Cu}_3(\text{im})_2(\text{H}_2\text{O})\}(\alpha\text{-B}-\text{XW}_9\text{O}_{33})_2\}^{14-}$ ^[54], $[\text{Cu}(\text{im})_4\{\text{Na}(\text{H}_2\text{O})_2\text{Co}(\text{im})\}_3(\alpha\text{-B}-\text{BiW}_9\text{O}_{33})_2]^{10-}$ ^[55], $[\text{Zn}_2(\text{H}_2\text{O})_{10}(\text{ZnCl})_6(\alpha\text{-B}-\text{BiW}_9\text{O}_{33})_2]^{8-}$ ^[56], and trimeric polyanions $[(\text{Np}_3\text{W}_4\text{O}_{15})(\text{H}_2\text{O})_3(\alpha\text{-B}-\text{BiW}_9\text{O}_{33})_3]^{18-}$ ^[57], $[\text{Bi}_2\text{Ag}_3\text{Na}(\text{W}_3\text{O}_{10})(\alpha\text{-B}-\text{BiW}_9\text{O}_{33})_3]^{19-}$ ^[58], $[\text{Bi}_6(\text{OH})_3(\text{H}_2\text{O})_3\text{V}_4\text{O}_{10}(\alpha\text{-B}-\text{BiW}_9\text{O}_{33})_3]^{12-}$ ^[59], tetrameric polyanions $[(\text{WO}_3)(\text{Bi}_6(\mu_3\text{-O})_4(\mu_2\text{-OH})_3)(\text{Ln}_3(\text{H}_2\text{O})_6\text{CO}_3)(\alpha\text{-B}-\text{BiW}_9\text{O}_{33})_4]^{22-}$ ^[60]. Above these reports, rare examples of dimeric polyanions containing tetranuclear metal clusters except for $[\text{Fe}_4(\text{C}_2\text{O}_4)_4(\text{H}_2\text{O})_2(\text{BiW}_9\text{O}_{33})_2]^{14-}$ ^[34] and $[\text{Cu}_4(\text{H}_2\text{O})_2(\text{BiW}_9\text{O}_{33})_2]^{10-}$ ^[28], and few examples of sandwich tungstobismutates serving as a catalyst have been reported^[12,35].

Taking into this account, our current synthetic strategy is to obtain new sandwich tungstobismutates containing multinuclear metal clusters with special properties applicable to magnetism, catalysis, medicine, or materials science through conventional solution syntheses. Here we reported the synthesis, structure, and some properties of new manganese(II) decorated tungstobismuthate(III)

$\text{Na}_9\text{H}[(\text{Mn}(\text{H}_2\text{O})_3)_2(\text{Mn}(\text{H}_2\text{O})_2)(\text{WO}_2)(\text{BiW}_9\text{O}_{33})_2] \cdot 30\text{H}_2\text{O}$ (1).

1 Experimental

1.1 Materials and measurements

All chemicals purchased were of reagent grade and used without further purification. $\text{Na}_9[\text{BiW}_9\text{O}_{33}] \cdot 16\text{H}_2\text{O}$ was synthesized according to the literature^[59] and characterized by IR spectra. Elemental analysis (C, H, and N) was performed on a Vario EL III CHN elemental analyzer. Na, Bi, W, and Mn were analyzed on an IRIS Advantage ICP atomic emission spectrometer. IR spectra were recorded on an EQUINOX55 IR spectrometer with KBr pellets. UV spectra were performed on a Shimadzu UV-2550 spectrophotometer. The powder X-ray diffraction (PXRD) data were recorded on a Rigaku RU200 diffractometer at 60 kV, 300 mA, and Cu $K\alpha$ radiation ($\lambda = 0.154\ 06\ \text{nm}$), with a scan speed of $5\ (^{\circ}) \cdot \text{min}^{-1}$ and a step size of 0.02° in a 2θ range of 5° – 50° . Thermogravimetric (TG) analysis was performed on a model Q600SDT analyzer in flowing N_2 with a heating rate of $10\ ^{\circ}\text{C} \cdot \text{min}^{-1}$. Magnetism measurements were performed on a Quantum Design MPMS SQUID magnetometer.

1.2 Synthesis of tungstobismuthate 1

$\text{Na}_9[\text{BiW}_9\text{O}_{33}] \cdot 16\text{H}_2\text{O}$ (2.886 g, 1 mmol) was dissolved in 20.0 mL H_2O to form solution A. $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$ (0.297 g, 1.5 mmol) was dissolved in 5.0 mL H_2O to form solution B. Then, solution B was added dropwise to solution A. The pH value of the solution was adjusted to 4.5 at room temperature by the addition of $1\ \text{mol} \cdot \text{L}^{-1}$ HCl. The mixture was kept at $80\ ^{\circ}\text{C}$ for about 1 h and then cooled to room temperature and filtered. Yellow prismatic crystals of **1** were isolated in a week (Yield: 36% based on W). Anal. Calcd. for $\text{H}_{77}\text{Bi}_2\text{Mn}_3\text{Na}_9\text{O}_{106}\text{W}_{19}$ (%): H, 1.28; Na, 3.41; Mn, 2.72; W, 57.67; Bi, 6.90. Found(%): H, 1.29; Na, 3.49; Mn, 2.67; W, 57.46; Bi, 7.05. IR (KBr, cm^{-1}): 3 417(s), 1 627(m), 929(m), 817(s), 680(m).

1.3 X-ray crystallography

The selected crystal of **1** was mounted on a glass fiber capillary for indexing and intensity data collection at 296 K on a BRUKER SMART APEX II CCD

diffractometer using Mo $K\alpha$ radiation ($\lambda = 0.071\ 073\ \text{nm}$). The structure was solved by direct methods (SHELXL-2018) and refined by the full-matrix-block least-squares method on F^2 . All heavy atoms (W, Mn, Na, and Bi) were refined anisotropically and other atoms were refined isotropically, and hydrogen atoms were not included. A summary of the crystal data and structure refinements for **1** is given in Table 1. Selected bond lengths and angles are listed in Table S1 (Supporting information).

CCDC: 2141242.

Table 1 Crystallographic data and structure refinement for the compound

Parameter	1
Empirical formula	$\text{H}_{77}\text{Bi}_2\text{Mn}_3\text{Na}_9\text{O}_{106}\text{W}_{19}$
Formula weight	6 056.19
T / K	296
Crystal system	Monoclinic
Space group	$P2_1/n$
a / nm	1.246 65(8)
b / nm	1.277 23(8)
c / nm	2.944 95(19)
$\beta / (^{\circ})$	100.783 0(10)
V / nm^3	4.606 3(5)
Z	2
$F(000)$	5 190
$D_c / (\text{g} \cdot \text{cm}^{-3})$	4.311
θ range for data collection / $(^{\circ})$	1.680–25.098
Limiting indices	$-14 \leq h \leq 14$, $-15 \leq k \leq 15$, $-35 \leq l \leq 30$
Reflection collected, unique	22 522, 8 147
μ / mm^{-1}	27.075
R_{int}	0.051 7
GOF on F^2	1.058
Final R indices [$I > 2\sigma(I)$] R_1, wR_2	0.050 6, 0.135 5
R indices (all data) R_1, wR_2	0.066 4, 0.144 5

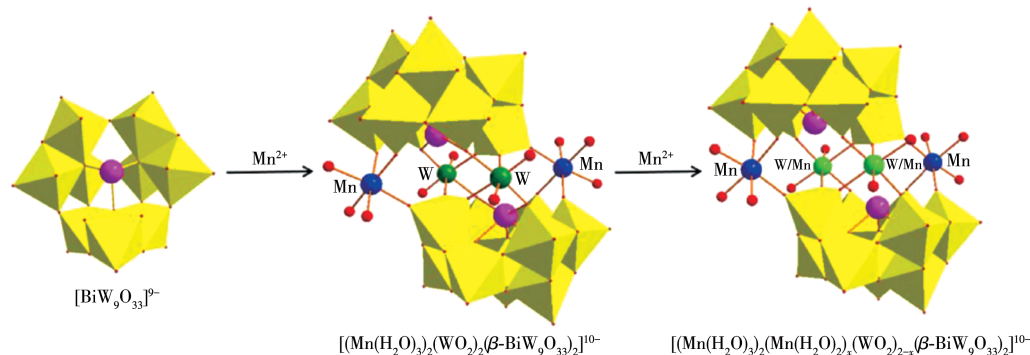
2 Results and discussion

2.1 Synthesis

Compound **1** was synthesized by mixing $\text{Na}_9[\text{BiW}_9\text{O}_{33}] \cdot 16\text{H}_2\text{O}$ and $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$ (1 : 1.5, n/n) in a pH 4.5 aqueous solution under conventional conditions. In view of the very recent work of Krebs^[15–16] and Kortz^[32], we find the ratio of Mn^{2+} to $[\text{BiW}_9\text{O}_{33}]^{10-}$ is a

phase-determining factor for the formation of the title compound. When the ratio was lower than 1:1, $[(\text{Mn}(\text{H}_2\text{O})_3)_2(\text{WO}_2)_2(\beta\text{-BiW}_9\text{O}_{33})_2]^{10-}$ was obtained. At a higher ratio (1.5:1), compound **1** was obtained. Last but not least, why the dimeric polyanions containing tetranuclear manganese cluster $[(\text{Mn}(\text{H}_2\text{O})_2)_4(\beta\text{-BiW}_9\text{O}_{33})_2]^{10-}$

was not obtained when the ratio was higher than 2:1? A reason is that the $[(\text{Mn}(\text{H}_2\text{O})_2)_4(\beta\text{-BiW}_9\text{O}_{33})_2]^{10-}$ polyanion is unstable and easily transforms into $[(\text{Mn}(\text{H}_2\text{O})_2)_2(\text{Mn}(\text{H}_2\text{O})_2)_2(\text{WO}_2)_{2-2x}(\beta\text{-BiW}_9\text{O}_{33})_2]^{10-}$ at the lower pH. We presume that the mechanism of formation of compound **1** is as follows (Scheme 1).



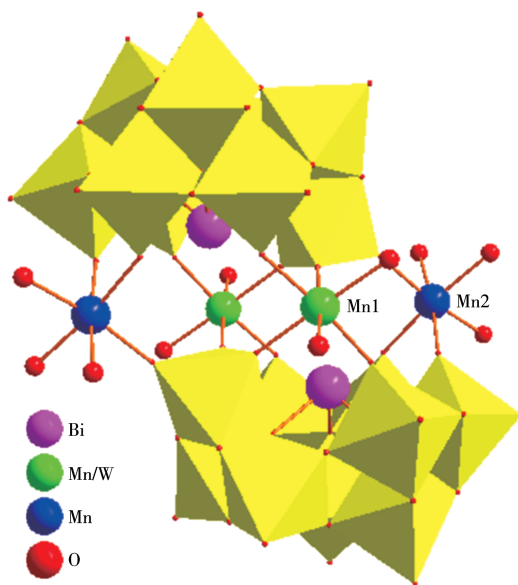
Scheme 1 Mechanism of formation of compound **1**

2.2 Structure description

Single crystal X-ray analysis reveals that compound **1** is composed of sandwich-type $[(\text{Mn}(\text{H}_2\text{O})_3)_2(\text{Mn}(\text{H}_2\text{O})_2)(\text{WO}_2)(\beta\text{-BiW}_9\text{O}_{33})_2]^{10-}$ polyanions, sodium cations, H^+ ion, and lattice water molecules^[15,40]. The sandwich-type $[(\text{Mn}(\text{H}_2\text{O})_3)_2(\text{Mn}(\text{H}_2\text{O})_2)(\text{WO}_2)(\beta\text{-BiW}_9\text{O}_{33})_2]^{10-}$ polyanion assembly of two trivalent $\beta\text{-B-[BiW}_9\text{O}_{33}]^{9-}$ Keggin fragments connected by two $[(\text{Mn}(\text{H}_2\text{O})_2)_{0.5}(\text{WO}_2)_{0.5}]^{2+}$ moieties and two $[\text{Mn}(\text{H}_2\text{O})_3]^{2+}$ subunits are located in the inner and outer positions, respectively (Fig. 1). The manganese atom Mn1 is disordered with tungsten atom W10 and shared with the occupancies of 50% Mn and 50% W, respectively. This trivalent $\beta\text{-B-[BiW}_9\text{O}_{33}]^{9-}$ unit derives from the Keggin structure by removing one W_3O_{13} fragment. The trivalent unit consists of three edge-sharing W_3O_{13} groups with the central Bi^{3+} which is surrounded pyramidally by three oxygen atoms. The lone pair is located on the top of the pyramid. Generally, $\beta\text{-B-[XW}_9\text{O}_{33}]^{9-}$ units can be derived from the $\alpha\text{-B-type}$ anions by 60° rotation of one W_3O_{13} group around the $\text{X-O}_{\text{W}3\text{X}}$ binding vector. In compound **1**, each $[(\text{Mn}(\text{H}_2\text{O})_2)_{0.5}(\text{WO}_2)_{0.5}]^{2+}/[\text{Mn}(\text{H}_2\text{O})_3]^{2+}$ unit links two $\beta\text{-B-[BiW}_9\text{O}_{33}]^{9-}$ units by four/three terminal-oxygen atoms from two $\beta\text{-B-[BiW}_9\text{O}_{33}]^{9-}$ units, and Mn1/Mn2 exhibits an octahedral coordination arrangement defined by two oxygen atoms of one $\beta\text{-B-[BiW}_9\text{O}_{33}]^{9-}$

moiety and two/one oxygen atoms of the other, the additional free coordination sites are completed by two/three water molecules. The Mn—O bond distances range from 0.209 0(14) to 0.228 0(20) nm with an average of 0.215 9 nm, while the O—Mn—O angles vary from $82.2(6)^\circ$ to $178.0(7)^\circ$.

In the packing arrangement of compound **1**, the



Only parts of manganese atoms are labeled, and all the Na atoms and water molecules are omitted for clarity

Fig.1 View of the novel polyanion of **1**, showing the coordination environments around Mn

adjacent sandwich-type polyoxoanions are stacked into a 3D supramolecular framework via the extensive H-bonding interactions between water molecules and the polyoxoanions as well as the electrostatic forces between Na^+ cations and the polyoxoanions (Fig.S1).

2.3 IR spectrum

The IR spectrum of compound **1** exhibited prominent characteristic peaks for the sandwich-type structure at 929, 817, and 680 cm^{-1} , which can be ascribed to the $\text{W}-\text{O}_\text{d}$, $\text{W}-\text{O}_\text{b}-\text{W}$, and $\text{W}-\text{O}_\text{c}-\text{W}$ vibrations of the polyoxoanion cluster (Fig.2). The strong peak at 1 627 cm^{-1} can be assigned to isolated solvent water molecules. The peak at 3 417 cm^{-1} can be assigned to the O—H vibration.

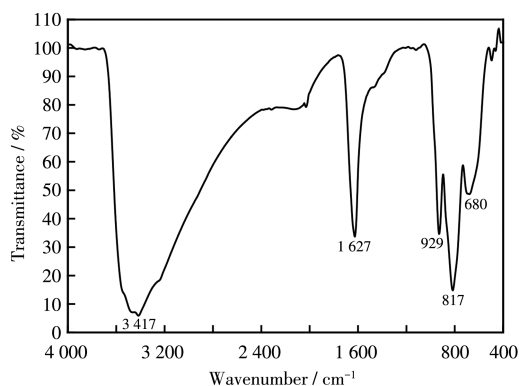


Fig.2 IR spectrum of compound **1**

2.4 UV spectrum

In the UV region (Fig.3), compound **1** exhibited two characteristic bands for the ligand to metal charge transfer in the polyanions. The more intense band corresponding to the $p_\pi(\text{O}_\text{d}) \rightarrow d_{\pi^*}(\text{W})$ transitions^[61] appeared at 195.8 nm. The broader band around 250.0 nm is assigned to a $p_\pi(\text{O}_{\text{b,c}}) \rightarrow d_{\pi^*}(\text{W})$ charge transfer

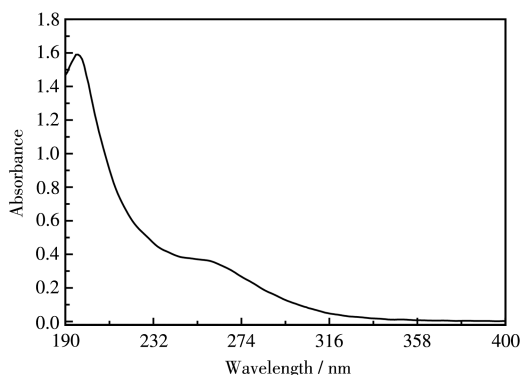


Fig.3 UV spectrum of compound **1** in aqueous solution

transition in the tri-centric bonds of POMs, which is consistent with the values in the literature (193.6 and 250.7 nm)^[48].

2.5 TG analysis

To examine the thermal stability of compound **1**, TG analysis was carried out. The TG curve of **1** showed one main weight loss (Fig.4). The TG curve of **1** showed the compound lost weight in a temperature range of 20–350 $^{\circ}\text{C}$, and the total weight loss was 11.59%, corresponding to the loss of lattice water molecules and coordinated water molecules. The value of weight loss from the TG curve for compound **1** (11.59%) was in agreement with the calculated value (11.95%).

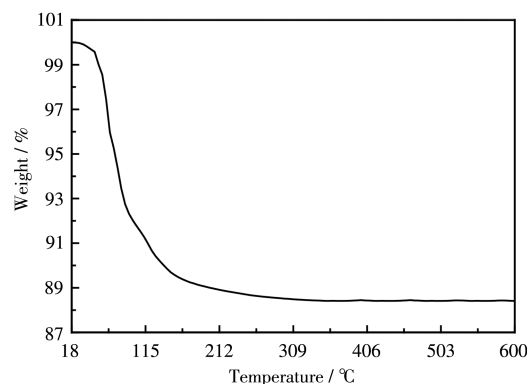


Fig.4 TG curve of compound **1**

2.6 PXRD analysis

In order to check the phase purity of compound **1**, PXRD experiment was carried out. As shown in Fig.5, the diffraction peaks on the pattern corresponded well in position, confirming that the product is a pure phase. The differences in reflection intensity are probably due to preferred orientation in the powder samples.

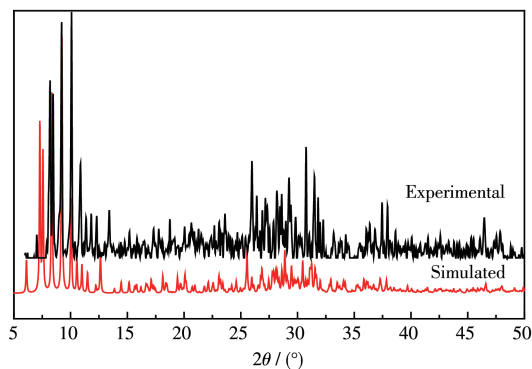


Fig.5 PXRD patterns from the single-crystal structure determination and as-synthesized product of compound **1**

2.7 Magnetic properties

Fig.6 shows the experimental data of **1** plotted as the $\chi_M T$ vs T and χ_M vs T . The $\chi_M T$ value of $12.68 \text{ cm}^3 \cdot \text{K} \cdot \text{mol}^{-1}$ at 300 K was close to that of three uncoupled manganese (II) ions ($13.13 \text{ cm}^3 \cdot \text{mol}^{-1} \cdot \text{K}$), which was larger than that expected for two manganese ions ($8.75 \text{ cm}^3 \cdot \text{mol}^{-1} \cdot \text{K}$) and smaller than that expected for four manganese ions ($17.50 \text{ cm}^3 \cdot \text{mol}^{-1} \cdot \text{K}$). This result also confirms the presence of sandwich-type $[(\text{Mn}(\text{H}_2\text{O})_3)_2(\text{Mn}(\text{H}_2\text{O})_2)(\text{WO}_2)(\text{BiW}_9\text{O}_{33})_2]^{10-}$ polyanion. Subsequently the $\chi_M T$ decreased continuously with decreasing temperature. Below 50 K, $\chi_M T$ quickly decreased and then reached a minimum value of $4.35 \text{ cm}^3 \cdot \text{mol}^{-1} \cdot \text{K}$ at 1.8 K. This behavior indicates the presence of relatively strong antiferromagnetic interactions between the Mn(II) ions.

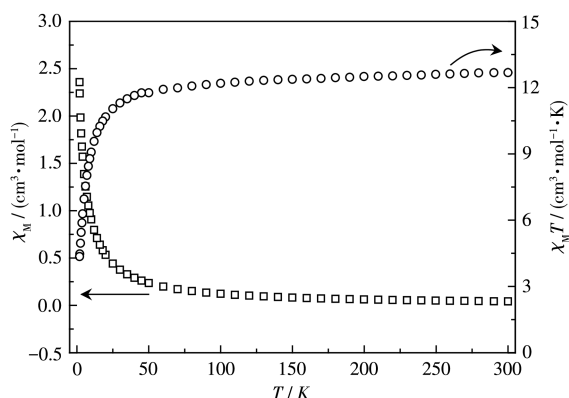


Fig.6 Temperature dependence of $\chi_M T$ and χ_M for **1**

The magnetic susceptibility followed the Curie-Weiss law over the entire temperature range with $C = 12.80 \text{ cm}^3 \cdot \text{K} \cdot \text{mol}^{-1}$ and $\theta = -4.29 \text{ K}$ (Fig.7). The nega-

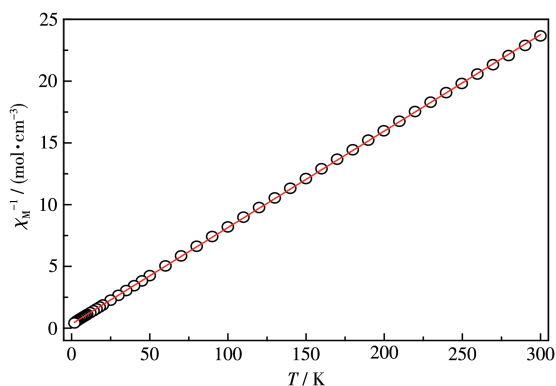


Fig.7 Plot of the temperature dependence of χ_M^{-1} for **1**, recorded on a powder sample at an applied field of 0.1 T

tive Weiss constant further demonstrates strong antiferromagnetic interactions between the Mn(II) ions through the oxygen bridges.

3 Conclusions

In summary, a new sandwich-type tungstobismuthate based on trivacant $\beta\text{-BiW}_9\text{O}_{33}]^{9-}$ Keggin polyanions and Mn(II) ions has been successfully synthesized by the aqueous solution method. Magnetic studies reveal that compound **1** exhibits relatively strong antiferromagnetic coupling interactions between Mn(II) ions in the central belt of polyoxoanion. The successful synthesis of **1** confirms that it is feasible to introduce the metal cations into the $[\text{BiW}_9\text{O}_{33}]^{9-}$ cluster for the construction of high-performance tungstobismuthates magnetics, and more investigations are underway.

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Supporting information is available at <http://www.wjhxxb.cn>

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