

A New Sandwich Polyoxometalate Constructed from a Zn_6^{12+} Hexagon Cluster Sandwiched by Two $B\text{-}\alpha\text{-}[BiW}_9O_{33}]^{9-}$

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Abstract A new sandwich polyoxometalate $Na_4Zn_2[Zn_2(H_2O)_{10}(ZnCl)_6(B\text{-}\alpha\text{-} BiW}_9O_{33})_2] \cdot 40.5H_2O$ (**1**) has been obtained in aqueous solution and characterized by IR, UV, element analysis, TG and single-crystal X-ray analysis. Polyoxoanion **1** is composed of a Zn_6^{12+} hexagon sandwiched by two $[BiW}_9O_{33}]^{9-}$ units, which is firstly observed in tungstobismutate. The crystal data for compound **1**: Triclinic, space group $P\bar{1}$, $a = 15.426(3)$ Å, $b = 15.467(3)$ Å, $c = 15.526(3)$ Å, $\alpha = 74.24(3)^\circ$, $\beta = 64.37(3)^\circ$, $\gamma = 60.73(3)^\circ$, $V = 2905.3(1)$ Å³, $Z = 1$.

Keywords Tungstobismutate · Sandwich polyoxometalate · Crystal structure · Zinc

Introduction

Polyoxometalates (POMs), as one kind of significant metal oxide cluster with nanosizes and abundant topologies, have been attracting extensive interest in fields such as catalysis, electrochemistry, electrochromism and magnetism [1, 2]. In the past decades, numerous novel transition-metal-substituted polyoxoanions have been synthesized, and a rapid progress in the synthesis and characterization of these new transition-metal-substituted POMs (TMSPs) is driven by interest in their structural diversity and fascinating properties with applications to catalysis, magnetism and electrochemistry [3, 4]. In the class of TMSPs, the sandwich-type polyoxoanions

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which are composed of a paramagnetic transition-metal cluster sandwiched by two lacunary polyoxoanions, are an important subclass. Recently, a great number of sandwich polyoxoanions have been reported, but mostly belong to the well-known Weakley-, Hervé-, Krebs- and Knoth-type sandwich structures [5, 6]. Therefore, the synthesis of new sandwich polyoxoanions with fundamentally novel structure continues to be a focus of considerable ongoing research.

The sandwich polyoxoanions with three or four transition metal cations were investigated extensively. However, the polyoxoanion containing a 5-fold coordination six-transition-metal-ion cluster sandwiched by two $[B\text{-}\alpha\text{-}XW_9O_{33}]^{12-}$ have been reported scarcely. The first examples of this polyoxoanion was obtained by Yamase et al. [7] in 2006 for $[(CuCl)_6(B\text{-}\alpha\text{-}AsW_9O_{34})_2]^{12-}$ and $[(MnCl)_6(B\text{-}\alpha\text{-}SbW_9O_{34})_2]^{12-}$. Hitherto, the Zn-containing analogues have never been reported.

In contrast to the well studied phosphotungstates, silicotungstates and tungstooarsenates sandwich polyoxoanions, the number of Bi-containing analogues is very small. Up to now, only several sandwich bismuth tungstates have been reported [8–13], for example: $K_{12}[(VO)_3(BiW_9O_{33})_2] \cdot 30H_2O$, $Na_8[Bi_2W_{20}Cu_2O_{68}(OH)_2(H_2O)_6] \cdot 26H_2O$, $Na_{10}[Cu_4(H_2O)_2(BiW_9O_{33})_2] \cdot 43H_2O$, $K_2Na_6(NH_4)_6[(VO)_2(BiW_9O_{33})_2] \cdot 41H_2O$.

Herein, we report the synthesis, characterization and crystal structure of a new sandwich tungstobismutate: $Na_4Zn_2[Zn_2(H_2O)_{10}(ZnCl)_6(B\text{-}\alpha\text{-}BiW_9O_{33})_2] \cdot 40.5H_2O$. The polyoxoanion **1** was composed of a Zn_6^{12+} hexagon sandwiched by two $[BiW_9O_{33}]^{9-}$ units, which was firstly observed in tungstobismutate.

Experimental

General Procedures

All chemicals purchased were commercially purchased and used without further purification. $Na_9[BiW_9O_{33}]$ was synthesized according to the literature [8] and characterized by IR spectrum. Bi, W, Cl, Zn and Na were analyzed on a PLASMA-SPEC(I) ICP atomic emission spectrometer. IR spectra were recorded in the range 400–4000 cm^{-1} on an Alpha Centaur FT/IR Spectrophotometer using KBr pellets. UV-vis absorption spectrum was obtained using a 752 PC UV-vis spectrophotometer. TG analysis was performed on Perkin-Elmer TGA7 instrument in flowing N_2 with a heating rate of 10 $^{\circ}C\ min^{-1}$.

Syntheses

Synthesis of $Na_4Zn_2[Zn_2(H_2O)_{10}(ZnCl)_6(B\text{-}\alpha\text{-}BiW_9O_{33})_2] \cdot 40.5H_2O$

In a typical synthesis procedure for **1**, $Na_9[BiW_9O_{33}]$ (2.0 g) was dissolved in water (30 mL). A solution of $ZnCl_2$ (0.01 mol) in water (10 mL) was added with stirring. The pH value of the mixture was carefully adjusted with a dilute HCl solution (1 M) to approximately 3.00. And then, the mixture was heated to 80 $^{\circ}C$ for 3 h. After cooling to room temperature, the filtrate was kept at room temperature, and slow

evaporation for two weeks resulted in the white crystals (Yield 60% based on $\text{Na}_9[\text{BiW}_9\text{O}_{33}]$). Anal. Calcd for **1** (%): Na, 1.38; H, 1.53; Cl, 3.20. Zn, 9.83; Bi, 6.28; W, 49.75. Found: Na, 1.35; H, 1.49; Cl, 3.23. Zn, 9.86; Bi, 6.24; W, 49.80. IR (KBr pellet): 948(s), 893(m), 819(s), 715(s), 649(m), 521(w), 447(m).

X-ray Crystallography

Single-crystal X-ray data for **1** was collected on a Rigaku R-AXIS RAPID IP diffractometer equipped with a normal focus 18 kW sealed tube X-ray source (Mo-K α radiation, $\lambda = 0.71073 \text{ \AA}$) operating at 50 kV and 200 mA. Data processing was accomplished with the RAXWISH processing program. A numerical absorption correction was applied. The structure was solved by direct methods and refined by full-matrix least-squares on F^2 using the SHELXL 97 software. All the non-hydrogen atoms were refined anisotropically. Further details of the X-ray structural analysis are given in Table 1. Selected bond lengths and angles are listed

Table 1 Crystal data and structure refinement for **1**

Complex	1
Chemical formula	$\text{H}_{101}\text{Na}_4\text{Zn}_{10}\text{Cl}_6\text{O}_{116.5}\text{Bi}_2\text{W}_{18}$
Formula weight	6651.43
T (K)	293(2)
λ (\AA)	0.71073
Crystal system	Triclinic
Space group	$P\bar{1}$
a (\AA)	15.426(3)
b (\AA)	15.467(3)
c (\AA)	15.526(3)
α ($^\circ$)	74.24(3)
β ($^\circ$)	64.37(3)
γ ($^\circ$)	60.73(3)
V (\AA^3)	2905.3(10)
Z	1
D_c (g/cm^3)	3.802 M
μ (mm^{-1})	23.04
F(000)	2977.0
Crystal size (mm)	0.32 \times 0.26 \times 0.24
θ range for data	3.03–25.00 $^\circ$
Limiting indices	$-17 \leq h \leq 18$, $-18 \leq k \leq 18$, $-18 \leq l \leq 18$
Reflections collected	9808
Independent reflections	7464 [$R(\text{int}) = 0.0822$]
Goodness of fit of F^2	1.028
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0497$, $wR_2 = 0.1106$
Largest diff. peak and hole	2.047 and $-2.432 \text{ e.\AA}^{-3}$

Note: $R_1 = \Sigma ||F_0| - |F_C|| / \Sigma |F_0|$; $wR_2 = [\sum [w(F_0^2 - F_C^2)^2] / \Sigma [w(F_0^2)^2]]^{1/2}$.

Table 2 Selected bond lengths (\AA) and angles ($^\circ$) for **1**

Bi(1)–O(9)	2.090(12)	W(1)–O(8)	1.724(11)
Bi(1)–O(10)	2.103(10)	W(1)–O(10)	2.258(11)
W(2)–O(11)	1.741(14)	W(3)–O(2)	1.726(13)
W(2)–O(6)	2.279(12)	W(3)–O(10)	2.285(12)
W(4)–O(3)	1.719(9)	W(5)–O(1)	1.723(11)
W(4)–O(6)	2.237(9)	W(5)–O(10)	2.247(10)
W(6)–O(4)	1.707(15)	W(7)–O(12)	1.712(11)
W(6)–O(9)	2.261(13)	W(7)–O(6)	2.273(10)
W(8)–O(18)	1.708(10)	W(9)–O(7)	1.720(10)
W(8)–O(9)	2.268(9)	W(9)–O(9)	2.266(9)
Zn(4)–O(25)	2.054(12)	Zn(3)–O(33)	2.052(11)
Zn(4)–O(21)	2.087(12)	Zn(3)–O(25)	2.110(11)
Zn(4)–Cl(2)	2.237(5)	Zn(3)–Cl(3)	2.240(4)
Zn(2)–O(21)	2.054(10)	Zn(1)–OW(18)	2.081(12)
Zn(2)–O(13)	2.103(11)	Zn(1)–O(3)	2.119(9)
Zn(2)–Cl(1)	2.237(4)	Na(1)–OW(17)	2.30(3)
Zn(5)–OW(8)	2.067(16)	Na(2)–OW(3)	2.38(2)
Zn(5)–OW(16)	2.197(19)	Na(2)–O(8)	2.440(15)
O(9)–Bi(1)–O(6)	85.4(4)	O(27)–W(1)–O(10)	72.9(4)
O(9)–Bi(1)–O(10)	86.6(4)	O(29)–W(1)–O(28)	158.8(5)
O(30)–W(2)–O(6)	73.5(4)	O(14)–W(3)–O(10)	72.5(4)
O(19)–W(2)–O(30)	160.4(5)	O(2)–W(3)–O(10)	170.9(5)
O(30)–W(4)–O(6)	74.0(4)	O(14)–W(5)–O(10)	72.7(4)
O(3)–W(4)–O(6)	169.3(4)	O(1)–W(5)–O(10)	168.6(4)
O(16)–W(6)–O(9)	73.1(5)	O(15)–W(7)–O(6)	73.5(4)
O(4)–W(6)–O(9)	168.3(4)	O(12)–W(7)–O(6)	167.2(5)
O(16)–W(8)–O(9)	73.0(4)	O(22)–W(9)–O(9)	73.0(4)
O(18)–W(8)–O(9)	167.1(6)	O(7)–W(9)–O(9)	170.9(6)
O(25)–Zn(4)–O(33)	79.9(4)	O(33)–Zn(3)–O(25)	79.3(4)
O(32)–Zn(4)–O(33)	139.7(4)	O(13)–Zn(3)–O(25)	139.2(4)
O(33)–Zn(4)–Cl(2)	114.6(3)	O(23)–Zn(3)–Cl(3)	115.3(3)
O(21)–Zn(2)–O(32)	80.4(5)	OW(6)–Zn(1)–OW(4)	89.6(6)
O(21)–Zn(2)–O(13)	139.0(4)	OW(18)–Zn(1)–O(3)	178.5(6)
O(32)–Zn(2)–Cl(1)	114.2(3)	OW(6)–Zn(1)–O(3)	86.0(4)
OW(9)–Zn(5)–OW(10)	85.4(6)	OW(13)–Na(1)–OW(17)	176.5(8)
OW(10)–Zn(5)–OW(16)	177.7(6)	O(8)–Na(2)–OW(17)	80.2(6)

in Table 2. And the crystal structure investigations may be obtained from the Fachinformationszentrum Karlsruhe, 76344 Eggenstein-Leopoldshafen, Germany (Fax: +49 7247 808 666; E-mail address: crysdata@fiz-karlsruhe.de), on quoting the depository number CSD 418548 for **1**.

Results and Discussion

Descriptions of the Structure

The compound **1** was synthesized from aqueous media and isolated as white block crystal. Single-crystal X-ray diffraction analysis shows that the heteropolyanion **1** is composed of a hexagon of six zinc groups sandwiched by two $\text{B}-\alpha\text{-}[\text{BiW}_9\text{O}_{33}]^{9-}$ units, which can also be described as a dimer of $[(\text{ZnCl})_3(\text{BiW}_9\text{O}_{33})]^{6-}$ building blocks related by an inversion center with a resultant D_{3d} symmetry [7]. A view of the anion is shown in Fig. 1. Each zinc atom adopts a square-pyramidal geometry, being coordinated by four terminal oxygen atoms from two $\text{B}-\alpha\text{-}[\text{BiW}_9\text{O}_{33}]^{9-}$ units with $\text{Zn}-\text{O}$ bond lengths of 2.052(11)–2.103(11) Å and one chlorine atom ($\text{Zn}-\text{Cl}$: 2.237(4)–2.240(4) Å). The six zinc atoms make an approximately equatorial hexagon by sharing the oxygen atoms (with a first-neighbor $\text{Zn}\dots\text{Zn}$ distance of 3.183(4) Å, neighboring $\text{Zn}-\text{Zn}-\text{Zn}$ angles of 119.97(1)°, and second-and third-neighbor $\text{Zn}\dots\text{Zn}$ distances of 5.478(8) and 6.422(3) Å (Fig. 2). In the center of each $[\text{BiW}_9\text{O}_{33}]^{9-}$ unit containing three corner sharing W_3O_{13} triads, the Bi(III) atom forms a BiO_3 trigonal pyramid with $\text{Bi}-\text{O}$ bond lengths of 2.090(12)–2.103(10) Å and the lone-paired electrons directed toward the opening of the unit.

Furthermore, in compound **1**, two μ_2 -oxygen atoms O(3) and O(3a) bridge the sandwich-type polyoxoanion $[(\text{ZnCl})_6(\text{BiW}_9\text{O}_{33})_2]^{12-}$ with Zn(1) and Zn(1a) respectively, with bond lengths W(4)–O(3) 1.719(9) Å, Zn(1)–O(3) 2.119(9) Å and band angle W(4)–O(3)–Zn(1) 174.6(8)°. Thus it can be concluded that the covalent interaction exists between Zn(1) and O(3) in **1**. As shown in Fig. 3, the

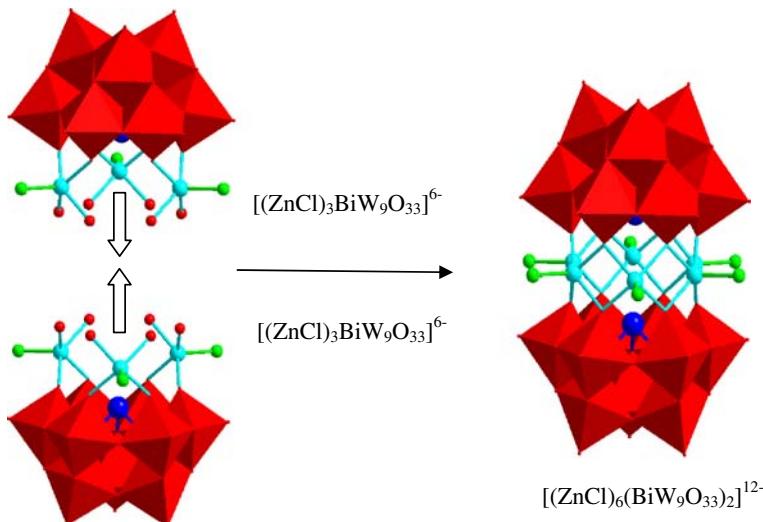


Fig. 1 The structure of $[(\text{ZnCl})_6(\text{BiW}_9\text{O}_{33})_2]^{12-}$ could be described as a dimer of $[(\text{ZnCl})_3(\text{BiW}_9\text{O}_{33})]^{6-}$ building blocks related by an inversion center with a resultant D_{3d} symmetry (Zn, sky blue; Bi, blue; Cl, green; O, red)

Fig. 2 Equilateral Zn_6^{12+} hexagon for **1**

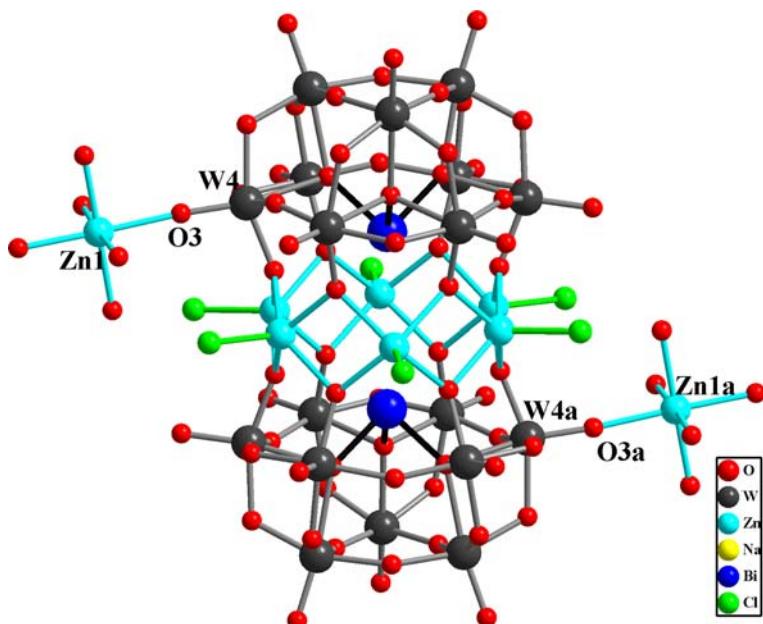
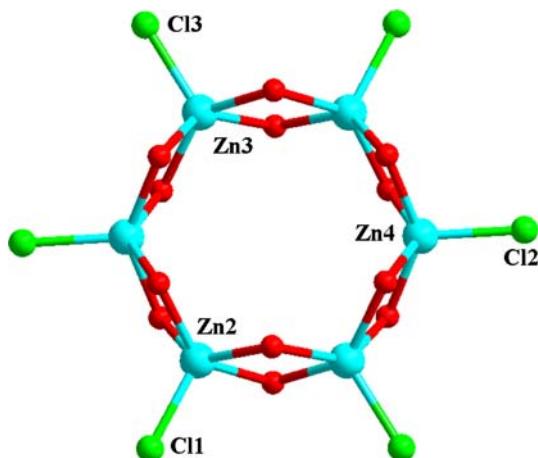


Fig. 3 Ball-and-stick representation of polyoxoanion **1**

Zn^{2+} ions coordinated to the sandwich-type polyoxoanions are in a six-coordinate environment with the other five sites occupied by five H_2O molecules (bond-valence sum calculations have given the proof of that). And there also existed two Zn^{2+} and four Na^+ to act as charge-compensating cations, which were interacted with the sandwich-type polyoxoanions to formed 3D supermolecule structure (Fig. S1) by hydrogen bonds ($O \dots OW$: 2.67–2.87 Å, $OW \dots OW$: 2.62–2.87 Å).

Spectroscopic Analyses

In the IR spectrum of compound **1** (Fig. S2), the peak at 948(s), 893(m), 819(s), 715(s), 649(m), 521(w), 447(m) can be attributed to v(W-Od), v(W-Oa), v(W-Ob) and v(W-Oc) in the polyoxoanion framework. In the UV spectrum for compound **1** (Fig. S3), the characteristic peaks are located at 223 and 260 nm, attributed to the characteristics of Keggin structure. Thus, the IR and UV spectra of compound **1** all indicate that the polyoxoanions of Keggin structure exists in compound **1**, which is consistent with the result of single-crystal X-ray diffraction analysis. And the luminescent property of the compound has also been investigated, but unluckily there is no fluorescence or phosphorescence has been found.

Thermal Analyses

Thermogravimetric analysis of compound **1** exhibits two weight loss steps in the temperature range 20–500 °C (Fig. S4), corresponding to the loss of the noncoordinated and coordinated water molecules, respectively. The whole weight loss (14.26%) is in good agreement with the calculated value (13.67%). It can be observed that the result of the TG analysis agrees with that of the structure determination.

Conclusions

In summary, we have successfully synthesized a new sandwich tungstobismutate: $\text{Na}_4\text{Zn}_2[\text{Zn}_2(\text{H}_2\text{O})_{10}(\text{ZnCl})_6(\text{B}-\alpha\text{-BiW}_9\text{O}_{33})_2] \cdot 40.5\text{H}_2\text{O}$. The polyoxoanion of compound **1** was composed of a Zn_6^{12+} hexagon sandwiched by two $[\text{BiW}_9\text{O}_{33}]^{9-}$ units, which was firstly observed in tungstobismutate.

Supplementary Materials

The IR spectrum, UV spectrum and the TG curve of compound **1** are available.

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