

Synthesis, Crystal Structure and Magnetic Property of Sandwich-Type Heteropolyoxometalate

$\text{Na}_9[\{\text{Na}(\text{H}_2\text{O})_2\}_3\{\text{Cu}(\text{H}_2\text{O})\}_3(\text{BiW}_9\text{O}_{33})_2] \cdot 42\text{H}_2\text{O}$

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The heteropolytungstate $\text{Na}_9[\{\text{Na}(\text{H}_2\text{O})_2\}_3\{\text{Cu}(\text{H}_2\text{O})\}_3(\text{BiW}_9\text{O}_{33})_2] \cdot 42\text{H}_2\text{O}$ is obtained by the reaction of $\text{Na}_2\text{WO}_4 \cdot 2\text{H}_2\text{O}$, $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ with $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ at $\text{pH} \approx 6$. The structure and chemical composition are determined by X-ray diffraction analysis and elemental analysis. The crystal data and main structure refinement are: $a = 1.410(3)$ nm, $b = 2.338(5)$ nm, $c = 3.173(6)$ nm, $\beta = 98.06(4)^\circ$, $V = 10.354(35)$ nm³, monoclinic crystal system, space group: $C2/c$, $Z = 4$, $R_1 = 0.0471$, $wR_2 = 0.0642$ [$I > 2\sigma(I)$], $R_1 = 0.1371$, $wR_2 = 0.0868$ (all data). $[\{\text{Na}(\text{H}_2\text{O})_2\}_3\{\text{Cu}(\text{H}_2\text{O})\}_3\text{W}_9\text{O}_{33}]^{9-}$ has D_{3h} symmetry. IR, UV-vis spectra, TG curve and magnetic property of the complex were also discussed. The compound exhibits an antiferromagnetic coupling with $J = -8.08$ cm⁻¹ and $g = 2.21$.

Keywords heteropolytungstate, crystal structure, copper, bismuth, magnetic property

Introduction

The chemistry of the sandwich-type heteropolyoxometalates encapsulating clusters of early transition metals is current of considerable interest with respect to the application of complexes in material science, medicine, catalysis and fundamental perspectives.¹⁻⁴ The great advantage of these complexes is the possibility of varying either the type of the metallic cluster or the heteroatom. The proximity of the transition metals possessing unpaired electrons facilitates their coupling through exchange, superexchange or dipolar interactions. In contrast with heteropolyoxometalates containing the subvalent main group atoms As^{III} and Sb^{III} which have been intensively studied, for instance $[\text{X}_2\text{W}_{20}\text{M}_2\text{O}_{70}(\text{H}_2\text{O})_6]^{(14-2n)-}$ ($\text{X} = \text{As}^{\text{III}}, \text{Sb}^{\text{III}}; \text{M} = \text{Co}^{\text{II}}, \text{Mn}^{\text{II}}, \text{Ni}^{\text{II}}, \text{Fe}^{\text{III}}$), $[\text{X}_2\text{W}_{18}\text{M}_3\text{O}_{66}(\text{H}_2\text{O})_3]^{12-}$ ($\text{X} = \text{As}^{\text{III}}, \text{Sb}^{\text{III}}; \text{M} = \text{Cu}^{\text{II}}, \text{Zn}^{\text{II}}, \text{Mn}^{\text{II}}$),⁵⁻⁸ only a little work has been carried out on the Bi^{III} analogues, and the structures of some species have been elucidated, e.g., $[\text{Bi}_2\text{W}_{22}\text{O}_{74}(\text{OH})_2]^{12-}$ and its 3d transition-metal-disubstituted complexes $[\text{Bi}_2\text{W}_{20}\text{M}_2\text{O}_{70}(\text{H}_2\text{O})_6]^{(14-2n)-}$ ($\text{M} = \text{Fe}^{\text{III}}, \text{Co}^{\text{II}}, \text{Zn}^{\text{II}}, \text{Mn}^{\text{II}}, \text{Ni}^{\text{II}}$),⁷⁻⁹ composed of trivacant $[\beta\text{-B}(\text{BiW}_9\text{O}_{33})]^{9-}$ units. Hitherto the structure of sandwich-type heteropolyanions $[\text{M}_3^{n+}(\text{H}_2\text{O})_x(\text{BiW}_9\text{O}_{33})_2]^{(18-3n)-}$,¹⁰ composed of trivacant

$[\alpha\text{-B}(\text{BiW}_9\text{O}_{33})]^{9-}$ units, has not been reported previously. We here report the synthesis and the structure of sandwich-type heteropolyanion of bismuth $[\{\text{Na}(\text{H}_2\text{O})_2\}_3\{\text{Cu}(\text{H}_2\text{O})\}_3(\alpha\text{-B-BiW}_9\text{O}_{33})_2]^{9-}$, which was also studied by means of elemental analyses, thermogravimetry, IR, UV-vis spectroscopy and magnetic measurement.

Experimental

Syntheses

All reagents were purchased commercially and used without further purification. $\text{Na}_2\text{WO}_4 \cdot 2\text{H}_2\text{O}$ (3.30 g, 10 mmol) was dissolved in a solution of water (20 mL) and HCl (6 mol · L⁻¹, 0.5 mL), and heated to 348 K, then $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ (0.48 g, 1 mmol) dissolved in HCl (6 mol · L⁻¹, 1 mL) was added dropwise with vigorous stirring ($\text{pH} \approx 6$). The solution was kept at 348 K for half an hour, $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ (0.17 g, 1 mmol) dissolved in the minimum water was added dropwise. The system was kept at this temperature for 15 min, the mixture was filtered and allowed to cool to ambient temperature. After a few days green crystals were produced. The yield was 1.94 g (94%, based on copper). Anal. calcd (Found) for $\text{Na}_9[\{\text{Na}(\text{H}_2\text{O})_2\}_3\{\text{Cu}(\text{H}_2\text{O})\}_3(\text{BiW}_9\text{O}_{33})_2] \cdot$

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42H₂O: W 53.66 (53.87), Bi 6.78 (6.64), Cu 3.09 (3.22), Na 4.47 (4.58), H₂O 14.88 (14.77).

X-ray crystallography

A green crystal of Na₉[[Na(H₂O)₂]₃{Cu(H₂O)}₃(BiW₉O₃₃)₂]·42H₂O with approximate 0.26 mm × 0.17 mm × 0.12 mm was mounted on a glass fiber capillary which was put on a Bruker Smart-1000 CCD diffractometer equipped with graphite monochromatic radiation Mo K α (λ =0.071073 nm). A total of 22517 (9875 independent, R_{int} =0.1440) reflections were collected at temperature 298(2) K. The crystal structure belongs to monoclinic, space group $C2/c$, with cell dimensions a =1.410(3) nm, b =2.338(5) nm, c =3.173(6) nm, β =98.06(4)°, V =10.354(35) nm³, Z =4, D_{calcd} =6.168 g/cm³, $F(000)$ =11020. The structure was solved by direct methods (SHELXTL-97) and refined by the full-matrix-block least-squares method on F^2 . Anisotropic temperature factors were applied to all nonhydrogen atoms. Structure solution and refinement based on 9875 reflections with $I > 2\sigma(I)$ and on 687 parameters gave R_1 =0.0471, wR_2 =0.0642. In the final difference map, the maximum and minimum residuals were 1.747 × 10³ and -1.620 × 10³ e/nm³, respectively.

Results and discussion

Structure of Na₉[[Na(H₂O)₂]₃{Cu(H₂O)}₃(BiW₉O₃₃)₂]·42H₂O

The crystal structure of the title compound is listed in Figure 1 with the atomic numbering scheme; selected bond lengths and bond angles are shown in Table 1.

IR and UV-vis spectra

IR spectra of the title compound have three absorp-

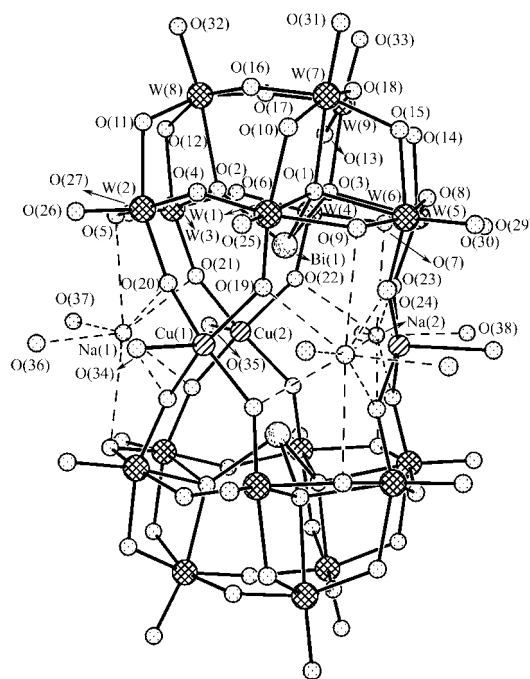


Figure 1 Structure of [[Na(H₂O)₂]₃{Cu(H₂O)}₃(BiW₉O₃₃)₂]⁹⁻.

tions at 945 (vs), 891 (vs), 752 (vs) cm⁻¹, attributed to the characteristic absorption of $\nu(\text{W}-\text{O}_d)$, $\nu(\text{O}_b-\text{W}-\text{O}_b)$ and $\nu(\text{W}-\text{O}_c)$, respectively. UV spectra have two absorption bands, the higher energy band at *ca.* 204 nm is attributed to the charge transfer of O_d-W , and the lower energy band at *ca.* 257 nm is attributed to that of $\text{O}_b/\text{O}_c-\text{W}$. In the visible region, Na₉[[Na(H₂O)₂]₃{Cu(H₂O)}₃(BiW₉O₃₃)₂]·42H₂O has two absorption bands at *ca.* 813, 376 nm respectively, attributed to the d-d

Table 1 Selected bond lengths (nm) and bond angles (°)

Bi(1)—O(2)	0.2076(11)	Bi(1)—O(3)	0.2109(12)	Bi(1)—O(1)	0.2131(11)
Cu(1)—O(20)#1	0.1895(12)	Cu(1)—O(20)	0.1895(12)	Cu(1)—O(19)#1	0.1981(13)
Cu(1)—O(19)	0.1981(13)	Cu(2)—O(24)#1	0.1913(13)	Cu(2)—O(22)	0.1913(13)
Cu(2)—O(23)#1	0.1916(12)	Cu(2)—O(21)	0.1916(12)		
O(2)—Bi(1)—O(3)	87.6(5)	O(2)—Bi(1)—O(1)	86.2(4)		
O(3)—Bi(1)—O(1)	86.3(5)	O(20)#1—Cu(1)—O(20)	166.2(7)		
O(20)#1—Cu(1)—O(19)#1	89.0(5)	O(20)—Cu(1)—O(19)#1	88.5(5)		
O(20)#1—Cu(1)—O(19)	88.5(5)	O(20)—Cu(1)—O(19)	89.0(5)		
O(19)#1—Cu(1)—O(19)	158.5(8)	O(20)#1—Cu(1)—O(34)	96.9(4)		
O(20)—Cu(1)—O(34)	96.9(4)	O(19)#1—Cu(1)—O(34)	100.7(4)		
O(19)—Cu(1)—O(34)	100.7(4)	O(24)#1—Cu(2)—O(22)	167.5(5)		
O(24)#—Cu(2)—O(23)#1	87.4(6)	O(22)—Cu(2)—O(23)#1	89.6(5)		
O(24)#1—Cu(2)—O(21)	91.5(5)	O(22)—Cu(2)—O(21)	87.3(6)		
O(23)#1—Cu(2)—O(21)	160.4(5)	O(24)#1—Cu(2)—O(35)	94.9(6)		
O(22)—Cu(2)—O(35)	97.6(6)	O(23)#1—Cu(2)—O(35)	100.6(6)		
O(21)—Cu(2)—O(35)	99.0(6)				

Symmetry transformations used to generate equivalent atoms: #1 $-x+2, y, -z+3/2$; #2 $-x+2, y+1, -z+3/2$; #3 $-x+2, -y+2, -z+2$; #4 $-x+3/2, y+1/2, -z+3/2$; #5 $-x+2, y-1, -z+3/2$; #6 $-x+3, y, -z+3/2$; #7 $-x+3/2, y-1/2, -z+3/2$; #8 $-x+3/2, -y+1/2, -z+2$.

Table 2 Bond lengths (nm) in several isostructural sandwich-type heteropolytungstates

	As ₂ W ₂₁ ¹²	Cu ₃ As ₂ W ₁₈ ¹¹	Cu ₃ Sb ₂ W ₁₈ ⁶	Cu ₃ Bi ₂ W ₁₈ (this paper)
W—O _a	0.229(3)—0.244(5)	0.219(7)—0.245(7)	0.2251(10)—0.2356(12)	0.2217(12)—0.2270(12)
W—O _{b/c}	0.190(4)—0.192(2)	0.186(5)—0.203(5)	0.1785(10)—0.2031(10)	0.1867(13)—0.2034(14)
W—O _d	0.163(6)—0.186(4)	0.161(7)—0.176(6)	0.1717(15)—0.1750(11)	0.1646(14)—0.1770(14)
W—O _t	—	0.175(4)—0.187(4)	0.1922(10)—0.1995(9)	0.1766(11)—0.1831(12)
X—O _a	0.177(4)	0.175(7)—0.188(7)	0.1941(12)—0.1995(9)	0.2076(11)—0.2131(11)
X···X	—	0.534	0.485	0.452

transitions of Cu^{II}.

TG-DTG curve

The TG-DTG curve of the title compound is showed in Figure 2. It is obvious that the thermal decomposition was completed in two steps: dehydration of crystal water and skeleton water. The residue amount of the first step is 87.37% (calcd 87.74%) from 293 to ca. 373 K, and that of the second step is 85.23% (calcd 85.12%) from ca. 373 K to ca. 673 K. Finally, the oxides are given as the final product.

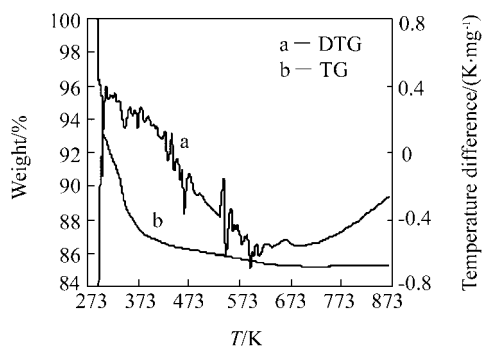


Figure 2 TG-DTG curve of title compound.

Magnetic property

The magnetic measurement was carried out on a powder sample with a CHAN 2000 Faraday-type magnetometer in the temperature range 75—300 K. Assuming that the magnetic cluster is formed by an equilateral triangle copper cluster (Figure 3) and the isotropic exchange Hamiltonian $H = -J[S_1S_2 + S_2S_3 + S_3S_1]$ has been used, the result is showed in Figure 4 in the form of T versus the molar magnetic susceptibility χ_m and the effective magnetic moment μ_{eff} .

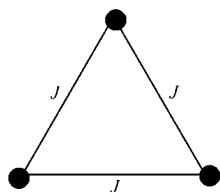


Figure 3 Exchange interaction of magnetic clusters.

Thus, $\chi_m T$ could be expressed as follows:

$$\chi_m T = (N\beta^2 g^2 / 4k) [(1 + 5x^{3/2}) / (1 + x^{3/2})]$$

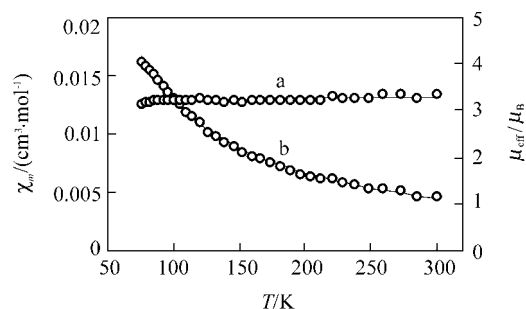


Figure 4 Temperature dependence of μ_{eff} (a) and χ_m (b).

with

$$x = \exp(J/kT)$$

The best fit is obtained for $J = -8.08 \text{ cm}^{-1}$, $g = 2.21$, showing that the Cu—Cu exchange interactions are antiferromagnetic.

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