A New Polynuclear Copper-Complex-Substituted Tungstoarsenate(V) Ruizhan Tong,^[a] Bin Liu,^[a] Ganglin Xue,^{*[a]} Huaiming Hu,^[a] Feng Fu,^[b] and Jiwu Wang^[b]

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Abstract. A new polynuclear copper-complex-substituted dimeric tungstoarsenate(V), $H_2[{Cu(2,2'-bpy)}_8(H_2O)_2(AsW_9O_{34})_2]\cdot 12H_2O$ (1) (2,2'-bpy = 2,2'-bipydine), was synthesized hydrothermally and its structure was determined by single-crystal X-ray diffraction. The title compound has *Ci* symmetry and consists of two trilacunary Keggin anions $[\alpha$ -AsW₉O₃₄]⁹⁻ supported by eight copper complex cations. The compound was also characterized by IR and fluorescence spectroscopy,

Introduction

Polyoxometalates (POMs) are a well-known class of metaloxygen cluster species with diverse properties and unique structural varieties that allow application in different scientific fields including catalysis, medicine and materials science [1-4]. In the development of POM 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]. The trivacant Keggin ion is one of the most important lacunary polyoxoanions and various types of its derivatives were reported. The dimeric sandwich TMSPs containing 2–6 transition metal cations in the central belt are the main such the disubstituted species. as polyoxoanion $[(VO)_2(BiW_9O_{33})_2]^{14-}$ [6]; the trisubstituted polyoxoanions $[(\alpha - XW_9O_{33})_2M_3(H_2O)_3]^{n-}$ $(n = 12, X = As^{3+}, Sb^{3+}, M = Cu^{2+}, Zn^{2+}; n = 10, X = Se^{4+}, Te^{4+}, M = Cu^{2+})$ [7]; the four transitionmetal-ion-substituted polyoxoanions $[M_4(H_2O)_2(GeW_9 O_{34}_{2}]^{12-}$ ($M = Mn^{2+}$, Cu^{2+} , Zn^{2+} , and Cd^{2+}) [8]; the pentacopper(II) substituted tungstosilicate [Cu₅(OH)₄(H₂O)₂(A-α-SiW₉-

TG analysis, and magnetic measurements. The emission spectrum of the compound in solid-state exhibits a redshift relative to those of $Na_8[A-HAsW_9O_{34}]$ ·11H₂O and the free ligand 2,2'-bpy. Magnetic measurements of the compound indicate competing ferro- and antiferromagnetic intramolecular coupling among the Cu^{II} atoms in the cluster anion.

 O_{33}_{2}]¹⁰⁻ [9]; and the six transition-metal-ion-substituted polyoxotungstates $[{Ni_6(H_2O)_4(\mu_2-H_2O)_4(\mu_3-OH)_2}(\gamma-SiW_9O_{34})_2]^{10-1}$ $[10] [(CuCl)_6(AsW_9O_{33})_2]^{12-} [11], and [(MnCl)_6(SbW_9O_{33})_2]^{12-}.$ Polymeric TMSPs with a higher number of transition metal (TM) atoms were also reported, such as, [Co₉(OH)₃- $(H_2O)_6(HPO_4)_2(B-\alpha-PW_9O_{34})_3]^{16-1}$ [12], [Ni₁₂(OH)₉WO₄- $(P_8W_{48}O_{184})]^{25-}$ [16], and $[H_{56}Fe_{28}P_8W_{48}O_{248}]^{28-}$ [17]. Even the record-sized heteropolytungstate anion $[As_{12}Ce_{16}-$ (H₂O)₃₆W₁₄₈O₅₂₄]⁷⁶⁻ [18] is an assembly of 12 [AsW₉O₃₃] groups linked by 16 Ce^{III} cations, additional tungsten atoms and four [W₅O₁₈] lacunary fragments.

Hybrid organic-inorganic POMs are of great interest because of their particular properties of the metal-oxo fragment with attached organic groups. A variety of hybrid organic-inorganic POMs based on the trivacant Keggin ion were reported, such as the phenyltin-substituted 9-tungstogermanate $[(C_6H_5)S_{1-1}]$ (OH)}₃ $(A-\alpha-GeW_9O_{34})$]⁴⁻ [19]; the dimethyltin-substituted $[{Sn(CH_3)_2(H_2O)}_{24}{Sn(CH_3)_2}_{12}(A-XW_9O_{34})_{12}]^{36-}$ cluster $(X = P^{5+}, As^{5+})$ [20] composed of twelve $(A-XW_9O_{34})$ Keggin moieties linked by 36 dimethyltin groups; the high-nuclear Ni^{II}-substituted polyoxometalate compounds functionalized by exogenous ligands $[Na{(A-\alpha-SiW_9O_{34})Ni_4(CH_3COO)_3(OH)_3}_2]^{15-}$ [21]; {[Cu(enMe)₂(H₂O)]₂[Cu₆(enMe)₂(SiW₉O₃₄)₂]}⁴⁻ [22]; etc. To date, three molecular copper complexes with trivacant Keggin ions as inorganic ligands in combination with the organic ligand 2,2'-bpy have been reported: $[{Cu(2,2'-bpy)(H_2O)}_2{Cu(2,2'-bpy)(H_2O)}_2]$ [23], $[{Cu(2,2'-bpy)(H_2O)} {Cu(2,2'$ bpy) $_{2}(\alpha-SbW_{9}O_{33})^{-}$ bpy) $_{4}(\alpha$ -GeW₉O₃₄) $_{2}$ [24], and [{Cu(2,2'-bpy)_{2}}{Cu(2,2'bpy) $_{3}(\alpha - AsW_{9}O_{33})^{-}$ [25]. Besides, two further polyoxoanions with asymmetric copper coordination modes were also reported: [{Cu₂(O₂CMe)₂(5,5'-dimethyl-2,2'-bipy)₂}{Cu(5,5'-dimethyl-2,2'bipy)₂ $SiW_{12}O_{40}$ [26] and [$\{Cu_8(2,2'-bpy)_8\}(PW_8O_{31})_2$]²⁻ [27].



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In this paper, we present the new discrete organic-inorganic dimer tungstoarsenate $H_2[\{Cu(2,2'-bpy)\}_8(H_2O)_2(AsW_9O_{34})_2]$ · 12H₂O (1). To the best of our knowledge, this compound is the first copper-complex-substituted POM based on the trivacant Keggin ion $[As^VW_9O_{34}]^{9-}$.

Experimental Section

Materials and Physical Measurements

All reagents used were of analytical grade and obtained from commercial sources without further purification. The infrared spectrum of compound 1 was recorded with a Nicolet AVATAR 360 FTIR spectrophotometer (KBr pellets in 400–4000 cm⁻¹ region). The TG measurement was performed with an Exstar 6000 analyzer under nitrogen with a heating rate of 10 °C·min⁻¹ from 25 to 1000 °C. Luminescent spectra were measured at room temperature with a Hitachi F4500 fluorescence spectrophotometer. Magnetic measurements were carried out using a Quantum Design MPMS-XL SQUID magnetometer.

Synthesis of $H_2[{Cu(2,2'-bpy)}_8(H_2O)_2(AsW_9O_{34})_2] \cdot 12H_2O$ (1)

A mixture of As_2O_3 (0.025 g, 0.125 mmol), WO₃ (0.232 g, 1.00 mmol), CuSO₄·5H₂O (0.15 g, 0.600 mmol), 2,2'-bpy (0.030, 0.192 mmol), and H₂O (10 mL) was stirred for 0.5 h. afterwards it was sealed in a Teflon-lined stainless steel autoclave (20 mL) and kept at 160 °C for 4 days after which the temperature was recovered to room temperature for 2 days. Blue block-shaped crystals were obtained. Yield 0.172 g (35 % based on Cu). Elemental analysis calcd. for $C_{80}H_{94}Cu_8As_2N_{16}O_{82}W_{18}$: C 14.65, H 1.44, As 2.28, N 3.42, Cu 7.75, W 50.5 %; found: C 14.54, H 1.41, As 2.4, N 3.38, Cu 8.1, W 50.1 %.

X-ray Crystallography

The crystallographic data of 1 were collected with a BRUKER SMART APEX II CCD diffractometer with graphite-monochromatized Mo- K_{α} radi-

Table 1. Crystal data and refinement parameters for compound 1.

Elemental composition	$H_{94}N_{16}C_{80}As_2Cu_8O_{82}W_{18}$	
crystal dimension /mm	$14 \times 12 \times 9$	
$M/g \cdot mol^{-1}$	6559.17	
space group	C2/c	
a /Å	41.1942(19)	
b /Å	18.6848(11)	
c /Å	19.7184(10)	
α	90.00	
β	107.8100(10)	
γ	90.00	
Volume /Å ³	14450.0(13)	
Ζ	4	
d calcd. $/g \cdot cm^{-1}$	3.015	
μ /cm ⁻¹	15.962	
total reflns	36101	
indep reflns	12867	
parameters	914	
GOF	1.025	
$R_1 \left[I > 2\sigma(I) \right]^{a}$	0.0380	
$wR_2 \left[I > 2\sigma(I)\right]^{a}$	0.0967	
R_1 (all data) ^{a)}	0.0589	
wR_2 (all data) ^{a)}	0.1081	
diff.peak and hole /e A^{-3}	1.840 and -1.618	

a) $R_1 = [\Sigma |F_0| - |F_c|] / [\Sigma |F_c|]; w R_2 = \{ [\Sigma w (F_0^2 - F_c^2)^2] / [\Sigma w (F_0^2)^2] \}^{1/2}.$

ation ($\lambda = 0.71073$ Å) radiation at 293(2) K. The structure was solved by direct methods and refined on F^2 by full-matrix least-squares using the SHELXTL-97 program package. All of the non-hydrogen atoms were refined anisotropically except the oxygen atoms of free water molecules were refined isotropically. The crystal data and refinement parameters for 1 are listed in Table 1. Selected bond lengths and angles are listed in Table 2.

Table 2. Selected bond lengths /Å and angles /° for 1.

As(1)-O(22)	1.654(7)	Cu(4)–N(2)	1.976(10)
As(1)–O(17)	1.682(7)	Cu(4) - N(1)	1.990(9)
As(1)–O(26)	1.683(7)	Cu(4)–O(6)	2.027(7)
As(1)–O(25)	1.698(7)	Cu(4)–O(28)	2.047(7)
Cu(1)–O(23)	1.907(8)	Cu(4)-O(7)	2.310(7)
Cu(1)–O(20)	1.928(8)	Cu(4)–O(4)	2.328(8)
Cu(1)–N(3)	1.975(9)	O(17)-As(1)-O(25)	105.7(4)
Cu(1)–N(4)	1.993(10)	O(22)-As(1)-O(26)	112.6(4)
Cu(1)–O(22)	2.437(7)	O(20)-Cu(1)-N(3)	93.9(4)
Cu(3)–O(21)	1.920(8)	O(23)-Cu(1)-N(3)	166.2(4)
Cu(3)–O(35)	1.997(7)	N(7)-Cu(3)-O(35)	94.5(4)
Cu(3)–N(7)	1.987(10)	O(21)-Cu(3)-N(7)	167.1(4)
Cu(3)–N(8)	2.009(10)	N(1)-Cu(4)-O(6)	93.0(4)
Cu(3)–O(33)	2.383(8)	N(1)-Cu(4)-O(28)	174.6(4)

Crystallographic data in cif format were deposited at the Cambridge Crystallographic Data Center. Copies of the data can be obtained free of charge on request from the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44-1223-336408, E-Mail: deposit@ccdc.cam.ac.uk or http:// www.ccdc.cam.ac.uk) quoting the deposition number CCDC-726209.

Supporting Information (see footnote on the first page of this article): Intra- and intermolecular π - π stacking interactions in compound 1, extended along the crystallographic *b* direction. TG curve for compound 1. Emission spectra of compound 1, the free ligand 2,2'-bpy and Na₈[*A*-HAsW₉O₃₄]·11H₂O.

Result and Discussion

Structure Description

The centrosymmetric dimer 1 consists of two trilacunary $[\alpha$ -AsW₉O₃₄]⁹⁻ anions and eight $[Cu(2,2'-bpy)]^{2+}$ complex cations (Figure 1a and Figure 1b). The $[\alpha$ -AsW₉O₃₄]⁹⁻ moiety is derived from the parent α -Keggin structure $[AsW_{12}O_{40}]^{3-}$ by removing three corner-sharing WO6 octahedra from three separate W3O13 triads. The $[\alpha$ -AsW₉O₃₄]⁹⁻ anion acts as a polydentate ligand towards four $[Cu(2,2'-bpy)]^{2+}$ cations, in which three of four $[Cu(2,2'-bpy)]^{2+}$ ion occupy the lacunary sites of $[\alpha-AsW_9O_{34}]^{9-}$ anion to form a copper substituted POM. The atoms Cu(1) and Cu(2) are located in a CuO₃N₂ square pyramid, corner-sharing with two WO₆ octahedra and one AsO₄ group [Cu–O = 1.907(7)– 2.437(7) Å, Cu–N = 1.975(9)–2.002(9) Å] (Figure 2a). Cu(3) as bridging atom is linked to one terminal oxygen atom of one lacunary anion, one water molecule and one terminal oxygen atom of another square pyramid [Cu-O = 1.920(8)-2.383(8) Å, Cu-N =1.987(10)-2.009(10) Å] (Figure 2b), which leads to the formation of a centrosymmetric dimer (Figure 1b). The copper atom of the fourth {Cu(2,2'-bpy)} unit, Cu(4), coordinates to the non-lacunary sites on the exterior of the POM by bonding to four bridging oxygen atoms with Cu–O distances in the range 2.027(7)– 2.328(8) Å (Figure 2c). The copper atoms Cu(1) and Cu(2) are connected by an oxygen bridge with a Cu(1)--Cu(2) distance of 3.4780(10) Å and a Cu(1)-O–Cu(2) angle of 104.011(345)°. The distance between the other copper atoms is longer than 4.4134(19) Å because they are separated by at least four bonds.





Figure 1. (a) View of the asymmetric molecular structure unit of compound 1. The polyhedra represent WO_6 and AsO_4 fragments. (b) View of the dimer.

On the basis of valence sum calculations, the oxidation states of all tungsten and copper atoms in **1** are +6 and +2 (for W $\sum S_{ij}$ = 5.96–6.27, mean 6.15; for Cu $\sum S_{ij}$ = 1.94–2.05, mean 2.01).

A similar bonding mode has been observed previously for the Cu₈-containing dimeric polyanion [{Cu(phen)}₈(β -AsW₈O₃₁)₂]²⁻ [28]. There are two remarkable differences between these two complexes besides different organic ligands. Firstly, the polyoxoanion [{Cu(phen)}₈(β -AsW₈O₃₁)₂]²⁻ is based on the tetravacant Keggin unit [β -AsW₈O₃₁]⁹⁻, whereas compound **1** is based on the

Figure 2. Ball and stick representations (a), (b), and (c) of the three copper coordination modes in compound 1.

trivacant Keggin unit $[AsW_9O_{34}]^{9^-}$. Secondly, six of eight Cu^{2^+} ions in the polyoxoanion $[\{Cu(phen)\}_8(\beta\text{-}AsW_8O_{31})_2]^{2^-}$ are in a square pyramidal environment, and the other two are tetracoordinated. In compound 1, six Cu^{2^+} ions are in a square pyramidal environment, however, the other two are in an octahedral environment.

The solid-state arrangement of compound 1 deserves special attention. Intense intra- and intermolecular π - π stacking interactions exist, which are extended along the crystallographic *b* direction (Figure S1). The intra- and intermolecular distances of the aryl planes of neighboring 2,2'-bpy ligands are in the range 3.10–3.30 Å. Besides, extensive hydrogen bonding and supermolecular interactions exist among neighboring molecules (C₃₇-H₃₇···O₂ 2.984 Å; C₂₂-H₂₂···O₁ 2.834 Å; C₁₃-H₁₃···O₁₅ 3.147 Å; C₃₄-H₃₄···O₁₀ 2.911 Å; C₁₂-H₁₂···O₁₁ 3.158 Å).

Synthesis of 1

Hydrothermal synthesis is a useful technique in the preparation of organic-inorganic hybrid materials. Compound 1 was synthesized under hydrothermal conditions by reaction of WO₃, CuSO₄·5H₂O and 2,2'-bpy with As₂O₃ at a pH value of 6.5. Several factors such as pH value, type of initial reactants and temperature have crucial effect on the final products in the synthesis of POMs. It is noticeable that the valence of arsenic was changed from +3 of the reactant to +5 of the product in the preparation of similar that the situation is to 1. of [Cu₄(Hen)₂As₂W₁₈O₆₈]•4H₂en•18H₂O [29] prepared by hydrothermal reaction of Na₂WO₄·2H₂O, Cu(CH₃COO)₂·H₂O, and ethylenediamine with As_2O_3 at pH = 4.0. In fact, the electromotive force value of AsO₄³⁻/AsO₃³⁻ increases with pH decrease, therefore As^{III} can be oxidized to As^V easily in mildly acidic condition [29]. We tried to improve the yield by using the pre-formed lacunary POM $[\alpha$ -AsW₉O₃₄]⁹⁻ instead of As₂O₃ as a precursor, but were unsuccessful. Compound 1 could not be obtained by reaction of $[\alpha$ -AsW₉O₃₄]⁹⁻ with Cu^{II} in the presence of 2,2'-bpy.

IR Spectroscopy

The IR spectrum of compound **1** exhibits four characteristic absorptions of the trilacunary $[\alpha$ -AsW₉O₃₄]⁹⁻ fragment below 1000 cm⁻¹ at 955, 889, 803, and 730 cm⁻¹, which are attributed to the characteristic absorption of v(W–O_d), v(W–O_b–W), v(As– O_a) and v(W–O_c–W), respectively. It indicates that the polyoxoanion in compound **1** has the basic Keggin structure, which is in agreement with the result of single-crystal X-ray diffraction analysis. In addition, the absorptions at 1601, 1496, 1472, and 1446 cm⁻¹ are assigned to the characteristic vibrations of 2,2'-bpy.

Thermal Analysis

The TG curve (Figure S2) indicates that the weight loss of the compound can be divided into two steps. The first weight-loss of 6.4 % occurs between 25 to 330 °C, corresponding to the loss of all fourteen water molecules and one 2,2'-bpy molecule (calcd. 6.2 %). The second weight loss of 16.7 % in the temperature range 330 to 776 °C is assigned to the decomposition of seven further 2,2'-bpy ligands (calcd. 16.6 %). The observed total weight loss (23.1 %) is in agreement with the calculated values (22.8 %). The remaining residues correspond to the mixed-metal oxides 8CuO·As₂O₅•18WO₃.

Fluorescent Properties

The emission spectra of compound 1, the free ligand 2.2'-bpy and Na₈[A-HAsW₉O₃₄]·11H₂O [30] in solid state at room temperature are compared (Figure S3). Compound 1 exhibits three emission peaks at ca. 415, 452, and 468 nm upon excitation at 260 nm. In contrast, the ligand 2,2'-bpy exhibits three weak emissions at ca. 393, 415, and 441 nm, which are assigned to the emissions between HOMO and LUMO energy levels. A strong broad band at ca. 360-399 nm and two emissions at ca. 451 and 465 nm, which correspond to $O_d \rightarrow W$ transition and $O_{b,c} \rightarrow W$ transition, respectively [31], are assigned to Na₈[A-HAsW₉O₃₄]·11H₂O. It is noticeable that the emission intensity of compound 1 is much stronger than that of free 2,2'-bpy ligand but weaker than that of Na₈[A-HAsW₉O₃₄]·11H₂O, furthermore, the broad emission bands of compound 1 exhibit somewhat redshift relative to those of Na₈[A-HAsW₉O₃₄]·11H₂O and the free 2,2'-bpy ligand. This may be caused by a change in the HOMO and LUMO energy levels of the ligand 2.2'-bpy coordinating to metal atoms, the chargetransfer transition between ligand and metal atoms [32] and the strong interaction between the $[\alpha$ -AsW₉O₃₄]⁹⁻ anion and the $[Cu(2,2'-bpy)]^{2+}$ complex.

Magnetochemistry

The magnetic susceptibility data of compound 1 measured at a field of 1 kOe and in a temperature range of 2–300 K are shown in Figure 3 as $\chi_{\rm M}^{-1}$ and $\chi_{\rm M}T$ vs. *T* plots. The $\chi_{\rm M}T$ value amounts 3.80 cm³·mol⁻¹·K at room temperature, which corresponds to the theoretical value for 8 isolated Cu²⁺ ions per molecule. Upon cooling, $\chi_{\rm M}T$ decreases smoothly to 3.69 cm³·mol⁻¹·K at 25 K, below which the $\chi_{\rm M}T$ value increases and reaches to 3.90 cm³·mol⁻¹·K at 3 K. As illustrated in the structural description, the centrosymmetrized compound contains two μ_3 -bridged Cu²⁺ dinuclear units (Cu1···Cu2) and six non interacting Cu²⁺ ions. Since the Cu1···Cu2 distance (3.48 Å) is much smaller than the others (larger than 4.41 Å), the magnetic interactions between the latter can be ignored, and the experimental data approximately follows the equation:



Figure 3. The χ_{M}^{-1} and $\chi_{M}T$ versus *T* plots for compound **1** under a field of 1 kOe.

$$\chi_{\rm M} = 2 \times \frac{2Ng^2\beta^2}{kT} \times \frac{1}{3 + e^{-2J/kT}} + 4 \times \frac{Ng^2\beta^2}{4kT}$$

which is the sum of the Bleaney–Bowers equation derived from the isotropic Hamiltonian $H = -JS_1S_2$ for two dinuclear Cu²⁺ entities and the Curie law for six monomer Cu²⁺ complexes. The bestfit parameters obtained between 25 and 300 K are J = -2.38 cm⁻¹, g = 2.25, and $R = 7.0 \times 10^{-5}$. The agreement factor R is defined as

$$\sum_{i} \left[\left(\chi_{\mathrm{M}} T \right)_{\mathrm{obsd}(i)} - \left(\chi_{\mathrm{M}} T \right)_{\mathrm{calcd}(i)} \right]^{2} / \sum_{i} \left[\left(\chi_{\mathrm{M}} T \right)_{\mathrm{obsd}(i)} \right]^{2}$$

which means that two dinuclear Cu^{2+} moieties interact antiferromagnetically [33]. Below 25 K, the upturn of the $\chi_M T$ value suggests that a weak ferromagnetic interaction exists, possibly caused by the interaction between the Cu_2 dimer and other Cu^{2+} ions. The susceptibility data is analyzed by the following revised equation

$$\chi_{\rm M} = \frac{Ng^2\beta^2}{k(T-\theta)} \left(\frac{4}{3+e^{-2J/kT}} + 1\right)$$

The fit parameters are $J = -11.15 \text{ cm}^{-1}$, g = 2.24, $\theta = 4.57 \text{ cm}^{-1}$ and $R = 6.6 \times 10^{-4}$. The positive θ value again confirms weak ferromagnetic interactions [34–36].

Conclusions

A discrete octa copper-complex-substituted dimeric arsenotungstate was synthesized by hydrothermal methods. The compound represents a new example of a hybrid organic-inorganic POMs composed of trivacant tungstoarsenate(V) Keggin ions and polynuclear copper complexes. The magnetic property of the compound is interesting, it indicate competing ferro- and antiferromagnetic intramolecular coupling among the Cu^{II} atoms in the cluster anion. Further research is focused on the reactions among other transition metal or rare earth ions, and lacunary POM units and organic ligands to obtain new types of hybrid organic-inorganic POMs containing large paramagnetic TM or rare earth complexes with interesting properties.

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