

RAPID COMMUNICATION

Hydrothermal Synthesis and Crystal Structure of an Unusual Compound: $[\text{Cu}(\text{en})_2]_4[\text{SiMo}_8\text{V}_4\text{O}_{40}(\text{V}^{\text{IV}}\text{O})_2][\text{MoO}_4]_2 \cdot 5\text{H}_2\text{O}$ Guoyou Luan,* Yangguang Li,* Enbo Wang,*¹ Zhengbo Han,* Changwen Hu,* Ninghai Hu,† and Hengqing Jia†

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A novel compound $[\text{Cu}(\text{en})_2]_4[\text{SiMo}_8\text{V}_4\text{O}_{40}(\text{V}^{\text{IV}}\text{O})_2][\text{MoO}_4]_2 \cdot 5\text{H}_2\text{O}$ has been hydrothermally synthesized and structurally characterized by single-crystal X-ray diffraction. Black crystals crystallize in the tetragonal system, space group $I4/m$, $a = b = 14.019(2)$ Å, $c = 20.341(4)$ Å, $V = 3997.9(11)$ Å³, $Z = 2$, $\lambda(\text{MoK}\alpha) = 0.71073$ Å ($R(F) = 0.0443$ for 1819 reflections). Data were collected on a Siemens P4 four-circle diffractometer at 293 K in the range of $1.76 < \theta < 24.98^\circ$ using the ω -scan technique. The structure was solved by the direct method and refined by the full-matrix least squares on F^2 method using the SHELXL-97 software. X-ray crystallographic study showed that the title compound contained a bicapped α -Keggin fragment $[\text{SiMo}_8\text{V}_4\text{O}_{40}(\text{V}^{\text{IV}}\text{O})_2]^{4-}$ polyoxoanion. © 2002 Elsevier

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Key Words: polyoxoanion; bicapped α -Keggin; hydrothermal synthesis; crystal structure.

INTRODUCTION

Polyoxometalates (POMs) containing Keggin moieties have received considerable attention in recent years as a consequence of their unusual electronic properties and interesting structural chemistry (1–3). During these years, however, owing to the limitation of synthesis methods, POMs with the capped Keggin structure feature have rarely been reported in comparison with numerous Keggin and transition-metal-substituted Keggin species (4,11,13). More recently, the introduction of hydrothermal techniques and the use of suitable templates have led to the appearance of various capped Keggin derivatives (5–20) pertaining to several systems. Among these systems, the V/

As/O system has been extensively studied, such as $[\text{AsV}_{14}\text{O}_{42}]^{9-}$ (5) and $[\text{H}_{12}\text{As}_3\text{V}_{12}\text{O}_{42}]^{3-}$ (6). The Mo/As/O system has also been reported, for example the mixed-valence species $[\text{As}_3\text{Mo}_{12}\text{O}_{40}]^{5-}$ (7). Furthermore, the Mo/Si/O system, such as $[\text{SiMo}_{14}\text{O}_{44}]^{4-}$ and $[\text{Si}_2\text{Mo}_{28}\text{O}_{84}(\text{H}_2\text{O})_2]^{6-}$ (8), the Mo/V/As/O system, exemplified by $[\text{As}_2^{\text{III}}\text{As}^{\text{V}}\text{Mo}_8\text{V}_4\text{O}_{40}]^{5-}$ (9,10), and the Mo/V/P/O system, such as $[\text{PMo}_{12}\text{O}_{40}(\text{VO})_2]^{5-}$ (11,12), $[\text{PMo}_8\text{V}_4\text{V}_2\text{O}_{40}\text{O}_{42}]^{5-}$ (13), and $[\text{Mo}_2^{\text{V}}\text{Mo}_6^{\text{VI}}\text{V}_8^{\text{IV}}\text{O}_{40}(\text{PO}_4)]^{5-}$ (14) have also been well studied. Other examples include $[\text{H}_4\text{PV}_{14}\text{O}_{42}]^{5-}$ (15), $[\text{H}_3\text{KV}_{12}\text{As}_3\text{O}_{39}(\text{AsO}_4)]^{6-}$ (16), $[\text{As}_4\text{V}_{12}\text{O}_{43}\text{H}_3]^{7-}$ (17), and $[\text{Mo}_8\text{V}_7\text{O}_{42}]^{7n-}$ (18–20), which are all synthesized by hydrothermal reactions. Nevertheless, POMs belonging to the Mo/V/Si/O system and exhibiting such a capped Keggin structure have rarely been observed. In this communication, we report the hydrothermal synthesis and crystal structure of $[\text{Cu}(\text{en})_2]_4[\text{SiMo}_8\text{V}_4\text{O}_{40}(\text{V}^{\text{IV}}\text{O})_2][\text{MoO}_4]_2 \cdot 5\text{H}_2\text{O}$, a novel Mo/V/Si/O bicapped α -Keggin POM with an unusual alternate arrangement of $\{\text{Mo}_4\}$ and $\{\text{V}_4\}$ layers in the polyoxoanion structure.

EXPERIMENTAL

General Procedures

All chemicals were commercially purchased and used without further purification. Elemental analyses (C, H and N) were performed on a Perkin-Elmer 2400 CHN Elemental Analyzer. V, Mo, Si, Cu were determined by a Leaman inductively coupled plasma (ICP) spectrometer. IR spectrum was recorded in the range $400\text{--}4000\text{ cm}^{-1}$ on an Alpha Centaur FT/IR Spectrophotometer using a KBr pellet. ESR spectrum was recorded on a Japanese JES-FE3AX spectrometer at 293 K. TG analysis was performed on a Perkin-Elmer TGA7 instrument in flowing N_2 with a heating rate of $10^\circ\text{C min}^{-1}$.

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TABLE 1
The Crystal Data and Structure Refinement for 1

Identification code	1023a
Empirical formula	C ₁₆ H ₇₄ Cu ₄ Mo ₁₀ N ₁₆ O ₅₅ SiV ₆
Formula weight	2918.20
Temperature	293(2) K
Wavelength	0.71073 Å
Crystal system	Tetragonal
Space group	I4/m
Unit cell dimensions	$a = 14.019(2)$ $b = 14.019(2)$ $c = 20.341(4)$ $\alpha = 90^\circ$ $\beta = 90^\circ$ $\gamma = 90^\circ$
Volume, Z	3997.9(11) Å ³ , 2
Density (calculated)	2.424 Mg m ⁻³
Absorption coefficient	3.330 mm ⁻¹
$F(000)$	2820
Crystal size	0.48 × 0.38 × 0.36 mm ³
θ Range for data collection	1.76–24.98°
Limiting indices	$-16 < h < 12$, $-16 < k < 12$, $-24 < l < 1$
Reflections collected	4243
Independent reflections	1819 ($R_{\text{int}} = 0.0389$)
Absorption correction	Psi-scan
Max. and min. transmission	0.7605 and 0.3065
Refinement method	Full-matrix least squares on F^2
Data / restraints / parameters	1819 / 0 / 149
Goodness-of-fit on F^2	1.098
Final R indices [$I > 2\sigma(I)$]	$R1 = 0.0443$, $wR2 = 0.1421$
R indices (all data)	$R1 = 0.0516$, $wR2 = 0.1461$
Largest diff. peak and hole	1.603 and $-1.005 \text{ e \AA}^{-3}$

Hydrothermal Synthesis

Compound **1** was prepared by hydrothermal reaction. A mixture of V₂O₅, H₂MoO₄, SiO₂, CuSO₄ · 5H₂O, NH₂CH₂CH₂NH₂ and H₂O in the mole ratio 2:2:1:1:1:500 was sealed in a 25 mL Teflon-lined reactor with 50% filling (pH = 6.0) and heated at 150°C for 120 h. Then the autoclave was cooled at 10°C h⁻¹ to room temperature. The resulting black block crystals of the compound were filtered off, washed with water, and dried in a desiccator at ambient temperature (yield 33% based on SiO₂). Elemental analyses found: C 6.62%, H 2.59%, N 7.61%, V 10.51%, Mo 32.96%, Si 0.99%, Cu 8.80%; Calc. for C₁₆H₇₄Cu₄Mo₁₀N₁₆O₅₅SiV₆, C 6.59%, H 2.56%, N 7.68%, V 10.47%, Mo 32.90%, Si 0.96%, Cu 8.71%.

X-Ray Crystallography

The crystal structure of the title compound was determined by single-crystal X-ray diffraction. Crystal data: C₁₆H₇₄Cu₄Mo₁₀N₁₆O₅₅SiV₆, $M = 2,918.20$, tetragonal, $I4/m$, $a = b = 14.019(2) \text{ \AA}$, $c = 20.341(4) \text{ \AA}$, $V = 3997.9(11) \text{ \AA}^3$, $Z = 2$, $D_c = 2.424 \text{ g cm}^{-3}$, $F(000) =$

2820, $\lambda = 0.71073 \text{ \AA}$, $T = 293 \text{ K}$. A single crystal with dimensions $0.48 \times 0.38 \times 0.36 \text{ mm}^3$ was fixed inside a glass capillary. Data were collected on a Siemens *P4* four-circle diffractometer with the ω scan mode in the range of $1.76 < \theta < 24.98^\circ$. A total of 4243 (1819 independent, $R_{\text{int}} = 0.0389$) reflections were measured. The structure was solved by direct methods and refined by full-matrix least squares on F^2 . All of the non-hydrogen atoms were refined with anisotropic temperature factors. The hydrogen atoms were placed in calculated positions with a C–H bond distance of 0.97 Å and a N–H bond distance of 0.90 Å. The calculations were performed with SHELXTL programs (21). Structure solution and refinement based on 1819 independent reflections with $I > 2\sigma(I)$ and on 149 parameters gave $R1(wR2) = 0.0443(0.1421)$ $\{R1 = \sum ||F_o| - |F_c|| / \sum |F_o|$; $wR2 = \sum [w(F_o^2 - F_c^2)^2] / \sum [w(F_o^2)^2]^{1/2}\}$. Crystal data and structure refinement, atomic coordinates, and selected bond lengths and angles are listed in Tables 1, 2, and 3, respectively. Anisotropic displacement parameters and hydrogen coordinates are available in supplementary materials.

RESULTS AND DISCUSSION

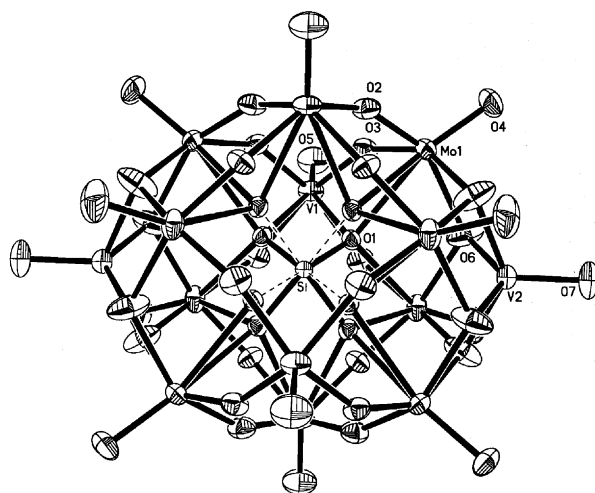
Compound **1** consists of an unusual discrete polyoxoanion $[\text{SiMo}_8\text{V}_4\text{O}_{40}(\text{V}^{\text{IV}}\text{O})_2]^{4-}$, $[\text{MoO}_4]^{2-}$, counter ions

TABLE 2
Atomic Coordinates [$\times 10^4$] and Equivalent Isotropic Displacement Parameters [$\text{\AA}^2 \times 10^3$] for 1. $U(\text{eq})$ Is Defined as One-Third of the Trace of the Orthogonalized U_{ij} Tensor

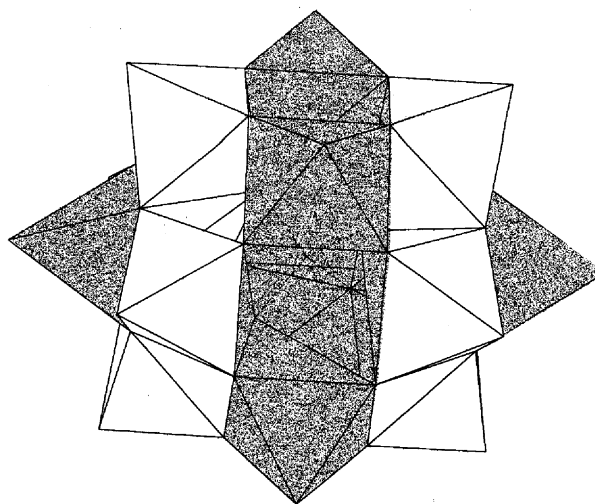
	x	y	z	$U(\text{eq})$
Mo(1)	8203(1)	546(1)	1167(1)	25(1)
Mo(2)	5000	0	2500	26(1)
V(1)	8812(1)	2239(1)	0	23(1)
V(2)	10,000	0	1977(1)	22(1)
Cu	7500	2500	2500	37(1)
Si	10,000	0	0	12(1)
O(1)	9556(6)	852(6)	456(4)	17(2)
O(2)	7703(7)	-145(7)	555(6)	28(2)
O(3)	8177(7)	1405(8)	567(5)	24(2)
O(4)	7474(4)	806(4)	1803(3)	41(1)
O(5)	8290(5)	3247(5)	0	41(2)
O(6)	9410(4)	1116(4)	1610(3)	42(2)
O(7)	10,000	0	2780(6)	45(3)
O(8)	4981(4)	1000(4)	1998(3)	44(2)
N(1)	8805(5)	2262(5)	2844(4)	37(2)
N(2)	7050(5)	1756(5)	3263(3)	40(2)
C(1)	8709(6)	1913(8)	3520(5)	56(3)
C(2)	7871(7)	1268(7)	3543(5)	54(3)
OW1	9370(30)	360(30)	5000	53(9)
OW2	8960(30)	-310(30)	5000	58(10)
OW3	5280(30)	310(30)	470(20)	110(14)
OW4	6120(30)	1740(30)	0	57(10)
O(3')	7990(8)	1765(8)	752(5)	22(3)
O(2')	7343(7)	-345(7)	772(5)	20(2)

TABLE 3
Selected Bond Lengths (Å) and Angles (°) for **1**

Mo(1)–O(4)	1.688(5)	Mo(1)–O(3)	1.715(9)
Mo(1)–O(2)	1.726(10)	Mo(1)–O(6)	2.077(5)
Mo(1)–O(1)	2.425(8)	V(1)–O(5)	1.592(7)
V(1)–O(3)	1.869(9)	V(1)–O(1)	2.392(9)
V(2)–O(6)	1.921(5)	V(2)–O(7)	1.634(11)
Cu–N(2)	1.974(7)	Cu–N(1)	1.987(6)
Si–O(1)	1.635(8)	N(1)–C(1)	1.466(13)
C(1)–C(2)	1.483(13)	N(2)–C(2)	1.455(11)
O(4)–Mo(1)–O(3)	112.4(4)	O(4)–Mo(1)–O(2)	115.4(4)
O(3)–Mo(1)–O(2)	82.6(5)	O(4)–Mo(1)–O(6)	94.5(3)
O(3)–Mo(1)–O(6)	93.2(4)	O(2)–Mo(1)–O(6)	149.3(4)
O(5)–V(1)–O(3)	109.6(4)	O(5)–V(1)–O(1)	157.2(2)
O(3)–V(1)–O(1)	57.3(4)	O(7)–V(2)–O(6)	112.9(2)



(a)



(b)

FIG. 1. (a) The structure of $[\text{SiMo}_8\text{V}_4\text{O}_{40}(\text{V}^{\text{IV}}\text{O})_2]^{4-}$ anion. The central atom Si is located at the inversion center (10,000, 0, 0), which shows that the central atom Si is surrounded by a cube of eight oxygen atoms with the site of each oxygen atom half-occupied. (b) Polyhedral representation of the anion (the white polyhedron represents Mo, while the gray polyhedron represents V).

$[\text{Cu}(\text{en})_2]^{2+}$, and water molecules. The polyoxoanion $[\text{SiMo}_8\text{V}_4\text{O}_{40}(\text{V}^{\text{IV}}\text{O})_2]^{4-}$ (Fig. 1) is based on the well-known α -Keggin structure of XM_{12} . The polyoxoanion $[\text{SiMo}_8\text{V}_4\text{O}_{40}(\text{V}^{\text{IV}}\text{O})_2]^{4-}$ of **1** can be best described as one α -Keggin core $[\text{SiMo}_8\text{V}_4\text{O}_{40}]^{8-}$ capped with two $\{\text{V}^{\text{IV}}\text{O}\}$ fragments. This bicapped α -Keggin structure, similar to those of $[\text{As}_2^{\text{III}}\text{As}^{\text{V}}\text{Mo}_8\text{V}_4\text{O}_{40}]^{5-}$ (9,10) and $[\text{PMo}_8\text{V}_4\text{V}_2\text{O}_{40}\text{O}_{42}]^{5-}$ (13), exhibits the common Keggin core consisting of four internally edge-shared octahedral $\{\text{Mo}_2\text{VO}_{13}\}$ connected with each other by corner-sharing oxygen atoms and enwrapping the central SiO_4 tetrahedron. In this compound, another interesting structural feature should be noticed. As shown in Fig. 1b, there exist two $\{\text{Mo}_4\}$ layers and one $\{\text{V}_4\}$ layer in the structure, which are distributed alternately. Similar structural features are only shown in the Mo/V/O system (18–20), while they have never been observed in other systems.

There are two crystallographically unique vanadium centers, that is, the $\{\text{V}^{\text{VO}}_6\}$ octahedra and the capped unit $\{\text{V}^{\text{VO}}_5\}$ pyramids. The bond lengths of V(1)–O in the octahedra are in the range 1.592(7)–2.392(9) Å, the V(2)–O distances in the capped fragments are in the range 1.634(11)–1.921(5) Å. There are also two crystallographically unique molybdenum centers, that is, the $\{\text{MoO}_6\}$ octahedra and the free anion $\{\text{MoO}_4\}$ tetrahedron. The bond lengths of Mo(1)–O in the octahedra are in the range 1.688(5)–2.425(8) Å, while the bond length of Mo(2)–O is 1.735(6) Å. The assignment of oxidation states for the vanadium and molybdenum atoms is consistent with their coordination geometries and is confirmed by valence sum calculations (22), which reveal that the values for V(1) and V(2) are 4.86 and 4.28, while the calculated valence sums for Mo(1) and Mo(2) are 6.09 and 6.37, respectively. The central atom Si is surrounded by a cube of eight oxygen atoms with each site of the oxygen atoms half-occupied. The Si–O average distance is 1.635(8) Å. The bond angles are in the range 108.7(3)–111.0(6)°.

In the unit cell of **1**, there exist the complex cation $[\text{Cu}(\text{en})_2]^{2+}$ and the free MoO_4^{2-} anions. In the complex cation $[\text{Cu}(\text{en})_2]^{2+}$, the average bond length of Cu–N is 1.981 Å. It is noteworthy that weak coordination interactions exist between the Cu^{2+} and the terminal oxygen atoms of polyoxoanions with the average distance of Cu–O 2.776 Å. Furthermore, there exist weak hydrogen bonds among the $\text{N}(1)\cdots\text{O}(8)$, $\text{N}(1)\cdots\text{O}(4)$, $\text{N}(2)\cdots\text{O}(8)$, and $\text{N}(2)\cdots\text{O}(4)$ with the distances of 2.991, 3.328, 2.893, and 3.312 Å, respectively. Owing to these weak coordinative interactions and hydrogen bonds, polyoxoanions and counter ions are linked together with regular space array (see Fig. 2).

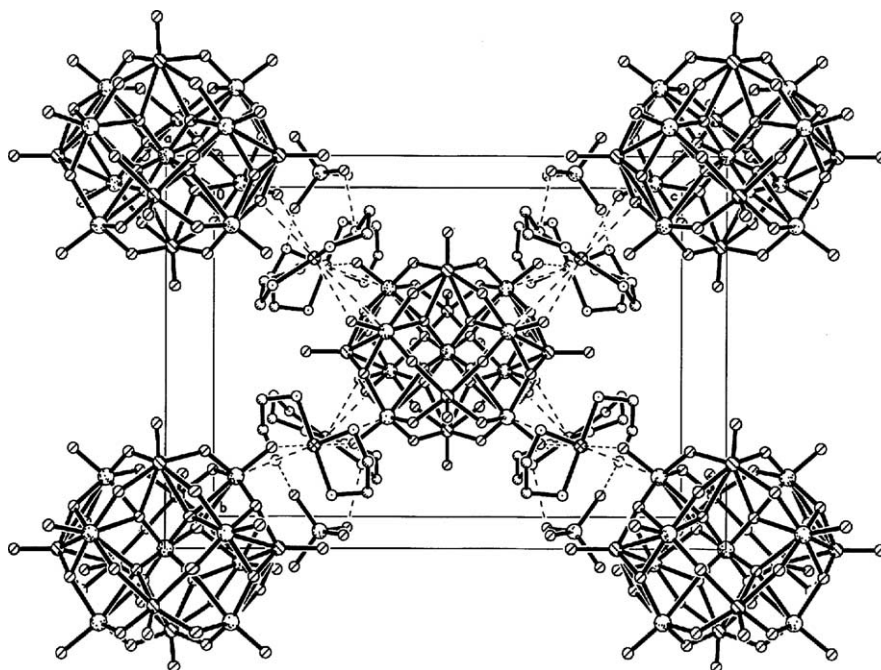


FIG. 2. View of crystal packing of compound **1** along *a*-axis.

The IR spectrum of **1** exhibits a complex pattern of bands at 1055, 988, 921, 873, and 783 cm^{-1} ascribed to $\nu(\text{Si-O})$, $\nu(\text{M}=\text{O})$, and $\nu(\text{M-O-M})$ ($\text{M} = \text{V}$ or Mo), respectively. The ESR spectrum of compound **1** (as shown in Fig. 3) shows the paramagnetic signal of V^{4+} at 273 K with $g = 1.962$, which is consistent with the result of valence sum calculations.

Thermogravimetric analysis (TGA) was carried out under N_2 with a heating rate of $10^\circ\text{C min}^{-1}$. The TG curve

of compound **1** (shown in Fig. 4) is divided into two stages. The first weight loss is 14.72% in the temperature range 230–380 $^\circ\text{C}$, and the second weight loss is 3.94% in the temperature range 390–480 $^\circ\text{C}$. These two weight losses correspond to the release of crystal water and the $\text{NH}_2\text{CH}_2\text{CH}_2\text{NH}_2$. The total weight loss (18.66%) is in agreement with the calculated value (19.52%). Compound **1** does not lose weight up to 650 $^\circ\text{C}$, the highest temperature in this experiment.

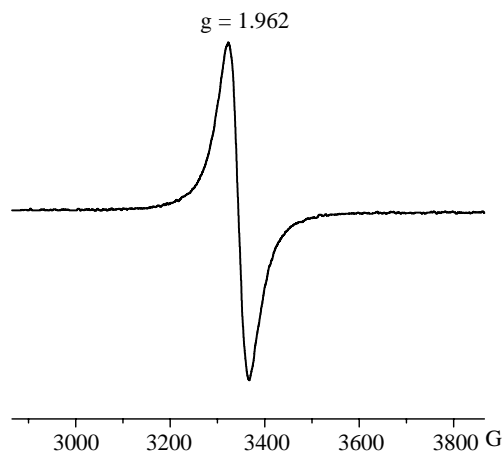


FIG. 3. ESR spectrum of compound **1**.

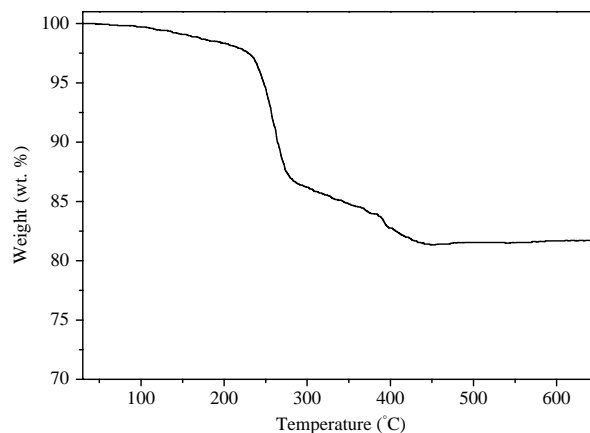


FIG. 4. TG curve of compound **1**.

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