Synthesis and Structural Characterization of a New Two-dimensional Organic-Inorganic Hybrid Molybdoarsenate: $[Cu(en)_2]_2[(CuO_6)Mo_6O_{18}(As_3O_3)_2]$

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A new organic-inorganic hybrid molybdoarsenate constructed from a unit with two (As_3O_3) rings capping Anderson-type moieties, $[Cu(en)_2]_2[(CuO_6)Mo_6O_{18}(As_3O_3)_2]$ (**1**) (en = ethylenediamine), has been hydrothermally synthesized and characterized by single-crystal X-ray diffraction and thermogravimetric analysis. The compound crystallizes monoclinically, space group $P2_1/c$, with unit cell dimensions $a = 9.1541(7)$, $b = 19.6348(14)$, $c = 14.5205(8)$ Å, $\beta = 129.082(3)^\circ$, $V = 364.20(4)$ Å^3, $Z = 2$, $T = 296(2)$ K. Complex **1** represents the first example of a 2D network of a POM polymer where $[(CuO_6)Mo_6O_{18}(As_3O_3)_2]^{4-}$ building blocks are connected by complex fragments $\{Cu(en)_2\}^{2+}$.

Key words: Polyoxometalate, Hydrothermal Synthesis, Crystal Structure, Anderson-type Unit

Introduction

Polyoxometalates (POMs) are a large family of metal-oxygen clusters with surprising compositional variability, electronic versatility and topological diversity [1]. These features endow them with applications in catalysis, medicine, material science, and photochemistry [2, 3]. One of the challenges in the synthesis of POM chemistry is to find multifunctional polyoxoanion building blocks and to connect them to one-, two-, or even three-dimensional extended solid frameworks.

It is well-known that Anderson-type polyoxoanions have abundant terminal oxygen atoms and can be used as multifunctional building blocks. Since the first Anderson-type anion $[TeMo_6O_{24}]^{6-}$ was reported in 1937 [4], these polyoxoanions have been extensively explored to construct 1D, 2D and even 3D compounds [5 – 12]. For example, in 2002, Das and coworkers reported the first 1D POM $[La(H_2O)_7Al(OH)_6Mo_6O_{18}]\cdot 4H_2O$ [5], and a 1D spiral-shaped inorganic-organic hybrid chain-like structure $[Cu(2,2'\text{-bipy})(H_2O)_2Al(OH)_6Mo_6O_{18}]$ [6]. In 2004, Krebs and coworkers published a series of 1D lanthanide derivatives $K_6(TeMo_6O_{24})[(Ln\text{-}(H_2O)_7)_2(TeMo_6O_{24})]\cdot 16H_2O$ (Ln = Eu^{III}, Gd^{III}) and $K_3[Ln(H_2O)_5(TeMo_6O_{24})]\cdot 6H_2O$ (Ln = Tb^{III}, Dy^{III}, Ho^{III}, Er^{III}) [8]. Later, Wang and coworkers published a series of 2D and 3D extended POM frameworks $[(H_2O)_5Na_2(C_6NO_2H_4)(C_6NO_2H_5)_3\text{-}Ag_2][Ag_2IMo_6O_{24}(H_2O)_4] \cdot 6.25H_2O$ [10] and $[(H_2O)_4Ag_3][Cr(OH)_6Mo_6O_{18}]\cdot 3H_2O$ [11], and networks $[(H_2O)_4Na_2(C_6NO_2H_5)_6Ag_3][IMo_6O_{24}]\cdot 6H_2O$ [10] and $[(C_6H_5NO_2)_2Ln(H_2O)_4]_2[IMo_6O_{24}]\cdot[NO_3]\cdot 4H_2O$ (Ln = Ce^{III}, La^{III}) [11]. Then, in 2007, Liu and coworkers reported two compounds with 1D chains constructed by alternating Anderson-type polyoxoanions and oxalate-bridged binuclear copper complexes, $[Cu_2(bpy)_2(\mu\text{-ox})][M(OH)_7Mo_6O_{17}]$ (M = Al^{III}, Cr^{III}) [12]. These compounds constitute an important subclass of inorganic chemistry with significance in the disciplines of magnetism and catalysis. However, compared to the abundance of these compounds based on typical Anderson-type POMs, examples based on two cyclic As_3O_3 groups capping Anderson-type POMs have rarely been reported. Typical examples with discrete cluster structures include $[Co(H_2O)_6]K_2[As_6CoMo_6O_{30}]$ [13], $Ni(en)_3[(Mo^{IV}O_6)Mo_670^{VI}O_{18}(As_3{}^{III}O_3)_2]\cdot H_2O$ [14], $Co^{III}(en)_3H_3O[(Co^{II}O_6)Mo^{VI}{}_6O_{18}(As^{III}{}_3O_3)_2]\cdot$

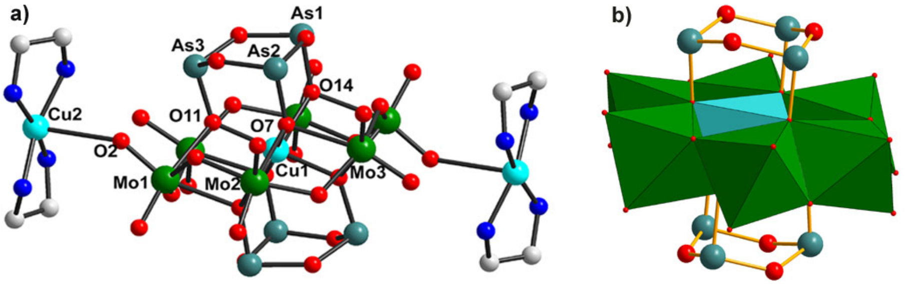

Fig. 1. a) The structural unit of **1** with labeling scheme adopted (H atoms omitted for clarity); b) polyhedral/ball-and-stick representation of the $[(CuO_6)Mo_6O_{18}(As_3O_3)_2]^{4-}$ anion.

$2H_2O$ [15], and $(C_5H_5NH)_2(H_3O)_2[(CuO_6)Mo_6O_{18}(As_3O_3)_2]$ [16].

Recently, Wang and coworkers reported (4,4′-bipy)-$[Zn(4,4'\text{-bipy})_2(H_2O)_2]_2[(ZnO_6)(As^{III}{}_3O_3)_2Mo_6O_{18}]\cdot 7H_2O$ and $[Zn(H4,4'\text{-bipy})_2(H_2O)_4][(ZnO_6)(As^{III}{}_3O_3)_2Mo_6O_{18}]\cdot 8H_2O$ [17], and Zhou and coworkers reported $[Cu(imi)_2]_2[(CuO_6)(As_3O_3)_2Mo_6O_{18}][Cu(imi)_2]_2$ [18]. However, all these 3D supramolecular frameworks are constructed *via* hydrogen bonding interactions. Therefore, in order to extend solid framework materials constructed by units $[(MO_6)Mo_6O_{18}(As_3O_3)_2]^{4-}$ (M = transition metal), we synthesized a new organic-inorganic hybrid molybdoarsenate $[Cu(en)_2]_2[(CuO_6)Mo_6O_{18}(As_3O_3)_2]$ (**1**) (en = ethylenediamine) under mild hydrothermal conditions. It is the most remarkable feature of **1**, that each $[(CuO_6)Mo_6O_{18}(As_3O_3)_2]^{4-}$ unit acts as a 4-connected node linking four $\{Cu(en)_2\}$ groups in a centrosymmetric manner generating a two-dimensional network with (4,4) topology. To the best of our knowledge, it is the fist example of a 2D POM network where $[(CuO_6)Mo_6O_{18}(As_3O_3)_2]^{4-}$ building blocks are connected by coordination to complex fragments $\{Cu(en)_2\}^{2+}$.

Table 1. Summary of crystal data and refinement results for **1**.

Formula	$C_8H_{32}As_6Cu_3Mo_6N_8O_{30}$
M_r	1936.23
Crystal size, mm^3	$0.25 \times 0.18 \times 0.14$
Crystal system	monoclinic
Space group	$P2_1/c$
a, Å	9.1541(7)
b, Å	19.6348(14)
c, Å	14.5205(8)
β, deg	129.082(3)
V, $Å^3$	2025.9(2)
Z	2
D_{calcd}, $g\,cm^{-3}$	3.17
$\mu(MoK_\alpha)$, cm^{-1}	0.8
θ range data collection, deg	2.07 – 26.00
$F(000)$, e	1825
hkl range	$-10 \le h \le 11$, $-23 \le k \le 24$, $-17 \le l \le 17$
Refl. measured / unique / R_{int}	11030 / 3955 / 0.079
Param. refined	277
$R1(F)/wR2(F^2)$ $[I \ge 2\sigma(I)]$	0.0347 / 0.0886
$R1(F)/wR2(F^2)$ (all refl.)	0.0399 / 0.0910
Gof (F^2)	1.018
$\Delta\rho_{fin}$ (max / min), e $Å^{-3}$	1.27 / −1.23

Experimental Section

General

Materials: All solvents and reagents are commercially available and were used without further purification.

Instrumentation: Elemental analysis of C, H and N was performed with a Perkin Elmer 240 analyzer. The IR spectra were recorded from KBr pellets with a Nicolet 170 SXFT-IR spectrometer in the range of 4000 – 400 cm^{-1}. Thermogravimetric analysis was performed in air on a Perkin Elmer 7 instrument with a heating rate of 10 °C min^{-1}.

Synthesis

As_2O_3 (0.12 g, 0.6 mmol), $Na_2MoO_4\cdot 2H_2O$ (0.50 g, 2 mmol), $CuCl_2\cdot 2H_2O$ (0.22 g, 1.3 mmol) and ethylenediamine (0.05 mL) were dissolved in water (8 mL, 30 °C), and the pH of the solution was adjusted to 5.7 by dilute hydrochloric acid (4 mol L^{-1}). After the reaction was complete, the solution was sealed in a 25 mL Teflon-lined autoclave and heated at 130 °C for 5 d. Then the autoclave was cooled with a rate 5 °C h^{-1} to r. t. The resulting blue rhombic crystals of **1** were filtered off, washed with water and dried at ambient temperature. The yield was 75 % based on As_2O_3. Anal.: calcd. C 4.96, H 1.66, N 5.79; found C 4.88, H 1.62, N 5.86 %.

X-Ray crystallographic study

A blue rhombic crystal with approximate dimensions of $0.25 \times 0.18 \times 0.14$ mm^3 was mounted on a glass fiber in a random orientation. The crystal data and refinement results are summarized in Table 1. Crystallographic data were collected with a Bruker CCD Apex-II diffractometer with graphite-monochromatized MoK_α

radiation (λ = 0.71073 Å). The structure was solved by Direct Methods using the SHELX-97 program package [19]. The remaining atoms were found from successive Fourier syntheses. Hydrogen atoms attached to carbon and nitrogen atoms were geometrically placed. Refinement was done with full-matrix least-squares on F^2 [19].

CCDC 743507 contains the supplementary crystallographic data. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/data-request/cif.

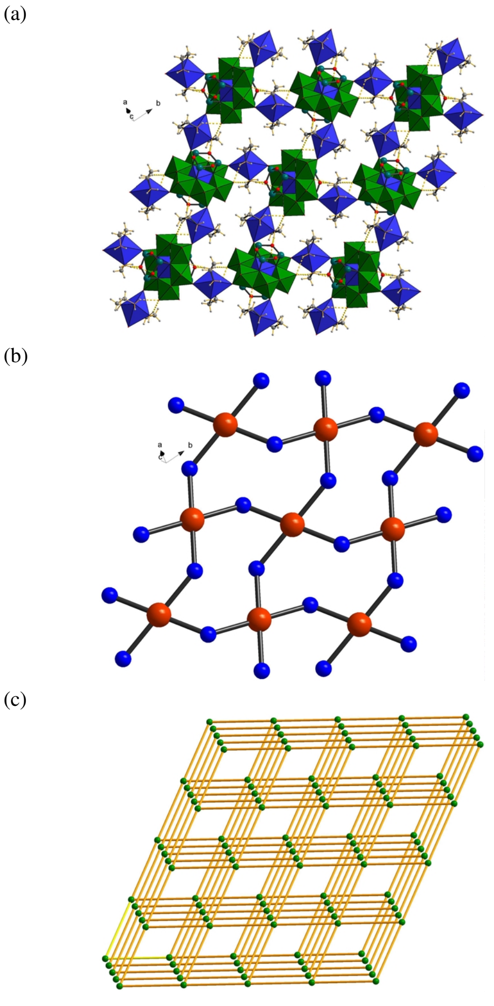

Fig. 2. a) Assembly of the 2D layer parallel to the crystallographic *ab* plane; b) schematic view of the combination between the Anderson-type $[(CuO_6)Mo_6O_{18}(As_3O_3)_2]^{4-}$ anions (red ball) and $\{Cu(en)_2\}^{2+}$ cations (blue ball); c) the 2D (4,4) topological network of **1** in the *ab* plane. The green spheres are the four-connected nodes and represent the $\{[Cu(en)_2]_2[(CuO_6)Mo_6O_{18}(As_3O_3)_2]\}$ subunits (color online).

Table 2. Selected bond lengths (Å) and angles (deg) of the title complex[a].

Mo(1)-O(1)	1.706(4)	Mo(1)-O(2)	1.714(4)
Mo(1)-O(3)	1.901(3)	Mo(1)-O(10)	1.908(4)
Mo(1)-O(14)#1	2.289(3)	Mo(1)-O(11)	2.458(3)
Mo(2)-O(5)	1.715(4)	Mo(2)-O(4)	1.709(4)
Mo(2)-O(3)	1.952(3)	Mo(2)-O(6)	1.908(3)
Mo(2)-O(7)	2.378(3)	Mo(2)-O(14)#1	2.298(3)
Mo(3)-O(8)	1.724(4)	Mo(3)-O(9)	1.700(4)
Mo(3)-O(6)	1.943(3)	Mo(3)-O(10)#1	1.920(3)
Mo(3)-O(11)#1	2.309(3)	Mo(3)-O(7)	2.294(3)
As(1)-O(14)	1.784(3)	Cu(1)-O(7)	1.982(3)
As(1)-O(12)	1.779(4)	Cu(1)-O(11)	1.988(3)
As(1)-O(13)	1.801(4)	Cu(1) -O(14)	2.266(3)
As(2)-O(12)	1.759(4)	Cu(2)-N(1)	1.984(5)
As(2)-O(7)	1.798(3)	Cu(2)-N(3)	2.009(5)
As(2)-O(15)	1.796(4)	Cu(2)-O(5)#2	2.571(4)
As(3)-O(11)	1.775(3)	Cu(2)-N(2)	1.989(4)
As(3)-O(15)	1.778(4)	Cu(2)-N(4)	2.007(6)
As(3)-O(13)	1.787(4)	Cu(2)-O(2)	2.610(4)
O(1)-Mo(1)-O(2)	104.3(2)	O(4)-Mo(2)-O(6)	99.27(16)
O(2)-Mo(1)-O(3)	96.83(17)	O(4)-Mo(2)-O(5)	105.64(19)
O(2)-Mo(1)-O(10)	101.10(17)	O(4)-Mo(2)-O(3)	102.68(16)
O(2)-Mo(1) -O(14)#1	159.11(16)	O(5)-Mo(2)-O(6)	101.98(17)
O(9) -Mo(3) -O(8)	107.1(2)	O(9)-Mo(3)-O(7)	88.91(19)
O(8)-Mo(3)-O(6)	95.67(17)	O(8)-Mo(3)-O(7)	161.82(18)
O(12)-As(1) -O(13)	98.36(17)	As(3)-O(15)-As(2)	128.1(2)
O(12)-As(1)-O(14)	100.66(16)	As(3)-O(13)-As(1)	131.1(2)
O(14)-As(1)-O(13)	97.73(16)	As(2)-O(12)-As(1)	133.8(2)
O(12)-As(2) -O(15)	99.62(18)	O(11)-As(3)-O(15)	98.42(16)
O(15)-As(2)-O(7)	100.19(16)	O(15)-As(3)-O(13)	100.65(18)
O(12)-As(2)-O(7)	99.63(16)	O(11)-As(3)-O(13)	101.93(16)
O(7)#1-Cu(1)-O(7)	180	O(7)-Cu(1)-O(14)	93.99(13)
O(7)-Cu(1)-O(11)	93.52(14)	O(11)-Cu(1)-O(14)	93.31(13)
O(7)-Cu(1)-O(11)#1	86.48(14)	O(11)#1-Cu(1)-O(14)	86.69(13)
N(1)-Cu(2)-N(2)	85.8(2)	N(2)-Cu(2)-O(5)#2	86.02(15)
N(3)-Cu(2)-N(4)	84.7(2)	N(3)-Cu(2)-O(2)	79.79(16)

[a] Symmetry transformations: #1 $-x, -y-1, -z+1$; #2 $x+1, -y-1/2, z+1/2$.

Results and Discussion

X-Ray crystal structure

Single-crystal X-ray diffraction analysis has revealed that the structural unit of **1** consists of an Anderson-type $[(CuO_6)Mo_6O_{18}(As_3O_3)_2]^{4-}$ unit capped by two As_3O_3 rings and two hexa-coordinate $[Cu(en)_2]^{2+}$ cations (Figs. 1a and 2a). Selected bond lengths and angles are collected in Table 2. Bond Valence Sum (BVS) calculations of **1** show that the oxidation states of all Mo, Cu and As atoms are +6, +2 and +3, respectively [20]. As shown in Fig. 1b, the $[(CuO_6)Mo_6O_{18}(As_3O_3)_2]^{4-}$ unit displays D_{3d} point symmetry and is derived from the well-known Anderson anion $[(CuO_6)Mo_6O_{18}]^{10-}$, in which a central $\{CuO_6\}$ octahedron is hexagonally surrounded shar-

Table 3. Hydrogen bond lengths (Å) and bond angles (deg)[a].

D–H···A	d(H···A)	d(D···A)	∠ (DHA)
N(1)–H(1D)···O(6)$^{\#4}$	2.29	3.189(7)	172.6
N(1)–H(1D)···O(8)$^{\#4}$	2.57	3.009(6)	110.8
N(2)–H(2C)···O(3)$^{\#2}$	2.16	2.970(6)	149.3
N(2)–H(2C)···O(15)$^{\#2}$	2.61	3.287(6)	132.2
N(2)–H(2D)···O(8)$^{\#1}$	2.15	3.018(6)	161.7
N(3)–H(3C)···O(8)$^{\#1}$	2.46	3.181(7)	137.0
N(3)–H(3D)···O(1)$^{\#5}$	2.48	3.095(6)	125.8
N(4)–H(4C)···O(4)$^{\#4}$	2.18	3.055(7)	162.2
N(4)–H(4D)···O(13)$^{\#6}$	2.58	3.302(7)	137.3

[a] Symmetry transformations: $^{\#1}$ $-x, -y-1, -z+1$; $^{\#2}$ $x+1, -y-1/2, z+1/2$; $^{\#3}$ $x-1, -y-1/2, z-1/2$; $^{\#4}$ $-x, y+1/2, -z+1/2$; $^{\#5}$ $x, -y-1/2, z+1/2$; $^{\#6}$ $x, -y-1/2, z-1/2$.

ing edges with the molybdate units. Two cyclic As_3O_6 trimers are capping opposite faces of the Anderson-type anion plane. Each As_3O_6 unit consists of three AsO_3 pyramids linked in a triangular arrangement by sharing corners and bonded to the central $\{CuO_6\}$ octahedron and two MoO_6 octahedra *via* μ_3-oxo groups. Concerning the As_3O_6 cyclic moiety, the three As–O bonds in each AsO_3 pyramid have distances in the range of 1.759(4) – 1.801(4) Å. In the $[(CuO_6)Mo_6O_{18}(As_3O_3)_2]^{4-}$ unit, three kinds of oxygen atoms exist in the cluster: terminal O_t, double-briging $O_{(\mu 2)}$, and tetracoordinate $O_{(\mu 4)}$. Thus, the Mo–O bond lengths fall into three classes: Mo–O_t = 1.700(4) – 1.724(4) Å, Mo–$O_{(\mu 2)}$ = 1.902(3) – 1.951(3) Å and Mo–$O_{(\mu 4)}$ = 2.288(3) – 2.458(3) Å. The six MoO_6 octahedra are distorted as expected, because each Mo atom is bound to three different types of oxygen atoms. The central copper atom Cu(1) adopts a distorted octahedral geometry due to the Jahn-Teller effect, where the Cu(1)–O distances vary from 1.982(3) to 2.266(3) Å, in agreement with previously reported values [18]. The other crystallographically independent copper atom Cu(2) is coordinated by two terminal oxygen atoms coming from two different Anderson anions (Cu(2)–O distances 2.571(4) and 2.610(4) Å) and four nitrogen donors from two en ligands (Cu(2)–N distances 1.984(5)–2.009(5) Å) furnishing a distorted octahedral geometry.

The most remarkable features of **1** are that each $[(CuO_6)Mo_6O_{18}(As_3O_3)_2]^{4-}$ unit links four $\{Cu(en)_2\}$ groups in a centrosymmetric manner, and that the $\{Cu(en)_2\}$ groups bridge two $(CuO_6)Mo_6O_{18}(As_3O_3)_2]^{4-}$ units to generate an unprecedented 2D networks in the *ab* plane (Fig. 2a, 2b). In comparison with the reported extended structure of $[Cu(imi)_2]_2[(CuO_6)(As_3O_3)_2Mo_6O_{18}][Cu(imi)_2]_2$ [18], in which the oxidation state +1 of the outer Cu atoms prevents further bonding to another $[(CuO_6)(As_3O_3)_2Mo_6O_{18}]^{4-}$ unit, the oxidation state +2 of the Cu(2) atoms in **1** allows for further bonding to $[(CuO_6)(As_3O_3)_2Mo_6O_{18}]^{4-}$ units to construct a 2D extended framework. The resulting gridlike coordination framework has (4,4) topology (Fig. 2c). Each layer shows square cavities with dimensions 8.6 × 16.8 Å^2 based on $d_{Cu\cdots Cu}$. Therefore, the successful synthesis of **1** gives guidance for the development of new coordination networks and topologies in POM chemistry. In addition, taking into account the strong hydrogen bonding interactions, a 3D supramolecular structure is generated through the N and the O atoms of the polyanions with N ··· O distances of 2.970(6) – 3.302(7) Å for **1**. The hydrogen bond lengths and bond angles are listed in Table 3. These hydrogen bonds make the crystal structure of compound **1** more stable.

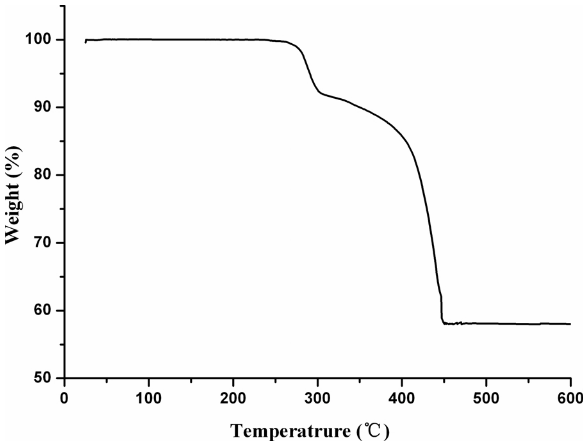

Fig. 3. TGA curve of compound **1** in flowing air atmosphere at 10 °C min^{-1}.

IR spectra

In comparison with the Keggin and Dawson types, IR spectroscopic studies of Anderson polyanions are rare, and the characteristic peaks have not been strictly assigned. In the low-wavenumber regions of the IR spectrum of **1**, the peaks at 932, 906 and 885 cm^{-1} are attributed to the Mo–O_t vibrations, those at 823, 787 and 669 cm^{-1} to the Mo–$O_{(\mu 2)}$ stretching modes, and those at 616 cm^{-1} to Cu–O_a stretching modes. Bands at 559, 533 and 461 cm^{-1} are assigned to the Mo–$O_{(\mu 4)}$ stretching vibration. The peaks in the range from 1035 to 1593 cm^{-1} are attributed to the ethylenediamine ligand.

Thermo-gravimetric analysis

The thermal decomposition of compound **1** is characterized by the loss of the organic groups and of As_2O_3 from 240 to 380 °C (Fig. 3). A 12.0 % weight loss is attributed to the loss of 4 en units (calculated 12.42 %). This is followed by a weight loss of *ca.* 30.04 % for the release of $3As_2O_3$ (calculated 30.65 %).

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