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# The synthesis, structure and properties of a new compound with 1D linear chain arsenomolybdate anion building block

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## ABSTRACT

The new inorganic–organic hybrid arsenomolybdate $\{Cu(2,2'\text{-}bpy)\}_2\{H_2As_2Mo_2O_{14}\}$ (2,2′-bpy = 2,2′-bipyridine) (1) has been hydrothermally synthesized and characterized by single-crystal X-ray diffraction analysis, elemental analyses, X-ray powder diffraction (XRPD), IR spectroscopy, UV spectroscopy, XPS spectroscopy and thermogravimetric analysis (TG). Compound 1 presents an infinite 1D chain structure based on the unprecedented $\{H_2As_2Mo_2O_{14}\}^{4-}$ fragment and transition-metal complex $\{Cu(2,2'\text{-}bpy)\}^{2+}$. Compound 1 displays obvious electrocatalytic activities toward the reduction of nitrite and better photocatalytic activities for the degradation of methylene blue.

Because polyoxometalates (POMs) have unique and novel structure, as well as excellent physical and chemical properties, it has great potential applications in medicinal chemistry [1], preparation of nanomaterials [2], photochemical [3], electrochemical [4], magnetic [5], catalysis [6] and other fields. Therefore, it becomes a hot research topic of modern inorganic chemistry. The arsenomolybdate is an important branch of POMs. Typical arsenomolybdate includes: (i) $As_2Mo_6$ type, e.g. the compound $[\{Cu(o\text{-}phen)(H_2O)_2\}_2Mo_6O_{18}(O_3AsOH)_2]$ [7], which has been reported by Zubieta group; (ii) $As_2Mo_{24}$ type, $[NBu_4]_6[Fe(C_5H_5)_2][HAsMo_{12}O_{40}]_2$ [8]; (iii) $As_2Mo_{18}$ type, $[Himi]_6[As_2Mo_{18}O_{62}]\cdot 11H_2O$ [9]; (iv) $As_6Mo_6$ type, $[Cu(arg)_2]_2[(CuO_6)Mo_6O_{18}(As_3O_3)_2]\cdot 4H_2O$ [10] and so on. However, as for the continuous exploration and improvement of experimental conditions, people are not only just focused on synthesizing the compounds with these typical arsenomolybdate anions, they are also studying the synthesis of compounds with distinctive arsenomolybdate anions. For example, in $As_2Mo_6$ type of compound, $PhAsO_3H_2$ is used as source material of arsenic in the compound, and then benzene ring structure is introduced in POM anion $[As_2Mo_6O_{26}]^{6-}$ to form a new arsenomolybdate anion $[Mo_6O_{18}(O_3AsPh)_2]^{4-}$ [11]; Baibin Zhou etc. [12] in our group has conducted structure improvement on the basis of original $[As_2Mo_{18}O_{62}]^{6-}$ anion, and prepared novel $As_2Mo_{18}$ type compound $[Cu(2,2'\text{-}bpy)_2][\{Cu(2,2'\text{-}bpy)\}_3\{As_2Mo_{18}O_{62}\}]\cdot 4H_2O$ and $(pyr)(imi)(Himi)_3[As_2(As_2Mo_{18}O_{62})]\cdot 3H_2O$ with Cu and As caps, respectively. In addition to the typical arsenomolybdates, many nonclassical arsenomolybdates have also been reported in the past of years, such as $Ag_{12.4}Na_{1.6}Mo_{18}As_4O_{71}$ [13], $(NH_4)_{11}[AgAs_2Mo_{15}O_{54}]_3\cdot 6H_2O\cdot 2CH_3CN$ [14], $[As^{III}{}_2Fe^{III}{}_5MMo_{22}O_{85}(H_2O)]^{n-}$ ($M = Fe^{3+}$, $n = 14$; $M = Ni^{2+}$ and $Mn^{2+}$, $n = 15$) [15] and so on. Therefore, novel arsenomolybdate structure is gaining more and more attention. Actually, we pay more attention on the arsenomolybdate modification process [16,17]. Moreover, we try to obtain the new arsenomolybdate with unusual structures and interesting properties.

Based on the results of previous work [18,19], we reported an organic–inorganic hybrid compound $\{Cu(2,2'\text{-}bpy)\}_2\{H_2As_2Mo_2O_{14}\}$ (1) with new arsenomolybdate anion fragment. In the anion of compound 1, the $\{AsO_4\}$ tetrahedra and the $\{MoO_6\}$ octahedra are connected by bridging oxygen atoms, forming unprecedented infinite 1D chain $\{H_2As_2Mo_2O_{14}\}_n^{4n-}$. Meanwhile, we also studied the compound 1 from the perspectives of electrochemistry and photocatalysis.

Compound 1 was synthesized by the self-assembly approach under hydrothermal condition. A mixture of $CuCl_2\cdot 2H_2O$ (0.4013 g, 2.35 mmol), $Na_3AsO_4\cdot 12H_2O$ (1.0017 g, 2.36 mmol), $MoO_3$ (0.5002 g, 3.47 mmol), 2,2′-bipyridine (0.2517 g 1.61 mmol) and $H_2O$ (18 mL, 1.00 mol) was stirred for 30 min. The pH value was adjusted to about 3.5 with 1.0 M HCl. The above mixture was placed in a Teflon-lined stainless steel autoclave reactor (25 mL) and heated at 160 °C for 6 days. After the mixture had been cooled to room temperature at a rate of 10 °C · $h^{-1}$, green block crystals of sample 1 were obtained in a 58% yield based on Mo. Anal. calcd for $C_{20}H_{18}As_2Cu_2Mo_2N_4O_{14}$

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

| Empirical formula | $C_{20}H_{18}As_2Cu_2Mo_2N_4O_{14}$ |
|---|---|
| Formula weight | 1007.20 |
| Crystal system | Monoclinic |
| Space group | Cc |
| *a* (Å) | 20.016(8) |
| *b* (Å) | 10.909(5) |
| *c* (Å) | 7.223(3) |
| $\alpha$ (deg) | 90 |
| $\beta$ (deg) | 106.001(5) |
| $\gamma$ (deg) | 90 |
| Z | 2 |
| Volume, (Å$^3$) | 1516.0(11) |
| $d_{calcd}$ (Mg cm$^{-3}$) | 2.202 |
| $\mu$ (Mo K$\alpha$), mm$^{-1}$ | 4.429 |
| *F* (000) | 1260 |
| GOF on $F^2$ | 1.007 |
| Final R indices [$I > 2\sigma(I)$] | $R_1{}^* = 0.0761$, $wR_2{}^* = 0.1884$ |

* $R_1 = \sum||F_o|\text{-}|F_c||/\sum|F_o|$, $wR_2 = \{R_w[(F_o)^2 - (F_c)^2]^2/R_w[(F_o)^2]^2\}^{1/2}$.

($M_r = 1007.20$): C, 23.83; H, 1.80; N, 5.56; Cu, 12.62; Mo, 19.05; As, 14.88%. Found: C, 23.84; H, 1.83; N, 5.60, Cu, 12.60; Mo, 19.02; As, 14.85%. IR data (KBr, cm$^{-1}$): 2357(s), 1606(s), 1446(m), 1385(m), 995(m), 920(s), 860(s), 794(s).

Single-crystal X-ray analysis [20] (Table 1) reveals that compound 1 is composed of $\{H_2As_2Mo_2O_{14}\}^{4-}$ fragment and $\{Cu(2,2'\text{-bpy})\}^{2+}$. The 1D structure is shown in Fig. 1. The basic unit of compound 1 (see Fig. 2) shows the coordination environment around the molybdenum, copper, and arsenic atoms. The anion $\{H_2As_2Mo_2O_{14}\}^{4-}$ is similar with the anion of reported $[As(phen)]_2[As_2Mo_2O_{14}]$ [18]. In the reported compound, each of anion is an independent $[As_2Mo_2O_{14}]^{6-}$ unit, while in compound 1, $\{MoO_6\}$ octahedra and $\{AsO_4\}$ tetrahedra are linked by the sharing oxygen atoms to form a 1D infinite chain.

In compound 1, each $\{AsO_4\}$ tetrahedron is linked to $\{MoO_6\}$ octahedra through O(3) and O(7). The two adjacent $\{MoO_6\}$ octahedra are connected through O(1) forming the limitless 1D chain. The bond lengths of As–O are between 1.708(14) and 1.735(11) Å. The bond lengths of Mo–O are in the range of 1.697(12)–2.277(11) Å. The range of bond angles of O–As–O and O–Mo–O are 107.3(6)–112.4(6)° and 75.2(5)–169.4(5)°, respectively.

For the sites of copper, the "4 + 2" geometry which is distorted on an axial basis is applied. The axial basis characterizes the $d^9$ Jahn–Teller cation. According to the definition of $\{CuO_4N_2\}$ site, it consists of two nitrogen donors and four oxo-groups, which come from the chelating 2,2′-bpy ligand and the $\{H_2As_2Mo_2O_{14}\}_n^{4n-}$ chain, respectively. Of it, in the cationic $\{Cu(2,2'\text{-bpy})\}^{2+}$, Cu is connected to tri-bridging oxygen atom O(3) and O(7) of two adjacent $\{MoO_6\}$ octahedra and also linked to the shared-oxygen atom O(1). The bond distance of Cu(1)–O(3) is 2.293(11)Å, while the Cu(1)–O(7) is 2.186(12)Å. At the same time, copper is also connected to O(2) of the $\{AsO_4\}$ tetrahedron. The bond length of Cu(1)–O(2) is 1.927(11)Å.

There are hydrogen bonds in compound 1 between carbon atoms of organic ligands and anions. As Fig. 3a shows, between the anion and the organic ligand, there are two groups of intermolecular hydrogen bonds, namely, C(4)–H(4)…O(4)$^{i}$ 3.24(2)Å and C(7)–H(7)…O(4)$^{i}$ 3.47(2)Å ((i) x,1 − y,1 / 2 + z). The two groups of hydrogen bonds construct the paralleling 1D chain into the 2D structure. In addition, the 2D plans of each layer form the 3D supramolecular structure through C(3)–H(3)…O(5)$^{ii}$ 3.50(2)Å ((ii) x,1 + y,z) (Shown in Fig. 3b). At the same time, there are two groups of intramolecular hydrogen bonds, C(1)–H(1)…O(2) 2.97(2)Å and C(10)–H(10)…O(5)$^{iii}$ 3.33(2)Å ((iii) x,1 − y,1 / 2 + z), respectively. The hydrogen bonds make the structure of compound 1 more stable.

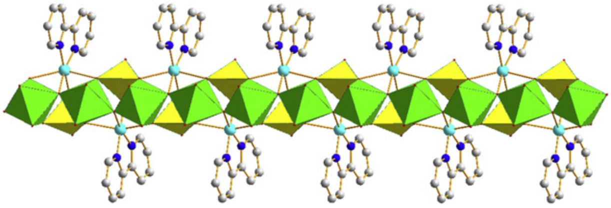

**Fig. 1.** Polyhedral and ball-stick representation of the 1D chain.

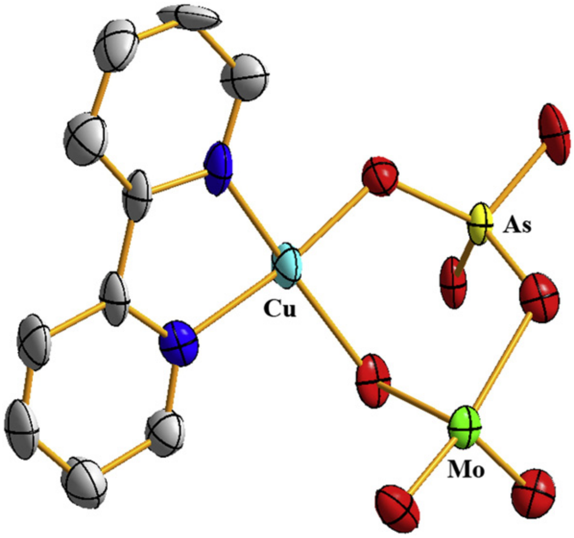

**Fig. 2.** ORTEP drawing of compound 1 with thermal ellipsoids at 50% probability.

IR spectrum of compound 1 is shown in Fig. S1, the strong absorption peaks at 920, 860, and 794 cm$^{-1}$ can be attributed to $\nu$(Mo–O–Mo). The absorption peak at 953 cm$^{-1}$ can be attributed to $\nu$(As–O). The absorption peak at 1606–1059 cm$^{-1}$ can be attributed to the characteristic

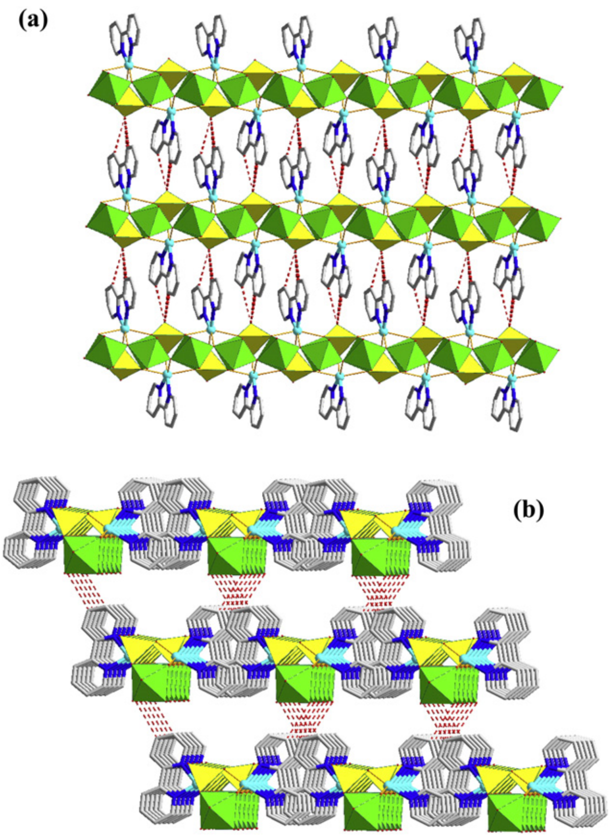

**Fig. 3.** The 2D and 3D polyhedral and ball-stick representation of compound 1 which was formed by hydrogen bonding interactions.