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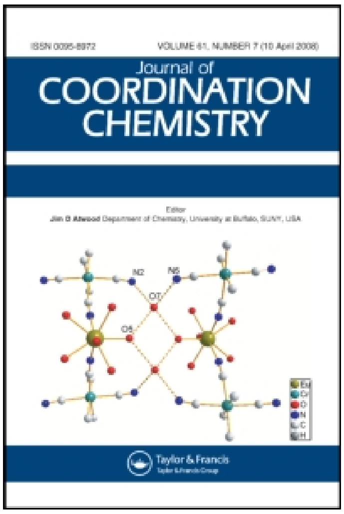

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A novel zigzag chain based on polyoxomolybdate decorated by glycine ligand in covalent bond

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A novel zigzag chain based on polyoxomolybdate decorated by glycine ligand in covalent bond

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An unusual compound, $K_2[Mo_4O_{13}(NH_3CH_2COO)_2]\cdot 2H_2O$ (**1**), has been synthesized and structurally characterized by the XRD, elemental analysis, IR spectrum, TG analyses and the single crystal X-ray diffraction. The structure of **1** exhibits a zigzag chain based on corner-shared tetramolybdate chelated by two bidentate glycine ligands.

Keywords: Hydrothermal synthesis; Crystal structure; Polyoxomolybdate; Glycine

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1. Introduction

Polyoxometalates have attracted attention due to their diverse structural properties and potential applications in catalysis, photochemistry, electrochromism, magnetism and medicine [1]. Research on polyoxometalate-based materials has focused on three main approaches: (1) under reducing conditions, some molybdenum-oxide based building blocks/fragments assemble into giant mixed-valence polyoxomolybdates with "big wheel" or "basket" architectures [2]; (2) vacant-species of the Keggin or Dawson type polyoxometalates linked by lanthanide or transition-metal ions to form magnetic clusters [3]; (3) polyoxometalates decorated by organic species or transition-metal coordination complexes to form organic–inorganic hybrid materials [4]. These materials exhibit abundant topologies and fascinating properties. In the third case, the association between polyoxometalate species and proteins has drawn attention due to the discovery of polyoxometalates as drugs against tumors and AIDs [5]. During research on models of polyoxometalate–protein interactions, amino acids, as the basic unit in biological systems, have found attention, and several examples have been reported recently. There are three main interaction models between polyoxoanions and amino acids or peptides: (1) amino acids as counterions interacting with polyoxoanions via hydrogen bonding [6], (2) amino acids forming covalent bonds [7], and (3) amino acids grafted into polyoxoanions by transition metals [8]. In the case of the covalent bond model, examples are mainly of discrete clusters; $[Mo_4O_{12}(\text{glycylglycylglycine})_2]\cdot 9H_2O$ [7d]

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is the only example of a one-dimensional chain, to our knowledge. Here, we report another chain-like polyoxomolybdate interacting with an amino acid by covalent bonds, $K_2[Mo_4O_{13}(NH_3CH_2COO)_2] \cdot 2H_2O$ (**1**).

2. Experimental

2.1. *Materials and methods*

All chemicals were reagent grade and used without further purification. The elemental analysis was performed with a German Elementary Vario EL III instrument. The IR spectrum of KBr pellets was recorded on a Nicolet FT-IR Magna 750 spectrophotometer. The thermogravimetric analysis was carried out with a NETZSCH STA449C unit, at a heating rate of $10^\circ C\,min^{-1}$ under an air atmosphere from 35 to 800°C. X-ray powder diffraction data were collected on an X-pert Pro diffractometer using Cu-Kα radiation ($\lambda = 1.5406$ Å).

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2.2. *Preparation of $K_2[Mo_4O_{13}(NH_3CH_2COO)_2] \cdot 2H_2O$ (1)*

A solution of $(NH_4)_6Mo_7O_{24} \cdot 4H_2O$ (0.2 mmol), glycine (10.0 mmol), KCl (5.0 mmol) and H_2O(10 mL) was stirred at room temperature for 10 min, and then the pH of mixture was adjusted to 3.9 with dilute HCl solution. The resulting suspension was sealed in a 25 cm^3 Teflon-lined reactor, which was kept at 110°C for 2 days. Colorless needles of **1** were isolated in 46% yield based on Mo. Element analysis for **1**. Calcd (%): H: 1.63, C: 5.56, N: 3.24; Found (%): H: 1.72, C: 5.65, N: 3.24. IR (cm^{-1}, KBr): 3427(s), 3255(s), 3127(s), 2981(m), 2850(m), 2670(m), 2582(m), 1606(s), 1588(s), 1495(s), 1443(m), 1413(s), 1338(s), 1116(m), 1037(m), 942(m), 916(s), 900(s), 867(m), 802(s), 716(m).

2.3. *X-ray crystallography*

A suitable single crystal with approximate dimensions ($0.15 \times 0.12 \times 0.03\,mm^3$) was used for X-ray diffraction analysis. The data collection was performed at 130 K on a Mercury CCD Diffractometer equipped with a graphite monochromator with Mo-Kα radiation ($\lambda = 0.71073$ Å). Empirical absorption corrections were applied by using the SADABS program [9]. The structure was solved with direct methods and all calculations were performed using the SHELXL package [10]. The structure was refined by full-matrix least squares with anisotropic displacement parameters for non-hydrogen atoms. The positions of H atoms (H2A, H2B) attached to carbon atoms were generated geometrically and treated as riding on the C2 atom. The hydrogen atoms of water (H10A, H10B) and nitrogen (H3, H4, H5) were located from difference maps. Details of the crystal data are listed in table 1. Selected bond lengths and angles are listed in table 2.

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Table 1. Crystal data and refinement parameters of compound **1**.

Empirical formula	$C_4H_{14}K_2Mo_4N_2O_{19}$
Formula weight	856.13
Crystal system	Monoclinic
Space group	$P2(1)/c$
a (Å)	8.0789(6)
b (Å)	14.6234(10)
c (Å)	8.1001(4)
β (°)	92.801(3)
V (Å^3)	955.81(11)
Z	2
D_{Calcd} (g cm^{-3})	2.975
μ (mm^{-1})	3.099
Reflections collected/unique	2192/1978
R_{int}	0.0304
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0269$, $wR_2 = 0.0610$
R indices (all data)	$R_1 = 0.0329$, $wR_2 = 0.0640$
Goodness-of-fit on F^2	1.093
Max, min $\Delta\rho$ (e Å^{-3})	0.72 and −0.72

Table 2. Selected bond lengths (Å) and angles (°) for compound **1**.

Mo(1)–O(1)	1.715(2)	Mo(2)–O(7)	1.713(3)
Mo(1)–O(3)	1.730(2)	Mo(2)–O(4)	1.718(3)
Mo(1)–O(6)	1.901(2)	Mo(2)–O(5)	1.8974(3)
Mo(1)–O(2)	1.931(2)	Mo(2)–O(2)	1.966(2)
Mo(1)–O(6)^a	2.176(2)	Mo(2)–O(6)^a	2.222(2)
Mo(1)–O(8)	2.419(2)	Mo(2)–O(9)	2.275(2)
C(1)–C(2)	1.508(5)	O(8)–C(1)	1.262(4)
C(2)–N(1)	1.489(4)	O(9)–C(1)	1.262(4)
O(1)–Mo(1)–O(3)	104.54(12)	O(7)–Mo(2)–O(4)	103.59(13)
O(1)–Mo(1)–O(6)	102.05(11)	O(7)–Mo(2)–O(5)	98.71(9)
O(3)–Mo(1)–O(6)	104.18(11)	O(4)–Mo(2)–O(5)	100.81(8)
O(1)–Mo(1)–O(2)	97.31(11)	O(7)–Mo(2)–O(2)	97.06(12)
O(3)–Mo(1)–O(2)	95.84(11)	O(4)–Mo(2)–O(2)	94.08(11)
O(6)–Mo(1)–O(2)	147.45(10)	O(5)–Mo(2)–O(2)	155.07(7)
O(1)–Mo(1)–O(6)^a	98.16(10)	O(7)–Mo(2)–O(6)^a	92.20(11)
O(3)–Mo(1)–O(6)^a	156.57(11)	O(4)–Mo(2)–O(6)^a	161.17(11)
O(6)–Mo(1)–O(6)^a	76.22(10)	O(5)–Mo(2)–O(6)^a	86.62(6)
O(2)–Mo(1)–O(6)^a	75.31(9)	O(2)–Mo(2)–O(6)^a	73.57(9)
O(1)–Mo(1)–O(8)	175.01(10)	O(7)–Mo(2)–O(9)	170.28(11)
O(3)–Mo(1)–O(8)	80.05(10)	O(4)–Mo(2)–O(9)	86.14(11)
O(6)–Mo(1)–O(8)	78.41(9)	O(5)–Mo(2)–O(9)	79.11(6)
O(2)–Mo(1)–O(8)	80.13(9)	O(2)–Mo(2)–O(9)	82.10(9)
O(6)^a–Mo(1)–O(8)	77.08(8)	O(6)^a–Mo(2)–O(9)	78.24(9)
O(8)–C(1)–O(9)	126.4(3)	O(8)–C(1)–C(2)	118.9(3)
N(1)–C(2)–C(1)	111.1(3)	O(9)–C(1)–C(2)	114.6(3)

Symmetry transformations used to generate equivalent atoms, a: $-x$, $-y+1$, $-z+2$.

3. Results and discussion

Compound **1** was obtained by self-assembly in K^+/molybdate/glycine system. By a series of parallel experiments, it was found that isolation of the title compound depended on the choice of amino acids, the reaction pH and the reaction time. In this reaction, longer reaction times resulted in discrete $\{Mo_8O_{26}(Gly)_2\}^{4-}$ (Gly = NH_3CH_2COO) clusters [11].

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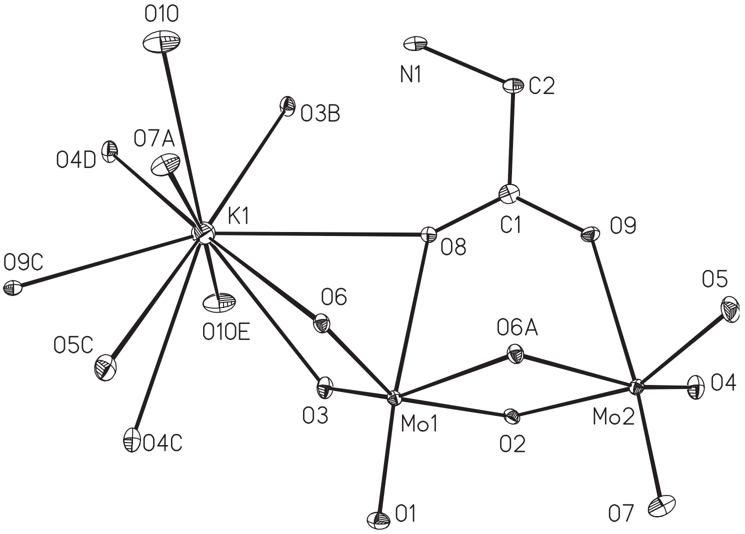

Figure 1. The coordination geometries of molybdenum and potassium in compound **1** (ellipsoids at 30% probability). Hydrogen atoms are omitted for clarity. Symmetry code: (a) $-x$, $1-y$, $2-z$; (b) x, $3/2-y$, $-1/2+z$; (c) $1+x$, y, z; (d) $1+x$, $3/2-y$, $-1/2+z$; (e) x, $3/2-y$, $1/2+z$.

The X-ray diffraction analysis reveals that the structure of **1** contains an infinite chain (parallel to the a axis) of zigzag corner-shared Mo_4O_{13} chelated by two bidentate glycine ligands. The basic building block is shown in figure 1. There are two crystallographically independent Mo atoms and one potassium atom. Each Mo atom is in a distorted octahedral environment with six oxygen atoms, one of which is from the carboxyl of the glycine ligand. Two molybdenum octahedra share two bridging oxygen atoms to form a $\{Mo_2O_7Gly\}$ subunit, in which a set of Mo1 and Mo2 atoms is bridged by a terminal carboxyl group of the bidentate glycine with a $Mo \cdots Mo$ separation of 3.281 Å, in good agreement with $Mo \cdots Mo$ distances for the edge-shared MoO_6 octahedra [7, 12]. Two such inversion center related subunits share an edge to give a $\{Mo_4O_{13}(Gly)_2\}$ unit, further linked into an infinite chain by corner-sharing, where glycine ligands are located, alternately, on each side of the chain (shown in figure 2). Oxygen atoms of the chain may be divided into five groups: terminal oxygen atoms (Mo–O distance of 1.713–1.73 Å); μ_2 oxygen atoms which bridge two Mo edge-sharing octahedra (Mo–O distance in 1.932–1.966 Å); μ_2 oxygen atoms which bridge two Mo corner-sharing octahedra (Mo–O distance in 1.897 Å); μ_3 oxygen atoms (Mo–O distance is 1.961–2.222 Å), and carboxyl–oxygen atom of glycine (Mo–O distance of 2.275–2.420 Å and Mo–O–C angle 125.37°–129.40°). Extensive bond valence sum calculation indicated the valences of Mo and O are +6 and −2, respectively. To keep the compound electrically neutral, one hydrogen atom must be added to NH_2 group of glycine. The packing of the $\{Mo_4O_{13}(Gly)_2\}_n$ chains shows a network of weak hydrogen bonds of $N \cdots O(\text{–Mo}) = 2.810(4)\text{–}3.110(4)$ Å and $O(\text{–}H_2) \cdots O(\text{–Mo}) = 2.745(4)\text{–}2.920(4)$ Å, respectively, which increase the stability. Nine of the eleven oxygen atoms located around potassium atom (K1) are from different polyoxomolybdate chains, the other two are from water. The K–O covalent bonds (in 2.781–3.326 Å) connect the polyoxomolybdate chains to a 3-D structure (shown in figure 3).

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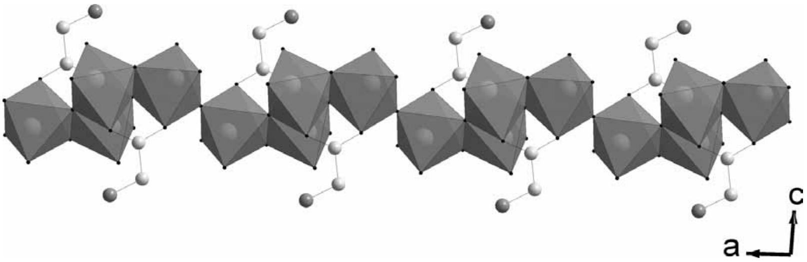

Figure 2. A polyhedral and ball-and-stick representation of the $\{Mo_4O_{13}(NH_3CH_2COO)_2\}_n$ chain in compound **1**; medium gray polyhedra belong to MoO_6 octahedra, ball-and-stick belong to Gly ligands, hydrogen atoms are omitted for clarity.

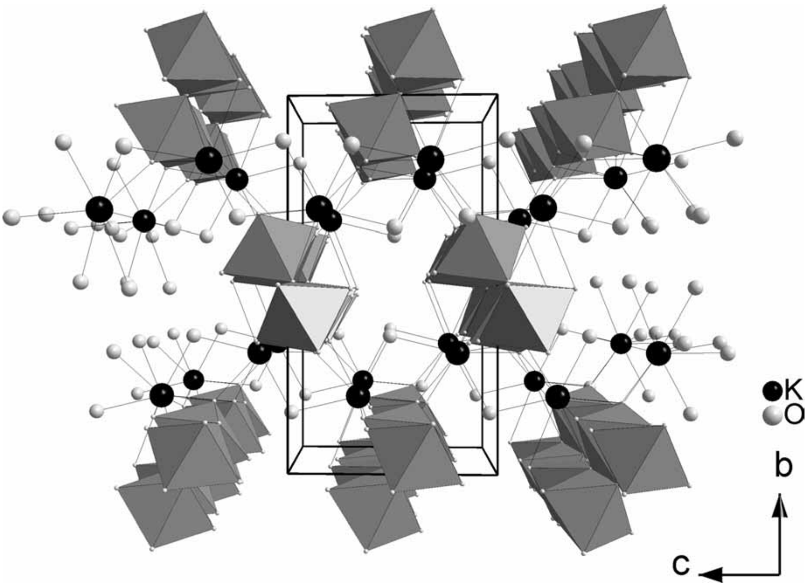

Figure 3. A polyhedral and ball-and-stick representation of compound **1** in cell packing; medium gray polyhedra belong to molybdate chain, C, H, N atoms are omitted for clarity.

To our knowledge, compound **1** is the second polyoxomolybdate decorated directly by amino acids with a chain-like structure. The first example was $[Mo_4O_{12}(\text{glycylglycylglycine})_2] \cdot 9H_2O$ reported by Professor Yamase in 1999 [7d]. The structures of the polyoxomolybdate chains in the two compounds are different. In $[Mo_4O_{12}(\text{glycylglycylglycine})_2] \cdot 9H_2O$, all MoO_6 octahedra are linked via edge-sharing to produce a rail-like polymeric chain. In contrast, in compound **1** four MoO_6 octahedra are assembled via edge-sharing to a tetramolybdate unit, which is further linked to a zigzag chain by corner-sharing. The structure is similar to the polyoxomolybdate chain in $[\{Cu(2,2'\text{-bpy})\}_2(tp)Mo_4O_{13}]$ [13] except that the tetramolybdate unit in the latter consists of two $\{MoO_6\}$ octahedra and two $\{MoO_5\}$ distorted square-pyramids in an edge-sharing arrangement. This is mostly due to the difference in the carboxyl coordination of the ligands. In compound **1**, two oxygen atoms of each carboxyl connect to two adjacent molybdenum atoms completing the

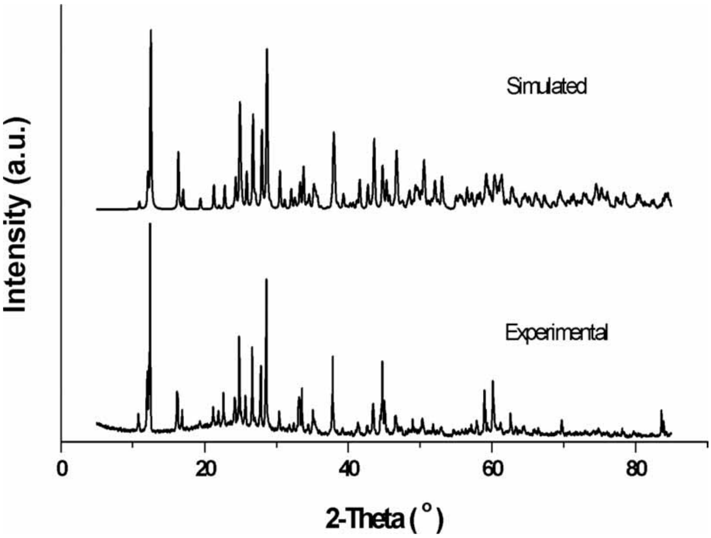

Figure 4. Experimental and simulated X-ray powder diffraction pattern of compound **1**.

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octahedron; while in [{Cu(2,2′-bpy)}$_2$(tp)Mo_4O_{13}], two oxygen atoms of each carboxyl connect to one molybdenum atom and one copper atom, resulting in {MoO_5} in the structure.

3.1. *Spectroscopic and thermal properties*

The experimental XRD pattern (powder X-ray diffraction) data were collected on a Philips X'Pert-MPD diffractometer with Cu-Kα radiation ($\lambda = 1.54056$ Å) for sample **1** and the simulated pattern on the basis of single crystal structure is shown in figure 4. The diffraction peaks of both patterns correspond well in position, indicating the purity of the sample. The IR spectrum of compound **1** shows stretching vibrations of C–H, N–H and O–H in the 2851–3492 cm^{-1} region and the stretching vibrations of glycine between 1000 and 1610 cm^{-1}. The strong bands in the region of 700–950 cm^{-1} may be assigned to the stretching vibrations of Mo–O and Mo–O–Mo bonds.

TGA measurement was performed on a NETZSCH STA 449C system. As shown in figure 5, the weight loss of compound **1** in the range 200–250°C (Calcd 4.2%, Found 4.6%) is in agreement with the removal of water. The second weight loss between 250 and 470°C is 17.3%, which is in agreement with the removal of the glycine ligands (Calcd 17.5%).

Supplementary material

Crystallographic data for the structure reported in this article have been deposited with the Cambridge Crystallographic Data Center as supplementary publication No. CCDC-286549. Copies of this information may be obtained free of charge from

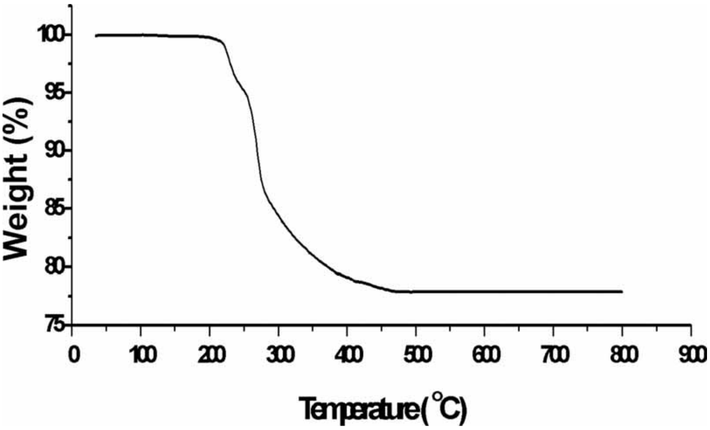

Figure 5. TGA-DTA of compound **1** in flowing air at 10°C min^{-1}.

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