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Short communication

A new hydrogen-bonding linked 3-D polyoxomolybdate

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ABSTRACT

The reactions under hydrothermal reaction conditions resulted in a hydrogen-bonding linked polyoxomolybdate $[(NH_4)_2M_4O_{13}]_n$ **1** with three-dimensional (3-D) polymeric structure. The compound **1** is composed of three distinct (MoO_6) and one (MoO_5) mixed polyhedral connected by edge-sharing within the asymmetric unit displaying a covalent bonding four-step ladder network, and the ladder units linked via corner-sharing between asymmetric units showing an extended covalent bonding 2-D layer structure, and the 2-D networks are further linked by multiple hydrogen bonds to result in a 3-D polyoxomolybdate.

1. Introduction

Polyoxometalates (POMs) are one of the most active and rapidly advancing areas of inorganic chemistry as they are an important class of compounds exhibiting a diverse structural versatility and chemical properties including redox and photochemical activity and catalytic properties [1,2]. These features are important in the area of practical applications such as catalysis whereby the structure and composition of a polyoxometalate can be varied based on the requirements [3–5]. The syntheses of tetramolybdates were reported in early nineteen sixties [6]. Among the obtained compounds of tetramolybdate $Mo_4O_{13}(C_5H_6N)_2$ and compounds of similar compositions were found in the system $MoO_3 - NH_3 - H_2O$, from which ammonium tetra-molybdates $4MoO_3 \cdot 2NH_3 \cdot H_2O$ and $4MoO_3 \cdot 3NH_3 \cdot 3H_2O$ were precipitated and characterized [6,7]. In nineteen eighties, the crystal structures of two polymorphs including orthorhombic and triclinic were observed. In the triclinic crystals infinite chains built of Mo_4O_{18} sub-units were tied in pairs by sharing edges to form Mo_8O_{26} groups, which were further connected in chains by sharing terminal edges. The orthorhombic polymorph contained Mo_4O_{18} sub-units linked by vertices into infinite ribbon chains. The infinite chains were additionally joined by vertices into a 2-D framework. The crystal structure of β-octamolybdate, $[Mo_8O_{26}]$ and a few similar discrete anions were described as containing centro-symmetric discrete poly-anions $[\beta\text{-}Mo_8O_{26}]^{4-}$ [8,9]. However, the three-dimensional network of the tetra-molybdates were not revealed. Herein we report reactions under hydrothermal reaction conditions that resulted in a hydrogen-bonding linked polyoxomolybdate $[(NH_4)_2M_4O_{13}]_n$ **1** with three-dimensional (3-D) polymeric structure. The compound **1** is composed of three distinct (MoO_6) and one (MoO_5) mixed polyhedral connected by edge-sharing within the asymmetric unit displaying a covalent bonding four-step ladder network, and the ladder units linked via corner-sharing between asymmetric units showing an extended covalent bonding 2-D layer structure, and the 2-D networks are further linked by multiple hydrogen bonds to result in a 3-D polyoxomolybdate.

The colorless crystals of **1**[1] are suitable for single crystal X-ray diffraction analysis. The details of the crystal structure solutions and refinements are listed in Table 1. The asymmetric unit of the structure **1** consists of four unique Mo metal atoms (Fig. 1). Among the four distinct Mo atoms, three Mo atoms (Mo2, Mo3 and Mo4) are coordinated by six oxygen atoms displaying distorted octahedral geometry while Mo1 atom is coordinated by five oxygen atoms (Please see also Figs. 3 and 4 for the full oxygen coordination around Mo atoms). The O—Mo1—O angles range between 71.37(6) and 162.66(7), the O-Mo2-O angles range between 72.30(6) and 170.64(7), the O-Mo3-O angles range between 72.30(6) and 176.17(10), the O-Mo4-O angles range between 73.92(7) and 168.72(7), respectively, differing from the ideal angle of 90 around Mo2, Mo3, and Mo4. The distances of Mo—O range from 1.6872(17) Å to 2.3811(18) Å (Mo(1)—O(5) 1.7053(18) Å; Mo(1)—O(4) 1.7200(18) Å; Mo(1)—O(3) 1.8731(17) Å; Mo(1)—O(1) 1.8874(16) Å; Mo(1)—O(2) 2.2713(16) Å. Mo(2)—O(9) 1.6872(17) Å; Mo(2)—O(7)#1 1.7346(18) Å; Mo(2)—O(8) 1.8950(17) Å; Mo(2)—O(6) 2.0000(17) Å; Mo(2)—O(1) 2.1446(17) Å; Mo(2)—O(7) 2.2749(18) Å. Mo(3)—O(11)

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[1] The synthesis if compound **1**: the reaction of Ammonium Molybdate Tetrahydrate (1.2358 g) with Nicotinic Acid (0.0615 g) and 4,4-Dipyridyl (0.1561 g), and water (3.0 ml) in the mole ratio of 2: 1: 2: 333 at 190 °C under hydrothermal conditions for 3.5 days produced colorless crystals of **1**.

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1387-7003/

Table 1
Crystal data and structure refinement for compound **1**[a].

Empirical formula	$H_8\,Mo_4\,N_2\,O_{13}$
FW	627.84
Space group	*Pbca*
a/Å	7.603(1)
b/Å	15.371(2)
c/Å	18.933(2)
V/Å^3	2212.7(4)
Z,	8
D_{calc}/gcm^{-3}	3.769
μ/mm^{-1}	4.507
Reflections collected	13,202
Independent reflections	2277 [$R_{int} = 0.0120$]
Refinement method	Full-matrix least-squares on F^2
Goodness-of-fit on F^2	1.343
Final R indices [$I > 4\sigma(I)$]	R1 = 0.0107, w$R2$ = 0.0323
R indices (all data)	R1 = 0.0112, w$R2$ = 0.0330

[a] Details of the structure solution, interatomic distances, angles and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. Click here for full crystallographic data (CCDC1435050).

1.7295(17) Å; Mo(3)—O(10)#1 1.7370(18) Å; Mo(3)—O(2) 1.8593(16) Å; Mo(3)—O(6) 1.9189(16) Å; Mo(3)—O(1) 2.1494(17) Å; Mo(3)—O(10)#1 2.3811(18) Å. Mo(4)—O(12) 1.7120(17) Å; Mo(4)—O(13) 1.7129(17) Å; Mo(4)—O(8)#2 1.8735(17) Å; Mo(4)—O(3) 1.9784(17) Å; Mo(4)—O(2) 2.1659(16) Å; Mo(4)—O(11)#3 2.3242(17) Å) (Table 2), which are comparable with those found in the literature [10]. The mixed polyhedral units are edge-shared within the asymmetric unit displaying a perspective view of a zig-zag four-step ribbon ladder covalent bonding network (Fig 1). The asymmetric edge-shared unit is linked through corner-sharing with other asymmetric units to display an extended 2-D network (Fig 2).

The two asymmetric NH_4^+ cations in **1** are linked through hydrogen bonds with oxygen atoms in the networks (Fig 3, and Fig 4). The N—H·O hydrogen bonds range between 2.795(3) Å and 3.083(9) Å that are comparable with the N—H·O hydrogen bonds found in coordination polymers [11]. The hydrogen bonds are listed in Table 3. Both cations are located between the layers affording strong hydrogen bonding interactions with both layers to result in a 3-D extended polymeric structure (Fig 5).

It should be noted that the 4,4-dipyridyl and nicotinate are not in the final structure of **1**. Syntheses without them as reactants were carried out and that didn't yield the crystals of **1**. The compounds 4,4-dipyridyl and nicotinate as reactants in the reaction may adjust the pH and act as a mineralizer in facilitating the growth of the crystals of the compound and in guiding the ultimate structure.

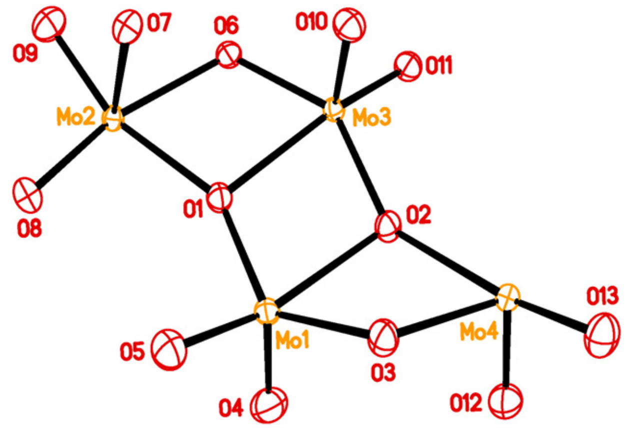

Fig. 1. View of the asymmetric unit showing the atom numbering scheme. Thermal ellipsoids are 80% equiprobability envelopes.

Table 2
Bond lengths [Å] and angles [deg] in compound **1**.

Mo(1)—O(5)	1.7053(18)
Mo(1)—O(4)	1.7200(18)
Mo(1)—O(3)	1.8731(17)
Mo(1)—O(1)	1.8874(16)
Mo(1)—O(2)	2.2713(16)
Mo(2)—O(9)	1.6872(17)
Mo(2)—O(7)[a]	1.7346(18)
Mo(2)—O(8)	1.8950(17)
Mo(2)—O(6)	2.0000(17)
Mo(2)—O(1)	2.1446(17)
Mo(2)—O(7)	2.2749(18)
Mo(3)—O(11)	1.7295(17)
Mo(3)—O(10)	1.7370(18)
Mo(3)—O(2)	1.8593(16)
Mo(3)—O(6)	1.9189(16)
Mo(3)—O(1)	2.1494(17)
Mo(3)—O(10)[a]	2.3811(18)
Mo(4)—O(12)	1.7120(17)
Mo(4)—O(13)	1.7129(17)
Mo(4)—O(8)[b]	1.8735(17)
Mo(4)—O(3)	1.9784(17)
Mo(4)—O(2)	2.1659(16)
Mo(4)—O(11)[c]	2.3242(17)
O(7)—Mo(2)[c]	1.7347(17)
O(8)—Mo(4)[d]	1.8734(17)
O(10)—Mo(3)[c]	2.3811(18)
O(11)—Mo(4)[a]	2.3241(17)
O(5)—Mo(1)—O(4)	104.20(9)
O(5)—Mo(1)—O(3)	101.24(8)
O(4)—Mo(1)—O(3)	105.44(8)
O(5)—Mo(1)—O(1)	104.05(8)
O(4)—Mo(1)—O(1)	103.79(8)
O(3)—Mo(1)—O(1)	134.83(7)
O(5)—Mo(1)—O(2)	162.66(7)
O(4)—Mo(1)—O(2)	93.13(8)
O(3)—Mo(1)—O(2)	73.36(7)
O(1)—Mo(1)—O(2)	71.37(6)
O(9)—Mo(2)—O(7)[a]	104.31(8)
O(9)—Mo(2)—O(8)	102.35(8)
O(7)[a]—Mo(2)—O(8)	98.03(8)
O(9)—Mo(2)—O(6)	95.71(8)
O(7)[a]—Mo(2)—O(6)	96.29(7)
O(8)—Mo(2)—O(6)	153.34(7)
O(9)—Mo(2)—O(1)	157.46(8)
O(7)[a]—Mo(2)—O(1)	96.09(7)
O(8)—Mo(2)—O(1)	83.89(7)
O(6)—Mo(2)—O(1)	72.30(6)
O(9)—Mo(2)—O(7)	85.00(7)
O(7)[a]—Mo(2)—O(7)	170.64(7)
O(8)—Mo(2)—O(7)	80.67(7)
O(6)—Mo(2)—O(7)	81.56(6)
O(1)—Mo(2)—O(7)	74.56(6)
O(11)—Mo(3)—O(10)	102.19(8)
O(11)—Mo(3)—O(2)	105.08(8)
O(10)—Mo(3)—O(2)	99.97(8)
O(11)—Mo(3)—O(6)	99.24(8)
O(10)—Mo(3)—O(6)	98.52(8)
O(2)—Mo(3)—O(6)	145.38(7)
O(11)—Mo(3)—O(1)	159.08(7)
O(10)—Mo(3)—O(1)	98.37(7)
O(2)—Mo(3)—O(1)	74.80(7)
O(6)—Mo(3)—O(1)	73.73(6)
O(11)—Mo(3)—O(10)[a]	80.64(7)
O(10)—Mo(3)—O(10)[a]	176.17(10)
O(2)—Mo(3)—O(10)[a]	81.65(7)
O(6)—Mo(3)—O(10)[a]	78.38(6)
O(1)—Mo(3)—O(10)[a]	78.65(6)
O(12)—Mo(4)—O(13)	103.72(8)
O(12)—Mo(4)—O(8)[b]	102.71(8)
O(13)—Mo(4)—O(8)[b]	98.78(8)
O(12)—Mo(4)—O(3)	97.36(8)
O(13)—Mo(4)—O(3)	96.83(8)
O(8)[b]—Mo(4)—O(3)	150.76(7)
O(12)—Mo(4)—O(2)	92.65(7)
O(13)—Mo(4)—O(2)	162.22(8)
O(8)[b]—Mo(4)—O(2)	84.04(7)

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