

Synthesis and characterization of a novel ring-like decamolybdate

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The reduction of heptamolybdate in acetic aqueous solution resulted in two polymorphic crystals with composition $(\text{NH}_4)_2[\text{Y}(\text{H}_2\text{O})_5]_2 \cdot [\text{Mo}^{\text{VI}}_6\text{Mo}^{\text{V}}_4\text{O}_{30}(\text{CH}_3\text{COO})_4] \cdot 16\text{H}_2\text{O}$. This polyanion exhibited a novel ring-like decamolybdate structure. Two Y atoms were captured by the polyanion and covered the central hole of the ring. $\text{Mo}^{\text{V}}\text{--}\text{Mo}^{\text{V}}$ bonds were also found in this mixed-valence compound.

Introduction

Polyoxometalate chemistry has been actively pursued owing to interest in the chemistry itself and its various applications in fields such as catalysis, electric conductivity, magnetism, nonlinear optical properties and medicine.¹ Since Berzelius reported the first examples of polyoxometalate in 1826,² extensive efforts have been made to synthesize such compounds and a considerable amount of data have been reported on their crystallographic and physical properties. Among the polyoxometalates studied to date, polyoxomolybdates constitute a large family and attract special attention.^{3–7} These high-nuclearity oxomolybdenum complexes have traditionally contained Mo^{VI} centers only (iso- and hetero-polymolybdates) or both Mo^{V} and Mo^{VI} centers with delocalized d-electrons (heteropoly blues).³ More recently, however, a new family of high-nuclearity oxomolybdenum complexes has emerged, one whose Mo^{V} d-electrons are localized in $\text{Mo}^{\text{V}}\text{--}\text{Mo}^{\text{V}}$ single bonds.^{8–11} The $\text{Mo}^{\text{V}}\text{--}\text{Mo}^{\text{V}}$ unit in polyoxomolybdates is known to occupy an $[\text{Mo}_2\text{O}_8]^{6-}$ environment with the $\text{Mo}^{\text{V}}\text{--}\text{Mo}^{\text{V}}$ bond distance lying in the 2.5–2.7 Å range. The substitution of Mo^{VI} with Mo^{V} in synthesis greatly helps to obtain novel and large polyoxomolybdates. On the other hand, this substitution results in highly charged nucleophilic compounds that need more positive charges to neutralize them. Rare earth elements are known to be highly oxophilic in the +3 state, so are chosen to be the central cations or linkage centers in those low valence polyoxomolybdates. From the reduction of heptamolybdate(VI) in aqueous solution in the presence of yttrium(III), a decamolybdate has been obtained and exhibits a novel ring-like structure. Here we report the synthesis and characterization of it and the comparison between it and other relevant polyoxomolybdates.

Results and discussion

Complex **1** has been characterized by elemental analysis and single-crystal X-ray diffraction. Two types of red crystals, chip-like ones (**1a**) and needle-like ones (**1b**), were separated from the reaction mixture of $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}$, $\text{CH}_3\text{COONH}_4$, $\text{N}_2\text{H}_4 \cdot \text{H}_2\text{SO}_4$, $\text{YCl}_3 \cdot x\text{H}_2\text{O}$ and hydrochloric acid aqueous solution, and were proved to be polymorphs.

Single-crystal X-ray diffraction shows that the polyanions in **1a** and **1b** are ring-like structures and each is constructed of ten edge-sharing $\text{Mo}\text{--}\text{O}$ polyhedra (Fig. 1). This decamolybdate lies on inversion centers thus the asymmetric unit consists of half a cluster. In each asymmetric unit, eight Mo atoms sit in the centers of distorted octahedra and can be divided into two pairs ($\text{Mo}(3)$ and $\text{Mo}(5)$ as well as $\text{Mo}(2)$ and $\text{Mo}(4)$). Two Mo

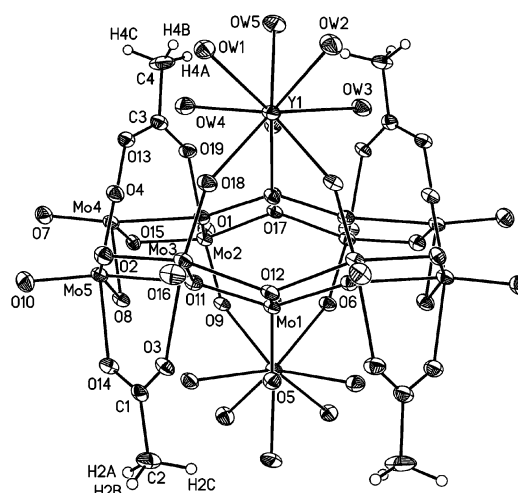


Fig. 1 The structure of compound **1** (showing 50% probability thermal ellipsoids).

centers of each pair are bridged by an acetic group *via* $\text{Mo}\text{--}\text{O}\text{--}\text{C}\text{--}\text{O}\text{--}\text{Mo}$ bonds. The residual Mo atom is coordinated by five oxygen atoms and sits in the center of a distorted trigonal bipyramidal geometry (Table 1). The distances between $\text{Mo}(4)$ and $\text{Mo}(5)$ are 2.5829(8) Å in **1a** and 2.5779(13) Å in **1b**, so an $\text{Mo}\text{--}\text{Mo}$ bond exists between them. $\text{Mo}(4)$ and $\text{Mo}(5)$ are of charge +5 according to bond-valence theory¹² and Ce^{4+} titration. The coordination environment of the $\text{Mo}^{\text{V}}\text{--}\text{Mo}^{\text{V}}$ unit, which is composed of a $[\text{Mo}_2\text{O}_8]^{6-}$ structure and two extra weakly coordinated $\mu_3\text{--}\text{O}$ (O(6)#1, O(11)), is similar to the $[\text{Mo}_2\text{O}_{10}]^{10-}$ structure described by Chae *et al.*⁸

A noticeable aspect of compound **1** is that two Y ions are captured by the anion (Fig. 1). Every Y ion is coordinated by three terminal oxygen atoms from three Mo centers and five water molecules. These two coordinating polyhedra lie above and below the ring plane and cover the central hole of the ring. Since the Y ion has a high charge of +3, it greatly decreases the negative charge of the polyanion and thus stabilizes the structure. The study on polyoxomolybdates with rare earth (RE) cations has progressed for over thirty years owing to interest in their ferroelectric properties and applications in laser or nuclear waste separation processing.¹³ The coordination number and Y–O bond lengths of compound **1** are all in the common range of the reported values.¹³ In fact, as in most polyoxomolybdate–RE complexes, the Y ions of compound **1** can be regarded as being encapsulated by the terminal oxygen atoms of the Mo centers. The nucleophilicity of these shared terminal oxygen

Table 1 Selected bond distances (Å) and angles (°) of complex **1**

	Crystal 1a	Crystal 1b		Crystal 1a	Crystal 1b
Mo(1)–O(5)	1.685(3)	1.694(7)	Mo(4)–O(4)	1.953(4)	1.960(7)
Mo(1)–O(12)	1.777(3)	1.768(7)	Mo(4)–O(15)	2.092(3)	2.059(7)
Mo(1)–O(6)	1.890(4)	1.877(6)	Mo(4)–O(13)	2.146(3)	2.135(7)
Mo(1)–O(11)	1.893(4)	1.890(6)	Mo(4)–O(6)#1	2.214(3)	2.214(6)
Mo(1)–O(17)#1	2.190(3)	2.221(7)	Mo(4)–Mo(5)	2.5829(8)	2.5779(13)
Mo(2)–O(1)	1.729(4)	1.724(7)	Mo(5)–O(10)	1.688(4)	1.698(6)
Mo(2)–O(9)	1.733(3)	1.754(7)	Mo(5)–O(4)	1.944(3)	1.946(7)
Mo(2)–O(15)	1.838(4)	1.824(7)	Mo(5)–O(8)	1.945(4)	1.919(7)
Mo(2)–O(17)	1.983(4)	2.003(6)	Mo(5)–O(2)	2.065(4)	2.060(7)
Mo(2)–O(6)#1	2.173(3)	2.185(6)	Mo(5)–O(14)	2.146(3)	2.158(7)
Mo(2)–O(19)	2.299(3)	2.313(7)	Mo(5)–O(11)	2.212(4)	2.184(6)
Mo(3)–O(16)	1.728(4)	1.719(7)	Y(1)–OW3	2.311(4)	2.351(6)
Mo(3)–O(18)	1.741(3)	1.752(7)	Y(1)–OW4	2.317(4)	2.342(7)
Mo(3)–O(2)	1.823(4)	1.848(7)	Y(1)–O(9)#1	2.349(4)	2.317(7)
Mo(3)–O(17)#1	2.007(4)	1.981(7)	Y(1)–OW1	2.349(4)	2.370(8)
Mo(3)–O(11)	2.176(3)	2.154(6)	Y(1)–O(18)	2.354(3)	2.354(7)
Mo(3)–O(3)	2.311(3)	2.293(7)	Y(1)–OW2	2.372(4)	2.360(7)
Mo(4)–O(7)	1.688(4)	1.681(6)	Y(1)–OW5	2.401(4)	2.363(7)
Mo(4)–O(8)	1.934(3)	1.949(7)	Y(1)–O(12)#1	2.419(3)	2.450(7)
O(5)–Mo(1)–O(12)	101.83(16)	103.0(3)	O(7)–Mo(4)–O(15)	92.94(16)	93.4(3)
O(5)–Mo(1)–O(6)	105.08(16)	106.5(3)	O(8)–Mo(4)–O(15)	88.52(14)	89.8(3)
O(12)–Mo(1)–O(6)	101.73(15)	102.1(3)	O(8)–Mo(4)–O(13)	162.66(15)	160.9(3)
O(5)–Mo(1)–O(11)	105.76(16)	105.4(3)	O(8)–Mo(4)–O(6)#1	86.40(14)	85.3(3)
O(12)–Mo(1)–O(11)	101.39(15)	101.9(3)	O(4)–Mo(4)–O(6)#1	88.00(14)	88.3(2)
O(6)–Mo(1)–O(11)	136.29(14)	134.2(3)	O(15)–Mo(4)–O(6)#1	73.06(13)	73.1(2)
O(12)–Mo(1)–O(17)#1	165.83(13)	166.3(3)	O(10)–Mo(5)–O(4)	105.90(16)	106.4(3)
O(1)–Mo(2)–O(9)	104.41(17)	104.5(3)	O(10)–Mo(5)–O(8)	104.19(17)	104.8(3)
O(1)–Mo(2)–O(15)	102.51(17)	104.1(3)	O(4)–Mo(5)–O(8)	93.91(14)	94.1(3)
O(9)–Mo(2)–O(15)	100.82(16)	101.0(3)	O(10)–Mo(5)–O(2)	92.81(17)	93.6(3)
O(1)–Mo(2)–O(17)	99.34(16)	98.1(3)	O(4)–Mo(5)–O(2)	89.28(14)	88.0(3)
O(9)–Mo(2)–O(17)	94.19(15)	94.0(3)	O(4)–Mo(5)–O(14)	163.13(15)	164.9(3)
O(9)–Mo(2)–O(6)#1	97.03(15)	97.6(3)	O(4)–Mo(5)–O(11)	87.30(14)	87.8(3)
O(15)–Mo(2)–O(6)#1	79.01(14)	78.4(3)	O(8)–Mo(5)–O(11)	88.66(14)	86.9(3)
O(17)–Mo(2)–O(6)#1	72.71(13)	72.7(3)	O(2)–Mo(5)–O(11)	72.84(14)	73.3(3)
O(9)–Mo(2)–O(19)	170.43(15)	170.3(3)	OW3–Y(1)–OW4	120.37(13)	116.5(2)
O(16)–Mo(3)–O(2)	102.48(17)	102.0(3)	OW3–Y(1)–OW1	139.69(13)	139.9(2)
O(16)–Mo(3)–O(17)#1	100.14(16)	100.1(3)	O(9)#1–Y(1)–O(18)	70.02(13)	69.1(2)
O(2)–Mo(3)–O(11)	78.39(15)	78.2(3)	OW1–Y(1)–O(18)	74.57(12)	72.3(3)
O(17)#1–Mo(3)–O(11)	72.69(13)	73.3(3)	OW3–Y(1)–OW2	76.79(13)	75.8(2)
O(16)–Mo(3)–O(3)	83.79(14)	82.3(3)	OW4–Y(1)–OW2	136.33(13)	143.5(3)
O(18)–Mo(3)–O(3)	168.74(15)	171.6(3)	O(9)#1–Y(1)–OW2	76.86(12)	71.4(2)
O(2)–Mo(3)–O(3)	82.73(14)	82.5(3)	OW1–Y(1)–OW2	69.15(13)	72.2(3)
O(17)#1–Mo(3)–O(3)	79.04(13)	79.6(3)	O(18)–Y(1)–OW2	113.62(13)	112.3(2)
O(11)–Mo(3)–O(3)	73.93(12)	75.1(2)	OW4–Y(1)–OW5	71.51(13)	74.1(2)
O(7)–Mo(4)–O(8)	106.51(16)	106.4(3)	O(9)#1–Y(1)–OW5	143.51(13)	144.3(2)
O(7)–Mo(4)–O(4)	104.60(17)	103.9(3)	OW2–Y(1)–OW5	78.50(14)	77.1(3)
O(8)–Mo(4)–O(4)	94.00(15)	92.7(3)	OW2–Y(1)–O(12)#1	146.76(13)	141.6(2)

Symmetry transformations used to generate equivalent atoms: **1a** #1 $-x + 1/2, -y + 1/2, -z$; **1b** #1 $-x + 2, -y, -z + 1$.

atoms are weakened and the Mo–O bonds are slightly stretched (Mo–O distances between 1.73–1.78 Å) if comparing the distances with the other Mo=O bonds of the anion (Mo–O distances between 1.68–1.73 Å).

As well as the giant wheel anions like {Mo₁₅₄}, {Mo₁₇₆} and their derivatives,¹⁴ many smaller polyoxomolybdates, such as the well-known Anderson structures¹⁵ [H_mXMo₆O₂₄]ⁿ⁻, the pentamolybdates [(RX)₂Mo₅O₂₁]⁴⁻ (X = P, As)¹⁶ and some octamolybdates,⁸ also have ring-like structures. But no decamolybdate having such ring-like structures has been reported so far. Special attention is now focused on one type of structure, [X₂Mo₆O₂₄]⁴⁻ (**2**), which is a hexamolybdoarsenate when X is an RAs group¹⁷ or the so-called α-octamolybdate when X is Mo=O.¹⁸ In these compounds, six MoO₆ octahedra share edges with adjacent ones to form a ring. Two XO₃ tetrahedra lie above and below the ring plane and cover the central hole of the ring, in similar positions to the Y ions in compound **1**. The structures of these anions are similar to that of compound **1**, but there are still some differences between them besides the number of component polyhedra: (1) all the Mo centers in anion **2** are of charge +6 and have two *cis* unshared oxygen atoms each, while four Mo centers of compound **1** are of charge +5 and have only

one terminal oxygen atom each; (2) all the ring components in anion **2** are MoO₆ octahedra while two of those in compound **1** are MoO₅ pyramids; (3) all the Mo centers of [X₂Mo₆O₂₄]⁴⁻ are the same, so the anion has a C_{3v} symmetry, but the five Mo centers in one unsymmetric unit of compound **1** have entirely different environments.

In conclusion, the resultant decamolybdate anion from the reduction of heptamolybdate shows a novel ring-like structure that has not been reported previously. This structure shows some similarity to hexamolybdoarsenate and α-octamolybdate reported before. The addition of Y cations possibly helps the formation of the polyanion. Further study on the reduced solution of molybdate in the presence of rare earth cations and organic acid is still in progress.

Experimental

Preparation of complex **1**

0.20 g (1.5 mmol) N₂H₄·H₂SO₄ was added to a solution of 1.36 g (1.08 mmol) (NH₄)₆Mo₇O₂₄·4H₂O and 3.00 g (39.0 mmol) CH₃COONH₄ in 60 ml (3.3 mol) water and stirred for

Table 2 Crystal data and refinement of complex **1**

	Crystal 1a	Crystal 1b
Formula	C ₈ H ₇₂ Mo ₁₀ N ₂ O ₆₄ Y ₂	C ₈ H ₇₂ Mo ₁₀ N ₂ O ₆₄ Y ₂
<i>M</i>	2361.88	2361.88
<i>T</i> /K	173	173
Crystal system	Monoclinic	Monoclinic
Space group	<i>C2/c</i>	<i>P2₁/c</i>
<i>a</i> /Å	24.345(5)	10.950(2)
<i>b</i> /Å	16.580(3)	22.521(5)
<i>c</i> /Å	15.355(3)	13.043(3)
β /°	101.16(3)	114.79(3)
<i>V</i> /Å ³	6081(2)	2921(1)
<i>Z</i>	4	2
μ /mm ⁻¹	4.005	4.168
No. of reflections collected/unique	25845/6943	12088/6587
<i>R</i> _{int}	0.050	0.061
Data/restraints/parameters	6943/0/420	6587/0/388
Final <i>R</i> indices [<i>I</i> > 2σ(<i>I</i>)]	<i>R</i> 1 = 0.035, <i>wR</i> 2 = 0.0772	<i>R</i> 1 = 0.061, <i>wR</i> 2 = 0.1377
<i>R</i> indices (all data)	<i>R</i> 1 = 0.055, <i>wR</i> 2 = 0.0816	<i>R</i> 1 = 0.103, <i>wR</i> 2 = 0.1511

10 minutes while the color changed from colorless to blue. 2.00 ml concentrated hydrochloric acid and 1.50 g YCl₃·xH₂O were introduced into the solution. The mixture was allowed to stand for one day and a brown solid precipitated from the blue solution. After filtration, the solution was left to stand for one week to give two types of red crystal, chip-like ones and needle-like ones, together with a little brown precipitate. The crystals were separated from the precipitate and washed with water and ethanol and dried in air. It was difficult to separate these two kinds of crystals. The entire yield was 0.93 g, 51% based on Mo. Found in **1a**: C, 4.1; H, 3.0; Mo, 40.4; N, 1.1; Y, 7.5%; Found in **1b**: C, 4.0; H, 2.9; Mo, 40.3; N, 1.2; Y, 7.4%. Calc. for C₈H₇₂Mo₁₀N₂O₆₄Y₂: C, 4.1; H, 3.0; Mo, 40.6; N, 1.2; Y, 7.5%.

Crystal structure determination

The crystallographic measurement was made on a Rigaku R-Axis RAPID image plate diffractometer with graphite monochromated Mo-Kα radiation ($\lambda = 0.71073$ Å). An absorption correction was applied as correction of the symmetry-equivalent reflections using the ABSCOR program.¹⁹ The structure was solved by direct methods and successive difference maps (SHELXS 97)²⁰ and refined by full-matrix least squares on *F*² using all unique data (SHELXL 97).²¹ The non-hydrogen atoms were refined anisotropically. The hydrogen atoms were included in their calculated positions with geometrical constraints and refined in the riding model. Selected bond distances and angles are presented in Table 1. Crystal data and the structure refinement are presented in Table 2.

In this experiment, like in some other experiments,²² NH₄⁺ and H₂O could not be distinguished in the crystal lattice according to the observed electron densities, all the positions of NH₄⁺ and H₂O were named O. Since the elemental analysis shows the presence of two NH₄⁺ cations per every one polyanion, one ninth of the so-called "O" positions are actually occupied by NH₄⁺ cations.

CCDC reference number 166172 for crystal **1a** and 166173 for crystal **1b**.

See <http://www.rsc.org/suppdata/dt/b1/b108997h/> for crystallographic data in CIF or other electronic format.

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