

# Hydrothermal synthesis and structure determination of a novel hexagonal ammonium molybdenum bronze, $\text{NH}_4\text{Mo}_6\text{O}_{18}$

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## Abstract

A new ammonium molybdenum bronze  $\text{NH}_4\text{Mo}_6\text{O}_{18}$  was synthesized by a hydrothermal method. Interesting features include the different location of the ammonium ions and the existence of lower-valence molybdenum atoms. © 1999 Elsevier Science S.A. All rights reserved.

**Keywords:** Hydrothermal methods; Hydroxylamine hydrochloride reduction; Hexagonal  $\text{MoO}_3$ ; Molybdenum bronze

In recent years, a series of transition metal (molybdenum, vanadium, cobalt and tin) phosphates and arsenates [1–6] with two-dimensional layered, three-dimensional open framework structures have been prepared under hydrothermal reactions. There are also some reports about the synthesis of non-reduced and reduced vanadium oxides [7–11]. All these compounds are distinctive for their structural diversity and technological importance. However, in contrast to the rich field of vanadium oxides, there have only been a few reports on the synthesis of molybdenum oxides by hydrothermal methods [12,13]. Moreover, all the molybdenum atoms in these structures are in the +6 oxidation state. In attempts to synthesize reduced molybdenum oxides by a hydrothermal method, we used hydroxylamine hydrochloride as the reducing agent. Hydroxylamine hydrochloride is used extensively in organic synthesis [14]. There are also reports that it is used to synthesize inorganic oxometalate clusters [15] and transition metal oxide particles [16]. Here we report the synthesis and the structure of  $\text{NH}_4\text{Mo}_6\text{O}_{18}$  prepared by a hydrothermal-reduction method. The compound is the first hexagonal molybdenum bronze synthesized by a hydrothermal method.

A mixture of  $\text{Na}_2\text{MoO}_4 \cdot 2\text{H}_2\text{O}$  (0.70 g),  $\text{NH}_2\text{OH} \cdot \text{HCl}$  (0.65 g),  $\text{H}_2\text{O}$  (10 ml) and hydrochloric acid (2 mol/l, 0.20 ml) was sealed in a 25 ml digestion bomb and heated at 170°C for 4 days. Blue hexagonal rod-shaped crystals (0.6 g) were isolated from the dark-blue solution after filtering, washing with water and air-drying. Single crystals were used

Table 1  
Atomic coordinates for  $\text{NH}_4\text{Mo}_6\text{O}_{18}$

Atom	x	y	z
Mo(1)	-0.1046(1)	-0.4593(1)	0.2500
O(1)	-0.2161(5)	-0.7172(5)	0.2500
O(2)	0.0792(5)	-0.5005(5)	0.2500
O(3)	-0.0091(6)	-0.2743(5)	0.2500
N(1)	0	0	0.1050(12)

for elemental analysis, TGA, FT-IR<sup>1</sup> and X-ray diffraction<sup>2</sup>. Atomic coordinates are given in Table 1, and bond lengths and angles in Table 2.

Single crystal diffraction gives the formula as  $\text{NH}_4\text{Mo}_6\text{O}_{18}$  and this is confirmed by chemical analysis. The compound has the same 3D framework as that of hexagonal  $\text{MoO}_3$  while the ammonium ions reside in the tunnels (Fig. 1). All the Mo atoms in the structure of  $\text{NH}_4\text{Mo}_6\text{O}_{18}$  are octahedrally coordinated by six oxygen atoms. Each octahedron is connected

<sup>1</sup> Elemental analysis: Calc. for  $\text{NH}_4\text{Mo}_6\text{O}_{18}$ : Mo, 65.29; N, 1.59. Found: Mo, 65.8; N, 1.54%. Main IR bands (KBr disc): 3475, 1626, 1401, 975, 911, 606, 525.

<sup>2</sup> Crystal data for  $\text{NH}_4\text{Mo}_6\text{O}_{18}$ :  $M = 881.68$ , space group  $P6_3/m$ ,  $a = 10.5760(10)$ ,  $b = 10.5760(10)$ ,  $c = 3.7280(10)$  Å,  $V = 361.12(11)$  Å<sup>3</sup>,  $F(000) = 407$ ,  $D_c = 4.036$  g cm<sup>-3</sup>, Mo-K $\alpha$  radiation,  $\lambda = 0.71069$  Å. Intensity data were collected on a Rigaku AFC6S diffractometer at 296 K and a total of 459 reflections were collected, of which 401 reflections were unique, the structure was solved with direct method and difference Fourier map using SHELXS97 and refined using SHELXL97. Final  $R1 = 0.0336$ ,  $wR2 = 0.0935$  for all data with 30 parameters and zero restraints,  $GOF = 1.235$ ; max (min) in final difference map = 1.652(-1.426) e Å<sup>-3</sup>.

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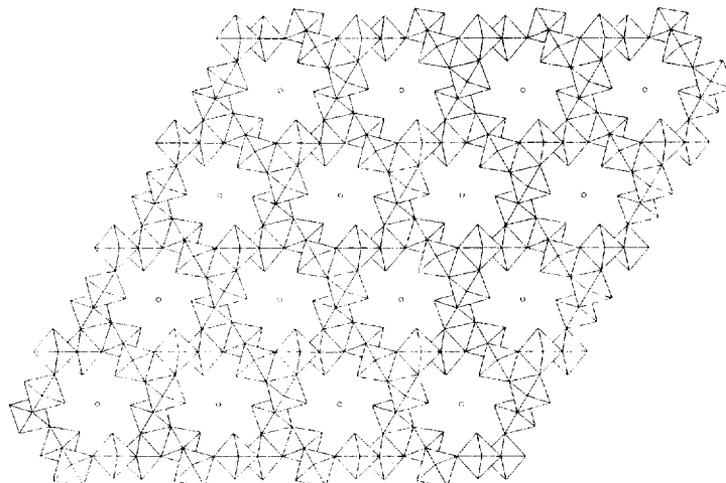
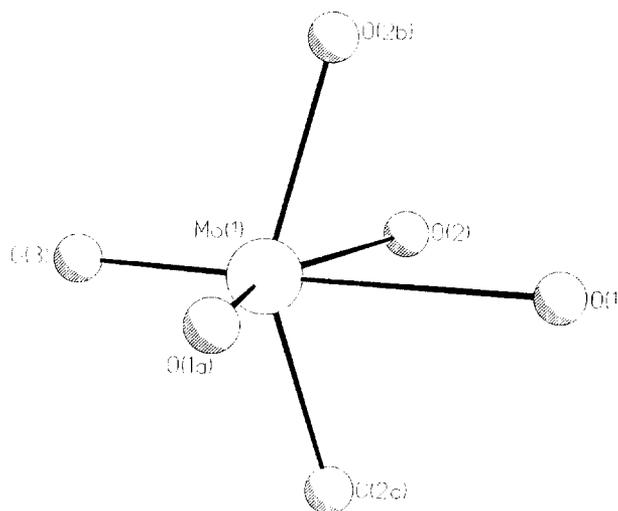
Fig. 1. Structure of  $\text{NH}_4\text{Mo}_6\text{O}_{18}$ .

Table 2

Bond lengths (Å) and bond angles (°) of  $\text{NH}_4\text{Mo}_6\text{O}_{18}$ 

Mo(1)–O(3)	1.695(5)	Mo(1)–O(2)	2.194(4)
Mo(1)–O(1)	2.368(5)	Mo(1)–O(2a)	1.9597(15)
Mo(1)–O(1a)	1.715(4)	Mo(1)–O(2b)	1.9597(15)
O(3)–Mo(1)–O(1a)	103.3	O(1a)–Mo(1)–O(2)	157.9
O(3)–Mo(1)–O(2a)	100.55	O(2a)–Mo(1)–O(2)	74.12
O(1a)–Mo(1)–O(2a)	101.52	O(2b)–Mo(1)–O(2)	74.12
O(3)–Mo(1)–O(2b)	100.55	O(3)–Mo(1)–O(1)	174.5
O(1a)–Mo(1)–O(2b)	101.52	O(1a)–Mo(1)–O(1)	82.2
O(2a)–Mo(1)–O(2b)	144.0	O(2a)–Mo(1)–O(1)	78.11
O(3)–Mo(1)–O(2)	98.8	O(2b)–Mo(1)–O(1)	78.11
O(2)–Mo(1)–O(1)	75.66		

Fig. 2. The oxygen coordination in  $\text{MoO}_6$  octahedron.

with another two octahedrons through edge-sharing and another two octahedrons through corner-sharing. In fact, the three corner-sharing  $\text{MoO}_6$  octahedrons can be viewed as the basic building unit. Neighboring units are connected through edge-sharing. The  $\text{MoO}_6$  octahedron is strongly distorted (Fig. 2). The Mo–O lengths to the corner-sharing oxygen O(1), O(1a), edge-sharing oxygen O(2), O(2a), O(2b) and terminal O(3) are 2.368, 1.715, 2.194, 1.9597, 1.9597, 1.695 Å, respectively.

The structure of hexagonal  $\text{MoO}_3$  was determined by Darriet and Galy [17] for  $\text{K}_{0.13}\text{V}_{0.13}\text{Mo}_{0.87}\text{O}_3$  and by Krebs and Paulat-Boschen [18] for  $\text{KH}_5\text{Mo}_5\text{O}_{18}$ . These two compounds represent two kinds of structure of hexagonal  $\text{MoO}_3$ : with and without vanadium atoms. The vanadium stabilized forms have a general composition  $\text{A}_{0.13}\text{V}_{0.13}\text{Mo}_{0.87}\text{O}_3 \cdot n\text{H}_2\text{O}$ . There are no vacancies in the framework and the vanadium atoms in the framework are charge-compensated by the A ions located in the tunnels. The same structure synthesized by other methods has also been reported [19,20]. The second kind of structure (without the vanadium atoms) or the pure molybdate forms have vacancies in the framework. Apart from  $\text{KH}_5\text{Mo}_5\text{O}_{18}$ , other similar structures have been reported:  $(\text{Na} \cdot 2\text{H}_2\text{O})(\text{H}_{4.5})_{0.67}\text{Mo}_{5.33}\text{O}_{18}$  [21];  $(\text{A} \cdot z\text{H}_2\text{O})\text{Mo}_{6-x}\text{O}_{18-x}(\text{H})_{4x-y}$  ( $\text{A} = \text{Na}, \text{NH}_4, \text{Ag}, \text{H}_3\text{O}$ ) [22].

Compared with all these structures, there are three important differences in the structure of  $\text{NH}_4\text{Mo}_6\text{O}_{18}$ . First, there are no molybdenum vacancies or vanadium atoms in the framework. Krebs and Paulat-Boschen [18] reported that in  $\text{KH}_5\text{Mo}_5\text{O}_{18}$  there was one Mo vacancy per unit cell while in  $(\text{Na} \cdot 2\text{H}_2\text{O})(\text{H}_{4.5})_{0.67}\text{Mo}_{5.33}\text{O}_{18}$  McCarron et al. [21] reported that there are two molybdenum vacancies for every three unit cells. Secondly, the position of the ammonium ion is different from that of  $\text{Na}^+$  or  $\text{K}^+$ . The position of  $\text{K}^+$  [18] and  $\text{Na}^+$  [21] is (0, 0, 0) and (0, 0, 0.25), respectively. Guo et al. [22] reported that the cations are disordered along the tunnels based on the powder diffraction data. But we find that the ammonium ion resides at (0, 0, 0.1050); the probable reason is that at this position the H atoms of the  $\text{NH}_4^+$  cation can form stronger hydrogen bonding interactions with the terminal oxygen atoms of the framework.

The third important difference is that there are lower-valence molybdenum atoms in the framework. From the formula, the average oxidation state of the molybdenum atoms is 5.83. Bond valence sum calculation [23] gives the result

as 5.81. The existence of molybdenum atoms in a lower oxidation state is obvious from the blue color of the crystals. Also worthy of mention is that  $\text{NH}_4\text{Mo}_6\text{O}_{18}$  is the first ammonium molybdenum bronze compound based on the hexagonal  $\text{MoO}_3$  structure. Its structure is different from most of the molybdenum bronzes already known. Molybdenum oxide bronzes have been the focus of research for many years due to their interesting structural and physical properties [24]. Usually they are prepared through high-temperature reaction, electrochemical reduction, chemical intercalation and ion exchange. There are also other reports adopting the reduction-crystallization method [16,25]. Most of their structures are layered and have the structural feature of  $\alpha\text{-MoO}_3$  or  $\beta\text{-MoO}_3$ . Only in recent years have there been reports that hexagonal  $\text{Li}_x\text{H}_y\text{MoO}_3$  [21] or  $\text{Li}_x\text{H}_y\text{V}_{0.13}\text{Mo}_{0.87}\text{O}_{2.935}$  [26] could be synthesized by the intercalation method and that H or Li could be inserted into the hexagonal  $\text{MoO}_3$  structure. However, single crystals have not been obtained and details about their structures have not been reported. So, to the best of our knowledge,  $\text{NH}_4\text{Mo}_6\text{O}_{18}$  is the first example of a hexagonal molybdenum bronze synthesized by a hydrothermal method.

In summary, a new ammonium molybdenum bronze has been synthesized by a hydrothermal-reduction method. Single crystals were obtained and the structure was determined. This method could open up a new route to the synthesis of other reduced transition metal oxides.

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