

Fig. 1. Projection along the  $c$  axis showing the atomic arrangement of  $\text{Ca}_2(\text{NH}_4)_2\text{P}_6\text{O}_{18}\cdot 6\text{H}_2\text{O}$ . The H atoms have been omitted for clarity.

$c/2$ . These rows are interconnected by the second ammonium polyhedron, the  $\text{CaO}_7$  polyhedra and the hydrogen bonds to form a three-dimensional network whose main geometrical features are reported in Table 2.

The program *STRUPLO* (Fischer, 1985) was used to prepare Fig. 1.

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## $(\text{NH}_4)\text{Mo}_3\text{O}_9$ , an Ammonium Molybdenum Bronze

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**Abstract.** Ammonium trimolybdate(V,2VI),  $M_r = 449.85$ , monoclinic,  $C2/m$ ,  $a = 14.819(4)$ ,  $b = 7.708(1)$ ,  $c = 6.386(2)$  Å,  $\beta = 93.56(3)^\circ$ ,  $V = 728.0$  Å<sup>3</sup>,  $Z = 4$ ,  $D_x = 4.10$  Mg m<sup>-3</sup>,  $\lambda(\text{Mo } K\alpha) = 0.71073$  Å,  $\mu = 5.0$  mm<sup>-1</sup>,  $F(000) = 836$ ,  $T = 296$  K. The structure was refined to  $R = 0.074$  for 882 absorption-corrected reflections. The bronze, prepared by hydrothermal decomposition of ammonium heptamolybdate, contains units of six edge-shared  $\text{MoO}_6$  octahedra [ $\text{Mo}(1)\text{—O} = 1.67\text{--}2.29$ ,  $\text{Mo}(2)\text{—O} = 1.68\text{--}2.38$  Å] which share vertices along  $[010]$  and  $[001]$  to form infinite layers. The ammonium ions completely occupy positions with an irregular eight-fold coordination ( $\text{N—O} = 2.74\text{--}3.14$  Å) between the layers.

**Introduction.**  $\text{NH}_3$  is a mild reducing agent for transition metal–oxygen compounds. This has been

demonstrated in a detailed study of the closed-system thermal decomposition of  $\text{NH}_4\text{VO}_3$  (Range & Zintl, 1983; Range, Zintl & Heyns, 1988) and  $(\text{NH}_4)_2\text{V}_6\text{O}_{16}$  (Range, Eglmeier, Heyns & De Waal, 1990). Redox reactions can also occur in the system  $\text{NH}_3\text{—MoO}_3\text{—H}_2\text{O}$ . The present paper describes the hydrothermal synthesis and structure refinement of a new ammonium molybdenum bronze,  $(\text{NH}_4)\text{Mo}_3\text{O}_9$ .

**Experimental.**  $(\text{NH}_4)\text{Mo}_3\text{O}_9$  was prepared by hydrothermal decomposition of ammonium heptamolybdate,  $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24}\cdot 2\text{H}_2\text{O}$  (silver ampoule, 500 bar, 625 K, 72 h, heating rate 5 K min<sup>-1</sup>, cooling rate 0.5 K min<sup>-1</sup>). The reaction product consisted of a mixture of black needles ( $\text{MoO}_2$ , main product) and bronze-coloured crystals with nearly rectangular shape. Chemical analysis of selected bronze-coloured crystals ( $\text{NH}_4$  found: 3.98, 4.12%; calculated: 4.01%) and EDX (only Mo, no Ag found) pointed to the stoichiometry  $(\text{NH}_4)\text{Mo}_3\text{O}_9$ .

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Table 1. Atomic coordinates and equivalent isotropic displacement parameters ( $\text{\AA}^2 \times 10^4$ )

$U_{eq}$  is defined as one third of the trace of the orthogonalized  $U_{ij}$  tensor. Starred atoms have been refined isotropically.

	x	y	z	$U_{eq}/U_{iso}$
Mo(1)	0.05781 (6)	0.2613 (1)	0.2702 (1)	75 (1)
Mo(2)	0.1178 (1)	0	0.6444 (2)	91 (3)
O(1)	0	0.258 (2)	0	90 (30)
O(2)	0.0805 (4)	0.237 (1)	0.5916 (9)	100 (10)*
O(3)	0.1666 (4)	0.259 (1)	0.214 (1)	140 (10)
O(4)	0.0386 (7)	0	0.309 (2)	50 (30)
O(5)	0.2183 (8)	0	0.529 (2)	140 (30)
O(6)	0.1454 (8)	0	0.904 (2)	160 (30)
O(7)	0.5385 (8)	0	0.296 (2)	130 (30)*
N	0.3149 (9)	0	0.177 (2)	150 (40)

Table 2. Selected interatomic distances ( $\text{\AA}$ )

Mo(1)—O(3)	1.674 (6)	Mo(2)—O(6)	1.682 (13)
—O(7)	1.871 (2)	—O(5)	1.702 (11)
—O(1)	1.878 (1)	—O(2)	1.932 (7) (2 ×)
—O(4)	2.051 (2)	—O(4)	2.355 (10)
—O(2)	2.068 (6)	—O(4)	2.378 (12)
—O(2)	2.289 (6)	<Mo(2)—O>	1.997
<Mo(1)—O>	1.972		
N—O(5)	2.739 (18)		
—O(2)	2.900 (11) (2 ×)		
—O(6)	2.967 (17)		
—O(3)	2.988 (11) (2 ×)		
—O(3)	3.138 (12) (2 ×)		
<N—O>	2.970		

which was finally confirmed by the structure refinement.

A crystal fragment (approximate dimensions  $0.015 \times 0.075 \times 0.075$  mm) was used for data collection on an Enraf-Nonius CAD-4 diffractometer (Mo  $K\alpha$ ,  $\lambda = 0.71073$  Å, graphite monochromator in incident beam,  $T = 296$  K). Lattice parameters were refined from  $2\theta$  values of 25 reflections in the range  $5.2 \leq \theta \leq 10.4^\circ$ . Intensities measured for  $2 \leq \theta \leq 35^\circ$ ;  $\omega$ -scan technique, scan width  $(2.0 + 0.4 \tan \theta)^\circ$ . Three standard reflections showed only small random fluctuations and indicated no loss of intensity throughout the data collection. Merging of the 2423 collected intensities ( $\sin \theta_{\max}/\lambda = 0.81 \text{ \AA}^{-1}$ ;  $-23 \leq h \leq 23$ ,  $-3 \leq k \leq 12$ ,  $0 \leq l \leq 10$ ) gave 1705 unique reflections, of which 882 with  $I > 0.8\sigma(I)$  were considered observed ( $R_{\text{int}} = 0.038$ ) and used for all calculations (program system *SDP* 3.1; Enraf-Nonius, 1988).

The structure was solved by routine direct methods, followed by successive difference Fourier syntheses. In the least-squares refinement  $|F|$  magnitudes were used to refine an overall scale factor, positional parameters, occupation factors and temperature factors of the non-hydrogen atoms, and an extinction factor. Convergence was obtained after a few cycles with s.o.f.'s for Mo, N and O corresponding to the stoichiometry  $(\text{NH}_4)\text{Mo}_3\text{O}_9$  within two standard deviations. Full occupancy of the nitrogen

position should especially be noted. Consequently, the s.o.f.'s were fixed again at 100% before performing a numerical correction for absorption (program *DIFABS*; Walker & Stuart, 1983). Transmission factors min. 0.66, max. 1.0. In the final refinement only Mo, N, O(1) and O(3)—O(6) could be refined anisotropically, O(2) and O(7) had to be refined isotropically. This behaviour, as well as the rather high value of  $R$  compared to  $wR$ , was obviously caused by insufficient absorption correction. Final  $R = 0.074$ ,  $wR = 0.041$  (including all reflections).  $w = k/\sigma^2(F)$ ,  $(\Delta/\sigma)_{\max} < 0.001$  in final refinement cycle, 61 variables,  $S = 0.98$ . Max. features in the final  $\Delta\rho$  map  $+1.7$ ,  $-2.1 \text{ e \AA}^{-3}$ . Atomic scattering factors and  $f'$ ,  $f''$  values were set by the *SDP* program. Bond distances and angles were calculated using the program *SADIAN* (Baur & Wenninger, 1969). Final atomic coordinates and equivalent isotropic displacement parameters are given in Table 1, derived bond distances in Table 2.\*

**Discussion.**  $(\text{NH}_4)\text{Mo}_3\text{O}_9$  is the first well characterized ammonium molybdenum bronze. It is basically isostructural with monoclinic red  $\text{K}_{1-x}\text{Mo}_3\text{O}_9$  (Stephenson & Wadsley, 1965). The structure comprises distorted  $\text{MoO}_6$  octahedra [ $\text{Mo}(1)\text{—O} = 1.67\text{—}2.29$ ,  $\text{Mo}(2)\text{—O} = 1.68\text{—}2.38$  Å] which are edge-shared to form six-octahedra units (Fig. 1a). These units share vertices along [010] and [001], thus creating infinite layers (Fig. 1b). The ammonium ions are situated between these layers and exhibit an irregular eightfold coordination ( $\text{N—O} = 2.74\text{—}3.14$  Å).

The size of the shared  $\text{MoO}_6$  octahedra determines the dimensions of the unit cell along [010] and [001].

\* Lists of structure factors and anisotropic parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 53068 (21 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

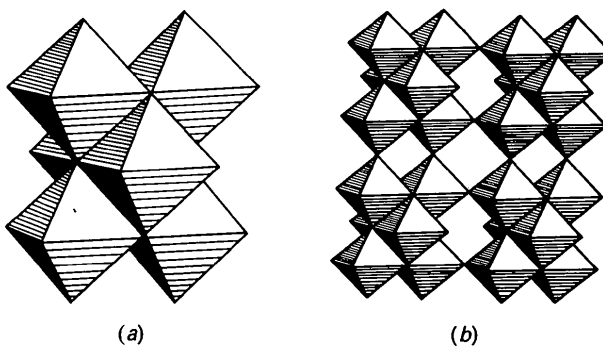


Fig. 1. (a) The unit of six  $\text{MoO}_6$  octahedra in  $(\text{NH}_4)\text{Mo}_3\text{O}_9$ . (b) Infinite layers formed by vertex sharing of the units shown in (a).

The lengths of the  $b$  and  $c$  axes in  $(\text{NH}_4)\text{Mo}_3\text{O}_9$  and  $\text{K}_{1-x}\text{Mo}_3\text{O}_9$  are therefore nearly identical. On the other hand, the difference in the radii of  $\text{NH}_4^+$  and  $\text{K}^+$  causes an increase of the  $a$  axis by  $0.54 \text{ \AA}$  in going from  $\text{K}_{1-x}\text{Mo}_3\text{O}_9$  to  $(\text{NH}_4)\text{Mo}_3\text{O}_9$ .

Assuming oxidation numbers of  $-3$  for N,  $+1$  for H, and  $-2$  for O, a mean oxidation number of  $+5.66$  can be calculated for Mo, *i.e.* the formula unit contains two  $\text{Mo}^{6+}$  and one  $\text{Mo}^{5+}$ . Keeping in mind the stoichiometric ratio of Mo(1) and Mo(2) as well as the different mean bond lengths Mo(1)—O ( $1.972 \text{ \AA}$ ) and Mo(2)—O ( $1.997 \text{ \AA}$ ) which are in agreement with the difference in the effective ionic radii for  $\text{Mo}^{6+}$  ( $0.59 \text{ \AA}$ ) and  $\text{Mo}^{5+}$  ( $0.61 \text{ \AA}$ ), both in octahedral coordination (Shannon, 1976), the chemical formula of the new ammonium molybdenum bronze may be written as  $(\text{NH}_4)\text{Mo}(\text{1})_2^{\text{6+}}\text{Mo}(\text{2})^{\text{5+}}\text{O}_9$ .

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## Structure of a Molybdenum(V) Phosphate $\beta\text{-KMo}_2\text{P}_3\text{O}_{13}$

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**Abstract.** Dimolybdenum potassium triphosphate,  $M_r = 531.90$ , monoclinic,  $P2_1/c$ ,  $a = 9.701(3)$ ,  $b = 18.848(2)$ ,  $c = 6.389(5) \text{ \AA}$ ,  $\beta = 106.96(3)^\circ$ ,  $V = 1117(2) \text{ \AA}^3$ ,  $Z = 4$ ,  $D_m$  not measured,  $D_x = 3.16 \text{ Mg m}^{-3}$ ,  $\lambda(\text{Mo } K\alpha) = 0.71073 \text{ \AA}$ ,  $\mu = 3.05 \text{ mm}^{-1}$ ,  $F(000) = 252$ ,  $T = 293 \text{ K}$ , 2624 reflections,  $R = 0.026$ ,  $wR = 0.025$ . The lattice is built up of  $\text{MoO}_6$ ,  $\text{PO}_4$  and  $\text{P}_2\text{O}_7$  groups delimiting tunnels where the  $\text{K}^+$  ions lie. The framework is more symmetrical than those of the Rb or Cs compounds.

**Introduction.** The  $A\text{-Mo-P-O}$  ( $A = \text{alkaline ions}$ ) system contains a very large number of compounds with molybdenum in oxidation states less than VI showing the great ability of the  $\text{PO}_4$  tetrahedra to form various frameworks with  $\text{MoO}_6$  octahedra.

The investigation, by several authors of the  $A\text{-Mo}^v\text{-P-O}$  system has shown the formation of  $\text{K}_4\text{Mo}_8\text{P}_{12}\text{O}_{52}$  (or  $\alpha\text{-KMo}_2\text{P}_3\text{O}_{13}$ ) (Leclaire, Monier & Raveau, 1983),  $\alpha$ - and  $\beta\text{-CsMo}_2\text{P}_3\text{O}_{13}$  (Lii & Haushalter, 1987),  $\beta\text{-RbMo}_2\text{P}_3\text{O}_{13}$  (Riou & Goreaud, 1989),  $\gamma\text{-CsMo}_2\text{P}_3\text{O}_{13}$  (Chen, Lii & Wang, 1988),  $\delta\text{-KMo}_2\text{P}_3\text{O}_{13}$  (Leclaire, Borel, Grandin & Raveau, 1989) and  $A\text{Mo}_5\text{P}_8\text{O}_{33}$  ( $A = \text{Li, Na, Ag}$ ) (Lii, Johnston, Goshorn & Haushalter, 1987).

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During the investigation of this system we obtained the  $\beta\text{-KMo}_2\text{P}_3\text{O}_{13}$  compound; its cell parameters correspond to those obtained from powder diffraction by Lii & Haushalter (1987) for  $\beta\text{-CsMo}_2\text{P}_3\text{O}_{13}$  but the  $a$  and  $c$  axes are inverted and the space group is  $P2_1/c$  instead of  $P2_1$ . Intrigued by this result we have determined the crystal structure of  $\beta\text{-KMo}_2\text{P}_3\text{O}_{13}$ .

**Experimental.** The preparation was performed in two steps. First,  $(\text{NH}_4)_2\text{HPO}_4$ ,  $\text{K}_2\text{CO}_3$  and  $\text{MoO}_3$  were mixed in an agate mortar in the molecular ratios needed to obtain the composition  $\text{KMo}_{1.67}\text{P}_3\text{O}_{13}$  and heated at 600 K to decompose the ammonium phosphate and the carbonate. The resulting mixture was then added to the required amount of molybdenum and placed in an evacuated silica ampoule. This mixture was heated for several days at 1300 K. Several forms of green crystals were obtained, yellow-green hexagonal prismatic crystals of  $\beta\text{-KMo}_2\text{P}_3\text{O}_{13}$  and emerald green polyhedral crystals of  $\delta\text{-KMo}_2\text{P}_3\text{O}_{13}$  (Leclaire *et al.*, 1989). Yellow-green crystal  $0.168 \times 0.036 \times 0.024 \text{ mm}$ .  $m$  symmetry with systematic absences  $l = 2n + 1$  for  $h0l$  and  $k = 2n + 1$  for  $0k0$ . Space group  $P2_1/c$ . Enraf-Nonius CAD-4