The Crystal Structure of Dipotassium Trimolybdate, $K_2Mo_3O_{10}$; a Compound with Five-co-ordinate Molybdenum(VI)

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As part of a general study of polymolybdates the crystal structure of dipotassium trimolybdate, $K_2Mo_3O_{10}$, has been determined by three-dimensional single-crystal *X*-ray diffraction techniques. It is well known that simple molybdates of type $M^I_2MoO_4$ contain tetrahedral MoO_4 groups, and Lindqvist[1] has reported that the dimolybdate, $Na_2Mo_2O_7$, contains no discrete $Mo_2O_7^{2-}$ unit but has a chain structure built up of MoO_6 octahedra and MoO_4 tetrahedra. We have shown that $K_2Mo_3O_{10}$ also has a chain structure, comprising edge-shared MoO_6 octahedral and MoO_5 square-pyramidal units.

It appears that as the Mo : O ratio changes from

1 : 3, as for example in the potassium molybdenum bronzes[2,3] and MoO_3,[4] through 3 : 10 in the trimolybdate, and 2 : 7 in the dimolybdate, to 1 : 4 in the simple molybdates, the co-ordination of Mo^{VI} ranges from purely octahedral through mixed square-pyramidal and octahedral, mixed tetrahedral and octahedral, to exclusively tetrahedral. This lack of a sharp transition from octahedral to tetrahedral stereochemistry of transition-metal oxides has been discussed by Orgel.[5]

Crystals in the form of white acicular prisms, obtained from a melt produced by the fusion of K_2CO_3 and MoO_3 in the molar ratio 1 : 3, are monoclinic with $a = 13{\cdot}838$, $b = 7{\cdot}900$, $c = 8{\cdot}889$ Å and $\beta = 98{\cdot}94°$, $D_m = 3{\cdot}60$ g. cm.$^{-3}$, for $Z = 4$, $D_c = 3{\cdot}64$ g. cm.$^{-3}$. Systematic absences indicate the space group as either $C2/c$ (C_{2h}^6, No. 15) or Cc(C_s^4, No. 9). The centrosymmetric space group $C2/c$ was chosen on the basis of the distribution of vectors in the Patterson function and confirmed by the refinement which proceeded smoothly. Cu-K_α radiation was used. (Preliminary data recorded by Lindqvist[6] are in agreement with our results.) The structure was solved by three-dimensional Patterson and Fourier techniques; the Mo and K atoms were initially located from the Patterson synthesis and their positions refined by Fourier methods. The oxygen atoms were then located unambiguously by a difference Fourier synthesis ($R = 0{\cdot}17$ for 365 independent reflections) and using anisotropic temperature-factors for the Mo and K atoms, four cycles of least-squares refinement reduced R to 0·10. Continued refinement should lower the residual value still further.

The structure consists of infinite chains of edge-shared MoO_6 octahedra and MoO_5 square-pyramids lying parallel to the needle (c) axis (Figure 1). Adjacent chains have no oxygen atoms in common, being held together by the potassium ions occupying inter-chain positions. The MoO_6 octahedra are distorted with Mo–O distances in the range 1·80—2·27 Å and angles differing considerably from 90° (Figure 2). The square-pyramidal units are similarly distorted, occurring in edge-shared pairs, there being a centre of symmetry midway between the two Mo atoms. The equatorial Mo–O distances vary from 1·71 to 2·11 Å with the Mo atom approximately 0·5 Å out-of-plane towards the apical oxygen, which is 1·62 Å from the central Mo atom, this being the shortest Mo–O distance in the structure. The Mo atoms at the centres of two square-pyramids with a common edge are 3·30 Å apart, and the distance between the Mo atoms at the centre of a square-pyramid and an octahedron (edge-shared) is 2·94 Å.

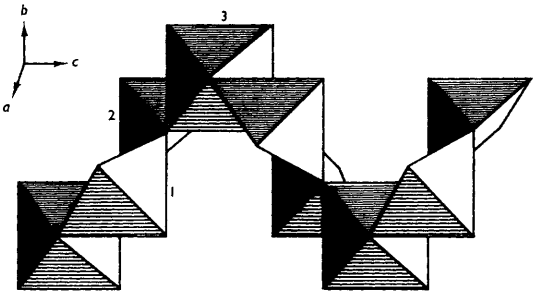

FIGURE 1. *The structure, in idealized form, of the infinite chain of octahedral and square-pyramidal units. 3 octahedron; 1 and 2 square-pyramids.*

This structure is, as far as we are aware, the first case where, with unambiguously located oxygen atoms, five-co-ordinate molybdenum(VI) has been reported in this type of compound.

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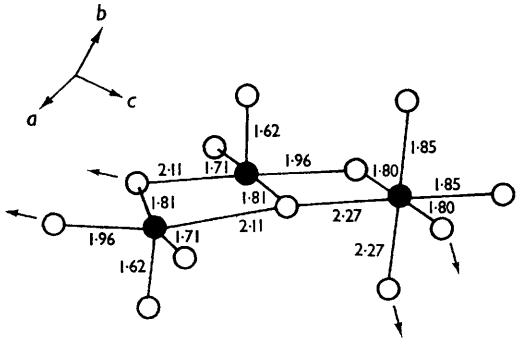

FIGURE 2. *Bond lengths in the octahedral and square-pyramidal units (dimensions in Å). Black circles represent molybdenum, white circles represent oxygen.*

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