The Chain Structure of Potassium Tetramolybdate, $K_2Mo_4O_{13}$

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Summary Potassium tetramolybdate has a chain structure, where the infinite chains of edge-shared MoO_6 octahedra are held together solely by interleaving potassium ions.

IN order to compare the structures adopted by the anhydrous alkali metal tetramolybdates $R^1_2Mo_4O_{13}$ (R = Na, K, Rb, Cs) with the infinite chain structures adopted by the dimolybdate $Na_2Mo_2O_7$[1] and trimolybdates $R^1_2Mo_3O_{10}$ (R = K, Rb, Cs)[2], an *X*-ray investigation has been carried out and we now report the crystal structure of $K_2Mo_4O_{13}$.

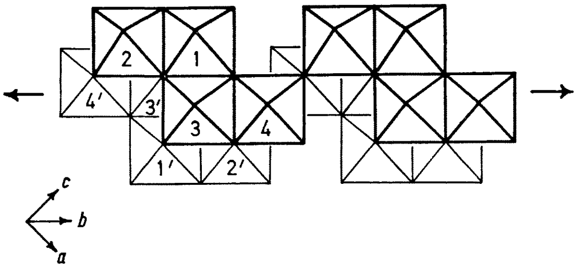

FIGURE. *A view normal to the* b*-axis of part of an infinite chain of idealised* MoO_6 *octahedra where two of the basic units of eight edge-shared octahedra are shown. The octahedra shown by heavy linework all lie at the one level and are edge-shared to the layer of octahedra beneath shown by fainter lines.*

White, tabular crystals of $K_2Mo_4O_{13}$ obtained from a melt produced by the fusion of K_2CO_3 and MoO_3 in the mole ratio 1 : 4, are triclinic, space group $P\bar{1}$, with $a = 7{\cdot}972$, $b = 8{\cdot}352$, $c = 10{\cdot}994$ Å, $\alpha = 119{\cdot}41°$, $\beta = 62{\cdot}70°$, and $\gamma = 109{\cdot}80°$; D_m 3·97, $Z = 2$, D_c 3·95 g cm^{-3}. A total of 1324 independent reflections obtained with a Weissenberg camera using Cu-K_α radiation, and corrected for absorption, were used in the structure determination, which was carried out by the usual three-dimensional Patterson and Fourier methods. Full-matrix least-squares refinement of the structure with individual isotropic temperature factors has reduced the reliability index to a present value of 0·120.

The structure consists of infinite chains built up of edge-shared MoO_6 octahedra running in the prism (*b*) axis direction. As shown in the Figure the four independent MoO_6 octahedra, designated 1, 2, 3, and 4, are linked by common edges (with the central molybdenum atoms almost coplanar) and this group of four octahedra is then joined by edge-sharing to an identical and symmetry related group of four octahedra (designated 1′, 2′, 3′, and 4′). Each basic unit of eight octahedra then links up with identical units through a common edge (across a centre of symmetry between octahedra 4 and 4′) to form the infinite chains; adjacent chains have no common oxygen atoms being held together solely by the potassium ions which occupy irregular eight-co-ordinate interchain positions.

The distortions present in the MoO_6 octahedra result in two short, two intermediate and two long Mo–O distances in each octahedron, which is apparently typical for many molybdate(VI) structures.[3] The repeating unit of eight edge-shared octahedra in the present structure is extremely similar to the basic structural units found in the two potassium molybdenum bronzes $K_{0\cdot26}MoO_3$ (red)[4] and $K_{0\cdot28}MoO_3$ (blue),[5] $CoMoO_4$,[6] and $Ag_6Mo_{10}O_{33}$,[7] and also to the discrete hepta- and octa-molybdate polyanions, $Mo_7O_{24}{}^{6-}$ and $Mo_8O_{26}{}^{4-}$ respectively.[8,9]

The tetramolybdate structure remains stable in the presence of the slightly larger rubidium ion as indicated by the isomorphous nature of $Rb_2Mo_4O_{13}$ and $K_2Mo_4O_{13}$, but the analogous caesium salt, $Cs_2Mo_4O_{13}$, is monoclinic and appears to adopt a different structure.[3] A single-crystal structure investigation of the latter is in progress.

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