The Crystal Structure of Potassium Heptamolybdate Tetrahydrate, $K_6Mo_7O_{24},4H_2O$

By B. M. GATEHOUSE* and P. LEVERETT

(*Department of Chemistry, Monash University, Clayton, Victoria, Australia* 3168)

ATTEMPTS[1-3] have been made to determine the crystal structure of ammonium heptamolybdate tetrahydrate, the most recent in an endeavour to explain the thermal decomposition properties of this compound.[2,3] We now report the complete crystal structure of potassium heptamolybdate tetrahydrate (which is isostructural with the ammonium and rubidium analogues) determined during a study of molybdates in general.[1]

$K_6Mo_7O_{24},4H_2O$ crystallises in the space group $P2_1/c$, with a unit cell, $a = 8{\cdot}20$, $b = 35{\cdot}61$, $c = 10{\cdot}31$ Å and $\beta = 115{\cdot}1°$; $D_m = 3{\cdot}34$, for $Z = 4$, $D_c = 3{\cdot}32$ g.cm^{-3}. A total of 2178 independent reflections obtained with a Weissenberg camera using Cu-K_α radiation, were used in the structural determination which was carried out by the usual three dimensional 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 0·121.

The structure consists of $Mo_7O_{24}{}^{6-}$ blocks stacked in the a-axis direction and held together by the potassium ions. The oxygen co-ordination around the potassium ions is irregular eightfold where in some cases water molecule oxygen atoms form part of the co-ordination polyhedron. Although the seven MoO_6 octahedra in the heptamolybdate anion are considerably distorted the actual framework of the Mo atoms exhibits a certain regularity with Mo(1), Mo(2), Mo(3) and Mo(4) lying at the corners of a flat rectangle and

Mo(6) situated approximately equidistant from the other six Mo atoms. The dihedral angle Mo(5)–Mo(6)–Mo(7) is 163·1°. Mo–O distances lie in the range 1·61 to 2·45 Å (standard deviations ±0·05 to ±0·10 Å) with the exception of one rather short distance, 1·51 ± 0·10 Å, and one long distance 2·62 ± 0·10 Å. There are quite marked differences in most of the Mo–O distances compared with those given by Shimao[3] for the analogous ammonium compound, and as a result, in contrast to Shimao's findings, we report that in each MoO_6 octahedron in the heptamolybdate ion there are two short, two intermediate, and two long Mo–O distances (as also found in MoO_3,[4] $Na_2Mo_2O_7$,[5] and $K_2Mo_3O_{10}$ [6]). The twelve shared edge O–O distances lie in the fairly close range 2·37—2·67 Å, with an average value of 2·56 Å, and as expected are somewhat shorter than the unshared edges.

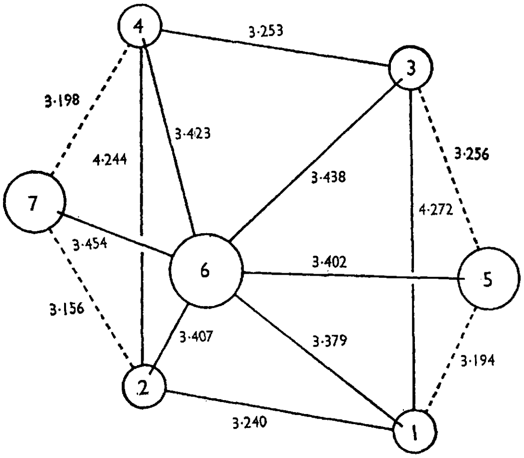

FIGURE. *Diagrammatic representation of the distribution of molybdenum atoms in the* $Mo_7O_{24}{}^{6-}$ *unit, showing metal–metal distances* (Å). *Inter-anion distances are much greater.*

Some of the potassium ions lie more or less between the heptamolybdate units and appear to be more strongly held in the structure than the remaining potassium ions which are found more towards the edges of the anion. This could explain the two-stage de-ammoniation of the isostructural ammonium heptamolybdate tetrahydrate.[2,3] In a similar way, of the four water molecules, two are found to bridge a pair of potassium ions between heptamolybdate blocks whilst two are situated elsewhere each bonded to a pair of cations, and are apparently not so strongly held in the structure. A thermogravimetric analysis of potassium heptamolybdate tetrahydrate in which two molecules of water were lost at 115° and two at 150° is in agreement with the above. The structure of the heptamolybdate anion is evidently a very stable arrangement of seven like octahedra and recently it was drawn to the authors' attention[7] that the same compact unit exists in $Ti_7O_{24}Et_{19}$,[8] which is the first hydrolysis product of titanium tetraethoxide.

This work forms part of a project supported by a grant from the Australian Research Grants Committee.

(*Received, April* 16*th*, 1968; *Com.* 456.)

[1] I. Lindqvist, *Arkiv Kemi*, 1950, **2**, 325.

[2] E. Shimao, *Nature*, 1967, **214**, 170.

[3] E. Shimao, *Bull. Chem. Soc. Japan*, 1967, **40**, 1609.

[4] L. Kihlborg, *Arkiv Kemi*, 1963, **21**, 357.

[5] M. Seleborg, *Acta Chem. Scand.*, 1967, **21**, 499.

[6] B. M. Gatehouse and P. Leverett, *J. Chem. Soc.* (*A*), in the press.

[7] A. F. Reid, private communication.

[8] K. Watenpaugh and C. M. Caughlan, *Chem. Comm.*, 1967, 76.