The Crystal Structure of Silver Decamolybdate, $Ag_6Mo_{10}O_{33}$

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Summary Silver decamolybdate, $Ag_6MO_{10}O_{33}$, has a layer structure where infinite sheets of edge and corner-shared MoO_6 octahedra are held together by silver ions.

AN investigation of the phase system Ag_2MoO_4–MoO_3 using *X*-ray single-crystal and powder-diffraction techniques shows the existence of two crystalline compounds, silver decamolybdate, $Ag_6Mo_{10}O_{33}$, and silver dimolybdate, $Ag_2Mo_2O_7$. The former compound crystallises over quite a wide compositional range in the phase system and this led us to initially assume the formula $Ag_2Mo_3O_{10}$.[1] Kohlmuller and Faurie[2] in a more recent investigation of the phase system considered this compound to be the tetramolybdate, $Ag_2Mo_4O_{13}$. However, the correct, and rather unexpected formula $Ag_6Mo_{10}O_{33}$ for this previously unreported compound has been determined after a complete crystal structure analysis which we now report.

$Ag_6Mo_{10}O_{33}$ crystallises in the triclinic system, space group $P\bar{1}$, $a = 7{\cdot}59$, $b = 8{\cdot}31$, $c = 11{\cdot}42$ Å, $\alpha = 82{\cdot}6°$, $\beta = 102{\cdot}9°$ and $\gamma = 106{\cdot}4°$; for $Z = 1$, $D_c = 5{\cdot}32$ g.cm.$^{-3}$. A total of 1267 independent reflections obtained with a Weissenberg camera using Cu-K_α radiation 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 anisotropic temperature factors for the silver atoms has reduced the reliability index to a present value of 0·076.

The description of the structure is made easier if the octahedral coordination of the molybdenum atoms is considered to be regular. The structure can be broken down into two fundamental groups, one of six octahedra sharing edges and the other a square arrangement of four octahedra sharing edges. Each group of six octahedra joins up with identical groups by edge-sharing to form infinite zig-zag chains running in the *a*-axis direction. The groups of four octahedra lie between these chains linking them by corner-sharing, forming infinite two dimensional sheets parallel to the (010) plane. As seen in Figure 1, this particular form of linkage of octahedra gives rise to

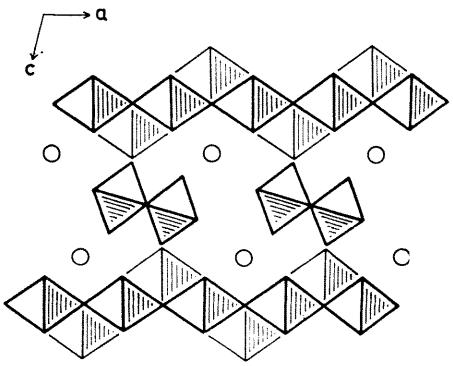

FIGURE 1. *A view, normal to the* (010) *plane, of an infinite sheet of idealized* MoO_6 *octahedra showing how the infinite chains are joined. The location of the silver ions* (*circles*) *in the voids is clearly seen.*

voids in the sheets, which are then filled with silver ions located in five-co-ordinate sites. Adjacent sheets have no common oxygen atoms, being held together by the remaining silver ions which occupy irregular seven-co-ordinate interlayer positions (Figure 2).

The distortions present in the MoO_6 octahedra result in two short, two intermediate and two long Mo–O distances in each octahedron (as also found in MoO_3,[3] $Na_2Mo_2O_7$,[4] $K_2Mo_3O_{10}$,[1] and $K_6Mo_7O_{24}{\cdot}4H_2O$[5]). The Mo–Mo distances vary between 3·23 and 3·84 Å for edge and corner-shared octahedra whilst the shortest intersheet Mo–Mo distance is about 4·9 Å. The repeating unit of six octahedra in the present structure is extremely similar to the basic structural

units found in the red[6] and blue[7] potassium molybdenum bronzes ($K_{0\cdot26}MoO_3$ and $K_{0\cdot28}MoO_3$ respectively) and

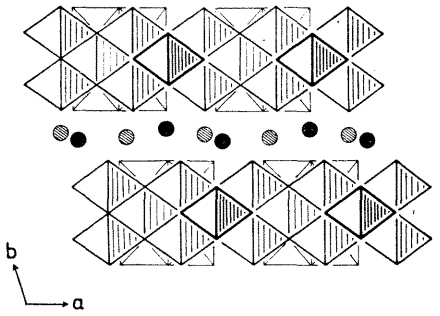

FIGURE 2. *Projection of the structure on* (001) *showing the idealized octahedral sheets linked by inter-layer silver ions. The lower chains in each sheet have been omitted for clarity. The almost coplanar silver ions represented by solid circles lie* ca. c/2 *above the almost coplanar silver ions represented by hatched circles.*

$CoMoO_4$,[8] and also to the sub-unit of six octahedra common to both the octa- and heptamolybdates which contain the discrete anions $(Mo_8O_{26})^{4-}$ and (Mo_7O_{24}).[6-9] Further, the units of four octahedra which are seen to link the infinite chains in this structure are also found in the octamolybdate anion where two such units are joined by common edges.

The Ag–O distances lie in the range 2·37—2·67 Å for the five-co-ordinate silver ions, and in the range 2·26—2·99 Å for the seven-co-ordinate silver ions, with an overall average value of 2·58 Å. The closest approach of any two silver ions is 3·22 Å, which may be compared with a distance of 2·889 Å in the metal.[10]

A single-crystal structure investigation of the second compound found to exist in the Ag_2MoO_4–MoO_3 phase system, apparently of formula $Ag_2Mo_2O_7$, is in progress.

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