# *X*-Ray Crystal Structure of $Ag_6O_2$

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*Summary* A single-crystal *X*-ray structural investigation of the material previously known as '$Ag_2O$ II' has shown the correct empirical formula to be $Ag_3O$.

A novel silver oxide, named '$Ag_2O$ II,' was reported in 1963;[1] *X*-ray powder photography, based on a unit cell with hexagonal axes $a$ = 3·072 (3) and $c$ = 4·941 (4) Å, suggested an anti-$CdI_2$ structure,[1] analogous with the subfluoride $Ag_2F$.[2] The agreement between observed and calculated intensities was rather poor ($R$ 0·25). We have succeeded in growing single crystals of '$Ag_2O$ II' from AgO by hydrothermal methods in silver tubes at moderate temperature and high pressure (*ca.* 80 °C, 4000 bar).[3] Diffractometer measurements revealed that the previously reported cell[1] was a subcell; the true cell has $a$ and $b$ axes longer than those of the subcell by a factor of $3^{\frac{1}{2}}$. Reflexions with $h - k \neq 3n$ are weak and extremely difficult to detect by powder methods.

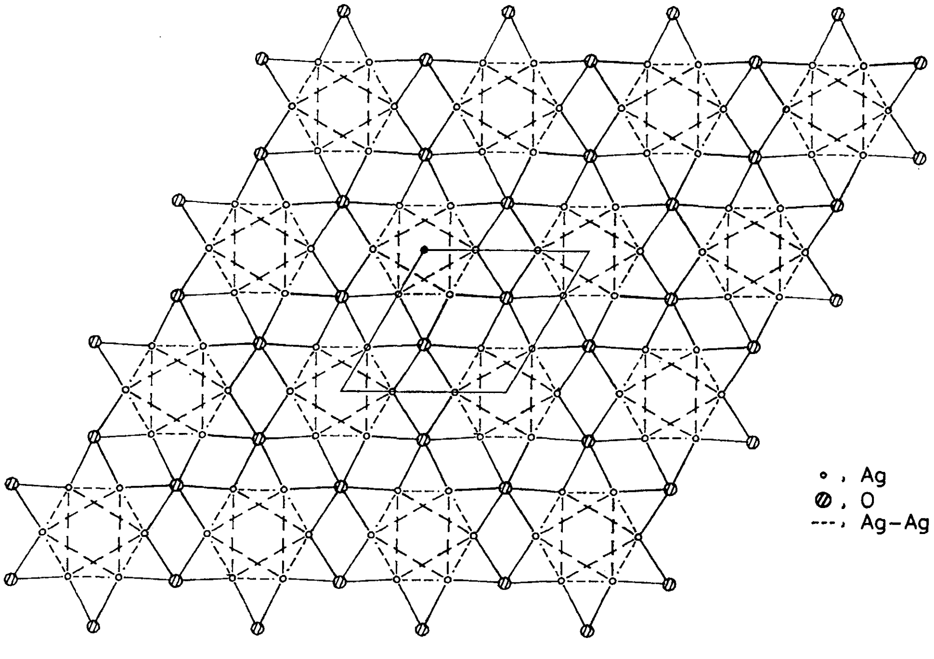

FIGURE. A projection of the structure down the $z$ axis. The origin is indicated by the black dot.

The successful structure solution and refinement prove the correct empirical formula to be $Ag_3O$. (This is confirmed by elemental analysis of a sample of single crystals, carefully dried *in vacuo* and free from adhering silver dust.)

To a first approximation the structure may be described as an hexagonal close-packed arrangement of Ag atoms, with the (larger) oxide ions filling 2/3 of the octahedral holes at $z = \frac{1}{2}$ (Ag–O 2·292 Å); this accounts for the metallic conductivity of $Ag_3O$, and is equivalent to an anti-$BiI_3$ structure (the short $c$ axis form of $BiI_3$[4]). An alternative, extreme description is in terms of $Ag_6^{4+}$ octahedra;[5] the Ag–Ag distances within the octahedra (2·863 and 2·757 Å) are significantly shorter than those between the octahedra (Ag–Ag $\geqslant$ 2·986 Å). In $BiI_3$ the reverse is true; the shortest I–I distance (4·175 Å) links two such octahedra. The apparent fractional charges on the Ag atoms (which are all crystallographically equivalent) may be accounted for by a model consisting of $Ag^+$ and $O^{2-}$ ions, with one additional electron-pair per $Ag_6$ octahedron, occupying an $a_{1g}$ symmetry molecular orbital located primarily within the octahedron.

*Crystal data:* $Ag_6O_2$, $M_r$ 679·22, trigonal, $P\bar{3}1m$, $a$ = 5·318(2), $c$ = 4·951(2) Å, $U$ = 121·3 Å$^3$, $Z$ = 1, $D_c$ = 9·30 g cm$^{-3}$, $F_{000}$ = 298, Mo-$K_\alpha$ radiation, $\lambda$ = 0·71069 Å, crystal size 0·22 × 0·06 × 0·06 mm, $\mu$ = 23·4 mm$^{-1}$. A complete sphere of data (1331 reflexions) in the range 7° $< 2\theta <$ 60° was collected on a Stoe 4-circle diffractometer. After Lorenz polarisation and absorption corrections, all 142 averaged unique reflexions were used for solution and refinement. Anisotropic refinement led to $R$ 0·020, $R_w$ 0·025, and final co-ordinates of Ag 0·3108, 0, 0·2228; O $\frac{1}{3}$, $-\frac{1}{3}$, $\frac{1}{2}$ (positions

*6k* and *2d* respectively). Final bond length e.s.d.'s were 0·002 Å.

The diffractometer control program[6] was written by Dr. W. Clegg; all other crystallographic programs by G. M. S. We thank the Verband der Chemischen Industrie for financial support, and the referees for helpful suggestions.

(*Received, 13th February* 1981; *Com.* 166.)

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