Gold(III) Oxide and Oxychloride

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Of all metals, gold shows the least tendency to form simple compounds with oxygen; anhydrous gold(III) oxide was until recently unknown. We have successfully prepared single crystals of gold(III) oxide and gold(III) oxychloride large enough to permit structure determination by X-ray crystallography.

Both preparations (1, 2) involve the heating in sealed quartz tubes of amorphous hydrated gold(III) oxide with perchloric acid and an alkali metal perchlorate — temperatures and pressures of the order of 250°C and 30 MPa are required. Small variations of reagent ratios, temperature and pressure result in different ratios of products and different crystal sizes.

X-ray diffraction data for both compounds have been collected on an automated diffractometer, and both structures have been elucidated (3, 4).

Gold(III) oxide exhibits the usual square planar co-ordination of the metal atom as shown here. The asymmetric unit (smallest unique group of atoms) consists of one gold and two oxygen atoms, one oxygen atom lying on a crystallographic two-fold axis. This oxygen atom (O2 in the diagram) is co-ordinated to two gold atoms, the other, O1, is co-ordinated to three gold atoms. This is reflected in the stronger (shorter) Au-O2 bond. A *trans* effect is observed, the Au-O1 bond *trans* to O2 being longest. The extended polymeric structure is best seen as a stereoview (3).

The structure of gold(III) oxychloride is also polymeric, with square planar co-ordination at the metal atom (by three oxygens and one chlorine); it also shows a *trans* effect, the AuO bond *trans* to Cl being longest.

Crystals of Au_2O_3 (maximum size 0.2 mm)

References

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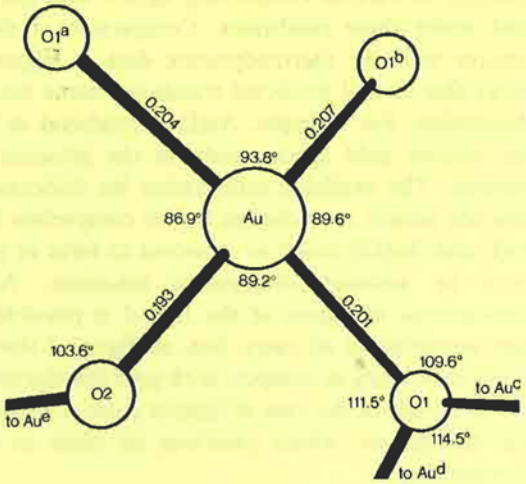
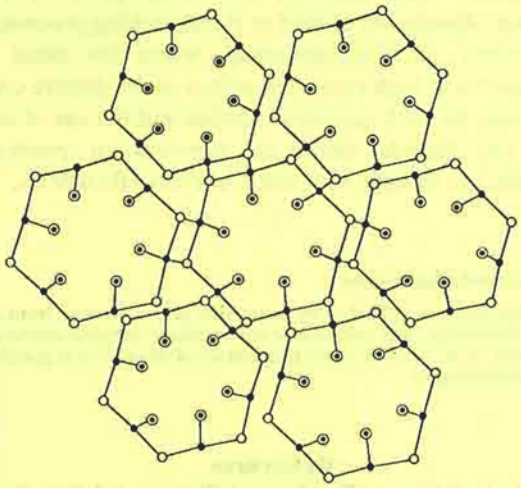


The square planar AuO_4 unit in Au_2O_3, showing unique bond lengths in nm and angles in degrees. The superscripts refer to symmetry equivalent atoms



The extended structure of AuOCl. Oxygen, chlorine and gold atoms are represented by open, dotted and filled circles respectively. The structure consists of linked hexameric rings; the gold atoms lie in a plane with oxygen atoms 0.029 nm and chlorine atoms 0.193 nm alternatively above and below this plane