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Gold(III) Oxide

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Abstract. Au_2O_3, $M_r = 441{\cdot}93$, orthorhombic, *Fdd*2, $a = 12{\cdot}827$ (3), $b = 10{\cdot}520$ (3), $c = 3{\cdot}838$ (1) Å, $U = 517{\cdot}9$ Å^3, $Z = 8$, $D_x = 11{\cdot}33$, $D_m = 10{\cdot}6$ Mg m^{-3}, μ(Mo $K\alpha$) = $108{\cdot}8$ mm^{-1}. Empirical absorption corrections were applied to allow for suspected inhomogeneity of the crystal; the structure was refined to $R = 0{\cdot}058$ for 373 unique reflexions. The structure is polymeric; the Au atom shows square-planar coordination, and a *trans* effect is observed. Angles at O atoms are approximately tetrahedral. One O atom lies on a twofold axis and is coordinated to two Au [Au—O 1·93 (2) Å]; the other lies on a general position and is coordinated to three Au [Au—O 2·01 (2), 2·04 (2), 2·07 (2) Å].

Introduction. Gold has the least tendency of all metals to form simple compounds with oxide or hydroxide ligands. Although several oxoaurates have been characterized (Hoppe & Arend, 1962; Wasel-Nielen & Hoppe, 1968, 1970; Klassen & Hoppe, 1976), Au^I oxide and hydroxide are unknown, and Au_2O_3 was until recently unknown in anhydrous form. [The unidentified oxide AuO_y reported by Muller, Newnham & Roy (1969) may be Au_2O_3 (Mohn, 1974).] We have previously reported the preparation of single crystals of Au_2O_3 (Schwarzmann, Mohn & Rumpel, 1976) and here report its crystal structure.

Intensities were measured with a Stoe four-circle diffractometer, monochromated Mo $K\alpha$ radiation and a crystal 0·2 × 0·2 × 0·1 mm. A complete sphere of data (1592 reflexions) was collected up to $2\theta = 60°$. Cell constants were obtained by least squares from strong high-angle reflexions. Lp corrections were applied, then empirical absorption corrections ($\mu = 108{\cdot}8$ mm^{-1}) based on measurements of strong equivalent reflexions at different azimuthal angles. Friedel opposites were also considered to be equal in deriving the absorption profile, since it was observed that reflexions with positive l were systematically weaker than those with negative l. A possible explanation of the observed absorption is that a non-crystalline region was embedded asymmetrically in the crystal. This is consistent with the low observed intensities, high backgrounds and poor agreement of measured and calculated densities, and is also reasonable in view of the method of preparation of the crystals. Equivalent reflexions (not including Friedel opposites) were merged, rejecting all those for which measurements of all possible equivalent reflexions were not available (a few measurements were rejected because of high and asymmetric background

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measurements). This procedure was adopted because the averaging of equivalent reflexions itself acts as a partial absorption correction. These extreme methods were considered necessary because of the very high absorption coefficient and suspected crystal inhomogeneity. Because of their empirical nature, little confidence can be attached to the absolute values of the atomic temperature factors.

With the 373 unique reflexions thus derived, the structure was solved by Patterson and Fourier methods, and refined with anisotropic Au and isotropic O to $R' = \sum w^{1/2}\Delta/\sum w^{1/2}|F_o| = 0{\cdot}062$, with a corresponding R of 0·058. The weighting scheme was $w = 1/[\sigma^2(F) + 0{\cdot}003F^2]$. Refinement of the opposite polar axis direction (generated by inverting all coordinates at the point $\frac{1}{8},\frac{1}{8},0$) did not result in a significantly different R, although the temperature-factor components were a little less satisfactory. The Friedel differences may be small because the Au atom lies on a pseudosymmetry centre, and the absorption corrections may have tended to reduce them. However, similar absorption procedures are in common use in protein crystallography, where accurate measurement of Friedel differences is important.

The results of the final refinement are shown in Table 1 and Fig. 1.* Complex neutral-atom scattering factors were taken from *International Tables for X-ray Crystallography* (1974).

* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 34281 (3 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. *Atomic coordinates* ($\times 10^4$) *and temperature factors* ($\text{Å}^2 \times 10^3$)

	x	y	z	U
Au	−458 (1)	1329 (1)	5000	*
O(1)	825 (17)	2334 (19)	6232 (54)	14 (3)
O(2)	0	0	8107 (86)	21 (6)

* Anisotropic temperature factors for Au: U_{11} 4 (1), U_{22} 14 (1), U_{33} 15 (1), U_{23} 0 (1), U_{13} 1 (1), U_{12} 0 (1). The temperature factor exponent takes the form $-2\pi^2(U_{11}h^2a^{*2} + \ldots + 2U_{12}hka^*b^*)$.

Discussion. The archetypal coordination geometry for Au^{III} is square planar, which it achieves in the Au_2O_3 polymer as shown in Figs. 1 and 2. The Au atom is coordinated by O(1), O(2) and two other O(1) atoms generated by symmetry transformations; the r.m.s. deviation of the five atoms from the AuO_4 least-squares plane is 0·044 Å. The coordinations about the two independent O atoms are different (although in both cases angles at O are approximately tetrahedral); O(1) is coordinated to three Au atoms, O(2) to two. This is reflected in the fact that the Au—O(2) bond is significantly shorter than the three Au—O(1) bonds, and also in a consequent *trans* effect, the longest Au—O(1) bond being *trans* to O(2). [The *trans* effect in Au^{III} compounds has been noted before, *e.g.* in $PhAu(SR_2)Cl_2$ (McPartlin & Markwell, 1973).] The average Au—O distance is 2·01 Å; this is significantly shorter than in any of the few structures containing Au—O bonds which are available for comparison. In the 1-hydroxy-2,3,4,5-tetraphenylauracyclopentadiene dimer (Peteau-Boisdenghien, Meunier-Piret & Van Meerssche, 1975) and the dimethylgold(III) hydroxide tetramer (Glass, Konnert, Miles, Britton & Tobias, 1968), both of which have O ligands *trans* to Au—C bonds, the Au—O distances are appreciably longer (averages of 2·21 and 2·15 Å respectively). This may be a further manifestation of the *trans* effect. In $Na_6Au_2O_6$, which contains $Au_2O_6^{6-}$ ions, the Au—O

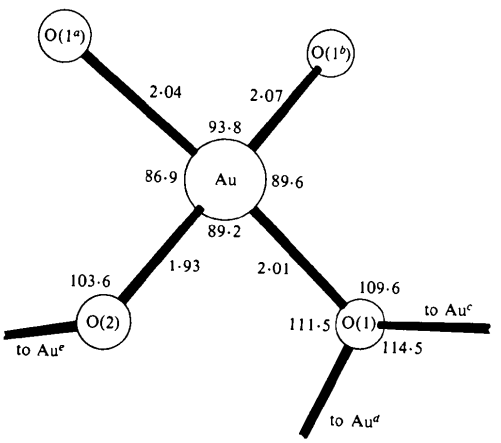

Fig. 1. The AuO_4 unit viewed perpendicular to the mean plane of the seven labelled atoms. Unique bond lengths (e.s.d. 0·02 Å) and angles (e.s.d. 1·5°) are indicated. Symmetry transformations: (*a*) $-\frac{1}{4}+x, \frac{1}{4}-y, -\frac{1}{4}+z$; (*b*) $-x, \frac{1}{2}-y, -\frac{1}{2}+z$; (*c*) $-x, \frac{1}{2}-y, \frac{1}{2}+z$; (*d*) $\frac{1}{4}+x, \frac{1}{4}-y, \frac{1}{4}+z$; (*e*) $-x, -y, z$. Other unique angles: O(1)—Au—O(1*a*) 174·8°, O(2)—Au—O(1*b*) 173·1°.

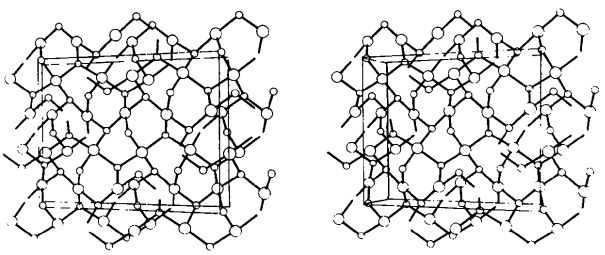

Fig. 2. Stereoview of the extended structure (*b* upwards, *a* across, *c* towards viewer).

bonds are 2·12 and 2·17 Å (Klassen & Hoppe, 1976), but here the O atoms are further coordinated to alkali-metal ions. This is also the case in the oxoaurates Li_5AuO_4, $Li_6Au_2O_6$ and $KAuO_2$, where powder data lead to Au—O distances of 2·03, 2·08 and 2·08 Å respectively (Wasel-Nielen & Hoppe, 1970), but these structures were not refined and no e.s.d.'s are given; in addition, Li_5AuO_4 has averaged Li/Au sites and so is not directly comparable.

The Au atom is weakly coordinated by four further O atoms: Au···O(1^c) 2·81, Au···O(2^a) 2·90, Au···O(1^f) 3·19, Au···O(2^g) 3·05 Å [symmetry transformations: (*a*) and (*c*), see Fig. 1; (*f*) $\frac{1}{4} - x, -\frac{1}{4} + y, -\frac{1}{4} + z$; (*g*) $x, y, -1 + z$]. These five atoms lie in a plane (r.m.s. deviation 0·07 Å) at 85° to the AuO_4 bonding plane, O(1^c) and O(2^a) lying above, O(1^f) and O(2^g) below the latter plane.

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Rare-Earth (and Yttrium)—Iridium and —Platinum Compounds with the Fe_3C Structure Type

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Abstract. Sm_3Ir, orthorhombic, *Pnma*, $Z = 4$, $a = 7·273$ (4), $b = 9·584$ (5), $c = 6·397$ (4) Å, $D_x = 9·58$ Mg m^{-3}, μ(Ag $K\alpha$) = 37·5 mm^{-1}; Y_3Pt, same type, $a = 7·101$ (4), $b = 9·584$ (7), $c = 6·454$ (6) Å, $D_x = 6·98$ Mg m^{-3}, μ(Mo $K\alpha$) = 73·8 mm^{-1}. The structures belong to the Fe_3C structure type. New compounds found to be isotypic are: La_3Ir, Pr_3Ir, Nd_3Ir, Sm_3Ir, Gd_3Ir, Tb_3Ir, Dy_3Ir, Ho_3Ir, Er_3Ir, Tm_3Ir, Lu_3Ir and Y_3Ir; and Gd_3Pt, Tb_3Pt, Dy_3Pt, Ho_3Pt, Er_3Pt, Tm_3Pt, Lu_3Pt and Y_3Pt.

Introduction. In the course of a review of the crystal structures of alloys containing rare-earth elements (and Y) and late transition elements (Parthé & Moreau, 1977; Le Roy, Moreau, Paccard & Parthé, 1978) it became evident that structural studies of rare-earth (*R*) rich alloys formed in the systems *R*–Ir and *R*–Pt were by no means complete. The only information found on such compounds was for La–Ir (Dmitrieva, Vorobev, Varekha, Domashev & Gusynin, 1974), Ce–Ir (Dmitrieva *et al.*, 1973), Yb–Ir (Iandelli & Palenzona, 1976), Nd–Pt, Er–Pt (Moffatt, 1978) and Yb–Pt (Iandelli & Palenzona, 1975). We report here the results of our investigations on other compounds belonging to these systems.

The alloys were made from commercially available elements of high purity by conventional arc-melting techniques. X-ray photographs from powdered samples were obtained on a Guinier camera with Cu $K\alpha$ radiation and were calibrated with Si powder. Small single crystals of Sm_3Ir (130 × 35 × 25 μm) and Y_3Pt (100 × 50 × 40 μm) were isolated by mechanical fragmentation. Intensities were measured with graphite-monochromated Ag $K\alpha$ (Sm_3Ir) and Mo $K\alpha$ (Y_3Pt) radiation on a computer-controlled Philips PW 1100 four-circle diffractometer in the θ–2θ scan mode.

Data collection for Sm_3Ir (Y_3Pt) was carried out to a limit of 0·71 (0·66) Å^{-1} in $\sin\theta/\lambda$, yielding 467 (561)

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