

atom is *trans* to a CO group, in the second it is *trans* to a Cl atom. A similar behaviour is observed for the Ru—Cl(1) distance, which is longer in (2) than in (1). In (2) the Cl atom is *trans* to a CO group, whereas in (1) it is *trans* to Cl. It is in accordance with the expected *trans* influence order and with that previously reported for *cis*-bis(2,2'-bipyridyl)carbonylchlororuthenium(II) perchlorate (Clear, Kelly, O'Connell, Vos, Cardin, Costa & Edwards, 1980). It seems that the uncoordinated pyridine does not have an important influence on the shortening of N(2)—Ru with respect to N(1)—Ru. This effect is present in both complexes, but it is more evident in the *cis*—*cis* compound [Ru—N(1) = 2.112 (2), Ru—N(2) = 2.049 (2) Å]. On the other hand the shorter Ru—N(2) distances with respect to the Ru—N(1) ones in both complexes are in agreement with the greater π acidity of the pyridazine ring. The C—O distances [1.126 (7), 1.132 (7) Å in (1) and 1.127 (4), 1.109 (4) Å in (2)] and the Ru—C—O angles [177.6 (5), 179.5 (5)° in (1) and 178.6 (3), 176.4 (3)° in (2)] are close to previously reported values (Clear, Kelly, O'Connell, Vos, Cardin, Costa & Edwards, 1980). The shortening of the C—O distance for the axial positions in the *cis*—*cis* compound with respect to the equatorial one in the *cis*—*trans* is noticeable.

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The Determination of Absolute Structure. VI.* The Structure of Zinc Digold(III) Octapropionate Dihydrate: Absolute Structure and Ghost Peaks

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Abstract. [Au₂Zn(C₃H₅O₂)₈(H₂O)₂], $M_r = 1079.9$, tetragonal, $I\bar{4}$, $a = 9.092$ (2), $c = 22.540$ (8) Å, $V = 1863.3$ Å³, $Z = 2$, $D_x = 1.925$ Mg m⁻³, $F(000) = 1040$, $\lambda(\text{Mo } K\alpha) = 0.71069$ Å, $\mu = 8.6$ mm⁻¹, $T = 293$ K. The structure was refined to $R = 0.030$ for 1631 unique observed reflections. The absolute structure was determined with an η refinement [$\eta = +1.06$ (3)]. A two-dimensional polymeric structure is observed; the Zn atom is coordinated octahedrally by four propionate oxygens and two *trans* waters, and the Au is coordinated by four propionate oxygens in a square plane. One propionate bridges Zn and Au, the other is only bonded to Au and has one non-coordinated O. The refinement of the wrong absolute structure led to a large

difference peak at 0, 0, 0.5, which could be successfully refined as an O atom. Incorrect absolute structure can thus lead to incorrect stoichiometry.

Introduction. In the course of our studies of gold(III) carboxylate complexes we have reported the structure of strontium digold(III) octaacetate dihydrate (Jones, 1984a). A detailed report of several other acetato-gold(III) complexes is in preparation. Here we show that the synthetic and structural principles can be extended to propionate complexes.

Experimental. Zinc digold(III) octahydroxide was prepared as a grey powder from aqueous solutions of NaAu(OH)₄ and Zn(ClO₄)₂, and immediately dissolved in warm propionic acid. On standing for several days,

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* Part V: Jones & Meyer-Bäse (1987).

colourless crystals, in the form of cubes and square prisms, were formed. They decompose at 427 K.

A crystal $0.15 \times 0.12 \times 0.12$ mm was sealed in a glass capillary and used to record 1934 profile-fitted intensities (Clegg, 1981) on a Stoe-Siemens four-circle diffractometer (monochromated Mo $K\alpha$ radiation, $2\theta_{\max} 50^\circ$, octants $+h+k+l$ and $-h-k-l$). Three check reflections showed no significant intensity change. An absorption correction based on ψ scans was applied (transmissions 0.44–0.48). Cell constants were refined from 2θ values of 48 reflections in the range 20 – 23° .

The apparent Laue symmetry was $4/mmm$, but the merging R value in this Laue group was poor (0.11). In $4/m$ the agreement was much better (0.04 with Friedel opposites merged, 0.025 otherwise), and the course of structure determination confirmed $4/m$ as correct; the space group is $I\bar{4}$, with 1659 unique reflections, $1643 > 4\sigma(F)$.

The structure was solved by inspection of the Patterson function (to obtain the Au and Zn positions); the light-atom positions were deduced gradually from subsequent difference syntheses, which gave multiple images of the structure until nearly all light atoms had been correctly located. Full-matrix least-squares refinement on F proceeded to R 0.030, wR 0.036 [all non-H atoms anisotropic, H atoms included using riding model; weighting scheme $w^{-1} = \sigma^2(F) + 0.0005F^2$; 103 parameters, max. Δ/σ 0.02, max. $\Delta\rho$ within $\pm 1.6 \text{ e } \text{Å}^{-3}$ near Au, $S = 1.2$]. Three reflections clearly in error were omitted. The absolute structure (Jones, 1984*b*) was determined using an η refinement (Rogers, 1981); η refined to $+1.06$ (3). The *SHELX* program system (Sheldrick, 1986; locally modified by its author) was used throughout. Scattering factors and anomalous-dispersion correction terms were from *International Tables for X-ray Crystallography* (1974).

Final atomic coordinates are given in Table 1, with derived bond lengths and angles in Table 2.*

Discussion. The Zn atom occupies the special position 0.5, 0.5, 0.5 with site symmetry $\bar{4}$; its coordination geometry is octahedral (see Fig. 1), with four equatorial propionate oxygen ligands O(22) and two axial water ligands (the water O lies on the twofold axis 0.5, 0.5, z). The Au atom lies on the twofold axis 0.5, 0, z and is coordinated by the propionate oxygens O(11) and O(21) and their equivalents in a square plane. The Au–O bond lengths of 1.971 (5) and 1.984 (6) Å are in good agreement with the values in strontium digold(III) octaacetate dihydrate [1.974–1.992 (9) Å (Jones, 1984*a*)].

* Lists of structure factors, anisotropic thermal parameters and H-atom parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 44838 (9 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 equivalent isotropic displacement parameters ($\text{Å}^2 \times 10^3$)

	x	y	z	U_{eq}^*
Zn(1)	5000	5000	5000	39 (1)
Au(1)	5000	0	5824.5 (1)	42 (1)
O(11)	3532 (7)	492 (6)	6437 (3)	57 (2)
C(11)	3719 (10)	1769 (9)	6695 (3)	55 (2)
O(12)	4750 (8)	2587 (7)	6572 (3)	67 (2)
C(12)	2575 (14)	2113 (12)	7151 (4)	87 (4)
C(13)	2533 (21)	3613 (18)	7364 (12)	208 (8)
O(21)	3566 (6)	485 (6)	5190 (2)	52 (2)
C(21)	3698 (8)	1761 (8)	4929 (3)	42 (2)
O(22)	4565 (6)	2702 (5)	5109 (2)	47 (2)
C(22)	2716 (12)	1942 (11)	4391 (4)	69 (3)
C(23)	2113 (25)	671 (24)	4103 (7)	188 (9)
O(1w)	5000	5000	5895 (3)	59 (3)

* Equivalent isotropic U defined as one third of the trace of the orthogonalized U_{ij} tensor.

Table 2. Molecular geometry

(a) Bond lengths (Å)

Zn(1)–O(22)	2.140 (5)	Zn(1)–O(1w)	2.017 (7)
Au(1)–O(11)	1.971 (6)	Au(1)–O(21)	1.984 (5)
O(11)–C(11)	1.310 (10)	C(11)–O(12)	1.229 (11)
C(11)–C(12)	1.496 (14)	C(12)–C(13)	1.446 (21)
O(21)–C(21)	1.306 (9)	C(21)–O(22)	1.232 (9)
C(21)–C(22)	1.516 (13)	C(22)–C(23)	1.435 (23)

(b) Bond angles ($^\circ$)

O(22)–Zn(1)–O(1w)	83.4 (1)	O(22)–Zn(1)–O(22 ⁱⁱ)	166.8 (3)
O(22)–Zn(1)–O(22 ⁱⁱ)	90.8 (1)	O(1w)–Zn(1)–O(22 ⁱⁱ)	96.6 (1)
O(1w)–Zn(1)–O(1w ⁱⁱ)	180.0 (1)	O(11)–Au(1)–O(21)	90.5 (2)
O(11)–Au(1)–O(11 ⁱⁱⁱ)	91.1 (3)	O(21)–Au(1)–O(11 ⁱⁱⁱ)	178.3 (2)
O(21)–Au(1)–O(21 ⁱⁱⁱ)	87.8 (3)	Au(1)–O(11)–C(11)	115.1 (5)
O(11)–C(11)–O(12)	122.3 (8)	O(11)–C(11)–C(12)	113.6 (8)
O(12)–C(11)–C(12)	124.0 (8)	C(11)–C(12)–C(13)	116.3 (12)
Au(1)–O(21)–C(21)	117.5 (5)	O(21)–C(21)–O(22)	121.8 (7)
O(21)–C(21)–C(22)	113.8 (7)	O(22)–C(21)–C(22)	124.4 (7)
Zn(1)–O(22)–C(21)	139.3 (5)	C(21)–C(22)–C(23)	120.0 (11)

Symmetry operators: (i) $1-x, 1-y, z$; (ii) $y, 1-x, -z$; (iii) $1-x, -y, z$.

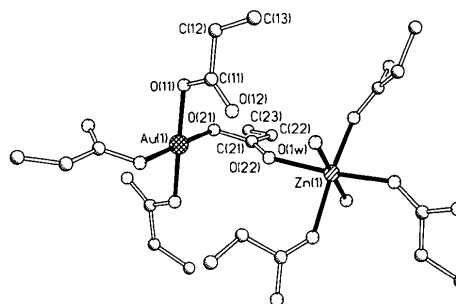


Fig. 1. The coordination spheres of the metal atoms in the title compound, showing the numbering scheme of the asymmetric unit. Radii arbitrary, H atoms omitted.

One propionate ligand bridges Au and Zn [via atoms O(21), O(22)], whereas the other is only bonded to Au [via O(11); O(12) does not coordinate any metal atom]. The extended structure thus formed is a sheet polymer (Fig. 2). Within the sheets, the contact $O(1w)\cdots O(12)$, 2.68 (2) Å, probably represents a hydrogen bond. There are no other $O\cdots O$ contacts under 3 Å.

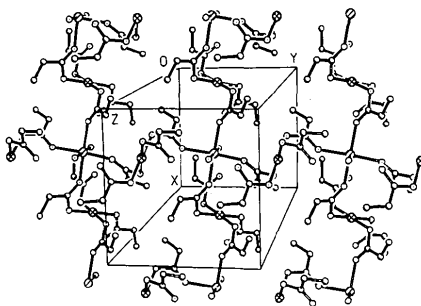


Fig. 2. One of the polymeric layers of the title compound. This layer runs through the cell in the region $z = 0.5$. Further such layers (not shown here) are at $z = 0$ and 1.

Absolute structure and ghost peaks. An earlier refinement of the title compound, in what proved to be the false absolute structure (η negative), showed a large difference peak at 0, 0, 0.5, which could be successfully refined as an O atom, and was assumed to belong to a water of crystallization. (A water with site symmetry $\bar{4}$ must involve some disorder – perhaps analogous to the structure of ice? – but the model was otherwise sensible, with O...O contacts of ca 2.7 Å to the apparent water.) After the η refinement, the absolute structure was inverted and the oxygen at 0, 0, 0.5 ‘disappeared’, i.e. its U value became impossibly high. An incorrect absolute structure can thus lead to a false apparent stoichiometry by giving rise to ghost peaks.

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A Mixed Chloride Acetate Complex of Lead(II) and Gold(III): [Pb₃(CH₃COO)₃Cl₂][AuCl₄]

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Abstract. Triacetato(dichloro)trilead(II) tetrachloroaurate(III), $M_r = 1208.4$, monoclinic, $C2/c$, $a = 41.29$ (2), $b = 10.657$ (4), $c = 8.832$ (4) Å, $\beta = 90.50$ (3)°, $U = 3887$ Å³, $Z = 8$, $D_x = 4.13$ Mg m⁻³, $\lambda(\text{Mo } K\alpha) = 0.71069$ Å, $\mu = 34.5$ mm⁻¹, $F(000) = 4160$, $T = 293$ K, $R = 0.051$ for 2683 unique observed reflections. The structure consists of two types of layers. The three independent lead atoms are linked by chloride and acetate ions to form a sheet polymer, and layers of AuCl₄⁻ ions run between these sheets. The layers are linked by Pb...Cl–Au contacts. The coordination at the Pb atoms is irregular and, when only the shorter contacts are considered, markedly one-sided.

Introduction. Our studies of acetate complexes of gold(III) have involved compounds of general formula MAu₂(CH₃COO)₈.xH₂O [$M = \text{Sr, Zn, Pb, Ca, Ba}$ (Jones, 1984; Schelbach, 1988)]. The lead compound was first described by Weigand (1906). Here we report the preparation and characterization of a lead(II) gold(III) acetate chloride.

Experimental. 200 mg HAuCl₄ was dissolved in 15 ml distilled water and then warmed with freshly precipitated Pb(OH)₂. The solution rapidly became colourless and a pH of 5–6 was attained. The insoluble orange product, presumably a mixed chloride/hydroxide of gold and lead, was dissolved in hot glacial acetic acid.

It is known that errors in intensity measurements lead to errors in electron density that are concentrated at special positions [in particular at the origin (Rees, 1977)], and it seems to be generally agreed among crystallographers that errors in the refinement model can lead to spurious electron density at special positions in space groups of high symmetry. However, we are not aware of any reference pointing out this fact.

Our findings represent a further reason for determining the absolute structure of a non-centrosymmetric structure as a matter of routine.

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