

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]

BY PETER G. JONES, RALF SCHELBACH, EINHARD SCHWARZMANN AND CARSTEN THÖNE
*Institut für Anorganische Chemie der Universität, Tammannstrasse 4, 3400 Göttingen,
Federal Republic of Germany*

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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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Yellow tabular crystals separated from the cooled solution after 2 weeks. Analysis: found Au 16.26, Pb 51.31, Cl 17.56%, calc. Au 16.37, Pb 50.86, Cl 17.43%. The product decomposes at 471 K.

A crystal $0.15 \times 0.12 \times 0.08$ mm was mounted in a glass capillary. 6868 profile-fitted intensities (Clegg, 1981) were recorded on a Stoe-Siemens four-circle diffractometer (monochromated Mo $K\alpha$ radiation, $2\theta_{\max} = 50^\circ$, hemisphere $\pm h \pm k + l$). Three check reflections showed no significant intensity change. An absorption correction based on ψ scans was applied; transmission factors were 0.26–0.99. Merging equivalents gave 3438 unique reflections ($R_{\text{int}} = 0.044$, index ranges $h -48$ to 48 , $k 0$ to 12 , $l 0$ to 10), of which 2683 with $F > 4\sigma(F)$ were used for all calculations via program system *SHELX76* (Sheldrick, 1976), locally modified by its author. Cell constants were refined from 2θ values of 34 reflections in the range 20–25°.

The structure was solved by the heavy-atom method and refined on F to $R = 0.051$, $wR = 0.044$. Au, Pb and Cl atoms were anisotropic, C and O isotropic; H atoms were not included. The weighting scheme was $w^{-1} = \sigma^2(F) + 0.0002F^2$. 141 parameters; max. $\Delta/\sigma = 0.03$; $\Delta\rho$ within $\pm 1.5 \text{ e } \text{Å}^{-3}$; $S = 1.6$. Scattering factors taken from *International Tables for X-ray Crystallography* (1974). Final atomic coordinates are presented in Table 1, with derived bond lengths and angles in Table 2.*

Discussion. The structure analysis shows that the title compound consists broadly of two parts, one involving lead and the other gold.

(i) *The gold-containing moiety.* Both Au atoms occupy special positions, Au(1) a twofold axis, $\frac{1}{2}, y, \frac{1}{4}$ and Au(2) a symmetry centre, $\frac{1}{2}, \frac{3}{4}, 0$. Both are coordinated solely by chloride ions, so that the well known anion AuCl_4^- is involved. There are no gold–acetate interactions within normal bonding distances. Three of the Au–Cl bond lengths are normal (Jones, 1981); the other, Au(2)–Cl(21), is rather long at 2.285 (5) Å. The reasons for this will be discussed below.

(ii) *The lead-containing moiety.* There are three independent Pb atoms, each occupying a general position. The coordination of each Pb atom by acetate and chloride ions is irregular, to such an extent that it is difficult to establish which interactions should be regarded as bonding. Pb(1) (Fig. 1*a*) is coordinated by three chlorides, Cl(3), Cl(4) and Cl(3ⁱⁱ), at 2.84–3.04 Å and by a chelating acetate, O(21ⁱ) and O(22ⁱ), at 2.65, 2.43 Å. Longer contacts (2.72, 3.16, 3.39 Å) extend to

* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 44839 (14 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}^*
Au(1)	5000	7421 (1)	2500	30 (1)
Cl(11)	4481 (1)	7486 (5)	1655 (5)	47 (2)
Cl(12)	5177 (1)	7392 (6)	81 (5)	58 (2)
Au(2)	2500	7500	0	38 (1)
Cl(21)	2618 (2)	5860 (6)	1579 (6)	71 (2)
Cl(22)	2869 (2)	8699 (6)	1234 (7)	71 (2)
Pb(1)	3412.0 (2)	5658.8 (7)	1821.3 (7)	36 (1)
Pb(2)	3490.3 (2)	9193.0 (6)	-1213.4 (7)	30 (1)
Pb(3)	3989.1 (2)	7568.4 (5)	4827.3 (6)	22 (1)
Cl(3)	3310 (1)	6532 (4)	-1414 (4)	39 (2)
Cl(4)	3668 (1)	8337 (4)	1733 (4)	37 (1)
O(11)	3443 (3)	8581 (10)	5478 (11)	30 (3)
O(12)	3402 (3)	6686 (10)	4640 (12)	31 (3)
C(11)	3271 (4)	7660 (13)	5123 (15)	19 (3)
C(12)	2914 (5)	7719 (16)	5268 (19)	39 (4)
O(21)	3947 (3)	5649 (11)	6360 (12)	40 (3)
O(22)	3924 (3)	4327 (10)	8193 (12)	36 (3)
C(21)	4075 (5)	5176 (15)	7481 (18)	30 (4)
C(22)	4398 (5)	5631 (17)	8100 (21)	45 (5)
O(31)	3997 (3)	8456 (10)	7664 (12)	30 (3)
O(32)	4049 (3)	9967 (10)	9279 (12)	31 (3)
C(31)	4175 (4)	9237 (14)	8343 (16)	24 (4)
C(32)	4530 (5)	9322 (18)	8056 (21)	48 (5)

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

Table 2. Molecular geometry

(a) Bond lengths (Å)

Au(1)–Cl(11)	2.264 (5)	Au(1)–Cl(12)	2.264 (5)
Au(2)–Cl(21)	2.285 (6)	Au(2)–Cl(22)	2.261 (6)
Pb(1)–Cl(3 ⁱⁱ)	2.841 (4)	Pb(1)–O(21 ⁱ)	2.645 (13)
Pb(1)–O(22 ⁱ)	2.428 (12)	Pb(1)–Cl(21)	3.392 (5)
Pb(1)–Cl(3)	3.031 (4)	Pb(1)–Cl(4)	3.044 (4)
Pb(1)–O(12)	2.720 (10)	Pb(1)–O(12 ⁱ)	3.155 (15)
Pb(2)–Cl(3)	2.937 (4)	Pb(2)–Cl(4)	2.847 (4)
Pb(2)–O(31 ⁱⁱⁱ)	2.453 (12)	Pb(2)–O(32 ⁱⁱⁱ)	2.485 (12)
Pb(2)–Cl(22)	3.411 (5)	Pb(2)–Cl(4 ^{iv})	3.284 (5)
Pb(2)–O(11 ⁱⁱⁱ)	2.999 (11)	Pb(2)–O(11 ^{iv})	2.811 (11)
Pb(3)–O(11)	2.569 (12)	Pb(3)–O(12)	2.605 (12)
Pb(3)–O(21)	2.460 (11)	Pb(3)–O(22 ⁱ)	2.496 (11)
Pb(3)–Cl(11)	3.476 (5)	Pb(3)–Cl(12 ^v)	3.451 (5)
Pb(3)–Cl(4)	3.137 (5)	Pb(3)–O(31)	2.678 (10)
Pb(3)–O(32 ^v)	2.683 (11)	O(11)–C(11)	1.249 (18)
O(12)–C(11)	1.246 (18)	C(11)–C(12)	1.485 (26)
O(21)–C(21)	1.228 (20)	O(22)–C(21)	1.269 (20)
C(21)–C(22)	1.517 (28)	O(31)–C(31)	1.257 (19)
O(32)–C(31)	1.251 (18)	C(31)–C(32)	1.494 (28)

(b) Selected bond angles (°)

Cl(11)–Au(1)–Cl(12)	90.1 (2)	Cl(11)–Au(1)–Cl(11 ^v)	176.5 (3)
Cl(12)–Au(1)–Cl(11 ^v)	90.0 (2)	Cl(12)–Au(1)–Cl(12 ^v)	178.5 (3)
Cl(21)–Au(2)–Cl(22)	90.0 (2)	Cl(21)–Au(2)–Cl(21 ^{vi})	180.0
Cl(22)–Au(2)–Cl(21 ^{vi})	90.0 (2)	Cl(22)–Au(2)–Cl(22 ^{vi})	180.0
Cl(3 ⁱⁱ)–Pb(1)–O(21 ⁱ)	77.3 (3)	Cl(3 ⁱⁱ)–Pb(1)–O(22 ⁱ)	82.2 (3)
O(21 ⁱ)–Pb(1)–O(22 ⁱ)	49.9 (4)	Cl(3)–Pb(2)–Cl(4)	79.0 (1)
Cl(3)–Pb(2)–O(31 ⁱⁱⁱ)	83.3 (3)	Cl(4)–Pb(2)–O(31 ⁱⁱⁱ)	93.0 (3)
Cl(3)–Pb(2)–O(32 ⁱⁱⁱ)	124.5 (3)	Cl(4)–Pb(2)–O(32 ⁱⁱⁱ)	73.5 (3)
O(31 ⁱⁱⁱ)–Pb(2)–O(32 ⁱⁱⁱ)	51.9 (4)	O(11)–Pb(3)–O(12)	49.3 (3)
O(11)–Pb(3)–O(21)	99.2 (4)	O(12)–Pb(3)–O(21)	70.4 (4)
O(11)–Pb(3)–O(22 ⁱ)	112.3 (4)	O(12)–Pb(3)–O(22 ⁱ)	64.9 (4)
O(21)–Pb(3)–O(22 ⁱ)	68.7 (4)	O(11)–C(11)–O(12)	119.6 (15)
O(11)–C(11)–C(12)	120.5 (14)	O(12)–C(11)–C(12)	119.9 (14)
O(21)–C(21)–O(22)	118.7 (17)	O(21)–C(21)–C(22)	122.2 (16)
O(22)–C(21)–C(22)	119.0 (15)	O(31)–C(31)–O(32)	118.9 (16)
O(31)–C(31)–C(32)	121.9 (14)	O(32)–C(31)–C(32)	119.2 (15)

Symmetry operators: (i) $x, 1-y, -0.5+z$; (ii) $x, 1-y, 0.5+z$; (iii) $x, y, -1+z$; (iv) $x, 2-y, -0.5+z$; (v) $1-x, y, 0.5-z$; (vi) $0.5-x, 1.5-y, -z$.

O(12) and O(12¹) and to Cl(21), which forms part of an AuCl₄⁻ anion. Pb(2) (Fig. 1b) has an inner coordination sphere consisting of a chelating acetate O(31ⁱⁱⁱ), O(32ⁱⁱⁱ) at 2.45, 2.49 Å and the chlorides Cl(3) and Cl(4) at 3.03, 3.04 Å, and longer contacts to O(11ⁱⁱⁱ) and O(11^{iv}) (3.00, 2.81 Å) and Cl(4^{iv}) and Cl(22) (3.28, 3.41 Å). Pb(3) (Fig. 1c) is essentially coordinated only by acetates, with chelating O(11) and O(12) at 2.57, 2.61 Å, O(21) and O(22¹) (non-chelating) at 2.46, 2.60 Å and O(31), O(32^{iv}) (also non-chelating) at 2.68, 2.68 Å. Three weaker contacts are observed to the chlorides Cl(4), Cl(11) and Cl(12²)

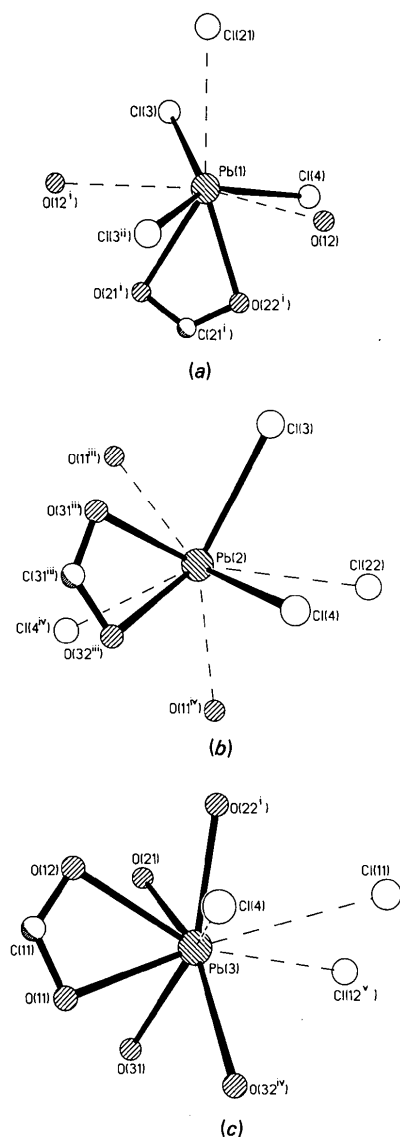


Fig. 1. The coordination spheres of the three independent Pb atoms. Radii are arbitrary. For bond lengths and angles and symmetry operators, see Table 2. Bonds longer than 2.7 Å to oxygen or 3.1 Å to Cl are dashed; this is an arbitrary division and should not be taken to imply any clear-cut difference in bonding type.

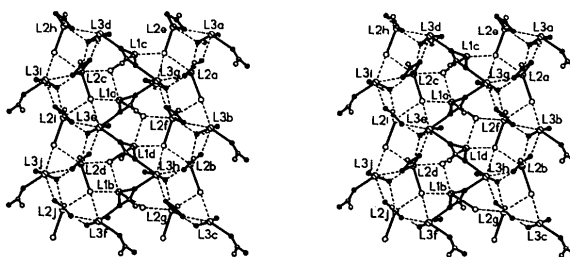


Fig. 2. Stereographic representation of part of the polymeric lead-containing sheet at $x \approx \frac{1}{8}$. The Pb atoms are given the symbol *L* rather than Pb to save space.

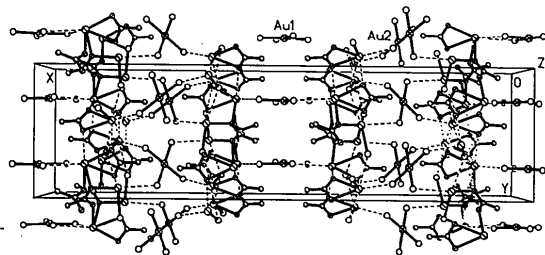


Fig. 3. Perspective view of the cell contents. The alternating lead and gold layers can be clearly distinguished. The gold layers are labelled to show whether they derive from Au(1) or Au(2).

(the latter two being tetrachloroaurate chlorides) at 3.14, 3.48 and 3.45 Å. The coordination at all lead atoms is markedly 'one-sided' as regards the shorter interactions.

Bridging acetate and chloride ions link the lead atoms to form polymeric cationic sheets $[\text{Pb}(\text{CH}_3\text{COO})_3\text{Cl}_2]_n^{n+}$ (Fig. 2), which run parallel to the *yz* plane at $x \approx \frac{1}{8}, \frac{3}{8}, \frac{5}{8}$ and $\frac{7}{8}$. The AuCl₄⁻ anions occupy the intervening layers at $x = 0, \frac{1}{2}$ for Au(1) and $\frac{1}{4}, \frac{3}{4}$ for Au(2) (Fig. 3). The gold and lead layers are linked by the Pb...Cl interactions discussed above, of which the shortest is Pb(1)...Cl(21) at 3.39 Å. This may account for the long Au(2)—Cl(21) bond, although other Pb...Cl interactions are not much longer. All these interactions involve the 'free' side of the lead coordination spheres.

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