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Diaquabis[tetrachloroaurate(III)-Cl¹, Cl²]zinc(II)

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Abstract. [Zn(AuCl₄)₂(H₂O)₂], $M_r = 779.0$, monoclinic, $P2_1/n$, $a = 7.576$ (2), $b = 12.113$ (2), $c = 15.355$ (3) Å, $\beta = 103.51$ (2)°, $V = 1370.1$ Å³, $Z = 4$, $D_x = 3.78$ Mg m⁻³, $\lambda(\text{Mo } K\alpha) = 0.71069$ Å, $\mu = 24.7$ mm⁻¹, $F(000) = 1376$, $T = 293$ K. The structure was refined to $R = 0.034$ for 2057 unique observed reflections. Discrete [Zn(AuCl₄)₂(H₂O)₂] molecules are observed; the coordination geometry at Zn is distorted octahedral and at gold square-planar. The water ligands are mutually *cis*. Two Cl atoms of each AuCl₄ ion bridge to zinc; the bridging Au–Cl bonds are appreciably longer than their non-bridging counterparts.

Introduction. Our recent studies of tetrachloroaurate(III) salts have involved both monatomic (Tl, Na) and polyatomic (SCl₃, SeCl₃, TeCl₃, PCl₄) cations (Jones, Schelbach & Schwarzmänn, 1987a; Jones, Hohbein & Schwarzmänn, 1988; Jones, Jentsch & Schwarzmänn, 1988; Jones, Schelbach & Schwarzmänn, 1987b; Jones, Jentsch & Schwarzmänn, 1986; Freire Erdbrügger, Jones, Schelbach, Schwarzmänn & Sheldrick, 1987). Many other crystallographic studies of AuCl₄⁻ salts have been performed; for a summary, see Jones (1981, 1983, 1986).

Two tetrachloroaurates of zinc have been described in the literature. von Bonsdorff (1829) reported a

dodecahydrate that was 'stable even in fairly moist air'. Topsøe (1874) reported an octahydrate that deliquesced even in quite dry air. It is not clear if these compounds are in fact identical.

We wished to ascertain if anhydrous zinc bis(tetrachloroaurate) exists. 100 mg gold(III) chloride and 45 mg zinc chloride (Fluka purum p.a., anhydrous) were sealed in a glass ampoule under nitrogen in 4 ml AsCl₃ as solvent. The ampoule was heated to 373 K for 12 h and allowed to cool. Two types of crystal separated; red (Au₂Cl₆) and yellow (the title compound). The nature of the yellow product was established by this structure determination. Because the compound is very moisture sensitive, crystals were sealed in glass capillaries under inert oil.

Experimental. A crystal 0.15 × 0.12 × 0.04 mm was used to record 4595 profile-fitted intensities (Clegg, 1981) on a Stoe–Siemens four-circle diffractometer (monochromated Mo K α radiation, $2\theta_{\text{max}} 50^\circ$, hemisphere $\pm h \pm k \pm l$). Three check reflections showed no significant intensity change. An absorption correction based on ψ scans was applied; transmissions ranged from 0.31 to 0.67. Merging equivalents gave 2400 unique reflections ($R_{\text{int}} 0.025$, index range $h -9$ to $+8$, $k 0$ to 14 , $l 0$ to 18), 2057 of which with $F > 4\sigma(F)$ were

used for all calculations [program system *SHELX* (Sheldrick, 1986), locally modified by its author]. Cell constants were refined from 2θ values of 46 reflections in the range $20\text{--}25^\circ$.

The structure was solved by the heavy-atom method and refined anisotropically on F to $R = 0.034$, $wR = 0.030$. H atoms were not located. The weighting scheme was $w^{-1} = \sigma^2(F) + 0.0001F^2$. An extinction correction of the form $F_{\text{corr}} = F_c/[1 + xF^2/\sin 2\theta]^{0.25}$ was applied; x refined to $4.4(2) \times 10^{-7}$. 119 parameters; $S = 1.5$; max. shift/e.s.d. = 0.002 ; max. residual electron density within $\pm 1.0 e \text{ \AA}^{-3}$ near Au(1). Scattering factors taken 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. If the oxygen atoms have been correctly identified as belonging to H_2O ligands, the composition of the yellow product is $\text{Zn}(\text{AuCl}_4)_2 \cdot 2\text{H}_2\text{O}$. It is surprising that the Zn retains traces of water so tenaciously, even in AsCl_3 as solvent. The assumption that the water arose from the nominally 'anhydrous' zinc chloride is lent weight by the observation that the use of $\text{ZnCl}_2 \cdot 4\text{H}_2\text{O}$ leads almost quantitatively to the title compound under the same conditions.

The structure consists of isolated $[\text{Zn}(\text{AuCl}_4)_2(\text{H}_2\text{O})_2]$ units (Fig. 1). Each tetrachloroaurate ion contributes two chlorines to the coordination sphere of the zinc, which thereby attains a distorted geometry (the 'bite' of an AuCl_4 ligand is not sufficient to give a Cl-Zn-Cl angle of 90°). The two water ligands are mutually *cis*.

The Zn-Cl bond lengths range from $2.474(3)$ to $2.547(3)$ Å. Most chlorozinc species in the crystallographic literature involve tetrahedrally coordinated zinc: in orthorhombic ZnCl_2 the bond lengths are $2.265(7)$ – $2.282(8)$ Å (Yakel & Brynstad, 1978); in the ZnCl_4 units of $\text{ZnCl}_2 \cdot \text{H}_2\text{O} \cdot \frac{1}{2}\text{HCl}$ $2.21(3)$ – $2.30(2)$ Å (Follner, 1970); in the ZnCl_4 units of $\text{ZnCl}_2 \cdot \frac{4}{3}\text{H}_2\text{O}$ $2.23(1)$ – $2.35(1)$ Å (Follner & Brehler, 1970); and in the assumed $\text{ZnCl}_3(\text{H}_2\text{O})$ units of $27.5 M$ aqueous ZnCl_2 2.28 Å [by X-ray diffraction from the solution (Kruh & Standley, 1962)]. Wells (1984) points out that 'the preference for tetrahedral coordination [of zinc] by Cl is very marked'. In the octahedral $\text{Zn}(\text{H}_2\text{O})_4\text{Cl}_2$ units of $\text{ZnCl}_2 \cdot \frac{4}{3}\text{H}_2\text{O}$ (Follner & Brehler, 1970) the Zn-Cl bond length is $2.60(1)$ Å, the Cl ions bridging to the tetrahedral zinc. It may be concluded that Zn-Cl bond lengths are greatly affected by coordination type.

* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 44840 (10 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 ($\text{\AA}^2 \times 10^3$)

	<i>x</i>	<i>y</i>	<i>z</i>	U_{eq}^*
Au(1)	6399.3 (5)	619.5 (3)	1344.4 (3)	33 (1)
Au(2)	2813.7 (5)	4774.1 (3)	481.1 (3)	33 (1)
Zn	3815 (2)	2687 (1)	2139 (1)	36 (1)
Cl(11)	3802 (4)	672 (2)	1872 (2)	43 (1)
Cl(12)	6904 (3)	2416 (2)	1780 (2)	50 (1)
Cl(13)	8955 (4)	586 (3)	819 (2)	60 (1)
Cl(14)	5869 (4)	-1171 (2)	946 (2)	58 (1)
Cl(21)	4270 (4)	4695 (2)	1968 (2)	41 (1)
Cl(22)	2291 (4)	2912 (2)	523 (2)	48 (1)
Cl(23)	1377 (4)	4834 (2)	-988 (2)	52 (1)
Cl(24)	3334 (5)	6611 (2)	472 (2)	62 (1)
O(1)	4933 (10)	2777 (6)	3474 (5)	54 (3)
O(2)	1333 (10)	2683 (6)	2424 (5)	57 (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)

Au(1)–Cl(11)	2.297 (3)	Au(1)–Cl(12)	2.283 (3)
Au(1)–Cl(13)	2.265 (3)	Au(1)–Cl(14)	2.263 (3)
Au(2)–Cl(21)	2.293 (2)	Au(2)–Cl(22)	2.294 (3)
Au(2)–Cl(23)	2.266 (3)	Au(2)–Cl(24)	2.261 (3)
Zn–Cl(11)	2.474 (3)	Zn–Cl(12)	2.547 (3)
Zn–Cl(21)	2.480 (3)	Zn–Cl(22)	2.496 (3)
Zn–O(1)	2.029 (7)	Zn–O(2)	2.028 (8)

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

Cl(11)–Au(1)–Cl(12)	88.2 (1)	Cl(11)–Au(1)–Cl(13)	179.4 (1)
Cl(12)–Au(1)–Cl(13)	91.3 (1)	Cl(11)–Au(1)–Cl(14)	90.5 (1)
Cl(12)–Au(1)–Cl(14)	178.4 (1)	Cl(13)–Au(1)–Cl(14)	90.0 (1)
Cl(21)–Au(2)–Cl(22)	88.7 (1)	Cl(21)–Au(2)–Cl(23)	79.4 (1)
Cl(22)–Au(2)–Cl(23)	90.8 (1)	Cl(21)–Au(2)–Cl(24)	90.2 (1)
Cl(22)–Au(2)–Cl(24)	178.8 (1)	Cl(23)–Au(2)–Cl(24)	90.4 (1)
Cl(11)–Zn–Cl(12)	78.8 (1)	Cl(11)–Zn–Cl(21)	161.0 (1)
Cl(12)–Zn–Cl(21)	86.9 (1)	Cl(11)–Zn–Cl(22)	87.7 (1)
Cl(12)–Zn–Cl(22)	91.9 (1)	Cl(21)–Zn–Cl(22)	80.3 (1)
Cl(11)–Zn–O(1)	101.8 (2)	Cl(12)–Zn–O(1)	92.2 (2)
Cl(21)–Zn–O(1)	91.1 (2)	Cl(22)–Zn–O(1)	170.2 (2)
Cl(11)–Zn–O(2)	93.8 (2)	Cl(12)–Zn–O(2)	172.5 (2)
Cl(21)–Zn–O(2)	100.6 (2)	Cl(22)–Zn–O(2)	88.7 (2)
O(1)–Zn–O(2)	88.4 (3)	Au(1)–Cl(11)–Zn	96.6 (1)
Au(1)–Cl(11)–Zn	95.0 (1)	Au(2)–Cl(21)–Zn	95.8 (1)
Au(2)–Cl(22)–Zn	95.3 (1)		

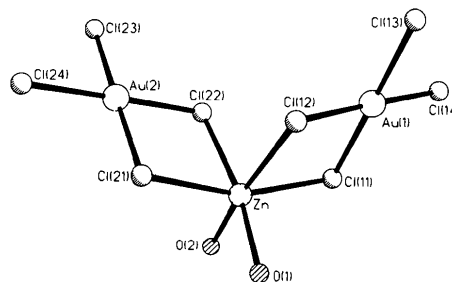


Fig. 1. The $[\text{Zn}(\text{AuCl}_4)_2(\text{H}_2\text{O})_2]$ unit in the crystal, showing the atom-numbering scheme. Radii are arbitrary.

The Zn–O bond lengths of $2.029(7)$, $2.028(8)$ Å are essentially the same as in the above-mentioned $\text{Zn}(\text{H}_2\text{O})_4\text{Cl}_2$ units [$2.02(2)$, $2.03(2)$ Å (Follner & Brehler, 1970)].

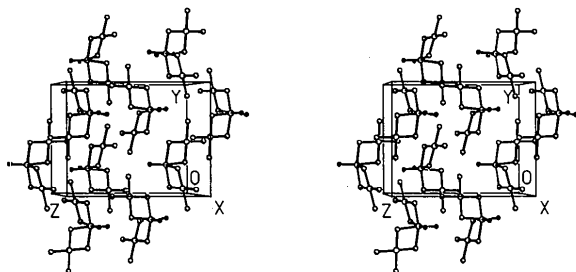


Fig. 2. Stereographic packing diagram of the title compound.

The Au—Cl bond lengths lie in the usual range (Jones, 1981, 1983, 1986); as would be expected, the bridging chlorines are involved in appreciably longer Au—Cl bonds than the non-bridging [mean 2.292 (3), 2.264 (3) Å respectively]. The Au atoms display the usual square-planar geometry.

A packing diagram of the structure is shown in Fig. 2. Selected non-bonded distances: O(2)···Cl(12) ($-1+x, y, z$) 3.29 (1), O(1)—Cl(14) ($1.5-x, 0.5+y, 0.5-z$) 3.35 (1), Cl(23)···Au(2) ($-x, 1-y, -z$) 3.47 (1) Å. There are several other O···Cl contacts in the range 3.3–3.6 Å. Within the title molecule, the Zn···Au distances are 3.565, 3.542 (2) Å.

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Anhydrous Sodium Tetrachloroaurate(III)

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Abstract. NaAuCl₄, $M_r = 361.8$, monoclinic, $P2_1/n$, $a = 11.277$ (5), $b = 11.234$ (5), $c = 20.584$ (12) Å, $\beta = 104.58$ (5)°, $V = 2524$ Å³, $Z = 16$, $D_x = 3.81$ Mg m⁻³, $\lambda(\text{Mo } K\alpha) = 0.71069$ Å, $\mu = 24.9$ mm⁻¹, $F(000) = 2528$, $T = 293$ K. The structure was refined to $R = 0.077$ for 3664 unique observed reflections. There are four formula units in the asymmetric unit. The anions show the expected square-planar geometry, with an average Au—Cl bond length of 2.277 (2) Å. Each Na ion is coordinated by seven chlorines; the Na···Cl contacts vary from 2.82 (1) to 3.19 (2) Å.

Introduction. Many salts of the AuCl₄⁻ anion have been structurally characterized; available results are reviewed by Jones (1981, 1983, 1986). The only

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structure determinations of anhydrous $M^+ \cdot \text{AuCl}_4^-$ salts are for $M = \text{K}$ [(Bonamico & Dessy, 1973) of limited precision because of pseudosymmetry], Rb (Strähle & Bärnighausen, 1970) and Tl [(Jones, Schelbach & Schwarzmann, 1987) isostructural with the Rb salt]. The structure of NaAuCl₄·2H₂O has been determined (Bonamico, Dessy & Vaciego, 1966).

We have obtained anhydrous NaAuCl₄ as orange prisms from the reaction between carbonyl gold(I) chloride and sodium tetrachloroaluminate in thionyl chloride.

Experimental. The crystals of the title compound are moisture sensitive and were therefore transferred from the reaction mixture into glass capillaries under inert oil.