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Tetraphenylarsonium Tetrachloroaurate(III)

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Abstract. $C_{24}H_{20}AsAuCl_4$, tetragonal, $P4/n$, $a=b=12{\cdot}448$ (4), $c=8{\cdot}034$ (2) Å, $U=1244{\cdot}9$ Å^3, $Z=2$, $D_x=1{\cdot}926$ g cm^{-3}. The structure consists of discrete $[AsPh_4]^+$ ions with crystallographic $\bar{4}$ symmetry, and $[AuCl_4]^-$ ions which lie on crystallographic fourfold axes but approximate closely to $4/mmm$ symmetry. The structure was refined to an R of 0·044 for 1181 diffractometer data.

Introduction. The structure of $Ph_4As^+AuCl_4^-$ has been determined to establish the precise anion geometry prior to ^{197}Au Mössbauer studies on a series of four-coordinated Au(III) complexes.

Pale-yellow crystals were obtained by slow evaporation from acetone, and were found to be stable to air and X-rays. Intensities were determined with an automated Stoe two-circle diffractometer, Mo $K\alpha$ radiation, graphite monochromator, and a crystal, $0{\cdot}2\times0{\cdot}2\times0{\cdot}15$ mm, (layers 0–22), mounted about [110]. After application of Lp and absorption corrections, inter-layer scale factors were derived by a linear least-squares analysis of equivalent reflexions from different layers. 3599 reflexions were measured; averaging equivalent reflexions gave 1181 unique reflexions with $F>2{\cdot}5\sigma(F)$ based on counting statistics. Cell dimensions were obtained by a least-squares analysis of 201 diffractometer zero-layer ω angle measurements.

The atoms were located from Patterson and difference syntheses; the Au and As atoms occupy special positions $(\frac{1}{4},\frac{1}{4},z)$ and $(\frac{1}{4},\frac{3}{4},0)$ respectively. A rigid phenyl group with C–C 1·395, C–H 1·08 Å and all angles 120° was employed in the final refinement because the reduction in R' (0·0008 for 12 additional parameters) when the C atoms were released was not considered to be significant. The H atom isotropic temperature factors were fixed at $U=0{\cdot}08$ Å^2. The final $R'=\sum w^{1/2}\Delta/\sum w^{1/2}|F_o|$ was 0·034, with a corresponding R of 0·044; the weighting scheme was $w=1/[\sigma^2(F)+0{\cdot}000101\ F^2]$ which led to a mean value of $w\Delta^2$ virtually independent of $\sin\theta$ or the magnitude of F_o. An empirical isotropic extinction parameter was included in the refinement; complex neutral-atom scattering factors were employed. Final atomic coordinates and thermal parameters are given in Table 1, and the resulting interatomic distances and angles in Table 2.*

* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 31155 (8 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

Table 1. *Atom coordinates* ($\times10^4$) *and temperature factors* (Å$^2\times10^3$)

The temperature exponent takes the form: $-2\pi^2(U_{11}h^2a^{*2}+\ldots+2U_{12}hka^*b^*+\ldots)$.

	x/a	y/b	z/c	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Au(1)	2500	2500	2001 (1)	72 (1)	72 (1)	36 (1)	0	0	0
As(1)	2500	7500	0	44 (1)	44 (1)	35 (1)	0	0	0
Cl(1)	915 (2)	1596 (2)	2025 (2)	81 (1)	100 (1)	79 (1)	−12 (1)	18 (1)	−14 (1)
C(1)	3696 (3)	7630 (3)	1412 (4)	45 (3)	53 (3)	41 (2)	−7 (2)	−1 (2)	7 (2)
C(2)	3744 (3)	7018 (3)	2864 (4)	52 (3)	80 (4)	51 (3)	12 (3)	0 (3)	13 (3)
C(3)	4589 (3)	7165 (3)	3983 (4)	67 (4)	98 (5)	46 (3)	−1 (3)	−7 (3)	29 (3)
C(4)	5384 (3)	7924 (3)	3649 (4)	70 (4)	84 (5)	72 (4)	−24 (4)	−29 (3)	12 (4)
C(5)	5335 (3)	8537 (3)	2197 (4)	80 (5)	77 (4)	91 (5)	1 (4)	−35 (4)	−18 (4)
C(6)	4491 (3)	8390 (3)	1078 (4)	64 (4)	59 (4)	63 (4)	−4 (3)	−19 (3)	−7 (3)
H(2)	3129 (3)	6429 (3)	3122 (4)						
H(3)	4627 (3)	6691 (3)	5107 (4)						
H(4)	6038 (3)	8038 (3)	4516 (4)						
H(5)	5951 (3)	9125 (3)	1939 (4)						
H(6)	4453 (3)	8864 (3)	−46 (4)						

Table 2. *Bond lengths* (Å) *and angles* (°)

Cl(1)–Au(1)	2·271 (4)	Cl(1)–As(1)	1·878 (5)
Cl(1)–Au(1)–Cl(1^{i})	179·0 (1)	Cl(1)–Au(1)–Cl(1^{ii})	90·0 (1)
C(2)–C(1)—As(1)	119·5 (2)	C(6)–C(1)—As(1)	120·3 (2)
C(1)–As(1)–C(1^{iii})	105·7 (3)	C(1)–As(1)–C(1^{iv})	111·4 (2)

The superscripts refer to the following equivalent positons:

(i) $0{\cdot}5-x,0{\cdot}5-y,z$ (ii) $0{\cdot}5-y,x,z$
(iii) $0{\cdot}5-x,1{\cdot}5-y,z$ (iv) $-0{\cdot}5+y,1-x,-z$
(v) $1-y,0{\cdot}5+x,-z$

Discussion. The Au atom lies 0·020 (2) Å from the plane of the four Cl atoms; since this is about one tenth of the r.m.s. thermal amplitude of the Au atom normal to the plane, for chemical purposes the ion may be considered to possess 4/*mmm* symmetry. The Au–Cl distance of 2·271 Å is consistent with previous measurements [*e.g.* 2·273 Å in ammonium tetrachloroaurate(III): Bonamico, Dessy, Furlani & Capece (1973)]. The cation has crystallographic $\bar{4}$ symmetry; the C–As bond is tilted by 4·1° with respect to the plane of the phenyl group, and the smallest dihedral angles about the C–As bond are: C(6)–C(1)–As–C(1)^{v} −15·1°, C(2)–C(1)–As–C(1)^{iii} 39·0°, C(2)–C(1)–As–C(1)^{iv} −82·1° and C(6)–C(1)–As–C(1)^{iv} 102·6°.* There are no short interionic contacts, which simplifies the interpretation of the Mössbauer spectra.

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* For symmetry transformations see Table 2.

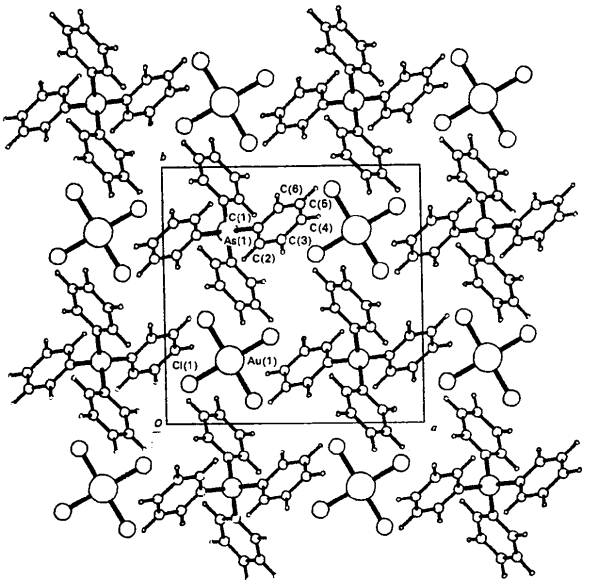

Fig. 1. The structure in projection down **c**.

Reference

BONAMICO, M., DESSY, G., FURLANI, C. & CAPECE, F. M. (1973). *Acta Cryst.* B**29**, 1737–1739.

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Calcium Divanadate Dihydrate

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Abstract. $Ca_2V_2O_7.2H_2O$, triclinic, $P\bar{1}$, $a=8{\cdot}1344$ (6), $b=8{\cdot}2019$ (7), $c=6{\cdot}8683$ (5) Å, $\alpha=96{\cdot}238$ (7)°, $\beta=113{\cdot}355$ (6)°, $\gamma=106{\cdot}192$ (8)°, $Z=2$, $D_x=2{\cdot}801$, $D_m=2{\cdot}81$ (2) g cm^{-3}. Anisotropic refinement of 1730 Mo $K\alpha$ counter-measured data to $R=0{\cdot}070$. The structure contains layers of packed $V_2O_7^{4-}$ groups and H_2O molecules, interleaved with Ca^{2+} ions.

Introduction. In a study of the chemistry of calcium vanadates in aqueous solution, Marvin & Magin (1959) obtained two crystalline products in the region of *p*H 8–9, which by analysis proved to be $Ca_2V_2O_7.2H_2O$ and $Ca_2V_2O_7$. We have carried out a crystal-structure determination of crystals from Marvin & Magin's original sample of the dihydrate, and the results are reported here. The crystals were prepared from a stock solution 0·04 *M* in CaO and 0·08 *M* in V_2O_5, having a *p*H of about 5, which was adjusted to about *p*H 8 by adding a solution of $Ca(OH)_2$, filtered and then evaporated at room temperature. A static thermogravimetric experiment (samples heated to various temperatures for 24 h, then cooled and weighed) showed that the dihydrate is converted to a monohydrate at 130 °C and to the anhydrous state at 220 °C (± 10°).

Schwendt, Petrovič & Žúrková (1971), in a study of solid alkaline earth divanadates, formed three compounds $Ca_2V_2O_7.2H_2O$, $Ca_2V_2O_7.H_2O$ and $Ca_2V_2O_7$. As far as we can tell from the meagre X-ray powder data of Schwendt *et al.* as compared with ours, our dihydrate and anhydrous phases are identical with their corresponding ones. They reported the results of DTA, TGA, and IR studies but gave no crystallographic information. According to Pedregosa, Baran & Aymonino (1973), $Ca_2V_2O_7$ is isostructural with tetragonal β-$Sr_2V_2O_7$.

$Ca_2V_2O_7.2H_2O$ forms colorless, lath-like, parallelogram-shaped crystals, bounded laterally by $\{1\bar{1}1\}$ and $\{2\bar{1}\bar{1}\}$ and flattened parallel to (100) (angle on face = 79·4°). The crystal used for intensity measurements was 0·15 × 0·15 × 0·015 mm in size, and was considered