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Tetraphenylarsonium Tetracyanoaurate(III) Dichloromethane Solvate

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Abstract. $[As(C_6H_5)_4][Au(CN)_4].CH_2Cl_2$, $M_r = 769{\cdot}3$, orthorhombic, *Pbcm*, $a = 9{\cdot}205$ (2), $b = 13{\cdot}776$ (2), $c = 23{\cdot}213$ (3) Å, $V = 2943{\cdot}6$ Å^3, $Z = 4$, $D_x = 1{\cdot}74$ Mg m^{-3}, λ(Mo $K\alpha$) = 0·71069 Å, $\mu = 6{\cdot}3$ mm^{-1}, $F(000) = 1480$, $T = 293$ K, $R = 0{\cdot}042$ for 2043 unique observed reflections. The Au atom occupies the special position $\frac{1}{2},\frac{1}{2},0$ with crystallographic symmetry $\bar{1}$, but the actual symmetry of the anion is close to the ideal $4/mmm$. The As atom lies in the mirror plane $x,y,\frac{1}{4}$. The solvent molecule is ordered, its central C atom lying on the twofold axis $x,\frac{3}{4},\frac{1}{2}$. The extended structure consists of two kinds of layers, one composed of cations and the other of anions and solvent. The Au—C bond lengths, 1·999 (7) and 2·014 (7) Å, are appreciably longer than in $Au(CN)_2^-$ complexes with large cations.

Introduction. We have recently reported the synthesis and structure of $Ph_4As^+.Au(SeCN)_4^-$ (Jones & Thöne, 1987); the compound had already been reported by Schmidtke & Garthoff (1967). The reaction between this compound and Ph_3As gave a colourless solution, from which the title compound could be isolated as a white powder. Presumably the reaction also leads to the formation of Ph_3AsSe, but we have not proved this. One of us (Jones, 1976) has already reported the synthesis of the title compound by other methods.

Experimental. The title compound was recrystallized by liquid diffusion of diisopropyl ether into a dichloromethane solution. Colourless prisms were obtained, which gradually became opaque on exposure to air. This loss of solvent is, however, slow enough to permit the crystals to be mounted in glass capillaries without special precautions.

A crystal 0·6 × 0·15 × 0·15 mm was used to collect 6752 profile-fitted intensities (Clegg, 1981) on a Stoe–Siemens four-circle diffractometer; $\omega/2\theta$ scans; monochromated Mo $K\alpha$ radiation, $2\theta_{max} = 50°$, octants $+h$ $+k$ $+l$ and $-h$ $-k$ $-l$ and some additional equivalents. Merging equivalents gave 2643 unique reflections ($R_{int} = 0{\cdot}025$, index ranges h 0 to 10, k 0 to 16, l 0 to 27), of which 2043 with $F > 4\sigma(F)$ were used for all calculations. The program system was *SHELX*76 (Sheldrick, 1976), locally modified by its author. An absorption correction based on ψ scans was applied; transmission factors 0·78–0·92. Three check reflections decreased in intensity by 14%, and an appropriate scaling was applied. Cell constants were refined from 2θ values of 44 reflections in the range 20–24°.

The structure was solved by the heavy-atom method and subjected to full-matrix anisotropic least-squares refinement on F. H atoms were included using a riding model. The solvent molecule was well-behaved. The final R was 0·042, $wR = 0{\cdot}037$; 177 parameters, $S = 1{\cdot}7$, weighting scheme $w^{-1} = \sigma^2(F) + 0{\cdot}00015F^2$, max. $\Delta/\sigma = 0{\cdot}014$, max. $|\Delta\rho| = 0{\cdot}8$ e Å^{-3}. Scattering factors were 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 three separate species present in the structure all exhibit crystallographic symmetry. The $Au(CN)_4^-$ anions are associated with symmetry centres $\frac{1}{2},\frac{1}{2},0$, but their actual symmetry is close to the ideal

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† 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 51307 (12 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Table 1. *Atomic coordinates* ($\times 10^4$) *and equivalent isotropic displacement parameters* ($Å^2 \times 10^3$)

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

	x	y	z	U_{eq}
Au	5000	5000	0	44 (1)
C(1)	6811 (7)	5118 (5)	−470 (3)	54 (2)
N(1)	7811 (7)	5183 (5)	−747 (3)	78 (3)
C(2)	5563 (8)	6189 (5)	452 (3)	52 (2)
N(2)	5882 (7)	6842 (5)	714 (3)	72 (3)
As	6268 (1)	5833·1 (7)	2500	39 (1)
C(11)	6737 (6)	5066 (4)	3159 (3)	41 (2)
C(12)	5742 (7)	4369 (5)	3329 (3)	54 (2)
C(13)	6098 (9)	3754 (5)	3775 (3)	67 (3)
C(14)	7404 (9)	3820 (5)	4044 (3)	68 (3)
C(15)	8404 (8)	4501 (6)	3875 (3)	67 (3)
C(16)	8071 (7)	5129 (5)	3427 (3)	55 (2)
C(21)	4237 (9)	6148 (6)	2500	44 (3)
C(22)	3530 (7)	6302 (5)	3018 (3)	60 (2)
C(23)	2120 (8)	6619 (6)	3010 (3)	76 (3)
C(24)	1401 (12)	6781 (8)	2500	69 (4)
C(31)	7290 (8)	7042 (6)	2500	38 (3)
C(32)	7592 (7)	7507 (5)	1984 (3)	58 (2)
C(33)	8216 (8)	8424 (5)	1992 (3)	72 (3)
C(34)	8517 (12)	8866 (7)	2500	72 (4)
C(10)	8962 (13)	7500	5000	90 (5)
Cl	9998 (3)	6729 (2)	4590 (1)	114 (1)

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

Au—C(1)	1·999 (7)	Au—C(2)	2·014 (7)
C(1)—N(1)	1·127 (9)	C(2)—N(2)	1·124 (9)
As—C(11)	1·910 (6)	As—C(21)	1·919 (8)
As—C(31)	1·912 (8)	C(11)—C(12)	1·385 (9)
C(11)—C(16)	1·378 (8)	C(12)—C(13)	1·377 (10)
C(13)—C(14)	1·358 (11)	C(14)—C(15)	1·372 (11)
C(15)—C(16)	1·388 (10)	C(21)—C(22)	1·383 (7)
C(22)—C(23)	1·369 (9)	C(23)—C(24)	1·374 (9)
C(31)—C(32)	1·386 (8)	C(32)—C(33)	1·387 (10)
C(33)—C(34)	1·356 (9)	C(10)—Cl	1·717 (7)
C(1)—Au—C(2)	90·2 (3)	Au—C(2)—N(2)	178·7 (6)
C(2)—Au—C(1^{i})	89·8 (3)	C(11)—As—C(31)	111·8 (2)
Au—C(1)—N(1)	178·2 (6)	C(11)—As—C(11^{ii})	106·5 (4)
C(11)—As—C(21)	110·2 (2)	As—C(11)—C(16)	121·8 (5)
C(21)—As—C(31)	106·4 (3)	C(11)—C(12)—C(13)	118·9 (6)
As—C(11)—C(12)	117·6 (4)	C(13)—C(14)—C(15)	120·5 (7)
C(12)—C(11)—C(16)	120·3 (6)	C(11)—C(16)—C(15)	119·7 (6)
C(12)—C(13)—C(14)	121·1 (7)	C(22)—C(21)—C(22^{ii})	120·6 (8)
C(14)—C(15)—C(16)	119·5 (7)	C(22)—C(23)—C(24)	121·3 (7)
As—C(21)—C(22)	119·6 (4)	As—C(31)—C(32)	120·1 (4)
C(21)—C(22)—C(23)	118·9 (6)	C(31)—C(32)—C(33)	119·5 (7)
C(23)—C(24)—C(23^{ii})	118·9 (10)	C(33)—C(34)—C(33^{ii})	120·8 (10)
C(32)—C(31)—C(32^{ii})	119·5 (8)		
C(32)—C(33)—C(34)	120·4 (7)		
Cl—C(10)—Cl^{iii}	112·5 (7)		

Symmetry operators: (i) $1-x$, $1-y$, $-z$; (ii) x, y, $0·5-z$; (iii) x, $1·5-y$, $1-z$.

$4/mmm$. The Ph_4As^+ cations possess crystallographic m symmetry (As on $x,y,\frac{1}{4}$) and the CH_2Cl_2 molecule crystallographic twofold symmetry (C on $x,\frac{3}{4},\frac{1}{2}$). All three species are shown, together with the numbering scheme of the asymmetric unit, in Fig. 1. Fig. 2 shows the crystal packing; there are two distinct layers, one type at $z = \frac{1}{4},\frac{3}{4}$ consisting of cations and the other, at $z = 0,\frac{1}{2}$, containing anions and solvent. Müller (1980) has discussed structural relationships of Ph_4E^+ salts, including a hypothetical structure type in *Pmab* (an alternative setting of the current space group *Pbcm*), but the present structure does not correspond to this type, because the cations are not parallel to each other in the y direction and because the anions are associated with special positions $4(a)$ rather than $4(c)$.

As far as we are aware, only two other structural studies of $Au(CN)_4^-$ salts have been carried out. In $H_5O_2^+.Au(CN)_4^-$ (Pennemann & Ryan, 1972) the Au—C bond lengths were 1·95, 1·99 (2) Å, and in $KAu(CN)_4.H_2O$ (neutron diffraction; Bertinotti & Bertinotti, 1970) 1·98 (1) Å (av.). In the current structure the Au—C bonds are slightly longer, 1·999 and 2·014 (7) Å. A rigid-body libration correction for the $Au(CN)_4^-$ ion indicated bond-length corrections of +0·009 Å for Au—C bonds, +0·006 Å for C(1)—N(1) and +0·005 Å for C(2)—N(2), but these corrections may not be completely reliable because of uncertainties in the anisotropic thermal parameters of the light atoms.

Several compounds containing the Au^I ion $Au(CN)_2^-$ have been structurally investigated, and the comparison of Au—C bond lengths for the different oxidation states of the metal seems worthwhile. The precision of Au—C bond lengths is inherently low, but some trends can be recognized. First, the Au—C bond lengths in $Au(CN)_2^-$ seem to depend on the nature of the

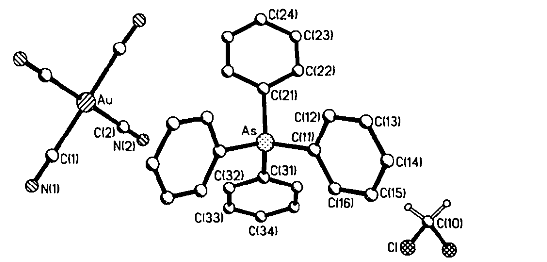

Fig. 1. Perspective view of the title compound in the crystal, showing the numbering scheme of the asymmetric unit. For a discussion of the various types of crystallographically imposed symmetry, see text. Radii are arbitrary; cation H omitted for clarity.

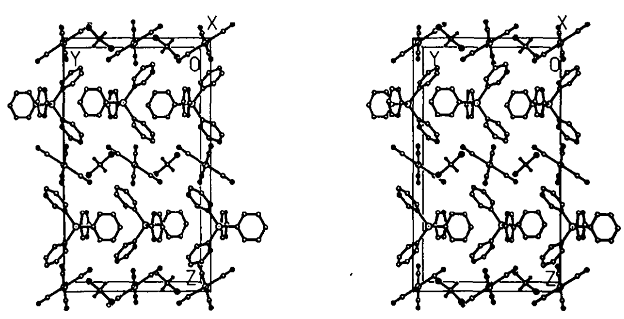

Fig. 2. Stereo packing diagram of the title compound. Radii are arbitrary, cation H omitted for clarity.

counterion. For monatomic counterions, the bond length is longer than for polyatomic {2·00 (3), 2·004 (19) Å in $Co[Au(CN)_2]_2$, Zyontz, Abrahams & Bernstein, 1981; 1·994 (11) Å in $KCo[Au(CN)_2]_3$, Abrahams, Bernstein, Liminga & Eisenmann, 1980; 1·993–1·998 (22) Å in $K_5[Au(CN)_2]_4[Au(CN)_2I_2]$.-$2H_2O$, Bertinotti & Bertinotti, 1972: *cf.* 1·939 (19) Å in a $C_{10}H_{10}S_4Se_2^{0.5+}$ salt, Kikuchi, Ishikawa, Saito, Ikemoto & Kobayashi, 1988; 1·88, 1·94 (2) Å in a potassium crown ether salt, Krasnova *et al.*, 1984}. This could be attributable to the effects of N···metal interactions. Secondly, for large counterions, the Au—C bond is longer for $Au(CN)_4^-$ than for $Au(CN)_2^-$; this may be a consequence of the better 'soft–soft' interactions for Au^I. These conclusions must be regarded as tentative, but are supported by observations of $AuCl_4^-$ and $AuCl_2^-$ salts, with more ionic bonding and less sensitivity of the Au—*X* bond length to oxidation state; a large number of $AuCl_4^-$ salts have Au—Cl bond lengths near the typical value of *ca* 2·27 Å (Jones, 1981), and various $AuCl_2^-$ salts show similar values, *e.g.* 2·257 (4) Å for the Bu_4N^+ salt (Braunstein, Müller & Bögge, 1986), 2·269–2·286 (6) Å for the Et_4N^+ salt (Helgesson & Jagner, 1987), and 2·260 (14), 2·293 (15) Å for the py_2Au^+ salt (Adams, 1980).

Future, more extensive measurements may enable us to distinguish the effects of other factors such as hybridization and electrostatic interactions.

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Structure of [3,3′-(2,2-Dimethylpropylene)diiminodipropionamide]copper(II) Perchlorate Monohydrate

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Abstract. $[Cu(C_{11}H_{24}N_4O_2)](ClO_4)_2.H_2O$, $M_r = 524·8$, monoclinic, $P2_1/c$, $a = 16·757$ (4), $b = 11·290$ (3), $c = 11·531$ (3) Å, $\beta = 108·28$ (2)°, $U = 2071·4$ (9) Å^3, $Z = 4$, $D_x = 1·683$ Mg m^{-3}, λ(Mo $K\alpha$) = 0·7093 Å, $\mu = 1·37$ mm^{-1}, $F(000) = 1084$, $T = 295$ (3) K, $R = 0·035$, $wR = 0·026$ for 3128 observed reflections. The Cu atom has coordination number six, two O(carbamoyl), two N(diamine) and two $O(ClO_4)$, forming a (4+2)-type complex. The central six-membered ring formed between the ligand and the Cu atom is in the chair conformation whereas the other two rings are twisted chairs. The solvate water molecules are hydrogen bonded to molecules of the complex, holding them together. The H atoms attached to the amino groups, NH, are on the same side of the least-squares plane of the Cu-coordinated atoms.

Introduction. Previous papers (Liu & Chung, 1985, 1986; Chao & Chung, 1987, 1988; Lee, Lu, Liu, Chung & Lee, 1984; Lee, Hong, Liu, Chung & Lee,

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