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THE CRYSTAL AND MOLECULAR STRUCTURE OF TETRABUTYLAMMONIUM TETRAPHENYLAURATE(III)

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Summary

An X-ray structure determination of tetrabutylammonium tetraphenylaurate(III) has shown that the tetraphenylaurate(III) anion consists of four phenyl rings σ-bonded to the central gold atom in a square-planar arrangement. The phenyl groups *trans* to each other are in the same plane. The crystals are monoclinic, space group, $I2/c$, a 17.15(3), b 10.31(2), c 22.76(5) Å, β 115.4(2)°, V 3635.2 Å^3, $Z = 4$, ρ_c 1.37 g cm^{-3}, μ(Cu-K_α) 79.12 cm^{-1}, $R = 0.0957$.

Introduction

Liddle and Parkin [1] have described the syntheses of a number of arylgold(III) complexes. The same workers also investigated a number of anionic arylgold complexes [2]. One of these compounds was believed to have the formula $[\mathrm{Bu}^n_4][\mathrm{Ph}_4\mathrm{Au}]$. An X-ray crystallographic investigation of this compound was undertaken in order to confirm the presence of the novel tetraphenylaurate(III) anion, and to elucidate the conformation of the anion.

Experimental

Tetrabutylammonium tetraphenylaurate crystallised from water as long, colourless needles with an oblique cross-section. The crystals were found to decompose very rapidly in the X-ray beam. Data were collected photographically, using six different crystals. Cu-K_α radiation was used, in spite of the large absorption coefficient, as the rate of decomposition was reduced compared to Mo-K_α radiation. The intensities of 1253 reflections were estimated visually from Weissenberg and precession photographs, and subsequently corrected for Lorentz and polarisation

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TABLE 1

CRYSTAL DATA AND DETAILS OF THE X-RAY INTENSITY MEASUREMENTS

Molecular formula	$AuC_{40}H_{56}N$	
M.W.	747.87	
Space group	*I*2/*c*	(*C*2/*c*)
a	17.15(3) Å	(21.85(4) Å)
b	10.31(2) Å	(10.31(2) Å)
c	22.76(5) Å	(22.76(5) Å)
β	115.4(2)°	(134.8(2)°)
U	3635.2 $Å^3$	(3635.2 $Å^3$)
Z	4	
D_c	1.37 g cm^{-3}	
D_m	1.37 g cm^{-3}	
μ(Cu-K_α)	79.12 cm^{-1}	
Radiation	Cu-K_α (λ 1.5418 Å)	
Data collection	Nonius integrating Weissenberg and Stoe precession camera	
Measured intensities (visual)	1422	
Unique reflections	1255	
$R = \Sigma \| \|F_0\| - \|F_c\| \| / \Sigma \|F_0\|$	0.0957	

effects. Reflections of the type *hkl*, with *l* odd were very weak. No attempt was made to measure these reflections, because of the rapid decomposition of the crystals. Computer programs for data reduction and subsequent refinement were supplied by Dr. N. Bailey, University of Sheffield.

Crystal structure determination

The structure was solved in the non-standard space group *I*2/*c*, in order to prevent parameter correlation as a result of the large β angle of the unit cell for *C*2/*c*. The parameters of the unit cells for both space groups, *C*2/*c*, and *I*2/*c*, are listed together in Table 1.

Structure factors for the Fourier calculations were initially calculated using the gold atom placed at the origin. All of the non-hydrogen atoms were located from a difference Fourier map. The structure was refined by a full matrix least squares procedure after the intensities had been corrected for absorption, to a conventional *R* value of 0.0957 (anisotropic thermal parameters used only for the gold atom). Lists of thermal parameters and structure factors may be obtained from the authors.

Results and discussion

The coordinates of all atoms are given in Table 2 (these correspond to the unit cell for the space group *I*2/*c*). The crystal structure shows an arrangement of gold atoms lying along the *c*-axis of the unit cell separated by a distance of 11.38 Å and an identical row of gold atoms lying along the line 1/2, 1/2, *c*. Exactly midway between the tetraphenylaurate(III) anions in the *c*-axis direction, there is a tetrabutylammonium cation. Alternate nitrogen atoms lie above and below the line 0, 0, *c* and similarly along 1/2, 1/2, *c*.

Each gold atom is at a centre of symmetry with *trans* phenyl rings centrosymmet-

TABLE 2

FRACTIONAL ATOMIC COORDINATES [a] AND ISOTROPIC THERMAL VIBRATION PARAMETERS, B

Atom	x/a	y/b	z/c	B (Å^2)
Au	0.0000	0.0000	0.0000	
C(1)	0.0997(16)	0.0167(40)	−0.0281(13)	3.96(09)
C(2)	0.156(29)	−0.0897(46)	−0.0191(22)	7.06(17)
C(3)	0.2247(32)	−0.0739(50)	−0.0409(24)	8.24(20)
C(4)	0.2405(26)	0.0209(68)	−0.0662(20)	8.44(18)
C(5)	0.1861(32)	0.1330(52)	−0.0716(24)	7.93(19)
C(6)	0.1165(25)	0.1240(40)	−0.0525(19)	5.40(13)
C(7)	0.0478(22)	0.1523(36)	0.0578(17)	4.62(12)
C(8)	0.0168(26)	0.2789(43)	0.0448(19)	6.03(15)
C(9)	0.0593(31)	0.3907(51)	0.0867(24)	7.73(19)
C(10)	0.1329(33)	0.3685(55)	0.1377(26)	8.47(21)
C(11)	0.1732(35)	0.2543(60)	0.1580(27)	9.07(22)
C(12)	0.1265(29)	0.1435(48)	0.1140(23)	7.04(17)
C(13)	0.0815(25)	0.0354(43)	0.2525(19)	7.13(18)
C(14)	0.0441(31)	−0.0491(48)	0.1962(24)	8.74(22)
C(15)	0.1317(38)	−0.1495(62)	0.2201(29)	9.84(25)
C(16)	0.1258(44)	−0.2494(76)	0.1644(34)	12.07(32)
C(17)	0.0299(33)	0.2086(54)	0.3095(24)	8.17(20)
C(18)	0.1160(46)	0.2825(78)	0.3279(36)	12.89(34)
C(19)	0.1402(54)	0.4023(86)	0.3796(42)	16.06(45)
C(20)	0.0926(50)	0.4999(48)	0.3432(40)	20.30(45)
N	0.0000	0.1300(46)	0.2500	5.49(16)

[a] Corresponding to the unit cell for space group $I2/c$.

rically related to each other. The four phenyl groups are σ-bonded to the gold atom, all five atoms being exactly in the plane. The square coordination plane is tilted in such a way that two *trans* phenyl rings lie above and below the glide plane. There is room for an n-butyl chain from one adjacent cation to project into the vacant space underneath one phenyl ring whilst the n-butyl chain of the adjacent cation on the "opposite" side of the anion occupies the space "above" the *trans* phenyl ring. The other two phenyl rings are cut by the glide plane, each ring tilted obliquely with respect to this plane. The packing of the molecules in the unit cell is shown in Fig. 2.

Table 3 gives details of the bond lengths and angles (the atom numbering scheme is shown in Fig. 1). The two independent gold carbon bonds lengths are 2.07(3) and 1.99(4) Å. These are not significantly different from that found in the neutral dichloro(phenyl)di-n-propylsulphidegold(III) complex, 2.00(1) Å [3]. These bond lengths are shorter than the mean value of the gold–carbon (perfluorophenyl) bonds (2.18, 2.12(9) Å) found in $Au^{III}Cl(C_6F_5)_2PPh_3$ [4]. Although the differences are only of low significance due to the large esds of the gold–carbon bond lengths under consideration, it is consistent with the phenyl group being a better σ-donor than the perfluorophenyl ligand. Organogold(III) complexes where the gold is bonded to four carbon atoms are rare. The structures of two ylide complexes of trimethylgold(III), $(CH_3)AuCH_2S(O)CH_3)_2$, and $(CH_3)_3AuCH_2P(C_6H_5)_3$ have been reported [5], but the $[AuPh_4]^-$ anion, provides the first example where four identical organic ligands are attached to the gold. The groups do not exert a mutual *trans* influence on each other. The carbon–carbon bonds of the phenyl rings average 1.40 Å.

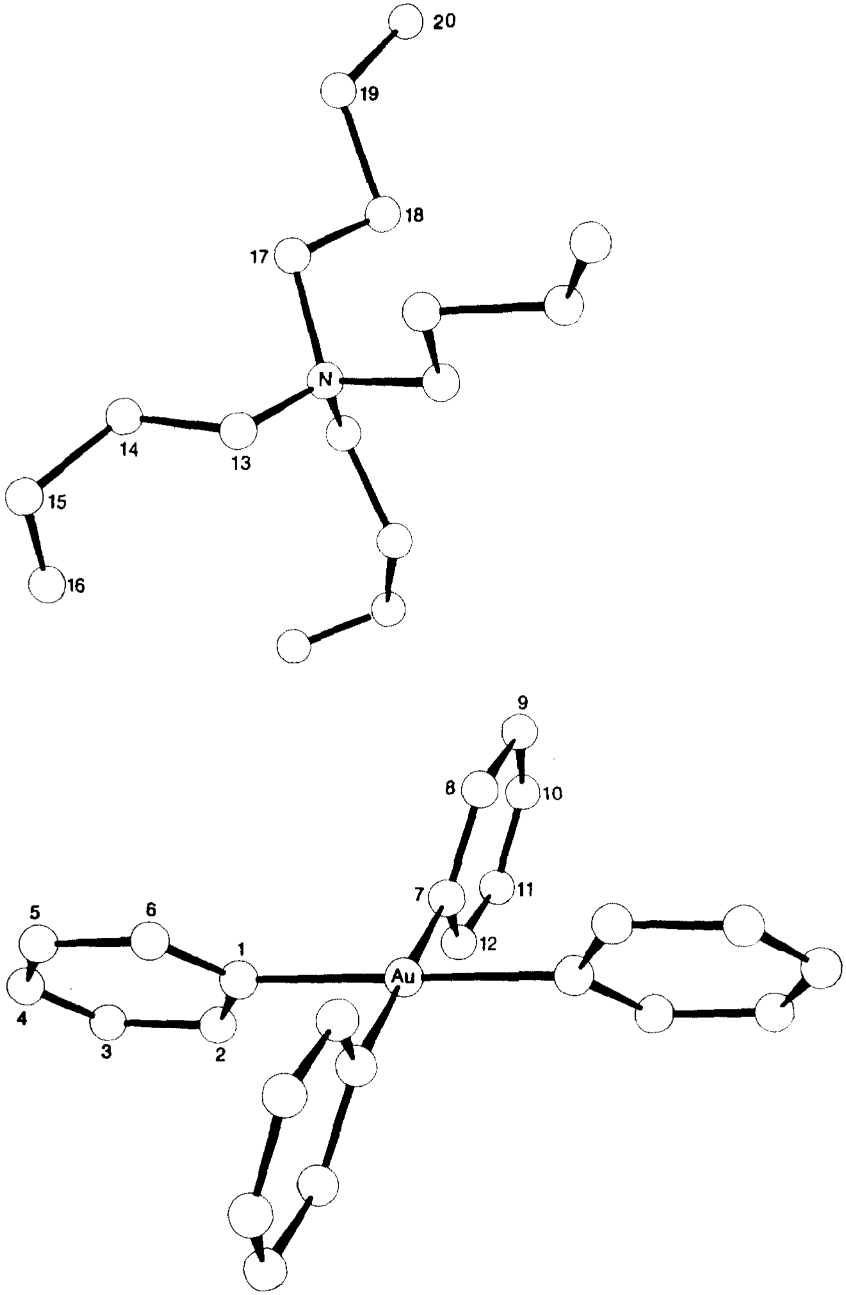

Fig. 1. Atom numbering scheme in tetrabutylammonium tetraphenylaurate.

The *ortho* carbon atoms of two *cis* phenyl rings approach each other, the separation between C(6) of one ring and C(8) of the other, being 3.69 Å. The orientation of the four phenyl rings is somewhat unexpected, as the most favourable orientation of four six-membered rings bonded in a square-planar configuration to a

TABLE 3

BOND LENGTHS (Å) AND BOND ANGLES (°) [a]

		(i) Tetraphenylaurate(III) anion		(ii) Tetrabutylammonium cation	
Au–C(1)	2.074(33)	C(1)–Au–C(7)	89(1)	C(13)–N–C(13'')	109(3)
Au–C(7)	1.990(40)	C(1)–Au–C(7')	91(1)	C(13)–N–C(17)	109(3)
C(1)–C(2)	1.42(6)	C(1)–Au–C(1')	180(2)	C(13)–N–C(17'')	108(3)
C(1)–C(6)	1.32(5)	C(7)–Au–C(7')	180(2)	C(17)–N–C(17'')	113(4)
C(2)–C(3)	1.47(7)	Au–C(1)–C(2)	120(2)	N–C(13)–C(14)	106(3)
C(3)–C(4)	1.22(8)	Au–C(1)–C(6)	124(3)	C(13)–C(14)–C(15)	95(3)
C(4)–C(5)	1.46(8)	C(2)–C(1)–C(6)	117(3)	C(14)–C(15)–C(16)	113(5)
C(5)–C(6)	1.44(7)	C(1)–C(2)–C(3)	117(4)	N–C(17)–C(18)	116(4)
C(7)–C(8)	1.39(6)	C(2)–C(3)–C(4)	128(5)	C(17)–C(18)–C(19)	119(6)
C(7)–C(12)	1.41(6)	C(3)–C(4)–C(5)	114(5)	C(18)–C(19)–C(20)	103(7)
C(8)–C(9)	1.47(7)	C(4)–C(5)–C(6)	121(5)		
C(9)–C(10)	1.32(8)	C(5)–C(6)–C(1)	123(4)		
C(10)–C(11)	1.34(8)	Au–C(7)–C(8)	126(3)		
C(11)–C(12)	1.50(8)	Au–C(7)–C(12)	121(3)		
N–C(13)	1.69(5)	C(8)–C(7)–C(12)	113(4)		
N–C(17)	1.47(6)	C(7)–C(8)–C(9)	124(4)		
C(13)–C(14)	1.45(7)	C(8)–C(9)–C(10)	117(5)		
C(14)–C(15)	1.71(8)	C(9)–C(10)–C(11)	128(6)		
C(15)–C(16)	1.60(10)	C(10)–C(11)–C(12)	113(5)		
C(17)–C(18)	1.55(10)	C(11)–C(12)–C(7)	126(4)		
C(18)–C(19)	1.63(12)				
C(19)–C(20)	1.34(12)				

[a] A prime refers to an atom at the equivalent position $-x$, $-y$, $-z$ with reference to an atom at x, y, z and double primes refers to an atom at the equivalent position $-x$, $-y$, $1/2-z$ with reference to an atom at x, y, z.

metal is a propeller arrangement where all of the rings have an identical orientation (usually 45° to the square plane) such as that found for the four pyrazine rings around cobalt in $CoCl_2(pyrazine)_2$ [6].

Each nitrogen of the tetrabutylammonium group is situated on a site of C_{2v} symmetry. The nitrogen–carbon bond lengths average 1.58(6) Å, and the C–C bond of the n-butyl chain average 1.55(9) Å.

There are three contacts, between carbon atoms of the n-butyl groups and phenyl ring (1) less than 3.70 Å (the sum of the Van der Waals radius of a methylene group, 2.0 Å, and the half-thickness of an aromatic ring, 1.70 Å [7]). These are C(1)...C(14) $(-x, -y, -z)$ of 3.57 Å, C(3)...C(18) $(x, -y, z-1/2)$, of 3.50 Å, and a shorter contact of 3.34 Å between C(6) and C(14) $(-x, -y, -z)$. These contacts are obviously determining the way in which the bulky tetrabutylammonium cations can pack into the space between the anions, giving a gold–nitrogen separation of 5.86 Å between an adjacent cation and anion. Thus a balance is being struck between the electrostatic attraction of the ions, and steric hindrance preventing closer contact.

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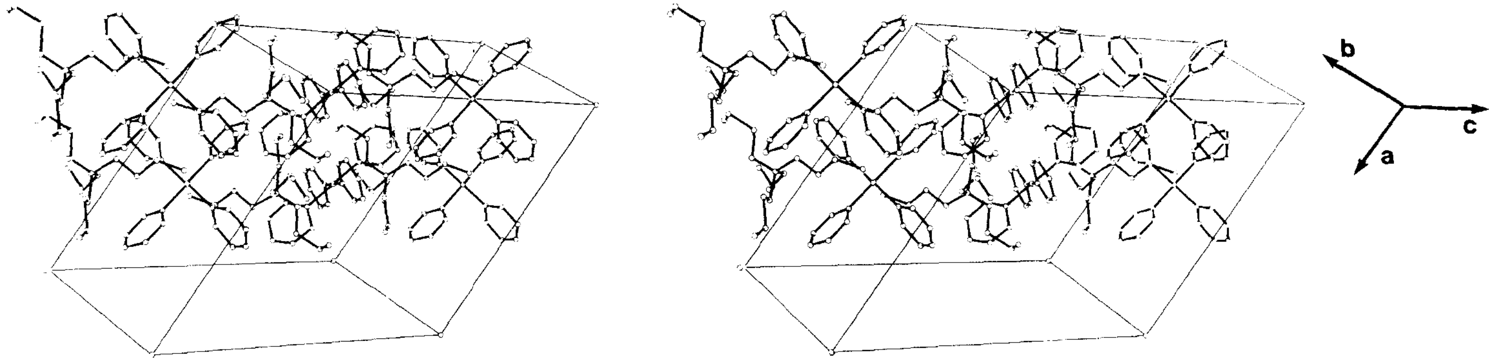

Fig. 2. Packing of the molecules in the unit cell.

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