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Bis(triphenylphosphine oxide)hydronium Tetrachloroaurate(III)

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Abstract. $C_{36}H_{31}O_2P_2^+AuCl_4^-$, $M_r = 896{\cdot}37$, monoclinic, $C2/c$, $a = 19{\cdot}676\,(8)$, $b = 9{\cdot}222\,(10)$, $c = 20{\cdot}285\,(8)$ Å, $\beta = 104{\cdot}55\,(3)°$, $U = 3563$ Å^3, $Z = 4$, D_m (flotation) $= 1{\cdot}66$, $D_x = 1{\cdot}671$ g cm^{-3}, μ(Mo $K\alpha$) $= 43{\cdot}5$ cm^{-1}. The Au atoms lie on twofold axes; the triphenylphosphine oxide moieties are joined by a centrosymmetrical hydrogen bond with $O\cdots O = 2{\cdot}39$ Å. The structure was refined to $R = 0{\cdot}070$ for 3467 unique reflexions.

Introduction. The carbonyl group of carbonylgold(I) chloride, (OC)AuCl, is easily replaceable by other ligands, thus providing a useful synthetic route to other Au compounds (Jones, 1976). The product may depend on whether solid (OC)AuCl or its conveniently prepared solution in thionyl chloride (Dell'Amico & Calderazzo, 1973) is used; thus addition of solid (OC)AuCl to a solution of diphenyl sulphide in dichloromethane yields Ph_2SAuCl, whereas addition of Ph_2S to a solution of (OC)AuCl in $SOCl_2$ gives Ph_2SAuCl_3 (Jones, 1976). The addition of triphenylphosphine oxide (TPPO) to such a solution causes slow effervescence of CO and the formation of a red solution, which on the removal of solvent *in vacuo* leaves a red oil. This may be crystallized from dichloromethane/diethyl ether as irregular yellow prisms. The nature of this compound could not be deduced by chemical means and a crystal structure determination was therefore performed.

A crystal 0·7 × 0·35 × 0·2 mm mounted about **b** was used to collect data on a Stoe STADI-2 two-circle diffractometer with Mo $K\alpha$ radiation and a graphite monochromator (5488 reflexions, layers 0–12). Darkening of the crystal indicated some decomposition. Systematic absences *hkl*, *h* + *k* odd, and *h*0*l*, *l* odd, indicated space group $C2/c$ or Cc. After application of Lp and numerical absorption corrections, averaging equivalent reflexions gave 3467 unique reflexions with $F > 4\sigma(F)$. Cell dimensions *a*, *c* and β were obtained by least squares from zero-layer diffractometer ω angle measurements, and *b* from 0*k*0 μ angle measurements.

A Patterson map showed only one high peak (at $0,0,\frac{1}{2}$). The Au atom lies on a special position $(0,y,\frac{3}{4})$ of twofold symmetry in $C2/c$; the closeness of *y* to 0·5 would give two Patterson peaks very close to, and symmetrically disposed about, the point $0,0,\frac{1}{2}$, thus

Table 1. *Atom coordinates* (×10^4) *and isotropic temperature factors* (Å^2 ×10^3)

	x	*y*	*z*	*U*
Au(1)	0	5129 (1)	7500	
Cl(1)	597 (2)	6866 (4)	7076 (2)	
Cl(2)	600 (2)	3389 (3)	7090 (1)	
P(1)	993 (1)	1572 (2)	5076 (1)	
O(1)	231 (3)	1203 (6)	5052 (2)	48 (1)
C(11)	1051 (2)	3458 (3)	4929 (2)	40 (1)
C(12)	1190 (2)	3984 (3)	4332 (2)	48 (2)
C(13)	1170 (2)	5472 (3)	4204 (2)	55 (2)
C(14)	1011 (2)	6434 (3)	4675 (2)	63 (2)
C(15)	872 (2)	5908 (3)	5273 (2)	57 (2)
C(16)	892 (2)	4420 (3)	5400 (2)	51 (2)
C(21)	1281 (2)	597 (4)	4441 (2)	39 (1)
C(22)	814 (2)	426 (4)	3803 (2)	58 (2)
C(23)	1009 (2)	−390 (4)	3301 (2)	75 (3)
C(24)	1671 (2)	−1035 (4)	3437 (2)	65 (2)
C(25)	2138 (2)	−864 (4)	4075 (2)	59 (2)
C(26)	1943 (2)	−48 (4)	4577 (2)	50 (2)
C(31)	1569 (2)	1121 (4)	5877 (2)	41 (1)
C(32)	2157 (2)	1962 (4)	6170 (2)	55 (2)
C(33)	2636 (2)	1486 (4)	6759 (2)	62 (2)
C(34)	2528 (2)	168 (4)	7055 (2)	74 (3)
C(35)	1941 (2)	−673 (4)	6762 (2)	80 (3)
C(36)	1461 (2)	−196 (4)	6173 (2)	65 (2)
H(12)	1313	3239	3967	95 (9)
H(13)	1277	5879	3742	95 (9)
H(14)	995	7586	4576	95 (9)
H(15)	749	6653	5637	95 (9)
H(16)	785	4013	5863	95 (9)
H(22)	301	925	3697	95 (9)
H(23)	648	−523	2807	95 (9)
H(24)	1822	−1667	3049	95 (9)
H(25)	2650	−1363	4181	95 (9)
H(26)	2304	84	5071	95 (9)
H(32)	2240	2982	5941	95 (9)
H(33)	3091	2137	6986	95 (9)
H(34)	2900	−201	7512	95 (9)
H(35)	1857	−1693	6991	95 (9)
H(36)	1006	−847	5945	95 (9)

Table 2. *Anisotropic temperature factors* (Å^2 ×10^3)

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

	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Au(1)	56 (1)	64 (1)	57 (1)	0	−3 (1)	0
Cl(1)	74 (1)	99 (1)	126 (1)	43 (2)	−6 (2)	−3 (2)
Cl(2)	115 (1)	95 (1)	75 (1)	26 (1)	40 (1)	32 (2)
P(1)	29 (1)	33 (1)	43 (1)	1 (1)	10 (1)	−5 (1)

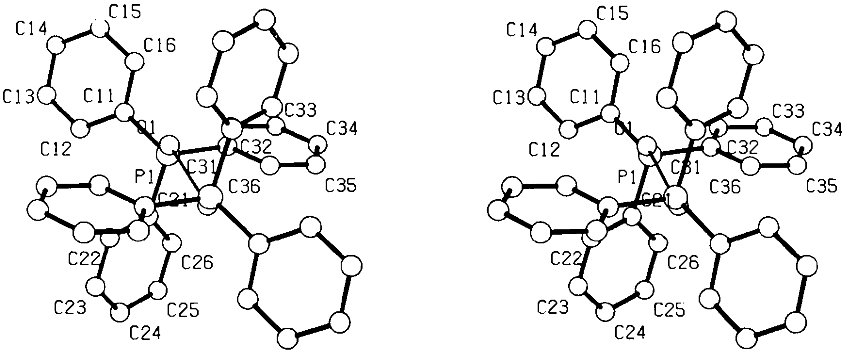

Fig. 1. Stereoview of the $(Ph_3PO\cdots H\cdots OPPh_3)^+$ ion (H atoms omitted) showing the labelling scheme for the unique TPPO. The hydrogen bond is indicated by a thin line.

Table 3. *Bond lengths* (Å) *and angles* (°)

Cl(1)–Au(1)	2·280 (6)	Cl(2)–Au(1)	2·269 (5)
O(1)–P(1)	1·526 (8)	C(21)–P(1)	1·777 (6)
C(11)–P(1)	1·773 (5)	C(31)–P(1)	1·780 (5)
Cl(2)–Au(1)–Cl(1)	89·6 (2)	Cl(1)–Au(1)–Cl(1^i)	90·7 (3)
Cl(2)–Au(1)–Cl(2^i)	90·0 (3)	C(21)–P(1)–O(1)	110·6 (3)
C(11)–P(1)–O(1)	108·5 (3)	C(11)–P(1)–C(21)	109·2 (3)
C(31)–P(1)–O(1)	111·9 (3)	C(31)–P(1)–C(21)	107·3 (3)
C(31)–P(1)–C(11)	109·3 (3)	C(22)–C(21)–P(1)	118·4
C(26)–C(21)–P(1)	121·6	C(12)–C(11)–P(1)	121·5
C(16)–C(11)–P(1)	118·3	C(32)–C(31)–P(1)	121·9
C(36)–C(31)–P(1)	117·7		

Symmetry transformation: (i) $-x, y, 1\cdot5-z$.

explaining an initial misinterpretation in which the Au atom was placed at the origin. Other atoms were located from a difference synthesis. Refinement (Au, Cl and P anisotropic) continued to $R = 0\cdot070$; rigid phenyl groups with C—C 1·395, C—H 1·08 Å and all angles 120° were employed, with a common H atom temperature factor. Interlayer scale factors and components of an anisotropic scaling tensor (Shakked & Rabinovich, 1977) were refined. The final $R' = \sum w^{1/2}\Delta/\sum w^{1/2}|F_o|$ was 0·085; the weighting scheme was $w = 1/[\sigma^2(F) + 0\cdot0015F^2]$.* A final difference map showed a maximum peak of 1·5 e Å^{-3}, associated with the Au atom. Final atomic parameters are given in Tables 1 and 2, bond lengths and angles in Table 3. Diagrams of the structure are given in Figs. 1 and 2.

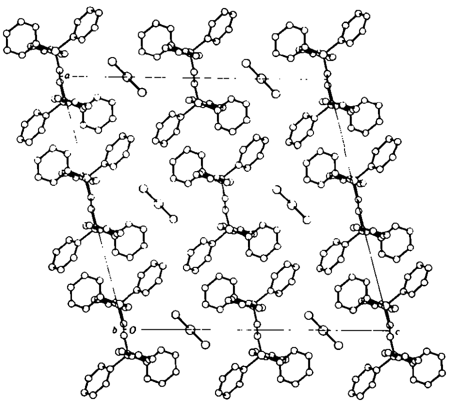

Fig. 2. Projection of the structure down **b**. The $AuCl_4^-$ ions are seen with two Cl atoms eclipsed.

Discussion. The anion is clearly $AuCl_4^-$; the requirement of electrical neutrality and the very short (2·39 Å) O···O distance between two TPPO molecules (at x,y,z and $-x, -y, 1-z$) suggest the presence of a symmetrical hydrogen bond; thus the compound is $(Ph_3PO\cdots H\cdots OPPh_3)^+AuCl_4^-$, consistent with chemical analysis (found, C 47·25, 47·36, H 3·54, 3·58%; required, C 48·23, H 3·49%).

Infrared spectroscopic studies of complexes of TPPO with strong acids (Hadži, 1962) led to the conclusion that the TPPO is not protonated. X-ray studies of the complexes TPPO–trichloroacetic acid (TCA) (Golič & Kaučič, 1976) and 2TPPO–dimethylmalonic acid (DMMA) (Declercq, Germain, Putzeys, Rona & Van Meerssche, 1974) have confirmed this; in both cases there are short P=O···H—O hydrogen bonds (O···O 2·50 Å in TPPO–TCA and 2·52, 2·58 Å in 2TPPO–DMMA), and the P—O distance (1·501, 1·492, 1·493 Å respectively) is lengthened with respect to TPPO itself [P—O = 1·483 Å (monoclinic form, Ruban & Zabel, 1976), 1·46 Å (orthorhombic form, Bandoli, Bortolozzo, Clemente, Croatto & Panattoni, 1970)].

In the present compound, since the $H(OPPh_3)_2^+$ cation lies on a centre of symmetry, the hydrogen bond is either symmetric or disordered; the O···O distance (2·39 Å) is one of the shortest known, indicating a symmetric H bond. The P—O···O angle is 124°. The P—O distance of 1·526 Å is appreciably longer than

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* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 33309 (16 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

that in either TPPO or its previously known complexes.

The $AuCl_4^-$ ion possesses approximate $4/mmm$ symmetry, as found in its other salts, *e.g.* $Ph_4AsAuCl_4$ (Jones, Guy & Sheldrick, 1975).

We thank the SRC for a contribution towards the cost of the diffractometer. The figures were drawn with *PLUTO* written by Dr W. D. S. Motherwell; all other crystallographic programs were written by GMS.

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Bis(acetylacetonato)bis(6-methylquinoline)cobalt(II)

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Abstract. $C_{30}H_{32}CoN_2O_4$, M_r = 543·53, monoclinic, a = 7·543 (1), b = 10·961 (1), c = 16·082 (1) Å, β = 97·15 (1)°, U = 1319·3 Å^3, Z = 2, D_x = 1·370, D_c = 1·368 g cm^{-3}, space group $P2_1/c$, $F(000)$ = 566, μ(Mo $K\alpha$) = 6·4 cm^{-1}, λ(Mo $K\alpha$) = 0·71069 Å. The structure was refined to R = 0·0375 for 3564 diffractometer data. The complex is centrosymmetric. The Co atom has an octahedral coordination with Co—N and mean Co—O distances of 2·262 (4) and 2·036 (3) Å respectively.

Introduction. The structure of the title compound has been determined as a preliminary to interpreting its magnetic susceptibility in terms of the model outlined by Gerloch & McMeeking (1975).

The complex was prepared by adding the stoichiometric amount of 6-methylquinoline to a solution of Co acetylacetonate dihydrate in toluene. Suitable crystals were obtained by recrystallizing from CH_2Cl_2.

The crystal system was determined from oscillation and Weissenberg photographs. Cell dimensions were obtained by least squares from the setting angles for fifteen reflexions automatically centred on a Nonius CAD-4 diffractometer. Intensities for 5616 reflexions (1·5 < θ < 33°) were recorded with graphite-monochromated Mo $K\alpha$ radiation, the $\omega/2\theta$ scan and a crystal 0·55 × 0·35 × 0·25 mm. All data were

Table 1. *Atom coordinates* (×10^4)

	x	y	z
Co	0	0	0
N(1)	1124 (2)	−1880 (1)	317 (1)
C(2)	1718 (2)	−2016 (2)	1117 (1)
C(3)	2505 (3)	−3091 (2)	1467 (1)
C(4)	2709 (3)	−4050 (2)	952 (1)
C(5)	2313 (3)	−4912 (2)	−487 (1)
C(6)	1731 (3)	−4790 (2)	−1319 (1)
C(7)	919 (2)	−3683 (2)	−1602 (1)
C(8)	707 (2)	−2734 (2)	−1072 (1)
C(9)	1317 (2)	−2847 (1)	−209 (1)
C(10)	2115 (2)	−3957 (1)	87 (1)
C(11)	1935 (5)	−5789 (2)	−1943 (2)
O(12)	2104 (1)	746 (1)	734 (1)
C(13)	3304 (2)	1391 (1)	469 (1)
C(14)	3655 (2)	1453 (2)	−364 (1)
C(15)	2774 (2)	793 (1)	−1034 (1)
O(16)	1393 (2)	144 (1)	−1007 (1)
C(17)	4442 (1)	2149 (2)	1115 (1)
C(18)	3496 (3)	848 (2)	−1867 (1)

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