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Tetrakis[acetatotriphenylphosphinesilver(I)]

BY ERNEST T. BLUES, MICHAEL G. B. DREW AND BANKOLE FEMI-ONADEKO

Department of Chemistry, The University, Whiteknights, Reading RG6 2AD, England

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Abstract. $C_{80}H_{72}O_8P_4Ag_4$, $M_r = 1716{\cdot}0$, monoclinic, space group $P2_1/c$ (systematic absences $h0l$, $l = 2n + 1$, $0k0$, $k = 2n + 1$), $a = 13{\cdot}616\ (11)$, $b = 12{\cdot}436\ (12)$, $c = 23{\cdot}489\ (17)$ Å, $\beta = 91{\cdot}28\ (11)°$, $U = 3976{\cdot}4$ Å^3, $Z = 2$, $d_m = 1{\cdot}43\ (1)$, $d_c = 1{\cdot}43$ g cm^{-3}, Mo $K\alpha$ radiation, $\lambda = 0{\cdot}7107$ Å, μ(Mo $K\alpha$) = 10·7 cm^{-1}. In the centrosymmetric tetramer, the two independent Ag atoms have different environments. One is bonded to a triphenylphosphine [Ag—P 2·376 (3) Å] and to two O atoms [2·241 (8), 2·260 (10) Å] while the other is bonded to a triphenylphosphine [2·354 (3) Å] and to three O atoms [2·226 (12), 2·320 (7), 2·475 (7) Å]. 2895 independent reflexions measured by counter methods have been refined to $R = 0{\cdot}067$.

Introduction. Crystals of $[Ag(PPh_3)(O_2CMe)]_4$ were prepared by reaction of AgO_2CMe with an equimolar amount of PPh_3 in toluene at reflux followed by filtration of the hot solution and recrystallization by slow evaporation of the same solvent. A crystal with

Table 1. *Final positional parameters* ($\times 10^4$) *with estimated standard deviations in parentheses*

	x	y	z		x	y	z
Ag(1)	6137 (1)	4821 (1)	4592 (0)	C(23)	8407 (10)	5603 (11)	1875 (6)
Ag(2)	6974 (1)	6974 (1)	4120 (0)	C(24)	7473 (12)	5441 (13)	1736 (7)
P(1)	6441 (2)	3568 (2)	3865 (1)	C(25)	6725 (10)	5784 (12)	2067 (6)
P(2)	8170 (2)	7139 (3)	3405 (1)	C(26)	6911 (9)	6256 (10)	2583 (5)
C(1)	4700 (8)	6831 (9)	4358 (5)	C(32)	9465 (9)	5974 (10)	4066 (5)
O(1)	4857 (5)	6041 (7)	4666 (3)	C(33)	10396 (10)	5668 (12)	4270 (6)
O(2)	5346 (6)	7225 (7)	4046 (4)	C(34)	11246 (9)	6154 (10)	4051 (6)
C(2)	3720 (9)	7388 (10)	4366 (5)	C(35)	11167 (9)	6877 (11)	3644 (6)
O(3)	7149 (7)	7265 (8)	5067 (4)	C(36)	10245 (9)	7237 (10)	3421 (5)
C(3)	7261 (9)	6486 (12)	5381 (6)	C(42)	5801 (9)	2999 (11)	2751 (6)
O(4)	7221 (8)	5564 (10)	5196 (5)	C(43)	5212 (11)	3146 (12)	2270 (6)
C(4)	7442 (12)	6653 (14)	6009 (8)	C(44)	4620 (10)	3933 (12)	2268 (6)
C(11)	8356 (7)	8491 (8)	3168 (4)	C(45)	4506 (12)	4649 (14)	2626 (8)
C(21)	7935 (7)	6430 (8)	2763 (4)	C(46)	5122 (9)	4537 (11)	3169 (6)
C(31)	9383 (8)	6766 (9)	3667 (5)	C(52)	5113 (8)	2105 (10)	4246 (5)
C(41)	5778 (7)	3763 (9)	3211 (5)	C(53)	4764 (10)	1028 (11)	4377 (6)
C(51)	6061 (7)	2222 (8)	4037 (4)	C(54)	5331 (10)	190 (11)	4280 (6)
C(61)	7727 (8)	3471 (9)	3682 (4)	C(55)	6262 (11)	299 (13)	4095 (7)
C(12)	8334 (10)	8811 (10)	2634 (5)	C(56)	6648 (9)	1321 (11)	3959 (5)
C(13)	8293 (10)	9921 (11)	2453 (6)	C(62)	8079 (8)	3703 (9)	3134 (5)
C(14)	8645 (9)	10621 (10)	2852 (6)	C(63)	9103 (9)	3633 (11)	3030 (5)
C(15)	8867 (10)	10308 (12)	3389 (6)	C(64)	9723 (10)	3352 (11)	3456 (6)
C(16)	8698 (9)	9268 (11)	3550 (5)	C(65)	9393 (9)	3103 (11)	4011 (6)
C(22)	8669 (9)	6093 (10)	2386 (6)	C(66)	8366 (8)	3195 (10)	4121 (5)

dimensions *ca* 0·5 × 0·35 × 0·7 mm was mounted with the a^* axis parallel to the instrument axis of a General Electric XRD 5 apparatus which was used to measure diffraction intensities and cell dimensions. 3688 reflexions with $2\theta < 35°$ were measured by the stationary-crystal–stationary-counter method with 10 s counts. 2895 reflections with $I > 2\sigma(I)$ were used in the subsequent calculations.

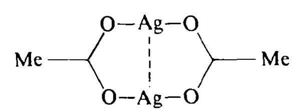
The structure was solved from the Patterson function and successive Fourier syntheses. Refinement by full-matrix least squares gave $R = 0{\cdot}067$. Ag and P atoms were refined anisotropically, O and C atoms isotropically. The phenyl ring H atoms were included in the structure factor calculations in trigonal positions but not refined. The final positions are listed in Table 1. The weighting scheme, chosen to give average values of $w\Delta^2$ for groups of reflections independent of the values of F_o and $\sin\theta/\lambda$, was $w^{1/2} = 1$ for $F_o < 80$ and $w^{1/2} = 80/F_o$ for $F_o > 80$. Calculations were performed on a CDC 7600 computer at the University of London Computer Centre with the XRAY set of programs (Stewart, 1972). Atomic scattering factors were taken from *International Tables for X-ray Crystallography* (1974) as were the corrections for the anomalous dispersion for the Ag and P atoms. There were signs of a disordered solvent molecule of toluene in the difference Fourier syntheses with an occupancy <0·5 around the centre of symmetry at 0,½,0 but this could not be refined successfully. In the final cycle of refinement all shifts were $<0{\cdot}25\sigma$. The dimensions of the tetramer are given in Table 2.*

Table 2. *Molecular dimensions*

The superscript i refers to the coordinates $1-x$, $1-y$, $1-z$ relative to the reference set in Table 1.

Ag(1)—P(1)	2·354 (3) Å	P(1)—Ag(1)—O(1)	129·2 (2)°
Ag(1)—O(1)	2·320 (7)	P(1)—Ag(1)—O(4)	127·7 (3)
Ag(1)—O(4)	2·226 (12)	P(1)—Ag(1)—O(1^{i})	109·4 (2)
Ag(1)—O(1^{i})	2·475 (7)	O(1)—Ag(1)—O(4)	99·8 (4)
Ag(2)—P(2)	2·376 (3)	O(1)—Ag(1)—O(1^{i})	78·9 (2)
Ag(2)—O(2)	2·241 (8)	O(4)—Ag(1)—O(1^{i})	95·5 (3)
Ag(2)—O(3)	2·260 (10)	P(2)—Ag(2)—O(2)	128·7 (2)
Ag(1)···Ag(2)	3·122 (1)	P(2)—Ag(2)—O(3)	128·6 (2)
Ag(1)—O(1)—Ag(1^{i})	101·1 (3)°	O(2)—Ag(2)—O(3)	97·9 (3)
P(1)—C(41)	1·782 (11) Å	Ag(1)—P(1)—C(41)	116·2 (4)°
P(1)—C(51)	1·801 (11)	Ag(1)—P(1)—C(51)	113·4 (4)
P(1)—C(61)	1·816 (11)	Ag(1)—P(1)—C(61)	113·7 (4)
P(2)—C(11)	1·791 (11)	C(41)—P(1)—C(51)	100·2 (5)
P(2)—C(21)	1·769 (11)	C(41)—P(1)—C(61)	106·1 (5)
P(2)—C(31)	1·810 (11)	C(51)—P(1)—C(61)	106·0 (5)
C(1)—O(1)	1·236 (11)	Ag(2)—P(2)—C(11)	113·9 (4)
C(1)—O(2)	1·257 (14)	Ag(2)—P(2)—C(21)	116·5 (3)
C(1)—C(2)	1·504 (16)	Ag(2)—P(2)—C(31)	111·8 (4)
O(3)—C(3)	1·225 (18)	C(11)—P(2)—C(21)	103·2 (5)
O(4)—C(3)	1·227 (19)	C(11)—P(2)—C(31)	102·2 (5)
C(3)—C(4)	1·505 (22)	C(21)—P(2)—C(31)	108·0 (5)
Ag(1)—O(1)—C(1)	126·7 (7)°	Ag(1)—O(4)—C(3)	129·6 (10)
Ag(2)—O(2)—C(1)	127·2 (7)	Ag(2)—O(3)—C(3)	118·3 (9)
O(1)—C(1)—C(2)	120·1 (10)	O(3)—C(3)—C(4)	119·7 (14)
O(2)—C(1)—C(2)	117·4 (10)	O(4)—C(3)—C(4)	118·7 (14)
O(1)—C(1)—O(2)	122·4 (10)	O(3)—C(3)—O(4)	121·5 (13)

Discussion. There has been little structural work on the Ag^I carboxylates. $Ag_2(O_2CCF_3)_2$ is a centrosymmetric dimer (Griffin, Ellett, Mehring, Bullitt & Waugh, 1972) with both acetates bridging both Ag atoms [Ag···Ag 2·967 (3), Ag—O 2·249 (6), 2·232 (6) Å]. This $Ag_2O_4C_2R_2$ unit (1) is also found in bis(3-hydroxy-4-phenyl-2,2,3-trimethylcyclohexanecarboxylato)disilver (I) dihydrate (Coggon & McPhail, 1972) with dimensions Ag···Ag 2·778 (5), 2·834 (5), Ag—O 2·20, 2·29 Å; and in silver perfluorobutyrate (Blakeslee & Hoard, 1956) with dimensions Ag···Ag 2·90 (2), Ag—O 2·25 (4) Å. Silver glycine nitrate (Rao & Viswamitra, 1972) also contains this dinuclear unit but the units are linked by further Ag—O interactions to give a polymeric structure similar to that found in copper(I) acetate (Drew, Edwards & Richards, 1973; Mounts, Ogura & Fernando, 1974). In all these examples the O—Ag—O angles are in the range 158–163°.



(1)

The structure of $Ag_4(O_2CMe)_4(PPh_3)_4$ is shown in Fig. 1. There are no Ag—Ag bonds as the shortest Ag···Ag distance is 3·122 (1) Å. The two independent Ag atoms have different environments. Ag(2) is bonded to triphenylphosphine [Ag(2)—P(2) 2·376 (3) Å] and is

* Lists of structure factors, anisotropic thermal parameters and dimensions of the benzene rings have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 32970 (9 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

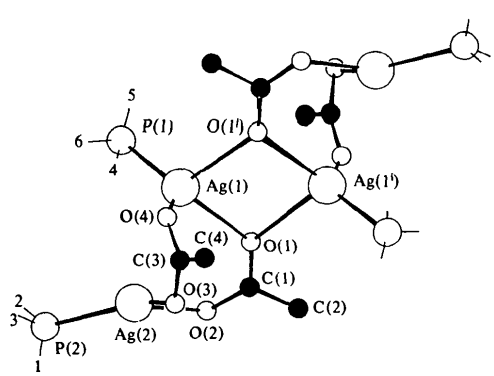


Fig. 1. The structure of $Ag_4(O_2CMe)_4(PPh_3)_4$ with phenyl rings omitted for clarity.

linked to Ag(1) *via* acetate groups [Ag(2)—O(2) 2·241 (8), Ag(2)—O(3) 2·260 (10) Å] in a similar fashion to that shown in (1) except that the O(2)—Ag—O(3) angle is only 97·9 (3)° and not 160° as found in the examples cited above. Ag(1) is also bonded to triphenylphosphine [Ag(1)—P(1) 2·354 (3) Å] and to two O atoms of acetates that bridge to Ag(2) [Ag(1)—O(1) 2·320 (7), Ag(1)—O(4) 2·226 (12) Å, O(1)—Ag—O(4) 99·8 (4)°]. In addition, Ag(1) is bonded to an O atom [Ag(1)—O(1^i) 2·475 (7) Å] of a second dinuclear unit. There is a precedent for the O—Ag—O angles in the tetramer; in bis(silvertrifluoroacetate)benzene (Hunt, Lee & Amma, 1974) there are two independent bridges of type (1), one with an angle of 98·3 and the other of 161·6°.

The geometries of the Ag(1), Ag(2) environments can be considered to be trigonal planar and tetrahedral, respectively, with large distortions caused by the ring formation. The Ag—O distances (mean 2·24 Å) are as expected except for Ag(1)—O(1) and Ag(1)—O(1^i), which are lengthened by bridge formation. The Ag—P distances can be compared with those found in $Ag_4(PPh_3)_4X_4$ (Teo & Calabrese, 1975, 1976) which are 2·372–2·386 (X = Cl), 2·429, 2·415 (X = Br) and 2·455, 2·466 Å (X = I). It was argued that these distances were different because of variations in steric crowding in the three molecules and therefore it is fitting that the Ag—P distances in the present uncrowded tetramer are comparable to those in the tetrachloride.

No report of the analogous $Cu(O_2CMe)(PPh_3)$ complex has been found but $Cu(O_2CMe)(PPh_3)_2$ is a monomer with a bidentate acetate ligand in which the metal atom has a distorted tetrahedral environment (Drew, Othman, Edwards & Richards, 1975). We have also prepared $Ag(O_2CMe)(PPh_3)_2$. Tetragonal silver(I) ketenide (2 g, 0·008 mol) was refluxed for 15 h with PPh_3 (2·45 g, 0·009 mol) in toluene. The toluene phase was filtered from unreacted silver ketenide, evaporated to dryness and the resulting solid was recrystallized from toluene. Found C 66·0%, H 4·73%, P 8·12%, Ag 16·2%. Calculated for $Ag(O_2CMe)(PPh_3)_2$ C 66·0%, H 4·78%, P 8·97%, Ag 15·6%. Powder patterns show that the Ag and Cu compounds are not isomorphous.

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2,3,7,8,12,13,17,18-Octaethyl-5-[2,2-bis(ethoxycarbonyl)vinyl]-22*H*,24*H*-porphine

By W. S. Sheldrick

Gesellschaft für Biotechnologische Forschung mbH, Mascheroder Weg 1, *D*-3300 *Braunschweig-Stöckheim, Federal Republic of Germany*

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Abstract. $C_{44}H_{56}N_4O_4$, triclinic, $P\bar{1}$, a = 14·590 (10), b = 15·439 (7), c = 9·692 (6) Å, α = 92·61 (3), β = 100·93 (4), γ = 66·98 (3)°, M_r = 737·0, Z = 2, D_x = 1·24 g cm^{-3}. The porphyrin skeleton is significantly ruffled, in particular in ring A, where atom deviations of −0·202 and −0·171 Å [C(2) and C(3)] from the N atom least-squares plane are observed. Although individual bond lengths and angles in the macrocycle are similar to those in porphine the geometry of the central 'hole' is distinctly rhomboid (neighbouring N···N distances: 2·78, 3·06, 2·79, 3·06 Å) rather than rhombic as in the parent compound.