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Acetatobis(triphenylphosphine)copper(I)

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Abstract. $C_{38}H_{33}O_2P_2Cu$, $M=647\cdot13$, monoclinic, $P2_1/a$ (systematic absences $h0l$; $h=2n+1$, $0k0$: $k=2n+1$), $a=18\cdot041$ (11), $b=11\cdot044$ (7), $c=19\cdot317$ (15) Å, $\beta=121\cdot87$ (10)°, $U=3268\cdot7$ Å^3, $Z=4$, $d_m=1\cdot32$, $d_c=1\cdot32$ g cm^{-3}, Mo $K\alpha$ radiation $\lambda=0\cdot7107$ Å, μ (Mo $K\alpha$) $=8\cdot21$ cm^{-1}. The copper atom is bonded to two triphenylphosphine ligands *via* phosphorus [Cu–P 2·233 (2) and 2·240 (3) Å] and to both oxygens of an acetate group [Cu–O 2·162 (5) and 2·257 (7) Å] to give a distorted tetrahedral monomeric complex. 2336 independent reflexions, measured by counter methods, have been refined to $R=0\cdot050$.

Introduction. Crystals of $Cu(O_2CCH_3)(PPh_3)_2$ were prepared by reaction of CuO_2CCH_3 with PPh_3 in toluene, followed by recrystallization by slow evaporation of the same solvent. A crystal with dimensions *ca* $0\cdot5\times0\cdot5\times0\cdot5$ mm was mounted with the $(20\bar{1})$ planes perpendicular to the instrument axis of a General Electric XRD 5 apparatus which was used to measure diffraction intensities and cell dimensions. It was equipped with a manual goniostat, scintillation counter and pulse-height discriminator. Molybdenum X-radiation, filtered with zirconium was used. 3178 reflexions with $2\theta<40°$ were measured by the stationary-crystal stationary-counter method. 2336 reflexions with $I>2\sigma(I)$ were used in the subsequent calculations. No crystal decay was observed in the course of the experiment. No absorption or extinction corrections were made.

The structure was solved from the Patterson function and successive Fourier syntheses. Refinement by least-squares calculations using seven large blocks gave $R=0\cdot050$. Copper, oxygen, phosphorus and carbon atoms were refined anisotropically; the phenyl ring hydrogen atoms were included in the structure-factor calculation but not refined. The final positions are listed in Table 1, the thermal parameters in Table 2. The weighting scheme was chosen to give average values of $w\Delta^2$ for groups of reflexions independent of the values of F_o and $\sin\theta/\lambda$. It was $\sqrt{w}=1$ for $F_o<47$ and $\sqrt{w}=47/F_o$ for $F_o>47$. Calculations were performed on a C.D.C. 7600 computer at the University of London Computer Centre using the X-RAY set of programs (Stewart, 1972). Atomic scattering factors for all atoms were taken from *International Tables for X-ray Crystallography* (1974) as were the corrections for the real and imaginary parts of the anomalous dispersion for the copper and phosphorus atoms. The anisotropic thermal parameters are defined as $\exp[-0\cdot25\pi^2\sum_i\sum_j U_{ij}h_ih_jb_ib_j]$ $(i,j=1,2,3)$, where b_i is the ith reciprocal cell dimension. The 842 zero reflexion showed no large discrepancies. There were no extraneous peaks in a difference Fourier synthesis and in the final cycle of refinement all shifts

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

	x	y	z
Cu(1)	3351 (1)	4426 (1)	2346 (1)
P(1)	3483 (1)	2880 (2)	3149 (1)
P(2)	4170 (1)	5096 (2)	1869 (1)
C(11)	2697 (5)	2898 (8)	3474 (4)
C(12)	2373 (5)	4015 (8)	3526 (4)
C(13)	1824 (5)	4084 (8)	3831 (5)
C(14)	1591 (5)	3064 (10)	4065 (5)
C(15)	1875 (5)	1949 (9)	3992 (5)
C(16)	2442 (5)	1865 (8)	3701 (5)
C(21)	3325 (5)	1417 (7)	2669 (5)
C(22)	4017 (6)	683 (8)	2812 (5)
C(23)	3839 (8)	−416 (9)	2363 (7)
C(24)	3003 (10)	−748 (9)	1813 (8)
C(25)	2327 (7)	−26 (10)	1657 (6)
C(26)	2470(6)	1066 (9)	2077 (5)
C(31)	4516 (5)	2787 (7)	4128 (4)
C(32)	4735 (5)	1832 (9)	4671 (5)
C(33)	5495 (7)	1884 (10)	5446 (6)
C(34)	6038 (6)	2887 (12)	5664 (6)
C(35)	5825 (6)	3823 (10)	5124 (7)
C(36)	5072 (5)	3767 (8)	4357 (5)
C(41)	4565 (4)	3950 (7)	1464 (4)
C(42)	4584 (6)	4106 (8)	758 (5)
C(43)	4946 (6)	3221 (9)	514 (6)
C(44)	5304 (6)	2186 (10)	970 (6)
C(45)	5275 (5)	2024 (8)	1664 (6)
C(46)	4901 (5)	2884 (8)	1992 (5)
C(51)	5168 (5)	5867 (6)	2626 (4)
C(52)	5941 (5)	5795 (7)	2617 (5)
C(53)	6687 (6)	6405 (9)	3202 (6)
C(54)	6667 (6)	7085 (10)	3784 (6)
C(55)	5921 (7)	7157 (9)	3806 (6)
C(56)	5170 (6)	6544 (9)	3225 (6)
C(61)	3633 (5)	6194 (7)	1042 (4)
C(62)	4063 (5)	7159 (8)	956 (5)
C(63)	3617 (7)	7910 (8)	272 (6)
C(64)	2767 (7)	7686 (9)	−305 (5)
C(65)	2324 (6)	6752 (9)	−231 (5)
C(66)	2749 (5)	6001 (7)	452 (5)
C(1)	2002 (5)	5721 (9)	1821 (5)
C(2)	1175 (6)	6473 (10)	1471 (7)
O(1)	1972 (3)	4718 (5)	1495 (3)
O(2)	2688 (4)	6104 (5)	2429 (4)

Table 2. *Anisotropic thermal parameters* ($\times 10^3$) *with estimated standard deviations in parentheses*

	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Cu(1)	36·7 (5)	49·3 (6)	40·1 (6)	3·7 (5)	21·4 (5)	7·2 (5)
P(1)	35·1 (11)	46·2 (13)	33·8 (11)	0·2 (10)	19·2 (10)	3·2 (10)
P(2)	31·6 (11)	40·8 (12)	33·1 (12)	1·4 (10)	16·5 (10)	4·0 (10)
C(11)	42 (4)	46 (5)	28 (4)	−5 (4)	10 (4)	−1 (4)
C(12)	39 (5)	66 (7)	37 (5)	−8 (4)	21 (4)	−3 (4)
C(13)	44 (5)	68 (7)	52 (6)	5 (5)	19 (5)	−5 (5)
C(14)	51 (5)	85 (8)	53 (6)	−3 (5)	35 (5)	−2 (5)
C(15)	50 (5)	81 (8)	57 (6)	−20 (5)	31 (5)	0 (5)
C(16)	48 (5)	57 (6)	42 (5)	−7 (4)	23 (4)	3 (4)
C(21)	49 (5)	43 (5)	53 (5)	−4 (4)	30 (5)	5 (4)
C(22)	70 (6)	61 (6)	59 (6)	6 (5)	34 (5)	5 (5)
C(23)	111 (9)	52 (7)	106 (9)	15 (6)	67 (8)	−3 (7)
C(24)	137 (11)	58 (8)	113 (10)	−26 (8)	92 (10)	−32 (7)
C(25)	74 (7)	86 (8)	69 (7)	−29 (6)	40 (6)	−33 (6)
C(26)	61 (6)	74 (7)	55 (6)	−12 (5)	33 (5)	−10 (5)
C(31)	46 (5)	50 (5)	35 (5)	3 (5)	26 (4)	−2 (5)
C(32)	50 (6)	84 (7)	53 (6)	8 (5)	27 (5)	13 (6)
C(33)	66 (7)	104 (9)	45 (6)	31 (6)	26 (6)	20 (6)
C(34)	40 (6)	114 (9)	52 (7)	14 (7)	13 (5)	−25 (7)
C(35)	47 (6)	82 (7)	69 (7)	2 (5)	21 (6)	−30 (6)
C(36)	46 (5)	46 (5)	56 (6)	−2 (4)	23 (5)	−11 (4)
C(41)	32 (4)	40 (5)	40 (5)	−1 (4)	14 (4)	−6 (4)
C(42)	70 (6)	59 (6)	40 (5)	5 (5)	35 (5)	3 (4)
C(43)	85 (6)	64 (7)	59 (6)	10 (6)	42 (6)	0 (6)
C(44)	68 (6)	91 (8)	64 (7)	13 (6)	40 (5)	−16 (6)
C(45)	48 (5)	63 (6)	52 (6)	23 (5)	5 (5)	3 (5)
C(46)	52 (5)	56 (6)	44 (5)	12 (5)	24 (4)	6 (5)
C(51)	41 (5)	39 (5)	31 (4)	4 (4)	15 (4)	5 (4)
C(52)	32 (5)	67 (6)	47 (5)	−8 (4)	13 (4)	−13 (5)
C(53)	56 (6)	79 (7)	77 (7)	−10 (5)	35 (6)	−20 (6)
C(54)	42 (6)	94 (8)	66 (7)	−18 (5)	13 (5)	−9 (6)
C(55)	102 (8)	85 (8)	54 (6)	−21 (7)	40 (6)	−35 (6)
C(56)	69 (6)	78 (7)	72 (6)	−13 (5)	51 (6)	−23 (6)
C(61)	47 (5)	39 (5)	41 (5)	11 (4)	24 (5)	9 (4)
C(62)	48 (5)	48 (5)	54 (6)	1 (5)	19 (5)	17 (5)
C(63)	76 (7)	57 (6)	86 (7)	6 (6)	58 (7)	17 (6)
C(64)	87 (8)	56 (6)	52 (6)	22 (6)	33 (6)	22 (5)
C(65)	62 (6)	70 (7)	45 (6)	7 (6)	18 (5)	21 (5)
C(66)	45 (5)	55 (6)	52 (5)	4 (4)	17 (5)	11 (5)
C(1)	38 (5)	61 (7)	38 (5)	5 (5)	13 (5)	6 (5)
C(2)	55 (6)	109 (9)	94 (8)	49 (6)	15 (6)	−4 (7)
O(1)	43 (3)	57 (4)	57 (4)	−1 (3)	21 (3)	−4 (3)
O(2)	58 (4)	61 (4)	60 (4)	1 (3)	30 (4)	−5 (3)

Table 3. *Molecular dimensions: distances* (Å) *and angles* (°)

The remaining individual dimensions have been deposited with the structure-factor table. Mean values are C–C 1·386 Å, P–C–C 120·4, C–C–C 120·0° with no significant variations.

Cu(1)–P(1)	2·233 (2)	P(1)—Cu(1)–P(2)	133·4 (1)
Cu(1)–P(2)	2·240 (3)	P(1)—Cu(1)–O(1)	107·5 (2)
Cu(1)–O(1)	2·162 (5)	P(1)—Cu(1)–O(2)	116·4 (2)
Cu(1)–O(2)	2·257 (7)	P(2)—Cu(1)–O(1)	112·4 (2)
		P(2)—Cu(1)–O(2)	104·3 (2)
		O(1)—Cu(1)–O(2)	59·4 (2)
C(1)—C(2)	1·519 (14)	Cu(1)–O(1)—C(1)	91·3 (4)
C(1)—O(1)	1·261 (11)	Cu(1)–O(2)—C(1)	87·4 (6)
C(1)—O(2)	1·247 (9)	O(1)—C(1)—O(2)	121·8 (8)
		O(1)—C(1)—C(2)	119·7 (7)
		O(2)—C(1)—C(2)	119·1 (9)
P(1)—C(11)	1·829 (11)	P(2)—C(41)	1·820 (9)
P(1)—C(21)	1·810 (8)	P(2)—C(51)	1·823 (6)
P(1)—C(31)	1·827 (6)	P(2)—C(61)	1·823 (7)
Cu(1)–P(1)—C(11)	114·4 (3)	Cu(1)–P(2)—C(41)	116·1 (3)
Cu(1)–P(1)—C(21)	113·3 (3)	Cu(1)–P(2)—C(51)	114·2 (3)
Cu(1)–P(1)—C(31)	116·0 (3)	Cu(1)–P(2)—C(61)	114·8 (3)
C(11)–P(1)—C(21)	104·2 (4)	C(41)–P(2)—C(51)	103·0 (4)
C(11)–P(1)—C(31)	101·4 (4)	C(41)–P(2)—C(61)	103·5 (4)
C(21)–P(1)—C(31)	106·2 (4)	C(51)–P(2)—C(61)	103·6 (3)

were $<0{\cdot}25\sigma$. The dimensions of the molecule are given in Table 3.*

Discussion. Amongst the copper(I)–triphenylphosphine complexes whose structures have been established by X-ray crystallography are a group of six monomeric distorted tetrahedral complexes of the type [Cu(chelating anion) $(PPh_3)_2$] (Table 4). We have suggested on the basis of spectroscopic data that $Cu(O_2CCH_3)(PPh_3)_2$ (I) is a further example of this type (Edwards & Richards, 1975) and this has been confirmed by the crystal structure determination. The molecule is shown in Fig. 1, together with the atomic numbering scheme.

In (I), the Cu–O distances of 2·162 (5) and 2·257 (7) Å are similar to those of $Cu(NO_3)(PPh_3)_2$ and Cu(*β*-diketonate) $(PPh_3)_2$ (Table 4) but longer than the Cu–O

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* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 31179 (7 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

Table 4. *Molecular dimensions of* [Cu (*chelating anion*) ($PPh_3)_2$] *complexes*

Compound [a]	Cu-P (Å)	Cu-X (Å)	P-Cu-P (°)	X-Cu-X (°)
$Cu(O_2CCH_3)(PPh_3)_2$ [b]	2·233 (2), 2·240 (3)	2·162 (5), 2·257 (7)	133·4 (1)	59·4 (2)
$Cu(NO_3)(PPh_3)_2$ [c]	2·256 (3)	2·22 (1)	131·2 (1)	57·5 (3)
Cu(TTA) $(PPh_3)_2$ [d]	2·242 (2), 2·252 (1)	2·104 (4), 2·100 (4)	127·53 (6)	88·7 (2)
Cu(HFA) $(PPh_3)_2$ [d]	2·239 (2), 2·236 (2)	2·123 (4), 2·117 (4)	127·10 (6)	86·6 (2)
Cu(TFA) $(PPh_3)_2$ [d]	2·258 (1), 2·256 (1)	2·096 (4), 2·077 (4)	126·46 (5)	88·8 (1)
$Cu(BH_4)(PPh_3)_2$ [e]	2·276 (1)	2·02 (5)	123·26 (6)	69·0 (3)
$Cu(B_3H_8)(PPh_3)_2$ [f]	2·274 (2), 2·288 (2)	1·84 (5), 1·85 (5)	119·97 (7)	103·0 (2)

(*a*) Abbreviations: TTA thenoyltrifluoroacetonate; HFA hexafluoroacetylacetonate; TFA trifluoroacetylacetonate. (*b*) This work. (*c*) Messmer & Palenik (1969). (*d*) Bartlett (1970). (*e*) Lippard & Melmed (1967). (*f*) Lippard & Melmed (1969).

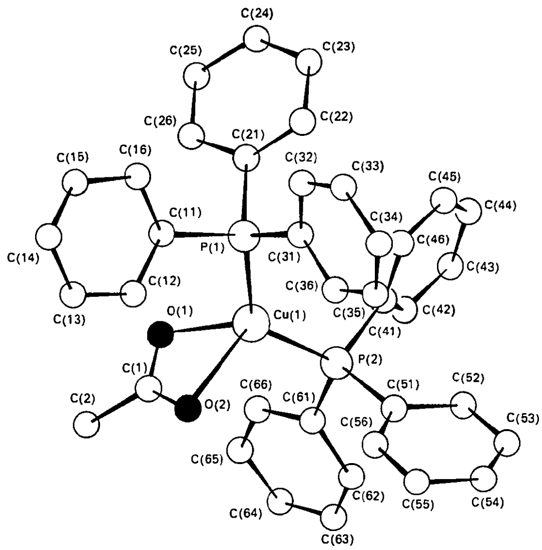

Fig. 1. Atomic numbering.

distances of uncomplexed copper(I) acetate [1·893 (17), 1·901 (18) Å] in which the acetate groups are bridging (Drew, Edwards & Richards, 1973). As expected the acetate group is planar. The slightly asymmetrical chelation of this group as demonstrated by the Cu–O bond lengths and also the Cu–O–C angles [91·3 (4), 87·4 (6)°] has been noted in other complexes, for example $(CH_3)_4N[Pb(O_2CCH_3)_3Ph_2]$ with Pb–O distances of 2·48 (2) and 2·55 (2) Å, (Alcock, 1972). The O–Cu–O angle is 59·4 (2)° as a result of the constrained geometry of the acetate group.

For copper(I)–triphenylphosphine complexes Cu–P distances range from 2·135 (1) Å in $(\eta\text{-}C_5H_5)Cu(PPh_3)$ (Cotton & Takats, 1970) to 2·303 (2) Å in one of the three crystallographically independent molecules of $Cu(BF_4)(PPh_3)_3$ (Gaughan, Dori & Ibers, 1974). In this context the distances of 2·233 (2) and 2·240 (3) Å found in (I) are unremarkable. However, the Cu–P distances in (I) are the shortest and the P–Cu–P angle of 133·4 (1)° in (I) is the largest found in the [Cu (chelating anion) $(PPh_3)_2$] series (Table 4). Lippard & Palenik (1971) note that within this series the P–Cu–P angles are largest for planar chelating anions and decrease as the non-planarity and general crowding of the anion increases. The present results agree well with these suggestions. The acetate group is planar, and not particularly crowded, the Cu–O distances are quite long and the P–Cu–P angle is the largest of the series.

It has alternatively been suggested that chelating anions can be regarded as simply negatively charged species occupying one coordination position (Davis, Belford & Paul, 1973). The geometry of the acetate complex could therefore be described as distorted trigonal planar. Although the P–Cu–P angle of 133·4 (1)° is less remarkable if considered in the light of an idealized value of 120°, this approach clearly has its limitations, particularly for (I) since a genuine monodentate acetate complex, $Cu(O_2CCH_3)(PPh_3)_3$ has been well characterized (Hammond, Jardine & Vohra, 1971).

There are no intermolecular contacts significantly less than the sum of the van der Waals radii.

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