

Table 2. Bond distances (Å) and angles (°) for $\text{Co}(\text{H}_2\text{O})_6^{2+}$ octahedra, SO_4^{2-} tetrahedra and hydrogen bonds

Water octahedron for Co(1)			
Co(1)—O(5)	2.103 (3)	O(5)—Co(1)—O(6)	91.7 (2)
—O(6)	2.048 (5)	O(5)—Co(1)—O(7)	95.5 (1)
—O(7)	2.102 (4)	O(6)—Co(1)—O(7)	88.0 (1)
Mean	2.084 (4)	Mean	91.7 (1)
Water octahedron for Co(2)			
Co(2)—O(8)	2.112 (4)	O(8)—Co(2)—O(9)	90.8 (1)
—O(9)	2.074 (4)	O(8)—Co(2)—O(10)	87.0 (1)
—O(10)	2.079 (4)	O(9)—Co(2)—O(10)	88.6 (2)
Mean	2.088 (4)	Mean	88.8 (1)
SO_4 tetrahedron			
S(1)—O(1)	1.488 (4)	O(1)—S(1)—O(2)	109.0 (2)
—O(2)	1.458 (4)	O(1)—S(1)—O(3)	106.2 (2)
—O(3)	1.497 (3)	O(1)—S(1)—O(4)	110.8 (2)
—O(4)	1.466 (4)	O(2)—S(1)—O(3)	110.3 (2)
Mean	1.477 (4)	O(2)—S(1)—O(4)	110.5 (3)
		O(3)—S(1)—O(4)	109.0 (2)
		Mean	109.3 (2)
Hydrogen bonds			
O(5)...O(1 ⁱ)	2.742 (4)	O(8)...O(1 ⁱⁱ)	2.783 (4)
O(5)...O(3 ⁱⁱ)	2.806 (4)	O(8)...O(2 ⁱⁱ)	2.663 (2)
O(6)...O(3 ⁱⁱ)	2.676 (5)	O(9)...O(2 ⁱⁱ)	2.698 (5)
O(6)...O(4 ⁱ)	2.781 (5)	O(9)...O(8 ⁱ)	2.984 (5)
O(7)...O(3 ⁱⁱⁱ)	2.947 (4)	O(10)...O(4 ⁱ)	2.756 (5)
O(7)...O(4 ⁱ)	2.856 (4)	O(10)...O(1 ⁱ)	2.806 (5)
Mean	2.791 (4)		

Symmetry-related positions: (i) x, y, z ; (ii) $-x, y, \frac{1}{2} - z$; (iii) $-x, -y, -z$.

Ruben & Templeton, 1964), between 1.45 (1) and 1.48 (1) Å in $\text{NiSO}_4 \cdot 6\text{D}_2\text{O}$ (O'Connor & Dale, 1966) and between 1.460 (4) and 1.482 (4) Å in $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ (Baur, 1964). Bond distances and angles are summarized in Table 2.

The six independent water molecules for two different $\text{Co}(\text{H}_2\text{O})_6$ octahedra around the Co(1) and Co(2) atoms are involved in hydrogen bonds in which the oxygen atoms of the sulfate group and an O(8) oxygen atom of water act as acceptors (Table 2). The

hydrogen-bonding scheme confirms the results of Zalkin *et al.* (1962). The average O...O hydrogen-bonding distance is 2.791 Å. The individual values range from 2.663 (4) to 2.984 (5) Å. They are shorter than the sum of the van der Waals radii which is given by Bondi (1964) as $r_{\text{O}} + r_{\text{O}} = 3.04$ Å. They were found by O'Connor & Dale (1966) to be between 2.69 (2) and 2.84 (2) Å and by Baur (1964) to be between 2.70 and 2.98 Å, in $\text{NiSO}_4 \cdot \text{D}_2\text{O}$ and $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ respectively.

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Structure of the Tetrakis(acetato)bis(triphenylphosphine)dicopper(II) Complex $\text{Cu}_2\text{Ac}_4(\text{PPh}_3)_2$

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Abstract. $[\text{Cu}_2(\text{C}_2\text{H}_3\text{O}_2)_4(\text{C}_{18}\text{H}_{15}\text{P})_2]$, $M_r = 887.84$, triclinic, $P\bar{1}$, $a = 9.149$ (7), $b = 9.559$ (3), $c = 14.709$ (3) Å, $\alpha = 61.00$ (2), $\beta = 72.67$ (5), $\gamma = 90.34$ (5)°, $V = 1056.3$ (2.1) Å³, $Z = 1$, $D_m = 1.40$, $D_x = 1.395$ g cm⁻³, $\text{Mo K}\alpha$, $\lambda = 0.71069$ Å, $\mu = 11.7$ cm⁻¹, $F(000) = 428$, $T = 293$ K, $R = 5.22\%$ for

1065 reflections. The crystal structure of $\text{Cu}_2\text{Ac}_4(\text{PPh}_3)_2$ comprises centrosymmetrical molecules each consisting of a dimeric unit Cu_2Ac_4 , similar to that found in the structure of copper(II) acetate monohydrate, with the PPh_3 molecules bonded to the Cu^{II} atoms. The interatomic distance Cu—Cu in the dimeric

unit is 2.709 (1) Å, bond distances Cu—O (average) and Cu—P are 1.956 (6) and 2.57 (2) Å, respectively.

Introduction. Copper(II) is usually reduced to copper(I) in reactions with triphenylphosphine. We have recently synthesized acetatocopper(II) and mixed-valence acetatocopper(I,II) complexes with PPh₃: Cu₂Ac₄-(PPh₃)₂ (Ondrejovič, Valigura, Máriássy & Mroziński, 1985) and Cu₄Ac₈(PPh₃)₄ (Valigura, Koman, Ďurčanská, Ondrejovič & Mroziński, 1986), respectively. The conditions of their syntheses showed a significant role of the dimeric structure of copper(II) acetate in the prevention of reduction and stabilization of Cu^{II} relative to Cu^I.

The spectral and magnetic properties of the Cu₂Ac₄-(PPh₃)₂ complex indicated that its structure might be similar to that of dimeric copper(II) acetate monohydrate (de Meester, Fletcher & Skapski, 1973). This paper presents the crystal and molecular structure of the Cu₂Ac₄(PPh₃)₂ complex.

Experimental. The complex Cu₂Ac₄(PPh₃)₂ presents green prism-shaped crystals, of which one measuring 0.30 × 0.20 × 0.30 mm was selected. *D_m* measured by flotation. Syntex P2₁ diffractometer, 15 reflections with 8 ≤ 2θ ≤ 17° for determining lattice parameters. Absorption and extinction ignored. 0 ≤ 2θ ≤ 55°, *h, k, l* range -11, -11, 0 to 10, 11, 11. Two standard reflections every 98, no significant intensity variation, 1065 independent reflections with *I* > 2σ(*I*). Cu and P atom positions from Patterson map, other non-H atoms from Fourier map. H atoms from difference Fourier map. Anisotropic full-matrix refinement (except H atoms) based on *F*, *R* = 0.052, *w* = 1, (*Δ*/σ)_{max} in final least-squares cycle 0.30, *Δ*ρ ≤ |0.7| e Å⁻³. Calculations performed on M-40-30 computer with NRC program (Pippy & Ahmed, 1968).

Discussion. Atomic coordinates are listed in Table 1; Table 2 gives the bond distances and angles.* The crystal structure consists of centrosymmetrical Cu₂Ac₄(PPh₃)₂ molecules (Fig. 1), where the centre of symmetry lies between the two Cu^{II} atoms. The two Cu^{II} atoms are bridge-bonded by four acetate groups as in copper(II) acetate monohydrate. Each Cu^{II} shows a fivefold coordination in the form of a square pyramid with the four O atoms of the bridging acetate groups in the basal plane and the P atom of a PPh₃ molecule at the apex.

The apical P atom is slightly displaced from the regular position and the Cu'—Cu—P angle is 169.67 (4)°. [See also the P—Cu—O(1) angles in Table

* 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 44499 (16 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

2.] Cu^{II} is displaced by 0.245 (1) Å out of the basal plane towards the apical P atom.

Table 1. Final atomic coordinates (×10⁴) with e.s.d.'s in parentheses and equivalent isotropic thermal parameters *B_{eq}*

	<i>x</i>	<i>y</i>	<i>z</i>	<i>B_{eq}</i> (Å ²)
Cu	-235 (1)	-208 (1)	1015 (1)	2.19
P	-230 (2)	-219 (2)	2765 (1)	3.68
O(1)	-2173 (6)	-1654 (6)	1506 (4)	6.47
O(2)	-1731 (6)	-1352 (6)	-152 (3)	5.58
O(3)	-927 (6)	2008 (6)	-1202 (3)	5.30
O(4)	-1271 (6)	1631 (6)	467 (4)	6.52
C(1)	-2553 (8)	-1911 (8)	837 (5)	4.22
C(2)	-4123 (9)	-2953 (9)	1267 (6)	5.36
C(3)	-1466 (9)	2368 (8)	-442 (5)	4.92
C(4)	-2309 (10)	3802 (9)	-755 (6)	6.45
C(11)	-1005 (8)	-2172 (7)	4079 (5)	3.70
C(12)	-239 (8)	-2716 (7)	4894 (5)	3.89
C(13)	-919 (8)	-4190 (8)	5847 (5)	4.34
C(14)	-2181 (9)	-5134 (9)	6050 (5)	5.38
C(15)	-2910 (10)	-4650 (9)	5289 (6)	6.28
C(16)	-2292 (9)	-3167 (9)	4256 (6)	5.35
C(21)	1739 (8)	414 (8)	2656 (5)	3.64
C(22)	2971 (8)	-176 (8)	2205 (5)	4.22
C(23)	4465 (9)	183 (9)	2158 (5)	5.60
C(24)	4772 (9)	1306 (8)	2475 (5)	5.09
C(25)	3576 (11)	1935 (10)	2897 (6)	6.75
C(26)	2063 (9)	1456 (8)	3019 (5)	5.31
C(31)	-1355 (8)	1179 (8)	3077 (5)	3.74
C(32)	-1049 (9)	2763 (9)	2189 (6)	5.21
C(33)	-1787 (9)	3988 (10)	2342 (6)	5.33
C(34)	-2852 (9)	3490 (9)	3387 (6)	5.73
C(35)	-3194 (8)	1941 (9)	4250 (5)	4.73
C(36)	-2440 (9)	728 (9)	4127 (6)	5.02

$$B_{eq} = \frac{8}{3} \pi^2 \sum_i \sum_j U_{ij} a_i^* a_j^* a_i \cdot a_j$$

Table 2. Selected bond distances (Å) and angles (°) with e.s.d.'s in parentheses

Cu—Cu'	2.709 (1)	P—Cu—O(1)	104.2 (2)
Cu—P	2.570 (2)	P—Cu—O(2)	90.3 (2)
Cu—O(1)	1.953 (6)	P—Cu—O(3)	96.8 (2)
Cu—O(2)	1.961 (5)	P—Cu—O(4)	97.2 (2)
Cu—O(3)	1.976 (6)	O(1)—Cu—O(3)	90.3 (2)
Cu—O(4)	1.934 (1)	O(1)—Cu—O(4)	89.2 (3)
O(1)—C(1)	1.260 (11)	O(2)—Cu—O(3')	89.8 (2)
O(2)—C(1)	1.248 (8)	O(2)—Cu—O(4)	87.1 (3)
C(1)—C(2)	1.512 (12)	O(1)—Cu—O(2')	165.5 (2)
O(3)—C(3)	1.288 (9)	O(3)—Cu—O(4)	165.6 (2)
O(4)—C(3)	1.243 (9)	O(1)—C(1)—O(2)	124.5 (7)
C(3)—C(4)	1.516 (13)	O(1)—C(1)—C(2)	117.3 (7)
P—C(11)	1.842 (6)	O(2)—C(1)—C(2)	118.2 (7)
C(11)—C(12)	1.448 (9)	Cu—O(1)—C(1)	120.7 (5)
C(12)—C(13)	1.376 (9)	Cu'—O(2)—C(1)	128.9 (5)
C(13)—C(14)	1.325 (11)	O(3)—C(3)—O(4)	122.7 (7)
C(14)—C(15)	1.364 (11)	O(3)—C(3)—C(4)	114.8 (7)
C(15)—C(16)	1.424 (11)	O(4)—C(3)—C(4)	122.4 (7)
C(16)—C(17)	1.387 (11)	Cu'—O(3)—C(3)	123.1 (5)
P—C(21)	1.833 (8)	Cu—O(4)—C(3)	128.5 (5)
C(21)—C(22)	1.397 (11)	Cu—P—C(11)	116.5 (2)
C(22)—C(23)	1.380 (12)	Cu—P—C(21)	111.5 (2)
C(23)—C(24)	1.418 (12)	Cu—P—C(31)	115.5 (3)
C(24)—C(25)	1.382 (13)	C(11)—P—C(21)	105.6 (3)
C(25)—C(26)	1.387 (13)	C(11)—P—C(31)	102.6 (3)
C(26)—C(21)	1.404 (11)	C(21)—P—C(31)	103.8 (3)
P—C(31)	1.839 (8)		
C(31)—C(32)	1.392 (11)		
C(32)—C(33)	1.432 (13)		
C(33)—C(34)	1.390 (11)		
C(34)—C(35)	1.356 (11)		
C(35)—C(36)	1.411 (13)		
C(36)—C(31)	1.412 (9)		

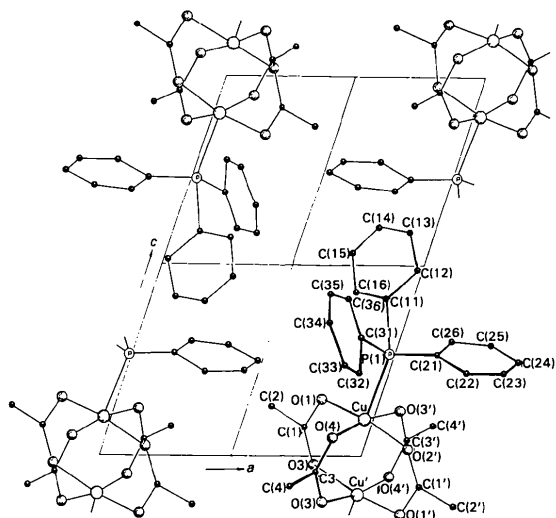


Fig. 1. View of the molecular packing, with atom-numbering scheme indicated.

The basal plane of the $\text{Cu}_2\text{Ac}_4(\text{PPh}_3)_2$ complex shows remarkable differences between the Cu—O bond distances. The long Cu—O(3) bond distance [1.976 (6) Å] corresponds to the long distance C(3')—O(3') [1.288 (9) Å] of the acetate group and indicates a weaker coordination of the O(3') oxygen atom in comparison with O(4) which occupies the *trans* position in the basal plane with bond distance Cu—O(4) 1.934 (5) Å.

The selected interatomic distances and Cu—basal plane distances (see Table 3) show that replacement of water molecules in $\text{Cu}_2\text{Ac}_4(\text{H}_2\text{O})_2$ by triphenylphosphine ligands led to an elongation of the Cu—Cu distance through displacement of the Cu atoms from the basal planes. The elongation of the Cu—Cu distance is followed by shortening of the Cu—O_{av} (in basal plane) distance. The replacement of water molecules

Table 3. Selected distances (Å) for aqua and for triphenylphosphine copper(II) carboxylates

Complex	Ligand	Interatomic distances			Cu—basal plane distance
		Cu—L	Cu—Cu	Cu—O _{av}	
$\text{Cu}_2\text{Ac}_4\text{L}_2$	H_2O^*	2.156 (4)	2.616 (1)	1.969 (3)	0.192
		2.161 (1)	2.614 (2)	1.969 (2)	0.191
Cu_2YL_2	PPh_3	2.570 (2)	2.709 (1)	1.956 (5)	0.245
		2.140 (3)	2.626 (2)	1.955 (4)	0.258
	PPh_3	2.570 (2)	2.676 (1)	1.967 (3)	0.226

Y = 2,9-bis(methoxymethyl)-2,9-dimethyl-4,7-dioxadecanedioate(2-) anion.

* de Meester, Fletcher & Skapski (1973); Brown & Chidambaram (1973).

† McCrindle, Ferguson, McAlees & Roberts (1981).

in $\text{Cu}_2\text{Y}_2(\text{H}_2\text{O})_2$ [Y = 2,9-bis(methoxymethyl)-2,9-dimethyl-4,7-dioxadecanedioate(2-) anion] by triphenylphosphine (McCrindle, Ferguson, McAlees & Roberts, 1981) causes smaller changes in Cu—Cu and Cu—O_{av} (in basal plane) distances. However, the displacements of the Cu atoms from the basal planes (see Cu—basal plane distance in Table 3) are in opposite directions. These differences can be explained by the different basicity of the ligands.

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The Structure of Di- μ -chloro-bis[chloro(η^6 -hexamethylbenzene)ruthenium(II)]-Chloroform (1/2)

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Abstract. $[\text{Ru}_2\text{Cl}_2(\text{C}_{12}\text{H}_{18})_2] \cdot 2\text{CHCl}_3$, $M_r = 907.26$, triclinic, $P\bar{1}$, $a = 10.192$ (1), $b = 10.953$ (1), $c =$

8.529 (2) Å, $\alpha = 100.26$ (1), $\beta = 106.64$ (1), $\gamma = 104.74$ (1)°, $V = 849.2$ (5) Å³, $Z = 1$, $D_x = 1.77$ g cm⁻³, Mo K α radiation ($\lambda = 0.71073$ Å), $\mu = 16.9$ cm⁻¹, $F(000) = 452$, $R_1 = 0.025$ for 2732 re-

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