Table 11 (*cont.*)

Bond angles	
O(IV)–O(V) —O(VI)	75·3
O(IV)–O(V) —O′(II)	131·5
O(VI)–O(V) —O′(II)	116·8
O(V) –O′(II)—O′(VI)	97·5
O′(II)–O′(VI) –O′(V)	106·6
O(II)^{i}–O″(VI)–O(I)^{ii}	122·8
P——O(II)——O′(V)	124·8
P——O(II)——O″(VI)	108·8
P^{i}——O(I) ——O″(VI)^{ii}	125·9
C(3′) –O(3′)——N′(2)	125·8
O(3′) –N′(2) —C′(2)	106·3

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Five-Coordinate Adducts of Cupric β-Diketone Complexes: the Structure of 4-Methylpyridine bis-(*o*-hydroxyacetophenonato)copper (II)

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4-Methylpyridine bis-(*o*-hydroxyacetophenonato)copper(II) is the first 'stable' 1:1 adduct of a cupric β-diketone to have its structure determined by X-rays. The copper atom is five-coordinated and has a tetragonal pyramidal environment. Four oxygen atoms form an approximate square-planar arrangement about the copper atom, which is raised slightly out of this plane towards the apical nitrogen atom. The discrete molecule has a twofold axis of symmetry. Copper–oxygen and carbon–oxygen bond distances indicate that the π-electron system of the coordinated β-diketone framework has been largely destroyed by the presence of a benzene ring in the *o*-hydroxyacetophenone residue. The crystals, which decompose during irradiation, crystallize in the orthorhombic system, space group *Pbcn*, with lattice constants $a = 9{\cdot}23 \pm 0{\cdot}05$, $b = 13{\cdot}99 \pm 0{\cdot}07$, $c = 15{\cdot}59 \pm 0{\cdot}08$ Å. The intensities of three-dimensional equi-inclination Weissenberg data were estimated visually and the structure was solved by Patterson and Fourier techniques. Refinement of atomic parameters was carried out by the method of least-squares.

Introduction

Cupric complexes with β-diketones have been extensively investigated in recent years, and X-ray crystallographic studies have shown that their structures are essentially square-planar, although in some cases there is evidence of weak axial interactions (Boyko, 1963; Barclay & Cooper, 1965; Hall, McKinnon & Waters, 1965). Graddon (1959) observed changes in the visible spectra of these compounds in chloroform, produced by increasing the concentrations of various heterocyclic bases, and he proposed the formation of

Table 1. *Observed and calculated structure amplitudes for* 4-*methylpyridinebis*-(*o-hydroxyacetophenonato*)*copper*(II)

Columns from left to right read *h*, *k*, *l*, F_o and F_c. Unobserved data have been omitted.

0	0	2	39.5	-37.7
0	0	4	85.9	84.5
0	0	6	77.8	-77.5
0	0	8	6.9	8.0
0	0	10	64.2	-58.0
0	0	12	41.8	38.3
0	0	14	22.9	-20.3
0	0	18	8.4	-8.3
0	2	1	83.3	-73.0
0	2	2	4.5	-4.2
0	2	3	5.6	3.8
0	2	5	21.2	-16.0
0	2	6	9.9	8.4
0	2	7	15.9	-13.3
0	2	8	7.6	-6.9
0	2	9	48.0	-39.5
0	2	10	13.0	9.4
0	2	11	33.2	30.9
0	2	12	8.2	-9.5
0	2	13	53.1	-40.6
0	2	14	6.6	6.0
0	2	16	6.2	-4.8
0	2	17	15.6	-9.5
0	2	19	16.4	11.0
0	4	0	218.9	-204.1
0	4	1	24.0	22.5
0	4	2	21.7	-16.1
0	4	3	30.9	-27.8
0	4	4	15.2	-15.2
0	4	5	6.5	5.9
0	4	6	34.7	27.3
0	4	7	7.1	-6.9
0	4	8	8.4	6.9
0	4	9	16.3	11.6
0	4	10	41.0	33.3
0	4	11	9.6	-7.7
0	4	12	28.9	-24.5
0	4	13	9.2	7.9
0	4	14	16.0	12.6
0	6	0	76.6	76.3
0	6	1	61.9	58.1
0	6	2	40.0	-38.0
0	6	3	17.1	-15.0
0	6	4	33.3	32.7
0	6	5	16.5	12.6
0	6	6	32.7	-33.4
0	6	7	9.1	7.2
0	6	8	23.1	20.4
0	6	9	21.6	21.8
0	6	10	22.7	-20.7
0	6	11	23.9	-19.1
0	6	12	23.6	18.6
0	6	13	25.4	22.4
0	6	14	10.1	-9.3
0	6	16	9.6	7.9
0	6	17	3.4	3.4
0	6	18	6.8	-5.0
0	8	0	79.0	78.1
0	8	1	18.4	-20.4
0	8	2	3.5	3.8
0	8	3	22.0	26.4
0	8	5	12.9	-12.2
0	8	6	10.7	-8.0
0	8	7	15.1	15.6
0	8	8	9.2	-9.2
0	8	9	25.0	-24.0
0	8	10	13.8	-12.8
0	8	11	19.7	20.4
0	8	12	10.3	10.8
0	8	13	20.5	-19.7
0	8	15	12.3	9.8
0	8	16	3.4	-3.6
0	8	17	14.8	-10.1
0	10	0	50.7	-44.6
0	10	1	7.7	-10.1
0	10	2	15.7	19.1
0	10	3	5.6	-5.6
0	10	4	15.8	-16.1
0	10	6	16.1	17.3
0	10	8	12.6	-8.0
0	10	9	6.5	-5.9
0	10	10	9.2	10.0
0	10	11	9.0	10.9
0	10	12	9.7	-9.3
0	10	13	12.7	-12.5
0	12	0	17.8	-21.5
0	12	1	12.1	15.0
0	12	3	12.2	-16.6
0	12	4	6.1	7.0
0	12	5	8.0	7.9
0	12	7	6.5	-7.2
0	12	8	9.0	11.4
0	12	9	9.3	12.7
0	12	11	8.4	-10.3
0	12	13	12.9	9.8
0	14	0	14.9	18.6
0	14	1	5.5	-6.1
0	14	3	10.4	12.0
0	14	4	4.4	5.3
0	14	5	9.8	-11.5
0	14	6	5.9	-7.5
0	14	7	8.1	9.4
1	0	2	23.6	-24.7
1	0	4	51.8	-45.9
1	0	6	22.3	15.2
1	0	8	6.2	-5.8
1	0	10	18.7	15.2
1	0	16	4.1	4.0
1	1	1	79.7	-88.6
1	1	2	40.8	41.3
1	1	3	50.3	53.7
1	1	4	30.4	-25.7
1	1	5	32.9	-34.0
1	1	6	7.5	-8.3
1	1	7	18.5	17.3
1	1	8	5.8	-5.0
1	1	9	31.0	-26.7
1	1	10	22.8	19.8
1	1	11	30.6	26.4
1	1	12	22.9	19.8
1	1	13	23.2	-20.3
1	1	14	12.6	-11.2
1	1	16	5.4	4.5
1	1	17	7.8	-6.3
1	1	18	4.4	-4.4
1	1	19	8.9	5.9
1	2	1	18.3	20.0
1	2	2	4.7	-1.4
1	2	3	16.8	15.9
1	2	4	8.1	-5.8
1	2	5	22.7	-17.3
1	2	7	5.8	4.8
1	2	8	9.3	-8.9
1	2	9	3.9	-3.9
1	2	11	7.3	6.2
1	2	12	2.9	-2.8
1	3	0	98.7	-129.3
1	3	1	29.5	-35.0
1	3	2	15.2	13.3
1	3	3	13.6	10.9
1	3	4	15.2	-16.1
1	3	5	3.6	1.8
1	3	6	42.0	35.2
1	3	7	9.5	-6.2
1	3	8	16.3	-11.0
1	3	9	3.5	-1.0
1	3	10	41.8	30.5
1	3	11	6.9	5.0
1	3	12	34.8	-26.0
1	3	13	6.8	-5.2
1	3	14	19.5	16.1
1	3	15	8.5	-6.4
1	3	16	9.9	-7.4
1	3	18	8.4	7.4
1	4	1	39.4	-40.2
1	4	2	25.5	23.8
1	4	3	7.7	-3.9
1	4	4	17.5	18.1
1	4	5	2.7	-3.8
1	4	7	8.6	6.6
1	4	8	3.4	-3.3
1	4	9	6.2	5.1
1	4	10	6.6	-6.9
1	4	16	3.9	-2.4
1	5	0	45.6	-50.5
1	5	1	56.6	64.2
1	5	2	2.5	-2.8
1	5	3	36.2	-40.1
1	5	4	3.7	2.3
1	5	5	35.3	31.3
1	5	6	8.5	7.4
1	5	7	20.6	-17.1
1	5	8	7.7	5.7
1	5	9	34.1	29.9
1	5	10	10.1	7.7
1	5	11	34.9	-29.1
1	5	12	7.6	-7.3
1	5	13	30.8	23.1
1	5	14	4.2	2.3
1	5	15	7.1	-6.8
1	5	17	11.5	8.6
1	6	1	7.5	-7.1
1	6	2	16.1	13.0
1	6	3	3.8	-3.9
1	6	4	4.2	-2.6
1	6	5	4.5	4.4
1	6	6	15.0	12.0
1	6	7	3.5	2.3
1	6	8	9.8	9.3
1	6	9	3.9	-2.9
1	6	14	7.3	5.2
1	7	0	68.5	72.5
1	7	1	16.7	-17.1
1	7	2	4.3	-6.0
1	7	3	25.7	24.3
1	7	4	5.8	10.3
1	7	5	22.5	-23.3
1	7	6	24.5	-22.5
1	7	7	18.3	17.1
1	7	8	11.7	8.0
1	7	9	12.2	-10.5
1	7	10	28.0	-24.2
1	7	11	6.1	5.3
1	7	12	20.9	20.0
1	7	14	18.0	-14.1
1	7	15	9.4	6.9
1	7	16	6.9	6.0
1	8	1	28.8	30.1
1	8	2	9.3	-10.2
1	8	3	10.4	8.8
1	8	4	3.5	-5.5
1	8	5	9.0	-6.9
1	8	6	3.8	3.7
1	8	9	15.2	-12.9
1	8	10	6.1	5.4
1	8	15	3.6	-2.7
1	9	1	30.1	-32.2
1	9	2	22.4	23.4
1	9	3	14.0	17.5
1	9	4	19.9	-20.2
1	9	5	14.1	-12.4
1	9	6	14.6	16.0
1	9	8	19.9	-19.7
1	9	9	8.0	9.0
1	9	10	11.5	10.2
1	9	11	8.6	7.6
1	9	12	9.4	-8.7
1	9	13	8.5	-6.2
1	9	14	8.3	8.2
1	9	15	3.3	-3.2
1	9	16	7.9	-7.5
1	10	2	9.7	-10.4
1	10	3	5.6	6.8
1	10	4	4.0	3.3
1	10	5	5.8	-6.0
1	10	6	9.4	-10.0
1	10	7	4.2	4.4
1	10	8	6.1	-4.8
1	10	14	6.8	-5.2
1	11	0	26.9	-31.9
1	11	1	13.8	16.4
1	11	3	13.3	-19.9
1	11	4	4.2	-4.0
1	11	5	17.2	19.2
1	11	6	11.5	10.5
1	11	7	16.9	-16.4
1	11	8	4.3	-3.5
1	11	9	12.8	14.8
1	11	10	14.5	15.0
1	11	11	12.0	-12.9
1	11	12	9.5	-12.1
1	11	13	6.8	7.6
1	11	14	10.3	10.0
1	11	15	8.0	-9.5
1	12	1	15.5	-17.4
1	12	6	4.3	-5.4
1	12	9	5.5	6.1
1	13	0	14.4	15.6
1	13	1	8.7	9.8
1	13	2	18.3	-20.8
1	13	4	14.3	16.9
1	13	5	4.2	3.4
1	13	6	11.1	-14.8
1	13	7	4.1	2.7
1	13	8	11.9	14.3
1	13	9	3.7	3.5
1	13	10	7.1	-8.6
1	13	12	7.5	7.5
1	14	2	4.2	4.9
1	15	1	6.6	-8.4
1	15	2	7.2	7.8
1	15	3	7.1	9.6
1	15	7	7.4	6.7
1	15	8	6.5	-5.7
1	15	9	4.7	-6.1
1	16	1	4.8	7.5
2	0	0	44.0	53.4
2	0	2	87.2	-95.3
2	0	4	74.7	77.0
2	0	6	79.1	-76.4
2	0	8	56.0	52.6
2	0	10	36.0	-35.7
2	0	12	22.0	20.8
2	0	14	24.2	-21.9
2	0	16	21.7	18.9
2	0	18	12.6	-11.1
2	1	1	21.0	21.3
2	1	2	23.3	-23.7
2	1	3	18.8	-14.4
2	1	4	22.8	20.2
2	1	5	5.6	2.9
2	1	6	13.1	-8.4
2	1	7	12.5	-11.9
2	1	8	24.1	23.0
2	1	9	9.2	9.3
2	1	10	9.4	-8.6
2	2	0	9.4	-7.8
2	2	1	23.0	-20.0
2	2	2	11.8	11.2
2	2	3	56.8	57.7
2	2	4	11.3	-9.8
2	2	5	36.7	-32.9
2	2	6	8.6	9.3
2	2	7	61.5	48.8
2	2	8	8.9	-8.2
2	2	9	16.5	-18.9
2	2	10	4.3	6.2
2	2	11	28.5	21.3
2	2	12	7.3	-5.1
2	2	13	15.6	-13.9
2	2	14	7.1	5.7
2	2	15	19.4	15.3
2	2	16	3.5	-2.8
2	2	17	17.8	-12.3
2	2	19	6.7	8.7
2	3	1	8.7	8.4
2	3	2	4.0	4.2
2	3	3	6.2	-4.0
2	3	5	13.8	10.4
2	3	6	7.5	-7.5
2	3	7	14.8	-11.2
2	3	8	12.0	-9.1
2	3	9	16.0	12.2
2	3	10	6.7	5.4
2	3	11	10.6	-7.6
2	3	12	7.4	5.5
2	4	0	16.1	-15.7
2	4	1	17.5	17.7
2	4	2	31.5	35.7
2	4	3	8.6	-7.7
2	4	4	39.7	-36.9
2	4	5	23.5	22.1
2	4	6	42.6	39.2
2	4	7	11.3	-11.5
2	4	8	28.9	-25.2
2	4	9	9.7	9.2
2	4	10	23.3	18.5
2	4	11	12.0	-11.2
2	4	12	7.9	-7.1
2	4	13	3.8	4.6
2	4	14	14.1	12.0
2	4	15	7.3	-6.4
2	4	16	14.0	-10.4
2	4	17	4.2	3.9
2	4	18	5.9	5.5
2	5	1	11.9	-15.3
2	5	2	11.3	13.7
2	5	3	11.3	9.7
2	5	4	5.0	-4.0
2	5	5	8.7	9.8
2	5	6	8.9	-6.8
2	5	7	2.9	2.2
2	5	8	4.5	-3.9
2	5	10	6.1	-5.7
2	5	11	6.9	-3.2
2	5	14	3.7	4.8
2	5	15	2.5	1.1
2	6	0	34.8	38.5
2	6	1	14.6	15.9
2	6	2	38.2	-43.0
2	6	3	35.5	-33.4
2	6	4	41.1	38.2
2	6	5	33.2	27.1
2	6	6	37.8	-33.9
2	6	7	32.5	-25.9
2	6	8	35.0	28.2
2	6	9	19.1	16.8
2	6	10	25.8	-22.0
2	6	11	13.5	-8.7
2	6	12	15.7	14.6
2	6	13	8.5	8.3
2	6	14	23.8	-15.5
2	6	15	12.5	-8.5
2	6	16	13.6	8.9
2	6	17	8.5	6.7
2	6	18	8.3	-8.0

Table 1 (*cont.*)

2	7	1	7.7	9.2
2	7	2	3.9	-3.7
2	7	3	13.1	-13.6
2	7	4	2.9	2.0
2	7	5	3.0	2.8
2	7	6	3.1	-2.9
2	7	7	5.7	-5.5
2	7	8	10.4	10.0
2	7	10	11.8	-10.3
2	7	11	3.8	2.7
2	7	13	5.9	6.0
2	8	0	10.3	9.1
2	8	1	24.4	-31.8
2	8	3	18.3	22.5
2	8	4	15.9	15.3
2	8	5	33.4	-34.4
2	8	6	12.2	-13.7
2	8	7	23.6	22.5
2	8	8	5.7	5.7
2	8	9	19.0	-18.6
2	8	10	10.0	-7.8
2	8	11	19.8	19.2
2	8	12	3.7	-1.9
2	8	13	12.0	-10.9
2	8	14	6.8	-4.9
2	8	15	13.4	11.6
2	8	16	3.7	3.8
2	9	1	7.9	9.8
2	9	2	8.4	-10.8
2	9	3	11.6	-14.0
2	9	6	5.0	4.0
2	9	7	11.0	-11.4
2	9	9	8.9	8.7
2	9	10	8.5	8.3
2	9	13	4.8	5.0
2	9	14	3.1	-4.9
2	10	0	14.8	-18.2
2	10	2	20.2	19.6
2	10	3	7.1	7.7
2	10	4	17.3	-18.5
2	10	5	10.4	-7.6
2	10	6	16.3	17.2
2	10	7	3.7	4.2
2	10	8	12.6	-14.1
2	10	9	7.6	-7.8
2	10	10	9.2	11.3
2	10	12	7.3	-6.7
2	10	13	3.2	-3.5
2	10	14	10.4	8.8
2	11	1	7.8	-9.0
2	11	3	4.5	5.7
2	11	4	4.6	-4.7
2	11	5	5.3	5.1
2	11	6	5.3	6.2
2	11	8	6.5	-7.8
2	11	9	5.2	6.3
2	11	10	11.4	9.6
2	11	11	8.4	-5.6
2	11	13	5.0	-4.4
2	12	1	12.6	16.7
2	12	2	10.7	-13.7
2	12	3	10.8	-11.5
2	12	5	18.7	18.9
2	12	7	11.5	-11.9
2	12	8	6.3	6.9
2	12	9	9.0	10.1
2	12	11	11.7	-10.4
2	12	12	9.8	8.4
2	12	13	4.2	5.9
2	13	2	7.5	9.6
2	13	6	3.6	2.2
2	13	10	4.2	-4.5
2	14	0	7.3	9.2
2	14	1	8.9	-12.3
2	14	2	7.2	-7.8
2	14	3	8.4	8.4
2	14	4	8.0	8.6
2	14	5	6.9	-6.9
2	14	6	10.6	-8.4
2	14	7	9.7	9.7
2	14	10	6.7	-5.8
2	14	12	6.7	3.3
2	15	1	5.8	7.6
2	16	1	5.8	-5.9
2	16	2	9.0	11.0
2	16	5	6.7	-7.2
3	0	2	19.3	21.3
3	0	4	4.6	-5.8
3	0	6	30.0	28.6
3	0	8	11.0	-12.3
3	0	10	5.5	-5.1
3	0	12	19.3	-18.4
3	0	14	5.1	-2.5
3	0	16	4.0	2.2
3	1	0	2.9	-2.0
3	1	1	2.8	2.1
3	1	2	8.1	4.5
3	1	3	36.2	41.5
3	1	4	49.9	53.1
3	1	5	48.7	-50.8
3	1	6	19.3	-20.3
3	1	7	34.4	36.7
3	1	8	11.2	11.8
3	1	9	31.9	-36.3
3	1	10	9.8	-8.5
3	1	12	17.5	-17.2
3	1	13	13.6	-13.2
3	1	14	5.1	-4.7
3	1	15	17.4	17.7
3	1	16	6.2	3.8
3	1	17	9.2	-9.1
3	2	1	7.7	-8.1
3	2	3	10.2	-8.1
3	2	4	5.7	-4.7
3	2	5	16.3	-17.7
3	2	6	6.1	5.5
3	2	7	13.7	10.4
3	2	8	2.8	-1.8
3	2	9	4.3	-2.2
3	2	10	8.5	6.2
3	2	11	9.0	7.7
3	3	0	7.5	-1 4
3	3	1	18.1	32.0
3	3	2	9.1	12.4
3	3	4	69.0	-65.2
3	3	5	20.1	-16.4
3	3	6	43.2	37.9
3	3	7	6.3	5.4
3	3	8	35.7	-29.3
3	3	9	17.1	-16.3
3	3	10	32.7	22.2
3	3	11	14.8	-12.9
3	3	12	8.0	3.3
3	3	14	17.8	14.8
3	3	15	6.9	8.1
3	3	16	14.4	-12.7
3	3	18	4.7	8.1
3	4	1	7.0	7.8
3	4	2	7.3	-7.6
3	4	3	19.0	16.8
3	4	4	4.5	-4.3
3	4	5	5.5	3.3
3	4	6	14.0	-11.2
3	4	7	2.8	2.3
3	4	9	4.5	-4.6
3	4	10	13.3	8.8
3	4	11	5.6	-3.3
3	4	12	14.1	11.7
3	5	0	5.8	4.3
3	5	1	13.1	12.4
3	5	2	7.9	-12.1
3	5	3	40.1	-45.7
3	5	4	24.5	-27.1
3	5	5	50.6	47.2
3	5	6	11.9	8.6
3	5	7	43.5	-38.9
3	5	8	9.5	-5.3
3	5	9	38.0	31.5
3	5	10	12.0	7.1
3	5	12	13.2	12.4
3	5	13	14.8	12.5
3	5	14	5.0	4.8
3	5	15	20.0	-15.8
3	5	17	6.8	9.0
3	6	1	4.2	3.0
3	6	2	4.3	5.9
3	6	3	12.2	10.1
3	6	4	3.8	-4.7
3	6	5	6.9	6.2
3	6	8	9.6	-8.1
3	6	9	4.2	-3.7
3	6	10	10.4	-8.2
3	6	11	3.6	-3.9
3	6	12	9.7	-8.1
3	7	0	6.0	5.5
3	7	1	18.3	-25.1
3	7	2	13.6	-16.2
3	7	3	6.9	7.3
3	7	4	45.4	44.8
3	7	5	5.2	-4.5
3	7	6	28.1	-28.1
3	7	7	12.3	12.5
3	7	8	24.3	20.5
3	7	10	17.4	-13.7
3	7	11	18.3	19.4
3	7	12	5.1	-4.2
3	7	13	7.8	-8.8
3	7	14	12.0	-8.4
3	7	16	9.9	8.4
3	8	1	8.1	-8.3
3	8	2	3.0	2.2
3	8	3	8.1	-8.3
3	8	5	14.4	-13.5
3	8	6	5.3	6.3
3	8	7	8.1	6.7
3	8	10	3.6	-2.8
3	8	11	10.3	9.0
3	8	12	6.6	-6.5
3	9	0	17.2	-21.7
3	9	1	8.5	9.8
3	9	2	23.9	27.0
3	9	3	12.8	11.5
3	9	4	10.4	-8.4
3	9	5	14.5	-13.7
3	9	6	15.7	14.2
3	9	7	14.7	15.8
3	9	8	12.1	-12.5
3	9	9	13.7	-13.3
3	9	10	8.5	7.2
3	9	11	3.5	-3.5
3	9	12	14.5	-16.4
3	9	13	7.8	-6.5
3	9	15	9.7	8.9
3	10	2	5.4	-5.8
3	10	4	5.0	4.5
3	10	5	6.7	-7.6
3	10	7	5.8	5.6
3	10	8	9.3	8.2
3	10	9	3.6	-2.0
3	10	10	7.1	6.0
3	10	11	3.4	4.6
3	10	12	10.1	7.9
3	11	0	5.6	-6.0
3	11	1	20.9	25.0
3	11	2	8.8	10.7
3	11	3	14.5	-15.1
3	11	4	22.5	-23.9
3	11	5	12.1	15.0
3	11	6	11.9	15.1
3	11	7	16.3	-16.2
3	11	8	10.5	-10.2
3	11	9	7.4	7.3
3	11	10	8.9	6.6
3	11	11	17.5	-14.4
3	11	12	5.8	4.0
3	11	13	9.4	8.7
3	11	14	3.0	3.4
3	12	3	6.3	6.7
3	12	4	3.6	4.0
3	12	5	6.3	6.1
3	12	6	5.1	-4.7
3	12	8	3.4	3.9
3	12	12	3.6	3.1
3	13	0	11.5	13.8
3	13	2	12.5	-16.4
3	13	3	3.5	-4.4
3	13	4	10.1	10.3
3	13	5	3.5	4.1
3	13	6	16.0	-12.5
3	13	7	8.7	-5.7
3	13	8	13.5	11.5
3	13	9	4.2	4.8
3	13	10	9.5	-8.3
3	13	12	16.1	12.0
3	15	0	6.2	-5.8
3	15	1	7.2	-9.9
3	15	2	5.7	5.3
3	15	3	6.7	5.1
3	15	5	7.4	-7.3
3	15	7	7.2	7.3
4	0	0	17.0	23.3
4	0	2	4.0	3.8
4	0	4	84.4	90.1
4	0	6	43.4	-45.2
4	0	8	40.9	40.1
4	0	10	47.7	-46.5
4	0	12	6.3	6.8
4	0	14	34.4	-28.7
4	0	16	27.5	23.6
4	0	18	17.7	-15.0
4	1	1	4.6	-4.4
4	1	2	3.0	3.3
4	1	3	14.8	-13.3
4	1	5	6.5	-4.5
4	1	6	6.8	-6.8
4	1	9	3.8	5.2
4	1	10	9.7	-10.6
4	1	11	4.3	5.7
4	2	0	14.7	-15.5
4	2	1	17.4	-17.9
4	2	2	12.3	11.6
4	2	3	61.8	64.2
4	2	4	22.8	-20.0
4	2	5	56.0	-51.8
4	2	6	8.8	9.8
4	2	7	37.1	34.7
4	2	8	3.0	-5.3
4	2	9	44.7	-42.0
4	2	10	6.5	4.7
4	2	11	14.0	-14.2
4	2	13	18.5	-12.8
4	2	15	16.7	11.8
4	2	17	4.7	-2.5
4	3	1	3.8	-4.2
4	3	2	2.3	-3.8
4	3	3	17.7	-15.8
4	3	4	4.3	-2.8
4	3	5	5.1	-3.8
4	3	9	4.0	3.5
4	3	10	11.5	7.0
4	3	11	7.6	6.3
4	3	12	3.1	3.1
4	3	13	5.9	5.7
4	4	0	7.9	-11.6
4	4	2	5.3	-5.6
4	4	3	14.5	-12.9
4	4	4	57.2	-60.0
4	4	5	12.4	10.0
4	4	6	27.2	24.8
4	4	7	18.1	-13.9
4	4	8	23.0	-18.9
4	4	9	16.9	13.3
4	4	10	29.5	24.9
4	4	12	10.5	7.0
4	4	13	11.8	9.7
4	4	14	18.0	13.9
4	4	15	8.0	-5.7
4	4	16	15.4	-12.2
4	4	17	3.0	3.7
4	5	2	3.6	-5.8
4	5	3	8.0	5.1
4	5	4	3.9	4.5
4	5	5	5.4	3.8
4	5	6	6.2	4.8
4	5	8	4.0	3.7
4	5	10	12.0	8.2
4	5	12	4.5	2.5
4	6	0	20.2	25.4
4	6	2	18.0	-19.6
4	6	3	26.8	-31.0
4	6	4	32.0	35.1
4	6	5	26.0	26.2
4	6	6	26.6	-26.2
4	6	7	24.5	-20.5
4	6	8	24.1	21.8
4	6	9	30.4	27.7
4	6	10	23.6	-20.6
4	6	11	13.5	11.5
4	6	12	14.1	13.3
4	6	13	12.6	9.9
4	6	14	18.2	-12.5
4	6	15	15.7	-10.1
4	6	16	15.8	11.4
4	6	17	3.5	2.5
4	7	3	11.6	9.7
4	7	4	6.0	5.2
4	7	10	7.1	-4.5
4	7	11	7.7	-5.8
4	7	13	7.2	-4.6
4	8	0	6.6	-5.5
4	8	1	22.1	-29.0
4	8	2	6.7	8.6
4	8	3	32.4	35.0
4	8	4	21.8	23.4
4	8	5	23.8	-26.2
4	8	6	6.7	-7.1
4	8	7	24.3	24.1
4	8	8	8.3	6.4
4	8	9	19.6	-18.5
4	8	10	10.5	-11.2
4	8	12	11.2	-7.4
4	8	13	16.9	-10.1
4	8	14	9.6	-7.0
4	8	15	8.9	5.4
4	8	16	7.5	6.6
4	9	2	5.8	5.5
4	9	10	6.2	-5.3
4	10	0	8.3	-7.4
4	10	1	3.0	-2.4
4	10	3	14.6	15.7
4	10	4	18.3	-17.8
4	10	5	11.8	-10.2
4	10	6	10.5	12.4
4	10	7	7.1	6.6
4	10	8	10.5	-11.4
4	10	9	8.2	-8.3

Table 1 (*cont.*)

4	10	10	16.9	12.9
4	10	11	13.9	-11.1
4	10	12	7.4	-7.3
4	10	14	4.0	8.5
4	11	3	7.1	-5.8
4	11	4	5.5	-4.2
4	11	11	3.6	2.9
4	11	13	2.8	3.2
4	12	0	14.8	16.4
4	12	1	10.5	11.8
4	12	2	12.3	-14.3
4	12	3	14.1	-16.4
4	12	5	13.2	13.0
4	12	6	6.1	-5.5
4	12	7	13.3	-13.5
4	12	9	12.7	11.7
4	12	13	5.5	7.4
4	14	0	6.4	6.0
4	14	1	8.0	-10.1
4	14	2	4.0	-4.0
4	14	4	12.2	11.0
4	14	6	5.0	-6.5
4	14	7	5.8	5.5
4	14	8	4.3	5.2
4	14	9	4.7	-3.7
4	14	10	5.0	-5.6
5	0	2	3.2	0.6
5	0	4	7.4	8.0
5	0	6	9.7	-10.4
5	0	8	3.4	3.6
5	0	10	3.9	-3.1
5	0	12	9.2	8.1
5	1	0	16.0	19.7
5	1	1	19.0	-19.4
5	1	2	22.8	-21.0
5	1	3	25.6	27.1
5	1	4	26.2	25.8
5	1	5	13.3	-13.5
5	1	6	11.1	-7.5
5	1	7	23.3	24.5
5	1	8	7.8	4.1
5	1	9	23.1	-23.5
5	1	10	11.7	-8.5
5	1	11	8.9	9.5
5	1	13	21.2	-21.4
5	1	15	12.5	12.0
5	1	17	7.2	-6.8
5	2	1	5.5	8.5
5	2	2	3.4	3.0
5	2	5	6.2	4.9
5	2	7	7.7	-7.3
5	2	10	6.2	-5.9
5	2	11	4.0	1.9
5	3	0	37.7	-30.8
5	3	1	7.2	7.7
5	3	2	38.5	27.4
5	3	4	39.3	-40.3
5	3	5	10.6	10.2
5	3	6	23.8	20.1
5	3	7	8.3	7.2
5	3	8	21.2	-18.4
5	3	9	8.1	-6.2
5	3	10	28.8	26.1
5	3	12	14.8	-9.0
5	3	13	11.7	-9.2
5	3	14	14.4	12.0
5	3	15	6.1	4.5
5	3	16	13.6	-9.1
5	4	3	11.0	-12.0
5	4	13	3.9	2.9
5	4	14	3.7	-3.5
5	5	0	4.4	-3.9
5	5	1	26.2	32.0
5	5	2	6.8	5.9
5	5	3	34.8	-34.6
5	5	4	7.1	-5.4
5	5	5	28.0	23.9
5	5	6	2.5	2.2
5	5	7	29.8	-26.2
5	5	9	33.5	28.4
5	5	10	5.7	5.1
5	5	11	10.0	-7.9
5	5	13	27.0	19.3
5	5	15	18.0	-13.0
5	6	1	3.1	-3.3
5	6	2	9.6	-10.5
5	6	10	11.2	8.2
5	6	11	2.8	-4.3
5	6	12	6.9	5.5
5	7	0	21.6	29.9
5	7	1	9.7	-10.0
5	7	2	17.4	-20.8
5	7	3	6.1	6.8
5	7	4	33.9	34.4
5	7	5	13.0	-15.7
5	7	6	17.3	-14.2
5	7	7	6.3	7.9
5	7	8	13.5	11.5
5	7	9	8.2	-9.8
5	7	10	17.9	-19.0
5	7	11	10.6	9.6
5	7	12	3.8	1.5
5	7	14	6.8	-7.6
5	7	15	7.9	6.4
5	7	16	4.2	3.9
5	8	2	6.4	6.0
5	8	3	10.0	9.0
5	8	5	7.3	6.5
5	8	11	6.7	6.0
5	8	14	5.1	2.5
5	9	0	15.6	-15.5
5	9	2	16.7	17.7
5	9	3	3.9	3.4
5	9	4	15.0	-17.1
5	9	5	4.0	-3.9
5	9	6	13.6	13.8
5	9	7	4.1	5.9
5	9	8	12.2	-13.6
5	9	9	15.0	-15.7
5	9	10	5.5	8.7
5	9	12	9.0	-7.1
5	9	13	14.5	-12.5
5	10	2	8.1	9.9
5	10	3	5.8	-6.5
5	10	8	5.6	-3.2
5	10	10	5.8	-6.8
5	10	12	5.3	-5.3
5	10	13	4.6	4.0
5	11	0	17.9	-21.4
5	11	1	17.5	18.4
5	11	2	12.0	12.2
5	11	3	13.6	-17.6
5	11	4	18.3	-22.1
5	11	5	15.7	17.6
5	11	6	6.9	7.6
5	11	7	14.6	-13.8
5	11	8	5.3	-5.3
5	11	9	12.5	11.8
5	11	10	11.6	10.5
5	11	11	10.1	-8.4
5	11	13	6.5	6.1
5	12	3	6.9	-6.8
5	12	10	6.6	6.2
5	13	0	8.1	8.2
5	13	2	12.5	-13.4
5	13	4	11.5	13.0
5	13	6	11.8	-10.6
5	13	9	7.7	7.1
5	13	10	8.7	-9.3
5	14	1	3.4	-0.3
5	14	3	4.7	4.9
6	0	0	56.4	56.4
6	0	2	37.7	-41.9
6	0	4	22.0	28.2
6	0	6	20.6	-20.2
6	0	8	24.6	22.8
6	0	10	29.3	-32.6
6	0	12	30.2	26.8
6	0	14	17.7	-18.3
6	0	16	11.2	9.9
6	1	1	7.5	-8.8
6	1	2	5.7	8.5
6	1	3	8.3	7.8
6	1	4	3.3	-2.7
6	1	5	3.7	-0.8
6	1	6	8.3	9.1
6	1	7	6.0	6.6
6	1	8	9.5	-9.9
6	1	10	7.3	7.8
6	1	11	6.4	1.5
6	2	0	7.2	-8.4
6	2	1	33.2	-38.9
6	2	2	8.6	9.7
6	2	3	30.5	22.7
6	2	4	9.6	-8.8
6	2	5	19.8	-17.1
6	2	6	7.3	5.8
6	2	7	21.7	17.3
6	2	8	8.3	-6.8
6	2	9	18.8	-16.3
6	2	10	7.3	9.3
6	2	11	27.3	24.2
6	2	12	3.6	-3.5
6	2	13	20.0	-18.2
6	2	14	3.3	2.9
6	2	15	8.4	5.9
6	3	2	5.1	1.3
6	3	3	9.5	7.9
6	3	5	5.7	-3.0
6	3	7	10.4	7.6
6	3	9	7.2	-5.6
6	3	10	5.2	-4.7
6	3	12	5.1	-2.3
6	4	0	43.0	-43.7
6	4	1	15.3	13.8
6	4	2	19.3	25.9
6	4	3	11.8	-10.2
6	4	4	9.9	-12.1
6	4	5	8.1	8.3
6	4	6	12.1	8.2
6	4	7	10.2	-9.4
6	4	8	11.2	-7.4
6	4	9	8.9	7.3
6	4	10	24.6	22.4
6	4	11	10.5	-9.5
6	4	12	26.0	-17.7
6	4	13	6.8	4.8
6	4	14	11.8	11.0
6	4	15	5.5	-5.4
6	5	1	9.2	13.4
6	5	2	7.0	-6.8
6	5	3	4.1	-2.8
6	5	6	5.8	-3.0
6	6	0	16.1	19.7
6	6	1	25.3	34.1
6	6	2	23.8	-32.2
6	6	3	10.6	-10.3
6	6	4	18.7	22.2
6	6	5	9.0	7.7
6	6	6	18.6	-16.6
6	6	7	10.2	-7.8
6	6	8	20.2	20.3
6	6	9	12.3	10.3
6	6	10	18.1	-18.1
6	6	11	16.1	-14.8
6	6	12	23.7	13.6
6	6	13	19.0	13.4
6	6	14	13.8	-12.0
6	7	1	4.7	-4.2
6	7	8	7.4	-9.0
6	7	10	5.1	5.0
6	8	0	19.8	23.2
6	8	1	22.8	-27.5
6	8	3	18.3	22.5
6	8	5	16.4	-17.9
6	8	7	15.8	17.0
6	8	9	18.5	-13.6
6	8	10	14.0	-11.0
6	8	11	18.7	13.9
6	8	12	10.6	8.3
6	8	13	9.4	-7.8
6	8	14	4.4	-5.0
6	9	1	9.7	-13.8
6	9	3	6.4	4.8
6	9	4	3.7	4.7
6	9	5	5.2	-4.0
6	9	7	9.0	9.6
6	9	11	4.3	3.9
6	10	0	9.1	-7.3
6	10	1	13.9	-14.5
6	10	2	15.3	17.4
6	10	4	9.0	-10.9
6	10	6	6.2	6.2
6	10	8	9.0	-11.3
6	10	10	14.9	11.1
6	11	4	8.8	6.4
6	11	8	10.0	8.9
6	11	10	7.5	-5.1
6	12	0	4.9	-5.5
6	12	1	12.6	14.5
6	12	2	9.8	-9.6
6	12	3	11.4	-12.2
6	12	4	4.7	6.7
6	12	5	9.2	9.1
6	12	6	5.9	-6.1
6	12	7	8.5	-8.8
6	12	8	10.4	8.0
6	13	1	9.0	8.3
6	13	2	7.7	-5.8
6	13	6	2.7	-2.9
6	14	0	3.9	4.3
6	14	1	3.9	-3.3
6	14	2	7.7	-9.1
6	14	3	9.0	8.6
6	14	4	4.4	6.4
6	14	5	6.7	-7.9
7	0	2	8.4	-7.7
7	0	4	8.4	8.7
7	0	6	15.7	-14.5
7	0	10	6.1	-6.7
7	0	14	6.5	-6.5
7	1	0	31.1	29.2
7	1	1	28.5	-36.7
7	1	3	12.5	12.8
7	1	5	11.2	-15.4
7	1	7	6.3	6.0
7	1	9	12.5	-12.5
7	1	10	15.7	-11.2
7	1	11	12.4	14.6
7	1	12	11.2	9.8
7	1	13	10.8	-12.1
7	1	14	6.0	-6.1
7	2	1	13.8	-19.2
7	2	3	6.5	-9.4
7	2	4	3.8	2.4
7	2	5	8.9	11.6
7	2	7	3.4	1.8
7	2	9	15.1	12.1
7	3	0	44.5	-45.9
7	3	1	11.6	-16.4
7	3	2	13.3	16.3
7	3	3	4.6	-3.6
7	3	4	12.0	-12.1
7	3	6	13.6	12.4
7	3	7	6.0	-5.6
7	3	8	9.5	-7.1
7	3	9	6.8	-2.4
7	3	10	24.5	17.4
7	3	11	3.6	3.9
7	3	12	13.8	-15.2
7	3	13	7.9	-4.9
7	3	14	12.1	9.4
7	4	1	6.6	6.8
7	4	2	5.6	3.8
7	4	5	7.6	6.2
7	4	7	6.1	-4.1
7	4	14	5.4	5.4
7	5	0	20.6	-23.4
7	5	1	28.8	32.8
7	5	3	16.2	-14.1
7	5	5	14.6	14.3
7	5	7	13.1	-9.3
7	5	9	17.3	13.9
7	5	10	6.2	5.7
7	5	11	28.0	-17.6
7	5	13	16.3	14.1
7	6	1	12.7	18.6
7	6	9	7.3	-5.5
7	6	10	7.0	-2.9
7	7	0	26.6	30.2
7	7	1	4.9	-3.5
7	7	2	11.1	-11.1
7	7	3	12.3	14.6
7	7	4	5.1	6.3
7	7	5	6.8	-7.1
7	7	6	8.2	-8.2
7	7	7	11.6	11.0
7	7	8	5.1	4.8
7	7	9	6.0	-4.7
7	7	10	18.1	-12.6
7	7	12	13.0	12.5
7	8	1	7.2	-6.6
7	8	2	3.6	-3.5
7	8	3	9.0	-6.3
7	8	4	3.6	2.4
7	8	5	7.0	7.1
7	8	6	3.6	-4.3
7	9	1	17.2	-16.7
7	9	2	14.7	15.1
7	9	4	11.6	-10.6
7	9	6	10.1	8.2
7	9	8	12.6	-12.1
7	9	10	8.4	5.1
7	9	11	9.1	7.1
7	10	1	8.9	-7.7
7	10	4	3.5	-2.8
7	10	5	5.6	5.8
7	10	6	3.4	5.0
7	10	9	8.2	6.3
7	11	0	12.1	-15.5
7	11	1	8.5	8.3
7	11	2	3.4	4.9
7	11	3	13.7	-13.2
7	11	5	11.3	9.4
7	11	6	6.2	4.3
7	11	7	11.9	-10.3
7	11	9	9.2	8.4
7	12	1	3.2	5.5
7	12	2	3.1	3.3
7	13	0	8.9	8.7
7	13	1	6.9	6.1
7	13	2	11.7	-12.6

five-coordinate complexes. Walker (1961) isolated a 1:1 adduct involving 4-methylpyridine but this proved to be unstable owing to loss of the base.

Since then there have been several studies of the adducts (Walker & Li, 1965; Graddon & Watton, 1961; Graddon & Schultz, 1965) in which formation constants of the 1:1 and 1:2 adducts were evaluated from solution spectra. May & Jones (1963) used calorimetric measurements to evaluate heats of formation and concluded that the fifth bond formed between the copper and the base is considerably weaker than the Cu–O bonds in the plane.

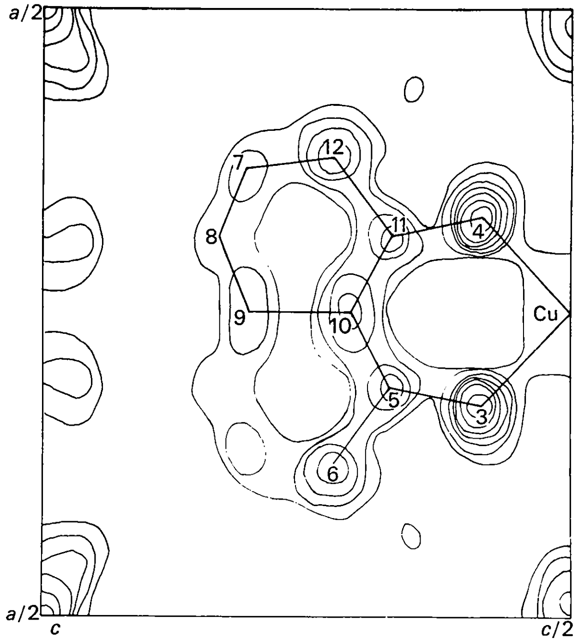

Fig. 1. A Patterson section perpendicular to [010] through the $(2x,2y,2z)$ Cu–Cu vector at (0,0·30,0·50). The *o*-hydroxyacetophenone residue is clearly recognizable and the positions of the atoms are marked. Contours are drawn at arbitrary levels except for the Cu–Cu vector for which no contours are drawn.

The structures of these adducts, however, had yet to be established. Graddon and his co-workers favoured five-coordinate tetragonal pyramidal structures for the 1:1 adducts, in which the coordinating atom of the base occupies the apical position above the square-planar arrangement of the β-diketone ligands about the copper atom. The alternative idealized five-coordinate geometry, *i.e.* the trigonal bipyramid, was felt to be less probable. Traill (1960), suggested that the copper atom was still four-coordinate owing to the opening of one chelate ring and replacement of one of the coordinated oxygen atoms by the donor atom of the base. The question of the stereochemistry of the copper was not resolved by crystal structure analysis because of the unstable nature of the adducts which had been isolated.

Recently Graddon & Mockler (1968) obtained a 1:1 4-methylpyridine adduct of the cupric complex of *o*-hydroxyacetophenone, which appeared to have a much greater stability than the corresponding complexes of simple β-diketones. This afforded an opportunity to obtain definite structural evidence on these types of compounds, as the absorption spectra of this complex (both in the solid state and in chloroform and 4-methylpyridine mixtures) closely resemble those of the simple 1:1 adducts referred to above, and they can, therefore, be regarded as being structurally similar.

Table 2. *Final fractional atomic coordinates and temperature factors for 4-methylpyridinebis-(o-hydroxyacetophenonato)-copper*(II)

	x/a	y/b	z/c	r.m.s.† standard deviations (Å)	Temperature factor (Å^2)
Cu(1)	0·0000 (00)*	0·1511 (01)	0·2500 (00)	0·002	2·55 (08)
N(2)	0·0000 (00)	0·3138 (10)	0·2500 (00)	0·014	3·52 (24)
O(3)	−0·1445 (08)	0·1406 (04)	0·1633 (04)	0·007	3·60 (15)
O(4)	0·1560 (07)	0·1236 (04)	0·1644 (04)	0·007	3·33 (14)
C(5)	−0·1198 (11)	0·1406 (06)	0·0772 (06)	0·010	3·00 (17)
C(6)	−0·2488 (15)	0·1474 (08)	0·0263 (08)	0·012	4·79 (27)
C(7)	−0·2419 (13)	0·1469 (08)	−0·0648 (08)	0·012	4·55 (25)
C(8)	−0·1129 (14)	0·1388 (08)	−0·1037 (08)	0·012	4·53 (24)
C(9)	0·0166 (11)	0·1285 (08)	−0·0585 (08)	0·011	3·71 (21)
C(10)	0·0134 (10)	0·1300 (07)	0·0351 (07)	0·010	3·07 (18)
C(11)	0·1504 (10)	0·1186 (06)	0·0830 (06)	0·009	2·76 (17)
C(12)	0·2919 (12)	0·1006 (08)	0·0372 (08)	0·012	4·49 (24)
C(13)	0·1144 (11)	0·3634 (05)	0·2827 (06)	0·009	2·63 (16)
C(14)	0·1168 (11)*	0·4638 (06)	0·2840 (06)	0·009	3·30 (18)
C(15)	0·0000 (00)	0·5136 (10)	0·2500 (00)	0·014	2·80 (24)
C(16)	0·0000 (00)	0·6247 (14)	0·2500 (00)	0·019	3·66 (31)

* Figures in brackets are the standard deviations of the observation and refer to the last two decimal places in the observation.

† These are the root mean square standard deviations in atomic positions except for atoms occupying special positions where the standard deviation of the y coordinate, in ångströms, is given.

Experimental

Crystals of 4-methylpyridinebis-(*o*-hydroxyacetophenonato)copper(II) were obtained as dull green plates by recrystallizing bis-(*o*-hydroxyacetophenonato)copper(II from 4-methylpyridine.

Zero level Weissenberg and precession photographs with use of Cu *Kα* and Mo *Kα* radiation, respectively, enabled the unit-cell dimensions to be determined and established the crystal class as orthorhombic. The space group *Pbcn* was determined uniquely from systematic absences in spectra.

4-*Methylpyridinebis-*(*o-hydroxyacetophenonato*)*copper-*(II) $CuC_{22}H_{21}O_4N$, F.W. = 426·9 .
Orthorhombic, $a = 9{\cdot}23 \pm 0{\cdot}05$, $b = 13{\cdot}99 \pm 0{\cdot}07$, $c = 15{\cdot}59 \pm 0{\cdot}08$ Å.
$U = 2012{\cdot}3$ Å^3, $D_m = 1{\cdot}43$ g.cc^{-1} (by flotation), $D_c = 1{\cdot}41$ g.cc^{-1}. $Z = 4$, $F(000) = 884$, space group *Pbcn* (D_{2h}^{14}).

The crystals decomposed in the X-ray beam and after several days no diffraction pattern could be obtained. It was therefore necessary to use a number of crystals for the collection of data. The intensity data were estimated visually from multifilm equi-inclination Weissenberg photographs collected about [100], (h=0,---7) and internally correlated with data collected about [010]. Lorentz and polarization corrections were applied on UTECOM to the 1124 independent reflexions by use of the program of Rollett (1961). Neither extinction nor absorption corrections were applied to these data and the observed and calculated structure amplitudes are listed for comparison in Table 1. The reliability index R for these observed data is 0·14, which is satisfactory in view of the poor data given by the decomposing crystals.

Structure determination and refinement

There are eight general equivalent positions in the space group *Pbcn*. The four molecules of 4-methylpyridinebis-(*o*-hydroxyacetophenonato)copper(II) must therefore each possess a centre of symmetry or a twofold axis. It is impossible to arrange the ligands around the copper atom so as to confer a centre of symmetry on the molecule. However, both the tetragonal pyramidal arrangements of ligands have a twofold axis of symmetry and in both cases this axis passes through the copper atom and the nitrogen and two carbon atoms of the solvent ligand. Moreover, if the environment of the copper atom is tetragonal bipyramidal, as predicted by Graddon, then it seemed probable that the *o*-hydroxyacetophenone residues in each molecule would assume an approximately planar arrangement about the copper atom and perpendicular to the twofold axis. The intermolecular vectors between copper atoms and the light atoms of these residues should then appear in the planes through the Cu–Cu vectors which are perpendicular to the [010] axis in the Patterson function. Fig. 1 shows a contour map representing such a plane and it was possible to determine the positions of thirteen of the sixteen atoms in the asymmetric unit from the three-dimensional Patterson function. The remaining atoms were located from difference Fourier syntheses.

Refinement of positional parameters and isotropic temperature factors was carried out by use of an IBM 7040 computer together with the *ORFLS* program of Busing, Martin & Levy (1962). The final coordinates and standard errors are listed in Table 2. These coordinates together with the unit-cell dimensions were used to derive the interatomic distances listed in Table 3 and the bond angles listed in Table 4. The standard errors in these values were computed from the variance-covariance matrix obtained in the final least-squares refinement and the unit-cell errors by use of the *ORFFE* program of Busing, Martin & Levy (1964). The standard deviation in the value of each observed. structure amplitude F_o was assumed to be $F_o/10$.

Table 3. *Bond distances within the molecule of* 4-*methylpyridinebis-*(*o-hydroxyacetophenonato*)*copper*(II)

The atomic numbering used is the same as in Table 2. Standard deviations are given in brackets and refer to the last two places of the preceding number.

Cu(1)-N(2)	2·270 (18)
-O(3)	1·900 (10)
-O(4)	2·000 (10)
O(3)—C(5)	1·360 (13)
O(4)—C(11)	1·270 (12)
C(12)-C(11)	1·510 (15)
C(5)—C(10)	1·400 (14)
C(11)-C(10)	1·480 (14)
C(5)—C(6)	1·430 (16)
C(6)—C(7)	1·420 (18)
C(7)—C(8)	1·340 (16)
C(8)—C(9)	1·400 (15)
C(9)—C(10)	1·460 (17)
N(2)—C(13)	1·360 (13)
C(13)-C(14)	1·400 (13)
C(14)-C(15)	1·390 (13)
C(15)-C(16)	1·550 (23)

Table 4. *The interatomic angles in the molecule of* 4-*methylpyridinebis-*(*o-hydroxyacetophenonato*)*copper*(II)

Angle	Value	Estimated standard deviation
N(2)—Cu(1)-O(3)	94·4°	0·2°
N(2)—Cu(1)-O(4)	101·1	0·2
O(3)—Cu(1)-O(4)	90·9	0·5
O(3)—Cu(1)-O(4)*	87·4	0·5
C(5)—O(3)—Cu(1)	125·6	0·7
C(11)-O(4)—Cu(1)	130·3	0·6
O(3)—C(5)—C(10)	127·5	0·9
O(3)—C(5)—C(6)	114·0	0·9
O(4)—C(11)-C(10)	122·2	0·8
C(6)—C(10)-C(11)	122·0	1·0
C(10)-C(11)-C(12)	121·3	0·9
O(4)—C(11)-C(12)	116·5	0·8
C(9)—C(10)-C(11)	119·1	0·8
C(5)—C(6)—C(7)	121·0	1·1

Table 4 (*cont.*)

Angle	Value	Estimated standard deviation
C(6)—C(7)—C(8)	120·0	1·2
C(7)—C(8)—C(9)	123·0	1·2
C(8)—C(9)—C(10)	119·1	0·9
C(9)—C(10)-C(5)	119·2	0·8
Cu(1)-N(2)—C(13)	120·6	0·6
C(13)-N(2)—C(13)*	119·0	1·3
N(2)—C(13)-C(14)	122·0	1·0
C(13)-C(14)-C(15)	119·0	1·0
C(14)-C(15)-C(14)*	120·0	1·3
C(14)-C(15)-C(16)	120·1	0·7

* Atom at $\bar{x}, y, \frac{1}{2}-z$.

The atomic form factors of Berghuis, Haanappel, Potters, Loopstra, MacGillavry & Veenendaal (1955) and Thomas & Umeda (1957) were used in structure factor calculations. The copper curve was corrected for the real component of the anomalous dispersion of Cu *Kα* radiation with the *Δf′* values given by Dauben & Templeton (1955).

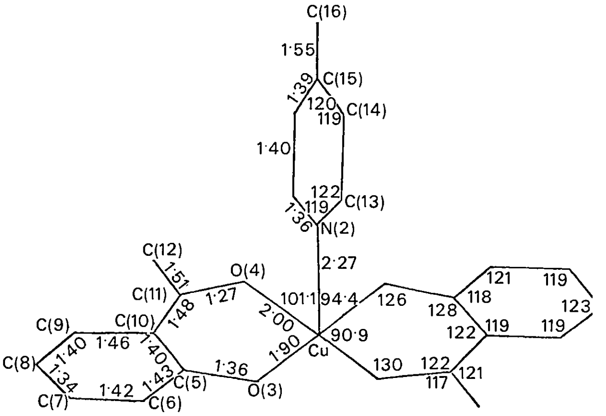

Fig. 2. A diagram of the 4-methylpyridinebis-(*o*-hydroxyacetophenonato)copper(II) molecule. A twofold axis passes through Cu(1), N(2), C(15) and C(16). Bond distances and angles are shown in the diagram.

Description of the structure

The structure of 4-methylpyridinebis-(*o*-hydroxyacetophenonato)copper(II) consists of discrete molecules in which the copper atom is five-coordinated and has the tetragonal pyramidal environment shown in Fig. 2. The four oxygen atoms form an approximate square-planar arrangement about the copper atom, which is raised slightly out of the mean plane of the oxygen atoms towards the apical nitrogen atom. The tetragonal distortion is evident in the length of the copper–nitrogen bond (2·27 Å) which is significantly greater than Cu–N bond distances (*ca.* 2·0 Å) found in square-planar environments of copper(II) complexes (Hanic, 1959; Dunitz, 1957; Mathieson & Welsh, 1952; Jarvis, 1961).

The two *o*-hydroxyacetophenone residues are equivalent, being related by the twofold axis through the copper atom. The planes of the chelate rings are slightly inclined to each other, so that the arrangement of the two residues about the axis of the pyramid is rather like that of two propeller blades attached to a shaft.

The pyridine ring is oriented about the twofold axis so that the non-axial carbons C(13) and C(14) lie above the space between the chelate rings at the base of the pyramid. The plane of the ring cuts across this space in a direction more towards the phenolic oxygens O(3) than the ketonic oxygens O(4) as can be seen in Fig. 3, which is a projection of the unit cell contents onto the (010) plane.

The closest intermolecular contacts are made between carbon atoms of *o*-hydroxyacetophenone residues

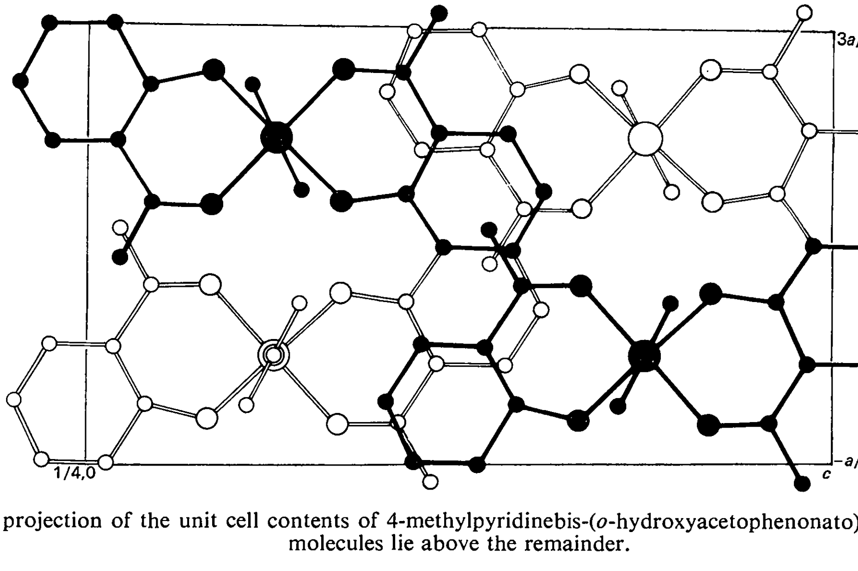

Fig. 3. An (010) projection of the unit cell contents of 4-methylpyridinebis-(*o*-hydroxyacetophenonato)copper(II). The shaded molecules lie above the remainder.

on neighbouring molecules and between the carbon atoms of the 4-methylpyridine ligand and oxygen atoms of adjacent molecules. The overlap of the *o*-hydroxyacetophenone residues in projection can be seen in Fig. 3 but the packing of the molecules in the unit cell can be seen more clearly in the (100) projection (Fig. 4) where some close contacts are indicated.

The environment of the copper atom

The tetragonal pyramidal environment of the copper atom is shown in Fig. 5. The two Cu–O bond lengths (1·90, 2·00 Å) are significantly different ($\Delta/\sigma=7{\cdot}1$) and the longer bond involves the ketonic oxygen. These values of the Cu–O bond lengths are within the range usually found for such bonds.

The plane of best fit through copper and the oxygen atoms of the coordinating molecules is perpendicular to the *b* axis and cuts this axis at 1·90 Å from the origin of the unit cell. Deviations from this plane, in ångströms, are Cu(1) 0·213, O(3) 0·066, O(4) −0·173. All deviations are significant, the phenolic oxygen O(3) being displaced toward the apical nitrogen atom. The copper atom is 0·266 Å above the plane through the

Table 5. *Least squares planes*

Equation in the form $Ax+By+Cz+D=O$, referred to the crystallographic axes, calculated after Schomaker, Waser, Marsh & Bergman (1959) with all weights equal to 1. All values have been multiplied by 10^5.

Plane	*A*	*B*	*C*	*D*	Atoms defining the plane
I	−438	0	899	−3504	N(2) C(13) C(14) C(15) C(16)
II	104	995	−7	−1820	C(5) C(6) C(7) C(8) C(9) C(10)
III	117	990	−81	−1697	Cu(1) O(3) O(4) C(5) C(10) C(11) C(12)

Deviations from planes (10^{-3} Å)

Plane	Cu(1)	N(2)	O(3)	O(4)	C(5)	C(6)	C(7)	C(8)	C(9)
I	—	—	—	—	—	—	—	—	—
II	—	—	—	—	13	−11	−3	13	−11
III	78		−113	−26	22				

	C(10)	C(11)	C(12)	C(13)	C(14)	C(15)	C(16)
I	—	—	—	−4	+4	—	—
II	−2	—	—	—	—	—	—
III	73	2	36				

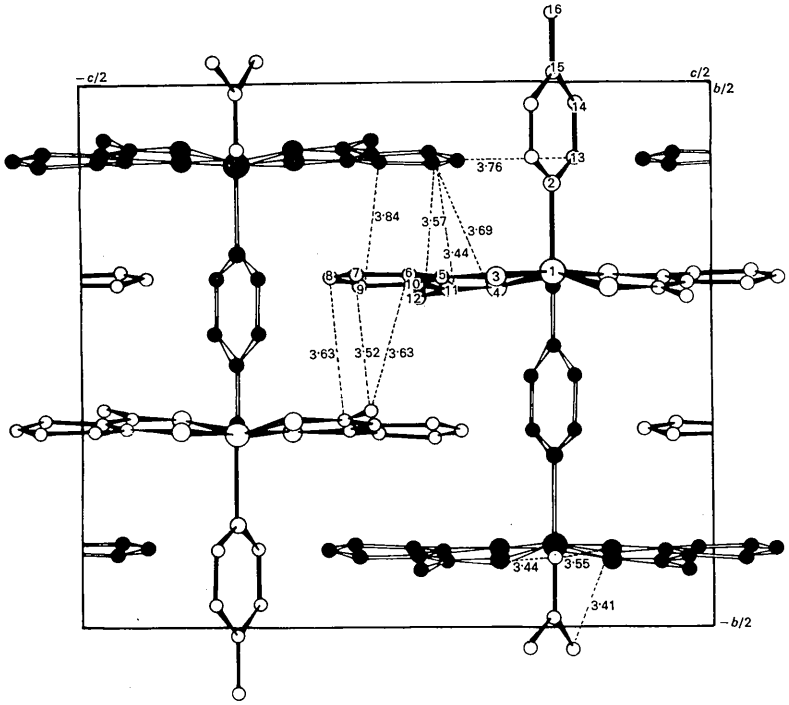

Fig. 4. A (100) projection of the unit-cell contents of 4-methylpyridinebis-(*o*-hydroxyacetophenonato)copper(II). The closest intermolecular contacts, shown by dotted lines, are between carbon atoms of *o*-hydroxyacetophenone residues on neighbouring molecules and between the carbon atoms of the 4-methylpyridine ligand and oxygen atoms of adjacent molecules.

four oxygen atoms in the direction of nitrogen atom N(2).

The Cu–N bond length of 2·27 Å is in close agreement with the value of 2·31 Å found by Hall, McKinnon & Waters (1965) for the corresponding bond length in pyridine *N*-methylsalicylaldiminatocopper(II). It also compares well with the Cu–N bond lengths found in the two crystalline forms of pyridine copper acetate, *i.e.* 2·13 Å in the monoclinic form (Barclay & Kennard, 1961) and 2·19 Å in the orthorhombic form (Hanic, Štempelová & Hanicová, 1964).

There is no evidence of interaction in the other axial site of the copper atom. This can be seen in Fig. 4. The closest intermolecular contacts made by the copper with carbon atoms of neighbouring molecules are all in excess of 4 Å, and none of the hydrogen atoms attached to these carbons lies in the vicinity of the axial approach.

The ligands

The plane of best fit through the 4-methylpyridine ligand is parallel to the *b* axis of the unit cell and contains the twofold molecular axis. The equation for this plane is given in Table 5 and the deviations of the atoms from this plane are not significant. The geometry of the pyridine ring does not significantly differ from that described by Bak, Hansen & Rastrup-Andersen (1954) whilst the C(15)–C(16) bond length of 1·55 Å shows good agreement with the values of 1·57 and 1·54 Å obtained for the C–CH_3 bonds in the structure of dichlorobis-(2-methylpyridine)copper(II) (Duckworth & Stephenson, 1969). The 4-methylpyridine ligand is oriented about the twofold axis towards the phenolic oxygen O(3). The phenolic oxygen side of the chelate ring is tilted towards the pyridine ring so that the O(3) atom is only 3·24 Å from the C(13) atom in pyridine ring.

The aromatic portion of the *o*-hydroxyacetophenone residue is planar and the equation of the plane of best fit through atoms C(5)–C(10) inclusive is listed in Table 5. None of the atoms deviate significantly from this plane. The mean value of 1·41 Å for the C–C bond lengths in the benzene ring agrees well with the value of 1·395 Å given for this bond by Sutton (1958). The mean value of the interatomic angles in the ring is 120° and no individual angle deviates significantly from this mean value.

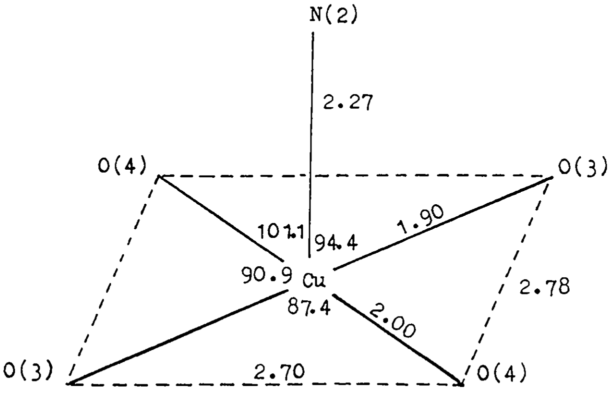

Fig. 5. A diagram illustrating the environment of the copper atom in 4-methylpyridinebis-(*o*-hydroxyacetophenonato)copper(II).

The chelate ring is only approximately planar; the equation of the plane of best fit through atoms Cu(1), O(3), O(4), C(5), C(10), C(11) and C(12) is given in Table 5. All atoms except C(5) and C(11) show significant deviations from this plane, which is inclined at an angle of 8° to the square coordination plane and 4° to the plane of the benzene ring. The two carbon–oxygen bond lengths, *i.e.* C(5)–O(3), 1·30 Å and C(11)–O(4), 1·27 Å are significantly different ($\Delta/\sigma=5{\cdot}2$). The value of 1·36 Å is also found for the corresponding C–O bond length in salicylic acid (Cochran, 1953) and copper salicylate tetrahydrate (Hanic & Michalov, 1960), whilst this bond length is 1·32 Å in bis(salicylaldehydato)copper (II). The values for the C–O bond length in the two crystalline forms of this latter complex (Hall, McKinnon & Waters, 1965; McKinnon, Waters & Hall, 1964) are 1·28 and 1·26 Å, which agree well with the value of 1·27 Å obtained in this present investigation.

Discussion

An unusual feature of this structure is the lack of any coordination to the copper atom in the sixth position of the coordination polyhedron; 4-methylpyridinebis-(*o*-hydroxyacetophenonato)copper(II) is an example of a discrete, five-coordinated complex of divalent copper.

In other monomeric, five-coordinated tetragonal pyramidal structures of copper(II) there is usually further interaction at the other axial site of the copper atom. Thus in the crystal of (*N*,*N'*-disalicylidenepropane-1,2-diamine)copper(II) monohydrate, the apical ligand is water, whilst in the sixth coordination position there is an oxygen atom, from another molecule, at a distance of 3·81 Å (Llewellyn & Waters, 1960). In the crystal of (diaquoacetylacetonato)copper(II) picrate the γ carbon stom of the β-diketone residue in a neighbouring molecule occupies the axial site at a distance of 3·1 Å from the copper atom (Gillard & Wilkinson (1963)]. The crystal structure of bis(*o*-hydroxyacetophenonato)copper(II) has not been determined but in the structures of the two crystalline forms of the closely related compound, bis(salicylaldehydato)copper(II), weak axial interactions between the copper atoms and neighbouring molecules exist. In the crystals of this compound obtained from alcohol, the benzene ring of the neighbouring molecule lies 3·21 Å above and below the copper atom. In the crystals obtained from chloroform, the copper atom is 3·13 Å from the planes of neighbouring chelate rings. It may be that packing requirements have overcome any tendency for weak interactions to occur in the molecule of 4-methylpyridinebis-(*o*-hydroxyacetophenonato)copper(II).

The significant differences in the two copper–oxygen bond lengths [Cu(1)–O(3), 1·90; Cu(1)–O(4), 2·00 Å] and the two carbon–oxygen bond lengths [C(5)–O(3), 1·36; C(1)–O(4), 1·27 Å] indicate that the presence of the fused benzene ring has largely destroyed any resonance system in the chelate ring, of the type found in some metal complexes with β-diketones, such as the acetylacetonato complexes (Calvin & Wilson, 1945).

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The Wurtzite *Z* Parameter for Beryllium Oxide and Zinc Oxide

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The z parameter in BeO and ZnO has been determined by single-crystal neutron diffraction measurements. For BeO, $z=0{\cdot}3786\pm0{\cdot}0015$, and for ZnO, $z=0{\cdot}3826\pm0{\cdot}0007$.

Introduction

BeO and ZnO crystallize in the polar space group $P6_3mc$ and have the wurtzite structure. There are two atoms of each kind in the unit cell and these are assigned to the special positions 2(*b*) so that metal atoms occupy the sites $\frac{1}{3},\frac{2}{3},0$ and $\frac{2}{3},\frac{1}{3},\frac{1}{2}$ while the oxygen atoms are at $\frac{1}{3},\frac{2}{3},z$ and $\frac{2}{3},\frac{1}{3},\frac{1}{2}+z$. There is only one structural parameter z and several attempts have been made to measure it because of its relevance to bonding calculations.

Structure analysis

(1) BeO

Jeffrey, Parry & Mozzi (1956) and later Smith, Newkirk & Kahn (1963) used single-crystal X-ray methods and obtained $z=0{\cdot}378$ and $0{\cdot}3786\pm0{\cdot}0005$ respectively Pryor & Sabine (1964) found a result of $0{\cdot}3778\pm0{\cdot}001$