Crystal Structure of Bis-[di-μ-(phenylmethoxo)-bis(pentane-2,4-dionato)dicopper(II)]

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The crystal and molecular structures of the title compound have been determined by single-crystal X-ray diffraction by use of three-dimensional photographic data, and refined anisotropically to R 10·1% for 1691 independent observed reflections. The blue crystals are monoclinic, space group $P2_1/c$, with a = 11·53 ± 0·03, b = 22·68 ± 0·05, c = 10·19 ± 0·03 Å, and β = 112·0° ± 0·3°. The unit cell contains two centrosymmetric tetrameric molecules, each consisting of two approximately planar benzoxy-bridged dimers (acac)Cu(μ-$OCH_2Ph)_2$Cu(acac) joined together by four apical Cu–O bonds involving one benzoxy and one acetylacetonate (acac) oxygen atom of each dimer, of lengths 2·42 Å (benzoxy) and 2·71 Å (acac). The Cu_2O_2 unit in the dimer is planar, with mean bond lengths 1·88(1) to the three- and 1·94(1) Å to the four-co-ordinate oxygen atom. The possible significance of the presence of both kinds of bridging atoms in relation to the magnetic properties of this and similar complexes is briefly noted.

In 1964, Bertrand and Caine [1] treated metal β-diketonates with sodium hydroxide in methanol and obtained compounds of the type M(chel)(OMe),MeOH (M = Co^{II} or Ni^{II}, Hchel = acetylacetone, salicylaldehyde, or *o*-hydroxyacetophenone), which have subsequently been shown to have tetrameric methoxy-bridged structures and interesting magnetic properties.[2] The copper complex Cu(acac)(OMe), however, which crystallised solvent-free, appeared from molecular-weight measurements in chloroform to be dimeric; its magnetic moment was low (0·75 B.M.), and in the light of spectroscopic evidence the planar structure (I) was suggested.[3]

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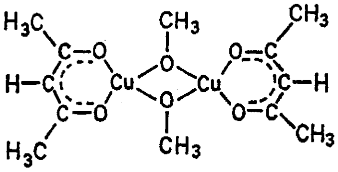
[1] J. A. Bertrand and D. Caine, *J. Amer. Chem. Soc.*, 1964, **86**, 2298.

[2] J. A. Bertrand and R. I. Kaplan, Abstracts *O* 20, 154th *Amer. Chem. Soc.* Meeting, September 1967; J. E. Andrew and A. B. Blake, *Chem. Comm.*, 1967, 1174 and *J. Chem. Soc.* (*A*), 1969, 1456; J. A. Bertrand, A. P. Ginsberg, R. I. Kaplan, C. E. Kirkwood, R. L. Martin, and R. C. Sherwood, *Inorg. Chem.*, 1971, **10**, 240; J. A. Barnes and W. E. Hatfield, *ibid.*, p. 2355.

[3] J. A. Bertrand and R. I. Kaplan, *Inorg. Chem.*, 1965, **4**, 1657.

Many compounds containing the Cu_2O_2 system are known, and most of them have subnormal magnetic moments.[4-10] This is generally supposed to be due to superexchange through the bridging oxygen atoms, and there is some evidence that the interaction depends on π-overlap between copper *d*- and oxygen *p*-orbitals, which would require an approximately planar arrangement of bonds around the bridging oxygen atom. Bertrand and Kelley found that the two compounds $Cu\{MeC(\vdots O)\cdot CH\cdot C(Me)\vdots N\cdot[CH_2]_n\cdot O\}$ ($n = 2$ or 3) have markedly different room-temperature magnetic moments (0·41 for $n = 2$ and 1·87 B.M. for $n = 3$) and they showed that the configuration at the bridging oxygen atoms is trigonal planar in the former (which is dimeric) and tetrahedral in the latter (which is tetrameric).[4] The difference is consistent with the view that π-overlap is the cause of the subnormal moment,[4,5] although some authors regard such a mechanism as improbable in copper complexes because of the energy required to place unpaired spin in the relevant metal orbitals.[10] Clearly, further detailed magnetic and structural information is needed to allow an assessment of the importance of bridge hybridisation and other factors in determining the strength of the interaction.



(I)

We have prepared a series of compounds of the type Cu(chel)OR which show magnetic moments in the range 0·7—1·4 B.M. at room temperature,[11] *i.e.*, values between those which, according to the π-overlap hypothesis, one might expect for planar and tetrahedral bridging oxygen atoms, respectively, and in order to throw some light on the factors operating here we have determined the structure of one of the compounds, $Cu(acac)(OCH_2Ph)$ (μ_{eff} 0·83 B.M. at 25 °C), by *X*-ray diffraction. The four acetylacetonates with R = Me, Et, Pr^n, $PhCH_2$ show sufficient similarity in their i.r. and mass spectra for the assumption that they have essentially the same structure.

EXPERIMENTAL

Cu(acac)OMe) was prepared by the method of ref. 3, and recrystallised from hot (150 °C) benzyl alcohol to give dark blue crystals of the analogous benzoxy-compound. The crystals used in the structure analysis were sealed in Lindemann glass capillary tubes to minimise atmospheric decomposition. Unit-cell dimensions were determined from zero-level Weissenberg photographs by use of three different oscillation axes.

Crystal data.—$C_{12}H_{14}O_3Cu$, $M = 269·7$, Monoclinic, $a = 11·53 \pm 0·03$, $b = 22·68 \pm 0·05$, $c = 10·19 \pm 0·03$ Å, $\beta = 112·0 \pm 0·3°$, $U = 2473 \pm 21$ Å^3, $D_m = 1·45$ (flotation), $Z = 8$, $D_c = 1·45$, $F(000) = 1112$. Cu-K_α radiation, $\lambda = 1·542$ Å; μ(Cu-K_α) $= 24·8$ cm^{-1}. Space group $P2_1/c$ from systematic absences: $0k0$ k odd, and $h0l$ l odd.

Timed-exposure, multiple-film photographs of the levels 0—$7kl$ and hk0—7 were taken by the equi-inclination Weissenberg method, by use of two crystals of dimensions *ca.* 0·3 × 0·3 × 0·15 mm, and the diffraction intensities were estimated visually. Only the 'elongated-spot' half of each film was measured, and reflections with $\sin\theta/\lambda > 0·5$, which appeared unreliable owing to spot-splitting, were excluded. Corrections were made for the Lorentz and polarisation effects and for spot elongation, but not for absorption, since intensity variation from this source was estimated to be <5%. The two sets of data were then merged by a comparison of common reflections. Of the *ca.* 2500 independent reflections available, 1691 had measurable intensity and were used in the subsequent refinement.

Structure Determination and Refinement.—A marked general tendency was noticed for reflections with $k + l$ even to be more intense than those with $k + l$ odd, suggesting that the copper atoms might be at centres of symmetry. A sharpened, three-dimensional Patterson synthesis showed, however, that in fact they occupied two sets of general positions, with the approximate fractional co-ordinates 0,0·07,0 and 0·25,0,0·06 respectively, so that four Cu atoms formed a 60° rhombus of side *ca.* 3 Å, with its shorter diagonal parallel to **b**, its longer diagonal at about 10° to **a**, and its centre at an inversion centre. These accidentally specialised approximate co-ordinates ($x = z = 0$ or $y = 0$) in $P2_1/c$ place the atoms in an *A*-centred arrangement, so that they contribute only to reflections with $k + l$ even. Hence only the latter data could be used in the first Fourier synthesis (phased on the copper positions), which consequently showed spurious *A*-centring corresponding to the superposition of two symmetry-related sets of light-atom positions. (A very similar situation was noted by Ibers in the case of $Ti(OEt)_4$, which has a structure related to that of the present compound.[12])

Two cycles of Fourier refinement and two of block-diagonal least-squares refinement led to reasonable positions for most of the half-atoms in the two superimposed structures, and gave *R* 0·26 for the $k + l$ even data, and it was then possible to pick out the correct arrangement of atoms in the asymmetric unit. A Fourier synthesis using all data then clearly showed all the non-hydrogen atoms in approximately their final positions, giving *R* 0·32.

The structure was further refined by least-squares in the

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[12] J. A. Ibers, *Nature*, 1963, **197**, 686.

block-diagonal approximation; two cycles refining only the atomic co-ordinates, four cycles with individual isotropic temperature factors, and five with anisotropic vibrational parameters for all atoms gave a final R of 0·101, all parameter shifts in the last cycle being $<\sigma$ (mean shift to σ ratio 0·15). The quantity minimised was $\Sigma w(|F_o| - |F_c|)^2$, and the weighting scheme used was that due to Cruickshank,[13] with parameters chosen so that the weighted errors showed no systematic dependence on sin θ or intensity. A three-dimensional difference-Fourier synthesis at this stage showed no features $> \pm 1{\cdot}3$ e Å^{-3}. No attempt was made to locate hydrogen atoms.

Atomic scattering factors were taken from ref. 14 for Cu^{2+}, C, and O. No dispersion corrections were applied. All major calculations were made on an Elliott 803 computer, with programs of refs. 15 and 16. Figures 1, 2, and 4 were drawn by use of the program PAMOLE.[17]

RESULTS AND DISCUSSION

Observed and calculated structure factors are listed in Supplementary Publication No. SUP 20666 (6 pp.).*

TABLE 1

Atomic fractional co-ordinates [a]

Atom	*x*	*y*	*z*
Cu(1)	0·2477(2)	−0·0065(1)	0·0554(3)
Cu(2)	0·0091(2)	−0·0721(1)	0·0035(3)
O(1)	0·0768(10)	−0·0117(4)	−0·0823(12)
O(2)	0·1761(10)	−0·0650(5)	0·1308(13)
O(3)	0·4055(12)	−0·0078(6)	0·2064(16)
O(4)	0·2959(11)	0·0495(5)	−0·0542(13)
O(5)	−0·1432(11)	−0·0799(5)	−0·1595(12)
O(6)	−0·0292(11)	−0·1372(5)	0·1016(13)
C(1)	0·0376(18)	−0·0041(7)	−0·2350(17)
C(2)	0·0538(15)	−0·0621(7)	−0·3050(19)
C(3)	0·1409(17)	−0·1035(8)	−0·2369(21)
C(4)	0·1546(21)	−0·1529(10)	−0·3070(25)
C(5)	0·0759(24)	−0·1615(10)	−0·4514(28)
C(6)	−0·0117(22)	−0·1197(10)	−0·5216(22)
C(7)	−0·0257(21)	−0·0702(8)	−0·4454(19)
C(8)	0·2384(17)	−0·0985(8)	0·2653(18)
C(9)	0·3081(15)	−0·1517(7)	0·2422(18)
C(10)	0·4118(19)	−0·1690(9)	0·3550(23)
C(11)	0·4771(23)	−0·2201(11)	0·3445(29)
C(12)	0·4339(21)	−0·2504(9)	0·2136(30)
C(13)	0·3324(22)	−0·2336(8)	0·1004(28)
C(14)	0·2675(17)	−0·1830(7)	0·1172(21)
C(15)	0·5003(17)	0·0262(9)	0·2174(24)
C(16)	0·6138(18)	0·0174(11)	0·3510(26)
C(17)	0·4975(21)	0·0671(10)	0·1223(27)
C(18)	0·4007(19)	0·0774(8)	−0·0096(24)
C(19)	0·4113(20)	0·1232(9)	−0·1151(28)
C(20)	−0·2108(16)	−0·1270(7)	−0·1918(19)
C(21)	−0·3063(19)	−0·1272(9)	−0·3406(19)
C(22)	−0·1951(17)	−0·1741(7)	−0·0997(21)
C(23)	−0·1149(17)	−0·1755(7)	0·0403(20)
C(24)	−0·1195(22)	−0·2265(9)	0·1351(25)

[a] In this and subsequent Tables, estimated standard deviations are given in parentheses, in units of the least significant digit.

TABLE 2

Ligand bond lengths (Å) and angles (°) [a]

(*a*) Benzoxy-groups

(i) Distances

O(1)–C(1)	1·46(2)	O(2)–C(8)	1·49(2)
C(1)–C(2)	1·54(3)	C(8)–C(9)	1·52(3)
C(2)–C(3)	1·36(3)	C(9)–C(10)	1·37(3)
C(3)–C(4)	1·37(3)	C(10)–C(11)	1·41(3)
C(4)–C(5)	1·42(4)	C(11)–C(12)	1·41(4)
C(5)–C(6)	1·37(4)	C(12)–C(13)	1·35(3)
C(6)–C(7)	1·41(3)	C(13)–C(14)	1·42(3)
C(7)–C(2)	1·39(3)	C(14)–C(9)	1·38(3)

(ii) Angles

Cu(1)–O(1)–C(1)	126·0(10)	Cu(1)–O(2)–C(8)	127·0(10)
Cu(2)–O(1)–C(1)	123·2(10)	Cu(2)–O(2)–C(8)	127·2(10)
Cu(2′)–O(1)–C(1)	105·1(9)	O(2)–C(8)–C(9)	111·3(14)
O(1)–C(1)–C(2)	110·5(14)	C(8)–C(9)–C(10)	116·4(16)
C(1)–C(2)–C(3)	123·2(16)	C(9)–C(10)–C(11)	119·8(20)
C(2)–C(3)–C(4)	120·4(19)	C(10)–C(11)–C(12)	117·5(23)
C(3)–C(4)–C(5)	119·9(22)	C(11)–C(12)–C(13)	123·6(24)
C(4)–C(5)–C(6)	120·2(23)	C(12)–C(13)–C(14)	116·8(24)
C(5)–C(6)–C(7)	118·5(21)	C(13)–C(14)–C(9)	121·2(18)
C(6)–C(7)–C(2)	120·3(19)	C(14)–C(9)–C(8)	122·5(16)
C(7)–C(2)–C(1)	116·2(16)	C(14)–C(9)–C(10)	121·0(17)
C(7)–C(2)–C(3)	120·6(17)		

(*b*) Acetylacetonate groups

(i) Distances

O(3)–C(15)	1·31(3)	O(5)–C(20)	1·29(2)
O(4)–C(18)	1·29(3)	O(6)–C(23)	1·29(2)
C(15)–C(16)	1·53(3)	C(20)–C(21)	1·52(3)
C(15)–C(17)	1·41(3)	C(20)–C(22)	1·38(3)
C(17)–C(18)	1·33(3)	C(22)–C(23)	1·40(3)
C(18)–C(19)	1·51(3)	C(23)–C(24)	1·50(3)

(ii) Angles

Cu(1)–O(3)–C(15)	125·4(13)	Cu(2)–O(5)–C(20)	124·5(11)
Cu(1)–O(4)–C(18)	124·2(13)	Cu(2)–O(6)–C(23)	123·3(12)
O(3)–C(15)–C(16)	114·5(19)	O(5)–C(20)–C(21)	113·9(16)
O(4)–C(18)–C(19)	113·4(18)	O(6)–C(23)–C(24)	114·0(17)
O(3)–C(15)–C(17)	123·7(21)	O(5)–C(20)–C(22)	123·4(17)
O(4)–C(18)–C(17)	124·0(20)	O(6)–C(23)–C(22)	125·6(17)
C(16)–C(15)–C(17)	122·6(20)	C(21)–C(20)–C(22)	120·4(18)
C(17)–C(18)–C(19)	121·7(21)	C(22)–C(23)–C(24)	122·7(17)
C(15)–C(17)–C(18)	127·1(23)	C(20)–C(22)–C(23)	125·7(18)

[a] Dimensions of the Cu_4O_{12} system are given in Figure 3.

Table 1 lists the atomic fractional co-ordinates, with their estimated standard deviations. The atomic vibrational parameters, which are not listed, showed no unexpected features. Figure 1 and Table 2 show the bond lengths and angles in the molecule, and Table 3 lists the equations of weighted mean planes passing through certain groups of atoms, the distances of

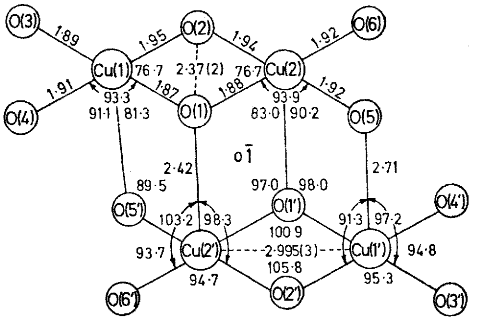

FIGURE 1 Dimensions of the Cu_4O_{12} system. Distances (Å) have σ 0·01 Å except where indicated, and angles (deg.) have σ 0·5°

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* For details see Notice to Authors No. 7 in *J.C.S. Dalton*, 1972, Index issue. (Items less than 10 pp. supplied as full-size copies.)

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various atoms from these planes, and the angles between the planes. Table 4 gives some distances between non-bonded atoms.

TABLE 3

Equations of planes of best (least-squares) fit to selected groups of atoms, distances of various atoms from planes, and angles between planes

(*a*) Atoms defining planes, and their distances (Å) [a]

Plane	Group	Atoms
(*A*)	Cu_2O_2	Cu(1) −0·002, Cu(2) −0·002, O(1) 0·01, O(2) 0·01
(*B*)	Cu_2O_2	Cu(1) 0·026, Cu(2′) 0·033, O(1) −0·09, O(6′) −0·11
(*C*)	CuO_4	Cu(1) −0·010, O(1) −0·04, O(2) 0·05, O(3) −0·04, O(4) 0·05
(*D*)	CuO_4	Cu(2) −0·072, O(1) 0·02, O(2) 0·08, O(5) 0·12, O(6) 0·02
(*E*)	acac	O(3) −0·02, O(4) 0·02, C(15) 0·0, C(16) 0·04, C(17) −0·05, C(18) −0·01, C(19) 0·01
(*F*)	acac	O(5) −0·05, O(6) 0·04, C(20) 0·0, C(21) 0·01, C(22) 0·09, C(23) 0·0, C(24) −0·08
(*G*)	Benzyl	C(2) 0·01, C(3) 0·0, C(4) 0·0, C(5) −0·01, C(6) 0·02, C(7) −0·02
(*H*)	Benzyl	C(9) 0·0, C(10) −0·01, C(11) 0·01, C(12) 0·0, C(13) 0·0, C(14) 0·01

(*b*) Equations of planes [b] in the form $lX + mY + nZ = p$

	10^4l	10^4m	10^4n	10^4p
(*A*)	5054	−7007	−5036	11775
(*B*)	5286	6427	−5545	9876
(*C*)	5036	−7235	−4721	12004
(*D*)	5743	−6716	−4681	12071
(*E*)	5700	−6916	−4437	14900
(*F*)	8253	−4677	−3165	5167
(*G*)	8306	4806	−2813	16045
(*H*)	−7573	−5659	3258	7030

(*c*) Distances (Å) of other atoms from planes

(*A*): Cu(2′) −2·35, O(3) −0·07, O(4) 0·12, O(5) 0·32, O(6) 0·15, C(1) 0·68, C(8) 0·0
(*C*): C(1) 0·59, C(8) 0·11, C(15) −0·11, C(18) −0·08
(*D*): C(1) 0·66, C(8) 0·12, C(20) 0·60, C(23) 0·44
(*E*): Cu(1) −0·11, O(1) −0·28, O(2) −0·15
(*F*): Cu(2) 0·31, O(1) 0·84, O(2) 1·05
(*G*): C(1) 0·08, O(1) −0·52
(*H*): C(8) 0·06, O(2) −0·63

(*d*) Interplanar angles (deg.)

(*A*)–(*C*)	2·2	(*C*)–(*E*)	4·5	(*A*)–(*E*)	5·1		
(*A*)–(*D*)	4·8	(*D*)–(*F*)	20·6	(*A*)–(*F*)	25·3		
(*A*)–(*B*)	84·5	(*A*)–(*G*)	77·0	(*A*)–(*H*)	98·6	(*G*)–(*H*)	6·9

[a] Atoms defining the planes were given weights proportional to their atomic numbers. [b] Orthogonal co-ordinates *X*, *Y*, *Z* are related to the fractional co-ordinates of Table 1 as follows: $X = ax + cz\cos\beta$, $Y = by$, $Z = cz\sin\beta$. *l*, *m*, *n* are the direction cosines of the plane normal, and *p* is in Å.

The molecule (Figure 2) consists of two approximately planar benzoxy-bridged dimers (acac)Cu(μ-OCH_2Ph)$_2$Cu(acac), having a structure analogous to that suggested [3] for the methoxy-compound (I), joined together by apical Cu–O bonds of length 2·42 Å from one copper atom, Cu(2), of each dimer to one of the two bridging oxygen atoms, O(1), of the other. The arrangement of the four bonds around these triply bridging oxygen atoms is roughly tetrahedral, the degree of distortion being indicated by the fact that the bonds O(1)–C(1) and O(1)–Cu(2′) make angles of 27 and 78° with the Cu_2O_2 plane, compared with the tetrahedral angle of 54·7°. The arrangement of bonds around the other bridging oxygen atoms, O(2) (which are 3·7 Å from the nearest

TABLE 4

Selected distances (Å) between non-bonded atoms [a]

Within dimer

Cu(1) ··· Cu(2)	2·995(3)		
Cu(1) ··· C(1)	3·04	Cu(1) ··· C(8)	3·02
Cu(2) ··· C(1)	3·00	Cu(2) ··· C(2)	3·38
Cu(2) ··· C(3)	3·41	Cu(2) ··· C(8)	3·03
O(1) ··· O(2)	2·37	O(2) ··· O(3)	2·78
O(1) ··· O(4)	2·80	O(2) ··· O(6)	2·80
O(1) ··· O(5)	2·82	O(3) ··· O(4)	2·80
O(5) ··· O(6)	2·81	O(1) ··· C(3)	2·87
O(3) ··· C(8)	3·03	O(4) ··· C(1)	3·10
O(5) ··· C(1)	3·01	O(5) ··· C(2)	3·17
O(6) ··· C(8)	3·04		

Between dimers in tetramer [b]

Cu(1) ··· Cu(1′)	5·399(3)		
Cu(1) ··· Cu(2′)	3·312(3)		
Cu(2) ··· Cu(2′)	3·276(3)		
Cu(2) ··· C(1′)	3·13	Cu(1) ··· C(20′)	3·42
O(1) ··· O(1′)	2·91	O(2) ··· C(1′)	3·41
O(6) ··· C(1′)	3·50	O(4) ··· C(20′)	3·49
C(18) ··· C(20′)	3·69	C(18) ··· C(22′)	3·70
C(15) ··· C(21′)	3·73		

Between tetramers [c]

C(1) ··· C(6^{I})	3·69	C(1) ··· C(7^{I})	3·62
C(7) ··· C(7^{I})	3·50	C(4) ··· C(13^{II})	3·63
C(5) ··· C(13^{II})	3·68	C(5) ··· C(24^{II})	3·71
C(13) ··· C(10^{II})	3·70	C(13) ··· C(11^{II})	3·73
C(19) ··· C(11^{II})	3·77	C(18) ··· C(15^{III})	3·62
C(19) ··· C(12^{III})	3·72	C(19) ··· C(15^{III})	3·80

[a] All distances O ··· O $\leqslant$ 3·0, O ··· C $\leqslant$ 3·5, and C ··· C $\leqslant$ 3·8 Å, are given except for those within an acac or benzoxy-group; Cu ··· C < 3·5 Å are also listed. [b] Primed and corresponding unprimed atoms are related by a centre of symmetry. [c] Roman numeral superscripts denote equivalent positions relative to *x*, *y*, *z*:

I $-x, -y, -z-1$
II $-x, -y-\frac{1}{2}, z-\frac{1}{2}$
III $-x+1, -y, -z$

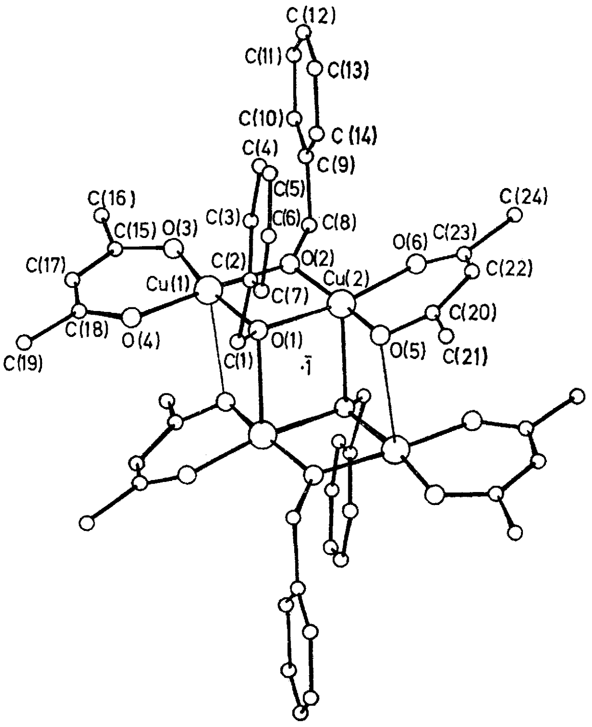

FIGURE 2 Perspective view of the molecule

copper atom in the other dimer), is planar. There is also what appears to be a weak bond between the other copper atom, Cu(1), and an acetylacetonate oxygen atom, O(5′), in the opposite dimer, at 2·71 Å. Two of these centrosymmetric, tetrameric molecules occupy the unit cell (Figure 3).

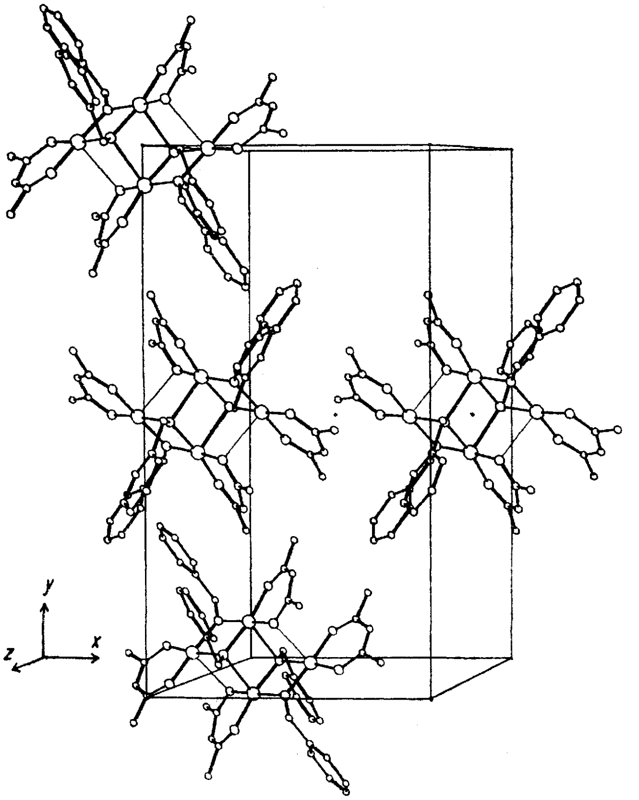

FIGURE 3 Unit cell viewed from the point with co-ordinates 50*a*,20*b*,120*c*. For clarity, only two of the molecules whose centres are at the corners of the cell are shown

The co-ordination of the copper atoms (Figure 1) is approximately square-pyramidal, Cu(2) being displaced 0·13 Å from the plane of O(1), O(2), O(5), and O(6) towards O(1′), while Cu(1) lies approximately in the plane of O(1)—(4). The four Cu–O(acac) bonds in the dimer average 1·91(1) Å and are equal, but the two Cu–O bonds to the three-co-ordinate bridging oxygen atom are significantly shorter [1·88(1) Å] than those to the four-co-ordinate bridging oxygen atom [1·94(1) Å], though the difference is not as great as that encountered in the titanium(IV) alkoxides.[12,18] (A similar, though less clear-cut, difference is also found in $[\mathrm{Cu[MeC(\dot{:}O)\cdot CH\cdot C(Me)\dot{:}N\cdot C_6H_4\cdot O]}]_2$.[6]) The dimensions of this Cu_2O_2 system are similar to those in other copper complexes in which the bridging group is the anion of an alcohol, phenol, or enol (Cu–O 1·9—2·0, Cu ··· Cu 3·0—3·1 Å [4-7]), but slightly different from those where it is hydroxide [Cu–O 1·9—2·0, Cu ··· Cu 2·8—3·0 Å (ref. 8)] or pyridine *N*-oxide [Cu–O 1·95—2·45, Cu ··· Cu 3·2—3·5 Å (ref. 9)]. These data perhaps indicate the extent to which a close Cu ··· Cu approach is easier when the bridging atoms are negatively charged.

All carbon–carbon and carbon–oxygen bond lengths and angles are as expected, and the benzene rings are planar. The acetylacetonate groups are approximately planar, but do not lie exactly in the plane of the dimer Cu_2O_2 system: the two acac groups which are involved in weak interdimer Cu–O interactions are tilted 25° outwards from the Cu_2O_2 plane (*i.e.* away from the opposite dimer), while the other two acac groups are tilted 5° inwards (Figure 4). The largest angle hitherto observed between the chelate ring and the CuO_4 plane in a copper β-diketone complex is 14° in bis-(3-phenylpentane-2,4-dionato)copper(II), where it is apparently the result of intermolecular forces.[19] The 25° distortion in the present case may represent a tendency towards tetrahedral hybridisation at O(5) as a result of the weak Cu–O bond. It seems unlikely that it is due to repulsive interactions, since the closest contact between adjacent tetramers is between two benzyl ring carbon atoms (3·50 Å, slightly greater than the 'thickness' of a benzene ring [20]), and the non-bonded distances (Table 4) between the acetylacetone group and the opposite dimer are all longer than the sums of the van der Waals radii [20] (O *ca.* 1·4, aromatic ring *ca.* 1·7, CH_3 *ca.* 2·0 Å). Moreover, the distance Cu(1) ··· C(20′), though short (3·42 Å), is considerably longer than Cu(2) ··· C(1) (3·13 Å).

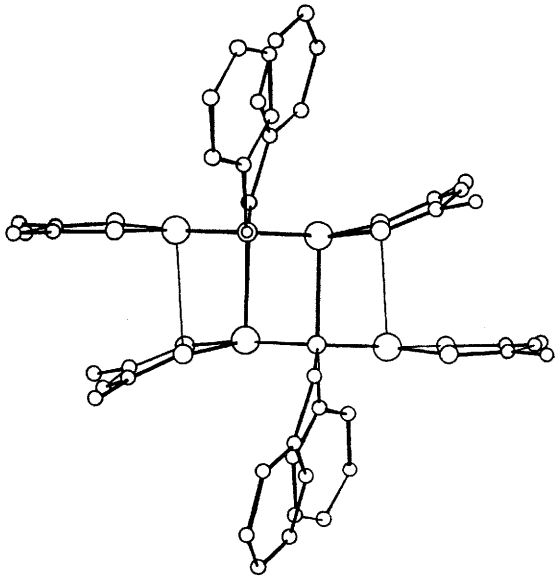

FIGURE 4 View of the molecule along the O(1) ··· O(2) axis, showing the distortion of the 'bridging' acac groups

The general arrangement in $[\mathrm{Cu(acac)(OCH_2Ph)}]_2$ is somewhat similar to that in $[\mathrm{Cu[MeC(\dot{:}O)\cdot CH\cdot}$

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[18] R. D. Witters and C. N. Caughlan, *Nature*, 1965, **205**, 1312; D. A. Wright and D. A. Williams, *Acta Cryst.*, 1968, **B**,**24**, 1107.

[19] J. W. Carmichael, jun., L. K. Steinrauf, and R. F. Belford, *J. Chem. Phys.*, 1965, **43**, 3959; I. Robertson and M. R. Truter, *J. Chem. Soc.* (*A*), 1967, 309.

[20] L. Pauling, 'The Nature of the Chemical Bond,' 3rd edn., Cornell University Press, Ithaca, New York, 1960, p. 261.

$\text{C(Me)}\text{:N}\cdot\text{C}_6\text{H}_4\cdot\text{O}]]_2$ (which also contains two dimeric units held together by long Cu–O bonds);[6] these compounds contain both μ_2 and μ_3 oxygen atoms, unlike $[\text{Cu}\{\text{MeC}(\text{:O})\cdot\text{CH}\cdot\text{C}(\text{Me})\text{:N}\cdot[\text{CH}_2]_3\cdot\text{O}\}]_2$ (μ_2 only) and $[\text{Cu}\{\text{MeC}(\text{:O})\cdot\text{CH}\cdot\text{C}(\text{Me})\text{:N}\cdot[\text{CH}_2]_2\cdot\text{O}\}]_4$ (μ_3 only).[4] The fact that the room-temperature magnetic moments of the two first-named compounds (0·83 and 1·37 B.M. [21]) are between those of the last two (0·41 and 1·87 B.M.) is consistent with the hypothesis that effective superexchange in the Cu_2O_2 system depends on the availability of oxygen π-orbitals and on the number of such π-pathways present. A fuller discussion of the magnetic properties of the alkoxy-bridged complexes will, however, be given elsewhere.[11]

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