Crystal and Molecular Structure of Tetrakis[copper(I) benzoate]

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Crystals of the title compound are triclinic, space group $P\bar{1}$, cell dimensions a = 15.408(7), b = 13.784(12), c = 15.034(9) Å, α = 92.43(6), β = 62.34(5), γ = 112.71(6)°, Z = 4. 2 262 Independent reflections above background were collected by counter methods; the structure was solved by direct methods and refined by full-matrix least squares to R 0.064. There are two independent tetramers in the asymmetric unit which have similar but not identical geometries in which four copper atoms form a parallelogram (internal angles 114.5, 65.5 and 108.8, 71.2° respectively in the two tetramers), with minimum Cu · · · Cu distances of 2.71 Å. The four benzoates bridge adjacent Cu · · · Cu atoms around the parallelogram and are alternately above and below the plane. The Cu–O distances are *ca.* 1.84 Å.

ALTHOUGH copper(I) formate and acetate were first isolated over seventy years ago,[1] it is only in the past few years that the chemistry of copper(I) carboxylates has been studied in any depth. This revival of interest stems from the knowledge that these compounds are involved as intermediates in decarboxylation reactions of organic acids [2] and in synthetic procedures such as the formation of esters from organic acids and alkyl halides in the presence of copper(I) oxide.[3] There has recently been some attention paid to the structural aspects of these compounds. Copper(I) acetate has been shown [4] to be a planar polymeric molecule in which chains of dinuclear units are linked together by further copper–oxygen interactions. In the dinuclear units each acetate group bridges the two copper atoms to afford an eight-membered ring. On the other hand, the acetate group is chelating in the distorted tetrahedral complex [Cu(O_2CMe)(PPh_3)$_2$].[5] The benzene π-complex [{Cu(O_2CCF_3)}$_4$(C_6H_6)$_2$] [6] shows another structural variation in that the four copper atoms are disposed at the corners of a planar parallelogram with bridging trifluoroacetate groups arranged approximately perpendicular to the Cu_4 plane. As a further example, we report here the structure of anhydrous copper(I) benzoate.

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EXPERIMENTAL

Preparation.—Copper(I) benzoate was prepared as before,[7] a sample (1.0 g) being subsequently recrystallised from sodium-dried xylene (150 ml) containing benzoic acid (2.0 g) under strictly anaerobic conditions.

Crystal Data.—$C_{28}H_{20}Cu_4O_8$, $M = 740.08$, Triclinic, $a = 15.408(9)$, $b = 13.784(12)$, $c = 15.034(9)$ Å, $\alpha = 92.43(6)$, $\beta = 62.34(5)$, $\gamma = 112.71(6)$°, $U = 2\,572.0$ Å^3, $D_m = 1.89$ g cm^{-3}, $Z = 4$, $D_c = 1.91$ g cm^{-3}, $F(000) = 1\,456$. Mo-K_α radiation, $\lambda = 0.7107$ Å, μ(Mo-K_α) = 34.4 cm^{-1}, space group $P1$ or $P\bar{1}$, confirmed as the latter by the successful refinement.

A crystal with dimension *ca.* 0.12 × 0.35 × 0.45 mm was mounted with the ($\bar{1}30$) 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. Zirconium-filtered molybdenum *X*-radiation was used. The stationary-crystal–stationary-counter method was used with a 4° take-off angle and a counting time of 10 s. Individual backgrounds were taken from plots of background as a function of 2θ. 3 650 independent reflections were measured with $2\theta < 40°$, of which 2 262 with $I > \sigma(I)$ were used in the refinement. Neither an absorption nor an extinction correction was made.

Structure Determination.—The positions of the eight independent copper atoms were obtained *via* direct methods using the SHEL-X set of programs [8] after many unsuccessful attempts with other programs. Fourier syntheses were then calculated to determine the positions of the remaining atoms. The structure was refined in two large blocks (one for each tetramer) by least squares The weighting scheme, chosen to give average values of $w\Delta^2$ for groups of reflections independent of the value of F_o and $\sin\theta/\lambda$, was $w^{\frac{1}{2}} = 1$ for $F_o < 140$ and $w^{\frac{1}{2}} = 140/F_o$ for $F_o > 140$. Calculations were made on a CDC 7600 computer at the University of London Computer Centre using programs of refs. 8 and 9, and with some of our own programs on an ICL 1904S at Reading University. Atomic scattering factors for Cu, O, C, and H were taken from ref. 10 as were the corrections for the real and imaginary part of the anomalous dispersion for copper. The anisotropic thermal factor was defined as $[-2\pi^2\sum_i\sum_j U_{ij}h_ih_jb_ib_j]$; $(i,j = 1,2,3)$, b_i being the i'th reciprocal cell dimension, and the isotropic thermal parameter as $\exp[-8\pi^2U\sin^2\theta/\lambda^2]$. The Cu atoms were refined anisotropically, the O and C atoms isotropically. Also included in the structure-factor calculation but not refined were the 40 H atoms on the eight independent benzene rings. These were given thermal parameters equivalent to those of the atoms to which they were bonded and given ideal trigonal positions. In the final cycle of refinement ($R = 0.064$) no shift was $> 0.10\sigma$. The 1 388 reflections given zero weight showed no large discrepancies. There were no significant peaks in a final difference-Fourier map. Positional co-ordinates and thermal parameters, together with their standard deviations are given in Tables 1 and 2. Molecular dimensions are given in Table 3. Observed and

TABLE 1

Atomic positions (× 10^4) and isotropic thermal parameters (× 10^3) for tetrakis[copper(I) benzoate]

Atom	*x*	*y*	*z*	*U*
Cu(11)	7 627(3)	5 700(3)	5 388(2)	*a*
Cu(12)	7 184(2)	3 636(3)	5 987(3)	*a*
Cu(13)	5 985(3)	3 610(3)	5 114(2)	*a*
Cu(14)	6 436(3)	5 683(3)	4 499(2)	*a*
O(111)	8 904(12)	5 691(13)	4 407(11)	75(5)
O(112)	8 556(12)	4 001(12)	4 900(10)	60(4)
C(111)	9 180(19)	4 926(21)	4 354(17)	61(7)
C(112)	10 321(19)	5 076(20)	3 580(17)	63(7)
C(113)	10 650(19)	4 259(19)	3 491(17)	65(7)
C(114)	11 719(21)	4 492(22)	2 775(19)	77(8)
C(115)	12 386(20)	5 444(23)	2 230(19)	77(8)
C(116)	12 061(21)	6 223(21)	2 298(19)	75(8)
C(117)	11 019(24)	6 072(24)	3 013(21)	94(9)
O(121)	5 855(12)	3 285(11)	7 151(10)	60(4)
O(122)	4 943(11)	3 473(12)	6 407(11)	67(5)
C(121)	5 029(18)	3 330(18)	7 161(17)	56(7)
C(122)	4 205(17)	3 397(17)	8 151(16)	53(7)
C(123)	4 211(20)	3 165(20)	9 089(19)	72(8)
C(124)	3 428(20)	3 228(20)	10 002(19)	73(8)
C(125)	2 604(21)	3 477(21)	10 104(19)	81(8)
C(126)	2 602(18)	3 683(18)	9 187(18)	62(7)
C(127)	3 377(17)	3 638(17)	8 258(16)	53(6)
O(131)	7 060(12)	3 783(13)	3 806(11)	67(5)
O(132)	7 372(11)	5 429(12)	3 305(11)	66(5)
C(131)	7 647(20)	4 633(21)	3 166(18)	66(7)
C(132)	8 687(18)	4 766(18)	2 300(16)	54(7)
C(133)	9 019(20)	3 909(20)	2 145(18)	72(7)
C(134)	9 996(21)	4 069(20)	1 391(19)	71(8)
C(135)	10 676(20)	5 022(22)	0 753(19)	77(8)
C(136)	10 374(20)	5 840(21)	0 865(19)	74(8)
C(137)	9 368(20)	5 705(20)	1 634(18)	72(8)
O(141)	5 595(11)	6 013(12)	5 731(11)	64(4)
O(142)	6 535(13)	5 944(13)	6 473(11)	78(5)
C(141)	5 747(19)	6 096(19)	6 469(19)	69(7)
C(142)	5 009(17)	6 293(17)	7 405(16)	47(6)
C(143)	5 079(17)	6 190(19)	8 319(18)	67(7)
C(144)	4 366(21)	6 380(21)	9 187(19)	78(8)
C(145)	3 621(21)	6 740(21)	9 240(19)	80(8)
C(146)	3 597(20)	6 893(20)	8 372(19)	72(7)
C(147)	4 255(18)	6 644(18)	7 479(17)	57(7)
Cu(21)	5 341(2)	−0 691(3)	7 339(2)	*a*
Cu(22)	6 402(2)	1 406(2)	7 348(2)	*a*
Cu(23)	5 433(2)	1 056(3)	6 164(2)	*a*
Cu(24)	4 403(3)	−1 079(3)	6 112(2)	*a*
O(211)	4 395(11)	−0 566(11)	8 619(10)	55(4)
O(212)	5 322(11)	1 145(12)	8 648(10)	56(4)
C(211)	4 554(18)	0 276(19)	9 077(16)	52(6)
C(212)	3 735(16)	0 097(17)	10 160(15)	42(6)
C(213)	3 921(18)	0 935(18)	10 702(17)	58(7)
C(214)	3 164(20)	0 760(20)	11 764(18)	67(7)
C(215)	2 294(20)	−0.183(22)	12 170(19)	77(8)
C(216)	2 098(22)	−0 965(23)	11 679(21)	88(9)
C(217)	2 837(19)	−0 851(19)	10 668(18)	66(7)
O(221)	7 595(12)	1 672(12)	6 126(11)	70(5)
O(222)	6 794(11)	1 328(11)	5 132(10)	55(4)
C(221)	7 586(19)	1 457(18)	5 236(17)	57(4)
C(222)	8 556(18)	1 450(19)	4 431(17)	58(7)
C(223)	9 437(20)	1 538(20)	4 577(18)	76(8)
C(224)	10 357(22)	1 448(22)	3 783(21)	92(9)
C(225)	10 414(21)	1 330(21)	2 848(20)	82(8)
C(226)	9 593(19)	1 253(18)	2 682(17)	63(7)
C(227)	8 695(20)	1 291(19)	3 450(18)	70(7)
O(231)	4 077(11)	0 774(12)	7 184(10)	56(4)
O(232)	3 231(12)	−0 934(13)	7 163(11)	73(5)
C(231)	3 263(18)	−0 107(19)	7 609(16)	54(7)
C(232)	2 324(16)	−0 250(16)	8 559(14)	37(6)
C(233)	2 313(17)	0 607(18)	9 051(16)	57(7)
C(234)	1 432(22)	0 488(22)	10 008(19)	83(8)
C(235)	0 589(22)	−0 515(24)	10 460(20)	87(9)
C(236)	0 611(19)	−1 352(20)	9 977(19)	71(7)
C(237)	1 479(19)	−1 232(19)	9 025(17)	62(7)
O(241)	5 539(13)	−1 368(12)	5 208(11)	73(5)
O(242)	6 333(11)	−0 972(11)	6 157(11)	59(4)
C(241)	6 313(19)	−1 240(18)	5 346(17)	58(7)
C(242)	7 190(18)	−1 501(18)	4 626(17)	57(7)

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TABLE 1 (*continued*)

Atom	x	y	z	U
C(243)	7 970(21)	−1 485(20)	4 798(19)	77(8)
C(244)	8 825(22)	−1 669(22)	4 086(22)	92(9)
C(245)	8 891(21)	−1 966(21)	3 186(20)	89(9)
C(246)	8 089(20)	−1 965(19)	2 999(18)	70(7)
C(247)	7 261(17)	−1 717(17)	3 706(16)	51(6)

[a] Anisotropic thermal parameters are in Table 2.

calculated structure factors are listed in Supplementary Publication No. SUP 21885 (4 pp., 1 microfiche).*

DISCUSSION

There are two independent tetramers in the asymmetric unit. These are numbered in an identical fashion but with a preceding digit of 1 or 2. They have similar but not identical structures, based on a parallellogram of copper atoms which are planar to within experimental error (Table 4). The benzoates bridge the four pairs of adjacent copper atoms around the parallelogram and are alternately above and below the plane. This structure is illustrated in the Figure. This tetrameric structure is not unique, being also found for tetrakis[(1,3-dimethyltriazino)copper(I)] [11] (1) and tetrakis[copper(I) trifluoroacetate]–benzene(1/2), (2).[6] Only preliminary details of these two structures are available; in (1) the parallelogram has the following dimensions (using our nomenclature) Cu(1) · · · Cu(2) 2.64(1), Cu(2) · · · Cu(3) 2.68(1), Cu(3) · · · Cu(4) 2.66(1), Cu(4) · · · Cu(1) 2.67(1) with Cu(1) · · · Cu(3) 2.97(1) Å and internal angles of [subtended at Cu(1) first] 112.5, 67.8, 111.7, and 67.6°. In (2) the structure is of limited accuracy because of disordered CF_3 groups; internal angles in the parallelogram are quoted as 113.1 and 66.8° with sides of *ca.* 2.8 Å. This latter figure seems rather high but may be an average including one or two diagonals. The dimensions in our two tetramers are very similar to these values. In tetramer 2, the mean internal ring angles are 114.5 and 65.5°, the larger angle being slightly greater than in (1) or (2). However, in tetramer 1 (angles 108.8 and 71.2°), the larger angle is smaller by *ca.* 4°. These differences are concomitant with Cu(1) · · · Cu(3) distances across the short diagonal in the two tetramers of 2.968(6) and 3.180(5) Å. This range of dimensions for the parallelogram of copper atoms suggests that Cu · · · Cu bonding is only of marginal significance within the tetramer and that the bridging benzoate groups are all-important in holding the tetramer together. Certainly this type of Cu_4 parallelogram is only found with bridging ligands of the carboxylate or triazino-type.

TABLE 2

Anisotropic thermal parameters (× 10^3) for the copper atoms in tetrakis[copper(I) benzoate]

Atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Cu(11)	74.8(24)	101.2(28)	73.7(23)	50.5(22)	−33.3(20)	−16.6(21)
Cu(12)	67.2(23)	83.7(25)	67.1(22)	35.2(20)	−30.5(19)	−12.3(19)
Cu(13)	79.2(25)	94.9(27)	53.1(20)	32.8(22)	−31.6(19)	−8.4(19)
Cu(14)	90.1(27)	103.7(29)	60.3(21)	54.3(23)	−36.3(20)	−15.9(20)
Cu(21)	77.5(24)	81.4(25)	59.0(20)	38.1(20)	−42.2(19)	−19.6(18)
Cu(22)	74.0(23)	75.0(24)	55.5(20)	21.8(20)	−33.0(19)	−13.6(18)
Cu(23)	64.5(22)	89.2(26)	64.6(21)	33.2(21)	−33.0(19)	−10.0(20)
Cu(24)	81.8(25)	111.4(30)	76.9(24)	56.2(24)	−52.2(21)	−37.2(22)

However in tetrakis[trimethylsilylmethylcopper(I)], the four copper atoms are also coplanar but form a square (Cu · · · Cu 2.42 Å) with the methylene carbon atoms lying in the same plane and bridging the edges and are presumably involved in three-centre two-electron bonds.[12] Ligands such as S_2CNEt_2 (diethyldithiocarbamate) and $S_2P(OPr^i)_2$ (di-isopropylphosphorodithioate) are also capable of bridging adjacent copper atoms in copper(I) complexes and indeed form the tetramers $[Cu_4(S_2CNEt_2)_4]$ [13] and $[Cu_4\{(Pr^iO)_2PS_2\}_4]$.[14] However, these compounds have markedly different structures from our present tetramers both in the mode of co-ordination of the ligands and the geometry of the Cu_4 unit. One of the sulphur atoms in each ligand bridges two copper atoms almost symmetrically whereas the other forms a bond with a third copper atom. The four copper atoms form a tetrahedron. It is not clear why two such different Cu_4 arrangements occur with ligands which potentially are capable of acting in an analogous way.† It may be significant that the Cu_4 planar parallelogram is only known to date in simple compounds in conjunction with first row elements (N for triazino, O for carboxylate, and C for CH_2SiMe_3) and the Cu_4 tetrahedral array only for second row elements (S in the above examples). A consequence of the change in the Cu_4 geometry is that each copper atom is two co-ordinate in the planar array but is three co-ordinate in the tetrahedral array (neglecting Cu · · · Cu interactions).

In $[Cu_4(benzoate)_4]$, there are no significant differences

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† A similar problem is found with the structures of related tetrameric copper(I) halide–phosphine complexes. The series $[\{Et_3PCuX\}_4]$ (X = Cl,[15] Br,[15] or I [16]) and $[\{Ph_3PCuCl\}_4]$ [16] have the four copper atoms arranged at the corners of a tetrahedron, the Cu_4X_4 unit being of the 'cubane' type. However in $[\{Ph_3PCuBr\}_4]$ [16] and $[\{Ph_3PCuI\}_4]$ [17] the structure changes dramatically to a 'step' type with the four copper atoms precisely coplanar. This Cu_4 planar parallelogram is also found in the structures of $[(CuX)_4(Ph_2PCH_2PPh_2)_2]$ (X = Cl, Br, and I).[18]

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TABLE 3

Dimensions in the two tetramers

(*a*) copper atoms

	tetramer 1	tetramer 2
Cu(1)–Cu(2)	2.742(6)	2.719(4)
Cu(1)–Cu(3)	3.180(5)	2.968(6)
Cu(1)–Cu(4)	2.720(6)	2.753(6)
Cu(2)–Cu(3)	2.709(6)	2.732(6)
Cu(3)–Cu(4)	2.756(7)	2.770(5)
Cu(1)–Cu(2)–Cu(3)	71.4(2)	66.0(1)
Cu(2)–Cu(3)–Cu(4)	108.8(2)	114.0(2)
Cu(3)–Cu(4)–Cu(1)	71.0(2)	65.0(1)
Cu(4)–Cu(1)–Cu(2)	108.8(2)	115.0(2)
Cu(2)–Cu(1)–Cu(3)	53.8(1)	57.2(1)
Cu(4)–Cu(1)–Cu(3)	55.0(1)	57.8(1)
Cu(2)–Cu(3)–Cu(1)	54.8(1)	56.8(1)
Cu(4)–Cu(3)–Cu(1)	54.0(1)	57.2(1)
Cu(1)–O(11)	1.835(16)	1.849(13)
Cu(1)–O(42)	1.856(17)	1.877(14)
Cu(2)–O(12)	1.862(13)	1.816(12)
Cu(2)–O(21)	1.854(14)	1.812(13)
Cu(3)–O(22)	1.815(13)	1.836(13)
Cu(3)–O(31)	1.838(15)	1.821(13)
Cu(4)–O(41)	1.863(15)	1.831(18)
Cu(4)–O(32)	1.833(15)	1.844(16)
O(11)–Cu(1)–O(42)	167.0(8)	170.4(9)
O(11)–Cu(1)–Cu(2)	82.8(6)	80.0(4)
O(11)–Cu(1)–Cu(4)	108.6(7)	109.8(6)
O(42)–Cu(1)–Cu(2)	102.9(5)	103.9(4)
O(42)–Cu(1)–Cu(4)	80.9(7)	76.7(6)
O(12)–Cu(2)–O(21)	175.3(9)	172.1(10)
O(12)–Cu(2)–Cu(1)	82.0(6)	85.1(5)
O(12)–Cu(2)–Cu(3)	104.4(7)	105.3(7)
O(21)–Cu(2)–Cu(1)	98.9(6)	97.0(5)
O(21)–Cu(2)–Cu(3)	80.3(6)	82.5(7)
O(22)–Cu(3)–O(31)	178.5(7)	179.5(7)
O(22)–Cu(3)–Cu(2)	84.9(6)	83.0(6)
O(22)–Cu(3)–Cu(4)	96.4(6)	99.3(5)
O(31)–Cu(3)–Cu(2)	94.5(7)	97.3(6)
O(31)–Cu(3)–Cu(4)	82.5(6)	80.1(5)
O(32)–Cu(4)–O(41)	174.6(8)	171.4(9)
O(32)–Cu(4)–Cu(3)	80.5(6)	82.4(5)
O(32)–Cu(4)–Cu(1)	91.6(7)	88.5(7)
O(41)–Cu(4)–Cu(3)	100.6(5)	101.5(5)
O(41)–Cu(4)–Cu(1)	83.8(7)	86.4(7)

(*b*) dimensions in the benzoates

In tetramer 1	n = 1	n = 2	n = 3	n = 4
O(n1)–C(n1)	1.27(4)	1.29(4)	1.26(3)	1.23(4)
O(n2)–C(n1)	1.28(3)	1.23(4)	1.30(4)	1.31(4)
C(n1)–C(n2)	1.53(3)	1.47(3)	1.47(3)	1.44(3)
Cu(m)*–O(n1)–C(n1)	125.2(12)	124.6(15)	126.6(18)	125.3(19)
Cu(m)–O(n2)–C(n1)	125.0(18)	122.9(18)	127.9(14)	127.1(17)
O(n1)–C(n1)–O(n2)	124.5(21)	125.9(16)	120.1(20)	122.6(23)
O(n1)–C(n1)–C(n2)	119.7(19)	115.9(25)	120.6(28)	120.6(29)
O(n2)–C(n1)–C(n2)	115.7(27)	117.3(27)	119.1(20)	116.7(27)
C(n1)–C(n2)–C(n3)	121.5(20)	120.4(21)	120.2(20)	119.9(27)
C(n1)–C(n2)–C(n7)	116.9(27)	123.0(26)	121.5(27)	123.5(26)
C(n3)–C(n2)–C(n7)	121.5(24)	116.6(20)	118.2(21)	116.5(21)
C(n2)–C(n3)	1.38(5)	1.46(4)	1.43(4)	1.44(4)
C(n3)–C(n4)	1.40(4)	1.37(3)	1.33(4)	1.36(4)
C(n4)–C(n5)	1.31(4)	1.38(5)	1.36(3)	1.39(5)
C(n5)–C(n6)	1.33(5)	1.42(5)	1.36(5)	1.35(5)
C(n6)–C(n7)	1.39(4)	1.37(3)	1.38(3)	1.38(3)
C(n7)–C(n2)	1.37(3)	1.38(3)	1.37(3)	1.38(4)
C(n2)–C(n3)–C(n4)	116.7(21)	119.1(30)	119.2(22)	118.1(31)
C(n3)–C(n4)–C(n5)	121.8(32)	124.0(31)	121.6(31)	124.1(31)
C(n4)–C(n5)–C(n6)	121.4(26)	116.1(23)	120.5(24)	117.5(25)
C(n5)–C(n6)–C(n7)	120.6(23)	121.7(30)	119.6(22)	120.9(32)
C(n6)–C(n7)–C(n2)	117.7(32)	122.5(27)	120.7(30)	122.6(28)
In tetramer 2				
O(n1)–C(n1)	1.32(3)	1.36(3)	1.27(2)	1.25(4)
O(n2)–C(n1)	1.23(2)	1.24(3)	1.30(3)	1.27(3)
C(n1)–C(n2)	1.48(3)	1.42(3)	1.43(3)	1.45(4)
Cu(m)–O(n1)–C(n1)	126.6(10)	124.7(15)	130.0(17)	122.5(16)
Cu(m)–O(n2)–C(n1)	124.5(15)	126.1(14)	125.4(13)	131.8(20)
O(n1)–C(n1)–O(n2)	123.3(18)	121.3(20)	119.8(18)	122.3(22)
O(n1)–C(n1)–C(n2)	114.9(16)	115.6(26)	123.9(21)	121.2(24)
O(n2)–C(n1)–C(n2)	121.8(21)	123.1(24)	116.2(17)	116.2(28)
C(n1)–C(n2)–C(n3)	116.9(16)	122.4(25)	118.4(17)	123.0(25)
C(n1)–C(n2)–C(n7)	124.1(21)	122.4(29)	122.2(21)	119.1(29)
C(n3)–C(n2)–C(n7)	119.0(18)	115.0(24)	119.2(17)	117.8(24)
C(n2)–C(n3)	1.40(3)	1.43(5)	1.37(3)	1.33(5)
C(n3)–C(n4)	1.43(3)	1.41(4)	1.40(3)	1.37(4)
C(n4)–C(n5)	1.35(3)	1.37(5)	1.39(3)	1.37(5)
C(n5)–C(n6)	1.30(4)	1.36(5)	1.34(4)	1.39(5)
C(n6)–C(n7)	1.38(3)	1.35(3)	1.39(3)	1.39(3)
C(n7)–C(n2)	1.38(3)	1.41(4)	1.37(3)	1.36(4)
C(n2)–C(n3)–C(n4)	117.7(17)	121.0(27)	120.2(18)	122.2(29)
C(n3)–C(n4)–C(n5)	118.1(24)	118.5(35)	119.2(26)	122.0(36)
C(n4)–C(n5)–C(n6)	125.0(22)	121.8(26)	120.2(22)	115.5(28)
C(n5)–C(n6)–C(n7)	118.6(21)	119.8(27)	120.5(20)	121.4(26)
C(n6)–C(n7)–C(n1)	121.3(24)	123.7(31)	120.6(23)	120.7(25)

* m is unspecified but refers to the number of the copper atom to which the oxygen atom is bonded. There is no ambiguity in this abbreviation.

TABLE 4

Least-squares planes in the form $Ax + By + Cz = D$, where x,y,z are the crystallographic fractional co-ordinates. Distances (Å) of relevant atoms from the planes are given in square brackets

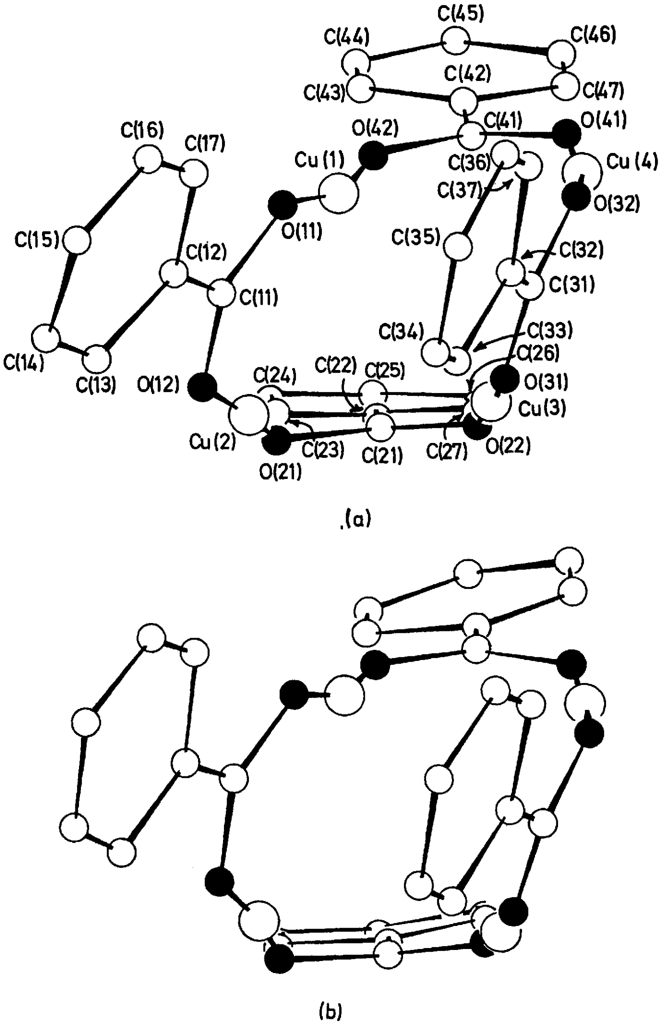
	A	*B*	*C*	*D*
Plane 1 Cu(1), Cu(2), Cu(3), Cu(4)				
tetramer 1	−6.69	4.08	8.97	2.05
[Cu(1) −0.00, Cu(2) 0.00, Cu(3) −0.00, Cu(4) 0.00]				
tetramer 2	9.54	−4.62	−6.13	0.93
[Cu(1) −0.02, Cu(2) 0.02, Cu(3) −0.02, Cu(4) 0.02]				
Plane 2 Cu(1), Cu(2), O(11), O(12)				
tetramer 1	10.39	1.76	13.61	16.26
[Cu(1) 0.00, Cu(2) −0.00, O(11) −0.01, O(12) 0.01, C(11) 0.07, C(12) 0.23]				
tetramer 2	14.04	−7.40	10.63	15.79
[Cu(1) 0.03, Cu(2) −0.03, O(11) −0.03, O(12) 0.03, C(11) 0.05, C(12) 0.19]				
Plane 3 Cu(2), Cu(3), O(21), O(22)				
tetramer 1	−0.64	12.92	1.96	5.35
[Cu(2) 0.06, Cu(3) −0.06, O(21) −0.08, O(22) 0.08, C(21) 0.03, C(22) 0.36]				
tetramer 2	−3.87	13.55	−1.15	−1.40
[Cu(2) 0.02, Cu(3) −0.02, O(21) −0.02, O(22) 0.02, C(21) 0.16, C(22) 0.45]				
Plane 4 Cu(3), Cu(4), O(31), O(32)				
tetramer 1	13.40	0.45	10.76	13.71
[Cu(3) −0.02, Cu(4) 0.02, O(31) 0.02, O(32) −0.02, C(31) 0.16, C(32) 0.62]				
tetramer 2	11.36	−5.80	13.47	13.86
[Cu(3) 0.00, Cu(4) −0.00, O(31) −0.00, O(32) 0.00, C(31) 0.16, C(32) 0.46]				
Plane 5 Cu(4), Cu(1), O(41), O(42)				
tetramer 1	1.46	11.43	−1.62	6.73
[Cu(1) 0.02, Cu(4) −0.02, O(41) 0.03, O(42) −0.03, C(41) 0.03, C(42) −0.00]				
tetramer 2	−0.52	11.71	−3.74	−3.80
[Cu(1) −0.03, Cu(4) 0.03, O(41) −0.03, O(42) 0.03, C(41) 0.02, C(42) −0.06]				

Angles between planes (°)

	tetramer 1	tetramer 2
1 and 2	108.0	106.2
1 and 3	82.9	83.0
1 and 4	86.9	86.2
1 and 5	103.2	103.9
6 * and 2	7.4	9.6
6 and 3	16.4	14.3
6 and 4	21.5	15.5
6 and 5	13.4	3.6

* Plane 6 is calculated from atoms C(n2)–C(n7) inclusive.

in the Cu–O distances whose mean value is an expected 1.84 Å. This is different from that observed in [{Cu($\mathrm{O_2CCF_3}$)}$_4$($\mathrm{C_6H_6}$)$_2$] [6] where Cu–O distances range between 1.83 and 2.2 Å. Details of the geometry of the benzoate fragments are illustrated *via* the least-squares planes of Table 4 (and the Figure). We have calculated the planes containing the pair of oxygen atoms from each benzoate together with the pair of copper atoms to which they are bonded. These four atoms are closely planar and intersect the $\mathrm{Cu_4}$ plane at angles significantly different from 90° ranging between 108.0 and 82.9°. It is significant (see Table 4 and the Figure) that these angles of intersection are very similar in the two independent tetramers with rings 1 bent away from the $\mathrm{Cu_4}$ plane (angles 108.0, 106.2° in tetramers 1 and 2 respectively) and rings 3 bent towards (86.9, 86.2°). Also planes 4 are bent away (103.2, 103.9°) while planes 2 are bent towards (82.9, 83.0°). This regularity must be due to intra- rather than inter-molecular contacts. A similar agreement is found in the dimensions of the two tetramers (O–Cu–O angles for example) despite the variation in the shape of the $\mathrm{Cu_4}$ parallelogram.



The two independent tetrakis[copper(I)benzoate] molecules. The numbering scheme of both molecules is identical

The angle between the Cu,Cu,O,O planes and the benzene rings is also variable (3.6—21.5°). However, this is primarily due to the ring being bent out of the plane rather than to any twist around the C(n1)–C(n2) axis. This is made clear by the deviations of C(n2) and to a lesser extent C(n1) atoms from the Cu,Cu,O,O plane, and also to the fact that the angles between planes O(n1), O(n2), C(n1), C(n2), and C(n2)—C(n7) inclusive, are much smaller (1.6—11.8°).

There are a large number of intermolecular contacts <3.5 Å and these are listed in Table 5. There are several Cu ··· O contacts among these, the shortest being 3.04, 3.08, and 3.11 Å. The shortest Cu ··· Cu contact between tetramers is 3.235 Å. It seems improbable that any of these distances represent even very weak interactions. In view of the cylindrical shape of the tetramer, each copper atom is more open to such contacts than a metal atom in a monomeric co-ordination compound and it is therefore not surprising that they are involved in the shortest intermolecular contacts.

TABLE 5

Intermolecular contacts <3.50 Å not involving hydrogen [a]

O(141) ··· C(242$^{\mathrm{I}}$)	3.276	C(114) ··· Cu(12$^{\mathrm{II}}$)	3.481
O(132) ··· C(245$^{\mathrm{I}}$)	3.403	Cu(11) ··· C(114$^{\mathrm{II}}$)	3.400
Cu(14) ··· C(246$^{\mathrm{I}}$)	3.316	C(111) ··· C(113$^{\mathrm{II}}$)	3.475
C(146) ··· O(211$^{\mathrm{I}}$)	3.302	Cu(12) ··· C(115$^{\mathrm{II}}$)	3.153
C(146) ··· Cu(21$^{\mathrm{I}}$)	3.222	Cu(12) ··· C(116$^{\mathrm{II}}$)	3.256
Cu(14) ··· C(247$^{\mathrm{I}}$)	3.364	C(135) ··· C(136$^{\mathrm{III}}$)	3.447
O(132) ··· C(246$^{\mathrm{I}}$)	3.307	Cu(13) ··· O(141$^{\mathrm{IV}}$)	3.422
C(147) ··· Cu(21$^{\mathrm{I}}$)	3.366	O(131) ··· C(147$^{\mathrm{IV}}$)	3.287
C(147) ··· O(242$^{\mathrm{I}}$)	3.394	C(147) ··· C(131$^{\mathrm{IV}}$)	3.338
C(145) ··· O(211$^{\mathrm{I}}$)	3.452	Cu(14) ··· O(141$^{\mathrm{IV}}$)	3.266
Cu(12) ··· Cu(23)	3.465	C(215) ··· Cu(22$^{\mathrm{V}}$)	3.387
O(121) ··· Cu(23)	3.321	C(215) ··· O(221$^{\mathrm{V}}$)	3.454
Cu(22) ··· O(121)	3.080	C(213) ··· C(211$^{\mathrm{V}}$)	3.495
O(231) ··· O(121)	3.471	Cu(21) ··· C(214$^{\mathrm{V}}$)	3.192
O(231) ··· C(121)	3.246	Cu(22) ··· C(216$^{\mathrm{V}}$)	3.487
O(221) ··· O(112)	3.193	C(213) ··· O(211$^{\mathrm{V}}$)	3.398
O(212) ··· O(121)	3.380	Cu(24) ··· Cu(23$^{\mathrm{VI}}$)	3.313
O(231) ··· O(122)	3.475	O(241) ··· Cu(13$^{\mathrm{VI}}$)	3.259
C(221) ··· O(112)	3.192	O(241) ··· Cu(23$^{\mathrm{VI}}$)	3.181
Cu(12) ··· O(221)	3.043	O(222) ··· Cu(24$^{\mathrm{VI}}$)	3.113
Cu(12) ··· C(221)	3.344	O(241) ··· O(231$^{\mathrm{VI}}$)	3.443
Cu(12) ··· O(222)	3.321	C(247) ··· O(122$^{\mathrm{VI}}$)	3.403
C(116) ··· Cu(22$^{\mathrm{II}}$)	3.409	O(222) ··· O(232$^{\mathrm{VI}}$)	3.487
O(112) ··· C(112$^{\mathrm{II}}$)	3.400	O(232) ··· C(227$^{\mathrm{VI}}$)	3.357
O(121) ··· C(115$^{\mathrm{II}}$)	3.134	C(235) ··· C(235$^{\mathrm{VII}}$)	3.422
O(121) ··· C(116$^{\mathrm{II}}$)	3.493	Cu(22) ··· Cu(12)	3.235

[a] Roman numerals as superscripts refer to the following equivalent positions relative to the *x,y,z* set in Table 1

I $x, 1 + y, z$
II $2 - x, 1 - y, 1 - z$
III $2 - x, 1 - y, -z$
IV $1 - x, 1 - y, 1 - z$
V $1 - x, -y, 2 - z$
VI $1 - x, -y, 1 - z$
VII $-x, -y, 2 - z$

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