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The Crystal Structure of Copper(II) Aspirinate

By Ljubica Manojlović-Muir

Chemistry Department, University of Glasgow, Glasgow G12 8QQ, Scotland

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Crystals of copper(II) aspirinate, $Cu(C_9H_7O_4)_2$, are monoclinic, space group $P2_1/c$, $a=8·208$ (3), $b=10·39$ (2), $c=21·56$ (1) Å, $\beta=104·74$ (5)°, $Z=4$. The intensities of 1635 independent reflexions were measured on a linear diffractometer with Mo $K\alpha$ radiation. The structure was determined by the heavy-atom method and refined by full-matrix least-squares to $R=0·078$. The crystal structure is built of binuclear $Cu_2(C_9H_7O_4)_4$ units, linked *via* Cu–O(acetyl) bonds to form polymeric chains parallel to the *a* axis. The metal atoms in each binuclear unit are bridged by four *syn–syn* carboxylate groups. The Cu–Cu, Cu–O(acetyl) and the average Cu–O(carboxylate) distances are 2·617 (3), 2·241 (8) and 1·963 (4) Å, respectively.

Introduction

Although salicylates are perhaps the most widely used drugs, having been available in synthetic form for over 90 years, the mechanism of their therapeutic action still remains obscure (Davison, 1971). It has been suggested, and supported by some experimental evidence, that the anti-fever and pain-relieving effects of acetylsalicylic acid (aspirin) may originate from its ability to form a chelate complex with copper ions *in vivo*, and thus reduce their concentration in the blood (Schubert, 1966). Hence we have made copper(II) aspirinate, and examined its solid-state structure using X-ray diffraction methods. A preliminary account of this work has been published earlier (Manojlović-Muir, 1967).

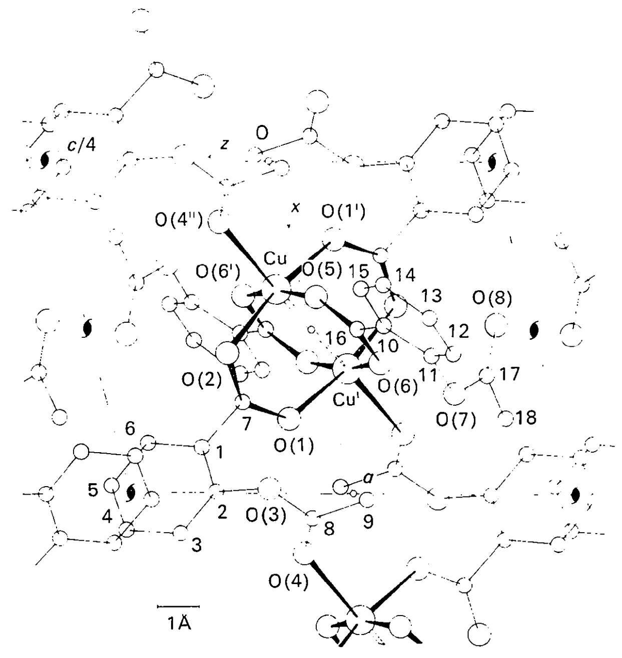

Fig. 1. The crystal structure of copper(II) aspirinate viewed down the *b* axis. The carbon atoms in the asymmetric unit are indicated by numbers 1–18. The significance of Roman numerals is as shown in Table 3.

Lewis, Mabbs, Royston & Smail (1969) have shown that copper(II) aspirinate, like many other copper(II) carboxylates, has anomalous magnetic properties. Recent interest in the magnetic interaction of copper(II) ions, and in the dependence of its magnitude on the structural properties of carboxylate residues, has led to intensive spectroscopic, magnetic and crystallographic investigations of these compounds (Jotham, Kettle & Marks, 1972; Porai-Koshits, Antsyshkina, Sadikov & Kukina, 1971). Structural data are now available for a number of copper(II) alkylcarboxylates, but for arylcarboxylates they have been determined only for copper(II) aspirinate and for copper(II) *o*-bromobenzoate monohydrate (Harrison, Rettig & Trotter, 1972).

Experimental

The crystals were prepared in the way described earlier (Manojlović-Muir, 1967). They were blue, transparent prisms elongated in the direction of the *b* axis. The specimen chosen for the subsequent analysis was of approximate dimensions 0·007 × 0·024 × 0·007 cm.

Crystal data

$Cu(C_9H_7O_4)_2$, F.W. 421·8. Monoclinic, space group $P2_1/c$, $a=8·208$ (3),[*] $b=10·39$ (2), $c=21·56$ (1) Å, $\beta=104·74$ (5)°, $U=1778·1$ Å^3, D_m (by flotation) $=1·58$ g cm^{-3}, $Z=4$, $D_c=1·576$ g cm^{-3}, $F(000)=860$, μ(Mo $K\alpha$) $=13·2$ cm^{-1}.

The unit-cell constants *a*, *c* and β were obtained by a least-squares treatment of 17 high-order reflexions recorded on a Weissenberg photograph, calibrated with powder lines from a thin aluminum wire (Cu $K\alpha_1$, $\lambda=1·5405$ Å). The constant *b* was determined from a

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[*] Throughout the paper, limits of error are estimated standard deviations and they are presented in parentheses. They are derived either from the appropriate least-squares matrix or, in the case of average values, from the range of individual measurements.

precession photograph and from setting angles on a linear diffractometer (Mo $K\alpha$, $\lambda = 0\cdot7107$ Å).

Intensity measurement

Intensities of the $h0l$–$h10l$ reflexions were measured on a Hilger–Watts linear diffractometer fitted with a scintillation counter and a pulse-height analyser. Molybdenum radiation was used in conjunction with balanced ZrO_2–SrO filters. After the correction for background was made, the intensities of 1635 independent reflexions were greater than zero, and only these were employed in the structure analysis. They were reduced to structure amplitudes by applying Lorentz and polarization factors appropriate to the equi-inclination Weissenberg geometry. No absorption correction was made.

Structure determination and refinement

The position of the copper atom was determined from a Patterson function, and the positions of the remaining non-hydrogen atoms from the subsequent Fourier syntheses of electron density.

The structure was refined by full-matrix least-squares. The function minimized was $\sum w\Delta^2$, where $\Delta = |F_o| - |F_c|$, and $|F_o|$ and $|F_c|$ are, respectively, the observed and calculated structure amplitudes. The atomic scattering factors were taken from *International Tables for X-ray Crystallography* (1962). The calculations were carried out on the Glasgow University KDF9 computer, using the programs developed by Professor D. W. J. Cruickshank and Drs W. S. McDonald, K. W. Muir, J. G. Sime and J. G. F. Smith.

The refinement of positional and isotropic thermal parameters of all atoms terminated at $R = 0\cdot100$. An allowance was then made for the anisotropic thermal vibrations, and the refinement converged at $R = 0\cdot078$ and $R' = 0\cdot083$, where $R' = (\sum w\Delta^2/\sum w F_o^2)^{1/2}$. In the later stages of refinement the least-squares weights were defined as $w = (80\cdot0/F_o)^2$ if $|F_o| \geq 80\cdot0$, otherwise $w = 1\cdot0$. An analysis of the mean $w\Delta^2$ values as a function of $|F_o|$, and of $\sin\theta/\lambda$, confirmed the adequacy of this weighting scheme. In the last cycle of refinement all parameters shifted by less than 0·20 of their estimated standard deviations. The function values in the final difference synthesis fluctuated between $-0\cdot51$ and

Table 1. *Observed structure amplitudes and calculated structure factors*

+0·66 e Å^{-3}, and the minimum peak height for a carbon atom in the final F_o synthesis was 4·52 e Å^{-3}.

The final calculated structure factors and the observed structure amplitudes are listed in Table 1, and the final atomic parameters are shown in Table 2.

Table 2. *Final atomic parameters*

The atoms were assigned anisotropic temperature factors of the form:

$$\exp\,(-2\pi^2 \sum_{i=1}^{3} \sum_{j=1}^{3} U_{ij} a_i^* a_j^* h_i h_j)\,.$$

(*a*) Fractional coordinates

	x	y	z
Cu	0·3842 (2)	0·0356 (2)	0·0284 (1)
O(1)	0·7719 (9)	0·0267 (10)	0·0507 (4)
O(2)	0·5739 (10)	0·0816 (8)	0·1011 (4)
O(3)	0·9849 (11)	0·2393 (9)	0·0928 (4)
O(4)	1·1825 (10)	0·1088 (9)	0·0725 (4)
O(5)	0·4052 (10)	0·1992 (9)	−0·0147 (4)
O(6)	0·6042 (10)	0·1391 (8)	−0·0627 (4)
O(7)	0·6940 (12)	0·3035 (9)	−0·1433 (4)
O(8)	0·4870 (16)	0·2013 (14)	−0·2084 (5)
C(1)	0·8597 (15)	0·1057 (13)	0·1568 (5)
C(2)	0·9957 (17)	0·1798 (13)	0·1547 (6)
C(3)	1·1237 (17)	0·2122 (16)	0·2060 (7)
C(4)	1·1154 (19)	0·1620 (18)	0·2663 (7)
C(5)	0·9785 (19)	0·0863 (18)	0·2701 (6)
C(6)	0·8482 (18)	0·0579 (15)	0·2164 (5)
C(7)	0·7230 (15)	0·0691 (11)	0·0984 (5)
C(8)	1·0763 (15)	0·1864 (13)	0·0536 (6)
C(9)	1·0194 (20)	0·2458 (19)	−0·0135 (7)
C(10)	0·4902 (15)	0·3473 (13)	−0·0820 (5)
C(11)	0·5801 (16)	0·3850 (13)	−0·1266 (6)
C(12)	0·5737 (20)	0·5083 (16)	−0·1517 (7)
C(13)	0·4659 (21)	0·5946 (15)	−0·1354 (7)
C(14)	0·3677 (20)	0·5662 (13)	−0·0931 (6)
C(15)	0·3806 (16)	0·4433 (12)	−0·0669 (6)
C(16)	0·4994 (15)	0·2197 (11)	−0·0512 (5)
C(17)	0·6376 (20)	0·2105 (16)	−0·1837 (7)
C(18)	0·7673 (27)	0·1156 (23)	−0·1926 (10)

Description of the structure and discussion

The crystal structure (Fig. 1) is built of binuclear units, with the composition Cu_2(aspirinate)$_4$. The geometry of these units is analogous to that of the dimeric *syn-syn* bridged metal carboxylates $M_2(RCO_2)_4L_2$, where L is a monodentate donor molecule (Martin & Waterman, 1959; Oldham, 1968). The molecular geometry of this type was first observed in copper(II) acetate monohydrate (van Niekerk & Schoening, 1953), and subsequently in a number of other copper(II) carboxylate monoadducts. However, while the $Cu_2(RCO_2)_4L_2$ dimers exist in the solid state as discrete molecules, the Cu_2(aspirinate)$_4$ units are associated *via* Cu–O(acetyl) bonds to form polymeric chains parallel to the crystallographic *a* axis. All interchain interactions are of the van der Waals type, as revealed by an examination of the appropriate interatomic distances shorter than 3·7 Å.

The Cu_2(aspirinate)$_4$ unit has C_i symmetry imposed crystallographically, and its geometry is shown in Fig. 1. The metal atoms are linked by four carboxylate bridges to form two cyclic $Cu_2(CO_2)_2$ fragments, which are planar and approximately perpendicular to one another. Each copper atom is in a distorted octahedral coordination and makes four relatively strong bonds with the oxygen atoms of the carboxylate groups and a relatively weak bond with an acetyl group oxygen from a neighbouring binuclear unit. Thus the latter oxygen atom forms the apex, and the coplanar car-

Table 2 (*cont.*)

(*b*) Vibrational parameters ($U_{ij} \times 10^3$ Å^2)

	U_{11}	U_{22}	U_{33}	$2U_{23}$	$2U_{31}$	$2U_{12}$
Cu	23 (1)	39 (1)	28 (1)	6 (1)	15 (1)	10 (2)
O(1)	22 (4)	78 (6)	41 (5)	− 4 (9)	10 (7)	−14 (9)
O(2)	41 (5)	49 (6)	42 (5)	−12 (8)	13 (8)	2 (8)
O(3)	44 (5)	46 (6)	64 (6)	− 4 (9)	30 (9)	15 (9)
O(4)	34 (5)	55 (6)	51 (5)	11 (9)	47 (8)	20 (8)
O(5)	39 (5)	52 (6)	47 (5)	12 (8)	39 (8)	5 (8)
O(6)	36 (5)	37 (5)	43 (5)	11 (8)	19 (8)	13 (8)
O(7)	64 (7)	51 (6)	70 (6)	2 (10)	56 (11)	18 (10)
O(8)	82 (9)	129 (12)	83 (8)	−47 (15)	10 (14)	73 (16)
C(1)	28 (6)	53 (8)	35 (6)	−17 (11)	2 (10)	6 (12)
C(2)	51 (8)	41 (8)	58 (8)	10 (12)	63 (14)	17 (13)
C(3)	35 (8)	79 (11)	64 (9)	−65 (16)	−22 (14)	− 1 (15)
C(4)	50 (9)	99 (13)	58 (9)	−18 (18)	23 (15)	16 (18)
C(5)	57 (10)	104 (14)	49 (8)	−58 (17)	25 (15)	30 (18)
C(6)	62 (9)	78 (11)	24 (6)	− 6 (13)	8 (12)	7 (16)
C(7)	41 (7)	38 (7)	30 (6)	9 (10)	16 (11)	11 (11)
C(8)	28 (7)	57 (9)	55 (8)	−20 (13)	22 (12)	7 (12)
C(9)	55 (10)	124 (16)	55 (9)	88 (19)	31 (16)	59 (20)
C(10)	29 (7)	49 (8)	36 (7)	− 4 (11)	− 5 (11)	16 (12)
C(11)	41 (8)	45 (8)	52 (8)	17 (12)	44 (13)	11 (12)
C(12)	78 (11)	67 (12)	75 (10)	26 (16)	75 (18)	15 (17)
C(13)	80 (11)	60 (10)	54 (9)	35 (15)	48 (16)	5 (17)
C(14)	81 (11)	39 (9)	50 (8)	5 (12)	23 (15)	1 (14)
C(15)	47 (8)	36 (8)	43 (7)	−11 (11)	−19 (12)	9 (12)
C(16)	39 (7)	29 (7)	34 (6)	1 (10)	− 6 (11)	4 (11)
C(17)	65 (10)	79 (12)	65 (9)	5 (16)	56 (16)	79 (18)
C(18)	109 (17)	128 (20)	111 (15)	8 (27)	112 (26)	86 (29)

boxylate oxygens (Table 4) the base of a square pyramid around the metal atom, which is displaced from the base and in the direction of the apex by 0·19 Å. A tetragonally distorted octahedron around the copper atom (Table 3) is completed by its centrosymmetrically related counterpart, the Cu–Cu$^{\mathrm{I}}$ distance being 2·617 (3) Å. The Cu–O(acetyl) and the average Cu–O(carboxylate) distances are 2·241 (8) and 1·963 (4) Å, respectively. The bond lengths and angles (Table 3) in the $\mathrm{Cu_2(C.CO_2)_4O_2}$ fragment are in very good agreement with those found in copper(II) *o*-bromobenzoate monohydrate, and they are in the range of values obtained in various copper(II) alkylcarboxylates, recently reviewed by Harrison, Rettig & Trotter (1972).

Of the two aspirinate groups in the asymmetric unit each is coordinated to two metal atoms in the same binuclear unit, but in addition, one is also bonded to a metal atom from a neighbouring binuclear unit. This difference in the mode of attachment to the metal atoms may account for the observed differences in the geometries of the two aspirinate residues (Tables 3 and 4). Thus the conformation of the bidentate aspirinate ligand is similar to that of aspirin itself (Wheatley, 1964); the carbonyl group is twisted by only 3·5° out of the benzene-ring plane, which makes an angle of 77·0° with the acetyl-group plane. The carbonyl and acetyl groups are bent away from each other, leading to angular distortions at the C(10) and C(11) atoms (Table 3) analogous to those observed in the molecule of aspirin and in the aspirinate residue of the acid salt KH(aspirinate)$_2$ (Manojlović & Speakman, 1967; Sequeira, Berkebile & Hamilton, 1967). In the tridentate aspirinate ligand, the acetyl group maintains the angle with the benzene ring plane at 73·4°. However, to bring the O(4) atom within the reach of the appropriate metal atom this acetyl group is bent in the direction of the carbonyl group, and consequently the angular distortions at the C(2) atom are a reversal of those at C(11). To minimize repulsion between the O(3) and O(1) atoms, which would have otherwise been unduly close to each other, the carbonyl group is twisted by 48·5° out of the benzene ring plane and the O(3)···O(1) separation is increased to 2·82 (1) Å.

Table 3. *Interatomic distances and angles in the* $\mathrm{Cu_2(C_9H_7O_4)_4}$ *unit*

The superscripts refer to the following transformations of atomic coordinates *x*,*y*,*z*:

I $1-x,-y,-z$ II $-1+x,y,z$

(*a*) Bond lengths (Å)

Cu-Cu$^{\mathrm{I}}$	2·617 (3)	O(3)—C(8)	1·38 (2)
		O(3)—C(2)	1·45 (2)
Cu-O(4$^{\mathrm{II}}$)	2·241 (8)	O(7)—C(17)	1·30 (2)
		O(7)—C(11)	1·38 (2)
Cu-O(1$^{\mathrm{I}}$)	1·964 (8)	C(8)—C(9)	1·53 (2)
Cu-O(2)	1·967 (8)	C(17)-C(18)	1·50 (3)
Cu-O(5)	1·966 (9)	Average	1·52 (2)
Cu-O(6$^{\mathrm{I}}$)	1·953 (8)		
Average	1·963 (4)	C(1)—C(2)	1·37 (2)
		C(2)—C(3)	1·36 (2)
O(1)-C(7)	1·27 (1)	C(3)—C(4)	1·42 (2)
O(2)-C(7)	1·25 (1)	C(4)—C(5)	1·39 (2)
O(5)-C(16)	1·25 (1)	C(5)—C(6)	1·39 (2)
O(6)-C(16)	1·27 (1)	C(6)—C(1)	1·40 (2)
Average	1·26 (1)	C(10)-C(11)	1·41 (2)
		C(11)-C(12)	1·39 (2)
C(1)—C(7)	1·51 (2)	C(12)-C(13)	1·37 (2)
C(10)-C(16)	1·48 (2)	C(13)-C(14)	1·39 (2)
Average	1·50 (2)	C(14)-C(15)	1·39 (2)
		C(15)-C(10)	1·44 (2)
O(4)-C(8)	1·18 (2)	Average	1·393 (6)
O(8)-C(17)	1·22 (2)		
Average	1·20 (2)		

(*b*) Non-bonding distances (Å) in the octahedron around the copper atom

O(1$^{\mathrm{I}}$)···O(5)	2·77 (1)	Cu$^{\mathrm{I}}$·····O(2)	3·145 (8)
O(5) ···O(2)	2·81 (1)	Cu$^{\mathrm{I}}$·····O(6$^{\mathrm{I}}$)	3·175 (8)
O(2) ···O(6$^{\mathrm{I}}$)	2·73 (1)	O(4$^{\mathrm{II}}$)···O(1$^{\mathrm{I}}$)	3·11 (1)
O(6$^{\mathrm{I}}$)···O(1$^{\mathrm{I}}$)	2·74 (1)	O(4$^{\mathrm{II}}$)···O(5)	3·08 (1)
Cu$^{\mathrm{I}}$ ····O(1$^{\mathrm{I}}$)	3·097 (7)	O(4$^{\mathrm{II}}$)···O(2)	3·13 (1)
Cu$^{\mathrm{I}}$ ····O(5)	3·048 (9)	O(4$^{\mathrm{II}}$)···O(6$^{\mathrm{I}}$)	3·15 (1)

Table 3 (*cont.*)

(*c*) Bond angles (°)

Cu$^{\mathrm{I}}$-Cu-O(4$^{\mathrm{II}}$)	176·0	C(7)—C(1)—C(6)	118 (1)
		C(16)-C(10)-C(15)	119 (1)
O(1$^{\mathrm{I}}$)-Cu-O(2)	169·0 (3)		
O(6$^{\mathrm{I}}$)-Cu-O(5)	168·7 (3)	C(7)—C(1)—C(2)	124 (1)
		C(16)-C(10)-C(11)	126 (1)
O(1$^{\mathrm{I}}$)-Cu-O(5)	89·5 (4)		
O(5) -Cu-O(2)	91·1 (3)	C(1)—C(2)—O(3)	114 (1)
O(2) -Cu-O(6$^{\mathrm{I}}$)	88·4 (3)	C(10)-C(11)-O(7)	121 (1)
O(6$^{\mathrm{I}}$)-Cu-O(1$^{\mathrm{I}}$)	88·9 (4)		
		C(3)—C(2)—O(3)	120 (1)
O(4$^{\mathrm{II}}$)-Cu-O(1$^{\mathrm{I}}$)	95·2 (3)	C(12)-C(11)-O(7)	115 (1)
O(4$^{\mathrm{II}}$)-Cu-O(5)	94·0 (3)		
O(4$^{\mathrm{II}}$)-Cu-O(2)	95·7 (3)	C(2)—O(3)—C(8)	119 (1)
O(4$^{\mathrm{II}}$)-Cu-O(6$^{\mathrm{I}}$)	97·2 (3)	C(11)-O(7)—C(17)	119 (1)
Cu$^{\mathrm{I}}$-Cu-O(1$^{\mathrm{I}}$)	83·8	C(9)—C(8)—O(3)	110 (1)
Cu$^{\mathrm{I}}$-Cu-O(5)	82·1	C(18)-C(17)-O(7)	115 (1)
Cu$^{\mathrm{I}}$-Cu-O(2)	85·4		
Cu$^{\mathrm{I}}$-Cu-O(6$^{\mathrm{I}}$)	86·7	C(9)—C(8)—O(4)	128 (1)
		C(18)-C(17)-O(8)	125 (2)
Cu-O(2)-C(7)	121·6 (7)		
Cu$^{\mathrm{I}}$-O(1)-C(7)	123·0 (7)	O(3)—C(8)—O(4)	122 (1)
Cu -O(5)-C(16)	125·9 (8)	O(7)—C(17)-O(8)	120 (1)
Cu$^{\mathrm{I}}$-O(6)-C(16)	120·7 (7)		
		C(1)—C(2)—C(3)	125 (1)
O(2)-C(7)—O(1)	126 (1)	C(2)—C(3)—C(4)	117 (1)
O(5)-C(16)-O(6)	125 (1)	C(3)—C(4)—C(5)	119 (1)
		O(1)—C(7)—C(1)	116 (1)
		O(2)—C(7)—C(1)	118 (1)
		O(5)—C(16)-C(10)	118 (1)
		O(6)—C(16)-C(10)	118 (1)
		C(4)—C(5)—C(6)	122 (1)
		C(5)—C(6)—C(1)	118 (1)
		C(6)—C(1)—C(2)	118 (1)
		C(15)-C(10)-C(11)	115 (1)
		C(10)-C(11)-C(12)	123 (1)
		C(11)-C(12)-C(13)	118 (1)
		C(12)-C(13)-C(14)	123 (1)
		C(13)-C(14)-C(15)	118 (1)
		C(14)-C(15)-C(10)	122 (1)

The acetyl groups of both aspirinate ligands show structural anomalies analogous to those observed in aspirin and in the KH(aspirinate)$_2$: the angular distortions around the central atoms C(8) and C(17) are

Table 4. *Mean planes through various sets of atoms*

(*a*) Parameters of the plane-equations in the form $lX+mY+nZ=p$. X, Y and Z are orthogonal coordinates in Å referred to a^*, b and c axes.

Plane	*l*	*m*	*n*	*p*
A	0·7121	−0·3160	−0·6269	2·3630
B	0·4953	−0·8194	−0·2885	2·0165
C	−0·7431	−0·3050	−0·5956	−2·3164
D	−0·0065	0·9323	−0·3616	0·4078
E	−0·7050	−0·3461	−0·6190	−2·2618
F	−0·6812	−0·7252	−0·0996	−7·1218
G	0·1311	0·5516	−0·8237	6·2072

(*b*) Displacements (Å) of atoms from the planes. Atoms not included in derivation of the planes are italicized. The significance of Roman numerals is as shown in Table 3.

A		*B*		*C*	
O(1^{I})	−0·003	C(1)	0·006	C(10)	−0·012
O(5)	0·002	C(2)	0·005	C(11)	0·022
O(2)	−0·002	C(3)	−0·010	C(12)	−0·017
O(6^{I})	0·003	C(4)	0·005	C(13)	0·003
Cu	−0·190	C(5)	0·005	C(14)	0·006
Cu$^{\text{I}}$	2·425	C(6)	−0·010	C(15)	−0·002
O(4^{II})	−2·430				

D		*E*		*F*	
O(1)	−0·001	O(5)	−0·002	O(3)	−0·002
O(2)	−0·001	O(6)	−0·002	O(4)	−0·002
C(7)	0·004	C(16)	0·006	C(8)	0·005
C(1)	−0·001	C(10)	−0·002	C(9)	−0·002

G	
O(7)	−0·007
O(8)	−0·008
C(17)	0·021
C(18)	−0·006

(*c*) Dihedral angles (°) between selected planes: *B,D* 48·5; *C,E* 3·5; *B,F* 73·4; *C,G* 77·0; *D,F* 50·5; *E,G* 76·9.

large, and each of the ester oxygen atoms, O(3) and O(7), makes a longer bond with the sp^2-carbon atom of the benzene ring than with the sp^2-carbon atom of the acetyl group (Table 3). Moreover, each of the two O(ester)–C(sp^2) bonds in the tridentate aspirinate ligand is longer than the corresponding one in the bidentate ligand. This might be associated with different functions of the two acetyl groups. That in the tridentate aspirinate ligand may act in a manner similar to that of the donor molecule L in $Cu_2(RCO_2)_4L_2$ complexes, where L is considered to reduce further the positive charge on the copper ion and thus facilitate formation of the binuclear structure (Lewis, Mabbs, Royston & Smail, 1969).

It is now obvious that more structural information is needed, especially for arylcarboxylates, before the relationship between the structural features of the parent carboxylate ions and the magnetic properties of *syn–syn* bridged copper(II) carboxylates can be fully understood.

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