

## Structures and Magnetic Properties of Dimeric Copper(II) Benzoylformates

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## Abstract

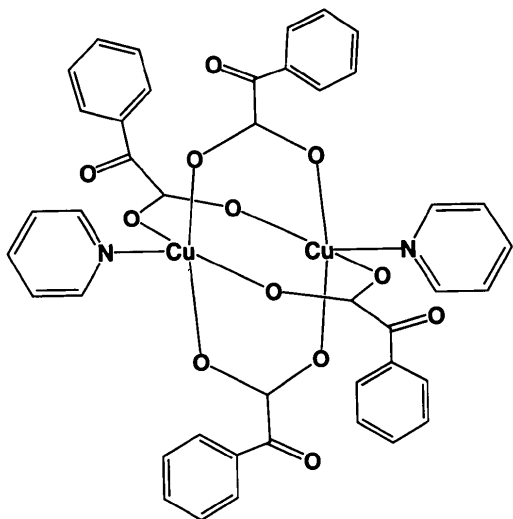
Structures of six dimeric copper(II) benzoylformates (I)–(VI) have been determined by single crystal X-ray diffraction and the magnitudes of the spin-exchange interaction ( $H = -2JS_1S_2$ ) have been determined based on the magnetic susceptibility measurement. (I): Tetrakis( $\mu$ -benzoylformato-*O,O'*)bis(pyridine)dicopper(II),  $[\text{Cu}(\text{C}_8\text{H}_5\text{O}_3)_2\text{C}_5\text{H}_5\text{N}]_2$ ,  $-2J = 648 \text{ cm}^{-1}$ . (II): Tetrakis( $\mu$ -benzoylformato-*O,O'*)bis(2-methylpyridine)dicopper(II),  $[\text{Cu}(\text{C}_8\text{H}_5\text{O}_3)_2\text{C}_6\text{H}_7\text{N}]_2$ ,  $-2J = 656 \text{ cm}^{-1}$ . (III): Tetrakis( $\mu$ -benzoylformato-*O,O'*)bis(3-methylpyridine)dicopper(II) monobenzene solvate,  $[\text{Cu}(\text{C}_8\text{H}_5\text{O}_3)_2\text{C}_6\text{H}_7\text{N}]_2 \cdot \text{C}_6\text{H}_6$ ,  $-2J = 649 \text{ cm}^{-1}$ . (IV): Tetrakis( $\mu$ -benzoylformato-*O,O'*)bis(4-methylpyridine)dicopper(II),  $[\text{Cu}(\text{C}_8\text{H}_5\text{O}_3)_2\text{C}_6\text{H}_7\text{N}]_2$ ,  $-2J = 625 \text{ cm}^{-1}$ . (V): Bis(2,3-dimethylpyridinium) tetrakis( $\mu$ -benzoylformato-*O,O'*)bis(chloride)dicopper(II) dibenzene solvate,  $2\text{C}_7\text{H}_{10}\text{N} \cdot [\text{Cu}(\text{C}_8\text{H}_5\text{O}_3)_2\text{Cl}]_2 \cdot 2\text{C}_6\text{H}_6$ ,  $-2J = 618 \text{ cm}^{-1}$ . (VI): Tetrakis(benzoylformato-*O,O'*)bis(caffeine)dicopper(II) dibenzene solvate,  $[\text{Cu}(\text{C}_8\text{H}_5\text{O}_3)_2\text{C}_8\text{H}_{10}\text{N}_4\text{O}_2]_2 \cdot 2\text{C}_6\text{H}_6$ ,  $-2J = 651 \text{ cm}^{-1}$  (caffeine = 3,7-dihydro-1,3,7-trimethyl-1*H*-purine-2,6-dione). In the binuclear cage structure the coordination geometry around the  $\text{Cu}^{\text{II}}$  atoms is typical square pyramidal with  $\text{Cu} \cdots \text{Cu}$  distances 2.725(1)–2.843(1) Å. An *ab initio* molecular orbital calculation for the benzoylformate ion indicates that the unusually strong antiferromagnetic interaction in dimeric copper(II) benzoylformates is attributed to the electronic effect of the  $\alpha$ -keto group in the bridging carboxylate moiety. This is in accordance with a positive linear relationship between  $-2J$  of the copper(II) carboxylates and the diagonal part of the  $2p_x$  orbital population of the carboxylate C atom in the symmetrical HOMO, highest occupied molecular orbital ( $x$  is parallel to the C—R bond axis in the  $\text{RCOO}^-$  ion).

## 1. Introduction

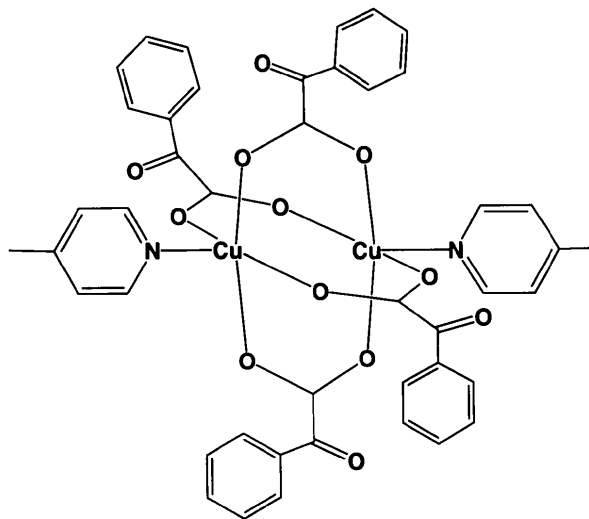
Dimeric copper(II) carboxylates generally take a cage structure and show the antiferromagnetic spin-exchange interaction. The magnitude of the exchange interaction, as measured by  $-2J$  (the energy difference between the triplet and singlet states) is mainly dependent on the atom,  $X$ , which is directly bonded to the bridging

carboxylate group. For acetates ( $X = \text{C}$ )  $-2J$  is ca  $330 \text{ cm}^{-1}$ . For formates ( $X = \text{H}$ )  $-2J$  is ca  $500 \text{ cm}^{-1}$ . Silanecarboxylates ( $X = \text{Si}$ ) show strong antiferromagnetic interaction with  $-2J$  around  $1000 \text{ cm}^{-1}$  (Steward, McAfee, Chang, Piskor, Schreiber, Jury, Taylor, Pletcher & Chen, 1986; Uekusa, Ohba, Saito, Kato, Steward, Tokii & Muto, 1990). The very strong antiferromagnetic interaction of silanecarboxylates is due to the electron-donating property of Si, which is reflected in the symmetrical HOMO of the bridge. Based on an *ab initio* molecular orbital calculation for the  $\text{Me}_3\text{SiCOO}^-$  ion, the diagonal electron population in the  $2p_x$  orbital of the carboxylate C atom in the symmetrical HOMO was estimated to be 0.044 e, which is apparently greater than those of  $\text{CH}_3\text{COO}^-$  (0.004 e) and  $\text{HCOO}^-$  (0.010 e) ions (Yamanaka, Uekusa, Ohba, Saito, Iwata, Kato, Tokii, Muto & Steward, 1991). Among the carbon carboxylate adducts ( $X = \text{C}$ ) studied so far, the largest  $-2J$  value was  $397 \text{ cm}^{-1}$  for  $[\text{Cu}(\text{Me}_3\text{CCOO})_2(\text{acridine})]_2$  (Kato & Muto, 1988). However, exceptional magnetic data are reported in this paper,  $-2J$  being  $\sim 650 \text{ cm}^{-1}$  for benzoylformates.

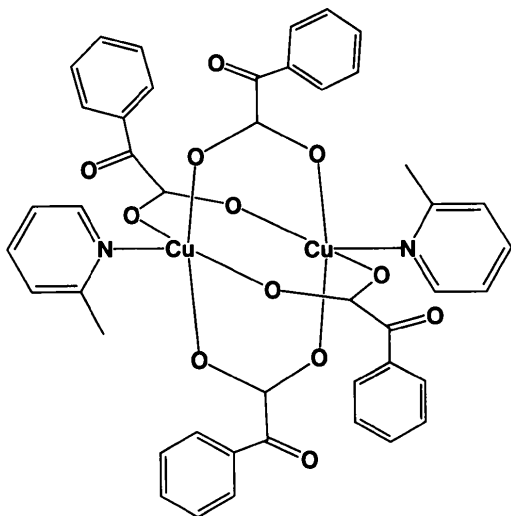
A magneto-structural correlation was revealed for dimeric copper(II) trichloroacetates: the  $-2J$  value decreases along with the deformation of the cage structure and with the transformation of the Cu coordination geometry from square pyramidal toward trigonal bipyramidal, TBP (Uekusa, Ohba, Tokii, Muto, Kato, Husebye, Steward, Chang, Rose, Pletcher & Suzuki, 1992). The TBP structure has also been found in certain adducts of dimeric copper(II) triphenylacetates (Steward, Kato, Chang, Sax, Chang, Jury, Muto, Tokii, Taura, Pletcher & Yoo, 1991; Yamanaka, Ohba, Tokii, Jury, Steward & Kato, 1993; Fujita, Ohba, Nagamatsu & Tokii, 1993). One of the authors (SO) wondered if the TBP structure may be observed in copper(II) dichlorophenylacetates, which have both the electronic effect of Cl and the steric effect of Ph. Unexpectedly, a reaction of  $\text{PhCCl}_2\text{COOH}$  and 2,3-lutidine with basic copper carbonate afforded the chloride-2,3-lutidinium adduct of copper benzoylformate (V). Since the observed  $-2J$  value of (V) is abnormally large compared with copper acetates, the pyridine (I), picoline (II–IV) and caffeine (VI) adducts were prepared using



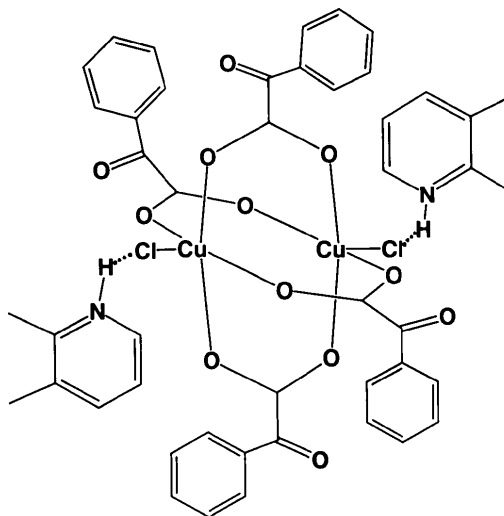
(I)



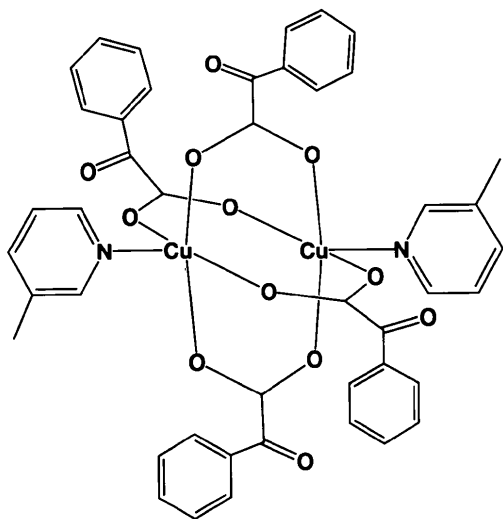
(IV)



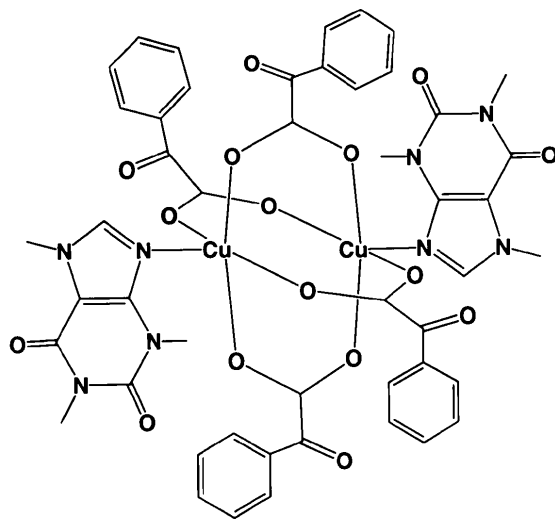
(II)



(V)



(III)



(VI)

benzoylformic acid from the beginning to confirm that the strong antiferromagnetic interaction is due to the benzoylformate bridge.

## 2. Experimental

### 2.1. Preparation of $[Cu(C_8H_5O_3)_2L]_2$

For pyridine and picoline adducts (I)–(IV): PhCO-COOH (120 mg, 0.8 mmol) and  $CuCO_3 \cdot Cu(OH)_2 \cdot H_2O$  (48 mg, 0.2 mmol) were suspended in aqueous ethanol (1:1; 20 ml); the solution was warmed for 30 min and then evaporated to dryness. The pale green residue was dissolved in ethanol (20 ml) to yield a green solution. After filtration two drops of the ligand *L* were added to the filtrate with stirring and the resulting blue solution was evaporated to dryness. The product was recrystallized from a mixture of benzene and ethanol (5:1). For preparation of the caffeine adduct, methanol was used instead of ethanol and caffeine (0.8 mmol) was solved in dichloromethane before the addition. Preparation of (V): Benzoylformic acid ethyl ester was reacted with  $PCl_5$  to afford dichlorophenylacetic acid ethylester (yield 65%), which was converted to the acid using KOH and then HCl. Fresh  $PhCCl_2COOH$  (0.588 mmol) and  $CuCO_3 \cdot Cu(OH)_2 \cdot H_2O$  (0.147 mmol) were suspended in aqueous methanol (1:1) and the solution was warmed for 30 min. The solution was evaporated to dryness and the residue was dissolved in methanol and filtered. To the pale green filtrate was added 2,3-lutidine solution (benzene:methanol 6:1) and the solution was evaporated to dryness. The product was recrystallized from a mixture of benzene and methanol.

### 2.2. Structure analysis

Crystal data, experimental condition and refinement information are listed in Table 1. The positional and anisotropic thermal parameters of non-H atoms were refined by full-matrix least-squares. H atom positions were calculated theoretically and only their isotropic thermal parameters were refined. Data collection, cell refinement: *AFC/MS* (Rigaku Corporation, 1993). Data reduction: local programs. Program used to solve and refine structure: *CRYSTAN-GM* (Edwards, Gilmore, Mackay & Stewart, 1995). Molecular graphics: *CRYSTAN-GM*. Software used to prepare material for publication: *CRYSTAN-GM*. Selected bond lengths and bond angles are listed in Table 2.\*

### 2.3. Magnetic measurement

Magnetic susceptibilities over the temperature range 80–300 K were determined by Faraday's method. Fresh

powder samples were prepared for this purpose. For (II) the paramagnetic impurities were relatively large, and the sample was prepared three times to obtain reasonable magnetic data. The crystal benzene in (III), (V) and (VI) was assumed to be evaporated under reduced pressure. The cryomagnetic data were fitted to the Bleaney–Bowers equation allowing for the presence of paramagnetic impurities (Ginsberg, 1971)

$$\chi_A = (Ng_i^2\beta^2/3kT)[1 + \exp(-2J/kT)/3]^{-1}(1 - P) + (Ng_i^2\beta^2P/4kT) + N\alpha,$$

where *A* is the paramagnetic susceptibility per metal atom after the correction for diamagnetism, *P* the mole fraction of the monomeric copper(II) impurities,  $g_i$  the average *g* factor of the impurity which was fixed at 2.2 and *Nα* the temperature-independent paramagnetism, which is assumed to be  $60 \times 10^{-6}$  cgs emu ( $1 \text{ cgs emu} = 4\pi \times 10^{-6} \text{ m}^3$ ) for copper(II) compounds. The best-fit parameters of  $-2J$ , *g* and *P* were obtained by least-squares (Table 3). The quantity-of-fit was estimated by means of a discrepancy index,  $\sigma_{\text{dis}} = [\sum(\chi_{\text{obs}} - \chi_{\text{calc}})^2 / \sum\chi_{\text{obs}}^2]^{1/2}$ . This value was in the range 0.016–0.022.

## 3. Discussion

### 3.1. Molecular structure

The dimeric copper benzoylformates have the usual cage structure with the Cu atoms in square-pyramidal coordination geometry (Fig. 1). Compared with the pyridine adduct with the corresponding formate, acetate and benzoate complexes, the Cu··Cu distance of the benzoylformate is longer by  $\sim 0.09 \text{ \AA}$ , which is the result of a larger deviation of the Cu atom toward the axial ligand from the  $O_4$  plane (Table 4). However, a vast compilation of magneto-structural data of dimeric copper(II) carboxylates (Kato & Muto, 1988) indicates that this and other geometrical parameters cannot be related to the abnormally large  $-2J$  value of the benzoylformate. One may wonder about the relation between the  $-2J$  values and the O—C—O bond angles in Table 4, but there is no relation. The average O—C—O angles in  $[Cu(Ph_2MeXCOO)_2\text{quinoline}]_2$  are  $125.0(4)^\circ$  for *X* = Si and  $125.6(2)^\circ$  for *X* = C, although the  $-2J$  values are 1036 and  $339 \text{ cm}^{-1}$ , respectively (Uekusa *et al.*, 1990). In (V) the axial ligand is the chloride ion, which is connected with the protonated 2,3-lutidine by a hydrogen bond. The Cl(1)··N(1) distance of  $3.078(5) \text{ \AA}$  is almost the same as that in the crystal of pyridinium chloride,  $3.010(5) \text{ \AA}$  (Mootz & Hocken, 1989). The 2,3-lutidinium ion is stacked with one of the phenyl groups of the bridging benzoylformate ions. The longest Cu··Cu distance of  $2.843(1) \text{ \AA}$  in (V) among (I)–(VI) is due to the largest shift of the Cu atom from the  $O_4$  plane,  $0.297(2) \text{ \AA}$ .

\* Lists of atomic coordinates, anisotropic displacement parameters, complete geometry and structure factors have been deposited with the IUCr (Reference: OA0006). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.



Table 2. Selected geometric parameters ( $\text{\AA}$ ,  $^\circ$ )

(I)			
Cu1—Cu1 <sup>i</sup>	2.735 (1)	Cu1—N1	2.131 (3)
Cu1—O1	1.981 (3)	O1—C1	1.249 (5)
Cu1—O2 <sup>i</sup>	1.953 (3)	O2—C1	1.256 (5)
Cu1—O3	1.960 (3)	O3—C9	1.217 (5)
Cu1—O4 <sup>i</sup>	1.969 (3)	O4—C9	1.275 (5)
Cu1 <sup>i</sup> —Cu1—N1	173.4 (1)	Cu1 <sup>i</sup> —O4—C9	122.4 (3)
O1—Cu1—O2 <sup>i</sup>	165.7 (2)	Cu1—N1—C17	124.3 (3)
O3—Cu1—O4 <sup>i</sup>	165.3 (2)	Cu1—N1—C21	119.8 (3)
Cu1—O1—C1	126.6 (3)	O1—C1—O2	127.2 (4)
Cu1 <sup>i</sup> —O2—C1	120.4 (3)	O3—C9—O4	127.6 (4)
Cu1—O3—C9	124.4 (3)		
(II)			
Cu1—Cu1 <sup>ii</sup>	2.757 (1)	Cu1—N1	2.162 (3)
Cu1—O1	1.972 (2)	O1—C1	1.243 (4)
Cu1—O2 <sup>ii</sup>	1.979 (2)	O2—C1	1.239 (4)
Cu1—O3	1.968 (3)	O3—C9	1.239 (4)
Cu1—O4 <sup>ii</sup>	1.976 (3)	O4—C9	1.257 (4)
Cu1 <sup>ii</sup> —Cu1—N1	174.4 (1)	Cu1 <sup>ii</sup> —O4—C9	123.0 (3)
O1—Cu1—O2 <sup>ii</sup>	164.7 (1)	Cu1—N1—C17	129.3 (3)
O3—Cu1—O4 <sup>ii</sup>	164.9 (1)	Cu1—N1—C22	113.0 (2)
Cu1—O1—C1	123.5 (2)	O1—C1—O2	128.0 (3)
Cu1 <sup>ii</sup> —O2—C1	123.8 (2)	O3—C9—O4	127.6 (3)
Cu1—O3—C9	124.5 (2)		
(III)			
Cu1—Cu2	2.725 (1)	Cu2—N2	2.121 (4)
Cu1—O1	1.979 (4)	O1—C1	1.260 (6)
Cu1—O3	1.987 (4)	O2—C1	1.233 (6)
Cu1—O5	1.965 (4)	O3—C9	1.247 (6)
Cu1—O7	1.992 (4)	O4—C9	1.254 (6)
Cu1—N1	2.123 (4)	O5—C17	1.243 (6)
Cu2—O2	1.974 (3)	O6—C17	1.252 (6)
Cu2—O4	1.975 (4)	O7—C25	1.254 (6)
Cu2—O6	1.978 (4)	O8—C25	1.234 (6)
Cu2—O8	1.990 (4)		
Cu2—Cu1—N1	178.6 (1)	Cu1—N1—C38	119.8 (4)
O1—Cu1—O5	167.1 (2)	Cu2—N2—C39	120.5 (3)
O3—Cu1—O7	164.9 (2)	Cu2—N2—C44	122.2 (3)
Cu1—Cu2—N2	178.2 (2)	O1—C1—O2	127.7 (5)
O2—Cu2—O6	164.3 (2)	O3—C9—O4	127.0 (5)
O4—Cu2—O8	166.8 (2)	O5—C17—O6	127.3 (5)
Cu1—N1—C33	122.3 (4)	O7—C25—O8	128.3 (5)
(IV)			
Cu1—Cu1 <sup>iii</sup>	2.729 (2)	Cu1—N1	2.127 (7)
Cu1—O1	1.964 (6)	O1—C1	1.246 (13)
Cu1—O2 <sup>iii</sup>	1.973 (6)	O2—C1	1.256 (13)
Cu1—O3 <sup>iii</sup>	1.986 (7)	O3—C9	1.255 (12)
Cu1—O4	1.981 (6)	O4—C9	1.240 (12)
Cu1 <sup>iii</sup> —Cu1—N1	177.1 (3)	Cu1—O4—C9	125.0 (6)
O1—Cu1—O2 <sup>iii</sup>	165.6 (3)	Cu1—N1—C17	121.0 (7)
O3 <sup>iii</sup> —Cu1—O4	165.9 (3)	Cu1—N1—C22	123.2 (7)
Cu1—O1—C1	122.5 (7)	O1—C1—O2	127.1 (9)
Cu1 <sup>iii</sup> —O2—C1	124.6 (6)	O3—C9—O4	128.2 (9)
Cu1 <sup>iii</sup> —O3—C9	120.8 (6)		
(V)			
Cu1—Cu1 <sup>i</sup>	2.843 (1)	Cu1—O4 <sup>i</sup>	2.000 (3)
C11—N1	3.078 (5)	O1—C1	1.246 (6)
Cu1—C11	2.395 (2)	O2—C1	1.241 (6)
Cu1—O1	1.988 (3)	O3—C9	1.249 (6)
Cu1—O2 <sup>i</sup>	1.977 (3)	O4—C9	1.247 (6)
Cu1—O3	1.975 (4)		
Cu1 <sup>i</sup> —Cu1—C11	173.4 (1)	Cu1—O3—C9	121.5 (3)
O1—Cu1—O2 <sup>i</sup>	162.5 (2)	Cu1 <sup>i</sup> —O4—C9	126.6 (4)
O3—Cu1—O4 <sup>i</sup>	163.0 (2)	O1—C1—O2	128.6 (5)
Cu1—O1—C1	124.2 (3)	O3—C9—O4	129.0 (5)
Cu1 <sup>i</sup> —O2—C1	124.6 (3)		
(VI)			
Cu1—Cu1 <sup>v</sup>	2.745 (1)	Cu1—N1	2.161 (5)
Cu1—O1	1.971 (4)	O1—C1	1.247 (7)

Table 2 (cont.)

Cu1—O2 <sup>v</sup>	1.974 (4)	O2—C1	1.243 (7)
Cu1—O3	1.980 (4)	O3—C9	1.240 (7)
Cu1—O4 <sup>v</sup>	1.977 (4)	O4—C9	1.231 (7)
Cu1 <sup>v</sup> —Cu1—N1	179.0 (2)	Cu1 <sup>v</sup> —O4—C9	119.8 (4)
O1—Cu1—O2 <sup>v</sup>	164.8 (2)	Cu1—N1—C17	114.3 (4)
O3—Cu1—O4 <sup>v</sup>	164.9 (2)	Cu1—N1—C24	143.5 (4)
Cu1—O1—C1	126.1 (4)	O1—C1—O2	127.6 (6)
Cu1 <sup>v</sup> —O2—C1	121.0 (4)	O3—C9—O4	128.8 (6)
Cu1—O3—C9	126.4 (4)		

Symmetry codes: (i)  $2-x, -y, 2-z$ ; (ii)  $1-x, -y, 2-z$ ; (iii)  $-x, 2-y, 2-z$ ; (iv)  $2-x, -y, 1-z$ ; (v)  $1-x, 1-y, 1-z$ .

Table 3. Magnetic data for dimeric copper(II) benzoylformates  $[\text{Cu}(\text{PhCOCOO})_2\text{L}]_2$ 

Compound	(I)	(II)	(III)	(IV)	(V)	(VI)
$L$	py	2-pic	3-pic	4-pic	$\text{Cl}^-$	Caffeine
$-2J$ ( $\text{cm}^{-1}$ )	648	656	649	625	618	651
$g$	2.22	2.20	2.22	2.24	2.20	2.25
$p$ (%)	1.2	3.5	1.1	2.2	1.3	0.6

Table 4. Comparison of the dimensions ( $\text{\AA}$ ,  $^\circ$ ) in  $[\text{Cu}(\text{RCOO})_2\text{pyridine}]_2$  and their  $-2J$  values

$R$	$\text{H}^{(a,b)}$	$\text{CH}_3^{(b)}$	$\text{Ph}^{(c,d)}$	$\text{PhCO}^{(e)}$
$\text{Cu} \cdots \text{Cu}$	2.641 (1)	2.641 (1)	2.658 (1)	2.735 (1)
$\text{Cu}-\text{N}$	2.145 (2)	2.191 (2)	2.170 (3)	2.131 (3)
$(\text{Cu}-\text{O})_{\text{min}}$	1.978 (2)	1.960 (2)	1.960 (2)	1.953 (3)
$(\text{Cu}-\text{O})_{\text{max}}$	1.986 (2)	1.980 (3)	1.979 (2)	1.981 (3)
Shift of $\text{Cu}^*$	0.207 (2)	0.208 (2)	0.217 (2)	0.248 (2)
$(\text{O}-\text{C}-\text{O})_{\text{av}}$	127.0 (3)	125.2 (3)	125.4 (5)	127.4 (4)
$-2J$ ( $\text{cm}^{-1}$ )	501	333	328	648
$pK_a \uparrow$	3.8	4.8	4.2	4.2

(a) Bernard, Borel, Busnot & Leclaire (1979). (b) Uekusa, Ohba, Saito, Kato, Tokii & Muto (1989). (c) Speier & Fulop (1989). (d) Kawata, Uekusa, Ohba, Furukawa, Tokii, Muto & Kato (1992). (e) Present work. \* The deviation of the Cu atom from the  $\text{O}_4$  plane.  $\uparrow$  The  $pK_a$  values of  $\text{RCOOH}$  in aqueous solution taken from Kortün, Vogel & Andrussov (1961).

In the benzoylformate bridge the phenyl group is coplanar with the carbonyl moiety and is almost perpendicular to the  $\text{COO}$  plane. As a whole, the arrangement of four benzoylformate ligands has a chemical fourfold rotational symmetry around the  $\text{Cu} \cdots \text{Cu}$  axis to minimize the steric repulsion between the phenyl groups. The twisted conformation of the benzoylformate ion avoids the short contact between one of the H atoms of Ph and carbonyl O atoms, for example, in (I) between H(16) bonds to C(16) and O(3) and O(4) atoms. A similar twisted conformation of  $\text{PhCOCOO}^-$  ligands has been observed in (benzoylformato- $O$ )-tris((2-pyridyl)methyl)amine- $N,N',N'',N'''$ )-methanolatoiron(II) perchlorate (Chiou & Que Jr, 1992). However, a planar conformation is seen in (benzoylformato- $O,O'$ )-tris(((6-methyl-2-pyridyl)methyl)amine)iron(II) perchlorate (Chiou & Que Jr, 1995), where the  $\alpha$ -keto oxygen and one of the carboxyl O atoms are coordinated to the Fe atom and the phenyl group is almost coplanar with the  $\alpha$ -keto acid moiety. The short intramolecular  $\text{O} \cdots \text{H}$  contact ( $\sim 2.41 \text{\AA}$ ) is reduced

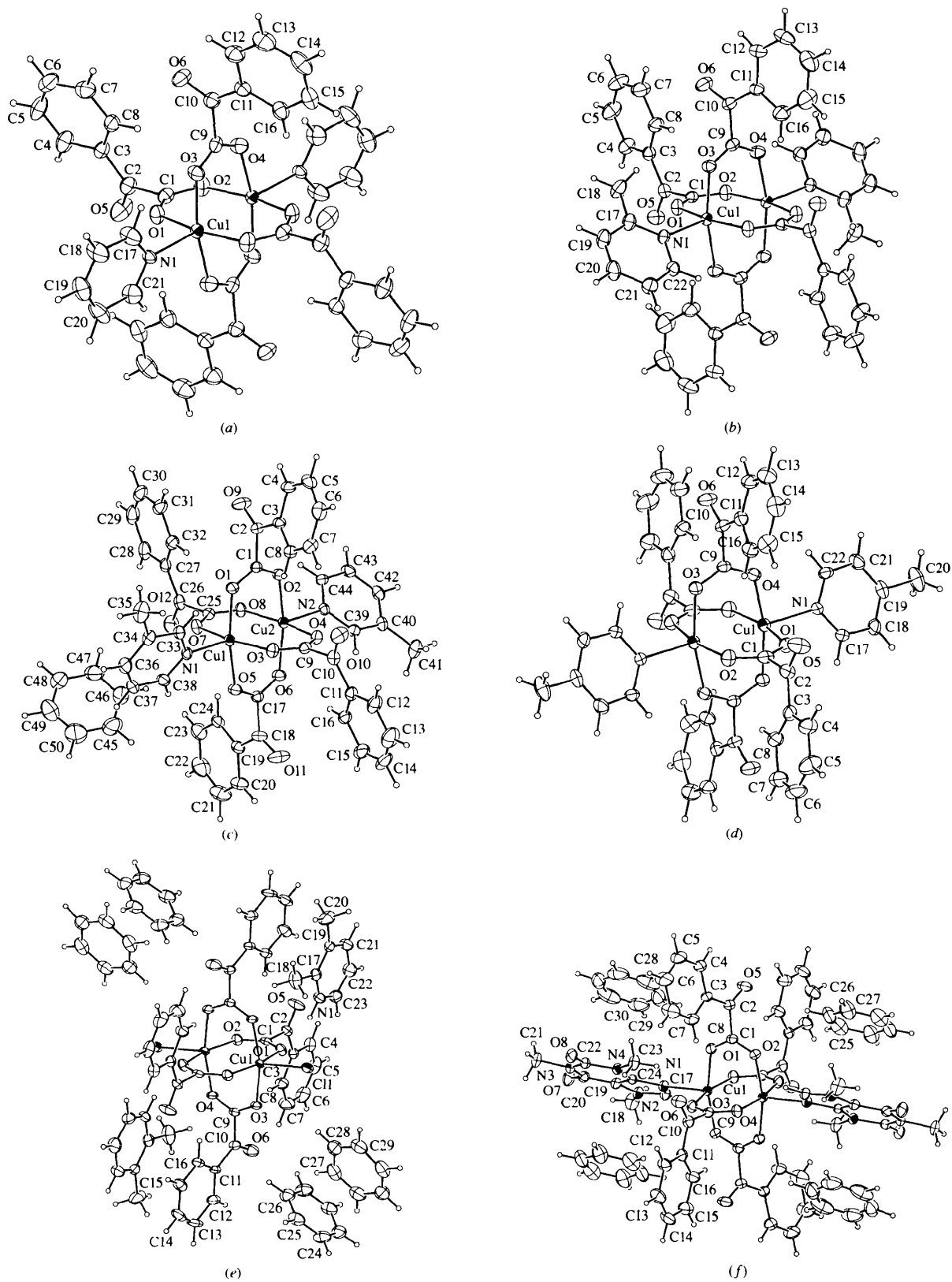


Fig. 1. The molecular structures of (I)–(VI) with thermal ellipsoids at the 20% probability level. H atoms are represented by circles of radius 0.1 Å.

by a widening of the C—C—C bond angle at the junction of Ph and carboxyl moieties. Intermolecular Ph··Ph stacking in this crystal seems to compensate in part the intramolecular strain energy. A search of the Cambridge Structural Database indicates that the benzyloxy moiety in organic compounds generally takes the twisted conformation, except for (3-chloro-4-hydroxyphenyl)glyoxylic acid methyl ester (McGahren, Martin, Morton, Hargreaves, Leese, Lovell, Ellestad, O'Brien & Holker, 1980), where the strained planar conformation with  $O\cdots H \simeq 2.27 \text{ \AA}$  is stabilized by the intermolecular  $\pi$ - $\pi$  stacking. The preparation of crystals of copper(II) complexes with other  $\alpha$ -keto acids,  $RCO_2COH$  ( $R = \text{Me, Et and benzyl}$ ), failed. The products were insoluble, suggesting the polymeric compounds. The  $\alpha$ -keto acid moiety in these ligands seems to prefer the planar conformation, where there is no strong interatomic non-bonded repulsion. Therefore, the twisted conformation of the benzoylformate ligand is essential to form a discrete binuclear copper complex.

### 3.2. Magneto-structural correlation

In the dimeric copper(II) carboxylates the unpaired electron of Cu occupies the  $d_{x^2-y^2}$  orbital and the symmetrical combination of the metal  $d_{x^2-y^2}$  orbitals

is interacted through the symmetrical HOMO's of the bridging carboxylate ions. Similarly, the asymmetrical combination of the copper  $d_{x^2-y^2}$  orbitals interacts through the asymmetric HOMO's of the bridging ligands. Hay, Thibeault & Hoffmann (1975) derived basic equations in their *ab initio* perturbational approach and indicated that the greater the square of the energy gap between the symmetrical and asymmetrical MO's of the binuclear complex, the greater the antiferromagnetic contribution. On the other hand, Kahn (1993) proposed the concept of natural magnetic orbitals, which are localized around each metal center, and showed that the greater the overlap between the magnetic orbitals, the greater the antiferromagnetic interaction.

In a previous study it is revealed that the  $-2J$  value of binuclear copper carboxylate correlates with the diagonal part of the  $2p_x$  electron population of the central C atom of the bridging carboxylate ion in the symmetrical HOMO (Yamanaka *et al.*, 1991). The local  $x$  axis in  $RCO_2^-$  is parallel to the  $R$ -C bond axis. The abnormally strong antiferromagnetic interaction in silanecarboxylates could be explained based on the electronic specificity in the bridge. Therefore, an *ab initio* molecular orbital calculation for  $\text{PhCOCOO}^-$  with the averaged and idealized geometry in the dimeric copper complexes has been carried out using an STO-6G basis set. Although the gross electron population of the COO

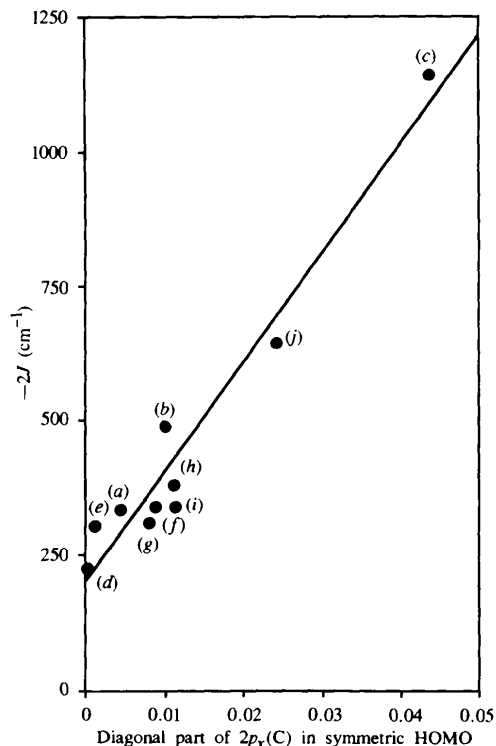


Fig. 2. The average  $-2J$  value of  $[\text{Cu}(\text{RCOO})_2\text{L}]_2$  (see Table 6 of Yamanaka *et al.*, 1991) versus the diagonal part of the  $2p_x(C)$  electron population in the symmetrical HOMO. The plots are for (a)  $R = \text{CH}_3$ , (b) H, (c)  $\text{SiMe}_3$ , (d)  $\text{CCl}_3$ , (e)  $\text{CHCl}_2$ , (f)  $\text{CH}_2\text{Cl}$ , (g)  $\text{CF}_3$ , (h)  $\text{CMe}_3$ , (i)  $\text{C}_2\text{H}_5$  and (j)  $\text{PhCO}$ .

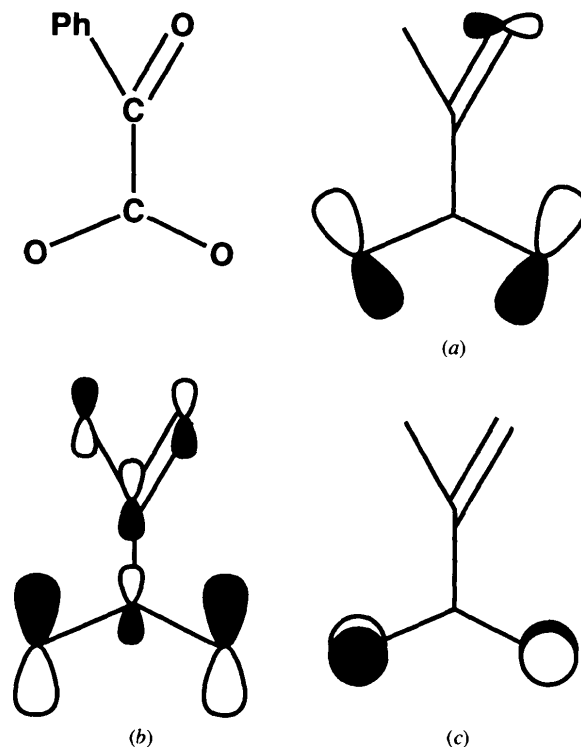


Fig. 3. The schematic drawing of three HOMO's of the benzoylformate ion: (a) asymmetrical HOMO, (b) symmetrical HOMO and (c)  $\pi$ -HOMO.

moiety is similar to those of the acetate and benzoate ions, the key factor is in the symmetrical HOMO. A plot of the average  $-2J$  value of several copper carboxylates versus the diagonal part of  $2p_x(\text{C})$  in the symmetrical HOMO is shown in Fig. 2. The  $-2J$  value and the electron population of the benzoylformate are  $644 \text{ cm}^{-1}$  and  $0.0242 e$ , the plot of which is in accordance with the linear correlation. In the symmetrical HOMO (orbital number 38) the  $2p_x$  atomic orbitals of the  $\alpha$ -keto group contribute considerably (Fig. 3) and alter the  $2p_x(\text{C})$  population in the bridge. Therefore, it can be concluded that the strong antiferromagnetic interaction in the benzoylformate is due to an electronic effect of the  $\alpha$ -keto group to the symmetrical HOMO of the bridging carboxylate ion. The  $\alpha$ -keto carboxylates have similarities with silanecarboxylates. The Si atom and the C=O group, which are directly bonded to the COO bridge, are both  $\sigma$ -donors and  $\pi$ -acceptors (Eaborn, 1960). The Si atom can form a  $\pi$  bond via the  $3d$  orbitals and the carbonyl C via the  $\pi^*$  levels of the C=O moiety.

In order to show the negligible influence of the ether O atom in the substitute group  $R$  in the bridging  $\text{RCOO}^-$  ion to the magnetic property, the aqua adduct of the dimeric copper(II) 2-furancarboxylate was prepared. The structure was determined to confirm that it is essentially the same as that reported by Charbonnier, Petit-Ramel, Faure & Loiseleur (1984). The  $-2J$  value was determined to be  $344 \text{ cm}^{-1}$ , which corresponds well with the diagonal electron population of  $2p_x(\text{C})$  in the symmetrical HOMO,  $0.0034 e$ . The preparation of the pyridine and picoline adducts of 2-furancarboxylate was not successful, suggesting the unusual stability of the aqua adduct.

#### 4. Conclusions

Dimeric copper(II) benzoylformates were prepared by a lucky accident and their strong antiferromagnetic properties ( $-2J \simeq 650 \text{ cm}^{-1}$ ) are attributed to the electronic effect of the  $\alpha$ -keto group in the symmetrical HOMO of the bridging carboxylate ions. The linear correlation between the  $-2J$  value of  $[\text{Cu}(\text{RCOO})_2\text{L}]_2$  and the diagonal part of the  $2p_x(\text{C})$  electron population in the symmetrical HOMO of  $\text{RCOO}^-$  ligands proposed in a previous paper (Yamanaka *et al.*, 1991) was confirmed without ambiguity. The linear relationship suggests the mechanism of spin super-exchange interaction through the  $\sigma$ -path. The natural magnetic orbitals mainly consist of copper  $d_{x^2-y^2}$  and oxygen  $2p$  orbitals parallel to the Cu—O bond, and have tails in the carboxylate bridges. Therefore, the  $2p_x(\text{C})$  orbital population in the symmetrical HOMO is an important factor which may determine the magnitude of the overlap between the two magnetic orbitals.

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