

Magneto-Structural Correlation in Dimeric Copper(II) Benzoates

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Abstract

The structures of six dimeric copper(II) benzoates, (I)–(VI), have been determined. Mo $K\alpha$ radiation was used throughout ($\lambda = 0.71073 \text{ \AA}$). Tetrakis(μ -benzoato- O, O')-bis(benzoic acid)dycopper(II), $[\text{Cu}(\text{C}_6\text{H}_5\text{COO})_2(\text{C}_6\text{H}_5\text{COOH})]_2$, (I), $M_r = 855.8$, monoclinic, $P2_1/n$, $a = 15.283(2)$, $b = 11.716(2)$, $c = 10.783(1) \text{ \AA}$, $\beta = 91.37(1)^\circ$, $V = 1930.2(5) \text{ \AA}^3$, $Z = 2$, $D_m = 1.48(2)$, $D_x = 1.47 \text{ Mg m}^{-3}$, $\mu = 1.165 \text{ mm}^{-1}$, $F(000) = 876$, $T = 300(2) \text{ K}$, $R = 0.034$ for 2990 observed unique reflections. Tetrakis(μ -benzoato- O, O')-bis(β -picoline)dycopper(II), $[\text{Cu}(\text{C}_6\text{H}_5\text{COO})_2(\text{C}_6\text{H}_7\text{N})]_2$, (II), $M_r = 797.8$, monoclinic, $P2_1/n$, $a = 17.326(2)$, $b = 10.554(1)$, $c = 10.655(2) \text{ \AA}$, $\beta = 95.56(1)^\circ$, $V = 1939.2(4) \text{ \AA}^3$, $Z = 2$, $D_m = 1.41(2)$, $D_x = 1.37 \text{ Mg m}^{-3}$, $\mu = 1.149 \text{ mm}^{-1}$, $F(000) = 820$, $T = 298(2) \text{ K}$, $R = 0.049$ for 2896 reflections. Tetrakis(μ -benzoato- O, O')-bis(4-methylquinoline)dycopper(II), $[\text{Cu}(\text{C}_6\text{H}_5\text{COO})_2(\text{C}_{10}\text{H}_9\text{N})]_2$, (III), $M_r = 897.9$, triclinic, $P\bar{1}$, $a = 10.684(3)$, $b = 10.780(2)$, $c = 10.207(2) \text{ \AA}$, $\alpha = 92.55(2)$, $\beta = 109.78(3)$, $\gamma = 68.44(2)^\circ$, $V = 1024.5(4) \text{ \AA}^3$, $Z = 1$, $D_m = 1.44(2)$, $D_x = 1.46 \text{ Mg m}^{-3}$, $\mu = 1.096 \text{ mm}^{-1}$, $F(000) = 462$, $T = 299(2) \text{ K}$, $R = 0.035$ for 3168 reflections. Tetrakis(μ -benzoato- O, O')-bis(7-methylquinoline)dycopper(II), $[\text{Cu}(\text{C}_6\text{H}_5\text{COO})_2(\text{C}_{10}\text{H}_9\text{N})]_2$, (IV), $M_r = 897.9$, monoclinic, $P2_1/n$, $a = 18.029(3)$, $b = 20.427(2)$, $c = 11.673(3) \text{ \AA}$, $\beta = 97.76(2)^\circ$, $V = 4260(1) \text{ \AA}^3$, $Z = 4$, $D_m = 1.41(2)$, $D_x = 1.40 \text{ Mg m}^{-3}$, $\mu = 1.054 \text{ mm}^{-1}$, $F(000) = 1848$, $T = 298(2) \text{ K}$, $R = 0.058$ for 3850 reflections. Tetrakis(μ -benzoato- O, O')-bis(4,7-dichloroquinoline)dycopper(II), $[\text{Cu}(\text{C}_6\text{H}_5\text{COO})_2(\text{C}_9\text{H}_5\text{Cl}_2\text{N})]_2$, (V), $M_r = 1007.7$, triclinic, $P\bar{1}$, $a = 10.657(2)$, $b = 11.047(2)$, $c = 10.640(2) \text{ \AA}$, $\alpha = 97.79(1)$, $\beta = 115.08(1)$, $\gamma = 69.13(1)^\circ$, $V =$

$1059.9(3) \text{ \AA}^3$, $Z = 1$, $D_m = 1.58(2)$, $D_x = 1.58 \text{ Mg m}^{-3}$, $\mu = 1.316 \text{ mm}^{-1}$, $F(000) = 510$, $T = 299(2) \text{ K}$, $R = 0.031$ for 4087 reflections. Tetrakis(μ -benzoato- O, O')-bis(cafeine)dycopper(II) dicaffeine, $[\text{Cu}(\text{C}_6\text{H}_5\text{COO})_2(\text{C}_8\text{H}_{10}\text{N}_4\text{O}_2)]_2 \cdot 2\text{C}_8\text{H}_{10}\text{N}_4\text{O}_2$, (VI), $M_r = 1338.3$, monoclinic, $P2_1/n$, $a = 12.922(2)$, $b = 22.122(2)$, $c = 10.898(1) \text{ \AA}$, $\beta = 99.42(1)^\circ$, $V = 3073.3(6) \text{ \AA}^3$, $Z = 2$, $D_m = 1.51(2)$, $D_x = 1.50 \text{ Mg m}^{-3}$, $\mu = 0.773 \text{ mm}^{-1}$, $F(000) = 1436$, $T = 298(2) \text{ K}$, $R = 0.053$ for 5036 reflections. The $-2J$ values from magnetic susceptibility measurements are in the range $316\text{--}350 \text{ cm}^{-1}$. The abnormally small antiferromagnetic interaction of the quinoline adduct, $-2J = 267 \text{ cm}^{-1}$, is probably due to the bent structure of the Cu—O—C—O—Cu bridges, which have a mean bending angle of $11.4(3)^\circ$.

Introduction

Dimeric copper(II) carboxylates $[\text{Cu}(\text{RCOO})_2L]_2$ are antiferromagnetic and the magneto-structural correlation has been studied extensively (Kato & Muto, 1988; Yamanaka, Uekusa, Ohba, Saito, Iwata, Kato, Tokii, Muto & Steward, 1991). The energy separation between the triplet state and singlet ground state, $-2J$, is usually similar if (i) the electron donation of the substituent R bonded to the carboxylate C atom is the same, (ii) the square-pyramidal coordination around the Cu atom is not deformed and (iii) the σ donation of the axial ligand (L) is similar. However, the quinoline adduct of dimeric copper(II) benzoate apparently shows a smaller $-2J$ value (267 cm^{-1}) than other copper(II) benzoate adducts, such as the pyridine adduct ($-2J = 328 \text{ cm}^{-1}$) for example. There are no abnormal bond lengths or bond angles in the quinoline adduct (Bencini, Gatteschi & Mealli, 1979). A possibility of accidental inconsistency between the crystal structure and the

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$-2J$ value, caused by polymorphism or a phase transition, was ruled out in this work. The abnormal $-2J$ value of $[\text{Cu}(\text{PhCOO})_2(\text{quinoline})]_2$ was confirmed several times by magnetic susceptibility measurements. Therefore we determined the crystal structures and the $-2J$ values of copper(II) benzoates with quinoline derivatives and other axial ligands in order to solve the conundrum of why the quinoline adduct has an abnormally small $-2J$ value. In the course of this investigation, little perturbation of the electronic structure of the PhCOO^- ion by rotation of the Ph group relative to the carboxylate plane was confirmed by *ab initio* molecular-orbital calculations.

Experimental

Crystals of (I) were obtained by evaporation of a methanolic solution prepared by stirring copper(II) carbonate with benzoic acid in methanol at 323 K. The powder (II) was prepared by addition of β -picoline to a methanolic solution of (I), followed by recrystallization from toluene. Crystals (III)–(VI) were obtained by slow diffusion of the relevant axial ligands into a methanolic solution of (I). Crystals of the quinoline adduct were also prepared by the diffusion method. The lattice constants of the quinoline adduct agreed with those reported by Benicini *et al.* (1979). Using this sample, the abnormally small $-2J$ value was confirmed by the magnetic susceptibility measurements. Differential scanning calorimetry in the temperature range 100–300 K showed no evidence of a phase transition. X-ray intensities of (I)–(VI) were measured on a Rigaku AFC-5 four-circle diffractometer with Mo $K\alpha$ radiation monochromatized by a graphite plate. Cell parameters were refined by least squares for 24–36 2θ values ($20 < 2\theta < 30^\circ$). Five standard reflections showed no significant variation. The structures were solved by Patterson and Fourier methods or by direct methods using *MULTAN78* (Main, Hull, Lessinger, Germain, Declercq & Woolfson, 1978). Coordinates and anisotropic thermal parameters of the non-H atoms were refined by block-diagonal least squares so as to minimize the function $\sum w(|F_o| - |F_c|)^2$ with $w^{-1} = \sigma^2(|F_o|) + (0.015|F_o|)^2$. H atoms were either located in difference syntheses or calculated theoretically and included in the refinement. The complex neutral-atom scattering factors were taken from *International Tables for X-ray Crystallography* (1974, Vol. IV). The calculations were carried out using the *UNICSIII* computation program system (Sakurai & Kobayashi, 1979) on a FACOM M-780/10 computer at Keio University. Experimental details are given below. (I): Blue–green hexagonal tablet crystal, $0.50 \times 0.35 \times 0.25$ mm, 4661 reflections measured ($2\theta \leq 55^\circ$, $h - 19 \rightarrow 19$,

$k 0 \rightarrow 15$, $l 0 \rightarrow 14$), 3149 observed with $|F_o| > 3\sigma(|F_o|)$, 2990 unique [$R_{\text{int}}(|F|) = 0.011$] after absorption correction by the Gaussian numerical integration method (Busing & Levy, 1957) (relative transmission factor, A 0.68–0.77). All of the 16 H atoms were found from difference syntheses, final $R(F) = 0.034$, $wR = 0.037$, $S = 1.43$ for 2990 unique reflections. Reflection/parameter (r/p) ratio 9.4, $\Delta/\sigma < 0.09$, $-0.47 < \Delta\rho < 0.27 \text{ e } \text{Å}^{-3}$. (II): Green prismatic crystal, $0.55 \times 0.50 \times 0.20$ mm, 4699 reflections measured ($2\theta \leq 55^\circ$, $h - 22 \rightarrow 22$, $k 0 \rightarrow 13$, $l 0 \rightarrow 13$), 3064 observed with $|F_o| > 3\sigma(|F_o|)$, 2896 unique ($R_{\text{int}} = 0.013$, $0.66 < A < 0.79$). Twelve of the 17 H atoms were found from difference syntheses and the others were calculated, $R = 0.049$, $wR = 0.075$, $S = 3.21$ for 2896 unique reflections. $r/p = 9.5$, $\Delta/\sigma < 0.13$, $-0.54 < \Delta\rho < 1.36 \text{ e } \text{Å}^{-3}$. (III): Green prisms, $0.40 \times 0.30 \times 0.20$ mm, 4952 reflections measured ($2\theta \leq 55^\circ$, $h - 13 \rightarrow 0$, $k - 14 \rightarrow 14$, $l - 13 \rightarrow 13$), 3342 observed with $|F_o| > 3\sigma(|F_o|)$, 3168 unique ($R_{\text{int}} = 0.013$, $0.73 < A < 0.84$). Fifteen of the 19 H atoms were found from difference syntheses and the others were calculated, $R = 0.035$, $wR = 0.037$, $S = 1.32$ for 3168 unique reflections. $r/p = 9.1$, $\Delta/\sigma < 0.17$, $-0.22 < \Delta\rho < 0.25 \text{ e } \text{Å}^{-3}$. (IV): Green prisms, $0.50 \times 0.30 \times 0.20$ mm, 10 088 reflections measured ($2\theta \leq 55^\circ$, $h 0 \rightarrow 23$, $k 0 \rightarrow 26$, $l - 15 \rightarrow 15$), 3982 observed with $|F_o| > 3\sigma(|F_o|)$, 3850 unique ($R_{\text{int}} = 0.022$, $0.71 < A < 0.82$). The B_{eq} values of the methyl C atoms of the 7-methylquinoline molecules are extraordinarily large, 18 and 26 Å^2 , suggesting orientational disorder of the axial ligands. Eight of the 38 H atoms were found from difference syntheses and the others calculated. H-atom parameters were not refined. $R = 0.058$, $wR = 0.061$, $S = 1.95$ for 3850 unique reflections. $r/p = 7.1$, $\Delta/\sigma < 0.27$, $-0.33 < \Delta\rho < 0.76 \text{ e } \text{Å}^{-3}$. (V): Green prisms, $0.40 \times 0.30 \times 0.25$ mm, 5125 reflections measured ($2\theta \leq 55^\circ$, $h - 13 \rightarrow 13$, $k - 14 \rightarrow 14$, $l 0 \rightarrow 13$), 4316 observed with $|F_o| > 3\sigma(|F_o|)$, 4087 unique ($R_{\text{int}} = 0.009$, $0.69 < A < 0.77$). All 15 H atoms were found from difference syntheses, $R = 0.031$, $wR = 0.040$, $S = 1.68$ for 4087 unique reflections. $r/p = 12.0$, $\Delta/\sigma < 0.18$, $-0.39 < \Delta\rho < 0.35 \text{ e } \text{Å}^{-3}$. (VI): Green prisms, $0.40 \times 0.35 \times 0.35$ mm, 7619 reflections measured ($2\theta \leq 55^\circ$, $h - 16 \rightarrow 16$, $k 0 \rightarrow 28$, $l 0 \rightarrow 14$), 5312 observed with $|F_o| > 3\sigma(|F_o|)$, 5036 unique ($R_{\text{int}} = 0.015$, $0.79 < A < 0.82$). 23 of the 30 independent H atoms were located from difference syntheses and the others calculated, $R = 0.053$, $wR = 0.066$, $S = 2.47$ for 5036 unique reflections. $r/p = 9.2$, $\Delta/\sigma < 0.15$, $-0.44 < \Delta\rho < 1.16 \text{ e } \text{Å}^{-3}$.

Magnetic susceptibilities in the temperature range 80–300 K were determined by one of the authors (TT) using the Faraday method. Correction for diamagnetic contribution was made using Pascal's constants (Selwood, 1956). The cryomagnetic data were

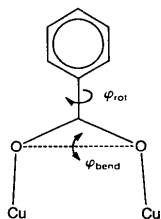
fitted to the Bleaney–Bowers equation (1) allowing for the presence of paramagnetic impurity (Ginsberg, 1971),

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

where P is the mole fraction of the noncoupled copper(II) impurity, g_i is the average g factor for the impurity which was fixed at 2.2 throughout the present study, and the other symbols have their usual meanings. The best-fit parameters of $-2J$, g and P were obtained by the non-linear least-squares fitting procedure.

Theoretical calculations

Mulliken population analyses (Mulliken, 1955) for the PhCOO^- ion were made by an *ab initio* SCF calculation using an STO-6G basis set with the program system *MOLYX* (Nambu, Nakata & Iwata, 1989) on VAX 11/750 and NEWS-830 computers. The C—O and C—Ph bond lengths, and the O—C—O bond angles were assumed to be 1.26, 1.53 Å, and 126° . The C—C and C—H bond distances in the phenyl group are assumed to be 1.395 and 1.084 Å with all bond angles 120° . The rotation angle of the Ph ring to the OCO plane, φ_{rot} , was fixed at (a) 0° , (b) 30° , or (c) 90° .



Discussion

Molecular structure

Atomic coordinates are listed in Table 1,* and selected bond lengths and bond angles in Table 2. Molecular structures are shown in Fig. 1 with the atom-numbering scheme. All the complexes except for (IV) have a crystallographic center of symmetry at the molecular center. In (I), there is an intramolecular hydrogen bond [$\text{O}(3)\cdots\text{O}(6) = 2.630$ (4) Å] between a bridging benzoate and axial benzoic acid. Owing to the hydrogen bond, the Cu—O(3) bond

distance is longer, by 0.050 (3) Å on average, compared with the other Cu—O bridge distances. The average dimensions of the central $\text{Cu}_2(\text{COO})_4$ cage and $-2J$ values of (I)–(VI) are compared in Table 3. Other copper(II) benzoates, the crystal structures of which have already been reported, are also included in Table 3. The complexes with the quinoline derivatives, (III)–(V), show normal $-2J$ values, $321\text{--}337\text{ cm}^{-1}$. Therefore, the abnormally small $-2J$ value of the quinoline adduct, 267 cm^{-1} , is not attributable to the small differences in bond lengths or the bond angles of the $[\text{Cu}_2(\text{COO})_4]$ cage. The coordination geometry around the Cu atoms is square pyramidal for all the complexes including the quinoline adduct and there is no tendency towards trigonal bipyramidal deformation. The imbalance in Cu—N—C angles involving the axial ligand owing to intramolecular repulsions is observed not only for the quinoline adduct [$\Delta(\text{Cu—N—C}) = 10.5$ (7°)] but also for its derivatives (III)–(V) [$\Delta(\text{Cu—N—C}) = 13.5$ (2)– 16.3 (2) $^\circ$] and for the caffeine adduct [35.8 (2) $^\circ$].

The molecular structure was projected along the Cu \cdots Cu axis in order to find the structural specificity of the quinoline adduct (see Fig. 2). The rotation angles of the Ph group relative to the COO moiety in the bridging benzoate ions, φ_{rot} , and the bending angles of the OCO moiety relative to the Cu—O \cdots O—Cu plane, φ_{bend} , are larger in the quinoline adduct than the other adducts. These deformations of the molecular structure are due to packing effects. For an isolated binuclear complex, the symmetric structure with $\varphi_{\text{rot}} = \varphi_{\text{bend}} = 0^\circ$ is expected to have the least strain energy. However, the molecular structure may deform in the crystals so as to improve the packing efficiency, where the increased intramolecular strain energy is compensated for by the intermolecular interactions. The reason why only the quinoline adduct is so deformed in the crystal is not clear at present.

Magneto-structural correlation

The magnitude of the spin-exchange interaction of the copper(II) benzoates is almost the same as that of the corresponding copper(II) acetates. For example, the $-2J$ value is 328 cm^{-1} for $[\text{Cu}(\text{PhCOO})_2\text{py}]_2$ and 333 cm^{-1} for $[\text{Cu}(\text{CH}_3\text{COO})_2\text{py}]_2$ (py = pyridine). In Table 3, the caffeine adduct shows a slightly larger $-2J$ value, 350 cm^{-1} , than the other adducts. This may be due to the effect of the axial ligand on the magnetic interaction, since the caffeine adduct of copper(II) acetate also has a larger $-2J$ value, 353 cm^{-1} , than the other adducts (Kato & Muto, 1988). However, the main factor which determines the magnitude of the antiferromagnetic interaction in the dimeric copper(II) carboxylates is the electronic

* Lists of structure factors, anisotropic thermal parameters, bond lengths and bond angles, and H-atom parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 54655 (210 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: AS0548]

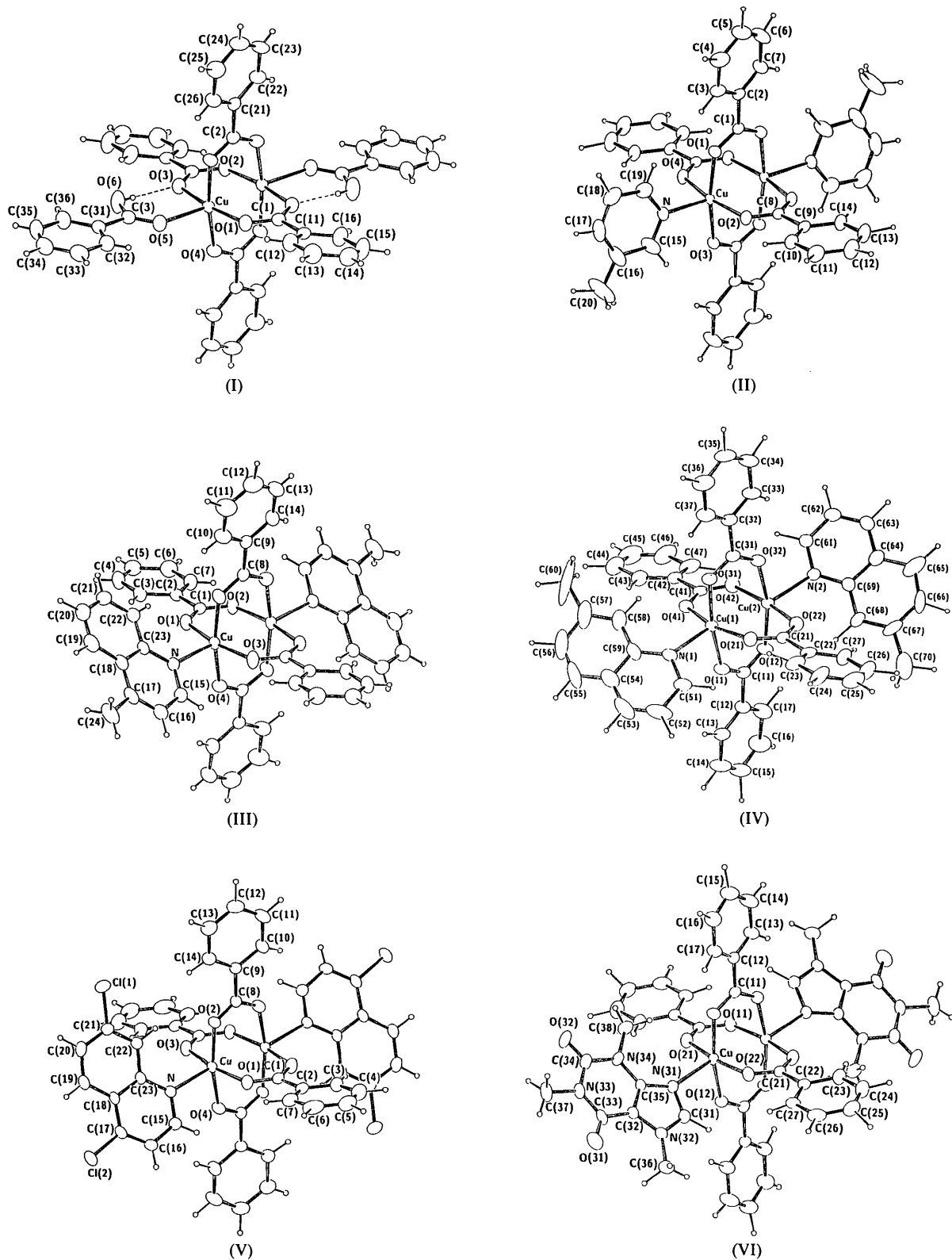


Fig. 1. ORTEPII drawings (Johnson, 1976) of molecules (I)–(VI). Thermal ellipsoids are scaled at 35% in (I), (V) and (VI), 30% in (III), and 25% in (II) and (IV). H atoms are represented by circles of radius 0.08 Å.

Table 1. *Positional parameters* ($\times 10^4$; for Cu $\times 10^5$) *and equivalent isotropic temperature factors* (Hamilton, 1959)

Compound (I)	<i>x</i>	<i>y</i>	<i>z</i>	$B_{eq}(\text{\AA}^2 \times 10)$	Compound (II)	<i>x</i>	<i>y</i>	<i>z</i>	$B_{eq}(\text{\AA}^2 \times 10)$
Cu	2084 (2)	10666 (3)	-1787 (19)	24	Cu	5025 (3)	5735 (5)	8397 (5)	25
O(1)	-158 (1)	1308 (2)	1527 (2)	33	O(1)	308 (2)	2023 (3)	-304 (3)	36
O(2)	1365 (1)	631 (2)	446 (2)	35	O(2)	-416 (2)	1052 (4)	1696 (3)	37
O(3)	542 (1)	500 (2)	-1854 (3)	33	O(3)	530 (2)	-1072 (3)	1733 (3)	37
O(4)	-1008 (1)	1199 (2)	-767 (3)	32	O(4)	1247 (2)	-99 (3)	-279 (3)	37
O(5)	598 (1)	2806 (2)	-691 (3)	37	N	1376 (2)	1486 (4)	2099 (4)	36
O(6)	1084 (2)	2514 (2)	-2590 (3)	58	C(1)	-151 (3)	2007 (5)	-1308 (5)	30
C(1)	-453 (2)	530 (2)	2205 (3)	28	C(2)	-239 (3)	3222 (5)	-2039 (5)	33
C(11)	-705 (2)	842 (2)	3491 (4)	28	C(3)	90 (4)	4328 (5)	-1530 (6)	44
C(12)	-450 (2)	1889 (3)	3959 (4)	43	C(4)	-28 (5)	5471 (6)	-2191 (7)	61
C(13)	-634 (3)	2194 (3)	5164 (4)	54	C(5)	-441 (5)	5483 (7)	-3360 (8)	71
C(14)	-1096 (3)	1458 (3)	5882 (4)	55	C(6)	-736 (5)	4382 (7)	-3875 (8)	82
C(15)	-1376 (3)	444 (4)	5421 (4)	58	C(7)	-650 (4)	3253 (6)	-3211 (6)	55
C(16)	-1173 (2)	111 (3)	4222 (4)	47	C(8)	-1082 (3)	755 (4)	1255 (5)	29
C(2)	1555 (2)	-368 (2)	811 (5)	28	C(9)	-1754 (3)	1246 (5)	1924 (5)	32
C(21)	2423 (2)	-586 (3)	1372 (5)	29	C(10)	-1613 (3)	2006 (5)	2976 (5)	42
C(22)	2677 (2)	-1674 (3)	1725 (5)	39	C(11)	-2242 (4)	2466 (6)	3577 (6)	53
C(23)	3472 (2)	-1850 (3)	2325 (5)	49	C(12)	-2973 (4)	2192 (7)	3132 (7)	63
C(24)	4025 (2)	-961 (3)	2541 (5)	51	C(13)	-3117 (3)	1432 (8)	2056 (7)	62
C(25)	3792 (2)	127 (3)	2191 (6)	50	C(14)	-2504 (3)	952 (6)	1459 (6)	43
C(26)	2987 (2)	319 (3)	1599 (6)	39	C(15)	1636 (5)	987 (6)	3180 (7)	67
C(3)	949 (2)	3154 (2)	-1611 (6)	32	C(16)	2298 (4)	1421 (7)	3944 (7)	73
C(31)	1262 (2)	4346 (2)	-1748 (6)	32	C(17)	2626 (4)	2457 (8)	3538 (8)	80
C(32)	1153 (2)	5095 (3)	-786 (7)	39	C(18)	2332 (5)	3080 (10)	2455 (8)	108
C(33)	1434 (2)	6218 (3)	-893 (7)	49	C(19)	1720 (5)	2505 (8)	1767 (7)	76
C(34)	1819 (2)	6569 (3)	-1957 (7)	54	C(20)	2634 (8)	777 (10)	5068 (12)	150
C(35)	1932 (3)	5832 (3)	-2914 (7)	57					
C(36)	1654 (2)	4716 (3)	-2826 (7)	46					
					Compound (III)				
					Cu	9246 (3)	2432 (3)	11537 (3)	28
					O(1)	964 (2)	-1357 (2)	2041 (2)	36
					O(2)	-821 (2)	1330 (2)	1537 (2)	40
					O(3)	567 (2)	1750 (2)	-124 (2)	43
					O(4)	2364 (2)	-943 (2)	383 (2)	41
					N	2492 (2)	804 (2)	2856 (2)	31
					C(1)	254 (3)	-2034 (2)	1373 (2)	29
					C(2)	398 (3)	-3267 (2)	2115 (3)	30
					C(3)	1173 (3)	-3591 (3)	3525 (3)	42
					C(4)	1272 (3)	-4724 (3)	4189 (3)	53
					C(5)	624 (3)	-5543 (3)	3466 (4)	51
					C(6)	-141 (4)	-5240 (3)	2068 (3)	49
					C(7)	-258 (3)	-4099 (3)	1394 (3)	40
					C(8)	-2069 (3)	1511 (3)	716 (3)	32
					C(9)	-3285 (3)	2516 (3)	1063 (3)	34
					C(10)	-3041 (3)	3214 (3)	2224 (3)	49
					C(11)	-4150 (4)	4175 (4)	2515 (4)	67
					C(12)	-5528 (4)	4478 (4)	1636 (4)	69
					C(13)	-5796 (4)	3791 (4)	493 (4)	69
					C(14)	-4674 (3)	2797 (4)	205 (3)	53
					C(15)	3345 (3)	1199 (3)	2460 (3)	38
					C(16)	4296 (3)	1745 (3)	3313 (3)	43
					C(17)	4378 (3)	1933 (3)	4660 (3)	41
					C(18)	3487 (3)	1513 (3)	5156 (3)	37
					Compound (IV)				
					Cu(1)	70985 (5)	15298 (4)	-8067 (8)	31
					Cu(2)	80696 (5)	9213 (4)	7952 (8)	32
					O(11)	6386 (3)	1149 (2)	122 (4)	43
					O(12)	7171 (2)	562 (2)	1354 (4)	44
					O(21)	7257 (3)	2264 (2)	344 (4)	42
					O(22)	7984 (3)	1713 (2)	1708 (4)	43
					O(31)	7952 (2)	1842 (2)	-1513 (4)	40
					O(32)	8766 (2)	1378 (2)	-135 (4)	44
					O(41)	7179 (2)	676 (2)	-1599 (4)	41
					O(42)	8026 (3)	190 (2)	-308 (4)	44
					N(1)	6139 (3)	2021 (3)	-1868 (5)	41
					N(2)	9043 (3)	511 (3)	1963 (5)	43
					C(11)	6526 (4)	748 (3)	928 (6)	35
					C(12)	5866 (4)	448 (3)	1382 (7)	39
					C(13)	5164 (4)	667 (4)	1018 (7)	50
					C(14)	4553 (5)	385 (4)	1418 (9)	72
					C(15)	4645 (5)	-113 (5)	2197 (9)	73
					C(16)	5338 (5)	-350 (5)	2540 (9)	83
					C(17)	5974 (5)	-61 (4)	2168 (8)	65
					C(21)	7610 (4)	2210 (3)	1331 (6)	34
					C(22)	7598 (4)	2776 (3)	2151 (7)	43
					C(23)	7287 (5)	3373 (4)	1720 (8)	58
					C(24)	7300 (6)	3905 (4)	2464 (8)	71
					C(25)	7564 (6)	3838 (4)	3573 (9)	79
					C(26)	7865 (6)	3250 (5)	4031 (8)	79
					C(27)	7867 (5)	2711 (4)	3302 (7)	59
					C(31)	8612 (4)	1699 (3)	-1034 (6)	37
					C(32)	9244 (4)	1958 (3)	-1638 (7)	43
					C(33)	9967 (4)	1762 (4)	-1232 (8)	57
					C(34)	10555 (4)	1999 (5)	-1777 (9)	71
					C(35)	10421 (5)	2423 (5)	-2656 (9)	76
					C(36)	9706 (5)	2638 (5)	-3056 (9)	80
					C(37)	9115 (5)	2395 (4)	-2537 (8)	60
					C(41)	7598 (4)	202 (3)	-1231 (6)	35
					C(42)	7562 (4)	-388 (3)	-2001 (7)	40
					C(43)	7203 (5)	-369 (4)	-3083 (8)	58
					C(44)	7164 (6)	-920 (5)	-3832 (8)	80
					C(45)	7505 (6)	-1485 (4)	-3343 (10)	90
					C(46)	7861 (6)	-1522 (4)	-2280 (9)	79
					C(47)	7912 (5)	-963 (4)	-1535 (8)	61
					C(51)	5729 (4)	2367 (4)	-1206 (8)	56
					C(52)	5000 (5)	2597 (4)	-1665 (10)	88
					C(53)	4705 (5)	2430 (5)	-2725 (10)	91
					C(54)	5102 (5)	2065 (4)	-3431 (8)	69
					C(55)	4795 (6)	1866 (6)	-4506 (9)	110
					C(56)	5230 (8)	1537 (6)	-5181 (9)	119
					C(57)	6022 (8)	1350 (6)	-4782 (9)	113
					C(58)	6273 (5)	1533 (5)	-3701 (8)	71
					C(59)	5835 (4)	1875 (3)	-2976 (7)	48
					C(60)	6445 (15)	986 (9)	-5624 (11)	260
					C(61)	9573 (4)	296 (5)	1389 (7)	57
					C(62)	10318 (5)	231 (5)	1898 (8)	68
					C(63)	10514 (4)	423 (4)	2998 (7)	59
					C(64)	9976 (5)	643 (4)	3652 (7)	49
					C(65)	10197 (6)	825 (4)	4862 (9)	85
					C(66)	9609 (6)	999 (4)	5409 (7)	71
					C(67)	8843 (5)	1016 (4)	4872 (8)	66
					C(68)	8647 (4)	841 (4)	3746 (7)	50
					C(69)	9212 (4)	663 (4)	3100 (6)	41
					C(70)	8257 (8)	1230 (9)	5633 (11)	176
					Compound (V)				
					Cu	9269 (3)	39519 (2)	46954 (3)	24
					Cl(1)	1611 (1)	-1427 (1)	5177 (1)	44
					Cl(2)	5532 (1)	-100 (1)	1996 (1)	46
					O(1)	2429 (2)	4657 (2)	6053 (2)	36
					O(2)	990 (2)	3072 (1)	6225 (2)	31
					O(3)	-867 (2)	3580 (1)	3446 (2)	35
					O(4)	555 (2)	5165 (1)	3264 (2)	36
					N	2521 (2)	2405 (2)	4005 (2)	26
					C(1)	2137 (2)	5677 (2)	6714 (2)	28
					C(2)	3403 (3)	6022 (2)	7804 (2)	30
					C(3)	3130 (3)	7148 (2)	8556 (3)	38
					C(4)	4278 (4)	7460 (3)	9613 (3)	51
					C(5)	5684 (4)	6668 (3)	9937 (3)	55
					C(6)	5990 (3)	5548 (3)	9215 (3)	54

Table 1 (cont.)

	x	y	z	$B_{eq}(\text{Å}^2 \times 10)$		x	y	z	$B_{eq}(\text{Å}^2 \times 10)$
C(7)	4832 (3)	5219 (2)	8122 (3)	40	C(23)	1739 (3)	-1832 (2)	-1063 (4)	37
C(8)	254 (2)	3662 (2)	6912 (2)	26	C(24)	1995 (4)	-2407 (2)	-1373 (5)	49
C(9)	345 (2)	2933 (2)	8053 (2)	27	C(25)	1237 (4)	-2847 (2)	-1669 (5)	47
C(10)	-221 (3)	3576 (2)	9013 (3)	40	C(26)	192 (4)	-2695 (2)	-1669 (4)	43
C(11)	-124 (3)	2919 (3)	10064 (3)	49	C(27)	-90 (3)	-2115 (2)	-1369 (4)	32
C(12)	520 (3)	1587 (3)	10179 (3)	43	O(31)	6020 (2)	1196 (2)	1284 (4)	53
C(13)	1081 (3)	936 (2)	9237 (3)	44	O(32)	5513 (2)	-756 (2)	2415 (3)	50
C(14)	1019 (3)	1590 (2)	8194 (3)	34	N(31)	2665 (2)	429 (1)	572 (3)	27
C(15)	3244 (3)	2868 (2)	3559 (3)	32	N(32)	3691 (2)	1223 (1)	301 (3)	29
C(16)	4198 (3)	2120 (2)	2945 (3)	34	N(33)	5764 (2)	214 (2)	1833 (3)	33
C(17)	4390 (2)	836 (2)	2786 (2)	29	N(34)	4070 (2)	-234 (1)	1560 (3)	28
C(18)	3680 (2)	265 (2)	3260 (2)	26	C(31)	2709 (3)	1000 (2)	136 (4)	32
C(19)	3849 (3)	-1073 (2)	3165 (3)	36	C(32)	4327 (3)	768 (2)	877 (4)	26
C(20)	3168 (3)	-1552 (2)	3695 (3)	40	C(33)	5422 (3)	770 (2)	1327 (4)	32
C(21)	2301 (3)	-731 (2)	4364 (2)	31	C(34)	5140 (3)	-293 (2)	1958 (4)	32
C(22)	2052 (2)	575 (2)	4437 (2)	28	C(35)	3681 (3)	298 (2)	1019 (3)	23
C(23)	2746 (2)	1100 (2)	3887 (2)	24	C(36)	4002 (4)	1827 (2)	-85 (5)	42
Compound (VI)					C(37)	6891 (3)	152 (3)	2339 (5)	55
Cu	10118 (3)	1137 (2)	3407 (4)	22	C(38)	3394 (3)	-749 (2)	1731 (5)	41
O(11)	893 (2)	-194 (1)	2007 (2)	32	O(41)	730 (3)	4143 (2)	-234 (4)	64
O(12)	812 (2)	399 (1)	-1393 (2)	32	O(42)	1238 (3)	2166 (2)	-1306 (4)	57
O(21)	1167 (2)	-715 (1)	-229 (3)	32	N(41)	-2082 (3)	3018 (2)	-2239 (4)	54
O(22)	539 (2)	913 (1)	837 (3)	32	N(42)	-1459 (4)	3987 (2)	-1273 (5)	75
C(11)	17 (3)	-396 (2)	2189 (3)	25	N(43)	985 (3)	3143 (2)	-770 (4)	39
C(12)	-60 (3)	-666 (2)	3430 (4)	25	N(44)	-418 (3)	2555 (2)	-1771 (4)	41
C(13)	-937 (3)	-1002 (2)	3573 (4)	38	C(41)	-2343 (5)	3582 (5)	-2011 (6)	98
C(14)	-987 (4)	-1277 (3)	4687 (5)	52	C(42)	-703 (4)	3571 (2)	-1198 (4)	36
C(15)	-180 (4)	-1206 (3)	5706 (5)	54	C(43)	362 (4)	3656 (2)	-699 (4)	39
C(16)	671 (4)	-859 (3)	5560 (4)	50	C(44)	642 (4)	2594 (2)	-1283 (4)	40
C(17)	743 (3)	-597 (2)	4429 (4)	39	C(45)	-1080 (4)	3038 (2)	-1749 (4)	41
C(21)	417 (3)	-1059 (2)	-673 (3)	23	C(46)	-1664 (8)	4529 (3)	-862 (8)	115
C(22)	687 (3)	-1681 (2)	-1040 (3)	26	C(47)	2101 (4)	3179 (3)	-284 (7)	71
					C(48)	-827 (5)	1962 (2)	-2285 (6)	60

Table 2. Selected bond lengths (Å) and bond angles (°)

Compound (I)		Compound (III)	
Cu...Cu ^I	2.610 (1)	Cu...Cu ^I	2.688 (1)
Cu—O(1)	1.956 (3)	Cu—O(1)	1.964 (2)
Cu—O(2)	1.945 (2)	Cu—O(2)	1.962 (2)
Cu—O(3)	2.002 (4)	Cu—O(3)	1.970 (2)
Cu—O(4)	1.956 (2)	Cu—O(4)	1.976 (2)
Cu—O(5)	2.197 (2)	Cu—N	2.207 (2)
Cu ^I —Cu—O(1)	85.6 (1)	O(1)—C(1)	1.259 (4)
Cu ^I —Cu—O(2)	85.4 (1)	O(2)—C(2)	1.260 (4)
Cu ^I —Cu—O(3)	83.3 (1)	O(3) ^y —C(1)	1.271 (3)
Cu ^I —Cu—O(4)	83.7 (1)	O(4) ^y —C(2)	1.264 (3)
Cu ^I —Cu—O(5)	173.6 (1)	C(1)—C(11)	1.493 (5)
O(1)—Cu—O(2)	89.5 (1)	C(2)—C(21)	1.495 (5)
O(1)—Cu—O(3)	168.9 (1)	O(3)—Cu—O(5)	90.2 (1)
O(1)—Cu—O(4)	90.1 (1)	O(4)—Cu—O(5)	96.1 (1)
O(1)—Cu—O(5)	100.8 (1)	Cu—O(1)—C(1)	123.8 (2)
O(2)—Cu—O(3)	88.7 (1)	Cu—O(2)—C(2)	122.1 (2)
O(2)—Cu—O(4)	169.1 (1)	Cu—O(3) ^y —C(1)	123.8 (2)
O(2)—Cu—O(5)	94.6 (1)	Cu—O(4)—C(2)	123.4 (2)
O(3)—Cu—O(4)	89.7 (1)	O(1)—C(1)—O(3) ^y	123.5 (3)
Compound (II)		O(1)—C(1)—C(11)	117.8 (3)
Cu...Cu ^I	2.664 (1)	O(3) ^y —C(1)—C(11)	118.7 (3)
Cu—O(1)	1.965 (3)	O(2)—C(2)—O(4) ^y	125.3 (3)
Cu—O(2)	1.975 (4)	O(2)—C(2)—C(21)	117.6 (3)
Cu—O(3)	1.979 (3)	O(4) ^y —C(2)—C(21)	117.1 (3)
Cu—O(4)	1.971 (4)	Compound (IV)	
Cu—N	2.151 (4)	Cu(1)...Cu(2)	2.688 (1)
O(1)—C(1)	1.270 (6)	Cu(1)—O(11)	1.951 (5)
Cu ^I —Cu—O(1)	82.8 (1)	Cu(1)—O(21)	2.008 (4)
Cu ^I —Cu—O(2)	85.6 (1)	Cu(1)—O(31)	1.949 (4)
Cu ^I —Cu—O(3)	84.7 (1)	Cu(1)—O(41)	1.989 (4)
Cu ^I —Cu—O(4)	81.6 (1)	Cu(1)—N(1)	2.226 (5)
Cu ^I —Cu—N	175.8 (1)	Cu(2)—O(12)	1.968 (4)
O(1)—Cu—O(2)	89.4 (1)	Cu(2)—O(22)	1.954 (4)
O(1)—Cu—O(3)	167.6 (1)	Cu(2)—O(32)	1.998 (4)
O(1)—Cu—O(4)	89.3 (1)	Cu(2)—O(42)	1.967 (4)
O(1)—Cu—N	96.1 (1)	Cu(2)—N(2)	2.235 (5)
O(2)—Cu—O(3)	89.1 (1)	O(11)—C(11)	1.247 (8)
O(2)—Cu—O(4)	167.2 (1)	O(12)—C(11)	1.260 (8)
O(2)—Cu—N	98.5 (1)	O(21)—C(21)	1.244 (8)
O(3)—Cu—O(4)	89.3 (1)	Cu(2)—Cu(1)—O(11)	81.1 (2)
O(3)—Cu—N	96.3 (1)	Cu(2)—Cu(1)—O(21)	81.9 (1)
		Cu(2)—Cu(1)—O(31)	88.2 (1)
		Cu(2)—Cu(1)—O(41)	80.6 (1)
		Cu(2)—Cu(1)—N(1)	168.5 (1)
		O(22)—C(21)	1.264 (8)
		O(31)—C(31)	1.278 (8)
		O(32)—C(31)	1.237 (8)
		O(41)—C(41)	1.267 (7)
		O(42)—C(41)	1.238 (8)
		N(1)—C(51)	1.341 (11)
		N(1)—C(59)	1.368 (9)
		N(2)—C(61)	1.314 (10)
		N(2)—C(69)	1.357 (9)
		C(11)—C(12)	1.498 (11)
		C(21)—C(22)	1.503 (10)
		O(31)—C(32)	1.514 (11)
		C(41)—C(42)	1.500 (9)
		O(32)—Cu(2)—O(42)	88.4 (2)
		O(32)—Cu(2)—N(2)	90.4 (2)
		O(42)—Cu(2)—N(2)	94.2 (2)
		Cu(1)—O(11)—C(11)	126.8 (5)
		Cu(2)—O(12)—C(11)	120.9 (4)

of the natural (non-orthogonalized) magnetic orbitals (Kahn, 1985). The natural magnetic orbital (NMO) of the Cu atom in the cage structure is mainly the $d_{x^2-y^2}$ orbital and has tails on the bridges. The spin super-exchange interaction increases along with the overlap integral of two NMO's. When the Cu—O—C—O—Cu bridge bends, the overlap between the $d_{x^2-y^2}$ orbital of the Cu²⁺ ion and the $2p_x$ orbital of the benzoate oxygen atoms in the symmetric HOMO decreases and the tails of the NMO on the bridge decrease. Consequently, the spin super-exchange interaction in the quinoline adduct is suppressed by the smaller overlap of the NMO's in the bent bridges [$\varphi_{\text{bend}} = 11.4(3)^\circ$] compared with

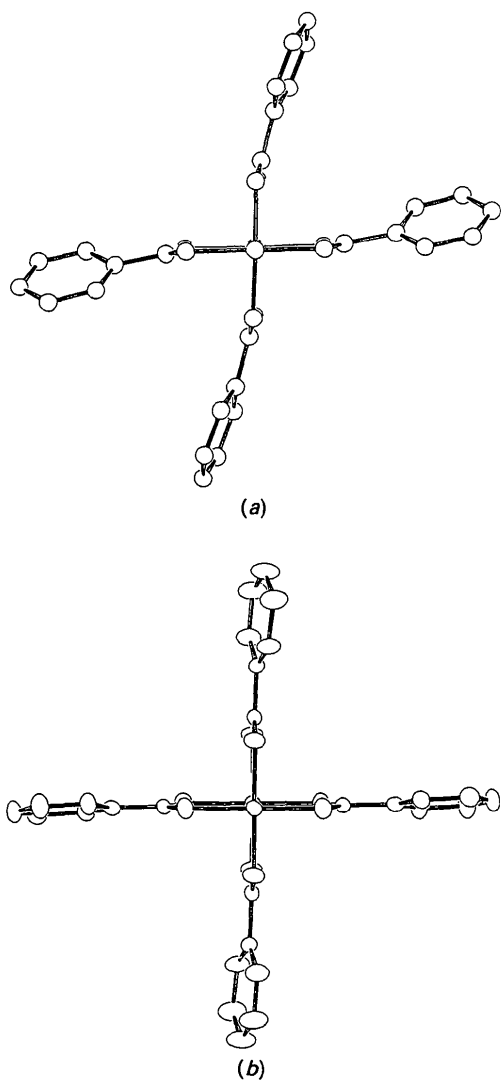


Fig. 2. Projections of the molecular structures of (a) quinoline and (b) caffeine adducts along the Cu...Cu axis. The axial ligands are omitted for clarity.

Table 4. Gross electron populations in the PhCOO⁻ carboxylate group

	$\varphi_{\text{rot}} = (a) 0, (b) 30, \text{ or } (c) 90^\circ$		
	(a)	(b)	(c)
Carbon			
s	3.075	3.075	3.076
$2p_x$	0.846	0.844	0.841
$2p_y$	0.882	0.884	0.889
$2p_z$	0.967	0.966	0.960
Total	5.771	5.770	5.765
Oxygen			
s	3.867	3.870	3.868
$2p_x$	1.747	1.745	1.735
$2p_y$	1.378	1.378	1.379
$2p_z$	1.512	1.513	1.520
Total	8.503	8.503	8.501

that in the coplanar bridges. The abnormally small $-2J$ values of [Cu(2,6-MeO₂-PhCOO)₂(H₂O)₂] [$-2J = 250 \text{ cm}^{-1}$, $\varphi_{\text{bend}} = 12.0(2)^\circ$] (Erre, Micera, Piu, Cariati & Ciani, 1985), [Cu(2-Br-PhCOO)₂(H₂O)₂] [$-2J = 250 \text{ cm}^{-1}$, $\varphi_{\text{bend}} = 7.3(2)^\circ$] (Lewis, Mabbs, Royston & Smail, 1969; Harrison, Rettig & Trotter, 1972) and [Cu(2,3-MeO₂-PhCOO)₂py]₂ [$-2J = 288 \text{ cm}^{-1}$, $\varphi_{\text{bend}} = 7.8(2)^\circ$] (Furukawa *et al.*, 1991) are also partly attributable to the bent structure of the bridges.

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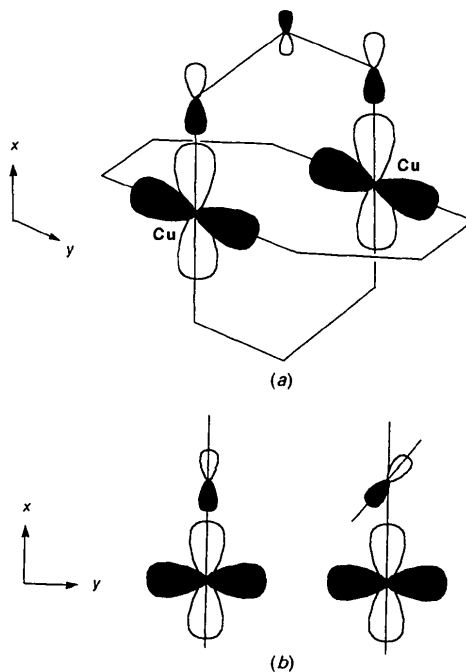


Fig. 3. Schematic drawing of the overlap between the $d_{x^2-y^2}$ orbitals of the Cu²⁺ ions and symmetric HOMO of the bridging carboxylate ion: (a) a perspective view and (b) partial projections of the normal and bent bridges along the Cu...Cu axis.

scanning calorimetry measurements on $[\text{Cu}(\text{PhCOO})_2(\text{quinoline})_2]$.

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Structural Analysis of the Fourfold Phase of Betaine Calcium Chloride Dihydrate at 90 K

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Abstract

The structure of the fourfold modulated phase of betaine calcium chloride dihydrate has been determined at 90 K. The refinement was performed using two different approaches: a standard one in space group $P2_1ca$ and a four-dimensional approach using a $P(Pnma):(1,s,-1)$ superspace group ($q = 0.25c^*$) assuming sinusoidal modulation; both refinements lead to similar R values but the four-dimensional method is more efficient for the refinement with fewer refinement parameters. The structural distortion is very similar to that of the incommensurate phase at 130 K. The amplitudes of the atomic modulations increase with respect to the incommensurate structure while the phases have approximately the same values. A symmetry-mode decomposition of the structural distortion of the

fourfold phase, as determined by the standard commensurate approach, shows that the A_3 mode, corresponding to the order parameter, is predominant, in accordance with the superspace refinement with a single harmonic. Other modes also have significant amplitudes. Data at 90 K: $(\text{CH}_3)_3\text{NCH}_2\text{-COOCaCl}_2 \cdot 2\text{H}_2\text{O}$, $M_r = 264.0$, $P2_1ca$, $a = 10.894$ (2), $b = 10.013$ (1), $c = 43.237$ (6) Å, $V = 4716$ (1) Å³, $Z = 16$, $D_x = 1.49$ g cm⁻³, $\lambda(\text{Mo } K\alpha) = 0.7107$ Å, $\mu = 9.5$ cm⁻¹, $F(000) = 2208$; for a total of 4493 independent reflections [$I > 3\sigma(I)$], final $R = 0.034$ in the commensurate refinement, and 0.046, 0.035, 0.075 and 0.56 for all, main, first- and second-order reflections, respectively, in the incommensurate refinement.

1. Introduction

Betaine calcium chloride dihydrate (BCCD) exhibits a long sequence of phase transitions giving rise to many commensurate and incommensurate (INC) phases modulated along the c axis with respect to a

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