

Structure of Tetra- μ -acetato-bis[benzimidazolecopper(II)]

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Abstract. $[\text{Cu}(\text{CH}_3\text{COO})_2(\text{C}_7\text{H}_6\text{N}_2)]_2$, orthorhombic, space group *Pbca*, $a = 21.631$ (5), $b = 14.411$ (4), $c = 8.037$ (2) Å, $V = 2505.3$ Å³, $Z = 2$, $D_m = 1.58$ (2), $D_x = 1.585$ Mg m⁻³. The structure of this new binuclear copper(II) acetate system has been determined by three-dimensional X-ray analysis. Full-matrix least-squares refinement using 1701 independent reflections has reached the *R* value of 0.068. The two Cu atoms in the molecule are held together in a dimer by the four carboxylate groups. Each Cu atom is bound in a square-pyramidal configuration to four carboxylate O atoms and to the N atom of a benzimidazole molecule. The mean Cu–O distance is 1.797 (4) Å. The Cu–N distance is 2.145 (5) Å. The Cu–Cu separation of 2.663 (1) Å is significantly greater than those found in similar dimer acetates. The binuclear molecules are connected in an infinite chain by hydrogen bonds between the imidazole –NH and the carboxylate groups.

Introduction. Partial spin pairing by antiferromagnetic coupling is common for dimeric copper(II) carboxylate monoadducts $[\text{Cu}(\text{RCOO})_2\text{L}]_2$, but no clear picture has yet emerged of the factors which determine the magnetic properties of these complexes. The phenomenon of antiferromagnetic interaction between copper(II) ions continues to be the subject of much interest among chemists (Doedens, 1976; Melnik, 1981). Complexes of copper(II) have occupied a special place in the study of intramolecular magnetic exchange because the theories of magnetic susceptibility are considerably simplified for d^9 systems. Studies of these interactions are believed to be important in a number of metalloprotein systems (Weser, 1979) and in magnetic-materials research. For monoadducts of copper(II) acetate it is interesting to relate the structural effects of variation of the axial donor ligand *L* upon the magnitude of the Cu–Cu interaction. The benzimidazole group has not before been investigated in such complexes as a ligand. We now report the synthesis and structure of dimeric copper(II) acetate monobenzimidazole.

Experimental. The crystals were prepared by adding 20 ml of a 1 *M* $\text{Cu}(\text{CH}_3\text{COO})_2$ solution to 20 ml of a 2 *M*

benzimidazole solution and the pH of the mixture was adjusted to about 5.0 by adding 2 *M* acetic acid. The solution was left at room temperature and well defined green prismatic crystals were formed within a few days.

The C, H and N content was determined by elemental analysis. Found: C, 41.7; H, 4.04; N, 9.0%; calculated for $\text{C}_{22}\text{H}_{24}\text{Cu}_2\text{N}_4\text{O}_8$: C, 44.07; H, 4.04; N, 9.35%. The lower results of the elemental analysis were caused by slight co-precipitation of copper acetate.

The crystal density measured by flotation in CHBr_3 /benzene indicated two formula units per unit cell. From rotation and corresponding Weissenberg photographs taken with Cu *K* α radiation it was concluded that the crystals are orthorhombic with the space group *Pbca*. The cell dimensions were determined by preliminary Weissenberg photographs and refined by least squares from diffractometer coordinates of 15 high-order reflections.

X-ray intensity data were measured at 295 K for a $0.03 \times 0.02 \times 0.04$ mm single crystal on a Syntex *P2*₁ four-circle diffractometer (Cu *K* α radiation, θ – 2θ scan, scintillation counter, graphite monochromator). A complete set of 1892 unique observations was measured in the range up to $(\sin \theta)/\lambda = 0.59$ Å⁻¹, 1701 of which were accepted as being statistically above background on the basis that $I \geq 1.96\sigma(I)$; zero weight was assigned to the rest. No absorption correction was made ($\mu = 22.5$ cm⁻¹).

The structure determination followed the usual routines of the heavy-atom method with a three-dimensional Patterson synthesis and subsequent Fourier synthesis. The Cu and O atoms were located from a Patterson map and the other non-H atoms from the Fourier maps.

The structure was refined by full-matrix least-squares techniques. The atomic scattering factors for Cu²⁺, O, N, C and H were taken from *International Tables for X-ray Crystallography* (1974). The refinement with individual isotropic temperature factors converged to a conventional *R* value of 0.12; the H atoms were not included. Anisotropic temperature factors were then applied to all non-H atoms and the *R* value dropped to 0.070. At this stage of refinement a difference Fourier map was made to locate the H atoms. Some peaks

Table 1. Positional parameters ($\times 10^4$) and approximate equivalent isotropic temperature factors ($\times 10^4$ for Cu, $\times 10^3$ for the other atoms)

$$U_{eq} = \frac{1}{3}(U_{11} + U_{22} + U_{33}).$$

	<i>x</i>	<i>y</i>	<i>z</i>	U_{eq} (\AA^2)
Cu	431 (1)	540 (1)	676 (1)	312 (4)
O(1)	-57 (2)	1550 (3)	-360 (6)	34 (2)
O(2)	-792 (2)	643 (3)	-1433 (6)	34 (2)
O(3)	-139 (2)	518 (3)	2595 (6)	35 (2)
O(4)	-864 (2)	-398 (3)	1489 (5)	30 (2)
C(1)	939 (3)	2350 (4)	2074 (8)	32 (4)
C(2)	1861 (3)	2182 (4)	3187 (8)	32 (4)
C(3)	2429 (3)	2264 (4)	3980 (8)	55 (5)
C(4)	2787 (4)	1478 (7)	4031 (11)	59 (5)
C(5)	2603 (3)	662 (6)	3279 (11)	51 (5)
C(6)	2038 (3)	572 (5)	2492 (10)	38 (4)
C(7)	1669 (3)	1351 (4)	2445 (8)	25 (3)
N(1)	1085 (2)	1481 (3)	1762 (7)	27 (3)
N(2)	1383 (3)	2810 (4)	2901 (8)	38 (3)
C(10)	-539 (3)	1412 (5)	-1163 (8)	29 (3)
C(20)	-850 (3)	2263 (4)	-1941 (8)	46 (4)
C(30)	-643 (3)	61 (4)	2678 (8)	27 (3)
C(40)	-982 (4)	70 (7)	4300 (9)	50 (4)

revealed could be assigned to H positions, but others could not. The H atoms of the benzimidazole ring were located from geometrical considerations assuming a C—H distance of 1.00 Å. No attempt was made to refine the H parameters. All parameter shifts in the final cycle were less than 0.3 of the standard deviation. The final *R* value was 0.068. The final atomic parameters are given in Table 1.* Maximum and minimum values of anisotropic thermal parameters U_{11} are 0.081 (6) Å² for C(4) and 0.022 (3) Å² for C(30). All calculations were carried out with the programs of the XRAY system (Stewart, Kundell & Baldwin, 1970) on a RIAD-32 computer.

Discussion. The crystal structure consists of centrosymmetric dimeric units, in which two Cu atoms are held together through four carboxylate bridges. Each Cu atom is further bonded to an atom of a benzimidazole molecule. The configuration of the binuclear complex is shown in Fig. 1. The interatomic bond distances and angles are listed in Table 2. The Cu atoms are coordinated by carboxylate atoms O(1), O(2)', O(3) and O(4)' at distances 1.983 (4), 1.971 (4), 1.976 (5) and 1.986 (4) Å, respectively, which are typical for short Cu—O bond lengths in such complexes. The four ligand atoms form a planar arrangement with the central Cu atom at a distance of

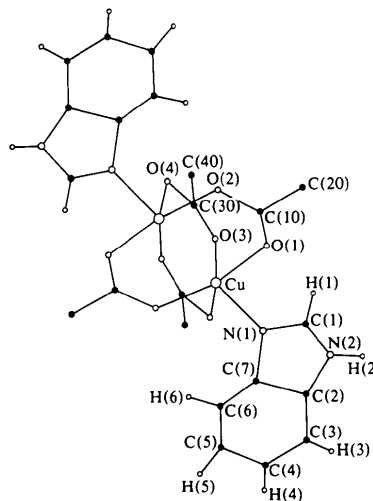


Fig. 1. The binuclear molecule viewed along the *z* axis.

0.215 (5) Å from their best plane. The fifth N atom of benzimidazole completes the square-pyramidal coordination around the Cu atom [Cu—N(1) = 2.145 (5) Å]. The N(1)—Cu—Cu' angle is 176.4 (3)° which results in N(1)—O(Ac) separations differing by about 0.14 Å. The O—O separations themselves are influenced by this deformation of tetragonal symmetry and range from 2.809 (4) [O(3)—O(1) separation] to 2.748 (6) Å [O(1)—O(4)' separation]. The Cu—Cu distance across the dimeric unit is 2.663 (1) Å. In this class of compounds, with a strong metal—metal bond, Cu—Cu separations were found in the wide range from 2.583 (1) Å in [Cu(CH₃COO)₂(pyrazine)] (Morosin, Hughes & Soos, 1975) to 2.886 (2) Å in [Cu(CF₃COO)₂(quinoline)] (Moreland & Doedens, 1975). The observed Cu—O—C—O—Cu' bridge lengths are in the range 6.41 (1) to 6.46 (1) Å (Doedens, 1976). The structures of binuclear copper(II) halogenates show a clear regularity: Cu—Cu distances are elongated when the acid strength increases (Melnik, 1981). The role of the axial ligand in determining the Cu—Cu distance was investigated in detail. The Cu—Cu distance of 2.663 (1) Å found in the present compound is distinctly greater than 2.616 (1) and 2.583 (1) Å observed in dimeric copper(II) acetate monohydrate (van Niekerk & Schoening, 1953; de Meester, Fletcher & Skapski, 1973) and in polymeric chains of pyrazine copper acetate and is comparable with the Cu—Cu separation in several dimeric copper(II) halogenoacetates (Melnik, 1981) and copper(II) *N*-acetylglycinate monohydrate where Cu—Cu = 2.666 (1) Å (Udupa & Krebs, 1979). The strength of the Cu—Cu bond in the present complex is confirmed by Cu—O—C—O—Cu' bridge lengths of 6.452 (8) and 6.494 (8) Å, which are close to the values found in the literature. The benzimidazole ligand is quite flat and

* Lists of structure factors, anisotropic thermal parameters and deviations from planes have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 36979 (14 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 2. Bond distances (Å) and angles (°) with their *e.s.d.*'s

(a) Coordination polyhedron

Cu—O(1)	1.983 (4)	Cu—O(4)	1.986 (4)
Cu—O(2)	1.971 (4)	Cu—N(1)	2.145 (5)
Cu—O(3)	1.976 (5)	Cu—Cu	2.663 (1)
O(1)—Cu—O(3)	90.4 (2)	O(4)'—Cu—O(1)	87.6 (2)
O(3)—Cu—O(2)'	89.5 (2)	N(1)—Cu—Cu'	176.4 (3)
O(2)'—Cu—O(4)'	89.7 (2)		

(b) Acetate groups

C(10)—O(1)	1.242 (8)	C(30)—O(3)	1.275 (8)
C(10)—O(2)	1.256 (7)	C(30)—O(4)	1.257 (8)
C(10)—C(20)	1.532 (9)	C(30)—C(40)	1.495 (10)
C(20)—C(10)—O(1)	116.9 (5)	O(3)—C(30)—C(40)	117.4 (6)
C(20)—C(10)—O(2)	116.4 (6)	C(40)—C(30)—O(4)	118.8 (6)
O(2)—C(10)—O(1)	126.7 (6)	O(4)—C(30)—O(3)	123.8 (6)

(c) Benzimidazole molecule

N(1)—C(1)	1.316 (7)	C(4)—C(5)	1.381 (13)
C(1)—N(2)	1.343 (9)	C(5)—C(6)	1.383 (10)
N(2)—C(2)	1.392 (9)	C(6)—C(7)	1.378 (9)
C(2)—C(3)	1.388 (9)	C(7)—N(1)	1.389 (8)
C(3)—C(4)	1.373 (11)	C(2)—C(7)	1.401 (8)
C(1)—N(1)—C(7)	105.7 (5)	C(5)—C(6)—C(7)	116.6 (7)
N(1)—C(1)—N(2)	113.1 (6)	N(2)—C(2)—C(7)	105.4 (6)
C(1)—N(2)—C(2)	107.0 (5)	N(1)—C(7)—C(2)	108.8 (5)
C(2)—C(3)—C(4)	116.3 (6)	C(3)—C(2)—N(2)	132.6 (6)
C(3)—C(4)—C(5)	121.8 (7)	C(6)—C(7)—N(1)	130.3 (6)
C(4)—C(5)—C(6)	122.3 (7)		

(d) Shortened interatomic contact

N(2)—O(4)	2.859 (7)
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inclined at 84.7 (5)° to the plane of the four coordinated O atoms. Bond distances and angles of the imidazole ring (Table 2) are close to the values of

noncoordinated and coordinated rings, tabulated by Freeman (1967). As is shown in Table 2, there are intermolecular hydrogen-bond contacts, N(2)—O(4), of 2.859 (7) Å.

The magnetic properties of the compound are being investigated by J. Mroziński in Wrocław.

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Structure of Bis(tetraphenylarsonium) Hexamolybdate(VI)

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Abstract. [As(C₆H₅)₄]₂[Mo₆O₁₉], 2C₂₄H₂₀As⁺. Mo₆O₁₉²⁻, *M_r* = 1646.4, monoclinic, *P*2₁/*c*, *a* = 16.939 (2), *b* = 30.641 (2), *c* = 21.423 (2) Å, β = 108.73 (1)°, *U* = 10530 Å³, *Z* = 8, *D_x* = 2.077 Mg m⁻³; Mo *K* α

radiation, λ = 0.71069 Å, μ = 2.66 mm⁻¹, *T* = 291 K; *R* = 0.082 for 7656 observed reflexions. In the hexamolybdate anion, six MoO₆ distorted octahedra are fused together so that they all share a common vertex. O atoms are of three types: central, terminal and bridging, bonded to six, one and two Mo atoms,

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