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Structure of a New Type of Copper Carboxylate Complex: $[Cu(C_{14}H_8O_3)(C_{10}H_8N_2)]_2.C_3H_7N.H_2O$

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Abstract. Bis[4,4′-Bipyridyl-μ-(9-hydroxy-9*H*-fluorene-9-carboxylato-*O*,μ-*O*′)copper] dimethylformamide monohydrate, $C_{48}H_{32}Cu_2N_4O_7.C_3H_7N.H_2O$, $M_r = 979\cdot01$, monoclinic, $P2_1/n$, $a = 10\cdot404$ (4), $b = 16\cdot454$ (5), $c = 13\cdot539$ (5) Å, $\beta = 103\cdot99$ (3)°, $V = 2249$ Å^3, $Z = 2$, $D_x = 1\cdot45$ g cm^{-3}, λ(Mo $K\alpha$) = 0·71069 Å, $\mu = 10\cdot48$ cm^{-1}, $F(000) = 1008$, $T = 296$ K, $R = 0\cdot068$ for 2707 observed reflections. Each Cu atom has a square pyramidal configuration; these two CuN_2O_3 square pyramids are combined by sharing an O—O edge, forming a binuclear unit. All binuclear units are connected through N atoms of the 4,4′-bipyridyl ligands, resulting in an infinite network structure.

Introduction. Copper(II) carboxylate complexes have been studied extensively (Doedens, 1976); most of them as the familiar binuclear molecule $[Cu(RCOO)_2L_2]_2$ with the quadruply bridged copper carboxylate structure (Hanic, Štempelová & Hanicová, 1964; Borel & Leclaire, 1976). However, some copper(II) complexes of an α-hydroxylated acid have a mononuclear structure (Prout, Armstrong, Carruthers, Forrest, Murray-Rust & Rossotti, 1968; Ahlgrén & Hämäläinen, 1975; Ahlgrén, Hämäläinen & Pajunen, 1977; Ahlgrén & Hämäläinen, 1977). Recently, we have successfully synthesized a series of binuclear copper(II) complexes of an α-hydroxylated acid, which have Cu_2O_2 core. As a first part of our systematic investigation, the crystal structure of the title compound is reported.

Experimental. Dark-green prismatic crystals were grown from DMF solution. Cell dimensions and crystal-orientation matrix determined on an AFC5R diffractometer by a least-squares treatment of the setting angles of 20 reflections in the range $10 < \theta < 15°$. Crystal dimensions 0·12 × 0·18 × 0·48 mm; intensities of reflections with indices h 0 to 12, k 0 to 20, l −16 to 16 with $2\theta < 52°$ measured; ω–2θ scans; ω-scan width $(1\cdot732 + 0\cdot400\tan\theta)°$, graphite-monochromatized Mo $K\alpha$ radiation. Intensities of three reflections measured every 150 reflections showed no evidence of crystal decay. 4904 reflections measured, 4609 unique, $R_{\rm int} = 0\cdot015$. 2707 with $I > 3\sigma(I)$ were used in structure solution and refinement. Data corrected for Lorentz and polarization factors and absorption effects [*DIFABS* (Walker & Stuart, 1983), max. and min. transmission factors 1·040 and 0·863; Gaussian integration: grid 6 × 6 × 6 (Coppens, Leiserowitz & Rabinovich, 1965)]. Space group $P2_1/n$ uniquely determined from systematic absences.

The crystal structure was solved by the heavy-atom method. Refinement was by full-matrix least-squares calculations with anisotropic thermal parameters for most non-H atoms and with isotropic thermal parameters for non-H atoms of the DMF and

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the H_2O molecules. Partial occupation of DMF and H_2O molecules proposed on the basis of peak heights in the difference Fourier map and thermal parameters. These occupation factors were also refined in the earlier refinement and then fixed (see Table 1). The final cycle of refinement included 295 variable parameters, $R = 0{\cdot}068$, $wR = 0{\cdot}098$, goodness-of-fit $= 2{\cdot}51$, $w = 1/\sigma^2(F_o)$. Max. shift/e.s.d. = 0·04, and the final residual electron density was $+1{\cdot}52$ $(-0{\cdot}36)\,\mathrm{e\,Å^{-3}}$; no chemically significant features. Scattering factors and anomalous-dispersion corrections for non-H atoms were taken from *International Tables for X-ray Crystallography* (1974, Vol. IV). All calculations were made on a MicroVAX II computer using the *TEXSAN* software package (Molecular Structure Corporation, 1985). Atomic coordinates and details of molecular geometry are given in Tables 1 and 2,* respectively.

Discussion. The title compound molecule is composed of one binuclear unit $[\mathrm{Cu_2(C_{14}H_8O_3)_2(C_{10}H_8N_2)_2}]$, one DMF solvent molecule and one H_2O molecule. The binuclear unit lies across a crystallographic centre at (0·5, 0, 0), as shown in Fig. 1. Atoms labelled with 'i' are related by the centre of inversion to those listed in Table 1. As illustrated in Fig. 2, the Cu atom is coordinated in a square-pyramidal geometry with the equatorial plane defined by two hydroxyl O atoms of two acid ligands, one carboxyl O atom of one acid ligand and one N atom of a 4,4′-bpy ligand, namely O(1), $\mathrm{O(1^i)}$, $\mathrm{O(3^i)}$ and N(1); the axial position is occupied by an N atom $\mathrm{N(2^{ii})}$ from a 4,4′-bpy ligand of a neighbouring molecule. The axial $\mathrm{Cu{-}N(2^{ii})}$ bond length [2·272 (6) Å] is longer than the normal axial Cu—N bond length (2·1 − 2·2 Å) in copper complexes with square-pyramidal configuration (Hanic, Štempelová & Hanicová, 1964; Davey & Stephens, 1970; Morosin, Hughes & Soos, 1975; Borel & Leclaire, 1976; Moreland & Doedens, 1978; Bukowska-Strzyzewska, Skoweranda & Tosik, 1982), while the equatorial bonds [Cu—O 1·941 (5) − 1·980 (5) Å, Cu—N 1·985 (6) Å] are similar to the corresponding bonds in the copper complexes mentioned above. The Cu atom is 0·329 Å out of the equatorial coordination plane. The Cu atoms are bridged in pairs by two hydroxyl O atoms of two 9-hydroxyfluorene-9-carboxylic acid ligands to form a binuclear unit $[\mathrm{Cu_2(C_{14}H_8O_3)_2(C_{10}H_8N_2)_2}]$ with Cu—Cu distance of 3·018 Å and angle $\mathrm{Cu{-}O(1){-}Cu^i}$ of 100·6 (2)°. This

Table 1. *Atomic coordinates and equivalent isotropic thermal parameters*

$$B_{\mathrm{eq}} = (4/3)[a^2\beta_{11} + b^2\beta_{22} + c^2\beta_{33} + (2ab\cos\gamma)\beta_{12} + (2ac\cos\beta)\beta_{13} + (2bc\cos\alpha)\beta_{23}].$$

	x	y	z	B_{eq}(Å^2)
Cu	0·60933 (9)	0·06246 (6)	0·02345 (7)	2·04 (4)
O(1)	0·4420 (5)	0·0383 (3)	−0·0780 (4)	2·0 (2)
O(2)	0·1200 (6)	0·0394 (4)	−0·2446 (5)	4·4 (3)
O(3)	0·2237 (5)	−0·0431 (4)	−0·1218 (4)	3·0 (3)
N(1)	0·6968 (6)	0·1318 (4)	−0·0610 (5)	2·4 (3)
N(2)	1·0232 (6)	0·3504 (4)	−0·3793 (5)	2·5 (3)
C(1)	0·6507 (8)	0·2014 (5)	−0·1024 (6)	2·7 (3)
C(2)	0·7156 (8)	0·2469 (5)	−0·1650 (6)	2·8 (3)
C(3)	0·8817 (8)	0·3477 (5)	−0·2620 (7)	3·0 (4)
C(4)	0·9431 (9)	0·3875 (5)	−0·3275 (7)	3·2 (4)
C(5)	1·0426 (8)	0·2713 (5)	−0·3644 (7)	2·8 (4)
C(6)	0·9849 (8)	0·2247 (5)	−0·3011 (7)	2·8 (3)
C(7)	0·8779 (8)	0·1440 (5)	−0·1426 (6)	2·8 (4)
C(8)	0·8126 (8)	0·1027 (5)	−0·0812 (7)	3·1 (4)
C(9)	0·8317 (7)	0·2167 (5)	−0·1847 (6)	2·2 (3)
C(10)	0·9001 (8)	0·2632 (5)	−0·2500 (6)	2·4 (3)
C(11)	0·237 (1)	0·1691 (8)	−0·0309 (8)	5·2 (5)
C(12)	0·203 (1)	0·248 (1)	−0·009 (1)	7·9 (8)
C(13)	0·225 (2)	0·312 (1)	−0·070 (2)	9 (1)
C(14)	0·274 (1)	0·3016 (7)	−0·150 (1)	7·4 (7)
C(15)	0·383 (1)	0·234 (1)	−0·336 (1)	7·8 (8)
C(16)	0·428 (1)	0·187 (1)	−0·410 (1)	10 (1)
C(17)	0·448 (1)	0·106 (2)	−0·402 (1)	10 (1)
C(18)	0·417 (1)	0·059 (1)	−0·3163 (8)	7·1 (7)
C(19)	0·3376 (7)	0·0784 (4)	−0·1488 (6)	2·3 (3)
C(20)	0·2942 (8)	0·1583 (5)	−0·1099 (7)	3·0 (4)
C(21)	0·309 (1)	0·2216 (6)	−0·172 (1)	4·4 (4)
C(22)	0·359 (1)	0·1908 (7)	−0·256 (1)	5·0 (5)
C(23)	0·3776 (8)	0·1072 (7)	−0·2451 (7)	3·6 (4)
C(24)	0·2171 (7)	0·0211 (5)	−0·1767 (6)	2·6 (3)
O(4)	0·064 (1)	0·0806 (9)	0·149 (1)	5·2 (3)*
N(3)	0·087 (2)	0·001 (1)	0·459 (2)	6·5 (5)*
C(25)	0·163 (3)	−0·016 (2)	0·387 (2)	7·4 (7)*
C(26)	0·098 (3)	0·088 (2)	0·504 (3)	9·2 (9)*
O(5)	0·199 (2)	0·030 (1)	0·336 (2)	9·3 (6)*
C(27)	0·004 (3)	−0·061 (2)	0·492 (2)	7·6 (7)*

* Refined isotropically with occupancy factor of 0·5.

Table 2. *Bond lengths* (Å) *and angles* (°)

Cu—O(1)	1·980 (5)	Cu—O(1')	1.941 (5)	Cu—O(3')	1.942 (6)
Cu—N(1)	1·985 (6)	Cu—N(2")	2.272 (6)	O(1)—C(19)	1.425 (9)
C(24)—O(2)	1·23 (1)	C(24)—O(3)	1.29 (1)	N(1)—C(1)	1.31 (1)
N(1)—C(8)	1·38 (1)	N(2)—C(5)	1.32 (1)	N(2)—C(4)	1.36 (1)
C(1)—C(2)	1·42 (1)	C(2)—C(9)	1.39 (1)	C(3)—C(4)	1.38 (1)
C(6)—C(10)	1·40 (1)	C(9)—C(10)	1.47 (1)	C(11)—C(20)	1.35 (1)
C(12)—C(13)	1·38 (3)	C(14)—C(21)	1.42 (2)	C(15)—C(22)	1.37 (2)
C(16)—C(17)	1·35 (3)	C(18)—C(23)	1.39 (2)	C(19)—C(23)	1.54 (1)
C(19)—C(24)	1·54 (1)	C(20)—C(21)	1.38 (1)	C(21)—C(22)	1.45 (2)
N(3)—C(25)	1·42 (3)	N(3)—C(27)	1.47 (4)	N(3)—C(26)	1.54 (4)
C(25)—O(5)	1·13 (3)	Cu—Cu(')	3.018		

O(1)—Cu—O(1')	79·4 (2)	O(1)—Cu—O(3')	159·0 (2)
O(1)—Cu—N(1)	99·5 (2)	O(1')—Cu—O(3')	83·2 (2)
O(1')—Cu—N(1)	156·4 (2)	O(3')—Cu—N(1)	91·7 (3)
N(2")—Cu—O(1)	97·2 (2)	N(2")—Cu—O(1')	97·8 (2)
N(2")—Cu—O(3')	96·8 (2)	N(2")—Cu—N(1)	105·7 (3)
Cu—O(1)—Cu(')	100·6 (2)	N(1)—C(1)—C(2)	122·5 (7)
C(4)—C(3)—C(10)	118·2 (8)	N(2)—C(5)—C(6)	124·2 (8)
C(9)—C(7)—C(8)	120·8 (8)	C(7)—C(9)—C(2)	117·9 (7)
C(6)—C(10)—C(3)	118·3 (7)	C(20)—C(11)—C(12)	118 (1)
C(14)—C(13)—C(12)	123 (1)	C(22)—C(15)—C(16)	116 (2)
C(16)—C(17)—C(18)	122 (2)	O(1)—C(19)—C(20)	114·1 (7)
O(1)—C(19)—C(24)	108·9 (6)	C(20)—C(19)—C(23)	101·1 (7)
C(11)—C(20)—C(21)	122 (1)	C(20)—C(21)—C(14)	120 (1)
C(15)—C(22)—C(23)	123 (1)	C(18)—C(23)—C(22)	123 (1)
O(2)—C(24)—O(3)	123·7 (8)	O(2)—C(24)—C(19)	120·4 (8)
O(3)—C(24)—C(19)	115·8 (7)	C(25)—N(3)—C(27)	122 (2)
C(27)—N(3)—C(26)	121 (2)	O(5)—C(25)—N(3)	127 (3)
Cu—O(1)—C(19)	140·6 (4)	Cu—O(1')—C(19')	114·6 (4)
Cu—O(3')—C(24')	116·4 (5)	Cu—N(1)—C(1)	125·2 (5)
Cu—N(1)—C(8)	117·2 (5)	C(1)—N(1)—C(8)	117·6 (7)
C(4)—N(2)—C(5)	117·0 (7)	Cu—N(2")—C(4")	113·1 (5)
Cu—N(2")—C(5")	129·9 (6)		

Symmetry code: (i) $1 - x, -y, -z$; (ii) $-\frac{1}{2} + x, \frac{1}{2} - y, \frac{1}{2} + z$.

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* Lists of structure factors, anisotropic thermal parameters, mean plane data, full bond lengths and angles, and torsion angles have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 54225 (32 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: HE0010]

Cu_2O_2 core has not been seen in copper(II) carboxylate complexes before, but a similar core was found in $[Cu_2(OH)_2L_n]$ type complexes (Casey, Hoskins & Whillans, 1970; Majeste & Meyers, 1970; Mitchell, Bernard & Wasson, 1970; Lewis, Hatfield & Hodgson, 1972). It is worth noting that there is no H atom in both α-hydroxyl groups for the title compound, while there are still OH ligands in the $Cu_2(OH)_2L_n$ complexes.

In this crystal each 9-hydroxyfluorene-9-carboxylic acid ligand is connected to two Cu atoms through a bridging hydroxyl O atom and a terminal carboxyl O atom, acting as a bivalent hydroxylated acid. The structural parameters of this acid are somewhat different from those of methyl 9-hydroxy-fluorene-9-carboxylate (Liu, Huang, Wang, 1988).

As a bridging ligand, every 4,4′-bipyridyl ligand is coordinated to two Cu atoms of two binuclear units through its two N atoms. All binuclear units are linked to each other *via* the bridging ligands, so that an infinite network structure is generated, as highlighted in Fig. 3. It is interesting to note that the two pyridine rings in a 4,4′-bpy ligand are not in the same plane, the dihedral angle between the two rings being 23·5°.

There is a weak intermolecular hydrogen bond O(4)—H···O(5) between the O atom [O(4)] of a water molecule and the carboxyl O atom [O(5)] of a DMF molecule, the distance of O(4)···O(5) being 2·72 Å.

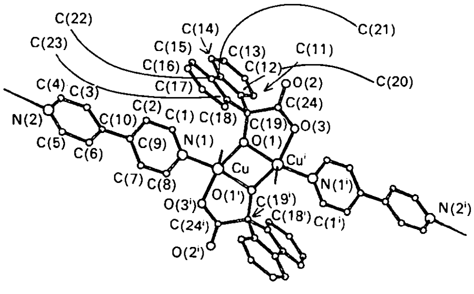

Fig. 1. View of $[Cu(C_{14}H_8O_3)(C_{10}H_8N_2)]_2$.

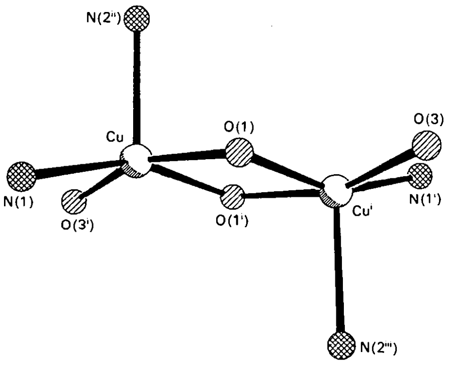

Fig. 2. Central coordination core around two Cu atoms in the title molecule.

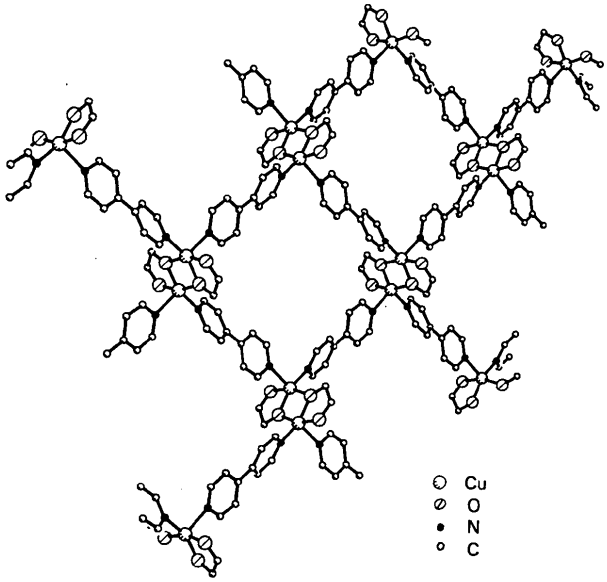

Fig. 3. View of molecules linked together one by one through the N atoms of 4,4′-bpy. Only two O atoms and two C atoms are used to represent an acid ligand for clarity.

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