

A Square-Pyramidal Copper Complex Containing both Monodentate and *anti-syn* Bridging Formate Groups: Crystal Structure of *catena-μ*-Formate-formatobis(pyridine)copper(II) Monohydrate

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Abstract

Crystals of the title complex, $\text{Cu}(\text{HCO}_2)_2(\text{pyridine})_2 \cdot \text{H}_2\text{O}$, are orthorhombic with $a = 9.731$ (1), $b = 14.351$ (1), $c = 10.302$ (1) Å, space group $Pnma$, $Z = 4$. The structure was refined to $R = 0.043$ for 1420 independent reflections. Both independent formate groups and the Cu atom lie on a mirror plane, and the complex has a polymeric chain structure. One formate is monodentate and the other bridges in an *anti-syn* fashion. Thus each Cu atom is coordinated to three formate groups and to two pyridine molecules. Coordination about Cu is essentially square-pyramidal, the base consisting of two *trans* pyridine N atoms ($\text{Cu}-\text{N} = 2.025$ Å) and two formate O atoms (mean $\text{Cu}-\text{O} = 1.959$ Å), while the apical atom is from a bridging formate with a relatively long $\text{Cu}-\text{O}$ of 2.313 Å. The water molecules are not coordinated, but are attached by hydrogen bonds to individual chains.

Introduction

Many Cu-carboxylate complexes have a dimeric structure based on that of $[\text{Cu}(\text{acetate})_2\text{H}_2\text{O}]_2$ (van Niekerk & Schoening, 1953; de Meester, Fletcher & Skapski, 1973), and show antiferromagnetic coupling, the nature of which is still a subject of debate (Catterick & Thornton, 1977). One such dimer is the emerald-green complex $[\text{Cu}(\text{HCO}_2)_2(\text{pyridine})_2]$ which has μ_{eff} of 1.15 BM (Gillard, Harris & Wilkinson, 1964). It can be obtained by heating a blue complex of formula $\text{Cu}(\text{HCO}_2)_2(\text{pyridine})_2 \cdot \text{H}_2\text{O}$, which has μ_{eff} of 1.88 BM, characteristic of magnetically normal Cu d^9 compounds. The structure of the latter complex was not known, and a number of possibilities could be envisaged, given that the stoichiometry allowed up to seven potential coordinating atoms per Cu atom. We have, therefore, determined its structure by X-ray diffraction, and find the complex to be a five-coordinate polymeric species with the water not coordinated to the metal.

Experimental

Crystals of the title complex were obtained by the method of King (1930) as modified by Goodgame (1977). Cupric formate (5 g) was dissolved in 1-propanol (40 ml) containing pyridine (10 ml) on a hot plate, and the solution filtered and allowed to cool. The resulting blue needles were washed with a little cold 1-propanol.

Photographs showed the needles to be orthorhombic with systematic absences $0kl: k + l = 2n + 1$, and $hk0: h = 2n + 1$. These are consistent with space groups $Pn2_1a$ and $Pnma$. Successful refinement showed the latter to be correct. Measurement of high-angle α_1 and α_2 reflections on a diffractometer gave $a = 9.731$ (1), $b = 14.351$ (1), $c = 10.302$ (1) Å, $U = 1438.7$ Å³ (at 283 K). $D_o = 1.52$ (by flotation), $D_c = 1.52$ Mg m⁻³ for $Z = 4$ and a formula $\text{C}_{12}\text{H}_{14}\text{CuN}_2\text{O}_5$, $M_r = 329.8$, $F(000) = 676$, $\mu(\text{Cu } K\alpha) = 2.38$ mm⁻¹.

A crystal $0.33 \times 0.13 \times 0.08$ mm was mounted with a parallel to the ϕ axis of a Siemens off-line automatic four-circle diffractometer. Intensities were measured with Cu $K\alpha$ radiation ($\lambda = 1.5418$ Å) at a

Table 1. Atomic coordinates with e.s.d.'s in parentheses

	<i>x</i>	<i>y</i>	<i>z</i>
Cu(1)	0.11500 (6)	$\frac{1}{4}$	0.14374 (6)
C(1)	0.0615 (4)	0.4410 (3)	0.2303 (4)
C(2)	0.0728 (5)	0.5363 (3)	0.2388 (5)
C(3)	0.1594 (5)	0.5825 (3)	0.1559 (4)
C(4)	0.2310 (6)	0.5309 (3)	0.0662 (5)
C(5)	0.2142 (5)	0.4354 (3)	0.0621 (4)
C(6)	0.1390 (5)	$\frac{1}{4}$	-0.1291 (5)
C(7)	0.3000 (4)	$\frac{1}{4}$	0.3529 (4)
N(1)	0.1316 (3)	0.3906 (2)	0.1438 (3)
O(1)	0.3937 (3)	$\frac{1}{4}$	0.2743 (3)
O(2)	0.0535 (3)	$\frac{1}{4}$	-0.0365 (3)
O(3)	0.2636 (4)	$\frac{1}{4}$	-0.1209 (4)
O(4)	0.1730 (3)	$\frac{1}{4}$	0.3267 (3)
O(5)*	0.0329 (6)	0.2855 (5)	0.5562 (5)

* The water is disordered and this atom has a site population parameter of 0.5.

take-off angle of 4.0° , a Ni β -filter, and a Na(Tl)I scintillation counter. The θ - 2θ scan technique was employed with a five-value measuring procedure (Allen, Rogers & Troughton, 1971). 1424 independent reflections were measured to $\theta = 70^\circ$, and of these 294 were considered to be unobserved with $I < 2.58\sigma(I)$. The 055 reflection was monitored as a reference every 50 reflections, and its net count did not alter noticeably. The data were scaled with the reference reflection, and Lorentz and polarization corrections applied.

At a later stage the data were corrected for absorption (Busing & Levy, 1957), with a $10 \times 10 \times 8$ grid and crystal path lengths determined by the vector analysis procedure (Coppens, Leiserowitz & Rabinovich, 1965).

Solution and refinement of the structure

An April 1974 version of the XRAY 72 system (Stewart, Kruger, Ammon, Dickinson & Hall, 1972) was used for the solution and refinement of the structure. The calculations were carried out on the University of London CDC 7600 computer with CRYLSQ used in the refinement. Steering tape generation, data processing and structural illustrations were done with the Imperial College CDC 6500/Cyber 174 machines.

An origin-removed Patterson synthesis showed the position of the Cu atom to give $R = 0.37$, and all other non-hydrogen atoms were located from a difference synthesis. Both formate groups and the Cu atom were on a mirror plane, while the water O atom was disordered, close to but significantly off the mirror plane. It was given a site population parameter of 0.5, and isotropic refinement in $Pnma$ reduced R to 0.084. Anisotropic refinement gave $R = 0.060$. After absorption correction, refinement gave $R = 0.054$. All the H atoms were located from a difference synthesis, and their inclusion as a fixed-atom contribution, with isotropic temperature factors of their parent C or O atoms, reduced R to 0.048. Introduction of a weighting scheme, an anomalous-dispersion correction, and the

Table 2. Fractional coordinates of the H atoms

Single-digit atomic numbers are the same as those of the parent C atoms; H(51) and H(52) are attached to O(5) and have site population parameters of 0.5.

	<i>x</i>	<i>y</i>	<i>z</i>
H(1)	-0.008	0.400	0.296
H(2)	-0.013	0.557	0.308
H(3)	0.179	0.653	0.163
H(4)	0.296	0.560	0.000
H(5)	0.279	0.387	0.004
H(6)	0.100	0.250	-0.221
H(7)	0.325	0.250	0.442
H(51)	0.058	0.273	0.475
H(52)	-0.058	0.260	0.563

removal from refinement of four strong low-angle reflections thought to be suffering from extinction gave the final R of 0.043. Refinement in $Pn2_1a$ resulted in only a negligible improvement in R and produced unacceptable divergence in the geometry of the two pyridine molecules.

The weighting scheme (Hughes, 1941) was $w = 1$ for $F < F^*$, $\sqrt{w} = F^*/F$ for $F \geq F^*$, with $F^* = 19$ as the optimum value. Scattering factors were those of Cromer & Waber (1965) and for H those of Stewart, Davidson & Simpson (1965); the anomalous-dispersion corrections for Cu were from Cromer & Liberman (1970). Table 1 lists the atomic coordinates; the unrefined coordinates of the H atoms are given in Table 2.†

Description of the structure and discussion

Fig. 1 shows the structure, which consists of a chain in which each Cu atom is bonded to two pyridine molecules, a monodentate formate group, and to two formate groups which bridge in an *anti-syn* fashion; the water molecules are not coordinated to the metal. The chain runs in the *a* direction, and translation along the chain is by a combination of a 2_1 screw axis and an *a* glide. The more important interatomic distances and bond angles are given in Table 3.

† Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 33968 (9 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

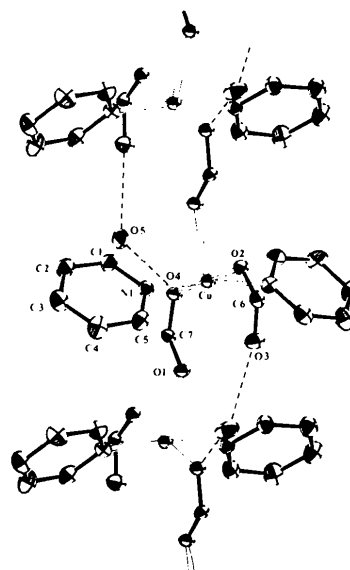


Fig. 1. Part of the chain structure of $\text{Cu}(\text{HCO}_2)_2(\text{pyridine})_2 \cdot \text{H}_2\text{O}$. Dashed lines indicate the hydrogen bonds which attach the water molecules to the chain. Thermal vibration ellipsoids are scaled to enclose 20% probability.

Both the crystallographically independent formate groups and also the Cu atom lie on a mirror plane, and Cu has an essentially square-pyramidal coordination. The base of the pyramid is formed by two *trans* pyridine N and two formate O atoms, one from a monodentate formate group and one from a bridging formate; the apex is an O atom from a second symmetry-related bridging group.

The Cu—N lengths are 2.025 Å; two basal Cu—O distances are 1.951 and 1.967 Å, the shorter of these two being to a monodentate formate. As expected, the apical Cu—O bond is weaker, with a length of 2.313 Å. On the side opposite to the apex the octahedral position is blocked by two formate O atoms at 3.03 and 3.09 Å from the Cu atom. Of the two links formed by the bridging formate, the *syn* link corresponds to the short basal bond, and the *anti* to the longer apical bond.

A distance of 0.066 Å of the Cu atom from the least-squares plane through the four basal atoms (Table 4) is unusually small for a square-pyramidal Cu complex, and in fact the two basal O atoms are fractionally further out of the plane in the apical direction. This distortion clearly arises because of the bridging groups, for which the angle O(apical)—Cu—O(basal) is 85.3°, with the Cu—O(apical) bond 4.1° from the normal to the basal plane.

anti-syn bridging by formate groups was originally postulated by Martin & Waterman (1959), and since

then only a few structures have been found which incorporate this type of bridge system. All of these are Cu complexes.

A formate complex, anhydrous Cu(HCO₂)₂ (Barclay & Kennard, 1961), and an acetate complex Cu(acetate)Br(NH₃)₂ (Belicchi Ferrari, Calzolari Capacchi, Gasparri Fava & Nardelli, 1972), both have the carboxylate bridge linking square-pyramidal coordinations base-to-base. In Cu(HCO₂)₂(H₂O)₂, one of the formate groups bridges in an *anti-syn* mode between octahedral Cu atoms (Bukowska-Strzyżewska, 1965). The only structure similar to that of the title complex is of μ -formato-(diethylenetriamine)copper(II) formate (Davey & Stephens, 1971) where the bridge links base-to-apex. In this compound the angle between the Cu—O(apical) bond and the normal to the base is 7.8°.

Both the formate groups are asymmetric, with C—O distances of 1.216 and 1.266 Å for formate centred on C(6), and 1.220 and 1.265 Å for that centred on C(7). The shortest of these bond lengths is associated with the non-coordinated O atom, while the other short distance is to the O atom involved in the long apical Cu—O bond. The two longer C—O distances are to O atoms involved in the strong basal Cu—O bonds.

Table 4 shows that the pyridine ring is closely planar, with the Cu atom *ca* 0.1 Å out of the ring plane. The plane of the pyridine ring is inclined 58.5° to that of the basal plane of the Cu coordination. Bond lengths and angles within the ring are typical of those found in other pyridine-containing compounds.

The disordered water molecule occupies one of two positions close to the mirror plane. It is associated with an individual chain by two O—H...O hydrogen bonds, of length 2.75 and 2.78 Å, to formate O atoms. As can be seen in Figs. 1 and 2 this hydrogen-bonding probably plays an important role in providing a secondary link in the chain to counterbalance the snaking covalently bonded strand.

Table 3. *Interatomic distances (Å) and bond angles (°) with e.s.d.'s in parentheses*

Superscripts refer to atoms in the following positions:
(I) $x - \frac{1}{2}, \frac{1}{2} - y, \frac{1}{2} - z$; (II) $x, \frac{1}{2} - y, z$; (III) $\frac{1}{2} + x, \frac{1}{2} - y, \frac{1}{2} - z$.

(a) Metal coordination			
Cu(1)—O(2)	1.951 (3)	Cu(1)—O(4)	1.967 (3)
Cu(1)—N(1)	2.025 (3)	Cu(1)—O(1 ^I)	2.313 (3)
Cu(1)...O(1)	3.027 (3)	Cu(1)...O(3)	3.087 (4)
N(1)—Cu(1)—N(1 ^{II})	170.87 (11)	O(2)—Cu(1)—O(4)	178.78 (13)
N(1)—Cu(1)—O(1 ^I)	94.24 (8)	N(1)—Cu(1)—O(2)	91.41 (8)
O(2)—Cu(1)—O(1 ^I)	93.54 (12)	N(1)—Cu(1)—O(4)	88.68 (8)
O(4)—Cu(1)—O(1 ^I)	85.25 (12)		
(b) Formate groups			
C(6)—O(3)	1.216 (7)	C(7)—O(1)	1.220 (5)
C(6)—O(2)	1.266 (6)	C(7)—O(4)	1.265 (5)
Cu(1)—O(2)—C(6)	121.0 (3)	Cu(1 ^{III})—O(1)—C(7)	117.0 (3)
O(2)—C(6)—O(3)	127.1 (5)	Cu(1)—O(4)—C(7)	119.0 (3)
		O(1)—C(7)—O(4)	126.1 (4)
(c) Pyridine ring			
C(1)—C(2)	1.375 (6)	C(4)—C(5)	1.381 (6)
C(2)—C(3)	1.371 (7)	C(5)—N(1)	1.329 (5)
C(3)—C(4)	1.374 (7)	N(1)—C(1)	1.335 (5)
Mean C—C	1.375	Mean C—N	1.332
N(1)—C(1)—C(2)	122.7 (4)	C(4)—C(5)—N(1)	122.1 (4)
C(1)—C(2)—C(3)	119.4 (4)	C(1)—N(1)—C(5)	118.0 (3)
C(2)—C(3)—C(4)	118.0 (4)	Cu(1)—N(1)—C(1)	119.9 (2)
C(3)—C(4)—C(5)	119.7 (4)	Cu(1)—N(1)—C(5)	122.0 (2)
(d) Hydrogen bonds			
O(4)...O(5)	2.777 (6)	O(4)—H(51)—O(5)	161
O(3)...O(5 ^{III})	2.751 (7)	O(3)—H(52)—O(5 ^{III})	157

Table 4. *Planarity of groups of atoms in the structure and distances (Å) from the least-squares planes*

Equations of the planes are expressed as $Px + Qy + Rz = S$ in direct space.

	$7.31x - 1.50y + 6.72z = 1.34$		
N(1)	0.006	C(1)	-0.001
C(3)	0.003	C(4)	0.002
		C(2)	-0.004
		C(5)	-0.006
Not defining plane: Cu(1) 0.096			
	$9.29x - 3.07z = 0.69$		
N(1)	0.087	O(2)	-0.085
N(1 ^{II})	0.087	O(4)	-0.089
Not defining plane: Cu(1) -0.066, O(1 ^I) -2.374			

Superscripts have the same meaning as in Table 3.

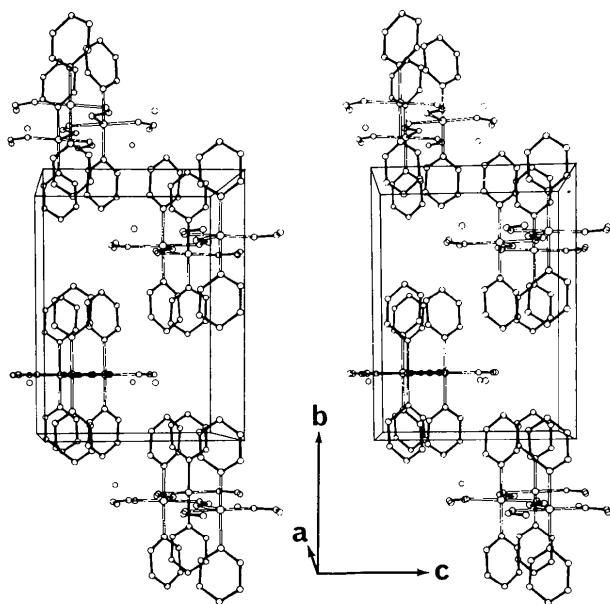


Fig. 2. A stereoscopic pair of drawings showing the packing of the chains in the structure. View is approximately down the length of the chains, and for the sake of clarity only one of each pair of disordered water molecules is drawn.

Fig. 2 (Johnson, 1965) shows how the chains are packed in the cell. Since cross-linking of chains by hydrogen bonds is not present, the forces holding them together are essentially of the van der Waals type. Although pairs of pyridine rings from different chains lie parallel across centres of symmetry, the perpendicular distance between them is $>4 \text{ \AA}$, much greater than the *ca* 3.3 \AA typical of structures where base stacking occurs.

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References

- ALLEN, F. H., ROGERS, D. & TROUGHTON, P. G. H. (1971). *Acta Cryst.* **B27**, 1325–1337.
- BARCLAY, G. A. & KENNARD, C. H. L. (1961). *J. Chem. Soc.* pp. 3289–3294.
- BELICCHI FERRARI, M., CALZOLARI CAPACCHI, L., GASPARRI FAVA, G. & NARDELLI, M. (1972). *J. Cryst. Mol. Struct.* **2**, 291–297.
- BUKOWSKA-STRZYŻEWSKA, M. (1965). *Acta Cryst.* **19**, 357–362.
- BUSING, W. R. & LEVY, H. A. (1957). *Acta Cryst.* **10**, 180–182.
- CATTERICK, J. & THORNTON, P. (1977). *Adv. Inorg. Chem. Radiochem.* **20**, 291–362.
- COPPENS, P., LEISEROWITZ, L. & RABINOVICH, D. (1965). *Acta Cryst.* **18**, 1035–1038.
- CROMER, D. T. & LIBERMAN, D. (1970). *J. Chem. Phys.* **53**, 1891–1898.
- CROMER, D. T. & WABER, J. T. (1965). *Acta Cryst.* **18**, 104–109.
- DAVEY, G. & STEPHENS, F. S. (1971). *J. Chem. Soc. A*, pp. 103–106.
- GILLARD, R. D., HARRIS, D. M. & WILKINSON, G. (1964). *J. Chem. Soc.* pp. 2838–2840.
- GOODGAME, D. M. L. (1977). Unpublished work.
- HUGHES, E. W. (1941). *J. Am. Chem. Soc.* **63**, 1737–1752.
- JOHNSON, C. K. (1965). *ORTEP*. Report ORNL-3794. Oak Ridge National Laboratory, Tennessee.
- KING, H. J. S. (1930). *J. Chem. Soc.* pp. 2307–2319.
- MARTIN, R. L. & WATERMAN, H. (1959). *J. Chem. Soc.* pp. 1359–1370.
- MEESTER, P. DE, FLETCHER, S. R. & SKAPSKI, A. C. (1973). *J. Chem. Soc. Dalton Trans.* pp. 2575–2578.
- NIEKERK, J. N. VAN & SCHOENING, F. R. L. (1953). *Acta Cryst.* **6**, 227–232.
- STEWART, J. M., KRUGER, G. J., AMMON, H. L., DICKINSON, C. & HALL, S. R. (1972). The XRAY 72 system. Technical Report TR-192. Computer Science Center, Univ. of Maryland, College Park, Maryland.
- STEWART, R. F., DAVIDSON, E. R. & SIMPSON, W. T. (1965). *J. Chem. Phys.* **42**, 3175–3187.