Tetrakis(μ-acetato-*O,O′*)bis[(4-cyano-pyridine-*N*)copper(II)]

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The title compound, $[Cu_2(C_2H_3O_2)_4(C_6H_4N_2)_2]$, has the familiar lantern-type structure that is characteristic of dimetal tetracarboxylates of copper and several other transition elements. The molecule lies about an inversion centre and the Cu atom is present in a distorted square-pyramidal coordination environment, consisting of four O atoms in equatorial positions and the pyridyl-N atoms of the two 4-cyanopyridine ligands in axial positions.

Comment

We have been investigating the coordination behaviour of 4-cyanopyridine (4-CNpy) in the hope of being able to prepare coordination polymers containing metal ions bridged by this unsymmetrical and potentially bidentate ligand, having two possible coordination sites at the pyridyl and nitrile N atoms. Polymeric species containing 4-CNpy as a bridging ligand are known (Carlucci *et al.*, 1994). In the absence of or at low concentrations of the acetate ion, the complex [CuCl₂(4-CNpy)₂] (Zhang *et al.*, 1997), which has a polymeric step-ladder chain structure (Barman *et al.*, 2000) in the solid state, is obtained in high yield. Using a reaction mixture of CuCl₂·2H₂O, 4-CNpy and NaCH₃COO·3H₂O in a 1:2:4 molar ratio in methanol, we were able to isolate dark-green crystals of the title compound, [Cu₂-(μ-O₂CCH₃)₄(4-CNpy)₂], (I), in good yield. This compound has previously been prepared by other routes and its magnetic and spectroscopic properties

have been reported in the literature (Dubicki & Martin, 1966; Muto *et al.*, 1984). It has been suggested by Uekusa *et al.* (1992) that there is a relationship between the coordination geometry of copper and the exchange coupling constant in dimeric structures of the copper(II) acetate hydrate type.

(I)
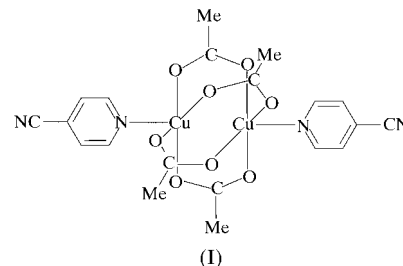
The molecular structure of (I) (Fig. 1) shows it to be structurally similar to copper(II) acetate hydrate. Both Cu atoms are present in general positions and are related by a crystallographic centre of symmetry at the midpoint of the Cu···Cu axis. The Cu—O bond lengths are close to 1.97 Å, but the Cu—N distance is longer at 2.188 (2) Å. The Cu···Cu distance of 2.600 (1) Å in (I) is shorter than the corresponding distances in $[Cu_2(\mu-O_2CCH_3)_4(H_2O)_2]$ [2.614 Å (Brown & Chidambaram, 1973) and 2.616 Å (de Meester *et al.*, 1973)], as well as those in the two forms of $[Cu_2(\mu-O_2CCH_3)_4(py)_2]$ [2.645 Å (Hanic *et al.*, 1964) and 2.630 Å (Barclay & Kennard, 1961)], but no bond is present between the Cu atoms. However, the Cu—O distances of (I) are comparable with those in the above compounds. The long Cu—*L* (*L* is an axial ligand) distances are characteristic of $[Cu_2(CH_3CO_2)_4L_2]$-type structures (Catterick & Thornton, 1977).

The distorted nature of the CuO₄N square pyramid can be understood from the O—Cu—O and O—Cu—N angles. While the former are found to be in the range 88.46 (10)–169.00 (7)°, the latter are in the range 93.03 (8)–98.21 (8)°. The Cu atom is 0.1523 (7) Å from the mean plane formed by the four equa-
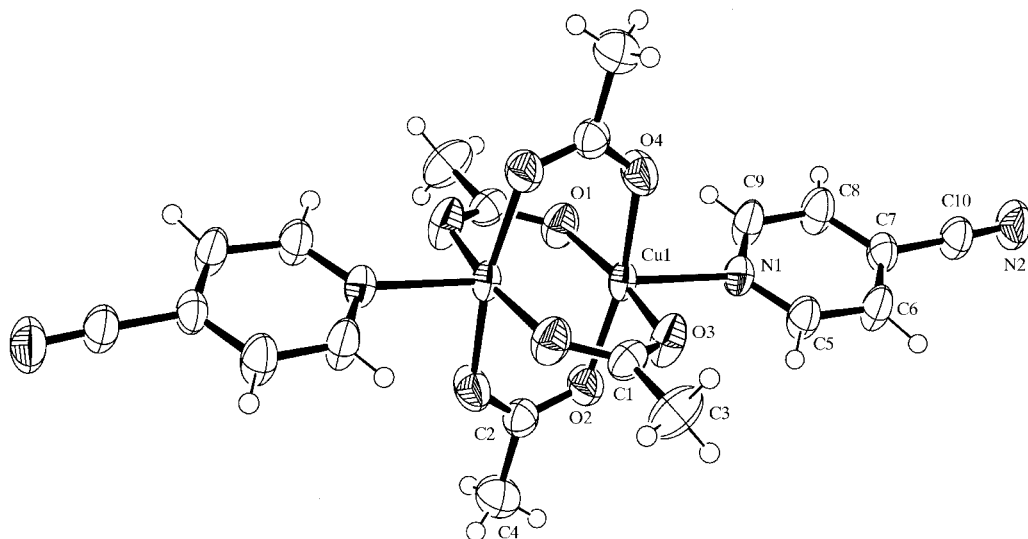
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Figure 1

The molecular structure of (I) showing 50% probability displacement ellipsoids and the atom-numbering scheme. H atoms are drawn as small spheres of arbitrary radii.

torial O atoms. On the other hand, the coordinated N atom also lies in the same direction, at a distance of 2.336 (3) Å from the plane. However, our data prove beyond doubt that the copper coordination geometry is by no means trigonal bipyramidal. Furthermore, an examination of the packing diagram shows that there are no significant intermolecular interactions involving discrete molecules of (I). The present crystal-structure analysis of (I) thus corroborates the validity of the chemical theory of Uekusa *et al.* (1992), in the sense that its previously reported antiferromagnetic (superexchange) coupling constant of 345 cm^{-1} (Muto *et al.*, 1984) is consistent with the observed structure which, we believe, is reported for the first time in the present paper. Our work also indicates that 4-CNpy is only a reluctant ligand with regard to coordination in a bidentate manner.

Experimental

A mixture of cupric chloride dihydrate (1 mmol), 4-cyanopyridine (2 mmol) and sodium acetate trihydrate (4 mmol) was mechanically stirred in methanol (20 ml) for 2 h. The small amount of light-blue precipitate which appeared was filtered off and the filtrate was kept at *ca* 278 K for 2 d. Large green crystals formed and these were filtered and washed with cold methanol (yield 68%). All crystals were clearly those of (I). A suitable single crystal was mounted on a glass fibre for the X-ray diffraction experiment.

Crystal data

[Cu$_2$(C$_2$H$_3$O$_2$)$_4$(C$_6$H$_4$N$_2$)$_2$]
M_r = 571.48
Triclinic, $P\bar{1}$
a = 7.734 (5) Å
b = 8.432 (3) Å
c = 9.782 (4) Å
α = 95.88 (4)°
β = 112.78 (4)°
γ = 92.09 (4)°
V = 583.0 (5) Å^3

Z = 1
D_x = 1.628 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 25
  reflections
θ = 8.2–14.3°
μ = 1.88 mm^{-1}
T = 293 (2) K
Irregular prism, dark green
0.34 × 0.28 × 0.16 mm

Data collection

Enraf–Nonius CAD-4 diffractometer
$\omega/2\theta$ scans
Absorption correction: ψ scan
  (North *et al.*, 1968)
  T_{min} = 0.700, T_{max} = 0.741
2222 measured reflections
2055 independent reflections
1845 reflections with $I > 2\sigma(I)$

R_{int} = 0.030
θ_{max} = 25°
h = 0 → 9
k = −10 → 10
l = −11 → 10
3 standard reflections
  every 200 reflections
  intensity decay: none

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.026
$wR(F^2)$ = 0.072
S = 1.11
2055 reflections
194 parameters
All H-atom parameters refined

$w = 1/[\sigma^2(F_o^2) + (0.0364P)^2 + 0.2826P]$
  where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.006
$\Delta\rho_{max}$ = 0.25 e Å^{-3}
$\Delta\rho_{min}$ = −0.30 e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

Cu1—O3	1.963 (2)	Cu1—N1	2.188 (2)
Cu1—O4	1.968 (2)	O2—C2	1.253 (3)
Cu1—O2	1.969 (2)	O3—C1	1.248 (3)
Cu1—O1	1.970 (2)	N2—C10	1.133 (3)
O3—Cu1—O4	90.76 (10)	O3—Cu1—N1	93.27 (9)
O3—Cu1—O2	89.35 (10)	O4—Cu1—N1	93.03 (8)
O4—Cu1—O2	168.73 (7)	O2—Cu1—N1	98.21 (8)
O3—Cu1—O1	169.00 (7)	O1—Cu1—N1	97.72 (9)
O4—Cu1—O1	88.46 (10)	N2—C10—C7	177.9 (3)
O2—Cu1—O1	89.28 (10)		

All H atoms were found in difference Fourier maps and were refined with isotropic atomic displacement parameters [C—H = 0.76 (5)–0.96 (6) Å].

Data collection: *CAD*-4 *Software* (Enraf–Nonius, 1989); cell refinement: *CAD*-4 *Software*; data reduction: local software; program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *ORTEP*-3 in *WinGX* (Farrugia, 1999).

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