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Copper(II)-induced methanolysis of a stable enediol: isolation and crystallographic characterization of chloro(methylpicolinato-*N*,*O*)(picolinato-*N*,*O*)-copper(II)

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A square-pyramidal geometry is found about the copper(II) centre in the title complex, [CuCl($C_6H_4NO_2$)($C_7H_7NO_2$)] or [Cu(2-pic)(2-picMe)Cl], a product of Cu^{II}-induced methanolysis of 1,2-di(2-pyridyl)-1,2-dihydroxyethylene. Each of the 2-pic and 2-picMe ligands chelates the copper centre *via* N and and one of their O-donor atoms. In the case of 2-picMe, the donor atoms span basal and axial positions *via* the N and O atoms, respectively. Weak secondary Cu$\cdots$Cl interactions link molecules of the complex in the crystal into centrosymmetric dimeric aggregates.

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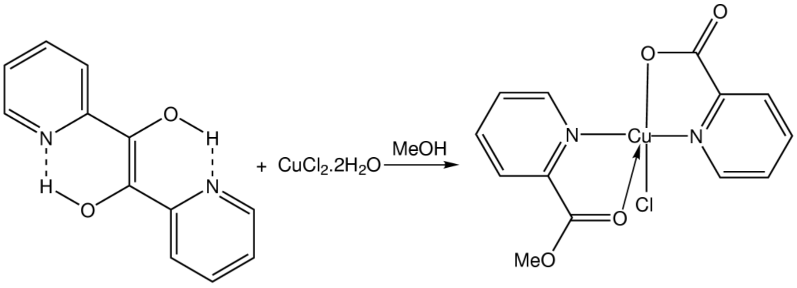
Key indicators

Single-crystal X-ray study
T = 173 K
Mean σ(C–C) = 0.004 Å
R factor = 0.028
wR factor = 0.081
Data-to-parameter ratio = 16.4

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

Comment

The coordination behaviour of 1,2-di(2-pyridyl)-1,2-dihydroxyethylene (H_2L) *versus* the first row transition metal ions has been documented (Brierley & Geary, 1967). However, the rather complex nature of some of the products calls for detailed structural studies.



H_2L (I)

The present communication indicates that a metal ion-induced solvolysis of the coordinated ligand in methanol solution has occurred when $CuCl_2{\cdot}2H_2O$ has been used as the metal ion precursor. The solvolysis generates the picolinic acid anion (2-pic) and methyl picolinate (2-picMe), both of which remain coordinated to the copper(II) centre in the mononuclear product, [Cu(2-pic)(2-picMe)Cl], (I), as proven crystallographically.

The copper(II) centre in (I) (Fig. 1 and Table 1) has a distorted square-pyramidal environment in which the basal plane is defined by the O1 and N1 atoms of the 2-pic anion, the N2 atom of the neutral 2-picMe ligand, and Cl1. The axial position is occupied by the carbonyl O3 atom of the 2-picMe ligand. Thus, both non-chloride ligands function as bidentate donors, forming five-membered rings in each case. There is some puckering in each of the chelate rings as manifested in the Cu—O1—C6—C1 and Cu—O3—C12—C7 torsion angles of 11.3 (2) and 16.5 (2)°, respectively. Within the basal plane of the square pyramid, the N atoms occupy mutually *trans* positions. The deviations of the Cl1, O1, N1 and N2 atoms

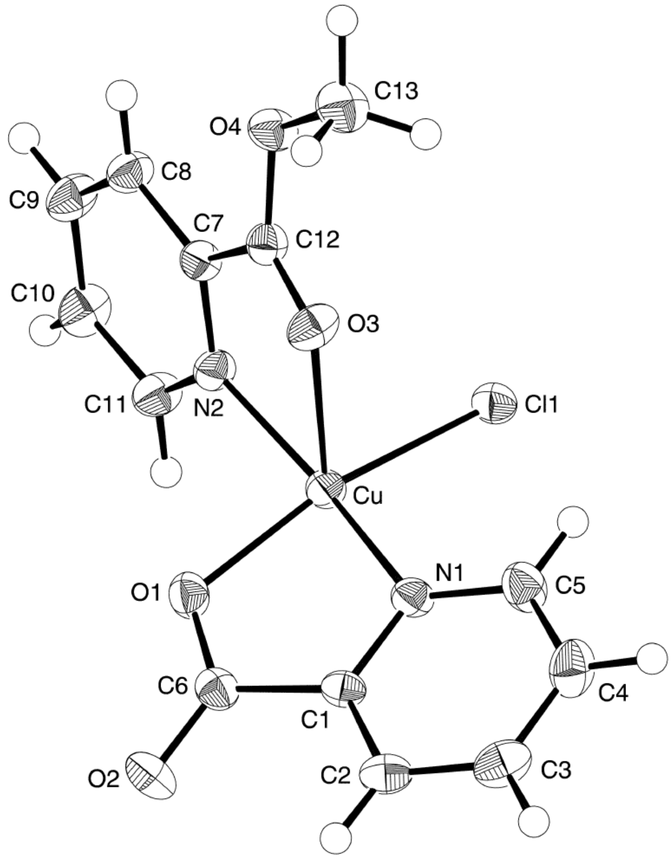


Figure 1
The molecular structure and crystallographic numbering scheme for [Cu(2-pic)(2-picMe)Cl]. Displacement ellipsoids are shown at the 50% probability level (Johnson, 1976).

from their least-squares plane are −0.1943 (6), −0.2609 (16), 0.2362 (19) and 0.2191 (19) Å, respectively, with the Cu atom lying essentially in the same plane [its displacement in the direction of the O3 atom is equal to 0.0367 (3) Å]. The Cu—N distances are similar to each other but the Cu—O1 distance of 1.9712 (17) Å is significantly shorter than the Cu—O3 distance of 2.3903 (17) Å reflecting, in part, the difference in donor strengths of the O1 and O3 atoms. The Jahn–Teller effect operating in this d^9 system will also cause elongation of the Cu—O3 bond.

The most significant intermolecular contact in the lattice occurs between the Cu atom and a symmetry related Cl1 atom so that Cu$\cdots$Cl1^{i} is 3.0634 (14) Å [symmetry code: (i) $-x$, $-y$, $1 - z$]. This association leads to the formation of centrosymmetric dimeric aggregates built around (Cu$\cdots$Cl)$_2$ rectangles. Finally, a short intermolecular contact between the C6—O2 carbonyl group and the symmetry-related quaternary C12($\frac{1}{2} - x$, $-\frac{1}{2} + y$, $\frac{1}{2} - z$) atom of 2.867 (3) Å is noted.

Experimental

A solution of $CuCl_2 \cdot 2H_2O$ (0.17 g, 1.0 mmol) in 20 ml of methanol was added dropwise to a stirred solution of 1,2-di(2-pyridyl)-1,2-dihydroxyethylene (0.21 g, 1.0 mmol), also in methanol (20 ml), to form a deep-green solution. The solution was stirred at room temperature for *ca* 4 h and filtered. The filtrate was rotary evaporated to *ca* 10 ml volume and stored at 277 K overnight; a blue crystalline compound precipitated. The product was collected by filtration, washed with a chilled methanol–diethyl ether mixture (2:1 *v*/*v*, 4 × 10 ml) and finally dried *in vacuo*. It was then recrystallized from acetonitrile solution. Yield: 85 mg (50%). The crop also contained a few diffraction quality crystals which were characterized as the title complex. Found: C 43.8, H 3.0, N 7.6%; calculated for $C_{13}H_{11}ClCuN_2O_4$: C 43.57, H 3.07, N 7.82%.

Crystal data

$[CuCl(C_6H_4NO_2)(C_7H_7NO_2)]$
$M_r = 358.24$
Monoclinic, $P2_1/n$
$a = 10.415$ (2) Å
$b = 9.466$ (2) Å
$c = 14.357$ (6) Å
$\beta = 105.88$ (2)°
$V = 1361.4$ (6) Å^3
$Z = 4$
$D_x = 1.748$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 19 reflections
$\theta = 7.2$–10.5°
$\mu = 1.82$ mm^{-1}
$T = 173$ K
Block, blue
0.27 × 0.27 × 0.17 mm

Data collection

Rigaku AFC-7*R* diffractometer
ω–2θ scans
3497 measured reflections
3130 independent reflections
2414 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.027$
$\theta_{\rm max} = 27.5°$
$h = 0 \rightarrow 13$
$k = 0 \rightarrow 12$
$l = -18 \rightarrow 17$
3 standard reflections every 400 reflections intensity decay: 1.2%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.028$
$wR(F^2) = 0.081$
$S = 1.03$
3130 reflections
191 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0394P)^2 + 0.7048P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\rm max} < 0.001$
$\Delta\rho_{\rm max} = 0.44$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.42$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

Cu—Cl1	2.2855 (8)	O3—C12	1.212 (3)
Cu—O1	1.9712 (17)	O4—C12	1.323 (3)
Cu—O3	2.3903 (17)	O4—C13	1.458 (3)
Cu—N1	1.981 (2)	N1—C1	1.340 (3)
Cu—N2	2.0058 (19)	N1—C5	1.332 (3)
O1—C6	1.274 (3)	N2—C7	1.342 (3)
O2—C6	1.233 (3)	N2—C11	1.337 (3)
O1—Cu—N1	82.62 (7)	N2—Cu—O3	75.70 (7)
O1—Cu—N2	90.89 (8)	Cl1—Cu—O3	89.73 (5)
N1—Cu—N2	166.23 (8)	C6—O1—Cu	114.66 (14)
O1—Cu—Cl1	165.21 (5)	C12—O3—Cu	105.94 (15)
N1—Cu—Cl1	95.96 (6)	C5—N1—Cu	128.36 (16)
N2—Cu—Cl1	93.36 (6)	C1—N1—Cu	112.32 (15)
O1—Cu—O3	105.05 (7)	C11—N2—Cu	122.09 (16)
N1—Cu—O3	94.21 (7)	C7—N2—Cu	119.31 (15)

The H atoms were placed in geometrically calculated positions and included in the final refinement in the riding-model approximation with an overall displacement parameter.

Data collection: *MSC*/*AFC Diffractometer Control Software* (Molecular Structure Corporation, 1996); cell refinement: *MSC*/*AFC Diffractometer Control Software*; data reduction: *TEXSAN for Windows* (Molecular Structure Corporation, 1997); program(s) used to solve structure: *DIRDIF* (Beurskens *et al.*, 1992); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); software used to prepare material for publication: *SHELXL*97.

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