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Bis[2-(pyrazol-3-yl)phenolato-κ^2N^2,O]-copper(II) dimethanol solvate

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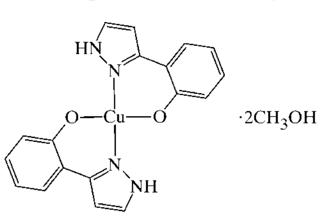
The title compound, $[Cu(C_9H_7N_2O)_2]\cdot 2CH_3OH$, contains a crystallographically centrosymmetric near-regular square planar Cu^{II} centre with *trans*-disposed chelating ligands. The complex molecules associate into a one-dimensional polymeric chain *via* hydrogen bonding to the solvent molecules.

Comment

We have recently described how complexation of $CuCl_2$ or $CuBr_2$ by 3{5}-*tert*-butylpyrazole in basic MeOH leads to a novel heptacopper aggregate structure, which is templated by $N-H\cdots X$ ($X^- = Cl^-, Br^-$) hydrogen bonding between the pyrazole ligands and non-coordinated halide anions (Liu *et al.*, 2001). As an extension of this work, we were keen to examine the Cu^{II} chemistry of pyrazole ligands containing additional hydrogen-bonding functionality, in addition to the N—H group of the pyrazole ring. 2-(Pyrazol-3-yl)phenol (H*L*) is one such ligand that is readily available (Catalan *et al.*, 1992), and we now report the structure of the mononuclear complex $[CuL_2]\cdot 2CH_3OH$, (I). No other complexes of L^- have been previously crystallographically characterized, although the crystal structure of one complex of the closely related ligand 2-(5-methylpyrazol-3-yl)phenol (H*L*′), $[FeL'_2(CH_3OH)_2]NO_3\cdot CH_4O$, has been reported (Ainscough *et al.*, 1980).



(I)

The asymmetric unit contains half a complex molecule, with Cu1 lying on the crystallographic inversion centre at $\frac{1}{2}, \frac{1}{2}, \frac{1}{2}$, together with one molecule of methanol. As in $[FeL'_2(CH_3OH)_2]NO_3\cdot CH_3OH$ (Ainscough *et al.*, 1980), the L^- ligands in (I) chelate to the Cu ion through their pyrazole N and phenoxide O donors, giving a four-coordinate Cu^{II} centre with a *trans*-N_2O_2 donor set. The coordination geometry at Cu1 is strictly planar by symmetry, and is almost perfectly square. The Cu^{II} ion stands proud of the least-squares plane of the chelating ligand, by 0.5784 (13) Å. This is also manifested in the dihedral angle between the square plane of donors at Cu1 [Cu1, N2, O13, N2^{i} and O13^{i}; symmetry code: (i) $1-x, 1-y, 1-z$] and the least squares plane of the L^- ligand (N2–O13), which is 24.73 (7)°. The pyrazole and phenoxide moieties of the ligand are twisted with respect to each other, with the dihedral angle between the least-squares planes N2–C7 and C8–O13 being 16.37 (11)°.

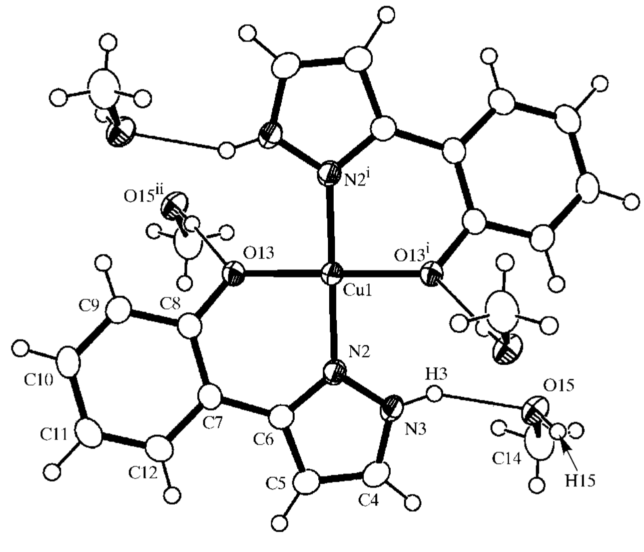


Figure 1
A view of the title compound with 50% probability displacement ellipsoids, showing the atom-numbering scheme employed. H atoms have arbitrary radii. [Symmetry codes: (i) $1-x, 1-y, 1-z$; (ii) $x, y, 1+z$.]

The methanol molecule accepts a hydrogen bond from the L^- pyrrolic N—H group, and donates a hydrogen bond to the phenoxide O-donor of a neighbouring molecule related by $x, y, 1-z$. This affords a one-dimensional polymeric chain of hydrogen-bonded molecules, running parallel to the z axis of the unit cell. Adjacent chains are linked by a π–π interaction between the phenyl rings C7–C12 and C7^{iii}–C12^{iii} (related by $-x, 1-y, 1-z$). The interacting rings are strictly coplanar by symmetry and are separated by 3.410 (5) Å, with their centroids being offset by 1.24 Å. These parameters imply a π–π interaction that is only weakly electrostatically attractive (Hunter & Sanders, 1990).

Experimental

A mixture of 2-(pyrazol-3-yl)phenol (0.32 g, 2.0 mmol; Catalan *et al.*, 1992), $CuBr_2$ (0.22 g, 1.0 mmol) and NaOH (0.040 g, 1 mmol) in MeOH (50 ml) was stirred at room temperature for 16 h, yielding a brown solution. Concentration of this solution to about half its original volume afforded a dark precipitate, which was removed by filtration. Storage of the filtrate at 263 K afforded dark-brown plates, which slowly degraded *in vacuo*. The dried material reproducibly analyses for $[CuL_2]\cdot xCH_4O\cdot(2-x)H_2O$ (x = *ca* 0.5): found C 53.4, H 4.5, N 12.9%; calculated for $C_{18}H_{14}CuN_4O_2\cdot 1.5CH_4O\cdot 0.5H_2O$: C 53.4, H 4.8, N 12.8%.

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Crystal data

$[Cu(C_9H_7N_2O)_2]\cdot 2CH_4O$	$D_x = 1.559$ Mg m^{-3}
$M_r = 445.96$	Mo $K\alpha$ radiation
Monoclinic, $P2_1/c$	Cell parameters from 10 193 reflections
$a = 7.5210$ (2) Å	$\theta = 2.8$–$27.5°$
$b = 15.6270$ (4) Å	$\mu = 1.19$ mm^{-1}
$c = 8.3657$ (3) Å	$T = 150$ (2) K
$\beta = 105.000$ (1)°	Plate, brown
$V = 949.72$ (5) Å^3	0.19 × 0.15 × 0.03 mm
$Z = 2$	

Data collection

Nonius KappaCCD diffractometer	1952 reflections with $I > 2\sigma(I)$
Area-detector scans	$R_{int} = 0.038$
Absorption correction: multi-scan (*SORTAV*; Blessing, 1995)	$\theta_{max} = 27.5°$
$T_{min} = 0.806$, $T_{max} = 0.965$	$h = -9 \rightarrow 9$
10 193 measured reflections	$k = -20 \rightarrow 20$
2172 independent reflections	$l = -10 \rightarrow 10$

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.053P)^2 + 0.359P]$ where $P = (F_o^2 + 2F_c^2)/3$
$R[F^2 > 2\sigma(F^2)] = 0.034$	$(\Delta/\sigma)_{max} = 0.001$
$wR(F^2) = 0.093$	$\Delta\rho_{max} = 0.37$ e Å^{-3}
$S = 1.06$	$\Delta\rho_{min} = -0.51$ e Å^{-3}
2172 reflections	Extinction correction: *SHELXL*97
178 parameters	Extinction coefficient: 0.032 (5)
All H-atom parameters refined	

Table 1
Selected geometric parameters (Å, °).

Cu1—N2	1.9390 (15)	Cu1—O13	1.9243 (12)
O13—Cu1—N2	90.07 (6)		

All H atoms were located in a Fourier difference map and allowed to refine freely. Refined C—H distances are in the range 0.88 (3)–1.02 (4) Å, while N3—H3 = 0.88 (3) and O15—H15 = 0.75 (3) Å.

Data collection: *COLLECT* (Nonius, 1999); cell refinement: *DENZO-SMN* (Otwinowski & Minor, 1997); data reduction: *DENZO-SMN*; program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1990); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *ORTEX* (McArdle, 1995); software used to prepare material for publication: local program.

Table 2
Hydrogen-bonding geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
N3—H3···O15	0.88 (3)	2.02 (3)	2.815 (2)	150 (2)
O15—H15···O13^{i}	0.75 (3)	1.97 (3)	2.724 (2)	177 (3)

Symmetry code: (i) $x, y, z-1$.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: BM1476). Services for accessing these data are described at the back of the journal.

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