metal-organic papers

Acetato(methanol)[*N*-phenyl-*N*,*N*-bis(2-pyridyl-methyl)amine]copper(II) hexafluorophosphate

**Anne Nielsen, Andrew D. Bond*
and Christine J. McKenzie**

University of Southern Denmark, Department of
Chemistry, Campusvej 55, 5230 Odense,
Denmark

Correspondence e-mail: adb@chem.sdu.dk

Key indicators

Single-crystal X-ray study
$T = 180$ K
Mean σ(C–C) = 0.004 Å
Disorder in solvent or counterion
R factor = 0.040
wR factor = 0.120
Data-to-parameter ratio = 20.4

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

The title copper complex, $[Cu(C_2H_3O_2)(CH_4O)(C_{18}H_{17}N_3)]$-$PF_6$, of the tridentate ligand *N*-phenyl-*N*,*N*-bis(2-pyridyl-methyl)amine (phbpa), displays a distorted octahedral coordination geometry in which the κ^2O,O'-acetate ligand approaches a κO-binding arrangement. One O atom of the acetate group also accepts an O—H···O hydrogen bond [O···O = 2.654 (2) Å] from a coordinated methanol molecule in a neighbouring complex.

Comment

Crystal structures of two copper(II) complexes incorporating the tridentate ligand *N*-phenyl-*N*,*N*-bis(2-pyridylmethyl)-amine (phbpa) have been published previously (Ugozzoli *et al.*, 2002). One is a mononuclear neutral dichloro derivative, (phbpa)CuCl$_2$, and the other involves a dinuclear chloro-bridged cation, $[(phbpa)_2Cu_2Cl_3]^+$. In both cases, copper(II) displays a distorted trigonal–bipyramidal coordination geometry. Octahedral cationic complexes $[(phbpa)_2M]^{2+}$ have also been reported for Ni and Rh (Hazell *et al.*, 2000; Bjer-nemose *et al.*, 2003).

(I)
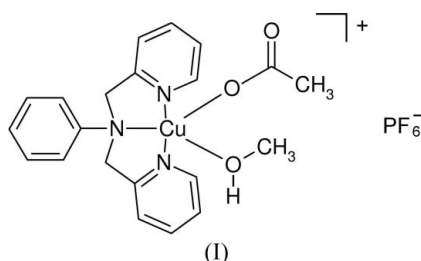
In the cation of the title complex, (I) (Fig. 1), atom Cu1 displays distorted octahedral coordination geometry (Fig. 2 and Table 1). The three N atoms of the phbpa ligand are approximately coplanar with Cu1 (the maximum deviation from the least-squares plane through the four atoms is 0.15 Å for Cu1), and the Cu—O bond to the coordinated methanol molecule lies approximately perpendicular to this plane. The binding geometry of the acetate ligand is such that atom O1 lies *ca* 0.85° from the plane and O2 forms a somewhat longer contact to Cu1 at an angle of *ca* 83° to the plane. The binding mode of the acetate ligand is described as κ^2O,O', although it approaches a κO description. The distorted geometry reflects the limited bite angle of the acetate ligand, coupled with the Jahn—Teller distortion around Cu^{II}. The C19—O2 bond [1.231 (3) Å] is significantly shorter than C19—O1 [1.260 (3) Å] and O2 also accepts an O—H···O hydrogen bond from a coordinated methanol molecule in a neigh-bouring complex (Fig. 3): O3—H3 = 0.84 Å, O3···O2^i =
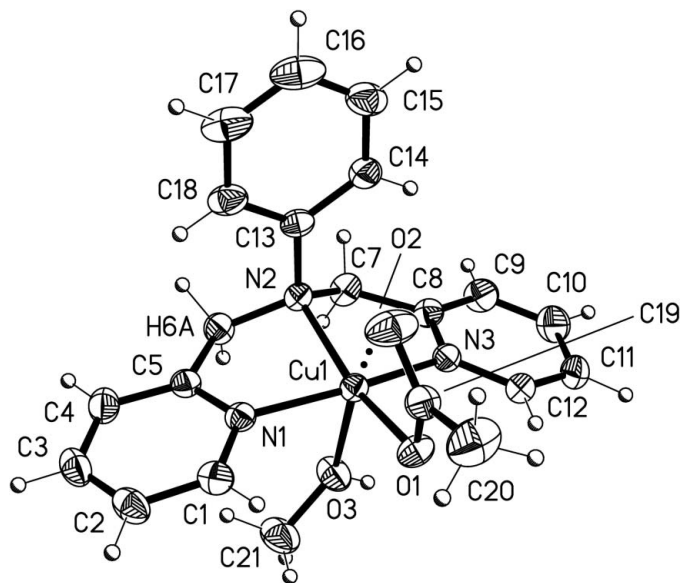
Figure 1
View of the cation of the title complex, showing displacement ellipsoids at the 50% probability level. H atoms are shown as spheres of arbitrary radius. The relatively long contact between Cu1 and O2 is shown as a dotted line.

2.654 (2) Å and O3—H3···O2^i = 170° [symmetry code: (i) $\frac{1}{2} - x, \frac{1}{2} - y, -\frac{1}{2} + z$].

Experimental

Cu(CH$_3$CO$_2$)$_2$·H$_2$O (17.4 mg, 0.087 mmol) in hot methanol (3 ml), NH$_4$Cl (4.6 mg, 0.086 mmol) in methanol (0.25 ml) and NH$_4$PF$_6$ (231.9 mg, 1.42 mmol) in methanol (2 ml) were added to *N*-phenyl-*N,N*-bis(2-pyridylmethyl)amine (phbpa; 23.8 mg, 0.086 mmol) in methanol (1 ml). Blue-green crystals precipitated overnight at low temperature (*ca* 250 K).

Crystal data

[Cu(C$_2$H$_3$O$_2$)(CH$_4$O)-(C$_{18}$H$_{17}$N$_3$)]PF$_6$
$M_r = 574.94$
Orthorhombic, *Pbcn*
$a = 18.8196 (7)$ Å
$b = 18.4938 (8)$ Å
$c = 13.5023 (6)$ Å
$V = 4699.4 (3)$ Å^3
$Z = 8$

$D_x = 1.625$ Mg m^{-3}
Mo *Kα* radiation
Cell parameters from 6956 reflections
$\theta = 2.9–27.3°$
$\mu = 1.07$ mm^{-1}
$T = 180 (2)$ K
Block, blue-green
$0.22 \times 0.16 \times 0.14$ mm

Data collection

Bruker–Nonius X8APEX-II CCD diffractometer
Thin-slice *ω* and *φ* scans
Absorption correction: multi-scan (*SADABS*; Sheldrick, 2003)
$T_{min} = 0.759$, $T_{max} = 0.864$
76538 measured reflections

7042 independent reflections
5365 reflections with $I > 2\sigma(I)$
$R_{int} = 0.034$
$\theta_{max} = 30.4°$
$h = -26 \rightarrow 26$
$k = -26 \rightarrow 26$
$l = -17 \rightarrow 19$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.040$
$wR(F^2) = 0.120$
$S = 1.05$
7042 reflections
346 parameters
H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0551P)^2 + 4.6723P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 0.75$ e Å^{-3}
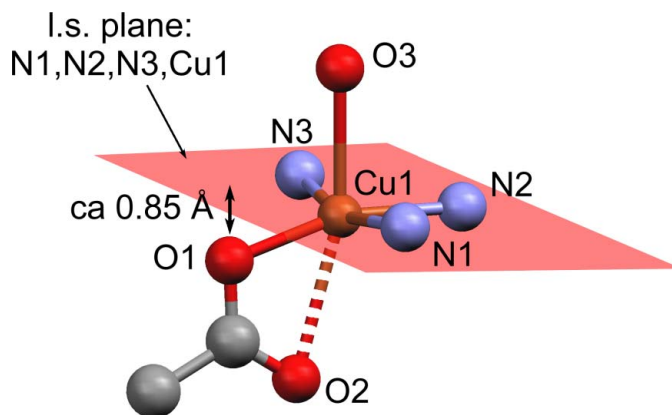$\Delta\rho_{min} = -0.45$ e Å^{-3}

Figure 2
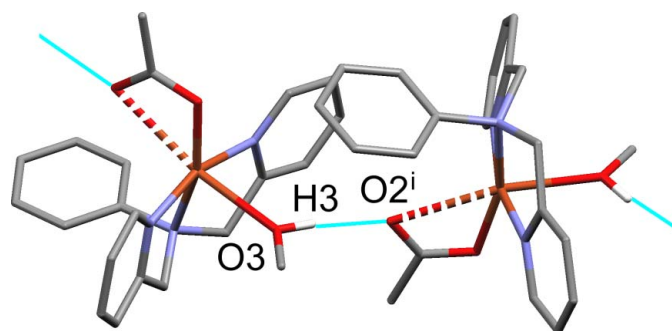The coordination geometry of Cu1.

Figure 3
O—H···O hydrogen bond between one O atom of the acetate ligand and a coordinated methanol molecule in a neighbouring complex.

Table 1
Selected geometric parameters (Å, °).

Cu1—O1	1.9519 (15)	Cu1—N2	2.0856 (17)
Cu1—N3	1.9650 (17)	Cu1—O3	2.3376 (16)
Cu1—N1	1.9655 (18)	Cu1—O2	2.6235 (18)
O1—Cu1—N3	97.04 (7)	N3—Cu1—O3	82.39 (7)
O1—Cu1—N1	98.47 (7)	N1—Cu1—O3	85.13 (6)
N3—Cu1—N1	162.35 (7)	N2—Cu1—O3	91.11 (7)
O1—Cu1—N2	162.21 (7)	N3—Cu1—O2	103.72 (7)
N3—Cu1—N2	84.03 (7)	N1—Cu1—O2	92.11 (7)
N1—Cu1—N2	83.79 (7)	N2—Cu1—O2	107.53 (6)
O1—Cu1—O3	106.65 (7)	O3—Cu1—O2	160.77 (6)

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

D—H···A	D—H	H···A	D···A	D—H···A
O3—H3···O2^i	0.84	1.82	2.654 (2)	170

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

While one PF$_6^-$ anion is well ordered (located on an inversion centre), the second (containing P2 and lying on a twofold axis) shows extensive rotational disorder. This disorder was approximated by modeling the PF$_6^-$ anion in two orientations, each with 50% site occupancy and restrained geometries. Anisotropic displacement

parameters were refined for all F atoms, showing considerable distortion approximately around the surface of a sphere centered on P2. Modeling the F atoms with isotropic displacement parameters gives *wR ca* 0.18 and a significantly less satisfactory refinement for the remainder of the structure (*i.e.* the geometry and standard uncertainties). Attempts to treat the disordered PF_6^- anion with a continuous solvent-area model (*SQUEEZE*; van der Sluis & Spek, 1990; Spek, 2003) were unsuccessful. H atoms bound to C atoms were positioned geometrically and allowed to ride during subsequent refinement, with C—H = 0.95 Å and $U_{iso}(H) = 1.2U_{eq}(C)$ for the H atoms of the pyridyl rings, C—H = 0.99 Å and $U_{iso}(H) = 1.2U_{eq}(C)$ for the methylene groups, and C—H = 0.98 Å and $U_{iso}(H) = 1.5U_{eq}(C)$ for the methyl groups. Atom H3, associated with the coordinated methanol molecule, was located in a difference Fourier map, then moved along the O3—H3 vector to give O—H = 0.84 Å. It was subsequently allowed to ride on O3 with $U_{iso}(H) = 1.2U_{eq}(O)$.

Data collection: *APEX2* (Bruker–Nonius, 2004); cell refinement: *SAINT* (Bruker, 2003); data reduction: *SAINT*; program(s) used to solve structure: *SHELXTL* (Sheldrick, 2000); program(s) used to refine structure: *SHELXTL*; molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL*.

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