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Bis{4-[α-(4-acetylphenylimino)benzyl]-3-methyl-1-phenylpyrazol-5-onato}-aquacopper(II)

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The Cu atom in the title complex, $[Cu(C_{25}H_{20}N_3O_2)_2(H_2O)]$, has a distorted trigonal-bipyramidal coordination environment, with two O atoms of the pyrazolone rings and a water O atom in the equatorial plane and two N atoms in axial positions [N—Cu—N = 159.34 (16)°]. The complex occupies a special position on a twofold axis running through the Cu atom and the water O atom. The Cu—O(H_2O) bond [2.549 (4) Å] is substantially longer than the rest of the bonds in the coordination polyhedron [Cu—O = 1.919 (2) Å and Cu—N = 1.990 (3) Å]. The pyrazolone ring is almost coplanar with the adjacent chelate ring, the dihedral angle formed by the mean plane of the pyrazolone ring and the planar part of the chelate ring being 2.91 (3)°.

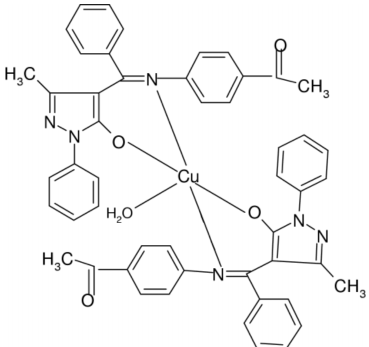
Key indicators

Single-crystal X-ray study
T = 293 K
Mean σ(C–C) = 0.008 Å
H-atom completeness 96%
R factor = 0.055
wR factor = 0.096
Data-to-parameter ratio = 10.4

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

Comment

Schiff base compounds are relatively easy to obtain and they frequently show high biological activity. Therefore, studies of Schiff bases and their metal complexes are the focal point of many research groups working in the fields of coordination chemistry, biomedicine and pharmaceutical chemistry (Vigoto, 1987).



(I)

4-Acyl-5-pyrazolones are enolizable β-diketones which afford stable chelate complexes with several metals (Miyazaki *et al.*, 1989; Morales *et al.*, 1988). A number of compounds derived from 4-acyl-5-pyrazolones and aromatic amines have been synthesized (Wang, Yu, Xu & Miao, 2002; Wang, Yu, Yang & Miao, 2002; Yu *et al.*, 2002). The ligand prepared by condensation of 1-phenyl-3-methyl-4-benzoyl-5-pyrazolone (PMBP) with p-aminoacetophenone was used for the synthesis of the title copper complex, (I), the structure of which is reported here.

The molecule has crystallographic twofold rotation symmetry, the axis passing through Cu1 and the coordinated water molecule. Atom Cu1 has a distorted trigonal-bipyramidal environment, with atoms N3 and N3^{i} [symmetry code:

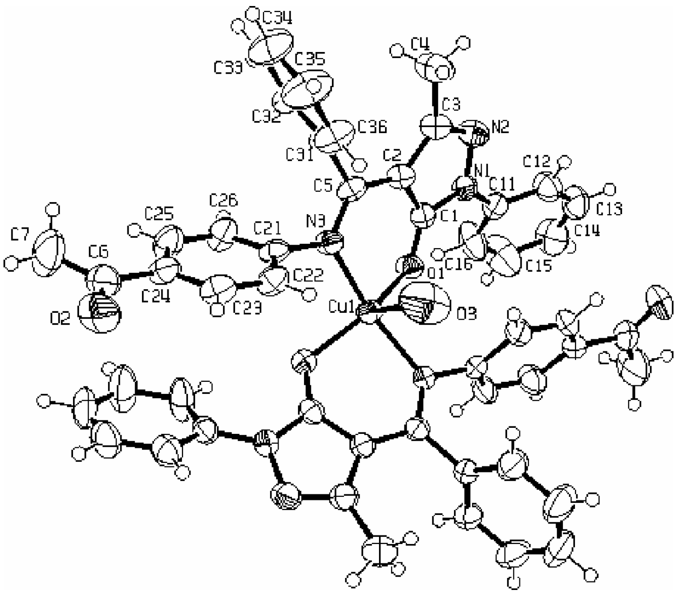


Figure 1
The molecular structure of (I), shown with 50% probability displacement ellipsoids.

(i) $-x, y, \frac{3}{2}-z$] in axial positions [N3—Cu1—N3^{i} = 159.34 (16)°] and both pyrazolone and water O atoms (O1, O1^{i} and O3) in the equatorial plane (Fig. 1). The Cu1—O3 bond [2.549 (4) Å] is substantially longer than other bonds in the coordination sphere of the Cu1 atom [Cu1—O1 = 1.919 (2) Å and Cu1—N3 = 1.990 (3) Å], which would be typical for square-planar Cu^{2+} complexes with additional coordination [4 + 1]. However, the description of the coordination as square-pyramidal, though in some sense logical, would be geometrically inaccurate, as the CuO_2N_2 fragment shows a pronounced tetrahedral distortion [O1—Cu1—O1^{i} = 144.56 (14)°]. A pentacoordinated copper complex similar to (I) was recently reported for the thiosemicarbazide derivative, aqua(3-hydroxy-5-hydroxymethyl-2-methyl-pyridine-4-carboxaldehyde 3-methylisothiosemicarbazone)(nitrato)-copper(II) nitrate (Leovac *et al.*, 2002).

The earlier studied PMBP complexes, however, had metal centers with higher coordination numbers [*e.g.* $(PMBP)_2Sn(t\text{-}C_4H_9)_2$ (Pettinari *et al.*, 1991) and $(PMBP)_2SnMe_2$ (Bovio *et al.*, 1993)].

The chelate ring Cu1—O1—C1—C2—C5—N3 has a sofa conformation with Cu1 displaced by 0.617 (4) Å from the mean O1/C1/C2/C5/N3 plane [maximum deviation of 0.042 (2) Å for atom C5]. The latter plane is almost coplanar with the mean pyrazolone ring plane; the dihedral angle formed by these planes [2.91 (3)°] is close to analogous dihedral angles in the Co(PMBP-*m*-chloroaniline) complex [2.47 (5) and 1.69 (6)°; Wang *et al.*, 2003]. Owing to steric hindrance, the chelate ring plane is nearly orthogonal to the rings planes C21–C26 and C31–C36 [respective dihedral angles are 84.39 (10) and 77.29 (9)°].

Though it was impossible to locate the water H atoms, it seems very likely that the intermolecular O2···O3^{ii} 2.725 (4) Å contact [symmetry code: (ii) $\frac{1}{2}+x, \frac{1}{2}-y, \frac{1}{2}+z$], in fact, corresponds to a hydrogen bond. These bonds link the molecules into infinite chains along the [101] direction.

Experimental

A mixture of 10 ml of 0.1 *M* *p*-aminoacetophenone ethanol solution and 10 ml of 0.1 *M* PMBP ethanol solution was refluxed for 4 h over a steam bath. The excess solvent was removed by evaporation. The Schiff base ligand was collected as a cream-colored powder and dried in air. 10 ml of 0.1 *M* $Cu(NO_3)_2\cdot H_2O$ ethanol solution was added dropwise to 10 ml of a 0.2 *M* solution of the ligand in ethanol. After vigorous stirring for 6–8 h at 343–353 K, a dark-brown product precipitated; this was filtered off, washed with cold anhydrous ethanol solution several times and dried in a vacuum desiccator over $CaCl_2$. The Cu complex was recrystallized from ethanol solution. Elemental analyses for *L* and CuL_2 respectively are as follows (calculated values in parentheses): C 76.60 (76.12) and 69.15 (69.00)%, H 5.41 (5.11) and 5.12 (4.86), N 10.81 (10.65) and 10.13 (9.66)%. IR spectra in the region 4000–400 cm^{-1} were determined with a KBr pellet on an AVATAR 360 (USA) IR spectrophotometer. The C═O absorption bands, observed at 1637 and 1505 cm^{-1} for PMBP, shifted to 1672 and 1662 cm^{-1} for the uncoordinated ligand, and to 1660 and 1630 cm^{-1} for the complex; the C═N absorption bands, observed at 1572 and 1541 cm^{-1} in the ligand, red shifted to 1570 and 1533 cm^{-1} in the complex, indicating that the carbonyl O and imine N atoms of the ligand are coordinated to the Cu atom in the complex.

Crystal data

$[Cu(C_{25}H_{20}N_3O_2)_2(H_2O)]$
$M_r = 870.35$
Monoclinic, $C2/c$
$a = 22.652$ (6) Å
$b = 16.228$ (5) Å
$c = 15.250$ (5) Å
$\beta = 130.636$ (14)°
$V = 4254$ (2) Å^3
$Z = 4$
$D_x = 1.359$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 790 reflections
$\theta = 2.3$–20.9°
$\mu = 0.57$ mm^{-1}
$T = 293$ (2) K
Block, dark brown
0.28 × 0.25 × 0.22 mm

Data collection

Bruker SMART 1000 CCD area-detector diffractometer
φ and ω scans
Absorption correction: none
8399 measured reflections
3765 independent reflections
2050 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.085$
$\theta_{\rm max} = 25.0°$
$h = -26 \rightarrow 25$
$k = -17 \rightarrow 19$
$l = -9 \rightarrow 18$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.055$
$wR(F^2) = 0.096$
$S = 0.97$
3765 reflections
362 parameters
All H-atom parameters refined
$w = 1/[\sigma^2(F_o^2) + (0.0266P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\rm max} = 0.001$
$\Delta\rho_{\rm max} = 0.27$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.27$ e Å^{-3}
Extinction correction: *SHELXL*97
Extinction coefficient: 0.00032 (12)

All aryl and methyl H atoms were located in a difference map and refined with isotropic displacement parameters [C—H = 0.83 (4)–1.02 (4) Å]. The H atoms of the aqua ligand (O3) were not located.

Data collection: *SMART* (Bruker, 1998); cell refinement: *SAINT* (Bruker, 1999); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *ORTEP*-3 *for Windows* (Farrugia, 1997); software used to prepare material for publication: *WinGX* (Farrugia, 1999).

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