[N,N'-Bis(salicylidene)-1,4-diimino-butane]copper(II)

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(I)

Abstract

In the title compound, {2,2'-[1,4-butanediylbis-(nitrilomethylidyne)]diphenolato-O,N,N',O'}copper(II), $[Cu(C_{18}H_{18}N_2O_2)]$, the Cu atom is coordinated by an N_2O_2 donor set from the imine–phenol ligand in a distorted planar coordination geometry, with the two phenolate O atoms being deprotonated. The Cu—O bond lengths are 1.898 (3) and 1.903 (3) Å, and the Cu—N bond lengths are 1.941 (3) and 2.000 (3) Å. The angles O1—Cu—N2 and O2—Cu—N1 are 144.0 (1) and 153.3 (1)°, respectively. The dihedral angle between the two salicylaldiminato groups around the central Cu atom is 42.7 (1)°.

Comment

The development of a $^{62}Zn/^{62}Cu$ radionuclide generator increases the potential utility of Cu-labeled radiopharmaceuticals as imaging agents in positron emission tomography (PET). ^{62}Cu–PTSM [PTSM is pyruvaldehyde bis(4-methylthiosemicarbazone)], a neutral and lipophilic Cu^{II} complex, has been investigated as a potential Cu tracer for imaging the heart and brain (Green, 1987). Additionally, neutral and lipophilic complexes of ^{67}Cu with a series of tetradentate Schiff base N_2O_2 ligands have also been evaluated as to their potential as cerebral blood-flow imaging agents (John, Bott & Green, 1994).

The chemistry of metal complexes with Schiff base ligands and their application have aroused considerable attention, mainly because of preparative accessibility, diversity and structural variability. For example, there has been interest in Cu^{II}–imine–phenols because of their color isomerism (Llewellyn & Waters, 1960; Hall & Waters, 1960), conformational influences (Clark, Hall & Waters, 1969; Baker, Hall & Waters, 1970a,b; Bhadbhade & Srinivas, 1993) and their potential as radiopharmaceuticals (John, Bott & Green, 1994). We describe here the synthesis and characterization of the title complex, (I).
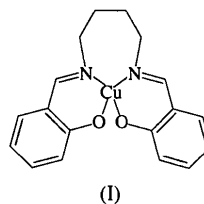
In (I), the coordination geometry about the Cu atom consists of a 6–7–6 chelate ring structure and a distorted coordination plane composed of two imine N atoms and two phenol O atoms. The molecule is neutral by deprotonation of the phenolic groups. The Cu—O bond lengths are 1.898 (3) and 1.903 (3) Å for Cu—O1 and Cu—O2, respectively, while the Cu—N bond lengths are 2.000 (3) and 1.941 (3) Å for Cu—N1 and Cu—N2, respectively. These values fall in the ranges 1.886–1.945 Å for Cu—O and 1.904–2.000 Å for Cu—N reported for analogs (Hall & Waters, 1960; Llewellyn & Waters, 1960; Baker, Hall & Waters, 1970a,b; Bhadbhade & Srinivas, 1993; Cheeseman, Hall & Waters, 1966).

Perhaps the most interesting comparative aspect of Cu complexes with imine–phenols involves the steric influence of the alkyl backbone upon the molecular structure. The Cu atom is displaced by 0.073 (2) Å above the best coordination plane (O1, O2, N1, N2). N1 and O2 are on the same side of the plane as Cu at distances of 0.453 (4) and 0.556 (4) Å, respectively, while N2 and O1 are on the opposite side at distances of 0.461 (4) and 0.556 (4) Å, respectively. The puckering resulting from the butyl group is significantly different from that of a normal square plane in, for example, [N,N'-bis(salicylidene)-1,2-diiminoethane]copper(II) with an ethyl backbone (Baker, Hall & Waters, 1970a). An alternative way of expressing the conformational variance is to note the expansion of the N—Cu—N angles [100.1 (1)°] from 90° and the compression of both trans-O—Cu—N angles [144.0 (1) and 153.3 (1)°] from 180°. As a
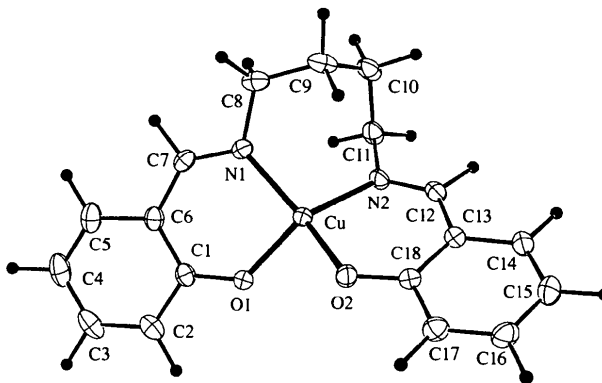

Fig. 1. A perspective view (ORTEPII; Johnson, 1976) of the title molecule with the atom-numbering scheme. Displacement ellipsoids are drawn at the 30% probability level.

result, the dihedral angle between the two planes defined by Cu, O1, N1 and Cu, O2, N2 is 42.7 (1)°, which is larger than that in [N,N'-bis(salicylidene)-2,2'-diiminobenzidine]copper(II) (37°), an analog with a 6–7–6 chelate ring structure (Cheeseman, Hall & Waters, 1966).

Experimental

N,N'-Bis(salicylidene)-1,4-diiminobutane was prepared by condensation of salicylaldehyde (60 mmol) and 1,4-butanediamine (30 mmol) in 100 ml of ethanol. The reaction mixture was stirred for 6 h and then placed in a freezer for 24 h. The yellow precipitate was collected by filtration and then washed with cold ethanol. After recrystallization yellow crystals with high purity were harvested and dried *in vacuo*. Copper(II) nitrate trihydrate (3 mmol) in 95% ethanol (20 ml) and N,N'-bis(salicylidene)-1,4-diiminobutane (3 mmol) in ethanol (100 ml) were mixed and heated at 333 K for 1 h. The solution was filtered and the filtrate kept in a beaker at 277 K for crystallization. Dark-blue crystals started appearing after 1–2 d and were then collected by filtration. Crystals suitable for X-ray diffraction were obtained by slow evaporation from a saturated ethanolic solution.

Crystal data

[Cu(C$_{18}$H$_{18}$N$_2$O$_2$)]
M_r = 357.90
Orthorhombic
Pbca
a = 10.3733 (10) Å
b = 14.724 (3) Å
c = 20.4710 (10) Å
V = 3126.6 (6) Å^3
Z = 8
D_x = 1.521 Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
λ = 0.7093 Å
Cell parameters from 25 reflections
θ = 7.50–16.56°
μ = 1.41 mm^{-1}
T = 293 K
Rhombohedron
0.49 × 0.25 × 0.16 mm
Dark blue

Data collection

Enraf–Nonius CAD-4 diffractometer
$\theta/2\theta$ scan
Absorption correction:
   empirical *via* ψ scans (North, Phillips & Mathews, 1968)
   T_{min} = 0.699, T_{max} = 0.798
3580 measured reflections
3580 independent reflections

2218 reflections with
   $I_{net} > 2.5\sigma(I_{net})$
θ_{max} = 27.41°
$h = 0 \rightarrow 13$
$k = 0 \rightarrow 19$
$l = 0 \rightarrow 26$
3 standard reflections
   frequency: 60 min
   intensity decay: 1.0%

Refinement

Refinement on F
R = 0.040
wR = 0.032
S = 2.19
2218 reflections
209 parameters
H atoms: see below
$w = 1/\sigma^2(F)$
$(\Delta/\sigma)_{max} < 0.001$

$\Delta\rho_{max}$ = 0.38 e Å^{-3}
$\Delta\rho_{min}$ = −0.44 e Å^{-3}
Extinction correction:
   Larson (1970)
Extinction coefficient:
   0.58 (3)
Scattering factors from *International Tables for X-ray Crystallography* (Vol. IV)

Table 1. *Selected geometric parameters (Å, °)*

Cu—O1	1.898 (3)	Cu—N1	2.000 (3)
Cu—O2	1.903 (3)	Cu—N2	1.941 (3)
O1—Cu—O2	87.38 (11)	Cu—O1—C1	129.0 (2)
O1—Cu—N1	94.29 (12)	Cu—O2—C18	128.0 (2)
O1—Cu—N2	144.00 (12)	Cu—N1—C7	120.8 (3)
O2—Cu—N1	153.28 (12)	Cu—N1—C8	125.7 (3)
O2—Cu—N2	93.85 (12)	Cu—N2—C11	118.2 (2)
N1—Cu—N2	100.12 (13)	Cu—N2—C12	125.2 (3)

H atoms were located in calculated positions. Refinement was by full-matrix least squares, with H atoms riding on the atoms to which they were bonded.

Data collection: *CAD-4 Software* (Enraf–Nonius, 1989). Cell refinement: *CAD-4 Software*. Data reduction: *NRCVAX DATRD2* (Gabe, Le Page, Charland, Lee & White, 1989). Program(s) used to solve structure: *NRCVAX SOLVER*. Program(s) used to refine structure: *NRCVAX LSTSQ*. Molecular graphics: *NRCVAX* and *ORTEP*II (Johnson, 1976). Software used to prepare material for publication: *NRCVAX TABLES* (version of January 1994).

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