Acta Crystallographica Section E
Structure Reports Online
ISSN 1600-5368

(Piperidine-κN)[*N*-(salicylidene)phenylalaninato-$\kappa^3 O,N,O'$]copper(II)

Ray J. Butcher,[a]* Garry M. Mockler[b] and Owen McKern[b]

[a]Department of Chemistry, Howard University, 525 College Street NW, Washington, DC 20059, USA, and [b]Department of Chemistry, University of Wollongong, NSW 2522, Australia

Correspondence e-mail: rbutcher@howard.edu

Key indicators

Single-crystal X-ray study
T = 293 K
Mean σ(C–C) = 0.005 Å
R factor = 0.036
wR factor = 0.082
Data-to-parameter ratio = 14.7

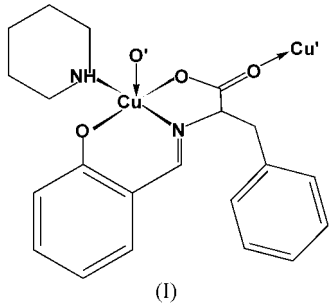
For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

Received 20 December 2002
Accepted 6 January 2003
Online 24 January 2003

The tridentate Schiff base ligand derived from the condensation of salicylaldehyde and L-phenylalanine, in the presence of piperidine, when reacted with copper sulfate pentahydrate, forms a polymeric square pyramidal five-coordinate copper complex, [Cu($C_{17}H_{14}O_3$)($C_4H_{10}N_2$)]. The axial position of the square pyramid is occupied by the carboxyl O atoms of a neighboring molecule.

Comment

Galactose oxidase is a type II copper protein that catalyses the oxidation of primary alcohols to aldehydes with a concomitant reduction of molecular oxygen (Whittaker, 1994). Its crystal structure (Ito *et al.*, 1994) reveals a unique mononuclear Cu site with two N donors (from histidine imidazole groups), two O donors (one axial and one equatorial tyrosine group), and an exogenous water or acetate molecule, all arranged in a distorted square-pyramidal coordination. Several different theories have been proposed to explain how galactose oxidase, which contains a single Cu atom, can catalyse a two-electron redox reaction. The currently accepted theory (Whittaker & Whittaker, 2001) suggests that the 'inactive' form of galactose oxidase is oxidized by the loss of one electron to produce the 'active' form, which contains a tyrosine (tyrosine 272) free radical ion coupled to the Cu^{II} ion. The active form is then reduced to the Cu^{I} species and the alcohol oxidized to the corresponding aldehyde.



(I)

There has been considerable interest in the study of model compounds of galactose oxidase in recent years (Butcher *et al.*, 2003*a*,*b*; Kruse *et al.*, 2002; Shimazaki *et al.*, 2002; Thomas *et al.*, 2002). One group of compounds that has attracted considerable interest consists of five-coordinate copper complexes with tridentate Schiff base ligands derived from the condensation of amino acids with substituted salicylaldehydes. In this type of complex, the Cu coordination sphere also contains a monodentate Lewis base. With two exceptions (Plesch *et al.*, 1997; Sivy *et al.*, 1994), X-ray crystallographic studies have shown that these Cu^{II} compounds contain Cu^{II} in a distorted square-

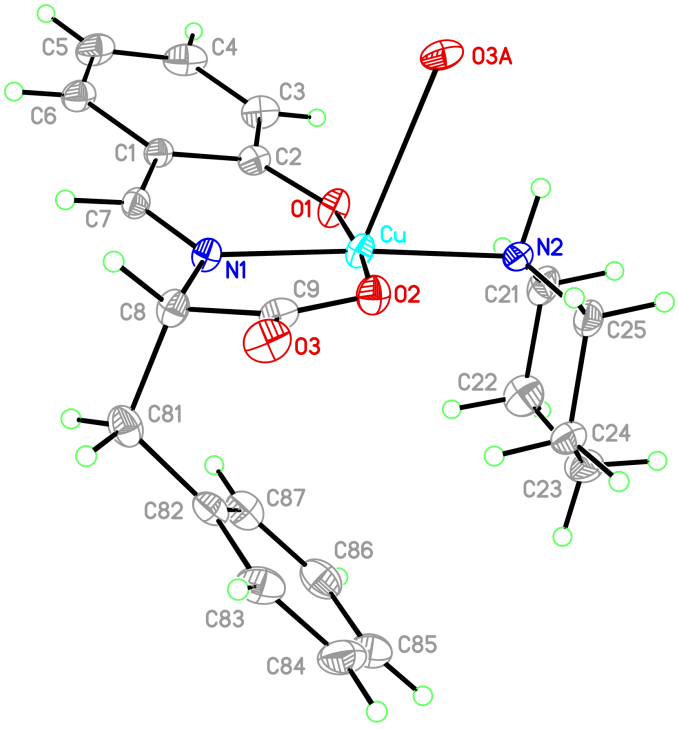


Figure 1
View of the coordination sphere of the Cu, showing the atom-labeling scheme. Displacement ellipsoids are drawn at the 20% probability level. H atoms are represented by circles of arbitrary size.

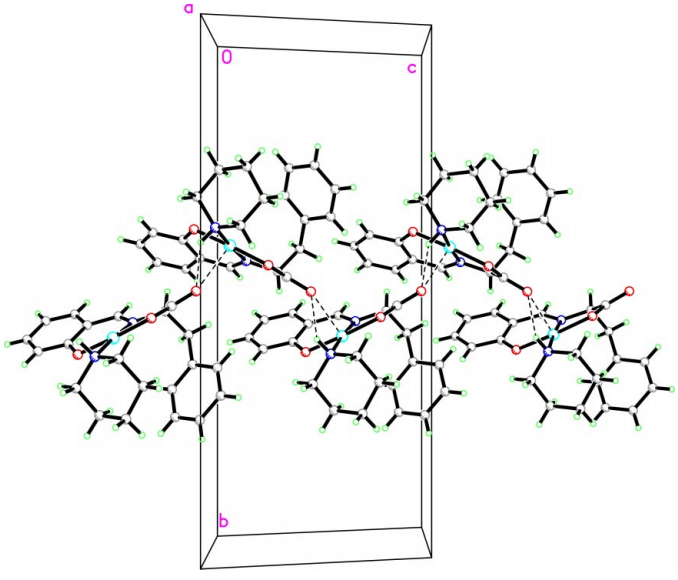


Figure 2
The molecular packing viewed along the *a* axis, showing the zigzag chain of complexes in the *c* direction, linked through the carboxyl O atoms.

pyramidal environment and fit into three main types:

(i) monomeric with a water molecule occupying the fifth coordination site (Butcher *et al.*, 2003*a*; Dawes *et al.*, 1982; Fujimaki *et al.*, 1971; Garcia-Raso *et al.*, 1996; Korhonen & Hamalainen, 1979; Ueki *et al.*, 1969; Warda *et al.*, 1996; Warda, 1997*g*; Warda, 1998*a*,*d*,*e*,*f*);

(ii) dimeric with an adjacent phenolic O atom occupying the fifth coordination site (Butcher *et al.*, 2003*b*; Davies, 1984; Hamalainen *et al.*, 1978; Hill & Warda, 1999; Warda, 1997*a*,*e*; Warda, 1998*b*,*c*,*e*,*g*; Warda, 1999; Warda *et al.*, 1998);

(iii) polymeric with the fifth coordination site occupied by an adjacent carboxyl O atom (Ueki *et al.*, 1967; Kettman *et al.*, 1993; Korhonen *et al.*, 1984; Plesch *et al.*, 1998; Warda *et al.*, 1997; Warda, 1997*a*,*b*,*c*,*d*,*f*; Sivy *et al.*, 1990).

The tridentate Schiff base ligand derived from the condensation of salicylaldehyde and L-phenylalanine, in the presence of piperidine, forms a square-pyramidal five-coordinate Cu complex, (I), of type iii. In this complex, the carboxyl O from an adjacent molecule occupies the apical site, at a distance of 2.674 (2) Å, forming a polymeric zigzag chain in the *c* direction. Unlike other square-pyramidal five-coordinate analogs, in this example, the Cu is only slightly displaced [0.012 (1) Å] from the basal plane formed by atoms O1, O2, N1, and N2, due to the comparatively weak out-of-plane bond to a neighboring carbonyl O donor. Neither the Cu—O1, Cu—O2, and Cu—N1 bond distances [1.918 (2), 1.964 (2), and 1.935 (2) Å, respectively] nor the Cu—N2 bond distance [2.002 (3) Å] differ significantly from those of similar type iii polymeric compounds mentioned above.

Experimental

The title complex was synthesized in two stages. In the first stage, 10 g of L-phenylalanine (phenala) and an equimolar amount of sodium hydroxide were dissolved in 300 ml of hot water. To this solution was added an equimolar quantity of copper sulfate pentahydrate dissolved in 100 ml of water. The blue–purple $[Cu(phenala)_2]\cdot nH_2O$ compound precipitated on cooling the solution. 6 g of this compound, two mole equivalents of salicylaldehyde, triethylamine (10 ml) and piperidine (10 ml) were refluxed in methanol for 1 h. The hot solution was filtered and allowed to stand until the dark green product precipitated from solution. X-ray quality crystals were grown by slow evaporation from a methanol–acetonitrile solution.

Crystal data

$[Cu(C_{17}H_{14}O_3)(C_4H_{10}N_2)]$
M_r = 415.96
Monoclinic, *Cc*
a = 8.7002 (9) Å
b = 22.6624 (15) Å
c = 9.9711 (8) Å
β = 106.010 (7)°
V = 1889.7 (3) Å^3
Z = 4
D_x = 1.462 Mg m^{-3}
Mo *K*α radiation
Cell parameters from 72 reflections
θ = 5.3–14.0°
μ = 1.18 mm^{-1}
T = 293 (2) K
Chunk, dark green
0.58 × 0.28 × 0.20 mm

Data collection

Siemens *P4S* diffractometer
ω scans
Absorption correction: ψ scan (North *et al.*, 1968)
T_{min} = 0.338, T_{max} = 0.475
3692 measured reflections
3609 independent reflections
2912 reflections with $I > 2\sigma(I)$
R_{int} = 0.000
θ_{max} = 32.5°
h = −13 → 0
k = 0 → 34
l = −14 → 15
3 standard reflections
every 97 reflections
intensity decay: 1%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.036$
$wR(F^2) = 0.082$
$S = 1.02$
3609 reflections
245 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0338P)^2 + 0.1576P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.002$
$\Delta\rho_{max} = 0.21$ e Å^{-3}
$\Delta\rho_{min} = -0.21$ e Å^{-3}
Extinction correction: *SHELXL*
Extinction coefficient: 0.0019 (5)
Absolute structure: Flack (1983), 180 Friedel pairs
Flack parameter = −0.001 (13)

Table 1
Selected geometric parameters (Å, °).

Cu—O1	1.918 (2)	Cu—N2	2.022 (3)
Cu—N1	1.935 (2)	Cu—O3*A*	2.674 (2)
Cu—O2	1.964 (2)		
O1—Cu—N1	91.49 (10)	O2—Cu—N2	94.24 (11)
O1—Cu—O2	173.91 (10)	O3*A*—Cu—O1	92.3 (1)
N1—Cu—O2	82.65 (10)	O3*A*—Cu—O2	88.1 (1)
O1—Cu—N2	91.69 (11)	O3*A*—Cu—N1	109.7 (1)
N1—Cu—N2	175.76 (11)	O3*A*—Cu—N2	73.0 (1)

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

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N2—H2*A*···O3^{i}	0.91	2.24	2.841 (4)	123

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

All H atoms were included in calculated positions with C—H distances ranging from 0.93 to 0.98 Å and N—H distances of 0.91 Å. The H atoms were then included in the refinement using a riding-motion approximation, with $U_{iso} = 1.2U_{eq}$ of the carrier atom.

Data collection: *XSCANS* (Siemens, 1994); cell refinement: *XSCANS*; data reduction: *XSCANS*; program(s) used to solve structure: *SHELXTL* (Sheldrick, 1997); program(s) used to refine structure: *SHELXTL*; molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL*.

RJB acknowledges the DoD ONR program for funds to upgrade his diffractometer.

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