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Aqua(pyridine-κN)(*N*-salicylidenetyrosinato-$\kappa^3 O,N,O'$)copper(II)

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Key indicators

Single-crystal X-ray study
T = 293 K
Mean σ(C–C) = 0.003 Å
R factor = 0.031
wR factor = 0.082
Data-to-parameter ratio = 16.6

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

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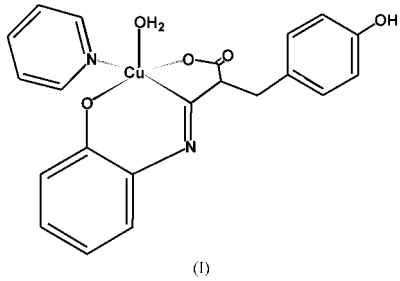
The tridentate Schiff base ligand derived from the condensation of salicylaldehyde and DL-tyrosine, in the presence of pyridine, forms a square-pyramidal five-coordinate Cu complex, $[Cu(C_{16}H_{13}NO_4)(C_5H_5N)(H_2O)]$, with a water molecule occupying the apical site.

Comment

Galactose oxidase is a type-II Cu protein that catalyses the oxidation of primary alcohols to aldehydes with 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 (Kruse *et al.*, 2002; Shimazaki *et al.*, 2002; Thomas *et al.*, 2002). One group of compounds that have attracted considerable interest consists of five-coordinate Cu 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-pyramidal environment and fit into three main types:

(i) monomeric with a water molecule occupying the fifth coordination site (Dawes *et al.*, 1982; Fujimaki *et al.*, 1971;

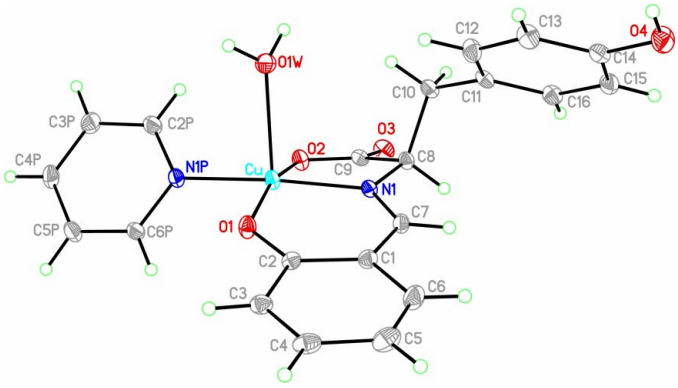


Figure 1
View of the title complex, showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 20% probability level. H atoms are represented by circles of arbitrary size.

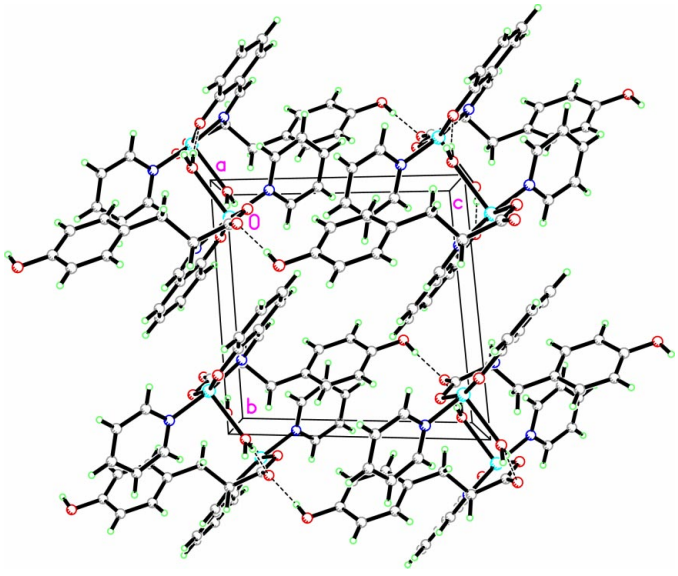


Figure 2
The molecular packing viewed along the *a* axis.

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 (Davies, 1984; Hamalainen *et al.*, 1978; Hill & Warda, 1999; Warda, 1997*e*; Warda, 1998*b*,*c*,*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 DL-tyrosine, in the presence of pyridine, forms a square pyramidal five-coordinate Cu complex of type (i) with a water molecule occupying the apical site at a distance of 2.375 (2) Å. Cu is displaced by 0.1861 (8) Å from the basal plane formed by O1, O2, N, and N1*P*. The Cu—O1, Cu—O2, and Cu—N1 bond distances in the equatorial plane [1.919 (1), 1.989 (1), and 1.939 (2) Å, respectively] do not differ significantly from those of similar dinuclear compounds mentioned above. Both the water molecule and the tyrosine phenolic group participate in strong hydrogen bonding interactions with the C=O groups of adjoining molecules, while the water molecule also forms a hydrogen bond to O1 from an adjoining molecule (see Table 2 and Fig. 2).

Experimental

The title complex was synthesized in two stages. In the first stage, 10 g of DL-tyrosine 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 compound $[Cu(tyr)_2]\cdot nH_2O$ precipitated on cooling the solution. 6 g of this compound, two mole equivalents of salicylaldehyde, triethylamine (10 ml) and pyridine (10 ml) were refluxed in methanol for one hour. 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

$[Cu(C_{16}H_{13}NO_4)(C_5H_5N)(H_2O)]$
M_r = 443.93
Triclinic, $P\overline{1}$
a = 10.0319 (13) Å
b = 10.0487 (11) Å
c = 10.1973 (14) Å
α = 81.973 (10)°
β = 72.624 (9)°
γ = 78.310 (9)°
V = 957.3 (2) Å^3
Z = 2
D_x = 1.540 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 42 reflections
θ = 4.8–17.3°
μ = 1.18 mm^{-1}
T = 293 (2) K
Plate, blue
0.58 × 0.46 × 0.15 mm

Data collection

Siemens *P4S* diffractometer
$2\theta/\omega$ scans
Absorption correction: by integration (Wuensch & Prewett, 1965)
T_{min} = 0.688, T_{max} = 0.883
4594 measured reflections
4347 independent reflections
3782 reflections with $I > 2\sigma(I)$
R_{int} = 0.021
θ_{max} = 27.5°
$h = 0 \rightarrow 12$
$k = -12 \rightarrow 13$
$l = -12 \rightarrow 13$
3 standard reflections
every 97 reflections
intensity decay: 0.1%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.031
$wR(F^2)$ = 0.082
S = 1.06
4347 reflections
262 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0343P)^2 + 0.4004P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.001
$\Delta\rho_{max}$ = 0.35 e Å^{-3}
$\Delta\rho_{min}$ = −0.27 e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

Cu—O1	1.9187 (14)	Cu—N1*P*	2.0086 (16)
Cu—N1	1.9394 (15)	Cu—O1*W*	2.3745 (15)
Cu—O2	1.9889 (14)		
O1—Cu—N1	93.61 (6)	O2—Cu—N1*P*	91.28 (6)
O1—Cu—O2	164.17 (6)	O1—Cu—O1*W*	99.82 (6)
N1—Cu—O2	83.13 (6)	N1—Cu—O1*W*	95.24 (6)
O1—Cu—N1*P*	90.30 (6)	O2—Cu—O1*W*	95.91 (6)
N1—Cu—N1*P*	172.18 (7)	N1*P*—Cu—O1*W*	90.76 (6)

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

D—H···A	D—H	H···A	D···A	D—H···A
O1W—H1W1···O1^{i}	0.87	1.92	2.793 (2)	175
O1W—H1W2···O3^{ii}	0.86	2.07	2.930 (2)	176
O4—H4···O3^{iii}	0.82	1.89	2.705 (2)	175

Symmetry codes: (i) $-x, -y, -z$; (ii) $1-x, -y, -z$; (iii) $x, y, z-1$.

All H atoms were included in calculated positions, with C—H distances ranging from 0.93 to 0.98 Å. The H atoms were then included in the refinement in riding-motion approximation, with $U_{iso} = 1.2U_{eq}$ of the carrier atom. The H atoms of the coordinated water molecule were located in a difference Fourier map and were refined with restrained O—H distances but an unrestrained H—O—H angle.

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*.

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