Aqua(pyridine-kN)(N-salicylidene tyrosinaot-k3 O,N,O')copper (II)

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Abstract
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.

Keywords
kn, n, k3, o, copper, aqua, ii, pyridine, salicylidenetyrosinaot

Disciplines
Medicine and Health Sciences | Social and Behavioral Sciences

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Aqua(pyridine-κN)(N-salicyldenetylrosinato-κ3O,N,O')copper(II)

The tridentate Schiff base ligand derived from the condensation of salicylaldehyde and d,l-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 CuII ion. The active form is then reduced to the CuI species and the alcohol oxidized to the corresponding aldehyde.

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 CuII compounds contain CuII 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;
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)$_2$]$_n$nH$_2$O 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 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$_5$H$_5$N)(H$_2$O)]

$M_f = 443.93$

Triclinic, $Par{1}$

$a = 10.0319 (13)$ Å

$b = 10.0487 (11)$ Å

$c = 10.1973 (14)$ Å

$\alpha = 81.973 (10)^\circ$

$\beta = 77.624 (9)^\circ$

$\gamma = 78.310 (9)^\circ$

$V = 957.3 (2)$ Å$^3$

$Z = 2$

$D_x = 1.540$ Mg m$^{-3}$

Mo $K\alpha$ radiation

Cell parameters from 42 reflections

min = 0.688, max = 0.883

4594 measured reflections

4347 independent reflections

3782 reflections with $I > 2\sigma(I)$

**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

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu–O1</td>
<td>1.9187 (14)</td>
</tr>
<tr>
<td>Cu–N1P</td>
<td>2.0086 (16)</td>
</tr>
<tr>
<td>Cu–N1</td>
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</tr>
<tr>
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<td>1.9889 (14)</td>
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<td>172.18 (7)</td>
</tr>
</tbody>
</table>

Selected geometric parameters (Å, °).

**Data collection**

Siemens P45 diffractometer

28780 scans

Absorption correction: by integration (Wuensch & Prewett, 1965)

$T_{	ext{min}} = 0.688, T_{	ext{max}} = 0.883$

4594 measured reflections

4347 independent reflections

3782 reflections with $I > 2\sigma(I)$

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included in the refinement in riding-motion approximation, with distances ranging from 0.93 to 0.98 A. The H atoms were then refined with restrained O–H distances but an unrestrained H–O–H angle.

All H atoms were included in calculated positions, with C–H distances ranging from 0.93 to 0.98 A. 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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References