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catena-Poly[[(pyridine-κN)copper(II)]-μ-*N*-salicylideneglycinato-$\kappa^4 O,N,O':O'$]

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Key indicators

Single-crystal X-ray study
T = 293 K
Mean σ(C–C) = 0.004 Å
R factor = 0.032
wR factor = 0.086
Data-to-parameter ratio = 14.9

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

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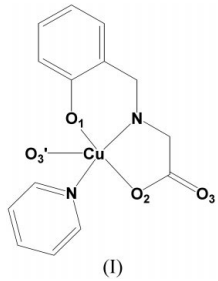
The tridentate Schiff base ligand derived from the condensation of salicylaldehyde and glycine, in the presence of pyridine, forms the title polymeric square-pyramidal five-coordinate copper complex, $[Cu(C_5H_5N)(C_9H_7NO_3)(C_5H_5N)]$, in which the copper centers are linked *via* the carboxyl O atoms of neighboring groups occupying the apical site.

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 from one axial and one equatorial tyrosine groups, 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*,*c*; 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-pyramidal environment and are of three

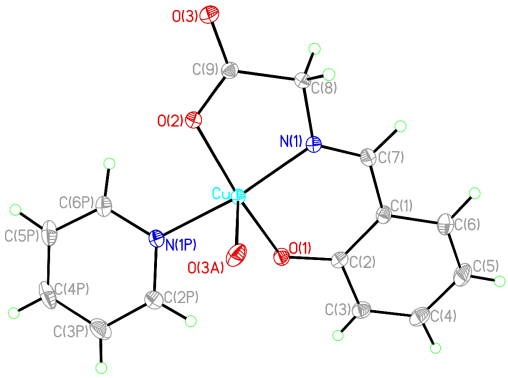


Figure 1
The asymmetric unit of (I), together with the completion of the Cu-atom coordination, showing the atom-labeling scheme. Displacement ellipsoids are drawn at the 20% probability level. H atoms are represented by circles of arbitrary size. Atom O3*A* corresponds to atom O3^{i} in Table 1.

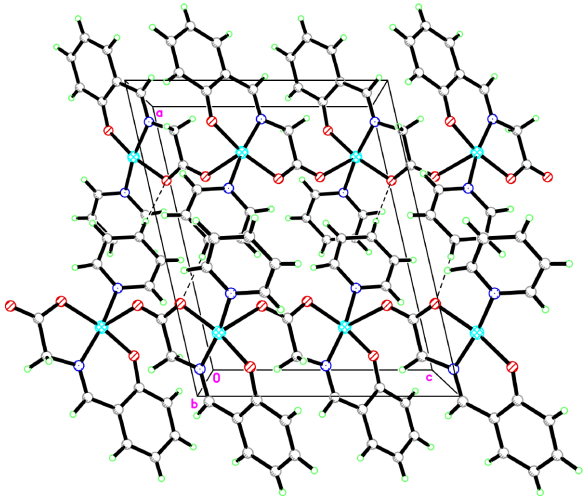


Figure 2
The molecular packing, viewed along the *b* axis, showing the chain of complexes linked through the carboxyl O atoms.

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*, 1998*a*,*d*,*e*,*f*); (ii) dimeric with an adjacent phenolic O atom occupying the fifth coordination site (Butcher *et al.*, 2003*c*; Davies, 1984; Hamalainen *et al.*, 1978; Hill & Warda, 1999; Warda, 1997*b*,*e*, 1998*b*,*c*,*e*,*g*, 1999; Warda *et al.*, 1998); (iii) polymeric with the fifth coordination site occupied by an adjacent carboxyl O atom (Butcher *et al.*, 2003*b*; Ueki *et al.*, 1967; Kettmann *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 glycine, in the presence of pyridine, forms a square-pyramidal five-coordinate Cu complex of type (iii). In this complex, the carboxyl O atom from an adjacent molecule occupies the apical site at a distance of 2.420 (2) Å, forming a polymeric chain in the *b* direction. The Cu atom is displaced by 0.1603 (9) Å from the basal plane formed by atoms O1, O2, N1, and N1*P*. The Cu—O1, Cu—O2 and Cu—N1 bond distances in the equatorial plane [1.928 (2), 1.976 (2) and 1.943 (2) Å, respectively] do not 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 glycine 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 $[Cu(gly)_2].nH_2O$ compound precipitated on cooling. 6 g of this compound, two molar equivalents of salicylaldehyde, triethylamine (10 ml) and pyridine (10 ml) were refluxed in methanol for 1 h. The hot solution was filtered and allowed to stand until a dark-green product precipitated from solution. X-ray quality crystals were grown by slow evaporation of a methanol/acetonitrile solution.

Crystal data

$[Cu(C_5H_5N)(C_9H_7NO_3)(C_5H_5N)]$
M_r = 319.80
Monoclinic, $P2_1/c$
a = 11.8517 (15) Å
b = 11.7867 (17) Å
c = 9.6046 (11) Å
β = 102.929 (8)°
V = 1307.7 (3) Å^3
Z = 4
D_x = 1.624 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 40 reflections
θ = 4.7–12.5°
μ = 1.68 mm^{-1}
T = 293 (2) K
Plate, green
0.79 × 0.63 × 0.12 mm

Data collection

Bruker *P*4 diffractometer
$2\theta/\omega$ scans
Absorption correction: ψ scan
North *et al.*, 1968
T_{min} = 0.447, T_{max} = 0.818
2698 measured reflections
2698 independent reflections
2267 reflections with $I > 2\sigma(I)$
θ_{max} = 27.5°
$h = -15 \rightarrow 15$
$k = 0 \rightarrow 15$
$l = 0 \rightarrow 12$
3 standard reflections
every 97 reflections
intensity decay: 0.2%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.032
$wR(F^2)$ = 0.086
S = 1.05
2698 reflections
181 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0464P)^2 + 0.4318P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.001
$\Delta\rho_{max}$ = 0.42 e Å^{-3}
$\Delta\rho_{min}$ = −0.28 e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

Cu—O1	1.9277 (17)	O1—C2	1.305 (3)
Cu—N1	1.9426 (19)	O2—C9	1.277 (3)
Cu—O2	1.9757 (16)	O3—C9	1.237 (3)
Cu—N1*P*	2.013 (2)	O3—Cu^{ii}	2.4197 (18)
Cu—O3^{i}	2.4197 (18)		
O1—Cu—N1	92.30 (8)	N1*P*—Cu—O3^{i}	87.45 (8)
O1—Cu—O2	169.10 (7)	C2—O1—Cu	127.09 (15)
N1—Cu—O2	83.39 (7)	C9—O2—Cu	116.18 (15)
O1—Cu—N1*P*	90.94 (8)	C9—O3—Cu^{ii}	131.54 (16)
N1—Cu—N1*P*	170.66 (8)	C7—N1—Cu	127.49 (16)
O2—Cu—N1*P*	91.86 (8)	C8—N1—Cu	113.35 (14)
O1—Cu—O3^{i}	98.79 (7)	C2*P*—N1*P*—Cu	120.59 (18)
N1—Cu—O3^{i}	100.69 (7)	C6*P*—N1*P*—Cu	121.86 (17)
O2—Cu—O3^{i}	91.86 (6)		

Symmetry codes: (i) $x, \frac{3}{2} - y, \frac{1}{2} + z$; (ii) $x, \frac{3}{2} - y, z - \frac{1}{2}$.

All H atoms were placed in calculated positions, with C—H distances ranging from 0.93 to 0.98 Å, and included in the refinement as riding, with $U_{iso}(H) = 1.2U_{eq}$ 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*.

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