Crystal structure of *cis*-bis[1-hydroxypyridine-2(1*H*)-thionato-*S*,*O*]copper(II), $Cu(C_5H_4NOS)_2$

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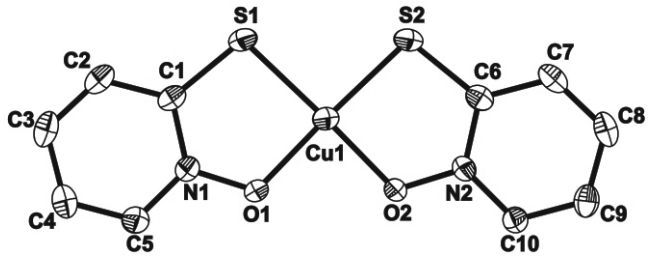

Abstract

$C_{10}H_8CuN_2O_2S_2$, monoclinic, $P12_1/n1$ (no. 14), a = 8.7845(7) Å, b = 13.673(1) Å, c = 9.889(1) Å, β = 97.670(1)°, V = 1177.1 Å^3, Z = 4, $R_{gt}(F)$ = 0.036, $wR_{ref}(F^2)$ = 0.098, T = 298 K.

Source of material

A process for the manufacture of 2-mercaptopyridine-1-oxide (Hmpo) and copper salts thereof, comprising the steps of oxidizing a 2-acetylaminopyridine with hydrogen peroxide in an inert solvent to give a 2-acetamidopyridine-1-oxide, cleaving the acetyl group with mineral acid to give a 2-aminopyridine-1-oxide, diazotizing the 2-aminopyridine-1-oxide and treating the diazonium salt with hydrochloric acid to give a 2-chloropridine-1-oxide, treating the latter with a sulfhydryl-donor to give a 2-mercaptopyridine-1-oxide was applied. A solution of $CuCl_2 \cdot 2H_2O$ (171 mg, 1 mmol) in water (5 mL) was dropped slowly into a solution of Hmpo (254 mg, 2 mmol) in EtOH (15 mL). The mixed solution was stirred for 2 h at 40 °C and then cooled to room temperature to give brown microcrystals, which were collected by filtration, washed successively with H_2O and EtOH, and dried *in vacuo*. Brown square crystals suitable for X-ray analysis were obtained by recrystallization of the precipitate from dichloromethane and ethanol (1:1).

Discussion

A number of structures have been reported for metal complexes of 2-substituted pyridine *N*-oxides [1-3]. These structures show that each ligand chelates to the metal atom via oxygen and the 2-substituted function donor to yield a five-or six-membered complex. We have been interested in the study of metal complexes of 2-mercaptopyridine-1-oxide due to the fact that these complexes have been successfully used as bactericidal and antifungal agents [4-6].

The copper atoms in the $Cu(mpo)_2$ complex are square-planar coordinated in *cis* configuration. In the literature [7], the molecule adopts a *trans*-square-planar configuration, with the Cu atom sited at a crystallographic centre of inversion.

In the title crystal structure, the Cu1 atom is coordinated by two sulfur atoms (d(Cu1—S1) = 2.142 Å; d(Cu1—S2) = 2.137 Å) and two oxygen atoms (d(Cu1—O1) = 1.876 Å; d(Cu1—O2) = 1.874 Å). The mean deviation from the plane constituted from the four coordination atoms around Cu1 was 0.004 Å. The dihedral angle between the Cu1/O1/N1/C1/S1 plane and the Cu1/O2/N2/C6/S2 plane is 3.09(1)°. The ring carbons are the atoms with the greatest deviation from the two planes indicating that the Cu(II) center and donor atoms are nearly co-planar. The two pyridine rings are bent slightly from the above planes by 1.77(2)° and 2.08(2)°, respectively. The angles are ∠S1–Cu1–S2 = 92.79(5)° and ∠O1–Cu1–O2 = 88.28(1)°, showing smaller deviation from a square donor atom arrangement than in $[Cu(6Mmpo)_2]$ (96.0(2)° and 85.8(5)°) [8]. The relatively short distances d(C—S) = 1.716 Å (av.) as observed in $Bi(mpo)_3$ (1.707 Å) and $[Bi(mpo)_2Ph]$ (1.700 Å) reveal partial double bond character, and are nearly 0.1 Å shorter than the distance for a single bond (1.81 Å) [4,9,10]. The angles ∠Cu–S–C = 96.99° (av.) and ∠Cu–O–N = 116.5° (av.) show that the bonding orbital of the sulfur atom is mainly of *p* character, while that of oxygen atom is of sp^2 character, almost the same as that in mpH_2-ligated complexes [11].

Table 1. Data collection and handling.

Crystal:	brown square, size 0.26 × 0.33 × 0.38 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ:	21.98 cm^{-1}
Diffractometer, scan mode:	Bruker SMART, φ/ω
$2\theta_{max}$:	50.04°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	5820, 2077
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\ \sigma(I_{obs})$, 1616
$N(param)_{refined}$:	155
Programs:	SHELXS-97, SHELXL-97 [12]

Table 2. Atomic coordinates and displacement parameters (in Å^2).

Atom	Site	x	y	z	U_{iso}
H(2)	4*e*	0.2859	0.1726	0.1769	0.058
H(3)	4*e*	0.3711	0.0205	0.2446	0.063
H(4)	4*e*	0.6038	0.0046	0.3864	0.063
H(5)	4*e*	0.7423	0.1415	0.4562	0.056
H(7)	4*e*	0.5919	0.7856	0.3621	0.057
H(8)	4*e*	0.8011	0.8587	0.4837	0.061
H(9)	4*e*	1.0019	0.7633	0.5861	0.056
H(10)	4*e*	0.9903	0.5961	0.5638	0.049

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Table 3. Atomic coordinates and displacement parameters (in Å^2).

Atom	Site	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Cu(1)	4*e*	0.60211(5)	0.43819(4)	0.35043(5)	0.0345(3)	0.0423(3)	0.0404(3)	0.0017(2)	–0.0011(2)	0.0022(2)
S(1)	4*e*	0.4051(1)	0.36861(9)	0.2401(1)	0.0354(6)	0.0516(7)	0.0472(7)	0.0015(5)	–0.0082(5)	–0.0015(5)
S(2)	4*e*	0.5158(1)	0.58140(8)	0.2988(1)	0.0396(6)	0.0462(7)	0.0594(8)	0.0075(5)	–0.0068(5)	0.0086(6)
N(1)	4*e*	0.5965(4)	0.2371(2)	0.3589(3)	0.034(2)	0.039(2)	0.036(2)	–0.004(2)	0.004(1)	–0.001(2)
N(2)	4*e*	0.7831(4)	0.5928(2)	0.4528(3)	0.037(2)	0.031(2)	0.040(2)	0.003(1)	0.008(2)	0.001(2)
O(1)	4*e*	0.6839(3)	0.3150(2)	0.4025(3)	0.036(2)	0.037(2)	0.048(2)	–0.002(1)	–0.011(1)	–0.001(1)
O(2)	4*e*	0.7797(3)	0.4946(2)	0.4449(3)	0.036(2)	0.029(2)	0.054(2)	0.001(1)	–0.005(1)	0.003(1)
C(1)	4*e*	0.4604(4)	0.2502(3)	0.2782(4)	0.033(2)	0.053(3)	0.027(2)	–0.005(2)	0.005(2)	–0.003(2)
C(2)	4*e*	0.3781(5)	0.1662(4)	0.2346(4)	0.037(2)	0.066(3)	0.041(3)	–0.013(2)	0.005(2)	–0.006(2)
C(3)	4*e*	0.4285(5)	0.0756(3)	0.2738(5)	0.056(3)	0.052(3)	0.053(3)	–0.022(2)	0.017(2)	–0.010(2)
C(4)	4*e*	0.5673(6)	0.0662(3)	0.3583(5)	0.062(3)	0.039(3)	0.058(3)	–0.005(2)	0.017(2)	0.003(2)
C(5)	4*e*	0.6494(5)	0.1475(3)	0.3996(4)	0.046(2)	0.046(3)	0.046(3)	–0.002(2)	0.001(2)	0.004(2)
C(6)	4*e*	0.6633(5)	0.6453(3)	0.3899(4)	0.041(2)	0.041(2)	0.036(2)	0.008(2)	0.012(2)	0.004(2)
C(7)	4*e*	0.6723(5)	0.7472(3)	0.4033(5)	0.058(3)	0.039(2)	0.047(3)	0.016(2)	0.014(2)	0.007(2)
C(8)	4*e*	0.7968(6)	0.7910(3)	0.4755(5)	0.070(3)	0.031(2)	0.056(3)	0.000(2)	0.021(2)	–0.002(2)
C(9)	4*e*	0.9166(5)	0.7340(3)	0.5366(5)	0.056(3)	0.045(3)	0.043(3)	–0.007(2)	0.015(2)	–0.009(2)
C(10)	4*e*	0.9094(5)	0.6347(3)	0.5240(4)	0.040(2)	0.038(2)	0.044(2)	0.001(2)	0.005(2)	–0.001(2)

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