Crystal structure of di(3-aminopyridine)disalicylatocopper(II), $C_{24}H_{22}CuN_4O_6$

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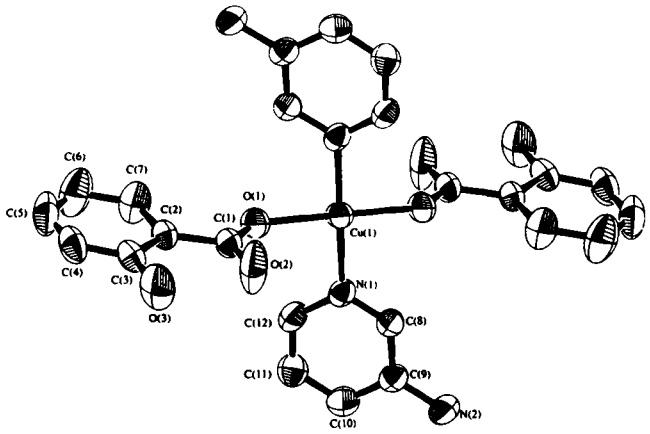

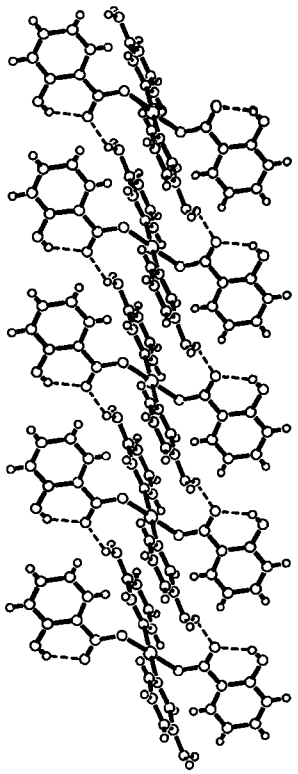

Abstract

$C_{24}H_{22}CuN_4O_6$, monoclinic, $P12_1/c1$ (No. 14), $a = 7.364(2)$ Å, $b = 6.455(1)$ Å, $c = 24.3816(7)$ Å, $\beta = 95.7579(7)°$, $V = 1153.1$ Å^3, $Z = 2$, $R_{gt}(F) = 0.036$, $wR_{ref}(F^2) = 0.044$, T = 296 K.

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Source of material

The title compound synthesized by two layered-solution approach in a tube of ca. 0.8 cm diameter with a 20 cm length. The upper layer was 3 ml of methanol solution of $Cu(CH_3COO)_2 \cdot H_2O$ (0.05 mol/l) and salicylic acid (0.2 mol/l). The bottom layer was 3 ml water solution of 3-aminopyridine (2 mol/l). After some days, crystals were obtained and filtered out.

Elemental analysis for $[Cu(C_7H_5O_3)_2(C_5H_6N_2)_2]$, calculated: C, 54.80%; N, 10.65%; H, 4.22%; found: C, 54.70%; N, 10.62%; H, 4.19%.

Discussion

Salicylate complexes of copper(II) containing N-donor ligands have been studied extensively due to interests from both biological and structural viewpoints [1]. In this paper, we report a new compound $Cu(C_7H_5O_3)_2(C_5H_6N_2)_2$ (**I**). In **I**, the copper atom is four-coordinated with a planar enviroment, involving two oxygen atoms from two salicylates and two pyridine nitrogen atoms from two 3-aminopyridine ligands. As expected, the Cu—O and Cu—N distances have the common magnitude [2,3]. Salicylates in complex **I** are singly deprotonated. The coordination mode of the carboxylato moiety of salicylate is monodentate terminal. The arrangement of two salicylates around copper center is the *trans* type (pseudo-pincer) comparing with pincer-like arrangement in $Cu(C_7H_5O_3)(py)_2$ [4]. The dihedral angle between rings of salicylate and 3-aminopyridine is 87.16(8)°, which suggests nearly perpendicular each other. The O3 atom of phenolic hydroxyl group involves in intra-molecular hydrogen bonding to the O2 atom of carboxyl group (d(O2···O3) = 2.537(4) Å). Hydrogen-bonding interaction exists intermolecularly between the neighboring units, carboxyl group of salicylate and amino group of 3-aminopyridine, through the pathway O2···N2 (d = 2.788(3) Å). Thus, monomer units are extended to one-dimensional zig-zag chain with double strands, having a separation of copper-copper of 6.453 Å (lower figure). Therefore, 3-aminopyridine serves as the second bridging group through hydrogen bonding.

Table 1. Data collection and handling.

Crystal:	green rod, size 0.10 × 0.10 × 0.80 mm
Wavelength:	Mo K_α radiation (0.7107 Å)
μ:	9.96 cm^{-1}
Diffractometer, scan mode:	Rigaku AFC7, ω
$2\theta_{max}$:	54.26°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	7743, 2513
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 3\,\sigma(I_{obs})$, 1751
$N(param)_{refined}$:	204
Programs:	SHELXS-97 [5], SHELXL [6]

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

Atom	Site	x	y	z	U_{iso}
H(1)	4*e*	0.405(7)	0.028(7)	–0.155(2)	0.12(2)
H(2)	4*e*	0.426(4)	–0.317(5)	–0.247(1)	0.076(9)
H(3)	4*e*	0.220(5)	–0.590(6)	–0.260(1)	0.09(1)
H(4)	4*e*	0.012(6)	–0.635(7)	–0.202(2)	0.11(1)
H(5)	4*e*	–0.024(5)	–0.415(6)	–0.136(1)	0.08(1)
H(6)	4*e*	–0.142(3)	0.419(4)	0.023(1)	0.039(6)
H(7)	4*e*	–0.305(4)	0.754(4)	0.024(1)	0.052(9)
H(8)	4*e*	–0.398(4)	0.817(5)	–0.023(1)	0.06(1)
H(9)	4*e*	–0.440(3)	0.628(4)	–0.110(1)	0.050(7)
H(10)	4*e*	–0.393(4)	0.321(4)	–0.153(1)	0.066(9)
H(11)	4*e*	–0.217(3)	0.072(4)	–0.105(1)	0.045(6)

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)	2*a*	0	0	0	0.0748(4)	0.0461(3)	0.0423(3)	0.0171(2)	0.0268(2)	0.0060(2)
O(1)	4*e*	0.0316(2)	–0.1224(3)	–0.07123(7)	0.064(1)	0.055(1)	0.047(1)	0.0124(9)	0.0245(9)	0.0015(8)
O(2)	4*e*	0.2765(5)	0.0455(4)	–0.0914(1)	0.158(3)	0.101(2)	0.082(2)	–0.077(2)	0.064(2)	–0.052(1)
O(3)	4*e*	0.4297(4)	–0.0450(5)	–0.1769(1)	0.101(2)	0.100(2)	0.074(2)	–0.044(2)	0.049(1)	–0.015(1)
N(1)	4*e*	–0.1685(3)	0.2223(3)	–0.03709(8)	0.045(1)	0.036(1)	0.048(1)	–0.0052(8)	0.0128(9)	–0.0028(9)
N(2)	4*e*	–0.3154(4)	0.7494(4)	–0.0097(1)	0.081(2)	0.042(1)	0.061(2)	0.011(1)	0.019(2)	–0.001(1)
C(1)	4*e*	0.1606(4)	–0.0896(4)	–0.1011(1)	0.066(2)	0.047(1)	0.040(1)	–0.002(1)	0.019(1)	–0.002(1)
C(2)	4*e*	0.1726(3)	–0.2304(4)	–0.14860(9)	0.041(1)	0.050(1)	0.037(1)	0.001(1)	0.007(1)	–0.003(1)
C(3)	4*e*	0.3093(4)	–0.2021(4)	–0.1841(1)	0.054(2)	0.066(2)	0.036(1)	0.000(1)	0.011(1)	0.001(1)
C(4)	4*e*	0.3287(5)	–0.3418(6)	–0.2259(1)	0.066(2)	0.089(2)	0.041(1)	0.014(2)	0.015(1)	–0.007(2)
C(5)	4*e*	0.2161(6)	–0.5032(6)	–0.2339(1)	0.093(3)	0.093(3)	0.057(2)	0.017(2)	0.007(2)	–0.034(2)
C(6)	4*e*	0.0785(6)	–0.5339(6)	–0.2004(2)	0.091(3)	0.084(3)	0.107(3)	–0.027(2)	0.012(2)	–0.044(2)
C(7)	4*e*	0.0589(4)	–0.3987(5)	–0.1579(1)	0.057(2)	0.074(2)	0.074(2)	–0.014(2)	0.020(2)	–0.023(2)
C(8)	4*e*	–0.1997(3)	0.4021(4)	–0.0119(1)	0.041(1)	0.040(1)	0.045(1)	–0.005(1)	0.013(1)	0.000(1)
C(9)	4*e*	–0.3019(3)	0.5619(4)	–0.0365(1)	0.046(1)	0.037(1)	0.054(1)	–0.004(1)	0.019(1)	0.001(1)
C(10)	4*e*	–0.3812(4)	0.5299(4)	–0.0899(1)	0.052(2)	0.052(2)	0.059(2)	0.005(1)	0.003(1)	0.006(1)
C(11)	4*e*	–0.3531(4)	0.3458(4)	–0.1158(1)	0.059(2)	0.056(2)	0.053(2)	–0.007(1)	–0.003(1)	–0.004(1)
C(12)	4*e*	–0.2471(4)	0.1963(4)	–0.0890(1)	0.055(2)	0.039(1)	0.056(2)	–0.004(1)	0.009(1)	–0.007(1)

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