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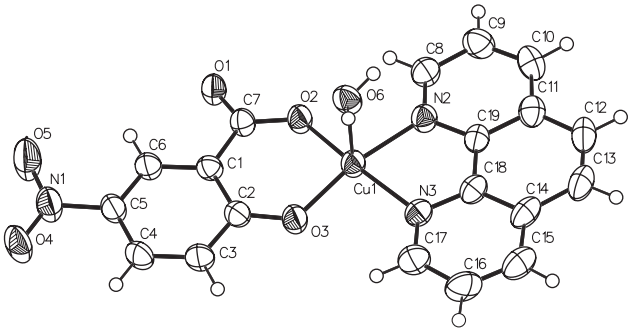
Crystal structure of aqua-(5-nitrosalicylato-κ²*O*,*O*′)-(1,10-phenanthroline-κ²*N*,*N*′)copper(II), $C_{19}H_{13}CuN_3O_6$



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Abstract

$C_{19}H_{13}CuN_3O_6$, monoclinic, $P2_1/c$, $a = 7.208(3)$ Å, $b = 21.720(8)$ Å, $c = 11.098(5)$ Å, $\beta = 99.085(17)°$, $V = 1715.8(12)$ Å^3, $Z = 4$, $R_{gt}(F) = 0.0428$, $wR_{ref}(F^2) = 0.1044$, $T = 293$ K.

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The asymmetric unit of the title crystal structure is shown in the figure. Tables 1 and 2 contain details of the measurement method and a list of the atoms including atomic coordinates and displacement parameters.

Source of material

A mixture of $Cu(NO_3)_2{\cdot}4H_2O$ (0.1 mmol), phenanthroline(phen) (0.1 mmol), 5-nitrosalicylic acid (0.2 mmol) and distilled water (10 mL) was added into a Teflon-lined autoclave (20 mL) and heated at 180°C for 72 h. Green chunk-like crystals of the title complex were collected from the reaction mixture.

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Table 1: Data collection and handling.

Crystal:	Green chunk
	Size 0.36 × 0.18 × 0.12 mm
Wavelength:	Mo $K\alpha$ radiation (0.71073 Å)
μ:	13.2 cm^{-1}
Diffractometer, scan mode:	TeXan-PC, ω
$2\theta_{max}$, completeness:	55°, >99%
$N(hkl)_{measured}$, $N(hkl)_{unique}$, R_{int}:	16553, 3944, 0.072
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\ \sigma(I_{obs})$, 2401
$N(param)_{refined}$:	268
Programs:	SHELX [6], TeXan-PC [7]

Table 2: Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2).

Atom	*x*	*y*	*z*	U_{iso}*/U_{eq}
Cu1	0.32548(5)	0.686288(17)	0.07623(3)	0.03931(14)
N1	−0.1219(5)	0.47485(13)	−0.3285(3)	0.0609(9)
N2	0.3834(3)	0.77545(12)	0.1188(2)	0.0385(6)
N3	0.5102(3)	0.67276(12)	0.2312(2)	0.0414(6)
O1	0.0068(3)	0.69591(9)	−0.25518(19)	0.0441(5)
O2	0.1849(3)	0.70907(9)	−0.07735(18)	0.0424(5)
O3	0.3215(3)	0.60067(10)	0.0427(2)	0.0497(6)
O4	−0.1081(4)	0.41922(11)	−0.3351(2)	0.0699(8)
O5	−0.2387(5)	0.50388(13)	−0.3993(3)	0.1158(15)
C1	0.1011(4)	0.60568(13)	−0.1447(3)	0.0352(7)
C2	0.2176(4)	0.57409(14)	−0.0488(3)	0.0392(7)
C3	0.2215(5)	0.50895(15)	−0.0547(3)	0.0471(8)
H3A	0.3017	0.4877	0.0050	0.057*
C4	0.1140(4)	0.47613(14)	−0.1432(3)	0.0473(8)
H4A	0.1192	0.4333	−0.1440	0.057*
C5	−0.0047(4)	0.50827(14)	−0.2332(3)	0.0431(8)
C6	−0.0082(4)	0.57179(14)	−0.2334(3)	0.0413(7)
H6A	−0.0867	0.5922	−0.2952	0.050*
C7	0.0955(4)	0.67432(13)	−0.1603(3)	0.0363(7)
C8	0.3204(4)	0.82558(15)	0.0599(3)	0.0455(8)
H8A	0.2422	0.8217	−0.0148	0.055*
C9	0.3667(5)	0.88439(16)	0.1053(3)	0.0509(9)
H9A	0.3223	0.9190	0.0603	0.061*
C10	0.4770(5)	0.89088(16)	0.2156(3)	0.0506(9)
H10A	0.5071	0.9300	0.2467	0.061*
C11	0.5452(4)	0.83914(16)	0.2824(3)	0.0436(7)
C12	0.6590(4)	0.83989(19)	0.4000(3)	0.0519(9)
H12A	0.6890	0.8775	0.4382	0.062*

Table 2 (continued)

Atom	x	y	z	U_{iso}*/U_{eq}
C13	0.7238(5)	0.78801(19)	0.4571(3)	0.0526(9)
H13A	0.7983	0.7904	0.5334	0.063*
C14	0.6804(4)	0.72873(18)	0.4026(3)	0.0476(9)
C15	0.7448(5)	0.67284(19)	0.4544(3)	0.0570(10)
H15A	0.8249	0.6721	0.5288	0.068*
C16	0.6899(5)	0.61889(19)	0.3956(3)	0.0597(10)
H16A	0.7320	0.5814	0.4299	0.072*
C17	0.5714(5)	0.62071(17)	0.2847(3)	0.0523(9)
H17A	0.5333	0.5837	0.2463	0.063*
C18	0.5645(4)	0.72620(15)	0.2890(3)	0.0397(7)
C19	0.4969(4)	0.78179(15)	0.2284(3)	0.0377(7)
O6	0.0710(3)	0.68764(10)	0.1829(2)	0.0469(5)
H1WB	0.059(5)	0.7222(8)	0.211(3)	0.056*
H1WA	0.079(5)	0.6601(12)	0.234(3)	0.056*

Experimental details

The aromatic H atoms were positioned geometrically and were included in the refinement in the riding-model approximation [C—H = 0.93 Å and $U_{iso}(H) = 1.2U_{eq}(C)$]. The H atoms of the water ligand were found in a difference Fourier map and were refined with distance restraints of O—H = 0.83(1) Å and $U_{iso}(H) = 1.2U_{eq}(O)$.

Discussion

Salicylic acid and its substituted derivatives continue to attract attention because of its versatile coordination modes and biological applications. Many complexes with salicylic acid derivatives and N-donor ligands were found to display diverse structure types [1–3]. Though the non-coordinating functional groups such as NO_2, NH_2, etc. are well known to form robust and strong hydrogen bonds, but metal-organic supramolecular assemblies employing organic ligands having NO_2 groups are limited [4, 5]. In the crystal structure of the title complex, Cu atom adopts a square-pyramidal N_2O_3 environment, with the basal plane defined by atoms O_2 and O_3 from one 5-(NO_2)sal ligand and the atoms N2 and N3 from one phen ligand, and finally atom O6 from coordinated water occupying the apical position. The water ligand shows a long Cu1—O6 distance of 2.336(3) Å. The 5-(NO_2)sal ligand is coordinated to Cu atom via one oxygen atom of the carboxylate group (O2) and one oxygen atom from the phenolate group (O3). The carboxylate group of the 5-(NO_2)sal ligand is approximately coplanar to the aromatic ring with a dihedral angle of 9.1(2)°. The adjacent mononuclear units are further connected to each other by O—H···O hydrogen bonds, resulting in extended 3D framework.

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