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Crystal structure of bis(*o*-acetamidobenzoato-κ^2:*O*:*O*2)-(1,10-phenanthroline-κ^2:*N*1:*N*2)copper(II), $Cu(C_{12}H_8N_2)(C_9H_8NO_3)_2$

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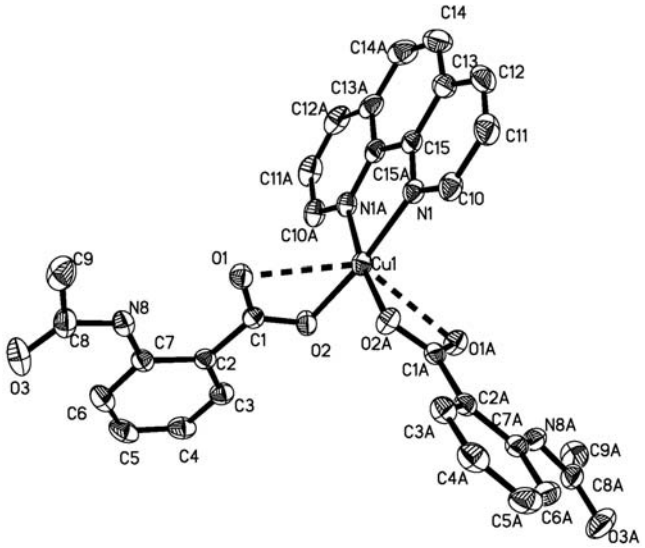

Abstract

$C_{30}H_{24}CuN_4O_6$, monoclinic, *C*12/*c*1 (no. 15), a = 11.882(4) Å, b = 11.182(3) Å, c = 20.282(7) Å, β = 103.871(2)°, V = 2616.2 Å^3, Z = 4, $R_{gt}(F)$ = 0.039, $wR_{ref}(F^2)$ = 0.115, T = 173 K.

Source of material

A mixture of *o*-acetamidobenzoic acid (0.036 g, 0.2 mmol), copper sulfate (0.025 g, 0.1 mmol) and 1,10-phenanthroline (0.020 g, 0.1 mmol) was dissolved in 15 ml of methanol. The pH value of the resultant mixture was adjusted to about 6.0 - 6.5 by adding three drops of triethylamine solution and the reaction was kept under water-bath condition at 333 K for 25 h. Afterwards, the mixture was filtered, and the filtrate was cooled to room temperature slowly. Deep blue single crystals suitable for X-ray diffraction analysis were obtained after fifteen days.

Experimental details

H atoms bound to C atoms were placed in calculted positions and treated as riding on their parent atoms, with d(C—H) = 0.95 Å, U_{iso}(H) = 1.2 U_{eq}(C) (aromtic) and d(C—H) = 0.95 Å, U_{iso}(H) = 1.5 U_{eq}(C) (methyl). H atoms attached to N atom was initially located in a difference Fourier map and restrained with d(N—H) = 0.88 Å and U_{iso}(H) = 1.2 U_{eq}(N).

Discussion

The study of the structural, spectroscopic, and electronic properties of metal centers present in biological systems is crucial to understand their role in nature [1,2]. These centers are often modeled by using small molecules containing donor atoms that reproduce the coordination around the metal ion [3,4]. The use of simple metal-containing systems with low molecular weight ligands is useful to understand the correlation between magnetic, electronic, and structural properties in more complex systems [5,6]. For this reason, the synthesis of complexes oriented to mimic metal sites of different types of metalloproteins constitutes an important branch in both inorganic and organic chemistry [7,8]. Copper and cobalt are present in a diverse group of metalloenzymes, in which the metal ions are coordinated by N, O and S atoms.

The crystal structure of the title complex contains a [Cu(1,10-phen)($C_9H_8NO_3$)$_2$] unit. The copper(II) ion is coordinated by two nitrogen atoms from one 1,10-phenanthroline molecule, four oxygen atoms from two *o*-acetamidobenzoate anions, forming a distorted octahedron with O1 and O1A at the axial positions and O2, O2A, N1 and N1A in the equatorial plane. The bond angle of O1–Cu1–O1A is 133.05°. At the equatorial plane, the bond angles N1–Cu1–N1A, N1A–Cu1– O2A, O2A–Cu1–O2 and O2–Cu1–N1 are 81.3(2)°, 92.9(1)°, 93.3(1)° and 92.9(1)°, respectively, with the sum of 360.28°. The bond length Cu1—O1 is 2.648(2) Å, indicating weak coordination bonds between the carbonyl oxygen atoms of *o*-carboxylaminobenzoate and the copper ion [8].

In the complex, the coordinated carbonyl oxygen atoms and the nitrogen atoms of *o*-acetamidobenzoate ligands are linked by strong hydrogen bonds: d(N8–H8···O1) = 1.940 Å, ∠N8–H8···O1= 139.0°. There exist weak hydrogen bonding interactions between the *o*-acetamidobenzoate ligands and 1,10-phenanthroline molecules: d(C10–H19···O2) = 2.56 Å, ∠C10–H19···O2 = 113° and d(C10–H19···O3) = 2.44 Å, ∠C10–H19···O3 = 124°.

Table 1. Data collection and handling.

Crystal:	blue block, size 0.20 × 0.20 × 0.20 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ:	8.89 cm^{-1}
Diffractometer, scan mode:	Bruker SMART APEX-II, φ/ω
$2\theta_{max}$:	49.58°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	5435, 2090
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\ \sigma(I_{obs})$, 1847
$N(param)_{refined}$:	178
Programs:	SHELXS-97, SHELXL-97 [10]

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

Atom	Site	x	y	z	U_{iso}
H(4)	8*f*	0.0880	0.4618	0.1198	0.066
H(5)	8*f*	0.1067	0.5352	0.0158	0.073
H(6)	8*f*	0.2545	0.4711	–0.0315	0.066
H(9A)	8*f*	0.5751	0.3070	–0.0902	0.101
H(9B)	8*f*	0.5613	0.2095	–0.0349	0.101
H(9C)	8*f*	0.6354	0.3281	–0.0117	0.101
H(3)	8*f*	0.2269	0.3309	0.1804	0.055
H(19)	8*f*	0.7559	0.0249	0.3264	0.061
H(20)	8*f*	0.8637	–0.1484	0.3583	0.075
H(21)	8*f*	0.7813	–0.3338	0.3322	0.076
H(23)	8*f*	0.5951	–0.4563	0.2783	0.083
H(8)	8*f*	0.4636	0.2597	0.0430	0.054

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*	½	0.08004(4)	¼	0.0323(3)	0.0432(3)	0.0322(3)	0	0.0065(2)	0
C(4)	8*f*	0.1507(3)	0.4368(3)	0.1016(2)	0.045(2)	0.047(2)	0.072(2)	0.007(2)	0.010(2)	–0.007(2)
C(5)	8*f*	0.1614(3)	0.4789(3)	0.0397(2)	0.049(2)	0.042(2)	0.083(3)	0.008(2)	–0.004(2)	0.008(2)
C(6)	8*f*	0.2492(3)	0.4414(3)	0.0116(2)	0.052(2)	0.047(2)	0.058(2)	–0.005(2)	–0.000(2)	0.013(2)
C(7)	8*f*	0.3312(3)	0.3593(3)	0.0461(2)	0.040(2)	0.035(2)	0.042(2)	–0.006(1)	0.002(1)	0.001(1)
C(8)	8*f*	0.4592(3)	0.3585(3)	–0.0345(2)	0.061(2)	0.057(2)	0.039(2)	–0.017(2)	0.009(2)	0.003(2)
C(9)	8*f*	0.5673(2)	0.2952(3)	–0.0436(1)	0.074(3)	0.077(3)	0.061(2)	–0.018(2)	0.034(2)	–0.002(2)
C(1)	8*f*	0.4028(1)	0.2258(2)	0.15103(8)	0.034(2)	0.036(2)	0.037(2)	–0.004(1)	0.004(1)	–0.001(1)
C(2)	8*f*	0.3225(1)	0.3172(2)	0.11063(8)	0.036(2)	0.034(1)	0.040(2)	–0.002(1)	0.005(1)	–0.003(1)
C(3)	8*f*	0.2326(1)	0.3579(2)	0.13688(8)	0.042(2)	0.045(2)	0.050(2)	0.002(1)	0.010(2)	–0.004(1)
C(10)	8*f*	0.7201(3)	–0.0508(3)	0.3155(2)	0.041(2)	0.069(2)	0.041(2)	0.009(2)	0.006(1)	–0.002(2)
C(11)	8*f*	0.7846(3)	–0.1544(4)	0.3345(2)	0.046(2)	0.088(3)	0.050(2)	0.022(2)	0.007(2)	0.005(2)
C(12)	8*f*	0.7361(4)	–0.2637(4)	0.3195(2)	0.071(3)	0.072(3)	0.053(2)	0.034(2)	0.023(2)	0.016(2)
C(13)	8*f*	0.6180(3)	–0.2735(3)	0.2850(2)	0.071(2)	0.052(2)	0.045(2)	0.015(2)	0.030(2)	0.009(2)
C(14)	8*f*	0.5562(4)	–0.3822(3)	0.2667(2)	0.096(3)	0.047(2)	0.073(3)	0.014(2)	0.041(2)	0.008(2)
C(15)	8*f*	0.5596(3)	–0.1653(3)	0.2676(2)	0.048(2)	0.049(2)	0.032(2)	0.005(1)	0.017(1)	0.001(1)
N(1)	8*f*	0.6091(2)	–0.0559(2)	0.2824(1)	0.035(2)	0.051(2)	0.034(1)	0.005(1)	0.007(1)	–0.002(1)
N(8)	8*f*	0.4232(2)	0.3190(2)	0.0205(1)	0.049(2)	0.045(1)	0.042(1)	–0.002(1)	0.011(1)	0.008(1)
O(1)	8*f*	0.4785(2)	0.1743(2)	0.1279(1)	0.041(1)	0.050(1)	0.043(1)	0.010(1)	0.012(1)	0.005(1)
O(2)	8*f*	0.3861(2)	0.1990(2)	0.2089(1)	0.047(1)	0.054(1)	0.037(1)	0.010(1)	0.012(1)	0.007(1)
O(3)	8*f*	0.4117(3)	0.4366(3)	–0.0729(1)	0.081(2)	0.089(2)	0.055(2)	–0.007(2)	0.013(1)	0.030(2)

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