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Crystal structure of aqua(phenanthroline-*N,N'*)(glycinato-*N,O*)copper(II) bromide hydrate, $[Cu(NH_2CH_2COO)(C_{12}H_8N_2)(H_2O)]Br \cdot H_2O$

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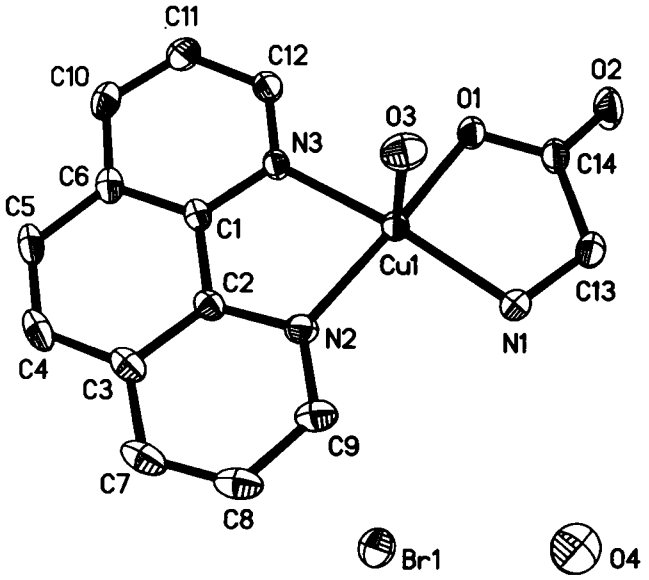

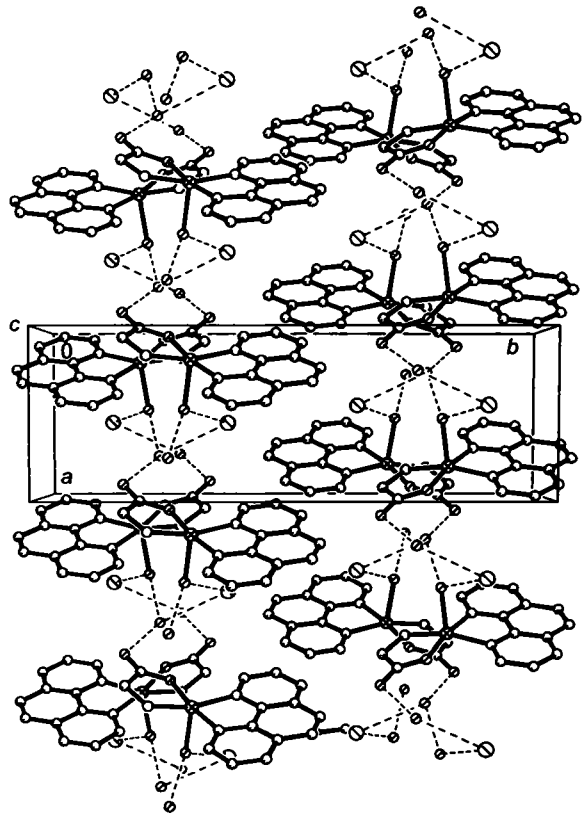

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Abstract

$C_{14}H_{16}BrCuN_3O_4$, monoclinic, $P12_1/c1$ (no. 14), a = 7.1063(2) Å, b = 21.0421(7) Å, c = 11.0447(4) Å, β = 95.974(2)°, V = 1642.6 Å^3, Z = 4, $R_{gt}(F)$ = 0.028, $wR_{ref}(F^2)$ = 0.078, T = 273 K.

Source of material

Synthesis of the title compound was carried out by stirring the solution of $CuBr_2$ (0.225 g, 1 mmol), 1,10-phenanthroline hydrate (0.198 g, 1 mmol), and glycine (0.075 g, 1 mmol) in ethanol (20 ml) for 6 hours at room temperature. After filtration, the filtrate was allowed to stand at room temperature. Slow evaporation of the solvent yielded blue crystals.

Experimental details

While the H atoms bonded to O atoms and involved in hydrogen bonds were localized from Fourier difference maps and refined freely, the other H atoms were added geometrically and treated as riding rigid body approximations.

Discussion

1,10-Phenanthroline and its substituted derivatives represent a widely investigated class of chelating agents [1]. Some intrinsic properties of phenanthroline such as the structural rigidity and luminescence make them attractive. The most fruitful field of exploitation of these ligands is coordination chemistry.

In the structure of the title compound $[Cu(gly)(phen)(H_2O)]Br \cdot H_2O$, the Cu(II) ion is five-coordinated with an oxygen atom from a water molecule and chelated by a gly ion and a phen molecule (gly = glycin monoanion, phen = 1,10-phenanthroline), both of which are bidentate ligands to form a distorted square-pyramid (figure, top). The gly and phen units are both asymmetrically coordinated to the copper atom (d(Cu1—N1) = 1.998(2) Å, d(Cu1—O1) = 1.939(2) Å, d(Cu1—N2) = 2.019(2) Å, d(Cu1—N3) = 2.006(2) Å) in the plane of the square pyramid with a water molecule occupying the fifth position. The Cu1—O3 distance (2.259(2) Å) is slightly longer than the four distances above, which is because of the weaker coordination ability of the water oxygen compared with the other four coordinated atoms of gly and phen [2]. One lattice water molecule and one non-coordinated bromine anion are also present in the unit cell. The title compound includes one chiral C atom (C14) and crystallizes as racemic mixture of the enantiomers.

The $[Cu(gly)(phen)(H_2O)]^+$, Br^- ions and H_2O molecules units are interconnected by six kinds of strong hydrogen bonds to form a one-dimensional infinite supramolecular chains, and then each one-dimensional chain is interlinked by π-π interactions to form a two-dimensional structure. The distance between the two adjacent phenanthroline planes is in the range 3.3 Å – 3.7 Å (d(C1···C4') =

3.541 Å, d(C2···C5′) = 3.510 Å, d(C3···C6′) = 3.520 Å; figure, bottom). In the similar compound [Cu(phen)(C_2O_4)(H_2O)] · H_2O [3], the second ligand is not gly but oxalate. The copper atoms have also a five-coordinated environment with a distorted square-pyramidal shape.

Table 1. Data collection and handling.

Crystal:	blue bar, size 0.20 × 0.30 × 0.50 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ:	37.84 cm^{-1}
Diffractometer, scan mode:	Bruker SMART CCD, φ/ω
$2\theta_{max}$:	56.6°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	17478, 4063
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\,\sigma(I_{obs})$, 3106
$N(param)_{refined}$:	224
Programs:	SHELXS-97 [4], SHELXL-97 [5]

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

Atom	Site	x	y	z	U_{iso}
H(1A)	4e	0.2843	0.2088	1.0434	0.044
H(1B)	4e	0.1066	0.2306	1.0842	0.044
H(4)	4e	0.3570	0.5671	1.1453	0.055
H(5)	4e	0.2251	0.5937	0.9567	0.052
H(7)	4e	0.4683	0.4800	1.3010	0.060
H(8)	4e	0.5096	0.3734	1.3397	0.061
H(9)	4e	0.3998	0.2996	1.1944	0.053
H(10)	4e	0.0765	0.5573	0.7456	0.052
H(11)	4e	−0.0298	0.4742	0.6216	0.054
H(12)	4e	0.0050	0.3708	0.6910	0.045
H(13A)	4e	−0.0468	0.1630	0.9744	0.048
H(13B)	4e	0.1440	0.1403	0.9291	0.048
H(3A)	4e	0.499(4)	0.312(1)	0.807(3)	0.06(1)
H(3B)	4e	0.560(4)	0.287(1)	0.913(3)	0.06(1)
H(4A)	4e	0.782(5)	0.281(2)	0.094(3)	0.08(1)
H(4B)	4e	0.681(7)	0.230(2)	0.070(5)	0.13(2)

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}
Br(1)	4e	0.44820(4)	0.62835(1)	0.39184(2)	0.0707(2)	0.0590(2)	0.0392(2)	−0.0154(1)	−0.0068(1)	−0.0037(1)
Cu(1)	4e	0.19005(4)	0.30513(1)	0.92762(2)	0.0398(2)	0.0239(1)	0.0288(2)	−0.0008(1)	−0.0024(1)	0.0004(1)
N(1)	4e	0.1682(3)	0.22378(8)	1.0182(2)	0.047(1)	0.030(1)	0.032(1)	0.0010(8)	0.0027(8)	0.0031(8)
N(2)	4e	0.2977(2)	0.35923(9)	1.0691(2)	0.036(1)	0.037(1)	0.0274(9)	−0.0017(7)	0.0016(7)	0.0004(8)
N(3)	4e	0.1331(2)	0.39040(8)	0.8511(2)	0.0348(9)	0.0230(9)	0.0314(9)	0.0016(7)	−0.0005(7)	−0.0021(7)
C(1)	4e	0.1936(3)	0.4393(1)	0.9261(2)	0.027(1)	0.026(1)	0.035(1)	−0.0012(8)	0.0039(8)	−0.0053(9)
C(2)	4e	0.2794(3)	0.4224(1)	1.0447(2)	0.029(1)	0.034(1)	0.031(1)	−0.0041(8)	0.0053(8)	−0.0059(9)
C(3)	4e	0.3415(3)	0.4704(1)	1.1275(2)	0.032(1)	0.047(1)	0.039(1)	−0.0077(9)	0.0084(9)	−0.015(1)
C(4)	4e	0.3172(3)	0.5351(1)	1.0905(2)	0.041(1)	0.041(1)	0.058(2)	−0.011(1)	0.013(1)	−0.024(1)
C(5)	4e	0.2379(3)	0.5510(1)	0.9783(2)	0.045(1)	0.026(1)	0.063(2)	−0.0070(9)	0.016(1)	−0.012(1)
C(6)	4e	0.1734(3)	0.5030(1)	0.8920(2)	0.032(1)	0.027(1)	0.047(1)	−0.0013(8)	0.0088(9)	−0.003(1)
C(7)	4e	0.4273(3)	0.4503(1)	1.2418(2)	0.041(1)	0.073(2)	0.035(1)	−0.012(1)	0.003(1)	−0.020(1)
C(8)	4e	0.4500(3)	0.3870(2)	1.2652(2)	0.044(1)	0.077(2)	0.030(1)	−0.004(1)	−0.002(1)	−0.003(1)
C(9)	4e	0.3834(3)	0.3426(1)	1.1769(2)	0.044(1)	0.056(2)	0.033(1)	−0.000(1)	−0.0001(9)	0.005(1)
C(10)	4e	0.0895(3)	0.5157(1)	0.7734(2)	0.045(1)	0.029(1)	0.057(2)	0.0045(9)	0.010(1)	0.008(1)
C(11)	4e	0.0275(4)	0.4663(1)	0.6998(2)	0.057(2)	0.038(1)	0.039(1)	0.008(1)	−0.001(1)	0.009(1)
C(12)	4e	0.0500(3)	0.4039(1)	0.7418(2)	0.047(1)	0.031(1)	0.034(1)	0.0020(9)	−0.0017(9)	−0.0031(9)
C(13)	4e	0.0641(3)	0.1771(1)	0.9375(2)	0.047(1)	0.028(1)	0.045(1)	−0.0010(9)	0.003(1)	0.003(1)
C(14)	4e	0.0030(3)	0.2040(1)	0.8129(2)	0.045(1)	0.027(1)	0.043(1)	0.0008(9)	0.001(1)	−0.002(1)
O(1)	4e	0.0543(2)	0.26086(7)	0.7915(1)	0.0544(9)	0.0268(8)	0.0348(8)	−0.0061(7)	−0.0070(7)	0.0005(7)
O(2)	4e	−0.0899(3)	0.16999(8)	0.7378(2)	0.080(1)	0.029(1)	0.059(1)	−0.0098(8)	−0.0189(9)	−0.0048(8)
O(3)	4e	0.4733(3)	0.2910(1)	0.8566(2)	0.044(1)	0.065(1)	0.045(1)	0.0039(9)	0.0066(9)	0.006(1)
O(4)	4e	0.7481(3)	0.2650(1)	0.0392(2)	0.068(1)	0.072(2)	0.058(2)	0.007(1)	−0.013(1)	0.001(1)

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