Crystal structure of 1,10-phenanthrolinecopper(II) dinitrate, $[\text{Cu}(\text{C}_{12}\text{H}_8\text{N}_2)](\text{NO}_3)_2$

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Abstract

$\text{C}_{12}\text{H}_8\text{CuN}_4\text{O}_6$, monoclinic, $P12_1/n1$ (no. 14), $a = 8.7008(2)$ Å, $b = 9.0614(3)$ Å, $c = 17.1132(3)$ Å, $\beta = 101.883(1)^\circ$, $V = 1320.3$ Å³, $Z = 4$, $R_{\text{gt}}(F) = 0.023$, $wR_{\text{ref}}(F^2) = 0.066$, $T = 153$ K.

Source of material

A mixture of $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ (0.3 mmol), NaOH (0.6 mmol), 1,10-phenanthroline (0.3 mmol) and 15 ml H_2O was sealed in a 25 ml Teflon-lined reactor and kept at 373 K for 3 days under autogenous pressure. After being cooled slowly to room temperature, blue crystals were collected in 76 % yield (based on Cu).

Discussion

In the last few years, much attention has been paid in organic chemistry field to the molecular structure and biological activity of coordinated complexes [1,2]. Among these complexes, the compounds constructed by phenanthroline (phen) and transition metal always have strong interactions with DNA molecules. The coordination modes of the complexes play a decisive role not only for the molecular structure of the complexes but also for the aggregation fashion of coordinated supermolecule as well as for the interaction mode with DNA with various biological activities [3,4].

The title structure consists of one Cu, one phenanthroline and two nitrate anions. The center Cu^{2+} is five-coordinated by two N atoms from one phen ligand with the Cu—N distances in the range of 1.997(1)–2.001(1) Å and three O atoms from three different nitrate anions with the Cu—O distances in the range of 1.957(1)–

2.318(1) Å. The bond lengths are in the reasonable ranges compared to the literature [5]. The N1, N2 atoms of phen ligand and O1, O4 atoms of nitrate anions define one equatorial plane, with the Cu atom approximately lying on the plane. The nitrate O6 occupies the axial positions, so the Cu^{2+} displays a distorted quadrihydrogen environment. The nitrate anions play two roles. One function is to equilibrate electrovalence, another function is to coordinate with Cu cations. The two nitrate anions have different coordinating modes with Cu atoms. The N4 nitrate anion as bridged ligand provides two O atoms (O4, O6) to coordinate two Cu atoms, forming a 1D zigzag chain along [001], while the N3 nitrate anion only offers one O atom to coordinate Cu. There are π – π stacking interactions between the phen rings of adjacent 1D chains with face to face distances of 3.585 Å, which is in the range of π – π stacking interactions, forming the supermolecular structure.

Table 1. Data collection and handling.

Crystal:	blue block, size $0.20 \times 0.27 \times 0.47$ mm
Wavelength:	Mo K_{α} radiation (0.71073 Å)
μ :	16.95 cm^{-1}
Diffractometer, scan mode:	Rigaku RAXIS-RAPID, ω
$2\theta_{\text{max}}$:	54.96°
$N(hkl)_{\text{measured}}$, $N(hkl)_{\text{unique}}$:	12679, 3026
Criterion for I_{obs} , $N(hkl)_{\text{gt}}$:	$I_{\text{obs}} > 2\sigma(I_{\text{obs}})$, 2911
$N(\text{param})_{\text{refined}}$:	209
Programs:	SHELXS-97 [6], SHELXL-97 [7], SHELXTL [8]

Table 2. Atomic coordinates and displacement parameters (in Å²).

Atom	Site	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> _{iso}
H(1)	4e	0.0788	0.8023	0.6175	0.022
H(2)	4e	−0.0504	0.8551	0.4863	0.024
H(3)	4e	0.0038	0.7161	0.3807	0.022
H(5)	4e	0.1633	0.5022	0.3353	0.024
H(6)	4e	0.3299	0.3061	0.3698	0.024
H(8)	4e	0.4932	0.1440	0.4809	0.026
H(9)	4e	0.5811	0.1031	0.6174	0.027
H(10)	4e	0.5170	0.2713	0.7095	0.024

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Table 3. Atomic coordinates and displacement parameters (in Å²).

Atom	Site	x	y	z	U ₁₁	U ₂₂	U ₃₃	U ₁₂	U ₁₃	U ₂₃
Cu	4e	0.33217(2)	0.57191(2)	0.696505(9)	0.0183(1)	0.0141(1)	0.0106(1)	0.00136(6)	0.00125(7)	0.00070(6)
O(1)	4e	0.4490(1)	0.4941(1)	0.79822(6)	0.0202(5)	0.0268(6)	0.0188(5)	−0.0028(4)	−0.0011(4)	0.0069(4)
O(2)	4e	0.6541(2)	0.6024(2)	0.77113(8)	0.0289(7)	0.0550(9)	0.0255(6)	−0.0110(6)	0.0055(5)	0.0134(6)
O(3)	4e	0.6738(1)	0.4695(2)	0.87856(7)	0.0251(6)	0.0326(6)	0.0260(6)	−0.0029(5)	−0.0070(5)	0.0101(5)
O(4)	4e	0.3107(1)	0.7665(1)	0.74779(6)	0.0220(5)	0.0156(5)	0.0146(5)	−0.0027(4)	0.0046(4)	−0.0005(4)
O(5)	4e	0.4542(2)	0.8483(1)	0.66662(7)	0.0364(7)	0.0236(6)	0.0309(6)	−0.0007(5)	0.0226(5)	−0.0027(5)
O(6)	4e	0.3805(1)	0.9971(1)	0.75107(7)	0.0212(5)	0.0162(5)	0.0254(6)	−0.0020(4)	0.0054(4)	−0.0069(4)
N(1)	4e	0.2020(1)	0.6334(1)	0.59143(7)	0.0182(6)	0.0147(6)	0.0130(5)	0.0008(4)	0.0029(4)	−0.0003(4)
N(2)	4e	0.3906(2)	0.4058(1)	0.63133(7)	0.0168(6)	0.0153(6)	0.0154(6)	0.0004(4)	0.0034(5)	0.0014(4)
N(3)	4e	0.5963(2)	0.5230(1)	0.81570(7)	0.0235(6)	0.0159(6)	0.0174(6)	−0.0015(5)	0.0067(5)	−0.0007(5)
N(4)	4e	0.3837(1)	0.8728(1)	0.72060(7)	0.0158(6)	0.0162(6)	0.0160(6)	0.0008(4)	0.0022(4)	0.0002(4)
C(1)	4e	0.1002(2)	0.7437(2)	0.57496(9)	0.0220(7)	0.0163(7)	0.0171(7)	0.0024(5)	0.0030(5)	−0.0020(5)
C(2)	4e	0.0231(2)	0.7763(2)	0.49637(9)	0.0211(7)	0.0158(7)	0.0213(7)	0.0035(5)	0.0007(6)	0.0022(5)
C(3)	4e	0.0544(2)	0.6940(2)	0.43407(9)	0.0204(7)	0.0193(7)	0.0149(6)	−0.0005(5)	−0.0002(5)	0.0029(5)
C(4)	4e	0.1624(2)	0.5762(2)	0.44997(9)	0.0177(7)	0.0168(7)	0.0144(7)	−0.0026(5)	0.0043(5)	0.0006(5)
C(5)	4e	0.2049(2)	0.4825(2)	0.39014(8)	0.0226(7)	0.0243(8)	0.0125(6)	−0.0008(6)	0.0043(5)	−0.0006(5)
C(6)	4e	0.3035(2)	0.3663(2)	0.41051(9)	0.0229(7)	0.0234(8)	0.0168(7)	−0.0011(6)	0.0087(6)	−0.0040(6)
C(7)	4e	0.3684(2)	0.3332(2)	0.49263(9)	0.0165(7)	0.0164(7)	0.0194(7)	−0.0013(5)	0.0069(5)	−0.0010(5)
C(8)	4e	0.4651(2)	0.2102(2)	0.5187(1)	0.0219(7)	0.0178(7)	0.0267(8)	0.0023(6)	0.0095(6)	−0.0022(6)
C(9)	4e	0.5183(2)	0.1869(2)	0.5991(1)	0.0208(7)	0.0180(7)	0.0292(8)	0.0049(6)	0.0058(6)	0.0022(6)
C(10)	4e	0.4790(2)	0.2879(2)	0.65410(9)	0.0211(7)	0.0181(7)	0.0192(7)	0.0019(5)	0.0030(5)	0.0037(5)
C(11)	4e	0.3342(2)	0.4265(1)	0.55194(9)	0.0139(6)	0.0142(6)	0.0153(6)	−0.0017(5)	0.0046(5)	0.0008(5)
C(12)	4e	0.2308(2)	0.5493(2)	0.53026(8)	0.0151(6)	0.0135(6)	0.0135(6)	−0.0016(5)	0.0035(5)	−0.0004(5)

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