Crystal structure of diaquanitrato(1,10-phenanthroline-*N,N'*)copper(II) nitrate, $[\text{Cu}(\text{H}_2\text{O})_2(\text{C}_{12}\text{H}_8\text{N}_2)(\text{NO}_3)]\text{NO}_3$

Y.-Q. Zheng*, J. Sun and J.-L. Lin

Ningbo University, Institute for Solid State Chemistry, Municipal Key Laboratory of Inorganic Materials Chemistry, Ningbo, Zhejiang, 315211 P. R. China

Received November 19, 2001, accepted and available on-line February 21, 2002; CCDC-No. 1267766

Abstract

$\text{C}_{12}\text{H}_{12}\text{CuN}_4\text{O}_8$, monoclinic, $P12_1/n1$ (No. 14), $a = 7.019(1) \text{ \AA}$, $b = 20.187(2) \text{ \AA}$, $c = 11.240(1) \text{ \AA}$, $\beta = 106.24(1)^\circ$, $V = 1529.1 \text{ \AA}^3$, $Z = 4$, $R_{\text{gt}}(F) = 0.068$, $wR_{\text{ref}}(F^2) = 0.159$, $T = 293 \text{ K}$.

Source of material

Under continuous stirring, 0.61 g (2.52 mmol) $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ was dissolved in 25 ml $\text{CH}_3\text{OH}-\text{H}_2\text{O}$ (1:1 v/v) containing 0.50 g (2.52 mmol) phenanthroline monohydrate and 0.42 g (3.62 mmol) maleic acid and then 1.0 ml (1.0 M) NaOH was dropwise added. The resulting blue solution (pH = 2.0) was maintained at 323 K. After three days, extremely slender needle-like blue crystal grew rapidly. The formed crystals were filtered out and the filtrate was allowed to stand at room temperature. Slow evaporation for one week afforded blue prismatic crystal in high yield.

Discussion

The crystal structure of the title compound is built up by the monovalent $[\text{Cu}(\text{H}_2\text{O})_2(\text{phen})(\text{NO}_3)]^+$ complex cations and nitrate anions. The Cu atoms in the complex cations are each square pyramidally coordinated by two N atoms of one phen ligand, three O atoms from two H_2O molecules and one nitrate ligand with one water molecule at the apical position ($d(\text{Cu}-\text{N}) = 1.995(3) \text{ \AA}$, $2.010(3) \text{ \AA}$; equatorial $d(\text{Cu}-\text{O}) = 1.978(2) \text{ \AA}$, $1.989(2) \text{ \AA}$; axial $d(\text{Cu}-\text{O}) = 2.234(3) \text{ \AA}$). The Cu atom is shifted by $0.133(1) \text{ \AA}$ from the equatorial plane through N(1), N(2), O(2) and O(3) atoms towards the apical O(1) atom. Through the intercationic hydrogen bonds with $d(\text{O}1 \cdots \text{O}5^{\text{I}}) = 2.789 \text{ \AA}$ and $\angle \text{O}1-\text{H} \cdots \text{O}(5)^{\text{I}} = 153^\circ$ (I: $x-1, y, z$), the complex cations are linked into 1D chains along the [100] direction with the chelating phen ligands extend-

ing parallelly on one side. Interdigitation of phen ligands from two adjacent chains leads to formation 1D double chains. The interplanar phen-to-phen distances alternatively of 3.39 $\text{\AA}$ and 3.47 $\text{\AA}$ suggest $\pi-\pi$ stacking interactions, in which the central benzene rings are engaged. The formed supramolecular double chains are arranged according to *pseudo* 1D close-packing pattern and the nitrate anions are situated in voids and are hydrogen bonded to water molecules from two double chains. Both nitrate and nitrate groups exhibit substantial deviation from the D_{3h} symmetry. Within the nitrate ligands, the N—O bond to the coordinating O3 atom of 1.285 $\text{\AA}$ is significantly longer than the remaining ones (1.217 $\text{\AA}$, 1.235 $\text{\AA}$). The N—O bond distances in the nitrate anions range from 1.199 $\text{\AA}$ to 1.249 $\text{\AA}$. The present monovalent $[\text{Cu}(\text{H}_2\text{O})_2(\text{phen})(\text{NO}_3)]^+$ complex cation is found to be the enantiomer of that reported in [1].

Table 1. Data collection and handling.

Crystal:	blue block, size $0.267 \times 0.489 \times 0.689 \text{ mm}$
Wavelength:	Mo $K\alpha$ radiation ($0.71073 \text{ \AA}$)
μ :	14.82 cm^{-1}
Diffractometer, scan mode:	Bruker P4, $\theta/2\theta$
$2\theta_{\text{max}}$:	54.98°
$N(hkl)_{\text{measured}}$, $N(hkl)_{\text{unique}}$:	4574, 3491
Criterion for I_{obs} , $N(hkl)_{\text{gt}}$:	$I_{\text{obs}} > 2 \sigma(I_{\text{obs}})$, 3087
$N(\text{param})_{\text{refined}}$:	275
Programs:	SHELXS-97 [2], SHELXL-97 [3]

Table 2. Atomic coordinates and displacement parameters (in $\text{\AA}^2$).

Atom	Site	x	y	z	U_{iso}
H(1)	4e	0.804(8)	0.212(3)	0.906(5)	0.08(2)
H(2)	4e	0.839(8)	0.213(3)	1.118(5)	0.09(2)
H(3)	4e	0.837(8)	0.122(3)	1.218(5)	0.08(2)
H(5)	4e	0.785(7)	−0.003(2)	1.212(4)	0.06(1)
H(6)	4e	0.722(7)	−0.103(2)	1.100(4)	0.07(1)
H(8)	4e	0.643(6)	−0.157(2)	0.877(4)	0.06(1)
H(9)	4e	0.616(7)	−0.141(2)	0.663(4)	0.07(1)
H(10)	4e	0.658(5)	−0.038(2)	0.599(3)	0.042(9)
HA(O1)	4e	0.33(1)	0.122(4)	0.617(7)	0.10(2)
HB(O1)	4e	0.389(6)	0.168(2)	0.682(4)	0.06(1)
HA(O2)	4e	0.932(7)	0.207(2)	0.702(4)	0.05(1)
HB(O2)	4e	0.762(6)	0.211(2)	0.609(4)	0.04(1)

* Correspondence author (e-mail: zhengcm@nbu.edu.cn)

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	0.73513(5)	0.10481(2)	0.70144(3)	0.0413(3)	0.0388(3)	0.0318(3)	−0.0016(1)	0.0136(2)	0.0021(1)
N(1)	4e	0.7735(4)	0.1184(1)	0.8824(2)	0.043(1)	0.043(1)	0.034(1)	−0.003(1)	0.016(1)	−0.001(1)
N(2)	4e	0.7059(4)	0.0098(1)	0.7467(2)	0.038(1)	0.041(1)	0.041(1)	−0.0014(9)	0.010(1)	0.001(1)
C(1)	4e	0.8026(6)	0.1745(2)	0.9459(3)	0.065(2)	0.048(2)	0.045(2)	−0.001(2)	0.024(2)	−0.004(1)
C(2)	4e	0.8253(7)	0.1757(2)	1.0738(4)	0.084(3)	0.064(2)	0.049(2)	−0.004(2)	0.029(2)	−0.014(2)
C(3)	4e	0.8168(6)	0.1185(2)	1.1359(3)	0.066(2)	0.080(2)	0.035(2)	0.000(2)	0.021(2)	−0.003(2)
C(4)	4e	0.7841(5)	0.0584(2)	1.0707(3)	0.038(1)	0.065(2)	0.037(1)	0.003(1)	0.014(1)	0.010(1)
C(5)	4e	0.7690(5)	−0.0045(2)	1.1253(3)	0.050(2)	0.069(2)	0.045(2)	0.005(2)	0.017(1)	0.020(2)
C(6)	4e	0.7356(5)	−0.0599(2)	1.0570(4)	0.051(2)	0.062(2)	0.063(2)	0.007(2)	0.021(2)	0.032(2)
C(7)	4e	0.7112(5)	−0.0587(2)	0.9255(3)	0.035(1)	0.048(2)	0.061(2)	0.001(1)	0.015(1)	0.013(1)
C(8)	4e	0.6704(6)	−0.1139(2)	0.8460(4)	0.059(2)	0.042(2)	0.080(3)	−0.002(2)	0.019(2)	0.012(2)
C(9)	4e	0.6487(7)	−0.1067(2)	0.7233(5)	0.068(3)	0.042(2)	0.077(3)	−0.007(2)	0.011(2)	−0.009(2)
C(10)	4e	0.6681(6)	−0.0437(2)	0.6759(4)	0.055(2)	0.046(2)	0.053(2)	−0.005(1)	0.011(2)	−0.004(1)
C(11)	4e	0.7277(4)	0.0023(1)	0.8702(3)	0.030(1)	0.041(1)	0.044(1)	0.003(1)	0.012(1)	0.008(1)
C(12)	4e	0.7634(4)	0.0613(2)	0.9433(3)	0.033(1)	0.048(2)	0.038(1)	0.001(1)	0.015(1)	0.005(1)
O(1)	4e	0.4185(4)	0.1375(2)	0.6441(3)	0.040(1)	0.073(2)	0.091(2)	0.004(1)	0.019(1)	−0.009(2)
O(2)	4e	0.8077(4)	0.1982(1)	0.6783(2)	0.058(2)	0.042(1)	0.041(1)	−0.002(1)	0.017(1)	0.0053(9)
N(3)	4e	0.9078(4)	0.0774(1)	0.5224(2)	0.064(2)	0.042(1)	0.036(1)	0.003(1)	0.023(1)	0.0031(9)
O(3)	4e	0.7285(4)	0.0814(1)	0.5295(2)	0.050(1)	0.061(1)	0.035(1)	−0.004(1)	0.0085(9)	−0.004(1)
O(4)	4e	0.9376(6)	0.0657(2)	0.4229(2)	0.123(3)	0.083(2)	0.045(1)	0.020(2)	0.048(2)	0.004(1)
O(5)	4e	1.0421(4)	0.0848(1)	0.6195(2)	0.049(1)	0.064(1)	0.051(1)	−0.000(1)	0.016(1)	0.000(1)
N(4)	4e	0.7708(4)	0.2521(1)	0.3768(2)	0.054(2)	0.042(1)	0.048(1)	−0.004(1)	0.011(1)	0.002(1)
O(6)	4e	0.9403(6)	0.2347(4)	0.4154(5)	0.049(2)	0.257(7)	0.140(4)	0.005(3)	0.009(2)	0.101(4)
O(7)	4e	0.6576(5)	0.2399(2)	0.4390(3)	0.075(2)	0.117(3)	0.063(2)	0.021(2)	0.029(2)	0.036(2)
O(8)	4e	0.7097(5)	0.2795(2)	0.2735(3)	0.075(2)	0.079(2)	0.047(1)	0.015(2)	0.024(1)	0.018(1)

Acknowledgments. The authors gratefully acknowledge the financial support of Zhejiang Provincial Natural Science Foundation of China (RC99034) and Municipal Natural Science Foundation of China (01J20130-1).

References

1. McFadden, D. L.; McPhail, A. T.; Gross, P. M.: Crystal and molecular structure of dinitrato(1,10-phenanthroline)cooper(II) and diaquanitrato-(1,10-phenanthroline)-copper(II) nitrate. *J. Chem. Soc. Dalton Trans.* (1975) 1993-1998.
2. Sheldrick, G. M.: Phase Annealing in SHELX-90: Direct Methods for Larger Structures. *Acta Crystallogr. A* **46** (1990) 467-473.
3. Sheldrick, G. M.: SHELXL-97. Program for the Refinement of Crystal Structures. University of Göttingen, Germany 1997.