Crystal structure of carbonatobis(1,10-phenanthroline-*N,N'*)copper(II) heptahydrate, $[\text{Cu}(\text{C}_{12}\text{H}_8\text{N}_2)_2(\text{CO}_3)] \cdot 7\text{H}_2\text{O}$

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Abstract

$\text{C}_{25}\text{H}_{30}\text{CuN}_4\text{O}_{10}$, monoclinic, $P12_1/c1$ (No. 14), $a = 9.930(1) \text{ \AA}$, $b = 26.346(2) \text{ \AA}$, $c = 10.548(1) \text{ \AA}$, $\beta = 106.083(8)^\circ$, $V = 2651.5 \text{ \AA}^3$, $Z = 4$, $R_{\text{gt}}(F) = 0.052$, $wR_{\text{ref}}(F^2) = 0.134$, $T = 293 \text{ K}$.

Source of material

10 ml CH_3OH was added to an aqueous solution of 0.34 g (1.36 mmol) $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ in 10 ml H_2O , and then 0.27 g (1.36 mmol) phenanthroline monohydrate and 0.18 g (1.36 mmol) L-aspartic acid were successively added and stirred. Insoluble solid was filtered out. Dropwise addition of 1.0 ml (1.0 M) Na_2CO_3 to the filtrate gave a dark blue solution. Slow evaporation at room temperature for several weeks afforded a small amount of greenish blue prismatic crystals.

Discussion

The title compound crystallizes isostructurally with $[\text{Ni}(\text{phen})_2\text{CO}_3] \cdot 7\text{H}_2\text{O}$ [1]. The $[\text{Cu}(\text{phen})_2\text{CO}_3]$ complex molecules and H_2O molecules build up the crystal structure. The Cu atom within the complex molecule is distorted octahedrally coordinated by two O atoms of one carbonate group and four N atoms of two phen ligands with $d(\text{Cu}—\text{O}) = 1.997 \text{ \AA}$, $2.345 \text{ \AA}$ and $d(\text{Cu}—\text{N}) = 2.038 \text{ \AA} - 2.222 \text{ \AA}$. Along the [001] direction, the complex molecules are stacked into columnar chains with the phen ligands containing N1 and N2 atoms outside so that each phen ligand containing N3 and N4 atoms is sandwiched by two crystallographically equivalents with the alternative interplanar distances of $3.29 \text{ \AA}$ and $3.32 \text{ \AA}$. The outside phen ligands of neighboring chains face antiparallelly at the interplanar distance

of $3.63 \text{ \AA}$. Above observation suggests that the π - π stacking interactions are responsible for the supramolecular assembly of the complex molecules into 2D supramolecular layers parallel to (001). Out of the seven crystallographically distinct H_2O molecules located between the 2D supramolecular layers, the five are situated at the corners of a hydrogen bonded (H_2O)₅ pentagon with $d(\text{O} \cdots \text{O}) = 2.798 \text{ \AA} - 2.893 \text{ \AA}$ and $\angle \text{O}—\text{H} \cdots \text{O} = 165^\circ - 174^\circ$ and the remaining two at the corners of a hydrogen bonded (H_2O)₄ rhombus with $d(\text{O} \cdots \text{O}) = 2.840 \text{ \AA}$, $2.927 \text{ \AA}$ and the corresponding angles $\angle \text{O}—\text{H} \cdots \text{O} = 178^\circ$, 165° . Along the [001] direction, the pentagonal (H_2O)₅ units are interlinked by hydrogen bonds ($d(\text{O} \cdots \text{O}) = 2.760 \text{ \AA}$, $2.762 \text{ \AA}$ and $\angle \text{O}—\text{H} \cdots \text{O} = 150^\circ$, 161°) to form 1D ribbons with pseudo pentagonal ring and pseudo rhombus ring alternating. Through hydrogen bonds ($d(\text{O} \cdots \text{O}) = 2.927 \text{ \AA}$ and $\angle \text{O}—\text{H} \cdots \text{O} = 172^\circ$), the formed ribbons are further bridged by the rhombus-like (H_2O)₄ units into 2D open networks. The carbonate group is significantly deviated from a D_{3h} symmetry due to the site and coordination effect, the C—O bond to the non-coordinating O atom being $1.235 \text{ \AA}$ substantially longer than those to the chelating ones ($1.271 \text{ \AA}$, $1.300 \text{ \AA}$). Three water molecules form strong hydrogen bonds to the carbonate O atoms ($d(\text{O} \cdots \text{O}) = 2.646 \text{ \AA} - 2.699 \text{ \AA}$ and $\angle \text{O}—\text{H} \cdots \text{O} = 170^\circ - 174^\circ$). It is clear that the 2D supramolecular layers are held together by the hydrogen bonded 2D networks.

Table 1. Data collection and handling.

Crystal:	greenish blue prism, size $0.422 \times 0.615 \times 0.778 \text{ mm}$
Wavelength:	Mo K_α radiation ($0.71073 \text{ \AA}$)
μ :	8.88 cm^{-1}
Diffractometer, scan mode:	Bruker P4, $\theta/2\theta$
$2\theta_{\text{max}}$:	55.02°
$N(hkl)_{\text{measured}}$, $N(hkl)_{\text{unique}}$:	7383, 6053
Criterion for I_{obs} , $N(hkl)_{\text{gt}}$:	$I_{\text{obs}} > 2\sigma(I_{\text{obs}})$, 5290
$N(\text{param})_{\text{refined}}$:	480
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	0.309(3)	0.097(1)	0.566(3)	0.041(7)
H(2)	4e	0.211(4)	0.065(1)	0.358(4)	0.07(1)
H(3)	4e	0.345(4)	0.036(1)	0.224(4)	0.07(1)
H(5)	4e	0.601(3)	0.023(1)	0.221(3)	0.052(9)
H(6)	4e	0.837(3)	0.029(1)	0.309(3)	0.051(8)
H(8)	4e	1.037(3)	0.058(1)	0.504(3)	0.046(8)
H(9)	4e	1.108(5)	0.085(2)	0.722(5)	0.10(2)
H(10)	4e	0.933(3)	0.111(1)	0.825(3)	0.038(7)

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Table 2. Continued.

Atom	Site	x	y	z	U _{iso}
H(13)	4e	0.795(3)	0.106(1)	1.020(3)	0.048(8)
H(14)	4e	0.927(3)	0.156(1)	1.180(3)	0.052(8)
H(15)	4e	0.930(3)	0.246(1)	1.157(3)	0.059(9)
H(17)	4e	0.834(3)	0.318(1)	1.018(3)	0.06(1)
H(18)	4e	0.692(3)	0.355(1)	0.825(3)	0.056(9)
H(20)	4e	0.522(3)	0.339(1)	0.605(3)	0.053(8)
H(21)	4e	0.411(3)	0.280(1)	0.445(3)	0.058(9)
H(22)	4e	0.448(3)	0.196(1)	0.484(3)	0.042(7)
HA(W1)	4e	0.140(4)	0.109(1)	1.061(3)	0.05(1)
HB(W1)	4e	0.231(4)	0.117(1)	1.008(3)	0.040(8)
HA(W2)	4e	0.291(5)	0.178(2)	0.733(4)	0.09(2)

Table 2. Continued.

Atom	Site	x	y	z	U _{iso}
HB(W2)	4e	0.159(5)	0.194(2)	0.740(5)	0.10(2)
HA(W3)	4e	0.092(4)	0.188(2)	0.914(4)	0.06(1)
HB(W3)	4e	0.076(5)	0.236(2)	0.880(5)	0.10
HA(W4)	4e	0.740(4)	-0.013(2)	0.032(4)	0.05(1)
HB(W4)	4e	0.695(4)	0.026(2)	-0.028(4)	0.07(1)
HA(W5)	4e	0.254(4)	0.178(2)	0.200(4)	0.06(1)
HB(W5)	4e	0.258(5)	0.223(2)	0.225(5)	0.10(2)
HA(W6)	4e	0.098(4)	0.021(2)	0.083(4)	0.07(1)
HB(W6)	4e	-0.037(4)	0.032(2)	0.093(4)	0.07(1)
HA(W7)	4e	0.175(5)	0.184(2)	0.388(5)	0.10
HB(W7)	4e	0.140(4)	0.191(2)	0.498(5)	0.08(1)

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	0.60261(2)	0.121417(9)	0.73817(2)	0.0248(2)	0.0334(2)	0.0279(2)	-0.00208(9)	0.0054(1)	-0.00440(9)
N(1)	4e	0.5000(2)	0.08695(7)	0.5651(2)	0.0287(8)	0.0356(9)	0.0317(8)	-0.0021(7)	0.0063(7)	-0.0054(7)
N(2)	4e	0.7740(2)	0.09421(7)	0.6784(2)	0.0306(9)	0.0340(9)	0.0350(9)	-0.0019(7)	0.0084(7)	-0.0042(7)
N(3)	4e	0.7236(2)	0.16199(7)	0.8925(2)	0.0267(8)	0.0349(9)	0.0304(8)	0.0001(6)	0.0066(7)	-0.0036(7)
N(4)	4e	0.5692(2)	0.20001(7)	0.6591(2)	0.0279(8)	0.043(1)	0.0313(9)	-0.0013(7)	0.0085(7)	-0.0001(7)
C(1)	4e	0.3636(2)	0.0838(1)	0.5119(2)	0.031(1)	0.050(1)	0.042(1)	-0.0043(9)	0.0085(9)	-0.008(1)
C(2)	4e	0.3047(3)	0.0635(1)	0.3858(3)	0.031(1)	0.065(2)	0.044(1)	-0.009(1)	-0.001(1)	-0.010(1)
C(3)	4e	0.3904(3)	0.0465(1)	0.3139(3)	0.047(1)	0.054(1)	0.036(1)	-0.008(1)	0.001(1)	-0.012(1)
C(4)	4e	0.5363(3)	0.04980(9)	0.3669(2)	0.042(1)	0.036(1)	0.034(1)	-0.0040(9)	0.0093(9)	-0.0066(8)
C(5)	4e	0.6356(3)	0.0344(1)	0.2980(3)	0.058(2)	0.043(1)	0.040(1)	-0.003(1)	0.018(1)	-0.015(1)
C(6)	4e	0.7749(3)	0.0391(1)	0.3547(3)	0.054(2)	0.043(1)	0.048(1)	0.004(1)	0.026(1)	-0.010(1)
C(7)	4e	0.8288(2)	0.05886(9)	0.4858(2)	0.039(1)	0.033(1)	0.045(1)	0.0034(9)	0.017(1)	-0.0018(9)
C(8)	4e	0.9721(3)	0.0641(1)	0.5512(3)	0.036(1)	0.048(1)	0.064(2)	0.005(1)	0.021(1)	-0.004(1)
C(9)	4e	1.0128(3)	0.0829(1)	0.6769(3)	0.029(1)	0.056(2)	0.061(2)	-0.001(1)	0.008(1)	-0.004(1)
C(10)	4e	0.9111(2)	0.0977(1)	0.7374(3)	0.032(1)	0.049(1)	0.044(1)	-0.0028(9)	0.0043(9)	-0.006(1)
C(11)	4e	0.7337(2)	0.07426(7)	0.5550(2)	0.032(1)	0.0262(9)	0.034(1)	-0.0008(7)	0.0102(8)	-0.0018(7)
C(12)	4e	0.5861(2)	0.07015(8)	0.4943(2)	0.033(1)	0.0280(9)	0.032(1)	-0.0021(7)	0.0094(8)	-0.0030(7)
C(13)	4e	0.8014(2)	0.1430(1)	1.0053(2)	0.034(1)	0.046(1)	0.035(1)	0.0037(9)	0.0065(9)	0.0007(9)
C(14)	4e	0.8821(3)	0.1732(1)	1.1071(2)	0.032(1)	0.066(2)	0.032(1)	0.004(1)	0.0035(9)	-0.003(1)
C(15)	4e	0.8797(2)	0.2244(1)	1.0920(2)	0.031(1)	0.063(2)	0.039(1)	-0.009(1)	0.0085(9)	-0.019(1)
C(16)	4e	0.7966(2)	0.24608(9)	0.9751(2)	0.028(1)	0.044(1)	0.040(1)	-0.0064(8)	0.0141(9)	-0.0139(9)
C(17)	4e	0.7844(3)	0.2998(1)	0.9521(3)	0.047(1)	0.041(1)	0.060(2)	-0.013(1)	0.025(1)	-0.021(1)
C(18)	4e	0.6990(3)	0.3187(1)	0.8404(3)	0.056(2)	0.031(1)	0.071(2)	-0.005(1)	0.034(1)	-0.008(1)
C(19)	4e	0.6206(2)	0.28637(9)	0.7373(2)	0.040(1)	0.034(1)	0.050(1)	0.0027(9)	0.025(1)	0.0041(9)
C(20)	4e	0.5314(3)	0.3040(1)	0.6173(3)	0.049(2)	0.047(1)	0.063(2)	0.015(1)	0.029(1)	0.021(1)
C(21)	4e	0.4658(3)	0.2704(1)	0.5234(3)	0.040(1)	0.074(2)	0.047(1)	0.014(1)	0.015(1)	0.023(1)
C(22)	4e	0.4880(2)	0.2184(1)	0.5472(2)	0.032(1)	0.061(2)	0.035(1)	0.001(1)	0.0090(9)	0.006(1)
C(23)	4e	0.6344(2)	0.23332(8)	0.7540(2)	0.0272(9)	0.032(1)	0.035(1)	-0.0008(7)	0.0147(8)	-0.0007(8)
C(24)	4e	0.7207(2)	0.21315(8)	0.8758(2)	0.0242(9)	0.034(1)	0.033(1)	-0.0027(7)	0.0121(8)	-0.0056(8)
C(25)	4e	0.4382(2)	0.08788(8)	0.8722(2)	0.035(1)	0.035(1)	0.039(1)	-0.0042(8)	0.0123(9)	-0.0037(8)
O(1)	4e	0.4289(2)	0.12765(7)	0.7973(2)	0.058(1)	0.041(1)	0.046(1)	0.0035(8)	0.0131(9)	0.0045(7)
O(2)	4e	0.5461(2)	0.06104(9)	0.8786(2)	0.046(1)	0.065(1)	0.074(1)	0.0160(9)	0.005(1)	-0.011(1)
O(3)	4e	0.3465(3)	0.07785(9)	0.9271(3)	0.108(2)	0.058(1)	0.125(2)	-0.019(1)	0.093(2)	-0.008(1)
O(4)	4e	0.1804(3)	0.12905(9)	1.0388(3)	0.063(1)	0.053(1)	0.060(1)	0.004(1)	0.024(1)	-0.002(1)
O(5)	4e	0.2286(3)	0.19706(9)	0.6941(2)	0.059(1)	0.075(1)	0.047(1)	0.020(1)	0.021(1)	0.011(1)
O(6)	4e	0.0561(2)	0.2053(1)	0.8584(2)	0.056(1)	0.063(1)	0.052(1)	0.006(1)	0.018(1)	0.008(1)
O(7)	4e	0.7679(2)	0.00651(9)	0.0091(2)	0.0338(9)	0.046(1)	0.067(1)	-0.0022(8)	0.0110(9)	0.0028(9)
O(8)	4e	0.2717(3)	0.1961(1)	0.2557(3)	0.069(2)	0.085(2)	0.052(1)	-0.010(1)	0.021(1)	-0.017(1)
O(9)	4e	0.0447(3)	0.04209(9)	0.1251(3)	0.048(1)	0.067(1)	0.071(1)	-0.008(1)	0.005(1)	-0.022(1)
O(10)	4e	0.1015(3)	0.1907(1)	0.4224(3)	0.053(1)	0.111(2)	0.052(1)	0.003(1)	0.015(1)	-0.000(1)

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