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Refinement of the crystal structure of bis(2-hydroxy-1,10-phenanthroline)dicopper(I), $Cu_2(C_{12}H_7N_2O)_2$

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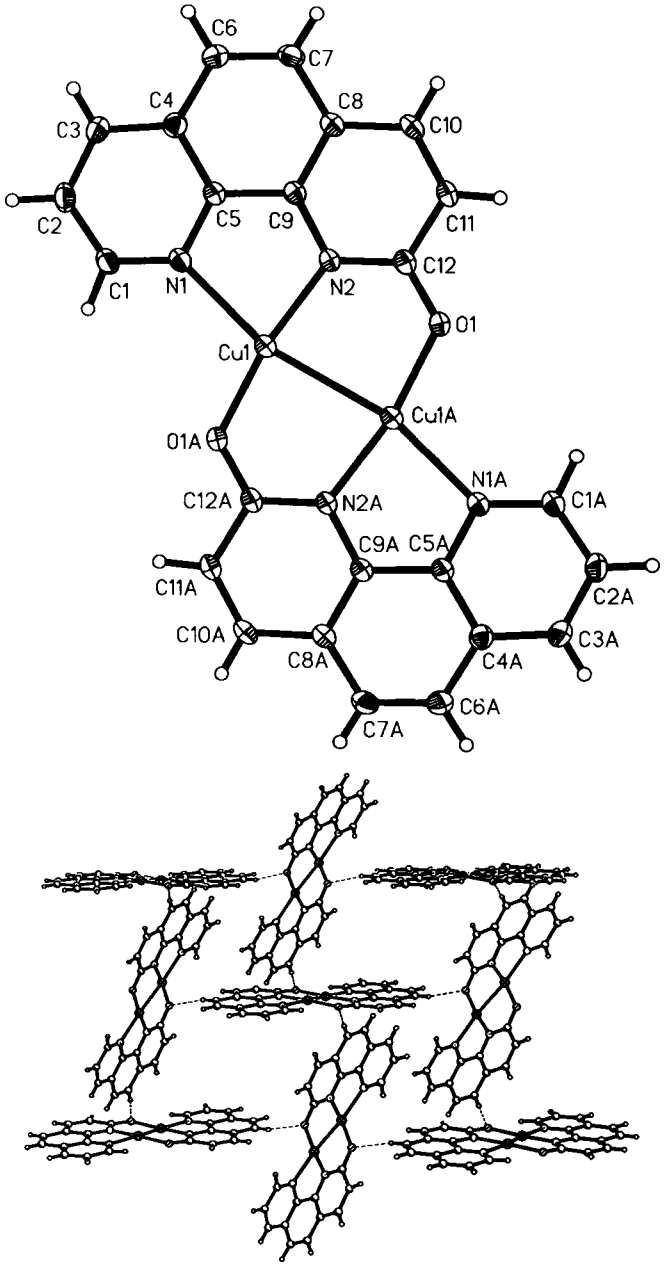

Abstract

$C_{24}H_{14}Cu_2N_4O_2$, monoclinic, $P12_1/n1$ (no. 14), a = 4.7747(4) Å, b = 12.688(1) Å, c = 15.446(1) Å, β = 95.316(1)°, V = 931.7 Å^3, Z = 2, $R_{gt}(F)$ = 0.023, $wR_{ref}(F^2)$ = 0.062, T = 293 K.

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Source of material

A mixture of $CuCl_2 \cdot 2H_2O$ (1 mmol), $Cu(CH_3COO)_2 \cdot H_2O$ (1 mmol), phen (1 mmol), and water (60 mL) in a molar ratio of 1:1:1:3333 was inside a programmable electric furnace at 185 °C for four days with starting pH = 9.95 adjusted by 2 M NaOH solution. After cooling the autoclave to room temperature for 32 h, blue block crystals were obtained.

Discussion

The considerable attention and driving force in the chemistry of copper(I) complexes with N-heterocyclic ligands, especially derivatives of 1,10-phenanthroline (phen) and 2,2′-bipyridine (2,2′-bpy), due to their unusual photophysical and electrochemical properties of mononuclear copper(I) complexes [1,2], as well as diverse luminescent properties of polynuclear copper(I) complexes [3-5]. At the same time it has to be pointed out these copper(I) complexes usually obtained by the so-called "anomalies" of reactivity of copper(II) compounds with N-heterocyclic ligands particularly phen and bpy [6,7], which can be interpreted by the Gillard mechanism [8]. Herein, we described a dinuclear copper(I) complex $[Cu_2(C_{12}H_7N_2O)_2]$, which was synthesized hydrothermally under basic environment. Although it was reported several years ago, our quality of crystallographic data and structure refinement is obviously higher than previously published one [9].

The crystal structure of the complex consists of two hydroxylated 1,10-phenanthroline molecules linked by two copper atoms via four nitrogen donors and two oxygen atoms (figure, top). The one crystallographically independent Cu^I atom adopts a trigonal environment, being defined by two nitrogen donors and one oxygen atom from the two different deprotonated 2-hydroxy-1,10-phenanthroline ligands. The Cu—N bond lengths are 1.946(2) Å and 2.194(2) Å and the Cu—O and Cu···Cu distances are 1.899(1) Å and 2.6299(5) Å, respectively, which are all obviously shorter than the previous report as a result of our higher data quality. Moreover, the Cu···Cu distance is between twice the Van der Waals radius of Cu^I (2.8 Å) and the Cu—Cu separation of 2.56 Å in metallic copper [10], indicating similar Cu^I–Cu^I bonding interactions. The remarkable structural feature of complex is the reduction of Cu^{II} by means of phen in the formation process. Bond valence sum (BVS) calculations demonstrate the valence sum of Cu center is 1.162 (+1) [11]. The phen acts as an effective agent to reduce from Cu^{II} to Cu^I, at the same time it was hydroxylated and coordinating to the reduced Cu^I ions to form the dinuclear copper(I) complex. More interestingly, discrete molecular units are connected by means of C–H···O hydrogen bonds (d(C7···O1A) = 3.345 Å) to form a two-dimensional supramolecular network (figure, bottom).

Table 1. Data collection and handling.

Crystal:	blue block, size 0.13 × 0.15 × 0.18 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ:	23.16 cm^{-1}
Diffractometer, scan mode:	Rigaku R-AXIS IP, φ
$2\theta_{max}$:	51°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	4856, 1735
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\,\sigma(I_{obs})$, 1550
$N(param)_{refined}$:	173
Programs:	SHELXS-97 [12], SHELXL-97 [13]

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

Atom	Site	x	y	z	U_{iso}
H(1)	4e	0.753(5)	0.797(2)	0.105(2)	0.042(6)
H(2)	4e	0.973(5)	0.631(2)	0.080(1)	0.037(6)
H(3)	4e	0.796(5)	0.542(2)	−0.044(2)	0.049(7)
H(6)	4e	0.466(5)	0.522(2)	−0.178(2)	0.050(7)
H(7)	4e	0.107(5)	0.596(2)	−0.265(2)	0.044(6)
H(10)	4e	−0.243(5)	0.739(2)	−0.297(1)	0.035(6)
H(11)	4e	−0.446(5)	0.896(2)	−0.255(2)	0.043(6)

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)	4e	0.20741(6)	0.93195(2)	0.01283(2)	0.0463(2)	0.0384(2)	0.0282(2)	0.0101(1)	−0.0087(1)	−0.0061(1)
O(1)	4e	−0.2960(3)	1.0012(1)	−0.12191(9)	0.0531(9)	0.0436(9)	0.0334(8)	0.0192(7)	−0.0159(7)	−0.0073(7)
N(1)	4e	0.4737(3)	0.7918(1)	0.0063(1)	0.0353(9)	0.0396(9)	0.0255(8)	0.0055(7)	−0.0032(7)	−0.0025(7)
N(2)	4e	0.0403(3)	0.8741(1)	−0.0967(1)	0.0334(9)	0.0328(8)	0.0239(8)	0.0035(7)	−0.0042(7)	−0.0010(6)
C(1)	4e	0.6872(4)	0.7527(2)	0.0572(1)	0.037(1)	0.048(1)	0.028(1)	0.006(1)	−0.0046(8)	−0.0026(9)
C(2)	4e	0.8158(5)	0.6573(2)	0.0409(1)	0.041(1)	0.052(1)	0.035(1)	0.013(1)	−0.005(1)	0.006(1)
C(3)	4e	0.7219(5)	0.6010(2)	−0.0315(2)	0.044(1)	0.038(1)	0.040(1)	0.014(1)	−0.001(1)	0.001(1)
C(4)	4e	0.4995(4)	0.6396(2)	−0.0885(1)	0.035(1)	0.032(1)	0.032(1)	0.0021(8)	0.0024(8)	0.0028(8)
C(5)	4e	0.3816(4)	0.7369(1)	−0.0663(1)	0.030(1)	0.0314(9)	0.0250(9)	0.0000(8)	0.0005(7)	0.0009(8)
C(6)	4e	0.3907(5)	0.5869(2)	−0.1657(1)	0.047(1)	0.033(1)	0.038(1)	0.005(1)	0.002(1)	−0.0045(9)
C(7)	4e	0.1758(5)	0.6285(2)	−0.2179(1)	0.045(1)	0.033(1)	0.030(1)	−0.0047(9)	−0.0005(9)	−0.0052(9)
C(8)	4e	0.0533(4)	0.7271(2)	−0.1975(1)	0.032(1)	0.033(1)	0.025(1)	−0.0039(8)	0.0006(8)	−0.0003(8)
C(9)	4e	0.1516(4)	0.7811(1)	−0.1222(1)	0.0299(9)	0.031(1)	0.0239(9)	−0.0011(8)	0.0009(7)	0.0014(7)
C(10)	4e	−0.1755(4)	0.7735(2)	−0.2492(1)	0.037(1)	0.041(1)	0.022(1)	−0.0049(9)	−0.0049(8)	−0.0024(8)
C(11)	4e	−0.2870(5)	0.8652(2)	−0.2246(1)	0.038(1)	0.042(1)	0.026(1)	0.0033(9)	−0.0080(9)	0.0009(9)
C(12)	4e	−0.1801(4)	0.9166(2)	−0.1455(1)	0.039(1)	0.037(1)	0.025(1)	0.0033(9)	−0.0040(8)	0.0014(8)

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