Crystal structure of aqua(1,10-phenanthroline)bis(2-thiophenecarboxylato)copper(II), $Cu(H_2O)(C_{12}H_8N_2)(C_4H_3SCOO)_2$

D.-M. Feng[I], H.-Y. He[I], H.-X. Jin[I] and L.-G. Zhu*[,II]

[I] Jiaxing College, Department of Chemical Engineering, Jiaxing, 314001 P. R. China
[II] Zhejiang University, Department of Chemistry, Hangzhou, 310027 P. R. China

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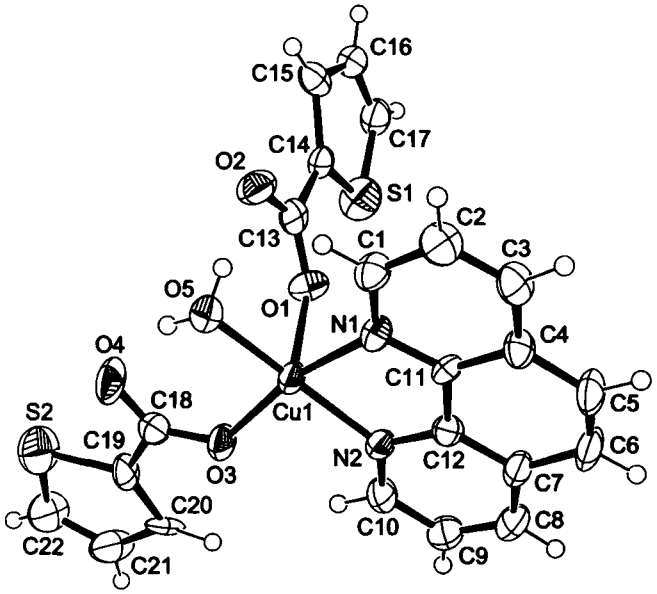

Abstract

$C_{22}H_{16}CuN_2O_5S_2$, monoclinic, $P12_1/c1$ (no. 14), $a = 8.4228(4)$ Å, $b = 19.7169(7)$ Å, $c = 12.4746(5)$ Å, $\beta = 91.041(2)°$, $V = 2071.3$ Å^3, $Z = 4$, $R_{gt}(F) = 0.067$, $wR_{ref}(F^2) = 0.199$, $T = 295$ K.

Source of material

A mixture of $Cu(CH_3COO)_2 \cdot H_2O$ (0.0586 g, 0.29 mmol) and 2-thiophenecarboxylic acid (0.0769 g, 0.6 mmol) in 10 ml water was added to a 10 ml CH_3OH solution of 1,10-phenanthroline (0.0614 g, 0.31 mmol). Then the resulting solution was set aside and the solvent allowed to evaporate at room temperature. After one day, green needle-shaped crystals were obtained.

Experimental details

The H atoms bonded to aromatic C atoms were generated geometrically and included in the refinements in the riding model approximation (d(C—H) = 0.93 Å, $U_{iso} = 1.2U_{eq}$(C)). The water H atoms were located from Fourier difference maps and refined with a distance restraint of d(O—H) = 0.85(1) Å and a fixed isotropic displacement parameter of U_{iso}(H) = 0.05 Å^2. The large R_{int} value indicates the low quality of the crystal. The small U value of the C20 atom is caused by a small part of disordering of the thiophene group. Sulfur occupies partially a position near the C20 position and, vice versa, carbon occupies a position near S2. The disorder parts were not resolved.

* Correspondence author (e-mail: chezlg@zju.edu.cn)

Discussion

The 2-thiophenecarboxylic acid (Htpc) has been intensively studied in biological systems [1] and its metal complexes can considerably increase their biological activities [2-3]. Recently, the Htpc ligand also has been used to prepare magnet and photoluminescence materials [4-5]. But so far single crystal structures of 2-thiophenecarboxylate complexes are still limited [4-8].

In the title monomer complex, the copper atom adopts a square pyramidal environment defined by two nitrogen donors from the 1,10-phenanthroline ligand, two carboxyl oxygen atoms from two 2-thiophenecarboxylato ligands and one oxygen atom from the coordinated water molecule. Atoms N1, N2, O3, and O5 are sitting on the basal plane, while atom O1 occupies the apical position. Each 2-thiophenecarboxylato ligand is mono-coordinated to the metal atom. The uncoordinated carboxyl oxygen atoms O2 and O4 form intra-molecular hydrogen bonds, which consolidates the solid structure. Two neighboring thiophenecarboxylato ligands stack each other with the distance of about 3.4 Å, indicating such materials can be used as electronic conductor.

The comparison with two benzoato (bez) complexes with aqua and 1,10-phenanthroline ligands, $[Cu(phen)(bez)_2(H_2O)]$ [9] and $[Mn(phen)(bez)_2(H_2O)]$ [10], shows similar coordination environments and bond lengths. In the title structure, there is only intramolecular hydrogen bonding, but in the benzoato structures intermolecular H-bonds extend the complexes into dimers.

Table 1. Data collection and handling.

Crystal:	green needle, size 0.03 × 0.05 × 0.52 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ:	12.96 cm^{-1}
Diffractometer, scan mode:	Bruker SMART APEX CCD, φ/ω
$2\theta_{max}$:	50°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	10400, 3639
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\,\sigma(I_{obs})$, 2331
$N(param)_{refined}$:	296
Programs:	SHELXS-97 [11], SHELXL-97 [12], ORTEP-3 [13], WinGX [14]

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

Atom	Site	x	y	z	U_{iso}
H(1)	4e	−0.0518	0.0305	0.1540	0.046
H(2)	4e	−0.0961	0.1250	0.0505	0.054
H(3)	4e	0.0056	0.2272	0.1042	0.049
H(5)	4e	0.1670	0.2943	0.2417	0.056
H(6)	4e	0.3216	0.2949	0.3916	0.060
H(8)	4e	0.4465	0.2281	0.5513	0.058

Table 2. Continued.

Atom	Site	x	y	z	U_{iso}
H(9)	4e	0.4826	0.1247	0.6334	0.059
H(10)	4e	0.3565	0.0309	0.5668	0.049
H(15)	4e	0.3772	−0.1065	−0.0488	0.044
H(16)	4e	0.6727	−0.0996	−0.0957	0.051
H(17)	4e	0.8457	−0.0687	0.0448	0.052

Table 2. Continued.

Atom	Site	x	y	z	U_{iso}
H(20)	4e	0.3625	−0.0835	0.6827	0.037
H(21)	4e	0.4369	−0.1820	0.8048	0.071
H(22)	4e	0.3469	−0.2884	0.7467	0.069
H(5B)	4e	0.043(7)	−0.070(3)	0.234(3)	0.050
H(5A)	4e	0.011(8)	−0.104(2)	0.326(4)	0.050

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	0.1385(1)	−0.00293(4)	0.36868(6)	0.0458(6)	0.0198(5)	0.0329(5)	−0.0039(4)	−0.0025(4)	−0.0008(3)
S(1)	4e	0.6422(3)	−0.0544(1)	0.1664(2)	0.069(2)	0.060(2)	0.071(2)	−0.001(1)	0.001(1)	−0.006(1)
S(2)	4e	0.2104(3)	−0.2466(1)	0.5970(2)	0.094(2)	0.041(1)	0.079(2)	0.007(1)	−0.001(1)	0.010(1)
N(1)	4e	0.0775(6)	0.0734(3)	0.2668(4)	0.033(3)	0.023(3)	0.040(3)	0.002(2)	−0.001(2)	−0.004(2)
N(2)	4e	0.2520(6)	0.0732(3)	0.4442(4)	0.042(3)	0.024(3)	0.028(3)	0.000(2)	−0.001(2)	−0.002(2)
O(1)	4e	0.3388(5)	−0.0379(2)	0.2694(3)	0.042(3)	0.048(3)	0.032(3)	0.003(2)	−0.005(2)	−0.009(2)
O(2)	4e	0.1890(6)	−0.0800(2)	0.1347(4)	0.047(3)	0.052(3)	0.041(3)	−0.009(3)	−0.001(2)	−0.014(2)
O(3)	4e	0.1742(6)	−0.0614(2)	0.4938(3)	0.076(4)	0.022(3)	0.038(3)	−0.009(2)	−0.006(2)	0.004(2)
O(4)	4e	0.0672(6)	−0.1582(2)	0.4354(4)	0.083(4)	0.024(3)	0.061(3)	−0.011(3)	−0.019(3)	0.011(2)
O(5)	4e	−0.0076(5)	−0.0668(2)	0.2927(4)	0.045(3)	0.037(3)	0.040(3)	−0.009(2)	0.000(2)	−0.001(2)
C(1)	4e	−0.0086(8)	0.0717(3)	0.1761(5)	0.037(4)	0.036(4)	0.040(4)	−0.003(3)	−0.009(3)	−0.002(3)
C(2)	4e	−0.0362(8)	0.1283(4)	0.1136(6)	0.048(5)	0.043(5)	0.044(4)	0.011(4)	−0.011(3)	0.008(3)
C(3)	4e	0.0249(8)	0.1886(3)	0.1453(5)	0.045(4)	0.032(4)	0.046(4)	0.010(3)	−0.003(3)	0.010(3)
C(4)	4e	0.1160(8)	0.1932(3)	0.2385(5)	0.038(4)	0.025(4)	0.041(4)	0.003(3)	−0.004(3)	0.006(3)
C(5)	4e	0.1848(9)	0.2539(3)	0.2784(6)	0.061(5)	0.021(4)	0.058(5)	−0.003(3)	−0.005(4)	0.008(3)
C(6)	4e	0.2756(9)	0.2544(3)	0.3685(6)	0.069(5)	0.018(4)	0.062(5)	−0.007(3)	−0.003(4)	−0.003(3)
C(7)	4e	0.3026(8)	0.1937(3)	0.4294(5)	0.047(4)	0.024(4)	0.041(4)	−0.006(3)	−0.003(3)	−0.003(3)
C(8)	4e	0.3979(9)	0.1895(4)	0.5232(6)	0.063(5)	0.035(4)	0.045(4)	−0.012(4)	−0.006(4)	−0.010(3)
C(9)	4e	0.4181(9)	0.1283(4)	0.5724(5)	0.065(5)	0.047(5)	0.033(4)	−0.013(4)	−0.008(4)	−0.004(3)
C(10)	4e	0.3428(8)	0.0720(3)	0.5313(5)	0.056(5)	0.031(4)	0.036(4)	−0.004(3)	−0.004(3)	0.008(3)
C(11)	4e	0.1389(7)	0.1331(3)	0.2963(5)	0.036(4)	0.020(3)	0.030(3)	0.003(3)	0.003(3)	−0.008(3)
C(12)	4e	0.2334(7)	0.1334(3)	0.3933(5)	0.039(4)	0.024(4)	0.032(4)	0.008(3)	0.002(3)	0.002(3)
C(13)	4e	0.3195(8)	−0.0621(3)	0.1769(5)	0.050(5)	0.018(3)	0.038(4)	0.007(3)	−0.006(3)	0.009(3)
C(14)	4e	0.4633(7)	−0.0712(3)	0.1092(4)	0.040(4)	0.019(3)	0.035(4)	−0.001(3)	0.000(3)	0.000(3)
C(15)	4e	0.4620(5)	−0.0936(2)	−0.0045(3)	0.041(3)	0.033(3)	0.037(3)	0.010(2)	0.011(2)	0.008(2)
C(16)	4e	0.6355(7)	−0.0897(3)	−0.0278(5)	0.060(5)	0.031(4)	0.037(4)	−0.003(3)	0.007(4)	−0.002(3)
C(17)	4e	0.7362(8)	−0.0715(3)	0.0521(5)	0.043(4)	0.032(4)	0.053(5)	−0.002(3)	0.008(4)	−0.003(3)
C(18)	4e	0.1522(8)	−0.1244(3)	0.4996(5)	0.053(5)	0.030(4)	0.037(4)	−0.001(3)	0.011(3)	−0.001(3)
C(19)	4e	0.2328(8)	−0.1596(3)	0.5922(5)	0.052(4)	0.017(3)	0.053(4)	0.005(3)	0.018(4)	0.005(3)
C(20)	4e	0.3330(7)	−0.1287(3)	0.6747(4)	0.048(4)	0.034(4)	0.010(3)	0.029(3)	0.003(3)	0.002(2)
C(21)	4e	0.376(1)	−0.1871(3)	0.7424(6)	0.080(6)	0.056(6)	0.042(5)	0.014(5)	0.000(4)	−0.010(4)
C(22)	4e	0.3231(9)	−0.2486(4)	0.7099(5)	0.078(6)	0.039(5)	0.054(5)	0.016(4)	−0.009(4)	0.007(4)

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