Corrected Version

Crystal structure of bis(1,10-phenanthroline-κ^2N,N')(sulfato-*O*)-copper(II) — propane-1,2-diol (1:1), $Cu(C_{12}H_8N_2)_2(SO_4) \cdot C_3H_8O_2$

Kai-Long Zhong*

Nanjing College of Chemical Technology, Department of Applied Chemistry, Nanjing 210048, P. R. China

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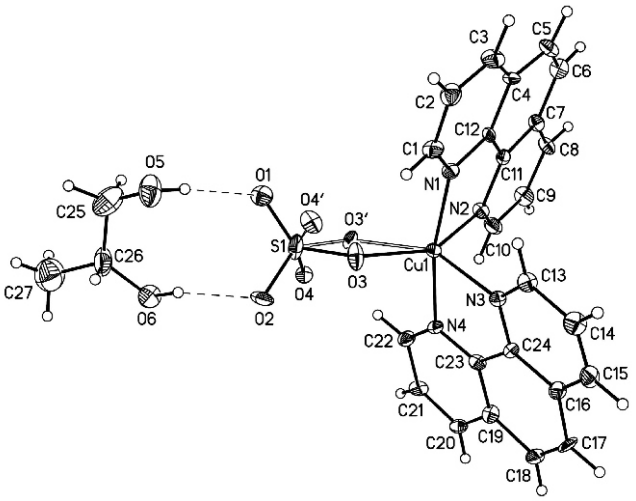

Abstract

$C_{27}H_{24}CuN_4O_6S$, monoclinic, *C*1*c*1 (no. 9), a = 17.405(7) Å, b = 13.074(6) Å, c = 13.267(7) Å, β = 123.45(2)°, V = 2519.1 Å^3, Z = 4, $R_{gt}(F)$ = 0.046, $wR_{ref}(F^2)$ = 0.126, T = 291 K.

Source of material

Reagents and solvents used were of commercially available quality. 1,10-Phenanthroline (phen, 0.2 mmol), melamine (0.1 mmol), $CuSO_4 \cdot 5H_2O$ (0.1 mmol), propane-1,2-diol (2.0 ml) and water (1.0 ml) were mixed and placed in a thick Pyrex tube, which was sealed and heated to 403 K for 72 h. The tube was cooled to ambient temperature spontaneously, and blue block-shaped crystals of the title compound were obtained.

Experimental details

The hydrogen atoms were positioned geometrically and allowed to ride on their parent atoms, with d(C—H) = 0.93 - 0.98 Å and U_{iso}(H) = 1.2 U_{eq}(C); d(O—H) = 0.82 Å and U_{iso}(H) = 1.5 U_{eq}(O). The sulfate ion is disorded over two positions with refined site occupancies of 0.51(1) and 0.49(1). The presence of pseudo-symmetry in the structure suggests the higher symmetry space group *C*2/*c* but attempts to refine the structure in this space group resulted in high R and wR values, moreover, the solvent propane-1,2-diol molecule does not exhibit two-fold symmetry. Hence the requirement to solve in *Cc*. The Flack parameter was refined as a full least-squares parameter, and the refined value of 0.49(3) suggests inversion twinning. The twinning has been applied in the refinement with 1539 Friedel pairs [1].

Discussion

The design and synthesis of metal-organic complexes or polymeric coordination networks is a rapidly developing field in coordination and supramolecular chemistry during the past decades [2-5]. Many N-containing bidentate ligands, such as 1,10-phenanthroline, 4,4′-bipyridine and 2,2′-bipyridine as auxiliary ligand have been widely applied in constructing coordination polymers [6,7]. In the past few years, we have synthesized and reported some transition metal complexes with bidentate-chelating sulfate auxiliary ligand via a alcohol-solvothermal reaction [8-15], the title compound was unexpectedly obtained during an attempt to synthesize a complex of Cu-complex with bidentate-chelating sulfate ligand by the similar route.

X-ray diffraction indicated that the Cu^{2+} ions are in a distorted square-pyramidal coordination formed by four N atoms (N1, N2, N3, N4) from two chelating phen ligands and an O atom (O3) from a monodentate sulfate ligand, the N1, N2, N3 and N4 atoms comprise a square, and the O3 atom the apex of a square pyramid. The Cu—N bond lengths and N–Cu–N angle are in the range of 1.991(7) - 2.154(8) Å and 80.4(3) - 80.7(3)°, respectively. The two chelating N–C–C–N groups subtend a dihedral angle of 84.9(4)°. This apical Cu—O3 distance is 1.40(1) Å.

In the crystal structure, the metal complex and solvent molecule are held together by intermolecular hydrogen bonds: d(O5–H51···O1) = 2.81(1) Å, O5–H51···O1 = 171.4° and d(O6–H61···O2) = 2.81(1) Å, O6–H61···O2 = 161.5°, which helps to further stabilize the crystal structure.

Table 1. Data collection and handling.

Crystal:	blue block, size 0.19 × 0.21 × 0.24 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ:	10.02 cm^{-1}
Diffractometer, scan mode:	Rigaku RAXIS-RAPID, ω
$2\theta_{max}$:	54.94°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	12107, 5404
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\ \sigma(I_{obs})$, 4684
$N(param)_{refined}$:	367
Programs:	SHELXS-97, SHELXL-97 [16]

* e-mail: zklong@tom.com

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

Atom	Site	Occ.	*x*	*y*	*z*	U_{iso}
H(1)	4*a*		0.8745	0.6292	0.8998	0.048
H(2)	4*a*		0.7731	0.6623	0.9434	0.061
H(3)	4*a*		0.6673	0.7890	0.8478	0.059
H(5)	4*a*		0.5838	0.9139	0.6604	0.052
H(6)	4*a*		0.5650	0.9710	0.4855	0.054
H(8)	4*a*		0.6293	0.9809	0.3518	0.051
H(9)	4*a*		0.7392	0.9221	0.3150	0.056
H(10)	4*a*		0.8517	0.8123	0.4497	0.061
H(13)	4*a*		0.9762	0.8065	0.9653	0.045
H(14)	4*a*		1.0943	0.9170	1.0978	0.063
H(15)	4*a*		1.1956	0.9751	1.0573	0.057
H(17)	4*a*		1.2542	0.9739	0.9173	0.053
H(18)	4*a*		1.2504	0.9049	0.7595	0.055
H(20)	4*a*		1.1716	0.7894	0.5783	0.048
H(21)	4*a*		1.0518	0.6751	0.4563	0.045
H(22)	4*a*		0.9545	0.6208	0.5245	0.046
H(25A)	4*a*		0.8384	0.0702	0.7065	0.134
H(25B)	4*a*		0.7983	0.1538	0.6050	0.134
H(26)	4*a*		0.9767	0.1201	0.7659	0.106
H(27A)	4*a*		0.8881	0.0220	0.5564	0.197
H(27B)	4*a*		0.9954	0.0276	0.6456	0.197
H(27C)	4*a*		0.9354	0.0213	0.6878	0.197
O(4')	4*a*	0.49	0.9127(8)	0.4812(9)	0.5729(9)	0.039(3)
H(51)	4*a*		0.8490	0.2685	0.7381	0.130
H(61)	4*a*		0.9719	0.2582	0.691	0.126

Table 3. Atomic coordinates and displacement parameters (in Å^2).

Atom	Site	Occ.	*x*	*y*	*z*	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Cu(1)	4*a*		0.9133(1)	0.69926(3)	0.7067(1)	0.0337(2)	0.0297(2)	0.0436(2)	0.0001(5)	0.0284(2)	0.0013(5)
S(1)	4*a*		0.9122(3)	0.46037(7)	0.7053(4)	0.0433(5)	0.0255(4)	0.0684(7)	0.002(1)	0.0080(5)	0.004(2)
C(1)	4*a*		0.8276(6)	0.6754(8)	0.8516(7)	0.044(5)	0.048(5)	0.038(4)	0.001(4)	0.029(4)	0.013(4)
C(2)	4*a*		0.7698(8)	0.6973(7)	0.880(1)	0.061(6)	0.046(5)	0.053(5)	0.002(4)	0.035(5)	0.006(4)
C(3)	4*a*		0.7041(7)	0.7702(9)	0.8201(8)	0.053(5)	0.067(6)	0.044(5)	0.003(5)	0.037(5)	0.009(4)
C(4)	4*a*		0.6912(6)	0.8170(8)	0.7174(8)	0.024(4)	0.040(5)	0.057(5)	0.003(3)	0.026(4)	0.009(4)
C(5)	4*a*		0.6236(7)	0.8898(8)	0.6397(8)	0.039(5)	0.051(5)	0.042(4)	0.011(4)	0.024(4)	0.006(4)
C(6)	4*a*		0.6131(7)	0.9269(7)	0.5361(7)	0.049(5)	0.048(5)	0.035(4)	0.001(4)	0.021(4)	0.002(3)
C(7)	4*a*		0.6773(6)	0.8964(7)	0.5078(7)	0.032(4)	0.034(4)	0.027(3)	0.008(3)	0.012(3)	0.006(3)
C(8)	4*a*		0.6744(7)	0.9344(7)	0.4040(8)	0.044(5)	0.039(4)	0.045(4)	0.016(3)	0.024(4)	0.007(3)
C(9)	4*a*		0.7405(7)	0.9004(8)	0.3827(8)	0.061(6)	0.049(5)	0.042(4)	0.013(4)	0.034(4)	0.024(4)
C(10)	4*a*		0.8082(7)	0.8334(8)	0.465(1)	0.053(6)	0.048(5)	0.068(5)	0.010(4)	0.043(5)	0.004(5)
C(11)	4*a*		0.7493(6)	0.8289(7)	0.5834(7)	0.038(5)	0.026(4)	0.044(4)	0.004(4)	0.027(4)	0.004(4)
C(12)	4*a*		0.7528(5)	0.7880(5)	0.6839(7)	0.020(3)	0.022(3)	0.036(3)	0.005(2)	0.010(3)	0.000(2)
C(13)	4*a*		1.0193(6)	0.8281(7)	0.9491(7)	0.045(5)	0.047(5)	0.028(3)	0.004(4)	0.024(3)	0.010(3)
C(14)	4*a*		1.0898(8)	0.8956(9)	1.0279(9)	0.057(6)	0.062(6)	0.039(4)	0.000(4)	0.027(4)	0.007(4)
C(15)	4*a*		1.1498(7)	0.9294(7)	1.0047(8)	0.046(5)	0.048(5)	0.035(4)	0.001(4)	0.014(4)	0.015(4)
C(16)	4*a*		1.1447(6)	0.8968(7)	0.9019(8)	0.038(5)	0.032(4)	0.051(5)	0.001(3)	0.024(4)	0.008(4)
C(17)	4*a*		1.2091(6)	0.9258(7)	0.8697(8)	0.026(4)	0.040(5)	0.060(5)	0.019(3)	0.020(4)	0.003(4)
C(18)	4*a*		1.2064(7)	0.8870(8)	0.7753(9)	0.035(5)	0.043(5)	0.065(6)	0.005(4)	0.031(4)	0.004(5)
C(19)	4*a*		1.1326(6)	0.8155(7)	0.6972(7)	0.046(5)	0.038(4)	0.030(3)	0.004(3)	0.026(3)	0.002(3)
C(20)	4*a*		1.1288(6)	0.7717(8)	0.5964(8)	0.036(4)	0.045(4)	0.055(5)	0.003(3)	0.036(4)	0.001(4)
C(21)	4*a*		1.0596(7)	0.7021(6)	0.5263(8)	0.044(4)	0.056(5)	0.039(4)	0.001(3)	0.039(4)	0.002(3)
C(22)	4*a*		0.9980(6)	0.6718(8)	0.5663(8)	0.039(5)	0.041(4)	0.044(4)	0.008(4)	0.028(4)	0.005(4)
C(23)	4*a*		1.0665(6)	0.7839(6)	0.7197(7)	0.036(4)	0.040(4)	0.030(3)	0.003(3)	0.026(3)	0.001(3)
C(24)	4*a*		1.0756(5)	0.8264(7)	0.8269(6)	0.027(4)	0.028(4)	0.028(3)	0.004(3)	0.014(3)	0.001(3)
C(25)	4*a*		0.8509(9)	0.136(1)	0.684(1)	0.126(8)	0.120(7)	0.114(7)	0.033(6)	0.081(6)	0.007(6)
C(26)	4*a*		0.9294(8)	0.1273(6)	0.680(1)	0.138(7)	0.037(3)	0.139(7)	0.003(4)	0.108(6)	0.002(4)
C(27)	4*a*		0.9377(9)	0.0313(9)	0.639(1)	0.149(8)	0.109(6)	0.148(8)	0.009(6)	0.090(6)	0.025(6)
N(1)	4*a*		0.8236(5)	0.7167(6)	0.7541(7)	0.036(4)	0.035(4)	0.035(4)	0.001(3)	0.026(3)	0.005(3)
N(2)	4*a*		0.8169(6)	0.7964(5)	0.5645(6)	0.039(4)	0.035(4)	0.029(3)	0.005(2)	0.025(3)	0.007(2)
N(3)	4*a*		1.0146(6)	0.7953(5)	0.8513(7)	0.033(4)	0.033(4)	0.043(4)	0.001(2)	0.025(3)	0.001(3)
N(4)	4*a*		1.0036(5)	0.7142(6)	0.6566(7)	0.028(4)	0.033(4)	0.043(4)	0.005(3)	0.024(3)	0.004(3)
O(3')	4*a*	0.49(1)	0.938(1)	0.561(1)	0.759(1)	0.10(1)	0.031(6)	0.051(8)	0.004(7)	0.055(8)	0.002(6)
O(3)	4*a*	0.51	0.8856(7)	0.5572(9)	0.651(1)	0.041(6)	0.026(5)	0.041(7)	0.009(4)	0.021(5)	0.003(5)
O(4)	4*a*	0.51	0.9149(8)	0.4809(9)	0.8288(8)	0.066(5)	0.055(5)	0.027(4)	0.011(3)	0.037(4)	0.001(3)
O(1)	4*a*		0.8294(5)	0.4005(6)	0.6516(6)	0.057(4)	0.062(4)	0.052(3)	0.004(3)	0.035(3)	0.011(3)
O(2)	4*a*		0.9941(4)	0.4037(6)	0.7525(8)	0.033(3)	0.068(5)	0.112(6)	0.003(3)	0.041(4)	0.023(4)
O(5)	4*a*		0.8622(8)	0.2120(6)	0.7703(8)	0.144(8)	0.058(5)	0.089(5)	0.004(4)	0.085(6)	0.012(4)
O(6)	4*a*		0.9678(6)	0.2073(5)	0.6522(8)	0.109(6)	0.063(5)	0.143(8)	0.013(4)	0.110(6)	0.042(5)

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