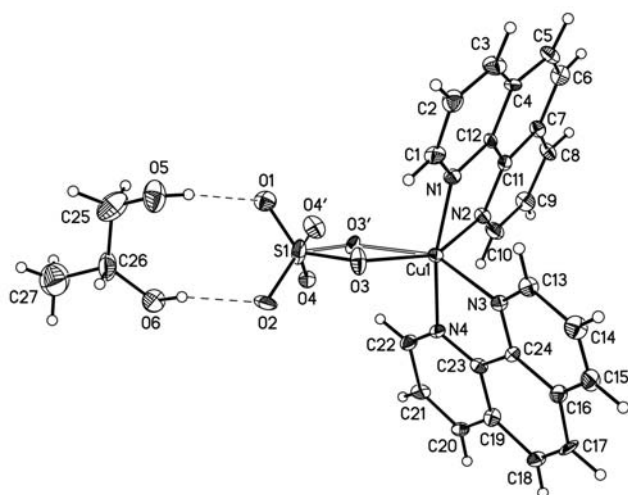


Crystal structure of bis(1,10-phenanthroline- κ^2N,N')(sulfato- κ^2O,O')-copper(II) — propane-1,2-diol (1:1), $\text{Cu}(\text{C}_{12}\text{H}_8\text{N}_2)_2(\text{SO}_4) \cdot \text{C}_3\text{H}_8\text{O}_2$

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Received February 8, 2011; accepted and available on-line April 27, 2011; CCDC no. 1267/3395



Abstract

$\text{C}_{27}\text{H}_{24}\text{CuN}_4\text{O}_6\text{S}$, monoclinic, $C1c1$ (no. 9), $a = 17.405(7)$ Å, $b = 13.074(6)$ Å, $c = 13.267(7)$ Å, $\beta = 123.45(2)^\circ$, $V = 2519.1$ Å³, $Z = 4$, $R_{\text{gt}}(F) = 0.046$, $wR_{\text{ref}}(F^2) = 0.126$, $T = 291$ K.

Source of material

Reagents and solvents used were of commercially available quality. 1,10-Phenanthroline (phen, 0.2 mmol), melamine (0.1 mmol), $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ (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 $d(\text{C}—\text{H}) = 0.93 - 0.98$ Å and $U_{\text{iso}}(\text{H}) = 1.2 U_{\text{eq}}(\text{C})$; $d(\text{O}—\text{H}) = 0.82$ Å and $U_{\text{iso}}(\text{H}) = 1.5 U_{\text{eq}}(\text{O})$. The sulfate ion is disordered over two positions with refined site occupancies of 0.51(1) and 0.49(1). The presence of pseudosymmetry in the structure suggests the higher symmetry space group $C2/c$ 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 an 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: $d(\text{O5}—\text{H51} \cdots \text{O1}) = 2.81(1)$ Å, $\angle \text{O5}—\text{H51} \cdots \text{O1} = 171.4^\circ$ and $d(\text{O6}—\text{H61} \cdots \text{O2}) = 2.81(1)$ Å, $\angle \text{O6}—\text{H61} \cdots \text{O2} = 161.5^\circ$, 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
$2\theta_{\text{max}}$:	54.94°
$N(hkl)_{\text{measured}}$, $N(hkl)_{\text{unique}}$:	12107, 5404
Criterion for I_{obs} , $N(hkl)_{\text{gt}}$:	$I_{\text{obs}} > 2 \sigma(I_{\text{obs}})$, 4684
$N(\text{param})_{\text{refined}}$:	367
Programs:	SHELXS-97, SHELXL-97 [16]

Table 2. Atomic coordinates and displacement parameters (in Å²).

Atom	Site	Occ.	x	y	z	U_{iso}
H(1)	4a		0.8745	0.6292	0.8998	0.048
H(2)	4a		0.7731	0.6623	0.9434	0.061
H(3)	4a		0.6673	0.7890	0.8478	0.059
H(5)	4a		0.5838	0.9139	0.6604	0.052
H(6)	4a		0.5650	0.9710	0.4855	0.054
H(8)	4a		0.6293	0.9809	0.3518	0.051
H(9)	4a		0.7392	0.9221	0.3150	0.056

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Table 2. Continued.

Atom	Site	Occ.	x	y	z	U _{iso}
H(10)	4a		0.8517	0.8123	0.4497	0.061
H(13)	4a		0.9762	0.8065	0.9653	0.045
H(14)	4a		1.0943	0.9170	1.0978	0.063
H(15)	4a		1.1956	0.9751	1.0573	0.057
H(17)	4a		1.2542	0.9739	0.9173	0.053
H(18)	4a		1.2504	0.9049	0.7595	0.055
H(20)	4a		1.1716	0.7894	0.5783	0.048
H(21)	4a		1.0518	0.6751	0.4563	0.045
H(22)	4a		0.9545	0.6208	0.5245	0.046

Table 2. Continued.

Atom	Site	Occ.	x	y	z	U _{iso}
H(25A)	4a		0.8384	0.0702	0.7065	0.134
H(25B)	4a		0.7983	0.1538	0.6050	0.134
H(26)	4a		0.9767	0.1201	0.7659	0.106
H(27A)	4a		0.8881	0.0220	0.5564	0.197
H(27B)	4a		0.9954	0.0276	0.6456	0.197
H(27C)	4a		0.9354	−0.0213	0.6878	0.197
O(4')	4a	0.49	0.9127(8)	0.4812(9)	0.5729(9)	0.039(3)
H(51)	4a		0.8490	0.2685	0.7381	0.130
H(61)	4a		0.9719	0.2582	0.691	0.126

Table 3. Atomic coordinates and displacement parameters (in Å²).

Atom	Site	Occ.	x	y	z	U ₁₁	U ₂₂	U ₃₃	U ₁₂	U ₁₃	U ₂₃
Cu(1)	4a		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)	4a		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)	4a		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)	4a		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)	4a		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)	4a		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)	4a		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)	4a		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)	4a		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)	4a		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)	4a		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)	4a		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)	4a		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)	4a		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)	4a		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)	4a		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)	4a		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)	4a		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)	4a		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)	4a		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)	4a		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)	4a		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)	4a		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)	4a		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)	4a		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)	4a		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)	4a		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)	4a		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)	4a		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)	4a		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)	4a		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)	4a		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)	4a		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')	4a	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)	4a	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)	4a	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)	4a		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)	4a		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)	4a		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)	4a		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)

Acknowledgment. This work was supported by the Scientific Research Foundation of Nanjing College of Chemical Technology (grant no. NHKY-2010-17).

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