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Crystal structure of diaqua-bis((*E*)-4-hydroxy-3-((2-hydroxyethylimino)-methyl)-5-(morpholinomethyl)benzenesulfonato)dicopper(II) diperchlorate hexahydrate, $[Cu_2(H_2O)_2(C_{14}H_{19}N_2O_3SO_3)_2][ClO_4]_2 \cdot 6H_2O$

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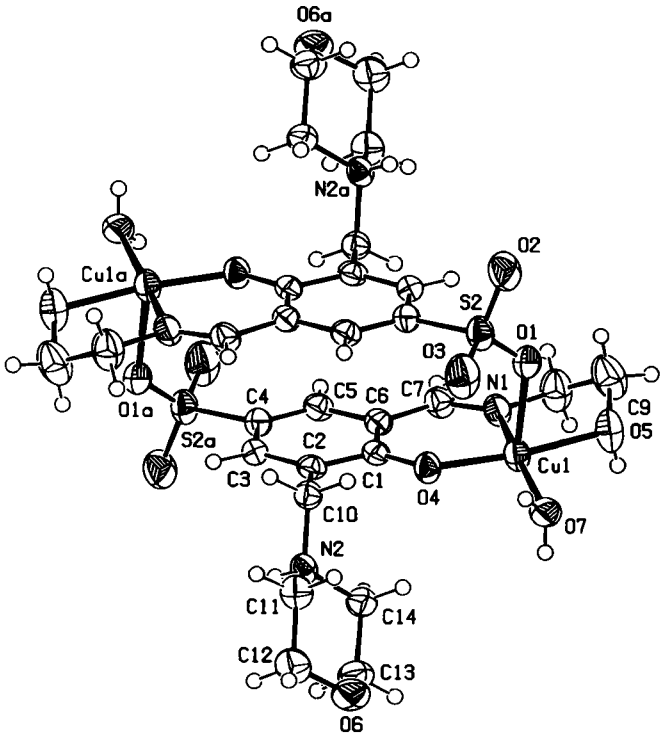

Abstract

$C_{28}H_{54}Cl_2Cu_2N_4O_{28}S_2$, triclinic, $P\bar{1}$ (no. 2), a = 8.6496(6) Å, b = 9.6240(7) Å, c = 13.7224(9) Å, α = 100.865(5)°, β = 100.956(5)°, γ = 93.997(6)°, V = 1094.8 Å^3, Z = 1, $R_{gt}(F)$ = 0.058, $wR_{ref}(F^2)$ = 0.175, T = 293 K.

Source of material

The solution of ethanolamine in 5 ml water was added slowly to 20 ml aqueous solution of 5 mmol sodium 3-formyl-4-hydroxy-5-morpholinomethyl-benzenesulfonate. After stirring vigorously for 30 min, 10 mmol $Cu(ClO_4)_2 \cdot 6H_2O$ was added to the resulting Schiff base. The mixture was refluxed for 1 h and cooled to room temperature. At first green square plate-shaped crystals were isolated from the precipitate, and then green needle-like crystals were obtained after a week by slowly evaporation of the solution at room temperature [1-4].

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Experimental details

The positions of the H atoms of the disordered hydrate water could not be analyzed.

Discussion

The crystal structure of the title compound consists of three fundamental units: metal complex cations, ClO_4^- anions and lattice water. In the complex, the hydrogen atom from phenol hydroxyl moved on to the nitrogen in the morpholine. Therefore, the phenol hydroxyl unit converts to the anion part with a single negative charge and the nitrogen combining a hydrogen atom converts to an ammonio unit with a single positive charge. The protonation of oxygen or nitrogen by lattice water or ethanolamine did not take place.

In the dinuclear complex cation, Cu is coordinated by three oxygen atoms and a nitrogen atom, among which two oxygen atoms (O4, O5) and one nitrogen (N1) come from Schiff base ligand, one oxygen atom (O7) is from the coordinated water. The bond lengths Cu1—O4, Cu1—N1, Cu1—O7 and Cu1—O5 are 1.878(3) Å, 1.933(4) Å, 1.980(3) Å and 2.007(3) Å, respectively. In the ClO_4^- anion, the refined distances Cl1—O8, Cl1—O10, Cl1—O9 and Cl1—O11 are 1.309(8) Å, 1.319(9) Å, 1.386(7) Å and 1.428(10) Å, respectively. There are weak and strong hydrogen bonds in the complex. The intramolecular hydrogen bonds include C5–H5···O3 and C10–H10A···O4. The intermolecular hydrogen bonds include C10–H10B···O2 and N2–H2C···O1. Oxygen O5 links the ligand and the lattice water O13 via C13–H13B···O5 and O5–H5C···O13 bonds. Except coordinated by Cu1, the coordinated O7 water forms strong hydrogen bonds via O7–H7B···O6 and O7–H7C···O16 (O16 from hydrate water), which is indicated by the hydrogen bond lengths of 2.03 Å and 1.86 Å, respectively. The C5–H5···O8 bond length of 2.59 Å shows that there is weak hydrogen bond between anion and ligand.

Table 1. Data collection and handling.

Crystal:	green square plate, size 0.11 × 0.23 × 0.29 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ:	12.90 cm^{-1}
Diffractometer, scan mode:	Bruker SMART CCD, φ/ω
$2\theta_{max}$:	50°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	5952, 3719
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\,\sigma(I_{obs})$, 2976
$N(param)_{refined}$:	301
Programs:	SHELXS-97 [5], SHELXL-97 [6], SHELXTL [7]

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

Atom	Site	x	y	z	U_{iso}
H(5O)	2*i*	0.4709	0.6978	0.2622	0.065
H(7A)	2*i*	0.3008	0.9072	0.3945	0.055
H(7B)	2*i*	0.3462	1.0383	0.3576	0.055
H(2)	2*i*	–0.3048	1.0591	0.2464	0.040
H(3)	2*i*	–0.3409	1.0158	0.0241	0.040
H(5)	2*i*	0.1460	1.3138	0.1097	0.042
H(7)	2*i*	0.0998	0.6242	–0.0370	0.047
H(8A)	2*i*	0.3655	0.5833	0.0024	0.071
H(8B)	2*i*	0.3363	0.5277	0.0988	0.071
H(9A)	2*i*	0.5965	0.6161	0.1390	0.082
H(9B)	2*i*	0.5600	0.7539	0.0966	0.082
H(10A)	2*i*	–0.1666	1.1920	0.1625	0.041
H(10B)	2*i*	–0.0090	1.1476	0.2195	0.041
H(11A)	2*i*	–0.0818	1.2604	0.3793	0.050
H(11B)	2*i*	–0.2439	1.2941	0.3198	0.050
H(12A)	2*i*	–0.2618	1.2844	0.4860	0.062
H(12B)	2*i*	–0.3814	1.1648	0.4095	0.062
H(13A)	2*i*	–0.3259	0.9284	0.3863	0.057
H(13B)	2*i*	–0.1676	0.8887	0.4463	0.057
H(14A)	2*i*	–0.0220	1.0000	0.3510	0.047
H(14B)	2*i*	–0.1514	0.8856	0.2773	0.047

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)	2*i*	0.29622(6)	0.84501(6)	0.21474(4)	0.0312(3)	0.0488(4)	0.0361(3)	0.0103(2)	0.0019(2)	0.0015(2)
Cl(1)	2*i*	0.0201(2)	0.5782(2)	0.2884(1)	0.089(1)	0.0398(7)	0.0645(9)	–0.0019(7)	0.0221(8)	–0.0030(6)
S(2)	2*i*	0.4307(1)	1.1930(1)	0.15574(9)	0.0329(6)	0.0484(7)	0.0384(6)	0.0083(5)	–0.0009(5)	0.0006(5)
O(1)	2*i*	0.4676(4)	1.0569(4)	0.1825(3)	0.033(2)	0.063(2)	0.042(2)	0.004(2)	0.001(1)	0.016(2)
O(2)	2*i*	0.5596(4)	1.2561(5)	0.1185(3)	0.038(2)	0.067(3)	0.076(3)	–0.005(2)	0.002(2)	0.024(2)
O(3)	2*i*	0.3871(5)	1.2924(5)	0.2364(3)	0.060(2)	0.086(3)	0.046(2)	0.023(2)	–0.002(2)	–0.010(2)
O(4)	2*i*	0.1129(4)	0.9372(3)	0.1893(2)	0.032(2)	0.047(2)	0.031(2)	0.008(1)	0.001(1)	0.001(1)
O(5)	2*i*	0.5007(4)	0.7570(4)	0.2319(3)	0.040(2)	0.052(2)	0.061(2)	0.014(2)	–0.004(2)	–0.001(2)
O(6)	2*i*	–0.1981(4)	1.0918(4)	0.4844(2)	0.059(2)	0.067(2)	0.031(2)	0.004(2)	0.011(2)	0.001(2)
O(7)	2*i*	0.3494(4)	0.9498(4)	0.3577(2)	0.038(2)	0.063(2)	0.035(2)	0.002(2)	0.007(1)	0.009(2)
O(8)	2*i*	0.049(1)	0.4455(8)	0.265(1)	0.192(9)	0.060(4)	0.36(2)	0.016(5)	0.14(1)	0.015(6)
O(9)	2*i*	0.154(1)	0.6752(8)	0.3082(5)	0.206(8)	0.112(5)	0.083(4)	–0.081(5)	0.013(4)	0.016(4)
O(10)	2*i*	–0.056(1)	0.610(2)	0.363(1)	0.19(1)	0.28(2)	0.20(1)	–0.01(1)	0.107(9)	–0.11(1)
O(11)	2*i*	–0.090(2)	0.593(2)	0.200(1)	0.21(1)	0.25(2)	0.22(1)	–0.01(1)	–0.11(1)	0.04(1)
N(1)	2*i*	0.2433(4)	0.7113(4)	0.0861(3)	0.031(2)	0.050(2)	0.039(2)	0.010(2)	0.006(2)	0.004(2)
N(2)	2*i*	–0.2008(4)	1.0881(4)	0.2743(3)	0.028(2)	0.039(2)	0.029(2)	0.003(2)	0.003(1)	–0.001(2)
C(1)	2*i*	–0.0032(5)	0.9029(5)	0.1106(3)	0.027(2)	0.040(2)	0.033(2)	0.000(2)	0.008(2)	0.011(2)
C(2)	2*i*	–0.1317(5)	0.9892(5)	0.1074(3)	0.030(2)	0.035(2)	0.033(2)	–0.001(2)	0.010(2)	0.009(2)
C(3)	2*i*	–0.2580(5)	0.9591(5)	0.0255(3)	0.029(2)	0.041(2)	0.031(2)	0.007(2)	0.007(2)	0.010(2)
C(4)	2*i*	0.2633(5)	1.1547(5)	0.0553(3)	0.029(2)	0.041(2)	0.033(2)	0.003(2)	0.004(2)	0.008(2)
C(5)	2*i*	0.1420(5)	1.2386(5)	0.0554(3)	0.033(2)	0.037(2)	0.033(2)	0.000(2)	0.008(2)	0.005(2)
C(6)	2*i*	–0.0100(5)	0.7890(5)	0.0275(3)	0.029(2)	0.037(2)	0.032(2)	0.003(2)	0.007(2)	0.007(2)
C(7)	2*i*	0.1143(5)	0.6976(5)	0.0197(3)	0.036(2)	0.042(2)	0.037(2)	0.007(2)	0.008(2)	0.001(2)
C(8)	2*i*	0.3627(7)	0.6121(7)	0.0737(5)	0.052(3)	0.061(3)	0.059(3)	0.020(3)	0.004(3)	0.000(3)
C(9)	2*i*	0.5208(7)	0.6852(8)	0.1319(5)	0.050(3)	0.077(4)	0.069(4)	0.018(3)	0.012(3)	–0.009(3)
C(10)	2*i*	–0.1200(5)	1.1157(5)	0.1907(3)	0.033(2)	0.036(2)	0.033(2)	0.005(2)	0.006(2)	0.007(2)
C(11)	2*i*	–0.1918(6)	1.2234(5)	0.3519(4)	0.048(3)	0.034(2)	0.038(2)	0.008(2)	0.008(2)	–0.005(2)
C(12)	2*i*	–0.2699(7)	1.1965(6)	0.4364(4)	0.054(3)	0.057(3)	0.039(3)	0.012(2)	0.012(2)	–0.007(2)
C(13)	2*i*	–0.2143(6)	0.9603(6)	0.4125(4)	0.051(3)	0.055(3)	0.037(2)	0.000(2)	0.011(2)	0.009(2)
C(14)	2*i*	–0.1351(6)	0.9756(5)	0.3257(3)	0.041(2)	0.042(3)	0.036(2)	0.008(2)	0.011(2)	0.009(2)
O(13)	2*i*	0.538(2)	0.5621(9)	0.3397(8)	0.32(1)	0.084(5)	0.147(7)	0.029(6)	–0.035(8)	0.039(5)
O(14)	2*i*	0.213(2)	0.429(2)	0.524(1)	0.31(2)	0.25(2)	0.27(2)	0.06(2)	0.05(2)	0.05(2)
O(15)	2*i*	0.2584(9)	0.2092(7)	0.3853(5)	0.145(6)	0.089(4)	0.112(5)	0.024(4)	0.057(4)	0.025(3)

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