Crystal structure of triaqua-4,4′-bipyridinecopper(II) sulfate dihydrate, $[Cu(4,4'\text{-bpy})(H_2O)_3](SO_4) \cdot 2H_2O$

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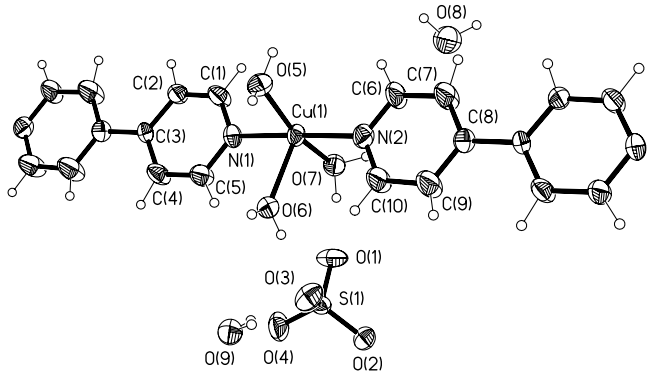

Abstract

$C_{10}H_{18}CuN_2O_9S$, hexagonal, $P6_5$ (No. 170), a = 11.211(2) Å, c = 21.582(4) Å, V = 2349.0 Å^3, Z = 6, $R_{gt}(F)$ = 0.055, $wR_{ref}(F^2)$ = 0.131, T = 298 K.

Source of material

For the synthesis, 0.250 g pentaaquacopper(II) sulfate (1 mmol) was dissolved in 10 mL water, then a solution of 4,4′-bipyridine (0.156g, 1.0 mmol) in ethanol (10 mL) was slowly added with stirring for four hours at 352 K. Lilac-blue crystals were deposited within five days (90% yield).

Experimental details

The refined Flack's parameter was 0.93(3).

Discussion

Self-assembly processes of metallic polymers into well-defined architecture have attracted a lot of attention in recent years, owing to their intriguing structural diversity and potential functions as microporous solids for molecular adsorption, ion exchange and heterogeneous catalysis [1,2]. By using exo-bidentate ligands and transition metal ions, various topologies, such as rectangles [3], two-dimensional networks [4], rhombic grids [5] have been reported. 4,4′-bipyridine (abbreviated as 4,4′-bpy) as a rod-like rigid spacer is chosen as a building block to synthesize the title compound by us. To our knowledge, the title compound, namely $[Cu(4,4'\text{-bpy})(H_2O)_3](SO_4) \cdot 2H_2O$ has not been reported so far, so we firstly report it here.

The crystal structure of the title compound comprises cationic $[Cu(4,4'\text{-bpy})(H_2O)_3]_n^{2n+}$ polymeric chains, crystal water molecules and sulfate counterions. The 1-D linear chain is made up of copper(II) ions, 4,4′-bpy molecules and coordinated water molecules. Three oxygen atoms from three coordinated water molecules and two nitrogen atoms from two 4,4′-bpy molecules form a quadratic pyramid around Cu atom CuO_3N_2: d(Cu1—N1) = 2.045(5) Å; d(Cu1—N2) = 2.061(5) Å; d(Cu1—O5) = 1.980(6) Å; d(Cu1—O6) = 2.225(5) Å; d(Cu1—O7) = 1.953(6) Å. Each pair of adjacent intrachain Cu(II) ions separated by 11.210(8) Å are alternately bridged by a 4,4′-bpy molecule to form the polymeric chains. There are strong interchain π-π interactions between the pyridyl rings of adjacent chains with the face-to-face separation of ca. 3.5 Å, resulting in an extended three-dimensional supramolecular array. The sulfate counterions occupy the cavities formed by the coordination chains and contact the adjacent interchain copper(II) ion by hydrogen-bonding interactions (d(O···O) = 2.805 Å) and the weaker link (d(Cu···O) = 2.672 Å) to furnish a wavy 3-D network structure.

Table 1. Data collection and handling.

Crystal:	lilac-blue prism, size 0.10 × 0.16 × 0.25 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ:	15.76 cm^{-1}
Diffractometer, scan mode:	CCD area detector, 520 frames, $\Delta\omega$ = 2°
$2\theta_{max}$:	54.2°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	10633, 3364
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\,\sigma(I_{obs})$, 2305
$N(param)_{refined}$:	280
Programs:	SHELX-97 [6], ORTEP-II [7]

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

Atom	Site	x	y	z	U_{iso}
H(1)	6*a*	0.678(3)	0.877(6)	0.026(4)	0.02(2)
H(2)	6*a*	0.877(7)	1.082(4)	0.020(4)	0.05(2)
H(3)	6*a*	1.087(4)	0.875(8)	0.033(3)	0.04(2)
H(4)	6*a*	0.862(8)	0.663(3)	0.028(5)	0.05(2)
H(5)	6*a*	0.278(7)	0.472(3)	0.010(3)	0.03(2)
H(6)	6*a*	0.076(7)	0.270(9)	–0.002(4)	0.07(3)
H(7)	6*a*	0.28(1)	0.062(7)	0.011(6)	0.11(4)
H(8)	6*a*	0.478(4)	0.274(9)	0.022(5)	0.08(3)
H(9)	6*a*	0.492(6)	0.638(9)	–0.073(4)	0.05(3)
H(10)	6*a*	0.568(6)	0.562(5)	–0.089(2)	0.01(2)
H(11)	6*a*	0.704(9)	0.432(9)	–0.035(2)	0.06(3)
H(12)	6*a*	0.704(7)	0.430(6)	0.034(2)	0.02(2)
H(13)	6*a*	0.60(1)	0.51(1)	0.130(5)	0.11(5)
H(14)	6*a*	0.481(3)	0.510(8)	0.124(4)	0.06(3)
H(15)	6*a*	0.17(1)	0.576(8)	0.083(3)	0.07(3)
H(16)	6*a*	0.062(4)	0.490(9)	0.126(4)	0.06(3)
H(17)	6*a*	0.802(4)	0.252(6)	–0.016(3)	0.04(2)
H(18)	6*a*	0.85(1)	0.34(1)	0.032(3)	0.09(4)

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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)	6*a*	0.57400(8)	0.57253(8)	0.02201(5)	0.0231(4)	0.0243(4)	0.0305(4)	0.0056(3)	–0.0010(4)	0.0007(4)
N(1)	6*a*	0.7578(5)	0.7531(5)	0.0268(3)	0.023(3)	0.030(3)	0.034(3)	0.007(2)	0.000(3)	–0.002(3)
N(2)	6*a*	0.3915(5)	0.3878(6)	0.0169(4)	0.028(3)	0.031(3)	0.039(4)	0.006(2)	–0.006(3)	0.001(3)
O(1)	6*a*	0.7082(7)	0.4778(6)	0.1816(3)	0.073(4)	0.066(4)	0.049(4)	0.056(4)	–0.004(3)	0.003(3)
O(2)	6*a*	0.7070(5)	0.2700(6)	0.2090(2)	0.042(3)	0.046(3)	0.025(3)	0.022(3)	0.003(2)	0.007(2)
O(3)	6*a*	0.7380(6)	0.3427(6)	0.1032(2)	0.071(4)	0.048(3)	0.025(3)	0.030(3)	0.002(3)	0.002(3)
O(4)	6*a*	0.9173(5)	0.4734(6)	0.1776(3)	0.028(3)	0.077(4)	0.061(5)	0.014(3)	0.003(3)	0.026(4)
O(5)	6*a*	0.5582(6)	0.6187(5)	–0.0650(3)	0.042(3)	0.036(3)	0.034(3)	0.020(3)	–0.004(2)	0.000(2)
O(6)	6*a*	0.6877(5)	0.4625(5)	–0.0003(3)	0.034(3)	0.032(3)	0.038(3)	0.018(2)	0.003(2)	0.004(3)
O(7)	6*a*	0.5671(5)	0.5584(6)	0.1123(3)	0.033(3)	0.039(3)	0.033(3)	0.016(3)	–0.004(2)	0.001(2)
O(8)	6*a*	0.1468(9)	0.519(1)	0.1147(4)	0.075(5)	0.128(7)	0.077(6)	0.067(5)	0.036(4)	0.056(5)
O(9)	6*a*	0.8808(6)	0.3144(6)	–0.0005(3)	0.043(3)	0.041(3)	0.050(4)	0.021(3)	0.007(3)	0.004(3)
S(1)	6*a*	0.7680(2)	0.3915(2)	0.16778(8)	0.0318(9)	0.040(1)	0.0264(9)	0.0221(8)	0.0017(7)	0.0048(8)
C(1)	6*a*	0.7641(7)	0.8764(7)	0.0259(5)	0.024(3)	0.029(4)	0.078(6)	0.013(3)	–0.002(4)	–0.003(4)
C(2)	6*a*	0.8839(7)	0.9999(7)	0.0240(5)	0.030(4)	0.025(4)	0.071(6)	0.015(3)	0.008(4)	0.011(4)
C(3)	6*a*	1.0101(6)	1.0052(7)	0.0226(4)	0.019(3)	0.026(3)	0.030(3)	0.008(3)	0.003(3)	0.000(3)
C(4)	6*a*	1.0037(7)	0.8787(7)	0.0263(5)	0.022(3)	0.032(4)	0.068(6)	0.012(3)	–0.007(4)	–0.006(4)
C(5)	6*a*	0.8786(7)	0.7567(8)	0.0282(5)	0.025(4)	0.025(4)	0.081(6)	0.009(3)	–0.006(4)	0.002(4)
C(6)	6*a*	0.2716(7)	0.3833(8)	0.0162(5)	0.023(4)	0.025(4)	0.096(8)	0.005(3)	0.004(5)	0.004(5)
C(7)	6*a*	0.1469(8)	0.2598(8)	0.0183(6)	0.026(4)	0.023(4)	0.116(8)	0.006(3)	–0.005(5)	–0.004(5)
C(8)	6*a*	0.1436(6)	0.1378(7)	0.0204(4)	0.029(3)	0.027(3)	0.032(4)	0.010(3)	–0.002(3)	–0.004(3)
C(9)	6*a*	0.2669(8)	0.1411(9)	0.0205(8)	0.030(4)	0.029(4)	0.15(1)	0.013(4)	0.006(6)	0.006(6)
C(10)	6*a*	0.3890(9)	0.2676(8)	0.0187(8)	0.025(4)	0.024(4)	0.17(1)	0.007(3)	0.007(7)	0.022(6)

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