Crystal Structure of [Cu(4,4'-bipyridine)(H₂O)₃(SO₄)]·2H₂O

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The crystal structure of the title complex, [Cu(4,4'-bipyridine)(H₂O)₃(SO₄)]·2H₂O, was determined by X-ray diffraction. This compound was crystallized in the monoclinic system, space group *Cc*, with *a* = 10.244(1) Å, *b* = 19.886(3) Å, *c* = 7.505(1) Å, β = 100.390(9)°, *Z* = 2, *V* = 1503.81(33) Å³. The structure consists of linear cationic chains of [Cu(4,4'-bipyridine)(H₂O)₃]²⁺ with SO₄²⁻ anions as spacers between the chains. A 3D supramolecular network was formed by hydrogen-bond interactions.

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The design and synthesis of organic/inorganic hybrid materials have attracted intense attention in recent years owing to their potential practical applications, such as electrical conductivity, size and shape selectivity, magnetism and catalysis.¹ For a long time, aromatic nitrogen-containing heterocycles, such as 4,4'-bipyridine, have been widely applied in constructing

supramolecular architectures,² storing energy and catalyzing oxidation.³ Hydrothermal synthesis has been proven to be a powerful method for designing novel organic/inorganic hybrid compounds.⁴ In this paper, we report on the hydrothermal synthesis and the X-ray structure of the title complex using 4,4'-bipyridine as a ligand.

The title complex, [Cu(4,4'-bipyridine)(H₂O)₃(SO₄)]·2H₂O, was prepared as good quality blue single crystals from a mixture of anhydrous CuSO₄ (0.48 g, 3 mmol), 4,4'-bipyridine (0.468 g, 3 mmol) and camphoric acid (0.504 g, 3 mmol) in a molar ratio of 1:1:1 and 10 mL of H₂O/ethanol (1:1), which was placed in a Parr Teflon-lined stainless-steel vessel (25 mL). The vessel was then sealed and heated to 180°C. The temperature was held for one day, and then the reactant mixture was cooled at a rate of 10°C day⁻¹, leading to the formations of blue crystals of a complex suitable for X-ray diffraction. Camphoric acid was first designed to form a complex with CuSO₄ and 4,4'-

Table 1 Crystal and experimental data

Empirical formula	C ₂₀ H ₃₆ Cu ₂ N ₄ O ₁₈ S ₂
Formula weight	811.73
Temperature	290 K
Wavelength	0.71073 Å
Crystal system, Space group	Monoclinic, <i>Cc</i>
Unit cell dimensions	<i>a</i> = 10.244(1) Å <i>b</i> = 19.886(3) Å β = 100.390(9)° <i>c</i> = 7.505(1) Å
Volume	1503.81(33) Å ³
<i>Z</i>	2
<i>D_x</i>	1.793 g/cm ³
Absorption coefficient	1.641 mm ⁻¹
<i>F</i> (0 0 0)	836
Crystal dimensions	0.44 × 0.34 × 0.32 mm
θ range for data collection	2.05 to 25.50°
Limiting indices	−12 ≤ <i>h</i> ≤ 12, −23 ≤ <i>k</i> ≤ 24, −9 ≤ <i>l</i> ≤ 8
Reflections collected/unique	2730/2521 [<i>R</i> (int) = 0.0131]
Absorption correction	Empirical
Max. and min. transmission	0.9856 and 0.8493
Data/restraints/parameters	2730/15/249
Goodness-of-fit on <i>F</i> ²	1.062
Final <i>R</i> indices [<i>I</i> > 2σ(<i>I</i>)]	<i>R</i> ₁ = 0.0257, <i>wR</i> ₂ = 0.0615
2θ _{max}	51.00° with Mo <i>K</i> _α
Largest diff. peak and hole	−0.256 eÅ ⁻³ and 0.256 eÅ ⁻³
Measurement	Siemens P4
Program system	SHELXL-97
Structure determination	direct method
Refinement	full-matrix least-squares on <i>F</i> ²
CCDC No.	283601

Table 2 Atomic coordinates (×10⁴) and equivalents isotropic displacement parameters (Å² × 10³)

Atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> (eq)
Cu(1)	5948(1)	2290(1)	5247(1)	21(1)
S(1)	2634(1)	1467(1)	5667(1)	21(1)
O(1)	5970(3)	2233(1)	2640(4)	31(1)
O(2)	5649(3)	2174(1)	7767(4)	27(1)
O(3)	7900(3)	2781(1)	6064(4)	32(1)
O(4)	3557(2)	1693(1)	4497(3)	28(1)
O(5)	2351(3)	747(1)	5415(4)	33(1)
O(6)	1367(2)	1845(1)	5227(4)	31(1)
O(7)	3246(2)	1601(1)	7575(3)	30(1)
O(8)	4792(3)	1084(1)	979(4)	40(1)
O(9)	3750(3)	104(2)	2984(5)	64(1)
N(1)	5018(3)	3214(1)	5056(4)	27(1)
N(2)	6875(3)	1381(1)	5417(4)	23(1)
C(1)	5653(4)	3781(2)	4851(8)	55(2)
C(2)	5091(4)	4410(2)	4946(7)	52(1)
C(3)	3795(3)	4471(2)	5210(5)	22(1)
C(4)	3136(4)	3876(2)	5323(7)	42(1)
C(5)	3767(4)	3270(2)	5246(7)	42(1)
C(6)	6295(4)	811(2)	5697(5)	32(1)
C(7)	6874(4)	189(2)	5666(6)	35(1)
C(8)	8155(3)	134(2)	5316(5)	22(1)
C(9)	8788(4)	733(2)	5070(6)	32(1)
C(10)	8134(4)	1340(2)	5136(6)	35(1)

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Table 3 Selected bond lengths (Å) and angles (°)

Cu(1)-O(1)	1.963(3)	Cu(1)-O(2)	1.983(3)
Cu(1)-N(2)	2.036(3)	Cu(1)-N(1)	2.062(3)
Cu(1)-O(3)	2.211(2)	Cu(1)-O(4)	2.688(2)
O(1)-Cu(1)-O(2)	167.15(11)	O(1)-Cu(1)-N(2)	85.57(12)
O(2)-Cu(1)-N(2)	89.26(12)	O(1)-Cu(1)-N(1)	94.03(12)
O(1)-Cu(1)-O(3)	97.44(12)	O(2)-Cu(1)-O(3)	94.24(11)
N(2)-Cu(1)-O(3)	89.22(10)	N(1)-Cu(1)-O(3)	90.51(11)
O(1)-Cu(1)-O(4)	86.57(10)	O(2)-Cu(1)-O(4)	81.76(10)
N(2)-Cu(1)-O(4)	91.04(9)	N(1)-Cu(1)-O(4)	89.26(10)
O(3)-Cu(1)-O(4)	175.99(9)	Cu(1)-O(1)-H(1A)	111(3)
Cu(1)-O(1)-H(1B)	127(5)	Cu(1)-O(3)-H(3A)	119(3)
Cu(1)-O(3)-H(3B)	112(3)	S(1)-O(4)-Cu(1)	132.00(14)
C(5)-N(1)-Cu(1)	120.9(3)	C(1)-N(1)-Cu(1)	122.4(3)
C(6)-N(2)-Cu(1)	123.8(2)	C(10)-N(2)-Cu(1)	119.5(2)

Table 4 Hydrogen bonds in crystal packing (Å, °)

D-H...A	d(D-H)/Å	d(H...A)/Å	d(D...A)/Å	∠DHA(°)	Symmetry
O(1)-H(1B)-O(6)	0.815(10)	1.89(3)	2.659(4)	156(7)	1/2+x, 1/2-y, -1/2+z
O(1)-H(1A)-O(8)	0.812(10)	1.968(13)	2.773(4)	171(4)	-1/2+x, 1/2-y, -1/2+z
O(2)-H(2A)-O(6)	0.818(10)	1.885(13)	2.695(4)	171(4)	1/2+x, 1/2-y, 1/2+z
O(2)-H(2B)-O(7)	0.817(10)	1.878(12)	2.693(4)	174(4)	
O(3)-H(3A)-O(4)	0.818(10)	1.931(11)	2.750(4)	179(4)	1/2+x, 1/2-y, 1/2+z
O(3)-H(3B)-O(7)	0.812(10)	2.196(14)	2.971(4)	160(3)	1/2+x, 1/2-y, -1/2+z
O(8)-H(8B)-O(7)	0.825(10)	2.32(4)	2.939(4)	132(5)	1/2+x, 1/2-y, -1/2+z
O(8)-H(8A)-O(9)	0.826(10)	1.965(12)	2.790(5)	176(4)	
O(9)-H(9A)-O(5)	0.827(10)	1.995(12)	2.821(4)	177(5)	1/2+x, 1/2-y, 1/2+z
O(9)-H(9B)-O(5)	0.826(10)	1.955(14)	2.764(4)	166(5)	1/2+x, -1/2+y, z

Fig. 1 Chemical structure of the title complex.

Fig. 2 ORTEP drawing of the title compound showing 30% probability displacement ellipsoids and the atom-numbering scheme. H atoms attached to C atoms have been omitted for clarity.

bipyridine; unfortunately, it was not contained in the complex.

X-ray data were collected on a Siemens P4 diffractometer equipped with graphite-monochromated Mo K_{α} radiation ($\lambda = 0.71073$ Å) at 290(2)K. The crystal structure of the title complex was solved by direct methods and refined on F^2 by full-matrix least-squares techniques using the program SHELXTL-97. The crystal data and experimental parameters are summarized in Table 1. The atomic coordinates and

Fig. 3 Packing diagram of the title compound, viewed along the c axis.

equivalent isotropic displacement parameters for the non-hydrogen atoms are listed in Table 2. The selected bond lengths and bond angles are given in Table 3. The hydrogen bonds in the crystal packing are demonstrated in Table 4. A chemical diagram of the title complex is shown in Fig. 1. An ORTEP drawing of the complex is illustrated in Fig. 2. A packing diagram is shown in Fig. 3.

As shown in Fig. 2, the Cu atom is coordinated with two pyridyl nitrogen donors from each of two 4,4'-bipyridine ligands, three aquo oxygen donors, and the oxygen of a sulfate anion. The coordination polyhedron around Cu is a distorted octahedron. The Cu-N distances are 2.062(3)Å (Cu-N(1)) and 2.036(3)Å (Cu-N(2)), respectively. The axial Cu-O(3) distance of 2.211(2)Å is significantly longer than the equatorial Cu-O(1) and Cu-O(2) distances of 1.963(3)Å and 1.983(3)Å, respectively. The Cu-O(4) distance is 2.688(2)Å, which indicates that the interaction of Cu-sulfate is weak.

The structure of the title complex consists of $\{Cu(4,4'-bipyridine)(H_2O)_3\}_n^{2+}$ chains parallel to the ab plane with SO_4^{2-} as spacers between the chains. An analysis of the crystal packing of the complex shows that a three-dimensional (3D) supramolecular network is formed by multiple hydrogen-bonding interactions (Fig. 3). All of the relevant hydrogen-bonding values and symmetry codes are listed in Table 4.

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