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Synthesis and Crystal Structure of a New 3D-Supramolecular Complex: $[Cu(C_{12}H_8N_2)_2Cl][C_6H_4N_3SO_3]\cdot H_2O$

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A novel complex $[Cu(C_{12}H_8N_2)_2Cl][C_6H_4N_3SO_3]\cdot H_2O$ was synthesized and characterized by IR spectra, elemental analysis and single-crystal X-ray. The crystal structure analysis shows that the Cu(II) is a five-coordinated in a trigonal dipyramidal environment, then complex packs in 3D-superamolecular network through intermolecular hydrogen bonds and π-π staking. The crystal is triclinic, space group P-1 with unit cell parameters: a = 10.318(2) Å, b = 11.759(2) Å, c = 12.960(3) Å, α = 67.90(3)º, β = 73.12(3)º, γ = 85.04(2)º, V = 1393.7(6) $Å^3$, Z = 2, Mr = 675.60, Dc = 1.610 Mg/cm^3, μ = 1.007 mm^{-1}, F(000) = 690, T = 293(2)K, R = 0.0456, wR = 0.0953 for 5467 reflections with $I > 2\sigma(I)$.

Key Words: Benzotriazole-4-sulfonic acid, Copper(II) complex, Crystal structure, Hydrogen bonds, π-π staking.

INTRODUCTION

1,10-Phenanthroline (phen) is a well-known motif for the synthesis of a large rang of strongly chelating ligands for various metal ions. The coordination capability of this easily accessible ligand has been used to develop biomimetic models of metalloenzymes and prepare supramolecules for molecular recognition and self assembling systems[1-5]. The five-coordinated copper(II) compounds comprised of both molecules of 1,10-phenanthroline and one monodentate co-ligands have been attracting great interest for interesting properties and potentials in spectroscopy, electrochemistry magnetism and biological activities[6-12]. However little attention has been paid to complexes derived from benzotriazole-4-sulfonic acid. Herein, reports a mononuclear complex in a formula as $[Cu(C_{12}H_8N_2)_2Cl][C_6H_4N_3SO_3]\cdot H_2O$.

EXPERIMENTAL

All reagents were of AR grade and used without further purification. Benzotriazole-4-sulfonic acid was prepared by a modified literature method[13]. Analyses for carbon, hydrogen and nitrogen were performed on a Perkin-Elmer 1400C analyzer. Infrared spectra (4000-400 cm^{-1}) were recorded with a Bruker Vector 22 FT-IR spectrophotometer on KBr disks.

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Synthesis: To a solution of benzotriazole-4-sulfonic acid (0.1 mmol) and $CuCl_2 \cdot 2H_2O$ (0.1 mmol) in water (15 mL) was dropped with 1 M HCl until the pH of solution is about 1.0. The solution was stirred for 10 min, then 0.2 mmol of 1,10-phenanthroline dissolved in 4 mL ethanol was added dropwise, resulting in a change from light blue to dark blue. After additional stirring of 10 min, the filtrate was evaporated for a week and blue block crystals were collected (yield: 47 %). Anal. calcd for $C_{30}H_{22}N_7O_4SClCu$: C, 53.33; H, 3.28; N, 14.51 %. Found: C, 53.67; H, 3.17; N, 14.72 %. IR (KBr, ν_{max}, cm^{-1}): 3447 (s), 3057 (w), 3011 (w), 1626 (m), 1587 (m), 1518 (s), 1497 (m), 1427 (s), 1385 (m), 1230 (s), 1215 (s), 1196 (s), 1142 (w), 1107 (w), 1047 (s), 991 (w), 950 (w), 852 (s), 800 (w), 748 (m), 723 (s), 665 (s), 634 (m), 577(m).

Crystal structure determination: A single crystal of compound with dimensions of 0.20 mm × 0.18 mm × 0.16 mm was selected for crystallographic data collection at 293(2)K and structure determination on a Siemens SMART CCD area-detector diffractometer with graphite-monochromatic MoKα radiation ($\lambda = 0.71073$ Å). A total of 13172 reflections were collected in the range of $3.01° \leq \theta \leq 26.00°$, of which 5467 reflections were unique with $R_{int} = 0.0413$. The data were integrate using the Siemens SAINT program[14]. With the intensities corrected for Lorentz factor, polarization, air absorption and absorption due to variation in the path length through the detector faceplate. Empirical absorption and extinction corrections were applied. The structure was solved by direct methods and expanded using Fourier techniques, and SHELXTL program[15] system was used in the solution and refinement of the structure. The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were added according to theoretical model. The final full-matrix least-squares refinement including 397 variable parameters for 5467 reflections with $I > 2\sigma(I)$ and converged with unweighted and weighted agreement factors of

$$R_1 = \Sigma(||F_0| - |F_C||)/\Sigma|F_0| = 0.0457 \quad (1)$$

and

$$wR_2 = \{\Sigma[w(F_0^2 - F_C^2)^2]/\Sigma w(F_0^2)^2\}^{1/2} = 0.0941 \quad (2)$$

where $w = 1/[\sigma^2(F_0^2) + (0.0734P)^2 + 4.665P]$ and $P = (F_0^2 + 2F_C^2)/3$. The maximum and minimum peaks on the final difference Fourier map are corresponding to 0.306 and -0.497 e/Å^3, respectively.

RESULTS AND DISCUSSION

The selected bond lengths and bond angles in Table-1. Fig. 1 shows the molecular structure of the title compound. Fig. 2 shows the packing diagram of the title compound. The title compound crystallizes in the triclinic lattice with P-1 space group. The asymmetric unit consists of one Cu atom, two phenanthroline molecules, one chlorine anion, one benzotriazole-4-sulfonate anion and one lattice water molecules. The Cu(II) atom has a flattened trigonal dipyramidal coordination geometry, formed by two phen molecules and one chlorine anion. The Cu-N(4) and Cu-N(6) bond distances in the apex directions are significantly shorter than Cu-N(5) and Cu-N(7) bond distances in the equatorial plane (Table-1).

TABLE-1
THE SELECTED BOND LENGTHS [Å] AND ANGLES [°]

Cu(1)-N(4)	1.995(3)	Cu(1)-N(5)	2.073(2)
Cu(1)-N(6)	1.987(3)	Cu(1)-N(7)	2.152(3)
Cu(1)-Cl(1)	2.2602(11)	S(1)-C(2)	1.766(3)
S(1)-O(1)	1.443(2)	S(1)-O(2)	1.436(2)
S(1)-O(3)	1.443(2)	–	–
N(6)-Cu(1)-N(4)	172.92(10)	N(6)-Cu(1)-N(5)	96.85(10)
N(4)-Cu(1)-N(5)	81.00(10)	N(6)-Cu(1)-N(7)	79.75(10)
N(4)-Cu(1)-N(7)	94.03(11)	N(5)-Cu(1)-N(7)	101.60(10)
N(6)-Cu(1)-Cl(1)	91.63(8)	N(4)-Cu(1)-Cl(1)	94.29(8)
N(5)-Cu(1)-Cl(1)	140.57(7)	N(7)-Cu(1)-Cl(1)	117.80(7)

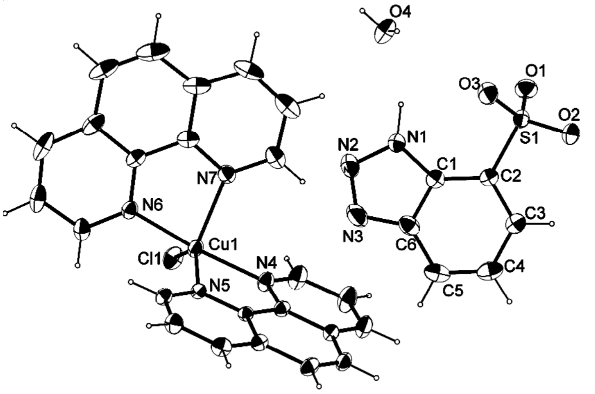

Fig. 1. The molecular structure of the title compound

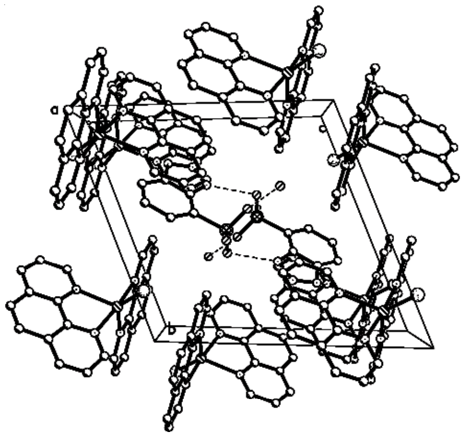

Fig. 2. View of a 3D supramolecular framework of title complex showing the intermolecular hydrogen bonding

In crystal packing, it is interesting to observe that the O-H···O, O-H···S, N-H···O, N-H···S intermolecular hydrogen bonds (Table-2) are formed between adjacent molecules and aromatic π-π staking interaction is existent between the neighboring 1,10-phenanthroline resulting in a 3D-supramolecular framework.

TABLE-2
HYDROGEN BOND DISTANCES AND [Å] AND ANGLES [°]

D-H…A	D-H	H…A	D…A	DHA
O(4)-H(4A)...O(2)#1	0.80	2.01	2.806(3)	169.4
O(4)-H(4B)...O(3)#2	0.96	1.92	2.879(4)	177.7
O(4)-H(4B)...S(2)#2	0.96	2.91	3.778(3)	151.9
N(1)-H(1)...O(1)#2	1.00	1.86	2.807(4)	156.8
N(1)-H(1)...S(1)#2	1.00	2.81	3.682(3)	145.1

Symmetry codes: #1 x - 1, y, z; #2 - x + 1, - y + 1, -z + 1.

Conclusion

A novel copper(II) complex with 3D-superamolecular structure has been synthesized and characterized by IR, elemental analysis and X-ray diffraction analysis.

Supplementary material: Crystallographic data for the structure reported in this communication have been deposited with the Cambridge Crystallographic Data Center as supplementary publication No. CCDC 737305.

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