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Synthesis and Crystal Structure of a New 3D-Supramolecular Complex: [Cu(phen)(C_2O_4)(H_2O)]·H_2O

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A novel complex [Cu(phen)(C_2O_4)(H_2O)]·H_2O, where phen = 1,10-phenanthroline, was synthesized and characterized by IR spectra, elemental analysis and single-crystal X-ray. The crystal structure analysis shows that the copper(II) is a five-coordinated in a slightly distorted square pyramidal geometry environment. The complex forms layer structure and packs in 3D-superamolecular network through some π-π stacking interactions and intermolecular hydrogen bonds. The crystal is monoclinic, space group P2(1)/c with unit cell parameters: a = 8.359(2)Å, b = 9.646(3)Å, c = 17.384(5)Å, $\alpha = 90^o$, $\beta = 103.523(4)^o$, $\gamma = 90^o$, V = 1362.8(6)$Å^3$, Z = 4, Mr = 367.8, Dc = 1.793 Mg/cm^3, μ = 1.639 mm^{-1}, F(000) = 748, T = 273(2)K, R = 0.0482, wR = 0.1225 for 3096 reflections with $I > 2\sigma(I)$.

Key Words: Cu(II) complex, π-π Stacking interactions, Crystal structure, Hydrogen bonds, Superamolecular.

INTRODUCTION

There has been increasing interest of Cu(II) and 1,10-phenanthroline complexes in the field of coordination chemistry[1-4]. At the same time, oxalates have played a prominent role in the design and construction of molecular magnetic material due to their stability and ease of chemical modification[5-10]. In an effort to bring these two research areas together, recently, in our laboratory, a series of copper(II) compounds have been synthesized and studied[11-14]. In this paper, we will report the synthesis and crystal structure of copper(II) complex [Cu(phen)(C_2O_4)(H_2O)]·H_2O.

EXPERIMENTAL

$Cu(ClO_4)_2 \cdot 6H_2O$ was prepared in our laboratory, the other reagents were of AR grade and used without further purification. IR spectra were recorded on a Nexus-870 spectrophotometer. Elemental analysis for C, H and N were performed on an Elementar Vario EL-III analyzer.

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Synthesis: To a 20 mL methanol solution of $Cu(ClO_4)_2 \cdot 6H_2O$ (371 mg, 1 mmol) were successively added a 10 mL methanol solution of 1,10-phenanthroline (198 mg, 1 mmol) and a 10 mL aqueous solution of $Na_2C_2O_4$ (111 mg, 1 mmol) with stirring. The mixture was refluxed for 3 h to obtain a clear blue solution, and after standing at room temperature for 3 weeks, well-shaped blue single crystals were obtained by slow evaporation. In the IR spectrum, maximal absorption wavelengths of 1,10-phenanthroline are 789, 723 cm^{-1}. The stretching vibrations of ν(C=N) are 1640 cm^{-1} and that of ν(C=O) is 1690 cm^{-1}. Elemental analysis confirmed the organic content. Found (Calcd.) (%): C 45.75 (45.70), H 3.30 (3.29), N 7.60 (7.62) for $[Cu(phen)(C_2O_4)(H_2O)] \cdot H_2O$.

Crystal structure determination: A single crystal of $[Cu(phen)(C_2O_4)(H_2O)] \cdot H_2O$ with dimensions of 0.95 mm × 0.65 mm × 0.60 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 (λ = 0.71073Å). A total of 10016 reflections were collected in the range of $3.04^o \leq \theta \leq 27.48^o$, of which 3096 reflections were unique with $R_{int} = 0.0248$. Lp effects and empirical absorption were applied in data corrections. The structure was solved by direct methods and expanded using Fourier techniques and SHELXS-97 program 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 220 variable parameters for 3096 reflections with $I > 2\sigma(I)$ and converged with unweighted and weighted agreement factors of

$$R_1 = \Sigma(||F_0|-|F_c||)/\Sigma|F_0| = 0.0224 \tag{1}$$

and

$$wR_2 = \{\Sigma[w(F_0^2 - F_C^2)^2]/\Sigma w(F_0^2)^2\} = 0.0624 \tag{2}$$

where $w = 1/[\sigma^2(F_0^2) +)0.0327P)^2 + 0.8457P]$ and $P = (F_0^2 + 2F_C^2)/3$. The maximum and minimum peaks on the final difference Fourier map are corresponding to 0.392 and $-0.478 e/Å^3$, respectively.

RESULTS AND DISCUSSION

The atomic coordinates and thermal parameters are listed in Table-1, and the selected bond lengths and bond angles in Table-2. Fig. 1 shows the molecular structure of the title compound. Fig. 2 shows the packing diagram of the title compound. From the Fig. 1, it is easy to conclude that the copper(II) ion is five-coordinated with two N atoms and three O atoms,which is very different from the normal copper(II) ion six-coordinated, because of the space encumbrance from the 1,10-phenanthroline molecule and the $C_2O_4^{2-}$ dianion.

TABLE-1
NON-HYDROGEN ATOMIC COORDINATES (× 10^4) AND THERMAL PARAMETERS (× 10^3 $Å^2$)

Atom	X	Y	Z	U(EQ)
Cu	-93	207	346	10(1)
N(1)	1417(1)	-1212(1)	4086(1)	11(1)
N(2)	931(1)	1426(1)	4385(1)	11(1)
O(1)	-1857(1)	1439(1)	3027(1)	13(1)
O(2)	-1372(1)	-1131(1)	2721(1)	15(1)
O(3)	-4306(1)	1498(1)	2172(1)	18(1)
O(4)	-3664(1)	-1190(1)	1759(1)	20(1)
O(5)	1748(2)	919(1)	2685(1)	22(1)
O(6)	2857(1)	-747(1)	1735(1)	18(1)
C(1)	-3027(2)	931(2)	2502(1)	12(1)
C(2)	-2694(2)	-600(2)	2297(1)	13(1)
C(3)	1628(2)	-2528(2)	3908(1)	14(1)
C(4)	2801(2)	-3378(2)	4399(1)	16(1)
C(5)	3767(2)	-2853(2)	5088(1)	14(1)
C(6)	3577(2)	-1453(2)	5286(1)	12(1)
C(7)	4566(2)	-779(2)	5973(1)	14(1)
C(8)	4332(2)	578(2)	6112(1)	14(1)
C(9)	3074(2)	1380(2)	5603(1)	12(1)
C(10)	2750(2)	2787(2)	5728(1)	14(1)
C(11)	1544(2)	3461(2)	5184(1)	16(1)
C(12)	655(2)	2753(2)	4511(1)	15(1)
C(13)	2114(2)	748(2)	4923(1)	11(1)
C(14)	2373(2)	-683(2)	4762(1)	11(1)

TABLE-2
SELECTED BOND DISTANCES (Å) AND ANGLES (°)

Bond	Length	Angle	(°)	Angle	(°)
Cu-O(1)	1.9397(11)	O(1)-Cu-O(2)	85.28(5)	N(1)-C(3)-C(4)	121.87(14)
Cu-O(2)	1.9535(11)	O(1)-Cu-N(1)	166.92(5)	O(2)-C(2)-C(1)	114.95(12)
Cu-N(1)	2.0015(13)	O(2)-Cu-N(1)	94.86(5)	O(4)-C(2)-C(1)	119.49(13)
Cu-N(2)	2.0135(13)	O(1)-Cu-N(2)	94.54(5)	O(4)-C(2)-O(2)	125.56(14)
Cu-O(5)	2.2063(2)	O(2)-Cu-N(2)	167.39(5)	O(1)-C(1)-C(2)	114.41(12)
N(1)-C(3)	1.392(18)	N(1)-Cu-N(2)	82.47(5)	O(3)-C(1)-C(2)	120.10(13)
N(1)-C(14)	1.3563(8)	O(1)-Cu-O(5)	94.17(5)	O(3)-C(1)-O(1)	125.49(14)
N(2)-C(12)	1.328(2)	O(2)-Cu-O(5)	96.72(5)	C(2)-O(2)-Cu	112.37(10)
N(2)-C(13)	1.3590(18)	N(1)-Cu-O(5)	98.79(5)	C(1)-O(1)-Cu	112.78(9)
O(1)-C(1)	1.2915(17)	N(2)-Cu-O(5)	95.78(5)	C(13)-N(2)-Cu	111.93(10)
O(2)-C(2)	1.2831(18)	C(3)-N(1)C(14)	118.57(13)	N(2)-C(12)C(11)	121.78(14)
O(3)-C(1)	1.2180(18)	C(3)-N(1)-Cu	128.88(10)	N(2)-C(13)-C(9)	123.47(13)
O(4)-C(2)	1.2249(18)	C(14)-N(1)-Cu	112.49(10)	N(2)-C(13)-C(14)	116.57(12)

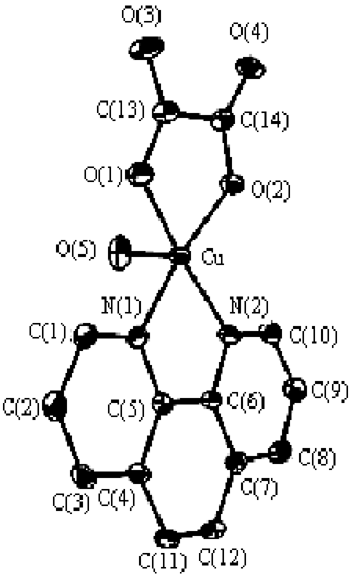

Fig. 1. Molecular strucutre of $[Cu(phen)(C_2O_4)(H_2O)]\cdot H_2O$

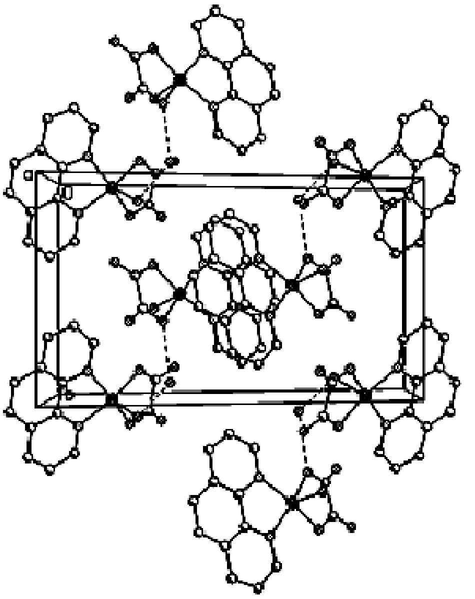

Fig. 2. Molecular packing arrangement in the unit cell

The two N atoms are from 1,10-phenanthroline molecule. The bond lengths are 2.0015(13)Å and 2.0135(13)Å. $O_{(1)}$ and $O_{(2)}$ come from a $C_2O_4^{2-}$ group. The bond lengths are 1.9397(11)Å and 1.9535(11)Å. The apical position is occupied by one coordinated water oxygen atom $O_{(5)}$, which is slightly elongated from the Cu center ($Cu–O_{(5)}$ = 2.2063(12)Å) due to the Jahn-Teller effects of the copper(II) atom with a d^9 electron configuration. All of the atoms of a 1,10-phenanthroline molecule and a $C_2O_4^{2-}$ group are respectively coplanar. The dihedral angle between the 1,10-phenanthroline molecule plane and the $C_2O_4^{2-}$ group plane is 167.3º. The bond angels of $O_{(1)}$-Cu-$O_{(5)}$, $O_{(2)}$-Cu-$O_{(5)}$, $N_{(1)}$-Cu-$O_{(5)}$, $N_{(2)}$-Cu-$O_{(5)}$ are in the range from 94.17(5)º to 98.79(5)º. The distances between $O_{(5)}$ and $O_{(1)}$, $O_{(5)}$ and $O_{(2)}$, $O_{(5)}$ and $N_{(1)}$, $O_{(5)}$ and $N_{(2)}$, $O_{(1)}$ and $O_{(2)}$, $O_{(2)}$ and $N_{(1)}$, $N_{(1)}$ and $N_{(2)}$, $N_{(2)}$ and $O_{(1)}$, $O_{(1)}$ and $N_{(1)}$, $O_{(2)}$ and $N_{(2)}$ are 3.042, 3.113, 3.198, 3.136, 2.637, 2.913, 2.647, 2.904, 3.916 and 3.943Å. In addition, The angels of $N_{(2)}$-$O_{(1)}$-$O_{(2)}$, $O_{(1)}$-$O_{(2)}$-$N_{(1)}$, $O_{(2)}$-$N_{(1)}$-$N_{(2)}$, $N_{(1)}$-$N_{(2)}$-$O_{(1)}$ are respectively 90.59, 89.60, 90.22 and 89.60º. So it can be suggested that the atoms $O_{(1)}$, $O_{(2)}$, $N_{(1)}$, $N_{(2)}$ are all but in a plane and $O_{(1)}\cdots O_{(2)}\cdots N_{(1)}\cdots N_{(2)}\cdots O_{(1)}$ is nearly a rectangle. The Cu atom is displaced by *ca.* 0.2212 Å out of the rectangle plane. By the above analyses, it is concluded that the copper(II) ion is five-coordinated in a slightly distorted square pyramidal geometry, the axial position is occupied by $O_{(5)}$ atom.

The hydrogen-bonded geometry involving coordinated and non-coordinated water molecules is characterized in Table-3 (Fig. 3). It can be seen that there are four kinds of hydrogen bonds in the crystal, through the anterior three kinds of ones: $O_{(5)}$-$H_{(1)}\cdots O_{(6)}$, $O_{(5)}$-$H_{(2)}\cdots O_{(2A)}$, $O_{(6)}$-$H_{(4)}\cdots O_{(1C)}$, the title compound molecule form a chain-link structure, and many chains make up of a two-dimensional polymer layer by another kind of hydrogen bond: $O_{(6)}$-$H_{(3)}\cdots O_{(4B)}$. In addition, between the layers the parallel phenanthroline ring lies alternately in a head-to-tail manner, forming a layer structure with the layer separation of about 3.506Å, implying the existence of some π-π stacking interactions between the phenanthroline rings[15]. Through the π-π stacking interactions, many of these layers pack in a 3-D net structure Supramolecular Complex and the shorest distance between the two layers is about 3.415 Å.

TABLE-3
HYDROGEN BOND DISTANCE (Å) AND ANGLES (°)

D-H···A	D-H	H···A	D···A	∠DHA
O(5)-H(1)···O(6)	0.894(16)	1.845(16)	2.7392(17)	178.0(2)
O(5)-H(2)···O(2A)#1	0.864(16)	2.067(16)	2.9287(18)	169.0(2)
O(6)-H(4)···O(1C)#3	0.876(15)	1.977(16)	2.8486(17)	172.6(19)
O(6)-H(3)···O(4B)#2	0.875(15)	2.099(16)	2.9305(18)	158.0(2)

Symmetry transformations used to generate equivalent atoms:
1-x,y+1/2,-z+1/2 #2 x+1,y,z #3 –x,y-1/2,-z+1/2

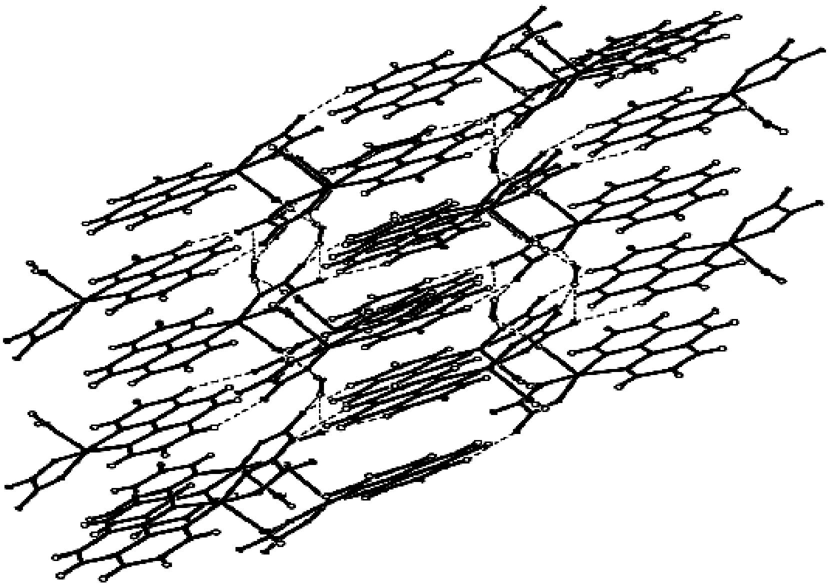

Fig. 3. View of the layered structure formed by hydrogen bonds and π-π stacking interactions with the hydrogen atoms omitted for clarity

Conclusion

Crystal structure of a novel 3D-superamolecular copper(II) complex with oxalate and 1,10-phenanthroline [Cu(phen)(C_2O_4)(H_2O)]·H_2O has been synthesized and characterized by IR, elemental analysis and X-ray diffraction analysis. The studies of the absorption and catalytic characteristics about this complex are in progress.

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