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Synthesis and Crystal Structure of a New Chiral Mononuclear Complex: $[Cu(C_{10}H_{12}N_2O)_2(NO_3)_2(H_2O)]$

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A novel chiral mononuclear complex $[Cu(C_{10}H_{12}N_2O)_2(NO_3)_2(H_2O)]$, where $C_{10}H_{12}N_2O$) is 3-(dimethylamino)-1-(pyridine-4-yl)prop-2-en-1-one, 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 with a chiral space group in a slightly distorted square pyramidal geometry environment. The crystal is monoclinic, space group Cc with unit cell parameters: a = 20.399(2)Å, b = 9.780(1)Å, c = 13.537(2)Å, α = 90º, β = 116.270(2)º, γ = 90º, V = 2421.8(5) Å^3, Z = 4, Mr = 558, Dc = 1.531 Mg/cm^3, μ = 0.964 mm^{-1}, F(000) = 1156, Flack x = 0.39(2), T = 291(2) K, R = 0.0561, wR = 0.0979 for 3513 reflections with I > 2σ(I).

Key Words: Chiral complex, Crystal structure, Hydrogen bonds, Superamolecular.

INTRODUCTION

Chirality has been of great importance in chemistry, pharmacy, biochemistry and materials science. Recently a major challenge in supramolecular chemistry is the design of simple molecular units that are capable of organizing into chiral architectures in view of possible applications such as enantioselective synthesis, asymmetric catalysis, porous materials, non-linear optical materials and magnetic materials[1-3]. There are numerous examples of achiral molecules including simple metal salts which crystallize in chiral space groups[4-7]. It is not well understood, however, how homochiral packing of helices in crystals can be induced. Herein, synthesis and crystal structure of a novel chiral copper complex produced by copper salt and 3-(dimethylamino)-1-(pyridine-4-yl)prop-2-en-1-one are reported.

EXPERIMENTAL

All reagents were of AR grade and used without further purification. 3-(Dimethylamino)-1-(pyridine-4-yl)prop-2-en-1-one was prepared by similar procedure reported in the literature[8]. Analyses for carbon, hydrogen and nitrogen were performed on a

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Perkin-Elmer 1400C analyzer. Infrared spectra (4000-400 cm^{-1}) were recorded with a Bruker Vector 22 FT-IR spectrophotometer on KBr disks.

Synthesis: To a 20 mL methanol solution of $Cu(NO_3)_2 \cdot 4H_2O$ (1 mmol) were successively added a 10 mL methanol solution of 3-(dimethylamino)-1-(pyridine-4-yl)prop-2-en-1-one (2 mmol) with stirring. The mixture was refluxed for 1 h to obtain a clear blue solution and after standing at room temperature for 2 weeks, well-shaped blue single crystals were obtained by slow evaporation. Anal. Calcd for $C_{20}H_{26}N_6O_9Cu$: C, 43.05; H, 4.70; N, 15.06 %. Found: C, 43.14; H, 4.68; N, 15.01 %. IR (KBr, cm^{-1}): 3088 (m), 1601 (m), 1523 (m), 1462 (m), 1385 (s), 1292 (w), 1021 (w), 825 (w).

Crystal structure determination: A single crystal of compound with dimensions of 0.32 mm × 0.24 mm × 0.20 mm was selected for crystallographic data collection at 291(2) K and structure determination on a Siemens SMART CCD area-detector diffractometer with graphite-monochromatic MoKα radiation (λ = 0.71073 Å). A total of 6316 reflections were collected in the range of $2.2° \leq \theta \leq 26.0°$, of which 3513 reflections were unique with $R_{int} = 0.059$. The data were collected using SMART and reduced by the program SAINT. All the structures were solved by direct methods and refined by full-matrix least squares method on F^2_{obs} by using SHELXTL-PC software package. Non-hydrogen atoms were placed in geometrically calculated positions. Hydrogen atoms were added according to theoretical model. The final full-matrix least-squares refinement including 334 variable parameters for 3513 reflections with $I > 2\sigma(I)$ and converged with unweighted and weighted agreement factors of

$$R_1 = \Sigma(||F_0|-|F_c||)/\Sigma|F_0| = 0.0561 \quad (1)$$

and

$$wR_2 = \{\Sigma[w(F_0^2-F_C^2)^2]/\Sigma w(F_0^2)^2\}^{1/2} = 0.0979 \quad (2)$$

where $w = 1/[\sigma^2(F_0^2) + (0.0254P)^2]$ and $P = (F_0^2 + 2F_C^2)/3$. The flack parameter is 0.39(2). The maximum and minimum peaks on the final difference Fourier map are corresponding to 0.44 and -0.28e/$Å^2$, respectively.

RESULTS AND DISCUSSION

A molecular structure with atom-numbering scheme and the packing diagram of title compoud are shown in Figs. 1 and 2, respectively. The selected bond lengths and bond angles in Table-1.

The molecular structure of title compound owns a mononuclear motif (Fig. 1), where each Cu(II) ion is bound by two oxygen atoms from two nitrate, one water molecule and two nitrogen atoms from two organic ligands, in a pentahedral fashion. Each ligand adopts a monodentate coordination pattern with a Z conformation.

In crystal packing, it is interesting to observe that the O–H···O and C–H···O intermolecular hydrogen bonds are formed between adjacent molecular motifs resulting in a 3D supramolecular framework.

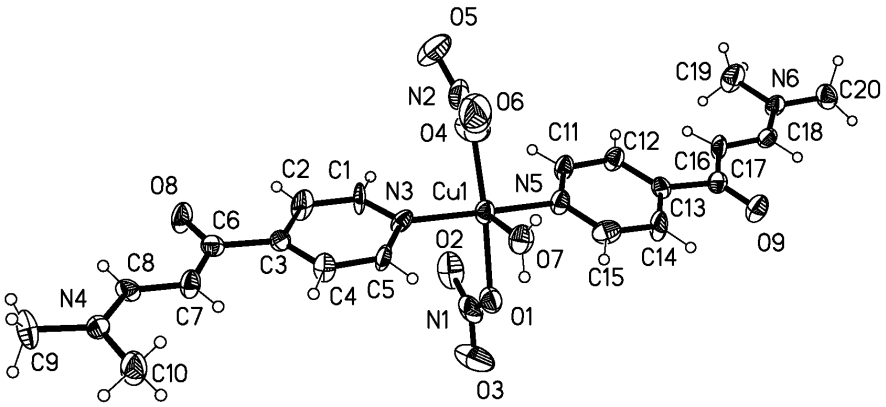

Fig. 1. Molecular structure of the title compound

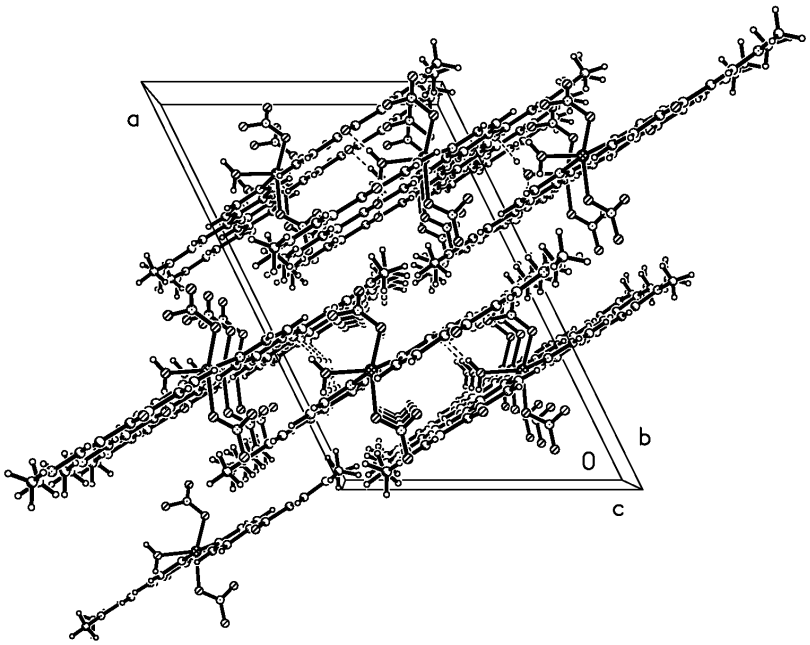

Fig. 2. Molecular packing arrangement in the unit cell

TABLE-1
SELECTED BOND DISTANCES (Å) AND ANGLES (º)

Cu(1)-N(3)	1.973(6)	N(3)-Cu(1)-O(4)	90.2(3)
Cu(1)-O(4)	1.975(8)	N(3)-Cu(1)-N(5)	167.7(3)
Cu(1)-N(5)	2.005(7)	O(4)-Cu(1)-N(5)	86.9(3)
Cu(1)-O(1)	2.044(6)	N(3)-Cu(1)-O(1)	90.2(2)
Cu(1)-O(7)	2.213(7)	O(4)-Cu(1)-O(1)	161.6(3)
N(5)-Cu(1)-O(1)	88.800(3)	O(4)-Cu(1)-O(7)	116.6(3)
N(3)-Cu(1)-O(7)	94.600(3)	N(5)-Cu(1)-O(7)	97.4(3)
O(1)-Cu(1)-O(7)	81.800(3)		

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

D–H···A	D–H	H···A	D···A	∠ DHA
O7-H7A···O8 #1	0.820	2.100)	2.748(10)	136.0
O7-H7B···O9 #2	0.83(9)	2.03(8)	2.813(10)	157(8)
C4-H4···O3 #3	0.930	2.590	3.468(1)	157.0
C5-H5···O2 #3	0.930	2.600	3.240(1)	127.0

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

Conclusion

Crystal structure of a novel chiral copper(II) complex with space group cc has been synthesized and characterized by IR, elemental analysis and X-ray diffraction analysis. The studies of the absorption and catalysis characteristics about this complex are in progress.

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 706837.

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