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Synthesis, Crystal and Supramolecular Structures of New Mononuclear Cu(II) Complex [Cu(pic)$_2$(py)$_2$]

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A new mononuclear Cu(II) complex, [Cu(pic)$_2$(py)$_2$] (where pic = picrate anion and py = pyridine), has been synthesized and characterized by single crystal X-ray crystallography. The crystal structure shows that Cu(II) ion has a distorted octahedral coordination geometry. The complex crystallizes in the orthorhombic crystal system with Pna 2(1), with a = 9.488(5) Å, b = 12.469(7) Å, c = 22.449(13) Å, and Z = 4. In the crystal, the short O···O contacts and hydrogen bonding interactions constitute a 2D supramolecular layer structure.

Keywords: Copper(II) complex, Crystal structure.

INTRODUCTION

The construction of crystal engineering has become rapidly expanding areas of research with implications for the rational design of functional materials[1,2]. Crystal engineering based on organic or organic and inorganic molecular building blocks has been rapidly developing because of the novel and diverse topologies and potential applications in catalysis, host-guest chemistry, electrical conductivity and magnetism[3-5]. Many studies have designed supramolecular contacts, particularly hydrogen bonding and π-π stacking interaction, between purely organic molecules to generate multidimensional arrays or networks[6,7]. The connection between organic or organic and inorganic molecular building blocks is established by exploiting non-covalent interactions[8,9]. In the transition metal complexes, these interactions are established mainly among the 'organic' parts of the molecules and choice a most appropriate ligands[10-14]. Copper(II) complexes are the most widely studied coordination compounds because of their widespread applications. Properties of copper(II) picrate and the coordination abilities of picrate ions can be using N-donor ligands with appropriate functionalization[15]. In brief, the chosen picrate ligand may show a propensity to exhibit different coordination modes depending upon the type of nitrogen donor ligand chosen. Herein, we report the synthesis and crystal structure of a mononuclear Cu(II) complex with pyridine and picrate.

EXPERIMENTAL

Salicylaldehyde (> 99 %) and 1,2-dibromoethane (= 99 %) were purchased from Alfa Aesar and used without further purification. 1,2-*bis*(Aminooxy)ethane was synthesized according to an analogous method reported earlier[16]. The others are the same as literature early[16].

Synthesis of H$_2$L: 2,2'-(Ethylenedioxy)*bis*(benzaldehyde) was prepared according to an similar method[17]. 2-[*O*-(1-Ethyloxy-amide)]oxime-phenol was synthesized by modification of the reported method[16]. The reaction of 2,2'-(ethylenedioxy)-bis(benzaldehyde) with 2-[*O*-(1-ethyloxy-amide)]oxime-phenol in hot ethanol gave the bis(salamo)-type ligand H$_2$L. Yield 77.3 %. m.p. 402-403 K. Anal. Calcd. for $C_{34}H_{34}N_4O_8$ (%): C, 65.17; H, 5.47; N, 8.94; found: C, 65.15; H, 5.46; N, 8.92.

Synthesis of Cu(II) complex: A solution of Cu(pic)$_2$·4H$_2$O (5.92 mg, 0.01 mmol) in ethanol (2 mL) was added dropwise to a solution of H$_2$L (3.13 mg, 0.005 mmol) in tetrahydrofuran (3 mL) and pyridine (0.5 mL) at room temperature. The mixing solution turned to green immediately. After continuing stirring for 2 h at room temperature, the mixture was filtered off and the filtrate was allowed to stand at room temperature for one day. Then green prismatical single crystals suitable for X-ray crystallographic analysis were obtained. Anal. Calcd. for $C_{22}H_{14}CuN_8O_{14}$(%): C, 38.98; H, 2.08; N, 16.53; Cu, 9.37; found: C, 38.97; H, 2.06; N, 16.52; Cu, 9.36.

X-ray structure determination: The single crystal of the title complex, with approximate dimensions of 0.28 mm × 0.26 mm × 0.22 mm was placed on a Bruker Smart 1000 diffractmeter equipped with Apex CCD area detector. The diffraction data were collected using a graphite monochromated MoK$_\alpha$ radition (λ = 0.71073 Å) at 296(2) K. The structure was solved by using the program SHELXS-97 and fourier difference

TABLE-1
CRYSTAL DATA AND STRUCTURE REFINEMENT FOR THE Cu(II) COMPLEX

Empirical formula	$C_{22}H_{14}N_8O_{14}Cu$
Formula weight	677.95
Temperature (K)	296(2)
Wavelength (Å)	0.71073
Crystal system	Orthorhombic
Space group	Pna2(1)
Cell dimensions, (Å, deg)	a = 9.488(5), b = 12.469(7), c = 22.449(13)
Volume (Å^3)	2656(3)
Z	4
Density (calculated) (mg/m^3)	1.696
Absorption coefficient (mm^{-1})	0.912
$F_{(000)}$	1372
Crystal size	0.28 × 0.26 × 0.22
Index ranges	$-10 \leq h \leq 11$, $-14 \leq k \leq 9$, $-25 \leq l \leq 26$
Reflections collected	13785/2350 [R(int) = 0.0266]
Independent reflections	4532
Data/restraints/parameters	2350/0/205
Goodness of fit indicator	1.045
R [I >2σ(I)]	R_1 = 0.0345, wR_2 = 0.0989
Largest diff. peak and hole (e Å^{-3})	0.549 and -0.273

techniques and refined by full-matrix least-squares method on F^2 using SHELXL-97. Details of the data collection and refinements of the Cu(II) complex are listed in Table-1. The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were added theoretically.

RESULTS AND DISCUSSION

Crystal structure of Cu(II) complex: X-ray crystallographic analysis reveals formation of a mononuclear structure, which consists of one Cu(II) atom, two picrate anions and two pyridine molecules. ORTEP-style drawing of the Cu(II) complex is shown in Fig. 1 and selected bond lengths and angles are listed in Table-2.

The Cu(II) complex is to be a Cu(II) atom coupled by both doubly phenoxo oxygen and nitro oxygen atoms of the picrate units and two N-pyridine. The coordination geometry around the center Cu(II) atom is regarded as a distorted octahedral geometry with hexa-coordination. One N-pyridine atom, two nitro oxygen atoms and one phenoxo oxygen atom are located on the equatorial plane of the central Cu(II) atom. The π-π stacking interaction between two benzene rings of the picrate anions is play a key role in formation, stability and crystallization of the Cu(II) complex and the centroid distance is 3.641(4) Å.

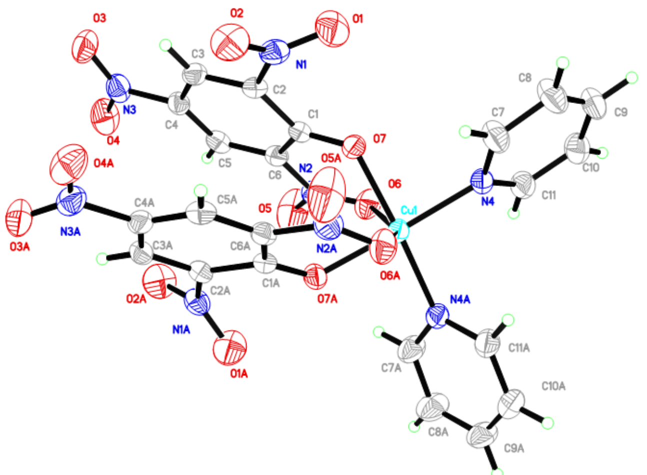

Fig. 1. ORTEP-style drawing of Cu(II) complex

Intermolecular interactions of Cu(II) complex: The extended layer structure is formed by intramolecular C-H···O hydrogen bonds and short intramolecular O-O contacts, intermolecular hydrogen bonds between two Cu(II) complexes. Hydrogen bond data are summarized in Table-3. And π-π stacking interaction drawing of the Cu(II) complex is shown in Fig. 2.

TABLE-3
DATA FOR HYDROGEN-BONDING INTERACTIONS (Å, °)

D-H···A	d(D-H)	d(H···A)	d(D···A)	∠D-H···A	Symmetry code
C10-H10···O4	0.93	2.57	3.257(5)	131	x, 1/2-y, -1/2+z
C11-H11···O3	0.93	2.47	3.304(4)	149	x, 1/2-y, -1/2+z

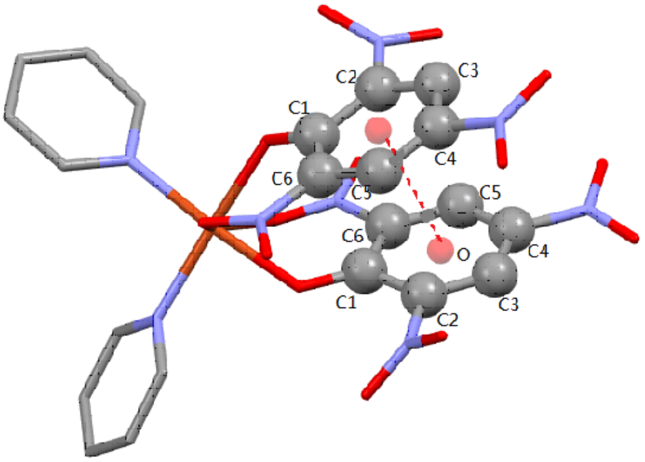

Fig. 2. View of intramolecular π-π stacking interactions of Cu(II) complex

TABLE-2
SELECTED BOND LENGTHS (Å) AND ANGLES (°) FOR THE Cu(IICOMPLEX

Bond	Lengths	Bond	Lengths	Bond	Lengths
Cu1-O7	1.9577(19)	Cu1-N4$^{\#A}$	1.996(2)	Cu1-O6	2.439(3)
Cu1-O7$^{\#A}$	1.9578(19)	Cu1-N4	1.996(2)	Cu1-O6$^{\#A}$	2.439(3)
Bond	**Angles**	**Bond**	**Angles**	**Bond**	**Angles**
O7-Cu1-O7	90.24(11)	O7-Cu1-N4	172.40(8)	O7-Cu1-N4$^{\#A}$	87.20(9)
O7-Cu1-N4	87.20(9)	O7-Cu1-N4$^{\#A}$	172.40(8)	N4-Cu1-N4	96.21(13)
O7-Cu1-O6$^{\#A}$	75.33(7)	O7-Cu1-O6$^{\#A}$	87.75(8)	N4-Cu1-O6$^{\#A}$	97.41(8)
N4-Cu1-O6	98.50(8)	O7-Cu1-O6	87.75(8)	O7-Cu1-O6$^{\#A}$	75.33(7)
N4-Cu1-O6$^{\#A}$	98.50(8)	N4-Cu1-O6	97.41(8)	O6-Cu1-O6	156.08(10)

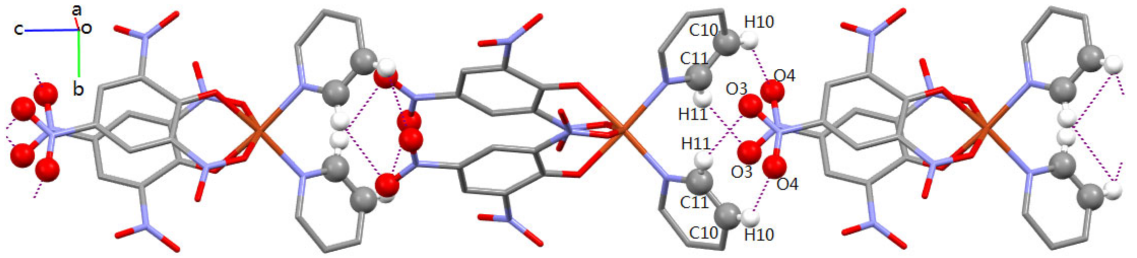

Fig. 3. View of the 1D chain motif of copper(II) complex units (hydrogen atoms, except those forming hydrogen bonds, are omitted for clarity)

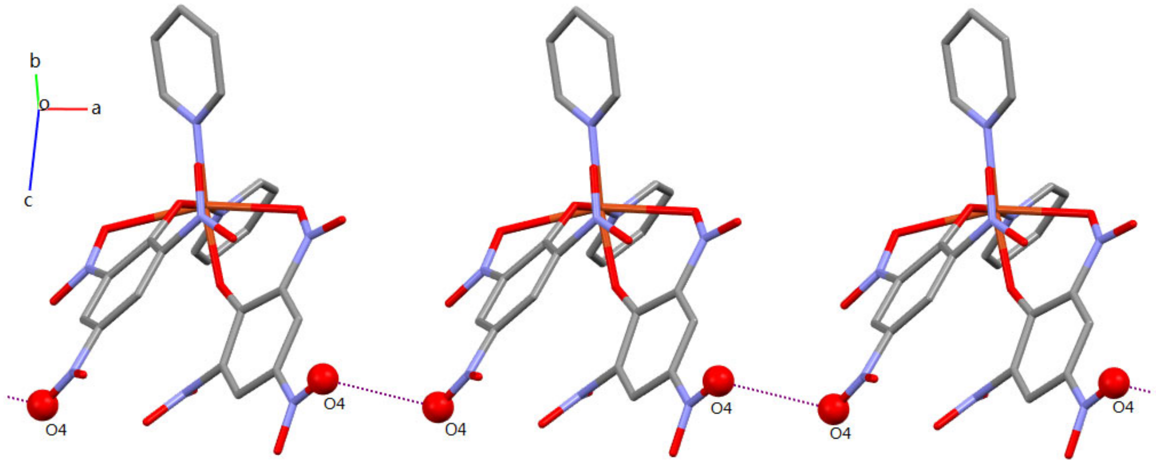

Fig. 4. View of the 1D chain motif of copper(II) complex units (hydrogen atoms, except those forming hydrogen bonds, are omitted for clarity)

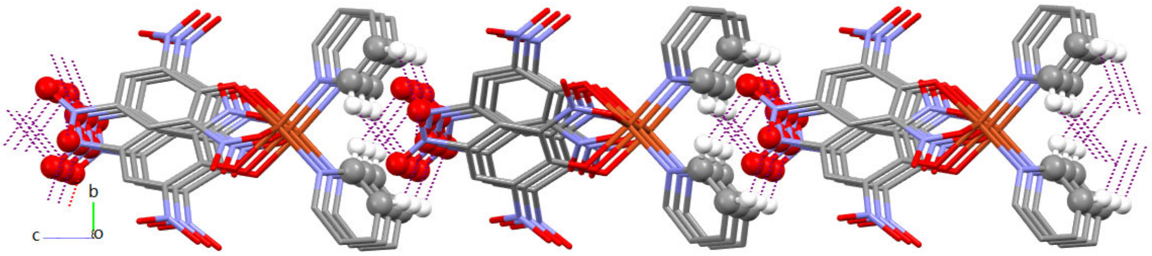

Fig. 5. View of the 2D supramolecular layer motif of copper(II) complex (hydrogen atoms, except those forming hydrogen bonds, are omitted for clarity)

The Cu(II) complex has two pairs of intramolecular C10-H10···O4 and C11-H11···O3 hydrogen-bonding interactions into an infinite 1D supramolecular chain (Fig. 3). Synchronously, this linkage is further stabilized by short intermolecular O4-O4 contacts between the nitro oxygen atoms of the picrate unit and that of another picrate unit, to form a 1D supramolecular chain-like structure (Fig. 4). A 2D supramolecular layer motif of the Cu(II) complexes is formed by hydrogen-bonding interactions and short intermolecular O4-O4 contacts (Fig. 5).

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