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Synthesis and Structure of Polymeric Copper(I) Compound with Single-Stranded Dihelicate Units involving Multiring Nitrogen-Heterocyclic Ligand

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The polymeric copper(I) complex $[Cu_2(L)I_2]$ (**1**) containing a new biologically relevant heterocyclic bis-bidentate ligand *viz.* 3,3′-dipyridine-2-yl-[1.1′]bi[imidazo[1,5-*a*]pyridineyl] (L) was synthesized and characterized by single-crystal X-ray diffraction analysis. The molecule lacks molecular center of symmetry where coordination environments around both Cu(1) and Cu(2) are distorted tetrahedral ($Cu\cdots Cu^{\#}$ separation of 3.5 Å). Compound in its solid-state structure shows π-π non-covalent interactions as well as C_{arene}-H---anion non-classical hydrogen bonding interactions that play dominant roles in shaping the extended structure of the molecule.

Keywords: Polymeric complex, Dihelicate units, N-Heterocyclic ligand, Non-covalent interactions, Hydrogen bonding.

INTRODUCTION

The programmed self-assembly of discrete helicates has been the topic of extensive research over the last few decades [1-8] because of their biomimetic relevance and aesthetic appeal [1,2,7]. Also the basic mechanistic and energetic findings provided by the study of formation, structure and properties of helicates help to understand the fundamental principles of molecular recognition and self-organization [4-6], which are important for the rational design of more complex architectures [1-3,7,9]. Among the various classes of ligands that are shown to be suitable for the construction of various types of helicates, polypyridines are particularly numerous [2,10-13]. Many transition metals with such ligands produce dihelicates. For dihelicates, double and triple stranded complexes of the types M_2L_2 and M_2L_3, where L is a bis-bidentate ligand, are particularly common [1,14]. Much less common are single-stranded dihelicates where a single ligand coordinates to two non-bridged metal ions in a helical motif [15].

Non-covalent interactions involving π-systems have been extensively studied in recent years [16]. Such interactions play a crucial role in many frontline areas of contemporary science, from molecular biology to crystal engineering [17,18]. For example, face to face π-stacking interactions involving aryl rings of nucleobase pairs are important for the stability of DNA double helix [19,19].

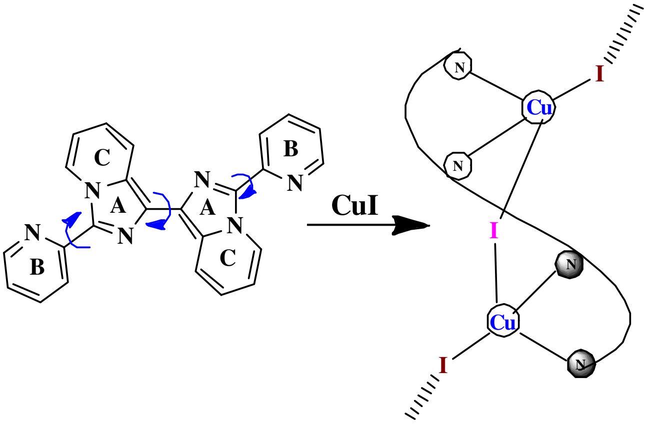
Recently, supramolecular chemistry has unveiled that non-conventional H-bonds, such as (a) C-H...X (X = O, N, F, Cl, Br, I), (b) X-H...π (X=N, O, C, Si & π = double, triple or aromatic), (c) X-H.....M (M as acceptors, M=Pt, Pd, Cu & X=N, O), M-H.....H (M as donors, M = Os, Ir) often play crucial structural and biological roles [20]. The theoretical and experi-mental studies on such interactions may lead to the develop-ment of novel approaches for the design of effective systems capable of exhibiting noncovalent recognition properties at molecular level.

A π-electron-deficient *N*-heterocyclic compound, *viz.* 3,3′-dipyridin-2-yl[1,1′]bi[imidazo[1,5-*a*] pyridinyl] (L) containing a pair of biologically relevant [21] imidazo[1,5-*a*]pyridine moieties were recently synthesized [22,23]. Ligand L is redox-active and capable of acting as a bis-bidentate ligand, and its copper(II) compound offers a unique example of valence tautomerism in solution [22]. Herein, the synthesis of polymeric Cu(I) compound with single stranded helicate units (1) of a nitrogen-rich electron deficient heterocyclic ligand (L) is reported. The compound has been characterized by single-crystal X-ray diffraction analysis.

EXPERIMENTAL

Bis-bidentate type ligand L was synthesized as described elsewhere [21,22]. The chemicals *viz*. CuI was purchased from Aldrich and all other reagents were commercially available and used as received. Solvents were of reagent grade, dried by standard methods [24] and distilled under nitrogen prior to their use. Elemental (C, H, N, and S) analyses were performed on a Perkin-Elmer model 2400 Series II CHNS Analyzer.The IR spectra were recorded on a Shimadzu model 8400S FT-IR spectrometer with samples prepared as KBr pellets.

Synthesis of [$Cu_2(L)I_2$] (1): CuI (38 mg, 0.2 mmol) in acetonitrile (5 mL) was carefully layered on to a solution of 3,3′-dipip (39 mg, 0.1 mmol) in dichloromethane (5 mL). Diffusion between the two layers over a period of *ca*. 5 days produced red crystals (**Scheme-I**). Yield: 30%. Anal. calcd. (found) % for $C_{24}H_{16}N_6I_2Cu_2$: C, 37.45 (37.44); H, 3.12 (3.01); N, 10.92 (10.61). FT-IR (KBr pellet, ν_{max}, cm^{-1}): 3465, 1589, 1458, 1305, 1249, 775, 688.



Scheme-I: Protocol followed for the synthesis of compound **1**

Refinement: Diffraction quality crystals of **1** (plate, red crystals, 0.030 × 0.020 × 0.002 mm^3 obtained from 1:1 (v/v) dichloromethane/acetonitrile) were grown by diffusion technique from the solvent combination as observed. Crystals were mounted on the glass fibers and aligned on a Bruker AXS platinum 200 CCD diffractometer. The crystal was coated with paraffin oil and were placed in the cold stream of nitrogen for low temperature data collection. Intensity data were collected with silicon 111 monochromatized synchrotron radiation ($\lambda = 0.77490$ Å) at 193(2) K using the ω-rotation scan techniques with narrow frames.

Here, absorption corrections based on multiscan using the SADABS software [25] were applied. The structures were solved by direct methods [25] and least square refinement [anisotropic displacement parameters, hydrogen atoms in the riding model approximation and a weighing scheme of the form $\omega = 1/[\sigma^2(F_0^2) + (aP)^2 + bP]$ for $P = (F_0^2 + 2F_c^2)/3)$] was on F^2 [25]. Bruker SHELXTL [25] was used both for structure solutions and refinements. Crystallographic parameters and the final residuals are given in Table-1. The positions of all non-hydrogen atoms were refined with anisotropic displacement factors. Data reductions were accomplished with Bruker SAINT and "Bruker SAINT V7.23a" software packages and crystallographic diagrams were drawn using Bruker SHELXTL at 30% probability level.

TABLE-1
SUMMARY OF X-RAY CRYSTALLOGRAPHIC DATA FOR **1**

Parameter	**1**
Composition	$C_{24}H_{16}N_6I_2Cu_2$
Formula weight	769.31
Crystal system	Triclinic
Space group	*P*-1
a (Å)	7.796(2)
b (Å)	10.102(3)
c (Å)	15.124(4)
α (°)	88.616(5)
β (°)	76.237(5)
γ (°)	75.710(5)
V $(Å)^3$	1116.5(5)
D_{calc} (Mg m^{-3})	2.288
Temperature (K)	193(2)
λ (Å)	0.77490
Z	2
F(000)/μ mm^{-1}	732/5.891
$2\theta_{max}$ (°)	48.31
Reflections collected/Unique	7193/271
R_{int}/GOF on F^2	0.0475/1.008
Number of parameters	307
$R1(F_0)$, $wR2(F_0)$ ($I \geq 2\sigma(I)$)	0.0398, 0.0926

RESULTS AND DISCUSSION

The bis-bidentate mode of the ligand in combination with tetravalent Cu(I) metal salt with counter anions like iodide favours the formation of relatively rare [15] single-stranded dihelicates. Strong tendency of iodide to bridge the metal centres facilitates the formation of polymeric $[Cu_2(L)I_2]_n$ (**1**) where the adjacent Cu(I) centers of the single stranded dihelicate units are connected both intra and intermolecularly through iodide. The ligand L has identical halves, each containing three different heterocyclic rings, *viz*. imidazole (A), isolated pyridine (B), and fused pyridine (C) rings, which will be designated as im, py and azopy rings, respectively. IR spectra of the complexes contain all the pertinent bands due to the coordinated bipyridine type ligands [26,27] appearing at *ca*. 1600, 1485, 1461, 1313, 1247, 770 cm^{-1} region as prominent features.

Structure: Compound **1** has an oligomeric structure comprising of monomeric units which are neutral binuclear Cu(I) species as revealed from X-ray crystallography. Perspective view of the monomeric unit of complex **1** is displayed in Fig. 1. Relevant metrical parameters are summarized in Table-2. The compound crystallizes in triclinic space group P-1 with two molecular units per cell.

As shown in Fig. 1 each non-equivalent Cu(I) center adopts highly distorted [28] (τ_4^{23} = 0.81) tetrahedral coordination geometry through the bonding of two iodine atoms and two chelating nitrogen donors from the bis-bidentate ligand L. The distortion is achieved by the bidentate chelating mode of L. Due to the planar five membered chelate ring formation, the N-Cu-N angles (79.4-79.9°) are significantly smaller than the ideal tetrahedral angle. The Cu-I (2.513(13)-2.655(16) Å) and

TABLE-2
SELECTED BOND DISTANCES (Å) AND ANGLES (DEG) FOR **1**

Bond distances (Å)				Bond angles (°)			
Cu(1)–N(1)	2.105(8)	Cu(2)–N(5)	2.034(6)	N(1)–Cu(1)–N(2)	79.90(3)	N(5)–Cu(2)–N(6)	79.40(3)
Cu(1)–N(2)	2.039(7)	Cu(2)–N(6)	2.128(7)	I(1)–Cu(1)–I(2)	108.53(5)	I(1)–Cu(2)–I(2)	107.89(5)
Cu(1)–I(1)	2.5139(13)	Cu(2)–I(1)	2.5608(14)	I(1)–Cu(1)–N(1)	123.34(19)	I(1)–Cu(2)–N(5)	119.40(2)
Cu(1)–I(2)	2.6556(16)	Cu(2)–I(2)	2.5942(15)	I(1)–Cu(1)–N(2)	122.10(2)	I(1)–Cu(2)–N(6)	116.40(2)
				I(2)–Cu(1)–N(2)	118.00(2)	I(2)–Cu(2)–N(5)	124.00(2)
				I(2)–Cu(1)–N(1)	101.20(2)	I(2)–Cu(2)–N(6)	105.80(2)

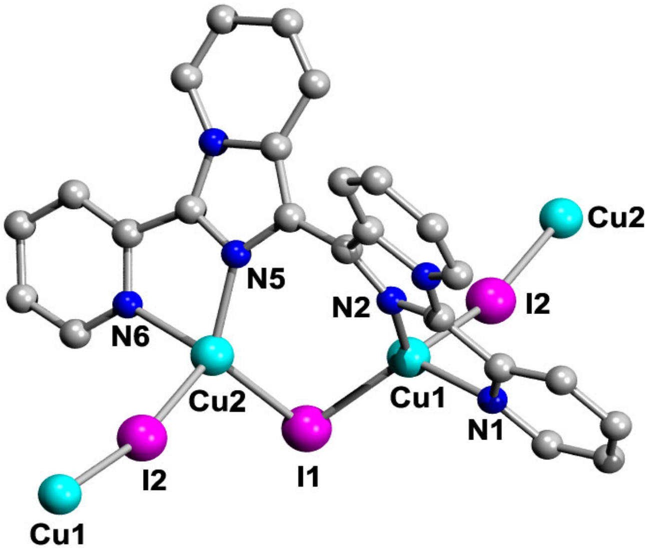


Fig. 1. Molecular structures of [$Cu_2(L)I_2$] (**1**) showing the atom-labeling scheme. Hydrogen atoms have been omitted for clarity

Cu-N (2.034(6)-2.128(7) Å) bond distances are in the expected range [29,30]. The dihedral angle between two central im rings is 49º. Such a twist makes it possible to bring the two Cu(I) centers to a close proximity (Cu(I)-Cu(I) distance 3.5 Å) that helps one iodide ion to bridge these metal centers in an intramolecular way.

The individual dinuclear units are further joined together intermolecularly also by bridging iodide to form infinite oligomeric chain (Fig. 2). In addition, there are three types of strong intermolecular π-stacking interactions in this molecule. Two of these exist between py and azopy (centroid-centroid distances 3.65 and 3.72 Å, respectively) and one between py and im ring (centroid-centroid distance 3.681 Å). The successive π-π interactions link neighboring polymeric chains together to form 2D array (Fig. 3). The linkages are further supported by strong C-H---I interactions, with the distances ranging from 3.02-3.06 Å.

Conclusion

Copper(I) complex (**1**) of nitrogen-rich electron deficient heterocyclic ligand (L) has been synthesized. The complex is polymeric, composed of several single-stranded helical units. The structure in the solid state involves multiple anion-π interactions. These noncovalent interactions play dominant role in shaping the extended structures of the compound in the solid state. Also compound establishes an array of C_{arene}-H---anion non-classical hydrogen bonds that reinforce these non-covalent interactions in the molecule.

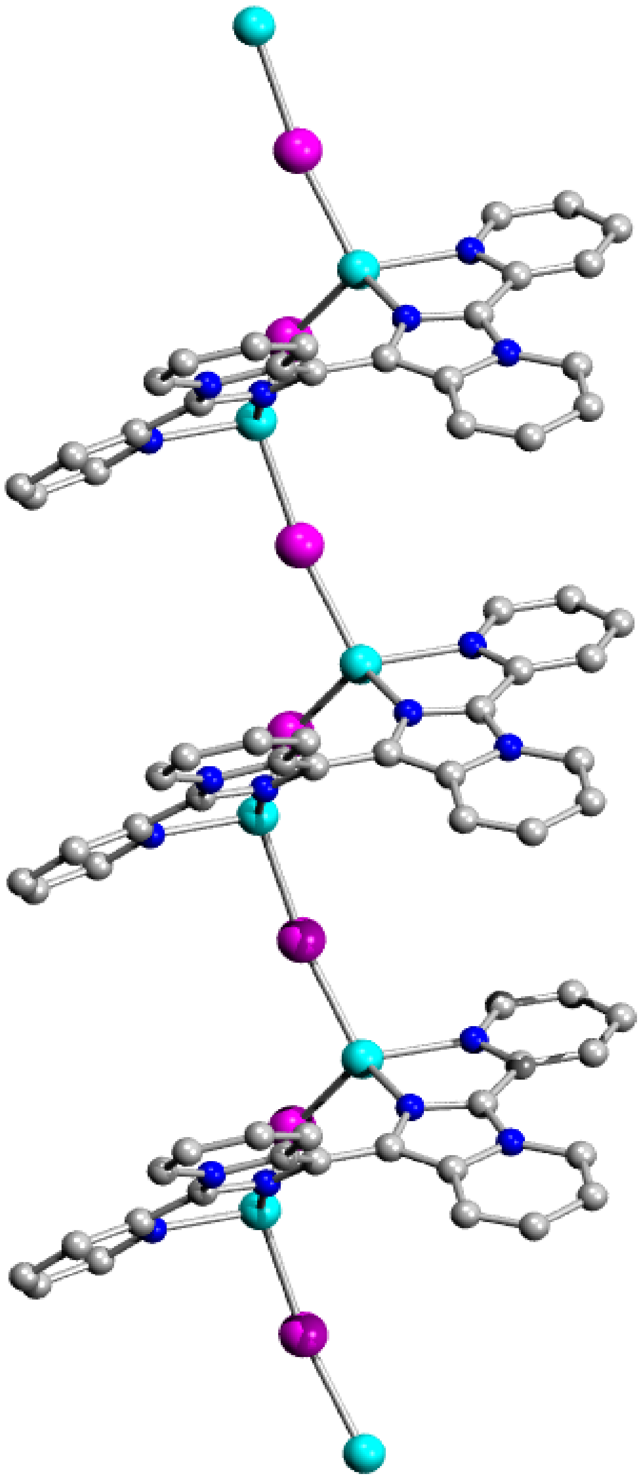


Fig. 2. Molecular structure of the neutral polymer **1**

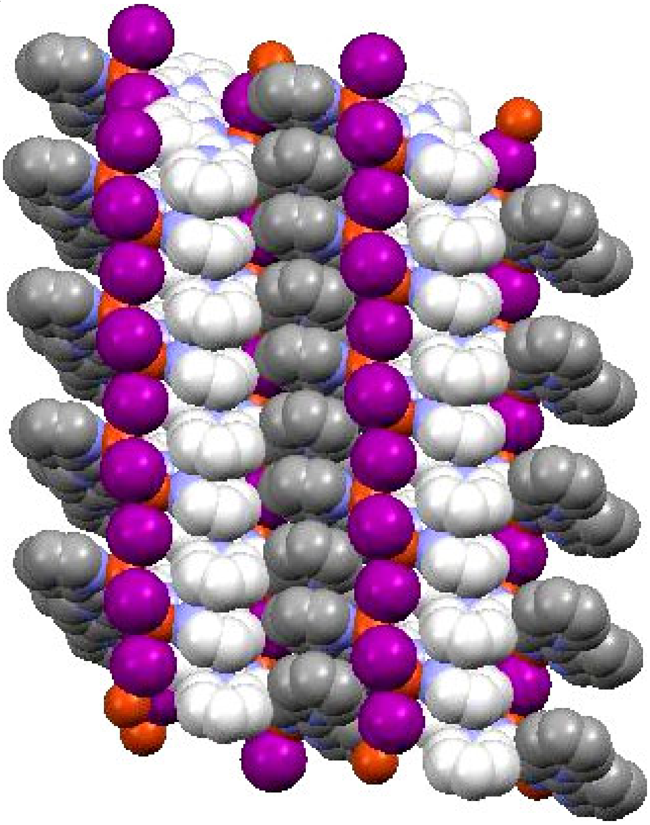


Fig. 3. Packing diagram of **1** depicting the π-π intermolecular interactions between py-azopy and py-im rings of L ligands from adjacent polymeric chains

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CONFLICT OF INTEREST

The authors declare that there is no conflict of interests regarding the publication of this article.

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