

Original Research Article

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Synthesis and Structure of a Single-Stranded Dihelicate of Copper (II) Involving Multiring Nitrogen-Heterocyclic Ligand

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ABSTRACT

Keywords

Single stranded dihelicate compound, N- heterocyclic ligand, X-ray diffraction analysis, π - π noncovalent interactions, Hydrogen bonding.

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The single stranded-helicate Copper (II) complex $[\text{Cu}_2(\text{L})\text{Cl}_4]\cdot\text{H}_2\text{O}$ (1) containing a new biologically relevant heterocyclic bis-bidentate ligand viz. 3, 3'-dipyridine-2-yl-[1,1']biimidazo [1, 5-a] pyridineyl (L) has been prepared and characterized by single-crystal X-ray diffraction analysis. The molecule is centrosymmetric where coordination environments around Cu (II) are distorted tetrahedral ($\tau_4 = 0.36$). The Cu (II) --- Cu (II) separation is 4.808 Å. Compound in its solid state structure shows π - π noncovalent interactions as well as hydrogen bonding interactions that play dominant roles in shaping the extended structure of the molecule.

Introduction

The helical geometrical motif is found in natural as well as in artificial structures including spiral arm of galaxies, right and left handed quartz¹, human art and architecture. In chemistry and biochemistry helicity is present in various systems². The most important among these is deoxyribonucleic acid (DNA) which exists as a double helix in which the two strands are connected by hydrogen binding between complementary bases³. It stores and transmits our genetic make-up and therefore is essential for the sustenance of life.

Helicity can be introduced in artificial supramolecular architecture by introducing

conformational restrictions in macromolecules,⁴ inter- or intramolecular hydrogen bonds,⁵ or coordination to metal ions.⁶

The term helicate was introduced by Lehn and coworkers in 1987 for metal complexes that contain one or more ligand strands and two or more metal centres.⁷ The number of coordinated ligand strands wraps about the metal centers in single, double and triple stranded helicates are one, two and three respectively. Identical coordinated strands lead to homostranded helicates while different ligand strands correspond to heterostranded helicates. Moreover coordinated ligand stands

possessing similar binding units with similar intrinsic information lead to homotopic helicate whereas ligand strands possessing different binding units form heterotopic helicate.

The first metallohelicate analyzed by X-ray diffraction was described by Lehn *et al.*, in 1987.⁷ It consists of two tris-(bipyridine) ligands and three Cu (I) ions. During the following decades, the helicate chemistry was dominated by ligands having bipyridine moieties⁸⁻¹⁰ located at several strategic positions as such compounds find applications in many new research areas.¹¹⁻²²

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.²³⁻²⁵ Much less common are single-stranded dihelicates where a single ligand coordinates to two non-bridged metal ions in a helical motif.²⁶⁻²⁸

Recently it has been observed that the weak or non-conventional hydrogen bonds like C-H...O, O-H..., C-H... are crucial and play distinctive roles in structural chemistry and biology.²⁹ The theoretical and experimental studies on such interactions may lead to the development of novel approaches for the design of effective systems capable of exhibiting noncovalent recognition properties at molecular level.

We have recently synthesized^{30,31} a *N*-heterocyclic compound, viz., 3,3'-dipyridin-2-yl[1,1']bi[imidazo[1,5-a] pyridinyl] (L) containing a pair of biologically relevant³² imidazo[1,5-a]pyridine moieties. The 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.³¹ Herein, we report the synthesis of a single stranded helicate

Cu(II) complex (1) of a nitrogen-rich heterocyclic ligand (L). The compound has been characterized by single-crystal X-ray diffraction analysis.

Experimental

Bis-bidentate type ligand L was prepared as described elsewhere.^{30,31} Copper chloride was purchased from Aldrich. All other reagents were commercially available and used as received. Solvents were reagent grade, dried by standard methods³³ 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 and crystallization

[Cu₂(L) Cl₄].H₂O (1)

A methanolic solution (5 mL) of CuCl₂.2H₂O (34 mg, 0.2 mmol) was carefully layered on to a solution of L (39 mg, 0.1 mmol) in dichloromethane (5 mL). Diffusion between the two layers over a period of 10 days produced dark green crystals. Yield: 24%. Anal. Calcd for C₂₄H₁₈N₆Cu₂OCl₄: C, 42.67; H, 2.67; N, 12.45. Found: C, 42.85; H, 2.64; N, 12.18%. FT-IR (KBr pellet, cm⁻¹): 3517, 3454, 1600, 1502, 1483, 1461, 1313, 1245, 781, 746, 696.

Refinement

Diffraction quality crystals of 1 (needle, dark green crystals, 0.13 x 0.024 x 0.016 mm³ obtained from 1:1 v/v dichloromethane/methanol) were grown by diffusion technique from the solvent combinations as noted. Crystal was mounted on glass fibers and aligned on a Bruker SMART APEX II CCD diffractometer.

Intensity data for the compound was measured employing a monochromatized MoK α radiation ($\lambda = 0.71073 \text{ \AA}$) source using phi and omega scan techniques at 296(2). In the case, absorption corrections based on multiscan using the SADABS software³⁴ were applied. The structures were solved by direct methods³⁴ and least square refinement [anisotropic displacement parameters, hydrogen atoms in the riding model approximation and a weighing scheme of the form $w = 1/[\sigma^2(F_0^2) + (aP)^2 + bP]$ for $P = (F_0^2 + 2F_c^2)/3$] was on F^2 .³⁴ Bruker SHELXTL³⁴ 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. The water bound hydrogen atoms could neither be placed nor found and were therefore, omitted during the refinements.

Result and Discussion

Synthesis

Being partitioned into two bidentate binding domains, the ligand combines with Cu(II) metal salt in presence of inert counter anion chloride to form relatively rare³⁵ single-stranded dihelicate $[\text{Cu}_2(3,3'\text{-dipip})\text{Cl}_4]$ (1) (Scheme 1). IR spectra of the complexes contain all the pertinent bands due to the coordinated bipyridine type ligands³⁶ appearing at ca. 1600, 1485, 1461, 1313, 1247, 770 cm^{-1} region as prominent features.

Structure

The molecular structure and the atom labeling scheme for 1 is shown in figure 1 and the relevant metrical parameters are compiled in table 2. The complex crystallizes in an orthorhombic space group $PbCn$ with four

molecular weight units per cell. The asymmetric unit comprises of one neutral binuclear species. The compound is centrosymmetric involving two Cu(II)Cl(1)Cl(2) centers connected by one bridging bis-bidentate ligand L through N(1) and N(2) donors to form single stranded dihelicate. The Cu(II)-N (2.014(5) and 2.022(4) \AA) and Cu(II)-Cl (2.242(15) and 2.248(17) \AA) bond lengths are consistent with the corresponding values found in analogues compounds.³⁷ The Cu(II)---Cu(II) separation is 4.808 \AA .

The copper centers with +II oxidation states exist in highly twisted coordination environments. The sum of the bond angles of ca. 678 $^\circ$ at the copper centers are closer to the idealized value for a tetrahedral geometry (ca. 657 $^\circ$) rather than a square planer (720 $^\circ$) one. The N(1)Cu(1)N(2)/Cl(1)Cu(1)Cl(2) dihedral angle is also significantly high (36.19 $^\circ$). Twisted environment around Cu (II) can also be explained by using the parameter τ_4 developed by Houser *et al.*,³⁸ The expression for τ_4 is shown by equation 1.

Where α and β are the largest angles in the four coordinate species. The calculated τ_4 value (0.36) also suggests the environments around Cu (II) are distorted. Such a twisted four coordinated Cu (II) centers have significant relevance to enzyme active sites.³⁹

There is a weak additional intermolecular interaction from Cl(1) to the copper center (Cu(1)'-Cl(1) 2.744 \AA) of a adjoining molecule (Figure 2). In effect, to avoid steric repulsion, the strongly coordinated Cl atoms are drifted away from each other to generate compressed *trans* angles [Cl(2)-Cu(1)-N(2), 146.64 $^\circ$ and Cl(1)-Cu(1)-N(1), 163.25 $^\circ$].

Table.1 Summary of X-ray crystallographic data for **1**

Parameter	1
Composition	C ₂₄ H ₁₆ Cl ₄ Cu ₂ N ₆ O
Formula wt.	673.31
Crystal system	Orthorhombic
Space group	<i>PbCn</i>
<i>a</i> , Å	15.422(4)
<i>b</i> , Å	11.180(3)
<i>c</i> , Å	14.830(4)
<i>α</i> , deg	90.00
<i>β</i> , deg	90.00
<i>γ</i> , deg	90.00
<i>V</i> , Å ³	2557.0(11)
<i>D</i> _{calc} , Mgm ⁻³	1.75
Temp, K	296(2)
<i>λ</i> , Å	0.71073
<i>Z</i>	4
<i>F</i> (000)/μ mm ⁻¹	1344/2.113
2θ _{max} [°]	41.76
Reflections Collected/Unique	18179/1344
<i>R</i> _{int} / GOF on <i>F</i> ²	0.0683/0.975
No of parameters	168
<i>R1</i> (<i>F</i> _o), <i>wR2</i> (<i>F</i> _o) (<i>I</i> ≥ 2σ(<i>I</i>))	0.0376, 0.1110
Largest diff. peak	0.42

Table.2 Selected bond distances (Å) and angles (deg) for **1**

Bond Distances (Å)			
Cu(1)—N(1)	2.014(5)	Cu(1)—Cl(1)	2.2422(15)
Cu(1)—N(2)	2.022(4)	Cu(1)—Cl(2)	2.2487(17)
Bond Angles (deg)			
N(1)—Cu(1)—N(2)	80.41(18)	N(1)—Cu(1)—Cl(2)	94.62(14)
N(1)—Cu(1)—Cl(1)	163.25(13)	N(2)—Cu(1)—Cl(2)	146.64(13)
N(2)—Cu(1)—Cl(1)	96.62(13)	Cl(1)—Cu(1)—Cl(2)	96.66(6)

Scheme.1 Protocol followed for the synthesis of compound **1**

Fig.1 Molecular structure of 1 showing atomic numbering scheme. Hydrogen atoms have been omitted for clarity

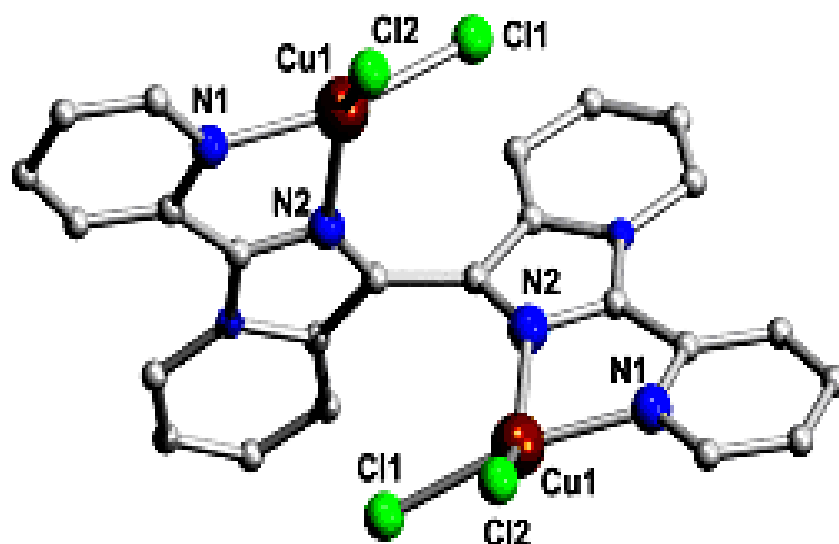


Fig.2 Partial view of the polymeric chain in 1

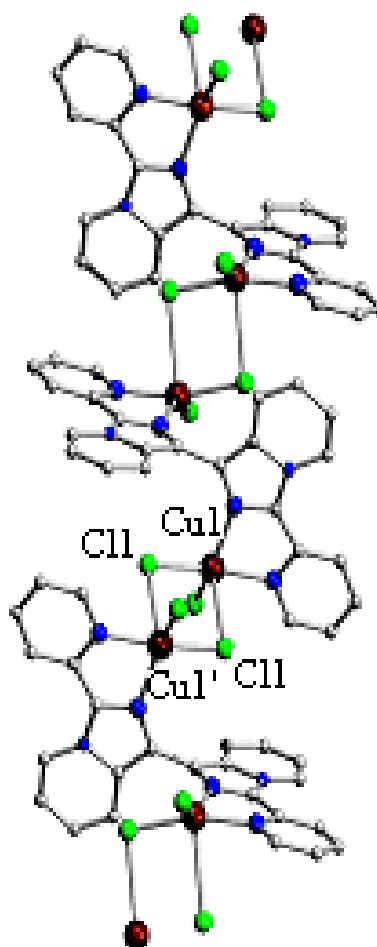
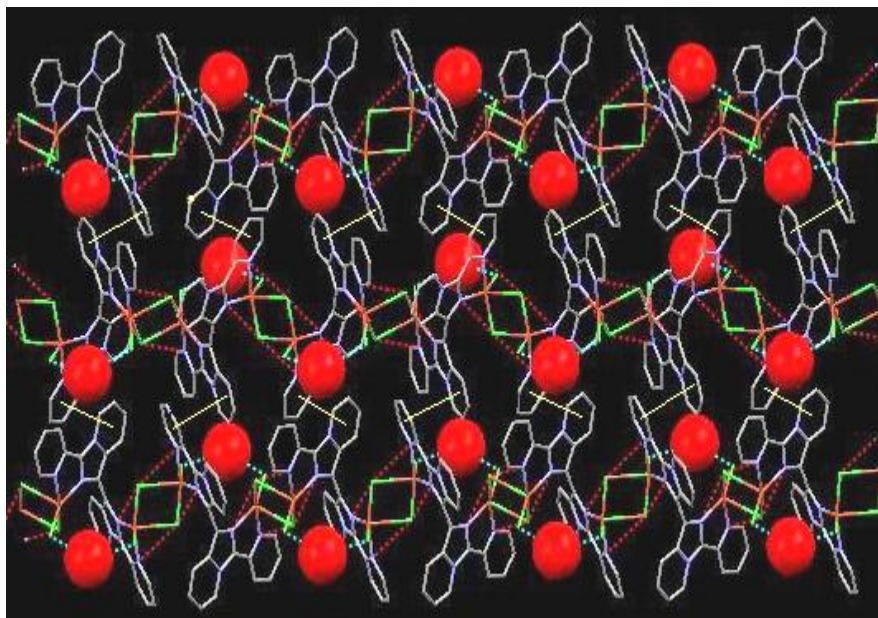


Fig.3 Representation of the F-type π - stacking and hydrogen bonding interactions in 1. Oxygen atoms of water molecules are represented in space-fill model



Finally, the dinuclear units are connected together intermolecularly by these weakly interacting Cl atoms which bind two adjacent Cu(II) centers of two dinuclear units (Cu(II)-Cu(II)' separation 3.709 Å), generating one dimensional oligomeric chain (Figure 2). Large im-im dihedral angle of 75° in the bis-bidentate ligand provides opportunities for the individual chains to stack *via* py-azopy overlapping creating aesthetically pleasing motif (Figure 3). These aromatic ring planes in the structure are separated by 3.579(4) Å and dihedral angle between them is 10.95°, giving clear indication of slightly off target classical π - π -stacking. The water molecules present in the compound participate in hydrogen bonding interactions with the coordinated Cl atoms (Figure 3).

Copper (II) complex (1) of the nitrogen-rich heterocyclic ligand (L) has been synthesized. The complex is dimeric with single-stranded helical topology. Finally, the dinuclear units are connected together intermolecularly by weakly interacting Cl atoms to generate one dimensional oligomeric chain The structure in

the solid state involves multiple π - 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 hydrogen bonds that reinforce these non-covalent interactions in the molecule.

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