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Noncovalent interactions and electrical conductance study of copper(II) coordination complex derived from 2,6-pyridinedicarboxylic acid and aminopyrimidine ligands

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Abstract : [Cu(pydc)$_2$(apym)]·3H$_2$O (1) (where, pydcH$_2$ = pyridine-2,6-dicarboxylic acid; apym = 2-aminopyrimdine) has been prepared and characterized by elemental analysis, IR spectroscopy and single crystal X-ray diffraction techniques. In complex 1, the aromatic molecules are connected by NH···π, lone pair···π, π···π and hydrogen bonds like different types of non covalent interactions. So these types of noncovalent interactions play an important role in the construction of supramolecular frameworks. The electrical current measured at ambient conditions in the order of 24 μA and 33 μA with bias +1 V before and after annealed respectively. The same experiment was done after one month which shows no deviation from cooler complex and annealed complex.

Keywords : Heterocycle based ligand, noncovalent interactions, electrical conductivity.

Introduction

Host-guest chemistry is the field of applied chemistry beyond that of molecules and focuses on the chemical systems composed of a discrete number of accumulated molecular subunits or constituents[1,2]. At the beginning of this chemistry, the focus was mainly emphasized on their synthesis and exceptional topologies, but recent trend is mostly associated with their potential efficacy in diverse technological and industrial areas, like heterogeneous catalysis[3], nanotechnology[4], gas adsorption and capture or storage[5], biomedicine[6], sensors[7], electrical conductivity and luminescence property[8] *etc*. Thus the interplay between chemistry and crystal engineering is the cross linking between the structure and properties of compounds on the one hand and those of extended togetherness of molecules on the other[9,10].

Pyridine-2,6-dicarboxylic acid (pydcH$_2$) and complexation compounds of pydcH$_2$ with different metallic ions have also attracted much attention in designing and synthesis of such compounds because of their interesting topologies, promising structural features, enthralling functionalities which promote wide practical utility in photoluminescence, molecular adsorption and gas storage, catalysis and magnetism[11–17]. The most commonly used practise for engineering the crystal structure of such complexes to conclude complexation compounds' important properties; employ non-covalent intermolecular forces (hydrogen bonding, aromatic ring stacking etc.)[18,19]. However, although extensive studies have been done on this ligand according to a survey of the Cambridge Structural Data base (CSD, Version 5.36, update 2015) on supramolecular systems, it still remains a challenging task to explore several compounds with different topological networks. In recent years, as a continuation of studies on dipicolinic acid, Porta *et al.* have described the formation of a novel Fe^{III} complex with pyridine-2,6-dicarboxylic acid ($pydcH_2$) and structural, electronic and optical properties were investigated[20]. Current research also deals the influence of water content on the topologies of MOFs of very similar dicarboxylic acid (chelidamic acid) and pyridine-3,5-dicarboxylate and metal ions under mild conditions[21]. On the other hand, carboxylate anion is well known as a ligand which can play an imperative role to construct novel MOFs in coordination chemistry[22]. Electrical conductivity of typical covalent polymers is well-known in material science and has taken a great attention of many researchers[23]. However this property of coordination polymers is yet very scarce. On the basis of recent new results of coordination polymer, it is motivated by high potential towards nanotechnological applications[24]. In addition, the serial incorporation of theoretical calculations seems to be extensive instruments to understand experimental measurements and design new electrically conductive polymers. In this endeavor, we have investigated electrical conductivity of the coordination complex of copper(II) ion.

Experimental

General methods and materials :

All reagents and chemicals (including $Cu(NO_3)_2 \cdot 6H_2O$) were of AR grade and procured from commercial sources (SD Fine Chemicals, India and Aldrich) and used without further purification.

Physical measurements :

Current (I)-Voltage (V) measurement at room temperature were taken before and after annealed by a Keithley 2611A source meter and Lab Tracer 2.0 software was used to collect the electrical data.

Synthesis :

Synthesis of $[Cu(pydc)_2(apym)] \cdot 3H_2O$ **(1)** :

The complex **1** has been prepared in the following literature method[25].

Device fabrication for electrical conductivity measurement :

Thin film of as prepared sample was fabricated on SiO_2 substrate by a simple drop-casting method. At the time of drop-casting the substrate were placed on a hot plate to evaporate the solvent from the aqueous solution of synthesized materials. Two parallel electrodes were drawn on the each film by conducting silver paint (Ted Pella) with average separation ~5 mm. For I-V characteristics of our devices, the probes were connected to a Keithley 2611A Source Meter and data was collected by Lab Tracer acquisition card.

Results and discussion

Noncovalent interactions of **1** :

The complex shows different kinds of weak interactions apart from H-bonding are π···π, lone pair···π and N-H···π in solid state structure that contributes to the self assembly process. The formation of a supramolecular 1D chain is ensured mainly by two additional π···π interactions (Fig. 1) (Table 1). Firstly, the chelate ring Cu1-N1-C6-C7-O3 is stacked over the same chelate ring of a neighbouring molecule of symmetry 1-x, 2-y, 1-z (3.460(5) Å). Secondly, the aromatic ring N(2)-C(8)-C(9)-C(10)-N(3)-C(11) is stacked over the chelate ring Cu1-N1-C6-C7-O3 neighbouring molecule of symmetry 1-x, 1-y, 1-z (3.534(5) Å). The solid state packing of compound **1** presents a relevant lone pair···π noncovalent interaction (Fig. 2) that is formed between the non coordinating carboxylate oxygen atom (O2) and the aromatic

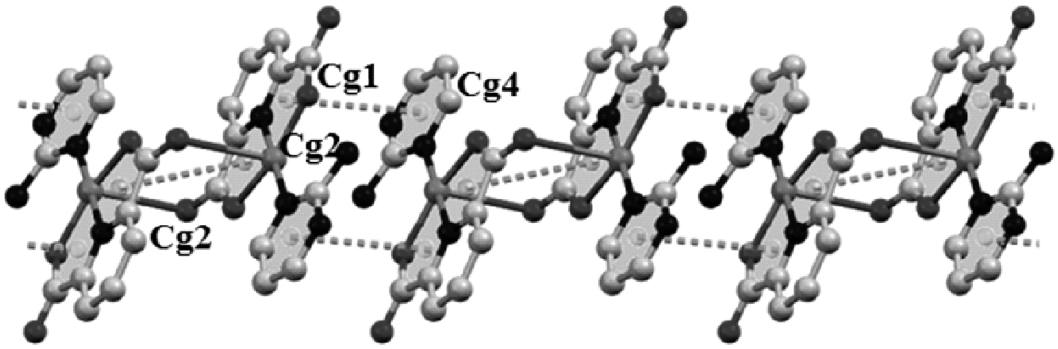


Fig. 1. 1D supramolecular chain generated through π···π interactions (H_2O molecules and H atoms are omitted for clarity).

Table 1. Geometric features (distances in Å and angles in degrees) of the π···π interactions obtained for complex **1**

Complex	Cg(Ring I)···Cg(Ring J)	Cg···Cg	Cg(I)···Perp	Cg(J)···Perp	α	β	γ	Symmetry
Complex **1**	Cg1···Cg4	3.534(5)	3.112	3.289	7.26	21.44	28.28	1-x, 1-y, 1-z
	Cg2···Cg2	3.460(5)	2.905	2.905	0.00	32.88	32.88	1-x, 2-y, 1-z

α = Dihedral angle between ring I and ring J (°); β = Cg(I)-->Cg(J) or Cg(I)-->Me vector and normal to plane I (°); γ = Cg(I)-->Cg(J) vector and normal to plane J (°); Cg-Cg = Distance between ring Centroids (Å); CgI----Perp = Perpendicular distance of Cg(I) on ring J (Å); CgJ----Perp = Perpendicular distance of Cg(J) on ring I (Å); Cg(1) = centre of gravity of ring [Cu(1)-O(1)-C(1)-C(2)-N(1)]; Cg(2) = centre of gravity of ring [Cu(1)-O(3)-C(7)-C(6)-N(1)] and Cg(4) = centre of gravity of ring [N(2)-C(8)-C(9)-C(10)-N(3)-C(11)].

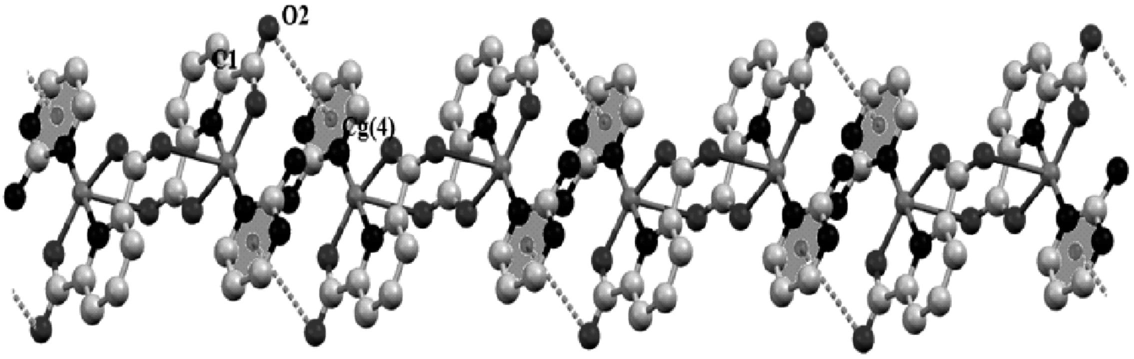


Fig. 2. 1D supramolecular chain generated through lone pair···π interactions (H_2O molecules and H atoms are omitted for clarity).

ring Cg(4) N(2)-C(8)-C(9)-C(10)-N(3)-C(11) of symmetry related moiety to create 1D crystalline supramolecular architecture (Table 2). This distance is very short (3.594 Å) indicating a strong interaction. Another kind of noncovealent interaction like N-H···π is involved in **1** (between noncoordinating N4-H4A

Table 2. Geometric features (distances in Å and angles in degrees) of the lone pair···π interaction obtained for complex **1**

Complex	C-H···Cg(Ring)	H···Cg (Å)	C-H···Cg (°)	C···Cg (Å)	Symmetry
Complex **1**	C1-O2···Cg4	3.593(8)	68.0(5)	3.398	1-x, 1-y, 1-z

For complex **1**, Cg(4) = centre of gravity of ring [N(2)-C(8)-C(9)-C(10)-N(3)-C(11)].

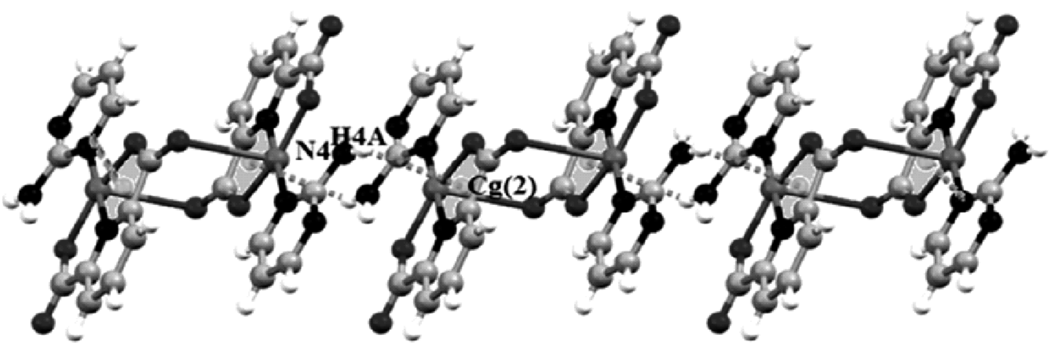


Fig. 3. 1D supramolecular chain generated through NH···π interactions (H_2O molecules and H atoms are omitted for clarity).

Table 3. Geometric features (distances in Å and angles in degrees) of the NH···π interaction obtained for complex **1**

Complex	C-H···Cg(Ring)	H···Cg (Å)	C-H···Cg (°)	C···Cg (Å)	Symmetry
Complex **1**	N2-H4A···Cg2	2.80	114	2.652	1-x, 1-y, 1-z

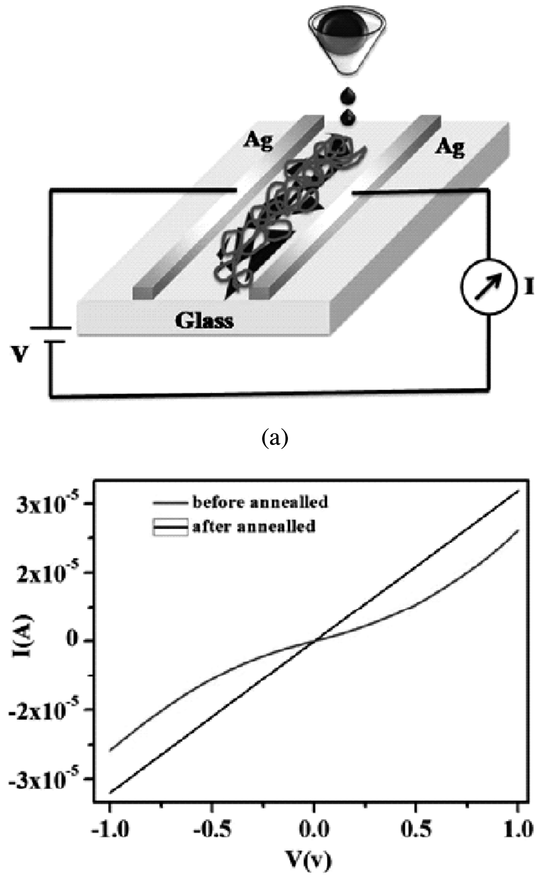
For complex **1**, Cg(2) = centre of gravity of ring [Cu(1)-O(3)-C(7)-C(6)-N(1)].

group and chelate ring Cg(2) defined by Cu(1)-O(3)-C(7)-C(6)-N(1) to form 1D supramolecular array with closest distance of 2.80 Å (Fig. 3) (Table 3).

Device fabrication and the measurement of electrical conductivity of **1** :

I-V characteristics of the complex shows linear symmetric nature within the range –1 to +1 V has depicted in Fig. 4. After annealing the film at 60°C for 30 min, the linear symmetric nature become more prominent but no significant change occurs in conductivity level, which demand that the conductivity is due to only the bulk of the coordination complex not for contact bias. Further confirm it, annealing process was continued but no significant improvement was observed for conductivity level of the prepared film. The range of electrical conductivity before or after annealed for coordination complex is much better than the conductivity of metal-metal based coordination type complexes and this better conductivity comes from the delocalization of carboxylate anions bridging linked with metal[26,27].

We have measured conductivity of the thin film after one month and no degradation was found, indicating air stability of synthesized compound have seen in Fig. 5. It is significant to note that measurements of conductivity depend on the polymer specimen, basically single crystals, thin film, hard-pressed



(a)

(b)

Fig. 4. (a) Schematic diagram of the device for measurement of electron transport, (b) Current-Voltage characteristics of the film realized with the compound **1**.

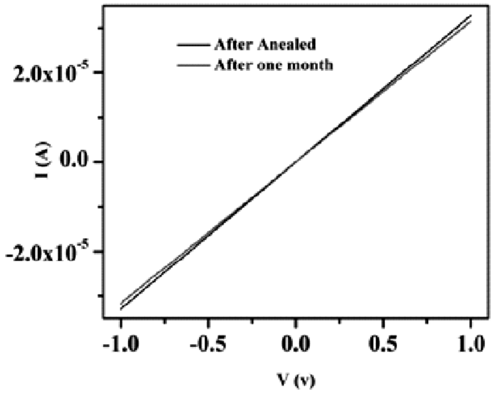


Fig. 5. Current-Voltage characteristics of the film realized with the compound **1** after one month.

pallets even nanowires may be taken into account even thermal variations. On the other hand our results designate that metal-to-metal interaction in coordination complex are vital but not necessary for conduction[23]. From this view it is clear that conductivity may improve due to metal-metal short distance when the metals are close to form intermetalic bond. However, conductivity positively decreases with increasing metal-metal distance it will not vanish completely.

Conclusion

Details of synthesis and crystal structure of $[Cu(pydc)_2(apym)]\cdot 3H_2O$ (where $pydcH_2$ = pyridine-2,6-dicarboxylic acid; apym = 2-aminopyrimidine) coordination complex were reported in previous literature work. But compared to previous work, weak non-covalent interactions like lone pair···π, NH···π and π···π interactions of said coordination complex are reported here. These studies also reveal that the "corner-sharing spirocylic" chain motif for tetramer is robust enough to be stabilized even in a metal-organic environment and is also flexible enough to accommodate additional water, keeping its basic tenet intact, and that might be attractive for theoretical modeling and understanding water's anomalous behavior. Knowledge obtained from this study may also aid to model various biological processes such as proton transfer, water structure inside channels and in energy-transduction proteins, and the role of ordered water in biological systems that often bear carboxylate and amino groups. In addition, from electrical conductivity study of thin film deposited on glass substrate illustrates that conduction is ohmic in nature and gives a good satisfactory result at ambient condition. Thus the nature of compound used indicates that the metal ions and ligands in coordination complex are highly relevance with electrical conductivity. The electrical conductivity of the film at ambient temperature is responsible for the coordination complex only. After one month of fabrication, there is nearly no change in I-V characteristics under high temperature or low temperature, this device may be used for commercial circuit component.

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