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Role of non-covalent interactions in three copper(II) 5-chloro-2-nitrobenzoate complexes with N-donor ligands: Syntheses, characterization and packing analyses of trans-[Cu(β-pic)$_2$(H$_2$O)$_2$(5-chloro-2-nitrobenzoate)$_2$], trans-[Cu(γ-pic)$_2$(5-chloro-2-nitrobenzoate)$_2$] and [trans-Cu(en)$_2$(H$_2$O)$_2$](5-chloro-2-nitrobenzoate)$_2$·2H$_2$O

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ABSTRACT

Three new copper(II) complexes trans-[Cu(β-pic)$_2$(H$_2$O)$_2$(5-chloro-2-nitrobenzoate)$_2$] **1**, trans-[Cu(γ-pic)$_2$(5-chloro-2-nitrobenzoate)$_2$], **2** and [trans-Cu(en)$_2$(H$_2$O)$_2$](5-chloro-2-nitrobenzoate)$_2$·2H$_2$O, **3** (where β-pic = β-picoline, γ-pic = γ-picoline and en = ethylenediamine) were prepared by the addition of β-pic, γ-pic and en, respectively, to the hydrated copper(II) 5-chloro-2-nitrobenzoate, suspended in methanol–water mixture (4:1, v/v). The newly synthesized complexes have been characterized by elemental analyses, TGA, spectroscopic techniques (FT-IR, UV–Vis and EPR), conductivity measurements, magnetic susceptibility studies and single crystal X-ray structure determination. Complex **1** crystallizes in monoclinic crystal system with $P2_1/c$ space group whereas the complexes **2** and **3** crystallizes in triclinic crystal system with $P\bar{1}$ space group. Single crystal X-ray structure determination revealed the presence of elongated octahedral geometry in all three complexes. Cu(II) center is covalently coordinated by two 5-chloro-2-nitrobenzoate, two β-pic moieties and two water molecules in complex **1**, two bidentate 5-chloro-2-nitrobenzoate and two γ-pic moieties in complex **2**. In complex **3**, the copper ion is coordinated to two chelating en ligands, two water molecules; with two 5-chloro-2-nitrobenzoate as counter anions and two water molecules of crystallization. The crystal lattice in complexes **1–3** is stabilized by an intricate network of hydrogen bonding interactions (C–H⋯O, O–H⋯O in complex **1**, C–H⋯O in complex **2** and O–H⋯O, N–H⋯O and C–H⋯O in **3**). Besides this, π⋯π stacking interactions in complex **1** and C–H⋯π interactions in complex **2** also contribute towards stability of the crystal lattice.

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1. Introduction

Methods that are reliable to organize molecules in a preconceived manner are pivotal to the design followed by successful synthesis of materials that possess required physical/chemical properties. The area of crystal engineering that deals with this concept as one of the important central themes have advanced exponentially in recent years [1–3]. The understanding that the

molecular aggregation can be controlled to a large extent by certain groups of atoms (i.e., functional groups) which interact strongly by non-covalent interactions has led to the identification of number of reliable and robust supramolecular synthons. In fact, supramolecular synthon concept has been extensively exploited for their potential application in host–guest chemistry, catalysis, electrical conductivity and magnetism [4–9]. Crystalline materials represent an extreme side of periodic organization of its constituent atoms, molecules or ions, however, till date, there is no foolproof method to predict how this organization happens, though great strides have been made to take control over molecular organization based on directed hydrogen bonding and metal

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assisted self-assembly [10–11]. In general, control of molecular organization in systems composed of organic compounds and metal ions is more tedious than in organic compounds themselves. This is because of the uncertainty over the occurrence of a particular supramolecular synthon which can be readily conceivable as expected in the organic realm. The primary reason for the increased difficulty in metal–organic compounds is based on the fact that the crystal packing occurs, in general, with a tradeoff between close packing and maximization of the utilization of intermolecular interactions. Mostly, the size/shape complementarity and considerable rigidity of the geometry around a metal center (octahedral, trigonal bipyramidal, etc.) becomes the impeding factor.

However, even in metal complexes, if the ligands are endowed with number of strongly interacting functional groups and considerable flexibility is possible (like the flapping of a benzene moiety), there can be a very good possibility of predictable reorganization of the metal units and counter ion(s). Analysis of such interaction patterns will be highly rewarding as insights can be developed about the chemical as well as geometrical requirements for interaction sustainability even by a metal center replacement (for example, replacement of Co by Ni or Cu) and associated coordination perturbation. The first level of difficulty is the choice of the metal center in the presence of suitable ligand so that an expected level of ligand...ligand secondary interactions (in the form of hydrogen bonds, π...π, C–H...π, etc.) are able to stabilize the lattice. The second level of difficulty is more tedious, which subtle variations should be considered within a given ligand (in terms of functional group substitution and their positional variation) without disturbing the size/shape complementarity to the extent that the tradeoff between the close packing and the directionality of the interactions are not pushed to one extreme. In the nutshell, a judicious selection of ligands is very crucial even if the same metal center is used to manifest the expected interaction patterns and to analyze their role in crystal lattice stability.

Our previous experience in copper(II) chemistry [12–14] led us to the selection of Cu(II) as the central metal atom and arylcarboxylates as first choice for the ligands providing oxygen donors involved in Cu(II) coordination sphere. It is worth noting that the carboxylates are often applied as building blocks in crystal engineering because of their versatility in coordination modes (monodentate, symmetric/asymmetric chelating, and bidentate/monodentate bridging) and ability to form strong and directional hydrogen bonds with predictable/desirable properties. Copper(II) arylcarboxylates are more potent and desirable drugs than their parent acids and some of their pharmacological activities such as super oxide dismutase and cytogenetic effects are enhanced in the presence of ancillary N-donor ligands [15–16].

In addition to the above mentioned role of arylcarboxylate anions, it is possible to adjust balance between the size and shape of a complex by introducing another ligand which is able to alter the coordination pattern of the carboxylic groups around the metal ion, but not at the expense of eliminating many secondary interactions that are crucial for lattice stabilization. It has been shown previously by us [17] that N-donor ligands have profound effect on the type of coordination mode exhibited by arylcarboxylates, what is essential for creating the supramolecular architectures in the resulting copper(II) complexes. In this backdrop, the ligands chosen are shown in Fig. 1. The selection of 5-chloro-2-nitrobenzoate has a special purpose. The presence of –NO₂ group *ortho* to –COO⁻ moiety can push the –COO⁻ from the plane of the aromatic ring making the conjugation less feasible and –Cl atom at *meta*-positions allows for its involvement in secondary interactions [18]. It has been shown that replacement of a chloro atom by a methyl group does not alter the crystal packing (Cl–CH₃ exchange rule) if the geometrical considerations are prominent in the 3D
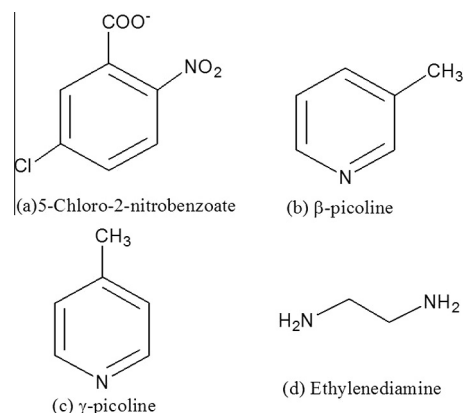

Fig. 1. Ligands employed in this study (a) 5-chloro-2-nitrobenzoate, (b) β-picoline, (c) γ-picoline and (d) ethylenediamine.

arrangement [19]. This prompted us to select β and γ-picoline as the N-donor ligands. The –CH₃ group in these ligands cannot participate in strong interactions but can act as space fillers to varying extent of different geometrical orientations (β versus γ disposition). The coordination of a very flexible ligand, ethylenediamine (Fig. 1) can generate a completely different packing mode (and interactions) than that of picolines and it would be very interesting to make a comparison. This paper attempts to rationalize the above mentioned issues through the syntheses and characterizing of electronic, crystal and molecular structures (by spectroscopic and X-ray crystallographic methods, respectively) of three new copper(II) 5-chloro-2-nitrobenzoate complexes with different nitrogen-donor ligands.

2. Experimental section

2.1. Materials and physical measurements

Analytical grade reagents were used without any further purification. Carbon, hydrogen and nitrogen were measured micro-analytically by an automatic Perkin Elmer 2400 CHN elemental analyzer and copper was determined gravimetrically [20]. FT-IR spectra were recorded using KBr pellets with a PERKIN ELMER SPECTRUM RXFT-IR system. Electronic spectra were recorded in methanol and water using a HITACHI 330 SPECTROPHOTOMETER. The EPR spectra of copper compounds were measured using a Bruker ELEXYS E500 spectrometer equipped with NMR teslameter (ER 036TM). The experimental EPR spectra were simulated using Doublet Exact program ($S = 1/2$) written by Dr. Andrew Ozarowski from NHMFL, University of Florida. The thermogravimetric analyses (TGA) were conducted with a SDT Q600 instrument. The samples contained in alumina pan were heated from 33 °C to 300 °C at a constant rate of 10 °C min⁻¹ under nitrogen environment with flux (flow rate) of 10 mL/min. Conductance measurement was performed by Pico Conductivity Meter (Model CNO4091201, Lab India) in aqueous medium at 25 °C using double distilled water. Magnetic measurements were carried out using the Gouy's method with following specifications: Pole face diameter: 10.2 cm; Pole gap: 4.0 cm; Current: 7.0 amp; Magnetic field: 6 k gauss. The calibrant employed was Hg[Co(SCN)₄] for which the magnetic susceptibility was assumed to be 1.644×10^{-5} cm⁻³ g⁻¹. All the measured susceptibility values were corrected for diamagnetism of the constituent atoms using the Pascal's constants. Magnetic moments were calculated according to the equation: $\mu = 2.83(\chi_M T)^{1/2}$.