



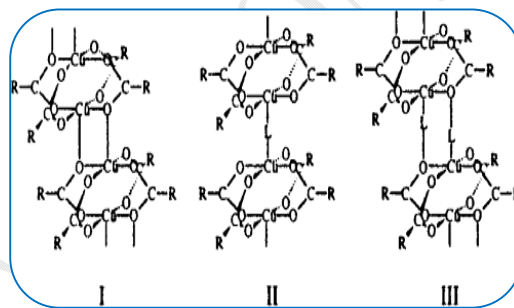
STRUCTURAL DIVERSITY OF COPPER(II) COMPLEXES WITH DIFFERENT CARBOXYLATES LIGANDS

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ABSTRACT :

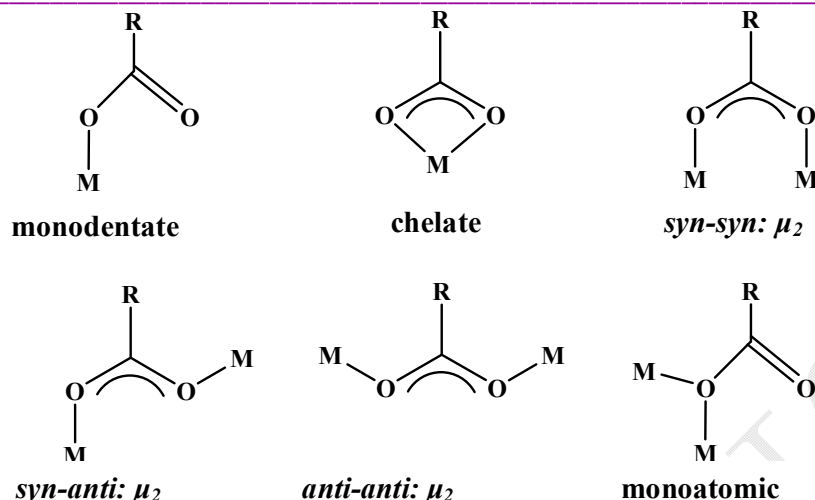
The paper deals with an overview on the mononuclear, dinuclear and polynuclear Cu(II) complexes of some carboxylate ligands. This paper also emphasize on versatile coordination behavior of carboxylates displaying distinct bonding modes toward metal cations, such as monodentate and chelate, as well as μ_2 bridging ligands in *syn-syn*, *syn-anti*, and *anti-anti* conformations. Long chain dicarboxylates are excellent structure directing anions due to their flexible bridging capability for the construction of metal-organic networks (MOF's).



KEYWORDS : Cu(II) complexes; carboxylate ligand; bridging mode; Dinuclear, Polynuclear, chelate, long chain.

INTRODUCTION:

Over the past decade, dimeric and polynuclear copper(II) carboxylates have received great attention in the studies of exchange-coupling interactions between adjacent metal centers,^{1,2} as well as for their special bioactive and biocatalytic functions.³ In addition, carboxylate anions exhibit a versatile coordination behavior displaying distinct bonding modes toward metal cations, such as monodentate and chelate, as well as μ_2 bridging ligands in *syn-syn*, *syn-anti*, and *anti-anti* conformations. Another type of coordination mode is the monatomic bridge,⁴ in which two metal ions are connected by a single oxygen atom of a carboxylate group. On the other hand, long chain dicarboxylates are excellent structure directing anions due to their flexible bridging capability for the construction of such metal-organic networks. This diversity of coordination modes assumed by carboxylate ligands is shown in scheme 1. Magnetic studies on structurally characterized carboxylato-bridged copper(II) complexes reveal that strong antiferromagnetic interactions are mediated by the *anti-anti* and *syn-syn* bridging modes,⁵ whereas weak either ferromagnetic or antiferromagnetic interactions^{6,5b} occur in the *syn-anti* mode.



A large variety of copper(II) coordination compounds containing carboxylate (such as acetate, benzoate etc) bridging anions have been described in the literature during the past years.⁷ Mononuclear, dinuclear, tetranuclear as well as polynuclear acetate/benzoate bridged Cu^{II} complexes have been reported using *syn-syn*, *syn-anti*, *anti-anti* bridging modes.⁷ A very rare *syn-anti*, *syn-anti* tetradentate bridging mode of acetate anions have been used to construct a beautiful two-dimensional network in (acetato)(methoxo)copper(II) complex.^{7c} Chakravarty, *et al*, reported⁸ some benzoate bridged dinuclear Cu^{II} complexes having weak antiferromagnetic coupling. There are also several examples which show that strong electron withdrawing group (trichloroacetate, trifluoroacetate) to the carbon atom in the carboxylato bridged compounds reduce the coupling constant.⁹

Cu(II) complexes dicarboxylate anions of glutaric acid, adipic acid, phthalic acid, biphenylcarboxylic acid & cyclobutanedicarboxylic acid.

The monodentate, *syn-syn*, *syn-anti*, *anti-anti* bridging mode of dicarboxylate anions (glutaric acid, adipic acid, phthalic acid, biphenylcarboxylic acid, cyclobutanedicarboxylic acid) have been used to construct several interesting polynuclear Cu^{II} complexes^{5c,10} (Figure 1). The structural analysis reveals that bridging glutarate gives rise to dinuclear and tetranuclear species, whereas the adipate dianion leads to octanuclear, one-dimensional and two-dimensional polymeric complexes.^{5c} Variable temperature magnetic susceptibility studies reveal antiferromagnetic coupling between Cu^{II} ions. One of the reported adipate compound exhibits an octanuclear cationic entity, arranged on an inversion center. Each adipate bridges four Cu^{II} ions; the central Cu(2) and Cu(3) atoms are bridged by three adipate and the other Cu(1) and Cu(2) are bridged by a single adipate dianion (Figure 1). The two independent crystallographic adipate dianions have different conformations (*gauche-anti-gauche* and *anti-anti-gauche*).

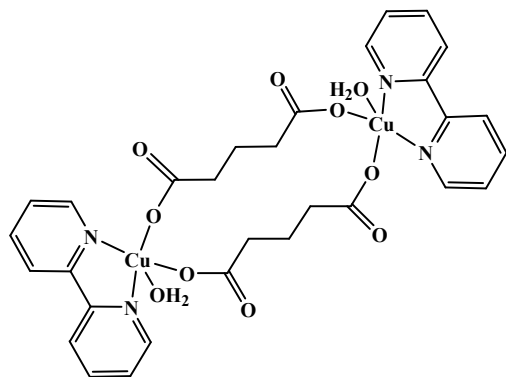


Figure 1a

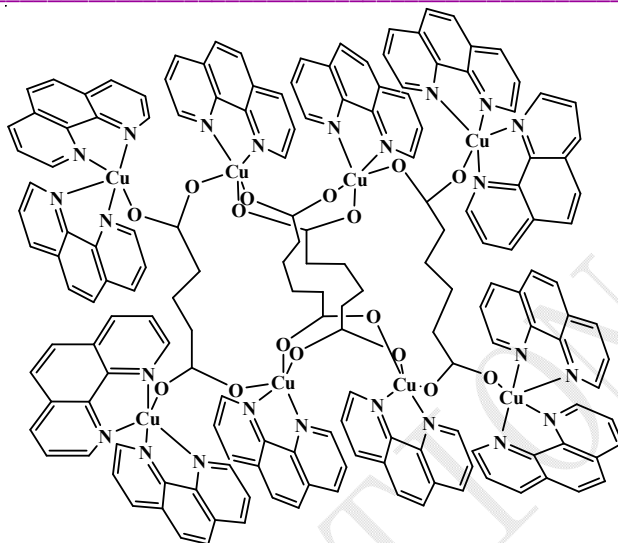


Figure 1b

Cu(II) complexes of malonate

A number of reports have been devoted to the malonate-containing copper(II) complexes. The versatility of malonate as a ligand is enhanced not only by the fact that it contains two carboxylate groups but also by the fact that they are located in the 1,3-positions. Consequently, malonate can simultaneously adopt chelating bidentate and different carboxylato-bridging coordination modes. A 1D chain compound with a regular alternation of aquabis(malonato)copper(II) and triaquacopper(II) units developing along the z axis have been reported by Ruiz-Pérez, *et al.*^{6b} The aquabis(malonato)copper(II) unit acts as a bridging ligand through two slightly different trans-carboxylato groups exhibiting an *anti-syn* coordination mode (Figure 2). Overall, ferromagnetic interaction between the Cu^{II} ions is observed in the complex.

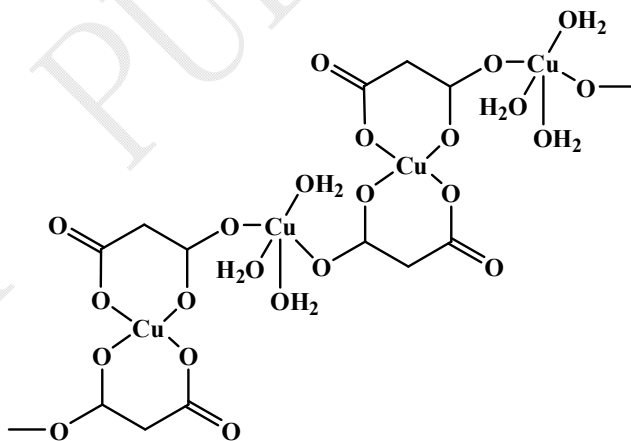


Figure 2: Perspective views of malonato-bridged copper(II) complex

Two unique 3D malonato bridged copper(II) compounds, $[\text{Cu}(\text{mal})(\text{DMF})]_n$ [DMF = N,N'-dimethylformamide] and $\{[\text{Cu}(\text{mal})(0.5\text{pyz})] \cdot \text{H}_2\text{O}\}_n$ [pyz = pyrazine, and mal = malonic acid] have been reported; they represent the first two examples of magnetic ordering in malonato-bridged complexes.¹¹ The structural analyses reveal that 3D structure of first complex are constructed by *syn-anti* as well as *anti-anti* carboxylate bridges, whereas in other complex Cu^{II} centres are linked to one another by only

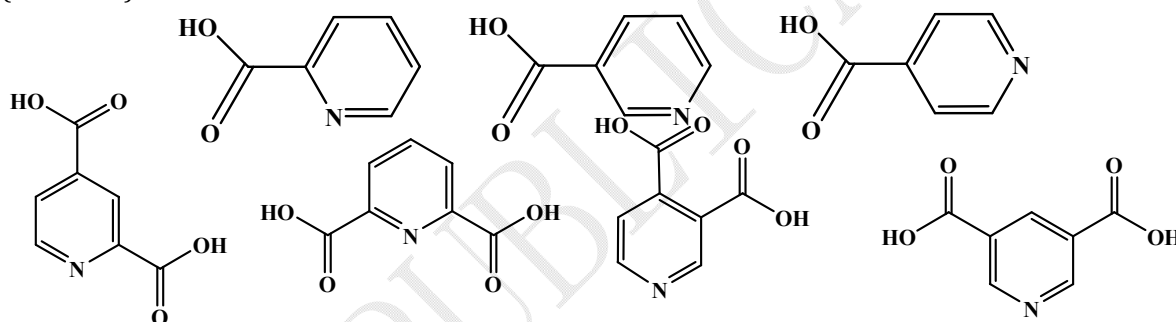
syn-anti carboxylate bridges. First compound exhibits ferromagnetic ordering below 2.6 K (T_c), and second complex displays a metamagnetic behavior below 3.2 K (T_N).

Cu(II) complexes of phenylmalonate, biphenylcarboxylate, cyclobutanedicarboxylate

A large number of structure and physical properties of polynuclear coordination compounds of Cu^{II} with different carboxylate bridging ligands, such as phenylmalonate, biphenylcarboxylate, cyclobutanedicarboxylate, etc., have been reported in the recent years.⁵ The 4,4'-bipyridine and 2,4'-bipyridine have been employed as a co-ligand to build two 2D *syn-anti* phenylmalonate-bridged copper(II) complexes.^{5a} Both the structures consist of layers of copper(II) ions with bridging bis-monodentate phenylmalonate and 4,4'-bipyridine ligands and terminal monodentate 2,4'-bipyridine groups. In 4,4'-bipyridine complex the Cu^{II} ions are bridged via *syn-anti* equatorial-apical carboxylate-bridge and 4,4'-bipyridine molecules. Whereas only *syn-anti* equatorial-equatorial carboxylate bridge links the copper(II) atoms in the other complex. Magnetic susceptibility measurements of both compounds in the temperature range 2-290 K show the occurrence of weak antiferromagnetic and ferromagnetic interactions between the copper(II) ions.

Cu(II) complexes of Pyridine substituted carboxylate

Pyridine substituted carboxylate are also of interest for the formation of extended coordination networks. This type of ligand possesses one or two carboxylic acid as coordination sites, which can be deprotonated, resulting in a mono-anionic or di-anionic ligand with a neutral nitrogen containing site (Scheme 2).



Scheme 2.

The three isomers of pyridine-carboxylic acid (2-picolinic acid, 3-picolinic acid, and 4-picolinic acid (Scheme 2) exhibit versatile coordination modes to metal ions. Among them, 2-picolinic acid (Hpic) is the most commonly used to obtain metal complexes, where, despite its different coordination modes, a chelating five-membered ring is invariably formed. A number of transition-metal-2-picolinate complexes with high nuclearity have been reported in the past two decades.¹² Interestingly, with Cu^{II} it usually produces the discrete, mononuclear 'inner metallic complex' $[\text{Cu}(\text{pic})_2]$.¹³ However, there are a few examples where some alkali¹⁴ or lanthanide metal ions (Figure 3)¹⁵ link the copper-picolinate units, and in one case the carboxylate group links the copper(II) ion in conjunction with a bridging chloride anion.¹⁶

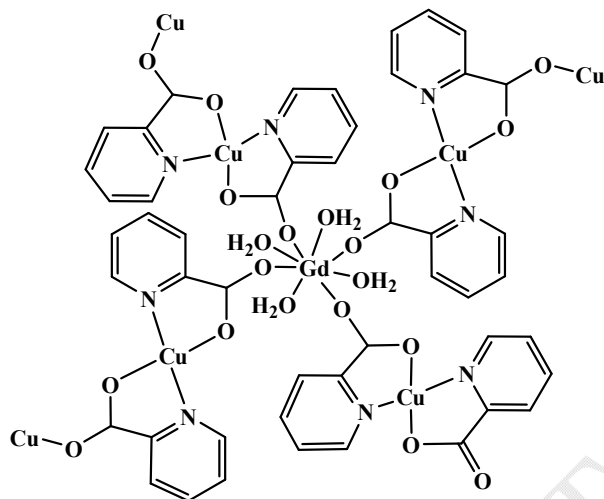


Figure 3.

Two new 3-D Cu^{II} coordination polymers [Cu(4-picolinate)₂][EtOH] and Cu(3-picolinate)₂ have been prepared by treating copper nitrate with 4-picolinic acid and 3-picolinic acid under hydro(solvo)thermal conditions, respectively.¹⁷ The Cu^{II} centers in 4-picolinate complex (Figure 4) adopt a slightly distorted square pyramidal geometry, while the Cu^{II} centers in 3-picolinate complex exhibit a coordination geometry intermediate between square pyramid and trigonal bipyramid. The Cu^{II} centers in both complexes coordinate to both pyridyl and carboxylate functionalities of the 4-picolinate and 3-picolinate bridging ligands, respectively, to result in complicated 3-D framework structures. Magnetic measurements indicated that first complex is a simple paramagnet with only very weak antiferromagnetic interactions, while in other exhibits more pronounced antiferromagnetic interactions.

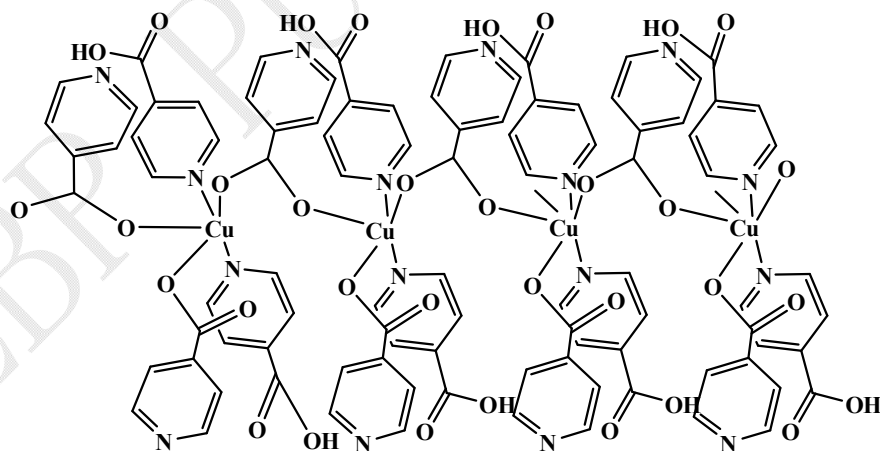


Figure 4.

Pyridine-2,6-dicarboxylate along with different N-heterocycles (4,4'-bipyridine, pyrazine and pyridine) have been used to form metal-organic framework structures of Cu^{II} under hydrothermal conditions.¹⁸ The dimensionality (1D, 2D or 3D) of the coordination polymers have been engineered with the help of different spacers (4,4'-bipyridine, pyrazine and pyridine). With 4,4'-bipyridine spacer,

a 2D network is formed where every alternate Cu^{II} ion in the 2D chain is coordinated terminally to an acyclic tetrameric water cluster (Figure 5). In all these three complexes pyridine-2,6-dicarboxylic acid linked copper(II) ions by *syn-anti* carboxylato bridging mode.

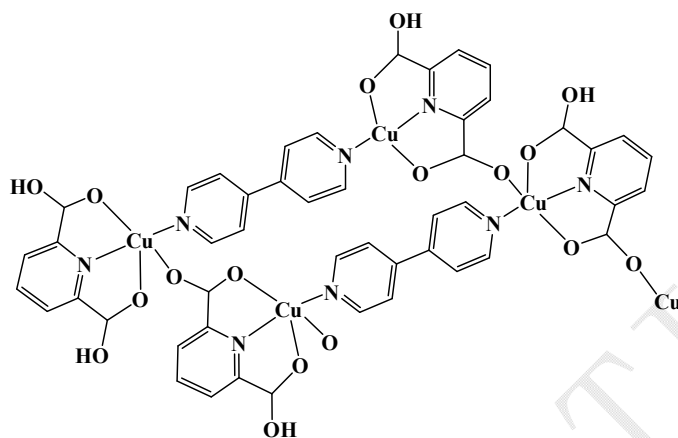


Figure 5

A polymeric one-dimensional (1D) zigzag chains of Cu^{II} has been reported with pyridine-2,6-dicarboxylic acid in μ -monoatomic oxygen bridging mode (Figure 6).¹⁹ Each copper(II) ion is in a distorted octahedral environment with a CuNO_5 core: two oxygen atoms and one nitrogen atom from one 2,6-dicarboxylate anion, one oxygen atom from an adjacent 2,6-dicarboxylate ligand and two oxygen atoms from coordinated water. Each 2,6-dicarboxylate anion connects two copper ions via a μ -oxygen atom

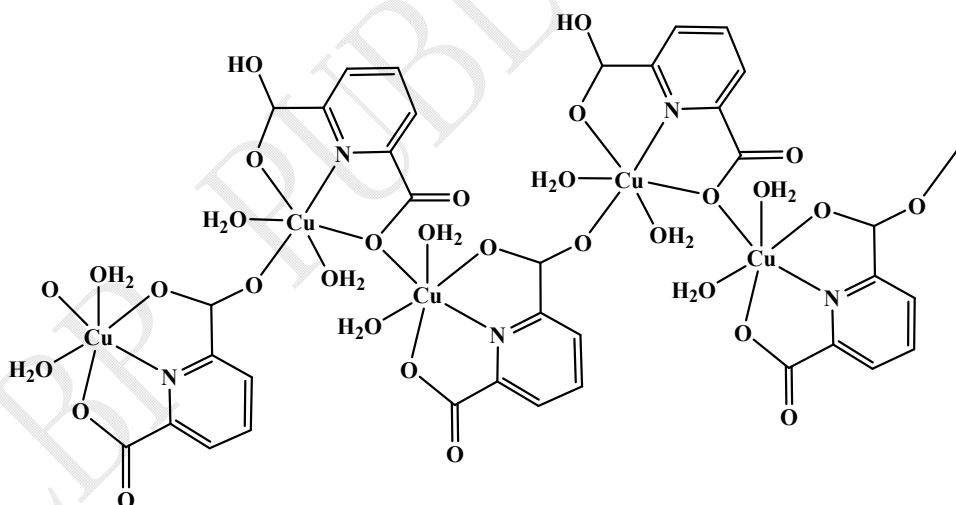


Figure 6

CONCLUSION

The paper contains a total of four sections of which section 1 deals with an overview on the $\text{Cu}(\text{II})$ complexes dicarboxylate anions of glutaric acid, adipic acid, phthalic acid, biphenylcarboxylic acid & cyclobutanedicarboxylic acid, section 2 and 3 describe the structural aspect of $\text{Cu}(\text{II})$ complexes of malonate and $\text{Cu}(\text{II})$ complexes of phenylmalonate, biphenylcarboxylate, cyclobutanedicarboxylate respectively. Whereas section 4 explains the structural diversity of $\text{Cu}(\text{II})$ complexes of Pyridine substituted carboxylates.

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