

Magnetic Properties of Carboxylato bridged manganese and copper complexes

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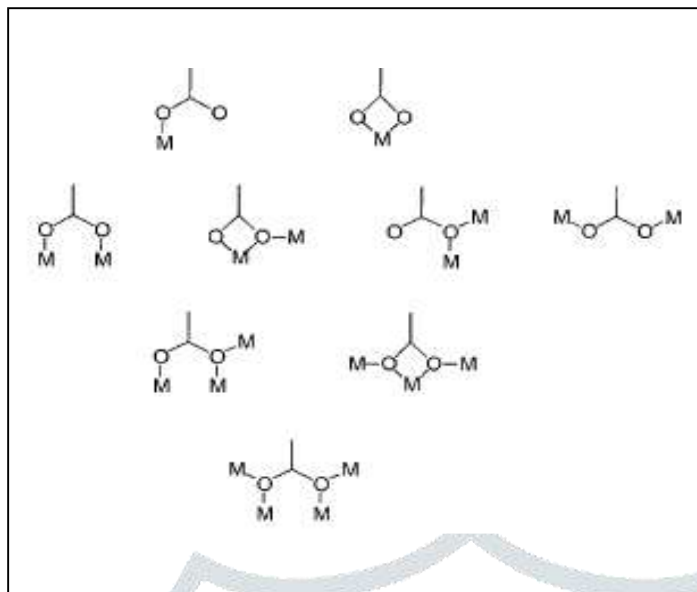
Abstract

Carboxylato bridged metal complexes has undergone quite impressive progress in the last decade in the field of molecular magnetism. Carboxylate group can bind two or more metal centres in monoatomic and triatomic *syn-syn*, *syn-anti*, and *anti-anti* fashion. Among the various transition metals, carboxylato bridged copper and manganese complexes show wide range of application in the field of molecular magnetism. The magnetic interaction among the metal centres will depend on the mode of coordination as well as the coordination environment around the metal centres. For mono atomic bridging fashion magnetic interaction will depend on the M-O-M bond angle θ . For small θ angles near 96° should lead to strong ferromagnetic interaction while larger value should make the interaction increasingly strongly antiferromagnetic.

Keywords: carboxylate bridging, copper, manganese, magnetic properties.

1.Introduction

There has been considerable interest in the coordination chemistry of transition metal ions involving nitrogen and oxygen donor ligands due to the increasing recognition of the role of this metal in biological systems [1-4]. These complexes are significant not only for their redox active role in several biochemical processes, but also for the diversity of their magnetic properties [5-7]. The field of molecular magnetism has undergone quite impressive progress in the last decade [8]. The magnetic exchange interactions between paramagnetic transition metal ions in multinuclear transition metal complexes are appropriate for the study of intramolecular magnetic exchange interactions, where the transition metal ions are the magnetic moment carrier. The magnetic exchange phenomenon within a molecule was first discovered by Guha et al. in year of 1951 [9], and then by Bleaney and Bowers [10], on a compound Cu(II) acetate monohydrate. These interactions may arise by the direct overlapping of magnetic orbitals of two connected metal centres or via superexchange through bridging atoms like O, N, S etc. Such interactions either decrease or increase the magnetic moment of the complex as a whole. To study the magnetic interaction, multinuclear copper(II), nickel(II) and manganese(II) complexes are very significant both from theoretical and practical viewpoints. For the preparation of these multinuclear complexes various bridging ligands or groups like carboxylate, phenolate, dicyanamide, azide, thiocyanate etc are employed as they can connect the metal centres in various bridging modes and significantly influence the category and magnitude of magnetic interaction. Multinuclear complexes containing bridging carboxylate groups are of current interest due to the fact that the carboxylate ions play a key role as a ligand in many biochemical systems involving mono- and polymetallic active sites [11-17]. Carboxylate is versatile anion that can assume many types of bridging conformations, the most important being monoatomic and triatomic *syn-syn*, *syn-anti*, and *anti-anti* [11,12] (Scheme 1).



Scheme 1. Some of the bridging conformations for the carboxylate group

In addition, the different bridging conformations of carboxylate group can bind two metal ions to give rise to a wide variety of multinuclear complexes ranging from discrete entities to three-dimensional systems [18-20] and their magnetic properties are closely related to the bridging conformation adopted by the carboxylate group in those multinuclear systems [21]. Multinuclear metal carboxylates are good candidates for the investigation of exchange-coupling interaction between adjacent metal ions [11,12,22,23]. Among metal(II) carboxylate polymers, structurally and magnetically characterised singly carboxylate-bridged chain complexes are rare [16,24-26] and those adopting the *anti-anti* conformation are rarer still.

There are several carboxylato bridged transition metal complexes reported in the literature, the present paper confined only on the discussion of carboxylato bridged copper and manganese complexes.

2. Synthesis:

2.1. Material

The source of carboxylic acid group is either the corresponding copper acetate or manganese acetate salts or the ligand itself may contain carboxylic acid group.

Synthesis of the ligands

In few cases direct carboxylic acid group containing ligands like anthranilic acid etc are used directly. On the other hand for most of the cases Schiff base type of ligand are prepared by the condensation of aldehyde or ketone with a amine or hydrazine group having carboxylic acid group.

2.2. Synthesis of the complexes

The corresponding metal acetate (copper or manganese) or any other salts are dissolved in methanol or ethanol and mixed with the alcoholic solution of the ligand with constant stirring generally at room temperature. The resulting solution was kept for few days and corresponding product was obtained.

2.3. Magnetic Study

Magnetic interaction between the metal centres through carboxylato bridging was measured using SQUID magnetometer in variable temperature range in a particular applied field.

3. Discussion

3.1. Carboxylato bridged Copper complexes

The carboxylato bridged copper(II) complexes are magnetically very important. Copper(II) complexes with monoatomic or *syn-anti* triatomic conformations exhibit very weak magnetic exchange interactions [15,27] whereas triatomic *syn-syn* and *anti-anti* conformations mediate large and weak to medium antiferromagnetic interactions, respectively [21,28]. The possibility of achieving strong magnetic interactions between magnetic centres which are linked through more and more extended bridges actually appears as a very active area of molecular magnetism. The dependence of J on the intramolecular metal–metal separation and thus to check if there is a limit distance for the exchange coupling to be propagated, chemists have prepared a great variety of dinuclear copper(II) complexes where the intra- molecular metal–metal separation is tuned in a wide range by using extended bridging ligands.

The magnetic interaction between the copper centres were estimated from a least-squares fitting of the susceptibility data by the corresponding Bleaney–Bowers expression derived through the Hamiltonian $\hat{H} = 2J\hat{S}_A\hat{S}_B$ with $S_A = S_B = 1/2$

Special attention has been paid to the bis-bidentate bridging groups of the oxalato type both from theoretical and experimental viewpoints. As for example, Colacio and co-workers reported a singly *anti-anti* carboxylato bridged zig-zag chain copper(II) Schiff base complex from a carboxylate containing tridentate Schiff base ligand (obtained by the condensation of 2-imidazolecarboxaldehyde and α -alanine) which shows weak antiferromagnetic interaction ($J = -0.40 \text{ cm}^{-1}$) [29].

For monoatomic carboxylato bridges between two paramagnetic transition metal centres, the magnetic interactions depend on the magnitude of bridging angle (θ) and other structural features [30]. This has been especially studied for oxygen bridged metal atoms such as Cu–O–Cu. Small θ angles near 96° should lead to strong ferromagnetic interaction while larger value should make the interaction increasingly strongly antiferromagnetic [31,32]. Besides a wide range of structural diversity is also observed in the reported copper(II) complexes [28, 29,33].

Among a helical-chain copper(II) complex $[\text{Cu}(\text{L})(\text{F}_3\text{CCO}_2)]_n$ (1) and a quasi-tetrahedral Cu_4 cluster $[\{\text{Cu}_4(\text{L})_4(\text{H}_2\text{O})_4\} \cdot 3.5\text{NO}_3 \cdot 0.5\text{N}_3]$ (2) (Figure 1) [$\text{L} = 2\text{-N-(2'-pyridylimine)benzoic acid}$] with single *syn-anti* carboxylato bridges first one exhibits very weak antiferromagnetic interaction whereas a weak ferromagnetic coupling has been established for latter[34].

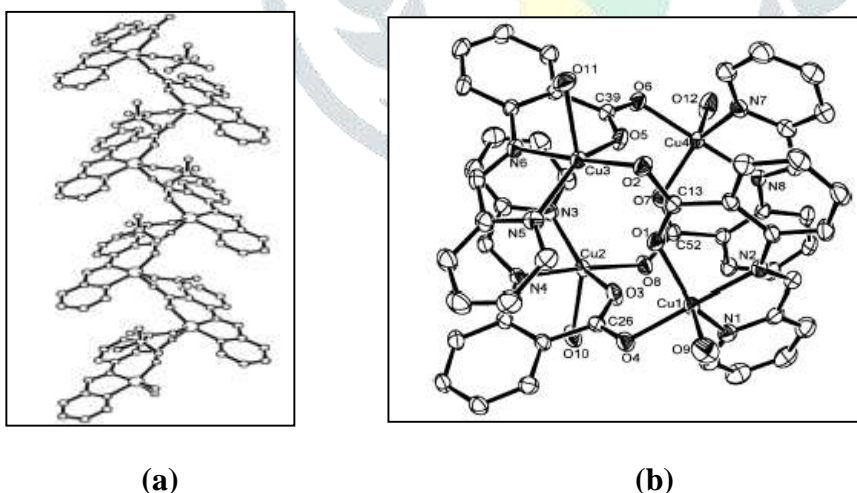


Figure 1. Perspective view of (a) $[\text{Cu}(\text{L})(\text{F}_3\text{CCO}_2)]_n$ (1) showing the formation of the helical polymeric chain; (b) $[\{\text{Cu}_4(\text{L})_4(\text{H}_2\text{O})_4\} \cdot 3.5\text{NO}_3 \cdot 0.5\text{N}_3]$ (2)

3.2. Carboxylato bridged Manganese Complexes

In recent years there has been significant research interest in the chemistry of manganese carboxylate complexes owing to: (i) their relevance to the biological Mn sites [35-37] and (ii) the realization of single-molecular magnets which are cluster complexes having abnormally large values of ground state spin [38,39]. Dinuclear manganese(II) complexes are of special attraction, since such systems are known to exist at the active centres of some manganese

containing enzymes [40]. Recently, dinuclear units with one to three carboxylato bridges were suggested to be plausible structure of the dinuclear sites in Mn catalases [40]. Considering the magnetic interaction, it has been observed generally μ_2 -carboxylato bridged manganese complexes show antiferromagnetic interactions [41,42] depending on the M-O-M bridging angle. One novel dinuclear manganese(III) complex using a quadridentate Schiff base, obtained by the condensation of 2-hydroxyacetophenone and 1,2-diaminopropane was reported by Mitra et.al which exhibits ferromagnetic intra-dimer interaction at low temperature [43].

To determine the exchange parameters *via* the double η^1 : μ -O_{carboxylate} bridge, (Figure 3) $\chi_M T$ was fitted to the equation [eq.(1)] for an isotropically coupled pair of $S = 5/2$ ions [44], where N is Avogadro's number, μ_B is the Bohr magneton and k_B is the Boltzmann constant. The best fit parameters for reproducing satisfactorily the experimental data, as shown in Figure 4, are $J_1 = -0.39\text{cm}^{-1}$, and $g = 1.97$ with $R = 2.7 \times 10^{-5}$ ($R = \sum_i (\chi T_{i\text{calc}} - \chi T_{i\text{exp}})^2 / (\chi T_{i\text{exp}})^2$)

$$\chi_M T = \frac{Ng^2\mu_B^2}{k_B} \frac{2\exp(J/k_B) + 10\exp(3J/k_B) + 28\exp(6J/k_B) + 60\exp(10J/k_B) + 110\exp(15J/k_B)}{1 + 3\exp(J/k_B) + 5\exp(3J/k_B) + 7\exp(6J/k_B) + 9\exp(10J/k_B) + 11\exp(15J/k_B)} \text{ eq. (1)}$$

The overall magnetic behavior of a μ_2 -dicarboxylato bridged dinuclear manganese(II) Schiff base complex $[\text{Mn}_2(\text{L}^1)_2(\text{NCS})_2]$ (**3**), corresponds to weak antiferromagnetically coupled systems (Figure 4). At room temperature, $\chi_M T$ shows a value of $8.395 \text{ cm}^3 \text{ K mol}^{-1}$ which is as expected for two manganese(II) ions ($8.75 \text{ cm}^3 \text{ mol}^{-1} \text{ K}$ per two Mn(II) with $g = 2.0$). On cooling, the $\chi_M T$ values remain constant, and below approximately 80K decreases quickly to $5.840 \text{ cm}^3 \text{ K mol}^{-1}$ at very low temperature (5 K) [45].

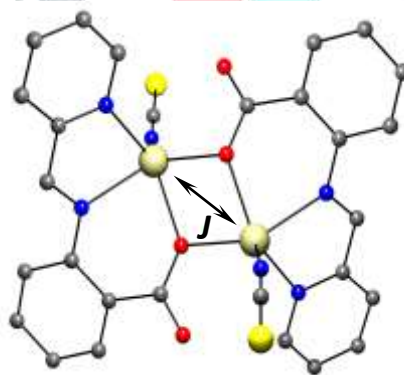


Figure 2. Dinuclear unit of complex

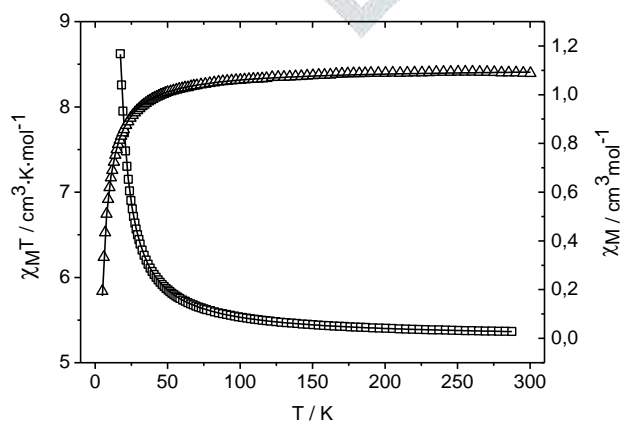


Figure 3. Plot of the $\chi_M T$ product (Δ) and the χ_M (\square) vs T for **1**, solid line shows the best fit of the data.

Magneto structural correlations in Mn(II) complexes with very weak magnetic coupling are very difficult to find. The only think is to try to compare with other ions with similar bridging ligands. For example, in the [Mn-O₂-Mn] entity, the angle Mn-O-Mn is close to 106.0°. In general, for a given cation, the angle closer to 90° smaller is the antiferromagnetic coupling [46].

Alternatively, manganese complexes with *syn-syn* and/or *syn-anti* carboxylato bridging exhibit weak to moderately strong antiferromagnetic interaction. One *syn-syn* and μ_2 -carboxylato bridged centro symmetric tetranuclear manganese(II) cluster [Mn₄(O₂CPh)₆{(py)CO₂}₂{(py)CHNOH}₂].0.6CHCl₃ (**4**), a 1D *syn-anti* carboxylato bridged manganese(II) coordination polymer [Mn(O₂CPh){(py)CO₂}{(py)CHNOH}]_n (**5**) and a double μ_2 - carboxylato bridged dinuclear manganese complex [Mn₂(O₂CMe)₂{(py)CO₂}₂{(py)CHNOH}₂] (**6**) [(py)CHNOH=2-pyridinealdoxime] (Figure 5) were reported by Perlepes et al. Variable-temperature magnetic susceptibility and EPR studies indicate weak antiferromagnetic exchange interactions is observed in case of the first complex [47].

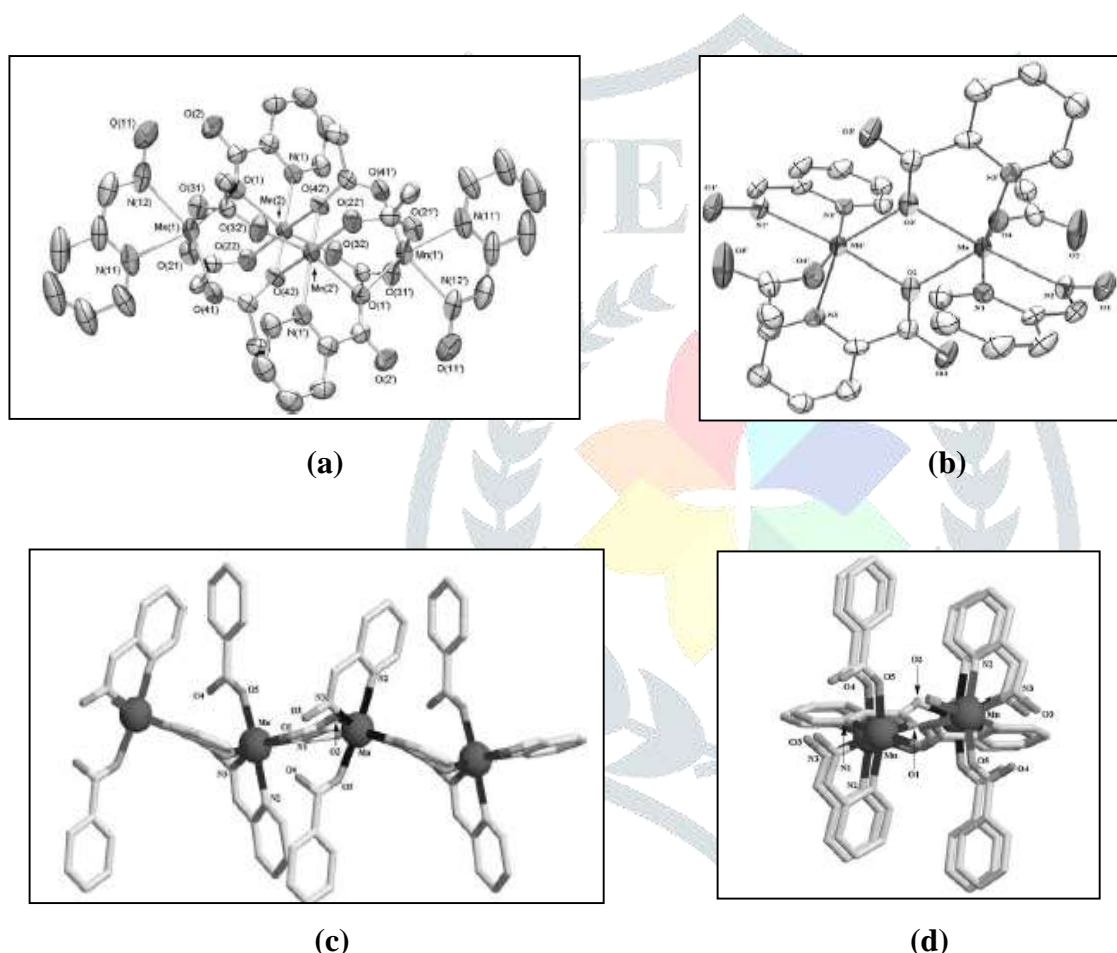


Figure 4. ORTEP plot of (a) [Mn₄(O₂CPh)₆{(py)CO₂}₂{(py)CHNOH}₂].0.6CHCl₃; (b) [Mn(O₂CPh){(py)CO₂}{(py)CHNOH}]_n; (c), (d) Views of Mn₂(O₂CMe)₂{(py)CO₂}₂{(py)CHNOH}₂ along b-axis (c) and c-axis (d) [66].

Between the two manganese(II) complexes, [Mn(mtm)(CH₃OH)₂(H₂O)]_n (**7**) and [Mn₂(mtm)₂(2,2'-bipy)₂]_n (**8**) (bipy=bipyridine, mtm= [bis(methylthio)methylene]malonate) (Figure 6) , in the first complex manganese(II) species extended by *syn-anti* carboxylate bridges and forms 2D structures through hydrogen bonds. Conversely, the two Mn(II) ions in the asymmetric unit of the second complex are bridged by μ_2 -carboxylato bridging group and the dimeric units are linked doubly by second carboxylates in *syn-anti* fashion, resulting in a chain structure. Both complexes show antiferromagnetic interaction [48].

In case of above mentioned complexes it is cleared that most of the cases antiferromagnetic interaction occurs between two manganese metal centres and depending on the mode of coordination the interaction is changes from weak to medium to strong.

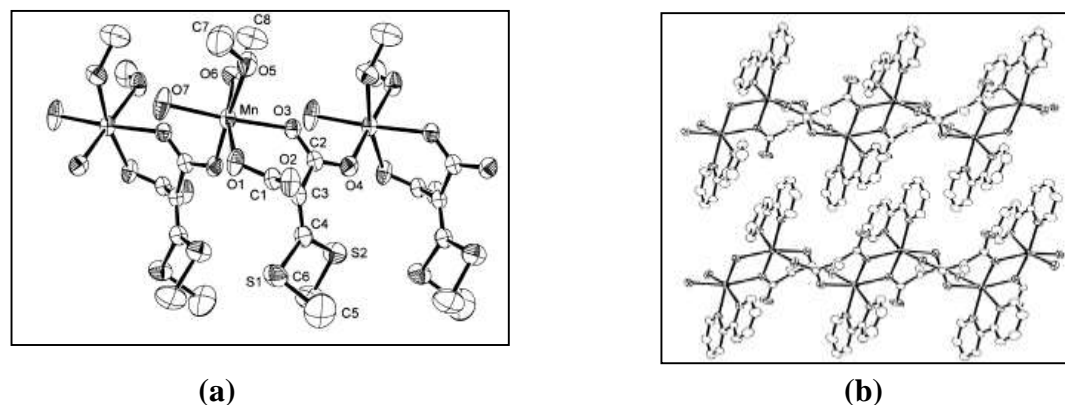


Figure 5. (a) ORTEP diagram of $[\text{Mn}(\text{mtm})(\text{CH}_3\text{OH})_2(\text{H}_2\text{O})]_n$; (b) View down along b -axis to show π -stacking of chains in $[\text{Mn}_2(\text{mtm})_2(2,2'\text{-bipy})_2]_n$,

4. Conclusion

As a bridging ligand carboxylate group is very much unique as it can bind the metal centres in various bridging mode resulting many interesting di and multi nuclear complexes. These complexes are very important not only from structural point of view but also from magnetic point of views. Carboxylato bridged copper and manganese complexes have lots of application in magnetic field as well as in biological field. Moreover synthesis processes of these complexes are not very expensive or time consuming. To synthesise these complexes choice of auxiliary ligand like Schiff bases, hydrazones etc is very much important. Some times auxiliary ligand itself contains the carboxylic acid group and bind two or more metal centres. Some multinuclear carboxylato bridged copper and manganese complexes show magnetic ordering which can be used as molecular magnets. Considering all the interesting properties of carboxylato bridged multinuclear copper and manganese complexes, many researchers are still give their attention to synthesis more new carboxylato bridged unique complexes till date.

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