Investigations of novel inorganic-organic hybrid framework assemblies constitute one of the most active areas of materials science and chemical research. The intense interest in these materials is driven to a large extent by their unique properties and potential in various applications relating to electrical conductivity\(^1\), magnetism\(^2\), photomechanism\(^3\), host-guest chemistry\(^4\), ion exchange, shape specificity and catalysis\(^5,6\), high-temperature and flame resistant fibrous materials\(^7\). Framework materials involving coordination metal complexes constitute major systems which are being probed and developed in the above contexts. Several of these metal-based compounds with low dimensional structures have long been investigated as materials with unusual properties. Molecular-based ferromagnets, conductors and non-linear optical materials represent several applications of such low dimensional coordination polymers\(^8-17\). The search for molecular building blocks in the design of new extended supramolecular architectures, with tailored electronic or catalytic properties, is a current interest in inorganic chemistry. The synthetic effort is directed mainly toward the preparation of molecular based magnets\(^18,19\) and of inorganic materials with inner cavities and channels mimicking zeolites\(^20-23\). A successful strategy leading to heteropolynuclear one-, two- and three-dimensional systems is the use of metal cations to link relatively stable coordination compounds containing potential bridging units.
Among the most oxidised forms of carbon which include −CO₂⁻, −CO₃²⁻ and −COOH, the carboxyl moiety provides key functional manifestations in chemical reactions, biological functions and also in modulating structural, electronic, magnetic and other material properties in systems containing the group. Carboxylic acids, besides being essential building blocks of many life molecules, are very useful functionality in generating hybrid framework materials by interacting with metal ions. The abilities of its anion to coordinate to metal ions in diverse and unique linking modes and switch its ligation characteristics with comparative ease towards metal ions depending on the reaction conditions and available molecular environments have made the carboxylate function versatile structure directing moiety. Owing to these reasons, the structural aspects of metal carboxylates have been well investigated. As evident, dicarboxylate compounds can generate a wide variety of polymeric metal complexes with diverse structural features because of their bifunctional nature and easily tunable coordination characteristics. While the main focus of the thesis is the generation and characterisations of interesting structural entities from polymeric metal dicarboxylates we feel it is worthwhile to discuss some of the interesting aspects of metal carboxylates in general.

1.1 **Monocarboxylates: Structure and Bonding**

Monocarboxylates by themselves are an attractive class of ligands for the coordination chemists. These versatile moieties bind to metal atoms in a variety of ways giving, in many instances, complexes with interesting structural manifestations and novel electronic, magnetic and other material properties which are also
Introduction

easily accessible. *Scheme I* shows some of the known modes of coordination of monocarboxylate anions. Unidentate (A) and symmetrical chelate coordination (B) modes are often found and well established, with the unidentate mode being more commonly observed. The presence of unidentate carboxylate can be comparatively easily established through IR spectra, by virtue of the inequivalence of the two C-O bonds in the coordinated anion. However, care must be exercised since the environment of the free carboxylate O atom (and even sample preparation) can influence their IR spectrum.\(^{[28-29]}\)

![Scheme I: Some coordination modes of monocarboxylate anions](image)

*Scheme I: Some coordination modes of monocarboxylate anions*

The most common bridging mode of coordination is *syn-syn* (E). The nature of metal-metal interactions as shown in (D) in such systems has been the subject of much study, with interaction varying from the relatively weak in dimeric Cu(II) complexes, to strongly M-M bonded species such as Mo$_2$(O$_2$CR)$_4$ which contain a formal quadruple bond. The two systems which have been most
studied are the bimetallic (I) and trimetallic (II) complexes, often referred to as ‘paddle-wheel’ and ‘triangular’ complexes, respectively.\(^\text{(30)}\)

Metal acetates and trifluoroacetates of weak Lewis acids are usually symmetric while those of very strong Lewis acids are often asymmetric.\(^\text{(31)}\) The other forms are not common, but anti-anti single bridging occurs in \([\text{Mnsal}_2\text{enCO}_2\text{Me}]_n\) and anti-syn in \([\text{Ph(CH}_2)_3\text{SnO}_2\text{CMe}]_n\). Trifluoroacetates are known only in unidentate and bridging forms. The syn-syn bridging \(\text{RCO}_2^-\) ligand is extremely common and important in compounds with M-M quadruple bonds.

In ‘ionic’ acetates or acetates in aqueous solution, the ‘free’ \(\text{CH}_3\text{CO}_2^-\) ion has symmetric and antisymmetric C-O stretching modes at \(~ 1415\) and \(~ 1570\) cm\(^{-1}\) respectively. These frequencies can vary by \(\pm 20\) cm\(^{-1}\) depending on the system. Since the symmetry of even the free ion is low and gives two IR active bands, evidence for the mode of coordination must be derived from the positions rather than the number of bands. When the carboxyl group is unidentate, one of the C-O bonds should have enhanced double-bond character
and should give rise to a high-frequency band. Such bands are observed in the 1590 to 1650 cm\(^{-1}\) region and are considered to be diagnostic of unidentate coordination.\(^{(29,32)}\)

Symmetrical bidentate coordination as in Zn(CH\(_3\)COO)\(_2\).2H\(_2\)O and Na[UO\(_2\)(CH\(_3\)CO\(_2\))]\(_3\) and symmetrical bridging, as in the M\(_2\)(O\(_2\)CCH\(_3\))\(_4\)L\(_2\) and M\(_3\)O(O\(_2\)CCH\(_3\))\(_6\)L\(_3\) types of molecules, leave the C-O bonds still equivalent; but the effect on the frequencies is not easily predictable. In general, multiple bands appear between 1400 and 1550 cm\(^{-1}\), the multiplicity being attributable to coupling between CH\(_3\)CO\(_2\) groups bonded to the same metal atom.

The only significant reaction of the carboxylate ligand is decarboxylation, which is often catalysed by transition metal species.\(^{(33)}\) Straight-chain alkyl carboxylic acids derived from petroleum and which also have a terminal cyclohexyl or cyclopentyl groups are known as naphthenic acids. They form complexes, presumably polymeric, with many transition metals, and are freely soluble in petroleum. There are, of course, more complicated carboxylic acids such as ethylenediaminetetraacetic acid that can function as multidentate ligands with both N and O bound to the metal. Also hydroxo carboxylic acids such as citric acid readily form complexes in which both carboxylate and hydroxo groups are involved in co-ordination. Among these, probably the best studied are tartrato complexes.\(^{(34)}\) A fairly common type of structure is one in which it bridges two metal atoms. A particular example is in the case of antimony complex which is known as tartar emetic (III).
Because of the chirality and multiplicity of bonding possibilities, many isomers of tartrate complexes are possible, and the relative stabilities of these can be explained in terms of steric constraints of the binuclear structure and conformation of the tartrato groups, and depend strongly on the coordination geometry around the metal.

Oxygen centred triangles\(^{(35)}\) are important units found widely in so-called "basic" carboxylates and a few other bridging anions of many transition metals like V, Cr, Mn, Fe, Co, Ru, Rh, Ir and Pt. For the +3 state they have the general formula \([\text{M}_3\text{O(OOCR)}_6\text{L}_3]^+\) where \(L\) is a ligand such as \(\text{H}_2\text{O}\) or pyridine and it has general structure as in IV.
Metal carboxylates, in general, are known to take multivarious structures.\textsuperscript{(36-38)} The acetate of Cu(I) is obtained as white air-sensitive crystals by reduction of Cu(II) acetate by Cu in pyridine or MeCN and has a planar chain structure (V). By contrast the trifluoroacetate \((\text{CuO}_2\text{CCF}_3)_4\cdot 2\text{C}_6\text{H}_6\), and benzoate \((\text{CuO}_2\text{CPh})_4\) complexes are tetramers with bridging carboxylates as in VI. However, this is the only one type of Cu\(_4\) polynuclear structure known.

\begin{center}
\textbf{V} \quad \textbf{VI}
\end{center}

Compared to the Cu(I) species mentioned above, copper(II) carboxylates are known to be binuclear with four carboxylate bridges and may additionally have end groups as in VII.

\begin{center}
\textbf{VII}
\end{center}
Polymeric species are known to be formed by interaction of tetrahydrothiophen (L) and CuCl$_2$, which gives [Cu$_{1}^{1}$Cu$_{1}^{II}$LCl$_{5}^{n}$] species while the action of P(OMe)$_3$ on copper(II) carboxylates gives Cu$_3$(O$_2$CR)$_5$[P(OMe)$_3$]$_2$ that may have units linked as in VIII.$^{(39)}$

![VIII](image)

Oxo-centred complexes can have $\mu_4$-tetrahedral oxygen in the center of a tetrahedron of divalent metal atoms as in M$_4$O(O$_2$CMe)$_6$ or in similar clusters. The best known complex is Be$_4$O(O$_2$CMe)$_4$. Similarly Zn$^{II}$ and Co$^{IV}$ analogues are also known.$^{(40)}$ The ‘manganic acetate’ is actually an oxo-centred species, [Mn$_3$O(O$_2$CMe)$_6$]CO$_2$Me. Interaction of the acetate with bipy in MeCN gives Mn$_4$O$_2$(O$_2$CMe)$_7$(bipy)$_2$, which is considered as a model for the Mn complex involved in photosynthesis.$^{(41)}$ One of the earliest Cr$^{II}$ compounds discovered (1844) was the acetate hydrate, Cr$_2$(O$_2$CCH$_3$)$_4$(H$_2$O)$_2$. It was long recognized as anomalous because it is red and diamagnetic, whereas the mononuclear Cr$^{II}$ compounds are blue or violet and strongly paramagnetic. This compound as well as numerous others of the general formula Cr$_2$(O$_2$CR)$_4$L$_2$, have the type of structure shown in IX.
It is now well understood that the chromium atoms are united by a quadruple bond in this dimer but the strength of this interaction is sensitive and depends as inverse function of the bonding strength of the axial ligand. It is also sensitive to the basicity of the RCO$_2$ groups.

1.2 Dicarboxylates: Structure and Bonding

Dicarboxylic acids are more complex than the corresponding monocarboxylic acid in transition metal coordination chemistry due to varied coordination behaviour in the resulting complexes.$^{(42-45)}$ Dicarboxylic acids being bifunctional molecules can bind metal ions through both of their carboxylate functions and can lead to extended polymeric systems. Besides the ability to exhibit diverse linking characteristics through –COO$^-$ groups resulting in highly tunable structural features, the nature of the spacer moiety between the two carboxylate functions can also contribute substantially to the structural architecture of the resulting framework materials. Dicarboxylic acids, as chelating ligands, control the oxidation state of transition metal and builds the skeleton of inorganic framework both as a part of the oxide sheet and pillars between layers. The three
dimensional framework of transition metal carboxylate opens a new series of transition metal complexes for engineering tailored materials. Hybrid inorganic-organic compounds are attracting interest as a class of materials that are well suited for the incorporation of transition metals into porous frameworks.\cite{46-48} In such materials, functionality can be introduced from either the inorganic species or the organic linker molecules. Transition metals are well known to confer redox character to zeolite hosts and may impart interesting magnetic and spectroscopic properties to porous materials. Organic species, on the other hand, can be used to adjust the channel size, after the surface of pores and impart chemical reactivity or chirality. For transition metal carboxylates, several examples of multidimensional metal-oxygen connectivity occur for materials made with linear dicarboxylic acids. Many researchers were interested in the use of the complexing properties of carboxylic acid to build open structure materials.\cite{49,50} In other words dicarboxylate ligands could be fruitfully used to obtain extended solids with open frameworks.\cite{51-54}

The simplest and most intensively studied among these dicarboxylic acids is oxalic acid (ethanedioic acid), which has no spacer entity between the two -COOH groups. Several coordination modes for this acid are possible and these are represented in Scheme 2. Unlike monocarboxylates, chelate coordination is favoured for oxalates over the unidentate mode. Of the two modes of chelate coordination, the formation of the larger chelate ring (D) is generally formed in preference to the four-membered chelate ring (C), with the latter becoming more common in higher members of the dicarboxylate series, where the two carboxylate groups are farther apart.
There are many possible bridging modes for this simplest dicarboxylic acid and among these, the tetradeutate bridging mode (F) is the most common. X-ray diffraction is the most reliable method of determining the coordination mode of the dicarboxylates, although chemical methods have been somewhat useful. For example, protonation reactions can reveal the presence of uncoordinated carboxylate groups, since these are easily protonated unlike the coordinated groups. Metal interactions in dicarboxylate complexes, particularly oxalate complexes, have been of interest, with copper complexes being the most studied. The magnetic properties of oxalate-bridged Cu$^{II}$ dimers $[\text{LCu(ox)CuL}']^{2+}$ have been found to be highly variable, and strongly influenced by the nature of the terminal ligands L and L$'$.\(^{(53)}$ Dicarboxylate complexes are usually synthesized by reaction of an aqueous solution of the alkali metal salt of the dicarboxylate with a metal halide, or by reduction of a metal salt by the dicarboxylic acid. For example, oxalic acid readily reduces iron oxides to form the iron(II) complex.
The oxalate ion has been known to function as a bis-bidentate ligand and its coordination to two metal ions affords a wide variety of polynuclear compounds.\textsuperscript{(56-59)} There are four types of polymerisation A-D, which are shown in \textit{Scheme 3}.

\textit{Scheme 3: Types of polymerisation in oxalate ion}

As in A linear chain structures are formed, in which the bridging oxalate ions coordinate in a monodentate fashion.\textsuperscript{(60,61)} In B each copper ion has a square-planar coordination geometry having bis-bidentate oxalate with adjacent, copper ions bridged by
Introduction

a single oxalate ion. The extended linear chain systems having bis-bidentate oxalate (C and D) are intriguing, concerning their magnetic behaviour, thermal and solid state reactions. Recently, compounds of the type C have been synthesised, whereas no single X-ray crystal structure of D has been reported in spite of its importance.

The occurrence of long range magnetic order in lattices composed of molecular transition metal complexes has been attracting increasing attention in recent years. Such compounds are of interest because they are insulating and frequently transparent and offer the opportunity of creating novel lattice architectures. They also offer the chemist the opportunity to investigate how magnetic exchange interactions are propagated through extended and conjugatively connected polyatomic ligands. Prominent among the latter is the ambidentate oxalate ion. Numerous dimeric and trimeric oxalate complexes have been prepared as models exhibiting novel properties. Exchange coupled clusters of transition metal ions are relevant to many different scientific areas ranging from chemistry to solid-state physics and to biology. There is active interest from the bio-inorganic community in heterometal polynuclear complexes because an increasing number of active centres in metalloproteins are found to contain more than one metal atom. The oxalato group has shown to be an excellent bridging ligand to achieve a strong antiferromagnetic interaction between metal ions far away from each other in homobimetallic complexes.

Polynuclear metal complexes are of considerable current interest in relation to the nature of magnetic exchange interaction between metal
ions through bridging ligands \(^{(70-73)}\) and as models for the active sites of metalloenzymes \(^{(74-76)}\). Many of these compounds are prepared in attempts to mimic the behaviour of various dicopper proteins such as hemocyanin, tyrosinase etc \(^{(77-80)}\). Various oxalato bridged metal complexes have structures like honey-comb layer \(^{(64,65,81)}\) (X), chicken wire sheet \(^{(82,83)}\) (XI-XII) and enantiomeric chains \(^{(83)}\) as shown in XIII.

![](image)

XIII

In the field of molecular based magnetism structurally two dimensional (2D) bimetallic oxalate bridged networks have attracted increasing interest in recent years \(^{(84)}\). Since the ambidentate oxalate ions act as mediators for magnetic exchange
interactions between the transition-metal centres, short range and long range magnetic ordering behaviour may occur, and consequently, from this molecular class of compounds emerge materials with distinct magnetic properties. The role of dipositive tris-chelated transition metal bipyridine complexes as templates in the formation and crystallization of chiral, three dimensional (3D) homo and bimetallic oxalate bridged networks is now well established.\textsuperscript{85} The topological, chemical and physical properties of the resulting polymeric frameworks are fascinating.

The oxalate ion is an efficient bridging ligand for the stepwise synthesis of homo and hetero-polynuclear complexes. This ion is known to be one of the few ligands for which systematic photochemical information regarding various metal ions exists.\textsuperscript{86,87} Oxidation-reduction is the principal photochemical reaction whereby in the complexes of tripositive metal ions, the metal ion is reduced from the trivalent to the divalent state and the oxalate ligand is finally oxidized to CO\textsubscript{2}. In addition to its reducing property, the oxalate ion is a versatile ligand since it can act as a mono, bi, tri and tetradeutate ligand capable of forming bridged polynuclear complexes.\textsuperscript{88} Self assembly of metal compounds by hydrogen bonds into one-, two- and three-dimensional supramolecular architectures, encompass biological and material areas and provide an opportunity to consider them in unison.\textsuperscript{89-91} Many oxalato bridged complexes have in fact very interesting 1D,\textsuperscript{92-94} 2D \textsuperscript{95,96} (XIV) and 3D framework structures \textsuperscript{97-101} (XV) and associated properties.
The coordination features of malonic acid which has a -CH$_2$-linker between the two -COOH groups is of current interest due to the versatile binding modes of its dianion (eg: syn-syn, syn-anti, anti-anti and monoatomic) which can simultaneously function as bidentate chelate as well as bridging ligand through the carboxylate groups to neighbour metal ions, which can propagate the electron transfer between paramagnetic centres leading to specially interesting magnetic materials.$^{[24-26,29]}$ Magnetic studies on the carboxylate bridged compounds generally indicate that syn-anti mode induces ferromagnetic interactions where as anti-anti and syn-syn induce antiferromagnetic interactions.

Several examples of metal complexes of malonate and bimalonate having polymeric$^{[102-105]}$, helical$^{[106]}$ and 3D network$^{[107,108]}$ are known of which a representative structure is given in XIV.
In addition to this, numerous layer-type polymeric malonato complexes have also been reported (XVII). These layers, which contain infinite puckered four-membered M-O-M-O rings in a pseudo-ternary symmetry, are formed by the metal and one independent malonate group. They are interconnected by the second independent malonate group, giving a three-dimensional framework. In this one malonate group is monodentate and triply bridging and chelating, whilst the other is doubly monodentate. The extensive network of hydrogen bonds and bridge bonds observed in this structure enhances the structure stability.
It is worthy to note that metal malonate and several of its analogue complexes are seen to have promising anti-tumor properties.\textsuperscript{(110)}

Succinate ions with -CH$_2$-CH$_2$- spacer between the two carboxylate functions are known to employ two distal carboxyl O atoms to link transition metal atoms into 1D polymeric or supramolecular chains.\textsuperscript{(111-114)} Previous investigations show that $\alpha,\omega$-dicarboxylate anions are interesting flexible bridging ligands to interlink metal atoms into supramolecular architectures with specific topologies.\textsuperscript{(115-118)} In addition, the succinato ligands polydentately link metal atoms to form 2D and 3D networks.\textsuperscript{(119,120)}

By adopting the hydrothermal techniques various metal succinates with 1D\textsuperscript{(121)}(XVIII), 2D\textsuperscript{(122-126)}(XIX, XX) and 3D\textsuperscript{(121,127)} (XXI, XXII) framework structures have been prepared. Under hydrothermal conditions, the temperature favours inorganic condensation (decrease of water polarity, modification of equilibrium constants). The condensation is therefore “perturbed” by the presence of the coordinated organic ligand. Under mild conditions, the stabilization of infinite networks comes from the bifunctional character of the
ligands, which can bridge metal centres. The suggested honeycomb structure\(^{(128)}\) of nickel succinate with hydroxyl group contains layers of edge-sharing NiO\(_6\) octahedra connected by isolated corner sharing NiO\(_6\) octahedra (XXIII). It may be considered as the first metal carboxylate with fully 3D M-O-M connectivity. The most prominent feature of the nickel succinate structure is the presence of unidimensional pores. The pores are lined almost entirely by the methylene groups of the dicarboxylate, which creates an exceptionally hydrophobic surface.
Benzoic acid–based ligands have led to a variety of structures as these ligands can form short bridges via one carboxylate end or longer bridges through the functionalized benzene ring. Recent reports of terephthalic acid (tpa) bridged Cu(II) centers have shown that the ligand can coordinate to the metal in either in chelating bis-bidentate\textsuperscript{(129)} (A) or bis-monodentate (B)\textsuperscript{(129-132)} or bridging bis-monodentate (syn-syn) (C)\textsuperscript{(133)} fashion (Scheme 4). The tpa ligand can form multidimensional compounds owing to its multibinding ability with regard to metal ions.\textsuperscript{(134)}
Increasing attention has been paid to the construction of two-dimensional (2D) or three-dimensional (3D) magnetic systems in order to gain a better understanding of the correlation between structure and magnetism. One strategy to build a spatially well-spanned framework, among others, is to utilize certain features of potentially bridging ligands, such as conformational flexibility, versatile binding modes, and the ability to form hydrogen bonds. The terephthalate ligand can form multidimensional compounds owing to its multi binding ability with regard to metal ions. The design of supramolecular structure with interesting inclusion and magnetic properties has been extensively studied in recent years. A rapidly developing area in this field is the synthesis of extended inorganic structures where the ability to control functionality along these networks is of much current interest.

There are several reports of terephthalato bridged complexes having 1D chain (XXIV), 2D layered (XXV, XXVI) and 3D network structures (XXVII).
In XXIV, tpa has a bridging bis-monodentate binding mode while in XXV, a mono-bidentate binding mode. In XXVI, there are two types of edge sharing MO₆ chains that are connected to each other by OH (M-O-M bridges) to form layers that are further joined together through terephthalate ion. Evidently these types of compounds exhibit unusual magnetic properties.

It is instructive to discuss in some details the relative magnitude of formation constants of ternary complexes involving dicarboxylate systems. The formation constants of the ternary complexes have been evaluated by a variety of methods depending upon the nature of the interaction between the metal ion.
and ligands, and the values are given in Table 1.1, along with those of the binary system.

**Table 1.1- Formation Constants of Ternary Complexes (Malonic Acid (A)-Cu(II)-Ligand(L) Complexes)**

<table>
<thead>
<tr>
<th>Ligand(L)</th>
<th>$\log K^M_{ML}$</th>
<th>$\log K^M_{ML^2}$</th>
<th>$\log \beta_{MAL}$</th>
<th>$\Delta \log K$</th>
<th>$\log X$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Oxalic acid</td>
<td>4.28</td>
<td>3.97</td>
<td>8.54</td>
<td>-0.57</td>
<td>0.72</td>
</tr>
<tr>
<td>Succinic acid</td>
<td>3.23</td>
<td>-</td>
<td>8.16</td>
<td>0.10</td>
<td>-</td>
</tr>
<tr>
<td>Maleic acid</td>
<td>4.02</td>
<td>2.82</td>
<td>9.39</td>
<td>0.54</td>
<td>3.83</td>
</tr>
<tr>
<td>Fumaric acid</td>
<td>3.19</td>
<td>-</td>
<td>6.28</td>
<td>-1.74</td>
<td>-</td>
</tr>
<tr>
<td>Phthalic acid</td>
<td>3.49</td>
<td>2.59</td>
<td>9.16</td>
<td>0.84</td>
<td>4.13</td>
</tr>
<tr>
<td>Salicylic acid</td>
<td>10.83</td>
<td>8.05</td>
<td>16.40</td>
<td>0.74</td>
<td>5.81</td>
</tr>
<tr>
<td>2,2'-Bipyridyl</td>
<td>8.00</td>
<td>5.60</td>
<td>14.61</td>
<td>1.78</td>
<td>7.51</td>
</tr>
<tr>
<td>Ethylenediamine</td>
<td>10.31</td>
<td>8.60</td>
<td>15.30</td>
<td>0.16</td>
<td>3.58</td>
</tr>
</tbody>
</table>

The stability constants of ternary complexes are characterized by the difference in stability constants ($\Delta \log K$) which is given by eq (1.1), and the disproportionation constant ($\log X$) which is given by eq (1.3), the equilibrium being represented by eq (1.2).

$$\Delta \log K = (\log K^M_{MAL} - \log K^M_{ML})$$

$$= (\log K^M_{MLA} - \log K^M_{MA})$$  \qquad \text{.........(1.1)}$$

$MA_2 + ML_2 \rightleftharpoons 2MAL$;
\[ X = \frac{[\text{MAL}]}{[\text{MA}_2][\text{ML}_2]} \] ........(1.2)

\[ \log X = 2 \log \beta_{\text{MAL}} - (\log \beta_{\text{MA}_2} + \log \beta_{\text{ML}_2}) \] ........(1.3)

The values expected for \( \Delta \log K \) and \( \log X \), from statistical arguments\(^\text{(159)}\) are –0.3 to –0.9 and 0.6, respectively. Higher values of \( \Delta \log K \) and \( \log X \) indicate that the ternary complex formation is favoured over the binary ones. The data presented in Table 1.1 show that the experimental \( \Delta \log K \) and \( \log X \) values are greater than the statistical ones, indicating that apart from the statistical factors the stability of the ternary complexes is also governed by other factors like ring size of chelate, neutralization of charge in the ternary complex formation and formation of \( \pi \)-bonds.

### 1.3 Carboxyl group in Biology

As mentioned earlier the -COOH groups are essential functionality of a variety of life molecules starting from amino acids. The group provides high compatibility for -NH\(_2\) function to form zwitter ions in terms of matching acid-base strengths.

Among several metalloenzymes it is noteworthy to mention some aspects about 'Carboxy peptidase A' (CPA). It is a type of enzyme, with a molecular weight of ~ 34, 600 which catalyzes the hydrolysis of the terminal peptide bond at the carboxyl end of proteins and other peptide chains. It is also effective toward correspondingly placed ester linkages. There is a marked preference for peptide bonds in which the side chain of the terminal residue is aromatic or a branched aliphatic chain. CPAs
have been found in the pancreas of many mammals including man. The carbonyl oxygen atoms of the peptide or ester link that is to undergo hydrolysis are coordinated to the Zn atom. This polarizes it in the O–C’ sense, thus making the C atom more prone to nucleophilic attack. The arginine -145 residue forms a strong hydrogen-bonded linkage (XXVIII) to the terminal carboxyl group. This accounts for the specificity of the enzyme for catalyzing hydrolysis of the terminal residue at the carboxyl end of a peptide. It also results in a good fit of a large non-polar side chain on the terminal residue into an available hydrophobic pocket. At this point, the so-called Michaelis complex is in fact formed. Beyond this, there has been considerable controversy as to how bond scission and generation of products is actually accomplished (Scheme 5).

![Diagram of XXVIII](image-url)
Scheme 5: A possible mechanism for the action of carboxypeptidase, X represents either O or NH, and the steps are not all written so as to be balanced with respect to protons.

A key point in favour of this scheme is that it can account for the accepted fact that following the Michaelis complex, another metastable complex (or intermediate) is formed, and only then is the product complex formed, from which the products, $\text{RCO}_2^-$ + $\text{HOCR'}\text{HCO}_2^-$ or $\text{RCO}_2^-$ + $\text{H}_3\text{NCR'}\text{HCO}_2^-$, promptly dissociate,
leaving the enzyme ready for the next cycle. This second complex must be one of the species in which there is an intermediate anhydride involving the carboxyl group of Glu-270. It is to be noted that another key step in the mechanism is the generation of a Zn-OH group, which is responsible directly for the attack on the carbonyl carbon atom. The zinc ion thus serves twice as a Lewis acid: once in binding and polarizing the carbonyl group and again in enhancing the acidity of the bound water molecule so that it can become the necessary OH nucleophile. There is indirect evidence for the occurrence of this Zn-OH attack on the mixed anhydride intermediate from study of model systems.\textsuperscript{[160]}

The naturally occurring polymeric carboxylic acid derivatives of vital biochemical importance are proteins (polyamino acids), polysaccharides (polycarbonates) and nucleic acids, (polynucleotides). Prostaglandins are naturally occurring carboxylic acids that are widely distributed in mammalian tissue. They play a vital role in many biological processes, including blood platelet aggregation (clotting), the regulation of blood pressure, the pain response and fertility control. The prostaglandins are all C\textsubscript{20} compounds related to eicosanoic acids or prostanoic acid in structure.\textsuperscript{[161,163,164]}

\begin{center}
\begin{tikzpicture}
\node[draw=none] (1) {eicosanoic acid};
\node[draw=none] (2) at (10,0) {prostanoic acid};
\end{tikzpicture}
\end{center}
Carboxyl group finds wide applications in biomedical and other related industries. Dacron, an important polyester formed from diethyl terephthalate and ethylene glycol\textsuperscript{(161)}, is of exceptional strength and is widely used to make fabrics and film backing for recording tapes.\textsuperscript{(162)} Dacron fabrics have been used to repair or replace segments to blood vessels and heart valves. The parabens-esters of p-hydroxy benzoic acids are used to inhibit moulds and yeast in cosmetics, pharmaceuticals and food.\textsuperscript{(162)} Various types of esters are used in the food and perfume industries as flavour and for fragrance compounds.\textsuperscript{(161)} Some are referred below.

\[
\begin{align*}
\text{ethyl formate} & \quad \text{(rum)} \\
\text{octyl acetate} & \quad \text{(oranges)} \\
\text{methyl salicylate (oil of wintergreen)} &
\end{align*}
\]

Olestra, ester of sucrose with fatty acids, is a nutritional novelty, a product that tastes like a cooking oil but that adds no calories to the diet.\textsuperscript{(165-167)} Metal naphthenates such as copper naphthenates are used as fungicides; aluminium naphthenates are used as a gelling agent in “napalm” and cobalt naphthenates find use in paints. Dilute solution of acetic acid is used as vinegar. Acetate ion is major intermediate in the metabolism of carbohydrate, lipids and proteins. Calcium and sodium salt of propanoic and sorbic acids are used in baked foods and processed cheese. They are also present in fruit juices, wines, soft drinks etc. Sodium benzoate is used as ingredient for beverages, syrups, pickles, fruit salads
Many of the insect pheromones are carboxylic acids or their derivatives. The interesting examples are given below.

\[ \text{isoamyl acetate} \quad \text{cis-7-Dodecenyl acetate} \]

(honey bee alarm pheromone) (cabbage looper sex pheromone)

Aspirin (acetyl salicylic acid) is the most widely used drug in the world. It is used as a pain reliever (analgesic), in the reduction of fever (antipyretic) and also as an agent for anticoagulation of blood. Nylon 6,6 an important polyamide, prepared from adipic acid and hexamethylenediamine, is more resistant to combustion and is immune to insect attack. In medicine, nylon is used in specialised tubing and as velour for blood contact surfaces. Nylon sutures were the first synthetic sutures and are still commonly used. High level of the omega-3 fatty acids in marine oils provides protection against diseases. Human milk contains ω-3-docosahexaenoic acid, which is essential for the retina and brain of infants.
The tartrate complex of antimony(III), $K_2[\text{Sb}_2(\text{d-C}_4\text{O}_6\text{H}_2)_2].3\text{H}_2\text{O}$, has been known in medicine for over 300 years. It is used for treatment of schistosomiasis and leishmaniasis and its toxic side effects can be mediated by pencilamine. Reports are available on several metal carboxylate complexes which are known to be exhibiting good anti-tumour activities having less toxic effects.\(^\text{[169,170]}\)

The important role of the dicarboxylic acids in life systems has long been well recognized by chemists and biologists. A wide range of simple aliphatic acids are ubiquitous in solids and plants viz., oxalic, malonic, malic, tartaric and citric, which are known for their metal-binding roles.\(^\text{[171]}\) Tiffen was the first to identify iron-citrate complex in plant xylem.\(^\text{[172,173]}\) This oxalato chromate(III) anion has been found in the leaf tissues of a plant species.\(^\text{[174]}\) For animal fluids also Ca\(^{2+}\) and Mg\(^{2+}\) citrate bindings are found. Ascorbic acid plays an important role in human iron metabolism— as one of the postulated factors aiding iron uptake. It reduces Fe\(^{III}\) to Fe\(^{II}\) and also reduce Cu\(^{II}\) to Cu\(^{I}\).\(^\text{[175]}\)

### 1.4 Metal Carboxylates as Synthetic Model Complexes

The report of a bioactive Cr-nicotinic acid complex sparked a brief but intense interest in the preparation of synthetic Cr-nicotinic acid complexes. Among the well-characterized Cr-nicotinic acid complexes, coordination of the ligand via the pyridine N and via the carboxylate oxygens have both been established.\(^\text{[176-178]}\) A Cr-nicotinic acid-gluthathione complex has demonstrated appreciable activity in rat adipocyte assays.\(^\text{[179]}\)
Well-characterized chromium-salt anion assemblies bridged by carboxylate ligands are few with the exception of those possessing the ‘basic acetate’ type structure $[\text{Cr}_3\text{O(O}_2\text{CR})_6\text{L}_3]^+$. ($L = \text{H}_2\text{O}, \text{py}$) \textbf{(XXIX)}.

These trinuclear oxo-centered metal carboxylate assemblies have been of intense interest for several decades; these compounds serve as important models to test theories of magnetic coupling between metal ions in multinuclear systems\textsuperscript{(180)} and as precursors to larger multinuclear assemblies whose novel magnetic properties have only recently been realized. Two tetranuclear, carboxylate-supported assemblies have been reported; $[\text{Cr}_4\text{S(OAc)}_8\text{(H}_2\text{O})_4]^{2+}$ \textsuperscript{(181)} and $[\text{Cr}_3\text{O}_2\text{(OAc)}_7\text{(bipy)}_2]^+$ \textsuperscript{(182)} which have interesting structures.

1.5 Metal carboxylates in Catalysis

Carboxylates of general formula $\text{Rh}_2(\mu_2\text{O}_2\text{CR})_4$ are known for their catalytic reactions such as hydrogenation or cyclopropanation of alkenes. They can act as hydrogenation catalyst in DMF and in presence of phosphenes. Cuprous carboxylate complexes are considered to be the first complexes involved in homogeneously catalysed hydrogenation reactions.\textsuperscript{(183,184)} Another example which
is of synthetical importance is Hurtely reaction, involving the condensation of benzoic acid units with \( \beta \)-carbonyls,\(^{185-187}\)

\[
\begin{align*}
\text{CO}_2\text{H} & + \text{H}_2\text{C}(\text{C}_\text{R}_1)\text{(C}_\text{R}_2) & \text{CO}_2\text{Na}^+ \text{NaOEt} & \text{[Cu]}_{\text{kat}} \\
\text{COR} & \text{COR} & \text{CHCOR}^2 & \text{COR}^1
\end{align*}
\]

Similarly Lead tetra acetate is known for its strong but selective oxidising property in organic chemistry,\(^{188}\)

\[
\begin{align*}
\text{n- C}_4\text{H}_9\text{O}_2\text{CCH-CHCO}_2\text{C}_4\text{H}_9^- n & + \text{Pb(OAc)}_4 \xrightarrow{\text{C}_6\text{H}_6} 2 \text{n- C}_4\text{H}_9\text{O}_2\text{CC}=\text{O} \\
\text{di-butyl tartrate} & \text{1-butyl 2-oxo-ethanoate}
\end{align*}
\]

The ability of some metal dicarboxylate complexes, especially manganese dicarboxylate complexes to act as functional models for the non-haem catalases which have been recently isolated from Lactobacillus plantrum, is known.\(^{189,190}\) Such biomimetic materials can be used not only to shed light on the chemistry of biological materials but also as catalysts in processes such as low temperature bleaching. The catalytic activity of these species for the disproportion of hydrogen peroxide, a reagent which is important for cell detoxification, has been investigated in detail inorder to establish the mode of action of the natural catalases,\(^{191}\)
1.6. **Scope and Objectives**

A closer look at the structural aspects of all the known metal dicarboxylate reveals that there is a major role for any additional ligand in deciding the final structure of the framework. This is evident from the structural details available for mixed ligand complexes of metal dicarboxylates having Lewis-bases as an additional constituent. The reports of such metal complexes often appear as random references and it is seen that their preparation involves combined interaction of metal salts, dicarboxylic acids and Lewis-bases in appropriate conditions. As evident from the synthetic procedure and their compositions these framework materials can be considered to be getting formed by chance rather than by choice or selection. Further, the anions of the metal salt employed are also seen to be complicating the nature of the final products. Therefore a more strategic route to generate varieties of tailored framework materials of mixed ligand complexes of choice could be the interaction of Lewis-bases directly with metal dicarboxylate complexes.

The present study is aimed at generating such molecular frameworks having diverse compositions and structural features by systematic study involving the interaction of polymeric metal dicarboxylates with varieties of Lewis-bases in various conditions and stoichiometry. It has also been well demonstrated that dicarboxylate systems with variable intervening spacer moieties when interacted with metal ions yield interesting and novel supramolecular architectures whose features and dimensionality get dictated by the nature of metal ion, spacer function and reaction
conditions.\textsuperscript{[192,193]} We could generate several new mixed ligand complexes with varying compositions by Lewis-bases mediated fragmentation of polymeric transition metal dicarboxylate systems.

The main focus made in the present study are on the following aspects.

1. The selection of the dicarboxylic acids is made such that they have varying nature of the spacer moiety between the two carboxylate functions. The dicarboxylic acids chosen are succinic acid (\(\text{H}_2\text{succ}\)), malonic acid (\(\text{H}_2\text{mal}\)), 1,4-benzene dicarboxylic acid (\(\text{H}_2\text{tpa}\)) and oxalic acid (\(\text{H}_2\text{ox}\)) having \(-\text{CH}_2\text{CH}_2-\), \(-\text{CH}_2-\), phenylene moieties respectively as spacer group for the first three and no spacer for the oxalic acid. The selection is made such that we get systems with both flexible and rigid functions. The Lewis-bases selected are ethylenediamine (en), 2,2'-bipyridyl (bipy), 1,10-phenanthroline (phen), 1,3-diaminopropane (pn) and pyridine (py) which are either chelating, conjugatively chelating or monodentate in nature so that the systems with diverse structural variations could be generated. We have confined our studies mostly to nickel(II), cobalt(II) and copper(II) ions.

2. Generation of metal succinates by various synthetic routes and their structural characterisation.

3. Systematic investigations on the nature of interaction of various Lewis-bases with the metal succinates developed above and characterisation of the resulting framework materials.
4. Attempts to grow single crystals of the above complexes and the crystal as well as the molecular structure determination by X-ray diffraction techniques.

5. Since there is the possibility of reversible adduct formation with some of the Lewis-bases and metal succinates with the possible structural modification, attempt has also been made to study the thermal decomposition features of the adduct formed in the above cases and also the evaluation of the associated thermodynamic parameters.

6. Developing various metal malonates and their characterisation by spectral and other analytical measurements.

7. Investigations on the Lewis-bases mediated fragmentation of the polymeric metal malonates with the various Lewis-bases and detailed structural characterisation of the resulting mixed ligand complexes as generated above.

8. Attempts to grow single crystal of some of the adducts of metal malonates and their detailed crystal and molecular structure characterisation by XRD technique.

9. Detailed thermal characterisation of both metal malonates and their various Lewis-base adducts and also the evaluation of the thermodynamic parameters.

10. Generation of metal oxalates by various synthetic routes and their characterisation by spectral and other analytical techniques.
11. Systematic and structural characterisation of the adducts generated by the interaction of various Lewis-bases with various metal oxalates.

12. Detailed investigation on the thermal features of both the metal oxalates as well as their various Lewis-base adducts generated as above.

13. Generation of metal terephthalate complexes and their interaction with various Lewis-bases and also the spectral and structural characterisation of the products formed. Investigations on the thermal decomposition features of the metal terephthalates and their various Lewis-base adducts are also attempted.
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