

CHAPTER 1

INTRODUCTION

The Fischer-Tropsch (FT) process is a complex process whereby coal or natural gas is converted to more valuable products such as liquid fuels. This technology was pioneered in the early 1900's and has since evolved into a highly lucrative industry.

FT technology is at the heart of Sasol's operations. It is the starting point for the evolution of many commercially important products and has proved to be an exceptionally efficient route to high quality synthetic fuels. Despite the high selectivity of FT catalysts to yield the desired products, undesirable products are also sometimes formed during FT processes. Oxygenates such as carboxylic acids are a common example and are undesirable in FT feed streams as they result in acid leaching of nickel-based hydrotreating catalysts which are found downstream of FT processes. It is therefore desirable to remove the carboxylic acids from the FT streams prior to hydrotreating to circumvent this problem.

In an initiative undertaken at Sasol Technology, workers have been engaged in studies to establish the best candidates to be used as commercial decarboxylation catalysts. It has been suggested that metal carboxylate interactions could be used to narrow the field in search of commercial decarboxylation catalysts¹. The proposal is that metals which yield carboxylates that decompose at low temperatures might also be capable of decomposing the carboxylic acids at low temperatures. Studies of the thermal

decomposition behaviour of various metal carboxylates have been reported. Despite this, literature dealing with metal carboxylates is scant.

While metal carboxylates are by no means inaccessible, complete characterisation has been, with the exception of the acetates, largely neglected. Few attempts have been made to conduct a systematic study across periods, down groups or with variation of the carboxylate chain length and thus deficiencies exist in the carboxylate literature.

1.1 Aims of this study

The primary aim of this study is the characterization – especially the thermal properties – of cobalt(II) carboxylates, which are of particular interest as they may form under FT conditions where cobalt catalysts are employed. By systematically varying the length of the organic part of the ligand, we hope to shed some light on the cobalt carboxylate complexes and in particular their thermal properties.

This study also attempts to summarize the known literature on metal carboxylate complexes, with particular emphasis on cobalt carboxylate chemistry, and to build on this knowledge to create an increased understanding of these compounds.

The scope of this project includes a study of the $C_2 - C_{10}$ carboxylates of cobalt(II). The spectroscopic and thermal properties of these compounds are discussed below. The bonding modes associated with carboxylate complexes are briefly introduced in the sections below.

1.2 Background

Many metal carboxylates have been known since ancient times. The first use of such materials appears to be in the formation of lead linoleates found in early paints used for mummification². The lubricating properties of these metallic carboxylates were also noticed as early as 1400 B.C., when lime soap thickened lubricants were used for the wheels of chariots. With the dawn of the industrial revolution in the 1800's, rapid progress in the field of metal carboxylates was made. During this time, the use of metal carboxylates in the paint industry also boomed and before long lead and manganese carboxylates were also being used as driers in paints². A large number of other uses for these compounds were discovered in later years, particularly as waterproofing materials and for adjusting the hardness of organic materials.

Despite their long history, the interest in the chemistry of metal carboxylates has persisted and many workers have investigated their fundamental characteristics such as carboxylate bonding modes, crystal structures and thermal properties. The most comprehensive reviews pertaining to metal carboxylates are contained in a text published by Mehrotra in 1983². In his book, Mehrotra discussed the physicochemical properties, synthesis, bonding and structure of a variety of metals and carboxylate species. Since the publication of Mehrotra's book, several new carboxylate structures have been reported. More recent areas of interest in the field of metal carboxylates include their use as precursors in catalyst synthesis³, initiators of photo-oxidative degradation in polymers⁴, rubber adhesion promoters in the tyre industry⁵ and in supramolecular chemistry⁶.

Metal carboxylate species stem from carboxylic acids. Carboxylic acids are ionized in aqueous solution to produce a resonance stabilized carboxylate

anion and a hydrated proton, shown in Fig. 1.1. Two resonance forms exist, which give rise to equivalent ions. Owing to the equivalence of these resonance forms, carboxylate ions are far more stable than their free acid counterparts.

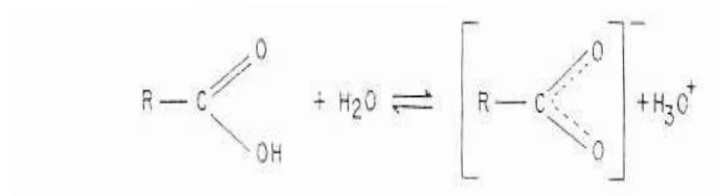
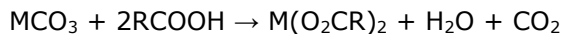
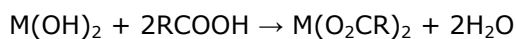
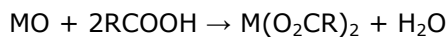


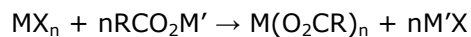
Fig. 1.1 Resonance in carboxylate ions²

The preparation of metal carboxylates can be achieved in a variety of ways, the most common of which are: (i) fusion method, (ii) precipitation method and (iii) reactions in non-aqueous media².

The fusion method involves refluxing a metal or metal oxide, hydroxide or carbonate with an appropriate molar ratio of a carboxylic acid, according to the reaction(s):



In the precipitation method, water-soluble salts of the metal are treated with stoichiometric amounts of the alkali salts of the desired carboxylic acid in aqueous solution, i.e.:



(Where $\text{M}' = \text{Na}^+, \text{K}^+, \text{NH}_4^+$; $\text{X} = \text{Cl}^-, \text{NO}_3^-, \text{SO}_4^{2-}$ etc.)

Reactions in non-aqueous media have been found to be useful for synthesizing carboxylates of less electropositive metals e.g. aluminium, the salts of which are highly susceptible to hydrolysis in aqueous media.

Electrochemical synthesis of transition metal carboxylates has also proved to be successful⁷, as has been the sol-gel method⁸.

The carboxylate complexes of the different elements can be divided into four categories depending on the nature of the $\text{M}-\text{O}_2\text{CR}$ interaction. Fig. 1.2 shows these various carboxylate bonding modes.

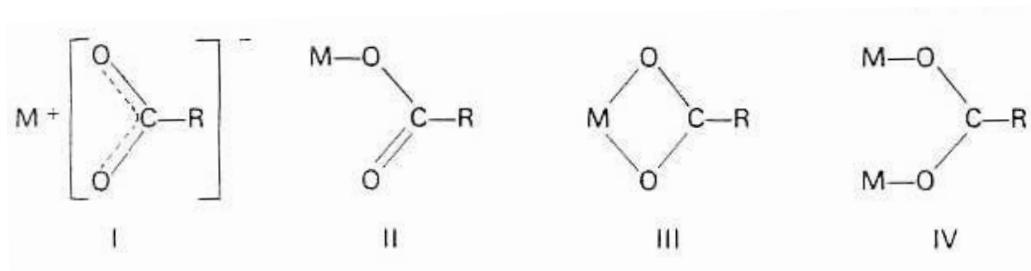


Fig. 1.2 Bonding modes of carboxylate ligands²

The carboxylates of highly electropositive elements such as sodium and potassium are ionic in nature (Fig. 1.2: I). The other bonding modes (Fig. 1.2: II – IV) are observed for most other metals.

Monodentate coordination (Fig. 1.2: II) is found in lithium and cobalt acetate².

Of all the possible modes of carboxylate coordination to a metal, the least favoured is bidentate chelating (Fig. 1.2: III) and only a few confirmed examples of this type of interaction are known. Four-membered ring zinc and uranyl complexes have been identified by X-ray crystallography⁹.

Even less common are eight coordinated metal complexes, such as $\text{Sn}(\text{O}_2\text{CCH}_3)_4$ ¹⁰. Steric crowding around the metal centre results in one carboxylate group assuming an asymmetrical arrangement. In such an instance the carboxylate moiety functions as a bidentate asymmetrical chelating group (Fig. 1.3).

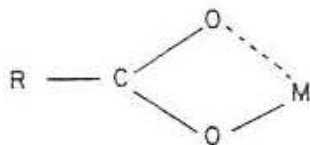


Fig. 1.3 Bidentate asymmetrical chelating $\text{M}(\text{O}_2\text{CR})_2$

The geometry of the carboxylate anions is particularly suited to the formation of complexes in which the carboxylate ligand is coordinated to the metal in a bridging mode (Fig. 1.2: IV). The common occurrence of polynuclear carboxylates reflects the strong bridging tendency of carboxylate anions.

Four types of carboxylate bridges (Fig. 1.4) have been identified:

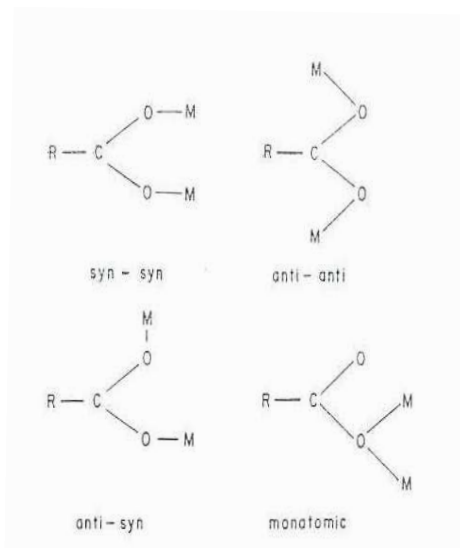


Fig. 1.4 Carboxylate bridges²

Anti-anti and *anti-syn* bridging has been known to give rise to an array of metallo-organo polymers¹¹. Polymers of this type include dimeric units linked to other dimeric units and monomeric units linked by bridging carboxylates (Fig. 1.5).

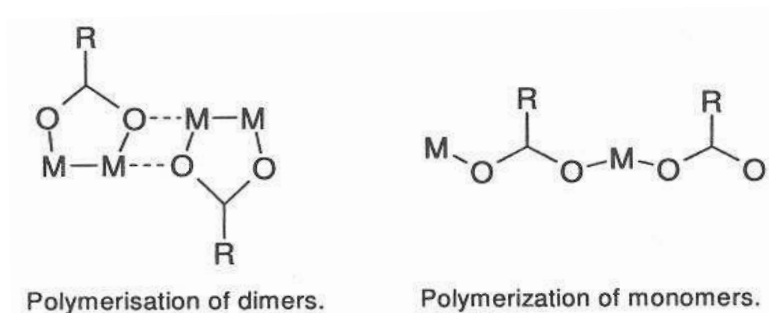


Fig. 1.5 Polymerisation modes of carboxylate units¹²

Syn-syn geometry brings metal atoms close enough together to form clustered structures with metal-metal bonds. Tetranuclear tungsten and molybdenum carboxylates¹³, polynuclear chromium(III) carboxylates¹⁴ and binuclear copper(II) carboxylates¹⁵ are well known examples. Fig. 1.6 illustrates the common structure for carboxylate-bridged metal dimers.

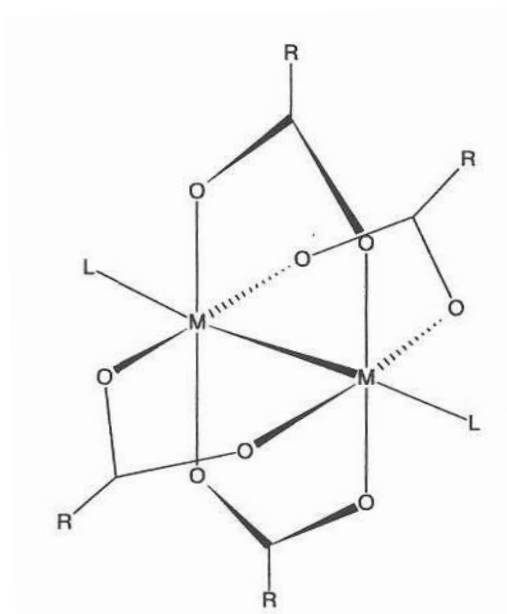


Fig. 1.6 Common structure for carboxylate-bridged metal dimers¹²

Mehrotra and Bohra observed that in an aqueous solution of metal carboxylates, their solubility, conductivity and solubilizing power decrease while viscosity, surface tension and refractive index increase with increasing length in their carboxylate chains². The solubility of metal carboxylates depends on a number of factors, such as temperature, nature of the acid, the presence of impurities and the nature of the carboxylate coordination.

Since both polar and non-polar groups are united within the same molecule in metal carboxylates, they exhibit orientation phenomena and form gels, sols and pastes. These characteristics of metal carboxylates have been exploited in a number of industrial applications¹⁶.

Due to the variety of bonding modes found in metal carboxylates, solid-solid phase transitions that entail shifting of the coordinated oxygen atoms to different metal centers are not uncommon e.g. copper carboxylates¹⁷. There are also documented cases of metal carboxylates, such as lead butyrate,

forming liquid crystalline phases between the isotropic liquid phase and crystal phases¹⁸.

1.3 Characterisation

1.3.1 Infrared spectroscopy

Monomeric carboxylic acids absorb strongly in the 1760-1770 cm^{-1} ⁽¹⁹⁾ region due to the presence of a carbonyl group. In metal carboxylates this band is replaced by two peaks arising from the symmetric and asymmetric stretches of the COO^- groups. This is because in the carboxylate ion, bond orders of both C-O groups become equal due to electron delocalization, as discussed previously. Since the degree of interaction between the cationic centre (metal) and the coordinated carboxylate group affects delocalization and consequently the stretching frequencies of the carboxylate ion, the importance of infrared spectroscopy becomes clear. Strong absorptions in the region 1550-1620 cm^{-1} are typical of the asymmetric stretching mode of the COO^- group and weaker absorptions around 1400 cm^{-1} arise from the symmetric COO^- stretching mode¹⁹.

Nakamoto and co-workers proposed that the difference between the symmetric and asymmetric stretch for the carboxylate ion ($\Delta\nu_{\text{COO}^-}$) could be used as an indication of its bonding mode in a carboxylate compound²⁰.

Stoilova and co-workers conducted a comprehensive study on a series of metal acetates and suggested that a separation of 105 – 140 cm^{-1} could be associated with monodentate bonding, 145 – 185 cm^{-1} could be associated with bidentate chelate bonding and that 180 – 190 cm^{-1} could be an indication

of bidentate bridging bonding, although values as high as 200 cm^{-1} have been observed²¹.

Compounds with monodentate carboxylate ligands have a lower symmetry than those of the other forms and could therefore be expected to show similarities to the spectra of the monomeric undissociated carboxylic acids themselves. It has been reported that for monodentate carboxylate groups, the asymmetric COO^- stretching frequency increases while the symmetric COO^- stretch decreases relative to the values observed in RCOONa and RCOOK ². The reason for this dissimilarity has been ascribed to the break down in equality of the carbonyl groups. This situation is unique to the monodentate form of coordination.

Carboxylate groups retain C_{2v} symmetry (as seen in the free, unbound carboxylate ion) when acting as a bidentate bridging or bidentate chelating group. In such cases, the COO^- frequencies would not be expected to be very different from those seen in the free ion spectrum. Although coordination to a heavy metal atom may cause shifting in these frequencies, these changes are small and care must be taken when using them to establish coordination modes or to distinguish between bridging and chelating configuration².

Although infrared spectroscopy is not necessarily the most powerful technique for studying metal carboxylates, its importance cannot be ignored and careful consideration has been given to the recording and interpretation of infrared spectra in this project.

1.3.2 Thermal analysis

Thermal decomposition of metal carboxylates has also attracted considerable attention because (i) the end products possess important electronic/surface properties, and (ii) the decomposition mechanism is of interest for fundamental purposes.

Thermal stability studies of metal carboxylates reveal that the initial change observed when heating these compounds is the loss of any adduct molecules e.g. water. In some cases this is accompanied by side-reactions like hydrolysis in the case of less electropositive metals²². Further decomposition of the carboxylates generally depends on a number of factors, such as the nature of the metal, length of the carboxylate chain as well as the heating conditions employed during analysis.

The alkali metal salts of the higher carboxylic acids exist in a number of polymorphic forms. As a result, these tend to undergo several transitions prior to melting². The heavy carboxylates of bi-, tri- and tetravalent metals generally exist in the form of an amorphous powder. The general properties of these metal carboxylates depend largely on the nature of their cations as well as the length of the hydrocarbon chain of carboxylate ions.

As expected, being the first member of a homologous series, the decomposition of formates follows a course different to those of other carboxylates; for example the initial step in the decomposition of formates generally consists of the formation of either $\text{H}_2 + \text{CO} + \text{M}_2\text{CO}_3$ or $\text{H}_2 + \text{M}_2\text{C}_2\text{O}_4$ ²³. In the second stage of the latter reaction path, metal carbonates are formed with the loss of carbon dioxide.

Acetates and the higher carboxylates generally decompose via the formation of the metal carbonate and an organic component ketone, both of which decompose according to their own characteristics, into the corresponding metal oxide. The decomposition of metal carbonate into carbon dioxide and metal oxide appears to be governed by the electropositive nature of the metal².

Carbonates of the alkali metals are stable to higher temperatures, the decomposition of alkaline earth carbonates occurs at much lower temperatures and those of less electropositive metals such as aluminium occur at such low temperatures that even in the initial stages, decomposition of the carboxylate is observed to occur with carbon dioxide evolution.

For other metals like silver, the final product is the metal rather than the metal oxide²⁴.

Systematic studies of the thermal properties of metal carboxylates have been largely limited to acetates in the past^{25,26,27}. More recently there have been reports published on oxalates, succinates and malonates^{28,29}. Work has focused largely on the effects of varying the cation (metal centre) for a particular carboxylate group e.g. acetate or oxalate, but no systematic studies have been completed to assess the effect of varying the organic chain length for the same cation.

Decomposition of compounds in this project has been studied using a combination of thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC). TGA shows mass loss as a function of temperature and DSC in turn shows energy changes as a function of temperature. The

combination of the two techniques provides a powerful tool for thermal characterisation.

1.4 References

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