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Synthesis and Characterisation of New Dimolybdenum (II,II) Dicarboxylates and Their Use as Polymerization Catalysts

Elizabeth Whelan
Technological University Dublin

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**Synthesis and Characterisation of
New Dimolybdenum(II,II) Dicarboxylates and their
use as Polymerization Catalysts**

Elizabeth Patricia Whelan

M.Sc.

1996

Synthesis and Characterisation of
New Dimolybdenum(II,II) Dicarboxylates and their use as
Polymerization Catalysts

Elizabeth Patricia Whelan B.Sc.

Chemistry Department

St. Patrick's College

Maynooth

Co. Kildare

A thesis presented to the National University of Ireland

for the degree of

Master of Science

August 1996

Research Supervisor: Dr. G.Malachy McCann (St. Patrick's College, Maynooth)

Dr. Michael Devereux (Dublin Institute of Technology)

Head of Department: Professor C.M. Quinn

DECLARATION

This thesis has not been submitted before,
in whole or in part, to any other university
for any degree, and is, except where
otherwise stated, the original work of the author.

Signed, *Elizabeth P. Whelan*

Elizabeth P. Whelan

ACKNOWLEDGEMENTS

I would like to thank Professor Martin Quinn for granting me the privilege of doing my M.Sc. research at St. Patrick's College, Maynooth. I would especially like to express my appreciation to my research supervisors Dr. Malachy McCann and Dr. Michael Devereux for all their advice and guidance over the past two years. I would also like to thank Dr. Eoghan Mac Giolla Coda, Dr. Andy Beaumont and Dr. Denise Rooney for their counsel at different stages of my research work.

I would like to thank the Dublin Institute of Technology for a scholarship to carry out this research. I would also like to thank Dr. Marlene Proctor for the use of facilities at the D.I.T., Bob Kavanagh for his help at administration and all the technicians and staff in the White House.

I wish to thank my research colleagues Fergal Humphries and Fergal Cronin for all their help during the past two years. I would like to thank Shane for all his help with the computer. To them and all the other postgrads., especially Martin Curran and Maura Jackman, Barry and Vivienne I express my appreciation for their friendship and encouragement. I would also like to thank the staff of the Chemistry Dept. St. Patrick's College Maynooth, particularly Rosemary, Martin MMC. and Ria for all their help and friendship over the past two years.

I thank my parents and family for all their support and understanding down through the years. Finally, and most importantly I would like to thank Brónagh and Abina for all their encouragement, optimism and friendship over the past few years.

*Ba mhaith liom
an tráchtas seo
a thoirbirt do mo
thuismitheoirí*

ABSTRACT

The purpose of this work was to prepare a series of new dimolybdenum(II,II) dicarboxylate complexes, to characterize the complexes and to investigate their use as potential catalysts for the ring-opening metathesis polymerization (ROMP) of the bicyclic monomer norbornene.

The known dimolybdenum(II,II) complexes $[\text{Mo}_2(\mu\text{-O}_2\text{CCH}_3)_4]$ and $[\text{Mo}_2(\text{CH}_3\text{CN})_8][\text{BF}_4]_4$ were employed as starting materials and a series of α,ω -dicarboxylic acids $\text{HO}_2\text{C}(\text{CH}_2)_n\text{CO}_2\text{H}$ ($n = 0-8$) and $\text{HO}_2\text{C}(\text{C}_6\text{H}_4\text{OCH}_2\text{CH}_2\text{O})\text{CO}_2\text{H}$ benzene-1,2-dioxyacetic acid (bdoaH₂) were used as the incoming ligands. New dimolybdenum(II,II) dicarboxylate complexes of general formula $[\text{Mo}_2(\text{O}_2\text{C}(\text{CH}_2)_n\text{CO}_2)(\text{CH}_3\text{CN})_x]_2[\text{BF}_4]_{4-y}\cdot y\text{CH}_3\text{CN}$ and $[\text{Mo}_2(\text{bdoa})\text{-}(\text{CH}_3\text{CN})_x]_2[\text{BF}_4]_{4-y}\cdot y\text{CH}_3\text{CN}$ ($n = 0-8$, $x = 0-6$, $y = 0-6$) were prepared. The X-ray crystal structure of the butanedioate complex $[\text{Mo}_2(\text{O}_2\text{C}(\text{CH}_2)_2\text{CO}_2)\text{-}(\text{CH}_3\text{CN})_6]_2[\text{BF}_4]_4\cdot 3\text{CH}_3\text{CN}$ showed it to be tetrameric (dimer of dimers), in which bridging bidentate $\text{O}_2\text{C}(\text{CH}_2)_2\text{CO}_2$ ligands link the four crystallographically identical molybdenum atoms.

In an attempt to improve the air-stability of the new complex salts $[\text{Mo}_2(\text{O}_2\text{C}(\text{CH}_2)_n\text{CO}_2)(\text{CH}_3\text{CN})_x]_2[\text{BF}_4]_{4-y}\cdot y\text{CH}_3\text{CN}$ the complexes themselves were reacted with the bidentate nitrogen donor ligands, 2,2'-bipyridine and 1,10-phenanthroline. These reactions resulted in the formation of purple tetrafluoroborate salts which proved difficult to handle and more air-sensitive than the parent complexes.

In the presence of EtAlCl₂ cocatalyst all of the complexes [Mo₂(O₂C(CH₂)_nCO₂)(CH₃CN)_n]₂[BF₄]₄·γCH₃CN and complex [Mo₂(bdoa)-(CH₃CN)_n]₂[BF₄]₄·γCH₃CN successfully polymerized norbornene. The complexes containing either 2,2'-bipyridine or 1,10-phenanthroline ligands also polymerized norbornene in the presence of EtAlCl₂, but proved to be less active catalysts than the parent complexes [Mo₂(O₂C(CH₂)_nCO₂)(CH₃CN)_n]₂[BF₄]₄·γCH₃CN.

¹³C {¹H} NMR studies of the polynorbornene samples revealed that, in general, there was a close similarity in the microstructures of the individual polymers produced by the various molybdenum(II) catalysts. The polymer yields and σ_c values were found to be similar to those previously obtained using other dimolybdenum(II,II) complexes. Gel permeation chromatographic analysis of the products from the polymerization reactions revealed that many of the catalysts produced low molecular weight oligomers in addition to high molecular weight polymers.

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ABBREVIATIONS

eda	ethanedioic acid
prda	propanedioic acid
bda	butanedioic acid
pda	pentanedioic acid
hxda	hexanedioic acid
hda	heptanedioic acid
oda	octanedioic acid
nda	nonanedioic acid
dda	decanedioic acid
bdoaH ₂	benzene-1,2-dioxyacetic acid
bipy	2,2'-bipyridine
phen	1,10-phenanthroline
py	pyridine
Hbim	benzimidazole
M.W.	molecular weight
IR	infrared
s, m, br, w	strong, medium, broad and weak intensity, respectively (IR)
ν	wavenumber (cm ⁻¹)
$\Delta\nu$	wavenumber separation (cm ⁻¹) { $\Delta\nu_{asym}$ - $\Delta\nu_{sym}$ }
<i>asym</i> , <i>sym</i>	asymmetric and symmetric, respectively
nmr	nuclear magnetic resonance
UV-Vis	ultraviolet - visible

ϵ	extinction coefficient ($\text{dm}^3 \text{mol}^{-1} \text{cm}^{-1}$)
λ_{max}	wavelength of maximum absorbance (nm)
Å	angström (10^{-10}m)
B.M.	Bohr magneton
T.B.A.P.	tetrabutylammonium perchlorate
G.C.	glassy carbon
Pt	platinum wire
Ag/AgCl	silver/silver chloride reference electrode (3.5 M in aqueous KCl)
L	ligand
Me	methyl
en	ethylenediamine
<i>ca.</i>	circa
GPC	gel permeation chromatography
ROMP	ring-opening metathesis polymerization
M_n	number average molecular weight
M_w	weight average molecular weight
P.D.	polydispersity

INTRODUCTION

I.1 CARBOXYLIC ACIDS

I.1.1 Monocarboxylic Acids

Carboxylic acids possess a carboxyl group and are represented by the formula RCO_2H (*Figure 1*), where R can be aliphatic, alicyclic or aromatic.

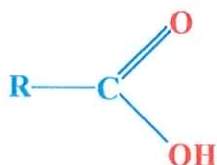


Figure 1

The saturated monocarboxylic acids are also referred to as the “fatty acids”, a name which arose from the fact that some of the higher members, particularly palmitic ($\text{CH}_3(\text{CH}_2)_{14}\text{CO}_2\text{H}$) and stearic ($\text{CH}_3(\text{CH}_2)_{16}\text{CO}_2\text{H}$) acid, occur in natural fats. Their general formula is $\text{C}_n\text{H}_{2n+1}\text{CO}_2\text{H}$, and since only one of the carboxyl group hydrogen atoms is replaceable by a metal ion the monocarboxylic acids are *monobasic*. The lower members of the saturated carboxylic acids are liquids at room temperature, but as the series is ascended the individual members become increasingly more viscous and those higher than decanoic acid ($\text{CH}_3(\text{CH}_2)_8\text{CO}_2\text{H}$) are crystalline solids. The lower members are far less volatile than is to be expected from their molecular weight, and this can be explained by intermolecular hydrogen bonding.

In the case of solid carboxylic acids the geometry of the carboxyl group has been determined using X-ray crystallography, and electron diffraction has been used to study liquid and gaseous samples. The average dimensions for crystalline dimers are shown in *Figure 2*.¹

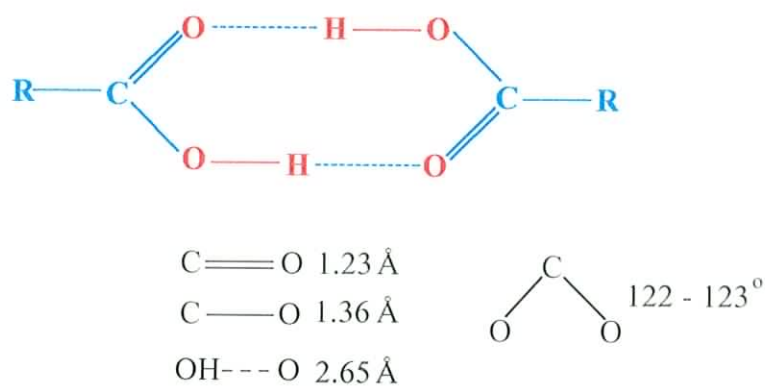


Figure 2

In aqueous solution carboxylic acids tend to dimerize in the open form (*Figure 3*) and not in the cyclic form (*Figure 2*). The latter form is observed in the solid and vapour states and also in non-ionizing solvents.²

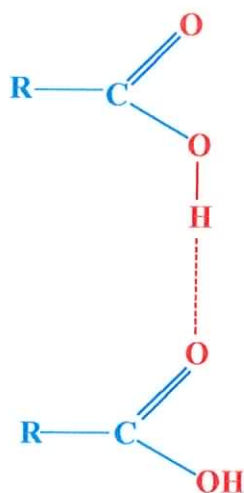


Figure 3

Carboxylic acids ionize to give carboxylate anions (*Figure 4*). The two C-O bond lengths (1.26 Å) are identical in the carboxylate ions.² While most carboxylic acids have a $\text{p}K_{\text{a}}$ value² of *ca.* 4.8 electron-withdrawing groups will stabilise the carboxylate anion by inductive effects, and thus, increase the acidity and lower the $\text{p}K_{\text{a}}$ value.

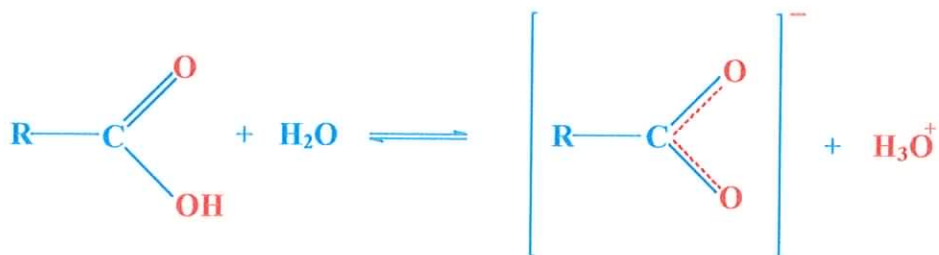


Figure 4

The principal IR absorption bands³ of free carboxylic acids are listed in *Table 1*.

Table 1. Principal IR bands found in carboxylic acids

Frequency (cm ⁻¹)	Remarks
3560-3500	Free O-H stretch
3300-2500	Broad hydrogen-bonded O-H stretch
1725-1700	C=O stretch for saturated and acyclic acids
1705-1690	C=O stretch for unsaturated acids

I.1.2 Dicarboxylic Acids

Dicarboxylic acids contain two carboxyl groups. The general formula of the saturated dicarboxylic acids is $\text{C}_n\text{H}_{2n}(\text{CO}_2\text{H})_2$, and the best known examples are those which have the two carboxyl groups at the opposite ends of the carbon chain, *i.e.* α,ω -dicarboxylic acids $\text{HO}_2\text{C}(\text{R})\text{CO}_2\text{H}$. The dicarboxylic acids are commonly known by names which indicate their source. For example, oxalic acid ($\text{HO}_2\text{CCO}_2\text{H}$) is so-called as it is found in plants of the *oxalis* group. All of the dicarboxylic acids are crystalline solids, the lower members being soluble in water and the solubility decreasing with an

increase in molecular weight. The structures and systematic names of a number of aliphatic dicarboxylic acids are given in *Table 2*.

Table 2. Some aliphatic dicarboxylic acids

IUPAC Name	Formula	Common Name
Ethanedioic	HO ₂ C-CO ₂ H	Oxalic
Propanedioic	HO ₂ C(CH ₂)CO ₂ H	Malonic
Butanedioic	HO ₂ C(CH ₂) ₂ CO ₂ H	Succinic
Pentanedioic	HO ₂ C(CH ₂) ₃ CO ₂ H	Glutaric
Hexanedioic	HO ₂ C(CH ₂) ₄ CO ₂ H	Adipic
Heptanedioic	HO ₂ C(CH ₂) ₅ CO ₂ H	Pimelic
Octanedioic	HO ₂ C(CH ₂) ₆ CO ₂ H	Suberic
Nonanedioic	HO ₂ C(CH ₂) ₇ CO ₂ H	Azealic
Decanedioic	HO ₂ C(CH ₂) ₈ CO ₂ H	Sebacic

Dicarboxylic acids have similar IR spectra to those of their monocarboxylic acid counterparts. However, some dicarboxylic acids have been found to exhibit two absorption bands in the carbonyl region.³ For example, ethanedioic acid shows ν_{\max} at 1710 and 1690 cm⁻¹, and propanedioic acid shows ν_{\max} at 1740 and 1710 cm⁻¹. This effect is reduced in butanedioic acid, which has a weak band at 1780 cm⁻¹ and a strong absorption band at 1700 cm⁻¹. Higher members of the series show only a single absorption band at 1700 cm⁻¹. Therefore, if the first few members of the series are ignored, the IR spectra of the dicarboxylic acids can be regarded as being typical of those of the monocarboxylic acids.

Dicarboxylic acids contain two carboxyl groups and thus they have two pK_a values. The pK_a values for the first and second dissociations (pK_a^1 and pK_a^2 , respectively) of a series of aliphatic dicarboxylic acids are listed in *Table 3*, along with the pK_a values of the corresponding monocarboxylic acids.

Table 3. pK_a values of carboxylic acids

Monocarboxylic Acid	pK_a	Dicarboxylic Acid	pK_a^1	pK_a^2
Ethanoic	4.76	Ethanedioic	1.23	4.27
Propanoic	4.87	Propanedioic	2.86	5.70
Butanoic	4.81	Butanedioic	4.21	5.64
Pentanoic	4.82	Pentanedioic	4.34	5.27
Hexanoic	4.88	Hexanedioic	4.41	5.28

From *Table 3* it is seen that the pK_a^1 values of the dicarboxylic acids are lower than the pK_a values of the corresponding monocarboxylic acids. However, the pK_a difference decreases as the chain length of the diacids increases. Also, the pK_a^2 values initially are much greater than the pK_a^1 values, but again this difference decreases as the chain length of the diacids increases. The relative values of pK_a^1 and pK_a^2 are dictated in terms of an electrostatic effect which is quite strong if the two carboxylate functions are close together, and this tends to inhibit double deprotonation of the diacid. pK_a^1 values tends towards pK_a^2 values as the separation between the two carboxylate groups increases.

I.2 METAL CARBOXYLATE COMPLEXES

I.2.1 Coordination Modes of Carboxylates²

Carboxylate complexes are known for almost every metal in the periodic table. They have a wide range of commercial and industrial applications, ranging from their use in ancient times as soaps and in paints, to their modern-day use as specialised homogeneous catalysts. Carboxylate anions with the general formula RCO_2^- are versatile ligands which are capable of (i) existing simply as a counterion or, (ii) binding to metal centres. Carboxylate complexes can be divided into the following four groups in accordance with the nature of the $\text{M-O}_2\text{CR}$ interaction.

Ionic Carboxylates

The carboxylate salts of Na, K, Rb, and Cs have been shown to be ionic, and the structure of sodium formate is shown in *Figure 5*.⁴

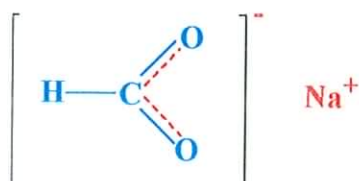


Figure 5

Unidentate Carboxylates

In lithium acetate dihydrate $\text{Li}(\text{O}_2\text{CCH}_3)(\text{H}_2\text{O})_2$ the acetate ion functions as a unidentate ligand (*Figure 6*).⁵

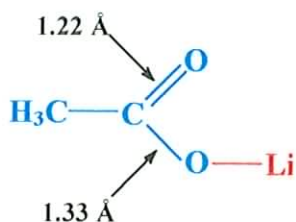


Figure 6

Bidentate Chelating Carboxylates

Carboxylates may chelate to the metal atom in either a symmetrical fashion (both metal-oxygen bonds are of equal length; *Figure 7a*) or in an unsymmetrical mode (one metal-oxygen bond is longer than the other; *Figure 7b*). In zinc acetate dihydrate $\text{Zn}(\text{O}_2\text{CCH}_3)_2 \cdot 2\text{H}_2\text{O}$ ⁶ the bonding mode of the acetate ligands is symmetrical bidentate chelating. The tin(IV) complex $[\text{Sn}(\text{O}_2\text{CCH}_3)_4]$ shows unsymmetrical bidentate chelation of the acetates.⁷



Figure 7

Bidentate Bridging Carboxylates

The geometry of the carboxylate ion is particularly suited to the formation of bridged complexes. Four modes of bridging are possible (*Figure 8*). The *syn-syn* configuration is the most common, and it is the only mode with a geometry which enables it to bridge bimetallic centres with short metal-metal bonds. This configuration has been observed for many metals, particularly those of the transition series *e.g.* $[\text{Mo}_2(\mu\text{-O}_2\text{CCH}_3)_4]$.⁸

The *anti-anti* and *anti-syn* configurations tend to give rise to polymeric structures. For example, the *anti-anti* axial ligand in the binuclear complexes $[\text{Ru}_2(\mu\text{-O}_2\text{CR})_4(\text{O}_2\text{CR})]$ bridges to neighbouring binuclear units to form polymeric chains (*Figure 9*).⁹

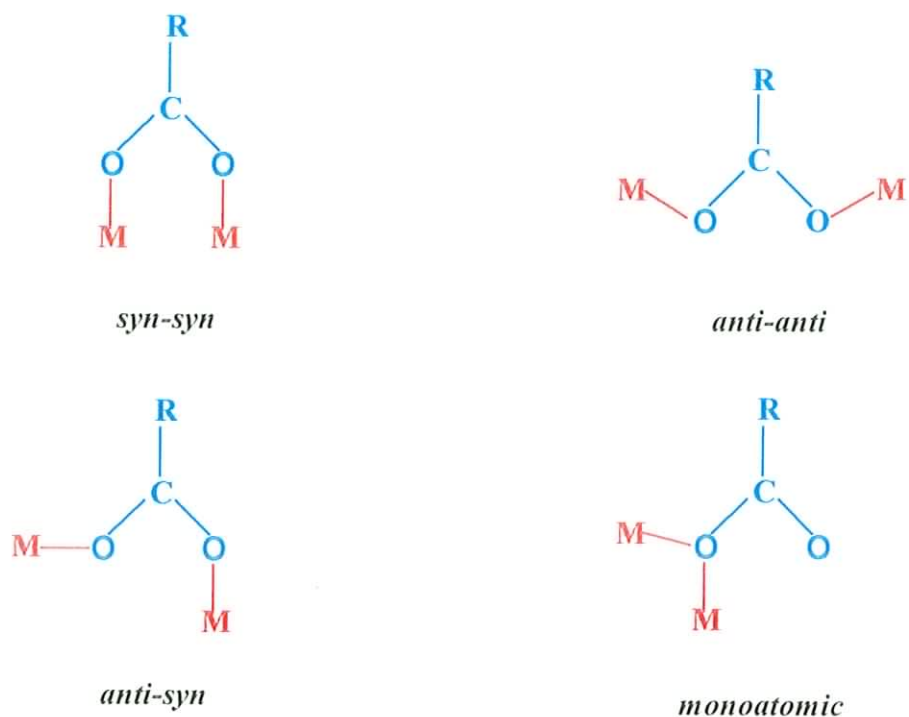


Figure 8

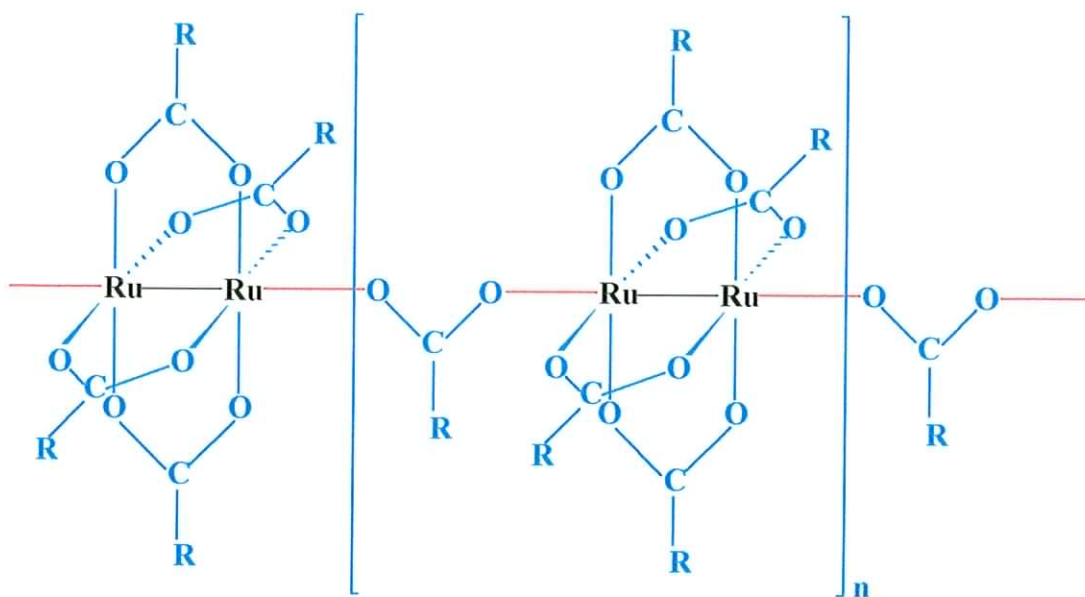


Figure 9

Copper(I) acetate displays a combination of *syn-syn* and *monoatomic* bridging modes (*Figure 10*).¹⁰ The complex contains copper ions bridged in pairs by acetate

groups to afford an essentially centrosymmetric eight-membered ring. In addition, one oxygen atom of each acetate is weakly coordinated to a copper atom of another binuclear unit to produce a planar polymeric structure.

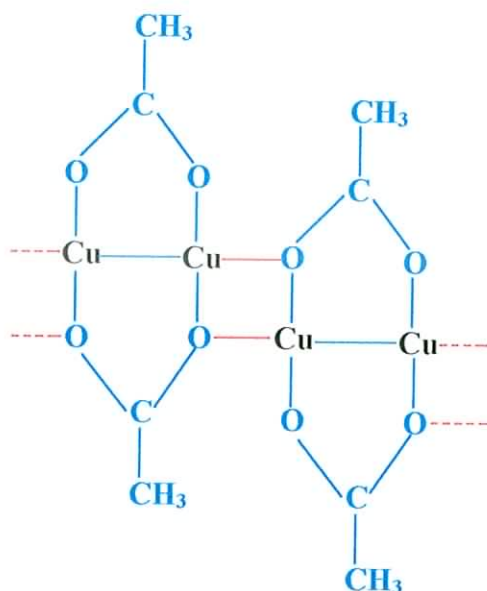


Figure 10

I.2.2 IR Spectra of Metal Carboxylates¹⁰

Detailed studies of carboxylic acids indicate that the carboxyl group shows five characteristic absorption bands at (i) 2500-2700 $\{\nu(\text{OH})\}$, (ii) 1700 $\{\nu(\text{C}=\text{O})\}$, (iii) & (iv) 1400 and 1200-1300 $\{\nu(\text{C}-\text{O})$ or $(\text{O}-\text{H})$ deformations $\}$ and (v) 900 cm^{-1} $\{(\text{O}-\text{H})$ deformations $\}$. The most characteristic bands in the IR spectra of metal carboxylate complexes are those due to the symmetric (ν_{sym}) and antisymmetric (ν_{asym}) stretching modes of the carboxylate O-C-O group. From the large quantity of IR data available for structurally characterised acetates and trifluoroacetate complexes Deacon and Phillips¹¹ compiled guidelines for diagnosing the nature of carboxylate coordination

from the IR spectrum (*Table 4*). These are based on the magnitude of the separation $\Delta\nu(\text{OCO}) \text{ cm}^{-1}$ between the symmetric and antisymmetric O-C-O stretching frequencies:

$$\Delta\nu(\text{OCO}) = [\nu_{\text{asym}}(\text{OCO}) - \nu_{\text{sym}}(\text{OCO})] \text{ cm}^{-1}$$

Ionic acetates have $\nu_{\text{sym}}(\text{OCO})$ at *ca* 1410 cm^{-1} and $\nu_{\text{asym}}(\text{OCO})$ at *ca* 1575 cm^{-1} , giving a value of *ca* 165 cm^{-1} for $\Delta\nu(\text{OCO})$. For trifluoroacetate complexes the values are $\nu_{\text{sym}}(\text{OCO})$ *ca* 1445 cm^{-1} , $\nu_{\text{asym}}(\text{OCO})$ *ca* 1680 cm^{-1} and $\Delta\nu(\text{OCO})$ *ca* 235 cm^{-1} . These frequencies are taken to represent the values corresponding to the free carboxylate ion, since there are only slight variations observed on changing the cation in the ionic salts.

The IR spectra of complexes containing unidentate carboxylate groups show a large increase in the $\nu_{\text{asym}}(\text{OCO})$ frequency and a similar decrease in the $\nu_{\text{sym}}(\text{OCO})$ frequency compared to those of ionic carboxylates. These frequencies correspond approximately to the $\nu(\text{C}=\text{O})$ and $\nu(\text{C}-\text{O})$ vibrations, respectively. The explanation for this is that the bonding of one oxygen to a metal, with the other oxygen free, increases the energy of the antisymmetric OCO stretching mode. Consequently, the difference in energy between $\nu_{\text{asym}}(\text{OCO})$ and $\nu_{\text{sym}}(\text{OCO})$ also increases. Values for $\Delta\nu(\text{OCO})$ which are substantially greater than those for the ionic carboxylates (i.e. $\Delta\nu(\text{OCO}) > 200 \text{ cm}^{-1}$ for acetate and $> 260 \text{ cm}^{-1}$ for trifluoroacetate) can therefore be diagnostic of unidentate coordination, but they are not exclusive. A smaller splitting may arise from intramolecular or intermolecular hydrogen bonding between the uncoordinated

carboxylate oxygen atom and a water molecule giving a “pseudo-bridging” arrangement *e.g.* $\Delta\nu(\text{OCO}) = 107 \text{ cm}^{-1}$ for $[\text{Ni}(\text{O}_2\text{CCH}_3)_2(\text{H}_2\text{O})_4]$.¹²

Complexes with $\Delta\nu(\text{OCO})$ values substantially less than the ionic values (*i.e.* $\Delta\nu(\text{OCO}) < 150 \text{ cm}^{-1}$ for acetates, and $< 200 \text{ cm}^{-1}$ for trifluoroacetates) indicates the presence of a chelating or bridging carboxylate. If the IR spectrum of a complex shows $\Delta\nu(\text{OCO})$ much less than the ionic value (*i.e.* $< 105 \text{ cm}^{-1}$ for acetate) the symmetric chelating mode of coordination is indicated. However, complexes in which the carboxylate ligand bridges short M-M bonds may also show small $\Delta\nu(\text{OCO})$ values *e.g.* $\Delta\nu(\text{OCO}) = 94 \text{ cm}^{-1}$ for $[\text{Mo}_2(\mu\text{-O}_2\text{CCH}_3)_4]$.⁸

Table 4. $\Delta(\text{OCO})$ values for acetate and trifluoroacetate complexes

$\Delta(\text{OCO})$ acetate (cm^{-1})	$\Delta(\text{OCO})$ trifluoroacetate (cm^{-1})	coordination mode indicated
<105	low	symmetric chelating or short bridging
<150	<200	chelating or bridging
<i>ca</i> 165	<i>ca</i> 235	assignments untrustworthy (ionic or “free” carboxylate)
>200	<260	unidentate

I.3 Dicarboxylate Complexes

I.3.1 Coordination Modes of Dicarboxylates

The coordination chemistry of dicarboxylate complexes will be considered in terms of the three structural types unidentate, chelating and bridging.

Unidentate Coordination

This mode of coordination is relatively rare among the dicarboxylic acids. The monomeric octahedral cobalt(III) complexes $[\text{Co}(\text{en})_2\text{X}(\text{O}_2\text{CCO}_2)]$ ($\text{X} = \text{halide}, \text{OH}^-$) (*Figure 11*) serve as some of the few examples of unidentate ethanedioate coordination, the conformation being determined from IR spectroscopy.¹³

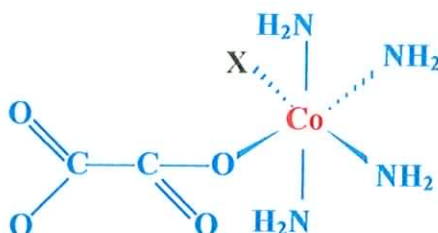


Figure 11

Chelate Coordination

There are numerous examples of structurally characterised chelating ethanedioate complexes.¹⁴ Chelation of dicarboxylates to a metal can occur in two different ways as illustrated in *Figure 12* for ethanedioate complexes.

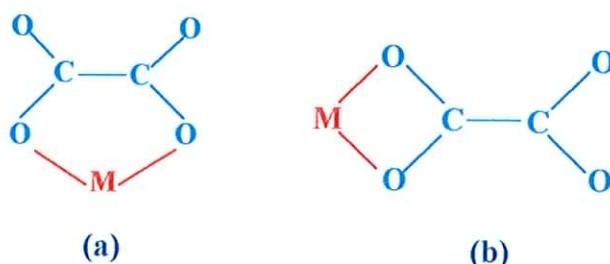


Figure 12

Chelation as in (a) shows two oxygen atoms from different carboxylate groups participating in the chelate ring, and this is probably the most common coordination mode with the lower members of the dicarboxylate series. An example of this mode of coordination is exhibited in the iron(III) complex anion $[\text{Fe}(\text{O}_2\text{CCO}_2)_3]^{3-}$ shown in Figure 13.¹⁵

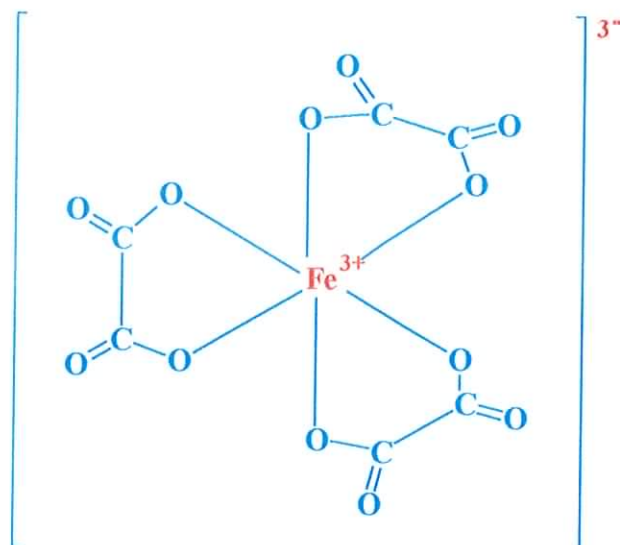


Figure 13

Bridging Systems

As with the monocarboxylate complexes this is the preferred form of coordination, with many possible bridging modes available to dicarboxylic acid ligands. A *cis* bridging system was implied¹⁶ from the IR spectrum of the cobalt(III) complex $[(\text{NH}_3)_4(\text{H}_2\text{O})\text{Co}(\text{O}_2\text{CCO}_2)\text{Co}(\text{NH}_3)_5]^{4+}$ (Figure 14a), whilst a *trans* structure¹⁷ was proposed for the heterobimetallic complex cation $[(\text{NH}_3)_5\text{Co}(\text{O}_2\text{CCO}_2)\text{Cr}(\text{H}_2\text{O})_5]^{4+}$ (Figure 14b).

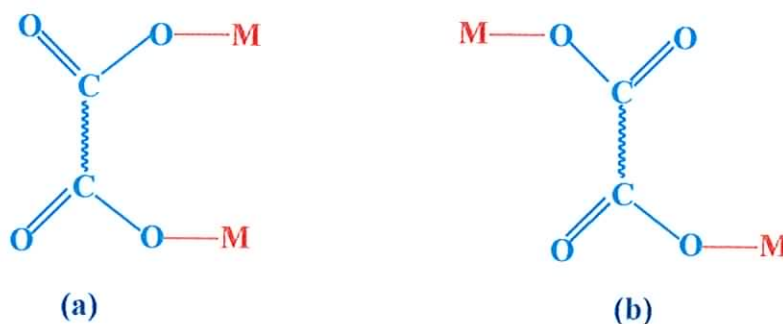


Figure 14

The propanedioate¹⁸ complex $[\text{Sc}(\text{OH})(\text{O}_2\text{C}(\text{CH}_2)\text{CO}_2)] \cdot 2\text{H}_2\text{O}$ and the ethanedioate¹⁹ complex $[\{(\text{NH}_3)_3\text{Co}\}_2(\text{NH}_3)_5\text{Co}(\text{OH})_2(\text{O}_2\text{CCO}_2)]^{5+}$ provide examples of the tridentate bridges shown in *Figure 15* (a) and (b), respectively.

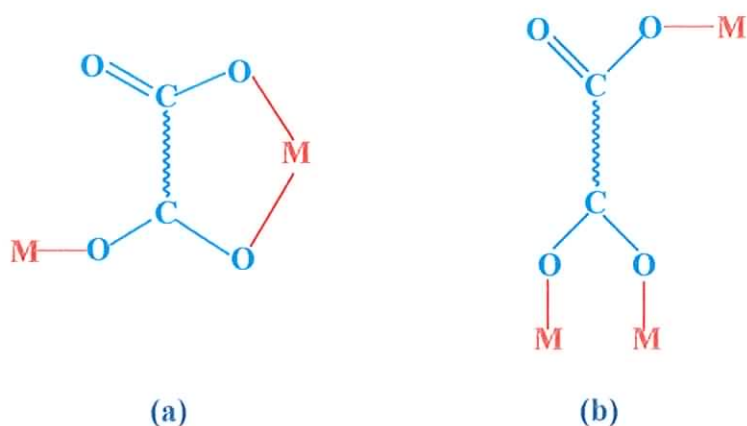


Figure 15

The structure of the ethanedioate complex cation $[\{(\text{NH}_3)_3\text{Co}\}_2(\text{NH}_3)_5\text{Co}(\text{OH})_2(\text{O}_2\text{CCO}_2)]^{5+}$ is shown in *Figure 16*.

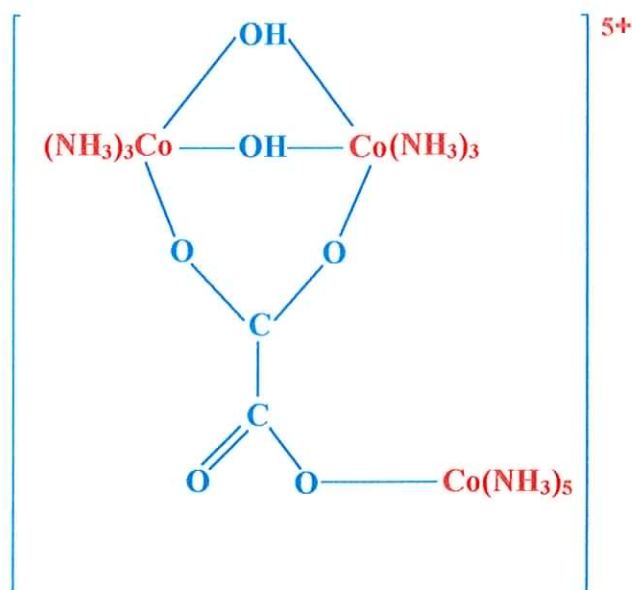


Figure 16

Tetradentate bridging of dicarboxylate groups is by far the most common, with the planar, doubly chelating system *Figure 17* being the most prevalent. Two different chelate ring systems in the ethanedioate complex $[\{\text{Bu}_3\text{P}(\text{Cl})\text{Pd}\}_2(\text{O}_2\text{CCO}_2)]$ were identified in 1938, but the first complete structural analysis was of the iron ethanedioate

mineral humboltine in 1957.²⁰ Since that date, many crystal structure determinations have demonstrated the extent of this coordination mode.

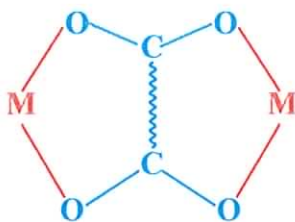


Figure 17

Tetradentate ligand behaviour, producing one six- and two four-membered rings, (*Figure 18*) is observed in the structurally characterised polymeric propanedioate complexes $[\text{Eu}_2(\text{O}_2\text{C}(\text{CH}_2)\text{CO}_2)_3 \cdot 8\text{H}_2\text{O}]_n$,²¹ and $[\text{Cd}(\text{O}_2\text{C}(\text{CH}_2)\text{CO}_2) \cdot \text{H}_2\text{O}]_n$.²²

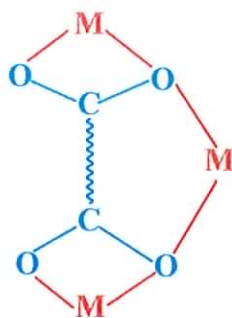


Figure 18

Part of the polymeric structure of $[\text{Cd}(\text{O}_2\text{C}(\text{CH}_2)\text{CO}_2)\text{H}_2\text{O}]_n$ is shown in *Figure 19*.

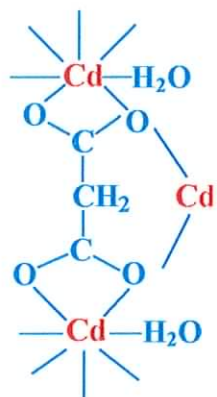


Figure 19

In the propanedioate neodymium(VI) complex $[\text{Nd}(\text{O}_2\text{C}(\text{CH}_2)\text{CO}_2)_3 \cdot 8\text{H}_2\text{O}]^{23}$ the four oxygen atoms of the two carboxylates are thought to bridge as in *Figure 20*.

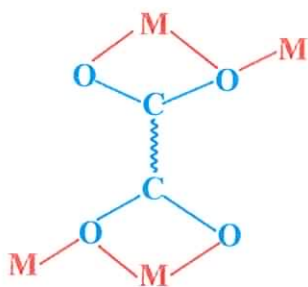


Figure 20

Two *syn-syn* bridges (Figure 21) often result in linked paddlewheel type dimers, as seen in the butanedioate (Figure 22) and pentanedioate complexes of copper(II).²⁴

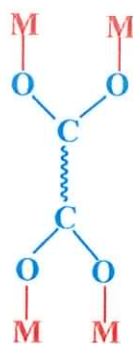


Figure 21

This type of coordination is most common in complexes involving relatively long chain dicarboxylic acids, and thus is very relevant to the present study.

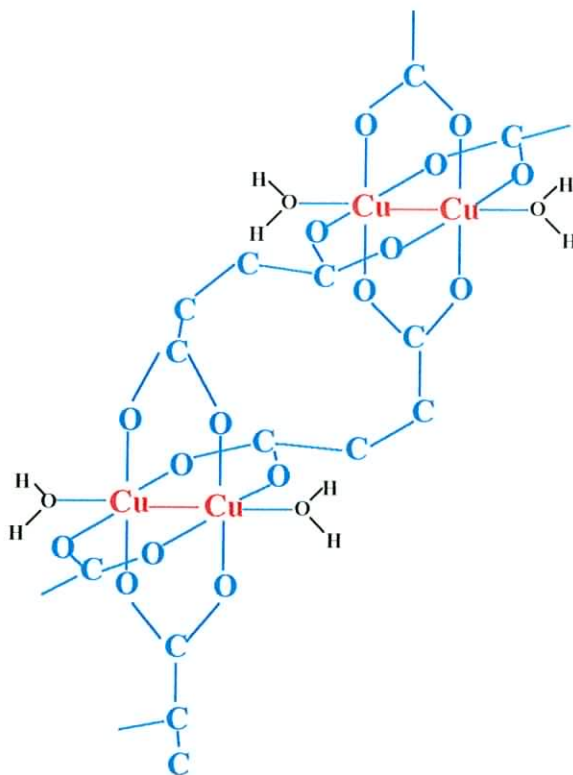


Figure 22

Mureinik²⁵ synthesised several long-chain polymeric molybdenum(II) dicarboxylate complexes with the type of bridging shown in *Figure 23*.

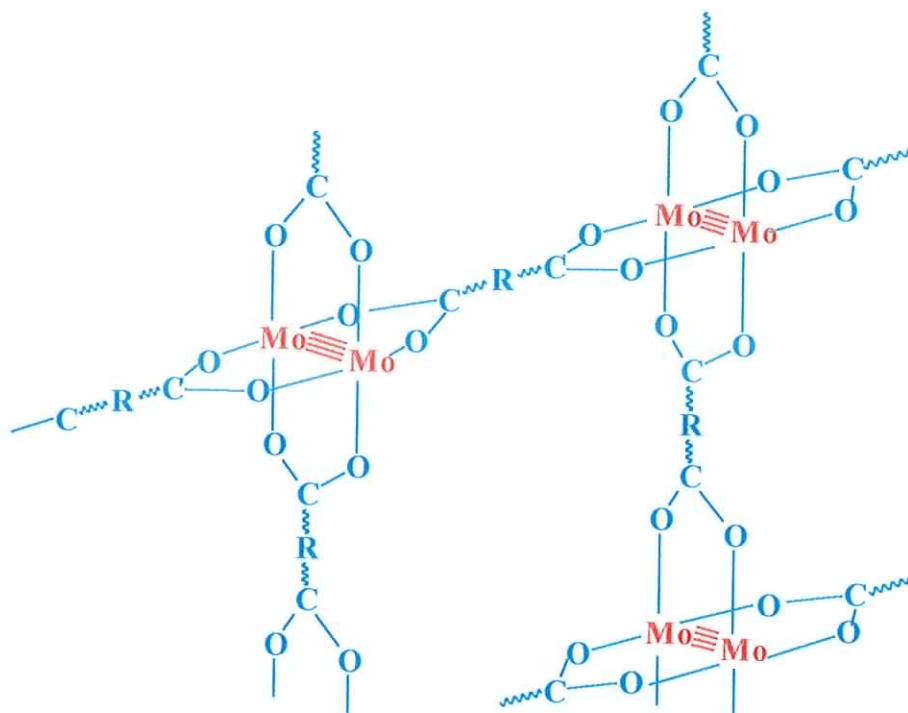


Figure 23

I.3.2 General Chemistry of Metal Dicarboxylate Complexes

The coordination chemistry of monocarboxylate metal complexes is well established. In contrast, relatively few papers have appeared in the literature concerning the coordination chemistry of dicarboxylates, and only a small number of these complexes have been structurally characterised. As a consequence of the difficulty in obtaining crystalline complexes, structural interpretation of the copper(II) complexes has relied a lot on magnetic susceptibility measurements. As with the monocarboxylates, it was the copper dicarboxylate complexes that were studied most.

In 1959, Asai *et al.*²⁶ reported the synthesis and magnetic susceptibilities of a

family of polymeric copper(II) complexes of formula $[\text{Cu}(\text{O}_2\text{C}(\text{CH}_2)_n\text{CO}_2)]$ ($n = 0-8$) and found that, with the exception of the propanedioic acid complex (which is magnetically “normal”), all of the materials had effective magnetic moments in the range of 1.20-1.45 B.M. per copper atom. These values were similar to those reported^{27,28} for hydrated copper(II) acetate (1.4 B.M. per copper) and considerably smaller than the theoretical spin-only value (1.73 B.M.). On the basis of the magnetic data the authors concluded that the complexes ($n = 0, 2-8$) contained bridging bidentate carboxylate ligands which held two copper atoms in close proximity, in the same manner as had been observed in the structurally characterised acetate complex $[\text{Cu}_2(\mu\text{-O}_2\text{CCH}_3)_4(\text{H}_2\text{O})_2]$ (Figure 24).^{29,30}

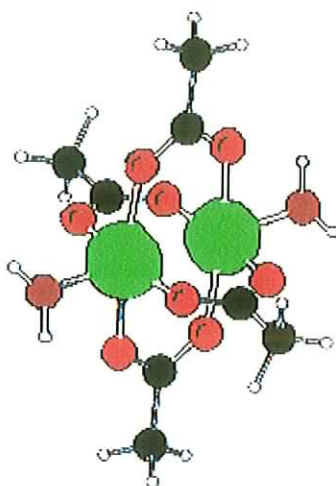


Figure 24

Verification of this structural prediction came when O'Connor and Maslen determined the X-ray crystal structure of the butanedioate complex $[\text{Cu}(\text{O}_2\text{C}(\text{CH}_2)_2\text{CO}_2)]$ (Figure 25).²⁴ $[\text{Cu}(\text{O}_2\text{C}(\text{CH}_2)_2\text{CO}_2)]$ was found to consist of infinite chains of covalently bonded binuclear units each of which closely resembled the copper(II) acetate structure. Each dicopper unit is bridged by four *syn-syn* carboxylate bridges from four butanedioate groups. The coordination number of each

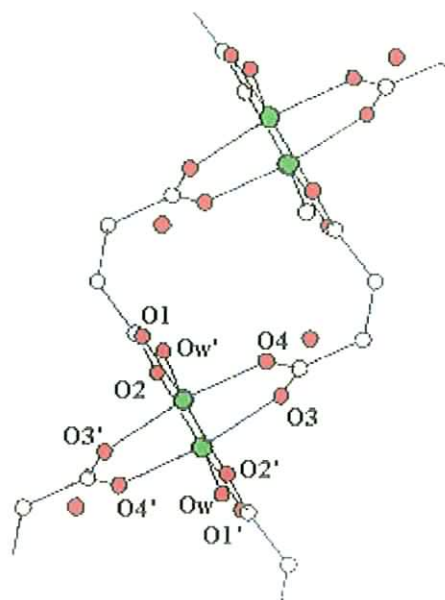


Figure 25

copper atom is six, the other two coordination sites being occupied by an axial water molecule and the neighbouring copper atom. Each of these paddlewheel dimers are linked through the C-C bonds of the butanedioate ligands to form linear chains parallel to the *a*-axis of the crystal, and a network of hydrogen bonds connects the chains. This complex, as with other copper(II) dicarboxylates, had a subnormal magnetic moment at room temperature (1.36 B.M.).³¹

Figgis and Martin carried out variable temperature magnetic susceptibility studies on a series of copper(II) dicarboxylates, and they concluded that the reduction in the magnetic moment as a function of temperature was due to anti-ferromagnetic coupling similar to that found in copper(II) acetate.^{29,30} The magnetic behaviour of the copper(II) heptanedioate and octanedioate complexes was very similar to that of the butanedioate complex.²⁴ This observation led Figgis and Martin to predict that these complexes had structures similar to that of butanedioate, except that they had the longer bridging sections $-(\text{CH}_2)_3-$ and $-(\text{CH}_2)_6-$, respectively, between the dimer units.

Gupta and his co-workers structurally characterised the nickel(II) butanedioate

complex $[\text{Ni}(\text{O}_2\text{C}(\text{CH}_2)_2\text{CO}_2)(\text{H}_2\text{O})_4]\cdot\text{H}_2\text{O}$ ³² and also the hexanedioate complex $[\text{Ni}(\text{O}_2\text{C}(\text{CH}_2)_4\text{CO}_2)(\text{H}_2\text{O})_4]$ (Figure 26).³³



Figure 26

More recently, they reported the X-ray crystal structure of the manganese(II) butanedioate complex $[\text{Mn}(\text{O}_2\text{C}(\text{CH}_2)_2\text{CO}_2)(\text{H}_2\text{O})_4]$ (Figure 27).³⁴

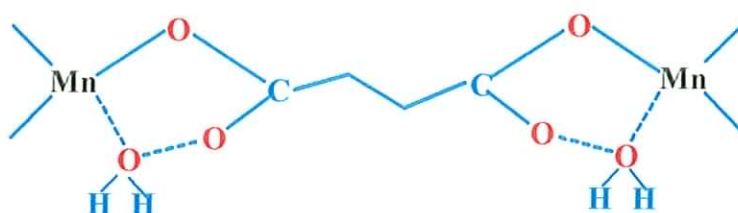


Figure 27

All three complexes were found to be structurally very similar, consisting of two linear polymeric chains of metal atoms bridged by dicarboxylate ligands. The metal ion is coordinated to six oxygen atoms, of which four come from the water molecules and two belong to two carboxyl groups of different dicarboxylate ions. These polymeric chains of dicarboxylate anions are linked by hydrogen bonds *via* water molecules. The coordination environment around the nickel atom in the hexanedioate complex (Figure 26) is very similar to that in nickel(II) acetate³⁵ which also contains a unidentate carboxylate ligand with hydrogen bonding between the non-coordinating carboxylate oxygen and the coordinated water molecules.

Hexanedioic acid was also employed as a ligand by Pajunen *et al.*³⁶ in their study of copper(II) complexes with mixed aliphatic diamines and aliphatic dicarboxylic acids. The X-ray crystal structure of the hexanedioate(*N,N*-diethyl-

ethylenediamine)copper(II) complex $[\text{Cu}_2(\text{O}_2\text{C}(\text{CH}_2)_4\text{CO}_2)(\text{H}_2\text{NCH}_2\text{CH}_2\text{N}(\text{C}_2\text{H}_5)_2)]$ (Figure 28) is in sharp contrast to the polymeric nickel hexanedioate (Figure 26).³³ Here, the addition of *N,N*-diethylethylenediamine ($\text{H}_2\text{NCH}_2\text{CH}_2\text{N}(\text{C}_2\text{H}_5)_2$) gives rise to a dimeric complex, where the hexanedioate ions and copper(II) ions form an eighteen-membered ring. The carboxylate groups are inclined towards the copper(II) ion in an attempt to complete the six coordination of the metal ion and resulting in a distorted octahedron.

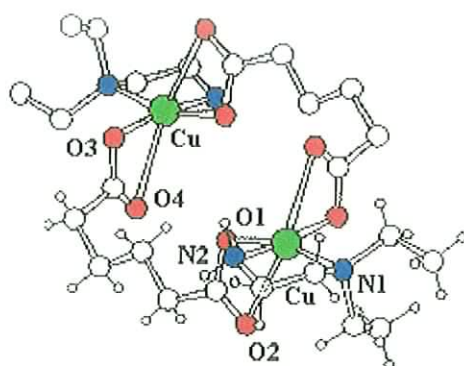
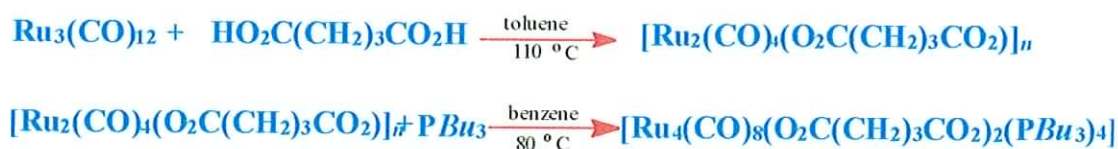


Figure 28

Bianchi *et al.* structurally characterised the non-polymeric tetraruthenium(I) pentanedioic acid complex $[\text{Ru}_4(\text{CO})_8(\text{O}_2\text{C}(\text{CH}_2)_3\text{CO}_2)_2(\text{PBu}_3)_4]$.³⁷ This complex was prepared using a two-stage synthetic strategy (Scheme 1). Firstly, dodecacarbonyltriruthenium(0) was reacted with pentanedioic acid in boiling toluene to give the polymeric complex $[\text{Ru}_2(\text{CO})_4(\text{O}_2\text{C}(\text{CH}_2)_3\text{CO}_2)]_n$. This highly insoluble complex was subsequently reacted with tributylphosphine to give yellow crystals of the tetramer $[\text{Ru}_4(\text{CO})_8(\text{O}_2\text{C}(\text{CH}_2)_3\text{CO}_2)_2(\text{PBu}_3)_4]$.



Scheme 1

The X-ray crystal structure of $[\text{Ru}_4(\text{CO})_8(\text{CH}_2)_3\text{CO}_2](\text{PBU}_3)_4$ (Figure 29) showed that each of the two dianionic diacid ligands are coordinated in a bridging bidentate fashion to separate diruthenium centres. The bridging of the ruthenium dimers by the pentanedioate ligands is similar to that found in $[\text{Cu}(\text{O}_2\text{C}(\text{CH}_2)_2\text{CO}_2)]$ (Figure 25).²⁴ However, in contrast to the polymeric copper(II) structure the ruthenium complex consists of discrete tetranuclear units, with the tributylphosphine acting as a capping ligand and thereby inhibiting polymerization of the complex *via* the bifunctional dicarboxylate ligand.

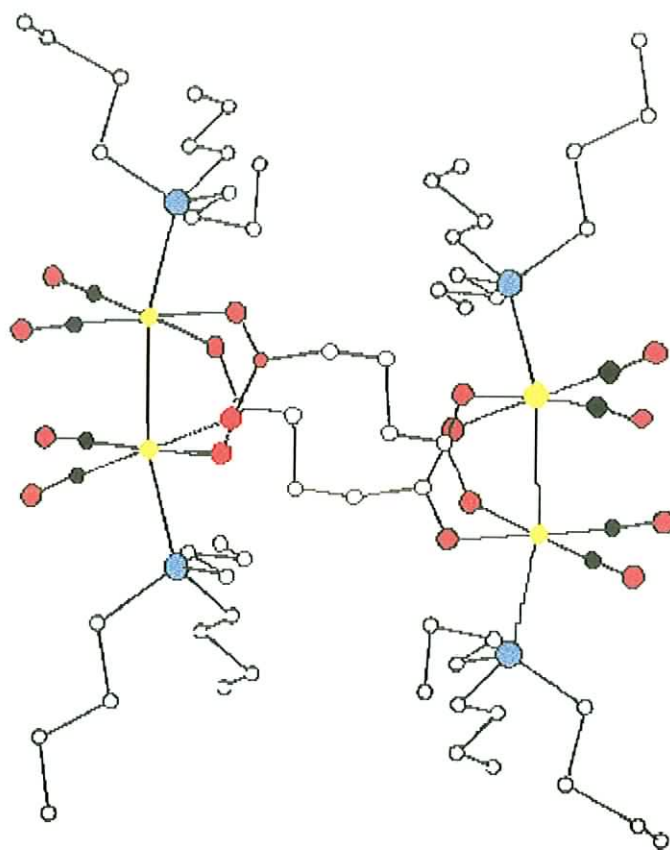
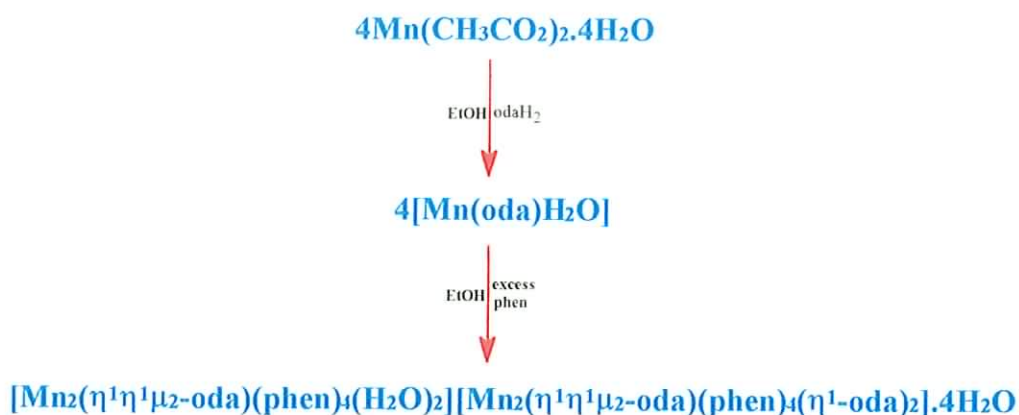


Figure 29

The effect of capping ligands like 1,10-phenanthroline (phen) and 2,2'-bipyridine (bipy) is seen in a number of copper(II) and manganese(II) complexes recently prepared by McCann and his co-workers.³⁸⁻⁴² Some examples of these are

outlined below. Octanedioic acid $\text{HO}_2\text{C}(\text{CH}_2)_6\text{CO}_2\text{H}$ (odaH_2) was reacted with manganese(II) acetate to give the white manganese(II) complex $[\text{Mn}(\text{oda})\text{H}_2\text{O}]$, which was further reacted with an excess of 1,10-phenanthroline to produce yellow crystals of the dimanganese(II,II) complex double salt $[\text{Mn}_2(\eta^1\eta^1\mu_2\text{-oda})(\text{phen})_4(\text{H}_2\text{O})_2][\text{Mn}_2(\eta^1\eta^1\mu_2\text{-oda})(\text{phen})_4(\eta^1\text{-oda})_2]\cdot 4\text{H}_2\text{O}$ (*Scheme 2*).³⁸



Scheme 2

The structures of the “concertina shaped” dianion $[\text{Mn}_2(\eta^1\eta^1\mu_2\text{-oda})(\text{phen})_4(\eta^1\text{-oda})_2]^{2-}$ and dication $[\text{Mn}_2(\eta^1\eta^1\mu_2\text{-oda})(\text{phen})_4(\text{H}_2\text{O})_2]^{2+}$ were found to be similar, with each of the two symmetry related manganese(II) atoms having a distorted octahedral N_4O_2 coordination geometry (*Figure 30*). Each metal is surrounded by two chelating phen groups and one carboxylate oxygen from the bridging oda^{2-} ligand. Both the dianion and the dication are comprised of two manganese centres bridged by a single oda^{2-} ligand which utilizes only one carboxylate oxygen from each end of the diacid. The uncoordinated carboxylate oxygen at either end of the bridging oda^{2-} ligand is on the limits of coordination distances to the metal. In the dianion, each manganese atom also has a unidentate oda^{2-} ligand, the other carboxylate moiety of the diacid remaining

uncoordinated. These uncoordinated carboxylate oxygens in the dianion, although on the limits of coordination distances to the metal, result in a distortion of the nitrogen-manganese-nitrogen angle from *ca.* 180° to 147.31°. This implies that the whole chromophore could possibly best be described as being pseudo eight-coordinate ($\text{MnN}_4\text{O}_2\text{O}_2$).

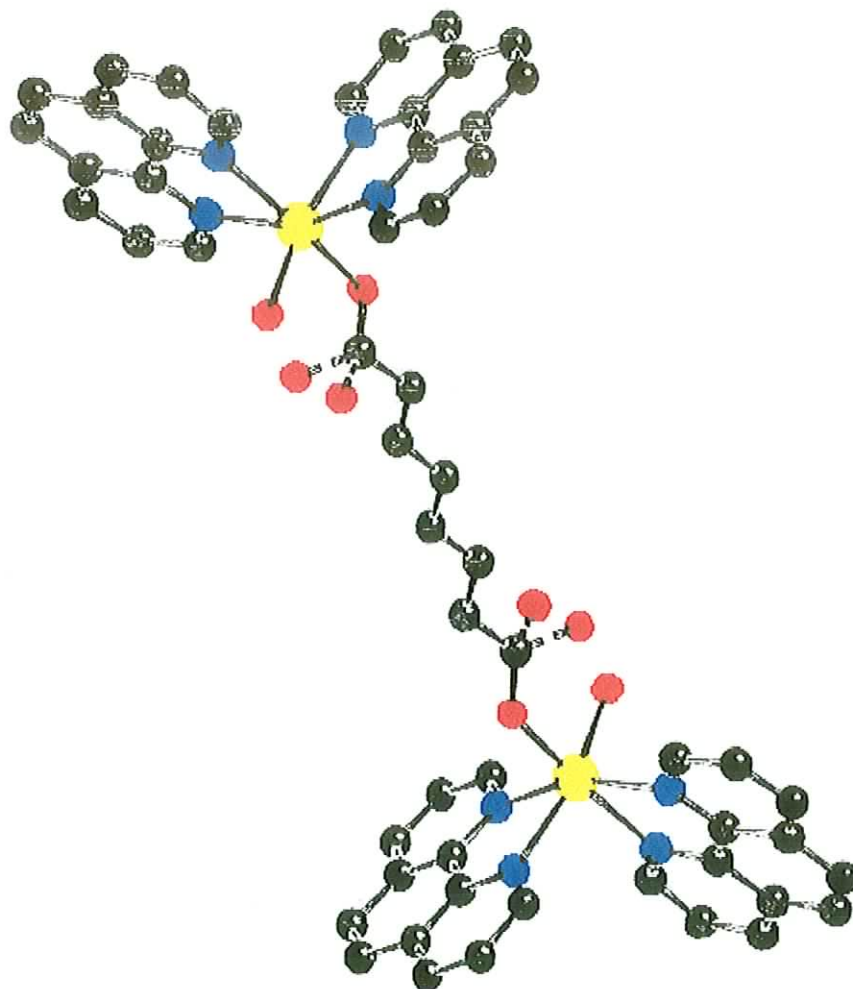


Figure 30

Van Albada *et al.*⁴³ reported the reaction of a series of copper(II) dicarboxylate complexes with benzimidazole (Hbim) to give blue crystalline complexes of empirical formula $\text{Cu}(\text{Hbim})_2(\text{A})$ (A = dianion of a dicarboxylic acid). The structure of the

polymeric heptanedioic acid derivative $\{[\text{Cu}_2(\text{Hbim})_4(\text{hda})(\text{Hhda})_2]\cdot 8\text{H}_2\text{O}\}_n$ is shown in *Figure 31*.

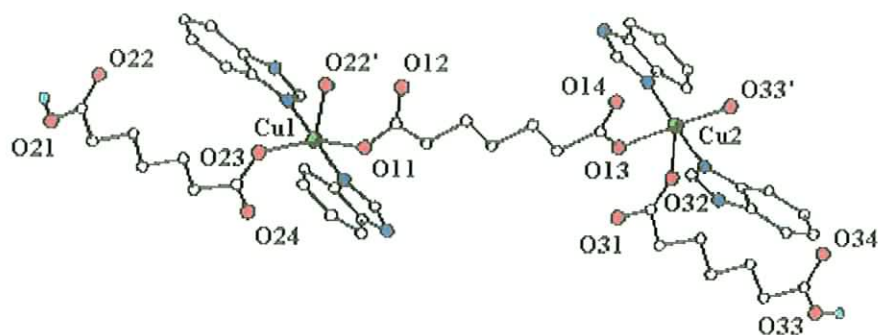


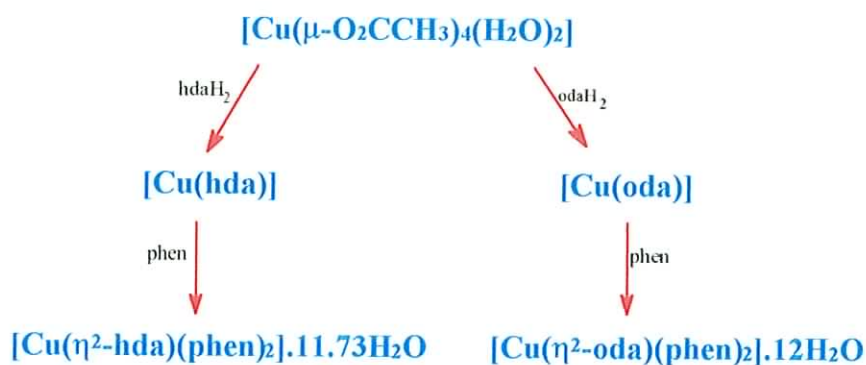
Figure 31

In this structure single dianionic and double monoanionic bridges link the metal centres into polymeric chains where each carboxylate or carboxylic acid group acts as a monodentate ligand. The copper(II) ions have a coordination number of five and a square-pyramidal $\text{CuN}_2\text{O}_2\text{O}$ chromophore. The authors concluded that α,ω -dicarboxylic acids can form polymeric chains comprising of copper(II) centres and carboxylate ions.

The above theory was supported by Baron *et al.* who synthesised the relatively long chain dicarboxylate copper(II) decanedioate complex $[\text{Cu}(\text{O}_2\text{C}(\text{CH}_2)_8\text{CO}_2)]$.⁴⁴ Although the X-ray crystal structure of the complex was not solved it was characterised by means of IR and electronic spectroscopy, as well as by variable temperature magnetic susceptibility measurements. The results (similar to those found by Van Albada *et al.*)⁴³ pointed to the existence of a complex containing Cu-Cu moieties bridged by carboxylate groups. The magnetic behaviour was found to be essentially similar to that of other copper(II) dicarboxylate complexes consisting of chains of magnetically isolated dimeric units joined by methylene bridges. Therefore, as in the

case of the copper(II) butanedioate complex $[\text{Cu}(\text{O}_2\text{C}(\text{CH}_2)_2\text{CO}_2)]$ (Figure 25), the magnetic behaviour of copper(II) decanedioate points to a structure similar to that of copper(II) acetate (Figure 24).²⁹

As part of their recent studies into the coordination chemistry of dicarboxylic acids, McCann and his co-workers have been examining the reactions of copper(II) salts with several relatively long-chained α,ω -dicarboxylic acids. $[\text{Cu}_2(\mu\text{-O}_2\text{CCH}_3)_4(\text{H}_2\text{O})_2]$ was found to react smoothly with heptanedioic acid ($\text{HO}_2\text{C}(\text{CH}_2)_5\text{CO}_2\text{H}$) (hdaH_2) and octanedioic acid ($\text{HO}_2\text{C}(\text{CH}_2)_6\text{CO}_2\text{H}$) (odaH_2) to form the polymeric copper(II) complexes $[\text{Cu}(\text{hda})]$ and $[\text{Cu}(\text{oda})]$, respectively (Scheme 3).³⁹ These reactions are similar to those described by Asai *et al.*²⁶



Scheme 3

$[\text{Cu}(\text{hda})]$ and $[\text{Cu}(\text{oda})]$ were found to be poorly soluble in most common organic solvents, and magnetic susceptibility measurements indicated a strong anti-ferromagnetic coupling between the metal centres in both complexes. The insolubility of the complexes, together with the magnetic and IR spectral data, suggested that they were probably isostructural with the polymeric copper(II) complex of butanedioic acid.²⁴ These somewhat insoluble polymeric complexes were then reacted with 1,10-phenanthroline to yield the highly soluble mononuclear species $[\text{Cu}(\eta^2\text{-hda})(\text{phen})_2] \cdot 11.73\text{H}_2\text{O}$ and $[\text{Cu}(\eta^2\text{-oda})(\text{phen})_2] \cdot 12\text{H}_2\text{O}$. Both complexes were

essentially isostructural, and the structure of $[\text{Cu}(\eta^2\text{-oda})(\text{phen})_2]\cdot 12\text{H}_2\text{O}$ is illustrated in *Figure 32*.

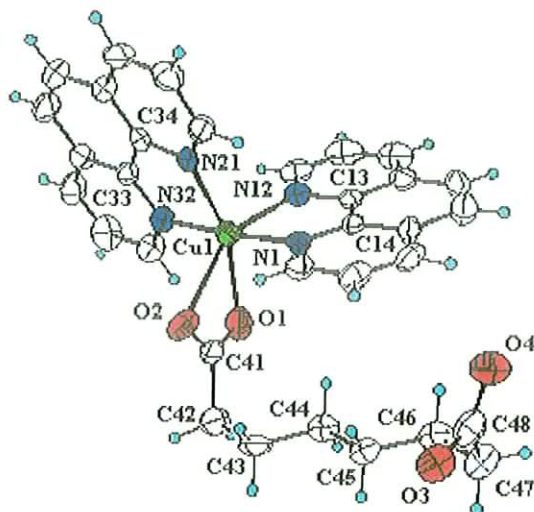


Figure 32

The copper(II) atom is at the centre of a distorted octahedron and is linked to four nitrogen atoms from two chelating phen ligands and two oxygen atoms from a single asymmetric chelating carboxylate function, with the remaining carboxylate group of the diacid uncoordinated. The IR spectra of $[\text{Cu}(\eta^2\text{-hda})(\text{phen})_2]\cdot 11.73\text{H}_2\text{O}$ and $[\text{Cu}(\eta^2\text{-oda})(\text{phen})_2]\cdot 12\text{H}_2\text{O}$ both displayed shifts in the position of the $\nu_{\text{asym}}(\text{OCO})$ band to lower frequency (by 35 and 30 cm^{-1} , respectively) compared to their precursors $[\text{Cu}(\text{hda})]$ and $[\text{Cu}(\text{oda})]$. This shift in the position of the $\nu_{\text{asym}}(\text{OCO})$ band possibly reflects the change in the coordination mode of the diacid ligands from bridging bidentate to chelating.⁴⁵

Recently, Devereux *et al.* reacted the copper(II) octanedioate complex $[\text{Cu}(\text{oda})]$ with an excess of pyridine to produce the blue crystalline copper(II) complex $\{\text{Cu}_2(\eta^1\eta^1\mu_2\text{-oda})_2(\text{py})_4(\text{H}_2\text{O})_2\}_n$ (*Figure 33*).⁴⁰ The structure consists of polymeric chains in which bridging oda^{2-} anions link two crystallographically identical copper(II)

atoms. The copper atoms are also ligated by two *transoidal* pyridine nitrogens and an oxygen atom from an apical water molecule, giving the metals an overall N_2O_3 square-pyramidal geometry. Interestingly, this complex, on being gently heated or allowed to stand in its mother liquor for prolonged periods, loses one molecule of pyridine and half

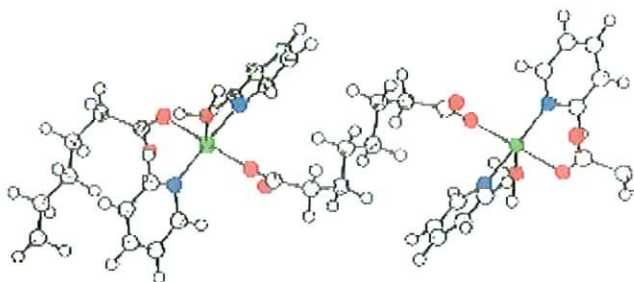


Figure 33

a molecule of water to form the green complex $\{Cu(oda)(py)(H_2O)_{0.5}\}_n$. This reaction was found to be completely reversed upon standing the green complex in a pyridine:water mixture for several days at room temperature. The mechanism of transformation is not clear, but it is possible that it may involve an intermediate complex in which the carboxylates are bound to the copper centres in a monodentate bridging mode. Lippard and his co-workers⁴⁶ have recently described this movement from monodentate bridging carboxylate to other binding modes as the “carboxylate shift”. Magnetic moment values for the green complex (1.34 B.M. per copper) indicate a strong antiferromagnetic coupling between adjacent metal centres. It was suggested that the structure of the green complex $\{Cu(oda)(py)(H_2O)_{0.5}\}_n$ is similar to that of the butanedioate complex $[Cu(O_2C(CH_2)_2CO_2)]$ discussed earlier (*Figure 25*).²⁴

An important aromatic dicarboxylic acid with respect to metal coordination is benzene-1,2-dioxyacetic acid (bdoaH_2) (Figure 34).

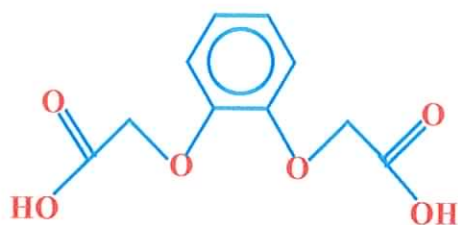


Figure 34

This aryloxydicarboxylic acid is a multifunctional ligand in that it has the potential to coordinate to metals in a number of different ways (Figure 35).

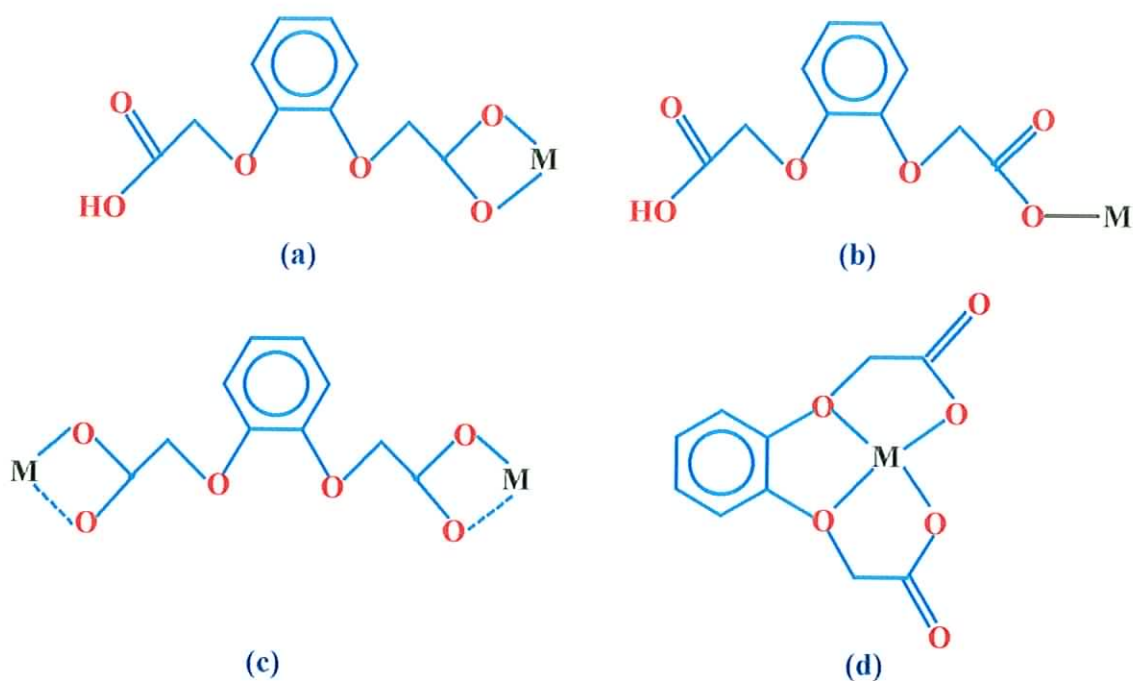


Figure 35

Green *et al.*⁴⁷ structurally characterised the complex $[\text{K}(\text{bdoaH})(\text{bdoaH})\text{H}]$ (Figure 36) in which the bdoaH^- ligand was shown to coordinate to the metal by using all of its six oxygens.

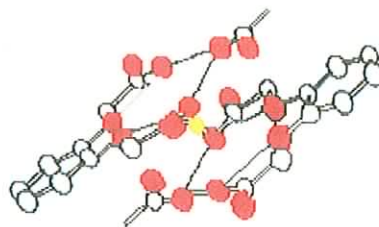
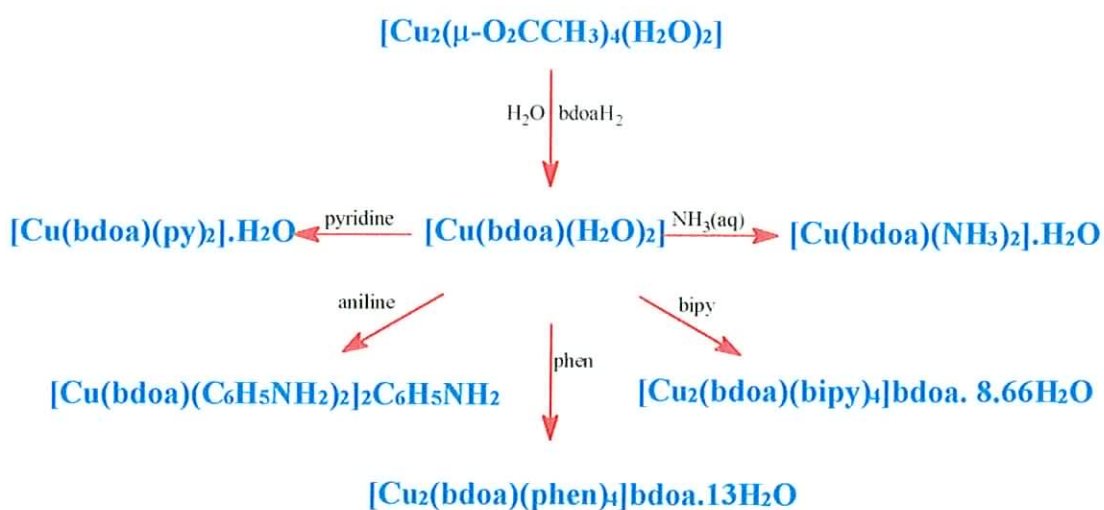


Figure 36

The potassium lies on a crystallographic two-fold axis and around the cation are ten oxygens whose geometry describes an irregular pentagonal antiprismatic polygon. The potassium is bound to four oxygens from each of two bdoaH⁻ ligands which sandwich it, and another two carboxylate oxygens from symmetry related bdoaH⁻ ligands. A hydrogen ion, located on a crystallographic inversion centre, is shared between the two sandwiching bdoaH⁻ ligands. Hydrogen bonding is also present between the bdoaH⁻ ligands. Thus, the net effect of the potassium ions and hydrogen bonds was to produce a two-dimensional polymer.

McCann *et al.* have recently synthesised several copper(II) bdoa complexes, and a summary of these reactions is presented in *Scheme 4*.



Scheme 4

Reaction of copper(II) acetate with bdoaH₂ in a 1:2 molar ratio in refluxing H₂O gave [Cu(bdoa)(H₂O)₂], and this complex was presumed to be the same as that reported by Suzuki *et al.*⁴⁸ who formed it by reacting copper(II) perchlorate with bdoaH₂ in water. This complex was then reacted with the nitrogen-donor ligands ammonia, aniline, pyridine, phen and bipy to give the corresponding adducts. X-ray crystal structures were determined for [Cu₂(bdoa)(bipy)₄]bdoa·8.66H₂O, [Cu(bdoa)(C₆H₅NH₂)₂]₂·C₆H₅NH₂ (Figure 37)⁴¹ and [Cu₂(bdoa)(phen)₄]bdoa·13H₂O (Figure 38).⁴²

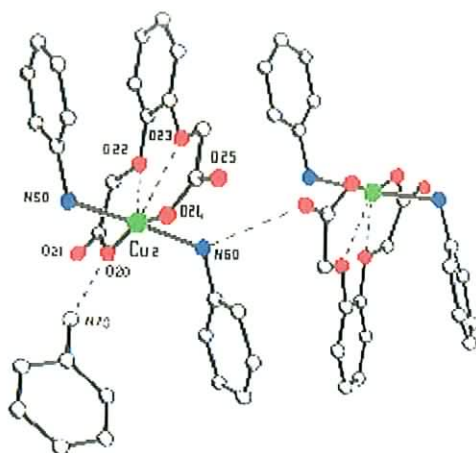
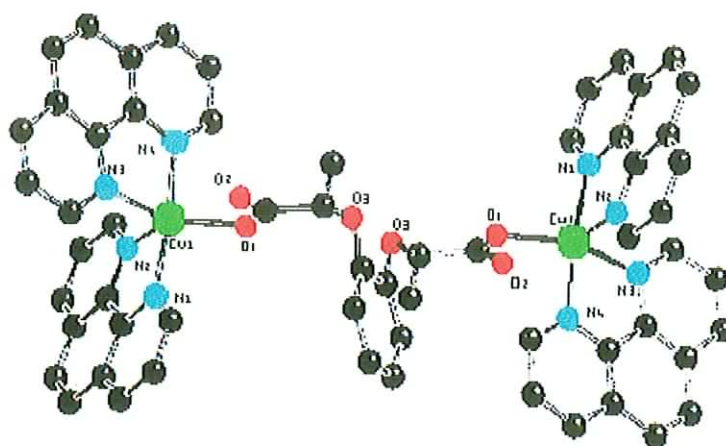


Figure 37



[Cu(bdoa)(L)₂] are produced, whilst addition of bidentate chelating nitrogen-donor ligands (*e.g.* LL = phen or bipy) induces formation of the binuclear complexes [Cu₂(bdoa)(LL)₄]bdoa. In the latter complexes the bdoa²⁻ ligand has each of its carboxylate groups unsymmetrically chelating to the metal centre, whereas in the mononuclear complexes the two ether oxygens, together with one oxygen atom from each of the two carboxylate moieties of the bdoa²⁻ ligand, bond to the metal.

As part of their continuing research into the coordination chemistry of dicarboxylic acids Devereux *et al.* reacted the copper(II) complex [Cu(bdoa)(H₂O)₂] with triphenylphosphine to produce the crystallographically characterised copper(I) complex [Cu(η^1 -bdoaH)(PPh₃)₃] (*Figure 39*).⁴⁹ In this complex the copper atom is at the centre of a distorted tetrahedron, and is ligated by the phosphorus atoms of the three triphenylphosphines and one carboxylate oxygen of the bdoaH⁻ ligand. In addition, there is significant intermolecular hydrogen-bonding between the pendant carboxylate OH function of one molecule and the uncoordinated “ketonic” oxygen of a neighbouring molecule. As in the case of the characterised dicopper(II,II) complex, [Cu₂(bdoa)(phen)₄]bdoa·13H₂O (*Figure 39*),⁴² the two “ketonic” carboxylate oxygens and the two ether oxygens of the diacid are not coordinated to the metal centre.

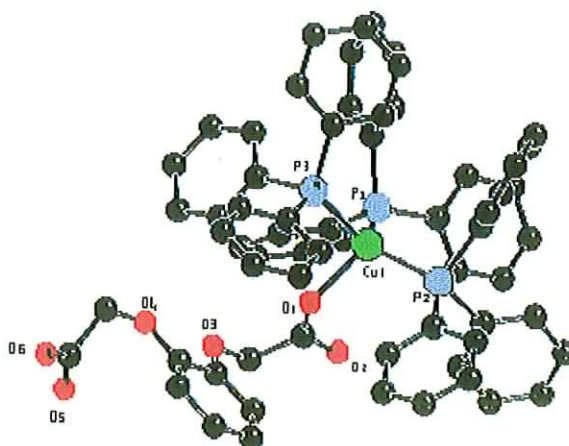


Figure 39

In addition to the work carried out on copper(I) and copper(II) bdoa complexes the mononuclear manganese(II) complex $[\text{Mn}(\text{bdoa})(\text{H}_2\text{O})_3]$ has very recently been structurally characterised by McCann *et al.* (Figure 40).⁵⁰ In this complex the metal is pseudo seven-coordinate. The quadridentate bdoa²⁻ dicarboxylate ligand forms an essentially planar girdle around the metal, being strongly bonded *transoid* by a carboxylate oxygen atom from each of the two carboxylate moieties and also weakly chelated by the two internal ether oxygen atoms. The coordination sphere about the manganese is completed by three meridional water molecules lying in the plane orthogonal to that of the bdoa²⁻ ligand. The coordination mode of the bdoa²⁻ ligand in $[\text{Mn}(\text{bdoa})(\text{H}_2\text{O})_3]$ is essentially the same as that in the mononuclear copper(II) aniline complex $[\text{Cu}(\text{bdoa})(\text{C}_6\text{H}_5\text{NH}_2)_2]_2\text{C}_6\text{H}_5\text{NH}_2$ (Figure 37)⁴¹, the only difference being that the metal to carboxylate oxygen distances are significantly shorter in the copper species.

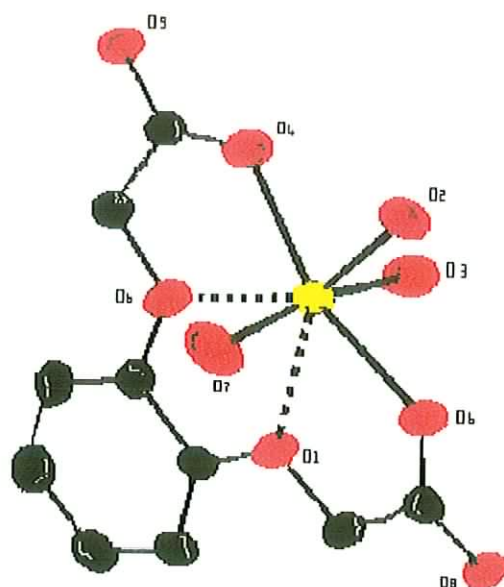


Figure 40

Hammond *et al.* prepared triphenylphosphine-stabilised dicopper(I,I) dicarboxylic acid complexes from copper(II) *cis*- and *trans*-1,2-butenedioate (maleate and fumarate, respectively), monochloromaleate and butanedioate (succinate). These complexes were formulated as $[(PPh_3)_2Cu(O_2C(R)CO_2)Cu(PPh_3)_2]$ (diacid = HO_2CRCO_2H) and, on the basis of their IR spectra, both of the carboxylate moieties were thought to be chelating. In addition, the authors also isolated the binuclear tris(triphenylphosphine) butanedioate dicopper(I,I) complex $[(PPh_3)_2Cu(O_2C(CH_2)_2CO_2)Cu(PPh_3)_2]$, where the two carboxylate functions of the diacid were believed to each act as a monodentate ligand, thus making each copper four-coordinate.

1.3.3 Uses of Dicarboxylate Complexes

Dicarboxylate complexes, although relatively unexplored, have already been shown to have wide applications. Menke's disease,⁵²⁻⁵⁴ a disorder characterised by severe neurologic, skeletal and developmental abnormalities, has been successfully treated by the administration of copper(II) salts in the presence of decanedioic acid $HO_2C(CH_2)_8CO_2H$.⁵⁵ This dicarboxylic acid has also been reported to be a useful ligand for the supplementation of essential trace metals as it is thought to facilitate the mobilisation of these metals through lipid membranes and similar biological barriers.⁴⁴

For the past decade, considerable attention has been focussed on the bioinorganic chemistry of manganese and, in particular, on multinuclear manganese metalloenzymes.⁵⁶ Manganese catalases, for example, are responsible for the catalytic disproportionation of hydrogen peroxide which is important for cell detoxification (*Scheme 5*). Recent work^{38,50} on manganese dicarboxylate complexes has shown that



Scheme 5

they also exhibit catalytic activity towards the disproportionation of hydrogen peroxide.

One of the principal routes to ethanedioate complexes depends upon its reduction of higher oxidation state metals. This reductive property of ethanedioic acid results in its ready dissolution of iron oxides, thus making it useful in the cleaning of nuclear power plants.⁵⁷

In the field of cancer research, metal complexes containing chelated dicarboxylate ligands (ethanedioate and propanedioate) have shown considerable activity against several types of cancerous tumours.⁵⁸ For example, the propanedioate $[\text{Pt}(\text{NH}_3)_2(\text{O}_2\text{C}(\text{CH}_2)\text{CO}_2)]$ complex has been successfully tested against the ADJ/PC6A tumour⁵⁹ and against advanced sarcoma - 180 tumours.⁶⁰ The exact nature of how these complexes inhibit tumour growth in the body is not clear, and research, so far, has failed to come up with a conclusive answer. However, analysis of aqueous solutions of these complexes by both UV spectroscopy and conductivity studies have shown them to be inert to substitution, and thus it is difficult to explain the anti-tumour effect in terms of leaving group ability. Propanedioic acid and several of its derivatives have also been reported⁶¹⁻⁶⁵ to have some tumour-inhibiting properties against several different types in mice.

I.4 DIMOLYBDENUM(II,II) MONOCARBOXYLATE COMPLEXES

I.4.1 Introduction to metal-metal bonds

From the 1900's to the 1960's transition metal chemistry was almost entirely based on the concept, developed by Alfred Werner,⁶⁶ of a central metal ion surrounded by a set of ligands. This "one-centre co-ordination chemistry" scheme focused on the characteristics of the central metal ion, its interaction with the surrounding ligands and the geometry and chemical characteristics of the ligand set.

From 1963 it was gradually realised that transition metals could also become involved in "multi-centre chemistry", with the recognition of the existence of chemical bonds with an order greater than 3. The quadruple bond was first discovered in 1964, and since then several hundred compounds containing it have been prepared and characterized.⁶⁶

In 1963 it was first shown that metal-metal bonds can be multiple. Molecular orbital analysis of the trirhenium(III,III,III) cluster $[\text{Re}_3\text{Cl}_{12}]^{3-}$ (*Figure 41*) showed that there were six doubly occupied bonding molecular orbitals covering the three Re-Re edges of the triangle, thus giving the molecular orbital equivalent of double bonds.⁶⁷

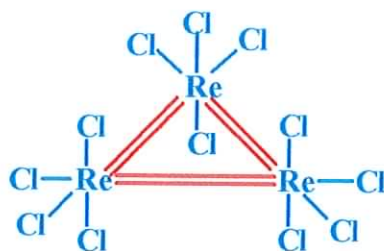


Figure 41

In late 1964 the existence of a quadruple bond in the dirhenium(III,III) anion $[\text{Re}_2\text{Cl}_8]^{2-}$ (*Figure 42*) was proposed and explained in detail.⁶⁸ Before the end of 1966 the first

triple bond between metal atoms was also reported,⁶⁹ in the dirhenium(II,III) complex $[\text{Re}_2\text{Cl}_5(\text{CH}_3\text{SCH}_2\text{CH}_2\text{SCH}_3)_2]$.

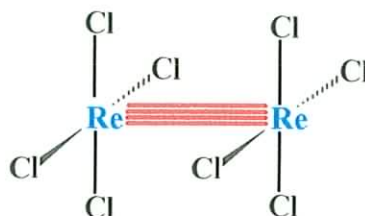


Figure 42

As early as 1959 the reaction between molybdenum hexacarbonyl and carboxylic acids had been investigated,⁷⁰ but there was no recognition of the possibility of metal-metal bonding in the complexes produced. In early 1965 the crystal structure of " $(\text{CH}_3\text{COO})_4\text{Mo}$ " was determined,⁷¹ and the molecular unit was found to be $[\text{Mo}_2(\mu\text{-O}_2\text{CCH}_3)]$ (*Figure 43*). The Mo-Mo distance in the complex was found to be extremely short (*ca.* 2.1 Å), even shorter than the Mo-Mo distance in metallic molybdenum. This, and the fact that molybdenum(II) is isoelectronic with rhenium(III), prompted the speculation that $[\text{Mo}_2(\mu\text{-O}_2\text{CCH}_3)_4]$ also contained a quadruple bond between the metal centres. Simultaneously with this report a paper was published⁷² proposing the existence of a quadruple bond in the technetium(II,III) complex anion $[\text{Tc}_2\text{Cl}_8]^{3-}$ (later found to have a Tc-Tc bond order of 3.5). In 1969 the molybdenum analogue of this compound, and of $[\text{Re}_2\text{Cl}_8]^{2-}$, *i.e.* the octachloro-dimolybdenum(II,II) anion $[\text{Mo}_2\text{Cl}_8]^{4-}$, was prepared and structurally characterized.⁷³

Since the 1960's hundreds of complexes containing metal-metal multiple bonds have been synthesized and characterized.⁶⁶ Quadruple bonds have been shown

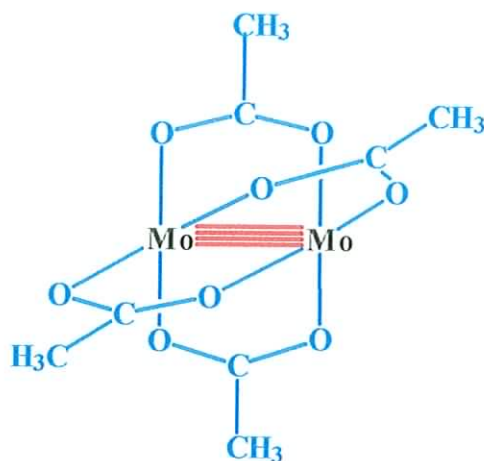


Figure 43

to be formed in chromium, molybdenum, rhenium, technetium and tungsten complexes. The chemistry of quadruply bonded dimolybdenum complexes will be discussed in detail in Section I.4.3.

I.4.2 Qualitative description of the quadruple bond

In 1964 Cotton *et al.*⁶⁸ proposed a qualitatively reliable description of the quadruple bond by considering only the interaction of the d-orbitals of the two metal atoms involved. When two "naked" transition metal atoms approach each other along the internuclear z-axis there are five possible overlaps of pairs of d-orbitals (*Figure 44*). The positive overlap of the two d_{z^2} orbitals gives rise to a σ -bonding orbital. Similarly a σ^* -antibonding orbital is formed from the negative overlaps. The overlaps of the d_{xz} orbitals and the overlaps of the d_{yz} orbitals give rise to degenerate pairs of π -bonding and π^* -antibonding orbitals. Finally, degenerate pairs of δ - and δ^* -orbitals are formed from the overlaps of the d_{xy} and the overlaps of the $d_{x^2-y^2}$ orbitals. The relative degrees of the three types of overlap, σ , π and δ , decrease in that order, and

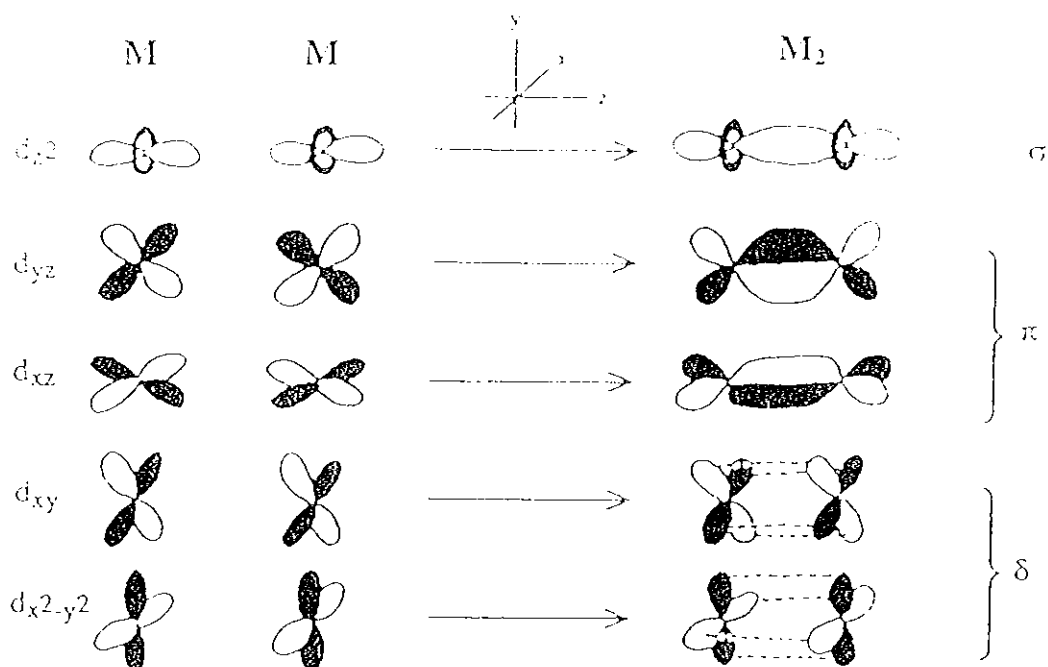


Figure 44

thus the ordering of bonding and antibonding orbitals might be expected to appear as in the column labelled M_2 of Figure 45, where, in energy terms, $\sigma < \pi < \delta < \delta^* < \pi^* < \sigma^*$.

This is the scenario in terms of the theoretical "naked" M_2 metal-metal system. When eight ligand donor atoms are introduced to this system (as in $[Mo_2Cl_8]^{4-}$ and $[Mo_2(\mu-O_2CCH_3)_4]$) the symmetry changes from being simple cylindrical to tetragonal prismatic. This results in a change in order of the molecular orbitals. As the M-M axis is defined as being in the z-direction, then the metal-ligand (M-L) bonds are in the x- and y-directions. The eight lobes of the overlapped $d_{x^2-y^2}$ orbitals point in the general direction of the ligands (along the +x, -x, +y and -y directions), therefore they can be assumed to be involved in the formation of M-L σ -bonds and not available for M-M bonding. One member of the δ set of M_2 drops to lower energy and becomes an

orbital and at the same time one member of the δ^* pair rises in energy and becomes an ML σ^* -orbital. These ML σ -orbitals are filled by electrons that contribute to M-L bonding and play no further role in M-M bonding. This is illustrated in the column labelled M_2L_8 in *Figure 45*.

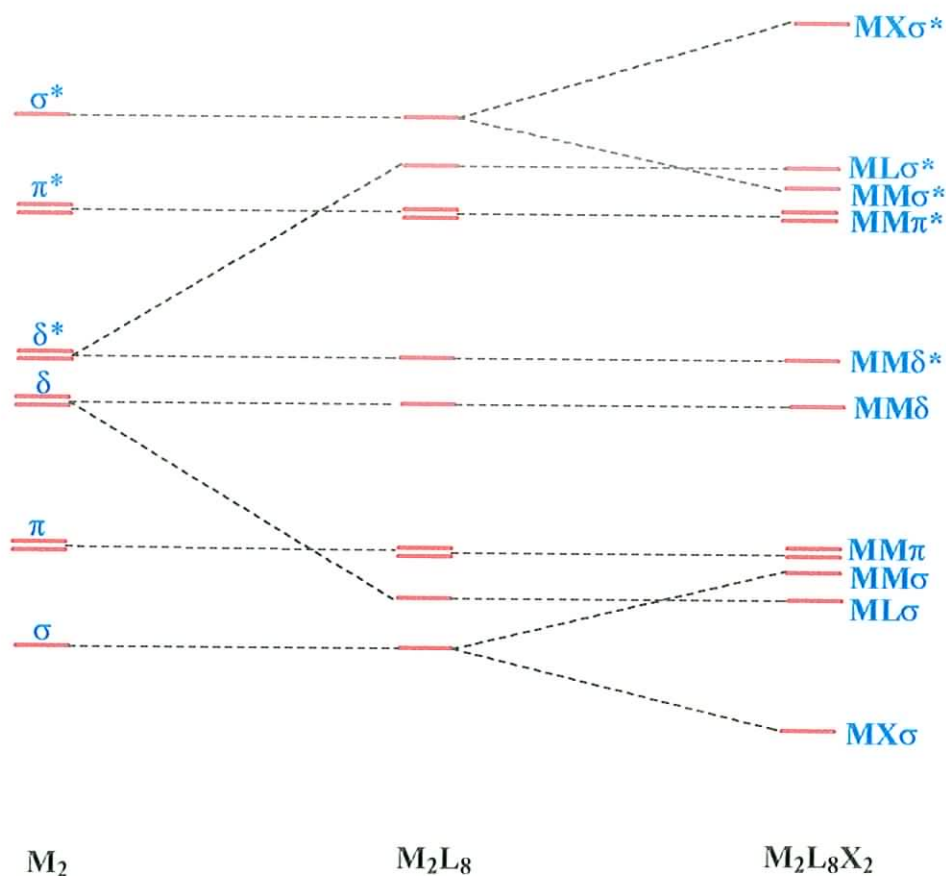


Figure 45

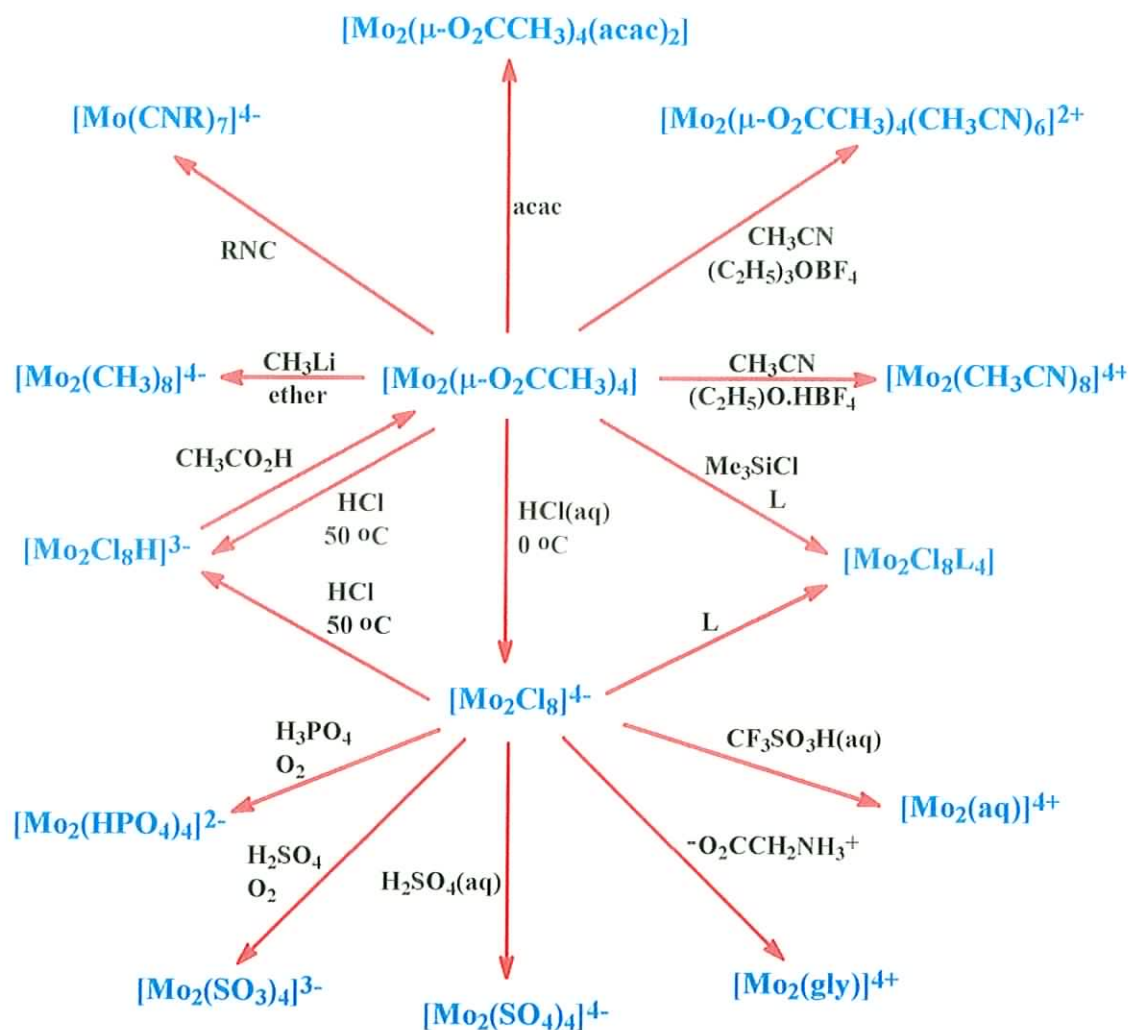
Due to the d^4 configuration of each metal in a dimolybdenum(II,II) complex (such as $[Mo_2Cl_8]^{4-}$) there are eight electrons to be placed in the orbitals involved in M-M bonding (the M-L σ -electrons having come from the ligands). This gives an electronic configuration of $\sigma^2\pi^4\delta^2\delta^{*0}\pi^{*0}\sigma^{*0}$. Conventional molecular orbital theory

defines the order of the bond as $(N_B - N_A)/2$ (where N_B and N_A are the numbers of electrons in bonding and antibonding molecular orbitals, respectively). In this case the bond order is 4 *i.e.* a quadruple bond. Similarly when a complex of the type $M_2L_8X_2$ (X = axial ligand) is considered, some of the M-M orbitals are altered, also resulting in a quadruple bond, albeit a weaker one (*Figure 45*). Theoretical⁷⁴ and spectroscopic studies⁷⁵ have given a more thorough picture of the M-M quadruple bond, but the above simple molecular orbital overlap representation remains qualitatively valid.

In M-M quadruply bonded complexes the δ -orbital is only weakly bonding whereas the δ^* -orbital is weakly antibonding. In energy terms, both orbitals are relatively close to each other. This means that an electron in the $\sigma^2\pi^4\delta^2$ ground state can be easily promoted to the $\sigma^2\pi^4\delta^1\delta^{*1}$ excited state, and this gives rise to an absorption band in the visible region of the spectrum. The characteristic royal blue colour of $[\text{Re}_2\text{Cl}_8]^{2-}$, intense red of $[\text{Mo}_2\text{Cl}_8]^{4-}$ and yellow of $[\text{Mo}_2(\mu\text{-O}_2\text{CCH}_3)_4]$ are due to $\delta \rightarrow \delta^*$ transitions at 700, 525 and 435 nm, respectively.

1.4.3 Dimolybdenum(II,II) carboxylates

At the present time the largest group of compounds that contain quadruple bonds are those of molybdenum. Some of these compounds and the reactions they are involved in can be seen in *Scheme 6*. One of the most important and useful of these complexes is the tetraacetate $[\text{Mo}_2(\mu\text{-O}_2\text{CCH}_3)_4]$ (*Figure 43*). The reaction between $\text{Mo}(\text{CO})_6$ and carboxylic acids was first examined in the late 1950's.⁷⁰ It was originally believed that the structure consisted of a polymer of tetrahedrally co-ordinated Mo(II) ions with no metal-metal bonding. However, it was later shown that an extremely short quadruple bond (2.093 Å) linked the two molybdenum atoms.⁷¹



Scheme 6

Many other analogues of the tetraacetate have been prepared by adapting the method first used by Wilkinson *et al.*⁸ This entails heating $\text{Mo}(\text{CO})_6$ with the appropriate carboxylic acid and anhydride (if available) in the high boiling solvent diglyme. This has consistently proved to give good yields of *ca.* 80%. The remaining molybdenum is converted to a number of higher oxidation state trinuclear compounds containing single Mo-Mo bonds.⁷⁶

Characterisation of these $[\text{Mo}_2(\mu\text{-O}_2\text{CR})_4]$ compounds has shown them to be isostructural with the tetraacetate and the Mo-Mo distances have been found to be relatively insensitive to the nature of the R group.⁷⁷ These complexes are reasonably

thermally stable ($[\text{Mo}_2(\mu\text{-O}_2\text{CCH}_3)_4]$ decomposes at *ca.* 300°C), but rather air-sensitive. Complexes of this type include the formate, trifluoroacetate, pivalate, benzoate, triphenylacetate and mandelate derivatives.⁶⁶ The molecules are generally ordered to form infinite chains in which there is weak axial co-ordination of each molecule to a carboxylate oxygen atom of its neighbour (*Figure 46*).

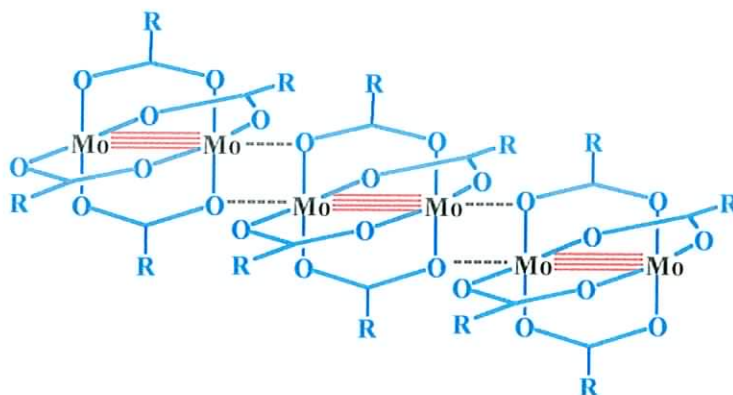


Figure 46

The tetracarboxylates readily form adducts where different ligands can co-ordinate axially to the Mo-Mo centre. This leads to a slight weakening and lengthening of the quadruple bond. Examples of these adducts include $[\text{Mo}_2(\mu\text{-O}_2\text{CC}_6\text{H}_5)_4(\text{diglyme})_2]$ ⁷⁸ and $[\text{Mo}_2(\mu\text{-O}_2\text{CCF}_3)_4(\text{py})_2]$ ⁷⁹ (*Figure 47*).

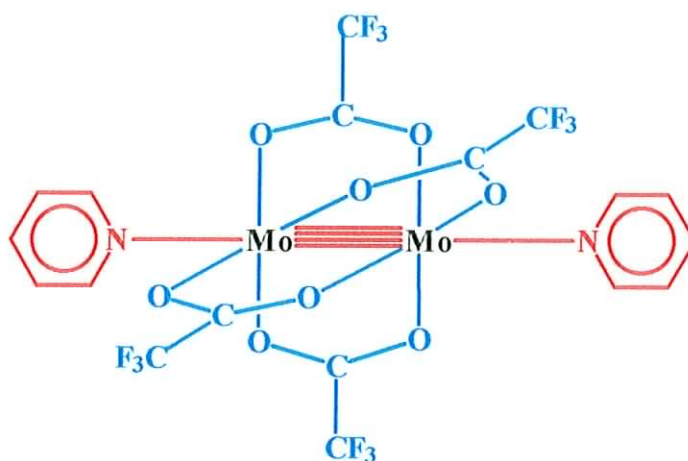


Figure 47

I.4.4 Partial replacement of carboxylate ligands

Dimolybdenum(II,II) complexes are also formed where there is replacement of some of the carboxylate groups of the $[\text{Mo}_2(\mu\text{-O}_2\text{R})_4]$ structure. There are several cationic species that contain carboxylate and nitrile ligands in the coordination sphere. Those that have been fully characterized contain the *cis*- $[\text{Mo}_2(\mu\text{-O}_2\text{CCH}_3)_2]^{2-}$ moiety, although the number of co-ordinated nitrile ligands varies. These dicationic complexes can be considered an intermediate stage in the conversion of $[\text{Mo}_2(\mu\text{-O}_2\text{CCH}_3)_4]$ to the tetracation $[\text{Mo}_2(\text{CH}_3\text{CN})_8]^{4+}$.⁶⁶

Telser and Drago⁸⁰ were the first to examine the interaction of strong non-complexing acids with $[\text{Mo}_2(\mu\text{-O}_2\text{CCH}_3)_4]$. The action of $\text{HBF}_4\cdot\text{Et}_2\text{O}$ produced a species which was assigned the dimolybdenum(II,II) formula $[\text{Mo}_2(\mu\text{-O}_2\text{CCH}_3)_2(\text{CH}_3\text{CN})_5][\text{BF}_3\text{OH}]_2$. The magenta-coloured crystals were stable indefinitely in an inert atmosphere but decomposed when exposed to air. As the oxidation state of both of the molybdenum atoms remained as molybdenum(II) this indicated that there was no cleavage of the Mo-Mo quadruple bond. Exposure of a solution of the complex to air caused it to change colour from red to yellow, and this implied that the Mo-Mo bond was broken and that a variety of monomeric species in more favourable oxidation states were formed. It was postulated that the BF_3OH^- ion was generated by an impurity present in the $\text{HBF}_4\cdot\text{Et}_2\text{O}$ solution.

Cotton *et al.*⁸¹ later examined the above reaction using Et_3OBF_4 and CH_3CN in CH_2Cl_2 solution, and succeeded in isolating red crystals of the salt $[\text{Mo}_2(\mu\text{-O}_2\text{CCH}_3)_2(\text{CH}_3\text{CN})_6][\text{BF}_4]_2$. Crystallographic studies revealed the $[\text{Mo}_2(\mu\text{-O}_2\text{CCH}_3)_2(\text{CH}_3\text{CN})_6]^{2-}$ cation to have the structure illustrated in *Figure 48*. The $[\text{Mo}_2(\mu\text{-O}_2\text{CCH}_3)_2]$ portion of the structure is similar to other cases which have two

cis-bridging carboxylate groups in association with four other equatorial ligand atoms (e.g. $[\text{Mo}_2((\text{pz})_2\text{Et}_2\text{B})_2]^{82}$). The Mo-Mo quadruple bond in $[\text{Mo}_2(\mu\text{-O}_2\text{CCH}_3)_2(\text{CH}_3\text{CN})_6][\text{BF}_4]_2$ is not as short (2.134 Å) as that in $[\text{Mo}_2(\mu\text{-O}_2\text{CCH}_3)_4]$ (2.093 Å), as the axial donor ligands share the same metal orbitals as those used to form the σ component of the Mo-Mo bond. The mean Mo-N equatorial distance (2.135 Å) is similar to the mean Mo-O distance (2.074 Å). However, the mean Mo-N axial distance (2.71 Å) is very long, suggesting the possibility of the easy dissociation of these ligands.

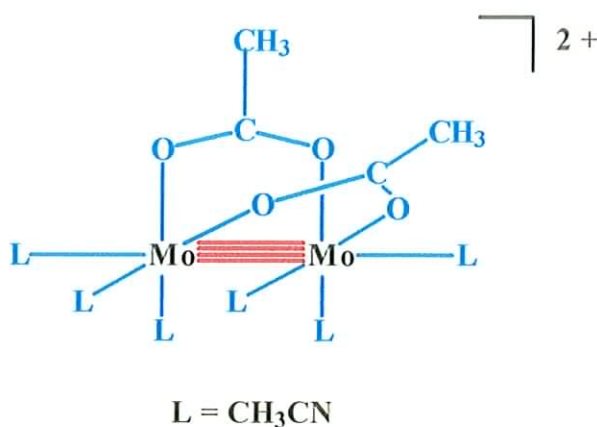


Figure 48

Clegg and his coworkers⁸³ also examined the structural and spectral properties of $[\text{Mo}_2(\mu\text{-O}_2\text{CCH}_3)_2(\text{CH}_3\text{CN})_6][\text{BF}_4]_2$. The presence of only one CH₃CN signal in the ¹H n.m.r. spectrum of a CD₃CN solution of this complex indicated that there was a rapid interchange between the axial and equatorial CH₃CN ligands. Due to this lability the displacement of these CH₃CN ligands was thought to offer a potential route for the formation of other complexes containing the $[\text{Mo}_2(\mu\text{-O}_2\text{CCH}_3)_2]^{2+}$ moiety, such as $[\text{Mo}_2(\mu\text{-O}_2\text{CCH}_3)_2(\mu\text{-dmpe})_2][\text{BF}_4]_2$.⁸⁴

$[\text{Mo}_2(\mu\text{-O}_2\text{CCH}_3)_2(\text{CH}_3\text{CN})_6][\text{BF}_4]_2$ has also been used as a starting point for the preparation of similar red dicationic complexes where the acetate groups have been replaced by unsaturated carboxylate ligands. Some of these new complexes, such as $[\text{Mo}_2(\mu\text{-O}_2\text{C}(\text{CH}_3)\text{C}=\text{CH}_2)_2(\text{CH}_3\text{CN})_4][\text{BF}_4]_2$ (Figure 49), have been successfully used as catalysts for the polymerization of norbornene and cyclopentadiene.⁸⁵

I.4.5 Total replacement of carboxylate ligands

The main examples of complex cations of the type $[\text{Mo}_2\text{L}_8]^{2+}$ (where L is a monodentate donor ligand) are the octakis(acetonitrile) derivatives. The complex

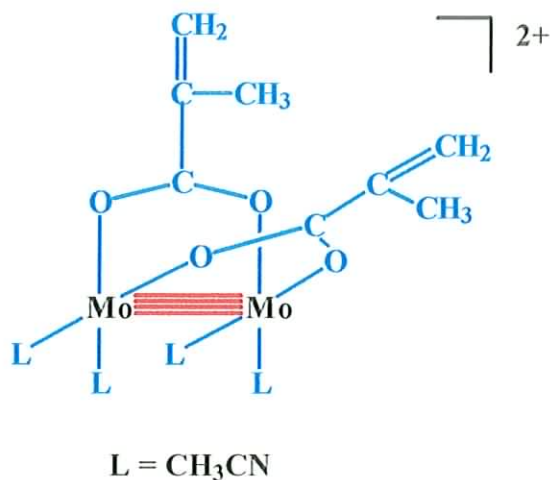


Figure 49

$[\text{Mo}_2(\text{CH}_3\text{CN})_8][\text{CF}_3\text{SO}_3]_2$ was obtained as blue crystals from the reaction of $[\text{Mo}_2(\text{CF}_3\text{SO}_3)_2(\text{H}_2\text{O})_4][\text{CF}_3\text{SO}_3]_2$ with CH_3CN .⁸⁶ Reaction of $[\text{Mo}_2(\text{CH}_3\text{CN})_8][\text{CF}_3\text{SO}_3]_2$ with acetic acid produces the yellow tetraacetate $[\text{Mo}_2(\mu\text{-O}_2\text{CCH}_3)_4]$.

The bright blue complex $[\text{Mo}_2(\text{CH}_3\text{CN})_8(\text{ax-CH}_3\text{CN})_2][\text{BF}_4]_4$ (*Figure 50*) prepared by reacting $[\text{Mo}_2(\mu\text{-O}_2\text{CCH}_3)_4]$ with (i) Et_3OBF_4 in acetonitrile,⁸⁷ and (ii) $\text{HBF}_4 \cdot \text{Et}_2\text{O}$.⁸⁸ $[\text{Mo}_2(\text{CH}_3\text{CN})_8(\text{ax-CH}_3\text{CN})_2][\text{BF}_4]_4$ is centrosymmetric and has a Mo-Mo distance of 2.187 Å. In addition, the complex exhibits a $\delta \rightarrow \delta^*$ electronic transition at 597 nm. The CH_3CN ligands are extremely labile thereby facilitating the use of this complex in the preparation of new dimolybdenum(II,II) complexes not readily synthesized by other means.⁸⁹

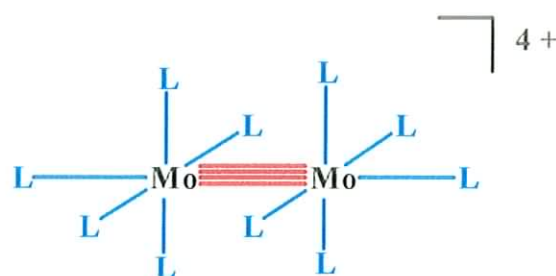


Figure 50

Addition of a slight excess of $\text{Ba}(\text{CF}_3\text{SO}_3)_2$ to a solution of $\text{K}_4[\text{Mo}_2(\text{SO}_4)_4]$ in trifluoromethanesulfonic acid results in the formation of a solution of the fully aquated red dimolybdenum(II,II) cation⁹⁰ represented as $[\text{Mo}_2(\text{aq})]^{4+}$. This red solution can be kept for long periods of time if oxygen is excluded.

The first cationic dimolybdenum(II,II) species to be isolated containing bidentate ligands was the orange ethylenediamine complex $[\text{Mo}_2(\text{en})_4]\text{Cl}_4$, which formed upon dissolving $\text{K}_4[\text{Mo}_2\text{Cl}_8]$ in neat ethylenediamine.⁹¹

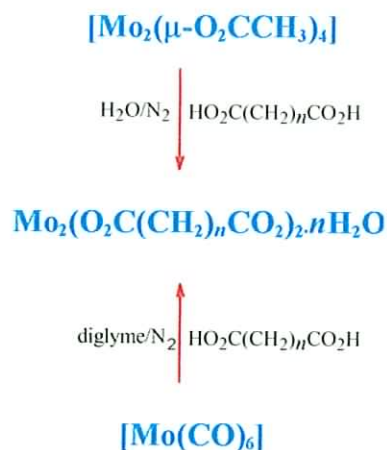
1.5 DIMOLYBDENUM (II,II) DICARBOXYLATES

The general lack of research into the whole area of dicarboxylate chemistry is evident for most metals in the periodic table and none more so than in the case of molybdenum. While molybdenum complexes make up the majority of complexes characterised in the overall picture of metal-metal bonded monocarboxylate chemistry, to date no X-ray crystal structures of molybdenum dicarboxylate complexes have been reported in the literature. Their synthesis, however, is unusual in that it is best conducted in aqueous media. Stephenson *et al.*⁸ observed that the interaction of $[\text{Mo}(\text{CO})_6]$ with dicarboxylic acids in dry diglyme afforded green powers of composition $[\text{Mo}(\text{O}_2\text{C}(\text{CH}_2)_n\text{CO}_2)]$ ($n = 3, 4$), while the green hydrates $\text{Mo}[\text{O}_2\text{C}(\text{CH}_2)_n\text{CO}_2] \cdot \text{H}_2\text{O}$ ($n = 2-4$) were obtained when "small amounts" of water were present in the reaction mixture. The IR spectra of these complexes showed strong bands in the $1400-1500 \text{ cm}^{-1}$ region due to asymmetric and symmetric carboxylate OCO stretches, while an additional broad band at $1700-1725 \text{ cm}^{-1}$ led the authors to assume that the dicarboxylate ligands coordinated *via* only one of their carboxylate functions.

In 1975, Mureinik²⁵ employed the same synthetic method as Stephenson *et al.* and prepared several new molybdenum(II) dicarboxylates of the general formula $\text{Mo}_2(\text{dicarboxylate})_2 \cdot n\text{H}_2\text{O}$. The names of a number of dicarboxylic acids used by Mureinik and their corresponding molybdenum complexes are illustrated in *Table 5*. In addition to using $[\text{Mo}(\text{CO})_6]$ as a starting material Mureinik also synthesised the same complexes *via* a ligand exchange reaction involving the diacids and $[\text{Mo}_2(\mu\text{-O}_2\text{CCH}_3)_4]$ (*Scheme 7*). The complexes were all obtained as fine amorphous powers, yellow coloured for the aliphatic and alicyclic acids, orange to red for the aromatic acids and almost black for *cis*-butenedioic and butyndioic acid. The complexes were all found to

Table 5.

Dicarboxylic Acids	Molybdenum Complexes
butanedioic (succinic acid)	Mo ₂ (butanedioate) ₂ ·2H ₂ O
hexanedioic (adipic acid)	Mo ₂ (hexanedioate) ₂ ·2H ₂ O
heptanedioic (pimelic acid)	Mo ₂ (heptanedioate) ₂ ·H ₂ O
<i>cis</i> -butenedioic (maleic acid)	Mo ₂ (butenedioate) ₂ ·2H ₂ O
propanedioic (malonic acid)	Mo ₂ (propanedioate)(acetate) ₂
butyndioic (acetylenedicarboxylic acid)	Mo ₂ (butyndioate)(acetate) ₂ ·2H ₂ O
1,2-benzenedioic (phthalic acid)	Mo ₂ (benzenedioate) ₂ ·H ₂ O Mo ₂ (benzenedioate) ₃ Mo ₂ (benzenedioate) ₄ ·H ₂ O
1,2-cyclohexanedicarboxylic acid	Mo ₂ (1,2-cyclohexanedicarboxylate) ₂
1,2-cyclohexene-4-dicarboxylic acid	Mo ₂ (1,2-cyclohexene-4-dicarboxylate) ₂
2,3-naphthalenedicarboxylic acid	Mo ₂ (2,3-naphthalenedicarboxylate) ₂ ·2H ₂ O
1,8-naphthalenedicarboxylic acid	Mo ₂ (1,8-naphthalenedicarboxylate) ₃ ·H ₂ O



Scheme 7

be air-sensitive to some extent but were stable under inert atmospheres. From the IR data Mureinik proposed a bis(dicarboxylato) formulation for the complexes. He assigned the band around 1730 cm^{-1} , not to an uncoordinated carboxylate function, but to a combination of carboxylate O-C-O and Mo-O stretching frequencies ($1400\text{ cm}^{-1} + 340\text{ cm}^{-1} = 1740\text{ cm}^{-1}$). The complexes were insoluble in all solvents and were believed to have a polymeric structure with two carboxylate groups of each diacid molecule coordinated to different dimolybdenum cores (*Figure 51*).

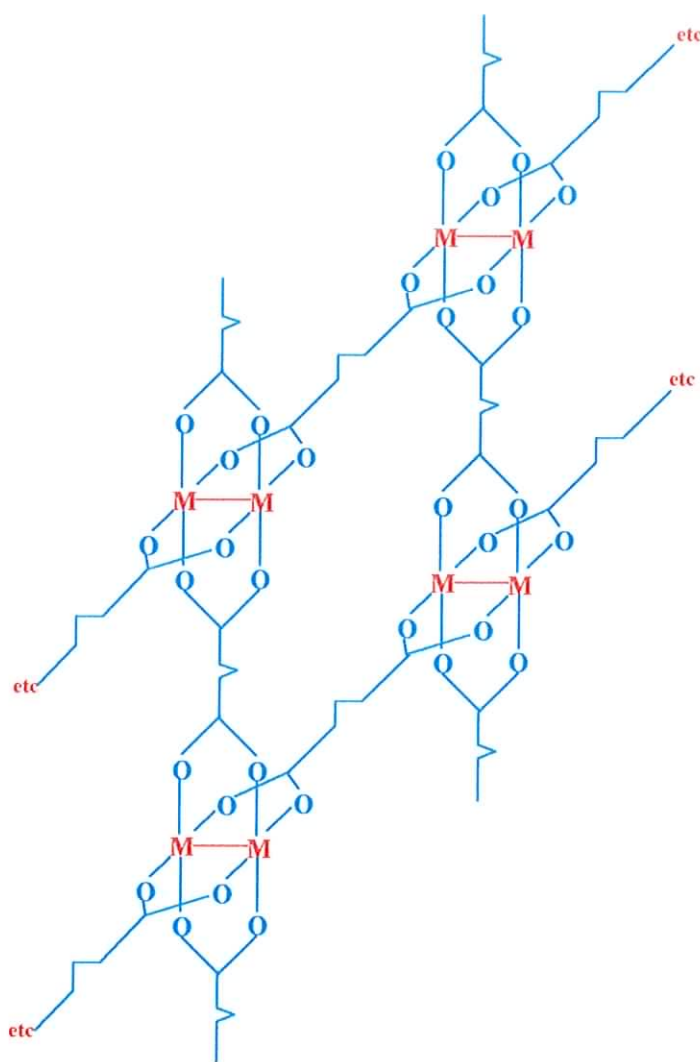


Figure 51

Mureinik proposed that for the ligand-exchange reaction the driving force was the formation of the highly insoluble polymeric complex, since it was assumed that the

new bonds formed were not markedly stronger than those broken. Depending upon the reaction conditions, 1,2-benzenedioic acid ($C_6H_4(CO_2H)_2$) reacted to give either $Mo_2(\text{benzenedioate})_2 \cdot H_2O$, $Mo_2(\text{benzenedioate})_3$ or $Mo_2(\text{benzenedioate})_4 \cdot H_2O$. In the case of propanedioic acid ($HO_2C(CH_2)CO_2H$) and butyndioic acid ($HO_2CC \equiv CCO_2H$) only partial substitution occurred to give the mixed carboxylate polymeric complexes $[Mo_2(O_2C(CH_2)CO_2)(O_2CCH_3)_2(H_2O)_2]_n$ and $[Mo_2(O_2CC_2CO_2)(O_2CCH_3)_2(H_2O)_2]_n$, respectively. Mureinik also reported the formation of complexes in which some of the diacids complexed *via* only one of their carboxylate functions. For example, 1,8-naphthalenedicarboxylic acid ($C_{10}H_6(CO_2H)_2$) reacted to give $[Mo_2(1,8\text{-naphthalenedicarboxylate})_3H_2O]$ (Figure 52). This tris diacid complex was considered to be composed of one molecule of acid dication bound to two Mo-Mo cores and two molecules of acid monocation acting monofunctionally per Mo-Mo unit.

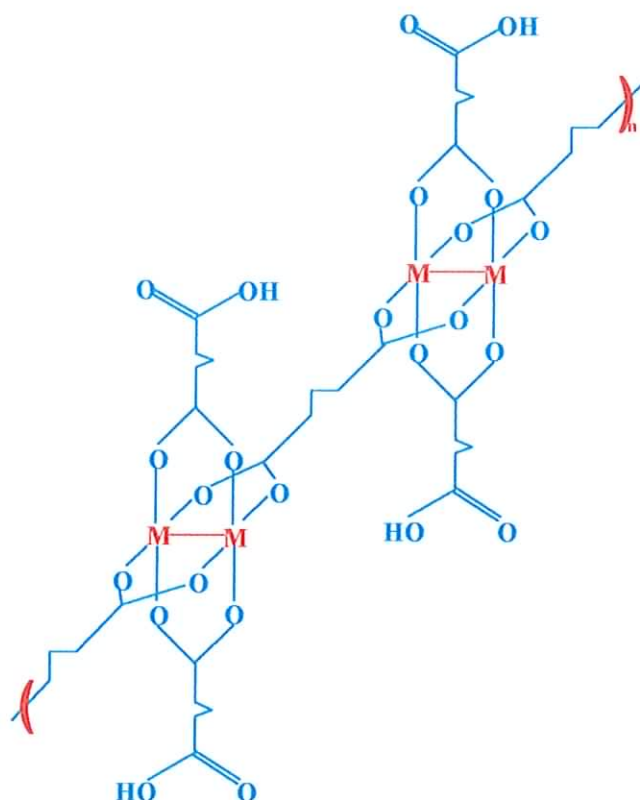


Figure 52

1.6 MOLYBDENUM CATALYSTS

1.6.1 The role of molybdenum in catalysis

Due to its variable oxidation state (0-VI), molybdenum forms many complexes which have found use as heterogeneous and homogeneous catalysts for a wide variety of reactions. Some examples of these catalysts and the reactions they catalyze are given in *Table 6*.

Classical Mo-SiO₂ catalysts are prepared by the impregnation of silica with an aqueous solution of ammonium heptamolybdate.⁹² Supported catalysts have also been prepared by the reaction of molybdenum species with the surface hydroxyl groups of silica.⁹³

Unsupported molybdenum species have also been used as heterogeneous catalysts. These include complexes used in conjunction with a cocatalyst (*e.g.* isopolyoxomolybdate(VI) salts with EtAlCl₂⁹⁴), and mixed-oxide catalysts often used in industrial processes.⁹⁵

In recent years, molybdenum complexes in solution have also found use as homogeneous catalysts. Quadruply-bonded dimolybdenum(II,II) carboxylate complexes in CH₃CN solution have proved to be useful catalysts for the polymerization of cyclopentadiene.⁸⁵ Polyoxomolybdate(VI) salts in aqueous solution containing, or in the presence of, an alkali or alkaline-earth metal cation have recently been used as photooxidation catalysts for the conversion of 2-butanol to 2-butanone.⁹⁶

Table 6. Heterogeneous and homogeneous molybdenum catalysts

CATALYST	REACTION CATALYZED	REF.
Supported catalysts:		
MoO ₃ -SiO ₂	Oxidative dehydrogenation of ethane	97
MoO ₃ -SiO ₂	Partial oxidation of methane	92,97
[Mo(CO) ₆]-SiO ₂	Olefin metathesis	98,99
[Mo(π-C ₃ H ₅) ₄]-SiO ₂	Olefin metathesis	100,101
	Hydrogenation of ethylene	102
MoCl ₅ -SiO ₂	Oxidation of methanol	93
MoS ₂ -Al ₂ O ₃	Hydrodesulphurization of hydrocarbons	103
Unsupported heterogeneous catalysts:		
[Mo(CO) ₆] / resorcinol	Metathesis of alkynes	104
MoCl ₅ / Ph ₄ Sn	Polymerization of phenylacetylene	105
(^t Bu ₄ N) ₂ [Mo ₆ O ₁₉] / Et ₂ AlCl ₂	Polymerization of norbornene	94
[Mo ₂ (μ-O ₂ CCH ₃) ₂ (MeCN) ₆][BF ₄] / EtAlCl ₂	Polymerization of norbornene	85
Bi ₂ O ₃ -MoO ₃ -UO ₂ -Sb ₂ O ₅	Synthesis of acrolein from propylene	95
CoO-MoO ₃	Synthesis of maleic anhydride from 1-butene	95
Homogeneous catalysts:		
[(Ph ₃ P) ₂ MoCl ₂ (NO) ₂]	Olefin metathesis	103
[MoH ₂ Cp ₂]	Olefin hydrogenation	106
[MoO ₅ (DMF)]	Olefin epoxidation	106
[Mo(NO) ₂ (MeCN) ₂ (DME) ₂] ²⁺	Polymerization of norbornadiene	107
(Et ₃ NH) ₃ [NaMo ₈ O ₂₆]	Photooxidation of 2-butanol	96
[Mo ₂ (μ-O ₂ CCH ₃) ₂ (MeCN) ₆][BF ₄]	Polymerization of cyclopentadiene	85

1.6.2 Unsupported catalysts

As early as 1969 Wilkinson *et al.*¹⁰⁸ investigated the protonation of quadruply-bonded transition metal carboxylates by HBF_4 , and hence produced homogeneous catalysts for the hydrogenation of olefins and alkynes. However, the catalyst derived from $[\text{Mo}_2(\mu\text{-O}_2\text{CCH}_3)_4]$ proved to be much less active than its dirhodium(II,II) and diruthenium(II,III) counterparts.

Diefenbach¹⁰⁹ prepared a wide range of bimetallic homogeneous catalysts for the metathesis of alkynes. For example, total conversion of hept-3-yne to the metathesis products hex-3-yne and oct-3-yne was achieved using $[\text{Mo}_2(\mu\text{-O}_2\text{CCH}_3)_2(\text{CH}_3\text{CN})_4][\text{CF}_3\text{SO}_3]_2$ in conjunction with $\text{Al}(\text{OC}_6\text{H}_4\text{Cl})_3$ in THF at 55 °C.

$[\text{Mo}_2(\mu\text{-O}_2\text{CCH}_3)_4]$ and $\text{K}_4[\text{MoCl}_8]$ have proved to be reasonably good catalysts for the ring-opening metathesis polymerization of 1-methyl-norbornene when EtAlCl_2 is employed as co-catalyst.¹¹⁰ $[\text{Mo}_2(\mu\text{-O}_2\text{CCH}_3)_2(\text{CH}_3\text{CN})_6][\text{BF}_4]_2$, and complexes derived from it and containing unsaturated carboxylate ligands, have been successfully used in the polymerization of norbornene, and also in the addition polymerization of cyclopentadiene.⁸⁵

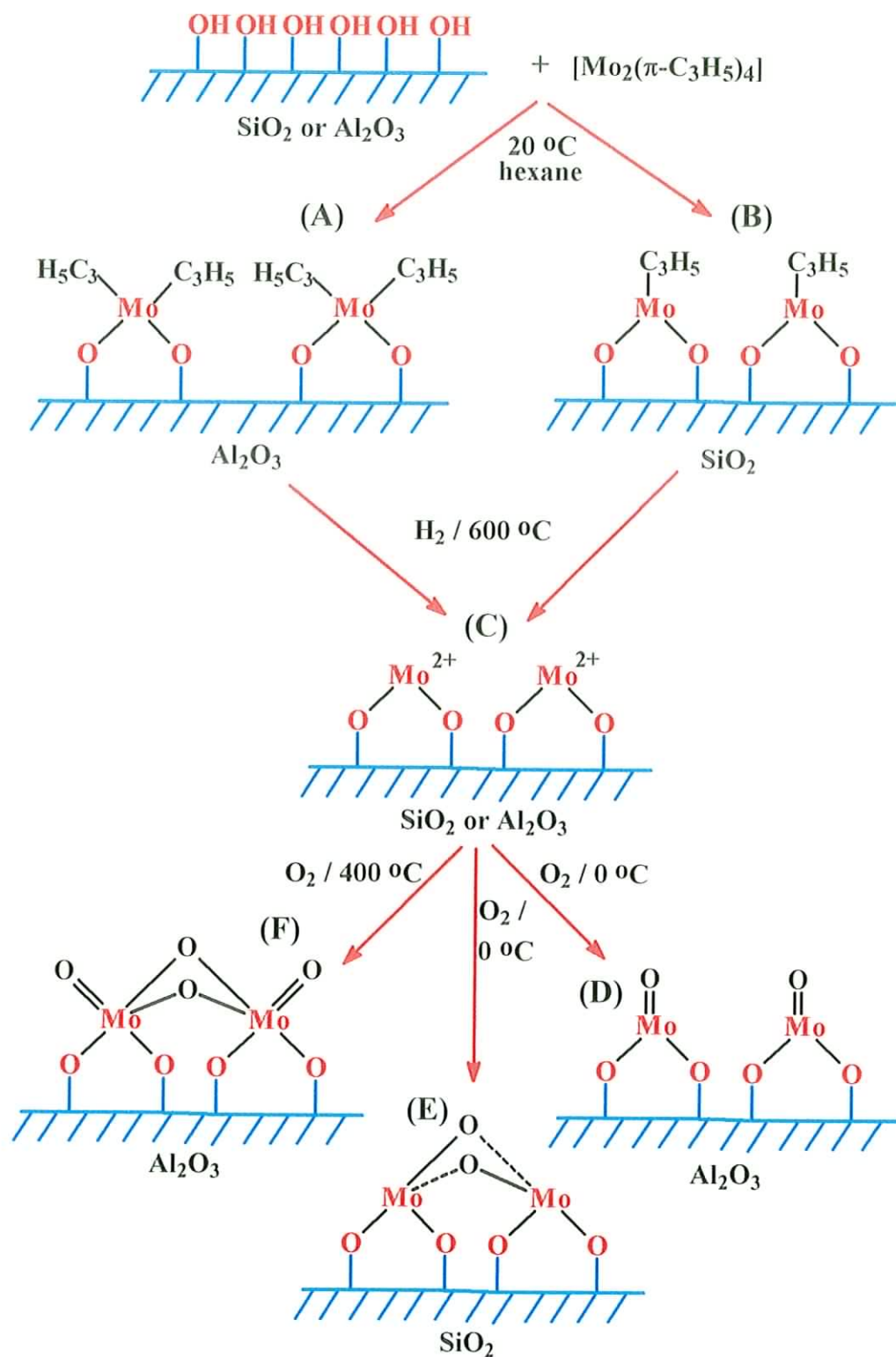
1.6.3 Supported catalysts

Candlin and his co-workers^{102,111} prepared heterogeneous catalysts by impregnating Al_2O_3 and SiO_2 with solutions of the dimolybdenum(II,II) allyl complex $[\text{Mo}_2(\pi\text{-C}_3\text{H}_5)_4]$. It was envisaged that the complex reacted with the surface hydroxyl groups of the support. No suggestions were made with respect to the structure of the supported species, or as to whether or not the Mo-Mo quadruple bond was retained after supporting the complex. The supported species proved active for the metathesis

of hex-1-ene and also for the polymerization of ethylene. However, as the monomolybdenum(IV) complex $[\text{Mo}(\pi\text{-C}_3\text{H}_5)_4]$ and its chromium, niobium, zirconium and tungsten analogues were also catalytically active for these reactions, it appears that it is the presence of the allyl groups rather than the dimolybdenum unit which is the source of the catalytic activity.

Iwasawa *et al.*¹¹²⁻¹¹⁴ also supported $[\text{Mo}_2(\pi\text{-C}_3\text{H}_5)_4]$ on SiO_2 and Al_2O_3 to produce a range of catalytically active grafted catalysts (*Scheme 8*). As before, it was found that $[\text{Mo}_2(\pi\text{-C}_3\text{H}_5)_4]$ bonded readily to the support *via* the hydroxyl groups giving species **A** (on Al_2O_3) and **B** (on SiO_2). Both **A** and **B** were reduced with H_2 at 600°C , which released the allyl ligands and produced species **C**. On exposure to O_2 at 0°C **C** was converted to either species **D** (on Al_2O_3) or species **E** (on SiO_2). At higher temperatures species **F** (on Al_2O_3) formed. All of the supported complexes **A-F** catalyzed reactions such as ethylene hydrogenation and the metathesis of propene. Using EXAFS it was found that the Mo-Mo distance for species **F** was *ca.* 3.15 \AA , and it was believed that this well-defined "paired structure" accounted for the greater activities of these catalysts compared to conventional supported mononuclear molybdenum catalysts.

Whan and his coworkers¹¹⁵ investigated the use of SiO_2 - and Al_2O_3 - supported $[\text{Mo}_2(\mu\text{-O}_2\text{CCH}_3)_4]$ and $[\text{Mo}_2(\text{CH}_2\text{SiMe}_3)_6]$ as catalysts for propene metathesis. Complexes soluble in cyclohexane were slurried with the support, whereas insoluble molybdenum complexes were simply dry-mixed with the silica or alumina. These workers were uncertain as to whether or not the Mo-Mo quadruple bond remained intact during the supporting procedure. Activation of the supported catalysts by heating them to $100\text{-}300^\circ\text{C}$ resulted in their oxidation, and this presumably occurred



Scheme 8

due to the interaction of co-ordinatively unsaturated molybdenum atoms with further hydroxyl groups. Catalysts formed from the less thermally stable carboxylate complex $[\text{Mo}_2(\mu\text{-O}_2\text{CCF}_3)_4]$, when activated at 300 °C, exhibited the highest activity for propene metathesis. The complexes behaved similarly to previous $[\text{Mo}(\text{CO})_6]$ precursors in that they provided labile sources of molybdenum to interact with the support. Oxidation of molybdenum(0) (as in $[\text{Mo}(\text{CO})_6]$) or molybdenum(II) (as in $[\text{Mo}_2(\mu\text{-O}_2\text{CCH}_3)_4]$) seemed to be a more efficient method of generating the active species compared to reduction of molybdenum(VI) (as in MoO_3).

Howe¹¹⁶ subsequently investigated the structure of Whan's supported dimolybdenum(II,II) complexes using EPR spectroscopy. It was found that at 100 °C the supported complex began to decompose. As the temperature of activation was increased the molybdenum(II) got oxidized to molybdenum(III), and finally to molybdenum(V), due to interaction with the surface oxygen groups. This supported molybdenum(V) species was believed to be identical to that derived from the oxidation of $[\text{Mo}(\text{CO})_6]$. However, as no correlation was found between the presence of molybdenum(V) and the activity of the catalyst for olefin metathesis, the exact nature of the active site could not be established.

Ichikawa *et al.*¹¹⁷ also investigated the nature of the active site in olefin metathesis catalysts derived from supported $[\text{Mo}_2(\mu\text{-O}_2\text{CCH}_3)_4]$. The catalyst was prepared by dry-mixing $[\text{Mo}_2(\mu\text{-O}_2\text{CCH}_3)_4]$ with activated SiO_2 . An ESR study of the system indicated that most of the original dimolybdenum(II,II) complex had been oxidized to the dimolybdenum(II,III) state upon mixing with the silica. The consequent change in the Mo-Mo bond order was from 4 to 3.5. Using EXAFS it was found that the Mo-Mo distance in the dimolybdenum(II,III) species (2.13 Å) remained similar to

that of the original complex (2.09 Å) up to 350 °C. Above this temperature the Mo-Mo distance lengthened (2.8 Å at 450 °C), indicating cleavage of the multiple bond. This cleavage occurred concurrently with the formation of an oxidized mononuclear molybdenum(V) species on the surface of the support. When activated at temperatures below 100 °C the supported complex showed no catalytic activity for olefin metathesis, whereas catalysts activated between 100-450 °C demonstrated good activity. Activation above 450 °C produced a catalyst which was inactive for olefin metathesis but which showed reasonable activity for ethylene homologation.

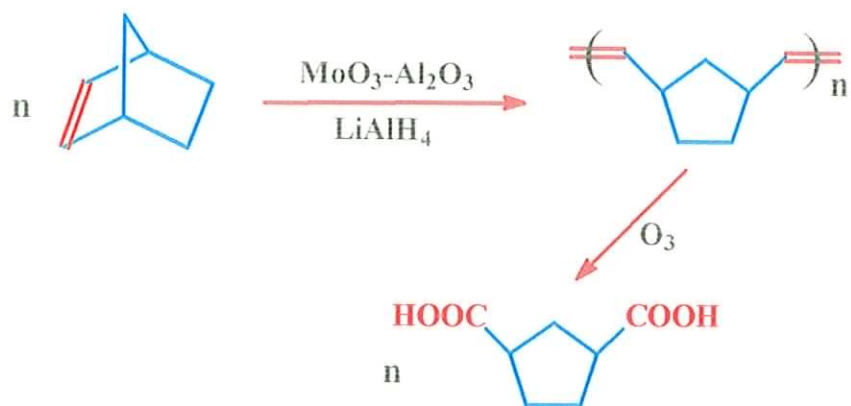
1.7 RING-OPENING METATHESIS POLYMERIZATION

1.7.1 Historical background

The ring-opening metathesis polymerization (ROMP) of cyclic alkenes has, in recent years, proven to be one of the most interesting fields of polymer chemistry. The reaction has been used to prepare a large number of elastomeric materials, only some of which have yet been commercially exploited. The study of ROMP has also proved to be an invaluable tool in the investigation of the mechanism of the general olefin metathesis reaction.

The first ROMP of a cyclic olefin was reported in a Dupont patent in 1955 by Anderson and Merckling¹¹⁸. Using a Ziegler-Natta catalyst they polymerized norbornene to a solid amorphous material with plastic properties. Shortly afterwards, in another Dupont patent, Eleuterio¹¹⁹ also reported the polymerization of norbornene and other cyclic alkenes such as cyclopentene, over a MoO₃-SiO₂ catalyst. Ozonolysis of the polymer prepared from norbornene produced *cis*-1,3-cyclopentane dicarboxylic acid. This indicated that a polymer with an unsaturated backbone had been formed by the opening of the cyclohexene ring on the norbornene (*Scheme 9*). Unfortunately, the low activity of the catalyst system used meant that not much importance was attributed to the discovery at the time. Truett *et al.*¹²⁰ later resumed the study of the polymerization of norbornene using more powerful Ziegler-Natta catalysts. The unsaturated nature of the polymer was again confirmed by ozonolysis.

During the 1960's Dall'Asta and his co-workers¹²¹⁻¹²³ carried out a comprehensive series of studies on the ring-opening polymerization of a large number of cyclic olefins. Using Ziegler-Natta catalysts they polymerized monomers such as cyclobutene,¹²² cyclopentene¹²¹ (*Scheme 10*), cyclooctene¹²¹ and dicyclopentadiene.¹²³



Scheme 9

Using different catalysts they were able to control, to a certain degree, the stereochemistry of the cyclopentene polymers produced.¹²¹ A molybdenum catalyst produced mostly *cis*-polypentenamer whereas a tungsten catalyst produced predominantly *trans*-polypentenamer.



Scheme 10

Until 1967 the chemistries of olefin disproportionation and ring-opening polymerization of cyclic olefins developed independently. The connection between the two different reactions was not immediately obvious. Disproportionation reactions were carried out at high temperatures over supported oxide catalysts such as $\text{MoO}_3\text{-SiO}_2$. On the other hand, Ziegler-Natta catalysts such as $\text{MoCl}_5/\text{Et}_3\text{Al}$ were employed for ring-opening polymerization reactions at much lower temperatures. The link that

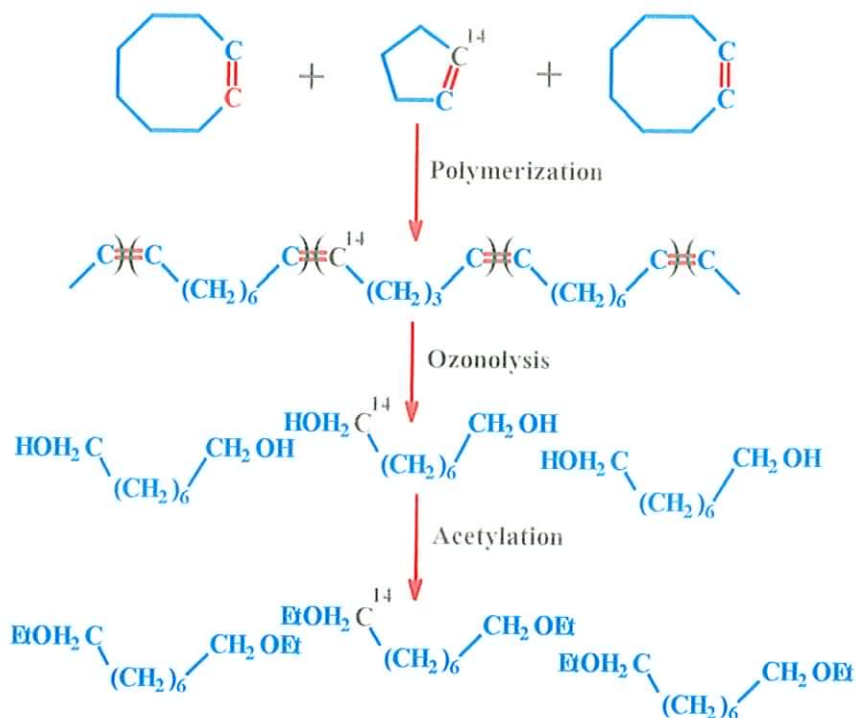
provided the connection between the two reactions was the discovery by Calderon that the $WCl_6/EtAlCl_2/EtOH$ system not only catalyzed the ring-opening polymerization of cyclooctene,¹²¹ but also the room-temperature disproportionation of pent-2-ene.¹²² It was then realized that the ring-opening *metathesis* polymerization of cyclic alkenes and the disproportionation of acyclic alkenes were both members of that branch of alkene reactions newly christened "olefin metathesis".¹²³

In 1968 Mol *et al.*¹²⁷ proved that the metathesis of acyclic olefins took place *via* cleavage of the double bond (transalkylidenation). To prove that in the ROMP of cyclic olefins the ring is also opened *via* cleavage of the double bond Dall'Asta¹²⁵ prepared copolymers of cyclooctene and isotopically labelled $[1-^{13}C]$ cyclopentene. The random copolymers produced were degraded by ozonolysis and the products were acetylated to their corresponding α,ω -diol acetates. All of the radioactivity was found to be localized in the $EtO(CH_2)_5OEt$ product, which indicated that ring-opening must have occurred by the breaking of the double bond (*Scheme 11a*). Ring-opening at a single bond adjacent to the double bond would have resulted in radioactive $EtO(CH_2)_8OEt$ (*Scheme 11b*).

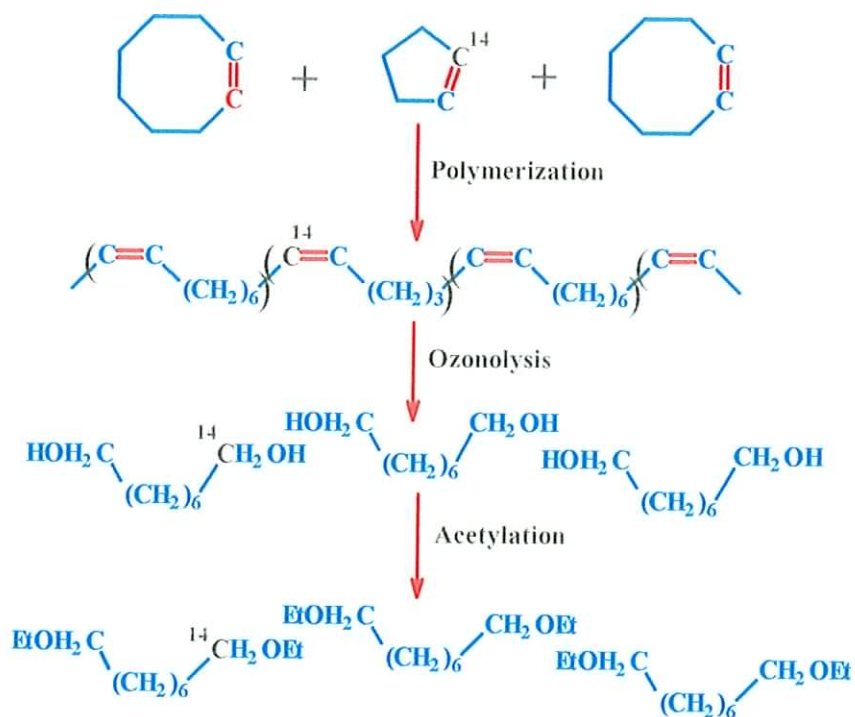
1.7.2 Reactants

ROMP has been carried out on most of the monocyclic olefins from cyclobutene to cyclododecene (except cyclohexene), and even higher members of the homologous series. A large number of bicyclic, tricyclic and polycyclic olefins have also been successfully polymerized. Some of the olefins which have been used as monomers for ROMP, together with the basic structure of the polymers produced, are outlined in *Table 7*.

(a) Ring-opening at the double bond









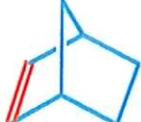

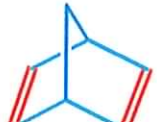
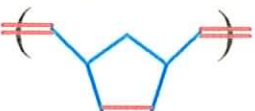
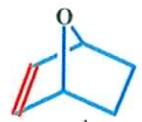


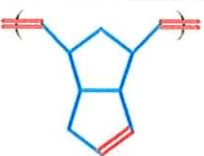




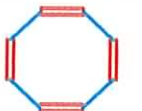

(b) Ring-opening at single bond next to double bond



Scheme 11

TABLE 7.

Monomers used in ROMP

MONOMER	POLYMER STRUCTURE	REF
 cyclobutene		122, 128
 cyclopentene		121, 129
 cyclooctene		119, 121, 130
 norbornene		see section I.8
 norbornadiene		131, 132
 7-oxanorbornene		133, 134
 <i>endo</i> -dicyclopentadiene		123, 130
 1,1,2,2-tetramethyl-1,2-disilacyclopent-3-ene		135
 benzvalene		136
 cyclooctatetraene		137, 138

The most important factor governing the ability of a particular olefin to undergo ROMP is the Gibbs Free Energy change (ΔG°) of the reaction.¹³⁰ This is related to the enthalpy change (ΔH°) and entropy change (ΔS°) of the reaction by the expression: $\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$. If ΔG° is negative then the ROMP reaction is thermodynamically probable if a suitable mechanism exists.

For the ROMP of the smaller monocyclic olefins such as cyclobutene the entropy change is negative ($\Delta S^\circ < 0$), therefore, entropy is not a driving force for the reaction.³ Cyclobutene is a highly strained ring system due to the considerable deviation of the ring angles from the normal tetrahedral angle of sp^3 -hybridized carbon atoms ($109^\circ 28'$).¹²⁹ Therefore, cyclobutene and similar small cyclic olefins do undergo ROMP due to the release of ring strain which provides substantial reaction enthalpy ($\Delta H^\circ < 0$) to offset the unfavourable reaction entropy.

The non-polymerizability of cyclohexene¹²¹ *via* ROMP is attributed to its low ring-strain ($\Delta H^\circ \approx 0$).¹³⁰ Cyclohexene usually exists in the "chair" conformation which is considerably more stable than the alternative "boat" conformation. This enhanced stability reduces the mobility of the molecule and the possibility of its conversion into other more reactive conformations. Attempts to polymerize cyclohexene using metathesis catalysts results only in the production of addition polymers which contain the even more stable cyclohexane ring as the repeating unit.¹²¹ In bridged multicyclic olefins, such as norbornene and dicyclopentadiene, the cyclohexene ring adopts the more strained boat conformation. The lower stability of the boat conformations in these olefins favours their ring-opening polymerization.

For larger monocyclic olefins the ring strain is very low ($\Delta H^\circ \approx 0$) but this is offset by a positive reaction entropy ($\Delta S^\circ > 0$). Consequently, these larger olefinic

rings undergo entropy-controlled ROMP. The relationship between polymerizability, ring-strain and reaction entropy has been investigated by Dainton¹³⁷ for the theoretical ring-opening polymerization of the slightly less-strained cycloalkane series (*Table 8*). In general, the trend is similar for the ROMP of cycloalkenes.¹³⁸

Table 8. Thermodynamic parameters for the theoretical ring-opening polymerization of cyclo-alkanes

Cycloalkane (CH ₂) _n n =	ΔH ⁰ (kJ mol ⁻¹)	ΔS ⁰ (kJ mol ⁻¹)	ΔG ⁰ (kJ mol ⁻¹)
3	-113	-69	-93
4	-105	-51	-89
5	-29	-43	-9
6	+3	-11	+6
7	-21	-3	-21
8	-35	+37	-46

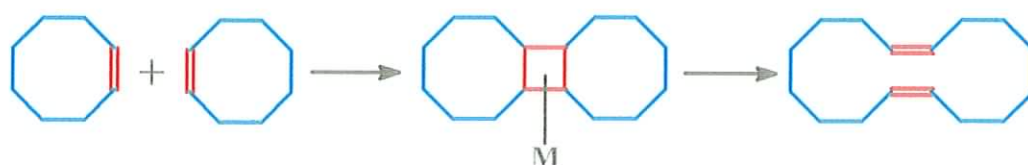
1.7.3 Mechanism

Originally, it was believed that the ring-opening of cyclic olefins occurred *via* cleavage of a carbon-carbon single bond adjacent to the double bond.¹²⁰ Subsequently, Dall'Asta¹²⁵ proved that cleavage occurred at the double bond itself. When the relationship between the ring-opening polymerization of cyclic olefins and the metathesis of acyclic olefins was finally identified it was realised that the former reaction must also occur by a metathetic mechanism.¹⁴¹

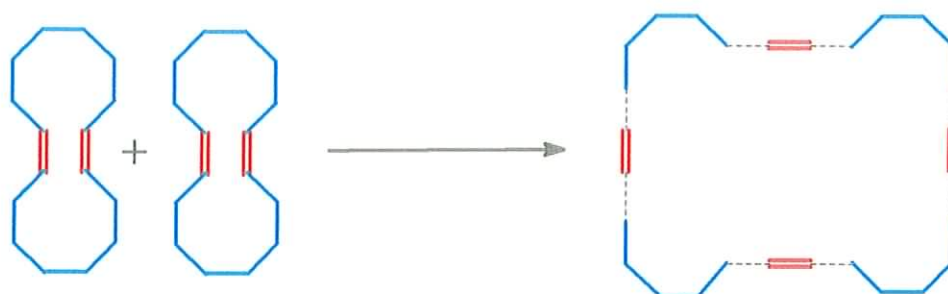
Calderon *et al.*¹⁴² proposed a mechanism for ROMP analogous to the “pairwise” mechanism previously proposed for the metathesis of acyclic olefins.^{124,143}

In the initiation step two cycloolefin molecules react *via* their double bonds with the transition metal catalyst to form a weakly held quasi-cyclobutane intermediate complex (Scheme 12).

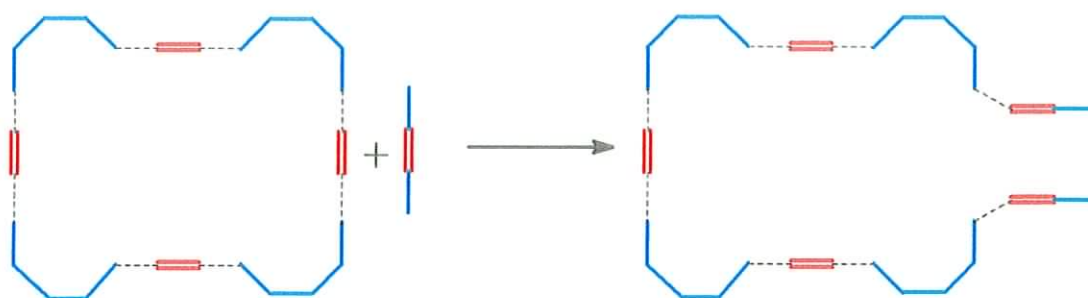
Initiation



Propagation



Termination



Scheme 12

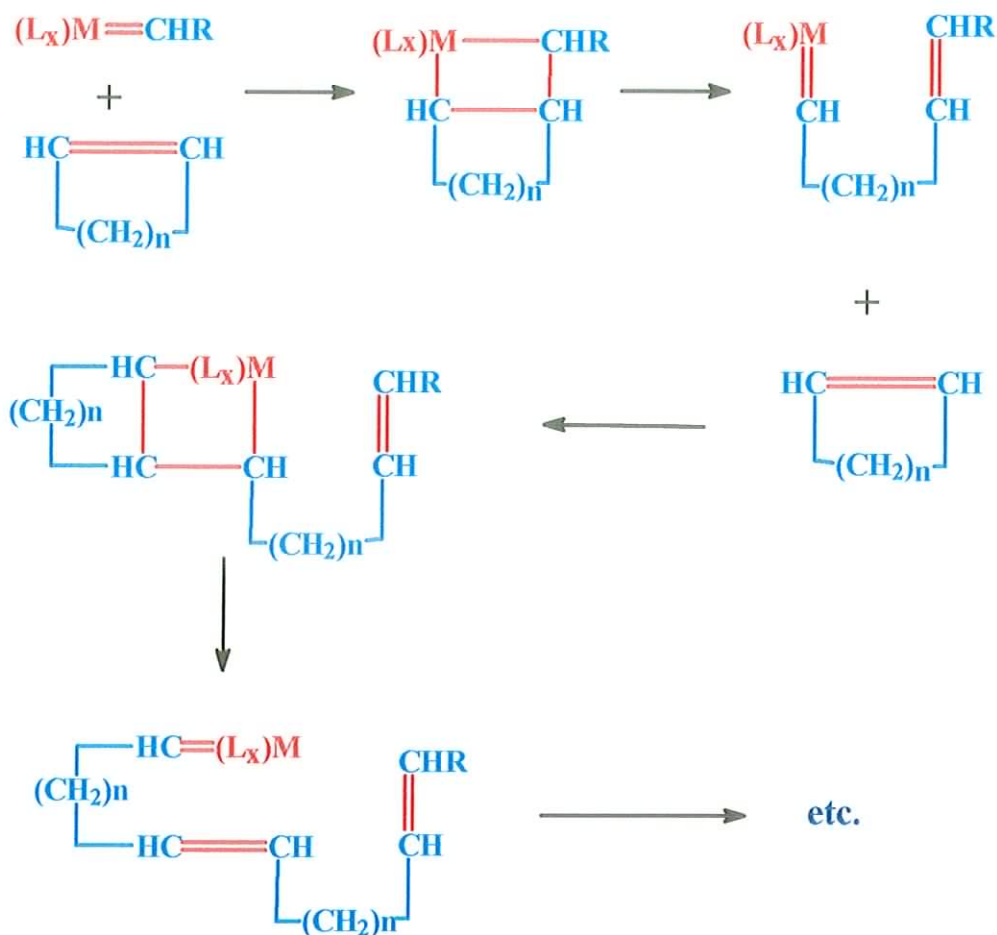
Rearrangement of this intermediate results in the formation of a dimeric cyclic olefin.

This dimer further reacts with other dimers or oligomers to form progressively larger

macrocyclic polyalkenamers. Cleavage of a macrocycle at a double bond with an acyclic olefin (alkenolysis) or a similar termination reaction results in the formation of a linear polymer. GLC and ^1H nmr analysis of the reaction mixture from the ROMP of cyclooctene confirmed the presence of unsaturated macrocyclic compounds.¹¹ It was also found that under normal ROMP conditions these cyclic oligomers could be converted into high polymer, and that the polymer could also be degraded into macrocyclic olefins.

In 1970, Herisson and Chauvin¹² proposed an alternative metathetic mechanism for ROMP based on an insertion-type reaction through a carbene species (*Scheme 13*). Propagation of the reaction occurs *via* a transient metallacyclobutane intermediate which rearranges to form a new metal carbene species as chain carrier at every stage. Herisson and Chauvin based their proposal on observing the products formed in the cross-metathesis of a cyclic olefin and an acyclic olefin.

Calderon's pairwise mechanism predicts that there would be a gradual increase in the molecular weight of the polymer formed by ROMP due to the increasing size of the macrocyclic oligomers. It also predicts that there would be a marked change in the relative proportions of the different oligomers as the reaction progresses. In practice, however, it has been found that: (a) cyclic oligomers and high polymer are formed concurrently in ROMP reactions (provided that the initial monomer concentration exceeds a certain critical value); (b) there is little change in the relative proportions of the different oligomers during the course of the reaction.^{11,12}

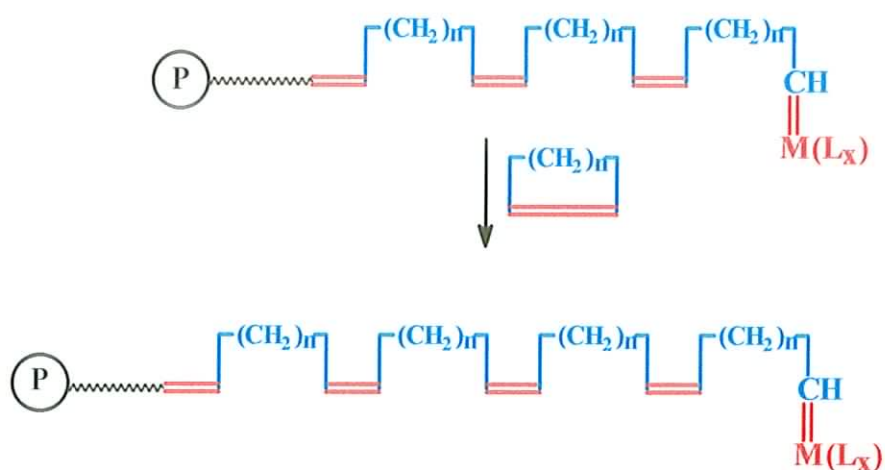


Scheme 13

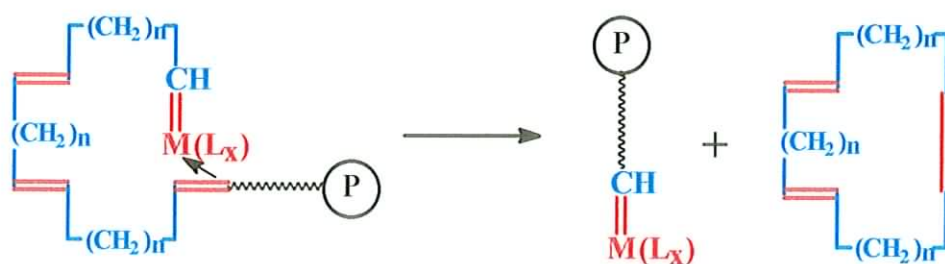
These two observations can only be reasonably interpreted in terms of a chain process such as the metal carbene mechanism.¹⁴² Competition occurs between the propagation of the ROMP reaction to form polymer and an intramolecular reaction (“back-biting”) to form cyclic oligomers (*Scheme 14*). At low monomer concentrations it is more likely that the growing polymer chain will react intramolecularly rather than with another monomer molecule, therefore, the production of cyclic oligomers will be favoured. Conversely, at high concentrations of monomer the propagation of the polymerization reaction will predominate. Double bonds on the backbone of a growing polymer chain some distance from the metallacarbene end of the polymer are unlikely to

come in contact, and react with the transition metal. This accounts for the fact that only small amounts of large oligomers are produced under normal polymerization conditions, and that there is little change in the relative proportions of the different oligomers as the reaction progresses.

(a) Propagation reaction



(b) Intramolecular reaction



Scheme 14

I.7.4 Catalysts

The range of effective catalysts for metathesis reactions is governed to a certain degree by the exothermicity of the reaction. The metathesis of acyclic olefins is essentially a thermoneutral reaction, therefore, only the more active molybdenum,

rhenium and tungsten catalysts are effective. On the other hand, the ROMP of cycloolefins containing a large degree of ring-strain, such as cyclobutene and norbornene, can be achieved using less active metathesis catalysts derived from other transition metals such as iridium, niobium, osmium, rhodium, ruthenium, tantalum, titanium and vanadium. Less strained cyclo-olefins, such as cyclopentene, usually require the use of more active catalysts under carefully controlled conditions.

Literally hundreds of transition metal complexes have been investigated as potential catalysts for ROMP reactions.^{139,140,142} A small sample of these different catalysts and the cyclic alkenes that they can polymerize is listed in *Table 9*. These catalysts can be divided into three general classifications depending on the method of formation of the initial metal carbene. The role and use of preformed metallocarbene catalysts will be examined in this section.

Although most isolable metal carbenes have proved disappointing as catalysts for the metathesis of acyclic olefins they have been successfully used as ROMP catalysts. The early Fischer carbenes have proved active only for the ROMP of highly strained cyclic olefins such as norbornene.¹⁴⁴ Addition of a cocatalyst such as TiCl_4 increases the activity of these carbenes for the polymerization of less-strained monomers. As one equivalent of CO is evolved per mole of added TiCl_4 it is assumed that the function of the cocatalyst is to open a site on the transition metal centre thus allowing the coordination of an olefinic monomer molecule. A less stabilized metal carbene complex developed by Casey¹⁴⁵ (*Figure 53*) has proved reasonably active for the ROMP of less-strained cyclic olefins, such as cyclooctene, even in the absence of a cocatalyst. Spectroscopic studies of the polymer produced revealed the presence of one phenylidene end-group per polymer chain, confirming that the original

Table 9.

Catalysts for ROMP

CATALYST	MONOMER	REF.
Catalysts requiring cocatalyst:		
TiCl ₄ / LiAlHep ₄	norbornene	120
WCl ₆ / Et ₃ Al	cyclopentene	121
ReCl ₅ / Me ₄ Sn	dicyclopentadiene	146
RuCl ₃ / H ₂ O	7-oxanorbornene	134
VCl ₄ / LiBu	cyclobutene	122
(Cl ₃ HI ₂) ₃ NH ₄ [Mo ₈ O ₂₆] / EtAlCl ₂	dicyclopentadiene	147
[Ru(H ₂ O) ₆ (tos) ₂] / EtO ₂ CCHN ₂	cyclooctene	129
(ⁿ Bu ₄ N) ₂ [MoO ₆ O ₁₉] / EtAlCl ₂	norbornene	94
Catalysts not requiring cocatalyst		
WCl ₆	norbornene	148
ReCl ₅	dicyclopentadiene	149
RhCl ₃ .H ₂ O	dicyclopentadiene	123
[Ru(H ₂ O) ₆ (tos) ₂]	7-oxanorbornene	129
[(<i>p</i> -cy)RuCl ₂].Pcy ₃	norbornene	150
IrCl ₃	cyclooctene	151
OsO ₄	norbornene	152
Metal carbene catalysts		
[(Me ₃ CCH ₂ O) ₂ Br ₂ W = CHBu ^t]	7-oxanorbornene	133
[(OBu ^t) ₂ (N-2,6-C ₆ H ₃ -Pr ^t ₂)Mo = CHBu ^t]	benznorbornadiene	153
[((CF ₃) ₂ MeCO) ₂ (N-2,6-C ₆ H ₃ -Pr ^t ₂)W = CHBu ^t]	methylocyclooctetraene	154
[(OBu ^t) ₂ (N-2,6-C ₆ H ₃ -Pr ^t ₂)Mo = CH(CPhMe ₂)]	3,3-diisopropylcyclobutene	155
[((CF ₃) ₂ MeCO) ₂ (N-2,6-C ₆ H ₃ -Pr ^t ₂)W = CHBu ^t]	benzvalene	156
[Cp ₂ Ti = CH ₂]	3,4-diisopropylidene-cyclobutene	157
[(PPh ₃) ₂ Cl ₂ Ru = CH(CHCPH ₂)]	norbornene	158

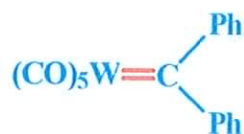


Figure 53

metallacarbene initiated the ROMP reaction.

Schrock and his coworkers¹⁵⁹ prepared tungsten-oxo-carbene complexes containing the neopentylidene group (Figure 54a), and these proved to be active ROMP catalysts in the presence of a Lewis acid cocatalyst. The role of the cocatalyst appears to be the removal of a chloride or phosphine ligand and open up a vacant site on the metal for the coordination of an olefin molecule. It is significant that a related five-coordinate metallacarbene complex (Figure 54b) does not require the addition of a cocatalyst to be active.

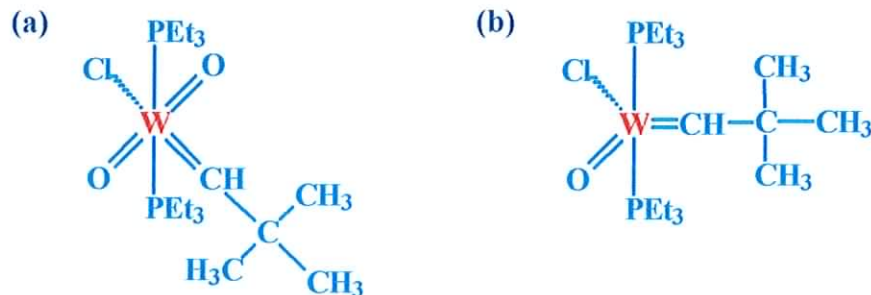
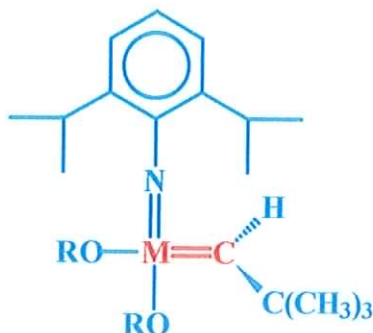


Figure 54

Schrock¹⁶⁰ later synthesized similar carbene complexes (Figure 55) in which the oxo ligand was replaced by a hindered aryl imino group (usually N-2,6-diisopropylphenyl). These metallacarbene complexes have proved to be extremely versatile ROMP catalysts whose activity can be “tuned” over a wide range of cyclic monomers by simply changing the nature of the alkoxy (OR) ligands. No cocatalysts

are required in these reactions. With these new carbene catalysts it has been possible to initiate the ROMP of unusual cyclic monomers which were not readily polymerized using the more traditional metathesis catalysts.



M = Mo; W

Figure 55

1.7.5 Applications of ROMP

The ROMP of cyclobutene and 1-methylcyclobutene produce the commercially important elastomers polybuta-1,4-diene and polyisoprene, respectively. These reactions have been fully investigated but have not been commercially developed as equivalent products may be manufactured more cheaply using existing technologies.¹⁶¹

For several years it appeared that the ROMP of cyclopentene had industrial potential as a route to a commercially viable elastomeric material.¹⁴⁰ Cyclopentene is an inexpensive monomer as it is readily available from the hydrogenation of cyclopentadiene, a by-product of naphta cracking. Polypentenamer obtained *via* ROMP is a good general purpose rubber which can be vulcanized to give products comparable with polybutadiene and polyisoprene. The physical properties of the polymer is dependent on its *cis* content which can be controlled by using different

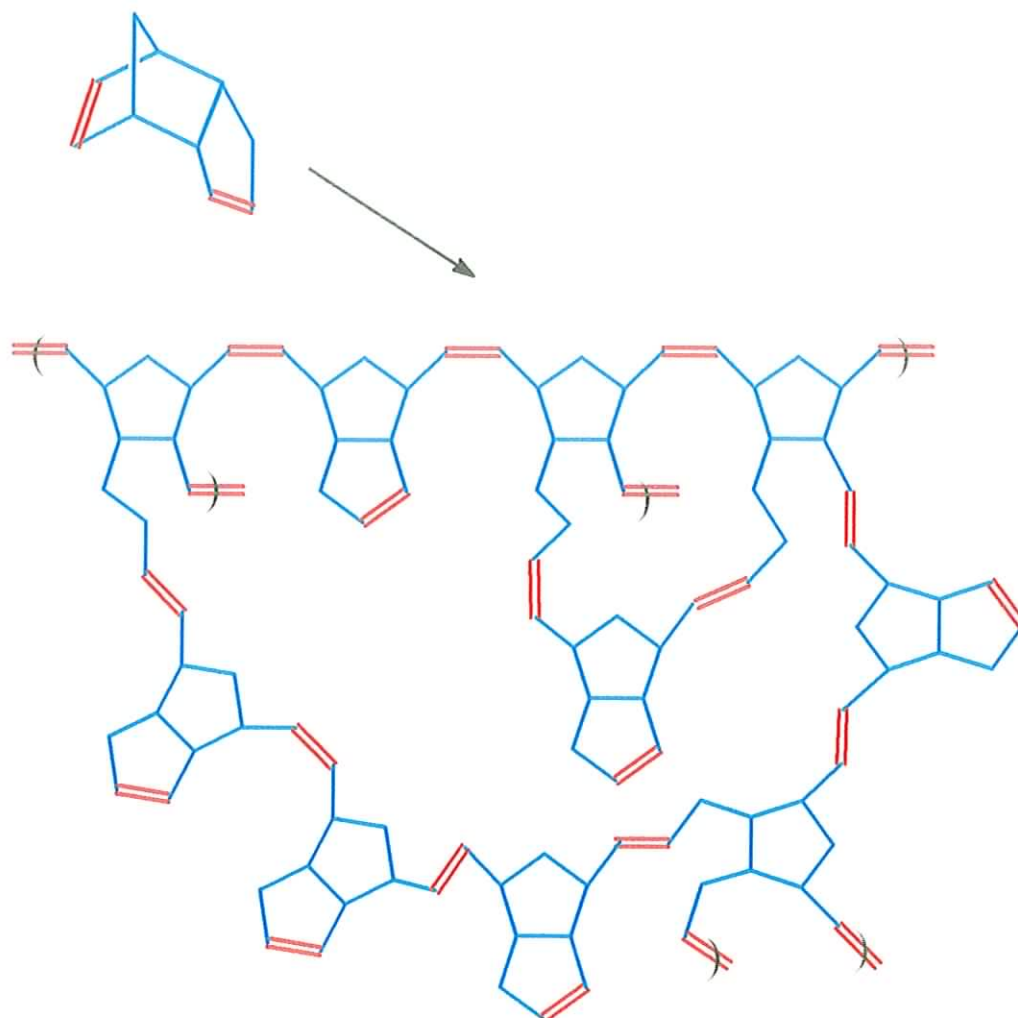
catalyst systems. The use of polypentenamer as a tyre-rubber has been seriously investigated. Unfortunately during road-testing the product failed dramatically, possibly due to metathesis depolymerization caused by residual catalyst.¹⁶²

At present the most successful polymer produced by ROMP in terms of production (12,000 tonnes per annum in 1988) is the low molecular weight *trans*-polyoctenamer obtained from *cis*-cyclooctene. This product is marketed as Vestenamer by Chemische Werke Hüls,¹⁴⁰ and it finds use as a viscosity-reducing agent in blends with other elastomers.

Polynorbornene, the first polymeric material to be prepared *via* ROMP,¹¹⁸ was not industrially exploited until twenty years later in 1976.¹⁶¹ The commercial elastomer is manufactured by CdF Chimie using a homogeneous RuCl_3 catalyst. The product which is marketed as Norsorex, contains *ca.* 90% *trans* double bonds and has a molecular weight of *ca.* 2×10^6 . Because of its capacity to absorb large volumes of solvents it has been used to mop up minor oil spillages.¹⁶³ The vulcanized versions of Norsorex exhibit high dynamic damping ability which make them useful in noise and vibration applications.^{164,165}

The commercial exploitation of the ROMP of dicyclopentadiene, a cheap tricyclic olefin, has attracted much attention over the last decade. In 1985 Hercules developed a production unit for the manufacture of polydicyclopentadiene *via* reaction injection moulding.¹⁶⁶ This plastic material, which is marketed under the name Metton, consists of ring-opened norbornene units cross-linked by the ring-opening of some of the cyclopentene rings (*Scheme 15*). Metton has extremely good mechanical properties and can be readily moulded into a variety of shapes. It is presently used in the

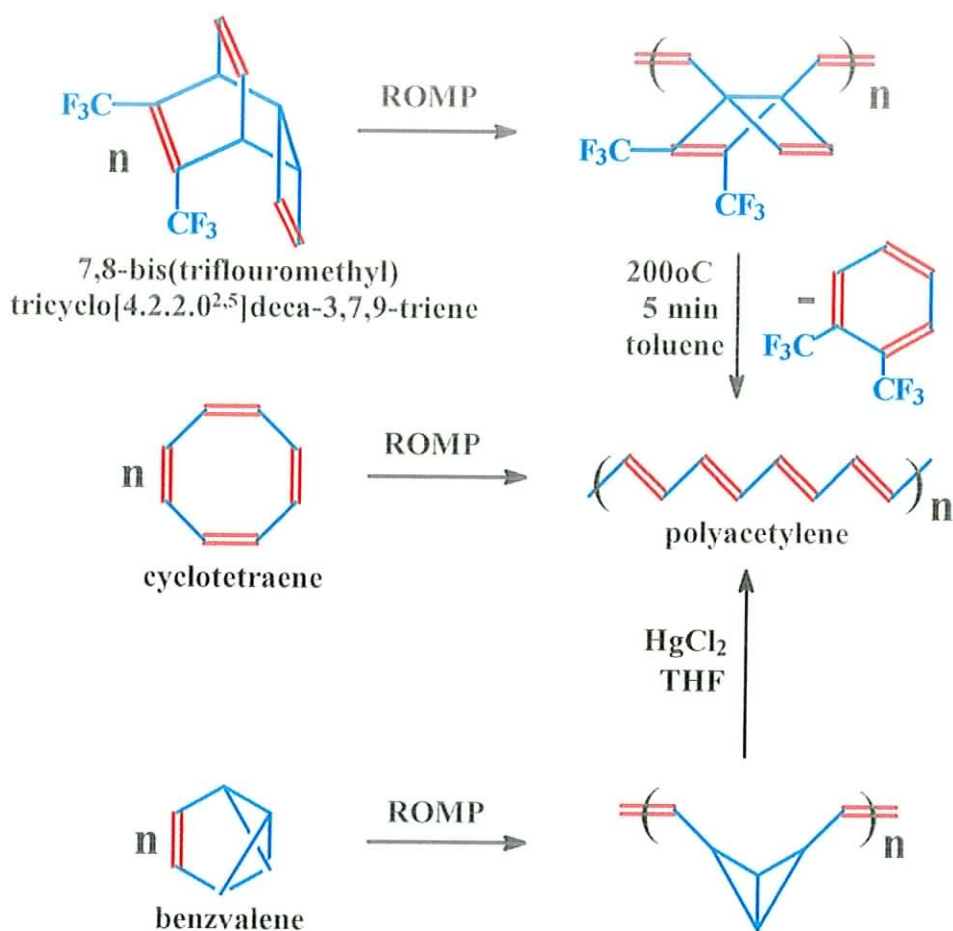
manufacture of the bodies of recreational equipment such as golf-carts and snowmobiles.¹⁶²



Scheme 15

Recently, there has been much interest in the possibility of preparing conjugated polymers with enhanced electrical conductivity properties, such as polyacetylene, *via* ROMP. The conductivity of polyacetylene can be increased by doping to values close to that of copper, and this gives it potential application in the field of non-linear optics.¹⁵⁶ Polyacetylenes prepared by most methods are usually insoluble, infusible materials which cannot be easily manipulated into useful shapes. Several new routes to

conjugated polymers involve the ROMP of cyclic olefins such as benzvalene¹⁵⁶, cyclooctatetraenes^{167,168} tricyclodecatrienes^{169,170} and diisopropylidene-cyclobutene¹⁵⁷ (Scheme 16). As concluded by Feast and Gibson:¹⁶¹ "It is clear that, if the appropriate initiator is used, the variety of polymerizable monomers is limited only by the imagination of the synthetic chemist".



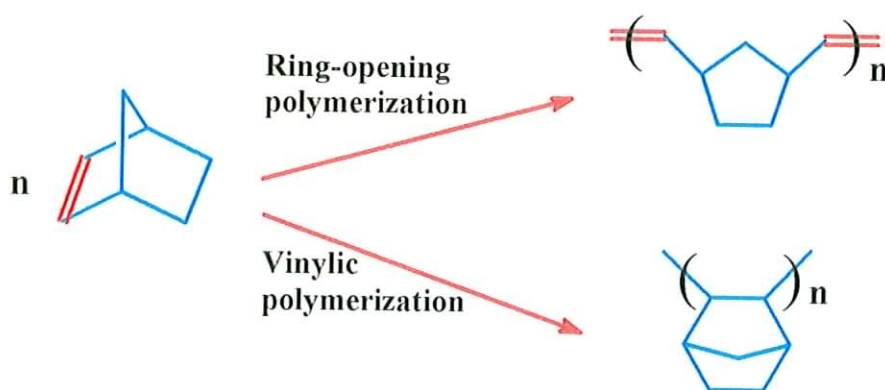
Scheme 16

1.8 ROMP OF NORBORNENE

1.8.1 Introduction

The ROMP of a cyclic olefin was first carried out by Anderson and Merckling¹¹⁸ in 1955 on norbornene (bicyclo[2.2.1]hept-2-ene), a strained bicyclic olefin. Using Ziegler-Natta catalyst systems, such as $\text{LiAl}(\text{butyl})_4/\text{TiCl}_4$, they produced a mixture of saturated and unsaturated polymers which could not be fully characterized at the time.

Using the similar catalyst system, $\text{LiAl}(\text{heptyl})_4/\text{TiCl}_4$, Truett *et al.*¹²⁰ also found that the polymerization of norbornene led to the formation of two distinct products. Vinylic (addition) polymerization at the double bond yielded a saturated polymer whereas ring-opening polymerization yielded an unsaturated polymer (*Scheme 17*). The relative proportions of these two types of polymer could be controlled by varying the Al:Ti ratio.



Scheme 17

Eleuterio¹¹⁹ used heterogeneous catalysts prepared by reducing chromium, molybdenum, tungsten or uranium oxides supported on alumina, titania or zirconia to

polymerize norbornene. It was found that the unsaturated polymer produced contained a mixture of *cis* and *trans* double bonds.

Michelotti and Keaveney¹⁷¹ carried out the ROMP of norbornene using RuCl₃, OsCl₃ and IrCl₃ hydrates in ethanol. The physical properties and microstructure of the polymer produced varied markedly with the catalyst used. OsCl₃ produced a polymer with a high content of *cis* double bonds, whereas IrCl₃ produced a polymer with a high content of *trans* double bonds. RuCl₃ produced a polymer with equal proportions of *cis* and *trans* configuration.

Oshika and Tabuchi¹⁴⁹ found that halides of tungsten, molybdenum and rhenium in CCl₄ or CS₂ solution were particularly active catalysts for the ROMP of norbornene. Again, the microstructure of the polynorbornene produced varied with the catalyst system used. MoCl₅ produced a polymer with a predominantly *trans* configuration, whereas ReCl₅ produced a polymer containing mostly *cis* double bonds.

Since the late 1960's numerous catalyst systems have been successfully used for the ROMP of norbornene.^{139,142,161} Generally, it has been found that any metathesis catalyst will effectively catalyze the ROMP of norbornene. Indeed, many research groups use this reaction to test the activity of potential novel metathesis catalysts.¹⁶¹ Norbornene as a monomer is cheap, being readily available from the reaction of cyclopentadiene with ethylene,¹⁶² and it can be easily functionalized which can impart unusual properties to the ring-opened polymer.¹⁶¹ However, despite numerous patents featuring novel uses of the ROMP product of norbornene and its derivatives¹⁷² only one commercial polymer, Norsorex, is as yet available.¹⁶⁵

Recently, McCann and his co-workers have developed novel catalyst systems which effect the ROMP of norbornene. The diruthenium(II,III) tetranorbornene-

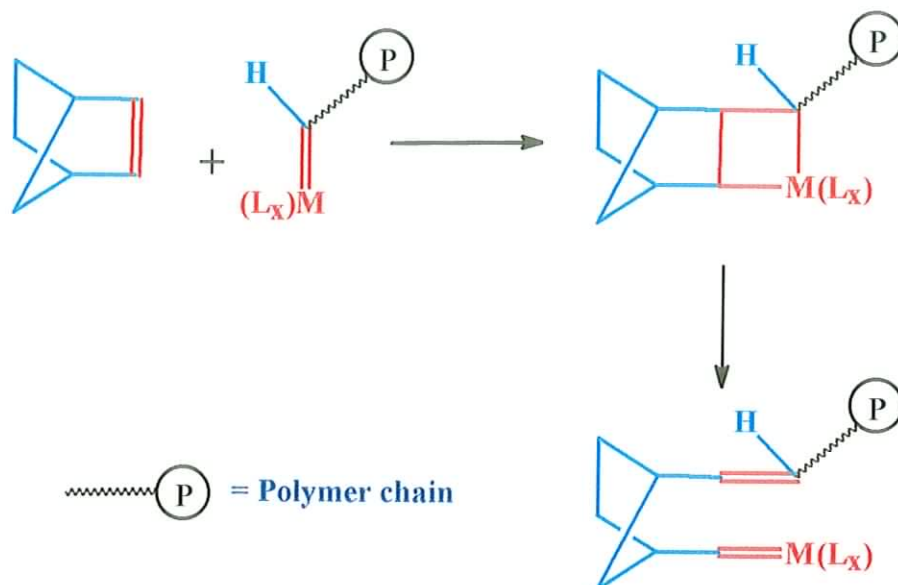
carboxylate chloride complex $[\text{Ru}_2(\mu\text{-O}_2\text{CC-H}_9)_4\text{Cl}]$ was co-polymerized with norbornene to give a polymeric material containing chemically bound $\text{Ru}_2(\text{II,III})$ units.¹⁷⁴ This copolymer itself was then used as a heterogeneous catalyst for the ROMP of norbornene in methanol solution at 120 °C, producing a polymer with a low *cis* content. Dimolybdenum(II,II) complexes, such as $[\text{Mo}_2(\mu\text{-O}_2\text{CCH}_3)_2(\text{CH}_3\text{CN})_6][\text{BF}_4]_4$, in the presence of EtAlCl_2 , also polymerize norbornene *via* ROMP to a polymer of low *cis* content.⁸⁵ Large single crystals of isopolyoxometallate(VI) salts, such as $(^n\text{Bu}_4\text{N})_2[\text{Mo}_6\text{O}_{19}]$ and $(^n\text{Bu}_4\text{N})_4[\text{W}_{10}\text{O}_{32}]$, when treated with EtAlCl_2 cocatalyst, were also found to be good catalysts for the ROMP of norbornene.^{174,85} The octahedral complex $[\text{Mo}(\text{bipy})\text{Me}_2\text{O}_2]$, when supported on a Montmorillonite clay catalysed the ROMP of norbornene at room-temperature even in the absence of added cocatalyst.¹⁷⁵

1.8.2 Stereochemistry of norbornene polymers

The ROMP of norbornene and its derivatives has been studied in great detail, not only because of the commercial potential of the resulting polymers, produced, but also because the reaction serves as a useful model for the study of olefin metathesis reactions in general. The stereochemistry of polynorbornene produced by different catalyst systems can serve as a probe into the mechanism of the catalytic reactions. Rooney and his co-workers¹⁷⁴⁻¹⁸³ have conducted comprehensive studies into the microstructure of the ROMP polymers obtained from norbornene and its derivatives using ^{13}C nmr spectroscopy.

It is now generally agreed that the ROMP of norbornene occurs *via* a metallacarbene intermediate (*Scheme 18*). The complete rupture of the double bond in

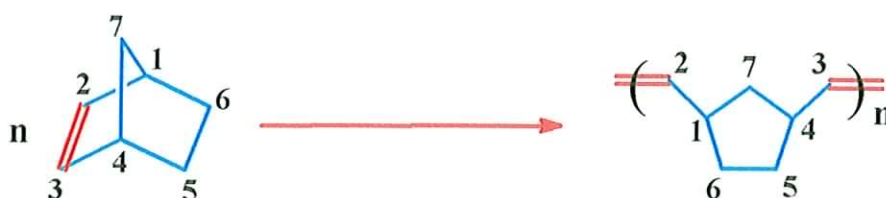
the strained norbornene molecule occurs with the simultaneous formation of a new double bond between the enchainment cyclopentane rings of the polymer.



Scheme 18

Examination of the molecular structure of the ring-opened polymer of norbornene reveals a number of interesting features:¹⁷⁴

(i) The chain bonds to a particular cyclopentane ring always have a *cis* relationship as they derive from the same double bond in the original norbornene molecule (*Scheme 19*).



Scheme 19

(ii) The double bonds of the polymer backbone may be either *cis* or *trans* and these carbons (C^2 and C^3 , *Scheme 19*) are labelled **c** and **t** accordingly. The carbon atoms of the enchained cyclopentane rings are labelled **cc**, **ct**, **tc** or **tt** where the first letter denotes the kind of link in the double bond nearest the carbon in question, and the second letter denotes the type of link in the double bond on the opposite side (*Figure 56*). Polymers in which extended sequences of *cis* or *trans* linkages occur are termed blocky. Polymers without this characteristic are termed random. The overall *cis* content of a polymer is expressed as a simple ratio, σ_c , where $\sigma_c = 1$ represents an all-*cis* polymer and $\sigma_c = 0$ represents an all *trans* polymer.

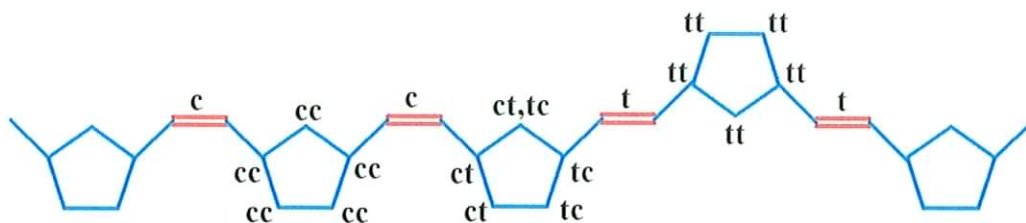


Figure 56

(iii) The ROMP of norbornene, a symmetrical monomer, gives rise to a polymer with two chiral centres per repeat unit. If the centres on each side of the double bond have the same chirality then a *racemic* (r) syndiotactic dyad is generated. Centres on each side of the double bond which have opposite chirality give rise to a *meso* (m) isotactic dyad (*Figure 57*). A polymer in which isotactic and syndiotactic dyads are randomly dispersed is termed atactic.

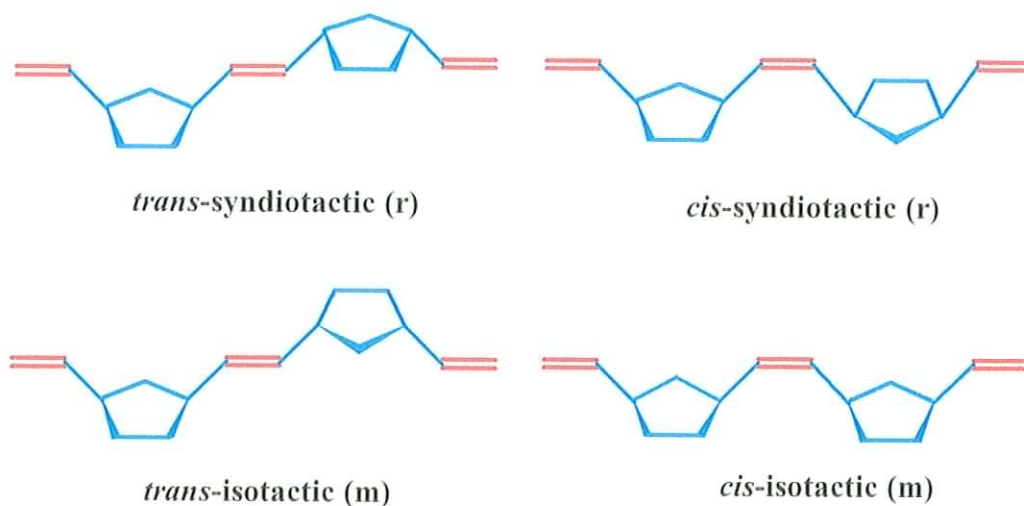
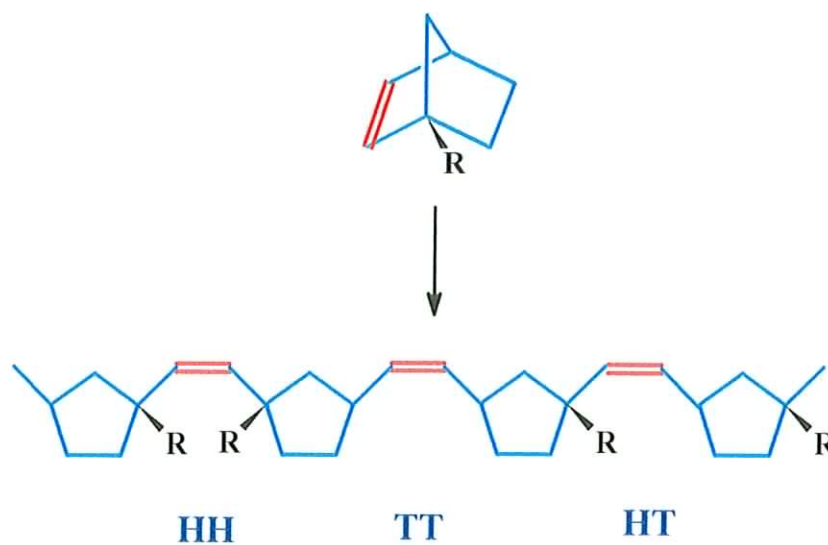


Figure 57

(iv) When the norbornene molecule is unsymmetrically substituted head-head (HH), tail-tail (TT) and head-tail (HT) incorporation of units is also possible (*Scheme 20*).



Scheme 20

The stereochemistry of the ROMP polymers of norbornene is difficult to rationalize in terms of the catalyst system used. Rooney *et al.*¹⁸¹ examined the ¹³C nmr spectra of polynorbornenes formed using various catalysts under different conditions. They proposed the existence of three kinetically different species. These species are based on a presumption that the double bond formed from the propagation of the last monomer remains coordinated to the metal centre of the catalyst (*Figure 58*). The presence of a coordinated *cis* double bond to the metal (*Figure 58a*) imposes some steric constraints on the entry of the next monomer molecule which is forced to adopt an orientation leading to the formation of another *cis* double bond. However, when the last double bond has a *trans* configuration then a much more sterically constrained situation arises (*Figure 58b*). This causes the ligands of the metal centre to move as far as possible from the carbene ligand and the coordinated double bond such that the catalyst cannot propagate with another monomer molecule. Propagation can only occur if the metal centre releases the coordinated *trans* double bond to produce a new species which can propagate the polymerization reaction (*Figure 58c*). While this species can propagate with a monomer molecule in any orientation the formation of a *trans* double bond is energetically favoured.

It has been found that the chirality of ring dyads (*m/r* tacticity) is, in general, governed by the chirality of the metal centre of the reaction intermediate.¹⁸¹ This control is expected to be stronger in the coordinated catalysts where *cis*-junctions are formed (*i.e. Figure 58a*) as the approach of the monomer molecule is already subject to a controlling factor. Therefore, catalysts which produce *cis* polymers also maintain a high degree of stereoregularity in the propagation step yielding syndiotactic polymers.

On the other hand, catalysts which produce *trans* polymers are not stereospecific and yield atactic polymers.

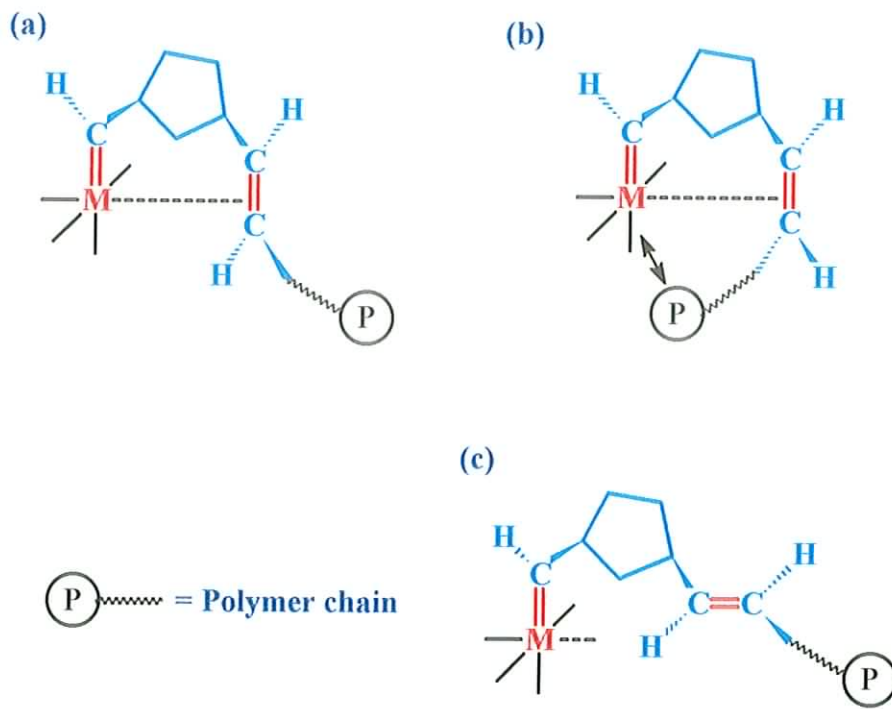


Figure 58

EXPERIMENTAL

E.1 INSTRUMENTATION

Infra-red spectra were recorded either in the region 4000-200 cm^{-1} on a Perkin-Elmer model 783 grating spectrometer or in the region 4000-400 cm^{-1} on a Nicolet Impact 400D FT-IR. Solids were run as potassium bromide discs. Selected bands are listed for each of the complexes and the IR spectra is included in the appendix.

Electronic spectra were obtained in 1 cm quartz cells on a Milton Roy Spectronic 3000 array.

Mass spectra were run on a Kratos Profile Double Focusing High Resolution Mass Spectrometer. Liquid Secondary Ion Mass Spectrometry (LSIMS) spectra were recorded using Cs^- as the primary ion.

Gel Permeation Chromatography was carried out on a Hewlett Packard 1050 Series HPLC instrument utilising a model 1050 Autosampler. A Polymer Laboratories PLgel 5 μm minimix-C column was used throughout. Chlorobenzene was the mobile phase solvent.

^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR spectra were recorded on a Bruker AC80 NMR spectrometer using either CDCl_3 or CD_3CN as the solvent. Chemical shifts are reported as δ -values in ppm. Positive shifts are universally reported downfield from the standard.

Cyclic voltammograms (*ca.* 20 $^\circ\text{C}$ and under N_2) were recorded using an EG&G Model 264A Polarographic Analyser and the data analysed using the EG&G Condecon software package. A glassy carbon disc and a platinum wire were used as the working and counter electrodes, respectively. Potentials were recorded with respect to a silver-silver chloride reference electrode (3.5 M aqueous KCl).

Tetrabutylammonium perchlorate (0.1 M) was used as the supporting electrolyte, and sample concentration was 4.0 mM.

Elemental analysis were performed by the Microanalytical Laboratories, University College, Cork. Due to the air- and moisture- sensitivity of the synthesised complexes it proved difficult to obtain good agreement between the theoretical and found microanalytical values. This phenomenon has also been observed and reported by Cotton.⁸¹

X-Ray crystal structure determinations were carried out on a Siemens P4 Four-circle Diffractometer by Dr. Vickie McKee, Queen's University, Belfast.

E.2 GENERAL SYNTHETIC PROCEDURES AND PURIFICATION OF SOLVENTS

Due to the air- and moisture-sensitivity of the dimolybdenum(II,II) complexes all syntheses and reactions were carried out under nitrogen using standard Schlenk techniques.¹⁸⁴ Dry, deoxygenated solvents were employed throughout, and samples were stored under nitrogen at 4°C. Ethylaluminium dichloride was used as a 1.8 M solution in toluene. Chemicals were purchased from commercial sources and were generally used without further purification.

Solvents were dried using standard literature methods.¹⁸⁵ Acetonitrile and dichloromethane were each dried by refluxing over P₂O₅ for *ca.* 2 hours and then distilled. Diglyme and toluene were dried by refluxing over sodium and distilling. Tetrahydrofuran was dried by refluxing with sodium and benzophenone under nitrogen until the dark blue colour (sodium benzophenone ketyl) was obtained. It was then subsequently distilled. All solvents were stored over activated 4A molecular sieves.

E.3 SYNTHESIS OF DIMOLYBDENUM(II,II) STARTING MATERIALS

E.3.1 $[\text{Mo}_2(\mu\text{-O}_2\text{CCH}_3)_4]$ (1)

This complex was prepared using the literature procedure.¹³⁰

IR (cm^{-1}): $\nu_{\text{asym}}(\text{CO}_2)$ 1512 (s), $\nu_{\text{sym}}(\text{CO}_2)$ 1440 (s), $\delta(\text{CO}_2)$ 675 (s)

E.3.2 $[\text{Mo}_2(\text{CH}_3\text{CN})_8][\text{BF}_4]_4$ (2)

This complex was prepared using the literature method.¹³⁰

IR (cm^{-1}): $\nu(\text{CN})$ 2317 (m), 2293 (m), $\nu[\text{BF}_4]^-$ 1040 (s)

E.3.3 $[\text{Mo}_2(\mu\text{-O}_2\text{CCF}_3)_4]$ (3)

This complex was prepared using the literature method.¹⁸⁶

IR (cm^{-1}): $\nu_{\text{asym}}(\text{CO}_2)$ 1598 (s), $\nu_{\text{sym}}(\text{CO}_2)$ 1460 (s)

$\nu(\text{C-F})$ 1250 (s), 1190 (s)

E.3.4 $[\text{Mo}_2(\mu\text{-O}_2\text{CCF}_3)_2(\text{bipy})_2](\text{O}_2\text{CCF}_3)_2$ (4)

This complex was made using two different methods taken from the literature.^{187,188}

IR (cm^{-1}): $\nu(\text{OCOCF}_3^-)$ 1687 (s), $\nu_{\text{asym}}(\text{CO}_2)$ 1600 (m), $\nu_{\text{sym}}(\text{CO}_2)$ 1430 (s)

$\nu(\text{C-F})$ 1200. $\nu(\text{C-N})$ 772 (m), 729 (m)

E.3.5 $[\text{Mo}_2(\mu\text{-O}_2\text{CCF}_3)_2(\text{phen})_2](\text{O}_2\text{CCF}_3)_2$ (5)

To a stirred suspension of $[\text{Mo}_2(\mu\text{-O}_2\text{CCF}_3)_4]$ (0.20 g, 0.31 mmol) in (10 cm³) CH₃CN was added 1,10-phenanthroline (0.123 g, 0.62 mmol). The resulting light brown solution was left stirring at room temperature for *ca.* 0.5 h. The solution was then reduced to low volume *in vacuo*. The resulting brown solid product was filtered off and dried *in vacuo*.

M.W. : 1003.88

Yield : 0.18 g (58%)

IR (cm⁻¹) : $\nu(\text{OCOCF}_3^-)$ 1701 (s), $\nu_{\text{asym}}(\text{CO}_2)$ 1519 (m), $\nu_{\text{sym}}(\text{CO}_2)$ 1428
1404 (m), $\nu(\text{C-F})$ 1187, 1144 (s), $\nu(\text{C-N})$ 742, 723 (s)

Calc. : C, 38.27, H, 1.61, N, 5.58

Found : C, 35.88, H, 1.55, N, 5.46

E.3.6 $[\text{Mo}(\text{CO})_4(\text{bipy})]$ (6)

This complex was made according to the literature procedure.¹⁸⁹

IR (cm⁻¹): $\nu(\text{CO})$ 2014 (m), 1911 (s), 1882 (w), $\nu(\text{C=N})$ 1440 (m)
 $\nu(\text{C-N})$ 770 (s)

E.3.7 [Mo(CO)₄(phen)] (7)

[Mo(CO)₆] (1.4 g, 5.0 mmol) and 1,10-phenanthroline (0.991 g, 5.0 mmol) were refluxed under nitrogen in toluene (50 cm³) for 1.5 h. The precipitated orange product was filtered off, washed with toluene and dried *in vacuo*.

M.W. : 387.94

Yield : 1.5 g (77%)

IR (cm⁻¹) : $\nu(\text{CO})$ 2004 (s), 1873 (m), 1844 (m), $\nu(\text{C}\equiv\text{N})$ 1424 (w)
 $\nu(\text{C-N})$ 842 (m), 740 (s)

Calc. : C, 49.51, H, 2.07, N, 7.22

Found : C, 49.94, H, 2.42, N, 7.20

E.3.8 [MoO₂(bipy)Br₂] (8)

This complex was made according to the literature procedure.¹⁹⁰

IR (cm⁻¹) : $\nu(\text{C}\equiv\text{N})$ 1598 (s), $\nu(\text{C-N})$ 772 (s), $\nu(\text{Mo-O})$ 932 (m), 903 (w)

E.4 SYNTHESIS OF DIMOLYBDENUM(II,II) DICARBOXYLATE COMPLEXES

E.4.1 [Mo₂(O₂CCO₂)(CH₃CN)_x][BF₄]₂ (9)

[Mo₂(MeCN)₈][BF₄]₄ (**2**) (0.20 g 0.23 mmol) was added to a stirred suspension of ethanedioic acid HO₂CCO₂H (0.021 g, 0.23 mmol) in CH₃CN (25 cm³). The resulting deep blue suspension was gently heated for *ca.* 1 h to give an orange solution.

The solution was reduced *in vacuo* to low volume at room temperature and the orange product precipitated out of solution. The orange product was then filtered off, washed with a very small volume of CH₂Cl₂ (2 cm³) and dried *in vacuo*.

Note: The reaction can also be conducted at room temperature over a period of 12 h.

M.W. : 1399.0

Yield: 0.13 g (47%)

IR (cm⁻¹): $\nu_{\text{asym}}(\text{CO}_2)$ 1556 (s), $\nu_{\text{sym}}(\text{CO}_2)$ 1305 (s), $\nu(\text{C}\equiv\text{N})$ 2283.6 (w)
 $\nu[\text{BF}_4]^-$ 1059 (s)

% Calc.: C, 24.03, H, 2.59, N, 12.0

% Found: C, 18.22, H, 2.66, N, 5.8

E.4.2 [Mo₂(O₂C(CH₂)CO₂)(CH₃CN)_x]₂[BF₄]_{4-y}CH₃CN (10)

[Mo₂(MeCN)₈][BF₄]₄ (**2**) (0.20 g 0.23 mmol) was added to a stirred suspension of propanedioic acid HO₂C(CH₂)CO₂H (0.024 g, 0.23 mmol) in CH₃CN (25 cm³). The resulting deep blue suspension was gently heated for *ca.* 1 h to give a red solution. The solution was reduced *in vacuo* to low volume at room temperature. A small volume of CH₂Cl₂ (3-5 cm³) was added to induce precipitation. The red product which precipitated was filtered off, washed with a very small volume of CH₂Cl₂ (2 cm³) and dried *in vacuo*.

Note: The reaction can also be conducted at room temperature over a period of 12 h.

M.W. : 1427.0

Yield: 0.12 g (37%)

IR (cm⁻¹): $\nu(\text{C}\equiv\text{N})$ 2283 (m), $\nu_{\text{asym}}(\text{CO}_2)$ 1536 (s)
 $\nu_{\text{sym}}(\text{CO}_2)$ 1381 (m), $\nu[\text{BF}_4]^-$ 1059 (s)

% Calc.: C, 25.24, H, 2.82, N, 11.77

% Found: C, 16.64, H, 2.83, N, 5.38

E.4.3 $[\text{Mo}_2(\text{O}_2\text{C}(\text{CH}_2)_2\text{CO}_2)(\text{CH}_3\text{CN})_6]_2[\text{BF}_4]_4 \cdot 3\text{CH}_3\text{CN}$ (11)

This butanedioic acid complex was synthesised using the same procedure as outlined in E.4.2.

Large X-ray quality crystals were obtained by adding hexane (*ca.* 10 cm³), which is immiscible with acetonitrile, to the red solution.

Over the following few days very small volumes of CH₂Cl₂ (1 cm³) were periodically added to the red solution, which eventually led to crystal formation.

Yield: 0.14 g (42%)

IR (cm⁻¹): $\nu(\text{CH})$ 3010 (w), 2942 (w), $\nu(\text{C}\equiv\text{N})$ 2290 (s), $\nu_{\text{asym}}(\text{CO}_2)$
1536 (s), $\nu_{\text{sym}}(\text{CO}_2)$ 1443 (m), $\nu[\text{BF}_4]^-$ 1059 (s)

% Calc.: C, 26.40, H, 3.0, N, 11.55

% Found: C, 20.30, H, 3.04, N, 6.91

UV-VIS (CH₃CN): $\lambda_{\text{max}} = 531 \text{ nm}$, $\epsilon = 1648 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$

E.4.4 $[\text{Mo}_2(\text{O}_2\text{C}(\text{CH}_2)_3\text{CO}_2)(\text{CH}_3\text{CN})_x]_2[\text{BF}_4]_4 \cdot y\text{CH}_3\text{CN}$ (12)

This pentanedioic acid complex was synthesised using the same procedure as outlined in E.4.2.

M.W. : 1483.0
Yield: 0.13 g (38%)
IR (cm⁻¹): $\nu(\text{CH})$ 2929 (w) 2854 (w), $\nu(\text{C}\equiv\text{N})$ 2283 (m), $\nu_{\text{asym}}(\text{CO}_2)$ 1510 (s), $\nu_{\text{sym}}(\text{CO}_2)$ 1430 (m), $\nu[\text{BF}_4]^-$ 1059 (s)
% Calc.: C, 27.52, H, 3.26, N, 11.33
% Found: C, 20.68, H, 3.02, N, 6.46

E.4.5 $[\text{Mo}_2(\text{O}_2\text{C}(\text{CH}_2)_4\text{CO}_2)(\text{CH}_3\text{CN})_x]_2[\text{BF}_4]_{4-y}\cdot y\text{CH}_3\text{CN}$ (13)

This hexanedioic acid complex was synthesised using the same procedure as outlined in E.4.1.

M.W. : 1511.0
Yield: 0.14 g (40%)
IR (cm⁻¹): $\nu(\text{CH})$ 2951 (w), $\nu(\text{C}\equiv\text{N})$ 2283 (m), $\nu_{\text{asym}}(\text{CO}_2)$ 1503 (s)
 $\nu_{\text{sym}}(\text{CO}_2)$ 1429 (m), $\nu[\text{BF}_4]^-$ 1057 (s)
% Calc.: C, 28.60, H, 3.47, N, 11.18
% Found: C, 21.42, H, 3.28, N, 5.50

E.4.6 $[\text{Mo}_2(\text{O}_2\text{C}(\text{CH}_2)_5\text{CO}_2)(\text{CH}_3\text{CN})_x]_2[\text{BF}_4]_{4-y}\cdot y\text{CH}_3\text{CN}$ (14)

This heptanedioic acid complex was synthesised using the same procedure as outlined in E.4.2.

M.W. : 1539.0
Yield: 0.12 g (34%)

IR (cm⁻¹): $\nu(\text{CH})$ 2929 (w) 2854 (w), $\nu(\text{C}\equiv\text{N})$ 2283 (m), $\nu_{\text{asym}}(\text{CO}_2)$
1523 (s), $\nu_{\text{sym}}(\text{CO}_2)$ 1424 (m), $\nu[\text{BF}_4]^-$ 1059 (s)
% Calc.: C, 29.64, H, 3.67, N, 10.92
% Found: C, 25.05, H, 3.42, N, 6.57

E.4.7 $[\text{Mo}_2(\text{O}_2\text{C}(\text{CH}_2)_6\text{CO}_2)(\text{CH}_3\text{CN})_x]_2[\text{BF}_4]_{4-x} \cdot y\text{CH}_3\text{CN}$ (15)

This octanedioic acid complex was synthesised using the same procedure as outlined in E.4.2.

M.W. : 1567.0
Yield: 0.17 g (47%)
IR (cm⁻¹): $\nu(\text{CH})$ 2933 (w) 2858 (w), $\nu(\text{C}\equiv\text{N})$ 2283 (m), $\nu_{\text{asym}}(\text{CO}_2)$
1505 (s), $\nu_{\text{sym}}(\text{CO}_2)$ 1423 (m), $\nu[\text{BF}_4]^-$ 1059 (s)
% Calc.: C, 30.64, H, 3.86, N, 10.72
% Found: C, 36.02, H, 5.30, N, 3.90

E.4.8 $[\text{Mo}_2(\text{O}_2\text{C}(\text{CH}_2)_7\text{CO}_2)(\text{CH}_3\text{CN})_x]_2[\text{BF}_4]_{4-x} \cdot y\text{CH}_3\text{CN}$ (16)

This nonanedioic acid complex was synthesised using the same procedure as outlined in E.4.2.

M.W. : 1595.0
Yield: 0.14 g (38%)
IR (cm⁻¹): $\nu(\text{CH})$ 2929 (w), 2855 (w), $\nu(\text{C}\equiv\text{N})$ 2283 (m), $\nu_{\text{asym}}(\text{CO}_2)$
1501 (s), $\nu_{\text{sym}}(\text{CO}_2)$ 1420 (m), $\nu[\text{BF}_4]^-$ 1059 (s)

% Calc.: C, 31.61, H, 4.04, N, 10.53

% Found: C, 25.64, H, 3.98, N, 7.93

E.4.9 $[\text{Mo}_2(\text{O}_2\text{C}(\text{CH}_2)_8\text{CO}_2)(\text{CH}_3\text{CN})_x]_2[\text{BF}_4]_{4-y} \cdot y\text{CH}_3\text{CN}$ (17)

This decanedioic acid complex was synthesised using the same procedure as outlined in E.4.2.

M.W. : 1623.0

Yield: 0.15 g (40%)

IR (cm⁻¹): $\nu(\text{CH})$ 2927 (w) 2852 (w), $\nu(\text{C}\equiv\text{N})$ 2283 (m), $\nu_{\text{asym}}(\text{CO}_2)$ 1507 (s), $\nu_{\text{sym}}(\text{CO}_2)$ 1425 (m), $\nu[\text{BF}_4]^-$ 1059 (s)

% Calc.: C, 32.54, H, 4.22, N, 10.35

% Found: C, 25.20, H, 3.79, N, 4.35

E.4.10 $[\text{Mo}_2(\text{bdoa})(\text{CH}_3\text{CN})_x]_2[\text{BF}_4]_{4-y} \cdot y\text{CH}_3\text{CN}$ (18)

This bdoaH₂ complex was synthesised using the same procedure as outlined in E.4.2. In this instance no CH₂Cl₂ was used as the red product precipitated easily out of the reaction solution.

M.W. : 1671.0

Yield: 0.18 g (47%)

IR (cm⁻¹): $\nu_{\text{asym}}(\text{CO}_2)$ 1546 (s), $\nu_{\text{sym}}(\text{CO}_2)$ 1433 (s), $\nu(\text{C}\equiv\text{N})$ 2288 (vw)
 $\nu[\text{BF}_4]^-$ 1058 (s)

% Calc.: C, 31.61, H, 3.13, N, 10.05

% Found: C, 27.95, H, 3.41, N, 8.79

**E.5 SYNTHESIS OF DIMOLYBDENUM(II,II) DICARBOXYLATE
COMPLEXES CONTAINING ADDITIONAL BIDENTATE NITROGEN
DONOR LIGANDS**

E.5.1 $[\text{Mo}_2(\text{O}_2\text{C}(\text{CH}_2)_2\text{CO}_2)(\text{bipy})_2]_2[\text{BF}_4]_4$ (19)

$[\text{Mo}_2(\text{MeCN})_8][\text{BF}_4]_4$ (2) (0.20 g 0.23 mmol) was added to a stirred suspension of butanedioic acid $\text{HO}_2\text{C}(\text{CH}_2)_2\text{CO}_2\text{H}$ (0.0272 g, 0.23 mmol) in CH_3CN (25 cm^3). The resulting deep blue suspension was gently heated for *ca.* 1 h to give a red solution. The flask was removed from the heat and left stirring for a further 1 h at room temperature. To the red solution was added 2,2'-bipyridine (0.072 g, 0.46 mmol) and the resulting purple solution was stirred for 0.5 h. The solution was reduced *in vacuo* to low volume at room temperature. A small volume of a CH_2Cl_2 : toluene mixture (1-3 cm^3) (50:50) was then added to the solution to induce precipitation. The resulting purple product was filtered off, washed with a very small volume of CH_3CN (*ca.* 1-2 cm^3) and dried *in vacuo*.

M.W. : 1915.0

Yield: 0.12 g (27%)

IR: $\nu(\text{CO})$ 1720 (s), $\nu_{\text{asym}}(\text{CO}_2)$ 1498 (m), $\nu_{\text{sym}}(\text{CO}_2)$ 1420 (m)
 $\nu(\text{Mo-O})$ 930 (w), $\nu(\text{C-N})$ 769 (s), $\nu[\text{BF}_4]^-$ 1050 (s)

Calc.: C, 32.95, H, 3.02, N, 10.48

Found: C, 30.0, H, 3.3, N, 7.0

E.5.2 $[\text{Mo}_2(\text{O}_2\text{C}(\text{CH}_2)_2\text{CO}_2)(\text{phen})_2]_2[\text{BF}_4]_4$ (20)

$[\text{Mo}_2(\text{MeCN})_8][\text{BF}_4]_4$ (**2**) (0.20 g 0.23 mmol) was added to a stirred suspension of butanedioic acid $\text{HO}_2\text{C}(\text{CH}_2)_2\text{CO}_2\text{H}$ (0.0272 g, 0.23 mmol) in CH_3CN (25 cm^3). The resulting deep blue suspension was gently heated for *ca.* 1 h to give a red solution. The flask was removed from the heat and left stirring for a further 1 h at room temperature. To the red solution was added 1,10-phenanthroline (0.091 g, 0.46 mmol) and the resulting purple solution was stirred for 0.5 h. The solution was reduced *in vacuo* to low volume at room temperature. A small volume of a CH_2Cl_2 : toluene mixture (1-3 cm^3) (50:50) was added to the solution to induce precipitation. The resulting purple product was filtered off, washed with a very small volume of CH_3CN (*ca.* 1-2 cm^3) and dried *in vacuo*.

M.W. : 2011.0

Yield: 0.1 g (21%)

IR: $\nu(\text{C}=\text{O})$ 1720 (s), $\nu_{\text{asym}}(\text{CO}_2)$ 1441 (w), $\nu_{\text{sym}}(\text{CO}_2)$ 1313 (m)
 $\nu(\text{Mo}=\text{O})$ 930 (w), $\nu(\text{C}-\text{N})$ 830 (m), 720 (m), $\nu[\text{BF}_4]^-$ 1050 (s)

Calc.: C, 34.9, H, 2.93, N, 10.17

Found: C, 35.41, H, 2.92, N, 6.38

E.5.3 $[\text{Mo}_2(\text{O}_2\text{C}(\text{CH}_2)_7\text{CO}_2)(\text{bipy})_2]_2[\text{BF}_4]_4$ (21)

This complex was synthesised using the same procedure as outlined in E.5.1.

M.W. : 2055.0

Yield: 0.13 g (27%)

IR: $\nu(\text{C}=\text{O})$ 1720 (s), $\nu_{\text{asym}}(\text{CO}_2)$ 1443 (w), $\nu_{\text{sym}}(\text{CO}_2)$ 1315 (m)
 $\nu(\text{Mo}=\text{O})$ 930 (w), $\nu(\text{C}-\text{N})$ 720 (m), $\nu[\text{BF}_4]^-$ 1050 (s)

Calc.: C, 40.31, H, 3.50, N, 6.48

Found: C, 40.52, H, 4.0, N, 6.20

E.5.4 $[\text{Mo}_2(\text{O}_2\text{C}(\text{CH}_2)_7\text{CO}_2)(\text{phen})_2]_2[\text{BF}_4]_4$ (22)

This complex was synthesised using the same procedure as outlined in E.5.2.

M.W. : 2151.0

Yield: 0.12 g (24%)

IR: $\nu(\text{C}=\text{O})$ 1720 (s), $\nu_{\text{asym}}(\text{CO}_2)$ 1427 (w), $\nu_{\text{sym}}(\text{CO}_2)$ 1310 (m)
 $\nu(\text{Mo}=\text{O})$ 940 (w), $\nu(\text{C}-\text{N})$ 720 (m), $\nu[\text{BF}_4]^-$ 1050 (s)

Calc.: C, 43.46, H, 3.32, N, 6.14

Found: C, 43.07, H, 3.50, N, 6.09

E.5.5 Complex (23)

This complex was synthesised using the same procedure as outlined in E.5.1.

Due to oxidation of the complex no formulation or structure was proposed.

M.W. : 2083.0

Yield: 0.12 g (25%)

IR: $\nu(\text{C}=\text{O})$ 1700 (s), $\nu_{\text{asym}}(\text{CO}_2)$ 1430 (w), $\nu_{\text{sym}}(\text{CO}_2)$ 1302 (m)
 $\nu(\text{Mo}=\text{O})$ 930 (s), $\nu(\text{C}-\text{N})$ 850 (m), 720 (m), $\nu[\text{BF}_4]^-$ 1050 (s)

Calc.: C, 41.0, H, 3.67, N, 6.38

Found: C, 43.64, H, 4.2, N, 7.7

E.5.6 Complex (24)

This complex was synthesised using the same procedure as outlined in E.5.2. As with complex (23) E.5.5, it is thought that complex (24) was also oxidised during preparation, and again no formulation or structure was proposed.

M.W. : 2179.0

Yield: 0.11 g (22%)

IR: $\nu(\text{C}=\text{O})$ 1700 (s), $\nu_{\text{asym}}(\text{CO}_2)$ 1427 (w), $\nu_{\text{sym}}(\text{CO}_2)$ 1302 (m)
 $\nu(\text{Mo}=\text{O})$ 931 (s), $\nu(\text{C}-\text{N})$ 850 (m), 720 (m), $\nu[\text{BF}_4]^-$ 1050 (s)

Calc.: C, 44.1, H, 3.50, N, 6.05

Found: C, 41.5, H, 4.44, N, 4.95

E.5.7 Complex (25)

To a stirred suspension of $[\text{Mo}_2(\mu\text{-O}_2\text{CCF}_3)_4]$ (0.20 g, 0.31 mmol) in CH_3CN (10 cm^3) was added 2,2' bipyridine (0.063 g, 0.62 mmol). The yellow solution immediately turned red in colour and to this was added a solution of decanedioic acid $\text{HO}_2\text{C}(\text{CH}_2)_8\text{CO}_2\text{H}$ (0.063 g, 0.31 mmol) in CH_3CN (10 cm^3). The resulting red/purple solution was left stirring at room temperature for a further 2 h and then reduced to low volume *in vacuo* at room temperature. A small volume of a CH_2Cl_2 : toluene mixture (1-3 cm^3) (50:50) was then added to the solution to induce precipitation. The resulting purple product was filtered off, washed with a very small volume of CH_3CN (*ca.* 1-2 cm^3) and dried *in vacuo*. It is thought that the complex became oxidised during the

preparation and therefore no formulation or structure was proposed.

M.W. : 929.88
Yield : 0.1 g (35%)
IR (cm⁻¹): ν (CO) 1700 (s), ν (C-F) 1200 (w), $\nu_{\text{asym}}(\text{OCO})$ 1430 (w),
 $\nu_{\text{sym}}(\text{OCO})$ 1302 (w), $\nu(\text{Mo=O})$ 930 (m), $\nu(\text{C-N})$ 772, 729 (m)
Calc. : C, 43.89, H, 3.47, N, 6.02
% Found: C, 54.07, H, 7.72, N, 1.01

E.5.8 Complex (26)

To a stirred suspension of $[\text{Mo}_2(\mu\text{-O}_2\text{CCF}_3)_4]$ (0.20 g, 0.31 mmol) in CH_3CN (10 cm³) was added 1,10-phenanthroline (0.123 g, 0.62 mmol). The yellow solution immediately turned red in colour and to this was added a solution of decanedioic acid $\text{HO}_2\text{C}(\text{CH}_2)_8\text{CO}_2\text{H}$ (0.063 g, 0.31 mmol) in CH_3CN (10 cm³). The resulting red/purple solution was left stirring at room temperature for a further 2 h and then reduced to low volume *in vacuo* at room temperature. A small volume of a CH_2Cl_2 : toluene mixture (1-3 cm³) (50:50) was then added to the solution to induce precipitation. The resulting purple product was filtered off, washed with a very small volume of CH_3CN (*ca.* 1-2 cm³) and dried *in vacuo*. As with complex (25) E.5.7, it is thought that complex (26) was also oxidised during preparation, and again no formulation or structure was proposed.

M.W. : 977.88
Yield: 0.10 g (50%)

IR (cm⁻¹): ν (CO) 1700 (s), ν (C-F) 1200 (w), $\nu_{\text{asym}}(\text{OCO})$ 1428 (w),
 $\nu_{\text{sym}}(\text{OCO})$ 1300 (w), $\nu(\text{Mo=O})$ 930 (m), $\nu(\text{C-N})$ 772, 729 (m)

Calc.: C, 46.64, H, 3.30, N, 5.73

% Found: C, 47.30, H, 4.65, N, 3.92

E.6 POLYMERIZATION OF BICYCLO[2.2.1]HEPT-2-ENE (NORBORNENE) USING SELECTED MOLYBDENUM(II,III) DIACID COMPLEXES AS CATALYSTS

E.6.1 $[\text{Mo}_2(\text{O}_2\text{C}(\text{CH}_2)_2\text{CO}_2)(\text{CH}_3\text{CN})_6]_2[\text{BF}_4]_4 \cdot 3\text{CH}_3\text{CN}$ (11)

A 1.8 M solution of ethylaluminium dichloride solution in toluene (0.3 cm³, 0.54 mmol) was added, under nitrogen, to the red complex (11) (0.1 g). The solid immediately turned black in colour. After *ca.* 5 min a solution of norbornene (0.5 g, 5.3 mmol) in chlorobenzene (5 cm³) was then added. The resulting reaction was exothermic and there was a significant increase in solution viscosity. The resulting mixture was agitated for 0.5 h and ethanol (10 cm³) was then added to quench the reaction and induce polymer precipitation. The combined solids {polynorbornene and complex (11)} were filtered off. Chloroform (40 cm³) was added to dissolve the polymer and this was separated from the solid catalyst by decantation. The residual complex (11) solid was washed with further portions of chloroform (3 × 10 cm³). The combined chloroform extracts were added to ethanol (200 cm³) containing concentrated HCl (1 cm³). The precipitated white polynorbornene was filtered off, washed with ethanol (3 × 10 cm³) and then dried *in vacuo*. Yield: 0.11 g (22%).

The following catalysts were also used to polymerize norbornene using the same procedure as outlined in E.6.1.

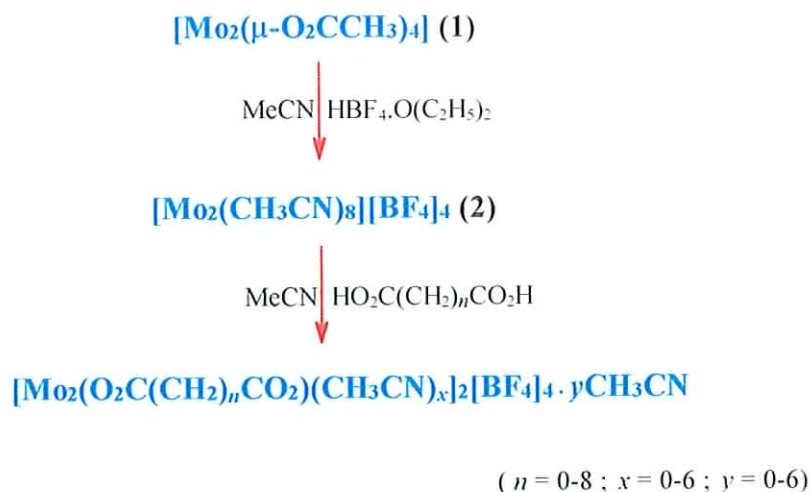
E.6.2	$[\text{Mo}_2(\text{O}_2\text{C}(\text{CH}_2)_3\text{CO}_2)(\text{CH}_3\text{CN})_6]_2[\text{BF}_4]_4$ (12)	Yield 0.11 g (22%)
E.6.3	$[\text{Mo}_2(\text{O}_2\text{C}(\text{CH}_2)_4\text{CO}_2)(\text{CH}_3\text{CN})_6]_2[\text{BF}_4]_4$ (13)	Yield 0.12 g (24%)
E.6.4	$[\text{Mo}_2(\text{O}_2\text{C}(\text{CH}_2)_5\text{CO}_2)(\text{CH}_3\text{CN})_6]_2[\text{BF}_4]_4$ (14)	Yield 0.1 g (20%)
E.6.5	$[\text{Mo}_2(\text{O}_2\text{C}(\text{CH}_2)_6\text{CO}_2)(\text{CH}_3\text{CN})_6]_2[\text{BF}_4]_4$ (15)	Yield 0.11 g (22%)
E.6.6	$[\text{Mo}_2(\text{O}_2\text{C}(\text{CH}_2)_7\text{CO}_2)(\text{CH}_3\text{CN})_6]_2[\text{BF}_4]_4$ (16)	Yield 0.1 g (20%)
E.6.7	$[\text{Mo}_2(\text{O}_2\text{C}(\text{CH}_2)_8\text{CO}_2)(\text{CH}_3\text{CN})_6]_2[\text{BF}_4]_4$ (17)	Yield 0.15 g (30%)
E.6.8	$[\text{Mo}_2(\text{bdoa})(\text{CH}_3\text{CN})_6]_2[\text{BF}_4]_4$ (18)	Yield 0.09 g (18%)
E.6.9	Complex (23)	Yield 0.05 g (10%)
E.6.10	Complex (24)	Yield 0.06 g (12%)

DISCUSSION

D.I PREPARATION OF MOLYBDENUM(II) DICARBOXYLATE COMPLEXES

Interest in molybdenum dicarboxylate complexes stems back as far as 1963 when Stephenson *et al.*⁸ reacted $[\text{Mo}(\text{CO})_6]$ with butanedioic, pentanedioic and hexanedioic acids to give molybdenum(II) complexes of the general formula $[\text{Mo}(\text{O}_2\text{C}(\text{CH}_2)_n\text{CO}_2)]\text{H}_2\text{O}$ ($n = 2, 3$ or 4). A few years later Mureinik²⁵ also synthesised molybdenum(II) dicarboxylate complexes by employing either $[\text{Mo}(\text{CO})_6]$ or $[\text{Mo}(\mu\text{-O}_2\text{CCH}_3)_4]$ as the starting material (Section I.5). To date, no X-ray crystal structure of a molybdenum dicarboxylate complex has been reported.

In the present work a series of dicarboxylic acids were reacted with the blue dimolybdenum(II) complex salt $[\text{Mo}_2(\text{CH}_3\text{CN})_8][\text{BF}_4]_4$ (**2**) to yield red solids of general formula $[\text{Mo}_2(\text{O}_2\text{C}(\text{CH}_2)_n\text{CO}_2)(\text{CH}_3\text{CN})_x]_2[\text{BF}_4]_{4 \cdot y}\text{CH}_3\text{CN}$. These reactions are represented in *Scheme 21*.



Scheme 21

The dicarboxylic acids used in the present synthesis are listed in *Table 10*.

Table 10. Dicarboxylic acids used in the synthesis of dimolybdenum(II)

complexes of formula $[\text{Mo}_2(\text{O}_2\text{C}(\text{CH}_2)_n\text{CO}_2)(\text{CH}_3\text{CN})_x]_2[\text{BF}_4]_{4-y}\text{CH}_3\text{CN}$

IUPAC Name	Formula	Common Name
ethanedioic (edaH ₂)	HO ₂ C-CO ₂ H	oxalic
propanedioic (prdaH ₂)	HO ₂ C(CH ₂)CO ₂ H	malonic
butanedioic (bdaH ₂)	HO ₂ C(CH ₂) ₂ CO ₂ H	succinic
pentanedioic (pdaH ₂)	HO ₂ C(CH ₂) ₃ CO ₂ H	glutaric
hexanedioic (hxdaH ₂)	HO ₂ C(CH ₂) ₄ CO ₂ H	adipic
heptanedioic (hdaH ₂)	HO ₂ C(CH ₂) ₅ CO ₂ H	pimelic
octanedioic (odaH ₂)	HO ₂ C(CH ₂) ₆ CO ₂ H	suberic
nonanedioic (ndaH ₂)	HO ₂ C(CH ₂) ₇ CO ₂ H	azealic
decanedioic (ddaH ₂)	HO ₂ C(CH ₂) ₈ CO ₂ H	sebacic
benzene-1,2-dioxyacetic acid	HO ₂ C(bdoa)CO ₂ H	bdoaH ₂

$[\text{Mo}_2(\text{CH}_3\text{CN})_8][\text{BF}_4]_4$ (**2**) reacted with the dicarboxylic acids in a 1:1 ratio in acetonitrile to give red solutions, except in the case of the ethanedioate complex $[\text{Mo}_2(\text{eda})(\text{CH}_3\text{CN})_x][\text{BF}_4]_2$ (**9**) where an orange solution was obtained. With the exception of the complexes $[\text{Mo}_2(\text{eda})(\text{CH}_3\text{CN})_x][\text{BF}_4]_2$ (**9**) and $[\text{Mo}_2(\text{bdoa})(\text{CH}_3\text{CN})_x]_2[\text{BF}_4]_{4-y}\text{CH}_3\text{CN}$ (**18**), where the product precipitated out of solution during the reaction, all of the other complexes were manipulated in order to induce precipitation of the product. The “manipulation” procedure involved decreasing the volume of the mother liquor (acetonitrile) *in vacuo* at room temperature followed by the addition of small amounts of dichloromethane.

The high solubility of the new molybdenum dicarboxylate complexes $[\text{Mo}_2(\text{O}_2\text{C}(\text{CH}_2)_n\text{CO}_2)(\text{CH}_3\text{CN})_x]_2[\text{BF}_4]_{4-y}\cdot\text{CH}_3\text{CN}$ in the reaction solvent (acetonitrile) presented difficulties in actually isolating the products in good yield. The products were highly insoluble in other common organic solvents like dichloromethane, alcohols and acetone but dissolved in pyridine to give greenish-yellow solutions which decomposed quite rapidly. The complexes $[\text{Mo}_2(\text{O}_2\text{C}(\text{CH}_2)_n\text{CO}_2)(\text{CH}_3\text{CN})_x]_2[\text{BF}_4]_{4-y}\cdot\text{CH}_3\text{CN}$ were air-sensitive and extremely hygroscopic and when they were exposed to air they changed to a dull red colour eventually decomposing to give a brown solid. Microanalytical data for the complexes is given in *Table 11*.

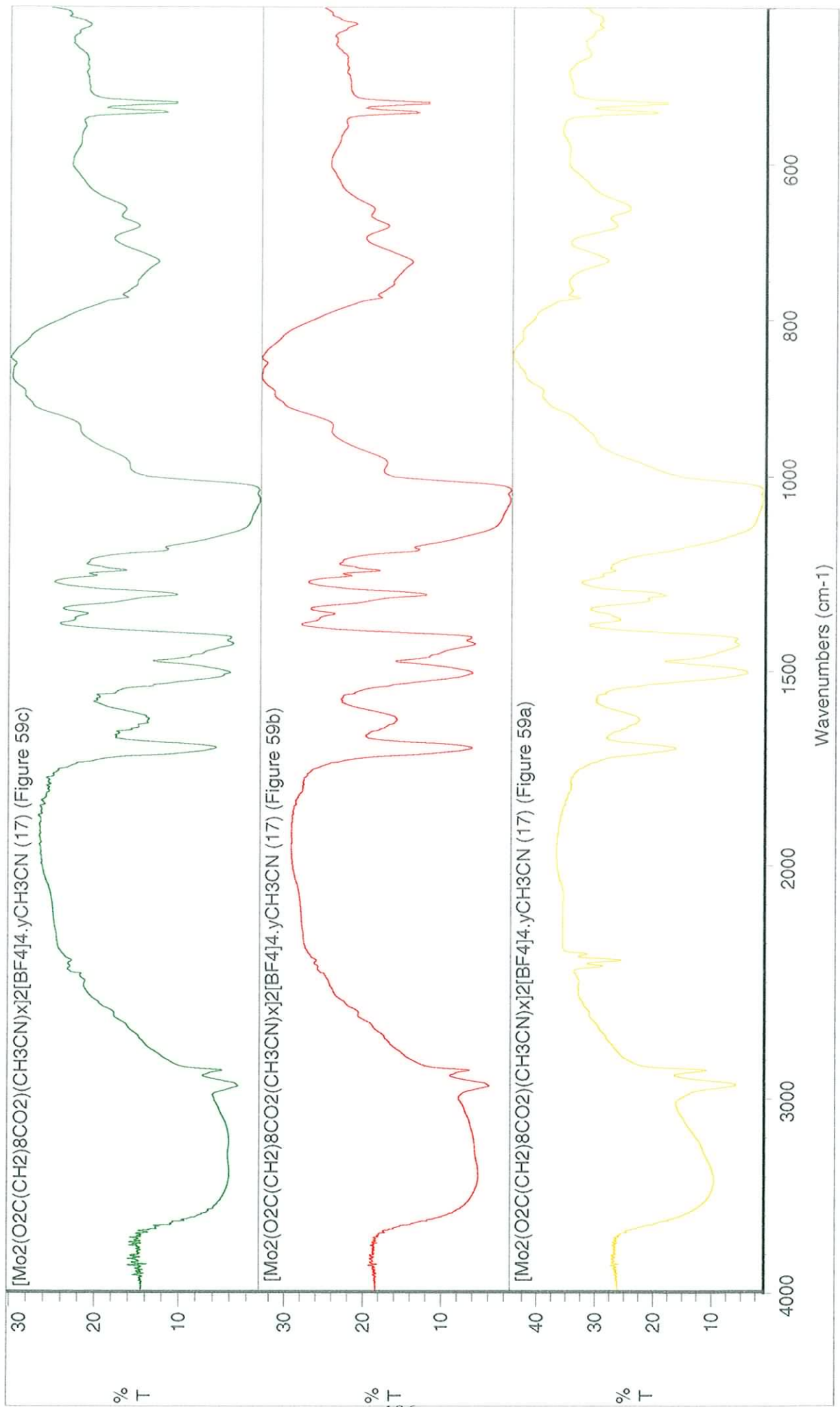
Table 11. Analytical data for $[\text{Mo}_2(\text{O}_2\text{C}(\text{CH}_2)_n\text{CO}_2)(\text{CH}_3\text{CN})_x]_2[\text{BF}_4]_{4-y}\cdot\text{CH}_3\text{CN}$

Complex	% Found			% Calc.		
	C	H	N	C	H	N
$[\text{Mo}_2(\text{eda})(\text{CH}_3\text{CN})_x][\text{BF}_4]_2$ (9)	18.22	2.66	5.80	24.03	2.59	12.0
$[\text{Mo}_2(\text{prda})(\text{CH}_3\text{CN})_x]_2[\text{BF}_4]_4$ (10)	16.64	2.83	5.38	25.24	2.82	11.77
$[\text{Mo}_2(\text{bda})(\text{CH}_3\text{CN})_x]_2[\text{BF}_4]_4$ (11)	20.30	3.04	6.91	26.40	3.0	11.55
$[\text{Mo}_2(\text{pda})(\text{CH}_3\text{CN})_x]_2[\text{BF}_4]_4$ (12)	20.68	3.02	6.46	27.52	3.26	11.33
$[\text{Mo}_2(\text{hxda})(\text{CH}_3\text{CN})_x]_2[\text{BF}_4]_4$ (13)	21.42	3.28	5.50	28.60	3.47	11.18
$[\text{Mo}_2(\text{hda})(\text{CH}_3\text{CN})_x]_2[\text{BF}_4]_4$ (14)	25.05	3.42	6.57	29.64	3.67	10.92
$[\text{Mo}_2(\text{oda})(\text{CH}_3\text{CN})_x]_2[\text{BF}_4]_4$ (15)	36.02	5.30	3.90	30.64	3.86	10.72
$[\text{Mo}_2(\text{nda})(\text{CH}_3\text{CN})_x]_2[\text{BF}_4]_4$ (16)	25.64	3.98	7.93	31.61	4.04	10.53
$[\text{Mo}_2(\text{dda})(\text{CH}_3\text{CN})_x]_2[\text{BF}_4]_4$ (17)	25.20	3.79	4.35	32.54	4.22	10.35
$[\text{Mo}_2(\text{bdoa})(\text{CH}_3\text{CN})_x]_2[\text{BF}_4]_4$ (18)	27.95	3.41	8.79	31.61	3.13	10.05

In many cases there is a large discrepancy between the microanalytical data found for the complexes and the theoretical values. This observation has previously been reported in the literature by Cotton⁸¹ and the inaccuracy is thought to be due to the extreme air- and moisture-sensitivity of the complexes. The air-sensitivity of the new dicarboxylate complex salts is in keeping with that previously reported for the neutral dicarboxylate complexes made by Stephenson *et al.*⁸ and also by Mureinik.²⁵ It is also notable that the air-stability of the present complexes varies with respect to the different dicarboxylate ligands. Those complexes containing shorter bridging units {*e.g.* propanedioate (**10**) and butanedioate (**11**)} appeared to be more air-sensitive than those complexes containing longer dicarboxylate ligands. The ethanedioate complex $[\text{Mo}_2(\text{O}_2\text{CCO}_2)(\text{CH}_3\text{CN})_x][\text{BF}_4]_2$ (**9**) proved to be the most stable complex of the present set.

The method used to precipitate the complexes from the acetonitrile mother liquor also appeared to affect their stability. Complexes requiring the addition of dichloromethane to the mother liquor in order to induce product precipitation were less air-stable than those where no additional solvent was required.

An IR spectral profile of the air-stability of $[\text{Mo}_2(\text{O}_2\text{C}(\text{CH}_2)_8\text{CO}_2)(\text{CH}_3\text{CN})_x]_2[\text{BF}_4]_{4-x}\cdot\text{CH}_3\text{CN}$ (**17**) is shown in *Figure 59 (a)-(c)*. A freshly prepared sample of the complex was ground up with KBr (in air) and the IR spectrum recorded (*Figure 59a*). The disc was then left exposed to the atmosphere for 5 days and the spectrum was again recorded (*Figure 59b*). A third spectrum of the same disc was recorded after a further 6 days (*Figure 59c*). The colour of the KBr disc of the freshly made sample was red (*a*) and this darkened considerably by the time the second and third spectra were recorded. The main difference between the three IR



spectra was the absence of the $\nu(\text{C}\equiv\text{N})$ band at 2283 cm^{-1} from (b) and (c) indicating the loss of acetonitrile ligands. Furthermore the relative intensity of the $\nu(\text{OH})$ band centred at *ca.* 3390 cm^{-1} increased with exposure time.

In general, the new molybdenum(II) complex salts appear to be more air-stable than the parent complex $[\text{Mo}_2(\text{CH}_3\text{CN})_8][\text{BF}_4]_4$ (**2**). All of the complexes are much more stable in acetonitrile solution than in the solid state, and under an atmosphere of N_2 the solutions appear to remain stable for up to three weeks.

D.1.2 X-ray crystal structure of the molybdenum(II) complex salt



The X-ray crystal structure of the molybdenum(II) butanedioate complex salt $[\text{Mo}_2(\text{O}_2\text{C}(\text{CH}_2)_2\text{CO}_2)(\text{CH}_3\text{CN})_6]_2[\text{BF}_4]_4 \cdot 3\text{CH}_3\text{CN}$ (**11**) is illustrated in *Figure 60* and packing diagrams are shown in *Figures 61-63*. The structure consists of a tetramer in which bridging bidentate bda^{2-} ligands link four crystallographically identical molybdenum atoms. Each molybdenum(II) atom is at the centre of a distorted octahedron, and is also ligated by two equatorially bound acetonitrile nitrogens and a third nitrogen from a weakly coordinated axial acetonitrile molecule. The butanedioate ligands have a dual role. Firstly, each of the dicarboxylate groups bridge the dimetallic Mo-Mo core and, secondly, each butanedioate ligand links the two halves of the tetramer together.

Selected bond distances and angles for the complex are listed in *Table 12*. In general, the bond distances for $[\text{Mo}_2(\text{O}_2\text{C}(\text{CH}_2)_2\text{CO}_2)(\text{CH}_3\text{CN})_6]_2[\text{BF}_4]_4 \cdot 3\text{CH}_3\text{CN}$ (**11**) are almost identical with those reported for the red molybdenum(II) salt $[\text{Mo}_2(\mu\text{-O}_2\text{CCH}_3)_2(\text{CH}_3\text{CN})_6][\text{BF}_4]_2$.⁸³ The mean Mo-N distance for the axial acetonitrile ligand

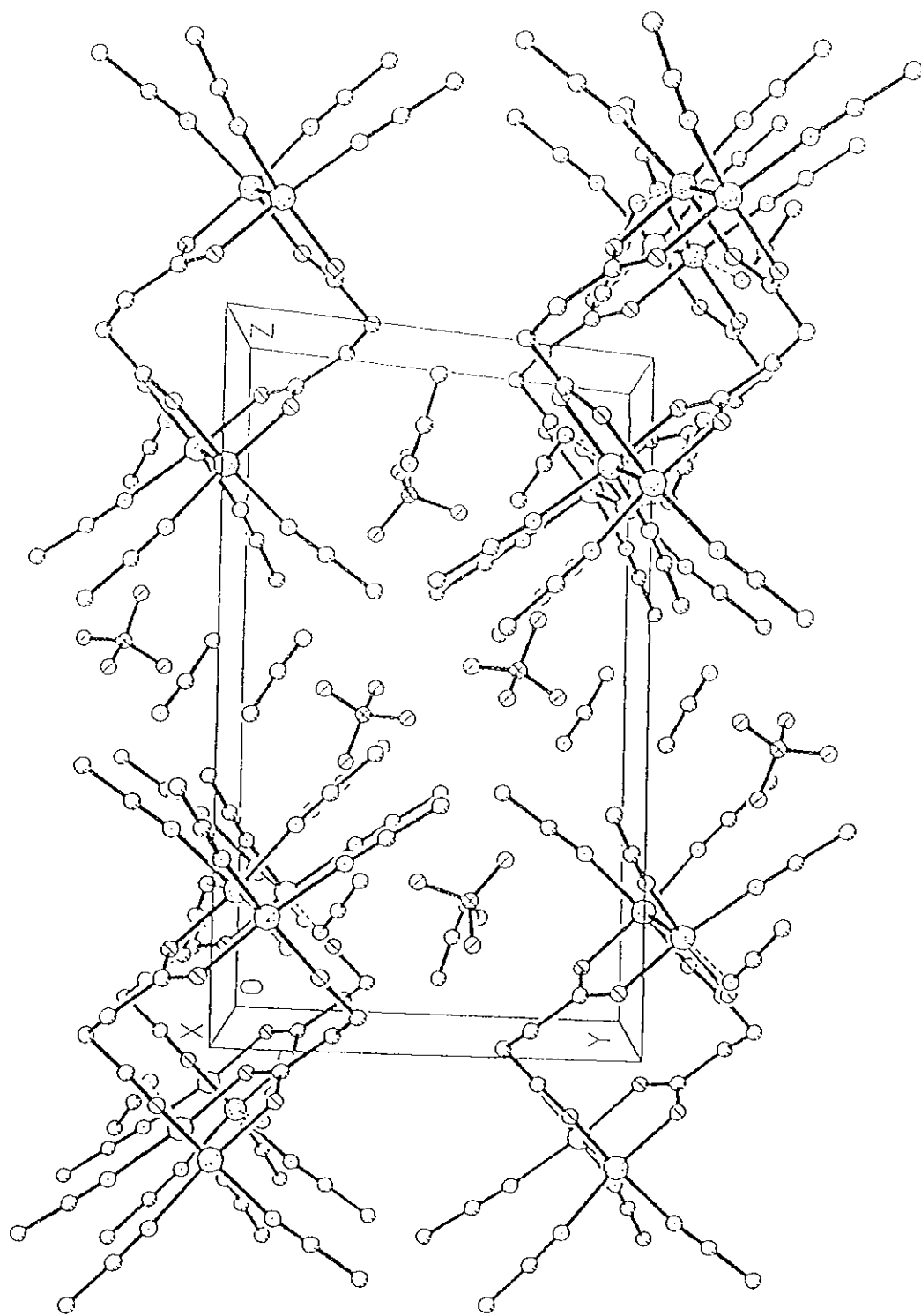


Figure 61

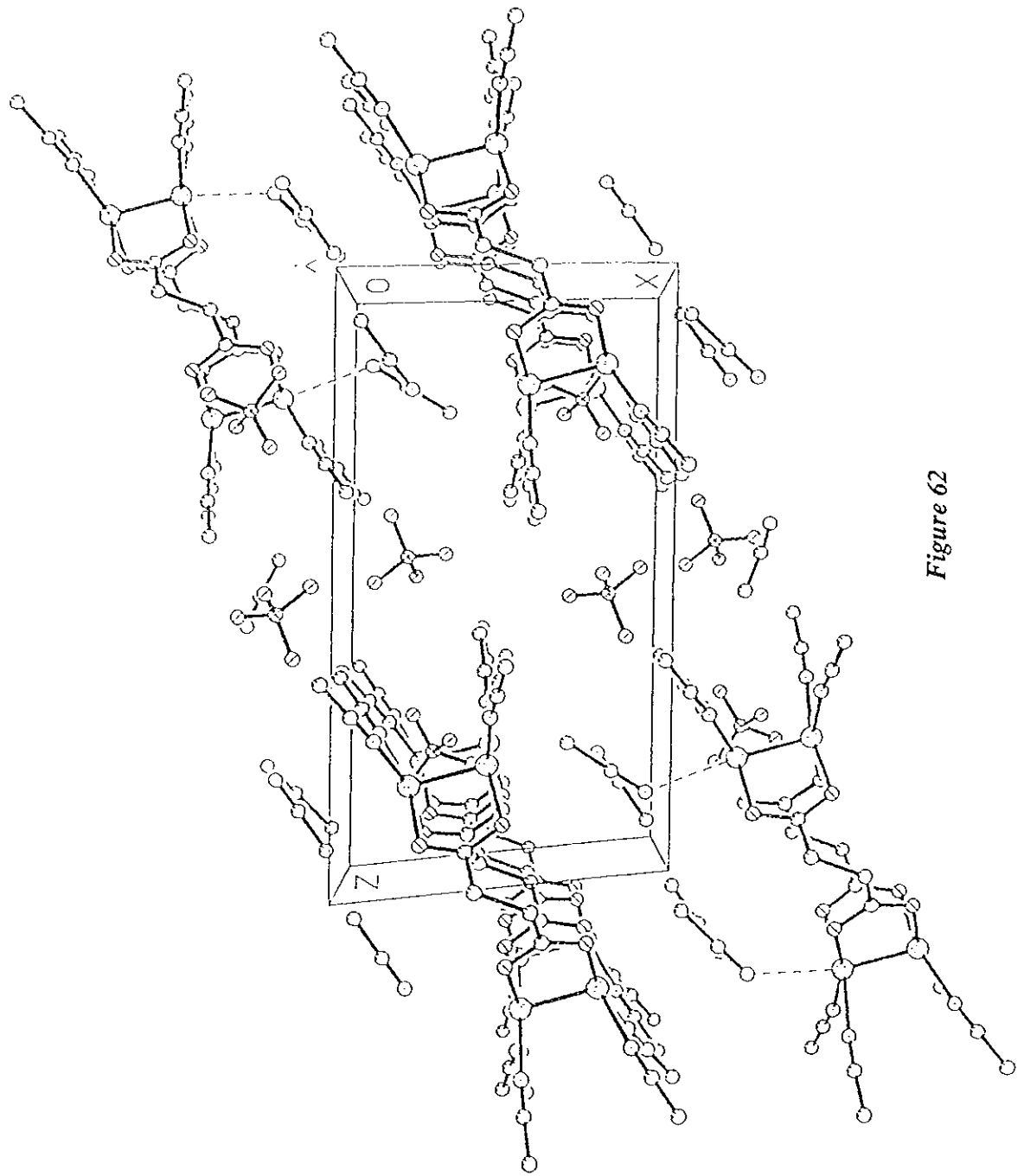


Figure 62

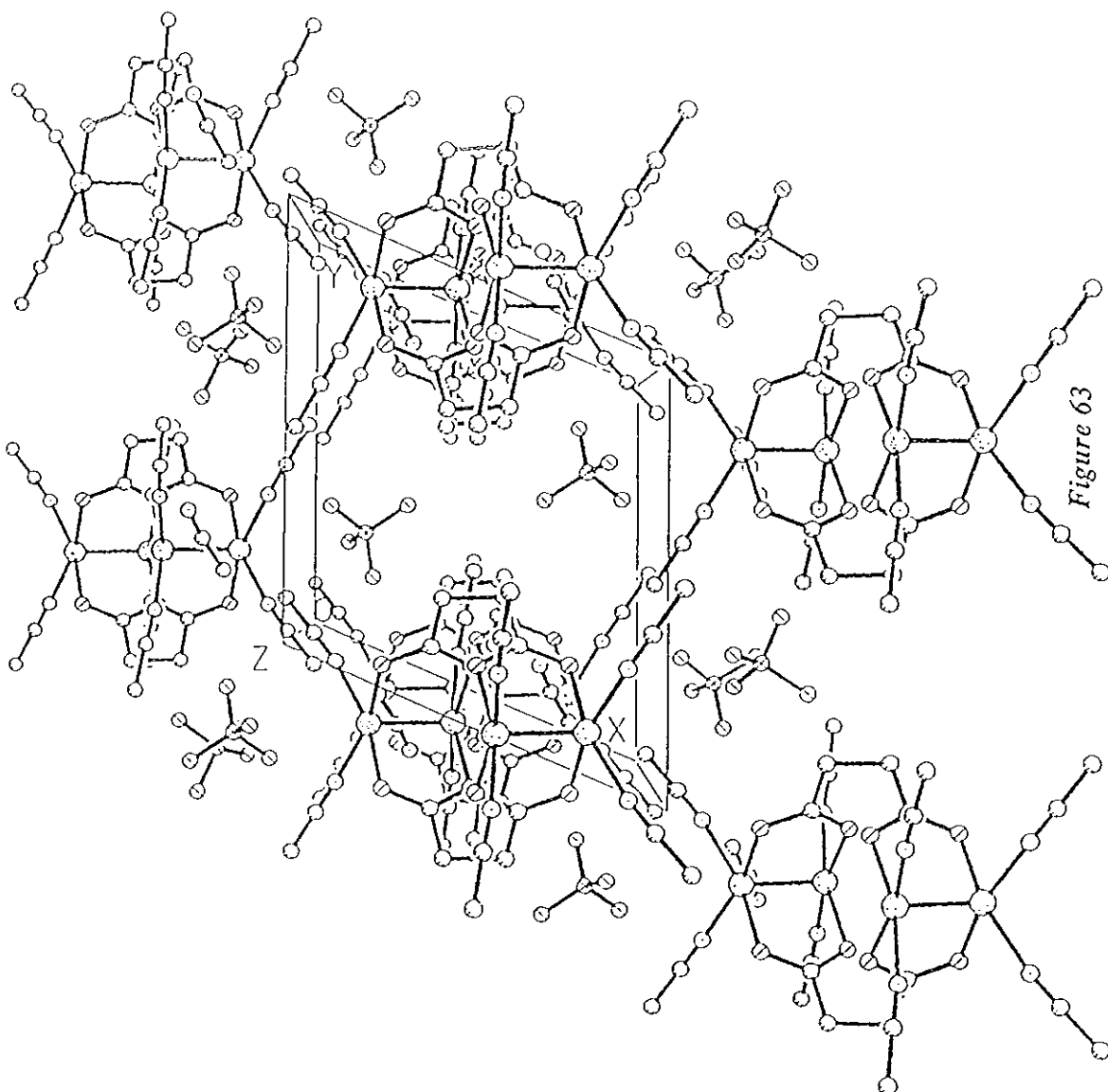


Figure 63

in complex (11) (2.693 Å) is only slightly shorter than in $[\text{Mo}_2(\mu\text{-O}_2\text{CCH}_3)_2(\text{CH}_3\text{CN})_6][\text{BF}_4]_2$ (2.7585 Å), whereas the mean equatorial acetonitrile ligand is marginally longer in complex (11) (2.162 Å) compared with that reported for $[\text{Mo}_2(\mu\text{-O}_2\text{CCH}_3)_2(\text{CH}_3\text{CN})_6][\text{BF}_4]_2$ (2.1475 Å). Interestingly the mean Mo-O bond lengths for both complexes are identical.

Table 12. Selected bond lengths [Å] and angles [°] for complex (11)

Mo(1)-O(3)	2.088(3)	Mo(1)-O(1)	2.091(3)
Mo(1)-Mo(2)	2.1451(6)	Mo(1)-N(10)	2.162(4)
Mo(1)-N(30)	2.172(4)	Mo(1)-N(50)	2.712(5)
Mo(2)-O(4)	2.077(3)	Mo(2)-O(2)	2.080(3)
Mo(2)-N(40)	2.152(4)	Mo(2)-N(20)	2.163(4)
Mo(2)-N(60)	2.674(5)		
O(3)-Mo(1)-O(1)	91.53(12)	O(3)-Mo(1)-Mo(2)	91.21(9)
O(1)-Mo(1)-Mo(2)	91.10(9)	O(3)-Mo(1)-N(10)	88.66(14)
O(1)-Mo(1)-N(10)	166.2(2)	Mo(2)-Mo(1)-N(10)	102.72(13)
O(3)-Mo(1)-N(30)	166.3(2)	O(1)-Mo(1)-N(30)	89.18(14)
Mo(2)-Mo(1)-N(30)	102.43(11)	N(10)-Mo(1)-N(30)	87.4(2)
O(3)-Mo(1)-N(50)	86.0(2)	O(1)-Mo(1)-N(50)	84.01(13)
Mo(2)-Mo(1)-N(50)	174.28(11)	N(10)-Mo(1)-N(50)	82.2(2)
N(30)-Mo(1)-N(50)	80.5(2)	O(4)-Mo(2)-O(2)	90.64(12)
O(4)-Mo(2)-Mo(1)	90.70(9)	O(2)-Mo(2)-Mo(1)	90.80(9)
O(4)-Mo(2)-N(40)	166.2(2)	O(2)-Mo(2)-N(40)	86.00(14)
Mo(1)-Mo(2)-N(40)	102.75(11)	O(4)-Mo(2)-N(20)	90.11(14)
O(2)-Mo(2)-N(20)	168.6(2)	Mo(1)-Mo(2)-N(20)	100.52(12)
N(40)-Mo(2)-N(20)	90.6(2)	O(4)-Mo(2)-N(60)	76.1(2)
O(2)-Mo(2)-N(60)	83.3(2)	Mo(1)-Mo(2)-N(60)	165.43(11)
N(40)-Mo(2)-N(60)	90.2(2)	N(20)-Mo(2)-N(60)	85.9(2)

Two complexes which show some structural similarity to the butanedioate complex $[\text{Mo}_2(\text{O}_2\text{C}(\text{CH}_2)_2\text{CO}_2)(\text{CH}_3\text{CN})_6]_2[\text{BF}_4]_4 \cdot 3\text{CH}_3\text{CN}$ (11) are the polymeric copper(II) butanedioate complex $[\text{Cu}(\text{O}_2\text{C}(\text{CH}_2)_2\text{CH}_2)]_n$ (Figure 25)²⁴ and the

tetrameric ruthenium(I) pentanedioate complex $[\text{Ru}_4(\text{CO})_8(\text{O}_2\text{C}(\text{CH}_2)_3\text{CO}_2)_2(\text{PBu}_3)_4]$ (Figure 29).³⁷ The copper(II) and the ruthenium(I) atoms in the above complexes each contain bridging bidentate dicarboxylate ligands.

The synthesis of the molybdenum(II) butanedioate complex (11) is thought to proceed *via* a ligand exchange reaction with the labile acetonitrile ligands of $[\text{Mo}_2(\text{CH}_3\text{CN})_6][\text{BF}_4]_4$ (2) easily replaced by the incoming bda^{2-} dianions.

The electronic spectrum of an acetonitrile solution of $[\text{Mo}_2(\text{O}_2\text{C}(\text{CH}_2)_2\text{CO}_2)(\text{CH}_3\text{CN})_6]_2[\text{BF}_4]_4 \cdot 3\text{CH}_3\text{CN}$ (11) contained a single broad *d-d* absorption band at 531 nm ($\epsilon = 1648 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$) (Figure 64).

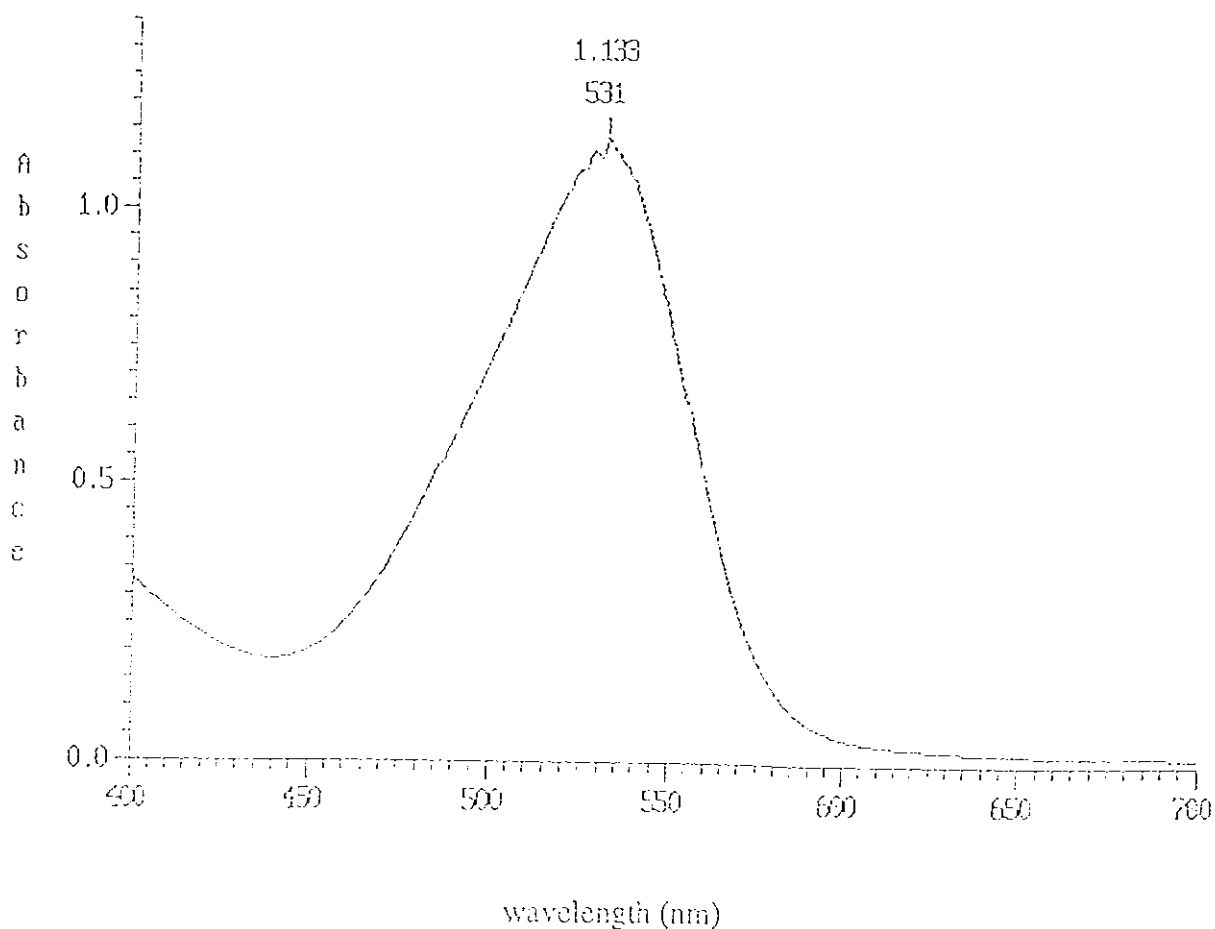


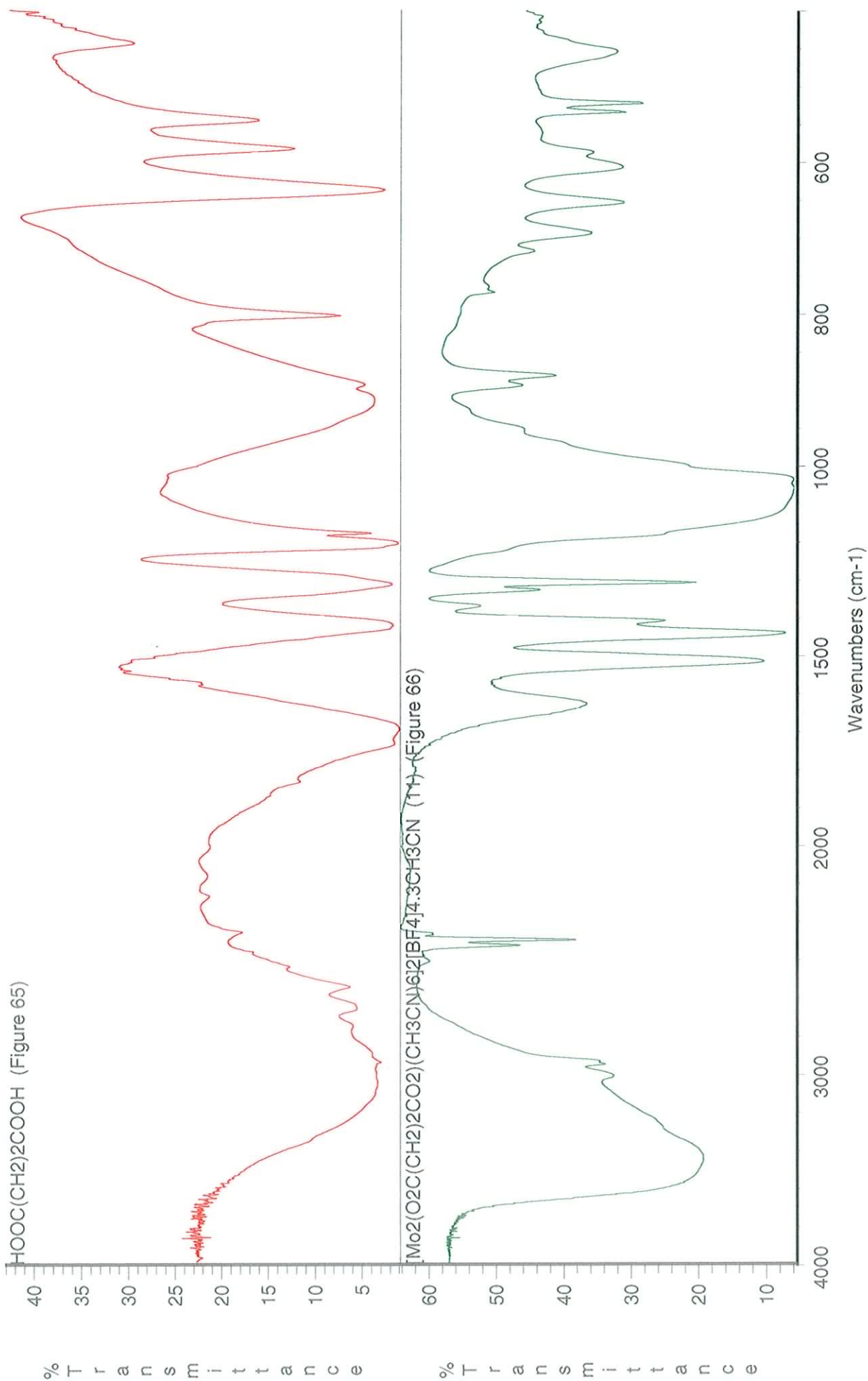
Figure 64

The IR spectrum of the free acid bdaH₂ contained a broad $\nu(\text{C}=\text{O})$ band centred around 1680 cm⁻¹ (*Figure 65*). When the acid is converted to the molybdenum(II) complex (**11**) the C=O band disappears and bands attributable to the $\nu_{\text{asym}}(\text{OCO})$ and $\nu_{\text{sym}}(\text{OCO})$ vibrations appear at 1536 cm⁻¹ and 1443 cm⁻¹, respectively ($\Delta\nu(\text{OCO}) = 93$ cm⁻¹) (*Figure 66*). The relatively low value of $\Delta\nu(\text{OCO})$ is in keeping with values recorded for complexes in which the carboxylate ligand bridges short M-M bonds (*e.g.* $\Delta\nu(\text{OCO}) = 94$ cm⁻¹ for [Mo₂(μ -O₂CCH₃)₄]).⁷¹

The cyclic voltammogram of (**11**) showed that the complex was electroinactive between the switching potentials of +2.0 and -2.0 volts.

D.1.3 Proposed structures for other molybdenum(II) dicarboxylate complexes

Selected IR data for complexes (**9**)-(18) is listed in *Table 13* and the actual IR spectra of the complexes are shown in Appendix 1. The IR spectra of the parent complexes [Mo₂(μ -O₂CCH₃)₄] (**1**) and [Mo₂(CH₃CN)₈][BF₄]₂ (**2**) are shown in *Figures 67* and *68*, respectively. The spectra of complexes (**10**)-(18) all contain prominent $\nu_{\text{asym}}(\text{OCO})$ stretching bands in the region 1550-1500 cm⁻¹ and $\nu_{\text{sym}}(\text{OCO})$ stretching bands in the region 1420-1430 cm⁻¹. The mean $\Delta\nu(\text{OCO})$ value (95 cm⁻¹) of the complexes (**10**)-(18) are consistent with the carboxylate ligands having a bridging bidentate coordination mode (Section 1.2.2). However, the ethanedioate complex [Mo₂(O₂CCO₂)(CH₃CN)_x][BF₄]₂ (**9**) had a $\Delta\nu(\text{OCO})$ value of 251 cm⁻¹ indicating a possible unidentate coordination mode for the dicarboxylate ligand.



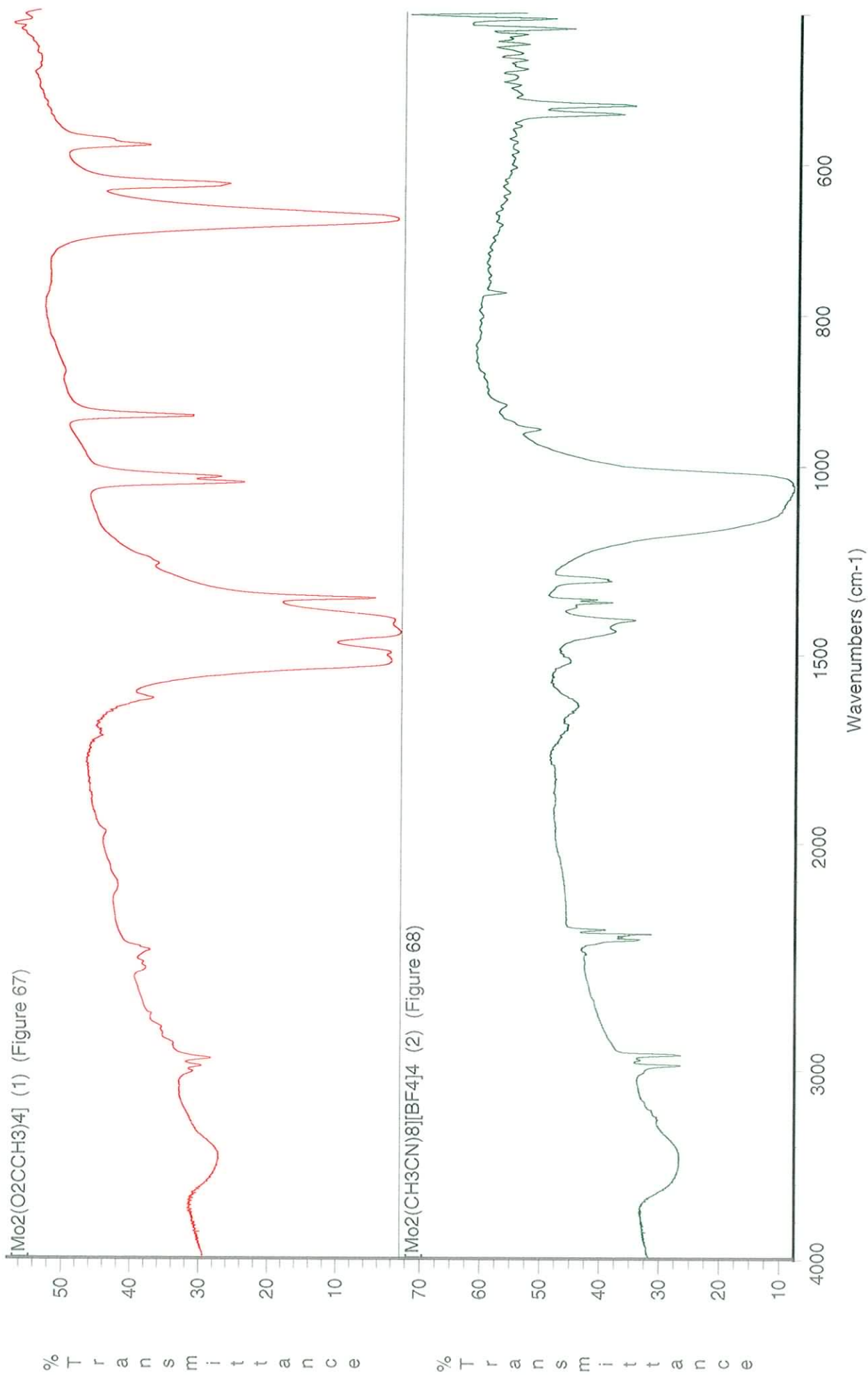
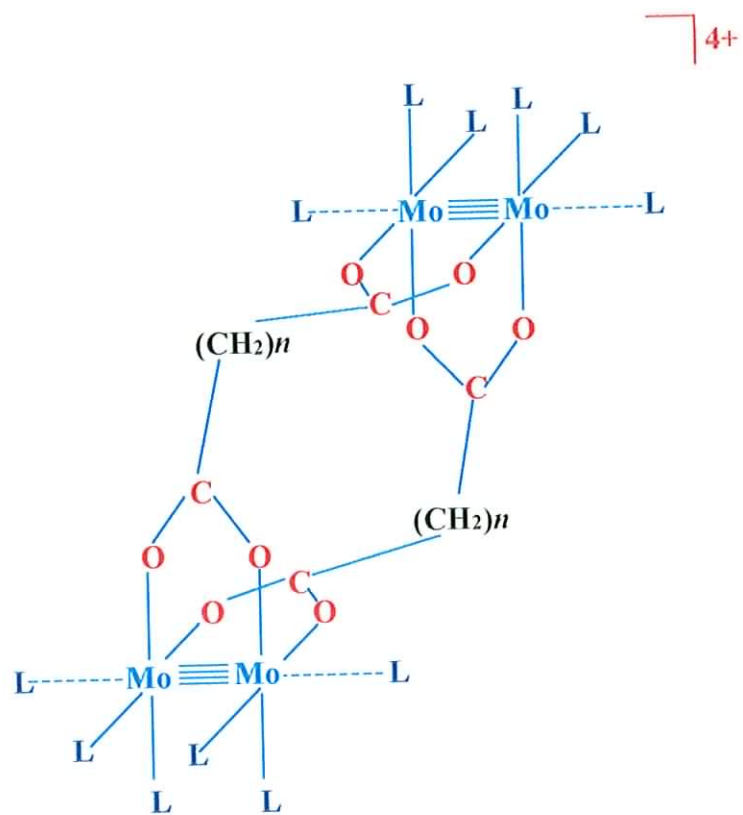


Table 13. Selected IR data (cm⁻¹) for the molybdenum(II) salts



Complex	$\nu_{\text{asym}}(\text{OCO}) \text{ cm}^{-1}$	$\nu_{\text{sym}}(\text{OCO}) \text{ cm}^{-1}$	$\Delta\nu(\text{OCO}) \text{ cm}^{-1}$
$[\text{Mo}_2(\text{eda})(\text{CH}_3\text{CN})_x][\text{BF}_4]_2$ (9)	1556	1305	251
$[\text{Mo}_2(\text{prda})(\text{CH}_3\text{CN})_x]_2[\text{BF}_4]_4$ (10)	1536	1381	155
$[\text{Mo}_2(\text{bda})(\text{CH}_3\text{CN})_x]_2[\text{BF}_4]_4$ (11)	1536	1443	93
$[\text{Mo}_2(\text{pda})(\text{CH}_3\text{CN})_x]_2[\text{BF}_4]_4$ (12)	1510	1430	80
$[\text{Mo}_2(\text{hxda})(\text{CH}_3\text{CN})_x]_2[\text{BF}_4]_4$ (13)	1503	1429	74
$[\text{Mo}_2(\text{hda})(\text{CH}_3\text{CN})_x]_2[\text{BF}_4]_4$ (14)	1523	1424	99
$[\text{Mo}_2(\text{oda})(\text{CH}_3\text{CN})_x]_2[\text{BF}_4]_4$ (15)	1505	1423	82
$[\text{Mo}_2(\text{nda})(\text{CH}_3\text{CN})_x]_2[\text{BF}_4]_4$ (16)	1501	1420	81
$[\text{Mo}_2(\text{dda})(\text{CH}_3\text{CN})_x]_2[\text{BF}_4]_4$ (17)	1507	1425	82
$[\text{Mo}_2(\text{bdoa})(\text{CH}_3\text{CN})_x]_2[\text{BF}_4]_4$ (18)	1546	1433	113

It is thought that the complexes of general formula $[\text{Mo}_2(\text{O}_2\text{C}(\text{CH}_2)_n\text{CO}_2)(\text{CH}_3\text{CN})_x]_2[\text{BF}_4]_{4-y}\cdot y\text{CH}_3\text{CN}$ (10)-(17) and $[\text{Mo}_2(\text{bdoa})(\text{CH}_3\text{CN})_x]_2[\text{BF}_4]_{4-y}\cdot y\text{CH}_3\text{CN}$ (18) are essentially isostructural with the structurally characterised complex $[\text{Mo}_2(\text{O}_2\text{C}(\text{CH}_2)_2\text{CO}_2)(\text{CH}_3\text{CN})_6]_2[\text{BF}_4]_4\cdot 3\text{CH}_3\text{CN}$ (11). Thus, the general structure of these new cationic dimolybdenum complex salts is illustrated in *Figure 69*. The shortest chain diacid (ethanedioic acid $\text{HO}_2\text{C}-\text{CO}_2\text{H}$) would not be capable of bridging two adjacent Mo-Mo units in the same manner as found in complex (11).

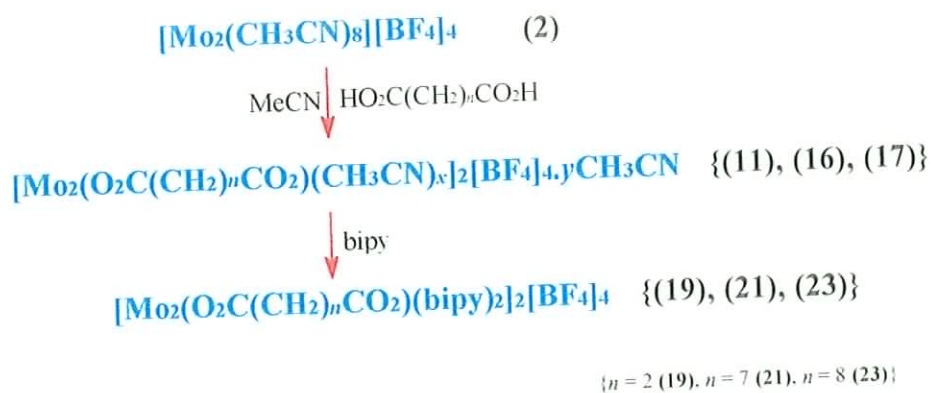


L = CH₃CN
 n = 0 - 8

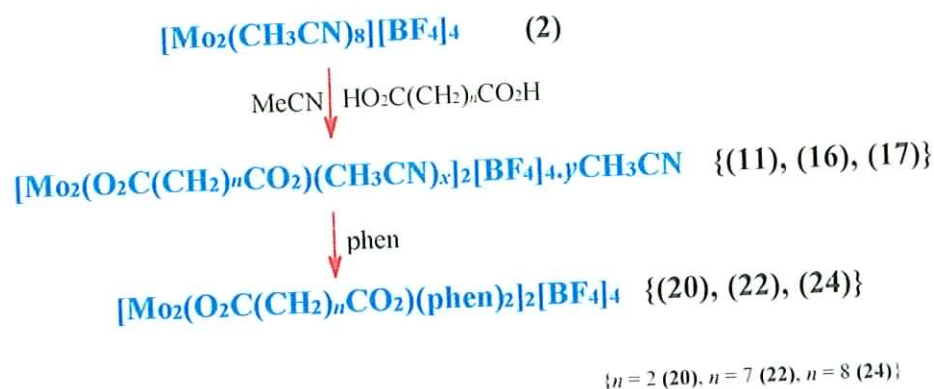
Figure 69

**D.2 PREPARATION OF DIMOLYBDENUM(II) DICARBOXYLATE
COMPLEXES CONTAINING BIDENTATE NITROGEN DONOR
LIGANDS**

The complex salts $[\text{Mo}_2(\text{O}_2\text{C}(\text{CH}_2)_n\text{CO}_2)(\text{CH}_3\text{CN})_x]_2[\text{BF}_4]_{4-y}\cdot\text{CH}_3\text{CN}$ (9)-(17) are air-sensitive, hygroscopic and sensitive to conditions of handling. Consequently, a series of experiments were conducted in an attempt to improve the stability of these dicationic complex salts. The general strategy was to replace the small labile acetonitrile ligands with larger, bulkier ligands which might provide more protection for the bimetallic $\text{Mo}_2(\text{II},\text{II})$ core from attack by O_2 and/or H_2O . It was also hoped that the addition of chelating ligands like 2,2'-bipyridine (bipy) and 1,10-phenanthroline (phen) would promote the breakdown of what had originally been thought to be polymeric dicarboxylate complexes into simpler binuclear structures, thus increasing the possibility of obtaining crystalline products. The reactions of complexes $[\text{Mo}_2(\text{O}_2\text{C}(\text{CH}_2)_2\text{CO}_2)(\text{CH}_3\text{CN})_6]_2[\text{BF}_4]_4\cdot 3\text{CH}_3\text{CN}$ (11), $[\text{Mo}_2(\text{O}_2\text{C}(\text{CH}_2)_7\text{CO}_2)(\text{CH}_3\text{CN})_x]_2[\text{BF}_4]_{4-y}\cdot\text{CH}_3\text{CN}$ (16) and $[\text{Mo}_2(\text{O}_2\text{C}(\text{CH}_2)_8\text{CO}_2)(\text{CH}_3\text{CN})_x]_2[\text{BF}_4]_{4-y}\cdot\text{CH}_3\text{CN}$ (17) with bipy and phen are summarised in *Schemes 22* and *23*, respectively.



Scheme 22



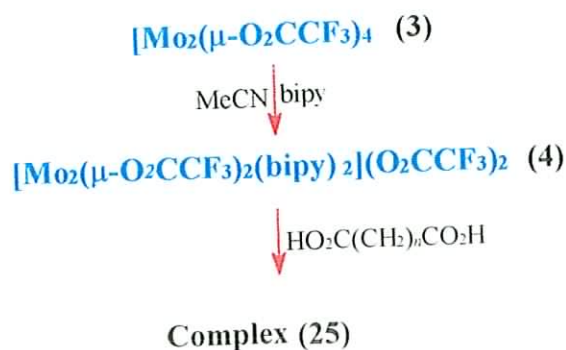
Scheme 23

Complexes (11), (16) and (17), reacted with bipy and phen in the ratio of 1:2 in acetonitrile to give purple solids of general formula $[\text{Mo}_2(\text{O}_2\text{C}(\text{CH}_2)_n\text{CO}_2)(\text{bipy})_2][\text{BF}_4]_4$ and $[\text{Mo}_2(\text{O}_2\text{C}(\text{CH}_2)_n\text{CO}_2)(\text{phen})_2][\text{BF}_4]_4$, respectively {(19)-(24)}. The reactions with bipy and phen proved to be very similar and involved manipulation of the resulting solution in order to induce precipitation of the product. Product isolation proved to be even more difficult than in the case of the parent complexes $[\text{Mo}_2(\text{O}_2\text{C}(\text{CH}_2)_n\text{CO}_2)(\text{CH}_3\text{CN})_x]_2[\text{BF}_4]_{4-y}\text{CH}_3\text{CN}$.

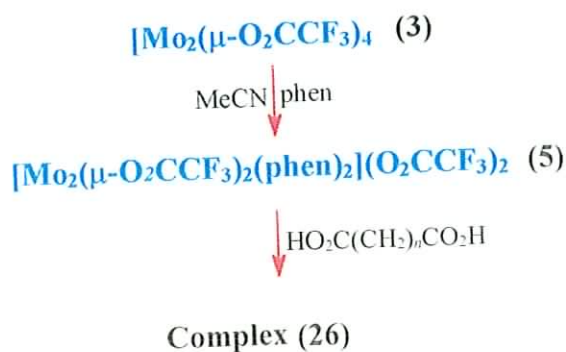
Complexes (19)-(24) were extremely soluble in acetonitrile and sparingly soluble in dichloromethane and in alcohols. The complexes were completely insoluble in toluene but dissolved in pyridine to give yellow solutions which decomposed rapidly. In the solid state the complexes appeared to be less air-sensitive and also less hygroscopic than their precursors $[\text{Mo}_2(\text{O}_2\text{C}(\text{CH}_2)_n\text{CO}_2)(\text{CH}_3\text{CN})_x]_2[\text{BF}_4]_{4-y}\text{CH}_3\text{CN}$. However, solutions of the bipy and phen complexes when stored under an atmosphere of N_2 changed colour from purple to black within a few days. Attempts to grow crystals of the bipy and phen complexes (19)-(24) were unsuccessful.

In a second series of reactions $[\text{Mo}_2(\mu\text{-O}_2\text{CCF}_3)_4]$ (3) was employed as the starting material for the preparation of the bipy and phen derivatives $[\text{Mo}_2(\mu\text{-$

$\text{O}_2\text{CCF}_3)_2(\text{bipy})_2](\text{O}_2\text{CCF}_3)_2$ (4)^{187,188} and $[\text{Mo}_2(\mu\text{-O}_2\text{CCF}_3)_2(\text{phen})_2](\text{O}_2\text{CCF}_3)_2$ (5), respectively. Complexes (4) and (5) were reacted with decanedioic acid to form complex (25) and complex (26), respectively (*Scheme 24* and *Scheme 25*).



Scheme 24



Scheme 25

Complexes (25) and (26) were obtained as purple solids, and both were precipitated from the acetonitrile reaction solution using a mixture of dichloromethane and toluene. As with complexes (19)-(24) the trifluoroacetate salts (25) and (26) also proved difficult to obtain in good yield.

Table 14. Analytical data for molybdenum(II) complexes (19)-(26)

Complex	% Found			% Calc.		
	C	H	N	C	H	N
[Mo ₂ (bda)(bipy) ₂][BF ₄] ₄ (19)	30.0	3.3	7.0	32.95	3.02	10.48
[Mo ₂ (bda)(phen) ₂][BF ₄] ₄ (20)	35.41	2.92	6.38	34.90	2.93	10.17
[Mo ₂ (nda)(bipy) ₂][BF ₄] ₄ (21)	40.57	4.0	6.2	40.31	3.50	6.48
[Mo ₂ (nda)(phen) ₂][BF ₄] ₄ (22)	43.07	3.50	6.09	43.46	3.32	6.14
Complex (23)	41.50	4.44	4.95			
Complex (24)	43.64	4.2	7.70			
Complex (25)	54.07	7.72	1.01			
Complex (26)	47.30	4.65	3.92			

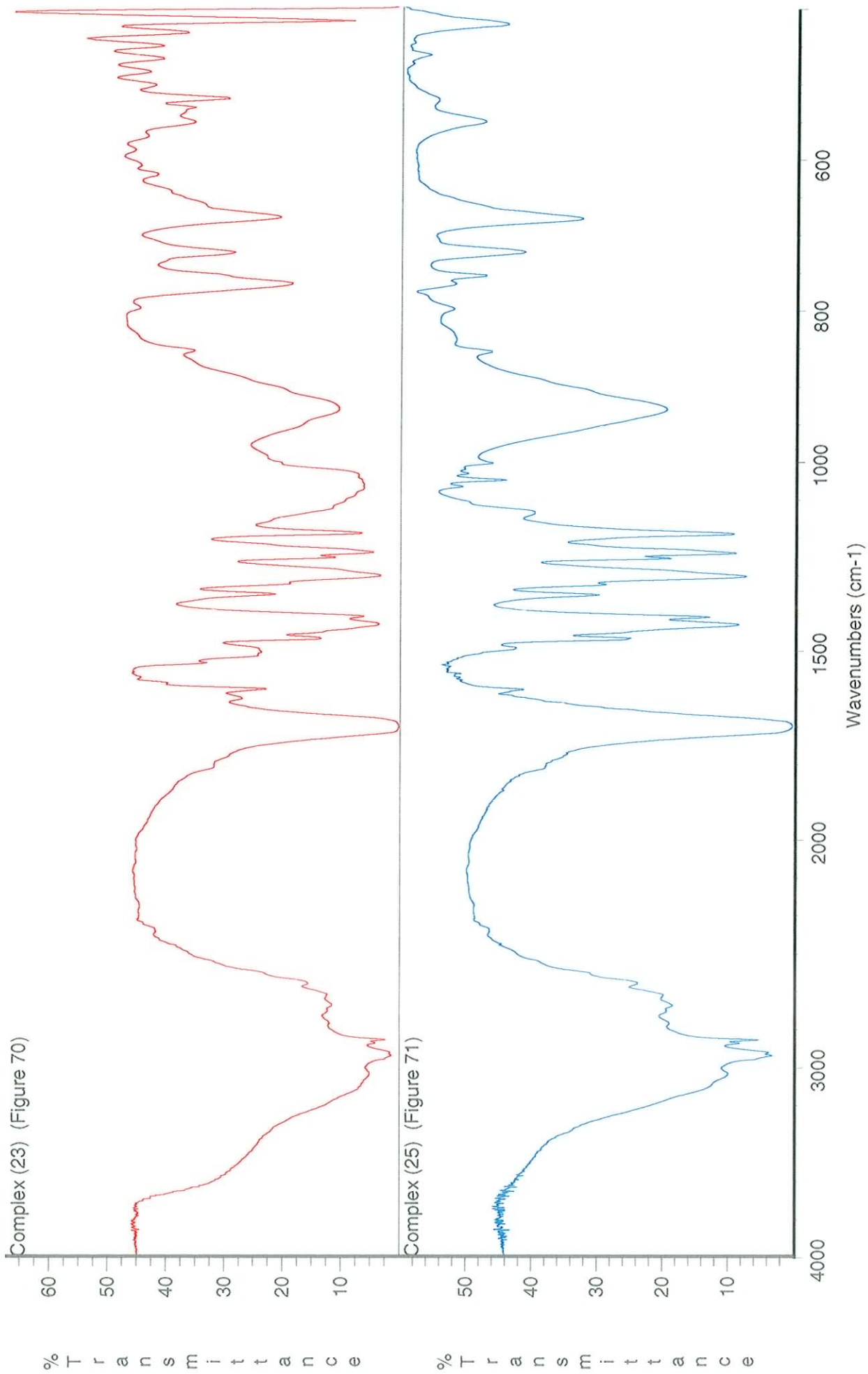
The IR spectra of complexes (19)-(26) are shown in Appendix 1. Selected IR data for the decanedioate complexes (23)-(26) are listed in *Table 15* and the IR spectra are shown in *Figures 70-73*. The complexes (19)-(26) all contain a strong absorption band at 1700 cm⁻¹ indicating the presence of a free acid group (COOH). Weak absorption bands for the carboxylate $\nu_{\text{asym}}(\text{OCO})$ and $\nu_{\text{sym}}(\text{OCO})$ stretches at 1600 and 1420 cm⁻¹, respectively, were also evident. In addition to the $\nu(\text{C}=\text{N})$ bands between *ca.* 700-760 cm⁻¹ associated with either the bipy or phen groups, the decanedioate complexes (23)-(26) contained a strong broad absorption band at *ca.* 930 cm⁻¹. This latter band was only very weak in complexes (19)-(22) and was thought to be due to $\nu(\text{Mo}=\text{O})$ stretching, thus indicating that oxidation had occurred in the decanedioate

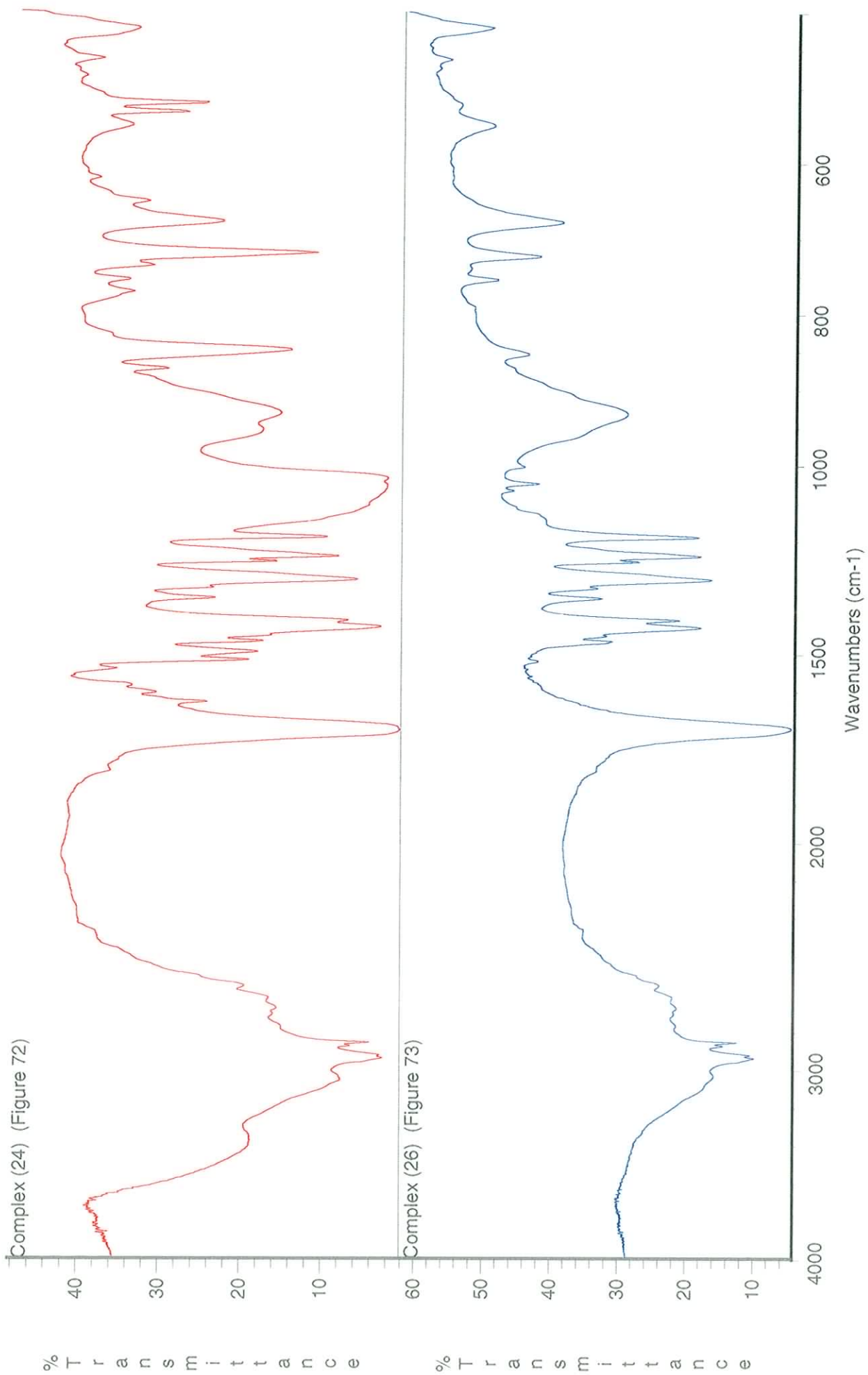
complexes. Previous work on oxymolybdate complexes¹⁹¹ details distinct bands in the IR spectrum appearing between 800-900 cm⁻¹.

Thus, it can be concluded that complexes (19)-(26) are even more sensitive to both air and conditions of handling than the parent complexes [Mo₂(O₂C(CH₂)_nCO₂)(CH₃CN)_x]₂[BF₄]_{4-y}·yCH₃CN (10)-(17) and on the basis of both the IR and microanalytical data alone it is difficult to postulate reasonable structures for these materials.

Table 15. Selected IR data for oxidised decanedioate complexes (23)-(26)

Complex	$\nu(\text{C}=\text{O})$	ν_{asym} (CO ₂)	ν_{sym} (CO ₂)	$\nu(\text{Mo}=\text{O})$
Complex (23)	1700	1430	1302	930
Complex (24)	1700	1427	1302	931
Complex (25)	1700	1430	1302	930
Complex (26)	1700	1428	1300	930



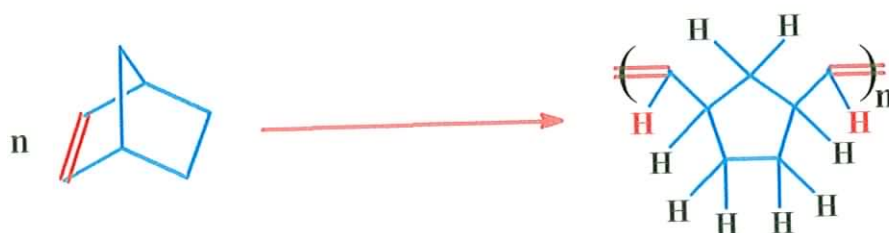


D.3 POLYMERIZATION OF NORBORNENE

D.3.1 Characterisation of polynorbornene

The polynorbornene obtained in these experiments was, in almost all cases, a fluffy white fibrous material which was totally soluble in chlorinated solvents and also reasonably soluble in toluene and benzene. It was insoluble in ethanol and in acetonitrile and upon exposure to air for long periods the polymer gradually crumbled to a yellow insoluble powdery material.

The ^1H n.m.r. spectrum of a polynorbornene sample is shown in *Figure 74*. Although there have been some studies of the stereochemistry of polynorbornene using ^1H nmr spectroscopy¹⁹² it is generally found that $^{13}\text{C}\{^1\text{H}\}$ nmr spectroscopy is a far more useful and adaptable tool for the study of the microstructure of these polymers. Nevertheless, a fair estimate of the degree of cross-linking in a polynorbornene sample can be made by calculating the ratio between the peaks due to the aliphatic protons and the peaks due to the olefinic protons (a/o) in the ^1H nmr spectrum. A value of 4 signifies that there are no cross-links present in the polynorbornene sample (*Scheme 26*). In the present study the polymers produced generally have an aliphatic : olefinic proton ratio of about 4-5:1, indicating that a small amount of cross-linking does indeed occur.



Scheme 26

The values for the structural parameters of polynorbornene, such as the relative amount of *cis* double bonds, σ_c , can be derived from the intensities of the $^{13}\text{C}\{^1\text{H}\}$ nmr spectral lines for carbons in different positions in the polymer chain.¹⁷⁴⁻¹⁸¹ It has been found, to a fair degree of approximation, that signal heights, rather than integrals, can be used as the indicator of the abundance of carbons in each configuration in the polymer chain.^{176, 183}

The $^{13}\text{C}\{^1\text{H}\}$ nmr spectrum of a typical polynorbornene obtained in the present study is shown in *Figure 75*. The pairs of carbons in the cyclopentene ring, C^1 , C^4 and C^5 , C^6 (*Scheme 19*) each give one or more of four possible lines in the $^{13}\text{C}\{^1\text{H}\}$ nmr spectrum, corresponding to the four conformations **cc**, **ct**, **tc**, or **tt**. The bridgehead carbon of the enchainment ring, C^7 , shows similar behaviour, except that for this carbon the **ct** and **tc** conformations are identical as C^7 is symmetrically placed between its two nearest olefin linkages. Therefore, the nmr signal for C^7 often has the appearance of a triplet. The olefinic carbons, C^2 and C^3 , show separate lines for *cis* and *trans* linkages. In well-resolved or high-field spectra, each of these lines is further subdivided into three components according to the configurations of the olefinic *triads* to which the carbon belongs, *i.e.* the configurations of the previous, present, and next olefinic links in the polymer chain.

The chemical shifts in p.p.m. of the carbons C^1 to C^7 in the different configurations¹⁷⁴ are shown in *Table 16*. The *cis* content, σ_c , for the three types of carbon, is given by the formulae below, where **cc**, **ct**, **tc**, and **tt** represent the line heights of the nmr signals for each carbon:

$$\text{Based on } \text{C}^7: \quad \sigma_c = (\text{ct} + \text{tc}) / (\text{ct} + \text{tc} + 2\text{tt})$$

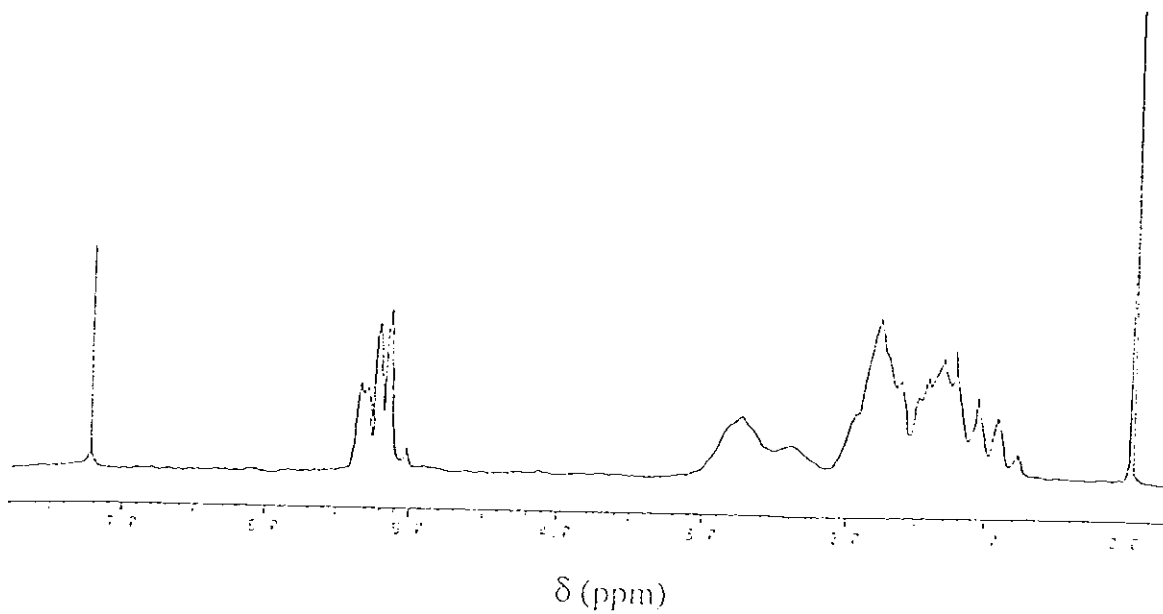


Figure 74: ^1H nmr spectrum of polynorbornene

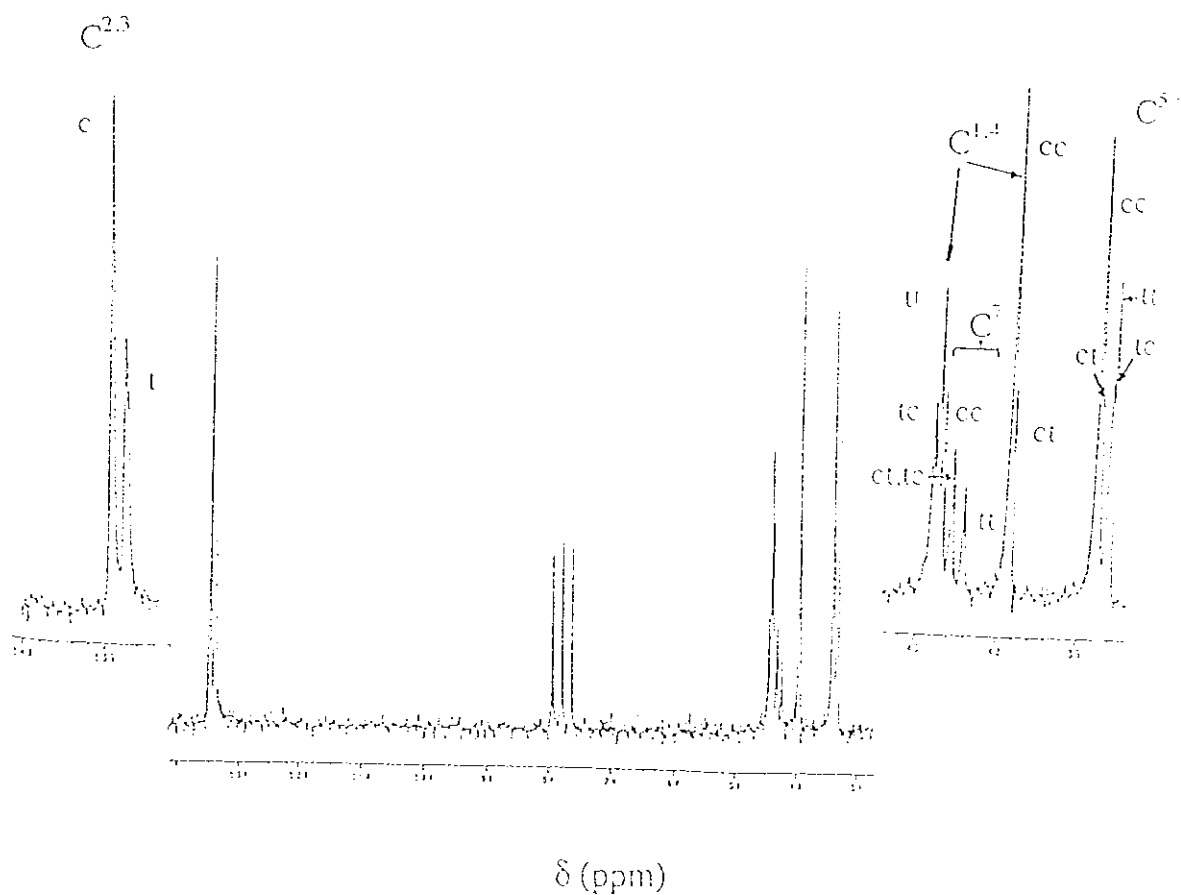


Figure 75: $^{13}\text{C}\{^1\text{H}\}$ nmr spectrum of polynorbornene

$$\text{Based on } C^1, C^4 \text{ and } C^5, C^6: \quad \sigma_c = (\text{cc} + \text{ct}) / (\text{cc} + \text{ct} + \text{tc} + \text{tt})$$

$$\text{Based on } C^2, C^3: \quad \sigma_c = (\text{c}) / (\text{c} + \text{t})$$

The blockiness of a polymer can be expressed in terms of the apparent reactivity ratios, r_t and r_c , where $r_t = \text{tt}/\text{tc}$ and $r_c = \text{cc}/\text{ct}$. The product $r_t r_c$ gives the ratio of linkages at which the configuration changes from *cis* to *trans* (or *vice versa*), to linkages at which the configuration remains *cis* or *trans*. Thus, in a polymer which tends to alternate *cis* with *trans* linkages, $r_t r_c$ is < 1 , and for a random polymer it is close to 1. In a blocky polymer, $r_t r_c$ is > 1 and becomes larger as the all-*cis* or all-*trans* sequences become longer.

Table 16. ^{13}C chemical shifts for the carbons in ring-opened polynorbornene.^a

	cc	ct	tc	tt	c	t
$C^{1,4}$	38.84	38.58	43.50	43.24		
$C^{5,6}$	33.27	33.06	32.54	32.37		
C^7	42.89	42.20	42.20	41.47		
$C^{2,3}$					133.96 134.04 134.17	133.04 133.17 133.26

a: ^{13}C chemical shifts given in p.p.m. relative to Me_4Si .

As the spectral lines for the different configurations seemed to be best resolved for the C^1, C^4 pair of carbons in the polynorbornene samples obtained in this study, all σ_c and $r_t r_c$ values are quoted for these carbons.

D.3.2 Polymerization of norbornene in the presence of a cocatalyst

It has been shown¹⁸³ that the neutral and tetraanionic dimolybdenum(II,II) complexes $[\text{Mo}_2(\mu\text{-O}_2\text{CCH}_3)_4]$ and $\text{K}_4[\text{Mo}_2\text{Cl}_8]$ catalyze the ring-opening metathesis polymerization (ROMP) of 1-methylnorbornene in the presence of added EtAlCl_2 cocatalyst at 20 °C. It is possible that the active catalyst in these systems is a mixed Mo/Al species. For example, it is known that $[\text{Mo}_2(\mu\text{-O}_2\text{CCH}_3)_4]$ reacts with aluminium isopropoxide to form the *trans* diacetate $[\text{Mo}_2(\mu\text{-O}_2\text{CCH}_3)_2\{\mu\text{-Al}[\text{OC}(\text{H})(\text{CH}_3)_2]_4\}_2]$.¹⁹³ Furthermore, Diefenbach¹⁰⁹ prepared and characterized Mo/Al complexes of the type $[\text{Mo}_2(\mu\text{-O}_2\text{CR})_2\{\text{Al}(\text{OC}_6\text{H}_4\text{Cl-}i>p)_4\}_2]$ ($\text{R} = \text{Me}, \text{Bu}^t$ or CF_3) and showed that they catalyzed alkyne metathesis reactions.

McCann *et al.*⁸⁵ have used the dianionic dimolybdenum(II,II) salt $[\text{NEt}_4]_2[\text{Mo}_2(\mu\text{-O}_2\text{CCH}_3)_2\text{Br}_4]$ and the dicationic dimolybdenum(II,II) salts $[\text{Mo}_2(\mu\text{-O}_2\text{CR})_2(\text{CH}_3\text{CN})_n][\text{BF}_4]_2$ ($\text{R} = \text{Me}, n = 6$; $\text{R} = \text{CH}_2=\text{C}(\text{CH}_3)_2, n = 4$) to catalyze the room temperature polymerization of norbornene in the presence of EtAlCl_2 . It was believed that the lability of the CH_3CN ligands in these complexes^{81,83} was a contributory factor in the polymerization process. It has also been found that, under certain conditions, that EtAlCl_2 can catalyze the ROMP of norbornene as well as the formation of oligomers *via* a Ziegler-Natta polymerization mechanism.¹⁹⁴ However, under the reaction conditions used in these studies EtAlCl_2 , by itself, has been found to be inactive in the polymerization of norbornene.

More recently, McCann *et al.*¹³⁰ employed the dimolybdenum(II,II) complex salts $[\text{Mo}_2(\text{CH}_3\text{CN})_8][\text{BF}_4]_4$ and $[\text{Mo}_2(\mu\text{-O}_2\text{CCH}_3)_2(\text{CH}_3\text{CN})_6][\text{BF}_4]_2$ supported on silica to catalyse the polymerization of norbornene both in the presence and absence of EtAlCl_2 . It was found that in the absence of EtAlCl_2 cocatalyst $[\text{Mo}_2(\text{CH}_3\text{CN})_8][\text{BF}_4]_4$ -

SiO₂ is an active catalyst for the ROMP of norbornene, and at 90 °C and a reaction time of 48 h the polymerization was essentially quantitative. The other catalysts, [Mo₂(CH₃CN)₈][BF₄]₄, [Mo₂(μ-O₂CCH₃)₂(CH₃CN)₆][BF₄]₂, and [Mo₂(μ-O₂CCH₃)₂(CH₃CN)₆][BF₄]₂-SiO₂ were found to be completely inactive in the absence of EtAlCl₂ even at elevated temperatures.

In the presence of EtAlCl₂ cocatalyst the complexes of general formula [Mo₂(O₂C(CH₂)_nCO₂)(CH₃CN)_x]₂[BF₄]_{4-y}CH₃CN **{(11)-(17)}** and [Mo₂(bdoa)-(CH₃CN)_x]₂[BF₄]_{4-y}CH₃CN **(18)**, complex **(23)** and complex **(24)** all polymerized norbornene at room temperature (*Table 17*). The complexes [Mo₂(O₂C(CH₂)_nCO₂)(CH₃CN)_x]₂[BF₄]_{4-y}CH₃CN **{(11)-(17)}** and [Mo₂(bdoa)-(CH₃CN)_x]₂[BF₄]_{4-y}CH₃CN **(18)** produced polynorbornene in moderate yield, whilst complex **(23)** and complex **(24)** gave a low yield of polymer. In all cases, the polymerization reaction was instantaneous.

The yields and σ_c values obtained for the polynorbornenes produced using [Mo₂(O₂C(CH₂)_nCO₂)(CH₃CN)_x]₂[BF₄]_{4-y}CH₃CN **(11)-(17)** and [Mo₂(bdoa)-(CH₃CN)_x]₂[BF₄]_{4-y}CH₃CN **(18)** in conjunction with EtAlCl₂ are similar to those previously obtained when other dimolybdenum(II,II) complexes were used with the same cocatalyst. Furthermore, the r_{1c} values obtained indicate that there is an almost random distribution of *cis* and *trans* double bonds in these polymers. In the earlier studies using [Mo₂(μ-O₂CCH₃)₄], [Mo₂(μ-O₂CCF₃)₄] and K₄[Mo₂Cl₈] catalysts σ_c values for the unsaturated poly-1-methylnorbornenes were 0.47, 0.41 and 0.46, respectively.¹⁸³ When the dimolybdenum(II,II) anionic and cationic complexes [NEt₄]₂[Mo₂(μ-O₂CCH₃)₂Br₄] and [Mo₂(μ-O₂CR)₂(CH₃CN)_n][BF₄]₂ (R = Me, n = 6; R = CH₂=C(CH₃)₂, n = 4), respectively, were employed to polymerize unsubstituted

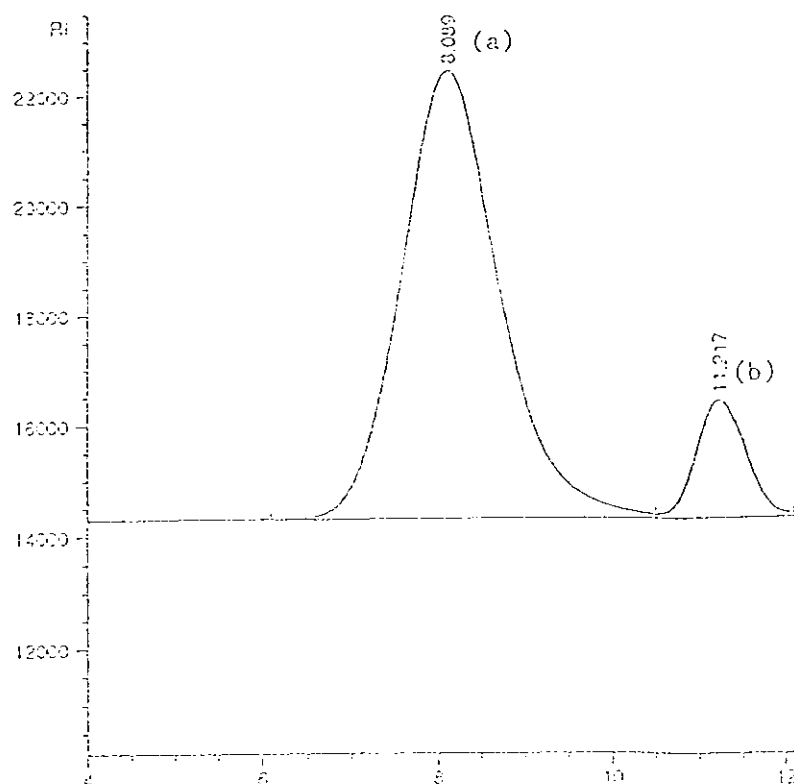
Table 17. Polymerization of norbornene in the presence of cocatalyst.^a

Catalyst	Polynorbornene Yield (%) ^b	σ_c	$r_t r_c$
[Mo ₂ (O ₂ C(CH ₂) ₂ CO ₂)(CH ₃ CN) _x] ₂ [BF ₄] _{4-y} ·CH ₃ CN (11)	17	0.44	1.4
[Mo ₂ (O ₂ C(CH ₂) ₃ CO ₂)(CH ₃ CN) _x] ₂ [BF ₄] _{4-y} ·CH ₃ CN (12)	15	0.42	1.4
[Mo ₂ (O ₂ C(CH ₂) ₄ CO ₂)(CH ₃ CN) _x] ₂ [BF ₄] _{4-y} ·CH ₃ CN (13)	19	0.43	1.3
[Mo ₂ (O ₂ C(CH ₂) ₅ CO ₂)(CH ₃ CN) _x] ₂ [BF ₄] _{4-y} ·CH ₃ CN (14)	18	0.39	1.5
[Mo ₂ (O ₂ C(CH ₂) ₆ CO ₂)(CH ₃ CN) _x] ₂ [BF ₄] _{4-y} ·CH ₃ CN (15)	24	0.47	1.7
[Mo ₂ (O ₂ C(CH ₂) ₇ CO ₂)(CH ₃ CN) _x] ₂ [BF ₄] _{4-y} ·CH ₃ CN (16)	22	0.41	1.4
[Mo ₂ (O ₂ C(CH ₂) ₈ CO ₂)(CH ₃ CN) _x] ₂ [BF ₄] _{4-y} ·CH ₃ CN (17)	25	0.34	1.3
[Mo ₂ (bdoa)(CH ₃ CN) _x] ₂ [BF ₄] _{4-y} ·CH ₃ CN (18)	16	0.27	1.3
Complex (23)	11	0.43	1.7
Complex (24)	13	0.29	1.3

a: solvent = chlorobenzene (5 cm³): mass of norbornene = 0.5 g; mass of catalyst = 0.1 g; volume of EtAlCl₂ solution = 0.3 cm³. b: chloroform-soluble polymer.

norbornene in the presence of EtAlCl₂, the σ_c values of the resulting polymers were *ca.* 0.36.⁸⁵ In general, it appears that changing the ligands on the dimolybdenum(II,II) core does not induce a significant change in the stereochemistry of the resulting polynorbornene.

The molecular weights of the polymers were determined using gel permeation chromatography (GPC) (see Appendix), and a typical chromatogram of polynorbornene catalysed by one of the molybdenum(II) dicarboxylate salts is shown in *Figure 76*. The chromatogram is bimodal, indicating the formation of both a high molecular weight polymer and a low molecular weight oligomer. Rooney and Laverty¹⁹⁵ have investigated the identities and yields of the low molecular weight products formed during the ROMP of norbornene in benzene using several unicomponent metal halide catalysts ([WCl₆], [MoCl₅], [ReCl₅], [RuCl₃] \cdot *x*H₂O, [OsCl₃] \cdot *x*H₂O, [IrCl₃] \cdot *x*H₂O).



(a) = peak 1, retention time (8.089 min) of high molecular weight polynorbornene.
 (b) = peak 2, retention time (11.217 min) of low molecular weight polynorbornene.
 solvent (chlorobenzene)

Figure 76

GPC trace of polynorbornene catalysed by
 $[\text{Mo}_2(\text{O}_2\text{C}(\text{CH}_2)_7\text{CO}_2)(\text{CH}_3\text{CN})_x]_2[\text{BF}_4]_{4-y}\text{CH}_3\text{CN}$ (16)

Dimers and trimers were observed in all cases for the polynorbornene samples but were only substantial relative to polymer yields for the catalysts $[\text{WCl}_5]$ and $[\text{ReCl}_5]$. In the present research, it is thought that the lower molecular weight oligomers is not due to the presence of dimers and trimers but may arise as a result of an intramolecular reaction ("back-biting") (Section I.8.3).

A summary of the molecular weight distributions of the polymers produced by the complexes $[\text{Mo}_2(\text{O}_2\text{C}(\text{CH}_2)_x\text{CO}_2)(\text{CH}_3\text{CN})_x]_2[\text{BF}_4]_{4-y}\text{CH}_3\text{CN}$ ((11)-(17)),

$[\text{Mo}_2(\text{bdoa})(\text{CH}_3\text{CN})_x]_2[\text{BF}_4]_4 \cdot y\text{CH}_3\text{CN}$ (**18**), and the 2,2' bipyridine and 1,10-phenanthroline complexes (**23**) and (**24**) is displayed in *Table 18*. Most of the products give bimodal chromatograms. For the monomodal chromatograms the polymers had unusually high polydispersities *ca.* polydispersity (P.D.) = 5-9.

The polymer samples had number average molecular weight (M_n) values between *ca.* 2.3×10^4 and 5.9×10^5 , whilst the lower molecular weight oligomers had M_n values between 400 and 500. The weight average molecular weight (M_w) values were found to lie between *ca.* 1.2×10^5 and 9.3×10^5 , whilst the lower molecular weight oligomers had M_w values between 400 and 600. Polydispersity (M_w/M_n) values range from between 1.3 -9.2 for the high molecular weight products. P.D. values > 6 are thought to be due to poor resolution of peaks in the chromatograms rather than the occurrence of a wide distribution of molecular weights in the polynorbornene samples. In the low molecular weight oligomers the P.D. values are *ca.* 1.

Table 18.

Molecular weights of polynorbornene samples

Catalyst	High Molecular Wt. Fraction (a.m.u.)	P.D.	Low Molecular Wt. Fraction (a.m.u.)	P.D.
Complex (11)	213,633 (M_w) 122,151 (M_n)	1.7	463 (M_w) 424 (M_n)	1.1
Complex (12)	690,918 (M_w) 201,610 (M_n)	3.4	568 (M_w) 527 (M_n)	1.0
Complex (13)	550,689 (M_w) 373,752 (M_n)	1.4		
Complex (14)	124,852 (M_w) 23,776 (M_n)	5.2		
Complex (15)	308,596 (M_w) 33,628 (M_n)	9.2		
Complex (16)	132,823 (M_w) 58,620 (M_n)	2.2	508 (M_w) 459 (M_n)	1.1
Complex (17)	143,988 (M_w) 33,369 (M_n)	4.3	492 (M_w) 454 (M_n)	1.1
Complex (18)	929,195 (M_w) 592,513 (M_n)	1.6		
Complex (23)	242,525 (M_w) 132,531 (M_n)	1.8	570 (M_w) 510 (M_n)	1.1
Complex (24)	477,907 (M_w) 359,116 (M_n)	1.3		

CONCLUSIONS

CONCLUSIONS

The blue dimolybdenum(II,II) complex salt $[\text{Mo}_2(\text{CH}_3\text{CN})_8][\text{BF}_4]_4$ reacted with selected dicarboxylic acids in acetonitrile to give red powders of composition $[\text{Mo}_2(\text{O}_2\text{C}(\text{CH}_2)_n\text{CO}_2)(\text{CH}_3\text{CN})_x]_2[\text{BF}_4]_{4-y}\cdot\text{CH}_3\text{CN}$ ($n = 0-8$) and $[\text{Mo}_2(\text{bdoa})-(\text{CH}_3\text{CN})_x]_2[\text{BF}_4]_{4-y}\cdot\text{CH}_3\text{CN}$. The complexes proved difficult to obtain in high yield but, in general, they were less air-sensitive and easier to handle than the parent complex $[\text{Mo}_2(\text{CH}_3\text{CN})_8][\text{BF}_4]_4$.

The X-ray crystal structure of the tetrameric molybdenum(II) butanedioate complex $[\text{Mo}_2(\text{O}_2\text{C}(\text{CH}_2)_2\text{CO}_2)(\text{CH}_3\text{CN})_6]_2[\text{BF}_4]_4\cdot 3\text{CH}_3\text{CN}$ was obtained. In this complex the bridging bidentate $^-\text{O}_2\text{C}(\text{CH}_2)_2\text{CO}_2^-$ ligands link four crystallographically identical molybdenum(II) atoms. On the basis of the IR spectra it is proposed that the complexes of general formula $[\text{Mo}_2(\text{O}_2\text{C}(\text{CH}_2)_n\text{CO}_2)(\text{CH}_3\text{CN})_x]_2[\text{BF}_4]_{4-y}\cdot\text{CH}_3\text{CN}$ are essentially isostructural with the butanedioate complex.

The $[\text{Mo}_2(\text{O}_2\text{C}(\text{CH}_2)_n\text{CO}_2)(\text{CH}_3\text{CN})_x]_2[\text{BF}_4]_{4-y}\cdot\text{CH}_3\text{CN}$ dicarboxylate complexes reacted with 2,2'-bipyridine and 1,10-phenanthroline to produce purple salts. As a result of their extreme air-sensitivity and hygroscopic nature these salts proved difficult to characterize.

In the presence of EtAlCl_2 cocatalyst the complexes of general formula $[\text{Mo}_2(\text{O}_2\text{C}(\text{CH}_2)_n\text{CO}_2)(\text{CH}_3\text{CN})_x]_2[\text{BF}_4]_{4-y}\cdot\text{CH}_3\text{CN}$ and $[\text{Mo}_2(\text{bdoa})-(\text{CH}_3\text{CN})_x]_2[\text{BF}_4]_{4-y}\cdot\text{CH}_3\text{CN}$ were moderately active catalysts for the ROMP of norbornene, and in all cases the polymerization reaction was instantaneous.

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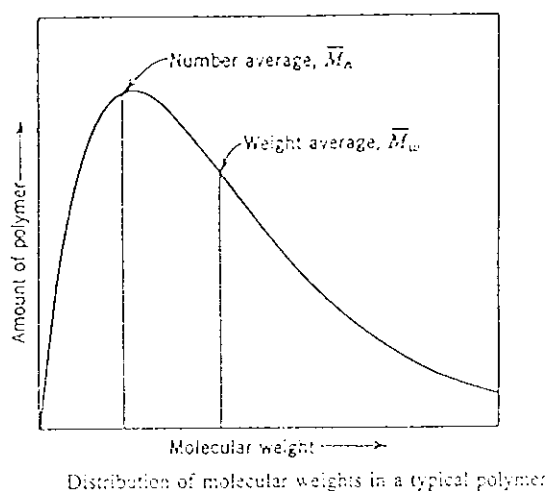
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APPENDIX

Gel Permeation Chromatography

One of the most important features distinguishing polymers from low-molecular weight species is the existence of a distribution of chain lengths and therefore degrees of polymerization. The distribution can be illustrated by plotting the weight of a given polymer against the molecular weight.



Because of the existence of the distribution in any finite sample of polymer, the experimental measurement of molecular weight can give only an average value. Several different averages are important. For example, some methods of molecular weight measurement in effect count the number of molecules in a known mass of material. Through knowledge of Avogadro's number, this information leads to the number average molecular weight (M_n) of the sample. For typical polymers the number average lies near the peak of the weight-distribution curve "or the most probable molecular weight".

If the sample contains N_i molecules of the i^{th} kind, for a total number of molecules $\sum_{i=1}^{\infty} N_i$, and each of the i^{th} kind molecule has a mass m_i , the total mass of all the molecules is $\sum_{i=1}^{\infty} N_i m_i$. The number average molecular mass is and

$$M_n = \sum_{i=1}^{\infty} m_i N_i / \sum_{i=1}^{\infty} N_i$$

multiplication by Avogadro's number gives the number-average molecular weight.

$$M_n = \sum_{i=1}^{\infty} M_i N_i / \sum_{i=1}^{\infty} N_i$$

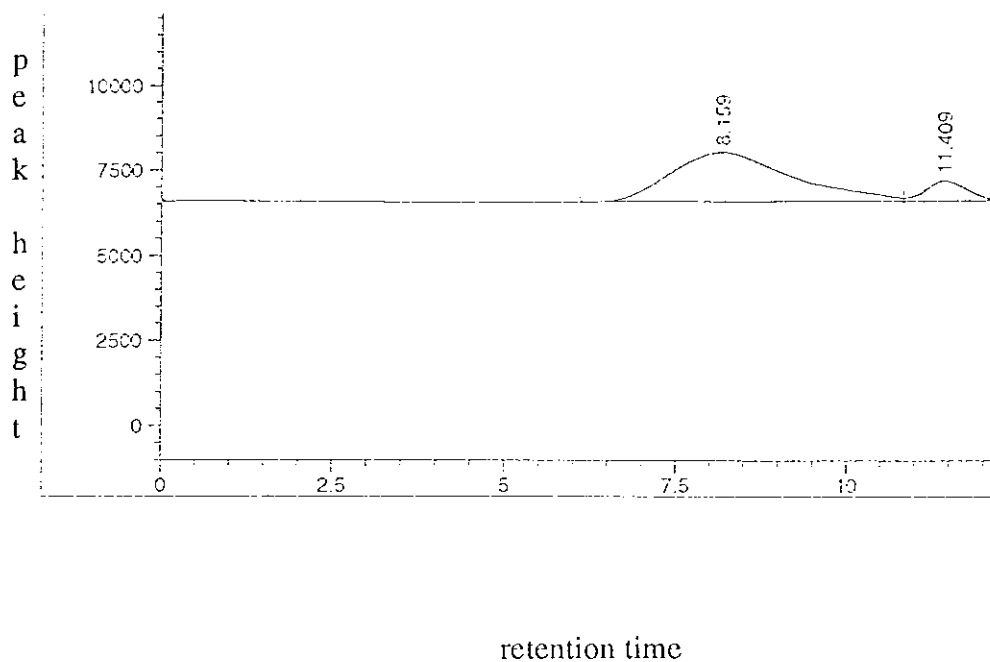
Number average molecular weights of commercial polymers usually lie in the range of 10,000-100,000 although some materials have values of M_n which are ten-fold higher and those which are ten-fold lower. In most cases the physical properties associated with typical high polymers are not well developed if M_n is below about 10,000.

After M_n , the next highest average molecular weight that can be measured is the weight-average molecular weight M_w . This quantity is defined as

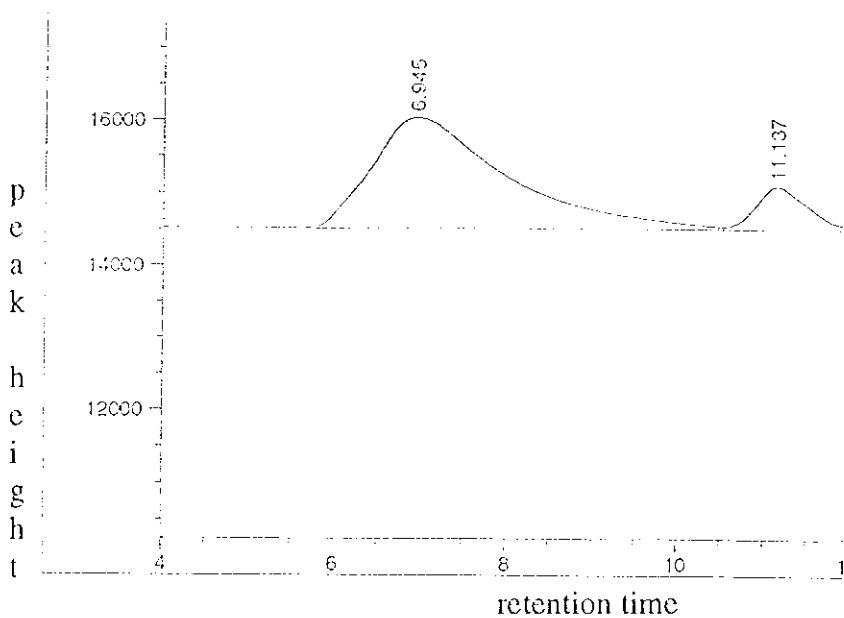
$$M_w = \sum_{i=1}^{\infty} N_i m_i^2 / \sum_{i=1}^{\infty} N_i m_i$$

In order to establish the average molecular weight of the polymer samples, it is first necessary to create a polystyrene calibration curve. Using polystyrene of known molecular weight, a graph is plotted of Log (or Ln) Molecular Weight *verses* Elution Volume (retention time of sample/elution time of solvent). From this calibration graph the slope and the intercept are calculated. The formula for the slope of a line $y = mx + c$ equates to:

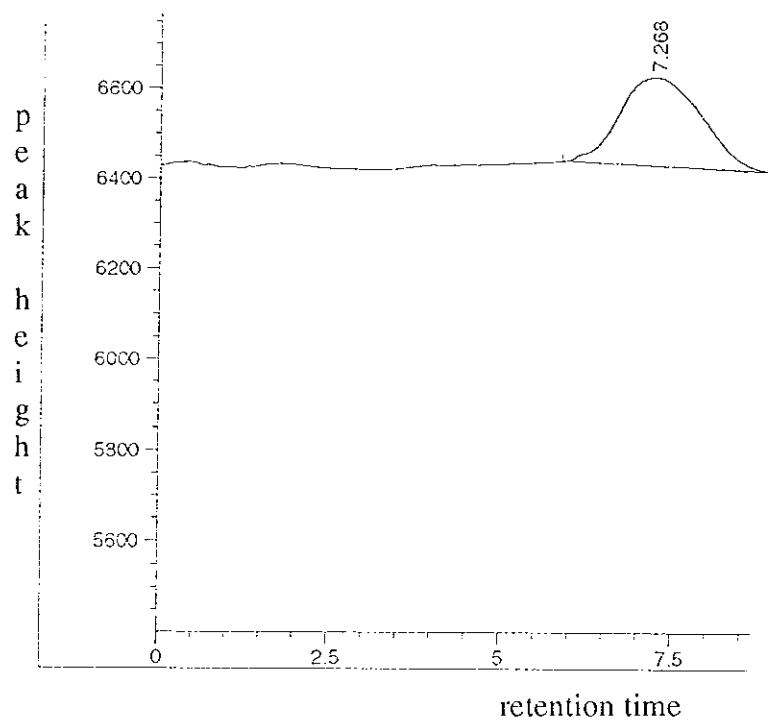
$$\text{Log } M_w = (\text{Slope of calibration curve})(\text{Elution Volume}) + \text{Intercept}$$



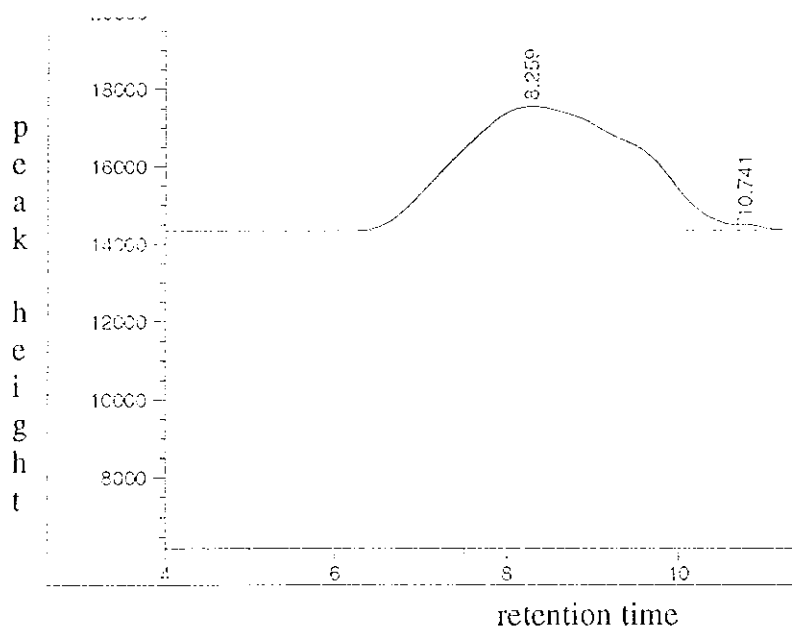
GPC trace of polynorbornene catalysed by
 $[\text{Mo}_2(\text{O}_2\text{C}(\text{CH}_2)_2\text{CO}_2)(\text{CH}_3\text{CN})_6]_2[\text{BF}_4]_4 \cdot 3\text{CH}_3\text{CN}$ (11)



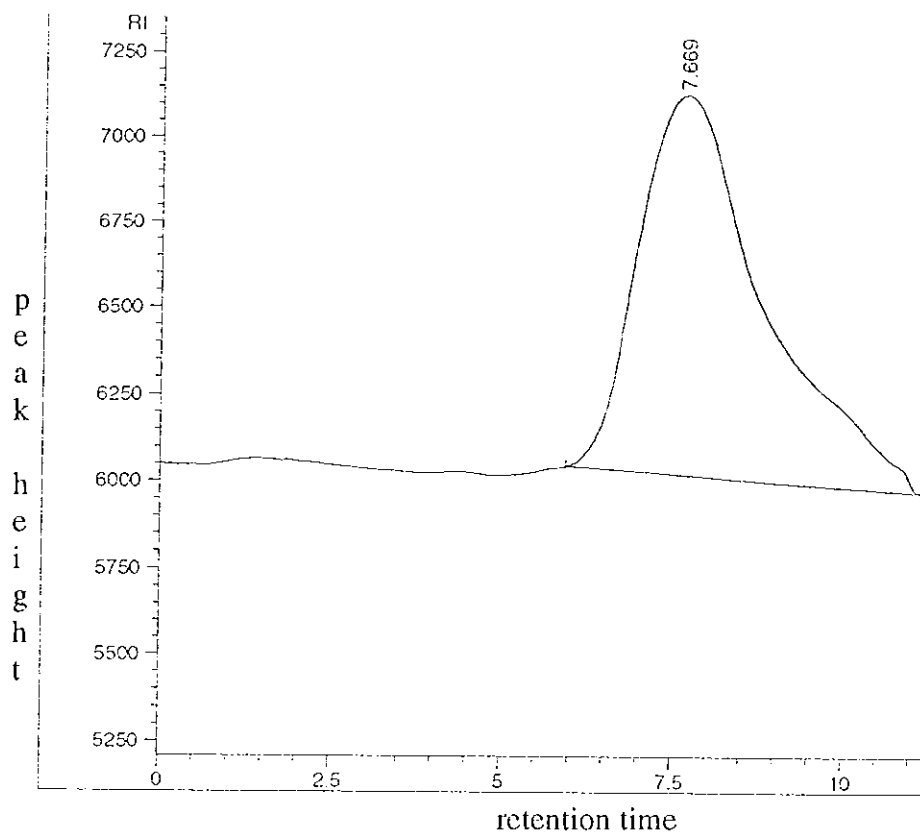
GPC trace of polynorbornene catalysed by
 $[\text{Mo}_2(\text{O}_2\text{C}(\text{CH}_2)_3\text{CO}_2)(\text{CH}_3\text{CN})_x]_2[\text{BF}_4]_4 \cdot y\text{CH}_3\text{CN}$ (12)



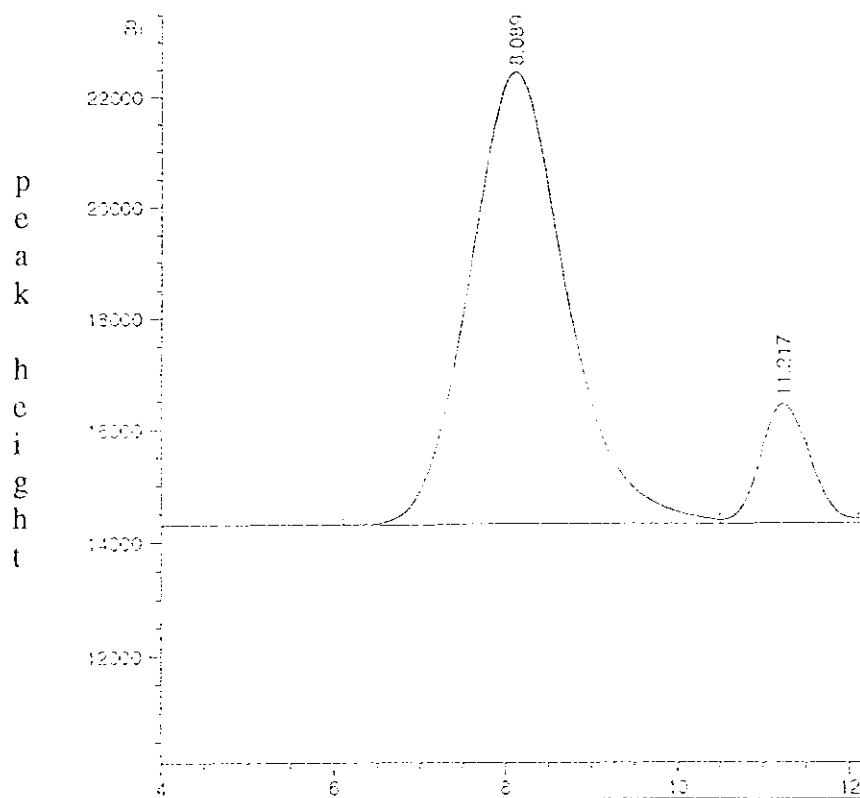
GPC trace of polynorbornene catalysed by $[\text{Mo}_2(\text{O}_2\text{C}(\text{CH}_2)_4\text{CO}_2)(\text{CH}_3\text{CN})_2][\text{BF}_4]_4 \cdot y\text{CH}_3\text{CN}$ (13)



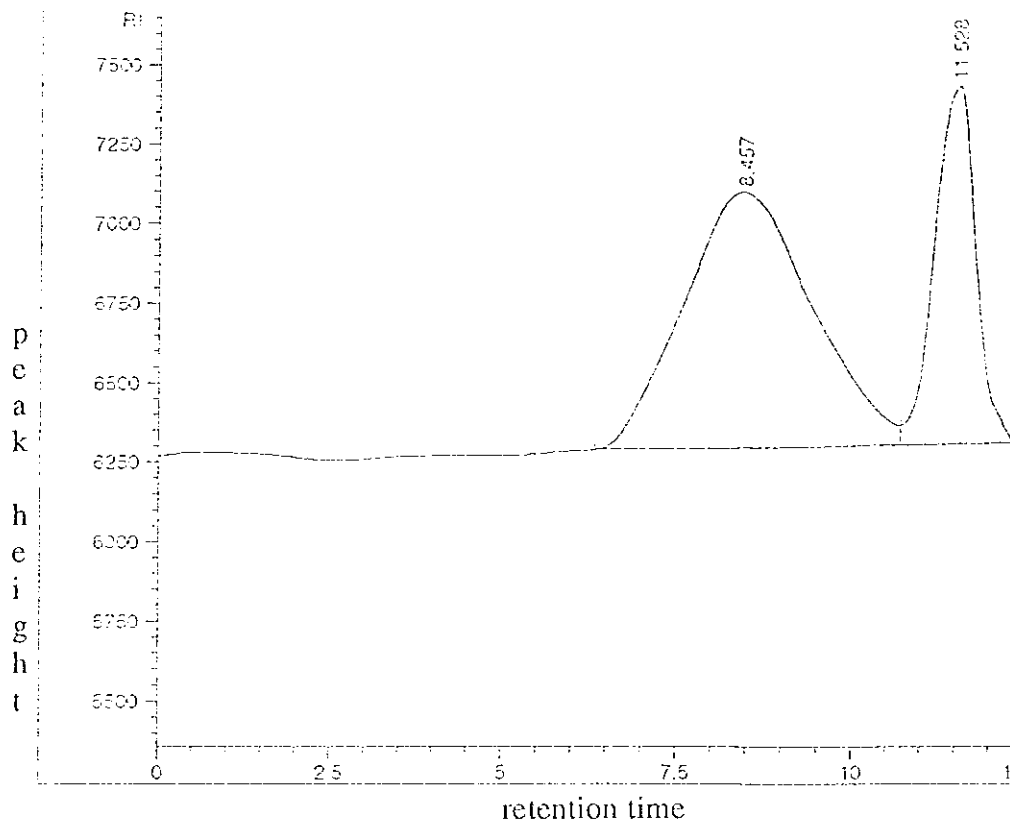
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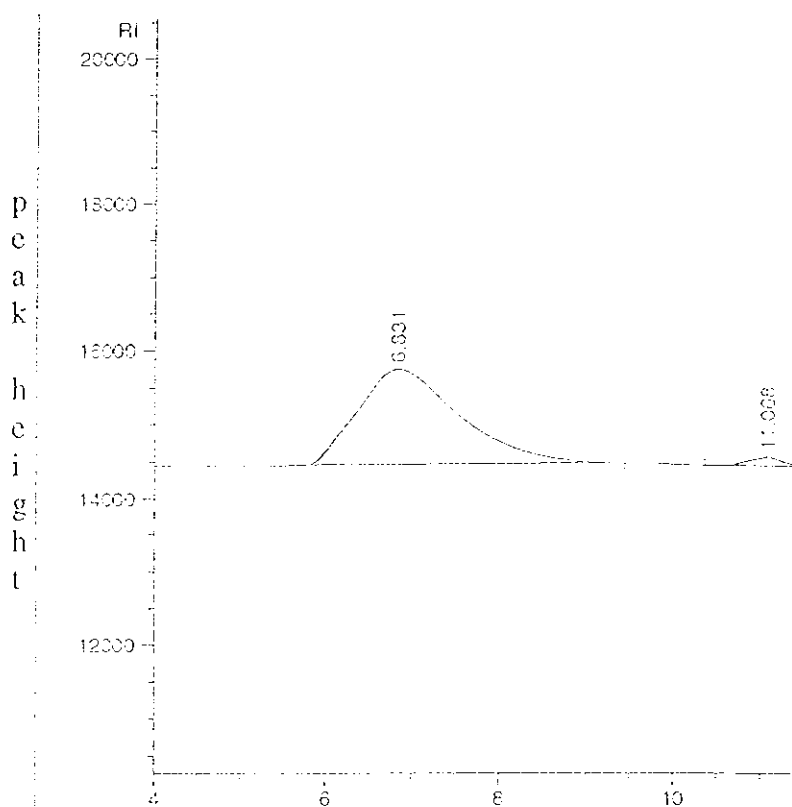
GPC trace of polynorbornene catalysed by
 $[\text{Mo}_2(\text{O}_2\text{C}(\text{CH}_2)_6\text{CO}_2)(\text{CH}_3\text{CN})_x]_2[\text{BF}_4]_y \cdot y\text{CH}_3\text{CN}$ (15)



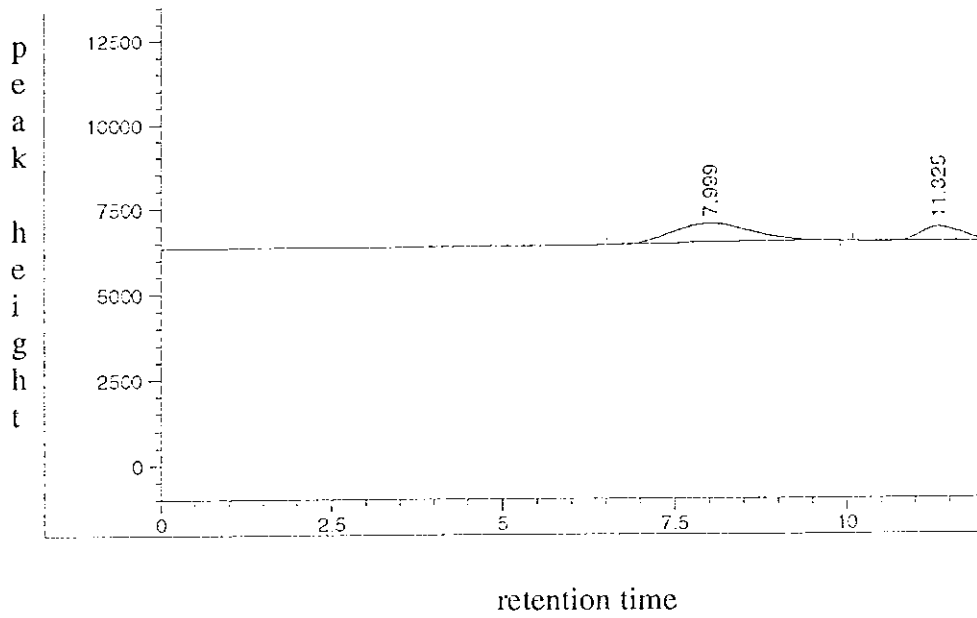
GPC trace of polynorbornene catalysed by
 $[\text{Mo}_2(\text{O}_2\text{C}(\text{CH}_2)_7\text{CO}_2)(\text{CH}_3\text{CN})_x]_2[\text{BF}_4]_y \cdot y\text{CH}_3\text{CN}$ (16)



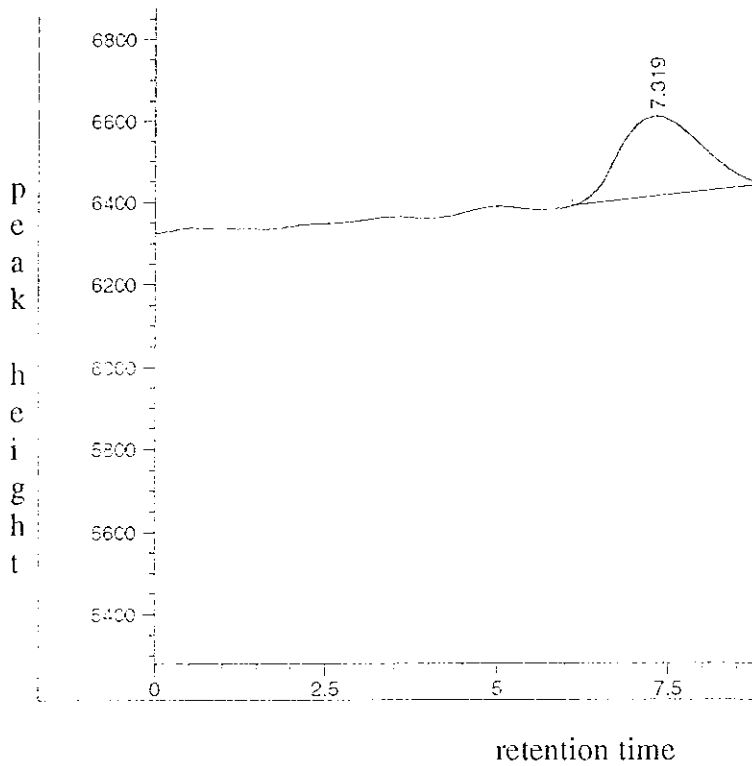
GPC trace of polynorbornene catalysed by
 $[\text{Mo}_2(\text{O}_2\text{C}(\text{CH}_2)_8\text{CO}_2)(\text{CH}_3\text{CN})_2][\text{BF}_4]_y\text{CH}_3\text{CN}$ (17)



GPC trace of polynorbornene catalysed by
 $[\text{Mo}_2(\text{bdoa})(\text{CH}_3\text{CN})_x][\text{BF}_4]_y\text{CH}_3\text{CN}$ (18)



**GPC trace of polynorbornene catalysed by
Complex 23**



**GPC trace of polynorbornene catalysed by
Complex 24**

