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A STUDY OF
SOME EARLY TRANSITION METAL HALIDE COMPLEXES

BY
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A dissertation submitted in part fulfilment of the requirements for the degree of Doctor of Philosophy at the University of Warwick.

September 1974.

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idem., J. Coord. Chem., paper in press.

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LIGAND ABBREVIATIONS

D:	A donor.
L:	A monodentate ligand.
B:	A bidentate ligand.
T:	A tridentate ligand.
diars:	<i>o</i> -phenylenebisdimethylarsine.
dien:	Diethylenetriamine.
en:	Ethylenediamine.
HMT:	Hexamethylcyclotrisilazane.
Me ₆ tren:	Tris (2-dimethylaminoethyl)amine.
OMT:	Octamethylcyclotetrasilazane.
pyr:	Pyridine.
THF:	Tetrahydrofuran.
THT:	Tetrahydrothiophene.
temen:	N,N,N',N'-tetramethylethylenediamine.
tetren:	Tetraethylenepentamine.
tren:	Tris (2-aminoethyl)amine.
triars:	Methylbis (<i>o</i> -dimethylarsinophenyl)arsine.
trien:	Triethylenetetramine.

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ABSTRACT

The coordination chemistry, in particular the position of the penta-coordinate state, of the halides of the early transition metals (titanium, vanadium and chromium) has been studied from two viewpoints.

1) The reactivity and stability of the metals in the penta-coordinate state has been investigated. A solution decomposition to a dimeric state, containing the metals in octahedral environments, was found to be active in the $MCl_3 \cdot 2NMe_3$ adducts. The nature of this decomposition and the reactivity of the product has been investigated.

2) The complex formation of the metals with bulky multi-dentate ligands, inducive to penta-coordination, was studied. The octahedral nature of the metal was found to be sufficiently powerful to control the donor roles of the ligands involved.

The zirconium/trimethylamine system has been investigated, in the (+4) and (+3) oxidation states. Here, in contrast to the first series metals, the ability of the metal to readily assume a coordination number greater than six is seen to play a major role in reaction. Possible structures for the adducts obtained are discussed in terms of eight coordinate polymeric species.

CHAPTER 1.

INTRODUCTION

1.1. NOMENCLATURE

The nomenclature used herein, where practical, follows that recommended by the International Union of Pure and Applied Chemistry. No attempt is made to give a detailed account of these recommendations, which may be found in the I.U.P.A.C. publication 'Nomenclature of Inorganic Chemistry',¹ but those of major concern to Coordination Chemistry are briefly set out.

Coordination Compounds

In general terms a coordination entity refers to molecules or ions in which there is an atom (A) to which are attached other atoms (B) or groups (C). For the purposes of nomenclature the older restriction on coordination compounds, that the atoms (B) or groups (C) are of a number in excess of that corresponding to the classical or stoichiometric valency of the atom (A), is dropped.

In such compounds the atom (A) is known as the 'nuclear' or 'central' atom, and all the other atoms which are directly attached to (A) are known as 'coordinating' or 'ligating' atoms. Each central atom (A) has a characteristic 'coordination number' or 'ligancy' which is the number of atoms directly attached to it. The atoms (B) and groups (C) are called 'ligands'. A group which contains more than one potential coordinating atom is referred to as a 'multidentate' ligand. The number of potential coordinating atoms present in a ligand are indicated by the multiplicative prefixes 'uni-', 'bi-', 'tri-' ('ter-'), etc.. A 'chelate' ligand is one attached to one central atom through two or more coordinating atoms, and a 'bridging group' is one attached to more than one centre of coordination. The whole assembly, with one or more central atoms and their ligands,

is referred to as a 'coordination entity', or more generally coordination compound or -complex.

Indication of Oxidation Number

The oxidation number of the central atom is given by bracketed Roman Numerals after the name of the atom.

Order of Citation of Ligands

The ligands are listed in alphabetical order regardless of their number. The multiplicative prefixes mono-, di-, tri-, tetra-, etc., are used to indicate the number of each simple ligand present. When complex ligands, generally those which may create structural ambiguity, are present the multiplicative prefixes bis-, tris-, tetrakis-, etc., are used, with the ligand being encased within brackets.

Names of Ligands

Anionic Ligands

The names for anionic ligands end in -o. In general if the anion ends in -ide, -ite or -ate, the final -e is replaced by -o to give -ido, -ito and -ato. Some common anions do not follow this convention; some examples of these are given below:

	<u>Ion</u>	<u>Ligand</u>
F ⁻	fluoride	fluoro
Cl ⁻	chloride	chloro
Br ⁻	bromide	bromo
I ⁻	iodide	iodo
O ²⁻	oxide	oxo
OH ⁻	hydroxide	hydroxo
CN ⁻	cyanide	cyano

Neutral and Cationic Ligands

The name of a coordinating molecule is used without change, except for the special cases of; water, which becomes aqua, and ammonia, which becomes ammine. Also the groups NO and CO, when linked directly to a metal atom, become nitrosyl and carbonyl respectively. All neutral ligands, with the exception of those cited above, are enclosed within brackets.

Structural Designations

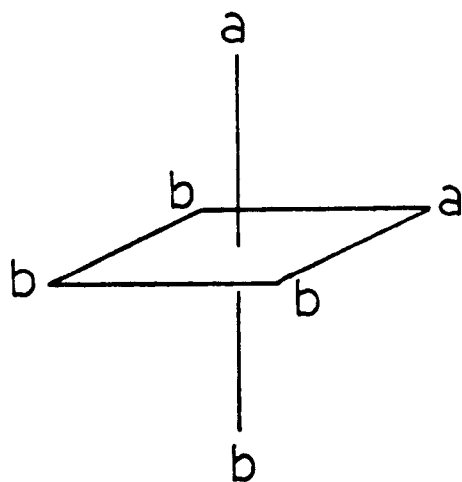
Bridging Atoms or Groups

- a). A bridging atom or group is indicated by adding $-\mu-$ immediately before its name and separating the name from the rest of the complex by hyphens.
- b). Two or more bridging groups of the same kind are indicated by a multiplicative prefix immediately prior to the $-\mu-$.
- c). The bridging groups are listed with the other groups in alphabetical order, unless the symmetry of the molecules permit simpler names by the use of multiplicative prefixes.
- d). Where the same ligand is present as a bridging ligand and as a non-bridging ligand, it is cited first as a bridging ligand.

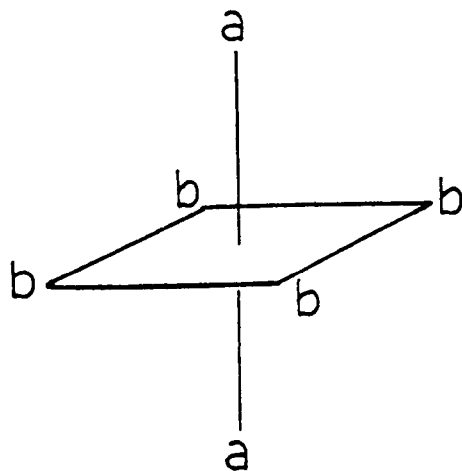
Geometric Isomerism

The prefixes cis-, trans-, fac- and mer- are used where they are sufficient to designate specific isomers.

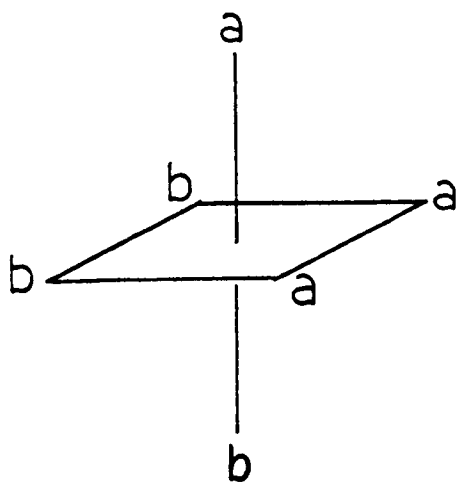
Example assignments for octahedral complexes are shown overleaf:



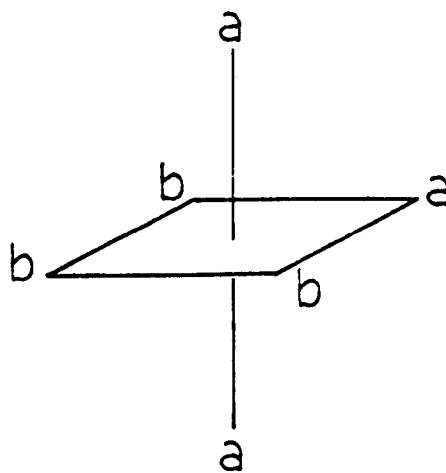
cis



trans

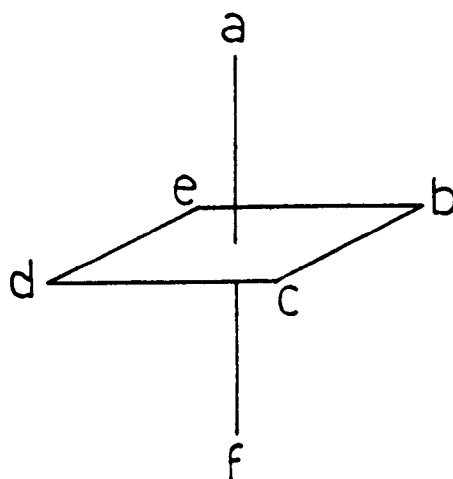
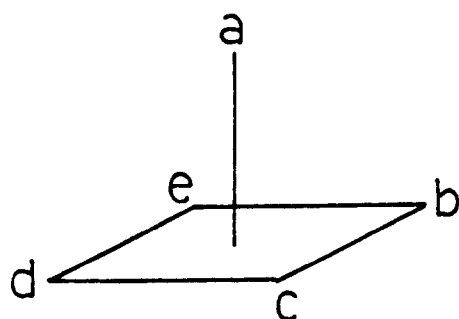
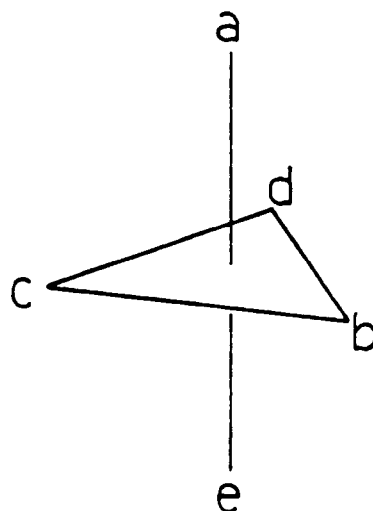
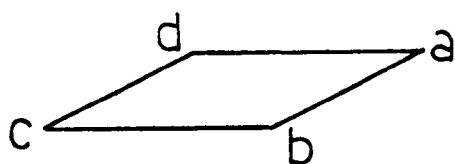


fac



mer

Where locant designators are used they are lower case letters.
Example assignments are shown overleaf:



The first ligand mentioned is given the lowest possible designator and the second ligand the next lowest possible designator, etc..

1.2. The Early Transition Metal Halides

The early transition metal halides may be regarded as those of the metallic elements of groups IVa, Va and VIa. The halides of the second and third transition series are in many ways similar, and to a large extent relate to those of the first series, but they have been the subject of far less study. The following sections are restricted to the binary halides of the early metals of the first transition series, i.e. titanium, vanadium and chromium, and their adduct forming reactions in non-aqueous media. The relevant chemistry of the second and third series metals will be introduced to the text as, and when, necessary.

This particular, and extensive, area of chemistry has been the subject of a number of reviews and textes, of which the works of Walton,² and Colton and Canterford^{3,4} are brought to note.

The Fluorides

Fluorine is characterised by its extreme electronegativity and its small ionic size, so that few of its compounds, especially those of the transition metals, resemble the other halides. In the context of the following dissertation the chemistry of the fluorides is not of direct relevance, but may be found as the subject of several recent review articles.^{5,6,7}

The Other Halides

The majority of the halides at room temperature are solids of polymeric structure, containing the metal atoms in a pseudo-octahedral environment. The exceptions to this are the tetrahalides, which are monomeric and tetrahedral. TiCl_4 and VCl_4 are liquids at room temperature, and TiBr_4 and TiI_4 low melting

solids. Of the remaining tetrahalides, VBr_4 melts with decomposition at -23°C ,⁸ and VI_4 ^{9,10} and CrCl_4 ¹¹ have only recently been detected in the vapour state. CrBr_4 and CrI_4 remain to be observed.

The tri- and dihalides all fall into one of four main structural types; these being the rutile, cadmium dichloride, cadmium diiodide and bismuth triiodide.

A). The structures of the dibromides and diiodides of titanium and vanadium all belong to the cadmium diiodide type, FIGURE 1.1..

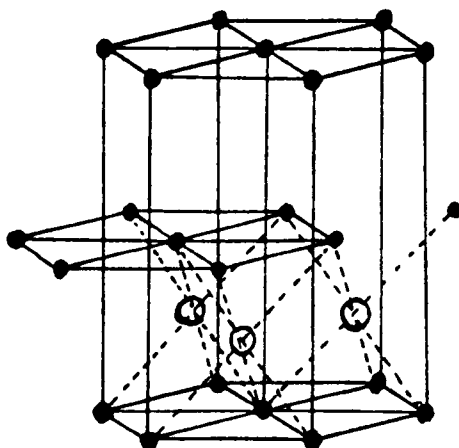


FIGURE 1.1. The Cadmium Diiodide Structure

This is a layer lattice in which the halogens, in hexagonal close packed arrangement, form planes, with the metal atoms filling the octahedral sites between alternate pairs of layers.

B). The dichlorides of titanium and vanadium are related to the cadmium dichloride structure. This is closely related to that of the diiodide, the difference in the structures arising from the arrangements of the lattice layers. The halogen planes in the diiodide represent an ABABABA type system, whereas those in the dichloride represent an ABCABCA type. This results

in a structure related to cubic close packing, but it remains that of a layer lattice similar to the diiodide.

C). The dihalides of chromium are all related to a tetragonally distorted rutile structure, FIGURE 1.2.. The metal atom

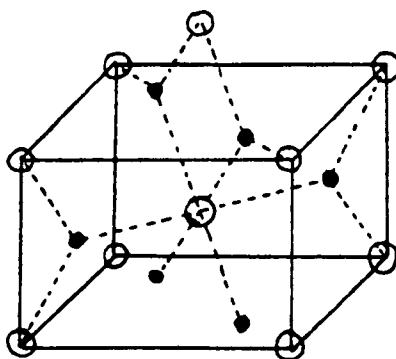


FIGURE 1.2. The Rutile Structure

is at the centre of a distorted octahedron, with four short and two long Cr-X bonds. This geometry is rationalised in terms of a Jahn-Teller distortion.

D). The structures of the trihalides are all related to the bismuth triiodide structure, FIGURE 1.3.. This is a layer

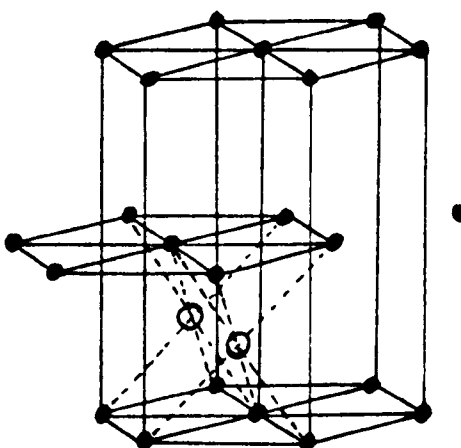


FIGURE 1.3. The Bismuth Triiodide Structure

lattice in which the halogens, in hexagonal close packed arrangement, form planes, with the metal atoms filling two-thirds of the octahedral sites between alternate pairs of layers. This structure readily gives rise to polymorphism, of which TiCl_3 is a classic example. It is known to exist in α -, β -, γ - and δ - forms, depending on the method used for preparation. The α - (the most common and widely studied form), γ - and δ - forms are all layer lattices, of the bismuth triiodide type, which differ only slightly in their packing arrangements. The β - form is quite different, consisting of single chains of TiCl_6 octahedra sharing two faces, FIGURE 1.4..

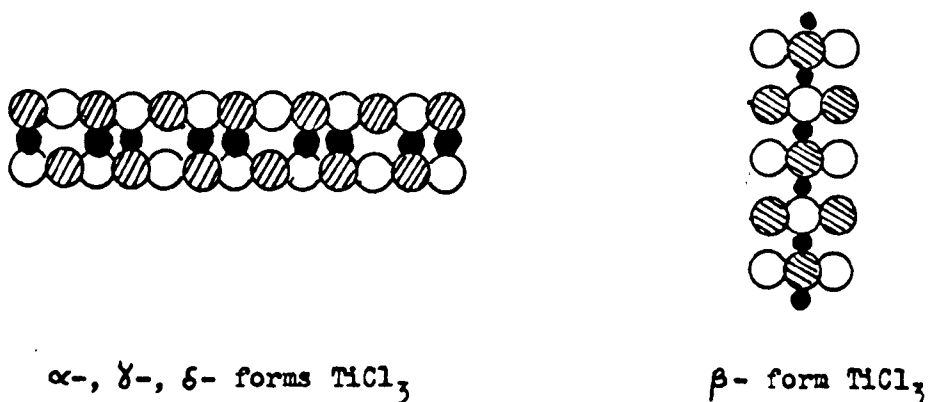


FIGURE 1.4.

The structures of the halides play a definite role in their reactivity, a decrease in reactivity usually being paralleled by an increase in the polymeric nature of the halide. For example VCl_4 , monomeric, VCl_3 , with a bismuth triiodide type layer lattice, and VCl_2 , with a cadmium dichloride type layer lattice, exhibit reactivity in the order $\text{VCl}_4 > \text{VCl}_3 > \text{VCl}_2$. The tetrachloride readily reacts with a wide range of donors, the trichloride reacts only with stronger donors, under somewhat more forcing conditions, whilst the dichloride under comparable conditions is virtually inert. Despite this observable

dependence on structure, however, reliable predictions of relative reactivity throughout the halides are not possible. The many influencing factors which are involved are often poorly understood; the complex kinetics, dominant at solid-liquid interfaces, being a major example.

1.3. Coordination Chemistry of the Early Transition Metal Halides

Coordination compounds of the transition metals have been the subject of study for a very long time. The structures of hydrates, double salts and ammonia compounds being widely discussed even before the beginning of the 19th century. At this time most attention was being given to the ammonia complexes, or ammonates as they were then known, the discovery of which is usually attributed to Tassaert.¹² The non-aqueous chemistry of the anhydrous metal halides has, however, only comparatively recently received much attention. This is mainly a result of the difficulties in handling these air-sensitive materials; which are readily hydrolysed by moist air, to hydroxy- and oxo-species.

The halides readily form a large number of adducts with ligands of various donor types, and, in the short history of this field, wide and extensive studies have been made. Many workers have been active, but few can vie with the contributions of Fowles and Clark and their co-workers.

As already noted, the structures of the halides themselves, often play a prime role in their reactions. In many cases the stable polymeric lattices are impervious to attack by the weaker donors, and require somewhat forcing conditions even with strong donors. As a direct result of this behaviour, ligand substit-

ution has become a prime route to many complexes. Where this method is employed, the halide lattice is first destroyed by attack with a strong donor, such as pyridine, acetonitrile or tetrahydrofuran, and the products, monomeric $\text{MX}_3 \cdot 3\text{L}$,¹³⁻¹⁶ from the trihalides, and normally $[\text{MX}_2 \cdot 2\text{L}]_n$,^{17,18} from the dihalides, then treated with an excess of the required ligand to induce a facile substitution.

The adducts are mainly of six coordinate octahedral geometry, though, an increasing number of five coordinate trigonal bipyramidal complexes are being isolated. Coordination numbers other than five and six are rare in this part of the periodic table, but are not completely unknown. To serve as an orient in this large field, there follows a brief survey of the main structural adduct types, with some illustrative examples.

Three Coordination

No true three coordinate halide adducts have been isolated, but several trigonal metal species obtained by halide substitution have been reported. The first of these being $[(\text{Me}_3\text{Si})_2\text{N})_3\text{Cr(III)}]$, prepared by Bürger and Wannagat,¹⁹ and $[(\text{Pr}^i)_2\text{N})_3\text{Cr(III)}]$, prepared by Bradley et al..²⁰ Later work in this area²¹⁻²³ has provided examples of such complexes for all the early trivalent transition metals.

Four Coordination

Four coordination is rare in adducts of the early transition metal halides. In 1966 the tetrahedral tetrahalogenovanadium(III) ion was isolated by Clark et al.,^{24,25} and some tetrahedral chromium(II) complexes of triphenylphosphine oxide, $[\text{CrX}_2 \cdot 2\text{Ph}_3\text{PO}]$ ²⁶ (X = Br, I), are also known. Several four co-

ordinate metal species, e.g. $\left[\left((\text{Me}_3\text{Si})_2\text{N} \right)_2\text{Cr}(\text{II}) \cdot 2\text{THF} \right]^{27}$ and $\left[(\text{Pr}^i_2\text{N})_3(\text{NO})\text{Cr}(\text{II}) \right]^{28}$, obtained by halide substitution, have also been reported.

Five Coordination

In recent years five has become an increasingly more common coordination number for complexes of the halides. The first complexes isolated, of this form, are normally attributed to Antler and Laubengayer,²⁹ when, from the reaction of trimethylamine with titanium tetrachloride, they obtained the adducts $\text{TiCl}_4 \cdot \text{NMe}_3$ and $\text{TiCl}_3 \cdot 2\text{NMe}_3$. A comprehensive review covering the extent of penta-coordination upto 1966, including the known transition metal compounds, has been given by Muetterties and Schunn.³⁰ In more recent years reviews on the structural^{31,32} and spectral^{33,34} aspects of this coordination number have appeared.

For the most part the complexes are monomeric trigonal bipyramidal species, of D_{3h} or C_{3v} symmetry. However, it must be said that, a great many of these complexes only exhibit penta-coordination either in solution, or in the solid state; often they achieve hexa-coordination in the second state via halogen bridging.

The only complex known for the +2 oxidation state is the trigonal bipyramidal chromium(II) complex, $\left[\text{Cr}(\text{Me}_6\text{tren})\text{X} \right] \text{X}$ ($\text{X} = \text{Cl}, \text{Br}, \text{I}$), prepared by Ciampolini.³⁵

By far the largest group of penta-coordinate adducts is that of the tervalent complexes, $\text{MX}_3 \cdot 2\text{L}$; these all show trans trigonal bipyramidal D_{3h} , or distorted D_{3h} , geometry. This class of complex has been isolated for many adducts of large bulky ligands containing nitrogen,^{15,29,36,38,39} sulphur^{38,40} and

phosphorus⁴¹ donors. More recently, a small number of adducts containing oxygen donor ligands has been isolated.^{42,43}

For the +4 oxidation state the amine complexes $\text{MX}_4 \cdot \text{NMe}_3$ ^{15,29,36} (M= Ti, V. X= Cl, Br) offer examples of this coordination number. These adducts were shown, by vibrational spectral analysis,³⁷ to have trigonal bipyramidal geometry of C_{3v} symmetry.

Six Coordination

The vast majority of the known complexes of these halides are of six coordinate pseudo-octahedral geometry; numbering far too many to be detailed to any extent.

Adduct formation occurs with numerous ligands, both mono- and multidentate, containing a large variety of donor atoms. They are both ionic and non-ionic, and often monomeric, though octahedral coordination may be obtained through halogen bridging to give polymeric species; the +2 oxidation state, in particular, typifies this behaviour.^{17,18}

The adducts with monodentate ligands are typified by those of the alkylnitriles,¹⁶ tetrahydrofuran¹⁴ and pyridine,^{13,15} and are of the $\text{MX}_n \cdot \text{L}_{6-n}$ type. A small, but interesting, class of adducts is that of the complex halides. The hexahalogenometalates and enneahalogenodimetalates have been the subjects of extensive structural, spectral and magnetic investigations,⁴⁴⁻⁴⁶ the enneahalogenodimetalates having an unusual triply halogen bridged structure.

The complexes of bidentate ligands often involve halide displacement, giving ionic species. The main adduct types may be represented by the adducts $\text{MX}_4 \cdot \text{B}$,⁴⁷ $[\text{MX}_2 \cdot 2\text{B}] \text{X}$ ⁴⁸ and $[\text{M} \cdot 3\text{B}] \text{X}_3$.⁴⁹

Complexes of tridentate ligands have been less well studied, but where the ligands exhibit maximum denticity they are typ-

ically of the types $\text{MX}_3 \cdot \text{T}$ ^{50,51} and $[\text{M} \cdot 2\text{T}] \text{X}_3$.⁵²

Seven Coordination

Seven coordinate complexes of monodentate ligands are rare, one example known for vanadium is $\text{K}_4[\text{V}(\text{CN})_7]$,⁵³ but this is not a halide adduct.

Multidentate ligands figure prominently in complexes of this coordination number, with N,N-dialkyldithiocarbamates being particularly common. Complexes of this type, $\text{Ti}(\text{S}_2\text{CNR}_2)_3\text{X}$, are known^{54,55} for $\text{R} = \text{Me}, \text{Et}, \text{Pr}^i, \text{Bu}^i$ and $\text{X} = \text{Cl}, \text{Br}$. Other donors include oxygen, nitrogen and arsenic, as found in the complexes, $\text{Ti}(\text{tropolonate})_3\text{Cl}$,⁵⁶ $\text{Ti}(\text{oxine})_3\text{Cl}$ ⁵⁷ and $\text{MCl}_4 \cdot \text{triars}$ ⁵⁰ ($\text{M} = \text{Ti}, \text{V}$).

Eight Coordination

There are exceedingly few halide complexes exhibiting this coordination number. Those which are known belong to the type $\text{MCl}_4 \cdot 2\text{diars}$ ^{58,59} ($\text{M} = \text{Ti}, \text{V}$). Other examples of eight coordination that may be cited include $\text{Ti}(\text{S}_2\text{CNR}_2)_4$ ⁵⁵ and $\text{Ti}(\text{NO}_3)_4$,⁶⁰ which are derived by halide displacement.

1.4. Electronic Spectra of the Early Transition Metals

Many analytical techniques are employed in the structural determination of coordination compounds, these including: conductivity, magnetic susceptibility and nuclear magnetic resonance, infrared and electronic spectroscopy. Each can provide useful structural information, but the generally most applicable and useful is electronic spectroscopy, this giving direct information on the coordination environment of the central metal atom. For this reason it is important to have a qualitative

knowledge of the spectra of these metals, though a quantitative understanding of the theoretical principles underlying the interpretations is not essential.

In a simple view the five degenerate d-orbitals of a transition metal ion, in the free state, will lose their degeneracy when placed in a spatially non-uniform electric field, such as that generated by a number of ligands surrounding the ion. This is because the five d-orbitals are not spatially identical, and those that are spatially in a position to interact most with a ligand generating such a field will increase in energy, those which do not directly interact will decrease in energy. FIGURES 1.5. and 1.6. show the splitting of these orbitals in five- and six-coordinate chromophores, the two most common geometries of the adducts of the halides. There now exists the potential for electrons in the lower energy d-orbitals to absorb energy on irradiation and jump to a higher energy position, thus causing an absorption in the spectrum of irradiation. These absorptions are normally found in the near infrared and visible regions of the spectrum, and from their number and position a great deal of information on the environment of the central metal ion may be obtained.

A more exact, though still by no means rigorous, view may be considered. The d-electrons of a transition metal may exist in a number of configurations or states, identified by a term symbol, which are not of equivalent energy. In an electric field, such as that generated by a number of surrounding ligands (termed ligand field), the energy, and any degeneracy, of these states will be reappraised. Spectral absorptions occur when an electron moves from one state to another, there being a number of theoretical rules governing such a transfer. One of such, is the

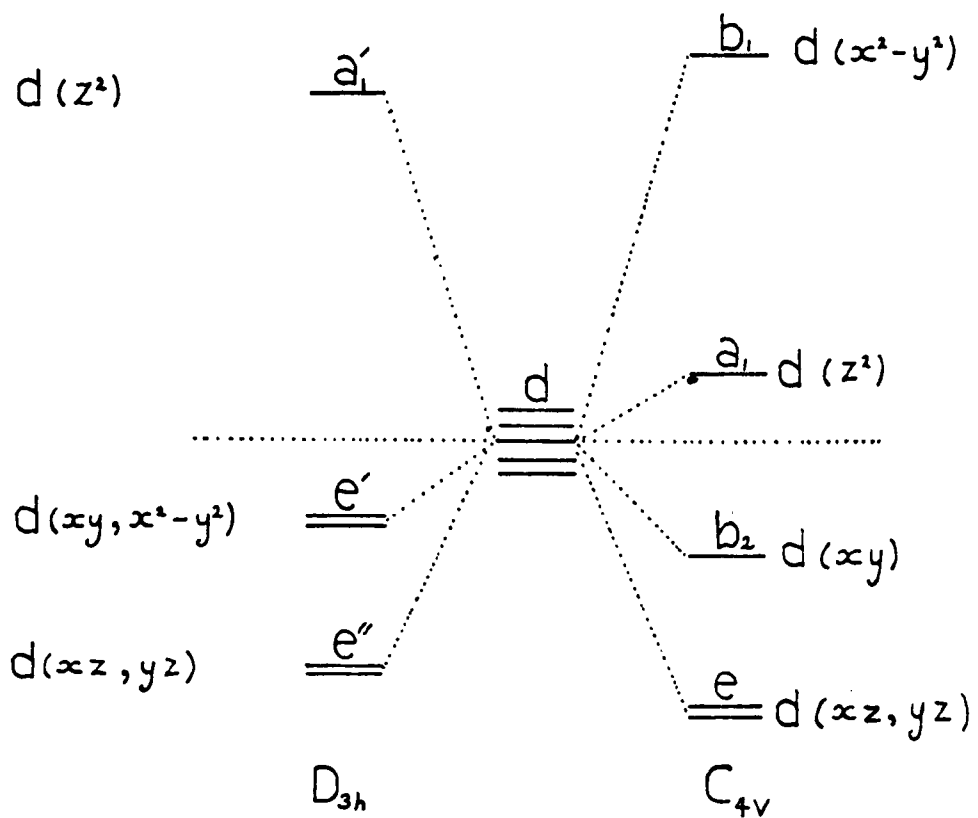


FIGURE 1.5. d-Orbital Splitting in Fields of D_{3h} and C_{4v} Symmetry

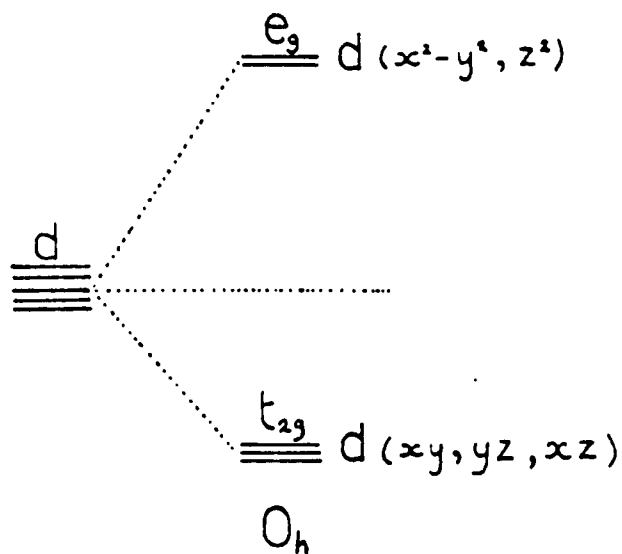


FIGURE 1.6. d-Orbital Splitting in Field of O_h Symmetry

electric dipole selection rule (or Laporte rule) which is that transitions must be odd \longleftrightarrow even, another is that transitions can only occur between states of the same spin multiplicity. As all the d-orbitals possess a centre of symmetry all 'd-d' transitions are forbidden by the Laporte selection rule. They are only observed because distortions in the geometry, caused by reasons such as vibrational displacement and 'p-d' orbital mixing, remove the centre of symmetry to some extent, thereby removing some of the "forbiddenness" of the transitions. For this reason all 'd-d' spectral absorptions are of low intensity.

The terms arising from various d^n configurations are given below:

<u>Configuration</u>	<u>Terms Arising</u>
d^1	2D
d^2	$^3F, ^3P, ^1G, ^1D, ^1S.$
d^3	$^4F, ^4P, ^2H, ^2G, ^2F, ^2D(2), ^2P.$

Any degeneracy in these terms are, in an octahedral field, split as shown below:

<u>State of Free Ion</u>	<u>States within an octahedral field</u>
S	A_1
P	T_1
D	$E + T_2$
F	$A_2 + T_1 + T_2$
G	$A_1 + E + T_1 + T_2$
H	$E + 2 T_1 + T_2$

2D is the only term arising from the d^1 configuration, and in an octahedral field its degeneracy splits with increasing field as shown in the Orgel Diagram, FIGURE 1.7.. The only possible transition is that from the ground state, $^2T_{2g}$, to the

excited state, 2E_g , and therefore only one 'd-d' absorption is seen in the electronic spectrum of an octahedrally coordinated d^1 ion.

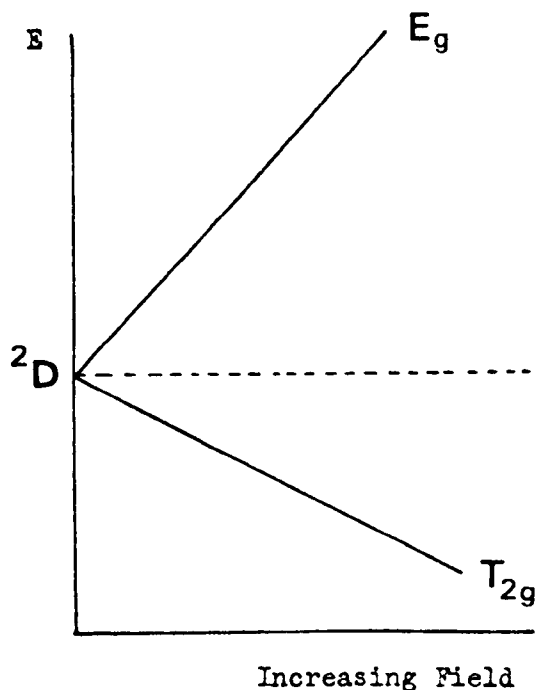


FIGURE 1.7. Orgel Diagram of d^1 configuration in an octahedral field

The energy level diagrams for the d^2 and d^3 ions in an octahedral field, FIGURES 1.8. and 1.9., are far more complex, but it can be seen that three transitions, between states of the same spin multiplicity, are expected from each of these ions in this environment.

Unfortunately, complete energy level diagrams for all these ions in five coordinate fields have not been fully calculated. However, the splitting schemes for trigonal bipyramidal fields, D_{3h} symmetry, are shown in FIGURES 1.10., 1.11. and 1.12..

In addition to the weak 'd-d' transitions, normally found in the $5,000 - 40,000 \text{ cm}^{-1}$ range, there occur a number of very

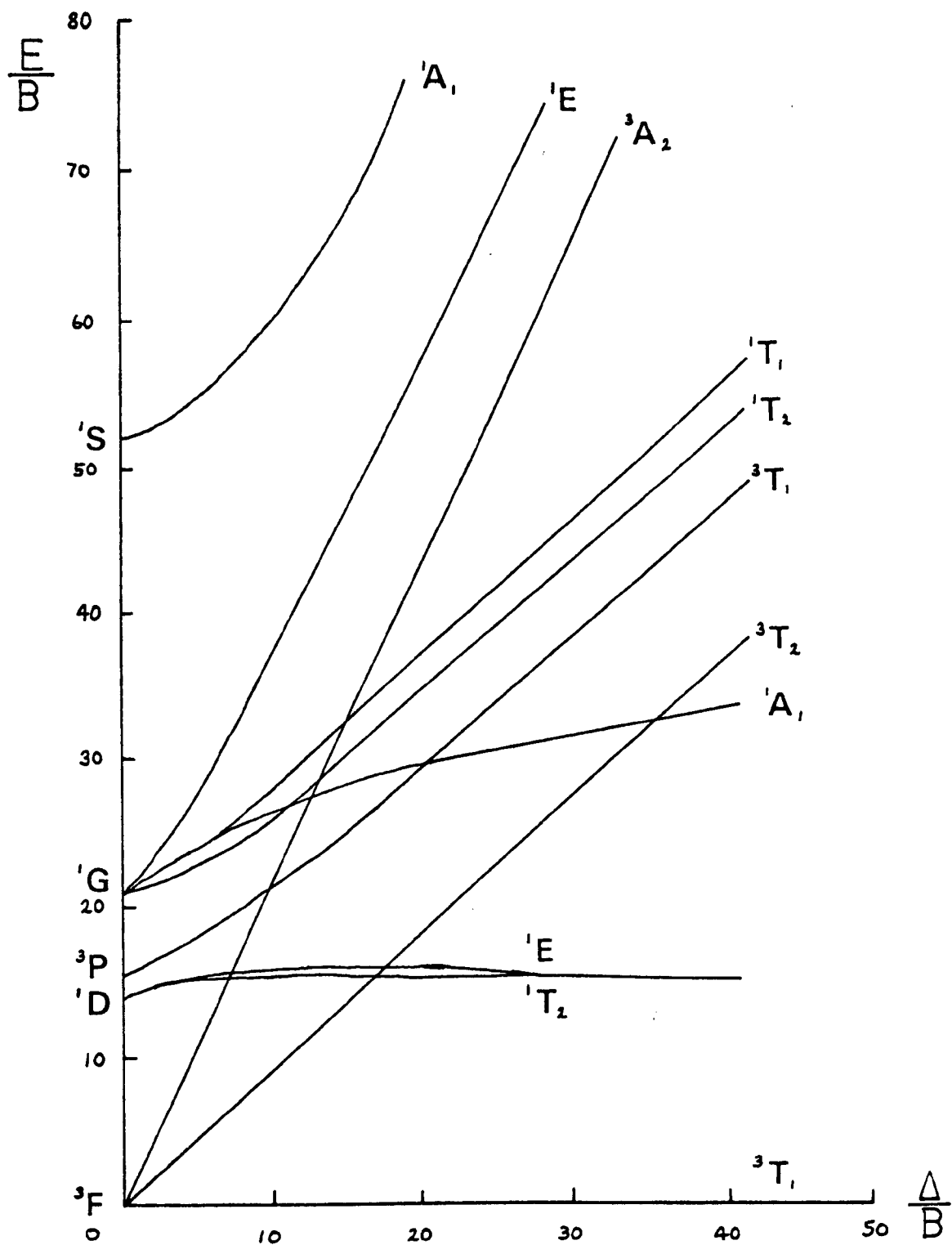


FIGURE 1.8. Energy Level Diagram for a d^2 -ion in an O_h Field

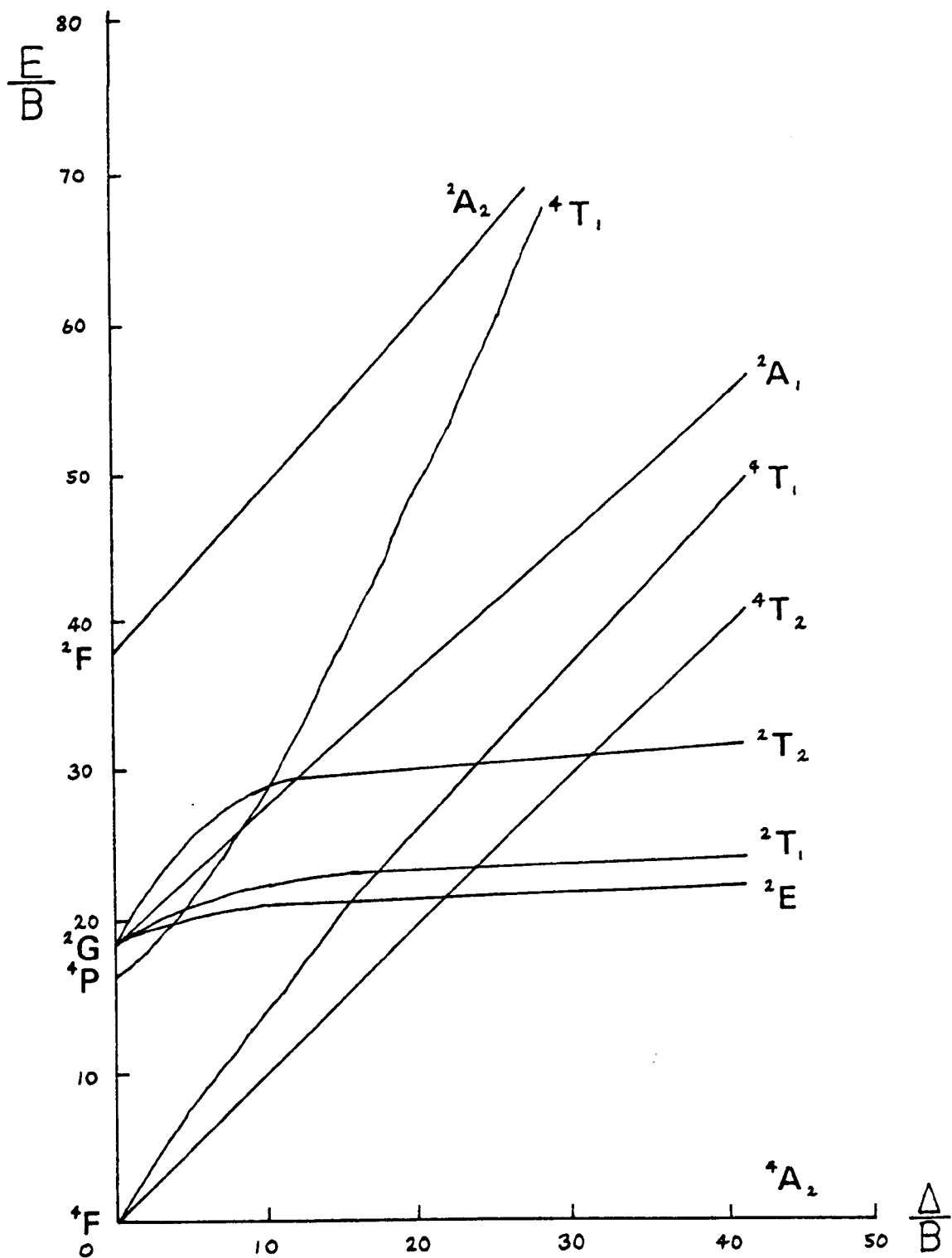


FIGURE 1.9. Energy Level Diagram for a d^3 -ion in an O_h Field

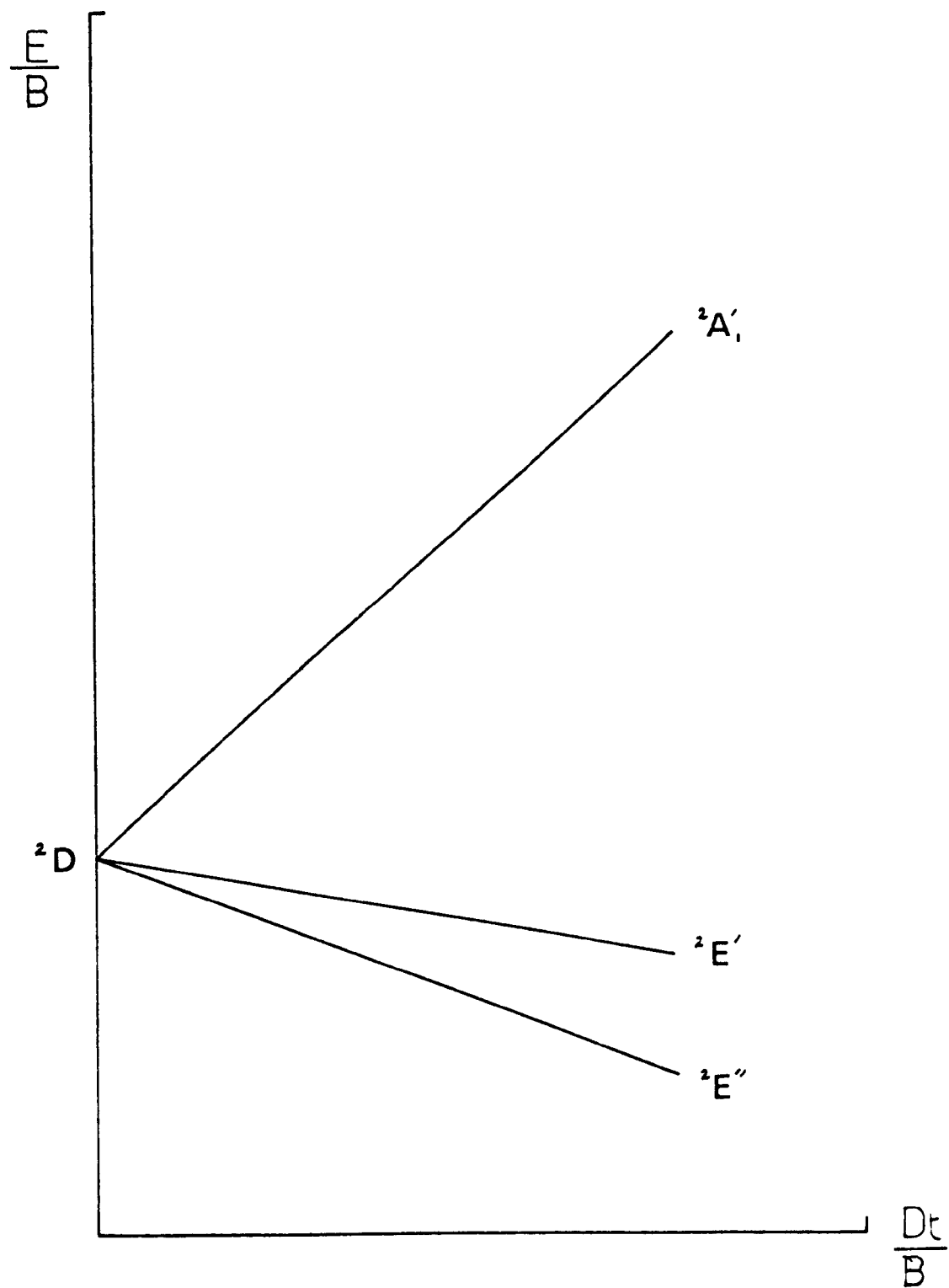


FIGURE 1.10. Energy Level Diagram for a d'-ion in a D_{3h} Field

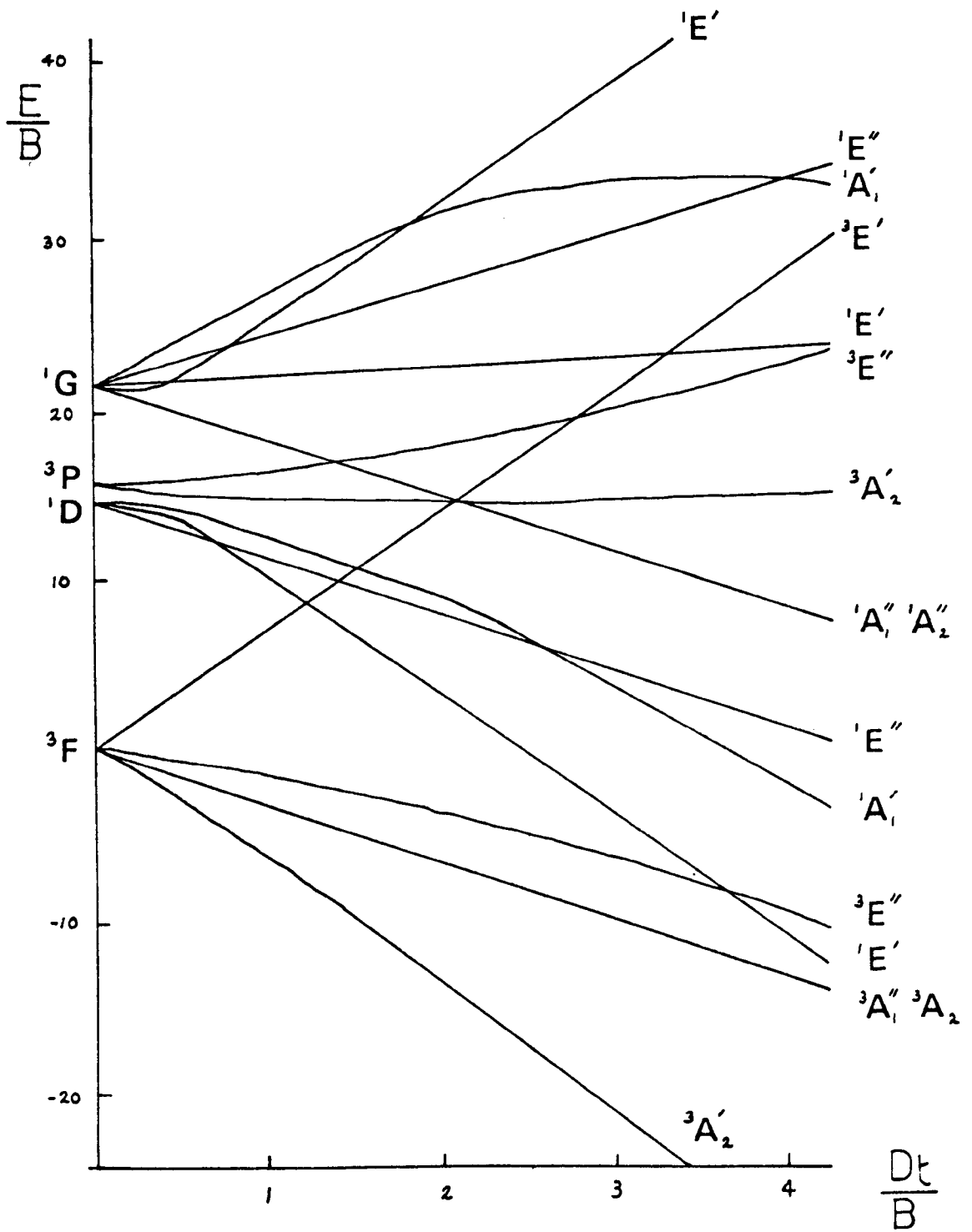


FIGURE 1.11. Energy Level Diagram for a

d^2 -ion in a D_{3h} Field

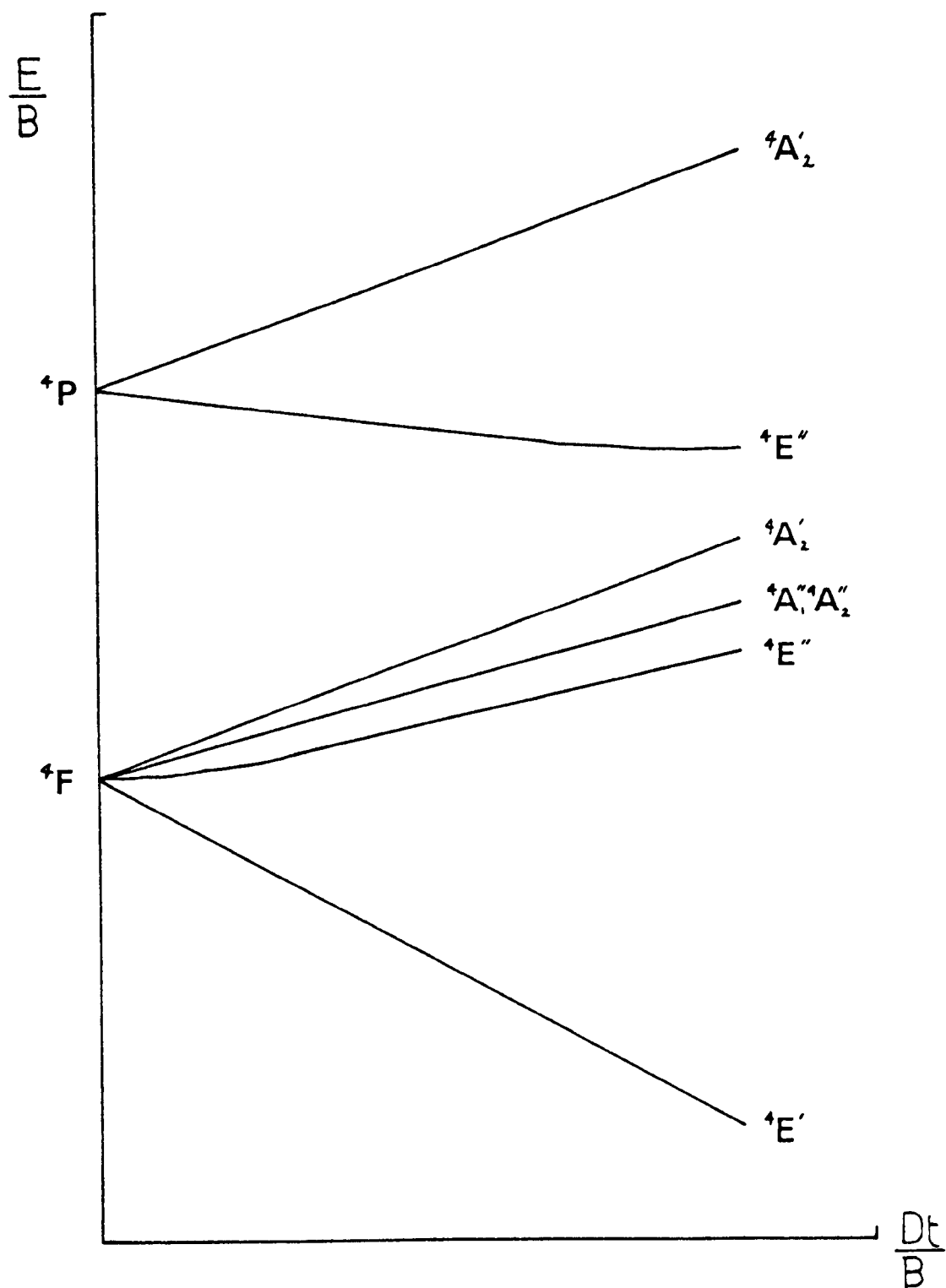


FIGURE 1.12. Energy Level Diagram for a d^2 -ion in a D_{3h} Field

high intensity bands in the region $\sim 30,000 \text{ cm}^{-1}$ onwards. They are known as charge transfer bands and are associated with the transfer of, normally non-bonding, electrons from ligand orbitals into metal d-orbitals. The most common of these are associated with metal \leftarrow halogen transitions.

For a more detailed and rigorous treatment of the spectra of 3d metal complexes the reader is referred to the excellent articles by Ciampolini³⁴ and Ferguson,⁶¹ and for a treatment of Ligand Field Theory, to Ballhausen.⁶²

CHAPTER 2.

REACTIVITY OF TRICHLOROBIS(TRIMETHYLAMINE)CHROMIUM(III)

2.1. INTRODUCTION

Readily obtained monomeric adducts of the early transition metal halides, particularly those of monodentate ligands, hold an important place in the synthetic coordination chemistry of these halides. They are frequently used as the starting materials in routes to new complexes; since their substitution reactions are far more facile than the corresponding addition reactions of the polymeric halides.

The primary area in which this technique is employed is in the chemistry of the trivalent metals. This indirect route is not required for reactions of the tetravalent halides, as they are, themselves, monomeric and show comparatively high reactivity. The chemistry of the divalent state has been little explored, but the adducts formed are normally of a polymeric nature. The practicality of ligand substitution in these complexes has, however, been demonstrated.¹⁸ The most widely employed adducts are of $MX_3 \cdot 3L$ formulation, where L = pyridine, acetonitrile and tetrahydrofuran, these being readily obtained, in high yield and purity, from direct reaction of the ligand with the appropriate metal halide.¹³⁻¹⁶ The use of these adducts has become an accepted part of synthetic coordination chemistry.^{2, 63, 64}

In this vein, the recently isolated five coordinate species, $MX_3 \cdot 2L$, being coordinatively unsaturated, and reactive, could offer a new, and extremely useful, labile starting material of this type. The adducts in the solid state are monomeric and of trigonal bipyramidal geometry.⁶⁵⁻⁶⁷ The two amine groups are positioned trans, occupying the axial positions of the polyhedron, thus achieving maximum separation. Distortions from pure D_{3h} symmetry are found in the bond angles in the equatorial plane;

$\text{TiBr}_3 \cdot 2\text{NMe}_3$: BrTiBr ; two angles of 121.25° one of 117.5°
 $\text{VCl}_3 \cdot 2\text{NMe}_3$: ClVCl ; two angles of 121° one of 113°
 $\text{CrCl}_3 \cdot 2\text{NMe}_3$: ClCrCl ; two angles of 124.2° one of 111.6°

The distortions of the titanium and chromium adducts can be rationalised in terms of a Jahn - Teller distortion, but that of the vanadium adduct, free from Jahn - Teller distortion, would seem to be a crystal packing effect.

Two advantages they offer, over their hexa-coordinate counterparts, are;

(i). Their lability; the adducts are all of large bulky ligands, and it is known that steric hindrance greatly reduces metal-ligand bond strength.⁶⁸⁻⁷⁰

(ii). Their solubility; being for the most part soluble in non-coordinating solvents, such as benzene, and even in some cases, aliphatic hydrocarbons.

The bis-trimethylamine adducts have already been used synthetically to advantage, by Fowles^{48,71} and Bradley,²¹ but no study has been made of the potentials, or restrictions, these adducts have when employed in this role. To this end we have studied the reactivity and stability of these five coordinate adducts, as represented by the trichlorobis(trimethylamine) chromium(III) complex, under a variety of conditions. The chromium adduct was chosen as it is readily prepared in high yield and purity, and because the chemistry of this metal has been extensively investigated and documented, thereby offering a useful control.

Reactions were carried out with three main types of ligand:

1) Strong donor ligands; as represented by pyridine, acetonitrile and tetrahydrofuran.

2) Weak donor ligands; as represented by diisopropylether and tetrakis(dimethylamino)diborane. If there exists sufficient lability, in the metal-ligand bond, these adducts might be expected to offer a synthetic route to complexes which would otherwise be extremely difficult, or impossible, to prepare, e.g. those of very weak donors.

3) Small covalent molecules: as represented by carbondioxide and carbondisulphide. These small molecules are known to undergo both, insertion reactions into metal-ligand bonds,⁷²⁻⁷⁶ and adduct formation⁷⁷⁻⁸⁰ with the transition metals. With their compactness, and the coordinatively unsaturated nature of the metal adducts, either of these reaction modes could be exhibited without substitution necessarily occurring.

We found that the substitution reactions of these adducts, even with strong donors, were not always straight forward. Two competing reactions were found to be taking place, one being substitution, the other, the decomposition of the five coordinate adduct. The indications are that this decomposition is not confined solely to the chromium(III) species, but is a common trait of the complexes $MCl_3 \cdot 2NMe_3$, where M= Ti, V, Cr. The nature of the decomposition product, including its formation, and reactivity, has been studied.

In addition to ligand substitution, halide substitution is also a viable proposition in these adducts, as demonstrated by Bradley et al..²¹ If all the halogens could be removed from the metal, and the 'naked' chromium stabilised with very readily displaced ligands, an extremely useful and versatile synthetic starting material would result. Perchlorate is an obvious choice for this ligand, being multidentate and having a very low Lewis basicity, indeed, until recently it was considered a non-coord-

inating anion. The first perchlorato complexes were not proposed until 1961,⁸¹⁻⁸³ but since that time many complexes of this ligand have been isolated.⁸⁴ To investigate this possibility we reacted the bis trimethylamine adduct with silver perchlorate, and isolated a new and very reactive perchlorato complex.

2.2. EXPERIMENTAL and RESULTS

Preparative and manipulative details are given in Appendices A and B.

A) Reaction of $\text{CrCl}_3 \cdot 2\text{NMe}_3$ with Hydrogen Chloride

When anhydrous HCl gas was either co-condensed with benzene onto, or bubbled through a benzene solution of, $\text{CrCl}_3 \cdot 2\text{NMe}_3$, an immediate reaction occurred, yielding a colourless solution and a purple precipitate. The solvent was removed in vacuo and the purple solid subjected to a soxhlet extraction with chloroform, which removed a soluble white crystalline solid that was identified as $\text{Me}_3\text{NH}^+\text{Cl}^-$. The purple residue that remained was chromium(III)chloride.

Anal. Calcd. for CrCl_3 : Cr, 32.9; Cl, 67.1 . Found: Cr, 32.1; Cl, 66.7 .

B) Reaction of $\text{CrCl}_3 \cdot 2\text{NMe}_3$ with Pyridine

When a benzene solution of $\text{CrCl}_3 \cdot 2\text{NMe}_3$ was added to excess pyridine, in vacuo, an immediate reaction occurred yielding a dark green solution and release of NMe_3 . The NMe_3 was trapped in an infrared gas cell and identified by its infrared spectrum.⁸⁵ The solvent and excess pyridine were removed in vacuo and the resulting dark green solid subjected to a soxhlet extraction with chloroform. The soluble dark green trichlorotris(pyridine) chromium(III) was obtained in 100% yield. The infrared spectrum was identical to that of an authentic sample.¹³

Anal. Calcd. for $\text{C}_{15}\text{H}_{15}\text{Cl}_3\text{N}_3\text{Cr}$: Cr, 13.1; Cl, 26.9 . Found: Cr, 13.1; Cl, 26.8 .

When the reaction was repeated using a 1:1 molar ratio of pyridine:metal immediate reaction occurred with release of NMe_3 and precipitation of a pink solid. The NMe_3 was trapped in an infrared gas cell and identified by its spectrum.⁸⁵ Removal of

the solvent in vacuo gave a pink solid that was insoluble in all the common organic solvents and of non-stoichiometric composition. The infrared spectrum contained bands at; 3110(w), 3060(m), 2990(w), 2956(w), 2922(w), 2900(w), 2848(w), 1603(m), 1482(m), 1461(w), 1446(s), 1360(w), 1261(w), 1217(m), 1066(m), 1047(m), 1016(m), 980(m), 818(m), 770(m), 755(m), 721(w), 696(s), 673(m), 641(m), 448(m), 378(m), 356(m), 342(s), 298(m) and 270(m) cm^{-1} respectively.

C) Reaction of $\text{CrCl}_3 \cdot 2\text{NMe}_3$ with Tetrahydrofuran

When a benzene solution of $\text{CrCl}_3 \cdot 2\text{NMe}_3$ was added to excess tetrahydrofuran, in vacuo, an immediate reaction occurred yielding release of NMe_3 , a pale purple solution and a purple precipitate. The NMe_3 was trapped in an infrared gas cell and identified by its spectrum.⁸⁵ Removal of the solvent and excess THF in vacuo gave the purple solid trichlorotris(tetrahydrofuran) chromium(III) in 100% yield. The infrared spectrum was identical to that of an authentic sample.⁸⁶

Anal. Calcd. for $\text{C}_{12}\text{H}_{24}\text{Cl}_3\text{O}_3\text{Cr}$: Cr, 13.9; Cl, 28.4 . Found: Cr, 13.8; Cl, 28.2 .

When the reaction was repeated using a 1:1 molar ratio of THF:metal immediate reaction occurred with release of NMe_3 and precipitation of a purple solid. The NMe_3 was trapped in an infrared gas cell and identified by its spectrum.⁸⁵ Removal of the solvent in vacuo gave a dark purple solid that was insoluble in all the common organic solvents and of non-stoichiometric composition. The infrared spectrum contained bands at; 3110(w), 3070(w), 3010(m), 2990(w), 2932(m), 2912(m), 2902(m), 2868(w), 2848(w), 1479(s), 1458(s), 1403(w), 1258(m), 1230(w), 1099(w), 1032(m), 1016(m), 976(s), 837(m), 816(s), 720(w), 681(s), 551(m), 522(m), 368(s) and 343(s) cm^{-1} respectively.

D) Reaction of $\text{CrCl}_3 \cdot 2\text{NMe}_3$ with Acetonitrile

When a benzene solution of $\text{CrCl}_3 \cdot 2\text{NMe}_3$ was added to acetonitrile in vacuo an immediate reaction occurred with release of NMe_3 and precipitation of a dark brown solid. The NMe_3 was trapped in an infrared gas cell and identified by its spectrum.⁸⁵ Removal of the solvent and excess MeCN in vacuo gave a dark brown/purple oily solid that was not amenable to purification.

E) Formation of $\text{Cr}_2\text{Cl}_6 \cdot 3\text{NMe}_3$

When a benzene solution of $\text{CrCl}_3 \cdot 2\text{NMe}_3$ was sealed into an ampoule, a slow reaction occurred (~ 2 weeks) precipitating a lilac solid, from the blue solution, and releasing NMe_3 . The NMe_3 was trapped in an infrared gas cell and identified by its spectrum.⁸⁵ Extraction of the solid product with benzene, in vacuo, removed the unreacted starting material and left the lilac solid tri- μ -chloro-trichlorotris(trimethylamine)dichromium(III). The product showed slight solubility in benzene and dichloromethane. Anal. Calcd. for $\text{C}_9\text{H}_{27}\text{Cl}_6\text{N}_3\text{Cr}_2$: C, 21.9; H, 5.4; Cl, 43.1; N, 8.5; Cr, 21.1. Found: C, 21.8; H, 5.3; Cl, 43.2; N, 8.4; Cr, 20.9. Mol. Wt. Calcd. 494; Observed (osmometric), 520.

Λ_m (298°K) = $2.1 \text{ ohm}^{-1} \text{ cm mole}^{-1}$ for a 10^{-3} M solution in CH_2Cl_2 .

Melting point: Decomposes at $T > 418^\circ \text{K}$.

Magnetic data;

Temp. ($^\circ \text{K}$)	χ'_m per Cr atom $\times 10^6$ c.g.s.u.	$\mu_{\text{eff.}}$ (BM)
297	5665	3.68
273	6180	3.68
243	6900	3.66
213	7775	3.64
183	8985	3.63
153	10490	3.59
123	12985	3.58
103	15010	3.51

The diamagnetic correction for $C_9H_{27}N_3Cl_6 = 270.42 \times 10^6$ c.g.s.u.

The infrared spectrum contained bands at; 3100(s), 3025(m), 2995(w), 2930(w), 2910(m), 2858(w), 2830(w), 2795(w), 1480(s), 1465(s), 1405(m), 1370(w), 1260(w), 1230(m), 1108(m), 1035(m), 1018(w), 980(s), 818(w), 720(m), 680(m), 530(m), 445(w), 425(w), 364(s), 354(s), 297(m), 255(m), 202(w), 176(w) and 151(w) cm^{-1} respectively.

The electronic spectrum gave bands at; 13,330, 18,520, 31,750(sh), 38,460(sh), 45,870(sh) and 51,280 cm^{-1} respectively, when run as the solid, and at; 13,600 and 18,350 cm^{-1} , when run as a solution in benzene.

This product was also obtained when the potential ligands CO_2 , CS_2 , Pr^i_2O and $(Me_2N)_2B-B(NMe_2)_2$ were present in the benzene solution. The reaction was independent of their presence.

F) Reaction of $CrCl_3 \cdot 2NMe_3$ with Silver Perchlorate

When a benzene solution of $CrCl_3 \cdot 2NMe_3$ was added to a similar solution of $AgClO_4$ (8:3 Ratio) in vacuo, an immediate reaction occurred. A red colouration initially imparted to the solution rapidly dispersed to give a dark green solution and a white precipitate, with release of NMe_3 . The NMe_3 was trapped in an infrared gas cell and identified by its spectrum.⁸⁵ The reaction mixture was extracted in vacuo with benzene to yield a white insoluble solid and a dark green solution. The precipitate was the stoichiometric yield of $AgCl$. Removal of the solvent in vacuo yielded the dark green solid triperchloratochromium(III). (WARNING: This solid is a thermal and mechanical shock sensitive explosive.) The infrared spectrum contained bands at; 1261(m), 1180(m), 1122(s), 1079(s), 1018(s), 981(m), 895(m), 850(m), 818(m), 722(w), 681(w), 655(m), 619(s), 602(s), 489(w), 390(m) and 348(w) cm^{-1} respectively.

The electronic spectrum contained bands at; 16,100, 22,500 and 37,000 cm^{-1} respectively when run as a solid, and at; 15,800 and 23,800 cm^{-1} respectively when run as a benzene solution.

G) Reaction of $\text{Cr}_2\text{Cl}_6 \cdot 3\text{NMe}_3$ with Trimethylamine

The reaction was carried out in a double ampoule, with neat NMe_3 being distilled onto the lilac $\text{Cr}_2\text{Cl}_6 \cdot 3\text{NMe}_3$. Immediate reaction occurred to give a colourless solution and a green solid. Removal of the NMe_3 in vacuo yielded an oily green solid that was insoluble in all the common organic solvents.

The infrared spectrum contained bands at; 3250(s), 3065(s), 3008(w), 2945(s), 2898(sh), 2852(m), 2801(w), 2730(w), 1467(s), 1449(sh), 1434(m), 1417(m), 1378(m), 1263(m), 1217(w), 1124(m), 1035(s), 1021(s), 981(m), 907(s), 816(w), 722(w), 468(m), 431(m), 354(s), 322(s), 293(m) and 250(m) cm^{-1} respectively.

H) Reaction of $\text{Cr}_2\text{Cl}_6 \cdot 3\text{NMe}_3$ with Hydrogen Chloride

When anhydrous HCl gas was either co-condensed with benzene onto, or bubbled through a benzene solution of, $\text{Cr}_2\text{Cl}_6 \cdot 3\text{NMe}_3$ an immediate reaction occurred, yielding a colourless solution and a purple precipitate. The solvent was removed in vacuo and the purple solid subjected to a soxhlet extraction with chloroform. This removed a soluble oily white solid of non-stoichiometric composition, leaving a purple/blue solid that was insoluble in all the common organic solvents, and of non-stoichiometric composition.

The infrared spectrum of the purple/blue solid contained bands at; 3110(s), 3015(m), 2959(w), 1474(sh), 1461(sh), 1451(s), 1418(w), 1372(w), 1242(m), 1013(m), 974(sh), 970(s), 802(m), 749(w), 718(w), 540(w), 452(w), 345(br-s), 321(br-s) and 268(m) cm^{-1} respectively.

I) Reaction of $\text{Cr}_2\text{Cl}_6 \cdot 3\text{NMe}_3$ with Pyridine

The reaction of $\text{Cr}_2\text{Cl}_6 \cdot 3\text{NMe}_3$ with warm pyridine occurred rapidly, under nitrogen, to yield a dark green solution and release of NMe_3 . The NMe_3 was trapped in an infrared gas cell and identified by its spectrum.⁸⁵ The solvent was removed in vacuo and the dark green solid obtained subjected to a soxhlet extraction with chloroform. This yielded the dark green trichlorotris(pyridine)chromium(III) in 100% yield. The infrared spectrum was identical to that of an authentic sample.¹³

Anal. Calcd. for $\text{C}_{15}\text{H}_{15}\text{Cl}_3\text{N}_3\text{Cr}$: Cl, 26.9; Cr, 13.1. Found: Cl, 26.7; Cr, 12.9.

J) Reaction of $\text{Cr}_2\text{Cl}_6 \cdot 3\text{NMe}_3$ with Acetonitrile

When excess acetonitrile was added to a benzene solution of $\text{Cr}_2\text{Cl}_6 \cdot 3\text{NMe}_3$ in vacuo an immediate reaction occurred yielding a dark purple precipitate. The solvent and excess acetonitrile was removed in vacuo to give a dark brown/purple oily solid, that was insoluble in the common organic solvents; and was not amenable to purification.

The infrared spectrum contained bands at: 2995(sh), 2860(m), 2890(w), 2830(m), 2790(m), 2760(sh), 2320(s), 2295(s), 2245(s), 1405(s), 1254(s), 1080(br-s), 1025(m), 940(m), 865(m), 820(sh), 798(s), 715(w), 675(m), 660(sh) and 345(br-s) cm^{-1} respectively. The electronic spectrum contained bands at ; 13,930(sh), 15,040, 21,150, 32,050(sh) and 42,020(sh) cm^{-1} respectively when run as the solid.

K) Reaction of $\text{Cr}_2\text{Cl}_6 \cdot 3\text{NMe}_3$ with Tetrahydrofuran

When excess THF was added to a benzene solution of $\text{Cr}_2\text{Cl}_6 \cdot 3\text{NMe}_3$ in vacuo an immediate reaction occurred yielding a dark purple precipitate. The solvent and excess THF were removed in vacuo to yield a dark brown/purple oily solid that was insoluble in

all the common organic solvents, and not amenable to purification.

The infrared spectrum contained bands at ;3110(sh), 3059(m), 3040(m), 3010(sh), 2955(s), 2898(w), 2850(sh), 1630(br-w), 1476(sh), 1460(sh), 1444(m), 1410(m), 1362(w), 1257(s), 1110(sh), 1081(s), 1013(s), 862(s), 798(br-s), 698(m), 682(m), 660(sh), 525(sh), 497(br-m), 389(s), 347(m), 320(m), 286(sh) and 260(sh) cm^{-1} respectively.

The electronic spectrum contained bands at; 13,600, 20,200, 37,040(sh), 38,460(sh) and 45,450(sh) cm^{-1} respectively when run as the solid.

L) Formation of $\text{V}_2\text{Cl}_6 \cdot 3\text{NMe}_3$

When a benzene solution of $\text{VCl}_3 \cdot 2\text{NMe}_3$ was sealed into an ampoule, a slow reaction occurred (~ 3 months) precipitating a dark brown solid and releasing NMe_3 . The NMe_3 was trapped in an infrared gas cell and identified by its spectrum.⁸⁵ Extraction of the solid product with benzene, in vacuo, removed the unreacted starting material and left the brown solid tri- μ -chloro-trichlorotris(trimethylamine)divanadium(III).

Anal. Calcd. for $\text{C}_9\text{H}_{27}\text{Cl}_6\text{N}_3\text{V}_2$: C, 22.0; H, 5.5; Cl, 43.3; N, 8.5 .

Found: C, 21.4; H, 5.4; Cl, 43.0; N, 8.2 .

Magnetic data:

Temp. ($^{\circ}\text{K}$)	χ'_m per V atom $\times 10^6$ c.g.s.u.	μ_{eff} (BM)
292	2774	2.55
259	2885	2.40
240	2971	2.32
225	3046	2.26
209	3105	2.17
195	3207	2.10
182	3311	2.03
166	3442	1.94
156	3535	1.88

The diamagnetic correction for $C_9H_{27}N_3Cl_6 = 270.42 \times 10^{-6}$ c.g.s.u.

Melting point: Decomposes at $T > 423^\circ K$.

The infrared spectrum contained bands at; 3090(s), 3025(sh), 3000(w), 2950(w), 2920(w), 2854(w), 2830(sh), 2780(w), 1478(s), 1462(s), 1406(m), 1372(m), 1251(m), 1090(m), 1040(w), 1012(m), 982(s), 804(m), 720(m), 668(w), 520(br-w), 448(m), 422(sh), 335(s), 315(s) and 283(m) cm^{-1} respectively.

The electronic spectrum contained bands at; 10,300, 17,700, 36,700(sh), 40,000(sh) and 47,600(sh) cm^{-1} respectively when run as the solid.

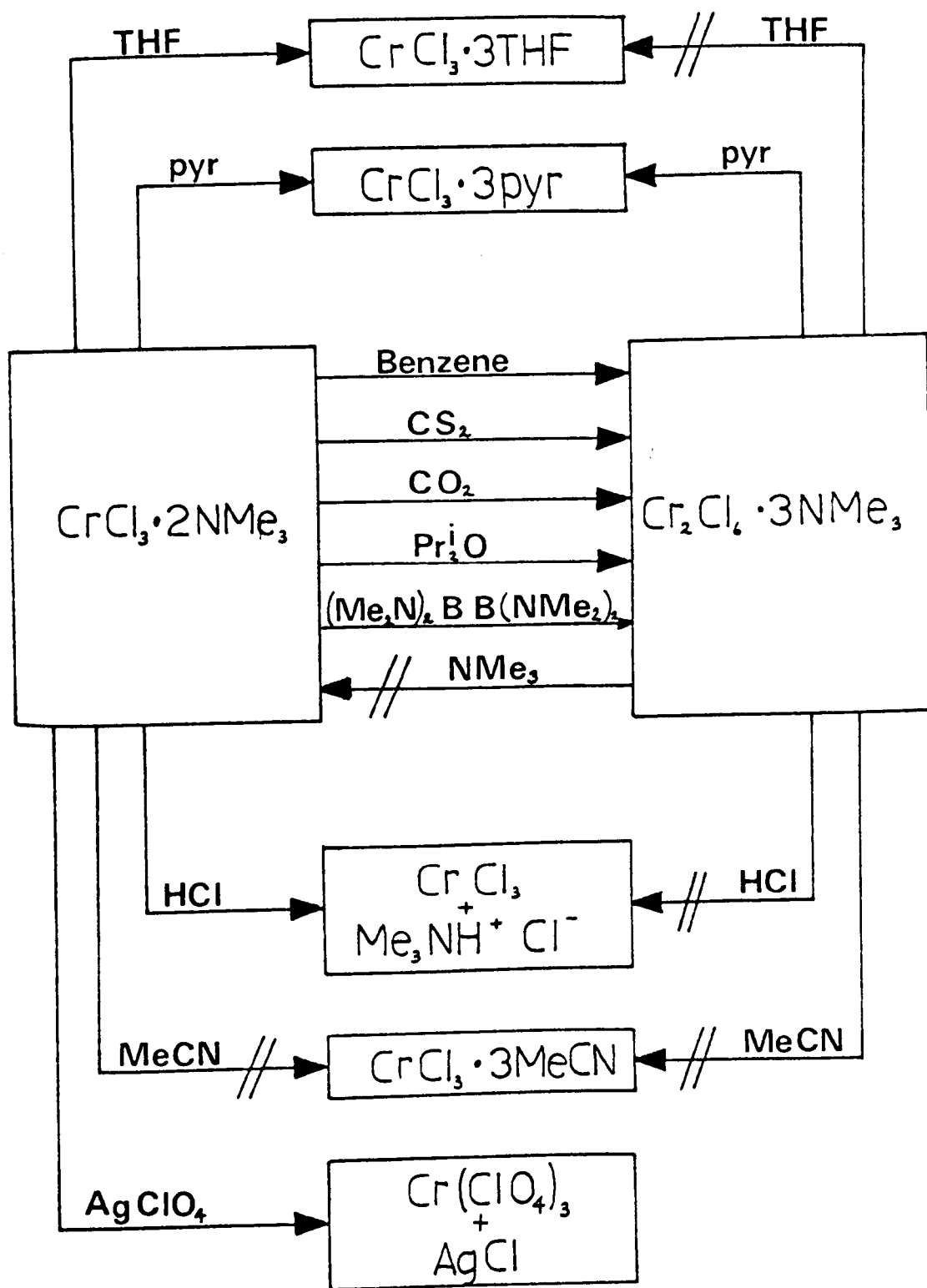


FIGURE 2.1. Reactions of $\text{CrCl}_3 \cdot 2\text{NMe}_3$ and $\text{Cr}_2\text{Cl}_6 \cdot 3\text{NMe}_3$

2.3. DISCUSSION

All the reactions in this section were carried out in benzene solution and, unless stated otherwise, an excess of ligand was used. The reactions are shown schematically in FIGURE 2.1..

2.3.A. Reactions of Trichlorobis(trimethylamine)chromium(III)

2.3.A.i. Reaction with Hydrogenchloride

Direct addition of anhydrous hydrogenchloride, either by bubbling or co-condensation with the benzene solvent, gave quantitative formation of trimethylamine hydrochloride (2 mols) and chromium(III)chloride (1 mol). These were the only products isolated from the reaction. Even under forcing conditions, e.g. many hours heating at $T > 473^\circ\text{K}$ in vacuo, the hexahalogenometalate, formed in a similar reaction with pyridinium hydrochloride,⁴⁴ was not produced. This result is in line with previous findings;^{44,46} that an excess of the amine hydrochloride is required for this reaction, and that the aromatic amine hydrochloride is a more effective source of chloride ion than is an aliphatic hydrochloride.

2.3.A.ii. Reactions Involving Trimethylamine Substitution

The reaction with excess pyridine, and the reaction with excess tetrahydrofuran, proceeded smoothly and rapidly, with release of trimethylamine and formation of the tris adducts, $\text{CrCl}_3 \cdot 3\text{pyr}$ ¹³ and $\text{CrCl}_3 \cdot 3\text{THF}$,⁸⁶ in 100% yield. The released trimethylamine was collected in an infrared gas cell and identified by its spectrum.⁸⁵ The solvent was removed from the reaction mixture in vacuo, and the adducts were identified by elemental analysis and comparison of their infrared spectra with those of authentic samples: prepared as described in the literature.^{13,14}

Addition using equimolar quantities of ligand and adduct again produced a rapid reaction, with release of trimethylamine. However, the insoluble products obtained, pink when pyridine was used as the ligand, and purple when tetrahydrofuran was used, proved to be of non-stoichiometric composition. Their infrared spectra contained bands attributable to both coordinated trimethylamine and the incoming ligand. The metal-halogen region, $400-200\text{ cm}^{-1}$, was poorly resolved in the THF adduct, but metal-halogen bridge bonding was clearly evident in the pyridine adduct. The bands found at 378 , 356 , 342 and 298 cm^{-1} respectively, being assignable to $\nu(\text{MCl})_{\text{terminal}}$, 378 and 356 cm^{-1} and $\nu(\text{MCl})_{\text{bridging}}$, 342 and 298 cm^{-1} modes. These products are seen to be polymeric material resulting from partial solvolysis, and the structure shown in FIGURE 2.2., previously proposed⁸⁷ for similar adducts, is favoured as their basis.

Rather surprisingly the reaction of the five coordinate adduct with excess acetonitrile failed to give the expected tris adduct, $\text{CrCl}_3 \cdot 3\text{MeCN}$. The product obtained was a brown/purple oily solid that proved impossible to purify. An explanation of this behaviour is difficult to find. Alkyl cyanides are known to reduce some transition metal species,^{16,88} but this action seems unlikely in the case of chromium(III). The most acceptable explanation seems to be that the product was a mixture of a number of partial and complete solvolysis products.

The outcome of the reaction with the potential ligands carbondioxide, carbondisulphide, diisopropylether and tetrakis-(dimethylamino)diborane proved most interesting. In these cases reaction occurred slowly, over a period of several days at room temperature, with release of trimethylamine and precipitation

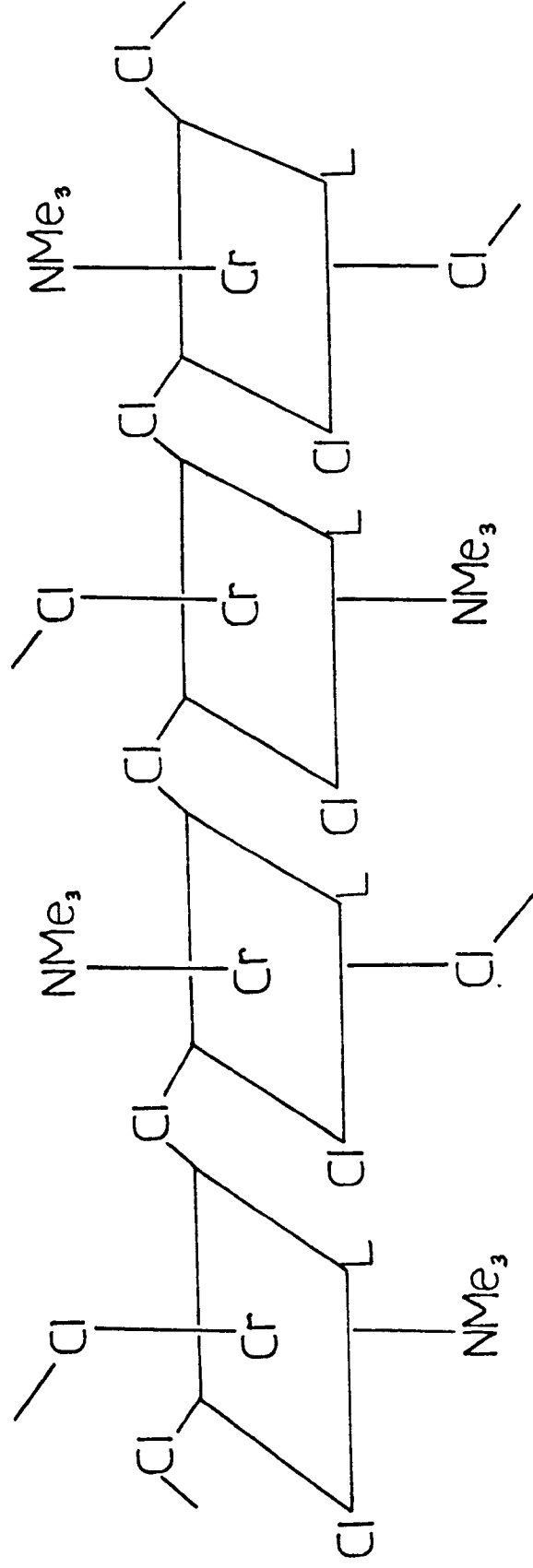


FIGURE 2.2. Possible Structure for Mixed Ligand Adducts

$\text{L} = \text{pyr or THF}$

of a lilac solid; that showed some solubility in benzene. The products from all these reactions proved to be identical, and devoid of the reacting ligand. Obviously an independent reaction was occurring, and it was no surprise when the identical product was again isolated by simply dissolving the bis trimethylamine adduct in dry de-gassed benzene, and leaving to react for two weeks.

The product from this solution decomposition of the five coordinate adduct was an air-moisture sensitive lilac solid of empirical formula $\text{Cr}_2\text{Cl}_6(\text{NMe}_3)_3$. It was non-conducting in dichloromethane solution, $\Lambda_m (298^\circ\text{K}) = 2.1 \text{ ohm}^{-1} \text{ cm mole}^{-1}$ at 10^{-3} M , and monomeric in benzene solution (vapour pressure osmometry). The electronic spectrum, TABLE 2.1., obtained in both the solid state and benzene solution, resembles those of both the hexahalogenometalate, CrCl_6^{3-} ,⁴⁴ and the enneahalogenodimetallate, $\text{Cr}_2\text{Cl}_9^{3-}$,^{45,46} ions; and can be interpreted in a similar manner.

TABLE 2.1. Electronic Spectrum of $\text{Cr}_2\text{Cl}_6 \cdot 3\text{NMe}_3$

Medium	Absorption Maxima (cm^{-1})
a	13,330; 18,520; 31,750(sh); 38,460(sh); 45,870(sh); 51,280.
b	13,600; 18,350.

a: nujol mull

b: benzene solution

The electronic transitions are essentially localised on adjacent chromium(III) ions, which are set in a pseudooctahedral environment. The peaks at $13,330 \text{ cm}^{-1}$ and $18,520 \text{ cm}^{-1}$ are assigned to the ${}^4\text{T}_{2g} \leftarrow {}^4\text{A}_{2g}$ and ${}^4\text{T}_{1g}(\text{F}) \leftarrow {}^4\text{A}_{2g}$ 'd-d' transitions respect-

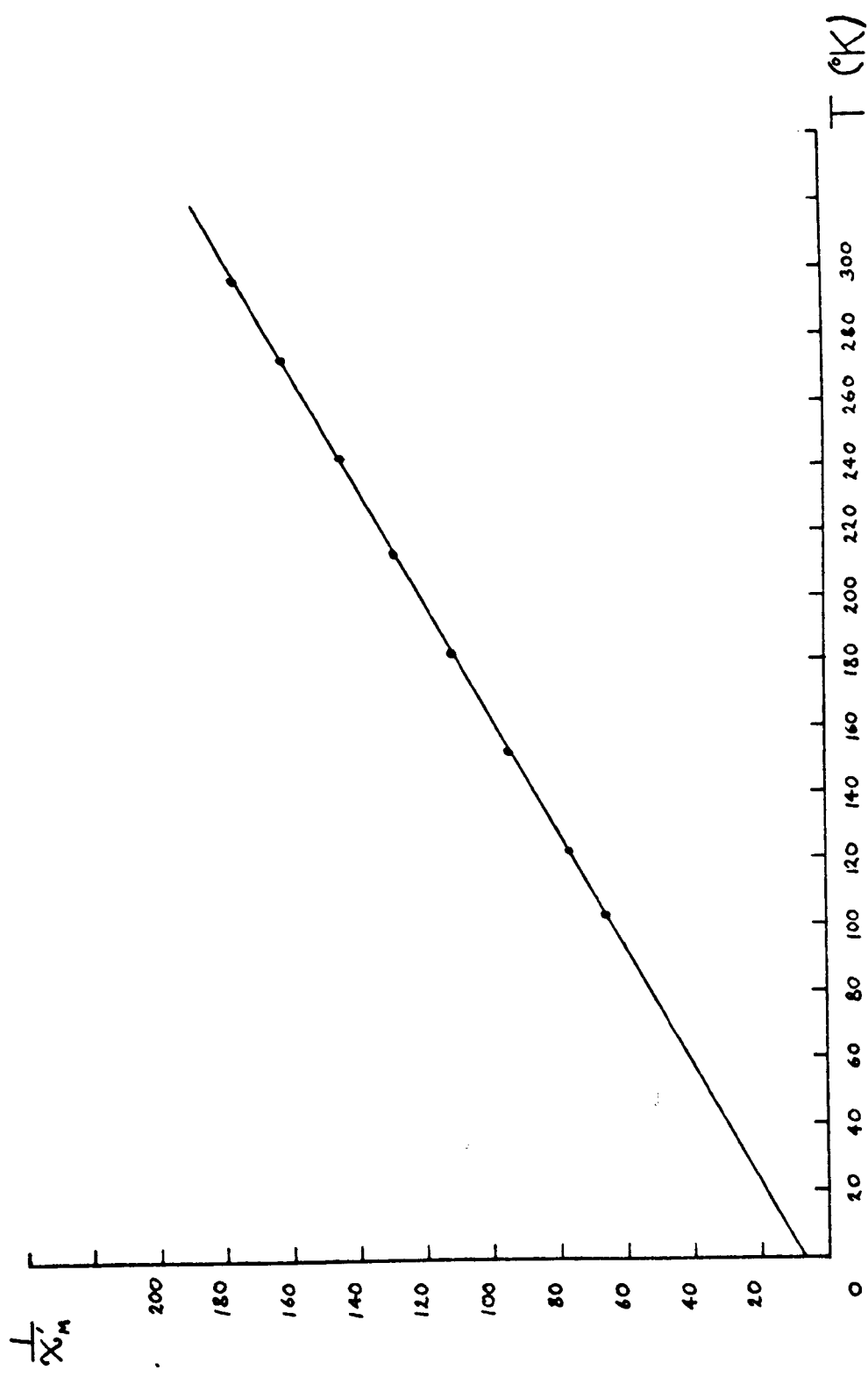


FIGURE 2.3. Curie-Weiss Plot $\text{Cr}_2\text{Cl}_6 \cdot 3\text{NMe}_3$

ively, and the remaining absorptions at 31,750(sh), 38,460(sh), 45,870(sh) and 51,280 cm^{-1} which effectively mask the third 'allowed' 'd-d' transition, ${}^4T_{1g}(P) \leftarrow {}^4A_{2g}$, are of charge transfer in origin, being of the type metal(d) \leftarrow chlorine(π).

The room temperature magnetic moment, of 3.68 BM, confirms the presence of genuine trivalent chromium(d^3). The magnetic susceptibility data, TABLE 2.2., shows excellent Curie-Weiss behaviour, FIGURE 2.3., over the temperature range 103°K - 297°K ($\Theta = 14^\circ$).

TABLE 2.2. Magnetic Data for $\text{Cr}_2\text{Cl}_6 \cdot 3\text{NMe}_3$

Temp. (°K)	297	273	243	213	183	153	123	103
$\chi \times 10^6$ c.g.s.u. per Cr atom	5665	6180	6900	7775	8985	10490	12985	15010

The similarity of this magnetic behaviour with that of the salts of the $\text{Cr}_2\text{Cl}_9^{3-}$ ion^{45,46,89} denies the presence of any significant metal-metal interaction within the dimer.

The assigned structure for this species, FIGURE 2.4., is that of two fused octahedra sharing a common face; as was determined by X-Ray analysis for $\text{Cs}_3\text{Cr}_2\text{Cl}_9$.⁹⁰

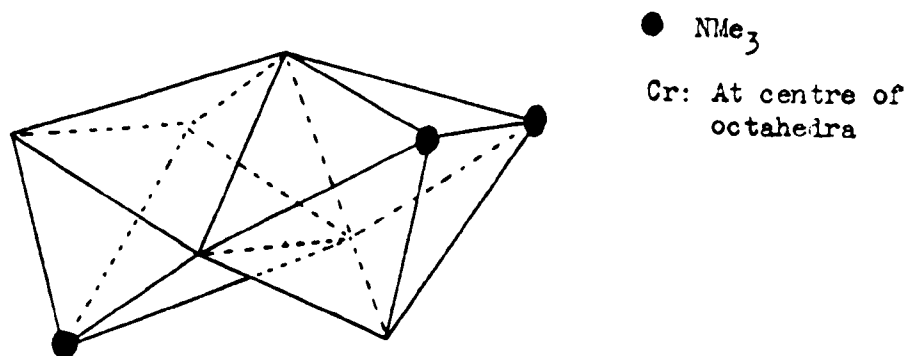


FIGURE 2.4. Assigned Structure of $\text{Cr}_2\text{Cl}_6 \cdot 3\text{NMe}_3$

The alternative structure with a trimethylamine occupying a common apical position, although favoured on symmetry grounds, is much less likely from a stereochemical and bonding viewpoint; as it would involve a bridging $\text{Cr} \cdots \text{NMe}_3 \cdots \text{Cr}$ linkage. A number of other possible structures can be disregarded, as apex-apex or edge-edge sharing of octahedra would be inconsistent with the molecular stoichiometry.

The infrared spectrum, $4000\text{--}400\text{ cm}^{-1}$, is very similar to that of the bis trimethylamine adduct, containing the characteristic bands of coordinated trimethylamine³⁸; $\nu_{\text{as}}(\text{CN})$ 1230, $\nu_{\text{s}}(\text{CN})$ 818, CH_3 rock 980, $(\text{CN})\text{def}_{\text{as}}$ 530 and $(\text{CN})\text{def}_{\text{s}}$ 445 cm^{-1} respectively. The $400\text{--}200\text{ cm}^{-1}$ region, containing the metal-halogen stretching frequencies, is very similar to that of the $\text{A}_3\text{Cr}_2\text{Cl}_9$ series, where $\text{A} = \text{K}, \text{Rb}, \text{Cs}, \text{Et}_4\text{N}$, with the two strong bands at 364 and 354 cm^{-1} and the two medium bands at 297 and 255 cm^{-1} being assigned to $\nu(\text{CrCl})_{\text{terminal}}$ and $\nu(\text{CrCl})_{\text{bridging}}$ vibrations respectively.

2.3.A.iii. Reactions Involving Chloride Substitution

The bis trimethylamine adduct reacted immediately with silver perchlorate, in a 1:3 molar ratio; releasing trimethylamine and giving a precipitate of silver chloride (3 mols), in a green solution of the perchlorate complex. The electronic spectrum, TABLE 2.3., of the complex is the same both in the solid state and in solution, implying that no change of geometry occurs between the two states. The chromium(III) ion is seen to be in an octahedral environment, with all three of the expected 'd-d' transitions, for this state, being observed. They were found at 16,100, ${}^4\text{T}_{2g} \leftarrow {}^4\text{A}_{2g}$ (10 Dq), 22,500, ${}^4\text{T}_{1g}(\text{F}) \leftarrow {}^4\text{A}_{2g}$ and 37,000, ${}^4\text{T}_{1g}(\text{P}) \leftarrow {}^4\text{A}_{2g}$, cm^{-1} respectively.

TABLE 2.3. Electronic Spectrum of $\text{Cr}(\text{ClO}_4)_3$

Medium	Absorption Maxima (cm^{-1})
a	16,100; 22,500; 37,000.
b	15,800; 23,800.

a: nujol mull

b: benzene solution

The three perchlorate groups are seen as producing this environment by each acting as a bidentate ligand. Hathaway and Underhill⁸³ have demonstrated the usefulness of the infrared spectra of this group in determining the bonding mode of the anion. The vibrations of the group as a function of symmetry are shown in FIGURE 2.5.. The degenerate ν_3 , asymmetric stretch, and ν_4 , asymmetric bend, vibrations are found in the ~ 1000 - 1100 cm^{-1} and ~ 600 - 700 cm^{-1} regions, respectively, for the free ion; which exhibits tetrahedral T_d symmetry. On coordination as a monodentate group the symmetry of the ion drops to C_{3v} , and these bands split into doublets. When coordination is as a bidentate group the symmetry further drops to C_{2v} and the bands are further split to triplets. The infrared spectrum of the adduct in the 1300 - 400 cm^{-1} region is shown in FIGURE 2.6.. The triplet structures derived from the original ν_3 and ν_4 bands are clearly visible in the expected spectral regions. The previously infrared inactive ν_1 and ν_2 vibrations appear as the active ν_2 and ν_4 modes at 981 and 390 cm^{-1} respectively. (not shown)

The proposed structure for the adduct, derived from the spectral data, is shown in FIGURE 2.7., but, unfortunately, at this point in the investigation the complex underwent a violent instantaneous decomposition (WARNING: The solution of this com-

State of ClO₄ Sym. Vibrations of ClO₄ Group^t

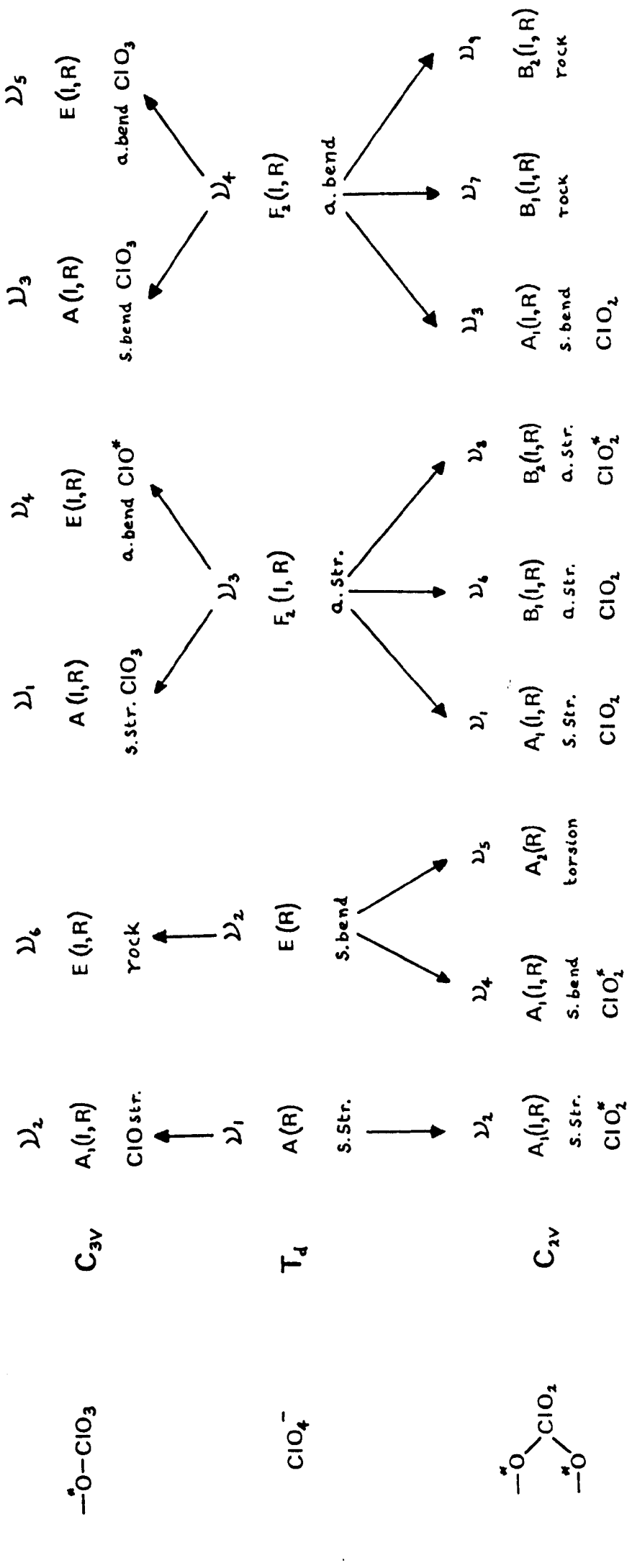


FIGURE 2.5. Vibrations of ClO_4 Group as a Function of Symmetry

t, Key on next page.

KEY to FIGURE 2.5.

(From, B.J.Hathaway and A.E.Underhill, J.Chem.Soc., 3091, 1961.)

- † A and B : Non degenerate
- E : Doubly degenerate
- F : Triply degenerate
- I : Infrared active
- R : Raman active
- s : Symmetric
- a : Antisymmetric
- ⋆ : Refers to coordinated oxygen

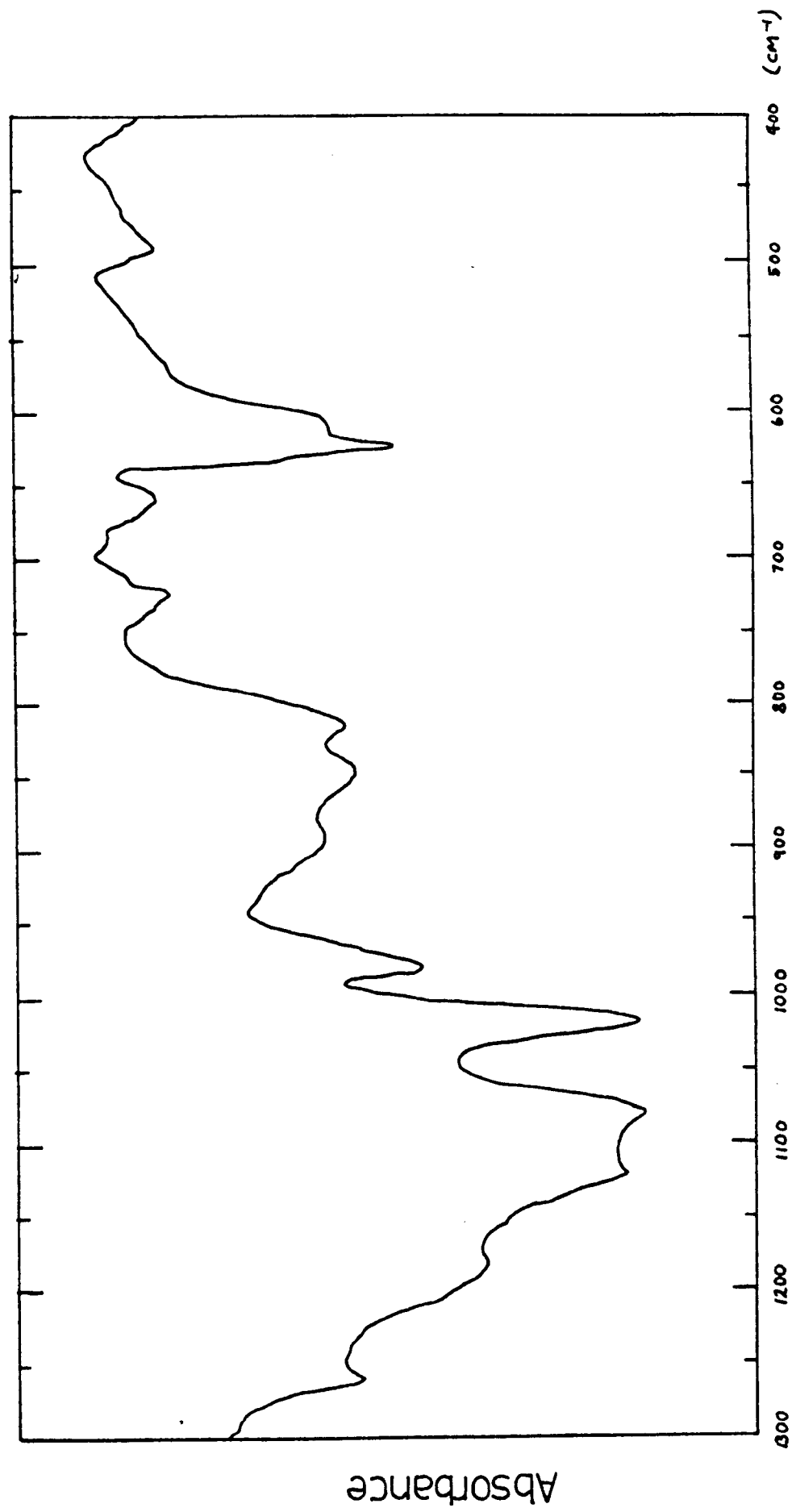


FIGURE 2.6. I.R. Spectrum of $\text{Cr}(\text{ClO}_4)_3$

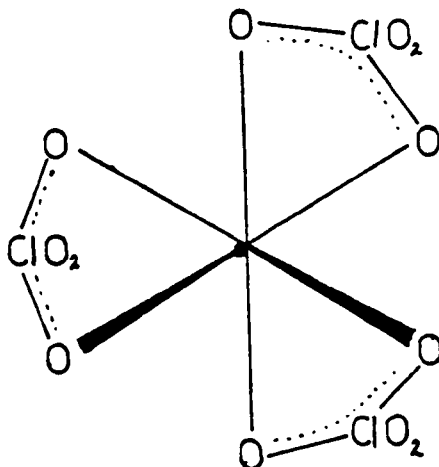
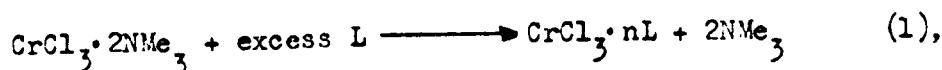


FIGURE 2.7. Proposed Structure for $\text{Cr}(\text{ClO}_4)_3$

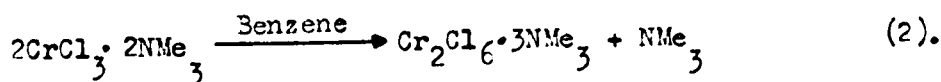
plex is extremely air-moisture sensitive, but the solid remaining on evaporation is very thermal, and mechanical, shock-sensitive, exploding with considerable violence.) and further structural information was not derived.

Conclusion

Two competing reactions are found to occur when the five coordinate adduct, $\text{CrCl}_3 \cdot 2\text{NMe}_3$, is reacted with potential ligands in benzene solution. One is ligand substitution of the type;



the other is an independent decomposition of the adduct;



With strong donor ligands reaction (1) is usually predominant, but in the presence of weak donor ligands reaction (2) gains dominance. Providing that strong donors, in a healthy excess, are employed there is no reason why the adducts $\text{MX}_3 \cdot 2\text{NMe}_3$ should not be used in ligand substitution reactions. Indeed the solubility of these adducts and their rapid reactions give them

advantages over several other adducts. However, where the strength of the incoming donor is low, or in doubt, great consideration should be given to their trait towards decomposition before their use is employed.

Provided that great care is exercised in its handling, the new triperchloratochromium(III) complex could prove a useful intermediate in the synthesis of non-halogen chromium(III) compounds.

2.3.B. Reactions of Tri-μ-chloro-trichlorotris(trimethylamine) dichromium(III)

2.3.B.i. Reaction with Trimethylamine

The decomposition of the $\text{CrCl}_3 \cdot 2\text{NMe}_3$ adduct by loss of trimethylamine was found to be irreversible. When the dimeric product was reacted with an excess of neat trimethylamine the product was an insoluble oily green solid. The trimethylamine obviously lacks the donor strength, probable due to steric hindrance, to break the metal-halogen bridge bonding and force the octahedral metal back to five coordination. This failure to cleave the bridge bonds is shown in the infrared spectrum of the impure product; with the strong bands at 354 and 322 cm^{-1} and the medium intensity bands at 293 and 250 cm^{-1} being characteristic of $(\text{CrCl})_{\text{terminal}}$ and $(\text{CrCl})_{\text{bridging}}$ vibrations respectively.

2.3.B.ii. Reaction with Hydrogenchloride

Direct reaction with anhydrous hydrogenchloride, by bubbling the gas through a benzene solution of the dimer, resulted in a purple/blue insoluble product being obtained. Even after Soxhlet extraction with chloroform, to remove any amine hydro-

chloride that may have been formed in the reaction, the infrared spectrum of the product still showed the presence of the trimethylamine group. The white soluble extract, which contained no metal ion, was non-stoichiometric and, by spectral comparison, not trimethylamine hydrochloride. Apart from the bands associated with the amine, the infrared spectrum of the purple/blue product gave bands, in the metal-halogen region, at 345(br-s), 321(br-s) and 268(m) cm^{-1} . This profile is the same as that given by $[\text{Et}_2\text{NH}]_3 [\text{Cr}_2\text{Cl}_9]$,⁴⁶ so again it would seem that the metal-halogen bridge bonding has not been cleaved.

A possible explanation of this result is shown in the equation:



This reaction is clearly not going cleanly to completion, probably because an excess of amine hydrochloride seems to be required to produce the dimetalate.^{44,46} However, the reaction is obviously a very attractive possibility, as the substitution would greatly relieve steric strain within the dimer.

2.3.B.iii. Reaction with Pyridine

This reaction occurs rapidly in warm solution, with loss of trimethylamine, to yield the expected mononuclear green $\text{CrCl}_3 \cdot 3\text{pyr}$. The pyridine is obviously a sufficiently strong donor, lacking the grosser steric restrictions of trimethylamine, to break the bridge bonding and cleave the dinuclear species.

2.3.B.iv. Reactions with Acetonitrile and Tetrahydrofuran.

The reactions of these ligands, in each case, precipitated out a brown/purple solid. On removal of the solvent, the solids obtained were found to be oily, and not amenable to purification.

The complexity of the low infrared spectra, though poorly resolved in the acetonitrile product, is indicative that, again, the dinuclear structure has not been completely destroyed; bridge bonding still being in evidence.

A product which is probably present as a result of these reactions is the species $[\text{CrCl}_2 \cdot 2\text{L}]^-$, previously reported for a number of vanadium(III) complexes.²⁴ The presence of these species in acetonitrile solutions of the enneahalogenodimetalate of titanium and vanadium has already been reported,⁴⁶ though they were not isolated. The counter ion to this adduct could be either the corresponding cationic adduct, $[\text{CrCl}_2 \cdot 4\text{L}]^+$, or the trimethylammonium ion. The latter case would involve a proton abstraction from one of the ligand sources to form the amine cation, but such a process is not unreasonable, particularly in acetonitrile.^{16,88} The deprotonated ligand would then be involved in some form of polymerisation, a process that would not be inconsistent with the observed results.

2.4. Decomposition of the $MCl_3 \cdot 2NMe_3$ Adducts in Benzene Solution

The decomposition of $CrCl_3 \cdot 2NMe_3$ in benzene solution is not an isolated characteristic of the chromium adduct, but is evident throughout the series $MCl_3 \cdot 2NMe_3$; where $M = Ti, V$ and Cr . When any of the metal adducts are placed in benzene solution the decomposition occurs, with loss of trimethylamine and precipitation of the product. The rate of decomposition varies markedly through the series in the order $Cr > V \gg Ti$.

The lilac product from the chromium decomposition has been detailed earlier in this chapter. The product from the vanadium reaction is a brown insoluble solid, with empirical formula $V_2Cl_6(NMe_3)_3$, that is formed at a very slow rate. The infrared spectrum in the $4000-400\text{ cm}^{-1}$ region is very similar to that of the chromium product, there being only minor frequency shifts in some of the bands. The $400-200\text{ cm}^{-1}$ region, containing the metal-halogen vibrations, exhibits bands at 335, 315 and 283 cm^{-1} and bears a very close resemblance to that of the $V_2Cl_9^{3-}$ ion.⁴⁶ The electronic spectrum, TABLE 2.4., of the product is typical of octahedral vanadium(III), with the first two 'd-d' transitions, the ${}^3T_{2g}(F) \leftarrow {}^3T_{1g}(F)$ and ${}^3T_{1g}(P) \leftarrow {}^3T_{1g}(F)$, being observed at 10,300 and $17,700\text{ cm}^{-1}$ respectively. This compares closely with the $V_2Cl_9^{3-}$ ion, where the comparable peaks are found at 10,600 $17,200\text{ cm}^{-1}$.⁴⁶

TABLE 2.4. Electronic Spectrum of $V_2Cl_6 \cdot 3NMe_3$

Medium	Absorption Maxima (cm^{-1})
a	10,300; 17,700; 36,700(sh); 40,000(sh); 47,600(sh).

a: nujol mull

The remaining high intensity charge transfer bands at 36,700(sh), 40,000(sh) and 47,600 cm^{-1} prevent the observation of the third allowed 'd-d' transition, the ${}^3A_{2g}(F) \leftarrow {}^3T_{1g}(F)$.

Due to the lack of solubility shown by this adduct, it was not possible to carry out a molecular weight determination. However, in view of the close chemical and spectral similarities with both $\text{Cr}_2\text{Cl}_6(\text{NMe}_3)_3$ and the $\text{V}_2\text{Cl}_9^{3-}$ ion, the adduct is assigned an analogous structure, of two fused octahedra sharing a common trigonal face of chlorine atoms.

The room temperature magnetic moment of 2.55 BM (2.54 BM for $[\text{Et}_2\text{NH}_2]_3 [\text{V}_2\text{Cl}_9]^{46}$) is significantly reduced from the normal value expected for magnetically dilute vanadium(III) complexes;⁹¹ and the moment shows a strong temperature dependence, TABLE 2.5.. This, and marked deviations from Curie-Weiss behaviour, gives evidence for definite magnetic interactions occurring in the solid.

TABLE 2.5. Magnetic Data for $\text{V}_2\text{Cl}_6(\text{NMe}_3)_3$

Temp. °K	292	259	240	225	209	195	182	166	156
$\chi_m \times 10^6$ c.g.s.u. per V atom	2774	2885	2971	3046	3105	3207	3311	3442	3535
μ_{eff} BM	2.55	2.40	2.32	2.26	2.17	2.10	2.03	1.94	1.88

The decomposition of $\text{TiCl}_3 \cdot 2\text{NMe}_3$ in benzene solution is extremely slow; a pale yellow/brown solid precipitating out of solution after a period of several months. The product yield was low, in the order of only 1%, even after a period of six months, and a sufficient quantity for structural investigations was not obtained.

The kinetics of the decomposition of the chromium and the vanadium bis trimethylamine adducts was investigated by spectrophotometrically following the loss of the five coordinate species in solution. Standard benzene solutions of the adducts, in sealed 1 cm silica cells, were monitored using a Cary 14 spectrophotometer, the cell compartment of which was thermostatted at 295°K. In the case of $\text{CrCl}_3 \cdot 2\text{NMe}_3$ the rate of loss of the five coordinate species was followed by monitoring the characteristic ${}^4\text{E}''(\text{F}) \leftarrow {}^4\text{E}'(\text{F})$ peak at $10,100 \text{ cm}^{-1}$. In the case of the vanadium adduct the loss was followed by monitoring the ${}^3\text{E}', {}^3\text{A}_2(\text{P}) \leftarrow {}^3\text{A}_2(\text{F})$ peak at $20,000 \text{ cm}^{-1}$.

No precipitation occurred in the chromium solutions provided that the concentrations were chosen such that the product concentration never exceeded 10^{-3} M . In such solutions the $\text{Cr}_2\text{Cl}_6 \cdot 3\text{NMe}_3$ adduct exhibited no absorption in the $10,000 \text{ cm}^{-1}$ region. The vanadium solutions precipitated out a very fine flocculent brown solid, which increased the measured optical density of the sample over that of the true solution. To avoid anomalously high readings being recorded, the cell was centrifuged before each reading. No problems were encountered with product absorptions in solution, as the adduct was completely insoluble in benzene.

Accurate values for the extinction coefficients of the absorptions being monitored were obtained by making plots of absorbance against time, for each solution, and extrapolating this back to zero time. From this zero time absorbance the extinction coefficients for the standard solutions were obtained. A comparison of the values gained in this way, with those previously reported, clearly show the results of this decomposition. The value obtained for the $\text{CrCl}_3 \cdot 2\text{NMe}_3$ ${}^4\text{E}''(\text{F}) \leftarrow {}^4\text{E}'(\text{F})$ absorption was 46.5, compared with the previously reported ³⁹ 23, and that

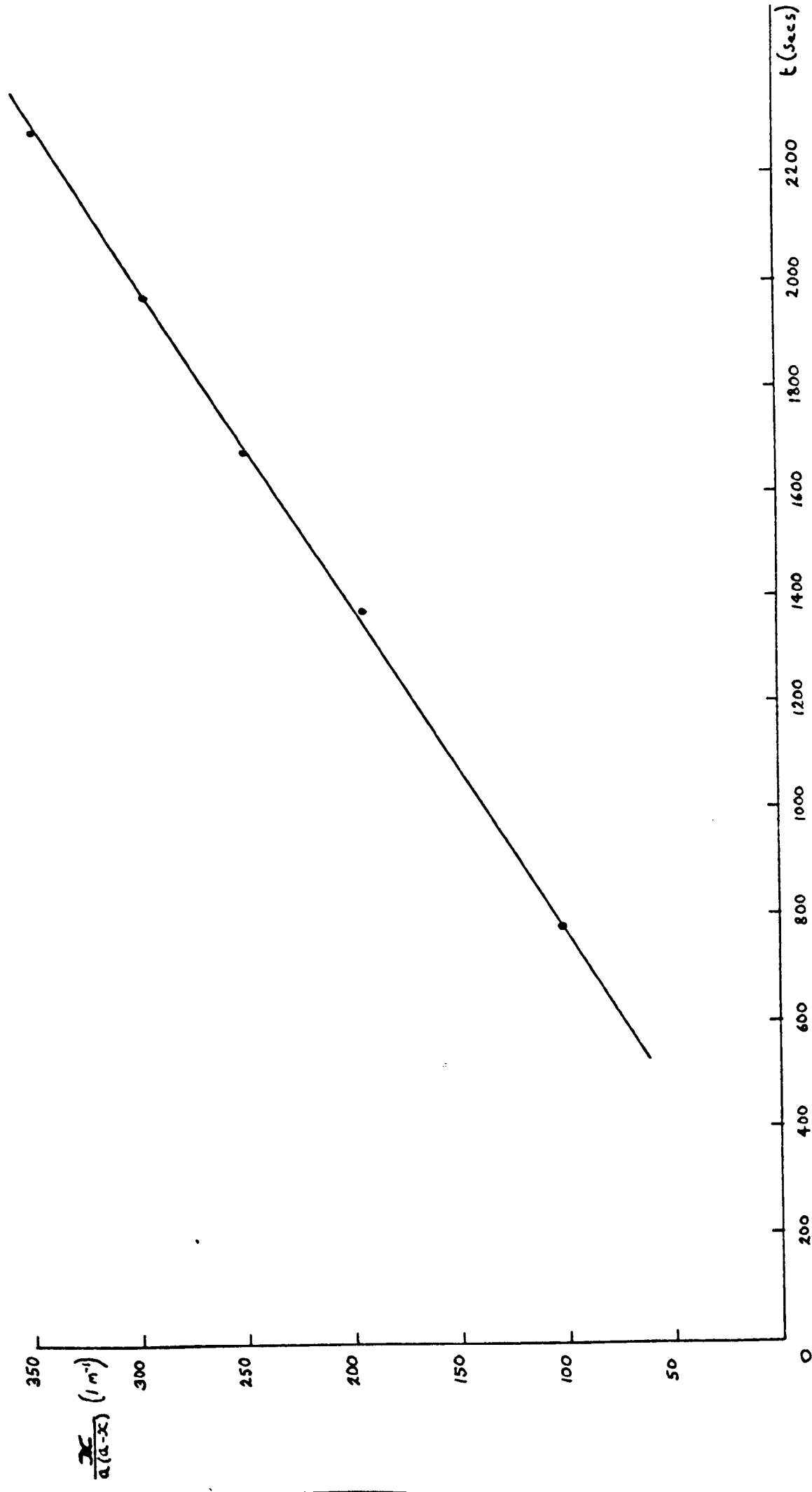


FIGURE 2.8. Second Order Rate Plot for $\text{CrCl}_3 \cdot 2\text{NMe}_3$ Decomposition

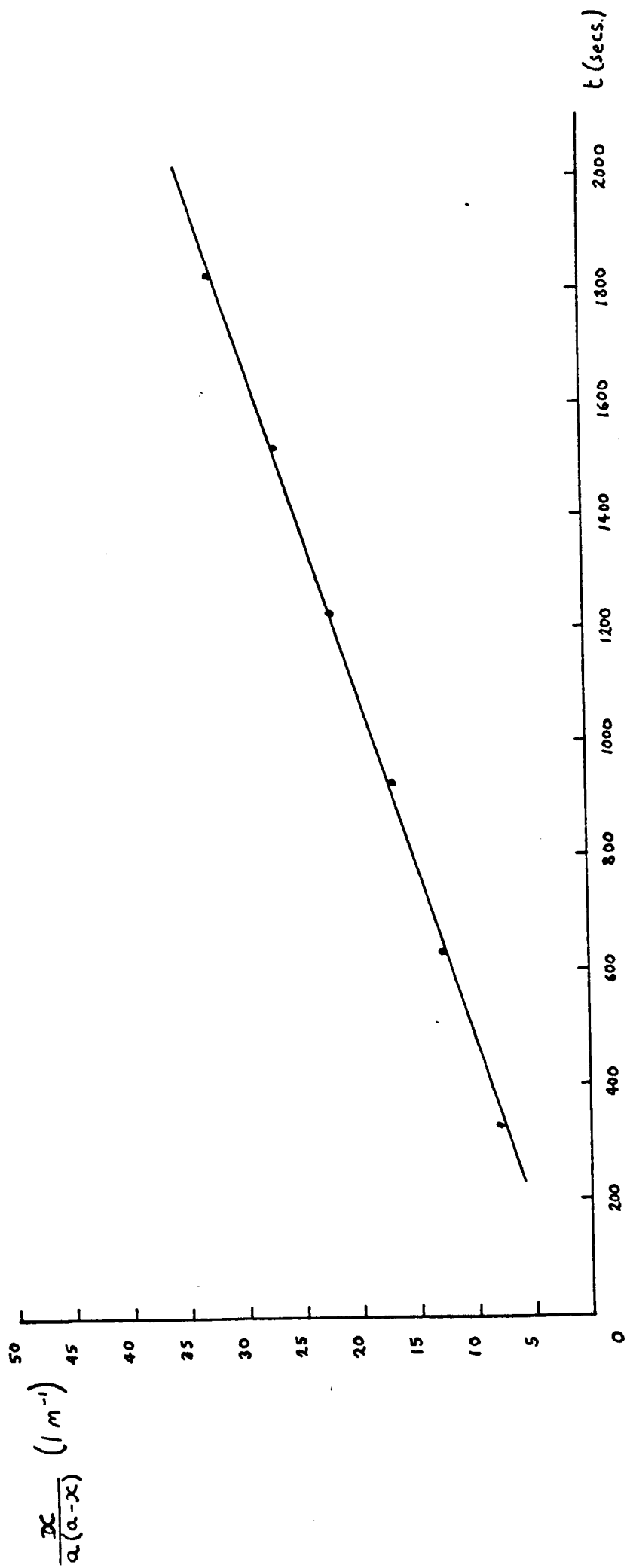


FIGURE 2.9. Second Order Rate Plot for $\text{VCl}_3 \cdot 2\text{NMe}_3$ Decomposition

for the $\text{VCl}_3 \cdot 2\text{NMe}_3$ ${}^3\text{E}'$, ${}^3\text{A}'_2(\text{P}) \leftarrow {}^3\text{A}'_2(\text{F})$ absorption was 26.5, compared with the previously reported ³⁸ 59. Obviously decomposition was well underway when the original spectra were recorded, with the precipitate in the vanadium case increasing the measured optical density.

From initial plots of log rate against log concentration, the reactions were found to be second order with respect to the adduct concentration. An integrated second order rate plot of $\frac{x}{a(a-x)}$ against t , where a = the initial concentration of the bis trimethylamine adduct, and x = the amount of the adduct that had reacted at the time t , has a slope of k , the rate constant. Plots of this form, FIGURES 2.8. and 2.9., gave the second order rate constants of $0.160 \text{ l m}^{-1} \text{ s}^{-1}$ for the $\text{CrCl}_3 \cdot 2\text{NMe}_3$ decomposition, and $0.0166 \text{ l m}^{-1} \text{ s}^{-1}$ for the $\text{VCl}_3 \cdot 2\text{NMe}_3$ decomposition.

The order in which the rate of decomposition increases for the adducts $\text{MCl}_3 \cdot 2\text{NMe}_3$, where $\text{M} = \text{Ti}, \text{V}$ and Cr , is that which one would expect, i.e. $\text{Cr} > \text{V} > \text{Ti}$. It can be seen from the relative d-orbital energy levels in ligand fields of D_{3h} and O_h symmetry, FIGURE 2.10., that the stability of octahedral over penta-coordinate geometry, in terms of crystal field stabilisation energy, increases for the series titanium(III) to chromium(III) in the order $\text{Cr}(\text{d}^3) > \text{V}(\text{d}^2) > \text{Ti}(\text{d}^1)$.

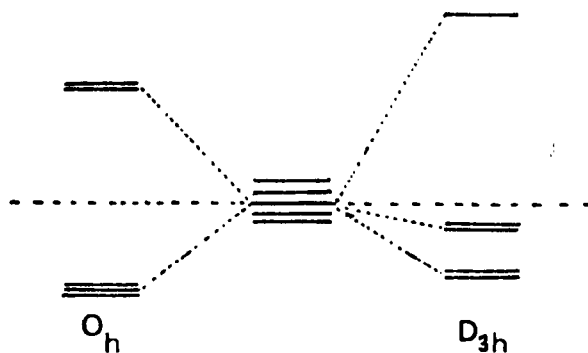
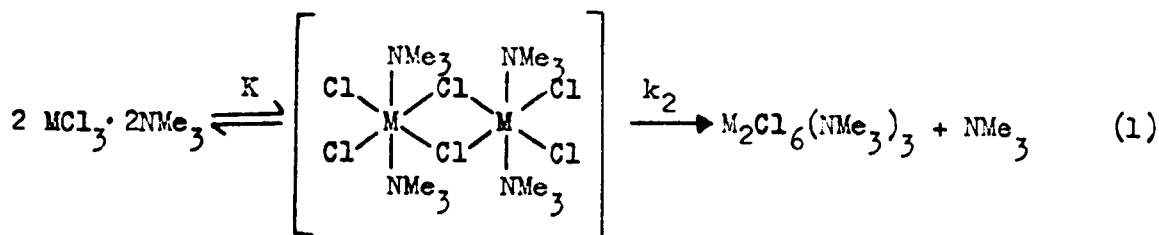


FIGURE 2.10. Relative d-orbital levels in O_h and D_{3h} fields

From this it would be expected that the drive towards octahedral coordination will be stronger in the chromium(III) species than either the vanadium(III) or the titanium(III).

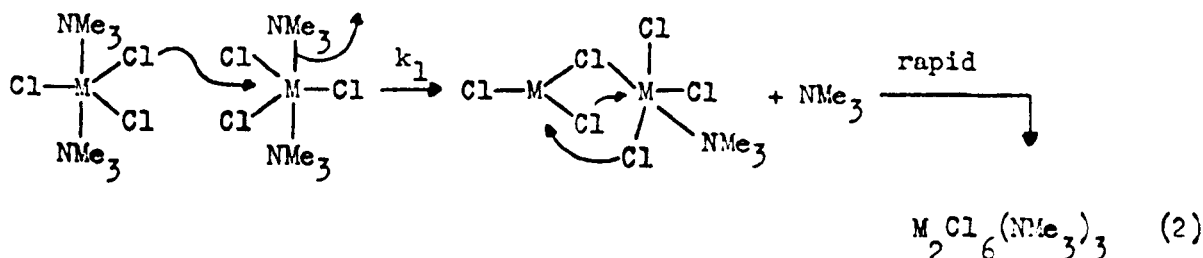
The mechanism by which this decomposition occurs is open to question. Few kinetic investigations have been carried out on five coordinate centres, and these have been on the late transition metals. In these studies the reaction behaviour has not been found to be rigid, both dissociative^{92,93} and associative⁹⁴ mechanisms have been found, and even both occurring simultaneously.⁹⁵ In the early transition metals, where four coordination under any circumstances is rare, a dissociative pathway is not intuitively favoured. Two mechanisms offer themselves as possible courses for the reaction;

One is an equilibrium dimer formation followed by a loss of trimethylamine with closing of the two octahedra;



$$\text{rate} = k_2 K [\text{CrCl}_3 \cdot 2\text{NMe}_3]^2.$$

A second possibility is for one molecule of the adduct to execute an $\text{S}_{\text{N}}2$ attack upon a second, this being followed by a rapid closure of the octahedra.



$$\text{rate} = k_1 \left[\text{CrCl}_3 \cdot 2\text{NMe}_3 \right]^2$$

Both of these reaction schemes fit the observed data and neither can be distinguished experimentally. However, the first scheme has a major point in its favour, in that it is well known for $\text{MX}_3 \cdot 2\text{L}$ species of the early metals to achieve octahedral coordination by dimer formation^{38,40} of the type shown as intermediate in reaction (1).

CHAPTER 3.

COMPLEXES OF 'BULKY' LIGANDS

3.1. INTRODUCTION

It is not possible to make accurate predictions as to under what conditions five coordinate complexes will and will not be formed. Even after several extensive investigations into this area of coordination chemistry, the requirements for penta-coordination remain indefinite. Several factors of obvious relevance have, however, been noted in recent researches, and may be regarded as gross, though not necessarily deciding, conditions for five coordination.

1) The size of the central metal atom; the larger this is, the less likely five coordination is, therefore higher oxidation states may be of particular relevance.

2) The size and shape of the ligand; multidentate ligands feature prominently in five coordinate complexes. Those which are designed with their interdonor distances and angles matching closely those required by the expected penta-coordinate polyhedra can often achieve success. Ligands of the general form $D(XD)_3$, where D is a donor atom linked by organic moieties X, such as $-(CH_2)-$ or $-C_6H_4-$, to three other donors D' , which may or may not be the same as D, have enabled the isolation of numerous trigonal bipyramidal complexes. The threefold symmetry of these ligands enable the donor atoms to readily occupy four sites in a trigonal bipyramidal complex.

The steric bulk of a ligand is of major, and often most significant, import in the determination of penta-coordination. Many five coordinate complexes have been prepared by using monodentate ligands of imposing steric bulk, such as tertiary amines and phosphines. In these situations the central metal atom is often forced into penta-coordination to minimise intramolecular contacts. Such non-bonding intramolecular interactions can have

significant effects in coordination chemistry, as recently noted by Wood;³² "...it is probable that structural studies of five coordinate molecules have made the inorganic chemist much more aware of the importance of formally non-bonding interactions in determining the finer details of the stereochemistry of coordination compounds."

The electronic factors of the central metal atom obviously plays an important role in this process, but, unfortunately, at the present time this role can not be defined exactly. By reference to FIGURE 2.10., it can be seen that for d^n configurations where $n = 1-3$, the crystal field stabilisation energy certainly favours octahedral coordination. In these cases five coordination must be mainly a result of ligand rather than metal requirements. A recent paper⁹⁶ has reported the isolation of several five coordinate complexes, mainly of the later transition metals, where it is said that the coordination is determined by the metal rather than ligand requirements. A five coordinate chromium(III) complex is also reported, and it is claimed that this is a complex "in which the coordination number and structure are determined primarily by the bonding characteristics of the metal." This obviously does not fit in with the octahedral nature of chromium(III). Unfortunately, the published data for this complex is scant, but the electronic spectrum shows a greater similarity to six, rather than five coordination. The lowest energy band is given at $16,000\text{ cm}^{-1}$, significantly higher than the expected ${}^4E''(F) \leftarrow {}^4E'(F)$ transition for trigonal bipyramidal chromium(III).

To clarify the depth of the metal's role in determining a specific coordination number, we have studied the reactions of the tervalent chlorides of titanium and chromium, predominantly octahedral species, with ligands that are sterically inductive of

penta-coordination.

We have found that the octahedral compulsion of these metals is strong enough, under most circumstances, to determine the coordination geometry, even to the extent of defeating the established coordination roles of the tripod ligands tren and Me₆tren.

3.2. EXPERIMENTAL and RESULTS

Preparative and manipulative details are given in appendices A and B.

A) Reaction between $\text{CrCl}_3 \cdot 2\text{NMe}_3$ and Tetrahydrothiophene

When excess THT was added to a concentrated benzene solution of $\text{CrCl}_3 \cdot 2\text{NMe}_3$ in vacuo an immediate reaction occurred releasing NMe_3 and giving a dark blue solution. The NMe_3 was trapped in an infrared gas cell and identified by its spectrum.⁸⁵ The solvent and excess THT were removed in vacuo and the remaining dark blue solid was thoroughly washed with n-hexane. This yielded the dark blue solid fac-trichlorotris(tetrahydrothiophene)chromium(III).

Anal. Calcd. for $\text{C}_{12}\text{H}_{24}\text{Cl}_3\text{S}_3\text{Cr}$: C, 34.0; H, 5.7; Cl, 25.1; S, 22.7; Cr, 12.3. Found: C, 33.8; H, 5.9; Cl, 24.9; S, 22.5; Cr, 12.4.

$\Lambda_m(298^\circ\text{K}) = 0.033 \text{ ohm}^{-1} \text{ cm mole}^{-1}$ for a 10^{-3} M solution in CH_2Cl_2 .

Magnetic data: At 293°K ; $\chi'_m = 5382.83 \times 10^{-6} \text{ o.g.s.u.}$, diamagnetic correction for $\text{C}_{12}\text{H}_{24}\text{Cl}_3\text{S}_3 = 244.74 \times 10^{-6} \text{ o.g.s.u.}$ and

$$\mu_{\text{eff}} = 3.56 \text{ BM.}$$

The infrared spectrum contained bands at; 2998(w), 2930(sh), 2920(s), 2900(sh), 2855(m), 1455(w), 1440(s), 1430(m), 1305(m), 1268(m), 1253(m), 1205(w), 1130(w), 1076(m), 1022(w), 958(m), 881(m), 817(m), 722(w), 668(m), 512(w), 471(w), 368(s), 341(s) and $292(\text{m}) \text{ cm}^{-1}$ respectively.

The electronic spectrum gave bands at; 13,510(sh), 14,600, 20,830, 28,570 and 39,370(sh) cm^{-1} respectively when run as the solid.

B) Reaction between CrCl_3 and Tetrahydrothiophene

Anhydrous CrCl_3 was sealed in a double ampoule with excess THT and a trace amount of zinc dust. An immediate vigorous reaction occurred giving a deep blue solution and a dark blue solid. Extraction by the normal double ampoule technique and then thorough washing with n-hexane yielded a dark blue solid product.

Analysis and spectral measurements confirmed this product to be identical with that described in A.

C) Isomerisation of fac-CrCl₃·3THT in Benzene Solution

The fac-CrCl₃·3THT was placed in a round bottomed flask and benzene was distilled onto it in vacuo. On warming to room temperature the dark blue solution immediately began to precipitate a lilac solid. After about two days stirring in vacuo the solution was only slightly coloured. The excess starting material was extracted with benzene to leave the lilac benzene insoluble solid mer-trichlorotris(tetrahydrothiophene)chromium(III).

Anal. Calcd. for C₁₂H₂₄Cl₃S₃Cr: C, 34.0; H, 5.7; Cl, 25.1; S, 22.7; Cr, 12.3. Found: C, 34.3; H, 5.2; Cl, 25.2; S, 20.2; Cr, 12.2.

$\Lambda_m(298^\circ\text{K}) = 0.095 \text{ ohm}^{-1} \text{ cm mole}^{-1}$ for a 10^{-3} M solution in CH₂Cl₂.

Magnetic data: At 292°K; $\chi'_m = 6218.6 \times 10^{-6} \text{ c.g.s.u.}$, diamagnetic correction for C₁₂H₂₄Cl₃S₃ = $244.74 \times 10^{-6} \text{ c.g.s.u.}$ and $\mu_{\text{eff}} = 3.81 \text{ BM.}$

The infrared spectrum contained bands at; 2998(w), 2930(s), 2920(s), 2900(sh), 2858(m), 1471(m), 1455(w), 1435(m), 1425(m), 1305(m), 1268(m), 1253(m), 1198(w), 1130(w), 1078(m), 956(m), 878(m), 804(m), 721(w), 696(m), 668(m), 510(w), 471(w), 380(s), 351(s), 293(m) and 278(s) cm⁻¹ respectively.

The electronic spectrum contained bands at; 14,300, 20,100, 26,300 and 38,460(sh) cm⁻¹ respectively when run as the solid.

D) Reaction between TiCl₃·3THF and N,N,N',N'-Tetramethylethylenediamine

Excess of temen was added to the solid TiCl₃·3THF in vacuo and the reaction sealed in an ampoule. After being placed on a mechanical shaker for 1 week a colourless solution and a dark grey solid were obtained. The excess temen was removed in vacuo and the solid product thoroughly washed with n-hexane. The pale grey solid product that was obtained was insoluble in all the

common organic solvents and its composition was non-stoichiometric. The infrared spectrum contained bands at; 3020(sh), 3005(m), 2980(sh), 2950(s), 2915(m), 2855(sh), 2630(sh), 2550(s), 2520(sh), 2435(s), 1537(br-m), 1492(sh), 1481(s), 1473(s), 1455(sh), 1433(m), 1408(m), 1289(s), 1156(s), 1139(m), 1008(s), 988(s) and broad bands at 845, 795, 720, 660, 570, 510, 460 and 375 cm^{-1} respectively.

The reaction was repeated using an excess of temen diluted about 1 in 20 in benzene. The immediate reaction yielded a colourless solution and a black precipitate. The solvent and excess temen were removed in vacuo and the black solid thoroughly washed with n-hexane. The black solid product, trichloro(tetrahydrofuran)bis(N,N,N',N'-tetramethylethylenediamine)titanium(III), was insoluble in most of the common organic solvents, but showed slight solubility in CH_2Cl_2 .

Anal. Calcd. for $\text{C}_{16}\text{H}_{40}\text{Cl}_3\text{N}_4\text{O Ti}$: C, 41.9; H, 8.7; Cl, 23.2; N, 12.2; Ti, 10.5. Found: C, 42.0; H, 8.6; Cl, 23.2; N, 12.1; Ti, 10.5.

$\Lambda_m(298^\circ\text{K}) = 0.60\text{ ohm}^{-1}\text{ cm mole}^{-1}$ for a 10^{-3} M solution in CH_2Cl_2 .

Magnetic data: At 292°K ; $\chi'_m = 994.2 \times 10^{-6}\text{ o.g.s.u.}$, diamagnetic correction for $\text{C}_{16}\text{H}_{40}\text{Cl}_3\text{N}_4\text{O} = 299.43 \times 10^{-6}\text{ o.g.s.u.}$ and

$\mu_{\text{eff}} = 1.52\text{ BM.}$

The infrared spectrum contained bands at; 3015(m), 2960(s), 2910(s), 2890(sh), 2835(m), 2795(sh), 2770(m), 2570(s), 2520(m), 2460(s), 2435(sh), 1468(s), 1441(sh), 1411(w), 1376(w), 1355(sh), 1284(s), 1262(w), 1155(s), 1121(s), 1103(sh), 1066(m), 1042(sh), 1018(sh), 1008(s), 987(s), 955(s), 923(w), 837(m), 800(s), 790(sh), 771(w), 721(w), 677(w), 586(m), 498(m), 474(sh), 444(w), 383(w), 340(sh), 320(sh) and 298 cm^{-1} respectively.

The electronic spectrum contained bands at; 12,500(sh), 13,200,

40,820(sh) and 49,020 cm^{-1} respectively when run as the solid.

E) Reaction between $\text{CrCl}_3 \cdot 3\text{THF}$ and N,N,N',N'-Tetramethylethylenediamine

Excess of temen was added to the solid $\text{CrCl}_3 \cdot 3\text{THF}$ in vacuo and the reaction sealed in an ampoule. After being placed on a mechanical shaker for 1 week a colourless solution and a green solid were obtained. The excess temen was removed in vacuo and the solid product thoroughly washed with n-hexane. The green solid product that was obtained was insoluble in all the common organic solvents and its composition was non-stoichiometric. The infrared spectrum contained bands at; 3270(br), 3010(m), 2950(s), 2915(s), 2850(sh), 2620(sh), 2555(s), 2510(sh), 2445(s), 2420(sh), 1620(br), 1469(s), 1439(sh), 1407(w), 1287(m), 1261(w), 1242(w), 1155(m), 1138(w), 1041(m), 1007(s), 986(s), 953(m), 852(m), 803(m), 768(w), 721(w), 586(sh), 503(br-s) and 329(br-s) cm^{-1} respectively.

The reaction was repeated using an excess of temen diluted about 1 in 20 in benzene. The immediate reaction yielded a colourless solution and a purple precipitate. The solvent and excess temen were removed in vacuo and the purple solid thoroughly washed with n-hexane. The purple solid product, dichlorobis-(N,N,N',N'-tetramethylethylenediamine)chromium(III)tetrachloro-(N,N,N',N'-tetramethylethylenediamine)chromate(III), was insoluble in most of the common organic solvents, but showed slight solubility in CH_2Cl_2 .

Anal. Calcd. for $\text{C}_{18}\text{H}_{48}\text{Cl}_6\text{N}_6\text{Cr}_2$: C, 32.5; H, 7.2; Cl, 32.0; N, 12.6; Cr, 15.6. Found: C, 33.0; H, 7.3; Cl, 30.1; N, 11.7; Cr, 15.4.

$\Lambda_m(298^\circ\text{K}) = 15.5 \text{ ohm}^{-1} \text{ cm mole}^{-1}$ for a 10^{-3} M solution in CH_2Cl_2 .

Magnetic data: At 292°K ; $\chi'_m = 12,817.9 \times 10^{-6} \text{ c.g.s.u.}$, diamag-

netic correction for $C_{18}H_{48}Cl_6N_6 = 402.66 \times 10^{-6}$ c.g.s.u.,

χ'_m per Cr atom = 6408.9×10^{-6} c.g.s.u. and $\mu_{eff} = 3.87$ BM.

The infrared spectrum contained bands at; 3035(m), 3005(m), 2985(s), 2905(s), 2830(w), 2730(w), 1470(s), 1456(sh), 1440(w), 1425(w), 1408(w), 1292(w), 1276(m), 1233(w), 1227(w), 1193(m), 1162(w), 1115(m), 1102(sh), 1063(m), 1043(w), 1029(w), 1010(m), 993(m), 981(m), 956(m), 943(s), 914(w), 802(sh), 795(s), 771(sh), 766(m), 722(w), 703(w), 680(w), 592(m), 519(m), 494(m), 454(w), 416(m), 398(w), 370(w), 340(m), 320(s), 273(w), 254(w) and 217(w) cm^{-1} respectively.

The electronic spectrum contained bands at; 14,080(sh), 14,700, 19,800, 20,490(sh), 25,000(sh), 33,333(sh), 38,460(sh) and 45,870(sh) cm^{-1} respectively when run as the solid.

F) Reaction between $TiCl_3 \cdot 2NMe_3$ and Tris(2-aminoethyl)amine

When a benzene solution of tren was added in vacuo to an equimolar quantity of $TiCl_3 \cdot 2NMe_3$, in benzene solution, an immediate reaction occurred with release of NMe_3 and precipitation of a green solid. The NMe_3 was trapped in an infrared gas cell and identified by its spectrum.⁸⁵ The solid product was thoroughly washed with benzene to remove any unreacted starting material. The product was the sage green solid trichloro(tris(2-aminoethyl)-amine)titanium(III).

Anal. Calcd. for $C_{6H_{18}Cl_3N_4Ti}$: C, 24.0; H, 6.0; Cl, 35.4; N, 18.7; Ti, 16.0. Found: C, 23.8; H, 6.2; Cl, 35.2; N, 18.6; Ti, 15.8.

$\Lambda_m(298^\circ K) = 0.011 \text{ ohm}^{-1} \text{ cm mole}^{-1}$ for a $10^{-3} M$ solution in CH_2Cl_2 .

Melting point: Decomposed at $T > 443^\circ K$.

Magnetic data: At $296^\circ K$; $\chi'_m = 710 \times 10^{-6}$ c.g.s.u., diamagnetic

correction for $C_{6H_{18}Cl_3N_4} = 171 \times 10^{-6}$ c.g.s.u. and $\mu_{eff} = 1.45$ BM.

The infrared spectrum contained bands at; 3198(s), 3130(s), 2945(m), 2898(m), 2720(w), 1580(m), 1475(m), 1320(w), 1290(m),

1144(m), 1070(m), 1060(m), 1030(m), 1010(m), 990(w), 885(m), 795(m), 725(m), 682(m), 672(m), 575(w), 543(w), 372(m) and 310(m) cm^{-1} respectively.

The electronic spectrum contained bands at; 12,300(sh), 12,900 and 39,200(sh) cm^{-1} respectively when run as the solid.

When slight excess, of a 2:1 molar ratio, of a benzene solution of tren was added in vacuo to a benzene solution of $\text{TiCl}_3 \cdot 2\text{NMe}_3$ an immediate reaction occurred; NMe_3 was released and a cream coloured solid precipitated. The NMe_3 was trapped in an infrared gas cell and identified by its spectrum.⁸⁵ The solid product was thoroughly washed with benzene to remove any unreacted starting material. The product was the cream/yellow solid bis(tris(2-aminoethyl)amine)titanium(III)chloride.

Anal. Calcd. for $\text{C}_{12}\text{H}_{36}\text{Cl}_3\text{N}_8\text{Ti}$: C, 32.3; H, 8.1; Cl, 23.8; N, 25.1; Ti, 10.7. Found: C, 31.9; H, 7.8; Cl, 23.6; N, 24.8; Ti, 10.5.

Melting point: Decomposed at $T > 403^\circ\text{K}$.

Magnetic data: At 295°K ; $\chi'_m = 700 \times 10^{-6}$ c.g.s.u., diamagnetic correction for $\text{C}_{12}\text{H}_{36}\text{Cl}_3\text{N}_8 = 282 \times 10^{-6}$ c.g.s.u. and $\mu_{\text{eff}} = 1.52$ BM.

The infrared spectrum contained bands at; 3180(s), 3120(s), 2942(m), 2880(m), 2640(w), 1595(m), 1472(m), 1330(m), 1294(m), 1150(m), 1080(m), 1060(m), 1035(m), 1010(m), 980(w), 880(m), 795(m), 720(m), 680(m), 670(m), 580(w) and 540(m) cm^{-1} respectively.

The electronic spectrum contained bands at; 12,150(sh), 12,800, 24,690(sh) 39,680(sh) cm^{-1} respectively when run as the solid.

G) Reaction between $\text{CrCl}_3 \cdot 2\text{NMe}_3$ and Tris(2-aminoethyl)amine

When a benzene solution of tren was added in vacuo to an equimolar quantity of $\text{CrCl}_3 \cdot 2\text{NMe}_3$, in benzene solution, an immediate reaction occurred with release of NMe_3 and precipitation of a blue solid. The NMe_3 was trapped in an infrared gas cell

and identified by its spectrum.⁸⁵ The solid product was thoroughly washed with benzene to remove any unreacted starting material. The product was the blue/grey solid trichloro(tris(2-aminoethyl)-amine)chromium(III).

Anal. Calcd. for $C_6H_{18}Cl_3N_4Cr$: C, 23.7; H, 5.9; Cl, 34.9; N, 18.4; Cr, 17.1. Found: C, 23.2; H, 6.2; Cl, 34.6; N, 18.1; Cr, 16.9.

$\Lambda_m(298^\circ K) = 0.086 \text{ ohm}^{-1} \text{ cm mole}^{-1}$ for a $10^{-3} M$ solution in CH_2Cl_2 .

Melting point: Decomposed at $T > 420^\circ K$.

Magnetic data: At $295^\circ K$; $\chi'_m = 6050 \times 10^{-6} \text{ c.g.s.u.}$, diamagnetic correction for $C_6H_{18}Cl_3N_4 = 171 \times 10^{-6} \text{ c.g.s.u.}$ and $\mu_{eff} = 3.83 \text{ BM}$.

The infrared spectrum contained bands at; 3195(s), 3110(s), 2950(m), 2890(w), 2850(w), 1578(m), 1465(m), 1358(w), 1262(m), 1151(m), 1075(m), 1043(m), 1030(m), 990(w), 885(w), 800(m), 720(m), 685(m), 675(m), 545(w), 338(s) and 300 cm^{-1} respectively.

The electronic spectrum contained bands at; 16,900, 24,500(sh) and $45,800 \text{ cm}^{-1}$ respectively when run as the solid.

When slight excess, of a 2:1 molar ratio, of a benzene solution of tren was added in vacuo to a benzene solution of $CrCl_3 \cdot 2NMe_3$ an immediate reaction occurred; NMe_3 was released and a pink solid precipitated. The NMe_3 was trapped in an infrared gas cell and identified by its spectrum.⁸⁵ The solid product was thoroughly washed with benzene to remove any unreacted starting material. The product was the pink solid bis(tris(2-aminoethyl)amine)chromium(III)chloride.

Anal. Calcd. for $C_{12}H_{36}Cl_3N_8Cr$: C, 32.0; H, 8.0; Cl, 23.6; N, 24.9; Cr, 11.5. Found: C, 31.8; H, 8.0; Cl, 23.6; N, 24.6; Cr, 11.4.

$\Lambda_m(273^\circ K) = 201 \text{ ohm}^{-1} \text{ cm mole}^{-1}$ for a $10^{-3} M$ solution in water.

Melting point: Decomposed at $T > 395^\circ K$.

Magnetic data: At $294^\circ K$; $\chi'_m = 6060 \times 10^{-6} \text{ c.g.s.u.}$, diamagnetic

correction for $C_{12}H_{36}Cl_3N_8 = 282 \times 10^{-6}$ c.g.s.u. and $\mu_{eff} = 3.86$ BM.

The infrared spectrum contained bands at; 3140(s), 3090(s), 2940(s), 2865(m), 2820(w), 1588(m), 1462(m), 1360(m), 1260(m), 1164(m), 1080(w), 1045(m), 1035(m), 992(w), 888(w), 800(m), 720(m), 690(w), 670(w), 550(w) and 508(w) cm^{-1} respectively.

The electronic spectrum contained bands at; 19,600, 25,780, 39,000(sh) and 45,500(sh) cm^{-1} respectively when run as the solid, and at; 20,060, 26,300 and 39,200(sh) cm^{-1} respectively when run as an aqueous solution.

H) Reaction between $TiCl_3 \cdot 2NMe_3$ and Tris(2-dimethylaminoethyl)amine

When a benzene solution of Me_6tren was added in vacuo to an equimolar quantity of $TiCl_3 \cdot 2NMe_3$, in benzene solution, an immediate reaction occurred with release of NMe_3 and precipitation of a pale blue solid. The NMe_3 was trapped in an infrared gas cell and identified by its spectrum.⁸⁵ The solid product was thoroughly washed with benzene to remove any unreacted starting material. The product was the duck-egg blue solid trichloro-(tris(2-dimethylaminoethyl)amine)titanium(III).

Anal. Calcd. for $C_{12}H_{30}Cl_3N_4Ti$: C, 37.5; H, 7.8; Cl, 27.6; N, 14.5; Ti, 12.5. Found: C, 37.3; H, 7.9; Cl, 27.2; N, 13.8; Ti, 12.6.

$\Lambda_m(298^\circ K) = 0.003 \text{ ohm}^{-1} \text{ cm mole}^{-1}$ for a $10^{-3}M$ solution in CH_2Cl_2 .

Melting point: Decomposed at $T > 408^\circ K$.

Magnetic data: At $293^\circ K$; $\chi'_m = 1486.3 \times 10^{-6}$ c.g.s.u., diamagnetic correction for $C_{12}H_{30}Cl_3N_4 = 242.5 \times 10^{-6}$ c.g.s.u. and $\mu_{eff} = 1.86$ BM.

The infrared spectrum contained bands at; 3030(m), 2983(sh), 2965(sh), 2918(sh), 2892(s), 2842(m), 2825(m), 2795(m), 2765(m), 1478(sh), 1460(s), 1440(sh), 1401(w), 1391(w), 1349(w), 1336(w), 1320(w), 1296(sh), 1288(w), 1276(m), 1259(m), 1232(m), 1170(w), 1161(w), 1150(m), 1100(m), 1084(sh), 1058(m), 1040(sh), 1030(sh), 1016(s), 1002(s), 996(sh), 988(sh), 968(m), 957(m), 947(m),

929(m), 896(w), 881(sh), 871(w), 860(w), 801(s), 790(sh), 776(s), 742(m), 723(m), 672(m), 616(w), 600(w), 581(m), 492(m), 460(w), 445(m), 410(w), 390(w), 355(s), 317(s) and 300(m) cm^{-1} respectively.

The electronic spectrum contained bands at; 12,420(sh), 13,000, 38,610(sh), 39,840(sh) and 46,510(sh) cm^{-1} respectively when run as the solid.

When the reaction was repeated using a five-fold excess of Me_6tren , the only product obtained was shown by analysis and spectral measurements to be identical to that described above.

I) Reaction between $\text{CrCl}_3 \cdot 2\text{NMe}_3$ and Tris(2-dimethylaminoethyl)amine

When a benzene solution of Me_6tren was added in vacuo to an equimolar quantity of $\text{CrCl}_3 \cdot 2\text{NMe}_3$, in benzene solution, an immediate reaction occurred with release of NMe_3 and precipitation of a green solid. The NMe_3 was trapped in an infrared gas cell and identified by its spectrum.⁸⁵ The solid product was thoroughly washed with benzene to remove any unreacted starting material. The product was the green solid trichloro(tris-(2-dimethylaminoethyl)amine)chromium(III).

Anal. Calcd. for $\text{C}_{12}\text{H}_{30}\text{Cl}_3\text{N}_4\text{Cr}$: C, 37.1; H, 7.7; Cl, 27.4; N, 14.4; Cr, 13.4. Found: C, 37.8; H, 7.8; Cl, 27.3; N, 13.9; Cr, 13.1.

$\Lambda_m(298^\circ\text{K}) = 0.0024 \text{ ohm}^{-1}\text{cm mole}^{-1}$ for a 10^{-3}M solution in CH_2Cl_2 .

Melting point: Decomposed at $T > 403^\circ\text{K}$.

Magnetic data: At 293°K ; $\chi'_m = 6322.5 \times 10^{-6} \text{ c.g.s.u.}$, diamagnetic correction for $\text{C}_{12}\text{H}_{30}\text{Cl}_3\text{N}_4 = 242.5 \times 10^{-6} \text{ c.g.s.u.}$ and $\mu_{\text{eff}} = 3.85 \text{ BM.}$

The infrared spectrum contained bands at; 3030(m), 2985(m), 2965(s), 2920(s), 2890(sh), 2842(sh), 2834(m), 2795(sh), 2770(m), 1480(sh), 1462(s), 1431(sh), 1400(w), 1391(w), 1383(w), 1372(w), 1340(w), 1334(sh), 1289(m), 1273(w), 1256(m), 1231(w), 1202(w), 1183(w), 1155(w), 1100(m), 1086(sh), 1051(m), 1038(m), 1027(m),

1012(s), 996(s), 977(sh), 950(s), 931(s), 893(w), 860(m), 795(m), 786(w), 764(s), 742(m), 672(w), 589(m), 572(m), 511(m), 430(m), 399(sh), 383(m), 349(s), 335(s) and 269(m) cm^{-1} respectively.

The electronic spectrum contained bands at; 14,100(sh), 15,430, 21,645, 36,900, 41,150 and 45,870(sh) cm^{-1} respectively when run as the solid, and at; 14,000(sh), 15,050 and 21,140 cm^{-1} respectively when run as a benzene solution.

When the reaction was repeated using a five-fold excess of Me_6tren , the only product obtained was shown by analysis and spectral measurements to be identical to that described above.

J) Reaction between TiCl_4 and Tris(2-aminoethyl)amine

TiCl_4 was co-condensed with benzene onto an equimolar quantity of tren, in vacuo. On warming to room temperature an immediate reaction occurred to give a pale yellow solution and a cream precipitate. The solvent was removed in vacuo and the solid thoroughly washed with benzene to remove any unreacted starting material. The product was the cream coloured solid bis(tris(2-aminoethyl)amine)titanium(IV)chloride.

Anal. Calcd. for $\text{C}_{12}\text{H}_{36}\text{Cl}_4\text{N}_8\text{Ti}$: C, 29.9; H, 7.4; Cl, 29.5; N, 23.2; Ti, 9.9. Found: C, 28.3; H, 7.2; Cl, 30.0; N, 22.3; Ti, 9.7.

The infrared spectrum contained bands at; 3045(s), 3006(s), 2952(s), 2930(sh), 2860(m), 1594(s), 1515(m), 1458(m), 1371(m), 1313(w), 1291(m), 1111(m), 1072(m), 1050(w), 1018(m), 979(w), 928(w), 860(w), 794(m), 721(m), 682(sh), 671(m), 599(m) and 528(w) cm^{-1} respectively.

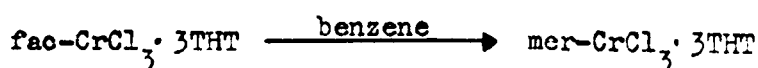
The electronic spectrum contained bands at; 41,666 and 50,000 cm^{-1} respectively when run as the solid.

3.3. DISCUSSION

3.3.A. Complexes of Tetrahydrothiophene

When complexes are prepared using ligands that lie on the border line of ability to stabilise penta-coordination, the metal requirements become critical. This has been aptly demonstrated by the dialkylsulphide complexes of vanadium(III) and chromium(III), the vanadium complexes being five coordinate bis adducts,^{38,40} and the chromium, six coordinate tris adducts.⁴⁰ Here the greater comparative stability of hexa- over penta-coordination of the chromium(III) is clearly demonstrated. Another ligand of this ilk is tetrahydrothiophene, its ability to stabilise five coordinate vanadium(III) having already been demonstrated.³⁸ We find its coordination to chromium(III) shows several interesting features.

Reaction of excess tetrahydrothiophene with either $\text{CrCl}_3 \cdot 2\text{H}_2\text{O}$, or chromic chloride in the presence of a trace amount of zinc, produced the dark blue hexa-coordinate solid $\text{CrCl}_3 \cdot 3\text{THT}$. As chromium(III) is a class A acceptor⁹⁷ complexes of this type, with sulphur donors, are less stable than those with nitrogen or oxygen donors, and few complexes of this class are known.^{40,98} The complex was soluble in the parent ligand, and dissolved in benzene, but with apparant decomposition; rapidly precipitating a lilac solid from the dark blue solution. This solid was insoluble in benzene, and most of the common organic solvents, showing only slight solubility in dichloromethane. Analysis showed this product to be $\text{CrCl}_3 \cdot 3\text{THT}$, though it was obviously different from the dark blue starting material. The reaction in benzene was infact an isomerisation;



Although octahedral chromium(III) complexes of the type $\text{CrX}_3 \cdot 3\text{L}$ can assume both fac- and mer- geometry, in practice it is rare, and one configuration is normally exclusively adopted; e.g. with $\text{L} = \text{THF}$ ⁸⁶ or pyridine,⁹⁹ the mer- configuration is favoured. For the multidentate ligand dien, both fac- and mer- isomers are known,¹⁰⁰ but they are not known to interconvert. Such an isomerisation, as occurs with the THT ligand, has been previously reported;¹⁰¹ the blue fac- $\text{CrCl}_3 \cdot 3\text{NH}_3$, on heating at 423°K for three days, converting to the green mer- $\text{CrCl}_3 \cdot 3\text{NH}_3$, but the individual adducts were not isolated.

Both isomers are non-conducting in dichloromethane solution, $\Lambda_m(298^\circ\text{K})$ at $10^{-3}\text{M} = 0.033$ and $0.095 \text{ ohm}^{-1} \text{ cm mole}^{-1}$ for the fac- and mer- isomers respectively. The value for the fac- isomer is not completely accurate as a slow isomerisation was evident whilst recording this value, however, both complexes are clearly non-electrolytes. The room temperature magnetic moment for the mer-complex, of 3.81 BM., is close to the expected spin only value⁹¹ of a magnetically dilute chromium(III) complex. The value obtained for the fac-complex, 3.56 BM., is somewhat low, but as this value was consistent for several separately prepared samples it is unlikely to be attributable to either impurities in the sample, or to decomposition of this air-sensitive material.

The electronic spectra, TABLE 3.1., are, in the solid state, typical of octahedrally coordinated chromium(III), the first two 'd-d' transitions, ${}^4\text{T}_{2g} \leftarrow {}^4\text{A}_{2g}$ and ${}^4\text{T}_{1g}(\text{F}) \leftarrow {}^4\text{A}_{2g}$, being observed at 14,600 and 20,830 cm^{-1} , and 14,300 and 20,100 cm^{-1} for the fac- and mer- isomers respectively. The weak absorption appearing as a shoulder at 13,510 cm^{-1} in the spectrum of the fac- isomer, is tentatively assigned to the spin forbidden ${}^2\text{E}_g \leftarrow {}^4\text{A}_{2g}$ transition, and as such is indicative of a trigonal

or lower symmetry distortion in the octahedral environment.¹⁰²

TABLE 3.1. Electronic Spectra of $\text{CrCl}_3 \cdot 3\text{THT}$

Complex	Medium	Absorption Maxima (cm^{-1})
$\text{fac-CrCl}_3 \cdot 3\text{THT}$	a	13,510(w-sh); 14,600; 20,830; 28,570; 39,370(w-sh).
	b	8,200(w); 13,550(w-sh); 14,350; 18,315(sh); 20,670.
	c	8,550; 13,520(sh); 14,336; 18,726; 19,530(sh).
$\text{mer-CrCl}_3 \cdot 3\text{THT}$	a	14,300; 20,100; 26,300; 38,460(sh).

a: nujol mull

b: THT solution

c: benzene solution

The remaining intense bands at $25,000 \text{ cm}^{-1}$ onwards, which mask the third 'allowed' 'd-d' transition, are of charge transfer in origin, associated with metal \leftarrow ligand/halide transitions.

The infrared spectra of the two complexes in the $4000\text{--}400 \text{ cm}^{-1}$ region are almost identical; containing bands assignable to coordinated THT.³⁸ The $\nu_{\text{as}}(\text{CSC})$ and $\nu_{\text{s}}(\text{CSC})$ modes, which appear in the free ligand at 819 and 685 cm^{-1} respectively, show the expected small shifts to lower frequency on coordination. The low infrared, $400\text{--}200 \text{ cm}^{-1}$, allows ready distinction to be drawn between the two isomers. The three $\nu(\text{CrCl})$ bands, at 380 , 351 and 278 cm^{-1} in the mer- isomer and the two $\nu(\text{CrCl})$ bands, at 368 and 341 cm^{-1} in the fac- isomer being in accord with the theoretical predictions for these two geometries.^{99,103} The additional less intense band found in each spectrum at $\sim 292 \text{ cm}^{-1}$

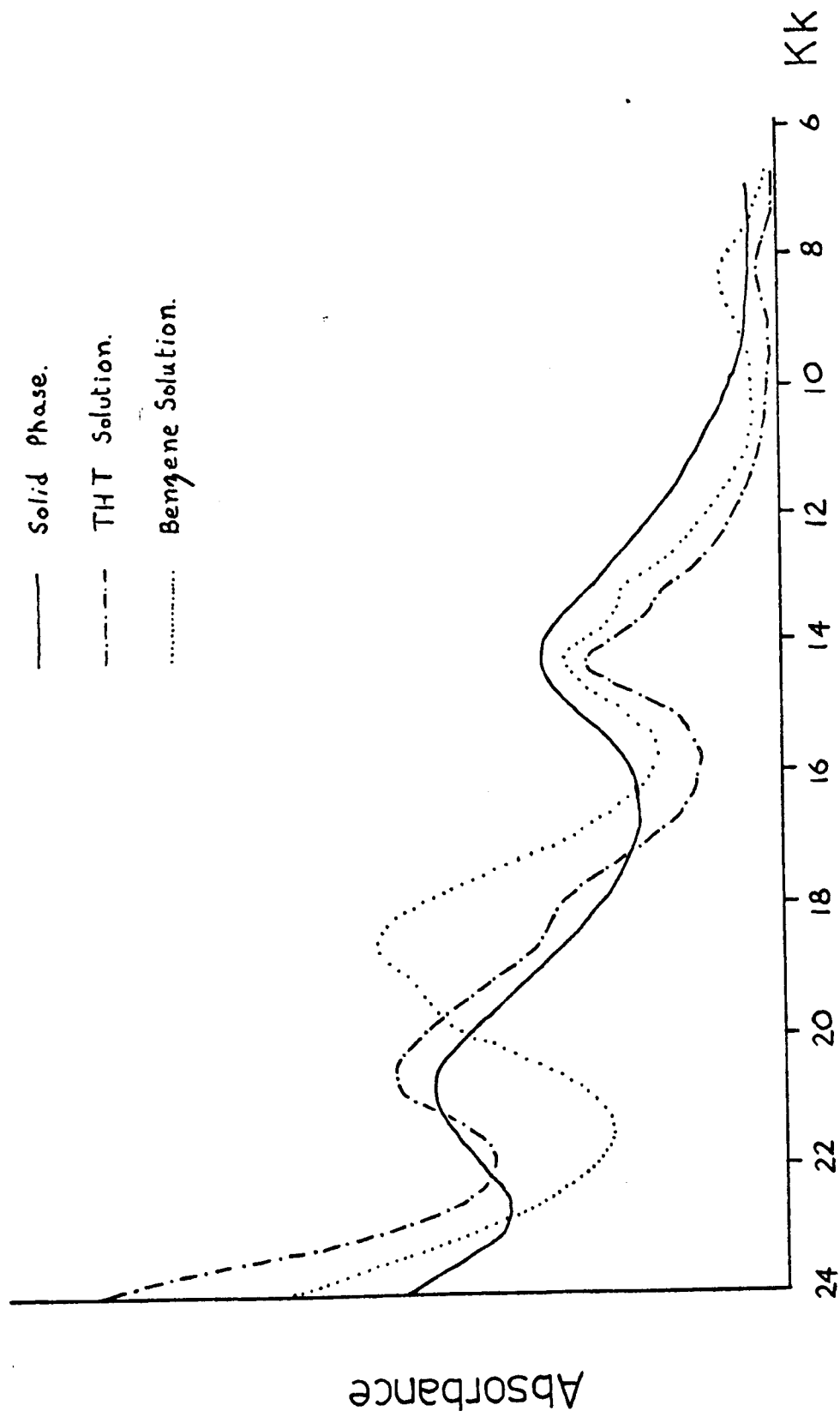


FIGURE 3.1. Electronic Spectra of $\text{fac-CrCl}_3 \cdot 3\text{THT}$

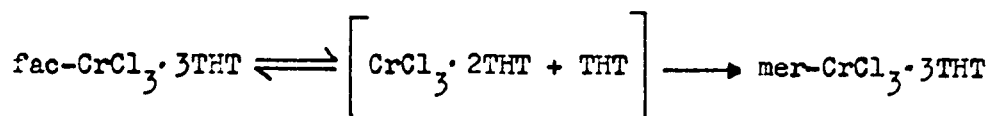
is assigned to a modified $\delta(\text{CSC})$ mode, which appears at 283 cm^{-1} in the free ligand.

Two points of interest that emerge from these complexes are the preferential formation of the fac- isomer and the mechanism of its subsequent isomerisation.

The first is consistent with observations in other octahedral complexes containing π -accepting ligands; where the ligands assume the facial arrangement to obtain a maximum share of the available metal $d\pi$ -electrons.

Concerning the second point, the isomerisation can occur either via a bond rupture mechanism, to give a five coordinate $\text{CrCl}_3 \cdot 2\text{THT}$ intermediate, or via a bond twist mechanism. Without a kinetic study a definite assignment can not be made, but a preference for the first mechanism is supported to some extent by solution spectral data, FIGURE 3.1.. By analogy with the solid phase spectrum the bands that are observed at 14,336 and 19,530(sh) cm^{-1} in the benzene solution spectrum of fac- $\text{CrCl}_3 \cdot 3\text{THT}$ can be assigned to the ${}^4\text{T}_{2g} \leftarrow {}^4\text{A}_{2g}$ and ${}^4\text{T}_{1g}(\text{F}) \leftarrow {}^4\text{A}_{2g}$ 'd-d' transitions respectively. The remaining absorptions are superfluous for an octahedral coordination environment, and can not be attributed to the mer- isomer as this is insoluble in benzene. These additional bands can, however, be interpreted in terms of a five coordinate chromium(III) species of D_{3h} symmetry.¹⁰⁴ The 8,550 cm^{-1} absorption may be assigned to the ${}^4\text{E}'' \leftarrow {}^4\text{E}'$ transition, the 13,520(sh) cm^{-1} absorption to the ${}^4\text{A}_1''$, ${}^4\text{A}_2'' \leftarrow {}^4\text{E}'$ and the 18,726 cm^{-1} absorption to the ${}^4\text{A}_2'$, ${}^4\text{E}''(\text{P})$, ${}^4\text{A}_2'(\text{P}) \leftarrow {}^4\text{E}'$. The shoulder at 13,520 cm^{-1} may also contain a contribution from the spin forbidden ${}^2\text{E}_g \leftarrow {}^4\text{A}_{2g}$ transition of the octahedral species.

This data would suggest a mechanism as depicted in the equation below:



In the presence of excess THT the first stage equilibrium would be forced to the left hand side and result in a repression of the isomerisation. However, from a closer spectral investigation it would appear that this equilibrium exists even in THT. The spectrum of the $\text{fac-CrCl}_3 \cdot 3\text{THT}$ in THT, FIGURE 3.1., contains two bands, at $14,350 \text{ cm}^{-1}$, ${}^4\text{T}_{2g} \longleftarrow {}^4\text{A}_{2g}$, and $20,670 \text{ cm}^{-1}$, ${}^4\text{T}_{1g}(\text{F}) \longleftarrow {}^4\text{A}_{2g}$, but, by increasing the sensitivity of the spectrophotometer by a factor of ten and using a very concentrated solution, further very weak absorptions are discernable. These are found at $8,200$, $13,550(\text{sh})$ and $18,315(\text{sh}) \text{ cm}^{-1}$ respectively, and may be interpreted in terms of a ligand field of D_{3h} symmetry; in the same manner as the comparable absorptions that are observed in the benzene solution.

The implications would seem to be that the five coordinate $\text{CrCl}_3 \cdot 2\text{THT}$ adduct does have some inherent stability, but that the steric requirements of the ligand are insufficient to overcome the preference for octahedral coordination shown by chromium(III). In these results the metal requirement is clearly seen as dominant; as it is also demonstrated that THT is capable of producing a five coordinate complex.

3.3.B. Complexes of N,N,N',N'-tetramethylethylenediamine

As noted, trimethylamine reacts with the trivalent halides of the early transition metals to produce the five coordinate adducts $\text{MX}_3 \cdot 2\text{NMe}_3$. The trans trigonal bipyramidal geometry of these adducts ⁶⁵⁻⁶⁷ serves to minimise the non-bonding interactions between the two amine groups. The bidentate amine N,N,N',N'-tetramethylethylenediamine can be viewed as two coupled

trimethylamine molecules, and might therefore, also be capable of stabilising a five coordinate adduct; though obviously its structure could not be a trans trigonal bipyramid.

Fowles et al. have recently investigated¹⁰⁵ the reactions of this ligand with the anhydrous halides of titanium(III) and vanadium(III), and found that five coordinate adducts were not produced. The products of the reactions were the hexa-coordinate ionic species, $[MX_2 \cdot 2temen] [MX_4 \cdot temen]$. However, the products formed in the reactions of these halides and their adducts are often critically dependent upon the reaction conditions;² and in studying the substitution reactions of the $MX_3 \cdot 3THF$ adducts ($M = Ti$ and Cr) with this ligand, we find it so in this case.

When the tris tetrahydrofuran adducts of titanium(III) and chromium(III) were reacted with excess temen, in the absence of any other solvent, they yielded grey and green solid products respectively. These products were found to be insoluble in all the common organic solvents, and analysis showed them to be of non-stoichiometric composition. Their infrared spectra were poorly resolved, particularly in the metal-halogen region, but indicated the presence of both coordinated THF and temen. The attempts made to isolate discrete adducts from these solids were without success, and it seems probable that these solid are mixtures of polymeric and partial solvolysis material.

These results would seem to stem from kinetic factors, as it has already been demonstrated that stable adducts of this ligand can be isolated. These reactions were therefore repeated adding benzene as a dilutant solvent, and by this method discrete adducts were isolated.

The reaction between $TiCl_3 \cdot 3THF$ and excess temen, diluted about 1 in 20 in benzene, yielded a black solid complex of the

composition $\text{TiCl}_3 \cdot 2\text{temen} \cdot \text{THF}$. The presence of the THF ligand was confirmed by the infrared spectrum, which contained the characteristic $\nu_a(\text{COC})$ and $\nu_s(\text{COC})$ absorptions of coordinated THF at 1008 and 837 cm^{-1} respectively. The complex showed slight solubility in dichloromethane, in which it was non-conducting and therefore not of an ionic formulation.

The room temperature magnetic moment of 1.52 BM. confirms the presence of tervalent titanium(d^1), and the electronic spectrum, TABLE 3.2., is that expected from such an ion experiencing an octahedral ligand field. The broad asymmetric band observed at $13,200\text{ cm}^{-1}$ is assigned to the ${}^2E_g \leftarrow {}^2T_{2g}$ transition, and those at 40,820 and $49,020\text{ cm}^{-1}$ to titanium(d) \leftarrow chlorine(π) charge transfers.

TABLE 3.2. Electronic Spectra of temen Adducts of Ti(III) and Cr(III)

Complex	Medium	Absorption Maxima (cm^{-1})
$\text{TiCl}_3 \cdot 2\text{temen} \cdot \text{THF}$	a	12,500(sh); 13,200; 40,820(sh); 49,020.
$\text{CrCl}_3 \cdot 1.5\text{ temen}$	b	14,080(sh); 14,700; 19,800; 20,490(sh); 25,000(sh); 33,330(sh); 38,460(sh); 45,870(sh).

a: nujol mull

b: KBr disc

The visualised structure of this adduct, FIGURE 3.2., bears some similarity to a recently proposed structure of another titanium(III) mixed ligand adduct.¹⁰⁶ Evidence in support of this structure is seen in the non-equivalence of the dimethylamino groups, which is revealed in the infrared spectrum. The spectrum contains, in particular, two distinct CH_3 rocking modes, observed

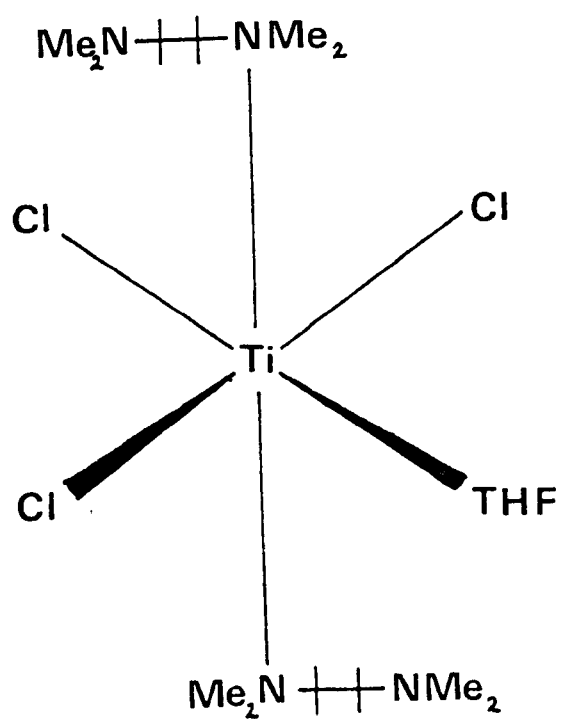


FIGURE 3.2. Proposed Structure for $\text{TiCl}_3 \cdot 2 \text{temen} \cdot \text{THF}$

at 1155 and 1121 cm^{-1} and two $\nu(\text{CN})$ modes, at 1066 and 1042 cm^{-1} . In addition, the bands observed in the 2750-2850 cm^{-1} region are indicative of there being some non-coordinated amine groups present in the adduct. It has been shown^{107,108} that the bands in this region are associated with the methylated amine group, and are only observed when the nitrogen lone pair is not involved in coordination. If these electrons are involved in bonding the peaks shift to higher frequency and are lost in the 'normal' CH absorptions. The peaks found in the 2400-2600 cm^{-1} region, though of unusually high intensity, are assigned to overtone and combination frequencies.¹⁰⁹

Although it was not possible to carry out a molecular weight determination, due to the lack of solubility shown by the adduct, any degree of polymerisation, either through the uncoordinated amines or via halogen bridging, is thought to be unlikely. The presence of any such association, in order to maintain the determined stoichiometry, would necessarily involve an increase in the coordination number of the titanium; an action for which there is no support.

The reaction between excess temen, diluted about 1 in 20 in benzene, and $\text{CrCl}_3 \cdot 3\text{THF}$ yielded the purple ionic product $[\text{CrCl}_2 \cdot 2\text{temen}] [\text{CrCl}_4 \cdot \text{temen}]$; analogous to those previously isolated for titanium and vanadium.¹⁰⁵ The recorded molar conductivity of 15.5 $\text{ohm}^{-1} \text{ cm mole}^{-1}$, at 10^{-3} M in dichloromethane, is that expected for a 1:1 electrolyte in this solvent.¹¹⁰ The infrared spectrum in the 4000-400 cm^{-1} region confirms the absence of THF, and bears extensive similarity to those reported¹⁰⁵ for the analogous titanium and vanadium complexes. This evidence is seen as support for their structural similarity. The absence of absorptions in the 2750-2850 cm^{-1} region is added confirm-

ation that all the amine ligands are acting as bidentate donors.

The electronic spectrum, TABLE 3.2., of the complex can be interpreted in terms of an octahedral field, and is clearly indicative of there being more than one absorbing species present. The first two absorptions of the spectrum, observed at 14,700 and 19,800 cm^{-1} show a doublet structure, with shoulders occurring at 14,080 and 20,490 cm^{-1} . The absorptions at 14,080 and 19,800 cm^{-1} may be assigned to the expected ${}^4\text{T}_{2g} \leftarrow {}^4\text{A}_{2g}$ and ${}^4\text{T}_{1g}(\text{F}) \leftarrow {}^4\text{A}_{2g}$ transitions, O_h symmetry, of the anion, and those at 14,700 and 20,490 cm^{-1} to the same transitions associated with the cation. This assignment is made following the ligand field order of $\text{temen} > \text{Cl}$.¹⁰⁵ The remaining high intensity bands at 25,000 cm^{-1} onwards, are of charge transfer in origin and prevent the observation of the third 'allowed' 'd-d' transition, the ${}^4\text{T}_{1g}(\text{P}) \leftarrow {}^4\text{A}_{2g}$.

The trans trigonal bipyramidal geometry of the bis trimethylamine adducts serves to minimise the non-bonding interactions between the amine groups. In complexes of temen, which has approximately the same steric volume as two trimethylamines, this separation is not possible. Therefore the relief from steric strain which can be gained by forming a five coordinate complex would not be as great as that gained in the bis trimethylamine adducts. This loss of driving force for penta-coordination is seen to allow the octahedral preference of the metal to take effect.

3.3.C. Complexes of Tris(2-aminoethyl)amine and Tris(2-dimethylaminoethyl)amine

Ligands of the general form $D(-(\text{CH}_2)_n\text{D})_3$, where D is a donor atom, exhibit a strong ability to stabilise five coordinate metal complexes. This is partly a result of their threefold symmetry enabling the donor atoms to readily occupy four sites of a trigonal bipyramidal structure; the most common geometry found for five coordinate complexes of the transition metals³².

Two ligands of this type are tris(2-aminoethyl)amine, (tren), and tris(2-dimethylaminoethyl)amine, (Me_6tren). The two atoms in each of the carbon chains of these ligands enable a network of three five membered chelate rings to be formed on complexation, endowing these ligands with powerful chelating properties.¹¹¹ Both ligands have already demonstrated their ability to give numerous five coordinate metal complexes,¹¹²⁻¹¹⁷ and tren has also shown the ability, not found in Me_6tren , to give six coordinate complexes.¹¹⁸⁻¹²⁵ For the most part the complexes have been of the divalent metals of the later transition series, though a five coordinate chromium(II) adduct has been isolated.³⁵

In the reactions of these ligands with the tervalent halides of titanium and chromium we see that the metal requirements are the dominant influence in complexation, and deny the ligand its usual tetradentate role.

3.3.C.i. Complexes of Tris(2-aminoethyl)amine

When the $\text{MCl}_3 \cdot 2\text{NMe}_3$ adducts ($M = \text{Ti}$ and Cr) were reacted with the ligand tren, in benzene solution, two types of adduct were obtained, depending upon the stoichiometry of the reactants. When an equimolar ratio of metal to ligand was used, the mono-adducts, $\text{MCl}_3 \cdot \text{tren}$, were obtained as green and blue/

purple solids for the titanium and chromium species respectively. When the reaction ratio was adjusted to a slightly more than 2:1 molar excess of ligand, the yellow/green titanium and pink chromium bis adducts, $\text{MCl}_3 \cdot 2\text{tren}$, were obtained.

In each case the reaction proceeded smoothly and rapidly with release of trimethylamine and precipitation of the appropriate adduct. The room temperature magnetic moments, $\text{TiCl}_3 \cdot \text{tren}$: 1.45 BM., $\text{TiCl}_3 \cdot 2\text{tren}$; 1.52 BM., $\text{CrCl}_3 \cdot \text{tren}$; 3.83 BM. and $\text{CrCl}_3 \cdot 2\text{tren}$; 3.86 BM., confirm that each adduct is a genuine trivalent titanium(d^1) or chromium(d^3) species, the magnetic moment being close to the appropriate spin only value.⁹¹

The mono-adducts decomposed immediately in donor solvents, such as acetonitrile, THF and methanol, and were insoluble in most non-coordinating solvents. They did, however, show slight solubility in dichloromethane, allowing conductivity measurements to be made in this solvent. They were found to be non-conducting, and so non-ionic.

The bis adducts were found to be insoluble in hydrocarbon and halogenated hydrocarbon solvents, and to generally decompose rapidly in donor solvents. An exception was the chromium complex, which at 273°K gave aqueous and methanolic solutions that were stable over a period of about ten minutes. In aqueous solution at this temperature the molar conductivity was $201 \text{ ohm}^{-1} \text{ cm mole}^{-1}$, at 10^{-3} M concentration. Conductivity quoted at this temperature is scarce, so for means of comparison the $[\text{Cr}(\text{en})_3] \text{Cl}_3$ complex was prepared,¹²⁶ and its conductivity in aqueous solution investigated. The results for a 10^{-3} M solution in the temperature range 273–298°K are shown in FIGURE 3.3.. From the value of $207 \text{ ohm}^{-1} \text{ cm mole}^{-1}$ obtained at 273°K we conclude that the chromium bis adduct shows ionic dissociation typical of a 3:1 electrolyte.

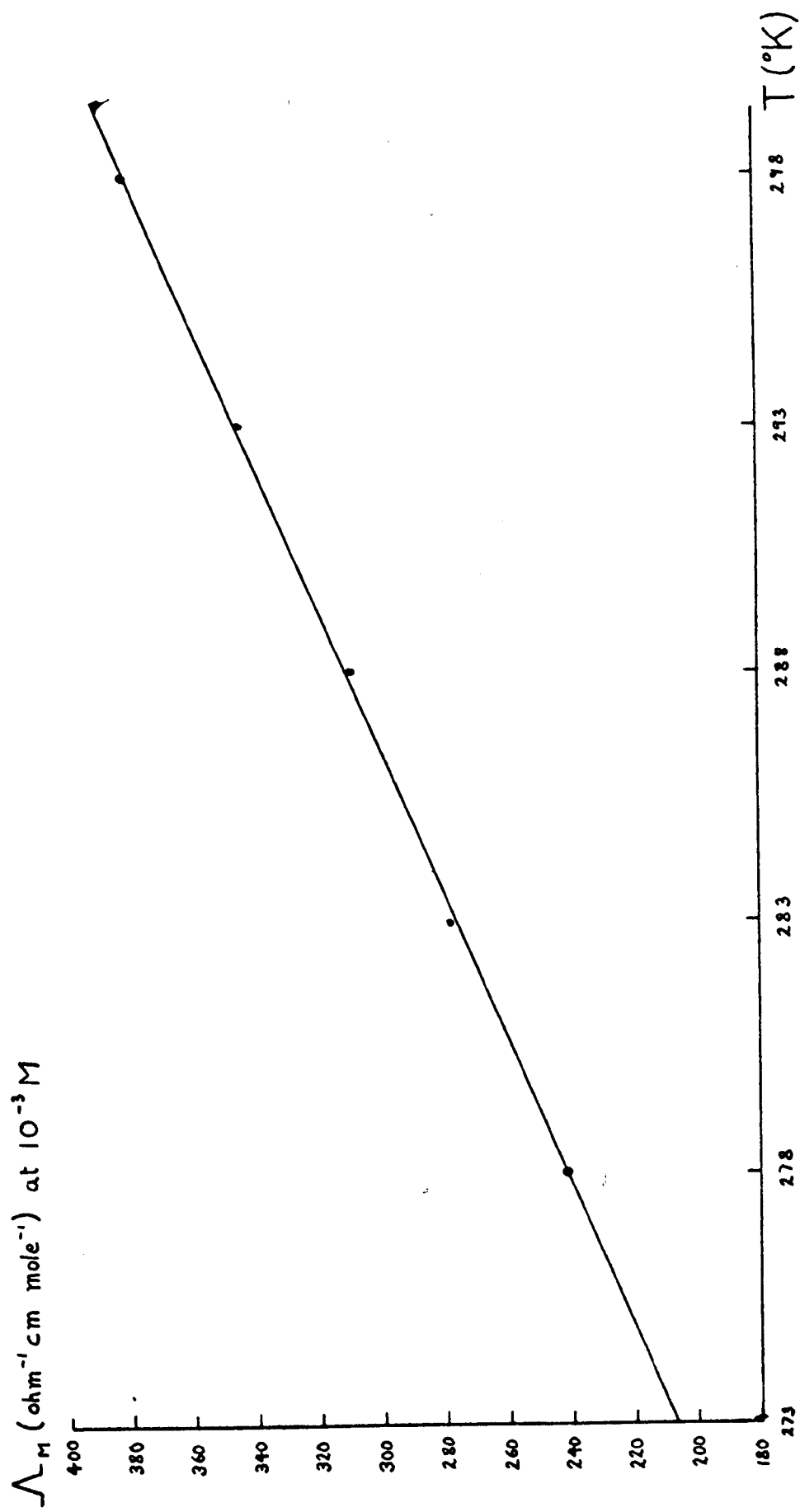


FIGURE 3.3. Temperature Dependence of Λ_m for $[\text{Cr}(\text{en})_3]\text{Cl}_3$

Further evidence in support of a $\left[\text{Cr}(\text{tren})_2 \right] \text{Cl}_3$ formulation was gained from a controlled metathetical reaction with sodium tetraphenylborate. The reaction, in standard aqueous solution at 273°K, was found to occur according to the equation:



The chromium cation was quantitatively precipitated out of solution as the tetraphenylborate salt, and titration of the remaining solution, by the Volhard method, indicated the presence of three equivalents of ionised chloride ion.

Unfortunately the analogous titanium complex was not amenable to similar studies as it decomposed rapidly on dissolution, even at 273°K. However, evidence for the two adducts having a common ionic formulation, $\left[\text{M}(\text{tren})_2 \right] \text{Cl}_3$, is obtained from the low infrared spectra, 500-200 cm^{-1} . Metal-halogen stretching frequencies for titanium(III) and chromium(III) chloro complexes are normally located in the 300-400 cm^{-1} region, appearing as intense broad absorptions. The spectra of the two bis adducts show no such bands in this region, infact no absorptions below 500 cm^{-1} were observed, and therefore a formulation involving covalent metal-halogen linkages is ruled out.

In contrast the low infrared of the non-ionic $\text{MCl}_3 \cdot \text{tren}$ complexes show two intense bands, at 372 and 310 cm^{-1} for the titanium adduct and 338 and 300 cm^{-1} for the chromium adduct, and are assigned to $\nu(\text{TiCl})$ and $\nu(\text{CrCl})$ modes respectively. The appearance of these bands is consistent with C_{3v} molecular symmetry, and an octahedral fac- arrangement of the chlorine ligands.¹⁰³

The electronic spectra, TABLE 3.3., of the two chromium adducts are readily interpreted in terms of a pseudo-octahedral

ligand field. The spectrum of the bis adduct in aqueous solution at 273°K is almost identical to that recorded in the solid state, implying that no change in stereochemistry occurs on dissolution.

TABLE 3.3. Electronic Spectra of the tren Adducts of Ti(III) and Cr(III)

Complex	Medium	Absorption Maxima (cm ⁻¹)
tren	a	rising to 40,000.
TiCl ₃ ·tren	b	12,300(sh); 12,900; 39,200(sh).
[Ti(tren) ₂]Cl ₃	b	12,150(sh); 12,800; 24,690(sh); 39,680(sh).
CrCl ₃ ·tren	b	16,900; 24,500(sh); 45,800(sh).
[Cr(tren) ₂]Cl ₃	c	19,600; 25,780; 39,000(sh); 45,500(sh).
	d	20,060; 26,300; 39,200(sh).

a: methanol solution

b: nujol mull

c: KBr disc

d: aqueous solution at 273°K

The bands at 20,060 cm⁻¹ and 26,300 cm⁻¹ are assigned to the ${}^4T_{2g} \leftarrow {}^4A_{2g}$ and ${}^4T_{1g}(F) \leftarrow {}^4A_{2g}$ transitions (O_h symmetry) respectively. The first band represents the ligand field splitting parameter 10Dq, and is similar to that found for other CrN₆ chromophores.⁶⁴ Similar assignments for the mono-adduct gives the ${}^4T_{2g} \leftarrow {}^4A_{2g}$ transition at 16,900 cm⁻¹ and the ${}^4T_{1g}(F) \leftarrow {}^4A_{2g}$ at 24,500 cm⁻¹.

By using the Dq values of 2006 cm⁻¹ for tren and 1345 cm⁻¹ for Cl⁻⁴⁴ the first ligand field band for CrCl₃·tren is computed at 16,755 cm⁻¹ by Jørgensen's rule of average environment, showing excellent agreement with the observed value.

The electronic spectrum of octahedrally coordinated tit-

anium(III) shows only one 'd-d' transition, the ${}^2E_g \leftarrow {}^2T_{2g}$ ($10Dq$), but this may be modified by the presence of distortions in the octahedral geometry. The observed 'd-d' transition for the titanium complexes, $12,900\text{ cm}^{-1}$ and $12,800\text{ cm}^{-1}$ for the mono and bis adducts respectively, are rather low for the $10Dq$ transition, compared with the values obtained for the chromium adducts, and are unlikely to be the ${}^2E_g \leftarrow {}^2T_{2g}$ transition. By analogy with the spectral analysis of $[\text{Cr}(\text{en})_3]^{3+}$ and $[\text{Ti}(\text{en})_3]^{3+}$ complexes,⁴⁹ these bands may be assigned to the ${}^2E_g \leftarrow {}^2A_1$ transition expected for an octahedrally coordinated titanium(III) species experiencing a strong trigonal field distortion.

The infrared spectra of these complexes contain several areas which proved diagnostically useful, and a number of important observations can be made from the spectra. The bands that are of major importance are shown in TABLE 3.4..

TABLE 3.4. Some Infrared Bands of the tren Adducts of Ti(III) and Cr(III)

Complex	Assignments (cm^{-1})				
	$\nu_{\text{as}}(\text{NH})$	$\nu_{\text{s}}(\text{NH})$	$\nu_{\text{s}}(\text{NH})$ calcd.*	CH_2 rock	$\nu(\text{MCl})$
tren	3358(s)	3282(s)	3283	904(m)	
$\text{TiCl}_3 \cdot \text{tren}$	3198(s)	3130(s)	3142	885(m)	372(m) 310(m)
$[\text{Ti}(\text{tren})_2]\text{Cl}_3$	3180(s)	3120(s)	3126	880(m)	
$\text{CrCl}_3 \cdot \text{tren}$	3195(s)	3110(s)	3140	883(w)	338(m) 300(m)
$[\text{Cr}(\text{tren})_2]\text{Cl}_3$	3140(s)	3090(s)	3089	888(m)	

* Calculated from the equation $\nu_{\text{s}} = 345.53 + 0.875 \nu_{\text{as}}$ ¹²⁷

The relevance of the absorptions in the metal-halogen region

of the complexes has already been discussed.

The absence of bands that are characteristic of coordinated trimethylamine ³⁸ confirms the observation that this amine was replaced in the adducts during the initial reaction with tren.

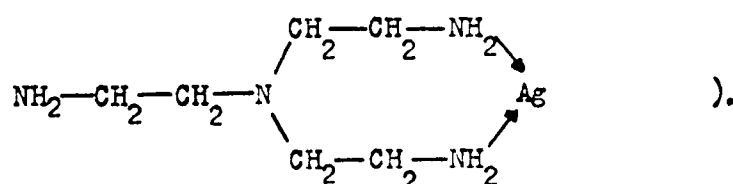
The two bands found in the 3200-3400 cm^{-1} region of tren can be assigned to the $\nu_{\text{as}}(\text{NH})$, 3358 cm^{-1} , and $\nu_{\text{s}}(\text{NH})$, 3282 cm^{-1} , modes of the primary amine groups. In the complexes these two bands are observed at frequencies lower by some 100-200 cm^{-1} from those of the free ligand. This reduction is characteristic of amine coordination, and is due to the drainage of electron density from the amine lone pair.¹²⁸ The fact that only two bands are observed suggests that all the primary amine groups are in identical environments; if this were not the case, a more complex peak profile would be expected.¹²³ This point was confirmed by applying the equation $\nu_{\text{s}} = 345.53 + 0.875 \nu_{\text{as}}$,¹²⁷ which relates the $\nu_{\text{s}}(\text{NH})$ and $\nu_{\text{as}}(\text{NH})$ modes of primary amines only when all the primary amines present are identical. The close agreement between the calculated $\nu_{\text{s}}(\text{NH})$ values and the observed values, TABLE 3.4., confirms that this is the case in the complexes.

One of the most important regions of the spectrum in complexes of this type lies between 750-900 cm^{-1} , and contains the CH_2 rocking modes of the metal-chelate ring. It has been shown that when a metal complex contains two or more five membered chelate rings that are non-coplanar, two CH_2 rocking modes are observed in this region, but only one if all the rings are coplanar.^{115,122,129-131} All the complexes isolated show only one band in this region of the spectrum. This means that the tren ligand can not be behaving as a tetradentate donor, as this would of structural necessity produce non-coplanar five membered chelate rings. Moreover, the necessary formulation that would be required for the mono-adducts,

$\left[\text{MCl}_2 \cdot \text{tren} \right] \text{Cl}$, has already been disproved.

The spectral evidence shows that the three primary amine groups of the ligand are in equivalent environments, which is a situation that can only occur in a fac-octahedral geometry. This geometry is also implied by the observed metal-halogen stretching frequencies. Therefore, from the accumulated data, tren in these complexes must be acting as a terdentate donor through the three primary nitrogens. To confirm the presence of an uncoordinated nitrogen in the complexes, a conductometric titration, with aqueous trichloroacetic acid, was carried out on the bis tren chromium adduct, at 273°K. The titration curve obtained, FIGURE 3.4., is typical of a strong acid-weak base system, and contains a break corresponding to an equivalence point of 1:1.9.

The exhibition of diminished denticity is not unknown for multidentate amines, as complexes of this type are already known for the ligands tetren,^{132,133} trien,¹³⁴ dien¹³⁵ and en.¹³⁶ However, this is the first time that the powerful chelation effects in tren have been broken; (although the structure of $\left[\text{Ag} \cdot \text{tren} \right]^+$ has been suggested¹³⁷ as being



Perhaps one of the oddest features of these complexes is the preferential formation of eight membered chelate rings as opposed to five membered, which are normally accepted as the more stable.¹¹¹ However, such behaviour is not unreasonable; the energy gain on forming a five membered ring is not large

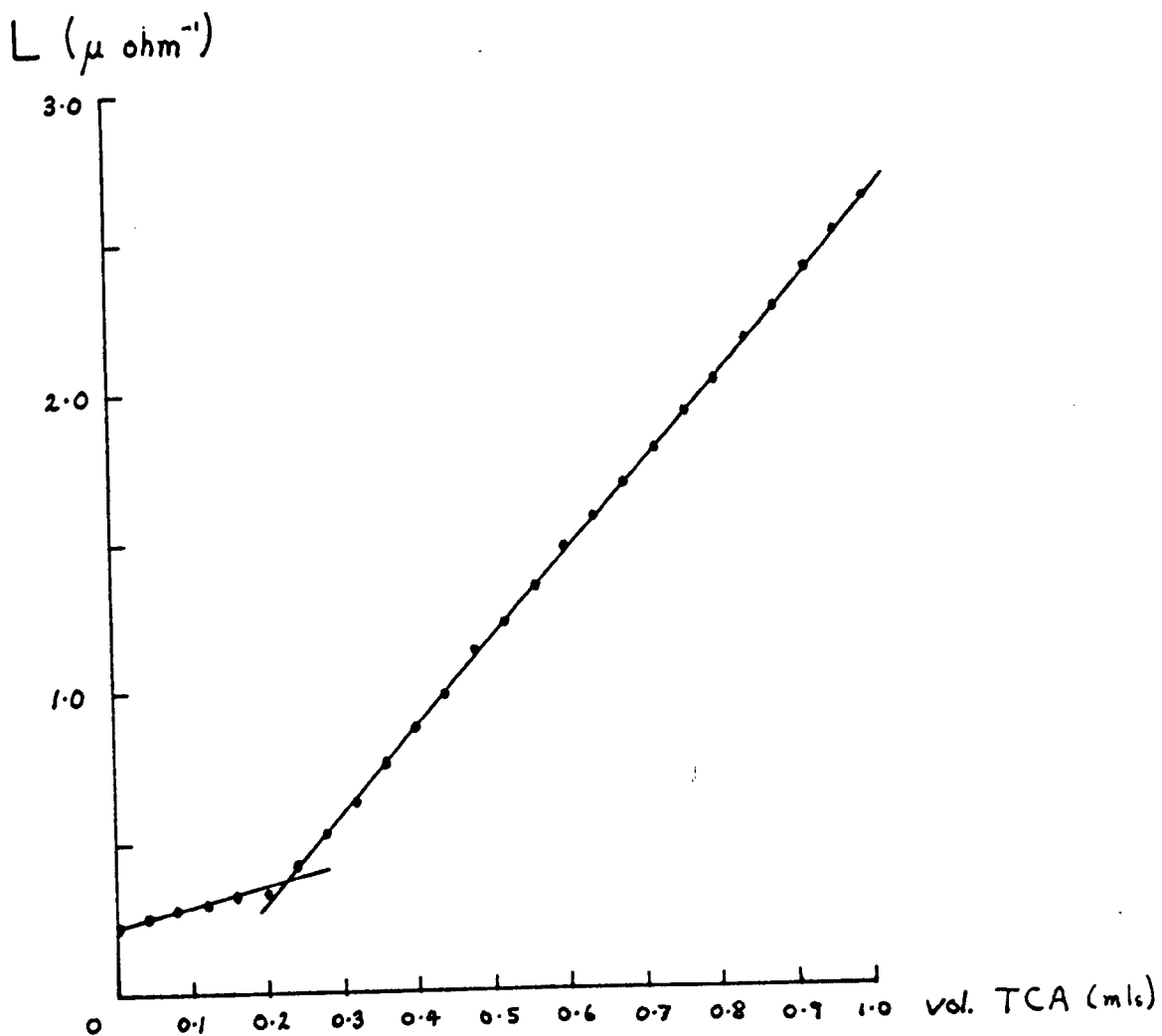


FIGURE 3.4. Conductometric Titration
of $[\text{Cr}(\text{tren})_2]\text{Cl}_3$ against TCA
100 mls $1.247 \times 10^{-3} \text{ M } [\text{Cr}(\text{tren})_2]\text{Cl}_3 \propto 0.993 \text{ M TCA}$.

and may easily be offset by other factors. Two such factors are present in the structure of tren.

One; the tertiary amine centre in tren is a weaker donor than the primary amine sites, this being mainly a result of steric factors.⁶⁸⁻⁷⁰

Two; the chelate rings that are formed in complexes of tren are linked rings, and in cases such as this, steric factors can reduce the effectiveness of five membered rings considerably. In these circumstances it is often found that larger rings are the more stable;¹³⁸ the greater available flexibility reducing steric strain.

3.3.C.ii. Complexes of Tris(2-dimethylaminoethyl)amine

The reactions between the $MCl_3 \cdot 2NMe_3$ adducts ($M = Ti$ and Cr) and the ligand Me_6tren , in benzene solution, proceeded smoothly and rapidly, with release of trimethylamine and precipitation of the solid product. The products obtained were found to be independent of the ligand concentration, and were of the formulation $MCl_3 \cdot Me_6tren$. The room temperature magnetic moments, of 1.86 BM. for the duck-egg blue $TiCl_3 \cdot Me_6tren$ and 3.85 BM. for the green $CrCl_3 \cdot Me_6tren$, were close to the expected spin only values,⁹¹ and confirmed them as being genuine trivalent titanium(d^1) and chromium(d^3) species respectively.

The complexes decomposed rapidly in donor solvents and were insoluble in most of the non-donor organic solvents, but did show slight solubility in dichloromethane. The chromium(III) species also showed a slight solubility in benzene, which was sufficient to make solution spectral measurements, but insufficient to allow a molecular weight determination. In dichloromethane solution each complex was found to be non-conducting,

and so of non-ionic formulation.

The electronic spectra, TABLE 3.5., may be interpreted on the basis of an octahedral ligand field. The spectrum of the chromium(III) complex is essentially the same both in the solid state and in benzene solution, the implication being that no change in the geometry of the complex occurs on dissolution.

TABLE 3.5. Electronic Spectra of the Me_6tren Adducts of Ti(III) and Cr(III)

Complex	Medium	Absorption Maxima (cm^{-1})
$\text{TiCl}_3 \cdot \text{Me}_6\text{tren}$	a	12,420(sh); 13,000; 38,610(sh); 39,840(sh); 46,510(sh).
$\text{CrCl}_3 \cdot \text{Me}_6\text{tren}$	a	14,100(sh); 15,430; 21,645; 36,900; 41,150; 45,870(sh).
	b	14,000(sh); 15,050; 21,140.

a: nujol mull

b: benzene solution

The first two expected 'd-d' transitions of O_h symmetry, the ${}^4T_{2g} \leftarrow {}^4A_{2g}$ and the ${}^4T_{1g}(F) \leftarrow {}^4A_{2g}$, are observed at $15,430 \text{ cm}^{-1}$ and $21,645 \text{ cm}^{-1}$ respectively, in the solid state. The remaining 'allowed' transition, the ${}^4T_{1g}(P) \leftarrow {}^4A_{2g}$, was undetected, as it was masked by the intense charge transfer absorptions, of the chromium(d) \leftarrow chlorine(π) type, present above $30,000 \text{ cm}^{-1}$. A lowering from pure O_h symmetry in this complex is apparent from the spectra. The weak shoulder that is found on the low energy side of the ${}^4T_{1g}(F)$ transition, at $14,100 \text{ cm}^{-1}$, may be assigned to the spin forbidden ${}^2E_g \leftarrow {}^4A_{2g}$ transition, and as such is indicative of a trigonal or lower symmetry distortion being present.¹⁰²

The electronic spectrum of the titanium adduct indicates

that a similar distortion is also present in this complex. The only observed 'd-d' transition occurs at $13,000\text{ cm}^{-1}$, which is similar to that observed in the analogous tren complex, $\text{TiCl}_3 \cdot \text{tren}$, at $12,900\text{ cm}^{-1}$. This low value, when considered against the 10Dq value of the chromium adduct, which shows a reduction from $16,900\text{ cm}^{-1}$ for $\text{CrCl}_3 \cdot \text{tren}$ to $15,430\text{ cm}^{-1}$ for $\text{CrCl}_3 \cdot \text{Me}_6\text{tren}$, is unlikely to be associated with the ${}^2\text{E}_g \leftarrow {}^2\text{T}_{2g}$ (10Dq) transition of a d^1 ion in a field of O_h symmetry. It may, however, be assigned to the ${}^2\text{E}_g \leftarrow {}^2\text{A}_1$ transition expected from such an ion experiencing an octahedral field with a strong trigonal distortion.

The low infrared of each complex shows two intense bands in the metal-halogen region, at 355 and 317 cm^{-1} for the titanium adduct and at 349 and 335 cm^{-1} for the chromium adduct. The appearance of these bands is consistent with the halogen atoms having the fac- geometry in the octahedral complexes.

The infrared spectra from $4000\text{--}400\text{ cm}^{-1}$ contained several areas from which important structural information could be gained. The evidence from the spectra suggests that the Me_6tren ligand is behaving in a similar manner to that of the analogous tren ligand, in that it is acting as a terdentate donor. A major difference that is apparent though, is that in the Me_6tren adducts donation is by the central nitrogen atom and two of the terminal amino groups, leaving an uncoordinated NMe_2 group.

The appearance of medium to strong bands in the $2750\text{--}2850\text{ cm}^{-1}$ region of the infrared spectrum is characteristic of an uncoordinated NMe_2 group, these bands on coordination moving to higher frequency and being lost in the 'normal' CH absorptions.^{107,108} The spectra of both complexes exhibit such bands in this region and are indicative of there being a free NMe_2 group present. Further evidence in support of this is gained from other regions of the spectra, where a clear non-equivalence of the terminal

dimehtylamino groups is shown. The strong NMe_2 stretch that is found at 1004 and 989 cm^{-1} in $\text{Me}_6\text{tren}\cdot 3\text{HCl}$ (assigned in comparison with the work of Mureinik and Robb¹⁰⁹) is observed as four bands in the spectra of the complexes, at 1016 , 1002 , 947 and 929 cm^{-1} respectively for the titanium adduct and at 1012 , 996 , 950 and 931 cm^{-1} respectively for the chromium adduct. The strong NMe_2 bending mode, found at 1291 cm^{-1} in $\text{Me}_6\text{tren}\cdot 3\text{HCl}$, also shows a distinct doublet profile, appearing at 1276 and 1259 cm^{-1} and at 1289 and 1256 cm^{-1} for the titanium and chromium adducts respectively.

Each complex shows two absorptions in the $750\text{--}900\text{ cm}^{-1}$ region, that are associated with the CH_2 rocking modes of the chelate rings. The appearance of these bands is indicative of the complexes containing two or more non-coplanar five membered chelate rings,^{115,122,129-131} and a fac- arrangement is suggested. This geometry, also indicated by the metal-halogen stretching modes, can be confirmed by reference to the work of Schmidtke and Garthoff.¹³¹ They have shown that in the metal complexes of the multidentate ligand dien, the fac- geometry, which gives rise to two non-coplanar chelate rings, shows three absorptions in the CH_2 wag region of the infrared spectrum, $1400\text{--}1500\text{ cm}^{-1}$. The Me_6tren complexes show the same profile in this region, as a strong peak with a distinct shoulder to both the high and low energy sides of this absorption.

The accumulated data again shows that the tetradentate role of the ligand is defeated by the octahedral requirements of the metal nucleus. This diminished denticity for Me_6tren is rare, there being only one brief mention in the literature¹¹⁷ prior to this work, and is indicative of the amount of control the metal ion has in determining the geometry of these complexes.

These adducts show great similarity to the analogous tren adducts, described earlier, the major points of divergence being in the choice of donor sites by the ligands. In the tren complexes the formation of five membered chelate rings is foregone in preference to the formation of a sterically less hindered complex, via donation of the primary amine groups. In Me_6tren all the potential donor sites present approximately equivalent steric bulk, and so little steric relief can be gained by donation solely through the terminal amine groups. In this situation the formation of the energetically more favourable five membered chelate rings is chosen, and achieved via donation through the central nitrogen and two of the terminal nitrogens.

A second point of divergence was the failure to produce the analogous bis adducts, $[\text{M}(\text{Me}_6\text{tren})_2]\text{Cl}_3$. This can obviously be seen as a direct result of the enormous steric bulk that two molecules of Me_6tren must represent to the metal centre.

3.3.D. The Reaction of TiCl_4 with Tris(2-aminoethyl)amine

For a considerable time after tren was first introduced into coordination chemistry, in 1925,¹³⁹ it was thought that its structure, with a donor atom at each corner of a tetrahedron, would be ideal for the preparation of tetrahedral metal complexes. Several complexes, particularly of nickel and platinum, were isolated and tentatively assigned a tetrahedral geometry. For the most part these complexes were later shown to have octahedral geometry. (e.g. see ref. 121.) To this date a tetrahedral metal complex of tren has not been isolated.

In this light titanium tetrachloride, being tetrahedral and monomeric, coupled with the ability shown by tren to displace

chloride from the first coordination sphere of the early transition metals, (see earlier in this chapter), seemed a potential precursor to such a complex. Accordingly, the reaction between this halide and the ligand tren was studied.

The reaction between TiCl_4 and tren, in benzene solution, proceeded smoothly and rapidly, precipitating a cream solid and leaving a pale yellow solution. On removal of the solvent a quantity of unreacted TiCl_4 was also removed, leaving a cream diamagnetic solid which analysed for $\text{TiCl}_4 \cdot 2\text{tren}$. No evidence for either ammonolysis or reduction was found.

The electronic spectrum of the adduct was typical of a titanium(IV) d^0 system; showing no absorptions in the near infra-red or visible, only intense charge transfer bands in the UV, at 41,666 and 50,000 cm^{-1} .

The infrared spectrum showed no absorptions in the metal-halogen region, in fact none were detected below 500 cm^{-1} , indicating that all the chlorides had been displaced from the inner coordination sphere of the metal. The spectrum between 4000-500 cm^{-1} was very similar to that recorded for the tervalent complex $[\text{Ti}(\text{tren})_2]\text{Cl}_3$. It would appear from this that the ligand is exhibiting the same donation behaviour as in the tervalent complex, i.e. donation through the three terminal amine groups. Further evidence for this can be derived from the observation of only two (NH) stretching modes, found at 3045 cm^{-1} , $\nu_{\text{as}}(\text{NH})$, and 3006 cm^{-1} , $\nu_{\text{s}}(\text{NH})$, indicating that all the primary amine groups are in equivalent environments. This point was confirmed by the application of the equation $\nu_{\text{s}} = 345.53 + 0.875 \nu_{\text{as}}$,¹²⁷ which gave the calculated $\nu_{\text{s}}(\text{NH})$ mode at 3010 cm^{-1} . The close agreement with the observed value is consistent with all the primary nitrogens being in identical environments.

The indications are that a tetrahedral geometry is not exhibited, but the octahedral ionic species $\left[\text{Ti}(\text{tren})_2 \right] \text{Cl}_4$, similar to the analogous trivalent complex $\left[\text{Ti}(\text{tren})_2 \right] \text{Cl}_3$, is formed. Each ligand acts as a terdentate donor through the three primary amine centres. Unfortunately, as the complex was insoluble in non-donor solvents and decomposed rapidly in donor solvents, even at low temperature, further structural confirmation, via conductivity and molecular weight, could not be gained.

CHAPTERS 2 and 3 :

EPILOGUE

Penta-coordination in the transition metals is a very recent area of research in chemistry. As late as 1966 only a few penta-coordinate complexes were known,³⁰ and they were viewed as unusual and anomalous examples of coordination. Since this date extensive research has yielded numerous examples of this state, and nowadays such a coordination number is looked upon as mildly unusual, but no longer anomalous. The majority of these complexes are of the metals of the first series, and are mostly found for the later metals; this coordination number still being relatively rare for the early transition metals. The small number of such complexes known for the second and third series metals may be a result of their increased size, diminishing the importance of steric restrictions within their coordination sphere, or may simply be due to a lack of suitable investigation.

Three predominant factors are recognised in the determination of a specific geometry for a coordination complex. These are the electronic requirements of the metal ion, the size of the metal ion and the size and shape of the ligand. In a five coordinate complex it is generally accepted that the steric requirements of the ligand, coupled to some extent with the size of the metal centre, is dominant in the decision of coordination geometry. That is to say, that by choosing a suitably bulky ligand, with suitably spaced donor atoms, the electronic requirements of a metal may quite easily be defeated, and a five coordinate complex formed.

This conclusion is quite acceptable for the later transition metals, as a variety of factors show trends that would support this view as one moves through the series.

For a series of metals of d^n configuration, as 'n' increases, the possible crystal field stabilisation energy increases for

low coordination number geometries. That is, the requirements of the metal for a coordination number greater than five becomes less important.

The contraction in the ionic radii of the metals along the series, due to the imperfect shielding of the d-electrons, also increases the steric control of the reactions. As the ions become smaller the available space within their coordination spheres rapidly diminishes and penta-coordination becomes an important choice for relieving steric strain.

Another important feature that follows from the contraction in ionic radii, is the stability of the complexes that are formed. This dependence of stability upon the reciprocal of the ionic radius of the central metal atom was first demonstrated by Irving and Williams¹⁴⁰ for octahedral complexes. From the analysis of a large quantity of data that was available, they showed that the stability of a transition complex increased as one went along the series, the order being independent of the nature of the ligand. This trait has also been demonstrated as being operative in five coordinate complexes of the transition metals.¹⁴¹

All these factors increase the favourability of penta-coordination in the transition series as the atomic number increases in a particular series. In these ways, by sometimes increasing the importance of the steric factors, and sometimes decreasing the importance of the metal requirements for higher coordination, penta-coordination becomes a more readily acceptable part of the coordination chemistry of the later transition metals.

But what of the early transition metals, of which relatively few examples of five coordination are known. At the beginning of the series the factors mentioned above are at a minimum, so what are the relative strengths of the steric requirements of

the ligand and of the metal's electronic requirements. The results of our work indicate that the metal requirements for octahedral coordination is the dominant factor, and the steric requirements of the ligand normally of secondary importance.

Both tren and Me₆tren are bulky, powerfully chelating ligands with a structure that is conducive to a trigonal bipyramidal geometry. Their ability to stabilise such a complex has been demonstrated many times in the later transition metals. However, we have found that the octahedral requirement of the early metals is sufficiently strong to defeat not only the normal denticity of these ligands, but in the case of tren, also the chelation effects of five membered rings. A similar effect is also noted in the reactions of the sterically hindered bidentate amine temen. Only in the case of the ligand tetrahydrothiophene was five coordination detected. Even in this case a discrete five coordinate adduct could not be isolated; it only existing in an equilibrium with a six coordinate species.

A question that arises from this is, how much is five coordination, in the early transition metals, a stable state in its own right, and how much is it simply an unstable condition forced onto the metal through gross steric restrictions.

A close look at the available data for the few five coordinate complexes of the early metals, shows that a great majority of them only exhibit penta-coordination under limited and specific conditions. A number of the potentially five coordinate trialkylphosphine complexes of vanadium(III) exhibit partial dimerisation to the hexa-coordinate state.¹⁴² The penta-coordinate (in the solid state) alkylphosphine complexes of titanium(III)⁴¹ when in solutions containing a 3:1 molar ratio of phosphine:metal exhibit hexa-coordination. The alkylsulphide complexes of vanadium(III)

only show penta-coordination in solution in non-donor solvents. In the solid state they gain octahedral coordination through halogen bridging, and in solution in the parent ligand a third ligand is associated with the complex to give a pseudo-octahedral geometry.^{38,143}

Some of the best known exceptions to this behaviour have been the bis trimethylamine adducts of the trivalent halides of titanium, vanadium and chromium. It appeared that these adducts exhibited stable penta-coordination not only in the solid state, but also in solutions of both the parent amine and of non-coordinating solvents. However, we have shown (chapter 2) that this stability is only apparent, and that these adducts decompose in non-donor solvents to achieve octahedral coordination via halogen bridging.

It has always been accepted that octahedral coordination is the preferred state of the early transition metals, and that penta-coordination is somewhat unusual, but it has become an accepted state. This work has indicated that the penta-coordinate state in these metals may not be as stable as is commonly thought. However, it has done little more than show that the preference for octahedral coordination is in most cases sufficiently strong to dominate the requirements a ligand may have in coordination. The instability of the penta-coordinate state and the constant drive of the metal to achieve hexa-coordination has also been demonstrated. Now a more thorough investigation of this field is required, not only in the preparative area, where most of the recent work has been centred, but also in the thermodynamics and kinetics associated with this state. By such investigations, the exact position of five coordination in the chemistry of the early transition metals may be clarified.

CHAPTER 4.

COMPLEXES OF CYCLOSILAZANES

4.1. INTRODUCTION

The cyclosilazanes are a class of inorganic ring compounds containing alternating silicon-nitrogen linkages. The rings may be represented by the formula $[R_2Si NR]_n$, and examples are known where $n = 2, 3$ and 4 and R is a hydrogen or virtually any alkyl or silyl group. There are a number of reviews that cover the preparations, properties and reactions of these ring systems.¹⁴⁴⁻¹⁴⁶

Cyclosilazanes were probably first prepared by Stock and his co-workers,¹⁴⁷ in 1921, by the ammonolysis of dichlorosilane, but they were never completely characterised. The first well defined systems were produced in 1948, when Brewer and Haber,¹⁴⁸ by the ammonolysis of dimethyl- and diethyldichlorosilanes, prepared the tri- and tetrameric rings. Since this time their interesting structure of alternating electron donor (nitrogen) and electron acceptor (silicon) atoms has ensured them extensive investigation.

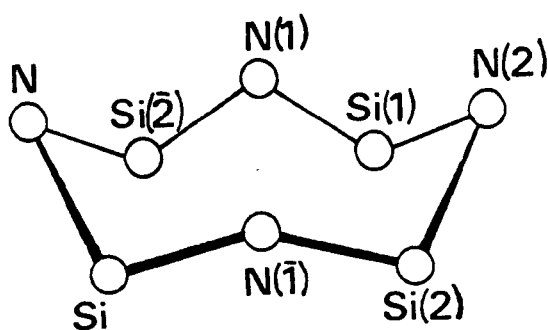
Much of the interest in these ring systems has stemmed from the possible p_π - d_π bonding that can result from their structure. The silicon contains a set of vacant, relatively low lying, d-orbitals into which it may accept electron density from the nitrogen lone pair and form a π -bond network within the ring. The presence of this nitrogen lone pair delocalisation is aptly demonstrated by the work of Pitt and Fowler.¹⁴⁹ They have shown that successive silylation of ammonia results in a hypsochromic shift of the UV absorptions recorded for these systems. They have shown that this absorption is due to a transition of the nitrogen lone pair, possibly into the Si-N σ^* -orbital. The spectral shift to higher energy can be accounted for by stabilisation of the nitrogen lone pair through delocalisation into the vacant silicon d-orbitals. This hypsochromic shift

may also contain a contribution from the possible partial re-hybridisation of the nitrogen atom from Sp^3 to Sp^2 . The resulting increase in s character of the Si-N σ -bonds would cause an increase in the energy of the anti-bonding orbital, and thus increase the energy associated with the spectral transition. Although such a change, or partial change, in hybridisation of a silylamine group is commonly accepted as being indicative of the presence of p_π - d_π bonding, it is not a necessary change.¹⁵⁰ Ebsworth has shown that sufficient orbital overlap between a silicon d-orbital and a nitrogen Sp^3 lobe may be achieved to result in a π -bond, though obviously, overlap with a π -type p-orbital maximises the bonding. The major effects of this p_π - d_π delocalisation are on the stereochemistry about the nitrogen, resulting from changes of hybridisation and the multiple bond characteristics of the Si-N linkages, and on the basicity of the amines.

Structural Features of (Si-N) Rings

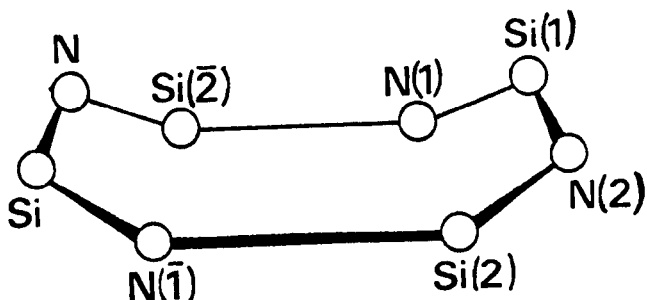
Hexamethylcyclotrisilazane has been the subject of several structural investigations, which led to some initial uncertainty about its structure. From the results of careful infrared measurements¹⁵¹ the ring was deduced to be planar, with D_{3h} molecular symmetry, it now, however, seems more likely that the ring is in fact slightly puckered. Electron diffraction studies^{152,153} have yielded a SiNSi angle of $117 \pm 4^\circ$ and a NSiN angle of $111 \pm 5^\circ$, though the detailed shape of the ring could not be determined. Calculations were later made¹⁵⁴ which tend to confirm these results, and if they are correct, the ring would have to pucker to accommodate the bond angles. The Si-N bond lengths, as found from electron diffraction, are 1.78 Å, which is a shorter bond

A) 'Chair' Form



Si(1) N(1)	1.788 Å	Si(1) N(1) Si(2̄)	132.4°
Si(1) N(2)	1.746 Å	Si(1) N(2) Si(2)	132.3°
Si(2) N(2)	1.734 Å	N(1) Si(1) N(2)	112.5°
Si(2) N(1̄)	1.727 Å	N(2) Si(2) N(1̄)	110.5°

B) 'Boat' Form



Si(1) N(1)	1.708 Å	Si(1) N(1) Si(2̄)	130.1°
Si(1) N(2)	1.741 Å	Si(1) N(2) Si(2)	133.1°
Si(2) N(2)	1.687 Å	N(1) Si(1) N(2)	110.3°
Si(2) N(1̄)	1.750 Å	N(2) Si(2) N(1̄)	110.3°

FIGURE 4.1. Crystal Data for $[\text{Me}_2\text{SiNH}]_4$

length than that expected for a pure Si-N single bond.¹⁵⁵

Octamethylcyclotetrasilazane has been the subject of an X-Ray crystal analysis.¹⁵⁶ The ring is found to crystallise in the monoclinic space group $P 2_1/c$, the crystals containing a 1:1 ratio of two ring conformers, the 'chair' and the 'boat'. The crystal data, FIGURE 4.1., shows that the Si-N bond lengths vary from 1.687 Å-1.788 Å, but these variations are probably due to crystal packing effects, and the mean value is of the same order as that found in the trimeric ring. The mean SiNSi angle of 131.9° is much larger than that of the trimer, 117° , but again may be the result of crystal packing effects, as electron diffraction studies^{152,153} give the angle at $123 \pm 4^\circ$ in the vapour phase.

In both rings the divergence of the SiNSi angle from that of an sp^3 hybrid, together with the shortening of the Si-N bond from the expected single bond length, is indicative of the presence of an extensive amount of lone pair delocalisation, through $p\pi - d\pi$ bonding.

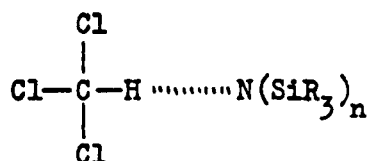
Basicity

The delocalisation of the nitrogen lone pair into the silicon d-orbitals has the effect of lowering the electron density on the nitrogen, and considerably reduces the basicity of the amine. The results of this are clearly shown by the planar trisilylamine,¹⁵⁷ which is a very much weaker base than the analogous trimethylamine. In place of the normal Lewis acid - Lewis base type reactions it frequently undergoes disproportionation and exchange with electron acceptors.

The basicity of an amine can be measured by its adduct forming ability with a standard reference acid. One of the simp-

best ways of obtaining a relative measure of the basicity of a silylamine is to measure its hydrogen bonding capacity to the reference acid chloroform.

i.e.



The shift in the ν (CH) peak in the infrared, on addition of excess amine, can be taken as a relative measure of the base strength of the amine.¹⁵⁸ In practice the acid deuteriochloroform is used, as the ν (CD) peak is in a 'cleaner' area of the spectrum, and is more readily distinguishable. Some of the results achieved by Abel and co-workers¹⁵⁸ are shown in TABLE 4.1..

TABLE 4.1. Infrared Shifts of the ν (CD) peak for CDCl_3 :Amine Mixtures

Amine	$\Delta\nu$ of ν (CD) (cm^{-1})	Ratio unshifted:shifted peak areas
$(\text{CH}_3)_3\text{CNH}\cdot\text{C}_2\text{H}_5$	89	1:100
$(\text{CH}_3)_3\text{Si N}(\text{CH}_3)_2$	62	1:12
$(\text{CH}_3)_3\text{Si N}(\text{C}_3\text{H}_7)_2$	77	1:1
$((\text{CH}_3)_3\text{Si})_2\text{NH}$	30	1:1
$((\text{CH}_3)_3\text{Si})_2\text{NCH}_3$	39	2:1
$[(\text{CH}_3)_2\text{Si NH}]_3$	31	1:4

$[(\text{CH}_3)_2\text{Si NH}]_4$ has been shown by Jarvie and Lewis¹⁵⁹ to be a slightly stronger base than the trimeric ring.

It can be seen from this data, that the silylamines show considerably lowered basicity compared with the alkylamines, and that successive silylation further lowers the donor capacity

of the amine. The ratio of the unshifted to shifted ν (CD) peak gives a relative measure of the steric accessibility of the nitrogen electrons for donation. From these values it can be seen that whilst the donor strength of the trimeric ring is about the same as its acyclic equivalent, $((\text{CH}_3)_3\text{Si})_2\text{NH}$, the nitrogen lone pair is sterically more accessible.

Even though the basicities of the silylamines are much reduced from the analogous alkylamines they are not zero, and a more quantitative picture may be gained from the heats of mixing with chloroform¹⁶⁰ recorded in TABLE 4.2..

TABLE 4.2. Heats of Mixing of Amines with CHCl_3 (cals/mole of solution)

Amine	Heat of Mixing
$n\text{-C}_4\text{H}_9\text{NH}_2$	714
$(n\text{-C}_4\text{H}_9)_2\text{NH}$	810
$(\text{C}_2\text{H}_5)_2\text{NH}$	866
$(\text{C}_2\text{H}_5)_3\text{N}$	870
$(\text{CH}_3)_3\text{SiNH}\cdot\text{CH}_3$	355
$(\text{CH}_3)_3\text{SiN}(\text{CH}_3)_2$	359
$(\text{C}_2\text{H}_5)_3\text{SiNH}_2$	272
$((\text{CH}_3)_3\text{Si})_2\text{NH}$	28
$[(\text{CH}_3)_2\text{SiNH}]_3$	196

Donor Behaviour

Although the basicities of the cyclosilazanes are low, they should be capable of donation to a suitable Lewis acid. Two modes of donation are open to the rings, one is π -donation from the delocalised electron system, the other is normal

σ -donation of the nitrogen lone pair. The latter would probably involve some withdrawal of electron density from the silicon d-orbitals and result in some structural changes to the rings.

Hexamethylcyclotriborazane is an analogous compound to the trimeric silazane and shows extensive delocalisation of the nitrogen lone pair throughout the ring, via $p\pi$ - $p\pi$ bonding. This is achieved by the Sp^2 hybridisation of both the boron and the nitrogen, which results in efficient π -overlap of the filled nitrogen p-orbital and the vacant boron p-orbital. The result is a 6π -electron aromatic system, and on coordination the ring has been shown to act as both a π and a σ -donor. As a π -donor the half sandwich compound analogous to π -benzenetricarbonyl-chromium has been isolated.¹⁶¹ Whereas, in the presence of the class A Lewis acid, $TiCl_4$, the $p\pi$ - $p\pi$ bonding within the ring is reduced and the ligand acts as a σ -donor through nitrogen.¹⁶²

The cyclosilazanes do not appear to contain the same extensive delocalisation as the borazines. The lack of a ring current in nonamethylcyclotrisilazane has been demonstrated by a nmr study of Lienhard and Rochow,¹⁶³ the lack of aromaticity indicating a non-continuous π system to be present in the ring. Another nmr study¹⁶⁴ has revealed there to be a lack of transmission of substituent effects through Si-N-Si linkages, seriously denying the presence of a continuous π bond through the silicon. The best description of the π -electron density within the rings is a system of localised three centre Si-N-Si bonds, with imperfect transmission through the silicon atom.

An earlier investigation of the donor properties of hexamethylcyclotrisilazane¹⁶⁵ revealed no evidence for π -donor capacity in the ring, but showed that it did react as a tentative σ -donor, through the nitrogen atoms, to yield stable adducts

of the type $MCl_3 \cdot [Me_2Si NH]_3$, ($M = Ti$ and V). In the following study we have investigated the donor role of the trimeric ring with $Ti(IV)$ and $Cr(III)$, and the potentially tetradentate tetrameric ring with $Ti(IV)$, $Ti(III)$, $V(III)$ and $Cr(III)$.

4.2. EXPERIMENTAL and RESULTS

Preparative and manipulative details are given in appendices A and B.

A) Reaction between TiCl_4 and Hexamethylcyclotrisilazane

TiCl_4 was co-condensed in vacuo with benzene onto a slight excess, for a 1:1 molar ratio, of HMT. On warming to room temperature an immediate reaction occurred to give a clear solution and a bright yellow precipitate. The solvent was removed in vacuo and the solid thoroughly washed with n-hexane. The product was the bright yellow solid di- μ -chloro-hexachloro- μ -(hexamethylcyclotrisilazane, N_1, N_2)-dititanium(IV).

Anal. Calcd. for $\text{C}_6\text{H}_{21}\text{Cl}_8\text{N}_3\text{Si}_3\text{Ti}_2$: C, 12.0; H, 3.5; Cl, 47.4; N, 7.0; Ti, 16.0. Found: C, 11.1; H, 3.7; Cl, 47.5; N, 7.7; Ti, 15.9.

$\Lambda_m(298^\circ\text{K}) = 0.02 \text{ ohm}^{-1} \text{ cm mole}^{-1}$ for a 10^{-3}M solution in CH_2Cl_2 .

Melting point: Decomposed at $T > 432^\circ\text{K}$.

The infrared spectrum contained bands at; 3350(s), 3280(s), 3240(sh), 2970(m), 2930(m), 1403(s), 1260(s), 1150(w), 953(s), 897(m), 863(s), 839(s), 804(s), 778(w), 743(m), 721(m), 681(w), 653(w), 633(w), 501(m), 441(m), 411(s), 348(s) and 277(m) cm^{-1} respectively.

The electronic spectrum contained bands at; 34,500, 39,100 and 45,000 cm^{-1} respectively when run as the solid, and at; 35,100(sh), 38,400 and 43,800 cm^{-1} respectively when run as a CH_2Cl_2 solution.

The proton nmr spectrum, in CH_2Cl_2 solution, gave bands at; 9.03, 9.25, 9.40 and 9.85 τ respectively, with relative intensities of 1:2:2:1.

B) Reaction between TiCl_4 and Octamethylcyclotetrasilazane

TiCl_4 was co-condensed in vacuo with benzene onto a slight excess, for a 1:1 molar ratio, of OMT. On warming to room temperature an immediate reaction occurred to give a clear solution

and a bright yellow precipitate. The solvent was removed in vacuo and the solid thoroughly washed with n-hexane. The product was the bright yellow solid di- μ -chloro-hexachloro- μ -(octamethylcyclotetrasilazane, N_1, N_3)-dititanium(IV).

Anal. Calcd. for $C_8H_{28}Cl_6N_4Si_4Ti_2$: C, 14.3; H, 4.2; Cl, 42.2; N, 8.3; Ti, 14.3. Found: C, 13.6; H, 4.0; Cl, 42.0; N, 8.3; Ti, 14.2.

$\Lambda_m(298^\circ K) = 0.28 \text{ ohm}^{-1} \text{ cm mole}^{-1}$ for a $10^{-3} M$ solution in CH_2Cl_2 .

Melting point: Decomposed at $T > 453^\circ K$.

The infrared spectrum contained bands at; 3225(s), 3180(s), 3125(sh), 2960(m), 2930(m), 1400(s), 1275(s), 1150(m), 930(m), 870(m), 800(s), 660(m), 600(w), 450(m), 350(s) and 300(w) cm^{-1} respectively.

The electronic spectrum contained bands at; 34,200, 39,400 and 45,500 cm^{-1} respectively when run as the solid, and at; 35,700(sh), 39,700(sh) and 43,820 cm^{-1} respectively when run as a CH_2Cl_2 solution.

The proton nmr spectrum, in CH_2Cl_2 solution, gave bands at; 9.15 and 9.40 τ respectively, with relative intensities of 1:1.

C) Reaction between $TiCl_3 \cdot 3THF$ and Octamethylcyclotetrasilazane

A benzene solution of OMT, sufficient for a slight excess of a 1:1 molar ratio, was added in vacuo to a benzene solution of $TiCl_3 \cdot 3THF$. An immediate reaction occurred to give a pale green solution and a green solid. The solvent was removed in vacuo and the solid thoroughly washed with n-hexane. The product was the bright green solid di- μ -chloro-tetrachloro- μ -(octamethylcyclotetrasilazane, N_1, N_3)-bis(tetrahydrofuran)dititanium(III).

Anal. Calcd. for $C_{16}H_{44}Cl_4N_6O_2Si_4Ti_2$: C, 25.8; H, 5.9; Cl, 28.6; N, 7.5; Ti, 12.8. Found: C, 26.4; H, 5.4; Cl, 28.8; N, 6.6; Ti, 12.8.

Mol. wt. Calcd: 745. Found (osmometric): 809.

$\Lambda_m(298^\circ\text{K}) = 0.11 \text{ ohm}^{-1} \text{ cm mole}^{-1}$ for a 10^{-3}M solution in CH_2Cl_2 .

Melting point: Decomposed at $T > 440^\circ\text{K}$.

The infrared spectrum contained bands at; 3275(m), 3150(m), 3090(sh), 2930(s), 2910(s), 2880(m), 2855(m), 2830(w), 1458(m), 1408(m), 1348(m), 1260(s), 1170(w), 1070(w), 1040(m), 1011(s), 960(w), 928(m), 852(s), 805(m), 722(w), 685(m), 630(w), 352(s) and 297(m) cm^{-1} respectively.

The electronic spectrum contained bands at; 12,390(sh), 13,250, 25,700(sh), 38,450(sh) and 44,200 cm^{-1} respectively when run as the solid.

D) Reaction between $\text{VCl}_3 \cdot 3\text{THF}$ and Octamethylcyclotetrasilazane

A benzene solution of OMT, sufficient for a slight excess of a 1:1 molar ratio, was added in vacuo to a benzene solution of $\text{VCl}_3 \cdot 3\text{THF}$. A slow reaction occurred, over a period of ~ 1 week, to give a colourless solution and a black solid. The solvent was removed in vacuo and the solid thoroughly washed with n-hexane. The product was the black solid di- μ -chloro-tetrachloro- μ -(octamethylcyclotetrasilazane, N_1, N_3)-bis(tetrahydrofuran) divanadium(III).

Anal. Calcd. for $\text{C}_{16}\text{H}_{44}\text{Cl}_6\text{N}_4\text{O}_2\text{Si}_4\text{V}_2$: C, 25.5; H, 5.8; Cl, 28.3; N, 7.5. Found: C, 25.4; H, 5.7; Cl, 28.1; N, 7.8.

$\Lambda_m(298^\circ\text{K}) = 0.29 \text{ ohm}^{-1} \text{ cm mole}^{-1}$ for a 10^{-3}M solution in CH_2Cl_2 .

Melting point: Decomposed at $T > 435^\circ\text{K}$.

The infrared spectrum contained bands at; 3289(m), 3220(m), 3140(sh), 2955(s), 2920(w), 2895(w), 2860(w), 1440(m), 1410(m), 1345(w), 1260(s), 1168(w), 1085(m), 1035(m), 1025(s), 960(m), 928(m), 852(m), 800(s), 712(w), 682(w), 630(w), 465(w), 345(s) and 305(w) cm^{-1} respectively.

The electronic spectrum contained bands at; 13,150, 20,610(sh), 34,450(sh), 40,800(sh) and 43,700 cm^{-1} respectively when run as

the solid, and at; 34,700(sh), 41,400(sh) and 43,800 cm^{-1} respectively, when run as a CH_2Cl_2 solution.

B) Reaction between $\text{CrCl}_3 \cdot 2\text{NMe}_3$ and Octamethylcyclotetrasilazane

A benzene solution of OMT, sufficient for a slight excess of a 1:1 molar ratio, was added in vacuo to a benzene solution of $\text{CrCl}_3 \cdot 2\text{NMe}_3$. An immediate reaction occurred to give a colourless solution and a purple precipitate. The solvent was removed in vacuo and the solid thoroughly washed with n-hexane. The product was the purple solid di- μ -chloro-tetrachloro- μ -(octamethylcyclotetrasilazane, N_1, N_3)-bis(trimethylamine)dichromium(III).
 Anal. Calcd. for $\text{C}_{14}\text{H}_{46}\text{Cl}_6\text{N}_6\text{Si}_4\text{Cr}_2$: C, 23.1; H, 6.3; Cl, 29.2; N, 11.5; Cr, 14.3. Found: C, 22.6; H, 5.8; Cl, 28.9; N, 10.1; Cr, 14.4.

$\Lambda_m(298^\circ\text{K}) = 1.26 \text{ ohm}^{-1} \text{ cm mole}^{-1}$ for a 10^{-3}M solution in CH_2Cl_2 .

Melting point: Decomposed at $T > 425^\circ\text{K}$.

The infrared spectrum contained bands at; 3200(m), 3110(m), 3080(sh), 3023(m), 2990(w), 2955(m), 2930(m), 2910(m), 2870(w), 2855(w), 2790(w), 2720(w), 1508(w), 1480(s), 1460(s), 1405(m), 1258(s), 1235(m), 1170(s), 1070(m), 1035(w), 975(s), 930(m), 890(m), 855(m), 815(s), 790(m), 675(m), 632(m), 525(m), 478(m), 370(s), 340(s), 287(w) and 250(w) cm^{-1} respectively.

The electronic spectrum contained bands at; 15,510, 19,510, 30,560 and 43,810 cm^{-1} respectively when run as the solid.

4.3. DISCUSSION

HMT reacted immediately with TiCl_4 , in benzene solution, to give the bright yellow solid adduct $(\text{TiCl}_4)_2 \cdot \text{HMT}$. All the attempts that were made to isolate an adduct between CrCl_3 and HMT met with failure. No adduct formation could be detected by direct addition of the ligand to the anhydrous metal halide, and substitution reactions of various CrCl_3 adducts all yielded products of non-stoichiometric composition. The infrared spectra of these products failed to reveal any skeletal $\nu(\text{SiNSi})$ modes, which is strongly suggestive that ring degradation has occurred. Such degradation is known to occur in the cyclosilazanes, via Si-N bond cleavage, in the presence of Al_2Cl_6 ,¹⁶⁶ CoCl_2 ,¹⁶⁷ and, CuCl_2 and FeCl_3 ,¹⁶⁸ with HMT showing greater susceptibility to such degradation than OMT.¹⁶⁹ It now seems that CrCl_3 can also initiate such a decomposition.

The reaction of OMT with the chlorides of the early transition metals yielded adducts of the types $(\text{MCl}_4)_2 \cdot \text{OMT}$ and $(\text{MCl}_3)_2 \cdot \text{OMT} \cdot 2\text{L}$, where $\text{L} = \text{THF}$ or NMe_3 . The reaction with TiCl_4 , in benzene solution, occurred immediately, precipitating out the bright yellow product. Reaction with the tervalent halides failed to give any apparent adduct formation. In these cases substitution reactions, carried out on the tris-tetrahydrofuran or bis-trimethylamine adducts of the halides, yielded isolable solid products that were green, black and purple for the Ti, V and Cr adducts respectively.

All the adducts isolated decomposed very rapidly in donor solvents and only showed very limited solubility in non-coordinating solvents. They were all found to be non-conducting in dichloromethane solution, and therefore of non-ionic formulation. Because of their limited solubility, molecular weight deter-

ination only proved to be feasible for the $(\text{TiCl}_3)_2 \cdot \text{OMT} \cdot 2\text{THF}$ adduct. This was recorded osmometrically in benzene solution, in which the adduct was found to be monomeric. A similar identity is proposed for the remaining adducts, by their similarity to the above, and to the $\text{MCl}_3 \cdot \text{HMT}$ analogues.¹⁶⁵

The infrared spectra of the adducts established several important points concerning their structure. In the $(\text{MCl}_3)_2 \cdot \text{OMT} \cdot 2\text{L}$ complexes, the ligands NMe_3 and THF are confirmed as being present, and coordinated in their normal mode. The $\nu_{\text{as}}(\text{CN})$ and $\nu_{\text{s}}(\text{CN})$ absorptions of the amine are decreased by $\sim 25 \text{ cm}^{-1}$ from the free ligand,³⁸ and the characteristic $\nu_{\text{as}}(\text{COC})$ and $\nu_{\text{s}}(\text{COC})$ absorptions of THF are decreased by $\sim 50 \text{ cm}^{-1}$ from those in the free ligand.¹⁴ The rings are seen to have retained their integrity, and not to have suffered degradation, as occurred in the case of the chromium(III) reaction with HMT. The absorptions associated with the skeletal $\nu_{\text{as}}(\text{SiNSi})$ and $\nu_{\text{s}}(\text{SiNSi})$, found at ~ 925 and 610 cm^{-1} respectively in the free ligand, show some small spectral shifts, but remain intact.

The absorptions in the $3500\text{--}3200 \text{ cm}^{-1}$ region of the spectrum, associated with the $\nu(\text{NH})$ mode, show that the ligands are not exhibiting their maximum denticity. Secondary amines give rise to a single absorption in this region, these are found at 3415 cm^{-1} and 3380 cm^{-1} for the trimeric and tetrameric rings respectively, in the free state. On coordination of an amine these bands characteristically lower in frequency, by $100\text{--}200 \text{ cm}^{-1}$, due to the drainage of electron density from the nitrogen into the metal's d-orbitals.¹²⁸ Each adduct shows two absorptions in this region, indicating that there are two types of nitrogen centres present in each complex. The lower frequency band shows a lowering of $\sim 200 \text{ cm}^{-1}$ from the position found in the free ligand, and may

be assigned to a nitrogen involved in lone pair donation to the metal. As the nitrogen involved in coordination withdraws its electron density from the silicon d-orbitals, for donation to the metal, the uncoordinated nitrogens increase their donation to the silicon to, in part, make good this loss. The result is a decrease in electron density on the uncoordinated nitrogen, which causes the second observed ν (NH) band, associated with it, to shift to a frequency $\sim 100 \text{ cm}^{-1}$ below that of the free ligand.

The spectra of the OMT adducts in the $3000\text{--}500 \text{ cm}^{-1}$ region are very much the same as that of the free ligand, with only small frequency shifts noted for some bands. This must mean that very little structural change has occurred upon coordination, perhaps the loss of electron density, from the ring to the metal d-orbitals, has been negated by increased donation from the uncoordinated nitrogens.

The spectrum of the HMT complex in this region is on the whole very similar to that of the free ligand, but does indicate the presence of two types of silicon atom. The $\nu_{\text{as}}(\text{SiC})$ and $\nu_{\text{s}}(\text{SiC})$ modes found at 865 and 680 cm^{-1} respectively in the free ligand, are found as distinct doublets at 863 and 839 cm^{-1} and at 681 and 653 cm^{-1} respectively in the complex.

The $400\text{--}200 \text{ cm}^{-1}$ region of the spectrum contains the absorptions associated with the metal-halogen vibrations. This region may be complicated by metal-ligand vibrations, or internal ligand modes, but these are normally weak in nature and the intense metal-halogen absorptions are generally readily detected. The adducts all show intense ν (MCl) bands that are, in position, indicative of octahedral coordination,¹⁰³ with weaker bands to lower frequency that may be assigned to metal-halogen bridging

vibrations. The observed bands, and their assignments, in the complexes are given in TABLE 4.3..

TABLE 4.3. Metal-Halogen Frequencies for the HMT and OMT Complexes

Complex	$\nu(\text{MCl})_{\text{terminal}} (\text{cm}^{-1})$	$\nu(\text{MCl})_{\text{bridging}} (\text{cm}^{-1})$
$(\text{TiCl}_4)_2 \cdot \text{HMT}$	348	277
$(\text{TiCl}_4)_2 \cdot \text{OMT}$	350	300
$(\text{TiCl}_3)_2 \cdot \text{OMT} \cdot 2\text{THF}$	352	297
$(\text{VCl}_3)_2 \cdot \text{OMT} \cdot 2\text{THF}$	345	305
$(\text{CrCl}_3)_2 \cdot \text{OMT} \cdot 2\text{NMe}_3$	370	287

The electronic spectra, TABLE 4.4., can all be assigned in terms of an octahedral ligand field. The spectra obtained in both the solid state and in solution are virtually identical, showing that no change in geometry occurs in the complexes on dissolution.

$(\text{TiCl}_4)_2 \cdot \text{HMT}$ and $(\text{TiCl}_4)_2 \cdot \text{OMT}$ are both d^0 systems and as such should show no absorptions in the near infrared or visible regions of the spectrum. This was found to be the case, and only the intense charge transfer absorptions observed in the UV were detected. The first two transitions of each complex are assigned to charge transfers of the type titanium(d) \leftarrow chlorine(π), and the third band to a modified internal ligand transition; found at $\sim 44,000 \text{ cm}^{-1}$ in the free ligands. All the adducts exhibited this absorption at $\sim 44,000 \text{ cm}^{-1}$, and in each case it is assigned to this internal ligand transition. It may be associated with either the nitrogen lone pair moving to the Si-N antibonding orbital, $\sigma^* \leftarrow n$, or to a $\pi^* \leftarrow \pi$ transition associated with the $p_\pi - d_\pi$ bonding within the ring.

TABLE 4.4. Electronic Spectra for the HMT and OMT Complexes

Complex	Medium	Absorption Maxima (cm ⁻¹)
HMT	a	44,100.
OMT	a	44,200.
(TiCl ₄) ₂ ·HMT	a	35,100(sh); 38,400; 43,800.
	b	34,500; 39,100; 45,000.
(TiCl ₄) ₂ ·OMT	a	35,700(sh); 39,700(sh); 43,820.
	b	34,200; 39,400; 45,500.
(TiCl ₃) ₂ ·OMT·2THF	b	12,390(sh); 13,250; 25,700(sh); 38,450(sh); 44,200.
(VCl ₃) ₂ ·OMT·2THF	a	34,700(sh); 41,400(sh); 43,800.
	b	13,150; 20,610(sh); 34,450(sh); 40,800(sh); 43,700.
(CrCl ₃) ₂ ·OMT·2NMe ₃	b	15,510; 19,510; 30,560; 37,740; 43,810.

a: dichloromethane solution

b: nujol mull

The (TiCl₃)₂·OMT·2THF adduct shows the single expected 'd-d' transition associated with an octahedral d¹ system, as a broad asymmetric band at 13,250 cm⁻¹, ${}^2E_g \leftarrow {}^2T_{2g}$. The shoulder that is found at 12,390 cm⁻¹ is indicative of the presence of a lower symmetry component, probably tetragonal, distorting the O_h field. The results of this would be a splitting of the degenerate ${}^2T_{2g}$ and 2E_g orbitals, causing the broadening of the transition. By using the 10Dq values for TiCl₆³⁻⁴⁶, TiCl₃·3THF¹⁷⁰ and TiCl₃·HMT¹⁶⁵, and Jørgensen's rule of averaged environments, the calculated ligand field band of (TiCl₃)₂·OMT·2THF is at 14,010 cm⁻¹. This difference in energy implies that the tetra-

meric ring has a weaker donor ability than the trimeric ring. Jarvie and Lewis¹⁵⁹ have already shown that the trimer is a stronger acid than the tetramer, and this apparant reversal must be due to steric effects, concerning either the bulkiness of the ring, or interdonor separation distances.

The spectrum of $(VCl_3)_2 \cdot OMT \cdot 2THF$ contains two bands in the visible region, at $13,150\text{ cm}^{-1}$ and $20,610\text{ cm}^{-1}$, which may be assigned to the ${}^3T_{2g} \leftarrow {}^3T_{1g}(F)$ and ${}^3T_{1g}(P) \leftarrow {}^3T_{1g}(F)$ transitions respectively, associated with a d^2 ion in an octahedral field. The intense vanadium(d) \leftarrow chlorine(π) transitions at $34,450\text{ cm}^{-1}$ and $40,800\text{ cm}^{-1}$ prevent the observation of the third 'allowed' 'd-d' transition, the ${}^3A_{2g} \leftarrow {}^3T_{1g}(F)$.

The spectrum of the $(CrCl_3)_2 \cdot OMT \cdot 2NMe_3$ adduct contains three bands in the visible region, and these may be assigned to the three expected 'd-d' transitions (O_h) of chromium(III). They are the ${}^4T_{2g} \leftarrow {}^4A_{2g}$ at $15,510\text{ cm}^{-1}$, the ${}^4T_{1g}(F) \leftarrow {}^4A_{2g}$ at $19,510\text{ cm}^{-1}$ and the ${}^4T_{1g}(P) \leftarrow {}^4A_{2g}$ at $30,560\text{ cm}^{-1}$. The intense absorption at $37,740\text{ cm}^{-1}$ can be assigned to a charge transfer of the type chromium(d) \leftarrow chlorine(π).

One of the major controlling factors in the coordination chemistry of the early transition metals is the drive towards octahedral coordination. In the adducts that have been isolated this geometry is achieved by the metal centre at the expense of maximum ligand donation. The proposed structures of the complexes are shown in FIGURES 4.2. and 4.3.. They are consistent with the spectral data, and the general structural features are not unknown. The achievement of octahedral coordination by halogen bridging is well established amongst complexes of the halides, and is infact shown by the tervalent halides themselves.² The addition of a third bridging group, donating in the manner pro-

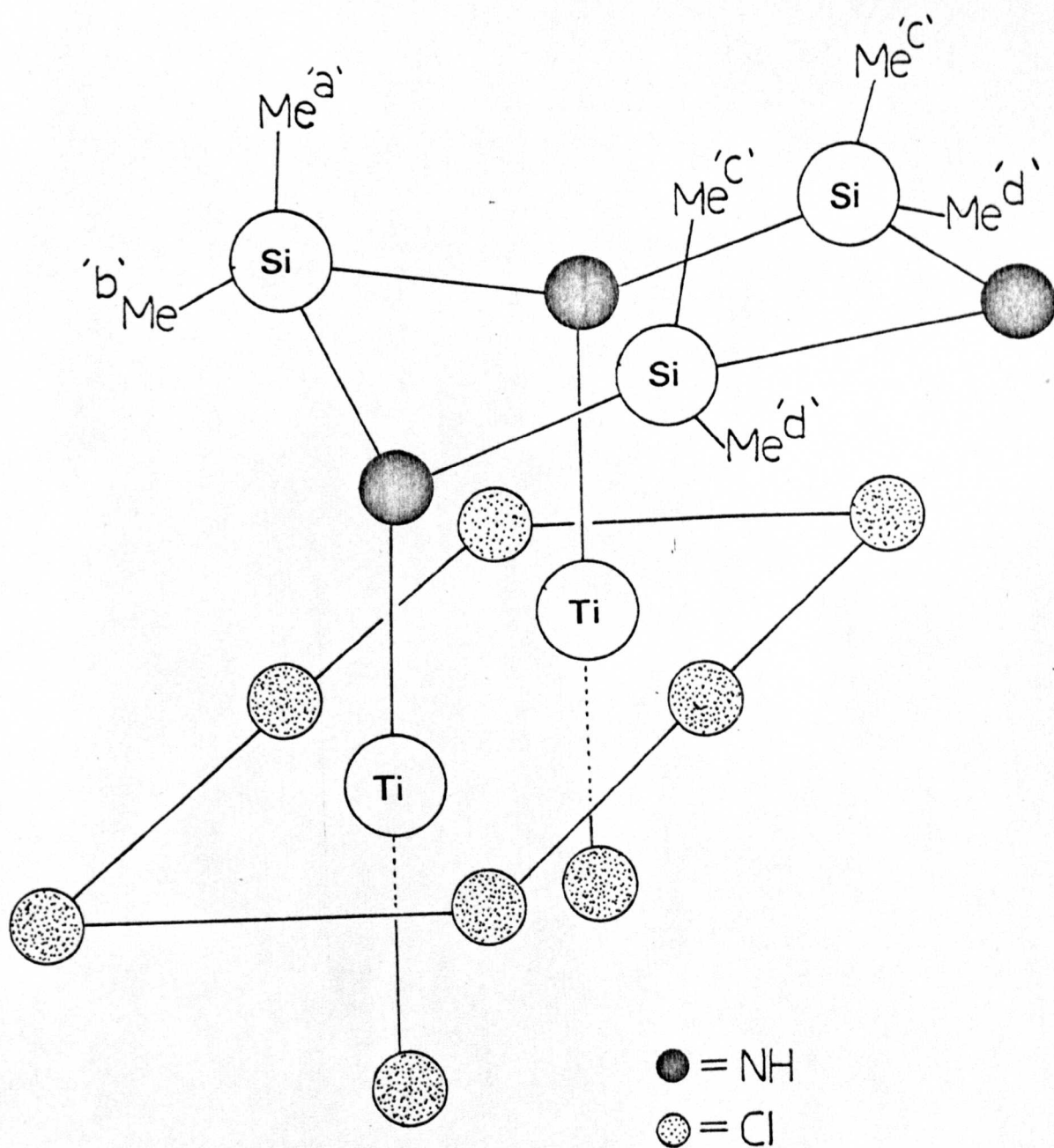


FIGURE 4.2. Proposed Structure for HMT Complex

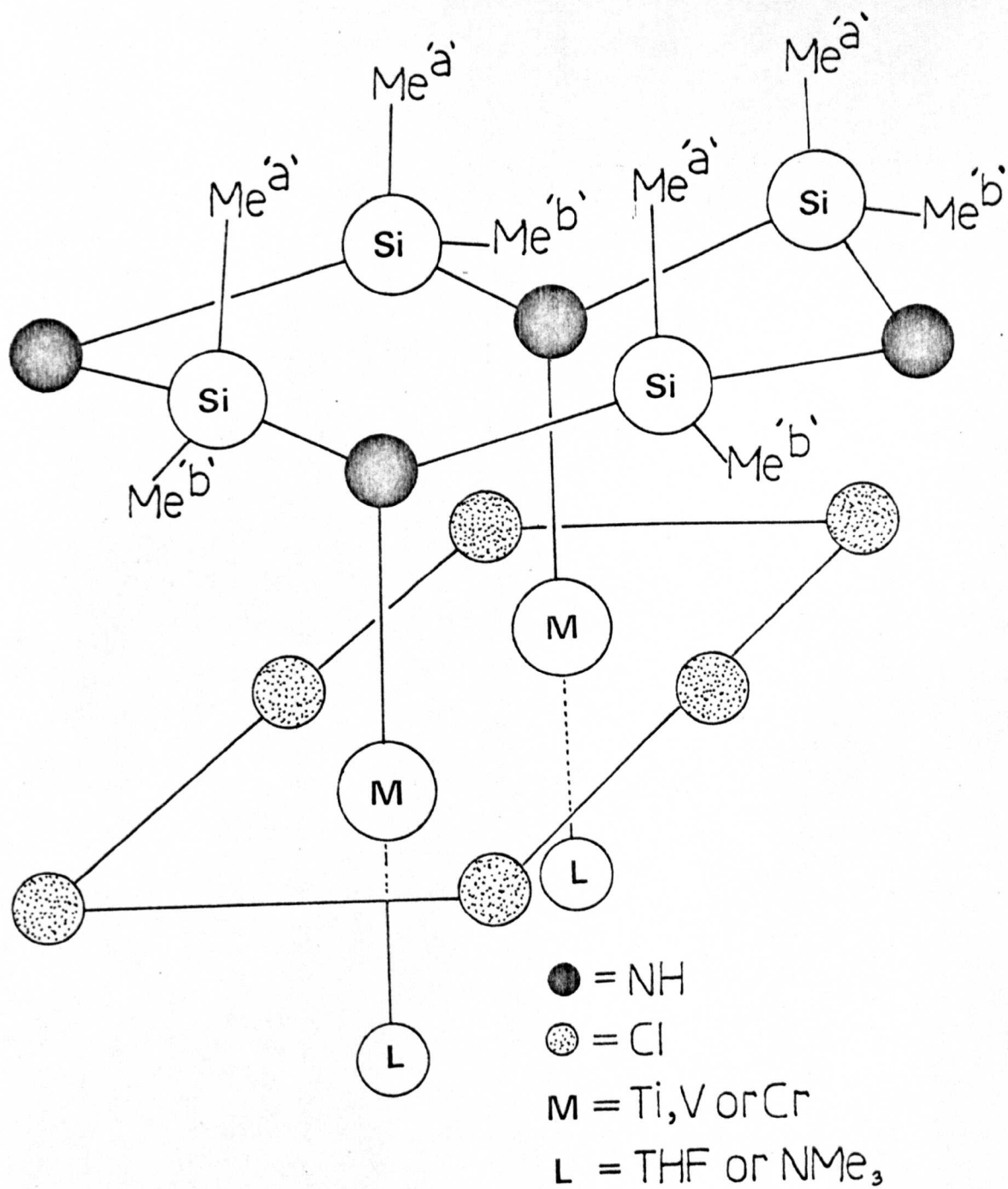


FIGURE 4.3. Proposed Structure for OMT Complexes

posed for the cyclosilazanes, has also been reported on several previous occasions.¹⁷¹⁻¹⁷³

In the adducts of the tervalent metals the additional ligands, either tetrahydrofuran or trimethylamine, are required to complete the octahedral environments of the metals, thus replicating the titanium(IV) framework. As a result of this requirement the formation reactions occur with incomplete substitution.

The proton nmr results, TABLE 4.5., that were obtained for the two tetravalent complexes, tend to substantiate these structures.

TABLE 4.5. Proton nmr of $(\text{TiCl}_4)_2 \cdot \text{HMT}$ and $(\text{TiCl}_4)_2 \cdot \text{OMT}$

Complex	Absorption Maxima* (τ)
HMT	9.90.
OMT	9.70.
$(\text{TiCl}_4)_2 \cdot \text{HMT}$	9.03(1); 9.25(2); 9.40(2); 9.85(1).
$(\text{TiCl}_4)_2 \cdot \text{OMT}$	9.15(1); 9.40(1).

* Recorded in dichloromethane solution with TMS as standard.

Relative intensities are given in parentheses.

The spectrum of $(\text{TiCl}_4)_2 \cdot \text{OMT}$ exhibits two signals of equal intensity, at 9.15 τ and 9.40 τ , that can be assigned to the methyl groups b and a, respectively. The b methyl groups experience a greater shielding effect from the chlorine atoms, thus move to lower field than the a methyls.

Similar shielding effects, coupled with the small effects of electron density redistribution in the ring, are observed in the $(\text{TiCl}_4)_2 \cdot \text{HMT}$ complex. Four signals are observed in the spectrum at 9.85 τ , 9.03 τ , 9.40 τ and 9.25 τ , with relative

intensities of 1:1:2:2, and may be assigned in the light of the above considerations to the methyl groups a, b, c and d respectively.

In these complexes there are three major factors that should be considered; the octahedral preference of the metal centres, the steric considerations of the ligands and the basicities of the ligands.

The requirements of octahedral coordination for the metal ions must again be viewed as the predominant factor in coordination. The dictates of the metal have determined the basic structures of the complexes, and restricted the possible donor roles of the ligands. Once this gross structure, of octahedral coordination, has been fixed by the metal the finer details are probably a result of ligand factors.

The result of 1:2 rather than 1:1 adducts can almost certainly be accounted for on steric grounds. The dimethylsilyl group is a very bulky structure, and the substitution of the coordinated nitrogen probably offers little less steric hindrance than that of a trimethylamine molecule; which is sufficient to determine penta-coordination in these metals. Therefore 1:2 adducts are formed to offer a relief from the probable steric hindrance that would be associated with a 1:1 adduct.

With regards to the basicities of the ligands, the metals proved themselves to be sufficiently good electron acceptors to induce a withdrawal of electron density from the ring. However, the delocalisation within the ring has a noticeably strong stabilising effect for the ligands. As the electron density is withdrawn to the metal d-orbitals the non-coordinated nitrogens, in part at least, make good this loss by further delocalisation of their electron density. This effect can be seen in the infra-

red spectra of the adducts. The $\nu(\text{NH})$ band of the uncoordinated nitrogens moves to lower wavenumber by some 100 cm^{-1} , showing the loss of electron density on this atom. Also the very small shifts noted for the skeletal (SiNSi) vibrations of the ligands, on coordination, are indicative of little bond order change within the rings. A direct result of this behaviour would be a further reduction in the basicity of the uncoordinated nitrogens. This, in conjunction with the steric factors, would greatly reduce the possibility of the ligand donating through all its potential donor sites; and is probably instrumental in the prevention of polymerisation through this free amine centre.

A further change in hybridisation might also be expected at these nitrogens. A move closer to pure Sp^2 hybrids, and greater planarity at these positions.

CHAPTER 5.

SOME COORDINATION CHEMISTRY OF ZIRCONIUM

5.1. INTRODUCTION

The coordination chemistry of the tervalent halides of zirconium is a field which has undergone very little exploration. Several adducts have been isolated,¹⁷⁴⁻¹⁷⁶ but for the most part they possess somewhat unusual stoichiometries. We felt that many of the reported results were due to a failure to break down the original halide lattice and produce discrete monomeric zirconium(III) species.

During an investigation to find such a discrete adduct, which might be suitable for further ligand substitution, we examined the zirconium tetrachloride-trimethylamine system. In the analogous titanium(IV) system reduction is known to occur, to yield the titanium(III) complex, $\text{TiCl}_3 \cdot 2\text{NMe}_3$ ^{15,29} and we wondered if a similar reduction might be feasible in this case. From the study no evidence of reduction was detected, but we obtained some interesting results which may help clarify the coordination behaviour of this metal.

5.2. EXPERIMENTAL and RESULTS

Preparative and manipulative details are given in appendices A and B.

A) Reaction between ZrCl_4 and Trimethylamine

NMe_3 was distilled in vacuo onto ZrCl_4 in a double ampoule. On warming to room temperature an immediate reaction occurred to give a pale yellow solution and a white solid. Extraction in the normal double ampoule manner gave a small amount, $\sim 2\%$ yield, of a yellow soluble product, and the bulk product, which was white and insoluble.

The yellow product analysed for $\text{ZrCl}_4 \cdot x\text{NMe}_3$, where $x = 2.5-3.5$. Melting point: Decomposed at $T > 318^\circ\text{K}$, to a brown solid.

The infrared spectrum contained bands at; 3260(m), 3150(s), 3028(m), 2990(m), 2960(m), 2940(sh), 2850(w), 2760(w), 1461(s), 1413(m), 1375(m), 1257(m), 1225(w), 1100(m), 1040(sh), 1012(s), 975(s), 887(s), 849(w), 804(s), 720(w), 671(w), 520(m), 465(m), 445(sh), 355(s), 332(s), 306(s), 236(s), 227(s) and 160(s) cm^{-1} respectively.

The electronic spectrum contained bands at; 28,410(sh), 39,525(sh), 46,085(sh) and 49,250(sh) cm^{-1} respectively when run as the solid.

The proton nmr spectrum contained a band at 7.66 τ with a weak secondary peak at 7.50 τ .

The white insoluble product analysed for $\text{ZrCl}_4 \cdot 2\text{NMe}_3$.

Anal. Calcd. for $\text{C}_{18}\text{H}_{18}\text{Cl}_4\text{N}_2\text{Zr}$: C, 20.5; H, 5.1; Cl, 40.4; N, 8.0; Zr, 26.0. Found: C, 20.1; H, 5.3; Cl, 41.1; N, 7.9; Zr, 25.9.

Melting point: Decomposed at $T > 318^\circ\text{K}$, to a brown solid.

The infrared spectrum contained bands at; 3258(m), 3155(s), 3031(m), 2993(m), 2962(w), 2944(m), 2840(w), 2730(w), 1459(s),

1414(m), 1381(m), 1252(m), 1209(w), 1108(w), 1043(m), 1012(m), 978(s), 888(s), 812(m), 721(w), 672(w), 540(w), 441(w), 373(w), 360(s), 342(s), 304(s), 232(s), 227(s) and 155(s) cm^{-1} respectively. The electronic spectrum contained bands at; 28,330(sh), 41,150(sh), 45,450(sh) and 51,020(sh) cm^{-1} respectively when run as the solid.

When the above reaction was repeated with a trace of zinc dust added to the reaction mixture an immediate reaction occurred giving a yellow solution and a white solid. Extraction in the normal double ampoule manner gave a white insoluble product, in $\sim 45\%$ yield, and a yellow soluble product. A second extraction of the soluble material with NMe_3 , in vacuo, yielded a white slightly soluble product and a yellow soluble product, contaminated with some white soluble material. A single extraction of the soluble material yielded an almost pure sample of the yellow product.

The white insoluble material and yellow soluble material were shown by analysis and spectral measurements, to be identical to the products of those colours obtained in the reaction in the absence of zinc dust.

The white soluble material analysed for $\text{ZrCl}_4 \cdot 2\text{NMe}_3$.
 Anal. Calcd. for $\text{C}_6\text{H}_{18}\text{Cl}_4\text{N}_2\text{Zr}$: C, 20.5; H, 5.1; Cl, 40.4; N, 8.0; Zr, 26.0 . Found: C, 20.4; H, 5.6; Cl, 40.3; N, 7.9; Zr, 26.3 .
 Melting point: Decomposed at $T > 323^\circ\text{K}$, to a brown solid.
 The infrared spectrum contained bands at; 3140(m), 3017(m), 2984(m), 2930(s), 2908(m), 2830(w), 2858(w), 2799(m), 2730(w), 1468(s), 1409(m), 1258(w), 1229(m), 1103(m), 1040(w), 1018(w), 976(s), 806(s), 722(w), 508(s), 424(w), 360(s), 343(s), 303(s),

233(s), 227(s) and 155(s) cm^{-1} respectively.

The electronic spectrum contained bands at; 28,160(sh) and 45,660(sh) cm^{-1} respectively when run as the solid.

B) Reaction between ZrCl_3 and Trimethylamine

NMe_3 was distilled in vacuo onto ZrCl_3 in a double ampoule. On warming to room temperature a slow reaction occurred giving a golden brown solution and a dark brown solid. Extraction in the normal double ampoule manner gave a pale brown solid, and left behind a dark brown/green insoluble solid.

Analysis for the extracted material was never consistent but gave $\text{ZrCl}_3 \cdot x\text{NMe}_3$, where $x = 1.25\text{--}2.5$.

The infrared spectrum contained bands at; 3130(m), 3012(w), 2945(m), 2910(m), 2850(w), 2725(w), 1461(s), 1404(m), 1251(m), 1230(m), 1098(w), 1040(sh), 1014(s), 978(s), 949(w), 812(s), 722(w), 665(w), 450(w), 308(s), 178(s) and 152(s) cm^{-1} respectively.

5.3. DISCUSSION

The reaction between zirconium(IV)chloride and trimethylamine has been previously investigated,¹⁷⁷ by the sealed ampoule technique, and found to yield the white insoluble bis-adduct, $\text{ZrCl}_4 \cdot 2\text{NMe}_3$. When we repeated this reaction using the double ampoule technique it appeared to proceed as reported, giving a clear solution and a white insoluble product. However, on close inspection it was seen that the solution was a very pale yellow in colour. Extraction, by the normal double ampoule method, yielded a small quantity, $\sim 2\%$ yield, of a yellow amine soluble product.

The reaction was also carried out in the presence of a trace amount of zinc dust, in the hope that this might facilitate the break up of the halide lattice; as is the case with chromium(III)chloride. In this case a soluble yellow product, a slightly soluble white product and a white insoluble product were obtained. The white insoluble product, $\sim 45\%$ yield, was purified by repeated extraction of the soluble products with the parent amine. The slightly soluble white product, $\sim 45\%$ yield, was then purified by extraction with the amine until all trace of the yellow product was removed. The total purification of the yellow product could not be achieved, as each extraction left it contaminated with a trace of the slightly soluble white product. However, a single extraction of the soluble material with trimethylamine yielded the yellow product with only a trace contaminant of the white.

No evidence for reduction could be detected in these reactions, and all the complexes were diamagnetic. The electronic spectra of the adducts, TABLE 5.1., were clear of absorptions in the visible and near infrared regions, only showing intense absorp-

tions in the UV, consistent with a d^0 system.

TABLE 5.1. Electronic Spectra of $ZrCl_4/NMe_3$ Adducts

Complex	Absorption Maxima* (cm^{-1})
White Insoluble	28,330(sh); 41,150(sh); 45,450(sh); 51,020(sh).
White Soluble	28,160(sh); 45,660(sh).
Yellow Soluble	28,410(sh); 39,525(sh); 46,085(sh); 49,250(sh).

*Recorded as nujol mulls.

The intense UV absorptions may be assigned to charge transfer transitions of the type zirconium(d) \leftarrow chlorine(π).

The infrared spectra of the adducts showed the white insoluble products, from each reaction, were the same, and the yellow soluble products, from each reaction, were the same. Their spectra, 4000-500 cm^{-1} , contained the bands associated with coordinated trimethylamine,³⁸ and were virtually identical. The spectrum of the white soluble adduct showed distinct variations from those of the other products. In particular, the first two adducts show two strong peaks at $\sim 975\text{ }cm^{-1}$ and $1012\text{ }cm^{-1}$, which are associated with the methyl rocking modes, the white soluble product only shows one such peak, at $976\text{ }cm^{-1}$. Also the $\nu_{as}(\text{CN})$ mode in this adduct is found at a position some $25\text{ }cm^{-1}$ to lower frequency, than found in the other adducts.

Analysis of the products revealed the formulations, $ZrCl_4 \cdot 2NMe_3$ for the white insoluble product, $ZrCl_4 \cdot 2NMe_3$ for the white soluble product and $ZrCl_4 \cdot xNMe_3$ (where $x = 2.5-3.5$) for the yellow product. The latter obviously contains an amount of associated,

but non-coordinated, amine. On either pumping in vacuo at room temperature for several hours, or washing for a few hours with benzene, it releases trimethylamine and reverts to the white insoluble adduct, $\text{ZrCl}_4 \cdot 2\text{NMe}_3$. The proton nmr of this complex, in benzene solution, gives a singlet absorption at 7.66 τ with a weak secondary peak at 7.50 τ , which may be associated with the 'free' amine.

The metal-halogen stretching frequencies of the complexes are shown in TABLE 5.2.. For comparison, the $\nu(\text{MCl})$ vibrations of $\text{ZrCl}_4 \cdot 2(\text{diars})$, a known eight coordinate adduct,¹⁷⁸ and ZrCl_4 ,¹⁷⁹ shown by X-Ray determination to have a six coordinate polymeric structure,^{180,181} are also included.

TABLE 5.2. Metal-Halogen Stretching Frequencies for Zirconium(IV)
Halide Systems

Complex	$\nu(\text{MCl})$ (cm^{-1})
White Insoluble ($\text{ZrCl}_4 \cdot 2\text{NMe}_3$)	360; 342; 304; 232; 227; 155.
White Soluble ($\text{ZrCl}_4 \cdot 2\text{NMe}_3$)	360; 343; 303; 233; 227; 155.
Yellow Soluble ($\text{ZrCl}_4 \cdot x\text{NMe}_3$)	355; 332; 306; 236; 227; 160.
ZrCl_4	431; 388; 283; 271; 233.
$\text{ZrCl}_4 \cdot 2(\text{diars})$	335; 303; 295.

Clark has demonstrated¹⁰³ how diagnostically useful these frequencies can be in the structural determination of halide complexes. One point in particular is that, for a given metal in a given oxidation state, as the coordination number of the

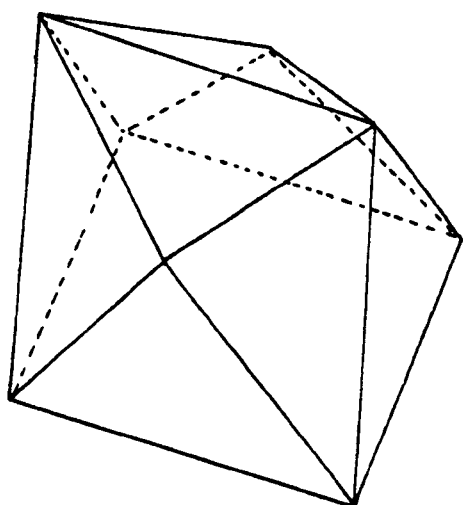
metal centre increases, the metal-halogen stretching frequency decreases. It can be seen from the table that the $\nu(\text{MCl})$ bands of the adducts are indicative of the complexes being eight coordinate, and hence polymeric, presumably through halogen bridging.

This coordination number is not at all unusual for zirconium,^{178,182} and has already been suggested by Fowles¹⁷⁷ as a possible structure for the white insoluble $\text{ZrCl}_4 \cdot 2\text{NMe}_3$ adduct that he isolated.

A molecular weight determination, by freezing point depression, was carried out on a benzene solution of the yellow product. The temperature depression observed was too small to be read to any degree of accuracy, implying at least an oligomeric structure for the adduct. The white soluble product proved to show too little solubility for a successful molecular weight determination to be made.

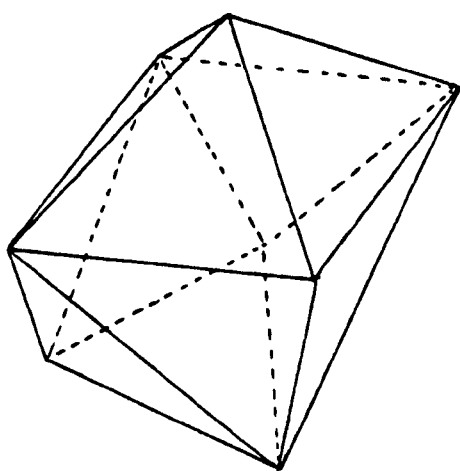
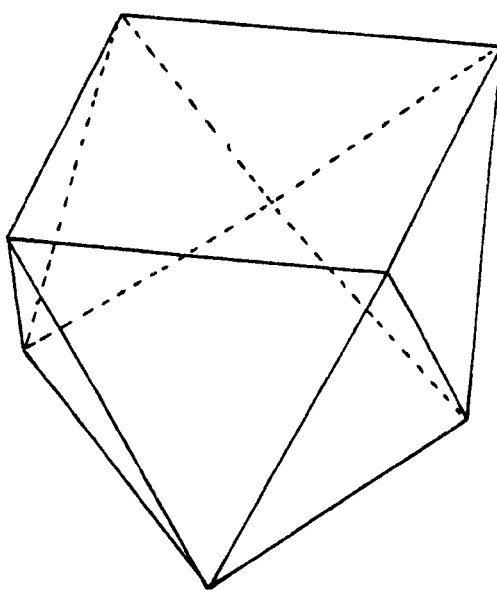
The low infrared spectra of the adducts clearly indicate the presence of metal-halogen bridge bonding, with vibrations due to these linkages observed at approximately 233, 227 and 155 cm^{-1} respectively. They also indicate a coordination number of eight for the metal centre, with the strong $\nu(\text{MCl})_{\text{octahedral}}$ band at $\sim 430 \text{ cm}^{-1}$ lowering to $\sim 355 \text{ cm}^{-1}$. We propose that the trimethylamine has failed to break down the zirconium(IV)chloride lattice, and yielded polymeric products by simple addition, without metal-halogen bridge bond cleavage.

There are a number of possible geometries for eight coordination, the most common, which have all been found for zirconium(IV) adducts,¹⁸² are shown in FIGURE 5.1.. The energy difference between the various geometries seems to be very small, and the final geometry chosen by an adduct is the result of



Hendecahedron

Square
Antiprism



Dodecahedron

FIGURE 5.1. Eight Coordinate Polyhedra

several varying factors.¹⁸² Dodecahedral is the geometry that is most commonly found in eight coordinate zirconium(IV) species.

It can be seen from FIGURE 5.1. that all the geometries are based on, and can be derived by simple distortions of, a cube. Therefore, for clarity, the following tentative proposals are based on a cubic structure, with the metal atom positioned at the centre of the cube.

The structure of zirconium(IV)chloride has been derived by Krebs^{180,181} and is that of zig-zag chains of ZrCl_6 octahedra sharing two common edges, FIGURE 5.2.. If the hypothesis that reaction occurs by simple addition, without metal-halogen bond cleavage, is correct, then four of the eight coordination positions about zirconium will be occupied by bridging chlorides. The two remaining chlorides and the two amine groups may then occupy any of the remaining four positions, leading to six potential structures, shown in FIGURES 5.3.(A-F).. In these diagrams only the amine positions are shown, the unmarked apices are occupied by chlorine atoms. From these diagrams it can be seen that structures A and B are the same, and that structures C and D are the same. This, therefore, limits the number of possible structures to four, A, C, E and F. Two of these, A and E, can be seen to involve the amine groups coordinated cis along the edge of the cube. The third, C, involves the sterically more favourable arrangement with the amines in trans facial positions, but still cis with respect to the metal. The fourth structure, F, seems sterically the most favourable, with the two bulky amine groups in trans diagonal positions. Therefore, on steric grounds, the structures C and F are the most probable to be assigned to the two isomeric $\text{ZrCl}_4 \cdot 2\text{NMe}_3$ adducts.

A choice of a structure for each isomer can be made on

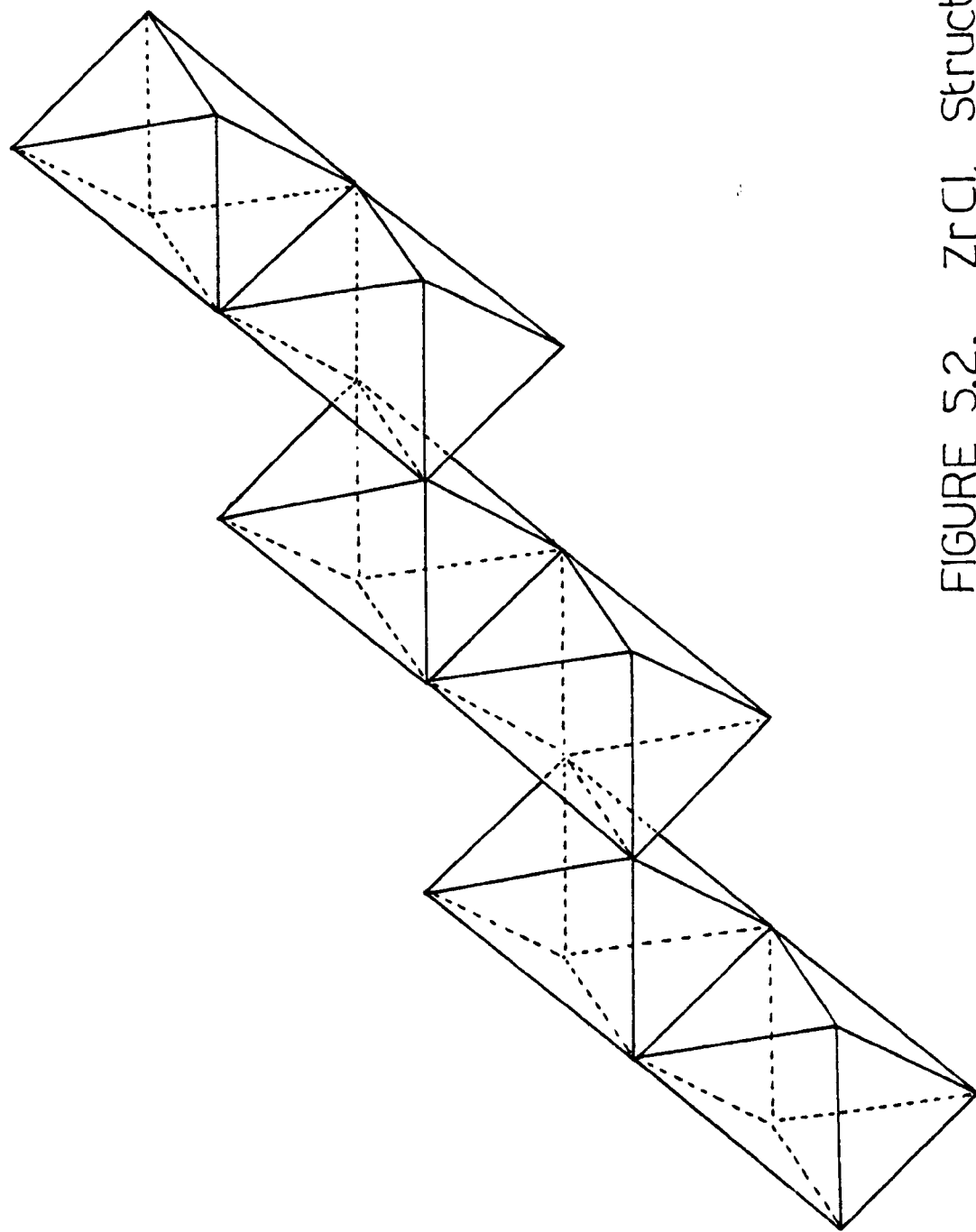


FIGURE 5.2. ZrCl_4 Structure

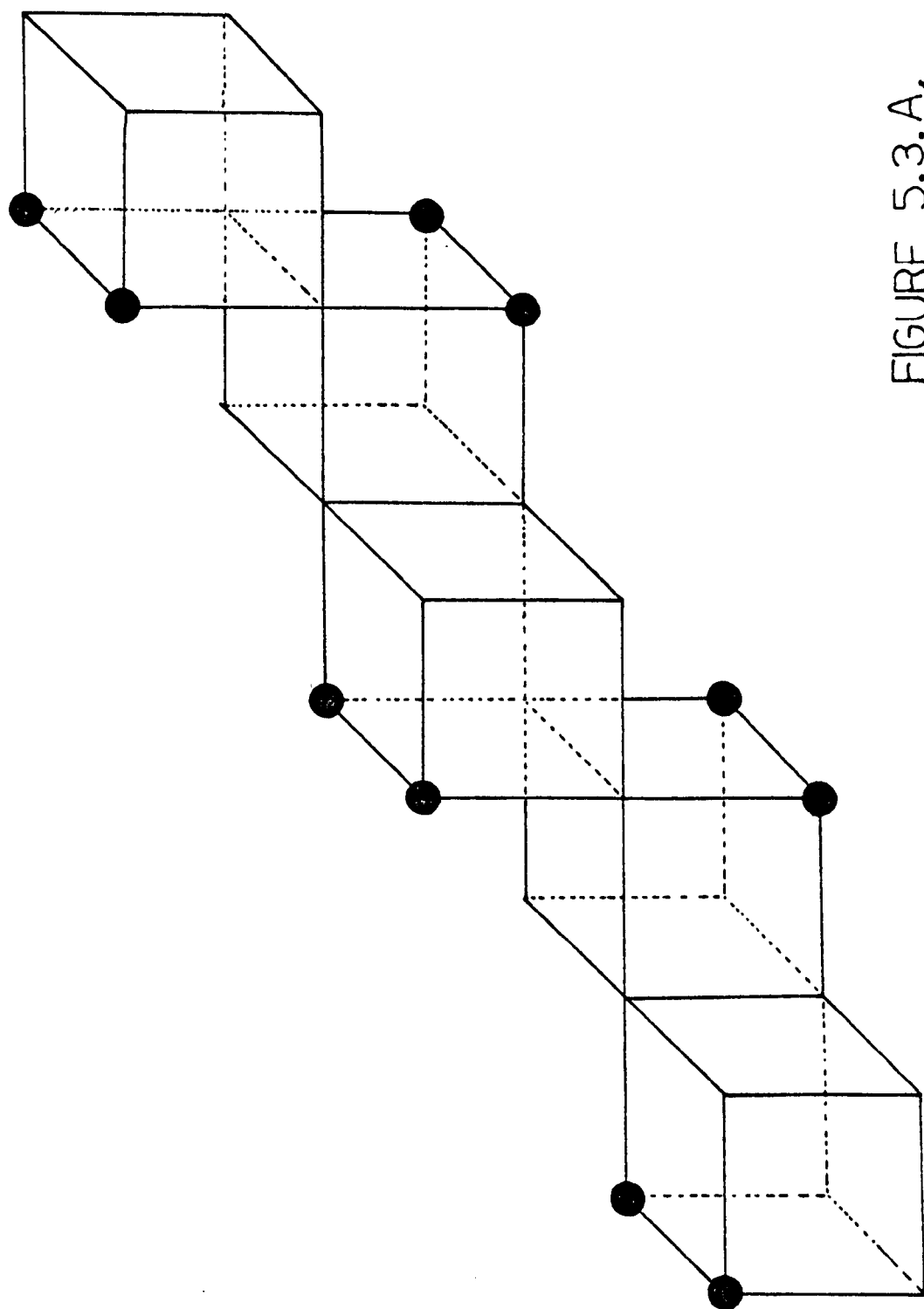


FIGURE 5.3.A.

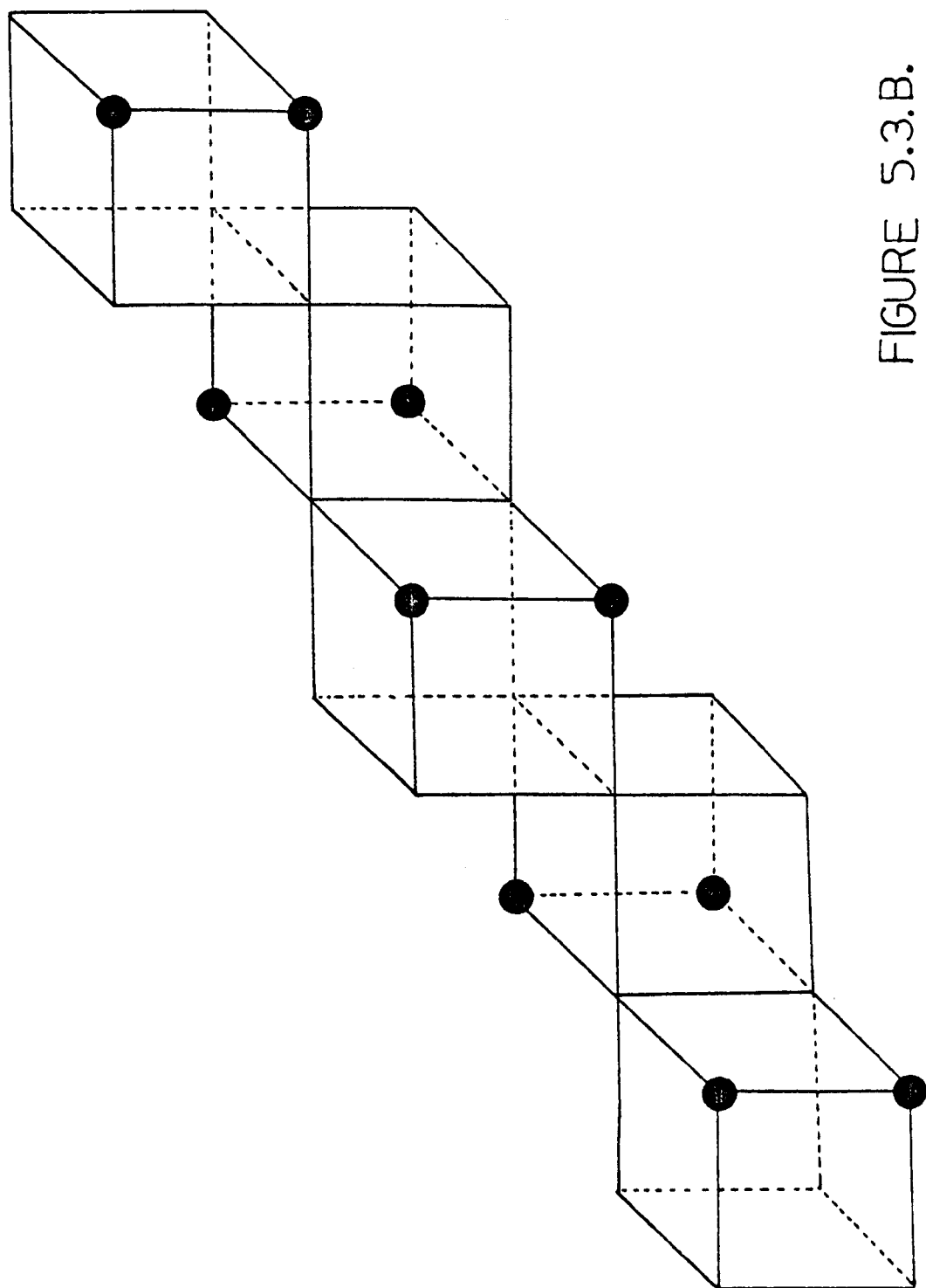


FIGURE 5.3.B.

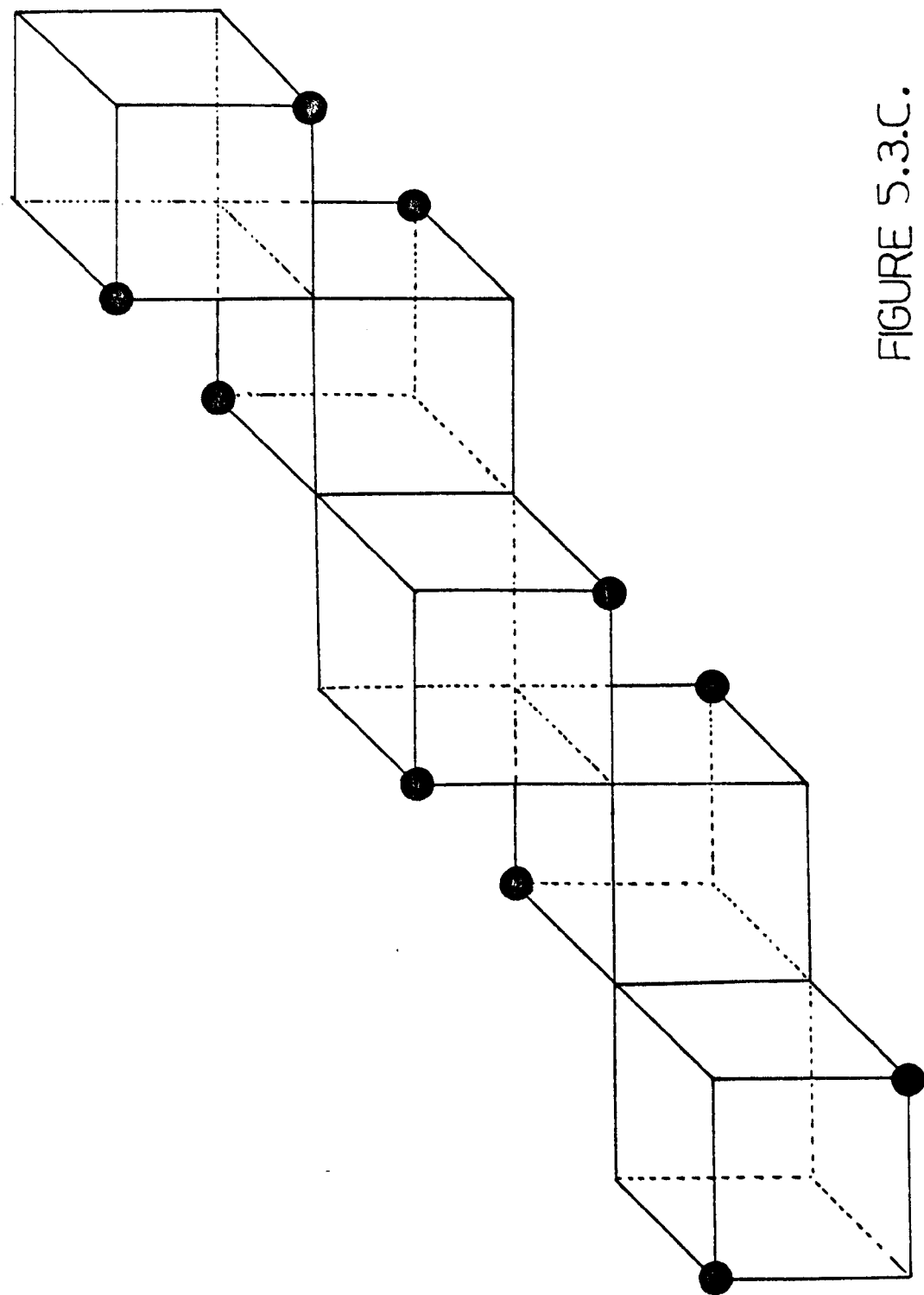


FIGURE 5.3.C.

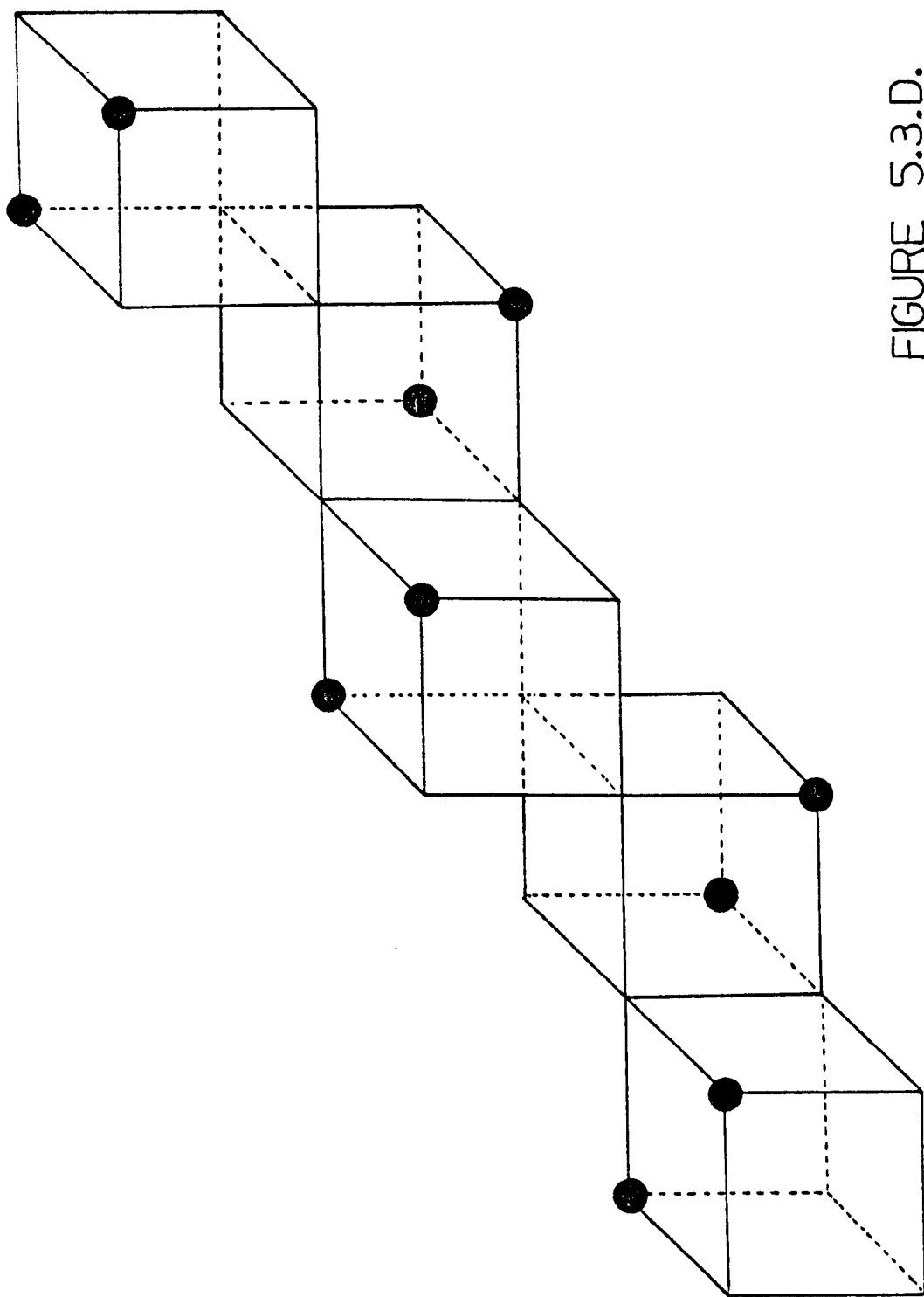


FIGURE 5.3.D.

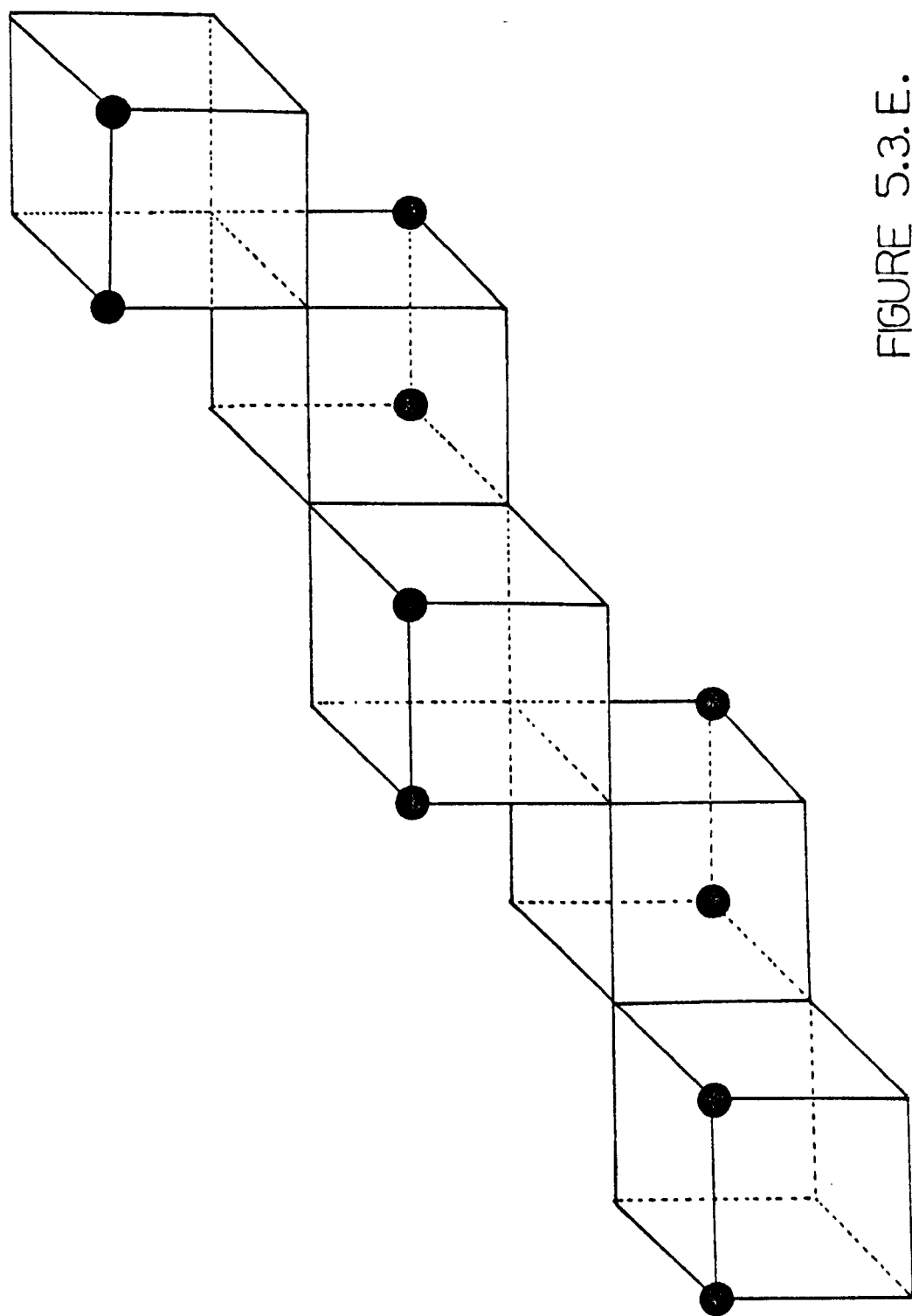


FIGURE 5.3.E.

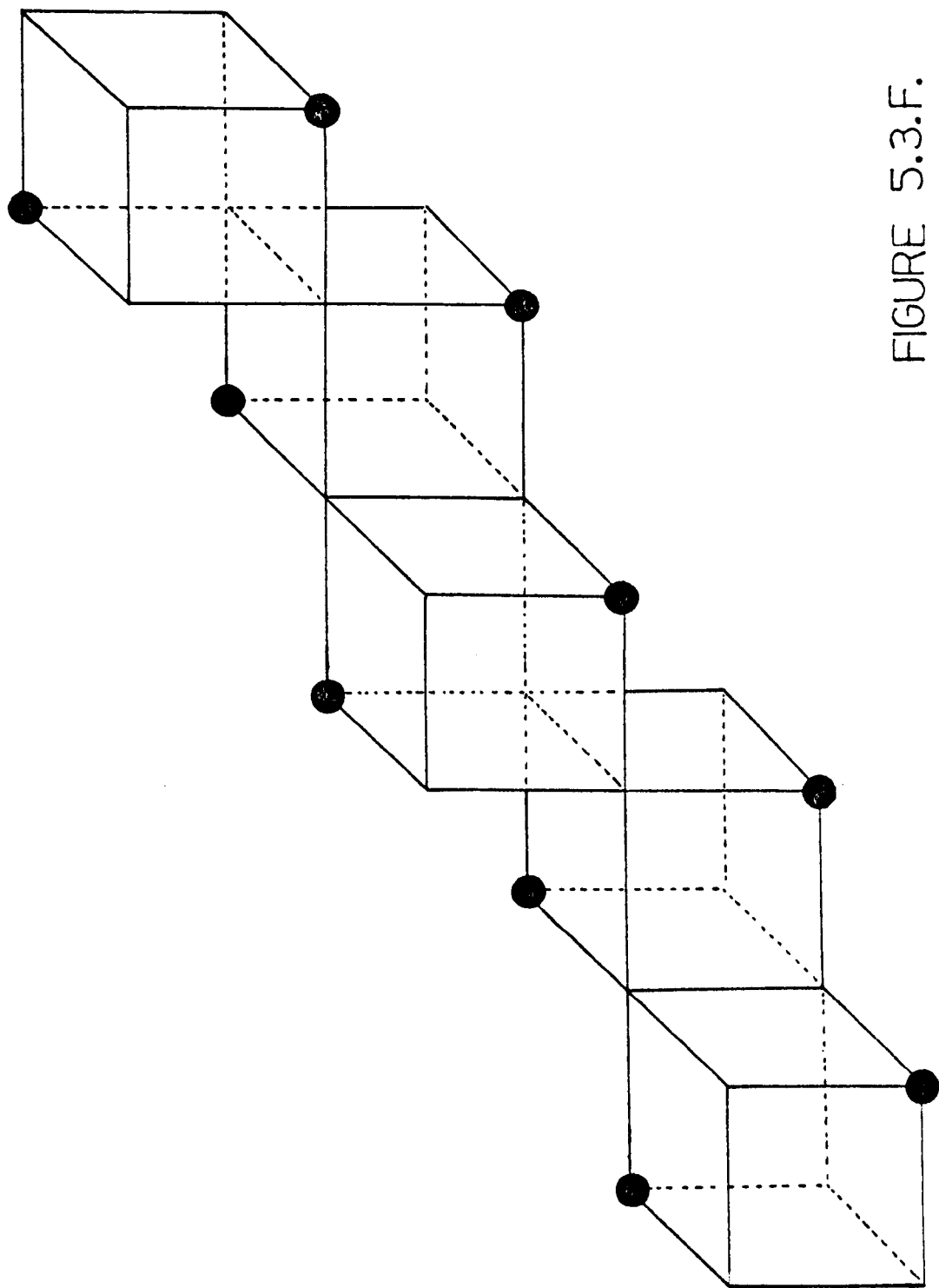
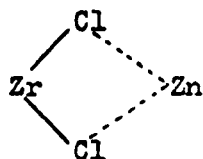


FIGURE 5.3.F.

consideration of their formation conditions. The kinetics of reactions at solid-liquid interfaces is complex and far from understood, so only a simple qualitative picture can be viewed. In the absence of zinc dust the insoluble isomer is formed to the exclusion of the soluble, and in the presence of zinc dust they are both formed to approximately equivalent yields. From a steric viewpoint, the energy of F should be the lower, as the amine groups have obtained maximum separation and achieved a position of minimum non-bonded interaction. Attack of the amine on the ZrCl_4 to produce this structure would also involve each amine attacking from opposite sides of the metal, which must represent the more favourable mode of attack. On this basis it would seem that F is the most probable structure for the insoluble isomer.

The role of the zinc in this reaction is not clear. It is, however, probably associated with the zirconium via some form of halogen bond.

e.g.



This would effectively block one side of the zirconium from attack by the amine. In such circumstances the amine attack could occur from only one side of the metal, the majority of the possible approaches being obscured by the other fused ZrCl_6 octahedra. This would result in a cis structure being formed, as in C.

In the light of these considerations a structure related to that depicted in FIGURE 5.3.F. is assigned to the insoluble adduct, and a structure related to that of FIGURE 5.3.C. to the soluble adduct.

The behaviour observed in these reactions leads one to ask

if this is an isolated example, or one common to the metal. Unfortunately the coordination chemistry of zirconium(IV)chloride has not been widely studied,^{176,178,182} but the adducts that have been obtained have all been insoluble solids. The structures have normally been proposed as six coordinate and octahedral, though polymerisation could not be ruled out, except in the case of the eight coordinate $\text{ZrCl}_4 \cdot 2(\text{diars})$ adduct. The structure of this complex has been confirmed by X-Ray analysis.⁵⁸

Three compilations of the available low infrared data on these complexes are available for study.^{178,183,184} In all cases the data shows the highest frequency $\nu(\text{MCl})$ band to be $\sim 360 \text{ cm}^{-1}$. This is far below the 431 cm^{-1} observed for octahedral ZrCl_6 ,¹⁷⁹ and consistent with an eight coordinate geometry.

The $\text{ZrCl}_4 \cdot 2\text{pyr}$ adduct has been reported¹⁸⁴ to combine with a third ligand molecule, which it loses on pumping in vacuo and returns to the bis adduct. This behaviour parallels that of the white insoluble $\text{ZrCl}_4 \cdot 2\text{NMe}_3$ adduct. In each case the metal-halogen region of the infrared spectrum remains virtually unchanged, indicating that marked changes to the coordination geometry of the complex does not occur.

It would seem that the stability of the zirconium(IV) halide lattice, combined with the ability of the metal to exhibit stable high coordination, is sufficient in most cases to prevent the formation of monomeric species. To define this situation adequately a single crystal X-Ray structure determination is required, but the insolubility of the adducts obtained have, to date, prevented the growth of such crystals.

The preceeding work was instigated by an investigation of the coordination chemistry of zirconium(III), and some unusual results we found in that field. In the light of the preceeding section these results have been somewhat clarified. It would appear that a similar behaviour, to that shown by the (+4) oxidation state, is also shown by the (+3) oxidation state.

When zirconium(III)chloride was reacted with trimethylamine, in a double ampoule, a golden brown solution and a dark brown/-green insoluble product were obtained. Extraction of the soluble material was carried out by standard double ampoule technique, with the parent amine. However, when the solution was evaporated to dryness a pale brown solid was obtained, which was then found to be insoluble in the amine. The analysis of this product never proved to be consistent, but varied between 1.5 and 2.5 amines being associated with each ZrCl_3 unit.

The infrared spectrum of the metal-halogen region, TABLE 5.3., shows distinct changes from that of the anhydrous halide, also shown. The metal centre in ZrCl_3 is octahedrally coordinated, in a lattice consisting of infinite chains of ZrCl_6 octahedra sharing opposite trigonal faces;^{185,186} similar to that of $\beta\text{-TiCl}_3$.

TABLE 5.3. Low Infrared Data for ZrCl_3 and its NMe_3 Adduct

Complex	Absorption Maxima (cm^{-1})
ZrCl_3	340; 277; 228; 191; 128; 115.
$\text{ZrCl}_3 \cdot x\text{NMe}_3$	308; 178; 152.

As is the case with the zirconium(IV) adducts the metal-halogen stretching frequencies are significantly reduced from those of the halide, implying an increase in the coordination

number of the metal centre. It would seem that a similar reaction, involving incomplete break down of the halide lattice and addition of amine, is also occurring in this oxidation state. The adducts are solvolysed by 'additional' associated amine, which is then, on evaporation to dryness, released to yield the stable insoluble adduct.

The lattice of the trihalide represents a much more compact structure than that of the tetrahalide, the bridging being achieved through trigonal faces. The addition of the amine in this case is less facile and not as complete as that recorded in the tetravalent system. The insoluble solid remaining in the reaction, after extraction of the soluble material, shows a high halide:ligand ratio, and spectral evidence indicates that it is mainly unreacted ZrCl_3 .

Although analogous behaviour between the two systems is implied it is far from defined. Far more extensive and detailed studies, including X-Ray structural investigations, are needed to adequately define this new, and as yet, little explored field of transition metal chemistry.

CONCLUDING REMARKS

CONCLUDING REMARKS

In the study of the penta-coordinate state of the early transition metals we used two approaches. We looked at:

A) The reactivity and stability of the five coordinate state, and at,

B) the metal ion in situations that were potentially conducive to the production of the five coordinate state.

Both approaches yielded the expected result, that octahedral coordination is the dominant influence in the chemistry of these metals. Moreover, the results showed how strong this influence is relative to penta-coordinate requirements.

Two points for consideration that emerged are:

1) When looking at the reactions of a five coordinate adduct, it must be borne in mind that a separate, and quite independent, reaction may be occurring. A decomposition, or rearrangement, of that species to a hexa-coordinate state; induced by the strong preference of these metals for octahedral coordination.

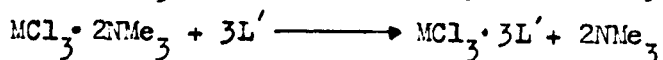
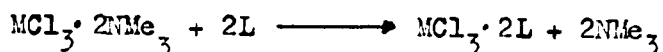
2) The powerful octahedral drive of the metals may be used to advantage. It has been demonstrated that this drive is sufficiently powerful to decree the bonding role of certain multidentate ligands, and may be used to control the donor capacity of some ligands.

This work in general has opened several possible lines for further investigation, many of which look inviting.

1) The five coordinate state: We have shown that the five coordinate $MCl_3 \cdot 2NMe_3$ ($M = Ti, V$ and Cr) adducts exhibit a decomposition trait in solution, allowing the metal to obtain an octahedral coordination geometry. How prevalent this behaviour is in the early transition series is an area that deserves further investigation, also the rates and mechanisms of these changes.

2) Kinetic studies of the five coordinate state: Few studies have been made on the reactions of five coordinate species, and these for the most part have concerned the later transition metals. Here both dissociative and associative pathways have been found,⁹²⁻⁹⁵ but in the early metals a dissociative pathway, to give a four coordinate intermediate, does not seem intuitively likely.

Initial investigations in this area have shown that the reactions;



are rapid and would require monitoring by a rapid technique, such as stopped flow.

A number of practical problems are present in the $\text{MCl}_3 \cdot 2\text{NMe}_3$ system:

- a) The air sensitive nature of the solutions; producing handling difficulties.
- b) The independent decomposition of the species in solution.
- c) The general insolubility of the products.

The third presents one of the biggest problems where the stopped flow technique is used. The solid precipitates could not only effect the optical density of the solutions, but also block the small bore tubes of the instrument. However, with a suitable choice of the system for investigation these problems could be overcome, and much valuable data collected.

3) Coordination chemistry of zirconium: We have seen that the zirconium/trimethylamine systems show evidence that the halide lattice is not completely broken down during reaction. Indeed there are indications that this behaviour is not restricted to the trimethylamine system. The behaviour is no doubt due to the strength of the halide lattice coupled with the ability of zirconium to assume coordination numbers higher than six.

The structural aspects of the coordination chemistry of zirconium requires further investigation; and efforts could be made particularly in the field of single crystal X-Ray determination.

In the preparative field there is wide scope for further work. A feasible line to follow would be to break down the halide lattice with multidentate ligands that could saturate the coordination sphere of the metal. This would reduce the likelihood of halogen bridging, and increase the possibility of gaining a monomeric species. Once a discrete monomeric species could be obtained ligand substitution might offer the correct route to further complexes.

APPENDIX A.

Starting Materials and Analytical Methods

APPENDIX A

Starting Materials and Analytical Methods

Materials

1) Gases

a) Ammonia: Was obtained as the anhydrous material from ICI Ltd., Teesside.

b) Carbon Dioxide: Was obtained from BDH Chemicals Ltd., Poole, and dried by passing through successive columns packed with anhydrous calcium chloride and silica gel.

c) Chlorine: Was obtained from ICI Ltd., Teesside, and dried by bubbling through concentrated H_2SO_4 , then passing through a column packed with silica gel.

d) Hydrogen Chloride: Was obtained from BDH Chemicals Ltd., Poole, and dried by passing through successive columns packed with anhydrous calcium chloride and silica gel.

e) Nitrogen: Was obtained from BOC Ltd., London, and dried by bubbling through concentrated H_2SO_4 , then passing through a column packed with molecular sieve type 4A and silica gel.

2) Liquids

a) Acetonitrile: Was obtained from Hopkin and Williams Ltd., Essex, and purified as follows:

Each 800 mls of liquid was refluxed, for ~1 hour, with 10 grms of anhydrous Na_2CO_3 and 15 grms of $KMnO_4$, then rapidly distilled under reduced pressure. The distillate was made slightly acidic with concentrated H_2SO_4 , decanted and distilled through a 12 inch column under a normal pressure of nitrogen.

b) Benzene: Was obtained from Koch-Light Laboratories Ltd., Colnbrook. It was stored over sodium wire and prior to use was

refluxed, for ~ 1 hour, with CaH_2 or Li AlH_4 and distilled under a normal pressure of nitrogen.

c) Carbon Disulphide: Was obtained from Hopkin and Williams Ltd., Essex. Prior to use it was refluxed, for ~ 1 hour, with CaH_2 or P_2O_5 and distilled under a normal pressure of nitrogen.

d) Dichloromethane: Was obtained from Hopkin and Williams Ltd., Essex. Prior to use it was refluxed, for ~ 1 hour, with CaH_2 or P_2O_5 and distilled under a normal pressure of nitrogen.

e) Dichlorodimethylsilane: Was obtained from Midland Silicones Ltd., Glamorgan.

f) Diisopropylether: Was obtained from Hopkin and Williams Ltd., Essex. It was stored over CaH_2 and sodium wire, and distilled from this, under a normal pressure of nitrogen, prior to use.

g) Ethylenediamine: Was obtained from Fisons Scientific Apparatus Ltd., Loughborough, and prior to use was distilled under a normal pressure of nitrogen from KOH .

h) Hexamethylcyclotrisilazane: Was prepared by the method of Osthoff and Kantor.¹⁸⁷

i) n-Hexane: Was obtained from BDH Chemicals Ltd., Poole. It was stored over sodium wire and prior to use was refluxed, for ~ 1 hour, with CaH_2 or Li AlH_4 and distilled under a normal pressure of nitrogen.

j) Pyridine: Was obtained from Fisons Scientific Apparatus Ltd., Loughborough, and prior to use was distilled under a normal pressure of nitrogen from KOH .

k) Tetrahydrofuran: Was obtained from Fisons Scientific Apparatus Ltd., Loughborough, and prior to use was refluxed, for ~ 1 hour, with LiAlH_4 and distilled under a normal pressure of nitrogen.

l) Tetrahydrothiophene: Was obtained from BDH Chemicals Ltd., Poole, and prior to use was refluxed, for ~ 1 hour, with CaH_2

and molecular sieve type 4A and distilled under a normal pressure of nitrogen.

m) Tetramethylethylenediamine: Was obtained from Ralph N. Emanuel Ltd., Wembley, and prior to use was distilled under a normal pressure of nitrogen from KOH.

n) Titanium Tetrachloride: Was obtained from Hopkin and Williams Ltd., Essex. It was stored over Cu powder and distilled in vacuo prior to use.

o) Triethylenetetramine: Was obtained as commercial grade material from Union Carbide UK Ltd., Southampton.

p) Trimethylamine: Was obtained from Hopkin and Williams Ltd., Essex. It was stored in vacuo over KOH and distilled in vacuo prior to use.

q) Tris(2-aminoethyl)amine: Was obtained either from, Strem Chemicals Inc., Danvers, Mass., or by extraction from commercial grade trien following the method of Forsberg et al.¹⁸⁸ Prior to use it was distilled under reduced pressure from KOH.

r) Tris(2-dimethylaminoethyl)amine: Was prepared from tren by the method of Ciampolini and Nardi.¹¹² Prior to use it was distilled under reduced pressure from KOH.

3) Solids

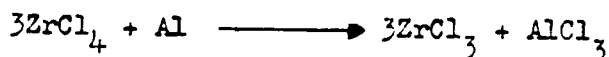
a) Aluminium Powder: Was obtained from BDH Chemicals Ltd., Poole.

b) $MCl_3 \cdot 2NMe_3$ ($M = Ti, V$ and Cr): Were prepared from the anhydrous metal trihalides and NMe_3 , using the double ampoule method of Fowles et al.³⁸

c) Chromium(III)chloride: Was obtained as the anhydrous material from Pfaltz and Bauer Inc., Flushing, NY.

d) Octamethylcyclotetrasilazene: Was prepared by the method of Osthoff and Kantor.¹⁸⁷

- e) Sodium Tetraphenylborate: Was obtained from BDH Chemicals Ltd., Poole, and oven dried at 373°K.
- f) Silver Perchlorate: Was obtained from BDH Chemicals Ltd., Poole, and dried in vacuo over P_2O_5 at 373°K.
- g) α -Titanium(III)chloride: Was obtained as the anhydrous material from K and K Laboratories, Plainview, NY.
- h) Trichloroacetic Acid: Was obtained from Fisons Scientific Apparatus Ltd., Loughborough, and dried in vacuo over P_2O_5 at room temperature.
- i) [Tris(ethylenediamine)chromium(III)] chloride: Was prepared by the method of Gillard and Mitchell.¹²⁶
- j) $MCl_3 \cdot 3THF$, (M = Ti, V and Cr): Were prepared by the method of Kern.¹⁴
- k) Vanadium(III)chloride: Was obtained as the anhydrous material from K and K Laboratories, Plainview, NY.
- l) Zirconium Powder: Was obtained from Cerac/Pure Inc., Menomonee Falls, Wisconsin.
- m) Zirconium Tetrachloride: Was prepared from zirconium metal and chlorine gas in the apparatus shown in FIGURE A.1.. A slow stream of chlorine, together with a stream of nitrogen carrier gas, was passed over the surface of the zirconium metal at $\sim 800^\circ K$. The zirconium tetrachloride sublimed out of the furnace and was 'chased' into the receiver with a bunsen burner. On completion of the reaction the receiver was removed to the vacuum line, under nitrogen, and pumped in vacuo for several hours.
- n) Zirconium Trichloride: Was prepared by the reduction of the tetrachloride with aluminium powder.



A very slight excess of the stoichiometric amount of $ZrCl_4$ was loaded with the aluminium powder into a glass tube, which was

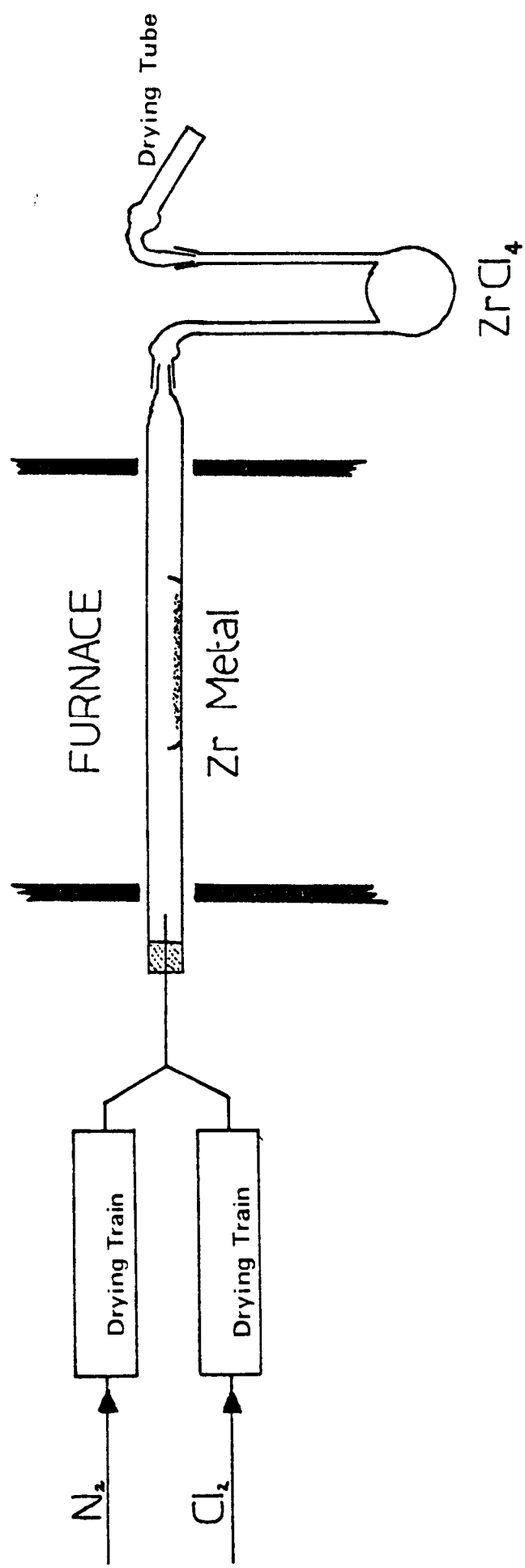


FIGURE A.1. Apparatus for the Preparation of ZrCl_4

then sealed under vacuum. The reagents were thoroughly mixed, using a mechanical mixer, and the tube placed in a furnace at $470-525^{\circ}\text{K}$. The tubes were removed from the furnace each day and the contents remixed. Reaction was complete after ~ 1 month, at which time the tubes were opened and the AlCl_3 and excess ZrCl_4 sublimed out, under vacuum, leaving the solid ZrCl_3 .

Analytical Methods

a) Chlorine: Was determined by the Volhard Method.¹⁸⁹

A small quantity of the sample (typically ~ 0.1 grms) was hydrolysed with aqueous HNO_3 , and the solution made up to 50 mls in a graduated flask. Determinations were then carried out on 10 ml aliquots in the normal manner. The AgNO_3 solution was standardised against NaCl , using K_2CrO_4 as indicator, and the KSCN solution, against the AgNO_3 solution, using ferric ion as indicator.

b) Chromium: Was determined spectrophotometrically following oxidation to chromate. A small quantity of the sample was hydrolysed and made up to a standard aqueous solution ($\sim 10^{-3}\text{M}$). A 10 ml sample of this solution was then made alkaline with KOH and treated with H_2O_2 to produce the yellow chromate solution. After excess H_2O_2 had been boiled off, the solution was made up to 100 mls (i.e. $\sim 10^{-4}$), and its optical density measured at 372 nm. At this wavelength ϵ for the CrO_4^{2-} ion is 4830. The concentration of chromate was then established from the equation:

$$\text{OD} = \epsilon cl$$

There; OD = Optical density.

ϵ = Molar extinction coefficient.

c = Concentration.

l = Path length.

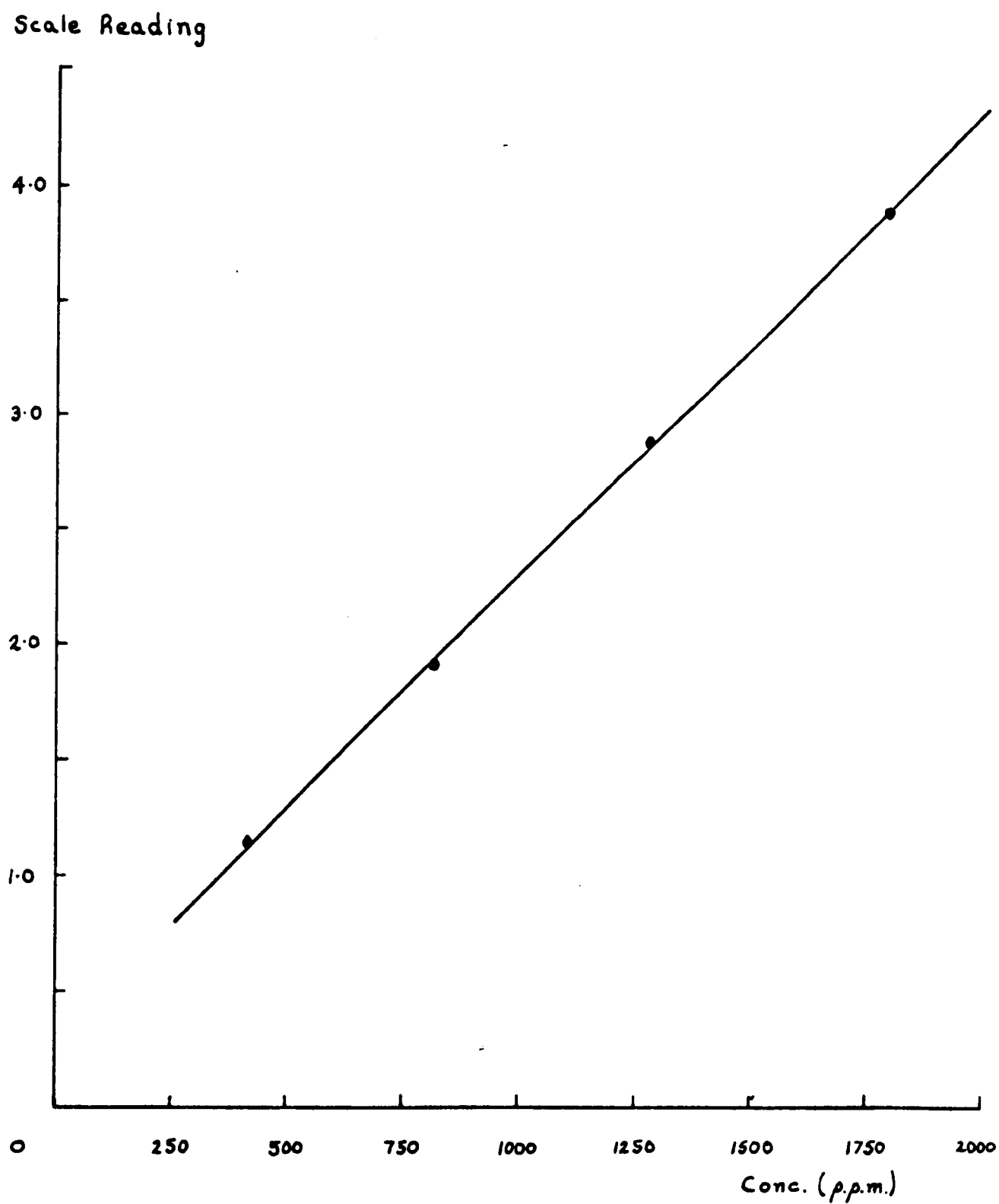


FIGURE A.2. Calibration of Atomic Absorption Spectrometer. Ti Lamp 364.3 nm.

c) Titanium: Was determined either, gravimetrically following combustion to the oxide, or spectroscopically by atomic absorption.

i) Gravimetrically: The sample, typically ~0.025 grms, was placed in a platinum crucible, previously heated to constant weight, and spotted with a few drops of concentrated HNO_3 . It was then heated gently, using a Meiker burner, until combustion occurred, after which it was heated strongly to constant weight. The weight of TiO_2 was then recorded.

ii) Atomic Absorption: The capacity of an element to absorb light of its characteristic resonance line, when in the atomic state, is directly proportional to its concentration. This capacity is used in atomic absorption spectrometry to determine the concentrations of unknown solutions of the element. Titanium was determined in 1:1 isopropanol:water using an EEL 140 atomic absorption spectrophotometer at 364.3 nm, employing a nitrous oxide/acetylene flame and an EEL type C831/Ti hollow cathode lamp. The machine was calibrated in the desired range using standard solutions of TiCl_4 in 1:1 isopropanol:water, see FIGURE A.2..

d) Zirconium: Was determined gravimetrically following combustion to the oxide. Typically ~0.025 grms of the sample was placed in a platinum crucible, previously heated to constant weight, and spotted with a few drops of concentrated HNO_3 . It was then heated gently, using a Meiker burner, until combustion occurred, after which it was heated strongly to constant weight. The weight of ZrO_2 was then recorded.

Elemental carbon, hydrogen, nitrogen, oxygen and sulphur analyses were carried out professionally at either, the A. Bernhardt Microanalytical Laboratory, Mullheim, Germany, or the National

Physical Laboratories, Middlesex, England.

APPENDIX B.

Experimental Techniques

APPENDIX B

Experimental Techniques

1) Preparative and Manipulative Techniques

Due to the extreme air/moisture sensitivity of the products, and many of the reactants, described in this thesis, a number of special preparative and manipulative techniques were employed. These all involved the handling of materials either, under an inert atmosphere, or in the absence of an atmosphere: in a high vacuum.

All glassware was thoroughly washed, in chromic acid, and dried prior to use. Drying was normally carried out by baking the apparatus in an oven at 398°K for several hours, and, where possible, then flaming the apparatus whilst being pumped in vacuo.

a) The 'Dry Box'

Much of the handling of materials was carried out in a steel glove box continually flushed with a supply of dry oxygen-free nitrogen. Two dishes of P_2O_5 were kept in the glove box, to remove residual traces of moisture. These were stirred daily, and replaced regularly, to ensure a continuing absence of moisture. Entry to the box was effected via an 'air' lock type entrance port, which was flushed with a rapid independent supply of dry oxygen-free nitrogen.

b) The Vacuum Line

The preparation and isolation of the products was carried out in sections of a standard all glass high vacuum system, FIGURE 3.1.. The vacuum was produced and maintained by a Genevac double stage rotary piston vacuum pump, type G.H.D.3, and an electrically heated mercury diffusion pump.

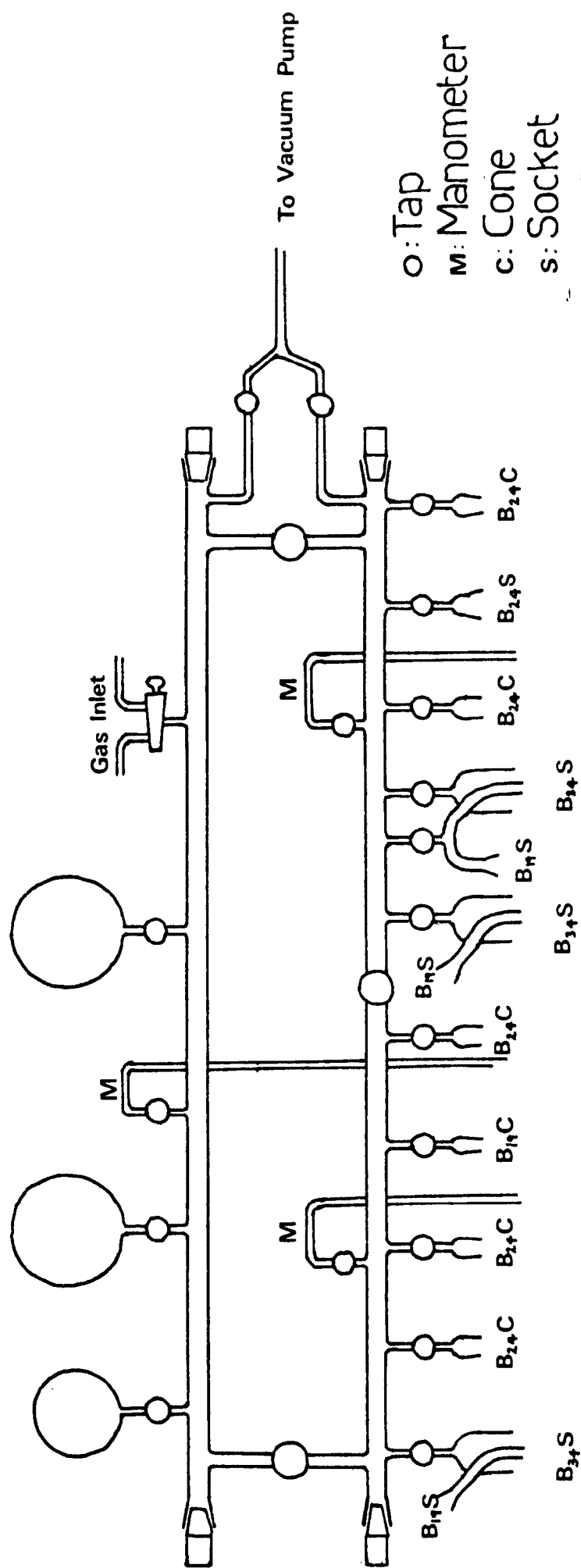


FIGURE B.1. The Vacuum Line

c) Weighings

The weighing of 'air' sensitive materials was generally carried out in a glove box, similar to that described above, specially fitted with a Stanton Instruments Unimatic CLX 4 balance; reading to better than 1 mg.

The weighing of materials for analytical determinations was made employing sealed ampoules and a Mettler Type H 16 balance; reading to better than 0.1 mg.

d) Solvent Drying

All solvents used in this work were rigorously dried by reflux with and distillation from CaH_2 , Li AlH_4 or P_2O_5 , under a nitrogen atmosphere. The use of specially designed solvent stills, FIGURE B.2., readily allowed a rapid reflux, collection and removal of solvents to be achieved. The glass sinter also allowed for the efficient degassing of solvents to be performed in situ, by passing dry nitrogen, via tap A, through the solvent during collection.

e) Reactions

Single Ampoule Method

The reactants, and solvent if any, were loaded into the ampoule, FIGURE B.3., which was then sealed under vacuum at point A. On completion of the reaction the ampoule was opened under vacuum via the break-seal B, broken by impact from the magnet C.

Double Ampoule Method

This method was used where the product of the reaction was soluble, but the starting materials insoluble. The reagents and solvent were loaded into flask A, FIGURE B.4., and the ampoule sealed under vacuum at point B. As the reaction proceeded the solution of the product was decanted through the sinter into flask C. The solvent was then distilled back to flask A, by

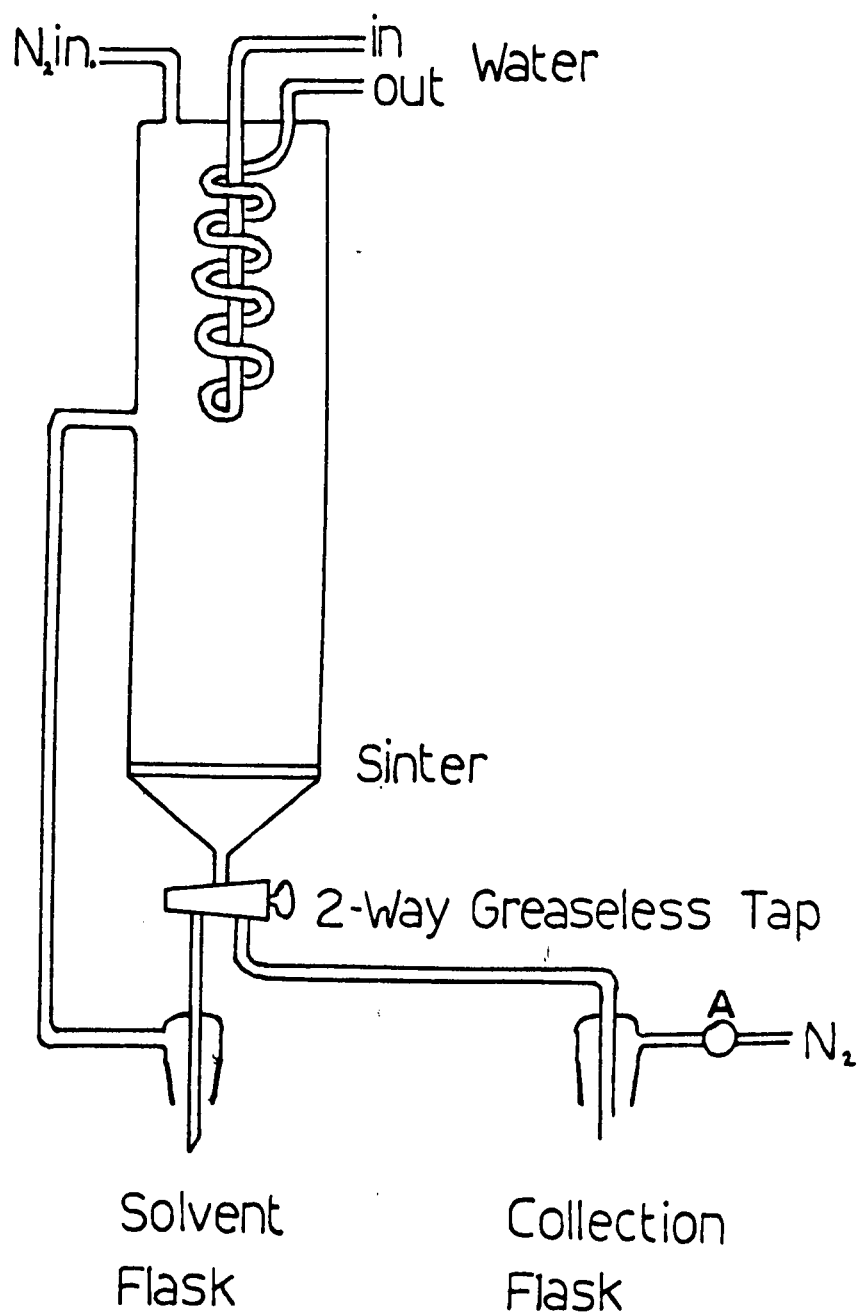


FIGURE B.2. Solvent Still

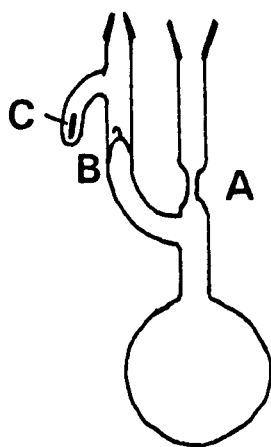


FIGURE B.3. Single Ampoule

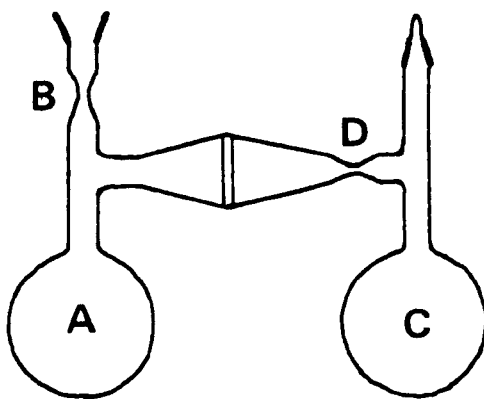


FIGURE B.4. Double Ampoule

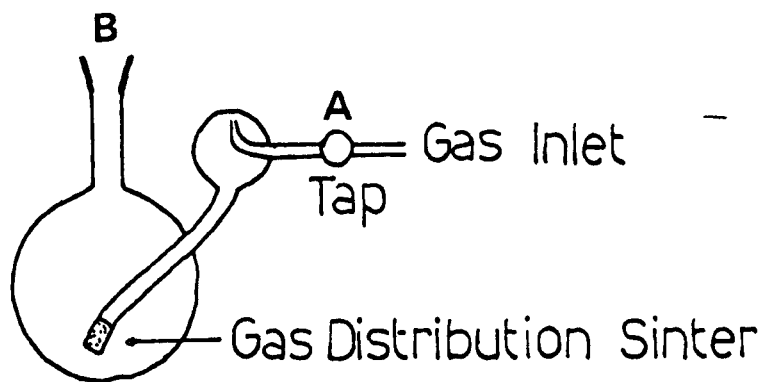


FIGURE B.5. Gas Reaction Flask

cooling this, and the process repeated until complete extraction had been achieved. The solvent was then frozen in flask A, and flask C, containing the product, sealed at point D. The product was then removed from the flask, when required, by opening this under a nitrogen atmosphere.

Gas Reactions

Reactions involving gases were carried out using either the above methods, by condensing the gas into the reaction vessel, or by bubbling the gas through a solution of the second reactant. In the latter case the apparatus shown in FIGURE B.5. was used, the gas being introduced via tap A and removed at point B.

f) Preparations

The general preparative procedure employed varied according to the states of the reactants, but could be ascribed to one of the three main procedures given below.

i) Reactions of the Solid + Solid Type

The two solid reactants are loaded into the reaction vessel in the dry box, the vessel is then removed to the vacuum line and evacuated. Dry degassed solvent is distilled, in vacuo, onto the reactants and the vessel sealed under vacuum. The sealed flask is then placed on a mechanical shaker, or in a water bath at a suitable temperature, until reaction is complete.

ii) Reactions of the Solid + Volatile Liquid Type

The solid reactant is loaded into the reaction vessel in the dry box, the vessel is then removed to the vacuum line and evacuated. A known quantity of the liquid reactant, from a graduated trap, is then condensed, in vacuo, with the dry degassed solvent onto the solid reactant, and the vessel sealed under vacuum. The sealed flask is then placed on a mechanical shaker, or in a water bath at a suitable temperature, until reaction is

complete.

iii) Reaction of the Solid + Slightly Volatile Liquid (Soluble Solid) Type

The solid reactant is loaded into the reaction vessel, and the slightly volatile liquid (soluble solid) into a flask, in the dry box. These are then removed to the 'extraction' system of the vacuum line, as shown in FIGURE B.6., and evacuated. Dry degassed solvent is then condensed, in vacuo, into both vessels, and allowed to thaw. By rotation of the flask and curved sinter about joint A the contents of flask B are added to the reaction vessel. The reaction mixture is then frozen and the vessel sealed under vacuum. The sealed flask is then placed on a mechanical shaker, or in a water bath at a suitable temperature, until reaction is complete.

As a general rule to enable ready purification of products; if the product was insoluble, only an excess of soluble starting materials was used in the reaction, and if the product was soluble, only an excess of insoluble starting materials was used in the reaction.

g) Product Isolation Procedures

The reaction vessel is placed on the 'extraction' system of the vacuum line as shown in FIGURE B.7.. The system is evacuated and the reaction vessel opened at the break-seal. The solvent is distilled out of the system and a suitable solvent for extraction of either the product or excess starting material distilled into flask A. With the system closed at tap B, the solution is decanted into flask C, and the solvent then distilled back to flask A. This process is repeated until complete extraction is achieved. The solvent is then removed from the system and the

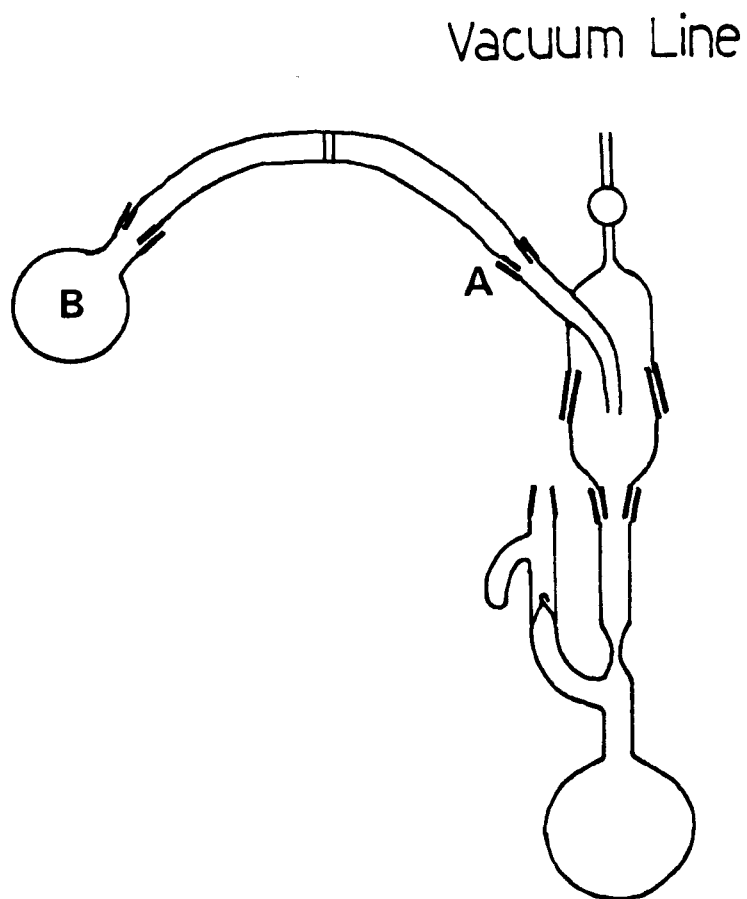


FIGURE B.6. Loading on Extraction System

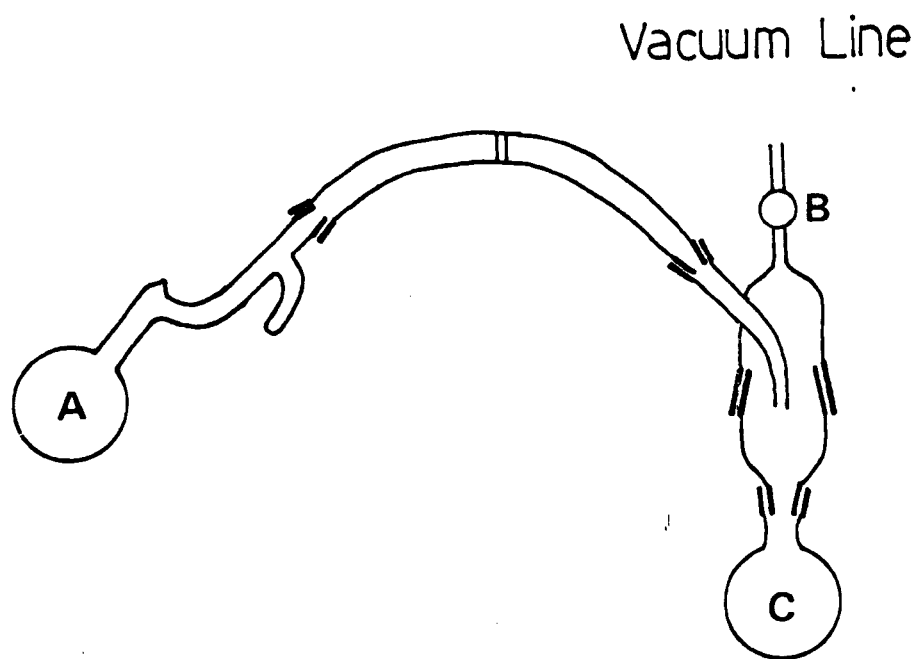


FIGURE B.7. Extraction on the
Vacuum Line

Vacuum Line

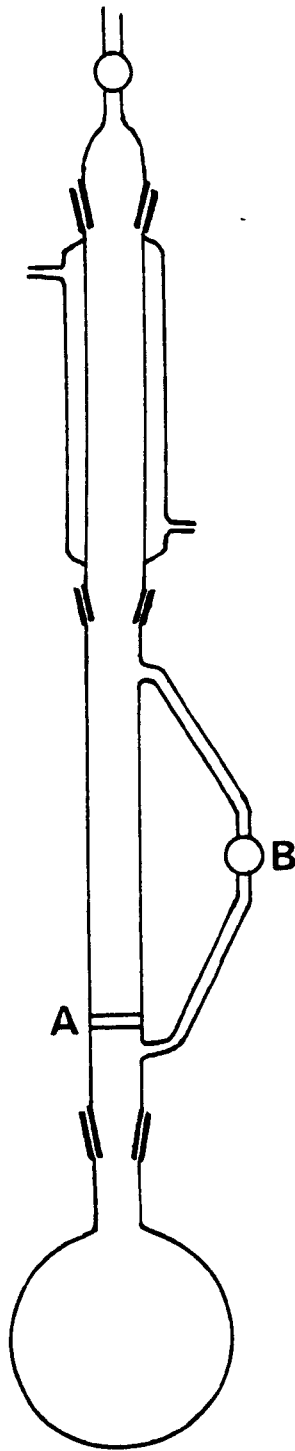


FIGURE B.8. Extraction Frit

product pumped in vacuo at room temperature for ~ 1 day.

When the material under extraction exhibits only slight solubility, an extraction frit may be employed, FIGURE B.8.. The material for extraction is laid on the fine glass frit A, and with the system under vacuum and tap B open, the solvent flask is gently warmed. The solvent collects on the material, and when the body of the apparatus is filled, the heat is removed and tap B closed. As condensation occurs in the solvent flask, the solvent on the frit is drawn through the material, extracting the required product. The process is repeated until extraction is complete.

All products, after being pumped in vacuo at room temperature for ~ 1 day, were sealed into glass ampoules, under an atmosphere of dry nitrogen.

2) Experimental Aspects of Structural Investigations

a) Molecular Weight Determinations

Where solubilities allowed, molecular weight determinations were carried out on the products isolated. These were recorded either cryoscopically or osmotically.

i) Cryoscopic

The vapour pressure of a dilute solution of a non-volatile solute follows Raoult's Law, and one may write the vapour pressure equation,

$$P = x_A P^\circ$$

where, P° = vapour pressure of solvent,

P = vapour pressure of solution,

x_A = mole fraction of solvent.

This may be rewritten to involve the mole fraction of the solute present,

$$P = (1 - x_s)P^\circ \quad \text{where, } x_s = \text{mole fraction of solute.}$$

$$\text{or } \frac{P^\circ - P}{P^\circ} = x_s$$

From this it can be seen, that for dilute solutions, the lowering of vapour pressure, $P^\circ - P$, from that of the pure solvent is dependent upon the mole fraction of solute present. Therefore molecular weights of non-volatile solutes may readily be determined from the vapour pressure lowering of dilute solutions of these compounds.

This lowering of vapour pressure causes a depression in the freezing point of the solution, as the freezing point is that point at which both the solid and the liquid have equal vapour pressures. This may readily be measured experimentally, and forms the basis for cryoscopic molecular weight determinations.

These were carried out, with the rigorous exclusion of moisture, using the specially designed apparatus shown in FIGURE B.9.. The molecular weight of the solute was obtained from the equation,¹⁹⁰

$$MW = \frac{1000WK}{S \Delta T} \quad \text{where, } MW = \text{molecular weight of solute,}$$

$$W = \text{weight of solvent,}$$

$$K = \text{freezing point depression constant,}$$

$$S = \text{weight of solute,}$$

$$\Delta T = \text{freezing point depression } (^{\circ}K).$$

ii) Osmometric

Vapour pressure osmometry is another technique that employs vapour pressure lowering of solutions to determine molecular weights. A drop of solution and a drop of solvent are suspended,

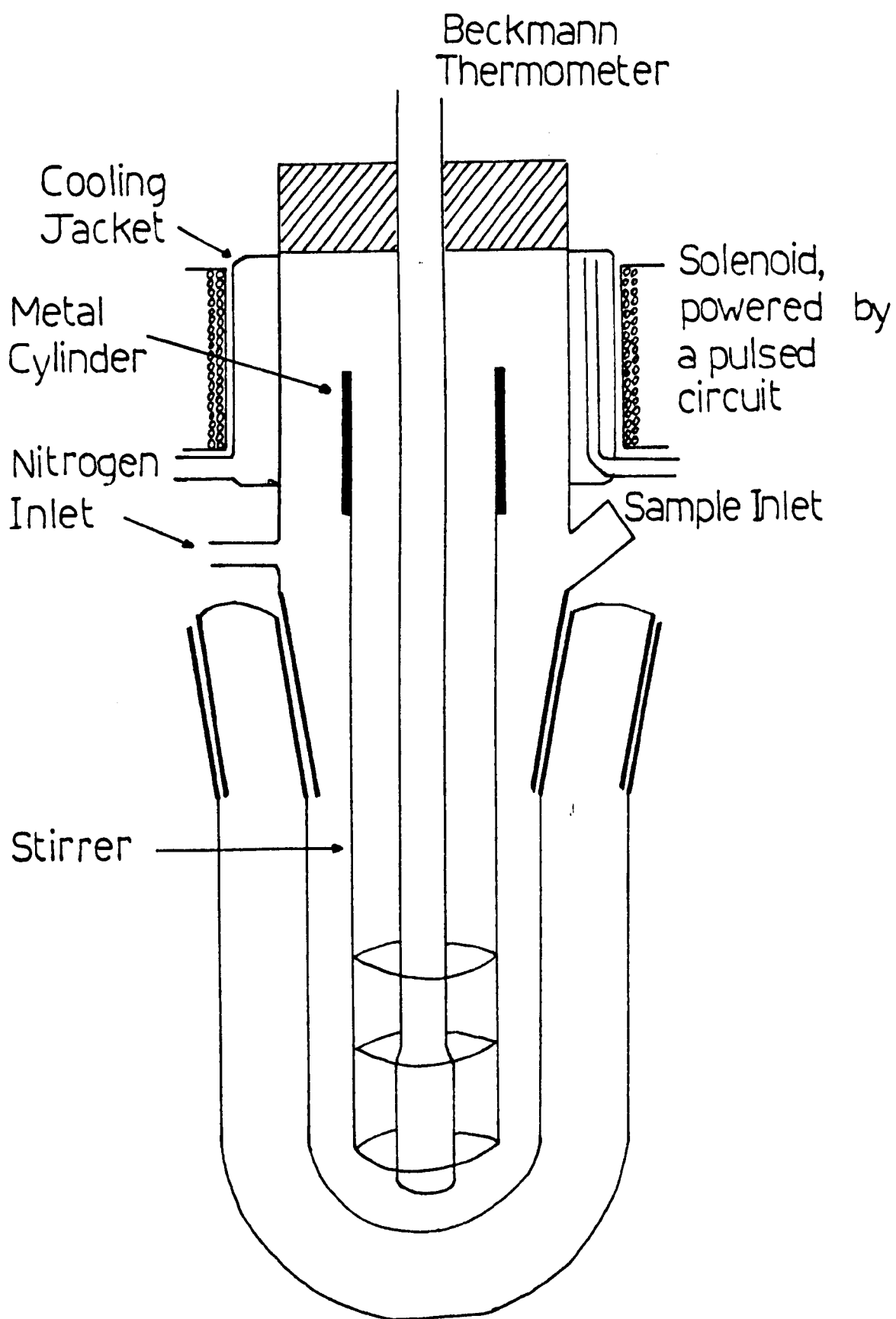


FIGURE B.9. Molecular Weight Apparatus

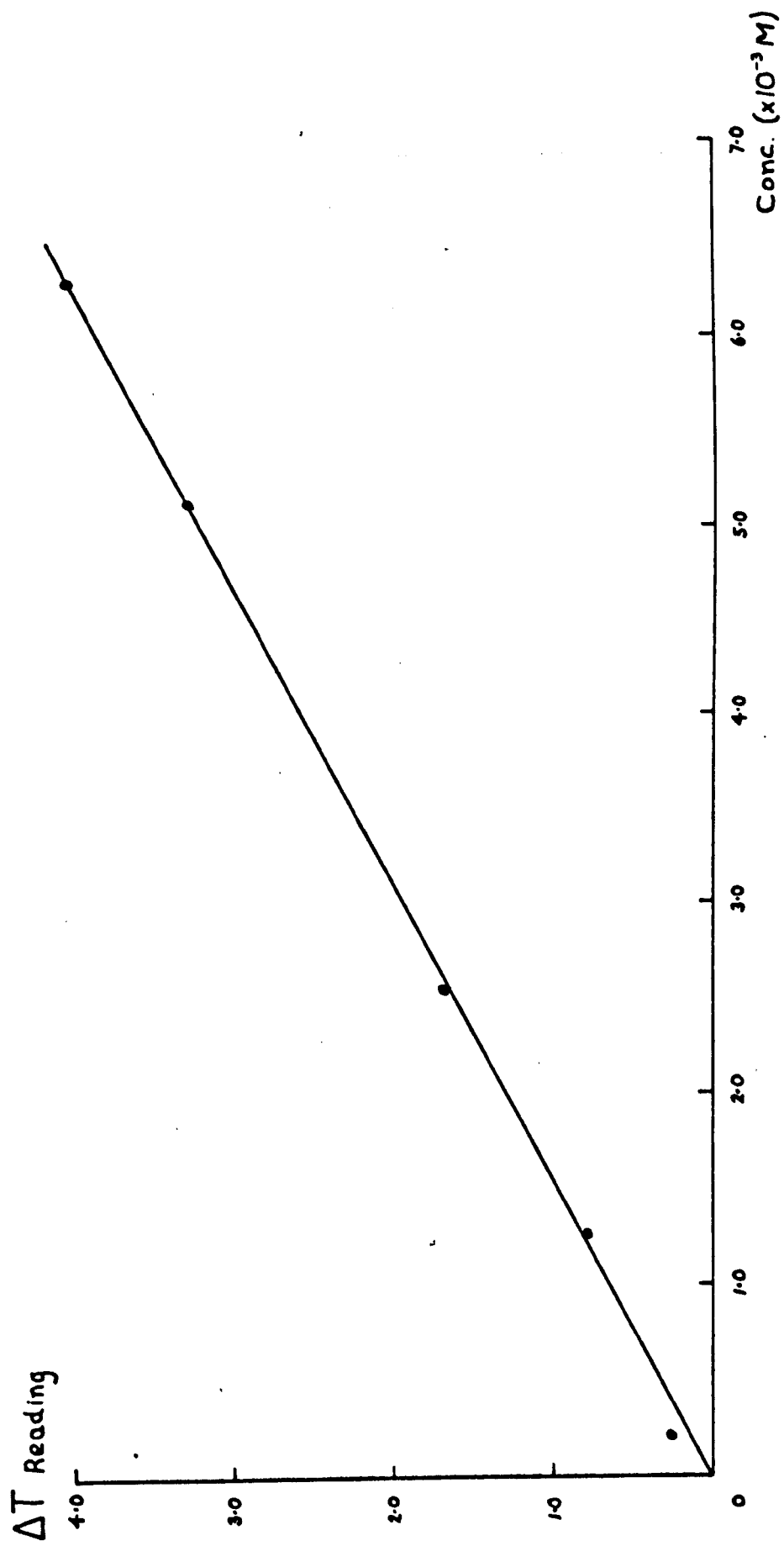


FIGURE B.10. Calibration of V.P. Osmometer. (Benzene)

side by side, in a closed chamber saturated with solvent vapour. Because of the difference in vapour pressures of the two drops, a differential mass transfer will occur between the two drops and the solvent vapour phase; resulting in greater condensation on (or lower evaporation from) the solution drop. This transfer will cause a temperature difference between the two drops (because of the heat of vapourisation); which is proportional to the vapour pressure lowering, and hence proportional to the solute concentration.

Molecular weights were determined in this manner using a Mechrolab Model 301 A vapour pressure osmometer, previously calibrated with benzene solutions of benzil, FIGURE B.10.. To enable the handling of 'air' sensitive materials on this machine, it was fully enclosed in a polythene glove bag, which was continually flushed with dry oxygen-free nitrogen.

b) Conductance

The conductance of solutions of a complex can give important information on the structural type of the complex. A non-ionic product would have an extremely low conductance (or high resistance), as the number of ions available to carry the charge through the solution is minimal. As the electrolyte type changes from non-electrolyte to 1:1 to 1:2 etc. the conductance of the solution increases, as the number of charge carriers increases. The molar conductance of a solution, Λ_m , which is that conductance measured in a cell with electrodes 1 cm apart and of large enough area so that the volume of solution contained between the plates contains one mole of the solute, generally varies within fixed limits for each electrolyte type. Therefore, a measurement of this quantity can give the electrolyte type of

the compound under investigation.

Experimentally, one measures the resistance, R , offered by a solution between two electrodes of a conductance cell. The conductance, L , is then the reciprocal of this value. As with metallic conductors, the resistance is proportional to the cross sectional area and length of the conductor,

$$R = \rho \frac{l}{A} \quad \text{where, } \rho = \text{specific resistance.}$$

Therefore,

$$L = \chi \frac{A}{l} \quad \text{where, } \chi = \text{specific conductance.}$$

Or,

$$\chi = \frac{l}{A} L$$

The value $\frac{l}{A}$ is a constant for a particular cell and may be derived by measuring the conductance of a solution of known specific conductance.

The molar conductance measures the current carrying ability of 1 mole of a solute, and may be obtained from the equation,

$$\begin{aligned} \Lambda_m &= \frac{1000}{c_m} \chi & \text{where, } C &= \text{the cell constant,} \\ &= \frac{1000 C L}{c_m} & c_m &= \text{the molar concentration} \\ & & & \text{of the solute.} \end{aligned}$$

This quantity is markedly temperature dependent and determinations are normally made at the standard temperature of 298°K.

Experimental determinations were carried out using the cell shown in FIGURE B.11. and a Wayne-Kerr Universal B 221 Conductance Bridge. The cell was calibrated using standard aqueous solutions of potassium chloride; the cell constant being determined as 0.3079 cm^{-1} .

The cell was pumped in vacuo for several hours prior to use, to ensure complete dryness, and then weighed. A known quantity of sample was then introduced to the cell in the dry box. The

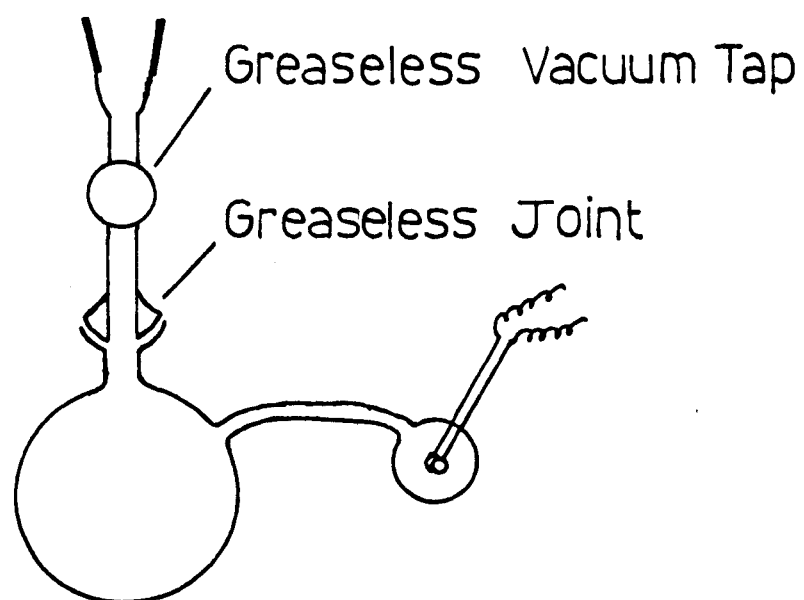


FIGURE B.11. Conductivity Cell

cell was returned to the vacuum line and the solvent distilled onto the sample, in vacuo. The conductance of the solution was measured with the cell thermostatted at $298 \pm 0.1^\circ\text{K}$, and the cell then reweighed. From the weight of the solution, and the density of the solvent at 298°K , the solute concentration was determined. This allowed the molar conductance of the sample to be found from the equation,

$$\Lambda_m = \frac{1000 C L}{c_m}$$

c) Magnetism

Four main types of magnetism may be observed in chemical compounds, they are; diamagnetism, paramagnetism, ferromagnetism and antiferromagnetism. In the coordination chemistry of the transition metals, of the four, paramagnetism holds the most important position.

Diamagnetism

Diamagnetism is a property exhibited by all matter to some extent. The effect is that the substance is repelled by a magnetic field. This behaviour is due to small magnetic moments that are produced by the field, but do not exist in the absence of the field. These moments are in opposition to the inducing field and so cause the substance to be repelled by the field. The magnitude of this effect is small.

Paramagnetism

A paramagnetic substance is attracted into a magnetic field. This form of magnetism is exhibited by substances which have a definite magnetic moment that exists in the absence of any external magnetic field. These substances generally contain ions, atoms or molecules which have unpaired electrons. In the simplest of views an electron is a charge spinning about its own axis,

thus giving rise to a magnetic field, the electron is also spinning about the nucleus, thus giving rise to a second magnetic field. The magnetic properties of any individual atom or ion will result from a combination of these two magnetic fields, that is, the spin moment and the orbital moment resulting from the motion of the unpaired electron.

In general, the magnetic moment of an atom or ion will be given by,

$$\mu = \sqrt{4S(S + 1) + L(L + 1)} \quad \text{BM}$$

where, μ = magnetic moment; measured in Bohr Magnetons,

S = the spin quantum number for the atom (ion),

L = the orbital angular momentum quantum number of the atom (ion).

Electric fields, due to other atoms, can often quench the orbital angular momentum term. This is particularly apparent in the first transition series and the recorded moment is close to the 'spin only' value,

$$\mu = \sqrt{4S(S + 1)} \quad \text{BM.}$$

Experimentally, magnetic moments are obtained from magnetic susceptibility data. The force experienced by a substance when suspended in a magnetic field, normally measured as a weight change, is proportional to the magnetic susceptibility, χ , which in turn is proportional to the magnetic moment.

$$\mu = 2.83 \sqrt{\chi_m T} \quad \text{BM.}$$

Where, χ_m = molar susceptibility,

T = temperature ($^{\circ}\text{K}$),

The susceptibility of a normal magnetically dilute substance varies with temperature, and closely follows the equation,

$$\chi_m = \frac{C}{T + \theta}$$

known as the Curie-Weiss Law. The constants C and Θ , the Curie and Weiss constants respectively, are dependent upon the magnetic interactions present within the substance. The susceptibility, however, shows no dependence on the applied field strength.

Experimental determinations were made using the non-uniform field, or Faraday, method.¹⁹¹ In this a sample of mass m and mass susceptibility χ , when suspended in a non-uniform field H , with a gradient of $\frac{\partial H}{\partial x}$, will experience a force, measured as a weight change Δw , in the direction of x .

$$\Delta w = m\chi H \frac{\partial H}{\partial x}$$

As very small samples are used in this method $H \frac{\partial H}{\partial x}$ will be a constant, β , for a particular machine setting. Therefore, $\Delta w = m\chi\beta$. Where, β = a calibration constant for the particular experimental conditions.

The apparatus used was a standard Faraday set up, incorporating a C.I. Electronics Mark 2 microbalance vacuum weighing head, with a remote control unit, and a Varian V-4005 electro-magnet powered by a Varian V-2900 current regulated power supply. The magnet was mounted on a hydraulically controlled variable position platform. Working temperatures, other than room, were achieved by the balance of a surrounding coolant bath, normally filled with liquid nitrogen, and an internally mounted electric heater. Temperatures were recorded using a Comark Type 1603 Electronic Thermometer with a Cr/Al thermocouple, incorporated into the apparatus at the sample position. Data was recorded at nine field strengths and averaged to obtain the required susceptibility data.

Calibration

The optimum position of the sample within the field was determined using a paramagnetic sample. The distance of the sample from an arbitrary position in the field, FIGURE B.12., was varied until the position for the maximum experienced force was found, FIGURE B.13..

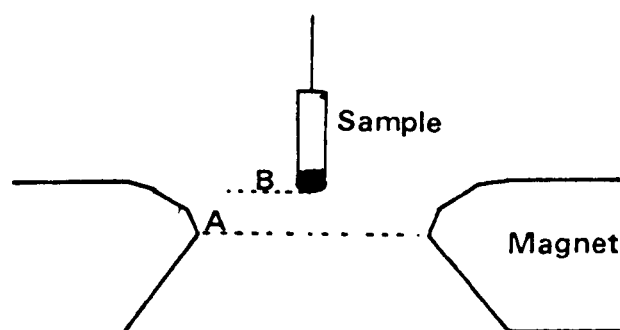


FIGURE B.12. Separation, AB, of sample from arbitrary position, A, in the field.

This position was then used in all subsequent determinations.

The diamagnetic correction required for the empty sample tube was then determined throughout the entire field range and temperature range, FIGURE B.14..

The machine constant β , $= \frac{H \Delta H}{\Delta x}$, was then determined, for

each field strength used, from a calibrant of known susceptibility. Two standard calibrants were used, $\text{Hg} [\text{Co}(\text{SCN})_4]$;
 $\chi_g = 16.44 \times 10^{-6}$ c.g.s.u. (293°K), and $[\text{Ni}(\text{en})_3] \text{S}_2\text{O}_3$;
 $\chi_g = 10.82 \times 10^{-6}$ c.g.s.u. (293°K), the results obtained being shown in TABLE B.1..

Temperature calibration, FIGURE B.15., was achieved by measuring the susceptibility of a known sample over the full

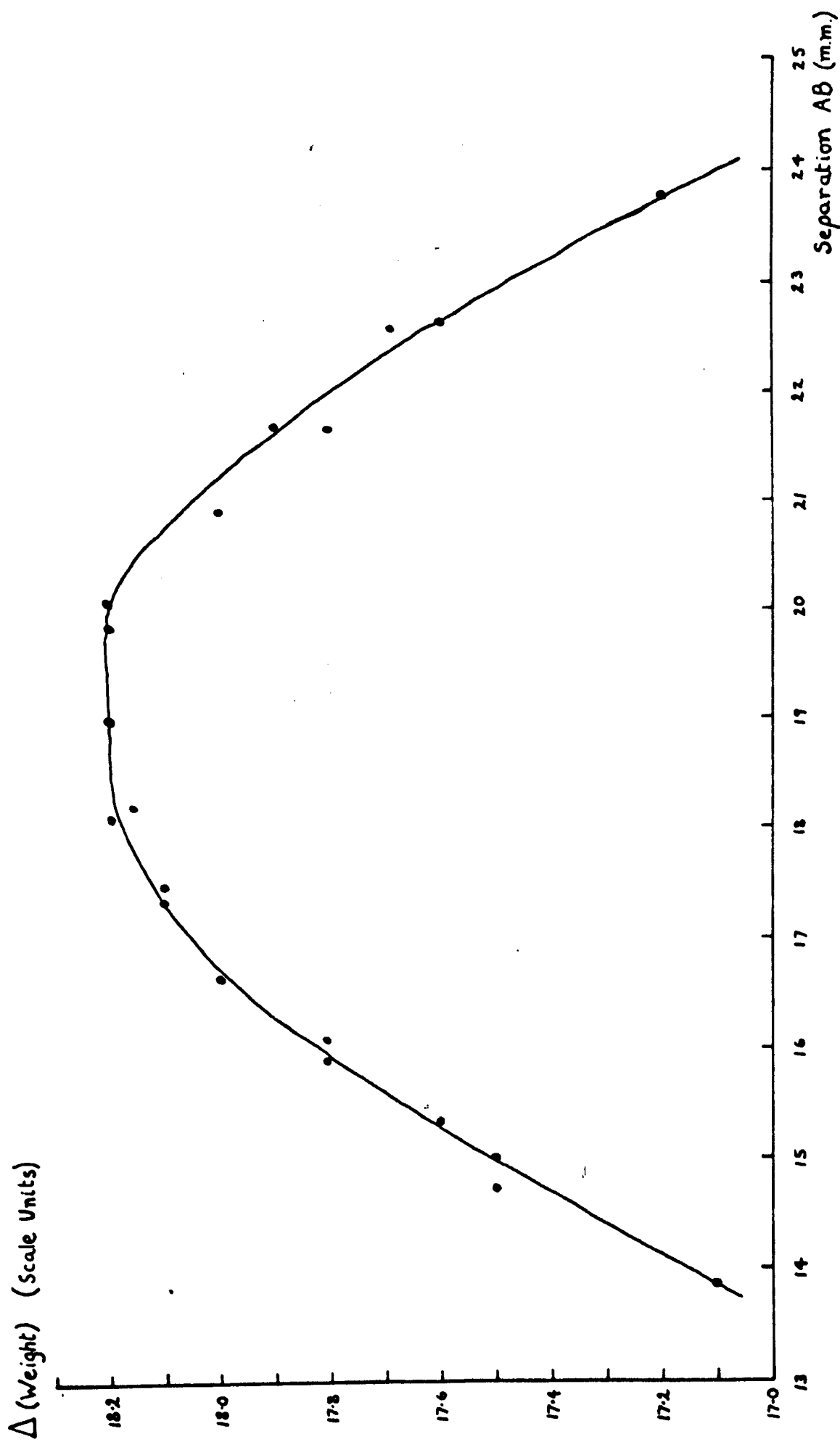


FIGURE B.13. Sample Position against Field Factor $H \frac{\partial H}{\partial x}$

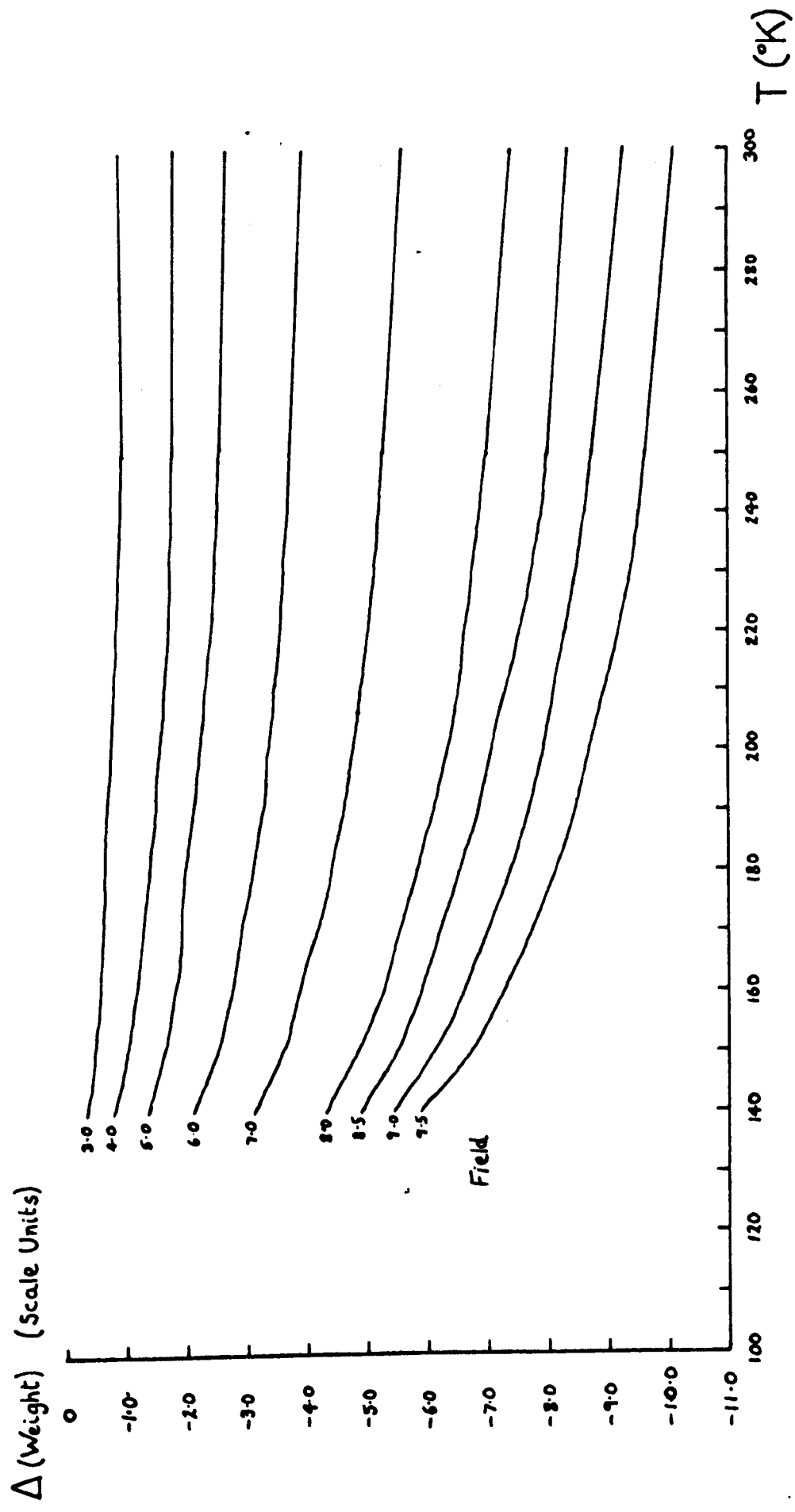


FIGURE B.14. Diamagnetic Correction for Sample Tube

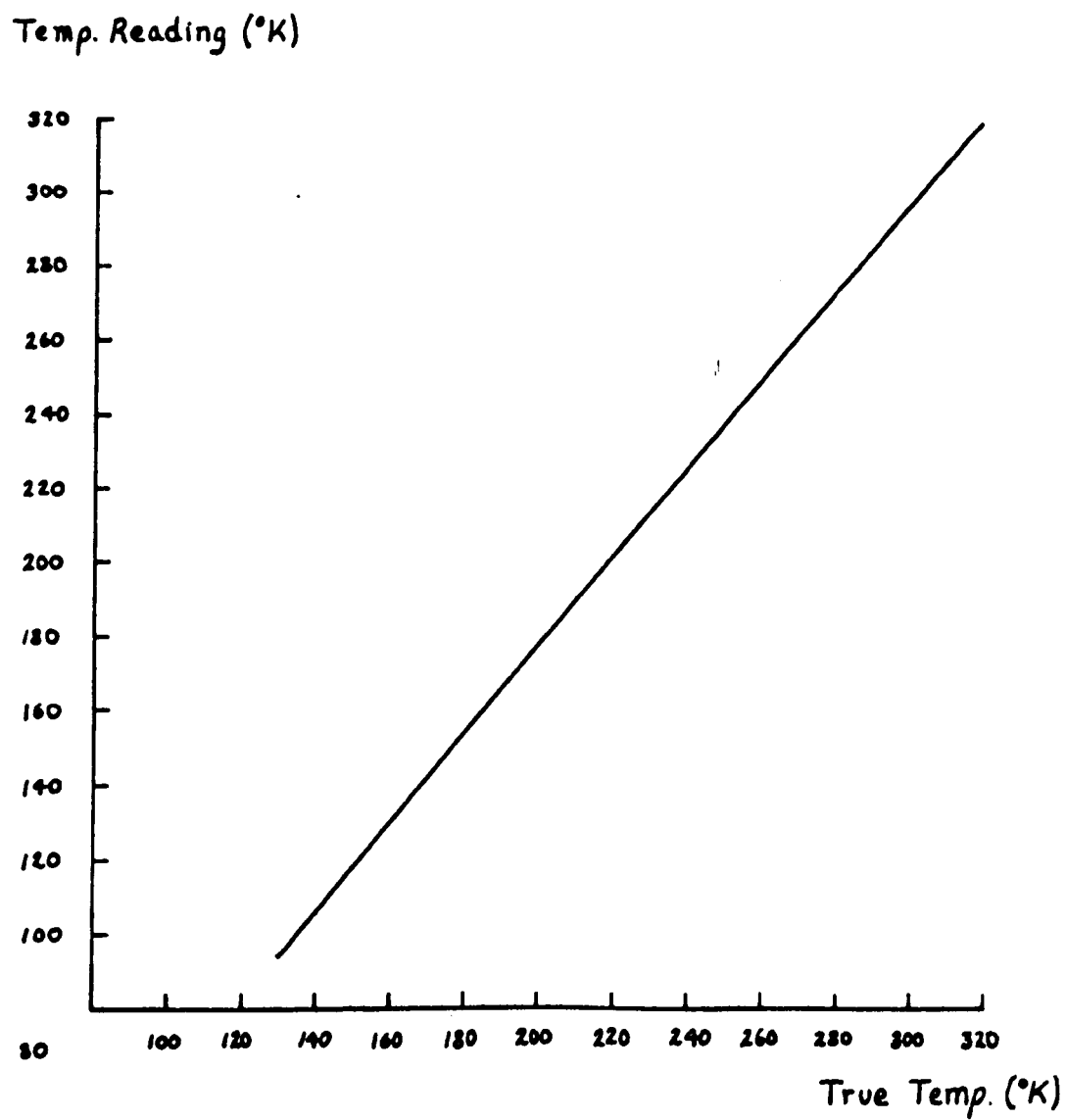


FIGURE B.15. Temperature Calibration

temperature range of the instrument, then relating the recorded temperature readings to the known temperatures.

TABLE B.1. Machine Constants for Faraday Balance

$\beta_{(\text{field strength})}$	From Hg $[\text{Co}(\text{SCN})_4]$	From $[\text{Ni}(\text{en})_3] \text{S}_2\text{O}_3$	Average
$\beta_{3.0}$	11.52	11.18	11.35
$\beta_{4.0}$	6.480	6.260	6.370
$\beta_{5.0}$	4.240	4.370	4.305
$\beta_{6.0}$	3.068	3.057	3.062
$\beta_{7.0}$	2.305	2.270	2.287
$\beta_{8.0}$	1.798	1.772	1.785
$\beta_{8.5}$	1.616	1.600	1.608
$\beta_{9.0}$	1.470	1.453	1.461
$\beta_{9.5}$	1.330	1.336	1.333

Ferromagnetism and Antiferromagnetism

These are two more forms of paramagnetism, but ones in which there is a complicated dependence of susceptibility on both temperature and applied field strength. They do not obey the Curie-Weiss Law, the plots of susceptibility against temperature for substances exhibiting these properties show discontinuities, as shown in FIGURE B.16..

The reason for this behaviour is the presence of interactions between the moments of the individual ions in the substance. For ferromagnetic substances below a certain temperature, T_c , the Curie temperature, the moments of the individual ions align themselves parallel, and thus reinforce one another. Above this temp-

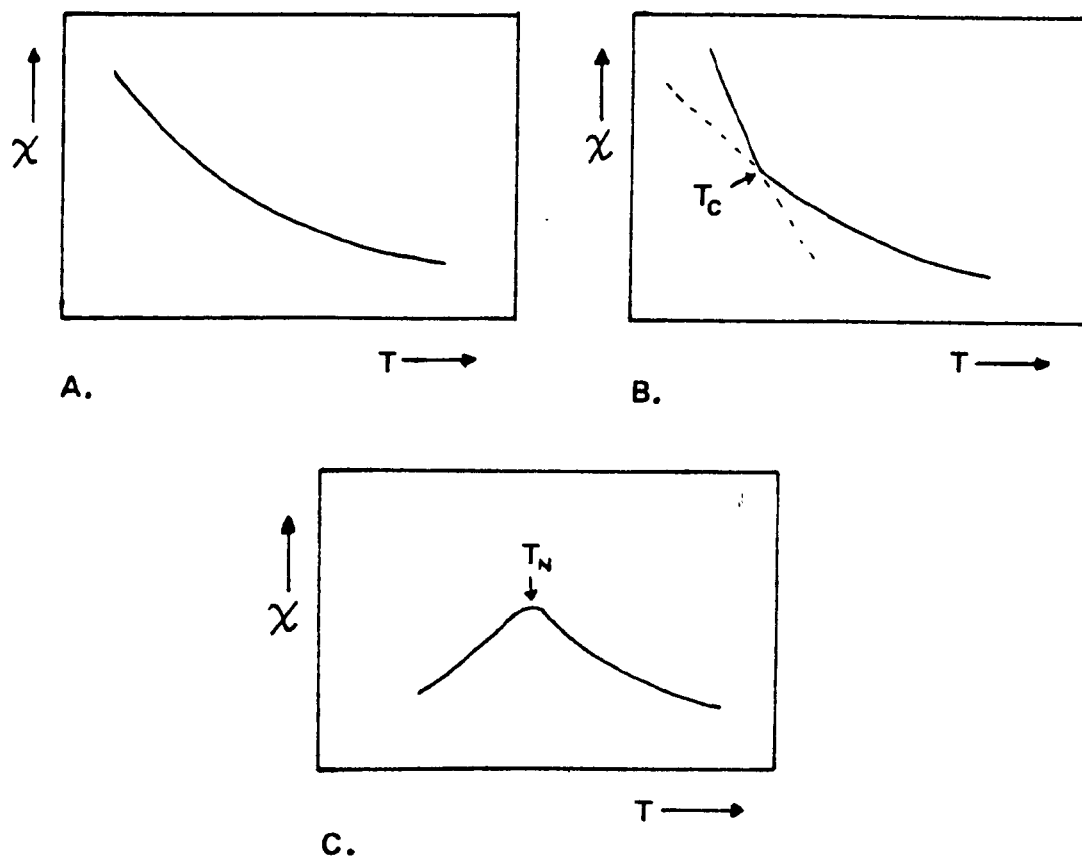


FIGURE B.16. Typical Plots of χ against Temperature for:

- A. Simple paramagnetism.
- B. Ferromagnetism.
- C. Antiferromagnetism.

erature thermal motion randomises the arrangement and the Curie-Weiss Law is often followed. For antiferromagnetic substances below the temperature T_N , the Neel temperature, the individual moments of the ions align themselves to cancel one another out. Above this temperature thermal motion again randomises the arrangement.

d) Spectral Measurements

i) Infrared Spectra (4000-200 cm^{-1}): Were recorded on a Perkin-Elmer 621 Grating Infrared Spectrophotometer. The spectra were calibrated at three points in the range, 2850, 1601 and 1028 cm^{-1} respectively, by use of a 0.05 mm polystyrene film. Samples were run as nujol and hexachlorobutadiene mulls held between caesium iodide plates. Solution spectra were recorded with the samples held in potassium bromide windowed infrared solution cells.

ii) Far Infrared Spectra (400-50 cm^{-1}): Were recorded on a Research and Industrial Instruments FS-720 Fourier Spectrophotometer. The machine was calibrated against the rotational spectrum of water vapour, as published by Rao et al.,¹⁹² and found to be accurate to $\pm 2 \text{ cm}^{-1}$. Samples were run as nujol mulls held between polythene plates.

iii) Electronic Spectra: Were recorded on a Cary 14 Spectrophotometer. Samples in the solid state were run as either, thin transparent KBr discs, or as nujol mulls held between silica plates. Solution spectra were recorded using sealed 1 cm silica cells, as shown in FIGURE B.17.. The sample was loaded into flask A in the dry box, and the solvent was then distilled into the flask in vacuo. The system was then sealed under vacuum at point B. This system allowed the ready dilution of solutions to be made in situ. Half the solution from the cell was tipped back to the reservoir, A, and the pure solvent then distilled back to the cell, thus diluting the solution.

iv) Proton Nuclear Magnetic Resonance Spectra (60 MHz): Were recorded on a Perkin-Elmer R 12 spectrometer. Spectra were calibrated against TMS as reference.

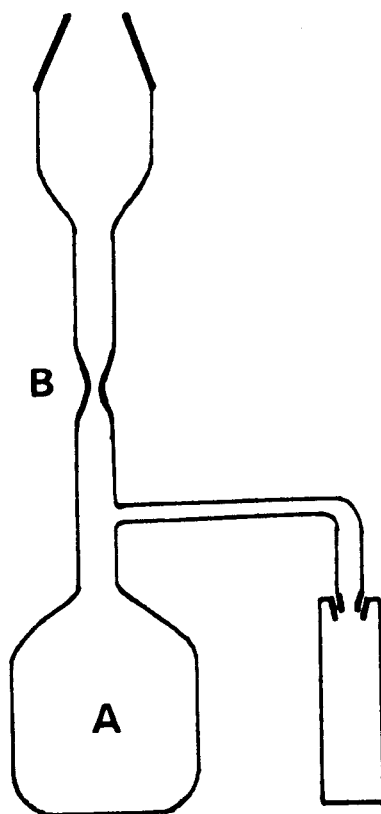


FIGURE B.17. UV Cell

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