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COMPLEXES OF DIVALENT AND TERVALENT TITANIUM

by

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FOREWORD

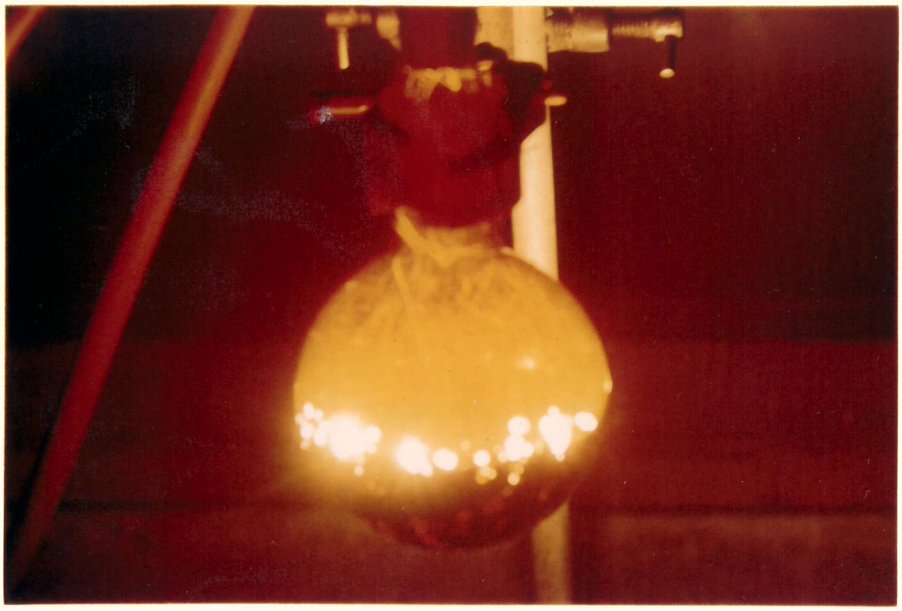
The work described in this thesis was carried out in the Departments of Chemistry at the Universities of Southampton and Reading between October 1964 and June 1967.

I wish to record my gratitude to Professor G.W.A. Fowles D.Sc. F.R.I.C. for his continual guidance and encouragement.

I would also like to thank Dr. J.S. Wood for his invaluable assistance in the crystallographic investigation and Dr. R.A. Walton for many helpful discussions.

Finally I acknowledge my debt to the technical staffs of both Universities, for their considerable help, and to the Science Research Council for a Research Studentship.

T.E. Lester.



PREPARATION OF TITANIUM(IV) BROMIDE

(Photograph by D.J. Tidmarsh)

ABSTRACT

FACULTY OF SCIENCE

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Doctor of Philosophy

COMPLEXES OF DIVALENT AND TERVALENT TITANIUM

by Timothy Edward Lester

The work described in this thesis concerns the complex chemistry of titanium halides. Titanium(III) iodide had been shown to form a range of adducts with organic ligands: TiI_3,3pyr; TiI_3,3γpic; TiI_3,2αpic; $2TiI_3$,3bipyr; $[TiI_2$,2phen$]I$; $TiI_3,3C_4H_8O_2$; $TiI_3,3C_4H_8O$ and $[TiI_2,2C_4H_{10}O_2]I$. Their magnetic moments have been measured at room temperature and are generally close to the values expected for titanium(III). Their spectra (infrared, visible and ultraviolet) are also reported and d-d transitions assigned.

Complexes of titanium(III) bromide with bidentate ligands which are reported include: $TiBr_3$,bipyr; $2TiBr_3$,3bipyr; $[TiBr_2$,2bipyr$]Br$ and $2TiBr_3,3C_4H_{10}O_2$ where $C_4H_{10}O_2$ is 1:2-dimethoxyethane). An X-ray structure on the latter has shown it to be ionic:

$[TiBr_2,2C_4H_{10}O_2][TiBr_4,C_4H_{10}O_2]$.

Complexes of the type $TiX_3,2L$ (where X = Cl, Br or I and L = $(CH_3)_2S$ or C_4H_8S) have been prepared and their properties investigated. The $TiCl_3,2L$ compounds exhibit strong antiferromagnetic exchange and structures based on interacting metal ions are postulated.

Reaction of titanium(IV) chloride with the ligands 3-methoxyproprionitrile and 3-dimethylaminoproprionitrile gave 1:2 adducts with donation from the cyanide in $TiCl_4,2CNCH_2CH_2OCH_3$. $TiCl_3,2N(CH_3)_3$ gave a compound $TiCl_3,2CNCH_2CH_2OCH_3$ but this was diamagnetic. Reaction of $TiCl_3$, $TiCl_3,2N(CH_3)_3$ or $TiCl_3,3CH_3CN$ with $CNCH_2CH_2N(CH_3)_2$ gave $TiCl_3,1.5L$ but the infrared suggested that an imine was formed.

The charge transfer spectra of a large number of titanium(III) and (IV) complexes have been measured. Those of $[TiCl_6]^{2-}$, $[TiBr_6]^{2-}$ and various others are discussed using Jørgensen's treatment.

Titanium(II) chloride, bromide and the salt Na_2TiCl_4 have been shown to form a wide range of organic ligand adducts: $TiCl_2,2CH_3CN$; $TiCl_2,2pyr$; $TiCl_2,2C_4H_8O$; $TiCl_2,2C_5H_{10}O$; $TiCl_2,bipyr$; $TiCl_2,phen$; $TiBr_2,2CH_3CN$; and $TiBr_2,bipyr$. These have very low magnetic moments and are considered to be magnetically concentrated. Their spectra show broad absorption and no d-d transitions are assigned. Reaction of $TiCl_2$ or Na_2TiCl_4 with dimethylamine or trimethylamine yields titanium(III) species. Reaction between titanium(II) chloride and pyridinium chloride gives $[PyH_3][TiCl_6]$.

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PREFACE

The work described in this thesis was directed by Professor G.W.A. Fowles as part of his research programme investigating the complex chemistry of the early transition metals.

Most of the work was concerned with organic ligand complexes of titanium(II) and (III) halides. The known chemistry of titanium(III) iodide has been considerably extended and the first sulphur donor complexes of titanium(III) bromide and iodide are reported. Titanium(II) chloride and bromide have been allowed to react with a wide range or organic molecules and titanium(II) and (III) compounds have been isolated. The reaction of titanium(III) bromide and 1:2-dimethoxyethane yielded a compound of empirical formula: $TiBr_3,1.5C_4H_{10}O_2$ and an X-ray single crystal structural determination showed that it was ionic: $[TiBr_2,2C_4H_{10}O_2]^+[TiBr_4,C_4H_{10}O_2]^-$. The ultraviolet spectra of titanium halide complexes are reported and discussed.

The experimental results are preceeded by a brief review of previous work in the field and a discussion of the physical techniques used to elucidate structures.

CHAPTER I

THE CHEMISTRY OF TITANIUM

Titanium is usually considered to be the first element of the first transition series, the neutral atom having the electronic configuration K, L, $3s^2, 3p^6, 3d^2, 4s^2$. As a typical transition metal titanium forms compounds in a number of oxidation states, the best known being Ti(IV), (III) and (II) with 0, 1 and 2 'd' electrons, respectively. These unpaired 'd' electrons, in titanium(III) and (II) give rise to paramagnetism and d-d spectral transitions in the visible region which contribute to the colour of the compounds.

The work in this thesis has been concerned with the titanium halides and their complexes and for brevity only these will be discussed.

Compounds of titanium(IV).

Titanium(IV) is the highest oxidation state and the one most frequently encountered in titanium compounds. All the titanium(IV) halides are known, the tetrachloride,[1] tetrabromide[2,3] and the tetraiodide being covalent tetrahedral molecules, their melting points rising with increasing molecular weight; the tetrabromide and tetraiodide have the tin(IV) iodide structure.[4] The structure of titanium(IV) fluoride does not appear to be known with certainty but it is a white powdery solid the bonds of which presumably have considerable ionic character; it is most readily prepared by the reaction of titanium(IV) chloride and hydrofluoric acid.[5] The other halides may be prepared by the direct reaction of the elements in the absence of water which causes rapid hydrolysis.

The oxydihalides, $TiOCl_2$,[6,7] $TiOBr_2$,[8] and $TiOI_2$,[9] are also known but the only reported thiohalide is $TiSCl_2$.[10]

Complexes

i) Neutral

The tetrahalides are all Lewis acids, the chloride and bromide in particular, forming a wide range of compounds[11,12-19] with donor molecules. These usually have the general formula $TiX_4,2L$ (where L is a monodentate ligand, e.g. C_4H_8O or CH_3CN) and can be formulated as simple octahedral species, but when the ligand is particularly bulky, e.g. trimethylamine,[20] triphenylphosphine or triphenylarsine,[21] the 1:1 adducts are formed. On the basis of molecular weight and infrared[22] studies these are considered to be five coordinate. 1:1 adducts may, however, attain six coordination by halogen bridging as shown from the X-ray structures of $(TiCl_4,POCl_3)_2$[23] and $(TiCl_4,CH_3COOC_2H_5)_2$.[24] O-phenylenebisdimethylarsine[25] (diars) forms a compound $TiCl_4$,2diars and an X-ray structure has shown that the titanium is indeed eight coordinated with a dodecahedral structure.[40] Nevertheless this compound dissociates in solution to give the six coordinate compound

$TiCl_4$, diars. Eight coordination is not, however, typical of bidentate ligands for both titanium(IV) chloride and bromide form 1:1 compounds with 2:2'-bipyridyl,[13,26] 1:2-dimethoxyethane[27] and the sulphur ligand $RSCH_2CH_2SR$.[74] Seven coordination of titanium(IV) has also been realised in two terdentate arsenic complexes[28] of the tetrachloride, $TiCl_4$,T.

While many compounds of the tetrachloride and tetrabromide are known with a large number of donor atoms (e.g. O, N, S, P, As,) comparatively few complexes of the other two halides are known. Emeleus and Rao[12] reported TiI_4,2pyr but Torrible[29] reports that he was unable to obtain a simple product from dioxan or thioxan reactions with titanium(IV) iodide. Clark[30] has recently prepared a range of compounds from titanium(IV) fluoride including TiF_4,2pyr and 1:1 adducts with 2:2'-bipyridyl and 1:10-phenanthroline. Dyer[31] has also prepared a number of the type TiF_4,L,L' where L and L' may or may not be identical (two typical ligands were para substituted pyridine-N-oxide and $CH_3CON(CH_3)_2$).

For compounds of the type TiX_4,2L, cis or trans isomers are possible, and for the pyridine adducts it was originally suggested[32] on the basis of infrared spectra that the chloride and bromide complexes were trans but the fluoride and iodide ones cis. X-ray results, however, indicate that all four are actually cis.[33] Dyer[34] has shown by N.M.R. that compounds $TiF_4,2L$ may be cis or trans depending on the ligands, a bulky one such as 2:6-dimethylpyridine-N-oxide giving the trans isomer.

The titanium(IV) oxydichloride and dibromide have been reported to form a few complexes including $TiOX_2,2pyr$ and $TiOCl_2,2\alpha pic$.[35]

ii) Cationic.

No cationic halide complexes have been reported.

iii) Anionic

Salts of the type $A_2[TiCl_6]$ have been reported for all the halogens with various cations and some structural work has been done.[36] Like the neutral compounds they are readily hydrolysed. The oxyhalo salts $[(CH_3)_4N]_3[TiOCl_5]$ and $[(C_2H_5)_4N]_2[TiOCl_4]$ have also been prepared recently.[35]

Compounds of titanium(III).

Halides

All four titanium(III) halides are known and may be prepared by reduction of the tetrahalides[37] or in the case of titanium(III) fluoride by reduction of $(NH_4)_2TiF_6$. The trihalides[3,4,38,39,41] all have structures which are basically close packed layers of halide ions containing metal ions in some of the octahedral holes.[9] Titanium(III) chloride exists in several forms which differ in the ordering of the metal ions; the α purple form has hexagonally close packed chloride ions with titanium ions occupying two-thirds of the octahedral holes between anion layers while in the brown β form titanium ions occupy one-third of the holes. The latter structure is equivalent to chains of $TiCl_6$ octahedra sharing opposite faces. The tribromide and triiodide also appear to exist in equivalent forms but are almost black.

The magnetic properties of the titanium(III) chloride and bromide have been studied[42-44] by several workers and are considered to be antiferromagnetic, although the trichloride is not straightforward as there is both a maximum and a minimum in the susceptibility vs temperature data. The triiodide[44] also has a low magnetic moment (χ'_m = 180 x 10^{-6}cgsu) and is probably antiferromagnetic, but rather suprisingly the trifluoride has a room temperature moment of 1.75 B.M. indicating little if any exchange.[45]

The oxychloride, TiOCl has also been reported.[46]

Complexes

i) Neutral

Many fewer complexes of titanium(III) halides are known than of titanium(IV) but a fair range of trichloride and tribromide adducts are now known[14,20,47-52] and these generally have the stoichiometry $TiX_3,3L$, where L is a monodentate ligand. This is consistant with formulation of the structures as octahedral monomers but direct X-ray evidence has not yet been obtained. Both cis and trans isomers are possible and it has been suggested from low infrared evidence that $TiCl_3,3C_4H_8O$ is trans but $TiCl_3,3CH_3CN$ cis.[53]

A number of compounds of the type $TiX_3,2L$ have also been prepared, particularly where L is a bulky ligand, and one of these,[54] $TiBr_3,2N(CH_3)_3$ has been shown by an X-ray structure to be trigonal bipyramidal, a number of others will be discussed later.

The bidentate ligands, 2:2'-bipyridyl[55] and 1:2-dimethoxyethane variously form compounds of the types TiX_3,B; $TiX_3,1.5B$ and $TiX_3,2B$ but although none of the structures are known with certainty all are postulated to contain octahedrally coordinated titanium and are discussed in greater detail later. Only a few titanium(III) iodide complexes are known, including two with methyl cyanide $[Ti(CH_3CN)_6][I_3]_3$,[75] and $[TiI_2,4CH_3CN]I$.[27]

ii) Cationic

Complexes of the type[56] $[TiA_6]Cl_3$ (where A = H_2O, CH_3OH etc.) are well known and although these cations do not contain halogen Schlafer[57] has recently suggested that $TiCl_3,6H_2O$ and $TiBr_3,6H_2O$ should actually be formulated $[Ti(H_2O)_4X_2]X,2H_2O$. The original interpretation of their spectra has historical connections with the development of ligand field theory.

iii) Anionic

Compounds of the type M_3TiX_6 are of interest as they contain the $[TiX_6]^{3-}$ anion which allows ready calculation of Dq for X^-. The fluoride anion $[TiF_6]^{3-}$ can be prepared for a number of cations[58] (NH_4^+, K^+, Na^+) but the hexachlorotitanate(III) and hexabromotitanate(III) have only recently been prepared,[59] although their presence had been deduced in fused salts;[60] a large number of cations were tried but only pyridinium gave satisfactory compounds. The mixed anion $[TiCl_4Br_2]^{3-}$ was also made, together with $[(C_2H_5)_4N][TiCl_4]$ and $[(C_2H_5)_4N][TiBr_4]$[59] but the latter salts, unlike the vanadium $[Ph_4As][VCl_4]$ and $[Ph_4As][VBr_4]$ do not contain tetrahedrally coordinated metal. A number of pseudohalide anions have also been reported, e.g. $[Ti(CN)_6]^{3-}$ [61] and $[Ti(SCN)_6]^{3-}$.[62]

Compounds of titanium(II).

Halides

Titanium(II) chloride[63] and bromide[64] are most readily prepared by disproportionation of the trihalides but may also be prepared by reduction of titanium(III) or (IV) halides under forcing conditions. Titanium(II) iodide[5] has been reported but not the difluoride. All three are black and very readily oxidised, reacting with water to give hydrogen. Baenziger and Rundle[65] deduced from powder photographs that titanium(II) chloride has the cadmium iodide structure which has close packed halide layers with half the octahedral holes occupied by metal atoms. Klemm and Grim, however, found that although one form of titanium (II) iodide had the cadmium iodide structure their dichloride did not and there is thus evidence for at least two forms of titanium(II) chloride.[66]

The magnetic properties of the dichloride and dibromide show marked deviations from the Curie-Weiss law and have very low moments at room temperature, with $\mu_{eff} \sim 1.1$ B.M.; they are presumed not to be magnetically dilute.[67] The iodide exists in two forms and both show anomalous behaviour in their variation of susceptibility with temperature.

Complexes

i) Neutral

Titanium(II) chloride reacts with liquid ammonia to give the compound $TiCl_2,4NH_3$[68] and with dimethylformamide to give $TiCl_2$,2DMF.[69] The latter has a moment of 1.17 B.M. at room temperature. No other neutral titanium(II) halide complexes have been reported but the cyclopentadienyl compound, $Ti(\pi\text{-}cp)_2$, has been prepared and is diamagnetic.[70]

ii) Cationic

No cationic complexes have been reported.

iii) Anionic

The salt Na_2TiCl_4 has been reported and although the room temperature moment of 2.43 B.M. is quite reasonable the susceptibility plot shows a break at about 200°k indicating that the system is not straightforward.[43] K_4TiF_6 is also known and is reported to be diamagnetic which is rather surprising.[67] The absorption spectrum of titanium(II) chloride in an aluminium(III) chloride melt has been studied and assigned on the assumption that the species present is $[TiCl_6]^{4-}$.[71]

Other oxidation states.

Two bipyridyl complexes have been reported, $Ti(bipyr)_3$ and $Ti(bipyr)_3^-$, in which the oxidation states are formally 0 and -1 respectively.[72] The analogous vanadium compound $V(bipyr)_3$ has been shown by X-rays to be a distorted octahedron and it has been shown by E.S.R. that all the nitrogens in $Ti(bipyr)_3$[73] are equivalent; this compound probably has a similar structure.

CHAPTER II

EXPERIMENTAL METHODS
for
STRUCTURE DETERMINATION

1. Electronic Spectra[76-78]

Transition metal compounds usually have absorption bands in the visible and ultraviolet regions of the spectrum and on the basis of extinction coefficients these fall fairly naturally into two classes, those with coefficients less than about 100 and those greater than 500. The former are due generally to transitions within the d levels while the latter usually arise from electron transfer between orbitals which are essentially metal and ligand in origin; i.e. the transitions are M → L or L → M.

i) d-d spectra

Titanium(III) and titanium(II) complexes are respectively d^1 and d^2 systems, the energy levels occupied by these electrons being subject to various forces. The largest of these is the central field due to the nucleus, which holds the atom together, but two others, the ligand field and inter-electron repulsion (between electrons in the same configuration or orbital) are of similar magnitude. Depending on whether the ligand field is greater or less than the electron repulsion it is said to be strong or weak. Spin-orbit coupling will also affect the levels but for the first row transition metals this is much smaller than inter-electron repulsion and the Russell-Saunders coupling scheme may therefore be used. The influence of various forces on the ^2D term arising from the Ti(III) free ion is shown in figure 2.1. For a d^1 system strong or weak fields lead to the same result and a single peak, ${}^2T_{2g} \longrightarrow {}^2E_g$, is expected for titanium(III) complexes. (Table 2.1 indicates the correspondence between the various labelling notations.) $[TiCl_6]^{3-}$ does indeed show a peak in the visible region but it has a distinct shoulder indicative of distortion from a perfect octahedron, which may be due to the Jahn Teller effect.[59] As the strength of the ligand field is increased, for instance in $[Ti(H_2O)_6]^{3+}$, the absorption moves to higher energy; the relationship between Dq and the energy of the transition is given by the Orgel diagram (fig. 2.2).

In the d^2 configuration T_{1g} terms arise from both the t_{2g}^2 and $t_{2g}e_g$ configurations and their interactions must be considered, the final results are shown in figures 2.3 and 2.4. Thus for octahedral Ti(II) three transitions might be expected, ${}^3T_{1g}(F) \longrightarrow {}^3T_{2g}(F)$; ${}^3T_{1g}(F) \longrightarrow {}^3T_{1g}(P)$ and ${}^3T_{1g}(F) \longrightarrow {}^3A_{2g}(F)$, but the last corresponds to a two electron transition ($t_{2g}^2 \longrightarrow e_g^2$) and is expected to be weaker than the other two. The only Ti(II) spectrum reported is that of titanium(II) chloride in an aluminium(III) chloride melt.[71]

These transitions are subject to certain selection rules.

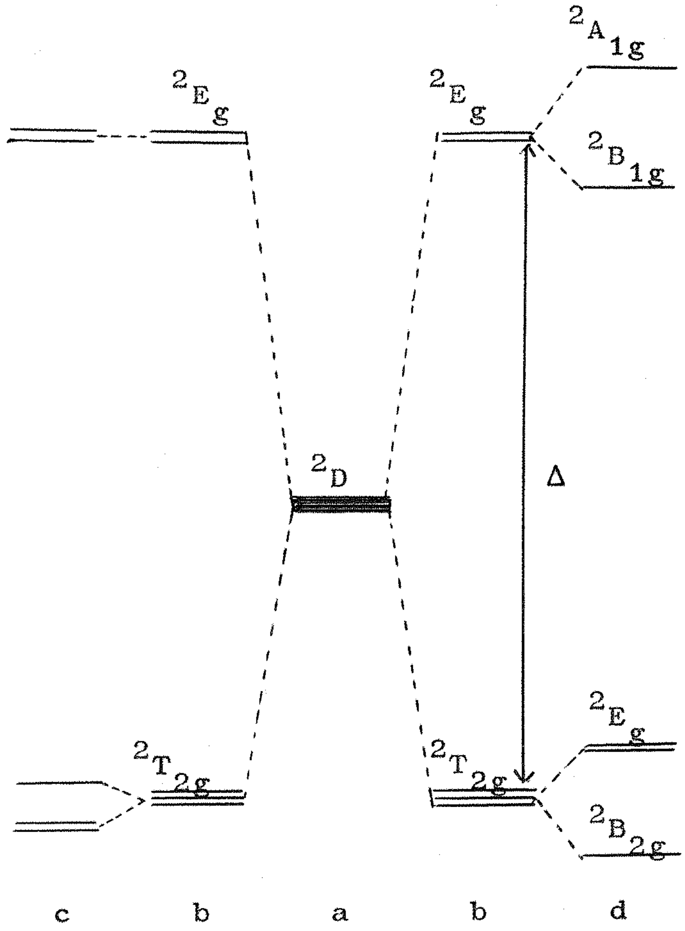


Fig. 2.1.

Energy levels of a ^2D term

a) Field-free ion

b) Octahedral field

c) Octahedral field + weak spin orbit coupling

d) Octahedral field + tetragonal distortion

Table 2.1

Correlation between Bethe and Mulliken notations for cubic-octahedral symmetry.	
Bethe	Mulliken
Γ_1	A_1
Γ_2	A_2
Γ_3	E
Γ_4	T_1
Γ_5	T_2

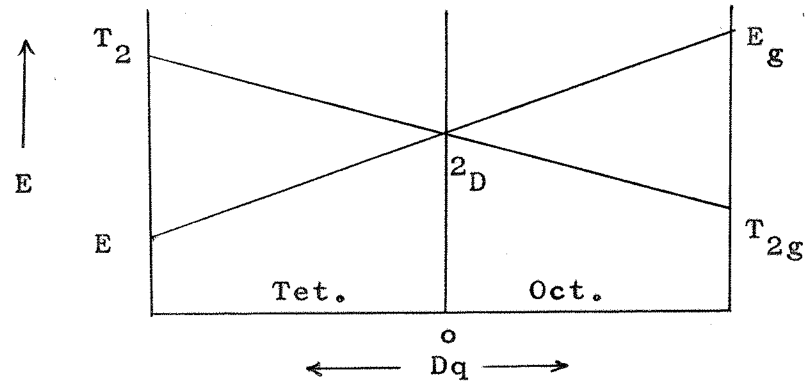


Fig. 2.2 Orgel diagram for a d^1 ion.

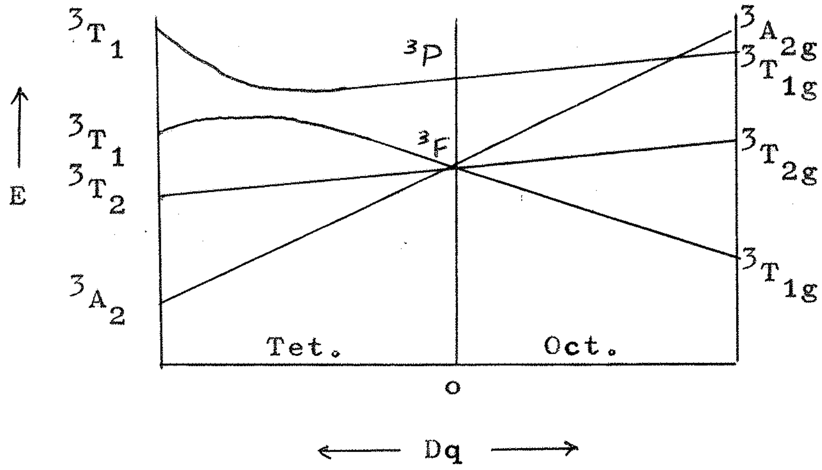
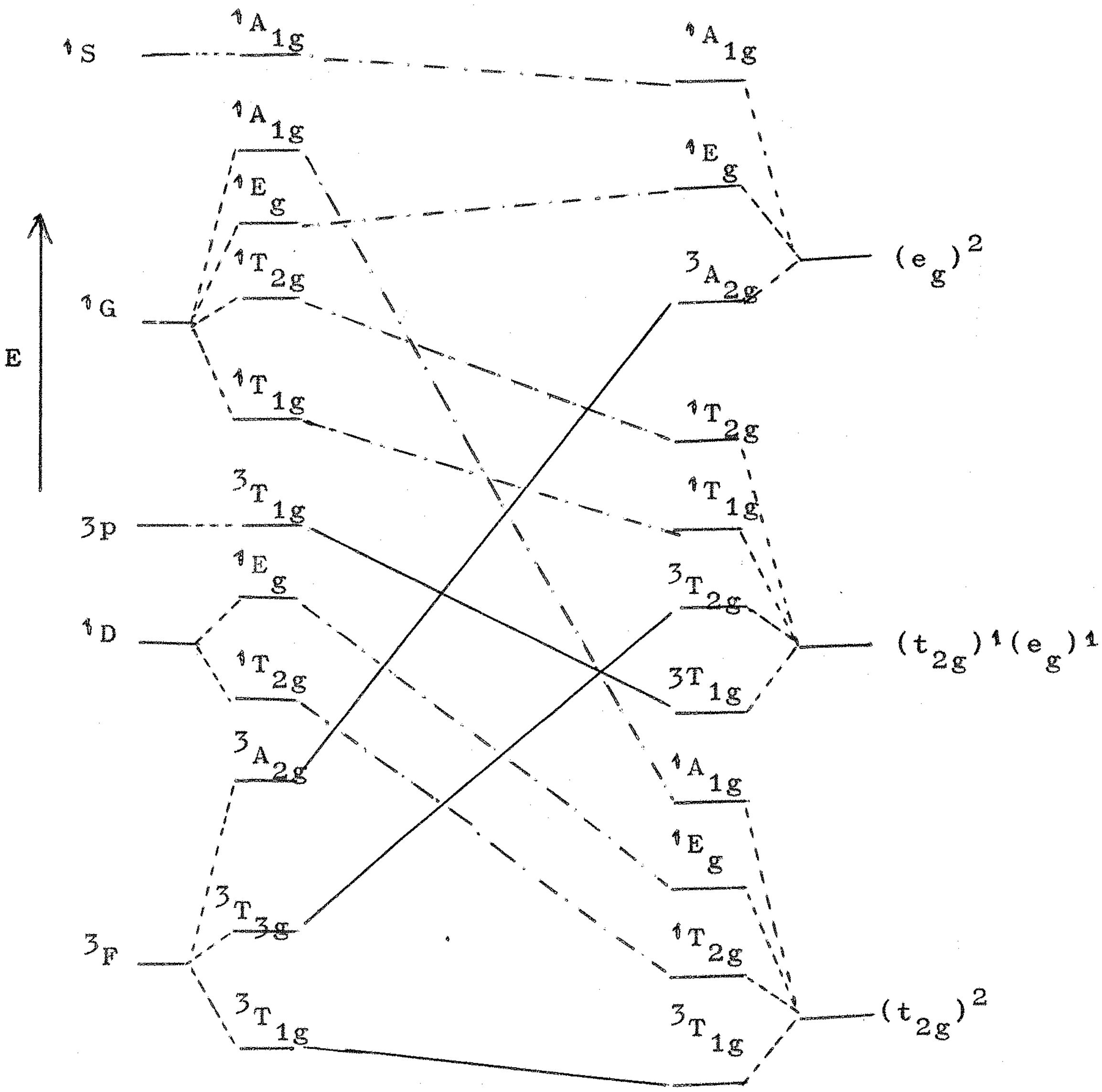


Fig. 2.4 Orgel diagram for a d^2 ion.



Correlation diagram for free ion → strong field configuration d^2 in O_h (e.g. Ti^{2+})

Fig. 2.3.

a) <u>Spin</u> The number of unpaired spins must not change. i.e. $\Delta s = 0$ for the transition to be allowed.

b) <u>Symmetry</u> i) $A_1 \longleftrightarrow T_1$ $A_2 \longleftrightarrow T_2$ $E \longleftrightarrow T_1$ $E \longleftrightarrow T_2$ $T_2 \longleftrightarrow T_2$ $T_1 \longleftrightarrow T_1$ and $T_1 \longleftrightarrow T_2$ transitions are allowed but all others are forbidden.

ii) g — u transitions are allowed but g — g and u — u transitions are forbidden (the Laporte rule).

In practice these selection rules are not rigorously obeyed, there being various mechanisms which break them down. In the presence of spin-orbit coupling the spin selection rule ceases to be strict and spin forbidden transitions are observed, albeit very weakly, e.g. in Mn^{2+} compounds. The Laporte rule is reduced in effect as 'u' vibrations of the molecule can mix with the electronic wavefunctions endowing them with partial 'u' character, the transition thus being 'vibronically' allowed. d-d transitions in tetrahedral molecules are usually more intense than in octahedral ones as the former have no centre of symmetry but even in the latter distortions and the presence of non-equivalent ligands serve to remove the centre of symmetry, allowing the possibility to some p-d mixing.

In spite of the relaxation of these selection rules d-d transitions are still about an order of magnitude weaker than allowed bands but this difference may be decreased when a d-d band occurs close to an intense charge-transfer peak for vibrational mixing can occur making the forbidden band more allowed (intensity 'stealing').

One striking feature of d-d peaks is that they are usually very broad and this is due to several factors. Since the field produced at the metal ion is a critical factor of its separation from the ligand, 10Dq is very sensitive to small changes in the metal-ligand distances, with the result that vibrations of the molecule can cause the transition to occur over a range of energy. It sometimes happens, however, that the energy difference between the ground and excited states remains the same as Dq is varied. If this is the case vibrational effects will not cause the band to be broadened. If the transition involves a T term the peak may be broadened as such a term is split by spin-orbit coupling; this effect is expected to be greater for the second and third row transition metals as these have much larger spin-orbit coupling constants. The third band broadening mechanism is due to the departure from cubic symmetry, whether because of crystal packing, inequivalent ligands or the Jahn Teller effect.

Information from d-d spectra

The most important parameter obtained from d-d spectra is 10Dq, the ligand field splitting. Jørgensen[80] has suggested a 'rule of average environment' for mixed ligand complexes which assumes a simple relationship between the numbers of each type of ligand and the position of the band. From the known compounds of titanium(III) the values of Dq for a number of ligands are known and this allows deductions to be made about the constituents of the first coordination sphere when a related compound is prepared. Δ_{tet} is much smaller than Δ_{oct} and if a tetrahedral Ti(III) compound is prepared it should be possible to distinguish it from the visible spectrum. Unfortunately the same is not true of Ti(III) if the structure is a trigonal bipyramid for two transitions are expected, the first being in approximately the octahedral position.

ii) Charge-transfer spectra

Charge-transfer spectra may be considered to belong to one of four types.

a) Metal → ligand (oxidation) transfer.

b) Ligand → metal (reduction) transfer.

c) Interaction spectra.

d) Solid state cooperative effects.

The first two are discussed in chapter VI in some detail and are not considered further here. (c)[81] arises when a mixture or compound contains a metal in two different oxidation states. If oxidation-reduction transfers occur between ions in the two states intense absorption bands can result. For example, when titanium(III) is placed in strong hydrochloric acid and some oxidation is allowed to take place an intense absorption is observed in the near ultraviolet. In close packed halide and oxide structures anomalous[82] absorptions are sometimes observed in the spectra (d), apparently as a result of the delocalisation of the d electrons to form bands similar to those found in semiconductors.

In addition to these charge-transfer transitions the ultraviolet may also contain peaks due to intra-ligand transitions; for instance 2:2'-bipyridyl has strong $\pi \rightarrow \pi^*$ absorptions in the ultraviolet and these are present in its complexes, although shifted somewhat as bonding to a metal ion affects the ligand's energy levels.

Although solution spectra usually show the best resolution the spectra of solids can be obtained and in this work diffuse reflectance has been used extensively. Solid spectra have the advantage that there is no possibility of reaction with a solvent but are frequently complicated by solid packing effects. To obtain the best results the solid should be finely ground and mixed with a non-absorbing diluent, for if these precautions are not followed significant shifts in the spectrum can result.[79]

Reflectance measurements also have the disadvantage that extinction coefficients cannot be measured, indeed large differences in the intensities observed in solution spectra generally appear to be greatly reduced in reflectance spectra.

2) Magnetic Measurements.[67,76]

Introduction

Two common magnetic effects are observed, the first is diamagnetism and arises from the motion of electrons if electrons considered as charged particles and the second is paramagnetism which results from an ion's spin or orbital angular momentum. As few cases occur in which an ion possesses orbital angular momentum in the absence of spin angular momentum, paramagnetism is normally associated with the presence of unpaired electrons. If the paramagnetic centres in a material are able to interact, because they are close together for instance, the substance is said not to be 'magnetically dilute' and two further effects, ferromagnetism and antiferromagnetism arise. Table 2.2 summarises the origins, magnitudes and signs of the various forms of magnetic behaviour.

When a paramagnetic substance is placed in a magnetic field two opposing effects operate; the magnetic field (H) tends to align the molecular dipoles and thermal

Table 2.2

Type of magnetic susceptibility	sign	approx magnitude x cgsu	dependence on H_o	origin
Diamagnetism	-	1×10^{-6}	independent	electronic charge
Paramagnetism	+	$0-10^{-4}$	independent	A.M.
Ferromagnetism	+	$10^{-2}-10^{4}$	dependent	dipole exchange
Antiferromagnetism	+	$0-10^{-4}$	may depend	dipole exchange

agitation tends to make their orientations random.

ii) Magnetic properties of free ions

The energy W of a wavefunction (ψ) in a magnetic field (H) is given by:-

$$W = W^o + W'H + W^2H^2 + \ldots\ldots\ldots$$

where W' and W^2 are the first and second order Zeeman effect coefficients. For a system composed of a term whose degeneracy may be lifted by a magnetic field (1st order Zeeman effect) and if the spin-orbit coupling constant is large so that states other than the ground state lie at $\gg$kt then it can be shown that:-

$$\mu_{eff} = g[J(J+1)]^{\frac{1}{2}}$$

This formula holds quite well for the lanthanides, or for other systems at low temperatures where the approximations are valid. 'g' is a small number, the 'Lande' or 'spectroscopic' splitting factor and is a measure of the amount of spin and orbital angular momenta which the state possesses. If a state specified by J arise from L and S then g is given by:-

$$g = 1 + \frac{[S(S+1)-L(L+1)+J(J+1)]}{2J(J+1)}$$

and when orbital angular momentum is quenched (L=0) then J = S and g = 2, giving the 'spin-only' formula:-

$$\mu_{eff} = 2[S(S+1)]^{\frac{1}{2}}$$

If the spin-orbit coupling constant (λ) is of the order of kt then more than one state may be thermally accessible and both contribute to the susceptibility, via the first order Zeeman effect, in the proportion of their Boltzmann population but there may also be a contribution from the second order Zeeman effect. This condition applies to the early first row transition metals which have $\lambda \sim 150\text{cm}^{-1}$.

iii) <u>Magnetic properties in complexes</u>

When a transition metal ion is surrounded by ligands the orbital angular momentum, about an axis, of any unpaired electron is affected. This can be visualised by the possibility of transforming the orbital it occupies into an exactly equivalent degenerate orbital, which does not contain an electron of the same spin as the first, by rotation about the axis in question. Thus, for example, while the $d_{x^2-y^2}$ and d_{xz} orbitals may contribute to orbital angular momentum in the free Ti(III) ion, formation of an octahedral complex eliminates this possibility as the two orbitals are no longer degenerate. There will, however, still be a contribution from the d_{xy}, d_{xz}, and d_{yz} orbitals but any distortion from octahedral will reduce this.

Complexes whose metal ions have A_g or E_g ground terms frequently have magnetic moments that differ appreciably from the spin only value. This arises partly from second order Zeeman contributions between the ground and higher states but also because spin-orbit coupling 'mixes in' other excited terms with the result that the orbital contribution to the moment is not completely quenched, although this might have been expected. The susceptibility should vary with temperature according to the Curie law with a small T.I.P. arising from the second order Zeeman effect.

The magnetic properties of complexes having T ground terms are obtained by summing the first and second order Zeeman contributions among the states arising from term splitting by spin-orbit coupling. The resulting moments are found to depend on temperature, as shown (fig. 2.5) for the ground $^2T_2$ term of octahedral Ti(III). As mentioned earlier, distortions from octahedral symmetry remove the orbital degeneracy of the $^2T_2$ term, but they also alter the energies of the levels between which thermal distribution occurs, having a profound effect on the μ_{eff} vs temperature plot (fig. 2.5). In general the temperature dependence decreases and the moment approaches the spin only value. When fitting the parameters λ and Δ (where Δ is defined as the ground state splitting) it is normal to consider an orbital reduction factor, k, which may be a measure of electron delocalisation onto the ligands, and again causes the moment to approach the spin only value as it results in a decrease of the system's orbital angular momentum.[84]

It has been calculated, using the free ion spin-orbit coupling constant, that at 300°k the moment for a Ti(III) octahedral complex should be 1.95 B.M. The alum, $CsTi(SO_4)_2,12H_2O$ has a moment of 1.84 B.M. but the hexahalogeno salts $[TiX_6]^{3-}$ have moments around 1.70 B.M., which suggests considerable distortion.[59] The splitting of the $^2T_{2g} \longrightarrow {}^2E_g$ transition in the spectra of these salts confirms that they are indeed appreciably distorted. The magnetic moments of three titanium(III) chloride adducts have been measured over a temperature range and the results fitted on the basis of a ground state distortion $\Delta \sim 600cm^{-1}$ with an orbital reduction factor k of ~ 0.7. At 298°k

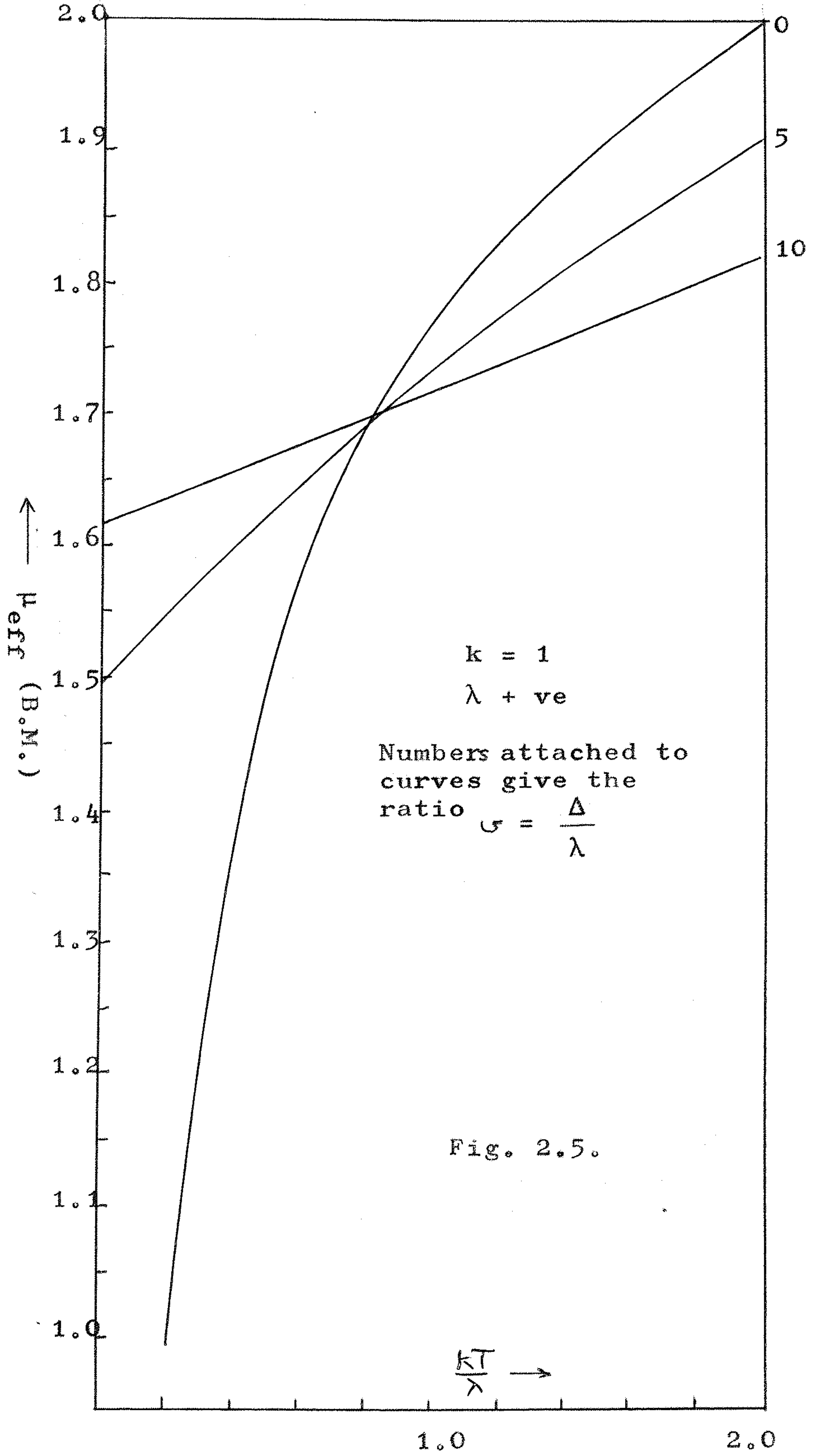
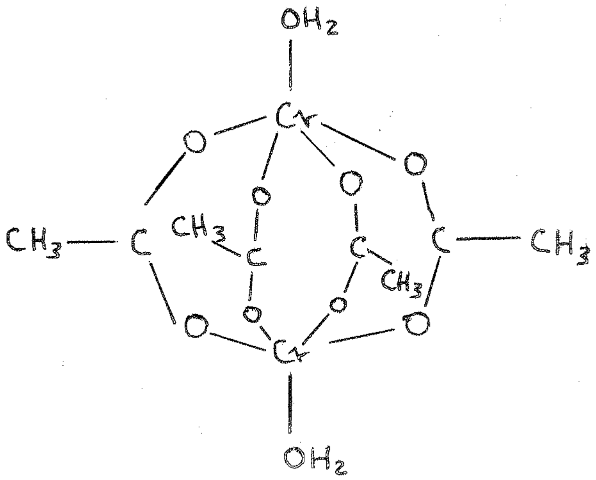

2.0
1.9
1.8
1.7
1.6
1.5
1.4
1.3
1.2
1.1
1.0
μ_{eff} (B.M.) →
0
5
10
k = 1
λ + ve
Numbers attached to curves give the ratio $\sigma = \frac{\Delta}{\lambda}$
$\frac{kT}{\lambda}$ →
1.0
2.0

Fig. 2.5.

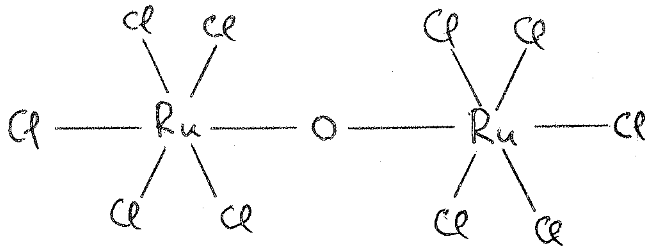
their moments are close to the spin only value.[67]

iv) Antiferromagnetism

It has previously been assumed that no interaction occurs between paramagnetic centres but in a considerable range of compounds, including most of the lower titanium halides this is not so. In these cases the metal ions interact, either directly as the result of their proximity or via an intermediate atom or atoms. The former is tantamount to a metal-metal bond and the latter is known as a super-exchange process. A classic case of direct interaction causing a reduction in magnetic moments occurs in copper(II) and chromium(II) acetates, e.g.:-



in this case the exchange is so great that the compound is diamagnetic.[5] Super-exchange is particularly prevalent in oxide and fluoride structures but also occurs in $(Ru_2OCl_{10})^{4-}$ where the exchange occurs via a single



intermediate atom.[67] In the $[ReX_6]^{2-}$ anions, however, interaction occurs via two non-magnetic atoms and the increase $F^- \longrightarrow I^-$ may be correlated with the increasing polarisability of the halogen.[67]

3) Conductivity Measurements

Conductivity measurements indicate the presence or absence of ionic species in solution and may provide information on the nature of the ions if they are present. A polar solvent is required to give conductances of measurable magnitude but such solvents are usually good donors and may react with the complex, and so complicate the interpretation of results.

The conductivities of a number of electrolytes in methyl cyanide were measured by Walden and Birr[85] who showed that the variation of conductance with concentration depended on the electrolyte type, e.g. 1:1 or 2:1. When equivalent conductivity Λ_e was plotted against $(\text{concentration})^{1/2}$ the slopes for 1:1 electrolytes were $\sim$400 while for 2 : 1 electrolytes they were

~1,500. Unfortunately little is known about the behaviour of complex compounds in methyl cyanide[83] and while non-conducting solutions are indicative of non-ionic solids other results should probably be interpreted with caution, particularly if the conductivity changes rapidly with concentration.

4) Infrared Spectra[86]

The energies required for vibrational transitions in molecules correspond to quanta of radiation in the infrared region of the spectrum but in order for a vibration to be excited by the absorption of radiation it must cause a change in the molecular dipole moment. This condition is not always satisfied, for instance in the stretching vibration of a homonuclear diatomic molecule, and is the first selection rule. The second selection rule states that only excitations which involve a unit increase in the vibrational quantum number can occur but this rule is not rigorously obeyed and transitions corresponding to $\Delta v = 2$ or 3 may be observed as overtones of the fundamental, although they are much weaker.

If a diatomic molecule is considered as a harmonic oscillator then ΔE, the energy between two adjacent vibrational levels is given by:

$$\Delta E = \left(\frac{h}{2\pi}\right) \left(\frac{k}{\mu}\right)^{\frac{1}{2}}$$

where h = Plank's constant; μ = reduced mass and k = the bond stretching force constant.

While the assumption that the molecule can be considered as a harmonic oscillator is rather naïve the expression indicates the dependence of frequency upon bond strength and the vibrating masses.

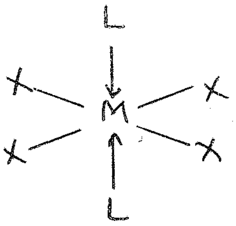
For a non-linear polyatomic molecule containing N atoms 3N - 6 normal modes of vibration are expected, but the empirical use of infrared spectra is greatly aided by the occurance of group vibrations; that is, certain chemical groupings have characteristic absorptions at specific frequencies which enable their presence to be diagnosed. This is particularly useful when the characterisation of an unknown compound is being carried out as the presence of certain ligands can be ascertained. A further advantage arises from the change in bonding adjacent to the donor atom on complex formation. When, for example, ethers such as tetrahydrofuran, coordinate to a metal a marked shift occurs in the frequency of the symmetric and assymetric C-O-C stretching vibrations. 1:4-dioxan, on the other hand, is a potentially bidentate ligand and the absence of the C-O-C stretching vibrations in the positions characteristic of uncoordinated dioxan indicate that both ends of the molecule are coordinated.

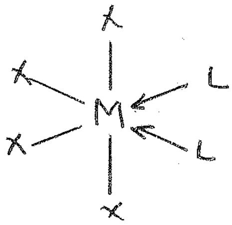
When methyl cyanide is bonded to a metal a weakening of the C≡N bond might be expected leading to a reduction in the C≡N stretching frequency; in practice an anomalous shift to higher energy is observed and various explanations have been suggested for this.[87,88] In addition to this stretching vibration at 2270 cm.$^{-1}$, methyl cyanide also has another band at 2295 cm.$^{-1}$ which is a combination of the 1375 cm.$^{-1}$ and 920 cm.$^{-1}$ bands. This also rises slightly on coordination as the frequencies of the component vibrations change when a complex is formed.

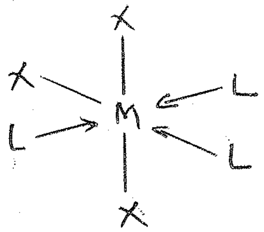
Recently compounds of succinonitrile[89] have been prepared in which the C≡N frequency is observed to decrease and on the basis of this and other evidence bonding via the triple bond is postulated.

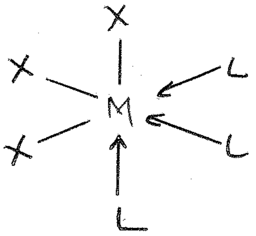
Examination of the modifications which occur in ligand spectra is a very valuable application of infrared spectra but much work has recently been directed to the study of the actual ligand-metal vibrations. Because of the heavier masses or weaker bonds involved these generally occur in the far-infrared region.
At present metal-halogen stretches are the best understood and only these will be discussed.

For both MX_4L_2 and MX_3L_3 type octahedral complexes cis or trans isomers are possible:









and it has been shown that the number of metal halogen stretching frequencies expected for the various isomers differ (table 2.3).[53] This assumes that coupling between M—L and M—X vibrations is not strong and that essentially M—X vibrations are observed.

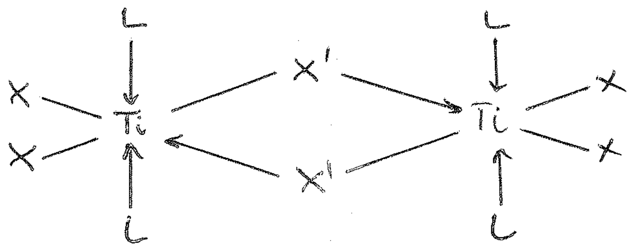
Table 2.3

Type	Isomer	No. of M—X bands
MX_4,2L	cis	4
	trans	1
MX_3,3L	cis	2
	trans	3

Thus it should be possible to distinguish between the isomers on the basis of their low-infrared spectra, and indeed a number of stereochemistries for titanium halide adducts have been assigned,[53] but for $TiCl_4$,2pyr conflicting results with an X-ray[90] examination suggest that such assignments should be treated with care.

This simple structural use of far-infrared spectra is complicated by various factors. Firstly, for the early transition metal halide complexes the bands are usually poorly resolved, and sometimes they are very broad indeed and obviously an envelope comprising several bands. This means that although the spectrum contains, say three peaks, only two may be observed, particularly if their separation is not great. Secondly, packing in the solid may distort the molecule sufficiently to cause splitting of the bands and more than the expected number for a given sterochemistry may be observed. Occasionally ligand modes, which are not observed in the free ligand, appear to increase in intensity on complex formation; for instance 2:2'-bipyridyl compounds[91] have a band at ~360cm^{-1} which is thought to be of this type.

A number of the compounds studied do not have simple octahedral structures and some of the $TiX_3,2L$ complexes, for example, are postulated to have a halogen bridged structure



in which even 'essentially' pure terminal metal-halogen stretches will not be observed as conditions are ripe for extensive coupling with the halogen bridge. The frequencies at which the bands are observed may therefore differ somewhat from those observed for monomeric octahedral compounds.

Fortunately the intensities of metal-halogen bands are usually high, enabling them to be distinguished from bands of the ligands, and when a peak is known to be due to M—X the frequency at which it is observed may provide valuable information. Clark[53] has suggested that as the coordination number decreases so the energy of the metal-halogen stretch rises, and an interesting example of this is found in the vanadium(III) compounds,[92] $VX_3,2S(CH_3)_2$ (where X = Cl or Br). These have their V—X stretches in the expected octahedral region in the solid but on dissolution in a non-polar solvent the band frequency increases by ~50 $cm.^{-1}$ confirming results from other techniques which show that the coordination number falls from six to five in this case.

The frequency of metal-halogen bands also show a dependence on oxidation state, the higher the oxidation state the greater the frequency; Ti(IV) has Ti—Cl bands ~10 $cm.^{-1}$ above Ti(III). This criterion can, however, be affected by the presence of charged species, with anions lowering the frequency and cations raising it, for instance $[InCl_2,2bipyr]^+$ $[InCl_4,bipyr]^-$ has a In—Cl stretching vibration at 301 $cm.^{-1}$ which is absent in $[Ph_4As]^+$ $[InCl_4,bipyr]^-$.

5) X-ray Structure [113,114]

The most decisive way of proving a molecular structure in the solid state is generally by carrying out a single crystal X-ray study. It is a property of X-rays that when they fall on a crystal they interact with the electrons and are scattered in all directions. The regions of greatest electron density correspond to atomic positions and these are related in a regularly repeating manner in a crystal, with the result that X-ray beams of significant intensity only emerge from the crystal in well defined directions. Bragg originally stated the criterion for constructive interference of X-rays scattered from crystal planes:

$$n\lambda = 2d\sin\theta$$

n = order of reflection.

λ = wavelength of the radiation.

d = spacing between the crystal planes.

θ = angle of incidence.

While the directions of the diffracted beams are a measure of the size of the repeating unit in the crystal (the unit cell) their intensities are related to the types of atoms present and their positions within the unit cell.

The electron density, which may be conveniently expressed by a Fourier series, as it is a continuous periodic function, is given by:

$$\rho(x,y,z,) = \frac{1}{V} \sum_{h} \sum_{k} \sum_{l}{}_{-\infty}^{\infty} F(hkl)\exp\left\{-2\pi i(hx+ky+lz)\right\}$$

where V = volume of the unit cell.

F(hkl) = structure factor for the plane (hkl).

$$F(hkl) = \sum_i f_i \exp\left\{2\pi i(hx+ky+lz)\right\}$$

f_i = atomic scattering factor.

Unfortunately, however, F(hkl) is a complex quantity which may be written $F = A + iB$

$$|F| = \sqrt{A^2 + B^2} \quad \text{and phase} \quad \alpha = \tan^{-1} {}^{B}/_{A}$$

although for a centrosymmetric crystal this simplifies since:

$$F = \pm A, \ B = 0 \text{ and } \alpha = 0 \text{ or } \pi$$

In the determination of a single crystal structure, following the accurate measurement of the unit cell dimensions, the intensities of a large number of reflected beams are measured and after correction these are proportional to F^2 but this only allows only relative values of $|F|$ to be obtained. Since $\rho(x,y,z)$ cannot therefore be calculated directly several ways around this problem (known as the 'phase problem') have been devised. One is the use of the Patterson function which at u,v,w, is given by:

$$P(u,v,w) = \frac{1}{V} \sum_h \sum_k \sum_{l=-\infty}^{\infty} |F(hkl)|^2 \cos 2\pi(hu+kv+lw)$$

This function gives information about interatomic vectors in the unit cell, the most intense peaks on the Patterson map, obtained by plotting P for u, v, and w, correspond to vectors between the heaviest atoms. Using the peaks corresponding to vectors between various atoms it is frequently possible to derive their positions and these may be used for the calculation and plotting of a Fourier map. Fortunately, the atoms most easily located by the Patterson method are the heaviest and these have the greatest influence in the Fourier calculation as approximately three-quarters of the signs (for F) are correct in a centrosymmetric structure when:

$$\sum A_h^2 = \sum A_1^2$$

where A_h and A_1 are the atomic numbers of the heavy and light atoms respectively. It should be possible from the Fourier map to locate the remaining light atoms and these may be incorporated in a further Fourier synthesis to yield more accurate coordinates for all the atoms. Further cycles of refinement are normally carried out until there is no further change in a quantity 'R' which is defined as:

$$R = \frac{\sum \left| \left(|F_o| - |F_c| \right) \right|}{\sum |F_o|}$$

CHAPTER III

COMPLEXES OF TITANIUM(III) IODIDE

Titanium(III) iodide has been known for several years[94] but few complexes have been reported.[40,75] The only ones containing a titanium-iodine covalent bond were prepared by Russ.[27]

The aim of this work was to prepare adducts with a range of organic ligands and to study their properties. The ligands used were those which had previously been examined with titanium(III) chloride and bromide, thus allowing a comparison between the three halides.

1. Reaction of titanium(III) iodide with tetrahydrofuran

Titanium(III) iodide was allowed to react with a large excess of ligand at room temperature for four days, and gave a red-brown solid which was slightly soluble in tetrahydrofuran. The solid was isolated by filtration, and pumped to remove excess ligand before being analysed.

	Ti%	I%	C%	H%
Found	7.6	59.2	18.6	3.8
$TiI_3,3C_4H_8O$ requires	7.4	59.0	22.3	3.8

The infrared spectrum showed that the C-O-C stretching frequencies had decreased and as there were no peaks corresponding to the free ligand all oxygens must be coordinated. The magnetic moment of the complex at room temperature was 1.64 B.M. The electronic spectra were measured for the solid (reflectance) and in tetrahydrofuran solution, they are reported in table 3.1, together with those for the other titanium(III) iodide compounds.

2. The reaction of titanium(III) iodide with 1:4-dioxan

Reaction under the same conditions as in (1) gave a red-brown solid which had the analyses:

	Ti%	I%	C%	H%
Found	6.6	55.1	20.4	3.7
$TiI_3,3C_4H_8O_2$ requires	6.9	54.9	20.8	3.5

The infrared spectrum showed peaks due to both coordinated and uncoordinated dioxan which is consistent with, but not proof that, each dioxan molecule was acting as a monodentate ligand. At 20°C μ_{eff} = 1.64 B.M.

3. Reaction of titanium(III) iodide with 1:2-dimethoxyethane

Reaction for one day at room temperature gave a red-brown solution and a small amount of an insoluble product which was probably unreacted halide. Filtration followed by evaporation of the solvent gave a brown solid. This had a Ti:I ratio of 1:1.8, and there was infrared evidence for a titanium-oxygen bond ($\sim$900br cm.$^{-1}$) indicating that oxygen had been abstracted from the ligand.

The reaction was therefore carried out using a $TiI_3:C_4H_{10}O_2$ mole ratio of ~1:4 with benzene as solvent. Three hours reaction gave an insoluble brown solid which was filtered off and washed with solvent. When the complex was pumped the colour lightened to yellow.

	Ti%	I%	C%	H%
Found	7.5	60.8	15.3	3.5
$TiI_3,2C_4H_{10}O_2$ requires	7.8	62.5	15.8	3.3

The infrared spectrum showed that both oxygen atoms were coordinated. Infrared data (1200-400 cm.$^{-1}$) on this and the previous oxygen-donor compounds are collected in table 3.2. The solution spectrum was not run in the ligand as further reaction was known to occur. The magnetic moment of the complex at 18°C was 1.73 B.M.

4. Reaction of titanium(III) iodide with pyridine

The triiodide (1 g) was allowed to react with pyridine in a mole ratio ~1:10 with benzene (~ 20 mls) as diluent. The golden-yellow solid which was formed was filtered off and washed with benzene.

	Ti%	I%	C%	H%	N%
Found	7.0	56.6	25.8	2.9	6.3
TiI_3,3pyr requires	7.2	57.2	27.0	2.2	6.3

The infrared spectrum gave no indication of pyridinium ion.[96] The magnetic moment at 20°C was 1.69 B.M. and the conductivity was measured over a limited range of concentration in both pyridine and methyl cyanide, fig. 3.1.

5. Reaction of titanium(III) iodide with α picoline

The reaction was carried out under the same conditions as the one with pyridine and yielded a brown solid.

	Ti%	I%	C%	H%	N%
Found	7.6	62.3	22.0	2.5	4.6
TiI_3,2αpic requires	7.8	62.0	23.4	2.3	4.6

At 18°C μ_{eff} = 1.65 B.M.

This compound was very rapidly hydrolysed and the triiodide, rather than TiI_3,2αpic, was dissolved in α picoline for measurement of the visible spectrum.

6. Reaction of titanium(III) iodide with γ picoline

Titanium(III) iodide and γ picoline were allowed to react in a mole ratio ~1:4 using benzene as solvent. Several hours refluxing resulted in the formation of a tan coloured solid which was filtered off, washed with benzene and pumped at 50°C prior to analysis.

	Ti%	I%	C%	H%	N%
Found	6.5	53.1	30.0	3.2	5.0
TiI_3,3γpic requires	6.8	53.8	30.6	3.0	5.9

The magnetic moment at 21°C was 1.97 B.M.

When the visible spectrum was being measured in γ picoline solution the colour of the solution varied from blue to green on different occasions, and showed an unusually strong absorption peak around 15,000 $cm.^{-1}$ (e = 250 for the green). This peak decayed very rapidly on exposing the cell to air (~1 sec.) and an orange solution was obtained. It is probable that the green solution resulted from a mixture of the orange and blue ones, a slight amount of oxidation or hydrolysis having taken place. The intensity of the peak is too great for a d-d transition and may be due to charge transfer but the species responsible is not known.

7. Reaction of titanium(III) iodide with 2:2'-bipyridyl

Reaction of titanium(III) iodide (2 g) with 2:2'-bipyridyl (1.5 g) in benzene (~20 mls) containing a trace of methyl cyanide ($<$0.5 ml), for two days gave a black insoluble solid.

	Ti%	I%	C%	H%	N%
Found	7.1	58.0	27.0	2.8	6.1
TiI_3,1.5bipyr requires	7.2	57.5	27.1	1.8	6.3

The infrared spectrum indicated that all the bipyridyl was coordinated and that no methyl cyanide remained in the complex. The conductivity, measured in methyl cyanide as a function of concentration is shown in figure 3.2.

At 19°C μ_{eff} = 1.39 B.M. but was also measured between 80-300°k (table 3.6, fig. 3.3 and 3.4).

8. Reaction of titanium(III) iodide with 1:10-phenanthroline

The reaction was carried out in benzene using the mole ratio TiI_3:phen of 1:2.5. Three weeks shaking gave an insoluble tan coloured solid.

	Ti%	I%	C%	H%	N%
Found	6.3	49.2	34.4	2.5	5.9
TiI_3,2phen requires	6.1	48.3	36.5	2.0	7.1

The conductivity was measured in methyl cyanide over a range of concentration (fig. 3.2). The magnetic moment at 18°C was 1.39 B.M.

9. Reaction of titanium(III) iodide with triphenylphosphine

Titanium(III) iodide was allowed to react with triphenylphosphine in the mole ratio ~ 1:3 using benzene as the solvent. Two weeks shaking gave a red-brown solid and a greenish solution. The solid was filtered off and washed with benzene, in which it was somewhat soluble.

	Ti%	I%
Found	6.6	54.8
TiI_3,PPh_3 requires	6.9	55.1

At 18°C μ_{eff} = 1.43 B.M. An attempt to repeat the reaction failed and the product was not studied further.

10. Reaction of titanium(IV) iodide with pyridine

Titanium(IV) iodide was allowed to react with pyridine using benzene as diluent. The brown insoluble product had Ti:I:pyr of 1:3.97:3.45. Magnetic measurements indicated that some reduction had taken place and the reaction was not studied further.

11. Reaction of titanium(IV) iodide with tetrahydrofuran

The green solution formed initially when titanium(IV) iodide was shaken with tetrahydrofuran rapidly changed to dark brown. Filtration and evaporation of the excess ligand left an intractable oil. The visible spectrum of the brown solution was recorded.

Table 3.1		Electronic Spectra	
$TiI_3,3C_4H_8O$	Refl.	10,900 14,200	~24,400vbr 38,000 45,000
	Soln. C_4H_8O	10,800 14,100	24,900
$TiI_3,3C_4H_8O_2$	Refl	11,350 14,100	~21,800vbr
	Soln. $C_4H_8O_2$	14,400sh(ε ~15)	20,300(ε6000) 25,000sh 31,800 35,500
$TiI_3,2C_4H_{10}O_2$	Refl.	11,230sh 14,700sh	23,300
	Soln. $C_4H_{10}O_2$	Not measured	
$TiI_3,3pyr$	Refl	11,900 14,810sh	20,700sh(w) 24,400 30,000 37,200 45,500
	Soln. pyr.	11,760sh 14,180sh	25,200(ε∿6000)
$TiI_3,3\gamma pic$	Refl.	∿12,900sh	20,800sh ∿29,000br ∿36,700sh 45,600
	Soln. in γ picoline	15,000(ε ∿250)	20,000sh 25,320(ε8000) ∿32,000sh
$TiI_3,2\alpha pic$	Refl.	14,390	21,200 27,300 37,500 45,300
	TiI_3 in αpic	11,500sh? 12,200 ∿14,800sh	20,300 24,500
$TiI_2,2phen$	Refl.	14,300sh	19,600sh 25,600
	Soln. CH_3CN		18,700 27,800sh
$TiI_3,1.5bipy$	Refl.	10,800w,sh 15,500	∿20,000
	Soln. CH_3CN		18,900sh 25,000sh ∿30,800sh 33,300

Table 3.2

Infrared Spectra

1200-400 cm.$^{-1}$

C_4H_8O	$TiI_3,3C_4H_8O$	$C_4H_8O_2$	$TiI_3,3C_4H_8O_2$	$C_4H_{10}O_2$	$TiI_3,2C_4H_{10}O_2$
1180w	1170w	1121vs*	1125s	1191s	1181m
1070s	1042m	1086m		∽1120vs	∽1102vw
					1079m
1032sh	991s	1048m	1047m		
					1060s
	950w		1027s		
	925m		1013w	1028s	∽1008vs
	915m				
		888m	895m	982m	
911s	845sh				
		875s+	872s	938m	
	820s				
			833m		
				925sh	
653w	678m		810s		
				853m	859s
			801s		
510w	575vw				
					842s
		612s	625m		
					798m
			615m		
					691s
		500w	470m		681s

* assymetric C-O-C stretching vibration

\+ symmetric C-O-C " "

Table 3.3 Infrared Spectra 2000-400 cm.$^{-1}$

Pyridine	TiI_3,3pyr	γpicoline	TiI_3,3γpic	αpicoline	TiI_3,2αpic
1600m 1590s	1605s	1605s 1561m	1628m 1608s 1590m	1595s 1565m	1603s 1560m
		N U J O L			
1215m	1220m	1225m	1240m	1298m	1300s
		1212m	1216m	1240w	1238w
1145m	1150m		1200w	1150m	1159m
1065m	1067m	1071w	1066m	1102w	1108m
	1063sh	1041m	1039m	1051m	1063m
1028s	1043m		1020s	1040sh	1035w
959s	1013sh	996m	810s	1000m	1018m
	1004m	972w		978w	1010w
747s	760m		785m	800w	
	755sh	800s	723m	753s	800m
705s	700sh				773s
605m	695s	727m	681s	730m	
	678w		675s	628m	765s
		514m		546w	721m
	638m		544m		647m
		483s	518w	470m	550m
			496s		468m
			474m		423s

Table 3.6 Magnetic Data $2TiI_3,3bipyr$

T °K	χ'_m ($x10^6$ cgsu)	μ_{eff} (B.M.)
313.2	837	1.449
303.2	837	1.426
293.2	737	1.316
283.2	916	1.441
273.2	890	1.395
253.2	991	1.417
233.2	1049	1.401
213.2	1177	1.417
193.2	1262	1.391
173.2	1342	1.356
153.2	1506	1.359
133.2	1661	1.331
113.2	1847	1.294
93.2	2112	1.255
83.2	2304	1.239

Results and Discussion

The ligands tetrahydrofuran, 1:4 dioxan, pyridine and γ picoline react with titanium(III) iodide to give complexes of the type $TiI_3,3L$ analogous to those which have been prepared from the trichloride and tribromide.[20,47,49-51] In contrast to these ligands methyl cyanide has been reported to give the compounds $[TiI_2,4CH_3CN]^+I^-$ [27] and $[Ti(CH_3CN)_6]^{3+}[I_3^-]_3$.[75] Unfortunately the compounds were completely insoluble in non-donor solvents, thus eliminating the possibility of molecular weight studies.

The conductivity of the pyridine adduct in pyridine solution, (fig. 3.1) while less than that expected for a 1:1 electrolyte, is significant. The rise in conductivity from the chloride to the iodide complex (table 3.4) may be due to the reaction:

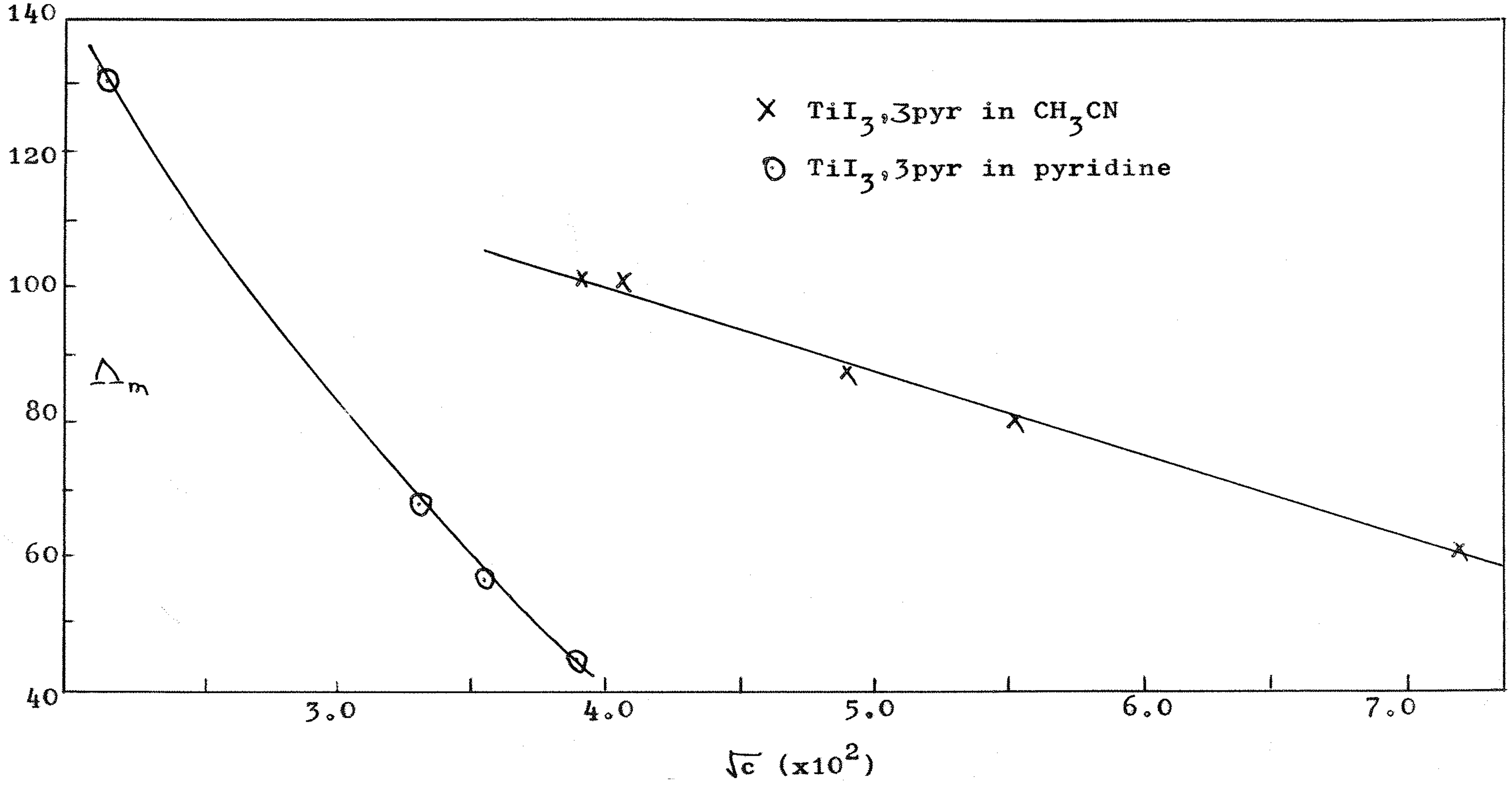
$$TiX_3,3pyr \quad + \quad pyr \quad \rightleftharpoons \quad [TiX_2,4pyr]^+ \quad + \quad X^-$$

Table 3.4

The conductivities of $TiX_3,3pyr$ adducts in pyridine

Compound	$\Lambda_m (ohm^{-1} cm^2)$	$c (x10^{-3} M)$
$(C_2H_5)_4NBr$	134	2.76
$TiCl_3,3pyr$	8	1.79
$TiBr_3,3pyr$	27	1.71
$TiI_3,3pyr$	65	1.00

Fig. 3.1.


140
120
100
80
60
40
Λ_m
3.0
4.0
5.0
6.0
7.0
$\sqrt{c}$ (x10^2)
× TiI_3,3pyr in CH_3CN
⊙ TiI_3,3pyr in pyridine

where the equilibrium constant is related to the metal-halogen bond strength. The very rapid rise in conductivity with dilution suggests that even further stages of ionisation may be occuring. Hoodless[20] found that $TiCl_3,3pyr$ behaved as a 1:1 electrolyte in methyl cyanide and the same effect was found for $TiBr_3,3pyr$.[50] The iodide complex behaved in a similar way and showed a linear plot of Λ_m against $\sqrt{c}$ (fig. 3.1). It was suggested that methyl cyanide displaced a chloride ion,

$$TiCl_3,3pyr + CH_3CN \rightleftharpoons [TiCl_2,3pyr,CH_3CN]^+ + Cl^-$$

but surprisingly the solution spectrum in methyl cyanide was very similar to that in pyridine.

α picoline forms 1:2 adducts with all three trihalides,[20,50] $TiCl_3,2\alpha pic$ was originally considered to be a halogen bridged dimer. The physical properties do, however, give some support to a trigonal bipyramidal structure. The trichloride compound shows a marked red shift of the d-d peak on being dissolved in α picoline although formation of the monomeric species, $TiCl_3,3\alpha pic$, should give a blue shift. Similar red shifts in ligand solution were also found with $TiCl_3,2N(CH_3)_3$[20] and $TiBr_3,2N(CH_3)_3$.[27] The latter is known to be trigonal bipyramidal in the solid[54] and the former is isomorphous with it.[27] A bridged structure might well give rise to magnetic exchange but this is not observed, the room temperature moment of $TiCl_3,2\alpha pic$ being close to that of the trimethylamine compound. The low infrared spectra of $TiCl_3,2\alpha pic$ and $TiCl_3,2N(CH_3)_3$ also show a marked similarity in the metal-halogen stretching region, except that an extra peak at 363 cm.$^{-1}$ was resolved in the α picoline complex. It seems likely that all three α picoline compounds have the same structure but without X-ray or near infrared reflectance studies it is unlikely to be determined.

The compound with 1:10-phenanthroline is formulated as $[TiI_2,2phen]^+I^-$ on the basis of its conductivity in methyl cyanide (fig. 3.2). The complex with 1:2-dimethoxyethane probably has a similar structure but its conductivity could not be measured owing to the probability of reaction with the usual solvents.

The bipyridyl compound, $2TiI_3,3bipyr$ is thought to be analogous to the chloride[55] and bromide[50] complexes which are discussed in detail in chapter IV. The conductivity (fig. 3.2) supports the ionic structure $[TiI_2,2bipyr]^+$ $[TiI_4,bipyr]^-$.

The magnetic moments, with the exception of three compounds, are all in the range expected for distorted octahedral titanium(III). The reason for the exceptionally high moment (1.97 B.M.) of the γ picoline complex is far from clear for although a high moment (1.97 B.M.) was also

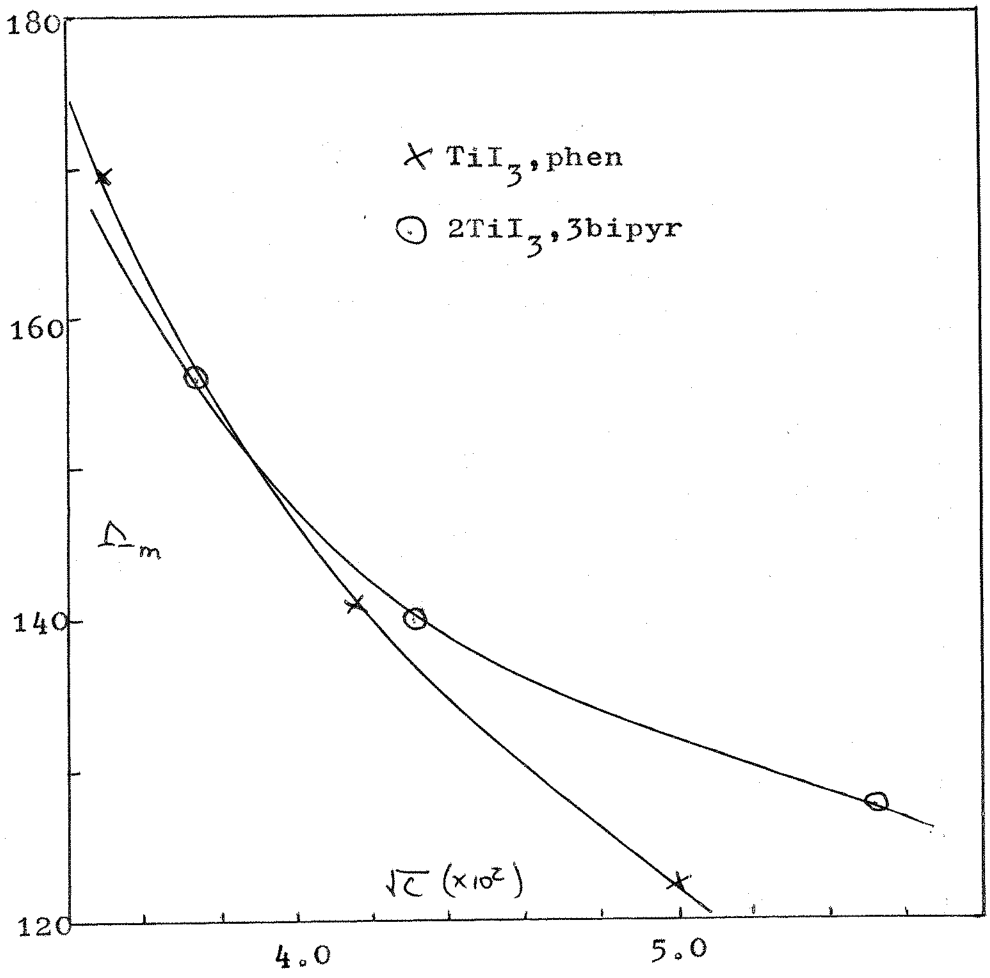

180
160
140
120
4.0
5.0
Λ_m
$\sqrt{c}$ ($\times 10^2$)
TiI$_3$,phen
2TiI$_3$,3bipyr

Fig. 3.2.

obtained for $TiCl_3,3\gamma pic$, impure halide was thought to be responsible in that case.[97] Both the phenanthroline and bipyridyl compounds have magnetic moments markedly below those of the other compounds and while oxidation is possible it is very unlikely with these ligands as they form exceptionally stable compounds with the trichloride and tribromide.

The plot of $1/\chi'_m$ vs T (fig. 3.3) for $2TiI_3,3bipyr$ shows that the Curie-Weiss law is obeyed with θ of 46°. The room temperature moment is too low to allow a curve to be fitted to the μ_{eff} vs T plot (fig. 3.4) by Figgis's method[84] and it seems that there must be some exchange between the titanium atoms. If $2TiI_3,3bipyr$ has the same structure as that postulated for the chloride and bromide (chapter IV) the exchange is presumably of the type:

$$Ti —— I- - -I —— Ti$$

This mechanism is found in the $[ReX_6]^{2-}$ salts, and is known to increase $F \rightarrow I$.[67] The low moment of the 1:10-phenanthroline complex can be explained in the same way.

The low infrared data for titanium(III) iodide and a number of the compounds are shown in table 3.5. The titanium-iodide stretching frequencies of $\sim$250 cm.$^{-1}$ are in accord with Clark's suggestion that:[98]

$$\frac{v_{M-I}}{v_{M-Cl}} \doteqdot 0.65$$

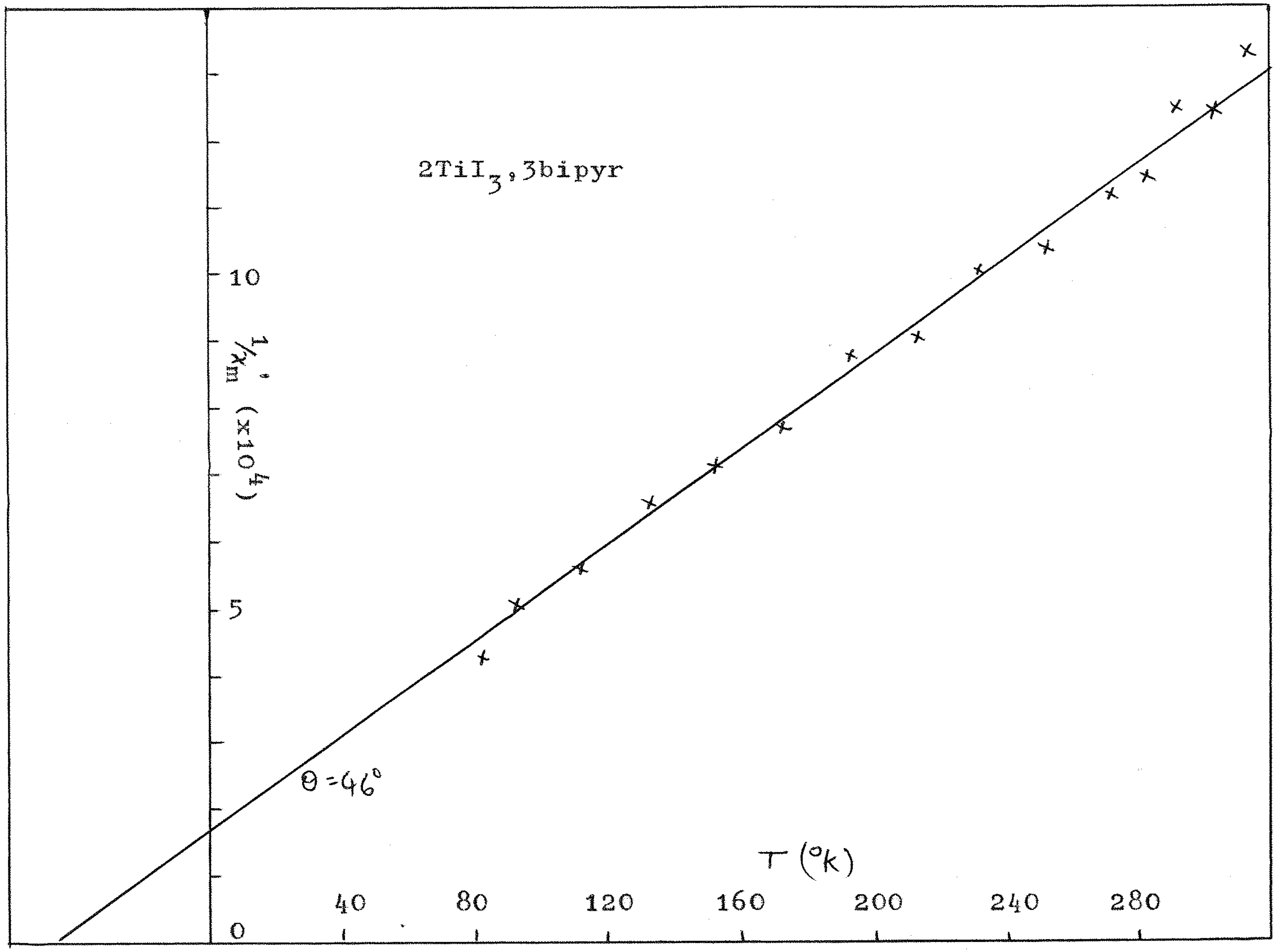


Fig. 3.3.

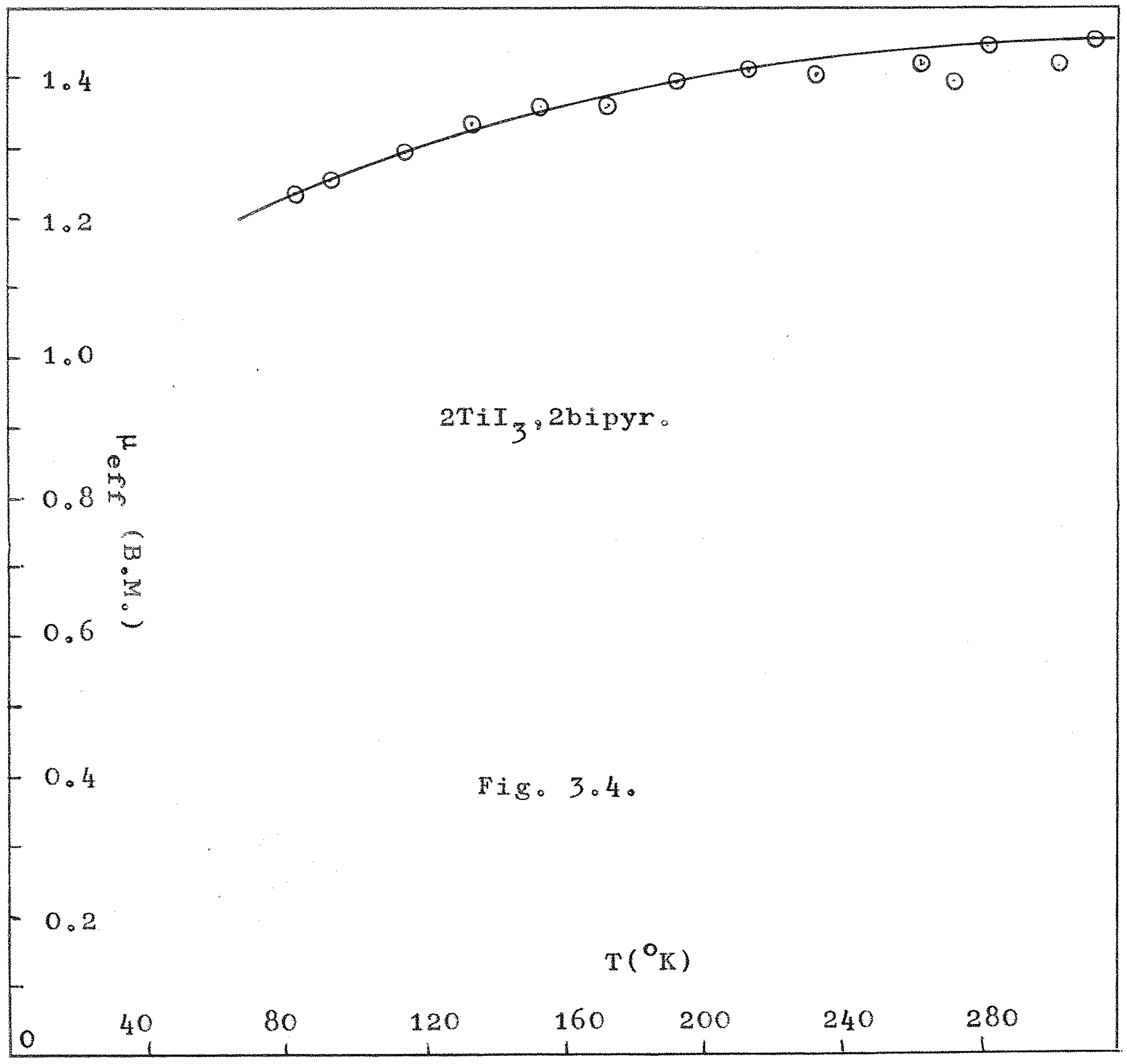

2TiI$_3$,2bipyr.
μ_{eff} (B.M.)
1.4
1.2
1.0
0.8
0.6
0.4
0.2
0
40
80
120
160
200
240
280
T(°K)

Fig. 3.4.

Table 3.5

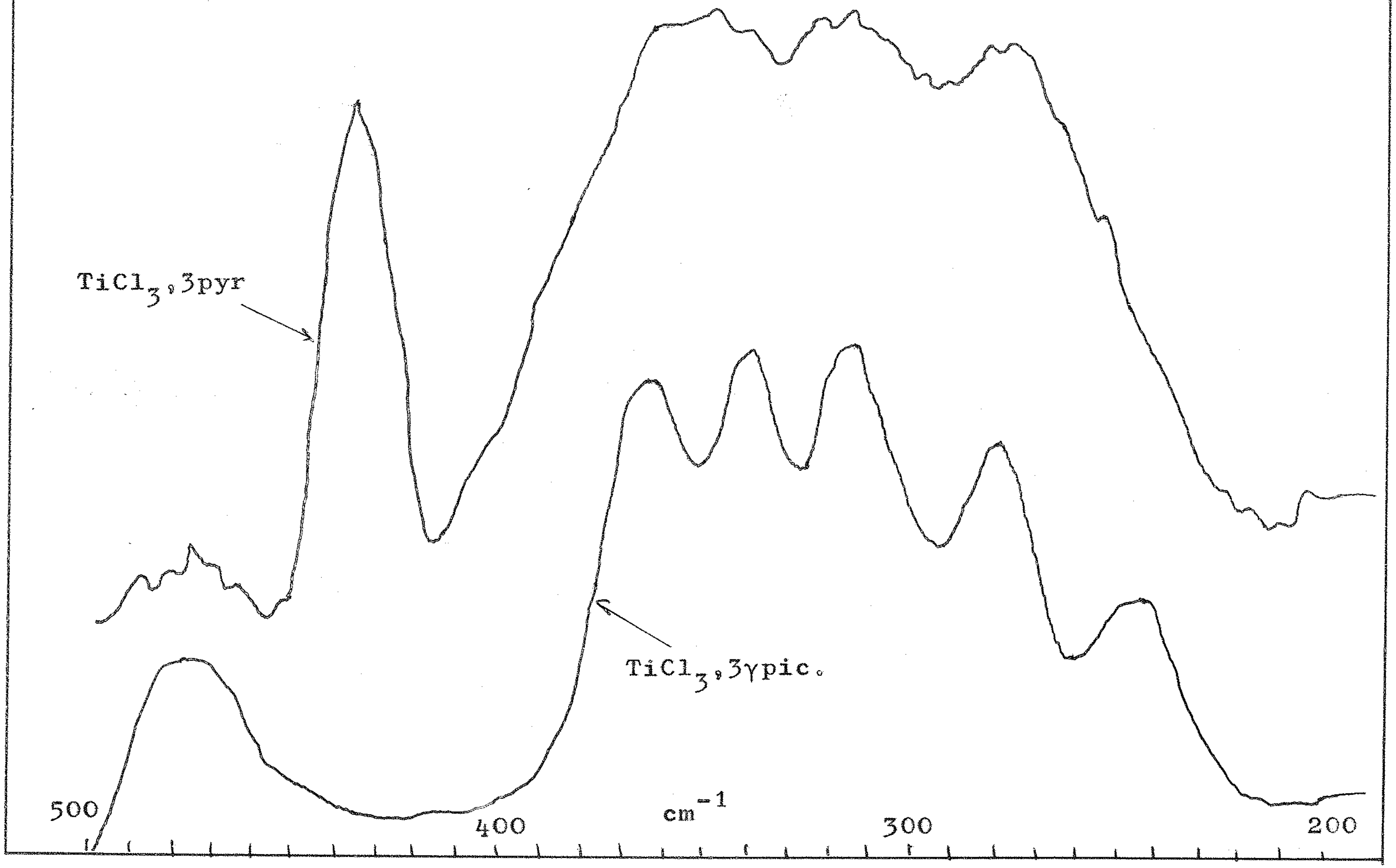
Low Infrared Spectra
(500-200 cm.$^{-1}$)

TiI_3	297w 241s ~200br
TiI_3,$3C_4H_8O$	260br
TiI_3,3pyr	434m 421sh 267s 240s,br
TiI_3,3γpic	475m,br 240br ~200br
TiI_3,2αpic	423m 375m 262s 247sh 237s
TiI_3,1.5bipyr	414m 360m 309m 290s 265s 239w,br 209w,br
TiI_2,2(1:10phen)	424s 320s 306s ~390br 268m 244m,br
$TiCl_3$,3pyr	432s 350s,br 319s,br 277s,br
$TiCl_3$,3γpic	476m,br 364s 343s 318s 282m 247m,br
$TiCl_3$,2αpic	428s 389s,br 363s,br ~338sh 298w 243m,br
$TiCl_3$,$2N(CH_3)_3$	437s 387s,br 330sh 254m
$TiBr_3$,3pyr	432m 283s 273sh

The distinction between cis and trans isomers was not made for the $TiI_3,3L$ compounds as the metal-halogen bands are broad and close to the instrumental limit of 200 cm.$^{-1}$. Metal-nitrogen bands are also expected in this region.[99] In order to avoid these problems measurements on a number of the analogous chloride compounds have been made and are included in the table. $TiCl_3,3\gamma pic$ has three well defined titanium-chlorine stretches and is probably trans while $TiCl_3,3pyr$ shows only two broad bands in the same region, (fig. 3.5). The position of metal-nitrogen vibrations in complexes of pyridine and related ligands is still not certain but Durig et al. have recently assigned bands in the 250-300 cm.$^{-1}$ region to M-N stretches.[99] The peaks around 280 cm.$^{-1}$ in these compounds may therefore be essentially titanium-nitrogen modes. $TiBr_3,3pyr$ shows only a single peak and a shoulder between 400 and 200 cm.$^{-1}$ and is probably cis. The Ti-N stretching frequency in $TiBr_3,3pyr$ is either very weak or more probably obscured by the bromine vibrations. Clark has suggested that $TiCl_3,3CH_3CN$ is cis while $TiCl_3,3C_4H_8O$ exists as the trans isomer.[53]

From conductance data $2TiI_3,3bipyr$ was considered to be $[TiI_2,2bipyr]^+[TiI_4,bipyr]^-$. If this is so the former ion should have two infrared active Ti-I bands (if the bipyridyl molecules are cis) while the latter

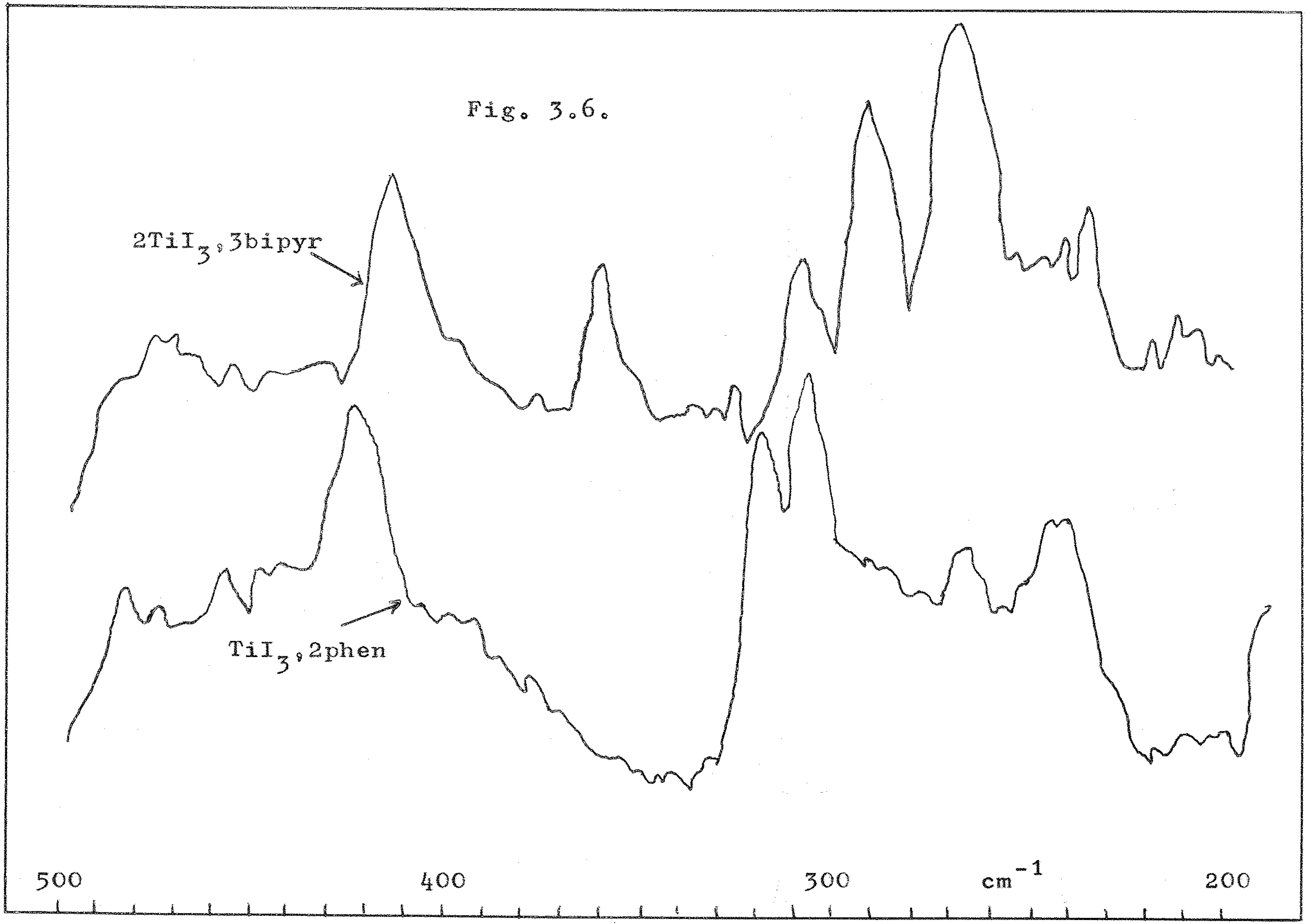
Fig. 3.5.



should have four. Coincidence of some of the bands is possible and it is expected that the cation should have stretching modes at higher energy than a neutral or anionic species.[93] Five peaks are observed below 310 $cm.^{-1}$, the peaks at 309 $cm.^{-1}$ and 290 $cm.^{-1}$ being at significantly higher energy than in the neutral compounds (as the 290 $cm.^{-1}$ band is one of the most intense bands in the spectrum it is probably not Ti-N). Peaks at 360 $cm.^{-1}$ and 414 $cm.^{-1}$ are characteristic of the ligand,[91] (fig. 3.6). The phenanthroline species $[TiI_2,2phen]^+I^-$ should have two Ti-I stretching vibrations for the cis isomer and this is consistent with the two sharp bands observed at 320 $cm.^{-1}$ and 306 $cm.^{-1}$. The correct assignment for the two broad peaks at 268 $cm.^{-1}$ and 244 $cm.^{-1}$ is not known. The band at 424 $cm.^{-1}$ is a ligand vibration, (fig. 3.6).

Three types of electronic transition are expected in the visible region of the spectrum. Those at lowest energy will be the d-d transitions $^2B_{2g} \longrightarrow {}^2B_{1g}$ and $^2B_{2g} \longrightarrow {}^2A_{1g}$. Charge transfer transitions $I(\pi) \longrightarrow Ti(d)$ are also expected, for on proceeding from $[TiCl_6]^{2-}$ to $[TiBr_6]^{2-}$ the first band, which is symmetry forbidden and therefore weak, moves from ~24,000 to ~22,000 $cm.^{-1}$.[100] The shift from $Cl \longrightarrow I$ reflects the decreasing optical electronegativity of the halogen (chapter VI). The third

Fig. 3.6.



type of transition Ti(d)⟶lig (π*) is expected for complexes with ligands which have comparatively accessible (π*) orbitals, such as 2:2'-bipyridyl.

Attempts to prepare a titanium(IV) iodide complex failed but the spectrum of the tetraiodide in tetrahydrofuran has the lowest band at 15,100 cm.$^{-1}$ which is fairly certainly due to an I(π)⟶Ti(d) transition. The equivalent transition in titanium(III) would be expected at rather higher energy since the optical electronegativity decreases as the oxidation state falls (chapter VI) and therefore transitions around 14,500 cm.$^{-1}$ are assigned to d-d.

The transition to lig(π*) is, to a first approximation independent of halide ion and is found in about the same position for the pyridine and bipyridyl complexes of both the trichloride and tribromide; it is about 18,500 cm.$^{-1}$ for the bipyridyl ones, (chapter IV).

The d-d spectra of the compounds with tetrahydrofuran, dioxan and pyridine, which appear to be the most straightforward, are very similar for the solid and for a solution in the ligand. These spectra confirm that at the concentrations at which they were measured reaction to give species of the type $[TiI_2,4L]^+I^-$ have not occurred to a significant extent.

The large splitting of the ^2E_g doublet by the unsymmetrical ligand field prevents meaningful calculations of 10Dq but it can be seen qualitatively that the assignments are self consistent. For instance the dioxan and tetrahydrofuran compounds have very similar spectra but the pyridine complex has bands at higher energy in agreement with the observations on the trichloride and tribromide complexes that $Dq_{pyr} > Dq_{C_4H_8O} \approx Dq_{C_4H_8O_2}$.[103] In the complex with 1:2-dimethoxyethane the presence of four oxygen atoms around each titanium shifts the d-d bands to higher energy than in the compounds of the other oxygen donors (since $Dq_{oxy.lig} > Dq_{I^-}$). The phenanthroline complex should show the same effect compared to the pyridine one but the position of the d-d band is obscured by a charge transfer transition $\sim$ 19,000 cm.$^{-1}$. The same is true of the bipyridyl complex except that a weak shoulder is observed at 10,800 cm.$^{-1}$ consistent with the presence of $[TiI_4,bipyr]^-$.

Both the phenanthroline and bipyridyl compounds show peaks $\sim$ 19,000 cm.$^{-1}$ which are assigned to $Ti(d) \rightarrow lig(\pi^*)$. The increase in the splitting of the excited state (^2E_g) in the iodide spectra compared to those of the chloride and bromide is explained by the increasing disparity between the Dq values and X^- and the other ligands used.

CHAPTER IV

COMPLEXES OF TITANIUM(III) BROMIDE
WITH
2:2'-BIPYRIDYL

In this chapter the preparation and characterisation of several new complexes of titanium(III) bromide with 2:2'-bipyridyl are described. The properties of the previously reported compounds $2TiX_3$,3bipyr, where X = Cl or Br, have also been investigated more fully and structures assigned.

1. Preparation of $TiBr_3$,bipyr

A 2:1 mole excess of 2:2'-bipyridyl was allowed to react with titanium(III) bromide in benzene containing a trace of methyl cyanide (~ 1%). The reactants were shaken in an ampoule for two weeks and the purple solid formed was filtered off, washed with benzene, pumped and analysed.

	Ti%	Br%	C%	H%	N%
Found	10.7	54.2	27.7	1.85	6.43
$TiBr_3$,2:2'-bipyr requires	10.8	54.1	27.0	1.80	6.31

The magnetic moment at 21°C was 1.88 B.M.

The infrared spectrum showed bands characteristic of coordinated bipyridyl (4,000-700 cm.$^{-1}$) and in particular the ring stretching vibrations, occurring between 1430 and 1590 cm.$^{-1}$, were shifted to slightly higher energy,[101] (~ 10 cm.$^{-1}$). There was no infrared evidence for the presence of methyl cyanide.

The conductivity of the product in methyl cyanide solution was measured at a concentration of 1.03 x 10^{-3}M; Λ_m was found to be 23.6 $ohm^{-1}cm^2$.

2. Preparation of $TiBr_3$,2bipyr,CH_3CN

Reaction of titanium(III) bromide and bipyridyl, in a mole ratio 1:2.1, using methyl cyanide as the solvent for one day gave a purple, slightly soluble product which was collected and analysed.

	Ti%	Br%	C%	H%	N%
Found	7.1	37.7	40.5	3.0	10.2
$TiBr_3$,2bipyr,CH_3CN requires	7.4	37.4	41.2	3.0	10.9

At 21°C μ_{eff} = 2.06 B.M.

The infrared spectrum was typical of coordinated bipyridyl but also contained a band at 2260 $cm.^{-1}$ typical of the C≡N stretching frequency of methyl cyanide when the nitrogen is not coordinated to a metal.

The conductivity was measured over a range of concentration in methyl cyanide and is plotted in fig. 4.1.

3. Preparation of $TiBr_3$,2bipyr,$CHCl_3$

Titanium(III) bromide and 2:2'-bipyridyl were allowed to react in a mole ratio of 1:2.1 using a mixture of chloroform (80%) and methyl cyanide (20%) as solvent. After two weeks reaction a purple solid was filtered off and analysed.

	Ti%	Br%	C%	H%	N%
Found	6.8	33.7	34.9	2.8	7.7
$TiBr_3$,2bipyr,$CHCl_3$ requires	6.7	33.4	35.0	2.4	7.8

The magnetic moment at 20°C was 1.85 B.M. The infrared spectrum gave no indication of methyl cyanide, chloroform could not be positively identified as the C-Cl stretching frequency at ~ 760 $cm.^{-1}$ was obscured by a bipyridyl vibration. Figure 4.1 shows a plot of conductance against $(concentration)^{\frac{1}{2}}$ for a solution in methyl cyanide.

4. Preparation of $TiBr_3$,2bipyr

$TiBr_3$,2bipyr,CH_3CN was heated under vacuo at 110-120°C for ninety minutes. In addition to the loss of methyl cyanide, indicated by the infrared spectrum, a small amount of bipyridyl was seen to sublime out and this was confirmed by slightly low carbon and nitrogen analyses on the residue.

	Ti%	Br%	C%	H%	N%
Found	8.3	39.6	37.3	3.2	9.2
$TiBr_3$,2bipyr requires	8.0	40.0	40.0	2.7	9.3

This compound was also purple but a deeper colour than $TiBr_3$,2bipyr,CH_3CN. An attempt was also made to prepare $TiBr_3$,2bipyr from $TiBr_3$,2bipyr,$CHCl_3$ but no reaction occurred on prolonged heating at 100°C and when the temperature was raised to 140°C bipyridyl was lost. It is interesting that the corresponding vanadium compound VBr_3,2bipyr,$CHCl_3$ did not lose chloroform to give VBr_3,2bipyr until 190°C.[102] The conductivity is given in figure 4.1.

5. Preparation of $2TiBr_3$,3bipyr

This was prepared using the method described by Walton involving the reaction of $TiBr_3$,$2N(CH_3)_3$ and 2:2'-bipyridyl in benzene.[50]

	Ti%	Br%	C%	H%	N%
Found	9.0	46.8	37.7	2.8	7.9
$2TiBr_3$,3bipyr requires	9.2	45.9	34.5	2.3	8.1

The magnetic moment at 20°C was found to be 1.72 B.M. and the conductivity was also measured in methyl cyanide over a range of concentration (fig. 4.2.).

6. Preparation of $2TiCl_3$,3bipyr

This was prepared by the reaction of titanium(III) chloride with 2:2'-bipyridyl in methyl cyanide, as done by Walton.[55]

	Ti%	Cl%	C%	H%	N%
Found	12.7	27.1	46.2	3.6	10.8
$2TiCl_3,3bipyr$ requires	12.3	27.2	46.4	3.9	10.8

The conductivity was measured in methyl cyanide (fig. 4.2).

7. Reaction of titanium(III) bromide with 1;10-phenanthroline

Titanium(III) bromide was allowed to react with 1;10-phenanthroline in methyl cyanide for a week. The dark blue solid obtained was washed very thoroughly with benzene but the analyses corresponded to $\sim TiBr_3,4phen$. Walton also reported non-stoichiometric products from this reaction.[50]

Table 4.1		Electronic Spectra ($cm.^{-1}$)
$TiBr_3$,2bipyr.	Refl.	16,000sh 19,250 26,300
	Soln. CH_3CN	15,150sh 15,900sh 19,050 31,800 35,300
$TiBr_3$,2bipyr, CH_3CN	Refl.	16,400sh 19,050 28,500sh
	Soln. CH_3CN	15,150sh 15,900sh($\varepsilon \doteqdot 50$) 19,050($\varepsilon \sim 300$) 31,900sh 33,300($\varepsilon \sim 20,000$)
$TiBr_3$,2bipyr, $CHCl_3$	Refl.	16,250sh 18,900 25,170
	Soln. CH_3CN	15,150sh 15,900sh 19,050 31,400 33,700
$TiBr_3$,bipyr.	Refl.	12,900wsh? 15,870 18,700
	Soln. CH_3CN	15,150wsh 18,000 31,900sh 32,900
2$TiBr_3$,3bipyr.	Refl.	15,850 18,700
	Soln. CH_3CN	15,400sh 18,500 31,600sh 32,800
2$TiCl_3$,3bipyr.	Refl.*	13,500sh 15,750 18,350 24,500
	Soln. CH_3CN	13,900wsh? 17,200sh 18,350 31,700sh 32,700

*measured by R.A. Walton.[103]

Table 4.2 Low Infrared Spectra (500-200 cm.$^{-1}$)

$TiBr_3$, bipyr.	410m	362m	313s	278s	247s
$TiBr_3$,2bipyr.	412s	358s	320s,br	272s,br	
$TiBr_3$,2bipyr, CH_3CN	412s	362s	$\sim$308s,v,br		
$TiBr_3$,2bipyr, $CHCl_3$	410s	358s	$\sim$303s,v,br		
2$TiBr_3$,3bipyr.	410m	360m	312s	272s	247s
2$TiCl_3$,3bipyr.	418m	362s,br	313s,br		

Results and Discussion

Titanium(III) chloride complexes with 2:2'-bipyridyl have been investigated previously and their preparations are summarised in the following scheme:[20,50,55,97,103]

$$\left.\begin{array}{lll}
1) & \mathrm{TiCl_3} + \text{bipyr (excess)} & \xrightarrow{150^\circ C} \\
2) & \mathrm{TiCl_3,3CH_3CN} + \text{bipyr (excess)} & \xrightarrow{\text{benzene}}
\end{array}\right\} \mathrm{TiCl_3,bipyr} \xrightarrow{\text{RCN}} \mathrm{TiCl_3,bipyr,RCN}$$

$$\begin{array}{lll}
3) & \mathrm{TiCl_3,2N(CH_3)_3} + \text{bipyr} & \xrightarrow{\text{RCN}} \mathrm{TiCl_3,bipyr,RCN}
\end{array}$$

$$\left.\begin{array}{lll}
4) & \mathrm{TiCl_3} + \text{bipyr (excess)} & \xrightarrow{\text{RCN}} \\
5) & \mathrm{TiCl_3,2N(CH_3)_3} + \text{bipyr} & \xrightarrow{\text{benzene}}
\end{array}\right\} \mathrm{2TiCl_3,3bipyr}$$

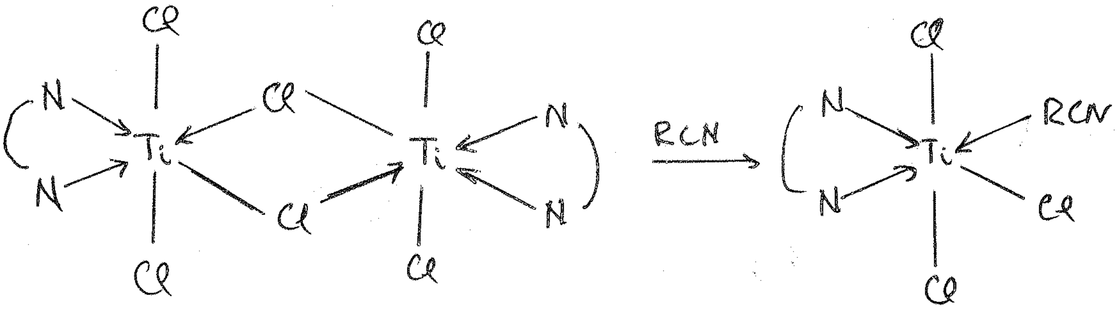
Certain similarities are noticed when titanium(III) bromide is used instead of the trichloride. Reaction (5) works for the bromide and (2) almost certainly would give $TiBr_3$,bipyr although the cyanide adduct was actually found 'in situ'. Reaction (4), however, gives $TiBr_3$,2bipyr,CH_3CN where methyl cyanide is present as a solvate molecule and can be replaced by chloroform if the latter is present as the major component of the solvent.

The reaction:

$$\mathrm{TiBr_3,2bipyr,S} \xrightarrow{\text{heat}} \mathrm{TiBr_3,2bipyr}$$

where S = solvate molecule, is not unexpected.

$TiCl_3$,bipyr was thought to be a halogen bridged dimer capable of breaking down in alkyl cyanides to give



a monomeric species which can be isolated from cyanide solution. A blue shift of the d-d peak in solution compared to reflectance supports this process since Dq for $^{bipyr}/_2 \approx CH_3CN > Cl^-$. The 1:1 bromide complex probably has the same structure but the d-d peaks are almost totally obscured by charge-transfer bands. The low conductivity supports a non-ionic formulation.

The 1:2 adducts, with and without solvate molecules, have very similar spectra, (fig. 4.4,) and conductivities, (fig. 4.1,) and are formulated as $[TiBr_2,2bipyr]^+Br^-$. The analogous vanadium(III) bromide compound has also been prepared.[102] It is interesting that the slopes of the conductivity plots (Λ_m against $\sqrt{c}$) are around 1,400, much greater than for such salts as tetraethylammonium bromide in the same solvent which have slopes ~450.[85] The absolute values of Λ_m at 10^{-3}M are also significantly lower than for the tetraalkyl

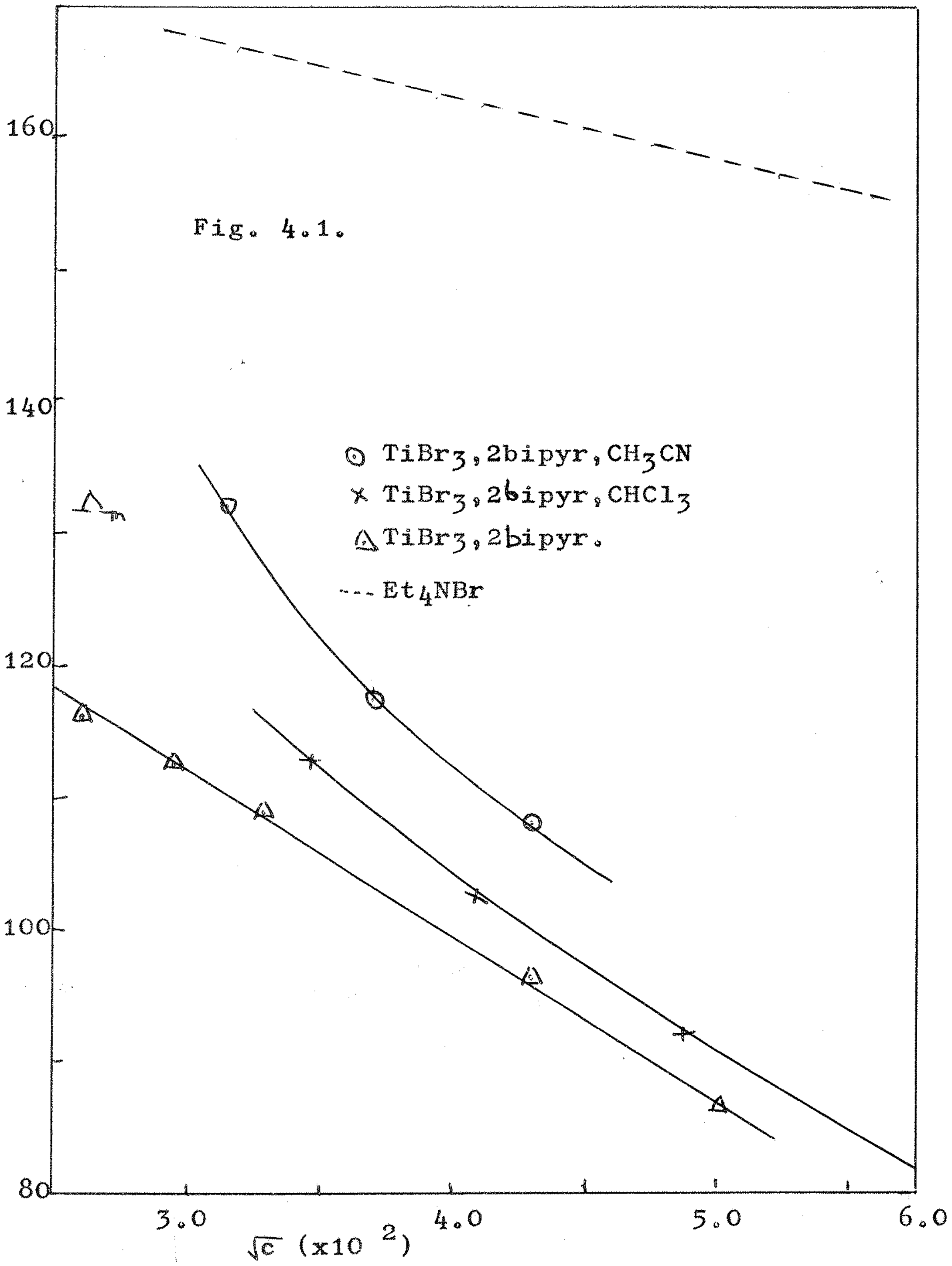


Fig. 4.1.
⊙ $TiBr_3$,2bipyr,CH_3CN
× $TiBr_3$,2bipyr,$CHCl_3$
△ $TiBr_3$,2bipyr.
--- Et_4NBr
Λ_m
160
140
120
100
80
3.0
4.0
5.0
6.0
$\sqrt{c}$ (x10 ^{2})

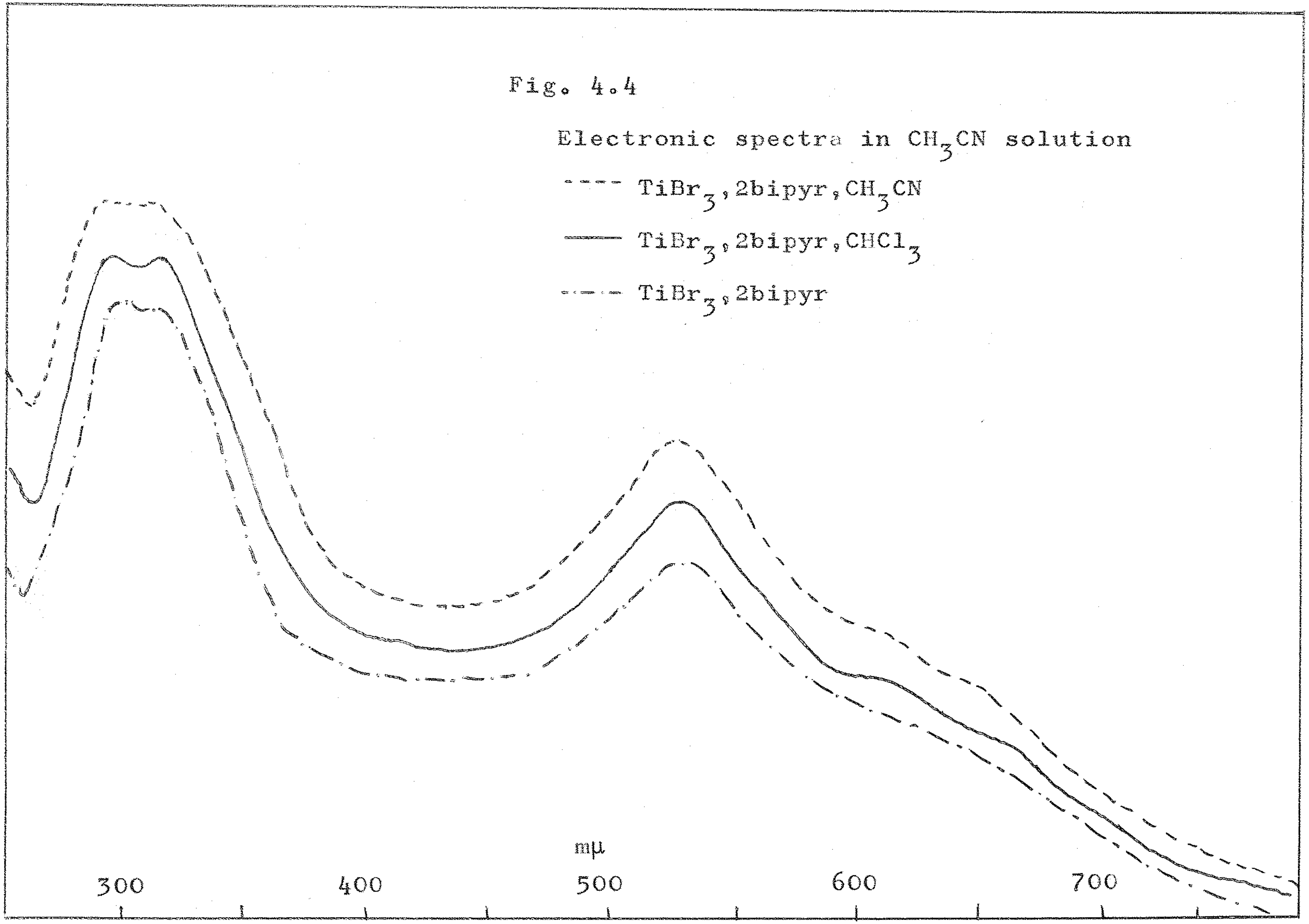
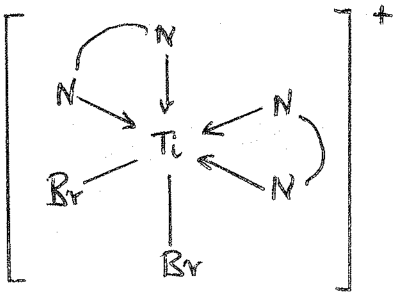


Fig. 4.4

Electronic spectra in CH_3CN solution

salts. These effects are consistent with ion pairing but it is also possible that some further ionisation is occurring at low concentrations. Ion pairing is favoured by the comparatively low dielectric constant of methyl cyanide ($e \doteqdot 36.7$) although the large cation size should help to reduce it.

The visible spectra show an absorption close to 16,000 cm.$^{-1}$ both for the solid and for the methyl cyanide solution but as it is only a shoulder the position is difficult to determine accurately, although using previously calculated values for Dq Br^- and bipyridyl (1040 and 3970 cm.$^{-1}$ respectively)[103] with respect to titanium(III) the d-d band for



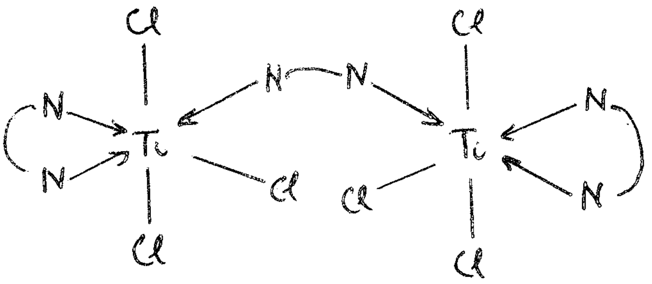
is predicted at 16,670 cm.$^{-1}$, in fair agreement with the observed position. The expected splitting of this shoulder due to the low symmetry is only resolved in methyl cyanide solution. Dependent upon whether the bipyridyl molecules are cis or trans the symmetry is C_2 or D_{2h} respectively; a smaller splitting of the ^2E_g

immediately turned it yellow showing that the blue form was unstable to hydrolysis. The conductivity of the blue solution was measured for a range of concentration and a very large slope for Λ_m against $\sqrt{c}$ was obtained (fig. 4.3). The ultra-violet spectrum was still characteristic of coordinated bipyridyl but the species responsible is not known.

Hoodless originally suggested that the compound $2TiCl_3,3bipyr$ was ionic with the structure:[20]

$$[TiCl_2,2bipyr]^+[TiCl_4,bipyr]^-$$

which was largely based on his value for Λ_m of $128 ohm^{-1}cm^2$ at 3.4×10^{-4} M. A similar structure has also been proposed for $2IrX_3,3(1{:}10phen)$.[106] Walton repeated the conductivity of $2TiCl_3,3bipyr$ and reported Λ_m to be $11 ohm^{-1}cm^2$ at 10^{-3} molar and accordingly proposed the non-ionic structure[55]

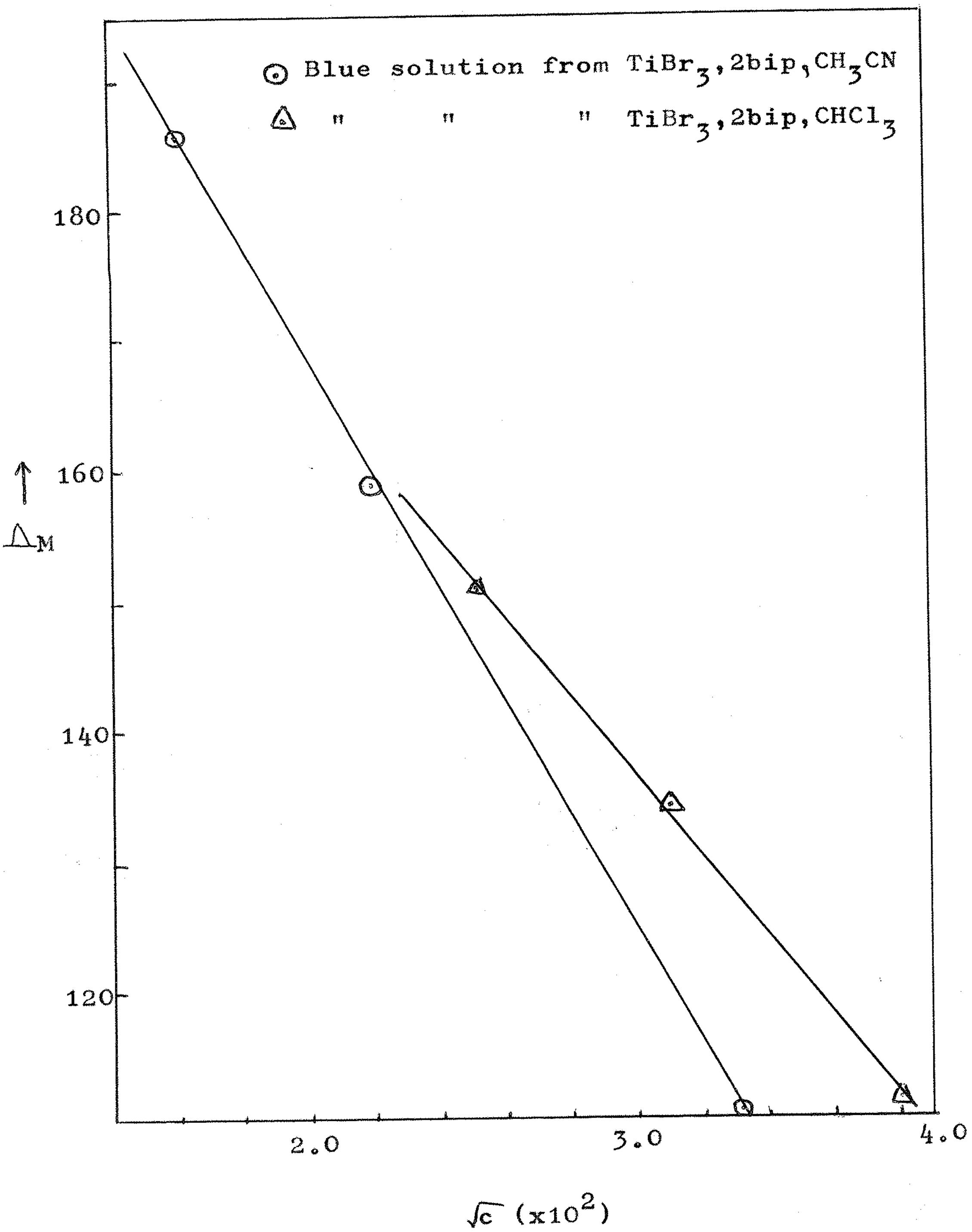


which had a bridging bipyridyl molecule. He also prepared $2TiBr_3,3bipyr$ which he considered to have the same structure although the conductivity was a great deal state would be expected for the former and this is consistent with the observed value of around 800 cm.$^{-1}$.[104]

In principle it should also be possible to distinguish between the isomers by the number of infrared active Ti-Br stretching frequencies. One (b_{1u}) is expected for the trans but two (a and b) are expected for the cis. The low infrared spectral results are given in table 4.2 but unfortunately very poorly resolved spectra were obtained; in any case titanium-nitrogen stretching frequencies may occur in the titanium-bromine region ($\sim$300 cm.$^{-1}$) complicating the issue.[99] Dwyer[105] expects the cis isomer to be more stable as it results in less steric interaction between the hydrogen atoms of the two rings but it seems doubtful if this would determine the stereochemistry.

During measurement of the conductivity and spectra of $TiBr_3$,2bipyr a blue solution was sometimes obtained instead of the usual purple one. It was found that a blue solution could be formed from the purple one by the admission of a very slight amount of air to the cell but when the solid was isolated from this blue solution there was no sign of an O-H stretch in the infrared, which may indicate that the decomposition was by oxidation rather than hydrolysis. This was supported by the observation that addition of a drop of water to the blue solution

Fig. 4.3.



⊙ Blue solution from $TiBr_3,2bip,CH_3CN$
△ " " " $TiBr_3,2bip,CHCl_3$
180
160
140
120
↑ Λ_M
2.0
3.0
4.0
$\sqrt{c}$ $(x10^2)$

higher with Λ_m = 57ohm^{-1}cm^2 for a concentration of 2.83 x 10^{-3}M.[50] These compounds have been reinvestigated, particular care being taken over the conductivities, which are plotted in figure 4.2, and while they are significantly less than those found for such 1:1 electrolytes as tetraethylammonium bromide they are nevertheless much higher than those normally found for a non-conducting species; for instance $TiCl_3,3CH_3CN$ has Λ_m = 18ohm^{-2}cm^2 at 10^{-3}M.[97] As suggested earlier the low values of Λ_m could be due to ion pairing although this is surprising in view of the bulky ions, however, little appears to be known about the behaviour of electrolytes such as these in non-aqueous solvents.[83] The analogous vanadium compound $2VCl_3,3$bipyr has conductivities in both methyl cyanide and nitromethane slightly below those expected for 1:1 electrolytes and an equivalent ionic structure has been assigned to it.[102] Unfortunately nitromethane has been found to oxidise titanium(III).[97]

The reflectance spectra, and also those in methyl cyanide solution if little reaction with the solvent has taken place at the concentrations employed, should show d-d peaks characteristic of both ions. As these would be split by the departure from O_h symmetry a single broad band might be expected. The spectra are listed (table 4.1) and it can be seen that only one band is

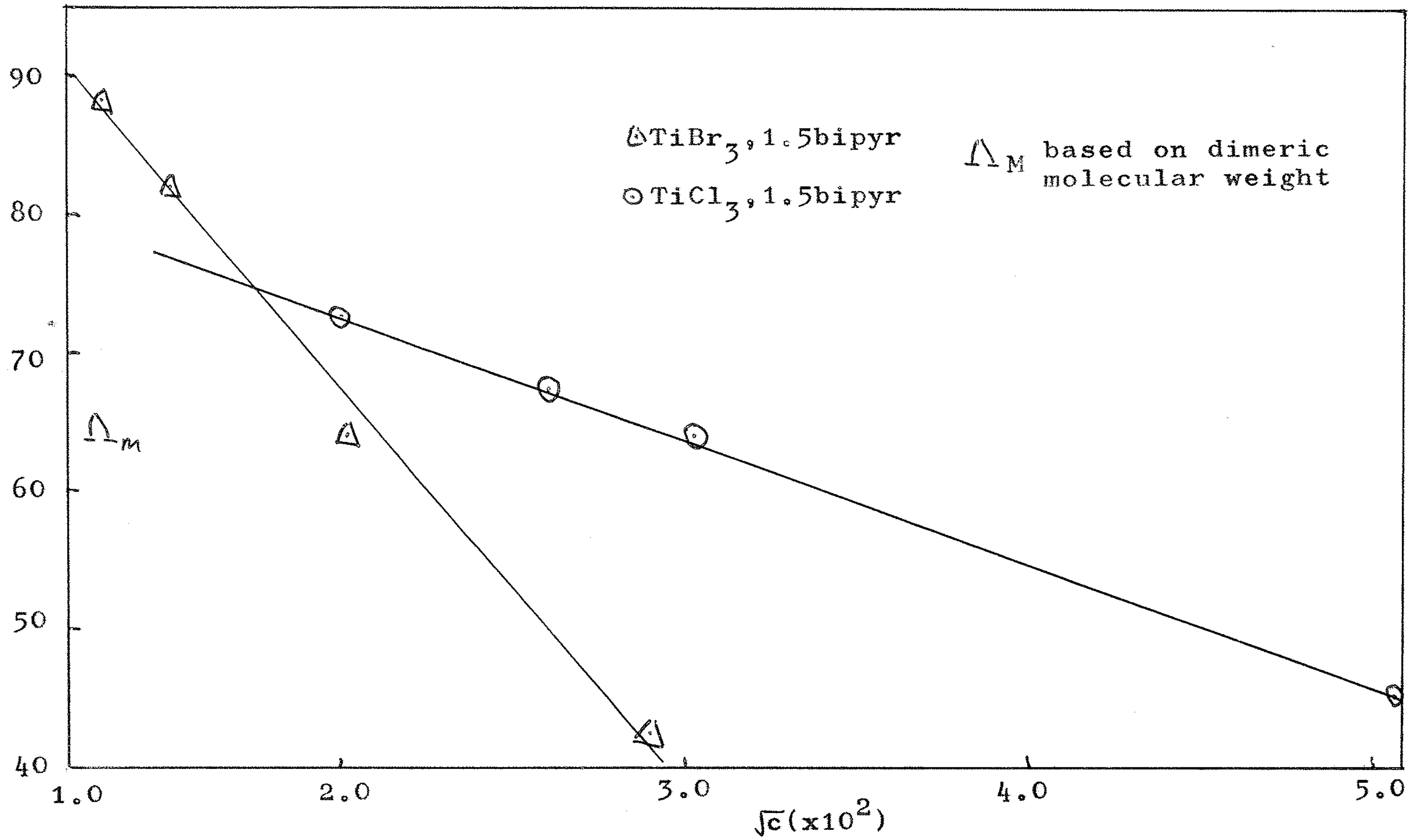

90
80
70
60
50
40
Λ_M
1.0
2.0
3.0
4.0
5.0
$\sqrt{c}(x10^2)$
△ $TiBr_3$,1.5bipyr
⊙ $TiCl_3$,1.5bipyr
Λ_M based on dimeric molecular weight

Fig. 4.2.

observed for the tribromide compound but that for the trichloride one there is some evidence for an absorption around 13,500 cm^{-1} which might be the low energy component of the transition for the $[TiCl_4,bipyr]^-$ ion.

Low infrared spectra should reveal six active titanium-halogen stretches for the two ions, $[TiX_2,2bipyr]^+$ and $[TiX_4,bipyr]^-$ if the former has the cis structure. Unfortunately the spectra are too poorly resolved to confirm or disprove the structures.

Walton[103] found that the reflectance spectra of $TiCl_3$,bipyr and $2TiCl_3$,3bipyr were identical and the same was found for the bromide compounds. To confirm that $2TiBr_3$,3bipyr was not a mixture of $TiBr_3$,bipyr and excess bipyridyl or another compound X-ray powder photographs were taken and although no attempt was made to index them the spacings and intensities were completely different.

The electronic spectra all show a peak between 18,000 and 19,000 $cm.^{-1}$ and this is assigned to a $Ti(d) \rightarrow bipyr(\pi^*)$ transition. Bands around 25,000 $cm.^{-1}$ in the complexes $TiCl_3$,3pyr, $TiCl_3$,3γpic and $TiCl_3$,2αpic have been assigned to a $Ti(d) \rightarrow lig(\pi^*)$ transfer.[20] This transition would be expected at lower energy in the bipyridyl complexes. The internal bipyridyl $\pi \rightarrow \pi^*$ transitions at 35,000 $cm.^{-1}$ moves to ~33,000 $cm.^{-1}$ in the compounds and it has been suggested[107] that this shift is due to the bipyridyl molecule isomerising from the trans configuration (in the free ligand) to the cis (in the complex) but the energies of the bipyridyl π orbitals will also be affected, probably significantly, on formation of the complex.

The magnetic moments for $TiBr_3$,bipyr and $TiBr_3$,2bipyr,S are appreciably higher than those normally found for titanium(III) but unfortunately the variable temperature balance was not available at the time of preparation although these compounds would merit further study.

In this chapter the preparation and properties of dimethyl sulphide and tetrahydrothiophene complexes of titanium(III) chloride, bromide, and iodide are described. Initial reports of the trichloride complexes have been made,[97,108] but only a limited number of measurements were carried out and in the case of the reaction with tetrahydrothiophene it seems that a different compound was obtained. The magnetic properties of the titanium(III) chloride complexes are of particular interest as they exhibit strong antiferromagnetic exchange.

1. Reaction of titanium(III) chloride with dimethyl sulphide

Titanium(III) chloride (~1g) was refluxed with excess dimethyl sulphide (~15mls) for two days and a green solution was obtained. Filtration and evaporation of the solvent gave a brown solid which was pumped for several hours to remove uncoordinated dimethyl sulphide.

	Ti%	Cl%
Found	17.0	37.8
$TiCl_3,2S(CH_3)_2$ requires	17.3	38.1

The magnetic properties of this and most of the subsequent compounds were measured between 80 and 300°k and are

CHAPTER V

SULPHUR COMPLEXES OF THE TITANIUM(III) HALIDES

given in table 5.1. The infrared spectrum (4,000 - 400 cm.$^{-1}$) showed that all the ligand was coordinated; essential details for all the compounds are given in table 5.2. The low infrared spectrum (400 - 200 cm.$^{-1}$) was also measured for a nujol mull (table 5,3). Electronic spectra for all the compounds, both in ligand solution and reflectance are given in table 5.4.

2. Reaction of titanium(III) chloride with tetrahydrothiophene

Once again titanium(III) chloride was treated with a large excess of ligand under reflux and gave a green solution and a purple solid. The green solution yielded a grey solid.

	Ti%	Cl%	C%	H%
Found	14.1	30.9	28.8	4.5
$TiCl_3,2C_4H_8S$ requires	14.5	32.1	29.1	4.8

The purple solid was also analysed

	Ti%	Cl%
Found	21.8	48.1
$TiCl_3,C_4H_8S$ requires	19.8	43.8

$Ti:Cl:C_4H_8S$ = 1:2.98:0.75 (C_4H_8S by difference)

Baker[108] reported that reaction of titanium(III) chloride and tetrahydrothiophene gave an insoluble purple solid with the stoichiometry : $TiCl_3,2C_4H_8S$. It is possible that the purple solid obtained in the present work was a mixture of unreacted titanium(III) chloride and the compound reported by Baker.

The usual measurements on the grey solid were made and results are listed in tables 1 - 4. The low infrared spectrum was measured both for a nujol mull and in ligand solution (fig.5.1).

3. Reaction of titanium(III) bromide with dimethyl sulphide.

Titanium(III) bromide (~1g) was allowed to react with dimethyl sulphide in a mole ratio ~1:4 using benzene (~20 mls) as a diluent. Reaction for eight hours gave a brown solution which was filtered off and the solvent evaporated, the solute was then pumped at room temperature for three hours.

	Ti%	Br%	C%	H%
Found	11.4	59.4	10.7	2.8
$TiBr_3,2S(CH_3)_2$ requires	11.6	58.3	11.6	2.9

The analyses on products from several runs indicated that the compound $TiBr_3,2S(CH_3)_2$ gradually lost dimethyl sulphide on prolonged pumping, even at room temperature. A small amount of an insoluble brown solid was filtered off during the preparation. This was not investigated further but was thought to be a mixture of unreacted halide and $TiBr_3,2S(CH_3)_2$.

4. Reaction of titanium(III) bromide with tetrahydrothiophene

Reaction of titanium(III) bromide with tetrahydrothiophene in a mole ratio ~1:4 using benzene as diluent gave a brown solution and an insoluble red-brown solid after eight hours. Both the soluble and insoluble solids were collected and pumped for twelve hours prior to analysis. The compound isolated as 'insoluble' did in fact dissolve in neat tetrahydrothiophene.

		Ti%	Br%	C%	H%
Found	Soluble	10.1	52.4	20.4	3.5
	Insoluble	10.1	51.8		
$TiBr_3,2C_4H_8S$ requires		10.3	51.7	20.7	3.4

The normal measurements were carried out on the soluble material but magnetic measurements were also made on the insoluble product; all five preparative runs gave abnormally high magnetic susceptibilities for this material (table 5.5).

Table 5.5 Magnetic measurements for 'insoluble' $TiBr_3,2C_4H_8S$

Approx. field (gauss)		2300	2700	3200	3600	4000
Run No.1	χ'_m (cgsux10^6)					2101
	μ_{eff} (B.M.)					2.21
No.2	χ'_m					2252
	μ_{eff}					2.30
No.3	χ'_m	2264	2148	2101	2002	1965
	μ_{eff}	2.30	2.24	2.22	2.17	2.14
No.4	χ'_m	1538				1411
	μ_{eff}	1.90				1.82
No.5	χ'_m	1554				1392
	μ_{eff}	1.91				1.81

5. Reaction of titanium(III) iodide with dimethyl sulphide

Titanium(III) iodide was allowed to react with dimethyl sulphide in a mole ratio ~1:4 using benzene as the solvent. Four hours' reaction gave a brown solution which after filtration and evaporation of the solvent yielded a black solid. This was pumped at room temperature for three hours.

	Ti%	I%	C%	H%
Found	8.7	67.8	8.1	1.9
$TiI_3,2S(CH_3)_2$ requires	8.7	68.9	8.7	2.2

A small amount of insoluble material was discarded.

6. Reaction of titanium(III) iodide with tetrahydrothiophene

When titanium(III) iodide was allowed to react with tetrahydrothiophene in a mole ratio ~1:4 using benzene as diluent a brown solution and black insoluble solid were obtained. Both soluble and insoluble solids were worked up.

		Ti%	I%
Found	Soluble	7.9	61.3
	Insoluble	7.8	63.9
$TiI_3,2C_4H_8S$ requires		7.9	62.0

The magnetic and spectral results for the soluble product are given in the usual tables 1 - 4. A magnetic susceptibility measurement on the insoluble compound gave an abnormally high value: μ_{eff} = 2.73 B.M.

χ_m' = 3162 (cgsu x10^6).

Prior to this preparation it was found that reaction of titanium(III) iodide and tetrahydrothiophene for two weeks gave a green solid, which was completely insoluble in the ligand, and a tan coloured solution. The analyses corresponded roughly to the 1:3 adduct.

	Ti%	I%	C%	H%
Found	6.6	54.3	22.8	4.4
$TiI_3,3C_4H_8S$ requires	6.9	55.0	20.8	3.5

The solid hydrolysed in dilute sulphuric acid to give a purple solution indicating that it contained titanium(III) but the magnetic moment at room temperature was only 0.64 B.M. It was not studied further.

Table 5.1

$TiCl_3,2C_4H_8S$

T°k	χ'_m (x10^{6}cgsu)	μ_{eff} (B.M.)	T°k	χ'_m (10^{6}cgsu)	μ_{eff} (B.M.)
313.2	548	1.17	213.2	363	0.79
298.2	541	1.13	193.2	333	0.71
293.2	536	1.12	173.2	287	0.63
283.2	528	1.09	153.2	263	0.57
273.2	509	1.05	133.2	265	0.53
253.2	468	0.97	113.2	241	0.47
233.2	428	0.89	93.2	234	0.42

$TiCl_3,2S(CH_3)_2$

T°k	χ'_m (x10^{6}cgsu)	μ_{eff} (B.M.)	T°k	χ'_m (10^{6}cgsu)	μ_{eff} (B.M.)
293.1	475	1.05	213.2	275	0.68
283.2	475	1.04	183.2	256	0.61
273.2	398	0.93	153.2	195	0.49
263.2	363	0.87	123.2	180	0.42
243.2	324	0.79	93.2	191	0.38

$TiBr_3.2C_4H_8S$

Soluble

$T^o k$	χ'_m (10^6 cgsu)	μ_{eff} (B.M.)	$T^o k$	χ'_m (10^6 cgsu)	μ_{eff} (B.M.)
313.2	1215	1.74	193.2	1821	1.68
303.2	1234	1.73	173.2	1973	1.65
293.2	1267	1.72	153.2	2204	1.64
283.2	1313	1.72	133.2	2517	1.64
273.2	1351	1.72	113.2	2927	1.63
253.2	1458	1.72	93.2	3521	1.62
233.2	1550	1.70	80.2	4018	1.60
213.2	1674	1.69			

$TiBr_3.2S(CH_3)_2$

$T^o K$	χ'_m (10^6 cgsu)	μ_{eff} (B.M.)	$T^o k$	χ'_m (10^6 cgsu)	μ_{eff} (B.M.)
298.2	1174	1.67	193.2	1679	1.61
291.2	1190	1.67	173.2	1844	1.60
283.2	1226	1.67	153.2	2016	1.57
273.2	1261	1.66	133.2	2254	1.55
253.2	1336	1.65	113.2	2551	1.52
233.2	1448	1.64	93.2	3059	1.51
213.2	1556	1.63	80.2	3325	1.46

$TiI_3,2S(CH_3)_2$					
$T^\circ k$	χ'_m ($x10^6$cgsu)	μ_{eff} (B.M.)	$T^\circ k$	χ'_m ($x10^6$cgsu)	μ_{eff} (B.M.)
298.2	1184	1.68	173.2	1800	1.58
283.2	1236	1.67	153.2	1977	1.56
273.2	1273	1.67	133.2	2195	1.53
253.2	1363	1.66	113.2	2454	1.49
233.2	1454	1.65	93.2	2776	1.44
213.2	1545	1.62	79.2	3033	1.39
193.2	1668	1.60			

Table 5.2 Infrared Spectra

Dimethyl Sulphide Complexes

Assign.[6]	Symm.	Liq.$(CH_3)_2S$	$TiCl_3 2L$	$TiBr_3 2L$	$TiI_3 2L$
C—S st	A_1	692m	688m	685m	665m
"	B_1	742w	725m	722m	730w
CH_3rock	B_2	972ms	983s	985s	978s
"	A_1	1027ms	1035s	1040s	1034s

Tetrahydrothiophene Complexes ($1300-400 cm.^{-1}$)

Free Ligand	$TiCl_3,2C_4H_8S$	$TiBr_3,2C_4H_8S$	$TiI_3,2C_4H_8S$	Average Shift
	1273w	1275w	1270w	
1259s	1258s	1260s	1258s	0
1215w	1215w	1213w	1210w	-2
1195m	1197w	1198w	1195w	+2
1134m	1135m	1132m	1130m	-2
1062w	1072m	1078w	1075w	+12
1035w	1035w	Several weak peaks, position uncertain		
958m	957m	961m	958m	+1
882m	882m	882m		
		878m	878m	
819m	810m	812m	807m	-10
	722mbr	734w	730w	
		722w	720w	
685m	670s	672s	665s	-16
515m	515m	515m	510m	
	468m	475m	470m	

Table 5.3

Low Infrared Spectra (500-200 cm.$^{-1}$)					
$TiCl_3,2(CH_3)_2S$	Solid	390sbr	323m		280br
$TiCl_3,2C_4H_8S$	Solid	390s	324m		290m
C_4H_8S	Soln.	373s	335w		
$TiBr_3,2(CH_3)_2S$	Solid	356vw	307s	272m	247w
$(CH_3)_2S$	Soln.		303s	275m	248w
$TiBr_3,2C_4H_8S$	Solid		304s	268s	250w
C_4H_8S	Soln.		301s	273m	253w
$TiI_3,2(CH_3)_2S$	Solid		292w	262s	244s
$(CH_3)_2S$	Soln.		288s	257m	
$TiI_3,2C_4H_8S$	Solid			257sh	237s
C_4H_8S	Soln.			244sbr	

Table 5.4 Electronic-Spectra

$TiCl_3,2C_4H_8S$	Soln.lig.	11,760 15,330 23,260wsh
	Refl.	12,200 17,250 25,800 30,200sh 37,200
$TiCl_3,2(CH_3)_2S$	Soln.lig.	12,050 15,600(ϵ=25) 23,000
	Refl.	11,400sh 17,300 25,000br 37,500
$TiBr_3,2C_4H_8S$	Soln.lig.	11,630sh 13,850(ϵ=13) 23,260 29,400
	Refl.	12,120sh 18,870
$TiBr_3,2(CH_3)_2S$	Soln.lig.	11,400sh 14,300(ϵ=12) 20,000wsh 25,000sh
	Refl.	11,800wsh 19,100 25,600 37,500 45,300
$TiI_3,2C_4H_8S$	Soln.lig.	12,560(ϵ=13) 15,750sh 20,700sh 24,390
	Refl.	10,810wsh 15,380 22,220
$TiI_3,2(CH_3)_2S$	Soln.lig.	14,900wsh 19,000sh 25,400sh 29,000sh
	Refl.	15,400br 21,200sh

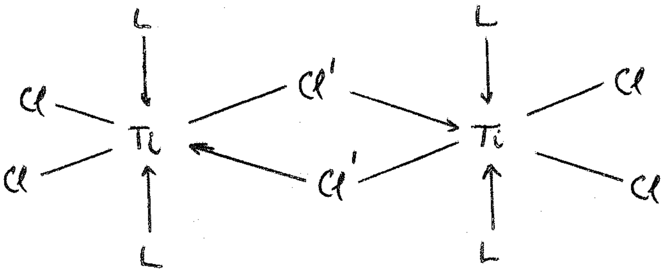
Results and Discussion

Sulphur complexes of the titanium(III) halides are not well known, the only ones reported are $TiCl_3,2S(CH_3)_2$,[97] $TiCl_3,2C_4H_8S$[108] (but neither are fully characterised) and the thioxan adducts $TiCl_3,C_4H_8OS$; $TiCl_3,2C_4H_8OS$; and $TiBr_3,2C_4H_8OS$.[49] Sulphur bonding was inferred in all the thioxan complexes although the 1:1 compound was thought to be a polymer involving bridging thioxan and is considered to be weakly antiferromagnetic.[109]

The presence of coordinated sulphur in thioethers is less easy to determine from the infrared spectrum than coordinated oxygen in ethers as the C-S-C stretching frequencies are rather weak and the shifts on coordination are small compared to the changes for ethereal C-O-C stretching frequencies. The infrared spectrum of dimethyl sulphide has, however, been assigned[110] and shifts of $\sim$15 cm.$^{-1}$ to lower frequency are observed for the A_1 and B_1 C-S stretches in the complexes. The CH_3 rocking vibrations B_2 and A_1 rise $\sim$ 10 cm.$^{-1}$ on coordination and these results (table 5.2) agree with those of Lewis et al. on the analogous gallium and aluminium trichloride compounds.[111] The infrared spectrum of tetrahydrothiophene does not appear to have been assigned but Lewis suggests that the 685 cm.$^{-1}$ peak in the ligand is a ring stretch involving sulphur which on coordination shifts to ~ 670 cm.$^{-1}$;[111] we also observe this shift and table 5.2 shows that several other bands also move ~ 10 cm.$^{-1}$ on coordination. Peaks characteristic of uncoordinated ligands were not observed indicating that both molecules of ligand are bonded to the titanium.

The molecular geometry of these compounds might reasonably be either trigonal bipyramidal or octahedral for the former has been shown to be the structure for both $TiBr_3,2N(CH_3)_3$[54] and $CrCl_3,2N(CH_3)_3$[112] while the latter is common for titanium(III). Dimethyl sulphide, like trimethylamine, is a bulky ligand which could cause five coordination and indeed the solution spectra (electronic and low infrared) of the vanadium compounds $VCl_3,2S(CH_3)_2$ and $VBr_3,2S(CH_3)_2$ in non-polar solvents show that they are trigonal bipyramidal.[92] Unfortunately the titanium compounds are very nearly insoluble in non-polar solvents such as benzene or dichloromethane. The slight solubility of $TiCl_3,2C_4H_8S$ (estimated at ~0.05% w/w) could be accounted for by the presence of a trace of free ligand resulting from slight decomposition. As the solubility was much too low for molecular weight studies, less direct methods for deducing stereochemistry had to be used. Solubility in non-polar solvents does not appear to be a criterion of structure since $TiX_3,2N(CH_3)_3$ (where X = CI or Br) are insoluble while $VX_3,2N(CH_3)_3$ are very soluble although it seems that all are trigonal bipyramidal.[27]

Far-infrared spectra (table 5.3) should enable one to distinguish between simple octahedral or five coordinate structures as the frequency of the metal-halogen stretch normally increases when the coordination number decreases.[53] Both $TiCl_3,2S(CH_3)_2$ and $TiCl_3,2C_4H_8S$ have strong titanium-chlorine vibrations at ∾ 390 $cm.^{-1}$ which is ∾ 15 $cm.^{-1}$ higher than usually found in titanium(III) octahedral complexes and initially suggested a five coordinate structure. Complications arise, however, as one of the most probable structures is



which has D_{2h} symmetry. Ignoring out of plane deformations the infrared active B_{2u} and B_{3u} modes will be compounded of both Ti-Cl and Ti-Cl' vibrations in addition to several in plane bending modes. The resulting 'terminal' titanium-chlorine 'stretches' may be so impure as to be meaningless for empirical assignments of stereochemistry. Regardless of whether the structure is five coordinate or bridged octahedral it may well change to a monomeric octahedral $TiCl_3,3L$ species in ligand solution and the far-infrared supports this change (fig. 5.1) for two peaks are then observed in the metal-halogen region, consistent with the octahedral cis isomer. The low infrared spectra of the bromide complexes are similar for both the solid and ligand solution (fig. 5.2). The highest energy titanium-bromine vibration occurs at $\sim$ 300 cm.$^{-1}$ while the five coordinate $TiBr_3,2N(CH_3)_3$ has a strong peak at 323 cm.$^{-1}$ which suggests that these compounds are not trigonal bipyramidal. The analogous vanadium compounds $VBr_3,2S(CH_3)_2$ and $VBr_3,2C_4H_8S$ are considered to be bridged octahedra in the solid and have their highest energy V-Br stretch at $\sim$ 300 cm.$^{-1}$. When dissolved in benzene this peak moves to $\sim$ 340 cm.$^{-1}$ and the molecular weights show that they are five coordinate.[92] The iodide spectra are recorded but it is not known which of the peaks observed are due to Ti-I stretching vibrations because a C-S-C deformation band is known to occur at 282 cm.$^{-1}$ in free dimethyl sulphide.[110]

The magnetic susceptibilities of the two titanium(III) chloride compounds exhibit strong antiferromagnetism

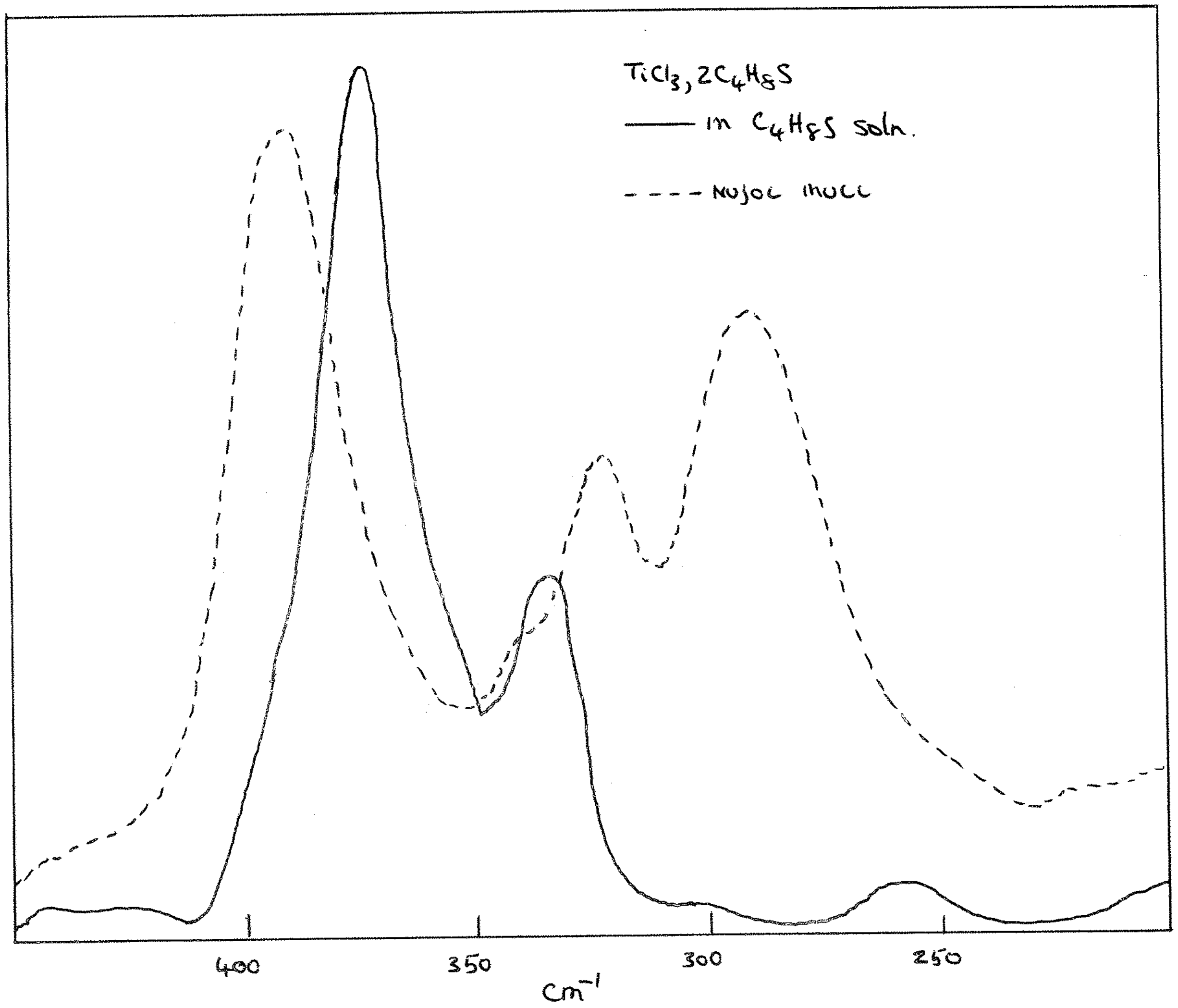


Fig 5.1.

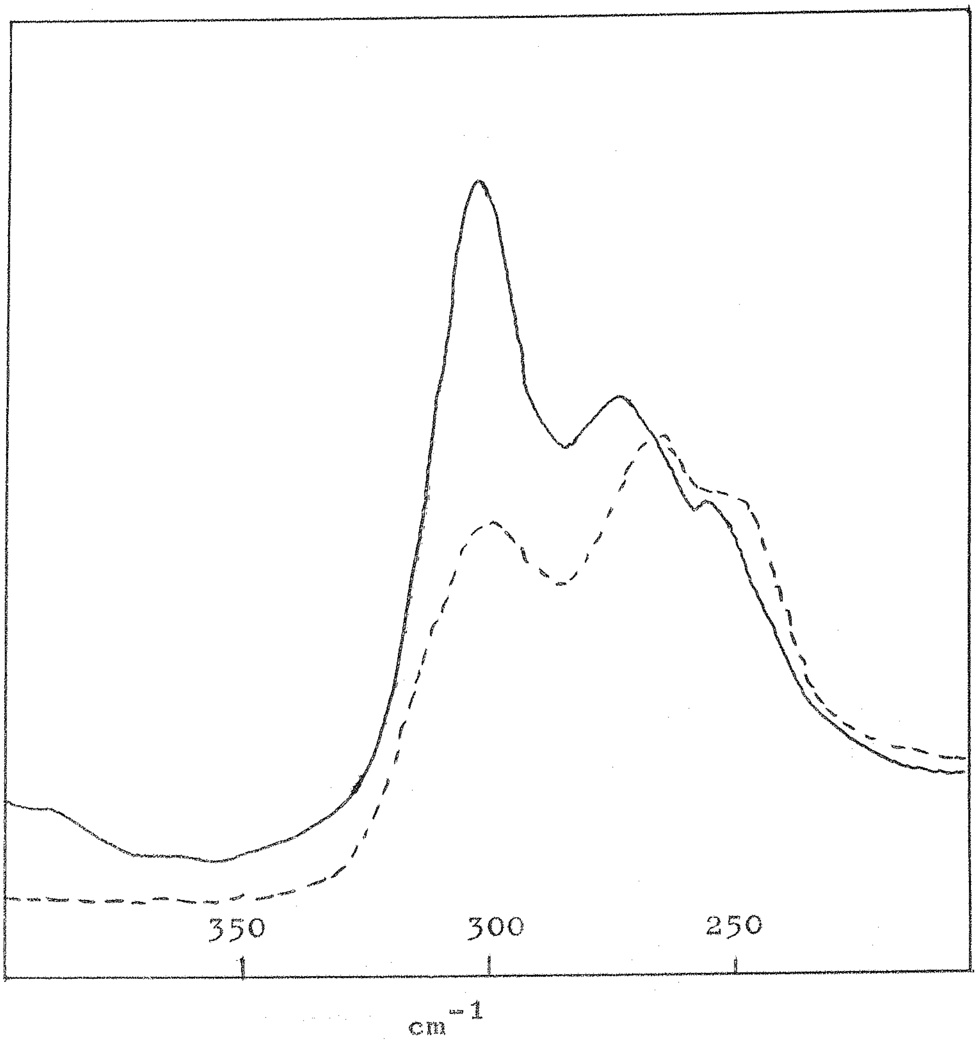


Fig. 5.2

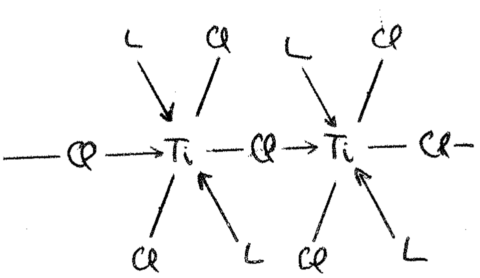
TiBr$_3$,2C$_4$H$_8$S
—— in C$_4$H$_8$S solution

---- Nujol mull

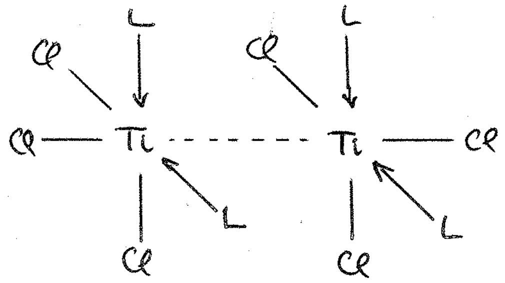
(fig. 5.3). The room temperature moments are well below the spin only value and the susceptibilities fall with decreasing temperature. Néel temperatures were estimated to be ~320°K but could not be found accurately owing to the thermal instability of the compounds; Baker reports that at 60°C the following disproportionation occurs:-[108]

$$TiCl_3,2S(CH_3)_2 \xrightarrow{60^{o}C} TiCl_4,2S(CH_3)_2 + Ti(II)?$$

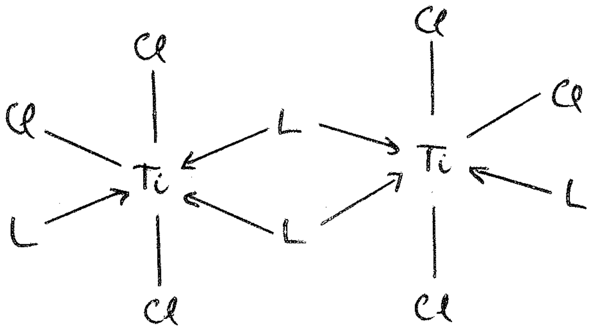
In view of the exchange, possible structures are (I) or



(II)



(III)



(IV)

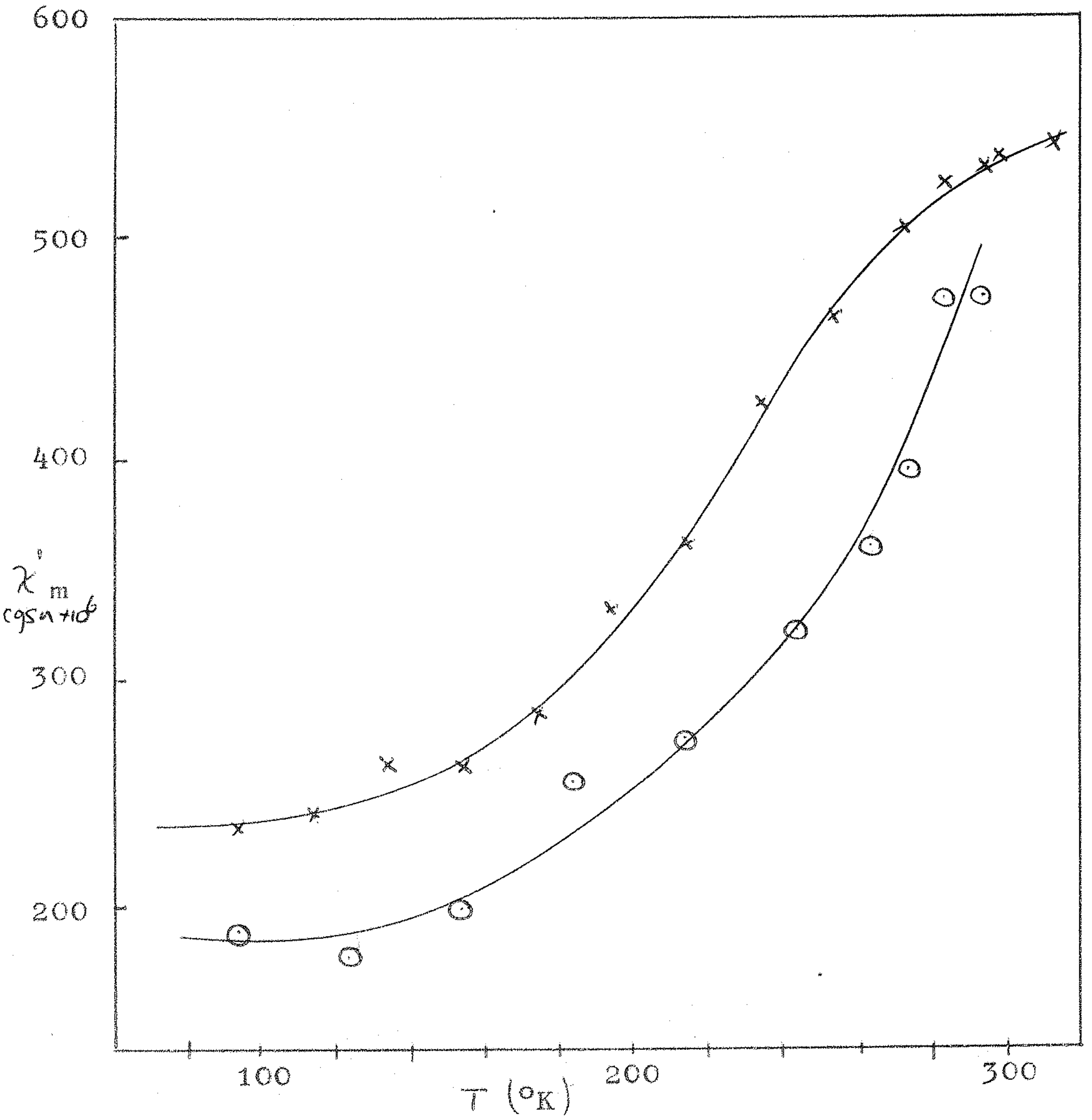


Fig. 5.3

x $TiCl_3,2C_4H_8S$

⊙ $TiCl_3,2S(CH_3)_2$

or any of their isomers. If (IV) were the structure for the chloride compounds it would also be reasonable to expect it for the bromide and iodide ones and as the bridge would remain essentially unchanged similar magnetic properties would be expected. These are not found and structure (IV) is not discussed further. The slight solubility in non-polar solvents is some evidence against (II). It is also doubtful if it would explain the magnitude of the exchange as the Néel temperature of these compounds is even higher than in titanium(III) chloride itself.[43] Structure(III) is intended to imply direct metal-metal interaction which might arise either from formation of a genuine metal-metal bond or from distortion of a five coordinate structure by crystal packing. A choice between (I) or (III) does not seem to be possible on the available evidence for both explain the far-infrared. Magnetic exchange in either of them might occur via metal-metal interaction but in (I) there is also the possibility of a super-exchange process. It is interesting that the vanadium compounds, $VCl_3,2S(CH_3)_2$ and $VCl_3,2C_4H_8S$, which as mentioned earlier are believed to be dimeric in the solid, exhibit little if any antiferromagnetism and obey the Curie-Weiss law.[92] Indeed the same trend is found in the trihalides themselves, titanium(III) chloride being antiferromagnetic with abnormal behaviour at low temperatures while vanadium(III) chloride has a room temperature moment of 2.7 B.M. which is close to the expected value.[67]

The bromide and iodide compounds obey the Curie-Weiss law (fig. 5.4) with θ in the range 30-60° Figgis has listed values of μ_{eff} as functions of the parameters T, λ, k and v for the $^2T_{2g}$ ground term under simultaneous perturbation by spin-orbit coupling and an axial component in the ligand field.[84] Δ is the separation between the orbital singlet and doublet levels resulting from the splitting of the ground term by the axial component of the ligand field and is positive when the singlet level lies lowest. T and λ are the temperature ($^\circ$k) and the spin-orbit coupling constant respectively. v is defined as $v = \frac{\Delta}{\lambda}$; k is the orbital reduction factor. Using the magnetic data for $TiBr_3,2S(CH_3)_2$ and $TiI_3,2S(CH_3)_2$ fits with theory could not be obtained. The 'best' fit required λ to be appreciably greater than the free ion value. Qualitatively the inability to obtain a good fit was due to the room temperature moment being too low for the considerable fall of μ_{eff} with temperature. Some residual antiferromagnetism would account for this behaviour and it therefore seems that these systems are still not magnetically dilute. The soluble product $TiBr_3,2C_4H_8S$ has more normal magnetic

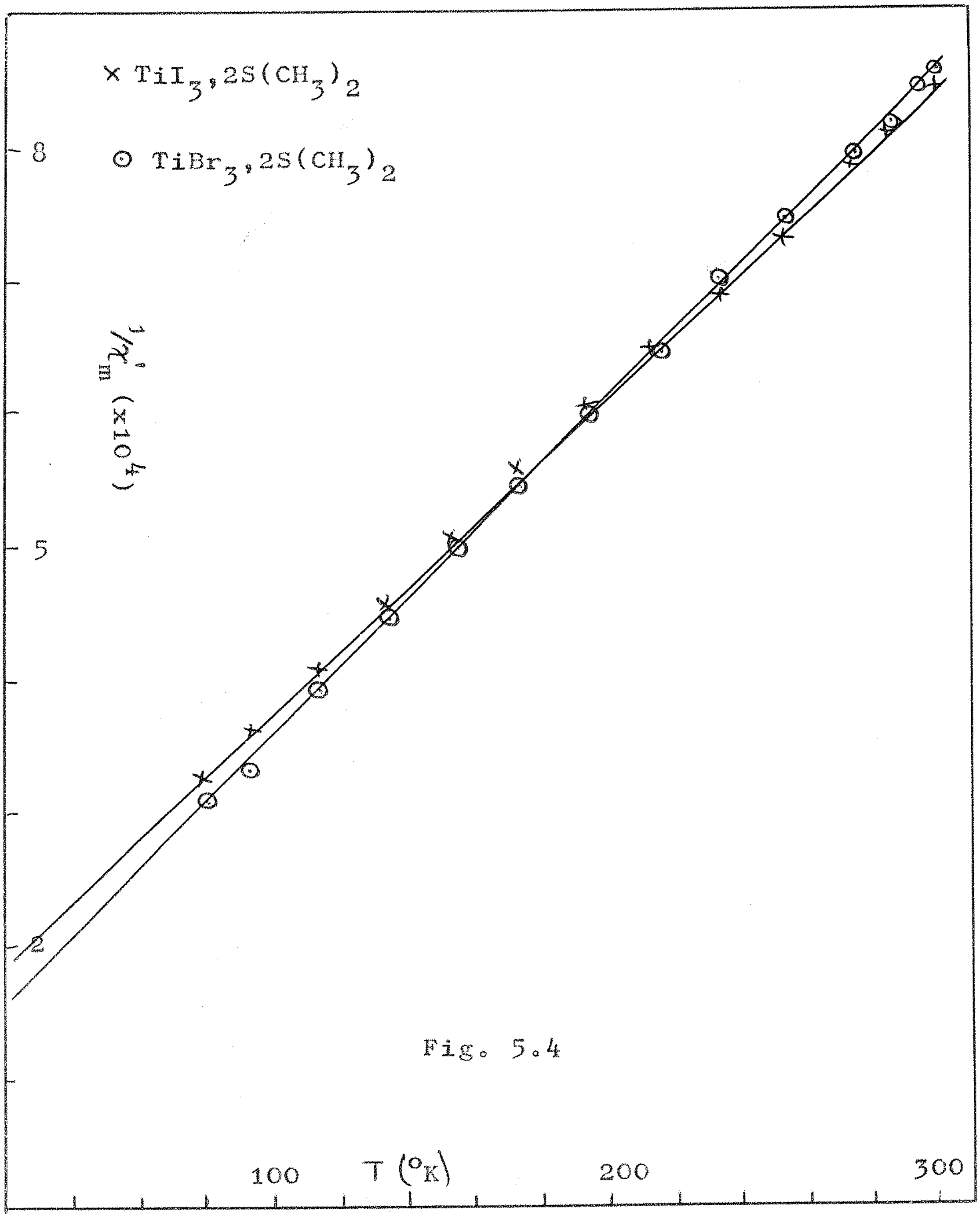


Fig. 5.4

behaviour and fits were obtained for the following parameters; $k = 0.8$, $v = +6$, $\lambda = 160$ cm.$^{-1}$ and $\Delta = 960$ cm.$^{-1}$ or $k = 0.7$, $V = +5$, $\lambda = 130$ cm.$^{-1}$, $\Delta = 650$ cm.$^{-1}$. (fig. 5.5). It is not suggested that these fits are the only possibilities since for magnetic moments which do not change appreciably with temperature unique fits are rarely obtained.[138]

The marked decrease in exchange on proceeding from the chloride to the bromide and iodide complexes is consistent with any structure involving halogen bridging regardless of the exchange mechanism. In view of the low infrared evidence structures (I) or (IV) are suggested.

The high, field-dependent moments obtained for the 'insoluble' $TiBr_3,2C_4H_8S$ are most readily explained by the presence of traces of a ferromagnetic impurity but both the titanium and aluminium metals were pure and the titanium(III) bromide prepared from them had a normal moment. It is possible that during the reaction a ferromagnetic substance was formed in varying amounts thus accounting for the lack of reproducibility of the susceptibilities. One sample of 'insoluble' $TiI_3,2C_4H_8S$ also had a high moment.

The compounds are all fairly soluble in the ligands and their visible spectra have been measured (table 5.4,

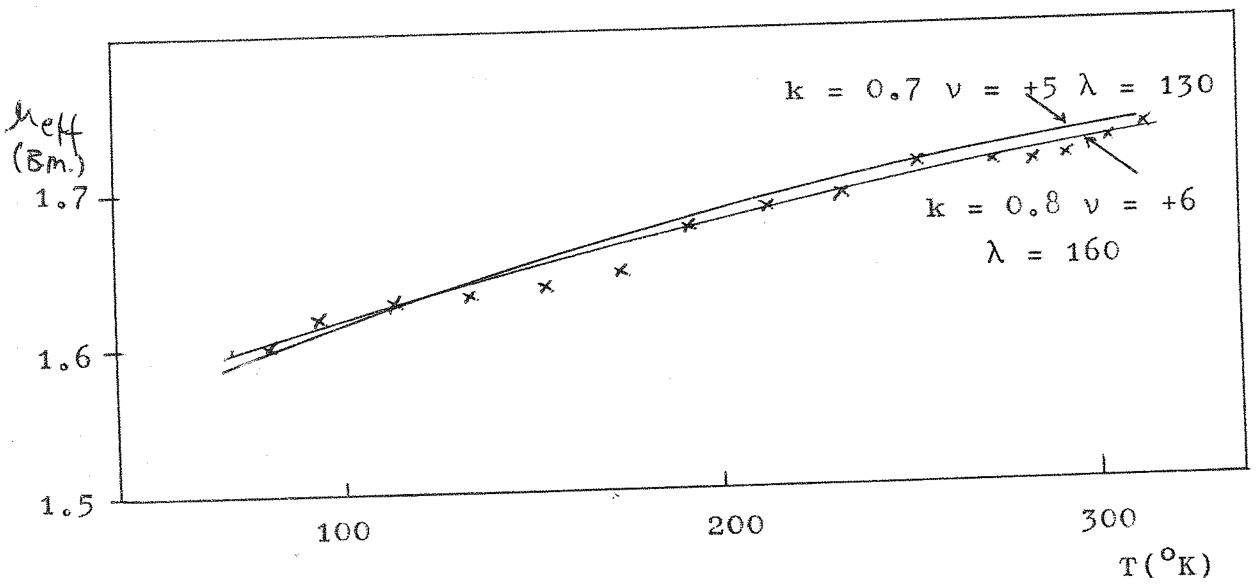


Fig. 5.5.

$TiBr_3,2C_4H_8S$

fig. 5.6). The chloride and bromide complexes both show two bands with $\epsilon < 50$ separated by $\sim 3,500$ cm.$^{-1}$. A single peak was observed in the visible region for $TiI_3,2C_4H_8S$ ($\epsilon = 13$) but $TiI_3,2S(CH_3)_2$ only showed a weak shoulder at rather higher energy which might be due to charge transfer. The peaks in the chloride and bromide compounds may be assigned to the transitions $^2B_{2g} \longrightarrow {}^2B_{1g}$ and $^2B_{2g} \longrightarrow {}^2A_{1g}$ assuming that a distorted $TiX_3,3L$ species is present in solution. The lower energy peaks in the bromide are consistent with the smaller values of Dq Br^- compared to Dq Cl^-. The peak observed at 12,560 cm.$^{-1}$ in $TiI_3,2C_4H_8S$ is assigned to $^2B_{2g} \longrightarrow {}^2B_{1g}$ and is presumably obscured by charge transfer in $TiI_3,2S(CH_3)_2$.

The solution spectra are significantly different from the solid (reflectance) spectra which confirms that a structural change occurs. In contrast to the low infrared the large splitting of the two bands suggests that the trans isomer is present in solution. The reflectance spectra of the chloride complexes show a peak and a shoulder, $\sim 17,500$ and 12,000 cm.$^{-1}$. If structure (I) is correct these can be assigned to the same d-d transitions as in solution but are split further and shifted to slightly higher energy. In the absence of more detailed structural information it is not clear

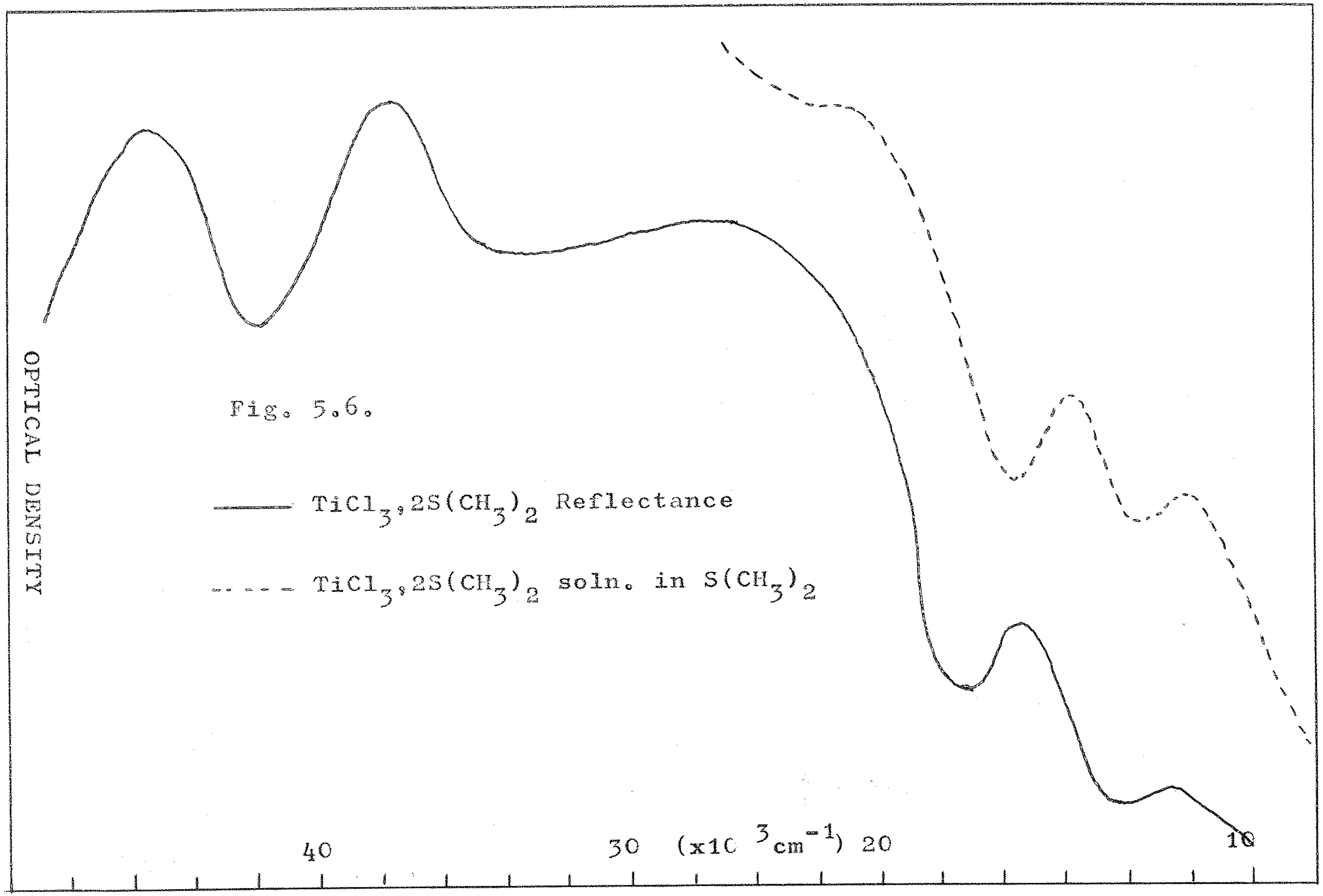


Fig. 5.6.

OPTICAL DENSITY
TiCl$_3$,2S(CH$_3$)$_2$ Reflectance
TiCl$_3$,2S(CH$_3$)$_2$ soln. in S(CH$_3$)$_2$
40
30
(x10^{3}cm^{-1})
20
10

where (III) would be expected to have transitions. The reflectance spectra of the bromide compounds show a shoulder ~ 12,000 cm.$^{-1}$ which may indicate that the E_g state splitting is small or simply that the other component is not observed. The next band at higher energy does not occur until ~ 19,000 cm.$^{-1}$ and is much more intense, probably being a Br→Ti charge transfer transition. The positions of the d-d peaks in the iodide spectra are obscured by charge transfer bands.

CHAPTER VI

THE ULTRAVIOLET SPECTRA OF TITANIUM(III) AND (IV) COMPOUNDS

Although the d-d spectra of the titanium(III) halides and their complexes have received a good deal of attention, little work has been directed towards the elucidation of their charge transfer spectra, or even those of titanium(IV) compounds. Fowles et al. have reported a few spectra and made tentative assignments but owing to the paucity of experimental data, correlations with other compounds were not possible.[48,115] In this chapter the ultraviolet spectra of a large number of previously prepared compounds are reported and discussed.

Sources of compounds

1. Tribromotris(tetrahydrofuran)titanium(III) was prepared by the reaction of titanium(III) bromide and tetrahydrofuran. A slightly soluble green solid was obtained.

	Ti%	Br%	C%	H%
Found	9.06	46.9	27.6	3.63
$TiBr_3,3C_4H_8O$ requires	9.52	47.6	28.6	4.76

The magnetic moment at 18°C was 1.75 B.M., which confirms the oxidation state.

2. Tribromotris(dioxan)titanium(III) was prepared by the reaction of titanium(III) bromide and 1:4-dioxan.

A pale green solid was obtained which was slightly soluble in 1:4-dioxan.

	Ti%	Br%
Found	9.1	46.3
$TiBr_3,3C_4H_8O_2$ requires	8.7	43.4

The sources of the remaining compounds are listed in table 6.1.

Table 6.1

$(PyH)_3TiCl_6$[a]

$TiI_3,3C_4H_8O_2$[a]

$TiI_3,3\gamma pic$[a]

$TiCl_3,2C_4H_8S$[a]

$TiI_3,3C_4H_8O$[a]

$TiBr_3,1{\cdot}5C_4H_{10}O_2$[a]

$TiCl_3,2S(CH_3)_2$[a]

$TiI_3,3pyr$[a]

$TiBr_3,2S(CH_3)_2$[a]

$TiI_3,2\alpha pic$[a]

$TiCl_3,3\gamma pic$[b]

$TiCl_3,2\alpha pic$[b]

$TiCl_3,3pyr$[b]

$TiCl_3,2N(CH_3)_3$[b]

$TiCl_3,3C_4H_8O_2$[c]

$TiCl_3,1{\cdot}5C_4H_{10}O_2$[c]

$TiCl_4,C_4H_8O_2$[d]

$TiBr_4,C_4H_8O_2$[d]

K_2TiCl_6[e]

$TiCl_4,2CH_3CN$[f]

$TiCl_4,bipyr$[f]

$TiBr_4,2CH_3CN$[f]

$TiBr_4,bipyr$[f]

$TiBr_3,3\gamma pic$[f]

$[(C_2H_5)_2NH_2]_2TiCl_6$[f]

$[(C_2H_5)_2NH_2]_2TiBr_6$[f]

$[(C_2H_5)_2NH_2]_2VCl_6$[f]

$(PyH)_3TiCl_4Br_2$[g]

$[(C_2H_5)_4N]TiCl_4$[g]

$TiBr_3,2N(CH_3)_3$[g]

$TiBr_4,C_4H_{10}O_2$[h]

K_2TiF_6[i]

a) Prepared by methods described elsewhere in this thesis.

b) Prepared by the method given in reference 20

c) " " " " " " " 47

d) " " " " " " " 26, 116

e) " " " " " " " 117

f) Kindly lent by Dr. R.A. Walton

g) " " " Dr. B.J. Russ

h) " " " Mr. P.C. Crouch

i) Supplied by C.A.F. Kahlbaum, Berlin

Table 6.2

Electronic absorption spectra of titanium(III) bromide and iodide compounds

Complex	Medium	Absorption maxima (47-18kK)				
$TiBr_3,3CH_3CN$*	Soln. CH_3CN		38.1	33.0	29.0	
$TiBr_3,3C_4H_8O_2$	Soln. $C_4H_8O_2$	40.5		34.4	29.9	
$TiBr_3,3C_4H_8O$	Soln. C_4H_8O				29.8	
$TiBr_3,1.5C_4H_{10}O_2$	Soln. $C_4H_{10}O_2$	41.0		34.5	29.9	
	Refl.	45.6	37.3		29.8	
$TiBr_3,3\gamma pic$	Refl.	44.4	37.6		30.2	23.6sh
$TiBr_3,3pyr$	Refl.	44.2	38.0	33.0sh	30.7	24.4
$TiBr_3,2N(CH_3)_3$	Refl.	44.8	35.6		27.7	~18.0sh
$TiBr_3,2(CH_3)_2S$	Refl.	45.3	37.5		25.6	19.1
$TiI_3,3C_4H_8O_2$	Soln. $C_4H_8O_2$		35.5	31.8	25.0	
$TiI_3,3C_4H_8O$	Refl.	45.0	38.0			~ 25.0vbr
$TiI_3,3pyr$	Refl.	45.5	37.2	30.0	24.4	20.7sh
$TiI_3,2\alpha pic$	Refl.	44.6	36.0	27.5	22.3	
$TiI_3,3\gamma pic$	Refl.	45.6	36.7	29.2	20.8	

* ref. 48

Table 6.3

Electronic absorption spectra of TiX_4,L_2 or TiX_4,B compounds

(X = Cl or Br)

Complex	Medium	Absorption maxima				(47-18kK)
$TiCl_4,2CH_3CN$	Refl.	45.2	37.2sh	34.8	28.4	
	Soln. CH_3CN^+	45.0		31.7		
$TiCl_4,C_4H_8O_2$	Refl.	45.2	37.8sh	35.0	28.2br	
	Soln. $C_4H_8O_2$	44.6		35.1	28.6	
$TiCl_4$,bipyr	Refl.	46.3	37.8sh	35.4	31.9*	26.6
$TiBr_4,2CH_3CN$	Refl.	45.7	37.1	27.8	21.4sh	18.8sh
	Soln. CH_3CN^+		36.6	25.0		
$TiBr_4,C_4H_8O_2$	Refl.	45.3	36.6	28.5	22.2	
	Soln. $C_4H_8O_2$		36.4	25.1		
$TiBr_4,C_4H_{10}O_2$	Refl.	44.8	36.6	27.0br	20.8sh	18.2sh
$TiBr_4$,bipyr	Refl.	44.7	37.2sh*	35.0	33.4sh 20.5wsh	27.0br 19.0
2:2'-bipyridyl	Refl.	45.0	37.6	32.9	31.4	

* Probably a bipyridyl absorption

\+ ref. 115.

Table 6.4

Electronic absorption spectra of halogeno salts and halides		
Complex	Medium	Absorption maxima $\varepsilon_{max} \times 10^{-3}$() (49-17kK)
K_2TiF_6	Refl.	45.2 ~37.8sh
K_2TiCl_6	Refl.	48.1 43.0sh 37.8sh 34.5 30.0 23.4
$[(C_2H_5)_2NH_2]_2$	Refl.	45.8 37.9 33.1 29.7 26.0sh
$TiCl_6$	Soln. CH_3CN*	42.5(4.4) ~38.5sh 31.8(2.2) ~29.0sh
	Soln. CH_3CN* + added Cl^-	43.5 ~ 39.0sh 36.8 33.0 ~28.2sh ~25.5sh?
Cs_2TiCl_6	12M HCl*	46.5 33.0sh,br
$[(C_2H_5)_2NH_2]_2$	Refl.	45.8 37.5 ~35.6sh 31.3 27.7 24.4sh 21.7
$TiBr_6$	Soln. CH_3CN*	44.2(9.5) 36.5(8.0) ~34.3sh? 27.0sh 25.2(5.9) ~22.0sh
$(PyH)_3TiCl_6$	Refl.	46.0 37.7 29.8 21.2sh
$(PyH)_3TiCl_4Br_2$	Refl.	46.0 37.6 ~ 29.2sh,br
$[(C_2H_5)_4N]TiCl_4$	Refl.	46.2 37.2 33.5 29.8 27.3 18.0

/cont'd....

Table 6.4 cont'd...

Complex	Medium	Absorption maxima ε_{max} x 10^{-3}() (49-17kK)
$TiCl_3$	Refl.	45.0 38.8 27.0 18.6
$TiBr_3$	Refl.	– broad absorption – 14.5
(PyH)Cl	Refl.	46.2 38.1 35.0sh,w

* Measured by Dr. B.J. Brisdon[100]

Table 6.5

Electronic absorption spectra of titanium(III) chloride complexes

Complex	Medium	Absorption maxima			(47-20kK)
$TiCl_3,3CH_3CN$	Soln. CH_3CN*	43.5	35.1	31.0sh	
$TiCl_3,3C_4H_8O_2$	Soln. $C_4H_8O_2$	44.8	36.6	31.2	
$TiCl_3,1.5C_4H_{10}O_2$	Refl.	45.0	37.6	30.8	
	Soln. $C_4H_{10}O_2$	41.8	37.4	31.7	
$TiCl_3,3\gamma pic$	Refl.	45.4	38.5	30.0sh	~23.0
$TiCl_3,2\alpha pic$	Refl.	44.7	38.4	30.2vbr	
$TiCl_3,2N(CH_3)_3$	Refl.	44.9	37.0	30.0	
$TiCl_3,2C_4H_8S$	Refl.	45.8	37.2	30.2sh	25.8
$TiCl_3,2S(CH_3)_2$	Refl.	45.1	37.5	~30.0br	

* ref. 48

Results and Discussion

The types of transition that might be expected in the region of the ultraviolet studied, 15-50kK, for halogen or mixed halogen/organic ligand complexes of the early transition metals are:

1) Halogen(π) $\longrightarrow$ Metal(d)
2) Organic donor(π) $\longrightarrow$ Metal(d)
3) Metal(d) $\longrightarrow$ Organic donor(π^*)

the last cannot, of course, occur for d^0 systems.

Jørgensen[78] reported that the hexachlorotitanate(IV) anion, $[TiCl_6]^{2-}$, had a single absorption band at 45.0kK which he assigned to $Cl(\pi) \longrightarrow Ti(t_{2g})$ and Fowles et al.[48,115] therefore assigned the spectra of the titanium(III) and (IV) chloride/methyl cyanide adducts according to the scheme:-

$TiCl_4,2CH_3CN$	45.0kK	$Cl(\pi) \longrightarrow Ti(d)$
	31.7	$CH_3CN(\pi) \longrightarrow Ti(d)$
$TiCl_3,3CH_3CN$	43.5	$Cl(\pi) \longrightarrow Ti(d)$
	35.1	$CH_3CN(\pi) \longrightarrow Ti(d)$
	31.0	$Ti(d) \longrightarrow CH_3CN(\pi^*)$

The observation of only two bands in the titanium(IV) compounds (d^0) was consistent with the assignment of one band in the titanium(III) adduct to a transition from the $Ti(t_{2g})$. To check the accuracy of these suggestions a wide range of complexes has been studied, for providing that a ligand(π)$\longrightarrow$Ti(d) transition is being observed, variation of the ligand should result in the shifting of one or more bands. This effect should be particularly marked if a ligand such as dioxan is compared with methyl cyanide which has comparatively low energy π orbitals. Examination of the spectra obtained, (fig. 6.4 and tables 6.3-5) revealed that the bands were virtually independent of the organic ligand but dependent upon the halogen, an observation that prompted further investigation of the $[TiX_6]^{2-}$ salts (where X = Cl or Br). Unlike most of the transition metal hexahalogeno spectra previously reported[78,118-120] these salts have d^o configurations which leaves little doubt that the transitions observed in the 15.0 to 50.0kK region are due to X(π)$\longrightarrow$Ti(d). The best way to study these spectra would be in solution, thus eliminating solid packing effects, but unfortunately they are not soluble in good ultraviolet solvents with which there is no possibility of reaction. Jørgensen originally reported the spectrum of $[TiCl_6]^{2-}$ in 12M hydrochloric acid,[8] but this species is only stable when the solution is saturated with HCl gas, and it is probable that the solution contained a species

$[TiO_nCl_{6-2n}]$ or $[Ti(OH)_nCl_{6-n}]$; indeed Jørgensen no longer believes that the spectrum measured was that of $[TiCl_6]^{2-}$.[121] The solvent chosen was methyl cyanide, as it can be rigorously dried and deoxygenated and other hexahalogeno salts are known to be stable when dissolved in it.[122-124] During measurement of the hexachlorotitanate(IV) spectrum excess chloride ion was added to suppress reaction of the type,[125]

$$[TiCl_6]^{2-} + CH_3CN = [TiCl_5,CH_3CN]^- + Cl^-$$

the change in the spectrum indicating that this takes place to a small extent.

The diffuse reflectance and solution spectra are quite similar and it therefore seems that the solutions do indeed contain the $[TiX_6]^{2-}$ chromophore. Comparison of the $[TiCl_6]^{2-}$ reflectance spectra for the potassium and dialkylammonium cations (fig. 6.2) show that the spectra are cation dependent, which may be due to differing distortion of the hexahalogeno ion as the result of crystal packing forces, or possibly to hydrogen bonding in the diethylammonium salt. Both these hexahalogeno ions violate the radius ratio rule, which may make them particularly prone to distortion, since the metal halogen bonds will be rather weak.

The conspicuous difference between these charge transfer bands and d-d peaks is their greater intensity,

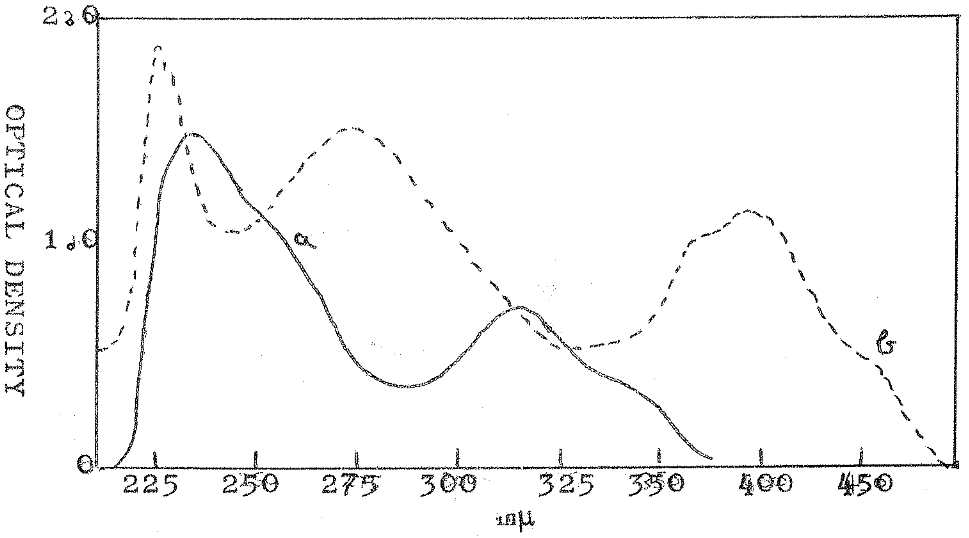


Fig. 6.1.

Solution Spectra of $[MX_6]^{2-}$ in CH_3CN

(a) $[TiCl_6]^{2-}$ (b) $[TiBr_6]^{2-}$

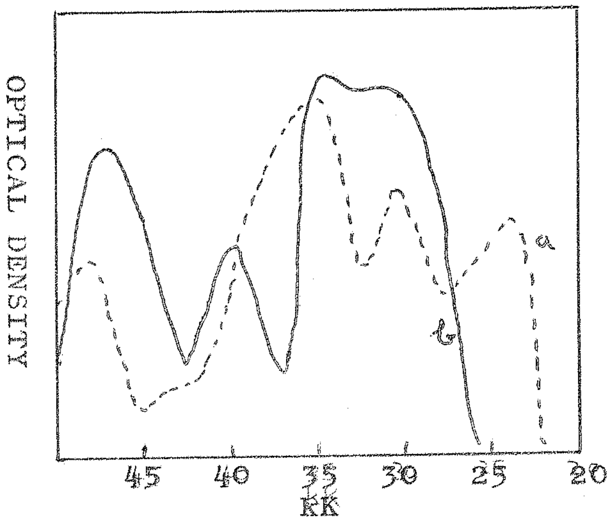


Fig. 6.2.

Diffuse reflectance spectra of

(a) K_2TiCl_6

(b) $[(C_2H_5)_2NH_2]_2 TiCl_6$

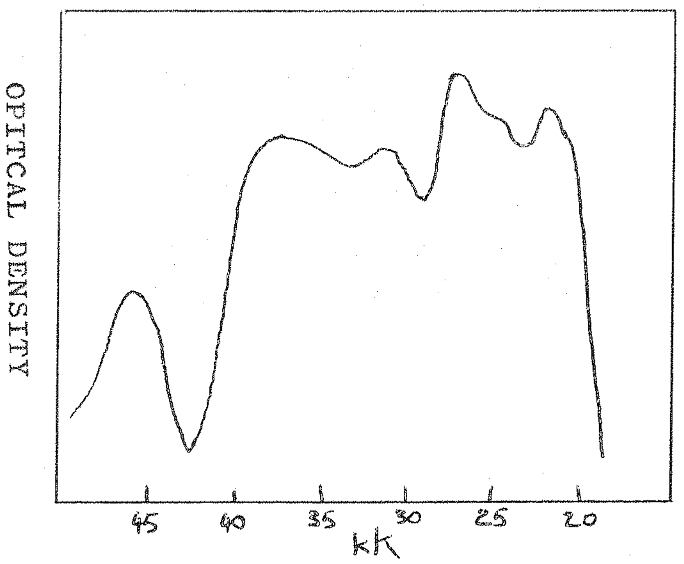


Fig. 6.3.

Diffuse reflectance spectrum of $[(C_2H_5)_2NH_2]_2TiBr_6$

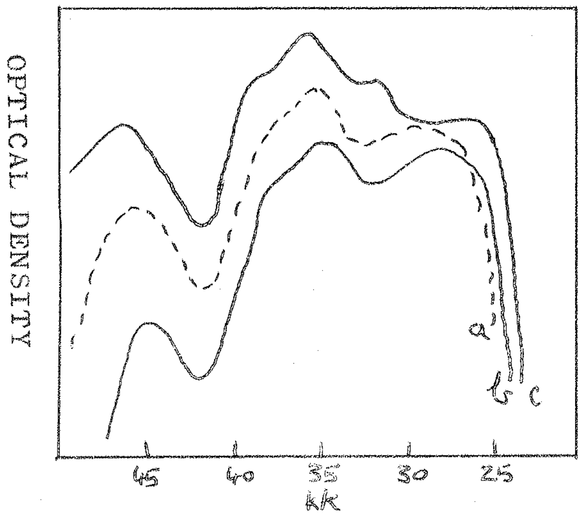


Fig. 6.4.

Diffuse reflectance spectra of

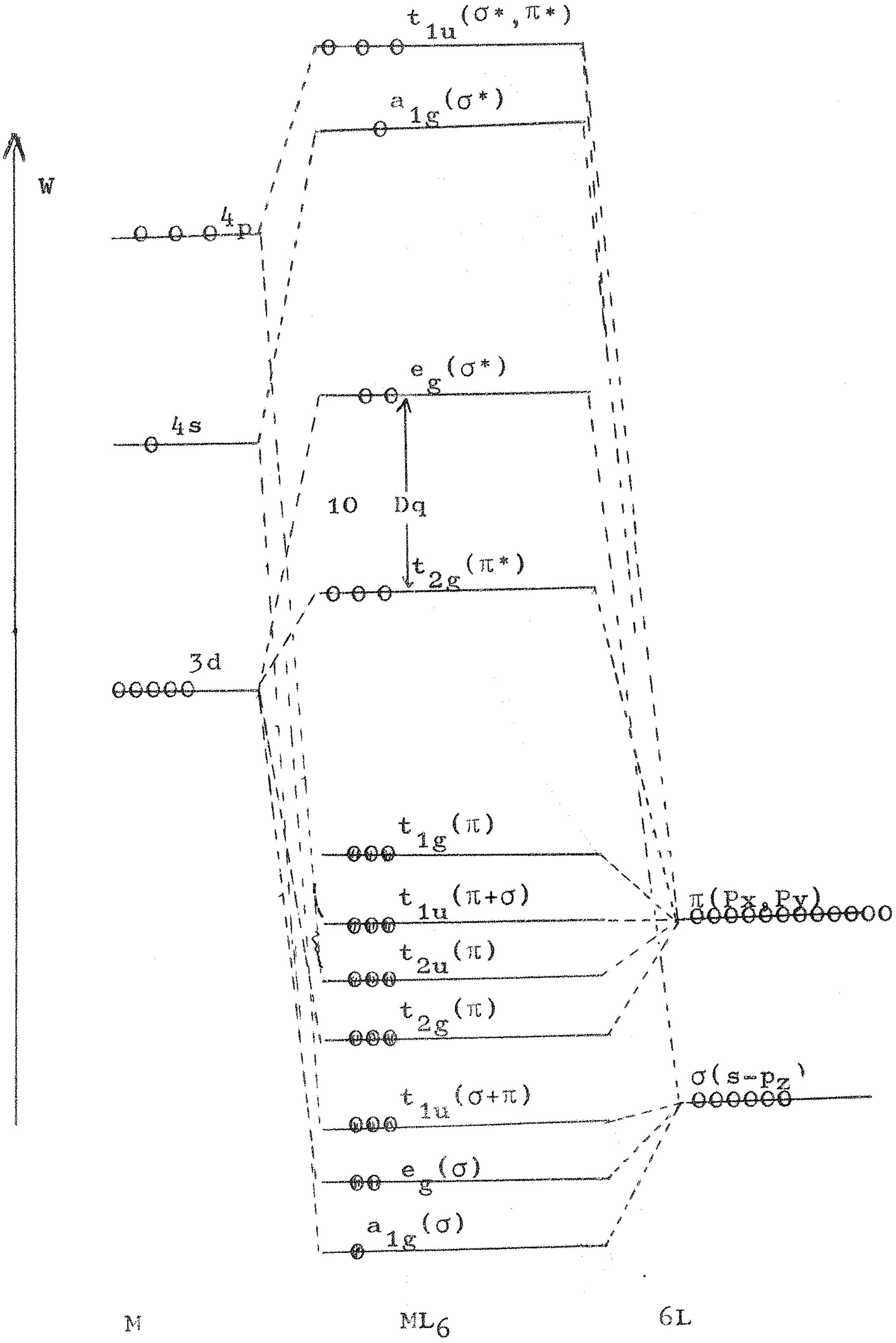
(a) $TiCl_4,2CH_3CN$ (b) $TiCl_4,C_4H_8O$ (c) $TiCl_4$,bipyr which arises because most of the charge transfer bands are parity allowed, being u-g transitions.

The molecular orbital diagram for an octahedral d^o complex, shown in fig. 6.5, is essentially the same as that of Ballhausen and Gray;[126] the only differences are that the $t_{1u}(\sigma)$ and $t_{1u}(\pi)$ can mix to some extent giving $t_{1u}(\sigma + \pi)$ and the relative energies of the t_{1u} and t_{2u} levels have been inverted because P.N. Schatz has shown,[121] using the Faraday effect, that this is the order in $[IrCl_6]^{2-}$.

Since the measurement of these spectra, Jørgensen and Ryan have reported those of $[TiCl_6]^{2-}$ and $[TiBr_6]^{2-}$ in methyl cyanide solution, and for the former they make the assignements:[121]

$t_{1g}(\pi) \longrightarrow t_{2g}(d)$	25.0kK
$t_{1u}(\sigma+\pi) \longrightarrow t_{2g}(d)$	29.6
$t_{2u}(\pi) \longrightarrow t_{2g}(d)$	31.8
$t_{1u}(\sigma+\pi) \longrightarrow e_g(d)$	43.8

Our spectra, however, (figs. 6.1 and 2; table 6.2) show an extra band at 38.0kK in both the solution and reflectance of both the salts and this casts some doubt on Jørgensen and Ryan's assignment of the 43.8kK band. Their results do, nevertheless, lead to a very acceptable value for 10Dq of around 14kK, compared to $[TiCl_6]^{3-}$



W
$t_{1u}(\sigma^*,\pi^*)$
$a_{1g}(\sigma^*)$
4p
$e_g(\sigma^*)$
4s
10 Dq
$t_{2g}(\pi^*)$
3d
$t_{1g}(\pi)$
$t_{1u}(\pi+\sigma)$
$\pi(P_x, P_y)$
$t_{2u}(\pi)$
$t_{2g}(\pi)$
$t_{1u}(\sigma+\pi)$
$\sigma(s-p_z)$
$e_g(\sigma)$
$a_{1g}(\sigma)$
M
ML_6
6L

Fg. 6.5.

where 10Dq is 12.8kK.[59] One explanation for this extra band is that the $t_{1g}(\pi) \longrightarrow e_g(d)$ transition is being observed but while the position is correct it is unlikely that this parity forbidden transition would be observed experimentally when sandwiched by two allowed bands; indeed it is interesting that even the $t_{1g}(\pi) \longrightarrow t_{2g}(d)$ transition is resolved.

Jørgensen has given an empirical expression relating the optical electronegativities of the halide and metal to the position of the first Laporte allowed charge transfer band:[127]

$$\sigma_{corr} = \left[\chi^{opt}_{Cl} - \chi^{opt}_{M}\right] \cdot 30\text{kK}$$

where χ_{Cl} and χ_M are the respective optical electronegativities of the halide and metal, and σ_{corr} is the position of the first allowed charge transfer band (in kK) corrected for electron repulsion, the correction being zero for a d^o system. This expression gives $\chi^{opt}_{Ti(IV)} = 2.06$ using the 28.2kK band of $[TiCl_6]^{2-}$ solution as the first allowed transition, the values of χ^{opt} for the halogens considered being taken as:[127]

F = 3.9 Cl = 3.0 Br = 2.8

K_2TiF_6 is white, and only one peak and a shoulder were observed, both at much higher energy than in the $[TiCl_6]^{2-}$ species. If the 45.2kK band is assigned to the $t_{1u}(\sigma+\pi) \longrightarrow t_{2g}(d)$ transition calculation of $\chi^{opt}_{Ti(IV)}$ gives a value of 2.4, which is in fair agreement with that obtained from the hexachloro anion. Clark has recently reported[30] that the bipyridyl adduct of titanium(IV) fluoride is white which also confirms the assignment of the low energy charge transfer transitions, causing the yellow and red colours of $TiCl_4$,bipyr and $TiBr_4$,bipyr respectively, as halogen(π)⟶Ti(d).

The spectrum of $[TiBr_6]^{2-}$ shows the expected shift to lower energy (fig. 6.3), reflecting the decrease in the optical electronegativity of bromide, and also has a more complex band structure than that of the hexachloro salt. Jørgensen has shown that the latter effect is to be expected as the Landé coupling parameter ε_{np} increases rapidly from chloride to bromide and iodide:-[78]

ε_{np} in kK Cl = 0.587. Br = 2.457. I = 5.069.

This results in significant splitting of the Γ_4 (t_1) and Γ_5 (t_2) energy levels:

$$^2\Gamma_4 \longrightarrow \Gamma_6 \quad \text{and} \quad \Gamma_8$$

$$^2\Gamma_5 \longrightarrow \Gamma_7 \quad \text{and} \quad \Gamma_8$$

and hence more transitions are expected.

To examine the effect of electron repulsion $[VCl_6]^{2-}$ and $[TiCl_6]^{2-}$ reflectance spectra were examined, since being d^1 systems excitation of a halogen(π) electron to the t_{2g}(d) set of orbitals should involve a repulsion term. The spectrum of $[VCl_6]^{2-}$ has been assigned:-[100]

$t_{1g}(\pi) \longrightarrow t_{2g}(d)$	~ 21kK
$t_{1u}(\sigma+\pi) \longrightarrow t_{2g}(d)$	28.2
$t_{2u}(\pi) \longrightarrow t_{2g}(d)$	36.4
$t_{1u}(\sigma+\pi) \longrightarrow e_g(d)$	45.4

and if these assignments are correct the spectrum is very similar to that of $[TiCl_6]^{2-}$ indicating that if the values of χ^{opt} for Ti(IV) and V(IV) are similar then the repulsion term is small. From the listed values of χ^{opt} for other pairs of adjacent metal ions in the same oxidation state,[127] it seems that the differences in χ^{opt} are probably less than 0.2 units and that electron repulsion has little effect in a d^1 system.

The only known salt of $[TiCl_6]^{3-}$ unfortunately contains the pyridinium cation which absorbs at 38.8 and ~ 45kK.[59] The first allowed charge transfer band occurs at 29.8kK, compared to Gray's predicted position of 37.0kK[128] and although this is only at slightly higher energy than in $[TiCl_6]^{2-}$ after a correction of 2.6kK for inter-electron repulsion it leads to $\chi^{opt}_{Ti(III)} = 1.9$.[78] The decrease in χ^{opt} with decreasing oxidation state is expected as reducing charge transfer to titanium(III) is harder than to titanium(IV).

Little information can be obtained from the spectrum of $(PyH)_3[TiCl_4Br_2]$ for at high energy pyridinium absorptions will contribute to the spectrum while at low energy discrete bands are not resolved.

It is interesting that titanium(III) chloride has the first intense charge transfer band at 18.0kK, which was first reported and assigned by Clark et al. to a $Cl(\pi) \longrightarrow Ti(d)$ transition.[51] Since the first allowed transition in $[TiCl_6]^{2-}$ is not observed until 28.2kK this suggests that the 18.6kK band may be characteristic of the polymeric chain of bridging halide ions and the presence of a strong band at 18.0kK in the reflectance spectrum of $[Et_4N][TiCl_4]$ confirms this, for magnetic and other spectral evidence show that $[TiCl_4]^-$ is not tetrahedral but contains halogen bridges.[59] While intensities estimated from diffuse reflectance may be misleading the peak in $[TiCl_4]^-$ appears appreciably less strong than in $TiCl_3$, which is consistent with the less polymeric nature of the former compound. As might be expected from these results titanium(III) bromide was also found to have strong absorption from 14.5kK upwards which is much lower than the first charge transfer transition found in discrete $TiBr_3,3L$ complexes.

The presence of intense low energy bands has recently been confirmed by single crystal spectra of $\alpha TiCl_3$ and $\alpha TiBr_3$.[129] Transitions of this type have been attributed to 'cooperative' effects between more than one metal ion,[78] presumably implying partial electron delocalisation along the chains. The strong antiferromagnetic exchange in titanium(III) chloride and also probably in $[TiCl_4]^-$, which has μ_{eff} = 1.21 B.M. at room temperature, confirms that the metal ions cannot be considered independently.[59]

The spectra of all the adducts are listed in tables 6.3-5, but no attempt has been made to give detailed assignments as the symmetry of only a few of them is known (i.e. whether cis or trans) and all those containing aromatic nitrogen ligands will have π-π^* transitions in the same region as the $X(\pi) \longrightarrow Ti(d)$ ones.

Transitions of the type $Ti(d) \longrightarrow lig.(\pi^*)$ have been considered in the discussion of the titanium(III) bromide bipyridyl compounds (chapter IV).

CHAPTER VII

REACTIONS OF TITANIUM(III) AND (IV) CHLORIDES WITH 3-METHOXYPROPRIONITRILE AND 3-DIMETHYLAMINOPROPRIONITRILE

The reactions of acceptor molecules with bidentate ligands in which the donor groups differ are of interest when deciding on the type of bonding favoured by the acceptor. Thus, for example, studies of titanium(III) and (IV) halide reactions with 1:4-thioxan show that sulphur is preferred to oxygen as a donor in these systems.[103] The aim of the work reported in this chapter was to assess the preference of titanium(III) and (IV) chlorides for the $-N(CH_3)_2$, $-OCH_3$ or $-CN$ groups.

1. Reactions of titanium(IV) chloride

a) Reaction of $TiCl_4$ with $CNCH_2CH_2OCH_3$

When $TiCl_4$ was allowed to react with $CNCH_2CH_2OCH_3$ in benzene (mole ratio ~ 1:5) a yellow solution was formed immediately and from this a canary yellow solid was obtained.

	Ti%	Cl%	C%	H%	N%
Found	13.9	39.8	26.5	4.1	6.1
$TiCl_4,2L$ requires	13.3	39.4	26.7	3.9	7.8

The infrared spectrum showed that the bonding occurred through the cyanide.

C≡N stretching frequency, free ligand = 2260 cm.$^{-1}$
$TiCl_4,2L$ = 2300 cm.$^{-1}$

The spectrum below 2000 cm.$^{-1}$ appeared similar to the free ligand and it therefore appears that the ethereal oxygen takes no part in bonding. The compound was slightly soluble in chloroform and an attempt was made to measure the N.M.R. spectrum but only a very weak signal was observed.

b) Reaction of $TiCl_4$ with $CNCH_2CH_2N(CH_3)_2$

Reaction of $TiCl_4$ with $CNCH_2CH_2N(CH_3)_2$ in benzene gave an immediate brown precipitate which was isolated and analysed.

	Ti%	Cl%	C%	H%	N%
Found	12.8	35.7	34.2	6.0	9.2
$TiCl_4$,2L requires	12.4	36.8	31.1	5.2	14.5

The infrared spectrum showed no shift of the C≡N stretching vibration at 2240 $cm.^{-1}$ but there was evidence for a weak band at 2300 $cm.^{-1}$ which was absent in the free ligand. Although there was no sign of an N-H stretching vibration ~ 3300 $cm.^{-1}$ there were bands at 1675, 1645 and 1640 $cm.^{-1}$, none of which were present in the free ligand. The compound was slightly soluble in chloroform, but not sufficiently for a satisfactory N.M.R. spectrum.

2. Reactions of $TiCl_3$, $TiCl_3,2N(CH_3)_3$ and $TiCl_3,3CH_3CN$

a) Reaction of $TiCl_3,2N(CH_3)_3$ with $CNCH_2CH_2N(CH_3)_3$

When $TiCl_3,2N(CH_3)_3$ was allowed to react with $CNCH_2CH_2N(CH_3)_2$ (mole ratio ~ 1:5) in benzene a green solution was quickly formed but after several days a green-brown solid separated. The colour and the analyses varied slightly from run to run.

	Ti%	Cl%	C%	H%	N%	μ_{eff}(B.M.)
Found Run 1	13.6	27.3			15.0	
2	13.3	30.5	33.4	6.5	12.1	1.43
3	15.4	33.5				1.31
4	15.4	35.0				1.68
$TiCl_3,2L$ requires	13.7	30.3	34.2	5.7	16.0	
$TiCl_3,1.5L$ "	15.9	35.2	29.9	5.0	13.9	

The infrared spectra on the products from all the runs showed a band at 3310 $cm.^{-1}$, and on those from runs 2 and 3 there was a weak C≡N peak at 2,200 $cm.^{-1}$ (cf free ligand at 2240 $cm.^{-1}$). In the products from runs 1 and 4 there was no trace of a C≡N stretching vibration. All the products showed two other peaks, which were absent in the free ligand, at 1580 $cm.^{-1}$ vs and 1670 $cm.^{-1}$ s. An attempt to isolate the initial green product using a short reaction time failed.

The reflectance spectrum of the product from run 4 showed a peak at 17,240 $cm.^{-1}$ with shoulders at

23,800 cm.$^{-1}$ and 13,000 cm.$^{-1}$.

b) Reaction of $TiCl_3$ with $CNCH_2CH_2N(CH_3)_2$

Titanium(III) chloride was allowed to react with and excess of $CNCH_2CH_2N(CH_3)_2$ in benzene and the brown solid obtained after two weeks was analysed.

	Ti%	Cl%	C%	H%	N%
Found	16.3	35.3	30.2	5.4	13.5
$TiCl_3$,1.5L requires	15.9	35.2	29.9	5.0	13.9

The infrared spectrum was the same as the $TiCl_3$,1.5L prepared in (a) run 4. There was no C≡N peak but there were peaks at 3310 cm.$^{-1}$ s, 1670 cm.$^{-1}$ m, and 1585 cm.$^{-1}$ s; none of which are present in the free ligand. The magnetic moment at room temperature was 1.62 B.M.

c) Reaction of $TiCl_3$,$3CH_3CN$ with $CNCH_2CH_2N(CH_3)_2$

$TiCl_3$,$3CH_3CN$ was allowed to react with $CNCH_2CH_2N(CH_3)_2$ in benzene for a week and the green insoluble solid that formed was collected.

	Ti%	Cl%
Found	15.9	34.5
$TiCl_3$,1.5L requires	15.9	35.2

The infrared spectrum was the same as that of the product from (b) except that there was still a weak ligand C≡N stretching vibration at 2220 cm.$^{-1}$. There was no evidence for methyl cyanide. The magnetic moment was 1.62 B.M. at room temperature.

d) Reaction of $TiCl_3,2N(CH_3)_3$ with $CNCH_2CH_2OCH_3$

When $TiCl_3,2N(CH_3)_3$ was allowed to react with $CNCH_2CH_2OCH_3$ in benzene a green solution was formed initially but after several hours an insoluble purple-brown solid separated out. This was isolated and analysed, it was insoluble in benzene but soluble in the ligand.

	Ti%	Cl%	C%	H%	N%
Found Run 1	15.0	30.4	27.2	6.4	9.2
2	14.9	32.0	29.0	6.4	9.5
3	14.7	30.9	29.5	4.6	8.7
4	15.1	33.8			
$TiCl_3$,2L requires	14.8	32.7	29.6	4.3	8.6

	Run 2	Run 3	Run 4
Valency state	3.13	3.11	3.00
χ_m(cgsu x 10^6)	-20	+21	+16

Valency change titrations and the purple colour of the hydrolysis solutions show that the oxidation state is Ti(III) but the compounds are essentially diamagnetic.

The infrared spectrum of $CNCH_2CH_2OCH_3$ shows the

C≡N stretching vibration at 2260 cm.$^{-1}$ and a strong band at 1120 cm.$^{-1}$ which is thought to be the C-O-C assymetric stretch. In the complexes the C≡N frequency had risen and either a single peak (2280 cm.$^{-1}$) or a doublet (2280 cm.$^{-1}$ and 2300 cm.$^{-1}$) was observed. In all the products the C-O-C frequency had decreased to 1075 cm.$^{-1}$ where a strong, rather broad peak was observed, but in some of them there was also evidence for a shoulder at 1120 cm.$^{-1}$

The reflectance spectrum of the product from run 4 had peaks at 22,200 cm.$^{-1}$ and 17,240 cm.$^{-1}$.

Results and Discussion

Titanium(IV) chloride is known to form complexes with alkyl cyanides,[12] tertiary amines,[97] and ethers[11] so that reaction of $TiCl_4$ with the ligands $CNCH_2CH_2OCH_3$ or $CNCH_2CH_2N(CH_3)_2$ should provide a comparison of its affinity for these donors. Their stereochemistry is such that neither is likely to chelate if it bonds in the usual way.

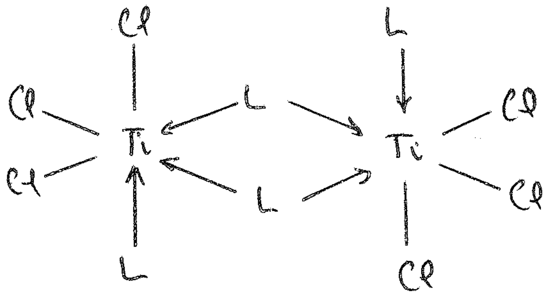
Both reactions yielded solids whose analyses correspond to the 1:2 adducts. The infrared evidence on tetrachlorobis(3-methoxyproprionitrile)titanium(IV) showed that bonding occurred via the cyanide group for the C≡N stretching frequency increased (40 cm.$^{-1}$) and peaks in the C-O-C stretching region appeared to be unchanged. In tetrachlorobis(3-dimethylaminoproprionitrile)titanium(IV) on the other hand the cyanide stretching vibration was largely unchanged, but the presence of a weak peak at 2300 cm.$^{-1}$ indicated some cyanide coordination. It was hoped to carry out an N.M.R. spectrum as the shifts of the methylene protons relative to the free ligand would have helped to prove bonding from the tertiary amine nitrogen but unfortunately the solubility was insufficient.

It therefore seems that titanium(IV) will choose cyanide donation in preference to a non-cyclic ether which is in agreement with the observations of Schwartz and Reski,[130] and Russ[27] that titanium(IV) chloride only forms a weak complex with diethylether. The type of bonding present in $TiCl_4,2CNCH_2CH_2N(CH_3)_2$ is not clear and the presence of extra peaks in the infrared suggests that the ligand may be undergoing reaction.

In marked contrast to this reaction between $TiCl_4$ and $CNCH_2CH_2N(CH_3)_2$ Jain and Rivest,[131] under very similar conditions, succeeded in preparing the 1:1 adduct which is apparently monomeric with bonding to the metal from the triple bond ($C{\equiv}N$). The $C{\equiv}N$ stretching frequency shows a marked decrease in the complex.

Titanium(III) chloride also forms complexes with alkyl cyanides,[48] tetriary amines[20] and non-cyclic ethers but diethylether does not displace trimethylamine in $TiCl_3,2N(CH_3)_3$.[27] Unfortunately simple adducts were not obtained in the reactions of titanium(III) with $CNCH_2CH_2OCH_3$ or $CNCH_2CH_2N(CH_3)_2$.

$TiCl_3,2N(CH_3)_3$ reacts with $CNCH_2CH_2OCH_3$ to give a 1:2 adduct in which there is infrared evidence for both cyanide and ether bonding. The valency state titrations showed that it was a compound of titanium(III) but it was diamagnetic. One possible structure is the ligand bridged one (I),



but from a model it seems that the titanium atoms are too far apart to interact. It is not clear what structure could cause such a low magnetic moment and an X-ray structural determination might be justified.

The reaction of titanium(III) chloride, and the compounds $TiCl_3,2N(CH_3)_3$ and $TiCl_3,3CH_3CN$ with 3-dimethylaminoproprionitrile is remarkable as the complex has little or no sign of a C≡N stretch in the infrared. This fact alone cannot be taken as a criterion for the absence of the C≡N group for Wilkinson has recently reported[132] some rhenium(III) chloride complexes containing methyl cyanide which have no C≡N peak in their infrared spectra, but in conjunction with the additional peaks at 1585 cm.$^{-1}$ s, 1670 cm.$^{-1}$ m, and 3310 cm.$^{-1}$ m, there is little doubt that the ligand has undergone reaction. The peak at 3310 cm.$^{-1}$ is characteristic of the N-H vibration in imines and it is suggested that the peak at 1580 cm.$^{-1}$ could be

-C=N- (although it is at rather low energy) and the 1670 cm.$^{-1}$ band due to -C=C-.[133] The ligand may therefore have reacted to give $HN=CHCH=CHN(CH_3)_2$ which will be indistinguishable by microanalyses. Unfortunately little appears to be known about the infrared spectra of imines[133] and the peaks to be expected when such a molecule is coordinated to a transition metal are open to question. The possibility that an imine might be formed during the reaction of methyl cyanide with rhenium halides has been suggested by Cotton and Walton but their evidence is not strong.[134]

The formation of the same product regardless of whether the starting material was $TiCl_3$, $TiCl_3,2N(CH_3)_3$ or $TiCl_3,3CH_3CN$ is interesting as the reaction was carried out in benzene using only a little ligand, for although the cyanide group of the ligand might have been expected to displace trimethylamine complete displacement of methyl cyanide is surprising.

CHAPTER VIII

COMPLEXES OF DIVALENT TITANIUM

Although complexes of titanium(III) and (IV) are well characterised very little work has been reported on titanium(II); apparently the only known halide adducts are $TiCl_2,2DMF$[69] (where DMF is dimethylformamide) and the ammine $TiCl_2,4NH_3$.[68] In this chapter the products of reactions between titanium(II) chloride and bromide and organic ligands are reported and discussed. The salt Na_2TiCl_4 and the cyanide adduct $TiCl_2,2CH_3CN$ were also used as starting materials.

1. Reaction between $TiCl_2$ and methyl cyanide

Titanium(II) chloride (~1.5g) was refluxed with methyl cyanide (~20mls) for two days when a dark-brown solution was obtained. A little solid which remained was thought to be unreacted halide. The solution was filtered and the solvent evaporated to leave a black solid which was pumped at ~50°C for twelve hours.

	Ti%	Cl%	C%	H%
Found Run 1	23.2	35.1	24.1	3.3
Run 2	23.3	35.4		
$TiCl_2,2CH_3CN$ requires	23.8	35.3	24.1	3.0

The rate of reaction appeared to vary with the batch of titanium(II) chloride; one particular sample failed to react significantly even after two weeks under reflux. The infrared spectrum of the product showed that the C≡N stretching frequency which occurs at 2270 cm.$^{-1}$ in the free ligand had risen to 2330 cm.$^{-1}$ indicating that all the methyl cyanide was coordinated. The conductivity in methyl cyanide solution at 1.64 x 10^{-3}M was 24.5 ohm^{-1}cm^{2} which suggests a non-ionic structure. The magnetic moment at 21°C was 1.07 B.M. The visible spectrum was measured for the solid (reflectance) and for a solution in methyl cyanide; it is reported, together with those of the other compounds listed in this chapter, in table 8.1.

In an attempt to prepare an adduct with more than two molecules of methyl cyanide the reaction was also carried out in a sealed tube at 120°C for one week but the black product obtained had analyses close to $TiCl_2,2CH_3CN$.

2. Reaction between Na_2TiCl_4 and methyl cyanide

Na_2TiCl_4 (~2g) was allowed to react with methyl cyanide (~20mls) for one day at room temperature. The dark-brown solution obtained was filtered through a porosity 4 sinter and the methyl cyanide evaporated off to give a black solid which was pumped for fifteen hours at ~50°C.

	Ti%	Cl%	C%	H%	N%
Found Run 1	22.8	34.5	22.3	3.2	
Run 2	23.6	33.6	23.6	3.8	11.5
$TiCl_2,2CH_3CN$ requires	23.8	35.3	24.1	3.0	14.1

The physical properties of this compound (e.g. infrared spectrum) showed that it was the same as the methyl cyanide adduct prepared directly from titanium(II) chloride and as it could be obtained fairly readily in considerable quantities it was a convenient starting material for substitution reactions. The molecular weight measured in boiling methyl cyanide was 475 ± ~ 30% (the monomer requires 201). The magnetic moment was measured between 80 and 300°K (table 8.2 and fig 8.1). It was also measured in methyl cyanide solution, at room temperature $\mu_{eff} = 1.35$ B.M.

3. Reaction of $TiCl_2,2CH_3CN$ with 1:10-phenanthroline

$TiCl_2,2CH_3CN$ was allowed to react with 1:10-phenanthroline in a mole ratio ~ 1:1.5 using methyl cyanide as solvent. The dark-blue insoluble solid, which was obtained after a week, was filtered off, washed once with methyl cyanide and pumped overnight.

	Ti%	Cl%	C%	H%	N%
Found	15.1	23.7	50.9	3.4	9.5
$TiCl_2$,phen requires	16.0	23.7	48.2	2.7	9.4

The infrared spectrum showed coordinated 1:10-phenanthroline but there was no evidence for the presence of methyl cyanide. The magnetic moment, which was 1.11 B.M. at room temperature, was also measured over a temperature range (table 8.2 and fig 8.2).

4. Reaction of $TiCl_2,2CH_3CN$ with 2:2'-bipyridyl

$TiCl_2,2CH_3CN$ was allowed to react with 2:2'-bipyridyl in a mole ratio ~1:2 using benzene as diluent. One week under reflux gave an insoluble dark-blue solid which was filtered off, washed several times with benzene, pumped and analysed.

	Ti%	Cl%	C%	H%	N%
Found	16.6	25.5	42.0	3.8	10.2
$TiCl_2$,bipyr requires	17.4	25.8	43.7	2.9	10.2

The infrared spectrum was characteristic of coordinated bipyridyl and indicated complete replacement of methyl cyanide. The magnetic moment was 1.09 B.M. at room temperature.

In an effort to obtain $TiCl_2$,2bipyr the 1:1 adduct was allowed to react at 140°C with an excess of molten bipyridyl. The sealed tube was opened after fifteen hours and the dark-blue solid it contained washed with benzene. Little if any reaction appeared to have taken place as the analyses corresponded to $\sim TiCl_2$, 1.25 bipyr, the slightly high ligand content was probably due to incomplete removal of the unreacted bipyridyl.

5. Reaction of $TiCl_2,2CH_3CN$ with pyridine

Reaction of $TiCl_2,2CH_3CN$ with pyridine ($\sim$1:4 mole ratio) in benzene gave a brown solution and a black insoluble solid, which was filtered off and pumped at $\sim 50^{\circ}C$ for eight hours.

	Ti%	Cl%	C%	H%	N%
Found	16.6	25.4	40.8	4.1	8.2
$TiCl_2$,2pyr requires	17.3	25.6	43.3	3.6	10.1

The infrared spectrum showed the presence of pyridine and once again indicated the complete replacement of methyl cyanide. The magnetic moment at $18^{\circ}C$ was 1.14 B.M. but was measured at five field strengths (table 8.3) and was field independent.

Table 8.3

Approx. Gauss:	2300	2700	3200	3600	4000
χ'_m :	532	533	513	534	527

The conductivity in pyridine solution at $1.5 \times 10^{-3}M$

had $\Lambda_m = 6.2$ ohm^{-1}cm^2 which confirmed the non-ionic formulation.

This method of preparing $TiCl_2$,2pyr was devised after failure of the direct reaction between titanium(II) chloride and pyridine. When titanium(II) chloride was allowed to react with pyridine at room temperature a transient blue solution was formed which changed to pale-green; filtration of this solution to remove unreacted halide and evaporation of the pyridine gave a dark-green solid. The analyses, Ti: Cl: N of 1: 2.5: 2.8 suggested that the major product was $TiCl_3$,3pyr. When Na_2TiCl_4 was allowed to react with pyridine a soluble green solid was again obtained.

	Ti%	Cl%
Found	11.6	24.7
$TiCl_3$,3pyr requires	12.2	27.2

6. Reaction of $TiCl_2$,$2CH_3CN$ with tetrahydrofuran

$TiCl_2$,$2CH_3CN$ was allowed to react with an excess of tetrahydrofuran for four days at room temperature when a brown solution was obtained. This yielded a black solid after filtration and evaporation of the solvent.

	Ti%	Cl%	C%	H%
Found Run 1	18.2	26.2	30.5	5.1
Run 2	18.8	26.6	31.8	6.5
$TiCl_2,2C_4H_8O$ requires	18.2	27.0	36.5	6.1

While the infrared spectrum showed the usual coordinated tetrahydrofuran peaks (1015 $cm.^{-1}$ s and 860 $cm.^{-1}$ s) there was no evidence for methyl cyanide. The magnetic moment at 20°C was 1.21 B.M.

7. Reaction of $TiCl_2,2CH_3CN$ with pentamethyleneoxide

The reaction was carried out in the same way as the one with tetrahydrofuran, a black solid being obtained.

	Ti%	Cl%	C%	H%
Found	17.1	25.6	36.2	6.6
$TiCl_2,2C_5H_{10}O$ requires	16.5	24.4	41.2	6.9

The infrared spectrum was, once again, typical of coordinated ligand and showed complete replacement of methyl cyanide. The magnetic moment, 0.99 B.M. at room temperature, was appreciably lower than that obtained for $TiCl_2,2C_4H_8O$ but this may have arisen from packing errors as the pentamethyleneoxide product was rather lumpy.

8. Reaction of titanium(II) bromide with methyl cyanide

Titanium(II) bromide was allowed to react with excess of methyl cyanide for five days at room temperature. The brown solution obtained was filtered and the solvent evaporated to give a black solid which was pumped at 85°C for twelve hours.

	Ti%	Br%	C%	H%	N%
Found	16.5	56.9	16.8	2.1	7.3
$TiBr_2,2CH_3CN$ requires	16.5	55.2	16.6	2.1	9.7

The infrared spectrum was typical of a cyanide adduct with the C≡N stretch and combination bands moved to 2340 $cm.^{-1}$ and 2310 $cm.^{-1}$. The conductivity, Λ_m = 10$ohm^{-1}cm^2$ at 4.9 x 10^{-3}M, showed that the compound was non-ionic. The magnetic moment was 1.11 B.M. at 20°C, close to that observed for the chloride compound, although the behaviour over a temperature range (table 8.2 and fig. 8.3) was significantly different to $TiCl_2,2CH_3CN$.

9. Reaction of $TiBr_2,2CH_3CN$ with 2:2'-bipyridyl

$TiBr_2,2CH_3CN$ was allowed to react with 2:2'-bipyridyl in a mole ratio ~1:2 using benzene containing a trace of methyl cyanide as the solvent. After the contents had been refluxed for four hours the ampoule was opened and a dark-blue solid filtered off, washed with the solvent (in which it was slightly soluble) and pumped.

	Ti%	Br%	C%	H%	N%
Found	12.6	44.1	30.2	4.1	7.8
$TiBr_2$,bipyr requires	13.2	44.0	33.0	2.2	7.7

The infrared spectrum (4000-400 cm.$^{-1}$) showed that all the methyl cyanide had been replaced; only peaks associated with 2:2'-bipyridyl were observed. The magnetic moment at 17°C was 1.10 B.M.

10. Reaction $TiBr_2$,$2CH_3CN$ with 1:10-phenanthroline

Reaction of $TiBr_2$,CH_3CN with 1:10-phenanthroline in a mole ratio ~ 1:2 using methyl cyanide as the solvent gave a slightly soluble purple solid after one week.

	Ti%	Br%
Found before further washing	6.7	23.3
Found after further washing	6.7	25.0
$TiBr_2$,3phen requires	6.4	21.4

The infrared spectrum showed that all the methyl cyanide had been replaced. The conductivity was extraordinarily high, Λ_m = 300ohm^{-2}cm^2 at ~ 10^{-3}M and the system was not investigated further.

11. Reaction of $TiBr_2$,$2CH_3CN$ with pyridine

Reaction of $TiBr_2$,$2CH_3CN$ with a very dilute solution of pyridine in benzene for three hours at room temperature yielded both soluble and insoluble solids, the former was almost black and the latter brown-green.

		Ti%	Br%
Found	Soluble	11.0	34.7
	Insoluble	9.9	41.9
$TiBr_2$,2pyr requires		13.1	43.7
$TiBr_3$,3pyr requires		9.1	45.7

It appears that during the reaction some oxidation of the titanium(II) bromide occurs to give $TiBr_3$,3pyr but that this is virtually insoluble in the very dilute pyridine solution. It was not, however, possible to isolate a pure sample of $TiBr_2$,2pyr as the soluble solid which may have been due to the presence of reduction products. The magnetic moment of the soluble product was close to those of the other titanium(II) adducts (μ_{eff} = 1.06 B.M. at 20°C). Prior to this reaction an attempt had been made to prepare $TiBr_2$,2pyr by direct reaction of the halide with pyridine. A turquoise solution was obtained after several days but following filtration and evaporation of the pyridine this gave a green-brown solid which appeared to be partially $TiBr_3$,3pyr. Analyses gave the ratio Ti: Br: pyr as 1: 2.5: 3.8.

using a mixture of methyl cyanide and benzene as the solvent but even after several months reaction no insoluble product had been formed.

15. Reaction of $TiCl_2,2CH_3CN$ with 1:4-dioxan

Reaction of $TiCl_2,2CH_3CN$ with 1:4-dioxan in cyclohexane as diluent gave brown solutions from which only non-stoichiometric products could be isolated.

16. Reaction of $TiCl_2,2CH_3CN$ with triphenylphosphine

$TiCl_2,2CH_3CN$ was allowed to react with triphenylphosphine in benzene containing a trace of methyl cyanide but analyses for the brown solid isolated after three days showed that it was unchanged $TiCl_2,2CH_3CN$.

17. Reaction of Na_2TiCl_4 with trimethylamine

Na_2TiCl_4 was allowed to react with trimethylamine in a double ampoule for two weeks. A green-blue solution was obtained which on filtration and evaporation of the ligand gave a blue solid.

	Ti%	Cl%
Found	17.4	39.4
$TiCl_3,2N(CH_3)_3$ requires	17.6	39.0

The analyses show that oxidation has occurred to give the well known titanium(III) chloride adduct. It was significant that the hydrolysis solution used for the analysis of this compound showed the characteristic purple colour of titanium(III) compounds and was unlike those obtained from titanium(II) compounds which gave a pale-brown solution fading in time to colourless.

18. Reaction of titanium(II) chloride with dimethylamine

An ampoule containing titanium(II) chloride and dimethylamine was made up by Lanigan[125] in 1959. Five years reaction yielded a green solution, large red crystals and a dark green insoluble solid. The products were separated and analysed but some of the red crystals were also pumped overnight at 45°C when a green-brown solid was obtained. This was also analysed.

	Ti%	Cl%	N%
Found red crystals	16.5	22.6	19.0
$TiCl_2,4NH(CH_3)_2$ requires	16.0	23.7	18.7
Found green soluble	17.6	27.8	15.3
$TiCl_2,3NH(CH_3)_2$ requires	18.8	27.9	16.5
Found red crystals + heat	18.8	29.5	16.3

The green insoluble solid gave a Ti: Cl: N ratio of 1: 1.35: 2.16 and as it was probably a complex mixture of reduction products it is not discussed further. Both the 1:4 and 1:3 adducts hydrolysed to give purple solutions and their magnetic moments were 1.78 and 1.43 B.M. respectively, both therefore appear to contain tervalent titanium. When Na_2TiCl_4 was allowed to react with dimethylamine a green solution and red crystals were obtained within a few days, but these were not satisfactorily isolated and analysed.

19. Reaction of titanium(II) chloride with [PyH][Cl]

Titanium(II) chloride was allowed to react with pyridinium chloride, in a mole ratio 1:4.1, using an oil bath at 150-160°C. Six hours reaction gave a yellow product and the ampoule was opened so that chloroform could be introduced. After it had been resealed, the ampoule was shaken for twelve hours to break up the lumps and dissolve excess pyridinium chloride. The yellow solid was then filtered off, washed with fresh chloroform, pumped and analysed.

	Ti%	Cl%	C%	H%	N%
Found	9.6	43.5	35.2	3.7	8.5
$[PyH]_3[TiCl_6]$ requires	9.6	42.5	35.9	3.6	8.4

The magnetic moment at 20°C was 1.80 B.M.

A similar product was obtained from the reaction of $TiCl_2,2CH_3CN$ and pyridinium chloride in a mixed solvent containing methyl cyanide (20%) and chloroform (80%). The solution was refluxed for fifteen hours after which the yellow insoluble solid was transferred to a soxhlet and given a prolonged washing with pure chloroform.

	Ti%	Cl%	
Found	8.4	37.0	Ti: Cl = 1: 5.96

The infrared spectrum confirmed the absence of methyl cyanide.

20. Reaction of $TiCl_2,2CH_3CN$ with $[(C_2H_5)_4N][Cl]$

A number of reactions were carried out between $TiCl_2,2CH_3CN$ and $[(C_2H_5)_4N]Cl$ using chloroform or mixed chloroform/methyl cyanide solutions. The analyses for the yellow-brown solids which were obtained varied but the Ti: Cl ratio usually lay in the range 1: 4.5-5.0 and it seems likely that oxidation had occurred once again.

Table 8.1		Electronic Spectra (cm.$^{-1}$)
$TiCl_2,2CH_3CN$	Reflectance	21,800?
	Soln. CH_3CN	14,000? 9,700cm^{-1}shw
$TiCl_2$,phen	Reflectance	~16,700sh vbr
	Soln. CH_3CN	~18,000sh vbr
$TiCl_2$,bipyr	Reflectance	~20,000br
	Soln. CH_3CN	19,000shw? 14,000shw?
$TiCl_2$,2pyr	Reflectance	24,400
	Soln. pyridine	25,200
$TiCl_2,2C_5H_{10}O$	Reflectance	~14,300shw?
$TiCl_2,2C_4H_8O$	Reflectance	22,200shw 16,100shw
$TiBr_2,2CH_3CN$	Reflectance	~15,400br
	Soln. CH_3CN	33,400($\varepsilon \gtrsim 3000$) 28,600sh 15,500sh($\varepsilon \sim 150$) ~8,000wsh?
$TiBr_2$,bipyr	Reflectance	~15,400br
	Soln. CH_3CN	32,200 ~17,000sh vbr

/cont'd....

Table 8.1 cont'd...

$TiCl_2$	Reflectance	44,600	37,200		~20,000vbr
$TiBr_2$	Reflectance	45,000			~ 20,000vbr
$(PyH)_3TiCl_6$	Reflectance	21,800sh		14,100	~11,800sh
	Soln. CH_3CN	25,350		16,300	

Table 8.2

$TiCl_2$,phen

T°K	χ'_m (x10^6cgsu)	μ_{eff} B.M.	T°K	χ'_m (10^6cgsu)	μ_{eff} B.M.
313.2	517	1.14	213.2	713	1.10
303.2	506	1.11	193.2	790	1.10
293.2	542	1.13	173.2	904	1.11
283.2	573	1.14	153.2	971	1.09
273.2	568	1.11	133.2	1084	1.07
253.3	635	1.13	113.2	1198	1.04
233.2	666	1.11	93.2	1420	1.03

$TiCl_2$,$2CH_3CN$

T°K	χ'_m	μ_{eff}	T°K	χ'_m	μ_{eff}
313.2	482.3	1.10	193.2	669.8	1.02
303.2	475.3	1.07	173.2	713.1	0.994
293.2	473.9	1.05	153.2	790.1	0.984
273.2	508.9	1.05	133.2	879.6	0.969
253.2	559.2	1.06	113.2	997.1	0.951
233.2	571.9	1.03	93.2	1172	0.935
213.2	618.0	1.03	83.2	1291	0.927

Table 8.2 cont'd..

$TiBr_2,2CH_3CN$					
T^oK	χ'_m	μ_{eff}	T^oK	χ'_m	μ_{eff}
323.2	534.7	1.18	213.2	713.5	1.10
313.2	552.6	1.18	193.2	752.0	1.10
303.2	562.6	1.17	173.2	818.0	1.01
293.2	571.8	1.16	153.2	886.7	1.00
283.2	584.2	1.15	133.2	981.6	1.00
273.2	598.0	1.14	113.2	1104	1.00
253.2	632.3	1.13	93.2	1268	0.97
233.2	687.3	1.13			

Table 8.4	Low Infrared Spectra (500-200 cm.$^{-1}$)								
$TiCl_2$						290w			
Na_2TiCl_4					~ 300w		~ 260w		
$TiBr_2$					303m			250m	
$TiCl_2$, phen	424m	366m	336m	317s	298m				237w
$TiCl_2$, bipyr		~350br			308s				
$TiCl_2$, 2pyr	432m	352s		317s			278m		
$TiCl_2$, $2C_4H_8O$		354s	326s			295m			
$TiCl_2$, $2CH_3CN$		~ 350vbr							
$TiBr_2$, $2CH_3CN$						~ 290vbr			
$TiBr_2$, bipyr	414m	360m				~ 280 br			210w

Results and Discussion

The aims of this work on titanium(II) halide systems were firstly to see whether a range of halide adducts could be prepared and secondly, to examine the spectral and magnetic properties of any compounds formed since titanium(II) is a d^2 system which has received little attention.

It was found that a considerable range of complexes could be prepared from titanium(II) chloride and a few were also prepared from titanium(II) bromide. These had the general formulae TiX_2,2L or TiX_2,B depending on whether a monodentate or a bidentate ligand was used. The methyl cyanide adducts, $TiX_2,2CH_3CN$, were widely used as starting materials in these preparations as the dihalides appeared to be oxidised by some ligands and replacement reactions occur more rapidly than reactions with the straight halides. Complete replacement of the methyl cyanide was achieved by the oxygen and aromatic nitrogen donors but no replacement occurred with triphenylphosphine. Infrared spectra (4000-400 $cm.^{-1}$) showed that the ligands were indeed coordinated and the conductivities of a number of the compounds showed that they were non-ionic. The compounds were insoluble in non-polar solvents which prevented the measurement of such physical properties as molecular weights in these solvents.

Two possible basic structures for the adducts TiX_2,2L and TiX_2,B were considered, either that the titanium was in an essentially tetrahedral environment or that it was octahedrally coordinated, with the coordination number raised by some form of bridging. The former structure implies discrete molecules and the largest single argument against it were the very low magnetic moments which are all ~ 1.0 B.M. instead of ~ 2.83 B.M. as expected for a d^2 system. On the other hand halogen bridging is known to occur in titanium halide compounds[23,24] and is presumed to be responsible for the very low moments of the dihalides themselves.[67] The bridged structure is therefore considered further, in spite of two rather surprising observations. Firstly, the solubilities of the $TiX_2,2CH_3CN$ and $TiCl_2$,2pyr complexes in the ligand appear to be very high, considerably greater than the monomeric titanium(III) ones, and secondly that the magnetic moment of $TiCl_2,2CH_3CN$ did not rise very much when dissolved in the ligand. The explanation of the latter effect seems to be given by the molecular weight of $TiCl_2,2CH_3CN$ in methyl cyanide which shows that the compound is at least dimeric even in boiling ligand

and may be even more associated at room temperature. Unfortunately molecular weights in solution could not be obtained with great accuracy and it is not known if the compound, when dissolved in methyl cyanide, immediately forms some stable species, say $[TiCl_2,3CH_3CN]_2$ or whether destruction of the halogen chain occurs gradually as a function of time, temperature or concentration. The room temperature magnetic moments of these compounds, and of $TiCl_2$,2DMF, are very similar to those of the dihalides, in spite of the magnetic dilution that would be expected on the introduction of ligands. By comparison Na_2TiCl_4[67] has a much higher moment (μ_{eff} = 2.43 B.M.). Lewis et al.[43] suggested that titanium(II) chloride was antiferromagnetic but were unable to decide whether the exchange occurred via a metal-metal or a superexchange mechanism. Starr et al. also studied the magnetic properties of titanium(II) chloride between 13.9 and 300°K and their plot for $1/\chi$ against temperature between 100 and 300°K is approximately linear, although it curves rapidly at lower temperatures.[42] Extrapolation for the range 100-300°K would give a value for θ, the Weiss constant of $\sim 300^{\circ}$. It is therefore interesting that both $TiCl_2,2CH_3CN$ and $TiCl_2$,phen appear to obey the Curie-Weiss law with θ between 30 and 50°. Although the significance

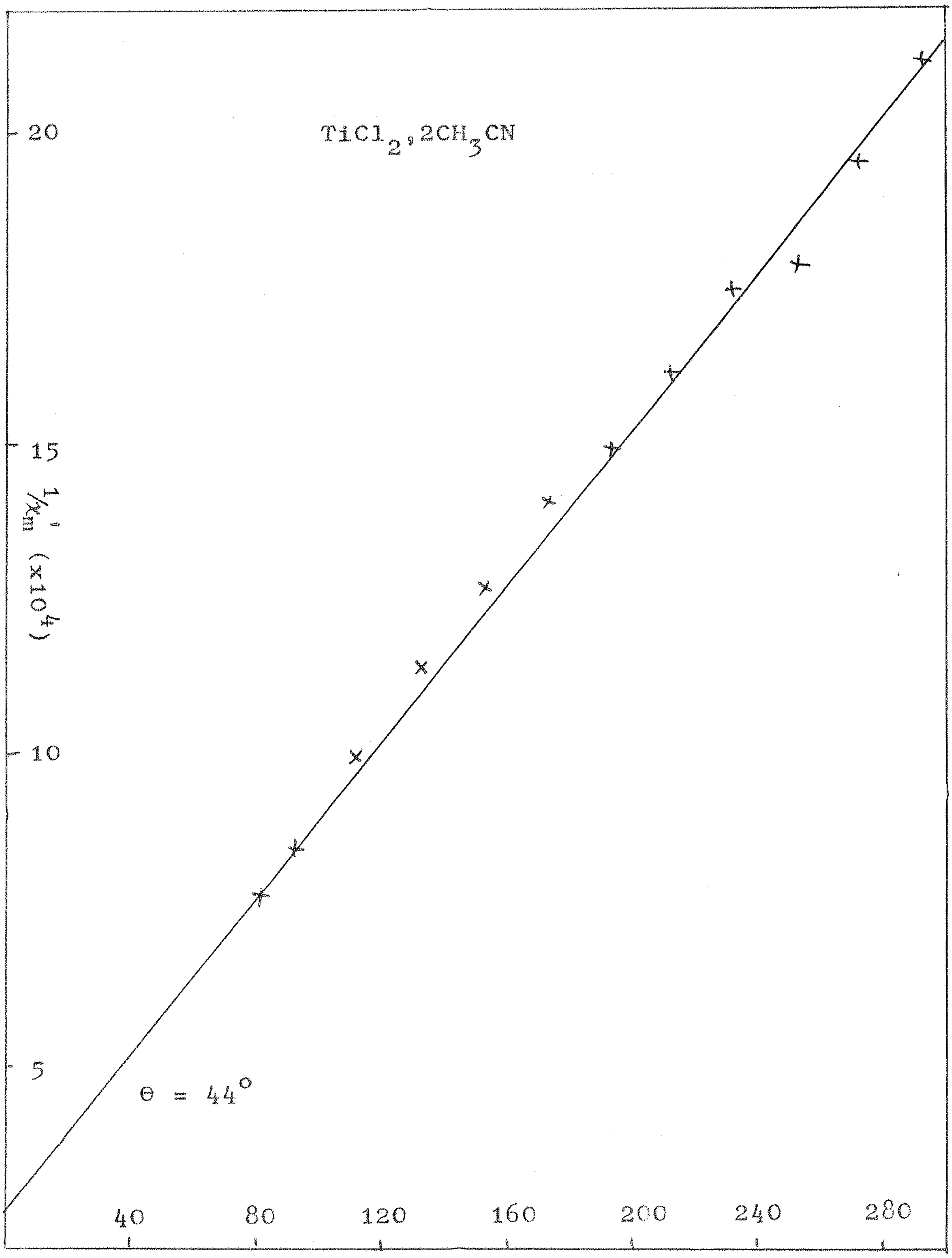

$TiCl_2,2CH_3CN$
$^1/\chi_m'$ (x10^4)
20
15
10
5
$\Theta = 44^\circ$
40
80
120
160
200
240
280

Fig. 8.1. T(°K)

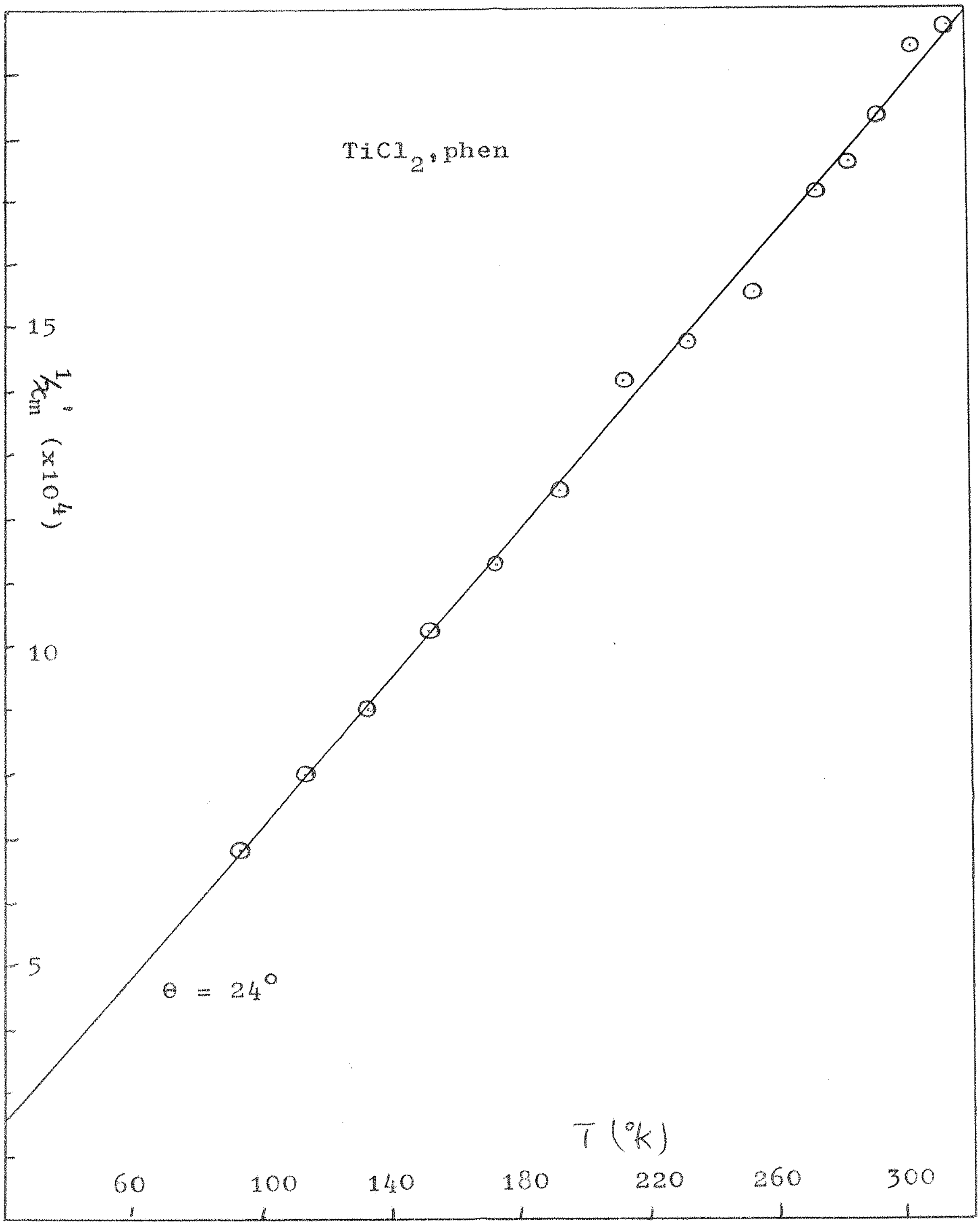


Fig. 8.2.

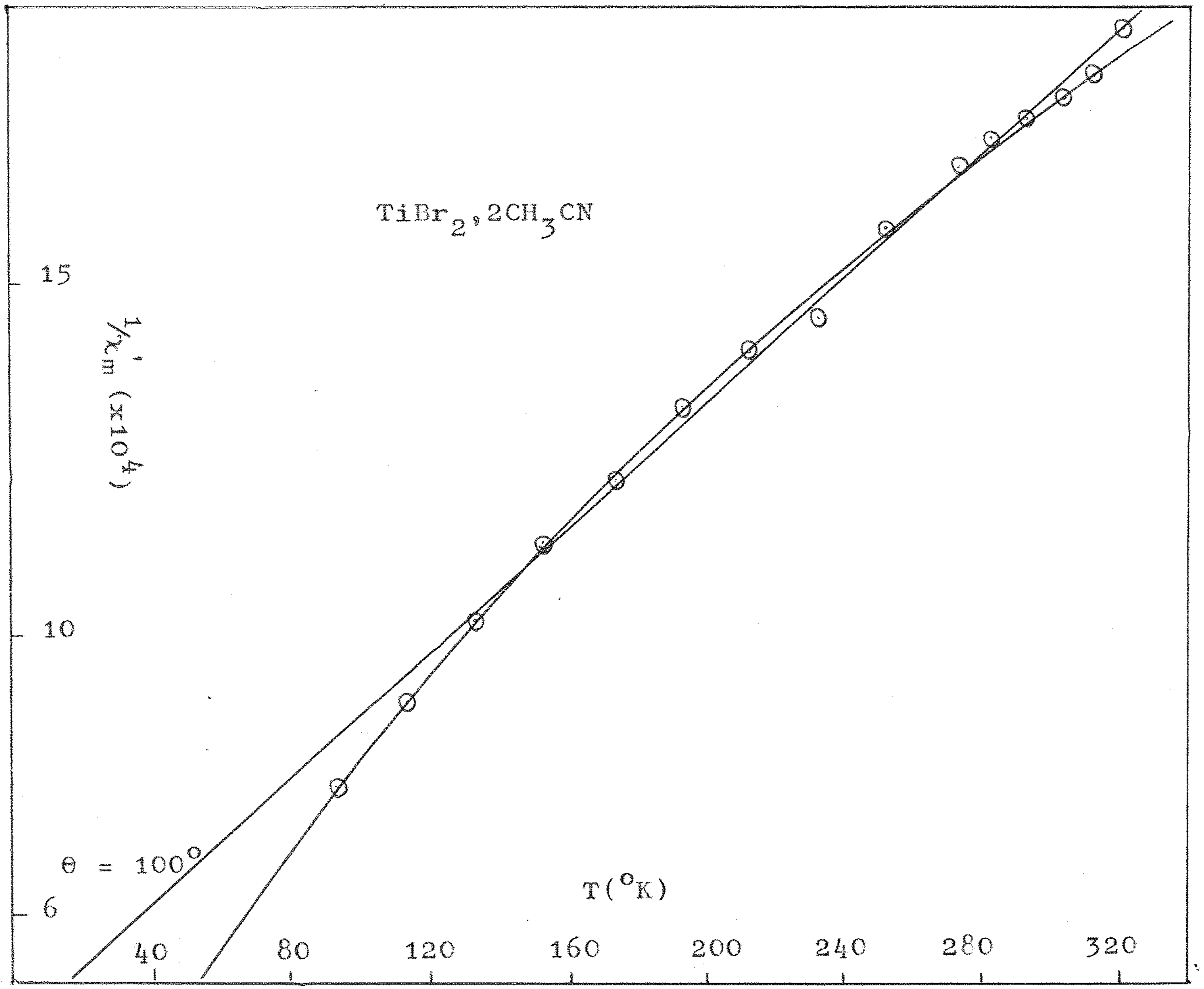
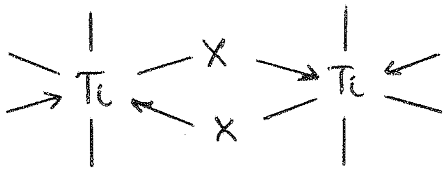
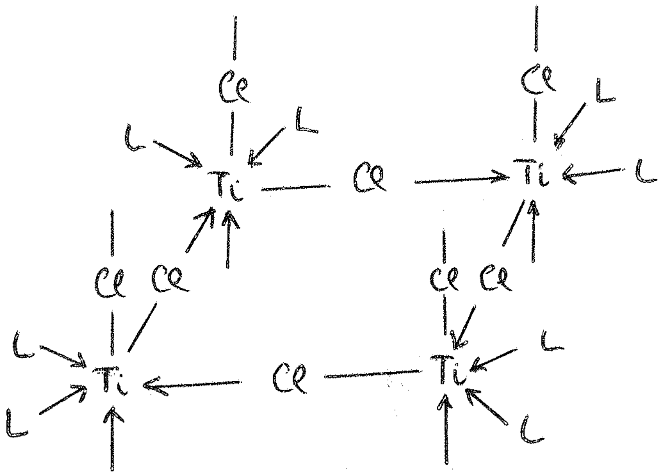
$TiBr_2, 2CH_3CN$
15
10
6
$^1/\chi_m'$ (x10^4)
θ = 100°
T(°K)
40
80
120
160
200
240
280
320

Fig. 8.3.

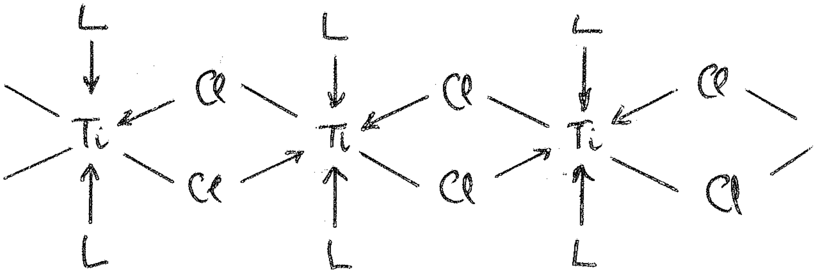
of this constant does not appear to be well understood the difference in its value, considering the chloride and complexes, may indicate that the mechanism of exchange has changed. The effect of field strength on the magnetic moments of $TiCl_2$,2pyr; $TiCl_2$,$2CH_3CN$; $TiCl_2$,phen and $TiBr_2$,CH_3CN was checked but no dependence was found; however this excludes neither of the exchange mechanisms mentioned earlier. There are a number of possible structures but assuming a six coordinated halogen bridged one the three essentially different possibilities are (I) a structure involving a single halogen bridge; (II) a structure with two halogens comprising a bridge and (III) with both types of bridge. (P.118)

Structure (I) is rather similar to the tetrameric MoF_5[135] but such single halogen bridges are more common with fluorine than chlorine. The magnetic results in methyl cyanide solution for $TiCl_2$,$2CH_3CN$ are more consistent with (III) as disruption of the single halogen bridge still leaves a dimeric species in which magnetic exchange is quite likely. The slight rise in the magnetic moment measured in solution can then be understood if most of the exchange occurs via the

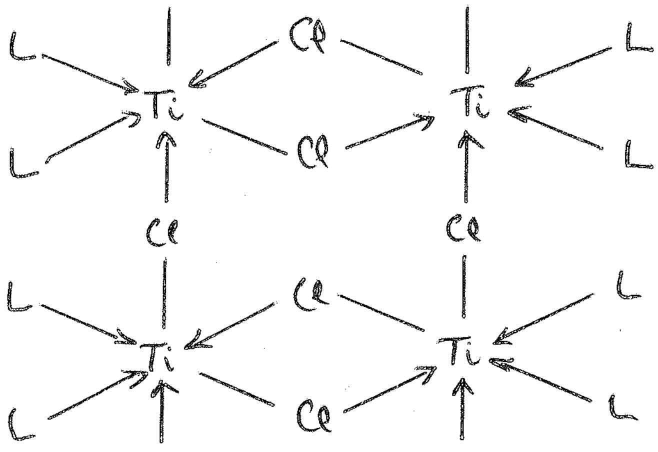




(I)



(II)



(III)

unit but a small amount results from the

$$\longrightarrow \mathrm{Ti} \,\text{—}\, X \longrightarrow \mathrm{Ti} \,\text{—}$$

system. The magnetic moment in solution is less easy to explain on the basis of structures (I) or (II) for the molecular weight suggests that comparatively small units are then present. A change in structure from an infinite polymer to a dimeric molecule should reduce the exchange by about 50% (structure (II)) or ~ 75% (structure (I)) if each bridge contributes equally to exchange. This does, however, assume that the degrees of association in methyl cyanide at room temperature and at 80°C are similar.

Structural evidence from other physical techniques is not forthcoming. Low infrared spectra (table 8.4) showed that the titanium-halogen bands were unusually broad and weak. In two cases, $TiCl_2,2pyr$ and $TiCl_2,2C_4H_8O$, the close resemblence of the spectra to those of $TiCl_3,3pyr$[136] and $TiCl_3,3C_4H_8O$[53] suggests that in spite of all precautions oxidation occurred during preparation of the mull or measurement. The spectra of $TiCl_2$ and Na_2TiCl_4 indicate that the titanium-chlorine stretching frequencies are ~ 300 $cm.^{-1}$ and the spectrum of the 1:10-phenanthroline compound shows a strong peak, presumably Ti-Cl, at 317 $cm.^{-1}$. This is appreciably lower than the Ti-Cl stretching frequencies in titanium(III) as these occur ~370 cm.$^{-1}$ and is consistent with the change in oxidation state.

Electronic spectra of most of the compounds have been measured in the solid state and solution (table 8.1). They show strong absorption from ~10,000 cm.$^{-1}$ to the limit of measurement in the ultraviolet (e.g. fig. 8.4). Superimposed upon this absorption, in the visible, there are a number of shoulders which are frequently weak but in the ultraviolet region a few peaks are observed. $TiBr_2$,bipyr, for example, shows the modified $\pi \rightarrow \pi^*$ transition of coordinated bipyridyl at 32,200 cm.$^{-1}$. The cause of this broad absorption is not clear and several possible explanations are considered. The intensity of the absorption (corresponding to an optical density of ~ 1.0 for reflectance throughout the visible region) indicates that it is not due to d-d transitions. Change transfer transitions of the type $Cl(\pi) \longrightarrow Ti(d)$ are expected at higher energy in titanium(II) than in titanium(III) (chapter VI) and should not start until ~30,000 cm.$^{-1}$. In any case experience with titanium(III) and (IV) and numerous other transition metal halide systems suggests that absorptions of this type can be resolved and do not give rise to the type of continuous absorption observed in this case. An interaction band arising

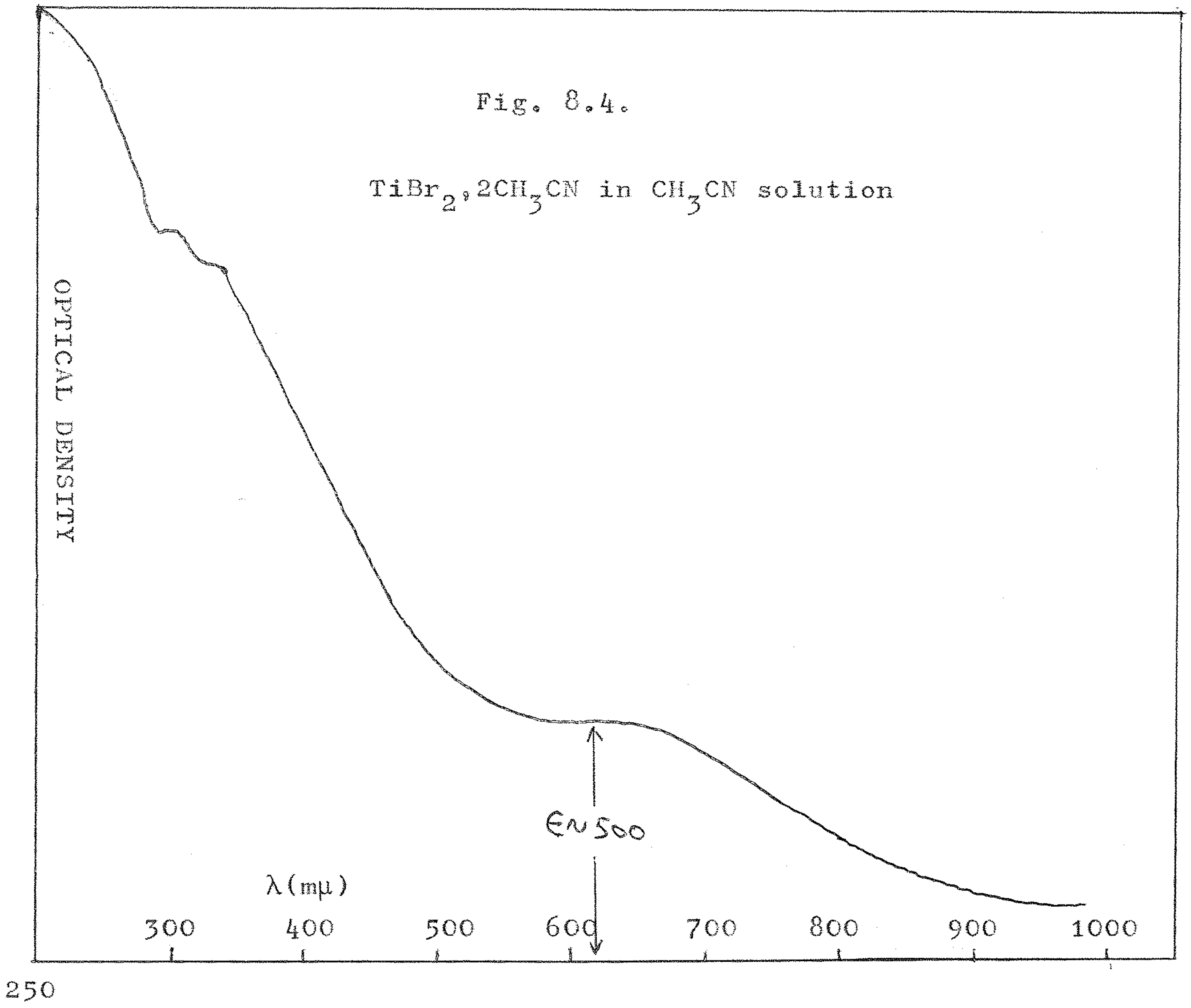


Fig. 8.4.

$TiBr_2, 2CH_3CN$ in CH_3CN solution

from the presence of titanium ions in two different oxidation states is a possible explanation but seems unlikely firstly because the analyses for a range of compounds are quite straightforward and secondly because the absorption is so broad; the Ti(III)-Ti(IV)[119] transition is very narrow by comparison. It is not anticipated that $L(\pi) \longrightarrow Ti(d)$ or $Ti(d) \longrightarrow L(\pi^*)$ bands would be expected at such low energy, particularly for $TiCl_2,2CH_3CN$ and $TiCl_2,2C_4H_8O$ (chapter VI).

It seems possible that this absorption is due to solid state cooperative effects, particularly in view of the strong magnetic exchange which shows that the metal atoms cannot be considered independently. The titanium(III) halides are known to show similar behaviour (chapter VI). The dihalides $TiCl_2$ and $TiBr_2$ (fig. 8.5) have similar low energy peaks. It is not clear whether the interactions are between pairs of titanium atoms or over a larger unit but if the latter is the case the width of the transition can be explained by promotion of delocalised electrons to a 'conduction' type band. The similarity of the spectra in solid and solution, however, suggests that a comparatively small unit is capable of causing the spectrum.

Efforts to obtain a more normal system by the

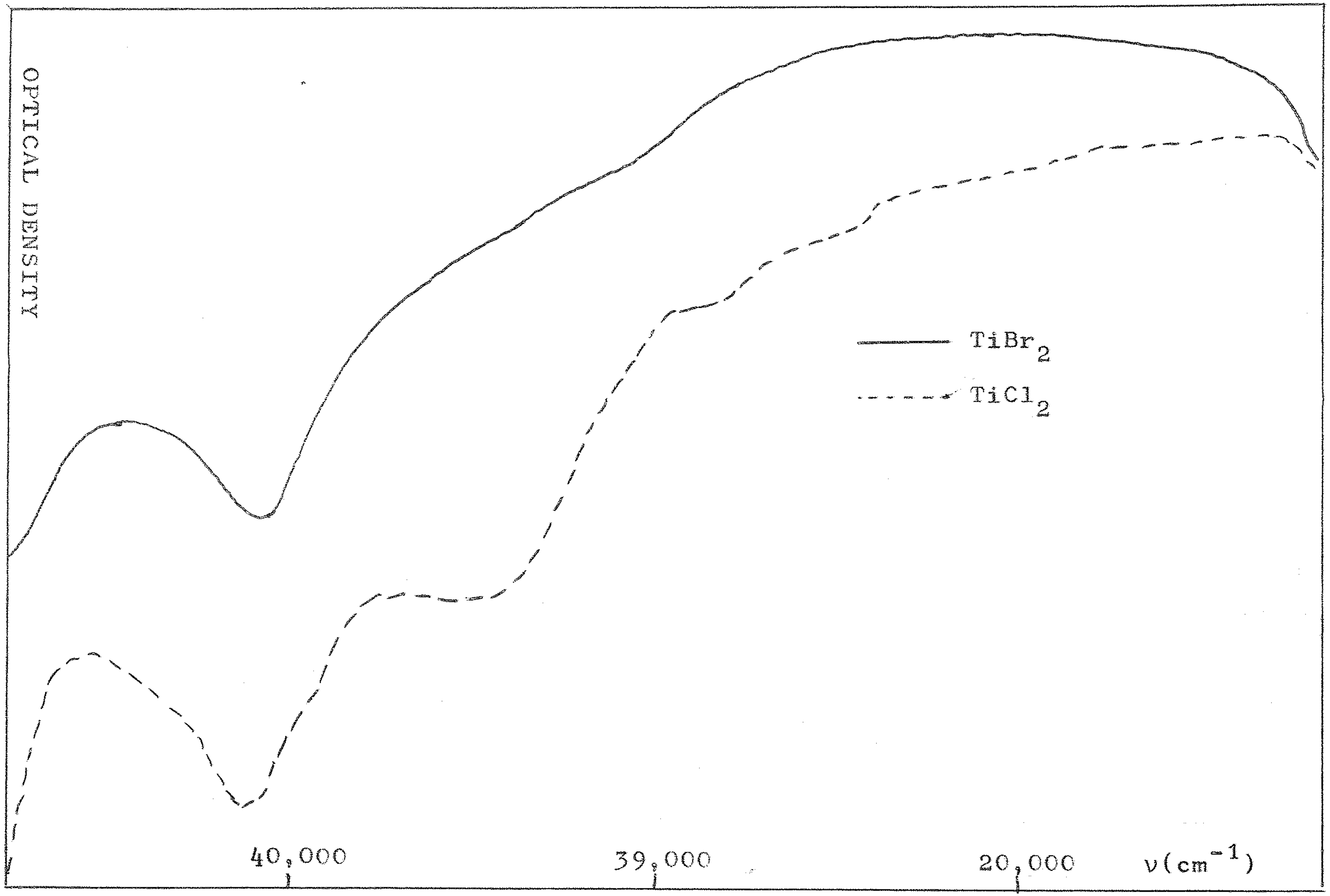


Fig. 8.5

introduction of more ligand (e.g. by fusion with 2:2'-bipyridyl) failed.

The reaction between titanium(II) chloride and pyridinium chloride was carried out to see if the ion $[TiCl_6]^{4-}$ was formed; although the high charge made this rather unlikely. In fact the hexachlorotitanate(III) was obtained and Greene[112] subsequently found that an analogous reaction occurs with vanadium(II) chloride to give $[PyH_3][VCl_6]$. The surprising observation is that the magnetic moment and visible spectrum of $[TiCl_6]^{3-}$ prepared in this way (fig. 8.6) are significantly different to those reported by Fowles and Russ[59] for their product which was prepared from titanium(III) chloride.

Source	μ_{eff} (B.M.)	visible reflectance ($cm.^{-1}$)	
$TiCl_6^{3-}$ from $TiCl_3$	1.68	12,800	11,000sh
" " $TiCl_2$	1.80	14,100	11,800sh

An X-ray powder photograph of the compound prepared from $TiCl_2$ would be useful for comparison with the results on the $TiCl_3$ product. The $[TiCl_6]^{3-}$ prepared from Ti(II) dissolves in methyl cyanide to give essentially the same spectrum as Hoodless reported for $TiCl_3$,3pyr in this solvent,[97] when the species present was thought to be $[TiCl_2,3pyr,CH_3CN]^+ Cl^-$.

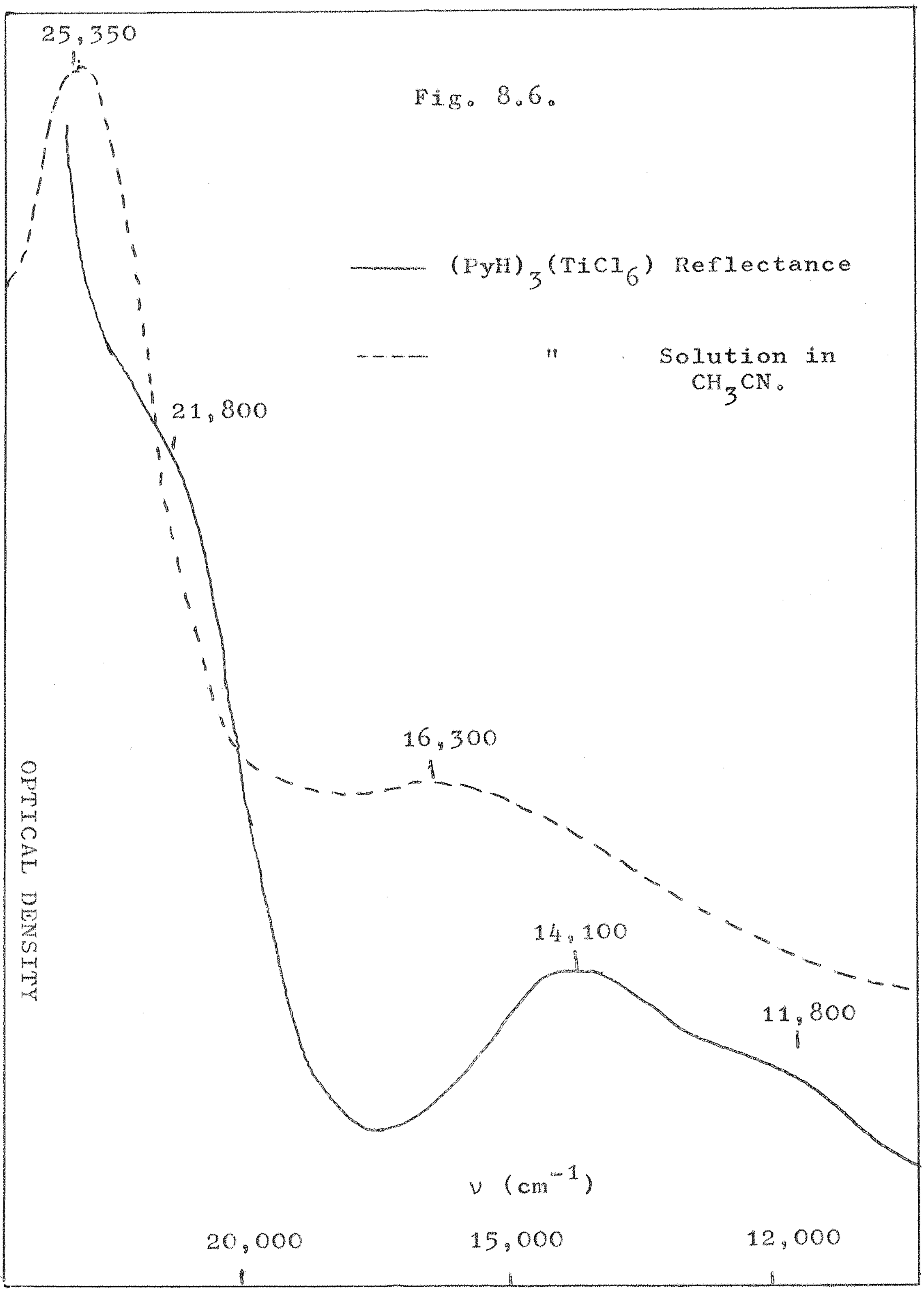
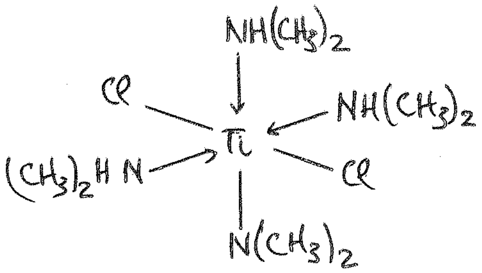


Fig. 8.6.

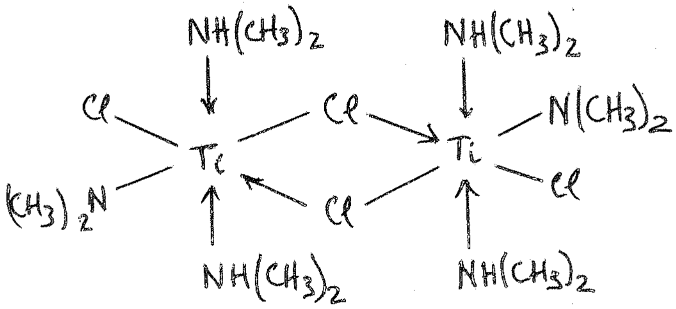
25,350
21,800
16,300
14,100
11,800
—— $(PyH)_3(TiCl_6)$ Reflectance
---- " Solution in CH_3CN.
OPTICAL DENSITY
ν (cm^{-1})
20,000
15,000
12,000

The reactions of $TiCl_2$ and Na_2TiCl_4 with amines are interesting in view of the reported ammine $TiCl_2,4NH_3$.[68] Trimethylamine causes complete oxidation of Na_2TiCl_4 giving $TiCl_3,2N(CH_3)_3$ although reaction with $TiCl_4$ gives reduction to the same product.[97] Neither mechanism is understood. Pyridine is another ligand which frequently causes reduction of the early transition metal halides in high oxidation states (e.g. of $TiCl_4$[97]) but which oxidises titanium(II) chloride and bromide.

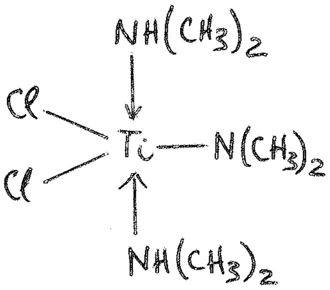
Titanium(III) chloride is known to form a green 1:3 adduct with dimethylamine, $TiCl_3,3NH(CH_3)_2$[103] and when a concentrated solution of this was prepared[137] for measurement of its magnetic moment a red crystal was formed in the tube. It seems likely that this red crystal had the same composition as those prepared from $TiCl_2$ and Na_2TiCl_4 reactions with dimethylamine. The latter appear to be titanium(III) compounds and the structure



is proposed. The red crystal observed in $TiCl_3/NH(CH_3)_2$ solution therefore corresponds to partial amminolysis (of $TiCl_3,3NH(CH_3)_2$) which is not surprising as both diethylamine and di-n-propylamine are known to cause aminolysis of titanium(III) chloride.[103] The green product $TiCl_2,3NH(CH_3)_2$ also appears to be a titanium(III) complex and the rather low moment may have been due to partial oxidation as this product was very unstable. The structure is not known but the most likely possibilities are:



or



CHAPTER IX

DIBROMOBIS(1:2-DIMETHOXYETHANE)TITANIUM(III) TETRABROMO(1:2-DIMETHOXYETHANE)TITANATE(III)

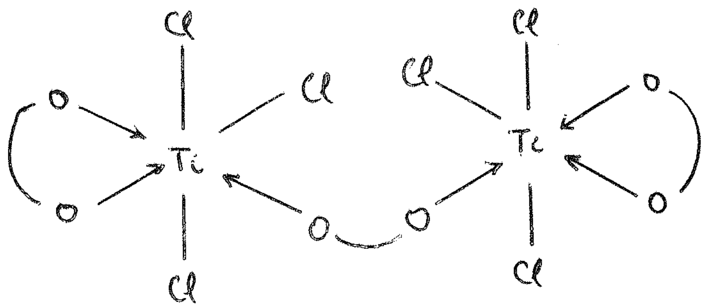
PREPARATION, STRUCTURE AND PROPERTIES

Reaction of titanium(III) bromide and excess 1:2-dimethoxyethane under reflux for eight hours gave green crystals and a pale green solution. The green crystals were separated and analysed:

	Ti%	Br%	C%	H%
Found	10.7	55.3	16.7	3.7
$TiBr_3,1.5C_4H_{10}O_2$ requires	11.3	56.7	17.0	3.5

The magnetic moment at 20°C was 1.67 B.M. confirming that the product was a compound of titanium(III).

1:2-dimethoxyethane had previously been found to form an analogous compound with titanium(III) chloride[47] and Greene has also prepared the complexes $VX_3,1.5C_4H_{10}O_2$[146] (where X = Cl or Br). A number of complexes of the early transition metals having this stoichiometry but with 2:2'-bipyridyl as the ligand are known, and have been discussed in chapter IV, but the structure of none of them is known with certainty. Two structures have been suggested for $TiCl_3,1.5C_4H_{10}O_2$,[47] either the ionic $[TiCl_2,2C_4H_{10}O_2]$ $[TiCl_4,C_4H_{10}O_2]$ or the ligand bridged one:



and the same possibilities arise for $TiBr_3,1.5C_4H_{10}O_2$. To clarify the situation it was decided to carry out an X-ray structure analysis.

Determination of the structure

A brief description of the principles involved is given in chapter II. Experimental details, e.g. mounting of the crystal and exposure times are given in appendix D.

The crystal selected was approximately 0.3 mm in all dimensions and did not have a sufficiently well defined axis for optical alignment. Orientation precession photographs were therefore taken, rotating the crystal by ten degrees between each photograph. These photographs were examined for evidence of the strong radial 'streaks' (associated with each reflection), whose ends define a circle, when a zero or principal reciprocal lattice level is perpendicular to the incident X-ray beam. In addition the orientation of the crystal in the other directions was also adjusted, using the goniometer arcs, during the efforts to find a principal plane; after about forty photographs had been taken one was located and centred by the arc and spindle adjustments outlined in the camera manual. A zero level photograph was then taken and this revealed what seemed likely to be a principal lattice row. Further orientation photographs were then taken, changing only the spindle setting, until a second prominent diffraction ring was found. A zero level photograph showed that a zero reciprocal lattice plane had been located in which the axes were orthogonal, and one quadrant of reflections unique. A first level photograph indicated that the crystal belonged to the monoclinic system, with the principal row located on the first zero level photograph being the third axis. The crystal rotation axis was found to be parallel to the b*c* diagonal (i.e. the reciprocal (011) direction). The first and second level photographs showed the systematic absences to be h, 0, 1, for 1 odd and 0, k, 0, for k odd thus determining the space group unambiguously as P_{2_1}/c. The cell dimensions were determined by measurement of the zero level photographs and found to be: a = 15.61 Å, b = 13.35 Å, and c = 14.05 Å. The angle between a* and the b*c* diagonal was determined from the camera spindle settings and β, the angle between the a and c axes was calculated. The density, determined by flotation, showed there to be eight monomer units in the unit cell, ρ_{reqd} = 2.08g/cc, ρ_{obs} = 2.00g/cc.

As it did not appear feasible to collect the necessary intensity data on precession photographs the crystal was transferred to the Weissenberg camera. This necessitated reorientation of the crystal so that the rotation axis lay along the (011) direction of the real cell, i.e. the bc diagonal (since for a monoclinic crystal only b and b* coincide). A zero level Weissenberg photograph revealed a number of spurious reflections and an attempt to eliminate them by narrowing the gap in the layer line screen was only partially successful. When an integrated Weissenberg photograph was taken some of these spurious spots overlapped with those whose intensities were required and it was therefore decided to take unintegrated photographs and estimate the intensities visually. Twelve reciprocal lattice levels (h,k,k - h,k,k+12) were photographed using the equi-inclination method. Indexing was difficult due to the low symmetry of the crystal, the spurious spots and the diagonal mounting. The last, however, helped to some extent as a number of spots measured on the lower levels were duplicated on the higher levels which allowed correlation of the intensities between levels, thus checking the indices. In spite of this it was not found possible to index levels higher than eight. Excluding systematic absences the eight levels gave 1,350 reflections of which 997 were independent and 201 of the latter unobserved. Lorentz-polarisation factors were applied graphically[147] and those reflections which had been measured twice were averaged. Unobserved reflections were assigned half the minimum observed intensity. Although the absorption coefficient for copper radiation is high (μ = 150 cm.$^{-1}$) owing to the relatively small size of the specimen and its approximately spherical shape absorption corrections were neglected, $\mu R = 2.0$ (R = radius of crystal).

Using the complete set of $F^2(hkl)$'s so obtained the three dimensional Patterson function was evaluated (at intervals of 1/40ths in x and 1/30ths in y and z) and a search made for the vectors arising from Br-Br interactions using the origin peak to calibrate the map. Although several possibilities for bromine positions were found, at this stage none was thought to be sufficiently reliable to be used in the derivation of phases on which to carry out an electron density calculation. The difficulty in locating the bromine atoms was due principally to the fact that, there being six per assymetric unit, the anticipated vector height is not sufficient to make then readily observable. Accordingly two sharpened Patterson maps were calculated (one sharpened for all atoms and one only for bromine atoms). Using these in conjunction with the unsharpened map, coordinates for two of the bromine atoms were derived, and tentative positions for two others were found. Rather than use all four, two were used to phase an electron density map and since the positions with the y coordinates interchanged are equally consistent with the Patterson, two Fourier maps were calculated. As anticipated one of these looked much more promising than the other and in fact gave the other four bromine atom positions, which fitted well with the sharpened Patterson. These positions indicated that the molecule was not dimeric. An electron density map phased on the six bromines showed the positions of the two titanium atoms and their coordinates together with those of the bromine atoms were used as variables in one cycle of full matrix least squares refinement (using O.R.F.L.S. in the X-ray 63 system). The new coordinates were used to derive phases for an electron density map which allowed the positions of all the oxygen atoms and four of the carbon atoms to be found. The residual now stood at 37%. Using the positions of all atoms except carbon a further cycle of least squares refinement brought R to 27% and a difference Fourier map with $(F_o - F_c)$ as coefficients allowed the remaining eight carbons to be located. After two more cycles of isotropic refinement R = 23.2%. The bond lengths and angles quoted in this thesis are based on the structure at this stage but refinement is being continued.

Calculations were performed using the X-ray 63 system on the I.B.M. 7090 computer at Imperial College and the Atlas at Harwell. Atomic scattering factors were from the International Tables for X-ray Crystallography Vol. III.

Description of the structure

Atomic coordinates and bond lengths are given in tables 9.1 and 9.2. The principal feature of the crystal structure is the existance of essentially isolated $TiBr_2,2L$ and $TiBr_4,L$ units, each titanium being octahedrally coordinated. The bromine atoms in the cation are cis and all the 1:2-dimethoxyethane molecules have the expected gauche conformation. The titanium-bromine distances in the cation are significantly shorter than in the anion (table 9.2) which is consistent with the greater steric repulsion of four

Table 9.1

Atom	X	Y	Z	B*
Br_1	0.7356	0.2493	0.0478	0.1557
Br_2	0.8153	0.0610	0.2544	0.9481
Br_3	0.4103	0.3318	0.3099	0.4992
Br_4	0.3759	0.0535	0.2919	1.7413
Br_5	0.9392	0.0924	0.0714	-0.4463
Br_6	0.0482	0.1702	0.3425	0.4989
Ti_1	0.8903	0.2021	0.1863	-0.2115
Ti_2	0.3711	0.1938	0.1855	1.1349
O_1	0.3198	0.0937	0.0482	-1.4381
O_2	0.2268	0.2115	0.1255	-4.2098
O_3	0.9495	0.3257	0.1545	-2.7071
O_4	0.8667	0.3217	0.2744	0.5517
O_5	0.5067	0.1696	0.1808	2.9439
O_6	0.3656	0.3340	0.0695	6.1364
C_1	0.9284	0.3622	0.0059	
C_2	0.3992	0.2920	0.0669	
C_3	0.9534	0.4100	0.2292	
C_4	0.9208	0.3885	0.4048	
C_5	0.2968	0.3688	0.0489	
C_6	0.1744	0.1446	0.0337	
C_7	0.3650	-0.0051	0.0108	
C_8	0.1791	0.2710	0.1799	
C_9	0.5737	0.1259	0.2729	
C_{10}	0.4639	0.2889	0.0671	
C_{11}	0.8764	0.4354	0.2502	
C_{12}	0.2534	0.2532	-0.0070	

*B gives the isotropic temperature factors. At this stage carbon temperature factors were not refined.

Table 9.2

Interatomic Distances and Angles

Bond	Length (Å)	S.D. (Å)	Bond	Length (Å)	S.D. (Å)
Ti_1-Br_1	2.51	0.04	Ti_1-O_3	2.02	0.09
Ti_1-Br_2	2.59	0.04	Ti_1-O_4	2.14	0.09
Ti_1-Br_5	2.51	0.04	Ti_2-O_1	2.22	0.08
Ti_1-Br_6	2.60	0.04	Ti_2-O_2	2.08	0.08
Ti_2-Br_3	2.44	0.04	Ti_2-O_5	2.17	0.11
Ti_2-Br_4	2.38	0.04	Ti_2-O_6	2.46	0.09

	Angle	S.D.		Angle	S.D.
$Br_1-Ti_1-Br_2$	91.8°	1.5°	$Br_3-Ti_2-Br_4$	101.9°	1.4°
$Br_1-Ti_1-Br_5$	95.7°	1.5°	$Br_3-Ti_2-O_1$	167.8°	2.5°
$Br_1-Ti_1-Br_6$	169.9°	1.5°	$Br_3-Ti_2-O_2$	97.5°	2.8°
$Br_2-Ti_1-Br_5$	93.3°	1.5°	$Br_3-Ti_2-O_5$	99.3°	2.7°
$Br_2-Ti_1-Br_6$	88.8°	1.5°	$Br_3-Ti_2-O_6$	80.5°	2.2°
$Br_5-Ti_1-Br_6$	91.1°	1.5°	$Br_4-Ti_2-O_1$	89.1°	2.5°
$O_3-Ti_1-Br_1$	90.6°	2.8°	$Br_4-Ti_2-O_2$	96.0°	2.8°
$O_3-Ti_1-Br_2$	172.5°	2.8°	$Br_4-Ti_2-O_5$	96.4°	2.8°
$O_3-Ti_1-Br_5$	92.9°	2.8°	$Br_4-Ti_2-O_6$	177.6°	2.7°
$O_3-Ti_1-Br_6$	88.7°	2.8°	$O_1-Ti_2-O_2$	75.7°	3.3°
$O_4-Ti_1-Br_1$	85.9°	2.8°	$O_1-Ti_2-O_5$	84.6°	3.5°
$O_4-Ti_1-Br_2$	99.6°	2.8°	$O_1-Ti_2-O_6$	88.6°	3.0°
$O_4-Ti_1-Br_5$	164.9°	2.8°	$O_2-Ti_2-O_5$	156.6°	3.8°
$O_4-Ti_1-Br_6$	87.3°	2.8°	$O_2-Ti_2-O_6$	84.0°	3.4°
$O_3-Ti_1-O_4$	73.6°	3.6°	$O_5-Ti_2-O_6$	82.7°	3.7°

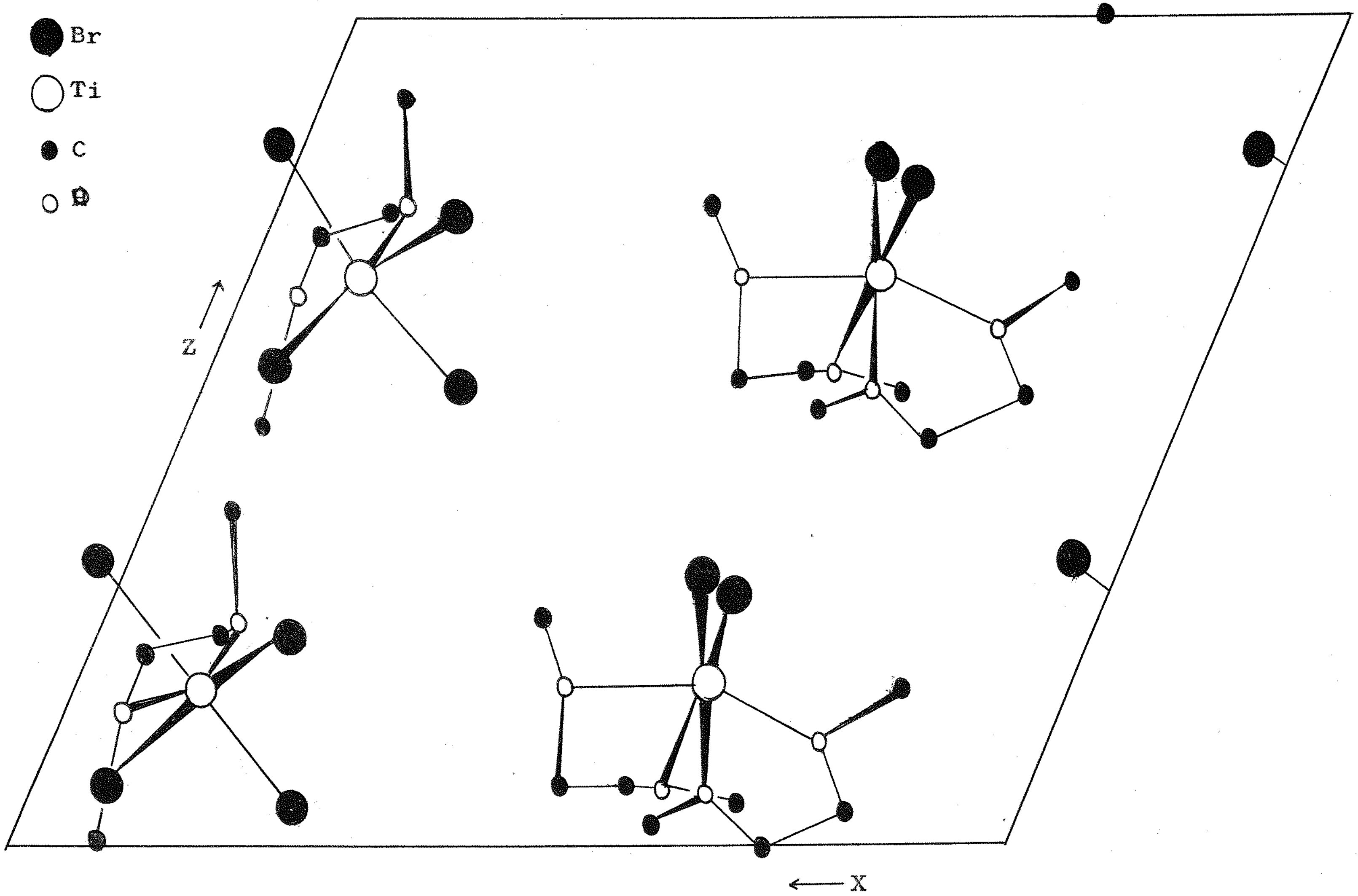
bromine atoms in the anion and the different charges on the ions. In the five coordinate $TiBr_3,2N(CH_3)_3$ the titanium-bromine distances were ~2.4Å and it therefore appears that the effect of a positively charged metal is approximately equivalent to a reduction in coordination number from six to five. The standard deviations on the light atoms are large, owing to the comparatively high R at this stage and the large number of heavy atoms, and only the titanium-oxygen distances are listed (table 9.2). The bromine-titanium-bromine angle in the cation (101 ± 1.4°) shows considerable distortion from an octahedron. Figures 9.1 and 9.2 show the distribution of molecules in the unit cell and the arrangement of ligands in each ion.

Discussion of properties

The structure shows that the compound is ionic and that the cation exists as the cis isomer. This is interesting as Greene[102] has postulated that $[VBr_2,2bipyr]Br$ and $[VCl_2,2phen]Cl$ have the cis structure on the basis of low infrared evidence.

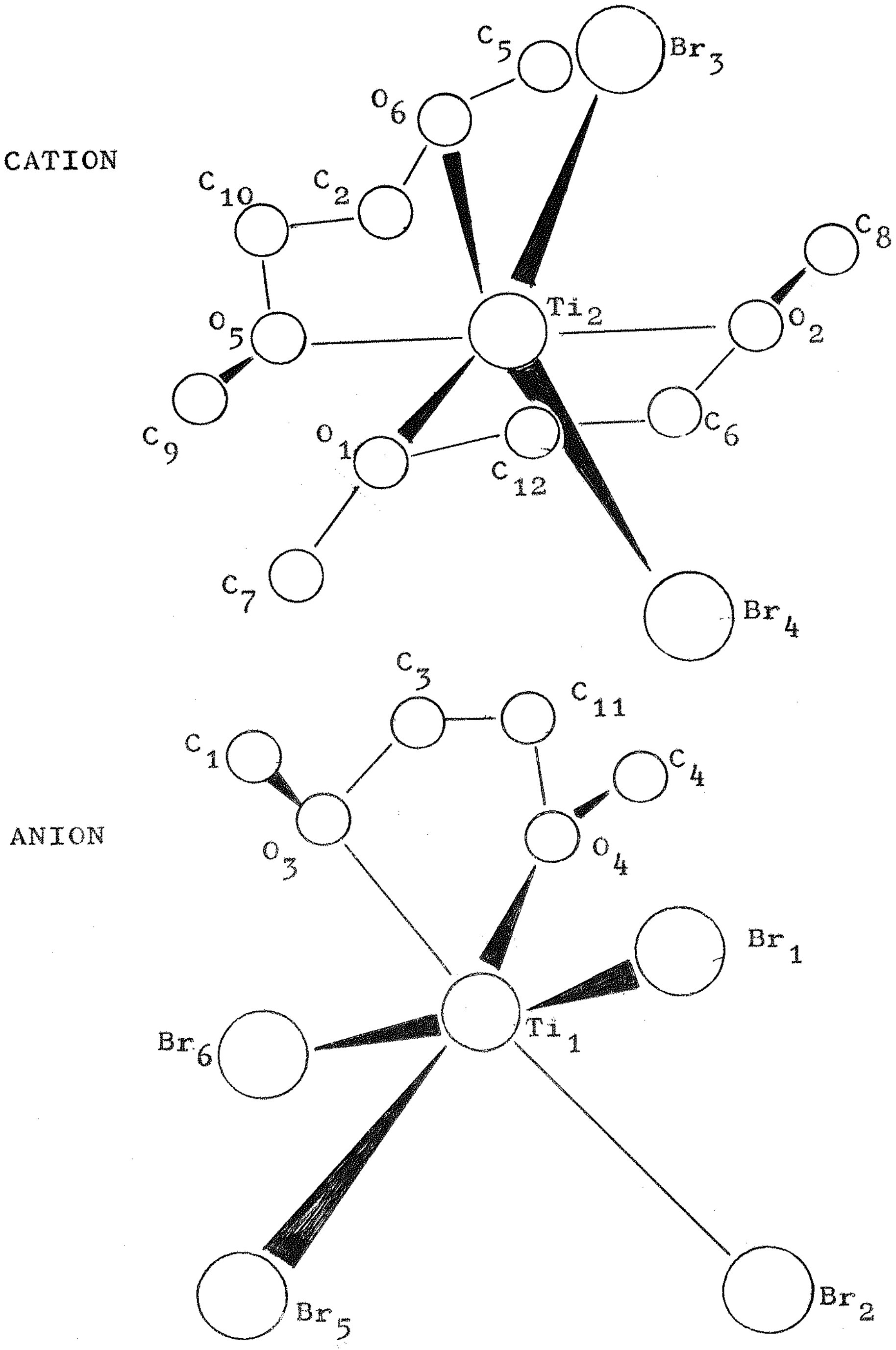
This appears to be the first structural determination of a $MX_3,1.5B$ type complex although it was suggested in 1964 that $IrX_3,1.5phen$ had the structure

Fig. 9.1



Projection on (010) for $y = 0 \rightarrow \frac{1}{2}$

Fig. 9.2


CATION

ANION

$[IrX_2,2phen][IrX_4,phen]$ (where X = Cl, Br or I).[106] It has also been shown in chapters III and IV that $TiX_3,1.5bipyr$ have the ionic structure and Greene[102] believes that the same is true of the analogous vanadium(III) chloride and bromide compounds. It is probable that $VCl_3,1.5C_4H_{10}O_2$; $VBr_3,1.5C_4H_{10}O_2$[146] and $TiCl_3,1.5C_4H_{10}O_2$[47] all have the same structure as $TiBr_3,1.5C_4H_{10}O_2$ and it therefore seems that the ionic structure is generally the favoured one.

The visible reflectance spectrum of $[TiBr_2,2C_4H_{10}O_2]$ $[TiBr_4,C_4H_{10}O_2]$ is consistent with the ionic structure for a very broad peak is observed which is composed of the d-d transitions for the two ions. The titanium(III) chloride compound also has a broad band and it is at slightly higher energy than in the bromide, as expected since $Dq_{Cl^-} > Dq_{Br^-}$.

Table 9.3

Electronic spectra (cm.$^{-1}$)	
$TiCl_3,1.5C_4H_{10}O_2$	
Refl.	13,800br 30,800 37,600 45,000
Soln. $C_4H_{10}O_2$	15,530 31,700sh 37,450 41,800
$TiBr_3,1.5C_4H_{10}O_2$	
Refl.	13,160vbr ~22,000sh 29,900 37,000 45,400
Soln. $C_4H_{10}O_2$	14,200(ε=12) 19,100sh 29,900 34,500sh 41,000sh

If Dq for $C_4H_{10}O_2$ is taken as $2 \times Dq_{C_4H_8O_2}$ (1660 cm.$^{-1}$) when the latter is acting as a monodentate ligand and values of 1370 cm.$^{-1}$ and 1040 cm.$^{-1}$ are used for Dq_{Cl^-} and Dq_{Br^-}[103] respectively then the positions of the d-d transitions due to the various species can be predicted using the 'average environment rule':[80]

X	$[TiX_2,2C_4H_{10}O_2]^+$	$[TiX_4,C_4H_{10}O_2]^-$
Cl	15,600	14,700
Br	14,500	12,460

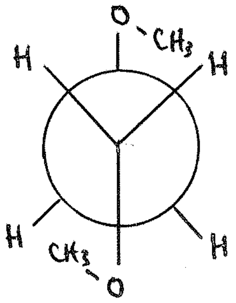
Table 9.3 shows that the spectra in ligand solution, are markedly different to reflectance. The visible band moves to higher energy and is sharper in solution but the explanation is not clear unless the reaction:

$$[TiBr_4,C_4H_{10}O_2]^- + C_4H_{10}O_2 = [TiBr_2,2C_4H_{10}O_2]^+ + 2Br^-$$

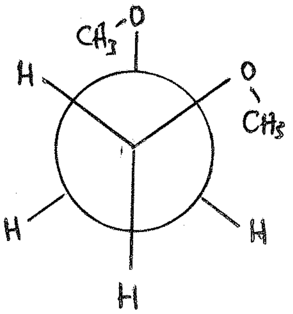
occurs.

The infrared spectrum of $[TiBr_2,2C_4H_{10}O_2]$ $[TiBr_4,C_4H_{10}O_2]$ shows that the 1:2-dimethoxyethane is fully coordinated as the C-O-C stretch, which occurs at 1120 cm.$^{-1}$, in the free ligand is not present in the complex. In principle 1:2-dimethoxyethane can exist in three forms and Miyake[148] has assigned CH_2

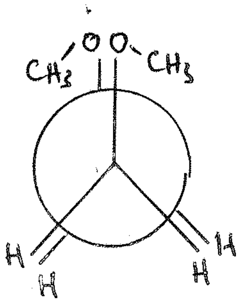
rocking modes at 853 cm.$^{-1}$ (which he considered to be due to the trans form) and 938 and 925 cm.$^{-1}$ (due to the gauche).



TRANS



GAUCHE



CIS

Clark has suggested that these assignments are incorrect as he has prepared the complexes $TiX_4,C_4H_{10}O_2$ where X = Cl or Br) and found that the 853 cm.$^{-1}$ band is present.[149] As these complexes are monomeric with chelating 1:2-dimethoxyethane the conformation cannot be trans and thus Miyake's assignment is incorrect. Clark points out that the 938 and 925 cm.$^{-1}$ peaks are missing in the complex, the inference being that one or both of these arise from the trans form. Chelation could occur via the cis or gauche conformations for although the cis form is sterically unstable in the free ligand, due to the methylene hydrogens being eclipsed, it might be stabilised in an adduct if the oxygen-oxygen separation was just correct for chelation to a particular metal. Clark came to the conclusion that for titanium(IV) the oxygen-oxygen separation would be more suitable for chelation in the gauche form.

If 1:2-dimethoxyethane was to bridge between two titanium atoms it would have to exist in the trans form but examination of the spectra for $MX_3,1.5C_4H_{10}O_2$ (where M = Ti or V and X = Cl or Br) always showed that the band ~850 cm.$^{-1}$ was present but that those around 930 cm.$^{-1}$ were absent, suggesting that the ligand chelated. Crouch,[150] however, has recently prepared $WOCl_4,\frac{1}{2}\,C_4H_{10}O_2$ in which the ligand must bridge but the infrared still shows a peak close to 850 cm.$^{-1}$ in addition to peaks ~950 cm.$^{-1}$ indicating that the presence or absence of a band close to 850 cm.$^{-1}$ does not serve as a criterion for the mode of coordination. One surprising feature about the spectrum of 1:2-dimethoxyethane is the apparent absence of a symmetric C-O-C stretching vibration. The infrared spectra of both the titanium(III) chloride and bromide adducts are given in table 9.4 but their low infrared spectra were unsatisfactory as the crystalline compounds refused to give satisfactory mulls.

Table 9.4

Infrared spectra (1300-400 cm.$^{-1}$)		
$C_4H_{10}O_2$ (liq.)	$TiCl_3,1.5C_4H_{10}O_2$	$TiBr_3,1.5C_4H_{10}O_2$
1301w		
1282w	1282m	1280m
1245m	1249m	1237m
1191s	1208w	1204w
1120vs.br	1188m	1184m
	1105w	1110w
	1074s	1067s
		1052s
1028m	1020s.br	1025s.br
982m	995sh	1002s
938m		980sh
925sh.w	895s	852s
853m	853s	839s
	804w	553w
	776w	852w
	553w	425w
	480w	410w

APPENDIX A

PREPARATION AND PURIFICATION
OF
STARTING MATERIALS

Sources of Reagents

Unless otherwise specified reagents were supplied by B.D.H. or Koch Light laboratories. 'Analar' or 'Pure' grades were used where available. Spectroscopic solvents (CH_3CN, CH_2Cl_2 and iso-octane) were supplied by Eastman Kodak.

1. Gases

B.O.C. White Spot nitrogen was dried by passage over Union Carbide 4A molecular sieves.

2. Liquids

Liquids were refluxed over a dehydrating agent for several hours as a preliminary drying and then transferred to the vacuum line where they were distilled several times from a variety of desiccants. Normally one day was allowed between distillations. Table A.1 shows the procedures used.

Titanium(IV) chloride was obtained from B.D.H. and distilled into small storage tubes which were sealed under vacuum.

3. Solids

Titanium metal was supplied in the form of granules by Imperial Metal Industries Ltd.

Table A.1.

Reagent	Desiccant for preliminary reflux	Desiccant for vacuum distillation	No. of Distillations
CH_3CN C_6H_6, CH_2Cl_2 CCl_4, $CHCl_3$, iso-octane	P_2O_5	P_2O_5 or 4A molecular sieves	4
pyr, αpic, γpic.	Freshly crushed barium oxide	Freshly crushed barium oxide	4
C_4H_8O, $C_4H_8O_2$ $C_5H_{10}O$, $C_4H_{10}O_2$	Freshly crushed CaH_2	Freshly crushed CaH_2. Finally K	3 + 1
$(CH_3)_2S$, C_4H_8S	Freshly crushed CaH_2	Freshly crushed CaH_2	4
$N(CH_3)_3$	———	P_2O_5 at $-78^\circ C$	4
$NH(CH_3)_2$	———	BaO at $-78^\circ C$	4
$CNCH_2CH_2OCH_3$ $CNCH_2CH_2N(CH_3)_2$	———	4A molecular sieves	2

Titanium(III) chloride was obtained from the Stauffer Chemical Co. and used without further purification.

	Ti%	Cl%
Found	31.2	69.6
$TiCl_3$ requires	31.0	68.9

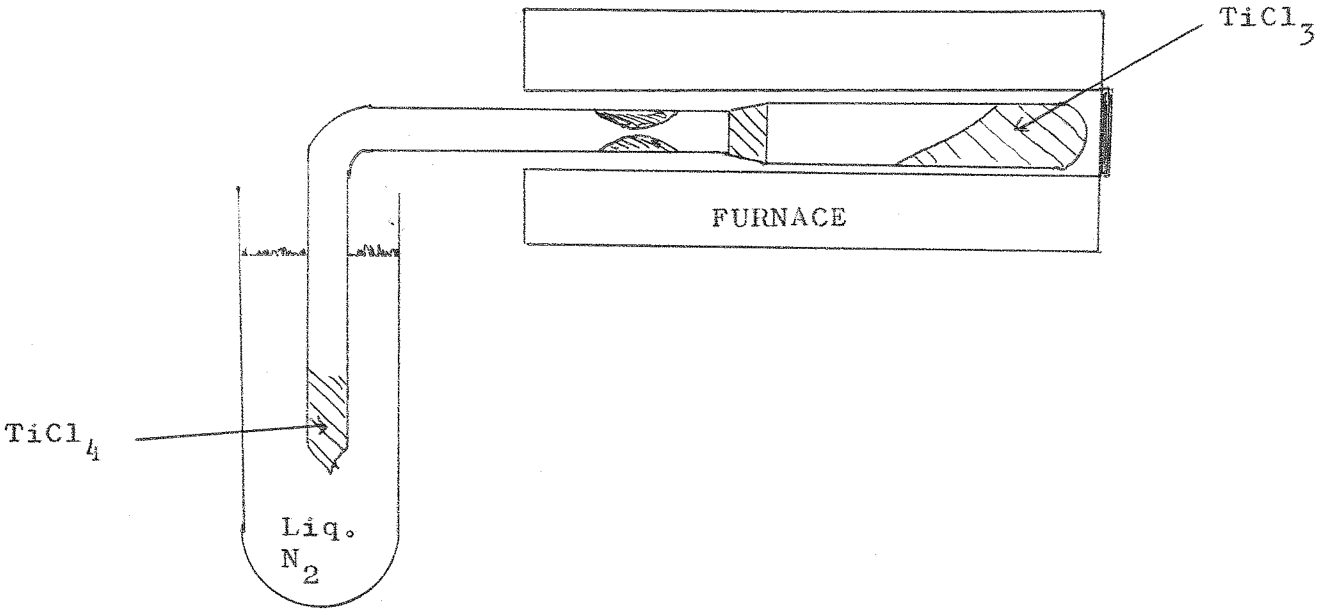
At 20°C μ_{eff} = 1.68 B.M.

Titanium(II) chloride was prepared by the disproportionation of titanium(III) chloride using a method similar to that of Clifton and MacWood.[63] Titanium(III) chloride was sealed in a glass tube (fig. A.1.) and placed in a furnace which was maintained accurately at 495°C. The protruding end of the tube was surrounded by an acetone-drikold slush bath to trap the titanium(IV) chloride which was formed. After several days the titanium(II) chloride was separated from the tetrahalide by sealing at the constriction.

	Ti%	Cl%
Found	40.3	60.3
$TiCl_2$ requires	40.3	59.6

Titanium(IV) bromide was prepared by the direct reaction of titanium metal and liquid bromine. Bromine (~200 mls.) was dried for several days over phosphorus pentoxide and then distilled into a round bottomed

Fig. A.1.



flask which was fitted with a reflux condenser. A few granules of titanium metal were added and the bromine warmed slightly to initiate the reaction. Titanium granules were then dropped down the condenser to maintain a steady rate of reaction. After about twelve grams of titanium had been added and allowed to react the excess bromine was distilled out and the titanium(IV) bromide was transferred to the vacuum line and sealed up under nitrogen.

	Ti%	Br%
Found	13.0	87.7
$TiBr_4$ requires	13.0	87.0

Titanium(III) bromide was prepared by aluminium reduction of titanium(IV) bromide. About 80% of the aluminium required for the reaction:

$$3TiBr_4 + Al = 3\ TiBr_3 + AlBr_3$$

was sealed, with the $TiBr_4$, in a tube having a constriction in the middle. The whole tube was then placed in a furnace at 220°C for several days. One end of the tube was then withdrawn from the furnace and the aluminium(III) bromide and excess titanium(IV) bromide were sublimed out. The titanium(III) bromide was isolated by sealing the tube in the middle and broken down to a powder by placing the tube on a shaker.

	Ti%	Br%
Found	16.4	82.2
$TiBr_3$ requires	16.8	83.2

At room temperature μ_{eff} = 1.20 B.M.

Titanium(II) bromide was prepared[64] in an analogous way to titanium(II) chloride but the disproportionation temperature was 400°C.

	Ti%	Br%
Found	23.0	76.3
$TiBr_2$ requires	23.1	76.9

Titanium(III) iodide. Titanium(IV) iodide was prepared by a modification of the method used by Blocher and Campbell[139] which utilised direct reaction between the elements, a slight excess of titanium granules being present. A sealed tube containing the reactants was placed in a furnace at 100°C and the temperature gradually raised to 250°C in the course of a week. The titanium(IV) iodide was sublimed to the end and the excess titanium sealed off at the constriction in the middle. The tetraiodide was transferred to a similar tube containing 90% of the aluminium required for the reaction:

$$3TiI_4 + Al = 3TiI_3 + AlI_3$$

and kept at 250°C for four days, after which time the excess tetraiodide and aluminium(III) iodide were sublimed off the titanium(III) iodide.

	Ti%	Br%
Found	11.1	88.1
TiI_3 requires	11.2	88.8

$TiCl_2$,2NaCl. This was supplied by the U.S. Industrial Chemical Co. and used without further purification.

	Ti%	Cl%
Found	19.8	59.4
$TiCl_2$,2NaCl requires	20.3	60.1

At room temperature μ_{eff} = 2.20 B.M. close to the value of 2.4 B.M. reported[43] for Na_2TiCl_4, which is considered to be the structure.

$ZrCl_2$,2NaCl was supplied by the U.S. Industrial Chemical Co.

	Cl%
Found	50.5
$ZrCl_2$,2NaCl requires	50.9

At room temperature μ_{eff} = 0.59 B.M.

$TiCl_3$,2$(CH_3)_3N$ was prepared as described by Fowles and Hoodless.[20]

	Ti%	Cl%
Found	17.5	39.4
$TiCl_3$,2$(CH_3)_3N$ requires	17.6	39.0

$TiBr_3,2(CH_3)_3N$ was supplied by Dr. B.J. Russ.

Pyridinium chloride was supplied by Dr. B.J. Russ.

2:2'-bipyridyl (I.C.I.), triphenylphosphine and tetraethylammoniumchloride were dried by prolonged pumping in the vacuum system.

1:10-phenanthroline was dried by vacuum sublimation.

$PhS\cdot CH_2\cdot CH_2\cdot SPh$ was obtained from Dr. K. Baker who prepared it by the method of Bell and Bennett.[140]

APPENDIX B

ANALYTICAL METHODS

About 0.2 g of product was transferred under nitrogen to a weighed glass tube which was then reweighed to give the amount of sample. The tube was quickly opened and immersed in sulphuric acid (1 M). After complete hydrolysis the solution was made up to a known volume and used for both metal and halogen determinations.

Titanium

A colorimetric method[141] involving hydrogen peroxide was used to estimate titanium. Excess hydrogen peroxide was added to an aliquot of the hydrolysis solution which was then made up to a known volume ensuring that the final solution was 1 M in sulphuric acid. The optical density of the orange solution at 410 mμ was measured on a Unicam SP.600 which had previously been calibrated using $TiCl_3,2(CH_3)_3N$. Iodide was removed before addition of hydrogen peroxide by boiling the hydrolysis solution to a small volume and oxidising it with concentrated nitric acid.

A gravimetric method was also used occasionally for the estimation of titanium, a known weight of compound being tipped into a weighed platinum crucible and decomposed with a few drops of concentrated nitric acid. After ignition at around 700°C for one hour the residue was weighed as TiO_2.

Zirconium

Zirconium was estimated gravimetrically in a similar manner to titanium except that the compound was decomposed using dilute ammonia.

Halogens

Chlorine, bromine and iodine were estimated by the gravimetric or Volhard methods. Very occasionally for bipyridyl compounds, chlorine or bromine were estimated by a microanalyst (Beiler, Vienna) as consistent analyses could not be obtained by either of the other methods.

Carbon, Hydrogen and Nitrogen

These elements were determined by a professional microanalyst (Weiler and Strauss, Oxford or Beiler, Vienna) but due to the rapid decomposition of some of the compounds on exposure to air it is doubtful if the accuracy quoted is justified.

Valence state determination

A weighed amount of the solid was immersed in N/20 ceric sulphate solution to oxidise Ti(III) to Ti(IV) and the excess ceric sulphate was titrated against N/10 ferrous ammonium sulphate enabling the valence state of the metal to be deduced.

APPENDIX C

EXPERIMENTAL PROCEDURES

The extreme sensitivity of many of the systems investigated to both water and oxygen made it essential that a vacuum line was used for much of the work. A simplified diagram of the vacuum line is shown in fig. A2 and some of the more frequently used operations will be described. To remove a piece of apparatus from the line for manipulations it was filled with dry nitrogen. As an aid to the handling of solid compounds, e.g. the preparation of infrared mulls, a dry-box was also set up and this is described later.

1. Preparations

a) Drying of solvents and liquid ligands

The drying of liquids was carried out using the left-hand side of the manifold and traps A, B and C. A little desiccant ($\sim$5g) was placed in each trap which was then evacuated and flamed out. Trap A was removed from the line and the liquid added, after replacing on the line air was removed by momentarily opening the tap to the pump several times. The liquid could then be distilled into B by surrounding B with liquid nitrogen or an acetone-drikold slush bath and opening the connecting taps. After about a day the liquid was distilled into C, four

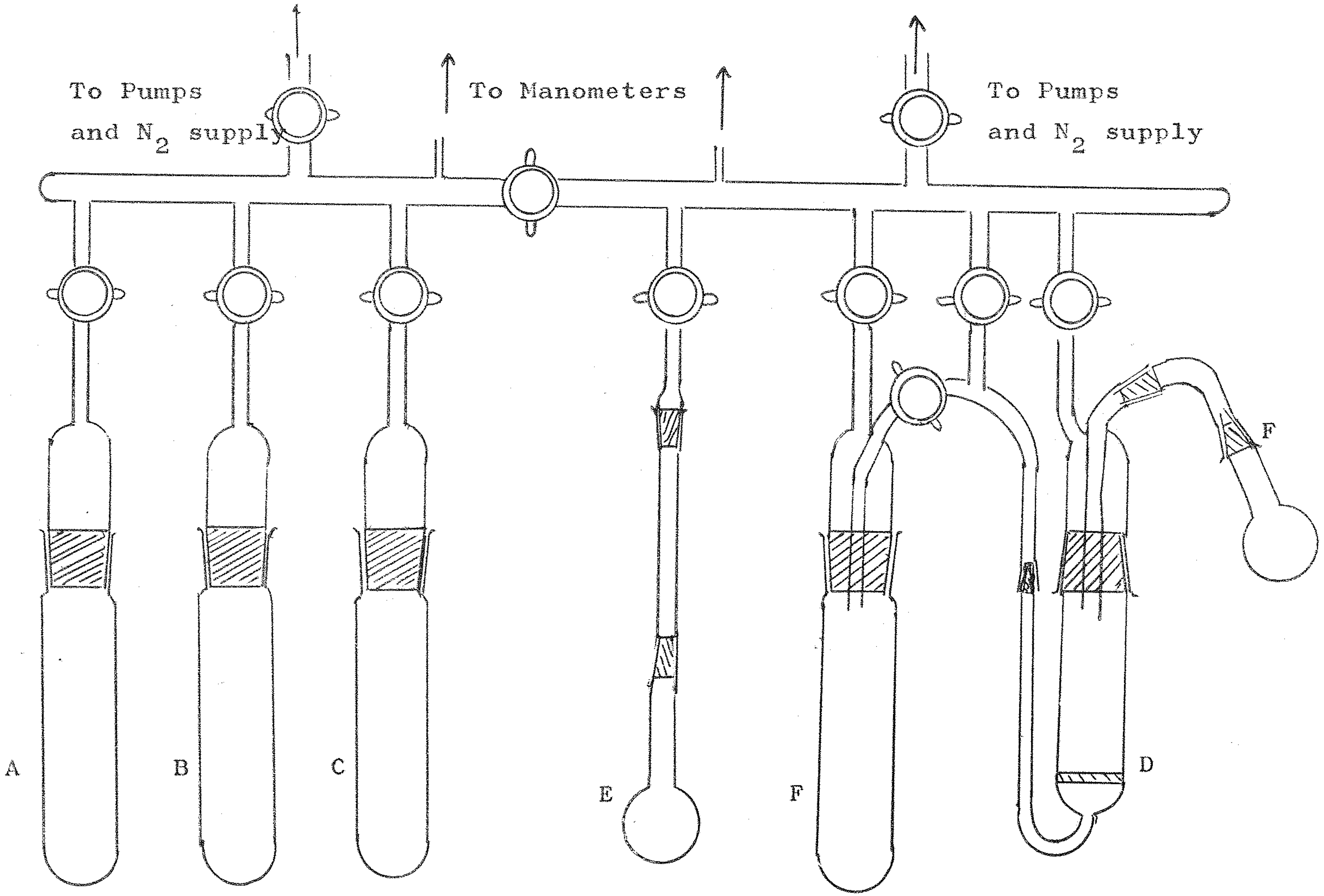


Diagram of the Vacuum System

Fig. A.2.

distillations normally being carried out during drying.

b) Preparation of ampoules

An ampoule was constructed (fig. A.2.E or fig. A.3) and flamed out with a bunsen while it was pumped. Solid halides were introduced from tubes having B14 cones by taking the ampoule off the line under nitrogen and tipping the halide in. The ampoule was then evacuated again and after the liquid ligand had been distilled in it was sealed off at the constriction while the liquid in the bulb was frozen. Solid ligands were introduced before the halide and pumped overnight. Titanium(IV) chloride, being a liquid, was distilled in from a storage ampoule which was broken open in the apparatus shown (fig. A.4).[145] Sealed tubes were filled in a similar manner.

If the reaction was to be carried out at room temperature the ampoule was placed on the shaker but elevated temperatures could be obtained by placing the ampoule on a heating mantle and allowing it to reflux gently.

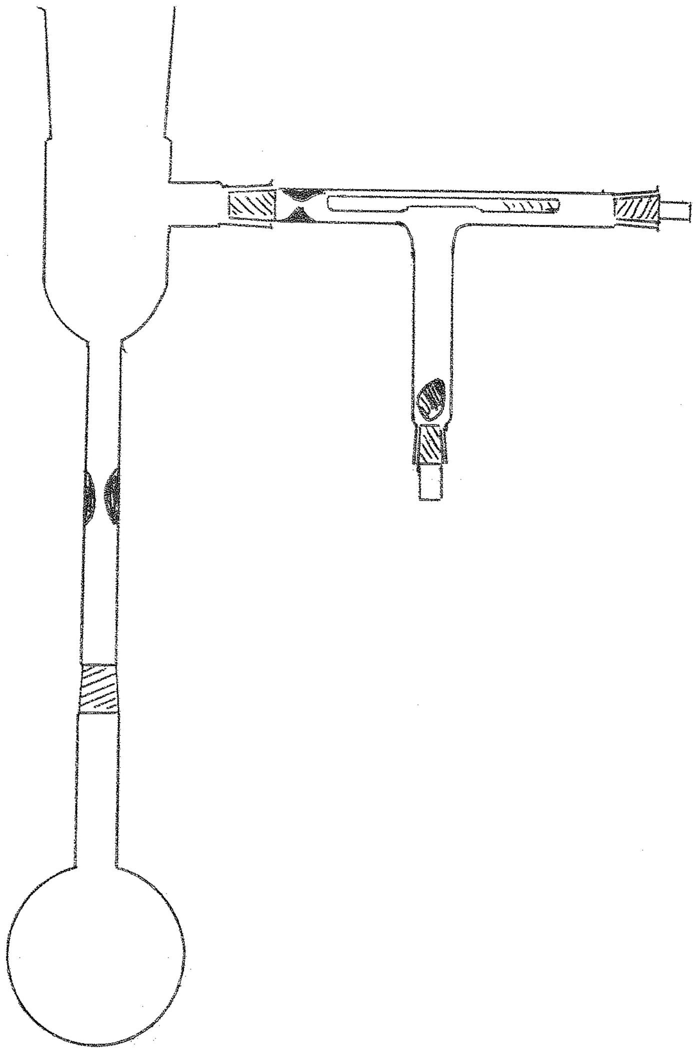


Fig. A.4.

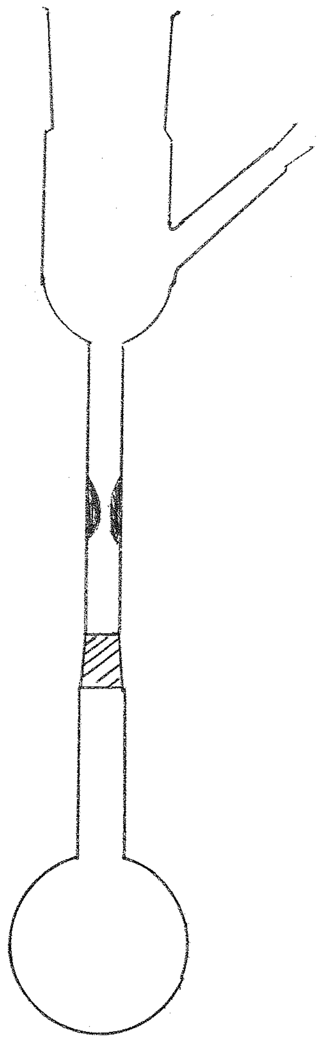


Fig. A.3.

c) Separation of products

i) Insoluble products

When an insoluble product had to be isolated the ampoule was frozen out and the filter adapter D (fig. A.2) flamed and evacuated. Nitrogen was admitted and after the top of the ampoule, above the B19 cone, had been removed by 'hot spotting' it was plugged into the B19 socket F. The ampoule was then pumped out while the contents were kept frozen, but after a few minutes the solvent was melted and tipped down onto the sintered disc, the filtrate being drawn through the pad by gently cooling trap F with the connecting tap open. The solid could be washed by distilling a solvent back into the ampoule and repeating the process. When more thorough washing was required a continuous procedure was used (fig. A.5). The reaction ampoule was plugged in at G and the solvent filtered through into the flask which was then gently heated to evaporate solvent up the bypass; on condensation it washed back through the solid on the pad. Solids were always pumped for 3-24 hours prior to analysis, the length of time depending on the solvent.

ii) Soluble products

The ampoule was opened as described above and

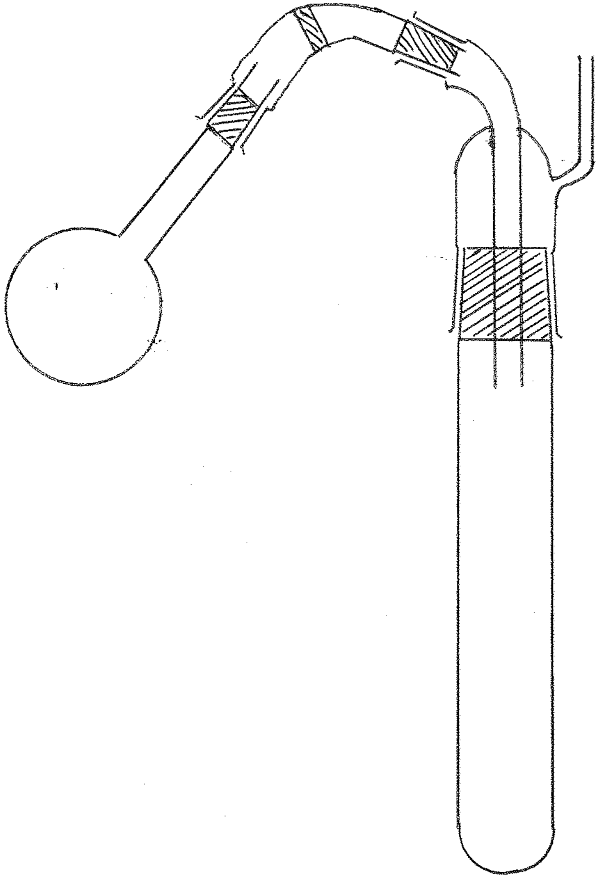


Fig. A.6.

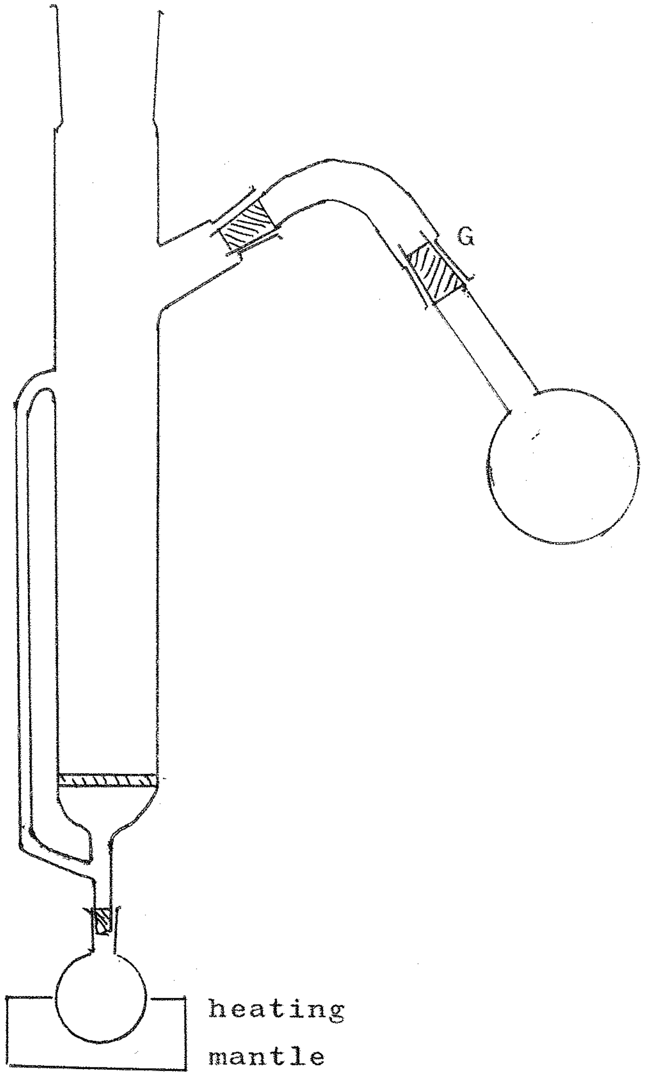


Fig. A.5.

plugged into the apparatus shown (fig. A.6). After filtration the solvent was evaporated from the trap, and the solute scraped off the walls and ground up with a glass or stainless steel rod.

Soluble solids were also collected by the double ampoule technique (fig. A.7) which is particularly useful for low boiling liquids as they can be filtered at room temperature.

After analysis samples were normally split into small quantities in a pig (fig. A.8) and sealed under vacuum. One tube was then used for each physical measurement thus minimising the chance of the remainder of the material decomposing.

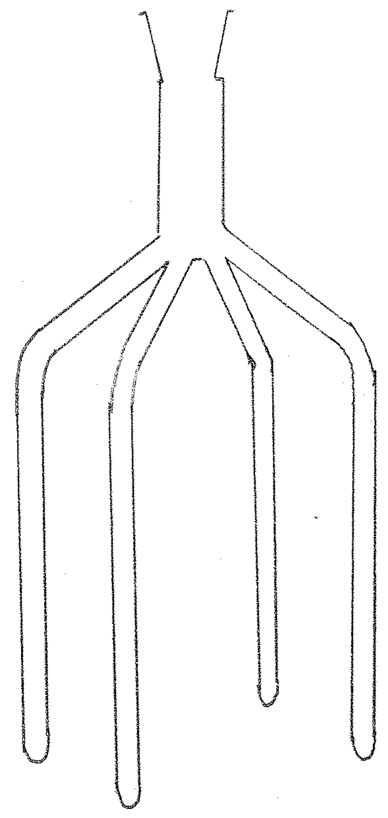


Fig. A.8.

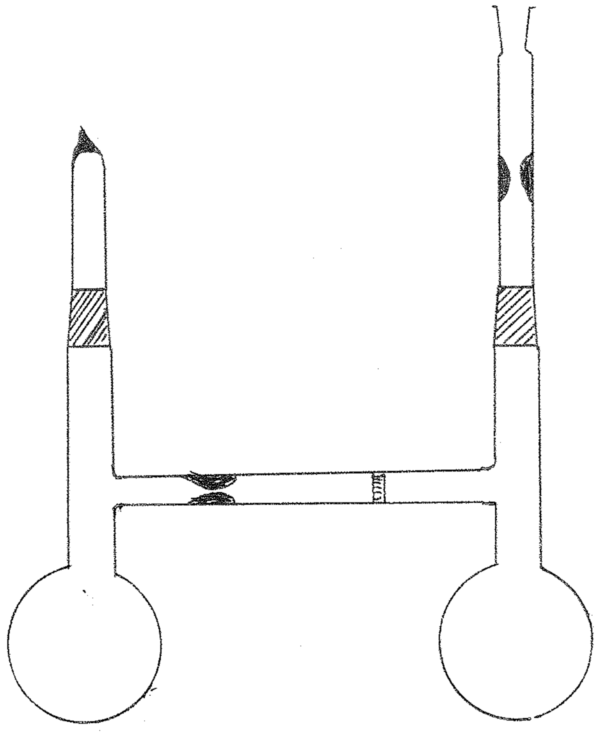


Fig. A.7.

APPENDIX D

STRUCTURAL STUDIES

a) Magnetic susceptibility measurements

i) At room temperature

The susceptibilities of the compounds were determined at room temperature using a Gouy type balance. A Newport electromagnet was used to provide a field of ~ 4,000 gauss (at 4 amps) and the weights measured with a semimicro air damped balance. Sample tubes were made of pyrex glass (~3mm diameter) and were fitted with a B7 socket at the top, the lower end having an internal flat and the length being about eleven centimetres. A scratch was made on the tube ~ 9.5 cms from the base and it was always filled to this level. Calibration was carried out using mercury tetrathiocyanatocobalt(II)[142] ($\chi_g = 16.44 \times 10^{-6}$ cgsu at 20°C) or trisethylenediamine-nickel(II) thiosulphate[143] ($\chi_g = 10.82 \times 10^{-6}$ cgsu at 20°C), the former was preferred as the packing was more reproducible. When calibrated the tube was evacuated, flamed, filled with nitrogen and weighed. The sample was then introduced slowly, with regular tapping to ensure uniform packing, from a sample tube via an appropriate adapter. In some cases measurements were repeated at more than one field strength.

Samples on which temperature range measurements were later carried out were repacked until a constant (± 1%) pull/weight ratio was obtained, an accurate room temperature moment being essential to the meaningful plotting of a $1/\chi$ vs T graph.

Calculation of moments

It can be shown that:

$$K_s = \frac{f_s}{f_c} [K_c - K_a] + K_a$$

where K_s, K_c and K_a are the volume susceptibilities of the sample, calibrant and air respectively; f_s and f_c are the forces on the sample and calibrant measured positive if the weight increases in a field. Since K_c and K_a are known and f_s and f_c are measured K_s can readily be found.

The gram susceptibility χ_g; the molar susceptibility χ_m and the corrected molar susceptibility χ'_m for a metal ion in a complex are given by the expressions:

$$\chi_g = \frac{K_s}{\text{Density}}$$

$$\chi_m = \chi_g \times \text{empirical molecular weight}$$

$$\chi'_m = \chi_m + \text{diamagnetic corrections for other atoms}^{144}$$

The effective magnetic moment μ_{eff} is then given by:

$$\mu_{eff} = 2.83 \sqrt{\chi'_m \times T} \quad \text{Bohr magnetons}$$

where T is the absolute temperature.

ii) Over a temperature range

For the investigation of the variation of susceptibility with temperature a Newport variable temperature Gouy apparatus was used, the temperature range was from -196 to + 100°C. The refrigerant was liquid nitrogen and the cryostat held the temperature steady to ± 0.1°C; the absolute value of the temperature was dependent on the accurate calibration of the thermocouple but is claimed to be ± 1°C. Measurements were not normally made above 40°C due to the possibility of the compounds decomposing and the danger of the stopper blowing out of the tube as the nitrogen inside expanded.

The procedure was as follows. A pyrex tube, similar to that used for the room temperature moments but fitted with a B5 joint, was filled with nitrogen and suspended from the balance. Nitrogen was flushed around the tube to displace any oxygen, which has temperature dependent paramagnetism, and the thrust on the tube measured at three field strengths (4,000 to 7,000 gauss) at intervals of 10 or 20°C.

A calibration curve, giving the diamagnetic correction for the tube, was then plotted. The tube was filled with sample ($\sim$ 9 cms) and the force on the tube and sample measured at the same field strengths over the range of temperature; using the tube calibration graph the net force on the sample at each temperature was determined.

χ_m at room temperature is known and since for nitrogen K_a is negligible;

$$\chi_m = A \cdot f_s$$

where A is a constant which is independent of temperature. Thus χ_m is found at each temperature for which the sample pull was measured and after diamagnetic corrections have been applied χ'_m is obtained.

b) Molecular weight determination

A Gallenkamp ebulliometer, combined with a thermister and bridge circuit, was used. The cell was modified so that dry nitrogen could slowly be flushed through the apparatus during measurement. Dry methyl cyanide (10 mls) was added from a pipette and the apparatus was calibrated with pellets of napthalene ($\sim$0.05 g), the first one serving to stabilise the boiling point. Small amounts of sample were then added from sealed glass tubes which were opened immediately before the addition, the weights being found by difference. The weights of napthalene and sample added were plotted against their respective resistance (temperature) changes and the molecular weight calculated:

$$\text{Unknown M.W.} = \text{M.W. of } C_{10}H_8 \times \frac{\text{Slope for } C_{10}H_8}{\text{Slope for unknown}}$$

c) Conductivity measurements

Measurements of conductivity were carried out in spectroscopic methyl cyanide or pyridine using a Mullard calibrated conductivity cell (E7597/A) with platinum electrodes in conjunction with a Pye 11700 bridge. Solutions were placed in a thermostat at 25°C prior to measurement.

The apparatus (fig. A.9) was steamed out with de-ionised water, rinsed with absolute ethanol and pumped for at least twelve hours with regular flaming. The sample was then introduced via (A) against a stream of dry nitrogen from a small tube which was weighed before and after the addition. After evacuation the cell was removed from the line and weighed; it was returned to the line and the solvent distilled in. After the solvent had been melted a

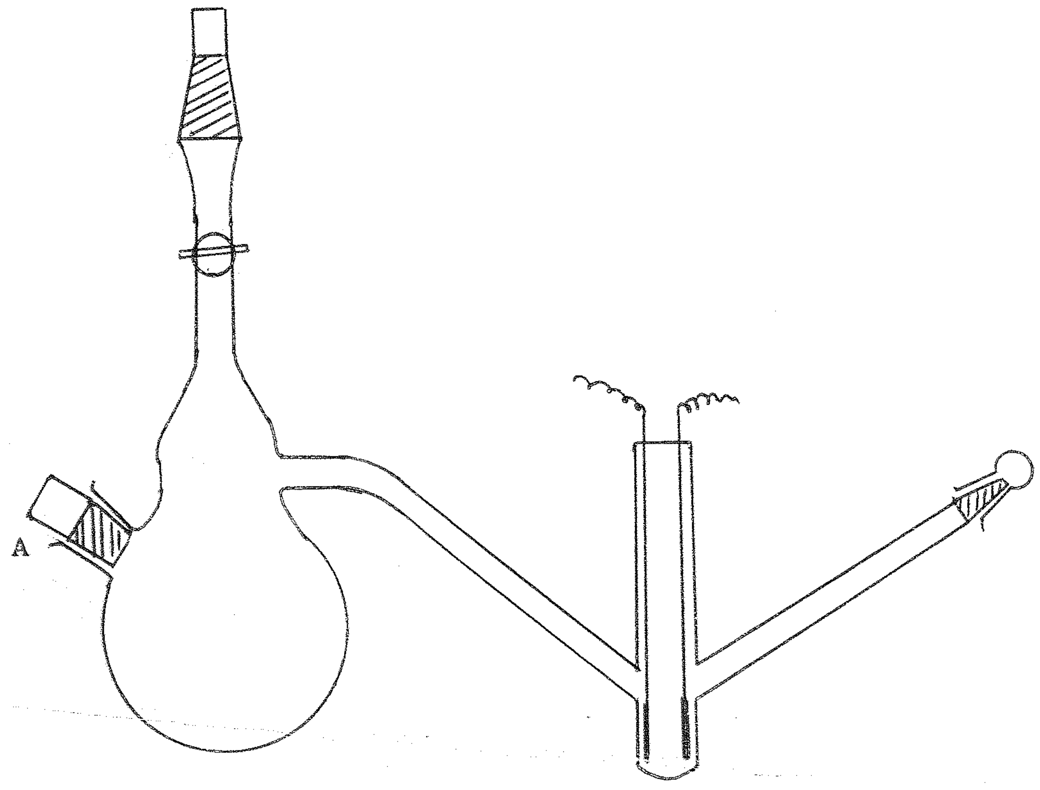


Fig. A.9.

check was made to ensure that all the solute dissolved; the cell was removed from the line and reweighed to give the weight and hence the volume of solvent. The solution was tipped down between the electrodes and the conductance measured; concentration or dilution could be carried out by replacing the cell on the line and distilling solvent in or out. The usual practice, when studying the conductivity over a concentration range, was to gradually dilute the solution but to do the final reading at a high concentration to check that no irreversible reaction had occurred during dilution. The molar conductivity was calculated from:-

$$\Lambda_m = \frac{\text{Cell const. x volume of soln. (cc's) x M.W.}}{\text{Resistance of soln. x weight of solute (g)}}$$

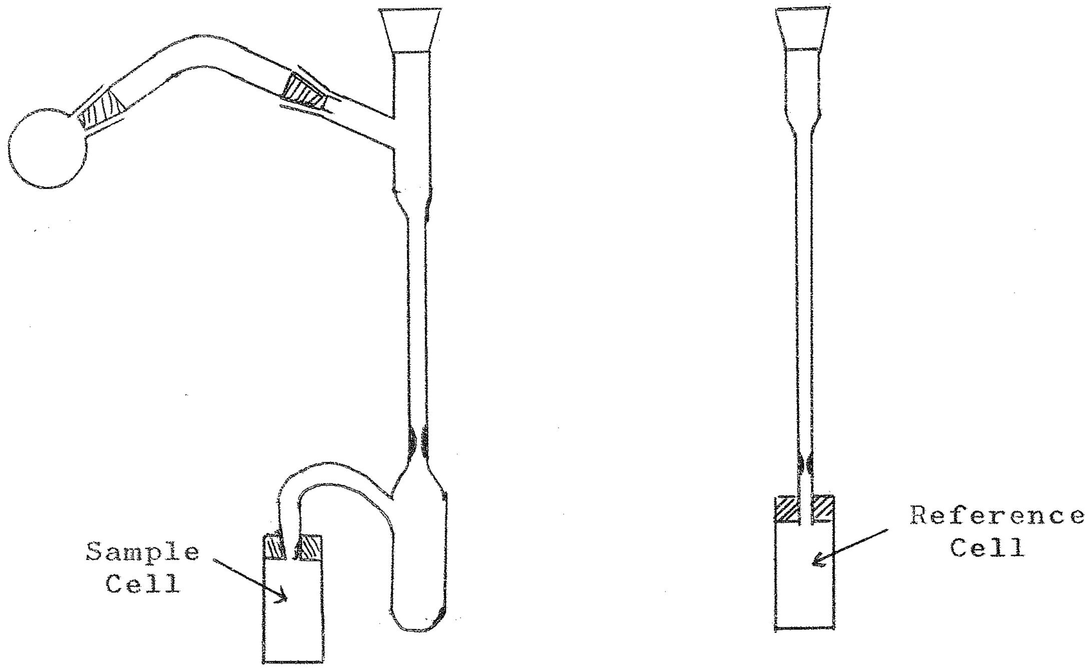
Although the concentration could be changed by a factor of ten it is the variation of conductivity with the square root of concentration which is of interest making the range studied rather narrow.

d) Spectral measurements

i) Solutions, Electronic spectra

Solution spectra in the region 4,000 to 45,000 cm.$^{-1}$ were measured on Unicam SP.500, 700 and 800 spectrophotometers. For the measurement of spectra the apparatus (fig. A.10) was evacuated and flamed out at intervals for several hours, the cell being gently warmed with a hot air blower. Nitrogen was then admitted and the sample tipped from a small tube into the flask; the apparatus was evacuated again and the solvent distilled in. The solvent was melted and the solute dissolved to give a solution which was filtered through the sinter and sealed up in the reservoir; a reference cell was generally filled from the same batch of solvent. If it was necessary to dilute the solution, to measure the ultraviolet region for instance, a few drops of the solution were tipped into the cell and pure solvent was then evaporated over by cooling the cell with an acetone-drikold swab. The ultraviolet spectrum measured in this way was considered to be reliable for if small traces of water were present they would react with some of the sample, but only a very small proportion which would be the same at all concentrations. If only sufficient sample was added to examine the very intense ultraviolet peaks the chances of a misleading spectrum would be much higher as a significant proportion of the sample might be decomposed. Extinction coefficients

Fig. A.10



were measured by weighing the amount of solid added and measuring the volume of solvent afterwards, values less than 100 should be quite accurate but if dilution was involved they could only be estimated.

The cells usually used were of glass or silica with a path length of 10 mm but 40 mm glass cells were also used for examining the d-d spectra of weakly absorbing or rather insoluble compounds. Silica cells of 1 mm path length were used to examine the near infrared of Ti(II) compounds in methyl cyanide as this solvent absorbs somewhat in this region.

ii) Low infrared

Low infrared spectra in solution were measured on a Grubb Parsons D.M.4 machine. The apparatus was as shown in fig. A.11 which also indicates how the polythene cells were constructed. As the sides of the cell touched when the apparatus was evacuated it was regularly filled with nitrogen and re-evacuated to ensure that no air remained inside. The sample was added and the solution made up as described for the electronic spectra except that the cell was sealed up at almost 1 atm. of nitrogen instead of under vacuum.

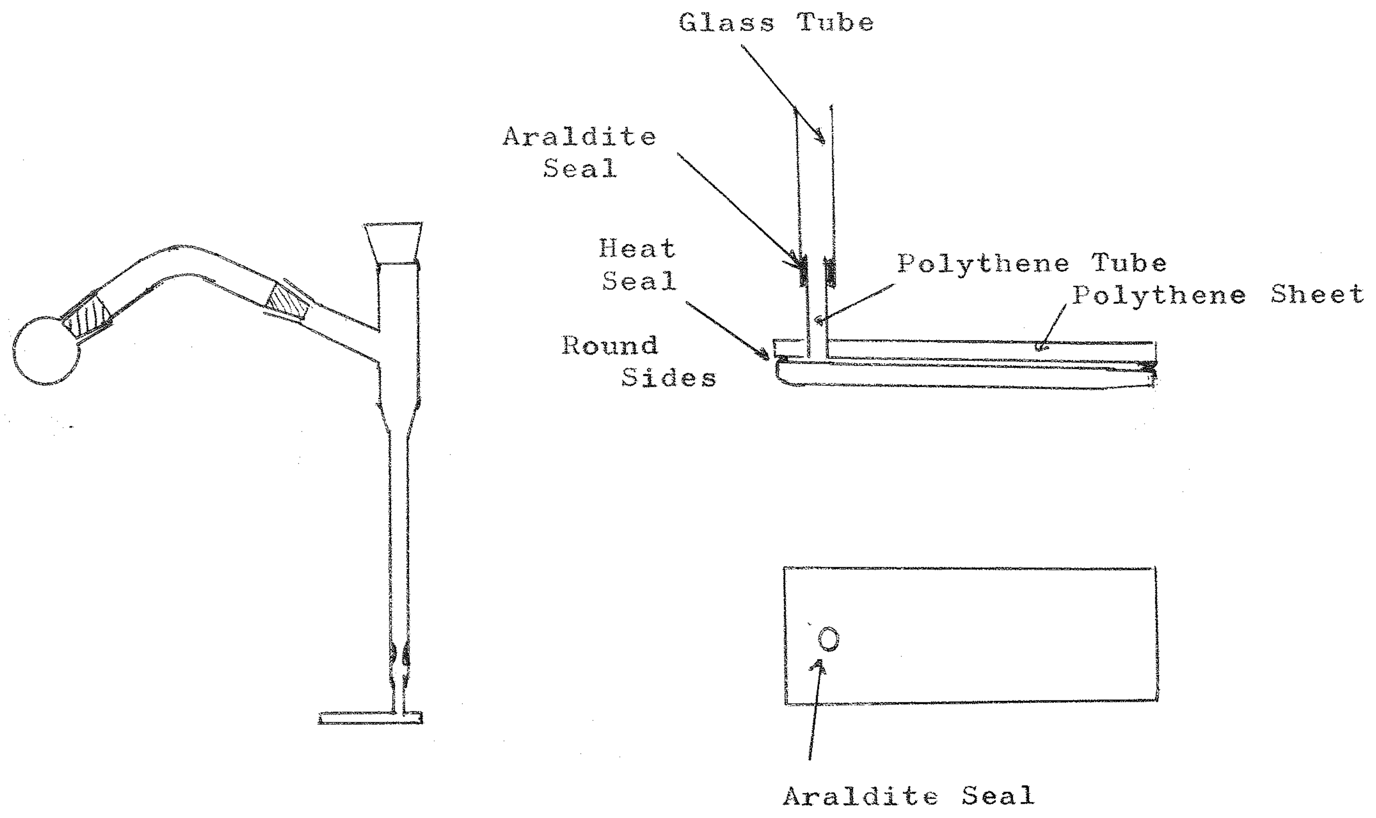

Glass Tube
Araldite Seal
Heat Seal
Round Sides
Polythene Tube
Polythene Sheet
Araldite Seal

Fig. A.11.

iii) Solids: Reflectance, Infrared and Low Infrared

Reflectance spectra were measured between 10,000 and 50,000 cm.$^{-1}$ using the Unicam SP.500 or 700 instruments equipped with their reflectance attachments; the standard sample holder was used with the 700 but for the 500 the compound was placed between two glass discs which were sealed around the edge with silicon grease. Magnesium oxide was used as the reference. Samples were finely ground but not diluted, although this can result in marked changed in the spectrum, due to the increased danger of decomposition.

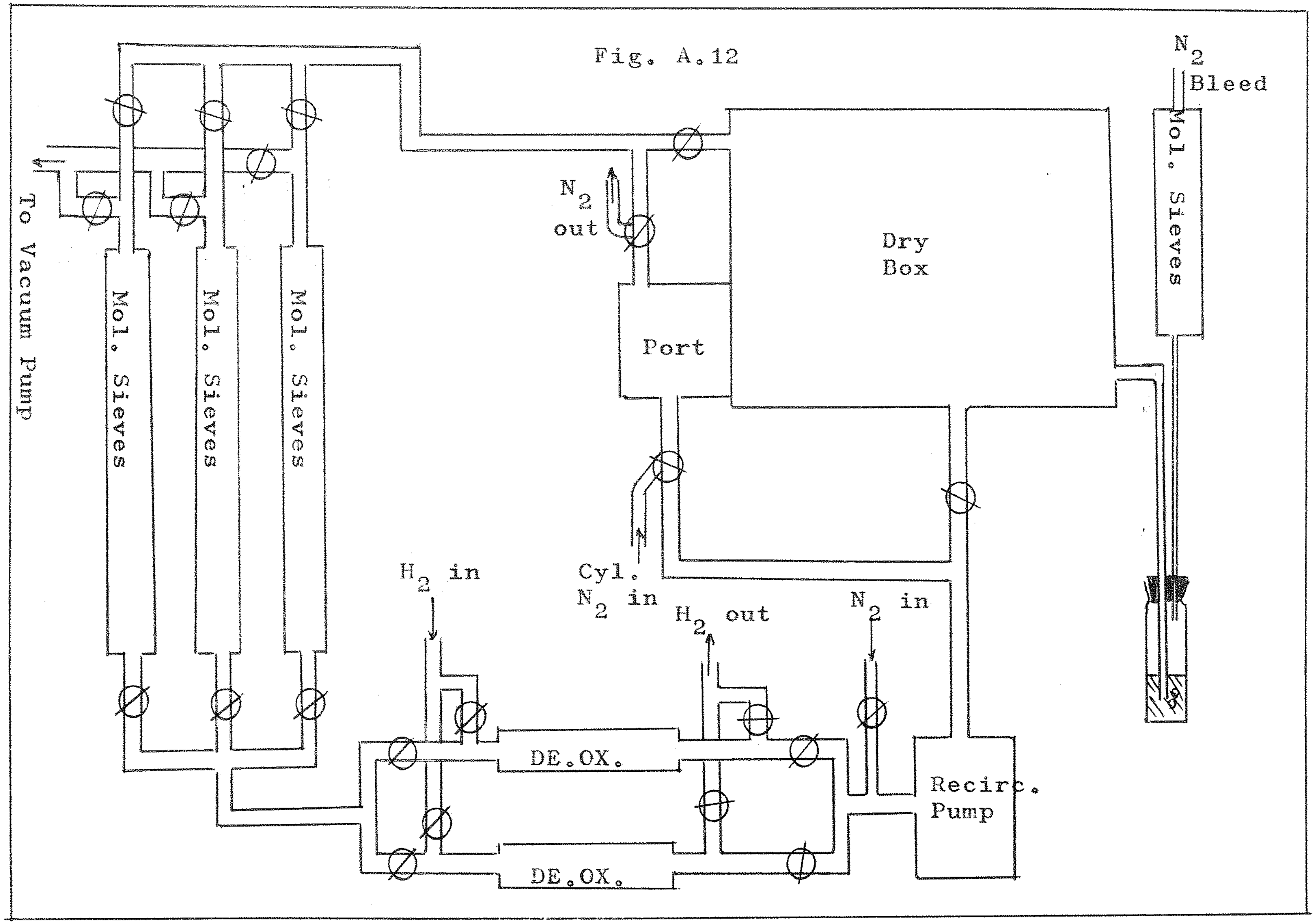
Infrared spectra were measured between 400 and 4,000 cm.$^{-1}$ using a Perkin Elmer 337 and in the range 200-500 cm.$^{-1}$ on the Grubb Parsons D.M.4. Nujol mulls were always used but the windows were of potassium bromide or polythene depending on the range being studied. All the manipulations involved in preparation of solid samples for spectral measurement were carried out in a dry-box.

Dry-box

The dry-box system was built in association with Mr. P.R. Marshall and Mr. P. Crouch with a great deal of help from the Workshop staff.

The box, which was supplied by Lintott, was equipped with a nitrogen recirculating system (fig. A12). Water was removed from the gas stream by molecular sieve columns, each containing about 1.5Kg of Union Carbide 5A sieves, and oxygen was abstracted using B.S.A.F. catalyst (B.T.S.), each column containing around 250 g, this being kept at 150°C by internal heating coils. Nitrogen was bled in slowly and the box maintained at a slight positive pressure. The recirculation rate was about 30 litres/minute achieved by a diaphram pump (Charles Austin), the total volume of the system was rather over 1,000 litres. The molecular sieve columns were reactivated by heating and pumping, each column being wound with a heating coil; the deoxygenation columns were activated by passing a slow stream of hydrogen over them for several hours, while they were kept at 150°C. The port, through which samples were introduced or removed, could be flushed either with nitrogen direct from the cylinder or with the recirculating gas. All the piping was of copper with brass taps and all joints were coated with polyurethane varnish to minimise leaks. Unfortunately no meters were available to test the water and oxygen content but phosphorus pentoxide showed no sign of absorbing water after a week.

Fig. A.12


N_2 Bleed
Mol. Sieves
Dry Box
Port
N_2 out
Cyl. N_2 in
H_2 in
H_2 out
N_2 in
Recirc. Pump
DE.OX.
DE.OX.
Mol. Sieves
Mol. Sieves
Mol. Sieves
To Vacuum Pump

e) X-Ray Studies

i) Powder measurements

A number of X-ray powder photographs were kindly taken by the Atomic Energy Authority. The samples were sealed up in Lindemann capillaries (0.3 mm diameter) which had been evacuated for at least twelve hours. The thin wall capillaries were connected to a Pyrex tube with black wax.

ii) The Single Crystal Study

The crystals of $2TiBr_3,3C_4H_{10}O_2$ were grown by refluxing 1:2-dimethoxyethane with titanium(III) bromide for twelve hours and were separated by filtration. A number were tipped into thin walled capillaries (0.3 mm diameter) and examined under a microscope to select one which was both well formed and firmly wedged in the tube. This was then mounted on a goniometer in plasticine which, after the capillary had moved during orientation of the crystal, was coated with Araldite.

The crystal density was found by flotation in a mixture of dry iso-octane and dry iodomethane, a value of 2.0 was obtained corresponding to 7.7 molecules per unit cell. The density was not expected to be very accurate because of the instability of the crystals.

All X-ray measurements were made using the General Electric XRD 6 generator in conjunction with their own tubes, the usual beam current was 30 ma at 50 kvp. Buerger precession (Charles Supper) and integrating Weissenberg (Nonius) cameras were used. Orientation precession photographs were taken using unfiltered molybdenum radiation, a 10° precession angle and twenty minute exposures. For precession layer photographs zirconium filtered molybdenum radiation, a 30° precession angle and twelve hour exposures were used. Oscillation orientation photographs were taken with copper radiation and a 15° oscillation angle. After thirty minutes exposure the crystal was rotated by 180° and a further ten minutes exposure given. The curvature of the two sets of rows allowed the correction necessary to align the crystal to be calculated.

The data was collected using equi-inclination Weissenberg layer photographs which were taken using nickel filtered copper radiation. Since the angle of rotation was greater than 180° two exposures were required for each level, the angles of rotation were noted and the exposures scaled to give a constant time per degree rotation. Three Ilford 'G' films, which were used throughout the study, were stacked in the film holder for each exposure. Data was collected from the first eight levels.

A comparison strip for estimating the intensities was prepared by isolating one well formed spot and taking twenty 4° oscillation photographs, each exposure being 1.2 times longer than the preceeding one. The eye is particularly sensitive to intensity differences in the middle of the wedge range and an effort was made to measure each spot on the film which gave the intensity in this range, although some spots inevitably had to be measured at the ends of the wedge range. A number of spots were measured carefully on each film to give the factor by which the spots were diminished in intensity on passing from one film to the next; it was estimated to be 2.45.

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