THE PREPARATION AND CHARACTERIZATION OF SOME MIXED-LIGAND COMPLEXES OF TITANIUM (III)

Thesis for the Degree of Ph. D.
MICHIGAN STATE UNIVERSITY
GLEN RICHARD HOFF
1970

This is to certify that the

thesis entitled

The Preparation and Characterization of Some
Mixed-Ligand Complexes of Titanium(III)

presented by

Glen Richard Hoff

has been accepted towards fulfillment
of the requirements for

Ph.D. degree in Chemistry

Carl H. Brubaker, Jr.
Major professor

Date August 18, 1970

O-169

ABSTRACT

THE PREPARATION AND CHARACTERIZATION OF SOME MIXED-LIGAND COMPLEXES OF TITANIUM(III)

By

Glen Richard Hoff

The complexes of titanium(III) chloride with the coordinating solvents acetonitrile, tetrahydrofuran, dioxane, and isopropanol were investigated. The solvent adducts $TiCl_3 \cdot nL$ were prepared by the direct reaction of the solvent with titanium trichloride or with many of the titanium(III) complexes. Addition of tetraethylammonium chloride to the solvent adducts suspended in the solvent yielded $(C_2H_5)_4N[TiCl_4 \cdot 2L]$. Compounds of the type $TiCl_3 \cdot L$ and the chloroalkoxo complex $Ti_2Cl_3(C_3H_7O)$ were obtained by heating the solvent adducts under vacuum. A new class of compounds of the type $TiCl_3L_2L'$, containing two different non-halide ligands, were prepared by the addition of ligand L' to the adduct $TiCl_3 \cdot nL$ suspended in the solvent L and by the dissolution of $TiCl_3 \cdot L'$ in the solvent L. The reactions and interconversions of all these compounds were studied, especially with regard to non-halide ligand substitution.

The infrared spectra of the complexes generally showed the shifts of absorption bands associated with coordination of the solvents. Far infrared spectra were too broad to provide useful information about the symmetries or bond strengths of the compounds. Two absorption bands were present in the visible spectra which indicated that all the compounds contained some elements of tetragonal or lower symmetry. Jorgensen's rule of average environment was obeyed in the complexes of the type $TiCl_3L_2L'$. The frequencies of the absorption bands increased with increasing chloride content of the complexes in contrast to Jorgensen's rule.

Magnetic studies over a range of temperatures indicated normal paramagnetism for most of the complexes and several ligand field parameters were obtained. As was expected, the distortion and t_{2g} electron delocalization decreased and the magnetic moment became more dependent upon temperature as the chloride:non-halide ligand ratio was increased. No correlations between several ligand field parameters were found in complexes of the type $TiCl_3L_2L'$. The compounds $TiCl_3 \cdot CH_3CN$ and $TiCl_3 \cdot C_4H_8O$ were antiferromagnetic and $Ti_2Cl_3(C_3H_7O)_3$ was diamagnetic.

The electron spin resonance spectra were measured at 297 and 77°K. The spectra indicated that compounds of the types $TiCl_3L_2L'$ and $(C_2H_5)_4N[TiCl_4 \cdot 2L]$ as well as $TiCl_3 \cdot 2C_4H_8O_2$ and $TiCl_3 \cdot 4C_3H_8O$ had cis configurations. In some complexes the separation of the t_{2g} sublevels was either too small or

too great to permit the observation of more than a single absorption peak even at 77°K. Since most of the complexes had an average g value close to 1.89 it was difficult to confirm the existence of any definite correlations of the g value with ligand field parameters. It appeared that distortion of the complexes and the approach of the g values toward 2.00 increased in the same order as the ligand field strengths of the complexes.

Several of the substances prepared changed color as they were cooled to 77°K. These thermochromic materials had charge-transfer bands which narrowed and shifted to higher frequencies to produce the color change. In addition, when some of the thermochromic substances were cooled to 77°K new peaks appeared in their esr spectra. It is felt that the thermochromism and unusual esr spectra of some of the substances is somehow related to the presence of both titanium(III) and titanium(IV).

THE PREPARATION AND CHARACTERIZATION OF SOME MIXED-LIGAND COMPLEXES OF TITANIUM(III)

By

Glen Richard Hoff

A THESIS

Submitted to
Michigan State University
in partial fulfillment of the requirements
for the degree of

DOCTOR OF PHILOSOPHY

Department of Chemistry

1970

To my wife, Janet, and our family

ACKNOWLEDGMENT

The author wishes to extend his thanks and appreciation to Professor Carl H. Brubaker, Jr. for his interest and guidance during this investigation.

Financial support from the National Science Foundation was deeply appreciated.

TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

INTRODUCTION

Ever since the beginning of coordination chemistry more than 170 years ago, chemists have been concerned with theories about the bonding in transition metal complexes. As the theories are developed and refined they are more able to account for many of the properties of these coordination complexes. Compounds of transition metals which have only one d electron provide the simplest of systems with which to test bonding theories as measurements such as the optical and electron spin resonance spectra and magnetic behavior can be correlated with the behavior of the lone d electron. The symmetries of the complexes generally are easy to predict and are only slightly distorted from ideal point group symmetry. Comparisons between molecular orbital parameters calculated from theoretical considerations and those obtained experimentally are especially useful for compounds in which the symmetry is lower than octahedral. The d^1 transition metal complexes studied in this laboratory include those of titanium(III),[1] vanadium(IV),[2] niobium(IV),[3] molybdenum(V),[4] and tungsten(V).[5]

There are several advantages in the use of titanium(III) instead of other metals in a study of d^1 transition metal complexes. The properties of titanium(III) compounds are generally sufficiently different from those of the other oxidation states of titanium so that the complexes can usually be isolated and characterized. In addition, titanium(III) does not form the oxo compounds which make up a large part of the chemistry of vanadium(IV), molybdenum(V), and tungsten(V). In most complexes with monodentate ligands the titanium atom is octahedrally coordinated. In those cases where the ligand:metal ratio is less than 6:1 one or more of the ligands often bridge two titanium atoms to complete the coordination sphere. Thus characterizations can be based upon distortion or reduction of octahedral point group symmetry. However, titanium(III) compounds are very susceptible to attack by oxygen and water and previous work in their characterization has been limited.

Titanium(III) chloride reacts with a number of coordinating solvents to form complexes of the type $TiCl_3 \cdot nL$ ($n = 1-4$). Few of the compounds are more than sparingly soluble in the solvent from which they were made and none will dissolve in any other solvent without reaction. The titanium atom appears to be six-coordinate in all of the complexes. In alkyl cyandides titanium trichloride reacts to form $TiCl_3 \cdot 3RCN$ (R = methyl, ethyl, n-propyl).[6-8] Titanium(III) chloride coordinates with three acetone molecules but only two diethylketones or benzophenones.[8,9] The complex $HTiCl_4 \cdot C_4H_{10}O$ is made from diethylether saturated with HCl.[1] Titanium trichloride adds three molecules of tetrahydrofuran(THF) but only two of dioxane and one of those is reported to be eliminated with prolonged heating and stirring in dioxane.[8,9] $TiCl_3 \cdot 1.5L$ is formed in 1,2-dimethoxyethane or ethylene glycol dimethyl ether.[9,10] While titanium(III) chloride reacts with ammonia to form the white hexammine complex,[11] it adds only two trimethylamines and undergoes solvolysis with methylamine or ethylamine.[12,13] Under appropriate conditions titanium trichloride forms $TiCl_3 \cdot 2.5$dimethylformamide,[14] $TiCl_3 \cdot 2$bipyridine,[15] and $TiCl_3 \cdot 1.5$bipyridine.[16] All three chlorides are ionic in the amine complexes $TiCl_3 \cdot 3L$ (L = ethylenediamine, propylenediamine) and $TiCl_3 \cdot$ 2diethylenetriamine.[7,17] $TiCl_3 \cdot 4$ethylenediamine has been reported but its existence is questioned.[7,18] In alcohols titanium forms complexes of the type $TiCl_3 \cdot 4L$ (L = methanol, ethanol, isopropanol, sec-butanol, cyclohexanol) in which one of the chlorides is ionic.[19,20] Titanium(III) bromide and iodide also react with coordinating solvents to form compounds analogous to those of the chloride.[6,18,20-22]

There are several alternative methods to prepare complexes of titanium(III) halides. Addition of the ligand to titanium trichloride suspended in another solvent is used to prepare compounds containing alcohols, alkoxide ions, nitriles, and amines.[1,16,23] In many cases an intermediate complex such as $TiCl_3 \cdot 2(CH_3)_3N$ or $HTiCl_4 \cdot Et_2O$ is used to prepare compounds not obtainable by direct synthesis.[6,24] Trimethylamine is displaced from $TiCl_3 \cdot 2(CH_3)_3N$ in dioxane and the very soluble $TiCl_3 \cdot 3$dioxane is formed.[9] Tetraethylammonium halide added to $TiX_3 \cdot 3CH_3CN$ (X = Cl, Br) in acetonitrile yields the polymeric $(C_2H_5)_4N[TiX_4 \cdot 2CH_3CN]$.[25] The intermediate $TiBr_3 \cdot 2(CH_3)_3N$, used to prepare a variety of titanium(III) bromide complexes, is prepared by the reduction of titanium(IV) bromide with trimethylamine.[22] $TiCl_3 \cdot nCH_3OH$ (n = 4,5) is made by the electrolytic reduction of titanium(IV) chloride in methanol.[24] Several complexes eliminate non-halide ligands when heated in a vacuum and compounds of the type $TiCl_3 \cdot 2L$ (L = NH_3, THF, DMF),[11,14,24] $TiCl_3 \cdot L$ (L = THF, CH_3CN),[25,26] and $(C_2H_5)_4N[TiX_4]$ (X = Cl, Br) are formed.[25]

Complexes in which the titanium atom is coordinated to six identical, non-bridging ligands generally exist only in solution. Systems of the type $[TiL_6]^n$ containing water, halides, alcohols, urea, acetonitrile, and amines have been characterized.[27-30] Solid compounds which have been isolated include the hexammine complex,[5] $(C_5H_5N)_3[TiX_6]$ (X = Cl, Br),[25] and $Ti(CH_3CN)_6(I_3)_3$ which has been prepared by the oxidation of powdered titanium metal with iodine in acetonitrile.[31]

Titanium(III), having only one d electron, has a ^2D ground state. In an octahedral ligand field this ground state is split into two levels (Figure 1). The upper level, ^2E_g, is separated from the ground level, $^2T_{2g}$, by an energy Δ_0. The orbital degeneracy in each of these two levels is lifted by components of lower symmetry. Generally the ligand field symmetry about the titanium atom is reduced from cubic (O_h) to tetragonal (D_{4h}) or trigonal (D_3) although other symmetries are also possible depending upon the nature of the ligands.

Trigonal distortion, caused by elongation or compression along the C_3 axis of the octahedron, leaves the ^2E_g state of the cubic field unchanged but splits the $^2T_{2g}$ state into a ^2E and a $^2A_1$ state, with an energy separation δ_1. Tetragonal deformation, caused by compression or elongation along the C_4 axis, splits the $^2T_{2g}$ ground state into an upper ^2E_g and a lower $^2B_{2g}$ level separated by an energy δ_1. The ^2E_g state of the octahedral field is split into a $^2A_{1g}$ level, and a $^2B_{1g}$ level, separated by an energy δ_2. The ordering of these two levels, shown in Figure 1, are those which are most widely used.[8,28,32] They are the reverse of those used by McDonald *et al.* which must be considered when spectrochemical data are compared.[7]

The $^2T_{2g} \rightarrow {}^2E_g$ transition in octahedral titanium(III) complexes falls between 13,000 and 20,000 cm^{-1}. The intensity of the peak ($\varepsilon \sim 3$ to 12) is consistent for transitions which are Laporte forbidden but which appear because of

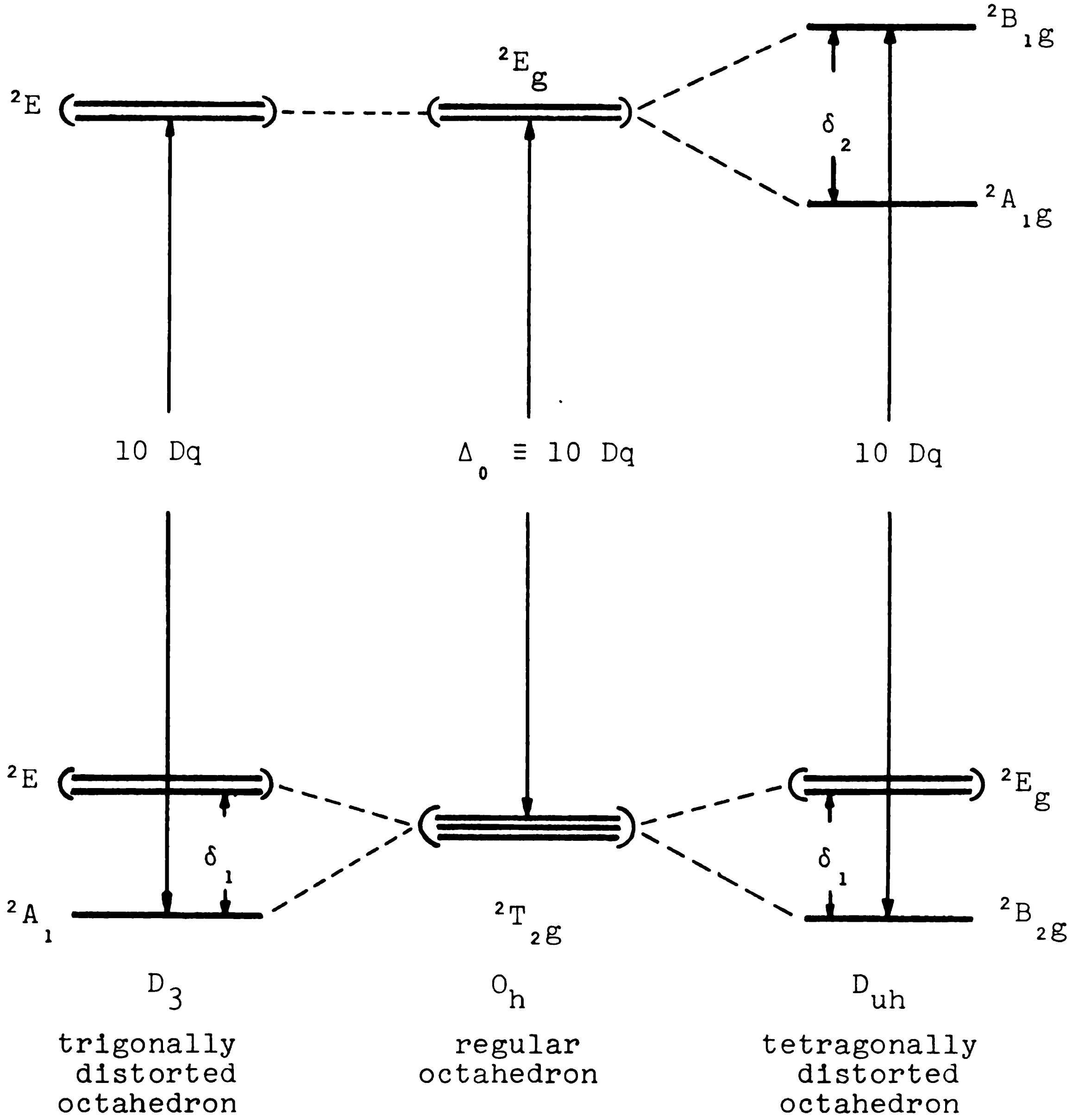

Figure 1. Relative energy of the titanium(III) d orbitals in octahedral, tetragonal, and trigonal environments.

vibronic coupling.[33] However, the expected sharp symmetrical ligand-field peak is not seen. The actual peak is broad and asymmetric, showing a distinct doublet structure which indicates that the ligand field must contain at least a tetragonal component. As previously indicated, a tetragonal deformation will split both the ground term ($^2T_{2g}$) and the upper term (^2E_g) so that two transitions, $^2B_{2g} \rightarrow {}^2A_{1g}$ and $^2B_{2g} \rightarrow {}^2B_{1g}$, would be expected. The tetragonal distortion is considered to be the result of the Jahn-Teller effect,[34,35] which removes the degeneracy of the original cubic field orbitals, and is on the order of 1,000 to 3,000 cm^{-1} for titanium(III) complexes.[8]

The difference in the energies of the two transitions corresponds to the separation energy δ_2 of the upper orbitals. Because data concerning the concommitant splitting of the ground level are not obtainable from optical spectroscopy, the usual practice for a d^1 system is to make no correction in either the upper or ground states for lower-symmetry components in the octahedral ligand field.[36] The energy Δ_o of the $^2T_{2g} \rightarrow {}^2E_g$ transition is taken to be that of the more intense upper band of the asymmetric ligand field band. The energy Δ_o is also equal to 10 Dq, where Dq is the cubic field splitting parameter.

To facilitate comparisons of ligand field strengths when the ligands are varied, the practice of ignoring lower ligand-field symmetries also extends to tetragonal and trigonal complexes. Although the perfect octahedral field no longer exists, the energy of the most intense d-d transition is set equal to 10 Dq. In tetragonal complexes this corresponds to the $^2B_{2g} \rightarrow {}^2B_{1g}$ transition. It can be seen from figure one that trigonal complexes have only one upper state. No amount of trigonal distortion, however great, removes the degeneracy of this E_g state. Thus only a single ligand field peak would be expected to appear in the optical spectrum. However, the spectrum of trigonal complexes shows the same double structure observed in octahedral and tetragonal complexes so a tetragonal component must also be present. For trigonal complexes the energy of the $A_{1g} \rightarrow B_{1g}$ transition is taken to be equal to 10 Dq.

Visible and ultraviolet spectra have been obtained for many of the titanium(III) complexes reported. All show the asymmetric or double structure caused by tetragonal distortion. Several ligands, along with their Dq values, fit into the spectrochemical series in the following order:

CH_3CN (2390) > H_2O (2010) > $(NH_2)_2CO$ (1754) > $(CH_3)_2CO$ (1710)

> CH_3OH (1680) > $C_4H_8O_2$ (1590) > C_4H_8O (1570) > Cl (1370).

It is assumed that Jorgensen's rule of average environment is obeyed.[37] The absorption spectrum of a solution of the trisacetonitrile complex of titanium(III) chloride is the same as the reflectance spectrum of the solid. However, the two spectra are clearly different for the tristetrahydrofuran or bisdioxane complexes which would indicate that the nature of the absorbing species in solution is different from that of the solid.[8]

Charge transfer bands, generally more intense than ligand field bands, appear in the ultraviolet region of the spectrum. They arise from transfer of the d electron of titanium to antibonding π molecular orbitals on the ligands or transfer of π-electrons from the ligands to vacant d orbitals of titanium. The exact nature of the transitions is unknown but tentative assignments have been made in some cases.[6,8,9]

The infrared spectra of titanium(III) complexes generally show band shifts and splittings associated with coordination. For example, the 2253 cm^{-1} band of CH_3CN is shifted 35 cm^{-1} higher in the compound $TiCl_3 \cdot 3CH_3CN$.[8] The bands assigned to symmetric and asymmetric C-O-C stretching vibrations of the cyclic ethers tetrahydrofuran and dioxane are shifted to lower wave numbers and split upon coordination through the oxygen.[8,9] Information about the symmetry of the complex may be obtained from the titanium-halogen bands in the far infrared spectrum. A <u>cis</u> (C_{3v})

complex should have two infrared active metal-halogen vibrations while a trans (C_{2v}) complex should have three. On this basis Clark has shown that $TiCl_3 \cdot 3C_4H_8O$ is trans and $TiCl_3 \cdot 3CH_3CN$ is cis.[38] However, the far infrared bands are often too broad to provide any useful information.

Data concerning the variation of the magnetic moment with temperature can provide useful information about axial distortion, spin-orbit coupling, and electron delocalization in titanium(III) complexes. Extensive reviews of this area are available[33,39,40] and only a brief summary will be given here.

Paramagnetic susceptibilities, from which the magnetic moments are calculated, vary inversely with temperature according to the Curie law

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

or the Curie-Weiss law

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

In these equations χ_m is the molar susceptibility, corrected for the diamagnetic contribution of titanium and the ligands, T is the absolute temperature, and C is the Curie constant, characteristic for each substance. θ, the Weiss constant which takes intermolecular interactions into account, is the temperature at which a plot of $1/\chi_m$ against T intercepts the T axis.

The magnetic moment is calculated from the molar susceptibility by

$$\mu = 2.84\ (\chi_m T)^{\frac{1}{2}}$$

for compounds which obey the Curie law.[40,41] The quantity $(T+\theta)$ must be used in place of T if the Curie-Weiss law is obeyed. However, in many cases the magnetic susceptibility data do not fit either law. The usual practice in these cases is to use the Curie law to determine the magnetic moment at a specific temperature and label this moment the effective magnetic moment μ_{eff} at the specified temperature.[42]

In the simplest case where there is no orbital angular momentum the magnetic behavior of the complex arises only from electron spin angular momentum. As a result, the spin-only magnetic moment is 1.73 Bohr magnetons for titanium(III). In molecules with a high degree of ligand field symmetry orbital angular momentum is present and will couple with the spin angular momentum. Spin-orbit coupling has a considerable effect upon the variation of the magnetic moment with temperature. Kotani has shown that the magnetic moment of a purely octahedral d^1 complex should approach zero as the temperature approaches zero.[43] However, there are no titanium(III) complexes which behave in this manner. Both axial distortion of the ligand field symmetry and orbital delocalization of the t_{2g} electron onto the ligands cause the magnetic moment to tend toward the spin-only value.

Figgis has presented a method for the treatment of the magnetic susceptibility data of titanium(III) systems from which estimates can be made of the following factors which quench the orbital angular momentum and cause the magnetic moment to approach the spin-only value:[44]

1. orbital delocalization (1-k) which is the fraction of time the t_{2g} electron spends upon the ligand atoms
2. spin orbit coupling λ' which is reduced from the free ion value λ by complexation[45]
3. energy separation δ_1 between the orbitals derived from the splitting of the ${}^2T_{2g}$ state by axial distortion.

Figgis has calculated theoretical, effective magnetic moments at several temperatures for a range of values for k (the amount of time the electron spends on the titanium atom) and v, where

$$v = \frac{\delta_1}{\lambda}$$

A positive value for v, and thus for δ_1, indicates that the orbital singlet from the splitting of the ${}^2T_{2g}$ state lies lowest and is the ground state. A plot is made of the experimental magnetic moments against kT/λ where k is the Boltzmann constant, T is the absolute temperature, and λ is the free ion spin orbit coupling constant. The resultant curve is compared to the theoretical curves of Figgis and the best values of k and v are determined by the best fit of the curves. The value of λ' is determined by substituting λ' for λ in the abscissa of the plot of the experimental data. The value of λ', a fraction of λ, is then adjusted until the best match of the curves is made. Although ligand fields of low symmetry cause the magnetic moment to tend toward the spin-only value, the effect is not great even for compounds which have axial ligand field components ten times the spin-orbit coupling constant. The effect of orbital delocalization is much greater.

In the preceeding discussion it has been assumed that the individual titanium atoms act independently of each other. Generally this is true but in at least two cases exchange interactions cause the compound to exhibit antiferromagnetism. Figure 2 shows the variation of χ_m with temperature for paramagnetic and antiferromagnetic substances. Above the Néel point the behavior of both types of compounds is similar, but below the Néel temperature χ_m of the antiferromagnetic compound rapidly decreases with temperature. Even above the Néel

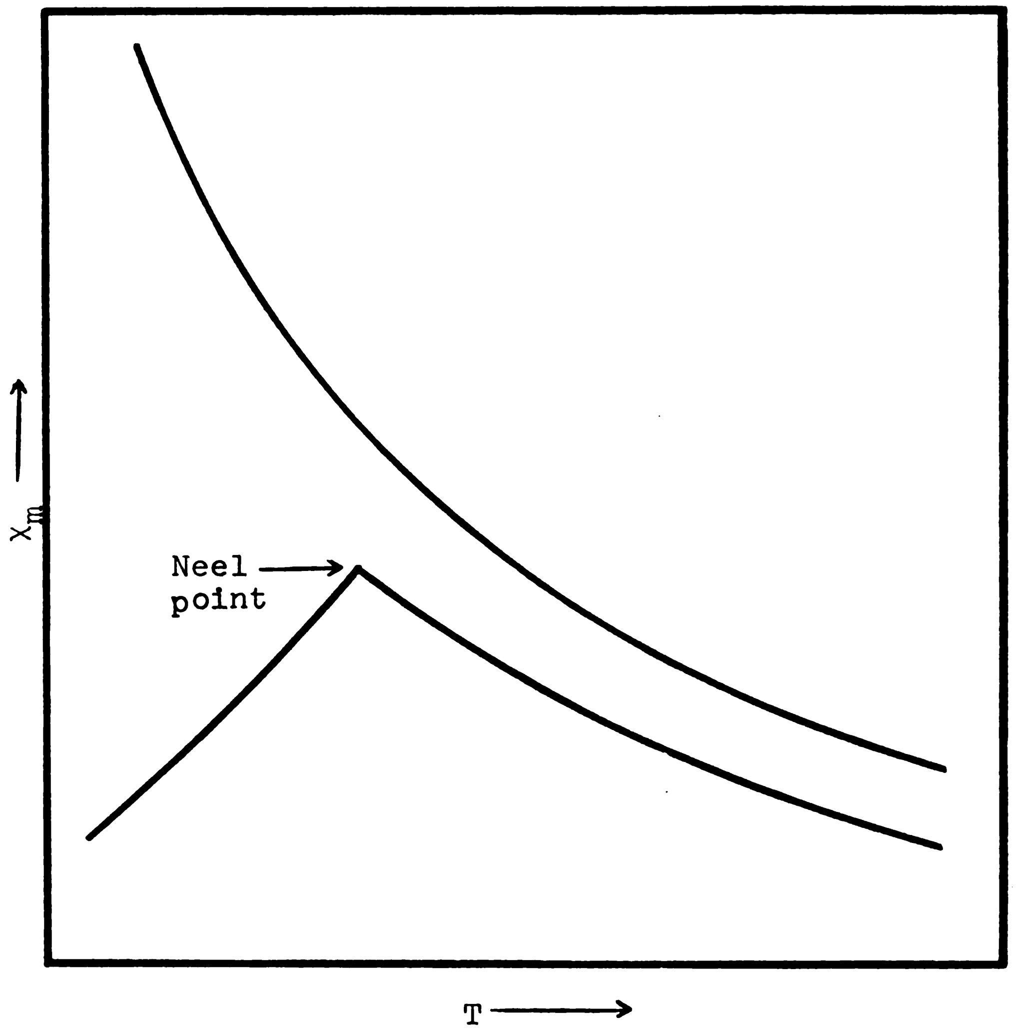

Figure 2. Magnetic behavior of typical (1) paramagnetic and (2) antiferromagnetic substances as a function of temperature.

temperature the magnetic moment of an antiferromagnetic titanium(III) compound is markedly reduced from the spin-only value.

Antiferromagnetism may come from intermolecular interactions, extending throughout the crystal, or intramolecular interactions, limited to within the molecule. With intermolecular interactions exchange between paramagnetic centers takes place through intervening atoms, known as "super-exchange." Super-exchange is destroyed when the interacting ions are separated by dissolution or dilution in a solid isomorphous diamagnetic host. Intramolecular interactions are unchanged by dissolution or dilution. Earnshaw *et al.*[46] have presented a mathematical treatment for the determination of the number of interacting spins S and the value of the exchange integral J for the equation $\Delta E = 2JS_iS_k$. The treatment of the magnetic data to find n, the number of spins and consequently the number of members of a polymeric chain, and J is similar to the treatment of magnetic data of paramagnetic complexes in the Figgis method. Titanium trichloride exhibits antiferromagnetism[47] but titanium tribromide does not.[48] The only complex reported to show antiferromagnetic behavior is $TiCl_3 \cdot CH_3CN$.[25]

Electron spin resonance (esr) measurements can provide valuable information concerning the structure, magnetic behavior, and molecular orbital parameters of transition metal complexes. There are many books and reviews which cover the fundamentals and applications of electron spin resonance.[49] Several references which deal specifically with titanium(III) in different crystal field symmetries are Kuska,[50] Carrington and Longuet-Higgens,[51] and Gladney and Swalen.[52]

It would be expected that titanium(III), as a d^1 electron system presenting the simplest of crystal field problems, would have been extensively studied. However, a review of the literature has shown that this is not the case. In octahedral lattice sites, such as with cesium titanium alum, the spin-lattice relaxation time is very short because of the presence of a low-lying excited state and resonance is only detected at liquid helium temperatures.[53-56]

Compounds of lower symmetry generally exhibit a resonance at room temperature, although the resonance may be anisotropic and only an average value of the gyromagnetic ratio is seen. Among the titanium(III) complexes of lower symmetry for which a resonance has been observed are those containing acetylacetone,[57,58] halides,[59] or alkoxides.[1,60] Giggenbach and Brubaker presented the esr spectrum of several mixed complexes containing chloride ion, methanol, methoxide ion, or acetonitrile.[1] The resonance spectrum of trichlortrisacetonitriletitanium(III) has been observed by McDonald _et_ _al_.[14] and Giggenbach.[61]

Ti^{48}, which has a natural abundance of 73.9%, has no nuclear spin and consequently does not give rise to hyperfine splitting of the epr spectrum. Ti^{47}, 7.3% natural abundance, and Ti^{49}, 5.5% natural abundance, have nuclear spins of 5/2 and 3/2 respectively. Hyperfine splittings caused by these two nuclei have been observed by Waters and Maki[59] and McGarvey.[57] The hyperfine patterns are best observed at -45° and at other temperatures the resonance broadens and only a broad asymmetric signal is seen.[1]

Thermochromism is the property of a compound to change color when the temperature is changed.[49,62] Generally this occurs in solids when a lowering of the temperature causes the charge transfer bands to sharpen and tail less into the visible region of the spectrum. In this case the color change should be gradual and no other changes in properties should take place. When thermochromism is associated with a phase change in the solid the color change should be abrupt (except for hysteresis) and other changes in the properties of the solid may occur. There are no previous reports of thermochromism being observed in titanium(III) complexes.

There are very few reports of titanium(III) complexes of the type $TiCl_3L_2L'$ where L and L' are different non-halide ligands. One of the objectives of this research was to prepare and characterize compounds of this type which contain acetonitrile, tetrahydrofuran, dioxane, and isopropanol as the non-halide ligands. Another objective was to prepare and study the series of compounds $TiCl_3 \cdot 3L$, $[TiCl_4 \cdot 2L]^-$, and $TiCl_3 \cdot L$. In $TiCl_3 \cdot L$ chloride ions bridge titanium atoms so that each titanium is coordinated to five chloride ions and one non-halide ligand. The experimental data were examined to find correlations between changes in the properties of the complexes and the nature of the ligands. In some cases the properties of the $TiCl_3L_2L'$ were expected to be intermediate to those of the parent complexes $TiCl_3 \cdot nL$ and $TiCl_3 \cdot nL'$. The location of the d-d absorption bands could be predicted from Jorgensen's rule of average environment and the Dq values of the ligands. The symmetries of the $TiCl_3L_2L'$ complexes were lower than those of the parent complexes. The changes in symmetry were expected to be apparent in the esr spectra and magnetic behavior of the compounds. The effect of an increased halide content was studied in the series $TiCl_3 \cdot 3L$, $(TiCl_4 \cdot 2L]^-$, $TiCl_3 \cdot L$. However, $TiCl_3 \cdot L$ may show additional changes because of the presence of bridging chloride ions. As very few esr spectra of titanium(III) chloride adducts have been reported, the spectra were obtained for all of the compounds in this research to observe the effect of the symmetry and the nature of the ligands upon the g value.

EXPERIMENTAL

A. Materials

Titanium Trichloride.--Anhydrous titanium trichloride was obtained from K & K Laboratories, Inc. and Research Organic/Inorganic Chemical Company. Titanium(III) and chloride determinations gave an analysis of 99.91% titanium (III) chloride and the compound was used without further purification. It was stored in a Schlenk vessel to facilitate subsequent transfer.[63]

Solvents.--[64]All solvents were refluxed with an appropriate drying agent under a nitrogen atmosphere except where indicated. Purity of the solvents was checked by examination of their proton magnetic resonance spectrum for evidence of impurities.

Acetonitrile was stirred with 200 mesh silica gel several hours and then stirred overnight with calcium hydride. After evolution of hydrogen had ceased, two grams of phosphorus pentoxide per liter of solvent was added and the acetonitrile was refluxed continuously. It was distilled at a high reflux ratio immediately before use.

Chloroform was washed with water and dried with calcium chloride. After the chloroform had refluxed 24 hours with phosphorus pentoxide it was distilled and stored in the absence of light before being used.

Dioxane was stored over sodium hydroxide. It was refluxed with sodium and distilled after the surface of the sodium had become shiny and the purple color of the disodium benzophenone complex was formed.[65]

Trimethylamine (anhydrous liquid from Eastman Organic Chemicals) was transferred to a Schlenk vessel and stored at -5°. It was distilled at a reduced pressure into the reaction vessel which was at -78°.

Isopropyl alcohol was continuously refluxed with sodium isopropoxide and distilled immediately before use.

Tetrahydrofuran, diethyl ether, and benzene were refluxed continuously with lithium aluminum hydride and distilled immediately before use.

<u>Tetraethylammonium Chloride</u>.--Tetraethylammonium chloride was obtained from Eastman Organic Chemicals. Twice it was ground, boiled with dry benzene to remove the water, and dried under vacuum. This method gave a product of higher purity than by merely drying the tetraethylammonium chloride in an oven at 100°.

<u>Gases</u>.--Oil-pumped prepurified nitrogen from Liquid Carbonics was passed through a heated activated copper catalyst (BTS catalyst - BASF R 3-11 from Badische Anilin- & Soda-Fabrik AG) at 150° to remove oxygen and through Aquasorb (indicating moisture absorbant, containing phosphorus pentoxide,

from Mallinckrodt Chemical Works) to remove water. The nitrogen in the controlled atmosphere box was continuously recirculated through the Aquasorb and heated BTS columns. The condition of the atmosphere in the controlled atmosphere box was checked by observing the burning time of an exposed light-bulb filament.

Hydrogen chloride from Matheson Gas Products was anhydrous and was used without further purification.

Analytical Reagents.--Silver nitrate was ground and dried at 180°, reground and stored in a vacuum desiccator. A 16.989 g sample was dissolved in one l of distilled water to make a 0.1000 N. solution.

A 0.100 N cerium(IV) sulfate solution was prepared from a standard solution from Fisher Scientific and the concentration checked by titration with ferrous ammonium sulfate. Ferroin (1,10-phenanthroline ferrous sulfate complex) was used as the indicator.

Dilute sulfuric acid was prepared by boiling demineralized distilled water, adding enough sulfuric acid to make a 4 M solution, boiling the mixture for another five minutes, and then cooling the solution in a special Schlenk vessel. Nitrogen was rapidly, and continuously bubbled through the solution during its preparation and cooling.

B. Analytical Methods

Carbon, Hydrogen, and Nitrogen Analysis.--These analyses were performed by the microanalytical laboratory of the Institute of Water Research, Michigan State University, East Lansing, Michigan. Although special handling precautions were taken to avoid decomposition of the samples, they reported the samples very difficult to analyze. Identical samples did not always give similar results.

Chloride Analysis.--Generally the solid sample was quickly dissolved in water but in cases where hydrogen chloride may be lost the sample was first cooled to 77°K and dilute sulfuric acid added. After the sample was slowly warmed to room temperature it was treated in the usual manner.

It was necessary to oxidize the titanium(III) catalytically with air prior to the chloride determination. This was done by the addition of one milliliter of a saturated solution of copper sulfate in 9M sulfuric acid to the dissolved sample and stirring the solution until the color changed from violet to yellow.

Chloride was determined by a differential potentiometric titration with a standard silver nitrate solution.[66] Silver-silver chloride electrodes and a Corning Model 10 pH meter were used.

Titanium(III) Analysis.--Titanium(III) was determined by a cerimetric technique. As the sample was sensitive to oxidation, it was cooled to 77° K in a Schlenk vessel and deoxygenated dilute sulfuric acid was added. After the solution had warmed to room temperature, it was titrated with cerium(IV) sulfate. Ferroin was used as the indicator. A nitrogen atmosphere was maintained over the solution during the dissolution and titration of the sample.

The total titanium content was determined spectrophotometrically as the titanium(IV) hydrogen peroxide complex in sulfuric acid.[67] Beer's law is obeyed at 410 nm for solutions containing up to 75 mg titanium(IV) per liter. The analysis was performed on a portion of the solution prepared for chloride analysis, in which the titanium(III) had been catalytically oxidized. Some samples could not be analyzed in this manner because the solution was turbid and the absorbance reading was thus abnormally high. Although the total titanium analysis also measured any titanium(IV) impurity present in the original sample, the two methods gave very close agreement in most cases.

C. Experimental Apparatus and Technique

All of the titanium(III) samples prepared were sensitive to water and oxygen. All reactions and manipulations were carried out under a nitrogen atmosphere. Schlenk tube techniques, similar to those recently presented by Herzog *et al.*,[63] were used throughout. One difference is that inner ground glass joints were generally used on Schlenk vessels to facilitate transfer and so that compounds would not come into contact with the silicone lubricant on the joint.

An important factor in the successful preparation of the titanium(III) complexes was the use of a vacuum manifold in connection with the nitrogen line. Whenever a glassware connection was made or broken, nitrogen was forced into the vessels through the side-arm stopcocks. This positive flow of nitrogen, about four liters per minute, prevented air from entering the vessel. When the vessel was closed, it was immediately evacuated and the atmosphere replaced with fresh nitrogen. Clean glassware, dried at 180° for several hours, was evacuated and filled with nitrogen several times while it cooled.

As the nitrogen of the controlled atmosphere box was not nearly as pure as that in the Schlenk vessels, which could be changed quickly, the box was little used except for the storage of compounds in Schlenk vessels and for the manipulations not amenable to Schlenk tube techniques. These included preparation of mulls for optical spectroscopy and the filling of esr and magnetic susceptibility tubes.

D. Preparation of the Compounds

Trichlorotrisacetonitriletitanium(III).--Eight grams of titanium trichloride was added to 300 ml of acetonitrile. The mixture was heated and the solvent allowed to reflux several hours. The color of the mixture changed from violet to blue during this time. Half of the solvent was then removed by vacuum evaporation which also served to cool the remaining mixture. The cold solution was filtered and the dark blue crystals were washed with portions of acetonitrile and dried under vacuum.

Analysis. Calc. for $TiCl_3C_6H_9N_3$: Ti, 17.27; Cl, 38.34; C, 25.98; H, 3.27; N, 15.15. Found: Ti, 17.29; Cl, 38.68; C, 26.34; H, 3.51; N, 14.78.

Trichlorotristetrahydrofurantitanium(III).--This compound was prepared in a manner similar to that of the above acetonitrile complex. Finely divided turquoise blue crystals were obtained.

Analysis. Calc. for $TiCl_3C_{12}H_{24}O_3$: Ti, 12.93; Cl, 28.70; C, 38.86; H, 6.53. Found: Ti, 12.98; Cl, 28.70; C, 38.84; H, 6.54.

Trichlorobisdioxanetitanium(III).--This compound was prepared in a manner similar to that of the above acetonitrile complex. The reaction time was about 16 hours. A pale green powder was collected.

Analysis. Calc. for $TiCl_3C_8H_{16}O_4$: Ti, 14.50; Cl, 32.19; C, 29.06; H, 4.89; Found: Ti, 14.54; Cl, 32.22; C, 28.78; H, 5.03.

Longer reaction times (60, 100, and 240 hours) gave a product similar in appearance, analysis, and behavior.

Trichlorotetrakis(2-propanol)titanium(III).--This compound was also prepared in a manner similar to that of the above acetonitrile complex. The reaction was complete in two hours and yeilded a blue powder.

Analysis. Calc. for $TiCl_3C_{12}H_{32}O_4$: Ti, 12.15; Cl, 26.96; C, 36.50; H, 8.18. Found: Ti, 12.13; Cl, 26.88; C, 36.00; H, 7.95.

Trichloroacetonitriletitanium(III).--A portion of $TiCl_3 \cdot 3CH_3CN$ was heated at 100° under a vacuum for several hours until the evolution of a gas ceased. The residue was a brown powder.

Analysis. Calc. for $TiCl_3C_2H_3N$: Ti, 24.42; Cl, 54.45; C, 12.28; H, 1.55; N, 7.17. Found: Ti, 24.54; Cl, 54.18; C, 11.98; H, 1.65; N, 6.86.

The reaction will proceed at 70° but at temperatures above 100° or with prolonged heating a dark violet-brown product was formed. This may contain $TiCl_3$ as titanium and chloride analyses were higher than those above.

In some cases a yellow sublimate was collected which appeared to be $TiCl_4 \cdot 2CH_3CN$. It was thermochromic, turning white as it was cooled to 77°K.

Analysis. Calc. for $TiCl_4C_4H_6N_2$: Ti, 17.62; Cl, 52.17. Found, Ti, 17.72; Cl, 53.12.

Trichlorotetrahydrofurantitanium(III).--A sample of $TiCl_3 \cdot 3C_4H_8O$ was heated under vacuum at 75°. A gas was evolved and the sample turned light green and then grey-green. The light green substance, which may be $TiCl_3 \cdot 2C_4H_8O$, could not be isolated. The gray-green solid turns violet as it is cooled to 77°K.

Analysis. Calc. for $TiCl_3C_4H_8O$: Ti, 21.16, Cl, 46.98; C, 21.20; H, 3.56. Found: Ti, 21.20; Cl, 46.80; C, 20.63; H, 3.62.

A thermochromic yellow sublimate, apparently $TiCl_4 \cdot 2C_4H_8O$, was also obtained when the samples were briefly exposed to the atmosphere.

Analysis. Calc. for $TiCl_4C_8H_{16}O$: Ti, 14.35; Cl, 42.47. Found: Ti, 14.58; Cl, 42.64.

Trichlorodioxanetitanium(III).--$TiCl_3$ $2C_4H_8O_2$ heated to 140° under vacuum gave a finely divided cream powder.

Analysis. Calc. for $TiCl_3C_4H_8O_2$: Ti, 19.76; Cl, 43.89; C, 19.81; H, 3.33. Found: Ti, 19.98; Cl, 43.74; C, 19.36; H, 3.31.

Trichlorotris(2-propoxy)dititanium(III).--A sample of $TiCl_3 \cdot 4C_3H_8O$ was heated under vacuum at 75° for ten hours. Hydrogen chloride and 2-propanol were evolved and the remaining solid turned red-brown.

Analysis. Calc. for $Ti_2Cl_3C_9H_{21}O_3$: Ti, 25.25; Cl, 28.03. Found: Ti, 26.70; Cl, 29.33.

Trichloroacetonitrilebistetrahydrofurantitanium(III).--Four grams of $TiCl_3 \cdot 3C_4H_8O$ was suspended in tetrahydrofuran and twenty milliliters of acetonitrile was added. After the solution was stirred and heated nine hours the volume was reduced by vacuum evaporation to forty milliliters. An equal quantity of hexane was added and the solution was stirred vigorously. The blue solid which precipitated was collected on a filter and dried under vacuum.

Analysis. Calc. for $TiCl_3C_{10}H_{19}O_2N$: Ti, 14.11; Cl, 31.33; C, 35.35; H, 5.65; N, 4.13. Found: Ti, 14.25; Cl, 31.30; C, 34.48; H, 6.02; N, 4.01.

A different preparative method was tried in which three milliliters of tetrahydrofuran was added to 5.85 g $TiCl_3 \cdot CH_3CN$ suspended in benzene. After the mixture was stirred and heated six hours it was filtered. The gray-green solid, collected by filtration and dried under vacuum, was thermochromic and appeared to be $TiCl_3 \cdot C_4H_8O$.

Trichloroacetonitrilebisdioxanetitanium(III).--Several grams of $TiCl_3 \cdot 3CH_3CN$ were suspended in dioxane and the mixture was heated and stirred five hours. The very thick blue-green mixture was filtered and the solid was washed with dioxane and dried under vacuum. The blue-green powder is difficult to handle as it becomes charged with static electricity when it is ground.

Analysis. Calc. for $TiCl_3C_{10}H_{19}O_4N$: Ti, 12.90; Cl, 28.63; C, 32.31; H, 5.16; N, 3.77. Found: Ti, 12.98; Cl, 28.66; C, 33.40; H, 5.15; N, 4.78.

The preparation worked equally well when $TiCl_3 \cdot CH_3CN$ was used as the starting material or when acetonitrile was added to $TiCl_3 \cdot 2C_4H_8O_2$ in dioxane.

Trichlorotetrahydrofuranbisdioxanetitanium(III).--A quantity of $TiCl_3 \cdot C_4H_8O$ was suspended in dioxane and the mixture was heated and stirred. After two hours the solid had dissolved and the solution was brown. The volume of the solution was reduced to forty milliliters under a vacuum and an equal quantity of diethyl ether was added. Immediate precipitation resulted and the solid was washed with dioxane and dried under a vacuum.

Analysis. Calc. for $TiCl_3C_{12}H_{24}O_5$: Ti, 11.90; Cl, 26.42; C, 35.79; H, 6.01. Found: Ti, 12.00; Cl, 26.38; C, 35.13; H, 5.31.

The use of $TiCl_3 \cdot 3C_4H_8O$ as the starting material often did not give a homogeneous precipitate.

Trichloro(2-propanol)bisdioxanetitanium(III).--Ten milliliters of isopropyl alcohol was added to six grams of $TiCl_3 \cdot 2C_4H_8O_2$ in dioxane and the mixture was stirred and heated overnight. The volume of the solution was reduced under vacuum to 40 ml and an equal quantity of diethyl ether was added while the mixture was vigorously stirred. The solution was filtered and the pale blue precipitate was dried under vacuum.

Analysis. Calc. for $TiCl_3C_{11}H_{24}O_5$: Ti, 12.26, Cl, 27.23; C, 33.84; H, 6.19. Found: Ti, 12.16; Cl, 27.28; C, 33.15; H, 6.08.

Tetraethylammonium Tetrachlorobisacetonitriletitanate(III).--A known quantity of $TiCl_3 \cdot 3CH_3CN$ was dissolved in a solution of 10% acetonitrile in chloroform. Upon addition of 2.3 equivalents of tetraethylammonium chloride to the blue solution, the mixture immediately turned yellow. After one-half hour the mixture was brown and after it had been stirred overnight the mixture was green. The solution was filtered and a pale blue-green product was collected and dried under vacuum.

Analysis. Calc. for $TiCl_4C_{12}H_{26}N_3$: Ti, 11.91; Cl, 35.27; C, 35.85; H, 6.52; N, 10.45. Found: Ti, 12.01; Cl, 35.15; C, 34.91; H, 6.14; N, 10.38.

Tetraethylammonium Tetrachlorobistetrahydrofurantitanate(III).--A known quantity of $TiCl_3 \cdot 3C_4H_8O$ was dissolved in tetrahydrofuran and 2.5 equivalents of tetraethylammonium chloride was added. The mixture was stirred overnight. The solution was filtered and a pale green powder was collected and dried under vacuum.

Analysis. Calc. for $TiCl_4C_{16}H_{36}O_2N$: Ti, 10.32; Cl, 30.55; C, 41.40; H, 7.82; N, 3.02. Found: Ti, 10.36; Cl, 30.52; C, 41.31; H, 8.12; N, 3.25.

When the green powder was washed with chloroform it immediately turned orange-brown. After it had been dried under vacuum, the powder was salmon and was thermochromic. This material was also obtained from a solution of 10% tetrahydrofuran in chloroform. The material was non-stoichiometric with a titanium:chloride ion ratio of 1:4.5.

Analysis. Found: Ti, 11.58, Cl, 37.58.

Tetraethylammonium Tetrachlorobisdioxanetitanate(III).--A weighed quantity of $TiCl_3 \cdot 2C_4H_8O_2$ was suspended in dioxane and 2.5 equivalents of tetraethylammonium chloride was added. After the mixture had been stirred overnight it was filtered and the pale green powder which was collected was dried under vacuum.

Analysis. Calc. for $TiCl_4C_{16}H_{36}O_4N$: Ti, 9.67; Cl, 28.64; C, 38.81; H, 7.31; N, 2.83. Found: Ti, 9.61; Cl, 28.70; C, 38.59; H, 7.52; N, 2.95.

The same material was also prepared from a solution of 10% dioxane in chloroform.

E. Spectroscopic Measurements

Optical Spectra.--The infrared spectra of the compounds were determined by means of Nujol mulls on sodium chloride plates on a Unicam SP-200 spectrophotometer. Far infrared spectra were recorded on a Perkin-Elmer 457 grating spectrophotometer with the sample enclosed in cesium iodide or polyethylene plates. The visible and ultraviolet spectra were obtained by use of a Unicam SP-800 spectrophotometer and a Cary 14 spectrophotometer. Solid samples were mulled with Nujol and enclosed in quartz plates. As most of the compounds dissolve only with reaction no solution spectra of the complexes were obtained. A Beckman DU spectrophotometer was used for the spectrophotometric analysis of titanium.

Electron Spin Resonance Spectra.--The X-band esr spectra of the solid complexes were recorded at 297°K and 77°K. Compounds which were thermochromic were also studied at a range of intermediate temperatures. The X-band spectrophotometers used were a Varian E-4 esr spectrometer system and the Varian 4501-04 spectrometer previously described.[49] First derivative curves were recorded on an X-Y recorder with the X axis proportional to the magnetic field strength. A sample of pitch in potassium chloride ($g = 2.0028$) was used as a calibration standard. An E-257 variable temperature unit was used in the variable temperature studies. At lower temperatures the microwave power had to be greatly reduced to avoid saturation of the samples. The g values were calculated from the klystron frequency and the measured magnetic field.

F. Magnetic Moment Measurements

Magnetic susceptibilities were measured by the Guoy method by use of equipment similar to that previously described.[69] A specially designed Dewar vessel was used for temperatures lower than room temperature. A constant flow of helium was used to provide heat transfer from the sample and to prevent water from condensing on the sample tube.

TABLE I.--Low Temperature Baths for Magnetic Susceptibilities.

Temperature	Bath
77°K	Liquid Nitrogen
148°K	Petroleum Ether Slush
175.5°K	Methanol Slush
195°K	Dry Ice-isopropanol
209.7°K	Chloroform Slush
250.3°K	Carbon Tetrachloride Slush

The magnetic susceptibility was calculated from the experimental data according to the equation

$$10^6\chi = \frac{\alpha+\beta(F-\delta)}{W_s}$$

where χ is the gram susceptibility of the sample, α is the correction for the displacement of air by the sample, β is the tube constant, F is the measured force on the sample and the tube, δ is the force on the empty tube, and W_s is the weight of the sample. The correction for displaced air, α, was eliminated by weighing the empty tube filled with nitrogen. The constants β and δ must be measured for every field strength and temperature used. Although borosilicate glass is diamagnetic, it was found that impurities caused δ to be positive and on the order of 10-15 milligrams. To evaluate β the tube was standardized with $Hg[Co(SCN)_4]$ which has a susceptibility of $16.44\text{x}10^6$ cgs units of 20°. This standard obeys the Curie-Weiss law with $\chi_m \propto (T+10)^{-1}$.[70]

The magnetic susceptibilities of all compounds were measured at 77, 195, and 297°K. If the sample exhibited normal paramagnetism the magnetic susceptibilities were also measured at several intermediate temperatures so that an accurate plot of the effective moment against $\frac{kT}{\lambda'}$ could be obtained. As is usual for titanium(III) solvent adducts, no corrections were made for the small temperature independent paramagnetism of the samples. The molar susceptibility was obtained by multiplying the gram-susceptibility by the molecular weight. The metal ion susceptibility was then found by applying corrections for the diamagnetism of the ligands as computed from Pascal's constants.[71]

RESULTS AND DISCUSSION

A. Preparation and Reactions of the Complexes

During the course of this research the complexes of titanium(III) chloride with several coordinating solvents were studied. A new class of compounds, containing two different non-halide ligands, as well as several new compounds of classes previously reported were prepared. In addition, several known compounds were prepared to complete the characterizations. The reactions of all these compounds were studied, especially with regard to non-halide ligand substitution.

Titanium trichloride reacted with the coordinating solvents acetonitrile, tetrahydrofuran, and isopropanol to form the adducts $TiCl_3 \cdot 3CH_3CN$, $TiCl_3 \cdot 3C_4H_8O$, and $TiCl_3 \cdot 4C_3H_8O$ respectively. When the adduct of one solvent was dissolved in another solvent, all of the non-halide ligands were replaced by the latter solvent. However, $TiCl_3(C_4H_8O)_2(CH_3CN)$ was formed when $TiCl_3 \cdot 3C_4H_8O$ was dissolved in a solution of 20% acetonitrile in tetrahydrofuran.

The solid adduct produced by the reaction of titanium(III) chloride with dioxane was $TiCl_3 \cdot 2C_4H_8O_2$ in which only two dioxanes were coordinated with the titanium. Clark <u>et al</u>.[8] had concluded from the uv spectra that a different species

exists in solution though the species was not identified. Fowles *et al*.[9] reported that a dioxane solution of the very soluble complex $TiCl_3 \cdot 3C_4H_8O_2$ gave a similar spectrum. Fowles *et al*. also reported that with prolonged reaction times (up to sixty hours) $TiCl_3 \cdot C_4H_8O_2$ was formed. However, in this investigation reaction times as long as 240 hrs. produced only $TiCl_3 \cdot 2C_4H_8O_2$. As each titanium was coordinated to only two dioxane molecules, compounds of the type $TiCl_3(C_4H_8O_2)_2L$ were prepared by the addition of the solvent ligand L to $TiCl_3 \cdot 2C_4H_8O_2$ suspended in dioxane. This type of complex was also produced when a titanium(III) solvent adduct was dissolved in dioxane.

When the solvent adducts $TiCl_3 \cdot nL$ (L = acetonitrile, tetrahydrofuran, dioxane) were heated under vacuum, compounds of the type $TiCl_3 \cdot L$ were formed. Fowles and Russ[25] had reported that a green product was obtained when $TiCl_3 \cdot 3CH_3CN$ was heated one-half hour at 100°. In this research it was found that longer heating times were necessary and that the substance which remained after the evolution of a gas had ceased was brown. However, elemental analysis of this substance showed it was $TiCl_3 \cdot CH_3CN$.

When $TiCl_3 \cdot 3C_4H_8O$ was heated under vacuum at 75° it first turned light green and then gray-green. The light green substance could not be isolated as the color of the material was never uniformly light green. Analysis of the gray-green compound showed it was $TiCl_3 \cdot C_4H_8O$. Seifert and Thurn[24] reported that a green compound, $TiCl_3 \cdot 2C_4H_8O$, was produced when $TiCl_3 \cdot 3C_4H_8O$ was heated under vacuum at 70°. If the temperature was then increased to 90° another mole of tetrahydrofuran was lost and gray $TiCl_3 \cdot C_4H_8O$ remained. During the course of the present research it was also found that if the samples had been previously exposed to air a yellow sublimate was also formed. The sublimates were primarily $TiCl_4 \cdot 2L$ but contained some titanium(III). The $TiCl_4 \cdot 2L$ complexes and $TiCl_3 \cdot C_4H_8O$ were thermochromic. When compounds of the type $TiCl_3(C_4H_8O_2)_2L$ were heated under vacuum at 70° they eliminated the ligand L to form $TiCl_3 \cdot 2C_4H_8O_2$. When the temperature was raised to 100° a mole of dioxane was then lost to produce the final product $TiCl_3 \cdot C_4H_8O_2$. $TiCl_3(C_4H_8O)_2(CH_3CN)$ yielded $TiCl_3 \cdot C_4H_8O$ when heated under vacuum to 80°.

Generally the compounds of the type $TiCl_3 \cdot L$ reacted with coordinating solvents in the same manner as titanium trichloride. However, in dioxane the ligand L was not eliminated when the titanium coordinated with two dioxane molecules. This is a convenient method of preparation of the complexes $TiCl_3(C_4H_8O_2)_2L$ (L = acetonitrile, tetrahydrofuran). Attempts were made to produce other compounds by similar methods. After the addition of acetonitrile to $TiCl_3 \cdot C_4H_8O$ or $TiCl_3 \cdot C_4H_8O_2$ in stoichiometric amounts to form $TiCl_3(CH_3CN)_2(C_4H_8O)$ and $TiCl_3(CH_3CN)_2(C_4H_8O_2)$ respectively, the starting materials were recovered unchanged.

When a stoichiometric amount of tetrahydrofuran was added to $TiCl_3 \cdot L$ (L = acetonitrile, dioxane) to produce compounds of the type $TiCl_3(C_4H_8O)_2L$, the only product was $TiCl_3 \cdot C_4H_8O$.

Both hydrogen chloride and isopropyl alcohol were liberated when $TiCl_3 \cdot 4C_3H_8O$ was heated under vacuum at 75°. The red material which remained was (probably) a polymeric chloroalkoxo complex with the simplest formula $Ti_2Cl_3(C_3H_7O)_3$. This material did not appear to react with coordinating solvents which indicated that the alkoxide ligands were not easily replaced.

The reaction of tetraethylammonium chloride with titanium(III) adducts $TiCl_3 \cdot nL$ in tetrahydrofuran or dioxane produced compounds of the type $(C_2H_5)_4N[TiCl_4 \cdot 2L]$. However, in acetonitrile the reaction yielded only non-stoichiometric materials with a variable chloride content. In a chloroform-acetonitrile or chloroform-dioxane solvent system the compounds $(C_2H_5)N[TiCl_4 \cdot 2L]$ (L = acetonitrile, dioxane) were produced. When the reaction took place in a chloroform-tetrahydrofuran system, or when $(C_2H_5)N[TiCl_4 \cdot 2C_4H_8O]$ was washed with chloroform, the tetrahydrofuran was eliminated from the complex and the composition of the solid product approached that of $(C_2H_5)_4N[TiCl_4]$. If complexes of the type $LiCl_3L_2L'$ were used in place of $TiCl_3 \cdot nL$ in the reactions, the ligand L' was eliminated and $(C_2H_5)_4N[TiCl_4 \cdot 2L]$ was formed.

B. Infrared Spectra

The infrared spectra of the complexes were determined in Nujol mulls and the results are presented in figures 3 through 17. In general the spectra showed the shifts in absorption bands associated with coordination of the solvents. The CN stretching vibration of acetonitrile (2253.5 cm^{-1}) was shifted upward 35 cm^{-1} upon coordination through the nitrogen. The combination band at 2288 cm^{-1} was shifted upward 25 cm^{-1}. In tetrahydrofuran coordination through the oxygen was indicated by the lowering and splitting of the symmetric (909 cm^{-1}) and asymmetric (1071 cm^{-1}) C-O-C stretching vibrations of the free ligand by ~60 cm^{-1}. Coordination through oxygen in dioxane lowered and split the free ligand bands occuring at 1125 and 883 cm^{-1}. The spectrum of $TiCl_3 \cdot 2C_4H_8O_2$ showed the presence of both free and coordinated oxygen while the spectrum of $TiCl_3 \cdot C_4H_8O_2$ showed only coordinated oxygen. It was apparent from the spectrum of $Ti_2Cl_3(C_3H_7O)_3$ that the compound was a chloroalkoxo complex and no isopropyl alcohol remained. The spectra of complexes of the type $TiCl_3L_2L'$ showed some shifts of absorbtion bands from their positions in the parent complexes $TiCl_3 \cdot nL$ and $TiCl_3 \cdot nL'$. Considerable changes in the spectra were observed when the chloride:non-halide ligand ratio of the complexes was increased. These changes may have arisen from changes in both the symmetries

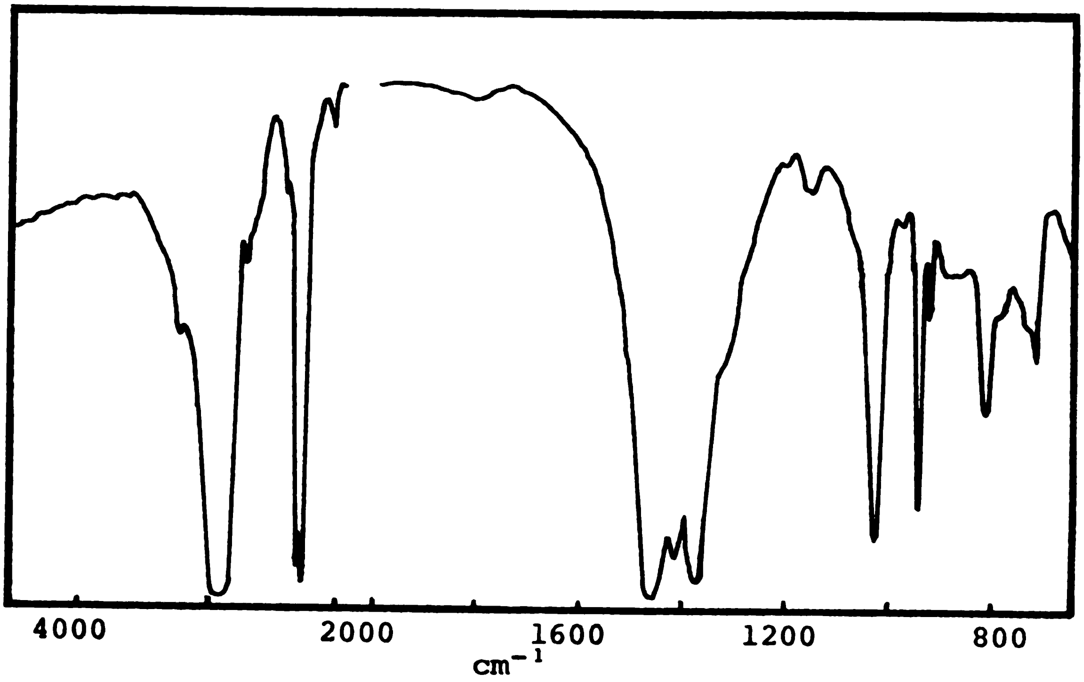

Figure 3. Infrared spectrum of $TiCl_3 \cdot 3CH_3CN$.

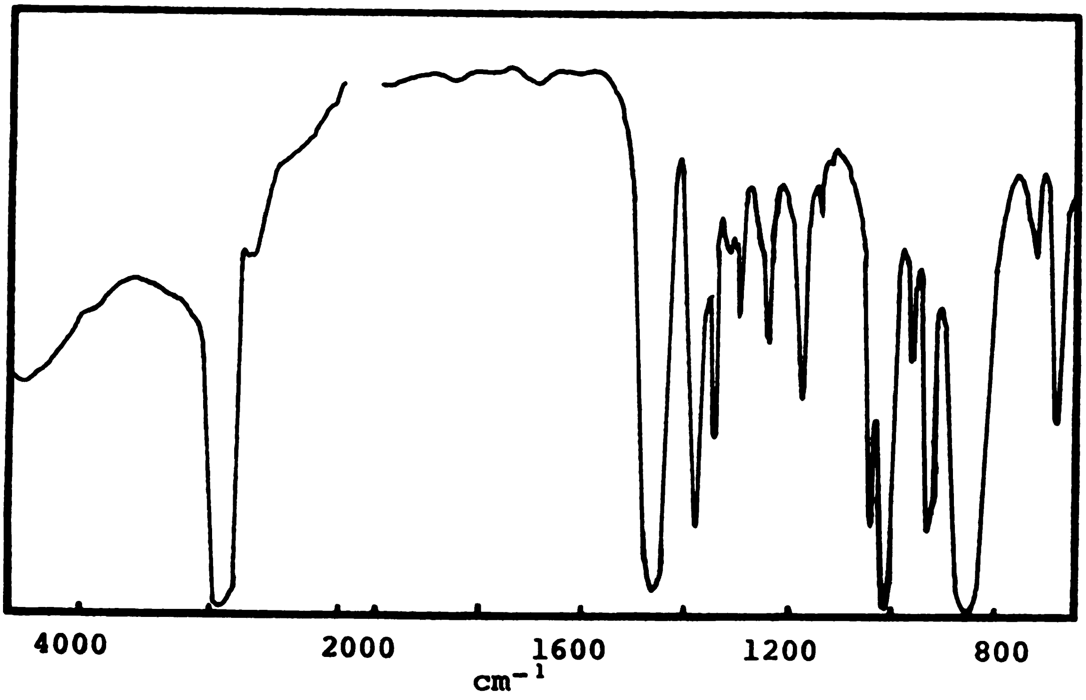

Figure 4. Infrared spectrum of $TiCl_3 \cdot 3C_4H_8O$.

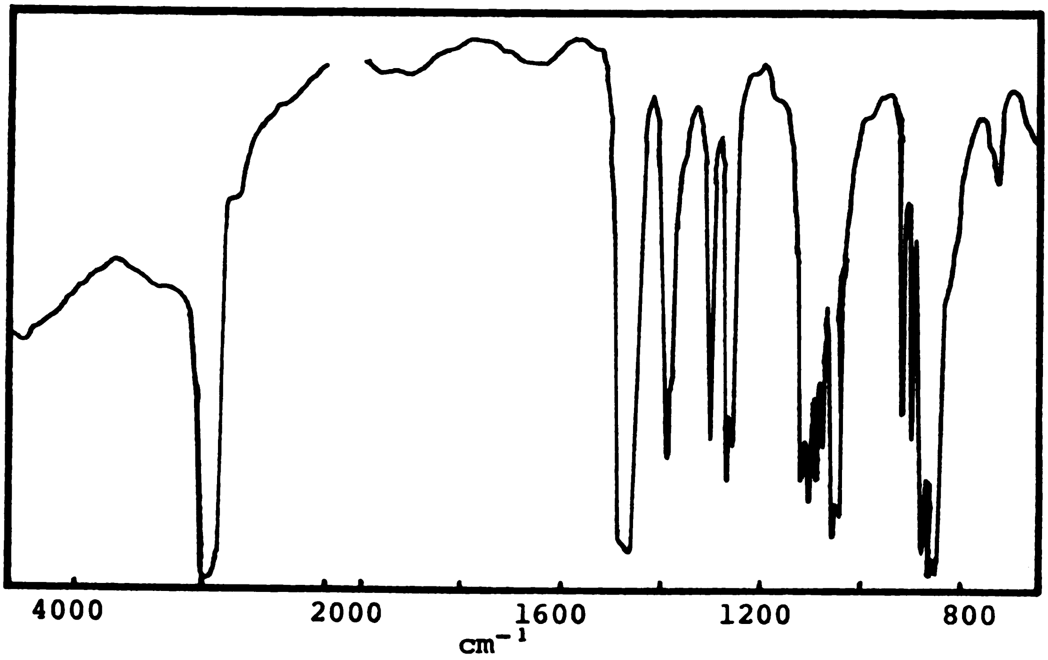

Figure 5. Infrared spectrum of $TiCl_3 \cdot 2C_4H_8O_2$.

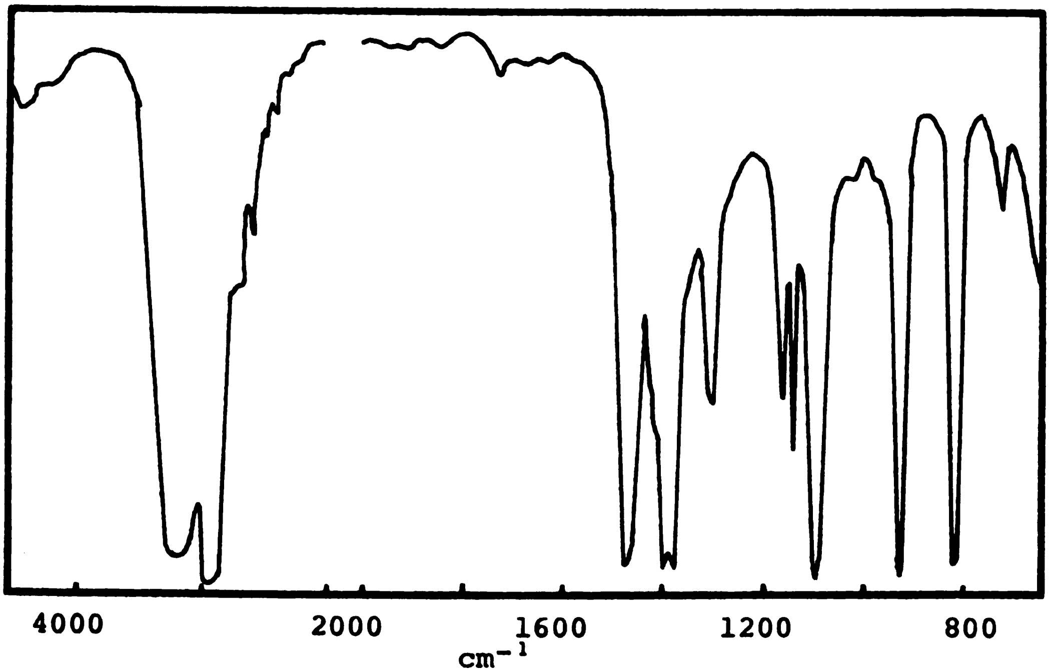

Figure 6. Infrared spectrum of $TiCl_3 \cdot 4C_3H_8O$.

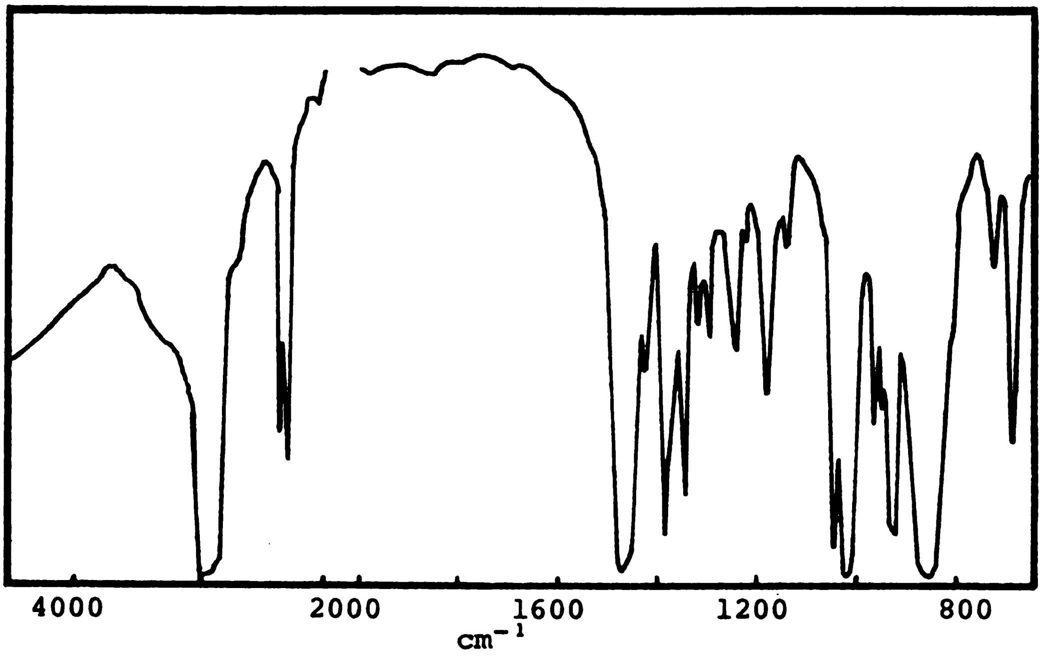

Figure 7. Infrared spectrum of $TiCl_3(C_4H_8O)_2(CH_3CN)$.

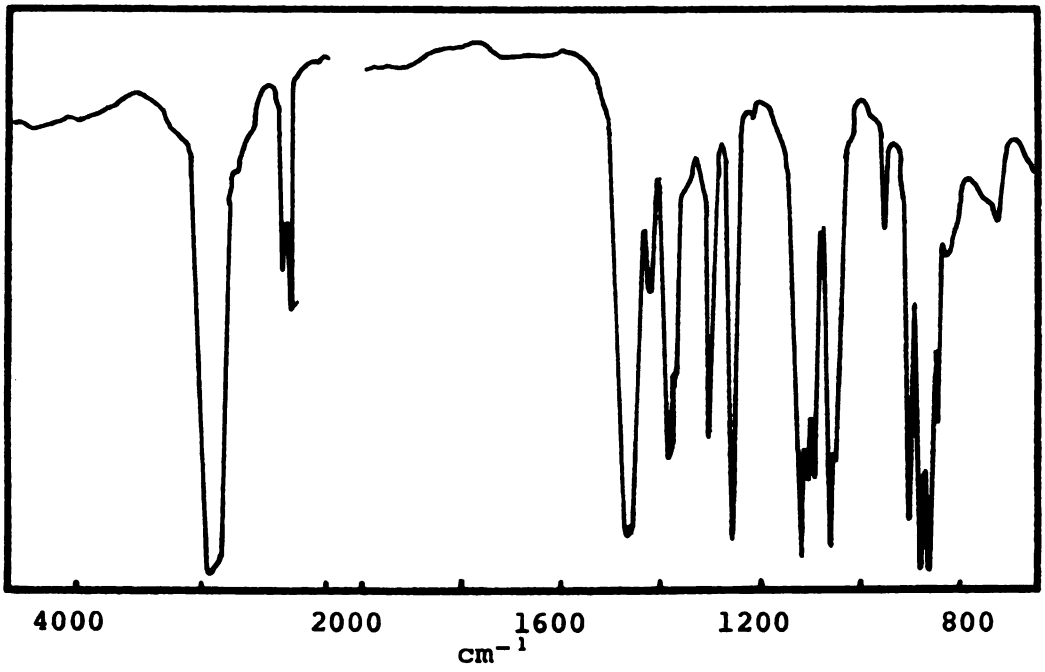

Figure 8. Infrared spectrum of $TiCl_3(C_4H_8O_2)_2(CH_3CN)$.

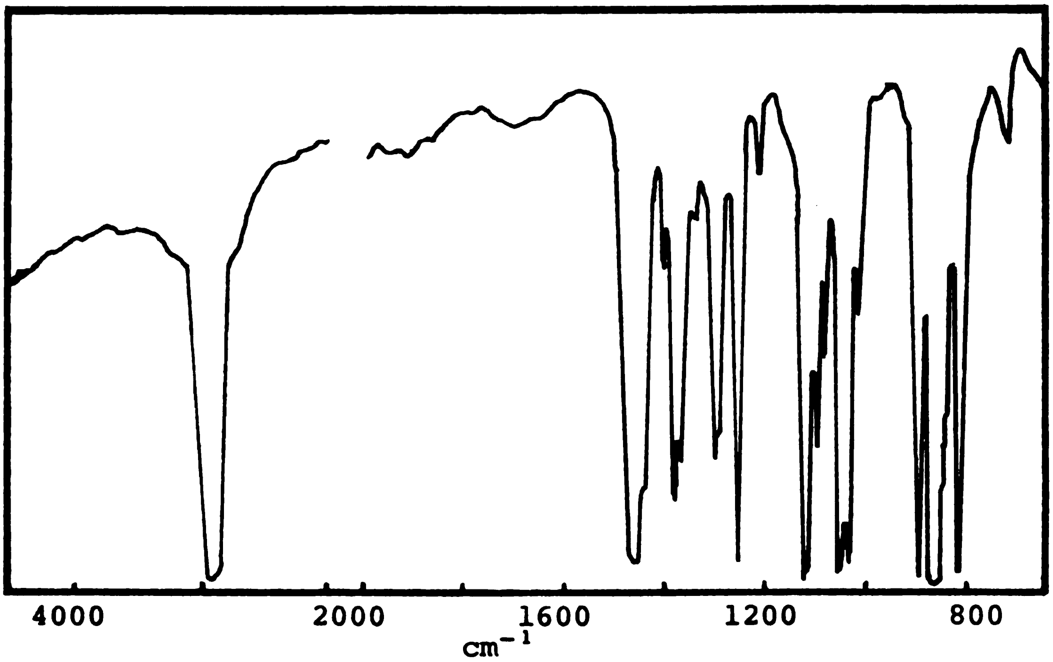

Figure 9. Infrared spectrum of $TiCl_3(C_4H_8O_2)_2(C_4H_8O)$.

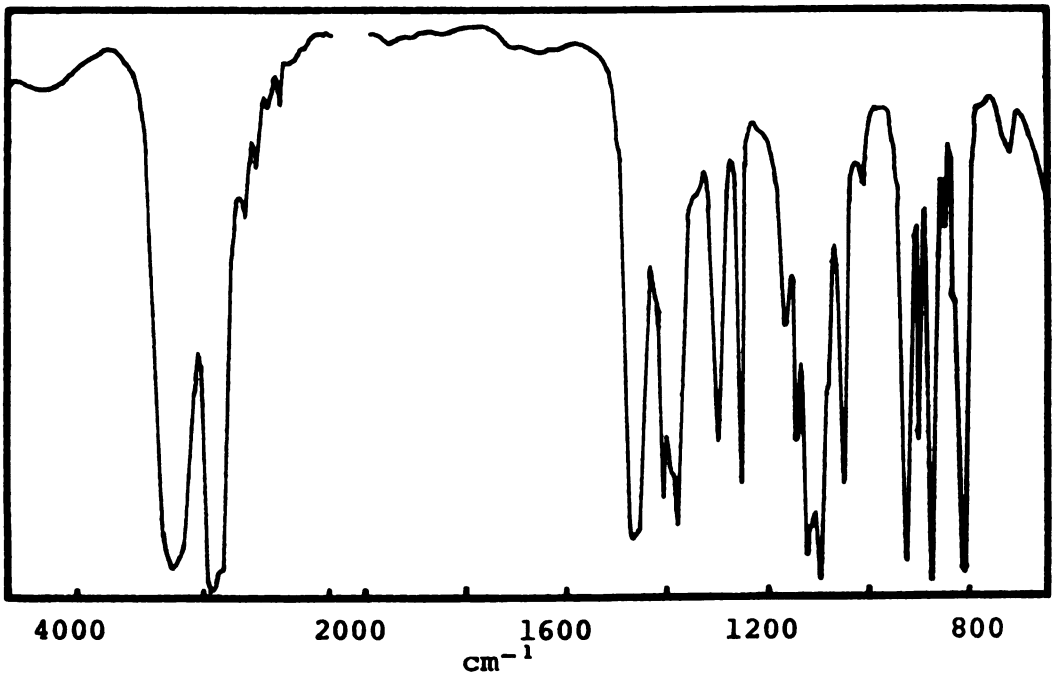

Figure 10. Infrared spectrum of $TiCl_3(C_4H_8O_2)_2(C_3H_8O)$.

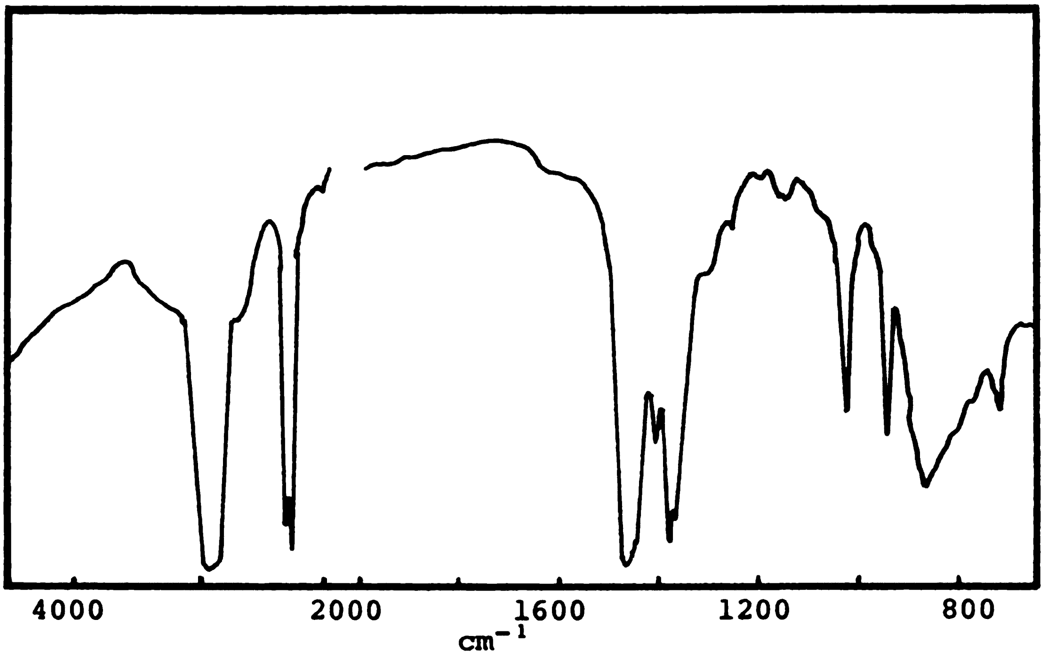

Figure 11. Infrared spectrum of $TiCl_3 \cdot CH_3CN$.

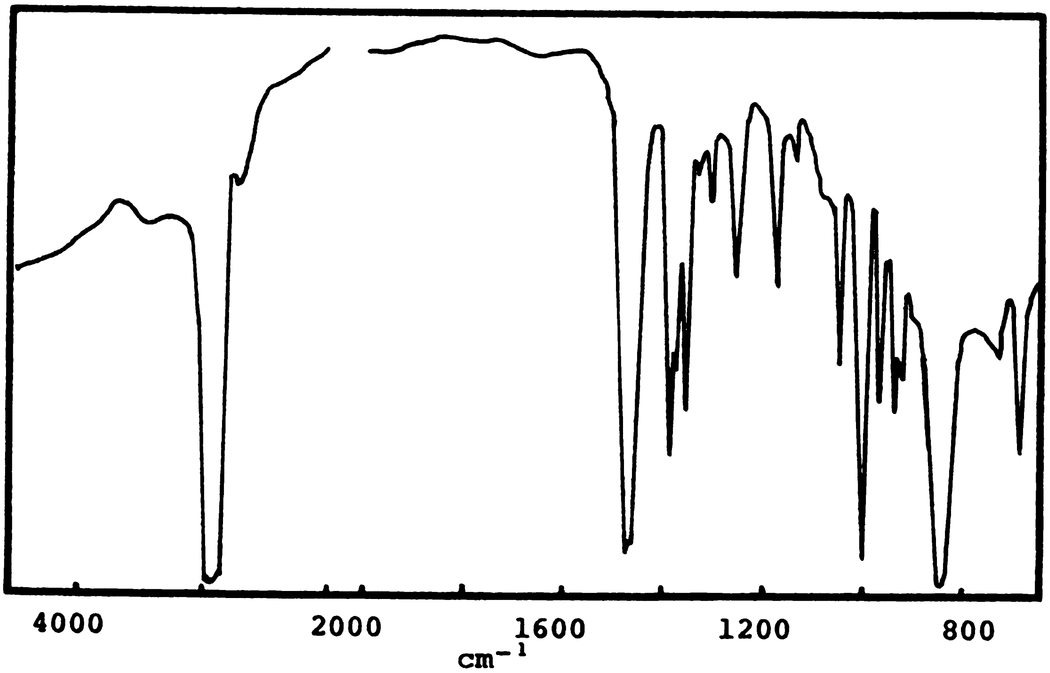

Figure 12. Infrared spectrum of $TiCl_3 \cdot C_4H_8O$.

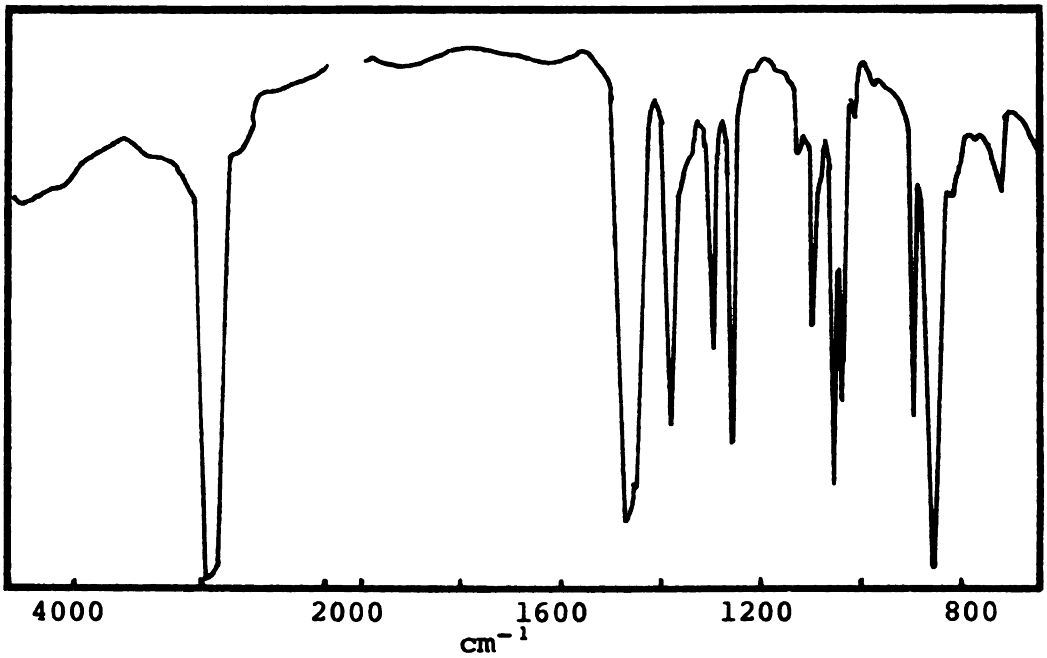

Figure 13. Infrared spectrum of $TiCl_3 \cdot C_4H_8O_2$.

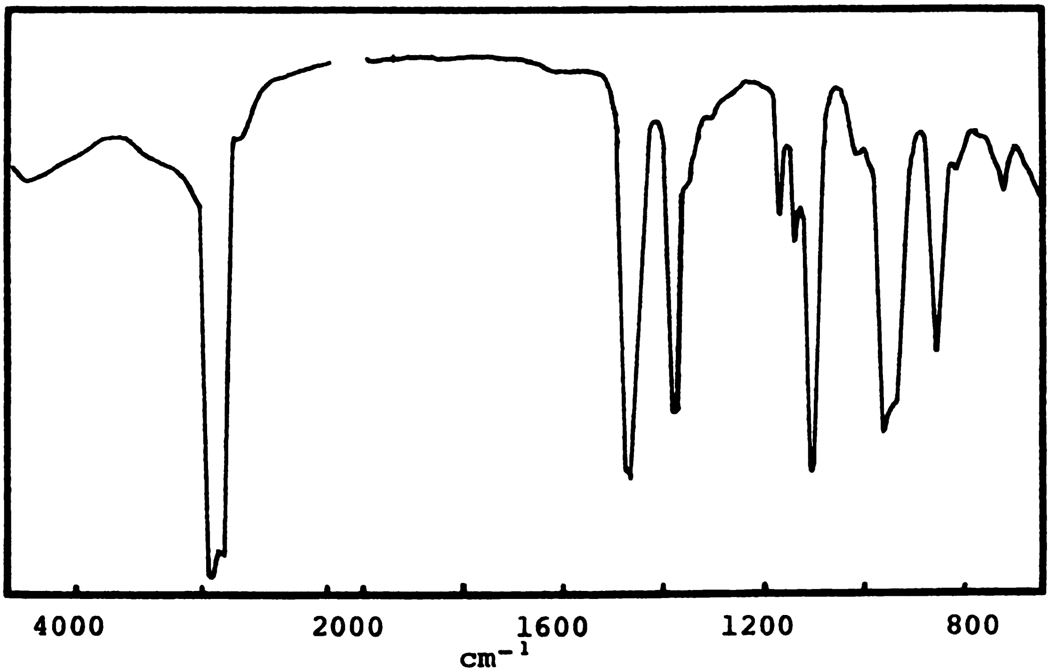

Figure 14. Infrared spectrum of $Ti_2Cl_3(C_3H_7O)_3$.

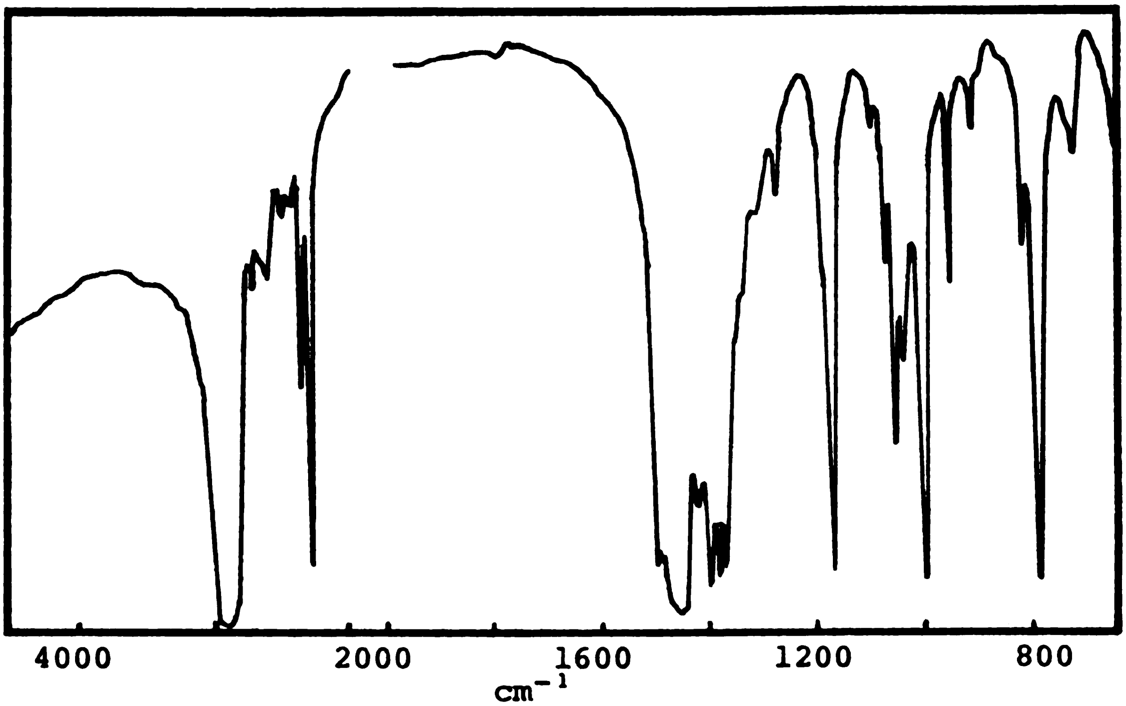

Figure 15. Infrared spectrum of $(C_2H_5)_4N[TiCl_4 \cdot 2CH_3CN]$

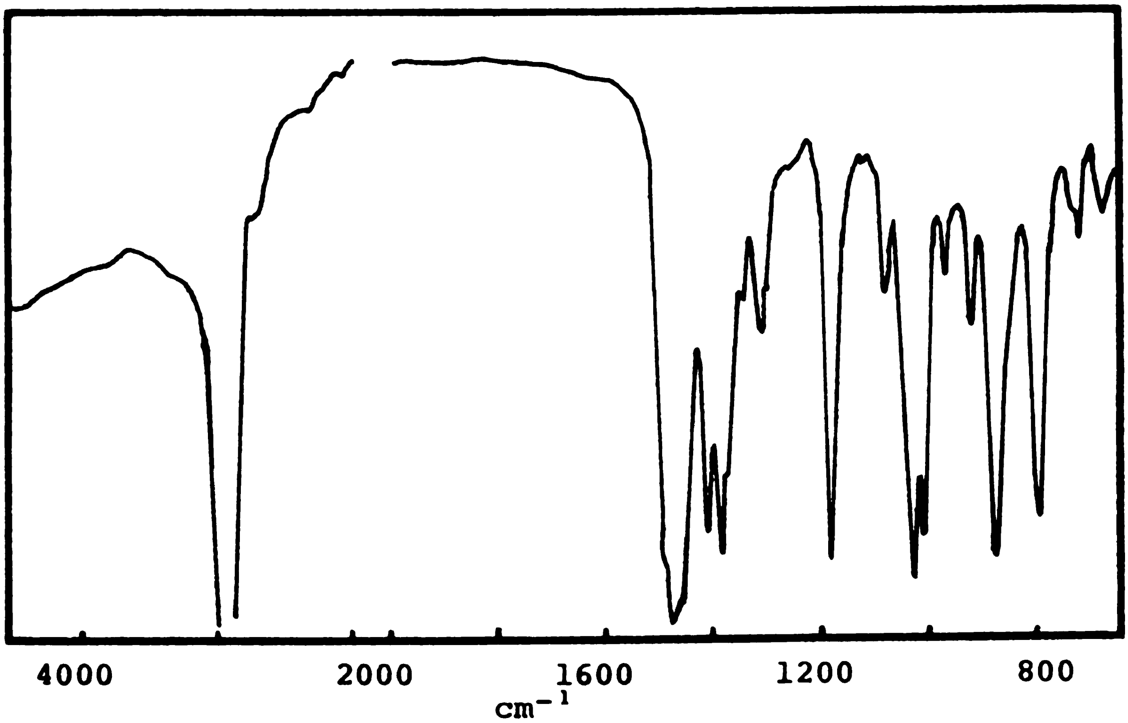

Figure 16. Infrared spectrum of $(C_2H_5)_4N[TiCl_4 \cdot 2C_4H_8O]$

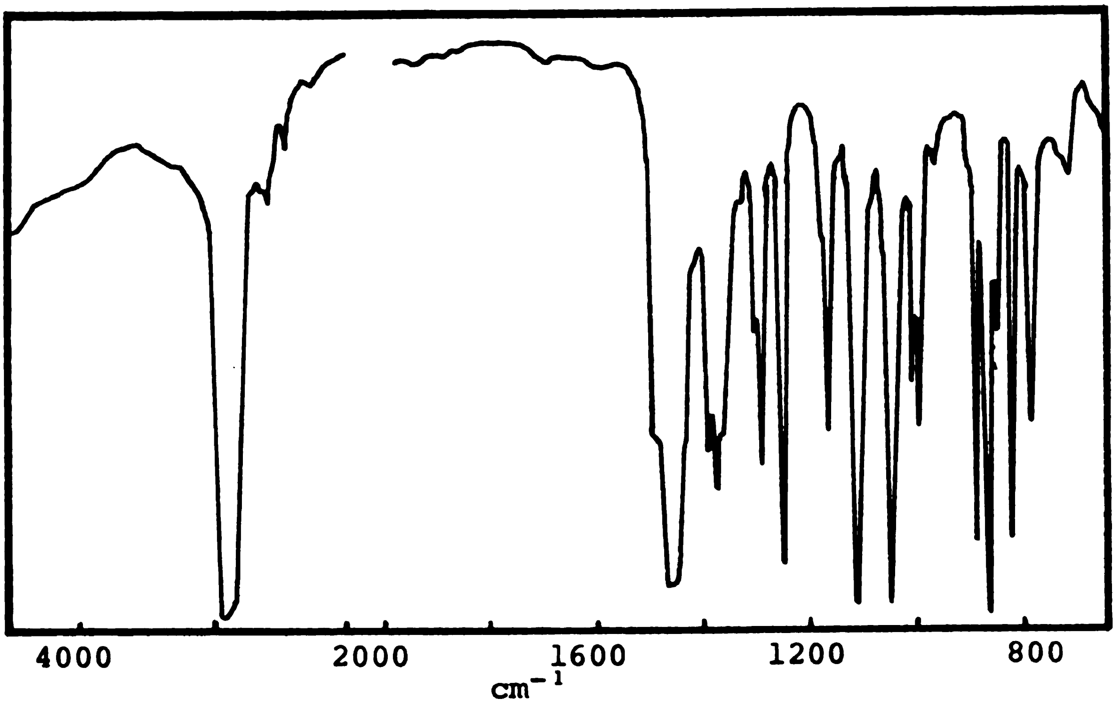

Figure 17. Infrared spectrum of $(C_2H_5)_4N[TiCl_4 \cdot 2C_4H_8O_2]$

and the ligand field strengths of the complexes. The far infrared spectra absorption bands were too broad to provide useful information about the symmetries or the ligand bond strengths.

C. Electronic Absorption Spectra

The electronic absorption spectra of the complexes were determined in Nujol mulls and the results are presented in Table II. Titanium was six-coordinate in all of the complexes which were studied. Although the symmetries of the complexes varied widely, all the spectra except that of $(C_2H_5)_4N[TiCl_n]$ had two d-d absorption bands. Since no amount of trigonal distortion of the basic octahedral point group symmetry would have removed the degeneracy of the upper ^2E d orbital level, the complexes contained some elements of tetragonal or lower symmetry.

The spectrochemical series for the ligands studied in this research is $CH_3CN > C_3H_8O > C_4H_8O_2 > C_4H_8O$. The locations of the absorption bands of the complexes of the type $TiCl_3L_2L'$ were about 100 cm^{-1} higher than the values predicted from Jorgensen's rule of average environment and the Dq values of the ligands. In the $[TiCl_4 \cdot 2L]^-$ complexes the locations of the absorption bands were almost identical, although Jorgensen's rule would have predicted $\nu_{CH_3CN} > \nu_{C_4H_8O_2} \simeq \nu_{C_4H_8O}$.

TABLE II.--Electronic Absorption Spectra of Compounds.[a,b]

Compound	Absorption Bands (cm^{-1})[c] $^2B_2 \rightarrow {}^2B_1$	Absorption Bands (cm^{-1})[c] $^2B_2 \rightarrow {}^2A_1$
$TiCl_3 \cdot 3CH_3CN$	17,100	14,700
$TiCl_3 \cdot 3C_4H_8O$	14,700	13,500
$TiCl_3 \cdot 2C_4H_8O_2$	14,800	12,800
$TiCl_3 \cdot 4C_3H_8O$	16,700	14,300
$TiCl_3(C_4H_8O)_2(CN_3CN)$	15,600(15,550)	14,000(13,900)
$TiCl_3(C_4H_8O_2)_2(CH_2CN)$	15,680(15,570)	13,325(13,433)
$TiCl_3(C_4H_8O_2)_2(C_4H_8O)$	14,780(14,770)	13,100(13,034)
$TiCl_3(C_4H_8)_2)_2(C_3H_8O)$	15,400(15,140)	13,220(13,110)
$TiCl_3 \cdot CH_3CN$	16,000(14,832)	11,900(12,900)
$TiCl_3 \cdot C_4H_8O$	17,300(14,032)	13,000(12,500)
$TiCl_3 \cdot C_4H_8O_2$	17,900(14,065)	14,600(12,270)
$Ti_2Cl_3(C_3H_7O)_3$	18,950	17,450
$(C_2H_5)_4N[TiCl_4 \cdot 2CH_3CN]$	15,150(15,800)	14,150(13,800)
$(C_2H_5)_4N[TiCl_4 \cdot 2C_4H_8O]$	14,900(14,200)	14,150(13,000)
$(C_2H_5)_4N[TiCl_4 \cdot 2C_4H_8O_2]$	15,000(14,270)	14,100(12,730)
$[(C_2H_5)_4N][TiCl_n]$	12,400	

---

[a] all spectra were determined in Nujol mulls.

[b] values in parentheses are those expected from Jorgensen's rule of average environment and the average Dq values of the ligands.

[c] assignments assume tetragonal or lower symmetry.

Only one low-lying absorption band was seen for the material with non-integral stoichiometry $(C_2H_5)_4N[TiCl_n]$. The absorption bands in compounds of the type $TiCl_3 \cdot L$ were considerably higher than would have been expected from Jorgensen's rule. In addition, the position of acetonitrile in the spectrochemical series was shifted so that it became the weakest of the ligands studied. It was expected from Jorgensen's rule that the location of the absorption bands would have shifted to lower frequencies as the chloride: non-halide ligand ratio was increased. However, in this investigation it was found that the frequencies of the absorption bands increased with increasing chloride content of the titanium(III) complexes.

D. Magnetic Moments

The magnetic susceptibilities and effective magnetic moments of the complexes at several temperatures are presented in Table III. Most of the compounds exhibited normal Curie-Weiss paramagnetism. The complexes $TiCl_3 \cdot CH_3CN$ and $TiCl_3 \cdot C_4H_8O$, in which chloride ions probably bridge two titanium atoms, were anti-ferromagnetic. A similar compound, $TiCl_3 \cdot C_4H_8O_2$, exhibited normal paramagnetism but with a much greater temperature dependence than the other paramagnetic complexes studied. The chloroalkoxo complex $Ti_2Cl_3(C_3H_7O)_3$ was diamagnetic.

Several ligand field parameters were obtained from graphs of μ_{eff} against kT/λ' (figures 18-29). The experimental

TABLE III.--Magnetic Properties of Titanium(III) Complexes.

Compound	Temp. °K	χ'_m x 10^6 cgs units	μ_{eff} B.M.
$TiCl_3 \cdot 3CH_3CN$	297	1241	1.72
	250.3	1420	1.69
	209.7	1645	1.67
	175.5	1902	1.64
	148	2222	1.63
	77	4019	1.58
$TiCl_3 \cdot 3C_4H_8O$	297	1246	1.72
	250.3	1438	1.70
	209.7	1646	1.67
	196	1738	1.66
	175.5	1931	1.65
	148	2220	1.63
	77	4021	1.58
$TiCl_3 \cdot 2C_4H_8O_2$	297	1232	1.72
	250.3	1391	1.68
	209.7	1614	1.65
	196	1705	1.64
	175.5	1873	1.63
	148	2122	1.59
	77	3670	1.51
$TiCl_3 \cdot 4C_3H_8O$	297	1270	1.74
	250.3	1416	1.69
	209.7	1616	1.65
	196	1692	1.64
	175.5	1859	1.62
	148	2120	1.59
	77	3738	1.52
$TiCl_3(C_4H_8O)_2(CH_3CN)$	297	1381	1.77
	250.3	1491	1.73
	209.7	1708	1.70
	196	1796	1.69
	175.5	1988	1.68
	148	2311	1.66
	77	4122	1.60
$TiCl_3(C_4H_8O_2)_2(CH_3CN)$	297	1230	1.72
	250.3	1370	1.66
	209.7	1575	1.63
	196	1621	1.60
	175.5	1745	1.57
	148	1957	1.53
	77	3302	1.43

TABLE III.--Continued.

Compound	Temp. ^{o}K	$\chi'_m \times 10^6$ cgs units	μ_{eff} B.M.
$TiCl_3(C_4H_8O_2)_2(C_4H_8O)$	297	1243	1.72
	250.3	1401	1.68
	209.7	1587	1.64
	196	1686	1.63
	175.5	1815	1.60
	148	2060	1.57
	77	3533	1.48
$TiCl_3(C_4H_8O_2)_2(C_2H_8O)$	297	1255	1.73
	250.3	1428	1.70
	209.7	1670	1.68
	196	1748	1.66
	175.5	1926	1.65
	148	2231	1.63
	77	3928	1.56
$TiCl_3 \cdot CH_3CN$	297	789	1.37
	196	971	1.24
	77	1928	1.09
$TiCl_3 \cdot C_4H_8O$	297	431	1.02
	196	356	0.75
	77	305	0.43
$TiCl_3 \cdot C_4H_8O_2$	297	1357	1.80
	250.3	1477	1.73
	209.7	1625	1.66
	196	1624	1.60
	175.5	1776	1.59
	148	1990	1.54
	77	2269	1.19
$Ti_2Cl_3(C_3H_7O)_3$		diamagnetic	
$(C_2H_5)_4N[TiCl_4 \cdot 2CH_3CN]$	297	1305	1.77
	250.3	1478	1.73
	209.7	1661	1.68
	196	1739	1.66
	175.5	1918	1.65
	148	2192	1.62
	77	3761	1.53

Table III.--Continued.

Compound	Temp. °K	$\chi'_m \times 10^6$ cgs units	μ_{eff} B.M.
$(C_2H_5)_4N(TiCl_4 \cdot 2C_4H_8O]$	297	1318	1.78
	250.3	1461	1.72
	209.7	1664	1.68
	196	1758	1.67
	175.5	1870	1.63
	148	2165	1.61
	77	3668	1.51
$(C_2H_5)_4N[TiCl_4 \cdot 2C_4H_8O_2]$	297	1265	1.74
	250.3	1394	1.68
	209.7	1600	1.64
	196	1638	1.61
	175.5	1765	1.58
	148	2008	1.55
	77	3242	1.42

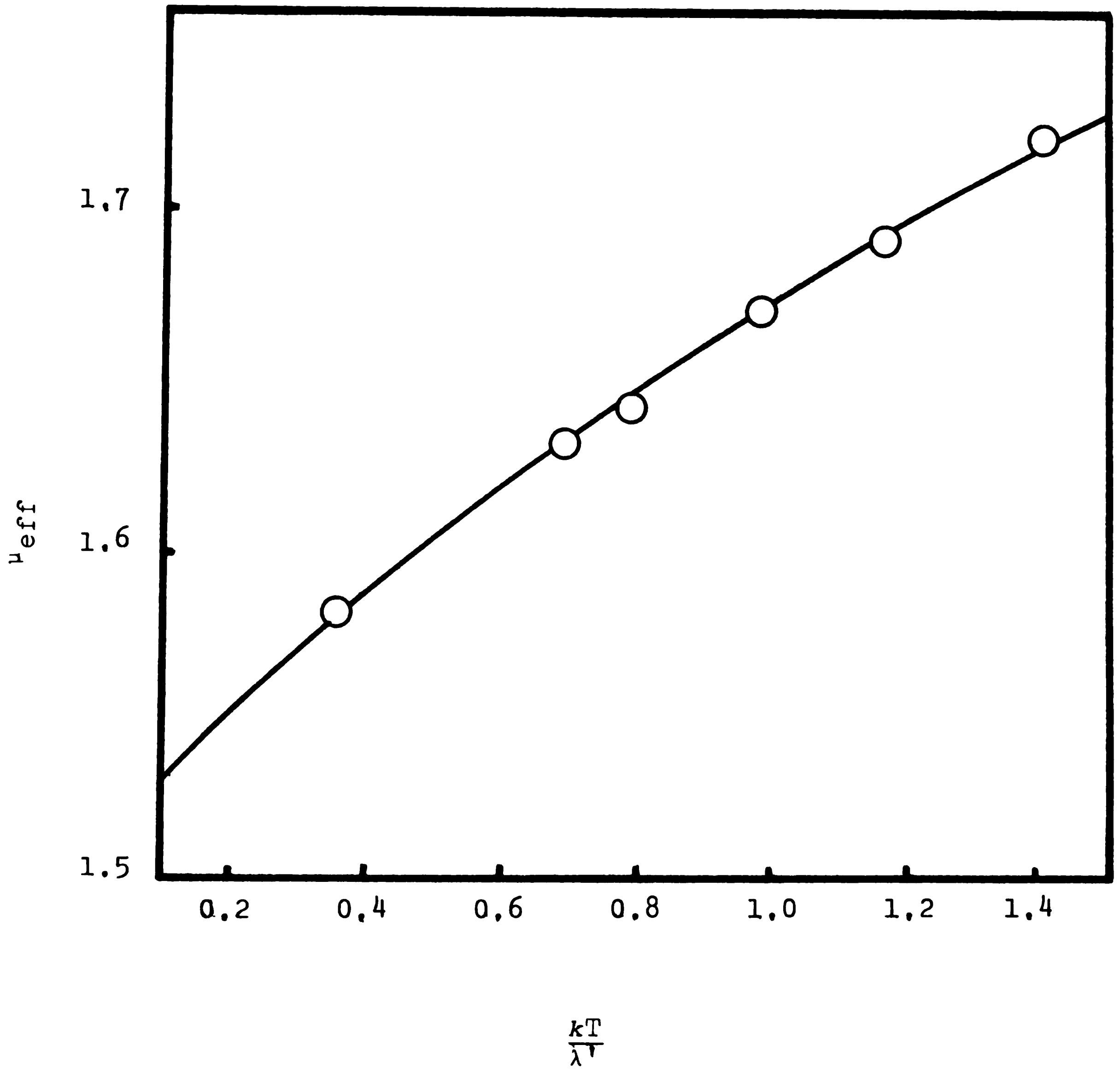

Figure 18. Graph of μ_{eff} vs. $\frac{kT}{\lambda'}$ for $TiCl_3 \cdot 3CH_3CN$. Circles are experimental points. Line calculated from reference 44 with $k = 0.7$, $v = 4.5$, $\lambda' = 0.95\ \lambda$.

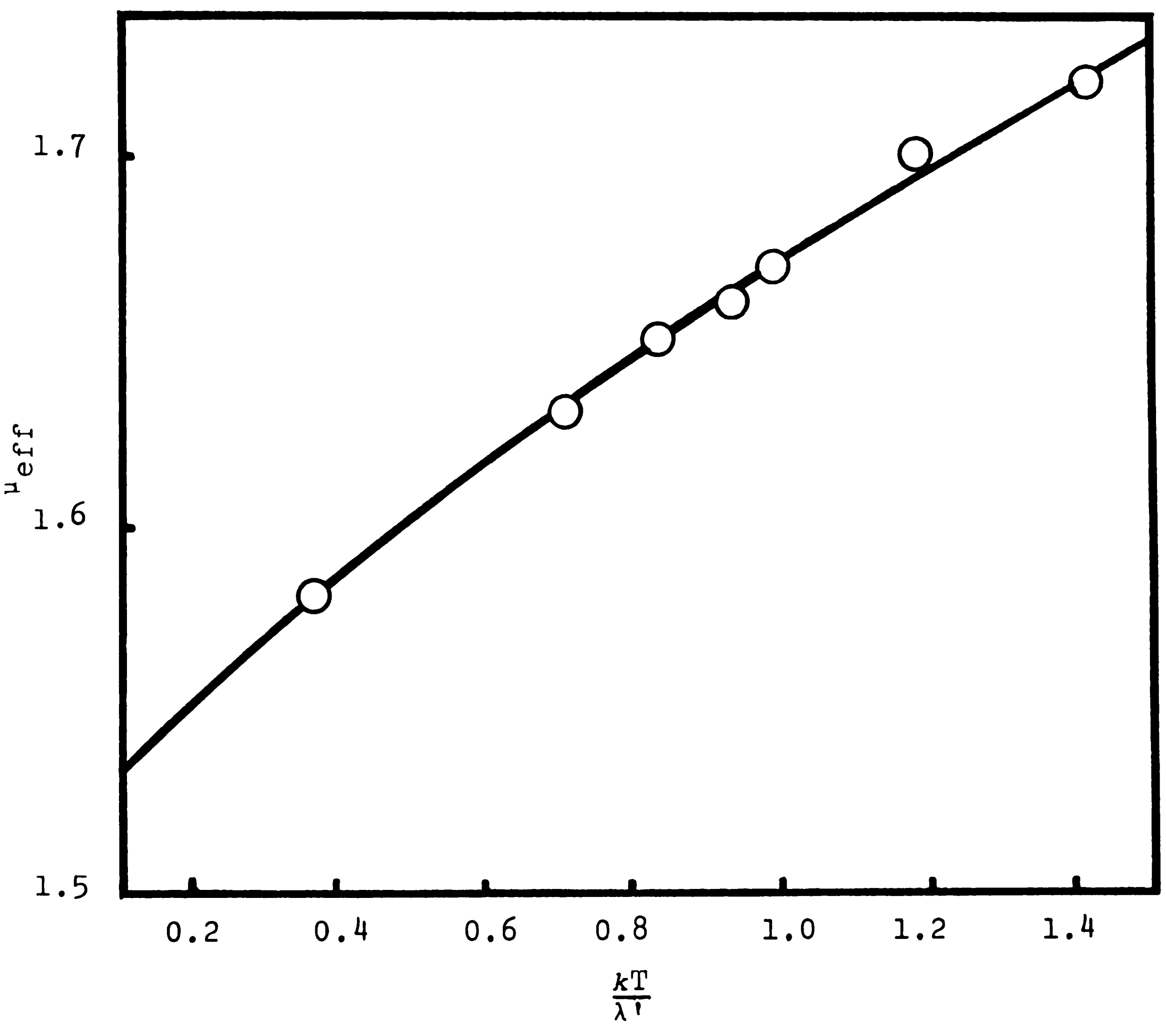

Figure 19. Graph of μ_{eff} vs. $\frac{kT}{\lambda'}$ for $TiCl_3 \cdot 3C_4H_8O$. Circles are experimental points. Line calculated from reference 44 with $k = 0.7$, $v = 4.5$, $\lambda' = 0.95\ \lambda$.

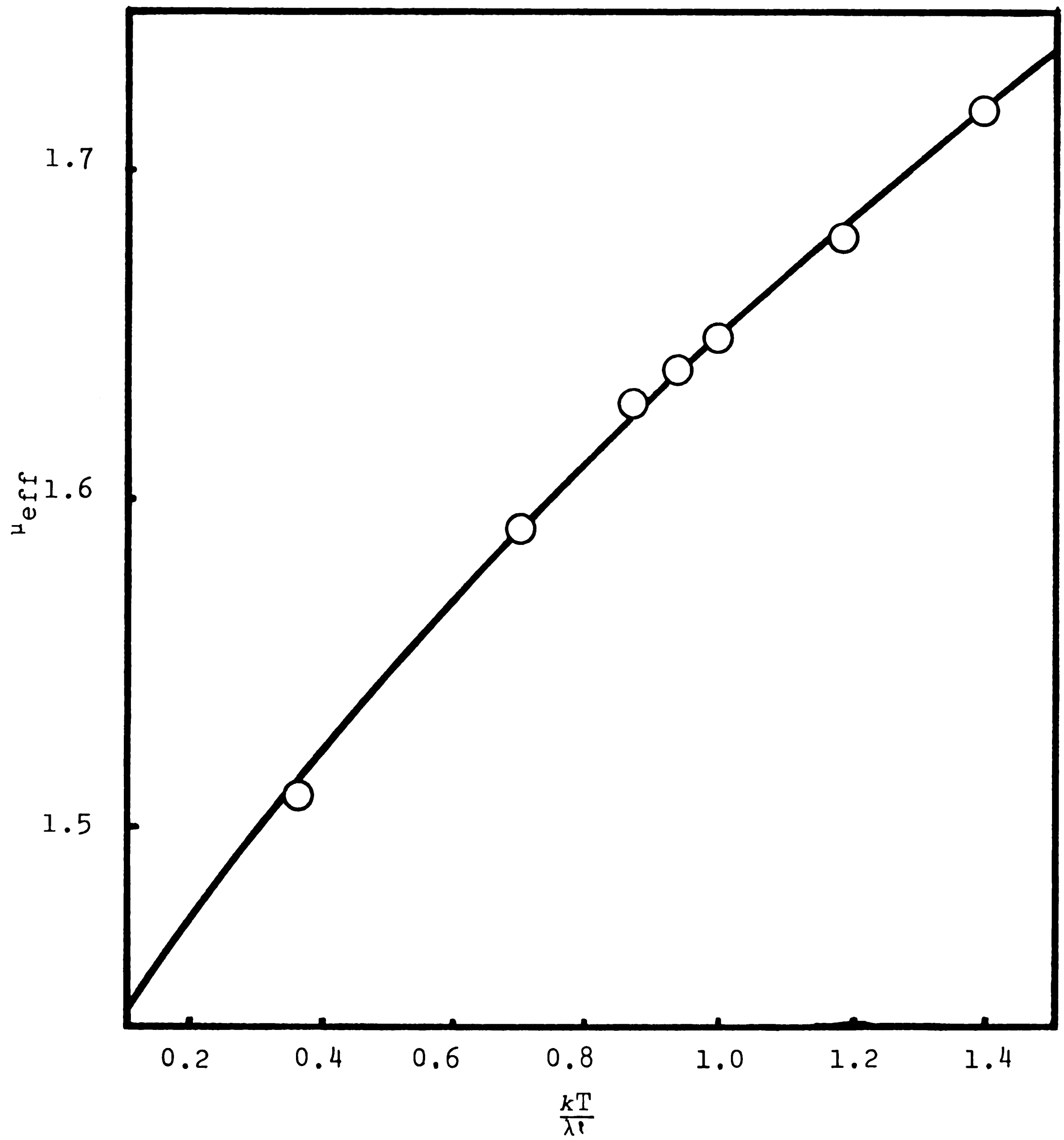

Figure 20. Graph of μ_{eff} vs. $\frac{kT}{\lambda'}$ for $TiCl_3 \cdot 2C_4H_8O_2$.
Circles are experimental points.
Line calculated from reference 44 with
$k = 0.7$, $v = 3$, $\lambda' = 0.95\ \lambda$.

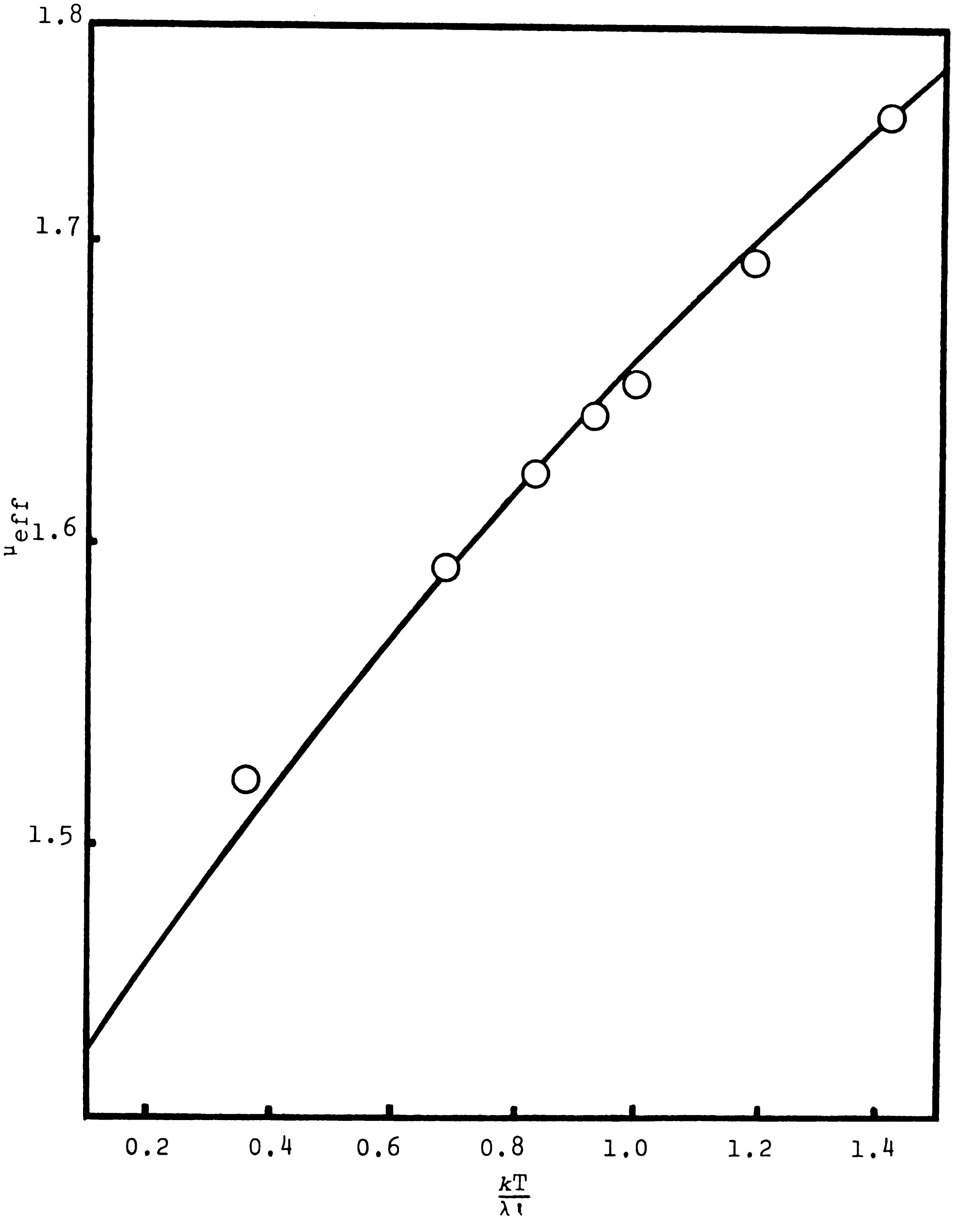

Figure 21. Graph of μ_{eff} vs. $\frac{kT}{\lambda'}$ for $TiCl_3 \cdot 4C_3H_8O$. Circles are experimental points. Line calculated from reference 44 with $k = 0.75$, $v = 3$, $\lambda' = 0.95\ \lambda$.

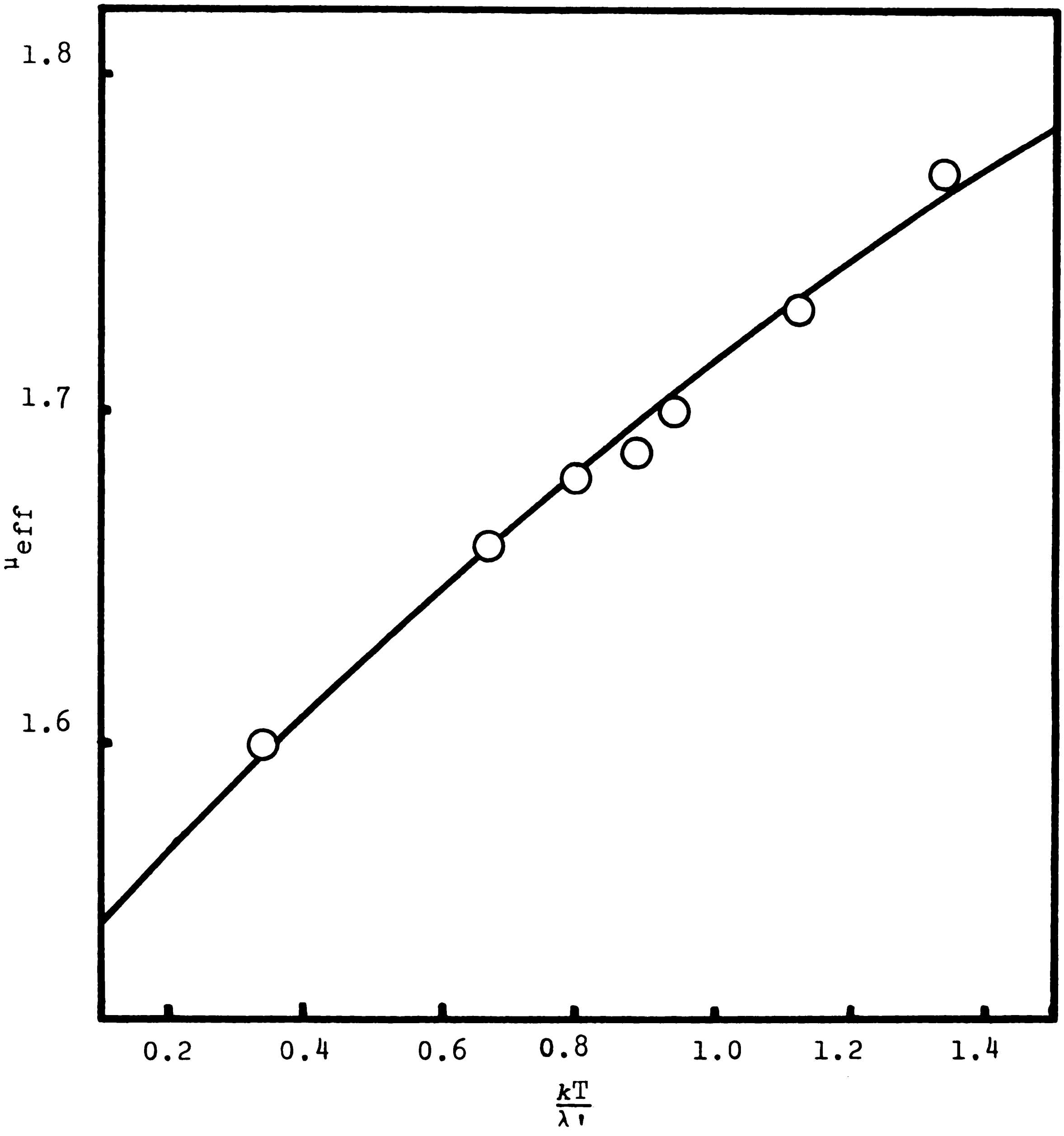

Figure 22. Graph of μ_{eff} vs. $\frac{kT}{\lambda'}$ for $TiCl_3(C_4H_8O)_2(CN_3CN)$. Circles are experimental points. Line calculated from reference 44 with $k = 0.9$, $v = 6$, $\lambda' = \lambda$.

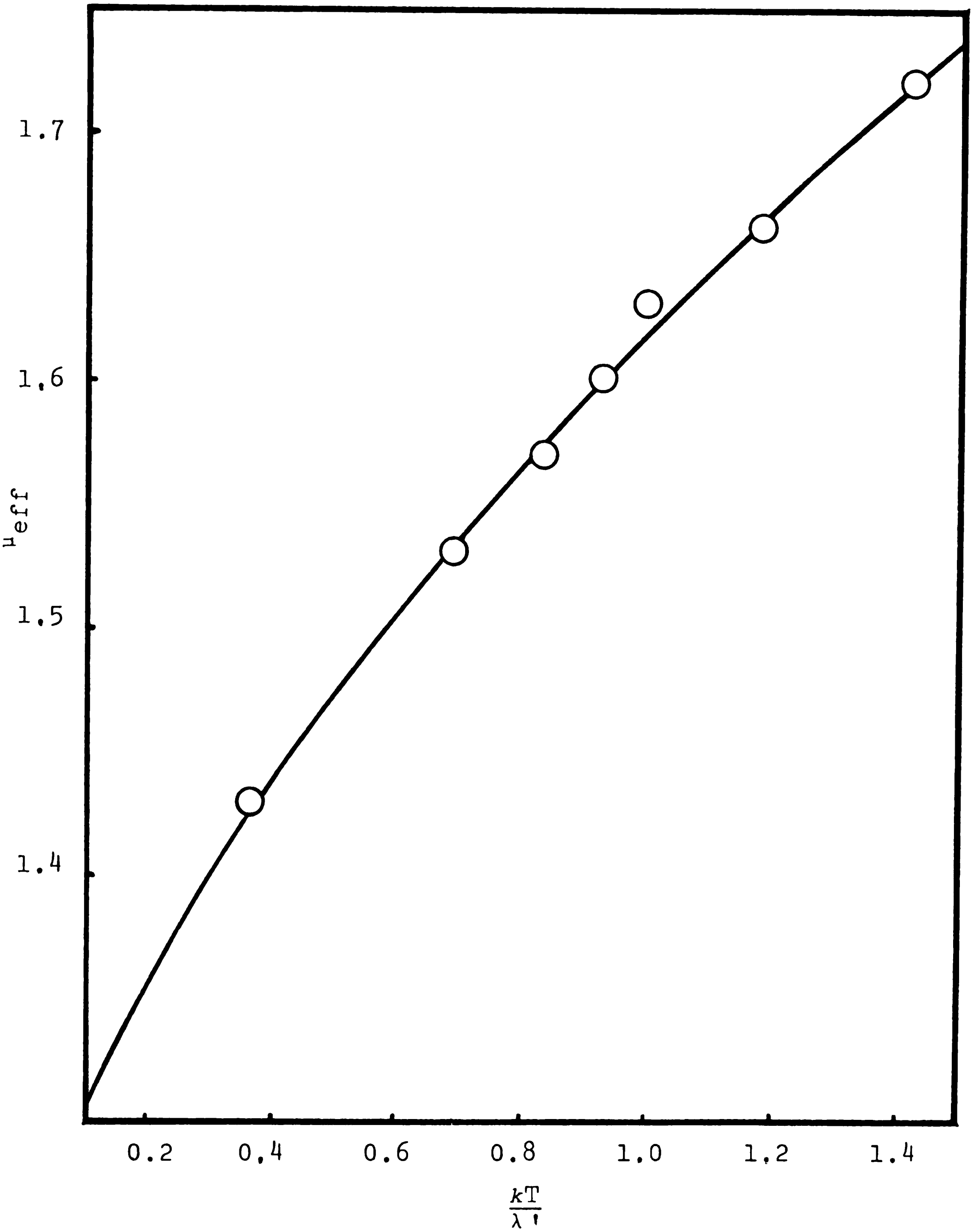

Figure 23. Graph of μ_{eff} vs. $\frac{kT}{\lambda'}$ for $TiCl_3(C_4H_8O_2)(CH_3CN)$. Circles are experimental points. Line calculated from reference 44 with $k = 0.7$, $v = 2$, $\lambda' = 0.95\ \lambda$.

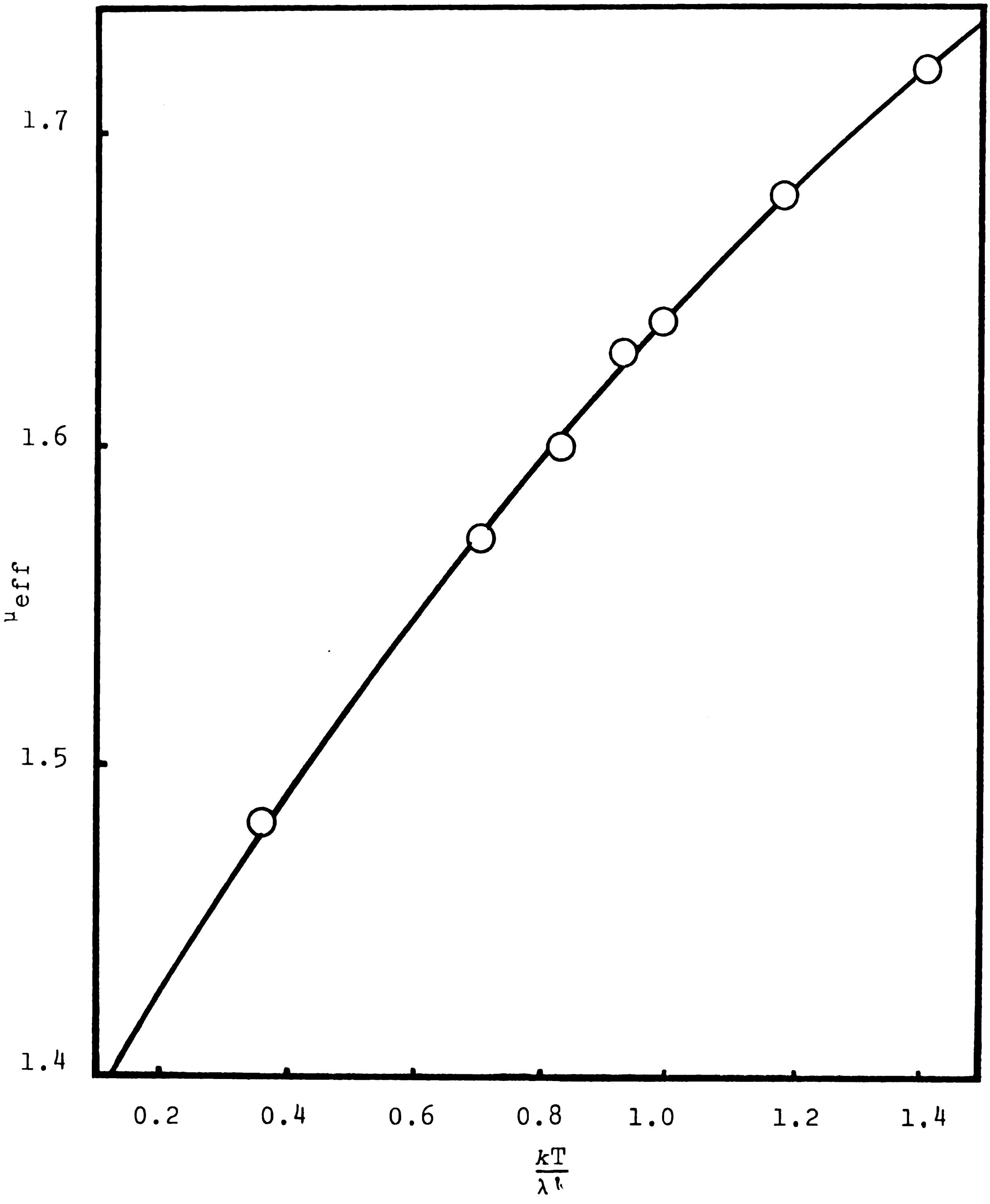

Figure 24. Graph of μ_{eff} vs. $\frac{kT}{\lambda'}$ for $TiCl_3(C_4H_8O_2)_2(C_4H_8O)$.
Circles are experimental points.
Line calculated from reference 44 with
$k = 0.7$, $v = 2.5$, $\lambda' = 0.95\ \lambda$.

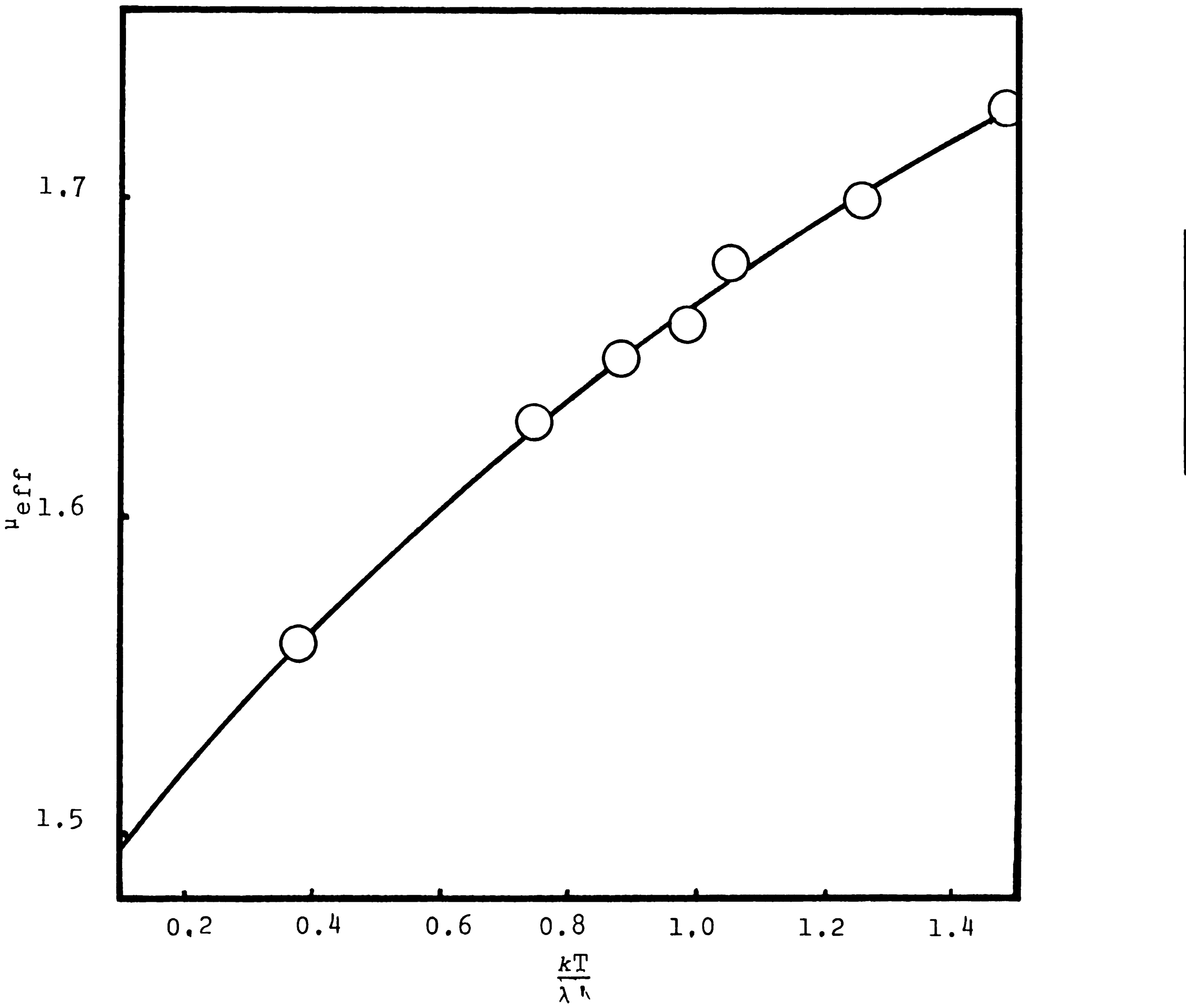

Figure 25. Graph of μ_{eff} vs. $\frac{kT}{\lambda'}$ for $TiCl_3(C_4H_8O_2)_2(C_3H_8O)$. Circles are experimental points. Line calculated from reference 44 with $k = 0.7$, $v = 4$, $\lambda' = 0.90\ \lambda$.

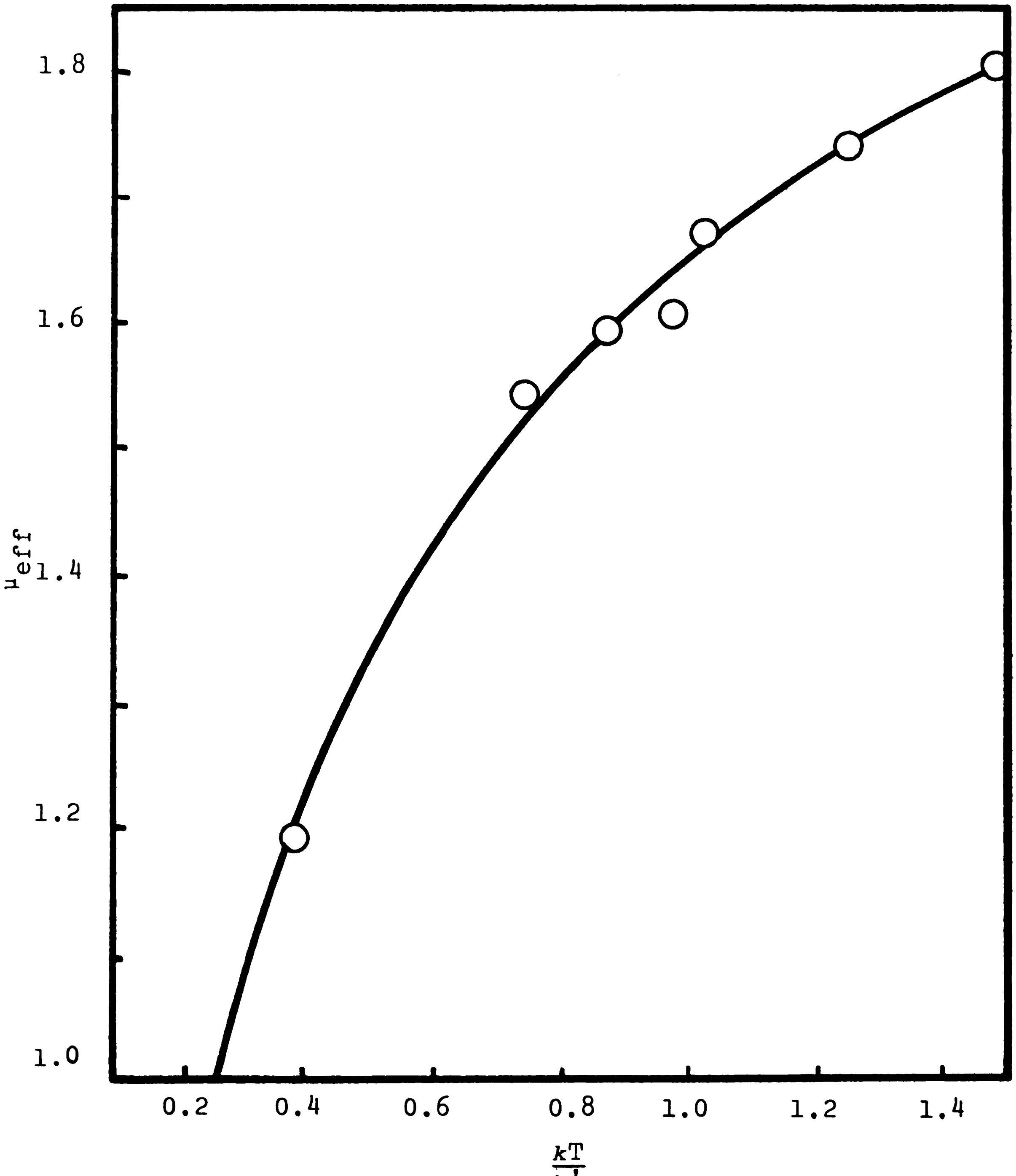

Figure 26. Graph of μ_{eff} vs. $\frac{kT}{\lambda'}$ for $TiCl_3 \cdot C_4H_8O_2$. Circles are experimental points. Line calculated from reference 44 with k = 0.8, v = 0.1, λ' = 0.90 λ.

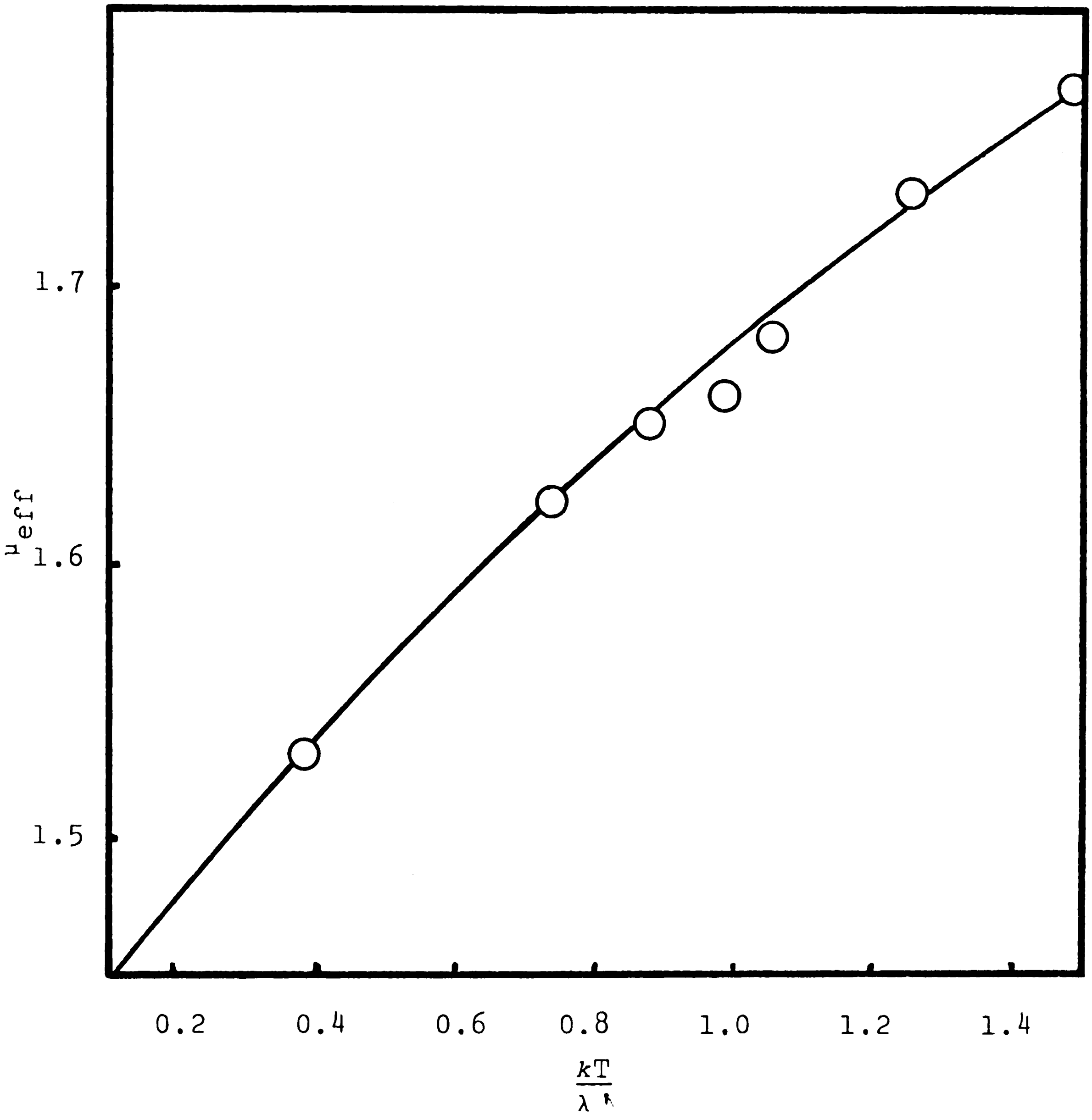

Figure 27. Graph of μ_{eff} vs. $\frac{kT}{\lambda'}$ for $(C_2H_5)_4N[TiCl_4 \cdot 2CH_3CN]$.
Circles are experimental points.
Line calculated from reference 44 with
$k = 0.8$, $v = 3.5$, $\lambda' = 0.90\ \lambda$.

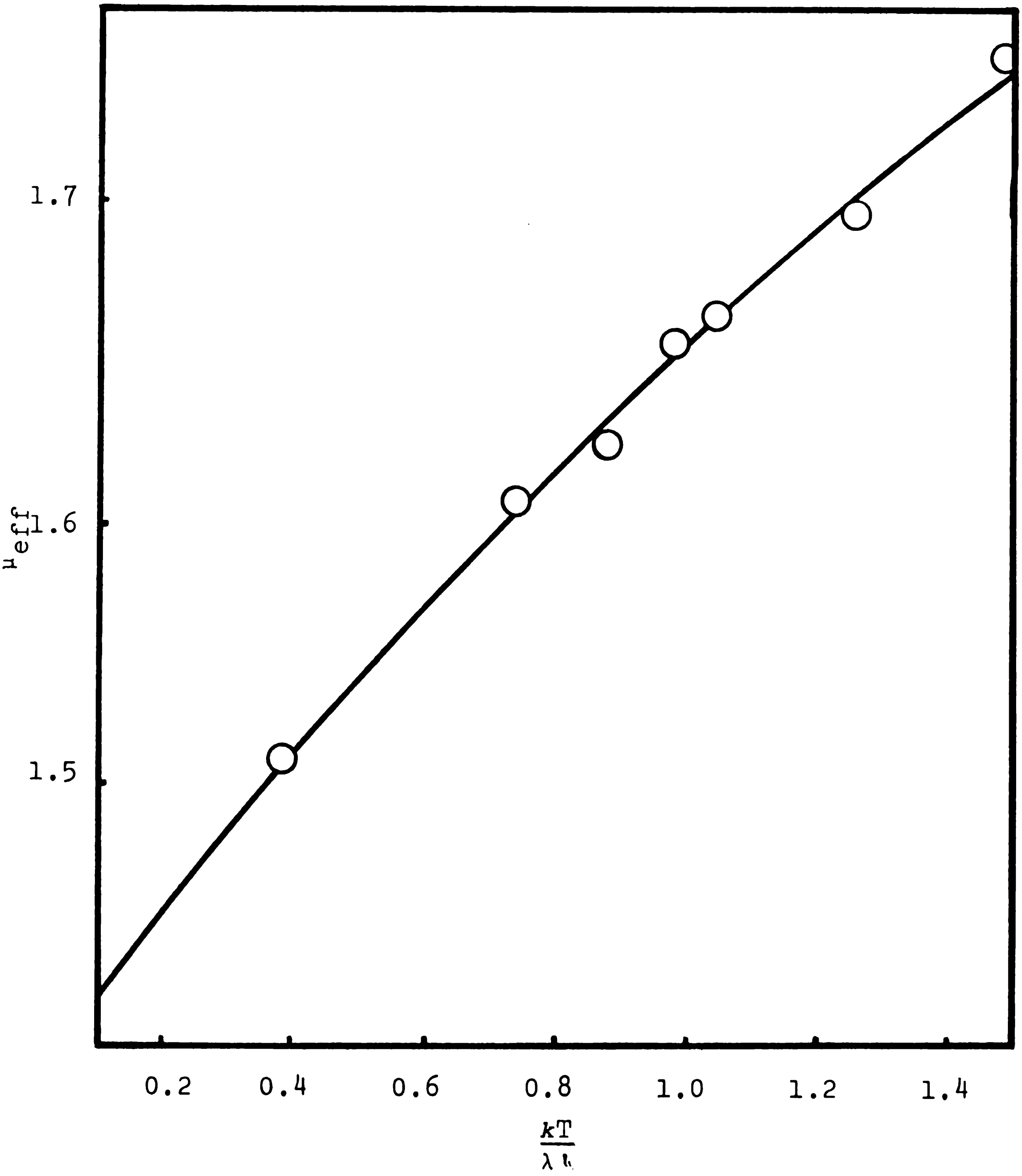

Figure 28. Graph of μ_{eff} vs. $\frac{kT}{\lambda'}$ for $(C_2H_5)_4N[TiCl_4 \cdot 2C_4H_8O]$. Circles are experimental points. Line calculated from reference 44 with $k = 0.8$, $v = 3.0$, $\lambda' = 0.90\ \lambda$.

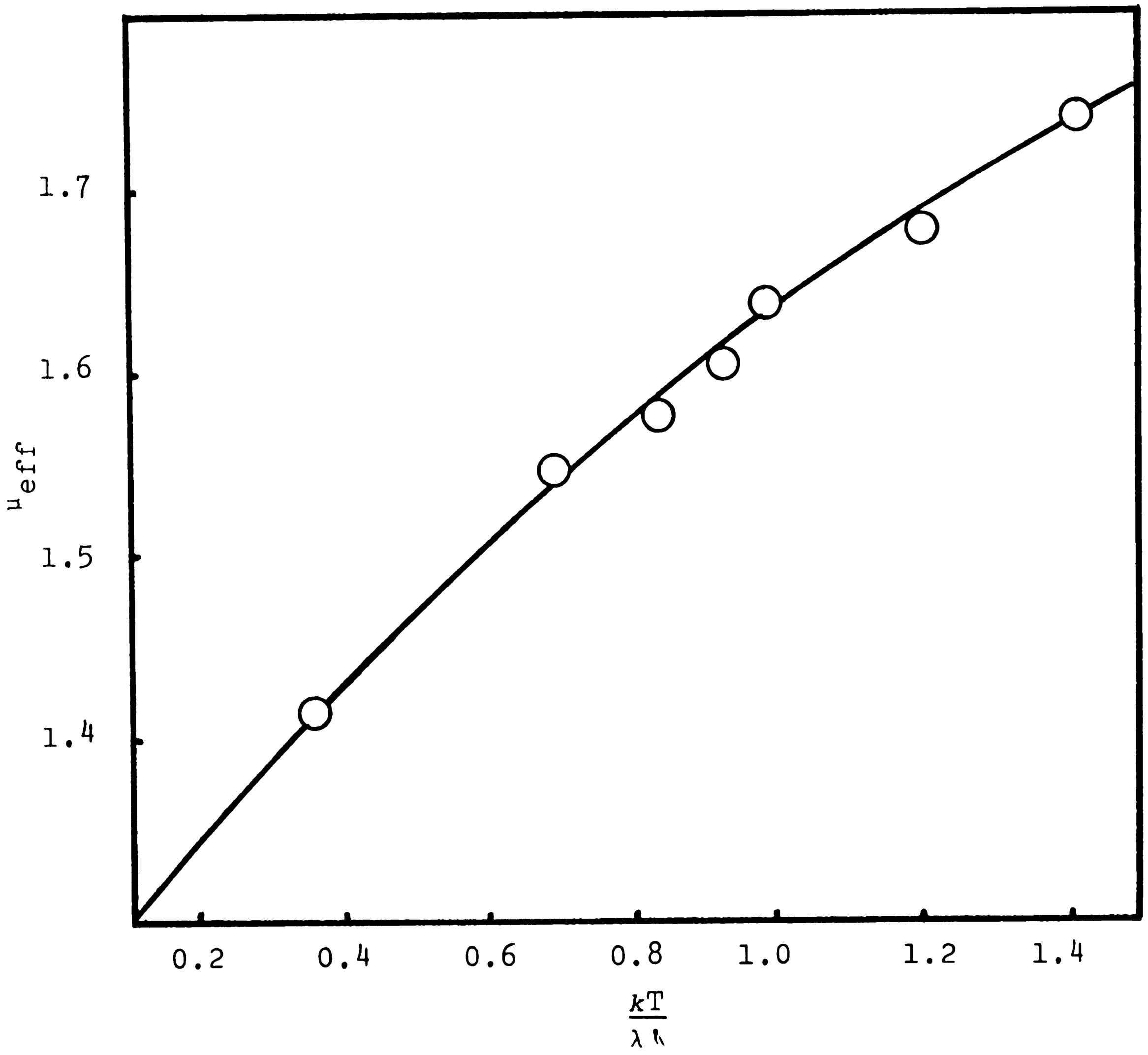

Figure 29. Graph of μ_{eff} vs. $\frac{kT}{\lambda'}$ for $(C_2H_5)_4N[TiCl_4 \cdot 2C_4H_8O_2]$.
Circles are experimental points.
Line calculated from reference 44 with
$k = 0.75$, $v = 2.0$, $\lambda' = 0.95\ \lambda$.

curves were fitted to the proper theoretical curves calculated from the values given by Figgis.[44] Values of k, the orbital delocalization factor, λ', the spin-orbit coupling constant, and v, the distortion factor, were obtained by this procedure. The energy of separation, δ_1, of the orbital levels derived from the $^2T_{2g}$ ground state term was calculated from the equation $v=\delta_1/\lambda$. The value of δ_1 was positive in all of the complexes which indicated that the orbital singlet derived from the $^2T_{2g}$ state was the lowest energy level. The ligand field parameters which were calculated from the magnetic data are given in Table IV.

The results were examined to find if any correlations existed between the values of the ligand field parameters β and δ_1 and other ligand field parameters of the complexes. Theoretically a complex which has an undistorted octahedral symmetry should have a magnetic moment which falls to zero as the temperature approaches zero. In complexes having lower symmetry and t_{2g} electron delocalization the moment approaches the spin-only value. Thus it would be expected that as the symmetries of the complexes were increased the magnetic moments should be more temperature dependent. This was the case in the series of compounds with different chloride:non-halide ligand ratio in which both the amount of orbital delocalization (1-k) and the energy of separation δ_1 decreased with increased chloride content. However, with the complexes of the type $TiCl_3L_2L'$ no correlations were found between the values of the ligand field parameters k

TABLE IV.--Ligand Field Parameters Calculated from Magnetic Data.

Compound	k	v	$\lambda'(cm^{-1})$	$\delta_1(cm^{-1})$
$TiCl_3 \cdot 3CH_3CN$	0.7	4.5	146	660
$TiCl_3 \cdot 3C_4H_8O$	0.7	4.5	146	660
$TiCl_3 \cdot 2C_4H_8O_2$	0.7	3.0	146	440
$TiCl_3 \cdot 4C_3H_8O$	0.75	3.0	146	440
$TiCl_3(C_4H_8O)_2(CH_3CN)$	0.9	6.0	154	925
$TiCl_3(C_4H_8O_2)_2(CH_3CN)$	0.7	2.0	146	290
$TiCl_3(C_4H_8O_2)_2(C_4H_8O)$	0.7	2.5	146	365
$TiCl_3(C_4H_8O_2)_2(C_3H_8O)$	0.7	4.0	139	550
$TiCl_3 \cdot C_4H_8O_2$	0.8	0.1	139	14
$(C_2H_5)_4N[TiCl_4 \cdot 2CH_3CN]$	0.8	3.5	139	485
$(C_2H_5)_4N[TiCl_4 \cdot 2C_4H_8O]$	0.8	3.0	139	415
$(C_2H_5)_4N[TiCl_4 \cdot 2C_4H_8O_2]$	0.75	2.0	146	290

and δ_1 and either the ligand field strength (10Dq) or δ_2, the energy of separation of the upper levels derived from the $^2E_{2g}$ state.

E. Electron Spin Resonance Spectra

The esr spectra of the powdered solid complexes were determined at 297 and 77°K. The results are presented in Table V. Figure 30 shows the three types of spectra generally found. Spectra of the type A occur when g, the Landé spectroscopic splitting factor, is isotropic or, more commonly, the temperature is too high to allow resolution of anisotropic g values. Compounds with type B spectra generally have an axis of symmetry and $g_x = g_y \neq g_z$. In the titanium(III) compounds investigated during the course of this research $g_\perp (g_x$ and $g_y)$ was greater than $g_{||}(g_z)$. Type C spectra are expected when the complex has no axial symmetry and $g_x \neq g_y \neq g_z$.

The esr spectra of $TiCl_3 \cdot 3CH_3CN$ and $TiCl_3 \cdot 3C_4H_8O$ are expected for the respective C_{3v} and C_{2v} symmetries.[38] Although the titanium atom is six-coordinate in $TiCl_3 \cdot 2C_4H_8O_2$ it is not certain which functional group bridges the titanium atoms. If the complex had a dioxane molecule in the sixth position or the two dioxane molecules present were trans, a type B spectrum would have been observed. Instead a three-line type C spectrum was observed which suggested that a bridging chloride ion occupied the sixth position and the complex had a cis configuration. $TiCl_3 \cdot 4C_3H_8O$, which had only two chloride ions coordinated to the titanium atom, also had a three-line type C spectrum and a cis configuration.

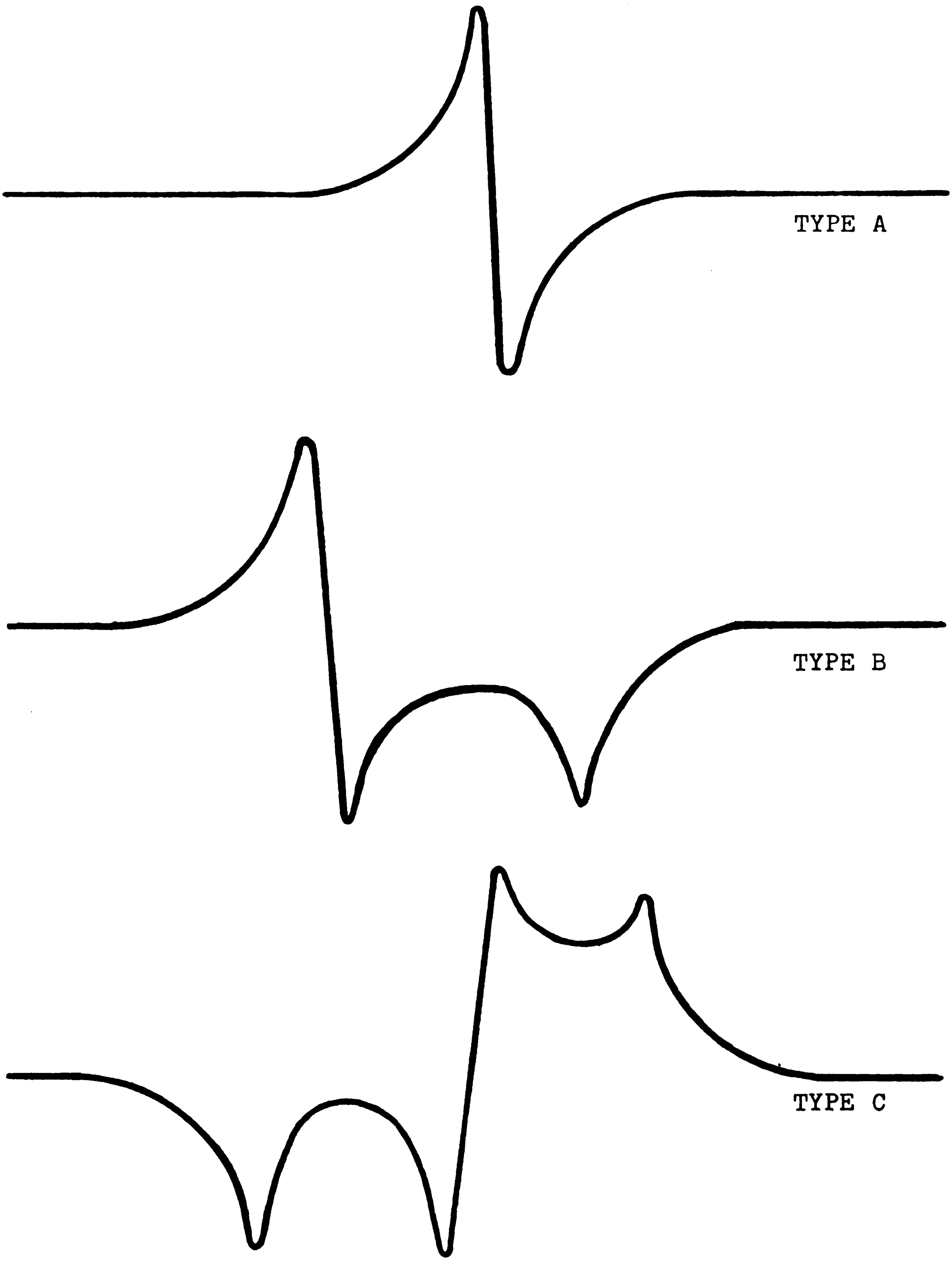

Figure 30. Representative electron spin resonance spectra.

TABLE V.--The g Values from esr Spectra of the Complexes.[a]

Compound	Temp. °K	Type of spectrum	g_1	g_2	g_3
$TiCl_3 \cdot 3CH_3CN$	297	A	1.907		
	77	B	1.921	1.883	
$TiCl_3 \cdot 3C_4H_8O$	297	A	1.884		
	77	B	1.894	1.849	
$TiCl_3 \cdot 2C_4H_8O_2$	297	B	1.972	1.880	
	77	C	1.982	1.880	1.826
$TiCl_3 \cdot 4C_3H_8O$	297	A	1.901		
	77	C	1.977	1.899	1.828
$TiCl_3(C_4H_8O)_2(CH_3CN)$	297	A	1.909		
	77	A	1.909		
$TiCl_3(C_4H_8O_2)_2(CH_3CN)$	297	C	1.963	1.890	1.836
	77	C	1.987	1.903	1.837
$TiCl_3(C_4H_8O_2)_2(C_4H_8O)$	297	A	1.885		
	77	C	1.939	1.898	1.827
$TiCl_3(C_4H_8O_2)_2(C_3H_8O)$	297	A	1.887		
	77	B	1.911	1.855	
$TiCl_3 \cdot CH_3CN$	297	A	1.911		
	77	A	1.907		
$TiCl_3 \cdot C_4H_8O$	297	A	1.898		
	77	A	1.898		
$TiCl_3 \cdot C_4H_8O_2$	297	A	1.879		
	77	A	1.881		
$(C_2H_5)_4N[TiCl_4 \cdot 2CH_3CN]$	297	C	1.941	1.869	1.807
	77	C	1.940	1.869	1.806
$(C_2H_5)_4N[TiCl_4 \cdot 2C_4H_8O]$	297	C	1.977	1.885	1.796
	77	C	1.978	1.886	1.796
$(C_2H_5)_4N[TiCl_4 \cdot 2C_4H_8O_2]$	297	C	1.983	1.886	1.815
	77	C	1.983	1.885	1.813

[a] for spectra of type B $g_1 = g_\perp$ and $g_2 = g_{||}$.

Compounds of the type $TiCl_3L_2L'$ have no axis of symmetry and were expected to give a three-line type C spectrum. However, this type of spectrum was observed only for $TiCl_3(C_4H_8O_2)_2(CH_3CN)$ and $TiCl_3(C_4H_8O_2)_2(C_4H_8O)$. The unsymmetrical spectrum of $TiCl_3(C_4H_8O_2)_2(C_3H_8O)$ may have been an unresolved three-line spectrum. The spectrum of $TiCl_3(C_4H_8O)_2(CH_3CN)$ remained a single absorption peak even at 77°K. This was caused by the large splitting of the ground state $^2T_{2g}$ (δ_1=990 cm^{-1} from the magnetic data) which quenched the orbital angular momentum and caused g to become approximately isotropic. The spectra of compounds of the type $TiCl_3 \cdot L$ were expected to show the axial symmetry of these complexes. However, the spectra had only a single absorption peak. The spectrum of $TiCl_3 \cdot C_4H_8O_2$ was very broad due to the small separation δ_1 of the t_{2g} sublevels. As $TiCl_3 \cdot CH_3CN$ and $TiCl_3 \cdot C_4H_8O$ were antiferromagnetic, the separation energy could not be evaluated from the magnetic data. Powdered antiferromagnetic substances generally give broad, inhomogeneous resonance spectra.[72] Compounds of the type $(C_2H_5)_4N[TiCl_4 \cdot 2L]$ gave three-line type C spectra even at room temperature. The spectra indicated that the compounds have cis configurations.

As the symmetries of the complexes became more distorted from octahedral symmetry, the orbital angular momenta were quenched and the average g values were expected to approach 2.00. Since most of the complexes had average g values close to 1.89 it was difficult to establish the existence of any definite correlations. However, the distortion of the complexes and the approach of the average g values to 2.00 appeared to be in the same order as the ligand field strengths of the complexes with the ligands in the order $CH_3CN > C_3H_8O > C_4H_8O_2 \simeq C_4H_8O > Cl$.

F. Thermochromism

Several of the complexes prepared during the course of this investigation were thermochromic. The compounds and the color changes that occur when they are cooled to 77°K are given in Table VI. Thermochromism may be caused by a change in phase or ligand geometry, in which case the color change is abrupt, or a narrowing and shifting of charge transfer bands into the ultraviolet region of the spectrum which causes a gradual change in color. There have been no previous reports of thermochromic titanium complexes.

TABLE VI.--Thermochromic Titanium Complexes.

Compound	Color at 297°K	Color at 77°K
$TiCl_3 \cdot C_4H_8O$	gray-green	violet
$TiCl_4 \cdot 2CH_3CN$	yellow	white
$TiCl_4 \cdot 2C_4H_8O$	yellow	white
$(C_2H_5)_4N[TiCl_4 \cdot 2CH_3CN]$	green	blue
"$(C_2H_5)_4N[TiCl_n]$"[a]	salmon	yellow

[a] a material with non-integral stoichiometry.

Several other physical properties of the thermochromic complexes were qualitatively examined to observe if the color changes could be correlated with other changes. The optical spectra showed a shift of the lowest-energy charge transfer band toward higher energies when the compounds were cooled. The shift was especially noticeable in the material with non-integral stoichiometry "$(C_2H_5)_4N[TiCl_x(C_4H_8O)_y]$", obtained from $(C_2H_5)_4[TiCl_4\cdot 2C_4H_8O]$, in which the charge-transfer band at 21,000 cm^{-1} at room temperature merged into the higher-energy bands. The charge-transfer band of $TiCl_3\cdot C_4H_8O$ was located such that the compound was thermochromic. In $TiCl_3\cdot C_4H_8O_2$ and $TiCl_3\cdot CH_3CN$ the energies of the first charge-transfer bands were respectively too high and too low for the compounds to exhibit thermochromism. No abrupt changes were found in the magnetic behavior of the thermochromic complexes as they were cooled.

Changes in the esr spectra and the average g value of the complexes occured when several of the compounds were cooled. The spectra of $TiCl_4\cdot 2CH_3CN$ and $TiCl_4\cdot 2C_4H_8O$ had a weak absorption peak at $g=1.937$ due to an unknown titanium(III) impurity. As the compound was cooled the spectrum of $TiCl_3\cdot 3CH_3CN$ appeared and at 77°K the intensity of this signal was very high. A similar change took place with $TiCl_4\cdot 2C_4H_8O$. The spectrum of "$(C_2H_5)_4N[TiCl_x(C_4H_8O)_y]$", which was prepared from $(C_2H_5)_4N[TiCl_4\cdot 2C_4H_8O]$, and

$(C_2H_5)_4N[TiCl_4 \cdot 2CH_3CN]$, which appeared to have been partially oxidized, showed only a very sharp, single absorption peak $g=2.00$ at room temperature. When the compounds were cooled this peak gradually disappeared and the spectra of the respective $(C_2H_5)_4N[TiCl_4 \cdot 2L]$ type compounds appeared. The changes were rapid and reversible as the temperatures were changed. In contrast, pure samples of the respective tetraethylammonium titanium complexes did not exhibit thermochromism or unusual esr spectra. It is felt that the thermochromism and the changes in the esr spectra of these compounds is somehow related to the presence of both titanium(III) and titanium(IV) in the samples though the connection is not apparent. The esr spectrum of $TiCl_3 \cdot C_4H_8O$ did not change except for the customary narrowing when the compound was cooled.

BIBLIOGRAPHY

BIBLIOGRAPHY

1. Giggenbach, W., and Brubaker, C. H., Jr., Inorg. Chem. 8, 1131 (1969).

2. Bereman, R. D., and Brubaker, C. H., Jr., Inorg. Chem. 8, 2480 (1969).

3. Wentworth, R. A. D., and Brubaker, C. H., Jr., Inorg. Chem., 3, 47 (1964).

4. Rillema, D. P., and Brubaker, C. H., Jr., Inorg. Chem., 8, 1645 (1969).

5. Reagan, W. J., and Brubaker, C. H., Jr., Inorg. Chem., 9, 827 (1970).

6. Duckworth, M. W., Fowles, G. W. A., and Hoodless, R. A., J. Chem. Soc., 5665 (1963).

7. McDonald, G. D., Thompson, M., and Larsen, E. M., Inorg. Chem., 7, 648 (1968).

8. Clark, R. J. H., Lewis, J., Machin, D. J., and Nyholm, R. S., J. Chem. Soc., 379 (1963).

9. Fowles, G. W. A., Hoodless, R. A., and Walton, R. A., J. Chem. Soc., 5873 (1963).

10. Fowles, G. W. A., Greene, P. T., and Lester, T. E., J. Inorg. Nucl. Chem., 29, 2365 (1967).

11. Schumb, W. C., and Sundström, R. F., J. Amer. Chem. Soc., 55, 596 (1933).

12. Fowles, G. W. A., "Progress in Inorganic Chemistry," Vol. VI, Cotton, F. A., ed., Interscience Publishers, New York, New York, 1964.

13. Antler, M. and Laubengayer, A. W., J. Amer. Chem. Soc., 77, 5250 (1955).

14. Ehrlich, P., and Siebert, W., Z. Anorg. Allg. Chem., 303, 96 (1960).

15. Fowles, G. W. A., Hoodless, R. A., and Walton, R. A., J. Inorg. Nucl. Chem., 27, 391 (1965).

16. Siddiqui, M. T., Ahmad, N., and Rahman, S. M. F., Z. Anorg. Allg. Chem., 336, 110 (1965).

17. Clark, R. J. H., and Greenfield, M. L., J. Chem. Soc., A, 409 (1967).

18. Edwards, D. A., Fowles, G. W.A., and Walton, R. A., J. Inorg. Nucl. Chem., 27, 1999 (1965).

19. Giggenbach, W. and Brubaker, C. H., Jr., Inorg. Chem., 7, 129 (1968).

20. Schlafer, H. L., and Gotz, R., Z. Anorg. Allg. Chem., 328, 1 (1964).

21. Fowles, G. W. A., Lester, T. E., and Russ, B. J., J. Chem. Soc., A, 805 (1968).

22. Fowles, G. W. A., and Walton, R. A., J. Chem. Soc., 4953 (1964).

23. Winter, G., Inorg. Nucl. Chem. Lett., 2, 198 (1966).

24. Seifert, J. J., and Thurn, F. M., Z. Anorg. Allg. Chem., 372, 79 (1970).

25. Fowles, G. W. A., and Russ, B. J., J. Chem. Soc., A, 517 (1967).

26. Kern, R. I., J. Inorg, Nucl. Chem., 24, 1105 (1962).

27. Schlafer, H. L., and Gotz, R., Z. Phys. Chem. (Frankfurt am Main), 41, 97 (1964).

28. Hartmann, H., Schlafer, H. L., and Hansen, K. H., Z. Anorg. Allg. Chem., 289, 40 (1957).

29. Schlafer, H. L., Lenz, W., and Staab, J., Z. Phys. Chem. (Frankfurt am Main), 62, 290 (1968).

30. Gutmann, V., Leitmann, O., Scherhauger, A., and Czuba, H., Monatsh. Chem., 98, 188 (1967).

31. Hathaway, B. J., and Holah, D. G., J. Chem. Soc., 537 (1965).

32. Ballhausen, C. J., and Gray, H. B., Inorg. Chem., 1, 111 (1962).

33. Figgis, B. N., "Introduction to Ligand Field Theory," Interscience Publishers, New York, New York, 1966.

34. Jorgensen, C. K., Acta. Chem. Scand., 11, 73 (1957).

35. Leihr, B., and Ballhausen, C. J., Ann. Phys., 3, 304 (1958).

36. Clark, R. J. H., J. Chem. Soc., 417 (1964).

37. Jorgensen, C. K., "Absorption Spectra and Chemical Bonding in Complexes," Pergamon Press, New York, New York, 1962, p. 109.

38. Clark, R. J. H., Spectrochim. Acta, 21, 955 (1965).

39. Figgis, B. N., and Lewis, J., "Progress in Inorganic Chemistry," Vol. VI, Cotton, F. A., Interscience Publishers, New York, New York, 1964.

40. Earnshaw, A., "Introduction to Magnetochemistry," Academic Press, New York, 1968.

41. Van Vleck, J. H., "Electric and Magnetic Susceptibilities," Oxford University Press, London, 1932.

42. Cotton, F. A., and Wilkinson, G., "Advanced Inorganic Chemistry," Interscience Publishers, New York, 1966 p. 641.

43. Kotani, M., J. Phys. Soc. Jap., 4, 293 (1949).

44. Figgis, B. N., Trans. Faraday Soc., 57, 198 (1961).

45. Dunn, T. M., J. Chem. Soc., 623 (1959).

46. Earnshaw, A., Figgis, B. N., and Lewis, J., J. Chem. Soc., A, 1656 (1966).

47. Lewis, J., Machin, D. J., Newham, I. E., and Nyholm, R. S., J. Chem. Soc., 2036 (1962).

48. Klemm, W., and Krose, E., Z. Anorg. Allg. Chem., 253, 209 (1947).

49. Bereman, R. D., Ph. D. Thesis, Michigan State University, 1969.

50. Kuska, H. A., Ph. D. Thesis, Michigan State University, 1965.

51. Carrington, A., and Longuet-Higgens, H. C., Quart. Rev. (London), 14, 427 (1960).

52. Gladney, H. M. and Swalen, J. D., J. Chem. Phys., 42, 1999 (1965).

53. Bijl, D., Proc. Phys. Soc. (London), A63, 405 (1950).

54. Bleany, B., Proc. Phys. Soc. (London), A63, 407 (1950).

55. Bleany, B., Bogle, G. S., Cooke, A. H., Duffus, R. J., O'Brien, M. C. M., and Stevens, K. W. H., Proc. Phys. Soc. (London), A68, 57 (1955).

56. Jarrett, H. S., J. Chem. Phys. 27, 1298 (1957).

57. McGarvey, B. R., J. Chem. Phys., 38, 388 (1963).

58. Waters, E. L., and Maki, A. H., Phys. Rev., 125, 233 (1962).

59. Gair'yanov, N. S., Danilova, A. V., and Shagidullin, R. R., Opt. Spektrosk., 13, 212 (1962).

60. Giggenbach, W. and Brubaker, C. H., Jr., Inorg. Chem., 7, 129 (1968).

61. Giggenbach, W., unpublished results.

62. Bereman, R. D., and Brubaker, C. H., Jr., J. Inorg. Nucl. Chem., in press.

63. Herzog, S., Dehnert, J., and Luhder, K., "Technique of Inorganic Chemistry," Vol. VII, Jonassen, H. B., and Weissberger, A., eds., Interscience Publishers, New York, New York, 1968.

64. Perrin, D. D., Armarego, W. L. F., and Perrin, D. R., "Purification of Laboratory Chemicals," Pergamon Press, Oxford, 1963.

65. Carter, H. V., McClelland, B. J. and Warhurst, E, Trans. Faraday Soc., 56, 343 (1960).

66. Walton, H. F., "Principles and Methods of Chemical Analysis," Prentice Hall, Inc., Englewood Cliffs, New Jersey, 1964, p. 236.

67. International Union of Pure Applied Chemistry, Commission on Spectroscopy and Other Optical Procedures for Analysis, "Tables of Spectrophotometric Absorption Data of Compounds Used for the Colorimetric Determination of the Elements," London: Butterworths, 1963.

68. Figgis, B. N., and Lewis, J., "Modern Coordination Chemistry," J. Lewis and R. G. Wilkins, Ed. New York: Interscience Publishers, Inc.

69. Vander Vennen, R. E., Ph. D. Thesis, Michigan State University, 1954.

70. Figgis, B. N. and Nyholm, R. S., J. Chem. Soc., 4190 (1958).

71. Foex, G., "Constantes Selectionnes: Diamagnetisme et Paramagnetisme. Relaxation Paramanetiquex," Masson & Cie, Paris, 1957.

72. Bersohn, M. and Baird, J. C., "An Introduction to Electron Paramagnetic Resonance," New York: W. A. Benjamin, Inc., 1966.