

In the absence of crystallographic investigations up to the present time, a combination of infrared and Raman spectroscopic measurements on the *solid* complexes seems the most rewarding means of establishing their structure. Thus from the present investigation the thallium(III) halides have been found to form complexes of coordination number four, five, or six, which are ionic, neutral and monomeric, or neutral and polymeric, and they thus resemble the indium(III) halides in their varied acceptor properties. However, in contrast to the latter halides,^{2,4} the factors which determine a particular structure and stereochemistry are not yet well understood.

The structure of species such as TiX_3Y^- , $TiCl_3 \cdot 2DMSO$, and $(TiX_3)_2 \cdot terpy$ can apparently be deduced from a study of their vibrational spectra, but it remains for crystallographic investigations to confirm or refute the conclusions of the present work.

Investigations are continuing on the spectroscopic properties of relatively simple thallium(III) halide species.

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Compounds of Titanium(III) Chloride from Nonaqueous Solvents

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The magnetic susceptibility of solid $Ti(CH_3CN)_3Cl_3$ was studied over the temperature range 88–300°K. The temperature dependence of the magnetic moments was found to fit Figgis' theory when the parameters $\lambda = 154 \text{ cm}^{-1}$, $\Delta = 770 \text{ cm}^{-1}$, and $k = 0.7$ were used. Out of an acetonitrile solution of titanium(III) chloride, compounds of composition $Ti(nc)_2Cl_3$, $Ti(en)_2Cl_3$, and $Ti(dien)_2Cl_3$ were obtained. In acetic anhydride or acetic acid slow acetate substitution for chloride occurred. From acetic anhydride solutions compositions of $Ti(Ac)_2Cl_3$ and $Ti(Ac)_2Cl$ were produced, but no trisubstituted product could be obtained. From a freshly prepared acetic acid solution and cesium chloride, $Cs_2TiCl_5 \cdot CH_3COOH$ precipitated. The magnetic data and infrared data of all these new compounds are reported.

The nonaqueous chemistry of titanium(III) has been little studied. Previous workers^{2–10} have prepared unidentate ligand adducts and have reported limited and sometimes conflicting magnetic data. Still fewer studies have been made on titanium(III) compounds with bidentate ligands.^{11–15}

Experimental Section

Reagents.— α -Titanium(III) chloride was obtained from Pittsburgh Plate Glass, New Martinsville, W. Va. The total reducing power of the reagent as titanium(III) was $99.9 \pm$

0.2% and the total titanium after reduction of any titanium(IV) present was $100.3 \pm 0.5\%$ titanium(III). Thus, within the limits of the analytical methods, the sample was considered free of titanium(II) and titanium(IV).

Acetonitrile was purified by fractional distillation from phosphorus pentoxide. The major fraction, which distilled at 81°, was collected over calcium hydride and then vacuum distilled (40° (140 mm)) directly off the calcium hydride into a transfer flask.

Acetic acid, dried by refluxing over phosphorus pentoxide for 1 hr, was distilled directly through an 80-cm fractionating column filled with glass helices. The middle fraction was collected in a storage bulb.

Acetic anhydride, to which was added two drops of 60% perchloric acid, was fractionally distilled through a Vigreux column. Only the middle fraction which distilled at 136–138° was collected in a storage bulb.

Nicotinamide (nc) (Eastman Kodak) was recrystallized from methanol before use.

Ethylenediamine (en) was refluxed over sodium hydroxide for 12 hr, fractionally distilled onto sodium metal, and then fractionally distilled off the sodium. The middle fraction was collected in a storage bulb and kept in a refrigerator.

Diethylenetriamine (dien) was dried over barium oxide and distilled through a Vigreux column at less than 1 μ . The fraction distilling at 56° was collected in a storage bulb.

Methods of Synthesis.—Inasmuch as titanium(III) chloride reacts rapidly with oxygen, it was necessary to carry out the syntheses in special all-glass equipment (Figure 1) which was loaded with reagents either in an inert-atmosphere box (water less than 40 ppm, oxygen about 100 ppm), on a vacuum line, or by gravity from a storage bulb interconnected with the partially

(1) This article is based on a dissertation submitted by G. D. McDonald in partial fulfillment of the requirements for the degree of Doctor of Philosophy at the University of Wisconsin.

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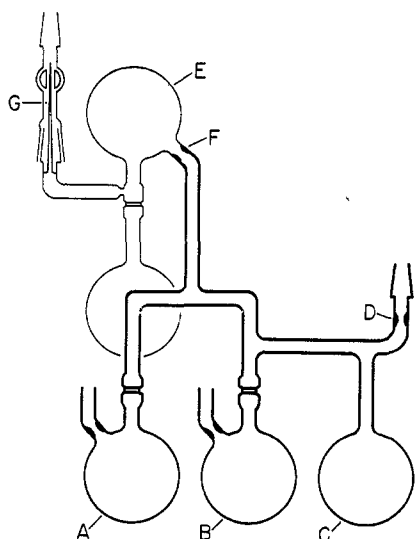


Figure 1.—Apparatus for synthesis of complexes.

evacuated system *via* a ground-glass joint. In general, systems were evacuated to less than 10 μ . Acetonitrile was the solvent used, except for cesium chloride where acetic acid was used because of a more favorable solubility. The analytical data on the products are tabulated in Table I.

TABLE I
ANALYTICAL DATA OF TITANIUM(III) REACTION PRODUCTS

Compound	% calcd			% found		
	Ti	Cl	Cs	Ti	Cl	Cs
TiCl ₃ (CH ₃ CN) ₃	24.19	53.50		24.10	53.49	
Ti(nc) ₂ Cl ₃	12.02	26.70		12.16	26.60	
Ti(dien) ₂ Cl ₃	13.28	29.49		13.25	29.39	
Ti(en) ₃ Cl ₃	14.32	31.80		14.30	31.77	
Ti(Ac) ₂ Cl ₂	26.93	39.87		27.21	40.25	
Ti(Ac) ₂ Cl	23.79	17.61		23.21	16.73	
Ti(Ac)Cl ₂ ·HAc	20.14	29.81		19.93	29.75	
Cs ₂ TiCl ₅ ·HAc	8.69	32.18	48.24	8.68	31.47	48.48

Ti(nc)₂Cl₃ and Cs₂TiCl₅·CH₃COOH.—Titanium(III) chloride (1 g) and nicotinamide (2.8 g) or cesium chloride (2.93 g) were placed in bulbs A and B, respectively, and sealed at the constrictions. Solvent was added to bulb C on the vacuum line, frozen, pumped on, and then sealed off at D. The solvent was transferred to bulbs A and B, and when the reactants had dissolved, the apparatus was inverted so that the solutions filtered into reaction bulb E. Precipitates formed immediately upon mixing, the nicotinamide reaction product being red-brown and the cesium chloride reaction product being greenish white. The apparatus was turned again so as to filter off the product, which was then sealed off at F and at a point below the filter disk. It was then reattached to the vacuum line by breaking the vacuum attachment G. The product was pumped on for 4 hr. The yields were quantitative.

Ti(en)₃Cl₃ and Ti(dien)₂Cl₃.—The reactions of the liquid amines with titanium(III) chloride were carried out in an apparatus modified by removing bulb C and replacing the filter disk above B with a break-seal. This construction kept the volatile ligand isolated from the rest of the system. Titanium(III) chloride (0.5–1.0 g) was introduced into bulb A and acetonitrile was added from the storage bulb. The solvent was frozen and pumped on, and the apparatus was sealed off. Ethylenediamine (2 ml) or diethylenetriamine was introduced into bulb B, frozen, pumped on, and sealed off at the constriction. After the titanium(III) had dissolved, the apparatus was inverted to filter the solution through the sintered disk into bulb E. The break-seal was ruptured allowing the amine to flow into reaction bulb E. Precipitates formed immediately. With diethylene-

triamine a very voluminous blue product formed accompanied by considerable evolution of heat. The reaction bulb was cooled to prevent decomposition. With ethylenediamine, a white precipitate formed initially which redissolved to give a blue product a few minutes later. The products were filtered off, sealed at F and at a point beyond the sintered disk, reattached to the vacuum line by breaking capillary G, and dried under vacuum for 4 hr. The yields were quantitative.

Ti(CH₃CN)₃Cl₃.—The acetonitrile adduct of titanium(III) chloride was prepared in an apparatus similar to but simpler than that shown in Figure 1. The titanium(III) chloride was placed in a reaction bulb and dissolved in acetonitrile which had been introduced into the system from the vacuum line. With the solvent frozen, the apparatus was evacuated, and the system was sealed off. The apparatus was inverted and the solution was filtered through a sintered disk into a second bulb. Half of the solvent was vacuum transferred from the solution, whereupon the light blue acetonitrile adduct separated out. The product was filtered by inverting the apparatus, the filtrate was sealed off, the apparatus was reconnected to the vacuum line, and the product was pumped on to remove any solvent. The yield was 50%.

Ti(CH₃COO)Cl₂, Ti(CH₃COO)₂Cl, and Ti(CH₃COO)Cl₂·CH₃COOH.—Titanium(III) chloride (3 g) was transferred to a reaction vessel constructed from a large test tube. Dry acetic anhydride was transferred into the reaction vessel, frozen, pumped on, and sealed off. The reaction system was rotated at room temperature for 2 weeks, during which time an insoluble yellow-brown product was slowly deposited. The insoluble product was recovered by filtration in the absence of oxygen and dried under vacuum for 2 hr. The yield was quantitative. The analytical data correspond to those for the disubstituted acetate.

Titanium(III) chloride (1 g) and acetic anhydride (30 ml) were mixed for 48 hr as described above. At this time there is still a small amount of dissolved titanium(III) as evidenced by the light green supernatant. The dried product was a very dark brown. The analytical data correspond to those for the monosubstituted acetate. With a 50:50 mixture of acetic acid and acetic anhydride, after 3 days of mixing, a monoacetate containing 1 mole of acetic acid solvent was obtained.

Measurement of Solution Spectra and Conductivity.—The visible and ultraviolet spectra and the conductivity were measured simultaneously in the apparatus shown in Figure 2. Absorption cell A was constructed from square quartz tubing and connected to the apparatus by a quartz-to-Pyrex graded seal. The conductance cell was constructed inside the absorption cell. Bright platinum plates were spot welded to tungsten leads which were brought through a quartz-to-tungsten graded seal. To prevent breaking of the brittle tungsten wires during repeated reattachment to the conductance bridge, the tungsten wires were spot welded to platinum wires. The cell was calibrated against standard potassium chloride solution and found to have a cell constant of 0.2218 cm⁻¹. The conductances were measured with an Industrial Instruments conductance bridge, Model RC 16B2.

The procedure for obtaining the spectra and conductance was as follows. Titanium(III) chloride was introduced into the apparatus in the inert-atmosphere box. The apparatus was evacuated, a known volume of pure acetonitrile was added, the solvent was frozen, and the system was evacuated and sealed off at D. The resulting solution was then filtered through the sintered disk E. A series of solutions of varying concentrations were prepared in the absorption cell from the stock solution by transferring pure solvent into the cell and then adding a drop of the stock solution by careful tilting. The transfer of pure solvent to the cell was accomplished by filling jacket B with coolant. Higher concentrations of titanium(III) were obtained by further additions of stock solution. After each addition, the apparatus was tipped so that the solution could flow into the empty bulb F for mixing. The visible and ultraviolet spectra were measured by placing the cell in the Cary-14 spectrophotometer. Errors due to positioning of the cell were eliminated by adjusting the height of an acetonitrile peak in the near-infrared region to a

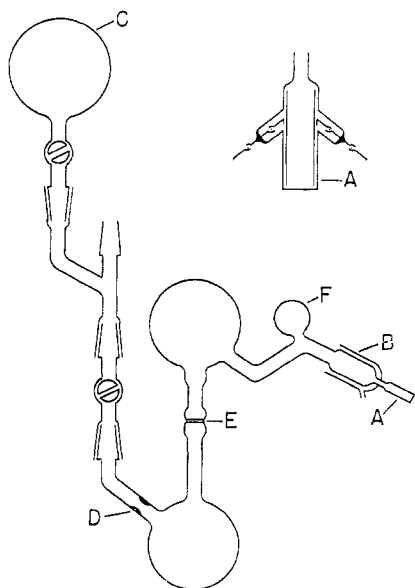


Figure 2.—Apparatus for measurement of absorption spectra and conductivity.

predetermined value. The molar absorptivity, ϵ , was determined to be 29.5 at 17,100 cm^{-1} compared to the 22 at 17,100 cm^{-1} reported by Clark,⁶ *et al.*

The conductivity data for titanium(III) chloride in acetonitrile are tabulated in Table II. Conductivity data for acetic acid solutions were complicated by the slow substitution of acetate for chloride and are not reported here.

TABLE II
CONDUCTIVITY DATA FOR TITANIUM(III)
CHLORIDE IN ACETONITRILE^a

$10^2\sqrt{C}$, $M^{1/2}$	Λ , $\text{cm}^2 \text{ohm}^{-1} \text{mole}^{-1}$	$10^2\sqrt{C}$, $M^{1/2}$	Λ , $\text{cm}^2 \text{ohm}^{-1} \text{mole}^{-1}$
21.31	2.486	15.17	3.582
20.82	2.566	14.49	3.706
19.86	2.670	13.64	3.960
18.62	2.840	13.30	4.056
17.67	3.017	12.81	4.259
17.34	3.103	12.26	4.361
16.65	3.269	11.56	4.592
16.33	3.318	11.06	4.811
15.75	3.469	9.31	5.263
15.54	3.521	7.82	5.681

^a Specific conductance of solvent was $2.66 \times 10^{-7} \text{ cm}^2 \text{ohm}^{-1} \text{mole}^{-1}$.

Magnetic Measurements.—Magnetic susceptibility measurements were made between 80 and 300°K by the Gouy method using $\text{HgCo}(\text{NCS})_4$ as the standard.¹⁸ These oxygen-sensitive titanium compounds were loaded in the inert-atmosphere box, sealed with a ground-glass stopper, and then permanently sealed off with a torch after removal from the box. The measurements were made at three different field strengths with three to five measurements made at each field strength and each temperature. The average values for each temperature and field strength were corrected for the diamagnetism of the glass tube. The experimental gram susceptibilities were converted to the molar susceptibilities, χ_m , by multiplying by the molecular weight corresponding to the simplest empirical formula of the compound. The molar susceptibilities were corrected for the diamagnetism of the atoms using Pascal's constants¹⁷ or experimental values

for the diamagnetic ligands. These corrected susceptibilities are designated as χ'_m .

All compounds prepared using nitrogen donors showed a linear field dependence (susceptibility decreasing with increasing field). The order in which these complexes showed increasing field dependence is $\text{CH}_3\text{CN} < \text{en} < \text{nc} < \text{dien}$, with variations of 1.4, 4.0, 7.0, and 10% at 90°K and 3.3, 9.0, 8.5, and 18% at 296°K over the field range of 4.4–6.2 kgauss. The per cent was taken as equal to the susceptibility at low field strength minus the value at high field divided by the average of the two times 100. Since the original titanium(III) chloride did not show this property, it is believed that the field dependence is a real property of these compounds although the cause is not understood. To interpret the data, the field dependence was removed by plotting χ'_m against the reciprocal of the field strength and extrapolating to infinite field in a so-called Honda–Owen plot.^{18,19} The assumption is made that the field-dependent phase contains such a small mole fraction of the total metal ion sites that it is valid to use the susceptibility at infinite field, χ'_m , in all subsequent calculations. The magnitude of the temperature-independent paramagnetism (TIP) was obtained from the intercept of a $\chi'_m \text{ vs. } 1/T$ plot for those compounds for which such a plot was linear. The magnetic data for all of the compounds prepared are given in Table III.

The temperature dependence of the magnetic moments was successfully treated using the techniques of Figgis^{20,21} for some of these compounds. Figgis has calculated theoretical magnetic moments for a metal ion with a T_{2g} ground state in an axially distorted field as a function of λ , the spin-orbit coupling constant, Δ , the splitting of the T_{2g} state by the axial field, and k , a parameter to allow for the t_{2g} electron not contributing to the orbital angular momentum for the fraction of the time it spends on the ligand. Tables of data included in ref 20 allow the determination of λ , Δ , and k , by comparison of the experimental and theoretical magnetic moments.

The energies of separation between the three pairs of doublets resulting from the effect of spin-orbit coupling were also calculated from equations supplied by Figgis,²⁰ as were the values for the gyromagnetic splitting factors.

Electron Paramagnetic Resonance Spectrum.—The spectrum of trichlorotriacetone-titanium(III) chloride diluted with potassium chloride was determined using a Varian 4502 epr unit. The 3-mm quartz tube used to hold the sample was filled in the inert-atmosphere box and sealed to prevent oxidation of the sample. A single, broad resonance (Figure 3) was obtained whose center was at 3436 gauss at a microwave field of 9910 Mcps.

Infrared Spectrum.—Nujol and Florolube mulls were prepared on cesium iodide plates in the inert-atmosphere box and the infrared spectrum was measured on a Beckman IR-10 spectrophotometer.

Analytical Methods.—The samples were stored in sealed ampoules and were weighed on a semimicrobalance. After the ampoule was broken cleanly in two to remove the sample, the two pieces were washed, dried, and reweighed to obtain the sample weight.

Titanium was determined as the oxide after oxidation of the titanium(III) by nitric acid. Chloride was determined by precipitation as silver chloride from the acidified filtrate of the titanium analysis. Cesium was determined as cesium chloride.

Discussion

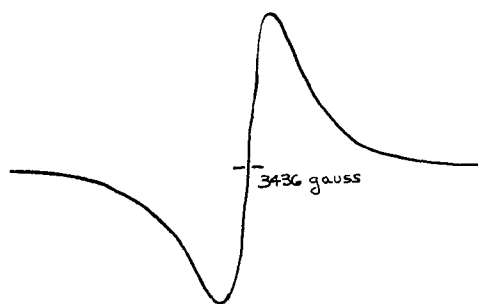
In general, these compounds, except for $\text{Cs}_2\text{TiCl}_5 \cdot \text{CH}_3\text{COOH}$, which has an X-ray pattern consisting of only broad, poorly defined lines, are noncrystalline, nonvolatile, and insoluble in all the solvents tried. This limits the structural information to that which

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TABLE III
 MAGNETIC SUSCEPTIBILITIES AND MAGNETIC MOMENTS OF TITANIUM(III) COMPOUNDS

Temp, °K	Ti(CH ₃ CN) ₃ Cl ₃		Ti(nc) ₂ Cl ₃		Ti(dien) ₂ Cl ₃		Ti(en) ₃ Cl ₃		TiCl(Ac) ₂		TiCl(Ac)·HAc		TiCl ₂ (ac)		C ₂ TiCl ₃ ·HAc	
	χ' _m [∞]	μ _{eff}	χ' _m [∞]	μ _{eff}	χ' _m [∞]	μ _{eff}	χ' _m [∞]	μ _{eff}	χ' _m ^{av}	μ _{eff}	χ' _m ^{av}	μ _{eff}	χ' _m [∞]	μ _{eff}	χ' _m [∞]	μ _{eff}
81.7																
83.3									1410	0.95						
84.1	3640	1.57	4180	1.69	1710	1.08										
87.6												1580	1.06		2820	1.41
91.1	3460	1.60	3900	1.69	1640	1.10	579	0.65	1440	1.03			2460	1.34	2770	1.43
99.5	3160	1.59	3570	1.69	1600	1.13	563	0.67	1440	1.08	1590	1.13	2440	1.40	2630	1.43
116.1							524	0.70					2370	1.49		
116.7	2760	1.61	3350	1.78	1520	1.19			1450	1.18	1590	1.22			2340	1.45
133.0							480	0.73								
133.8	2470	1.63	3060	1.82	1420	1.23			1450	1.25	1570	1.30			2200	1.54
149.3			2790	1.84	1320	1.26	451	0.74					2310	1.67		
151.0	2210	1.64							1420	1.31	1560	1.38			2080	1.59
166.0			2640	1.88	1240	1.29	430	0.76								
168.2	1970	1.63							1400	1.38	1550	1.45			1990	1.64
183.9			2410	1.89	1140	1.30	413	0.78					2370	1.88		
185.6	1820	1.67							1370	1.43	1500	1.50			1910	1.69
201.6			2230	1.90	1030	1.30	399	0.81								
203.5	1720	1.68							1290	1.46	1460	1.55			1800	1.72
219.7			2150	1.95	1000	1.33	390	0.83					2440	2.08		
221.7	1600	1.69							1260	1.50	1400	1.58			1750	1.77
236.8			2040	1.97	990	1.38	379	0.85								
239.1	1460	1.68							1230	1.54	1360	1.62			1650	1.78
254.5			1970	2.01	940	1.38	368	0.87					2510	2.27		
257.1	1390	1.70							1200	1.57	1310	1.65			1590	1.82
272.4			1910	2.05	900	1.38	360	0.90					2490	2.34		
275.4	1320	1.71							1150	1.60	1270	1.68			1490	1.82
296.2															1420	1.84
296.6					850	1.42					1220	1.70				
297.7	1220	1.71														
298.5			1810	2.08												
299.2	1210	1.71							1080	1.61						
300.2							344	0.93					2330	2.38		


 Figure 3.—Electron paramagnetic resonance of TiCl₃(CH₃CN)₃ at a 9100-Mcps microwave field.

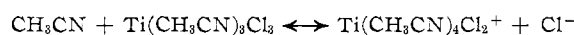
can be deduced from the infrared spectra and the magnetic data.

The infrared spectrum of α -titanium(III) chloride shows only a strong band centered on 275 cm⁻¹. The exact value must be used with some reservation since we are operating at the limit of the instrument. It is reasonable to conclude that the absorption is due to a chlorine-metal-chlorine mode, since in α -titanium(III) chloride itself, the halogens are close-packed with titanium(III) ions occupying two-thirds of the octahedral holes in alternate layers.²² Now, since the coordination number of the metal is six, each chloride on the average must be bonded to two titanium ions to preserve the stoichiometry of 1:3; therefore, the chlorides within the occupied layer must be bridging groups.

(22) J. W. Reed, Ph.D. Thesis, The Ohio State University, 1957; *Dissertation Abstr.*, **17**, 1479 (1957).

In acetonitrile solutions of titanium(III) chloride, the absorbing species has been assumed to be molecular trichlorotriacetone-titanium(III) since the solution has a low conductivity,^{5,6} and the reflectance spectrum of the solid with this composition is the same as the absorption spectrum of the solution.⁵ Now, in addition, the infrared spectrum of the solid shows a strong absorption at 330 cm⁻¹ which can be assigned to the terminal chlorine-metal stretching frequency. This assignment is consistent with the α -titanium(III) chloride spectrum and the data of Clark²³ for metal-chlorine bonds in coordination compounds of composition MX₃L₃. In principle, we should be able to decide whether the three chlorides are in *cis* or *trans* positions, but the absorption is so broad that it is impossible to tell whether it is made up of two (*cis*-C_{3v}) or three (*trans*-C_{2v}) absorptions. The remainder of the spectrum is consistent with that previously reported.^{2,3}

The conductivity in acetonitrile over the titanium(III) concentration range of 0.6 × 10⁻² to 4.5 × 10⁻² M gave specific conductances (corrected for solvent) of 3.478 × 10⁻⁵ to 11.29 × 10⁻⁵ cm² ohm⁻¹ mole⁻¹, respectively. Since the solutions behaved as typical weak electrolytes, the assumption was made that the Debye-Hückel theory was applicable. For the dissociation



(23) R. J. H. Clark and C. S. Williams, *Inorg. Chem.*, **4**, 350 (1965).

the equilibrium constant written in terms of c , the stoichiometric concentration of titanium(III), f , the mean activity coefficient of the dissociated species, and γ , the fraction of solute free to carry current, is $K = (c\gamma)^2 f^2 / c(1 - \gamma)$. From the measured specific conductance, k , and the estimated limiting conductance, Λ_0 , obtained by extrapolation of the data in Table II, a numerical value of γ was obtained using the procedure of Kraus and Fuoss.²⁴ This involved a reiterative process in which Λ/Λ_0 was substituted for γ on the right side of the Debye relationship $\gamma = \Lambda/[\Lambda_0 - \alpha(c\gamma)^{1/2}]$, and a new γ was calculated. After six reiterations, a constant value of γ was obtained. With this value of γ , f was computed using the Debye-Hückel limiting law. As required by the equilibrium constant expression, a plot of $(1 - \gamma)^{1/2}/\gamma$ against $c^{1/2}f$ gave a straight line, and from the slope the value of 1.39×10^{-4} was obtained for the equilibrium constant. It can be concluded that the dissociated species $\text{Ti}(\text{CH}_3\text{CN})_4\text{Cl}_2^+$ is present in concentrations too low to be detected spectrophotometrically unless it has an unusually high absorbancy. Therefore, the absorption spectrum can indeed be attributed to molecular trichloroacetonitriletitanium(III).

A comparison of the theoretical and experimental values of the magnetic moments of the acetonitrile adduct as a function of temperature using the values of $\lambda = 154 \text{ cm}^{-1}$, $k = 0.7$, and $\Delta = 770 \text{ cm}^{-1}$ is shown in Figure 4. These values differ somewhat from those of $\lambda = 154 \text{ cm}^{-1}$, $k = 0.6$, and $\Delta = 600 \text{ cm}^{-1}$ reported by Nyholm,⁶ who had only limited magnetic data to work with. It is seen from the figure that the application of the Figgis procedure adequately explains the manner in which the magnetic moment varies with temperature. Additionally, the average gyromagnetic splitting factor as obtained from the magnetic data, 1.8, compares favorably with the value of 1.89 obtained at room temperature by direct esr measurement. This gives confidence to the interpretation of the magnetic data based on the Figgis theory. The magnetic moment of 1.71 BM at 299.2° is significantly higher than the 1.58–1.68 values at 302° obtained by Nyholm on different samples of the acetonitrile adduct. Low values for their samples may represent some oxidation during handling.

The complete splitting diagram showing the effects of axial distortion and spin-orbit coupling on the acetonitrile adduct is shown in Figure 5. The positive value of Δ is evidence that the singlet ${}^2B_{2g}$ level lies lowest. The splittings of the Kramers doublets were calculated from the equations provided by Figgis. The separation of the higher E states from the ground state is 3.5–4.5 times kT at room temperature, and therefore the contribution of these states to the magnetic moment is *via* the second-order Zeeman effect thus accounting for the relatively large TIP of 290×10^{-6} cgs unit. As can be seen, the splitting due to the axial distortion is small compared to the ligand field effect.

(24) C. A. Kraus and R. M. Fuoss, *J. Am. Chem. Soc.*, **55**, 476 (1933).

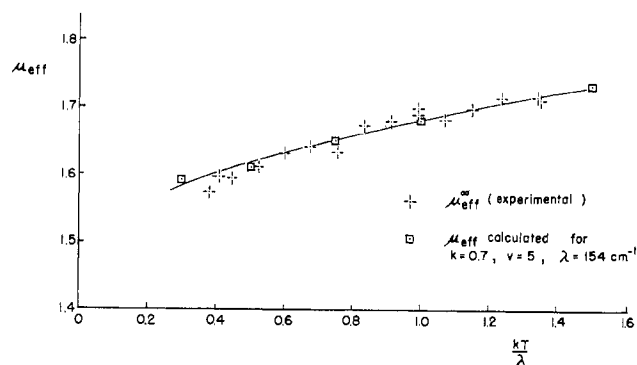


Figure 4.—Comparison of theoretical and experimental magnetic moments of the acetonitrile adduct.

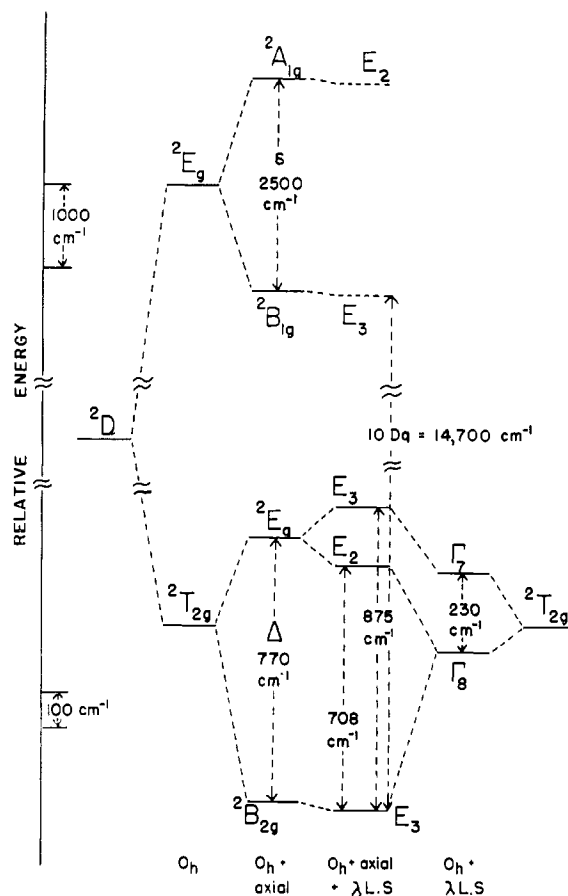


Figure 5.—Splitting diagram for $\text{Ti}(\text{CH}_3\text{CN})_3\text{Cl}_3$.

The splitting of the upper 2E state into a lower B_{1g} and upper A_{1g} is the inverse of the assignment used by Nyholm,⁶ but is consistent with the assignment used by Moffitt,²⁵ Ballhausen,²⁶ and Figgis²⁷ for a d^1 species with axial distortion. The assignment of the B_{1g} term as lower lying rather than the A_{1g} results in different numerical values for the quantity $10Dq$ ($B_{1g} \rightarrow B_{2g}$) than previously reported^{2,8} and also in a somewhat different order for the spectrochemical series of ligands. Along with the reassigned $10Dq$ values, the ligands fit into the order: CN^- (18,900 cm^{-1}), H_2O (17,400), HCO_2H (16,100), CH_3CN

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

(27) B. N. Figgis, *J. Chem. Soc.*, 4887 (1965).

(14,700), morpholine (14,000), furan (13,500), dioxane (13,400), CH_3COOH (13,000), $(\text{CH}_3)_2\text{CO}$ (12,700), Cl^- (12,000).

It should be noted that the absorption spectrum of titanium(III) chloride in acetic acid (freshly prepared) shows at least four peaks. This complexity undoubtedly arises from the slow substitution reaction which results in a mixture of species in solution. The peaks at 13,000 and 18,400 cm^{-1} correspond to those at 14,700 and 17,200 cm^{-1} in acetonitrile. The lower intensity peaks at 21,930 and 23,640 cm^{-1} remain unidentified. The color of the solution to the eye is always green and never blue as previously described.⁵ It is believed that the blue color is due to water in acetic acid.

The nicotinamide complex, $\text{Ti}(\text{nc})_2\text{Cl}_3$, presents a more complex problem. To preserve electrical neutrality with this composition, the nicotinamide must be present as a neutral molecule. The infrared absorption spectrum shows a strong, broad absorption at 315 cm^{-1} which is taken to mean that terminal chlorides bound to the metal are present. Whether all of the chlorides are bound cannot be determined.

The nature of the amide bonding is ambiguous. The amide I band, which is principally a C–O stretch, occurs in nicotinamide at 1681 cm^{-1} and in the complex at 1660 cm^{-1} . This lowering is generally taken to mean that the amide group is coordinated through the oxygen. However, when this occurs, the amide III band, which is largely associated with the C–N stretch, normally shifts to higher frequencies.²⁸ In the titanium(III) complex, however, the amide III band is found at 1376 cm^{-1} compared to that at 1394 cm^{-1} in the free ligand, a shift normally associated with nitrogen coordination. The known sensitivity of the amide I band to hydrogen bonding makes the interpretation of shifts difficult. Indeed, the N–H modes which normally appear as sharp bands in nicotinamide at 3365 and 3158 cm^{-1} broaden out in the infrared spectrum of the complex with minima appearing at 3330, 3200, and 3100 cm^{-1} . Although the role of hydrogen bonding in these shifts is unknown, a structural feature must be present in the complex which is not present in the free ligand. The amide II band, which is principally an $-\text{NH}_2$ bending mode with some C–N contribution, shows essentially no shift upon complex formation, but this is consistent with its known insensitivity to metal bond formation. However, ring nitrogen coordination to metal can be established by shifts in the C–C out-of-plane bending mode. In nicotinamide this occurs at 401 cm^{-1} , while in the titanium(III) adduct it is found at 430 cm^{-1} . This increase in frequency is indicative of bonding through the ring nitrogen²⁹ and has been observed in pyridine and other nicotinamide–metal complexes. The conclusion seems to be that nicotinamide is bound to a metal by both the ring nitrogen and

the amide sites. This is the conclusion reached by Yamasaki³⁰ for metal complexes with pyridine-2-carboxamide, the *ortho* isomer of nicotinamide. Now, although the *ortho* isomer can act as a bidentate group to one metal ion, this is physically impossible for the *meta* isomer. Therefore if nicotinamide is acting as a bidentate group it must be to two metal ions. Two other possibilities suggest themselves to account for the shifts normally associated with ring nitrogen–metal and amide–metal bonding. These are random distribution of monodentate nicotinamide ligands between the two coordination sites or a species in which the nicotinamide ligands are all ring nitrogen–metal bonded, with all of the rings so oriented to result in a particularly favorable amide group interaction *via* hydrogen bonding. Whether the latter would explain the amide shifts observed is not known. Neither of these two alternatives seems to be preferred to nicotinamide as a bidentate ligand. In any event a monomeric species is not likely if coordination number six is to be preserved.

The dependence of the magnetic moments of the nicotinamide–titanium complex on temperature can be satisfactorily explained using the Figgis theory for the effect of axial distortion and spin–orbit coupling on a six-coordinate species. The values for the parameters which yield a fit of the data are $\lambda = 85 \text{ cm}^{-1}$, $k = 0.95$, and $\Delta = 300 \text{ cm}^{-1}$. An energy-level diagram similar to Figure 5 can be constructed, except that the ligand field is unknown for nicotinamide, although again it must be large compared to Δ . It is interesting to note that the effect of axial distortion results in a considerably smaller Δ for nicotinamide than for the acetonitrile complex. This in turn means a smaller separation between the Kramers doublets. It is calculated that the E_3 and E_2 terms resulting from the resolution of the lower 2E_g state by spin–orbit coupling lie 363 and 268 cm^{-1} above the ground state. The high value for the electron delocalization factor is consistent with the lack of evidence for superexchange through the ligands and the fact that the nicotinamide is a *meta*-substituted ligand which does not favor electron delocalization. The low spin–orbit coupling constant and the high k are consistent with the higher than spin-only value of 2.08 BM at 298.5°. The magnetic data are therefore not inconsistent with a polymeric species of metal coordination number six in which the bridging groups do not allow for electron interaction. If the nicotinamide ligands are bidentate between two metal ions, a trimer is the smallest polymer which will yield an electrically neutral unit.

The spectra of the diethylenetriamine, $\text{Ti}(\text{dien})_2\text{Cl}_3$, and the ethylenediamine, $\text{Ti}(\text{en})_3\text{Cl}_3$, complexes show no strong, broad absorptions in the 300- cm^{-1} region leading to the conclusion that metal–chlorine bonds are not present. The sharp, medium absorptions which do occur in this region have been assigned

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to NH_2 modes³¹ or to N-M-N ring deformations.³² There is a question of whether the two sharp absorptions at 392 and 363 cm^{-1} in the ethylenediamine complex could be metal-chlorine stretching frequencies, since such frequencies have been assigned as high as 366 cm^{-1} .³³ However, they are more likely to be N-C-C deformations.³² In any event, to incorporate chlorides into the structure would require monodentate amines in either monomeric or polymeric species, and there is no evidence for other than bound amine frequencies. All of the NH_2 modes in the ethylenediamine complex are shifted to lower frequencies than in the free amine,³¹ and although similar data are not available for dien owing to the complicated nature of its spectrum,³² it seems safe to conclude that all of the amine functions are bound to the metal in both compounds. It is not possible to decide whether the amines are bidentate with respect to one or to two metal ions, although the spectrum of the ethylenediamine complex corresponds closely with the monomeric $\text{Co}(\text{en})_3\text{Cl}_3$, $\text{Cr}(\text{en})_3\text{Cl}_3$, and $\text{Rh}(\text{en})_3\text{Cl}_3$.^{34,35} It should be pointed out that we found no evidence for the compound of composition $\text{Ti}(\text{en})_4\text{Cl}_3$ as reported by Fowles.¹⁵ The reported infrared spectrum has some points of correspondence with our spectrum, but the analytical data are certainly different. Except for the fact that this compound appears to have been prepared from pure ethylenediamine and the compound in this work was prepared in acetonitrile solution, there seems to be no explanation for the different compositions.

The low magnetic moments for the amine complexes could not be fit to the Figgis tables of theoretical values unless spin-orbit coupling constants greater than the free-ion value were used. This explanation is not satisfactory and we can only conclude that either the parameter k is much less than 0.7, data for which are not provided in the Figgis tables, or that electron interaction *via* metal-metal bonding or bridging ligands is responsible for the low magnetic moments. In view of the large Weiss constants (-250 and -130°K), it appears that the low moments are best interpreted in terms of polymeric species with bridging ligands.

A freshly prepared solution of titanium(III) chloride in acetic acid reacts with cesium chloride to yield insoluble $\text{Cs}_2\text{TiCl}_5 \cdot \text{CH}_3\text{COOH}$, analogous to $\text{Cs}_2\text{TiCl}_5 \cdot \text{OH}_2$ obtained from water solutions.³⁶ The infrared spectrum of the acetic acid solvate shows a strong, broad absorption at 300 cm^{-1} associated with the chlorine-metal stretching frequency. In addition, there is also a medium-strong absorption at 1660 cm^{-1} , presumably the C=O stretching frequency; there are no other important features in the spectrum. In pure, associated acetic acid, the C=O stretching frequency occurs at 1720 cm^{-1} and is known to occur at lower frequencies in acetic acid adducts.³⁷ It is

assumed that molecular acetic acid assumes the sixth coordination position in the TiCl_5^{2-} group.

The magnetic moments could be fit to the Figgis theoretical moments for the parameters $\lambda' = 139 \text{ cm}^{-1}$, $\Delta = 200 \text{ cm}^{-1}$, and $k = 0.85$. However, the plot of $\chi'_{\text{m}} \text{ vs. } 1/T$, while linear over the range 88–222°, becomes nonlinear at higher temperatures. Extrapolation of the linear part of the curve gives a very high TIP value of 1100×10^{-6} cgs unit. As in the nicotinamide complex, the ligand field separation is not known but it must be large compared to Δ . From Δ and λ' it is calculated that the E_3 and E_2 terms resulting from the resolution of the 2E_g state by spin-orbit coupling lie at 481 and 236 cm^{-1} , respectively, above the ground state. The nonlinearity at higher temperatures reflects the electron population of these higher levels. There seems to be no need to invoke structures more complicated than a monomer.

The substituted acetate products may not be pure compounds, since the acetate substitution for chloride probably is continuous without the production of a unique phase. The extreme insolubility of the product makes it unlikely that equilibrium conditions exist, and the fact that products of reasonable stoichiometry were obtained may be the result of fortuitous sampling. Nevertheless some interesting relationships do appear in the spectral and magnetic data. The infrared spectra of all of the products are very much alike regardless of the extent of acetate substitution. They all show the strong, broad absorption centered on 290 cm^{-1} of the metal-chlorine stretching frequency. The intense band at 1530 cm^{-1} is assigned to the asymmetric stretch of the COO^- group. This may be compared to the 1578- cm^{-1} frequency in the free acetate ion. A broad absorption at 1445 cm^{-1} is assigned to the methyl deformation comparable to the 1433- and 1430- cm^{-1} absorptions in sodium acetate, while the shoulder at 1400 cm^{-1} is taken to be the symmetric stretching frequency³⁸ which occurs in sodium acetate at 1410 cm^{-1} . This decrease in frequency is indicative of bidentate rather than unidentate bonding. Further evidence for symmetrical bidentate bridging comes from Nakamoto,³⁹ who has noted that in compounds with symmetrical coordination of carboxylate groups, both symmetrical and antisymmetrical COO^- frequencies, as observed here, are shifted in the same direction as one metal is changed for another. Further support for the presence of a bridging carboxylate is found in the dimer $\text{Pd}(\text{OCOR})_2\text{CH}_3\text{CO}_2$,⁴⁰ in which the asymmetric stretch occurs at 1540 cm^{-1} compared to 1530 cm^{-1} in the substituted titanium(III) compounds. There is no way to determine whether the acetate is bidentate to one or two metal ions, but, in most of the structures in which the acetate is known to be a bridging ligand, it is between two metals, and this assumption is made here.

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Under no circumstances were we able to prepare a trisubstituted product. This leads to the conclusion that the remaining chlorides are not suitably located for bidentate coordination. These chlorides could occur as pairs along a common edge, or as unique chlorides perpendicular to a square plane bearing four ligand atoms and a titanium at the center. Bridging chlorides at a common edge create the problem that the resulting titanium-titanium distances are probably too great to be spanned by the COO^- group.

In general, the magnetic properties of the compounds formulated as $\text{TiCl}_2(\text{Ac})\cdot\text{HAc}$ and $\text{TiCl}(\text{Ac})_2$ are similar, and the magnetic properties of $\text{TiCl}_2(\text{Ac})$ differ from the other two. The monoacetate-solvate and the diacetate show essentially no field dependence; the monoacetate is strongly field dependent. χ_g decreased 20% on increasing the magnetic field strength from 4.4 to 6.2 kgauss. The monoacetate-solvate and diacetate both show a broad Néel point at 100°K ; in fact, their susceptibility *vs.* temperature curves parallel one another; the monoacetate product has a susceptibility which is essentially independent of temperature. The monoacetate-solvate and the diacetate have room-temperature magnetic moments of 1.61 and 1.70 BM, while the monoacetate has a room-temperature magnetic moment of 2.38 BM. These data can be interpreted⁴¹ in terms of antiferromagnetic interactions between pairs of titanium ions, the values of $-J$ (the exchange integral) being 60 cm^{-1} for the diacetate and 70 cm^{-1} for the monoacetate-solvate (Figure 6).

The similarity in properties of the $\text{Ti}(\text{Ac})\text{Cl}_2\cdot\text{HAc}$ and $\text{Ti}(\text{Ac})_2\text{Cl}$ may at first seem surprising, especially since the solvate is obtained from the acetic acid-acetic anhydride mixture, while the monoacetate and diacetate are obtained from acetic anhydride solutions. However, if we consider the monoacetate-solvate to contain a bridge acetate which is bidentate to two metals and a unidentate acetic acid molecule with its carbonyl oxygen bonded to one titanium and its proton near a chloride which is bonded to a second titanium,

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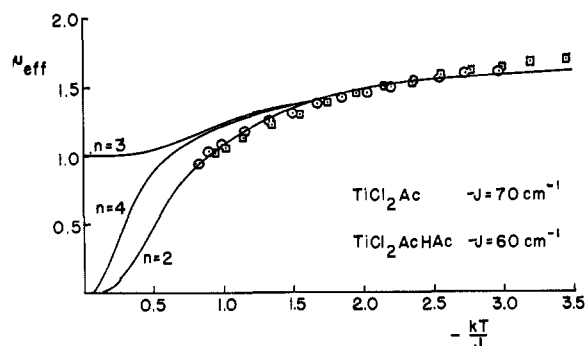


Figure 6.—Fit of experimental μ_B for $\text{TiCl}(\text{Ac})\cdot\text{HAc}$ (\square) and $\text{TiCl}(\text{Ac})_2$ (\circ) against theoretical curves for different values for n (chain length).

then the solvate can be converted to the diacetate by elimination of hydrogen chloride and the formation of a second acetate bridge. The structure can be completed to give the proper stoichiometry and electrical neutrality by the formation of cyclic dimers or trimers similar to the structures of $\text{Cu}(\text{Ac})_2\cdot 2\text{H}_2\text{O}$,⁴² $\text{Cr}(\text{Ac})_2\cdot 2\text{H}_2\text{O}$,⁴³ $\text{Cr}_3(\text{Ac})_6\text{O}^+$,⁴⁴ or $\text{Re}_2(\text{Ac})_6\text{Cl}_2$.⁴⁵ A little work with paper and pencil will show that the diacetate structure is not so easily related to an unsolvated monoacetate structure. This type of structure accounts for the unique chloride positions, but it also requires a coordination number of five for the metal. This might not be important but it does seem to invite metal-electron interactions with which the high magnetic moments reported here would seem to conflict. A more thorough structural investigation by X-rays will have to await the production of a crystalline product.

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