

1117. Some Complexes of Titanium(III) Chloride.

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Titanium(III) chloride reacts with 1,4-dioxan, 1,4-thioxan, morpholine, and ketones to form compounds of the types $\text{TiCl}_3 \cdot 3\text{L}$, $\text{TiCl}_3 \cdot 2\text{L}$, and $\text{TiCl}_3 \cdot \text{L}$, the product depending upon the experimental conditions and ligand used; reaction with ethylene glycol dimethyl ether gives a compound of empirical formula $\text{TiCl}_3 \cdot 1.5(\text{CH}_2 \cdot \text{OMe})_2$. The spectra of these compounds have been measured and interpreted.

RELATIVELY few complexes of trivalent titanium have been reported, largely because of the experimental difficulties of handling these compounds that are sensitive to both oxidation and hydrolysis. Recently, however, Clark *et al.*¹ prepared and characterised several titanium(III) complexes, including two ($\text{TiCl}_3 \cdot 2\text{C}_4\text{H}_8\text{O}_2$ and $\text{TiCl}_3 \cdot 3\text{C}_3\text{H}_6\text{O}$) which we report here. Also, complexes with tertiary amines have been prepared,² and a complex with a ditertiary phosphine is said to exist.³ Before this the main investigations of titanium(III) complexes were carried out by Hartmann and his co-workers,⁴ who reported complexes of the type $[\text{TiA}_6]\text{Cl}_3$ in which the titanium atom is in an octahedral environment of identical ligands. This field (O_h) splits the 2D term into the ground (T_{2g}) and upper (E_g) terms. One ligand-field peak is accordingly predicted as resulting from the $E_g \leftarrow T_{2g}$ transition. Experimentally the peak is found to be a doublet, and this is said to arise through a Jahn-Teller distortion that splits the ground term into 2E_g and ${}^2B_{2g}$ components and the upper term into ${}^2A_{1g}$ and ${}^2B_{1g}$ components; the two peaks are assigned to the transitions ${}^2A_{1g} \leftarrow {}^2B_{2g}$ and ${}^2B_{1g} \leftarrow {}^2B_{2g}$. The separation of these peaks gives a measure of the splitting of the upper 2E_g term (δ' cm^{-1}). The separation (δ cm^{-1}) between the orbital levels derived from T_{2g} can be estimated from measurements of the variation in magnetic susceptibility over a temperature range.

According to Clark *et al.*,¹ the distortions amount to ~ 1200 — 2400 cm^{-1} in the excited state and 400 — 800 cm^{-1} in the ground state. The complexes reported in this present paper will also be expected to have at least tetragonal distortions with consequent complications in the spectra. The asymmetric nature of the field will result in the quenching of any orbital angular momentum, so that magnetic susceptibility values at room temperature should be close to 1.73 B.M.⁵

Clark *et al.*¹ found that a complex $\text{TiCl}_3 \cdot 2\text{C}_4\text{H}_8\text{O}_2$ was formed from titanium(III) chloride and dioxan. Our work confirms a compound of this overall composition when the time of reflux is relatively short (~ 8 hours), but we have found that more prolonged reaction leads to the compounds containing less dioxan, the composition tending to $\text{TiCl}_3 \cdot \text{C}_4\text{H}_8\text{O}_2$. If dioxan is treated at room temperature with the trimethylamine adduct, $\text{TiCl}_3 \cdot 2\text{NMe}_3$,² the trimethylamine is displaced and a dioxan compound $\text{TiCl}_3 \cdot 3\text{C}_4\text{H}_8\text{O}_2$ is formed. Whereas the other dioxan compounds are insoluble in non-ionising organic solvents, including dioxan, the 1:3 adduct is very soluble in dioxan, forming a blue solution. It also dissolves in methyl cyanide to give a deep blue solution that is virtually non-conducting ($\lambda_m = 12$ $\text{ohm}^{-1} \text{cm}^{-2}$), but the visible spectrum of this (cf. Fig. 1) is identical with that of $\text{TiCl}_3 \cdot 3\text{MeCN}$,^{1,6} and it is clear that the co-ordinated dioxan is displaced by methyl cyanide.

The solution of $\text{TiCl}_3 \cdot 3\text{C}_4\text{H}_8\text{O}_2$ in dioxan shows absorptions at 15,150 and 20,800 cm^{-1} , the second peak being less well-defined. The reflectance spectrum of the solid is similar,

¹ Clark, Lewis, Machin, and Nyholm, *J.*, 1963, 379.

² Fowles and Hoodless, *J.*, 1963, 33.

³ Chatt and Hayter, *J.*, 1962, 1343.

⁴ Hartmann and Schafer, *Z. phys. Chem. (Leipzig)*, 1951, **197**, 116; Ilse and Hartmann, *ibid.*, p. 239; Hartmann, Schäfer, and Hansen, *Z. anorg. Chem.*, 1956, **284**, 153; 1957, **289**, 40.

⁵ Figgis and Lewis, "Modern Co-ordination Chemistry," Interscience Publ., Inc., New York, 1960, p. 430.

⁶ Duckworth, Fowles, and Hoodless, *J.*, 1963, 5665.

except that for a shoulder at $13,400\text{ cm}^{-1}$, but the second peak has moved to a somewhat higher wave number.

Clark *et al.*¹ found in the diffuse reflectance spectrum of the compound $\text{TiCl}_3 \cdot 2\text{C}_4\text{H}_8\text{O}_2$ a peak at $14,800\text{ cm}^{-1}$ with a shoulder at $12,800\text{ cm}^{-1}$. Our work (Fig. 2) confirms this, but we found an additional peak at $21,000\text{ cm}^{-1}$; this shows to some extent as a plateau in the curve published by Clark *et al.* These workers found the complex $\text{TiCl}_3 \cdot 2\text{C}_4\text{H}_8\text{O}_2$ to be sufficiently soluble in dioxan for spectra measurement and observed peaks at $15,750$ and $20,900\text{ cm}^{-1}$, which agree well with our observations on the spectrum of the complex $\text{TiCl}_3 \cdot 3\text{C}_4\text{H}_8\text{O}_2$ in dioxan; it seems that the absorbing species are the same. It is difficult to account for both peaks on the basis of a single absorbing species of trivalent titanium such as $\text{TiCl}_3 \cdot 3\text{C}_4\text{H}_8\text{O}_2$, since splitting of the 2E_g level rarely amounts to more than 2000 cm^{-1} , and this in any case is presumably responsible for the splitting observed for the $15,150\text{ cm}^{-1}$ peak. A similar difficulty exists in explaining the spectrum of the 1 : 3 adduct formed with tetrahydrofuran.¹ In each case the peaks have similar intensities, with ϵ_{max} values not greater than 50, so that both peaks appear to be of the $d-d$ rather than of the charge-transfer type. However, Clark *et al.* tentatively suggest that the peak of

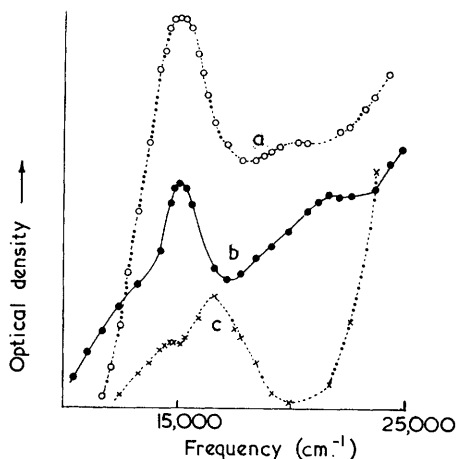


FIG. 1. Spectrum of $\text{TiCl}_3 \cdot 3\text{C}_4\text{H}_8\text{O}_2$.

(a) In dioxan. (b) Diffuse reflectance.
(c) In methyl cyanide.

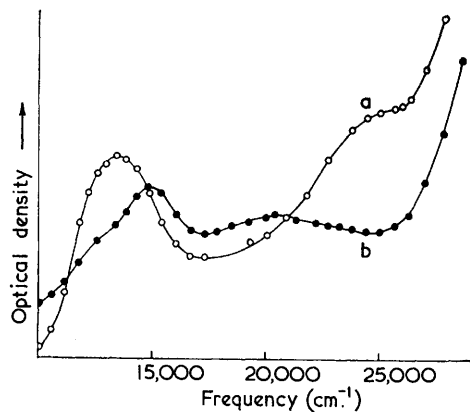


FIG. 2. Diffuse reflectance spectra of (a) $\text{TiCl}_3 \cdot \text{C}_4\text{H}_8\text{O}_2$ and (b) $\text{TiCl}_3 \cdot 2\text{C}_4\text{H}_8\text{O}_2$.

higher energy may be a charge-transfer band involving the π -electrons of the chlorine ligands. Since the 1 : 3 adducts formed by titanium(III) chloride with ligands such as pyridine² and alkyl cyanides⁶ give non-conducting solutions in an excess of the ligand, it also seems unlikely that the dioxan and tetrahydrofuran compounds will contain ionic species.

As dioxan is lost and the composition of the product approaches $\text{TiCl}_3 \cdot \text{C}_4\text{H}_8\text{O}_2$, so the two main peaks become further apart; as Fig. 2 shows, the peaks are found at $13,500$ and $25,000\text{ cm}^{-1}$.

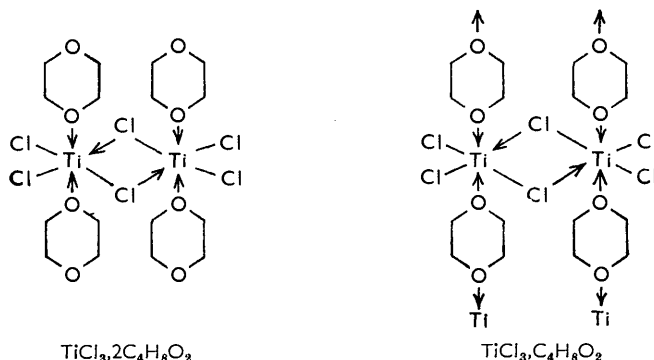
The infrared spectra provide evidence for the extent to which both oxygen atoms of the dioxan molecule may co-ordinate to titanium, since the asymmetric C-O-C stretching vibration, present in the free ligand at 1125 cm^{-1} , should disappear when both oxygen atoms co-ordinate. Rolsten and Sisler⁷ found no such band for the complex $\text{TiBr}_4 \cdot \text{C}_4\text{H}_8\text{O}_2$ and consider that dioxan here acted as a bidentate ligand. Similarly, this band is also missing for the analogous compound by titanium(IV) chloride, but a modified band occurs around

⁷ Rolsten and Sisler, *J. Amer. Chem. Soc.*, 1957, **79**, 1068, 1819.

1040 cm^{-1} ; the peak found at 883 cm^{-1} with the free ligand splits to give two peaks at 865 and 845 cm^{-1} in the complex.⁸ Thus, if we take the criterion that the disappearance of the 1125 and 883 cm^{-1} peaks and the appearance of new peaks at lower frequency indicate co-ordination of the oxygen atoms, it is apparent that in the 1 : 2 and 1 : 3 adducts there are both free and co-ordinated oxygen atoms in roughly equal amounts. However, with the 1 : 1 adduct there are strong bands associated with the co-ordinated oxygen, but those resulting from oxygen atoms that are not co-ordinated are considerably less intense.

The 1 : 1 and 1 : 2 complexes may be formulated as polymer and dimer, respectively. Thus the loss in intensity of the C-O-C antisymmetric stretching frequency occurs when additional polymerisation takes place and the dioxan molecules co-ordinate through both their oxygen atoms.

The analogous reaction of titanium(III) chloride with 1,4-thioxan was slow but gave a brown compound of composition $\text{TiCl}_3 \cdot \text{C}_4\text{H}_8\text{OS}$, which was insoluble in non-polar organic



solvents (including thioxan). At the same time a pale yellow thioxan-soluble compound was formed, but this did not contain an integral number of thioxan molecules ($\text{TiCl}_3 : \text{C}_4\text{H}_8\text{OS} = 1 : 2.4$). The spectra of the soluble and the insoluble compound were quite different: the latter showed peaks at 13,500 and 22,000 cm^{-1} , resembling those of the

TABLE 1.

Spectra of titanium(III) chloride complexes.

Compound	Peak positions (cm^{-1})
$\text{TiCl}_3 \cdot 3\text{C}_4\text{H}_8\text{O}^*$	14,700
$\text{TiCl}_3 \cdot 3\text{C}_4\text{H}_8\text{O}_2^*$	13,400sh; 15,150; 21,800
$\text{TiCl}_3 \cdot 2\text{C}_4\text{H}_8\text{O}_2^*$	12,800sh; 14,800
$\text{TiCl}_3 \cdot 2\text{C}_4\text{H}_8\text{O}_2$	12,500sh; 14,800; 20,500
$\text{TiCl}_3 \cdot \text{C}_4\text{H}_8\text{O}_2$	13,500br; 25,000sh
$\text{TiCl}_3 \cdot \text{C}_4\text{H}_8\text{OS}$	13,500; 21,800
$\text{TiCl}_3 \cdot 3\text{C}_4\text{H}_8\text{ON}$	14,000; 15,500
$\text{TiCl}_3 \cdot 1.5\text{C}_4\text{H}_{10}\text{O}_2$	12,400; 13,800; 20,000
$\text{TiCl}_3 \cdot 3\text{Me}_2\text{CO}^*$	15,400 (37)
$\text{TiCl}_3 \cdot 3\text{Me}_2\text{CO}$	15,400; 24,700br
$\text{TiCl}_3 \cdot 2\text{Et}_2\text{CO}$	15,600 (140); 24,200br (2200)
$\text{TiCl}_3 \cdot 2\text{Ph}_2\text{CO}$	15,600; 25,600
$\text{TiCl}_3 \cdot 3\text{MeCN}^*$	14,700 (13); 17,100 (22)
$\text{TiCl}_3 \cdot 3\text{MeCN}^\dagger$	14,700 sh (15); 17,200 (31); 31,000sh (500); 35,100 (1100); 43,500 (400)
$\text{TiCl}_3 \cdot 3\text{EtCN}^\dagger$	14,700; 17,200

* Ref. 1. † Ref. 6.

1 : 1 dioxan product and it is probable that the two products have similar polymeric structures.

The infrared spectrum of the thioxan compound does not show the strong band at

⁸ Fowles and Walton, unpublished observations.

⁹ Hendra and Powell, *J.*, 1960, 5105.

1105 cm^{-1} (the antisymmetric C–O–C stretch) that is found for the free ligand, so that thioxan certainly co-ordinates to titanium through the oxygen atom. It is more difficult to show that co-ordination also occurs through the sulphur, since C–S stretching frequencies are much weaker and are found in the 600–700 cm^{-1} region where a number of skeletal vibrations occur. However, there is evidence for the bonding of thioxan through sulphur in the complexes formed by titanium(IV) chloride and bromide, $\text{TiX}_4 \cdot 2\text{C}_4\text{H}_9\text{OS}$,⁸ since the infrared spectra of these adducts in the 800–1200 cm^{-1} region are identical with that of thioxan itself, thus ruling out co-ordination through oxygen. Bonding in the tervalent complex is therefore also likely to involve the sulphur atom of the thioxan ligand. Co-ordination through sulphur is also evident in the complexes formed by the dichlorides of platinum, copper, and mercury, $\text{MX}_2 \cdot 2\text{C}_4\text{H}_9\text{OS}$, since in every case the infrared spectrum shows⁹ the 1105 cm^{-1} peak almost unchanged.

The blue product formed in the reaction of titanium(III) chloride with morpholine, $\text{TiCl}_3 \cdot 3\text{C}_4\text{H}_9\text{ON}$, has a diffuse reflectance spectrum typical of the octahedral 1 : 3 complexes (cf. Table 1), there being a peak at 15,400 cm^{-1} with a shoulder at 13,300 cm^{-1} . Morpholine evidently forms bonds to titanium through nitrogen rather than through oxygen, since in the infrared spectrum of the complex the C–O–C antisymmetric stretch (at 1095 cm^{-1} for morpholine itself) is almost unchanged, whereas the N–H stretching frequency is lowered from ~ 3320 in the free ligand to 3205 cm^{-1} in the complex.

The blue compound formed in the reaction of titanium(III) chloride with ethylene glycol dimethyl ether has the overall composition $\text{TiCl}_3 \cdot 1.5(\text{CH}_2 \cdot \text{OMe})_2$. There are two obvious explanations of the composition, either the compound is polymeric with the bidentate ether linking titanium atoms, or it is ionic and contains titanium in both cationic and anionic form, e.g., $[\text{TiCl}_2 \cdot 2(\text{CH}_2 \cdot \text{OMe})_2]^+ [\text{TiCl}_4(\text{CH}_2 \cdot \text{OMe})_2]^-$. Unfortunately, the compound is insoluble in solvents with which it does not react, so that conductivity measurements cannot be made; it dissolves in methyl cyanide, but the spectrum of the solution is identical with that formed by the complex $\text{TiCl}_3 \cdot 3\text{MeCN}$. The diffuse reflectance spectrum shows a very broad peak around 13,800 cm^{-1} and a second peak at 20,400 cm^{-1} . The ionic formulation, with two different absorbing titanium species, could account for the two peaks, although two similar peaks were observed for the dioxan system where all the evidence pointed to a polymeric structure. The infrared spectrum of the compound still shows a weak peak at 1125 cm^{-1} (found as a strong band in the free ligand) corresponding to a C–O–C stretch, and a much stronger new band at 1075 cm^{-1} . This suggests that some ether molecules bridge the titanium atoms, and others act as monodentate ligands.

Titanium(III) chloride reacts with ketones to give the complexes: $\text{TiCl}_3 \cdot 3\text{R}_2\text{CO}$ (R = Me, Et, or Ph). The acetone complex was reported by Clark *et al.* and our work confirms their findings that it behaves as a non-electrolyte in acetone solution which gives a rather broad peak at 15,400 cm^{-1} typical of octahedral titanium species. In addition, we observed a very much stronger band at $\sim 25,000$ cm^{-1} that is clearly charge-transfer in origin. This may be analogous to the band¹⁰ at 27,500 cm^{-1} for the acetylacetone complex, $\text{Ti}(\text{acac})_3$, assigned to a transition of the *d*-electron of titanium to an antibonding $[\pi_4(e)]$ orbital associated with the acetylacetone groupings.

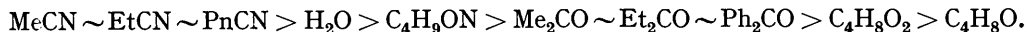
Diethyl ketone and benzophenone may be restricted to forming 1 : 2 complexes by steric considerations, but it seems likely that the titanium atoms will retain their octahedral environment in the solid state through chlorine bridging. The diethyl ketone complex dissolves in the ligand, however, to give a non-conducting solution, the spectra of which closely resembles that of the acetone complex. Thus in solution the chlorine bridging is presumably broken down and a 1 : 3 complex is formed.

For all three compounds, co-ordination results in an appreciable lowering of the carbon–oxygen stretching frequency: R = Me, 1670 and 1560 (Me_2CO , 1715); Et, 1655 (Et_2CO , 1720); Ph, 1560 cm^{-1} (Ph_2CO 1680 cm^{-1}). This characteristic lowering of the carbonyl

¹⁰ Barnum, *J. Inorg. Nuclear Chem.*, 1961, **21**, 221; **22**, 183.

stretching frequency has also been observed in the ketone complexes formed by titanium(IV) chloride.¹¹

The spectra of the known complexes of titanium(III) chloride are summarised in Table I. If Dq values are taken as 1320 and 2010 cm^{-1} for titanium(III) co-ordinated octahedrally by chloride ions and water molecules, respectively,¹ then on the basis of the position of the lowest-energy main peak the ligands may be fitted into the spectrochemical series:



EXPERIMENTAL

Analysis.—Titanium, halogen, and nitrogen were determined as described previously.¹³ Carbon, hydrogen, and sulphur were determined by a professional microanalyst.

Spectra.—Visible and ultraviolet spectra were measured by means of a Unicam S.P. 500 spectrophotometer equipped with a reflectance attachment, modified to make it suitable for measurements on compounds that reacted with air and moisture. Infrared spectra were measured for Nujol mulls, with Unicam S.P. 100 and Infracord (KBr) spectrophotometers.

Magnetic-susceptibility Measurements.—These were made by the Gouy procedure at room temperature only.

Conductivity.—This was measured in specially adapted cells with a Phillips PR 9500 bridge.

Valency-state.—This was determined by treating the product with a known excess of cerium(IV) sulphate solution and back-titration with iron(II) sulphate solution.

Materials.—Titanium(III) chloride, supplied by Union Carbide, was used without further purification (Found: Cl, 67.4; Ti, 31.3. Calc. for TiCl_3 : Cl, 69.0; Ti, 31.0%). The ligands and solvents were fractionated and dried by repeated distillation *in vacuo* from drying agents, usually calcium hydride and phosphoric oxide.

Reactions.—Reactions were carried out by standard vacuum-line procedures, great care being taken to exclude moisture.

(i) *Reaction of titanium(III) chloride with morpholine.* Blue crystals of a complex [Found: Cl, 25.5; N, 10.1; Ti, 11.3; $\text{TiCl}_3 \cdot 3\text{C}_4\text{H}_9\text{ON}$ requires Cl, 25.6; N, 10.1; Ti, 11.5%], μ , 1.60 B.M. and a green solution resulted.

(ii) *Reaction of titanium(III) chloride and dioxan.* The nature of the product depended on the reflux time, as Table 2 shows. The insoluble products were blue-green.

TABLE 2.
Insoluble products of the $\text{TiCl}_3\text{-C}_4\text{H}_8\text{O}_2$ reaction.

Reflux time (hr.)	Found (%)				Ratios found			Valency state	μ * (B.M.)
	C	H	Cl	Ti	$\text{C}_4\text{H}_8\text{O}_2 : \text{Cl} : \text{Ti}$				
4.5	29.0	4.7	31.3	14.2	2.09	2.98	1.00	—	1.74
8	—	—	31.5	14.5	2.02	2.92	1.00	3.04	—
14	—	—	39.5	18.2	1.26	2.93	1.00	—	1.54
18	—	—	40.0	19.0	1.18	2.84	1.00	3.13	1.73
60	20.1	3.8	41.6	19.6	1.07	2.87	1.00	—	1.67

* At 20°.

$\text{TiCl}_3 \cdot 2\text{C}_4\text{H}_8\text{O}_2$ requires C, 29.1; H, 4.9; Cl, 32.2; Ti, 14.5%.

$\text{TiCl}_3 \cdot \text{C}_4\text{H}_8\text{O}_2$ requires C, 19.7; H, 3.3; Cl, 43.9; Ti, 19.8%.

Reaction of trichlorobis(trimethylamino)titanium(III) with dioxan gave a solution from which a blue-green solid complex, μ 1.69 B.M., was obtained (Found: Cl, 24.4; Ti, 11.6. $\text{TiCl}_3 \cdot 3\text{C}_4\text{H}_8\text{O}_2$ requires Cl, 25.4; Ti, 11.4%). The compound was fairly soluble in dioxan and also dissolved in methyl cyanide to give a deep blue non-conducting solution (λ_m 12 $\text{ohm}^{-1} \text{cm}^2$). The visible spectrum of this solution (cf. Fig. 1c) was the same as that of titanium(III) chloride in methyl cyanide.

(iii) *Reaction of titanium(III) chloride with thioxan.* Trichloro-(1,4-thioxan)titanium(III), μ 1.65 B.M., was prepared as a brown solid by reaction under reflux for 50 hr. (Found: C, 18.0;

¹¹ Susz and Lachavanne, *Helv. Chim. Acta*, 1958, **41**, 634.

¹² Fowles and Nicholls, *J.*, 1959, 990.

H, 3.3; Cl, 41.3; S, 12.0; Ti, 19.1. $\text{TiCl}_3 \cdot \text{C}_4\text{H}_8\text{OS}$ requires C, 18.6; H, 3.1; Cl, 41.2; S, 12.4; Ti, 18.5%). Reaction was not complete when shorter reflux times were used. The compound was insoluble in non-ionising organic solvents. Some thioxan-soluble product was also formed and removal of thioxan from the filtrate left a brown solid (Found: Cl, 25.2; Ti, 12.2%).

(iv) *Reaction of titanium(III) chloride with ketones.* Reaction with acetone gave a greenish-brown solution from which a brown solid *complex*, μ 1.61 B.M., was obtained by removal of excess of acetone at the pump (Found: Cl, 32.3; Ti, 15.0. $\text{TiCl}_3 \cdot 3\text{C}_3\text{H}_6\text{O}$ requires Cl, 32.4; Ti, 14.6%). The analogous reaction with diethyl ketone gave a dark green *complex*, μ 1.61 B.M. (Found: Cl, 32.6; Ti, 14.8. $\text{TiCl}_3 \cdot 2\text{C}_5\text{H}_{10}\text{O}$ requires Cl, 32.6; Ti, 14.7%). Titanium(III) chloride reacted when refluxed for three days with a solution of benzophenone in benzene to give a steel-blue solid *complex* (Found: C, 59.5; H, 4.2; Cl, 20.1; Ti, 9.5. $\text{TiCl}_3 \cdot 2\text{C}_8\text{H}_{10}\text{O}$ requires C, 60.2; H, 3.9; Cl, 20.1; Ti, 9.2%).

(v) *Reaction of titanium(III) chloride with ethylene glycol dimethyl ether.* Reaction at room temperature gave a blue solid *complex*, μ 1.74 B.M. [Found: Cl, 36.8, 36.6; Ti, 16.8, 16.9%; valence state, 3.05. $2\text{TiCl}_3 \cdot 3(\text{CH}_2\text{OCH}_3)_2$ requires Cl, 36.8; Ti, 16.6%], and a purple solution.

We gratefully acknowledge the support of this work by the D.S.I.R. through research awards to R. A. H. and R. A. W.

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[Received, May 23rd, 1963.]
