# 59. Complexes of Titanium Trichloride.

By R. J. H. Clark, J. Lewis, D. J. Machin, and R. S. Nyholm.

Titanium trichloride reacts with acetonitrile, tetrahydrofuran (THF), and dioxan to form, respectively, the complexes $TiCl_3$,3MeCN, $TiCl_3$,3THF, and $TiCl_3$,2Dioxan. The properties of these complexes have been investigated and, in particular, their spectra and magnetic moments over a temperature range have been measured and employed to determine the distortion from octahedral of the ligand field about the titanium ion. The spectral data indicate that the distortion in the excited state is ~1200—2400 cm.$^{-1}$ in the complexes studied, while the magnetic data indicate that the distortion in the ground state is ~400—800 cm.$^{-1}$. The spectra of the complex $VCl_3$,3MeCN have been analysed on the basis of an average *Dq* for the ligands. A comparison of the *Dq* values for analogous titanium and vanadium complexes is given. The relative position of the solvent molecules in the spectrochemical series has also been elucidated from the spectral measurements.

Relatively few complexes of titanium(III) have been unambiguously established, undoubtedly because of the experimental difficulties involved in their preparation and characterisation. The best known are the hexahydrate [1] and the alum [2] in each of which the titanium(III) ion is octahedrally co-ordinated to six water molecules. These complexes have a historical connection with ligand-field theory in that Ilse and Hartmann [3] first interpreted the weak ($\varepsilon$ 5·7) band, which occurs at 20,100 cm.$^{-1}$, as being caused by an electronic transition between the levels formed by splitting the $^2D$-ground term of titanium(III) by an octahedral ligand field (Fig. 1).[4] Other complexes of titanium(III) which have been reported to contain this ion in an octahedral environment of equivalent ligands include [4] $[Ti(C_2H_5{\cdot}OH)_6]Cl_3$, $[Ti(CH_3{\cdot}OH)_6]Cl_3$ (both with $\varepsilon = 4$), $[Ti(Bu^iOH)_6]Cl_3$, and [5] $[Ti(urea)_6]I_3$ ($\varepsilon = 10$). In all cases, the ligand-field peak shows distinct double structure, indicating that the field must contain at least a tetragonal component. The latter has the effect of splitting both the ground ($^2T_{2g}$) and the upper ($^2E_g$) term, so that two transitions are expected in the 20,000 cm.$^{-1}$ region, *e.g.*, from $^2B_{2g}$ to $^2A_{1g}$ and to $^2B_{1g}$ in $D_{4h}$. The split in the $^2E_g$ state is of the order of 1500—3000 cm.$^{-1}$ in these complexes, and is believed to be the result of a Jahn–Teller distortion of the complex ion.[6]

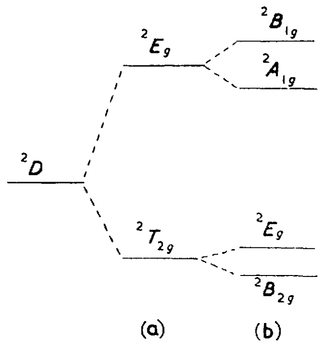

Fig. 1. Splitting of the ground term of Ti(III) ($^2D$) with (a) an octahedral field, $O_h$, and (b) a tetragonal field, $D_{4h}$. Terminology after Wilson, Decius, and Cross, "Molecular Vibrations," McGraw-Hill, New York, 1955.

It has been shown that when the effect of spin–orbit coupling in a $d^1$-configuration is considered the magnetic moment of a perfectly octahedral $d^1$-complex should approach

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[1] Hartmann and Schläfer, *Z. phys. Chem.*, 1951, **197**, 116.

[2] Lipson, *Proc. Roy. Soc.*, 1935, *A*, **151**, 347.

[3] Ilse and Hartmann, *Z. phys. Chem.*, 1951, **197**, 239.

[4] Hartmann, Schläfer, and Hansen, *Z. anorg. Chem.*, 1956, **284**, 153.

[5] Hartmann, Schläfer, and Hansen, *Z. anorg. Chem.*, 1957, **289**, 40.

[6] Jørgensen, *Acta Chem. Scand.*, 1957, **11**, 73; Liehr and Ballhausen, *Ann. Phys.*, 1958, **3**, 304.

zero as the temperature approaches zero.[7] However, the magnetic moment of a $d^1$-complex can approach the spin-only value (1·73 B.M.) at all temperatures if the asymmetric component of the ligand field increases relatively to the cubic component and if orbital delocalisation of the $t_{2g}$-electron occurs.[8] Magnetic data may now be analysed by Figgis's method [8] to estimate the extent of orbital delocalisation $(1 - k)$ and the separation ($\delta$) between the orbital levels derived from $T_{2g}$. The parameter $k$ ($\leqslant 1$) is the factor by which the orbital angular momentum part of the magnetic moment operator $\{(L + 2S)\beta\}$ is reduced by complex formation, and this reduction may be associated with $t_{2g}$-electron delocalisation on to the ligands (cf. the implications of the paramagnetic resonance spectrum of the $IrCl_6^{2-}$ ion).[9]

An investigation of the reactions between titanium trichloride and certain electron-donor solvents has been carried out to determine the stoicheiometry and stability of possible complexes and in order to estimate the distortion of pseudo-octahedral complexes from true octahedral symmetry.

We have found that titanium trichloride is soluble to the extent of 0·1M in tetrahydrofuran (THF) and in dioxan, to give in each case a deep red solution, in acetonitrile to give a blue solution (~1M), and in acetone to give a greenish-red solution (~1M). The complexes $TiCl_3,3C_4H_8O$, $TiCl_3,2C_4H_8O_2$, and $TiCl_3,3MeCN$ have been isolated from the appropriate solvents and the complex $[TiCl_3,3COMe_2]$ has been identified in acetone solution. They will now be discussed separately.

*Tetrahydrofuran System.*—Trichlorotristetrahydrofurantitanium(III) is obtained as bluish-green crystals by refluxing titanium trichloride with anhydrous tetrahydrofuran. The compound is extremely labile towards water, acetone, acetonitrile, and alcohols. This property nullifies any conductivity measurements. It is insoluble in non-polar solvents. The infrared spectrum, which compares favourably with that found by Pregaglia *et al.*,[10] indicates that co-ordination of the ligand is through the oxygen atom, because the symmetric ($A_1$ species, 909 cm.$^{-1}$) and the asymmetric ($B_1$ species, 1071 cm.$^{-1}$) C–O–C stretching vibrations of free tetrahydrofuran are split and lowered by ~60 cm.$^{-1}$ on co-ordination. A similar phenomenon is observed in the infrared spectrum of the corresponding titanium(IV) complex, $TiCl_4,2C_4H_8O$. The crystals belong to the space group $P2_1/c$ with $a = 17{\cdot}67$, $b = 12{\cdot}67$, $c = 15{\cdot}37$ Å, $\beta = 91{\cdot}5°$, $\rho = 1{\cdot}445$ g./c.c., leading to an $X$-ray molecular weight of 748·5. As the formula weight is 370·6 and the space group requires a minimum of 4 molecules per unit cell, the latter must contain either four dimers {*e.g.*, of the type $[Ti(THF)_4Cl_2]^+[Ti(THF)_2Cl_4]^-$} or two sets each of four monomers $[TiCl_3,3THF]$, the sets being oriented differently with respect to the cell edges. Complete structure analysis of the complex has not been carried out, but the diffuse reflectance spectrum of the powdered solid suggests the second possibility. It shows a broad maximum (Fig. 2) stretching from 13,500 to 14,700 cm.$^{-1}$, indicating that the upper ($^2E_g$) term of titanium(III) is split by 1200 cm.$^{-1}$. The dimeric model would be expected to give a more complicated spectrum. The magnetic moment of the complex has been measured between 283° and 80°K (see Table 1). The value at room temperature is 1·72 B.M., *i.e.*, close to the spin-only value of 1·73 B.M. These data have been fitted [8] to an orbital delocalisation factor $k = 0{\cdot}7$ and a distortion $v = 4{\cdot}5$ (Fig. 3). The parameter $v = \delta/\lambda'$, where $\lambda' = 0{\cdot}9\lambda$, $\lambda$ being the spin–orbit coupling constant pertinent to the lowest term for the free ion [155 cm.$^{-1}$ for titanium(III)] [11] and $\lambda'$ being the value to which $\lambda$ is reduced in the complex.[12] These results lead to $\delta = 630$ cm.$^{-1}$, the positive value implying that the orbital singlet derived from $^2T_{2g}$ lies lowest.

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[7] Kotani, *J. Phys. Soc. Japan*, 1949, **4**, 293.

[8] Figgis, *Trans. Faraday Soc.*, 1961, **57**, 198, 204.

[9] Griffiths, Owen, and Ward, *Proc. Roy. Soc.*, 1953, *A*, **219**, 526.

[10] Pregaglia, Mazzanti, and Moreno, *Ann. Chim.* (*Italy*), 1959, **49**, 1784.

[11] Dunn, *Trans. Faraday Soc.*, 1961, **57**, 1441.

[12] Dunn, *J.*, 1959, 623.

TABLE 1.

Magnetic susceptibility measurements.

| $TiCl_3,3C_4H_8O$ | | $TiCl_3,2C_4H_8O_2$ | | $TiCl_3,3CH_3CN$ | |
|---|---|---|---|---|---|
| Temp. (K) | $10^6\chi$(Ti) | Temp. (K) | $10^6\chi$(Ti) | Temp. (K) | $10^6\chi$(Ti) |
| 282·8° | 1304 | 301·2° | 1225 | 302·3° | 1155 |
| 257·4 | 1405 | 279·3 | 1308 | 282·0 | 1228 |
| 232·6 | 1520 | 255·8 | 1395 | 257·7 | 1328 |
| 217·4 | 1631 | 231·2 | 1499 | 233·3 | 1436 |
| 196·4 | 1747 | 207·0 | 1622 | 208·5 | 1568 |
| 178·3 | 1901 | 183·4 | 1787 | 186·2 | 1770 |
| 160·6 | 2084 | 163·2 | 1947 | 163·3 | 1978 |
| 144·1 | 2308 | 140·5 | 2203 | 119·5 | 2619 |
| 127·7 | 2568 | 118·5 | 2534 | 103·0 | 2949 |
| 126·0 | 2589 | 102·7 | 2864 | 92·3 | 3270 |
| 115·9 | 2827 | 92·8 | 3113 | 79·5 | 3793 |
| 104·1 | 3096 | 79·0 | 3567 | | |
| 80·6 | 3911 | | | | |

The absorption spectrum of a solution of titanium trichloride in tetrahydrofuran has been recorded (Fig. 2). It is clearly different from the reflectance spectrum of the crystalline compound $TiCl_3$,3THF, and so the nature of the absorbing species is also different. The separation between the two bands ($\nu_a = 20{,}400$ cm.$^{-1}$, $\varepsilon_a = 36$; $\nu_b = 15{,}500$ cm.$^{-1}$, $\varepsilon_b = 20$) is greater than would be expected for a single Ti(III) species, if both bands are due to ligand-field effects. While the reduced magnetic moment in solution ($\mu_{\text{eff}} = 1·4 \pm 0·15$ B.M. at 0·112M) and the isopiestically determined molecular weight (550 as compared with 371 for the monomeric $TiCl_3$,3THF) suggest the presence of dimers in solution, neither $\varepsilon_a/\varepsilon_b$ nor the shape of the spectrum changes between 20° and 52°C; furthermore, $\varepsilon_a/\varepsilon_b$ does not depend on the concentration of Ti(III), as would be expected for a monomer–dimer equilibrium. Application of the rule of average environment indicates that the most strongly perturbing of the possible species present in solution, $[Ti(THF)_6]^{3+}$, would absorb at ~15,700 cm.$^{-1}$, *i.e.*, in a position corresponding approximately with that of $\nu_b$. The low dielectric constant of tetrahydrofuran itself, and the ligand exchange in more polar solvents, precluded the positive conductometric identification of the species $[Ti(THF)_6]^{3+}$ in solution and hence this assignment of $\nu_b$ is tentative. It is suggested

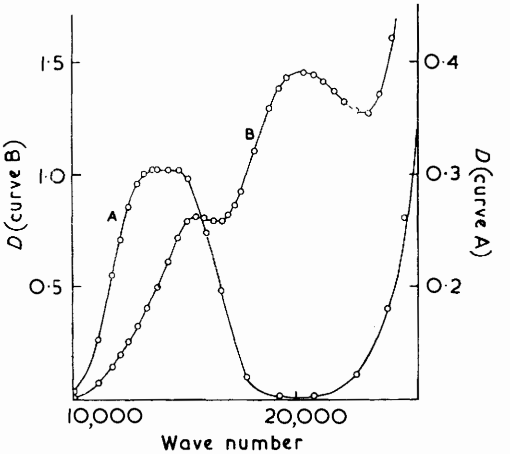

FIG. 2. Spectra of the titanium trichloride–tetrahydrofuran system. (A) Diffuse reflectance spectrum of $TiCl_3,3C_4H_8O$. (B) Absorption spectrum of $TiCl_3$ in tetrahydrofuran.

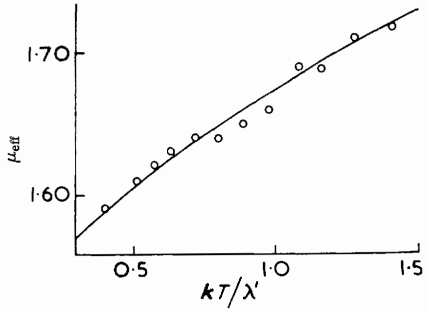

FIG. 3. Plot of $\mu_{\text{eff}}$ against $kT/\lambda'$ for $TiCl_3,3C_4H_8O$. Circles are experimental points; the line is calculated from ref. 8 with $v = 4·5$ and $k = 0·7$.

that $\nu_a$ is a charge-transfer band, similar to that found at 18,500 cm.$^{-1}$ in the reflectance spectrum of titanium trichloride itself.[13] Experiment shows that $\nu_a$ is not due to traces of $[Ti(H_2O)_6]^{3+}$ which is known to absorb at this frequency (albeit with a much lower extinction coefficient).[4] It also seems improbable that $\nu_a$ is the $3d$–$4s^1$ transition because in the free ion the latter configuration lies 80,378 cm.$^{-1}$ above the $\cdots 3d^1$ configuration.[14] While this value may be reduced on complex formation, it is unlikely to be reduced as far as 20,400 cm.$^{-1}$.

*Dioxan System.*—Trichlorobisdioxantitanium(III) is prepared by refluxing an excess of anhydrous dioxan with titanium trichloride and it is deposited as small green crystals. The general properties of the complex are very similar to those of the tetrahydrofuran complex. In its infrared spectrum, the complicated splitting of the bands which occur at ~1120 and ~880 cm.$^{-1}$ for free dioxan is taken to imply bonding to the ethereal oxygen atoms. It is not clear from this spectrum whether the complex is five-co-ordinate or whether it attains six-co-ordination because the dioxan behaves as a bidentate group. Five-co-ordination has been considered possible[15] for the Ti(III) ion in the compound $TiCl_3,2N(CH_3)_3$, while it has been suggested that dioxan functions as bidentate ligand in the compound $TiBr_4$,dioxan.[16] (The compound $TiCl_4$,dioxan has also been prepared but it is not possible to decide from its infrared spectrum whether the dioxan is functioning as a monodentate or as a bidentate ligand.) However, the diffuse reflectance spectrum of the complex $TiCl_3,2C_4H_8O_2$ (Fig. 4) is typical of octahedral $d^1$ complexes. The main transition is at 14,800 cm.$^{-1}$ with a shoulder at 12,800 cm.$^{-1}$, *i.e.*, the separation between the levels arising from $^2E_g$ is 2000 cm.$^{-1}$. The magnetic moment at 300°K is 1·72 B.M., falling to 1·51 B.M. at 79°K (Table 1). These values fit $k = 0{\cdot}7$, $v = 3{\cdot}0$, $\lambda' = 0{\cdot}95\lambda$, and hence $\delta = 440$ cm.$^{-1}$ (Fig. 5).

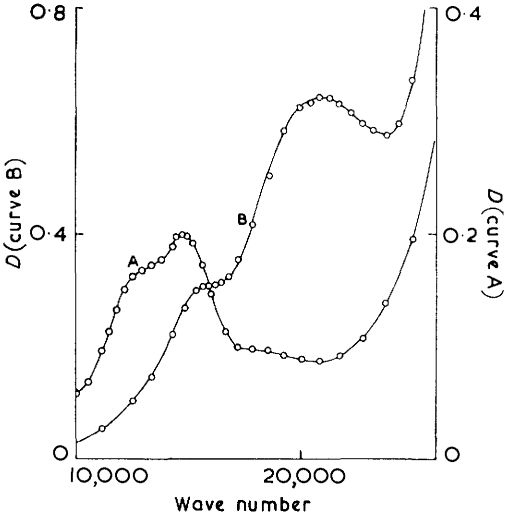

FIG. 4. Spectra of the titanium trichloride–dioxan system. (A) Diffuse reflectance spectrum of $TiCl_3,2C_4H_8O_2$. (B) Absorption spectrum of $TiCl_3$ in dioxan.

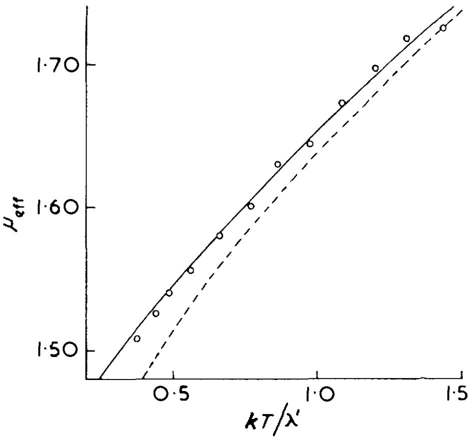

FIG. 5. Plot of $\mu_{eff}$ against $kT/\lambda'$ for $TiCl_3,2C_4H_8O_2$. Circles are experimental points; the lines are calculated from ref. 8, with $k = 0{\cdot}7$; full line, $v = 3{\cdot}0$; broken line, $v = 2{\cdot}5$.

The absorption spectrum of titanium trichloride in dioxan (Fig. 4) is quite different from the diffuse reflectance spectrum of the compound $TiCl_3$,2dioxan, indicating that a

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[13] Clark and Dunn, unpublished work.

[14] " Atomic Energy Levels," ed. Charlotte E. Moore, U.S. Bur. Stand., Circ. no. 467.

[15] Antler and Laubengayer, *J. Amer. Chem. Soc.*, 1955, **77**, 5250.

[16] Rolsten and Sisler, *J. Amer. Chem. Soc.*, 1957, **79**, 1068, 1819.

different absorbing species exists in solution. The spectrum, which consists of two peaks ($\nu_a = 20{,}900$ cm.$^{-1}$, $\varepsilon_a = 50$; $\nu_b = 15{,}750$ cm.$^{-1}$, $\varepsilon_b = 24$) is very similar to the absorption spectrum of titanium trichloride in tetrahydrofuran. It seems probable that the absorbing species in the two solutions are analogous.

*Acetonitrile System.*—Trichlorotriacetonitriletitanium(III) is prepared by refluxing anhydrous acetonitrile with titanium trichloride, the solution depositing blue crystals of the complex on cooling. These appear to be less stable than those of the ethers. The CN stretching vibration ($A_1$ species) in the complex is 35 cm.$^{-1}$ above that in free acetonitrile (2253·5 cm.$^{-1}$),[17] this shift being characteristic of co-ordination of the ligand through the nitrogen atom;[18] *e.g.*, it is as much as 111 cm.$^{-1}$ in $BF_3,CH_3{\cdot}CN$ [19] for which an *X*-ray analysis has shown that co-ordination is to nitrogen.[20] We find the corresponding shift in the complex [19] $TiCl_4,2CH_3{\cdot}CN$ to be 30 cm.$^{-1}$. The band of medium intensity at 2288 cm.$^{-1}$ in free acetonitrile, which is considered [17] to arise from a combination of $\nu_3$, the symmetric $CH_3$ deformation vibration ($A_1$), at 1372 cm.$^{-1}$, and $\nu_4$, the symmetric C–C stretching vibration ($A_1$), at 917 cm.$^{-1}$, is also raised on complex formation. It occurs at 2313 cm.$^{-1}$ in the titanium(III) complex, with $\nu_3 = 1372$ cm.$^{-1}$ and $\nu_4 = 942$ cm.$^{-1}$ and at 2302 cm.$^{-1}$ in the titanium(IV) complex, with $\nu_3 = 1359$ cm.$^{-1}$ and $\nu_4 = 944$ cm.$^{-1}$. The complex is virtually a non-electrolyte in acetonitrile, as $\Lambda = 4{\cdot}3$ cm.$^2$ mho mole$^{-1}$ at $3{\cdot}14 \times 10^{-2}$M and 22°C. 1 : 1 Electrolytes have equivalent conductances $\Lambda \sim 150$ cm.$^2$ mho mole$^{-1}$ in this solvent.[18] The diffuse reflectance spectrum of the powdered solid is identical with the absorption spectrum of a solution of titanium trichloride in acetonitrile (Fig. 6), and thus the common absorbing species is clearly $[TiCl_3,3CH_3{\cdot}CN]^0$. The ligand field peak is at 17,100 cm.$^{-1}$ ($\varepsilon$ 22) with a shoulder at 14,700 cm.$^{-1}$ ($\varepsilon$ 13), implying that the separation between the components of $^2E_g$ is 2400 cm.$^{-1}$. The extinction coefficients are independent of titanium(III) concentration. There is some doubt as to the exact magnetic moment of this complex at room temperature, values between 1·58 and 1·68 B.M. having

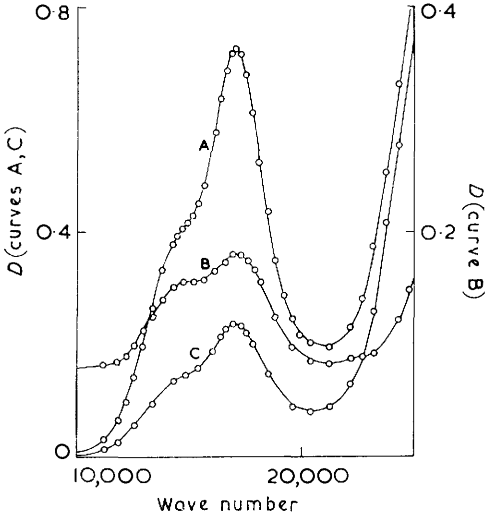

FIG. 6. Spectra of the titanium trichloride–acetonitrile system. (A, C) Absorption spectra of $TiCl_3$ in $CH_3{\cdot}CN$; (A) $3{\cdot}13 \times 10^{-2}$M, and (C) $1{\cdot}13 \times 10^{-2}$M. (B) Diffuse reflectance spectrum of $TiCl_3,3CH_3{\cdot}CN$.

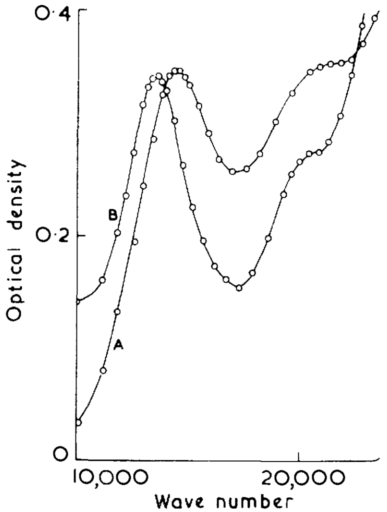

FIG. 7. Diffuse reflectance spectra of (A) $VCl_3,3CH_3{\cdot}CN$ and (B) $Ph_4As[VCl_4,2CH_3{\cdot}CN]$.

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[17] Venkateswarlu, *J. Chem. Phys.*, 1951, **19**, 293.

[18] Nyholm and Scaife, unpublished work.

[19] Coerver and Curran, *J. Amer. Chem. Soc.*, 1958, **80**, 3522.

[20] Buzzell, Hoard, Owen, and Salmon, *Acta Cryst.*, 1950, **3**, 130.

been obtained with different samples. The magnetic moments over a temperature range have been adjusted so that the value at 302°K is 1·68 B.M., this having been considered the most reliable value for this temperature. The data fit $k = 0{\cdot}6$, $v = 4$, and $\delta \approx 600$ cm.$^{-1}$.

By way of comparison we have further investigated the properties of the complex formed between vanadium trichloride and acetonitrile.[18] The analytical values obtained by Scaife implied that there were 4·4 molecules of acetonitrile associated with each molecule of vanadium trichloride, but the infrared spectrum suggested that both free and co-ordinated acetonitrile were present. We find that the complex is isomorphous with the complex $[TiCl_3,3CH_3{\cdot}CN]^0$ and hence that it should be formulated as $[VCl_3,3CH_3{\cdot}CN]^0$. Further, the diffuse reflectance spectrum of the powdered solid (Fig. 7) is practically identical with the absorption spectrum of a solution of vanadium trichloride in acetonitrile,[18] and hence the absorbing species in solution is also considered to be $[VCl_3,3CH_3{\cdot}CN]^0$. The two transitions in the visible region of the spectrum, normally assigned as $\nu_a$, ${}^3T_{2g} \longleftarrow {}^3T_{1g}(F)$ and $\nu_b$, ${}^3T_{1g}(P) \longleftarrow {}^3T_{1g}(F)$, occur at 14,400 and 21,400 cm.$^{-1}$ (Fig. 8). The diffuse reflectance spectrum of the complex $Ph_4As[VCl_4,2CH_3{\cdot}CN]$ has also been recorded, and is found to agree with the absorption spectrum of the complex. This confirms the view that $[VCl_4,2CH_3{\cdot}CN]^-$ is the absorbing species in an acetonitrile solution of the complex; $\nu_a = 13{,}500$ and $\nu_b = 20{,}400$ cm.$^{-1}$.

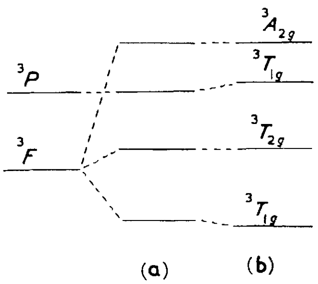

FIG. 8. Splitting of the ground terms of V(III) ($d^2$) with (a) an octahedral field, $O_h$, and (b) configurational interaction.

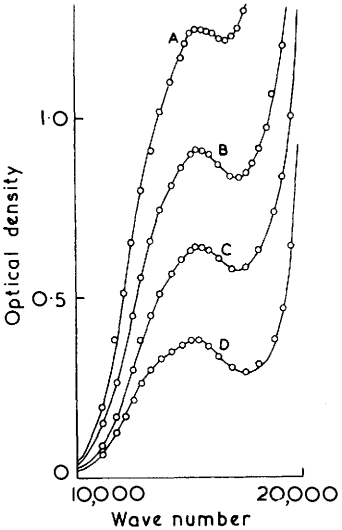

FIG. 9. Absorption spectra of $TiCl_3,3(CH_3)_2CO$. (A) $3{\cdot}15 \times 10^{-2}$M, $\varepsilon = 32$. (B) $1{\cdot}85 \times 10^{-2}$M, $\varepsilon = 39$. (C) $1{\cdot}37 \times 10^{-2}$M, $\varepsilon = 37$. (D) $0{\cdot}83 \times 10^{-2}$M, $\varepsilon = 37$.

*Acetone System.*—Titanium trichloride dissolves in acetone to a red solution from which we were not able to precipitate a complex, but which on complete removal of solvent yields a red solid whose analysis corresponds to the formula $TiCl_3,3(CH_3)_2CO$. The glutinous nature of the complex prevented measurement of many of its physical properties, but it is virtually a non-electrolyte in acetone ($\Lambda = 2{\cdot}1$ cm.$^2$ mho mole$^{-1}$ at $8{\cdot}33 \times 10^{-3}$M and 22°C). The absorption spectrum (Fig. 9) is typical of octahedral titanium(III) spectra, containing a single asymmetric peak, the band maximum being at 15,400 cm.$^{-1}$ ($\varepsilon = 37$) and the shoulder at 13,300 cm.$^{-1}$ ($\varepsilon = 28$), *i.e.*, the ${}^2E_g$ term is split by 2100 cm.$^{-1}$. The extinction coefficients are independent of titanium(III) concentration between 3·15 and $0{\cdot}83 \times 10^{-3}$M. The magnetic moment of a 1·06M-solution of the complex in acetone is 1·5 ± 0·15 B.M. On the above evidence, the complex has been formulated as $[TiCl_3,3(CH_3)_2CO]^0$.

It is noted here also that titanium trichloride will dissolve in acetic acid to a deep blue solution having $\nu \approx$ 14,000 cm.$^{-1}$ ($\varepsilon \sim 60$). The shape of the ligand-field band changes with change of titanium(III) concentration, and no definable complex could be precipitated from the solution.

*General Discussion.*—It appears from the ease with which titanium trichloride dissolves in the above solvents that it is likely to do so in most electron-donor solvents. With strongly co-ordinating ligands, *e.g.*, water or urea, ions of the type $Ti(ligand)_6^{3+}$ are formed, but with less strongly co-ordinating ligands, complexes of the type $TiCl_3,(ligand)_3$ or $TiCl_3,(ligand)_2$ are formed. The latter ligands do not appear to stabilise the tervalent state of titanium, whereas the hexaurea complex is known to be very stable.[5] In solution the titanium(III) ion appears always to be six-co-ordinated, although formally it is possible for the ion to be five-co-ordinate in the crystalline compound $TiCl_3$,2dioxan.

The results have been summarised in Table 2 together with those for hexaureatitanium(III) perchlorate [21] and for titanium(III) alum.[22] Using these data and the values $Dq$ = 1370 and 2010 cm.$^{-1}$ for titanium(III) octahedrally co-ordinated with chloride ions [13] and with water molecules,[4] we have fitted the ligands into the spectrochemical series $CH_3{\cdot}CN > H_2O > (CH_3)_2CO > C_4H_8O_2 > C_4H_8O > Cl^-$. We have assumed that Jørgensen's rule of average environment is valid.[23] It is apparent from Table 2 that if three of the ligands (L) co-ordinated to the titanium(III) ion in $[TiCl_3,L_3]$ (*e.g.*, L = $CH_3{\cdot}CN$) are replaced by three ligands which are closer to the chloride ion in the spectrochemical series (*e.g.*, L = tetrahydrofuran), then the energy separation ($\delta'$) between the levels derived from $^2E_g$ is reduced. This result is consistent with the knowledge that, by such a replacement, the field about the titanium ion is approaching octahedral. It is known that the $Dq$ value for urea [5] is 1754 cm.$^{-1}$ in the complex $[Ti(OCN_2H_4)_6]I_3$, and hence urea may be inserted between water and acetone in the above series; the $Dq$ value for methanol [4] is 1680 cm.$^{-1}$ in the complex $[Ti(CH_3{\cdot}OH)_6]Cl_3$, so that this ligand may be inserted between acetone and dioxan. The distortions ($\delta$) in the ground term ($^2T_{2g}$) of titanium(III) for the acetonitrile, dioxan, and tetrahydrofuran complexes are ~600, 440, and 630 cm.$^{-1}$, respectively, the positive value of $\delta$ implying in each case that the orbital singlet lies lowest. It is not possible theoretically to correlate the distortions in the ground and the excited states, but it is interesting that they are found to be of the same order of magnitude. The orbital delocalisation of the $t_{2g}$ electron is of the order of 0·3 (*i.e.*, $k$ = 0·7) for these complexes. It is difficult to estimate the accuracy to which $k$ has been determined, for the latter is particularly sensitive to the absolute value of the magnetic moment at a particular

TABLE 2.

Summary of results on titanium(III) complexes.

| | $TiCl_3$,3THF | $TiCl_3$,2dioxan | $TiCl_3,3(CH_3)_2CO$ |
|---|---|---|---|
| 10$Dq$ (cm.$^{-1}$) | 14,700 | 14,800 | 15,400 |
| $\delta'$ (cm.$^{-1}$) | 1200 | 2000 | 2100 |
| $\delta$ (cm.$^{-1}$) | 630 | 440 | — |
| $k$ | 0·7 | 0·7 | — |
| $\mu_{eff}$ (25°) (B.M.) | 1·72 | 1·72 | ~1·5 |
| | $TiCl_3,3CH_3{\cdot}CN$ | $Ti(urea)_6(ClO_4)_3$ | Ti(III) alum |
| 10$Dq$ (cm.$^{-1}$) | 17,100 | 17,540 | 20,100 |
| $\delta'$ (cm.$^{-1}$) | 2400 | 1540 | ~2350 |
| $\delta$ (cm.$^{-1}$) | ~600 | 420 | ~800 |
| $k$ | ~0·6 | 0·7 | ~0·9 |
| $\mu_{eff}$ (25°) (B.M.) | ~1·68 | 1·72 | 1·73 |

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[21] Lewis, Machin, Newnham, and Nyholm, *J.*, 1962, 2036.

[22] Bose, Chakravarty, and Chatterjee, *Proc. Roy. Soc.*, 1960, *A*, **255**, 145.

[23] Jørgensen, 10$^e$ Conseil de l'Institut International de Chimie Solvay, 1956, p. 355.

temperature. We estimate $k$ to be accurate to $\pm 0{\cdot}05$. Similar values of these parameters, $k$ and $\delta$, have been found previously for other complexes, *e.g.*, $k \sim 0{\cdot}9$ for $Cr(H_2O)_6^{3+}$; $k \sim 0{\cdot}8$, $\delta \sim 1200$ cm.$^{-1}$ for $V(H_2O)_6^{3+}$ in vanadium alum;[24] $\delta \sim 1000$ cm.$^{-1}$ for $Ti(H_2O)_6^{3+}$ in an $AlCl_3,6H_2O$ lattice;[25] $k = 0{\cdot}87$ for $K_3Fe(CN)_6$.[26] The magnetic moments over a temperature range also imply that there is a small reduction in the spin–orbit coupling constant of the metal ion on complex formation. This phenomenon has been discussed previously.[12]

The spectrum of $VCl_3,3CH_3{\cdot}CN$ has been analysed by a first-order perturbation treatment [27] to yield an average $Dq$ value of 1550 cm.$^{-1}$ and a $^3P$–$^3F$ term separation of 8100 cm.$^{-1}$ (the free ion value is 12,925 cm.$^{-1}$) [14] (Table 3). A similar analysis for the $[VCl_4,2CH_3{\cdot}CN]^-$ ion yields $Dq = 1460$ cm.$^{-1}$ and $^3P$–$^3F = 8000$ cm.$^{-1}$. In Table 3, the $Dq$ values of analogous titanium and vanadium complexes are listed. The uniformly higher values of $Dq$ for titanium(III) complexes are caused primarily through assuming that $10Dq$ corresponds to the energy difference between the ground state and the upper of the two levels derived from $^2E_g$ and not the centre of gravity of these levels.

TABLE 3.

Comparative spectral data for titanium(III) and vanadium(III).

| Species | $Dq$ (Ti) | $Dq$ (V) | $^3P$–$^3F$ (V) | Refs. |
|---|---|---|---|---|
| $M(H_2O)_6^{3+}$ | 2010 | 1850 | 9000 | 1, 2, 3 |
| $MCl_3,3CH_3{\cdot}CN$ | 1710 | 1550 | 8100 | |
| $M(CH_3{\cdot}OH)_6^{3+}$ | 1680 | 1600 | 8800 | 1, 4 |
| $[MCl_4,2CH_3{\cdot}CN]^-$ | — | 1460 | 8000 | |

$Dq$ and the $^3P$—$^3F$ term separation are in cm.$^{-1}$.

References: (1) Hartmann, Schläfer, and Hansen, *Z. anorg. Chem.*, 1956, **284**, 153. (2) Furman and Garner, *J. Amer. Chem. Soc.*, 1950, **72**, 1785. (3) Hartmann and Furlani, *Z. phys. Chem.* (*Frankfurt*), 1956, **9**, 162. (4) Hartmann and Schläfer, *Z. Naturforsch.*, 1951, **6a**, 754.

The reduction in the $^3P$–$^3F$ term separation from that found for the free ion has been observed previously,[12,28] and is ascribed to a decreased effective charge on the central metal ion owing to increased screening brought about by the donated $\sigma$-electrons.

## EXPERIMENTAL

*Spectra.*—The absorption spectra were recorded on a Unicam S.P. 500 spectrophotometer. Solutions were made up from the anhydrous halide under oxygen-free nitrogen in a container connected directly to a 1 cm. silica cell, which, after having been filled, could be sealed from the atmosphere. The diffuse reflectance spectra were recorded by using the standard attachment to the Unicam S.P. 500 spectrophotometer. Infrared spectra were recorded on a Grubb-Parsons double-beam grating spectrophotometer type GS2A for both hexachlorobutadiene and Nujol mulls between sodium chloride plates.

*Conductivities.*—Conductivities were measured by breaking a tared ampoule of the complex under nitrogen into a glass apparatus which contained the anhydrous solvent. The electrodes were incorporated in the apparatus.

*Magnetic Susceptibilities.*—The magnetic susceptibilities of complexes at room temperature were determined by the Gouy method. The complexes were sealed from the air. The measurements of the relative values of the susceptibility at different temperatures were made on equipment described previously.[29] The susceptibilities of solutions of titanium trichloride were

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[24] Figgis, Lewis, and Mabbs, *J.*, 1960, 2480; Pryce and Runciman, *Discuss. Faraday Soc.*, 1958, **26**, 34.
[25] Wong, *J. Chem. Phys.*, 1960, **32**, 598.
[26] Bleaney and O'Brien, *Proc. Phys. Soc.*, 1956, **69**, *B*, 1216.
[27] Ballhausen, *Z. phys. Chem.* (*Frankfurt*), 1957, **11**, 205.
[28] Owen, *Proc. Roy. Soc.*, 1955, *A*, **227**, 183.
[29] Figgis and Nyholm, *J.*, 1959, 331.

determined by the Gouy method at room temperature and at a magnetic field of 10,000 gauss. The sample volume was 7 ml.

*Other Techniques.*—*X*-Ray powder photographs of the acetonitrile complexes were taken with a Phillips Debye–Scherrer camera of 114·8 mm. diameter and copper-$K_\alpha$ radiation with a nickel filter. The complexes were sealed in Lindemann glass capillaries. The molecular weight of titanium trichloride in tetrahydrofuran was determined by Clark's modification [30] of the Signer isothermal distillation method. The density of the compound $TiCl_3$,3THF was determined by the method of flotation.

*Preparation of Compounds.*—British Oxygen Company's "white spot" nitrogen was deoxygenated by passage through an activated copper column [31] at 280° and dehydrated by passage through a magnesium perchlorate column. Solvents were either fractionally distilled and/or redistilled under nitrogen from lithium aluminium hydride or calcium hydride immediately before use and directly into the reaction flask. The titanium trichloride was refluxed with the solvent under nitrogen until reaction was complete ($\frac{1}{2}$—6 hr.). The crystals were filtered under nitrogen and dried in a vacuum. Once prepared, the complexes were sealed in glass manifolds under a vacuum.

*Analyses.*—Titanium was determined by titration under nitrogen against standard ferric ammonium alum.[32] Chloride was determined potentiometrically. Carbon, hydrogen, and nitrogen analyses were carried out by the microanalytical service of this department. These methods gave the following results:

*Trichlorotristetrahydrofurantitanium*(III). Found: C, 36·9; H, 6·3; Cl, 28·6; Ti, 12·8. $C_{12}H_{24}Cl_3O_3Ti$ requires C, 38·9; H, 6·5; Cl, 28·7; Ti, 12·9%.

*Trichlorobisdioxantitanium*(III). Found: C, 27·7; H, 4·9; Cl, 33·0; Ti, 15·1. $C_8H_{16}Cl_3O_4Ti$ requires C, 29·1; H, 4·9; Cl, 32·2; Ti, 14·5%.

*Trichlorotriacetonitriletitanium*(III). Found: C, 26·6, 25·4; H, 3·5; N, 15·7; Ti, 17·4. $C_6H_9Cl_3N_3Ti$ requires C, 26·0; H, 3·3; N, 15·2; Ti, 17·3%.

*Trichlorotriacetonetitanium*(III). Found: C, 30·3; H, 5·3; Cl, 29·2; Ti, 13·4. $C_9H_{18}Cl_3O_3Ti$ requires C, 32·9; H, 5·5; Cl, 32·4; Ti, 14·6%. This compound contains a small amount of very finely powdered titanium dioxide which causes a small lowering of all the analytical figures (including that of Ti, for the volumetric method used for determining this element is not sensitive to it in the form of titanium dioxide).

Tetrachlorobistetrahydrofurantitanium(IV). Found: C, 28·8; H, 4·8; Cl, 42·3; Ti, 14·5. Calc. for $C_8H_{16}Cl_4O_2Ti$: C, 29·1; H, 4·8; Cl, 42·5; Ti, 14·4%.

Tetrachlorodiacetonitriletitanium(IV). Found: C, 17·6; H, 2·6; N, 10·0; Cl, 51·8; Ti, 17·6. Calc. for $C_4H_6Cl_4N_2Ti$: C, 17·7; H, 2·2; N, 10·3; Cl, 52·2; Ti, 17·6%.

We are indebted to British Titan Products Co. Ltd. for a scholarship to one of us (R. J. H. C.), to Dr. P. J. Pauling for the *X*-ray analysis of $TiCl_3,3C_4H_8O$, and to Drs. T. M. Dunn and B. N. Figgis for helpful discussions.

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[*Received, May* 21*st*, 1962.]

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[30] Clark, *Ind. Eng. Chem.*, *Analyt.*, 1941, **13**, 820.
[31] Meyer and Ronge, *Angew. Chem.*, 1939, **52**, 637.
[32] Nakazono, *Sci. Reports Res. Inst.*, *Tôkohu Univ.*, 1925, **14**, 109.