value of $K_4 > 10^{14}$ *M* for $Ni(CN)_4^{2-}$. The difference is, of course, in the associative path of the square-planar substitution reactions. In the present case, once intermediates such as III form, they must react readily to add cyanide and break the nickel–nitrogen bonds to trien.

Lack of more detailed knowledge of the kinetic behavior of labile octahedral to square-planar reactions forces a somewhat speculative discussion. This is an interesting area for additional investigation. The fact remains that from pH 5 to 7.5 cyanide reacts 2.5 times faster with nickel–trien than it does with aquonickel to form tetracyanonickelate(II).

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The Preparation and Optical and Electron Spin Resonance Spectra of Some Chloro(methanol) Complexes of Titanium(III)

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Several new chloro complexes of titanium(III) have been isolated: $H[TiCl_4(C_4H_{10}O)]$, $TiCl_3(CH_3OH)_3$, $(C_5H_6N)TiCl_4$, $(C_5H_6N)[TiCl_4(CH_3OH)_2]$, and $(C_5H_6N)_2[TiCl_5(CH_3OH)]$. These new compounds have been characterized and magnetic susceptibilities and optical spectra are reported. Esr spectra have been determined for these and previously reported[1] compounds of similar types. Three of the complexes, $[TiCl(CH_3OH)_5]Cl_2$, $TiCl_3(CH_3OH)_3$, and $(C_5H_6N)_2[TiCl_5(CH_3OH)_2]$, exhibited axial symmetry. No esr signals could be observed for the hexachlorotitanate(III), for the octachlorotitanate(III), or for $(C_5H_6N)_2[TiCl_5(CH_3OH)]$. Three distinct *g*'s were observed for the other compounds. The nature of species present in methanol solutions of titanium(III) is discussed as are the electronic spectra of such species.

In a continuation of previous work[1] on solutions of titanium(III) in methanol solutions, we have prepared some new compounds, characterized them, and applied esr measurements to all of the series of compounds which gave esr signals.

Experimental Section

Materials and Experimental Techniques.—Solvents were purified as described in a previous study.[1] All other chemicals were reagent grade and were used without further purification. All operations were carried out as before under nitrogen, mainly by use of Schlenk-tube techniques. Nitrogen was purified by passing it through columns filled with BTS catalyst (BASF), calcium chloride, and magnesium perchlorate.

$H[TiCl_4(C_4H_{10}O)]$.—A 7.7-g sample of $TiCl_3$ was added to 50 ml of anhydrous ether saturated with HCl. The mixture was stirred vigorously for 1 day and was then resaturated with HCl. The resulting yellow-brown compound, which was slightly soluble in ether, was filtered and washed with dry ether (12.6 g). *Anal.* Calcd for $TiCl_4C_4H_{11}O$: Ti, 18.1; Cl, 53.8. Found: Ti (vol), 17.75; Ti (grav), 18.3; Cl, 52.8.

$TiCl_3(CH_3OH)$.—A 6.6-g sample of $TiCl_4HC_4H_{10}$ was added to a mixture of 50 ml of dry benzene and 3.0 ml of methanol. After being stirred for 1 day, the solution was filtered and its volume was reduced under reduced pressure. Pale blue crystals separated (4.8 g). They were filtered and washed with benzene and petroleum ether (bp 37.5–46.8) and were dried under vacuum. If the reaction is carried out with $TiCl_3$ and methanol in benzene, 1 week of vigorous stirring is required before the product is obtained. *Anal.* Calcd for $TiCl_3C_3H_{12}O_3$: Ti, 19.14; Cl, 42.49. Found: Ti (vol), 18.93; Ti (grav), 19.12; Cl, 42.36.

$TiCl_4(C_5H_6N)$.—A 7.7-g sample of $TiCl_3$ was added to a mixture of 4.0 ml of pyridine in 50 ml of anhydrous ether which was saturated with HCl. After 1 day of vigorous stirring the resulting pea green powder (13.5 g) was filtered and dried. *Anal.* Calcd for $TiCl_4C_5H_6N$: Ti, 17.75; Cl, 52.56; $C_5H_6N^+$, 29.69. Found: Ti (vol), 16.87; Ti (grav), 17.12; Cl, 51.98; $C_5H_6N^+$, 30.07.

$(C_5H_6N)[TiCl_4(CH_3OH)_2]$.—A 6.8-g sample of $(C_5H_6N)TiCl_4$ was added to a mixture of 2.0 ml of anhydrous methanol in 50 ml of anhydrous ether. After being stirred for 1 day, the turquoise product (8.4 g) was filtered, washed with ether, and dried *in vacuo*. *Anal.* Calcd for $TiCl_4C_7H_{14}O_2N$: Ti, 14.44; Cl, 42.73; $C_5H_6N^+$, 24.14. Found: Ti (vol), 14.22; Ti (grav), 14.31; Cl, 42.75; $C_5H_6N^+$, 24.33.

$(C_5H_6N)_2[TiCl_5(CH_3OH)]$.—A 7.7-g sample of $TiCl_3$ was added to a mixture of 8.0 ml of pyridine and 2.0 ml of methanol in 50 ml of anhydrous ether or chloroform saturated with HCl. After 1 day of vigorous stirring, the yellow product (20 g) was filtered, washed with chloroform and ether, and dried under vacuum. *Anal.* Calcd for $TiCl_5C_{11}H_{16}ON_2$: Ti, 11.47; Cl, 42.48; $C_5H_6N^+$, 38.38. Found: Ti (vol), 11.23; Ti (grav), 11.39; Cl, 42.24; $C_5H_6N^+$, 38.18.

Attempts to Prepare a Monomeric Titanium(III)–Chloro(methoxo) Complex.—From the behavior of tungsten(V)–,[2] molybdenum(V)–,[3] and niobium(IV)–chloro[4] compounds one could anticipate the formation of titanium(III)–chloro(methoxo) complexes by the reaction of higher titanium(III)–chloro complexes with methanol with elimination of HCl.

When methanol was added to a yellow suspension of $(C_5H_6N)_4H[TiCl_8]$ in chloroform, a green precipitate was obtained and proved to be $(C_5H_6N)_2[TiCl_5(CH_3OH)_2]$. This suspension was then

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

(2) R. A. D. Wentworth and C. H. Brubaker, Jr., *ibid.*, **2**, 551 (1963); **3**, 47 (1964).

(3) H. Funk, F. Schmeil, and H. Scholz, *Z. Anorg. Allgem. Chem.*, **310**, 86 (1961).

(4) D. P. Rillema, W. J. Reagan, and C. H. Brubaker, Jr., *Inorg. Chem.*, **8**, 587 (1969).

stirred and caused to reflux while a steady stream of nitrogen was passed through the system to carry away volatile products. After 3 hr the green compound had turned into a bright orange precipitate consisting of clear hexagonal platelets. Analysis and the ir spectrum suggested the formation of a $CHCl_3$ adduct to $(C_5H_6N)_3TiCl_6$. The reflectance spectrum and the magnetic data are identical with those of the compound $(C_5H_6N)_3TiCl_6$. *Anal.* Calcd for $TiCl_6(C_5H_6N)_3 \cdot CHCl_3$: Ti, 7.7; Cl, 34.2; $C_5H_6N^+$, 38.8. Found: Ti (vol), 7.65; Ti (grav), 7.78; Cl, 34.73; $C_5H_6N^+$, 39.23.

The substance was also obtained by adding 1 equiv of pyridine to $(C_5H_6N)_4H[TiCl_8]$ in $CHCl_3$. Addition of 3 equiv of pyridine resulted in the formation of a yellow-green compound whose analysis corresponded to $(C_5H_6N)_2[TiCl_5(C_5H_5N)_2]$. The ir spectrum showed the typical bands for coordinated and protonated pyridine. *Anal.* Calcd for $TiC_5C_{22}H_4$: Ti, 8.8; Cl, 32.6; C_5H_5N, 58.6. Found: Ti (vol), 8.41; Ti (grav), 8.58; Cl, 32.09; C_5H_5N, 58.12.

On addition of methanol to a suspension of $(C_5H_6N)_2[TiCl_5(C_5H_5N)_2]$ in dichloroethane a deep red solution was obtained. When this solution was caused to reflux in a nitrogen stream, the starting material was regenerated.

When HCl was bubbled through a suspension of $(C_5H_6N)_2[TiCl_5(C_5H_5N)_2]$ in dichloroethane, the orange $(C_5H_6N)_3TiCl_6$ was formed.

On addition of methanol to a suspension of $(C_5H_6N)_3TiCl_6$ in dichloroethane, the formation of the green compound $(C_5H_6N)_2[TiCl_5(CH_3OH)_2]$ was also observed. If the solution was boiled and the methanol was driven off, the hexachloro complex was regenerated.

When $(C_5H_6N)_2[TiCl_5(CH_3OH)_2]$ in a nonpolar solvent was allowed to reflux for 1 day, the methanol was driven off and a pink-brown solid was formed whose analysis suggested the formation of the compound $(C_5H_6N)_2TiCl_5$. Infrared and reflectance spectra indicated that the decomposition was not complete even after prolonged boiling. *Anal.* Calcd for $TiCl_5C_{10}H_{12}N_2$: Ti, 12.6; Cl, 46.00; $C_5H_6N^+$, 41.7. Found: Ti (vol), 11.1; Ti (grav), 11.36; Cl, 42.01; $C_5H_6N^+$, 41.5.

Spectra.—Visible and ultraviolet spectra were determined by use of a Unicam SP-800 and a Cary Model 14 spectrometer. Reflectance spectra were recorded on a Spectronic 500 spectrophotometer, which was equipped with the reflectance attachment for the range 12,500–30,000 cm^{-1} and barium carbonate was used as reference reflector. For measurements below 12,500 cm^{-1} a thick paste of the compound and mineral oil was placed between a pair of glass plates and was brought into the cell compartment of the Cary model 14 spectrometer. The intensity of the reference beam was reduced mechanically. The spectra were recorded as if they were ordinary absorption spectra.

Infrared spectra were determined in mineral oil mulls and a Unicam Model SP-200 was used.

Esr spectra were obtained with a Varian V-4500-10A spectrometer with 100-kHz modulation. The spectra were calibrated by use of a Hewlett-Packard 524C frequency counter. The klystron frequency was 9.5 GHz at room temperature and 9.2 GHz for liquid nitrogen measurements.

Relative spin concentrations were determined by multiplying the peak-to-peak height of the derivative signal by the square of the maximum slope width. Absolute concentrations were estimated by use of spectrophotometrically standardized benzene solutions of diphenylpicrylhydrazyl.[5]

Magnetic Moments.—Magnetic susceptibilities were obtained as previously described.[5]

Spectrophotometric Titrations.—The titrations were carried out in a three-necked flask, equipped with a magnetic stirrer, a nitrogen inlet, and a 50-ml buret. The upper end of the stoppered buret was connected to the flask through a side arm to permit pressure equalization in the closed system. During the titrations, samples were withdrawn by means of an all-glass syringe. The spectroscopic cells and the esr tubes were filled and closed under purified nitrogen.

The solutions were prepared under purified nitrogen from reagent grade materials in volumetric flasks equipped with side arms. The concentrations of the solutions were determined by weighing the starting material or by analyses (Cl^- and I^-, potentiometrically with $AgNO_3$; $C_5H_6N^+$, spectrophotometrically).[1]

The following solutions in methanol were used: $TiCl_3$, 6.43 g/100 ml (0.418 *M*); HCl, 41.6 g/100 ml (11.42 *M*); C_5H_6NCl, 70.8 g/100 ml (6.12 *M*); C_5H_6NCl + HCl, (71.8 g + 25.4 g)/100 ml; KI, 12.9 g/100 ml (0.78 *M*); $NaOCH_3$, 1.0 g of Na/100 ml (4.36 *M*).

Results and Discussion

Reflectance Spectra.—All of the monomeric complexes $TiCl_n(CH_3OH)_{6-n}{}^{3-n}$ (n = 1–6), $(C_5H_6N)_2[TiCl_5(CH_3OH)_2]$, and $(C_5H_6N)_4H[TiCl_8]$ exhibited reflectance spectra consisting of two bands of varying relative intensity, the high-energy band always being the more intense one. With increasing number of Cl^- ions in the coordination sphere, the charge-transfer bands moved progressively into the visible part of the spectrum. The results are given in Table I, which includes compounds already described in a previous study.[1]

TABLE I

	Reflectance spectra, $10^3 \times cm^{-1}$		Solution spectra, $10^3 \times cm^{-1}$		Remarks
	$\bar{\nu}_1$	$\bar{\nu}_2$	$\bar{\nu}_1$	$\bar{\nu}_2$	
$[Ti(CH_3OH)_6]Cl_3$	...	...	16.8	15.1	*a*
$[TiCl(CH_3OH)_5]Cl_2$	18.6	15.2	...	...	*b*
$[TiCl_2(CH_3OH)_4]Cl$	18.2	15.0	15.5	13.9	*c*
$TiCl_3(CH_3OH)_3$	16.9	13.8	15.1	13.4	*d*
$(C_5H_6N)[TiCl_4(CH_3OH)_2]$	15.7	12.9	14.6	12.7	*e*
$(C_5H_6N)_2[TiCl_5(CH_3OH)]$	13.6	11.4	...	...	*b*
$(C_5H_6N)_3[TiCl_6]$	12.9	11.0	13.7	11.8	*f*
$(C_5H_6N)_3[TiCl_6] \cdot CHCl_3$	12.9	11.0	...	...	
$(C_5H_6N)_2[TiCl_5(CH_3OH)_2]$	15.6	12.9	...	...	*b*
$(C_5H_6N)_4H[TiCl_8]$	12.9	10.9	13.4	10.9	*f*
$H[TiCl_4] \cdot C_4H_{10}O$	22.5	16.6	...	...	*b*
$(C_5H_6N)[TiCl_4]$	16.1	10.9	...	...	*b*
$(C_5H_6N)_2[TiCl_5]$	20.0	...	...	...	*b*
$(C_5H_6N)_2[TiCl_5(C_5H_5N)]$	23.8	13.4	...	...	
$Ti(OCH_3)(CH_3OH)_nCl_{5-n}{}^{2-n}$	...	...	20.6	14.6	*g*

[a] In pure methanol. [b] Not observed in solution. [c] In solution with 2 *M* Cl^-. [d] In supernatant ether from the preparation. [e] In solution with 6 *M* Cl^-. [f] In supernatant acetonitrile from the preparation. [g] In methanol solution containing OCH_3^- or I^-.

Magnetic Moments.—The calculations outlined by Figgis[6,7] have been used to obtain values for k (delocalization of the d electron onto the ligands) and Δ (the splitting of the t_{2g} levels in an axial field) in the case of the paramagnetic compounds and to obtain n (the number of members in a polyatomic chain) and J (the exchange integral) in the case of the antiferromagnetic chloro complexes. Since measurements were made at only three temperatures, these values should be regarded as being only approximate. The magnetic moments of $(C_5H_6N)_2[TiCl_5]$ have been corrected for the presence of the impurity of $(C_5H_6N)_2[TiCl_5(CH_3OH)_2]$ (Table II).

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(5) J. A. Lyons and W. F. Watson, *J. Polymer Sci.*, **87**, 141 (1955).

(6) B. N. Figgis, *Trans. Faraday Soc.*, **157**, 198 (1961).

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

TABLE II

MAGNETIC DATA

	$10^{-6}\chi_M'$, cgsu	μ_{eff} BM 292°	195°	77°	θ, °K	κ	Δ, cm^{-1}
$TiCl_3(CH_3OH)$	1341	1.79	1.73	1.65	−18	1	1250
$(C_5H_6N)[TiCl_4(CH_3OH)_2]$	1373	1.79	1.73	1.64	−20	1	1100
$(C_5H_6N)[TiCl_5(CH_3OH)]$	1348	1.79	1.69	1.54	−44	0.9	450

	$10^{-6}\chi_M'$, cgsu	μ_{eff}, BM 292°	195°	75°	Probable geometry	n	J, cm^{-1}
$H[TiCl_4]\cdot C_4H_{10}O$	256	0.78	...	0.32	...	...	...
$(C_5H_6N)[TiCl_4]$	716	1.31	0.96	0.47	Chain	>4	160
$(C_5H_6N)_2[TiCl_5]$	578	1.27	1.15	0.99	Ring	3	90

The reflectance spectra of the series of compounds with the general fomula $TiCl_n(CH_3OH)_{6-n}{}^{3-n}$ may be used to test the validity of the rule of average environment proposed by Jørgensen.[8] This rule states that the optical absorption of octahedral complexes containing two different ligands in varying ratios can be predicted by use of the relationship

$$\bar{\nu}_{MX_nY_{6-n}} = {}^1/_6[n\bar{\nu}_{MX_6} + (6 - n)\bar{\nu}_{MY_6}]$$

In the case of the titanium(III)–chloro(methanol) complexes, this equation is satisfied best with values of 19,900 ± 800 cm^{-1} assumed for the high-energy band and 15,200 ± 900 cm^{-1} for the low-energy band of the unknown complex $[Ti(CH_3OH)_6]Cl_3$. This also shows that the deviations from the predicted values are not greater than 5% for the first and 6% for the second band in spite of the largely different symmetries of these complexes (Figure 1).

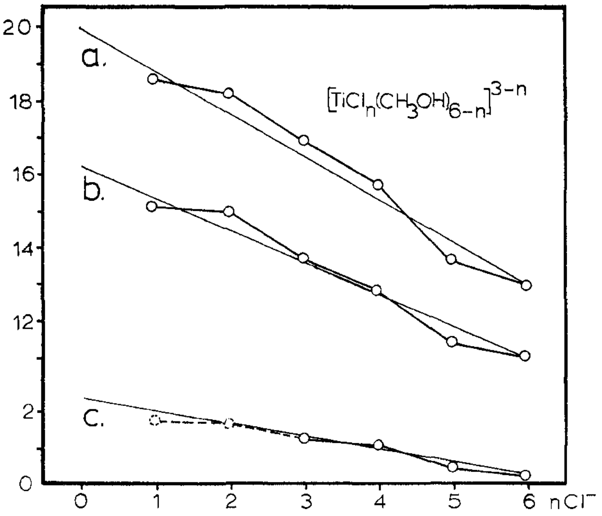

Figure 1.—(a and b) Position of the absorption bands in the reflectance spectra of the complexes $TiCl_n(CH_3OH)_{6-n}{}^{3-n}$. Circles represent experimental data; the straight line indicates values expected from the rule of average environment by assuming $\bar{\nu}_1 = 19.9 \times 10^3\ cm^{-1}$ and $\bar{\nu}_2 = 15.2 \times 10^3\ cm^{-1}$ for the species $Ti(CH_3OH)_6{}^{3+}$. (c) The values of the splitting of the lower orbitals derived from magnetic data.

The obvious axial symmetry of the compound $[TiCl(CH_3OH)_5]Cl_2$ was confirmed by its esr spectrum (Figure 2). The low value of Dq for $TiCl_6{}^{3-}$ of 1100 cm^{-1} compared to the estimated value of 1520 cm^{-1} for $Ti(CH_3OH)_6{}^{3+}$ would suggest a somewhat smaller interaction between the ligands and the d orbitals of the central atom along the fourfold axis containing one Cl^- ion and one CH_3OH molecule than in the equatorial plane formed by four methanol molecules. Such interactions would lead to a splitting of the cubic t_{2g} and e_g levels into a low-lying e_g level followed with increasing energy by b_{2g}, a_{1g}, and b_{1g}. The magnetic moments observed on this complex, however, require the presence of a low-lying orbital singlet with the next orbitals more than 1500 cm^{-1} above. In the case of the complex $(C_5H_6N)_2[TiCl_5(CH_3OH)]$, the more strongly interacting CH_3OH molecule in the axial position should lead to a well-separated orbital singlet ground state. The magnetic moments, however, indicate a rather small splitting of about 490 cm^{-1} between the B_{2g} ground state and higher excited states.

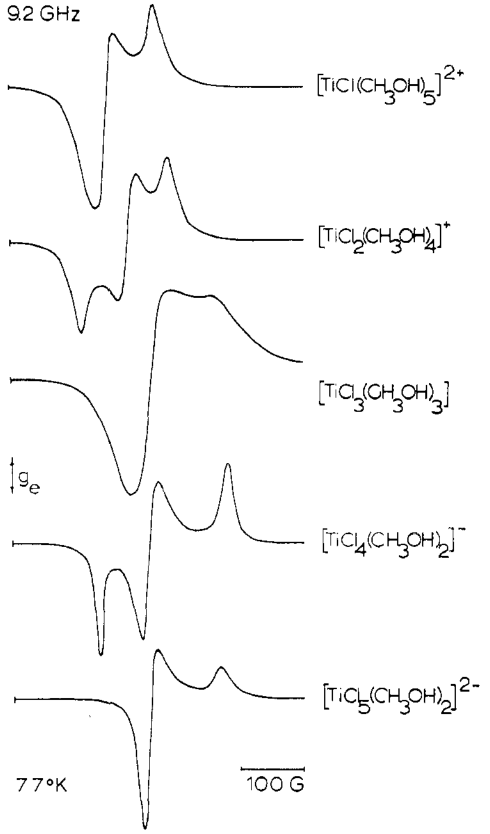

Figure 2.—Esr spectra of the solid undiluted compounds at liquid nitrogen temperature.

These effects may be explained by the ability of the Cl^- ion to form π bonds to the central atom, thus increasing the Ti–Cl bond strength which in turn means a shorter bond and a stronger electrostatic potential in the Ti–Cl bond direction. On the other hand, additional π bonding would lead to a reduction of the positive charge on the Ti atom and a decrease in the over-all electrostatic potential between Ti and the ligands as indicated by decreasing Dq values with increasing number of Cl^- ions in the coordination sphere.

For the complexes $[TiCl_2(CH_3OH)_4]Cl$ and $(C_5H_6N)[TiCl_4(CH_3OH)_2]$ *trans* and *cis* configurations are possible. The three-line esr spectrum indicates nonaxial symmetry and, therefore, *cis* configurations for these compounds. Only detailed calculations, however, may establish the ordering of the d orbitals, according to their energy, without ambiguity.

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(8) C. K. Jørgensen, "Absorption Spectra and Chemical Bonding in Complexes," Pergamon Press Inc., New York, N. Y., 1962, p 109.

The esr spectra of the compound $TiCl_3(CH_3OH)_3$ suggest axial symmetry. By assuming C_{3v} symmetry and taking the threefold axis as a new axis of quantization, the d_{z^2} orbital with the symmetry a_{1g} would have the lowest energy, followed by two degenerate levels e_g' and e_g'' at different energies. Magnetic moment measurements showed that the first level e_g' is separated from the a_{1g} level by about 1250 cm^{-1}. The transition from the A_{1g} state into the E_g'' state should then cause the absorption in the visible part of the spectrum. Since no distortion, no matter how strong, along the trigonal axis can remove the degeneracy of the e_g levels, one would expect only one band. The reflectance spectra, however, show clearly two bands at 16,900 and 13,800 cm^{-1}. The relatively large splitting of about 3000 cm^{-1} could be explained by some additional distortion with a strong component in a direction perpendicular to the trigonal axis. A similar problem[9] exists for a complex $TiCl_3(CH_3CN)_3$ whose esr spectrum[10] at 77°K also consists of two lines with values for $g_{\parallel} = 1.907$ and $g_{\perp} = 1.949$.

TABLE III

g VALUES OF VARIOUS SOLID TITANIUM(III)–CHLORO(METHANOL) COMPLEXES AT 77°K[a]

	g_1	g_2	g_3
$TiCl(CH_3OH)_5^{2+}$	1.927	1.927	1.869
$TiCl_2(CH_3OH)_4^{+}$	1.937	1.894	1.860
$TiCl_3(CH_3OH)_3$	1.869	1.869	1.815
$TiCl_4(CH_3OH)_2^{-}$	1.923	1.877	1.813
$TiCl_5(CH_3OH)^{2-}$		Not obsd	
$TiCl_6^{3-}$		Not obsd	
$TiCl_5(CH_3OH)_2^{2-}$	1.875	1.875	1.817
$H[TiCl_8]^{4-}$		Not obsd	

[a] Counterions are $C_5H_6N^+$ or Cl^-. For axial symmetry, $g_1 = g_2 = g_{\perp}$.

The compound $(C_5H_6N)_2[TiCl_5(CH_3OH)_2]$ exhibits an esr spectrum (Figure 2) whose two lines could signify D_{5h} symmetry, corresponding to a pentagonal-bipyramidal structure. However, again a strong additional orthorhombic distortion has to be assumed to explain the removal of the degeneracy of the E_g' ground state in D_{5h} symmetry. The optical absorption bands for this complex are much closer to those observed for $(C_5H_6N)[TiCl_4(CH_3OH)_2]$ than to those for $(C_5H_6N)_2[TiCl_5(CH_3OH)]$ (see Table I). In addition, the separation of the lower orbitals determined from magnetic moment measurements is, at 1250 cm^{-1}, very close to that for the tetrachloro complex $(C_5H_6N)[TiCl_4(CH_3OH)_2]$.

The fact that no esr signal could be found for the complex $(C_5H_6N)_4H[TiCl_8]$ at 77°K either in solution or in the solid state indicated that the unpaired electron occupies a d orbital which is close enough to other appropriate d orbitals to give rise to strong spin–orbit interaction. The strong temperature dependence of the magnetic moments and the resulting large Weiss constant of −72° confirm these considerations. Assuming that all Cl^- ions are coordinated to the Ti atom, one has to consider mainly the possible arrangements: the Archimedean antiprism (D_{4d}), the dodecahedron (D_{2d}), the cube (O_h), the trigonal prisms with two ligands either in the center of two end faces (D_{3h}) or in the center of two side faces (C_{2v}). The first two arrangements lead to well-separated orbital singlets[11,12] and therefore have to be excluded. Since the matrix elements of L_z between the d_{z^2} and $d_{x^2-y^2}$ wave functions of the low-lying ^2E_g term are zero, no strong orbital angular momentum contribution is expected for the third configuration. In D_{3h} the degenerage d_{xy} and $d_{x^2-y^2}$ orbitals form the gound state giving rise to angular momentum. In C_{2v} a pair of low-lying (A_1 and A_2) orbitals is close together and is primarily made up of the same two d_{xy} and $d_{x^2-y^2}$ orbitals. Thus one of the last two arrangements for the $TiCl_8^{5-}$ ion $(C_5H_6N)_4H[TiCl_8]$ would be supported by the spectra and the magnetic susceptibility.

The importance of the compounds $H[TiCl_4]\cdot C_4H_{10}O$, $(C_5H_6N)TiCl_4$, and $(C_5H_6N)_2TiCl_5$ lies mainly in their use to prepare mixed titanium(III)–chloro complexes with various ligands which might not be accessible otherwise. $H[TiCl_4]\cdot C_4H_{10}O$ can be substituted for $TiCl_3$ in many cases in preparing neutral $TiCl_3L_3$ complexes, if 3 equiv of the neutral ligands is added to a suspension of the tetrachlorooxonium salt in a nonpolar solvent. A similar method may be used to prepare complexes like $(C_5H_6N)[TiCl_4L_2]$ and $(C_5H_6N)_2[TiCl_5L]$ from $(C_5H_6N)TiCl_4$ and $(C_5H_6N)_2TiCl_5$. The low magnetic moments of these compounds indicated strong antiferromagnetic interactions and a polymeric structure with chloride bridges.

Spectrometric Titrations.—Since the optical and esr spectra of all of the compounds $TiCl_n(CH_3OH)_{6-n}{}^{3-n}$ were known, it appeared worthwhile to investigate the position of the equilibria $TiCl_n(CH_3OH)_{6-n}{}^{3-n} + Cl^- \rightleftarrows TiCl_{n+1}(CH_3OH)_{5-n}{}^{2-n}$ as a function of the Cl^- ion concentration.

On addition of Cl^- in the form of HCl, C_5H_6NCl, or a mixture of both to a solution of $TiCl_3$ in methanol, the characteristic double band with maxima at 16,800 and 15,100 cm^{-1} was gradually changed to a broad, structureless band with a maximum at 15,300 cm^{-1} and the molar absorptivity changed from ϵ 4.8 to ϵ 6.3 at the highest maxima. On further addition of Cl^- ions, this broad band gradually shifted to lower frequencies while a new absorption appeared at about 13,000 cm^{-1} and steadily increased. At a concentration of 6 *M* Cl^- the green compound $(C_5H_6N)_2[TiCl_5(CH_3OH)_2]$ precipitated and redissolved on further addition of Cl^-. In very concentrated solutions, saturated with C_5H_6Cl and then HCl, the yellow compound $(C_5H_6N)_4H[TiCl_8]$ separated and the yellow supernatant solution showed an absorption band which had a maximum at 13,900 cm^{-1} with a shoulder at 13,000 cm^{-1}.

A comparison of the spectroscopic data for the compounds $TiCl_n(CH_3OH)_m{}^{3-n}$ in Table I shows little direct relationship between the reflectance and solution spec-

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[9] G. D. McDonald, M. Thompson, and E. L. Larsen, *Inorg. Chem.*, **7**, 648 (1968).

[10] W. Giggenbach, unpublished result.

[11] G. Gliemann, *Theoret. Chim. Acta*, **1**, 14 (1962).

[12] M. Randic, *J. Chem. Phys.*, **36**, 2094 (1962).

tra. This disparity, the large widths of the absorption bands (half-widths ~6000 cm^{-1}), and the narrow range in which they occur (10,000–19,000 cm^{-1}) made it impossible to determine the nature of the molecule or molecules formed in solutions of different Cl^- concentrations by optical spectroscopy.

On the other hand, the distinct and relatively sharp esr absorption curves (Figure 2) suggested that there might be a means of identifying the species present during a titration. In the initial solution of $TiCl_3$ in methanol one predominant paramagnetic species could be detected at 77°K. The signal at 77°K consisted of three lines corresponding to a nonaxial species with g values of 1.987, 1.897, and 1.854 and is probably due to the compound $[TiCl_2(CH_3OH)_4]Cl$. The difference between the experimental g values of the powder spectrum and the spectrum in frozen methanol is possibly caused by the difference in line width of the signals (Figure 3). The frozen solution spectrum is considerably broader (ΔH = 65 G, compared to a maximum slope width of ΔH = 26 G for the powder spectrum). There were no indications of the presence of the compound $[TiCl(CH_3OH)_5]Cl_2$ in solution.

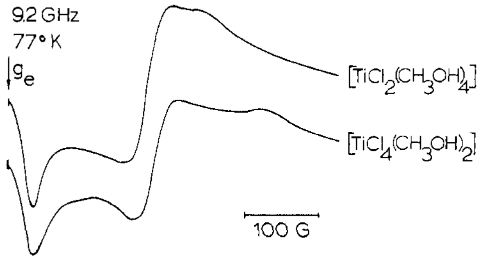

Figure 3.—Esr spectra of the Ti(III) species observed in 2 and 6 M Cl^- methanol solutions.

After Cl^- ion was added, the esr spectrum of $[TiCl_2(CH_3OH)_4]Cl$ was gradually replaced by a three-line signal which has g's equal to 1.981, 1.885, and 1.808 and which is probably due to $(C_5H_6N)[TiCl_4(CH_3OH)_2]$. The spectrum of the frozen methanol solution showed broader lines with ΔH = 65 G, compared to ΔH = 26.5 G for the powder spectrum (Figure 3). On further addition of Cl^- ions, the green compound $(C_5H_6N)_2[TiCl_5(CH_3OH)_2]$ precipitated but no corresponding esr signal could be detected in the supernatant liquid. If the solution was cooled slowly to permit the crystallization of the pentachloro complex in the esr tube, the typical two-line spectrum could be observed at 77°K. After the esr tube had been warmed and the solid redissolved, the signal again disappeared.

In solutions containing more Cl^- a third very broad single line (ΔH = 225 G) was observed which might be due to one of the compounds $(C_5H_6N)_2[TiCl_5(CH_3OH)]$, $(C_5H_6N)_3TiCl_6$, or $(C_5H_6N)_4H[TiCl_8]$. The precipitation of $(C_5H_6N)_4H[TiCl_8]$ in these solutions does not necessarily imply any appreciable concentration of such a species in solution.

In Figure 4 these relationships are shown. The concentrations of different species are given as the percentage of the amount of Ti(III) present in solution.

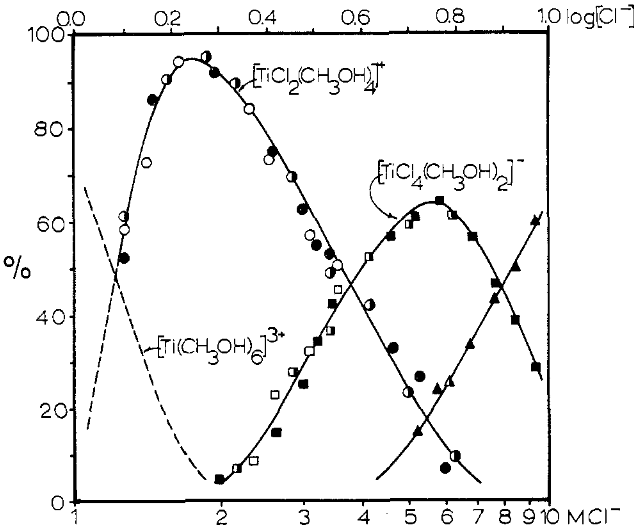

Figure 4.—Concentrations of Ti(III) species present in methanol solutions containing varying amounts of Cl^- as determined by esr spectra. Open symbols represent experimental values obtained from solutions containing HCl and half-filled symbols correspond to C_5H_5HCl-containing solutions, whereas filled symbols indicate experimental values obtained from solutions containing both C_5H_6NCl and HCl (see text).

The concentration for Cl^- ions in the case of C_5H_6NCl is the analytical concentration. It has been found that the concentration of HCl had to be about 2.33 times higher than that of C_5H_6NCl to cause similar changes in the esr spectra. Therefore, Figure 4 has been plotted by use of the empirical relationship $\gamma_{HCl} = 0.43\gamma_{C_5H_6NCl}$ and the assumption that $\gamma_{C_5H_6NCl} = 1$, where γ's are fitted, molar-scale activity coefficients.

From the preceding observations it was not possible to determine the nature of the species present in solutions of $TiCl_3$ in pure methanol. The complex isolated from these solutions, $TiCl_3(CH_3OH)_5$, exhibited a two-line esr spectrum typical of axial symmetry and the structural formula $[TiCl(CH_3OH)_5]Cl_2$. The reflectance spectrum consisted of two bands of about equal intensity of 18,600 and 15,200 cm^{-1}. In solution, however, the absorption spectrum showed two bands of slightly different intensity at 16,800 (ϵ 4.8) and 15,100 cm^{-1} (ϵ 4.6) and the esr spectrum at 77°K seems best ascribed to the complex $[TiCl_2(CH_3OH)_4]Cl$. As can be seen from Figure 4, the concentration of $[TiCl_2(CH_3OH)_4]Cl$ was 50% of the total Ti(III) concentration as determined from esr spectra of solutions of $TiCl_3$ in methanol alone. On addition of about 1 equiv of HCl the intensity of the esr absorption reached a maximum and the bands at 18,600 and 15,200 cm^{-1} were replaced by the broad absorption band with its maximum at 15,600 cm^{-1}. Because of the absence of a corresponding esr signal, the missing 50% of the Ti(III) and the double-banded optical spectrum must be due to a species different from $[TiCl(CH_3OH)_5]Cl_2$.

A species causing a sharp esr absorption was detected by Waters and Maki[13] in $TiCl_3$ in methanol solutions which contained methoxide ion. This signal consists of an intense central line accompanied by a series of hyperfine lines representing the hyperfine pattern expected

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

for ^{47}Ti and ^{49}Ti in their natural abundance. The hyperfine patterns are best observed at −45°. At higher or lower temperatures the signal broadens and at 77°K a rather broad asymmetric signal is observed. The intensity of this signal reaches a maximum in solutions containing 1 mol of sodium methoxide per mole of $TiCl_3$, but it also could be observed in solutions of $TiCl_3$ in pure methanol. The absolute concentration of this species was estimated as described in the Experimental Section and it was found to account for only about 2% of the total Ti(III) concentration in pure methanol and for about 10% in solutions containing 1 equiv of methoxide. It was, therefore, necessary to consider the possibility of the presence of a third species which could be ascribed to the remaining 48% of Ti(III) in pure methanol and which had an absorption spectrum with bands at 16,800 and 15,200 cm^{-1}. No esr absorption could be detected whose behavior toward changes in Cl^- concentration corresponded to the changes in the optical absorption and may be explained by the large width of the esr signal of a species whose t_{2g} sublevels are only slightly separated. The highly symmetric complex $[Ti(CH_3OH)_6]Cl_3$ would fulfill this requirement.

In order to support the idea of the formation of the hexamethanol complex, we tried to replace the rather strongly coordinating Cl^- ions by ions whose tendency to enter the Ti(III) coordination sphere is expected to be rather low: ClO_4^- and NO_3^- were rapidly reduced by Ti(III) whereas BF_4^- appeared to give off F^- ions to form Ti–F complexes. The only ion tried which did not interact with Ti(III) directly was the I^- ion. Addition of a concentrated solution of KI to the blue solution of $TiCl_3$ in methanol caused the precipitation of KCl without any significant change in the absorption spectrum until about 1.5 mol per mole of $TiCl_3$ had been added and an equivalent amount of KCl had been precipitated. On further addition of KI, the color of the solution changed from blue to violet to yellow as two new bands in the optical spectrum at 20,600 and 14,600 cm^{-1} appeared. An isosbestic point at 18,900 cm^{-1} indicates that two species participate in this equilibrium but the esr spectra at 77°K revealed that there is still about 10% of $TiCl_2(CH_3OH)_4^+$ present even in solutions saturated with KI. These esr spectra also showed a much stronger, broad, asymmetric signal consisting of two lines with experimental values of $g_\perp = 1.960$ and $g_\| = 1.944$. With rising temperature this signal narrowed considerably and changed into the characteristic eight-line hyperfine spectrum observed in solutions of $TiCl_3$ in methanol containing methoxide. The calculated $\langle g \rangle = 1.954$ from the spectrum at 77°K is very close to the experimental isotropic g value of the signal at −45° with $g = 1.953$. The isotropic hyperfine constant,[13] A_{Ti}, is 16.3×10^{-4} cm^{-1} and corresponds to that observed for methoxide-containing solutions, $(16.2 \pm 0.2) \times 10^{-4}$ cm^{-1}. The absolute concentration of the corresponding species reached about 55% of the total Ti(III) concentration and it seems reasonable to ascribe the two new optical bands at 20,600 and 14,600 cm^{-1} to this species, probably $Ti(OCH_3)(CH_3OH)_5^{2+}$.

On addition of another 0.5 equiv of some alkali methoxide to a solution of $TiCl_3$ in methanol containing 1 equiv of methoxide, the concentrations of the complexes $[TiCl_2(CH_3OH)_4]Cl$ (as indicated by its esr spectrum) and $[Ti(CH_3OH)_6]Cl_3$ (as indicated by its optical spectrum) reached zero, and the eight-line hyperfine esr spectrum also disappeared. Very weak signals observed in these solutions are probably best ascribed to impurities.

The equilibria existing in these $TiCl_3$ solutions containing various amounts of CH_3O^- or I^- can probably be represented by

$$[TiCl_2(CH_3OH)_4]Cl \underset{+Cl^-}{\overset{+CH_3OH}{\rightleftarrows}} [Ti(CH_3OH)_6]Cl_3 \underset{+HCl}{\overset{+OCH_3^-}{\rightleftarrows}}$$

$$[Ti(OCH_3)(CH_3OH)_5]Cl_2 \underset{+HCl}{\overset{+OCH_3^-}{\rightleftarrows}} TiCl_{1.5}(OCH_3)_{1.5}(CH_3OH)_2$$

$$[TiCl_2(CH_3OH)_4]Cl \underset{+Cl^-}{\overset{+CH_3OH}{\rightleftarrows}} [Ti(CH_3OH)_6]Cl_3 \underset{+HCl}{\overset{+I^-}{\rightleftarrows}}$$

$$[Ti(OCH_3)(CH_3OH)_5]I_2$$

From the preceding discussion of the esr titrations one can conclude that in methanol containing Cl^- ion only the species $[Ti(CH_3OH)_6]Cl_3$, $[TiCl_2(CH_3OH)_4]Cl$, and $(C_5H_6N)[TiCl_4(CH_3OH)_2]$ occur in significant concentrations. The data of the optical spectra of these solutions are given in Table I. They show that the solution spectra appear at considerably lower frequencies than the corresponding reflectance spectra. From Figure 5 one can see that the rule of average environment can also be applied to these data. One also can see that the differences between the solution spectra and the reflectance spectra decrease with decreasing number of coordinated methanol molecules. The complex $(C_5H_6N)_3TiCl_6$ is not stable in methanol, but if its optical data are calculated by use of the rule of average environment and the available solution data of the other compounds, the calculated values are very close to those obtained from reflectance spectra. This observation supports the idea that the differences of the solution and reflectance data are mainly determined by the number of coordinated CH_3OH molecules and have to be explained by strong interactions between coordinated and solvent CH_3OH molecules through hydrogen

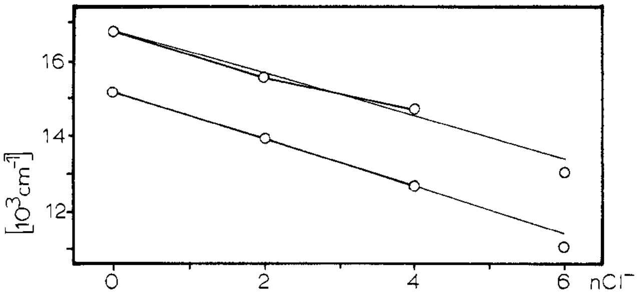

Figure 5.—Position of the absorption bands of some Ti(III) complexes stable in methanol solutions containing Cl^- ions. The straight line corresponds to values expected from the rule of average environment. The data for $TiCl_6^{3-}$ are those of the reflectance spectrum.

bonds. A similar effect has been observed on two compounds in acetonitrile solutions also investigated during this study. The reflectance spectra of $(C_5H_6N)_3[TiCl_6]$ and $(C_5H_6N)_2[TiCl_5CH_3CN]$ have strong maxima at 12,900 and 14,000 cm^{-1}, respectively. In solution these bands appear at higher energies at 13,700 cm^{-1} (+800 cm^{-1}) for the hexachloro complex and at 15,200 cm^{-1} (+1200 cm^{-1}) for the pentachloroacetonitrile complex. Thus, acetonitrile has the opposite effect of methanol.

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Excitation Energy Transfer from Chromium in the Cation to Chromium in the Anion in Some Crystalline Compounds: $[CrA_6][Cr(CN)_6]\cdot xH_2O$

BY HANS L. SCHLÄFER, HANS GAUSMANN, AND CHRISTIAN H. MÖBIUS

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Luminescence measurements indicate, in a series of double complex salts $[CrA_6][Cr(CN)_6]\cdot xH_2O$ and $[Cr(A\text{-}A)_3][Cr(CN)_6]\cdot xH_2O$, where A and (A-A) are mono- or bidentate neutral ligands with oxygen or nitrogen as coordinating atoms, an excitation energy transfer from chromium in the cation (donor, D) to chromium in the anion (acceptor, A). Relative emission intensities and lifetimes of the phosphorescence $^2E_g \rightarrow {}^4A_{2g}$ of the acceptor are reported. It is suggested that a doublet–doublet transfer D*(doublet) + A(quartet) → D(quartet) + A*(doublet) is operating. Possible types of mechanism are discussed.

A. Introduction

In a previous paper[1] we reported an excitation energy transfer from the cation to the anion in the double complex salt $[Cr(OC(NH_2)_2)_6][Cr(CN)_6]\cdot 3H_2O$. This was concluded on the basis of luminescence measurements from the fact that excitation of the cationic component, *i.e.*, absorption in a spectral region where only the hexaureachromium(III) entity absorbed, yielded a phosphorescence emission $^2E_g(an) \rightarrow {}^4A_{2g}(an)$ located in the hexacyano part. The corresponding phosphorescence emission of the cation $^2E_g(ct) \rightarrow {}^4A_{2g}(ct)$ and also the fluorescence $^4T_{2g}(ct) \rightarrow {}^4A_{2g}(ct)$ which are seen in $[Cr(ur)_6]Cl_3\cdot H_2O$ or $[Cr(ur)_6](ClO_4)_3$ were both totally quenched in the double salt. The emission of the $Cr(CN)_6{}^{3-}$ part in the double salt was greatly increased compared to the emission of $K_3[Cr(CN)_6]$.

The present work has been undertaken to clarify the luminescence behavior of similar double complex salts of the type $[CrA_6][Cr(CN)_6]\cdot xH_2O$ or $[Cr(A\text{-}A)_3][Cr(CN)_6]\cdot xH_2O$, where A is a monodentate and (A-A) a bidentate neutral molecule. Compounds with oxygen or nitrogen coordination of the cationic Cr^{3+} and with different distances $Cr^{3+}(ct)$–$Cr^{3+}(an)$ have been investigated in the hope of obtaining information about the relationships between the efficiency of energy transfer, the cation–anion distance, and the nature of the coordinating atom of the cation. These double salts have been selected to fulfill the following conditions. (1) The absorption spectra of the double salts should be very nearly a superposition of the spectra of the individual constituent ions. (2) A spectral region should exist where only the cationic part of the double salts absorbs. At an appropriate wavelength, excitation of only the cation is then possible. (3) The lowest doublet state $^2E_g(an)$ of $Cr(CN)_6{}^{3-}$ from which the emission originates should be located at somewhat lower energy than the lowest doublet $^2E_g(ct)$ of the cationic component.

On mixing aqueous solutions of $Cr(CN)_6{}^{3-}$ with $CrA_6{}^{3+}$ or $Cr(A\text{-}A)_3{}^{3+}$ [A = urea (ur), antipyrine (atp), imidazolone (imid), or ammonia; (A-A) = ethylenediamine (en), propylenediamine (pn), or trimethylenediamine (tn), respectively], one easily obtains crystalline precipitates of the corresponding double complex salts.

B. Results and Discussion

The reflectance spectra of the double salts are very nearly a superposition of the individual spectra of the cation and the anion (Figures 1–7), indicating little or no coupling between the two chromium(III) centers. Therefore it is possible to discuss the energy states of the double complex salts from the point of view of two Cr^{3+} entities, each of which consists of a chromium(III) metal ion surrounded octahedrally by six identical ligands A or CN^- or by three equal bidentate ligands (A-A). Also it seems reasonable to regard the electronic excitation of the double complex salts as at least temporarily completely localized in the cation or the anion part.

Figures 8 and 9 show the term diagrams for the different compounds, obtained using the spectral data of Figures 1–7. On the right the electronic energy states

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[1] H. L. Schläfer, H. Gausmann, and H. Witzke, *J. Chem. Phys.*, **46**, 1423 (1967).