85. *Transition-metal Halide–Methyl Cyanide Complexes.*
Part III.[1] Titanium, Vanadium, and Chromium.

By B. J. HATHAWAY and D. G. HOLAH.

Titanium metal is oxidised by chlorine and bromine in methyl cyanide solution to titanium(IV) and yields the complexes $TiCl_4,MeCN$ and $TiBr_4,2MeCN$. Iodine yields titanium(III) as the polyiodide $[Ti(MeCN)_6])(I_3)_3$. All three halogens oxidise vanadium metal to vanadium(III), and give the complexes $(VCl_3,3MeCN)MeCN$, involving a molecule of unco-ordinated methyl cyanide, $(VBr_2,4MeCN)(Br_3)$, containing the tribromide anion, and $[V(MeCN)](I_3)_3$ analogous to the titanium polyiodide complex. Chromium metal is oxidised by all three halogens to chromium(III) and gives the complexes $(CrCl_3,3MeCN)MeCN$, $(CrI_2,4MeCN)I$, and a bromide of variable composition, $CrBr_3,2$—$3MeCN$. The magnetic moments at room temperature, and the infrared and electronic reflectance spectra are reported and indicate that all the complexes involve octahedral co-ordination of the transition-metal ions.

RECENTLY several authors [2,3] have obtained complexes of titanium-(III) and -(IV) and of vanadium(III) by crystallisation of the appropriate halide from methyl cyanide solution. The following complexes were obtained: $TiCl_3,3MeCN$; $TiCl_4,2MeCN$; $VCl_4,2MeCN$; $VCl_3,4·4MeCN$; $TiBr_3,3MeCN$; $TiBr_4,2MeCN$; $VCl_3,3MeCN$; $VBr_3,3MeCN$. Spectral and magnetic properties [2,3] have been used to deduce that the complexes $TiCl_3,3MeCN$ and $VCl_3,3MeCN$ are monomeric and octahedral, while $VCl_3,4·4MeCN$ [4] contains both free and co-ordinated methyl cyanide. Solutions of the metal halides in methyl cyanide solution have been used for the preparation of tetrahedral vanadium(III) complexes [5] by addition of tetraethylammonium chloride or bromide. The complexes $(Et_4N)(VX_4),2MeCN$, $(X = Cl^-$ and $Br^-)$ were obtained; the methyl cyanide is easily removed by evacuation at $80°$.

Continuing our investigation of the properties of methyl cyanide as a ligand,[1,6] we have examined the products of reaction of the halogens with the metals titanium, vanadium,

TABLE 1.

The complexes isolated and their analysis.

Complex	Reaction time	Colour	Found (%)			Required (%)		
			Metal	Halide	Halogen	Metal	Halide	Halogen
$TiCl_4,L$	30 min.	Yellow	20·6	61·6	—	20·75	61·5	—
$TiBr_4,2L$	5 min.	Red	10·6	70·9	—	10·65	71·1	—
$TiI_9,6L$	5 min.	Black	3·25	81·0 *	53·1	3·3	79·5 *	53·0
$VCl_3,4L$	2 hr.	Green	16·1	33·1	—	15·9	33·0	—
$VBr_5,4L$	5 min.	Brown	8·25	64·7 *	24·6	8·3	65·0 *	26·0
$VI_9,6L$	2 days	Black	3·7	79·2 *	52·75	3·5	79·35 *	52·9
$CrCl_3,4L$	3 hr.	Grey	16·1	33·0	—	16·1	33·0	—
$CrBr_3,xL$	10 min.	Green	9·5—13·5	54·0—64·2	—	—	—	—
$CrI_3,4L$	1 hr.	Red-brown	8·7	64·0	—	8·7	63·78	—

L = Methyl cyanide.   * See Experimental section for details.

and chromium in methyl cyanide solution. The complexes obtained, their colours and analysis are given in Table 1 along with an estimation of the time required for complete reaction. The suggested stereochemical formulation of the complexes isolated, their

[1] Parts I and II. *J.*, 1964, 2400 and 2408.
[2] Clark, Lewis, Machin, and Nyholm, *J.*, 1963, 379.
[3] Fowles, Symposium on the Early Transition Elements, *Proc. Chem. Soc.*, 1962, 375; Duckworth, Fowles, and Hoodless, *J.*, 1963, 5665.
[4] Scaife and Nyholm, unpublished work.
[5] Nyholm, *Croat, Chem. Acta*, 1961, **33**, 157.
[6] Hathaway, Holah, and Underhill, *J.*, 1962, 2444.

magnetic moments at room temperature, infrared and electronic reflectance spectra are given in Table 2.

Titanium Complexes.—From the magnetic properties and stoicheiometries of the titanium complexes, it is clear that chlorine and bromine oxidise titanium metal to titanium(IV), d^0, while iodine only oxidises it to titanium(III), d^1, which is consistent with the weaker oxidising properties of iodine compared with those of the other two halogens. In each complex, all the methyl cyanide is co-ordinated as indicated by the shift to higher frequencies of the C≡N vibration.[1,2] The $TiBr_4,2MeCN$ complex is presumed to involve six-co-ordination, while the $TiCl_4,MeCN$ complex implies five-co-ordination, but this is probably increased to six by halogen bridging, although there is no evidence for this. The iodide complex may be formulated as containing the octahedral $(Ti(MeCN)_6)^{3+}$ cation and three tri-iodide anions, although in the reflectance spectra of this complex the first d–d transition, $^2E_g \longleftarrow {}^2T_{2g}$, which should occur in octahedral titanium(III) at approximately 20,000 cm.$^{-1}$ is obscured by the adsorption due to the tri-iodide ion. The formulation of this complex as $[Ti(MeCN)_6](I_3),3I_2$ is not considered likely, because the free iodide anion is a much stronger co-ordinating ligand than methyl cyanide and would displace
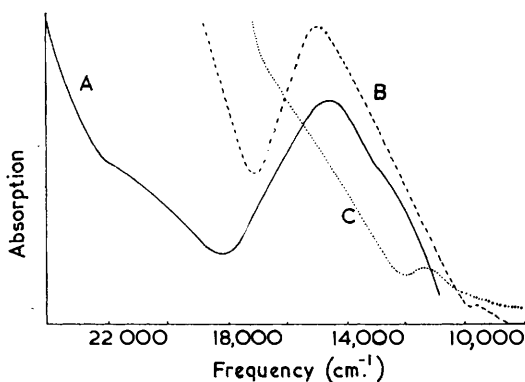

Fig. 1. The reflectance spectra of some solid vanadium(III) complexes.

A: $[VCl_3(MeCN)_3]MeCN$;
B: $[VBr_2(MeCN)_4](Br_3)$;
C: $[V(MeCN)_6](I_3)_3$.

the methyl cyanide from the co-ordination shell of the titanium(III) cation.[1] The large size and single negative charge of the tri-iodide anion would give it very little co-ordinating power so that the tri-iodide anion is unlikely to displace co-ordinated methyl cyanide, although lattice energy effects may determine the actual result.

Vanadium Complexes.—All three halogens oxidise vanadium metal to vanadium(III), although the iodide complex was too unstable to allow an accurate measurement of the magnetic moment to confirm this. In the bright green, very hygroscopic chloride complex, the infrared spectrum shows that there are both co-ordinated and unco-ordinated methyl cyanide molecules present. The latter is not removed by evacuation at room temperature, although at 80° a molecule of methyl cyanide is lost to give a dark brown product, the infrared spectrum of which shows no free methyl cyanide. The reflectance spectrum of the green complex is shown in Fig. 1, in which the band at 14,700 cm.$^{-1}$ is assigned as the $^3T_{2g}(F) \longleftarrow {}^3T_{1g}(F)$, with the $^3T_{1g}(P) \longleftarrow {}^3T_{1g}(F)$ seen as a shoulder at 21,700 cm.$^{-1}$ on the side of a charge-transfer band. With this assignment, the spectrum is consistent with the formulation of the complex as $(VCl_3,3MeCN),MeCN$ involving octahedral vanadium.[2] The shoulder at approximately 12,000 cm.$^{-1}$ would suggest a distortion of the octahedral $(VCl_3,3MeCN)$ consistent with the presence of six non-equivalent ligands, but it is odd that this shoulder is lost when the molecule of unco-ordinated methyl cyanide is removed. The results from the reflectance spectra of $VCl_3,3MeCN$ then agree very closely with the values of 14,500 and 21,000 cm.$^{-1}$ reported for this complex in solution.[2]

In the reaction between vanadium metal and bromine in methyl cyanide, which is complete in a few minutes, a reaction also occurs between the bromine and the methyl

cyanide to give a white, volatile fuming solid, which collects in the condenser above the reaction flask, but which it has not been possible to identify. The pale brown complex of vanadium(III) obtained from this reaction gave off traces of white fumes when the complex was exposed to the atmosphere and, although the analysis was good, the slightly low magnetic moment of 2·65 B.M. may arise from this impurity, but it is still consistent with the presence of two unpaired electrons [7] and hence of vanadium(III). The infrared results show that all the methyl cyanide is co-ordinated, and the reflectance spectrum (Fig. 1) is consistent with octahedral vanadium(III). The band at 14,900 cm.$^{-1}$ is assigned as the $^3T_{2g}(F) \longleftarrow {}^3T_{1g}(F)$ transition, the other spin-allowed transitions to $^3T_{1g}(P)$ and $^3A_{2g}(F)$ are hidden under the absorption bands of the tribromide anions. This evidence and the analysis of the complex suggest the formulation as (VBr$_2$,4MeCN)(Br$_3$)

The complex iodide of vanadium(III) is rather unstable and quickly loses iodine, and this invalidates any magnetic measurements. The reflectance spectrum is dominated by the very intense absorption of the tri-iodide anion, but there is some evidence of a shoulder at 15,000 cm.$^{-1}$, which could well be the first spin-allowed transition of octahedral vanadium(III). By comparison with the titanium iodide complex the vanadium complex is formulated as [V(MeCN)$_6$](I$_3$)$_3$. The reflectance spectra of all three vanadium complexes show traces of weak absorptions between 900 and 12,000 cm.$^{-1}$; these are probably due

Fig. 2. The reflectance spectra of some solid chromium(III) complexes.

A: [CrCl$_3$(MeCN)$_3$]MeCN;
B: CrBr$_3$,2—4MeCN;
C: [CrI$_2$(MeCN)$_4$]MeCN.
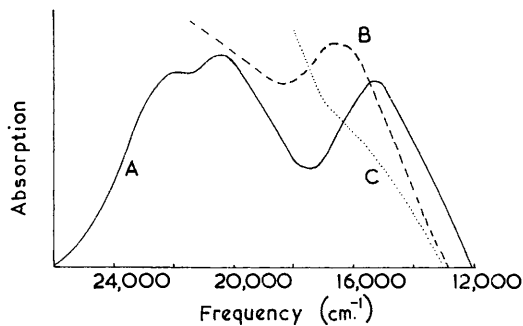
to spin-forbidden transitions to doublet levels, which have been observed in the spectrum of the vanadium(III) ion in aluminium oxide.[8]

The values of D_q have been calculated for (VCl$_3$,3MeCN),MeCN and (VBr$_2$,4MeCN)(Br$_3$) by using Ballhausen's theory,[9] and give the values of 1623 and 1645 cm.$^{-1}$, respectively. In the latter complex, there are four molecules of methyl cyanide co-ordinated to the vanadium ion, while there are only three in the former; this accounts for the slightly higher value of D_q in the bromide. A value for D_q of 1550 cm.$^{-1}$, based on the results of solution spectra has previously been calculated for VCl$_3$,3MeCN.

Chromium Complexes.—From the magnetic [7] properties and the stoicheiometries of the chromium complexes, all three halogens oxidise chromium metal to chromium(III). In the chloride, the infrared spectrum indicates the presence of both free and co-ordinated methyl cyanide. The reflectance spectrum (Fig. 2) of the chloride shows two main peaks typical of the octahedrally co-ordinated chromium(III) cation at 15,400 and 20,200 cm.$^{-1}$ which are assigned as the $^4T_{2g}(F) \longleftarrow {}^4A_{2g}$ and $^4T_{1g}(F) \longleftarrow {}^4A_{2g}$ transitions, respectively. The band at 20,200 cm.$^{-1}$ has a definite shoulder at 22,200 cm.$^{-1}$; this splitting has only been observed in a few cases of octahedral chromium complexes,[10] for example *trans*-[Cr(H$_2$O)$_4$F$_2$]$^+$ ion, where the tetragonal distortion of the octahedron produces a splitting of 2400 cm.$^{-1}$.

[7] Figgis and Lewis, " Modern Coordination Chemistry," ed. Lewis and Wilkins, Interscience, Publ. Inc., New York, 1960, p. 400.
[8] McClure, *J. Chem. Phys.*, 1962, **36**, 2757.
[9] Ballhausen, *Z. phys. Chem. (Frankfurt)*, 1957, **11**, 205.
[10] McClure, " Advances in the Chemistry of the Coordination Compounds," ed. Kirschner, Macmillan and Co., New York, 1961, p. 498.

The molecule of unco-ordinated methyl cyanide may be removed by heating the complex to 80° under vacuum, to give a purple solid containing no free methyl cyanide and showing no trace of the shoulder at 22,200 cm.$^{-1}$. The complex is therefore formulated as (CrCl$_3$,3MeCN),MeCN, and the splitting in the reflectance band would appear to be caused by a distortion of the lattice owing to the presence of unco-ordinated methyl cyanide, as occurs with the vanadium chloride complex and with some cobalt(II) complexes of methyl cyanide.[1]

No definite complex has been obtained from the reaction between chromium metal and bromine in methyl cyanide solution and, although all the reactions yielded dark green crystalline products, their analyses, while indicating chromium tribromide, gave variable amounts of methyl cyanide in the range of two to four molecules per chromium atom. There is no evidence of unco-ordinated methyl cyanide (Table 2) or, from the analyses, of

TABLE 2.

Magnetic moments and infrared and electronic (reflectance) spectra.

Complex formulated as	Magnetic moments (B.M.)	Infrared spectra (cm.$^{-1}$)			Electronic spectra (cm.$^{-1}$)		
TiCl$_4$,L	Diamagnetic	—	2272	2292	Nil		
TiBr$_4$,2L	Diamagnetic	—	2275	2295	Nil		
(TiL$_6$)(I$_3$)	1·80	—	2280	2300	—	—	—
(VCl$_3$L$_3$)L	2·85	2255	2285	2305	12,000sh, w	14,000	21,700sh
(VBr$_2$L$_4$)(Br$_3$)	2·65	—	2280	2300	9750vw	14,900	—
(VL$_6$)(I$_3$)$_3$	—	—	2287	2308	11,100vw	15,000sh	—
(CrCl$_3$L$_3$)L	3·90	2255	2285	2305	15,400	20,200	22,200sh
CrBr$_3$,xL	—	—	2285	2305	16,600	—	—
(CrI$_2$L$_4$)I	3·78	—	2285	2300	16,000	—	—

sh = shoulder, v = very, and w = weak.

any free bromine. The reflectance spectrum shows a band at 16,600 cm.$^{-1}$ consistent with the $^4T_{2g}(F)$ ◄— $^4A_{2g}$ transition in octahedral chromium; the higher energy spin-allowed bands of the chromium(III) are obscured by the charge-transfer bands of the bromide anion.

The magnetic moment of the complex CrI$_3$,4MeCN is consistent with the presence of chromium(III), and the infrared spectrum show that all four molecules of the methyl cyanide are co-ordinated to the metal ion. Little can be deduced from the reflectance spectrum (Fig. 2), since this only shows a weak shoulder at 16,000 cm.$^{-1}$ on the side of a much more intense charge-transfer band of the iodide ion, but this is approximately in the right position for the first ligand field band of the octahedral chromium(III) ion. The complex is therefore formulated as (CrI$_2$,4MeCN)I.

Conclusions.—The use of methyl cyanide as a solvent has been shown to effect a reaction between chlorine, bromine, and iodine and the first-row transition metals in all the cases examined. The products in a number of the reactions are the same as those from the dissolution of the respective halides in methyl cyanide, but the present route avoids the need to prepare the anhydrous halides. Of the three halogens, iodine yields the lowest oxidation state for a given metal which is consistent with its slower oxidation properties, but in no case has an unusual oxidation state been produced, because methyl cyanide is such a weak donor that it cannot stabilise either high or low states of oxidation. Iodine tends to produce complexes M(MeCN)$_6$MX$_4$ involving the tetrahedral anion MI$_4^{2-}$, with only titanium and vanadium giving complexes involving the tri-iodide anion. With bromine, there is no tendency for the tetrabromo-anion to be formed, but there is a preference for six-co-ordinate complexes and polybromide anions to be formed with vanadium, manganese, cobalt, nickel, and copper.[11] Chlorine has given rise to mainly six-co-ordinate complexes with no evidence for the formation of the trichloro-anion, which is consistent with the much lower stability of these anions.[12]

[11] Hathaway and Holah, unpublished results.
[12] Chattaway and Hoyle, *J.*, 1923, **123**, 654.

EXPERIMENTAL

Methyl cyanide was dried and purified as described in Part I.[1]   The details of the apparatus used in the reactions of the halogens and the metals described in this Paper are also given in Part I.[1]   The magnetic moments at room temperature, and the infrared and electronic (reflectance) spectra were measured as described previously.[13]   The metals were analysed by the methods given in Vogel,[14] titanium by reaction with Cupferron and subsequent ignition to titanium dioxide (p. 474), vanadium by oxidation to vanadium(v) followed by reduction to vanadium(iv) with sulphur dioxide, and subsequent titration with $0\cdot02$N-potassium permanganate (p. 319), and the chromium as dichromate after persulphate oxidation (p. 297).   The halides were estimated gravimetrically as the silver halide, and the free halogen by titration with sodium thiosulphate after addition of excess of potassium iodide.   The free bromine in the vanadium tribromide complex reacts with water according to the equilibrium

$$H_2O + Br_2 \rightleftharpoons Br^- + HOBr + H^+,$$
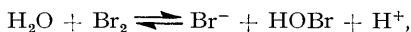
which lies completely to the right-hand side in the presence of silver nitrate.[15]   The hypobromous acid then oxidises vanadium(iii) to vanadium(v), liberating bromide ions.   Consequently, five bromide ions are estimated with silver nitrate, but only two bromine atoms are estimated in the thiosulphate titration.   The free iodine in the tri-iodide complex reacts with silver nitrate as follows [16]

$$H_2O + I_2 + AgNO_3 = HOI + HNO_3 + AgI.$$
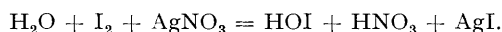
The hypoiodous acid produced is unstable and decomposes:

$$2HOI = 2HI + O_2,$$
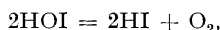
consequently, all the iodine atoms in the tri-iodide complexes are estimated as iodide with silver nitrate.

THE UNIVERSITY, HULL.

[13] Hathaway, Holah, and Hudson, *J.*, 1963, 4586.
[14] Vogel, " Textbook of Quantitative Inorganic Analysis," Longmans, Green and Co., London, 1961.
[15] Mellor, " Comprehensive Treatise on Inorganic and Theoretical Chemistry," Longmans, 1956, Supplement II, Part I, p. 713.
[16] Ref. 15, p. 870.