1082. *Reaction of Alkyl Cyanides with Chlorides and Bromides of Tervalent Titanium and Vanadium, and with Vanadium*(IV) *Chloride.*

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The trichlorides and tribromides of titanium and vanadium have been shown to react with alkyl cyanides, RCN (R = Me, Et, Pr^n), to give as products MX_3,3RCN. Vanadium(IV) chloride forms a complex, VCl_4,2RCN, but, with an excess of cyanide, reduction occurs and compounds VCl_3,3RCN are produced.

The properties of these compounds have been studied, and in particular ultraviolet, visible, and infrared spectra have been measured.

As part of an investigation of the reaction of the halides of elements of the titanium, vanadium, and chromium sub-groups with monodentate ligands, the reactions of titanium trichloride and tribromide, and of vanadium tri- and tetra-chloride and tribromide with a number of alkyl cyanides have been examined. During these studies, other workers [1] published their work on the $TiCl_3$–MeCN system.

We briefly include the results we obtained for the same system, since they contain ultraviolet (u.v.) spectral measurements on the product, and we report analogous compounds obtained from the other reactions.

EXPERIMENTAL

Materials.—Vanadium(III) chloride was prepared [2] by heating vanadium(V) oxide with sulphur monochloride under reflux for 8 hr.; the product was filtered off and washed with carbon disulphide in a closed system, then kept *in vacuo* overnight (Found: Cl, 67·2; V, 31·5. Calc. for VCl_3: Cl, 67·7; V, 32·4%). Vanadium(IV) chloride was prepared by chlorination of metallic vanadium sponge (Magneson Elektron) at 400° (Found: Cl, 72·5; V, 26·6. Calc. for VCl_4: Cl, 73·6; V, 26·4%). Vanadium(III) bromide was made by passing bromine vapour (in a stream of argon) over metallic vanadium at 400° (Found: Br, 82·7; V, 17·5. Calc. for VBr_3: Br, 82·3; V, 17·5%). The various alkyl cyanides, which were of the highest grade available, were finally dried by repeated distillation *in vacuo* from phosphoric oxide.

Analysis.—Chlorine and bromine were determined gravimetrically as the silver halides. Nitrogen was determined by the Kjeldahl method, the reflux time being 3—4 days. Vanadium was determined as previously described; [3] bromine interfered, however, and was removed by evaporation in the presence of nitric acid and sulphuric acid.

Reaction of Titanium(III) *Chloride and Bromide with Alkyl Cyanides.*—Reaction of titanium(III) chloride with methyl, ethyl, or propyl cyanide in a sealed ampoule gave in each case a blue solid and a blue solution; the solids were isolated by filtration and pumped for 6 hr. at room temperature before analysis. Reaction of the complex $TiCl_3,2NMe_3$ [4] with methyl cyanide gave the same product as did titanium(III) chloride. Titanium(III) bromide dissolved in methyl cyanide to give a green solution, from which a green solid was obtained by removal of the excess of cyanide. Table 1 gives the analytical and magnetic susceptibility data of the *compounds.* The compounds were insoluble in such organic solvents as benzene, carbon tetrachloride, and chloroform, but soluble in the corresponding alkyl cyanide.

Reaction of Vanadium(III) *Chloride and Bromide with Alkyl Cyanides.*—The halides reacted only very slowly at room temperature, but complete reaction took place under reflux. Green and brown products given, respectively, by the chloride and bromide, were filtered off and kept *in vacuo* before analysis, although one sample of the VCl_3–MeCN reaction product (†) was treated with both benzene and chlorobenzene (to test solubility) before analysis (cf. Table 2).

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[1] Clark, Lewis, Machin, and Nyholm, *J.*, 1963, 379.
[2] Kurras, *Naturwiss.*, 1959, **46**, 171.
[3] Fowles and Pleass, *J.*, 1957, 1674.
[4] Fowles and Hoodless, *J.*, 1963, 33.

TABLE 1.

Products of the TiX_3–RCN reactions.

Reactants		Products						
		Found (%)			$TiX_3,3RCN$ requires (%)			Magnetic moment
Halide, etc.	R in cyanide	X	N	Ti	X	N	Ti	μ (B.M.) *
$TiCl_3$	Me	38·1	15·4	17·2	38·4	15·2	17·3	1·58 (290°)
$TiCl_3,2NMe_3$	Me	37·6	15·2	18·0	38·4	15·2	17·3	—
$TiCl_3$	Et	32·9	13·1	15·4	33·3	13·2	15·0	1·53 (293°)
$TiCl_3$	Pr^n	29·8	11·5	13·6	29·5	11·6	13·3	1·61 (293°)
$TiBr_3$	Me	57·3	10·4	12·1	58·4	10·2	11·7	1·51 (292°)

* Figures in parentheses give the temperatures in °K.

TABLE 2.

Products of the VX_3–RCN reactions.

Reactants		Products							
		Found (%)			$VX_3,nRCN$ requires (%)				Magnetic moment *
Halide, X	R in cyanide	X	N	V	X	N	V	n	(μ (B.M.))
Cl †	Me	36·0	15·7	17·9	37·9	14·3	18·2	3	2·75
Cl	Me	33·1	17·5	16·0	32·2	17·4	15·8	4	—
Cl	Et	32·0	13·3	15·8	33·0	13·0	15·8	3	2·59
Br	Me	52·7	12·2	11·4	52·7	12·3	11·2	4	2·56
Br	Et	51·9	9·4	11·3	52·6	9·2	11·2	3	2·50

* Values for 293°K.

All these *compounds* were slightly soluble in the alkyl cyanide at room temperature; the chloro-compounds also appeared to dissolve slightly in benzene, giving a brown solution, although the bromo-compounds were insoluble in this solvent.

The thermal stability of the adducts was studied by heating them *in vacuo* for 2 hr. at each of several temperatures over the range 20—200°; any liberated alkyl cyanide was immediately trapped out in a liquid-oxygen bath. The results of these experiments are summarised in Fig. 1.

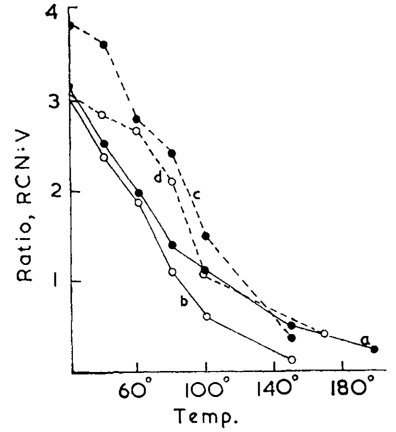

FIG. 1. Thermal decomposition of complexes of (a) VCl_3–MeCN, (b) VCl_3–EtCN, (c) VBr_3–MeCN, and (d) VBr_3–EtCN.

Reaction of Vanadium(IV) *Chloride with Alkyl Cyanides.*—(*a*) *In the presence of an additional inert solvent.* Vanadium(IV) chloride reacted with methyl cyanide in carbon tetrachloride solution to give a dark purple residue whose composition corresponded to $VCl_4,2MeCN$ (Found: Cl, 50·3; N, 10·9; V, 18·3. $VCl_4,2MeCN$ requires Cl, 51·6; N, 10·2; V, 18·5%). The *product* sublimed readily *in vacuo* at 80°, and the purple-black product then had an analysis even closer to the theoretical value (Found: Cl, 51·6; N, 10·1; V, 18·7%). It had a magnetic moment

(μ) of 1·77 B.M. at 20°; it was insoluble in " iso-octane," moderately soluble in benzene, and gave a green solution in methyl cyanide.

The analogous *ethyl cyanide compound*, which was prepared and purified by sublimation in a similar manner, was also purple-black (Found: Cl, 47·0; N, 9·1; V, 17·3%; *M*, 144. VCl_4,2EtCN requires Cl, 46·8; N, 9·25; V, 16·8%; *M*, 303.

(*b*) *Direct reaction.* Vanadium(IV) chloride and methyl cyanide reacted to give a greenish-brown sludge and a brown solution, filtration of which gave a green solid. The brown solution deposited a brown residue on removal of the excess of methyl cyanide at the pump. The compositions of the green and the brown solid varied somewhat from experiment to experiment, although the V : Cl ratio was always quite close to 1 : 3 for both. Typical analytical data were: (for green insoluble product) Cl, 36·0; N, 15·7; V, 17·8%; corresponding to Cl : N : V = 2·93 : 3·18 : 1·00; (for brown soluble product) Cl, 31·2; N, 18·2; V, 15·2%; corresponding to Cl : N : V = 2·99 : 4·35 : 1·00. Direct titration of the products with a standard solution of an oxidising agent (ceric sulphate or potassium permanganate) showed that in both cases the vanadium was in oxidation state +3. Thermal decomposition of the green product gave a similar curve to that obtained for VCl_3,3MeCN (cf. Fig. 1). Since vanadium is evidently reduced to the tervalent state, and one atom of chlorine is lost to the system, attempts were made to identify the oxidation products of the methyl cyanide. The methyl cyanide solution contained a great deal of hydrogen chloride (identified with silver nitrate) but no chlorinated species (*i.e.*, compounds containing a C–Cl bond) could be isolated by fractionation; an unidentified dark brown tarry residue remained. In an attempt to prepare a more concentrated solution of the oxidised product, an ampoule was made up containing only a small excess of methyl cyanide; the infrared spectrum of the distillate then showed strong peaks at 710 and 773 cm.$^{-1}$.

Spectra.—Visible and ultraviolet spectra measurements were made with a Unicam S.P. 500 spectrophotometer. Solutions were prepared in 1 cm. or 1 mm. silica cells attached to the vacuum-line, the cells being sealed before removal from the line. Infrared spectra were recorded on S.P. 100, S.P. 200, and Infracord (KBr) spectrophotometers, for Nujol mulls (between potassium bromide discs) and solutions in the alkyl cyanides. Special precautions were taken [5] to avoid oxidation or hydrolysis of the compounds.

Conductivities.—These were measured by means of a Phillips PR 9500 conductivity bridge and a cell specially adapted to be filled on the vacuum-line.

Magnetic Susceptibility and Molecular-weight Measurements.—These were made as described previously.[3,4]

RESULTS AND DISCUSSION

The compounds formed by the trichlorides of titanium and vanadium are non-electrolytes since their solutions in the alkyl cyanide are virtually non-conducting (cf. Table 3).

TABLE 3.

Molar conductivity of compounds MCl_3,3RCN in RCN.

Compound	Molar conductivity * (ohm^{-1} cm.^{2})	Compound	Molar conductivity * (ohm^{-1} cm.^{2})
MeCN as solvent		EtCN as solvent	
Et_4NBr	159	Et_4NBr	156
$TiCl_3$,3MeCN	18	$TiCl_3$,3EtCN	14
VCl_3,3MeCN	3·3	VCl_3,3EtCN	2·5

* For ~10^{-3}M-solutions.

The conductivities of the analogous bromo-compounds were not measured, but the compounds are also likely to be non-electrolytes. Because the compounds are insufficiently soluble in solvents such as benzene and nitrobenzene, molecular-weight measurements could not be made, so it is not possible to prove that the compounds are monomeric. The analogous tervalent molybdenum complex, $MoBr_3$,3Pr^{n}CN, is, however, known [6] to be

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[5] Duckworth and Fowles, *J. Chem. Educ.*, 1962, **39**, 474.

[6] Allen and Fowles, unpublished observations.

monomeric in benzene solution and, since tervalent titanium and vanadium do not normally show covalencies greater than six, we suppose that their cyanide complexes are also octahedral.

The infrared spectra of the complexes are given in Table 4, together with the spectra of the cyanides themselves; only peaks of medium to strong intensity are recorded. Two regions are of particular interest. The C≡N stretching frequency (~2300 cm.$^{-1}$) in every case increases by 20—30 cm.$^{-1}$ when the cyanide co-ordinates, and this increase evidently arises through coupling of the M–N and C≡N stretching vibrations.[7] By means of equations (suitably modified) originally used for chloroacetylene,[8] and a simple linear model $M \longleftarrow N{\equiv}C{-}Me$, Beattie[9] has calculated that the observed frequency increase is of the order to be expected. There is no splitting of the peak, which shows that there can be no significant coupling through the metal atoms, since such a coupling would result in several peaks. Two peaks are observed for the methyl cyanide compounds, but these are also present in methyl cyanide; one (2260 cm.$^{-1}$) is the C≡N stretching frequency, and the other (2295 cm.$^{-1}$) has been assigned to either a combination band of the symmetric CH_3 deformation vibration and the symmetric C–C stretching vibration[10] or to an overtone.[11]

TABLE 4.

Infrared spectra of $MCl_3,3RCN$ compounds (in cm.$^{-1}$).

	Metal in $MCl_3,3MeCN$			Metal in $MCl_3,3EtCN$				
MeCN *	Ti	V	EtCN *	Ti	V	Pr^{n}CN †	$TiCl_3,3Pr^nCN$ †	Assignment
2295m	2305m	2300s						Combination band
2260s	2280s	2270s	2260s	2295s	2275s	2265s	2295s	CN str.
		1610s			1605s			
		1600s						
1460s	N	N	1480s	N	N	1470s	N	
						1435s	1430s	
1390s	N	N	1400s	N	N	1395s	N	
			1300s	1320s	1315s	1350s	1350s	
						1340m	1330m	
1050s	1040m	1160m	1090s	1085m	1075s	1110m	1115m	
		1035s						
			1020m	1010m	1010m	1060m	1055m	
930s	950m	980s			995m	920m	930m	
	890s	945s		890s		880m	880s	
			845m	860m	855m	845m	850m	
	790s	825s	790s	790m	790s	770m	790m	
750s	730m		760m	730m		745m	745m	
			545s	560m	562m			
	408m	421s		400s	414s			M–Cl str.

N = Nujol. * Measured as liquid films between KBr discs. † Not measured below 700 cm.$^{-1}$.

The peaks found between 400 and 421 cm.$^{-1}$ may be metal–chlorine stretching frequencies, although such frequencies for octahedral complexes of quadrivalent elements are usually below 400 cm.$^{-1}$. Thus, in the complex $SnCl_4,2MeCN$ they are found at 365, 339, and 306 cm.$^{-1}$,[12] and in $TiCl_4$,dipyr they are reported[13] to occur between 350 and 390 cm.$^{-1}$. In our complexes, the metal is in the tervalent state, however, and this may result in a small increase in the metal–chlorine stretching frequencies.

The visible spectra of solutions of the complexes in the alkyl cyanide are also in agreement with octahedral configurations. Clark *et al.*[1] found that the absorption spectrum

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[7] Nightingale, Proc. 7th Internat. Conf. Co-ordination Chemistry, Stockholm, 1962, p. 217.
[8] Richardson and Goldstein, *J. Chem. Phys.*, 1950, **18**, 1314.
[9] Beattie, personal communication.
[10] Venkateswarlu, *J. Chem. Phys.*, 1951, **19**, 293.
[11] Herzberg, " Infrared and Raman Spectra," Van Nostrand, New York, 1945, p. 332.
[12] Beattie, McQuillan, Rule, and Webster, *J.*, 1963, 1514.
[13] Clark, *J.*, 1963, 1377.

of a solution of titanium(III) chloride in methyl cyanide showed a peak and a shoulder in the visible region, and they observed that the solid $TiCl_3,3MeCN$ showed the same two peaks in its diffuse reflectance spectrum. Our solution measurements (cf. Fig. 2 and Table 5) were made on solutions of the recrystallised products, rather than titanium(III) chloride, since the latter was usually contaminated with traces of other materials. The spectra of all three chloride products $TiCl_3,3RCN$ (R = Me, Et, and Pr^n) were almost identical, within the limits of the spectrophotometer. The peak positions and extinction coefficients are in good agreement with those obtained for the methyl cyanide adduct by Clark, and we agree with the assignments: 14,700 cm.$^{-1}$, $^2A_{1g} \leftarrow {}^2B_{2g}$; 17,200 cm.$^{-1}$, $^2B_{1g} \leftarrow {}^2B_{2g}$.

TABLE 5.

Spectra of $MX_3,3RCN$ in RCN.

Compound	Peak positions (cm.$^{-1}$) (ε in parentheses)
$TiCl_3,3MeCN$	14,700sh (~15); 17,200 (31); 31,000sh (~500); 35,100 (1100); 43,500 (400)
$TiBr_3,3MeCN$	16,300 (50)
$TiCl_3,3EtCN$	14,700; 17,200
$TiCl_3,3Pr^nCN$	14,700; 17,200
$VCl_3,3MeCN$	14,400 (28); 20,000sh (~20); 30,850 (4400); 41,800 (8700)
$VCl_3,3EtCN$	14,600 (20); 30,900 (4500); 41,600 (9100)
$VBr_3,3MeCN$	14,000 (25); 21,000 (~1300); 24,200 (2800); 36,400br (7000); 42,000sh (~10,000)
$VBr_3,3EtCN$	13,900 (35); 21,000 (~1400); 24,200 (3300); 35,700br (8000); ~42,000sh (~10,000)

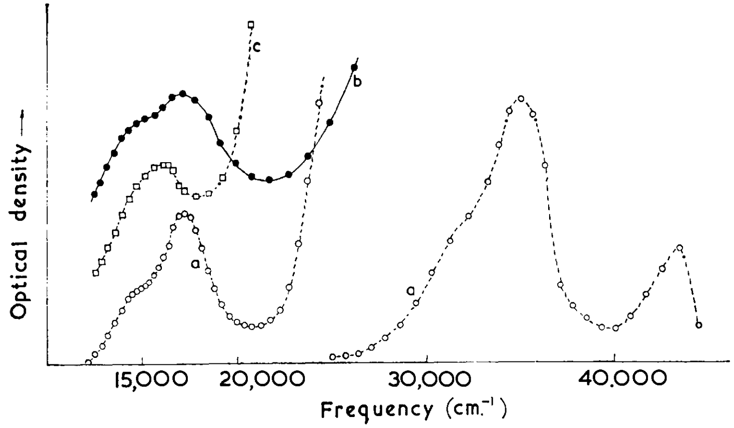

FIG. 2. Spectra of (a) $TiCl_3,3MeCN$ in MeCN, (b) $TiCl_3,3MeCN$ (diffuse reflectance), and (c) $TiCl_3,3EtCN$ in EtCN.

The bromide complex, $TiBr_3,3MeCN$, shows a similar spectrum, although the shoulder is no longer observed except as a broadening and asymmetry of the main peak. The separation of the components of the ^2E_g level is thus less than it is with the chloride complex. Furthermore, the main peak shows a shift of some 1000 cm.$^{-1}$ to lower wave numbers; this agrees with the accepted ligand-field strength order Cl > Br. A similar shift was observed with the trimethylamine complexes, $TiX_3,2NMe_3$.[4]

The ultraviolet spectrum of a solution of the complex $TiCl_3,3MeCN$ in methyl cyanide shows two peaks, at 35,100 and 43,500 cm.$^{-1}$, the former having a strong shoulder at 31,000 cm.$^{-1}$. None of these peaks has a very large extinction coefficient, but the values (400—1100) show that the peaks are of the charge-transfer type. While the exact nature of the transitions is unknown, it is possible to comment on the general type of charge-transfer band to be expected in such compounds and make tentative assignments. There are two general types: (*a*) transfer of the *d*-electron of titanium to antibonding π-molecular orbitals associated with the ligands; (*b*) transfer of π-electrons from the ligands to vacant *d*-levels of the titanium. The transfer of electrons from the titanium–ligand σ bonds is much less likely and can be ruled out.

Measurements of the ultraviolet spectra of several related complexes have been made, and provisional assignments have been suggested (cf. Table 6). The complexes of quadrivalent titanium only show peaks corresponding to transfer of charge from the ligands to titanium, or possibly $\pi \rightarrow \pi^*$ transitions for suitable ligands such as pyridine. The peak observed at 45,050 cm.$^{-1}$ for the hexachlorotitanate(IV) anion must be associated with the transfer of the chlorine π-electrons, and it seems reasonable to suppose that such charge-transfer bands in any chloro-complex of quadrivalent titanium will occur in the 45,000 cm.$^{-1}$ region. The additional band at 31,750 cm.$^{-1}$ observed for the methyl cyanide complex, $TiCl_4$,2MeCN, has therefore been considered[15] to involve the π-electrons of the co-ordinated methyl cyanide ligands. A similar pair of peaks (at 45,700 and 33,400 cm.$^{-1}$) has been observed[15] for the zirconium complex ZrCl,2MeCN; the shift to higher wave numbers, compared with those for titanium, agrees with the chemical fact that it is harder to reduce zirconium to the tervalent state.

TABLE 6.

Ultraviolet spectra of titanium complexes.

Complex	Spectra peaks (cm.$^{-1}$)	Assignments	Ref.
$[TiCl_6]^{2-}$	45,050	$Cl(\pi) \rightarrow Ti$	14
$TiCl_4$,2MeCN	45,050	$Cl(\pi) \rightarrow Ti$	15
	31,750	$MeCN(\pi) \rightarrow Ti$	
$Ti(acac)_3$	32,400	$\pi_3 \rightarrow \pi_4$	16
	27,500	$Ti(d) \rightarrow \pi_4(e)$	
$TiCl_3$,3THF	20,400	$Cl(\pi) \rightarrow Ti$	1
$TiCl_3$	18,500	$Cl(\pi) \rightarrow Ti$	1
$[TiCl_2py_3(MeCN)]^+$	42,550	$\pi \rightarrow \pi^*$	4
	35,710	$MeCN(\pi) \rightarrow Ti$	
	25,640	$Ti(d) \rightarrow$ Ligand	

Extension of the arguments to the cyanide complexes of tervalent titanium suggests that analogous bands should occur, and the peak at 35,100 cm.$^{-1}$ is believed to result from the transfer of π-electrons from the methyl cyanide ligands. The shoulder at ~31,000 cm.$^{-1}$ could correspond to the transfer of the titanium *d*-electron to an antibonding molecular orbital associated with the methyl cyanide ligands. This may be compared with the assignments made for the spectrum of the acetylacetone complex; Barnum[16] calculated that the peak at 27,500 cm.$^{-1}$ corresponded to a transition from the titanium $^2B_{2g}$ level to an antibonding $\pi_4(e)$-orbital of the acetylacetone groups. The band found at 43,500 cm.$^{-1}$ for the complex, $TiCl_3$,3MeCN, is, we believe, associated with the transfer of the chlorine π-electrons.

Our provisional assignments are not in accord with those suggested by Clark *et al.*[1] for the complex $TiCl_3$,3THF and for titanium trichloride, where the bands in the 18,000—20,000 cm.$^{-1}$ region were considered to involve the transfer of the chlorine π-electrons.

The methyl cyanide complex of vanadium(III) chloride, VCl_3,3MeCN, shows two peaks in the visible region of its spectrum (cf. Fig. 3), one at 14,400 and the other (a shoulder) at ~20,000 cm.$^{-1}$; the spectrum is the same for a solution in methyl cyanide and for the solid. These peaks have been assigned[1] to the transitions $^3T_{2g} \leftarrow {}^3T_{1g}$ (F) and $^3T_{1g}$ $(P) \leftarrow {}^3T_{1g}$ (F). The spectrum of the analogous ethyl cyanide complex shows one ligand field peak at 14,600 cm.$^{-1}$, but the second peak is not detected, even as a shoulder,

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[14] Jørgensen, " Absorption Spectra and Chemical Bonding in Complexes," Pergamon, Oxford, 1962, p. 284.

[15] Fowles, Walton, and Williams, unpublished observations.

[16] Barnum, *J. Inorg. Nuclear Chem.*, 1961, **21**, 221; **22**, 183.

and must be obscured by the charge-transfer bands. In the analogous bromo-complexes, $VBr_3,3RCN$, the first peak is again found (cf. Fig. 4) although it has shifted to around 14,000 cm.$^{-1}$ as might be expected in view of the smaller ligand field of bromine than of chlorine. The charge-transfer bands for the bromo-complexes come much more into the visible region than do those for the chloro-complexes, and they completely eclipse the second ligand-field band.

The ultraviolet spectra of the chloro-complexes show two main peaks, around 31,000 and 42,000 cm.$^{-1}$, and by analogy with the spectra of the titanium complexes these peaks can be assigned, respectively, to transitions involving the π-electrons of the co-ordinated alkyl cyanide groups and the π-electrons of the chlorine atoms. There is thus a small shift of the peaks to lower wave numbers than with the titanium analogues, and this is in line with the observation that it is somewhat easier to reduce tervalent vanadium than tervalent titanium. As Fig. 3 shows, the spectra of both complexes show an additional shoulder and this could be associated with transitions involving the *d*-electrons.

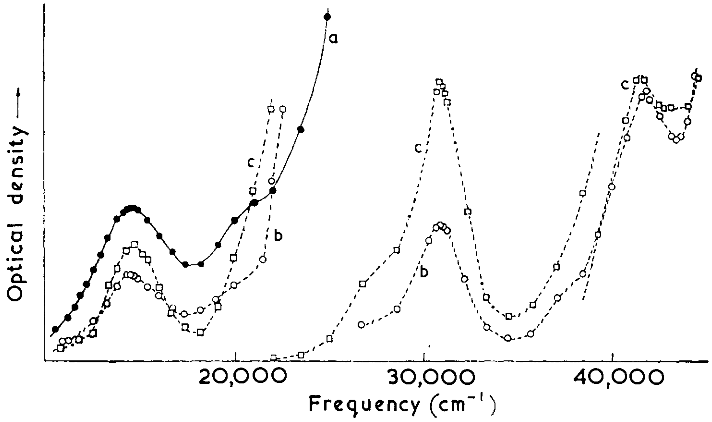

FIG. 3. Spectra of (a) $VCl_3,3MeCN$ (diffuse reflectance), (b) $VCl_3,3MeCN$ in MeCN, and (c) $VCl_3,3EtCN$ in EtCN.

The ultraviolet spectra of the bromo-complexes are much more complicated, there being five peaks in all, the two at the highest wave numbers being broad and ill-defined. All the peaks are at much lower wave numbers than for the chloro-complexes, and it is clear that the π-electrons of the bromine atoms can be transferred much more readily than those of the chlorine atoms. It is doubtful whether any detailed assignments can be made in such a complex system.

The magnetic moments of the four alkyl cyanide complexes of titanium are somewhat below the spin-only value, and range from 1·51 for $TiBr_3,3MeCN$ to 1·61 for $TiCl_3,3Pr^nCN$. Clark *et al.* report inconsistent values between 1·58 and 1·68 B.M. for $TiCl_3,3MeCN$, and suggest that the highest value may be the most reliable. For this particular compound we obtained consistent results, but they were always very close to 1·58 B.M. A very recent report[17] on $TiCl_3,3EtCN$, gives a value of 1·59 B.M. for the room-temperature magnetic moment. The magnetic moment of the methyl cyanide complex formed by vanadium(III) chloride is close to the spin-only value; but the other complexes have somewhat lower moments, between 2·5 and 2·6 B.M. Similar moments have been observed for other vanadium(III) complexes.[18]

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[17] Kern, *J. Inorg. Nuclear Chem.*, 1963, **25**, 5.

[18] Duckworth, Fowles, and Williams, *Chem. and Ind.*, 1962, 1285.

Funk and his co-workers[19] reported that a complex $VCl_4,2MeCN$, was formed when carbon tetrachloride solutions of vanadium(IV) chloride and methyl cyanide were mixed. We have confirmed this and prepared also the ethyl cyanide complex. Both compounds sublime readily *in vacuo* as purple-black crystals that dissolve in benzene to brown solutions. Molecular-weight measurements on these solutions show an approximately two-fold depression, indicating extensive dissociation, presumably of the type: $VCl_4,2RCN \rightleftharpoons VCl_4,RCN + RCN$. This is in agreement with the conclusions of Ulich *et al.*,[20] who studied the dipole moments of the analogous ethyl cyanide complexes of tin(IV) chloride and titanium(IV) chloride in benzene solution. Similarly, Beattie and his co-workers[12] have found that the infrared spectrum of the tin complex $SnCl_4,2MeCN$ in benzene solution is different from that in a Nujol mull, and they consider that a 1 : 1 adduct may be present. A strong band at 402 cm.$^{-1}$ was thought to be associated with a tin–chlorine stretching frequency. The vanadium(IV) chloride methyl cyanide and ethyl cyanide complexes in benzene solution show strong peaks at 438 and 432 cm.$^{-1}$, respectively, and these peaks are not given by Nujol mulls. This suggests that, while the vanadium atom may be octahedrally co-ordinated in the solid, it is five-co-ordinate in benzene solution, since the vanadium–chlorine stretching frequencies, which would be expected to be below 400 cm.$^{-1}$ for octahedral complexes, would be somewhat higher for compounds of lower co-ordination number. Vanadium–chlorine stretching frequencies for the five-co-ordinate complexes $VCl_3,2L$ have been assigned[18] to peaks at 444, 424, and 427 cm.$^{-1}$ for L = NMe_3, SMe_2, and SEt_2, respectively.

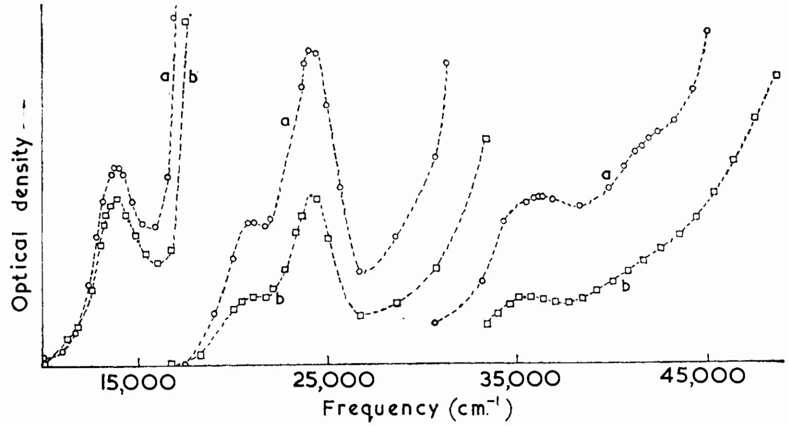

FIG. 4. Spectra of (a) $VBr_3,3MeCN$ in MeCN and (b) $VBr_3,3EtCN$ in EtCN.

The visible spectra of the vanadium(IV) complexes (cf. Fig. 5) in benzene solution are rather ill-defined. Thus, for the complex, $VCl_4,2MeCN$, there is rising absorption towards the ultraviolet with indications of at least two shoulders at ~20,000 and ~22,000 cm.$^{-1}$ ($\varepsilon_{max.} \sim 500$) together with a definite peak at 30,000 cm.$^{-1}$ (ε 900). We cannot comment in detail on these spectra, in view of the unsymmetrical nature of the absorbing species, except to suggest that the peak at 30,000 cm.$^{-1}$ is of the charge-transfer type and may be associated with the transfer of charge from the π-electrons of the methyl cyanide to one of the vacant *d*-orbitals.

While the compounds formed by the reaction of vanadium(IV) chloride with alkyl cyanides in the presence of a solvent are undoubtedly of quadrivalent vanadium ($\mu = 1{\cdot}77$ B.M. for $VCl_4,2MeCN$), quantitative reduction to the tervalent state takes place in the presence of

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[19] Funk, Mohaupt, and Paul, *Z. anorg. Chem.*, 1959, **302**, 199.
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an excess of alkyl cyanide. The reduction of transition-metal halides by alkyl cyanides in not unknown. For instance, Schneider reports[21] the reduction of copper(II) bromide by methyl cyanide to the copper(I) state, and in these laboratories we have found[22] that any alkyl cyanide reduces molybdenum(V) chloride and the chlorides and bromides of quinque- and sexi-valent tungsten to the quadrivalent state, with the formation of complexes of the type $MX_4,2RCN$. Schneider found that bromine was liberated in the reaction. In the reaction of alkyl cyanides with vanadium(IV) chloride, however, we found no chlorine gas, but a very high yield of hydrogen chloride. Since hydrogen chloride is formed, a hydrogen atom must be removed from the methyl group (in methyl cyanide), leaving the radical $\cdot CH_2\cdot CN$ that may dimerise or initiate polymerisation of the methyl cyanide. Hydrogen chloride forms an unstable compound with methyl cyanide that has been formulated[23] as $[CH_3\cdot CNH]^+[HCl_2]^-$. Such a complex loses hydrogen chloride *in vacuo* and its infrared spectrum does not show a C–Cl stretching frequency. However, although no volatile chloro-compound (other than hydrogen chloride) could be detected in the normal reactions between vanadium(IV) chloride and methyl cyanide, concentration of the products formed in reactions in which there was only a slight excess of methyl cyanide gave a volatile liquid whose infrared spectrum showed quite strong C–Cl stretching frequencies (713 and 773 cm.$^{-1}$). Evidently some chlorination of the methyl cyanide takes place under these conditions. The nature of the oxidation products of the alkyl cyanides is being further investigated.

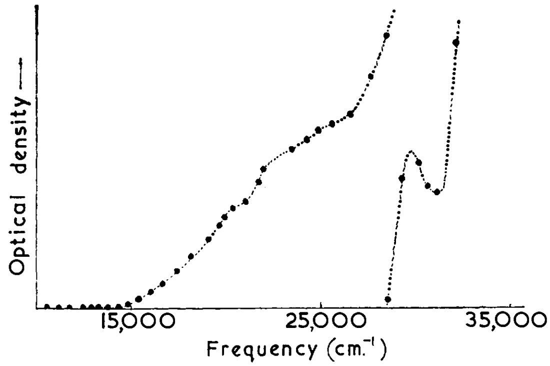

FIG. 5. Spectrum of $VCl_4,2MeCN$ in benzene.

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