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## Preparations, Structures, Electronic Spectra, and Magnetism of Vanadium(III) Alcoholates<sup>1</sup>

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Vanadium trichloride is shown to react with methyl, ethyl, *n*-propyl, isopropyl, *n*-butyl, isobutyl, *sec*-butyl, and cyclohexyl alcohols to form alcoholates. As demonstrated by detailed conductance measurements, the complexes when dissolved in the parent alcohol behave as 1:1 electrolytes and should therefore be formulated as  $[V(\text{ROH})_4\text{Cl}_2]\text{Cl}$  in solution. Their electronic spectra have been recorded and assigned. The complexes isolated from the above solutions may possess not only the formula  $\text{VCl}_3 \cdot 4\text{ROH}$  (with the above structure) but also the formula  $\text{VCl}_3 \cdot 3\text{ROH}$  (these being six-coordinate neutral monomers). The diffuse reflectance spectra of the complexes are compared with the solution spectra and also assigned. The magnetic moments of the complexes have been measured at 12–23 points over the range 321–80°K and the data have been analyzed in terms of the splitting of the ground  ${}^3T_{1g}$  term (in  $O_h$  nomenclature) by the asymmetry of the ligand field and in terms of other magnetic parameters. Vanadium–chlorine stretching frequencies occur near  $330\text{ cm}^{-1}$  in these complexes. One bromo complex,  $[V(i\text{-C}_3\text{H}_7\text{OH})_4\text{Br}_2]\text{Br}$ , has also been prepared and studied by the above techniques. It is concluded that alcohols, unlike water and urea, are not able to displace all of the halogen atoms from the first coordination sphere of the parent trihalide.

### Introduction

Complex ions of the type  $\text{ML}_6^{3+}$  ( $M = \text{Ti}$  or  $\text{V}$ ;  $L =$  neutral ligand) are comparatively rare.<sup>2</sup> Among the few established cases are the ions<sup>3–6</sup>  $\text{Ti}(\text{H}_2\text{O})_6^{3+}$ ,  $\text{V}(\text{H}_2\text{O})_6^{3+}$ ,  $\text{Ti}(\text{urea})_6^{3+}$ , and  $\text{V}(\text{urea})_6^{3+}$ , for all of which a variety of physical data are available both for the dissolved and for the crystalline states.<sup>2</sup> It has also been reported that ions of the types  $\text{Ti}(\text{ROH})_6^{3+}$  ( $R = \text{CH}_3$ ,  $\text{C}_2\text{H}_5$ , or *i*- $\text{C}_3\text{H}_7$ )<sup>7</sup> and  $\text{V}(\text{ROH})_6^{3+}$  ( $R = \text{CH}_3$ ,  $\text{C}_2\text{H}_5$ , or *i*- $\text{C}_4\text{H}_9$ )<sup>4</sup> exist, both in solution in the parent alcohol and as the crystalline chloro complexes.

Subsequent work on the titanium(III) complexes of methyl,<sup>3</sup> isopropyl, *sec*-butyl, and cyclohexyl<sup>9</sup> alcohols indicated that their correct stoichiometry is  $\text{TiCl}_3 \cdot 4\text{ROH}$ , although the complex  $\text{TiCl}_3 \cdot 5\text{CH}_3\text{OH}$  has also been reported.<sup>8</sup> A reinvestigation of the vanadium trichloride–methanol system<sup>10</sup> indicated the existence of the complexes  $\text{VCl}_3 \cdot 5\text{CH}_3\text{OH}$  (with the fifth methanol molecule only loosely bound),  $\text{VCl}_3 \cdot 4\text{CH}_3\text{OH}$ , and  $\text{VCl}_3 \cdot 3\text{CH}_3\text{OH}$  but not  $\text{VCl}_3 \cdot 6\text{CH}_3\text{OH}$ . With ethanol, the previous workers<sup>10</sup> isolated the complex  $\text{VCl}_3 \cdot 3\text{C}_2\text{H}_5\text{OH}$  and with isopropyl alcohol, the complexes  $\text{VCl}_3 \cdot 4i\text{-C}_3\text{H}_7\text{OH}$  and  $\text{VCl}_3 \cdot 3i\text{-C}_3\text{H}_7\text{OH}$ ; in no case, however, was the structure established.

If the vanadium(III) alcoholates were correctly formulated as  $\text{V}(\text{ROH})_6^{3+}$ , the frequencies of the two observed spin-allowed d–d transitions would imply that

the ligand field strengths of alcohols are much lower than those of other oxygen-donor ligands.<sup>2</sup> In the belief that this situation is unlikely, we set out to study the reactions of vanadium trichloride (and in one case of vanadium tribromide) with a large series of alcohols ( $\text{CH}_3\text{OH}$ ,  $\text{C}_2\text{H}_5\text{OH}$ , *n*- and *i*- $\text{C}_3\text{H}_7\text{OH}$ , *n*-, *i*-, and *sec*- $\text{C}_4\text{H}_9\text{OH}$ , and  $\text{C}_6\text{H}_{11}\text{OH}$ ) in order to ascertain the correct absorbing species in solution and in the solid state. All of the complexes are found to be formulated, on the basis of conductance and spectral work, as  $[\text{V}(\text{ROH})_4\text{Cl}_2]\text{Cl}$  in solution, and in the solid state either in the same way or as  $\text{VCl}_3 \cdot 3\text{ROH}$ . Detailed measurements of the magnetic moments of the solid complexes have been carried out between room and liquid nitrogen temperatures in order to compare the various derived magnetic parameters with those found previously for other titanium(III)<sup>11</sup> and vanadium(III)<sup>12,13</sup> complexes.

### Experimental Section

**Trichloride.**—The anhydrous trichloride used for the syntheses was the British Drug Houses Ltd. product. That used for the conductivity measurements was the BDH product, chlorinated to  $\text{VCl}_4$ , twice distilled, and then decomposed<sup>2</sup> to  $\text{VCl}_3$ .

**Tribromide.**—The anhydrous compound was obtained from K & K Laboratories Inc. Another sample was obtained by passing a stream of  $\text{N}_2$  and  $\text{Br}_2$  over powdered vanadium at  $\sim 470^\circ$ . The brown tribromide condensed in the cooler part of the tube.<sup>2</sup> This material reacted more quickly than the commercial one, but the products appeared to be the same. Both the trichloride and tribromide were analyzed satisfactorily for halogen.

**Treatment of the Alcohols.**—The various alcohols were dried as follows:  $\text{CH}_3\text{OH}$ , treated with iodine-activated magnesium;  $\text{C}_2\text{H}_5\text{OH}$ , first treated with a molecular sieve and then with sodium metal and finally refluxed with diethyl succinate; *n*- $\text{C}_3\text{H}_7\text{OH}$ , treated with iodine-activated magnesium; *i*- $\text{C}_3\text{H}_7\text{OH}$ , treated with aluminum isopropoxide and then fractionated; *n*- $\text{C}_4\text{H}_9\text{OH}$ , first treated with sodium metal and then refluxed with dibutyl phthalate; *i*- and *sec*- $\text{C}_4\text{H}_9\text{OH}$  and  $\text{C}_6\text{H}_{11}\text{OH}$ , all

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TABLE I  
ANALYTICAL DATA

Complex	Color	% C		% H		% Cl		% V	
		Calcd	Found	Calcd	Found	Calcd	Found	Calcd	Found
VCl <sub>3</sub> ·4CH <sub>3</sub> OH	Green	16.8	17.3	5.6	6.4	37.3	37.0	17.8	17.0
VCl <sub>3</sub> ·3C <sub>2</sub> H <sub>5</sub> OH	Green	24.4	23.9	6.1	6.2	36.0	36.0	17.2	16.3
VCl <sub>3</sub> ·4 <i>n</i> -C <sub>3</sub> H <sub>7</sub> OH	Brown	36.2	35.2	8.1	7.6	26.7	26.9	12.8	13.2
VCl <sub>3</sub> ·4 <i>i</i> -C <sub>3</sub> H <sub>7</sub> OH	Green	36.2	36.3	8.1	8.7	26.7	26.1	12.8	12.4
VBr <sub>3</sub> ·4 <i>i</i> -C <sub>3</sub> H <sub>7</sub> OH	Green	27.1	27.6	6.1	6.4	45.2 <sup>a</sup>	46.7 <sup>a</sup>	9.6	9.9
VCl <sub>3</sub> ·3 <i>n</i> -C <sub>4</sub> H <sub>9</sub> OH	Brown	37.9	37.4	8.0	8.6	28.0	27.5	13.4	12.6
VCl <sub>3</sub> ·3 <i>i</i> -C <sub>4</sub> H <sub>9</sub> OH	Brown	37.9	37.6	8.0	8.9	28.0	27.0	13.4	13.9
VCl <sub>3</sub> ·3 <i>sec</i> -C <sub>4</sub> H <sub>9</sub> OH	Brown	37.9	37.3	8.0	8.5	28.0	27.3	13.4	12.8
VCl <sub>3</sub> ·4 <i>sec</i> -C <sub>4</sub> H <sub>9</sub> OH	Green	42.3	41.4	8.9	8.0	23.4	23.0	11.2	11.4
VCl <sub>3</sub> ·4C <sub>6</sub> H <sub>11</sub> OH	Pale brown	51.7	49.4	8.7	8.3	19.1	19.2	9.1	9.4

<sup>a</sup> Bromine.

treated with an ethereal solution of ethylmagnesium bromide and then fractionated.

**Preparation of Complexes.**—The general method for the preparation of the complexes was to distil the alcohol in excess (~125 ml) onto the vanadium trihalide (~5 g) and then to reflux gently for *ca.* 1 hr. The mixture was then cooled and treated as indicated below to precipitate the required adduct. The reactions appeared to be complete (judged by the evident disappearance of the trihalide) in general within *ca.* 10 min. If the reflux was continued for periods longer than 1 hr, no change in any properties (including analyses of the products) could be brought about. Most of the conductance data (below) were obtained on the complexes prepared in the above manner. All operations were carried out under rigorously dried nitrogen on a vacuum line. Cyclohexyl alcohol reacts much slower than the other alcohols.

The precipitation procedures specific to each complex were as follows. CH<sub>3</sub>OH complex: this precipitated after removal of half of the solvent under vacuum followed by cooling in a Dry Ice-acetone mixture. Recrystallization from methanol was not successful. C<sub>2</sub>H<sub>5</sub>OH complex: on cooling the solution to -40° and saturating it with hydrogen chloride, a green solid precipitated from the then dark brown solution. *n*-C<sub>3</sub>H<sub>7</sub>OH complex: as removal of the solvent under vacuum did not result in the formation of any precipitate, the complex was isolated in the way described for the C<sub>2</sub>H<sub>5</sub>OH complex. The brown solid then precipitated from the brown solution. *i*-C<sub>3</sub>H<sub>7</sub>OH complex: the solid complex precipitated immediately on treatment of the trichloride with the alcohol; it may be recrystallized from isopropyl alcohol. *n*-C<sub>4</sub>H<sub>9</sub>OH complex: this precipitated after removal of two-thirds of the alcohol in the form of a brown solid. *i*-C<sub>4</sub>H<sub>9</sub>OH: isolated as for the C<sub>2</sub>H<sub>5</sub>OH complex; it precipitated as a brown solid from a brown solution. *sec*-C<sub>4</sub>H<sub>9</sub>OH: after removal of half of the alcohol, a brown solid precipitated from the green solution; if the latter was filtered off and then cooled to 0° and allowed to stand overnight, a green solid was deposited. *t*-C<sub>4</sub>H<sub>9</sub>OH: no solid could be obtained except by evaporation of seven-eighths of the solvent; this procedure caused extensive decomposition of the complex. C<sub>6</sub>H<sub>11</sub>OH: after reflux of the mixture for 4-5 hr, a yellow-brown solid precipitated; an equal volume of anhydrous diethyl ether was added to the solution to assist in the filtration of the solid. In general, the complexes were washed several times with freshly distilled diethyl ether and then filtered off, dried *in vacuo*, and transferred to glass manifolds which were evacuated and sealed off.

**Analyses.**—Carbon, hydrogen, and halogen analyses were determined at professional analytical laboratories. Vanadium was determined both by Nakazono's method<sup>14</sup> and also by atomic absorption spectrophotometry. The results are in Table I.

**Conductance Measurements.**—The equivalent conductances of the complexes were determined by breaking a tared ampoule of the trihalide or of the complex under argon into a glass ap-

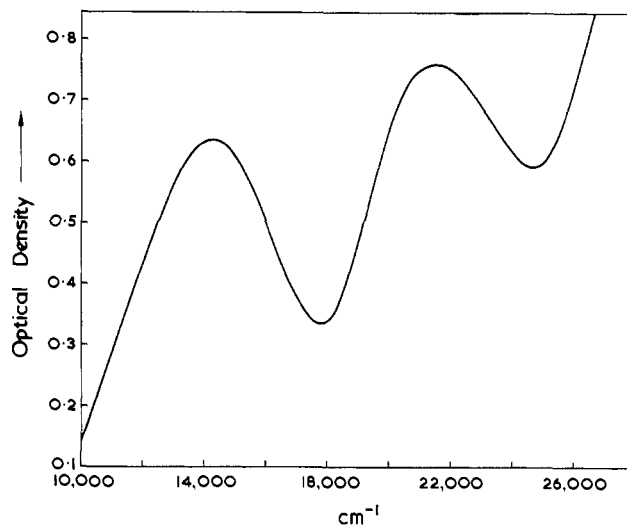


Figure 1.—Diffuse reflectance spectrum of the complex [V(*sec*-C<sub>4</sub>H<sub>9</sub>OH)<sub>4</sub>Cl<sub>2</sub>]Cl.

paratus containing the anhydrous, deoxygenated alcohol. The electrodes were incorporated in the apparatus. In the case of ethanol, the same conductance was obtained by use of the complex as for the trihalide itself (within ±6%), and thus, to conserve materials, the conductances of the other complexes were determined using the trihalide as outlined above. The conductances of the complexes were not a function of time.

Measurements were made at room temperature (19.5°) except for those in cyclohexanol which were carried out at 35°. The volume of solvent used ranged from 27.5 to 29.5 ml. Using a Wayne-Kerr universal bridge, the cell was calibrated against the conductance of aqueous KCl.

Measurements have also been carried out on (C<sub>2</sub>H<sub>5</sub>)<sub>4</sub>NCl in the various alcohols; prior to use, the (C<sub>2</sub>H<sub>5</sub>)<sub>4</sub>NCl was dried at 100° for 2 hr.

**Electronic Spectra.**—The solution and diffuse reflectance spectra of the complexes were recorded using a Cary 14 spectrophotometer. As all of the complexes are very unstable to air and to moisture, the solution cells were sealed from the air, and the solid samples were held between silica plates, the edges of which had been greased.

**Magnetism.**—The magnetic susceptibilities of the complexes were determined by the Gouy method by use of an electromagnet with a field strength of 8150 ± 50 Oe; the field strength was checked every six runs. The thermocouple was calibrated by reference to the susceptibility of HgCo(NCS)<sub>4</sub>. The temperatures are believed to be correct to ±0.5° at 300°K and ±0.8° at 90°K. For each compound, two or three measurements were taken at another field strength (usually about 6000 Oe); the magnetic susceptibilities were independent of field strength to

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TABLE II  
CONDUCTANCE DATA

Alcohol	Sp cond, 10 <sup>6</sup> K, cm <sup>-1</sup> ohm <sup>-1</sup>	$(C_2H_5)_4NCl$		VCl <sub>3</sub>	
		Concn × 10 <sup>3</sup> , M	Molar cond, cm <sup>2</sup> mol <sup>-1</sup> ohm <sup>-1</sup>	Concn × 10 <sup>3</sup> , M	Molar cond, cm <sup>2</sup> mol <sup>-1</sup> ohm <sup>-1</sup>
CH <sub>3</sub> OH	3.18	2.02	107.5	6.03	80.9
		6.61	101.0	13.39	69.1
		9.20	98.5	27.8	61.3
C <sub>2</sub> H <sub>5</sub> OH	0.32	2.04	46.07	1.291	39.9
		4.90	40.4	7.45	28.5
		8.24	36.5	16.15	23.3
<i>n</i> -C <sub>3</sub> H <sub>7</sub> OH	0.302	1.115	23.8	1.545	20.9
		2.53	19.25	6.76	15.17
		5.59	16.05	9.05	11.61
<i>n</i> -C <sub>4</sub> H <sub>9</sub> OH	0.251	1.201	11.27	0.722	10.49
		4.749	7.14	8.68	5.78
		6.68	6.42	11.93	4.48
<i>i</i> -C <sub>4</sub> H <sub>9</sub> OH	0.167	1.091	13.38	0.711	11.02
		4.611	8.02	7.46	6.20
		6.61	6.70	10.21	4.71
<i>sec</i> -C <sub>4</sub> H <sub>9</sub> OH	0.122	1.122	14.97	1.002	12.28 <sup>a</sup>
		3.714	8.87	7.33	6.81
		8.32	6.72	10.91	4.92
C <sub>6</sub> H <sub>11</sub> OH	0.0256	0.786	0.595	2.48	1.021
		2.849	0.372	6.42	0.581
		7.17	0.319	11.70	0.482

<sup>a</sup> Data refer to the green form [V(*sec*-C<sub>4</sub>H<sub>9</sub>OH)<sub>4</sub>Cl<sub>2</sub>]Cl; the brown form VCl<sub>3</sub>·3*sec*-C<sub>4</sub>H<sub>9</sub>OH behaves as a nonelectrolyte in *sec*-C<sub>4</sub>H<sub>9</sub>OH.

TABLE III  
ELECTRONIC SPECTRA OF THE COMPLEXES AS SOLUTIONS IN THE PARENT ALCOHOL

Complex	Concn, M	Band max, cm <sup>-1</sup> , and extinction coefficients (in parentheses)		
		<sup>2</sup> T <sub>2g</sub> ← <sup>2</sup> T <sub>1g</sub> (F)	<sup>2</sup> T <sub>1g</sub> (P) ← <sup>2</sup> T <sub>1g</sub> (F)	<sup>2</sup> T <sub>1g</sub> (P) ← <sup>2</sup> T <sub>1g</sub> (F)
[V(CH <sub>3</sub> OH) <sub>4</sub> Cl <sub>2</sub> ]Cl	0.0428	12,800 (4.3) <sup>a</sup>	14,900 (7.9)	22,050 (12.0)
[V(C <sub>2</sub> H <sub>5</sub> OH) <sub>4</sub> Cl <sub>2</sub> ]Cl	0.0250	13,400 (7.6)	14,750 (10.5)	21,900 (13.6)
	0.0578	13,300 (6.3)	14,800 (9.1)	21,800 (13.5)
[V( <i>n</i> -C <sub>3</sub> H <sub>7</sub> OH) <sub>4</sub> Cl <sub>2</sub> ]Cl	0.0272	13,100 (14.9)	14,450 (18.5)	21,900 (12.2)
[V( <i>i</i> -C <sub>3</sub> H <sub>7</sub> OH) <sub>4</sub> Cl <sub>2</sub> ]Cl	0.0128	13,250 (21.9)	14,300 (26.5)	21,300 (14.2)
	0.0143	13,150 (22.2)	14,300 (28.0)	21,350 (12.0)
[V( <i>i</i> -C <sub>3</sub> H <sub>7</sub> OH) <sub>4</sub> Br <sub>2</sub> ]Br	0.00886	...	14,100 (36.8)	21,200 (8.1)
	0.0116	...	14,100 (38.5)	21,300 (10.6)
[V( <i>n</i> -C <sub>4</sub> H <sub>9</sub> OH) <sub>4</sub> Cl <sub>2</sub> ]Cl	0.0290	13,900 (18.6)	14,500 (20.4)	22,000 (15.3)
[V( <i>i</i> -C <sub>4</sub> H <sub>9</sub> OH) <sub>4</sub> Cl <sub>2</sub> ]Cl	0.0326	13,100 (16.4)	14,350 (21.2)	21,450 (11.8)
[V( <i>sec</i> -C <sub>4</sub> H <sub>9</sub> OH) <sub>4</sub> Cl <sub>2</sub> ]Cl	0.0129	...	14,350 (43.3)	21,050 (17.8)
	0.0165	...	14,300 (44.6)	21,100 (26.3)
[V(C <sub>6</sub> H <sub>11</sub> OH) <sub>4</sub> Cl <sub>2</sub> ]Cl	0.0060	...	13,950 (40.8)	21,050 (28.2)

<sup>a</sup> The band reported in this column appears only as a shoulder (poorly resolved) on the side of the main band

within 1–2%. Samples of ~0.5 g in each case were sealed into Pyrex tubes. The susceptibilities are based on the experimentally found percentages of vanadium in each compound.

The magnetic parameters for the complexes were initially derived by graphical procedures and then refined by use of a program written by Dr. M. Gerloch for the University of London Atlas computer.

**Infrared Spectra.**—The infrared spectra of the complexes were determined by use of a Perkin-Elmer 225 spectrometer as Nujol mulls using CsI plates. In order to protect the surfaces of the latter, they were coated with a thin film of polythene.

### Results and Discussion

It is clear from the preparations outlined above (in particular, from the difference in color between the solution and the precipitate in some cases) that the species present in solution are not necessarily the same as those isolated from the solutions. It is thus desirable to discuss the physical measurements pertaining to each state separately. Accordingly we present first the solution data (conductance and electronic spectra) followed by

the solid-state data (diffuse reflectance spectra, magnetism, and infrared spectra).

**A. Solution Data. Conductance.**—The equivalent conductance of vanadium trichloride in the various alcohols was measured at three concentrations in each case and compared with that of tetraethylammonium chloride in the same alcohol at comparable concentrations. The data are given in Table II. The equivalent conductances of tetraethylammonium chloride in methanol, ethanol, and 1-propanol are in agreement with those found for other alkylammonium halides in these solvents.<sup>15</sup> The equivalent conductance of tetraethylammonium chloride in the higher alcohols decreases as the size of the alkyl group increases, this being related to the decrease in the dielectric constants and the increase in the viscosities of the higher alcohols. Moreover the specific conductances (*K*) of the alcohols

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TABLE IV  
 SPECTRAL PARAMETERS FOR THE ALCOHOLATES  
 IN SOLUTION

	$Dq,$ $\text{cm}^{-1}$	$B,$ $\text{cm}^{-1}$	$\beta$	$c$	$A$
$[\text{V}(\text{CH}_3\text{OH})_4\text{Cl}_2]\text{Cl}$	1605	553	0.64	-0.321	1.266
$[\text{V}(\text{C}_2\text{H}_5\text{OH})_4\text{Cl}_2]\text{Cl}$	1591	548	0.635	-0.321	1.266
$[\text{V}(n\text{-C}_3\text{H}_7\text{OH})_4\text{Cl}_2]\text{Cl}$	1562	575	0.665	-0.312	1.278
$[\text{V}(i\text{-C}_3\text{H}_7\text{OH})_4\text{Cl}_2]\text{Cl}$	1542	541	0.63	-0.319	1.269
$[\text{V}(i\text{-C}_3\text{H}_7\text{OH})_4\text{Br}_2]\text{Br}$	1523	552	0.64	-0.315	1.274
$[\text{V}(n\text{-C}_4\text{H}_9\text{OH})_4\text{Cl}_2]\text{Cl}$	1567	578	0.67	-0.313	1.277
$[\text{V}(i\text{-C}_4\text{H}_9\text{OH})_4\text{Cl}_2]\text{Cl}$	1548	548	0.635	-0.318	1.271
$[\text{V}(sec\text{-C}_4\text{H}_9\text{OH})_4\text{Cl}_2]\text{Cl}$	1542	523	0.605	-0.323	1.264
$[\text{V}(\text{C}_6\text{H}_{11}\text{OH})_4\text{Cl}_2]\text{Cl}$	1506	547	0.635	-0.316	1.273
$\text{VCl}_3 \cdot 3\text{C}_2\text{H}_5\text{OH}^a$	1500	537	0.63	-0.317	1.272

<sup>a</sup> Data derived from the diffuse reflectance spectrum of the solid.

themselves also decrease progressively for the higher alcohols, indicating that they are less ionizing solvents. Indeed, the values for the specific and the equivalent conductances in cyclohexanol are so low that no conclusion as to the ionic type of a compound in this solvent can be drawn.

**Electronic Spectra**—The electronic spectra of the complexes as solutions in the parent alcohol are given in Table III. The two accessible spin-allowed d-d transitions for an octahedrally coordinated  $d^2$  species are assigned as  ${}^3T_{2g} \leftarrow {}^3T_{1g}(\text{F})$  at lower energy ( $\nu_1$ ) and  ${}^3T_{1g}(\text{P}) \leftarrow {}^3T_{1g}(\text{F})$  at higher energy ( $\nu_2$ ). For the chloro alcoholates under discussion,  $\nu_1$  occurs in the range 14,000–14,900  $\text{cm}^{-1}$ , although the band is asymmetric with a shoulder on the low-frequency side. The shoulder arises from resolution of the  ${}^3T_{2g}$  term by low-symmetry components to the ligand field; these are undoubtedly present, owing to the nonequivalence of all six ligands attached to the metal atom. The second ligand-field band,  $\nu_2$ , occurs in the range 21,050–22,050  $\text{cm}^{-1}$ . The methanol complex gives rise to the highest values for both  $\nu_1$  and  $\nu_2$ , and there is a general trend for both bands to move progressively to lower energies the higher the alcohol. This implies that the higher alcohols have slightly lower ligand field strengths than methanol.

The band maxima and the extinction coefficients for the methyl, ethyl, and isobutyl alcohol solutions agree

 TABLE V  
 DIFFUSE REFLECTANCE SPECTRA OF THE ALCOHOLATES (10,000–45,000  $\text{cm}^{-1}$ )

Complex		Shoulder	${}^3T_{2g} \leftarrow {}^3T_{1g}(\text{F})$	${}^3T_{1g}(\text{P}) \leftarrow {}^3T_{1g}(\text{F})$	Charge-transfer bands		
$\text{VCl}_3 \cdot 4\text{CH}_3\text{OH}$	$\text{cm}^{-1}$	10,450?	14,800	22,300	34,500	41,050	...
	$D^a$	0.24	0.64	0.76	1.48	1.44	...
$\text{VCl}_3 \cdot 3\text{C}_2\text{H}_5\text{OH}$	$\text{cm}^{-1}$	10,900?	13,900	20,850	33,800	40,900	...
	$D$	...	0.71	0.92	1.45	1.44	...
$\text{VCl}_3 \cdot 4n\text{-C}_3\text{H}_7\text{OH}$	$\text{cm}^{-1}$	10,450?	13,750	20,550	29,150	36,550	41,950
	$D$	...	0.78	0.98	1.28	1.38	1.40
$\text{VCl}_3 \cdot 4i\text{-C}_3\text{H}_7\text{OH}^b$	$\text{cm}^{-1}$	...	14,550	21,900	29,700	36,800	42,000
	$D$	...	0.33	0.41	0.60	0.73	0.84
$\text{VBr}_3 \cdot 4i\text{-C}_3\text{H}_7\text{OH}$	$\text{cm}^{-1}$	12,100	14,400	...	23,450	33,800	41,350
	$D$	0.80	1.01	...	0.94	1.29	1.35
$\text{VCl}_3 \cdot 3n\text{-C}_4\text{H}_9\text{OH}$	$\text{cm}^{-1}$	...	14,100	20,800	30,600	36,250	41,500
	$D$	...	0.74	1.05	1.39	1.41	1.43
$\text{VCl}_3 \cdot 3i\text{-C}_4\text{H}_9\text{OH}$	$\text{cm}^{-1}$	10,950	13,750	20,400	31,250	36,200	42,300
	$D$	0.34	0.51	0.58	1.19	1.33	1.34
$\text{VCl}_3 \cdot 3sec\text{-C}_4\text{H}_9\text{OH}$	$\text{cm}^{-1}$	12,000	13,700	20,750	30,750	36,050	42,200?
	$D$	0.31	0.40	0.54	1.16	1.33	1.36
$\text{VCl}_3 \cdot 4sec\text{-C}_4\text{H}_9\text{OH}$	$\text{cm}^{-1}$	13,050	14,200	21,500	31,000	36,100	42,100
	$D$	0.57	0.64	0.76	1.35	1.45	1.47
$\text{VCl}_3 \cdot 4\text{C}_6\text{H}_{11}\text{OH}$	$\text{cm}^{-1}$	13,050	13,600	20,950	31,550	35,650	42,500 sh
	$D$	0.25	0.26	0.39	0.94	1.27	1.19

<sup>a</sup>  $D$  is the nominal optical density of a peak at its maximum. <sup>b</sup> Diluted 1:1 with  $\text{MgCO}_3$ .

In the other alcohols, the vanadium species present in solution have equivalent conductances in each case (reproducible to  $\pm 4\%$ ) a little below those of tetraethylammonium chloride in the same alcohol. The vanadium species in solution are thus 1:1 electrolytes and are accordingly formulated as  $[\text{V}(\text{ROH})_4\text{Cl}_2]\text{Cl}$  in each case. The vanadium-containing cations, being heavier than the tetraethylammonium ion, would be expected to have lower mobilities than the latter, consistent with the lower equivalent conductances of their chloro salts. Treatment of the conductivity results by the method outlined by Feltham and Hayter<sup>16</sup> also leads to the conclusion that the vanadium species in solution are 1:1 electrolytes.

closely with those originally reported by Hartmann and Schläfer.<sup>4</sup> However, our conductance data (see above) and the diffuse reflectance spectral data (see below) clearly show that the absorbing species are not  $\text{V}(\text{ROH})_6^{3+}$  as then reported but are  $\text{V}(\text{ROH})_4\text{Cl}_2^+$ .

The extinction coefficients of  $\nu_1$  and  $\nu_2$  lie between 8 and 45. One interesting and unexplained feature of these extinction coefficients is that whereas with the lower alcohols,  $\nu_1$  is less intense than  $\nu_2$ , the reverse is true for the higher alcohols (propanols and above).

The data have been analyzed in terms of a first-order perturbation treatment<sup>2,17</sup> in which  $Dq$  and the Racah parameter  $B$  are determined by the frequencies of  $\nu_1$  and  $\nu_2$ . The results are given in Table IV, together

TABLE VI  
 TEMPERATURE-RANGE MAGNETIC DATA

$\text{VCl}_3 \cdot 4\text{CH}_3\text{OH}$ ( $\chi_{\text{dia}} = 169.5$ cgsu)									
Temp, °K	294.5	275.0	268.0	256.0	244.0	227.5	215.0	203.5	195.0
$10^6\chi_V'$ , cgsu	3169	3360	3516	3599	3753	3978	4207	4369	4576
$\mu$ , BM	2.73	2.72	2.745	2.715	2.705	2.69	2.69	2.665	2.67
Temp, °K	184.5	167.0	146.0	135.0	125.5	107.0	97.0	86.0	
$10^6\chi_V'$ , cgsu	4803	5238	5987	6361	6802	7888	8538	9364	
$\mu$ , BM	2.665	2.645	2.645	2.62	2.615	2.60	2.575	2.54	
$\text{VCl}_3 \cdot 3\text{C}_2\text{H}_5\text{OH}$ ( $\chi_{\text{dia}} = 183$ cgsu)									
Temp, °K	293.0	274.5	255.5	244.5	231.0	209.0	187.5	180.2	166.5
$10^6\chi_V'$ , cgsu	3172	3387	3586	3717	3889	4261	4625	4864	5209
$\mu$ , BM	2.725	2.725	2.705	2.695	2.68	2.67	2.635	2.65	2.635
Temp, °K	155.0	142.5	128.8	120.2	110.0	104.0	95.5	85.0	
$10^6\chi_V'$ , cgsu	5464	5848	6460	6948	7380	7958	8398	9299	
$\mu$ , BM	2.605	2.58	2.58	2.585	2.55	2.575	2.535	2.515	
$\text{VCl}_3 \cdot 4n\text{-C}_3\text{H}_7\text{OH}$ ( $\chi_{\text{dia}} = 264$ cgsu)									
Temp, °K	294.0	280.5	261.0	241.0	221.0	204.0	187.0	165.5	148.8
$10^6\chi_V'$ , cgsu	3355	3448	3673	3911	4152	4391	4797	5242	5954
$\mu$ , BM	2.81	2.78	2.77	2.745	2.71	2.675	2.68	2.635	2.66
Temp, °K	140.0	123.0	108.5	96.0					
$10^6\chi_V'$ , cgsu	6176	6915	7805	8533					
$\mu$ , BM	2.63	2.61	2.605	2.56					
$\text{VCl}_3 \cdot 4i\text{-C}_3\text{H}_7\text{OH}$ ( $\chi_{\text{dia}} = 264$ cgsu)									
Temp, °K	293.0	286.0	279.0	263.5	255.8	243.5	228.0	218.8	207.0
$10^6\chi_V'$ , cgsu	3135	3245	3315	3457	3550	3694	3846	3995	4168
$\mu$ , BM	2.71	2.725	2.72	2.70	2.695	2.68	2.65	2.645	2.625
Temp, °K	199.0	189.0	171.5	156.0	147.2	138.2	123.0	115.0	106.5
$10^6\chi_V'$ , cgsu	4319	4477	5012	5348	5618	6021	6560	6976	7534
$\mu$ , BM	2.62	2.60	2.62	2.585	2.57	2.58	2.54	2.535	2.535
Temp, °K	97.0	90.0	79.9						
$10^6\chi_V'$ , cgsu	8219	8735	9733						
$\mu$ , BM	2.525	2.51	2.495						
$\text{VBr}_3 \cdot 4i\text{-C}_3\text{H}_7\text{OH}$ ( $\chi_{\text{dia}} = 298$ cgsu)									
Temp, °K	293.5	280.0	260.0	236.0	216.5	196.0	175.0	161.0	140.0
$10^6\chi_V'$ , cgsu	3032	3134	3358	3712	4006	4408	4894	5252	5864
$\mu$ , BM	2.67	2.65	2.64	2.645	2.635	2.63	2.615	2.60	2.56
Temp, °K	129.5	114.8	97.5	91.5					
$10^6\chi_V'$ , cgsu	6375	7116	8077	8180					
$\mu$ , BM	2.57	2.565	2.51	2.445					
$\text{VCl}_3 \cdot 3n\text{-C}_4\text{H}_9\text{OH}$ ( $\chi_{\text{dia}} = 254$ cgsu)									
Temp, °K	321.5	306.0	300.0	289.5	280.0	274.0	257.0	242.5	224.5
$10^6\chi_V'$ , cgsu	2915	3211	3197	3340	3371	3529	3609	3856	4014
$\mu$ , BM	2.74	2.805	2.77	2.78	2.75	2.78	2.725	2.735	2.685
Temp, °K	206.0	188.0	172.0	165.0	154.0	143.5	133.5	117.0	108.0
$10^6\chi_V'$ , cgsu	4329	4625	5064	5161	5457	5807	6248	6959	7455
$\mu$ , BM	2.67	2.635	2.64	2.61	2.595	2.58	2.585	2.55	2.54
Temp, °K	98.5	86.0	84.5	83.0	81.0				
$10^6\chi_V'$ , cgsu	7946	8727	8919	9118	9271				
$\mu$ , BM	2.50	2.45	2.455	2.46	2.45				
$\text{VCl}_3 \cdot 3i\text{-C}_4\text{H}_9\text{OH}$ ( $\chi_{\text{dia}} = 254$ cgsu)									
Temp, °K	296.5	280.0	262.0	239.5	224.0	207.0	185.5	166.8	148.8
$10^6\chi_V'$ , cgsu	3439	3487	3531	3651	3715	3787	3959	4092	4280
$\mu$ , BM	2.855	2.795	2.72	2.645	2.58	2.505	2.425	2.335	2.255
Temp, °K	128.5	109.0	101.0	92.5	80.5				
$10^6\chi_V'$ , cgsu	4480	4783	4919	5026	5098				
$\mu$ , BM	2.145	2.04	1.995	1.93	1.81				
$\text{VCl}_3 \cdot 4\text{sec-C}_4\text{H}_9\text{OH}$ ( $\chi_{\text{dia}} = 312$ cgsu)									
Temp, °K	295.5	293.0	276.5	257.0	242.5	235.0	220.0	207.0	188.0
$10^6\chi_V'$ , cgsu	3077	3062	3263	3455	3612	3668	3897	4065	4321
$\mu$ , BM	2.695	2.68	2.685	2.665	2.645	2.625	2.62	2.595	2.55
Temp, °K	180.0	165.0	144.0	121.0	110.0	93.0	80.0		
$10^6\chi_V'$ , cgsu	4587	4915	5607	6528	7068	8046	9151		
$\mu$ , BM	2.57	2.545	2.54	2.515	2.495	2.445	2.42		

TABLE VI (Continued)

VCl <sub>3</sub> ·3 <i>sec</i> -C <sub>4</sub> H <sub>9</sub> OH ( $\chi_{\text{dia}} = 254$ cgsu)									
Temp, °K	301.0	276.0	268.0	244.5	226.0	204.0	182.5	164.0	155.0
10 <sup>6</sup> $\chi_V'$ , cgsu	3047	3284	3295	3545	3755	4052	4459	4883	5125
$\mu$ , BM	2.71	2.695	2.66	2.635	2.605	2.57	2.55	2.53	2.52
VCl <sub>3</sub> ·4C <sub>6</sub> H <sub>11</sub> OH ( $\chi_{\text{dia}} = 371$ cgsu)									
Temp, °K	293.0	274.0	249.5	229.2	210.0	190.0	173.0	153.0	132.0
10 <sup>6</sup> $\chi_V'$ , cgsu	3460	3663	3789	3889	4065	4255	4504	4655	5091
$\mu$ , BM	2.85	2.835	2.75	2.67	2.615	2.545	2.495	2.385	2.32
Temp, °K	111.0	99.0	85.8						
10 <sup>6</sup> $\chi_V'$ , cgsu	5676	5949	6359						
$\mu$ , BM	2.245	2.17	2.09						

with the derived values of  $\beta$  ( $B(\text{complex})/B(\text{free ion})$ ) in each case. Also included in Table IV are the calculated values of the parameters  $c$  and  $A$ , the latter being required subsequently for the interpretation of the magnetic data. The parameter  $c$  is the mixing coefficient in the ground ( ${}^3T_{1g}$ ) term wave functions, and the parameter  $A$  is defined<sup>18</sup> by  $A = (1.5 - c^2)/(1 + c^2)$ .

By use of the rule of average environment,<sup>19</sup> together with the value 1265 cm<sup>-1</sup> for  $Dq$  for the VCl<sub>6</sub><sup>3-</sup> ion,<sup>2</sup> it may be calculated that  $Dq$  for the as yet unprepared V(C<sub>2</sub>H<sub>5</sub>OH)<sub>6</sub><sup>3+</sup> ion would be 1750 cm<sup>-1</sup>; *i.e.*, the ligand field strength of ethanol is identical with that of urea. As both ligands are oxygen donors, this result was to be expected, although both have lower ligand field strengths than water ( $Dq = 1850$  cm<sup>-1</sup>) and higher ligand field strengths than tetrahydrofuran ( $Dq = 1535$  cm<sup>-1</sup>, derived similarly from the parameters  $Dq = 1400$  cm<sup>-1</sup> and  $B = 555$  cm<sup>-1</sup> for the complex VCl<sub>3</sub>·3C<sub>4</sub>H<sub>9</sub>O, for which  $\nu_1 = 12,900$  cm<sup>-1</sup> and  $\nu_2 = 20,200$  cm<sup>-1</sup>).

The ligand field strengths of the alcohols fall in the order CH<sub>3</sub>OH > C<sub>2</sub>H<sub>5</sub>OH > *n*-C<sub>3</sub>H<sub>7</sub>OH ~ *n*-C<sub>4</sub>H<sub>9</sub>OH > *i*-C<sub>3</sub>H<sub>7</sub>OH ~ *i*-C<sub>4</sub>H<sub>9</sub>OH ~ *sec*-C<sub>4</sub>H<sub>9</sub>OH. Steric hindrance of the branched alcohols possibly contributes to their lower ligand field strengths. The lower ligand field strength of the V(*i*-C<sub>3</sub>H<sub>7</sub>OH)<sub>4</sub>Br<sub>2</sub><sup>+</sup> ion compared with the corresponding chloro ion is consistent with the relative positions of bromide and chloride in the spectrochemical series.

#### B. Solid-State Data. Diffuse Reflectance Spectra.

—The band maxima observed in the diffuse reflectance spectra of the solid complexes which crystallized from the various alcohol solutions are given in Table V, together with an indication of their relative intensities.

As demonstrated in the previous section, all of the complexes exist in the form [V(ROH)<sub>4</sub>Cl<sub>2</sub>]Cl in solution. For those cases in which complexes of the same stoichiometry could be precipitated from solution, the band maxima in the diffuse reflectance spectra of the powdered solids lie at frequencies almost identical with those for the corresponding complexes in solution. This is the situation for the complexes of CH<sub>3</sub>OH,

*i*-C<sub>3</sub>H<sub>7</sub>OH, *sec*-C<sub>4</sub>H<sub>9</sub>OH, and C<sub>6</sub>H<sub>11</sub>OH. (The isopropyl alcohol adduct has been isolated once previously.<sup>19</sup>) For those cases in which complexes with the stoichiometry VCl<sub>3</sub>·3ROH are precipitated from solution (*i.e.*, R = C<sub>2</sub>H<sub>5</sub> and *n*-, *i*-, and *sec*-C<sub>4</sub>H<sub>9</sub>), the frequencies of  $\nu_1$  and  $\nu_2$  are ~700 and ~1000 cm<sup>-1</sup>, respectively, lower than the corresponding solution values. These shifts are fully consistent with the replacement of one alcohol molecule by the chloride in the first coordination sphere of the vanadium ion. *sec*-Butyl alcohol complexes with both stoichiometries were isolated.

The value of  $Dq$  (1500 cm<sup>-1</sup>) derived from the diffuse reflectance spectrum of the complex VCl<sub>3</sub>·3C<sub>2</sub>H<sub>5</sub>OH is about 90 cm<sup>-1</sup> lower than that of [V(C<sub>2</sub>H<sub>5</sub>OH)<sub>4</sub>Cl<sub>2</sub>]Cl (Table IV). This is in agreement with the fact that ethanol has a higher ligand field strength than chloride and with the value 1750 cm<sup>-1</sup> derived above for the as yet unprepared V(C<sub>2</sub>H<sub>5</sub>OH)<sub>6</sub><sup>3+</sup> ion.

The only solid complex for which ambiguity as to the correct formulation arises is that derived from *n*-C<sub>3</sub>H<sub>7</sub>OH. From a comparison of the solution spectrum with the diffuse reflectance spectrum, it would be concluded that the solid had the formula VCl<sub>3</sub>·3*n*-C<sub>3</sub>H<sub>7</sub>OH, yet the analytical data are in agreement with the empirical formula VCl<sub>3</sub>·4*n*-C<sub>3</sub>H<sub>7</sub>OH.

**Magnetic Data.**—The magnetic moments of the solid complexes have been determined at 12–23 points over the range ~300 to ~80°K (Table VI). In all cases, the magnetic moments fall with decreasing temperature in agreement with the behavior expected for  ${}^3T_{1g}$  ground terms. The variation with temperature is less than that predicted for an octahedrally coordinated d<sup>2</sup> ion in a precisely cubic field and is in accord with the presence of axial distortions to the cubic field (nonequivalence of the ligands would in itself bring this situation about).

In order to obtain an estimate of the splitting ( $\Delta$ , cm<sup>-1</sup>) of the ground  ${}^3T_{1g}$  term by the axial field into an orbital doublet and an orbital singlet, the magnetic data have been analyzed by standard procedures<sup>18</sup> in terms of the following parameters:  $v = \Delta/\lambda$ , where  $\lambda$  is the spin-orbit coupling constant of vanadium(III) in the complex (105 cm<sup>-1</sup> in the free ion),<sup>20</sup>  $k$ , the orbital reduction factor, and  $A$ , which is defined in the elec-

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tronic spectral section. A value of  $A = 1.27$  was used in all cases, this being the average value of the parameter as determined from the spectral calculations. The resulting values for the other parameters are listed in Table VII.

TABLE VII  
VALUES FOR THE MAGNETIC PARAMETERS OF THE  
ALCOHOLATES ( $A = 1.27$ )

Compound	$k$	$\lambda$ , $\text{cm}^{-1}$	$\nu$	$\Delta$ , $\text{cm}^{-1}$
$[\text{V}(\text{CH}_3\text{OH})_4\text{Cl}_2]\text{Cl}$	0.7	80	7.0	560
$\text{VCl}_3 \cdot 3\text{C}_2\text{H}_5\text{OH}$	0.65	75	5.5	410
$\text{VCl}_3 \cdot 3n\text{-C}_3\text{H}_7\text{OH}$	0.75	65	6.5	420
$[\text{V}(i\text{-C}_3\text{H}_7\text{OH})_4\text{Cl}_2]\text{Cl}$	0.65	80	5.0	400
$[\text{V}(i\text{-C}_3\text{H}_7\text{OH})_4\text{Br}_2]\text{Br}$	0.7	90	6.0	540
$\text{VCl}_3 \cdot 3n\text{-C}_4\text{H}_9\text{OH}$	0.7	65	4.5	290
$\text{VCl}_3 \cdot 3i\text{-C}_4\text{H}_9\text{OH}^a$	1.0	115	1.0	115
$[\text{V}(sec\text{-C}_4\text{H}_9\text{OH})_4\text{Cl}_2]\text{Cl}$	0.7	70	5.0	350
$\text{VCl}_3 \cdot 3sec\text{-C}_4\text{H}_9\text{OH}$	0.7	70	5.0	350
$[\text{V}(\text{C}_6\text{H}_{11}\text{OH})_4\text{Cl}_2]\text{Cl}^a$	1.0	120	2.5	300

<sup>a</sup> These compounds are anomalous in that a fit can only be obtained if  $\lambda$  is increased above the spin-only value.

The orbital reduction factor depends principally on the absolute value of the magnetic moment, being greatest in those cases for which the moment is highest. Its value lies near 0.7 for the alcoholates, with two exceptions. The spin-orbit coupling constant in the complexes is lower than the free-ion value in most cases. The distortion parameter and hence  $\Delta$  are determined mainly by the curvature of the plot of the magnetic moment against  $kT/\lambda$  and partly also by the value of  $\lambda$ . It is positive in each case, and hence the orbital singlet derived from the  ${}^3T_{1g}$  term lies lower than the orbital doublet; this appears to be the case for all the octahedral  $d^2$  complexes which have been studied so far. Apart from two cases which appear to be anomalous because their magnetic moments imply  $\lambda$  values greater than that in the free ion ( $\text{VCl}_3 \cdot 3i\text{-C}_4\text{H}_9\text{OH}$  and  $\text{VCl}_3 \cdot 4\text{C}_6\text{H}_{11}\text{OH}$ ), the  $\Delta$  values vary from 290 to 560  $\text{cm}^{-1}$ . This is the same order of magnitude as found for a variety of other octahedral vanadium(III) complexes<sup>12,13</sup> in which dissimilar ligands are attached to the metal ion.

**Infrared Spectra.**—The infrared spectra of all the complexes have been recorded over the range 4000–200  $\text{cm}^{-1}$ . The data above 400  $\text{cm}^{-1}$  in each case are simply indicative of the coordinated ligand. The only features of interest occur near 330  $\text{cm}^{-1}$ ; bands in this

region are assigned as vanadium–chlorine stretching frequencies in agreement with earlier assignments<sup>13,21,22</sup> for these vibrations in other octahedrally coordinated vanadium(III) complexes. The data thus confirm that the complexes contain six-coordinate molecules or ions.

The 4:2 complex ions appear to have the *cis* stereochemistry in most cases, owing to the appearance in their spectra of two bands in this region (Table VIII). The corresponding bands in the spectra of the 3:3 complexes are especially broad and it is not considered that deductions regarding the stereochemistries of these complexes can be made. Solution infrared spectra did not prove to be feasible and so it is not known whether a stereochemical change occurs on dissolution in the parent alcohol.

TABLE VIII  
INFRARED SPECTRA OF THE ALCOHOLATES IN THE  
VCl STRETCHING FREQUENCY REGION ( $\text{cm}^{-1}$ )

Compound <sup>a</sup>	$\nu(\text{VCl})$
$[\text{V}(\text{CH}_3\text{OH})_4\text{Cl}_2]\text{Cl}$	372 s
$[\text{V}(n\text{-C}_3\text{H}_7\text{OH})_4\text{Cl}_2]\text{Cl}$	330 m, sh, 310 s, vbr
$[\text{V}(i\text{-C}_3\text{H}_7\text{OH})_4\text{Cl}_2]\text{Cl}$	340 vs, 314 s
$[\text{V}(sec\text{-C}_4\text{H}_9\text{OH})_4\text{Cl}_2]\text{Cl}$	345 m, vbr, 315 s, vbr
$[\text{V}(\text{C}_6\text{H}_{11}\text{OH})_4\text{Cl}_2]\text{Cl}$	325 s, 305 m
$\text{VCl}_3 \cdot 3\text{C}_2\text{H}_5\text{OH}$	330–270 s, vbr
$\text{VCl}_3 \cdot 3n\text{-C}_4\text{H}_9\text{OH}$	333 m, br, 310 s, vbr
$\text{VCl}_3 \cdot 3i\text{-C}_4\text{H}_9\text{OH}$	323 m, br, 305 s, vbr

<sup>a</sup> Recorded as Nujol mulls. The VO stretching frequencies probably occur near 400  $\text{cm}^{-1}$  but could not be assigned with certainty.

## Conclusions

With the preparative methods used, it is clear that alcohols are not capable of displacing all of the halide ions from the first coordination sphere of the parent trihalide. Instead, complexes of the type  $[\text{V}(\text{ROH})_4\text{Cl}_2]\text{Cl}$  are formed in solution. In the solid state, the alcoholates either have the same formulation or are of the type  $\text{VCl}_3 \cdot 3\text{ROH}$ .

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