Acetic Acid Complexes of Vanadium(III) and Titanium(III)

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Vanadium(III) halide–acetic acid complexes of the type $A[VX_4(AcOH)_2]$ ($A = Et_4N$, Me_4N, or pyH, $X = Cl$ or Br) have been prepared from acetyl halide solutions. Co-ordination of the acetic acid to the metal has been demonstrated by analytical and spectroscopic methods. The complexes are intensely coloured and exhibit thermochromism. Visible and u.v. spectra, halogen nuclear quadrupole resonance spectra, i.r. spectra, and magnetic properties are reported. The method has been extended to the preparation of the corresponding titanium(III) compound, $Et_4N[TiCl_4(AcOH)_2]$, which is reported for the first time.

Metal compounds containing acetic acid were recently reviewed by van Leeuwen and Groeneveld.[1] However, few of these compounds involved transition metals or direct co-ordination of the acid to the metal. In $ReCl_3(AcOH)_2$, isolated by treating $ReCl_3$ with acetic acid in the absence of air, the acetic acid was considered to be co-ordinated to the metal in the axial positions of a trigonal bipyramid.[2] Hexa-acetic acid complexes of manganese, cobalt, copper, and nickel could be prepared when the anion was large, *viz.*, BF_4^-, ClO_4^-, and NO_3^- (ref. 1). The appropriate hexahydrated salt was allowed to react with acetic anhydride to yield the complex, but with $NiCl_2,6H_2O$ no pure product could be obtained from similar treatment.[1]

Several copper, nickel, and chromium halide or acetate compounds containing acetic acid were isolated by Hardt and his co-workers, but in all cases the acid appeared to be present only as solvate.[3-6] However, the acid was assumed[7] to be co-ordinated directly to the metal in the titanium(III) compounds $Cs_2[TiCl_5(AcOH)]$ and $TiCl_2(AcO)(AcOH)$. The only reported acetic acid complex of vanadium is $Et_4N[VBr_4(AcOH)_2]$ which was prepared from vanadium pentoxide by reduction with a mixture of acetic acid and hydrobromic acid.[8]

During investigations of the reactions of the hydrated vanadium(III) halides $VX_3,6H_2O$ in the acetyl halides AcX (X = Cl or Br) we have found that in the presence of nitrogen base cations compounds of the type $A[VX_4(AcOH)_2]$ are precipitated. We now report the first systematic study of the preparations and structural properties of vanadium complex compounds containing acetic acid. A similar titanium(III) compound is reported and conclusive evidence for the direct co-ordination of the acid to the metal in all compounds is given.

RESULTS AND DISCUSSION

The intensely coloured vanadium complexes precipitated from the acetyl halide were extremely sensitive to moisture and air. They were very soluble in water, slightly soluble in other polar solvents, though not dissolving unchanged, and insoluble in non-polar solvents. Subsequent experiments showed that $Et_4N[VCl_4(AcOH)_2]$ could also be prepared from $VCl_3,6H_2O$ and Et_4NCl in acetic acid–thionyl chloride mixtures, and from the same reactants in acetic acid by precipitation with hydrogen chloride.

The vanadium compounds were titrated potentiometrically with sodium hydroxide to determine the free acetic acid. The direct titration showed an end-point at close to five equivalents of base, as expected for two equivalents for the acetic acid and three for $V(OH)_3$. Addition of the calculated amount of disodium ethylenediaminetetra-acetic acid[9] reduced the titre to four equivalents of base, now representing two for the acetic acid and two for the acid released from the edta salt owing to complexing with the vanadium. We note that whereas we were able to titrate directly the co-ordinated acetic acid, Seifert[9] could not titrate directly the formic acid in the compound $V(HCO_2)_3,HCO_2H$.

The i.r. spectra of the vanadium and titanium compounds contain bands which are characteristic of acetic acid which is strongly hydrogen-bonded.[10,11] Acetic acid in the solid state has been shown to have a polymeric

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structure with hydrogen-bonding between adjacent carbonyl and hydroxy-groups.[12] The i.r. spectrum of the solid polymer is contrasted with that of the gaseous monomer of acetic acid in Table 1. Also in Table 1 are data from spectra of the solid complex compounds and of $Et_4N[VCl_4(AcOD)_2]$ from the spectrum of partially deuteriated $Et_4N[VCl_4(AcOH)_2]$. Both the O–H and C=O stretching bands are at much lower frequencies in the complexes than in the acid monomer. This suggests either that the carbonyl oxygen is co-ordinated to the metal and the hydroxy-group is hydrogen-bonded to halides or other acid groups, or that the acid is present only as solvate and that intermolecular hydrogen-bonding exists between solvate molecules. However, the latter proposition would require in the compound a polymeric complex anion, $[VX_4]_n^-$, which can be ruled out on the basis of the visible spectrum (see later). A significant lowering of the carbonyl stretching frequency on co-ordination to the metal as above has also been reported for several Lewis acid adducts with acetic acid (*e.g.*, $SbCl_3$,AcOH) [13] and for the complex compounds mentioned in the introduction, *i.e.*, $M(AcOH)_6X_2$ [1] and Cs_2TiCl_5,AcOH.[7] The same behaviour is also observed for the carbonyl stretching band for esters co-ordinated to metal ions.[14]

TABLE 1

I.r. spectra/cm^{-1} of acetic acid–halide complexes

1	2	3	4 [a]	5	6	7	8	9	Assignment
3113s,vbr	2970s,vbr	3073s,vbr	2277s,vbr	3050s,vbr	3050s,vbr	3190s,vbr	3583	2927	νOH
1615s,br	1639s,br	1658vs	1642vs	1648m	1612vs	1652s	1788	1652	νC=O
1293s	1274s	1291vs	1350s	1293s	1288s	1285s	1182	1268	νC–O
1415s	1416s	1417s	1067m	1412s	1412s	1415s	1264	1411	δOH
1448sh	1436sh	1449sh	1448w	1450sh	1450w	1451sh	1430	1440	δ_aCH_3
1360m	1361m	1365s	1373m	1361m	—	1359m	1382	1351	δ_sCH_3
1051w	1049w	1038vw	—	—	1047w	1052vw	1048	1047	ρ_aCH_3
1016w	1024m	1016sh	1014m	1017w	1011vw	1014vw	989	1019	ρ_sCH_3
636m	623s	634s	610s	623s	*b*	623s	642	629	δCOO
582vw	575vw	576w	555w	559w	*b*	*b*		592	γCCO
490m	481m	491s	484s	486m	*b*	*b*	581	450	δCCO or νM–O
343sh	279sh	333vs,vbr	332s	295sh	*b*	*b*			νM–X
315s,vbr	263s,vbr	303s	302m	276vs,vbr	*b*	*b*			
			641s						γOD ?

[a] OD bands. [b] Not recorded in this region. 1 = $Me_4NVCl_4(AcOH)_2$, 2 = $Me_4NVBr_4(AcOH)_2$, 3 = $Et_4NVCl_4(AcOH)_2$, 4 = $Et_4NVCl_4(AcOD)_2$, 5 = $Et_4NVBr_4(AcOH)_2$, 6 = $(pyH)VCl_4(AcOH)_2$, 7 = $Et_4NTiCl_4(AcOH)_2$, 8 = AcOH monomer (ref. 10), 9 = AcOH polymer (0 °C) (ref. 11).

Although the 1500—1300 cm^{-1} region is complicated by the presence of bands due to the cation the strong O–H bending and C–O stretching vibrations can be assigned at *ca.* 1415 and 1290 cm^{-1} respectively. The presence of these bands and the O–H stretching band indicates the absence of the acetate ion from the compounds.

Nicholls and Wilkinson [8] reported that when $Et_4N[VBr_4(AcOH)_2]$ was heated *in vacuo* at 77 °C, acetic acid only was evolved, leaving a brown residue. In our experiments, similar treatment of the tetraethylammonium chloride and bromide produced dark blue and dark green residues, respectively. The i.r. spectra of the liquid distillates indicated that acetic acid was present but analysis of the solid residues showed that halide had also been removed, leaving solids which contained cation : vanadium : halide = *ca.* 1 : 1 : 3·2 and then exhibited i.r. acetate bands.

The vanadium compounds are orange and dark red for the chlorides and bromides respectively, but on immersion in liquid nitrogen the chlorides become paler and the bromides turn yellow. This type of thermochromic effect has been reported also for the similar acetonitrile compounds $Et_4NVX_4(MeCN)_2$ (X = Cl or Br or both).[15] The solid reflectance spectra as measured at room temperature are listed in Table 2. From the visible spectra of the hexa-acetic acid complexes of nickel and cobalt, it was found that the ligand field strength of acetic acid was slightly greater than that of urea.[1] Using these results and the band positions [16] for $V(urea)_6^{3+}$ we estimate that the ion $V(AcOH)_6^{3+}$ should have ligand fields bands at *ca.* 16,000 and 24,500 cm^{-1}. Then average field calculations based on these values and those [17] for the ions VCl_6^{3-} and VBr_6^{3-} lead to band positions at 12,930 and 20,170, and 12,740 and 19,360, for the ions $VCl_4(AcOH)_2^-$ and $VBr_4(AcOH)_2^-$, respectively. Thus Table 2 shows that the solid vanadium compounds have visible spectra which are consistent with a pseudo-octahedral environment of four halide ions and two acetic acid molecules around the vanadium. The bromide complexes also show charge-transfer bands near 23,000 cm^{-1} and the results for $Et_4NVBr_4(AcOH)_2$ are similar to those previously reported.[8] For the titanium compound, the band positions are at slightly lower energy than in $TiCl_4(MeOH)_2^-$ [18] as would be expected for acetic acid with a weaker ligand field than methanol.

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The band positions in Table 2 also show that the chlorides differ considerably from the polymeric $Et_4N[VCl_4]$, which exhibits[19] bands at 10,870, 16,560, and 20,000 cm^{-1}.

The solution spectra of vanadium trichloride in acetic acid have also been investigated (Table 3). Vanadium trichloride dissolves in acetic acid giving a green solution, which turns orange on addition of hydrogen chloride, although no solid precipitates. From the average ligand field calculation above, it appears that the orange solution contains the ion $VCl_4(AcOH)_2^-$. However for the green solution, although the lower-energy band suggests that $V(AcOH)_6^{3+}$ is present, the higher-energy ligand-field band is significantly lower than the predicted value of 24,500 cm^{-1}.

TABLE 2

Reflectance spectra of acetic acid complexes

Compound	Band positions/cm^{-1}			
	$^3T_{1g} \longrightarrow {}^3T_{2g}$	$^3T_{1g} \longrightarrow {}^3T_{1g}$ (P)	Other bands	
Vanadium				
$Me_4NVCl_4(AcOH)_2$ Purple	13,100	18,320 20,580	26,460(sh), 29,670, 32,300 (vbr)	37,900(vbr)
$Et_4NVCl_4(AcOH)_2$ Orange	12,700	20,330	27,170 30,400, 31,750 (vbr)	37,450(vbr)
$pyHVCl_4(AcOH)_2$ Pink	12,000	19,600	*ca.* 29,000(vbr)	
$Me_4NVBr_4(AcOH)_2$ Red	11,930		23,300, 26,180, 33,400(vbr)	36,800(vbr)
$Et_4NVBr_4(AcOH)_2$ Red	12,500	20,240(sh)	23,200, 25,770(vbr), 30,000(vbr)	33,600(vbr) 37,000(vbr)
$Et_4NVBr_4(AcOH)_2$ [a]	11,760	20,410(sh) 22,220		
	$^2T_{2g} \longrightarrow {}^2E_g$			
Titanium				
$Et_4NTiCl_4(AcOH)_2$ Green	12,800(sh) 14,900		*ca.* 28,000(vbr)	

[a] From ref. 8.

TABLE 3

Solution spectra of vanadium(III) halides in acetic acid

Colour	Band positions/ cm^{-1}	Origin or preparation of solution
Green	16,300, 22,600	VCl_3 in AcOH
Red	12,800, 19,900	HCl gas passed into above solution
Red	13,100, 20,500	$VCl_3,6H_2O$ in AcOH, passed HCl gas
Red	15,300 (ε = 80) 21,000 (ε = 2100) 35,500 (ε = 1900)	$Et_4NVCl_4(AcOH)_2$ in AcCl
Red	12,700 Intense charge-transfer bands	AcBr solution from $Et_4NVBr_4(AcOH)_2$ preparation

Further evidence on the stereochemistry of these complexes can be obtained from the low-frequency i.r. data. Absorptions assignable to COO and CCO deformations[11] and metal–halogen stretching modes have been observed (Table 1). The bands near 630 and 590 cm^{-1} appear to correspond to the COO bending mode and the CCO wagging mode, respectively. However, the band near 490 cm^{-1} can be assigned either to the CCO bending mode or to the metal–oxygen stretching mode. The former lies in the range 450—480 cm^{-1} in the free acid polymer,[11] while vanadium–oxygen stretching bands have been observed at 531 and 368 cm^{-1} in a vanadium(III) oxalate complex[20] and at 442 cm^{-1} in $VO(AcO)_2$.[21] The vanadium–halogen bands observed are in the range expected for octahedral vanadium(III) halides. The presence of two distinct bands in this region seems to preclude a *trans*-configuration for which only one metal–halogen stretching band would be expected, whereas for a *cis*-configuration four bands should be observed.[22] The compound $SnCl_4(AcOH)_2$ has bands at 351 and 327 cm^{-1} and was assigned a *cis*-configuration on this basis.[23] Other vanadium(III) chloro-complexes $Et_4NVCl_4(pyridine)_2$ and Et_4NVCl_4(phenanthroline) have similar vanadium–chlorine stretching frequencies.[24] These must be assumed to have the *cis*-configuration because of the bidentate phenanthroline ligand.

Nuclear quadrupole resonance (n.q.r.) spectra (Table 4) have been observed for four of the vanadium complexes, the tetraethylammonium complexes showing interesting variations of frequency with temperature (see Figure). At room temperature both complexes exhibit two lines, although in each case the higher-frequency line disappears at low temperature. The presence initially of two lines favours a *cis*-configuration for, unless there is some crystallographic asymmetry, a *trans*-configuration with four equivalent halogens should exhibit one resonance.

The n.q.r. line which disappears is the less intense of the two lines and possesses a ' normal ' negative temperature coefficient. The stronger line possesses a small positive temperature coefficient for both the chloride and

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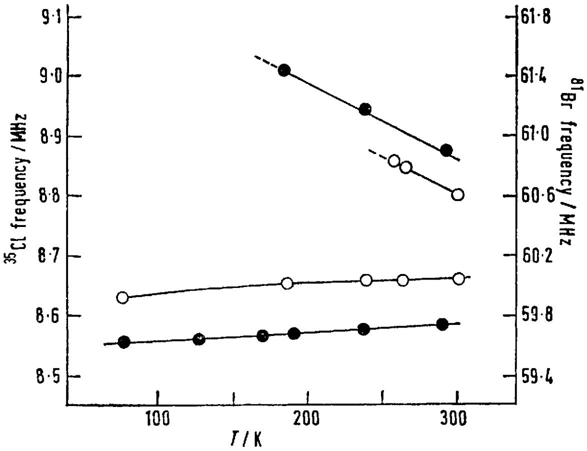
bromide. The majority of halides studied by n.q.r. methods have resonance frequencies which increase linearly with decreasing temperature.[25] However, positive temperature coefficients have been associated with π-bonding,[25] phase transitions,[26] and hydrogen bonding.[27,28] The different temperature-dependences of the resonance lines in these vanadium compounds cannot be explained by either π-bonding or phase transitions. The small separation between the two lines indicates that each type of vanadium–halogen bond has similar π-bonding, yet the positive temperature coefficient is not shown by both resonance lines. Also, it would be unlikely that a phase transition would affect one type of vanadium–halogen bond but not the other. Therefore the explanation of the temperature-dependences must lie with hydrogen bonding.



Temperature-dependence of n.q.r. lines in the complexes $Et_4NVX_4(AcOH)_2$; ○, Cl; ●, Br

TABLE 4

^{35}Cl and ^{79,81}Br n.q.r. spectra

$Me_4NVCl_4(AcOH)_2$			$Et_4NVCl_4(AcOH)_2$			$Me_4NVBr_4(AcOH)_2$			$Et_4NVBr_4(AcOH)_2$		
T/K	MHz	S/N	T/K	MHz	S/N	T/K	MHz	S/N	T/K	MHz	S/N
298	8·545	2	291	8·660	3	298	59·14	3	291	59·742	9
				8·800	2		70·76 [a]	3		60·891	4
Not observed at 77 K			77	8·629	8	Not observed at 77 K				71·507 [a]	9
										72·83 [a]	4
									77	59·620	10

[a] ^{79}Br resonance. S/N = Signal-to-noise ratio.

Previous investigations of the effect of hydrogen bonding on n.q.r. lines have dealt only with compounds containing no π-bonding. In such compounds, as the temperature is lowered the increased hydrogen bonding draws electron density away from the metal–halogen bond and reduces its covalency, thereby lowering the resonance frequency. But in a π-bonded compound this electron-withdrawal will also reduce the π-bond strength, with a resultant shift of the resonance to a higher frequency. This increase will approximately cancel the low-frequency shift resulting from the reduction in σ-bond strength, so that hydrogen bonding in compounds with significant π-bonding will result in a 'normal' negative temperature coefficient for n.q.r. lines.

The temperature-dependence shown in the Figure can now be rationalised if the lower-frequency line is assigned to a pair of vanadium–halogen bonds which are π-bonded but not hydrogen bonded, the line therefore having a positive temperature coefficient. The higher-frequency line is assigned to a pair of vanadium–halogen bonds which are involved with both π-bonding and hydrogen bonding, and the negative temperature coefficient is explained. Some supporting evidence for this explanation is obtained from the n.q.r. data for the similar compound $Et_4N[VCl_4(MeCN)_2]$ in which no hydrogen bonding is possible and in which two n.q.r. lines both with positive temperature coefficients are observed.[15]

The disappearance of the high-frequency line can also be explained on the basis of hydrogen bonding. For $NaAuCl_4,2H_2O$, Sasane *et al.*[28] observed that one n.q.r. line, which was assigned to the only gold–chlorine bond involved with hydrogen bonding, was much broader than the other three lines. The broadening effect was attributed to magnetic dipole interaction with the protons. Hence, for the acetic acid compounds, if as the temperature is lowered the hydrogen bonding is increased, the magnetic dipole interaction should increase until the resonance is so broad it can no longer be detected. For the lower-frequency line, with no hydrogen bonding involved, the resonance intensity actually increases as the temperature is lowered.

For the tetramethylammonium compounds, only one very weak resonance was observed at room temperature. No resonance could be detected for the pyridinium–vanadium compound, and the n.q.r. spectrum was not recorded for the titanium compound.

Magnetic measurements were recorded over the temperature range 77 K to room temperature with the results shown in Table 5. The room-temperature magnetic moments of the chloride complexes are slightly depressed below the spin-only value for octahedral vanadium(III) and are further depressed in the case of the bromides. Our value of $\mu_{eff} = 2{\cdot}59$ B.M. compares

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well with the value reported[8] at room temperature for $Et_4NVBr_4(AcOH)_2$. The magnetic moments reported[8,15,19,24] for the complex ions $VX_4(MeCN)_2^-$ (X = Cl or Br) are also similar to those listed here. However, the magnetic moments for the acetic acid complexes decrease more markedly with temperature than the acetonitrile compounds. The magnetic data[19] for the latter compound were in agreement with the behaviour of a $^3T_{1g}$ ground-state ion under simultaneous perturbation by spin–orbit coupling and an axially distorted ligand field, with ground-state splittings of *ca.* 800 cm^{-1}. For the acetic acid complexes the more marked dependence on temperature of the magnetic moments suggests that the ground-state splittings are smaller than for the acetonitrile compounds. This observation can be correlated with the relative ligand-field strengths of the two ligands.

TABLE 5

Magnetic results

$Me_4NVCl_4(AcOH)_2$					
$\chi'_M/cm^3\ mol^{-1}$	3218	3414	3713	4092	4566
μ_{eff}/B.M.	2·74	2·72	2·68	2·64	2·60
T/K	290·9	270·1	241·3	213·0	184·8
$\chi'_M/cm^3\ mol^{-1}$	5194	6012	7203	8237	
μ_{eff}/B.M.	2·55	2·50	2·43	2·33	
T/K	156·7	129·9	102·3	81·3	
$Et_4NVCl_4(AcOH)_2$					
$\chi'_M/cm^3\ mol^{-1}$	3309	3531	3865	4262	4775
μ_{eff}/B.M.	2·76	2·74	2·71	2·67	2·63
T/K	287·5	266·4	237·7	209·6	181·7
$\chi'_M/cm^3\ mol^{-1}$	5439	6337	7594	9094	
μ_{eff}/B.M.	2·59	2·55	2·47	2·40	
T/K	154·4	128·0	100·6	79·5	
$(pvH)VCl_4(AcOH)_2$					
$\chi'_M/cm^3\ mol^{-1}$	3137	3409	3707	4053	4461
μ_{eff}/B.M.	2·74	2·74	2·71	2·66	2·61
T/K	297·0	272·5	244·7	216·3	188·8
$\chi'_M/cm^3\ mol^{-1}$	5010	5743	6775	8546	
μ_{eff}/B.M.	2·55	2·49	2·42	2·30	
T/K	161·0	133·9	106·9	77·0	
$Et_4NVBr_4(AcOH)_2$					
$\chi'_M/cm^3\ mol^{-1}$	2878	3037	3254	3515	3844
μ_{eff}/B.M.	2·59	2·56	2·51	2·45	2·39
T/K	291·3	269·3	241·2	213·3	185·8
$\chi'_M/cm^3\ mol^{-1}$	4245	4792	5553	6647	
μ_{eff}/B.M.	2·32	2·24	2·14	2·00	
T/K	158·4	131·0	103·3	77·5	
$Me_4NVBr_4(AcOH)_2$					
$\chi'_M/cm^3\ mol^{-1}$	2942	3093	3319	3600	3939
μ_{eff}/B.M.	2·62	2·60	2·55	2·49	2·44
T/K	289·6	270·9	242·4	214·1	187·1
$\chi'_M/cm^3\ mol^{-1}$	4389	4970	5692	6924	
μ_{eff}/B.M.	2·38	2·31	2·21	2·10	
T/K	159·6	132·8	106·4	79·1	

An unusual feature of the plots of reciprocal susceptibility against temperature is the marked curvature towards the temperature axis. This feature can also be observed from the magnetic data for other vanadium(III) halide complexes, *viz.*, $Et_4NVBr_4(MeCN)_2$, $(Et_4N)_3V_2Cl_9$, Et_4NVCl_4,[19] $(Et_2NH_2)_3V_2Cl_9$,[29] and M_2VCl_5 (M = Rb and Cs).[30]

EXPERIMENTAL

Preparations.—All materials were handled by standard vacuum-line techniques.

All five vanadium complexes were obtained by refluxing the trihalide hexahydrate in the appropriate acetyl halide until dissolved, whereupon the nitrogen base halide was added. The complexes precipitated immediately and were filtered off and dried at room temperature *in vacuo*. The trihalide hydrates were prepared as reported.[30]

$Et_4NVCl_4(AcOH)_2$. This *complex* was also isolated by treating $VCl_3,6H_2O$ and Et_4NCl,H_2O with acetic acid and thionyl chloride or by passing dry HCl into a solution of the same reactants dissolved in acetic acid. The complex was soluble in water (turning brown), in acetyl chloride (orange), dimethyl sulphoxide and dimethylformamide (yellow), and pyridine (intense violet); slightly soluble in acetic anhydride (yellow) and ethanol, methanol, and acetone (green); and insoluble in acetic acid, chloroform, ether, benzene, dichloromethane, tetrahydrofuran, and methyl cyanide (Found: Cl, 31·2; Et_4N, 29·3; V, 11·4%; oxidation state, 3·02. $C_{12}H_{28}Cl_4NO_4V$ requires Cl, 32·0; Et_4N, 29·4; V, 11·5%). In potentiometric titration with sodium hydroxide the end-point occurred at mole ratio NaOH : V = 4·94 and at 4·05 after the stoicheiometric quantity of Na_2(edta) was added. Similarly prepared were the *complexes* $Me_4NVCl_4(AcOH)_2$ (Found: Cl, 35·9, 36·7; V, 13·1, 13·3%; oxidation state, 3·00. $C_8H_{20}Cl_4NO_4V$ requires C, 36·7; V, 13·2%), and $Et_4NVBr_4(AcOH)_2$ (Found: Br, 51·4, 51·2; Et_4N, 20·7, 21·1; V, 8·1%; oxidation state, 2·99. $C_{12}H_{28}Br_4NO_4V$ requires Br, 51·5; Et_4N, 21·0; V, 8·2%).

$Me_4NVBr_4(AcOH)_2$. Initial attempts to prepare this *complex* resulted in coprecipitation of a brown solid. Acetic acid was added to the reaction mixture, which was warmed, and allowed to cool slowly. Small red crystals were present after standing for about two weeks (Found: Br, 57·9, 57·2; V, 8·8%; oxidation state, 3·00. $C_8H_{20}Br_4NO_4V$ requires Br, 56·6; V, 9·0%).

$(pyH)VCl_4(AcOH)_2$. This *complex* had a potentiometric titration end-point with NaOH : V = 4·95 mol ratio (Found: Cl, 36·3, 35·9; V, 12·6, 12·6%; oxidation state, 2·97. $C_9H_{14}Cl_4NO_4V$ requires Cl, 36·1; V, 13·0%).

$Et_4NTiCl_4(AcOH)_2$. The green *complex* was prepared as for the vanadium complexes from $TiCl_3,6H_2O$ which was prepared by refluxing titanium metal powder in 12M-hydrochloric acid under nitrogen, precipitation being effected by passage of hydrogen chloride (Found: Cl, 31·4, 31·7; Et_4N, 28·9, 29·2; Ti, 9·8(v), 10·0%(g); oxidation state, 3·03. $C_{12}H_{28}Cl_4NO_4Ti$ requires Cl, 32·7; Et_4N, 29·6; Ti, 10·9%).

Deuteriated complexes. $Et_4NVCl_4(AcOD)_2$ was partially deuteriated by crystallising the compounds from acetyl chloride and AcOD, the latter being generated *in situ* by the addition of D_2O to the acetyl chloride.

Analyses.—The vanadium oxidation state was determined by direct titration with cerium(IV) sulphate in 2N-sulphuric acid, and total vanadium by oxidation of the complexes in nitric–sulphuric acid mixtures, reduction with sodium sulphite, followed by titration with cerium sulphate. It was found that ferroin and *N*-phenylanthranilic acid were not suitable indicators but nitro-ferroin was

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[29] P. C. Crouch, G. W. A. Fowles, and R. A. Walton, *J. Chem. Soc.* (*A*), 1969, 972.

[30] L. P. Podmore and P. W. Smith, *Austral. J. Chem.*, submitted for publication.

used successfully. Titanium was titrated directly with cerium(IV) sulphate, and also determined gravimetrically by ignition of the compound to TiO_2. Halogens were determined by the Volhard method and cations were estimated gravimetrically with sodium tetraphenylboron.

Potentiometric titrations were performed with a Radiometer model 23 pH meter, the complexes being titrated directly in distilled water. For the vanadium complex, the stoicheiometric amount of the disodium salt of edta was added and the complex titrated according to reaction[9] (1).

$$V^{3+} + \mathrm{edta}H_2^{2-} \longrightarrow V(\mathrm{edta})^- + 2H^+ \qquad (1)$$

Instrumental.—The visible–u.v. spectra were recorded on a Zeiss PMQII or Perkin-Elmer Spectracord 4000A spectrophotometer. Magnetic measurements were recorded by the Gouy technique as described previously. N.q.r. spectra were recorded on a Wilks NQRIA spectrometer, with low-temperatures obtained by passing cold nitrogen gas over the sample in a vacuum-jacketed tube, the temperature being measured by a copper–constantan thermocouple. I.r. spectra were recorded on a Perkin-Elmer model 221 spectrophotometer with caesium bromide interchange for the 650—260 cm^{-1} range. Samples were mulled in petroleum jelly, hexachlorobutadiene, and Kel F.

Two of us (L. P. P. and R. S.) acknowledge Commonwealth Postgraduate Scholarships. We thank the Australian Research Grants Committee for equipment and maintenance grants.

[2/1682 *Received*, 17*th July*, 1972]