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SOME COMPLEX HALIDES OF VANADIUM(II) AND VANADIUM(III). THE CRYSTAL AND MOLECULAR STRUCTURE OF TETRAKIS(METHYLAMMONIUM) HEXACHLOROVANADATE(III) CHLORIDE

DOST M. HALEPOTO, LESLIE F. LARKWORTHY,* DAVID C. POVEY,
GALLIENUS W. SMITH and VIJAYALAKSMI RAMDAS

Department of Chemistry, University of Surrey, Guildford GU2 5XH, U.K.

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Abstract—Some complex chlorides of vanadium(II), $A_2[VCl_4(CH_3CO_2H)_2]$, where A = $NMeH_3$, $C(NH_2)_3$ (guanidinium) and $C_4H_{12}N_2$ (pyrazinium), have been isolated from vanadium(II) chloride in acetic acid and characterized by magnetic and spectroscopic measurements. By controlled aerial oxidation of the vanadium(II) complexes or directly from VCl_3, a series of hexachlorovanadates (III), $A_4[VCl_6]Cl$, has been prepared in which A = $NMeH_3$, NMe_2H_2, $NEtH_3$, NPr^nH_3 and $NBzH_3$. A single crystal X-ray investigation has been carried out on the methylammonium salt. There are two independent VCl_6 octahedra in the structure. Both are regular, with V—Cl distances in the range 2.380(2)–2.401(2) Å and the internal Cl—V—Cl angles all within 0.5° of 90°. The complexes $[Hpy]_3[VCl_6]$, $[NBu^nH_3]_2[VCl_5]$ and $[NMeH_3]_4[VBr_6]Br$ have also been isolated. From VCl_3 and the alkylammonium chloride in acetic acid or propionic acid as appropriate, the salts $A_2[VCl_5(CH_3CO_2H)]$ (A = NMe_2H_2 and $NEtH_3$) and $A_2[VCl_5[C_2H_5CO_2H)]$ (A = NPr^nH_3 and NBu^nH_3) have been obtained.

Many complex halides of vanadium(III) exist, containing four, five and six halide ligands, but few are known for vanadium(II).[1] Those of vanadium(II) are predominantly of the type AVX_3, where A is a monovalent cation and X is halide, containing $(VX_3)_n^{n-}$ chains, although there are some with mononuclear anions, e.g. $Cs_2[VCl_4(H_2O)_2]$.[2] Anhydrous complex halides of vanadium(II) are generally prepared by high temperature dry routes.[1] However, $RbVCl_3$[2,3] and $CsVBr_3$[4] are formed by thermal dehydration of the hexahydrates, previously obtained from $VX_2 \cdot nH_2O$ prepared by electrolyte reduction. Vanadium(II) chemistry is somewhat restricted by the reactivity of the oxidation state and the lack of suitable starting materials.[1] We have found that the vanadium(II) complex halides, $A_2[VCl_4(CH_3CO_2H)_2]$, where A = $NMeH_3$, $C(NH_2)_3$ (guanidinium) and $C_4H_{12}N_2$ (piperazinium) can be isolated (Table 1) from acetic acid containing ACl and $[VCl_2(CH_3CO_2H)_4]$, which can in turn be obtained from vanadium metal and hydrogen chloride gas in acetic acid.[5] Oxygen reacts with the vanadium(II) complex halides in solution to give vanadium(III) complex halides, for example $[NMeH_3]_4[VCl_6]Cl$, the crystal structure of which has been determined. The formulation of the complex has been confirmed by its preparation from anhydrous vanadium(III) chloride and methylammonium chloride. A series of similar hexachlorovanadates (III) has been produced by these methods. Previously, only $[HPy]_3[VCl_6]$[6] and the alkali metal salts were known.[7] Some salts of the new anions $[VCl_5(RCO_2H)]^{2-}$ (R = Me or Et) have also been isolated.

EXPERIMENTAL

All preparations were carried out under nitrogen. The vanadium(II) starting materials $[VCl_2(CH_3$

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* Author to whom correspondence should be addressed.

Table 1. Analysis and magnetic properties of the vanadium(II) and vanadium(III) complexes

	Analyses[a] (%)					μ_{eff}			
	C	H	N	Cl	V[b]	295 K	90 K	θ°[c]	$10^6\chi L$[d]
Vanadium(II) complexes									
$[NMeH_3]_2[VCl_4(CH_3CO_2H)_2]$ green	19.0 (19.1)	5.4 (5.3)	7.7 (7.4)	37.3 (37.0)	13.4 (13.5)	3.99	3.84	11	305
$[C(NH_2)_3]_2[VCl_4(CH_3CO_2H)_2]$ green	17.1 (16.7)	4.7 (4.2)	19.1 (19.5)	32.3 (32.9)	11.7 (11.8)	3.89	3.89	0	305
$[C_4H_{12}N_2][VCl_4(CH_3CO_2H)_2]$ light green	23.95 (22.9)	5.0 (5.2)	6.7 (7.6)	35.8 (35.6)	12.3 (12.7)	3.68	3.71	−2	212
Vanadium(III) complexes									
$[NMeH_3]_4[VCl_6]Cl$ dark pink	12.0 12.2 (11.2)	5.9 6.3 (5.7)	13.3 14.4 (13.1)	57.8 — (58.1)	11.8[e] 13.0[f] (11.19)	2.64	2.19	74	257
$[NMe_2H_2]_4[VCl_6]Cl$ dark pink	19.5 20.6 (19.9)	6.2 6.2 (6.7)	11.0 9.95 (11.6)	51.0 — (51.3)	11.0[e] —[f] (10.5)	2.81	2.47	44	304
$[NEtH_3]_4[VCl_6]Cl$ orange–pink	20.6 21.5 (19.9)	6.6 6.65 (6.7)	11.8 11.1 (11.6)	51.2 — (51.3)	10.4[e] —[f] (10.5)	2.69	2.25	67	305
$[NPr^nH_3]_4[VCl_6]Cl$ pink	25.5 (26.7)	7.2 (7.5)	9.5 (10.4)	46.2 (46.0)	9.4[e] (9.45)	2.69	2.42	34	352
$[Hpy]_3[VCl_6]$ rose–red	35.8 (35.7)	3.7 (3.6)	8.2 (8.3)	42.2 (42.2)	10.0[e] (10.1)	2.90	2.76	15	270
$[N_2H_5]_3[VCl_6]\cdot 0.25CH_3CN$ red–brown	1.85 (1.60)	4.6 (4.25)	23.9 (23.4)	57.0 (57.0)	13.8 (13.7)	2.55	2.30	33	190
$[NBzH_3]_4[VCl_6]Cl$ orange–pink	46.6 (45.95)	5.9 (5.5)	8.3 (7.65)	33.0 (33.9)	6.7[e] (7.0)	2.38	2.27	13	366
$[NPhH_3]_6[VCl_6]Cl_3$ pink	46.9 (46.25)	5.4 (5.2)	9.0 (9.0)	34.1 (34.1)	5.4[e] (5.45)	2.52	2.05	85	570
$[NBu^nH_3]_2[VCl_5]$ orange–pink	24.9 (25.5)	6.0 (6.4)	7.8 (7.4)	47.5 (47.1)	13.8[e] (13.5)	2.50	2.24	35	217
$[NMeH_3]_4[VBr_6]Br\cdot 0.5CH_3CO_2H$ yellow–brown	7.7 7.5 (7.8)	3.55 3.75 (3.4)	7.5 7.3 (7.30)	72.8[g] — (72.8)	6.6[h] —[i] (6.6)	2.68	2.13	100	232
$[NMe_2H_2]_2[VCl_5(CH_3CO_2H)]$ dark pink	19.0 (18.9)	6.0 (5.3)	7.4 (7.35)	46.35 (46.6)	13.3[e] (13.4)	2.45	2.21	34	213
$[NEtH_3]_2[VCl_5(CH_3CO_2H)]$ dark pink	18.7 (18.9)	5.55 (5.3)	7.35 (7.35)	46.0 (46.6)	13.5[e] (13.4)	2.68	2.23	72	213
$[NPr^nH_3]_2[VCl_5(C_2H_5CO_2H)]$ pink	24.95 (25.6)	6.7 (6.2)	7.4 (6.6)	42.0 (41.95)	12.1[e] (12.1)	2.54	2.27	36	248
$[NBu^nH_3]_2[VCl_5(C_2H_5CO_2H)]$ dark pink	31.4 (29.3)	7.5 (6.7)	6.5 (6.2)	—	—[e]	2.14	1.95	29	272

[a] Calculated values in parentheses.
[b] As vanadium(II).
[c] Curie–Weiss law taken as $\chi_v^{-1}\alpha(T+\theta)$.
[d] Diamagnetic correction in c.g.s.u. (SI = c.g.s.u. × $4\pi/10^6$).
[e] From VCl_3.
[f] From $[VCl_2(CH_3CO_2H)_4]$.
[g] From $[V(CH_3CO_2H)_6]Br_2$ and bromide analysis.
[h] Total vanadium as V_2O_5.
[i] From VBr_3.

$CO_2H)_4]$ and $[V(CH_3CO_2H)_6]Br_2$ were prepared from vanadium metal (Aldrich) as described[5]. VCl_3 (Aldrich) and VBr_3 (Alpha Chemicals) were used as-received. Magnetic susceptibility studies of samples in sealed tubes were carried out by the Gouy method from room temperature to liquid-nitrogen temperature. The field was calibrated with $Hg[Co(NCS)_4]$ and $[Ni(en)_3]S_2O_3$. The diffuse reflectance spectra of samples in sealed cells were recorded on a Beckman Acta MIV spectrophotometer. IR spectra of Nujol mulls made up in an inert atmosphere box were recorded on a Perkin–Elmer 577 spectrophotometer.

Preparation of vanadium(II) *compounds*

To prepare bis(guanidinium) bis(acetic acid) tetrachlorovanadate(II) $[VCl_2(CH_3CO_2H)_4]$ (1.77 g, 0.0049 mol) was dissolved in hot glacial acetic (40 cm^3) to give a blue solution. To this was added guanidinium chloride (1.10 g, 0.0115 mol) and the reaction mixture was heated for 1 h. A green complex separated on cooling. It was filtered off, washed with glacial acetic acid and dried by continuous pumping at room temperature for 6 h (yield 70%). The green compound turned brown in a few minutes in air. The methylammonium and piperazinium salts were prepared similarly (Table 1). An aqueous solution of the methylammonium salt, prepared under nitrogen, has the electronic spectrum of the hydrated ion, $[V(H_2O)_6]^{2+}$. The known complexes $CsVCl_3$ and $CsVBr_3$ have been isolated respectively from solutions of VCl_2 in acetic acid and VBr_2 in propionic acid. The solutions were prepared from the metal and the hydrogen halide gas; the concentration of VX_2 was determined from the weight of metal which had dissolved. The molar ratios of reactants were such that Cs_2VX_4 or Cs_4VX_6 might have been formed but only trihalogenato complexes separated.

Tetrakis(*methylammonium*) *hexachlorovanadate*(III) *chloride*

Vanadium(III) chloride (0.91 g, 0.0057 mol) was suspended in glacial acetic acid (25 cm^3). To this, methylammonium chloride (1.56 g, 0.022 mol) was added. A pink product separated on heating, but this re-dissolved on further heating to give a green solution which was then allowed to cool slowly. Dark pink needles crystallized after a few hours, and these were filtered off, washed with acetic acid and dried at the pump. They soon became green in air.

This complex was also obtained from a solution of vanadium(II) chloride in glacial acetic acid (50 cm^3) prepared from HCl (g) and the metal (0.15 g, 0.0029 mol), to which methylammonium chloride (1.25 g, 0.0185 mol) was added. The reaction mixture was heated gently to dissolve some pink solid which had separated and the green–blue solution was then allowed to stand overnight. The dark pink crystals which appeared were filtered off, washed with glacial acetic acid and dried by continuous pumping at room temperature for 10 h. One such crystal was used in the structure determination.

Tetrakis(*dimethylammonium*) *hexachlorovanadate*(III) *chloride*

To vanadium(III) chloride (0.90 g, 0.0057 mol) suspended in acetonitrile (100 cm^3), dimethylammonium chloride (1.50 g, 0.0184 mol) was added. The reaction mixture was heated to boiling and a pink solid separated from the hot solution. This solid was filtered off after the liquid had cooled, washed with acetonitrile and dried by pumping for 5 h. This complex was also prepared by the action of oxygen (as air, *ca* 100 cm^3) on a mixture of $[VCl_2(CH_3CO_2H)_4]$ (2.17 g, 0.006 mol) and dimethylammonium chloride (1.00 g, 0.0144 mol) suspended in acetic acid (30 cm^3). The reaction mixture was heated gently until all the dimethylammonium chloride had dissolved and then the resulting green solution was shaken and allowed to cool undisturbed. The dark pink crystals which appeared were filtered off, washed with glacial acetic acid and dried by pumping. The compound rapidly turned green in air.

Tetrakis(*ethylammonium*) *hexachlorovanadate*(III) *chloride*

This complex was prepared as an orange–pink solid from vanadium(III) chloride and ethylammonium chloride in acetonitrile as above. It was also synthesized by reaction of a dark blue solution of $[VCl_2(C_2H_5CO_2H)_n]$, obtained by reaction of HCl (g) with vanadium (0.10 g, 0.0020 mol) in propionic acid (50 cm^3), with ethylammonium chloride (0.64 g, 0.0078 mol) in propionic acid. Some dark pink crystals separated rapidly; these were re-dissolved by gentle heating to give a greenish blue solution from which a mass of dark pink crystals separated on slow cooling. The crystals were filtered off, washed with propionic acid and dried at the pump for 8 h.

Tetrakis(n-propylammonium) and tetrakis (benzylammonium) hexachlorovanadate(III) chloride were prepared as above from VCl_3 and the ammonium halide in boiling acetonitrile, as was tris(pyridinium) hexachlorovanadate(III), but from n-butylammonium chloride a pentachlorovanadate(III) was obtained. From hydrazinium chloride and VCl_3, a reddish brown product analyzing as $[N_2H_5]_3[VCl_6]\cdot 0.25CH_3CN$ was obtained. The pink solid isolated from 1 : 3 molar quantities of VCl_3 and anilinium chloride after reflux analyzed as hexakis(anilinium) hexachlorovanadate(III) trichloride.

Tetrakis(methylammonium) hexabromovanadate(III) *bromide*·0.5 *acetic acid*

The vanadium(II) salt[5] $[V(CH_3CO_2H)_6]Br_2$ (2.00 g, 0.0035 mol) was dissolved in hot glacial acetic acid (50 cm^3) to give a dark green solution to which methylammonium bromide (1.50 g, 0.0133 mol) was added. Oxygen (as air ~ 100 cm^3) was admitted and the mixture heated. Yellowish brown crystals separated from a dark green solution on cooling. These were filtered off, washed with glacial acetic acid and dried by pumping (yield 50%).

The complex was also prepared from vanadium(III) bromide (0.80 g, 0.0027 mol) suspended in glacial acetic acid (50 cm^3) with methylammonium bromide (1.0 g, 0.0089 mol). The mixture was heated under reflux for 2 h. Dark brown crystals separated from the reddish brown solution on cooling. They were filtered off, washed with glacial acetic acid and dried under vacuum at room temperature. The complex soon became dark green in air.

Bis(dimethylammonium) mono(acetic acid)pentachlorovanadate(III)

Vanadium(III) chloride (1.50 g, 0.0095 mol) was suspended in glacial acetic acid (75 cm^3). To this, dimethylammonium chloride (2.63 g, 0.038 mol) was added. The reaction mixture was heated until all the reactants had dissolved. The dark pink crystals obtained from the green solution on cooling were filtered off, washed with acetic acid and dried by pumping. The pink ethylammonium salt was prepared in the same way. Both salts soon became green in air.

Bis(n-propylammonium) pentachloromono(propionic acid)vanadate(III)

Vanadium(III) chloride (1.27 g, 0.0080 mol) was dissolved in hot propionic acid (100 cm^3). To this was added n-propylammonium chloride (3.00 g, 0.0314 mol). Some pink compound which separated was re-dissolved by heating to give a dark green solution. On cooling, dark pink needles separated. They were filtered off, washed with propionic acid and dried at the pump. The n-butylammonium salt was analogously obtained. Both become green in air.

X-ray crystal structure analysis of $[NMeH_3]_4[VCl_6]Cl$

Crystals prepared as described above were sealed under nitrogen in Lindemann capillaries.

Crystal data

$C_4H_{24}Cl_7N_4V$, $M = 427.38$, monoclinic, $a = 15.968(4)$, $b = 7.295(3)$, $c = 16.030(4)$ Å, $\beta = 103.60(3)°$, $U = 1815.0$ (2) Å^3, space group = $P2/n$, $Z = 4$, $D_c = 1.564$ g cm^{-3}, pink, air-sensitive needles of approximate dimensions 0.3 × 0.2 × 0.2 mm, $F(000) = 872$, graphite-monochromated Mo-K_α radiation ($\lambda = 0.71073$ Å), μ(Mo-K_α) = 15.54 cm^{-1}.

Data collection and processing

Cell parameters were determined on a CAD4 diffractometer using 25 accurately centred reflections in the range $13° \leqslant \theta \leqslant 15°$. Data were collected to a θ limit of 26° ($-19 \leqslant h \leqslant 19, 0 \leqslant k \leqslant 9, 0 \leqslant l \leqslant 19$) in the ω–2θ scan mode with a scan speed of 3.3° min^{-1}. This yielded a total of 3989 reflections, 2204 having $I \geqslant 3\sigma(I)$. Systematic absences were observed only for $h\ 0\ l$, $h+l$ odd, while the intensity statistics indicated the presence of a centre of symmetry. Space group $P2/n$ was therefore adopted. Psi data were not available for an empirical absorption correction.

Structure analysis and refinement

The structure was partially solved using SHELX86[8] and interpretation of the Patterson map to give positions of the vanadium and chlorine atoms. The light atoms were subsequently located on a difference Fourier map. Isotropic refinement converged smoothly to $R = 0.083$ and the hydrogen atoms of the CN groups were observed on a difference map. Their positions were added to the atoms list and their coordinates regularized to give ideal tetrahedral geometry with $d_H = 1.0$ Å. An absorption correction was applied by the program DIFABS,[9] which gave min/max corrections of 0.90/1.16. At this stage there was uncertainty about the correct identity of the carbon and nitrogen positions. Refinement of the occupancy factors of these eight sites was inconclusive, but a 4.0 Å search about these atoms disclosed that four sites were ~3.2 Å from the chlorine atoms Cl(7) and Cl(8),

Table 2. Bond lengths (Å) and angles (°) for $[NMeH_3]_4[VCl_6]Cl$ with e.s.d. values in parentheses

V(1)—Cl(1)	2.389(2)	V(2)—Cl(5)	2.401(2)	N(3)—C(3)	1.438(12)
V(1)—Cl(2)	2.384(1)	V(2)—Cl(6)	2.380(2)	N(4)—C(4)	1.452(13)
V(1)—Cl(3)	2.384(2)	N(1)—C(1)	1.433(12)		
V(2)—Cl(4)	2.386(2)	N(2)—C(2)	1.411(12)		
Cl(1)—V(1)—Cl(2)	90.36(6)	Cl(2)—V(1)—Cl(3)	90.07(6)	Cl(4)—V(2)—Cl(6)	90.03(6)
Cl(1)—V(1)—Cl(3)	90.24(6)	Cl(4)—V(2)—Cl(5)	90.56(6)	Cl(5)—V(2)—Cl(6)	90.10(6)

while the other four sites were ~3.6 Å from these atoms. The former sites were taken to be the nitrogen positions, since it is on these atoms where the charge resides and therefore the most likely to form hydrogen bonds with the chlorines.

Full-matrix anisotropic refinement was started, initially with vanadium and chlorine anisotropic, then with all non-hydrogen atoms, resulting in convergence at $R = 0.048$, $R_w = 0.076$, $S = 1.126$, using a weighting scheme[10] $w^{-1} = [(\sigma(F))^2 + (0.04F)^2 + 4.0]$. The highest peak in a final difference map was 0.46 electrons. All calculations were performed with the Enraf-Nonius structure determination package.[11] Selected bond lengths and angles are given in Table 2, and the atom numbering scheme is shown in Fig. 1. The unit cell is shown in Fig. 2.

RESULTS AND DISCUSSION

Vanadium(II) *complex halides*

The use of acetic acid as solvent has permitted the isolation from $[VCl_2(CH_3CO_2H)_4]$ of a number of new vanadium(II) complex halides $A_2[VCl_4(CH_3CO_2H)_2]$, where A = $NMeH_3$, $C(NH_2)_3$ and $C_4H_{12}N_2$; and the known complexes $CsVCl_3$ and $CsVBr_3$, previously obtained by high temperature dry routes or by thermal dehydration of the hexahydrate ($CsVBr_3$)[1,4]. The complexes $A_2[VCl_4(CH_3CO_2H)_2]$ have effective magnetic moments which are close to the spin-only value for a $3d^3$ ion (3.87) and essentially independent of temperature (Table 1), as expected for magnetically-dilute complexes. The diffuse reflectance spectra of $A_2[VCl_4(CH_3CO_2H)_2]$ contain three absorption bands (Table 3), assignable to the transitions ${}^4A_{2g} \rightarrow {}^4T_{2g}$ (ν_1), ${}^4A_{2g} \rightarrow {}^4T_{1g}$ (*F*) (ν_2) and ${}^4A_{2g} \rightarrow {}^4T_{1g}$ (*P*) (ν_3), as expected for vanadium(II) in an octahedral complex.[12] On dissolution in water under nitrogen, the characteristic spectrum of $[V(H_2O)_6]^{2+}$ is obtained. IR spectra of the complexes show bands due to the cations and additional bands due to the coordinated acetic acid. Vanadium–chloride and vanadium–oxygen stretching vibrations occur near 270 and 450 cm^{-1}, respectively (Table 3). *Trans*–octahedral structures are proposed for the complex anions, although

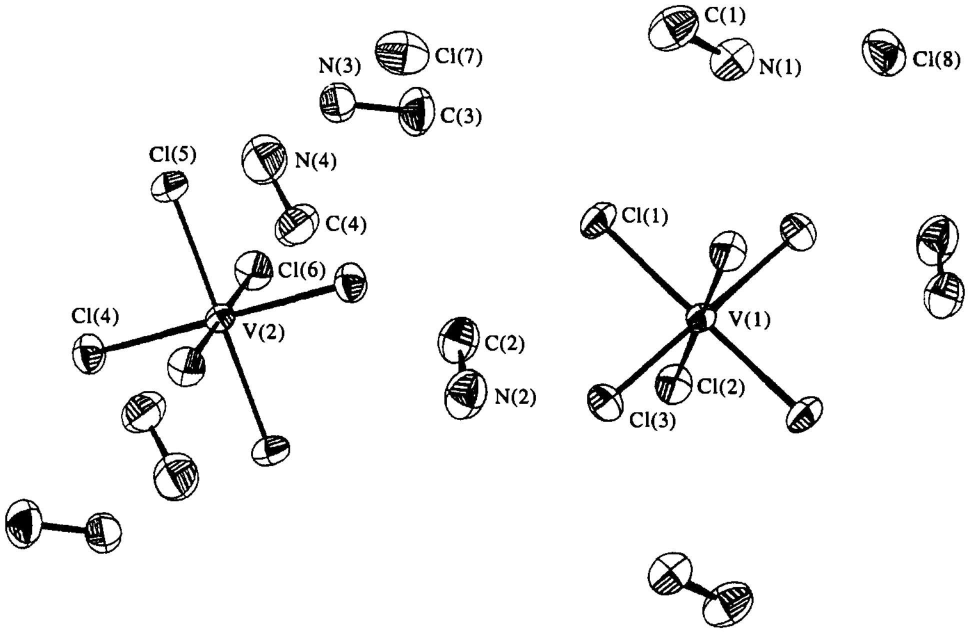

Fig. 1. Atom numbering scheme for $[NMeH_3]_4[VCl_6]Cl$.

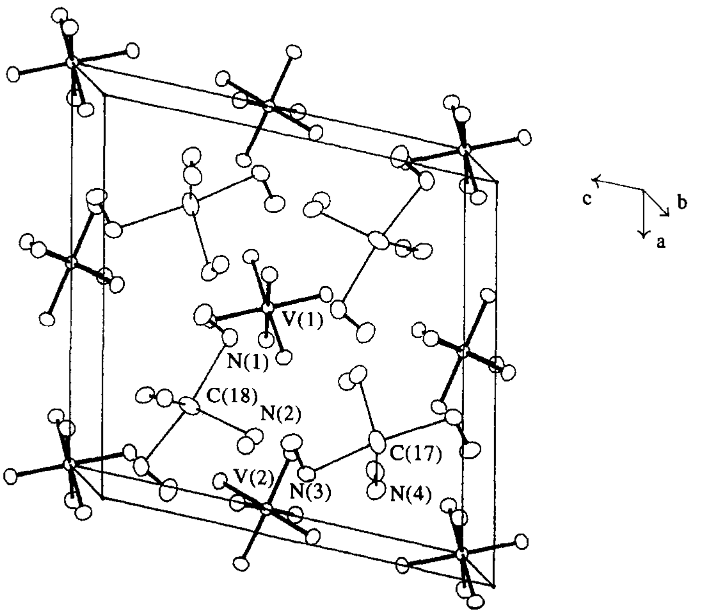

Fig. 2. Unit cell of $[NMeH_3]_4[VCl_6]Cl$.

Table 3. Electronic and IR absorption bands of the complexes

	Reflectance spectra (cm^{-1} × 10^{-3})			IR bands (cm^{-1})		
	ν_1	ν_2	ν_3	ν(C═O)	ν(v—Cl)	ν(V—O)
Vanadium(II) complexes						
$[NMeH_3]_2[VCl_4(CH_3CO_2H)_2]$	10.0m,br	15.3m,br	26.5s	1670	270	480
$[C(NH_2)_3]_2[VCl_4(CH_3CO_2H)_2]$	10.0m,br	15.55m,br	26.5s	1650	270	450
$[C_4H_{12}N_2][VCl_4(CH_3CO_2H)_2]$	9.6m,br	15.2m,br	26.9s	1670	260	450
Vanadium(III) complexes						
$[NMeH_3]_4[VCl_6]Cl$	11.8m,br	18.5m	26.7s		310	
$[NMe_2H_2]_4[VCl_6]Cl$	11.6sh 12.5m,br	19.05m	27.9s		320	
$[NEtH_3]_4[VCl_6]Cl$	11.6m	18.35m	26.9s		320	
$[NPr^nH_3]_4[VCl_6]Cl$	11.7sh 12.5m	19.3m	28.1s		310	
$[Hpy]_3[VCl_6]$	11.8sh 12.55m	19.6m	27.4s		320	
$[N_2H_5]_3[VCl_6]\cdot 0.25CH_3CN$	12.5sh 14.3m,br	19.6m	27.8m		310	
$[NBzH_3]_4[VCl_6]Cl$	12.8m	20.0m	27.8m		310	
$[NPhH_3]_6[VCl_6]Cl_3$	11.9br	18.5m	27.55s		310	
$[NBu^nH_3]_2[VCl_5]$	12.9br	20.8br			330	
$[NMeH_3]_4[VBr_6]Br\cdot 0.5CH_3CO_2H$	11.05m	16.1sh	24.4s,vbr		230	
$[NMe_2H_2]_2[VCl_5(CH_3CO_2H)]$	12.5m,vbr	18.9m	27.2s	1660	320	475
$[NEtH_3]_2[VCl_5(CH_3CO_2H)]$	12.3m,vbr	18.9m	27.4s	1660	310	405
$[NPr^nH_3]_4[VCl_5(C_2H_5CO_2H)]$	12.0br	18.9m	27.0s	1660	310	400
$[NBu^nH_3]_2[VCl_5(C_2H_5CO_2H)]$	12.5vbr	19.05m	28.2s	1660	310	400

no X-ray study has been carried out because of the lack of suitable crystals. Analogous anions of vanadium(III) have been isolated, i.e. $A[VCl_4(CH_3CO_2H)_2]$ (A = NEt_4, NMe_4 or Hpy). These, as would be expected, show *d–d* transitions and V—Cl stretching vibrations at higher wavenumbers than the vanadium(II) anions.[13]

Preparation of vanadium(III) *complexes*

During some preparations of $[NMeH_3]_2[VCl_4(CH_3CO_2H)_2]$ and other vanadium(II) complexes from $[VCl_2(CH_3CO_2H)_4]$, small amounts of crystalline pink solids separated when the reactants were mixed. These were first thought to be vanadium(II) complexes because the microanalyses fitted best with the general formula $A_4[VCl_6]$ (A = $NMeH_3$, $NEtH_3$ and NMe_2H_2). However, the magnetic moments were low for vanadium(II), the reflectance spectra were atypical and analyses showed zero vanadium(II) content. Finally, a single crystal X-ray study showed the methylammonium salt to be $[NMeH_3]_4[VCl_6]Cl$. It appears that the vanadium(III) complexes were being formed through inadvertent admission of traces of oxygen and/or through oxidation by protons from the acetic acid or propionic acid reaction media. To increase the yields of the vanadium(III) complexes, approximately stoichiometric amounts of oxygen as air were admitted to the reaction mixture in the preparation of some complexes, and the preparation of several, also from vanadium(III) chloride, confirmed their formulations.

The magnetic moments of the vanadium(III) complexes are generally below the spin-only value (2.83) for the $3d^2$ configuration and decrease markedly with temperature. Since hexahalogenovanadate(III) complexes would be expected to be magnetically dilute the variation of magnetic moments arises from a combination of distortion and delocalization effects and spin-orbit coupling, as found in other six-coordinate vanadium(III) complexes.[14]

The reflectance spectra of the vanadium(III) compounds contain bands which can be assigned [12] to the three spin-allowed *d–d* transitions: ${}^3T_{1g}(F) \rightarrow {}^3T_{2g}(F)$ (ν_1), ${}^3T_{1g}(F) \rightarrow {}^3T_{1g}(P)$ (ν_2) and ${}^3T_{1g}(F) \rightarrow {}^3A_{2g}(F)$ (ν_3). Usually, the third bank is not observed because it is weak and frequently masked by charge-transfer transitions. Slightly lower wavenumbers are observed for the bromo complex $[NMeH_3]_4[VBr_6]Br$, as expected. The spectrum of $[NBuH_3]_2[VCl_5]$ shows band positions similar to those observed for the complexes containing $[VCl_6]^{3-}$ ions, suggesting an octahedral vanadium(III) environment through chloride bridging. The ν(V—Cl) absorption bands are found in the far-IR spectrum at 310–320 cm^{-1} (Table 3), at higher wavenumber than for the vanadium(II) chloro complexes.

Discussion of the structure of $[NMeH_3]_4[VCl_6]Cl$

The unit cell volume indicates a very open structure, since the average unit atomic volume is ~30 Å^3, substantially higher than usual. The stability of the structure is attained by the hydrogen bonding which occurs between the charged end of the methylammonium ions and the two independent chloride ions, which are sited on the diad axes. Figure 2 shows the four methylammonium ions clustered around the chloride positions. Table 4 lists closest contacts between the nitrogen atoms and all the chlorine sites less than 3.5 Å. It will be seen that in addition to the hydrogen bonded atoms Cl(7)—N(3) (3.19 Å), Cl(7)—N(4) (3.23 Å), Cl(8)—N(1) (3.18 Å) and Cl(8)—N(2) (3.29 Å), there exist other contacts to the two independent VCl_6 groups which must play a part in stabilizing the structure. These contacts have not been shown in the diagram for the sake of clarity. All the carbon–chloride sites exceed 3.6 Å.

The two VCl_6 octahedra are very regular with all the internal angles within 0.5° of 90°. The V—Cl distances around V(1) are very similar, ranging from 2.384 to 2.389 Å, while those around V(2)

Table 4. Short contacts between the nitrogen and chlorine sites

	Distance (Å)
N(1)—Cl(8)^a	3.19
N(1)—Cl(3)^b	3.25
N(1)—Cl(3)^a	3.43
N(1)—Cl(1)^b	3.48
N(1)—Cl(1)^a	3.49
N(2)—Cl(8)^b	3.29
N(2)—Cl(3)^a	3.32
N(2)—Cl(4)^b	3.34
N(2)—Cl(5)^b	3.43
N(3)—Cl(7)^a	3.19
N(3)—Cl(6)^b	3.26
N(3)—Cl(6)^a	3.34
N(3)—Cl(4)^b	3.43
N(3)—Cl(5)^a	3.46
N(4)—Cl(7)^a	3.23
N(4)—Cl(5)^a	3.28
N(4)—Cl(2)^c	3.37
N(4)—Cl(1)^d	3.42

Symmetry codes: ^{a} x, y, z; ^{b} $\bar{x}, \bar{y}, \bar{z}$; ^{c} $\frac{1}{2}+x, \bar{y}, \frac{1}{2}+z$; ^{d} $\frac{1}{2}-x, y, \frac{1}{2}-z$.

[V(2)—Cl(4) 2.386 Å and V(2)—Cl(6) 2.380 Å] are almost the same, but V(2)—Cl(5) is significantly different at 2.401 Å. There appears to be no obvious reason for this difference, although it should be noted that the Cl(5)—N(4) length of 3.28 Å is suggestive of a weak hydrogen bond, along with Cl(6)—N(3) (3.26 Å) and Cl(3)—N(1) (3.25 Å). Similar V—Cl distances occur in $[VCl_2(H_2O)_4]Cl \cdot 2H_2O$ (2.361 Å),[15] $Cs_2[VCl_2(H_2O)_4]Cl_3$ (2.361 Å),[16] $Cs_3[VCl_2(H_2O)_4]Cl_4$ (2.377 Å)[17] and in $[V_3(\mu\text{-O})(CH_3CO_2)_6(CH_3CO_2H)_2(thf)][VCl_4(CH_3CO_2H)_2]$ (2.336 Å).[18]

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