Preparation, Properties, and Crystal and Molecular Structures of *trans*-Tetrakis(acetic acid)dichlorovanadium(II) and Hexakis(acetic acid)vanadium(II) Dibromide†

David G. L. Holt, Leslie F. Larkworthy,* David C. Povey, and Gallienus W. Smith
Department of Chemistry, University of Surrey, Guildford GU2 5XH
G. Jeffery Leigh
A.F.R.C. Institute of Plant Science Research, Nitrogen Fixation Laboratory, University of Sussex, Brighton BN1 9RQ

The vanadium(II) complexes $[VCl_2(CH_3CO_2H)_4]$ and $[V(CH_3CO_2H)_6]Br_2$ have been obtained from reactions between vanadium, acetic acid and HX (X = Br or Cl). Crystal structure analysis confirms that in each case acetic acid molecules are bonded by the carbonyl oxygen rather than the hydroxyl oxygen. In *trans*-octahedral $[VCl_2(CH_3CO_2H)_4]$ the mean co-ordination sphere bond distances are V–O 2.125 and V–Cl 2.497 Å. There is considerable intramolecular hydrogen bonding. In $[V(CH_3CO_2H)_6]Br_2$ the cations are regular octahedra (mean V–O 2.114 Å) and they are hydrogen bonded to the anions throughout the lattice. The reactions of HX with vanadium in some other non-aqueous solvents have been investigated.

Few carboxylic acid or even carboxylato complexes of vanadium(II) or vanadium(III) have been reported.[1] An attempt to prepare vanadium(II) acetate by dissolving freshly precipitated vanadium(II) carbonate in acetic acid gave a product[2] heavily contaminated with vanadium(III). The trinuclear complex $[V_3(\mu_3\text{-}O)(CH_3CO_2)_6(thf)_3]$ (thf = tetrahydrofuran) formally contains one vanadium(II) and two vanadium(III) atoms.[3] Several vanadium(III) carboxylates, $[V(CH_3CO_2)_3]$,[4,5] $[V_2(RCO_2)_6]$ (R = CH_3 or C_6H_5[6]), and $[V_3(\mu_3\text{-}O)(CH_3CO_2)(CH_3CO_2H)_2(thf)][VCl_4(CH_3CO_2H)_2]$[3] are known. The formulation of the last compound as a salt of a trinuclear, oxo-centred cation containing bridging acetate and terminal acetic groups, and an octahedral anion with co-ordinated acetic acid, is based on the crystal structure data and the preparative method. The anion[3] $[VCl_4(CH_3CO_2H)_2]^-$ is also present[7,8] in $[A][VX_4(CH_3CO_2H)_2]$ [A = NMe_4 or NEt_4, X = Cl or Br; A = pyridinium (Hpy), X = Cl].

Hexakis(acetic acid)metal(II) cations have been reported for Mg, Mn, Co, Ni, Cu, and Zn as BF_4^-, ClO_4^-, and NO_3^- salts.[9] Only the nickel complex $[Ni(CH_3CO_2H)_6][BF_4]_2$ has been examined structurally.[10] The nickel atom is surrounded octahedrally by oxygen atoms and, as was inferred earlier from infrared and other studies,[9] is bonded to the carbonyl oxygen, not to the hydroxyl oxygen. This paper describes the preparation and structural characterization of the first vanadium(II) complexes containing co-ordinated acetic acid.

Experimental

Preparations and physical measurements were carried out with the exclusion of air. Vanadium turnings (99.7%) were obtained from Aldrich; acetic acid (AnalaR) was used as received from May and Baker Ltd. as were the anhydrous hydrogen halides (AnalaR) from BDH.

Tetrakis(*acetic acid*)*dichlorovanadium*(II).—Hydrogen chloride was passed through glacial acetic acid (75 cm^3) over vanadium turnings (5 g) until rapid effervescence was observed from the metal surface. The reaction mixture was then heated at 90 °C for 8—10 h to give a dark blue solution. When there was no further effervescence the solution was filtered from the excess of metal (4 g), cooled and concentrated to half volume under vacuum. The colour changed gradually from blue to green on concentration. On standing for 6—12 h blue *crystals* separated from the green solution. These were filtered off, washed once with acetic acid, and dried *in vacuo* (9.9 g, 79%) (Found: C, 27.0; H, 5.50; V, 13.4. $C_8H_{16}Cl_2O_8V$ requires C, 26.6; H, 4.45; V, 14.1%). As with the complexes below, the vanadium was determined as vanadium(II) by titration with iron(III) alum and neutral red indicator.

The effective magnetic moment of $[VCl_2(CH_3CO_2H)_4]$ is 3.86 at 90 K and 3.87 at 295 K, and the complex obeys the Curie law ($\theta = 0$). Reflectance spectrum (cm^{-1}): 12 500s(br) (ν_1), 16 500s (ν_2), and 27 200m (ν_3). I.r. spectrum (cm^{-1}): 3 340m(br) [ν(OH)], 2 505m, 2 300m, 2 160m, 1 790m, 1 675vs [ν(C=O)], 1 360m [$\delta(CH_3)$], 1 260vs [ν(C–OH)], 1 055m, 1 020s [δ(OH)], 900m, 850s, 840s, 630vs [$\delta(CO_2)$], 490s [ν(MO)?], and 290s [ν(V–Cl)].

Hexakis(*acetic acid*)*vanadium*(II) *Dibromide*.—Hydrogen bromide was passed through acetic acid (75 cm^3) over vanadium turnings (5 g) until gas effervesced rapidly from the metal surface. The reaction mixture was then heated at 90 °C for 8—10 h to give a dark green solution. After the effervescence had ceased the solution was filtered from the excess of metal (4.1 g), cooled, and concentrated to half volume under vacuum. Over 6—12 h, purple *crystals* separated from the green solution. These were filtered off, washed once with acetic acid, and dried *in vacuo* (9.9 g, 75%) (Found: C, 25.9; H, 4.70; V, 8.3. $C_{12}H_{24}Br_2O_{12}V$ requires C, 25.3; H, 4.25; V, 8.9%).

The effective magnetic moment of $[V(CH_3CO_2H)_6]Br_2$ is 3.90 at 90 K and 3.85 at 295 K. The complex obeys the Curie–Weiss law [$\chi_v^{-1} \propto (T + \theta)$] with $\theta = -4°$. Reflectance spectrum (cm^{-1}): 12 100s(br) (ν_1), 18 100s (ν_2), and 27 400m (ν_3). I.r. spectrum (cm^{-1}): 3 170m(br) [ν(OH)], 1 655s [ν(C=O)], 1 340m, 1 220s [ν(COH)], 1 045m, 1 020s [δ(OH)], 550m, 467s [ν(MO)], and 310s.

If, after the HCl/HBr has been passed, the reaction mixture is

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† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1990, Issue 1, pp. xix—xxii.

Table 1. Final atomic co-ordinates for non-hydrogen atoms in [$VCl_2(CH_3CO_2H)_4$] with estimated standard deviations (e.s.d.s) in parentheses

Atom	*x*	*y*	*z*
V	0	0	0
Cl(1)	0.147 9(1)	−0.329 5(1)	0.266 0(1)
Cl(2)	−0.146 2(1)	0.330 1(1)	−0.268 3(1)
O(11)	0.206 6(4)	−0.121 2(4)	−0.208 8(4)
O(12)	0.144 4(7)	0.096 1(7)	−0.504 8(5)
O(21)	0.194 7(3)	0.119 1(3)	0.010 5(4)
O(22)	0.124 9(5)	0.451 3(4)	−0.185 1(6)
O(31)	−0.206 4(3)	0.121 9(4)	0.203 3(3)
O(32)	−0.161 1(6)	−0.104 3(5)	0.509 5(5)
O(41)	−0.187 8(4)	−0.116 1(4)	−0.012 4(4)
O(42)	−0.144 8(4)	−0.435 1(4)	0.200 8(4)
C(11)	0.241 0(5)	−0.072 6(5)	−0.382 2(5)
C(12)	0.406 5(8)	−0.215 8(7)	−0.483 7(6)
C(21)	0.224 4(4)	0.279 2(4)	−0.059 8(4)
C(22)	0.373 5(5)	0.294 3(5)	0.010 3(6)
C(31)	−0.247 6(5)	0.077 7(5)	0.382 7(5)
C(32)	−0.394 2(6)	0.212 1(6)	0.467 8(5)
C(41)	−0.223 3(5)	−0.274 6(5)	0.053 6(5)
C(42)	−0.362 4(5)	−0.305 5(6)	−0.005 5(6)

Table 2. Bond lengths (Å) and angles (°) for [$VCl_2(CH_3CO_2H)_4$] with e.s.d.s in parentheses

V–Cl(1)	2.493(1)	O(22)–C(21)	1.310(4)
V–Cl(2)	2.500(1)	O(31)–C(31)	1.244(4)
V–O(11)	2.145(3)	O(32)–C(31)	1.316(4)
V–O(21)	2.149(3)	O(41)–C(41)	1.223(5)
V–O(31)	2.116(2)	O(42)–C(41)	1.305(4)
V–O(41)	2.090(4)	C(11)–C(12)	1.572(6)
O(11)–C(11)	1.196(4)	C(21)–C(22)	1.513(7)
O(12)–C(11)	1.280(4)	C(31)–C(32)	1.407(5)
O(21)–C(21)	1.207(4)	C(41)–C(42)	1.461(7)
Cl(1)–V–Cl(2)	179.60(2)	V–O(11)–C(11)	138.4(2)
Cl(1)–V–O(11)	88.46(6)	V–O(21)–C(21)	139.2(2)
Cl(1)–V–O(21)	88.34(6)	V–O(31)–C(31)	139.9(2)
Cl(1)–V–O(31)	92.20(6)	V–O(41)–C(41)	141.7(3)
Cl(1)–V–O(41)	91.78(6)	O(11)–C(11)–O(12)	124.4(1)
Cl(2)–V–O(11)	91.18(6)	O(11)–C(11)–C(12)	123.0(3)
Cl(2)–V–O(21)	91.50(6)	O(12)–C(11)–C(12)	112.6(3)
Cl(2)–V–O(31)	88.16(6)	O(21)–C(21)–O(22)	124.5(4)
Cl(2)–V–O(41)	88.38(6)	O(21)–C(21)–C(22)	119.8(3)
O(11)–V–O(21)	91.2(1)	O(22)–C(21)–C(22)	115.5(4)
O(11)–V–O(31)	179.2(1)	O(31)–C(31)–O(32)	122.0(3)
O(11)–V–O(41)	88.3(1)	O(31)–C(31)–C(32)	123.5(3)
O(21)–V–O(31)	89.2(1)	O(32)–C(31)–C(32)	114.4(3)
O(21)–V–O(41)	179.5(1)	O(41)–C(41)–O(42)	121.0(5)
O(31)–V–O(41)	91.3(1)	O(41)–C(41)–C(42)	126.6(3)
		O(42)–C(41)–C(42)	112.3(4)

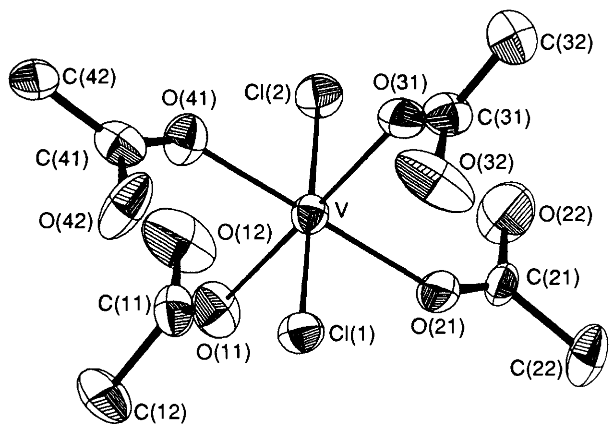

Figure 1. Atom numbering scheme for [$VCl_2(CH_3CO_2H)_4$]

allowed to stand for several days before heating, the yield can be increased. An excess of metal was used to maintain a reducing environment.

Reactions of Vanadium with HX (X = Cl *or* Br) *in Other Solvents*.—Some preliminary investigations of the reactions of HCl and HBr with vanadium in solvents other than acetic acid have been carried out. A dark blue solution formed from the metal and HCl in propionic acid but on concentration an intractable dark blue oil developed. However, some complex halides of vanadium(II) have been isolated from the solution.[11] From formic acid under conditions as for the preparation of [$VCl_2(CH_3CO_2H)_4$], the green vanadium(III) complex [$VCl_3(HCO_2H)_3$] was isolated (Found: C, 12.8; H, 3.1. $C_3H_6Cl_3O_6V$ requires C, 12.2; H, 2.1%).

The metal also reacts with HX in neutral non-aqueous solvents. Oxidation to vanadium(III) by HCl occurred in methanol from which a green solid analysing approximately as [$VCl_3(CH_3OH)_3$] was isolated, but HBr gave a solid analysing as [$VBr_2(CH_3OH)(H_2O)$] although the vanadium(II) content determined by direct titration was low.

Vanadium reacts with HCl in thf, 1,2-dimethoxyethane and diethyl ether, and with HBr in diethyl ether, but intractable oils generally formed on removal of the solvents and the reactions were not investigated further.

X-*Ray Crystal Structure Analysis of* [$VCl_2(CH_3CO_2H)_4$].—Crystals prepared as described above were satisfactory for structure determination and one of approximate dimensions 0.6 × 0.25 × 0.2 mm was sealed in a Lindemann capillary under dinitrogen.

Crystal data. $C_8H_{16}Cl_2O_8V$, $M = 362.06$, triclinic, space group $P1$, $a = 7.821(1)$, $b = 7.873(2)$, $c = 7.864(1)$ Å, $\alpha = 61.50(2)$, $\beta = 70.72(1)$, $\gamma = 63.83(2)°$, $U = 377.5$ Å^3, $Z = 1$, $D_c = 1.592$ g cm^{-3}, $F(000) = 185$, graphite-monochromated Mo-K_α radiation ($\lambda = 0.710\ 73$ Å), μ(Mo-K_α) = 10.18 cm^{-1}.

Data collection. Cell parameters were determined on an Enraf-Nonius CAD4 diffractometer using 25 accurately centred reflections in the range $14 \leqslant \theta \leqslant 16°$. The intensity data were measured in the range $1 \leqslant \theta \leqslant 26°$ ($0 \leqslant h \leqslant 9$, $-9 \leqslant k \leqslant 9$, $-9 \leqslant l \leqslant 9$), for a hemisphere of reciprocal space using the ω—2θ scan mode, which yielded a total of 1 597 reflections, 1 467 having $I \geqslant 3\sigma(I)$. Corrections were applied for Lorentz and polarization effects and for a 2.1% decay in the monitored reflection over the period of data collection. No suitable reflections were available for ψ measurements and consequently no semi-empirical absorption correction could be applied.

Structure solution and refinement. The near perfect centrosymmetric nature of the molecule dominated the intensity distribution of the diffraction pattern such that the $N(z)$ statistical test gave a near perfect centric distribution, and so, initially, all calculations were done in the wrongly assumed space group of $P\bar{1}$. From the Patterson map vectors were chosen for V–Cl and two V–O distances. These corresponded to the expected octahedral co-ordination around the vanadium atom. On the assumptions that the space group was $P\bar{1}$ and that the cell volume could only accommodate one molecule, the vanadium atom was sited at the origin, and conventional heavy-atom refinements produced the remaining atoms of the structure. However, isotropic refinement of all atoms did not yield an R value below 0.20. On changing the space group to $P1$ and introducing the other half of the molecule as independent non-symmetry related atoms, isotropic refinement converged

Table 3. Final atomic co-ordinates for non-hydrogen atoms in $[V(CH_3CO_2H)_6]Br_2$ with e.s.d.s in parentheses

Atom	x	y	z
Br	0.006 02(7)	0.214 90(4)	0.392 80(8)
V	0	0.500	0
O(1)	−0.077 7(4)	0.364 6(2)	−0.069 8(4)
O(2)	0.226 0(4)	0.453 2(2)	0.056 7(4)
O(3)	−0.041 6(4)	0.457 0(3)	0.210 0(4)
O(11)	−0.159 4(5)	0.219 1(3)	−0.079 9(6)
O(21)	0.463 3(5)	0.424 5(3)	0.155 6(5)
O(31)	−0.132 1(5)	0.419 4(3)	0.410 9(4)
C(1)	−0.051 0(6)	0.281 3(4)	−0.058 6(7)
C(2)	0.331 3(6)	0.462 0(4)	0.159 7(6)
C(3)	−0.113 7(6)	0.477 4(4)	0.304 3(6)
C(11)	0.100 1(8)	0.240 1(5)	−0.026 5(9)
C(21)	0.326 6(8)	0.512 6(4)	0.300 9(6)
C(31)	−0.189 6(8)	0.568 8(5)	0.312 9(7)
H(1)	−0.28(1)	0.257(6)	−0.10(1)
H(2)	0.440(9)	0.382(6)	0.058(9)
H(3)	−0.082(6)	0.383(3)	0.406(6)

Table 4. Bond lengths (Å) and angles (°) for $[V(CH_3CO_2H)_6]Br_2$ with e.s.d.s in parentheses

V–O(1)	2.113(3)	O(21)–C(2)	1.312(7)
V–O(2)	2.121(3)	O(21)–H(2)	1.07(8)
V–O(3)	2.109(4)	O(31)–C(3)	1.309(7)
O(1)–C(1)	1.212(6)	O(31)–H(3)	0.70(5)
O(2)–C(2)	1.220(6)	C(11)–C(11)	1.465(9)
O(3)–C(3)	1.202(7)	C(2)–C(21)	1.485(8)
O(11)–C(1)	1.309(7)	C(3)–C(31)	1.480(9)
O(11)–H(1)	1.20(9)		
O(1)–V–O(2)	92.3(1)	O(11)–C(1)–C(11)	113.7(5)
O(1)–V–O(3)	84.6(1)	O(2)–C(2)–O(21)	121.6(5)
O(2)–V–O(3)	90.1(1)	O(2)–C(2)–C(21)	125.7(5)
C(1)–O(11)–H(1)	111(4)	O(21)–C(2)–C(21)	112.8(5)
C(2)–O(21)–H(2)	102(4)	O(3)–C(3)–O(31)	122.3(5)
C(3)–O(31)–H(3)	105(4)	O(3)–C(3)–C(31)	124.4(5)
O(1)–C(1)–O(11)	121.3(5)	O(31)–C(3)–C(31)	113.4(5)
O(1)–C(1)–C(11)	125.0(5)		

rapidly at $R = 0.075$. An absorption correction by DIFABS[12] reduced R to 0.062 (min., max. correction 0.78, 1.17).

The hydrogen atoms attached to the methyl carbon atom were included in calculated positions (C–H 1.0 Å). Full anisotropic refinement (V and Cl at first, then all non-hydrogen atoms) converged at $R = 0.033$, $R' = 0.051$, estimated standard deviations (e.s.d.s) of unit weight = 1.15, using the weighting scheme[13] $w = (\sigma F)^2 + (0.04F)^2 + 4.0$ where the coefficients were adjusted to give a near linear δR *versus* normal probability plot[14] of slope 1.08. Near the end of the refinement a difference map showed small peaks of 0.6—0.8 electrons. These were taken to be the associated hydrogen atoms of the hydroxyl oxygen atoms O(12), O(22), O(32), and O(42) (Figure 1).

The hydrogen atom of O(12) was displaced from its expected position, but the other three were better placed, O–H distances being in the range 0.9—1.07 Å, but the angle H(12)–O(12)–C(11) was 90° compared with 102—105° for the other three. The positions of these four hydrogen atoms were included in the final stages of refinement, but not refined. No other significant peaks were present in the difference map, the highest peak amounting to 0.3 electrons. The unusually short distance of 1.407(5) Å between C(31) and C(32) is thought to arise from some local disorder of these atoms. Final atomic co-ordinates are given in Table 1 and bond distances and angles in Table 2. All calculations were performed using the Enraf-Nonius Structure Determination Package.[15]

X-Ray Crystal Structure Analysis of $[V(CH_3CO_2H)_6]Br_2$.—A crystal of the vanadium(II) complex of approximate dimensions 0.3 × 0.3 × 0.2 mm, obtained as described above, was sealed in a Lindemann capillary under dinitrogen.

Crystal data. $C_{12}H_{24}Br_2O_{12}V$, $M = 571.08$, monoclinic, space group $P2_1/n$, $a = 9.017(1)$, $b = 14.256(3)$, $c = 9.133(5)$ Å, $\beta = 100.08(03)°$, $U = 1\,155.9$ Å^3, $Z = 2$, $D_c = 1.643$ g cm^{-3}, $F(000) = 570$, graphite-monochromated Mo-K_α radiation ($\lambda = 0.710\,73$ Å), μ(Mo-K_α) = 38.91 cm^{-1}.

Data collection. Cell parameters were determined on a CAD4 diffractometer using 25 accurately centred reflections in the range $10 \leqslant \theta \leqslant 13°$. The intensity data from two octants of reciprocal space were measured in the range $1 \leqslant \theta \leqslant 25°$ ($0 \leqslant h \leqslant 10$, $0 \leqslant k \leqslant 16$, $-10 \leqslant l \leqslant 10$), which yielded a total of 2 263 reflections, 1 491 having $I \geqslant 3\sigma(I)$. The space group was determined by inspection of the systematic absences occurring for $h0l$ ($h + l$ odd) and $0k0$ (k odd).

After the usual Lorentz and polarization corrections, a correction was made for a 6.9% decay in the monitored reflection over the period of data collection. A semi-empirical absorption correction was applied using ψ data (min., max., = 0.887, 0.999) with an average correction of 0.940.

Structure solution and refinement. Since there are only two vanadium atoms in the unit cell, they must be sited at centres of symmetry. From the Patterson function the positions of the bromine atoms and the correct relative pair of centres of symmetry for the vanadium atom were chosen. Least-squares refinement of these two atoms followed by an electron density calculation served to produce the rest of the structure. Isotropic refinement of all atoms converged at $R = 0.132$.

The program DIFABS[12] was used to supply an absorption correction. A further refinement with the bromine and vanadium atoms anisotropic, the remainder isotropic, converged at $R = 0.064$. Full anisotropic refinement of all atoms converged at $R = 0.047$. From a difference Fourier synthesis, the hydrogen atoms of the hydroxyl groups were identified along with the hydrogen atoms of the methyl group. The latter hydrogen atoms were kept fixed, but the hydroxyl hydrogen atoms were included in the last three cycles of refinement when R converged to 0.042, $R' = 0.054$ and S (estimated standard deviation of observation of unit weight) = 1.162, using the weighting scheme as above. The highest residual peak in a final difference map was 0.32 electrons. Atomic co-ordinates are given in Table 3 and selected bond distances and angles in Table 4.

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom co-ordinates, thermal parameters, and remaining bond lengths and angles.

Results and Discussion

Tetrakis(acetic acid)dichlorovanadium(II) and hexakis(acetic acid)vanadium(II) dibromide are typical vanadium(II) complexes, with effective magnetic moments which are close to the spin-only value for a $3d^3$ ion (3.87) and essentially independent of temperature. The infrared spectra contain bands assignable to co-ordinated acetic acid.

The diffuse reflectance spectra of $[V(CH_3CO_2H)_4Cl_2]$ and $[V(CH_3CO_2H)_6]Br_2$ contain absorption bands which are assignable to the transitions $^4A_{2g} \longrightarrow {}^4T_{2g}$ (ν_1), $^4A_{2g} \longrightarrow 4T_{1g}(F)$ (ν_2), and $^4A_{2g} \longrightarrow {}^4T_{1g}(P)$ (ν_3), as expected for vanadium(II) in octahedral symmetry. The difference between the spectra of the two complexes is due to the number of oxygen atoms co-ordinated to the vanadium atom and to tetragonal

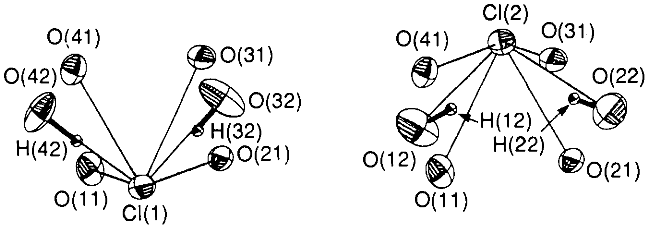

Figure 2. Arrangement of oxygen atoms and hydrogen bonding around each chlorine atom in [$VCl_2(CH_3CO_2H)_4$]

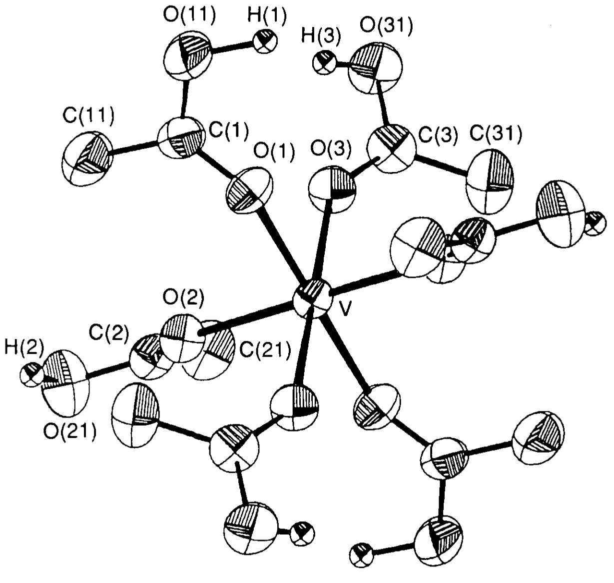

Figure 3. Atom numbering scheme for [$V(CH_3CO_2H)_6$]Br_2

distortion in *trans*-[$VCl_2(CH_3CO_2H)_4$] causing some broadening of the ν_1 band and possibly of the ν_2 band. As expected the band positions are close to those reported previously for [$VCl_2(C_2H_5OH)_4$] and [$V(C_2H_5OH)_6$]Br_2.[16]

The *X*-ray structure determination shows the expected *trans* structure for [$VCl_2(CH_3CO_2H)_4$] and in the VCl_2O_4 co-ordination sphere the internal angles are 88.2—92.2°, the average V–Cl distance is 2.497 Å and the average V–O distance is 2.125 Å [range 2.090(4)—2.149(3) Å] (Table 2 and Figure 1). The vanadium(III) anion [$VCl_4(CH_3CO_2H)_2$]$^-$ has an octahedral structure[3] with internal angles of 87—92° an average V–Cl distance of 2.336 Å and an average V–O distance of 2.089 Å. The V–Cl distances of the vanadium(III) anion are shorter by approximately 0.17 Å, but the oxidation state difference has less effect on the V–O distances. The average V–O distance of 2.125 Å is close to those reported previously for other vanadium(II) complexes, [$V(CH_3OH)_6$]Cl_2 (V–O 2.132 Å)[17] and [$V(H_2O)_6$][CF_3SO_3]$_2$ (V–O 2.120 Å).[18] The average V–Cl distance of 2.497 Å is also close to the value in [$VCl_2(py)_4$][19] (V–Cl 2.462 Å). A bond scan around each chlorine atom shows that six oxygen atoms cluster in a hemisphere around each chlorine atom, with distances 3.01—3.34 Å suggesting weak hydrogen bond interactions. Figure 2 shows the arrangement for each chlorine atom, for which the closest approach distances are: Cl(1)$\cdots$O(42) 3.01, Cl(1)$\cdots$O(32) 3.01, Cl(2)$\cdots$O(12) 2.97, and Cl(2)–O(22) 3.02 Å. The hydrogen bonding is unusual in being entirely intramolecular and there are no close contacts between molecules.

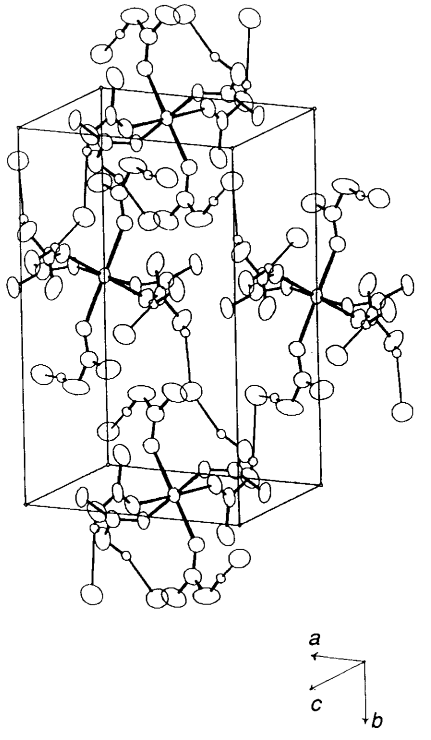

Figure 4. Packing of [$V(CH_3CO_2H)_6$]$^{2+}$ cations showing hydrogen bonding to bromide ions

In [$V(CH_3CO_2H)_6$]Br_2, the VO_6 octahedron is symmetrical with internal angles of 84.6—92.3° (Table 4 and Figure 3). The average V–O distance of 2.114 Å is close to those discussed above and is greater than the Ni–O value of 2.06 Å found in the analogous nickel(II) complex [$Ni(CH_3CO_2H)_6$][BF_4]$_2$,[10] reflecting the smaller metal ion radius of Ni^{2+}. Each bromide ion is surrounded by three hydroxyl groups with Br–O distances of 3.13—3.19 Å and Br–H distances of 1.96—2.53 Å suggesting that the hydroxyl groups are intermolecularly hydrogen bonded to the bromide ions (Figure 4). A similar pattern is also observed in the above nickel(II) complex, where the hydroxyl hydrogens are intramolecularly hydrogen bonded to a tetrafluoroborate fluorine atom whilst simultaneously being intramolecularly hydrogen bonded to the carbonyl oxygen. The latter is not observed in [$V(CH_3CO_2H)_6$]Br_2.

In both structures the shorter C–O bond of each acetic acid molecule is held to the vanadium atom indicating that the doubly bonded oxygen is co-ordinated. This is confirmed by the identification of the hydroxyl hydrogen atom on the adjacent oxygen atoms. The dimensions of the acetic acid molecules are close to those found[3,10,20] in the other complexes of acetic acid, [$VCl_4(CH_3CO_2H)_2$]$^-$, [$Ni(CH_3CO_2H)_6$]$^{2+}$, and [$CrBr_4(CH_3CO_2H)_2$]$^{2-}$.

Most vanadium(II) complexes are prepared *via* vanadium(II) starting materials obtained by electrolytic or chemical reduction of compounds in higher oxidation states. Occasional use has been made of anhydrous vanadium(II) halides prepared by high-temperature dry routes. Electrolytic and high-temperature procedures are complicated and time-consuming, and chemical reduction can lead to contamination from the reductant.[1] The present paper shows that vanadium(II) compounds can be obtained more conveniently from the metal and HCl or HBr under non-aqueous conditions. It is also now clear[18] that aqueous vanadium(II) solutions can be produced directly from the metal and hydrochloric, hydrobromic, trifluoromethanesulphonic, and tetrafluoroboric acids. The two routes should allow easier preparation of vanadium(II) complexes and application of vanadium(II) as a reducing agent.

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