Facile Synthesis of Complexes of Vanadium(II) and the Crystal and Molecular Structures of Hexaaquavanadium(II) Trifluoromethylsulphonate

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Abstract

The new vanadium(II) salt $[V(H_2O)_6](CF_3SO_3)_2$ was crystallised from solutions obtained by dissolving metallic vanadium in aqueous trifluoromethylsulphonic acid. The cations in this complex are regular octahedra (V–O distance = 2.119(1) Å) and are extensively hydrogen-bonded to the anions throughout the lattice. The salt is soluble in several organic solvents and should be a useful starting material in the preparation of vanadium(II) complexes. Thus $[V(ethylenediamine)_3](CF_3SO_3)_2$ has been prepared by the addition of ethylenediamine to a solution of $[V(H_2O)_6](CF_3SO_3)_2$ in ethanol. The preparation of $[VCl_2(H_2O)_4]$, $[V(H_2O)_6]Br_2$ and $[V(H_2O)_6](BF_4)_2$ from vanadium and the appropriate aqueous acid has been confirmed.

Introduction

Investigations of vanadium(II) chemistry are restricted because of the unavailability of simple vanadium(II) compounds for synthetic work and because the materials are often air- and moisture-sensitive. Hydrated vanadium(II) salts, the sulphate and the halides, have been isolated from solutions obtained by electrolytic reduction of vanadyl(IV) salts at a mercury cathode [1]. Aqueous vanadium(II) solutions have long been prepared by reduction of acidified vanadyl(IV) solutions with amalgamated zinc [2]. More recently, non-aqueous methods have been used: VCl_3 in tetrahydrofuran (thf), with zinc dust gives '$VCl_2(thf)_2$', now known to be $[V_2(\mu\text{-}Cl)_3(thf)_6]_2[Zn_2Cl_6]$ [3, 4]; $[VCl_3(thf)_3]$ in thf with AlR_2OR gives $[V_2(\mu\text{-}Cl)_3(thf)_6][AlCl_2R_2]$ [5] and VCl_3/MeCN with $ZnEt_2$ provides $[V(MeCN)_6][ZnCl_4]$ [6]. The zinc or aluminium often cannot be removed although the aluminium-containing salts [6] rapidly produce $[V(MeOH)_6]Cl_2$ and $[VCl_2(MeOH)_4]$ with methanol.

Anodic oxidation of vanadium [7] is now known to give vanadium(III) [8] compounds. Vanadium metal is said to be unreactive towards non-oxidising acids other than HF [9], and this was previously our experience with vanadium powder, but there is a brief report [10] that crystalline vanadium (99.99% pure) will dissolve on reflux in moderately concentrated aqueous HCl, HBr, HI or HBF_4 to give violet solutions from which the hydrated vanadium(II) salts crystallise on cooling. Although initially doubtful, the results for the chloride, bromide and tetrafluoroborate with vanadium turnings have been confirmed but no reaction has been found with hydriodic acid. However, vanadium metal dissolves readily in refluxing dilute trifluoromethylsulphonic acid (triflic acid) to give violet solutions from which hexaaquavanadium(II) triflate was crystallised, the properties of which are described here.

Experimental

Preparations were carried out under purified dinitrogen in glass apparatus. Solids were transferred in a glove box with a recirculatory gas-purification system, manufactured by Faircrest Engineering Ltd., Croydon, U.K. Magnetic measurements on samples in sealed tubes were carried out by the Gouy method. Electronic spectra were recorded on a Beckman Acta MIV spectrophotometer fitted with a diffuse reflectance sphere. The vanadium(II) triflate was in a sealed cell. Infrared spectra were recorded on a Perkin-Elmer 577 spectrophotometer (Nujol mull and KBr plates). Vanadium turnings (99.7%) and triflic acid were obtained from Aldrich; hydrochloric acid (AR) and hydrobromic acid (AR) were used as received from BDH Ltd.; ethylenediamine (Aldrich) was distilled from sodium hydroxide pellets and stored over molecular sieve 4A under nitrogen. Microanalyses were carried out by the Analytical Unit, Department of Chemistry, University of Surrey. Vanadium(II) was analysed by titration with acidic iron(III) ammonium sulphate, using 0.1% neutral red indicator.

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Hexaaquavanadium(II) Triflate

Vanadium turnings (5 g) were heated under reflux with a mixture of acid (20 cm^3) and water (20 cm^3). A light blue–green colour developed, turning to dark blue after heating for about 12 h. The solution was allowed to cool, during which time a purple colour developed. Purple crystals separated from this solution. The mixture was reheated to redissolve the crystals and the solution was decanted from the excess of metal. Purple needles separated on cooling. These were filtered off and washed once with anhydrous diethylether. The residual metal weighed 4.5 g, so that approximately 0.5 g had reacted. Based on this, a 20% yield of the hexahydrate was obtained although no attempt was made to optimise the yield.

When the metal is heated with the neat acid it slowly becomes coated with a blue–green material, which dissolves when water is added. An excess of metal was used to maintain a reducing environment. The vanadium(II) solution is easily decanted from the turnings; metal powder, although it reacts with the acid, is less suitable for handling.

The effective magnetic moment for $[V(H_2O)_6](CF_3SO_3)_2$ is 3.86 BM at 90 K and 3.83 BM at 295 K. The complex obeys the Curie–Weiss Law, $[\chi_V{}^{-1} \propto (T+\theta)]$, with $\theta = -2°$. The reflectance spectrum has bands (cm^{-1}) at 11800s, br (ν_1), 17400s (ν_2) and 26600m (ν_3).

$[V(H_2O)_6](CF_3SO_3)_2$ is soluble in acetone, methanol, ethanol, n-butanol, ethyl acetate and 1,2-dimethoxyethane giving purple solutions. It does not dissolve in diethylether, toluene or dichloromethane. Marked colour changes occur with pyridine, acetonitrile, tetrahydrofuran, 1,4-dioxan and dimethylformamide.

Tetraaquadichlorovanadium(II)

Vanadium turnings (5 g) and hydrochloric acid (50 cm^3) were heated under reflux for 3 h. The resultant deep purple solution was filtered from the excess of metal (4.3 g) and evaporated to dryness *in vacuo* to yield a blue solid. This was washed with diethylether and dried *in vacuo* (yield 85%).

Hexaaquavanadium(II) Dibromide

Vanadium turnings (5 g) and hydrobromic acid (50 cm^3) were heated under reflux for 3 h. The resultant deep purple solution was filtered from the excess of metal (3.65 g) and evaporated to dryness *in vacuo* to yield a purple solid. This was washed with cold ethyl acetate and dried *in vacuo* (yield 60%).

Hexaaquavanadium(II) Tetrafluoroborate

Vanadium turnings (5 g) and fluoroboric acid (40 cm^3) were heated under reflux for 3 h. The resultant deep purple solution was filtered from the excess of metal (4.3 g) and concentrated *in vacuo*. A purple solid crystallised and was filtered off, washed once with diethylether and dried *in vacuo* (yield 65%).

The effective magnetic moment of $[V(H_2O)_6](BF_4)_2$ is 3.74 BM at 195 K and 3.78 BM at 295 K. The complex obeys the Curie–Weiss Law, $[\chi_V{}^{-1} \propto (T+\theta)]$, with $\theta = -4°$. The reflectance spectrum has bands (cm^{-1}) at 11900s (ν_1), 18000s (ν_2) and 27500m (ν_3).

Tris(ethylenediamine)vanadium(II) Triflate

To a purple solution of $[V(H_2O)_6](CF_3SO_3)_2$ (0.9 g, 1.96 mmol) in ethanol (40 cm^3) was added ethylenediamine (0.53 cm^3, 7.87 mmol) to give a green solution. This was concentrated to half its original volume under vacuum and stored at −20 °C. After one week the green solid which crystallised was filtered off and washed once with diethylether and dried *in vacuo* (yield 50%).

The reflectance spectrum has bands (cm^{-1}) at 15900s (ν_1), and 21700s (ν_2).

Microanalytical and infrared spectral data are given in Tables 1 and 2.

The X-ray Crystal Structure Analysis of $[V(H_2O)_6](CF_3SO_3)_2$

Crystal data

$C_2H_{12}F_6O_{12}S_2V$, $M_r = 457.17$, monoclinic, $a = 18.516(4)$, $b = 6.975(2)$, $c = 6.584(1)$ Å, $\beta =$

TABLE 1. Analytical data (%)[a]

Complex	C	H	N	V^{II}
$[V(H_2O)_4Cl_2]$		4.25(4.20)		25.2(26.3)
$[V(H_2O)_6]Br_2$		3.85(3.79)		15.5(16.0)
$[V(H_2O)_6](BF_4)_2$		3.90(3.60)		
$[V(H_2O)_6](CF_3SO_3)_2$	5.75(5.25)	2.45(2.65)		
$[V(en)_3](CF_3SO_3)_2$	18.6(18.2)	4.70(4.50)	15.6(15.9)	9.0(9.6)

[a] Calculated values in parentheses.

TABLE 2. Infrared data (cm^{-1})

$[V(H_2O)_6](CF_3SO_3)_2$	$[V(en)_3](CF_3SO_3)_2$	Assignment [11–13]
3480s, vbr		ν(OH)
	3340s	$\nu(NH_2)$
	3290s	$\nu(NH_2)$
	3180m	$\nu(NH_2)$
1660m		
1640m		
	1570s	$\delta(NH_2)$
1255s, vbr	1250s, br	$\nu(SO_3)$
	1225m	
1195s	1150vs	ν(CF)
	1100s	ν(CF)
1040s, br	1030vs	ν(CF)
	970m	
	760s	
645m	640vs	
590s	570s	
525m	515s	
	475m	

103.86(1)°, $V = 825.6$ Å^3, space group $C2/m$, $Z = 2$, $D_c = 1.839$ g cm^{-3}, $F(000) = 458$, graphite-monochromated Mo Kα radiation ($\lambda = 0.71067$ Å), μ(Mo Kα) = 9.34 cm^{-1}.

Determination of the structure

A crystal of the vanadium(II) complex of approximate dimensions 0.4 × 0.6 × 0.15 mm was sealed in a Lindemann capillary under dinitrogen. The dimensions of the unit cell were determined by least-squares refinement of a set of 25 reflections in the range $13° \leqslant \theta \leqslant 15°$.

The intensity data were measured in the range $1° \leqslant \theta \leqslant 24°$, ($-21 \leqslant h \leqslant 21$, $0 \leqslant k \leqslant 8$, $0 \leqslant l \leqslant 7$), using the $\omega/2\theta$ scan mode, which yielded a total of 758 reflections, 632 having $I \geqslant 3\sigma(I)$. After the usual Lorentz polarization correction, a correction was made for a 1.1% decrease in the monitored reflection over the data collection period, followed by an empirical absorption correction (min./max. correction 0.95/1.0).

TABLE 3. Fractional atomic coordinates for $[V(H_2O)_6][CF_3SO_3]_2$ with e.s.d.s in parentheses and B_{eq} thermal parameters (Å^2)

Atom	x	y	z	B_{eq}[a]
V	0	0	0	3.32(1)
S	0.37465(4)	0	0.3114(1)	3.82(2)
F(1)	0.2609(2)	0	0.4708(5)	11.3(1)
F(2)	0.2454(1)	0.1538(5)	0.1907(6)	15.10(8)
O(1)	0.3808(2)	0	0.0982(4)	5.01(5)
O(2)	0.3997(1)	0.1717(3)	0.4228(3)	6.03(4)
O(3)	−0.0522(2)	0	0.2534(4)	5.30(6)
O(4)	0.0718(1)	0.2191(3)	0.1539(3)	5.71(4)
C	0.2748(3)	0	0.2866(9)	7.3(1)
H(3)	−0.068(1)	0.096(4)	0.306(4)	6.6(7)
H(4A)	0.080(1)	0.248(3)	0.297(4)	4.3(6)
H(4B)	0.087(1)	0.303(4)	0.071(4)	6.7(6)

[a]The B_{eq} values are calculated according to the equation $B_{eq} = (4/3)\Sigma_i\Sigma_j B_{ij}a_i a_j$.

From a statistical analysis of the intensity data, the crystal was taken to be centrosymmetric, confirming space group $C2/m$, and leading to the position of the V atom on a centre of symmetry. The positions of the S atoms were obtained from a Patterson map and the remaining atoms by the usual heavy atom methods. Isotropic refinement converged at $R = 0.16$ and following a second absorption correction by DIFABS [14] R fell to 0.116 (min./max. correction 0.60/1.36). Full-matrix anisotropic refinement of non-hydrogen atoms converged at $R = 0.047$, $R_w = 0.080$, $S = 0.931$ using weighting scheme $w^{-1} = (0.5 + 0.029F + 0.01F^2)$ where the coefficients were adjusted to give a linear δR–normal probability plot [15] of slope 0.96. The hydrogen atoms of the water molecules were located in a difference map and refined in the last three cycles of refinement. The largest peak in a final difference map was 0.38 electrons. Atomic coordinates are given in Table 3, and selected bond distances and angles in Table 4. All calculations were performed using the Enraf Nonius Structure Determination Package [16] on a DEC PDP 11/73 computer.

TABLE 4. Bond lengths (Å) and bond angles (°) with e.s.d.s in parentheses

V–O(3)	2.120(3)	S–O(2)	1.423(3)	O(3)–H(3)	0.84(4)
V–O(4)	2.118(2)	S–C	1.817(7)	O(4)–H(4A)	0.94(4)
S–O(1)	1.435(3)	F(1)–C	1.299(8)	O(4)–H(4B)	0.89(5)
F(2)–C	1.296(6)				
S–C–F(1)	110.0(5)	O(1)–S–O(2)	114.3(1)	S–C–F(2)	110.1(4)
O(3)–V–O(4)	91.4(1)	O(1)–S–C	103.3(3)	F(1)–C–F(2)	107.5(5)
O(4)–V–O(4)′[a]	92.4(2)	O(2)–S–O(2)′	114.7(2)	F(2)–C–F(2)′	111.7(8)
O(2)–S–C	104.2(2)				

[a]Symmetry code is $x, -y, z$.

Discussion

Hexaaquavanadium(II) triflate, tris(ethylenediamine)vanadium(II) triflate and hexaaquavanadium(II) tetrafluoroborate are typical vanadium(II) complexes with effective magnetic moments which are close to the spin-only value for a $3d^3$ ion (3.87 BM), and essentially independent of temperature.

The diffuse reflectance spectra of $[V(H_2O)_6](CF_3SO_3)_2$, $[V(H_2O)_6](BF_4)_2$ and $[V(en)_3](CF_3SO_3)_2$ contain absorption bands, assignable to the transitions $^4A_{2g} \rightarrow {}^4T_{2g}$ (ν_1), $^4A_{2g} \rightarrow T_{1g}(F)$ (ν_2), and $^4A_{2g} \rightarrow T_{1g}(P)$ (ν_3), expected for vanadium(II) in octahedral symmetry. The values for the hexaaqua complex are close to those reported earlier [17] for $[V(H_2O)_6](SO_4)$ and $A_2[V(H_2O)_6](SO_4)_2$ ($A = NH_4$, K, Rb or Cs) and the values for the tris(ethylenediamine) complex are close to those [13] for $[V(en)_3]Br_2$ and $[V(en)_3]I_2$ (en = ethylenediamine).

Although both vanadium metal and triflic acid are comparatively expensive, this synthetic route to a simple vanadium(II) compound would seem preferable to electrolytic reduction for many purposes. Its synthetic potential is suggested by the synthesis of the tris(ethylenediamine) complex and by the marked colour changes seen with donor solvents.

The halide syntheses work with vanadium powder or with the turnings. However, with the powder the reaction is harder to control and it is not easy to separate the reaction solution from the excess powder.

The X-ray investigation of $[V(H_2O)_6](CF_3SO_3)_2$ shows that in the VO_6 octahedron (Fig. 1 and Table 4) all the V–O distances are equal as expected for a $3d^3$ complex. The mean value of 2.119(1) Å agrees closely with those found for the $V–OH_2$ distances in $[V(H_2O)_6]SO_4$ (2.131 Å) [18] and $(NH_4)_2[V(H_2O)_6](SO_4)_2$ (2.15 Å) [19] and the V–O distance (2.132 Å) in $[V(CH_3OH)_6]Cl_2$ [5]. The mean $V–OH_2$ bond distance [20] in the vanadium(III) triflate $[V(H_2O)_6][H_5O_2](CF_3SO_3)_3$ is 1.995 Å, smaller by approximately 0.13 Å.

The triflate anions have dimensions similar to those reported recently [20], and they are extensively hydrogen-bonded to the coordinated water molecules. Eight anions form a cage around each $[V(H_2O)_6]$ octahedron, and the framework of twelve hydrogen bonds consists of two independent contacts from each of the four O(4) water molecules to different triflate anions [O(4)–O(1) = 2.839 Å

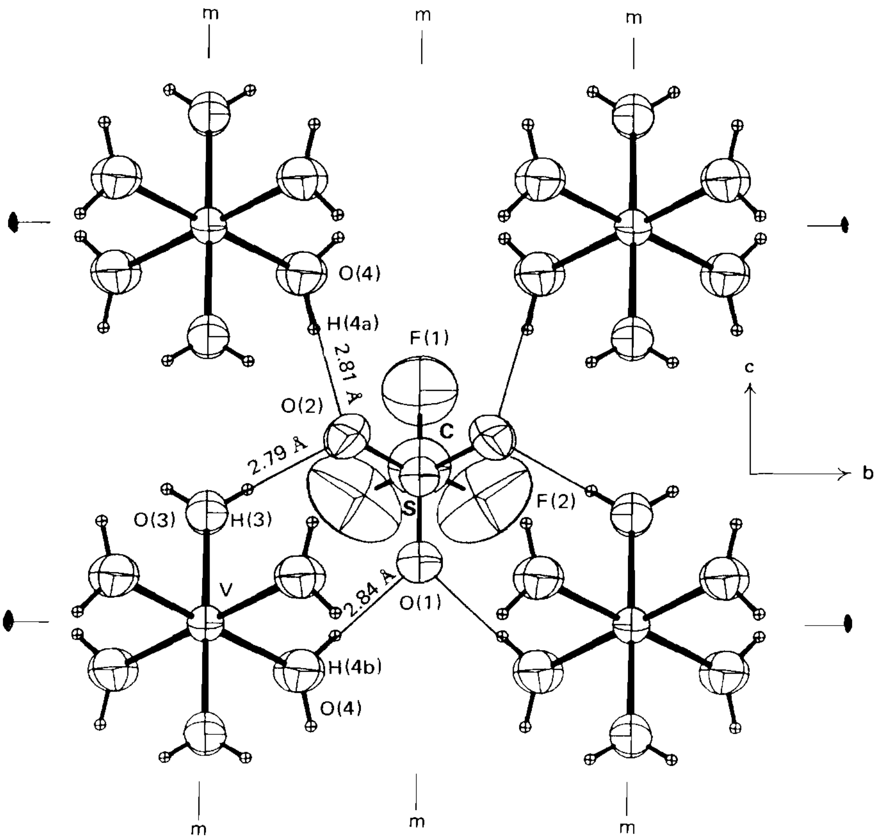

Fig. 1. Atom numbering scheme, structure and arrangement of hydrogen bonds of $[V(H_2O)_6](CF_3SO_3)_2$.

involving H(4b); O(4)–O(2) = 2.814 Å involving H(4a)], and two symmetrical contacts between each water molecule O(3) and the O(2) atoms of two anions [O(3)–O(2) = 2.785 Å involving H(3)]. The hydrogen bonding clearly contributes to the stability of the lattice.

References

1 M. Kranz, *Inorg. Synth.*, *7* (1963) 94; H. J. Seifert and B. Gerstenberg, *Z. Anorg. Allg. Chem.*, *315* (1962) 56; H. J. Seifert and T. Auel, *Z. Anorg. Allg. Chem.*, *360* (1968) 50; L. F. Larkworthy, K. C. Patel and D. J. Phillips, *J. Chem. Soc. A*, (1970) 1095; G. Brauer, *Handbook of Preparative Inorganic Chemistry*, Vol. 2, Academic Press, London, 2nd edn., 1965, p. 1277.

2 A. I. Vogel, *Quantitative Inorganic Analysis*, Longmans, London, 3rd edn., 1964, p. 337.

3 F. A. Cotton, S. A. Duraj, M. W. Extine, G. E. Lewis, W. J. Roth, C. D. Schmulbach and W. Schwotzer, *J. Chem. Soc., Chem. Commun.*, (1983) 1377; F. A. Cotton, S. A. Duraj and W. J. Roth, *Inorg. Chem.*, *24* (1985) 913.

4 R. J. Bouma, J. H. Teuben, W. R. Beukema, R. L. Bansemer, J. C. Huffman and K. G. Caulton, *Inorg. Chem.*, *23* (1984) 2715.

5 F. A. Cotton, S. A. Duraj, L. E. Manzer and W. J. Roth, *J. Am. Chem. Soc.*, *107* (1985) 3850.

6 P. Chandrasekhar and P. H. Bird, *Inorg. Chim. Acta*, *97* (1985) L31.

7 J. J. Habeeb, L. Neilson and D. G. Tuck, *Can. J. Chem.*, *55* (1977) 2631.

8 F. A. Cotton, G. E. Lewis and W. Schwotzer, *Inorg. Chem.*, *25* (1986) 3528.

9 F. A. Cotton and G. Wilkinson, *Advanced Inorganic Chemistry*, Wiley, Chichester, 4th edn., 1980, p. 710; N. V. Sidgwick, *The Chemical Elements and Their Compounds*, Vol. 1, Clarendon, Oxford, 1950, p. 807.

10 A. F. Zueva, O. N. Efimov and A. G. Ovcharenko, *Russ. J. Inorg. Chem.*, *21* (1976) 1075.

11 D. Dolphin and A. Wick, *Tabulation of I.R. Spectral Data*, Wiley, New York, 1977, p. 469.

12 N. E. Dixon, G. A. Lawrence, P. A. Lay and A. M. Sargeson, *Inorg. Chem.*, *23* (1984) 2940.

13 M. M. Khamar, L. F. Larkworthy, K. C. Patel, D. J. Phillips and G. Beech, *Aust. J. Chem.*, *27* (1974) 41.

14 N. Walker and D. Stuart, *Acta Crystallogr. Sect. A*, *39* (1983) 158.

15 S. C. Abrahams, *Acta Crystallogr. Sect. B*, *30* (1974) 261.

16 *Structure Determination Package*, B. A. Frenz and Associates, College Station, TX 77840, 1985.

17 L. F. Larkworthy, K. C. Patel and D. J. Phillips, *J. Chem. Soc. A*, (1968) 2936.

18 F. A. Cotton, L. R. Falvello, R. Llusar, E. Libby, C. A. Murillo and W. Schwotzer, *Inorg. Chem.*, *25* (1986) 3423.

19 H. Montgomery, R. V. Chastain, J. J. Natt, A. M. Witkowska and E. C. Lingafelter, *Acta Crystallogr.*, *22* (1967) 775.

20 F. A. Cotton, C. K. Fair, G. E. Lewis, G. N. Mott, F. K. Ross, A. J. Schultz and J. M. Williams, *J. Am. Chem. Soc.*, *106* (1984) 5319.