

Pentaaquovanadium(IV) bis(trifluoromethanesulfonate)

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The structure of the pentaaquovanadium(IV) ion in a salt with singly charged counter-ions is presented. In $[\text{VO}(\text{H}_2\text{O})_5](\text{CF}_3\text{SO}_3)_2$, the six-coordinate V atom is coordinated to the oxo group with a short bond [1.577 (2) Å]. The equatorial V–O bond lengths are 2.0262 (18) and 2.0277 (17) Å. The aqua ligand *trans* to the oxo group is subject to its *trans* influence, which leads to a somewhat longer V–O bond [2.175 (2) Å]. In the structure, the cation and both anions are situated on crystallographic mirror planes. The cation and anions engage in a number of relatively long hydrogen bonds [2.725 (2)–2.834 (2) Å].

Comment

The archetypical mono-oxo complex of transition metals is the vanadyl ion (VO^{2+} ; Jørgensen, 1957; Ballhausen & Gray, 1962). Although numerous structural characterizations of anionic and neutral complexes containing the vanadyl group have been undertaken (Nugent & Mayer, 1988), there exist very few structurally characterized examples of cationic vanadyl complexes (Seifert & Uebach, 1981). Prompted by its simple electronic structure and by its use as a spin-probe in bioinorganic and materials chemistry, several studies have dealt with the structure of the vanadyl aqua ion in solution (Smith *et al.*, 2002; Mustafi *et al.*, 1999; Mustafi & Makinen, 1988; van Willigen *et al.*, 1982). The solution structure has been determined by combined application of electron paramagnetic resonance (EPR), high-frequency (high-field) EPR, electron nuclear double resonance and UV–vis spectroscopies. In the solid state, the vanadyl aqua ions have been characterized in various hydrated sulfate salts; however, the majority of these are either oligomeric or contain coordinated sulfate (Palma-Vittorelli *et al.*, 1956). The parent aqua ion, $[\text{VO}(\text{H}_2\text{O})_5]^{2+}$, is only present in $\text{VO}(\text{SO}_4)\cdot 6\text{H}_2\text{O}$ and one of the modifications of $\text{VO}(\text{SO}_4)\cdot 5\text{H}_2\text{O}$ (Hawthorne *et al.*, 2001; Tachez & Théobald, 1980). Recently, Tézé *et al.* (2000) isolated, for the first time, a structure without sulfate counter-ions, containing the pentaaquovanadium(IV) complex, namely $[\text{Na}(\text{H}_2\text{O})_2]$

$[\text{VO}(\text{H}_2\text{O})_5][\text{SiW}_{12}\text{O}_{40}]\cdot 4\text{H}_2\text{O}$. Refinement of this fairly complicated structure yielded a structure with 0.01–0.02 Å standard deviations on the V–O bond lengths. We have found that metathesis of vanadyl sulfate with barium triflate to yield a salt of the weakly coordinating trifluoromethanesulfonate ion, *viz.* $[\text{VO}(\text{H}_2\text{O})_5](\text{CF}_3\text{SO}_3)_2$, (I), is possible. This salt, although very hygroscopic, can be crystallized from aqueous solution. The cation in (I), which is depicted in Fig. 1, is six-coordinate, with a vanadium–oxo bond length of 1.577 (2) Å, which is slightly, but significantly, shorter than the

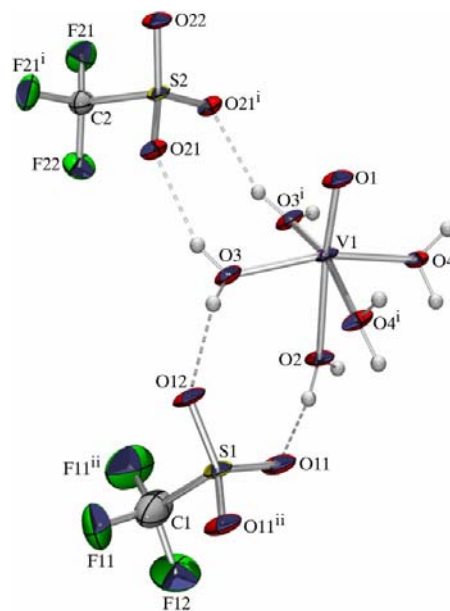


Figure 1

The molecular structure of the ionic components of the title compound. [Symmetry code: (i) $x, -y + \frac{1}{2}, z$; (ii) $x, -y + \frac{3}{2}, z$.]

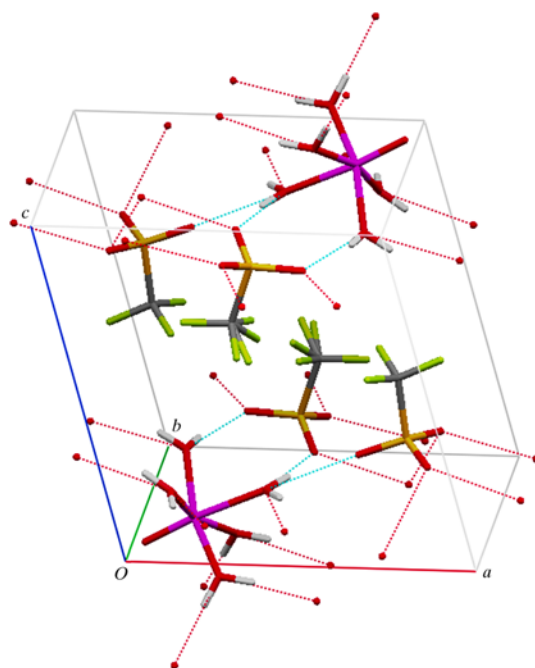


Figure 2

The packing and hydrogen bonding in $[\text{VO}(\text{H}_2\text{O})_5](\text{CF}_3\text{SO}_3)_2$.

average of structurally characterized vanadyl(IV) systems. The equatorial water ligands are coordinated at normal distances [2.0262 (18) and 2.0277 (17) Å], while the *trans* influence [V—O(*trans*) = 2.175 (2) Å] is less pronounced than for most other six-coordinate vanadium(IV) systems. In the present structure, all of the H atoms were located from a difference density map, which allows for comments on the coordination mode of the aqua ligands. These are found to have neither purely tetrahedral nor purely planar coordination, but the *trans* aqua ligand approaches the planar coordination mode with its plane bisecting the bond directions from vanadium to the equatorial ligands. This conformation is the same as that found in the sulfates (Tachez & Théobald, 1980). The V atom is raised out of the plane of the four equatorial O-atom donors towards the terminal oxo group by 0.2880 (12) Å, which is an unexceptional degree of pyramidalization for V^{IV}, but significantly larger than usually found for cationic complexes of Mo^{IV} (0.11 Å; Bendix & Bøgevig, 1998*a*) or W^{IV} (0.10–0.17 Å; Bendix & Bøgevig, 1998*b*). The O(oxo)—V—O(*trans*) unit is almost linear, with a bond angle of 174.23 (12)°, indicating only weak interaction of the *trans* water ligand with the counter-ions (see below).

As expected from the composition, the structure is held together by several hydrogen bonds, although these are not very short. The symmetry-independent equatorial water molecules each engage in two roughly linear hydrogen bonds to the O atoms of neighbouring trifluoromethanesulfonate anions. The water molecule *trans* to the oxo group is expected to be less acidic and, in line with this, it only engages in a single hydrogen bond, which is longer than the others. The packing including these hydrogen bonds is shown in Fig. 2 and the hydrogen-bond lengths are tabulated in Table 2. The structures of the trifluoromethanesulfonate counter-anions are unexceptional and their lack of coordination is expected.

The structure determined here agrees well with the earlier literature. Specifically, we find all the V—O bond distances except that to the *trans*-situated aqua ligand identical within experimental error to those determined by Tézé *et al.* (2000).

Experimental

A solution of vanadyl sulfate (25.3 g, 0.100 mol in 200 ml water) was treated with a solution of barium triflate (17.3 g, 0.101 mol) in 0.1 M trifluoromethanesulfonic acid (*ca* 200 ml). The resulting precipitate of barium sulfate was removed by filtration. The filtrate was concentrated by rotary evaporation and left in a desiccator for several weeks to produce crystals a few centimetres in size. From one of these very hygroscopic crystals, a piece suitable for X-ray diffraction was cut under an atmosphere of dry dinitrogen.

Crystal data

[VO(H ₂ O) ₅](CF ₃ SO ₃) ₂	<i>Z</i> = 2
<i>M_r</i> = 455.16	<i>D_x</i> = 2.017 Mg m ⁻³
Monoclinic, <i>P</i> ₂ ₁ / <i>m</i>	Mo <i>K</i> α radiation
<i>a</i> = 9.688 (2) Å	<i>μ</i> = 1.07 mm ⁻¹
<i>b</i> = 7.7579 (17) Å	<i>T</i> = 122 (1) K
<i>c</i> = 10.219 (4) Å	Prism, blue
<i>β</i> = 102.684 (19)°	0.43 × 0.26 × 0.26 mm
<i>V</i> = 749.3 (4) Å ³	

Data collection

Nonius KappaCCD area-detector diffractometer	18866 measured reflections
<i>ω</i> and <i>φ</i> scans	1588 independent reflections
Absorption correction: Gaussian integration (Coppens, 1970)	1429 reflections with <i>I</i> > 2σ(<i>I</i>)
<i>T</i> _{min} = 0.747, <i>T</i> _{max} = 0.843	<i>R</i> _{int} = 0.141
	<i>θ</i> _{max} = 26.0°

Refinement

Refinement on <i>F</i> ²	<i>w</i> = 1/[σ ² (<i>F</i> _o ²) + (0.0498 <i>P</i>) ² + 0.7459 <i>P</i>]
<i>R</i> [<i>F</i> ² > 2σ(<i>F</i> ²)] = 0.038	where <i>P</i> = (<i>F</i> _o ² + 2 <i>F</i> _c ²)/3
<i>wR</i> (<i>F</i> ²) = 0.104	(Δ/ <i>σ</i>) _{max} < 0.001
<i>S</i> = 1.07	Δ <i>ρ</i> _{max} = 0.48 e Å ⁻³
1588 reflections	Δ <i>ρ</i> _{min} = -0.56 e Å ⁻³
131 parameters	
H-atom parameters constrained	

Table 1

Selected geometric parameters (Å, °).

V1—O1	1.577 (2)	V1—O3	2.0262 (18)
V1—O2	2.175 (2)	V1—O4	2.0277 (17)
O1—V1—O2	174.23 (12)	O3—V1—O4	163.52 (7)
O1—V1—O3	99.97 (8)	O3—V1—O2	84.15 (7)
O1—V1—O4	96.43 (8)	O4—V1—O2	79.62 (7)

Table 2

Hydrogen-bond geometry (Å, °).

<i>D</i> —H... <i>A</i>	<i>D</i> —H	H... <i>A</i>	<i>D</i> ... <i>A</i>	<i>D</i> —H... <i>A</i>
O2—H2...O11	0.88	2.02	2.834 (2)	154
O3—H3A...O12	0.90	1.96	2.808 (2)	157
O3—H3B...O21	0.83	1.95	2.725 (2)	156
O4—H4A...O21 ⁱ	0.88	1.87	2.734 (2)	166
O4—H4B...O11 ⁱⁱ	0.90	1.87	2.752 (2)	168

Symmetry codes: (i) $-x, -y - \frac{1}{2}, -z$; (ii) $-x + 1, y - \frac{1}{2}, -z$.

During the refinement of the title complex, the trifluoromethyl group on one of the trifluoromethanesulfonate anions was found to be disordered. The large anisotropic displacement parameters for the C1/F11₂/F12 unit suggests disorder due to rotation of the trifluoromethyl group. The disorder was resolved by refining the F11 atom over two positions. The large *R*_{int} value is probably caused by slow decay of the crystal due to the highly hygroscopic nature of the title compound.

Data collection: COLLECT (Nonius, 1999); cell refinement: DIRAX (Duisenberg, 1992); data reduction: EVALCCD (Duisenberg, 1998); program(s) used to solve structure: SHELXS97 (Sheldrick, 1997); program(s) used to refine structure: SHELXL97 (Sheldrick, 1997); molecular graphics: ORTEPII (Johnson, 1976) and MERCURY (Macrae *et al.*, 2006); software used to prepare material for publication: SHELXL97.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: IZ3014). Services for accessing these data are described at the back of the journal.

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