acidified to pH 4–5 and was subjected to continuous extraction for 1 week with ether using a modified Dean-Stark trap. (Strongly acidic conditions had to be avoided to suppress the generation of I_2 during the continuous extraction process, presumably arising from residual iodate salts in the aqueous phase; otherwise, further purification became awkwardly complicated.) After continuous extraction, the ether solution was dried and carefully concentrated to 0.5–1.0 mL, and the isotopically labeled cyclopropanecarboxylic acids were purified by VPC on column C at 170 °C. The yields ranged from 50 to 70%.

Typical Procedure for Preparation of Labeled Phenyl Cyclopropyl Ketones for NMR Chiral Shift Reagent Analysis. The isotopically labeled cyclopropanecarboxylic acid (26.2 mg, 0.29 mmol) was washed from a VPC collection tube into the reaction vessel with dry THF (3 mL) and the flask was cooled to 0 °C. A 2.7 M solution of phenyllithium (0.77 mL, 2.08 mmol, Aldrich Chemical Co.) in 7:3 cyclohexane/ether was quickly syringed into the solution followed by 1.5 h of stirring at 0 °C. Trimethylsilyl chloride[18] (0.76 mL, 7.00 mmol) was rapidly added, the cooling bath was removed, and the mixture was stirred 30 min at room temperature. The bis(trimethylsilyl) derivative was then hydrolyzed by addition of aqueous 1 M HCl (2 mL) and rapid stirring for 1 h. The layers were separated, the aqueous phase was extracted with ether (2 × 10 mL), and the combined organic phases were dried and concentrated to ~0.5 mL. The ketone product was purified for shift reagent analysis by VPC on column A at 145 °C. Yields of 80 to 90% were realized.

General Procedure Used for Determining Enantiomeric Ratios with NMR Chiral Shift Reagent Eu(hfc)$_3$. The VPC purified sample was dissolved in dry benzene-d_6. The optimum sample size was about 15 mg. This gave an adequate signal-to-noise ratio in the NMR allowing reasonably accurate and precise integrations to be measured, yet kept the substrate concentration low enough so that an excessively large amount of shift reagent was not required to produce the necessary peak separations. The shift reagent was added in about 50-mg portions to the NMR tube. After each addition the solution was agitated to dissolve the shift reagent, nitrogen was bubbled through the solution for 5 min with a drawn out Pasteur pipet, and the spectrum was measured. The integral ratios reported were an average of at least 10 scans with a 30-s delay between each scan. Commercial Eu(hfc)$_3$ contains an insoluble trace impurity; samples requiring large amounts of shift reagent (>300 mg) were therefore filtered and deoxygenated once more before the final spectral determinations were made.

Acknowledgment. We thank the Research Corporation and the National Science Foundation for partial support of this work.

Registry No. (2*R*,3*R*)-(+)-**1**-*t*, 88546-86-5; (*S*,*S*,*S*)-**1**-*a*, 91230-87-4; **3**, 91230-88-5; **4**, 71777-36-1; **6**, 54522-92-8; **7**, 91230-89-6; **8**, 91230-90-9; **9**, 91230-91-0; **10**, 91230-93-2; **11**, 91230-94-3; $I^{13}CH_3$, 4227-95-6; *dl*-menthyl α-deuteriodiazoacetate, 80594-25-8; *d*-menthyl *trans*-1-(*S*),2(*R*),3(*R*)-trideuterio-2-phenylcyclopropanecarboxylate-*3*-^{13}C, 91230-92-1; *l*-menthyl *trans*-1(*S*),2(*R*),3(*R*)-trideuterio-2-phenylcyclopropanecarboxylate-*3*-^{13}C, 91279-52-6; *d*-menthyl *cis*-1(*R*),2(*R*),3(*R*)-trideuterio-2-phenylcyclopropanecarboxylate-*3*-^{13}C, 91279-51-5; *l*-menthyl *cis*-1(*R*),2(*R*),3(*R*)-trideuterio-2-phenylcyclopropanecarboxylate-*3*-^{13}C, 91279-53-7.

Precise Structural Characterizations of the Hexaaquovanadium(III) and Diaquohydrogen Ions. X-ray and Neutron Diffraction Studies of $[V(H_2O)_6][H_5O_2](CF_3SO_3)_4$

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Abstract: The title compound, a new one, the preparation of which is described, has been investigated structurally by both X-ray diffraction at ca. 295 K and neutron diffraction at ca. 20 K. The space group is $P\bar{1}$ and the unit cell has the following dimensions, where in each case the X-ray value is given first followed by the neutron value: a = 8.950 (1) Å, 8.942 (8) Å; b = 9.112 (1) Å, 8.902 (8) Å; c = 8.928 (2) Å, 8.774 (8) Å; α = 103.38 (1)°, 103.4 (2)°; β = 93.75 (2)°, 95.2 (1)°; γ = 70.19 (1)°, 69.9 (2)°; V = 666.4 (3) Å^3, 638 (2) Å^3. The structure was first solved and refined (211 variables) by using 2605 independent X-ray reflections with $F^2 > 3\sigma(F^2)$ to R = 0.046. Neutron data, 2137 reflections with $F^2 > 2\sigma(F^2)$, were then used to refine 261 variables including all hydrogen atoms anisotropically to R = 0.067. The structure consists of centrosymmetric $[V(H_2O)_6]^{3+}$ and $H_5O_2^+$ cations and $CF_3SO_3^-$ anions. All hydrogen atoms participate in hydrogen bonds. The $H_5O_2^+$ ion appears to be truly centrosymmetric with an O···O distance of 2.430 (3) Å at 20 K; the configuration at each oxygen atom is highly pyramidal. The $[V(H_2O)_6]^{3+}$ cation has nearly flat water molecules (i.e., sums of bond angles about oxygen atoms are 357.7–359.7°), and these are arranged to give the hexaaquo ion essentially D_{3d} symmetry of the sort in which the six hydrogen atoms of three mutually cis water molecules are essentially coplanar. Possible reasons for the adoption of this particular highly symmetric arrangement are discussed.

Definitive structural information on hydrated ions is surprisingly scarce,[2-7] considering the importance of the subject. The principal difficulty, of course, is that a full description of such species requires accurate knowledge of hydrogen atom positions and the only generally applicable source of precise data on this point is neutron crystallography. Of course, there are several requirements to obtain accurate and useful neutron diffraction data. Crystals of considerably greater volume than those used for X-ray crystalography are needed (typically at least 100 times greater), and for many interesting compounds such crystals cannot be grown. Furthermore, as in X-ray work, it is desirable to have well-ordered crystals. Finally, to obtain the fullest benefit from the neutron diffraction data, it is best to collect it at a very low temperature and this means that the crystal must not undergo any interfering

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(1) (a) Texas A&M University. (b) Research Reactor Facility, University of Missouri. (c) Argonne National Laboratory.

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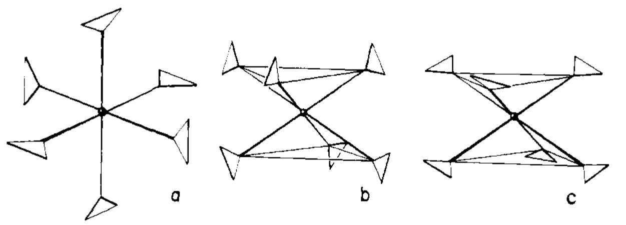

Figure 1. The three most symmetrical arrangements of six planar water molecules about a central metal ion where the MO_6 core has O_h symmetry. (a) T_h symmetry, (b) all-vertical D_{3d} symmetry, (c) all-horizontal D_{3d} symmetry.

phase transition between room temperature and the temperature used for data collection.

With regard to aquo metal cations, two questions of considerable interest are (1) the orientation of each water molecule relative to the metal–oxygen bond and (2) the orientations of the water molecules around a given ion relative to one another. The first question is concerned with whether the $M-OH_2$ unit is *flat* or *pyramidal* (and if pyramidal, to what degree). In the event that the configuration of each individual water molecule is flat (or nearly so), and we are dealing with a hexaaquo ion, the second question is concerned with the point symmetry of the $[M(H_2O)_6]^{n+}$ arrangement. The O_h symmetry of the central MO_6 group is necessarily reduced by the hydrogen atoms, but a considerable amount of symmetry may still be retained. The three most symmetrical arrangements are shown in Figure 1. In the first one a form of cubic symmetry, T_h, is retained. Also shown are the two arrangements that have D_{3d} symmetry. There are two ways to pass from one of these to the other by a concerted set of rotations about the M–O bonds; these pathways traverse ranges of intermediate structures having either S_6 or D_3 symmetry. It should be noted that the all-horizontal D_{3d} arrangement is also consistent with pyramidal water molecules, while the other two are not (i.e., the water molecules in those must lie in symmetry planes).

With regard to hydrated forms of the hydrogen ion[8] there has been more information available, but still there is a great deal to be learned. One of the most important species is the diaquo hydrogen ion, $H(H_2O)_2^+$ or $H_5O_2^+$. The existing data suggest that in this ion the configurations at the oxygen atoms are characteristically pyramidal, but there is some variation in the O···O separation, which is reported to vary over a range[9a] with the approximate limits 2.41 to 2.45 Å. Another important variable is the location of the shared proton, i.e, the presence or absence of a center of symmetry. The fact that the $H_5O_2^+$ ions in a given structure reside on crystallography centers of inversion does not, of course, imply that the individual $H_5O_2^+$ ions are necessarily centric, since the crystallography requirement can be met by a disordered array of non-centric $H_5O_2^+$ ions or a distorted H_3O^+ ion bound to a H_2O molecule and having a very short O···O distance and *no* center of symmetry between the oxygen atoms.[9b]

In the context of the foregoing discussion, we recognized that the title compound presented an unusually auspicious opportunity to acquire valuable data concerning the structures of hydrated cations, both a hydrated metal ion and a hydrated hydrogen ion. When the compound was prepared and subjected to X-ray structure determination it became clear that is possessed not only interesting components, i.e., both the $[V(H_2O)_6]^{3+}$ and $H_5O_2^+$ ions, but also properties well suited to a low-temperature neutron diffraction study. Such a study has been carried out (at 20 K) and the results, along with the X-ray results and other information, are reported and discussed here.

Table I. Data Collection and Analysis Parameters

	X-ray	neutron
formula (fw)	$VS_4F_{12}O_{20}C_4H_{17}$	(792.39)
sample temp	295 K	20 K
unit cell parameters		
a, Å	8.950 (1)	8.942 (8)
b, Å	9.112 (1)	8.902 (8)
c, Å	8.928 (2)	8.774 (8)
α	103.38 (1)	103.4 (2)
β	93.75 (2)	95.2 (1)
γ	70.19 (1)	69.9 (2)
vol, $Å^3$	666.4 (3)	638 (2)
space group	$P\bar{1}$	$P\bar{1}$
wavelength, Å	0.71073	1.068 (3)
type of data measured	$+h, \pm k, \pm l$	$\pm h, \pm k, \pm l$
max $(\sin\theta)/\lambda$, $Å^{-1}$	0.6497	0.662
total no. reflcns	3050	8290
no. unique reflcns used in refinement	2605[a]	2137[b]
merging R factor		0.044
value of P in σ calcn[c]	0.05	0.04
linear absorptn coeff, cm^{-1}	8.175	1.4[d]
extinctn parameter, $g10^{-4}$		6.7 (4)
no. variables	211	261
final R factors		
$R(F^2)$	0.046	0.067
$R_w(F^2)$	0.068	0.090
error in observn of unit wgt.	2.204	2.566

[a] Data with $F^2 > 3\sigma(F^2)$. [b] Data with $F^2 > 2\sigma(F^2)$; $\sigma(F^2) = [\sigma_0(F^2) + (PF^2)^2]^{1/2}$, where $\sigma_0(F^2)$ is determined from counting statistics. [d] No absorption correction applied (see text).

Experimental Section

Synthesis. All chemical operations were conducted in an atmosphere of argon. Water was purged with argon, distilled in an argon atmosphere immediately before use, and transferred by syringe. The title compound was prepared by dissolving $[V_3(\mu_3\text{-}O)(CH_3CO_2)_6(CH_3CO_2H)_2(C_4H_8O)][VCl_4(CH_3CO_2H)_2]$[10] in water and pouring the solution on to a Dowex 50W × 2 cation exchange column. Elution with 2 M trifluoromethanesulfonic acid gave only a single blue band. Slow evaporation of the blue eluate gave large blue-violet crystals.

X-ray Structure Determination. A crystal approximately 0.3 × 0.4 × 0.4 mm was sealed in a Lindemann glass capillary. The crystallographic data and data collection conditions are summarized in Table I. Data were collected on an Enraf-Nonius CAD-4 diffractometer with Mo Kα radiation ($\lambda = 0.71073$ Å, $2\theta_{max} = 55°$) monochromated in the incident beam with a graphite crystal. In view of the low linear absorption coefficient, no absorption correction was made. The structure was solved by the direct methods program MULTAN, whereby the vanadium atom and two sulfur atoms were located. Difference maps alternating with cycles of least-squares refinement were then used to locate the other non-hydrogen atoms. After anisotropic refinement of all these atoms a difference Fourier map revealed the six hydrogen atoms of the water molecules coordinated to the vanadium atom. These hydrogen atoms were then included in the refinement with isotropic thermal parameters. The hydrogen atoms in the $H_5O_2^+$ ion were located later and their contributions included in F_c values, but they were not refined. Tables of positional parameters, anisotropic thermal parameters, and structure factors are available as supplementary material.

Neutron Diffraction Data Collection and Analysis. Several blue-purple crystals were sealed in lead glass capillaries under an atmosphere of argon. The crystals were initially characterized using the neutron time-of-flight single-crystal diffractometer at the Argonne Intense Pulsed Neutron Source.[11] The best single crystal, which was approximately spherical in shape, with a diameter of approximately 3 mm, was transported to the University of Missouri Research Facility and mounted inside a helium-filled canister which was attached to the cold stage of a Displex closed-cycle helium refrigerator. The sample was kept at a constant temperature of 20 K throughout data collection on the 2XE neutron diffractometer. There was no significant deviation of the intensities of four standard reflections measured periodically during the data collection. A summary of the data collection and analysis parameters is presented in Table I.

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[8] For a summary of $H_5O_2^+$ geometries in crystal structures, see: Lundgren, J.-O.; Olovsson, I. "The Hydrogen Bond"; Schuster, P., Zundel, G., Sandorfy, C., Eds.; North-Holland: Amsterdam, 1976; Vol. II, p 471–526.

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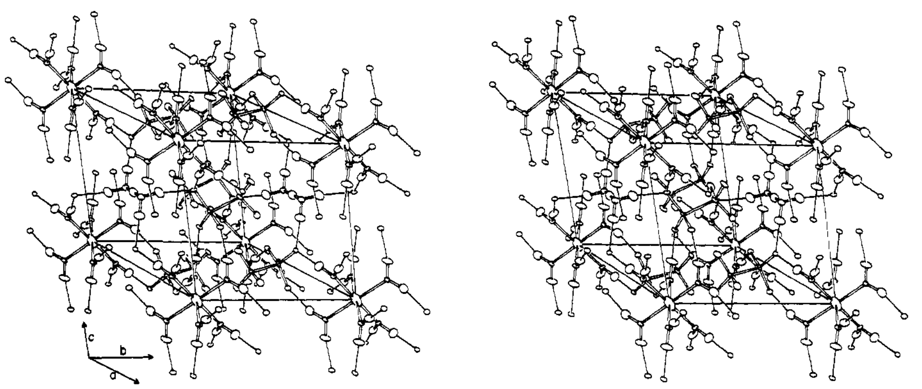

Figure 2. Stereoscopic view of the unit cell, based on the neutron diffraction results. The terminal atoms outside the unit cell boundaries are $CF_3SO_3^-$ oxygen atoms.

Table II. Positional Parameters and Equivalent Isotropic Thermal Parameters from the Neutron Diffraction Study

atom	*x*	*y*	*z*	*B*, Å^2
V(1)	0.0000	0.0000	0.0000	0.7 (7)[a]
S(1)	−0.1733 (2)	0.2535 (7)	0.4968 (7)	0.7 (1)
S(2)	0.6362 (7)	0.7736 (7)	0.0920 (7)	0.6 (1)
F(1)	−0.1312 (4)	0.4956 (4)	0.7074 (4)	1.14 (6)
F(2)	−0.3714 (4)	0.5474 (4)	0.6133 (4)	1.22 (6)
F(3)	−0.1822 (4)	0.5454 (4)	0.4769 (4)	1.22 (6)
F(4)	0.6491 (4)	0.4805 (4)	−0.0626 (4)	0.95 (6)
F(5)	0.8670 (4)	0.4924 (4)	0.0593 (4)	1.26 (6)
F(6)	0.6655 (4)	0.5099 (4)	0.1878 (4)	1.24 (7)
O(1)	0.2219 (3)	−0.1402 (4)	−0.0614 (3)	0.72 (5)
O(2)	−0.0012 (3)	−0.1310 (4)	0.1535 (3)	0.70 (5)
O(3)	−0.0935 (3)	−0.1398 (4)	−0.1675 (4)	0.74 (5)
O(4)	−0.2796 (4)	0.2455 (4)	0.3632 (3)	0.81 (6)
O(5)	−0.0058 (3)	0.1957 (4)	0.4630 (4)	0.81 (6)
O(6)	−0.2142 (3)	0.1952 (4)	0.6229 (3)	0.73 (5)
O(7)	0.6665 (4)	0.8014 (4)	−0.0551 (4)	0.80 (6)
O(8)	0.4717 (3)	0.8248 (4)	0.1338 (4)	0.78 (6)
O(9)	0.7367 (3)	0.8253 (4)	0.2203 (3)	0.68 (5)
O(10)	0.3566 (4)	0.0439 (4)	0.4795 (4)	1.03 (6)
C(1)	−0.2190 (3)	0.4754 (3)	0.5784 (3)	0.77 (5)
C(2)	0.7093 (3)	0.5500 (3)	0.0676 (3)	0.75 (5)
H(1)	0.2525 (7)	−0.1843 (8)	−0.1720 (7)	2.0 (1)
H(2)	0.3161 (7)	−0.1542 (8)	0.0082 (6)	1.6 (1)
H(3)	−0.0976 (7)	−0.1516 (8)	0.1810 (7)	1.9 (1)
H(4)	0.0815 (7)	−0.1550 (8)	0.2331 (7)	1.7 (1)
H(5)	−0.1810 (7)	−0.1756 (8)	−0.1439 (7)	2.1 (1)
H(6)	−0.0676 (7)	−0.1685 (8)	−0.2787 (7)	2.1 (1)
H(7)	0.5000	0.000	0.5000	1.9 (2)
H(8)	0.3058 (8)	0.0986 (8)	0.5806 (8)	2.3 (1)
H(9)	0.3162 (8)	−0.0456 (8)	0.4366 (8)	2.2 (1)

[a] This atom only was refined isotropically. The isotropic equivalent thermal parameter is defined as $(^4/_3)[a^2B(1,1) + b^2B(2,2) + c^2B(3,3) + ab(\cos\gamma)B(1,2) + ac(\cos\beta)B(1,3) + bc(\cos\alpha)B(2,3)]$.

The positional parameters of the non-hydrogen atoms as determined from the X-ray structure were used to calculate phases for a difference Fourier map from which the locations of the hydrogen atoms were obtained. All atoms except the vanadium atom were refined by using anisotropic thermal parameters. Since the coherent neutron scattering length for vanadium is nearly zero ($b_V = -0.05 \times 10^{-12}$ cm), it was not possible to refine the temperature factor of the vanadium atom anisotropically. The neutron scattering lengths used for all atoms were those tabulated by Bacon.[12a] No absorption correction was applied since $\mu R = 0.21$ is small and the correction factors would vary by less than 1%. The refinement of the neutron structure was carried out at the University of Missouri with a locally modified SDP-Plus program package. Table II contains the atomic positional and equivalent isotropic thermal parameters obtained from the final least-squares cycle. The anisotropic thermal parameters and structure factors are available as supplementary material.

Table III. H···O Hydrogen Bond Distances (Å) and Associated O–H···O Angles (deg)

	distance	angle
O(1)–H(1)···O(4)	1.652 (4)	172.6 (4)
O(1)–H(2)···O(8)	1.681 (4)	177.5 (4)
O(2)–H(3)···O(9)	1.641 (5)	176.0 (4)
O(2)–H(4)···O(6)	1.667 (4)	176.3 (4)
O(3)–H(5)···O(7)	1.722 (5)	164.1 (4)
O(3)–H(6)···O(5)	1.733 (5)	167.7 (4)
O(10)–H(8)···O(9)	1.746 (5)	165.5 (4)
O(10)–H(9)···O(6)	1.818 (5)	170.9 (4)

Table IV. Bond Distances (Å)

	X-ray	neutron
V(1)–O(1)	1.993 (1)	1.991 (2)
V(1)–O(2)	1.988 (1)	1.978 (2)
V(1)–O(3)	2.003 (1)	2.013 (2)
mean	1.995 [4]	1.994 [8]
S(1)–O(4)	1.445 (1)	1.446 (4)
S(1)–O(5)	1.431 (1)	1.441 (4)
S(1)–O(6)	1.451 (1)	1.448 (5)
S(2)–O(7)	1.430 (1)	1.434 (5)
S(2)–O(8)	1.435 (1)	1.437 (4)
S(2)–O(9)	1.449 (1)	1.466 (4)
mean	1.440 [4]	1.445 [5]
S(1)–C(1)	1.821 (2)	1.851 (4)
S(2)–C(2)	1.829 (2)	1.835 (4)
C(1)–F(1)	1.317 (3)	1.331 (3)
C(1)–F(2)	1.310 (3)	1.321 (3)
C(1)–F(3)	1.318 (3)	1.319 (3)
C(2)–F(4)	1.304 (3)	1.330 (2)
C(2)–F(5)	1.307 (3)	1.327 (3)
C(2)–F(6)	1.327 (3)	1.318 (3)
mean	1.314 [3]	1.324 [2]
O(10)–O(10)′	2.360 (2)	2.430 (3)
O(1)–H(1)		0.984 (2)
O(1)–H(2)		0.984 (4)
O(2)–H(3)		1.000 (5)
O(2)–H(4)		0.973 (4)
O(3)–H(5)		0.995 (5)
O(3)–H(6)		0.977 (4)
O(10)–H(7)		1.215 (2)
O(10)–H(8)		0.975 (4)
O(10)–H(9)		0.971 (5)

An attempt was made to refine the structure in the noncentrosymmetric space group *P*1 in order to remove the crystallographic center of inversion imposed by space group *P*$\bar{1}$ on the $H_5O_2^+$ and $[V(H_2O)_6]^{3+}$ cations. With twice the number of variables the *R* factors decreased, and the O···H···O bond in the $H_5O_2^+$ cation did become noncentered. However, the temperature factors of 26 out of 58 atoms became nonpositive definite, and some of the bond distances and angles became chemically unreasonable. We therefore conclude that the centrosymmetric space group *P*$\bar{1}$ is correct.

Results

The structure consists of $[V(H_2O)_6]^{3+}$ ions residing on inversion centers at (0,0,0) and $H_5O_2^+$ ions residing on inversion centers at $(^1/_2,0,^1/_2)$, together with two crystallographically independent

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(12) (a) Bacon, G. E. "International Tables for X-ray Crystallography"; Kynoch Press: Birmingham, 1974; Vol IV, p 270. (b) Bond, W. L. *Ibid.* 1959; Vol. II, p 302.

Table V. Bond Angles (deg)

	X-ray	neutron
O(1)-V(1)-O(2)	91.70 (6)	91.18 (9)
O(1)-V(1)-O(3)	91.93 (6)	92.29 (8)
O(2)-V(1)-O(3)	91.61 (6)	92.28 (9)
O(4)-S(1)-O(5)	115.6 (1)	116.2 (3)
O(4)-S(1)-O(6)	112.2 (1)	112.5 (3)
O(4)-S(1)-C(1)	105.0 (1)	104.3 (2)
O(5)-S(1)-O(6)	114.28 (9)	114.8 (3)
O(5)-S(1)-C(1)	104.4 (1)	103.8 (3)
O(6)-S(1)-C(1)	103.7 (1)	103.3 (2)
O(7)-S(2)-O(8)	114.8 (1)	116.1 (3)
O(7)-S(2)-O(9)	114.69 (9)	113.1 (3)
O(7)-S(2)-C(2)	103.9 (1)	104.7 (2)
O(8)-S(2)-O(9)	113.69 (9)	113.2 (3)
O(8)-S(2)-C(2)	103.9 (1)	105.3 (3)
O(9)-S(2)-C(2)	104.0 (1)	102.6 (2)
S(1)-C(1)-F(1)	109.6 (2)	108.9 (2)
S(1)-C(1)-F(2)	110.6 (2)	111.1 (2)
S(1)-C(1)-F(3)	109.9 (2)	110.2 (2)
F(1)-C(1)-F(2)	108.1 (2)	109.4 (2)
F(1)-C(1)-F(3)	107.3 (2)	108.1 (2)
F(2)-C(1)-F(3)	111.3 (3)	109.1 (2)
S(2)-C(2)-F(4)	111.8 (2)	110.5 (2)
S(2)-C(2)-F(5)	110.5 (2)	110.5 (2)
S(2)-C(2)-F(6)	109.5 (2)	109.7 (2)
F(4)-C(2)-F(5)	108.3 (2)	108.8 (2)
F(4)-C(2)-F(6)	107.4 (2)	108.5 (2)
F(5)-C(2)-F(6)	109.3 (2)	108.9 (2)
V(1)-O(1)-H(1)		121.7 (3)
V(1)-O(1)-H(2)		125.7 (3)
H(1)-O(1)-H(2)		111.3 (4)
V(1)-O(2)-H(3)		124.5 (3)
V(1)-O(2)-H(4)		123.1 (3)
H(3)-O(2)-H(4)		110.1 (4)
V(1)-O(3)-H(5)		121.1 (3)
V(1)-O(3)-H(6)		124.8 (3)
H(5)-O(3)-H(6)		113.8 (4)
S(1)-O(4)-H(1)		133.8 (3)
S(1)-O(5)-H(6)		123.4 (2)
S(1)-O(6)-H(4)		118.4 (2)
S(1)-O(6)-H(9)		115.4 (2)
H(4)-O(6)-H(9)		113.1 (2)
S(2)-O(7)-H(5)		138.3 (3)
S(2)-O(8)-H(2)		125.9 (2)
S(2)-O(9)-H(3)		119.8 (3)
S(2)-O(9)-H(8)		129.3 (3)
H(3)-O(9)-H(8)		110.0 (2)
H(7)-O(10)-H(8)		108.4 (3)
H(7)-O(10)-H(9)		113.7 (3)
H(8)-O(10)-H(9)		106.8 (4)

$CF_3SO_3^-$ ions, each on a general position. Figure 2 shows a stereospecific view of the unit cell contents. All oxygen and hydrogen atoms are involved in hydrogen bonds, and an extensive network of hydrogen bonds links all the ions. Table III lists the distances and angles in the hydrogen bonds. The other bond distances and angles are listed in Tables IV and V, respectively.

In Tables IV and V the results obtained by X-ray and neutron diffraction are compared. For bonds not involving hydrogen the differences are generally insignificant, especially the average values for sets of chemically equivalent bonds. The one difference that requires comment is the O···O distance in the $H_5O_2^+$ ion, which was found to be 2.360 (2) Å in the X-ray work and 2.430 (3) Å in the neutron work. Presumably this is mainly attributable to the effect of thermal motion, which is much larger at room temperature (X-ray) than at 20 K (neutron).

The distances to H atoms found in the X-ray work were all reasonable but quite inaccurate and are of little interest now that the neutron results are at hand. Excluding H(7), the atom at the center of the $H_5O_2^+$ ion, the H···O distances in hydrogen bonds range from 1.641 (5) to 1.818 (5) Å and the O–H···O angles range from 165.5 (4)° to 177.5 (4)°. The observed geometries for the O–H···O bonds in this structure are thus fairly typical for hydrogen bonds involving water molecules in other neutron diffraction structures.[6]

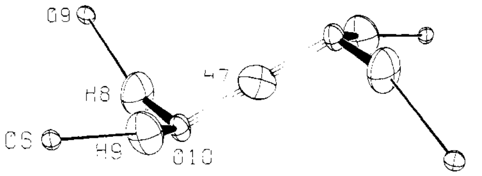

Figure 3. A perspective view of the $H_5O_2^+$ ion. Hydrogen bonds to the O(6) and O(9) atoms of $CF_3SO_3^-$ anions are also shown.

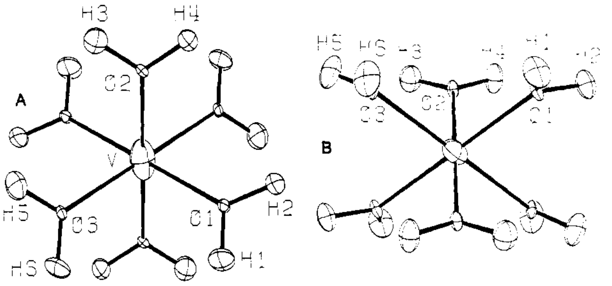

Figure 4. Two views of the $[V(H_2O)_6]^{3+}$ ion, which has virtual D_{3d} symmetry. (A) A view down the C_3 axis; (B) a view perpendicular to the C_3 axis.

Table VI. Some Least-Squares Best Planes and Deviations Therefrom (Å)[a]

Plane 1: $0.4926x + 0.8623y - 0.1171z = 0.0$			
O(1)	-0.060 (3)	O(1)′	0.060 (3)
H(1)	0.023 (7)	H(1)′	-0.023 (7)
H(2)	0.024 (6)	H(2)′	-0.024 (6)
V	0.0		
Plane 2: $0.1301x - 0.7375y - 0.6627z = 0.0$			
O(2)	0.082 (3)	O(2)′	-0.082 (3)
H(3)	-0.032 (6)	H(3)′	0.032 (6)
H(4)	-0.032 (6)	H(4)′	0.032 (6)
V	0.0		
Plane 3: $-0.4210x + 0.8895y - 0.1775z = 0.0$			
O(3)	-0.030 (3)	O(3)′	0.030 (3)
H(5)	0.012 (7)	H(5)′	-0.012 (7)
H(6)	0.012 (7)	H(6)′	-0.012 (7)
V	0.0		
Plane 4: $-0.0024x - 0.09859y - 0.1676z = 1.3476$			
H(1)	0.100 (7)	H(4)	0.027 (7)
H(2)	-0.080 (7)	H(5)	0.041 (7)
H(3)	-0.016 (7)	H(6)	-0.071 (7)

[a] In each case, all atoms listed were used to compute the best plane. Dihedral angles between planes (1,2), (1,3), and (2,3) are 119.6°, 54.5°, and 126.4°, respectively.

$H_5O_2^+$ Cation. Because this cation resides on a crystallographic center of inversion, the O···H···O bond appears to be centered and linear. It is shown in Figure 3. The O···O distance of 2.430 (3) Å is within the range of other known $H_5O_2^+$ structures.[8] The geometry of O(10) is pyramidal and each terminal hydrogen atom is hydrogen bonded to an oxygen atom of a $CF_3SO_3^-$ anion.

$[V(H_2O)_6]^{3+}$ Cation. The vanadium atom resides on an inversion center, and the VO_6 unit has O_h symmetry within experimental error. However, when the hydrogen atoms are included the symmetry is necessarily lower. Two view of the cation are shown in Figure 4, and it can be seen that the arrangement is, within experimental error, the all-horizontal type of D_{3d} symmetry shown in Figure 1. In ideal form this D_{3d} symmetry would require the hydrogen atoms to lie exactly in two parallel planes. Table VI, which gives various least-squares planes for the $[V(H_2O)_6]^{3+}$ ion, includes, as plane 4, the plane of the six crystallographically independent hydrogen atoms. All deviations from this mean plane are ≤ 0.1 Å, with the average absolute deviation being 0.056 Å.

As noted in the introduction, this form of D_{3d} symmetry is achievable whether the water molecules are planar or pyramidal. In fact, in this case the water molecules are not fully planar, but they come close. For truly pyramidal molecules, i.e., those derived from an approximately tetrahedral set of orbitals on the oxygen atom, the sum of the three angles subtended by the M and two H atoms at the oxygen atom[13] should be about 330°. For the oxygen atoms in the $H_5O_2^+$ ion the sum is 329 ± 1°. For the three independent water molecules in the $[V(H_2O)_6]^{3+}$ ion the sums are 358.7 (10)°, 357.7 (10)°, and 359.7 (10)° at O(1), O(2), and O(3), respectively. While this sum of angles criterion is perfectly valid, it does not provide a particularly sensitive measure of small deviations from planarity. It is, therefore, well to look directly at the mean planes and deviations therefrom, as given in Table VI. The planes 1–3 are those defined by the pairs of centrically related water molecules. These results show that while the water molecules in $[V(H_2O)_6]^{3+}$ are not planar within the experimental errors, the deviations are all less than 0.1 Å.

Discussion

$H_5O_2^+$ Ion. Surveys of high-precision neutron diffraction studies of short hydrogen bonds (O···O = 2.40–2.50 Å) nearly always indicate that the bond is noncentered if crystallographic symmetry is not imposed.[14,15] Presumably this is because when the two oxygen atoms experience different crystal environments they appear chemically different to the shared hydrogen atom. For those cases where crystallographic symmetry is imposed, it is still possible to infer a static or dynamic disorder of a noncentered hydrogen bond if the hydrogen thermal ellipsoid is unduly extended in the O···O direction, indicative of a potential function that is broad and flat or has a double minimum. However, in this structure the thermal ellipsoid of O(7) is very nearly isotropic, as seen in Figure 3, and we believe that this is a truly centric hydrogen bond.

$[V(H_2O)_6]^{3+}$ Ion. This study provides a considerably more precise description of the structure of a hexaaquo transition-metal ion than any that has previously been reported. Moreover, the structure so obtained has two well-defined features for which explanations must be considered. These are (1) the practically planar water molecules and (2) the all-horizontal D_{3d} structure.

To explain the planarity of the water molecules, two factors suggest themselves. It has previously been noted[3,7] that there is a general tendency for a higher charge-to-radius ratio of the metal ion to favor the planar arrangement. Such an electrostatic factor may well have its place in a complete explanation of the present structure. However, in dealing with a transition-metal ion, which has a partially filled d shell, electronic factors, specifically the possibility of π interaction between lone pairs on the water molecules and the d_{xz}, d_{yz}, and d_{xy} orbitals of the metal atom, should also be considered. To the extent that such ligand-to-metal dative π bonding can contribute to the stability of the molecule, it will lead to a preference for flat water ligands. Studies by either experimental or theoretical means, or both, will be required to assess the actual importance of this factor.

The question of why the observed all-horizontal D_{3d} structure is adopted is also one to which it is not now possible to provide an unequivocal answer. Again, two potential contributions must be considered, viz., (1) an electronic preference for this structure due to the d^2 configuration of the metal ion and (2) lower crystal energy derived from the suitability of this cation structure for hydrogen bonding, as compared to other possible structures. While we shall reserve a detailed discussion for a future paper, the electronic factor merits a preliminary examination here.

For an "octahedrally" coordinated V^{3+} ion having true O_h symmetry, or also T_h symmetry (see Figure 1), there would be a degenerate ground state (${}^3T_{1g}$ or ${}^3T_g$). According to the Jahn-Teller theorem this should not be stable. A change to either of the D_{3d} structures of course splits the t_{2g} orbitals into an a_{1g} and a pair of e_g orbitals. It turns out[16] that the vertical D_{3d} structure would give $E(a_{1g}) < E(e_g)$ and hence an ${}^3E_g$ ground state based on an $a_{1g}{}^1e_g{}^1$ configuration. The horizontal D_{3d} structure gives the reverse splitting, $E(e_g) < E(a_g)$, and hence an $e_g{}^2$ configuration, from which a ${}^3A_{2u}$ ground state would be derived. The latter splitting thus conforms with the requirements of the Jahn–Teller theorem and also gives twice the stabilization energy (in the center-of-gravity rule approximation of crystal field theory) given by the former. Thus, the observed horizontal D_{3d} structure is the one that would be "predicted" by consideration of metal–oxygen π bonding and the Jahn–Teller theorem. Of course, this does not prove that the electronic factor is necessarily the one that determines this structure.

By similar arguments we would conclude that for a d^1 ion the vertical D_{3d} structure is preferred while for a d^3 ion there would be no preference among the three structures shown in Figure 1 or any intermediate ones. Thus, similar compounds containing the Cr^{3+} ion might adopt whatever structure is most favored by hydrogen bonding, and might thus provide a test of the importance of hydrogen bonding. On the other hand, compounds of the Ti^{3+} ion should show a tendency to have this ion in the vertical D_{3d} structure if the electronic effects are dominant. However, the attainment of optimal hydroge bonding might overwhelm the electronic tendency and dictate some other result. Further studies of structures containing $[Ti(H_2O)_6]^{3+}$, $[V(H_2O)_6]^{3+}$, and $[Cr(H_2O)_6]^{3+}$ ions by low-temperature neutron diffraction would thus be of interest and will be undertaken if suitable crystals can be grown.

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Registry No. $[V_3(\mu_3\text{-}O)(CH_3CO_2)_6(CH_3CO_2H)_2(C_4H_8O)][VCl_4(CCh_3CO_2H)_2]$, 82188-50-9; $[V(H_2O)_6][H_5O_2](CF_3SO_3)_4$ complex, 91238-34-5; $4CF_3SO_3H\cdot V\cdot 8H_2O$, 91230-59-0.

Supplementary Material Available: Tables of X-ray positional parameters, anisotropic thermal parameters, and structure factors for both the X-ray and neutron diffraction studies (30 pages). Ordering information is given on any current masthead page.

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[13] Friedman and Lewis[3] have addressed this question in a formal way defining an angle θ_+ as follows: $\theta_+ = 360° - \angle MOH' - \angle MOH'' - H'OH'$ where $\theta_+ = 0°$ for ideally trigonal water and $\theta_+ = 31.5°$ for ideally tetrahedral (pyramidal) water. In the $[V(H_2O)_6]^{3+}$ cation in this structure, the three independent water molecules have an almost perfect trigonal orientation, with θ_+ values of 1.3°, 2.3°, and 0.3°.

[14] Olovsson, I.; Jonsson, P.-G., ref 8, pp 393–456.

[15] Joswig, W.; Fuess, H.; Ferraris, G. *Acta Crystallogr., Sect. B* **1982**, *B38*, 2798–2801.

[16] These orbital splittings can be deduced by qualitative arguments, but they have also been confirmed by calculations using the Fenske–Hall method.