Neutron and X-ray Structural Characterization of the Hexaaquavanadium(II) Compound VSO₄·7H₂O

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The title compound, for which crystals are more reactive toward oxygen than the chemically similar compound VSO₄·6H₂O, has been prepared as large single crystals and characterized by both X-ray diffraction at room temperature and neutron diffraction at 11−16 K. VSO₄·7H₂O crystallizes in the monoclinic space group $P2_1/c$, $Z = 4$, with the following cell dimensions, where in each case the room temperature X-ray value is given first followed by the 11−16 K neutron value: $a = 14.130(3), 14.013(2)$ Å; $b = 6.501(1), 6.481(1)$ Å; $c = 11.017(2), 10.981(2)$ Å; $\beta = 105.64(2), 105.39(1)°$; $V = 974.5(3), 961.5(3)$ Å³. The structure was refined to residuals of $R = 0.0289$ and 0.0766 and quality of fit $= 1.047$ and 1.427 for X-ray and neutron data, respectively. It consists of two independent centrosymmetric $V(H_2O)_6^{2+}$ ions connected to a sulfate ion and an interstitial water molecule by an extensive network of hydrogen bonds. The room temperature and low-temperature structures are qualitatively identical. Each hydrogen atom is involved in a hydrogen bond. The network of hydrogen bonds is implicated in the stability of VSO₄·7H₂O in the solid state in dry surroundings.

Introduction

Until recently, the chemistry of vanadium(II) showed a very slow growth. Fortunately, a systematic study of its reactions and the factors that affect the stability of its compounds have finally given us enough information to understand the pathways necessary to obtain a variety of compounds ranging from mononuclear to dinuclear species.[2]

In our early studies, we found that one of the major barriers to the advance of this chemistry was the lack of easy-to-prepare, thermodynamically stable starting materials that are both reactive toward substitution and easy to handle without complex manipulations.[3] One of the compounds that was found to be very useful in the preparation of other vanadium(II) compounds is $[V(H_2O)_6]SO_4$.[4] It has been used to synthesize a variety of relatively air-stable vanadium(II) compounds, many of which contain vanadium(II)-to-water bonds, such as [V(saccharinate)₂-(H₂O)₄]·2H₂O[3a] and [V(picolinate)₂(H₂O)₂]·2H₂O.[2a] The high stability toward air in this type of compound has been associated with the presence of extended arrays of hydrogen bonds.

In most instances, the anhydrous materials can be easily prepared by azeotropic distillation of the water molecules using pyridine.[2a,3a] More recently, we have used [V(H₂O)₆]SO₄ for the preparation of anhydrous materials even from aqueous solutions. Examples of the later compounds are V(bpy)₂SO₄ and [V(en)₃]SO₄.[5]

In our studies, we also found that when crystals of [V(H₂O)₆]-SO₄ were recrystallized using an aqueous solution with a less acidic pH, the crystals that were obtained were more sensitive to reaction toward oxygen, particularly when the atmospheric humidity was high. We therefore decided to study this type of crystal in more detail. It was then found that the crystals obtained under these conditions were in fact those of the heptahydrate.

Another part of the motivation for this study was our interest in the structural features of the hexaaquadipositive ions of the first transition series.[6] Only a handful of hexaaquavanadium(II) compounds have been structurally characterized, namely $[V(H_2O)_6]SO_4$,[4] $[V(H_2O)_6]SiF_6$,[6] $[V(H_2O)_6](CF_3SO_3)_3$,[7] the deuterated and protic ammonium Tutton salts,[6,8] and a solid solution of $[(V_{1-x}Ni_x)(H_2O)_6]SO_4$.[9]

More recently, a number of studies have appeared in which theoretical calculations have been used to compare the binding energies in species of the type $M(H_2O)_6^{2+}$.[10] These have been augmented by spin and charge density determinations for species of the first transition series[11] and for vanadium(II) species in particular.[12]

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We also decided to undertake this study of [V(H$_2$O)$_6$]SO$_4$·H$_2$O (*vide infra*) because it would afford a structural comparison of the V(H$_2$O)$_6$ entity with that of a previously studied vanadium-(III) compound, namely [V(H$_2$O)$_6$][H$_5$O$_2$](CF$_3$SO$_3$)$_4$.[13]

Experimental Section

All manipulations were carried out under nitrogen using standard Schlenk techniques. The solvents were deoxygenated by prolonged reflux under a nitrogen atmosphere and were freshly distilled under nitrogen prior to use. [V(H$_2$O)$_6$]SO$_4$ was prepared as described before.[4,14]

[V(H$_2$O)$_6$]SO$_4$·H$_2$O. [V(H$_2$O)$_6$]SO$_4$ (1.85 g, 7.25 mmol) was dissolved in a solution prepared by mixing 0.10 mL of concentrated H$_2$-SO$_4$ in 17.5 mL of water. To the violet solution was added a layer of 15 mL of ethanol, and then it was cooled to 0 °C. After several days, very large violet single crystals were separated by filtration and washed with small amounts of a 70–30% mixture of ethanol–water. For drying, the crystals were briefly held under vacuum (1.50 g, 76% yield). The homogeneity of the crystalline sample was established by unit cell determinations from many crystals.

Crystallographic Studies

X-ray Structure Determination. A small block-shaped crystal (0.35 × 0.35 × 0.33 mm), which had been cut from a larger sample, was mounted at the end of a glass fiber and covered with a thin layer of epoxy. The unit cell parameters and orientation matrix were established by routine procedures. Data were collected on the +h,+k,±l quadrants. The R_{int} was 0.0321. During the course of intensity data collection—a time lapse of less than 1 day—the intensities of three monitor reflections decreased to about two-thirds each of their original values. By the end of the data collection, a noticeable portion of the crystal had changed from its original color, purple, to a light pale green. We suspect that the observed decomposition was a result of interaction between the crystal and the epoxy, since unmounted crystals from the same batch did not show signs of decomposition at the time of the end of data collection—and for that matter, for some time thereafter.

The data were processed by routine procedures.[16] The two independent vanadium atoms were placed at their expected positions, and the remainder of the structure was developed and refined in the usual cycle of least-squares refinements and difference Fourier maps.[17] All of the unique intensity data, in the form of F_o^2, were used in the refinement. The hydrogen atoms were located in a difference map and were refined independently, each with its own isotropic displacement parameter. The refinement converged with the residuals given in Table 1.

Neutron Structure Determination. Neutron diffraction data were gathered at the Intense Pulsed Neutron Source at Argonne National Laboratory, on the time-of-flight single-crystal diffractometer. Details of the experimental arrangement were identical to those given in the accompanying paper on (NH$_4$)$_2$[Cr$_{0.10}$Zn$_{0.90}$(H$_2$O)$_6$](SO$_4$)$_2$.[18] Parameters specific to this structure determination are summarized in Table 1. After an initial determination of the cell and orientation matrix[19] from the data in one histogram, 25 three-dimensional histograms were accumulated, covering a quadrant of reciprocal space. The intensities of the diffraction maxima were derived by a procedure that optimizes the value of $I/\sigma(I)$ using a variable ellipsoidal model.[20]

The initial structural model consisted of the independent vanadium and oxygen atoms, which were placed at positions reported previously

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Table 1. Crystal Data for VSO$_4$·7H$_2$O

	X-ray	neutron
formula	VSO$_{11}$H$_{14}$	
fw	273.11	
space group	P2$_1$/c	
a, Å	14.130(3)	14.013(2)
b, Å	6.501(1)	6.481(1)
c, Å	11.017(2)	10.981(2)
β, deg	105.64(2)	106.39(1)
V, Å^3	974.5(3)	961.5(3)
Z	4	
d_{calcd}, g/cm^3	1.861	1.886
T, K	298(2)	11–16
μ (Mo Kα), cm^{-1}	12.7	
λ, Å	0.710 73	
λ range, Å		0.7–4.2
data collcn technique		time-of-flight Laue^a
μ(incoherent + coherent), cm^{-1}		1.428
μ(abs, 1.8 Å), cm^{-1}		2.037
transm factors: max, min	0.94–0.92	
R^b	0.0289 (1460 data with $I > 2\sigma(I)$)	0.0755
wR2^c	0.0798	
$R_w{}^d$		0.0766
weighting function	w^e	w^f

^{a} Using 30 × 30 cm^2 position-sensitive detector. ^{b} $R = \sum||F_o| - |F_c||/\sum|F_o|$. ^{c} wR2 = $[\sum w(F_o^2 - F_c^2)^2/\sum w(F_o^2)^2]^{1/2}$. ^{d} $R_w = [\sum w(F_o - F_c)^2/\sum w F_o^2]^{1/2}$. ^{e} $[\sigma^2(F_o^2)^2 + 0.0507(\max(F_o^2, 0) + 2F_c^2)/3 + 0.24(\max(F_o^2, 0) + 2F_c^2)3]^{-1}$. ^{f} $4F_o^2/(\sigma^2(F_o^2) + (0.04F_o^2)^2 + 3000)$
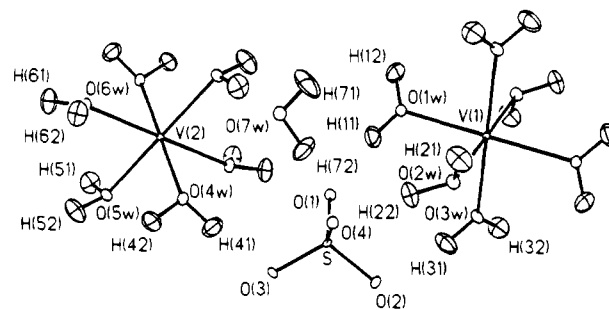
Figure 1. Thermal ellipsoid plot of the neutron crystal structure of VSO$_4$·7H$_2$O, showing the atom naming scheme. Atoms V(1) and V(2) sit on crystallographic inversion centers. Non-vanadium atoms are represented by their 50% probability ellipsoids.

for an X-ray structure determination of FeSO$_4$·7H$_2$O.[15] Isotropic refinement was followed by a difference Fourier map, in which all of the independent hydrogen atoms were located. The structure was then refined routinely. For the final refinement, all of the oxygen and hydrogen atoms had anisotropic displacement parameters. The two independent vanadium atoms—barely visible under neutron diffraction due to the vanadium scattering length of nearly zero—were assigned fixed isotropic displacement parameters (U) of 0.003 Å^2. The final residuals are summarized in Table 1. Positional and displacement parameters are given in Table 2. Selected bond distances and bond angles are given in Table 3. The hydrogen bonding interactions are given in Table 4.

Results and Discussion

The structure of VSO$_4$·7H$_2$O is shown in Figure 1, which also indicates the labeling scheme. The general features of this structure are similar to that of the iron analog.[15] There are two independent V(H$_2$O)$_6^{2+}$ ions for which the vanadium center is octahedral, with deviations from regularity. In both cases, the vanadium atoms are located on crystallographic inversion centers at (0, 0, 0) and ($^1/_2$, $^1/_2$, 0), respectively. The sulfate ion as well as the interstitial water molecule serve as bridges between the hexaaquavanadium(II) species through a network of hydrogen bonds; this network extends in three directions, with no single direction or plane predominating. Figure 2, a *y*-axis

Table 2. Atomic Positional and Equivalent Isotropic Displacement Parameters from the X-ray (Roman Type) and Neutron (Italic Type) Structures of VSO₄·7H₂O

| atom	x	y	z	U_{eq},[a] Å²
V(1)	0.0000	0.0000	0.0000	0.003
V(1)	*0.0000*	*0.0000*	*0.0000*	*0.0022(1)*
V(2)	0.5000	0.5000	0.0000	0.003
V(2)	*0.5000*	*0.5000*	*0.0000*	*0.0021(1)*
S	0.2255(3)	0.4740(9)	0.1729(4)	0.004(1)
S	*0.2267(1)*	*0.4755(1)*	*0.1751(1)*	*0.0021(1)*
O(1)	0.2036(2)	0.4746(5)	0.0331(2)	0.007(1)
O(1)	*0.2054(1)*	*0.4762(2)*	*0.0361(2)*	*0.0030(1)*
O(2)	0.1348(2)	0.5387(5)	0.2089(2)	0.007(1)
O(2)	*0.1380(1)*	*0.5413(3)*	*0.2109(2)*	*0.0033(1)*
O(3)	0.3061(2)	0.6197(4)	0.2251(2)	0.007(1)
O(3)	*0.3079(1)*	*0.6181(3)*	*0.2267(2)*	*0.0034(1)*
O(4)	0.2534(2)	0.2640(5)	0.2228(2)	0.007(1)
O(4)	*0.2538(1)*	*0.2670(3)*	*0.2237(2)*	*0.0033(1)*
O(1w)	0.1237(2)	0.0995(5)	−0.0605(2)	0.008(1)
O(1w)	*0.1122(2)*	*0.1216(4)*	*−0.0709(2)*	*0.0054(1)*
O(2w)	0.0974(2)	−0.0405(5)	0.1860(2)	0.008(1)
O(2w)	*0.1014(2)*	*−0.0395(3)*	*0.1810(2)*	*0.0037(1)*
O(3w)	−0.0280(2)	0.2981(5)	0.0672(2)	0.009(1)
O(3w)	*−0.0300(2)*	*0.2929(3)*	*0.0695(2)*	*0.0035(1)*
O(4w)	0.4774(2)	0.4502(5)	0.1815(2)	0.008(1)
O(4w)	*0.4785(2)*	*0.4555(3)*	*0.1812(2)*	*0.0033(1)*
O(5w)	0.5717(2)	0.7867(5)	0.0634(2)	0.009(1)
O(5w)	*0.5693(2)*	*0.7878(3)*	*0.0589(2)*	*0.0035(1)*
O(6w)	0.6447(2)	0.3551(5)	0.0569(2)	0.008(1)
O(6w)	*0.6436(1)*	*0.3630(3)*	*0.0597(2)*	*0.0035(1)*
O(7w)	0.3653(2)	0.0058(5)	0.1158(2)	0.009(1)
O(7w)	*0.3624(2)*	*0.0045(3)*	*0.1167(2)*	*0.0036(1)*
H(11)	0.1542(5)	0.2373(11)	−0.0404(6)	0.024(2)
H(11)	*0.1418(28)*	*0.2287(64)*	*−0.0510(35)*	*0.0070(12)*
H(12)	0.1284(4)	0.0595(13)	−0.1438(5)	0.024(2)
H(12)	*0.1216(23)*	*0.0782(52)*	*−0.1291(32)*	*0.0045(9)*
H(21)	0.1171(5)	−0.1847(11)	0.2063(6)	0.025(2)
H(21)	*0.1200(24)*	*−0.1510(53)*	*0.2046(29)*	*0.0048(9)*
H(22)	0.1565(4)	0.0482(12)	0.2052(5)	0.024(2)
H(22)	*0.1458(25)*	*0.0359(51)*	*0.2017(31)*	*0.0046(10)*
H(31)	0.0206(5)	0.3873(13)	0.1209(6)	0.027(2)
H(31)	*0.0102(30)*	*0.3827(63)*	*0.1163(40)*	*0.0085(13)*
H(32)	−0.0884(4)	0.3765(12)	0.0359(6)	0.024(2)
H(32)	*−0.0789(25)*	*0.3646(49)*	*0.0436(30)*	*0.0049(9)*
H(41)	0.4208(4)	0.5167(12)	0.2002(5)	0.024(2)
H(41)	*0.4307(29)*	*0.5037(50)*	*0.1919(36)*	*0.0054(11)*
H(42)	0.5323(4)	0.4667(12)	0.2576(5)	0.022(1)
H(42)	*0.5229(29)*	*0.4579(54)*	*0.2363(38)*	*0.0055(12)*
H(51)	0.5921(5)	0.8691(12)	0.0000(5)	0.024(2)
H(51)	*0.5872(25)*	*0.8469(53)*	*0.0091(32)*	*0.0054(10)*
H(52)	0.6292(5)	0.7827(13)	0.1358(6)	0.027(2)
H(52)	*0.6167(32)*	*0.7867(61)*	*0.1231(40)*	*0.0080(13)*
H(61)	0.7011(4)	0.4228(12)	0.0386(6)	0.024(2)
H(61)	*0.6947(26)*	*0.4236(53)*	*0.0389(31)*	*0.0055(9)*
H(62)	0.6668(4)	0.2703(11)	0.1334(5)	0.022(1)
H(62)	*0.6594(22)*	*0.2960(50)*	*0.1157(29)*	*0.0041(9)*
H(71)	0.3368(6)	−0.1275(12)	0.0929(8)	0.035(2)
H(71)	*0.3390(26)*	*−0.0999(61)*	*0.0986(33)*	*0.0060(12)*
H(72)	0.3171(5)	0.0909(13)	0.1432(7)	0.028(2)
H(72)	*0.3261(29)*	*0.0821(65)*	*0.1385(38)*	*0.0074(13)*

[a] The equivalent isotropic displacement parameter U_{eq} is calculated as: $U_{eq} \sum U_{ij} a_i \cdot a_j a^*_i a^*_j$. $i, j = 1, 3$.

Table 3. Selected Bond Distances (Å) and Bond Angles (deg) from the X-ray (Roman Type) and Neutron (Italic Type) Structures of VSO₄·7H₂O[a]

V(1)−O(1w)	2.102(2)	V(2)−O(6w)	2.151(2)
	2.115(2)		*2.170(3)*
V(1)−O(2w)	2.134(2)	S−O(1)	1.479(2)
	2.150(2)		*1.483(4)*
V(1)−O(3w)	2.137(2)	S−O(2)	1.475(2)
	2.141(3)		*1.488(4)*
V(2)−O(4w)	2.118(2)	S−O(3)	1.466(2)
	2.125(2)		*1.467(6)*
V(2)−O(5w)	2.130(2)	S−O(4)	1.469(2)
	2.139(3)		*1.481(6)*
O(1w)−V(1)−O(2w)	90.51(9)	O(2)−S−O(1)	108.97(10)
	91.77(10)		*108.5(3)*
O(1w)−V(1)−O(3w)	92.31(9)	O(3)−S−O(1)	108.62(10)
	94.22(10)		*109.2(3)*
O(2w)−V(1)−O(3w)	85.43(8)	O(4)−S−O(1)	109.91(10)
	84.89(11)		*110.3(3)*
O(4w)−V(2)−O(5w)	90.24(8)	O(3)−S−O(2)	110.23(11)
	90.05(10)		*109.8(3)*
O(4w)−V(2)−O(6w)	91.06(9)	O(4)−S−O(2)	109.05(5)
	91.44(9)		*108.7(3)*
O(5w)−V(2)−O(6w)	87.25(8)	O(3)−S−O(4)	110.04(10)
	87.71(11)		*110.3(3)*

[a] Numbers in parentheses are estimated standard deviations in the least significant digits.
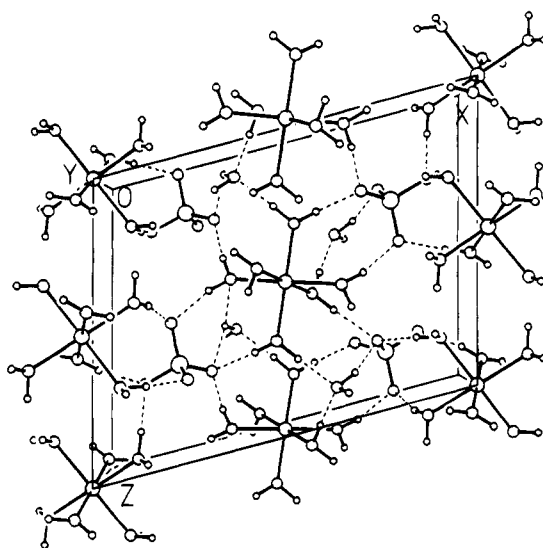
Figure 2. Drawing of the extended structure of VSO₄·7H₂O, as viewed along [010]. Data for this drawing were taken from the neutron structure determination.

projection of the extended structure, shows the rich pattern of hydrogen bonding. As Table 4 shows, every hydrogen atom in the structure in involved in a hydrogen bond. Atom H(71) of the interstitial water molecule serves as donor atom in a bifurcated hydrogen bond. Each oxygen atom of the sulfate group is an acceptor in three different H-bonding interactions. The oxygen atom, O(7w), of the interstitial water molecule, serves as acceptor in two hydrogen bonds, while only one of the oxygen atoms of V(H₂O)₆²⁺, namely O(6w), is involved as an acceptor. The hydrogen bonding pattern clearly is a stabilizing factor for the crystalline material. In Tables 3 and

4 the results obtained by X-ray and neutron diffraction are compared. The agreement is very good, even though direct comparisons cannot be made since the temperatures used for the two determinations were quite different, namely 11−16 K for the neutron *vs* 293 K for the X-ray analysis. It is important to note that, as Table 4 shows, the hydrogen bonding network is qualitatively identical at the two temperatures; in other words, the two structures are rigorously isotypic. This behavior cannot be taken for granted, and indeed in the Tutton-salt solid solutions described in the following paper we see a minor rearrangement of hydrogen bonds upon changing from room temperature to approximately 15 K. In the present structure, the vanadium-to-oxygen distances are 0.01−0.02 Å longer for the neutron data, which is probably due to the presence of less libration in the crystal at lower temperatures. The same is also true for the oxygen-to-oxygen distances shown in Table 4, for which hydrogen bonding is important. As expected, the oxygen-to-hydrogen distances are also 0.06−0.24 Å longer for the neutron

Table 4. Hydrogen Bonding Interactions from the X-ray (Roman Type) and Neutron (Italic Type) Structures of $VSO_4 \cdot 7H_2O^a$

donor−H···acceptor	D···A, Å	D−H, Å	H···A, Å	D−H···A, deg	acceptor coords
O(1w)−H(11)···O(1)	2.757(3)	0.81(4)	1.96(4)	166(4)	x, y, z
	2.758(4)	*0.990(7)*	*1.788(7)*	*165.7(6)*	
O(1w)−H(12)···O(2)	2.739(3)	0.74(4)	2.00(4)	177(3)	$x, {}^1/_2 - y, -{}^1/_2 + z$
	2.729(3)	*0.970(5)*	*1.762(6)*	*174.3(7)*	
O(2w)−H(21)···O(2)	2.777(3)	0.79(3)	2.02(3)	162(3)	$x, -1 + y, z$
	2.776(4)	*0.984(8)*	*1.809(7)*	*167.1(6)*	
O(2w)−H(22)···O(4)	2.877(3)	0.78(3)	2.11(3)	169(3)	x, y, z
	2.893(4)	*0.984(7)*	*1.923(7)*	*168.0(7)*	
O(3w)−H(31)···O(2)	2.945(3)	0.88(4)	2.10(4)	162(4)	x, y, z
	2.859(4)	*0.966(8)*	*1.907(7)*	*168.1(6)*	
O(3w)−H(32)···O(1)	2.863(3)	0.82(3)	2.05(4)	174(3)	$-x, 1-y, -z$
	2.828(4)	*0.968(7)*	*1.861(7)*	*176.9(6)*	
O(4w)−H(41)···O(3)	2.798(3)	0.78(4)	2.02(4)	177(4)	x, y, z
	2.793(3)	*0.971(6)*	*1.826(6)*	*173.8(7)*	
O(4w)−H(42)···O(7w)	2.723(3)	0.75(4)	1.98(4)	172(4)	$1 - x, {}^1/_2 + y, {}^1/_2 - z$
	2.709(4)	*0.980(6)*	*1.732(6)*	*175.3(5)*	
O(5w)−H(51)···O(7w)	2.739(3)	0.77(4)	1.97(4)	178(4)	$1 - x, 1 - y, -z$
	2.716(3)	*0.979(6)*	*1.741(6)*	*174.3(7)*	
O(5w)−H(52)···O(4)	2.963(3)	0.83(5)	2.13(5)	174(4)	$1 - x, {}^1/_2 + y, {}^1/_2 - z$
	2.914(4)	*0.971(7)*	*1.944(7)*	*177.4(8)*	
O(6w)−H(61)···O(1)	2.823(3)	0.91(4)	1.93(4)	169(3)	$1 - x, 1 - y, -z$
	2.799(3)	*0.970(6)*	*1.846(5)*	*166.6(6)*	
O(6w)−H(62)···O(3)	2.770(3)	0.74(3)	2.03(3)	175(3)	$1 - x, -{}^1/_2 + y, {}^1/_2 - z$
	2.768(4)	*0.983(6)*	*1.789(6)*	*173.7(5)*	
O(7w)−H(71)···O(3)	2.979(3)	0.76(4)	2.43(4)	131(3)	$x, -1 + y, z$
	2.986(4)	*0.957(8)*	*2.304(9)*	*127.7(7)*	
···O(6w)	3.067(3)		2.50(4)	133(3)	$1 - x, -y, -z$
	2.991(4)		*2.274(9)*	*131.0(7)*	
O(7w)−H(72)···O(4)	2.763(3)	0.80(4)	1.97(4)	169(4)	x, y, z
	2.761(4)	*0.980(6)*	*1.799(7)*	*166.6(7)*	

^{a} Numbers in parentheses are estimated standard deviations in the least significant digits.

determination. It is noteworthy, however, that the dispositions of the hydrogen atoms with respect to their parent oxygen atoms—as seen in the bond angles—are quite similar in the two determinations. This accords well with the generally accepted notion that X-ray diffraction shows the electron density of a hydrogen atom at a mean position displaced toward the parent atom.

Table 5 lists all structurally characterized vanadium(II) compounds with vanadium-to-water bonds. The range of V−O distances is rather small. If only room temperature determinations are used, they range from 2.102 to 2.151 Å, a difference of only 0.05 Å, which is smaller than those found in other M(II)−water compounds of the first transition series.[6] We do not know yet if the constancy of the vanadium-to-oxygen distance is intrinsic to this type of bond or if this is only observed here because of the limited number of compounds of this type that are known.

In the only two neutron crystal structure determinations containing vanadium(II)-to-water bonds, for the $V(H_2O)_6{}^{2+}$ species in $VSO_4 \cdot 7H_2O$ and $(ND_4)_2[V(H_2O)_6](SO_4)_2$, the V−O distances vary from 2.111 to 2.170 Å. These are much longer than the vanadium-to-oxygen bond lengths of 1.993, 1.988, and 2.003 Å found in the $V(H_2O)_6{}^{3+}$-containing compound $[V(H_2O)_6][H_5O_2](CF_3SO_3)_4$ which is in accord with the difference in the oxidation state of the vanadium center.

A comparison of chemical behavior of $VSO_4 \cdot 6H_2O$ and $VSO_4 \cdot 7H_2O$ is important. We have found that the former is easily handled in the atmosphere when the crystals are dried. However, under similar conditions the latter is more reactive. The decomposition is much faster if the atmospheric humidity is high. From a comparison of the structural data it is not immediately clear to us why this behavior is so different, although as noted above the interstitial water molecule in the heptahydrate plays an important role in the stabilization of the crystalline material by hydrogen bonding. A wet environment may offer other stable arrangements for the interstitial water

Table 5. Vanadium(II)−Water Distances in Compounds of the Type $V(H_2O)_nL_m$

compound	distances, Å		temp,^{e}	ref
	I	II		
$[V(H_2O)_6]SO_4 \cdot H_2O^{a,b}$			11	this work
	2.115(2)	2.125(2)		
	2.150(2)	2.139(3)		
	2.141(2)	2.170(3)		
			RT	this work
	2.102(2)	2.118(2)		
	2.134(2)	2.130(2)		
	2.137(2)	2.151(2)		
$[V(H_2O)_6]SO_4{}^a$			RT	4
	2.131(2)	2.150(2)		
	2.123(2)	2.120(2)		
	2.136(2)	2.124(2)		
$[V(H_2O)_6]SiF_6$	2.1214(7)		213	6
	2.123(2)		RT	
$(ND_4)_2[V(H_2O)_6](SO_4)_2{}^b$	2.130(5)		5.8	8a
	2.111(7)			
	2.114(6)			
$(NH_4)_2[V(H_2O)_6](SO_4)_2$	2.133(1)		RT	6
	2.136(1)			
	2.116(1)			
$[V(H_2O)_6](CF_3SO_3)_2$	2.120(3)		RT	7
	2.118(2)			
$[V(Sac)_2(H_2O)_4] \cdot 2H_2O^c$	2.120(2)		278	4
	2.124(2)			
$[V(Pic)_2(H_2O)_2] \cdot 2H_2O^d$	2.134(1)		RT	2a

^{a} There are two independent molecules in the crystal. ^{b} Neutron structure. ^{c} Sac = saccharinate. ^{d} Pic = picolinate. ^{e} RT = room temperature.

molecule, to the detriment of the crystal. It remains true, though, that in both cases, hydrogen-bonding networks exist which in general tend to impede the reaction with oxygen of the crystalline forms of this type of compound.[2a,4] From a synthetic point of view, it is easier to handle and store $[V(H_2O)_6]SO_4$ samples, and consequently, care should be taken to crystallize

the product from solutions in which the acid concentration is higher.[4] This dependence of the type of product formed from aqueous–acidic solutions is relatively well known. A recent example of this was provided by the study of MSiF$_6$, M = Cr and Cu, in aqueous hexafluorosilic acid.[21]

Supplementary Material Available: Tables of crystallographic data, complete bond distances and bond angles, anisotropic displacement parameters, and ΔMSDA (5 pages). Ordering information is given on any current masthead page.

(21) Cotton, F. A.; Daniels, L. M.; Murillo, C. A. *Inorg. Chem.* **1993**, *32*, 4868.