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A Coordination Chemistry Study of Hydrated and Solvated Cationic Vanadium Ions in Oxidation States +III, +IV, and +V in Solution and Solid State

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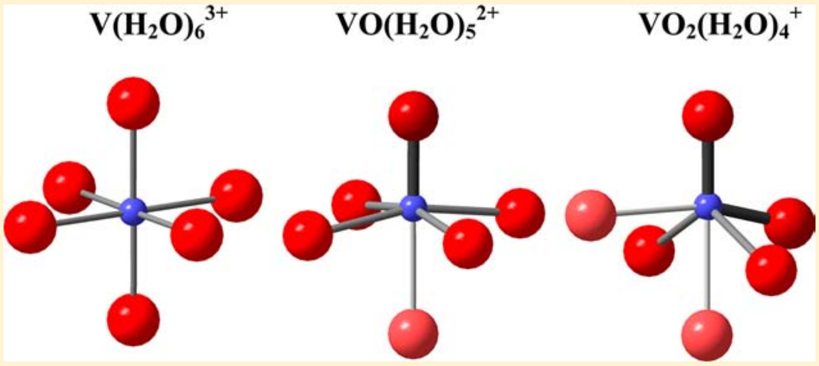
Supporting Information



ABSTRACT: The coordination chemistry of hydrated and solvated vanadium(III), oxovanadium(IV), and dioxovanadium(V) ions in the oxygen-donor solvents water, dimethyl sulfoxide (DMSO), and *N*,*N*′-dimethylpropyleneurea (DMPU) has been studied in solution by extended X-ray absorption fine structure (EXAFS) and large-angle X-ray scattering (LAXS) and in the solid state by single-crystal X-ray diffraction and EXAFS. The hydrated vanadium(III) ion has a regular octahedral configuration with a mean V−O bond distance of 1.99 Å. In the hydrated and DMSO-solvated oxovanadium(IV) ions, vanadium binds strongly to an oxo group at ca. 1.6 Å. The solvent molecule trans to the oxo group is very weakly bound, at ca. 2.2 Å, while the remaining four solvent molecules, with a mean V−O bond distance of 2.0 Å, form a plane slightly below the vanadium atom; the mean $O{=}V{-}O_{perp}$ bond angle is ca. 98°. In the DMPU-solvated oxovanadium(IV) ion, the space-demanding properties of the DMPU molecule leave no solvent molecule in the trans position to the oxo group, which reduces the coordination number to 5. The $O{=}V{-}O$ bond angle is consequently much larger, 107°, and the mean V═O and V−O bond distances decrease to 1.58 and 1.97 Å, respectively. The hydrated and DMSO-solvated dioxovanadium(V) ions display a very distorted octahedral configuration with the oxo groups in the cis position with a mean V═O bond distance of 1.6 Å and a $O{=}V{=}O$ bond angle of ca. 105°. The solvent molecules trans to the oxo groups are weakly bound, at ca. 2.2 Å, while the remaining two have bond distances of 2.02 Å. The experimental studies of the coordination chemistry of hydrated and solvated vanadium(III,IV,V) ions are complemented by summarizing previously reported crystal structures to yield a comprehensive description of the coordination chemistry of vanadium with oxygen-donor ligands.

■ INTRODUCTION

Vanadium plays a number of roles in biological systems, especially in marine environments. It is, e.g., present in haloperoxidases as vanadium(V),[1−5] as vanadium(III) or vanadium(IV) complexes in tunicate blood cells,[6,7] and also as amavadine, a vanadium(IV) complex produced by the mushroom genus *Amanita*.[8−10] Some species in the family *Ascidiidae* accumulate vanadium at concentrations in excess of 350 mmol dm^{-3}, corresponding to about 10^{7} times that found in seawater,[11] and the transport function of vanadium into ascidians has been recently described.[12] The role of vanadium in biological systems is both structural, seen by the maintenance of various biological structures, and functional, there by bringing key reactivity to active centers of proteins, enzymes, and coenzymes.[7] Vanadium(IV) salts have been utilized in the treatment of diabetes for some time, and the insulin-mimetic behavior of vanadium(IV,V) coordination compounds has been studied extensively.[13−19] Vanadium toxicity is often associated with the production of reactive oxygen species, causing lipid peroxidation and an alteration in the enzymatic antioxidant defense.[20] The coordination chemistry and role of vanadium in biological systems have been reviewed in many publications and books.[1,5−10,21−23] Vanadium compounds have received increased attention as catalysts in a number of applications as recently reviewed.[24]

Vanadium(III) has well-defined coordination chemistry retaining octahedral complexes in most systems, while the coordination chemistry of vanadium(IV) and vanadium(V) is much more

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Table 1. Concentrations of All Ions and, Wherever Appropriate, a Solvent Medium in mol dm^{-3} of the Vanadium Solutions Studied by LAXS (L) and EXAFS (E), Including Their Densities ρ, Linear Absorption Coefficients μ, and pH[a]

sample	$[V_{tot}]$	$[Cl^-]$	$[ClO_4^-]$	$[CF_3SO_3^-]$	$[SO_4^{2-}]$	[solvent]	ρ/g cm^{-3}	μ/cm^{-1}	pH	note
V^{3+} in water	0.50	1.50	0.10			xs			0.60	E, **L0**
V^{3+} in water	0.50	1.50	0.10			xs			1.22	E, **L0**$_{hyd}$
VO^{2+} in water	1.228		2.556			53.228	1.273	4.123	0.53	L, **L1a**
VO^{2+} in water	4.433		8.866			11.512	1.386	10.880	0.4	L, **L1b**
VO^{2+} in water	0.70		1.40			xs			0.5	E, **L1c**
VO^{2+} in DMSO	0.369		0.738			13.282	1.136	5.460		L, **L2a**
VO^{2+} in DMSO	0.18		0.36			xs				E, **L2b**
VO^{2+} in DMPU	0.18		0.36			xs				E, **L3**
VO_2^+ in water	1.833				7.237	32.953	1.449	6.181	<0	L, **L4a**
VO_2^+ in water	0.87				3.435	xs			<0	E, **L4b**
VO_2^+ in DMSO	1.374		3.822			11.693	1.401	7.503		L, **L5a**
VO_2^+ in DMSO	0.50		0.50			xs				E, **L5b**
VO_2^+ in DMPU	0.20		0.20			xs				E, **L6**

[a] The label xs denotes excess solvent.

Table 2. Crystallographic Data and Structure Refinement Details for Vanadium Compounds 1, 2a, 3, and 5

	1	2a	3	5
structure formula	$[VO(H_2O)_5](CF_3SO_3)_2$	$[VO(DMSO)_5](ClO_4)_2$	$[VO(DMPU)_4](CF_3SO_3)_2$	$[VO_2(DMSO)_4]CF_3SO_3$
sum formula	$C_2H_{10}F_6O_{12}S_2V$	$C_{10}H_{30}Cl_2O_{14}S_5V$	$C_{26}H_{48}F_6N_8O_{11}S_2V$	$C_9H_{24}F_3O_9S_5V$
M_w	455.16	656.48	877.80	544.55
diffractometer system	Bruker SMART CCD	Bruker SMART CCD	Bruker SMART CCD	Bruker SMART CCD
radiation, λ/Å	0.71073	0.71073	0.71073	0.71073
cryst syst	monoclinic	monoclinic	monoclinic	monoclinic
space group	$P2_1/m$ (No. 11)	$P2_1/c$ (No. 14)	$P2_1/c$ (No. 14)	$P2_1/c$ (No. 14)
a/Å	9.7598(11)	11.0482(15)	16.590(4)	13.756(3)
b/Å	7.8650(9)	10.8796(15)	27.137(6)	6.4360(13)
c/Å	10.2154(11)	24.928(3)	18.215(4)	24.660(5)
α/deg	90	90	90	90
β/deg	102.555(2)	109.297(5)	98.667(5)	92.291(4)
γ/deg	90	90	90	90
V/Å^3	765.39(15)	2828.0(7)	8107(3)	2181.5(7)
Z	2	4	8	4
T/K	295(2)	295(2)	295(2)	295(2)
D_c/g cm^{-1}	1.975	1.542	1.438	1.658
F^2	454	1356	3656	1120
μ/mm^{-1}	1.043	0.962	0.436	0.993
cryst size/mm^3	0.50 × 0.40 × 0.30	0.60 × 0.30 × 0.14	0.55 × 0.45 × 0.40	0.40 × 0.22 × 0.20
θ range/deg	2.0−25.7	1.7−25.0	1.4−25.7	1.5−25.7
index ranges	$-8 \le h \le 11$	$-13 \le h \le 12$	$-20 \le h \le 19$	$-16 \le h \le 10$
	$-9 \le k \le 9$	$-12 \le k \le 12$	$-33 \le k \le 24$	$-7 \le k \le 7$
	$-12 \le l \le 12$	$-29 \le l \le 26$	$-22 \le l \le 21$	$-29 \le l \le 29$
measd reflns	4087	13771	42469	11340
unique reflns	1567	4950	15320	4116
obsd reflns, $I > 2\sigma(R_{int})$	1275 (0.028)	2477 (0.054)	6205 (0.077)	1717 (0.161)
data/restraints/param	1561/11/143	4950/78/337	15320/49/1012	4116/0/285
GOF	0.99	0.93	0.93	0.98
refinement method	full-matrix least squares on F^2	full-matrix least squares on F^2	full-matrix least squares on F^2	full-matrix least squares on F^2
final R1, wR2 $[I > 2\sigma(I)]$[a]	0.0392, 0.1062	0.0735, 0.2255	0.0904, 0.2948	0.0795, 0.1402
largest diff peak, hole/e Å^{-3}	−0.44, 0.49	−0.45, 0.68	−0.54, 1.72	−0.35, 0.33

[a] R values are defined as $R1 = \sum||F_o| - |F_c||/\sum|F_o|$, $wR2 = [\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]]^{0.5}$.

flexible, with several configurations and coordination numbers reported.[23]

Vanadium(V) has different speciation and coordination depending on the level of the pH in aqueous solution.[25] At low pH, vanadium(V) is present as the cationic vanadyl(V) ion, VO_2^+, while in neutral and alkaline solution, it is present as tetrahedral vanadate(V) ions, $H_nVO_4^{(3-n)-}$. The dominating vanadium(V) species in weak acidic solution, $2 \le pH \le 6$, is the decamer $[V_{10}O_{28}]^{6-}$. The acidic constants of vanadic acid, H_3VO_4, pK_{a1} = 3.5, pK_{a2} = 7.8, and pK_{a3} = 12.5, respectively,[6] resemble closely those of phosphoric acid, H_3PO_4, pK_{a1} = 2.1, pK_{a2} = 7.2, and pK_{a3} = 12.7.[26] This makes the chemical properties of orthophosphoric and orthovanadic acid systems very similar in neutral and alkaline aqueous solution, although the vanadate(V) ion is slightly larger than the phosphate ion. The mean V−O and P−O bond distances are 1.72 and 1.54 Å, respectively, and no evidence for the presence of orthovanadic acid has been put forward.[27,28] A more detailed overview of the hydrolysis and polymerization of vanadium(V) is given elsewhere.[25]

No structures of the hydrated dioxovanadium(V) ion have been reported so far in the solid state, but one five-coordinate neutral solvate[29] and a few additional five- and six-coordinate anionic hydrated and solvated complexes have been reported;[30−32] see Table S4a−e in the Supporting Information. In six-coordinate dioxovanadium(V) complexes, the bonds trans to the oxo groups are significantly longer than those in the cis position.[31,32] In the five-coordinate trigonal-bipyramidal complexes, where no true trans position exists, all three V−O bond distances are similar.[29,30]

The characteristic of the coordination chemistry of oxovanadium(IV) complexes is the strong V═O double bond.[33] The uniquely stable oxovanadium(IV) [vanadyl(IV)] ion, VO^{2+}, possibly the most stable diatomic ion known,[34] can withstand many types of redox reactions and form complexes with a large variety of ligands. Vanadium(IV) starts to hydrolyze and dimerize at pH ≈ 4; the pK_a value of the $[VO(H_2O)_5]^{2+}$ ion has been reported to be in the range 5.3−6.0.[35] At pH = 5, insoluble $\{VO(OH)_2\}_n$ starts to form,[36] which converts to water-soluble $[(VO)_2(OH)_5]^-$ and $[VO(OH)_3]^-$ complexes in strong alkaline aqueous solution.[37,38]

Nine pentaaquaoxovanadium(IV) structures have been reported in the solid state with a strong V═O bond, with mean bond distance $d_{V═O}$ = 1.586 Å. They all feature four near-perpendicularly bound water molecules, with mean $d_{V−O}$ = 2.024 Å, and a fifth water molecule in the trans position to the V═O bond more weakly bound, with mean $d_{V−O}$ = 2.189 Å, forming a distorted octahedral structure;[39] see Table S3a in the Supporting Information. Additionally, four dimethyl sulfoxide (DMSO) and urea solvates of oxovanadium(IV) display a coordination pattern very similar to that of the hydrates, with mean bond distances 1.583, 2.022, and 2.183 Å,[40] respectively; see Table S3b in the Supporting Information.

The hydrated vanadium(II) and vanadium(III) ions, with d^3 and d^2 electron configuration, respectively, have regular octahedral configurations based on the structures in the solid state and from theoretical simulations,[39−43] although this has not yet been confirmed by experimental structural studies in aqueous solution. A limited number of solid-state structures containing hexaaquavanadium(II) and hexaaquavanadium(III) ions have been reported with mean V−O bond distances of 2.130 and 1.995 Å, respectively; see Tables S1a and S2a in the Supporting Information. Similarly, the reported structures containing solvated vanadium(II) and vanadium(III) ions are also octahedral, with mean V−O bond distances similar to those in the hydrates, 2.132 and 1.982 Å, respectively; see the Tables S1b and S2b in the Supporting Information. The hydrolysis properties of vanadium(III) were recently studied, showing that vanadium(III) starts to hydrolyze already at pH ≈ 1, with maximal dominance of $[VOH]^{2+}$(aq) and $[V(OH)_2]^+$(aq) at pH = 3 and 4, respectively.[44] This shows that vanadium(III) starts to hydrolyze at somewhat lower pH than previously reported.[25]

The objective of the present work is to investigate the structures of the hydrated and solvated cationic vanadium(III), oxovanadium(IV), and dioxovanadium(V) ions in the oxygen-donor solvents water, DMSO, and *N*,*N*′-dimethylpropyleneurea (DMPU) in both solution and solid state. The structures of solid $[VO(OH_2)_5](CF_3SO_3)_2$, $[VO(DMSO)_5](ClO_4)_2$, $[VO(DMPU)_4](CF_3SO_3)_2$, and $[VO_2(DMSO)_4]CF_3SO_3$ have been determined by single-crystal X-ray diffraction and extended X-ray absorption fine structure (EXAFS) at room temperature, with some additional information on solid dioxovanadium(V) perchlorate, VO_2ClO_4, obtained through powder diffraction. The structures of the hydrated and hydrolyzed vanadium(III) ions in aqueous solution and the hydrates and solvates of the oxovanadium(IV) and dioxovanadium(V) ions in aqueous, DMSO, and DMPU solution have been determined by means of large-angle X-ray scattering (LAXS) and EXAFS. The studies performed here are complemented with the information obtained from the two crystallographic databases Cambridge Structure Database[41] and Inorganic Crystal Structure Database,[42] yielding a comprehensive description of the coordination chemistry of cationic vanadium ions with oxygen-donor ligands. Additionally, the UV−vis spectra of the respective solutions were recorded, providing spectrophotometric characterization of the studied solutions.

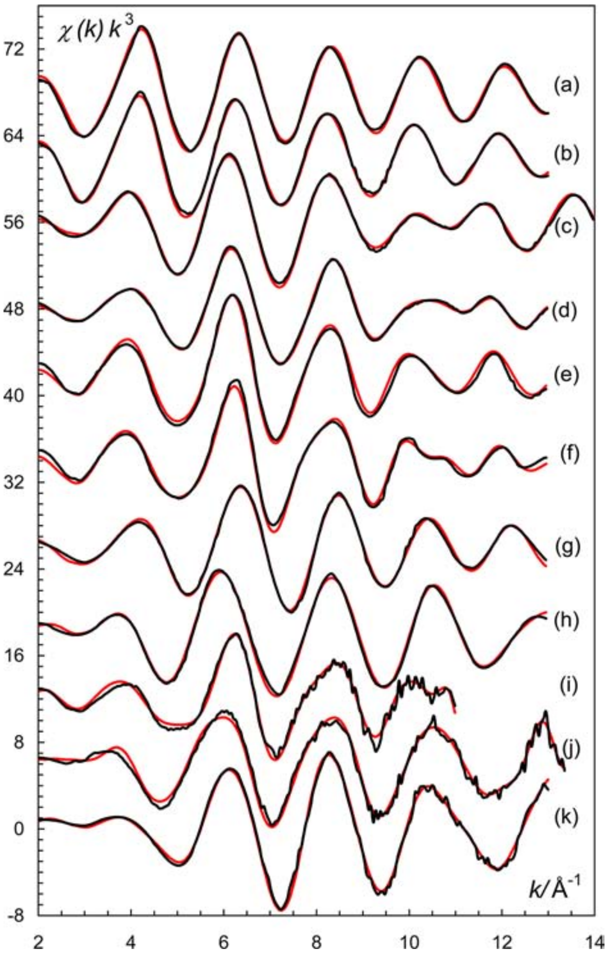

Figure 1. Experimental EXAFS data (black lines) fitted with a model (Table 3) formed by ab initio calculated scattering paths from the *FEFF* program (red lines): (a) $[V(H_2O)_6]^{3+}$ in water; (b) $[V(OH)_3(H_2O)_3]$ in water; (c) $[VO(H_2O)_5]^{2+}$ in water; (d) solid $[VO(H_2O)_5]SO_4$; (e) $[VO(OSMe_2)_5]^{2+}$ in DMSO; (f) solid $[VO(OSMe_2)_5](CF_3SO_3)_2$; (g) $[VO(ON_2C_6H_{12})_4]^{2+}$ in DMPU; (h) $[VO_2(H_2O)_4]^+$ in water; (i) $[VO_2(OSMe_2)_4]^+$ in DMSO; (j) solid $[VO_2(OSMe_2)_4]CF_3SO_3$; (k) $[VO_2(ON_2C_6H_{12})_3]^+$ in DMPU. Incremental offset: 6.

■ EXPERIMENTAL SECTION

Solvents. Deionized water was used throughout this study. Dimethyl sulfoxide (DMSO), $(CH_3)_2SO$ (Merck), and *N*,*N*′-dimethylpropyleneurea

Table 3. Mean Bond Distances, *d*/Å, Number of Distances, *N*, and Temperature Coefficients, *b*/Å^2 (LAXS), or Debye−Waller Coefficients, *σ*/Å^2 (EXAFS), from the LAXS (L) and EXAFS (E) Studies of the Hydrated and DMSO- and DMPU-Solvated Vanadium(III), Oxovanadium(IV), and Dioxovanadium(V) Ions in Solution and the Solid State at Room Temperature

species	interaction	*N*	*d*	*b*/*σ*^{2}	method
V^{3+} in Perchloric Acidic Water, 0.50 mol dm^{-3}, **L0**					
$[V(H_2O)_6]^{3+}$	V−O	6	1.992(1)	0.0038(1)	E
	MS (VO_6)	3 × 6	3.998(11)	0.012(2)	
Hydrolyzed Vanadium(III) in Water, 0.50 mol dm^{-3}, **L0$_{hyd}$**					
$[V(OH)_3(H_2O)_3]$	V−O	6	2.014(2)	0.0039(1)	E
	MS (VO_6)	3 × 6	4.026(12)	0.011(2)	
VO^{2+} in Water, 1.228 mol dm^{-3}, **L1a**					
$[VO(H_2O)_5]^{2+}$	V=O	1	1.615(5)	0.0024(5)	L
	V−O$_{eq}$	4	2.024(7)	0.0061(5)	
	V−O$_{ax}$	1	2.20(5)	0.020(3)	
	V···O$_{II,eq}$	8	4.06(2)	0.040(3)	
ClO_4^-/aq	Cl−O	4	1.453(5)	0.0022(4)	
water bulk	O···O	2	2.890(6)	0.0200(8)	
VO^{2+} in Water, 4.433 mol dm^{-3}, **L1b**					
$[VO(H_2O)_5]^{2+}$	V=O	1	1.607(5)	0.0020(5)	L
	V−O$_{eq}$	4	1.993(7)	0.0061(5)	
	V−O$_{ax}$	1	2.18(5)	0.021(3)	
	V···O$_{II,eq}$	8	4.06(2)	0.040(3)	
ClO_4^-/aq	Cl−O	4	1.436(4)	0.0022(4)	
water bulk	O···O	2	2.860(5)	0.0098(8)	
VO^{2+} in Water, 0.700 mol dm^{-3}, **L1c**					
$[VO(H_2O)_5]^{2+}$/aq	V=O	1	1.588(1)	0.0006(2)	E
	V−O$_{eq}$	4	2.027(2)	0.0041(1)	
	V−O$_{ax}$	1	2.21(5)	0.015(5)	
Solid $[VO(H_2O)_5]SO_4$					
$[VO(H_2O)_5]^{2+}$/aq	V=O	1	1.585(2)	0.0004(2)	E
	V−O$_{eq}$	4	2.009(2)	0.0028(2)	
	V−O$_{ax}$	1	2.21(5)	0.015(5)	
	MS ($VO_{4,eq}$)	3 × 4	4.00(4)	0.042(10)	
	V···S	1	2.883(7)	0.0083(8)	
	V−O−S	2	3.120(4)	0.0053(4)	
VO^{2+} in DMSO, 0.369 mol dm^{-3}, **L2a**					
$[VO(OS(CH_3)_2)_5]^{2+}$	V=O	1	1.605(8)	0.0064(4)	L
	V−O$_{eq}$	4	2.010(9)	0.0056(10)	
	V−O$_{ax}$	1	2.24(4)	0.015(5)	
	V···S$_{eq}$	4	3.236(8)	0.0127(11)	
	V···S$_{ax}$	1	3.36(3)	0.011(4)	
ClO_4^-	Cl−O	4	1.425(4)	0.003(1)	
VO^{2+} in DMSO, 0.18 mol dm^{-3}, **L2b**					
$[VO(OS(CH_3)_2)_5]^{2+}$	V=O	1	1.583(2)	0.0051(3)	E
	V−O$_{eq}$	4	2.021(2)	0.0043(2)	
	V−O$_{ax}$	1	2.20(4)	0.013(2)	
	V···S$_{eq}$	4	3.189(6)	0.0146(7)	
	V−O−S	4	3.338(13)	0.014(2)	
	MS (VO_4)	3 × 4	4.06(2)	0.026(4)	
Solid $[VO(OS(CH_3)_2)_5](ClO_4)_2$, **2a**					
$[VO(OS(CH_3)_2)_5]^{2+}$	V=O	1	1.615(3)	0.0075(5)	E
	V−O$_{eq}$	4	2.004(2)	0.0068(3)	
	V−O$_{ax}$	1	2.220(12)	0.013(2)	
	V···S$_{eq}$	4	3.166(3)	0.0102(3)	
	V−O$_{eq}$-S$_{eq}$	8	3.325(6)	0.0070(8)	
	MS ($VO_{4,eq}$)	3 × 4	4.08(2)	0.030(5)	
VO^{2+} in DMPU, 0.20 mol dm^{-3}, **L3**					
$[VO(DMPU)_4]^{2+}$	V=O	1	1.579(2)	0.0052(3)	E
	V−O$_{eq}$	4	1.971(1)	0.0033(2)	
	V···C$_{eq}$	4	2.965(10)	0.0121(14)	
	V−O$_{eq}$−C$_{eq}$	8	3.072(11)	0.020(3)	

Table 3. continued

species	interaction	N	d	b/σ^2	method
VO_2^+ in Sulfuric Acid, 1.833 mol dm^{-3}, **L4a**					
$[VO_2(H_2O)_4]^+$/aq	V═O	2	1.621(5)	0.0024(5)	L
	$V-O_{cis}$	2	1.987(13)	0.0054(7)	
	$V-O_{trans}$	2	2.215(17)	0.019(3)	
	$V\cdots O_{II,cis}$	4	4.16(2)	0.019(3)	
	$V\cdots O_{II,trans}$	4	4.27(2)	0.029(4)	
	$V\cdots S_{sulfate}$	2	3.556(3)	0.0197(5)	
SO_4^{2-}/aq	S−O	4	1.495(6)	0.0027(4)	
VO_2^+ in Dilute Sulfuric Acid, 0.87 mol dm^{-3}, **L4b**					
$[VO_2(H_2O)_4]^+$/aq	V═O	2	1.628(2)	0.0012(5)	E
	$V-O_{cis}$	2	2.004(2)	0.0021(3)	
	$V-O_{trans}$	2	2.224(17)	0.0063(4)	
VO_2^+ in DMSO, 1.833 mol dm^{-3}, **L5a**					
$[VO_2(DMSO)_4]^+$	V═O	2	1.628(5)	0.0024(5)	L
	$V-O_{cis}$	2	2.014(13)	0.0125(7)	
	$V-O_{trans}$	2	2.25(17)	0.0175(13)	
	$V\cdots S_{cis}$	4	3.205(2)	0.020(3)	
	$V\cdots S_{trans}$	4	3.393(2)	0.025(4)	
	$V\cdots S_{sulfate}$	2	3.556(3)	0.0197(5)	
Solid $[VO_2(OS(CH_3)_2)_5]CF_3SO_3$, **5**					
$[VO_2(DMSO)_4]^+$	V═O	2	1.646(3)	0.0010(5)	E
	$V-O_{cis}$	2	2.046(7)	0.0017(10)	
	$V-O_{trans}$	2	2.22(1)	0.006(2)	
	V···S	2	3.175(9)	0.0068(10)	
	V−O−S	4	3.26(2)	0.0016(3)	
VO_2^+ in DMPU, 0.20 mol dm^{-3}, **L6**					
$[VO_2(DMPU)_3]^+$	V═O	2	1.652(3)		E
	V−O	3	2.049(2)		
	V−C	3	3.016(6)		
	V−O−C	6	3.148(9)		

(DMPU), $C_6H_{12}N_2O$ (BASF), were distilled over calcium hydride, CaH_2 (Fluka), and stored in dark bottles over 3 Å molecular sieves.

Chemicals. Vanadium(III) chloride, VCl_3 (Merck), vanadium(IV) sulfate pentahydrate, $VOSO_4\cdot 5H_2O$ (**S1**; Merck), vanadium(V) oxide, V_2O_5 (Merck), barium perchlorate, $Ba(ClO_4)_2$ (Kebo), barium trifluoromethanesulfonate, $Ba(CF_3SO_3)_2$ (Aldrich), trifluoromethanesulfonic acid, CF_3SO_3H (Riedel-de Haën), and perchloric acid (BDH, 70%) were used as purchased.

Solids. *Pentaaquaoxovanadium(IV) Trifluoromethanesulfonate, $[VO(OH_2)_5](CF_3SO_3)_2$ (**1**).* A dilute trifluoromethanesulfonic acidic aqueous oxovanadium(IV) trifluoromethanesulfonate solution was prepared by mixing aqueous solutions of oxovanadium(IV) sulfate pentahydrate and barium trifluoromethanesulfonate in a molar ratio of 1:1, as described elsewhere.[45] The formed barium sulfate was filtered off after the mixture was cooled in a refrigerator for 1 week. The volume of the filtered solution was reduced to a final concentration of ca. 4 mol dm^{-3}. This concentrated solution was placed in a refrigerator, and crystals of **1** of sufficient quality for single-crystal X-ray diffraction studies were obtained.

*Pentakis(dimethyl sulfoxide)oxovanadium(IV) Perchlorate, $[VO(OS(CH_3)_2)_5](ClO_4)_2$ (**2a**), and Pentakis(dimethyl sulfoxide)oxovanadium(IV) Trifluoromethanesulfonate, $[VO(OS(CH_3)_2)_5](CF_3SO_3)_2$ (**2b**).* DMSO was added to a concentrated aqueous solution of oxovanadium(IV) perchlorate or trifluoromethanesulfonate. Water and most of the excess of DMSO were evaporated off under reduced pressure. The salts crystallized after cooling in a refrigerator, and they were recrystallized twice from freshly distilled DMSO.

*Tetrakis(N,N′-dimethylpropyleneurea)oxovanadium(IV) Trifluoromethanesulfonate, $[VO(OCN_2(CH_3)_2(CH_2)_3)_4](CF_3SO_3)_2$ (**3**).* **3** was prepared in a manner analogous to that described for **2b**, using DMPU instead of DMSO.

*Dioxovanadium(V) Perchlorate and Trifluoromethanesulfonate Hydrates, **4**.* Vanadium(V) oxide, V_2O_5, was dissolved in dilute sulfuric acid, an equimolar amount of barium perchlorate or triflouromethanesulfonate, dissolved in water, was added, and the formed barium sulfate was filtered off. The obtained solutions were evaporated under reduced pressure until a fine-grained deep-red precipitate was formed, and the solutions were put in a refrigerator for continued crystallization. The precipitates were filtered off and studied by powder diffraction. The powders were found to be only partially crystalline, as indicated by the powder diffraction data of the perchlorate salt shown in Figure S6 in the Supporting Information.

*Tetrakis(dimethyl sulfoxide)dioxovanadium(V) Trifluoromethanesulfonate, $[VO_2(OS(CH_3)_2)_4]CF_3SO_3$ (**5**).* A DMSO solution of dioxovanadium(V) trifluoromethanesulfonate was prepared by adding trifluoromethanesulfonate acid (Riedel-de Haën) to a vanadium(V) oxide/DMSO slurry. The mixture was stirred and heated to 363 K for about 48 h until most of the vanadium(V) oxide had reacted. The excess of DMSO was removed by the slow evaporation under reduced pressure of a filtered solution. **5** crystallized after cooling in a refrigerator, and it was recrystallized once from pure DMSO. ***Caution!*** *Note that perchlorate salts cannot be prepared by this route due to the explosive reaction between DMSO and aqueous perchloric acid.*

Solutions. An aqueous solution of vanadium(III) chloride (**L0**) was prepared by dissolving anhydrous vanadium(III) chloride in 0.1 mol dm^{-3} perchloric acid degassed with nitrogen for 15 min. Concentrated perchloric acid was added dropwise until a clear blue solution of vanadium(III) was obtained; the pH was measured to 0.60. A hydrolyzed vanadium(III) solution, $\mathbf{L0_{hyd}}$, was prepared by adjusting the pH with a dilute sodium hydroxide solution until a significant color change to bluish-green was observed; the pH was measured to 1.22 in this solution. Vanadium(III) seems to be perfectly stable for weeks under these conditions. The UV−vis spectra of the aqueous vanadium(III) solutions studied (Figure S1 in the Supporting Information) are in full agreement with those reported by Kanamori.[46]

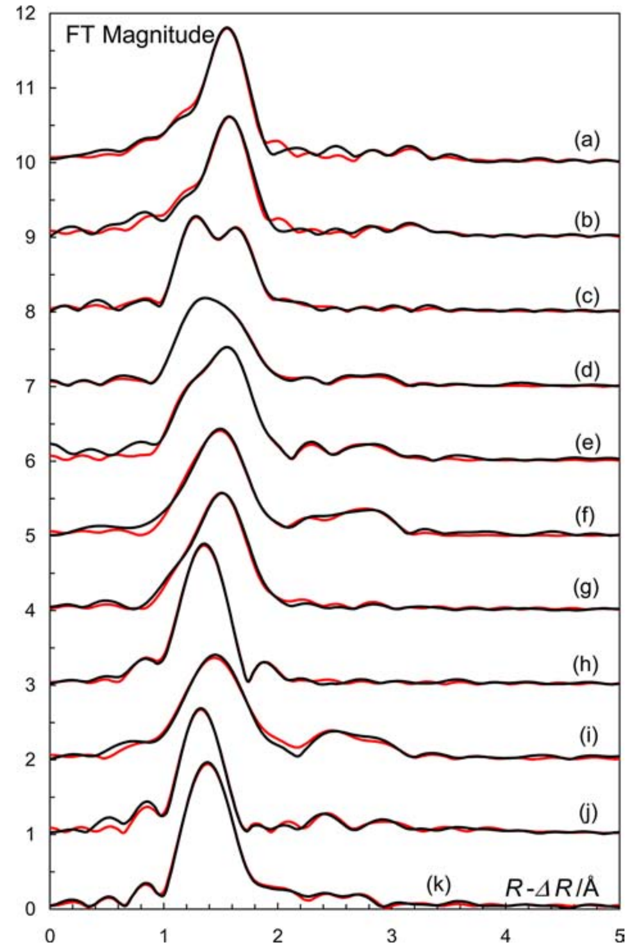

Figure 2. Experimental (black lines) and modeled (red lines) Fourier transforms of the EXAFS data: (a) $[V(H_2O)_6]^{3+}$ in water; (b) $[V(OH)_3(H_2O)_3]$ in water; (c) $[VO(H_2O)_5]^{2+}$ in water; (d) solid $[VO(H_2O)_5]SO_4$; (e) $[VO(OSMe_2)_5]^{2+}$ in DMSO; (f) solid $[VO(OSMe_2)_5](CF_3SO_3)_2$; (g) $[VO(ON_2C_6H_{12})_4]^{2+}$ in DMPU; (h) $[VO_2(H_2O)_4]^+$ in water; (i) $[VO_2(OSMe_2)_4]^+$ in DMSO; (j) solid $[VO_2(OSMe_2)_4]CF_3SO_3$; (k) $[VO_2(ON_2C_6H_{12})_3]^+$ in DMPU. Incremental offset: 1.

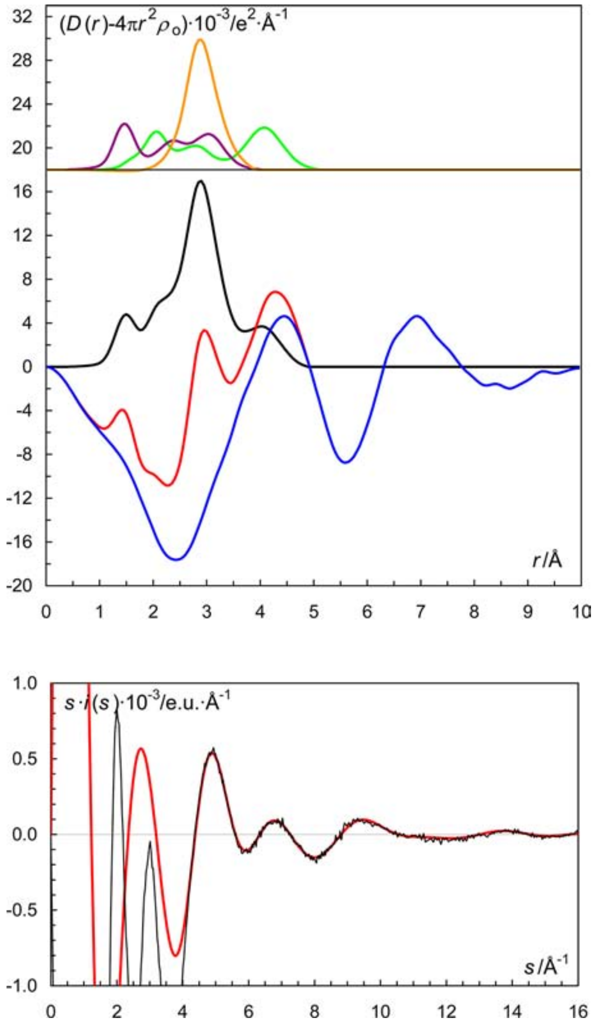

Figure 3. (Top) LAXS RDF curves for a 1.228 mol dm^{-3} aqueous solution of oxovanadium(IV) perchlorate, **L1a**. Upper part: Separate model contributions (offset: 18) of the hydrated oxovanadium(IV) ion (green line), the perchlorate ion (purple line), and aqueous bulk structure (orange line). (Middle) Experimental RDF: $D(r) - 4\pi r^2\rho_0$ (red line); sum of the model contributions (black line); difference (blue line). (Bottom) Reduced LAXS intensity functions $si(s)$ (black line); model $si_{calc}(s)$ (red line).

Aqueous solutions of oxovanadium(IV) perchlorate, $VO(ClO_4)_2$ (**L1a-c**), were prepared by mixing aqueous solutions of vanadium(IV) oxide sulfate (Merck) and barium perchlorate (Merck), and the barium sulfate precipitate was filtered off. The final solutions were prepared by removing water by evaporation to the desired concentration.

DMSO solutions of oxovanadium(IV) perchlorate (**L2a-b**) were prepared by dissolving **2a** in freshly distilled DMSO.

A DMPU solution of oxovanadium(IV) trifluoromethanesulfonate (**L3**) was prepared by adding a stoichiometric amount of trifluoromethanesulfonic acid (Riedel-de Haën) to a vanadium(IV) oxide/DMPU slurry. The mixture was stirred and heated to 373 K for about 60 h until most of the vanadium(IV) oxide had reacted, and the remaining starting material was filtered off.

Acidic aqueous solutions of dioxovanadium(V) sulfate (**L4a-b**) were prepared by adding a considerable excess of highly concentrated sulfuric acid (98% by weight, Merck) to a vanadium(V) oxide/water slurry heated to 350 K. The mixture was stirred and heated to 360 K until all vanadium(V) oxide had reacted. The obtained solution was cooled and diluted to the desired concentration.

Acidic DMSO solutions of dioxovanadium(V) sulfate (**L5a-b**) were prepared by adding DMSO to a dioxovanadium(V) sulfate solution in sulfuric acid prepared as described above.

A DMPU solution of dioxovanadium(V) trifluoromethanesulfonate (**L6**) was prepared by adding a stoichiometric amount of trifluoromethanesulfonic acid (Riedel-de Haën) to a vanadium(V) oxide/DMPU slurry as described above.

The concentrations of all ions and solvents, wherever appropriate, for all solutions studied by EXAFS and LAXS are summarized in Table 1. UV−vis spectra of the studied solutions after appropriate dilution are shown in Figure S1 in the Supporting Information.

Single-Crystal X-ray Diffraction. The crystals were taken out of the mother liquid and mounted in glass capillaries, which were sealed by burning immediately after mounting. Data collections were performed on a Bruker SMART platform equipped with a CCD area detector[47] and a graphite monochromator using Mo Kα (λ = 0.7107 Å) radiation at ambient room temperature. A hemisphere data set was collected for each structure using the ω scan method, with 1271 frames and a crystal-to-detector distance of 5.0 cm for all compounds studied, **1**, **2a**, **3**, and **5**. Appropriate absorption correction was applied using overlapping multiscans. The structures were solved by direct methods in *SHELXL*[48] and refined using full-matrix least squares on F^2. Hydrogen atoms were added to the water molecules in **1**, allowing the distance to be refined, whereas hydrogen atoms were calculated in ideal positions riding on their respective carbon atom in **2a**, **3**, and **5**. Selected bond distances and angles are given in the

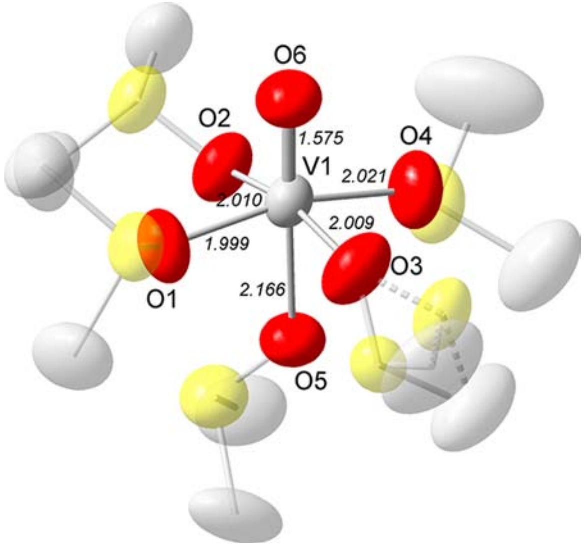

Figure 4. Representation of the oxovanadium(IV) cation complex in **2a**. The thermal ellipsoids are set at 50% probability. The carbon and sulfur atoms have been faded and the hydrogen atoms and counterions removed for clarity. The alternate position of one of the sulfur atoms is indicated by a dashed bond (faded).

Supporting Information, and the CIF files have been deposited at the Cambridge Crystallographic Data Centre as CCDC 864570−864573.

EXAFS: Data Collection. V K-edge X-ray absorption spectra were recorded at the wiggler beamline 4-1 (old station) at the Stanford Synchrotron Radiation Lightsource (SSRL). The EXAFS station was equipped with a Si[220] double-crystal monochromator. SSRL operated at 3.0 GeV and a maximum current of 100 mA. The data collection was performed in transmission mode and at ambient temperature. Higher-order harmonics were reduced by detuning the second monochromator to 40% of the maximum intensity at the end of the scans. The solutions were placed in cells with Mylar foil windows and 1−5 mm Teflon spacers. The energy scale of the X-ray absorption spectra was calibrated by assigning the first inflection point of the K edge of a vanadium foil to 5465.2 eV.[49] For each sample, three to six scans were averaged, giving satisfactory data (k^3-weighted) in the k range 2−13 Å^{-1}. The *EXAFSPAK* program package was used for the primary data treatment.[50]

EXAFS: Data Analysis. The *EXAFSPAK* program package was used for data treatment,[50] including refinement of structure parameters using FEFF-calculated EXAFS parameters.[51] The standard deviations reported for the refined parameters in Table 2 are obtained from k^3-weighted least-squares refinements of the EXAFS function $\chi(k)$ and do not include systematic errors of the measurements. These statistical error values allow reasonable comparisons of, e.g., the significance when relative shifts in the distances are compared. However, variations in the refined parameters, including the shift in the E_0 value (for which $k = 0$), using different models and data ranges, indicate that the absolute accuracy of the distances given for the separate complexes is within ±0.005−0.02 Å for well-defined interactions. The "estimated standard deviations" given in the text have been increased accordingly to include estimated additional effects of systematic errors.

LAXS. A large-angle θ−θ diffractometer was used to measure the scattering of Mo Kα radiation (λ = 0.7107 Å) on the free surface of aqueous, DMSO, and DMPU solutions of oxovanadium(IV) and dioxovanadium(V) perchlorate. The solutions were contained in a Teflon cuvette inside a radiation shield with beryllium windows. After monochromatization of scattered radiation, by means of a focusing LiF crystal, the intensity was measured at 450 discrete points in the range $1 < \theta < 65°$ (the scattering angle was 2θ). A total of 100000 counts were accumulated at each angle, and the whole angular range was scanned twice, which corresponds to a statistical uncertainty of about 0.3%. The divergence of the primary X-ray beam was limited by 1 or $^1/_4$° slits for different θ regions with overlapping of some parts of the data for scaling purposes.

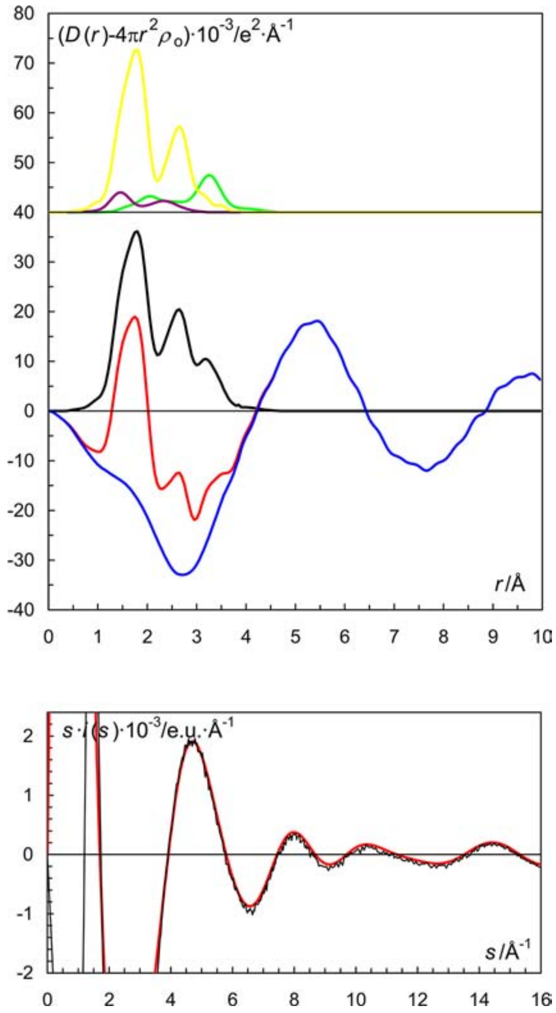

Figure 5. (Top) LAXS RDF curves for a 0.369 mol dm^{-3} DMSO solution of oxovanadium(IV) perchlorate, **L2a**. Upper part: Separate model contributions (offset: 40) of the hydrated oxovanadium(IV) ion (green line), the perchlorate ion (purple line), and DMSO (yellow line). (Middle) Experimental RDF: $D(r) - 4\pi r^2\rho_0$ (red line); sum of the model contributions (black line); difference (blue line). (Bottom) Reduced LAXS intensity functions $si(s)$ (black line); model $si_{\text{calc}}(s)$ (red line).

All data treatment was carried out by using the *KURVLR* program,[52] which was previously described in more detail.[53] The experimental intensities were normalized to a stoichiometric unit of volume containing one vanadium atom, using the scattering factors f for neutral atoms, including corrections for anomalous dispersion, $\Delta f'$ and $\Delta f''$,[54] and values for Compton scattering.[55,56] To receive a better alignment of the intensity function, a Fourier back-transformation was applied to eliminate spurious peaks below 1.2 Å not related to any interatomic distances in the radial distribution function (RDF).[57] Least-squares refinements of the model parameters were performed by means of the *STEPLR* program[58] to minimize the error square sum $U = \sum w(s)[i_{\text{exp}}(s) - i_{\text{cal}}(s)]^2$.

RESULTS AND DISCUSSION

Hydrated and Hydrolyzed Vanadium(III) Ions in Aqueous Solution, L0 and L0$_{\text{hyd}}$. The EXAFS data of the

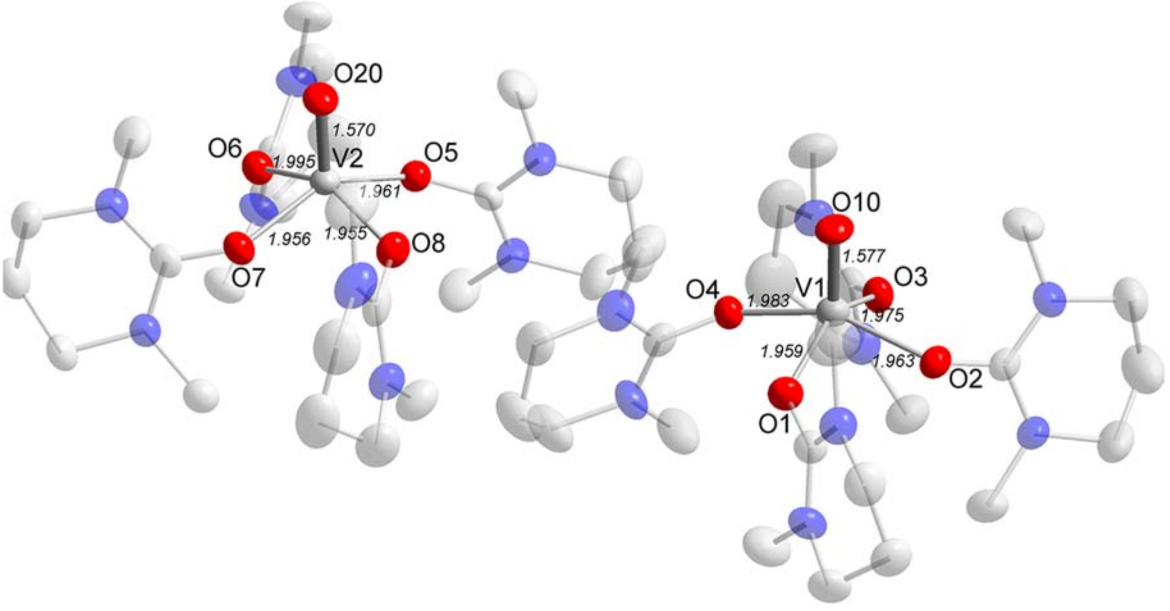

Figure 6. Representation of the two crystallographically independent oxovanadium(IV) cation complexes in **3**. The thermal ellipsoids are set at 30% probability. The carbon and nitrogen atoms have been faded and the hydrogen atoms and counterions removed for clarity.

hydrated and hydrolyzed vanadium(III) ions in aqueous solution display simple backscattering patterns typical for regular octahedral complexes with only one coordination shell of oxygen atoms as the backscatterer (Figure 1). The hydrolyzed vanadium(III) complex, most likely present as $[V(OH)(H_2O)_5]^{2+}$,[44] has a significantly shorter phase than the hydrated vanadium(III) ion (Figure 1). Refinement of the structure parameters gave mean V−O bond distances of 1.992(3) and 2.014(5) Å for hydrated and hydrolyzed vanadium(III) ions, respectively, and with matching linear multiple-scattering path lengths within the octahedral VO_6 entities (Table 3). The longer mean V−O bond distance of the hydrolyzed vanadium(III) complex is due to the larger radii of the oxygen atoms in the hydroxide ion, 1.37 Å, than in the coordinated water, 1.34 Å.[59,60] The observed difference in the V−O bond distance between hydrated and hydrolyzed complexes is therefore expected.

Confirmation of the Crystal Structure of 1. The crystal structure of pentaaquaoxovanadium(IV) triflouromethanesulfonate, **1**, has been reported previously.[39i] The reported structure, crystallizing in space group $P2_1/m$ (No. 11), is confirmed in this study with near-identical structure parameters (Table 2 and Figure S2 in the Supporting Information). Selected bond distances and angles are listed in parts a and b of Table S5 in the Supporting Information, respectively.

Structure of the Hydrated Oxovanadium(IV) Ion in Aqueous Solution. The EXAFS and LAXS data show that the structure of the hydrated oxovanadium(IV) ion in aqueous solution is, in principle, the same as that observed in the solid state. The refinement of the EXAFS data gave mean V═O, V−O_{perp}, and V−O_{trans} bond distances of 1.588(3), 2.026(3), and 2.24(6) Å, respectively (Table 3 and Figures 1 and 2). The RDF from the LAXS experiments on the aqueous oxovanadium(IV) perchlorate solutions reveals a total of four peaks or shoulders at 1.5, 2.1, 2.9, and 4.1 Å (Figure 3). The peak at 1.5 Å corresponds to the Cl−O bond distance in the perchlorate ion and the V═O bond in the oxovanadium(IV) ion. The structure of the hydrated perchlorate ion is identical with those reported in previous studies of perchlorate salts in aqueous solution, with Cl−O bond distances of 1.453(5) and 1.436(6) Å, in dilute and concentrated solutions, respectively.[61] The peak/shoulder at 2.05 Å corresponds to the perpendicularly bound water molecules, while the peak at 4.1 Å corresponds with the second hydration shell of water molecules hydrogen bound to perpendicularly bound water molecules. The peak at 2.9 Å corresponds to O···O distances in the aqueous bulk. The refined structure parameters from the LAXS measurements are summarized in Table 3. The V═O bond distance of the strongly bound oxo group in the hydrated oxovanadyl(IV) ion is 1.61(1) Å; the water molecules bound perpendicularly to the V═O bond display a V−O bond distance of 2.03(2) Å, while the water molecule trans to the oxo group is significantly more weakly bound at ca. 2.20 Å (Table 3).

DMSO-Solvated Oxovanadyl(IV) Ion, $VO(DMSO)_5^{2+}$. The structure of solid pentakis(dimethyl sulfoxide)-oxovanadium perchlorate (**2a**) was solved and refined in the monoclinic space group $P2_1/c$ (No. 14) with improved structural parameters compared to a previously reported determination of the same compound using the nonstandard setting $P2_1/n$ (No. 14).[40b] The sole crystallographically independent pentakis(dimethyl sulfoxide)oxovanadium(IV) structural unit has a short V═O bond, $d_{V=O}$ = 1.575(5) Å, four longer ones perpendicular to the V═O bond in the range of 1.999−2.021 Å, mean 2.007 Å, while the fifth DMSO molecule, trans to the V═O bond, is much more weakly bound, d_{V-O} = 2.168(5) Å (Figure 4). The deviation from the horizontal plane is within 7.5 ± 1.0° for the four DMSO ligands, and the trans O═V—O bond angle is 178°. In one of the DMSO ligands, the sulfur atom has an alternate position with a refined 50:50 distribution. One of the trifluoromethanesulfonate ions was refined with a structural disorder with two superimposed ions sharing a common S−C bond. Crystallographic data and selected bond distances and angles are listed in Tables 2 and S6a,b in the Supporting Information, respectively.

The EXAFS and LAXS data show that the DMSO-solvated oxovanadium(IV) ion has the same structure in solution as in the solid pentakis(dimethyl sulfoxide)oxovanadium(IV) perrhenate,[40d] perchlorate,[40b] and iodide[40c] salts reported previously (Table S3b in the Supporting Information) and in this study. The refined structure parameters of the DMSO-solvated oxovanadium(IV) are given in Table 3, and the fits of the experimental data are given in Figures 1, 2, and 5.

DMPU-Solvated Oxovanadium(IV) Ion, $VO(DMPU)_4^{2+}$. The structure of tetrakis(*N*,*N'*-dimethylpropyleneurea)oxovanadium trifluoromethanesulfonate (**3**) was solved and refined in the monoclinic space group $P2_1/c$ (No. 14). The structure consists of discrete tetrakis(*N*,*N'*-dimethylpropyleneurea)oxovanadium(IV) and trifluoromethanesulfonate ions. Because of the space-demanding properties of the DMPU ligand, the oxovanadium(IV) ion binds only four DMPU molecules at a mean V−O bond distance of 1.971 Å and the V═O distance is 1.576 Å (Figure 6). The trans position is unoccupied because of the space required by the four DMPU molecules, which also cause or allow the equatorial V−O bonds to be slightly shorter than those in the pentasolvated oxovanadium(IV) ions. Furthermore, the O═V—O bond angle deviation from a theoretical horizontal plane of a regular square-pyramidal structure is much larger with a mean value of about 17°. In the structural refinement, one point of unusually high residual electron density (1.7 e) was located trans to the V1═O10 bond but cannot be logically attributed to any real atom. Crystallographic data and selected bond distances and angles are listed in Tables 2 and S7a,b in the Supporting Information, respectively. The structure of the DMPU-solvated oxovanadium(IV) ion is maintained in a DMPU solution with mean V═O and V−O bond distances of 1.580(5) and 1.971(3) Å, respectively. The refined structure parameters of the DMPU-solvated oxovanadium(IV) are given in Table 3, and the fits of the experimental data are given in Figures 1 and 2.

Hydrated Dioxovanadium(V) Ion. The hydrated dioxovanadium(V) ion, $VO_2^+(aq)$, has been studied in acidic aqueous solution. Several attempts to crystallize the hydrated dioxovanadium(V) ion with perchlorate and trifluoromethanesulfonate as counterions failed; see Experimental Section. The hydrated dioxovanadium(V) ion seems to be stabilized in concentrated sulfuric acid; the high sulfate concentration allows complexation with sulfate or hydrogen sulfate ions. The Fourier transform of the hydrated dioxovanadium(V) ion shows three different V−O distances, 1.6, 2.0, and 2.1 Å, corresponding to the oxo groups, which from other oxovanadium(V) complexes are shown to be in the cis configuration, and to the water molecules in the cis and trans positions to the oxo groups, respectively. The same structure modeled the LAXS data very well. The refined structure parameters from the EXAFS and LAXS studies are summarized in Table 3, and the fits of the experimental data are given in Figures 1, 2, and 7.

DMSO-Solvated Dioxovanadyl(V) Ion, $VO_2(DMSO)_4^+$. The crystal structure of tetrakis(dimethyl sulfoxide)dioxovanadium(V) trifluoromethanesulfonate (**5**) was solved and refined in the space group $P2_1/c$ (No. 14). The oxovanadium(V) cation is solvated by four DMSO molecules through their oxygen atoms. The coordination around vanadium is a highly distorted octahedron with the strongly bound oxo groups in the cis configuration with V═O bond distances of 1.591(5) and 1.594(5) Å and an O═V═O angle of 104.0(3)° (Figure 8). These V═O distances are slightly shorter than analogous distances in dioxovanadium(V) compounds reported before, which usually have values longer than 1.6 Å in complexes with inorganic as well organic oxygen-donor ligands (Table S4 in the Supporting Information).[23−26] However, the current compound is, to the best of our knowledge, the first such example of a discrete dioxovanadium(V) cation being six-coordinate with noncharged ligands. The V−O distances trans to the oxo groups are relatively long, 2.201 and 2.206 Å, while the DMSO molecules perpendicular to both oxo groups have V−O bond distances of 1.985 and 2.048 Å. These two perpendicular DMSO molecules are disordered and split into two alternative positions (O13 and O13b and O16 and O16b), which were refined with occupancy factors of 55 and 45% for each pair, respectively. All O−V−O angles deviate significantly from 90 and 180°. In addition, the vanadium atom is displaced from the center of the octahedron toward the two terminal oxo ligands. The O═V═O angle in **5**, 104.0(3)°, is in close agreement those observed in $[VO_2(SO_4)_2(OH_2)_2]^{3-}$ at 103.80°,[31c] and $VO_2IO_3(H_2O)_2$ at 104.82°.[30b] In comparison, in the dioxovanadium(V) complexes with organic molecules, the cis O═V═O angle is generally 3−4° larger[23−26] than that reported here.

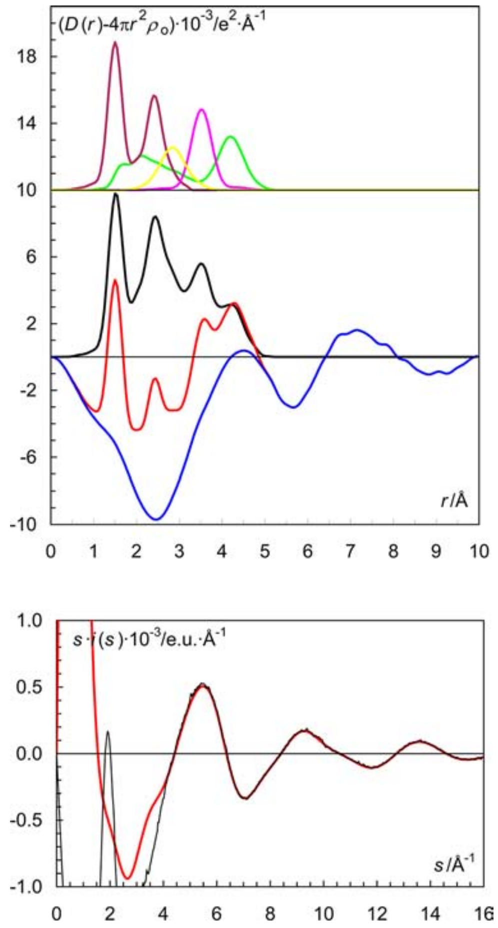

Figure 7. (Top) LAXS RDF curves for a 1.833 mol dm^{-3} aqueous solution of dioxovanadium(IV) sulfate (**L4a**). Upper part: Separate model contributions (offset: 18) of the hydrated dioxovanadium(V) ion (green line), the sulfate ion (purple line), aqueous bulk structure (yellow line), and V···S distances (magenta line). (Middle) Experimental RDF: $D(r) - 4\pi r^2\rho_0$ (red line); sum of model contributions (black line); difference (blue line). (Bottom) Reduced LAXS intensity functions $si(s)$ (black line); model $si_{calc}(s)$ (red line).

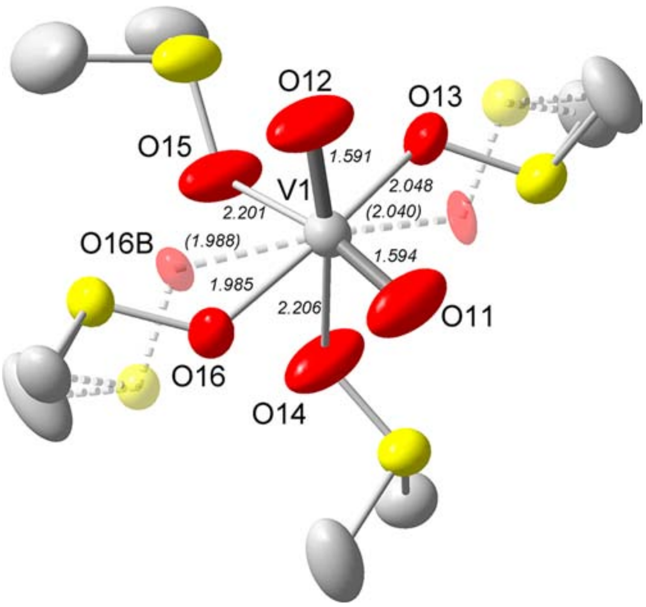

Figure 8. Representation of the oxovanadium(IV) cation complex in **5**. The thermal ellipsoids are set at 50% probability. The carbon and sulfur atoms have been faded and the hydrogen atoms and counterions removed for clarity. The alternate positions of atoms are shown faded with dashed bonds.

The intramolecular bond distances within the DMSO molecules in **5** are in good agreement with distances found for other compounds with oxygen-coordinated DMSO ligands.[41] The mean V−O−S angle in **5**, 120.2°, is significantly smaller than that in **2a**, 128.4°, which may indicate a higher degree of covalency in the V^{V}−O bonds than the corresponding V^{IV}−O ones. The atomic positions of the trifluoromethanesulfonate ions are fairly well-defined and give bond distances in good agreement with other determinations.[41]

The RDF of the DMSO solution of dioxovanadium(V) sulfate studied by LAXS is shown in Figure 9. The S−O interactions from the sulfate anion and the S−O and C−S interactions from the DMSO molecule are all contained within the broad unresolved peak around 1.6 Å. The broad peak at about 2.2 Å corresponds to the V−O bond interactions but also to the nonbonding interactions within the sulfate and DMSO species. The small peak at 3.15 Å is due to the V···S distance from coordinated DMSO molecules and coordinated sulfate ions. DMSO is known to reveal a strong proton-accepting ability.[62] In the case of the presence of considerable excess amounts of sulfuric acid in this solution, the bis(dimethyl sulfoxide) cations, $(DMSO)_2H^+$, are formed, which results in an extremely short O···O distance at about 2.5 Å.[63]

DMPU-Solvated Dioxovanadium(V) Ion. The structure of the DMPU-solvated dioxovanadium(V) ion, $VO_2(DMPU)_3^+$ (**L6**), has been studied in a DMPU solution by EXAFS. The mean V=O and V−O bond distances are 1.652(2) and 2.048(3) Å, respectively, which clearly indicate that vanadium is strongly solvated by three DMPU molecules in a manner similar to that previously shown for triphenylphosphine oxide, another ligand known to be space-demanding upon coordination.[28] The V···C and V−O−C scattering paths are 3.02(1) and 3.15(2) Å, giving a V−O−C bond angle of 130°. Several attempts to crystallize the DMPU-solvated dioxovanadium(V) ion with both perchlorate and trifluoromethanesulfonate as counterions unfortunately failed.

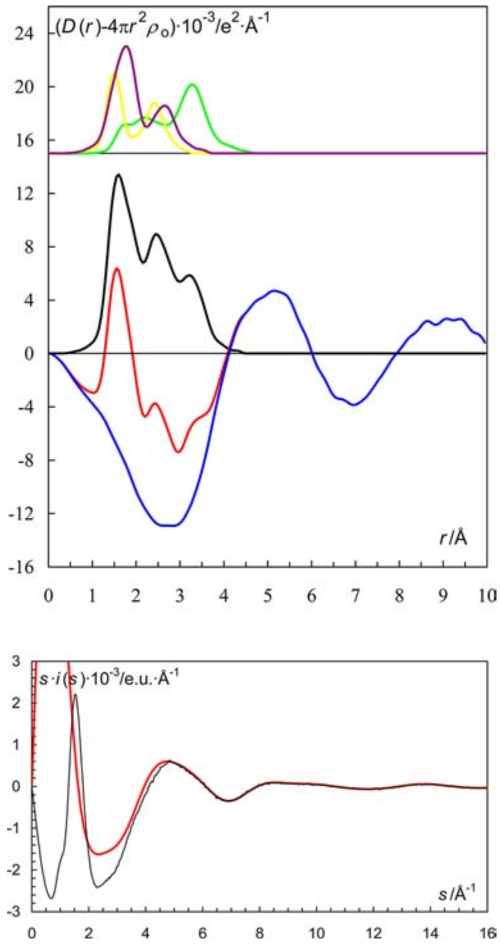

Figure 9. (Top) LAXS RDF curves for a 0.50 mol dm^{-3} DMSO solution of oxovanadium(IV) perchlorate (**L5a**). Upper part: Separate model contributions (offset: 18) of the hydrated oxovanadium(IV) ion (green line), the perchlorate ion (purple line), and DMSO (yellow line). (Middle) Experimental RDF: $D(r) - 4\pi r^2\rho_0$ (red line); sum of model contributions (black line); difference (blue line). (Bottom) Reduced LAXS intensity functions $si(s)$ (black line); model $si_{calc}(s)$ (red line).

■ CONCLUSIONS

The hydrated vanadium(III) ion has a regular octahedral geometry with a mean V−O bond distance of 1.99 Å, yielding an ionic radius of 0.65 Å, which is in excellent agreement with the value reported by Shannon.[59] Hydrated oxovanadium(IV) ions have distorted octahedral configurations with a mean V=O bond distance to the oxo group of 1.586 Å, a mean V−O bond distance to the four water molecules almost perpendicular to the V=O bond of 2.02 Å, and the V−O bond trans to the oxo group only weakly bound at ca. 2.2 Å. The solvated oxovanadium(IV) ions with small solvent molecules display structures very similar to that of the hydrate, while solvates with solvent molecules demanding space at coordination, such as DMPU, are five-coordinate with a distorted square-pyramidal geometry. The V=O and V−O bond distances of the DMPU-solvated oxovanadium(IV) ion are 1.58 and 1.97 Å, respectively. The hydrated and solvated dioxovanadium(V) ions have very distorted octahedral configurations with O=V=O angles in the range 103−109°. The mean V=O bond distance is 1.63 Å, and the V−O bond distances in the cis and trans positions to the oxo groups are 1.99 and 2.20 Å, respectively. A solvate of dioxovanadium(V) with a space-demanding solvent molecule, such as DMPU and triphenylphosphate, shows a bicapped trigonal configuration with mean V═O and V−O bond distances of 1.617 and 2.020 Å, respectively.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

X-ray crystallographic data in CIF format, summary of reported V−O and V═O bond distances of hydrate and solvate complexes of vanadium in the oxidation states II+, III+, IV+, and V+ (Tables S1−S4), selected bond distances and angles of **1**, **2a**, **3**, and **5** (Tables S5−S8), UV−vis spectra (Figure S1), and packing of unit cells of **1**, **2a**, **3**, and **5** (Figures S2−S5), powder diffractogram of **4** (Figure S5). This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

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