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 Material

Table S1a. Vanadium(II) hydrates

Ref. or CSD/ICSD code(s)		avg. $d_{V\text{-}O}$	Structure	$d_{V\text{-}O}$/Å	Comment
VEPSUE	68779	2.118 Å	$[V(H_2O)_6](CF_3SO_3)_2$	2·(2.118, 2.118, 2.119)	
	66150	2.121? Å	$(ND_4)_2[V(D_2O)_6](SO_4)_2$	2·(2.113, 2.129, ???)	Only two distances listed!
		2.125 Å	$[V(H_2O)_6]SiF_6$	6·2.125 Å	Cotton, F. A.; Daniels, L. M.; Murillo, C. A.; Quesada, J. F. *Inorg. Chem.*, **1993**, *32*, 4861-4867
	75461	2.129 Å	$[V(H_2O)_6]SO_4{\cdot}H_2O$	(2·(2.102, 2.134, 2.137) + 2·(2.118, 2.130, 2.151))	X-ray data
		2.129 Å	$(NH_4)_2[V(H_2O)_6](SO_4)_2$	2·(2.116, 2.133, 2.135)	Cotton, F. A.; Daniels, L. M.; Murillo, C. A.; Quesada, J. F. *Inorg. Chem.*, **1993**, *32*, 4861-4867
	61263	2.131 Å	$[V(H_2O)_6]SO_4$	(2·(2.123, 2.131, 2.136) + 2·(2.120, 2.124, 2.150))	
	75462	2.140 Å	$[V(H_2O)_6]SO_4{\cdot}H_2O$	(2·(2.115, 2.141, 2.150) + 2·(2.125, 2.139, 2.170))	Neutron data
	14345	2.148 Å	$[V(H_2O)_6](NH_4)_2(SO_4)_2$	2·(2.118, 2.161, 2.164)	
	Mean:	**2.130 Å [8 structures]**			

Excluded structures (3): YEGSAF (more likely V^{3+}, see Table S2), 15232 (mixed V^{2+}/Ni^{2+}), 66151 (mixed V^{2+}/Zn^{2+})

Table S1b. Vanadium(II) solvates

CSD	ICSD	avg. $d_{V\text{-}O}$	Structure	$d_{V\text{-}O}$/Å	Comment
SIJFAS		2.114 Å	$[V(CH_3COOH)_6]Br_2$	2·(2.109, 2.113, 2.121)	acetic acid
DATBUV		2.140 Å	$[V(CH_3OH)_6]Cl_2$	2·(2.133, 2.139, 2.147)	methanol
SUJNUG		2.142 Å	$[V(OC_4H_8)_6](C_{24}BF_{20})_2{\cdot}2C_4H_8O$	2·(2.131, 2.147, 2.149)	thf
	Mean:	**2.132 Å [3 structures]**			

Table S2a. Vanadin(III) hydrates

CSD	ICSD	avg. $d_{V\text{-}O}$	Structure	$d_{V\text{-}O}$/Å	Comment
FEMHOV	170206	1.990 Å	$[V(H_2O)_6](C(NH_2)_3)(SO_4)_2$	3·(1.987, 1.993)	
	81830	1.991 Å	$K[V(H_2O)_6](SO_4)_2{\cdot}6H_2O$	6·1.991	
	81832	1.991 Å	$Cs[V(H_2O)_6](SO_4)_2{\cdot}6H_2O$	6·1.991	
	96936	1.993 Å	$Cs[V(D_2O)_6](SO_4)_2{\cdot}6D_2O$	6·1.993	10 K
	201210	1.993 Å	$Cs[V(H_2O)_6](SO_4)_2{\cdot}6H_2O$	6·1.993	
COLNUM01	201679	1.994 Å	$[V(H_2O)_6](H_5O_2)(CF_3SO_3)_4$	2·(1.978, 1.991, 2.013)	10 K, neutron
COLNUM	201678	1.995 Å	$[V(H_2O)_6](H_5O_2)(CF_3SO_3)_4$	2·(1.988, 1.993, 2.003)	295 K, X-ray
	81831	1.996 Å	$Rb[V(H_2O)_6](SO_4)_2{\cdot}6H_2O$	6·1.996	
	96936	1.996 Å	$Cs[V(D_2O)_6](SO_4)_2{\cdot}6D_2O$	6·1.996	15 K
	74004	2.007 Å	$Cs[V(H_2O)_6](SO_4)_2{\cdot}6H_2O$	6·2.007	
	Mean:	**1.995 Å [10 structures]**			

Excluded structures (1): YEGSAF (reported as V^{2+}, mean value at 1.958 Å)

Table S2b. Vanadin(III) solvates

CSD	ICSD	avg. $d_{V\text{-}O}$	Structure	$d_{V\text{-}O}$/Å	Comment
HURVTI01		1.93*5* Å	$[V(OC(NH_2)_2)_6]I_3$	6·1.93 *(in text)*	urea, 90 K, 2.86 Å in CSD
HURVTI		1.98*5* Å	$[V(OC(NH_2)_2)_6]I_3$	6·1.98 *(in text)*	urea, 300 K, 2.96 Å in CSD
PIZBIJ		2.027 Å	$Li_3[V(OC_{12}H_{19}O_5)_6]C_6H_5CH_3$	2·(2.020, 2.028, 2.033)	substituted glucanofuranose
	Mean:	**1.982 Å [3 structures]**			

Excluded structures (6): VAACAC, VAACAC01, VAACAC02, VAACAC12, VAACAC13, VAACAC14 (all anionic)

Table S3a. Vanadium(IV) hydrates

CSD	ICSD	$d_{V=O}$/Å;	$d_{V\text{-}O perp}$/Å;	$d_{V\text{-}O trans}$/Å	Structure	Comment
	51489	1.570;	2.030, 2.030, 2.030, 2.030;	2.210	$[Na(H_2O)_2]_2[VO(H_2O)_5][SiW_{12}O_{40}]\cdot 4H_2O$	
OBUZUH		1.576;	2.028, 2.035, 2.036, 2.049;	2.171	$[VO(H_2O)_5](C_7H_5SO_6)\cdot 2H_2O$	
LEYMIL		1.577;	2.007, 2.013, 2.023, 2.059;	2.177	$[VO(H_2O)_5][Cu_2C_{16}H_{14}N_8O_{13}S_3]\cdot 7H_2O$	
SIBGEQ		1.577;	2.026, 2.026, 2.028, 2.028;	2.175	$[VO(H_2O)_5](CF_3SO_3)_2$	
	92978	1.582;	2.019, 2.019, 2.034, 2.034;	2.231	$[VO(H_2O)_5]SO_4$	
	8103	1.584;	1.993, 2.006, 2.008, 2.019;	2.182	$[VO(H_2O)_5]SO_4$	
	10433	1.586;	2.004, 2.021, 2.023, 2.029;	2.160	$[VO(H_2O)_5]SO_4\cdot H_2O$	
	23308	1.591;	2.017, 2.017, 2.031, 2.031;	2.217	$[VO(H_2O)_5]SO_4$	
	69125	1.599;	2.010, 2.021, 2.024, 2.032;	2.161	$[VO(H_2O)_5]SO_4\cdot H_2O$	
	Mean:	**1.586 Å**	**2.024 Å**	**2.189 Å [9 structures]**		

Excluded structures: *WAJKOI (a.k.a. 99952; anionic), XACTOK (a.k.a. 151325; anionic), 15748 (anionic), 24839 (anionic), 40420 (anionic), 55332 (anionic)*

Table S3b. Vanadium(IV) solvates

CSD	ICSD	$d_{V=O}$/Å;	$d_{V\text{-}O perp}$/Å;	$d_{V\text{-}O trans}$/Å	Structure	Comment
	39393	1.527;	1.996, 2.002, 2.005, 2.015;	2.190 Å	$[VO(OC(NH_2)_2)_5)Br_2\cdot OC(NH_2)_2\cdot HBr\cdot H_2O$	urea
VODMSO01		1.593;	2.022, 2.039, 2.042, 2.047;	2.191 Å	$[VO(OS(CH_3)_2)_5](ClO_4)_2$	dmso
BAVCUW		1.603;	1.980, 2.020, 2.026, 2.034;	2.169 Å	$[VO(OS(CH_3)_2)_5]I_2$	dmso
DMSVRE		1.610;	1.941, 2.028, 2.065, 2.084;	2.180 Å	$[VO(OS(CH_3)_2)_5](ReO_4)_2$	dmso
	Mean:	**1.583 Å**	**2.022 Å**	**2.183 Å [4 structures]**		

Excluded structures (2): VDMSOP10 (incorrect; no coord.) and VODMSO (no coord.)

Table S4a. Vanadium(V) hydrates

CSD	ICSD	$d_{V=O}$/Å;	$d_{V\text{-}O perp}$/Å;	$d_{V\text{-}O trans}$/Å	∠O=V=O/°	Structure	Comment
			~ none listed ~				

Table S4b. Vanadium(V) solvates

CSD	ICSD	$d_{V=O}$/Å;	$d_{V\text{-}O}$/Å	∠O=V=O/°	Structure	Comment
XOKNAN		1.606, 1.621;	2.014, 2.019, 2.027	108.3	$[VO_2(OPC_{18}H_{15})_3]Cl_2$	

Table S4c. Vanadium(V) anionic hydrates (CN = 5)

CSD	ICSD	$d_{V=O}$/Å;	$d_{V\text{-}O}$/Å	∠O=V=O/°	Structure	Comment
	51784	1.592, 1.682;	1.917, 1.941, 2.002 +	108.1	$K_3(VO_2)_2(PO_4)(HPO_4)\cdot H_2O$	*tbp*
		1.613, 1.645;	1.927, 1.999, 2.022	107.5		
	166893	1.619, 1.640;	1.971, 2.014, 2.038	105.8	$Na(VO_2)(IO_3)_2\cdot 2H_2O$	*tbp*
	51098	1.629, 1.632;	1.984, 1.995, 2.018	106.4	$Ba_2(VO_2)(PO_4)(HPO_4)\cdot H_2O$	*tbp*
	Mean:	**1.631 Å**	**1.986 Å [3 structures]**			

Excluded: 93843 (CN=5&6)

Table S4d. Vanadium(V) anionic hydrates (CN = 6)

CSD	ICSD	$d_{V=O}$/Å;	$d_{V\text{-}O perp}$/Å;	$d_{V\text{-}O trans}$/Å	∠O=V=O/°	Structure	Comment
	158951	1.573, 1.654;	1.993, 2.027;	2.109, 2.256	107.6	$Rb((VO_2)(SO_4)(H_2O)_2)\cdot H_2O$	
	158948	1.588, 1.596;	1.985, 2.000;	2.153, 2.311	108.9	$K((VO_2)(SO_4)(H_2O)_2)\cdot H_2O$	
	363	1.594, 1.682;	1.982, 2.037;	2.094, 2.237	104.8	$VO_2IO_3\cdot 2H_2O$	
	158950	1.605, 1.658;	2.004, 2.032;	2.140, 2.287	103.7	$Tl((VO_2)(SO_4)(H_2O)_2)\cdot H_2O$	
	280295	1.621, 1.635;	2.003, 2.010;	2.230, 2.255	103.8	$(NH_4)_3(VO_2)(SO_4)_2\cdot 1.5H_2O$	
	158949	1.637, 1.674;	2.061, 2.068;	2.205, 2.273	110.2	$NH_4((VO_2)(SO_4)(H_2O)_2)\cdot H_2O$	
	410957	1.645, 1.656;	1.918, 1.955;	2.191, 2.395	103.0	$Cd(VO_2)(PO_4)\cdot H_2O$	
	416841	1.649, 1.655;	1.954, 1.963;	2.163, 2.471	103.3	$(NH_4)_4((VO_2)_2(Te_2O_8(OH)_2))\cdot 2H_2O$	
	Mean:	**1.632 Å**	**1.999 Å**	**2.236 Å [8 structures]**			

Excluded: 91845 (odd bond distribution),93843 (CN=5&6), 109614 (odd bond distribution; V^{4+}?), 109862 (odd bond distribution)

Table S4e. Vanadium(V) anionic solvates (CN = 6)

CSD	ICSD	$d_{V=O}$/Å;	$d_{V\text{-}Operp}$/Å;	$d_{V\text{-}Otrans}$/Å	∠O=V=O/°	Structure	Comment
AOXOVA01		1.626, 1.667;	1.983, 2.027;	2.186, 2.258	103.8	$(NH_4)_3VO_2(O_2C_2O_2)\cdot 2H_2O$	bidentate
KOXALV	109849	1.628, 1.638;	1.995, 2.009;	2.158, 2.230	104.3	$K_3(O_2C_2O_2)(VO_2)\cdot 3H_2O$	bidentate
KOXALV01	109850	1.630, 1.643;	1.992, 2.014;	2.165, 2.237	104.3	$K_3(O_2C_2O_2)(VO_2)\cdot 3H_2O$	bidentate
AOXOVA		1.634, 1.648;	1.973, 1.988;	2.184, 2.235	103.8	$(NH_4)_3VO_2(O_2C_2O_2)\cdot 2H_2O$	bidentate
OJEHOB		1.641, 1.641;	1.977, 1.977;	2.181, 2.181	104.4	$(NH_4)(C_5H_4NO_3)_2(VO_2)\cdot 3H_2O$	bidentate
	Mean:	**1.640 Å**	**1.994 Å**	**2.202 Å [5 structures]**			

Excluded: DAQSET, (strained bidentate), FAPJEL (strained bidentate)

Table S5a – Selected bond distances in Å for **1**.

V1-O1	1.569(3)
V1-O11	2.0304(19)
V1-O11_c	2.0304(19)
V1-O12	2.023(2)
V1-O12_c	2.023(2)
V1-O13	2.183(3)
S2-O21	1.432(2)
S2-O22	1.440(3)
S2-C2	1.812(8)
C2-F21	1.305(8)
C2-F22	1.264(5)
S3-O31	1.4480(18)
S3-O32	1.424(3)
S3-C3	1.830(5)
C3-F31	1.311(3)
C3-F32	1.309(5)

Table S5b – Selected bond angles in degrees for **1**.

O1-V1-O11	99.38(10)
O1-V1-O11_c	99.38(10)
O1-V1-O12	96.67(10)
O1-V1-O12_c	96.67(10)
O1-V1-O13	175.11(14)
O11-V1-O11_c	88.48(8)
O11-V1-O12	87.68(8)
O11-V1-O12_c	163.90(9)
O11-V1-O13	84.09(8)
O11_c-V1-O13	84.09(8)
O11_c-V1-O12	163.90(9)
O11_c-V1-O12_c	87.68(8)
O12-V1-O12_c	91.71(9)
O12-V1-O13	79.96(8)
O12_c-V1-O13	79.96(8)

Table S6a – Selected bond distances in Å for **2a**.

V1-O6	1.575(5)
V1-O1	1.999(5)
V1-O2	2.010(5)
V1-O3	2.009(6)
V1-O4	2.021(5)
V1-O5	2.166(5)
O1-S1	1.521(5)
S1-C11	1.780(10)
S1-C12	1.748(9)
O2-S2	1.528(5)
S2-C21	1.731(10)
S2-C22	1.749(10)
O3-S3A	1.397(7)
S3A-C31	1.792(12)
S3A-C32	1.711(11)
O3-S3B	1.381(7)
S3B-C31	1.813(11)
S3B-C32	1.624(12)
O4-S4	1.481(5)
S4-C41	1.715(10)
S4-C42	1.738(13)
O5-S5	1.490(5)
S5-C51	1.777(10)
S5-C52	1.777(11)

Table S6b – Selected bond angles in degrees for **2a**.

O6-V1-O1	97.9(2)
O6-V1-O2	98.4(3)
O6-V1-O3	96.6(3)
O6-V1-O4	97.3(2)
O6-V1-O5	178.2(3)
O1-V1-O2	88.2(2)
O1-V1-O3	90.2(2)
O1-V1-O4	164.8(2)
O1-V1-O5	83.8(2)
O2-V1-O3	165.0(2)
O2-V1-O4	89.6(2)
O2-V1-O5	81.3(2)
O3-V1-O4	88.1(2)
O3-V1-O5	83.8(2)
O4-V1-O5	81.0(2)
V1-O1-S1	124.9(3)
V1-O2-S2	124.3(3)
V1-O3-S3A	132.9(4)
V1-O3-S3B	137.7(4)
V1-O4-S4	127.1(3)
V1-O5-S5	129.7(3)

Table S7a – Selected bond distances in Å for **3**.

V1-O10	1.577(5)
V1-O1	1.959(4)
V1-O2	1.964(4)
V1-O3	1.975(5)
V1-O4	1.984(4)
V2-O20	1.570(5)
V2-O5	1.961(4)
V2-O6	1.995(5)
V2-O7	1.956(4)
V2-O8	1.955(5)
O1-C1	1.285(9)
O2-C2	1.277(8)
O3-C3	1.275(9)
O4-C4	1.271(8)
O5-C5	1.277(7)
O6-C6	1.267(9)
O7-C7	1.275(8)
O8-C8	1.286(10)
C1-N11	1.333(10)
C1-N12	1.324(11)
C2-N21	1.314(10)
C2-N22	1.321(10)
C3-N31	1.321(10)
C3-N32	1.337(9)
C4-N41	1.360(9)
C4-N42	1.303(9)
C5-N51	1.321(9)
C5-N52	1.336(10)
C6-N61	1.324(10)
C6-N62	1.341(10)
C7-N71	1.334(8)
C7-N72	1.326(8)
C8-N81	1.316(13)
C8-N82	1.349(11)

Table S7b – Selected bond angles in degrees for **3**.

O10-V1-O1	109.5(2)
O10-V1-O2	105.1(2)
O10-V1-O3	108.3(2)
O10-V1-O4	104.2(2)
O1-V1-O2	86.13(17)
O1-V1-O3	142.1(2)
O1-V1-O4	84.63(18)
O2-V1-O3	85.29(18)
O2-V1-O4	150.7(2)
O3-V1-O4	85.13(18)
O20-V2-O5	107.3(2)
O20-V2-O6	105.1(2)
O20-V2-O7	108.0(2)
O20-V2-O8	106.6(2)
O5-V2-O6	85.51(18)
O5-V2-O7	144.8(2)
O5-V2-O8	85.25(18)
O6-V2-O7	86.02(18)
O6-V2-O8	148.3(2)
O7-V2-O8	84.30(17)
V1-O1-C1	136.7(4)
V1-O2-C2	136.6(5)
V1-O3-C3	136.7(4)
V1-O4-C4	135.4(4)
V2-O5-C5	136.2(5)
V2-O6-C6	135.1(4)
V2-O7-C7	137.9(4)
V2-O8-C8	131.8(4)

Table S8a – Selected bond distances in Å for **5**.

V1-O11	1.594(6)
V1-O12	1.591(5)
V1-O13	2.048(11)
V1-O13B	2.040(12)
V1-O14	2.206(5)
V1-O15	2.202(6)
V1-O16	1.985(11)
V1-O16B	1.998(13)
O13-S13	1.521(12)
S13-C131	1.748(8)
S13-C132	1.815(9)
O13B-S13B	1.537(13)
S13B-C131	1.734(9)
S13B-C132	1.811(9)
O14-S14	1.490(6)
S14-C141	1.779(7)
S14-C142	1.741(9)
O15-S15	1.505(5)
S15-C152	1.755(10)
S15-C151	1.745(9)
O16-S16	1.531(12)
S16-C161	1.764(8)
S16-C162	1.832(10)
O16B-S16B	1.541(13)
S16B-C161	1.758(8)
S16B-C162	1.828(10)

Table S8b – Selected bond angles in degrees for **5**.

O11-V1-O12	104.0(3)
O11-V1-O13	106.3(4)
O11-V1-O13B	84.0(4)
O11-V1-O14	92.2(2)
O11-V1-O15	164.9(2)
O11-V1-O16	85.6(4)
O11-V1-O16B	108.3(4)
O12-V1-O13	83.4(4)
O12-V1-O13B	108.8(4)
O12-V1-O14	163.7(3)
O12-V1-O15	91.1(3)
O12-V1-O16	105.3(4)
O12-V1-O16B	86.3(4)
O12-V1-O16B	86.3(4)
O13-V1-O14	90.8(4)
O13-V1-O15	75.5(3)
O13-V1-O15	75.5(3)
O13-V1-O16	163.3(4)
O13B-V1-O14	71.1(4)
O13B-V1-O15	91.7(4)
O13B-V1-O16B	158.1(5)
O14-V1-O15	72.7(2)
O14-V1-O16	76.9(4)
O14-V1-O16B	90.0(4)
O15-V1-O16	89.9(3)
O15-V1-O16B	71.7(4)

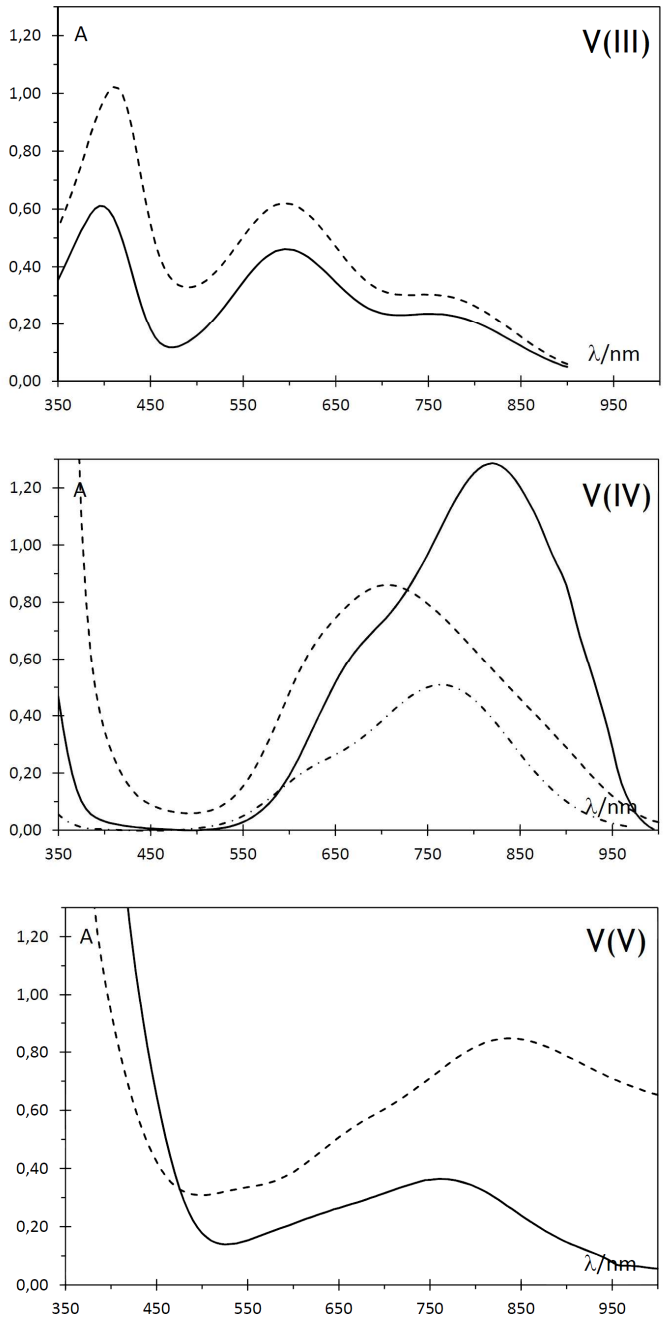

Figure S1. UV-Vis spectra of the studied vanadium solutions. (top) vanadium(III) in water at pH=0.60 (**L0**, solid line) and pH=1.22 (dashed line, $\mathbf{L0_{hyd}}$), the solutions are diluted ca. 5 times, $c_V = 0.1$ mol·dm^{-3}; (middle) vanadium(IV) in water (dot dashed line, **L1a**), dmso (solid line, **L2a**) and dmpu (dashed line, **L3**), the solutions are diluted ca. 25 times; and (bottom) vanadium(V) in water (solid line, **L4b**) and dmso (dashed line, **L5a**), the solutions are diluted ca. 100 times.

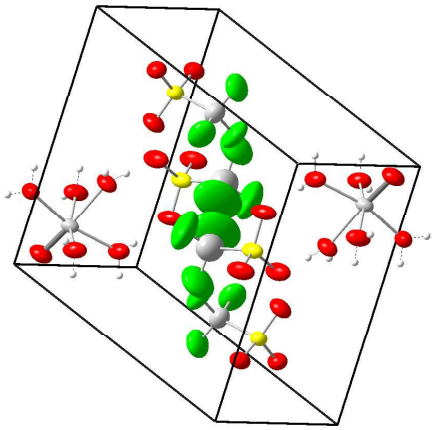

Figure S2. Representation of the unit cell for **1**. Thermal ellipsoids are set at 30 % probability.

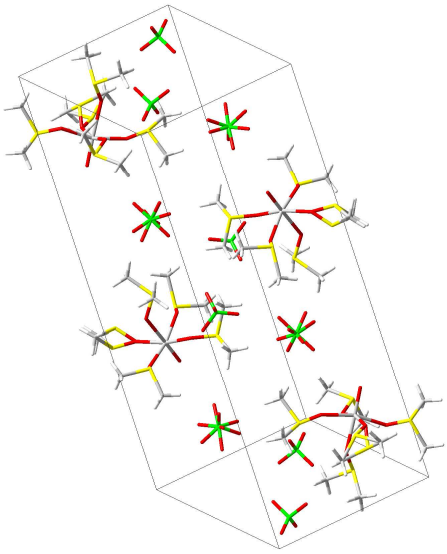

Figure S3. Representation of the unit cell for **2a**. The alternative positions for the disordered perchlorate ions are represented as shown.

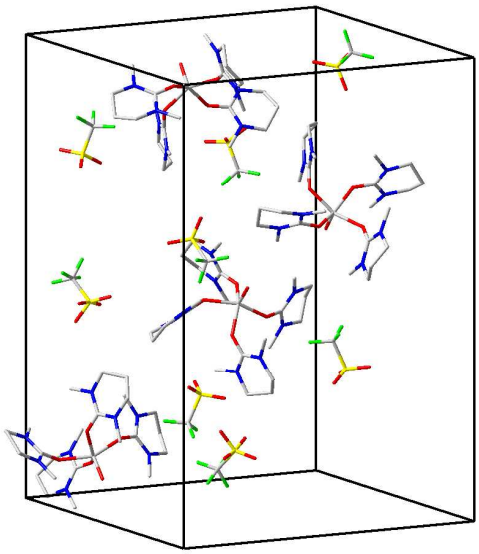

Figure S4. Representation of the unit cell for **3**.

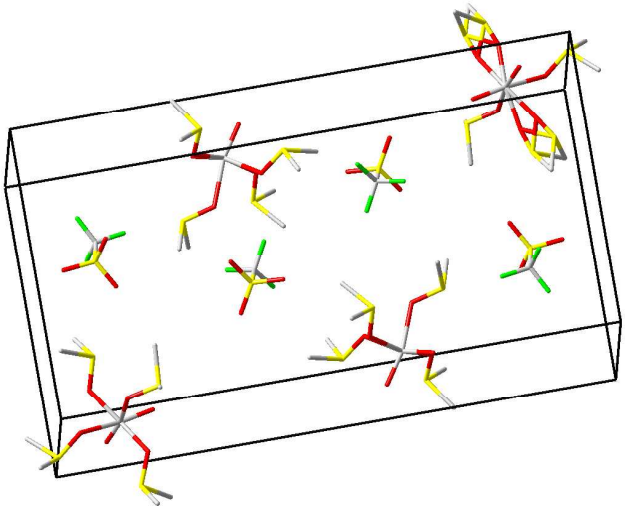

Figure S5. Representation of the unit cell for **5**. The alternative positions for the equatorial dmso molecules are only shown on one of the complexes.

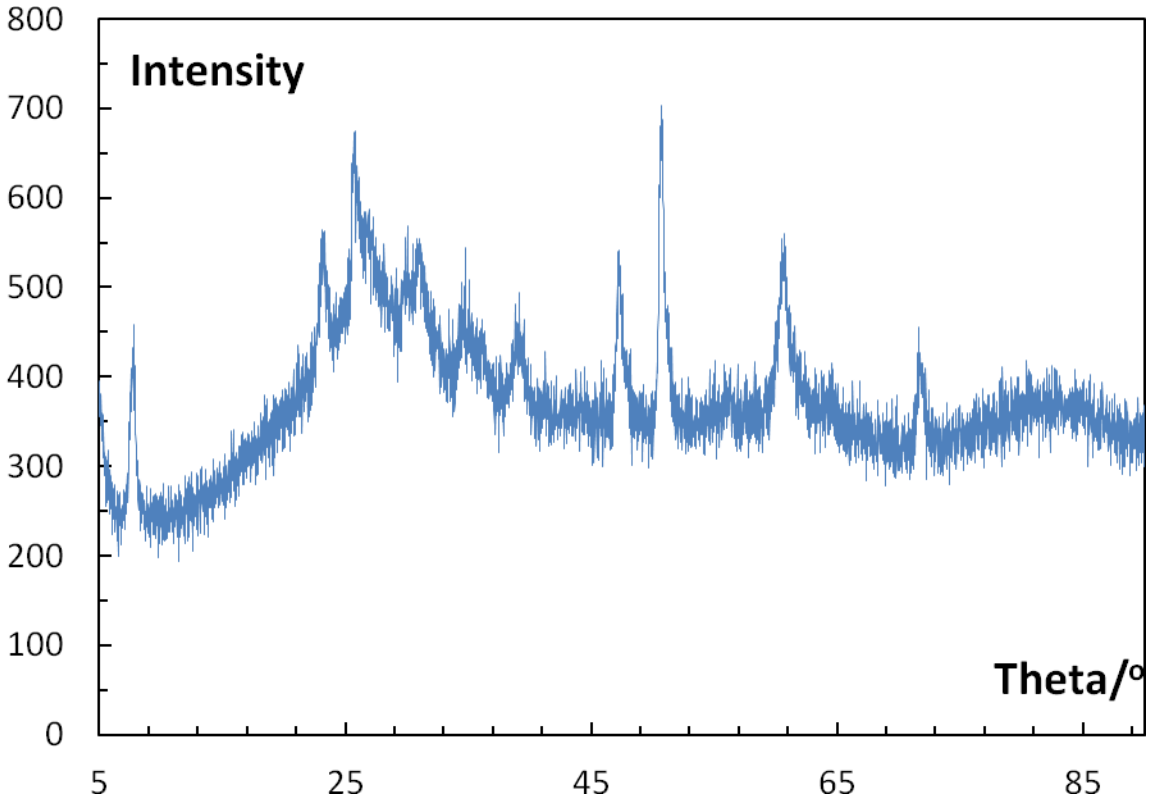

Figure S6. Powder diffraction data of dioxovanadium(V) perchlorate.