Supporting Information

Coordination Environment and EPR Properties of Vanadyl Centers: A Comparative DFT Study of VOPc and Silica-Supported VO Species

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Topics in Catalysis

S0. Computational details: program settings

Gaussian 09, Rev. D.01 (geometries). Each structure was computed as a chain of linked jobs: stability test of the initial unrestricted wave function, optimization, stability test at the optimized geometry. Route sections:

```
# UPBE1PBE gen EmpiricalDispersion=GD3 Stable=Opt SCF=Tight Int=(UltraFine,acc2e=12) nosymm
# opt UPBE1PBE gen EmpiricalDispersion=GD3 geom=allcheck guess=read SCF=Tight Int=(UltraFine,acc2e=12) nosymm
# UPBE1PBE Chkbasis EmpiricalDispersion=GD3 geom=allcheck guess=read Stable=Opt SCF=Tight Int=(UltraFine,acc2e=12) nosymm
# nmr=giao UPBE1PBE Chkbasis EmpiricalDispersion=GD3 geom=allcheck guess=read   (Gaussian EPR parameters, Table S1)
```

Basis sets: Wachters+f on V, 6-311G(d,p) on all other atoms (gen). SMD calculations: SCRF=(SMD,Solvent=Water) in optimization and property steps. Constrained V–O_w distances (Table S8): opt=modredundant with the V–O_w bond frozen.

ORCA 5.0.4 (EPR parameters, single points on the Gaussian geometries). Example input (model e):

```
! UKS PBE0 D3ZERO 6-311G(d,p) TightSCF DEFGRID3 NoTRAH
%basis  NewGTO V "CP(PPP)" end  end
%method SpecialGridAtoms 23  SpecialGridIntAcc 7  end
* xyzfile -1 2 vosi_3f_H2O.xyz
%eprnmr
  GTensor true
  Nuclei = all V  {AISO, ADIP, AORB}
  Nuclei = all O  {AISO, ADIP}
  Nuclei = all H  {AISO, ADIP}
  Nuclei = all Si {AISO, ADIP}
  ORI GIAO
end
```

RIJCOSX with the def2/J auxiliary basis (ORCA 5 default for hybrid functionals); spin–orbit operator SOMF(1X) (default); ^{14}N: AISO, ADIP. B3LYP and BHandHLYP (Table S6): same input without D3ZERO. SMD single points: keyword CPCM with `%cpcm smd true; SMDsolvent "water" end`. For VOPc with BHandHLYP the SCF was started from the PBE0 orbitals (MORead); the default guess converged to a V=O π^* solution 55 kcal mol^{-1} higher in energy.

$\langle S^2 \rangle$ (PBE0): 0.756–0.775 for all systems in the main text.

Frequencies. Frequencies were computed at the optimization level. Full Hessian: VOPc, the weakly bound VOPc–X (X = MeCN, CO, PH_3), the aqua ion and all silica models. Partial Hessian (V, oxo O, four equatorial donors and the axial ligand unfrozen): the other VOPc–X systems.

Table S1: Gaussian and ORCA g and ^{51}V hyperfine for all vanadyl models (incl. cluster-size test). Vanadyl ($V^{IV}O^{2+}$, $S = \frac{1}{2}$) in three environments: phthalocyanine, water and silica. g and ^{51}V hyperfine principal values ordered $\perp_1$ / $\perp_2$ / $\parallel$. Gaussian 09: UPBE0-D3, Wachters+f (V) / 6-311G(d,p), optimized geometries (no spin–orbit term in A; Δg about twice too large for V, cf. VOPc); ORCA 5.0.4: UKS PBE0-D3, CP(PPP) (V) / 6-311G(d,p), GIAO, SOMF(1X), single points on the Gaussian geometries.

			$g_{\perp1}/g_{\perp2}/g_{\parallel}$		$A(^{51}\mathrm{V})$ (MHz)				
System	Model	q	Gaussian	ORCA	Gaussian	ORCA	a_{iso} (ORCA)	$\langle S^2\rangle$	Remark
Phthalocyanine (N_4 macrocycle)									
VOPc	gas phase	0	1.9740/1.9740/1.9419	1.9885/1.9885/1.9743	−154/−154/−447	−151/−151/−457	−253	0.764	
VOPc	exp., 1:1000 in TiOPc [1]		1.987/1.987/1.966		168/168/477		271		benchmark
Aqua ion (O_4 + trans H_2O, distorted octahedron)									
$[VO(H_2O)_5]^{2+}$	gas phase	2	1.9659/1.9653/1.8791	1.9847/1.9845/1.9470	−237/−236/−536	−233/−233/−554	−340	0.773	
$[VO(H_2O)_5]^{2+}$	SMD water	2	1.9621/1.9606/1.8889	1.9834/1.9828/1.9527	−202/−197/−509	−200/−195/−522	−306	0.771	
$[VO(H_2O)_5]^{2+}$	exp., frozen solution [2]		1.9792/1.9772/1.9335		208.5/208.5/547.0		321		benchmark
Silica-supported V=O: cluster models of Dinse et al. [3] (Si–H terminated)									
a	$VOH(OSi)_3$	0	1.9528/1.9179/1.8706	1.9787/1.9630/1.9420	−160/−17/−361	−176/−27/−386	−196	0.757	$\lvert A_{\parallel}\rvert$ too small, rhombic $A_{\perp}$: excluded
b	$VOH(OSi)_4$	−1	1.9338/1.9135/1.8579	1.9718/1.9614/1.9361	−75/−71/−386	−100/−83/−402	−195	0.758	$\lvert A\rvert$ too small: excluded
c	$VO(OSi)_3$	−1	1.9731/1.9623/1.7289	1.9883/1.9827/1.8829	−185/−180/−492	−187/−176/−537	−300	0.760	$g_{\parallel}$ too low
d	$VO(OSi)_4$	−2	1.9600/1.9600/1.8842	1.9820/1.9820/1.9501	−178/−178/−496	−177/−177/−513	−289	0.761	4 eq. O donors
Silica: model c with a fourth equatorial O donor (e–g, this work)									
e	$VO(OSi)_3(OH_2)$	−1	1.9729/1.9620/1.8243	1.9879/1.9827/1.9225	−205/−204/−512	−203/−199/−540	−314	0.763	V–O_w 2.28 Å
f	$VO(OSi)_3(HOSiH_3)$	−1	1.9681/1.9584/1.8110	1.9857/1.9813/1.9170	−202/−189/−504	−201/−187/−534	−307	0.763	V–O 2.11 Å
g	$VO(OSi)_3(O(SiH_3)_2)$	−1	1.9705/1.9593/1.8230	1.9868/1.9816/1.9220	−204/−192/−505	−201/−189/−533	−308	0.763	V–O 2.14 Å
e, SMD water	$VO(OSi)_3(OH_2)$	−1	1.9712/1.9526/1.8448	1.9875/1.9791/1.9325	−192/−189/−503	−189/−185/−524	−299	0.762	SMD opt.: V–O_w 2.20 Å
Silica: cluster size (second silica shell added)									
c, large cluster	26 atoms	−1	1.9740/1.9638/1.7231	1.9887/1.9834/1.8806	−195/−189/−502	−196/−186/−548	−310	0.760	cf. c (14 atoms)
e, large cluster	29 atoms	−1	1.9736/1.9627/1.8262	1.9883/1.9832/1.9235	−211/−211/−519	−209/−206/−547	−320	0.763	cf. e (17 atoms)
VO/SBA-15	exp., pulsed EPR/ENDOR [3]		1.9871/1.9846/1.9391		±214/±199/±551 (same sign)		321		reference
VO/SBA-15	exp., high-field EPR [4]		1.9808/1.9738/1.9330		104/64/550				$A_{\perp}$ differs from [3]

Charges follow from VO^{2+} (V^{IV}, d^1) + one −1 per ≡Si–O^- anchor; V–OH adds +1; H_2O, silanol and siloxane are neutral. The fifth O donor stays bound after optimization in all three cases (V–O distances from the Gaussian geometries; 2.25 Å for the large e cluster); with silanol and siloxane one V–OSi bond lengthens to 2.07–2.12 Å. Perpendicular components are listed in decreasing magnitude. Dinse et al. [3] computed only $A(^{51}\mathrm{V})$ (Gaussian, BHandHLYP, no spin–orbit term): a 53/ − 196/ − 281, b −64/ − 65/ − 391, c −223/ − 232/ − 550, d −19/ − 49/ − 68 MHz. Experimental a_{iso} of [2] from the principal values. [1] Atzori et al., JACS 2016, 138, 2154. [2] Grant et al., J. Phys. Chem. B 1999, 103, 10627. [3] Dinse et al., J. Phys. Chem. C 2013, 117, 16921. [4] Dinse et al., J. Phys. Chem. C 2008, 112, 17664.

Table S2: VOPc series: neutral ligands (trans to oxo). Gaussian 09: UPBE0-D3, Wachters+f (V) / 6-311G(d,p) (other atoms), optimized geometries, ΔE; ORCA 5.0.4: UKS PBE0-D3(zero), CP(PPP) (V) / 6-311G(d,p), DEFGRID3, GIAO, SOMF(1X), single points on the Gaussian geometries.

			ORCA		$g_{\perp 1}/g_{\perp 2}/g_{\parallel}$		ORCA hyperfine (MHz)			
System	d(V–X) (Å)	ΔE (eV)	ρ_{V}	$\langle S^2 \rangle$	Gaussian	ORCA	$A(^{51}\mathrm{V})$ $\perp_1$ / $\perp_2$ / $\parallel$	a_{iso}(V)	a_{iso}(X)	$a_{\mathrm{iso}}(^{14}\mathrm{N_{in}})$
VOPc	–	–	1.21	0.764	1.9740/1.9740/1.9419	1.9885/1.9885/1.9743	−151/−151/−457	−253	–	−7.1
H_2O	2.66	−0.49	1.22	0.764	1.9728/1.9727/1.9464	1.9879/1.9879/1.9763	−140/−140/−444	−241	−0.8	−7.2
NH_3	2.55	−0.54	1.23	0.765	1.9720/1.9720/1.9486	1.9875/1.9875/1.9773	−136/−136/−436	−236	0.3	−7.3
py	2.72	−0.58	1.23	0.764	1.9723/1.9722/1.9481	1.9877/1.9877/1.9771	−137/−137/−438	−237	0.2	−7.3
Im	2.57	−0.61	1.23	0.765	1.9720/1.9718/1.9487	1.9875/1.9875/1.9773	−136/−135/−436	−235	0.2	−7.4
MeCN	3.35	−0.36	1.21	0.764	1.9736/1.9735/1.9435	1.9883/1.9883/1.9750	−148/−148/−454	−250	0.1	−7.2
CO	3.51	−0.17	1.21	0.764	1.9739/1.9739/1.9421	1.9885/1.9885/1.9744	−150/−150/−456	−252	0.3	−7.1
PH_3	3.75	−0.24	1.21	0.764	1.9738/1.9737/1.9426	1.9884/1.9884/1.9746	−149/−149/−455	−251	1.0	−7.2

Principal values ordered $\perp_1$ / $\perp_2$ / $\parallel$ (perpendicular components in decreasing magnitude), as in Table S1. Hyperfine values are signed ORCA totals (incl. SOC term); a_{iso}(V) is the mean of the three principal values. ΔE: Gaussian binding energy. The parent VOPc is given as reference. Italic rows: weakly bound ligands (binding energy −0.17 to −0.36 eV).

Table S3: VOPc series: anions. Gaussian 09: UPBE0-D3, Wachters+f (V) / 6-311G(d,p) (other atoms), optimized geometries, ΔE; ORCA 5.0.4: UKS PBE0-D3(zero), CP(PPP) (V) / 6-311G(d,p), DEFGRID3, GIAO, SOMF(1X), single points on the Gaussian geometries.

			ORCA		$g_{\perp1}/g_{\perp2}/g_{\parallel}$		ORCA hyperfine (MHz)			
System	d(V–X) (Å)	ΔE (eV)	ρ_V	$\langle S^2\rangle$	Gaussian	ORCA	$A(^{51}\mathrm{V})$ $\perp_1$ / $\perp_2$ / $\parallel$	a_{iso}(V)	a_{iso}(X)	$a_{iso}(^{14}\mathrm{N_{in}})$
VOPc	–	–	1.21	0.764	1.9740/1.9740/1.9419	1.9885/1.9885/1.9743	−151/−151/−457	−253	–	−7.1
F^-	1.95	−3.97	1.23	0.768	1.9708/1.9708/1.9510	1.9871/1.9871/1.9782	−142/−142/−433	−239	12.3	−7.1
Cl^-	2.61	−1.16	1.23	0.766	1.9700/1.9700/1.9517	1.9867/1.9867/1.9786	−132/−132/−428	−231	1.1	−7.5
Br^-	2.83	−1.06	1.23	0.766	1.9703/1.9703/1.9515	1.9869/1.9869/1.9786	−132/−132/−428	−230	4.6	−7.5
I^-	3.24	−0.76	1.22	0.765	1.9701/1.9701/1.9518	1.9867/1.9867/1.9789	−132/−132/−432	−232	3.2	−7.5
CN^-, C-bound	2.32	−1.55	1.25	0.768	1.9696/1.9696/1.9512	1.9863/1.9863/1.9784	−131/−131/−422	−228	−7.9	−7.7
CN^-, N-bound*	2.22	−1.61	1.24	0.767	1.9697/1.9697/1.9515	1.9864/1.9864/1.9786	−132/−132/−427	−230	−0.7	−7.5
OH^-	1.99	−4.03	1.24	0.768	1.9712/1.9707/1.9505	1.9871/1.9869/1.9780	−144/−142/−431	−239	−0.1	−7.0
OCH_3^-	2.00	−3.00	1.24	0.767	1.9719/1.9712/1.9503	1.9875/1.9870/1.9779	−141/−140/−431	−237	0.1	−7.0
CH_3^{-a}	2.31	−2.81	1.26	0.771	1.9710/1.9695/1.9478	1.9870/1.9860/1.9765	−147/−139/−425	−237	−18.9	−7.9

Principal values ordered $\perp_1$ / $\perp_2$ / $\parallel$ (perpendicular components in decreasing magnitude), as in Table S1. Hyperfine values are signed ORCA totals (incl. SOC term); a_{iso}(V) is the mean of the three principal values. ΔE: Gaussian binding energy. The parent VOPc is given as reference. [a]Guided SCF start. CN^- binds through C (cyanide) or through N (isocyanide); *more stable isomer (N-bound by 1.5 kcal/mol, Gaussian). Omitted (strong spin contamination, $\langle S^2\rangle > 0.825$): H^- (1.79).

Table S4: VOPc series: first-shell variants. Gaussian 09: UPBE0-D3, Wachters+f (V) / 6-311G(d,p) (other atoms), optimized geometries, ΔE; ORCA 5.0.4: UKS PBE0-D3(zero), CP(PPP) (V) / 6-311G(d,p), DEFGRID3, GIAO, SOMF(1X), single points on the Gaussian geometries.

			ORCA		$g_{\perp1}/g_{\perp2}/g_{\parallel}$		ORCA hyperfine (MHz)			
System	d(V–X) (Å)	ΔE (eV)	ρ_V	$\langle S^2\rangle$	Gaussian	ORCA	$A(^{51}\mathrm{V})$ $\perp_1$ / $\perp_2$ / $\parallel$	a_{iso}(V)	a_{iso}(X)	$a_{iso}(^{14}\mathrm{N_{in}})$
VOPc	–	–	1.21	0.764	1.9740/1.9740/1.9419	1.9885/1.9885/1.9743	−151/−151/−457	−253	–	−7.1
[C,O]-cis	C 2.03/O 2.13	0.00	1.21	0.764	1.9795/1.9724/1.9347	1.9911/1.9878/1.9710	−157/−151/−457	−255	–	−7.2
[C,O]-trans	C 2.01/O 2.12	0.08	1.21	0.764	1.9810/1.9735/1.9361	1.9918/1.9884/1.9715	−148/−147/−449	−248	–	−7.1
[C,S]-cis[a]	C 2.07/S 2.35	0.00	1.20	0.764	1.9785/1.9748/1.9406	1.9908/1.9889/1.9741	−142/−139/−441	−241	–	−6.8
[C,S]-trans	C 1.99/S 2.38	0.22	1.20	0.764	1.9813/1.9730/1.9363	1.9919/1.9883/1.9721	−138/−134/−435	−236	–	−6.5

Principal values ordered $\perp_1$ / $\perp_2$ / $\parallel$ (perpendicular components in decreasing magnitude), as in Table S1. Hyperfine values are signed ORCA totals (incl. SOC term); a_{iso}(V) is the mean of the three principal values. ΔE: Gaussian energy relative to the more stable (cis) isomer. The parent VOPc is given as reference. [a]Guided SCF start.

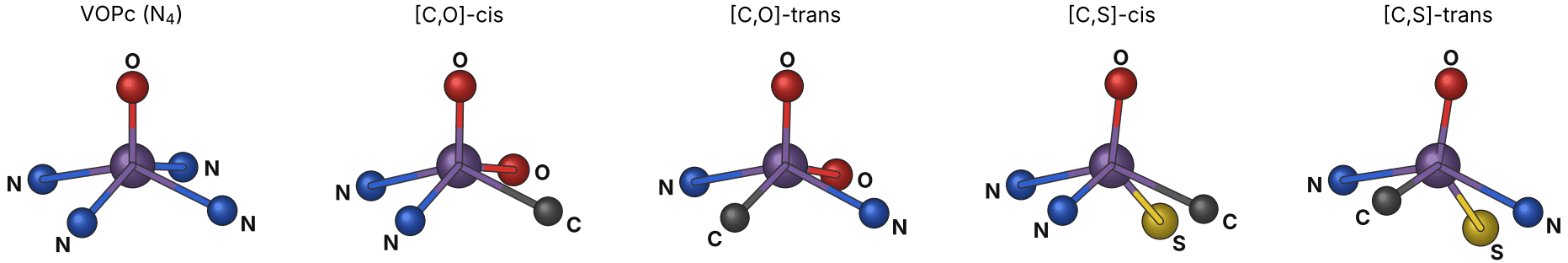

Figure S1: First-shell variants of VOPc (Table S4): two of the four inner N atoms of the phthalocyanine ring are replaced by one C and one O (or S) atom, on adjacent (cis) or opposite (trans) positions. Optimized geometries (UPBE0-D3) in their Cartesian frame, viewed as in Figure 1 of the main text (z up); only V, the oxo group and the four equatorial donor atoms are shown, the rest of the macrocycle is omitted. V–C/V–O(S) distances: [C,O]-cis 2.03/2.13, [C,O]-trans 2.01/2.12, [C,S]-cis 2.07/2.35, [C,S]-trans 1.99/2.38 Å; V–N 2.00–2.10 Å. Color code: V violet, O red, N blue, C dark grey, S yellow.

Table S5: Model d computed as a *neutral* cluster, as in Dinse et al. [3], compared with d at the charge required for V^{IV} ($q = -2$). "Vertical": $q = 0$ at the optimized $q = -2$ geometry; "optimized": $q = 0$ geometry optimized with Gaussian (UPBE0-D3). g and A: principal values (for $q = 0$ there is no V=O-type axial pattern). BHandHLYP without D3.

Model d	Geometry	Method	ρ_V	Spin located on	g	$A(^{51}V)$ (MHz)	$\langle S^2 \rangle$
$q = -2$ (V^{IV})	optimized ($q = -2$)	ORCA PBE0	1.14	V (d_{xy})	1.9820/1.9820/1.9501	−177/−177/−513	0.761
$q = 0$	vertical	ORCA PBE0	−0.25	4 eq. O (4 × 0.30)	2.0196/2.0196/2.0306	−10/−10/23	0.786
$q = 0$	vertical	ORCA BHandHLYP	−0.35	4 eq. O (4 × 0.33)	2.0219/2.0219/2.0462	−5/−5/32	0.815
$q = 0$	optimized ($q = 0$)	Gaussian PBE0	−0.20	4 eq. O (4 × 0.30)	2.0120/2.0120/2.0259	−24/−24/−7	0.770
$q = 0$	optimized ($q = 0$)	ORCA PBE0	−0.21	mainly 2 eq. O (2 × 0.40)	2.0041/2.0134/2.2099	−14/−26/−39	0.786
$q = 0$	optimized ($q = 0$)	ORCA BHandHLYP	−0.18	mainly 1 eq. O (0.71)	2.0083/2.0115/2.0282	−18/−36/−37	0.784
$q = 0$	Dinse et al. [3]	Gaussian BHandHLYP	–	–	–	−19/−49/−68	–
VO/SBA-15	exp. [3]				1.9871/1.9846/1.9391	±214/±199/±551	

Neutral d is not a V^{IV} site: in every calculation the unpaired electron sits on the equatorial siloxide O atoms (V^{V} + $O^{\bullet -}$), ρ_V is small and negative (spin polarization), $g > 2$ and $|A(^{51}V)| < 40$ MHz; Dinse et al. likewise obtained small ^{51}V couplings ($\leq$68 MHz) for this neutral model. How far the O hole is delocalized depends on the method (four, two or one O atom); the conclusion does not. ρ_V: Mulliken spin population.

Table S6: Functional dependence (ORCA, CP(PPP)/6-311G(d,p), SOMF(1X), same geometries; HF exchange fraction in parentheses). $\Delta g_\parallel$ and $\Delta|A_\parallel|$: deviation of the computed value from experiment (VOPc [1], aqua ion [2], VO/SBA-15 [3]). No empirical correction is applied.

System	Functional	$g_{\perp1}/g_{\perp2}/g_\parallel$	$A(^{51}\mathrm{V})$ (MHz)	a_iso	$\Delta g_\parallel$	$\Delta\lvert A_\parallel\rvert$ (%)	$\langle S^2\rangle$
Benchmarks							
VOPc	B3LYP (20 %)	1.9892/1.9892/1.9753	−117/−117/−429	−221	0.009	−10	0.760
	PBE0 (25 %)	1.9885/1.9885/1.9743	−151/−151/−457	−253	0.008	−4	0.764
	BHandHLYP (50 %)	1.9836/1.9836/1.9667	−172/−172/−504	−283	0.001	6	0.770
VOPc	exp. [1]	1.987/1.987/1.966	168/168/477	271			
$[VO(H_2O)_5]^{2+}$, gas	B3LYP (20 %)	1.9858/1.9856/1.9500	−185/−184/−512	−294	0.016	−6	0.766
	PBE0 (25 %)	1.9847/1.9845/1.9470	−233/−233/−554	−340	0.014	1	0.773
	BHandHLYP (50 %)	1.9778/1.9769/1.9367	−273/−272/−609	−385	0.003	11	0.800
$[VO(H_2O)_5]^{2+}$	exp. [2]	1.9792/1.9772/1.9335	208.5/208.5/547.0	321			
Silica models							
c	B3LYP (20 %)	1.9891/1.9835/1.8960	−148/−137/−497	−261	−0.043	−10	0.758
	PBE0 (25 %)	1.9883/1.9827/1.8829	−187/−176/−537	−300	−0.056	−3	0.760
	BHandHLYP (50 %)	1.9836/1.9794/1.8606	−213/−203/−596	−337	−0.078	8	0.765
e	B3LYP (20 %)	1.9889/1.9836/1.9285	−161/−157/−500	−273	−0.011	−9	0.760
	PBE0 (25 %)	1.9879/1.9827/1.9225	−203/−199/−540	−314	−0.017	−2	0.763
	BHandHLYP (50 %)	1.9822/1.9786/1.9082	−233/−229/−599	−354	−0.031	9	0.770
d	B3LYP (20 %)	1.9830/1.9830/1.9532	−138/−138/−478	−251	0.014	−13	0.759
	PBE0 (25 %)	1.9820/1.9820/1.9501	−177/−177/−513	−289	0.011	−7	0.761
	BHandHLYP (50 %)	1.9774/1.9774/1.9409	−196/−196/−561	−318	0.002	2	0.767
VO/SBA-15	exp. [3]	1.9871/1.9846/1.9391	±214/±199/±551	321			

PBE0 rows are the PBE0-D3 single points of Table S1; the B3LYP and BHandHLYP single points are run without D3 (not parametrized for BHandHLYP in ORCA 5). D3 does not enter g or A at fixed geometry. VOPc/BHandHLYP converges to the d_{xy} ground state only when started from the PBE0 orbitals; the default guess leads to a V=O π^* solution 55 kcal/mol higher in energy. BHandHLYP gives $\langle S^2\rangle = 0.800$ for the aqua ion.

Table S7: Hyperfine couplings to neighboring nuclei (ORCA PBE0, MHz). ^{1}H: signed principal values of the proton with the largest coupling. ^{29}Si: isotropic couplings of the Si atoms bonded to the V–O–Si anchors.

Nucleus	System	A_1	A_2	A_3	a_{iso}	Note
^{1}H (V–OH_2)	e	−2.7	−3.6	15.1	2.9	V–O–H 86°, H-bonded; V–O_w 2.28 Å
^{1}H (V–OH_2)	e, large cluster	−2.2	−3.0	15.3	3.4	V–O–H 86°
^{1}H (Si–OH)	f	−1.2	−1.7	9.9	2.3	
^{1}H (Si–H)	g	−1.8	−2.1	4.6	0.2	no O–H near V
^{1}H (Si–H)	d	0.8	−2.1	−2.2	−1.2	no O–H near V
^{1}H (eq. H_2O)	$[VO(H_2O)_5]^{2+}$, SMD	−3.4 to 4.8	−4.8 to 5.3	10.2 to 20.3	0.7 to 10.1	8 protons, β = 11–130°; a_{iso} follows $11.07 - 12.86\cos^2\beta$ [6]
^{1}H (eq. H_2O)	$[VO(H_2O)_5]^{2+}$, gas	2.0	2.4	15.7	6.7	two waters, $\beta = 69°$
^{1}H (eq. H_2O)	$[VO(H_2O)_5]^{2+}$, gas	−5.4 to −6.0	−6.7	6.9 to 7.9	−1.4 to −1.9	two waters, $\beta = 0/180°$ (plane contains V=O)
^{1}H (eq. H_2O)	$[VO(H_2O)_5]^{2+}$, exp. [5,6]	1.8–3.9	2.2–4.2	16.4–17.9	7.0 to 8.7	in-plane waters, single crystal
^{1}H (ax. H_2O)	$[VO(H_2O)_5]^{2+}$, gas	−3.1	−3.2	6.8	0.2	
^{1}H (ax. H_2O)	$[VO(H_2O)_5]^{2+}$, SMD	−3.3	−3.5	7.9	0.4	
^{1}H (ax. H_2O)	$[VO(H_2O)_5]^{2+}$, exp. [5,6]	−3.4	−3.1	6.5	−0.04, 0.01	single crystal
^{1}H (V–OH)	a	16.6	19.2	31.8	22.5	too large
^{1}H (V–OH)	b	−3.1	−7.9	11.9	0.3	
^{1}H	VO/SBA-15, exp. [3]	$\lvert A\rvert$ = 0.5 / 0.5 / 17(2)			±6(1)	as-prepared sample; signs not determined
^{29}Si (anchor)	c		–		−11.3, −11.2, −0.3	
^{29}Si (anchor)	c, large cluster		–		−11.9, −11.5, 1.5	
^{29}Si (anchor)	e		–		−7.5 (×2), −0.3	
^{29}Si (anchor)	e, large cluster		–		−6.5 (×2), 0.9	
^{29}Si (anchor)	f		–		−6.2, −4.5, −2.7	silanol Si −1.8
^{29}Si (anchor)	g		–		−6.5, −3.3, −2.2	siloxane Si −3.4, −2.5
^{29}Si (anchor)	d		–		−0.06 (×4)	

Experimental aqua-ion values: a_{iso} + dipolar principal values from single-crystal ENDOR of $[VO(H_2O)_5]^{2+}$ in $Mg(NH_4)_2(SO_4)_2{\cdot}6H_2O$ [5], as tabulated in [6] (signs relative to $A(^{51}V)$, taken as negative); range over the four protons of the two in-plane equatorial waters. Larsen [6] relates a_{iso} of an equatorial water proton to the water orientation ($a_{\mathrm{iso}} \approx 11.1 - 12.9\cos^2\beta$, β = O=V–O–H dihedral). In e the $\cos^2\beta$ dependence holds qualitatively (rotating the flattened water gives the largest a_{iso} at $\beta = \pm 90°$ and the smallest, slightly negative, at 0/180°), but with a much smaller amplitude (1.2 vs. 11 MHz at ±90°): the constants are specific to the aqua-ion geometry. No orientation raises a_{iso} above the optimized, H-bonded one, which is also the most stable. The difference to the aqua ion (3 vs. 6–9 MHz) comes from the V–O_w distance (2.28 vs. 2.06–2.11 Å), which is very soft: a relaxed scan and an unconstrained SMD optimization (2.195 Å) both bring the proton closer to experiment; in the relaxed scan A_3 and a_{iso} reach the experimental range at 2.15 Å (Table S8). [3] Dinse et al., J. Phys. Chem. C 2013, 117, 16921. [5] Atherton & Shackleton, Mol. Phys. 1980, 39, 1471. [6] Larsen, J. Phys. Chem. A 2001, 105, 8333.

Table S8: Bound water in e: rigid orientation scan, relaxed distance scan, SMD water and two explicit second-shell waters (ORCA PBE0 single points). Orientation rows: only the water moved, rest = Gaussian optimized geometry. Tilt: angle between V→O_w and the water bisector (97° = optimized); rot: rotation of the flattened water about V–O_w. Where the two protons differ, both are given in the order of the β column (separated by ";"). ΔE relative to the optimized orientation.

Water orientation	V–O–H	β	ΔE (kcal/mol)	^{1}H $A_1/A_2/A_3$	^{1}H a_{iso}	$g_\parallel$	$\lvert A_\parallel\rvert(^{51}V)$	$\langle S^2\rangle$
optimized (tilt 97°)	86°	±128°	0	−2.7/−3.6/15.1	2.9	1.9225	540	0.763
tilt 75°	99°	±127°	1.9	−1.5/−2.1/12.2	2.9	1.9225	540	0.762
tilt 50°	113°	±121°	6.4	−1.4/−1.7/9.7	2.2	1.9220	540	0.762
tilt 25°	124°	±108°	10.9	−1.7/−1.8/8.1	1.5	1.9209	540	0.762
tilt 0° (flat)	128°	±90°	13.4	−1.9/−2.0/7.5	1.2	1.9201	539	0.761
tilt 0°, rot 45°/135°	128°	135/−45°	14.0	−2.3/−2.6/6.9; −2.7/−3.0/6.7	0.6; 0.3	1.9191	540	0.761
tilt 0°, rot 90°	128°	180/0°	14.9	−3.4/−3.9/5.7; −3.1/−3.7/6.1	−0.5; −0.3	1.9178	541	0.761
V–O_w frozen, everything else optimized (Gaussian relaxed scan; ΔE relaxed; EPR from ORCA)								
V–O_w 2.20 Å	88°	±128°	0.2	−1.9/−2.7/16.8	4.1	1.9268	538	0.763
V–O_w 2.15 Å	89°	±128°	0.6	−1.1/−1.9/18.1	5.0	1.9296	536	0.763
V–O_w 2.10 Å	91°	±128°	1.4	−0.1/−0.9/19.6	6.2	1.9323	534	0.763
Unconstrained optimization in SMD water (Gaussian): V–O_w 2.195 Å; two inequivalent protons								
SMD geometry, ORCA gas phase	104°	119/−132°	–	−0.0/0.5/14.8; −0.4/−1.1/13.8	5.1; 4.1	1.9309	532	0.765
SMD geometry, ORCA SMD	104°	119/−132°	–	0.2/−0.4/14.3; −0.7/−1.4/13.3	4.7; 3.8	1.9325	524	0.762
Unconstrained gas-phase optimization with two explicit second-shell waters: V–O_w 2.193 Å								
2 explicit waters, ORCA gas phase	102/112°	68/−177°	–	−0.5/−1.0/14.2; −3.2/−4.1/8.7	4.3; 0.5	1.9290	532	0.763
second-shell water protons (V–H 2.85–3.73 Å)				largest component 3.1–7.6	−0.1 to 0.2			
VO/SBA-15, exp. [3]				$\lvert A\rvert$ 0.5/0.5/17	±6	1.9391	551	

Orientation: no orientation reaches the experimental proton a_{iso}, and the ^{51}V parameters do not change; the rotation rows follow Larsen's $\cos^2\beta$ trend (largest a_{iso} at ±90°, smallest at 0/180°) with a ∼10 times smaller amplitude. Distance: shortening V–O_w raises a_{iso} and the largest proton component; in the relaxed scan the cost is only 0.2–1.4 kcal/mol, the water stays H-bonded (V–O–H 88–91°), and at 2.15 Å the proton tensor is close to the experimental one (A_3 and a_{iso} within the experimental uncertainty). In SMD water the unconstrained minimum moves by itself to V–O_w = 2.195 Å, the water becomes less bent (V–O–H 104°), $g_\parallel$ reaches 1.931–1.933 (exp. 1.939) and the small proton components match experiment; $\lvert A_\parallel\rvert$ and the largest proton component decrease slightly (as SMD also lowers $\lvert A\rvert$ of the aqua ion by ∼6 %). Orientation rows: ORCA; relaxed, SMD and explicit-water rows: ORCA single points on the Gaussian geometries.

Table S9: V^{IV}–O–V^{V} model h: model c whose fourth equatorial position is occupied by the oxo group of a neighboring $V^{V}O(OSiH_3)_2$ unit ($q = -2$, doublet). Two minima were found: a *bent* bridge (V–O–V 123°; V^{IV}–O_{br} 2.09 Å, O_{br}–V^{V} 1.65 Å, O=V^{IV}–O_{br} 94°), and an almost *linear* bridge (174°; 2.12/1.62 Å, 92°) that is 4.2 kcal/mol higher (Gaussian). In both, O_{br} binds to V^{IV} in the equatorial plane. Compared with the monomer models of Tables S1, S6 and S8 (same functional).

			ρ (Mulliken)		$A(^{51}V^{IV})$ (MHz)		$A(^{51}V^{V})$, neighbor (MHz)	
Model	Functional	$g_{\parallel}$	V^{IV}	V^{V}	$A_{\perp}$ / $A_{\parallel}$	a_{iso}	$A_1/A_2/A_3$	a_{iso}
c (no fourth donor)	PBE0	1.8829	1.09	–	−187/−176 / −537	−300	–	–
e	PBE0	1.9225	1.14	–	−203/−199 / −540	−314	–	–
i	PBE0	1.9290	1.10	–	−197/−193 / −532	−308	–	–
h (bent bridge, minimum)	PBE0	1.9292	1.15	0.018	−196/−193 / −532	−307	1.1/−1.7/−5.7	−2.1
h, linear bridge (4.2 kcal/mol)	PBE0	1.9245	1.14	0.033	−200/−197 / −534	−310	−5.6/−7.0/−14.7	−9.1
e	BHandHLYP	1.9082	1.17	–	−233/−229 / −599	−354	–	–
h (bent bridge, minimum)	BHandHLYP	1.9180	1.18	0.013	−223/−220 / −587	−343	−0.1/2.2/−3.1	−0.3
h, linear bridge	BHandHLYP	1.9130	1.18	0.023	−228/−225 / −592	−348	−3.6/−4.5/−9.6	−5.9
VO/SBA-15, exp.		1.9391			±214/±199 / ±551	321		≈4.5 (HYSCORE, sign n.d.)

$\langle S^2 \rangle$: 0.764 (PBE0), 0.771–0.772 (BHandHLYP). The linear minimum came from an optimization in Cartesian coordinates (started after a V^{V}–O–Si angle reached 180° in redundant internals); continuing in redundant internals gave the lower, bent minimum. BHandHLYP without D3, at the same geometries. Experimental neighbor coupling: off-diagonal HYSCORE peaks of H_2-reduced samples, isotropic part ≈4.5 MHz, interpreted by Dinse et al. as ∼1 % spin transfer through a covalent V–O–V bridge.

Cartesian coordinates (Å) of the optimized structures (Gaussian UPBE0-D3)

VOPc

N	-3.348345	0.253746	0.141180
N	-1.272886	1.481634	0.228789
N	0.253746	3.348345	0.141180
N	1.481634	1.272886	0.228789
N	3.348345	-0.253746	0.141180
N	1.272886	-1.481634	0.228789
N	-0.253746	-3.348345	0.141180
N	-1.481634	-1.272886	0.228789
C	-2.635287	1.361719	0.155704
C	-3.225811	2.681028	0.052770
C	-0.949029	2.810391	0.155726
C	-2.164265	3.592986	0.052828
C	-4.544865	3.108215	-0.048183
C	-4.768597	4.473665	-0.141713
C	-3.703810	5.388395	-0.141619
C	-2.387699	4.961359	-0.048018
C	1.361719	2.635287	0.155704
C	2.681028	3.225811	0.052770
C	2.810391	0.949029	0.155726
C	3.592986	2.164265	0.052828
C	4.961359	2.387699	-0.048018
C	3.108215	4.544865	-0.048182
C	5.388395	3.703810	-0.141619
C	4.473665	4.768597	-0.141713
C	2.635287	-1.361719	0.155704
C	3.225811	-2.681028	0.052770
C	2.164265	-3.592985	0.052828
C	0.949029	-2.810391	0.155726
C	2.387699	-4.961359	-0.048018
C	3.703810	-5.388395	-0.141619
C	4.768597	-4.473665	-0.141713
C	4.544865	-3.108215	-0.048183
C	-1.361719	-2.635287	0.155704
C	-2.810391	-0.949029	0.155726
C	-2.681028	-3.225811	0.052770
C	-3.592985	-2.164265	0.052828
C	-3.108215	-4.544865	-0.048182
C	-4.961359	-2.387699	-0.048018
C	-4.473665	-4.768597	-0.141713
C	-5.388395	-3.703810	-0.141619
H	-5.357890	2.391377	-0.050374
H	-5.784570	4.846713	-0.217044
H	-3.919438	6.448999	-0.216876
H	-1.556506	5.657048	-0.050063
H	5.657048	1.556506	-0.050063
H	2.391377	5.357890	-0.050374
H	6.448999	3.919439	-0.216876
H	4.846713	5.784570	-0.217044
H	3.919439	-6.448999	-0.216876
H	5.784570	-4.846713	-0.217044

H	5.357890	-2.391377	-0.050374
H	1.556506	-5.657048	-0.050063
H	-2.391377	-5.357890	-0.050374
H	-5.657048	-1.556506	-0.050063
H	-4.846713	-5.784570	-0.217044
H	-6.448999	-3.919438	-0.216876
V	0.000000	0.000000	0.814044
O	0.000000	0.000000	2.373525

$[VO(H_2O)_5]^{2+}$ (gas)

V	-0.030122	0.001793	-0.024566
O	-0.128009	0.001168	1.503540
O	2.031500	0.002953	-0.251414
H	2.558210	0.778978	-0.015638
H	2.559029	-0.772676	-0.016165
O	-0.018234	2.069188	-0.216807
H	-0.066823	2.673523	0.536260
H	0.033401	2.586866	-1.029813
O	-2.046246	0.000918	-0.512485
H	-2.598701	-0.775251	-0.346407
H	-2.599531	0.776360	-0.345775
O	-0.016088	-2.065437	-0.218385
H	0.036137	-2.582428	-1.031790
H	-0.064037	-2.670406	0.534214
O	0.111867	0.002700	-2.257779
H	0.923605	0.003325	-2.779291
H	-0.627451	0.002556	-2.877693

$[VO(H_2O)_5]^{2+}$ (SMD)

V	0.060216	0.087539	-0.098158
O	0.081107	-0.037610	1.456478
O	2.052595	0.249199	-0.602416
H	2.535971	0.870394	-0.042021
H	2.517977	-0.595089	-0.536477
O	0.066539	2.130685	-0.322426
H	-0.763020	2.550261	-0.059529
H	0.765517	2.563586	0.184884
O	-1.997902	0.133386	-0.443100
H	-2.335886	-0.739166	-0.683554
H	-2.497864	0.410967	0.335027
O	0.107273	-2.010493	-0.332483
H	-0.041384	-2.460500	0.508343
H	-0.567093	-2.346244	-0.936971
O	-0.103573	-0.125604	-2.362437
H	0.702327	-0.480205	-2.755155
H	-0.811414	-0.708671	-2.660003

a

V	0.047071	-0.147877	0.218442
O	0.186705	-0.057785	1.968272
H	0.628789	0.661041	2.431321

O	1.632235	-0.125552	-0.646673
Si	1.648303	-0.015281	-2.297965
H	2.992923	-0.001160	-2.874093
O	0.766759	1.333186	-2.706032
O	-0.771190	1.279537	-0.526448
Si	-0.805779	1.419335	-2.175250
H	-1.492041	2.621176	-2.649382
O	-1.535613	0.021319	-2.716273
O	-0.763532	-1.459952	-0.645389
Si	-0.824788	-1.422060	-2.322998
H	-1.527915	-2.577911	-2.877470
O	0.748074	-1.313731	-2.830371

b

V	0.008547	0.004313	0.140115
O	-0.038885	0.063664	1.899328
O	1.795452	-0.003836	-0.519060
Si	2.062351	-0.003242	-2.115761
H	3.491992	-0.003977	-2.486192
O	1.345983	1.346068	-2.779961
O	0.008361	1.790828	-0.512697
Si	0.003430	2.062388	-2.111169
H	0.001748	3.494944	-2.470846
O	-1.349345	1.350237	-2.768347
O	-1.781817	0.005918	-0.503226
Si	-2.061777	0.002894	-2.100033
H	-3.496063	0.006653	-2.452739
O	-1.352494	-1.345250	-2.765351
O	0.008368	-1.785740	-0.509115
Si	-0.001668	-2.061579	-2.104431
H	-0.006801	-3.493353	-2.466434
O	1.340063	-1.346679	-2.781291
H	-0.666965	0.716680	2.224523

c

V	0.031541	-0.054279	0.336093
O	-0.074811	0.129603	1.906582
O	1.680297	-0.014166	-0.598735
Si	1.637220	0.002939	-2.225166
H	2.968492	-0.003900	-2.862955
O	0.764880	1.325086	-2.746820
O	-0.812952	1.407658	-0.575442
Si	-0.814249	1.410199	-2.188141
H	-1.484793	2.572005	-2.804207
O	-1.530008	0.000187	-2.747293
O	-0.827989	-1.461679	-0.598748
Si	-0.821299	-1.416291	-2.225170
H	-1.481014	-2.572722	-2.862779
O	0.764684	-1.324639	-2.749568

d

```
V      0.000000    0.000000    0.212735
O      0.000000    0.000000    1.795193
O      1.877176    0.000000   -0.504929
Si     2.058470    0.000000   -2.090687
H      3.480052    0.000000   -2.551774
O      1.347131    1.347131   -2.784542
O      0.000000    1.877176   -0.504929
Si     0.000000    2.058470   -2.090687
H      0.000000    3.480052   -2.551774
O     -1.347131    1.347131   -2.784542
O     -1.877176    0.000000   -0.504929
Si    -2.058470    0.000000   -2.090687
H     -3.480052    0.000000   -2.551774
O     -1.347131   -1.347131   -2.784542
O      0.000000   -1.877176   -0.504929
Si     0.000000   -2.058470   -2.090687
H      0.000000   -3.480052   -2.551774
O      1.347131   -1.347131   -2.784542
```

e

```
V      0.009363   -0.110589    0.500540
O     -0.293426    0.327070    1.982348
O      1.723423   -0.000016   -0.456112
Si     1.693268   -0.010466   -2.081275
H      3.036696   -0.033914   -2.696487
O      0.828810    1.281814   -2.671861
O     -0.791009    1.304493   -0.546277
Si    -0.765090    1.346150   -2.149617
H     -1.429700    2.509472   -2.770827
O     -1.457367   -0.062776   -2.743867
O     -0.874367   -1.526642   -0.537011
Si    -0.775997   -1.462290   -2.158069
H     -1.378693   -2.630271   -2.833567
O      0.845072   -1.369212   -2.578164
O      1.111899   -2.016084    1.097780
H      0.507985   -2.467948    0.485662
H      1.826839   -1.690199    0.526427
```

f

```
V      0.349423   -0.087234    0.540741
O      0.372737    0.515903    1.994738
O      1.871714    0.218624   -0.563207
Si     1.739463    0.206977   -2.174059
H      3.018663    0.395528   -2.884827
O      0.640488    1.355802   -2.685092
O     -0.797864    1.104027   -0.442642
Si    -0.893819    1.181711   -2.043514
H     -1.779535    2.231939   -2.582737
O     -1.423240   -0.313348   -2.602475
O     -0.476671   -1.728594   -0.522207
Si    -0.485682   -1.606585   -2.172136
```

H	-0.972404	-2.830664	-2.831420
O	1.060403	-1.250789	-2.661980
O	1.097572	-1.963706	1.154637
H	1.700228	-2.163805	1.869437
Si	0.261959	-3.285456	0.407262
H	-1.122839	-3.632544	0.843251
H	0.666733	-3.849873	-0.918687
H	1.027549	-4.300070	1.280036

g

V	-0.245294	-0.406797	0.472655
O	-0.872790	-0.214053	1.904126
O	1.671037	-0.301129	-0.315119
Si	1.774662	-0.140798	-1.963533
H	3.162870	-0.198962	-2.449790
O	1.070364	1.287398	-2.406185
O	-0.736289	1.203158	-0.462426
Si	-0.566714	1.427676	-2.042107
H	-1.064430	2.712936	-2.568432
O	-1.292398	0.164033	-2.863730
O	-1.081228	-1.565131	-0.793973
Si	-0.801948	-1.353868	-2.373866
H	-1.418458	-2.379229	-3.236521
O	0.858923	-1.350221	-2.638423
O	0.949596	-2.073189	1.082910
Si	2.597949	-1.766473	0.627620
H	3.075087	-3.004148	1.410573
H	3.160586	-2.181478	-0.695583
H	3.359139	-0.727885	1.376834
Si	0.361949	-3.406735	1.895323
H	-1.116667	-3.316913	1.891788
H	0.787650	-4.661857	1.216448
H	0.857950	-3.437512	3.299439

e (SMD)

V	0.050355	-0.161502	0.459603
O	-0.350127	0.310697	1.933162
O	1.722270	0.060444	-0.518877
Si	1.693379	0.024085	-2.143880
H	3.021272	0.005868	-2.774547
O	0.808220	1.321529	-2.721539
O	-0.775852	1.310096	-0.570638
Si	-0.781132	1.381726	-2.181704
H	-1.456198	2.551476	-2.764403
O	-1.477932	-0.023982	-2.781220
O	-0.898104	-1.482163	-0.592131
Si	-0.792110	-1.440489	-2.213769
H	-1.401176	-2.597984	-2.884859
O	0.825254	-1.324216	-2.640137
O	1.086939	-1.944546	1.209662
H	0.606340	-2.677780	0.804882
H	1.936308	-1.924668	0.750019

i

V	0.116184	-0.653826	0.327082
O	-0.623723	-0.691776	1.724332
O	1.803384	0.116842	-0.380053
Si	1.873499	0.437293	-1.972492
H	3.211078	0.864153	-2.429909
O	0.742511	1.542942	-2.465769
O	-0.926232	0.721918	-0.568387
Si	-0.838970	1.092949	-2.122336
H	-1.758507	2.144215	-2.599424
O	-1.073395	-0.298640	-3.034601
O	-0.337327	-1.973063	-1.038689
Si	-0.102530	-1.571806	-2.597385
H	-0.299830	-2.704789	-3.523197
O	1.471464	-1.002965	-2.761051
O	1.418759	-2.245047	1.090133
H	0.800324	-2.997983	1.155139
H	2.108000	-2.485130	0.440723
O	-0.891763	-3.740622	0.972503
H	-1.270841	-3.041072	1.516546
H	-0.872250	-3.320181	0.090458
O	3.398567	-2.150985	-0.768393
H	2.913084	-2.184249	-1.602876
H	3.157762	-1.259335	-0.454394

h (bent bridge)

V	-0.594357	-1.452691	0.454998
O	-1.999916	-2.118689	0.729968
O	-0.040001	0.293215	1.108591
Si	1.073905	1.100913	0.276985
H	1.603084	2.299941	0.971405
O	0.497573	1.581057	-1.222198
O	-1.011763	-0.633463	-1.323329
Si	0.004777	0.271365	-2.154727
H	-0.503476	0.795740	-3.450529
O	1.418461	-0.584710	-2.460231
O	1.041568	-2.251141	-0.366884
Si	2.095319	-1.238945	-1.074456
H	3.386947	-1.859697	-1.434138
O	2.367675	0.094509	-0.093016
O	0.290256	-2.252684	2.168932
V	1.669317	-3.151503	2.130995
O	1.901072	-3.706100	3.599160
O	3.146152	-2.141922	1.738591
Si	4.052928	-0.883229	2.210854
H	3.294873	0.319294	2.661368
H	4.914797	-1.273514	3.387123
H	5.019606	-0.471526	1.146843
O	1.552788	-4.614594	1.055814
Si	1.063183	-4.885649	-0.485696
H	-0.325528	-4.473133	-0.818600
H	2.028945	-4.467649	-1.544648
H	1.048115	-6.398823	-0.615823

c, large cluster

V	0.040805	-0.054776	0.590388
O	-0.097735	0.106694	2.157104
O	1.653763	0.282793	-0.353792
Si	1.600722	0.284819	-1.968661
O	0.520094	1.428061	-2.497991
O	-1.051668	1.227358	-0.332360
Si	-1.043222	1.225764	-1.935116
O	-1.501133	-0.275876	-2.498761
O	-0.546618	-1.593515	-0.354835
Si	-0.551085	-1.536569	-1.969690
O	0.984145	-1.173021	-2.501090
O	3.046899	0.508711	-2.690106
Si	4.006372	-0.157849	-3.836883
H	4.496032	-1.504917	-3.430793
H	3.301378	-0.288222	-5.143110
H	5.186879	0.730761	-4.028602
O	-1.971240	2.371339	-2.636188
Si	-1.865277	3.589028	-3.724081
H	-0.940730	4.663680	-3.266173
H	-1.399234	3.105412	-5.054576
H	-3.222479	4.180756	-3.893103
O	-1.069468	-2.904959	-2.690878
Si	-2.139543	-3.420828	-3.817117
H	-3.546710	-3.176181	-3.394265
H	-1.921684	-2.757157	-5.133332
H	-1.952709	-4.888133	-3.996784

e, large cluster

V	-0.098118	0.128597	0.441852
O	-0.552251	0.861653	1.756284
O	1.708659	0.047724	-0.336284
Si	1.838676	-0.288905	-1.908414
O	1.082943	0.855460	-2.847211
O	-0.746408	1.304281	-0.957441
Si	-0.544203	1.016418	-2.518291
O	-1.204116	-0.467131	-2.899499
O	-0.900830	-1.461939	-0.396196
Si	-0.620257	-1.711349	-1.965038
O	1.028163	-1.713336	-2.220681
O	0.874208	-1.595541	1.518384
H	0.347767	-2.195360	0.965796
H	1.675085	-1.428351	0.996016
O	3.383547	-0.431494	-2.423666
Si	4.319969	-0.013769	-3.700347
H	5.636621	-0.696138	-3.550404
H	3.718627	-0.436992	-4.996103
H	4.560457	1.455588	-3.749505
O	-1.187196	2.166678	-3.486385
Si	-2.002327	3.574171	-3.269985
H	-1.197610	4.573856	-2.514644
H	-2.297781	4.137703	-4.618452
H	-3.294584	3.366365	-2.559816

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O     -1.249536   -3.110512   -2.529644
Si    -2.076984   -3.678388   -3.823485
H     -3.463572   -3.136063   -3.872891
H     -1.396710   -3.351809   -5.108138
H     -2.160948   -5.161652   -3.702763
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