

## Electronic Supplementary Information (ESI)

### **Magnetic and relaxation properties of Vanadium(IV) complexes: An integrated $^1\text{H}$ relaxometric, EPR and DFT study**

*Valeria Langostina,<sup>a</sup> Fabio Carniato,<sup>b</sup> David Esteban-Gómez,<sup>c</sup> Carlos Platas-Iglesias\*,<sup>c</sup> Mario Chiesa\*<sup>a</sup> and Mauro Bottà\*<sup>b</sup>*

*<sup>a.</sup> Department of Chemistry, University of Turin, Via Giuria 9, 10125 Torino, Italy. E-mail: mario.chiesa@unito.it*

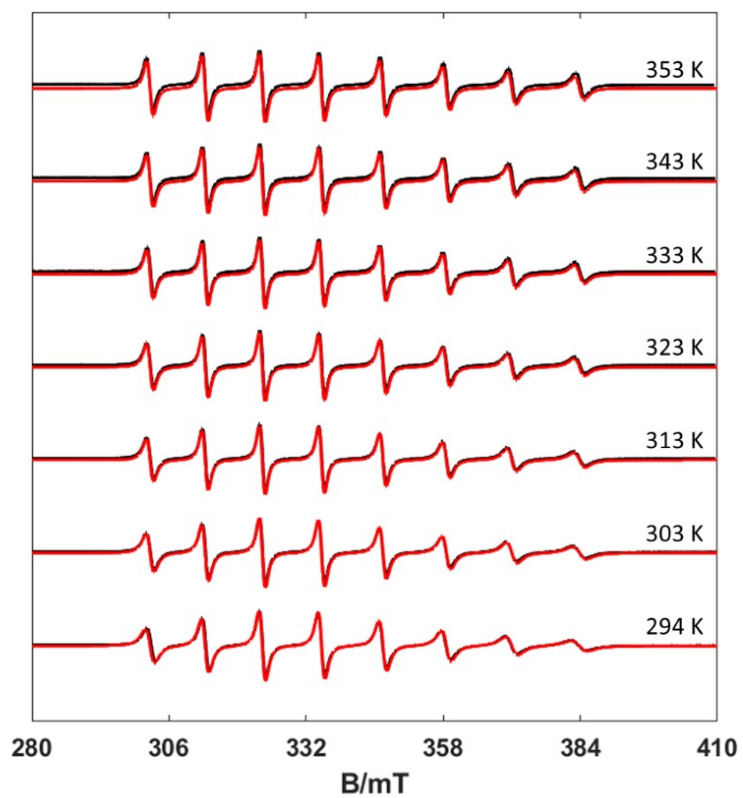
*<sup>b.</sup> Dipartimento di Scienze e Innovazione Tecnologica, Università del Piemonte Orientale "A. Avogadro", Viale T. Michel 11, 15121 Alessandria, Italy. E-mail: mauro.botta@uniupo.it*

*<sup>c.</sup> Universidade da Coruña, Centro de Investigacións Científicas Avanzadas (CICA) and Departamento de Química, Facultade de Ciencias, 15071, A Coruña, Galicia, Spain.*

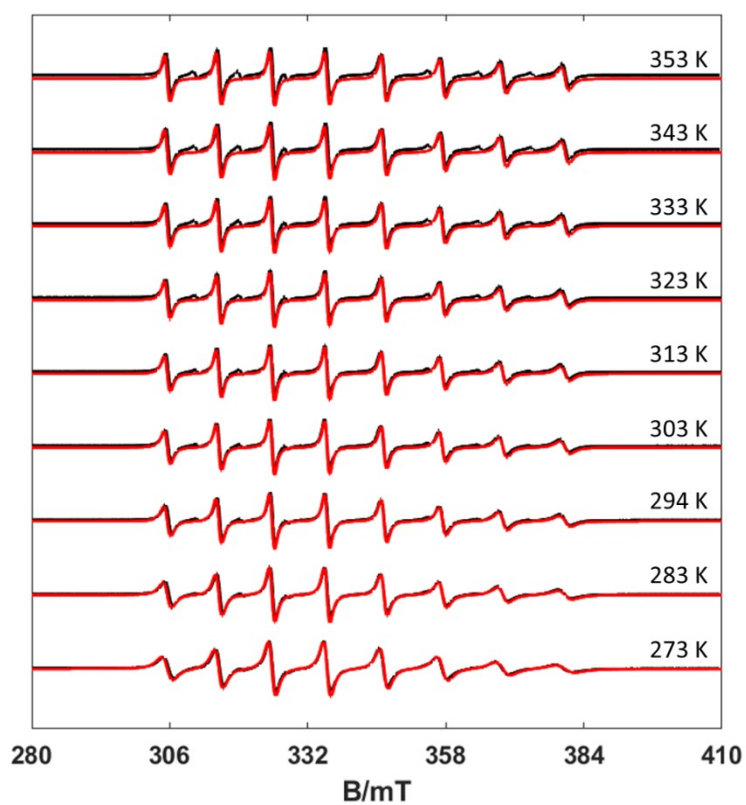
## Contents:

Figure S1. X-band CW EPR spectra of $[\text{VO}(\text{H}_2\text{O})_5]^{2+}$ at variable temperature experimental (black) and simulation (red) 10 mW power and 0.5 mT modulation amplitude.....	4
Figure S2. X-band CW EPR spectra of $[\text{VO}(\text{ox})_2]^{2-}$ at variable temperature experimental (black) and simulation (red) 10 mW power and 0.5 mT modulation amplitude. ....	5
Figure S3. X-band CW EPR spectra of $[\text{VO}(\text{dtpa})]^{3-}$ at variable temperature experimental (black) and simulation (red) 10 mW power and 0.5 mT modulation amplitude.....	6
Figure S4. Rotational correlation time as a function of temperature of $[\text{VO}(\text{H}_2\text{O})_5]^{2+}$ (black), $[\text{VO}(\text{dtpa})]^{3-}$ (blue), $[\text{VO}(\text{ox})_2]^{2-}$ (orange) and $[\text{VO}(\text{nta})]^-$ (green). ...	7
Figure S5. Plots of the rotational correlation time as a function of temperature for $[\text{VO}(\text{H}_2\text{O})_5]^{2+}$ (black), $[\text{VO}(\text{dtpa})]^{3-}$ (blue), $[\text{VO}(\text{ox})_2]^{2-}$ (orange) and $[\text{VO}(\text{nta})]^-$ (green). The slopes of the linear fits ( $E_R/R$ ) were used to calculate the activation energy for rotation, while the intercepts afford $\ln(\tau_R^{298})$ . ...	8
Figure S6. Variable Temperature electron spin echo decay (left) and inversion recovery (right) data for $[\text{VO}(\text{H}_2\text{O})_5]^{2+}$ at 1215 mT and 33.985 GHz: 20 K (blue), 50 K (light blue), 80 K (green), 120 K (yellow), 150 K (orange) and 200 K (red). .	9
Figure S7 Variable Temperature electron spin echo decay (left) and inversion recovery (right) data for $[\text{VO}(\text{ox})_2]^{2-}$ at 1206 mT and 33.748 GHz: 20 K (blue), 50 K (light blue), 80 K (green), 120 K (yellow), 150 K (orange) and 200 K (red). .	9
Figure S8. Variable Temperature electron spin echo decay (left) and inversion recovery (right) data for $[\text{VO}(\text{nta})]^-$ at 1207 mT and 33.748 GHz: 20 K (blue), 50 K (light blue), 80 K (green), 120 K (yellow), 150 K (orange) and 200 K (red). ....	10
Figure S9. Variable Temperature electron spin echo decay (left) and inversion recovery (right) data for $[\text{VO}(\text{dtpa})]^{3-}$ at 1209 mT and 33.827 GHz: 20 K (blue), 50 K (light blue), 80 K (green), 120 K (yellow), 150 K (orange) and 200 K (red). ....	10
Figure S10. Variable Temperature electron spin echo decay (left) and inversion recovery (right) data for $[\text{VO}(\text{acac})_2]$ at 1206 mT and 33.693 GHz: 20 K (blue), 50 K (light blue), 80 K (green), 120 K (yellow), 150 K (orange) and 200 K (red).....	11
Table S1. Rotational correlation time ( $\tau_R$ ( $10^{-11}$ s)) of VO-complexes calculated by EasySpin simulations. ....	11
Table S2. $T_1^e$ and amplitude fitting values for VO-complexes.....	12

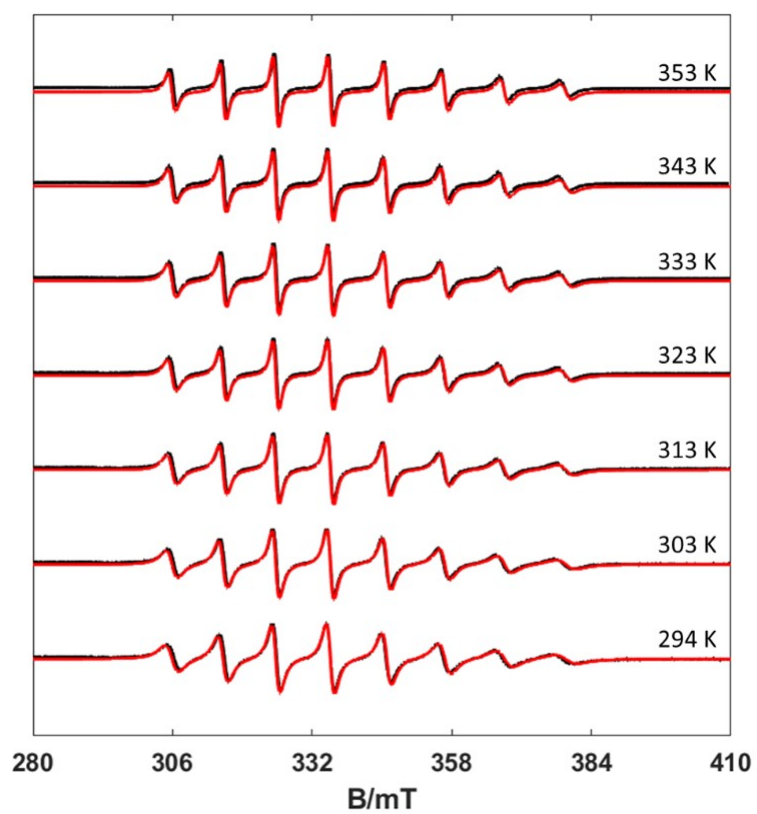
Table S3. $T_m^e$ and stretch fitting values as a function of temperature for VO <sup>2+</sup> complexes. ....	13
Table S4. Cartesian coordinates (Å) obtained with DFT calculations for the [VO(H <sub>2</sub> O) <sub>5</sub> ] <sup>2+</sup> system.....	14
Table S5. Cartesian coordinates (Å) obtained with DFT calculations for the [VO(nta)(H <sub>2</sub> O)] <sup>-</sup> system.....	15
Table S6. Cartesian coordinates (Å) obtained with DFT calculations for the [VO(nta)(H <sub>2</sub> O)] <sup>-</sup> ·2H <sub>2</sub> O system.....	16
Table S7. Cartesian coordinates (Å) obtained with DFT calculations for the [VO(Hdtpa)] <sup>2-</sup> system.....	17
Table S8. Cartesian coordinates (Å) obtained with DFT calculations for the [VO(ox) <sub>2</sub> (H <sub>2</sub> O)] <sup>2-</sup> system.....	18
Table S9. Cartesian coordinates (Å) obtained with DFT calculations for the [VO(ox) <sub>2</sub> (H <sub>2</sub> O)] <sup>2-</sup> ·2H <sub>2</sub> O system.....	19
Table S10. Cartesian coordinates (Å) obtained with DFT calculations for the [VO(acac) <sub>2</sub> (H <sub>2</sub> O)] system.....	20
Table S11. Cartesian coordinates (Å) obtained with DFT calculations for the [VO(acac) <sub>2</sub> (H <sub>2</sub> O)]·2H <sub>2</sub> O system.....	21



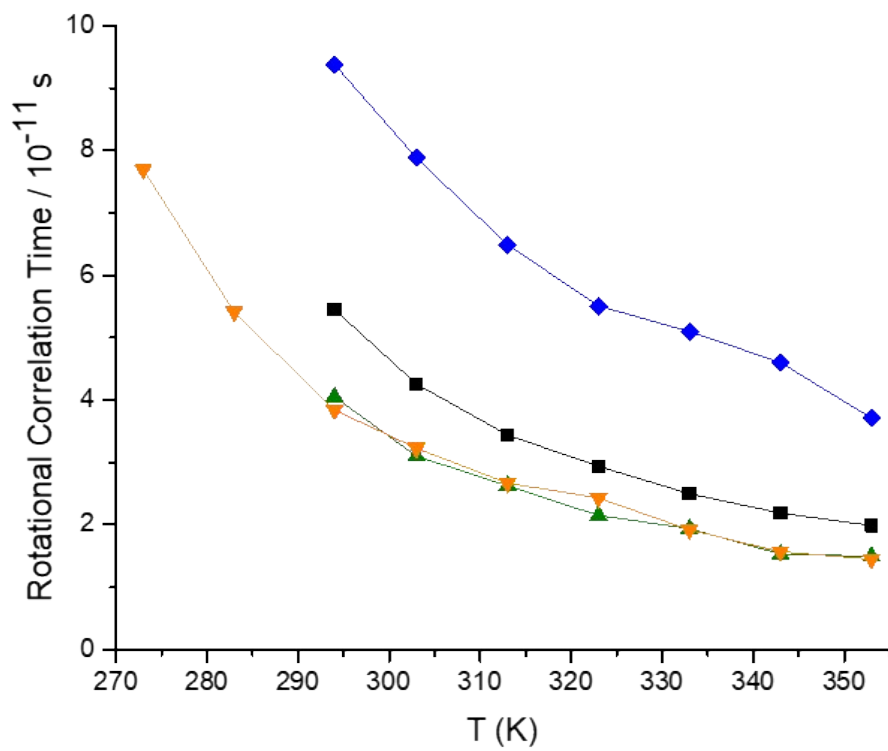
**Figure S1.** X-band CW EPR spectra of  $[\text{VO}(\text{H}_2\text{O})_5]^{2+}$  at variable temperature experimental (black) and simulation (red) 10 mW power and 0.5 mT modulation amplitude.



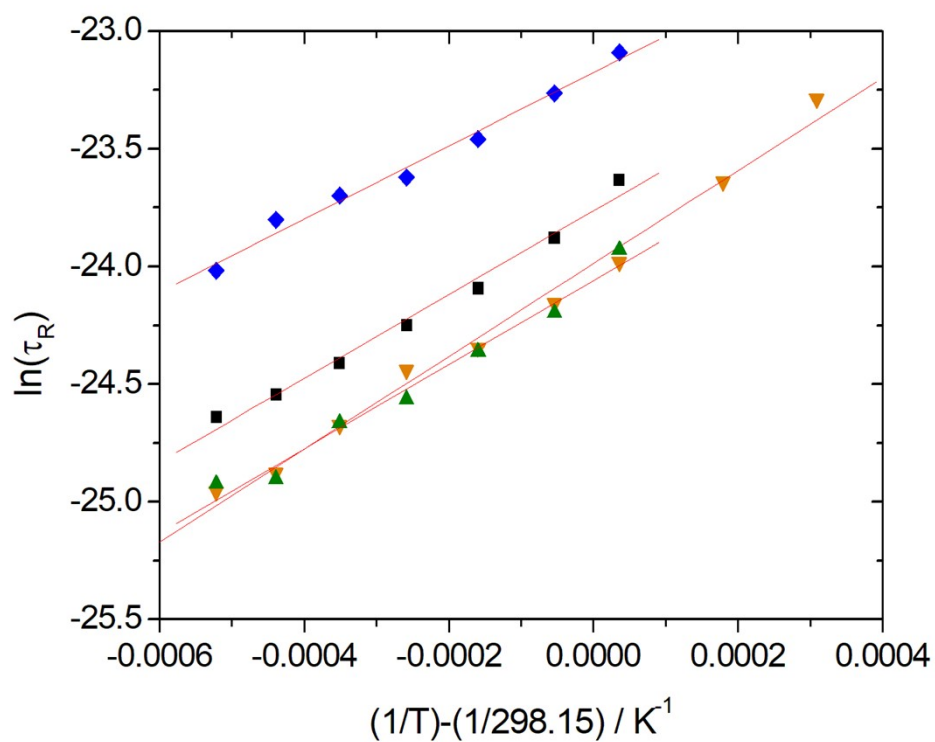
**Figure S2.** X-band CW EPR spectra of  $[\text{VO}(\text{ox})_2]^{2-}$  at variable temperature experimental (black) and simulation (red) 10 mW power and 0.5 mT modulation amplitude.



**Figure S3.** X-band CW EPR spectra of  $[\text{VO}(\text{dtpa})]^{3-}$  at variable temperature experimental (black) and simulation (red) 10 mW power and 0.5 mT modulation amplitude.

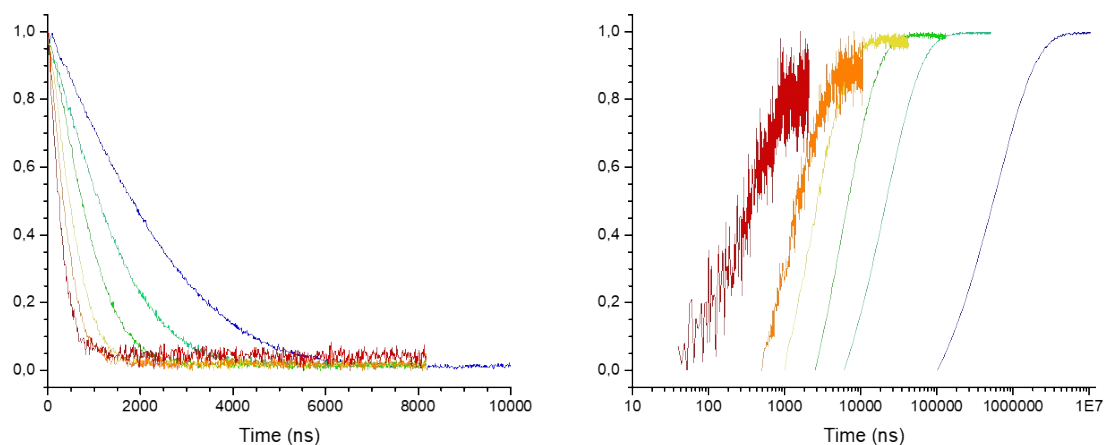


**Figure S4.** Rotational correlation time as a function of temperature of  $[\text{VO}(\text{H}_2\text{O})_5]^{2+}$  (black),  $[\text{VO}(\text{dtpa})]^{3-}$  (blue),  $[\text{VO}(\text{ox})_2]^{2-}$  (orange) and  $[\text{VO}(\text{nta})]^-$  (green).

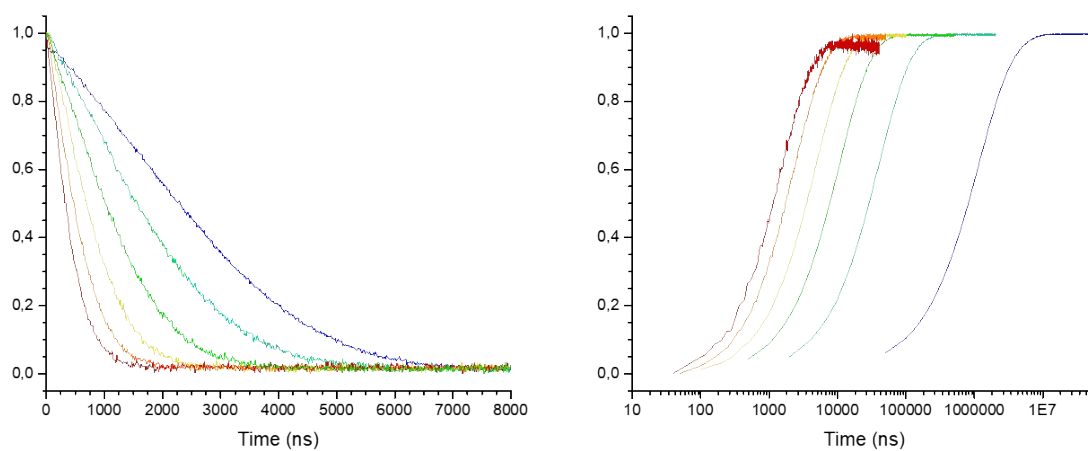


**Figure S5.** Plots of the rotational correlation time as a function of temperature for  $[\text{VO}(\text{H}_2\text{O})_5]^{2+}$  (black),  $[\text{VO}(\text{dtpa})]^{3-}$  (blue),  $[\text{VO}(\text{ox})_2]^{2-}$  (orange) and  $[\text{VO}(\text{nta})]^-$  (green). The slopes of the linear fits ( $E_R/R$ ) were used to calculate the activation energy for rotation, while the intercepts afford  $\ln(\tau_R^{298})$ .

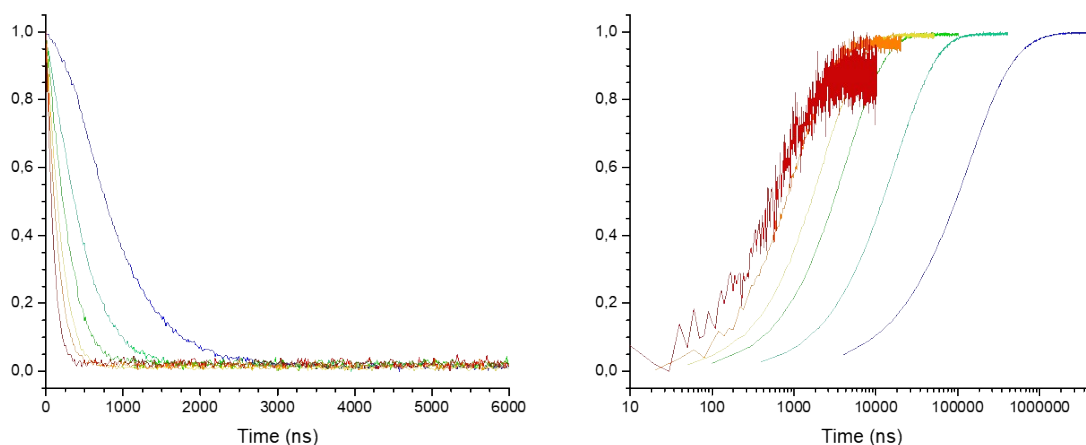




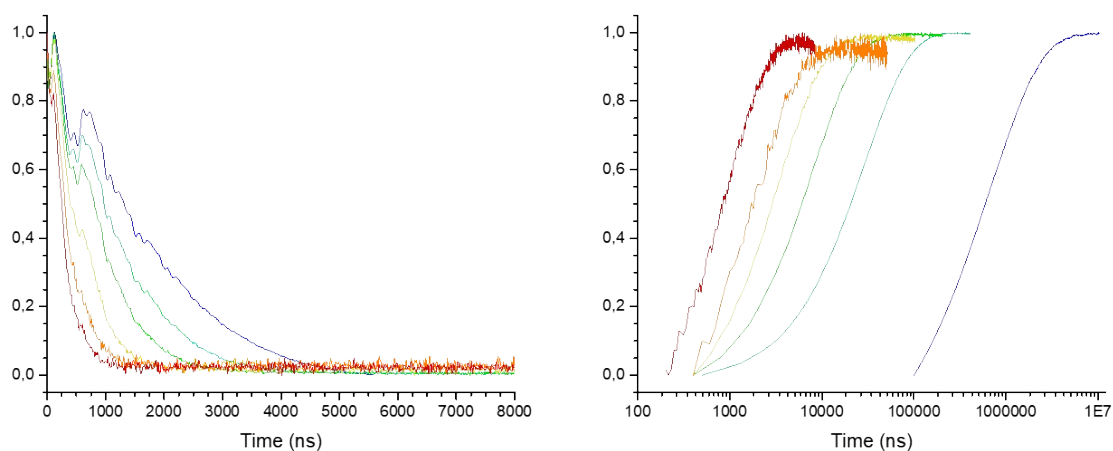
**Figure S6.** Variable Temperature electron spin echo decay (left) and inversion recovery (right) data for  $[\text{VO}(\text{H}_2\text{O})_5]^{2+}$  at 1215 mT and 33.985 GHz: 20 K (blue), 50 K (light blue), 80 K (green), 120 K (yellow), 150 K (orange) and 200 K (red).



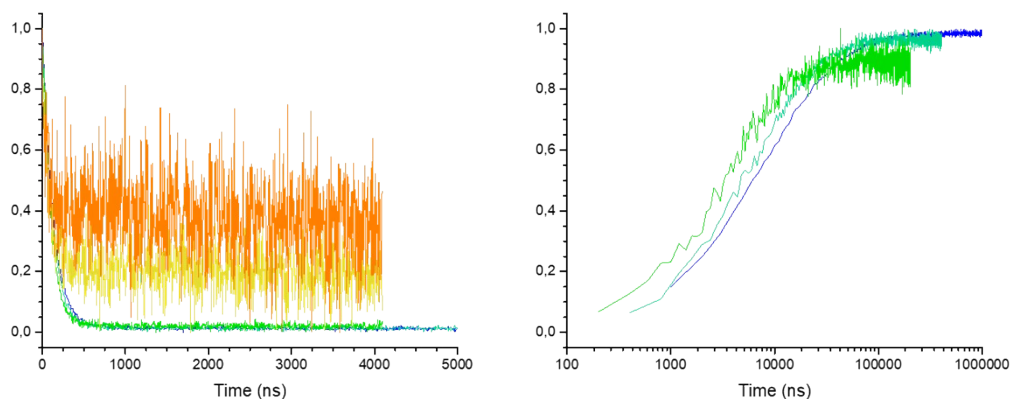
**Figure S7** Variable Temperature electron spin echo decay (left) and inversion recovery (right) data for  $[\text{VO}(\text{ox})_2]^{2-}$  at 1206 mT and 33.748 GHz: 20 K (blue), 50 K (light blue), 80 K (green), 120 K (yellow), 150 K (orange) and 200 K (red).



**Figure S8.** Variable Temperature electron spin echo decay (left) and inversion recovery (right) data for [VO(nta)]<sup>3-</sup> at 1207 mT and 33.748 GHz: 20 K (blue), 50 K (light blue), 80 K (green), 120 K (yellow), 150 K (orange) and 200 K (red).



**Figure S9.** Variable Temperature electron spin echo decay (left) and inversion recovery (right) data for [VO(dtpa)]<sup>3-</sup> at 1209 mT and 33.827 GHz: 20 K (blue), 50 K (light blue), 80 K (green), 120 K (yellow), 150 K (orange) and 200 K (red).



**Figure S10.** Variable Temperature electron spin echo decay (left) and inversion recovery (right) data for  $[\text{VO}(\text{acac})_2]$  at 1206 mT and 33.693 GHz: 20 K (blue), 50 K (light blue), 80 K (green), 120 K (yellow), 150 K (orange) and 200 K (red).

**Table S1.** Rotational correlation time ( $\tau_R$  ( $10^{-11}$  s)) of VO-complexes calculated by EasySpin simulations.

T (K)	$[\text{VO}(\text{H}_2\text{O})_5]^{2+}$	$[\text{VO}(\text{dtpa})]^{3-}$	$[\text{VO}(\text{nta})]^-$	$[\text{VO}(\text{ox})_2]^{2-}$	$[\text{VO}(\text{acac})_2]$
273	-	-	-	7.69	-
283	-	-	-	5.41	-
295	5.45	9.38	4.05	3.84	7.7
303	4.26	7.88	3.10	3.23	-
313	3.44	6.49	2.63	2.67	-
323	2.94	5.51	2.15	2.43	-
333	2.50	5.10	1.94	1.92	-
343	2.19	4.60	1.53	1.57	-
353	1.99	3.71	1.50	1.45	-

**Table S2.**  $T_1^e$  and amplitude fitting values for VO-complexes.

Samples	T (K)	$T_1^e$ long (ns)	Amplitude ( $k_m$ )	$T_1^e$ short (ns)	Amplitude ( $k_n$ )
[VO(H <sub>2</sub> O) <sub>5</sub> ] <sup>2+</sup>	20	9,16*10 <sup>5</sup>	83000	3,22*10 <sup>5</sup>	44980
	50	16386	66744	31028	58775
	80	6755	47007	2909	10710
	120	2447	23221	1059	887
	150	1331	7342	516	909
	200	368	-	368	-
[VO(nta)] <sup>-</sup>	20	2,48*10 <sup>5</sup>	17552	53592	12846
	50	23247	20255	7345	8247
	80	6373	15768	2189	5404
	120	2763	11863	1125	3364
	150	1375	6904	42	483
	200	-	-	-	-
[VO(ox) <sub>2</sub> ] <sup>2-</sup>	20	2,03*10 <sup>6</sup>	19493	8,33*10 <sup>5</sup>	24437
	50	53576	16464	27641	9577
	80	13881	14430	7861	9403
	120	5834	14604	3228	4850
	150	2768	11293	1650	3715
	200	1548	8951	681	123
[VO(dtpa)] <sup>3-</sup>	20	1,09*10 <sup>6</sup>	66250	329033	39265
	50	36538	151048	126411	40286
	80	10123	53584	4108	17233
	120	4220	26632	1650	6880
	150	2130	9198	330	2239
	200	873	22792	4,5	10290
[VO(acac) <sub>2</sub> ]	20	38657	8592	6444	19521
	50	17595	5868	4030	8094
	80	11404	3841	3290	11979
	120	-	-	-	-
	150	-	-	-	-
	200	-	-	-	-

**Table S3.**  $T_m^e$  and stretch fitting values as a function of temperature for VO<sup>2+</sup> complexes.

Samples	T (K)	$T_m^e$ (ns)	Stretch factor ( $\beta_m$ )
[VO(H <sub>2</sub> O) <sub>5</sub> ] <sup>2+</sup>	20	2408	1.37
	50	1505	1.39
	80	966	1.41
	120	616	1.37
	150	439	1.29
	200	302	1.2
[VO(nta)] <sup>-</sup>	20	569	1.09
	50	419	11.8
	80	293	1.21
	120	193	1.17
	150	142	1.12
	200	105	1.12
[VO(ox) <sub>2</sub> ] <sup>2-</sup>	20	3004	1.61
	50	2027	1.46
	80	1329	1.42
	120	888	1.4
	150	610	1.31
	200	438	1.26
[VO(dtpa)] <sup>3-</sup>	20	2511	1.30
	50	1393	1.40
	80	1028	1.39
	120	630	1.29
	150	424	1.35
	200	331	1.41
[VO(acac) <sub>2</sub> ]	20	130	1.01
	50	120	1.03
	80	104	1.04
	120	64	0.77
	150	-	-
	200	-	-

**Table S4.** Cartesian coordinates (Å) obtained with DFT calculations for the  $[\text{VO}(\text{H}_2\text{O})_5]^{2+}$  system.

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	8	0	0.053171	1.535329	1.085141
2	8	0	1.172072	-1.036773	1.153597
3	1	0	2.118703	-0.846649	1.224208
4	8	0	-1.589064	-0.657255	1.258546
5	1	0	-2.119863	-1.357732	0.852615
6	8	0	-1.426979	0.925705	-1.219444
7	1	0	-1.104154	1.566389	-1.870258
8	8	0	1.354520	0.731070	-1.194452
9	1	0	1.728909	0.043624	-1.764017
10	8	0	-0.296632	-1.542478	-1.076019
11	1	0	-0.848457	-1.624739	-1.864501
12	1	0	-2.321047	1.197581	-0.966524
13	1	0	2.054895	1.365761	-0.987414
14	1	0	0.883276	-1.384263	2.010388
15	1	0	-2.161502	-0.149982	1.851187
16	1	0	0.150539	-2.387487	-0.938275
17	23	0	-0.091833	0.260088	0.188876

E(UTPSSh) = -1401.4694392 Hartree

Zero-point correction = 0.129419

Thermal correction to Energy = 0.144493

Thermal correction to Enthalpy = 0.145437

Thermal correction to Gibbs Free Energy = 0.089972

Sum of electronic and zero-point Energies = -1401.340020

Sum of electronic and thermal Energies = -1401.324946

Sum of electronic and thermal Enthalpies = -1401.324002

Sum of electronic and thermal Free Energies = -1401.379467

**Table S5.** Cartesian coordinates (Å) obtained with DFT calculations for the [VO(nta)(H<sub>2</sub>O)]<sup>-</sup> system.

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	23	0	0.349408	-0.126231	0.870958
2	8	0	-3.442890	1.241265	1.500400
3	8	0	-1.349009	0.488121	1.669403
4	8	0	0.841012	1.720994	0.360380
5	8	0	-0.458406	-1.858718	0.361623
6	8	0	1.164403	-0.420991	2.223202
7	8	0	1.839664	-0.667516	-0.548818
8	7	0	-0.968748	0.352875	-1.042096
9	6	0	-2.385748	0.863626	0.996570
10	6	0	-2.271845	0.831598	-0.528182
11	6	0	0.553142	2.282948	-0.776815
12	6	0	-0.231900	1.405362	-1.757269
13	8	0	0.906907	3.412844	-1.099080
14	6	0	-1.045313	-2.104440	-0.772780
15	6	0	-1.086586	-0.928321	-1.753979
16	8	0	-1.502109	-3.197485	-1.092625
17	1	0	2.116867	-1.593191	-0.514516
18	1	0	2.645101	-0.133714	-0.514778
19	1	0	-3.078737	0.200393	-0.906524
20	1	0	-2.468624	1.841980	-0.892948
21	1	0	-0.882754	2.029922	-2.374422
22	1	0	0.503510	0.937654	-2.414681
23	1	0	-0.226720	-1.045106	-2.416431
24	1	0	-1.990241	-0.988015	-2.365851

E(UTPSSh) = -1834.8344352 Hartree

Zero-point correction = 0.159633

Thermal correction to Energy = 0.176262

Thermal correction to Enthalpy = 0.177206

Thermal correction to Gibbs Free Energy = 0.112451

Sum of electronic and zero-point Energies = -1834.674802

Sum of electronic and thermal Energies = -1834.658174

Sum of electronic and thermal Enthalpies = -1834.657229

Sum of electronic and thermal Free Energies = -1834.721985

**Table S6.** Cartesian coordinates (Å) obtained with DFT calculations for the [VO(nta)(H<sub>2</sub>O)]·2H<sub>2</sub>O system.

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	23	0	0.001691	-0.521690	-0.265951
2	8	0	-0.013486	1.525896	3.285028
3	8	0	-0.004219	0.003321	1.651362
4	8	0	1.928496	-0.021052	-0.445063
5	8	0	-1.925798	-0.026681	-0.451945
6	8	0	0.004752	-2.111357	-0.042755
7	8	0	0.005810	-0.461773	-2.350231
8	7	0	-0.000201	1.844622	-0.353356
9	6	0	-0.006306	1.214982	2.093733
10	6	0	0.003774	2.327430	1.045814
11	6	0	2.342646	1.169277	-0.788062
12	6	0	1.238719	2.192145	-1.064887
13	8	0	3.521159	1.463802	-0.949032
14	6	0	-2.342987	1.163967	-0.789694
15	6	0	-1.242208	2.192134	-1.059532
16	8	0	-3.522029	1.455501	-0.952127
17	1	0	-0.801501	-0.926525	-2.691935
18	1	0	0.814531	-0.927414	-2.687213
19	1	0	-0.864995	2.963936	1.226580
20	1	0	0.886507	2.944339	1.226795
21	1	0	1.595469	3.196687	-0.824363
22	1	0	1.049934	2.150390	-2.139389
23	1	0	-1.055625	2.160168	-2.134818
24	1	0	-1.602089	3.193432	-0.810391
25	8	0	-2.416165	-1.536301	-2.804990
26	1	0	-2.481391	-2.498642	-2.774540
27	1	0	-2.621879	-1.233411	-1.901172
28	8	0	2.429806	-1.540399	-2.788851
29	1	0	2.491615	-2.502765	-2.752702
30	1	0	2.631355	-1.233512	-1.885405

E (UTPSSh) = -1987.7904187 Hartree

Zero-point correction = 0.209399

Thermal correction to Energy = 0.231174

Thermal correction to Enthalpy = 0.232118

Thermal correction to Gibbs Free Energy = 0.157372

Sum of electronic and zero-point Energies = -1987.581019

Sum of electronic and thermal Energies = -1987.559245

Sum of electronic and thermal Enthalpies = -1987.558301

Sum of electronic and thermal Free Energies = -1987.633047



**Table S7.** Cartesian coordinates (Å) obtained with DFT calculations for the [VO(Hdtpa)]<sup>2-</sup> system.

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	23	0	3.916782	1.692652	-0.017927
2	8	0	5.298074	1.459505	-0.813991
3	8	0	2.539011	1.634859	-1.448533
4	8	0	0.436800	1.196102	-2.072667
5	8	0	3.952896	3.684578	0.073676
6	8	0	2.992414	5.670540	0.435644
7	8	0	3.357921	-0.136594	0.516616
8	8	0	3.583743	-1.812174	1.982601
9	8	0	7.399990	6.559266	0.877750
10	8	0	7.790317	5.414241	2.791243
11	8	0	11.044586	1.302741	2.658591
12	8	0	9.334955	2.198294	3.841019
13	7	0	1.879793	2.258332	1.022607
14	7	0	4.531655	1.677385	2.103506
15	7	0	8.037192	3.093172	1.690911
16	6	0	2.039605	1.854506	2.430306
17	6	0	3.416756	2.267660	2.918520
18	6	0	5.746673	2.489196	2.424529
19	6	0	7.027727	1.986281	1.764809
20	6	0	0.878156	1.490699	0.268231
21	6	0	1.278341	1.435769	-1.210291
22	6	0	1.691631	3.713148	0.858293
23	6	0	2.965677	4.441993	0.433151
24	6	0	4.718781	0.240069	2.442470
25	6	0	3.809397	-0.665391	1.614796
26	6	0	7.666715	4.203986	0.747555
27	6	0	7.616900	5.531806	1.547166
28	6	0	9.415315	2.542266	1.481780
29	6	0	9.981731	1.945870	2.793889
30	1	0	8.071400	3.586885	2.614597
31	1	0	1.283915	2.317632	3.075525
32	1	0	1.904714	0.775582	2.493842
33	1	0	3.550719	1.987321	3.967353
34	1	0	3.519260	3.351322	2.852898
35	1	0	5.523263	3.500788	2.088200
36	1	0	5.878516	2.516258	3.510965
37	1	0	6.842879	1.644469	0.747121
38	1	0	7.492950	1.197221	2.350704
39	1	0	-0.130675	1.899840	0.368553
40	1	0	0.869827	0.463992	0.636183
41	1	0	0.949887	3.893026	0.077578
42	1	0	1.303631	4.170034	1.772769
43	1	0	5.739484	-0.051640	2.193770
44	1	0	4.571221	0.060655	3.509651
45	1	0	6.692652	3.996975	0.305798
46	1	0	8.403605	4.256366	-0.050247
47	1	0	10.052805	3.368289	1.167126
48	1	0	9.379015	1.803726	0.682563

E (UTPSSh) = -2481.9306069 Hartree

Zero-point correction = 0.357959

Thermal correction to Energy = 0.386300

Thermal correction to Enthalpy = 0.387244

Thermal correction to Gibbs Free Energy = 0.295400  
 Sum of electronic and zero-point Energies = -2481.572648  
 Sum of electronic and thermal Energies = -2481.544307  
 Sum of electronic and thermal Enthalpies = -2481.543363  
 Sum of electronic and thermal Free Energies = -2481.635207

**Table S8.** Cartesian coordinates (Å) obtained with DFT calculations for the  $[\text{VO}(\text{ox})_2(\text{H}_2\text{O})]^{2-}$  system.

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	8	0	-0.508140	1.946810	-1.268865
2	8	0	0.587009	-0.878003	0.879511
3	8	0	-1.653912	0.763737	1.052205
4	8	0	-1.638139	-0.687047	-1.074445
5	8	0	1.098244	-0.252669	-1.559017
6	8	0	1.113763	1.692441	0.854305
7	1	0	1.754589	2.220853	0.361457
8	1	0	1.612466	1.003060	1.317706
9	23	0	-0.305593	0.602672	-0.400964
10	6	0	1.748960	-1.293887	-1.152100
11	6	0	1.418424	-1.687649	0.320233
12	6	0	-2.701289	-0.859335	-0.344945
13	6	0	-2.708512	0.018014	0.942848
14	8	0	-3.638566	-0.022564	1.738923
15	8	0	-3.621289	-1.620617	-0.610249
16	8	0	1.937021	-2.674339	0.840861
17	8	0	2.561539	-1.927351	-1.821694

E(UTPSSh) = -1850.8843546 Hartree  
 Zero-point correction = 0.080395  
 Thermal correction to Energy = 0.096177  
 Thermal correction to Enthalpy = 0.097122  
 Thermal correction to Gibbs Free Energy = 0.035603  
 Sum of electronic and zero-point Energies = -1850.803960  
 Sum of electronic and thermal Energies = -1850.788177  
 Sum of electronic and thermal Enthalpies = -1850.787233  
 Sum of electronic and thermal Free Energies = -1850.848751

**Table S9.** Cartesian coordinates (Å) obtained with DFT calculations for the  $[\text{VO}(\text{ox})_2(\text{H}_2\text{O})]^{2-} \cdot 2\text{H}_2\text{O}$  system.

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	8	0	-0.791500	1.904637	-1.023683
2	8	0	0.688786	-1.090429	0.600458
3	8	0	-1.605481	0.354425	1.247977
4	8	0	-1.726367	-0.800188	-1.041768
5	8	0	0.886454	-0.107624	-1.763277
6	8	0	1.017670	1.540833	0.869621
7	1	0	1.293689	2.388909	0.454894
8	1	0	1.799983	1.090068	1.271504
9	8	0	1.133733	3.769194	-0.687312
10	1	0	0.330882	3.267406	-0.965625
11	1	0	0.800482	4.565542	-0.257255
12	8	0	3.085541	0.223822	2.116958
13	1	0	3.969429	0.564468	1.935214
14	1	0	3.063693	-0.664788	1.700490
15	23	0	-0.406456	0.482778	-0.327989
16	6	0	1.754860	-1.031119	-1.513887
17	6	0	1.742615	-1.458646	-0.021522
18	6	0	-2.714075	-1.120507	-0.259269
19	6	0	-2.634251	-0.427393	1.132754
20	8	0	-3.477873	-0.625447	1.997492
21	8	0	-3.628279	-1.879571	-0.549960
22	8	0	2.716945	-2.037855	0.485066
23	8	0	2.531171	-1.523799	-2.328470

E(UTPSSh) = -2003.8408704 Hartree

Zero-point correction = 0.130359

Thermal correction to Energy = 0.150910

Thermal correction to Enthalpy = 0.151854

Thermal correction to Gibbs Free Energy = 0.079621

Sum of electronic and zero-point Energies = -2003.710512

Sum of electronic and thermal Energies = -2003.689960

Sum of electronic and thermal Enthalpies = -2003.689016

Sum of electronic and thermal Free Energies = -2003.761249

**Table S10.** Cartesian coordinates (Å) obtained with DFT calculations for the [VO(acac)<sub>2</sub>(H<sub>2</sub>O)] system.

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	8	0	-0.204392	0.393633	-2.446250
2	8	0	-1.580493	-1.181290	-0.591895
3	8	0	1.157186	-1.323990	-0.722780
4	8	0	1.317316	1.427080	-0.343972
5	8	0	-1.421391	1.577601	-0.231887
6	8	0	-0.093495	-0.158773	1.590075
7	1	0	0.507796	0.477292	1.998264
8	1	0	0.285177	-1.024488	1.790153
9	23	0	-0.152586	0.178983	-0.864708
10	6	0	-2.666456	1.457124	0.039267
11	6	0	-2.808387	-0.993590	-0.280774
12	6	0	2.578472	1.199435	-0.350215
13	6	0	2.435280	-1.249129	-0.683898
14	6	0	-3.375175	0.250479	0.016778
15	6	0	-3.371022	2.732268	0.411508
16	1	0	-2.884063	3.169584	1.286598
17	1	0	-3.273695	3.450344	-0.406285
18	1	0	-4.425177	2.570224	0.627812
19	6	0	-3.658101	-2.233314	-0.237779
20	1	0	-3.632471	-2.722365	-1.214566
21	1	0	-3.235532	-2.933855	0.486656
22	1	0	-4.689725	-2.014159	0.030563
23	1	0	-4.425663	0.278277	0.268834
24	6	0	3.159158	-0.060002	-0.536760
25	1	0	4.237552	-0.125997	-0.514332
26	6	0	3.162024	-2.560823	-0.788890
27	1	0	2.832188	-3.220808	0.017060
28	1	0	2.897051	-3.044207	-1.732418
29	1	0	4.241845	-2.436707	-0.736417
30	6	0	3.451447	2.400582	-0.116442
31	1	0	3.257459	3.142760	-0.894716
32	1	0	3.187050	2.857657	0.840147
33	1	0	4.509150	2.144792	-0.115851

E(UTPSSh) = -1786.6843756 Hartree

Zero-point correction = 0.251678

Thermal correction to Energy = 0.274121

Thermal correction to Enthalpy = 0.275065

Thermal correction to Gibbs Free Energy = 0.199057

Sum of electronic and zero-point Energies = -1786.432698

Sum of electronic and thermal Energies = -1786.410255

Sum of electronic and thermal Enthalpies = -1786.409311

Sum of electronic and thermal Free Energies = -1786.485318

**Table S11.** Cartesian coordinates (Å) obtained with DFT calculations for the [VO(acac)<sub>2</sub>(H<sub>2</sub>O)]·2H<sub>2</sub>O system.

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	8	0	-0.017798	-0.282798	-2.209224
2	8	0	-1.317326	-1.587631	-0.156450
3	8	0	1.471250	-1.279965	-0.113072
4	8	0	1.182189	1.477685	-0.458227
5	8	0	-1.607911	1.189851	-0.503193
6	8	0	-0.255047	0.179538	1.689634
7	1	0	0.050921	1.057714	2.000271
8	1	0	0.216098	-0.515528	2.195946
9	8	0	0.546239	2.816914	1.935049
10	1	0	0.710919	2.669918	0.984780
11	1	0	-0.200104	3.427033	1.972475
12	8	0	1.061212	-2.097310	2.549627
13	1	0	1.217049	-2.156751	1.588422
14	1	0	0.451582	-2.816737	2.753281
15	23	0	-0.089123	-0.091840	-0.624306
16	6	0	-2.838827	0.921435	-0.277946
17	6	0	-2.582269	-1.529098	0.028811
18	6	0	2.441843	1.418846	-0.706023
19	6	0	2.698199	-1.027380	-0.400010
20	6	0	-3.348296	-0.358462	-0.027800
21	6	0	-3.766911	2.104737	-0.289502
22	1	0	-3.439693	2.824954	0.464453
23	1	0	-3.705847	2.601819	-1.260663
24	1	0	-4.798574	1.819428	-0.093316
25	6	0	-3.248893	-2.842944	0.330669
26	1	0	-3.063907	-3.538794	-0.491252
27	1	0	-2.800268	-3.275157	1.228529
28	1	0	-4.321565	-2.734756	0.478628
29	1	0	-4.410816	-0.447595	0.148750
30	6	0	3.183364	0.233651	-0.763791
31	1	0	4.237403	0.316174	-0.986973
32	6	0	3.645076	-2.188073	-0.288435
33	1	0	3.643259	-2.559853	0.739666
34	1	0	3.295583	-3.001533	-0.928443
35	1	0	4.660658	-1.914751	-0.566643
36	6	0	3.128575	2.739835	-0.905056
37	1	0	2.638835	3.282036	-1.717271
38	1	0	3.021664	3.344056	-0.000268
39	1	0	4.186008	2.620393	-1.131048

E (UTPSSh) = -1939.6333193 Hartree

Zero-point correction = 0.301741

Thermal correction to Energy = 0.329230

Thermal correction to Enthalpy = 0.330174

Thermal correction to Gibbs Free Energy = 0.242921

Sum of electronic and zero-point Energies = -1939.331578

Sum of electronic and thermal Energies = -1939.304089

Sum of electronic and thermal Enthalpies = -1939.303145

Sum of electronic and thermal Free Energies = -1939.390399