

ELECTRONIC SUPPLEMENTARY INFORMATION (ESI)

V^{IV}O complexes with antibacterial quinolone ligands and their interaction with serum proteins

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Table S1. Cartesian coordinates of the isomer *SPY-5-12*-[VO(nal)₂] optimized by DFT methods at the level of theory B3P86/6-311g.^a

Atom	<i>x</i>	<i>y</i>	<i>z</i>
C	-5.549628	2.594408	-0.412917
C	-6.682280	1.825115	-0.070127
C	-5.372156	-0.073927	0.127448
C	-4.196432	0.617769	-0.210868
C	-4.312834	1.991598	-0.483343
N	-5.306336	-1.434572	0.406078
C	-4.111302	-2.066134	0.359524
C	-2.925331	-1.451508	0.032774
C	-2.922723	-0.064914	-0.281003
C	-6.528305	-2.170410	0.798989
O	-1.880354	0.615228	-0.608638
C	-1.690867	-2.295185	0.056102
O	-0.561143	-1.693538	-0.251294
O	-1.783383	-3.494737	0.380462
C	5.549626	-2.594414	-0.412891
C	6.682297	-1.825095	-0.070223
C	5.372153	0.073918	0.127490
C	4.196433	-0.617771	-0.210857
C	4.312832	-1.991604	-0.483315
N	5.306337	1.434568	0.406098
C	4.111306	2.066134	0.359527
C	2.925336	1.451510	0.032773
C	2.922726	0.064914	-0.281000
C	6.528307	2.170407	0.799006
O	1.880356	-0.615229	-0.608630
C	1.690874	2.295189	0.056090
O	0.561147	1.693538	-0.251289
O	1.783386	3.494736	0.380470
V	0.000002	0.000001	-0.995112
O	0.000006	0.000004	-2.579865
H	-5.663994	3.649420	-0.617181
H	-3.413360	2.533593	-0.739973
H	-4.090425	-3.121241	0.595597
H	-7.349709	-1.753313	0.223262
H	-6.378703	-3.206357	0.497374
H	5.663979	-3.649443	-0.617075
H	3.413352	-2.533606	-0.739909
H	4.090431	3.121243	0.595590
H	7.349717	1.753287	0.223304
H	6.378718	3.206346	0.497360
N	6.583578	-0.514029	0.196474
N	-6.583576	0.514026	0.196464
C	8.042802	-2.437641	0.013544

H	8.773189	-1.680174	0.284362
H	8.069220	-3.234057	0.760774
H	8.333500	-2.880369	-0.941739
C	-8.042821	2.437610	0.013408
H	-8.773250	1.680085	0.283947
H	-8.069415	3.233896	0.760772
H	-8.333321	2.880499	-0.941860
C	-6.808239	-2.060897	2.290626
H	-6.980075	-1.022823	2.571864
H	-7.702181	-2.633733	2.542372
H	-5.977935	-2.451937	2.880218
C	6.808217	2.060934	2.290651
H	6.980039	1.022867	2.571921
H	7.702160	2.633770	2.542394
H	5.977907	2.451999	2.880219

^a Energy = -2622.53990613 a.u.

Table S2. Cartesian coordinates of the isomer SPY-5-13-[VO(nal)₂] optimized by DFT methods at the level of theory B3P86/6-311g.^a

Atom	<i>x</i>	<i>y</i>	<i>z</i>
C	-3.532531	3.491377	0.160911
C	-4.922580	3.386493	-0.060637
C	-4.758073	1.079711	-0.193488
C	-3.367791	1.094750	0.019686
C	-2.762779	2.349714	0.201173
N	-5.413658	-0.133215	-0.374276
C	-4.696727	-1.276935	-0.341907
C	-3.336909	-1.333017	-0.129701
C	-2.607231	-0.135141	0.065234
C	-6.884843	-0.109018	-0.591666
O	-1.331871	-0.067491	0.269456
C	-2.707755	-2.692871	-0.157989
O	-1.415720	-2.743686	0.058702
O	-3.432068	-3.677334	-0.403624
C	3.712807	3.302896	0.254540
C	5.102923	3.129210	0.077165
C	4.831818	0.831406	-0.037820
C	3.437554	0.915485	0.131028
C	2.888290	2.200287	0.281880
N	5.426944	-0.414652	-0.177258
C	4.654832	-1.524858	-0.159244
C	3.289015	-1.513480	0.003408
C	2.616007	-0.275091	0.161482
C	6.888237	-0.521478	-0.387556
O	1.340109	-0.141857	0.321090
C	2.591079	-2.840262	-0.031334
O	1.290029	-2.819054	0.126230
O	3.273390	-3.864002	-0.229706
V	-0.045399	-1.551808	0.738943
O	-0.083053	-1.600365	2.321380
H	-3.087939	4.466690	0.300131
H	-1.696134	2.372285	0.372572
H	-5.209264	-2.214052	-0.495908
H	-7.068335	0.553846	-1.435842
H	-7.327788	0.373087	0.279273
H	3.312102	4.299988	0.370263
H	1.819197	2.276007	0.419595
H	5.141677	-2.482699	-0.283233
H	7.353737	0.257087	0.210188
H	7.187748	-1.492098	0.005250
C	-7.496480	-1.475526	-0.827915
H	-7.093998	-1.965324	-1.715188
H	-7.372779	-2.144208	0.024389

H	-8.567502	-1.345119	-0.985364
C	7.268471	-0.374198	-1.853433
H	6.988087	0.610622	-2.224776
H	8.347809	-0.485783	-1.967672
H	6.782921	-1.133526	-2.467779
C	6.035036	4.296856	0.043901
H	7.055184	3.951456	-0.098687
H	5.779412	4.980992	-0.768470
H	5.984677	4.865928	0.974947
C	-5.797735	4.596865	-0.110124
H	-5.486833	5.275251	-0.907915
H	-6.827729	4.299579	-0.286285
H	-5.749293	5.155168	0.827541
N	-5.513948	2.195731	-0.232808
N	5.641360	1.910378	-0.066588

^a Energy = -2622.52875181 a.u.

Table S3. Cartesian coordinates of the isomer *OC-6-32*-[VO(nal)₂(H₂O)] optimized by DFT methods at the level of theory B3P86/6-311g.^a

Atom	<i>x</i>	<i>y</i>	<i>z</i>
C	6.031177	-1.503746	0.925411
C	6.748736	-0.342246	0.568177
C	4.847827	0.573335	-0.388377
C	4.058999	-0.546318	-0.069810
C	4.694636	-1.600794	0.606330
N	4.272652	1.640439	-1.064194
C	2.965534	1.581674	-1.406302
C	2.135272	0.522560	-1.124608
C	2.654544	-0.601451	-0.424421
C	5.073378	2.846622	-1.367592
O	1.979552	-1.647345	-0.094331
C	0.724363	0.641981	-1.613893
O	-0.095868	-0.340036	-1.323206
O	0.399291	1.657723	-2.262227
C	-5.919828	-1.312862	-1.445258
C	-6.655560	-0.209205	-0.965645
C	-4.852374	0.475188	0.316660
C	-4.052876	-0.600746	-0.105325
C	-4.624194	-1.504450	-1.016330
N	-4.329675	1.400434	1.210790
C	-3.061873	1.246568	1.660850
C	-2.220753	0.228032	1.282272
C	-2.688128	-0.751801	0.358869
C	-5.136364	2.566306	1.628149
O	-2.007191	-1.751133	-0.077482
C	-0.876350	0.188590	1.944195
O	-0.057822	-0.751865	1.534998
O	-0.623049	1.019364	2.844633
V	-0.015286	-1.954509	-0.248854
O	0.031310	-3.217458	-1.223570
H	6.537802	-2.304325	1.445492
H	4.102052	-2.468246	0.857541
H	2.547323	2.422511	-1.942274
H	6.076555	2.510097	-1.614350
H	4.627806	3.300585	-2.251863
H	-6.377787	-1.993749	-2.148632
H	-4.013450	-2.327639	-1.358946
H	-2.693554	1.969535	2.375464
H	-6.166625	2.230103	1.706021
H	-4.783505	2.851130	2.618894
O	0.169008	-3.146224	1.473946
H	0.785681	-3.882898	1.530886
H	0.283021	-2.423137	2.130245

C	5.105546	3.821190	-0.199368
H	5.579295	3.362926	0.667621
H	5.680361	4.707591	-0.472639
H	4.100460	4.140371	0.079027
C	-5.022323	3.722859	0.645536
H	-5.403193	3.431558	-0.332313
H	-5.609393	4.571197	1.001568
H	-3.987072	4.047506	0.533827
C	-8.062787	0.040286	-1.404581
H	-8.460690	0.910120	-0.888965
H	-8.110784	0.220824	-2.481135
H	-8.701470	-0.819555	-1.191093
C	8.200604	-0.193525	0.889939
H	8.554285	0.778920	0.558569
H	8.377135	-0.285179	1.963857
H	8.793021	-0.967692	0.396654
N	6.156119	0.673203	-0.075509
N	-6.120634	0.665730	-0.101252

^a Energy = -2699.15551270 a.u.

Table S4. Cartesian coordinates of the isomer OC-6-34-[VO(nal)₂(H₂O)] optimized by DFT methods at the level of theory B3P86/6-311g.^a

Atom	<i>x</i>	<i>y</i>	<i>z</i>
C	2.005813	3.317164	-1.517400
C	3.297648	3.724672	-1.119896
C	3.809232	1.563504	-0.462204
C	2.542826	1.074360	-0.829252
C	1.633738	1.999107	-1.371126
N	4.747659	0.689483	0.067858
C	4.429346	-0.615953	0.215070
C	3.211317	-1.161602	-0.119625
C	2.197237	-0.320292	-0.650872
C	6.066796	1.193105	0.510409
O	1.006702	-0.698254	-0.981244
C	3.072410	-2.638304	0.094245
O	1.911242	-3.174204	-0.194596
O	4.054016	-3.277732	0.522590
C	-5.235940	0.074467	-2.150799
C	-5.925398	0.950532	-1.286458
C	-4.309802	0.659480	0.348736
C	-3.560685	-0.222807	-0.449324
C	-4.058927	-0.507851	-1.731297
N	-3.863350	0.966476	1.627825
C	-2.711753	0.412293	2.080413
C	-1.929095	-0.452132	1.355216
C	-2.323396	-0.810515	0.032802
C	-4.623150	1.911112	2.473161
O	-1.679703	-1.594625	-0.752029
C	-0.722358	-1.018050	2.042148
O	-0.063171	-1.927295	1.368551
O	-0.447168	-0.619904	3.195692
V	0.155882	-2.488974	-0.706805
O	-0.002577	-3.067912	-2.181251
H	1.322940	4.043989	-1.934022
H	0.658475	1.636291	-1.662020
H	5.183836	-1.276921	0.619104
H	6.761871	0.358955	0.424529
H	6.362915	1.969700	-0.189208
H	-5.638199	-0.132650	-3.132343
H	-3.490940	-1.186973	-2.351777
H	-2.394662	0.662551	3.083717
H	-5.676868	1.751803	2.261586
H	-4.426879	1.631746	3.507726
O	-0.414804	-4.180831	0.389953
H	0.276005	-4.853782	0.287215
H	-0.354261	-3.741830	1.269725

N	4.175174	2.854414	-0.601592
N	-5.460190	1.233369	-0.060286
C	-4.236891	3.359107	2.208464
H	-4.464746	3.632823	1.178982
H	-4.800575	4.020269	2.868744
H	-3.173931	3.524732	2.389888
C	-7.205594	1.603738	-1.697887
H	-7.581646	2.222284	-0.887549
H	-7.060958	2.231564	-2.580208
H	-7.963078	0.858846	-1.951621
C	3.743270	5.144566	-1.257496
H	3.125628	5.809806	-0.649361
H	4.776689	5.240186	-0.935892
H	3.663501	5.484026	-2.292437
C	6.023229	1.735521	1.931347
H	7.018211	2.069342	2.229977
H	5.345933	2.586096	1.995905
H	5.694872	0.972081	2.637648

^a Energy = -2699.15481390 a.u.

Table S5. Cartesian coordinates of the isomer *OC-6-24*-[VO(nal)₂(H₂O)] optimized by DFT methods at the level of theory B3P86/6-311g.^a

Atom	<i>x</i>	<i>y</i>	<i>z</i>
C	3.704240	-0.486874	3.303870
C	4.562398	-1.484641	2.796325
C	3.852808	-1.039299	0.637474
C	2.971388	-0.030038	1.058627
C	2.913020	0.235693	2.436970
N	3.950397	-1.343113	-0.717061
C	3.195950	-0.652510	-1.600001
C	2.318785	0.354063	-1.260776
C	2.162066	0.708014	0.109273
C	4.892053	-2.417544	-1.125716
O	1.362540	1.604361	0.570439
C	1.601869	1.002118	-2.406460
O	0.910262	2.085921	-2.145520
O	1.714858	0.503167	-3.547292
C	-2.724670	-2.700781	-2.098904
C	-3.868165	-3.155204	-1.410415
C	-3.789904	-1.316492	-0.002565
C	-2.642161	-0.797539	-0.626890
C	-2.117006	-1.526516	-1.705823
N	-4.362122	-0.622793	1.055420
C	-3.803210	0.543629	1.466331
C	-2.685656	1.108778	0.905819
C	-2.029814	0.446195	-0.178491
C	-5.545525	-1.171016	1.749357
O	-0.972807	0.866832	-0.758000
C	-2.227012	2.408961	1.489857
O	-1.185644	2.973162	0.934425
O	-2.857984	2.887488	2.457536
V	0.137187	2.810159	-0.472426
O	0.939617	4.179869	-0.337659
O	-1.182523	3.452578	-1.954256
H	3.676619	-0.297229	4.367481
H	2.239232	1.010979	2.773368
H	3.276036	-0.901580	-2.646725
H	4.598189	-3.319779	-0.590355
H	5.874055	-2.141705	-0.743634
H	-2.338632	-3.274258	-2.929854
H	-1.242615	-1.132246	-2.205172
H	-4.275099	1.060341	2.290927
H	-6.086232	-0.320886	2.163926
H	-6.167241	-1.646296	0.995452
H	-0.724415	3.119429	-2.749730
H	-1.488564	4.364154	-2.012354

C	4.939245	-2.663260	-2.620680
H	3.978353	-2.986431	-3.022541
H	5.271402	-1.786747	-3.178023
H	5.657106	-3.461551	-2.811351
C	5.443910	-2.288138	3.696875
H	5.965931	-3.046969	3.120430
H	6.185371	-1.652119	4.186583
H	4.865403	-2.776030	4.484009
N	4.626327	-1.749566	1.482364
N	-4.384114	-2.467756	-0.380747
C	-4.560449	-4.422907	-1.797932
H	-5.418270	-4.586104	-1.151160
H	-4.904975	-4.382368	-2.833714
H	-3.889018	-5.280508	-1.713002
C	-5.166310	-2.167579	2.835288
H	-6.065015	-2.531323	3.336352
H	-4.648455	-3.022851	2.402993
H	-4.521574	-1.708664	3.586206

^a Energy = -2699.15060318.

Table S6. Cartesian coordinates of the isomer OC-6-23-[VO(nal)₂(H₂O)] optimized by DFT methods at the level of theory B3P86/6-311g.^a

Atom	<i>x</i>	<i>y</i>	<i>z</i>
C	-5.288385	-0.329470	-1.961081
C	-5.996549	0.569635	-1.135129
C	-4.269229	0.560842	0.408106
C	-3.495834	-0.329230	-0.356791
C	-4.045058	-0.776415	-1.570321
N	-3.776788	1.017622	1.623854
C	-2.557612	0.606293	2.043823
C	-1.751185	-0.265776	1.350812
C	-2.197796	-0.780643	0.101324
C	-4.564950	1.974385	2.431060
O	-1.537243	-1.596407	-0.642110
C	-0.421264	-0.580691	1.967782
O	0.311574	-1.494760	1.376503
O	-0.076502	0.046018	2.990665
C	1.818305	3.207695	-1.930699
C	2.975420	3.758851	-1.341231
C	3.557524	1.689890	-0.475109
C	2.430291	1.058911	-1.031686
C	1.551070	1.864892	-1.772378
N	4.460673	0.946335	0.272934
C	4.240089	-0.377733	0.439661
C	3.154308	-1.054847	-0.064482
C	2.177109	-0.355943	-0.827477
C	5.626028	1.650727	0.867769
O	1.116245	-0.889132	-1.333115
C	3.123534	-2.530238	0.189808
O	2.003489	-3.152690	-0.099280
O	4.155188	-3.089605	0.613369
V	0.113476	-2.664409	-0.165425
O	-0.626833	-3.979553	0.329021
O	0.335653	-3.190330	-2.193956
H	-5.731446	-0.662004	-2.889047
H	-3.464543	-1.471101	-2.160737
H	-2.192826	0.994227	2.985077
H	-5.610319	1.700217	2.319428
H	-4.271661	1.821429	3.468770
H	1.153495	3.844241	-2.497746
H	0.676549	1.392540	-2.197109
H	4.966563	-0.950533	0.993944
H	5.229351	2.434910	1.511988
H	6.143083	2.154897	0.052528
H	0.769278	-2.375650	-2.516510
H	0.917652	-3.960603	-2.268961

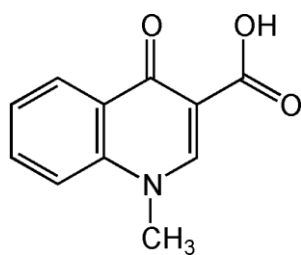
C	-7.350525	1.075242	-1.515674
H	-8.070087	0.255583	-1.580020
H	-7.701363	1.786703	-0.773201
H	-7.329437	1.564641	-2.491790
C	-4.339459	3.415180	1.996991
H	-4.663146	3.558314	0.966925
H	-4.918520	4.087672	2.631874
H	-3.287979	3.694210	2.078432
C	3.307393	5.209842	-1.481817
H	2.541135	5.834454	-1.016271
H	4.260429	5.416570	-1.002651
H	3.369613	5.501142	-2.532547
C	6.569846	0.745685	1.634539
H	6.088879	0.266896	2.487846
H	7.010627	-0.027842	1.004717
H	7.386324	1.356296	2.021347
N	3.822766	3.004262	-0.627546
N	-5.485594	1.002265	0.026889

^a Energy = -2699.14620770 a.u.

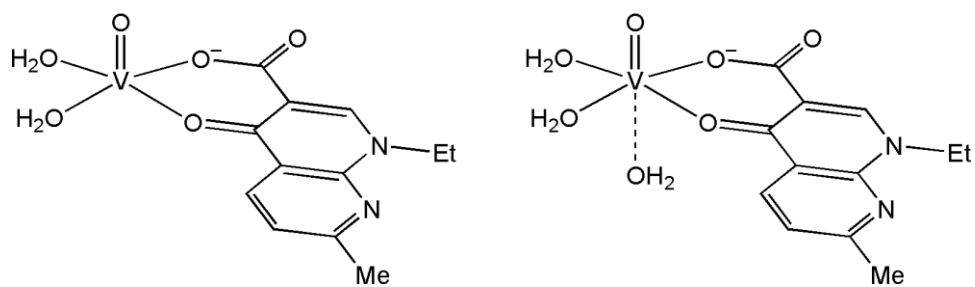
Table S7. ^{51}V A values calculated at the level of theory BHandHLYP/6-311+g(d) with Gaussian 09 software for the $\text{V}^{\text{IV}}\text{O}$ species formed by the model ligand L^{Q} .^{a,b}

	Isomer	$A_{\text{iso}}^{\text{calcd}}$	$A_{\text{x}}^{\text{calcd}}$	$A_{\text{y}}^{\text{calcd}}$	$A_{\text{z}}^{\text{calcd}}$	$A_{\text{z}}^{\text{exptl}}$	PD ^c
$[\text{VO}(\text{L}^{\text{Q}})(\text{H}_2\text{O})_2]^+$	–	-112.0	-75.7	-78.7	-181.6	-175.4	3.5
$[\text{VO}(\text{L}^{\text{Q}})(\text{H}_2\text{O})_3]^+$	–	-107.5	-72.3	-74.0	-176.2	-175.4	0.5
<i>cis</i> - $[\text{VO}(\text{L}^{\text{Q}})_2(\text{H}_2\text{O})]$	OC-6-23	-99.4	-62.5	-67.2	-168.5	-174.6	-3.5
<i>cis</i> - $[\text{VO}(\text{L}^{\text{Q}})_2(\text{H}_2\text{O})]$	OC-6-24	-102.0	-66.1	-69.7	-170.2	-174.6	-2.5
<i>cis</i>-$[\text{VO}(\text{L}^{\text{Q}})_2(\text{H}_2\text{O})]$	OC-6-32	-105.3	-70.9	-71.5	-173.6	-174.6	-0.6
<i>cis</i>-$[\text{VO}(\text{L}^{\text{Q}})_2(\text{H}_2\text{O})]$	OC-6-34	-105.2	-70.3	-72.2	-173.3	-174.6	-0.7
$[\text{VO}(\text{L}^{\text{Q}})_2]$	SPY-5-12	-99.1	-61.1	-66.5	-169.6	-168.1	0.9
$[\text{VO}(\text{L}^{\text{Q}})_2]$	SPY-5-13	-96.6	-58.4	-64.2	-167.1	-168.1	-0.6
<i>trans</i> - $[\text{VO}(\text{L}^{\text{Q}})_2(\text{H}_2\text{O})]$	OC-6-42	-93.1	-55.2	-62.6	-161.7	-168.1	-3.8
<i>trans</i> - $[\text{VO}(\text{L}^{\text{Q}})_2(\text{H}_2\text{O})]$	OC-6-43	-89.2	-50.9	-59.5	-157.2	-168.1	-6.5
<i>cis</i>-$[\text{VO}(\text{L}^{\text{Q}})_2(\text{MeIm})]$	OC-6-32	-96.0	-61.6	-63.2	-163.3	-169.1	-3.4
<i>cis</i>-$[\text{VO}(\text{L}^{\text{Q}})_2(\text{MeIm})]$	OC-6-34	-96.3	-61.4	-64.1	-163.5	-169.1	-3.3

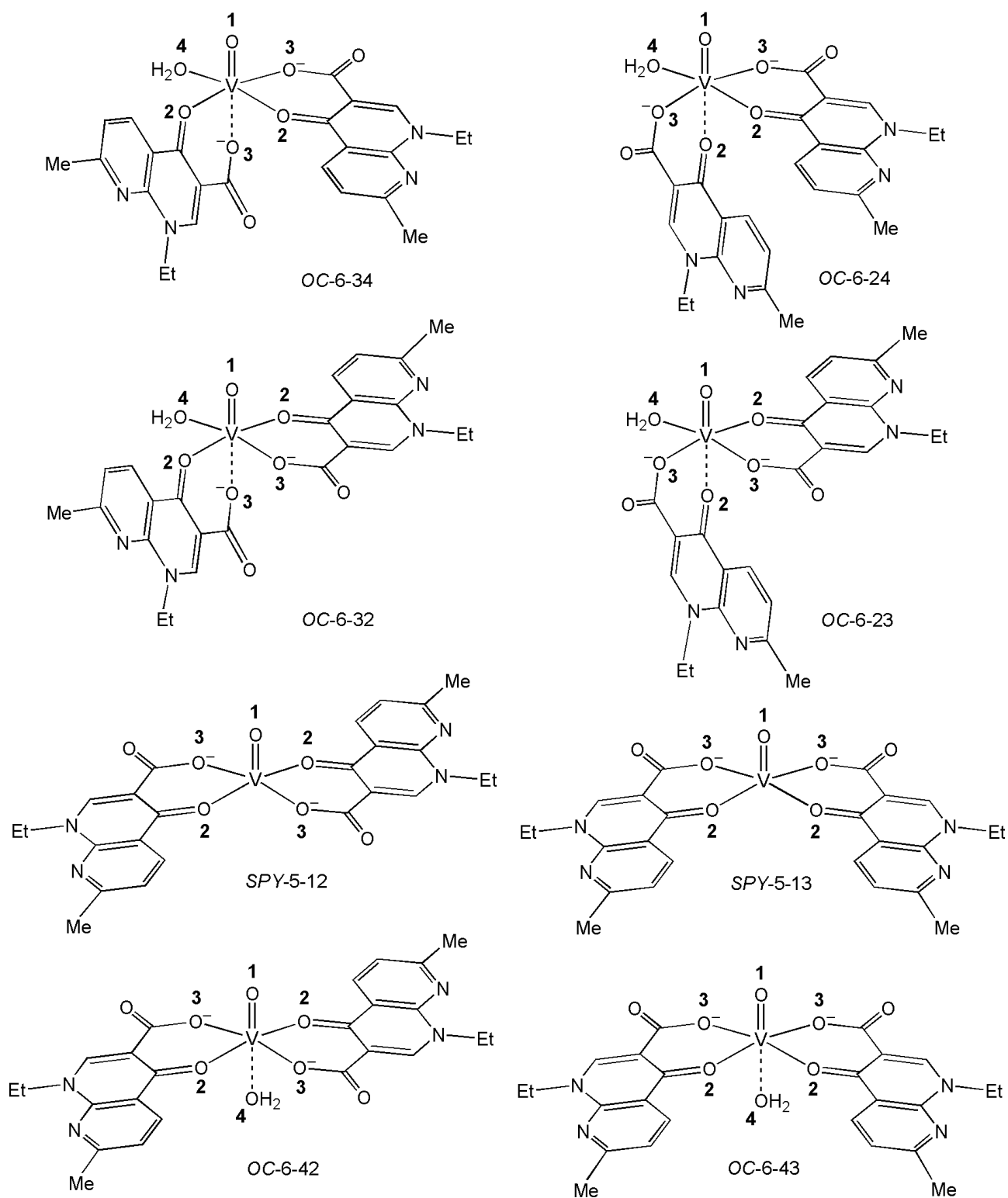
^a All the A values are in 10^{-4} cm^{-1} . ^b In bold the species probably formed in solution. ^c Percentage deviation (PD) respect to the absolute experimental value calculated as: $100 \times [(|A_{\text{z}}|^{\text{calcd}} - |A_{\text{z}}|^{\text{exptl}})|/|A_{\text{z}}|^{\text{exptl}}]$.



Scheme S1. Structure of the model ligand 1-methyl-4-oxo-1,4-dihydroquinoline-3-carboxylic acid (L^Q).



Scheme S2. Possible structures of the mono-chelated $V^{IV}O$ species of nalidixic acid.



Scheme S3. Possible structures of the bis-chelated $V^{IV}O$ species of nalidixic acid.

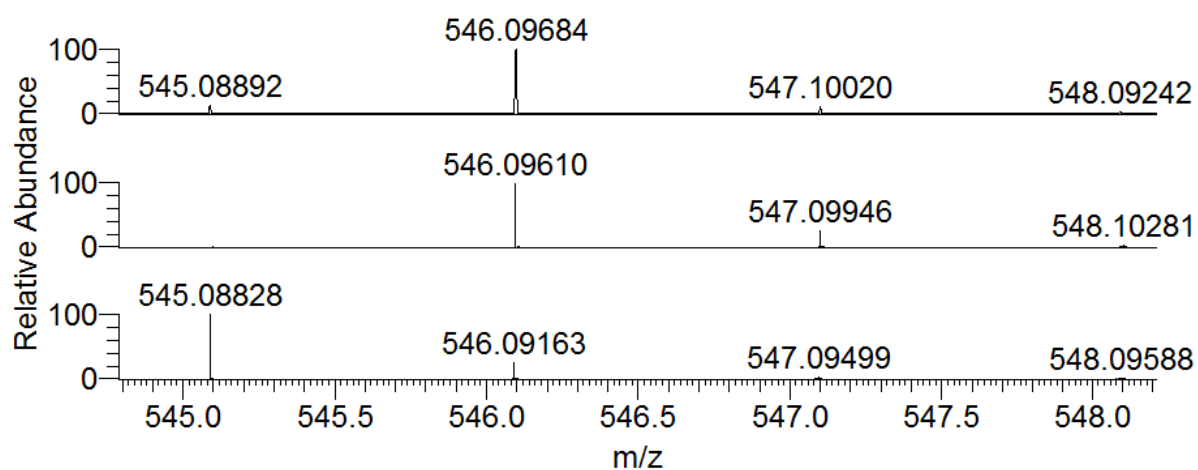


Figure S1. Experimental (above) and calculated isotopic pattern for the peak of $[\text{V}^{\text{IV}}\text{O}(\text{nal})_2(\text{OH})]^-$, (centre) and $[\text{V}^{\text{V}}\text{O}_2(\text{nal})_2]^-$ (below) revealed at $m/z = 546.10$ and 545.09 , respectively, in the negative ESI-MS spectrum recorded on the system $\text{V}^{\text{IV}}\text{O}^{2+}/\text{Hnal}$ 1:2 (ultrapure LC-MS water, V concentration 5.0×10^{-6} M).

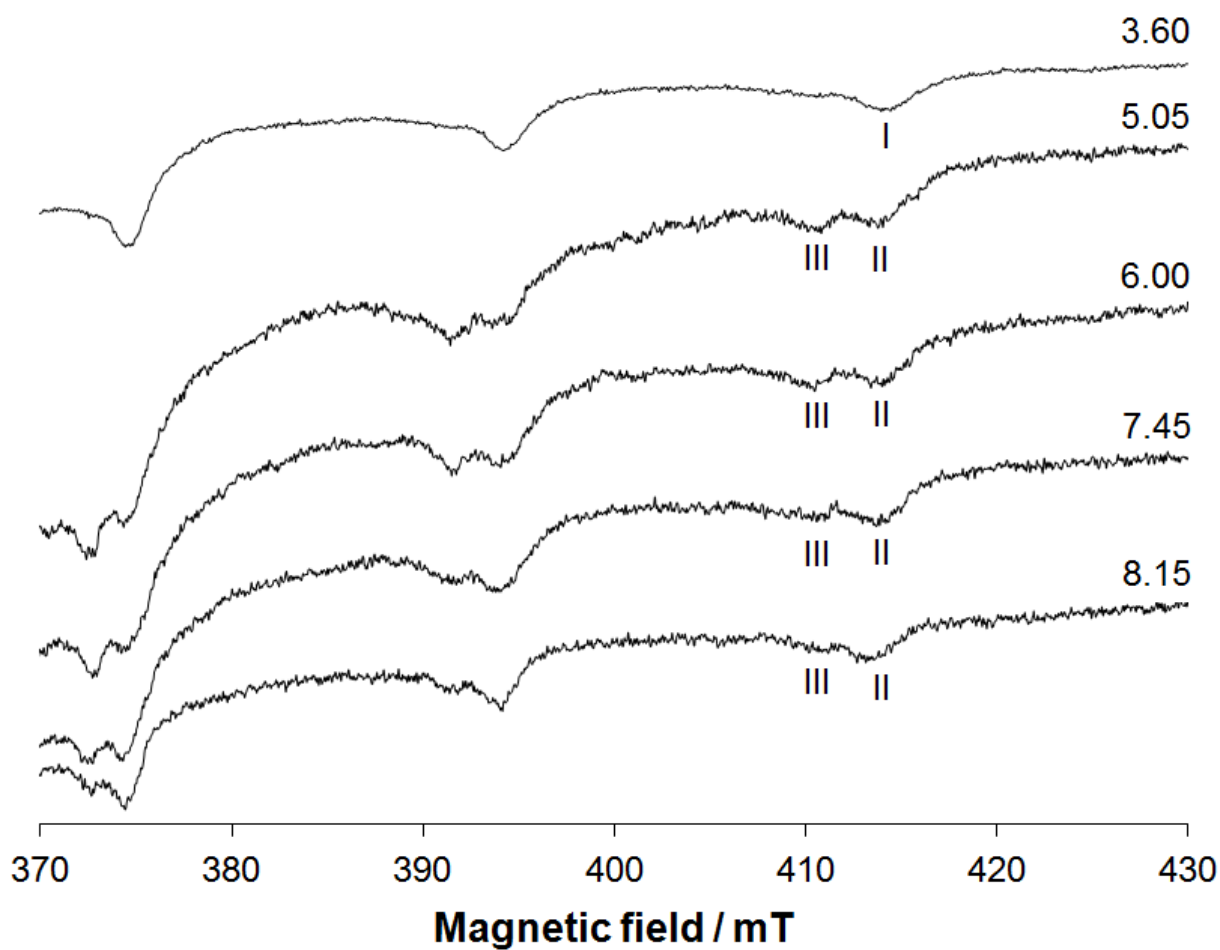


Figure S2. High field region of the X-band anisotropic EPR spectra recorded in H₂O at 120 K as a function of pH in the system V^{IV}O²⁺/Hlev (HL) with a metal to ligand molar ratio of 1:2 and V concentration of 1.0×10^{-3} M. With **I**, **II** and **III** are indicated the $M_I = 7/2$ resonances of the species [VO(HL)(H₂O)₃]²⁺, *cis*-[VOH_{*x*}L₂(H₂O)]^{*x*+} (OC-6-32) and [VOH_{*x*}L₂]^{*x*+} (SPY-5-12) with *x* = 0-2.

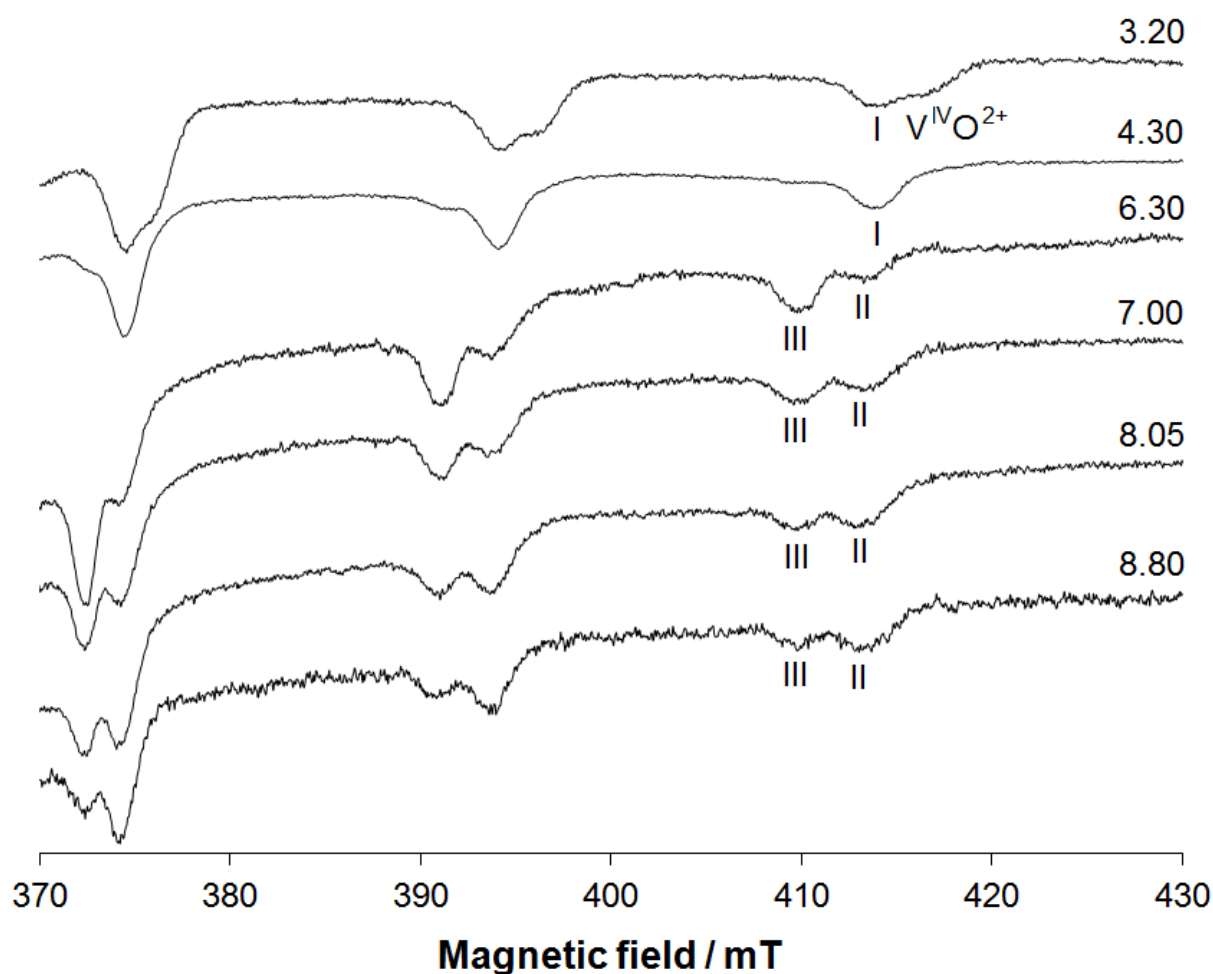


Figure S3. High field region of the X-band anisotropic EPR spectra recorded in a mixture $\text{H}_2\text{O}/\text{DMSO}$ 50/50 (w/w) at 120 K as a function of pH in the system $\text{V}^{\text{IV}}\text{O}^{2+}/\text{Hlev}$ (HL) with a metal to ligand molar ratio of 1:2 and V concentration of 1.0×10^{-3} M. With $\text{V}^{\text{IV}}\text{O}^{2+}$, **I**, **II** and **III** are indicated the $M_I = 7/2$ resonances of the species $[\text{VO}(\text{H}_2\text{O})_5]^{2+}$, $[\text{VO}(\text{HL})(\text{H}_2\text{O})_3]^{2+}$, *cis*- $[\text{VOH}_x\text{L}_2(\text{H}_2\text{O})]^{x+}$ (OC-6-32) and $[\text{VOH}_x\text{L}_2]^{x+}$ (SPY-5-12) with $x = 0-2$.

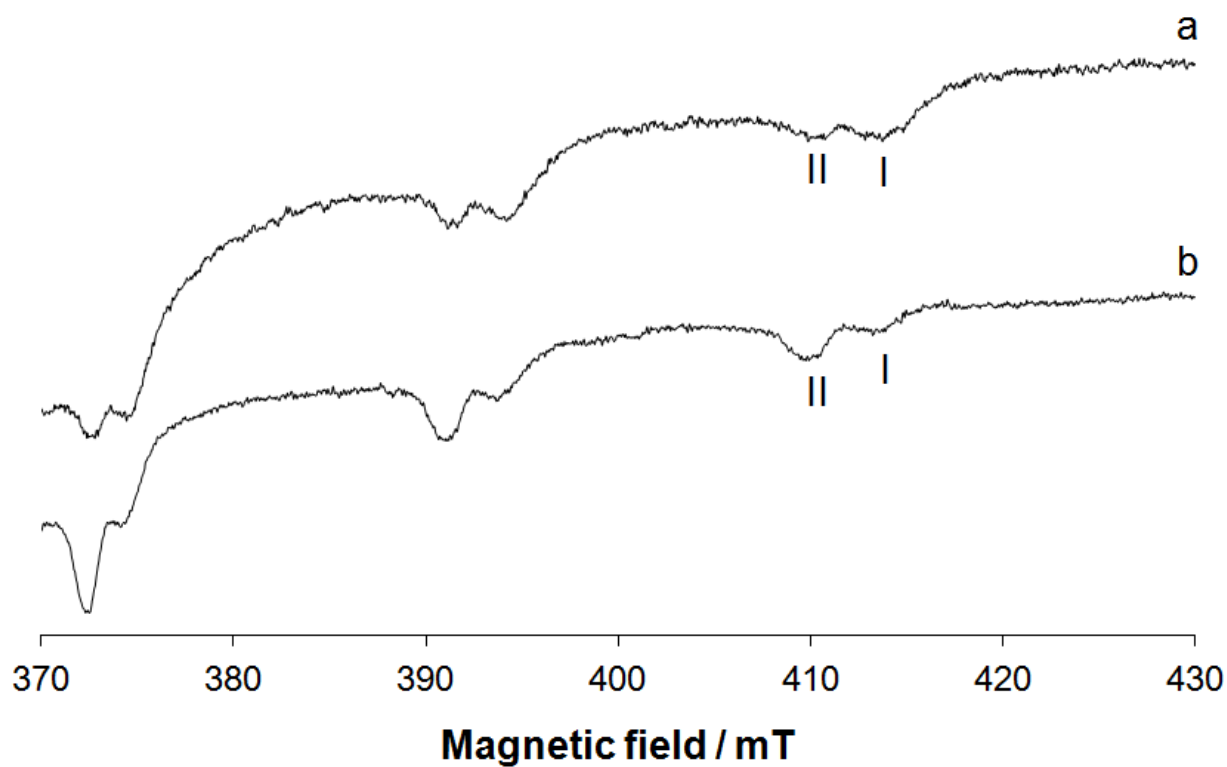


Figure S4. High field region of the X-band anisotropic EPR spectra recorded at 120 K in the system $V^{IV}O^{2+}/Hlev$ (HL) with a metal to ligand molar ratio of 1:2 and V concentration of 1.0×10^{-3} M: (a) spectrum recorded in H_2O at pH 6.80 and (b) spectrum recorded in a mixture $H_2O/DMSO$ 50/50 (w/w) at pH 6.30. With **I** and **II** are indicated the $M_I = 7/2$ resonances of the species *cis*- $[VOH_xL_2(H_2O)]^{x+}$ (OC-6-32) and $[VOH_xL_2]^{x+}$ (SPY-5-12) with $x = 0-2$.

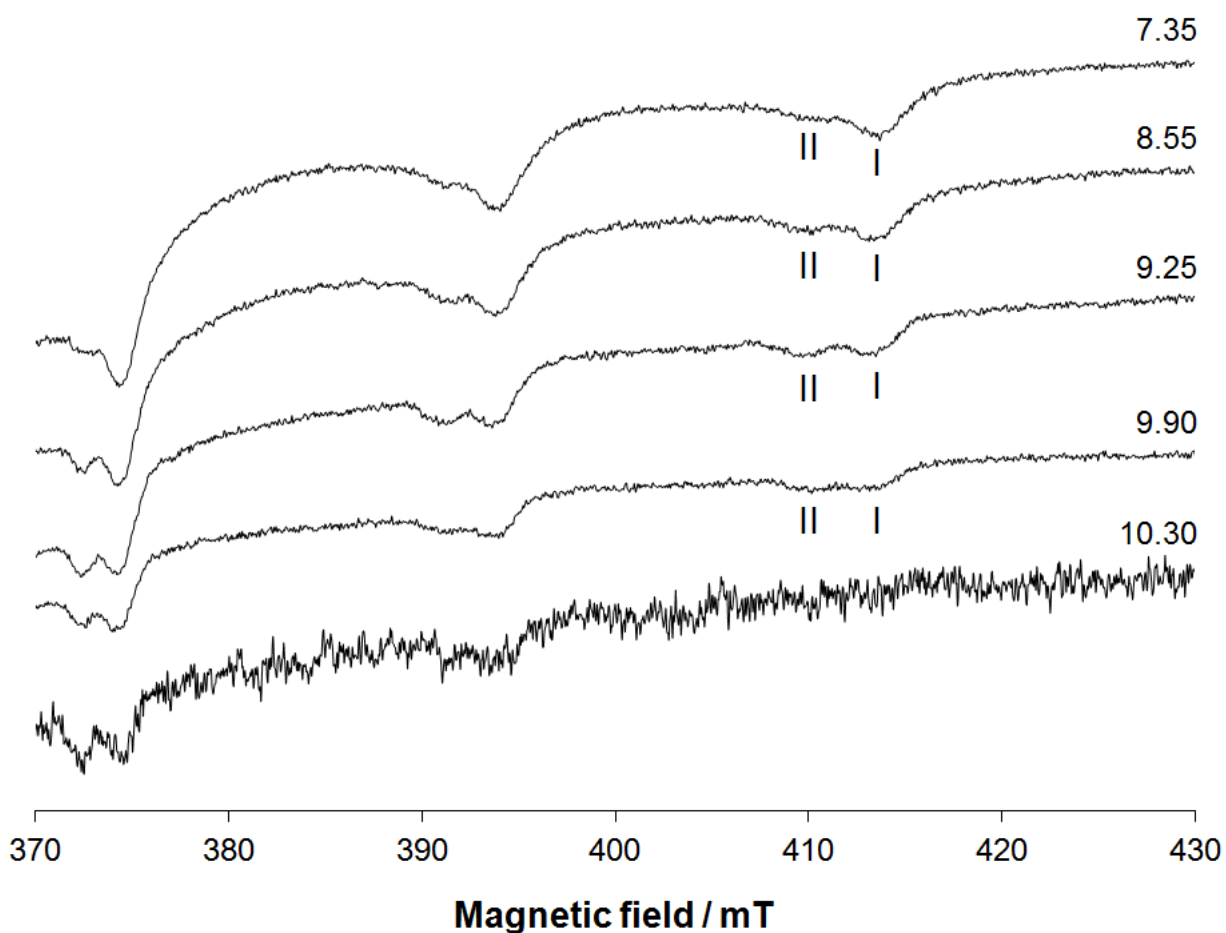


Figure S5. High field region of the X-band anisotropic EPR spectra recorded in a mixture $\text{H}_2\text{O}/\text{DMSO}$ 50/50 (w/w) at 120 K in the system $\text{V}^{\text{IV}}\text{O}^{2+}/\text{Hcip}$ (HL) with a metal to ligand molar ratio of 1:2 and V concentration of 1.0×10^{-3} M. With **I** and **II** are indicated the $M_I = 7/2$ resonances of the species $\text{cis}[\text{VOH}_x\text{L}_2(\text{H}_2\text{O})]^{x+}$ (OC-6-32) and $[\text{VOH}_x\text{L}_2]^{x+}$ (SPY-5-12) with $x = 0-2$.

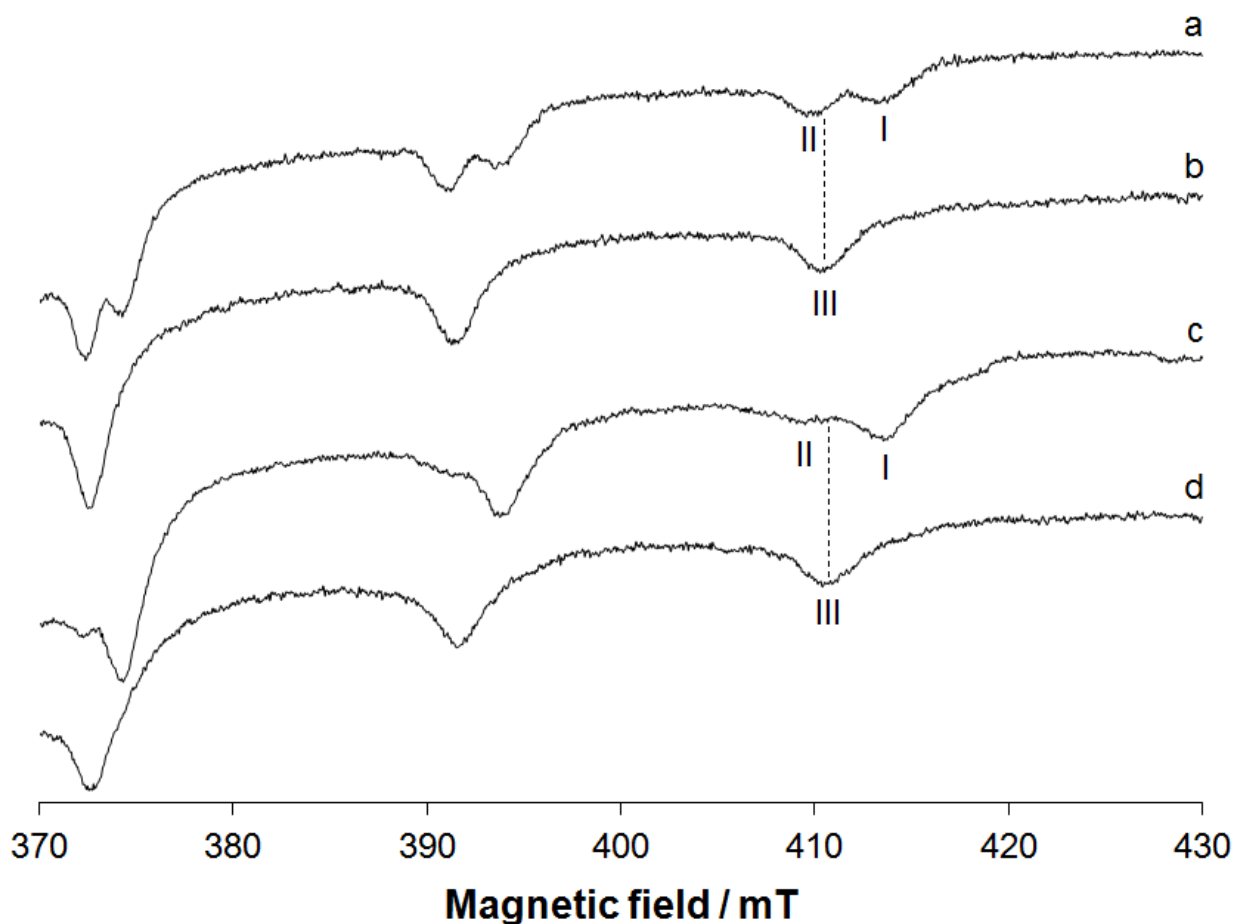


Figure S6. High field region of the X-band anisotropic EPR spectra recorded at 120 K in H₂O at pH 7.0 in the systems: (a) V^{IV}O²⁺/Hlev 1:2; (b) V^{IV}O²⁺/Hlev/MeIm 1:2:4; (c) V^{IV}O²⁺/Hspar 1:2 and (d) V^{IV}O²⁺/Hspar/MeIm 1:2:4. V concentration was 1.0×10^{-3} M. With **I**, **II** and **III** are indicated the $M_I = 7/2$ resonances of the species *cis*-[VOH_xL₂(H₂O)]^{x+} (OC-6-32), [VOH_xL₂]^{x+} (SPY-5-12) and [VOH_xL₂(MeIm)]^{x+} (OC-6-32), with $x = 0-2$ and L = lev, spar. The $M_I = 7/2$ resonance of [VOH_xL₂(MeIm)]^{x+} is also denoted with the dotted line.