SUPPLEMENTARY INFORMATION

Influence of the temperature on the equilibria of oxidovanadium(IV) complexes in solution

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Table S1 Experimental (g_0, A_0, g_z, A_z) and DFT calculated (A_z^{calcd}) spin Hamiltonian parameters for V complexes studied in this work.[a]

Complex	Isomer	g_0	A_0	g_z	A_z	A_z^{calcd}	PD [b]
$[VO(dhp)_2]$	*SPY*-5-12	1.976	84.1	1.953	158.1	158.97	0.6
	SPY-5-13					159.19	0.7
cis-$[VO(dhp)_2(H_2O)]$	*OC*-6-23	-	-	1.940 [c]	169.0 [c]	166.27	-1.4
	OC-6-34					166.65	-1.6
cis-$[VO(dhp)_2(MeIm)]$ [d]	*OC*-6-34 (154°)	-	-	1.947	162.8	159.64	-1.9
	OC-6-34 (345°)					159.21	-2.2
	OC-6-23 (149°)					158.66	-2.5
	OC-6-23 (336°)					158.63	-2.6
$[VO(ma)_2]$	*SPY*-5-12	1.975 [e]	90.4 [e]	1.948 [f]	161.1 [f]	160.63	-0.3
	SPY-5-13					162.29	0.7
cis-$[VO(ma)_2(H_2O)]$	*OC*-6-32	1.969	95.7	1.943	168.9	168.61	-0.2
	OC-6-34					168.63	-0.2
cis-$[VO(ma)_2(MeIm)]$ [d]	*OC*-6-32 (3°)	[g]	[g]	1.948 [h]	164.8 [h]	161.66	-1.9
	OC-6-32 (187°)					162.11	-1.6
	OC-6-34 (9°)					162.17	-1.6
	OC-6-34 (198°)					162.18	-1.6
cis-$[VO(pic)_2(H_2O)]$	*OC*-6-23	1.975	91.9	1.946	163.8	163.50	-0.2
	OC-6-24					160.94	-1.7
cis-$[VO(pic)_2(OH)]^-$	*OC*-6-23	[g]	[g]	1.949	160.7	154.19	-4.1
	OC-6-24					154.32	-4.0
cis-$[VO(pic)_2(MeIm)]$ [d]	*OC*-6-23 (212°)	[g]	[g]	1.951	159.5	155.31	-2.6
	OC-6-24 (188°)					155.88	-2.3

[a] A values reported in 10^{-4} cm^{-1}. [b] Percent deviation (PD) with respect to the absolute experimental A_z value calculated as: $100\times[(|A_z|^{calcd}-|A_z|)|/|A_z|]$. [c] Measured in H_2O/MeOH 9/1. [d] The isomers listed in tables S3, S4 and S5 are reported with the corresponding $O{=}V{-}N_{MeIm}{-}C_{MeIm}$ dihedral angle in parentheses. [e] Measured in $CHCl_3$/toluene 6/4 v/v. [f] From ref. D. Sanna et al., *Eur. J. Inorg. Chem.*, 2012, 1079-1092. [g] Not measurable. [h] From refs. D. Sanna et al., *Metallomics*, 2012, **4**, 33-36; D. Sanna et al., *Inorg. Chem.*, 2010, **49**, 174-187).

Table S2 Gibbs free energy values (at 298.15 and 120 K) for *spy* and *cis-Oh* isomers of the $V^{IV}O^{2+}$ complex formed by dhp ligand.[a,b]

Isomer [c]	G_{aq} (298.15 K)	G_{aq} (120 K)
OC-6-34	-1288197.71	-1288173.88
OC-6-32	-1288198.65	-1288174.47
OC-6-24	-1288198.50	-1288174.31
OC-6-23	-1288198.75	-1288174.60
SPY-5-12	-1240121.82	-1240099.28
SPY-5-13	-1240120.98	-1240098.85

[a] Values reported in kcal mol^{-1}. [b] Calculations performed at the B3P86/6-311g(d,p) level of theory using the SMD model for water. [c] Structures are shown in Scheme S1.

Table S3 Gibbs free energy values (at 298.15 and 120K) for the most stable isomers of $[VO(dhp)_2(MeIm)]$ complex.[a,b]

Isomer	Dihedral angle $O{=}V{-}N_{MeIm}{-}C_{MeIm}$ [c]	G_{aq} (298.15 K)	G_{aq} (120 K)
cis-$[VO(dhp)_2(MeIm)]$[d]	153.69	-1407234.36	-1407207.55
cis-$[VO(dhp)_2(MeIm)]$[d]	345.35	-1407233.91	-1407207.43
cis-$[VO(dhp)_2(MeIm)]$[e]	149.24	-1407235.10	-1407207.95
cis-$[VO(dhp)_2(MeIm)]$[e]	335.75	-1407234.54	-1407207.81

[a] Values reported in kcal mol^{-1}. [b] Calculations performed at the B3P86/6-311g(d,p) level of theory using the SMD model for water. [c] The values were obtained after optimization of the structures at the minimum points in the scan calculation. [d] Structure obtained from *OC*-6-34 substituting water molecule with MeIm with two different dihedral angles. [e] Structure obtained from *OC*-6-23 substituting water molecule with MeIm with two different dihedral angles.

Table S4 Gibbs free energy values (at 298.15 and 120K) for the most stable isomers of [VO(ma)$_2$(MeIm)] complex. [a,b]

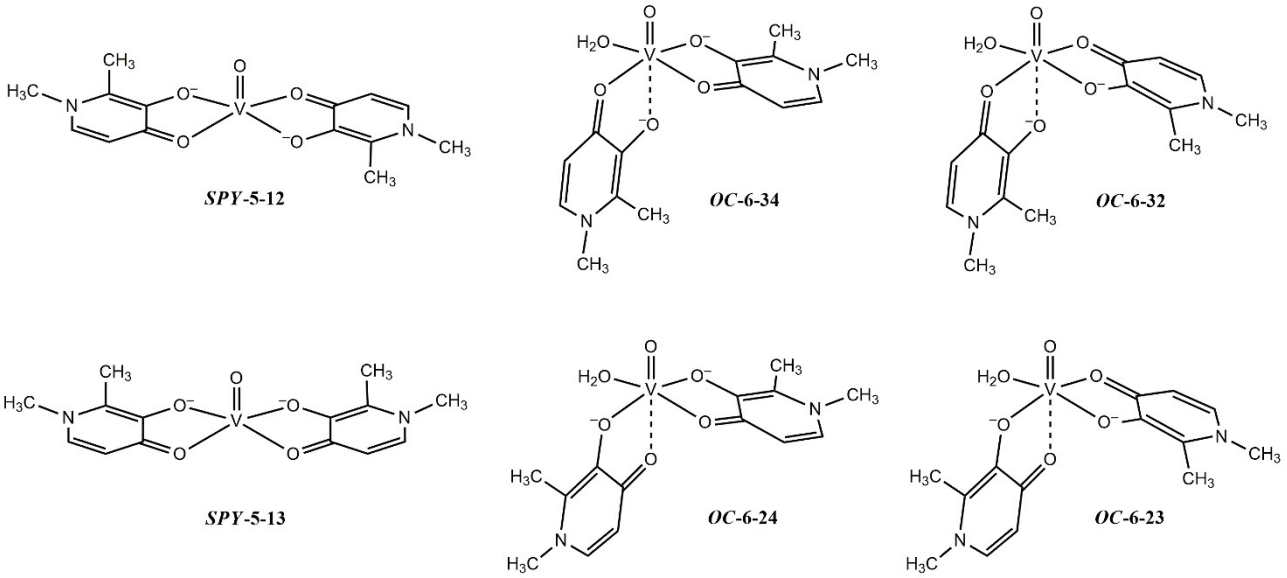
Isomer	Dihedral angle O=V–N_{MeIm}–C_{MeIm} [c]	G_{aq} (298.15 K)	G_{aq} (120 K)
cis-[VO(ma)$_2$(MeIm)][d]	3.41	-1382652.47	-1382626.90
cis-[VO(ma)$_2$(MeIm)][d]	186.59	-1382652.46	-1382626.84
cis-[VO(ma)$_2$(MeIm)][e]	8.82	-1382654.66	-1382628.38
cis-[VO(ma)$_2$(MeIm)][e]	197.85	-1382654.75	-1382628.41

[a] Values reported in kcal mol^{-1}. [b] Calculations performed at the B3P86/6-311g(d,p) level of theory using the SMD model for water. [c] The values were obtained after optimization of the structures at the minimum points in the scan calculation. [d] Structure obtained from *OC*-6-32 substituting water molecule with MeIm with two different dihedral angles. [e] Structure obtained from *OC*-6-34 substituting water molecule with MeIm with two different dihedral angles.

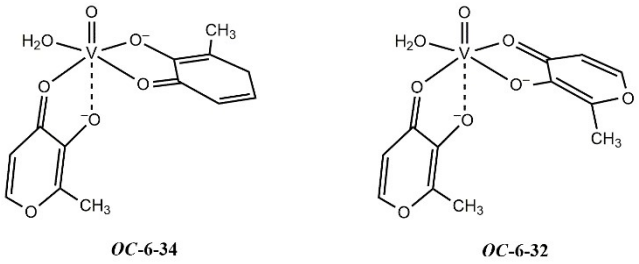
Table S5 Gibbs free energy values (at 298.15 and 120 K) for the most stable isomers of [VO(pic)$_2$(MeIm)] complex. [a,b]

Isomer	Dihedral angle O=V–N_{MeIm}–C_{MeIm}[c]	G_{aq} (298.15 K)	G_{aq} (120 K)
cis-[VO(pic)$_2$(MeIm)][d]	192.29	-1356210.74	-1356186.11
cis-[VO(pic)$_2$(MeIm)][d]	211.58	-1356211.19	-1356186.21
cis-[VO(pic)$_2$(MeIm)][e]	182.35	-1356209.63	-1356184.92
cis-[VO(pic)$_2$(MeIm)][e]	187.87	-1356209.79	-1356184.83

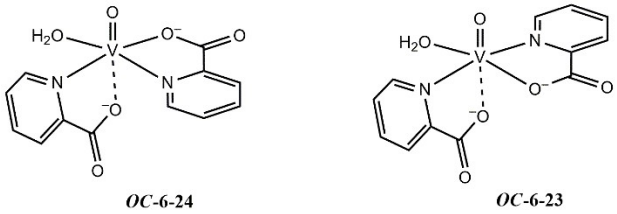
[a] Values reported in kcal mol^{-1}. [b] Calculations performed at the B3P86/6-311g(d,p) level of theory using the SMD model for water. [c] The values were obtained after optimization of the structures at the minimum points in the scan calculation. [d] Structure obtained from *OC*-6-24 substituting water molecule with MeIm with two different dihedral angles. [e] Structure obtained from *OC*-6-23 substituting water molecule with MeIm with two different dihedral angles.



Scheme S1 Possible isomers for the penta-coordinated $[VO(dhp)_2]$ and hexa-coordinated *cis*-$[VO(dhp)_2(H_2O)]$ species.



Scheme S2 Most stable isomers for the hexa-coordinated *cis*-$[VO(ma)_2(H_2O)]$ species.



Scheme S3 Most stable isomers for the hexa-coordinated *cis*-$[VO(pic)_2(H_2O)]$ species.

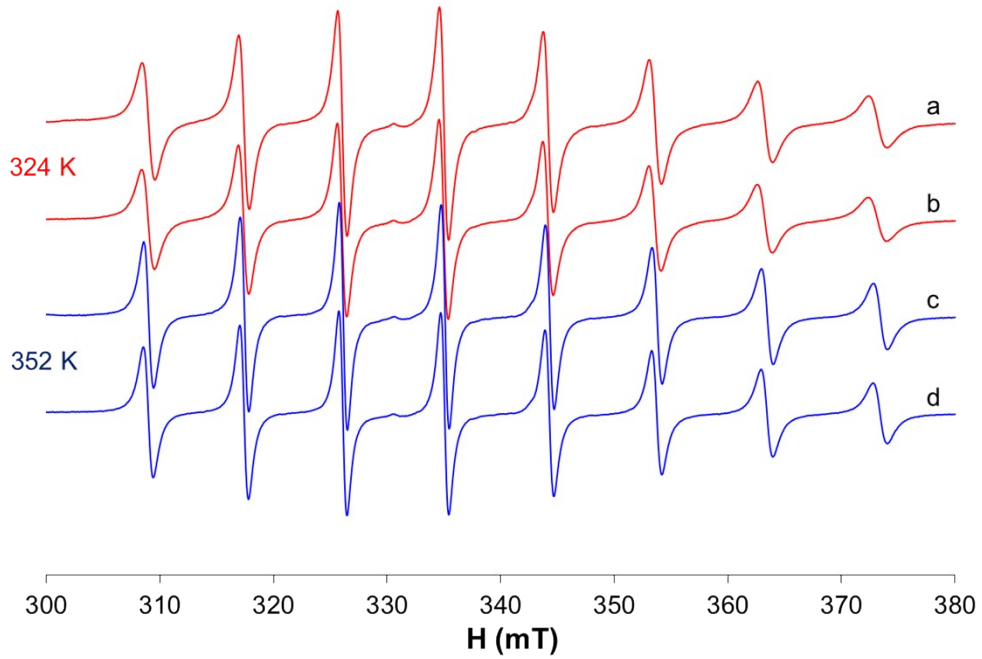


Fig. S1 Isotropic EPR spectra recorded at variable temperature on solutions containing: a) VO^{2+}/dhp 1/2, VO^{2+} 1 mM, in HEPES 0.1 M pH 7.40; b) VO^{2+}/dhp /MeIm 1/2/4, VO^{2+} 1 mM, in HEPES 0.1 M pH 7.40; c) VO^{2+}/dhp 1/2, VO^{2+} 1 mM, in HEPES 0.1 M pH 7.40; d) VO^{2+}/dhp /MeIm 1/2/4, VO^{2+} 1 mM, in HEPES 0.1 M pH 7.40.

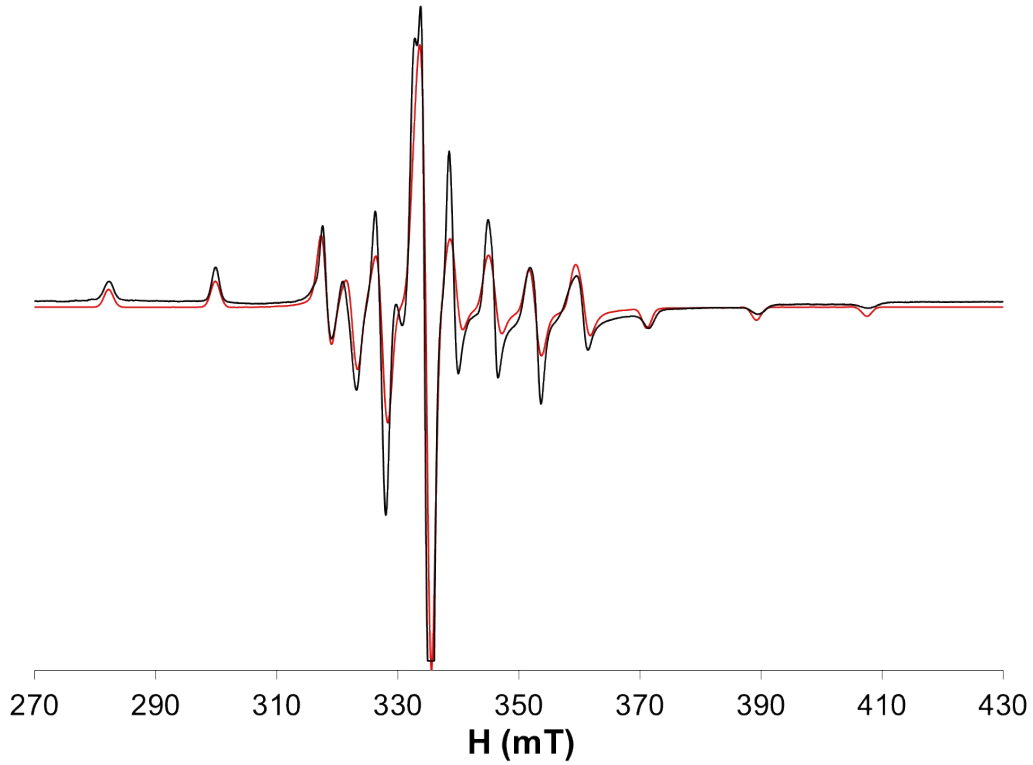


Fig. S2 Experimental (black) anisotropic EPR spectrum recorded at 120 K on frozen solution containing VO^{2+}/dhp/MeIm 1/2/4, VO^{2+} 1 mM, in HEPES 0.1 M pH 7.40. The spectrum was simulated (red) with the following parameters: A_x 54.5 × 10^{-4} cm^{-1}, A_y 55.5 × 10^{-4} cm^{-1}, A_z 162.8 × 10^{-4} cm^{-1}, g_x 1.980, g_y 1.972, g_z 1.947. The spectrum has been assigned to the species *cis*-[$VO(dhp)_2$(MeIm)].

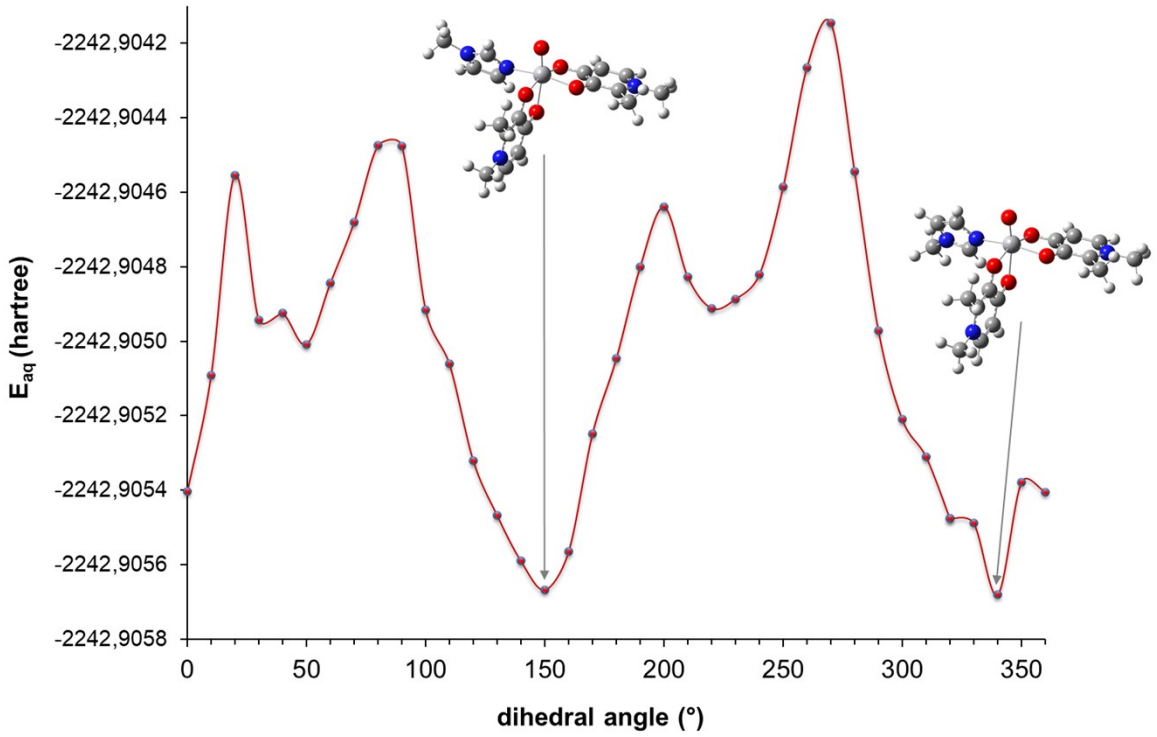


Fig. S3 Electronic energy values in solution (E_{aq}, 298.15 K) in function of the O=V–N_{MeIm}–C_{MeIm} dihedral angle. Relaxed scan calculation performed on *cis*-[VO(dhp)$_2$(MeIm)] structure obtained substituting water molecule with MeIm from *OC*-6-23.

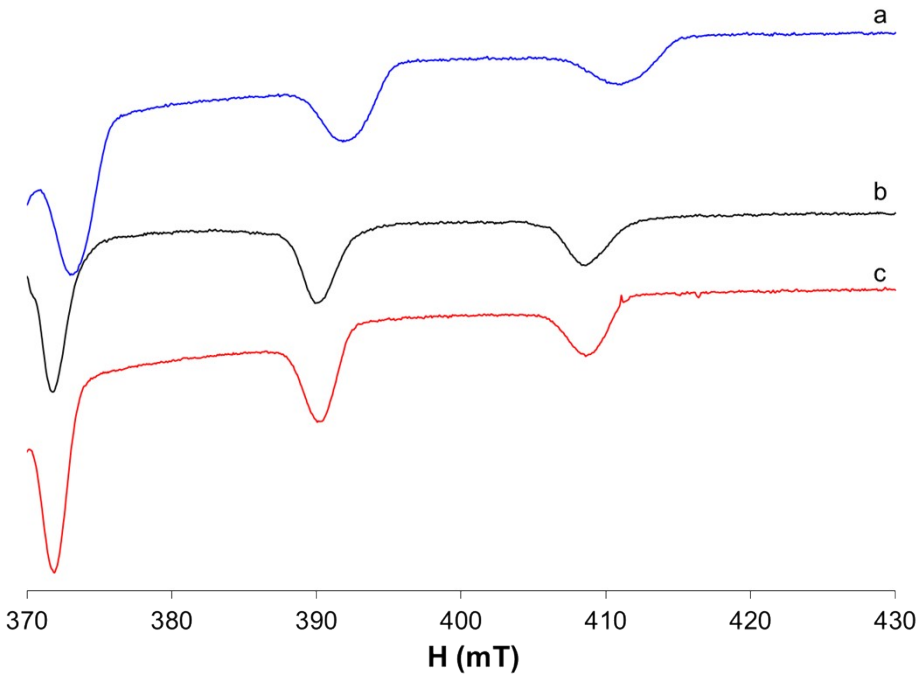


Fig. S4 Anisotropic EPR spectra recorded at 120 K on frozen solutions containing: a) VO^{2+}/ma 1/2, VO^{2+} 1 mM, in HEPES 0.1 M pH 7.40; b) VO^{2+}/ma/Mb 1/2/1, VO^{2+} 1 mM, in HEPES 0.1 M pH 7.40; c) VO^{2+}/ma/MeIm 1/2/4, VO^{2+} 1 mM, in HEPES 0.1 M pH 7.40.

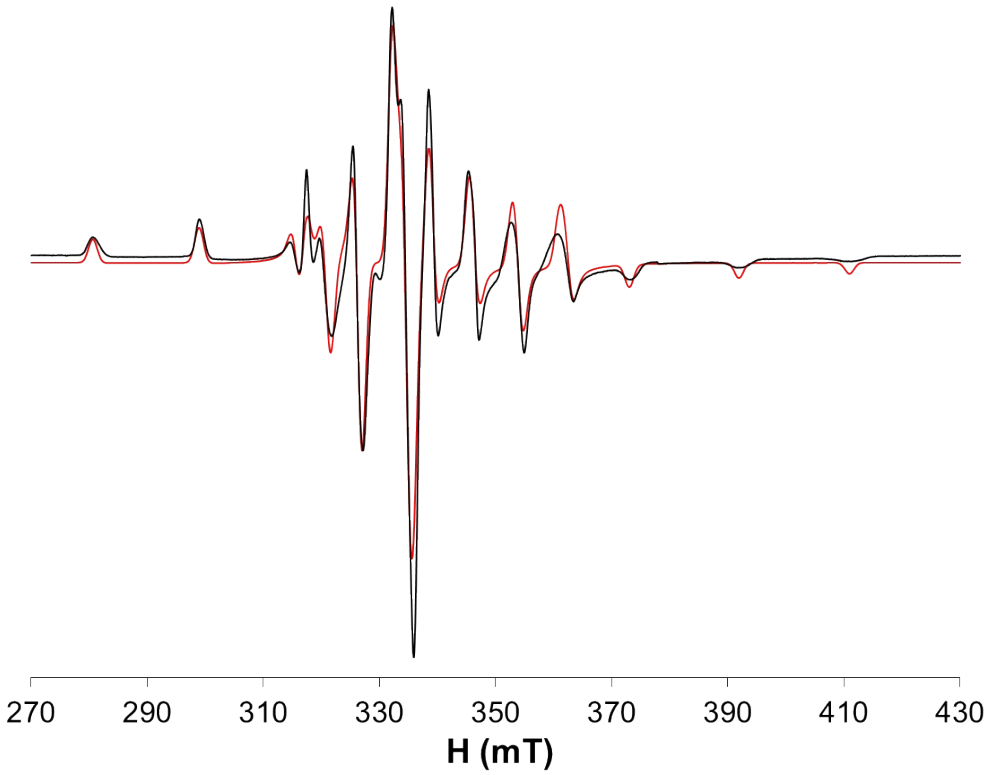


Fig. S5 Experimental (black) anisotropic EPR spectrum recorded at 120 K on frozen solutions containing VO^{2+}/ma 1/2, VO^{2+} 1 mM, in HEPES 0.1 M pH 7.40. The spectrum was simulated (red) with the following parameters: A_x 58.0 × 10^{-4} cm^{-1}, A_y 62.0 × 10^{-4} cm^{-1}, A_z 168.9 × 10^{-4} cm^{-1}, g_x 1.977, g_y 1.976, g_z 1.942. The spectrum has been assigned to the species *cis*-[$VO(ma)_2(H_2O)$].

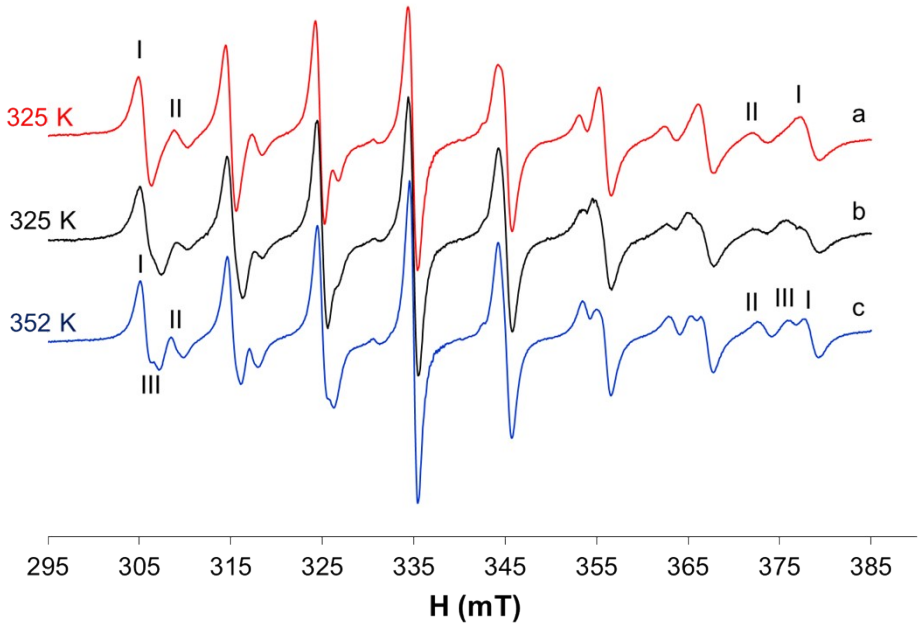


Fig. S6 Isotropic EPR spectra recorded at variable temperature on solutions containing: a) VO^{2+}/ma 1/2, VO^{2+} 1 mM, in HEPES 0.1 M, pH 7.37; b) VO^{2+}/ma/MeIm 1/2/4, VO^{2+} 1 mM, in HEPES 0.1 M, pH 7.40, 325 K.; c) VO^{2+}/ma/MeIm 1/2/4, VO^{2+} 1 mM, in HEPES 0.1 M pH 7.40. With **I**, **II** and **III** the resonances of *cis*-[$VO(ma)_2(H_2O)$], *trans*-[$VO(ma)_2(H_2O)$] and *cis*-[$VO(ma)_2(MeIm)$] are indicated.

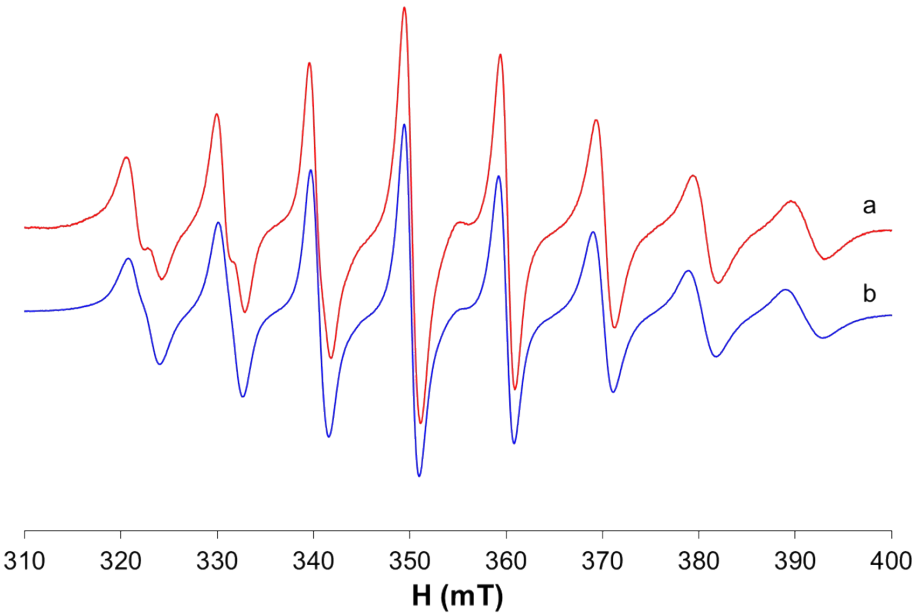


Fig. S7 Isotropic EPR spectra recorded at 298 K on solutions containing: a) VO^{2+}/pic 1/2, VO^{2+} 1 mM, in HEPES 0.1 M pH 7.52; b) VO^{2+}/pic/MeIm 1/2/4, VO^{2+} 1 mM, in HEPES 0.1 M pH 7.52.