DT-ART-05-2017-001776 (Revised)

Exploring the effect of hydroxylic and non-hydroxylic solvents on the reaction of [$V^{IV}O(\beta\text{-diketonate})_2$] with 2-Aminobenzoylhydrazide in aerobic and anaerobic conditions. Valence delocalisation in mixed-valence V^{IV}-O-V^{V} species

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Electronic Supporting Information (ESI)

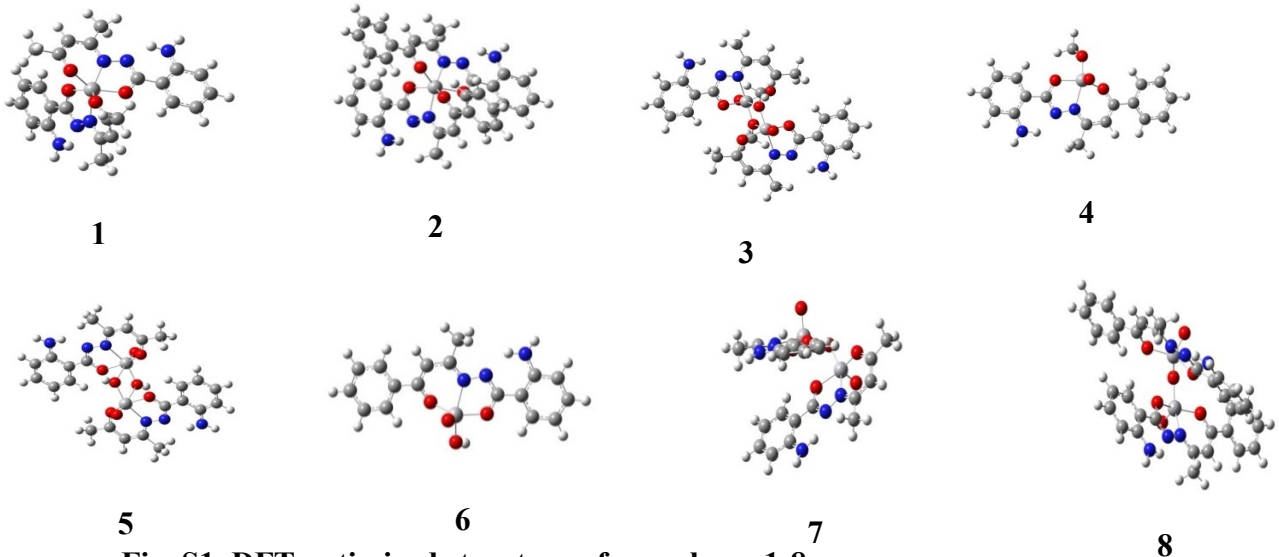
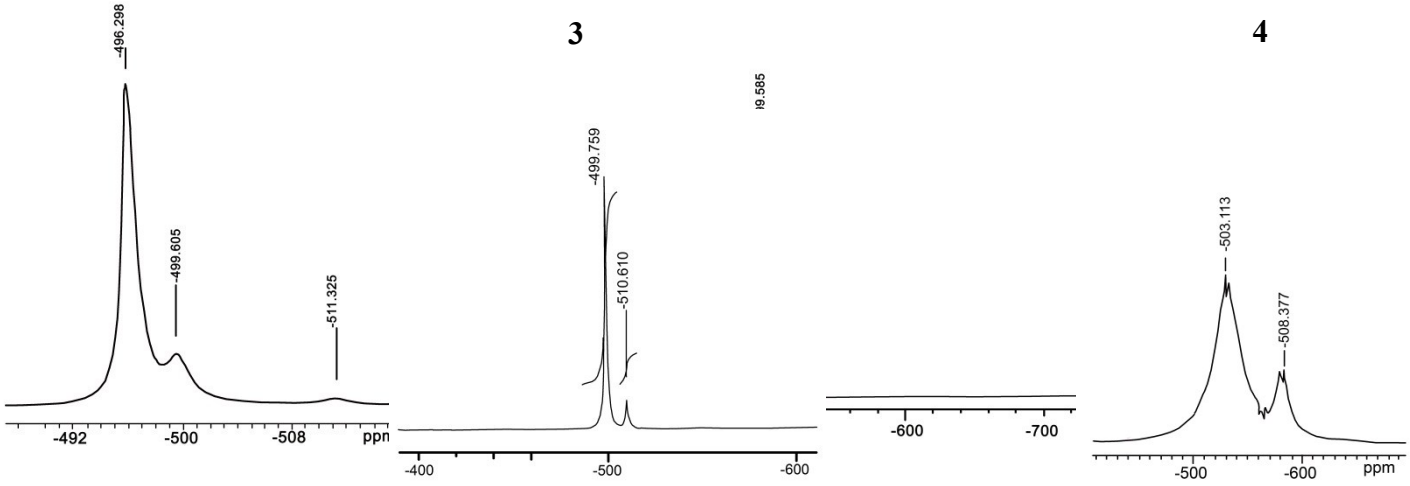


Fig. S1. DFT optimized structure of complexes 1-8



8

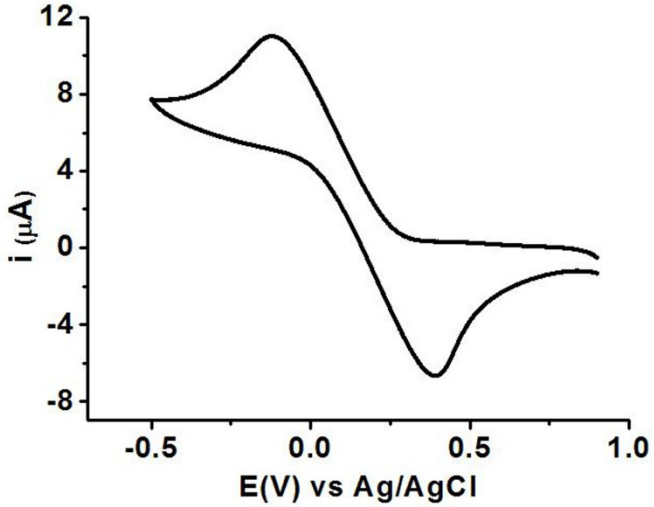


Fig. S2. ^{51}V NMR of co
4, **7** and **8** in $CDCl_3$ solu

Fig. S3. Cyclic voltammogram of **3** in CH_2Cl_2

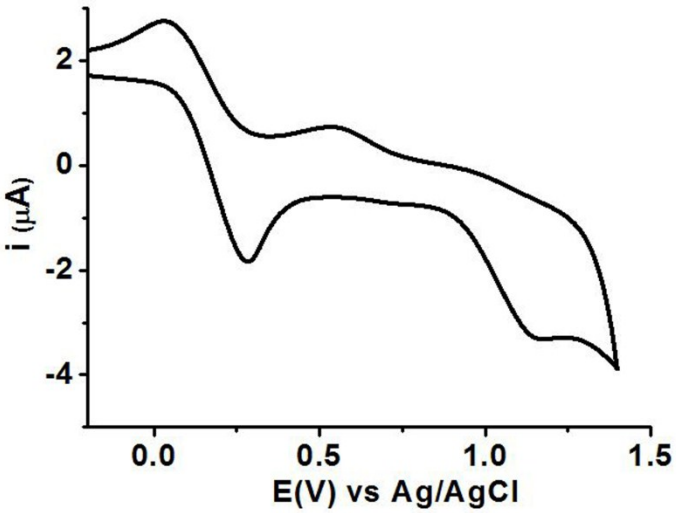


Fig. S4. Cyclic voltammogram of **7** in CH_2Cl_2.

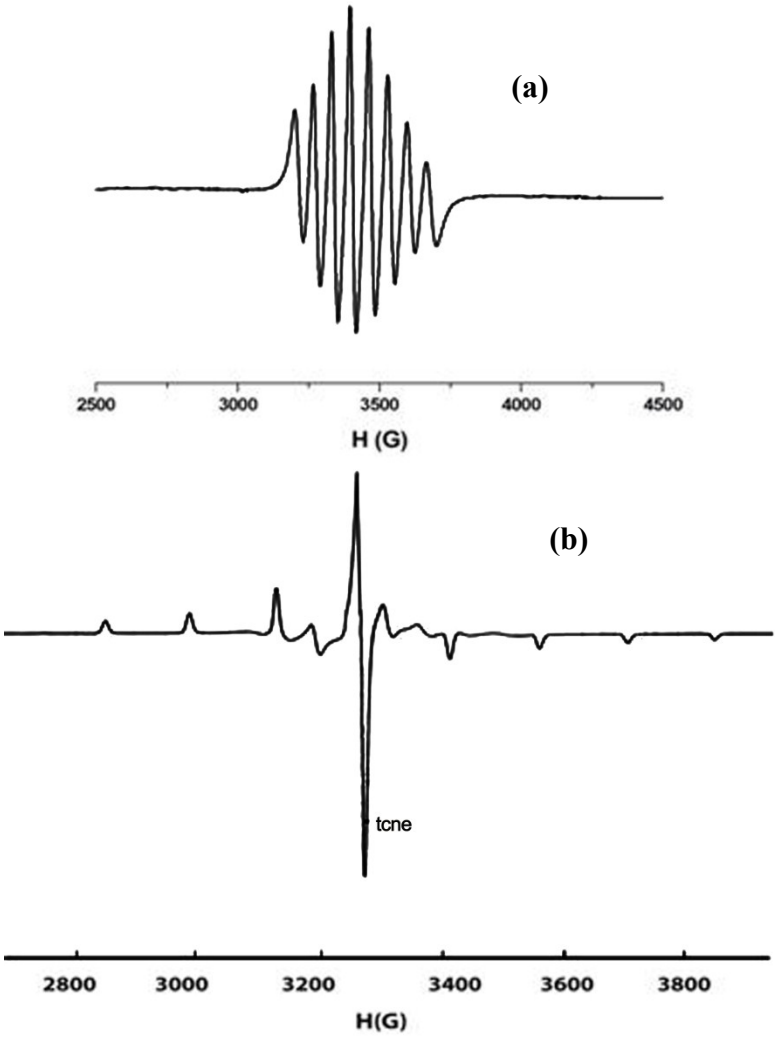


Fig. S5. X-band EPR spectra of complex **1** in CH_2Cl_2 solution (a) at 300 K and (b) at 77 K.

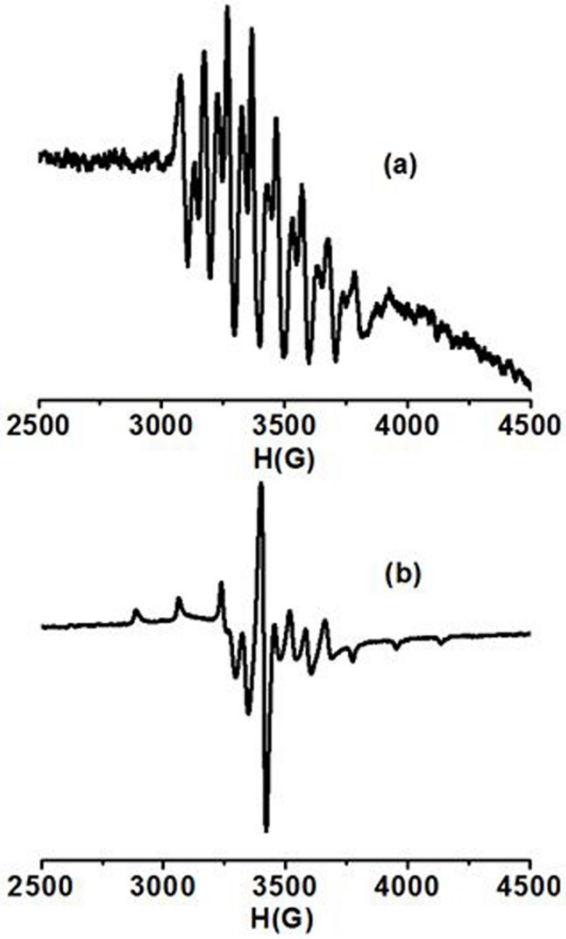


Fig. S6. X-band EPR spectra of **8a** in CH_2Cl_2 solution (a) at 300 K and (b) at 77 K.

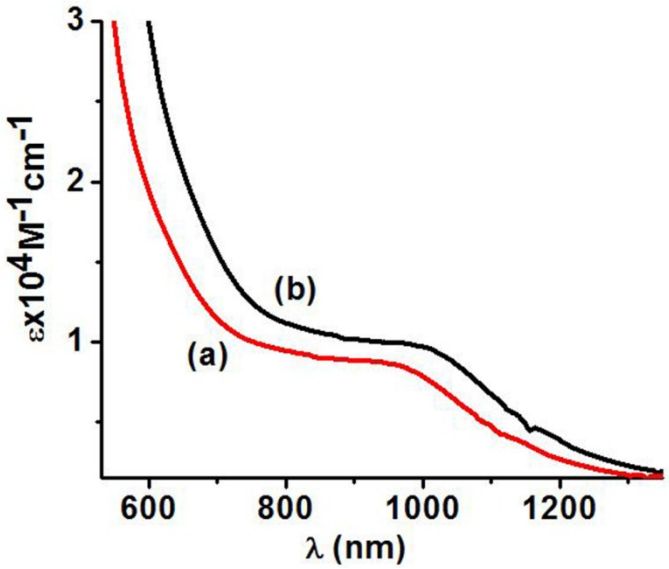


Fig. S7. Electronic spectra of complexes **7a** (a) and **8a** (b) in CH_2Cl_2 solution at room temperature.

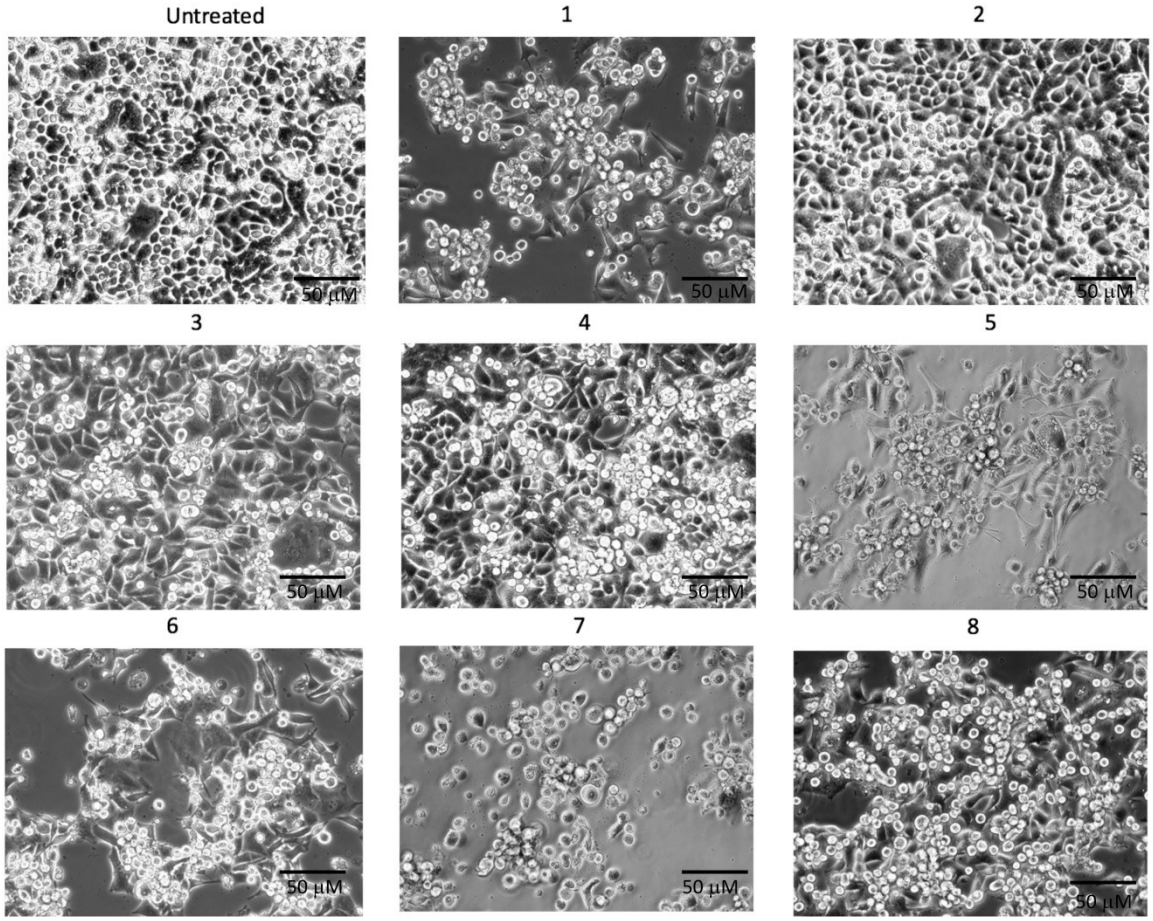


Fig. S8. Experimental proof of cell death treated with the complexes **1**-**8**.

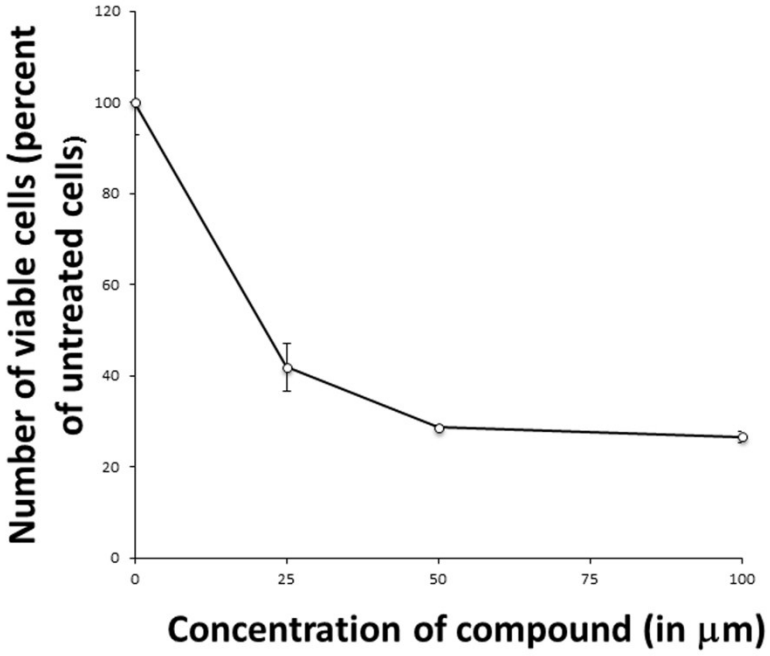


Fig. S9. Cytotoxic activity of $VOSO_4$ at different concentrations.

Table S1. Calculated Geometrical parameter for complex 2

bond lengths, Å	
V-O1	1.940
V-O2	1.918
V-O3	1.940
V-O4	1.918
V-N1	2.064
V-N4	2.064
bond angles, deg	
O1-V-O2	134.77
O1-V-O3	82.13
O1-V-O4	86.12
O2-V-O3	86.13
O2-V-O4	130.05
O3-V-O4	134.75
O1-V-N1	83.39
O2-V-N1	74.42
O3-V-N1	134.55
O4-V-N1	86.56
O1-V-N4	134.55
O2-V-N4	86.56
O3-V-N4	83.39
O4-V-N4	74.42
N1-V-N4	134.22

Table S2. Calculated Geometrical parameters for complexes 3 and 4

Complex	**3**	**4**
bond lengths, Å		
V-O1	1.590	1.592
V-O2	1.886	1.879
V-O3	1.918	1.920
V-O4	1.809	1.783
V-N1	2.136	2.093
V-O4$^{(i)}$	2.578	
bond angles, deg		
O1-V-O2	101.24	106.60
O1-V-O3	102.80	110.51
O1-V-O4	104.40	108.37
O2-V-O3	148.64	138.51
O2-V-O4	100.51	97.10
O3-V-O4	92.70	88.37
O1-V-N1	97.46	97.51
O2-V-N1	82.93	83.09
O3-V-N1	74.27	74.42
O4-V-N1	156.64	152.76
O1-V-O4$^{(i)}$	175.57	
O2 -V-O4$^{(i)}$	78.81	
O3-V-O4$^{(i)}$	78.75	
O4-V-O4$^{(i)}$	71.30	
N1-V-O4$^{(i)}$	86.94	

Table S3. Calculated Geometrical parameter for complex 8

bond lengths, Å

V1-O1	1.590
V1-O2	1.856
V1-O3	1.932
V1-O4	1.798
V1-N1	2.104
V2-O4	1.796
V2-O5	1.590
V2-O6	1.856
V2-O7	1.932
V2-N4	2.105
V1-V2	3.126

bond angles, deg

O1-V1-O2	104.77
O1-V1-O3	105.30
O1-V1-O4	109.82
O1-V1-N1	98.74
O2-V1-O3	144.48
O2-V1-O4	99.27
O2-V1-N1	82.81
O3-V1-O4	87.87
O3-V1-N1	74.36
O4-V1-N1	149.57
O5-V2-O4	109.77
O5-V2-O6	104.94
O5-V2-O7	105.45

O5-V2-N4	98.48
O6-V2-O4	99.35
O6-V2-O7	144.18
O6-V2-N4	82.86
O7-V2-O4	87.75
O7-V2-N4	74.34
O4-V2-N4	149.81
V1-O4-V2	120.78

Table S4. Vertical excitation energies (E_{cal}), oscillator strengths (f_{cal}) and type of excitations of the excited states obtained from TD-DFT calculations of 1-8

Complex	$E_{cal/nm}$	f_{cal}	Excitation
1	380.13	0.2929	HOMO-1→LUMO+2 (0.57689)
			HOMO-2→LUMO (0.34231)
2	421.54	0.1991	HOMO→LUMO+3 (0.65378)
			HOMO-2→LUMO (0.53933)
3	371.24	0.2976	HOMO-1→LUMO+7 (0.32328)
			HOMO→LUMO+6 (0.41386)
4	376.81	0.1803	HOMO-1→LUMO+1 (0.61192)
			HOMO→LUMO+3 (0.29007)
5	380.84	0.3053	HOMO-1→LUMO+7 (-0.30482)
			HOMO →LUMO+6 (0.47970)
6	469.5	0.237	HOMO →LUMO+1 (0.44957)
			HOMO →LUMO+2 (-0.42639)
7	371.8	0.1234	HOMO-8→LUMO (0.38858)
			HOMO-1→LUMO+6 (0.41808)
8	510	0.2504	HOMO-1→LUMO+3 (0.30856)
			HOMO→LUMO+2 (0.48814)