Electronic Supplementary Information

A Manganese Oxido Complex Bearing Facially Coordinating Trispyridyl Ligands – Is Coordination Geometry Crucial for Water Oxidation Catalysis?

Hans-Martin Berends,[a] Anne-Marie Manke,[a] Christian Näther,[a] Felix Tuczek*[a] and Philipp Kurz*[a]

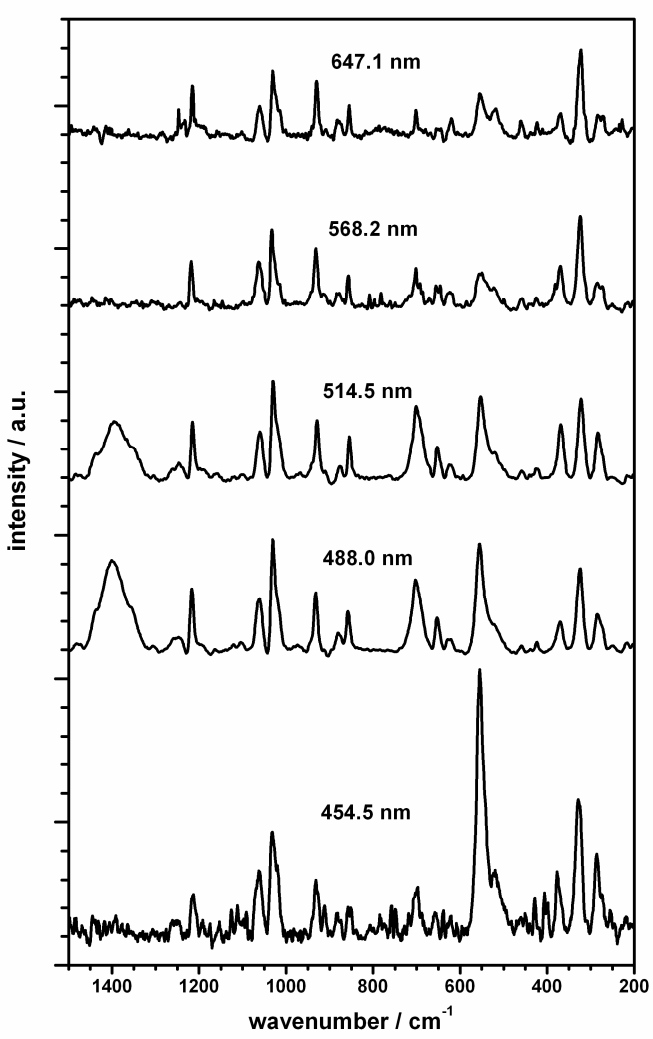

Fig. SI 1 Resonance Raman spectra recorded with different excitation wavelengths.

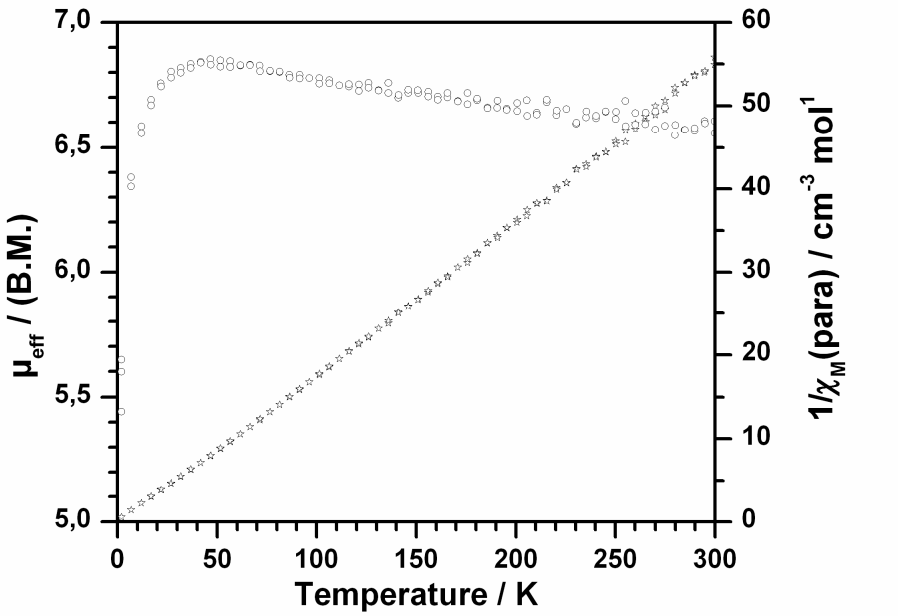

Fig. SI 2 Plots of inverse magnetic susceptibility and effective magnetic moment per dinuclear complex versus temperature at H = 0.1 T for a polycrystalline sample of complex **1**.

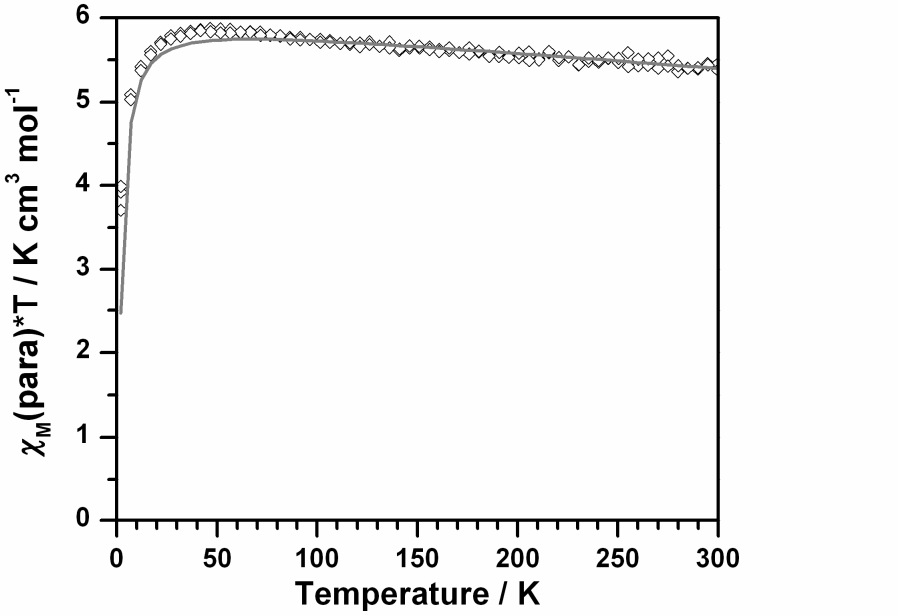

Fig. SI 3 Plot of χT vs. T at H = 0.1 T for a polycrystalline sample of complex **1**. The solid line shows a least square fit to the Bleaney-Bowers equation for a $S_1 = S_2 = 2$ dimer resulting in weak antiferromagnetically coupling ($J = -0.25$ cm^{-1}, $H = -2JS_1S_2$).[1]

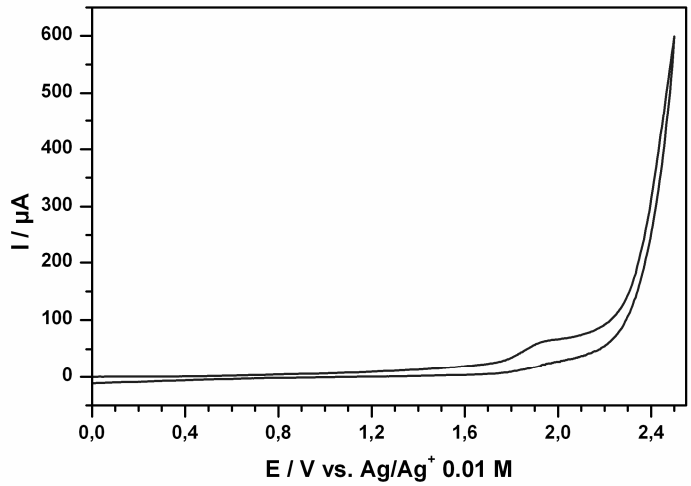

Fig. SI 4 Cyclic voltammogram of the ligand tpdm measured in acetonitrile.

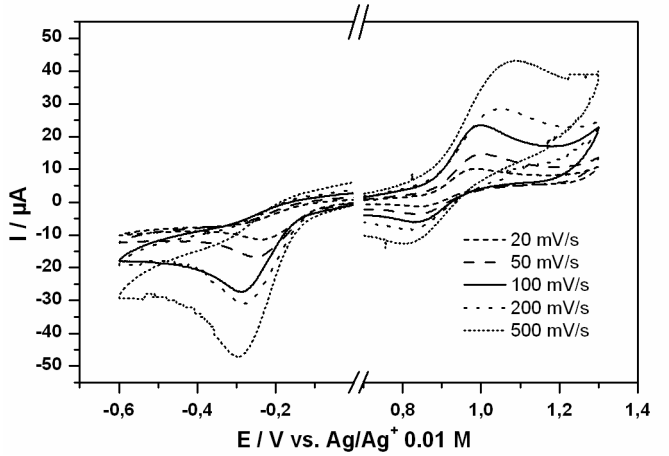

Fig. SI 5 Cyclic voltammogram of **1** measured with different scan rates.

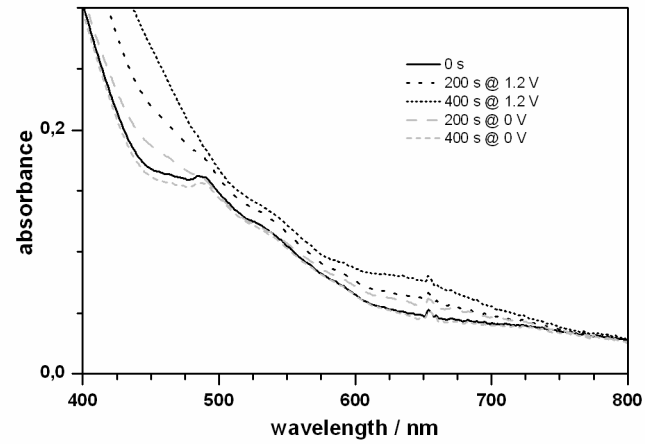

Fig. SI 6 Changes observed for absorption spectra of **1** (2.5 mM in acetonitrile / 0.1 M $TBAClO_4$) in an OTTLE cell (1mm path length) recorded during the electrochemical oxidation of the complex at a potential of +1 200 mV vs. Ag/Ag^+ and following re-reduction at 0 mV.

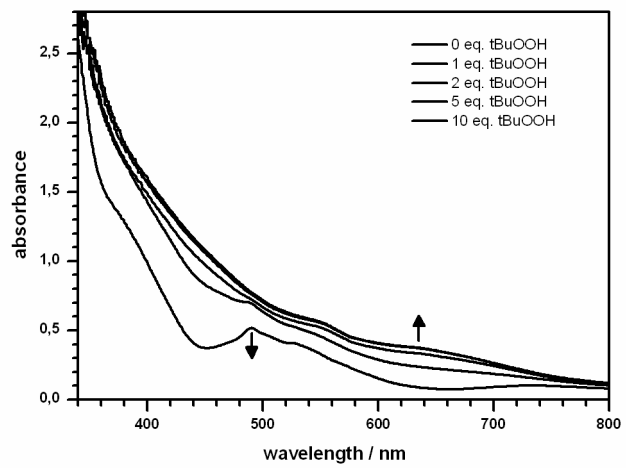

Fig. SI 7 UV/Vis spectra of **1** recorded after oxidation with *t*BuOOH.

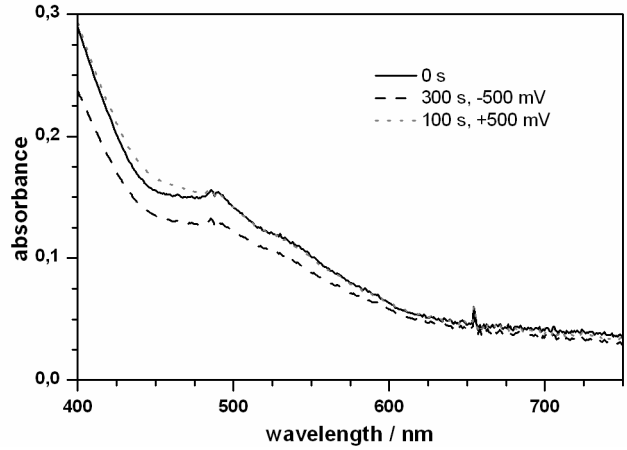

Fig. SI 8 Changes observed for absorption spectra of **1** (2.5 mM in acetonitrile / 0.1 M $TBAClO_4$) in an OTTLE cell (1mm path length) recorded during the electrochemical reduction of the complex at a potential of -500 mV vs. Ag/Ag^+ and following re-oxidation at +500 mV.

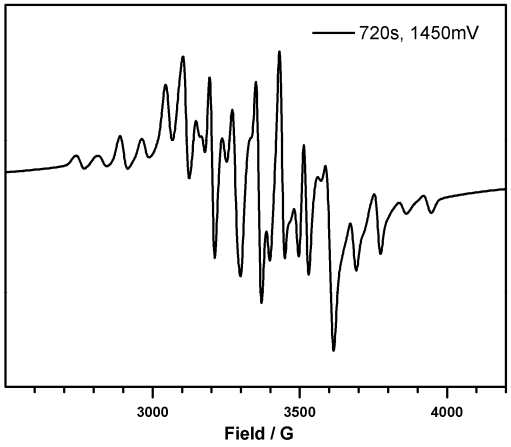

Fig. SI 9 EPR spectrum of **1** recorded after electrochemical oxidation at a potential of 1450 mV vs. Ag/Ag^+.

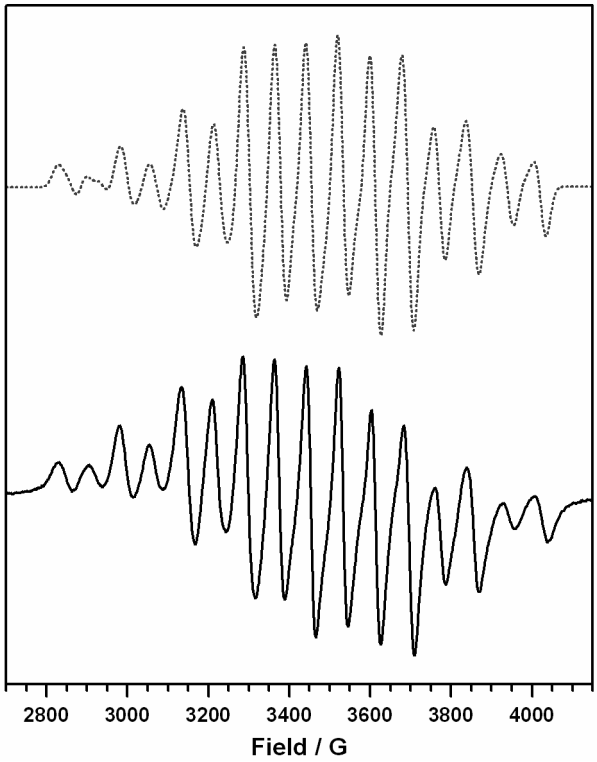

Fig. SI 10 Experimental (solid line) and simulated (dotted line) X-band EPR spectra for **1** oxidized chemically with five equivalents of *t*BuOOH.

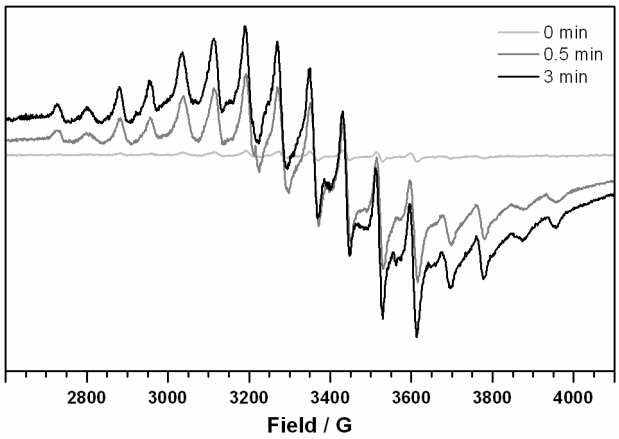

Fig. SI 11 X-band EPR spectra for **1** reduced electrochemically at -400 mV vs. Ag/Ag^{+}.

Table SI 1 X-Sophe parameters for the $Mn_2^{III,IV}$ form of **1** obtained by electrochemical oxidation.

Experiment Title	G4b_5K_2mW_DM*1000 esp
Operator	xuser
Spin Hamiltonian =	(Mn : beta B.g.S + S.A.I[Mn] + S.A.I[Mn1]). ;
Experiment Type	Continuous Wave
Spectrum Type	Randomly Oriented Spectrum
Method	Matrix Diagonalisation
Superhyperfine Method	Matrix Diagonalisation
Spin System	
Number of Paramagnetic Centres	1
Atomic Element for Electron Spin	Mn
Electron Spin	0.5
Number of Nuclei	2
Atomic Element for Nuclear Spin	Mn
Number of Equivalent Nuclei	1
Number of Isotopes	1
Nuclear Spin - Mn-55	2.5
Nuclear g value - Mn-55	1.3874800
Natural Abundance - Mn-55	100.0000%
Atomic Element for Nuclear Spin	Mn1
Number of Equivalent Nuclei	1
Number of Isotopes	1
Nuclear Spin - Mn1-55	2.5
Nuclear g value - Mn1-55	1.3874800
Natural Abundance - Mn1-55	100.0000%
Instrument Parameters	
Abscissa - 1	Magnetic Field
Center Field [G]	3500.000200
Sweep Width [G]	2000.000000
Number of Points	5000
Abscissa - 2	None
Temperature [K]	0.000000
Microwave Frequency [GHz]	9.644088
Harmonic	First
Phase	Normal
Units	Gauss
Cavity Mode	Perpendicular
Magnetic Field - 1 Theta [deg]	0.000000
Magnetic Field - 1 Phi [deg]	90.000000
Magnetic Field - 2 Theta [deg]	90.000000
Magnetic Field - 2 Phi [deg]	90.000000
File/Execution Information	
Sophe Input File Version	1.0.1
Sophe Output File Version	1.0.1
Rewrite Input File [y/n]	n
Input Spectrum Directory	/home/xuser/.../echem
Input Spectrum Filename	G4b_5K_2mW.par
Output Spectrum To	Xepr
Output Spectrum Directory	/home/xuser/.../echem
Output Spectrum Filename	echem_d
Input Format	Bruker ESP
Output Format	Bruker ESP

Hostname	ESP
Execution Mode	Single Interactive
Batch File Name	File

Sophe Parameters	
Number of Theta Orientations	25
Number of Field Segments	10
Interpolation Step [G]	1.000000
Symmetry	Orthorhombic

Line Shape Parameters	
Line Shape Model	Angular Dependence of g
Electron Spin / Nucleus	Mn Mn
Line Shape	Gaussian
Line Shape Cutoff [No. Std. Dev.]	6.000000
Linewidth Units	Gauss

Transition Probabilities	
Transition Threshold	0.010000
Number of Transitions	0

Optimisation Parameters	
Method	Simplex
Error Function	Raw Data
Error	6.000000e-03
Normalisation Method	Peak Extrema
Total Number of Iterations	1000
Output Results Every N Iterations	25
Output Parameters To	Disk
Output Spectra To	Disk

Matrix/ Tensor	Values			Deviation			Parameter Space Half Width			Means of Varying Par.
Mn-g	1.99811	0.00000	0.00000	0.500000	0.00000	0.00000	0.500000	0.00000	0.00000	1 0 0
	0.00000	2.00369	0.00000	0.00000	0.500000	0.00000	0.00000	0.500000	0.00000	0 2 0
	0.00000	0.00000	1.98482	0.00000	0.00000	0.500000	0.00000	0.00000	0.500000	0 0 3
Mn-A	-149.992	0.00000	0.00000	2.00000	0.00000	0.00000	20.0000	0.00000	0.00000	4 0 0
	0.00000	-168.994	0.00000	0.00000	2.00000	0.00000	0.00000	20.0000	0.00000	0 5 0
	0.00000	0.00000	-107.989	0.00000	0.00000	2.00000	0.00000	0.00000	20.0000	0 0 6
Mn1-A	82.9967	0.00000	0.00000	1.00000	0.00000	0.00000	20.0000	0.00000	0.00000	7 0 0
	0.00000	72.0060	0.00000	0.00000	1.00000	0.00000	0.00000	20.0000	0.00000	0 8 0
	0.00000	0.00000	79.9954	0.00000	0.00000	1.00000	0.00000	0.00000	20.0000	0 0 9
Linewidth x		15.5031		1.00000			20.0000	10		
Linewidth y		15.5031		1.00000			20.0000	10		
Linewidth z		15.5031		1.00000			20.0000	10		

Table SI 2 EPR parameters for the $Mn_2^{III,IV}$ form of **1** obtained by chemical oxidation as determined by a simulation of the signal using the X Sophe software suite. Hyperfine coupling constants A are given in gauss.

	g	A^{III}	A^{IV}
x	2.005	-168	72
y	1.996	-149	83
z	1.985	-107	79

1. C. J. O'Connor, *Prog. Inorg. Chem.*, 1982, **29**, 203-283.