

Chelate Electronic Properties control the Redox Behaviour and Superoxide Reactivity of Seven-Coordinate Manganese(II) Complexes

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X-ray crystal structure determinations of 1, 2 and H₂Dcphp:

Suitable single crystals were coated with protective perfluoropolyalkylether oil and mounted in the cold nitrogen gas stream of a Bruker-Nonius KappaCCD diffractometer. Data were collected at 100 K using MoK α radiation (graphite monochromator). Diffraction intensities were corrected for Lorentz and polarization effects. A semi-empirical absorption correction based on multiple measurements of reflections was applied for **1** ($T_{\min} = 0.918$, $T_{\max} = 0.993$),¹ while a numerical absorption correction based on the description of crystal faces was applied for **2** ($T_{\min} = 0.826$, $T_{\max} = 0.902$) and **H₂Dcphp** ($T_{\min} = 0.982$, $T_{\max} = 0.990$).² The structures were solved by direct methods and refined by full-matrix least-squares procedures on F^2 .³ All non-hydrogen atoms were refined with anisotropic displacement parameters. With the exception of the hydrogen atoms of the two methanol solvent molecules of **1**, which were placed in calculated positions of optimized geometry, the positions of all other hydrogen atoms were derived from difference fourier maps. The positional parameters of the H atoms in **1** and **2** were refined while those of **H₂Dcphp** were kept

in their originally derived positions. The isotropic displacement parameters of all hydrogen atoms were tied to those of their adjacent carrier atoms by a factor of 1.2 or 1.5. The solvent water molecule in the crystal structure of **H₂Dcphp** is disordered. Two alternative sites have been identified that are occupied by approximately 87% (O3) and 13% (O3A).

CCDC 720837 - 720839 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif

- ¹ *SADABS*, 2.10, Bruker AXS, Inc., 2002, Madison, WI, USA.
- ² P. Coppens (1970). In *Crystallographic Computing*, edited by F.R. Ahmed, S.R.Hall & C.P.Huber, pp 255-270. Copenhagen: Munksgaard.
- ³ *SHELXTL* NT 6.12, Bruker AXS, Inc., 2002, Madison, WI, USA.

Table S1 Crystallographic data, data collection and refinement details of the X-ray crystal structure determinations of **1**, **2** and **H₂Dcphp**.

	1	2	H₂Dcphp
	CCDC-720837	CCDC-720838	CCDC-720839
Molecular formula	C ₂₁ H ₂₉ MnN ₇ O ₆	C ₁₉ H ₂₃ Cl ₂ MnN ₇ O ₁₀	C ₁₇ H ₁₇ N ₇ O ₃
<i>M_r</i>	530.45	635.28	367.38
Temperature [K]	100(2)	100(2)	100(2)
Wavelength [Å]	0.71073	0.71073	0.71073
Crystal description	yellow needle	orange prism	colourless block
Crystal size [mm]	0.25 × 0.10 × 0.07	0.28 × 0.24 × 0.17	0.23 × 0.18 × 0.12
Crystal system	monoclinic	monoclinic	monoclinic
Space group	<i>C2/c</i> (No. 15)	<i>C2/c</i> (No. 15)	<i>P2₁/n</i> (No. 14)
<i>a</i> [Å]	25.251(2)	10.9947(6)	11.9352(9)
<i>b</i> [Å]	7.6250(5)	31.380(4)	8.3106(3)
<i>c</i> [Å]	27.574(2)	7.9492(6)	17.982(2)
β [°]	113.044(5)	108.613(5)	102.780(7)
<i>V</i> [Å ³]	4885.4(6)	2599.1(4)	1739.4(2)
<i>Z</i>	8	4	4
<i>F</i> (000)	2216	1300	768
ρ_{calc} [g cm ⁻³]	1.442	1.623	1.403
μ [mm ⁻¹]	0.591	0.780	0.101
Total reflections	55979	31490	26980
Unique reflections	5386	3105	3843
Observed refl. [<i>I</i> > 2 σ (<i>I</i>)]	4235	2482	2853
<i>R</i> (int)	0.0550	0.0653	0.0832
Scan range θ [°]	3.21 to 27.10	3.40 to 27.87	3.50 to 27.10
Completeness to θ_{max} [%]	99.8	99.7	99.8
Index ranges	-32 ≤ <i>h</i> ≤ 32 -9 ≤ <i>k</i> ≤ 9 -35 ≤ <i>l</i> ≤ 35	-14 ≤ <i>h</i> ≤ 14 -41 ≤ <i>k</i> ≤ 41 -10 ≤ <i>l</i> ≤ 10	-15 ≤ <i>h</i> ≤ 15 -10 ≤ <i>k</i> ≤ 9 -22 ≤ <i>l</i> ≤ 23
Data / restraints / parameters	5386 / 0 / 383	3105 / 0 / 212	3843 / 0 / 253
Goodness-of-fit on <i>F</i> ²	1.129	1.052	1.030
<i>RI</i> , <i>wR2</i> [<i>I</i> > 2 σ (<i>I</i>)]	0.0396, 0.0827	0.0331, 0.0701	0.0463, 0.0949
<i>RI</i> , ¹ <i>wR2</i> (all data)	0.0602, 0.0882	0.0538, 0.0754	0.0756, 0.1051
Max./min. el. density [e.Å ⁻³]	+0.344, -0.311	+0.423, -0.609	+0.318, -0.256

Table S2 Selected bond distances (Å) and bond angles (°) of **1** and **2**.

Bond distances (Å)			
1			
Mn1-O4	2.194(2)	N2-C6	1.310(3)
Mn1-N5	2.265(2)	N2-N3	1.384(2)
Mn1-N2	2.269(2)	N5-C12	1.308(3)
Mn1-O3	2.282(2)	N5-N6	1.390(2)
Mn1-N1	2.332(2)	O1-C6	1.290(2)
Mn1-N7	2.360(2)	O2-C12	1.280(2)
Mn1-N4	2.467(2)		
2			
Mn1-O1a [#]	2.216(2)	Mn1-N4	2.330(2)
Mn1-O1	2.216(2)	Mn1-N4a [#]	2.330(2)
Mn1-N1	2.313(2)	N2-C6	1.293(2)
Mn1-N2a [#]	2.328(2)	N2-N3	1.356(2)
Mn1-N2	2.328(2)		
Bond angles (deg)			
1			
O4-Mn1-O3	177.62(6)	N5-Mn1-N7	69.20(6)
O4-Mn1-N5	86.08(6)	N2-Mn1-N7	152.37(6)
O4-Mn1-N2	100.07(6)	O3-Mn1-N7	83.67(6)
N5-Mn1-N2	134.93(6)	N1-Mn1-N7	135.26(6)
N5-Mn1-O3	94.12(6)	O4-Mn1-N4	83.04(6)
N2-Mn1-O3	81.47(6)	N5-Mn1-N4	156.51(6)
O4-Mn1-N1	94.11(6)	N2-Mn1-N4	67.77(6)
N5-Mn1-N1	67.64(6)	O3-Mn1-N4	95.93(6)
N2-Mn1-N1	67.41(6)	N1-Mn1-N4	133.78(6)
O3-Mn1-N1	88.15(6)	N7-Mn1-N4	90.87(6)
O4-Mn1-N7	94.20(6)		
2			
O1a [#] -Mn1-O1	169.95(8)	O1-Mn1-N4	80.76(5)
O1a [#] -Mn1-N1	95.02(4)	N1-Mn1-N4	134.07(4)
O1-Mn1-N1	95.02(4)	N2a [#] -Mn1-N4	154.10(5)
O1a [#] -Mn1-N2a [#]	100.64(5)	N2-Mn1-N4	68.49(5)
O1-Mn1-N2a [#]	83.25(5)	O1a [#] -Mn1-N4a [#]	80.76(5)
N1-Mn1-N2	67.47(4)	O1-Mn1-N4a [#]	92.22(5)
O1a [#] -Mn1-N2	83.25(5)	N1-Mn1-N4a [#]	134.07(4)
O1-Mn1-N2	100.64(5)	N2a [#] -Mn1-N4a [#]	68.49(5)
N1-Mn1-N2a [#]	67.47(4)	N2-Mn1-N4a [#]	154.10(5)
N2a [#] -Mn1-N2	134.95(7)	N4-Mn1-N4a [#]	91.85(7)
O1a [#] -Mn1-N4	92.22(5)		

[#] symmetry transformation: -x+2, y, -z+0.5

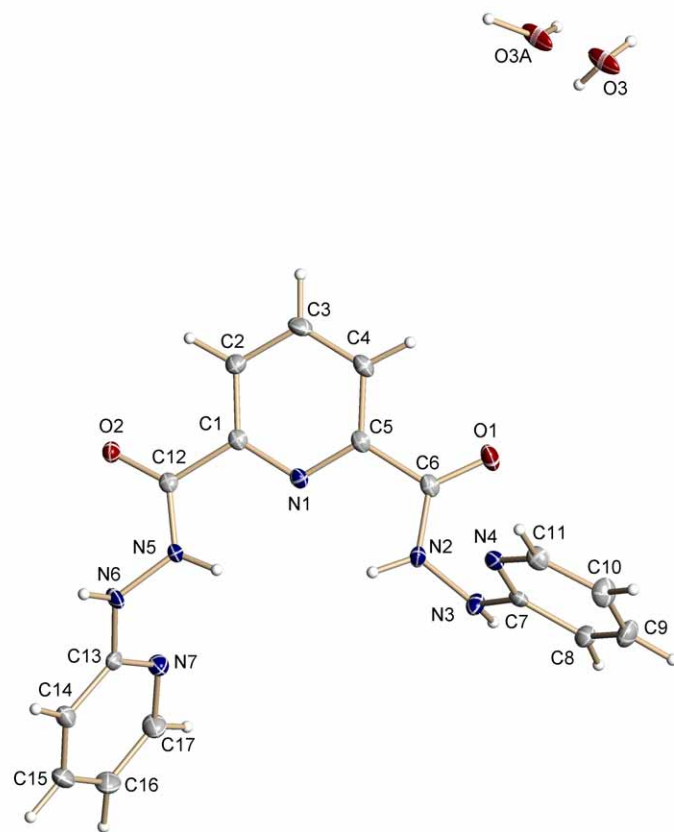


Figure S1 Thermal ellipsoid plot of the molecular structure of **H₂Dcphp** (50% probability).

Table S3 Selected bond distances (Å) of **H₂Dcphp**.

Bond distances (Å)			
O1-C6	1.226(2)	N5-N6	1.388(2)
O2-C12	1.237(2)	N5-H5N	0.89
N2-C6	1.347(2)	N6-C13	1.372(2)
N2-N3	1.387(2)	N6-H6N	0.89
N2-H2N	0.91	C5-C6	1.507(2)
N3-C7	1.369(2)	C1-C12	1.507(2)
N3-H3N	0.92		

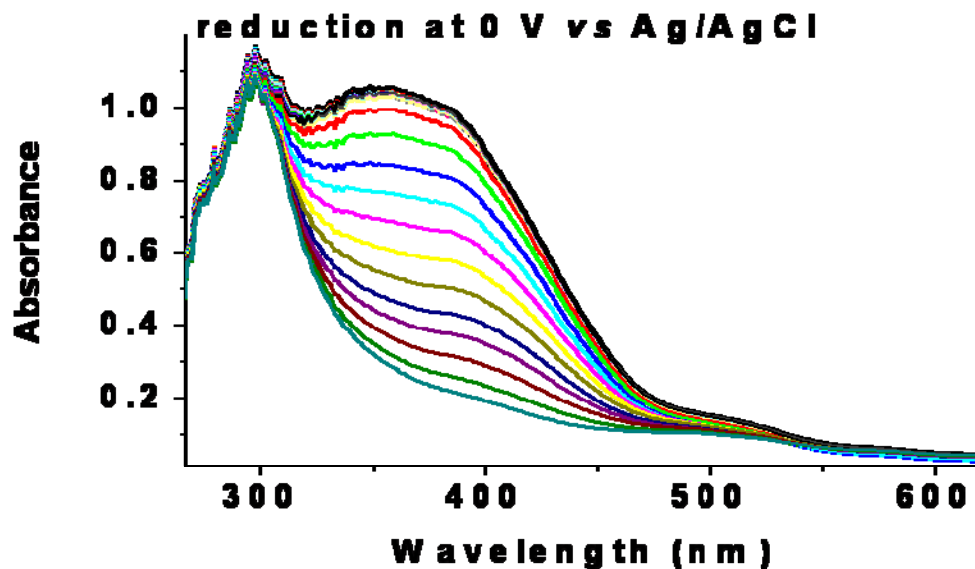


Figure S2 Reduction of the Mn^{III} species of **1** at 0 V vs Ag/AgCl.

Quantum Chemical Methods:

All structures have been preoptimized at the UHF/LANL2MB[A,B,C] level of theory and characterized as minima by computation of vibrational frequencies. We performed hybrid density functional structure optimizations using the B3LYP functional[B3LYP] and the LANL2DZ basis set with effective core potentials,[C,LANL2DZ] augmented with polarization functions on nonhydrogen atoms,[pol] further denoted as B3LYP/LANL2DZp. The influence of the bulk solvent was evaluated via single-point calculations using the CPCM [CPCM] formalism, that is, B3LYP(CPCM)/LANL2DZp//B3LYP/LANL2DZp and water as solvent. Corrections for zero-point vibrational energy (UHF/LANL2MB) were made, and all wave functions were tested for stability. The GAUSSIAN suite of programs was used.[G03]

[A] Hehre, W. J.; Stewart, R. F.; Pople, J. A. *J. Chem. Phys.* 1969, 51, 2657-2664.

[B] Collins, J. B.; von Rague' Schleyer, P.; Binkley, J. S.; Pople, J. A. *J. Chem. Phys.* 1976, 64, 5142-5151.

[C]

(a) Hay, P. J.; Wadt, W. R. *J. Chem. Phys.* 1985, 82, 270-283.

(b) Hay, P. J.; Wadt, W. R. *J. Chem. Phys.* 1985, 82, 284-298.

(c) Hay, P. J.; Wadt, W. R. *J. Chem. Phys.* 1985, 82, 299-310.

[B3LYP]

- (a) Becke, A. D. *J. Phys. Chem.* 1993, 97, 5648-5652.
- (b) Lee, C.; Yang, W.; Parr, R. G. *Phys. Rev. B.* 1988, 37, 785-789.
- (c) Stephens, P. J.; Devlin, F. J.; Chabalowski, C. F.; Frisch, M. J. *J. Phys. Chem.* 1994, 98, 11623-11627.

[LANL2DZ]

Dunning, T. H., Jr.; Hay, P. J. *Mod. Theor. Chem.* 1976, 3, 1-28.

[pol]

Huzinaga, S., Ed. *Gaussian Basis Sets for Molecular Calculations*; Elsevier: Amsterdam, The Netherlands, 1984.

[CPCM]

- (a) V. Barone, M. Cossi, *J. Phys. Chem. A* 1998, 102 1995 –2001.
- (b) M. Cossi, N. Rega, G. Scalmani, V. Barone, *J. Comp. Chem.* 2003, 24, 669– 681.

[G03]

M. J.Frisch, G.W. Trucks,H.B. Schlegel, G. E. Scuseria,M.A.Robb, J. R. Cheeseman, J. A. Montgomery, Jr., T. Vreven, K. N. Kudin, J. C. Burant, J. M. Millam, S. S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G. A. Petersson, H.Nakatsuji,M.Hada,M. Ehara, K. Toyota,R.Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J. E. Knox,H. P.Hratchian, J. B. Cross, V. Bakken, C.Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. Ochterski, P. Y. Ayala, K. Morokuma, G. A. Voth, P. Salvador, J. J. Dannenberg, V. G. Zakrzewski, S. Dapprich, A. D. Daniels, M. C. Strain, O. Farkas, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. V. Ortiz, Q. Cui, A. G. Baboul, S. Clifford, J. Cioslowski, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, M. Challacombe, P. M. W. Gill, B. G. Johnson, W. Chen, M. W. Wong, C. Gonzalez and J. A. Pople, *GAUSSIAN 03* (Revision C.02), Gaussian, Inc., Wallingford, CT, 2004.

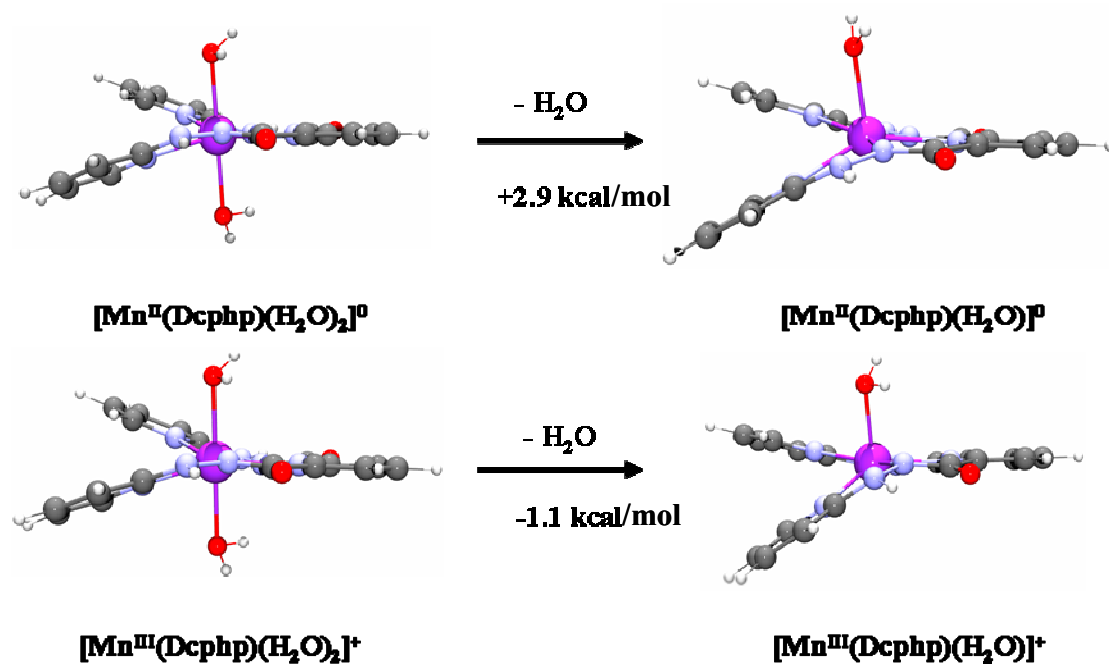


Figure S3 Calculated (B3LYP(CPCM)/LANL2DZp//B3LYP/LANL2DZp + ZPE (HF/LANL2MB)) water dissociation energy (ΔE) for $[\text{Mn}^{\text{II}}(\text{Dcphp})(\text{H}_2\text{O})_2]^0$ and $[\text{Mn}^{\text{III}}(\text{Dcphp})(\text{H}_2\text{O})_2]^+$.

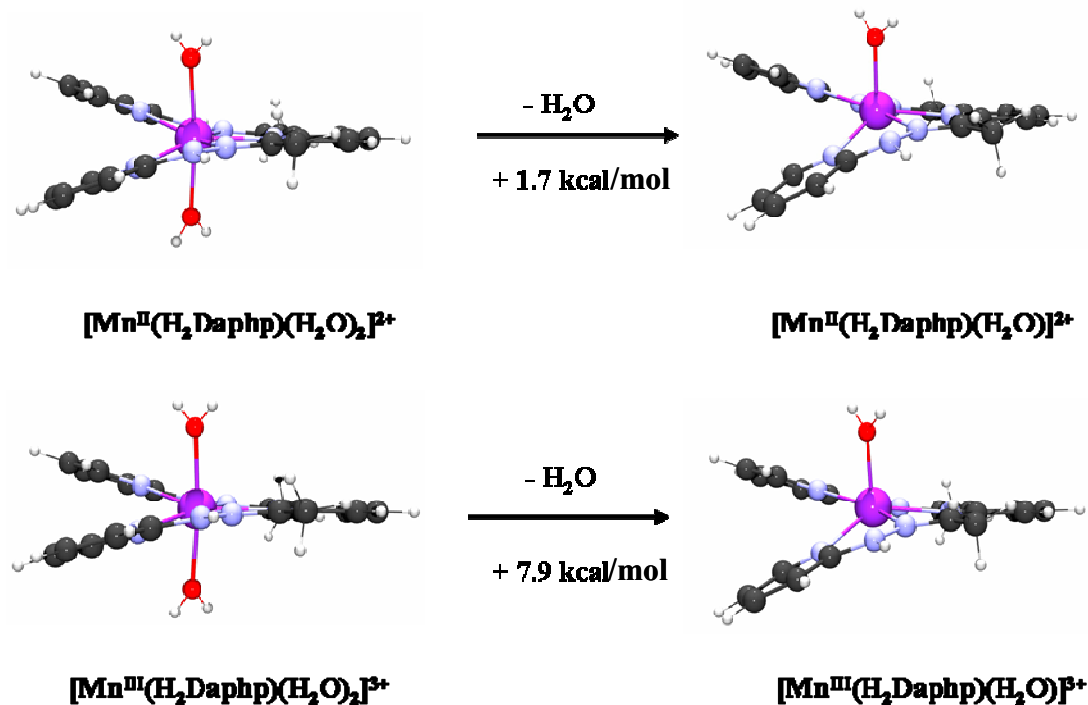


Figure S4 Calculated (B3LYP(CPCM)/LANL2DZp//B3LYP/LANL2DZp + ZPE (HF/LANL2MB)) water dissociation energy (ΔE) for $[\text{Mn}^{\text{II}}(\text{H}_2\text{Daphp})(\text{H}_2\text{O})_2]^{2+}$ and $[\text{Mn}^{\text{III}}(\text{H}_2\text{Daphp})(\text{H}_2\text{O})_2]^{3+}$.