

Supporting Information for

Manganese-Hydroxido Complexes Supported by a Urea/Phosphinic Amide Tripodal Ligand

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Table S1. Crystallographic Data and Structure Refinement Parameters

Complex	K ₂ [Mn ^{III} H ₂ POUT(OH)]	K[Mn ^{III} H ₂ POUT(OH)]
Empirical Formula	C ₃₆ H ₆₁ K ₂ MnN ₈ O ₆ P	C ₃₆ H ₆₁ KMnN ₈ O ₆ P
Formula weight	866.03	776.87
Crystal system	Orthorhombic	Triclinic
Space group	Pbca	P $\bar{1}$
a (Å)	17.8861(7)	11.5758(11)
b (Å)	21.3269(8)	13.6752(13)
c (Å)	23.3999(9)	14.4278(14)
α (°)	90°	70.2118(11)°
β (°)	90°	72.9494(11)°
χ (°)	90°	73.1226(12)°
Volume (Å ³)	8926.0(6)	2007.7(3)
Z	8	2
δ calc (Mg/m ³)	1.289	1.285
GOF	1.015	1.032
R1	0.0343	0.0377
wR2	0.0823	0.092
CCDC Code	1849229	1849228

Preparative Methods for Mn-Oxido Complexes.

Preparation of Low-Temperature [Mn^{III}H₂pout(O)]²⁻ EPR Samples. A solution of [Mn^{III}H₂pout(OH)]⁻ (~15 mM, 250 μ L) in a DMF:THF mixture was transferred to an EPR tube and sealed with a rubber septum. The tube was brought out of the dry box and placed in a -30 °C acetonitrile/dry ice bath and allowed to equilibrate for fifteen minutes. A 0.5 M (0.028 g, 0.25 mmol) stock solution of KO^tBu was prepared in a DMF:THF mixture and one equiv (8 μ L) was added via a syringe. After mixing by careful shaking of the tube, the EPR tube was quickly removed from the cold bath, wiped clean of acetonitrile, and frozen in liquid nitrogen before analysis.

Preparation of Low-Temperature [Mn^{IV}H₂pout(O)]⁻ EPR Samples. Samples were prepared in an analogous manner as described above with the following modifications: subsequent addition of one equivalent of FcBF₄ (18 μ L of a 220 mM stock solution). Sample was prepared in a -80 °C acetone/dry ice bath.

Generation of [Mn^{III}H₂pout(O)]²⁻ at Low Temperature using UV-vis Spectroscopy. For a typical experiment, a stock solution of [Mn^{III}H₂pout(OH)]⁻ at 20 mM concentration (0.013 g, 0.020 mmol) was prepared in a DMF:THF mixture (1 mL) and stored at -35 °C. To a 1 cm cuvette

was added 2 mL of DMF:THF mixture and 40 μ L of metal complex solution giving the desired experiment concentration (400 μ M). The cuvette was sealed with a rubber septum then transferred to the precooled UV-vis spectrometer cryostat and allowed to equilibrate for at least 15 minutes at - 30 $^{\circ}$ C under a flow of argon gas. A 45 mM (0.010 g, 0.089 mmol) stock solution of KO^tBu was prepared in 1 mL of a DMF:THF mixture and one equiv (18 μ L) was added via a syringe and the progress of the reaction monitored optically.

Generation of [Mn^{IV}H₂pout(O)]⁻ at Low Temperature using UV-vis Spectroscopy. Experiments were performed in an analogous manner as described above with the following modifications: subsequent addition of one equivalent (20 μ L) of a 40 mM FcBF₄ (0.011 g, 0.040 mmol) stock in 1 mL of DMF:THF mixture at - 80 $^{\circ}$ C.

Computational Methods. The DFT calculations were performed with Gaussian '09 using the hybrid functional B3LYP and the basis set 6-311G.¹

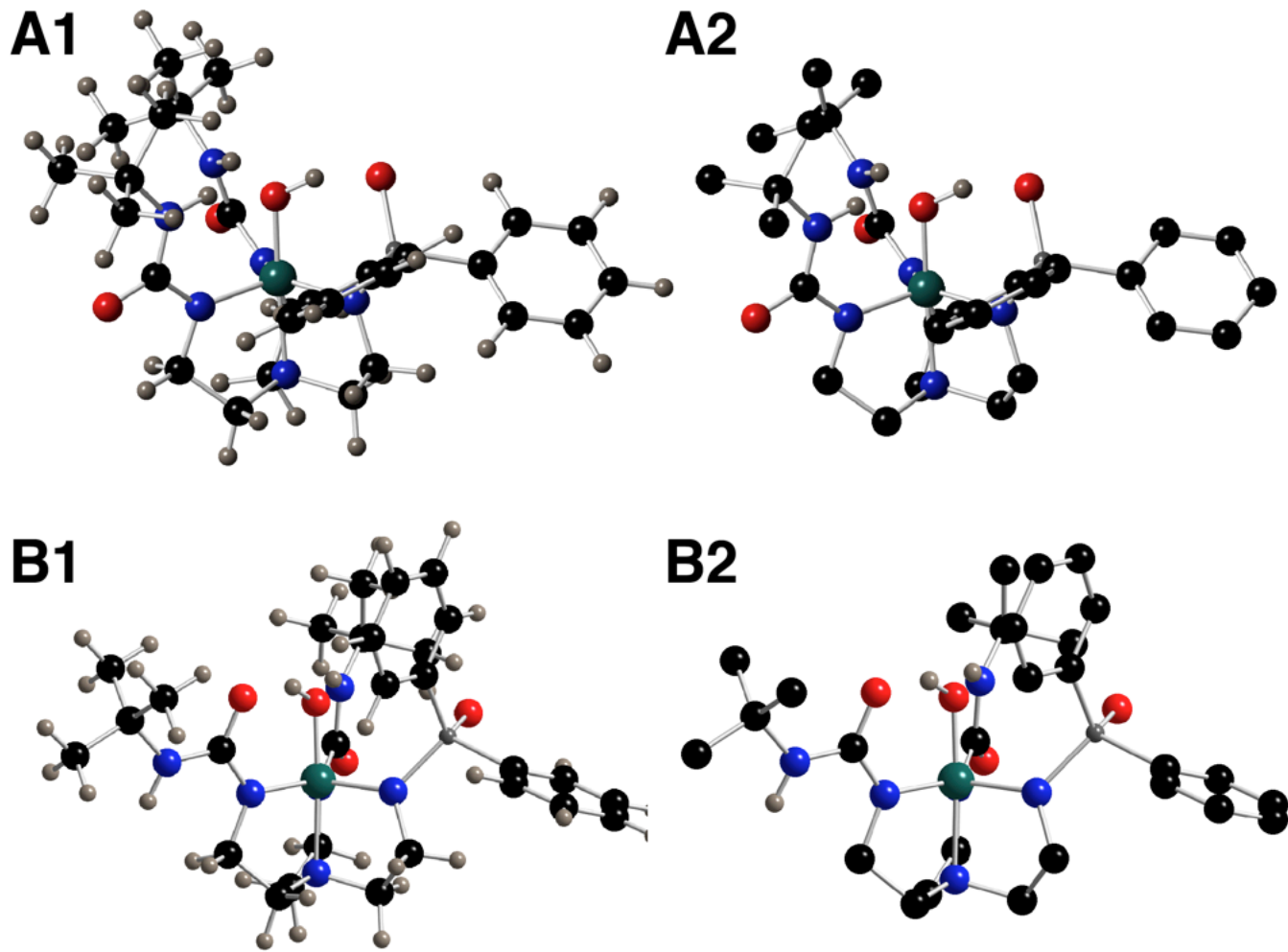


Figure S1. Possible structures for the two Mn^{IV}-OH complexes of [Mn^{IV}H₂pout(OH)] determined from DFT. Hydrogens removed for clarity in A2 and B2.

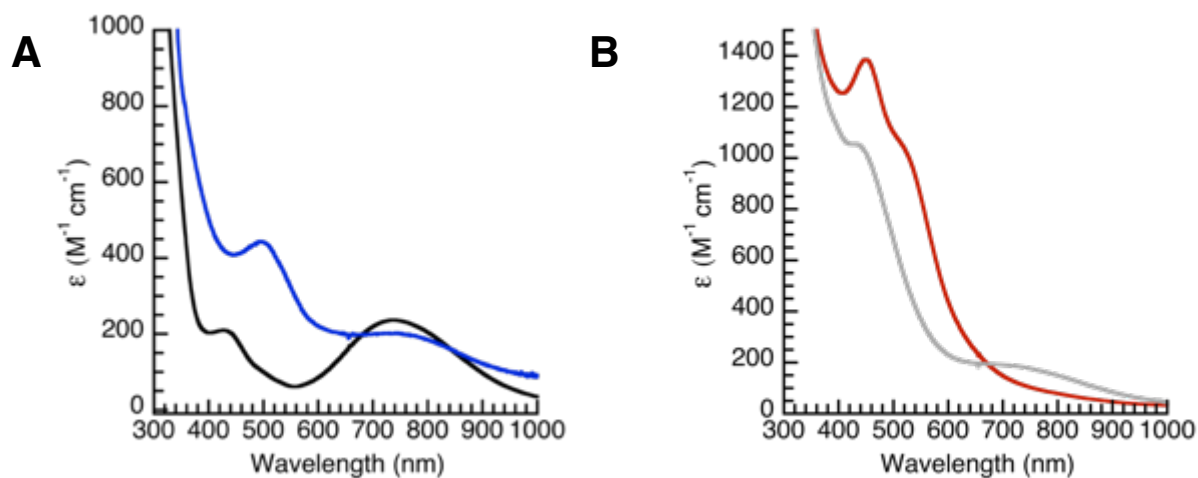


Figure S2. Overlaid UV-visible spectra of $[\text{Mn}^{\text{III}}\text{H}_2\text{pout}(\text{OH})]^{2-}$ (—), $[\text{Mn}^{\text{III}}\text{H}_2\text{pout}(\text{O})]^{2-}$ (—) (A), $[\text{Mn}^{\text{IV}}\text{H}_2\text{pout}(\text{OH})]^{-}$ (—) and $[\text{Mn}^{\text{IV}}\text{H}_2\text{pout}(\text{O})]^{-}$ (—) (B). Spectra were recorded in a 1:1 DMF:THF mixture at $-30\text{ }^{\circ}\text{C}$ and $-80\text{ }^{\circ}\text{C}$, respectively.

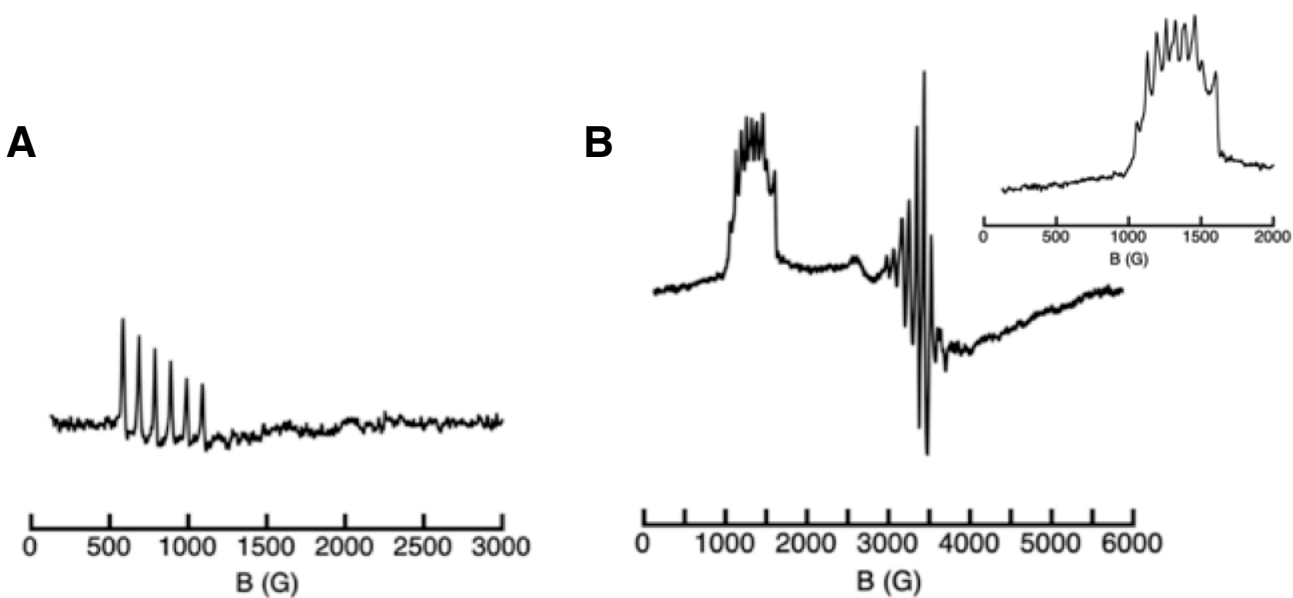


Figure S3. Parallel-mode EPR spectrum of a frozen solution of $[\text{Mn}^{\text{III}}\text{H}_2\text{pout}(\text{O})]^{2-}$ (A) and perpendicular-mode EPR spectrum of a frozen solution $[\text{Mn}^{\text{IV}}\text{H}_2\text{pout}(\text{O})]^{-}$ (B) in 1:1 DMF:THF. Inset: Zoom of low-field region. Sample temperature was 10 K.

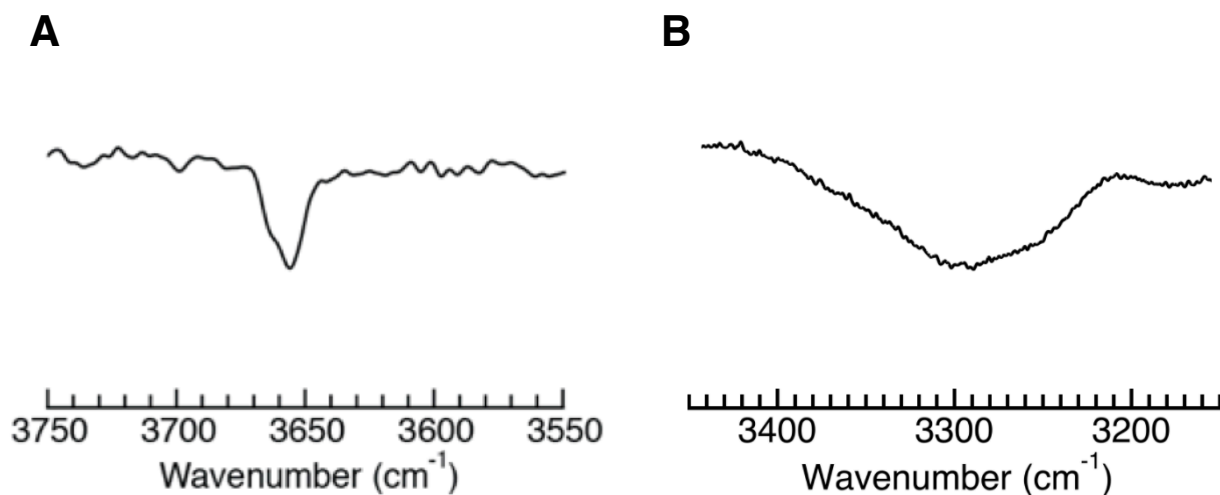


Figure S4. FTIR spectra for $[\text{Mn}^{\text{II}}\text{H}_2\text{pout}(\text{OH})]^{2-}$ (A) and $[\text{Mn}^{\text{III}}\text{H}_2\text{pout}(\text{OH})]^{-}$ (B) illustrating the region for the O-H vibration.

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