Supporting Information:

Preparation and Properties of a Monomeric High-Spin Mn^V–Oxo Complex

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Contents

Experimental Section

General Methods

All reagents were purchased from commercial sources and used as received, unless otherwise noted. Solvents were sparged with argon and dried over columns containing Q-5 and molecular sieves. DMF was stored over activated 4 Å molecular sieves for two days in a Vacuum Atmospheres, Co. drybox under an Ar atmosphere, then decanted onto a second portion of 4Å molecular sieves for two days before use. The syntheses of metal complexes were conducted in an Ar atmosphere. The preparation of $[Cp_2Fe]BF_4$ followed the literature procedure.[1]

Synthesis and Sample Preparation

Potassium[tris(N'-tert-butylureaylato)N-ethyl]aminato(oxo)]manganate(III)], $K_2[Mn^{III}H_3buea(O)]$. $K_2[Mn^{II}H_3buea(OH)]$ (153 mg, 0.2 mmol), prepared by literature methods,[2] was dissolved in 7 mL of DMA and treated with $[Cp_2Fe]BF_4$ (55 mg, 0.2 mmol) in 2 mL of DMA under an argon atmosphere. A rapid color change occurred, with the reaction mixture changing from light yellow to green. After stirring for 1 h, the solution was treated with solid KO^tBu (27 mg, 0.24 mmol), causing a color change to purplish-brown. The solution was stirred for an additional hour and filtered through a medium glass fritted funnel. Diffusion of Et_2O into the filtrate resulted in purple-brown crystals, whose spectroscopic features matched those published previously for the potassium salt of $[Mn^{III}H_3buea(O)]^{2-}$ (81 mg, 53 %).

Samples for UV-Vis Absorbance Measurements

A quartz cuvette containing DMF (1.5 mL) and THF (1.5 mL) under an argon atmosphere was cooled to -80˚C within the spectrophotometer and stirred for 15 min. A solution of $K_2[Mn^{III}H_3buea(O)]$ (0.50 µmol, 20 µL of a 25 mM solution in DMF) was added via injection with a gas tight syringe, the mixture was stirred for 1 min, and then treated with 2 equiv of $[Cp_2Fe]BF_4$ (1.0 µmol, 20 µL of a 50 mM solution in DMF) to produce $[Mn^{V}H_3buea(O)]$ and 1 equiv of $[Cp_2Fe]BF_4$ for preparing $[Mn^{IV}H_3buea(O)]^-$ (0.5 µmol, 10 µL).

Samples for EPR Measurements

A solution of $K_2[Mn^{III}H_3buea(O)]$ (3.1 µmol, 200 µL of a 15 mM solution in 90%THF/10%DMF) in an EPR tube was cooled to -78˚C in an acetone/dry ice bath. For generating $[Mn^{IV}H_3buea(O)]^-$, 1.3 equiv of $[Cp_2Fe]BF_4$ (4.0 µmol, 40 µL of a 100mM solution in DMF) was injected with a gas tight syringe. A similar procedure was used for $[Mn^{V}H_3buea(O)]$; in total 3.2 equiv of $[Cp_2Fe]BF_4$ (10 µmol, 100 µL of a 100mM solution in DMF) was injected to assure complete oxidation. The solution was allowed to sit for an additional 15 min and then frozen in liquid N_2.

Samples for Resonance Raman Measurements

A solution of $K_2[Mn^{III}H_3buea(O)]$ (6.0 µmol, 60 µL of a 100 mM solution in DMF) was combined with THF (150 µL) and DMF (30 µL) in an EPR tube and cooled to -78˚C in an acetone/dry ice bath. After 15 min, the solution was treated with 2 equiv of $[Cp_2Fe]BF_4$ (12 µmol, 60 µL of 200 mM solution in DMF) via injection with a gas tight syringe, resulting in a rapid color change from red-purple to dark brown. The solution was allowed to sit for an additional 15 min and then frozen in liquid N_2. A similar procedure was used to generate $[Mn^{IV}H_3buea(O)]^-$ using 1 equiv of $[Cp_2Fe]BF_4$ (6 µmol, 30 µL).

Samples for Mnβ X-ray Emission Measurements

A solution of $K_2[Mn^{III}H_3buea(O)]$ (25 µmol, 250 µL of a 100 mM solution in DMF) was combined with THF (500 µL) and $[Cp_2Fe]BF_4$ solution (50 µmol, 250 µL of a 200 mM solution in DMF) at -80˚C under argon in a drybox cold-well; a color change from red-purple to dark brown was observed. After mixing for 2 min, a portion of the solution was transferred anaerobically to a pre-cooled XES sample holder and frozen in liquid N_2.

Physical Methods

Electronic absorbance spectra were recorded with an 8453 Agilent UV-Vis spectrometer equipped with an Unisoku Unispeks cryostat. Cyclic voltammetric experiments were conducted using a CHI600C electrochemical analyzer following methods described previously.[3] A 2.0 mm glassy carbon electrode was used as the working electrode at scan velocities between 0.010 and 1.0 Vs^{-1}. A ferrocenium /ferrocene couple

($[FeCp_2]^{+/0}$) was used as an internal reference to monitor the reference electrode (Ag^+/Ag).

Resonance Raman spectra were recorded on an Acton 506 spectrometer using a Princeton Instruments LN/CCD-11100-PB/UBAR detector and ST-1385 controller interfaced with Winspec software. The spectra were obtained at -196 °C using backscattering geometry. Excitation at 647.1 nm was provided by a Spectra-Physics BeamLok 2060-KR-V Krypton ion laser. Raman shifts were externally referenced to liquid indene and internally referenced to solvent (DMF/THF).

Manganese Kβ X-ray emission spectral measurements were performed at wiggler beamline 6-2 of the Stanford Synchrotron Radiation Laboratory (SSRL), with an operating ring current of 300 mA. The beamline monochromator, using two cryogenically cooled Si crystals in (111) reflection, was used to set the incident photon energy to 10.0 keV. The X-ray beam was focused to 0.7 x 1 mm by means of vertical and horizontal focusing mirrors. The X-ray dose was set below the threshold of radiation damage over several scans. All spectra were normalized to the incident flux (I_o) as monitored by an ionization chamber detector filled with helium gas and calibrated to the published 6490.40 eV for the first moment of Mn_2O_3 (peak top position is 6491.01) taken in the energy range of 6485–6495 eV. Incident X-rays angle relative to the sample surface was set to 45°. Samples were protected from radiation damage by maintaining them at a temperature of approximately 10 K in a continuous flow liquid helium cryostat (Oxford Instruments CF1208) and under an ambient pressure.

Emission spectra were recorded by means of a high-resolution crystal-array spectrometer, using 14 spherically bent Si(440) crystals (100 mm diameter, 1 m radius of curvature), aligned on intersecting Rowland circles. An energy resolved Si drift detector (Vortex) was positioned at the focus of the 14 diffracting elements. The spectrometer energy was calibrated by measuring the energy of the elastically scattered beam as a function of spectrometer position. The overall experimental resolution was estimated to 0.6 eV, sufficient to detect small shifts of the fluorescence lines. A helium-filled polyethylene bag was sited between the cryostat and the spectrometer to minimize signal attenuation due to air absorption.

X-band EPR spectra were recorded on a Bruker 300 spectrometer equipped with an Oxford ESR-910 liquid helium cryostat and a dual mode microwave cavity. The quantification of signals is relative to a CuEDTA spin standard. The microwave frequency was calibrated with a frequency counter and the magnetic field with a NMR gaussmeter. The modulation frequency and amplitude was 100 kHz and 1.0 mT_{pp}. The EPR simulation software package SpinCount was used to analyze the data.[4] The software diagonalizes the spin Hamiltonian H = $\beta_e \mathbf{B}\cdot\mathbf{g}\cdot\mathbf{S} + D\{\mathbf{S}_z^2 - S(S+1)/3 + E/D(\mathbf{S}_x^2 - \mathbf{S}_y^2)\} + \mathbf{S}\cdot\mathbf{A}\cdot\mathbf{I}$, where the parameters have the usual definitions. The quantitative simulations are least-squares fits of the experimental spectra generated with consideration of all intensity factors, which allows computation of simulated spectra for a specified sample concentration. The Windows software package (SpinCount) is available for general application to any mono- or dinuclear metal complex by contacting M. Hendrich.

References.

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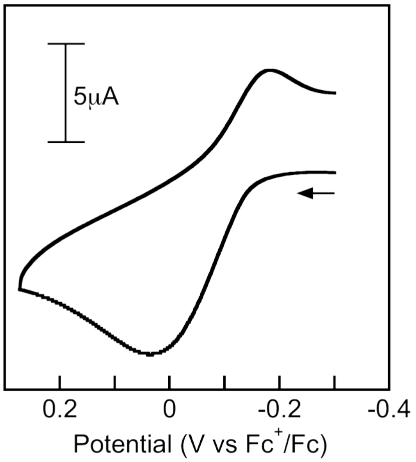

Figure S1. Cyclic voltammogram illustrating the second oxidation of $[Mn^{III}H_3buea(O)]^{2-}$ at -60 °C in DMF at a scan rate of 0.10 V/s.

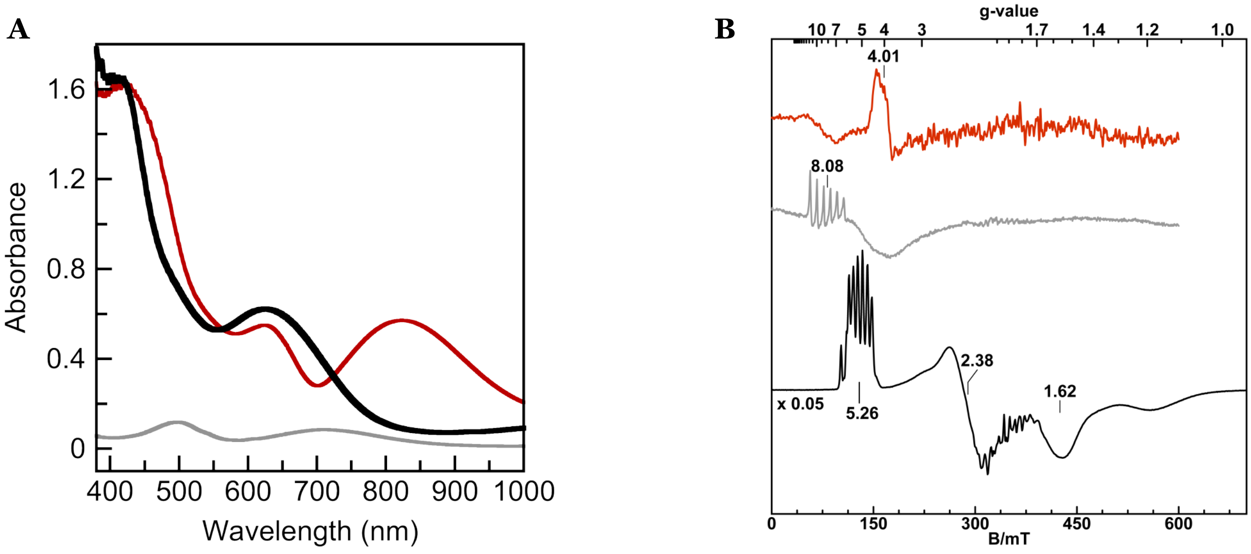

Figure S2. (**A**) Absorbance and (**B**) EPR spectra monitoring the comproportionation reaction described by eq 1: spectra of reactant complexes $[Mn^{III}H_3buea(O)]^{2-}$ (gray) and $[Mn^{V}H_3buea(O)]$ (red), and the product $[Mn^{IV}H_3buea(O)]^{-}$ (black). The reactions were done at -80 °C in 1:1 THF/DMF.