Supplementary Material (ESI) for Chemical Communications

X-ray photoreduction of a di(μ-oxo)$Mn^{III}Mn^{IV}$ complex occurs at temperatures as low as 20 K

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Electronic supplementary information

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I. Synthesis of 1. $\{[Mn_2(pda)_2(O)_2]Na(H_2O)_3\}_n$

In an erlenmeyer flask 0.112 g (0.5 mmol) of H_2pda[1] were neutralized by a saturated solution of sodium hydrogenocarbonate. 15 mL of acetone were added and the solution cooled down to -20°C. Then a chilled solution of manganese(II) nitrate (60 mg, 0.35 mmol) in acetone was added followed by a solution of 23 mg of potassium permanganate in the minimum amount of water. The resulting green-black solution was evaporated under vacuum at low temperature and the resulting product washed with acetonitrile and crystallized from a 50:50 mixture of acetone and water producing 100 mg (yield: 65%) of green black needles.

Mass spectrometry (ESI-MS, negative mode): ***m/z*** **$[M-Na]^-$: 586.**

II. X-ray Crystallography.

Diffraction data were taken using a Bruker SMART CCD area detector three-circle diffractometer (MoK_α radiation, graphite monochromator, λ = 0.71073Å). Data collection was performed at -50°C on a crystal of 0.15x0.15x0.5 mm.

The crystal-detector distance was 5 cm. For three settings of Φ and 2Θ, 1271 narrow data frames were collected for 0.3° increments in ω with a 180 s exposure time. A full hemisphere of data was collected for each complex. At the end of data collection, the first 50 frames were recollected to establish that crystal decay had not taken place during the collection. Unique intensities with $I>10\sigma(I)$ detected on all frames using the SAINT program[2] were used to obtain and refine the values of the cell parameters. The substantial redundancy in data allows empirical absorption corrections to be applied using multiple measurements of equivalent reflections with the SADABS Bruker program.[2] Space groups were determined from systematic absences, and they were confirmed by the successful solution of the structure (see Table S1). Complete information on crystal data and data collection parameters is given in Table S1.

The structure was solved by direct methods using the SHELXTL 5.03 package,[3] and all atoms were found by difference Fourier syntheses. All non-hydrogen atoms were anisotropically refined on F2. Hydrogen atoms were included in calculated positions and refined isotropically. Bond lengths and angles are listed in Table S3.

Table 1. Crystal data and structure refinement for NaMn2PDA2.

Identification code	NaMn2PDA2
Empirical formula	C20 H38 Mn2 N4 Na O19
Formula weight	771.41
Temperature	298(2) K
Wavelength	0.71073 A
Crystal system	Monoclinic
Space group	C2/c
Unit cell dimensions	a = 18.9552(19) A alpha = 90 deg. b = 6.7285(7) A beta = 94.816(2) deg. c = 24.535(3) A gamma = 90 deg.
Volume, Z	3118.2(6) A^3, 4
Density (calculated)	1.643 Mg/m^3
Absorption coefficient	0.912 mm^-1
F(000)	1596
Crystal size	0.15 x 0.15 x 0.5 mm
Theta range for data collection	1.67 to 28.96 deg.
Limiting indices	-21<=h<=24, -9<=k<=8, -28<=l<=31
Reflections collected	9671
Independent reflections	3730 [R(int) = 0.0629]
Absorption correction	None
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	3730 / 0 / 210
Goodness-of-fit on F^2	1.165
Final R indices [I>2sigma(I)]	R1 = 0.0829, wR2 = 0.2217
R indices (all data)	R1 = 0.0995, wR2 = 0.2322
Extinction coefficient	0.0122(7)
Largest diff. peak and hole	1.887 and -1.258 e.A^-3

Table 2. Atomic coordinates and equivalent isotropic displacement parameters (A^2) for NaMn2PDA2. U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

	x	y	z	U(eq)
Mn	0.29417(2)	0.69927(7)	0.542908(18)	0.01702(11)
O(1)	0.28231(11)	0.9079(3)	0.49543(9)	0.0218(5)
O(2)	0.23448(13)	0.7827(4)	0.60698(12)	0.0320(6)
O(3)	0.15570(15)	0.6470(5)	0.65767(13)	0.0479(8)
O(4)	0.37741(12)	0.8121(3)	0.58523(9)	0.0211(5)
O(5)	0.45130(13)	0.7704(4)	0.65965(10)	0.0284(6)
O(6)	0.5000	0.3828(7)	0.7500	0.0699(18)
O(7)	0.38999(16)	0.8384(5)	0.77510(13)	0.0475(8)
N(1)	0.30900(12)	0.4585(4)	0.59713(10)	0.0164(5)
N(2)	0.36565(14)	0.5192(4)	0.50207(11)	0.0203(6)
C(1)	0.32679(17)	0.2782(4)	0.56594(14)	0.0222(7)
C(2)	0.37278(17)	0.3315(4)	0.52113(13)	0.0208(7)
C(3)	0.41535(18)	0.1949(5)	0.49794(15)	0.0279(8)
C(4)	0.45106(19)	0.2529(6)	0.45336(17)	0.0331(9)
C(5)	0.44463(19)	0.4450(7)	0.43438(16)	0.0361(9)
C(6)	0.40232(18)	0.5753(6)	0.45984(14)	0.0285(8)
C(7)	0.24020(16)	0.4351(5)	0.62169(14)	0.0244(7)
C(8)	0.20748(17)	0.6371(5)	0.62986(14)	0.0259(7)
C(9)	0.36746(18)	0.5143(5)	0.63913(13)	0.0236(7)
C(10)	0.40128(16)	0.7120(5)	0.62804(13)	0.0207(7)
Na	0.5000	0.7241(3)	0.7500	0.0284(5)
O(8)	0.3197(3)	1.0837(8)	0.6959(2)	0.1213(17)
O(9)	0.3117(2)	0.5009(6)	0.77371(19)	0.0782(13)
O(10)	0.00194(16)	0.6656(4)	0.64939(14)	0.0418(8)

Table 3. Bond lengths [A] and angles [deg] for NaMn2PDA2.

Mn-O(1)#1	1.810(2)
Mn-O(1)	1.826(2)
Mn-O(4)	1.967(2)
Mn-O(2)	2.089(3)
Mn-N(1)	2.100(3)
Mn-N(2)	2.130(3)
Mn-Mn#1	2.6665(9)
O(1)-Mn#1	1.810(2)
O(2)-C(8)	1.259(4)
O(3)-C(8)	1.243(4)
O(4)-C(10)	1.297(4)
O(5)-C(10)	1.238(4)
O(5)-Na	2.350(2)
O(6)-Na	2.296(5)
O(7)-Na	2.353(3)
N(1)-C(1)	1.488(4)
N(1)-C(7)	1.490(4)
N(1)-C(9)	1.496(4)
N(2)-C(2)	1.350(4)
N(2)-C(6)	1.349(4)
C(1)-C(2)	1.503(5)
C(2)-C(3)	1.377(5)
C(3)-C(4)	1.390(5)
C(4)-C(5)	1.376(6)
C(5)-C(6)	1.373(6)
C(7)-C(8)	1.514(5)
C(9)-C(10)	1.511(5)
Na-O(5)#2	2.350(2)
Na-O(7)#2	2.353(3)
O(1)#1-Mn-O(1)	85.66(11)
O(1)#1-Mn-O(4)	179.15(10)
O(1)-Mn-O(4)	95.19(10)
O(1)#1-Mn-O(2)	92.13(10)
O(1)-Mn-O(2)	103.19(10)
O(4)-Mn-O(2)	87.72(10)
O(1)#1-Mn-N(1)	94.63(10)
O(1)-Mn-N(1)	179.29(10)
O(4)-Mn-N(1)	84.52(9)
O(2)-Mn-N(1)	77.45(10)
O(1)#1-Mn-N(2)	92.43(10)
O(1)-Mn-N(2)	100.74(10)
O(4)-Mn-N(2)	87.37(10)
O(2)-Mn-N(2)	155.91(10)
N(1)-Mn-N(2)	78.61(10)
O(1)#1-Mn-Mn#1	43.06(7)
O(1)-Mn-Mn#1	42.60(7)
O(4)-Mn-Mn#1	137.79(7)
O(2)-Mn-Mn#1	100.46(8)
N(1)-Mn-Mn#1	137.69(7)
N(2)-Mn-Mn#1	98.99(8)
Mn#1-O(1)-Mn	94.34(10)
C(8)-O(2)-Mn	113.1(2)
C(10)-O(4)-Mn	115.9(2)
C(10)-O(5)-Na	140.2(2)
C(1)-N(1)-C(7)	111.4(2)
C(1)-N(1)-C(9)	111.8(2)

C(7)-N(1)-C(9)	111.8(2)
C(1)-N(1)-Mn	109.10(19)
C(7)-N(1)-Mn	105.21(18)
C(9)-N(1)-Mn	107.14(18)
C(2)-N(2)-C(6)	119.0(3)
C(2)-N(2)-Mn	114.7(2)
C(6)-N(2)-Mn	126.2(2)
N(1)-C(1)-C(2)	110.6(2)
N(2)-C(2)-C(3)	121.8(3)
N(2)-C(2)-C(1)	115.4(3)
C(3)-C(2)-C(1)	122.6(3)
C(2)-C(3)-C(4)	118.6(3)
C(5)-C(4)-C(3)	119.7(3)
C(4)-C(5)-C(6)	119.0(4)
N(2)-C(6)-C(5)	121.9(3)
N(1)-C(7)-C(8)	109.9(3)
O(3)-C(8)-O(2)	124.9(3)
O(3)-C(8)-C(7)	118.2(3)
O(2)-C(8)-C(7)	116.9(3)
N(1)-C(9)-C(10)	113.4(3)
O(5)-C(10)-O(4)	122.6(3)
O(5)-C(10)-C(9)	118.8(3)
O(4)-C(10)-C(9)	118.6(3)
O(6)-Na-O(5)#2	97.63(8)
O(6)-Na-O(5)	97.63(8)
O(5)#2-Na-O(5)	164.73(16)
O(6)-Na-O(7)	109.09(10)
O(5)#2-Na-O(7)	89.79(10)
O(5)-Na-O(7)	85.23(10)
O(6)-Na-O(7)#2	109.09(10)
O(5)#2-Na-O(7)#2	85.23(10)
O(5)-Na-O(7)#2	89.79(10)
O(7)-Na-O(7)#2	141.8(2)

Symmetry transformations used to generate equivalent atoms:
#1 -x+1/2,-y+3/2,-z+1 #2 -x+1,y,-z+3/2

Table 4. Anisotropic displacement parameters (A^2) for NaMn2PDA2.
The anisotropic displacement factor exponent takes the form:
-2 pi^2 [h^2 a*^2 U11 + ... + 2 h k a* b* U12]

	U11	U22	U33	U23	U13	U12
Mn	0.0140(2)	0.0153(2)	0.0216(2)	-0.00173(17)	0.00113(16)	-0.00162(17)
O(1)	0.0174(9)	0.0234(11)	0.0251(11)	-0.0034(9)	0.0043(8)	-0.0090(9)
O(2)	0.0255(12)	0.0189(12)	0.0514(15)	0.0034(11)	0.0016(11)	0.0027(10)
O(3)	0.0393(13)	0.0484(17)	0.0603(17)	0.0107(14)	0.0297(12)	0.0162(13)
O(4)	0.0208(10)	0.0168(10)	0.0252(11)	-0.0011(9)	-0.0004(8)	-0.0023(8)
O(5)	0.0270(11)	0.0261(12)	0.0306(12)	0.0007(10)	-0.0061(10)	-0.0094(10)
O(6)	0.128(5)	0.025(2)	0.055(3)	0.000	-0.004(3)	0.000
O(7)	0.0375(14)	0.0549(19)	0.0513(17)	-0.0144(15)	0.0118(13)	0.0039(14)
N(1)	0.0133(10)	0.0110(11)	0.0250(12)	-0.0006(9)	0.0034(9)	-0.0023(9)
N(2)	0.0200(12)	0.0130(11)	0.0276(13)	0.0034(10)	-0.0002(10)	0.0001(10)
C(1)	0.0274(15)	0.0109(13)	0.0290(15)	0.0010(12)	0.0070(13)	0.0005(12)
C(2)	0.0229(14)	0.0111(13)	0.0284(15)	0.0015(11)	0.0027(12)	-0.0034(11)
C(3)	0.0250(15)	0.0194(15)	0.0395(18)	-0.0025(14)	0.0043(14)	0.0008(13)
C(4)	0.0244(15)	0.0295(18)	0.047(2)	-0.0052(16)	0.0126(15)	0.0047(14)
C(5)	0.0281(16)	0.048(2)	0.0336(18)	0.0062(17)	0.0109(14)	-0.0073(17)
C(6)	0.0254(15)	0.0280(17)	0.0322(17)	0.0085(14)	0.0032(13)	-0.0048(14)
C(7)	0.0188(13)	0.0214(15)	0.0338(17)	0.0068(13)	0.0078(12)	-0.0003(12)
C(8)	0.0208(14)	0.0240(15)	0.0334(16)	0.0019(14)	0.0060(13)	0.0072(13)
C(9)	0.0260(15)	0.0208(15)	0.0229(15)	0.0014(12)	-0.0039(12)	0.0004(13)
C(10)	0.0181(13)	0.0197(14)	0.0245(14)	-0.0017(12)	0.0037(11)	0.0031(12)
Na	0.0291(9)	0.0255(10)	0.0299(9)	0.000	-0.0008(8)	0.000
O(8)	0.098(3)	0.117(3)	0.158(4)	0.093(3)	0.066(3)	0.060(3)
O(9)	0.077(2)	0.052(2)	0.109(3)	-0.016(2)	0.023(2)	-0.011(2)
O(10)	0.0375(14)	0.0239(13)	0.0645(18)	0.0018(13)	0.0061(14)	0.0000(12)

Table 5. Hydrogen coordinates and isotropic displacement parameters (A^2) for NaMn2PDA2.

	x	y	z	U(eq)
H(1A)	0.2836	0.2162	0.5502	0.027
H(1B)	0.3514	0.1833	0.5905	0.027
H(3)	0.4201	0.0665	0.5118	0.033
H(4)	0.4792	0.1623	0.4364	0.040
H(5)	0.4686	0.4860	0.4048	0.043
H(6)	0.3988	0.7060	0.4476	0.034
H(7A)	0.2478	0.3674	0.6566	0.029
H(7B)	0.2083	0.3551	0.5978	0.029
H(9A)	0.4035	0.4117	0.6404	0.028
H(9B)	0.3488	0.5193	0.6747	0.028

III. X-ray absorption spectroscopy measurements

XAS spectra at the Mn K-edge were collected at the European Synchrotron Radiation Facility (ESRF, Grenoble, France), on the undulator beamline ID26.[4] The storage ring operating conditions were 6 GeV electron energy and 150-185 mA electron current. A Si(220) double-crystal monochromator was used for these experiments. The beamline was first calibrated at Cu K-edge based on an absolute calibration of the first inflection point of the Cu foil K-edge at 8983.32 eV.[5] Then, for all experiments, a reference foil of metallic Mn was used to provide an internal and accurate energy calibration of the monochromator for all spectra. The first inflection point of the Mn K-edge was set at 6539 eV. The energy reproducibility for these experiments was ± 0.05 eV. Two mirrors (amorphous silicon before, and SiO_2 after the monochromator) were used to remove the high-energy harmonics from the incident X-ray beam (cutting energy at 8 keV). XAS data for **1** were collected in the transmission mode from 6440 to 7440 eV at 20 K. Details of the sample preparation for powdered XAS measurements have been described previously.[6] The acquisition time is 17 min for one spectrum. After each spectrum, the beamline was quickly realigned during 1 min, and another spectrum was recorded without changing the sample position. 9 spectra have been successively recorded.

Data analysis was made as previously described[7,8] with the SEDEM software package.[9] The structural parameters were obtained as described earlier.[7,8] Ab initio calculations were performed with the FEFF 7.02 code[10] for a single absorber-scatterer pair Mn-O at 1.80 Å distance, a single Mn-N interaction at 2.10 Å, and a single Mn-Mn interaction at 2.65 Å. Since N_i and σ_i^2 are strongly correlated, N_i was held fixed to chemically reasonable integer values and only R_i and σ_i^2 were optimized.

1 D. D. Cox, S. J. Benkovic, L. M. Bloom, F. C. Bradley, M. J. Nelson, L. Que Jr and D. E. Wallick, *J. Am. Chem. Soc.,* 1988, ***110***, 2026.
2 Siemens Analytical X-ray Instruments Inc.: Madison, WI, 1995.
3 G. M. Sheldrick; Sheldrick, G. M., Ed.; University of Göttingen: Germany, 1994.
4 C. Gauthier, V. Solé, R. Signorato, J. Goulon and E. Moguiline, *J. Synchrotron Rad.,* 1999, ***6***, 164.
5 R. Pettitfer and C. Hermes, *J. Appl. Cryst.,* 1985, ***18***, 404.
6 L. Jacquamet, D. Aberdam, A. Adrait, J. L. Hazemann, J. M. Latour and I. Michaud-Soret, *Biochemistry,* 1998, ***37***, 2564.
7 A. Adrait, L. Le Pape, A. Gonzalès de Peredo, D. Aberdam, J. L. Hazemann, J. M. Latour and I. Michaud-Soret, *Biochemistry,* 1999, ***38***, 6248.
8 L. Jacquamet, F. Dole, C. Jeandey, J. L. Oddou, E. Perret, L. Le Pape, D. Aberdam, J. L. Hazemann, I. Michaud-Soret and J. M. Latour, *J. Am. Chem. Soc.,* 2000, ***122***, 394.
9 D. Aberdam, *J. Synchrotron Rad.,* 1998, ***5***, 1287.
10 S. Zabinsky, J. Rehr, A. Ankudinov, R. Albers and M. J. Eller, *Phys. Rev. B,* 1995, ***52***, 2995.