Supporting Information

Tsui and Agapie 10.1073/pnas.1302677110

Refinement Details

In each case, crystals were mounted on a glass fiber or nylon loop using Paratone oil, then placed on the diffractometer under a nitrogen stream. Low-temperature (100 K) X-ray data were obtained on a Bruker APEXII CCD-based diffractometer (Mo sealed X-ray tube, $K_\alpha = 0.71073$ Å). All diffractometer manipulations, including data collection, integration, and scaling, were carried out using the Bruker APEXII software (1). Absorption corrections were applied using SADABS (2). Space groups were determined on the basis of systematic absences and intensity statistics, and the structures were solved by direct methods using XS (3) (incorporated into SHELXTL) and refined by full-matrix least squares on F^2. All nonhydrogen atoms were refined using anisotropic displacement parameters. Hydrogen atoms were placed in idealized positions and refined using a riding model. The structure was refined (weighted least squares refinement on F^2) to convergence.

It should be noted that due to the size of these compounds, most crystals included solvent-accessible voids, which tended to contain disordered solvent. In addition, due to a tendency to desolvate, the long-range order of these crystals and amount of high-angle data we were able to record was in some cases not ideal. These disordered solvent molecules were largely responsible for the alerts generated by the checkCIF protocol. For two compounds ([**1**-Sr]$_2$ and **1**-Zn), the disordered noncoordinated solvents were removed using the SQUEEZE protocol included in PLATON (ref. 4, see special refinement details). We are confident this additional electron density is from solvent in the crystal lattice and not from unaccounted counterions.

Special Refinement Details for [LSrMn$_3$O$_4$(OAc)$_3$(DMF)]$_2$·DMF ([1-Sr]$_2$). The structure is a dimer of two molecules bridged by a highly disordered *N*,*N*-dimethylformamide (DMF) molecule. Restraints and populations were used to model this bridging ligand as a DMF molecule disordered in two positions. Restraints were also used to treat the displacement parameters of the coordinated DMF molecule to acceptable sizes. The crystal lattice also contained electron density corresponding to uncoordinated solvent molecules. One DMF molecule could be located, while the remaining electron density could not be satisfactorily modeled. SQUEEZE was used to produce a bulk solvent correction to the observed intensities. The program accounted for 91 electrons per unit cell. This is in reasonable agreement with what would be expected for a disordered molecule of DMF (40 electrons/molecule).

Special Refinement Details for LZnMn$_3$O$_4$(OAc)$_3$·C$_6$H$_6$ (1-Zn). The compound crystallized with two solvent molecules in the lattice. One molecule could be modeled as a single benzene molecule, while the other was disordered and likely a mixture of benzene and diethyl ether. The electron density could not be satisfactorily modeled, and SQUEEZE was used to produce a bulk solvent correction to the observed intensities. The program accounted for 78 electrons per unit cell. This is in reasonable agreement with what would be expected for a molecule of benzene (42 electrons/molecule) or a molecule of diethyl ether (42 electrons/molecule).

Special Refinement Details for [LYMn$_3$O$_4$(OAc)$_3$(DMF)$_2$][OTf]·2(DMF) ([1-Y][OTf]). The structure contains two DMF ligands coordinated to yttrium. One DMF ligand is slightly disordered, but the difference peaks were low, suggesting that the disordered population is low. The structure also contains two free DMF molecules and an outer-sphere trifluoromethanesulfonate counterion, which were all satisfactorily modeled.

Special Refinement Details for LScMn$_3$O$_4$(OAc)$_3$(DMF)·H$_2$O (2·DMF). The structure contains a DMF ligand coordinated to scandium. Additionally, there is a water molecule in the lattice (O15). The hydrogen atoms were not located, but the distance between O15 and O1 (2.805 Å) is consistent with a hydrogen bonding interaction.

1. Bruker Analytical X-Ray Systems (2006, June) *APEX2, Version 2 User Manual, M86-E01078* (Bruker Analytical X-Ray Systems, Madison, WI).
2. Sheldrick GM (2008) *SADABS (Version 2008/1): Program for Absorption Correction for Data from Area Detector Frames* (Univ of Göttingen, Germany).
3. Sheldrick GM (2008) A short history of *SHELX*. *Acta Crystallogr A* 64(Pt 1):112–122.
4. Spek AL (2009) Structure validation in chemical crystallography. *Acta Cryst* D65(2):148–155.

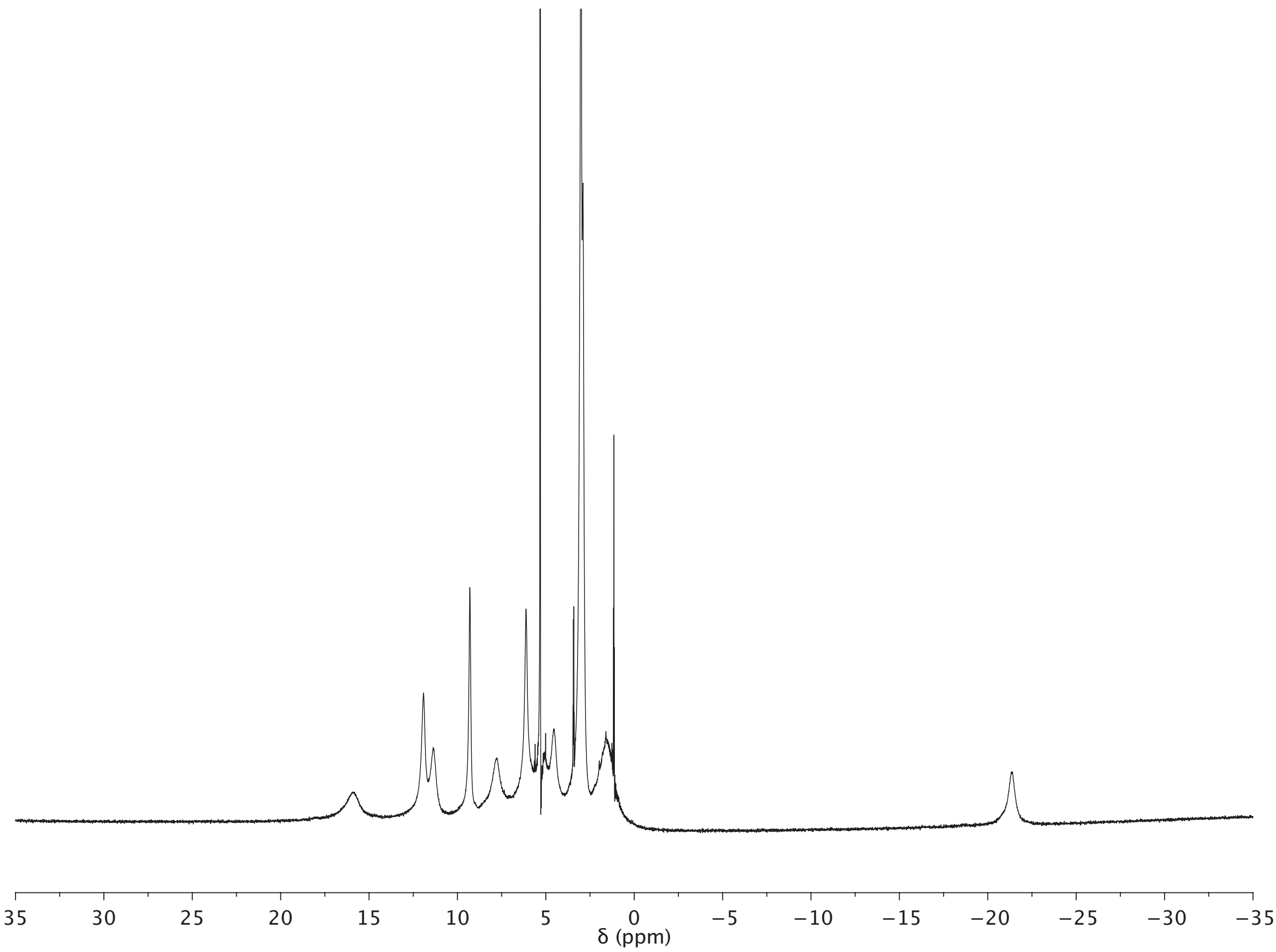

Fig. S1. ^{1}H NMR spectrum of [**1**-Y][OTf] in CD_2Cl_2 at 25 °C. Solvent signals are offscale.

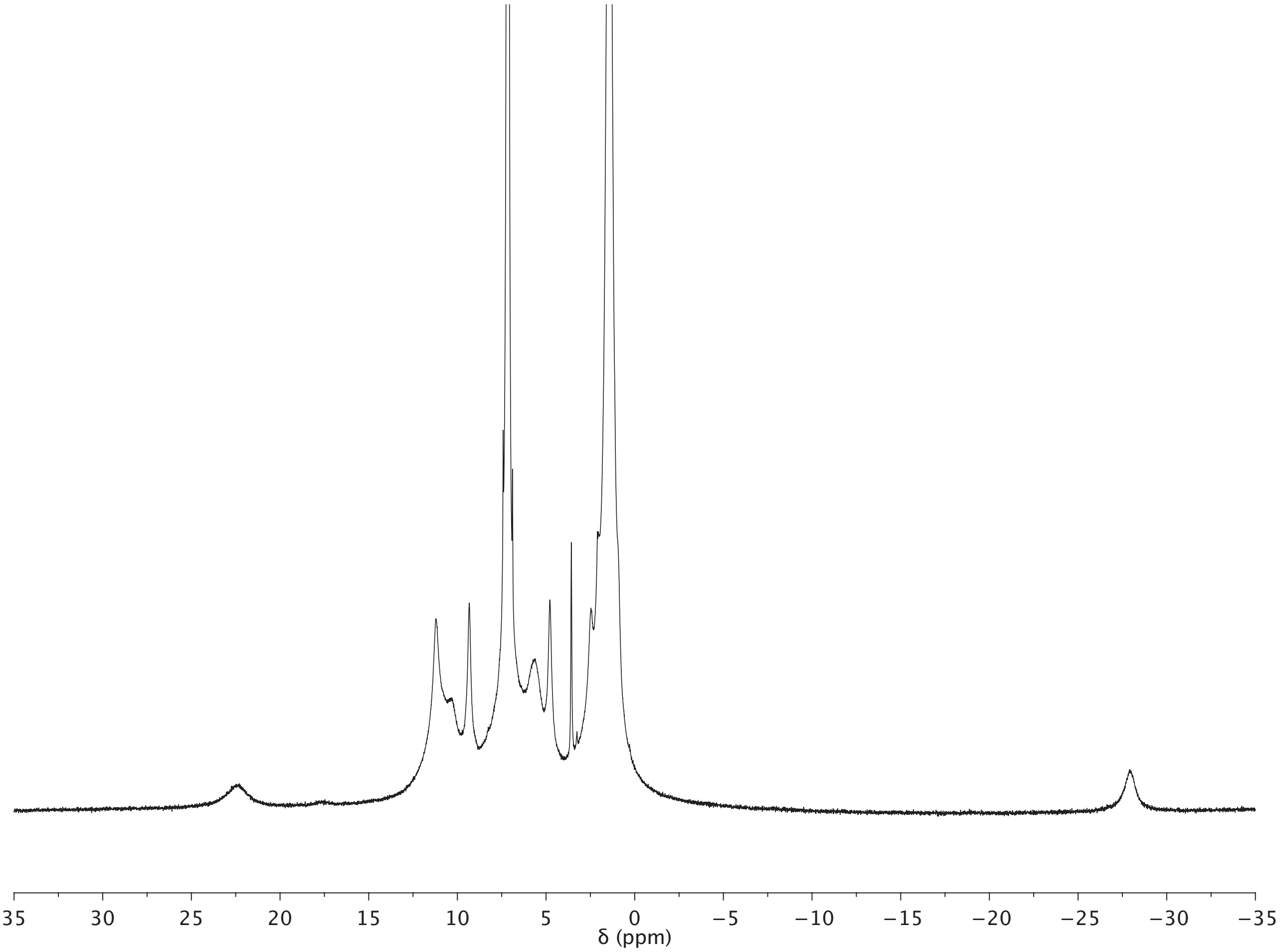

Fig. S2. ^{1}H NMR spectrum of **2**·tetrahydrofuran in C_6D_6 at 25 °C. Solvent signals are offscale.

Table S1. Crystal and refinement data for reported complexes

	[**1**-Sr]$_2$	**1**-Zn	[**1**-Y][OTf]	**2**·DMF
Empirical formula	$C_{69}H_{55}Mn_3N_8O_{15}Sr$	$C_{69}H_{54}Mn_3N_6O_{13}Zn$	$C_{76}H_{76}F_3Mn_3N_{10}O_{20}SY$	$C_{66}H_{55}Mn_3N_7O_{15}Sc$
CCDC no.	923216	923217	923218	923219
Formula wt	1,488.65	1,405.37	1,742.26	1,395.95
T, K	100	100	100	100
a, Å	14.4394(9)	13.5517(7)	12.9611(6)	13.8808(6)
b, Å	14.5514(9)	15.2198(8)	14.9934(7)	14.6307(6)
c, Å	18.0485(11)	16.9998(8)	19.8287(9)	14.8415(6)
α, °	80.763(3)	70.865(2)	84.492(2)	84.969(2)
β, °	71.236(3)	81.612(2)	82.070(2)	82.052(2)
γ, °	73.470(3)	82.158(3)	87.566(2)	78.193(2)
V, Å^3	3,432.3(4)	3,262.4(3)	3,797.2(3)	2,916.5(2)
Z	2	2	2	2
Crystal system	Triclinic	Triclinic	Triclinic	Triclinic
Space group	P-1	P-1	P-1	P-1
d_{calcd}, g/cm^3	1.440	1.431	1.568	1.590
θ range, °	1.82–29.02	1.99–33.15	1.78–30.74	1.86–32.88
μ, mm^{-1}	1.383	0.998	1.360	1.336
Absorption correction	Semiempirical from equivalents	Semiempirical from equivalents	Semiempirical from equivalents	Semiempirical from equivalents
Goodness of fit*	1.186	1.046	1.237	1.542
R1† wR2‡ (I > 2σ(I))	0.0668, 0.1559	0.0433, 0.1053	0.0536, 0.1250	0.0511, 0.0710

CCDC, Cambridge Crystallographic Data Centre.

*$GOF = S = \{\sum[w(F_o^2 - F_c^2)^2]/(n-p)\}^{1/2}$.

$^†R1 = \sum||F_o| - |F_c||/\sum|F_o|$.

$^‡wR2 = \{\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]\}^{1/2}$.

Table S2. BVS calculations for manganese atoms in $[1\text{-Sr}]_2$ (ref. 1)

Mn atom	Mn^{II}	Mn^{III}	Mn^{IV}
Mn1	4.45	4.10	**4.02**
Mn2	4.47	4.12	**4.04**
Mn3	4.47	4.12	**4.04**

The bolded value is the closest to the charge for which it was calculated. The oxidation state is the nearest whole number to the bold value. BVS, bond valence sum.

1. Thorp HH (1992) Bond valence sum analysis of metal-ligand bond lengths in metalloenzymes and model complexes. *Inorg Chem* 31(9):1585–1588.

Table S3. BVS calculations for manganese atoms in 1-Zn (ref. 1)

Mn atom	Mn^{II}	Mn^{III}	Mn^{IV}
Mn1	4.49	4.14	**4.06**
Mn2	4.41	4.07	**3.99**
Mn3	4.46	4.12	**4.04**

Bolded value is the closest to the charge for which it was calculated. The oxidation state is the nearest whole number to the bold value.

1. Thorp HH (1992) Bond valence sum analysis of metal-ligand bond lengths in metalloenzymes and model complexes. *Inorg Chem* 31(9):1585–1588.

Table S4. BVS calculations for manganese atoms in [1-Y][OTf] (ref. 1)

Mn atom	Mn^{II}	Mn^{III}	Mn^{IV}
Mn1	4.47	4.12	**4.04**
Mn2	4.47	4.13	**4.05**
Mn3	4.47	4.12	**4.05**

Bolded value is the closest to the charge for which it was calculated. The oxidation state is the nearest whole number to the bold value.

1. Thorp HH (1992) Bond valence sum analysis of metal-ligand bond lengths in metalloenzymes and model complexes. *Inorg Chem* 31(9):1585–1588.

Table S5. BVS calculations for manganese atoms in 2·DMF (ref. 1)

Mn atom	Mn^{II}	Mn^{III}	Mn^{IV}
Mn1	3.62	3.34	3.27
Mn2	4.21	3.88	**3.81**
Mn3	4.37	4.03	**3.96**

Bolded value is the closest to the charge for which it was calculated. The oxidation state is the nearest whole number to the bold value.

1. Thorp HH (1992) Bond valence sum analysis of metal-ligand bond lengths in metalloenzymes and model complexes. *Inorg Chem* 31(9):1585–1588.

Table S6. Reduction potentials of [$\mathrm{MMn^{IV}{}_3O_4}$] compounds in *N*,*N*-dimethylacetamide (0.1 M $\mathrm{NBu_4PF_6}$)

Compound	pK_a of M(aqua)$^{n+}$	Potential vs. Fc/Fc$^+$, mV
$\mathrm{LMn_4O_4(OAc)_3}$	0.1	290 (ref.1)
[**1**-Sc][OTf]	4.7	−250
[**1**-Y][OTf]	8.0	−430
1-Zn	9.3	−630
1-Ca	12.6	−940 (ref.1)
1-Sr	13.2	−940

Reported potentials are an average of duplicate measurements from different samples and referenced to Fc/Fc$^+$.

1. Kanady JS, Tsui EY, Day MW, Agapie T (2011) A synthetic model of the $\mathrm{Mn_3Ca}$ subsite of the oxygen-evolving complex in photosystem II. *Science* 333(6043):733–736.

Other Supporting Information Files

Dataset S1 (TXT)