Supporting Information

Emerson *et al.* 10.1073/pnas.0711179105

SI Text

Analysis of X-Ray Crystallography Data. In the high-resolution structures of Mn-HPCD and Fe-HPCD, slightly asymmetric rather than spherical electron density is apparent at one of the solvent coordination sites in two of the subunits. Because no small ligand that can account for the observed density is present in purification or crystallization solutions, solvent at partial occupancy in two slightly different positions was modeled at these sites.

Analysis of EPR Spectra

EPR spectra of spin $S = 3/2$ and $S = 5/2$ complexes were analyzed according to the following spin Hamiltonian equations, respectively:

$$\hat{H}_e = g_o\beta_e\vec{S}\vec{H} + D[S_z^2 - 5/4 + E/D(S_x^2 - S_y^2)] \quad [1]$$

$$\hat{H}_e = g_o\beta_e\vec{S}\vec{H} + D[S_z^2 - 35/12 + E/D(S_x^2 - S_y^2)], \quad [2]$$

where D and E/D are zero field-splitting parameters and the other parameters have their usual definitions. The value of g_o is generally assumed to be 2.0, but small deviations from this value sometimes occur because of symmetry perturbations. The term E/D is a measure of the departure of the electronic environment of the iron from axial symmetry and can assume values between 0 and 1/3 [Blumberg WE, Peisach J (1973) The measurement of zero field splitting and the determination of ligand composition in mononuclear nonheme iron proteins. *Ann NY Acad Sci* 222:539–560], the extreme values representing the axial and completely rhombic cases, respectively. The absolute value of E/D can be calculated from the g-values and is used as a convenient method to compare spectra of samples with $S > 1/2$.

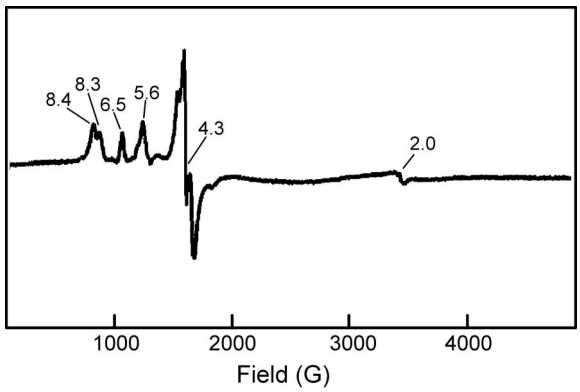

Fig. S1. EPR spectra of as-isolated Fe-MndD. As-isolated Fe-HPCD exhibits essentially no EPR spectrum.

Table S1. X-ray data collection and refinement statistics

Dataset	Mn-HPCD
PDB ID code	3BZA
Space group	$P2_12_12$
Monomer/AU	4
Cell dimensions, Å	110.5, 152.2, 96.3
Cell angles, °	90, 90, 90
Resolution range,* Å	28.8–1.70 (1.74)
Reflections, observed/unique	834,470/176,615
R_{merge},*† %	8.8 (55.5)
Mean $\langle I\rangle/\sigma\langle I\rangle$*	15.3 (2.3)
Completeness,* %	99.3 (98.4)
R, R_{free}, test,‡ %	17.0, 19.7, 5.0
RMSD§ bond length, Å	0.011
RMSD§ angles, °	1.297
ESU,¶ Å	0.064
Ramachandran plot	
Allowed regions, %	99.7
Generously allowed regions, %	0.3

*Values for the highest-resolution shell are given in parenthesis.

†$R_{merge} = \Sigma\ |I_i - \langle I\rangle|/\Sigma\ |I_i|$, where I_i is the integrated intensity of a given reflection, and $\langle I\rangle$ is the mean value for that reflection.

‡$R = (\Sigma\ |F_{obs} - kF_{calc}|)/\Sigma\ |F_{obs}|$, where k is a scale factor. The R_{free} value was calculated with the indicated percentage of reflections not used in the refinement.

§Root-mean-square deviation (RMSD) from ideal geometry in the final models.

¶Estimated overall coordinate error (ESU) based on maximum likelihood.