Supporting Information to Accompany:

NMR Paramagnetic Relaxation of the Spin 2 Complex MnIII-TSPP: a Unique Mechanism

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**Reference Note (22)**

**NMR Relaxation Measurement: Experimental Technique.**

Spin lattice relaxation times were measured using the phase shifted triplet sequence $\{D_tD_r(D/2)D_r(D/2)D_r\}^n$, in which the magnetization is sampled by pulse triplets at successive intervals, $D_t$, during the decay: the triplet samples the magnetization with a $\pi/2$ pulse, refocuses the magnetization as a spin echo with a phase-shifted $\pi$ pulse, and then returns the magnetization to the z-axis with a second $\pi/2$ pulse. The reproducibility of this method on a given sample is $\pm 1.0\%$ as long as $\frac{D_t}{D_d} \leq 0.01$. At low field strengths the signal to noise ratio was relatively poor and averaging was used as needed to obtain reproducibility of the measured $R_1$ of $3\%$ or better. Sample probe temperature was maintained within $\pm 0.5 \, ^\circ\text{C}$ via a stream of dry nitrogen.

**Reference Note (39)**

**Test of Chemical Stability for Mn$^{III}$TSPP in Solution and PA gels**

Polyacrylamide (PA) gel samples were monitored by UV-VIS spectroscopy over the course of four months in order to test the chemical stability as a function of time of the Mn$^{III}$TSPP (Figure 1S-A), particularly the possibility that manganese oxidation or reduction might result from the presence of free radicals of the gelation mechanism. Spectra were collected at increasing times (indicated by the arrow) following initiation of the polymerization reaction, with the pre-gelation control spectrum at $t = 0$ of the figure. Gelation caused some spectral broadening and increased scattering as the sample aged.
Neither band shifts nor appearance of new bands, indicative of changes in oxidation state of metal ions \(^2\), are apparent.

**Reference Note (45)**

**Test of Mn\(^{III}\)TSPP Sample Aggregation**

The possibility of solute aggregation, which occurs in aqueous H\(_2\)TSPP \(^3\)\(^4\) solutions and in solutions of some metallated TSPP solutes \(^5\)\(^6\), was examined in the control experiments of Figure 1S-B, which compares spectra of Mn\(^{III}\)TSPP at 2.1 \(\mu\)M and 1.14 mM, buffered at pH 8. The more concentrated solution was observed at a path length of approximately 0.0025 mm by layering two drops of the sample solution between two Corning microscope cover slips. Porphyrin aggregation is known \(^7\)\(^8\)\(^9\) to cause shifts the order of 15 nm in the Soret band of the porphyrin as well as large perturbations in the Q-bands. Upon 500-fold dilution, the spectra, normalized at the Soret Bands, are almost superimposable (Figure 1S-B), showing the absence of aggregation in these samples. Kellar and Foster \(^10\) similarly concluded that aqueous Mn\(^{III}\)TSPP does not aggregate at millimolar concentrations from their NMR relaxation study, based on the effect of addition of acetone, a presumed disaggregating agent \(^11\)\(^12\), on the water proton fdp.
Reference Note (46)

Outer Sphere and Scalar Contributions to $R_{1p}$ for Mn$^{III}$TSPP

The outer sphere (intermolecular) contribution to the water proton $R_{1p}$ was estimated using MD simulation as described previously $^{13,14,15}$. This calculation requires the translational diffusion correlation time, $\bar{D}$, defined as:

$$\bar{D} = \frac{d_c^2}{(D_1 + D_2)}$$  \hspace{1cm} (S1)

where $d_c$ is the metal-proton distance of closest approach, and $D_1$ and $D_2$ are the self diffusion coefficients of the solvent and solute. The distance of closest approach was estimated from a radial distribution function (rdf) generated by MD simulations of the [Mn$^{III}$TSPP•(H$_2$O)$_2$]/water solution, and were performed using the Dynamics Simulation Module of Cerius2 (Biosim-Molecular Simulations, Inc.). The simulations were performed under constant NVE with a unit cell containing a single [Mn$^{III}$TSPP•(H$_2$O)$_2$] molecule and 48 water molecules, with periodic boundary conditions. The unit cell dimensions were chosen to give a solution density of 1.000 g/ml. The solution structure for [Mn$^{III}$TSPP•(H$_2$O)$_2$] (Figure 2S) was taken from the x-ray structure for [Mn$^{III}$TPP•(H$_2$O)$_2$] $^{16}$ (TPP = tetraphenylporphyrin), to which sulfonate groups were added. This structure for [Mn$^{III}$TSPP•(H$_2$O)$_2$] was then constrained to remain constant during the simulation. The rdf (Figure 3S) shows both intramolecular and intermolecular metal-proton distances. The peaks in the plot correspond to the intramolecular hydrogens, while the background corresponds to the protons of the intermolecular water molecules. The distance of closest approach is taken from this plot to be 3.9 angstroms, the minimum distance of the intermolecular proton background. The self-diffusion
The coefficient of water was measured by NMR \(^{17}\) and diaphragm cells \(^{18}\) with a value of \(D_1 = 2.2 \times 10^{-9} \text{ m}^2\text{s}^{-1}\). The solute self-diffusion coefficient, \(D_2\), was set an order of magnitude smaller for \([\text{Mn}^{\text{III}}\text{TSPP}\bullet(\text{H}_2\text{O})_2]\), as the significantly larger molecule will diffuse much more slowly. The reorientational correlation time of \([\text{Mn}^{\text{III}}\text{TSPP}\bullet(\text{H}_2\text{O})_2]\) was calculated as described below. Using these values in conjunction with the parameters of Table I from the article, the outer sphere contribution was found to be less than 2-3\% of the measured \(R_{1p}\).

Chemical exchange and scalar coupling can also contribute to the NMR-PRE. The measured relaxation rate is related to the relaxation rate, \(R_{1p}\), of the protons of the axial water ligands as seen in the Luz-Meiboom \(^{19}\) equation:

\[
R_{1p} = \frac{f_m}{T_{1m} + \tau_m}
\]

where \(f_m\) is the mole ratio of bound/free solvent ligand, \(T_{1m}\) is the spin lattice relaxation time, and \(\tau_m\) is the chemical exchange lifetime of the bound solvent molecule.

Chemical exchange times for H\(_2\)O ligands on related Mn(III) porphyrins have been measured by Kellar \textit{et al} \(^{20}\) using \(^{17}\)O NMR linewidths, and found to be 21.4 ns for Manganese (III) tetrakis(N-methylpyrid-4-yl) porphyrin and 47.4 ns for manganese (III) protoporphyrin IX. These values are \(\sim\)2 orders of magnitude longer than \(\tau_m^{(1)}\), meaning \(\tau_m\) is slow relative to other contributions to the dipolar correlation time in eqn. 8, and will not contribute to the relaxation. Because the \(\tau_m\) is fast on the NMR timescale, \(\tau_m\) is negligible in eq S2 and the measured \(R_{1p}\) is a direct measure of the NMR-PRE. The scalar coupling was investigated using the scalar coupling constants.
of water protons as measured \(^{21}\) by NMR for aqueous metal ions. The scalar
contribution to the water proton \(R_{1p}\) is negligible compared to the dipolar relaxation,
and is therefore assumed to be zero.

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Figure 1S. UV-VIS spectra of Mn$^{III}$TSPP samples, gelled and aqueous.

A) Spectra of a gelled sample over 4 months, time follows arrow.

B) Test for aggregation in pH = 8 buffer sample.
Figure 2S. A) top and B) side views of the crystal structure of \([\text{Mn}^{III} \text{TPPS} (\text{H}_2\text{O})_2]^{+1}\)
Figure 3S. Radial distribution function for protons relative to metal center in Mn$^{III}$ TSPP. Peaks are intramolecular hydrogens, described in text. The background is for intermolecular waters, the shortest distance being the distance of closest approach.