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Aqueous Speciation and Electrochemical Properties of a Water-Soluble Manganese Phthalocyanine Complex[#]

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Abstract

The speciation behavior of a water-soluble manganese(III) tetrasulfonated phthalocyanine complex was investigated with UV-visible and electron paramagnetic resonance (EPR) spectroscopies, as well as cyclic voltammetry. Parallel-mode EPR (in dimethylformamide:pyridine solvent mix) reveals a six-line hyperfine signal, centered at a g-value of 8.8, for the manganese(III) monomer, characteristic of the $d^4 S=2$ system. The color of an aqueous solution containing the complex is dependent upon the pH of the solution; the phthalocyanine complex can exist as a water-bound monomer, a hydroxide-bound monomer, or an oxo-bridged dimer. Addition of coordinating bases such as borate or pyridine changes the speciation behavior by coordinating the manganese center. From the UV-visible spectra, complete speciation diagrams are plotted by global analysis of the pH-dependent UV-visible spectra, and a complete set of pK_a values is obtained by fitting the data to a standard pK_a model. Electrochemical studies reveal a pH-independent quasi-reversible oxidation event for the monomeric species, which likely involves oxidation of the organic ligand to the radical cation species. Adsorption of the phthalocyanine complex on the carbon working electrode was sometimes observed. The pK_a values and electrochemistry data are discussed in the context of the development of mononuclear water-oxidation catalysts.

Keywords

coordination chemistry; pH dependence; water-oxidation catalysis; global analysis; pK_a determination

Introduction

The aqueous coordination chemistry of manganese complexes has received less attention than it deserves. This is somewhat surprising, as manganese has known roles in a diverse number of important natural and artificial systems. For example, manganese catalases and synthetic manganese complexes show high activity for dismutation of hydrogen peroxide.¹ An oxo-hydroxo bridged dimer of manganese and iron plays an important role in the class 1c ribonucleotide reductases.² Manganese serves as a water-oxidation catalyst in both the oxygen-evolving complex of photosystem II,³ and in model water-oxidation catalysts.⁴

[#]Dedicated to Professor David Cole-Hamilton on the occasion of his retirement and for his outstanding contribution to transition-metal catalysis.

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Despite this motivation, even the pK_a values of bound water molecules to manganese centers are little known, and the resulting hydroxo or oxo complexes can dimerize or oligomerize. Additionally, manganese has several accessible oxidation states. In aqueous solutions under moderately oxidizing conditions, states from +II to +V have been observed, depending on the ligand set. In some cases, oxidation of the metal center can be coupled to deprotonation of bound water due to the marked change in the Lewis acidity of the metal center.

In one particularly informative study, Pecoraro and co-workers described the redox and pK_a behavior of bridging hydroxo/oxo ligands in a dimanganese complex which can have the (III,IV) or (IV,IV) oxidation state.⁵ Our group has measured the pK_a value for water in the $[Mn(terpyridine)(OH_2O)]_2^{4+}$ complex, and its possible relevance to water-oxidizing chemistry. Specifically, pH-dependent electrochemistry data show that the pK_a of water bound to the (IV,IV) oxidation state of the dimer is 1.8.⁶ Other work has examined the properties of mononuclear manganese complexes. Work from Stack and co-workers showed that, for the manganese(III) complex of a neutral pentapyridyl ligand, water is bound and deprotonated reflecting the high Lewis acidity of the metal complex.⁷ Busch and co-workers have also studied pH effects on the activity and protonation state of a manganese(IV) complex bearing a neutral tetradentate ligand that is effective for hydrogen atom abstraction from C-H bonds.⁸

These studies highlight the complexity of working with manganese, as the high-spin d^5 manganese(II) ion can be very labile, introducing complications to studies of speciation in aqueous solution due to ligand exchange or complex decomposition. Thus, most work on manganese is done with chelating multidentate ligands.⁹ Along this line, phthalocyanines are an attractive class of ligands for transition metals due to their high binding affinity. This is a key feature, because they tightly bind manganese even in its labile +II oxidation state. Moreover, the strong donor power of the phthalocyanine ligand results in manganese complexes that are rather easily oxidized to the manganese(III) state, even by dioxygen.¹⁰ Thus, phthalocyanines have found utility in oxidation catalysis and oxygen-reduction chemistry.¹¹

The phthalocyanine ligand itself is very oxidation resistant, and is stable under a diverse array of conditions, having been incorporated into metal-organic frameworks, zeolite materials, electrode materials, and heterogeneous catalysts.¹² Phthalocyanines are also very insoluble, in part due to favorable π - π stacking interactions. However, this insolubility can be reversed by installing sulfonic acid groups ($pK_a < 0$) on the periphery of the ligand. For the tetrasulfonated ligand, the normally water-insoluble species becomes quite soluble in aqueous solutions at all relevant pH values. Thus, metal complexes can be assembled that tightly bind the transition metal of choice, are fully soluble in water, and maintain the appealing spectral properties and stability of the phthalocyanine ligand framework.

We now report studies of the aqueous speciation behavior of manganese(III) tetrasulfonated phthalocyanine, **MnPc'**. Using parallel-mode EPR spectroscopy, we confirm that the oxidation state of the metal center in the phthalocyanine complex is +III. Using global analysis of UV-visible spectra collected over the pH range 1–13 in water, we can track the interconversion of the various water-bound derivatives of the complex, namely the aqua-bound monomer (**1**), the hydroxide-bound monomer (**2**), and the oxo-bridged dimer (**3**) (see Scheme 1). By addition of 2 eq. of pyridine or borate as an exogenous ligand to the water-bound complex, we perturb the aqueous speciation, resulting in stabilization of the hydroxide-bound species over the aqua complex. This additional ligand also results in a rise in the pK_a for formation of the oxo-bridged dimer. pH-dependent electrochemical studies carried out with the complex in potassium nitrate electrolyte show that a ligand-centered

oxidation process occurs at around 1050 mV vs. NHE. Under some conditions, adsorption of the complex onto the electrode surface is observed.

Results

Preparation and characterization of the macrocyclic complex

The manganese(III) complex was obtained by metallation of the tetrasulfonated phthalocyanine ligand with standard methods.¹³

In order to confirm the oxidation state of the manganese center in the compound, we looked to electron paramagnetic resonance (EPR) spectroscopy.¹⁴ Manganese(III) is a non-Kramer's, integer spin system (d^4 , $S = 2$ if high-spin, $S = 0$ if low-spin), and, thus, the parallel mode was required. Parallel-mode spectra of manganese(III) complexes at X-band are relatively rare due to a need for appropriate zero-field splitting parameters. One notable relevant example is the parallel-mode spectrum of manganese(III)-salen (Jacobsen's catalyst) published by Britt *et al.*¹⁵

Following a screen of several typical solvent mixtures, we found that the manganese(III) EPR signal was best observed in either dimethylformamide (DMF) containing ten equivalents of pyridine, or a 2:1 ethylene glycol:water mixture at *ca.* 6 K. In the two cases, either pyridine or water is likely bound to the metal center, which helps overcome the strong π - π interactions in the solid **MnPc'**. The parallel-mode spectrum obtained at X-band in each case is shown below in Figure 1.

The spectra shown above in Figure 1 are consistent with hyperfine coupling to one $I = 5/2$ $^{55}\text{Mn(III)}$. In the case of the spectrum collected in DMF with 10 eq. of pyridine (Figure 1, upper panel) the six-line signal is centered at $g = 8.7$. The average hyperfine splitting is 44 G. For the lower spectrum in 2:1 ethylene glycol:water, the six-line signal is centered at 8.5, with an average hyperfine splitting of 43 G. The two spectra are quite similar, as expected. The differences likely arise from differences in the axial coordination of the phthalocyanine complex: in the first case, pyridine, and in the second, water.

pH-dependent UV-visible spectra

Having assigned the oxidation state, we next turned our attention to characterizing the aqueous speciation of the manganese(III) complex. Upon addition to water, the compound readily dissolves and gives solutions that vary in color from forest green at lower pH values to light blue at higher pH. In Figure 2, the UV-visible spectra of the complexes are shown at various pH values.

The strong band centered at 720 nm and the weaker band at 511 nm have been previously assigned¹⁶ to the monomeric species with $-\text{OH(H)}$ ligands in organic solvents (**1**). Based on analogy with structural data available for analogous manganese(III) porphyrins, the 720 nm band can confidently be assigned to manganese(III) with two bound waters.¹⁷ Additional work from Williamson and Hill¹⁸ showed that addition of a single equivalent of water to the unsubstituted manganese(III) phthalocyanine gave the five-coordinate aqua-bound monomer. They also showed that addition of two equivalents of water gave essentially quantitative yield of the six-coordinate di-aqua manganese(III) complex.¹⁹ We are, thus, confident that the spectra we observe arise in every case from nearly octahedral manganese(III) centers with six ligands. Related crystallographic work (described below) shows many examples of manganese(III) porphyrins with two axial ligands that can include chloride, hydroxide, water, or ethanol.

However, the initial protonation state of the complex in acidic water has been unclear in the past. In a related system, Bruice *et al.* have found a pK_a of 4.4 for deprotonation of water bound to a manganese(III) tetrasulfonated octachloroporphyrin.²⁰ Considering that this highly substituted porphyrin is likely a poorer donor ligand than unsubstituted phthalocyanine, this pK_a is consistent with our assignment of the diaqua species **1** in acidic water.²¹

Upon increasing the pH to around 9, the band at 628 nm increases in intensity, corresponding to formation of what we assign as the hydroxide-bound monomer (**2**) with a second bound water in the *trans* site. Finally, upon increasing the pH to 12, the band at 685 nm becomes dominant, indicating conversion to a new species that has been assigned to the μ -oxo dimer (**3**) with water or hydroxide in the terminal axial positions. Calvin and co-workers saw similar band interconversions upon pH changes in their work with unsubstituted phthalocyanines in mixed methanol:water solutions.²² Calvin's 1968 report described a 630 nm band corresponding to the complex with hydroxide and pyridine bound, which compares well with our spectra.²³ Because dioxygen is a potential reactant, we have verified that our UV-vis spectra do not match those previously obtained for dioxygen adducts obtained by direct treatment of the manganese(II) phthalocyanine with molecular oxygen.²⁴

However, our compound does not display isosbestic behavior, as is apparent in Figure 2. Since multiple species are titrating over a tight pH range, the spectra are complex. Notably, below pH 7, the spectra for the compound in water that is free of additional ligands do not show significant changes. Moreover, above pH 12, there are no significant changes.

However, because the compound has two axial ligands bound, we can change the speciation of the system by changing the ligand in the axial position *trans* to the bound water. We selected two additional ligands for study along this line: pyridine and borate. Selected spectra showing the effect of adding pyridine appear in Figure 3. Clearly, the equilibrium has been shifted from the case in which water occupies both sites, because we noticed no spectral changes in the pH range of 3 to 7 in the previous case. Despite this change in speciation however, the electronic properties of the manganese center are not be perturbed markedly, because the absorbance maxima for each of the three main peaks remained as before: 628, 685, and 720 nm. Addition of borate also causes shifts in the speciation, as observed in the UV-vis spectra, but the wavelengths of the absorbance maxima are again unchanged. This is consistent with Calvin and co-workers' study.²³

Global analysis and calculation of pK_a values

The pH-dependent shift of the maximum absorption band between 600 and 750 nm indicated that a global analysis of UV-visible spectra would provide us with a method for determining the aqueous speciation of the system. Global analysis allows us to fit the complete set of spectral data to a model. In this case, the model that best fits the data is one in which, as the pH is raised, there is a first deprotonation event that forms a hydroxide-bound species **2** from the initially water-bound species **1**, followed by dimerization *via* the hydroxide ligand. Depending on the identity of the axial ligand in the position *trans* to the bound water, the pK values of these pH-dependent equilibria are shifted. The complete set of three speciation diagrams is shown in Figure 4.

In the case of the phthalocyanine complex with only water as a possible ligand, the only major species in solution under acidic and neutral conditions is the aqua-bound monomer **1**. However, above pH 8, there are multiple species in solution. First, the hydroxide-bound monomer **2** appears, followed quickly by the oxo-bridged dimer **3** as the pH is raised further. However, upon addition of two equivalents of pyridine, the first deprotonation of the

monomer **1** is shifted down to near pH 7. Conversely, the appearance of the dimer **3** is shifted to greater than pH 10, versus pH 8 in the case of the water-only speciation. Similar changes are apparent in the speciation of the solution containing two equivalents of borate. In this case, the pK_a of the aqua species **1** is even further perturbed, though, with an apparent value near 4. The formation of the dimer **3** is similar to that of the system with the presence of pyridine.

Next, we moved to fit the data provided by the global analysis to a standard pK_a model and compute the actual pK_a values for the various species. These pK_a values roughly correspond to the crossing points of the dashed traces shown in Figure 4. The dashed traces were obtained by fitting the global analysis concentration vs. pH data to a diprotic model, as has been done previously in our group.²⁵ In such a model, the concentration of the species **2** depends on both the pK_{obs1} of the aqua/hydroxo equilibrium and the pK_{obs2} of the hydroxo-monomer/oxo-dimer equilibrium. This is shown in Equation 1:

$$[2] = \frac{[2]_{max}}{1 + \frac{[H^+]}{K_{obs1}} + \frac{K_{obs2}}{[H^+]}} \quad (\text{Equation 1})$$

The concentration curve for the hydroxo-bound monomer (**2**) could be well fit in each case using Equation 1. The related equation for a monoprotic equilibrium of **1** or **3** could also be used to fit the relevant concentration curves for those species obtained from the global analysis. Thus, for the two pK_{obs} values apparent in each of the three data sets, two values could be obtained and averaged to give the pK_{obs} values reported in Table 1.

Having, thus, characterized the aqueous speciation behavior of our manganese(III) system, we next moved to interrogate its electrochemical properties by cyclic voltammetry. Significant work has been done to characterize the electrochemistry of manganese phthalocyanines. Perhaps most notable was the work done by Lever and co-workers beginning in the late 1950s.²⁶ In this work, they began with the interesting observation that dioxygen could oxidize the manganese(II) compound²⁷ to form the manganese(III) oxo-bridged dimer and release one equivalent of water.^{16,28} Later, it was found that the manganese(II) phthalocyanine, when dissolved in suitable organic solvents showed several redox events, including the II/III couple for oxidation of manganese near 0 V.²⁹ There is an additional higher potential oxidation wave near 870 mV vs. SCE in DMF (approx. 1.1 V vs. NHE), which has been assigned to a phthalocyanine ligand-based oxidation to form the ligand radical species. Scattered reports have assigned this oxidation to formation of higher valent manganese species,³⁰ but this does not appear to be the case. Most reliable data on phthalocyanine electrochemistry describe this second oxidation as purely ligand based.³¹ Additional work on the magnesium and zinc complexes of unsubstituted phthalocyanines supports this assignment, with a reversible oxidation of the ligand usually found between 700 and 800 mV vs. SCE in organic solvents such as dimethylacetamide.³² Finally, the oxo-bridged dimer of unsubstituted manganese(III) phthalocyanine can be oxidized at 350 mV vs. SCE (591 mV vs. NHE), forming what appears to be the mixed valence $Mn_2(III,IV)$ oxo-bridged dimer, although ligand involvement in this oxidation should not be discounted.³³

For our system, cyclic voltammetry of a solution containing **1** at pH 1 is shown in Figure 5. Around 1 V vs. NHE, there is a single oxidation event, which corresponds to formation of the ligand-based radical cation. Raising the pH to 7 of the same solution causes no major changes to the redox process observed at lower pH values. However, increased background water oxidation is observed above 1.6 V (dashed line, Figure 5). We have not so far seen any catalytic production of oxygen by **MnPc'** under any conditions.³⁴ The redox process at 1 V is quasi-reversible, with a peak separation $\Delta E_p = 225$ mV, which implies that there is

slow interfacial electron transfer, a subsequent chemical process which occurs following oxidation, or that there contributions of multiple species to the voltammetry. However, the peak currents do follow the expected behavior of a diffusional process, with peak currents linearly related to the scan rate (see Figure 6). Nonetheless, the waveform does not exactly match the waveform expected of a diffusional, one-electron process. This may be due to adsorption effects.

Previously, it has been found that even water-soluble tetrasulfonated phthalocyanine complexes adsorb readily onto graphite electrodes.³¹ This occurs under various conditions, but often the solutions of macrocycle are made in organic solvents or deposited by allowing aqueous solutions of the macrocycle to stand on the electrode for extended time periods.³⁵ This contrasts with our method, in which a freshly prepared electrode was immediately exposed to a fresh solution of the 10^{-3} mol L⁻¹ manganese(III) phthalocyanine in 0.1 M KNO₃ solution. Our studies suggest adsorption or aggregation of the metal complexes onto the electrode surface does occur. This is illustrated below in Figure 7 with cyclic voltammograms collected on a solution of compound **1**. In the case of the data shown in Figure 7, on the first run of cyclic voltammetry, the expected quasi-reversible feature centered near 1050 mV is not present. Instead, an unusual voltammogram is obtained, showing evidence for an adsorption process with an onset near 1.2 V vs. NHE. On the return pass, a seemingly paired reduction feature is present with a peak current around 1050 mV. The oxidative and reductive features are consistent with an oxidation event coupled with adsorption which occurs upon oxidation, followed by reduction and release of the adsorbed species.³⁶ Related observations come from the well-known behavior of Cu⁺¹/Cu⁰ and Ag⁺¹/Ag⁰ and at a gold electrode, and the appearance of the metal deposition features.³⁷

On a second run several minutes following the first, the appearance of the cyclic voltammogram had changed markedly. As shown in Figure 7, the onsets of the oxidative and reductive currents now both shift to less positive potentials. Moreover, the sharp features characteristic of adsorption or desorption are attenuated. Following another pH change and a further delay of several minutes, the voltammetry converged to the limiting voltammogram shown in Figure 5. (We had originally intended the data shown in Figure 7 as a pH-dependent study similar to that presented in Figure 6; this was the motivation for the changes in pH. Unfortunately, in this set of experiments, there was the conflated signal of adsorption of **1** on the electrode surface. Changes made to the solution pH itself cause no changes to the redox chemistry of **1** as shown in Figure 5.) We ascribe this behavior to aggregated and poorly dissolved phthalocyanine in solution, which over the timescale described here, fully dissolves. When the stirring and dissolution time was insufficient, behavior such as that shown in Figure 7 was observed. Aggregation of phthalocyanines has been observed previously in many systems, although it has not been investigated extensively for the tetrasulfonated phthalocyanines. Notably, this behavior is somewhat irreproducible, suggesting that the adsorption processes are dependent on many factors, including preparation of the electrode surface, concentration of the phthalocyanine, and solution pH.

Discussion

This work characterizes the pK_a transitions of water bound to manganese(III) phthalocyanine complexes. In the case of the solely water-bound system, pK transitions were found around pH values of 9.2 and 10.5. In our model, these transitions correspond to conversion of water-bound **1** to hydroxide-bound **2**, and hydroxide-bound **2** to oxo-dimer **3** (structures given in Figure 1). This is in excellent agreement with previous work done on related porphyrin systems by Harriman and Porter, who found similar pK_a values of 8.6 and 11.6 in the case of the analogous tetrasulfonated porphyrin system.³⁸ Considering the greater

donor power of the porphyrin ligand versus the phthalocyanine ligand,^{21,39} it is unexpected that the first pK_a of the porphyrin system is lower than that of the phthalocyanine, though.

We were surprised to see the observed shifts in pK_a for the systems containing pyridine and borate as ligands to the site *trans* to the bound water. Originally, we expected that the added ligands would serve as better sigma-electron donors, and, thus, increase the pK_a of the bound water. Conversely, we found that the pK_a of the bound water decreased to 7.2 in the case of pyridine as *trans* ligand, and in the case of borate to 4.4. However, analogous crystal structures of water-bound manganese(III) tetraphenylporphyrin give key information to interpret these results. In the structure of the diaqua manganese(III) system characterized by Hill *et al.*,¹⁹ the bond lengths to the two bound waters are both 2.270 Å. However, this contrasts with the case of a water- and triazole-bound manganese(III) tetraphenylporphyrin, in which the bond to the triazole was 2.283 Å, but the bond to bound water was shortened to 2.20 Å.⁴⁰ This corresponds to a shortening of the $Mn^{III}-OH_2$ bond of nearly 0.1 Å, and suggests that the metal center has become more Lewis acidic, which would promote the deprotonation of bound water.

One contribution to this difference may also be the mild π -accepting character of the pyridine ligand, which would be expected to result in increased Lewis acidity of the metal center. Supporting this hypothesis are the data obtained for borate-bound manganese(III), which results in a further shift of the pK_a of bound water to 4.4. Although we found no structural data for borate-bound manganese(III) systems, the empty π orbital of the boron center in the planar borate anion is expected to exert an influence on the manganese center. This would in turn increase the acidity of manganese-bound water in an analogous fashion to the pyridine-bound system.

It is interesting here to note that the pK_a of hexa-aqua manganese(III) is around 0.1.⁴¹ Thus, without additional electron-donating ligands to the metal center, water deprotonates spontaneously when the pH is above zero. Thus, in this case with tetrasulfonated phthalocyanine as a ligand, we see a marked increase to pH 9.2 for the deprotonation of a bound water to the manganese(III) center. This has important repercussions in catalytic applications, where precise tuning of the protonation state of bound water and oxidation state of the metal center is necessary. For example, rate accelerations of up to 40 $\times$ were observed for a manganese(IV) oxo complex versus the corresponding manganese(IV) hydroxo complex.⁸

Along this line, because phthalocyanines are among the most stable and oxidation resistant ligands known, we were interested in the possibility that our complex might function as a water oxidation catalyst. Among the various metals considered for use as catalysts for water oxidation, manganese is perhaps the most attractive due to its high abundance and known role in natural light-driven water oxidation.³ This is an especially tantalizing idea, because mononuclear iridium and ruthenium catalysts have recently been described.^{42,43} However, no mononuclear catalysts for water oxidation with manganese are currently known. In this study, we find no evidence for water oxidation with the mononuclear forms of the manganese(III) tetrasulfonated phthalocyanine. The electrochemistry of the complex does not show any evidence of above-background current, and formation of the ligand-based radical cation likely precludes formation of higher-valent species. Such higher valent species are necessary for water oxidation.^{4,6,42} For the dimeric complex **3**, we have not been able to assign any observed processes to water oxidation, although distinguishing poor water-oxidation catalysis from background oxidation is difficult.

Conclusions

The speciation behavior of a water-soluble manganese(III) tetrasulfonated phthalocyanine complex has been described with complete speciation diagrams prepared by global analysis of pH-dependent UV-visible spectra. Parallel-mode EPR spectra confirm the oxidation state of the metal center as +III. The complete set of pK_a values for interconversion of the aqua monomer (**1**), hydroxo monomer (**2**), and oxo-bridged dimer (**3**) species was obtained by fitting the data to a standard pK_a model. Electrochemical studies reveal a pH-independent quasi-reversible oxidation event for the monomeric species, which results in formation of the ligand-based organic radical cation. These electrochemical results suggest that the monomeric manganese phthalocyanine species are not suitable candidate ligands for water-oxidation catalysts. Future studies examining the Lewis acidity of higher-valent manganese complexes will provide key details on the properties required for effective water-oxidation catalysts.

Experimental

General

The manganese(III) tetrasulfonated phthalocyanine complex was obtained by metallation of the free tetrasulfonated phthalocyanine ligand (a mixture of regioisomers; from Frontier Scientific, Logan, Utah), using a previously reported procedure.¹³ Briefly, the free ligand was refluxed with manganese(II) acetate in absolute ethanol for 18 hours in air, followed by precipitation with a MeOH/H₂O mix to give the manganese(III) tetrasulfonated phthalocyanine, **MnPc'**.

UV-visible spectra were collected with a Cary 50 UV-visible spectrometer. Samples were prepared by setting the pH of an initial solution using either nitric acid or sodium hydroxide, adding 50 μ L of an initially 0.95 mM concentrated solution to 2 mL of the pH-controlled solution, and then recording the pH of the combined solution ($[Mn]_{final} = 23 \mu M$). The spectrum was then collected. Speciation diagrams were generated with the SPECFIT/32 global analysis program (SPECTRUM Software Associates, version 3.0.40 for 32-bit Windows). pH measurements were obtained with a Corning 440 pH meter, and a single-junction pH electrode. pK_a values were computed based on the speciation diagrams using the diprotic model discussed above with OriginLab version 8.5.0.

Electron paramagnetic resonance

EPR spectra were collected at X-band with a Bruker Biospin Elexsys E500 spectrometer, using a dual-mode cavity. Temperature control was achieved with an Oxford ESR900 liquid helium cryostat and an Oxford ITC4 temperature controller. The nominal temperature for the experiments was 5–7 K. The data were recorded with a time constant of 41 ms.

Cyclic Voltammetry

The measurements were made on a Princeton Applied Research model 273 potentiostat/galvanostat using a standard three-electrode configuration. A basal-plane graphite electrode (surface area: 0.09 cm²) was used as the working electrode to minimize background oxidation current. The preparation and treatment of the basal-plane graphite electrode has been described previously.⁴² A platinum wire was used as the counter electrode, and a standard calomel electrode (SCE; Accumet) was used as the reference (SCE vs. NHE: +241 mV). Experiments were generally carried out in unbuffered solutions containing 0.1 M KNO₃ (Johnson Matthey, electronics grade) as the supporting electrolyte. The solution pH was adjusted with dilute potassium hydroxide or nitric acid in some experiments, as noted.

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Figure 1.

X-band parallel-mode EPR spectra of manganese(III) complexes formed from **MnPc'**. Top panel: spectrum collected in DMF with 10 eq. of pyridine added. Lower panel: spectrum collected in 2:1 ethylene glycol:water. Conditions: 5–7 K; [Mn] = 1 mM; microwave frequency was *ca.* 9.374 GHz for the experiments. The spectra confirm that the oxidation state of the manganese is +III.

Figure 2.

UV-visible spectra of aqueous solutions of MnPc' at the indicated pH values as marked in legend. $[\text{Mn}]_{\text{total}}$ is 10^{-6} M. Assignment of the species, as detailed in the text, is included above the major peaks.

Figure 3. UV-visible spectra of the manganese(III) phthalocyanine in water at the indicated pH values with 2 eq. of added pyridine. $[\text{Mn}]_{\text{total}}$ is 10^{-6} M, and $[\text{pyr}]/[\text{Mn}]_{\text{total}} = 2$.

Figure 4.

pH-dependent aqueous speciation diagrams for manganese(III) tetrasulfonated phthalocyanine containing no additional ligand (upper panel), 2 equivalents of pyridine (middle panel), or 2 equivalents of borate (lower panel). Black points and dashed line: aqua-bound monomer **1**; green points and dashed line: hydroxide-monomer **2**; blue points and dashed trace: oxo-bridged dimer **3**. Data were fit as described in main text and Experimental Section. Dashed lines represent fits of the speciation data to the standard pK_a model described in the text.

Figure 5. Aqueous cyclic voltammetry data collected for **1**. Conditions: 10^{-3} M **1** in 0.1 M KNO₃ at pH values as indicated in the inset; scan rate: 100 mV/s; working electrode: basal-plane graphite.

Figure 6.

Dependence of the aqueous cyclic voltammetry of **1** on scan rate. Left panel: voltammograms for various scan rates, as indicated in the inset. Right panel: dependence of peak current on the square root of the scan rate. Data collected with a basal-plane graphite working electrode in a 10^{-3} -M solution of **1** at pH 6.5. Based on the linear dependence, the redox process is diffusional in nature, rather than arising from a surface-bound species or film.

Figure 7.

Sequential cyclic voltammograms of an aqueous solution containing **1**. Approximately three minutes elapsed between each experiment, showing deaggregation of the compound from the electrode surface. Conditions: 1 mM **1** in 0.1 M KNO₃; scan rate: 20 mV/s; working electrode: basal-plane graphite.

Scheme 1.

Structure of the **MnPc'** skeleton (left) and the compounds discussed in this work. On the right, the pH-dependent speciation relationships of the aqua-bound monomer **1**, hydroxide-bound monomer **2**, and oxo-bridged dimer **3** are shown. In this study, L = water, pyridine, or borate (i.e., H_2BO_3^-). Manganese is in the +III oxidation state in all structures.

Table 1

Summary of pK_{a} data obtained from global analysis and fitting. Given errors come from averaging the individual errors of the mono- and di-protic fits as described in the main text.

6 th ligand	pK_{obs1} (1,2)	pK_{obs2} (2,3)
water	9.16 ± 0.04	10.53 ± 0.07
pyridine	7.20 ± 0.05	11.59 ± 0.23
borate	4.42 ± 0.02	12.04 ± 0.20