which create an effective plane of symmetry on the NMR time scale thereby making both sides of the benzene ring equivalent. By analogy the *trihapto*-7-azabenzyl derivatives IV are expected to exhibit similar fluxional properties. If the coalescence temperatures of the *trihapto*-7-azabenzyl derivatives IV are lower than that of the *trihapto*-benzyl derivative V, such fluxional properties could persist even below room temperature thereby making both sides of the benzene ring equivalent even at the lowest temperatures at which NMR spectra were taken. The broadening of the ortho carbon resonances in $[(CH_3)_2CNNC_6H_5]M(CO)_2C_5H_5$ (M = Mo and W) observed at −28 °C could arise from incipient freezing out of the fixed structure IV. The ortho carbon resonance in a fluxional compound of structure IV should broaden before the meta carbon resonance on cooling since in a frozen structure IV the bonding of the metal to an ortho carbon but to neither meta carbon would make the chemical shifts of the two ortho carbons more different than those of the two meta carbons. In our opinion the ambiguity between the *N,N-dihapto* structures III and the *trihapto*-7-azabenzyl structures IV for the complexes $[(CH_3)_2CNNC_6H_5]M(CO)_2C_5H_5$ (M = Mo and W) will only be satisfactorily resolved when x-ray structural data become available.

One of the several methods that we have used to prepare the ketoximato complexes[1] $RR'CNOM(CO)_2C_5H_5$ (I, M = Mo and W) uses the reaction of $C_5H_5M(CO)_3Cl$ (M = Mo and W) with excess ketoxime in pyridine solution at ~70 °C. An analogous reaction of $C_5H_5Mo(CO)_3Cl$ with excess acetone phenylhydrazone failed to give any $[(CH_3)_2CNNC_6H_5]Mo(CO)_2C_5H_5$ but instead gave the pyridine complex[13] $C_5H_5Mo(CO)_2(NC_5H_5)Cl$. This suggests that the $(CH_3)_2CNNC_6H_5$ ligand forms weaker chemical bonds with transition metals than the RR′CNO ligands in I.

The "pyridine method", although it fails for the preparation of $[(CH_3)_2CNNC_6H_5]Mo(CO)_2C_5H_5$ from acetone phenylhydrazone, provides an alternative to the previously reported[6] preparation of the 1,3-diphenyltriazenido complex $(C_6H_5)_2N_3Mo(CO)_2C_5H_5$ (II, M = Mo). Similarly, the ultraviolet irradiation of $C_5H_5W(CO)_3Cl$ with excess 1,3-diphenyltriazene in pyridine solution gives the previously unreported $(C_6H_5)_2N_3W(CO)_2C_5H_5$ (II, M = W). The carbon-13 NMR spectra of the 1,3-diphenyltriazenido complexes $(C_6H_5)_2N_3M(CO)_2C_5H_5$ (II, M = Mo and W) (Table I) indicate equivalence of the two metal carbonyl groups in accord with the symmetry of the 1,3-diphenyltriazenido ligand, at least on an NMR time scale.

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Registry No. II (M = Mo), 53092-57-2; II (M = W), 63641-12-3; III (M = Mo), 63641-13-4; III (M = W), 63641-14-5; IV (M = Mo), 63641-15-6; IV (M = W), 63641-16-7; $C_5H_5Mo(CO)_3Cl$, 12128-23-3; $C_5H_5W(CO)_3Cl$, 12128-24-4; ^{13}C, 14762-74-4.

References and Notes

(1) For part 10 of this series see: R. B. King and K. N. Chen, *Inorg. Chem.*, **16**, 1164 (1977).
(2) Postdoctoral research associate, 1975–1977.
(3) R. B. King and W. M. Douglas, *Inorg. Chem.*, **13**, 1339 (1974).
(4) G. P. Khare and R. J. Doedens, paper presented at the 170th National Meeting of the American Chemical Society, Chicago, Ill., Aug 1975; Abstracts, No. INOR 67.
(5) G. P. Khare and R. J. Doedens, *Inorg. Chem.*, **16**, 907 (1977).
(6) R. B. King and K. C. Nainan, *Inorg. Chem.*, **14**, 271 (1975).
(7) O. A. Gansow, A. R. Burke, and W. D. Vernon, *J. Am. Chem. Soc.*, **94**, 2550 (1972).
(8) R. O'Connor, *J. Org. Chem.*, **26**, 4375 (1961).
(9) T. S. Piper and G. Wilkinson, *J. Inorg. Nucl. Chem.*, **3**, 104 (1956).
(10) J. B. Stothers, "Carbon-13 N.M.R. Spectroscopy", Academic Press, New York, N.Y., 1972, Table 5.58 on p 197.
(11) R. B. King and A. Fronzaglia, *J. Am. Chem. Soc.*, **88**, 709 (1966).
(12) F. A. Cotton, *Acc. Chem. Res.*, **1**, 257 (1968).
(13) R. B. King and K. N. Chen, unpublished results.

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Thin-Layer Spectroelectrochemical Study of Tetrakis(4-*N*-methylpyridyl)porphinecobalt(III)

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Reports have recently appeared dealing with the reactions of the water-soluble metalloporphyrin tetrakis(4-*N*-methylpyridyl)porphinecobalt(III) ($Co^{III}TMpyP$) with a variety of reducing agents.[3-5] These studies led to a determination of the absorbance maximum in the Soret region for the diaquo form of $Co^{II}TMpyP$ as 429 nm and an estimate of $+0.3 \le E^{\circ\prime} \le +0.8$ V vs. NHE for $CoP(H_2O)_2^{5+} + e^- \rightarrow CoP(H_2O)_2^{4+}$. In order to determine more precisely these important parameters, we have applied the optically transparent thin-layer electrode (OTTLE) technique to this cobalt porphyrin system.[6]

Experimental Section

$(CoTMpyP)I_5$ was prepared, purified, and converted to the chloride form by methods described elsewhere.[7,8] Solutions of the porphyrin were prepared by dissolving the solid in 0.5 M $NaNO_3$/0.01 M HNO_3 in doubly distilled water. The metalloporphyrin concentration was 2.04×10^{-4} M, somewhat beyond the concentration range previously investigated for adherence to Beer's law behavior.[7] The spectral properties of these solutions lead us to conclude that monomeric $CoP(H_2O)_2$ is the only chromophore present in appreciable amounts.

Cyclic voltammetry and spectropotentiostatic experiments were performed with a potentiostat of conventional operational amplifier design, an X-Y recorder (Houston Omnigraphic Model 2000), and a digital voltmeter (Fluke Model 8000A). A Cary 14 spectrophotometer, with cell compartment modified to permit introduction of electrical leads, was used for the spectropotentiostatic experiment. The spectroelectrochemical cell was an OTTLE of the minigrid-microscope slide design.[6,9,10] The cell was constructed by sandwiching a gold minigrid electrode (500 wires/in., 60% transmittance; Buckbee-Mears Co., St. Paul, Minn.) between two glass microscope slides which were separated by Teflon tape spacers along the edges. Calibration of this OTTLE by controlled potential coulometry of a standard potassium ferricyanide solution[9] gave an electrochemical cell volume of 43 μL and an optical path of 0.022 cm. The reference and auxiliary electrodes were a saturated sodium chloride calomel electrode (H cell) and a platinum wire, respectively. The potential of the reference electrode was found to be within 2 mV of the potential of the conventional SCE (saturated with KCl).

In a typical experiment the OTTLE was first positioned in the Cary 14 cell compartment which was then purged with argon and the top sealed with clear polyethylene. The sample was deoxygenated by argon bubbling and transferred to the electrochemical cell by a previously reported method.[9] Electrochemical and spectroelectrochemical measurements were then performed while continuously flushing the cell compartment with argon.

Results and Discussion

Thin-layer cyclic voltammograms of $(Co^{III}TMpyP)^{5+}$ and of the supporting electrolyte are shown in Figure 1. A deoxygenated solution of 0.5 M $NaNO_3$/0.01 M HNO_3 gives a wide potential window extending from +0.900 to −0.450 V vs. SCE on the gold minigrid OTTLE as shown by the dotted line. The voltammogram of $(Co^{III}TMpyP)^{5+}$ exhibited well-defined reduction and oxidation waves for the $Co^{III} \rightleftarrows Co^{II}$ couple. A scan, initiated at +0.500 V vs. SCE in the negative direction, caused reduction of Co(III) to Co(II) with a cathodic peak potential (E_{pc}) of +0.135 V. Scan reversal at 0 V vs. SCE resulted in oxidation of Co(II) to Co(III) with an anodic peak potential (E_{pa}) of +0.210 V vs. SCE. Three consecutive cycles on the same solution gave identical voltammograms, indicating that the cobalt oxidation state can be reversibly cycled between III and II in the thin-layer cell. An

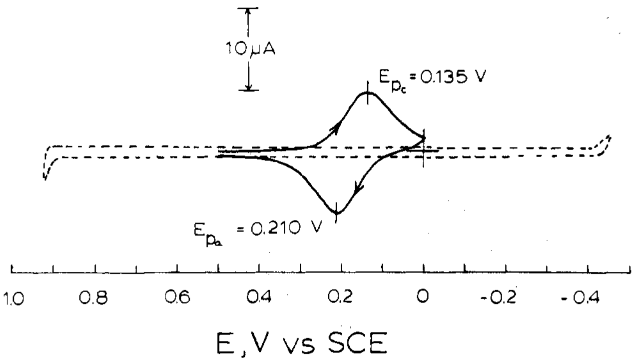

Figure 1. Cyclic voltammogram of 2.04×10^{-4} M $(CoTMpyP)Cl_5$ in 0.5 M $NaNO_3$/0.01 M HNO_3. Scan rate 2.0 mV s^{-1}, initial potential +0.500 V vs. SCE. Dotted line is potential window of the supporting electrolyte solution.

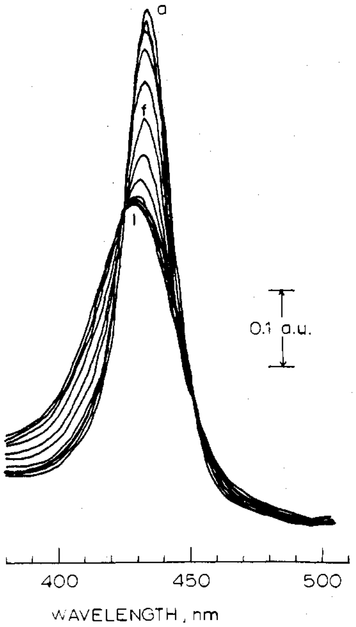

Figure 2. Spectra of 2.04×10^{-4} M $(CoTMpyP)Cl_5$ from spectropotentiostatic experiment. Co(III) → Co(II) process. $E_{applied}$: (a) open circuit, (b) +0.250, (c) +0.230, (d) +0.210, (e) +0.190, (f) +0.170, (g) +0.150, (h) +0.130, (i) +0.100, (j) +0.075, (k) +0.025, (l) -0.050 V vs. SCE.

$E^{\circ\prime}$ value of +0.173 V vs. SCE (+0.415 V vs. NHE) was calculated by averaging the cathodic and anodic peak potentials.

The thin-layer aspect of the OTTLE enables the ratio of the concentrations of oxidized and reduced forms in the cell to be controlled by the potential applied to the transparent minigrid. When the controlling potential is changed, the ratio [O]/[R] adjusts by electrolysis at the minigrid to the ratio demanded by the Nernst equation

$$E_{applied} = E^{\circ\prime} + \frac{RT}{nF} \log \frac{[O]}{[R]} \qquad (1)$$

Since cell thicknesses are typically only 0.02 cm, equilibrium is achieved within 2–3 min. The optical transparency of the gold minigrid enables spectra to be recorded through the OTTLE for each potential applied to the cell. Figure 2 shows spectra in the Soret region for the reduction of $(Co^{III}TMpyP)^{5+}$ by a series of increasingly negative applied potentials which incrementally convert Co(III) to Co(II). The 434-nm peak of Co(III) diminishes and a peak at 429 nm characteristic of the Co(II) species[3-5] appears. Incremental oxidation of Co(II) to Co(III) by moving the potential positively returns the spectrum to its original appearance, once again indicating the reversibility of the III, II conversion. An absorbance vs. applied potential plot, Figure 3, summarizes the spectral change at 434 nm for the Co(III) ⇄ Co(II) redox couple. Nernst plots of $E_{applied}$ vs. log [O]/[R] at λ 434 nm for both the reduction and oxidation processes are shown in Figure 4. The value of [O]/[R] for each potential is calculated from the spectra by the equation

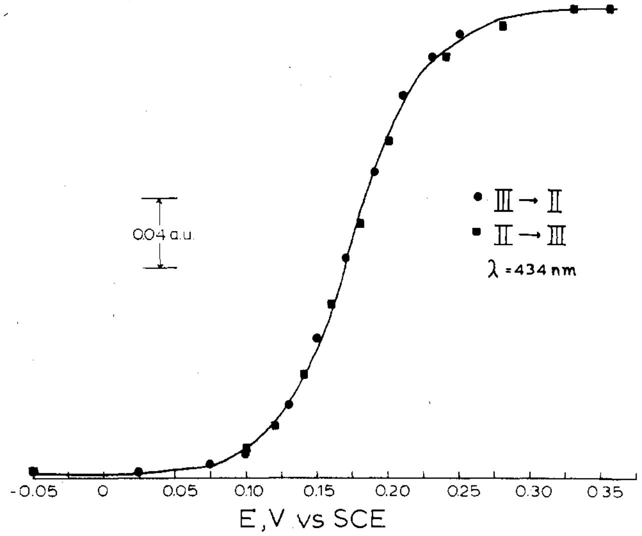

Figure 3. Absorbance vs. potential plot for $(CoTMpyP)Cl_5$, Co(III) → Co(II) and Co(II) → Co(III) processes, from spectra of Figure 2.

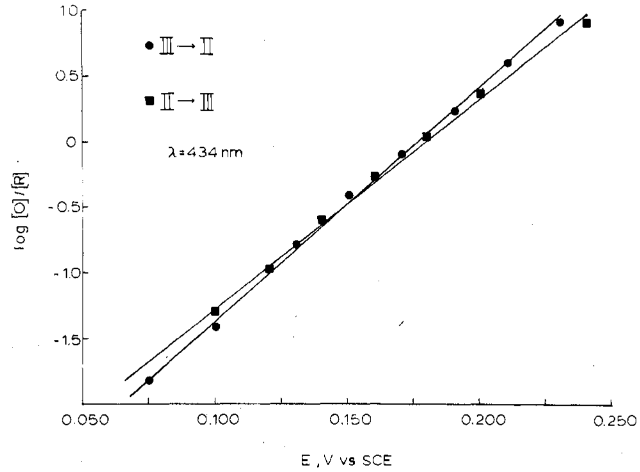

Figure 4. Plot of $E_{applied}$ vs. log [O]/[R] for $(CoTMpyP)Cl_5$, Co(III) → Co(II) and Co(II) → Co(III) processes, from plot in Figure 3.

$$[O]/[R] = \frac{A_2 - A_1}{A_3 - A_2}$$

where A_3 is the absorbance of the completely oxidized form, A_1 is the absorbance of the completely reduced form, and A_2 are the absorbances for the mixtures of oxidized and reduced forms. For the III → II process, the least-squares line has a slope of 55.4 mV, resulting in $n = 1.07$; the intercept (log [O]/[R] = 0) yields $E^{\circ\prime} = +0.175$ V vs. SCE (+0.417 V vs. NHE). For the oxidation process the slope is 62.0 mV, corresponding to $n = 0.955$; an $E^{\circ\prime}$ value of +0.178 V vs. SCE (+0.420 V vs. NHE) is calculated from the intercept. Correlation coefficients for the two lines are 0.999 and 0.997, respectively.

Thus the data from the present electrochemical study are consistent with the results of redox reactions of $Co^{III}TMpyP$ with chromium(II),[3] sodium dithionite,[4] and hexaammineruthenium(II)[5] and permit a calculation of the self-exchange rate constant for this cobalt porphyrin. The electron-transfer mechanism for the reaction of $\mathrm{Co^{III}TMpyP}$ with $\mathrm{Ru(NH_3)_6^{2+}}$ is certainly of the outer-sphere type and the Marcus theory[11] can be applied to this system. According to this theory, for an outer-sphere electron-transfer reaction for which $\Delta G°$ is not too negative

$$k_{12} = (k_{11}k_{22}K_{12})^{1/2}$$

where k_{12} and K_{12} are the rate and equilibrium constants, respectively, for the electron transfer reaction and k_{11} and k_{22} are the appropriate self-exchange rate constants.

The equilibrium constant K_{12} for the reaction

$$\mathrm{CoP(H_2O)_2{}^{5+} + Ru(NH_3)_6{}^{2+} \rightleftarrows CoP(H_2O)_2{}^{4+} + Ru(NH_3)_6{}^{3+}}$$

is calculated from the present results and $E°' = -0.066$ V for $\mathrm{Ru(NH_3)_6^{2+} \rightleftarrows e^- + Ru(NH_3)_6^{3+}}$ at $\mu = 0.5$ M.[12] This calculation leads to $K_{12} = 8.9 \times 10^5$. Since $k_{12} = 1.2 \times 10^5$ $\mathrm{M^{-1}\,s^{-1}}$[5] and $k_{11} = 8.2 \times 10^2$ $\mathrm{M^{-1}\,s^{-1}}$ for $\mathrm{Ru(NH_3)_6^{2+/3+}}$[13] we obtain that $k_{22} = 20$ $\mathrm{M^{-1}\,s^{-1}}$ for $\mathrm{CoTMpyP^{4+/5+}}$.

Electron transfer to metalloporphyrins can occur through axial ligands or through the porphyrin ring system with the preferred pathway quite likely dependent upon the nature of the axial ligands as well as on the metalloporphyrin and reducing agent.[3] Sutin has suggested that for low-spin iron porphyrins in which electron transfer proceeds via the porphyrin π system, the self-exchange rate may be approximated by a value derived from the $\mathrm{Fe(phen)_3^{2+/3+}}$ system.[14] It is thus implicitly assumed that three 1,10-phenanthroline molecules with their highly delocalized electron densities provide a ligand environment sufficiently similar to the porphyrin ligand that the self-exchange rates are comparable provided that the spin state of the metal is the same in both complexes. It has been shown, for example, that the $\mathrm{Fe(phen)_3^{2+/3+}}$ estimate is not applicable to high-spin iron porphyrins.[15]

A direct comparison of the self-exchange rates of $\mathrm{CoTMpyP^{4+/5+}}$ and $\mathrm{Co(phen)_3^{2+/3+}}$ can be attempted with the knowledge that the oxidized form of both complexes involves low-spin cobalt[7,16] although the spin state of the aquo complex of $\mathrm{CoTMpyP^{4+}}$ is less certain. The self-exchange rate constant for $\mathrm{Co(phen)_3^{2+/3+}}$ is 21 $\mathrm{M^{-1}\,s^{-1}}$[17,18] while the value for $\mathrm{CoTMpyP^{4+/5+}}$ is 20 $\mathrm{M^{-1}\,s^{-1}}$. The close agreement of the rates substantiates the Sutin hypothesis and suggests that, for the reduction of the diaquo form of $\mathrm{Co^{III}TMpyP}$ by $\mathrm{Ru(NH_3)_6^{2+}}$, electron transfer involves the π system of the porphyrin ligand.

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References and Notes

(1) University of Cincinnati.
(2) Ithaca College.
(3) R. F. Pasternack and N. Sutin, *Inorg. Chem.*, **13**, 1956 (1974).
(4) R. F. Pasternack, M. A. Cobb, and N. Sutin, *Inorg. Chem.*, **14**, 866 (1975).
(5) R. F. Pasternack, *Inorg. Chem.*, **15**, 643 (1976).
(6) (a) R. W. Murray, W. R. Heineman, and G. W. O'Dom, *Anal. Chem.*, **39**, 1666 (1967); (b) W. R. Heineman, B. J. Norris, and J. F. Goelz, *ibid.*, **47**, 79 (1975).
(7) (a) R. F. Pasternack and M. A. Cobb, *J. Inorg. Nucl. Chem.*, **35**, 4327 (1973); (b) *Biochem. Biophys. Res. Commun.*, **51**, 507 (1973).
(8) R. F. Pasternack, E. G. Spiro, and M. Teach, *J. Inorg. Nucl. Chem.*, **36**, 599 (1974).
(9) D. F. Rohrbach, E. Deutsch, and W. R. Heineman, "Characterization of Solutes in Non-Aqueous Solvents", G. Mamantov, Ed., Plenum Press, to be published.
(10) T. P. DeAngelis and W. R. Heineman, *J. Chem. Educ.*, **53**, 594 (1976).
(11) R. A. Marcus, *Annu. Rev. Phys. Chem.*, **15**, 155 (1964), and references cited therein.
(12) D. K. Lavallee, C. Lavallee, J. C. Sullivan, and E. Deutsch, *Inorg. Chem.*, **12**, 570 (1973).
(13) T. J. Meyer and H. Taube, *Inorg. Chem.*, **7**, 2369 (1968).
(14) N. Sutin, *Chem. Br.*, **8**, 148 (1972).
(15) R. F. Pasternack and E. G. Spiro, in preparation.
(16) T. J. Przystas and N. Sutin, *J. Am. Chem. Soc.*, **95**, 5545 (1973).
(17) J. V. McArdle, H. B. Gray, C. Creutz, and N. Sutin, *J. Am. Chem. Soc.*, **96**, 5737 (1974).
(18) B. R. Baker, F. Basolo, and H. M. Neumann, *J. Phys. Chem.*, **63**, 371 (1959).

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Water-Exchange Studies on Aqueous Manganese(II)- and Cobalt(II)-*o*-Phenylenediaminetetraacetate Complexes

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Previous oxygen-17 NMR studies[1] on $\mathrm{Mn^{II}}$–EDTA complexes have shown the presence of a seven-coordinate complex in aqueous solution. Lingafelter and Rose[2] and co-workers have recently done x-ray work on the Co(II) complexes of EDTA and *o*-phenylenediaminetetraacetate (PhDTA) finding a significant difference in structure, the EDTA complex being roughly octahedral, while PhDTA produces a more trigonal-prismatic structure. We thought it of interest to apply the oxygen-17 NMR techniques[3] to this ligand.

Experimental Section

The pure ligand was kindly prepared and supplied by Dr. E. F. K. McCandlish via Dr. Norman J. Rose. A cobalt(II) complex solution was prepared in 1% $\mathrm{^{17}OH_2}$; [Co(II)] = 0.0595 *M*, [PhDTA] = 0.0655 *M*, pH 6. The solution did not appear to undergo oxidation in air (Rose et al. found none also). The Mn(II) complex did appear air sensitive and was therefore prepared under a nitrogen atmosphere, giving a light rosy pink color. The composition was [Mn(II)] = 0.0493 M, [PhDTA] = 0.0543 M, pH 6.3. For these studies 1% $\mathrm{^{17}OH_2}$ was used as the blank or reference. The NMR techniques, equipment, and data treatment are discussed previously.[1]

Results

For the Co(II) solution at 30 and 80 °C only small line broadening and shift were seen (close to detection limit). For one $\mathrm{H_2O/Co(II)}$ we expected ca. 150 Hz shift (paramagnetic) and found ca. 18 Hz.

For Mn(II) large line broadenings and shifts were observed from 25 to 84 °C (see Table I). The shift data showed the water exchange to be in a fast-exchange limit. Treatment of the data in the usual way gave the following parameters: k_1(25 °C) (rate constant for a single $\mathrm{H_2O}$ exchange) = 3.5×10^8 $\mathrm{s^{-1}}$, $\Delta H^{\ddagger} = 8.1$ kcal $\mathrm{mol^{-1}}$, $\Delta S^{\ddagger} = 7.6$ cal $\mathrm{mol^{-1}\,deg^{-1}}$, and A/h (scalar coupling constant) = 6.04×10^6 Hz.

Discussion

The results on the Co(II) complex are consistent with those of Rose et al.,[2] namely, that the complex is predominantly six-coordinate at pH 6–7, without bound water.

A comparison of the $\mathrm{Mn^{II}EDTA}$ and $\mathrm{Mn^{II}PhDTA}$ results is of interest. The analogous parameters for $\mathrm{Mn^{II}EDTA}$ are k_1(25 °C) = 4.4×10^8 $\mathrm{s^{-1}}$, $\Delta H^{\ddagger} = 7.7$ kcal $\mathrm{mol^{-1}}$, $\Delta S^{\ddagger} = 6.8$ cal $\mathrm{mol^{-1}\,deg^{-1}}$, and $A/h = 6.04 \times 10^6$ Hz. These are remarkably similar to the PhDTA values and suggest to us that the present Mn(II) species is $\mathrm{Mn(PhDTA)(H_2O)^{2-}}$ (seven-coordinate). We do not have direct evidence that the ligand is completely ligated in this case so that we can only be sure that there is one $\mathrm{H_2O}$ per Mn and the total coordination number is simply speculative. The "counting" of bound water is done assuming that A/h is constant (per $\mathrm{H_2O}$) for Mn(II) complexes regardless of the presence of other ligands and here