Electrochemistry and Spectroscopy of Sulfate Complexes of (Tetraphenylporphyrinato)manganese

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The electrochemical and spectroscopic properties of $[Mn_2(tpp)_2(SO_4)]$ (H_2tpp = tetraphenylporphyrin = 5,10,15,20-tetraphenyl-21*H*,23*H*-porphine) were studied to characterize the stability of this compound as a function of solvent, redox state, and sulfate concentration. In non-coordinating solvents such as 1,2-dichloroethane, the dimer was stable, and two cyclic voltammetric waves were observed in the region for Mn^{III} reduction. These waves correspond to reduction of the dimer to $[Mn^{II}(tpp)]$ and $[Mn^{III}(tpp)(OSO_3)]^-$, and reduction of $[Mn^{III}(tpp)(OSO_3)]^-$ to $[Mn^{II}(tpp)(OSO_3)]^{2-}$, respectively. In the coordinating solvent DMSO, $[Mn_2(tpp)_2(SO_4)]$ was unstable and dissociated to form $[Mn^{III}(tpp)(DMSO)_2]^+$. A single voltammetric wave was observed for Mn^{III} reduction in this solvent, corresponding to formation of $[Mn^{II}(tpp)(DMSO)]$. In non-coordinating solvent systems, addition of sulfate (as the bis(triphenylphosphoranylidene)ammonium (PPN^+) salt) resulted in dimer dissociation, yielding $[Mn^{III}(tpp)(OSO_3)]^-$. Reduction of this monomer produced $[Mn^{II}(tpp)(OSO_3)]^{2-}$. In DMSO, addition of SO_4^{2-} led to displacement of solvent molecules forming $[Mn^{III}(tpp)(OSO_3)]^-$. Reduction of this species in DMSO led to $[Mn^{II}(tpp)(DMSO)]$.

Introduction. – The chemistry of porphyrinatometals has been of considerable interest during the past 25 years due to the importance of these compounds in a number of biological processes [1]. Synthetic porphyrinatometals have often been used as models for the chemistry occurring within natural systems that contain metalloproteins. As a result, porphyrinatometals containing a wide variety of anionic axial ligands have been synthesized and characterized to date. One such ligand, the sulfate ion (SO_4^{2-}), has been shown to react with (tetraphenylporphyrinato)manganese(III) to form a porphyrinatomanganese(III) dimer, $[Mn_2(tpp)_2(SO_4)]$ (H_2tpp = tetraphenylporphyrin = 5,10,15,20-tetraphenyl-21*H*,23*H*-porphine), which is bridged by the sulfato ligand [2]. This complex has been characterized by spectroscopic methods (UV/VIS and IR spectroscopy) and X-ray crystallography, and its photochemical reactions have been examined [2]. Structurally, this dimeric species is similar to that of the analogous iron derivative, $[Fe_2(tpp)_2(SO_4)]$ [3][4]. For both $[Mn_2(tpp)_2(SO_4)]$ and $[Fe_2(tpp)_2(SO_4)]$, the sulfato ligand bridges the two metal atoms in a monodentate fashion [2–4]; this coordination was confirmed by both the X-ray structures and IR spectra. In addition, the VIS spectrum of $[Mn_2(tpp)_2(SO_4)]$ dimer showed no unusual features compared to other porphyrinatomanganese complexes, indicating only a weak interaction between the two porphyrin moieties [2].

Although the structure and spectroscopic properties of $[Mn_2(tpp)_2(SO_4)]$ have been characterized, the electrochemical properties of this substance have not previously been examined. In addition, the association/dissociation equilibria of this complex in coordinating solvents and in the presence of excess ligand have not been investigated. In this report, we present a study of the electrochemical and spectroscopic properties of the sulfato-bridged dimer $[Mn_2(tpp)_2(SO_4)]$. The major aim was to characterize the dimer's equilibria, and to understand its stability as a function of solvent strength, redox state, and sulfate concentration. The iron analog, $[Fe_2(tpp)_2(SO_4)]$, has been shown to be stable only in non-coordinating solvents [5]. In coordinating solvents and in the presence of excess sulfate, the iron derivative dissociates [5] [6]. The behavior of $[Mn_2(tpp)_2SO_4]$ will, therefore, be compared to that of the corresponding iron derivative under similar conditions.

Experimental Part

Materials. Chloro[5,10,15,20-tetraphenyl-21*H*,23*H*-porphinato(2 –)-κN^{21},κN^{22},κN^{23},κN^{24}]manganese ([Mn(tpp)(Cl)]), bis(triphenylphosphoranylidene)ammonium chloride ((PPN)(Cl), $CHCl_3$, CH_2Cl_2, benzene, acetone, and tetrabutylammonium borohydride ($(Bu_4N)BH_4$) were purchased from *Aldrich Chemical Co.* $ClCH_2CH_2Cl$, dimethylsulfoxide (DMSO), dimethylformamide (DMF), Na_2SO_4, and $(Bu_4N)ClO_4$ were purchased from *Fisher Scientific*. Acetone was obtained from *Curtin Matheson Scientific*. All solvents were of the highest purity available and were used without further purification. Small amounts of $(Bu_4N)ClO_4$ were dried *in vacuo* at 90° for 4–6 h prior to use and stored in a dessicator. *Care must be exercised during the heating and handling of* TBAP *($(Bu_4N)ClO_4$)* since all perchlorates have the potential to decompose explosively.

The {μ-[sulfato(2 –)-κO:$\kappa O'$]bis[5,10,15,20-tetraphenyl-21*H*,23*H*-porphinato(2 –)-κN^{21},κN^{22},κN^{23},κN^{24}]dimanganese ($[Mn_2(tpp)_2SO_4)]$, was synthesized from [Mn(tpp)Cl] and Ag_2SO_4 in a biphasic CH_2Cl_2/H_2O system [2]. The product was characterized by comparison of the UV/VIS and IR spectra with the reported spectra.

Bis(triphenylphosphoranylidene)ammonium sulfate ($(PPN)_2SO_4$) was prepared by the metathesis reaction of (PPN)Cl and excess Na_2SO_4 in H_2O [7]. The product, recrystallized from acetone/Et_2O, exhibited distinctive IR bands corresponding closely to those of the free sulfate ion [8].

Cyclic Voltammetry. CHI-Instruments 6000 voltammetric analyzer; scan rates from 100 mV/s to 300 mV/s. Half-wave potentials ($E_{1/2}$) were measured as the average of the cathodic and anodic peak potentials [9]. A three-electrode *Bioanalytical Systems* (*BAS*) cell was used for all experiments, consisting of a *BAS* Pt-disk (1.6 mm) electrode, a *BAS* Pt-wire auxiliary electrode, and a *BAS* Ag/$AgNO_3$ (0.1M in MeCN) reference electrode (SRE). Deoxygenation of all solns. was accomplished by passing a gentle, constant stream of prepurified N_2 through the soln. for 15 min and maintaining a blanket of the inert gas over the soln. during the experiment. In the case of CH_2Cl_2 and $ClCH_2CH_2Cl$, the N_2 was saturated with the solvent prior to entering the electrochemical cell to minimize evaporation. Sulfate-ion concentrations were varied by adding appropriate amounts of $(PPN)_2SO_4$ directly to the test solns., followed by several minutes of additional deoxygenation.

Spectroelectrochemical Experiments. They were performed with an optically transparent thin-layer electrode (OTTLE). The cell design has been described previously [10]. This cell had a Pt-mesh working electrode and an optical path length of 0.2 mm. The reference was a *BAS* Ag/$AgNO_3$ (0.1M in MeCN) reference electrode (SRE). Test solns. were deoxygenated for 30 min. The VIS-spectral data were obtained following controlled potential electrolysis at the desired potentials. Potential control was maintained using a *BAS CV-27* voltammograph.

VIS Spectra. Perkin-Elmer Lambda-3 UV/VIS spectrophotometer connected to an *IBM* computer (also for spectroelectrochemical experiments). Besides the OTTLE cell, a 1-mm quartz cell was used to obtain the *Soret* region, and a 1-cm quartz cell was used to measure the spectral data in the long wavelength (500–800 nm) region.

IR Spectra. Analect RFX-30-FT IR spectrometer; solid samples as KBr pellets, soln. samples in a 0.1-mm NaCl liquid cell (*Wilmad Glass Co.*).

Chemical Reduction of [Mn(tpp)Cl]. Addition of an excess of the reducing agent $(Bu_4N)BH_4$ to either a CH_2Cl_2 or a DMSO soln. of [Mn(tpp)Cl] while under a blanket of N_2 maintained in a glove bag gave the soln. for VIS analysis. The UV/VIS cells were sealed tightly with rubber septa to exclude O_2 prior to removing the solns. from the N_2 atmosphere.

Results. – *Spectroscopy.* The VIS spectrum of $[Mn_2(tpp)_2(SO_4)]$ in CH_2Cl_2 has been reported previously [2]. The spectrum for the sulfato-bridged dimer is similar to those reported for high-spin porphyrinatomanganese(III) complexes [11] [12]. VIS-Spectral data for $[\mathrm{Mn_2(tpp)_2(SO_4)}]$ in several different solvents were recorded and are listed in *Table 1*. The VIS spectra of [Mn(tpp)Cl] were also determined for comparison. The spectrum of the sulfato-bridged dimer in the non-coordinating solvent $\mathrm{CHCl_3}$ between 400 and 750 nm exhibited a *Soret* band with an absorbance maximum at 466 nm, $\mathrm{Q_a}$ and $\mathrm{Q_b}$ band maxima at 577 and 612 nm, respectively, and an additional broad band at 530 nm (*Fig. 1*), in close agreement with the reported spectrum [2]. By comparison, the spectrum of [Mn(tpp)Cl] in $\mathrm{CHCl_3}$ exhibited absorbances similar to the literature values [13], with a *Soret* band at 479 nm and other VIS bands at 528, 583, and 618 nm. The spectral features observed for both $[\mathrm{Mn_2(tpp)_2(SO_4)}]$ and [Mn(tpp)Cl] in other non-coordinating (or weakly coordinating) solvents were similar to those in $\mathrm{CHCl_3}$ (*Table 1*). The solution IR spectrum of $[\mathrm{Mn_2(tpp)_2(SO_4)}]$ in $\mathrm{ClCH_2CH_2Cl}$, after background subtraction, was essentially the same as that observed for the spectrum of the solid.

Table 1. *VIS Spectra (Tetraphenylporphyrinato)manganese(III) Complexes* a)

	Solvent	*Soret* band b)	Other VIS bands b)
$[\mathrm{Mn_2(tpp)_2(SO_4)}]$	$\mathrm{CHCl_3}$	466 (215)	530 (10.9), 577 (22.5), 612 (18.9)
	$\mathrm{CH_2Cl_2}$ c)	466 (172)	528 (7.1), 575 (15.4), 612 (13.5)
	benzene	468 (75.8)	531 (4.3), 577 (8.9), 613 (7.3)
	toluene	468 (119)	532 (6.2), 577 (12.8), 613 (10.5)
	MeCOMe d)	468	527, 572, 609
	DMF	440(sh), 466 (185)	524 (14.2), 568 (23.0), 604 (17.9)
	DMSO	439 (sh), 465 (258)	523 (12.6), 567 (23.1), 604 (17.9)
[Mn(tpp)Cl]	$\mathrm{CHCl_3}$	479 (115)	528 (6.3), 583 (10.8), 618 (11.7)
	$\mathrm{CH_2Cl_2}$	478 (119)	529 (6.6), 583 (11.2), 618 (13.0)
	$\mathrm{ClCH_2CH_2Cl}$	478 (101)	530 (5.6), 583 (8.7), 619 (10.5)
	benzene	477 (124)	523 (5.8), 585 (9.3), 621 (11.2)
	toluene	478 (12.5)	532 (5.7), 586 (9.2), 622 (11.2)
	DMSO	465 (132)	518 (6.2), 567 (11.2), 603 (8.7)
$[\mathrm{Mn(tpp)}]^{+}$ e)	DMSO	465 (124)	515 (13.1), 567 (17.4), 602 (15.0)
$[\mathrm{Mn(tpp)(OSO_3H)}]$ c)	$\mathrm{CH_2Cl_2}$	470 (51.8)	521 (3.5), 574 (7.2), 608 (5.9)
$[\mathrm{Mn(tpp)(OSO_3)}]^{-}$	$\mathrm{CHCl_3}$	469 (159)	531 (7.0), 578 (13.1), 613 (12.1)
	$\mathrm{ClCH_2CH_2Cl}$	470 (119)	531 (5.6), 579 (10.5), 615 (10.3)
	MeCOMe	469 (66.9)	531 (3.4), 578 (6.3), 615 (6.3)
	DMF	441 (80.7), 465 (82.3)	530 (6.1), 575 (11.0), 614 (10.9)
	DMSO	440 (sh), 466 (109)	528 (5.7), 576 (10.0), 614 (8.9)

a) VIS Spectral data between 400 and 750 nm. b) $\lambda_{\max}$ in nm, ε (in parentheses) in $\mathrm{cm^{-1} \cdot mM^{-1}}$. c) [2]. d) Sample not completely soluble in this solvent system. e) [14].

In the coordinating solvent DMSO, the spectra for both $[\mathrm{Mn_2(tpp)_2(SO_4)}]$ and [Mn(tpp)Cl] were essentially the same and similar to that reported for $[\mathrm{Mn(tpp)(DMSO)_2}]^{+}$ [14], with a *Soret* band maximum at 465 nm, Q bands at 567 and 603 nm, and a broad band at *ca.* 520 nm (*Table 1*, *Fig. 2*). A small absorbance was observed at 439 nm in the spectrum of the sulfato-bridged dimer that was not observed in the spectrum of [Mn(tpp)Cl].

Addition of sulfate ion (as the $\mathrm{PPN^{+}}$ salt) to solutions of $[\mathrm{Mn(tpp)_2(SO)_4}]$ in various solvents produced significant changes in the VIS spectra (*Figs. 1* and *2*). In

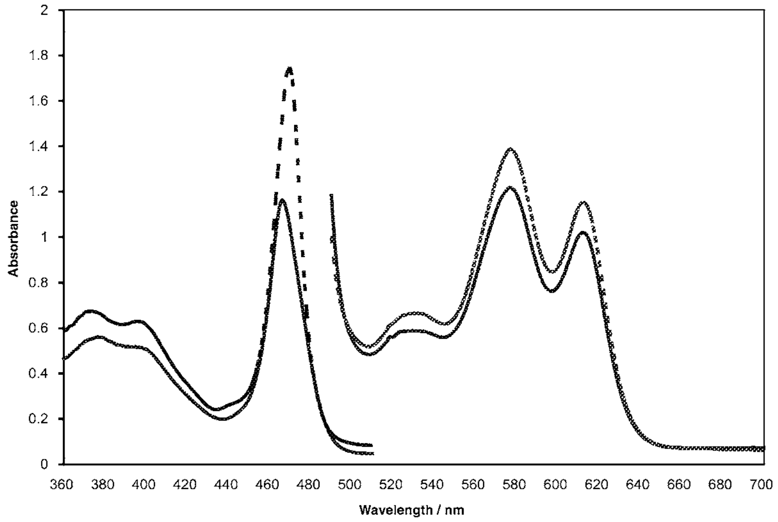

Fig. 1. *VIS Spectrum of [Mn(tpp)$_2$(SO$_4$)]* (0.054 mM) *in CHCl$_3$ in the presence and absence of sulfate: 0 mM (PPN)$_2$SO$_4$* (solid line) *and 10.4 mM (PPN)$_2$SO$_4$* (dashed line) (360–490 nm in 1-mm cell; 490–700 nm in 1-cm cell)

CHCl$_3$, addition of excess sulfate shifted the *Soret* band from 466 to 469 nm (*Fig. 1*). Only minor shifts in the wavelengths of the longer wavelength bands were observed. However, the excess sulfate ion resulted in a definite increase in the absorbances of each of these bands. The changes observed were nearly stoichiometric with addition of sulfate, and no isosbestic points were observed. In addition, the spectrum remained unchanged at higher concentrations of the ligand, *i.e.*, at greater than 1 equiv. of added sulfate. Similar spectral results were observed in other non-coordinating/weakly coordinating solvents. The IR spectrum of the dimer [Mn$_2$(tpp)$_2$(SO$_4$)] in ClCH$_2$CH$_2$Cl following the addition of 15 equiv. of sulfate exhibited non-porphyrin bands at 1286, 1109, 1032, 943, and 880 cm^{-1} following subtraction of solvent, PPN$^+$, and free sulfate bands.

In the coordinating solvent DMSO, addition of excess sulfate ion to the [Mn$_2$(tpp)$_2$(SO$_4$)] solution resulted in a spectrum with absorbances at 441, 466, 528, 576, and 615 nm (*Fig. 2,a*). Isosbestic points were detected at 456, 470, 502, 576, 593, and 609 nm during the spectral changes in this solvent for the dimer as the sulfate concentration was increased from 0 to 23 equiv. (*Fig. 2,b*).

Addition of excess sulfate ion to solutions of [Mn(tpp)Cl] under analogous conditions produced identical spectra to those of the dimer following sulfate addition. In addition, isosbestic points were also observed in the spectrum of [Mn(tpp)Cl] in DMSO at the same wavelengths (456, 470, 502, 576, 593, and 609 nm) as those noted for the dimer in DMSO as the amount of sulfate was increased.

Chemical reduction of [Mn(tpp)Cl] with borohydride (BH$_4^-$) (as the Bu$_4$N$^+$ salt) in ClCH$_2$CH$_2$Cl produced a spectrum consistent with a five-coordinate, anion-complexed manganese(II) species [15][16], yielding absorbance maxima at 613, 573, and 441 nm. The same spectrum was observed for the reduced product in the presence of added

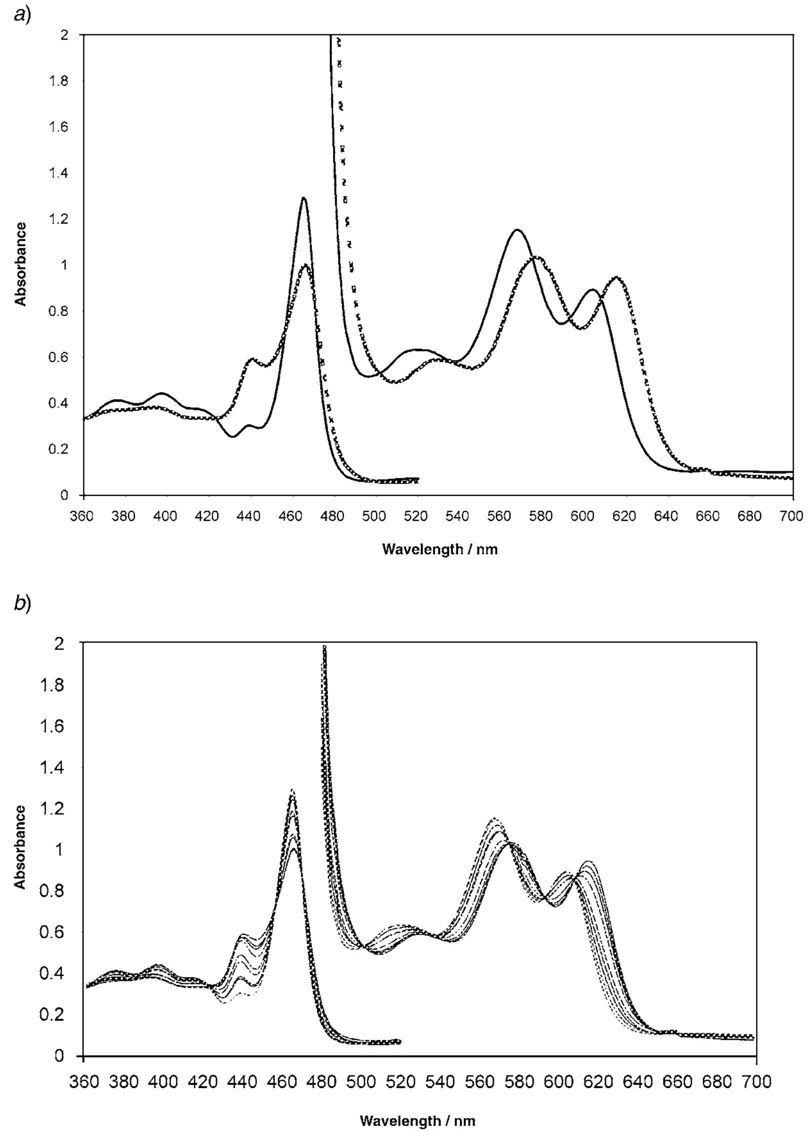

Fig. 2. a) *VIS Spectrum of* $[Mn_2(tpp)_2(SO_4)]$ (0.052 mM) *in DMSO in the presence and absence of sulfate: 0* mM $(PPN)_2SO_4$ (solid line) *and 11.6* mM $(PPN)_2SO_4$ (dotted line) (360–490 nm in 1-mm cell; 490–700 nm in 1-cm cell). b) *VIS-Spectral changes for* $[Mn_2(tpp)_2(SO_4)]$ (0.052 mM) *in DMSO with varying concentrations of* $(PPN)_2SO_4$ (0–11.6 mM) (360–480 nm in 1-mm cell; 480–700 nm in 1-cm cell)

sulfate ion. Borohydride reduction of [Mn(tpp)Cl] in DMSO lead to a spectrum consistent with that of $[Mn^{II}(tpp)(DMSO)]$ [15][16], with absorbances observed at 606, 567, and 435 nm. This spectrum was unaltered after addition of sulfate ion to the solution. Addition of only 1 equiv. of borohydride to a solution of $[Mn_2(tpp)_2(SO_4)]$ in

CH_2Cl_2 resulted in a spectrum possessing *Soret* bands at both 435 and 467 nm, indicative of the presence of both Mn^{II} and Mn^{III} species.

To better understand and characterize the products of the reactions between the porphyrinatomanganese complexes and the sulfate ion, the molar absorptivity ratio of bands Q_b and Q_a was calculated for the various spectra (*Table 2*) [16]. By using the terminology of *Boucher* [11], these bands are numbered III and IV, respectively. In the non-coordinating solvent $ClCH_2CH_2Cl$, the ratio $\varepsilon_{III}/\varepsilon_{IV}$ is 1.21 for [Mn(tpp)Cl], in close agreement with the reported value of 1.17 [16]. Similar values (1.08 – 1.21) were also observed in other non-coordinating solvents. In DMSO, this ratio for [Mn(tpp)Cl] was 0.78. This latter value is somewhat lower than the reported value of 0.99 [16], but could be repeated multiple times under the conditions used in this study. Addition of a large excess of sulfate to [Mn(tpp)Cl] solutions in various solvent systems produced spectra with similar ratios, *i.e.*, $\varepsilon_{III}/\varepsilon_{IV} = 0.89 - 1.00$, thus implying that the same product is formed in each solvent. The same ratios (0.93 – 1.00) were also obtained after addition of sulfate to the $[Mn_2(tpp)_2(SO_4)]$ in all solvents utilized. Following the chemical reduction of [Mn(tpp)Cl] in $ClCH_2CH_2Cl$, the ratio $\varepsilon_{III}/\varepsilon_{IV}$ was determined to be 1.08, in keeping with the reported values for $[Mn^{II}(tpp)Cl]^-$ in non-coordinating or weakly coordinating solvent systems [16]. A ratio of 1.03 was calculated for the reduced product following sulfate addition to the solution. In DMSO, the reduced species gave $\varepsilon_{III}/\varepsilon_{IV} = 0.90$ both in the absence and presence of added sulfate, implying that sulfate does not coordinate to Mn^{II} in this solvent system.

Table 2. *Spectroscopic Properties as a Function of Solvent for (Tetraphenylporphyrinato)manganese(III) Complexes*

	Solvent	$\varepsilon_{III}/\varepsilon_{IV}$ [a])	$\varepsilon_{IV}/\varepsilon_{V}$ [b])
$[Mn_2(tpp)_2(SO_4)]$	$CHCl_3$	0.84	0.10
	CH_2Cl_2	0.88	0.090
	benzene	0.82	0.12
	toluene	0.82	0.11
	DMF	0.78	0.12
	DMSO	0.77	0.090
[Mn(tpp)Cl]	$CHCl_3$	1.08	0.094
	CH_2Cl_2	1.16	0.094
	$ClCH_2CH_2Cl$	1.21	0.086
	benzene	1.20	0.075
	toluene	1.22	0.074
	DMSO	0.78	0.085
$[Mn(tpp)(OSO_3H)]$	CH_2Cl_2	0.82	0.14
$[Mn(tpp)(OSO_3)]^-$	$CHCl_3$	0.92	0.082
	$ClCH_2CH_2Cl$	0.98	0.088
	MeCOMe	1.00	0.094
	DMF	0.99	0.13
	DMSO	0.89	0.092

[a]) Molar absorptivity ratios of bands III (λ 599 – 618 nm) and IV (λ 564 – 582 nm). [b]) Molar absorptivity ratios of bands IV (λ 564 – 582 nm) and V (*Soret* band, λ 462 – 474 nm).

Electrochemistry. The redox properties of $[Mn_2(tpp)_2(SO_4)]$ were investigated by cyclic voltammetry. A representative voltammogram for this porphyrinatomanganese complex in $ClCH_2CH_2Cl$ is provided in *Fig. 3*. All reductions were found to be diffusion-controlled as evidenced by constant current functions at all scan rates employed [9][17]. Three waves were exhibited during cyclic voltammetry of the sulfato-bridged $[Mn_2(tpp)_2(SO_4)]$ (0.5 mM) in $ClCH_2CH_2Cl$ between -0.2 and -2.2 V (*vs.* SRE) (*Fig. 3*). The first two waves, waves Ia and Ib, appeared in the potential region for the Mn^{III}/Mn^{II} redox couple [18]. Wave Ia, observed at a potential of *ca.* -0.55 V, appeared as a shoulder to wave Ib at $E_{pc} = -0.71$ V. Qualitatively, the voltammogram was similar to that expected for a reversible two-electron charge transfer in which $\Delta E^\circ = -90$ mV [17], with the exception that only one oxidation wave was observed during the reverse sweep. This wave occurred at $E_{pa} = -0.47$ V. The third wave, wave II, was observed at a potential of -1.91 V and corresponds to reduction of the porphyrin ring to form the anion radical [18]. This process was irreversible in this solvent system, in agreement with the reported behavior of $[Mn(tpp)(ClO_4)]$ under similar conditions [18]. The voltammetric response of [Mn(tpp)Cl] was analogous to that reported previously [18][19].

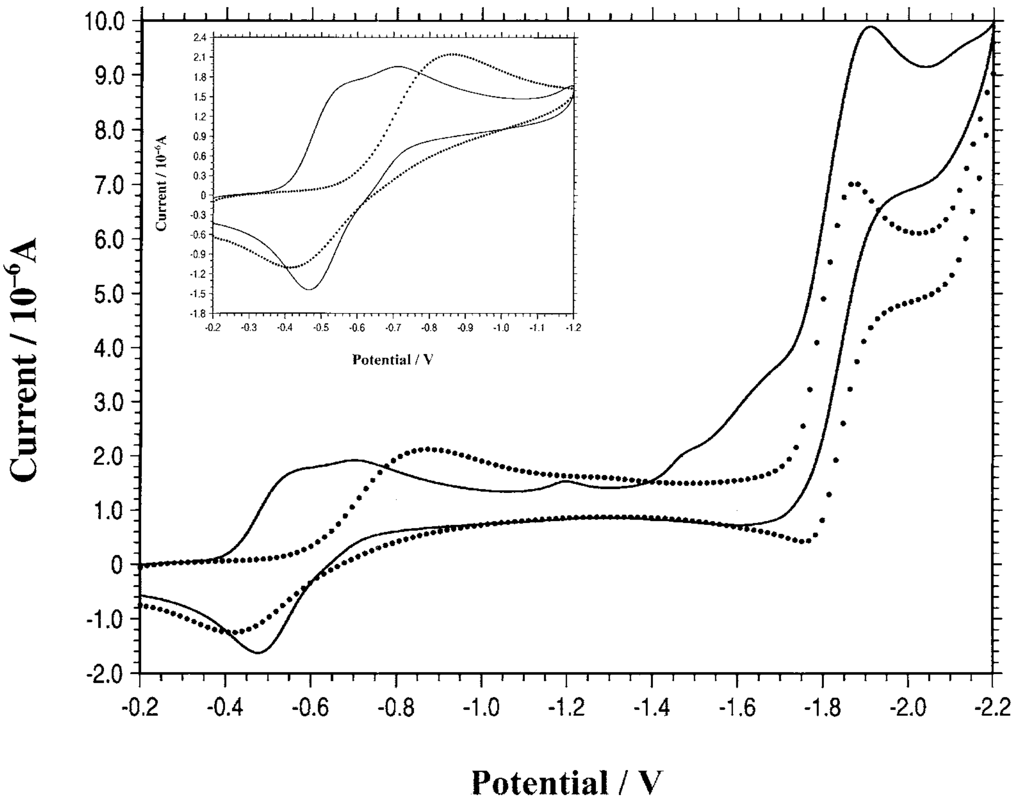

Fig. 3. *Cyclic voltammetry of* $[Mn(tpp)_2(SO_4)]$ (0.52 mM) *in* $ClCH_2CH_2Cl$*: 0* mM $(PPN)_2SO_4$ (solid line) *and 10.0* mM $(PPN)_2SO_4$ (dotted line). Conditions: Pt-disk working electrode, SRE, $(Bu_4N)ClO_4$ (0.1M) supporting electrolyte, 100 mV/s

The spectroelectrochemistry of the sulfato-bridged [$Mn_2(tpp)_2(SO_4)$] in CH_2Cl_2 was examined by using an OTTLE cell. The results for the *Soret* region are shown in *Fig. 4*. As the potential was stepped through and the negative of the first two voltammetric waves, the *Soret* band for the Mn^{III} species was replaced by a broad band at 440 nm. This feature is associated with the spectra of five-coordinate porphyrinatomanganese(II) complexes that are axially coordinated by anionic ligands [15][16][20]. It seems noteworthy that the *Soret* band associated with the Mn^{III} species was not diminished completely at potentials at which the Mn^{II} species begins to develop, *i.e.*, potentials more positive than –0.6 V. In the long-wavelength region, the Q_a and Q_b bands at 577 and 612 nm shifted to 572 and 612 nm, respectively. No isosbestic points were observed during the spectroelectrochemical reduction of [$Mn_2(tpp)_2(SO_4)$] in this solvent system.

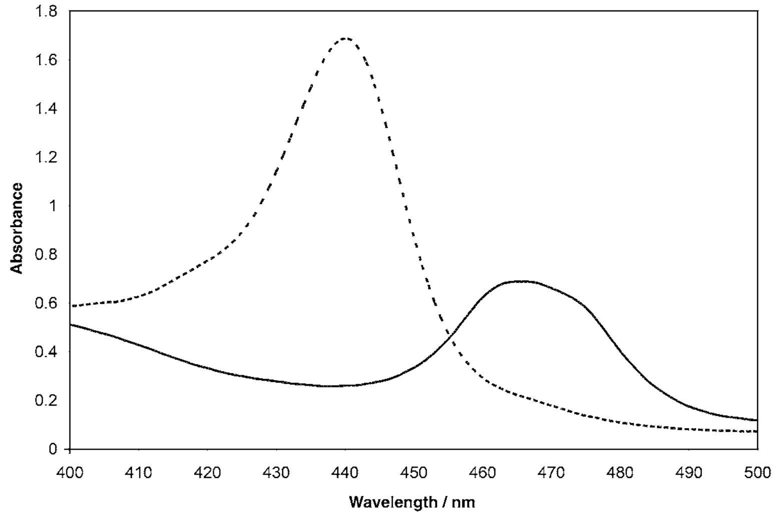

Fig. 4. *Spectroelectrochemistry of [$Mn_2(tpp)_2(SO_4)$]* (0.089 mm) *in CH_2Cl_2 with (Bu_4N)ClO_4* (0.1m) *in OTTLE cell: –0.2 V* vs. *SRE* (solid line) *and –1.0 V* vs. *SRE* (dashed line)

The cyclic voltammetric behavior of [$Mn_2(tpp)_2(SO)_4$)] (0.05 mm) in DMSO between –0.2 and –2.0 V differed significantly from that in $ClCH_2CH_2Cl$ (*Fig. 5*). Only two voltammetric waves were observed during the reduction, as is typically observed for porphyrinatomanganese complexes [18]. The first wave for the dimer, representing the Mn^{III}/Mn^{II} redox couple, occurred at $E_{1/2} = -0.68$ V. The second reduction, representing the first ring reduction, was observed at $E_{1/2} = -1.71$ V. By comparison, [Mn(tpp)Cl], which completely dissociates in DMSO to form [$Mn(tpp)(DMSO)_2$]$^+$ [18], yielded reduction waves at –0.66 V and –1.69 V.

The spectroelectrochemistry of the sulfato-bridged dimer was also carried out in DMSO. Stepping the potential negative of the Mn^{III}/Mn^{II} redox couple produced a spectrum with a *Soret* band at 434 nm, typical of five-coordinate [$Mn^{II}(tpp)(S)$] (S = axial solvent molecule) [15][16]. The reduced product also exhibited absorbances at 522, 563, and 605 nm.

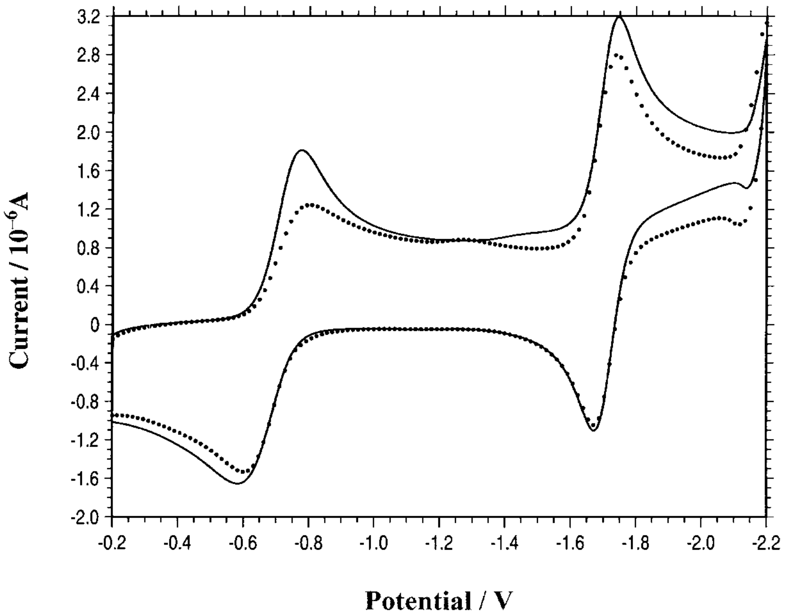

Fig. 5. *Cyclic voltammetry of [Mn(tpp)$_2$(SO$_4$)]* (0.52 mM) *in DMSO: 0* mM *(PPN)$_2$SO$_4$* (solid line) *and 30.0* mM *(PPN)$_2$SO$_4$* (dotted line). Conditions: Pt-disk working electrode, SRE, (Bu$_4$N)ClO$_4$ (0.1M) supporting electrolyte, 100 mV/s

Addition of sulfate ion (as the PPN$^+$ salt) to solutions of [Mn$_2$(tpp)$_2$(SO$_4$)] in ClCH$_2$CH$_2$Cl resulted in the disappearance of wave Ia (*Fig. 3*). At sulfate/dimer concentrations greater than 1:2, this reduction process could no longer be observed in the voltammogram. In addition, wave Ib became more quasi-reversible, and its peak current increased by 1/3 with increasing ligand concentration. At 10 mM sulfate, ΔE_p = 0.45 V (*vs.* 0.25 V for the dimer) and $E_{pc} = -0.86$ V for wave Ib. At sulfate concentrations greater than 10:1, the cathodic peak potential was essentially independent of sulfate concentration. Wave II was unaffected by addition of sulfate below concentrations of 10:1. Addition of sulfate concentrations above this amount shifted E_{pc} to slightly more-positive values, and enhanced the reversibility of wave II due to the growth of a new anodic process at – 1.77 V. At 10 mM sulfate, $E_{pc} = -1.87$ V and $E_{1/2} = -1.82$ V. The $E_{1/2}$ for wave II was independent of sulfate concentration. Cyclic voltammetric reduction of [Mn(tpp)Cl] in the presence of a large excess of sulfate ion resulted in a voltammogram similar to that of [Mn$_2$(tpp)$_2$(SO$_4$)] under analogous conditions.

Spectroelectrochemical reduction of [Mn$_2$(tpp)$_2$(SO$_4$)] in CH$_2$Cl$_2$ in the presence of added sulfate was also investigated. Stepping the potential through the region of the Mn^{III}/Mn^{II} redox couple produced a VIS spectrum with a *Soret* band at 441 nm. Significantly, isosbestic points were observed at *ca.* 405 and 455 nm as the potential was stepped through the region of Mn^{III} reduction.

Addition of excess sulfate ion to [Mn$_2$(tpp)$_2$(SO$_4$)] in DMSO also resulted in some changes in the voltammetric behavior. However, these changes were not as dramatic as those observed in the non-coordinating solvent system. The potential of the first wave shifted negatively with increasing ligand concentration. However, between 0 and 30 mM sulfate, $E_{1/2}$ differed by only 25 mV. The wave for the first ring reduction was unaffected by added sulfate in DMSO. [Mn(tpp)Cl] yielded similar voltammetric results in DMSO in the presence of added sulfate. The one-electron reduction of the dimer in DMSO with added sulfate by using the OTTLE cell produced a spectrum with a *Soret* band at 434 nm, consistent with $[\mathrm{Mn^{II}(tpp)(DMSO)}]$ [15][16].

Discussion. – *Effect of Solvent on [Mn$_2$(tpp)$_2$(SO$_4$)] Structure and Electrochemistry.* $[\mathrm{Mn_2(tpp)_2(SO_4)}]$ was apparently stable in non-coordinating solvents during the time period over which the experiments were performed. No evidence of decomposition was observed in the VIS spectrum of the dimer in non-coordinating solvents such as $CHCl_3$ within 30 min. In addition, the solution IR spectrum of the dimer in $ClCH_2CH_2Cl$, after appropriate background subtraction, was the same as that of the solid. The voltammetric and VIS-spectral data indicate, however, that the sulfato-bridged dimer was not stable in DMSO. Dissociation of the dimer occurred in this solvent, forming primarily the solvent-coordinated complex, $[\mathrm{Mn(tpp)(DMSO)_2}]^+$, although a small amount of a sulfato-coordinated species may be present in this solution also. Analogous to the behavior of the corresponding iron derivative [5][6], the equilibria of *Eqns. 1* and *2* are proposed to occur for the dimer in DMSO based on the data. In this solvent system, the reaction of *Eqn. 1* apparently goes to completion, whereas the reaction of *Eqn. 2* favors the products at equilibrium. Although the chemistry of the sulfato-bridged dimer in DMF was not investigated in detail (*Table 1*), it seems reasonable to assume that dissociation of the dimer also occurs in this solvent given the similarities between the spectra for the dimer in both DMF and DMSO. $[\mathrm{Fe_2(tpp)_2(SO_4)}]$ has been shown to dissociate according to *Eqns. 1* and *2* in DMSO [5][6].

$$[\mathrm{Mn_2(tpp)_2(SO_4)}] + 2\mathrm{DMSO} \rightleftarrows [\mathrm{Mn(tpp)(DMSO)_2}]^+ + [\mathrm{Mn(tpp)(SO_4)}]^- \quad (1)$$

$$[\mathrm{Mn(tpp)(SO_4)}]^- + 2\mathrm{DMSO} \rightleftarrows [\mathrm{Mn(tpp)(DMSO)_2}]^+ + \mathrm{SO_4^{2-}} \quad (2)$$

In non-coordinating solvents, reduction of the sulfato-bridged complex apparently involves dimer cleavage concerted with electron transfer. The mechanism according to *Eqns. 3–5* is proposed based on the electrochemical and spectrochemical data.

$$[\mathrm{Mn_2(tpp)_2(SO_4)}] + \mathrm{e^-} \rightleftarrows [\mathrm{Mn^{II}(tpp)}] + [\mathrm{Mn^{III}(tpp)(SO_4)}]^- \quad (3)$$

$$[\mathrm{Mn(tpp)(SO_4)}]^- + \mathrm{e^-} \rightleftarrows [\mathrm{Mn(tpp)(SO_4)}]^{2-} \quad (4)$$

$$[\mathrm{Mn(tpp)(SO_4)}]^{2-} \rightleftarrows [\mathrm{Mn(tpp)}] + \mathrm{SO_4^{2-}} \quad (5)$$

The reaction of *Eqn. 3* was observed as wave Ia during the cyclic voltammetric reduction of the sulfato-bridged adduct, and the reaction of *Eqn. 4* as wave Ib. The following results support this mechanism: *a*) The dimer $[\mathrm{Mn_2(tpp)_2(SO_4)}]$ was stable in the non-coordinating solvent systems, and two waves were observed in the potential region for the $\mathrm{Mn^{III}/Mn^{II}}$ redox couple. *b*) No isosbestic points were observed during the spectroelectrochemical reduction of the dimer in CH_2Cl_2, supporting the presence of more than two species, such as $[Mn_2(tpp)_2(SO_4)]$, $[Mn^{III}(tpp)(SO_4)]^-$, $[Mn^{II}(tpp)]$, and $[Mn^{II}(tpp)(OSO_3)]^{2-}$, in the solution during the spectral changes. *c*) Both Mn^{II} and Mn^{III} species were observed in the spectrum following one-electron borohydride reduction of the dimer. *d*) The spectrum of the totally reduced product clearly showed the presence of a porphyrinatomanganese(II) adduct. *e*) Spectral and electrochemical data with added sulfate indicated that wave Ib is due to a sulfato-complexed Mn^{III} species different from the dimer. *f*) Wave Ia was apparently irreversible, *i.e.*, the oxidation observed at -0.47 V was coupled to wave Ib. Such behavior is expected if dimer cleavage occurs following the initial reduction. Reoxidation would involve bringing two monomeric porphyrinato complexes together at the electrode surface, a process expected to be kinetically less facile than reoxidation of an intact dimeric species. The electrochemical behavior exhibited for $[Mn_2(tpp)_2(SO_4)]$ in non-coordinating solvents was consistent with that reported for the analogous iron derivative under similar conditions [5].

The apparent lack of spectral features attributable to [Mn(tpp)] [21] in the spectroelectrochemical results in CH_2Cl_2 must be addressed, since both [Fe(tpp)] and $[Fe(tpp)(SO_4]^{2-}$ have been observed during spectroelectrochemical reduction of $[Fe_2(tpp)_2(SO_4)]$ under similar conditions [5]. Comparison of the relative ε values for the anion-complexed Mn^{II} adduct generated during spectroelectrochemistry of the dimer with added sulfate *vs.* that in the absence of added ligand shows that the former is 1.7 times the latter. This result would be expected if spectroelectrochemical reduction in the absence of added ligand does not convert all Mn^{III} species to $[Mn^{II}(tpp)(SO_4]^{2-}$. Although the exact reason is not known, spectral overlap may mask the spectrum of [Mn(tpp)], a conclusion supported by the broadness of the *Soret* band observed in the absence of added sulfate.

In DMSO, reduction of $[Mn_2(tpp)_2(SO_4)]$ involved the bis-solvent-coordinated Mn^{III} complex, forming $[Mn^{II}(tpp)(DMSO)]$. This is supported by both the spectroelectrochemistry of the dimer in this solvent and the nearly identical $E_{1/2}$ values for the dimer and [Mn(tpp)Cl].

Further reduction of the Mn^{II} state in both solvent systems involves porphyrinato-ring reduction.

Effect of Added Sulfate on $[Mn_2(tpp)_2(SO_4)]$ Structure and Electrochemistry. The sulfato-bridged dimer reacted with additional ligand in all solvents studied to form a sulfato-coordinated porphyrinatomanganese(III) monomer. In non-coordinating solvents, the monomer was produced as the result of dimer dissociation according to *Eqn. 6*. In DMSO, this occurred as the result of solvent displacement according to *Eqn. 7*.

$$[Mn_2(tpp)_2(SO_4)] + SO_4^{2-} \rightleftarrows 2\,[Mn(tpp)(SO_4)]^- \qquad (6)$$

$$[Mn(tpp)(DMSO)_2]^+ + SO_4^{2-} \rightleftarrows [Mn(tpp)(SO_4)]^- + 2DMSO \qquad (7)$$

Several pieces of evidence support this conclusion. *a*) The IR spectrum of $[Mn_2(tpp)_2(SO_4)]$ in $ClCH_2CH_2Cl$ with a large excess of added sulfate, following appropriate background subtraction, was consistent with $[Mn(tpp)(SO_4)]^-$. Qualitatively, the IR spectrum of the product species was similar to that reported for the corresponding hydrogen sulfate adduct [2]. The splitting of the free sulfate band at 1104 cm^{-1} into bands at 1109 and 1032 cm^{-1} was consistent with monodentate coordination of sulfate [8]. *b*) The VIS spectrum observed for the reaction product was different from that observed for $[Mn_2(tpp)_2(SO_4)]$ and [Mn(tpp)Cl], and the reported spectrum of $[Mn(tpp)(HSO_4)]$ [2]. *c*) The VIS spectrum and the $\varepsilon_{III}/\varepsilon_{IV}$ ratio of the product were similar to those reported for other monomeric [Mn(tpp)X] complexes containing 'hard' axial ligands [13]. Additionally, the $\varepsilon_{III}/\varepsilon_{IV}$ and $\varepsilon_{IV}/\varepsilon_{V}$ ratios calculated for the product were different from those observed for the parent dimer and the reported spectrum of $[Mn(tpp)(HSO_4)]$. *d*) The spectral properties of this sulfate complex were similar in the various solvent systems, indicating that the same or similar species were generated in each case. In addition, reaction of [Mn(tpp)Cl] with excess sulfate led to a product with the same VIS-spectral characteristics. Reaction of both $[Fe(tpp)_2(SO_4)]$ and [Fe(tpp)Cl] has been shown to lead to formation of a monomeric, sulfato-coordinated Fe^{III} adduct [5][6].

Sulfate apparently does not bond as strongly to $[Mn^{III}(tpp)]^+$ as it does to the analogous iron derivative. Addition of a high excess concentration of sulfate resulted only in a 70 mV shift in $E_{1/2}$ for [Mn(tpp)Cl] in $ClCH_2CH_2Cl$, whereas a 320-mV difference in $E_{1/2}$ between [Fe(tpp)Cl] and the sulfate complex has been observed [5]. This may indicate a significantly greater degree of ionic bonding between the axial sulfato ligand and porphyrinatomanganese complexes compared to their iron counterparts [11][13]. As with the porphyrinatoiron complexes [5], the sulfate ion forms a stronger complex with the porphyrinatomanganese adduct in non-coordinating solvents than in coordinating solvents, where the dimer exists primarily as a bis-solvent-coordinated complex in the absence of excess sulfate. This phenomenon may be due in part to stronger solvation of the dianionic sulfate ion in the more strongly coordinating solvents. As a result, higher concentrations of sulfate are needed before this ligand can coordinate to the metal.

Reduction in the presence of excess sulfate ion involves the sulfato-coordinated monomer in both non-coordinating solvents and DMSO. The negative shift in potential with increasing sulfate concentration is consistent with stabilization of Mn^{III} over Mn^{II}. In CH_2Cl_2, the spectroelectrochemical results indicate that sulfate remained coordinated to the metal following the metal-centered reduction (*Eqn. 4*). The quasi-reversibility of this process may be the result of a large out-of-plane displacement that the Mn-atom of the sulfato complex undergoes upon reduction. This would have the effect of increasing the inner-shell activation barrier and decreasing the rate of electron transfer [15]. Alternatively, the quasi-reversibility could be due to the slow rate of ligand coordination [5]. In DMSO, the solvent binds preferentially to the reduced state, even in the presence of a large excess of the sulfate ion. Thus, a solvent molecule displaces the sulfate ion upon reduction of $[Mn^{III}(tpp)(OSO_3)]^-$ in this solvent.

The slight shift in potential and the enhanced reversibility for the reduction of $[Mn^{II}(tpp)]$ in $ClCH_2CH_2Cl$ at higher sulfate concentrations (*Fig. 3*) indicates slight stabilization of the reduced ring species over [Mn(tpp)] under these conditions. Such stabilization has been attributed previously to interactions between the porphyrinato π ring and coordinating solvent molecules [18][22]. The exact cause of these observations in the present study is not known and was not investigated further. However, it is conceivable that a weak π interaction could occur between the porphyrinato radical anion and the phenyl groups of the PPN^+ ion under these conditions.

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