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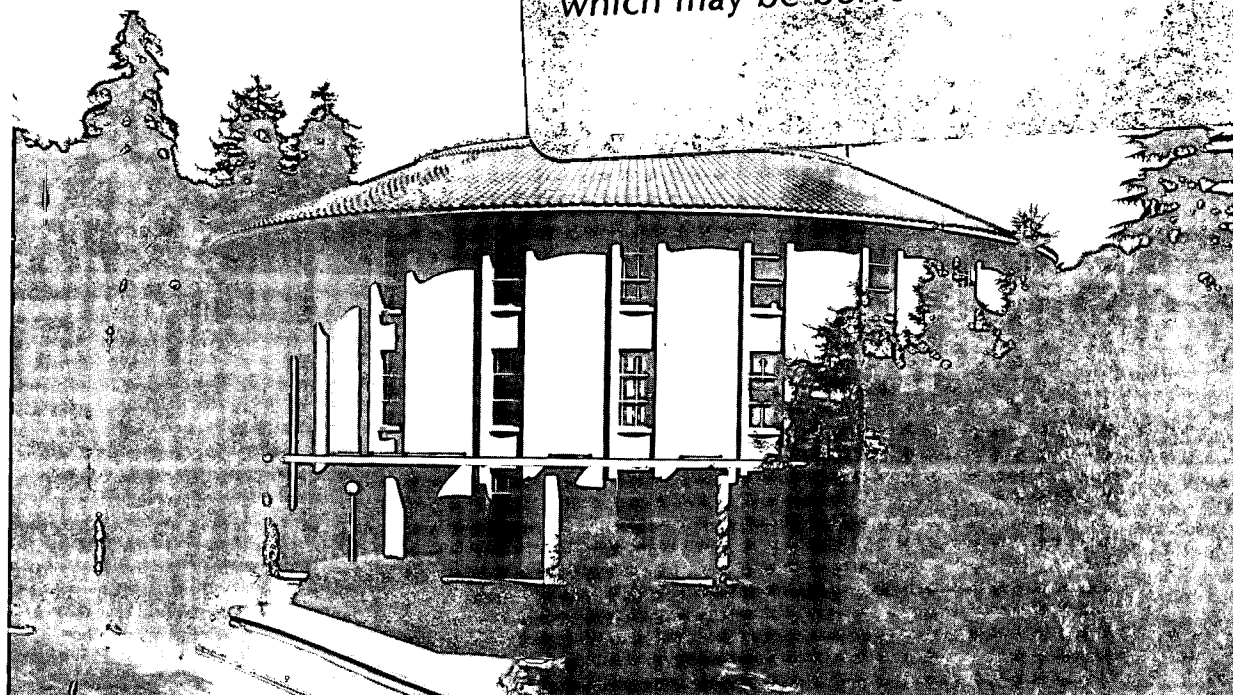
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PORPHYRIN CATION RADICAL AND ITS CONVERSION  
TO Mn<sup>IV</sup> BY LIGAND METATHESIS

L.O. Spreer, A.C. Maliyackel, S. Holbrook,  
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SYNTHESIS AND CHARACTERIZATION OF A Mn<sup>III</sup> PORPHYRIN  
CATION RADICAL AND ITS CONVERSION TO Mn<sup>IV</sup> BY LIGAND METATHESIS

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ABSTRACT

The complex (5,10,15,20-tetraphenylporphinato) manganese chloro hexachloroantimonate, 1, MnTPP(Cl)(SbCl<sub>6</sub>), was synthesized by the oxidation of MnTPP(Cl) with phenoxathiin hexachloroantimonate in dichloromethane. The assignment of 1 as a manganese(III) porphyrin  $\pi$ -cation radical species was based on its X-ray crystal structure, visible and infrared spectra, and its magnetic properties. The crystal structure was determined as a tetrachloroethane solvate. The manganese in the compound is five-coordinated with the chloride anion axially bound to the Mn with 50% occupancy at sites above and below the porphyrin ring. The second anion, SbCl<sub>6</sub><sup>-</sup>, is displaced from the Mn with Mn-Cl-Sb angle of 132°. The porphyrin core carbon and nitrogen atoms as well as Mn are coplanar. Variable-temperature magnetic susceptibility measurements on the solid gave  $\mu_{\text{eff}} = 4.9 \mu_{\text{B}}$  which is close to that expected for a Mn<sup>III</sup> cation ( $d^4$ )  $S = 2$ ,  $\pi$ -cation radical  $S = \frac{1}{2}$ , with independent spin states. Magnetic susceptibility measurements on solutions of 1 gave a range of values for  $\mu_{\text{eff}}$  between 5.7 and 6.7  $\mu_{\text{B}}$ . This suggests that the spin independent state of 1 in the solid changes into a ferromagnetically coupled state, resultant spin of five halves, in the solution phase. The IR spectrum of 1, with four solvent molecules (C<sub>2</sub>H<sub>2</sub>Cl<sub>4</sub>) present, shows a peak at 1280 cm<sup>-1</sup>. A band in this region has been suggested as diagnostic of metallotetraphenyl porphyrin  $\pi$ -cation radical species. The 1280 cm<sup>-1</sup> band observed for 1 disappeared when all the solvent molecules from 1 were removed under vacuum. The crystalline nature of the solid was lost by the removal of the solvent

molecules; however, magnetic moment ( $4.7 \mu_B$ ) and the visible spectrum remained virtually unchanged. We believe that the  $1280 \text{ cm}^{-1}$  band in 1 is associated with the solvent molecules; neat  $\text{C}_2\text{H}_2\text{Cl}_4$  also shows strong absorption in the  $1280 \text{ cm}^{-1}$  region. Treatment of 1 with basic methanol, or oxidation of  $\text{MnTPP}(\text{Cl})$  with phenoxathiin hexachloroantimonate in the presence of basic methanol gave another species whose visible and EPR spectra are identical to that reported for  $\text{Mn}^{\text{IV}}\text{TPP}(\text{OCH}_3)_2$ . These results suggest that the site of oxidation in  $\text{MnTPP}(\text{Cl})$  is shifted from the ligand to the metal in the presence of the strong  $\pi$ -donating ligand,  $\text{CH}_3\text{O}^-$ .

## INTRODUCTION

The development of stable and efficient oxidation catalysts is difficult but essential to work aimed at producing an artificial photosynthesis assembly capable of converting solar energy to storable high energy chemical compounds. A useful oxidation catalyst in an assembly designed to split water would mediate the four-electron conversion of water to oxygen. An alternate goal would be the use of an oxidation catalyst to produce more useful intermediate oxidants.<sup>1</sup> In connection with our interest in artificial photosynthesis we have examined manganese porphyrin compounds as potential redox catalysts.

Our interest in manganese porphyrin compounds is longstanding<sup>2-4</sup> and originated in the knowledge that some type of manganese complex is involved in the oxidation cycle of natural chloroplasts. The porphyrin ligands are resistant to irreversible oxidation or reduction reactions, and this is a very desirable property since it increases the possibility for the central metal ion to participate in redox reactions. A primary requisite for a multiple electron redox catalyst is the accessibility of a variety of oxidation states, and manganese porphyrin species have been characterized with manganese in the +2,<sup>5</sup> +3<sup>5</sup> and +4<sup>6</sup> levels and species have been proposed for the +5<sup>7</sup> state. In addition, there have been recent reports of the use of manganese porphyrins as oxidation catalysts for a variety of organic substrates.<sup>8</sup> We report here results of work on a one-electron oxidation product of MnTPPCl; TPP = 5,10,15,20-tetraphenylporphyrin, which we believe is best classified as a manganese-III porphyrin  $\pi$ -cation radical. Addition of a hard base ligand, such as methoxide ion, to a solution containing  $\text{Mn}^{\text{III}}\text{TPP}^+$  produces another species whose spectral properties are consistent with  $\text{Mn}^{\text{IV}}\text{TPP}(\text{OCH}_3)_2$ .

## EXPERIMENTAL AND INSTRUMENTATION

Visible spectra of the compounds were recorded on a Hewlett-Packard 8450A spectrometer.

Infrared spectra of solid samples were recorded as KBr pellets (4-6 weight percent sample) on a Perkin-Elmer 299B spectrometer.

Variable-temperature magnetic susceptibility measurements in solid state were carried out on a SQUID apparatus (SHE Corp. VPS 800 susceptometer). The SQUID apparatus had been calibrated by using  $\text{HgCo}(\text{SCN})_4$  as a standard.

The magnetic moment in solution was determined by the Evan's method<sup>9</sup> using a 200 MHz Fourier transform  $^1\text{H}$  NMR instrument (UCB-200). In this method, shifts in the proton resonance lines of inert molecules caused by the paramagnetic molecules (eg. manganese porphyrin) are measured and the magnetic moment of the paramagnetic substance was calculated by the standard procedure.<sup>9</sup> In a typical experiment, the manganese porphyrin was accurately weighed (1-2 mg) and dissolved in a known volume (0.3-0.5 ml) of dichloromethane- $\text{d}_2$  (99.6+ atom percent) containing tetramethylsilane (TMS) as an internal standard. The solution was placed in the inner tube of a 5 mm double concentric tube (Wilmad Glass Co.). The solvent containing TMS was then placed in the outer portion of the tube. The frequency shifts due to manganese porphyrin were then measured from the TMS signal and that of the residual protons of the solvent. The shifts in both the cases agreed within 0.2 Hz and the average value was taken for the calculation of magnetic susceptibility. The possible thermal decomposition of the compound was minimized by carrying out the experiment within 5 minutes of the preparation of the solution; the amount of decomposition (as checked from the visible spectrum) was less than 5%.

X-band EPR spectra were recorded on a Varian Model E109 spectrometer equipped with a low temperature dewar (Air Products, Ltd.).

Spectroelectrochemistry was performed in an optically transparent thin layer electrode assembly<sup>10</sup> in dichloromethane with tetrabutylammonium perchlorate as supporting electrolyte with an IBM EC/225 Voltametric Analyzer potentiostat.

Elemental analyses were performed by the Microanalytical Laboratory operated by the Department of Chemistry, University of California, Berkeley.

### Materials

Mn<sup>III</sup>TPP(OAc) was synthesized by literature methods.<sup>11</sup> The chloride form of this compound was made by the addition of an ice-cold aqueous solution of sodium chloride to a cold solution (5°C) of MnTPP(OAc) in DMF. The green precipitate formed was filtered, washed several times with water, and air dried. The crude sample so obtained was dissolved in dichloromethane and loaded on an alumina column. The manganese porphyrin was then eluted with methanol-chloroform (1:9 v/v). The eluent was then evaporated to dryness, dissolved in methanol, and reprecipitated by the addition of an equal volume of 6 M HCl. The green precipitate was filtered, washed with water, and air dried. The sample was recrystallized by dissolving in benzene and precipitating by the addition of hexane. The precipitate was then filtered, washed with hexane and dried in vacuum. Purity of this compound was checked by its elemental analysis and visible and IR absorption spectra.

Phenoxathiin hexachloroantimonate [ $(\text{C}_6\text{H}_4\text{SC}_6\text{H}_4\text{O})\text{SbCl}_6$ ], was synthesized<sup>12</sup> by reacting stoichiometric amounts of phenoxanthiin and antimony pentachloride in dichloromethane. The cation radical formed was filtered under a stream of nitrogen and dried under vacuum. Purity of the compound was checked by elemental analysis.

Dichloromethane was purified by refluxing over calcium hydride followed by distillation in a N<sub>2</sub> atmosphere onto activated molecular sieves. Hexane, chloroform and tetrachlorethane were HPLC grade, or the best commercially available grade, and were used without further purification.

Synthesis of MnTPP(Cl)(SbCl<sub>6</sub>). MnTPP(Cl), 0.5 g (0.71 mmol), was dissolved in 50 ml of CH<sub>2</sub>Cl<sub>2</sub> at room temperature and phenoxathiin hexachloroantimonate, 0.55 g (1.03 mmol), was added to it. The reaction



was carried out in a nitrogen atmosphere. The solution was stirred for 30 min and filtered into 100 ml of cold (5°C) hexane. The resulting precipitate was collected by filtration, rinsed with hexane, and air dried to yield amorphous powder of  $\text{MnTPP}(\text{Cl})(\text{SbCl}_6)$ .

Crystal Growth. Diffraction-quality single crystals of  $\text{MnTPP}(\text{Cl})(\text{SbCl}_6) \cdot 4 \text{C}_2\text{H}_2\text{Cl}_4$ , 1, were grown by dissolving the amorphous powder of  $\text{MnTPP}(\text{Cl})(\text{SbCl}_6)$  in a minimum quantity of 1,1,2,2-tetrachloroethane and adding an equal volume of hexane to it. The solution was then left undisturbed at -20°C for 24 hrs. The resultant black crystals were filtered, rinsed carefully with hexane and dried in air. The sample crystallized with four solvent molecules as determined from the carbon and chlorine analysis. Calculated for  $\text{MnTPP}(\text{Cl})(\text{SbCl}_6) \cdot 4\text{C}_2\text{H}_2\text{Cl}_4$ : C 36.56; H 2.11; N 3.28; Cl 47.68; Mn 3.22; Sb 7.15. Found: C 36.57; H 2.05; N 3.25; Cl 46.20; Mn 3.22; Sb 7.98. Purity of the compound was judged mainly from the ratios of C/N and Mn/N which were in good agreement with the calculated values. An attempt to grow crystals from dichloromethane was not successful.

Crystallographic Methods. A shiny black crystal of approximate dimensions 0.20 x 0.30 x 0.36 mm, mounted with epoxy on a glass fiber, was used for collection of the X-ray diffraction data. Intensities were collected on an Enraf-Nonius CAD-4 automatic diffractometer at room temperature. The data reduction was standard, with the exception that no absorption corrections were made. The structure was solved by first locating the Sb atom, using Patterson and direct methods, and then locating other atoms by iterative difference Fourier maps. The program SHELX<sup>13</sup> was used for both the structure solution and the refinement. During the latter stages of the refinement the phenyl groups attached to the porphyrin ring were constrained to an ideal geometry in order to reduce the number of overall parameters. After it was clear that the chloride attached to the manganese was distributed between two sites, their occupancies and temperature factors were refined in alternate cycles due to the high correlation between these parameters. All atoms were refined anisotropically, except for the phenyl atoms which were assigned rigid body anisotropic thermal parameters (which can be

converted to atomic isotropic temperature factors). No hydrogen positions were included in the model. The largest peaks in the final difference Fourier were the correct distance from appropriate atoms and were likely due to hydrogens.

### RESULTS AND DISCUSSION

Oxidation of  $\text{Mn}^{\text{III}}\text{TPP}(\text{Cl})$  in dichloromethane by one equivalent of the one-electron oxidant phenoxathiin hexachloroantimonate,  $\text{C}_6\text{H}_4\text{SC}_6\text{H}_4\text{O}(\text{SbCl}_6)$  followed by recrystallization of the crude material from  $\text{C}_2\text{H}_2\text{Cl}_4$  leads to black crystals of  $\text{MnTPP}(\text{Cl})(\text{SbCl}_6) \cdot 4\text{C}_2\text{H}_2\text{Cl}_4$ , 1, which exhibits the visible spectrum shown in Fig. 1. An identical spectrum obtains when  $\text{Mn}^{\text{III}}\text{TPPCl}$  is electrochemically oxidized by one electron at a gold minigrad electrode in a thin-layer cell. (Oxidation at +1.1 V relative to an SCE reference electrode in dichloromethane containing 0.1 M tetrabutylammonium perchlorate). The spectrum shown in Fig. 1 is that of the one-electron oxidation product of  $\text{Mn}^{\text{III}}\text{TPP}(\text{Cl})$ , and the peak in the spectrum at 476 nm is not due to residual  $\text{Mn}^{\text{III}}\text{TPP}(\text{Cl})$ , as excess phenoxathiin oxidant or prolonged electrochemical oxidation does not change the spectrum. Similar electronic spectra of oxidized MnTPP species have been reported by Harriman<sup>14</sup> and Goff.<sup>15</sup>

The assignment of 1 as a  $\text{Mn}^{\text{III}} \pi$ -cation radical compound is based on its crystal structure, the magnetic susceptibility of both the solid and its solution, its solution visible spectrum and its spectral behavior upon ligand metathesis. The results are summarized briefly below and then followed by detailed comments.

Magnetic susceptibility measurements on the solid gave a magnetic moment  $\mu_{\text{eff}} = 4.91 \mu_{\text{B}}$ . This is close to the calculated value of  $\mu_{\text{eff}} = 5.19 \mu_{\text{B}}$  for a  $\text{Mn}^{\text{III}}$  species, which is  $d^4(S = 2)$  together with an independent spin ( $S = \frac{1}{2}$ ) on the oxidized porphyrin ring. Table 1 shows the magnetic moments for this configuration (A) as well as other possible ones for a one-electron oxidation product of  $\text{Mn}^{\text{III}}\text{TPP}$ .

Table 1

Calculated Magnetic Moments for Manganese Porphyrin  
Configurations

Configuration	$\mu_{\text{eff}}$ (calc) ( $\mu_B$ )
A Mn <sup>III</sup> TPP <sup>+</sup> . Independent spins	5.19
B Mn <sup>IV</sup> TPP 3	3.87
C Mn <sup>III</sup> TPP <sup>+</sup> . Ferromagnetic coupling	5.91
D Mn <sup>III</sup> TPP <sup>+</sup> . Anti-ferromagnetic coupling	3.87

Species B is ruled out on two counts. The  $\mu_{\text{eff}}$  value of 3.8 is not consistent with the observed one of 4.91, and the visible solution spectrum shows no evidence of bands at 420 and 535 nm that are characteristic of a Mn<sup>IV</sup> porphyrin.<sup>7</sup>

Species C and D in the solid are also ruled out, both by their mismatch of  $\mu_{\text{eff}}$  with the observed value and by evidence from the X-ray crystal structure, which shows that the C and N atoms of the porphyrin ring as well as the Mn atom are all coplanar. Magnetic coupling of the two spin sites is only possible if the ring is puckered.

In solution, 1 appears to change to state C as shown by the increase of its  $\mu_{\text{eff}}$  to a value between 5.7 and 6.7. Then upon substitution of CH<sub>3</sub>O<sup>-</sup> ligands for Cl<sup>-</sup> and SbCl<sub>6</sub><sup>-</sup>, an electron is moved from the metal center to the porphyrin ligand with the production of a Mn<sup>IV</sup> porphyrin species as shown by visible and EPR spectra.

## Electronic Spectra

Numerous studies of electronic spectra of metalloporphyrin species have led to the compilation of a few "empirical rules" that help to distinguish between a  $\pi$ -radical and a porphyrin where the central metal ion has been oxidized.<sup>16</sup> In general, the broadening of a Soret band with less intensity relative to that of unoxidized-metallo porphyrins was taken as indicative of  $\pi$ -cation species. The appearance of the visible spectrum of 1 with a broadened Soret of diminished intensity is consistent with the formulation of 1 as a  $\pi$ -radical species. For a  $Mn^{IV}$  porphyrin species a Soret band with maximum around 420 nm region with a single band about 535 nm is expected.<sup>7</sup>

Structure. A drawing of  $MnTPP(Cl)(SbCl_6) \cdot 4C_2H_2Cl_4$ , showing the coplanarity of the porphyrin core atoms with the manganese atom, is shown in Fig. 2. The four solvent molecules are not shown in Fig. 2 but are included in the stereo view of the crystal packing in the unit cell as shown in Fig. 3. Important bond distances and the crystal parameters are given in Table 2.

The structure (Fig. 3) consists of parallel rows of MnTPP units with centers offset; an  $SbCl_6$  anion is located equidistant between porphyrin cores. A chloride is axially bound to the Mn and has a 50% occupancy at sites above and below the porphyrin ligand. The  $SbCl_6$  anion is not situated on this Mn-Cl axis but rather is displaced with a Mn-Cl-Sb angle of  $132^\circ$ ; the closest approach of a Cl of the  $SbCl_6$  anion to the Mn is 4.72 Å. Thus, the manganese is five coordinate and as such might be expected to be displaced out of the nitrogen plane toward the ligand in an analogous pattern to  $Mn^{III}TPPX$  compounds.<sup>5</sup> With the present case of disorder of the chloride sites, the manganese atom would exhibit an elongated vibrational ellipsoid, but our data do not show this result. The porphyrin core carbon atoms, as well as the nitrogen and manganese, are coplanar with only random small deviations from the mean plane (the largest displacement is 0.12 Å of a meso carbon and the average absolute deviation is 0.05 Å).

Table 2

Crystallographic Data for  
 $\text{Mn}^{\text{III}}\text{TPP}(\text{Cl})(\text{SbCl}_6) \cdot 4\text{C}_2\text{H}_2\text{Cl}_4$

Space Group -  $P_1$

Cell Parameters       $a = 12.1969(14)$ ,  $b = 12.4478(9)$ ,  
                               $c = 12.9537(12)$   
                               $\alpha = 64.795(7)^\circ$ ,       $\beta = 70.701(8)^\circ$ ,  
                               $\gamma = 87.398(7)^\circ$   
                              VOLUME =  $1669 \text{ \AA}^3$ ,  $Z = 1$

Radiation =  $\text{MoK}_\alpha$  ( $\lambda = 0.71073 \text{ \AA}$ )

Data Collection - 4352 data ( $2\theta = 3-45$  degrees)

4048 data greater than  $3.0 \text{ sigma } F_0$

$R$  (4163 data) - 4.22%

$R_w$  (4048 data) - 4.57%

Important distances

Mn-N                     $2.00(8) \text{ \AA}$  (average of four distances)

Mn-Cl                    $2.32(1) \text{ \AA}$

Mn-Cl( $\text{SbCl}_6$ )       $4.72$

Magnetic Susceptibility. The planarity vs. ruffling of metallo-porphyrin cation radical species has been judged to be important in determining spin state.<sup>19</sup> The generalization is that loss of  $D_{4h}$  symmetry by ruffling of the porphyrin atoms destroys the orthogonality of the ligand  $a_u$  and the metal  $d$  magnetic orbitals, thereby providing an overlap pathway for ferromagnetic or antiferromagnetic coupling of unpaired metal  $d$  electrons and a  $\pi$ -cation radical unpaired electron. Conversely, a strictly planar metalloporphyrin cation radical species would be expected to have independent spin states of the paramagnetic metal and cation radical. Magnetic susceptibility measurements (SQUID method) on the x-ray diffraction crystalline material show normal paramagnetism over the temperature range of 5-100 K with no variation in susceptibility at field strengths ranging from 5,000-40,000 gauss. After application of diamagnetic corrections for all metalloporphyrin and solvent atoms, a plot of  $1/\chi_M$  vs temperature yielded a straight line

with the temperature intercept of +0.38 K, indicating Curie-Weiss behavior. With use of the equation  $\mu_{\text{eff}} = 2.83 (\chi_M(T - \theta))^{\frac{1}{2}}$  and the experimental Weiss constant of +0.38 K the magnetic moment was calculated to be  $4.91 \mu_B$ .

In the oxidation of  $\text{Mn}^{\text{III}}\text{TPP}(\text{Cl})$  the electron could come from the metal-centered orbital to form an  $\text{Mn}^{\text{IV}}\text{TPP}^{+2}$  ion.  $\text{Mn}^{\text{IV}}$  is a  $d^3$  ion and would have an expected spin-only moment of  $3.87 \mu_B$ . Three different spin states can be distinguished if 1 is a  $\text{Mn}^{\text{III}}$ ,  $S = 2$ ,  $\pi$ -cation radical species,  $S = \frac{1}{2}$ : (A) The antiferromagnetic state with a resultant spin of three halves and expected moment of  $3.87 \mu_B$ ; the ferromagnetic coupled state with a resultant spin of five halves and spin-only magnetic moment of  $5.91 \mu_B$ ; the independent spin  $S = 2$ ,  $S = \frac{1}{2}$  state ( $\mu = (\mu_1^2 + \mu_2^2)^{\frac{1}{2}}$ ) with an expected moment of  $5.19 \mu_B$ . The observed value of  $4.91 \mu_B$  in the solid sample excludes a  $\text{Mn}^{\text{IV}}\text{TPP}^{+2}$  species as well as antiferromagnetic-coupled  $\text{Mn}^{\text{III}}$   $\pi$ -cation radical. The  $4.91 \mu_B$  value is closer to that expected for an independent spin system and this choice is consistent with the structure determination, that is, the planarity of the molecule maintains strict orthogonality of porphyrin and metal magnetic orbitals. This provides no means of overlap leading to exchange and coupling.

Repeated magnetic susceptibility measurements in dichloromethane- $d_2$  solution ( $^1\text{H}$  NMR shift method) gave a range of values from  $5.7$ - $6.7 \mu_B$ . Two approaches were used in determining these values. One was to dissolve weighed samples of 1 in dichloromethane and the other was to titrate  $\text{Mn}^{\text{III}}\text{TPPCl}$  with phenoxathiin hexachloroantimonate (both in  $\text{CD}_2\text{Cl}_2$ ). Both methods lead to higher  $\mu_B$  values in solution than in the solid. This suggests that in solution the planarity of the metallo-porphyrin metal and porphyrin core is lost and the ferromagnetically coupled spin system is favored. Our results differ from Goff, *et al.*<sup>15</sup> who prepared  $\text{MnTPPCl}(\text{ClO}_4)$  by electrochemical oxidation. The electronic spectrum given by these workers agrees with Fig. 1 in this work, but they report a solution magnetic moment of  $4.9 \mu_B$  and they observe a  $g = 2.0$  X-band EPR signal at 77 K. Species 1 is EPR silent to 8 K. Goff and co-workers also conclude that  $\text{MnTPPCl}(\text{ClO}_4)$  is a manganese-III

$\pi$ -cation radical and the only difference with 1 is in the ligands present.

We are currently examining a series of oxidized MnTPP(X)(X') species to further explore possible spin state changes and changes in magnetic interactions as a function of coordinating anions.

IR Spectra. A recent paper by Goff, Reed and co-workers concluded that a characteristic infrared band in the  $1250-1300\text{ cm}^{-1}$  can be used as a diagnostic tool for metallotetraphenylporphyrin  $\pi$ -cation radical species.<sup>18</sup> The appearance or absence of this band has been cited as evidence in a number of papers concerning oxidized metalloporphyrin compounds. The infrared spectra of MnTPPCl and 1, MnTPPClSbCl<sub>6</sub>·4C<sub>2</sub>H<sub>2</sub>Cl<sub>4</sub> are given in Fig. 4. A new band at  $1280\text{ cm}^{-1}$  appears for 1. There are also changes in the  $600-800\text{ cm}^{-1}$  region. We noted that prolonged exposure of solid samples of 1 to vacuum leads to deterioration of the crystalline nature of the material and elemental analyses confirmed that the solvate molecules were lost from the lattice. A material that analyzed as MnTPP(Cl)(SbCl<sub>6</sub>), 2, yielded spectrum C in Fig. 5. The "diagnostic"  $\pi$ -cation radical band at  $1280\text{ cm}^{-1}$  disappeared and there were accompanying changes in the  $600-800\text{ cm}^{-1}$  region. With varying lengths of exposure to vacuum, materials could be obtained which gave analyses appropriate for removal of two or three solvent molecules. These materials, intermediate between 1 and 2, exhibit consistent diminution of the  $1280\text{ cm}^{-1}$  band as well as changes in the  $600-800\text{ cm}^{-1}$  region. The solvent, C<sub>2</sub>H<sub>2</sub>Cl<sub>4</sub>, shows broad intense absorptions at  $600-800\text{ cm}^{-1}$  and  $1000-1300\text{ cm}^{-1}$ .

Our results seem to indicate that the band at  $1280\text{ cm}^{-1}$  as well as others in the  $600-800\text{ cm}^{-1}$  region are due to C<sub>2</sub>H<sub>2</sub>Cl<sub>4</sub> solvent molecules in the lattice. Samples of material 2 when dissolved in dichloromethane gave an electronic spectrum identical to that of 1. Magnetic susceptibility measurements (SQUID) were also made on samples of 2. These showed normal paramagnetism with a strictly linear Curie-Weiss plot over the temperature range 5-100 K with a Weiss constant of 0.16 K. There was no field dependence over a 5000-40,000 gauss range. The

experimental magnetic moment was  $4.71 \mu_B$  which compares to the  $4.9 \mu_B$  of samples of 1 which include four solvent molecules. This comparison would suggest that there were no major spin state changes in transforming the crystalline solid of 1 to the amorphous powder of solid 2, even though the band at  $1280 \text{ cm}^{-1}$  disappears.

Many metallotetraphenylporphyrin oxidation studies are carried out in chlorocarbon solvents and the possibility exists that incorrect interpretation of the appearance of infrared bands in the  $1250\text{-}1300 \text{ cm}^{-1}$  region have been made. However, we believe the best interpretation of our experimental results of electronic spectrum, x-ray structure and magnetic susceptibility measurements is that 1 is indeed a  $\text{Mn}^{\text{III}}$   $\pi$ -cation radical species. In the absence of a definitive study of the origin of the  $1250\text{-}1300 \text{ cm}^{-1}$  band no conclusion regarding the validity of the use of the generalized diagnostic marker can be made.

Ligand Metathesis. Indirect evidence for assignment of 1 as a  $\text{Mn}^{\text{III}}$ -porphyrin cation radical is provided by ligand exchange reactions. Several species have been characterized as  $\text{Mn}^{\text{IV}}\text{TPPX}_2$  compounds, with  $X = \text{N}_3$ ,  $^{19}\text{NCO}^{20}$  and  $\text{OCH}_3^{20}$ . The addition of an approximately tenfold excess of  $\text{NaOCH}_3$  in methanol to a  $\text{CH}_2\text{Cl}_2$  solution of 1 at  $0^\circ\text{C}$  caused an immediate change in intensity in the brown solution. The visible spectrum of the new species, 3, was dramatically different from that of 1 (Fig. 5). In a different experiment an equivalent amount of the oxidant phenoxathiin hexachloroantimonate was added to a solution of  $\text{Mn}^{\text{III}}\text{TPP}(\text{Cl})$  in  $\text{CH}_2\text{Cl}_2$  which also contained a fivefold excess of  $\text{NaOCH}_3$  in methanol. In the absence of methoxide ion phenoxathiin hexachloroantimonate oxidizes  $\text{Mn}^{\text{III}}\text{TPP}$  to the  $\pi$ -cation radical (Fig. 5a); in the presence of methoxide ion spectrum 5b is produced. Spectrum 5b can be attributed to that of  $\text{Mn}^{\text{IV}}\text{TPP}(\text{OCH}_3)_2$  as its absorption and EPR (see below) spectra are very similar to that reported for  $\text{Mn}^{\text{IV}}\text{TPP}(\text{OCH}_3)_2$ .<sup>20</sup> Thus  $\text{Mn}^{\text{IV}}\text{TPP}(\text{OCH}_3)_2$  can be generated from either  $\text{MnTPP}(\text{Cl})$  or the  $\text{MnTPP}$  cation radical.

Additional confirmation of the identity of 3 as a manganese-IV species is provided by its X-band EPR. Species 1 is EPR silent from



200-10,000 gauss at 8 K. If a solution of 1 in  $\text{CH}_2\text{Cl}_2$  is warmed to about  $-50^\circ\text{C}$  and  $\text{NaOCH}_3$  is added with the temperature then lowered to 8 K, the EPR spectrum exhibits a signal at  $g = 5.4$  and a broad poorly resolved signal in the  $g = 2$  region. This spectrum is similar to that observed for  $\text{Mn}^{\text{IV}}\text{TPP}(\text{OCH}_3)_2$ .<sup>20</sup> The electronic spectrum of the sample from the EPR measurements was identical to that shown in Fig. 5b.

Taken together, these results indicate that coordination by methoxide, a strong  $\pi$ -donating ligand, has shifted the site of oxidation in the porphyrin ring in 1 to the manganese in 3.

### Redox Catalyst

In solution, after a time, 1 reverts to the original  $\text{Mn}^{\text{III}}\text{TPP}$  species, as determined by the electronic spectrum. With purified, dried dichloromethane as the solvent this reduction occurs over a 10-15 minute period. If the dichloromethane is not rigorously free of HCl or if small amounts of methanol, water or similar solvents are added the process occurs more rapidly. In none of these cases has the reducing agent or its oxidized products been identified. The reactivities of  $\text{Mn}^{\text{III}}\text{TPP}^+$ ,  $\text{Mn}^{\text{IV}}\text{TPP}$ ,<sup>20</sup> and other high-valent manganese porphyrin complexes,<sup>6,8</sup> as evidenced by their reactions with water, HCl and other organic substrates, justify interest in them as potential redox catalysts in artificial photosynthesis assemblies. Spectral measurements indicate that oxidation of  $\text{Mn}^{\text{III}}\text{TPP}$  to  $\text{Mn}^{\text{III}}$  porphyrin  $\pi$ -cation radical followed by return to  $\text{Mn}^{\text{III}}\text{TPP}$  can be repeated many times without significant degradation of starting materials. Our observation that the site of oxidation in  $\text{Mn}^{\text{III}}\text{TPP}$  compounds can be controlled by the ligands coordinated to the manganese ion is also of potential importance. Conversion of  $\text{Mn}^{\text{III}}$  porphyrin  $\pi$ -cation radical to a  $\text{Mn}^{\text{IV}}$  porphyrin by addition of a methoxide ion, a strong  $\pi$ -donating ligand, suggests that adjustment of redox reactivities and oxidation potentials may be possible by variation of coordinating ligands.

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Figure Captions

Figure 1. Quantitative optical absorption spectra of  $\text{Mn}^{\text{III}}\text{TPP}(\text{Cl})$  (—) and 1,  $\text{Mn}^{\text{III}}\text{TPP}(\text{Cl})(\text{SbCl}_6) \cdot 4\text{C}_2\text{H}_2\text{Cl}_4$  (----) in dichloromethane.

Figure 2. ORTEP diagram of 1,  $\text{Mn}^{\text{III}}\text{TPP}(\text{Cl})(\text{SbCl}_6) \cdot 4\text{C}_2\text{H}_2\text{Cl}_4$ . Each atom is represented by its vibrational ellipsoid (50%) having the shape and the relative size concomitant with its thermal motion in the crystal. Hydrogen atoms and solvent molecules are omitted for clarity. The chloride axially bound to Mn has 50% occupancy at sites above and below the plane of the porphyrin.

Figure 3. Stereo view of the crystal packing diagrams of 1,  $\text{Mn}^{\text{III}}\text{TPP}(\text{Cl})(\text{SbCl}_6) \cdot 4\text{C}_2\text{H}_2\text{Cl}_4$  as viewed perpendicular to the crystallographic BC plane. Molecules lying within 2 unit cells in the B and C directions and one cell in the A direction are included in the diagram.

Figure 4. Infrared spectra (in KBr) of  $\text{Mn}^{\text{III}}\text{TPP}(\text{Cl})$  (a); 1,  $\text{Mn}^{\text{III}}\text{TPP}(\text{Cl})(\text{SbCl}_6) \cdot 4\text{C}_2\text{H}_2\text{Cl}_4$  (b); and 2,  $\text{Mn}^{\text{III}}\text{TPP}(\text{Cl})(\text{SbCl}_6)$  (c). Spectra were recorded at room temperature. Compound 2 was obtained upon prolonged exposure of 1 to vacuum.

Figure 5. Optical absorption spectra of 1,  $\text{Mn}^{\text{III}}\text{TPP}(\text{Cl})(\text{SbCl}_6) \cdot 4\text{C}_2\text{H}_2\text{Cl}_4$  (----) and 3,  $\text{Mn}^{\text{IV}}\text{TPP}(\text{OCH}_3)$  (—) in dichloromethane. Compound 3 was obtained either by addition of  $\text{NaOCH}_3$  to 1, or by oxidation of  $\text{Mn}^{\text{III}}\text{TPPCl}$  by phenoxanthiin hexachloroantimonate in the presence of  $\text{NaHCO}_3$ .

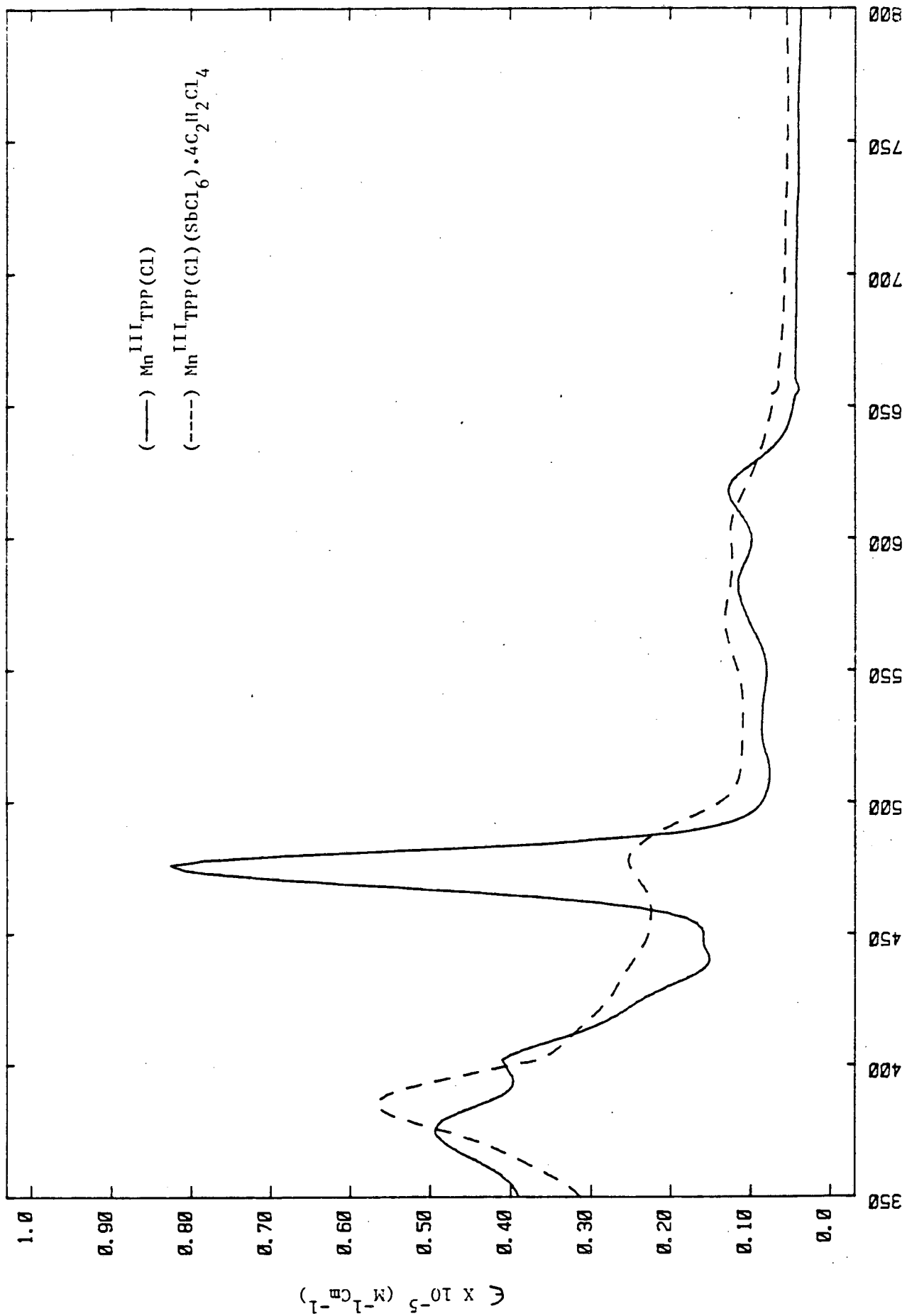


FIGURE 1 WAVELENGTH (nm)

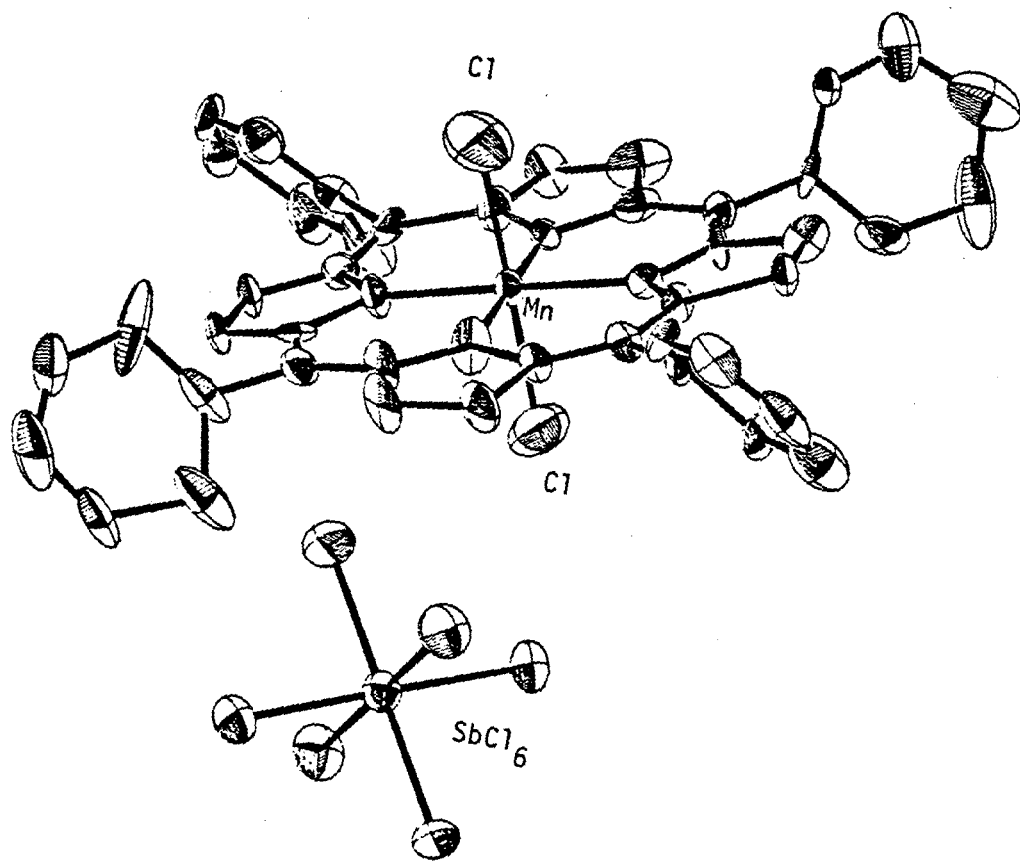


FIGURE 2

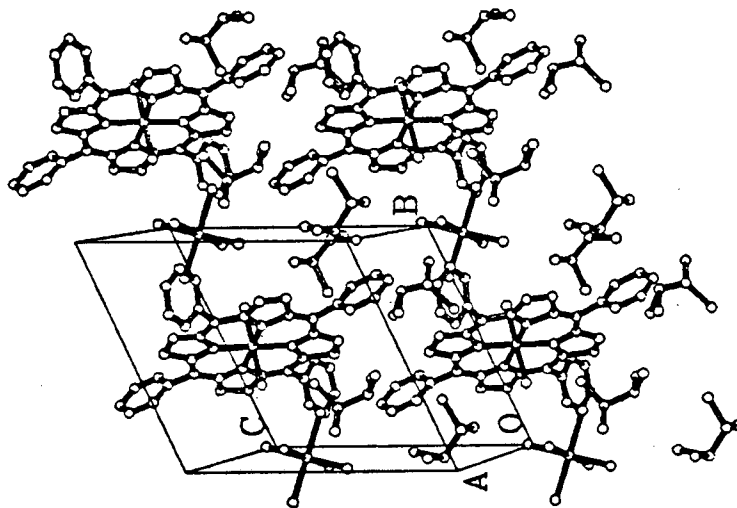
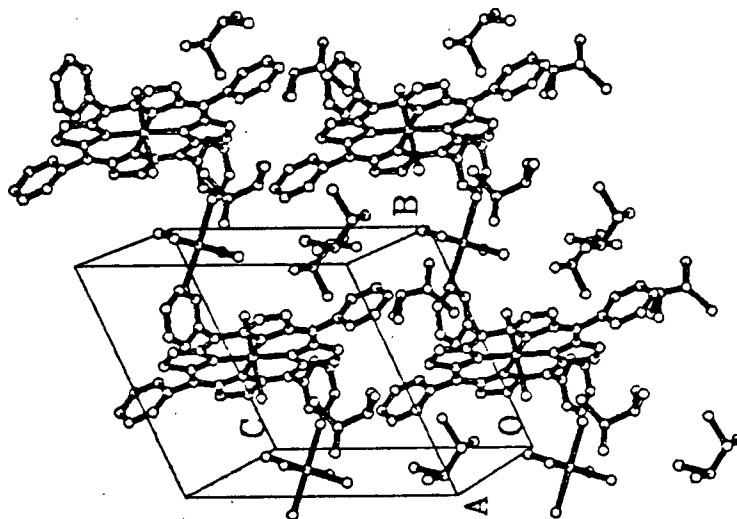


FIGURE 3



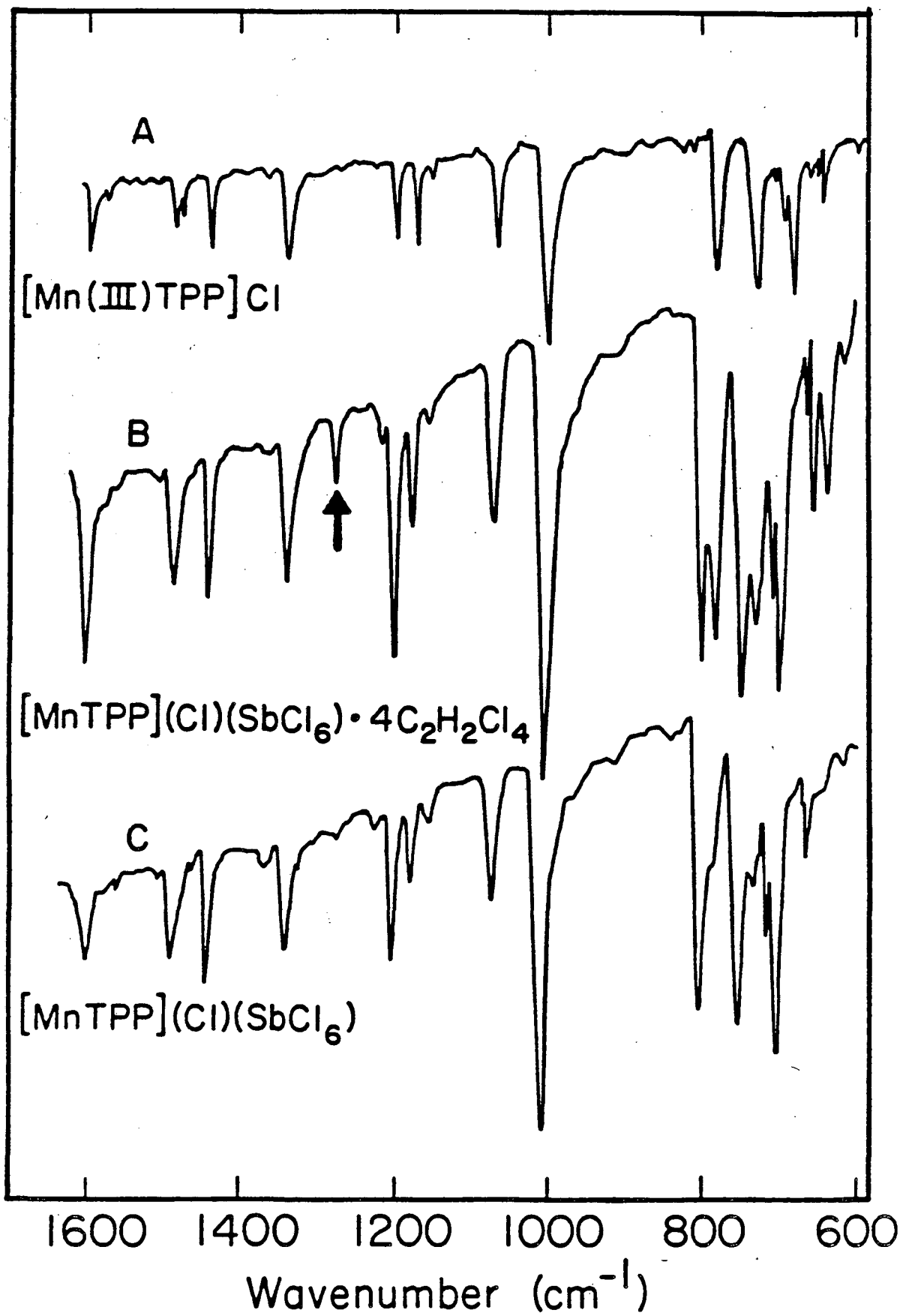


FIGURE 4

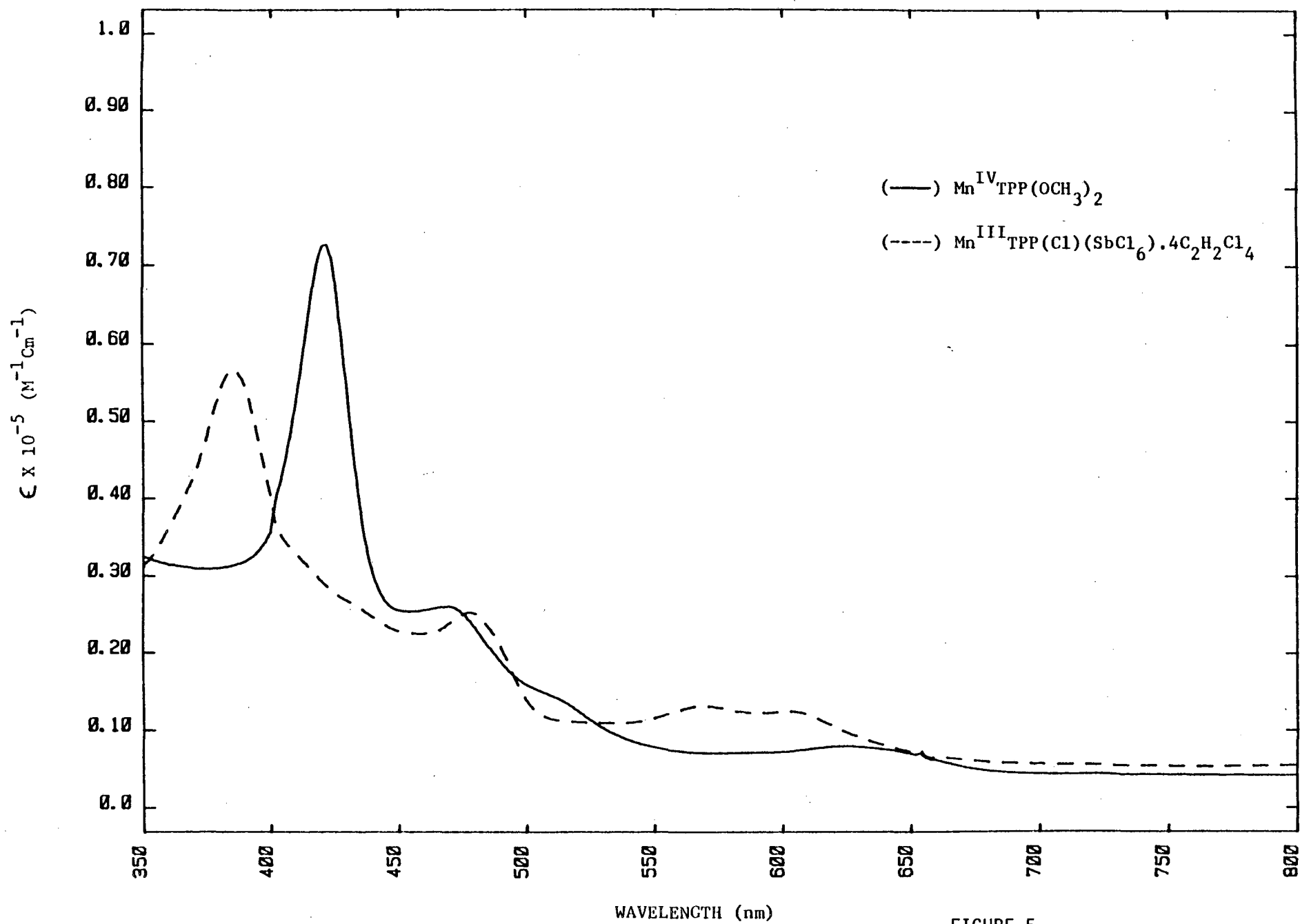
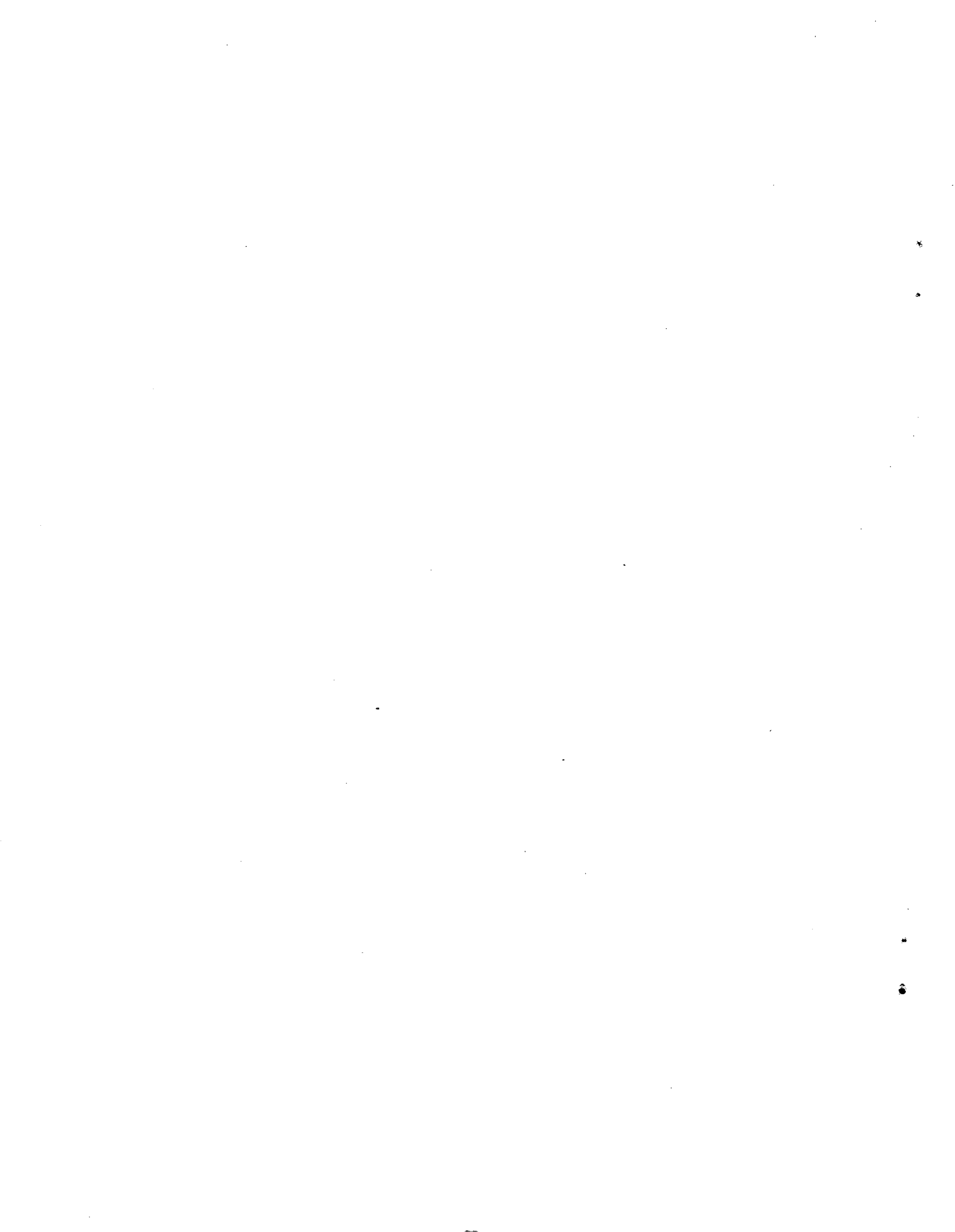


FIGURE 5



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