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## Coordination of Pyridine to Phthalocyaninomanganese and Etioporphyrin I-Manganese Complexes

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Coordination of pyridine to two phthalocyaninomanganese complexes and to (etioporphyrin I)acetatomanganese(III) was studied. The electronic spectra and chemical behavior are markedly affected by the presence of pyridine. Quantitative determination of the amount of pyridine sorbed was made by using a sensitive quartz helix balance. Two molecules of pyridine per manganese were found to add to phthalocyaninomanganese(II), and one to (etioporphyrin I)acetatomanganese(III). One pyridine per manganese bonds to  $\mu$ -oxo-bis[phthalocyaninomanganese(III)], and another is weakly held. The coordinated pyridine can be removed by heating *in vacuo*. The properties of a phthalocyaninomanganese oxide are re-examined in the light of a recent X-ray structural analysis, and part of the previously reported oxidation-reduction mechanism of phthalocyaninomanganese in pyridine solution is revised.

In a previous discussion<sup>1</sup> we showed that pyridine plays an important role in both oxidation and reduction reactions of phthalocyaninomanganese and etioporphyrin I-manganese complexes. In the present investigation, the effect upon the electronic spectra of coordination of pyridine to the manganese atom has been studied, and the amount of pyridine bound has been determined using a quartz helix balance. Some observations on the magnetically anomalous phthalocyaninomanganese oxide are reported, and the structure of the complex is reexamined.

### Experimental Section

**Apparatus.**—Electronic spectra were taken with a Beckman Model DK-2 recording spectrophotometer, in specially constructed quartz or Pyrex cells which could be evacuated. The spectra of solid samples were obtained by subliming the sample onto the walls of the evacuated optical cell at about 400°.

**Infrared spectra** were measured on a Beckman IR-7 spectrophotometer using KBr pellets.

**Magnetic susceptibility** measurements of solid specimens were carried out by a Faraday method as reported previously.<sup>1</sup> Solution susceptibilities were measured on a Gouy balance. The authors wish to thank Professor B. B. Cunningham for the use of his apparatus.

**Quartz helix balances** having a calibrated sensitivity of about 1 cm/mg (Microchemical Specialties Co.) were used to study the sorption and desorption of pyridine. The sample, placed in an aluminum pan suspended from the balance, could be heated under vacuum by an electric tube furnace. The balance setup is fully described in ref 2.

**Electron Spin Resonance.**—A standard X-band reflection spectrometer employing a Varian cavity with 100-kcps modulation and a phase-sensitive detection unit was used for esr measurements.

**Preparation of Compounds.**—Phthalocyaninomanganese(II) and "phthalocyaninomanganese oxide" were prepared as reported previously.<sup>1</sup> The latter is now identified as  $(\text{MnPc-Py})_2\text{O} \cdot 2\text{Py}$ . Analyses are given in Table I.

**(Etioporphyrin I)acetatomanganese(III).**—Etioporphyrin I (0.47 g, 1.0 mmol) and manganese(II) acetate (0.63 g, 5.5 mmol) were heated for several hours at about 80° in 50 ml of glacial acetic acid containing 8 ml of acetic anhydride. Completion of the reaction producing the Mn(III) complex was confirmed by the electronic spectrum, which revealed no metal-free etioporphyrin. The solution was evaporated to dryness and taken up with chloroform. The excess solid manganese acetate was filtered off, and the filtrate was concentrated to a small volume. Concentration of all chloroform solutions was accomplished using a rotary evaporator at room temperature *in vacuo*.

Chromatography of the concentrated chloroform solution on a column of activated alumina (Woelm, activity grade I, or Merck, chromatographic grade) showed at least three distinct bands, one of which was nearly insoluble in chloroform but soluble in pyridine. The main, chloroform-soluble fraction was further purified by removing the solvent and then subliming the solid at 350–400° under vacuum. This procedure yields  $\text{Mn}^{\text{II}}\text{Etp} \cdot \text{HOAc}$ ; impurities and by-products of the reduction do not sublime with the complex, which upon exposure to the atmosphere is oxidized to  $\text{Mn}^{\text{III}}\text{Etp}(\text{OAc})$ . Probably the acetic acid is liberated during the reduction; as  $\text{Mn}^{\text{II}}\text{Etp}$  condenses in a cool part of the vessel, it resorbs the acetic acid vapor. The infrared spectrum of the compound in air (oxidized form) has several peaks which do not appear in the spectra of the corresponding  $\text{Ni}^{\text{II}}$ ,  $\text{Zn}^{\text{II}}$ , or  $\text{Co}^{\text{II}}$  chelates, nor in that of metal-free etioporphyrin, none of which contains acetate. A band at  $1594 \text{ cm}^{-1}$  is believed to correspond to the asymmetric  $\text{CO}_2^-$  vibration; that at  $1338 \text{ cm}^{-1}$ , to the symmetric vibration of the chelated car-

(1) G. Engelsma, A. Yamamoto, E. Markham, and M. Calvin, *J. Phys. Chem.*, **66**, 2517 (1962).

(2) L. K. Phillips, Ph.D. Thesis, Department of Chemistry, University of California, Berkeley, Calif., 1967.

TABLE I  
 CHEMICAL ANALYSIS OF PHTHALOCYANINOMANGANESE COMPOUNDS

Sample	% found				% calcd				Composition
	C	H	N	Mn <sup>e</sup>	C	H	N	Mn	
a	67.76	2.78	19.74	9.50	67.73	2.84	19.75	9.68	MnPc
b	68.42	3.33	18.79	7.85	68.34	3.57	19.10	7.49	(MnPcPy) <sub>2</sub> O·2Py
c	67.83	3.61	19.17	7.51	68.75	3.41	19.17	7.92	(MnPcPy) <sub>2</sub> O·Py
d	66.73	2.96	19.06	9.29	66.78	2.80	19.48	9.55	(MnPc) <sub>2</sub> O

<sup>a</sup> Prepared as in ref 1. <sup>b</sup> The crystals prepared from MnPc by oxidation in pyridine were washed with pyridine and diethyl ether and dried in air. <sup>c</sup> The crystals were washed with pyridine and dried overnight in a vacuum desiccator. <sup>d</sup> The crystals were heated *in vacuo* for 4 hr at 120°. <sup>e</sup> The manganese content was estimated from the amount of ash, assuming the ash was in the form of Mn<sub>3</sub>O<sub>4</sub>.

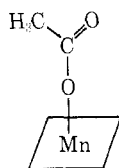
boxylate. Weakly adsorbed acetic acid as well is indicated by a peak at 1714 cm<sup>-1</sup>.

*Anal.* Calcd for Mn<sup>III</sup>Etp(OAc), C<sub>34</sub>H<sub>38</sub>N<sub>4</sub>O<sub>2</sub>Mn: C, 69.1; H, 6.7; N, 9.5; O, 5.4; Mn, 9.3. Found: C, 68.1; H, 6.6; N, 9.7; O (by difference), 6.1; Mn, 9.5. (Manganese content was estimated as ash, assuming that the ash consisted of Mn<sub>3</sub>O<sub>4</sub> only.) The empirical formula is C<sub>33</sub>H<sub>38</sub>N<sub>4</sub>O<sub>2</sub>Mn.

## Results

**(A) Coordination of Pyridine to (Etioporphyrin I)acetatomanganese(III).**—The reaction of (etioporphyrin I)acetatomanganese with pyridine vapor was studied using the quartz helix balance. The sample readily sorbs pyridine (Figure 1, stage I); when the system is again evacuated, 1 equiv of pyridine is held tightly at room temperature (stage II) but can be removed at higher temperatures (stage III). Although the rate of surface adsorption, in excess of the chemisorbed pyridine, varies among samples, both the rate and the stoichiometry of the chemical absorption are reproducible.

The absorption and desorption of 1 equiv of pyridine is in agreement with the proposed structure, in which the base would occupy the sixth coordination position on the manganese



When (etioporphyrin I)acetatomanganese(III) is sublimed *in vacuo* onto the wall of an optical cell, the spectrum obtained is that corresponding to divalent manganese, probably (etioporphyrin I(acetic acid))-manganese(II) (Figure 2). The coordination of pyridine causes an over-all intensity increase and a sharpening of the bands, as well as a shift of the Soret band from 402 to 442 m $\mu$ . The introduction of air, with no pyridine present, causes rapid oxidation to trivalent manganese,<sup>2</sup> which explains the difficulty of obtaining divalent etioporphyrin-manganese complexes. In pyridine solution, (etioporphyrin I)manganese(II) is similarly oxidized by air, and in turn the manganese(III) chelate can be photoreduced in the absence of air.

The effect of pyridine vapor on the spectrum of the sublimed metal-free etioporphyrin is very small, supporting the contention that the base is bound to the metal atom rather than to the porphyrin itself.

## (B) Coordination of Pyridine to Phthalocyanino-

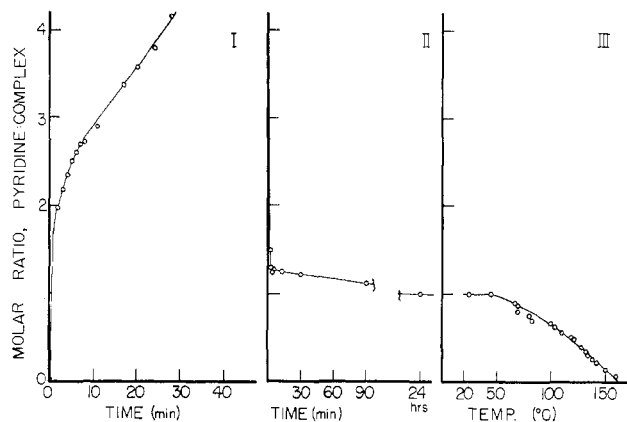


Figure 1.—Sorption and desorption of pyridine by etioporphyrinacetatomanganese(III). Molar ratio after sorption and evacuation, in subsequent experiments: 1.01, 1.00. I, sorption of pyridine vapor ( $P = 18$  torr); II, evacuation at room temperature; III, heating *in vacuo*.

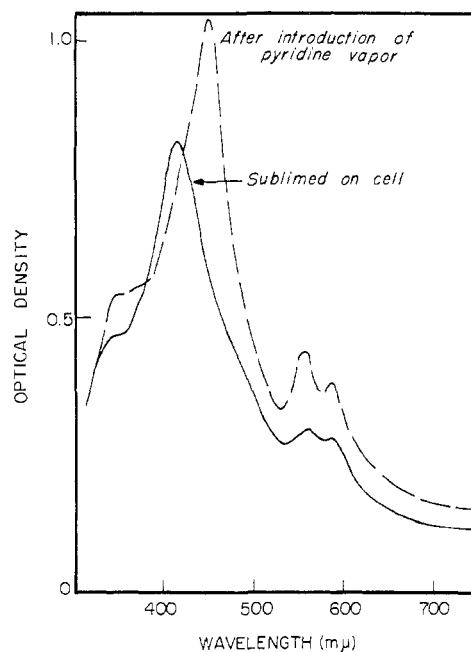


Figure 2.—Effect of pyridine vapor on the spectrum of a thin film of (etioporphyrin I)manganese(II).

**manganese(II).**—A thin film of phthalocyaninomanganese(II) is prepared by sublimation onto the walls of an optical cell *in vacuo*. When pyridine vapor is introduced into the cell in the absence of air, a remarkable change in the spectrum is observed (Figure 3). This change initially takes place rapidly, then rather

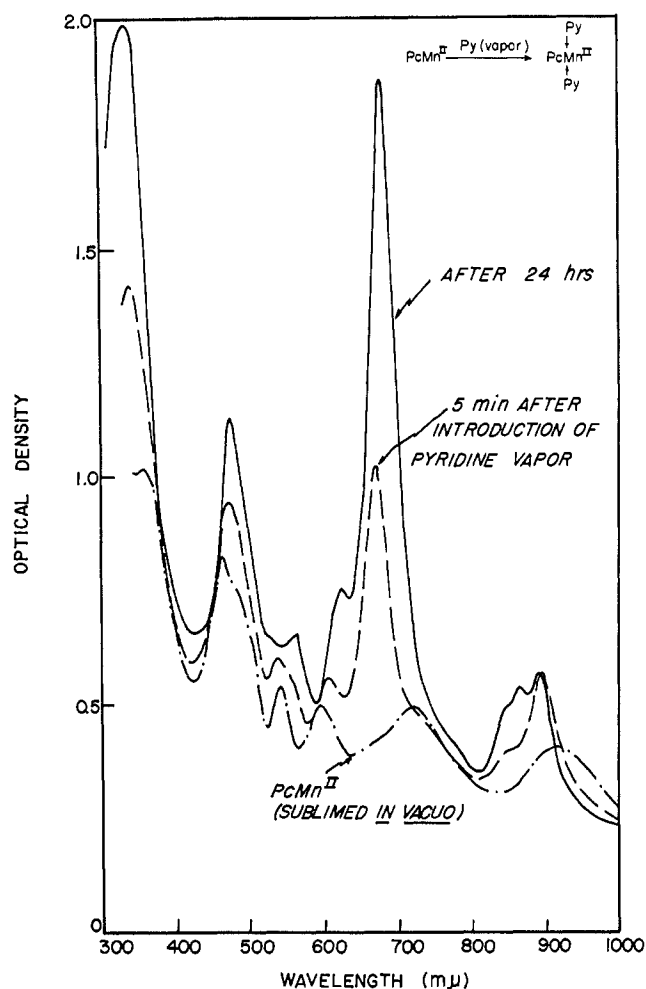
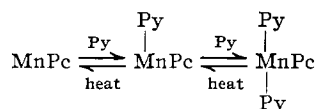


Figure 3.—Effect on the electronic spectrum of phthalocyaninomanganese(II) due to coordination of pyridine.

slowly. The resemblance of the spectrum after introduction of pyridine to that of phthalocyaninomanganese(II) in pyridine solution<sup>1</sup> suggests that the base is coordinated similarly in both solution and the solid state. Furthermore, the spectrum of phthalocyaninomanganese(II) coordinated with pyridine is reversibly affected by change of temperature (Figure 4), possibly owing to a shift of the equilibrium



(Pc, phthalocyanine anion,  $\text{C}_{32}\text{H}_{16}\text{N}_8^{2-}$ ; Py, pyridine). When the cell is evacuated and heated at  $100^\circ$  for 1 hr, the pyridine is desorbed and the original spectrum of solid phthalocyaninomanganese(II) is restored.

The sorption of pyridine on phthalocyaninomanganese in the absence of air was investigated on the quartz helix balance. The rate of sorption varied tremendously from sample to sample and was increased by heating for a given sample. After removing the loosely absorbed pyridine by evacuating the system, up to two molecules of pyridine was found to be absorbed firmly on the complex. All of the pyridine could be removed

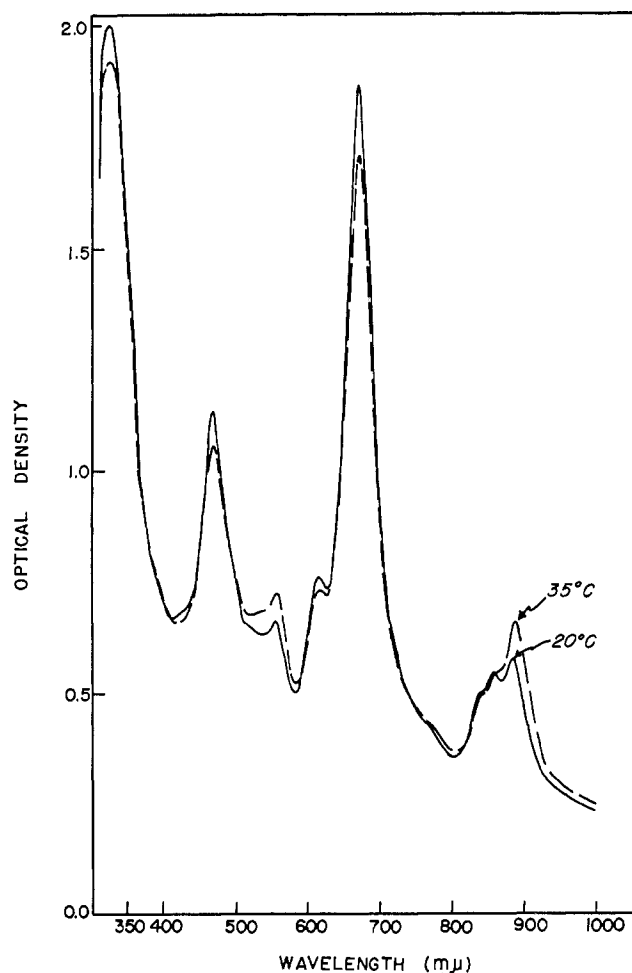


Figure 4.—Effect of temperature on the electronic spectrum of solid phthalocyaninomanganese(II) coordinated with pyridine. Note that the longest wavelength peak, which increases more rapidly than its shoulders upon exposure to pyridine (Figure 3), seems to be associated with the complex containing less pyridine.

by heating at  $50$ – $60^\circ$ . The process is illustrated in Figure 5.

From these observations, the following conclusions may be drawn. The rate of pyridine sorption depends upon surface characteristics of the sample, which are difficult to control. However, the effect of pyridine on the electronic spectrum of  $\text{Mn}^{\text{II}}\text{Pc}$  indicates that the base is chemically as well as physically sorbed. The limiting value of 2 equiv of pyridine which is strongly absorbed suggests that it occupies the two vacant coordination positions of the manganese(II).

(C) Structure of "Phthalocyaninomanganese Oxide."—By aerial oxidation of phthalocyaninomanganese(II) (I) in pyridine, a compound for which Elvidge and Lever<sup>8</sup> proposed the structure oxophthalocyaninopyridinemanganese(IV) (II) is obtained as purple rhombic crystals. The oxidation of I to II and the reduction of II to I proceed through an intermediate trivalent manganese complex (III), and we previously proposed a tentative scheme for this reaction<sup>1</sup> (Scheme I). Trivalency of the intermediate complex (III) having

(8) J. A. Elvidge and A. B. P. Lever, *Proc. Chem. Soc.*, 195 (1959).

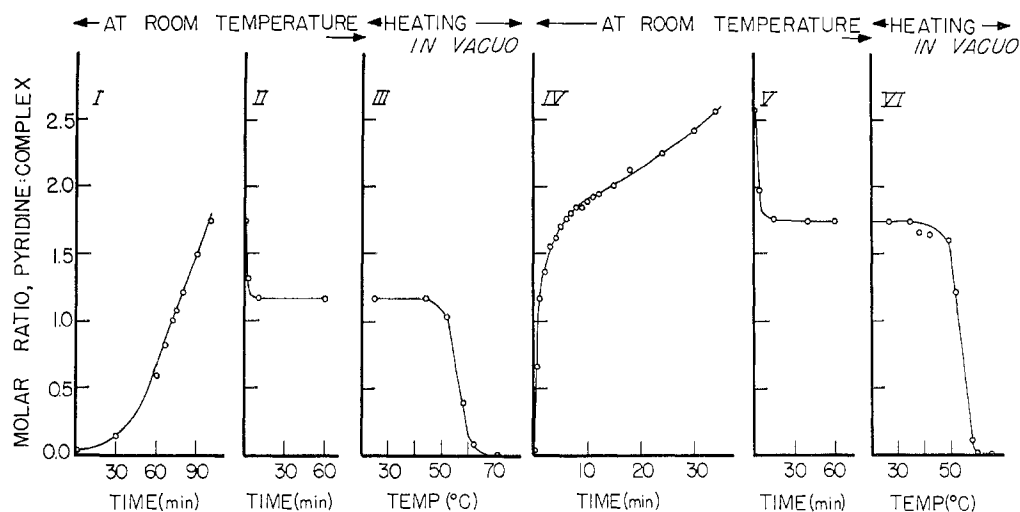
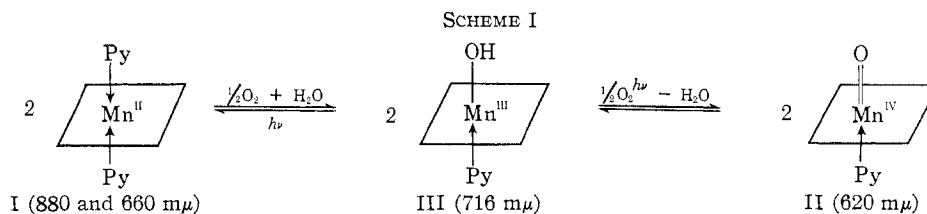
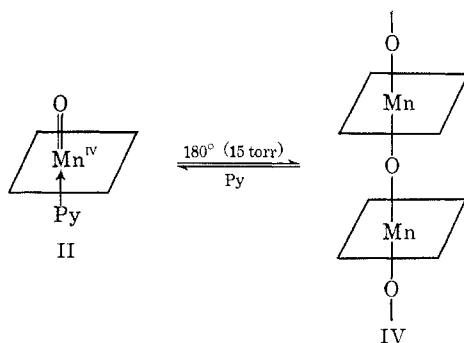


Figure 5.—Sorption of pyridine vapor on phthalocyaninomanganese(II) in the absence of air: I, sorption of pyridine vapor ( $P = 15$  torr); II, evacuation at room temperature; III, heating *in vacuo*; IV, pyridine vapor readmitted ( $P = 15$  torr); V, evacuation at room temperature; VI, heating *in vacuo*. In heating experiments, temperature was increased at the rate of  $1^\circ/\text{min}$ . Molar ratio: after stage II, 1.17; after stage V, 1.74.



an absorption maximum at  $716 \text{ m}\mu$  was established by isolating a variety of trivalent phthalocyanine-manganese complexes with unequivocal analytical and magnetic susceptibility data. However, there remained some doubt concerning the structure of II.

According to Elvidge and Lever, the infrared absorption spectrum of II shows characteristic bands of pyridine and a strong band at  $1096 \text{ cm}^{-1}$  assigned to the  $\text{Mn}=\text{O}$  linkage. Heating the compound at  $180^\circ$  (15 torr) gives a thermostable product ( $\mu_{\text{eff}} = 3.77 \text{ BM}$ ), which, they conclude, has an extended six-coordinate lattice structure (IV) with an infrared absorption band at  $820 \text{ cm}^{-1}$  assigned by them to  $\text{Mn}-\text{O}-\text{Mn}$  vibration.



Some of our results differ from theirs. The infrared spectra of the complex before and after heat treatment ( $10^{-3}$  torr,  $100^\circ$ ) were compared with that of  $\text{Mn}^{\text{II}}\text{Pc}$ . The band assigned by Elvidge and Lever to the  $\text{Mn}=\text{O}$  linkage was observed in the spectrum of the unheated compound at  $1098 \text{ cm}^{-1}$ ; bands of medium intensity at  $1220$  and  $1440 \text{ cm}^{-1}$  and other weak bands are apparently due to pyridine.<sup>4</sup> These bands

were not seen in the spectrum of  $\text{Mn}^{\text{II}}\text{Pc}$ . However, no shift of any band was observed either in the  $\text{NaCl}$  region or in the  $\text{CsI}$  region down to  $350 \text{ cm}^{-1}$  upon substitution of  $^{16}\text{O}$  by  $^{18}\text{O}$ . When the sample was heated *in vacuo* at  $100^\circ$ , the above-mentioned bands disappeared and the spectrum obtained was essentially the same as that of  $\text{Mn}^{\text{II}}\text{Pc}$ . The band at  $820 \text{ cm}^{-1}$  which Elvidge and Lever observed with their heated sample and which they ascribed to  $\text{Mn}-\text{O}-\text{Mn}$  vibration was not observed.

Magnetic susceptibility of "phthalocyaninomanganese oxide" compounds depends greatly on the history of the sample. In the solid state, the pyridine adduct is generally diamagnetic before correction for ligands (phthalocyanine,  $-422 \times 10^{-6}$  cgs unit; pyridine,  $-49 \times 10^{-6}$  cgs unit).<sup>1</sup> Because measurements are often close to experimental limits, we can only say that the magnetic moment is considerably lower than that expected for one unpaired electron.

After some or all of the pyridine has been removed from this compound by heating *in vacuo*, the room-temperature magnetic moment corresponds approximately to one unpaired electron. The moment decreases with increasing magnetic field, suggesting anti-ferromagnetic interactions. The susceptibility does not follow the Curie-Weiss law. Magnetic moments at a low-field value are given in Table II.

The magnetic behavior of these compounds is not compatible with the proposed structures II and IV and prompted us to investigate their reactions with pyridine using the quartz helix balance. The results

(4) N. S. Gill, R. H. Nuttall, D. E. Scaife, and D. W. A. Sharp, *J. Inorg. Nucl. Chem.*, **18**, 79 (1961).

TABLE II  
MAGNETIC MOMENTS<sup>a</sup> OF HEATED  
PHTHALOCYANINOMANGANESE OXIDE<sup>b</sup>

Sample	Temp, °K			
	302	296	230	77
1	1.57		1.47	1.18
2	2.07		1.94	1.45
3		2.2	1.9	1.3

<sup>a</sup> Calculated from  $\mu_{\text{eff}} \text{ (BM)} = 2.84\sqrt{\chi_M(\text{cor})T}$ . <sup>b</sup> The compound is taken to be  $(\text{MnPcPy})_2\text{O}$ .

of a typical experiment are shown in Figure 6. The crystals used were obtained from phthalocyaninomanganese(II) by aerial oxidation in pyridine solution and washed with pyridine and dry diethyl ether. More recently, an X-ray structural analysis has

desorption behavior may be explained by a change in crystal structure during heating, which is not surprising in view of Vogt's observation that removal of pyridine leads to crystalline disorder. Usually our samples were evacuated for about 1 day, and close to 1.5 mol of pyridine per g-atom of manganese remained. This led us to suspect that an adduct of this composition was formed with the unheated compound II. Indeed, a similar phenomenon occurs with a complex similar to II, bis(dibenzoylmethano)oxovanadium.<sup>6</sup> Thermogravimetry and infrared spectra show that initially pyridine adds not only in the vacant coordination position of the vanadium, but also elsewhere, possibly to the oxygen, to form a 2:1 adduct. After heating, only a 1:1 adduct is observed.<sup>6</sup> However,

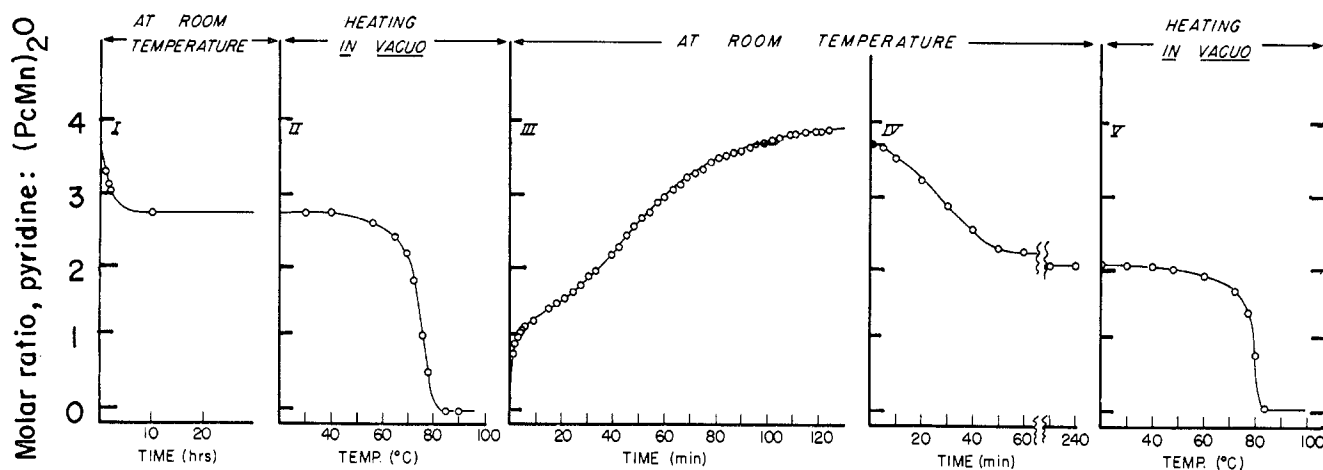


Figure 6.—Determination of pyridine contained in  $(\text{MnPcPy})_2\text{O} \cdot 2\text{Py}$ : I, evacuation at room temperature; II, heating *in vacuo*; III, exposure to pyridine vapor (15–17 torr); IV, evacuation at room temperature; V, heating *in vacuo*.

been reported<sup>5</sup> for the dinuclear complex  $(\text{Mn}^{\text{III}}\text{PcPy})_2\text{O} \cdot 2\text{Py}$ , in which the manganese atoms are joined by an oxygen bridge. The preparation of this compound differed from ours in that the crystals were washed only in pyridine, and pains were taken not to let them dry: The easily lost pyridines of crystallization seem essential for a well-ordered crystal. Dr. L. H. Vogt, Jr., kindly provided L. K. P. with a sample of the material used for the X-ray structural determination.<sup>5</sup> An experiment like that in Figure 6 was carried out, with similar results. Table III compares stoichiometries found in these two experiments.

The chemical analyses of our phthalocyaninomanganese compounds (Table I) agree with the formula of the dinuclear complex. The interstitial pyridine molecules are loosely held, although their loss can be very slow: both our preparation and Vogt's required several weeks under vacuum at room temperature to reach the composition  $(\text{MnPcPy})_2\text{O}$ . After all of the pyridine is removed by heating, the readsorbed interstitial pyridines are readily lost again. The coordinated pyridines, on the other hand, come off in the same way on the first and second heatings (Figure 6).

The difference between initial and subsequent gas

TABLE III  
PYRIDINE ADDUCTS OF  
 $\mu$ -OXO-BIS(PHTHALOCYANINOMANGANESE)

Source			
Vogt		Yamamoto <sup>b</sup>	
Treatment	Molar ratio <sup>a</sup>	Treatment	Molar ratio <sup>a</sup>
Initial	3.55		
In air 3 hr	3.45	In air	3.84
In air 80 days	3.21		
Under vacuum 3 days	2.06	Under vacuum 1 day	2.85
Under vacuum 21 days	1.96		
Heated 7 hr under vacuum, to 116°	(0)	Heated 8 hr under vacuum, to 60°	(0)
Pyridine atmosphere $\geq 16$ hr under vacuum	$\geq 3.98^c$	Pyridine atmosphere 1 hr under vacuum	3.94
Heated under vacuum to about 110°	1.99 <sup>c</sup>	Heated under vacuum to 116°	2.35
	0.27 <sup>c</sup>		0.05

<sup>a</sup> Py:  $(\text{MnPc})_2\text{O}$ . <sup>b</sup> Table I, sample b. <sup>c</sup> Averages for four cycles.

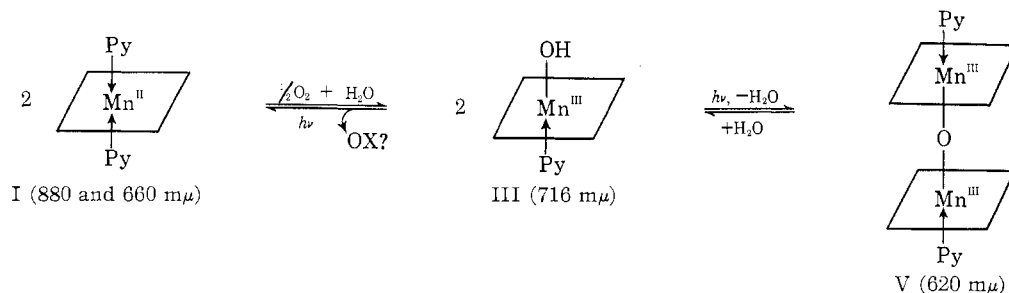
in the case of  $(\text{MnPc})_2\text{O}$ , the X-ray analysis rules out any direct bonding of the complex with more than two pyridines (per two manganese atoms), and apparently the effect of heating is simply to increase the rate of desorption.

The near-diamagnetism of  $(\text{PcMnPy})_2\text{O}$  becomes plausible once we know that the compound contains

(6) S. Ikeda, A. Yamamoto, S. Kurita, K. Takahashi, and T. Wanatabe, *ibid.*, **5**, 611 (1966).

(5) L. H. Vogt, Jr., A. Zalkin, and D. H. Templeton, *Science*, **151**, 569 (1966); *Inorg. Chem.*, **6**, 1725 (1967).

SCHEME II



manganese(III). Complete spin pairing is unusual for this ion but is possible under two conditions: (a) antiferromagnetic interactions often occur between oxygen-bridged manganese ions; (b) in  $\text{Mn}^{\text{II}}\text{PcPy}_2$ , the  $d_{xz}, d_{yz}$  orbitals are the lowest lying of the manganese d orbitals; the manganese has only one unpaired electron, in the  $d_{xy}$  orbital.<sup>2</sup> Then we might expect the manganese(III) analog to have its four d electrons paired up in the  $d_{xz}, d_{yz}$  level.

Still a mystery is the increase in magnetic moment on heating; we should comment that Elvidge and Lever's more drastic heating yielded a product with magnetic moment higher than that of our heated compound, but not yet high enough to correspond to the expected four unpaired electrons. An X-ray structural analysis of these two products would be valuable.

Establishment of the molecular structure of the oxide complex as an oxygen-bridged trivalent manganese compound requires us to revise part of our previously proposed mechanism<sup>1</sup> for the oxidation and reduction reactions of phthalocyaninomanganese. We

tentatively propose Scheme II for the reactions of this complex in pyridine solution.

The revised scheme explains reasonably well most but not all of our observations.<sup>1</sup> We suggest that the reaction  $\text{III} \rightarrow \text{V}$  is a dimerization rather than an oxidation. An absorption peak at about 630  $m\mu$  has been reported for the associated species of various complexes of a tetrasulfonated phthalocyanine.<sup>7</sup> However, it is difficult to reconcile this reaction with the apparent disproportionation of the 716- $m\mu$  species to the 620- and 660- $m\mu$  species. The requirement of air for the photochemical change of the 716- to the 620- $m\mu$  species<sup>1</sup> is also puzzling.

To understand the whole picture of the oxidation and reduction reactions, a further study focused on the role and the fate of water in combination with pyridine is required.

**Acknowledgments.**—This work was supported, in part, by the U. S. Atomic Energy Commission.

(7) K. Bernauer and S. Fallab, *Helv. Chim. Acta*, **44**, 1287 (1961); H. Kobayashi, Y. Torii, and N. Fukada, *Nippon Kagaku Zasshi*, **81**, 694 (1960).

CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,  
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## Ligand Field Theory for Pentacoordinate Molecules. I. The Electronic Spectra of Species with $D_{3h}$ and $C_{3v}$ Symmetry

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Application of the point charge model to the calculation of the energy levels of first-row transition metal ions in ligand fields of  $D_{3h}$  symmetry has been made. The results are used to make an assignment of the bands in the electronic spectra of molecules of the types  $\text{MX}_3 \cdot 2\text{L}$  and  $\text{M}(\text{TD})\text{X}$  where L is a unidentate ligand, TD is a tetradentate amine ligand, and X is halogen. Ligand field strengths for the different ligand combinations are calculated and it is shown that to obtain reasonable agreement with the observed spectra, reduction in the interelectron repulsion parameters from their free ion values must be assumed. The amount of reduction for the different ligand combinations follows the same trend as found in complexes of cubic symmetry. While the compounds of formulation  $\text{M}(\text{TD})\text{X}$  do not deviate appreciably from  $D_{3h}$  symmetry, it appears qualitatively that better agreement with the observed spectra would be found for a model of  $C_{3v}$  symmetry. Some of the band assignments made for these molecules differ from those given previously.

### Introduction

The current interest in pentacoordinate molecules of the first-row transition series elements has led to the application of a crystal field model to the interpretation of their spectra.<sup>1</sup> However, apart from the pentachlorocuprate ion,  $\text{CuCl}_5^{3-}$ , for which a molecular orbital

study has also been made,<sup>2</sup> none of the molecules considered possesses the symmetries of the two idealized

(1) (a) M. Ciampolini, *Inorg. Chem.*, **5**, 35 (1966); (b) M. J. Norgett, J. M. Thornley, and L. M. Venanzi, *J. Chem. Soc., A*, 540 (1967); (c) W. E. Hatfield and T. S. Piper, *Inorg. Chem.*, **3**, 841 (1964).

(2) W. E. Hatfield, H. D. Bedon, and S. M. Horner, *Inorg. Chem.*, **4**, 1181 (1965).