

labilized, while isocyanide is considered a nonlabilizing ligand.^{16,17}

As for molybdenum(II) compounds the formal positive charge, the ability to reach coordination number 7,

(16) G. Cetini and O. Gambino, *Atti Accad. Sci. Torino, Cl. Sci. Fis., Mat. Natur.*, **97**, 1189 (1963).

(17) R. J. Angelici, *Organometal. Chem. Rev.*, **3**, 194 (1968).

and the possibility of a more complicated mechanism¹⁸ than an SN1 or an SN2 remove the obstacles to ready and complete substitution of CO groups by isocyanides.

Acknowledgments.—This work was supported by Consiglio Nazionale delle Ricerche.

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Manganese Porphyrin Complexes. IV. Reduction of Manganese Porphyrins¹

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The polarographic reduction of a number of (anion)porphyrinmanganese(III) complexes was carried out at the dropping mercury electrode in acetonitrile and dimethylformamide solution. The polarograms show three separate reversible one-electron reductions which can be ascribed to the Mn(III) → Mn(II) reduction at -0.15 to -0.49 V (*vs. sce*) and to the first and second porphyrin reductions at -1.14 to -1.67 and -1.62 to -2.05 V, respectively. The half-wave potentials are dependent on the anion and the porphyrin. The porphyrin order, $-E_{1/2}$, for the three waves is etioporphyrin I \geq mesoporphyrin IX dimethyl ester $>$ deuteroporphyrin IX dimethyl ester \geq hematoporphyrin IX dimethyl ester $>$ protoporphyrin IX dimethyl ester $>$ $\alpha, \beta, \gamma, \delta$ -tetraphenylporphine $>$ methyl pheophorbide_a. The dependence of the Mn(III) → Mn(II) half-wave potentials on the anion was determined for the etioporphyrin I and protoporphyrin IX dimethyl ester derivatives. The anion order, $-E_{1/2}$, is $F^- > OCN^- \geq N_3^- \geq OAc^- > OH^- \geq Cl^- > SCN^- \geq Br^- > I^-$. The electronic spectra of chemically generated manganese(II) complexes were also measured.

The role that manganese plays in the photosynthetic liberation of oxygen from water is undoubtedly linked to the ability of the metal ion to function as a redox catalyst.² The utility of the metal ion in this process depends on the potential resulting from the changes between the oxidation states and the availability of suitable oxidation states. Both of these are a function of the ligand field around the metal ion.³ Although the binding site of manganese in the photosynthetic unit has not been assigned, the donor atoms surrounding the metal will most probably be nitrogen or oxygen (or less likely sulfur) of a prosthetic group or of an apoprotein.⁴ The ligand field may be composed of all of one kind of donor atom or a mixture of several kinds. Good model ligands for the nitrogen donor prosthetic group are porphyrins. In addition to being peripatetic biological ligands, they form complexes with manganese(II), manganese(III), and manganese(IV).⁵ The Mn(III) → Mn(II) potential has been determined for a few cases either by titration with dithionite or by polarographic reduction. The hydroxide complexes studied

have included those of mesoporphyrin IX,⁶ hematoporphyrin IX,^{5,7} hematoporphyrin IX dimethyl ester,^{5,7} and methyl pheophorbide_a.⁸ No detailed assessment of the factors that influence the magnitude of the redox potential was made in these studies.

We have studied the polarography of a number of manganese(III) porphyrins with a variety of anions and porphyrins. (See Figure 1.) For the case of reversible reductions, polarography provides a convenient way of determining redox potentials.⁹ By examining complexes with porphyrins of varying basicity and with axial anions of differing coordinating characteristics, we can determine the relative importance of in-plane and axial interaction on the redox potentials of manganese(III) porphyrins.

Experimental Section

Materials.—Manganese porphyrin complexes were prepared and purified according to the procedure set out in previous papers.^{10,11} Tetra-*n*-propylammonium perchlorate was prepared by a standard method.¹² Acetonitrile was purified according to the procedure of Coetzee.¹³ Dimethylformamide was refluxed

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(5) P. A. Loach and M. Calvin, *Biochemistry*, **2**, 361 (1963).

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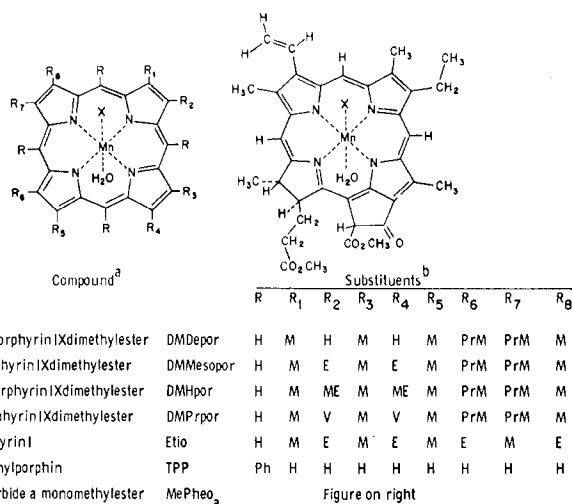
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^aX = anion; see Tables One and Two

^bM = CH₃; E = CH₂CH₃; V = CH=CH₂; ME = CHOCH₃; PrM = CH₂CH₂CO₂CH₃; Ph = C₆H₅

Figure 1.—Structural representation of manganese porphyrin complexes.

over CaH₂ and fractionated.¹⁴ All other materials used were reagent grade.

Polarographic Measurements.—Current-potential measurements were made at 23–25° with a Sargent Model XVI polarograph equipped with an *iR* compensator.¹⁵ A three-electrode cell was used with a dropping mercury electrode, mercury pool anode, and a saturated aqueous calomel reference electrode. The junction of the reference electrode and the solution was made through a coarse frit and a potassium chloride-agar salt bridge. The bridge was placed in the organic solvent only long enough (<10 min at a time) to make the measurements. In order to prevent deterioration the bridge was frequently replaced. The dme had a flow rate of 0.995 mg/sec and a drop time of 5.62 sec on an open circuit. The supporting electrolyte was 0.1 *M* N(*n*-C₃H₇)₄ClO₄. The complexes were generally only sparingly soluble in acetonitrile, while a little more soluble in dimethylformamide. Concentrations of the solutions used were 2 × 10⁻⁴ *M* in complex in most cases and lower in cases where saturated solutions were used (~1 × 10⁻⁴ *M*). High-purity dry nitrogen which had been passed through a presaturator containing the solvent was bubbled through the solutions for 10 min before each measurement to remove oxygen and was passed continuously over the surface of the solutions during the run (~5 min). The half-wave potentials and *n* values were obtained from the polarographic data in the standard way¹⁶ except that a computer program was used to obtain a least-squares fit. Each current-potential measurement was made at least twice, and in most cases, two different samples of the complex were used. The half-wave potentials are reproducible to within ±0.01 V and the *n* values to within ±0.05.

Chemical Reductions.—Reductions were carried out with a fivefold excess of sodium dithionite in 1:1 pyridine-water at pH 11.¹⁷ Manganese(III) chloride complexes of the porphyrins were dissolved in the solvent (~5 × 10⁻⁴ *M*) and the spectra were recorded on a Cary Model 14 spectrophotometer at room temperature. The solid reducing agent was then added and the solution cells were then tightly stoppered. There was no apparent reoxidation of the manganese(II) complex in the 15 min it took fully to record the spectra. When the solutions were allowed to stand in air in an unstoppered cell for several hours,

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(17) P. S. Clezy and D. B. Morrell, *Biochim. Biophys. Acta*, **71**, 165 (1963).

the complexes were reoxidized to the manganese(III) porphyrins. The final spectra were identical with those of the original solutions before reduction.

Results

Polarography.—The measurements were made in acetonitrile since it is a good polarographic solvent¹⁸ and also it is a weak electron-pair donor;¹⁹ *i.e.*, axial anions are not likely to be displaced. Dimethylformamide was also used so that we could compare our results with the extensive literature on the polarographic reduction of metalloporphyrins in this solvent.¹⁴ A typical polarogram of a manganese(III) porphyrin in acetonitrile is given in Figure 2. Although the waves

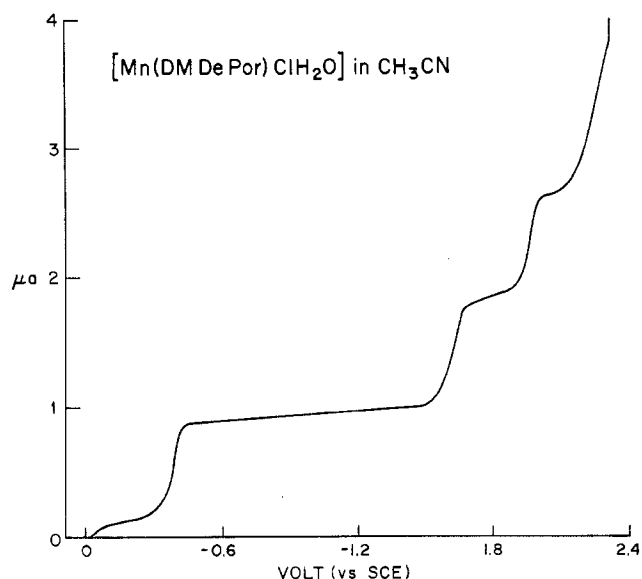


Figure 2.—Polarogram for aquo(chloro)(deuteroporphyrin IX dimethyl ester)manganese(III) in acetonitrile.

are shifted by ~+0.05 V, the same pattern is seen for dimethylformamide solutions. The polarograms show three well-defined one-electron waves of equal height in the 0 to -2.4 V region. There is also a prewave seen at ~-0.1 V. This prewave seems to be general for metalloporphyrins¹² and has been ascribed to an adsorption process at the surface of the mercury electrode.²⁰ The half-wave potentials of the first wave and their respective *n* values for the various porphyrins and anion complexes of manganese(III) are given in Tables I and II. The *n* values generally are near 1, which is con-

TABLE I
Mn(III) → Mn(II) HALF-WAVE POTENTIALS
(vs. SCE) OF Mn(Por)ClH₂O

Por	Acetonitrile		Dimethylformamide	
	<i>E</i> _{1/2} , V	<i>n</i>	<i>E</i> _{1/2} , V	<i>n</i>
Etio	-0.45	0.99	-0.40	0.95
DMMesopor	-0.43	1.00	-0.40	0.86
DMDePor	-0.38	0.99	-0.33	0.99
DMHpor	-0.37	0.75	-0.32	0.94
DMPrpor	-0.35	1.00	-0.31	0.93
TPP	-0.23	1.00	-0.22	1.00
MePheo _a	-0.23	0.86	-0.21	0.88

(18) E. O. Sherman and D. C. Olson, *Anal. Chem.*, **40**, 1174 (1968).

(19) R. S. Drago and K. F. Purcell, *Progr. Inorg. Chem.*, **10**, 304 (1964).

(20) D. G. Davis and J. G. Montalvo, Jr., *Anal. Chem.*, **41**, 1195 (1969).

TABLE II
Mn(III) → Mn(II) HALF-WAVE POTENTIALS (*vs.* SCE)
OF Mn(Por)XH₂O IN ACETONITRILE

X ⁻	Protoporphyrin IX dimethyl ester		Etioporphyrin I	
	<i>E</i> _{1/2} , V	<i>n</i>	<i>E</i> _{1/2} , V	<i>n</i>
F ⁻	... ^a	...	-0.49	0.99
Cl ⁻	-0.35	1.00	-0.45	0.99
Br ⁻	-0.32	0.93	-0.41	0.90
I ⁻	-0.29	0.92	-0.29	0.83
C ₂ H ₃ O ₂ ⁻	... ^a	...	-0.48	0.74
OH ⁻	-0.35	0.67	-0.45	1.00
N ₃ ⁻	-0.39	0.76	-0.48	0.99
SCN ⁻	-0.32	0.98	-0.40	0.96
OCN ⁻	-0.38	0.90	-0.46	1.00

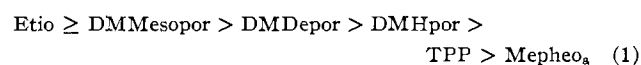
^a Insufficient solubility.

sistent with a one-electron reversible reduction. The plot of $\log(i/(i_d - i))$ *vs.* potential, whose slope yields *n*, gives good straight lines in all cases. However, in several instances the *n* values are considerably less than 1 and fall below 0.9, well outside the experimental error of our determinations. This might arise from applying "reversible" theory to slightly "irreversible" reactions and from kinetic control of the current. However, the electrode reaction appears to be diffusion controlled since a plot of the diffusion current *i*_d *vs.* the concentration in the region of our measurements, (0.5–2.5) × 10⁻⁴ M, gives a straight line. In addition, it was found that a plot of *i*_d *vs.* the square root of the mercury reservoir height gave a straight line, indicating diffusion rather than any type of kinetic control. The value of the half-wave potential was also found to be independent of concentration and drop time. All this is indicative of diffusion-controlled reversible electrode reaction. The low *n* values might be due to an adsorption of the highly surface-active porphyrin molecule on the mercury drop. This phenomenon has been noted and thoroughly substantiated for the polarography of manganese(III) hematoporphyrin IX in aqueous solutions. Although it appears likely that all the polarographic reductions listed in the tables represent reversible reductions and that the deviation of the *n* values from 1 results from adsorption phenomenon, a slight irreversibility cannot be ruled out until detailed cyclic voltammetric measurements are made. Initial measurements, however, on aquo(hydroxo)(protoporphyrin IX dimethyl ester)manganese(III) (where *n* = 0.67 from polarography) give voltgrams that are consistent with a reversible reduction⁹ ($\Delta E_p = 58$ mV).

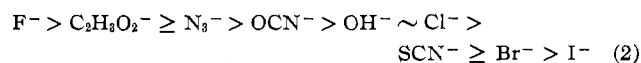
The first polarographic wave can be assigned to the Mn(III) → Mn(II) reduction. The redox potentials of (hydroxo)(hematoporphyrin IX dimethyl ester)-manganese(III) have been measured in aqueous ethanol both potentiometrically with sodium dithionite and polarographically at the dropping mercury electrode. The redox potential -0.51 V⁵ agrees quite well with the half-wave potential -0.52 V⁷ at pH 9. The product of the potentiometric reduction has been identified by its spectra and magnetic properties as a manganese(II) porphyrin.⁵ The corresponding half-wave potential for acetonitrile solutions is -0.37 V, about 0.15 V more positive than the value for aqueous solutions.

This is in agreement with a liquid junction potential for acetonitrile-water of +0.15 V (pilot ion method).²¹ Therefore it seems reasonable to assume that the first wave represents the Mn(III) to Mn(II) reduction in acetonitrile. The only other possibility for a one-electron reduction would be that of the aromatic porphyrin ligand.¹⁴ This is unlikely since this generally occurs at much higher potential. Further the esr spectra of chemically reduced manganese porphyrins do not show a signal typical of a porphyrin anion radical but do show lines arising from a manganese(II) porphyrin.²²

The Mn(III) → Mn(II) half-wave potentials are dependent on the porphyrin and on the anion.²³ The order of -*E*_{1/2} for different porphyrins in both acetonitrile and dimethylformamide is



The order of -*E*_{1/2} for different anions for both the etioporphyrin I and protoporphyrin IX dimethyl ester derivatives is



In general, the half-wave potentials for all the anions are ~0.1 V more negative for the etioporphyrin I than for the protoporphyrin IX dimethyl ester complexes. An interesting exception to this rule is the iodide complex which gives the same half-wave potential for both porphyrins. Infrared measurements have previously shown that OCN⁻ and SCN⁻ are bound to the manganese(III) through the oxygen and nitrogen atoms, respectively.²⁴

The second and third polarographic waves are seen at more negative potentials than for the Mn(III) → Mn(II) wave. These waves can be assigned to the first and second reduction of the aromatic porphyrin ligand of the manganese(II) complex. The waves are diffusion controlled and appear to arise from one-electron reversible reductions. The half-wave potentials for acetonitrile solution are given in Table III. Similar data are obtained from dimethylformamide solutions

TABLE III
PORPHYRIN REDUCTION POTENTIALS (*vs.* SCE)
OF Mn(Por) IN ACETONITRILE

Por	<i>E</i> _{1/2} , V	<i>E</i> _{1/2} , V
Etio	-1.66 (-1.60) ^a	-2.05
DMMesopor	-1.67 (-1.57)	-2.00
DMDepor	-1.60 (-1.52)	-1.95
DMHpor	-1.50 (-1.41)	...
DMPrpor	-1.54 (-1.44)	-1.87
TPP	-1.38 (-1.31)	-1.70
Mepheo _a	-1.30 (-1.14)	...

^a In dimethylformamide, entry in parentheses.

(21) J. F. Coetzee, D. K. McGuire, and J. L. Hedrick, *J. Phys. Chem.*, **67**, 1815 (1963).

(22) T. Yonetani, H. R. Drott, J. S. Leigh, G. H. Reed, M. Waterman, and T. Ansakura, *J. Biol. Chem.*, **245**, 2998 (1970).

(23) R. Felton, G. M. Sherman, and H. Linschitz, *Nature (London)*, **203**, 637 (1969).

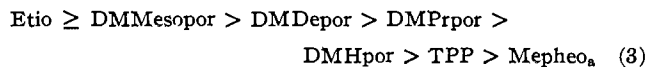
(24) L. J. Boucher in "Coordination Chemistry," S. Kirschner, Ed., Plenum Press, New York, N. Y., 1969, p 128.

TABLE IV
 ABSORPTION MAXIMA^a OF MANGANESE(II) PORPHYRIN COMPLEXES IN PYRIDINE-WATER

Band	Por						
	Etio	DMMEpor	DMDepor	DMHpor	DMPpor	TPP	Mepheo _a
A	... ^b	14.1	~14.3	13.8	~14.1	... ^b	9.7
B	...	~15.2	15.1		~15.4	~15.2	11.4
α	17.2	17.2	17.2	17.0	16.9	16.3	15.2
β	18.2	18.2	18.2	18.0	17.9	17.4	16.1, 17.5, 19.0
Soret	23.5	23.5	23.7	23.4	22.9	22.7	23.3

^a In kK (1000 cm⁻¹). ^b Insufficient solubility.

except that the half-wave potentials are all ~0.08 V more positive than for acetonitrile solutions. Further, the values appear to be independent of the axial anion originally bound to manganese(III). The order of the $-E_{1/2}$ values is



Due to experimental difficulties, the second wave for the methyl pheophorbide_a complex as well as that for the hematoporphyrin IX dimethyl ester derivative did not yield good estimates of the half-wave potentials. The half-wave potentials for the porphyrin reductions have been measured for several divalent metalloporphyrins in dimethyl sulfoxide and dimethylformamide.^{12,14} The position of the first two waves falls in the region of the waves observed here. In fact, for the same solvents, dimethylformamide and acetonitrile, the values for manganese(II) are equal to those for zinc(II) porphyrins. Further, for manganese(II) the difference in half-wave potentials for the two porphyrin reduction waves is equal to 0.37 ± 0.03 V which is in the range for other divalent metalloporphyrins.^{12,14} It has been unambiguously shown by esr spectroscopy that the polarographic reduction wave observed for the divalent metalloporphyrins corresponds to the formation of a radical anion of the porphyrin aromatic system.^{12,14} The close correspondence of the polarogram of manganese(II) porphyrins to those of similar divalent metalloporphyrins leaves no doubt that the second and third waves observed here correspond to porphyrin ligand reductions.

Visible Spectra and Chemical Reductions.—When excess sodium dithionite is added to a pyridine-water solution of a manganese(III) porphyrin at pH 11, the complex is rapidly reduced to the manganese(II) porphyrin. In the absence of air, these solutions are fairly stable and their electronic spectra can be easily measured. Similar spectra are obtained for solutions that have been electrolytically reduced and from spontaneous reductions *in vacuo* in the gas phase.²⁵ A typical spectrum of a manganese(III) porphyrin solution before and after addition of a reducing agent is given in Figure 3 and the data are collected in Table IV. Under the conditions used, the original chloro-complexed manganese(III) porphyrin is transformed into the pyridine complex in solution. Previous work has shown that the axial coordination positions of manganese(II) porphyrins are occupied by pyridine mole-

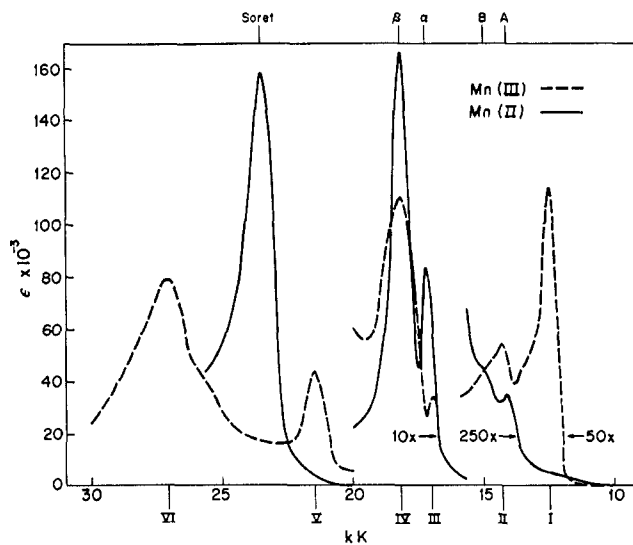


Figure 3.—Visible absorption spectra of aquo(chloro)(meso-porphyrin IX dimethyl ester)manganese(III) in 1:1 pyridine-water with Na₂S₂O₄ added (—) and without Na₂S₂O₄ (---).

cules.^{6,7} In addition to the expected α , β , and Soret bands of a divalent metalloporphyrin, two weak bands are seen in the red end of the visible spectrum. In the case of the etioporphyrin I and TPP complexes, the manganese(II) porphyrins are not sufficiently soluble to observe the weak near-ir bands. With the other porphyrins, a slow base-catalyzed hydrolysis of the methyl ester occurs during the time it takes fully to record the spectra. Fortunately, the formation of the metalloporphyrin-free acid does not affect the spectrum. Further, the spectrum does not vary when the water to pyridine ratio is varied from 4:1 to 1:4. The magnetic susceptibility of the manganese(III) porphyrin solutions before and after addition of the reducing agent gives effective magnetic moments of 4.9 and 5.9 BM, respectively.⁵ We have confirmed this result using the nmr method of determining the magnetic susceptibility of solutions.

The visible spectra of the manganese(III) porphyrins in acetonitrile were recorded. Although the absorption maxima blue shifted, the frequency order is the same for acetonitrile solutions as for chloroform solutions¹¹ for the different anion and porphyrin complexes. Thus it appears that the complexes behave the same way in chloroform as in acetonitrile and that the anions remain coordinated in acetonitrile.

Discussion

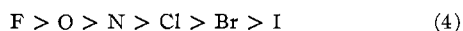
Unlike most ligands porphyrins stabilize the +3 oxidation state of manganese to a great extent. This is

(25) L. Edwards, D. H. Dolphin, and M. Gouterman, *J. Mol. Spectrosc.*, in press.

undoubtedly a consequence of the strong ligand field of the porphyrin. An additional perturbation is supplied by the ligand field of the axial ligands. The fifth and sixth coordination positions of the manganese atom above and below the porphyrin are filled by anions and/or solvent molecules. In all combinations of porphyrins and ligands examined so far, the magnetic moments are ~ 4.9 BM which is consistent with a high-spin d^4 configuration for the manganese. In no case is spin pairing observed. Although unstable in the presence of air, manganese(II) porphyrins have been prepared and studied. Again the spin state of manganese is always that of a high-spin d^5 configuration. Aside from the additional electron, there appears to be no spin state change in the Mn(III) \rightarrow Mn(II) reduction. It is therefore a straightforward operation to interpret the redox potentials for this process.

The observed redox potential for Mn(III) \rightarrow Mn(II) appears to be dependent on the porphyrin and the axial ligands. Varying the substituents on the porphyrin ring changes the redox potential by as much as 0.22 V. Order (1), given above, corresponds closely to the pK_a order of the porphyrins.²⁶ The higher the basicity toward the proton, the higher the pK_a (for the dissociation of the protonated form of the porphyrin) and the more negative the half-wave potential, *i.e.*, the stronger the porphyrin-manganese interaction, the more stable the manganese(III) porphyrin. The strongest donor, etioporphyrin I, gives the most negative potential while the weakest donor, tetraphenylporphine gives the most positive potential. In the same way the relatively positive half-wave potential reflects the assumed weak donor strength of the chlorophyll derivative, methyl pheophorbide_a.

Similarly, varying the axial anion changes the redox potential by as much as 0.20 V. Order (2) generally follows the electronegativity of the donor atom



While the azide ion fits into its proper place in this order, the thiocyanate is surprisingly quite low in the series. The most electronegative species, F^- , gives the most negative redox potential while the least electronegative species, I^- , gives the most positive potential. For the cases known, order (4) is also the order for the stability of manganese(III) complexes.²⁷ Further, spectrophotometric measurements on solution equilibria indicate that fluoride is more strongly bound than iodide and that dimethyl sulfoxide is more strongly bound than pyridine to manganese(III) porphyrins.²⁴ In a general way, then, the anion that forms the strongest bond with manganese(III) stabilizes this oxidation state to the greatest extent. This is also observed for the manganese(III) porphyrin complexes with pyridine and other nitrogen heterocycles.⁷ For example, imidazole binds more strongly to manganese(III) and stabilizes it more toward reduction than does pyridine. The anion order observed here has been seen for other series of

(26) W. S. Caughey, W. Y. Fujimato, and B. P. Johnson, *Biochemistry*, **5**, 3830 (1966).

(27) G. Davies, *Coord. Chem. Rev.*, **4**, 199 (1969)

transition metal complexes, *e.g.*, $Co(NH_3)_5X^{2+}$.²⁸ In contrast to the present case, however, the reduction of the cobalt complexes is completely irreversible and the half-wave potentials are a measure of the rate of reduction and not of the normal redox potential. Both the anion and porphyrin trends noted here reflect the common observation that strongly binding ligands stabilize the high oxidation states of transition metal ions. Also implicit in this discussion is that the manganese(III) appears to behave as a hard acid toward the axial anions.

A comparison of the properties of manganese and iron porphyrin complexes seems desirable. In both aqueous and nonaqueous solutions, the hydroxide²⁹ and chloride complexes of iron(III) porphyrins are more easily reduced than the corresponding manganese(III) porphyrins; *i.e.*, $E_{1/2}$ is 0.03–0.05 V more positive. The stability of iron(III) with respect to that of manganese(III) is further decreased in the dipyrindine complex; *i.e.*, $E_{1/2}$ is ~ 0.39 V more positive for iron(III).²⁹ The large change in stability of the iron(III) complex when changing the axial ligand from chloride to a nitrogen heterocycle is a result of spin pairing in the dipyrindine complexes with placement of the iron in the plane of the porphyrin.³⁰ This option of spin state and configuration change is apparently not open to manganese. The manganese(III) potential still can vary appreciably by varying the porphyrin, anion, and dielectric medium. For example, manganese(III) complexes with polarizable axial ligands like sulfur atoms and weak donors like a chlorophyll derivative bound in the interior of a protein should give a low redox potential. On the other hand, when manganese(III) is bound to a strong donor porphyrin like mesoporphyrin IX and a hard axial anion like OH^- in an aqueous environment, the reduction potential will be quite negative. In the former case, manganese(II) will be a poor reducing agent while in the latter case, it will be a good reducing agent. In fact, manganese(II) porphyrin complexes are more potent reducing agents than the comparable iron(II) derivatives.

Visible Spectra of Manganese(II) Porphyrins.—The electronic spectra of manganese(II) porphyrins are very similar to those of other divalent metalloporphyrins³¹ and show the usual α , β , and Soret bands (see Table IV). These absorptions can be assigned to the a_{1u} , $a_{2u} \rightarrow e_g^*$ transitions.³² An additional feature of the spectra is the presence of weak bands in the red end of the visible region, labeled A and B in Table IV. Presumably the bands arise from the allowed ligand to metal charge-transfer bands, *e.g.*, a_{1u} , $a_{2u} \rightarrow d\pi$, much like those observed for manganese(III) porphyrins.¹⁰ The bands are blue shifted and their intensity decreases by a factor of 10 in going from manganese(III) to manganese(II). The blue shift is a consequence of the destabilization of the metal d orbitals.

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tals with the decrease in oxidation state and the intensity decrease is consistent with a decreased porphyrin π character in the $d\pi$ metal orbital. This results from a decreased metal-porphyrin π interaction in manganese(II) over manganese(III). It is interesting to note the enhanced intensity and sharpening of the visible absorption bands when going from manganese(III) to manganese(II). This is consistent with the notion that there is considerable charge-transfer character in the bands of manganese(III) but very little for manganese(II). Although it may be coincidental, band IV of the manganese(III) derivatives appears at exactly the same frequency as the β band of the manganese(II) complex. Substituting one porphyrin for another produces shifts in all the band frequencies. The order of the band position agrees with that observed for other divalent metalloporphyrins²⁶ and also for manganese(III) porphyrins.¹¹ The redox potentials for the first and second porphyrin reduction also parallel the spectral order. This is undoubtedly related to the identity of the substituents on the porphyrin macrocycle. Electron-donating alkyl groups increase the electron density in the ring and it is more difficult to add on another electron during reduction. This accounts for the increase in $-E_{1/2}$ of 0.29 V in going from the β -hydrogen substituents of tetraphenylporphine to the alkyl substituents of etioporphyrin I. The exocyclic ring and the reduction of ring IV in methyl pheophorbide_a also lower the redox potential.²³

The normal visible spectrum of manganese(II) porphyrins in contrast to the unusual nature of the spectrum of manganese(III) porphyrins implies that the special interaction (and/or geometry) of the latter is not present in the former. Manganese(II) is a high-spin d^5 case with symmetrically half-filled d orbitals. The fact

that the $d_{x^2-y^2}$ orbital is singly occupied in these materials is consistent with the notion that the metal is out of the plane of the porphyrin. Indirect evidence for this is the result of molecular orbital calculations which show that a planar configuration would give rise to an intermediate spin state for manganese(II).³² More to the point, it is known that the isoelectronic iron(III) porphyrins adopt a nonplanar configuration when the metal is in the high-spin state.³³ The marked instability of the manganese(II) porphyrins to dissociation in aqueous solution²⁰ is consistent with a structure in which the manganese metal is considerably out of the plane of the porphyrin. In this configuration the porphyrin retains a high negative charge and the metal retains a high positive charge.³² The high potential of the manganese(II) porphyrin ligand reductions is consistent with this description. Further, the relatively strong binding of an axial ligand (more strongly bound than to manganese(III)) is in line with the relatively high positive charge on the metal.⁷ The strong axial interaction is also displayed in the esr spectra of manganese(II) porphyrins which show a relatively low zero-field parameter.²² This can be interpreted as due to axial interactions which are comparable in magnitude to the porphyrin interaction.

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Iodonium Salts of Complex Anions. III.¹ Isolation and Reactions of Diphenyliodonium Tris(*N*-cyanodithiocarbimato)cobalt(III)

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Isolation and reactions of diphenyliodonium tris(*N*-cyanodithiocarbimato)cobalt(III), $(dpi)_3[Co(cdc)_3]$ (I) have been carried out. Pyrolysis reactions of I show that the reactive sites in the anion are the coordinated sulfur atoms of the same ligand. Partial reduction of the metal ion to the bivalent state and liberation of iodobenzene and phenyl disulfide occur simultaneously. In pyridine solution also ligand phenylation occurs; however, arylated ligand decomposes under these reaction conditions. Nonarylated ligand dissociates into thiocyanate and reduction of metal ion to cobalt(II) also occurs in the pyridine reaction. From this solution $Co(py)_4(NCS)_2$ has been isolated; this complex has been converted into the corresponding *o*-phenanthroline and α, α' -dipyridyl complexes. The electronic spectra of the compounds have been recorded.

Introduction

Recently studies of the reactions of chelated ligands have assumed a place of considerable interest in the

field of coordination chemistry.^{2,3} Almost all the reactions studied make use of an external reagent and a suitable complex under specific conditions. The di-

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