

Electrochemical studies have also been done on the iron(III) porphyrin chlorides and hydroxides of the basket-handle porphyrins.¹⁸ The substituents had large effects on the reduction potentials. The effect of the ether substituents was attributed to steric interference with solvation of the negatively charged species. The effects of the amide linkages were attributed to specific interactions involving either hydrogen-bonding or dipole-dipole interactions.

These literature results suggest that several factors contribute to the effects of ortho substituents on iron porphyrins. The relative importance of these factors varies from reaction to reaction. The factors that influence the rates of reaction of the iron porphyrin hydroxide may be quite different from those for oxygen binding because of the charge on the hydroxide ligand. Since the electrochemical studies were performed in polar solvents in the

presence of high electrolyte concentrations, the solvation of the iron complexes is probably quite different from that in CCl₄ as used in the studies in this paper. Nonetheless, there is increasing evidence that both ether and amide substituents can have both general and specific effects on iron porphyrin reactions.

Acknowledgment. The partial support of this work by National Institutes of Health Grant GM21156 is gratefully acknowledged. S.S.E. thanks the National Science Foundation for a Visiting Professorship for Women, 1984.

Registry No. III, 98170-58-2; IV, 98170-59-3; V, 98170-60-6; Fe(TP-OC₂)Cl, 98170-53-7; Fe(TTP-OC₂)Cl, 98170-54-8; Fe(TTP-OC_{1A})Cl, 98170-55-9; Fe(TTP-OC_{2A})Cl, 98170-56-0; Fe(TTP-OC_{4A})Cl, 98170-57-1; Fe(TTP-OC₂)OH, 98170-61-7; Fe(TTP-OC₂)O-H, 98170-62-8; Fe(TTP-OC_{1A})OH, 98170-63-9; Fe(TTP-OC_{2A})OH, 98170-64-0; Fe(TTP-OC_{4A})OH, 98170-65-1.

Notes

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1,4,7,10,13,16,19-Heptaazacycloheneicosane. A Large, Potentially Dinucleating Polyazacycloalkane. Synthesis and Equilibria between Hydrogen and Copper(II) Ions

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Received January 11, 1985

Although there has been a considerable number of publications dealing with metal complexes of saturated polyazamacrocycles, relatively few studies are available on metal complexes of large polyazacycloalkanes (more than six nitrogens as donor atoms). These macrocycles are interesting mainly because they are potentially dinucleating ligands, able to incorporate more than one metal ion for each ligand molecule. In a previous paper¹ we have studied the coordination capabilities of the large polyazacycloalkane 1,4,7,10,13,16,19,22-octaazacyclotetrasosane (bistrien). Continuing our studies on dinucleating polyazamacrocyclic ligands, we report here the synthesis of the large polyazacycloalkane 1,4,7,10,13,16,19-heptaazacycloheneicosane (L₁) and thermodynamic and electrochemical studies on its Cu(II) complexes.

Experimental Section

Synthesis of the Compounds. All chemicals were reagent grade and utilized without purification. Macrocycle L₁ has been synthesized by the general procedure (see Figure 1) of Atkins et al.² Experimental details of the synthetic procedure are reported in Table I. A dinuclear complex of formula Cu₂(L₁)Cl(ClO₄)₂·H₂O can be isolated as a microcrystalline solid by mixing hot ethanolic solutions of copper(II) perchlorate and neutralized solutions of (L₁)·7HCl. (Anal. Calcd for C₁₄H₃₇N₇O₁₃Cu₂Cl₄: C, 21.54; H, 4.78; N, 12.56; Cl, 18.17. Found: C, 21.4; H, 4.9; N, 12.5; Cl, 18.1.) The magnetic moment of the complex measured by the Faraday method, is given by μ_{eff} = 2.81 μ_B at 298 K.

EMF Measurements. All potentiometric measurements were carried out in 0.5 mol dm⁻³ NaClO₄. The potentiometric titrations were carried out by using equipment (potentiometer, buret, stirrer, thermostated cell, microprocessor, etc.) that has been already described.⁴ The computer program SUPERQUAD⁵ was used to process data and calculate basicity and stability constants.

Electrochemical Measurements. Electrochemical analysis by cyclic voltammetry was performed with the following apparatus: a potentiostat (Amel Model 552), pen recorder (Amel Model 862/A) and a classical three-electrode cell. The working electrode was a platinum microsphere, the auxiliary electrode was a platinum disk, and the reference was an

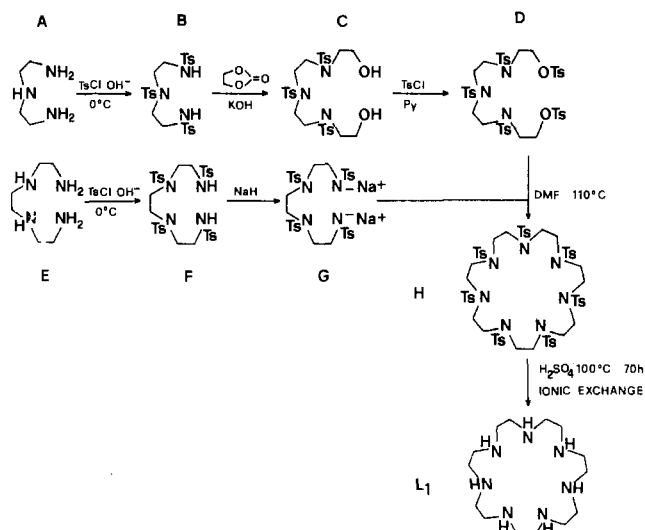


Figure 1. Reaction sequence for the synthesis of the macrocycle (L₁).

SCE electrode. Before each experiment the solution was carefully deoxygenated. Electronic spectra were recorded on a Varian Cary Model 17 spectrophotometer.

Results and Discussion

Protonation. The stepwise protonation constants for the macrocycle (L₁) are reported in Table II. For comparison, the protonation constants for the similar macrocycle bistrien are also reported. As already observed for polyazamacrocycles, values for the basicity constants constitute two groups.^{1,4,6} The macrocycle (L₁) behaves as a strong base in the first three steps of protonation and as much weaker base in the last steps of protonation. Such a behavior can be easily rationalized in terms of electrostatic repulsion among the positive charges on the protonated cyclic polyamines.⁶

Copper(II) Complexes (Equilibrium Studies). Species and stability constants for the Cu(II) complexes with L₁ are reported

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Table I. Experimental Details and References Relative to the Synthesis of the Compounds Reported in Figure 1

compd	yield, %	mp, °C	anal.			TLC (R_f) ^a	ref	
				% C	% H			% N
B	81	173–175	calcd	53.08	5.52	7.43	0.82	2
			found	53.2	5.5	7.4		
C	60	110–112	calcd	53.27	6.01	6.43	0.72	2
			found	53.4	6.0	6.4		
D	44	147–149	calcd	53.68	5.34	4.38	0.85	2
			found	53.6	5.3	4.4		
F	94	219–220	calcd	53.52	5.55	7.34	0.52	3
			found	53.4	5.5	7.3		
H	42	264–268	calcd	54.80	5.62	7.10	0.92	2
			found	54.9	5.6	7.1		
(L ₁) ₂ ·7HCl ^b	87		calcd	30.21	7.60	17.61		
			found	30.3	7.6	17.5		

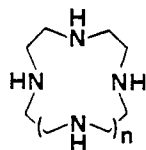
^a TLC measurements were carried out on precoated TLC plates of silica gel 60 F-254 (Merck) by using a methylene chloride, *n*-hexane, and methanol (8:4:1) mixture as eluent. ^b ¹³C NMR spectrum (water with 15% D₂O, 20 MHz) consists of only one signal at 43.8 ppm (CH₂).

Table II. Basicity and Formation Constants of Cu(II) Complexes of L₁ in Aqueous Solution, at 25 °C in 0.5 mol dm⁻³ NaClO₄ (Standard State = 1 mol dm⁻³)

reaction	log K	
	L = L ₁	L = bistrien ^a
H ⁺ + L = HL ⁺	9.83 (1) ^b	10.01
HL ⁺ + H ⁺ = H ₂ L ²⁺	9.53 (1)	9.50
H ₂ L ²⁺ + H ⁺ = H ₃ L ³⁺	8.84 (1)	9.10
H ₃ L ³⁺ + H ⁺ = H ₄ L ⁴⁺	6.72 (1)	8.29
H ₄ L ⁴⁺ + H ⁺ = H ₅ L ⁵⁺	4.04 (2)	5.01
H ₅ L ⁵⁺ + H ⁺ = H ₆ L ⁶⁺	2.43 (2)	3.71
H ₆ L ⁶⁺ + H ⁺ = H ₇ L ⁷⁺	2.30 (4)	2.98
H ₇ L ⁷⁺ + H ⁺ = H ₈ L ⁸⁺		1.97
Cu ²⁺ + L = CuL ²⁺	24.4 (1) ^b	
Cu ²⁺ + L + 2H ⁺ = CuLH ₂ ⁴⁺	34.4 (1)	
CuL ²⁺ + 2H ⁺ = CuLH ₂ ⁴⁺	10	
2Cu ²⁺ + L = Cu ₂ L ⁴⁺	30.7 (1)	36.63
CuL ²⁺ + Cu ²⁺ = Cu ₂ L ⁴⁺	6.3	
2Cu ²⁺ + L + 2H ⁺ = Cu ₂ LH ₂ ⁶⁺		42.02
Cu ₂ L ⁴⁺ + 2H ⁺ = Cu ₂ LH ₂ ⁶⁺		5.39
Cu ₂ L ⁴⁺ + OH ⁻ = Cu ₂ LOH ³⁺	4.8	3.21

^a Taken from ref 1. ^b Values in parentheses are standard deviations in the last significant figure.

in Table II. The macrocycle (L₁), with seven donor atoms, is a dinucleating ligand as indicated by the high stability of the dinuclear species Cu₂(L₁)⁴⁺. This species is, as expected, significantly less stable than the corresponding dinuclear species formed by bistrien (log *K* = 36.63) where eight nitrogen atoms are involved in the coordination to the two Cu(II) ions. Among the most important species in the system Cu(II)/L₁ there also is a very stable mononuclear complex Cu(L₁)²⁺ (see Table II). If one imagines a series of polyazacycloalkanes derived by adding the -CH₂-CH₂-NH- group to the smallest azamacrocycle 1,4,7-triazanonane, the ligand (L₁) is the only one in the series that forms



$n = 0, \dots, 5$

$n = 4$ L₁

$n = 5$ bistrien

both mononuclear and dinuclear species. The smaller macrocycle 1,4,7,10,13,16-hexaazacyclononadecane ($n = 3$) forms only mononuclear species,⁷ while the larger macrocycle bistrien ($n = 5$) forms only dinuclear species (see Table II). In the Cu(II)/L₁

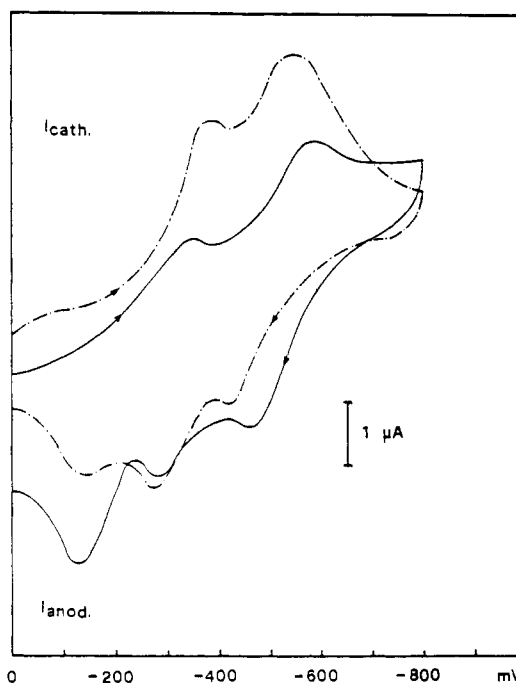


Figure 2. Cyclic voltammograms of 0.1 mmol dm⁻³ Cu₂(L₁)⁴⁺ (—) in 0.1 mol dm⁻³ KCl at 50 mV s⁻¹ with a platinum microsphere as working electrode and of Cu₂(bistrien)⁴⁺ (---) under the same experimental conditions, taken from ref 1.

system there are two species, Cu(L₁)H₂⁴⁺ and Cu₂(L₁)OH³⁺. Cu(L₁)²⁺ has a poor tendency to be protonated, as shown by the equilibrium constant corresponding to the addition of two protons to the complex (see Table II). These values of protonation are much smaller than the sum of those for the protonation of the first two nitrogen atoms in the free ligand (log β₂ = 19.36; see Table II). This big difference (9.36 log units) cannot be explained only in terms of electrostatic repulsion, which will contribute to make the protonation of the bipoisitive Cu(L₁)²⁺ ion (Cu(L₁)²⁺ + 2H⁺ = Cu(L₁)H₂⁴⁺) less favorable with respect to the neutral ligand (L₁ + 2H⁺ = (L₁)H₂²⁺). It may be considered as indirect evidence for the fact that there are not uncoordinated nitrogens, and to some extent, all donor atoms seem to be involved in the coordination to the metal ion in the mononuclear species. Although the formation of hydroxo species in Cu(II)/polyazamacrocycles systems is very rare, L₁ forms a very stable dinuclear hydroxo species Cu₂(L₁)OH³⁺, as shown by the equilibrium constant for the addition of the hydroxide ion to the dinuclear complex (log *K* = 4.8).

Electrochemical Studies. An aqueous solution obtained by dissolving a well-known amount of the solid complex Cu₂(L₁)-Cl(ClO₄)₃ has been investigated by using the CV technique. Cyclic voltammetry curves are reported in Figure 2, where the electrochemical behavior of Cu₂(L₁)⁴⁺ is compared with that of the parent

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complex $\text{Cu}_2(\text{bistrien})^{4+}$. The current/potential profile shows two consecutive peaks in reduction, followed, in the reverse scan, by two oxidation peaks. The separation between the peaks in the reduction scan is about 193 mV. The peaks do not shift on the potential axis as a function of scan rate. The intensity of each peak, compared with a mono-electronic standard,⁸ would correspond to the addition of 1 e. It is worth noting that the two peaks in reduction are more separate ($\Delta E_{1/2} = 190$ mV) than those in $\text{Cu}_2(\text{bistrien})^{4+}$ ($\Delta E_{1/2} = 140$ mV) (see Figure 1), indicating that in the $\text{Cu}_2(\text{L}_1)^{4+}$ complex the reduction of the first Cu(II) is easier than that in the corresponding $\text{Cu}_2(\text{bistrien})^{4+}$ complex. The opposite is true for the second Cu(II) ion, which is more easily reduced in $\text{Cu}_2(\text{bistrien})^{4+}$. These facts can be related to the overall minor stability of the dinuclear species $\text{Cu}_2(\text{L}_1)^{4+}$ when compared to that of $\text{Cu}_2(\text{bistrien})^{4+}$ and to the possibility that the smaller macrocycle (L_1) forms stable mononuclear species. An anodic peak appears in the oxidation scan at ca. -140 mV whose intensity increases with the decreasing of the scan rate. This peak, which does not disappear even at high scan rate, can be ascribed to anodic stripping due to the oxidation of deposited copper metal.⁹ Controlled-potential electrolysis at the potential of the first peak of reduction (-400 mV) causes deposition of copper metal, which plates the platinum electrode surface. This suggests that the $\text{Cu}^{\text{II}}\text{Cu}^{\text{I}}(\text{L}_1)^{3+}$ species is unstable with respect to the disproportionation by which copper metal is produced. In the case of $\text{Cu}_2(\text{bistrien})^{4+}$ the anodic stripping peak appears only at low scan rate, and deposition of copper metal by controlled-potential electrolysis only occurs in correspondence with the second reduction peak when the $\text{Cu}^{\text{I}}\text{Cu}^{\text{I}}(\text{bistrien})^{2+}$ species is present.

Acknowledgment. Financial support from Progetto Finalizzato Chimica Fine e Secondaria of the Italian Research Council (CNR) is gratefully acknowledged.

Registry No. A, 111-40-0; B, 56187-04-3; C, 74461-29-3; D, 97783-00-1; E, 112-24-3; F, 55442-07-4; H, 52601-76-0; L₁, 296-85-5; (L₁)₇HCl, 56187-10-1; $\text{Cu}_2(\text{L}_1)\text{Cl}(\text{ClO}_4)_3$, 97783-02-3.

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Manganese(IV) in Discrete O₃S₃ Coordination

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Received April 16, 1985

Trivalent and tetravalent manganese are implicated in photo-synthetic oxygen evolution.^{1,2} The chemistry³ of these oxidation states is therefore of particular interest. Surprisingly few well-characterized discrete mononuclear manganese(IV) species are known at present. Among these just two tris chelate types occur— $\text{Mn}^{\text{IV}}\text{O}_6$ in sorbitolato⁴ and catecholato^{5,6} species and $\text{Mn}^{\text{IV}}\text{S}_6$ in dithiocarbamates.⁷⁻⁹ In the present work we describe

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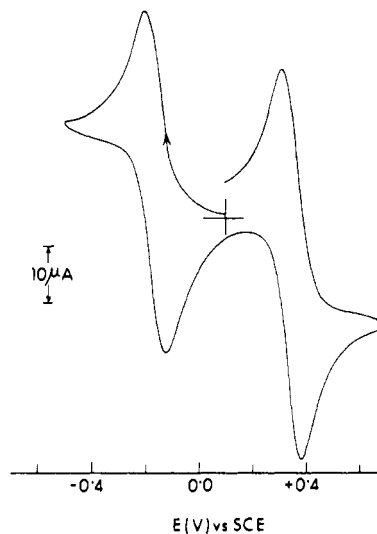
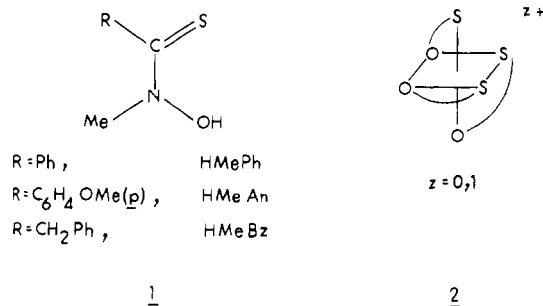


Figure 1. Cyclic voltammogram (scan rate 50 mV s^{-1}) of $\sim 10^{-3} \text{ M}$ solution of $\text{Mn}(\text{MePh})_3$ in acetonitrile (0.1 M TEAP) at a platinum electrode (298 K).

the intermediate type, $\text{Mn}^{\text{IV}}\text{O}_3\text{S}_3$, furnished by thiohydroxamic acids. Because of the siderophoric role of such acids their transition-metal chemistry,^{10,11} including that of manganese(II,III),^{12,13} has received recent attention.

Results and Discussion

Synthesis. The three ligands HMePh, HMeAn, and HMeBz used in the present work are of type 1 and are generally abbreviated as HMeR (H refers to the dissociable OH proton). The



manganese(IV) complexes $\text{Mn}(\text{MeR})_3^+$ are furnished in high yield by dichlorine oxidation of $\text{Mn}(\text{MeR})_3$ in acetonitrile solution and are isolated as dark-colored hexafluorophosphates. The manganese(III) precursor is synthesized either as reported^{12,13} or by the essentially quantitative displacement reaction (1) carried out in ethanol at room temperature (Hacac = acetylacetonate).



In solution $[\text{Mn}(\text{MeR})_3]\text{PF}_6$ behaves as a 1:1 electrolyte and its magnetic moment conforms to the d^3 configuration. Selected

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