

At present, we have no evidence for the intervention of low-lying excited states, and qualitatively, the labilization can be accounted for by the inductive effect of converting bpy into bpy^- , as noted above. It should also be noted that reduction of bpy to bpy^- is expected to increase the σ -donor ability of bpy markedly, which would have the effect of destabilizing the $d\sigma^*$ levels relative to the unreduced complexes, which would tend to increase the energy

gap between the $(d\pi)^6(\pi_1^*)(\pi_2^*)$ and $(d\pi)^6(\pi_1^*)(d\sigma^*)$ states; note eq 18.

In future papers we will demonstrate the use of the ligand-based reductive chemistry in the electrocatalysis of H_2 production from H_2O and of CO_2 reduction. An important feature in such applications appears to be the role of the ligand-based reductions in inducing substitution and in providing an "electron reservoir" for the necessary reductive redox equivalents on demand.

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Registry No. [Os(bpy)₂Cl₂], 79982-56-2; [Os(bpy)₂(CH₃CN)Cl](PF₆), 81831-14-3; [Os(bpy)₂(py)Br](PF₆), 97335-07-4; [Os(bpy)₂(PPh₃)Cl](PF₆), 81831-16-5; [Os(bpy)₂(CO)Cl](PF₆), 80502-54-1; [Ru(bpy)₂Cl₂], 19542-80-4; [Ru(bpy)₂(py)Cl](PF₆), 36413-31-7; [Ru(bpy)₂(py)NO₂](PF₆), 36309-80-5; [Ru(bpy)₂(py)CN](PF₆), 97335-09-6; [Ru(bpy)₂(PPh₃)Cl](PF₆), 67710-99-0; [Ru(bpy)₂(CO)(O₂CH)](PF₆), 84117-41-9; [Ru(bpy)₂(CO)Cl](PF₆), 79850-20-7; [Ru(bpy)₂(CO)(CH₃CN)](PF₆), 97335-10-9; [Os(bpy)₂(NH₂CH₂CH₂NH₂)](PF₆), 97277-66-2; [Ru(bpy)₂(py)(CH₃CN)](PF₆), 72525-79-2; TEAP, 2567-83-1; bpy, 366-18-7; CH₃CN, 75-05-8; Cl₂, 7782-50-5.

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- (23) In this paper the periodic group notation is in accord with recent actions by IUPAC and ACS nomenclature committees. A and B notation is eliminated because of wide confusion. Groups IA and IIA become groups 1 and 2. The d-transition elements comprise groups 3 through 12, and the p-block elements comprise groups 13 through 18. (Note that the former Roman number designation is preserved in the last digit of the new numbering: e.g., III → 3 and 13.)

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Electrochemistry and Spectroelectrochemistry of Indium(III) Porphyrins. Reactions of Five-Coordinate Ionic Complexes

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The electrochemistry and spectroelectrochemistry of In(III) tetraphenyl- and octaethylporphyrins were investigated in nonaqueous media. Counterions on the In(III) complexes were either Cl⁻ or ClO₄⁻. Each oxidized and reduced species was characterized by UV-visible spectroscopy, and ESR spectra were obtained for each of the generated cation and anion radicals. Singly oxidized species gave rise to ESR spectra with values of $g \approx 2.00$ but with values of ΔH that varied between 16.8 and 221 G depending upon the nature of the porphyrin ring and the composition of the solvent-supporting electrolyte system. Analysis of the ESR data indicated π -ring-centered reactions with a small amount of spin density residing upon the metal.

Introduction

Recently, indium(III) porphyrins have been demonstrated to be an essential starting product in the synthesis of novel groups of metalloporphyrins with metal-metal bonds.^{2,3} The second metal σ -bonded to the In center in these bimetallic complexes may be Mo, W, Cr, Mn, Fe, or Co. In(III) porphyrins are also the starting product for the formation of In(III) complexes containing σ -bonded alkyl or aryl groups.⁴ These latter species have been shown to insert carbon dioxide into the In-carbon σ bond⁵ or alternatively to insert sulfur dioxide between the metal atom and the alkyl or aryl group of In(III).⁶

For the case of the metal-metal-bonded species, indium can exist as a formal In(III) or an In(I) species and the overall complex can be reduced by two single-electron-transfer reactions without cleavage of the metal-metal bond.³ Likewise, the σ -bonded alkyl or aryl complexes can be reduced by two single-electron transfers without cleavage of the metal-carbon bond. This stability does

not occur for the case of oxidations where both series of compounds are highly reactive and undergo either metal-metal or metal-alkyl (aryl) bond cleavage after the addition of either one or two electrons.

In order to better understand the stability and reactivity of In porphyrins with σ -bonded metal complexes or with alkyl (aryl) axial ligands, we have undertaken a series of parallel studies on the electrochemistry of different σ -bonded and ionic In(III) porphyrins. The first of these studies involved an investigation of 16 different σ -bonded alkyl tetraphenylporphyrin and octaethylporphyrin derivatives in nonaqueous media and is presented in another paper.⁷ This present study describes detailed investigations on the tetraphenyl and octaethylporphyrin complexes where the complex is ionic and the associated counterion is Cl⁻ or ClO₄⁻. Partial electrochemical characterization for reduction of one of these compounds, (TPP)InClO₄,³ has been published, but no UV-visible spectral data of the reduction products were reported. This is now given in the present manuscript. In addition, we present the first UV-visible and ESR spectra of electrooxidized In(III) porphyrins.

Experimental Section

Instrumentation. UV-visible spectra were taken with a Tracor Northern 1710 holographic optical spectrometer multichannel analyzer or an IBM 9430 spectrophotometer. ESR spectra were recorded on an IBM Model ER 100D spectrometer equipped with an ER 040-X microwave bridge and an ER 080 power supply. IR spectra were performed

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on a Perkin-Elmer 1330 spectrometer. Samples were 1% dispersions in CsI pellets.

Cyclic voltammetric measurements were obtained with the use of a three-electrode system where the working electrode was a platinum button and the counter electrode a platinum wire. A saturated calomel electrode (SCE) served as a reference electrode and was separated from the bulk of the solution by a fritted glass bridge. An EG&G Model 174A polarographic analyzer, an EG&G Model 175 universal programmer, a Houston Instruments Model 2000 X-Y recorder, a BAS-100 electrochemical analyzer, a HIPLLOT DMP-40 plotter, and an EPSON Model FX80 printer were used.

Controlled-potential electrolysis was performed by using an EG&G Model 173 potentiostat or a BAS-100 electrochemical analyzer. Both the reference electrode and the platinum-wire counter electrode were separated from the bulk solution by means of fritted glass bridges.

Thin-layer spectroelectrochemical measurements were performed with an IBM EC 225 voltammetric analyzer coupled with a Tracor Northern 1710 holographic optical spectrometer multichannel analyzer to obtain time-resolved spectral data. The utilized optically transparent thin-layer electrode (OTTLE) has been described in previous publications.^{8,9}

Chemicals. Reagent grade methylene chloride (CH_2Cl_2) and benzonitrile (PhCN) were distilled over P_2O_5 and stored over a 4-Å activated molecular sieves. Tetrabutylammonium perchlorate (TBAP) (Fluka) was recrystallized from ethanol. Tetrabutylammonium hexafluorophosphate ($\text{TBA}(\text{PF}_6)$) (Fluka) was recrystallized from ethyl acetate. (TPP)InCl and (OEP)InCl were synthesized according to literature procedures.¹⁰ The corresponding perchlorate derivatives, (TPP)InClO₄ and (OEP)InClO₄, were generated by adding a stoichiometric amount of AgClO_4 in boiling tetrahydrofuran. Their physicochemical characteristics are as follows. (TPP)InCl: UV-vis in CHCl_3 , λ (nm ($\epsilon \times 10^{-3}$)) 424 (653), 516 (1.3) 557 (30.4), 597 (16.8); $\nu_{\text{In-Cl}}$ (cm^{-1}) = 390. (OEP)InCl: UV-vis in CHCl_3 , λ (nm ($\epsilon \times 10^{-3}$)) 405 (327), 497 (3.9), 537 (15.7), 574 (15.9); $\nu_{\text{In-Cl}}$ (cm^{-1}) = 350. (TPP)InClO₄: UV-vis in CHCl_3 , λ (nm ($\epsilon \times 10^{-3}$)) 421 (637), 554 (28.9), 595 (14.9); $\nu_{\text{In-ClO}_4}$ (cm^{-1}) = 1140, 1100, 1020, 890, 625. (OEP)InClO₄: UV-vis in CH_2Cl_2 , λ (nm ($\epsilon \times 10^{-3}$)) 403 (314), 535 (13.4), 573 (14.0); $\nu_{\text{In-ClO}_4}$ (cm^{-1}) = 1160, 1080, 875, 620.

Results and Discussion

Electrochemistry of (OEP)InX and (TPP)InX, Where X = Cl⁻, ClO₄⁻. The electrooxidation and electroreduction of (OEP)InX and (TPP)InX were investigated in CH_2Cl_2 and PhCN containing 0.1 M TBAP. The electrochemistry of these compounds is straightforward and is not unlike the electrochemistry reported¹¹ for other group 13²³ metalloporphyrins such as (OEP)AlOH, (OEP)GaOH, (OEP)InOH, and (OEP)TlOH.

For the case of (OEP)InOH, two oxidations and two reductions are observed, all four of which have been postulated to occur at the porphyrin π -ring system. This postulate was based¹¹ on a 2.27-V separation between half-wave potentials for the first oxidation and the first reduction as well as differences in half-wave potentials of 0.28 and 0.40 V between the first and second oxidation and the first and second reduction of (OEP)InOH, respectively. These separations between half-wave potentials fit perfectly the trend expected for a series of π -ring-centered reactions of octaethylporphyrins and, with several exceptions, are not too unlike results in this study for oxidation and reduction of (OEP)InX and (TPP)InX.

Both (OEP)InX and (TPP)InX can be reduced or oxidized in a total of four single-electron-transfer steps. This is illustrated in Figure 1, and the electrode reactions are summarized by eq 1-4, where P = OEP²⁻, TPP²⁻ and X = Cl⁻, ClO₄⁻.

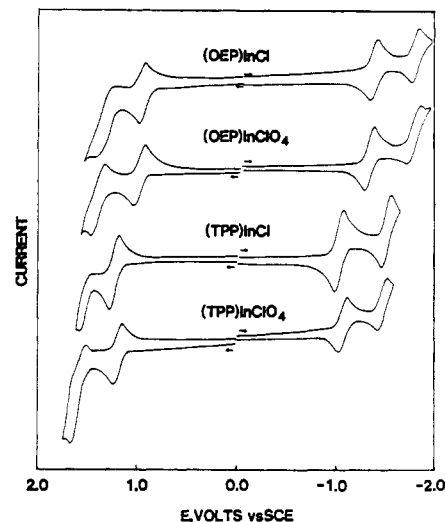
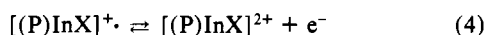
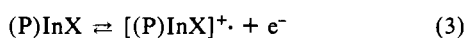
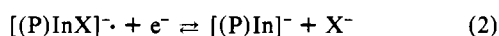
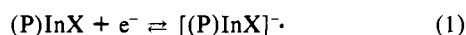


Figure 1. Cyclic voltammograms of various (P)InX complexes in CH_2Cl_2 (0.1 M TBAP) at 100 mV/s.

Table I. Half-Wave Potentials (V vs. SCE) of (P)In^{III}Cl and (P)In^{III}ClO₄ in CH_2Cl_2 and PhCN (0.1 M TBAP)^b

compd	solvent	2nd oxidn	1st oxidn	1st redn	2nd redn
(TPP)InCl	CH_2Cl_2	1.45	1.16	-1.09	-1.48
	PhCN	1.52 ^a	1.21	-1.09	-1.48
(TPP)InClO ₄	CH_2Cl_2	1.49	1.08	-1.12	-1.50
	PhCN	1.56	1.18	-1.04	-1.45
(OEP)InCl	CH_2Cl_2	1.49	1.05	-1.29	-1.72
	PhCN	1.53	1.07	-1.29	-1.77
(OEP)InClO ₄	CH_2Cl_2	1.55	1.12	-1.30	-1.80

^a E_{pa} measured at a scan rate of 100 mV/s. ^b Scan rate 100 mV/s.

Potentials for both series of compounds in CH_2Cl_2 and PhCN are given in Table I, and typical voltammograms in CH_2Cl_2 are represented in Figure 1. The reduction potentials of (TPP)InCl are identical in CH_2Cl_2 and PhCN, but differences exist for all the other reactions. As expected,¹³ reduction potentials for the octaethylporphyrins are negatively shifted from those of the tetraphenylporphyrins due to the increased basicity of the porphyrin ring. This, however, is not generally true for the oxidations, which show some variations between the different series of compounds. In addition, the potentials generally fit the trends for ring-centered reactions but certain exceptions can be noted.

The absolute potential differences between the first and second reduction of (P)InX range between 0.38 and 0.50 V and seem to suggest the formation of anion radicals and dianions. The absolute potential difference between the first oxidation and the first reduction of (P)InX ranges between 2.20 and 2.36 V for three of the compounds, suggesting cation radical and anion radical formation, but for (OEP)InClO₄ in CH_2Cl_2 this absolute potential difference is 2.42 V. Finally, the potential separation between the first and second oxidation is quite variable for (OEP)InX and (TPP)InX and ranges between 0.29 and 0.46 V depending upon the porphyrin ring, the type of counterion, and the solvent. These differences can be due simply to the varying degrees of metalloporphyrin-counterion interaction and do not necessarily suggest the possibility of In(IV) or In(II) formation upon electrooxidation or electroreduction.

Electronic Absorption Spectra of Oxidized and Reduced (OEP)InX and (TPP)InX in PhCN (0.3 M TBAP). Controlled-potential electrolysis was carried out after each reduction, and the products were characterized by electronic absorption and ESR spectroscopy. For the first reduction 1.0 ± 0.1 electron was added to the starting species to give a product generally characteristic of an anion radical. This is best illustrated by the electronic absorption spectra of the singly reduced (TPP)InCl and

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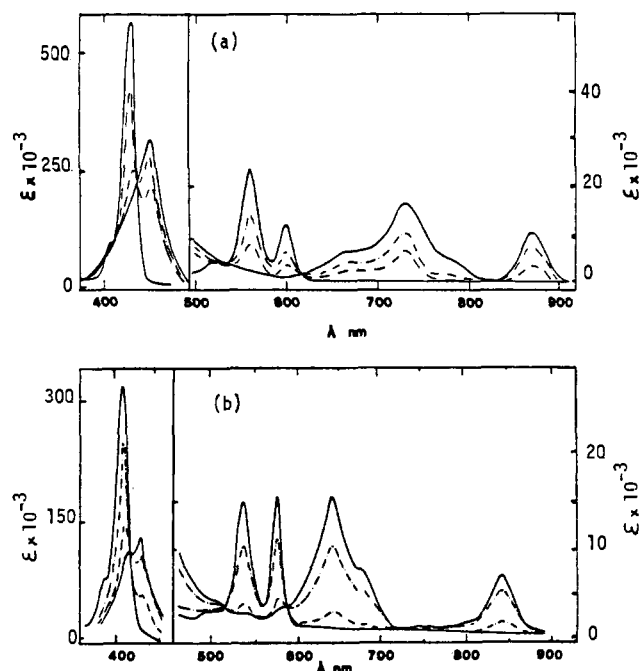


Figure 2. UV-visible spectra of the first reduction product of (a) 5×10^{-4} M (TPP)InCl and (b) 5×10^{-4} M (OEP)InCl in PhCN (0.3 M TBAP).

Table II. Maximum Absorbance Wavelengths (λ_{\max}) and Corresponding Molar Absorptivities (ϵ) for Oxidized^a and Reduced (OEP)InX and (TPP)InX in PhCN (0.3 M TBAP, $c = 5 \times 10^{-5}$ M)

compd	λ_{\max} , nm ($10^{-3}\epsilon$)			
(TPP)InCl	428 (560)	561 (23.0)	601 (13.1)	
(TPP)InClO ₄	428 (546)	561 (22.4)	601 (12.7)	
(OEP)InCl	411 (318)	541 (15.3)	578 (15.4)	
(OEP)InClO ₄ ^b	411 (301)	539 (12.0)	576 (12.4)	
[(TPP)InCl] ⁻	452 (315)	733 (16.2)	874 (10.9)	
[(TPP)InClO ₄] ⁻	452 (315)	734 (16.1)	874 (11.0)	
[(OEP)InCl] ⁻	431 (130)	636 (15.4)	820 (7.0)	
[(OEP)InClO ₄] ⁻ ^b	430 (128)	637 (15.1)	822 (6.4)	
[(TPP)InCl] ⁺	420 (220)	519 (11.4)	609 (13.2)	
[(TPP)InClO ₄] ⁺	421 (212)	524 (10.5)	608 (13.7)	
[(OEP)InCl] ⁺	399 (174)	651 (7.4)		
[(OEP)InClO ₄] ⁺ ^b	392 (179)	645 (7.2)		

^a Oxidized and reduced compounds are shown without loss of anion upon oxidation or reduction. This is only to designate the starting species and may not be representative of the actual species in solution. ^b Spectra are for solutions with 0.5 M TBAP in CH₂Cl₂.

(OEP)InCl derivatives represented in Figure 2.

The spectrum of five-coordinate (TPP)InCl has been described in the literature.¹⁰ In PhCN, a Soret peak is observed at 428 nm and two visible bands are located at 561 and 601 nm. Upon reduction at -1.3 V, the Soret peak decreases in intensity and shifts to 452 nm. At the same time the two bands in the visible region completely disappear while two new broad peaks characteristic of anion radicals appear¹⁴ at 733 and 874 nm. Several smaller peaks are also present at 619 and 669 nm. In addition, three isosbestic points are present at 440, 538, and 610 nm, indicating the presence of only (TPP)InCl and [(TPP)InCl]⁻ (or (·TPP)In) in solution. These spectral changes are totally reversible, and the spectrum of the starting species could be regenerated upon application of a controlled potential more positive than -1.0 V.

Spectral changes associated with reduction of (OEP)InCl are very similar to those observed after reduction of (TPP)InCl. This is shown in Figure 2b and Table II, which summarizes wavelengths and molar absorptivities for each of the neutral and reduced complexes. During controlled-potential reduction at -1.4 V, the

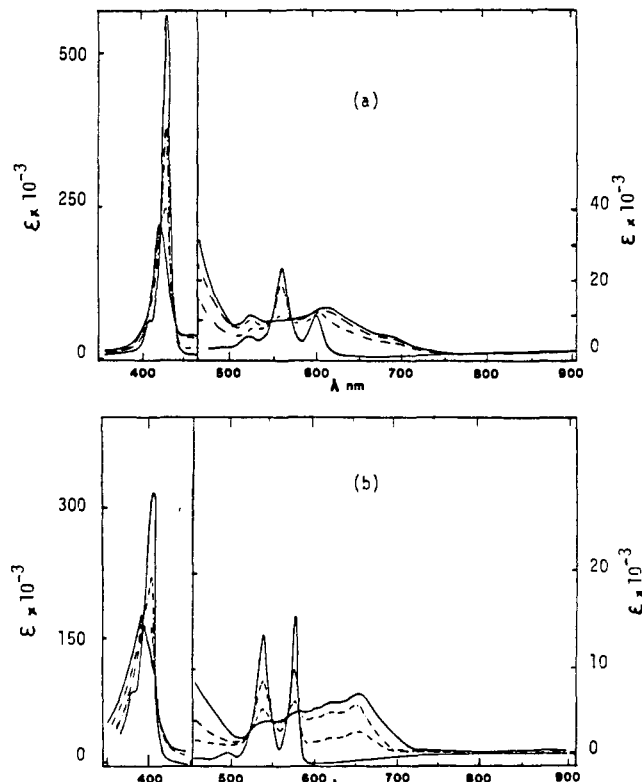


Figure 3. UV-visible spectra of the first oxidation product of (a) 1×10^{-4} M (TPP)InClO₄ and (b) 1×10^{-4} M (OEP)InClO₄ in PhCN (0.3 M TBAP).

Table III. ESR Data of Singly Oxidized and Reduced (P)InX in CH₂Cl₂ (0.1 M TBAP) at 120 K

compd	1st redn		1st oxidn	
	ΔH , G ^a	g^b	ΔH , G ^a	g^b
(TPP)InCl	162	2.001	201	2.002
(TPP)InClO ₄	161	2.001	221	2.002
(OEP)InCl	168	2.001	52.5	2.001
(OEP)InClO ₄	167	2.002	16.8	2.002

^a The total width, ΔH , was measured between field strengths corresponding to about 5% of the derivative peak heights. ^b g values given with respect to DPPH signal.

Soret peak of (OEP)InCl decreased in magnitude and shifted toward longer wavelengths. At the same time the visible bands at 541 and 578 nm disappeared and were replaced by the two broad absorbances with maxima at 636 and 820 nm. Again isosbestic points are obtained at 418, 518 and 587 nm, indicating the lack of any spectral intermediates during the electroreduction. This reduction is also spectrally reversible, and the starting species could be regenerated by controlled-potential oxidation at -1.1 V. Spectral changes associated with reduction of (TPP)InClO₄ and (OEP)InClO₄ were identical with those observed for reduction of (TPP)InCl or (OEP)InCl. For a given OEP or TPP complex the UV-visible spectra of the reduced species are very similar. This suggests a lack of anion association to the singly reduced species or (as is the case) a spectrum which is independent of the bound anion.

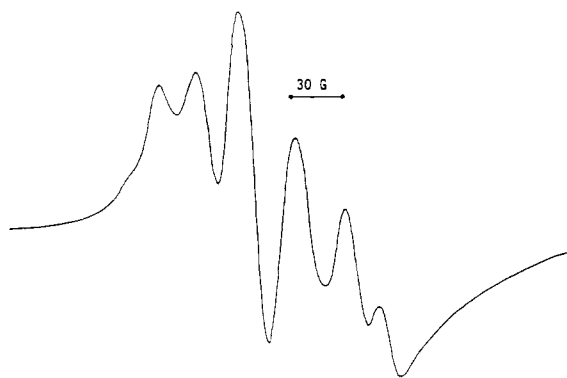
Unlike the case for reductions, the electronic absorption spectra of oxidized (TPP)InX and (OEP)InX depend upon the counterion of the starting material. This is shown in Figure 3 and Table II, which illustrate the spectra obtained during electrooxidation in an OTTLE cell. Oxidation of (TPP)InClO₄ or (OEP)InClO₄ (Figure 3) leads to a species with a diminished-intensity Soret band and broad peaks in the visible region of the spectra. The α and β bands of the starting material completely disappear after abstraction of one electron, and the resulting spectrum is very typically that of a cation radical.¹⁴ Also, the final absorption maxima and molar absorptivities of [(TPP)InClO₄]⁺ and

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Table IV. ESR Data of Singly Oxidized (TPP)InX and (OEP)InX in Various Solvent-Supporting Electrolyte Mixtures^a

compd	solvent	supporting electrolyte		T, K	ΔH , G ^{b,d}	g ^c	A _M , G
		type	concn, M				
(TPP)InCl	CH ₂ Cl ₂	TBAP	0.1	298	160	2.003	14.1
				234	173	2.002	14.0
				173	186	2.002	
				120	201	2.002	
(TPP)InClO ₄	CH ₂ Cl ₂	TBAP	0.1	298	160	2.002	14.1
				120	221	2.002	
(OEP)InCl	CH ₂ Cl ₂	TBAP	0.1	298	30.7 (16.1)	2.001	
				182	33.9 (19.1, 5.1)	2.002	
				120	52.5 (6.7)	2.001	
	CH ₂ Cl ₂	TBA(PF ₆)	0.1	298	30.9 (18.7)	2.001	
				120	61.3 (5.1)	2.001	
				298	26.9 (16.5)	2.001	
(OEP)InClO ₄	CH ₂ Cl ₂	TBAP	0.1	165	31.2 (17.3, 5.9)	2.001	
				120	36.5 (5.6)	2.001	
				298	23.6 (8.8)	2.002	
				175	16.8 (4.7)	2.002	
				120	16.8 (4.7)	2.002	

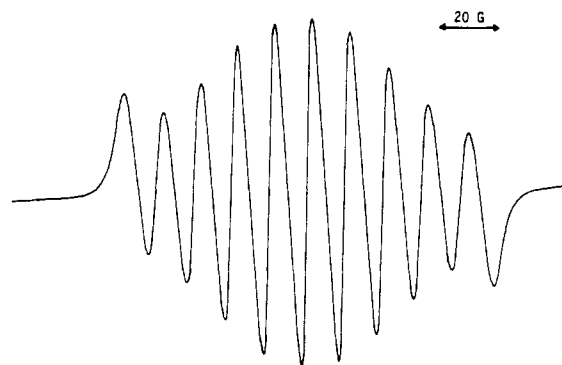
^aPotential applied 100–150 mV positive of $E_{1/2}$ for first oxidation. ^bThe total width, ΔH , was measured between field strengths corresponding to about 5% of the derivative peak heights. ^cg values given with respect to DPPH signal. ^dValues in parentheses are peak to peak values of ΔH .

**Figure 4.** ESR spectrum of the first reduction product of 6×10^{-4} M (TPP)InCl at 120 K in CH₂Cl₂ (0.1 M TBAP).

[(TPP)InCl]⁺, or [(OEP)InClO₄]⁺, and [(OEP)InCl]⁺, are not identical as seen in Table II.

ESR of Oxidized and Reduced (OEP)InX and (TPP)InX. Exhaustive electrolysis of (TPP)InCl at -1.2 V gave a solution whose ESR spectrum is shown in Figure 4. The g factors and ΔH width of the signals for the reduced OEP and TPP derivatives were identical in CH₂Cl₂ and PhCN and were independent of the counterion as shown in Table III. For all compounds the g factors are close to the free spin value of 2.0023. In addition, the total widths are about 160 G, while the widths between points of the maximum slope are about 70 G. The obtained spectra are also symmetrical about the center. This type of broad signal was reported by Felton for zinc porphyrin radical anions.¹⁵ However, in the case of zinc complexes, the width between the inflection points was only in the range of 15–20 G whereas the total width was about 80–100 G. No unambiguous explanations for the zinc porphyrin radical ESR spectra have been proposed. The observed g factors and total widths of the indium monoanion derivatives suggest that the site of primary reduction may be at the metal ion rather than at the π -ring center. However, these views are not supported by the morphology of the ESR spectra consisting of poorly resolved lines.

The one-electron oxidation of (TPP)InCl at 1.1 V leads to a species that exhibits an ESR spectrum at room temperature (Figure 5) consisting of 10 well-resolved lines reflecting coupling of the unpaired electron with the nuclear spin of ¹¹⁵In ($I = 9/2$). The g factors (≈ 2.002) and isotropic coupling constants (≈ 14 G) are given in Tables III and IV and are in good agreement with a metallic paramagnetic center type complex ion. However, this splitting accounts only for a spin density of 0.41% at the indium

**Figure 5.** Room-temperature ESR spectrum of the first oxidation product of 4×10^{-4} M (TPP)InCl in CH₂Cl₂ (0.1 M TBAP).

nucleus, considering that its optimal hyperfine coupling constant is about 3400 G.¹⁶ Moreover, since these complexes display highly isotropic ESR signals both at room temperature and at low temperature, the splitting can be considered as a superhyperfine coupling between the electron, essentially localized on the macrocycle, and the metal.

Delocalization of spin onto the metal of the porphyrin has been detected for oxidized cobalt,^{17,18} zinc,^{19–21} and thallium²² derivatives. With the exception of thallium porphyrins, these compounds generally exhibit optical spectra typical of an A_{2u} state. The A_{2u} ground state is characterized by high spin density at the meso position, enough spin density at the nitrogens to induce a coupling constant, no detectable spin density at the β pyrrole positions, and enough spin density on the metal to yield detectable coupling constants. This behavior is typified by oxidized zinc tetra-

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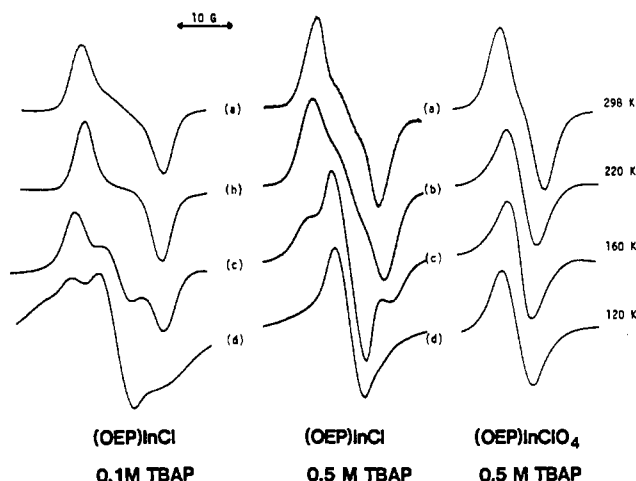


Figure 6. ESR spectra of (OEP)InCl (0.1 M TBAP), (OEP)InCl (0.5 M TBAP), and (OEP)InClO₄ (0.5 M TBAP) at various temperatures in CH₂Cl₂: (a) 298 K; (b) 220 K; (c) 160 K; (d) 120 K.

Table V. Coupling Constants for Different Cation Radicals of (P)M(L) and (P)M(L)₂

metal	axial ligand, L	<i>a</i> _M , G		ref ^a
		TPP	OEP	
Co(III)	ClO ₄ ⁻	5.7	1.2	16, 17
Zn(II)	ClO ₄ ⁻	1.22	≈0	18-20
In(III)	Cl ⁻	14.1	≈0	tw
	ClO ₄ ⁻	14.1	≈0	tw
Tl(III)	ClO ₄ ⁻	11.8	65.5	21
	CN ⁻	55.8	19.5	21

^atw = this work.

phenylporphyrin complexes. In contrast, the octaethylporphyrinic cation radicals [(OEP)Mg]⁺ and [(OEP)Zn]⁺ have optical spectra typical of an A_{1u} state and display no coupling with the metal.¹⁸ In the present study, the same behavior is observed for the octaethylporphyrin derivatives [(OEP)InCl]⁺ and [(OEP)InClO₄]⁺. Indeed, the one-electron oxidation of (OEP)InCl yields radicals with a characteristic singlet ESR signal as shown in Figure

6. However, at temperatures below 200 K, the oxidized complex leads to a spectrum with two singlet ESR signals and shows a reversible temperature dependence. If the concentration of the supporting electrolyte is increased to 0.5 M TBAP and the temperature is lowered, the signal observed at room temperature disappears. This is shown in Figure 6c,d. In contrast, the oxidized (OEP)InClO₄ complex exhibits only one singlet in the range 293-120 K but the total width of this singlet is smaller at low temperature. The above observations clearly indicate that ESR spectra of the (OEP)InX derivatives exhibit the same line-width variations depending on the temperature and the nature of the anion of the supporting electrolyte. We, therefore, ascribe the evolution of the ESR signals to the fact that the metal interacts with the anion of the supporting electrolyte at low temperature.

Finally, it is of interest to compare the above results to those observed for other metalloporphyrin radical cations. As shown in Table V, the metal couplings depend strictly on the nature of the macrocyclic and axial ligands. For the cobalt, zinc, and indium series, the ratio of the coupling constants, *a*_M(TPP)/*a*_M(OEP), demonstrates that the origin of the metal couplings arise from a σ-π spin polarization mechanism while both the σ-π spin polarization and direct π interaction mechanisms are involved for the thallium series.

In summary, the electrochemical, spectroelectrochemical, and ESR results are consistent with the formation of anion and cation radicals and give no evidence for the formation of discrete In(II) or In(IV) oxidation states. These data, however, do not rule out the formation of a highly oxidized or highly reduced indium atom in those metalloporphyrins containing a metal-metal or metal-carbon σ bond.

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Registry No. TBAP, 1923-70-2; (TPP)InCl, 63128-70-1; [(TPP)InCl]²⁺, 97644-36-5; [(TPP)InCl]⁺, 97644-35-4; [(TPP)InCl]⁻, 97644-33-2; [(TPP)InCl]²⁻, 97644-34-3; (TPP)InClO₄, 91312-86-6; [(TPP)InClO₄]²⁺, 97644-40-1; [(TPP)InClO₄]⁺, 97644-39-8; [(TPP)InClO₄]⁻, 97644-37-6; [(TPP)InClO₄]²⁻, 97644-38-7; (OEP)InCl, 32125-07-8; [(OEP)InCl]²⁺, 97644-44-5; [(OEP)InCl]⁺, 97644-43-4; [(OEP)InCl]⁻, 97644-41-2; [(OEP)InCl]²⁻, 97644-42-3; (OEP)InClO₄, 96363-81-4; [(OEP)InClO₄]²⁺, 97644-48-9; [(OEP)InClO₄]⁺, 97644-47-8; [(OEP)InClO₄]⁻, 97644-45-6; [(OEP)InClO₄]²⁻, 97644-46-7; TBA(PF₆), 3109-63-5.

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Reactions of σ-Bonded Alkyl- and Aryliron Porphyrins with Nitric Oxide. Synthesis and Electrochemical Characterization of Six-Coordinate Nitrosyl σ-Bonded Alkyl- and Aryliron Porphyrins

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The synthesis and physical characterization of 12 six-coordinate nitrosyl σ-bonded alkyl- and aryliron porphyrins were investigated in nonaqueous media. The ligands σ bonded to the nitrosyliron octaethylporphyrin or tetraphenylporphyrin complexes were CH₃, *n*-C₄H₉, C₆H₅, C₆H₄Me-*p*, C₆H₄OMe-*p*, and C₆F₅H. Each neutral complex was characterized by ¹H NMR, IR, and UV-visible spectroscopy, and on the basis of these data, the central metal was assigned as being in the Fe(II) oxidation state. The electrochemistry of two complexes, (OEP)Fe(C₆H₅)(NO) and (TPP)Fe(C₆H₅)(NO), was carried out, and results of this study were evaluated with respect to the spectroscopic characterization of the complexes. Finally, comparisons were made between the reactivities and physicochemical properties of the investigated six-coordinate complexes and other related iron σ-bonded alkyl and iron nitrosyl complexes in the literature.

Introduction

Studies on the binding and activation of small molecules by metalloporphyrins are of major interest due to the potential im-

portance of these reactions in catalytic processes involving biological reactions.²⁻⁵ Evidence has been provided for the formation

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