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Gold Porphyrin Complexes. Evidence for Electrochemically Inert Gold(III)

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Gold(III) tetraphenylporphine tetrachloroaurate, gold(III) etioporphyrin I tetrachloroaurate, and gold(III) mesoporphyrin IX dimethylester acetate were synthesized and characterized by visible spectral and electrochemical (classical and cyclic voltammetry and coulometry) studies. The gold porphyrin complexes show spectral properties similar to those reported for other metalloporphyrins, except Mn and Mo, and electrochemical properties similar to those of metalloporphyrins with a stable central metal ion. Interestingly, in these gold complexes the tripositive metal ion is electrochemically inert.

Introduction

Metalloporphyrin complexes occur widely in nature in such complex biological systems as hemoglobin, myoglobin, and the cytochromes. In each biological metalloporphyrin, precise oxidation–reduction fine-tuning of the complex is vital to its function. Hemoglobin, for example, which contains iron(II) protoporphyrin IX, reversibly binds oxygen during respiration in higher animals, while methemoglobin, which contains iron(III) protoporphyrin IX in an identical environment, cannot perform this function [1]. Cytochrome *c* serves as an electron-transfer agent during photosynthesis; its precise oxidation–reduction behavior allows the photosynthetic process to continue. Recently many simple metalloporphyrin complexes have been examined as model systems for the more complicated biological originals. Extensive spectral and electrochemical studies have been conducted on these prototypes to determine their exact behavior and so expand our knowledge of their function in living systems [2–15]. In the course of these model studies, much has been learned about the porphyrin ligand itself; it is an aromatic macrocycle with a rich and varied chemistry, including redox chemistry, of its own; it is also an excellent ligand, which may have a large effect upon the chemical behavior of its central metal ion [2, 3]. The porphyrin ligand is useful more than just as a component of biological model systems; it is a valuable tool through which to study the chemical behavior of metal ions.

X-ray photoelectron spectroscopic studies [16] and theoretical calculations [17] have indicated that a large amount of negative charge is associated with the nitrogen donor atoms of the porphyrin ligand; calculations have indicated further that nitrogen-to-central metal binding in most metalloporphyrins is primarily electrostatic. Because of the size constraint imposed by the structure of the ligand [18], the extreme polarizability of the ligand, and the large electrostatic attraction, the porphyrin ligand is expected to stabilize the higher oxidation states of metal ions, and, in fact, many porphyrin complexes of metal ions in unusual oxidation states have been prepared. A stable silver(III) porphyrin complex has been isolated [11] and iron(IV) porphyrin dimers have been generated in solution [19]. Presumably the porphyrin ligand might be used to stabilize the higher oxidation states of other metal ions.

The oxidation–reduction chemistry of gold in simple coordination complexes has been studied and recently summarized [20]. Gold(I) and gold(III) are the principal oxidation states, though gold species in both states are highly reactive redox species and are readily reduced to the metal. Very recently, the synthesis of a complex of gold(V) was reported [21], but no redox study has appeared. Controversy has existed for some time concerning complexes of gold(II) [20, 22–26]; some electrochemical evidence indicates the possible formation of a gold(II) complex by electrolysis [27], but in general gold(III) undergoes a two-electron reduction to gold(I) and then a one-electron reduction to gold(0).

This study is an examination of the electrochemical behavior of gold in porphyrin complexes, undertaken to determine the effect of gold upon the porphyrin ligand and the effect of the porphyrin ligand upon gold. Compounds of gold(III) with three different porphyrin ligands were synthesized: gold(III) tetraphenylporphine tetrachloroaurate, [Au(TPP)] [$AuCl_4$], gold(III) mesoporphyrin IX dimethylesteracetate, [Au(Meso)] [$C_2H_3O_2$] and gold(III) etioporphyrin I tetrachloroaurate, [Au(Etio)] [$AuCl_4$]. The ligands were chosen to cover large extremes of peripheral substitution on the porphyrin ring. The complexes were characterized by visible spectrophotometry, voltammetry, and coulometry. A unique, new kind of complex of gold is reported: one in which gold is electrochemically inert throughout the full range of voltammetric examination.

Experimental

Solvents and Supporting Electrolytes

Dimethylsulfoxide, DMSO, was purified by fractional distillation from calcium hydride. Butyronitrile, BN, was purified by a modification of the method of Van Duyne and Reilley [28]. Both DMSO and BN were stored in the dark under nitrogen. Spectral grade chloroform was used without further purification.

Tetraethylammonium perchlorate, TEAP, obtained from Eastman Organic Chemicals, was prepared for electrochemical use by recrystallization from distilled water and drying at reduced pressure. Polarographic grade tetrabutylammonium perchlorate (TBAP), obtained from Southwestern Analytical Chemicals, Inc., was dried under reduced pressure. Both supporting electrolyte compounds were placed in stoppered bottles in a desiccator.

Porphyrin Ligands

Tetraphenylporphine (H_2TPP) was prepared by the method of Adler *et al.* [29]. Mesoporphyrin IX dimethylester (H_2Meso) was obtained from ICN Pharmaceuticals, Inc., and used without purification. Etioporphyrin I (H_2Etio) was prepared by the method of Smith [30], from 5-bromo-3,4′-diethyl-3′,4,5′-trimethylpyrromethene perbromide, which was prepared by the method of Fischer and Orth [31].

Preparation of the Gold Porphyrin Complexes

All of the cationic gold porphyrin complexes were prepared by a modification of the procedure of Dorough, Miller, and Huennekens [32] for the preparation of metallotetraphenylporphines. The synthesis of $[Au(TPP)][AuCl_4]\cdot 5H_2O$ by this method was previously reported by Fleischer and Laszlo [33]. Interestingly, the tetraphenylporphine and etioporphyrin complexes crystallized as the tetrachloroaurate salt, while the mesoporphyrin complex crystallized as the acetate. For anodic voltammetric studies in BN, either counter ion was acceptable, because neither acetate nor tetrachloroaurate is electroactive in the 0 to +2V potential range. Tetrachloroaurate is reducible in DMSO, however, and it was necessary to eliminate it in order to examine the cathodic behavior of the cationic porphyrin complexes. This was done by controlled-potential reduction of the $AuCl_4^-$ ion to Au(0) at a platinum gauze electrode; the electrode was then removed from the solution, thus eliminating the interference. Because of large molar absorptivities of the porphyrin complexes in the visible range, the small absorption due to $AuCl_4^-$ did not interfere in spectral measurements.

$[Au(TPP)][AuCl_4]$ was prepared by adding 20 mmol of $KAuCl_4$ and 200 mmol of anhydrous sodium acetate to one liter of 2×10^{-4} *F* H_2TPP in glacial acetic acid. While the resulting solution was continuously stirred, it was heated to boiling and then cooled. The solution was then treated with 400 ml of benzene and 400 ml of water. Finally the benzene layer was separated, washed with water, and evaporated to dryness. The dark residue was recrystallized from methanol, leaving dark purple micro-crystals, which were air dried; yield 41.3%. *Anal.* Calcd for $[Au(TPP)][AuCl_4]$, $C_{44}N_4H_{28}Au_2Cl_4$: C, 46.02; H, 2.46; N, 4.87%. Found: C, 46.20; H, 2.51; N, 4.32%.

$[Au(Meso)](CH_3COO)$ was prepared starting with H_2Meso by a procedure identical with that used for $[Au(TPP)][AuCl_4]$. The residue from the reaction was dissolved in a minimum of methanol and the product was thrown out of the solution by the addition of ice. The dark purple micro-crystals were collected and air-dried; yield 18.8%. *Anal.* Calcd for $[Au(Meso)](C_2H_3O_2)$, $C_{38}N_4H_{43}O_6Au$: C, 53.78; H, 5.11; N, 6.60%. Found: C, 54.51; H, 5.36; N, 6.45%.

$[Au(Etio)][AuCl_4]$ was prepared by the same method as the other complexes, but the reaction mixture was not taken to dryness. Instead, the volume of the benzene layer was reduced to 2 ml and the mixture was filtered. The product was obtained as dark purple micro-crystals; yield 5.5%. *Anal.* Calcd for $[Au(Etio)][AuCl_4]$, $C_{32}N_4H_{36}Au_2Cl_4$: C, 37.96; H, 3.58; N, 5.53%. Found: C, 35.10; H, 3.14; N, 4.30%.

Physical Measurements

Spectra were obtained on a Cary Model 14 spectrophotometer with matched quartz spectral cells of 1.00 cm path length. Molar absorptivities were calculated from spectral data collected with a Beckman D. U. spectrophotometer. Because of very large molar absorptivities, solutions of concentration 5×10^{-5} to 1×10^{-6} *F* were used for spectral measurements.

All voltammetric curves were obtained with a controlled-potential polarograph as previously described [34]. A three-compartment polarographic cell was used, in which medium porosity glass frits separated the working, reference, and auxiliary electrode compartments. Solutions were de-aerated fully prior to each experiment, and a blanket of nitrogen was maintained above the solution in the working electrode compartment throughout the measurement. The reference electrode was a saturated calomel electrode (aq.); the auxiliary, a platinum foil electrode; and the working, either a dropping mercury electrode (DME), a rotated platinum electrode (RPE), or a stationary platinum electrode (SPE).

Controlled-potential coulometry was performed with a Wenking Model 61-RS potentiostat. The working electrode was a rotated platinum gauze electrode; the other electrodes were the same as for the voltammetric measurements.

For spectroelectrochemical measurements, controlled-potential electrolyses were conducted with a Wenking potentiostat as above and spectra were recorded on a Cary 14 spectrophotometer. The entire experiment, up until the actual recording of the spectrum, was conducted in an inert atmosphere system as previously described [35].

Results and Discussion

The three gold(III) porphyrin complexes were characterized by visible spectral studies, by classical and cyclic voltammetry, and by coulometry. For comparison purposes, the three ligands were characterized in the same way. In addition, the one- and two-electron reduction products of gold(III) tetraphenylporphine were characterized by visible spectrophotometry.

Visible Spectral Study

The visible spectra of the free base porphyrin compounds and corresponding gold(III) porphyrin complexes were examined in DMSO, 0.1*F* in TEAP; $CHCl_3$, 0.1*F* in TBAP; and BN, 0.1*F* in TBAP. The spectra of each complex or ligand in the three solvent systems showed only slight differences due to solvent effects.

The spectra of the three porphyrin ligands are very similar to each other; they consist of four low energy and low intensity bands, I–IV, of increasing molar absorptivity and one higher energy and higher intensity band (Soret). The spectral data for all the porphyrin ligands are presented in Table I, along with some literature values. No evidence was found for any association, dissociation, or chemical reaction of the porphyrin ligands.

The three gold porphyrin complexes also show spectral features similar to each other, but these are

TABLE I. λ_{max} and Molar Absorptivity Data for the Free Base Porphyrins.

Compound	Solvent	Soret[a] (ε)[b]	I[a] (ε)[b]	II[a] (ε)[b]	III[a] (ε)[b]	IV[a] (ε)[b]	Reference
H_2TPP	DMSO[c]	419 (3.9 x 10^5)	649 (4.1 x 10^3)	591 (4.2 x 10^3)	551 (6.3 x 10^3)	515 (1.4 x 10^4)	this work
H_2TPP	CF[d]	419 (3.6 x 10^5)	650 (3.3 x 10^3)	591 (3.9 x 10^3)	551 (5.5 x 10^3)	516 (1.3 x 10^4)	this work
H_2TPP	BN[d]	415 (4.2 x 10^5)	649 (4.6 x 10^3)	591 (5.3 x 10^3)	547 (7.8 x 10^3)	513 (1.8 x 10^4)	this work
H_2TPP	DMF	418 (4.7 x 10^5)	647 (3.7 x 10^3)	590 (5.1 x 10^3)	548 (8.0 x 10^3)	513 (1.8 x 10^4)	15
H_2Meso	DMSO[c]	399 (1.4 x 10^5)	621 (4.1 x 10^3)	567 (6.3 x 10^3)	531 (8.8 x 10^3)	498 (1.3 x 10^4)	this work
H_2Meso	CF[d]	400 (1.4 x 10^5)	623 (4.3 x 10^3)	568 (5.7 x 10^3)	534 (8.6 x 10^3)	499 (1.2 x 10^4)	this work
H_2Meso	BN[d]	395 (1.3 x 10^5)	622 (3.3 x 10^3)	567 (4.1 x 10^3)	529 (6.1 x 10^3)	497 (8.7 x 10^3)	this work
H_2Meso	DMF	397 (1.9 x 10^5)	620 (6.1 x 10^3)	566 (8.0 x 10^3)	529 (1.1 x 10^4)	496 (1.7 x 10^4)	14
H_2Etio	DMSO[c]	398 (1.1 x 10^5)	621 (3.7 x 10^3)	566 (5.1 x 10^3)	531 (7.2 x 10^3)	497 (1.0 x 10^4)	this work
H_2Etio	CF[d]	398 (1.1 x 10^5)	622 (3.8 x 10^3)	567 (5.0 x 10^3)	533 (7.7 x 10^3)	499 (1.1 x 10^4)	this work
H_2Etio	BN[d]	395 (8.5 x 10^4)	622 (3.9 x 10^3)	567 (5.1 x 10^3)	529 (7.5 x 10^3)	497 (1.0 x 10^4)	this work
H_2Etio	DIOX	399.5 (1.6 x 10^5)	621 (5.2 x 10^3)	566 (6.0 x 10^3)	528 (9.5 x 10^3)	496 (1.4 x 10^4)	36, 37

[a] Wavelength in nanometers. [b] Molar absorptivity. [c] 0.1*F* TEAP. [d] 0.1*F* TBAP.

TABLE II. λ_{max} and Molar Absorptivity Data for the Gold(III) Porphyrins.

Complex	Solvent	Soret[a] (ε)[b]	α[a] (ε)[b]	β[a] (ε)[b]	Reference
Au(TPP)$^+$	DMSO[c]	413 (2.1×10^5)	609 (2.7×10^3)	526 (1.4×10^4)	this work
Au(TPP)$^+$	CF[d]	410 (1.7×10^5)	594 (3.1×10^3)	523 (1.0×10^4)	this work
Au(TPP)$^+$	BN[d]	407 (2.8×10^5)	589 (4.6×10^3)	523 (2.1×10^4)	this work
Au(TPP)$^+$	CF	412 (3.3×10^5)	–	521 (2.0×10^4)	33
Au(Meso)$^+$	DMSO[c]	393 (4.2×10^4)	549 (3.0×10^3)	514 (2.4×10^3)	this work
Au(Meso)$^+$	CF[d]	390 (5.9×10^4)	547 (5.6×10^3)	512 (4.0×10^3)	this work
Au(Meso)$^+$	BN[d]	388 (6.9×10^4)	546 (5.7×10^3)	512 (4.2×10^3)	this work
Au(Etio)$^+$	DMSO[c]	392 (9.0×10^4)	548 (6.2×10^3)	511 (4.4×10^3)	this work
Au(Etio)$^+$	CF[d]	388 (6.7×10^4)	547 (7.1×10^3)	511 (4.0×10^3)	this work
Au(Etio)$^+$	BN[d]	388 (8.2×10^4)	546 (5.8×10^3)	509 (3.9×10^3)	this work

[a] Wavelength in nanometers. [b] Molar absorptivity. [c] 0.1*F* TEAP. [d] 0.1*F* TBAP.

very different from those of the free base porphyrins. In these cases, there are two low intensity and low energy bands (α and β) and one high intensity, high energy band (Soret). The spectral data for the gold(III) porphyrin complexes appear in Table II. These data indicate that the complexes also do not undergo any association, dissociation, or chemical reaction.

The spectra observed for the gold(III) porphyrin complexes are typical metalloporphyrin spectra [3]; they indicate the formation of a simple coordination complex between the central gold(III) ion and the porphyrin macrocycle. One feature of importance in the spectra of the complexes is their great similarity, which indicates the dominance of the porphyrin core and the lesser perturbations caused by peripheral substituents. Another is the presence of two lower energy bands in the spectrum of each complex instead of the four corresponding bands in the spectrum of each ligand; this results from the higher symmetry of the metalloporphyrin compared to that of the free base porphyrin [38]. A third important feature is the position of the high energy Soret peak. In each complex the shift in the Soret peak position upon complexation of the porphyrin ring with the gold ion is nearly the same, and it is always to shorter wavelength. Apparently the high positive charge of the central gold(III) ion causes electron density to be drawn toward the center of the ring, making the motion of charge to the periphery of the ring more difficult. The Soret absorption in simple metalloporphyrin complexes has been attributed to the $\pi \rightarrow \pi^*$ transitions of the porphyrin macrocycle, with the motion of charge to the periphery of the ring [38, 39]. The spectra of the gold(III) porphyrin complexes then arise from the porphyrin macrocycles themselves, with only minor perturbations caused by the gold ion, and they appear to indicate the formation of a simple metalloporphyrin complex.

Classical Voltammetry and Coulometry

To attain the maximum possible potential range for electrochemical study, two solvent systems and two electrodes were employed; BN (0.1*F* TBAP) was used for anodic voltammetric studies at a rotated platinum electrode and DMSO (0.1*F* TEAP) was used for cathodic voltammetric studies at a rotated platinum electrode, and a dropping mercury electrode. Coulometric studies were performed at controlled potential with a rotated platinum gauze electrode.

The voltammetric and coulometric behavior of the free base porphyrins was examined so that the data for the ligands might be compared to those for the gold complexes. Data for the porphyrin ligands are shown in Table III, along with some data from the literature. The porphyrin ligands undergo a series of

TABLE III. Cathodic and Anodic Voltammetry and Coulometry of the Free Base Porphyrins.

Compound	Electrode, Solvent	1st step			2nd step			Reference
		$E_{1/2}{}^{a,b}$	$i_L{}^c$	n^d	$E_{1/2}{}^a$	$i_L{}^c$	n^d	
CATHODIC								
H_2TPP	Pt^e, $DMSO^f$	–1.03	1.00	1.0^g	–1.42	0.98	1.0^g	this work
H_2TPP	DME, $DMSO^f$	–1.02	1.00	–	–1.43	0.95	–	this work
H_2TPP^h	DME, DMF^f	–1.08	1.0	1.0^i	–1.45	1.0	1.0^i	15
H_2Meso	Pt^e, $DMSO^f$	–1.30	1.00	1.0^g	–1.71	1.08	1.1^g	this work
H_2Meso	DME, $DMSO^f$	–1.30	1.00	–	–1.68	0.95	–	this work
H_2Meso^h	DME, DMF^f	–1.34	1.0	1.0^i	–1.73	1.0	1.0^i	14
H_2Etio	Pt^e, $DMSO^f$	–1.32	1.0	–	–1.72	1.07	–	this work
H_2Etio	DME, $DMSO^f$	–1.27	1.00	–	–1.78	1.01	–	this work
H_2Etio^h	DME, DMF^j	–1.37	1.0	1.0^k	–1.80	1.0	1.0^i	12
ANODIC								
H_2TPP	Pt^e, BN^l	+1.06	1.00	$–^{g,m}$	+1.19	1.00	$2.1^{g,m}$	this work
H_2TPP	Pt, BN^n	+0.97	–	1.0^o	(+1.12)	–	–	40
H_2Meso	Pt^e, BN^l	+0.88	1.00	1.1^g	+1.44	0.78	$1.3^{g,p}$	this work
H_2Meso	Pt, BN^n	+0.78	–	1.0^o	–	–	–	40
H_2Etio	Pt^e, BN^l	+0.88	1.00	–	+1.44	0.82	–	this work
H_2Etio	Pt, BN^n	+0.77	–	1.0^o	–	–	–	40

[a] V *vs.* SCE. [b] All values were reproducible to ±0.01 V. Each value was the result of two or more independent measurements. [c] Limiting current values are normalized to i_L (1st step). [d] Number of mol of electrons per mol of free base porphyrin. [e] $E_{1/2}$ values were measured at the RPE; coulometric experiments were performed with a rotated platinum gauze electrode. [f] 0.1*F* TEAP. [g] Measured by controlled-potential coulometry. [h] Four cathodic waves were reported; only the first two are listed here. [i] Measured by polarographic slope analysis. [j] 0.1*F* TPAP. [k] Measured by analogy with reaction with metallic sodium. [l] 0.1*F* TBAP. [m] The two oxidation waves were so close that they could not successfully be separated for coulometric study; the second value is the sum of both steps. [n] 0.1*F* $LiClO_4$. [o] Measured by voltammetric curve analysis. [p] Value includes impurity wave and second oxidation.

TABLE IV. Cathodic and Anodic Voltammetry and Coulometry of the Gold(III) Porphyrins[a].

Complex	Electrode, Solvent	1st step			2nd step			3rd step	
		$E_{1/2}{}^{b,c}$	$i_L{}^d$	n^e	$E_{1/2}{}^b$	$i_L{}^d$	n^e	$E_{1/2}{}^b$	$i_L{}^d$
Cathodic									
$Au(TPP)^+$	Pt^f, $DMSO^g$	–0.52	1.00	1.0	–0.96	0.92	0.9	–1.67	1.04
$Au(TPP)^+$	DME, $DMSO^g$	–0.50	1.00	–	–0.92	1.12	–	–1.66	0.96
$Au(Meso)^+$	Pt^f, $DMSO^g$	–0.73	1.00	1.1	–1.23	0.92	1.0	–	–
$Au(Meso)^+$	DME, $DMSO^g$	–0.79	1.00	–	–1.26	1.19	–	–1.92	0.94
$Au(Etio)^+$	Pt^f, $DMSO^g$	–0.78	1.00	–	–1.30	0.80	–	–	–
$Au(Etio)^+$	DME, $DMSO^g$	–1.04	1.00	–	–1.29	1.00	–	–	–
Anodic									
$Au(TPP)^+$	Pt^f, BN^h	+1.68		0.9					
$Au(Meso)^+$	Pt^f, BN^h	+1.57		1.1					
$Au(Etio)^+$	Pt^f, BN^h	+1.54		–					

[a] All values are from this work. [b] V *vs.* SCE. [c] All values are reproducible to ±0.01 V. Each value was the result of two or more independent measurements. [d] Limiting current values are normalized to i_L (1st step). [e] Number of mol of electrons per mol of gold(III) porphyrin was determined by controlled-potential coulometry. [f] $E_{1/2}$ values were measured at the RPE; coulometric experiments were performed with a rotated platinum gauze electrode. [g] 0.1*F* TEAP. [h] 0.1*F* TBAP.

reductions in DMSO–TEAP and a series of oxidations in BN–TBAP. Limiting current data suggest that the oxidations and reductions are all one-electron changes; this is confirmed by coulometric data. No large differences exist between half-wave potentials for the reductions at the platinum and mercury electrodes.

Voltammetric patterns for the gold(III) porphyrins are very similar to each other, as well as to those of the corresponding ligands. In DMSO–TEAP, there is a series of reductions and in BN–TBAP, one oxidation before solvent background. Again limiting current and coulometric data suggest that each oxidation and each reduction involves one electron. Data for the voltammetric and coulometric experiments are shown in Table IV.

No large differences appear between the cathodic half-wave potentials measured for the complexes at the platinum and at the mercury electrodes. In addition, no differences are observed in the electrochemical steps when different anions are present to counter the charge of the cationic gold porphyrin complexes. Tetrachloroaurate, chloride, and acetate were the counter ions examined. This suggests that the gold(III) ion, of d^8 configuration, does not bind closely additional ligands beyond the square plane provided by the porphyrin ring, though it might loosely bind DMSO molecules. This behavior is expected for a d^8 ion in square planar configuration [20].

Cyclic Voltammetry

Cyclic voltammetric studies were conducted at a stationary platinum electrode. Again both the free base porphyrins and the gold(III) porphyrins were examined so that comparison might be made. The cyclic voltammetric data for the free base porphyrins

TABLE V. Cyclic Voltammetry of the Free Base Porphyrins[a,b].

Compound	1st step			2nd step		
	E[c]	i_{p_r}/i_{p_f}[d]	Δ[e]	E[c]	i_{p_r}/i_{p_f}[d]	Δ[e]
Cathodic (initial sweep)						
H_2TPP	−1.03	0.94	60	−1.41	1.03	60
H_2Meso	−1.30	0.95	60	−1.70	1.01	60
H_2Etio	−1.31	0.88	60	−1.74	0.88	60
Anodic (initial sweep)						
H_2TPP	+1.08	0.93	80	+1.23	0.99	70
H_2Meso[f]	+0.89	0.87	60	–	–	–
H_2Meso[g]	+0.89	0.43	60	+1.41	0.28	110
H_2Etio[f]	+0.86	1.00	60	–	–	–
H_2Etio[g]	+0.86	0.33	60	+1.40	0.30	120

[a] All values are from this work. [b] All solutions for cathodic studies were 0.1*F* TEAP in DMSO and for anodic studies, 0.1*F* TBAP in BN; the working electrode was the SPE. [c] Potential halfway between anodic and cathodic peak potentials; V *vs.* SCE ± 0.01 V. [d] Ratio of return to forward peak currents. [e] $E_{p_{anodic}} - E_{p_{cathodic}}$. [f] Only the first oxidation was included in the scan. [g] First and second oxidations were included in the scan.

TABLE VI. Cyclic Voltammetry of the Gold(III) Porphyrins[a,b].

Complex	1st step			2nd step			3rd step		
	E[c]	i_{p_r}/i_{p_f}[d]	Δ[e]	E[c]	i_{p_r}/i_{p_f}[d]	Δ[e]	E[c]	i_{p_r}/i_{p_f}[d]	Δ[e]
Cathodic (initial sweep)									
$Au(TPP)^+$	−0.54	1.03	60	−0.98	1.00	70	−1.69	1.03	70
$Au(Meso)^+$	−0.74	1.11	100	−1.25	0.92	60	–	–	–
$Au(Etio)^+$	−0.77	1.12	90	−1.30	1.04	70	–	–	–
Anodic (initial sweep)									
$Au(TPP)^+$	+1.69	0.91	80						
$Au(Meso)^+$	+1.58	0.67	100						
$Au(Etio)^+$	+1.57	0.81	100						

[a] All values are from this work; cathodic initial sweep values were taken from scans including two or three reduction steps. [b] All solutions for cathodic studies were 0.1*F* TEAP in DMSO and for anodic studies 0.1*F* TBAP in BN; the working electrode was the SPE. [c] Potential halfway between anodic and cathodic peak potentials; V *vs.* SCE. [d] Ratio of return to forward peak current. [e] $E_{p_{anodic}} - E_{p_{cathodic}}$; mV ± 10 mV.

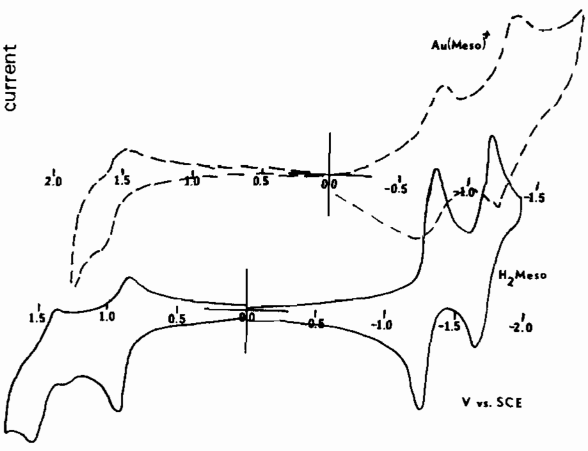

Figure 1. Composite cyclic voltammograms for H_2Meso and Au(Meso)$^+$ at 12 V/min at a stationary platinum electrode. The negative potential region was studies in DMSO (0.1*F* TEAP) and the positive potential region in butyronitrile (0.1*F* TBAP).

agree in general with the voltammetric data already presented (Tables III and V). The free base porphyrins undergo a series of reversible one-electron reductions in DMSO–TEAP and a series of reversible one electron oxidations in BN–TBAP. As in the classical voltammetric behavior, the cyclic voltammetric behavior of the gold complexes is very similar to that of the free base porphyrins. The complexes were observed to undergo a series of apparently reversible one-electron reductions in DMSO–TEAP and one quasi-reversible one-electron oxidation in BN–TBAP at a scan rate of 12 volts per minute (cyclic voltammetric examination of the gold(III) tetraphenylporphine and gold(III) mesoporphyrin IX dymethylester acetate complexes at scan speeds of 6 to 30 volts per minute showed no change in peak potentials). Data for the cyclic voltammetric study of the complexes are presented in Table VI.

Of particular interest in the electrochemical examination of the gold(III) porphyrins is their similarity to the free base porphyrins. In the voltammetric experiments, the result of complexation with the gold ion is a change in the potentials of the redox steps, but no change in the pattern of behavior, an effect similar in nature to that noted in the spectral examination. The cyclic voltammograms of H_2Meso and Au(Meso)$^+$ in Figure 1 demonstrate this point. Again the dominance of the porphyrin macrocycle and the minor perturbations caused by replacement of the two protons of the free base porphyrin by the gold(III) ions are obvious. The entire voltammogram has been shifted to more positive potential; as more negative charge from the ligand is drawn to the center of the ring by the gold ion, the ring becomes easier to reduce and harder to oxidize. There are no new oxidation or reduction processes which can be attributed to the gold(III) ion itself, as each peak in the voltammogram of the complex has a counterpart in the voltammogram of the ligand.

Spectroelectrochemistry

The one- and two-electron reduction products of Au(TPP)$^+$ were generated electrochemically by controlled-potential electrolysis and characterized by visible spectrophotometry. The spectral data for the complex and its reduction products are shown in Table VII. In each case a porphyrin Soret peak appears, but in each of the reduction products the Soret peak is significantly diminished in absorptivity.

TABLE VII. λ_{max} and Molar Absorptivity Data for Gold(III) Tetraphenylporphine^a.

Complex	Soret^b (ε)	Visible Bands^b	
		(ε)	(ε)
Au(TPP)$^+$	413^c (2.1 × 10^5)	526^c (1.4 × 10^4)	609^c (2.7 × 10^3)
Au(TPP)·	445^d (2 × 10^4)	735^d (2 × 10^3)	
Au(TPP)$^-$	375^d (1 × 10^4)	560^d (4 × 10^3)	625^d (2 × 10^3)

^{a}All solutions were 0.1*F* TEAP in DMSO. ^{b}Wavelength in nanometers. ^{c}Wavelength measured ±1 nm. ^{d}Wavelength measured ±5 nm.

Conclusions

Because of their value as biological model compounds and as intrinsically interesting complexes, metalloporphyrin complexes have generated a great deal of experimentation, particularly among electrochemists and spectroscopists. Recently many novel metalloporphyrin complexes have been prepared [41]; some contain metal ions bonded to the porphyrin ring through two or three nitrogen donor atoms [42]. The vast majority of metalloporphyrin complexes, however, are coordination complexes in which the central metal ion lies approximately in the center of the porphyrin ring, bonded through all four nitrogen donor atoms. The simple metalloporphyrin complexes are characterized by the similarity of their spectral and electrochemical behavior; they typically show a three-banded visible spectrum with one high intensity, high energy (Soret) band. They show a series of reversible one-electron oxidations, characterized by predictable half-wave potential separations. Fajer *et al.* [6], Fuhrhop, Kadish, and Davis [4], and Felton and Linschitz [10] have tabulated standard half-wave potential separations for simple metalloporphyrin complexes. The existence of these standard potential separations

TABLE VIII. Significant Half-Wave Potential Separations (Δ) in Porphyrin Electrochemistry.

Electrochemical Steps	Compounds	Δ	Reference
$E^{oxid'n}_{1/2(2)} - E^{oxid'n}_{1/2(1)}$	$M^{II}(TPP)$	0.29 ± 0.05 V	6
$E^{red'n}_{1/2(1)} - E^{red'n}_{1/2(2)}$	$M(OEP)^{a}$	0.42 ± 0.05 V	4
$E^{oxid'n}_{1/2(1)} - E^{red'n}_{1/2(1)}$	$M(OEP)^{a}$	2.25 ± 0.15 V	4
$E^{red'n}_{1/2(1)} - E^{red'n}_{1/2(2)}$	$M(TPP)^{b}$	0.44 ± 0.04 V	10
$E^{red'n}_{1/2(1)} - E^{red'n}_{1/2(1)}$	$M^{II}(TPP)–M^{II}(Etio)$	0.27 ± 0.02 V	10

[a] Metals of oxidation states (II), (III), and (IV) were considered. [b] Metals of oxidation states (II) and (IV) were considered.

(Table VIII) for complexes containing a wide variety of peripheral substituents and a wide variety of central metal ions indicates the slight effect of the metal ion upon the ligand behavior. When the metal ion itself is electroactive, however, the electrochemical pattern changes; now steps corresponding to the oxidation or reduction of the metal also appear. The characteristic porphyrin pattern, however, is still maintained; the metal steps are simply superimposed upon the pattern. The standard pattern of porphyrin electrochemistry has been used as a criterion for assigning the mechanism of electrochemical reaction for porphyrin complexes [34, 43, 44].

The gold(III) porphyrin complexes reported here show the standard pattern of porphyrin electrochemistry; as was indicated above, no new waves resulted from the replacement of the two ionizable hydrogens in the ligands by the gold ion. The half-wave potential separations for $Au(TPP)^+$, $Au(Meso)^+$, and $Au(Etio)^+$, and the average half-wave potential separation value from the ligand redox steps of a number of simple metalloporphyrins are, respectively: for Oxid'n(1) – Red'n(1): 2.20 V, 2.30 V, 2.32 V, and 2.25 ± 0.15 V; for Red'n(1) – Red'n(2): 0.44 V, 0.50 V, 0.52 V, and 0.40 ± 0.10 V; and for Red'n(2) – Red'n(3): 0.71 V [$Au(TPP^+)$] and 0.70 ± 0.10 V (average half-wave potential separation value). These results establish that only the ligand is electroactive. From the spectral data, it is clear that the complex between gold and the porphyrin ligand is a simple coordination complex; from the electrochemical data, it is clear that while the ligand itself is highly electroactive, the central gold(III) ion is electrochemically inert.

This conclusion is supported by the results of the spectroelectrochemical experiment (Table VII). The pattern of spectral behavior of the one- and two-electron reduction products of $Au(TPP)^+$ is like that reported by Closs and Closs for similar reduction products of Zn(TPP), a metalloporphyrin with an inert central metal ion [13]. Upon reduction by one electron, the Soret band shifts to longer wavelength and is diminished in intensity; upon reduction by a second electron, the Soret band shifts back to shorter wavelength, but remains diminished in intensity. Just as the electrons appear to enter the porphyrin π-cloud in Zn(TPP) [13], so they appear to enter the porphyrin π-cloud in $Au(TPP)^+$. Thus based upon this spectral–electrochemical experiment, the gold(III) ion appears to be electrochemically inert in the gold(III) porphyrin complexes.

Complexes of gold(III) with porphyrin ligands therefore appear to be simple coordination complexes with spectral properties similar to those reported for other metalloporphyrins, except Mn and Mo, and electrochemical properties similar to those of metalloporphyrins with a stable central metal ion. The unusual feature of these gold complexes is the inertness of the tripositive metal ion. Apparently the porphyrin ligand, known to stabilize high oxidation states of transition metals, stabilizes gold in the (III) state and so renders it inert throughout the entire range of voltammetric measurement. This represents the first reported example where gold(III) is electrochemically inert. Additional experiments are currently being conducted to study the effect of more drastic electronic changes in the porphyrin ligand upon the electrochemical behavior of gold.

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