Table III. Effect of Ionic Strength on k^a

I, M	$10^3k, M^{-1}$ sec^{-1}	I, M	$10^3k, M^{-1}$ sec^{-1}
0.22	4.79 ± 0.03	2.02	6.11 ± 0.05
0.47	4.08 ± 0.04	2.52	8.17 ± 0.06
1.02	4.28 ± 0.01	3.23	12.6 ± 0.2

[a] At 25.0°, $[HClO_4] = 0.220\,M$, $[Np(V)]_0 = 1.40 \times 10^{-3}\,M$, and $[Br(V)]_0 = 2.15 \times 10^{-2}\,M$. Ionic strength maintained with $LiClO_4$. Uncertainties are average deviations from replicate experiments.

observed, competition between bromous acid disproportionation and its reduction by V(IV) has been suggested.[9] With the potentially multiequivalent reducing agents HN_3,[5] H_2O_2,[17] and Br^-,[7] however, the sole fate of the bromous acid appears to be reduction to hypobromous acid.

Clearly, the demonstration of the validity of the full reaction scheme (a)-(c) proposed for these intriguing systems will require considerable additional investigation. The present study, because of its apparent simplicity, will hopefully provide a foundation on which further results can be added.

Registry No. Np, 7439-99-8; BrO_3^-, 15541-45-4.

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Electrochemical Behavior of Copper, Nickel, Cobalt, and Metal-Free Hemiporphyrazines in a 50% v/v Dimethyl Sulfoxide-Benzene Mixture

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The electrochemical behavior of the copper(II), nickel(II), and cobalt(II) complexes of hemiporphyrazine (hpM) and of metal-free hemiporphyrazine (hpH_2) has been examined by voltammetry at the dme and rpe, by cyclic voltammetry, and by coulometry. For hpCo and hpNi, these studies established that the polarographic reduction steps of these two hemiporphyrazines involve 1:1:2:1 electrons and the oxidation step involves one electron. In the case of hpCu and hpH_2, the reduction steps involve 1:1:3 and 1:1:2:1 electrons, respectively. No oxidation step was observed for the latter two compounds. The electrochemical studies supported by polarography in the presence of the protic source benzoic acid indicate the hemiporphyrazines hpNi, hpCo, and hpH_2 undergo reductions involving only molecular orbitals of primarily ligand character. Importantly, in the case of hpCu, the first reduction step can be designated as involving a molecular orbital of primarily metal character with the remaining steps involving orbitals of primarily ligand character.

Introduction

Phthalocyanine with four nitrogens bridging four isoindole rings is an attractive and easily obtainable model compound for the porphyrin skeleton. Complexes of phthalocyanine and phthalocyanine itself, therefore, have received a great deal of attention. Of special interest is the recent report of the preparation of a compound in which a trans pair of isoindoles in the phthalocyanine molecule is replaced by two pyridines.[1-5] The aromaticity of the restricted coordination environment of the metal complexes of this macrocycle, hemiporphyrazine,[5] has been shown to be considerably less than that of the complexes of phthalocyanine.[6,7] In view of the interesting electrochemical data in the literature on metallophthalocyanines and metalloporphyrins[8] and the lack of any such data on metallocomplexes of this less aromatic macrocycle, we have examined the electrochemical behavior of the copper(II), cobalt(II), and nickel(II) complexes of hemiporphyrazine (Figure 1) and of the metal-free species in 50:50 (by volume) dimethyl sulfoxide-benzene.

Experimental Section

Materials. Dimethyl sulfoxide (DMSO) from Crown Zellerbach was distilled two times from calcium hydride under reduced pressure (*ca.* 1 mm, 35°). The middle 80% of the distillate was collected each time. The final product was stored under dry nitrogen, with no noticeable change in composition over a period of several months. Reagent grade benzene was refluxed over concentrated sulfuric acid for 3-4 hr, decanted, and distilled. The initial and final 10% portions of the distillate were discarded.

The purified DMSO and benzene were examined by gas chromatography with a Chromosorb 102 (60-80 mesh) column. The water content of the purified DMSO was found to be 10^{-2} *M*. The detection limit was 10^{-3} *M*. The peak heights of dimethyl sulfide in the gas chromatograms were usually about that of water. Because of the possibility of dimethyl sulfide resulting from decomposition of DMSO at the operating temperatures of the gas chromatograph, no attempt was made to determine the quantity of dimethyl sulfide. Instead, small amounts of dimethyl sulfide were added to the solutions used in the voltammetric studies, and no change in the electrochemical results was noted. Purified benzene contained no detectable impurities.

Tetraethylammonium perchlorate (Et_4NClO_4), Eastman Organic Chemicals, was recrystallized one or two times from water. The purified salt was dried *in vacuo* at *ca.* 70° and stored over Drierite. Maleimide from Aldrich Chemical Co. was sublimed before use. Reagent grade benzoic acid (Merck) was used without further purification. Solid tetramethylammonium hydroxide was obtained by heating a 10% solution of the hydroxide from Eastman Organic Chemicals to dryness *in vacuo* with an infrared lamp. The white, hygroscopic crystals were stored over Drierite.

Preparation of Compounds. Metal-Free Hemiporphyrazine, hpH_2. The method reported by Esposito, Sutton, and Kenney was followed.[6]

When 0.2 mol of phthalonitrile and 0.2 mol of 2,6-diaminopyridine were combined, the yield of purified product was 40%. The dried product melted at 340-342° (lit.[1] mp 344°). *Anal.* Calcd for hpH_2: C, 70.9; H, 3.67; N, 25.4. Found: C, 71.1; H, 3.69; N, 25.6.

Cobalt, Nickel, and Copper Hemiporphyrazines, hpCo, hpNi, and hpCu. Procedures for the preparation of hpCu,[1] hpNi,[1] and hpCo[5] have been described previously. In this study, hpCo was

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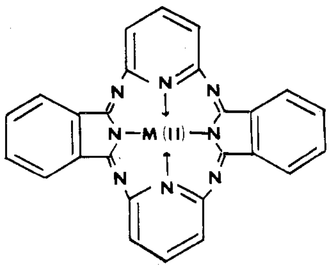

Figure 1. Metal hemiporphyrazine.

prepared in a manner similar to that used for the copper and nickel complexes. The metal hemiporphyrazines were recrystallized from nitrobenzene. Yields based on hemiporphyazine were 60–90%. hpNi precipitated as brown needles which yielded a green powder when ground; hpCu was green and hpCo was violet. The melting points were as follows: hpNi, 394–395° (lit.[1] mp 386°); hpCu, 400–402° (lit.[5] mp >400°); hpCo, 398°. *Anal.* Calcd for hpNi: C, 62.8; H, 2.84; N, 22.5; Ni, 11.8. Found: C, 62.7; H, 2.94; N, 22.6; Ni, 12.2. Calcd for hpCu: C, 62.2; H, 2.82; N, 22.3; Cu, 12.7. Found: C, 60.2; H, 2.72; N, 21.8; Cu, 12.6. Calcd for hpCo: C, 62.8; H, 2.84; N, 22.5; Co, 11.9. Found: C, 60.0; H, 3.53; N, 22.0; Co, 13.3.

Alkali Metal Derivatives of hpH_2. The monolithium and disodium salts of hemiporphyrazine (hpHLi and $hpNa_2$) were prepared according to procedures described by Sutton and Kenney.[7] hpHNa was prepared by adding an equimolar mixture of sodium hydride (as 57% mineral oil dispersion) and hpH_2 to diphenyl ether and refluxing the mixture for several hours. The monosodium salt was obtained on cooling the mixture to room temperature. The purified product recrystallized from dimethylformamide and dried at 175° *in vacuo* was red-brown.

1,3-Diiminoisoindoline. The preparation of this compound has been previously described.[9]

Potassium 1,3-Diiminoisoindoline. This salt was prepared in a manner similar to that described for potassium phthalimide.[10] Because of the appreciable solubility of the potassium salt in ethanol, most of the solvent had to be stripped off to recover the product, which was yellow.

Analytical Methods. The metals in the metallohemiporphyrazines were determined electrogravimetrically.[11] The hemiporphyrazines were decomposed by heating to near dryness with 4:1 (v/v) HNO_3-$HClO_4$ and with 4:1 HNO_3-H_2SO_4. Deposition was made on a weighed platinum gauze electrode. Copper was deposited from a slightly acidic solution, 5 ml of H_2SO_4 and 3 ml of HNO_3 in 200 ml of solution; nickel, from a solution neutralized with ammonia and made ammoniacal to the extent of 30 ml of ammonia in 200 ml of solution; and cobalt, from a solution neutralized with ammonia and containing 15 ml of excess ammonia, 3 g of ammonium chloride, and 0.1 g of hydroxylamine hydrochloride in 100 ml of solution. Upon completion of electrolysis, *ca.* 1 hr, the electrode was washed with water and then with acetone and dried at 75–100° for several minutes.

Carbon, hydrogen, and nitrogen analyses were performed by Schwarzkopf Microanalytical Laboratory, Inc. The hemiporphyrazines were dried *in vacuo* at 200° before submission for analysis.

Electrochemical Measurement. Voltammetry. Polarographic and slow-scan voltammetric studies were carried out with an instrument designed by Underkofler and Shain[12] and modified by Marcus and Hawley,[13] along with a Moseley 7030A X-Y recorder. For polarographic work, a scan rate of 0.5 V/min was used. For studies at the rotating platinum electrode, the scan rate was 1 V/min, and for the slow-scan cyclic voltammetric investigations, 3–60 V/min. For cyclic voltammetric examinations at scan rates from 60 to 2000 V/min, an instrument designed by White[14] and an oscilloscope equipped with a Polaroid Land camera were utilized.

The dropping mercury electrode in 50:50 (v/v) DMSO–benzene 0.10 *F* in Et_4NClO_4 on an open circuit had a drop time of 3.8 sec and a flow rate of 0.96 mg of mercury/sec at a column height of 58.0 cm. Because the drop time changed significantly with potential, the relative step heights of the polarographic wave were corrected with the data from an electrocapillary curve of drop time *vs.* potential.

The rotating platinum electrode was a platinum wire, sealed into a glass tube so that 1 mm of the wire extended from the tip of the tube, rotated at 600 rpm with a Sargent synchronous motor. This platinum electrode was also used in the cyclic voltammetric studies.

For the hanging mercury drop electrode, a platinum wire was sealed into a glass tube with one end of the wire recessed about 1 mm from the tip of the glass. After electrolytic deposition of a film of mercury on the platinum surface from a slightly acidic mercuric nitrate solution, mercury drops collected from the dme on a Teflon scoop were attached to the mercury-plated wire. Keeping the electrode tip immersed in water eliminated the need for repeating the deposition of mercury film on the platinum wire between runs.

A three-compartment cell was used in all the voltammetric work. The center compartment was separated from the two side compartments, placed on opposite sides, by glass frits of medium porosity. The working electrode was placed in the center compartment and the auxiliary (platinum) and reference (saturated aqueous calomel) electrodes were placed in the other compartments. A Luggin-Haber reference electrode[15] was constructed to minimize the effect of uncompensated *iR* drop in the cyclic voltammetric studies at high scan rates. Also in these studies, the concentration of electroactive species was kept as low as possible and the electrode area as small as possible to minimize ohmic potential distortion. The cell was equipped with two capillary tubes, one to deaerate the solution and the other to keep nitrogen over the solution during the course of measurement. Nitrogen from Linde and Air Products was purified by passage first through a tower of Linde 4X molecular sieves and then over copper metal heated to 400°.

The solutions for the voltammetric investigation were *ca.* 10^{-4} *F* in electroactive material and 0.10 *F* in Et_4NClO_4 and were 50:50 (v/v) DMSO–benzene. The mixed solvent increased the solubility of the hemiporphyrazines just to the point where the solutions could be examined voltammetrically. hpCo was the least soluble at 1×10^{-4} *F*, and hpH_2 was the most soluble at 4×10^{-4} *F*. The DMSO-benzene solutions 0.10 *F* in Et_4NClO_4 contained no electrochemically detectable impurities. For the DMSO–benzene mixture, the anodic–cathodic limit at the dropping mercury electrode was +0.3 to −2.7 V and at the platinum electrode was +1.0 to −1.7 V *vs.* sce.

For comparison of half-wave potentials in the DMSO–benzene solution with those in DMSO, the half-wave potentials for the oxidation of ferrocene in DMSO–benzene and in DMSO were determined. $E_{1/2}$ in DMSO–benzene 0.10 *F* in Et_4NClO_4 was found to be +0.470 V *vs.* sce, and in DMSO 0.10 *F* in Et_4NClO_4 it was found to be +0.446 V.

Coulometry. The controlled-potential coulometric assembly has been previously described.[16] Owing to the low solubilities of the hemiporphyrazines, the background currents were a significant part of the total current; and corrections for these currents were made.

Electron Paramagnetic Resonance, Epr. Epr spectral studies were carried out on a Varian V-4500-10A spectrometer equipped with an X-band microwave klystron and V-4560 100-kc field modulator. A Varian V-4551 rapid-scan unit connected to a C-1024 time-averaging computer (CAT) was used to obtain the spectra of short-lived radicals.

The epr cell consisted of a flat quartz cell containing a gold minigrid screen (1000 lines/in.) for the working electrode, a sce for the reference electrode, and a platinum wire for the auxiliary electrode. For studies of short-lived radicals, a flow technique was employed. Fresh solution of the electrolyte was caused to pass over the working electrode in the cavity of the epr spectrometer by withdrawing solution at the bottom of the cell with a syringe. The syringe was inserted through a Teflon-coated rubber septum at the bottom of the cell.

Electronic Absorption Spectra. Ultraviolet, visible, and near-infrared spectra were recorded on a Cary 14 spectrophotometer.

Results

Voltammetry and Coulometry. The voltammetric behavior

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Table I. Voltammetric and Coulometric Data for Metal-Free, Cobalt, Nickel, and Copper Hemiporphyrazines[a] (Half-Wave Potentials *vs.* Sce)

Compd	Potential at dme, V	$E_{1/2} - E_{3/4}$,[c] mV	Potential at rpe,[d] V	$E_{1/4} - E_{3/4}$,[c] mV	Rel step heights	n^e
hpH_2	−1.19	47	−1.23	60	1	0.7
	−1.55	47	−1.62	69	1	0.6
	−1.95	80			2	1.7
	−2.2	63			1	0.9
hpCo			+0.42[b]	60	1	0.7
	−0.99	56	−1.02	63	1	0.6
	−1.66	56	−1.67	56	1	0.8
	−2.01	53			2	*f*
	−2.2	40			1	*f*
hpNi			+0.80[b]	45	1	*f*
	−0.99	55	−0.99	69	1	0.9
	−1.56	54	−1.58	57	1	0.8
	−1.92	47			2	1.5
	−2.2	100			1	*f*
hpCu	−0.72	55	−0.73	55	1	0.8
	−1.69	60	−1.69	70	1	0.8
	−1.91	49			3	2.6

[a] Reduction steps, except as otherwise noted. Water content of solutions *ca.* 10^{-2} *F*. [b] Oxidation step. [c] For a reversible one-electron electrochemical step, this value is 56 mV, and for a two-electron step, 28 mV. [d] Cathodic solvent limit is −1.7 V. [e] Moles of electron per mole of electroactive material from coulometry (±0.1). [f] Evaluation of *n* made difficult by large background current.

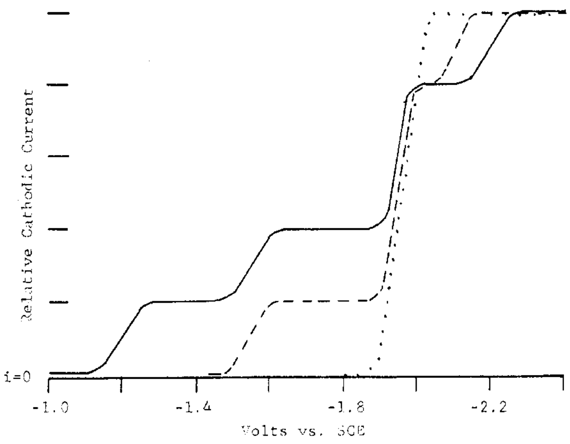

Figure 2. Effect of the addition of tetramethylammonium hydroxide on the polarographic behavior of hpH_2 in 50:50 v/v DMSO–benzene (1.0×10^{-4} *F* hpH_2, 0.10 *F* TEAP): ——, no base added; - - - - -, 1 equiv of base/mol of hpH_2; · · · · ·, 2 equiv of base/mol of hpH_2.

of the cobalt(II), copper(II), and nickel(II) complexes of hemiporphyrazine and of hemiporphyrazine itself is summarized in Table I. The information was obtained at the dropping mercury electrode (dme) and the rotating platinum electrode (rpe). In the potential region where both electrodes could be used, essentially the same electrochemical behavior was observed. Coulometric studies support the voltammetric data in the assignment of 1:1:2:1 electrons for the reduction steps of hpCo and hpNi and of one electron for the single oxidation step. For hpCu and hpH_2, the reduction steps have been established as being 1:1:3 and 1:1:2:1 electrons, respectively. No oxidation step was observed for the latter two compounds. The last reduction step for hpH_2, hpCo, and hpNi varied in height and in potential between −2.1 and −2.3 V, depending on the residual water content of the solutions.

Except in the case of hpCu, the addition of benzoic acid (HBz) to solutions of the hemiporphyrazines caused the height of the first reduction wave to increase significantly. At a 3:1 mole ratio of HBz to hpH_2, the first wave was 3 times the original height, and for the same mole ratio of HBz to hpNi and HBz to hpCo, *ca.* 3.5 and 1.5 times, respectively. In the case of solutions of hpCu, addition of HBz did not result in any change in the current of the first reduction step. The second wave for hpH_2, hpNi, and hpCu decreased rapidly in height with the addition of HBz. At a 2:1 mole ratio of HBz to hpNi, this step was completely absent, and for hpCu, this occurred at a mole ratio of HBz to hpCu of 4:1. Interestingly, only with hpCo did the second step increase in height. At a 2:1 mole ratio of HBz to hpCo, the limiting current was 1.5 times the original. Along with these changes in the first and second waves, in every case, additional changes were noted in the current-voltage curves. These changes are fully described elsewhere;[17] it suffices to say here that the waves near −2 V in all cases rapidly decreased in height with added HBz and were completely absent when the mole ratio of HBz to hpM or HBz to hpH_2 was between 1:1 and 4:1. Despite the wide variation in current on addition of HBz, the potentials of the reduction steps varied only slightly, from a few millivolts to 50 mV at the most.

The voltammetry of solutions of hpH^- and of hp^{2-} was examined at the dme by (1) the addition of stoichiometric amounts of tetramethylammonium hydroxide to a solution of hpH_2 and (2) the use of solutions of the mono- and disodium salts of hpH_2 and the addition of benzoic acid to the solution of hp^{2-}. The results of the voltammetric study of solutions of hpH_2 treated with tetramethylammonium hydroxide are summarized in Figure 2. Of special importance is the constancy of the reduction current at −2.4 V, which suggests that the first two reduction steps do not involve direct proton (acidic isoindoline hydrogen) reduction. This observation is consistent with the first and second reduction steps appearing at the same potential at the dme and rpe. An overvoltage effect would have been noted at the dme if direct reduction of the acidic isoindoline hydrogen were taking place. The polarograms of solutions of $hpNa_2$ and of hpHNa and of these solutions treated with benzoic acid were essentially identical with those obtained by the treatment of hpH_2 with tetramethylammonium hydroxide, except for the absence in the case of solutions of $hpNa_2$ of the last reduction step.

The reduction of hpH_2, hpH^-, and hp^{2-} at the dme and rpe follows the same pattern as that of solutions of 1,3-

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(17) C. G. Birch, Ph.D. Thesis, University of Kansas, 1971.

Table II. Electrochemical Data on 1,3-Diiminoisoindoline and Its Potassium Salt (Potentials Reported in Volts *vs.* Sce)

Polarography

Compd	Half-wave potentials Anodic steps		Cathodic steps		
1,3-Diiminoisoindoline			−1.60 (1)[a]		−2.22 (1)
1,3-Diiminoisoindoline +Me_4NOH	+0.55 (1)[b]	−0.5 (1)[c]			−2.22 (2)
Potassium 1,3-Diiminoisoindoline	+0.51 (1)[b]	−0.5 (1)[c]		−2.04 (1)[d]	−2.26 (2)
Potassium 1,3-Diiminoisoindoline +CF_3COOH			−1.64 (1)	−2.03 (1)[d]	−2.22 (1)

Cyclic Voltammetry

	1st cathodic step				2nd cathodic step			
Compd	$E_{p,c}$[e]	$E_{p,a}$[f]	$i_{p,a}/i_{p,c}$[g]	E_λ[h]	$E_{p,c}$	$E_{p,a}$	$i_{p,a}/i_{p,c}$	E_λ
1,3-Diiminoisoindoline at the hmde	−1.80	−1.41	0.06	−1.93	−2.4	−2.3	1.0	−2.53
1,3-Diiminoisoindoline at the spe	−1.70	−1.41	0.03	−1.88	[i]			

[a] The numbers enclosed in parentheses indicate the moles of electrons required per mole of electroactive material. [b] At the rpe. [c] Mercury dissolution wave in the presence of the anionic form of the imide (absent at rpe). [d] Potassium ion reduction. [e] Cathodic peak potential. [f] Anodic peak potential. [g] Scan rate 9 V/min. [h] Switching potential. [i] Beyond cathodic background at Pt electrode.

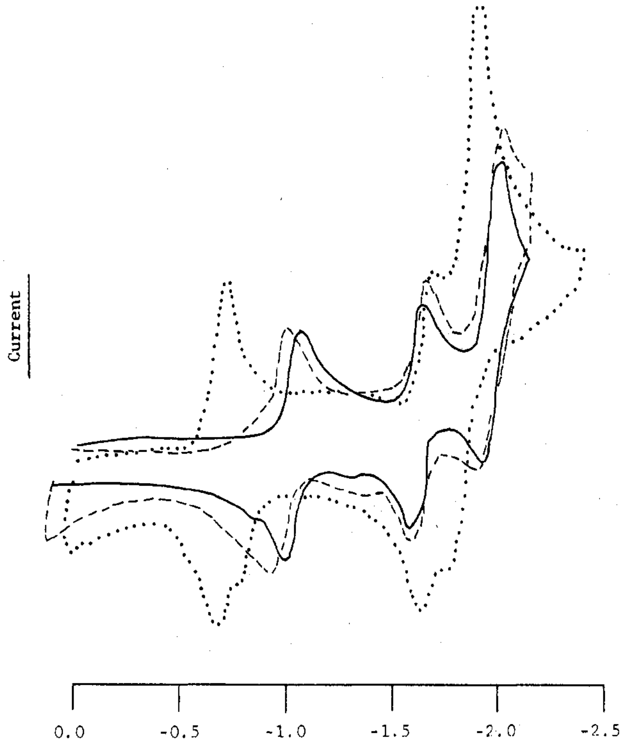

Figure 3. Cyclic voltammograms for hpNi, hpCo, and hpCu obtained at 9 V/min with a hmde in 50:50 v/v DMSO-benzene (0.10 *F* TEAP): ———, hpNi; - - - -, hpCo, · · · · ·, hpCu.

diiminoisoindoline in the absence and presence of tetramethylammonium hydroxide and of solutions of the potassium salt of 1,3-diiminoisoindoline in the absence and presence of benzoic acid. The results are summarized in Table II. The deprotonation and protonation steps are reversible; the total reduction current of diiminoisoindoline is unaffected by treatment of solutions of the compound with base, that of the anion is unaffected by treatment of solutions of the salt with acid, and the first reduction step of the acidic form of the compound is not affected on switching from the dme to the rpe.

Cyclic Voltammetry. The cyclic voltammetric behavior of the metal hemiporphyrazines at the hanging mercury drop electrode (hmde) in 50:50 v/v DMSO-benzene at 9 V/min is summarized in Figure 3. The voltammetric data are in excellent agreement with those obtained at the dme and rpe. The fourth wave in the cyclic voltammograms of hpCo and hpNi is poorly defined and is not reproducible; this step is not shown in the current-potential curves for hpCo and hpNi in Figure 3. Reversibility of the first two reduction steps for the three metal hemiporphyrazines was firmly established by the $E_{p(\text{anodic})} - E_{p(\text{cathodic})}$ values and the anodic to cathodic peak current ratios. The former values were close to 58 mV, and the latter were essentially unity. In addition, solutions of the one-electron and two-electron reduction products obtained by controlled-potential electrolyses yielded the same redox data as those obtained with the parent metal hemiporphyrazines. Although cyclic voltammetry at 9 V/min shows $hpCo^+$ to be a stable species, bulk electrolysis studies indicated it to be unstable in the longer time period involved in this technique; no reduction step was observed for the solution on examination following complete oxidation of hpCo. Cyclic voltammetry at 9 V/min showed the anodic step for hpNi to be completely irreversible; no cathodic return step was observed.

The cyclic voltammetric behavior of hpH_2 at a scan rate of 9 V/min is summarized in Figure 4. Similar results were obtained at scan rates between 3 and 20 V/min. For the first reduction step, absence of a return peak and decrease in the peak height with successive scans were noted. The second reduction step showed the same features as the first step, except in this case a partial return was observed.

At the hmde, examination of the third reduction step was possible. The study of the fourth reduction step, however, was plagued by lack of reproducibility. The third step with a peak height equal to those of each of the first two steps showed a return anodic step of the same peak height as the cathodic step. In addition, interestingly, a new anodic peak appeared at −1.3 V when the cathodic scan was carried out past the third step.

Increase in the cyclic voltammetric scans to 600-2000 V/min resulted in the appearance at both the hmde and the spe of a return peak for the first reduction step of hpH_2. The ratio of the anodic peak current to the cathodic peak current was near unity at 2000 V/min. On scans at 2000 V/min covering the first and the second reduction step (observed at −1.6 V at scan rates of 3-20 V/min), it was

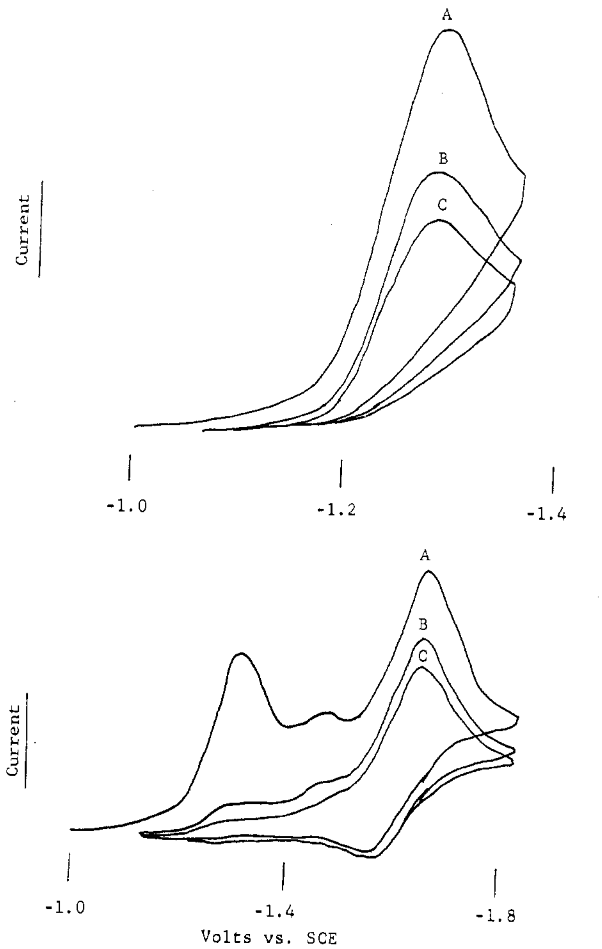

Figure 4. Cyclic voltammograms of *ca.* 5×10^{-4} *F* hpH_2 in 50:50 v/v DMSO-benzene (0.10 *F* TEAP), obtained at a stationary platinum electrode at 9 V/min. Repetitive scans: A, first; B, second; C, third.

noted that the peak current of the second step was only a few per cent of the first peak. Accompanying this reduction in the peak current of the second step was the appearence of a reduction step at -1.9 V of almost the same peak height as the first step. A cathodic peak of approximately the same height as the small peak at -1.6 V was observed at -2.0 V. At 2000 V/min, both the cathodic step at -1.9 V and the first reduction step at -1.2 V have substantial anodic returns following reversal of scan at -2.3 V.

The cyclic voltammograms of solutions of hpH^- at a scan rate of 600 V/min showed a value of 1 for the anodic to cathodic peak height ratio of the first reduction step at -1.6 V. The potential for this step is identical with that obtained in the slow-scan voltammetric studies. At 600 V/min, there were two other reduction steps, at -1.9 and -2.3 V. The peak height ratios of the three cathodic steps for hpH^- were 1:2:2, with a change to 1:2:1 at 2000 V/min. The dianion hp^{2-} showed a single reduction peak at -1.9 V, in agreement with the polarographic observations which were described earlier.

Use of the diagnostic criteria described by Nicholson and Shain[18] established the electrochemical processes at -1.2 and -1.6 V as involving a reversible electron-transfer step followed by an irreversible chemical reaction. From the available cyclic voltammetric data, estimates were made of the rate constants for the irreversible chemical follow-up reactions. The analyses were complicated by distorted voltammograms resulting from uncompensated resistance at the high scan rates employed, and although appropriate adjustments have been made in the analyses, the results can only be considered rough estimates. Because increase in $E_{p(anodic)} - E_{p(cathodic)}$ with increase in scan rate at the highest scan rates is suggestive of significant uncompensated resistance and/or irreversible electron transfer,[19] the peak potential separation at the hmde of the first step at -1.2 V and the second at -1.6 V at constant scan rate was plotted as a function of the sum of the cathodic and anodic peak currents (faradaic and capacitive) and extrapolated to zero current. An approximation of the actual peak potential separation that reflected the reversibility of the electron-transfer step was thus obtained. At 2000 V/min, this residual peak potential separation was approximately 60 mV for the two reduction steps. The large values of peak potential separation appear to be essentially the result of uncompensated resistance. $E_{1/2}$ values for these two steps, therefore, were estimated by taking half of the sum $E_{p(anodic)} + E_{p(cathodic)}$ of cyclic voltammograms in which the total anodic current was equal to the total cathodic current, *i.e.*, where the distortions of the cathodic and anodic regions were the same. Values of -1.30 and -1.61 V were obtained.

For the evaluation of the rate constants, a working curve of anodic to cathodic peak current ratio *vs.* $k_f\tau$ was employed (k_f is the homogenous rate constant of the irreversible chemical step and τ is the time from $E_{1/2}$ to $E_{switching}$).[18] A tentative value of k_f obtained from the $i_{p,a}/i_{p,c}$ *vs.* $k_f\tau$ curve by the use of the previously estimated value for $E_{1/2}$ was utilized to compute a value of $E_p - E_{1/2}$ (from the expression $E_p = E_{1/2} - (RT/nF)(0.780 - \ln\sqrt{k_f RT/nFv}$, where v is the scan rate), and comparison was made of this $E_p - E_{1/2}$ quantity with that involving the estimated $E_{1/2}$. When necessary, the estimated value of $E_{1/2}$ was adjusted until the value of k_f yielded, by computation, $E_p - E_{1/2}$ in agreement with $E_p - E_{1/2}$ (estimated). For k_{f_1}, the rate constant for the chemical step in the first step, a value of $(1.6 \pm 0.5) \times 10^2$ sec^{-1} was obtained, and for k_{f_2}, 0.8 ± 0.1 sec^{-1} was obtained.

Electron Paramagnetic Resonance. The spectra of hpCu and $hpCu^{2-}$ at room temperature are shown in Figure 5. Differences in *g* values and in peak-to-peak line widths are evident. Attempts to obtain the spectra of these samples at liquid nitrogen temperature were unsuccessful. No epr signal was observed for solutions of the monoanion $hpCu^-$ obtained by electrolytic reduction of hpCu.

The spectra of solutions of hpCo and $hpNi^-$ could not be secured at room temperature or at liquid nitrogen temperature. Likewise, attempts to obtain the spectra of $hpH_2\cdot^-$ and $hpH\!:^{2-}$ were not successful. In connection with the study of the reduction products of hpH_2, it was demonstrated that the five-line spectrum of the short-lived keto form of the one-electron reduction product of phthalimide[20,21] could be obtained by the technique employed.

Visible Spectral Studies. The spectra of solutions of hpH_2, hpHNa, and $hpNa_2$ in 50:50 v/v DMSO-benzene are shown in Figure 6. The hpH^- and hpH_2 solutions used to obtain these spectra were prepared by protonation of the disodium salt in 50:50 v/v DMSO-benzene with

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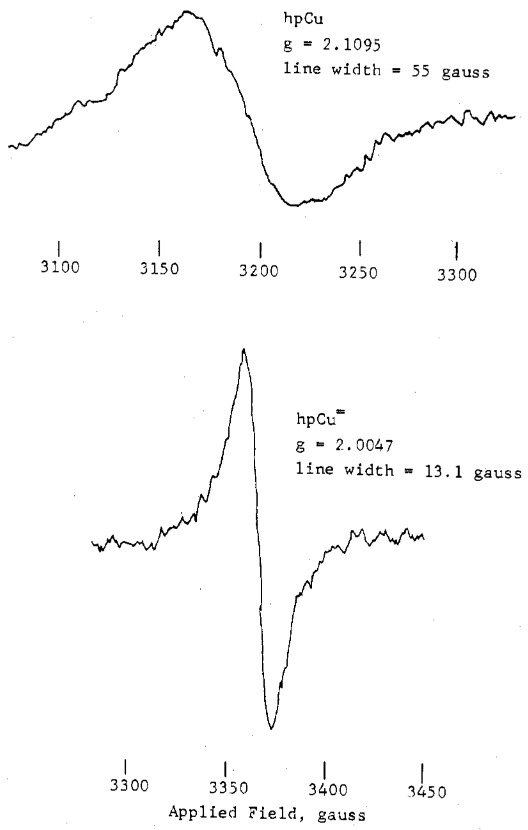

Figure 5. First-derivative epr spectra of hpCu and $hpCu^{2-}$ in 50:50 v/v DMSO-benzene (0.10 *F* TEAP), 25°.

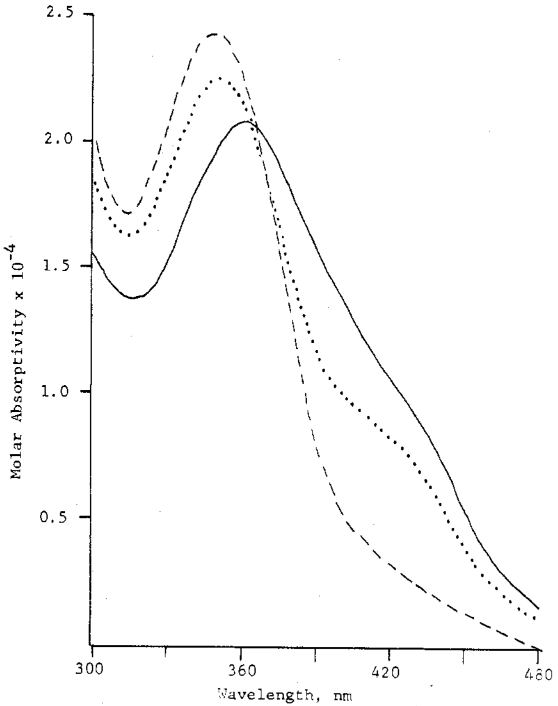

Figure 6. Visible spectrum of *ca.* 3 × 10^{-4} *F* $hpNa_2$ in 50:50 v/v DMSO-benzene (0.10 *F* TEAP) and the effect of benzoic acid addition: ———, no acid added; ------, 1 equiv of acid/mol of $hpNa_2$; ······, 2 equiv of acid/mol of $hpNa_2$.

stoichiometric amounts of benzoic acid. Essentially identical spectra were observed on starting with a solution of hpH_2 and adding stoichiometric quantities of Me_4NOH to obtain hpH^- and hp^{2-} solutions.

Controlled-potential electrolysis of solutions of hpH_2 at −1.4 V yielded a solution with a spectrum identical with that of hpH^-, and subsequent bulk electrolysis at −1.8 V produced a solution with a spectrum similar to that of a solution of hp^{2-}.

For solutions of the metal hemiporphyrazines, the spectra in the region 310-700 nm are shown in Figure 7. The absorption bands in the 500-700-nm region are an order of magnitude less in intensity than in the 310-500-nm region. There is a good deal of similarity in the spectra of the three complexes.

The visible spectra for solutions of the monoanions of the three metal hemiporphyrazines obtained by bulk electrolysis are shown in Figure 8. The presence of small amounts of unreduced metal hemiporphyrazines in the solutions is indicated by the small peaks characteristic of the unreduced material on the broad bands in the 300-500-nm region. Of primary interest is the noticeable difference in the spectrum of the monoanion of copper hemiporphyrazine, particularly in the 500-1100-nm region, from those for the monoanions of the nickel and cobalt complexes.

Discussion

In the initial step in the examination of the effect of change in the coordination environment resulting from the replacement of an opposite pair of isoindoles in phthalocyanine with two pyridines [a voltammetric (with dme, rpe, and spe) and coulometric study of hpCo, hpCu, hpNi, and hpH_2 in 50:50 DMSO-benzene solutions], it was observed that the four reduction steps of hpNi and of hpCo occur at about the same potential and involve the same number of electrons as those for hpH_2, *i.e.*, 1:1:2:1. Each of the first two reduction steps of hpH_2 occurs at the same potential at the rpe and at the dme, indicating electron transfer to a ligand orbital rather than direct reduction of the acidic isoindoline hydrogens. The constancy of the total reduction current at −2.4 V for a solution of hpH_2 upon treatment with Me_4NOH to give hpH^- and hp^{2-} solutions also suggests that the first two reduction steps do not involve direct reduction of the acidic isoindoline hydrogens but introduction of electrons into ligand orbitals. All four reduction steps of hpNi and hpCo, therefore, appear to involve molecular orbitals of primarily ligand character. The much more positive potential for the first reduction step of hpCu than for those of hpCo, hpNi, and hpH_2 is strongly indicative of a step involving a molecular orbital unlike those in the case of the other three hemiporphyrazines. The orbital involved is very likely one of primarily metal character.

To establish firmly the nature of the reduced species, an epr study was made of solutions of the hemiporphyrazines prior and subsequent to electrolysis. Unfortunately, spectral data on only hpCu and its reduction products could be obtained, but the limited results are highly informative. Electrolytic reduction of a solution of hpCu at a potential which produces the one-electron reduction product resulted in the disappearance of the epr signal for hpCu: $g = 2.1095$; line width 55 G. Continued electrolysis to the two-electron reduction product caused the reappearance of an epr signal, but this signal had a *g* value of 2.0047 and was much narrower in width, 13.1 G, than the signal for hpCu. The disappearance of the epr signal for hpCu on electrolysis to $hpCu^-$ and the *g* value and line width of the new epr signal of solutions of the two-electron reduction product are explainable in terms of the electrochemical picture of the first reduction step involving a molecular orbital of primarily metal character, *i.e.*, metal

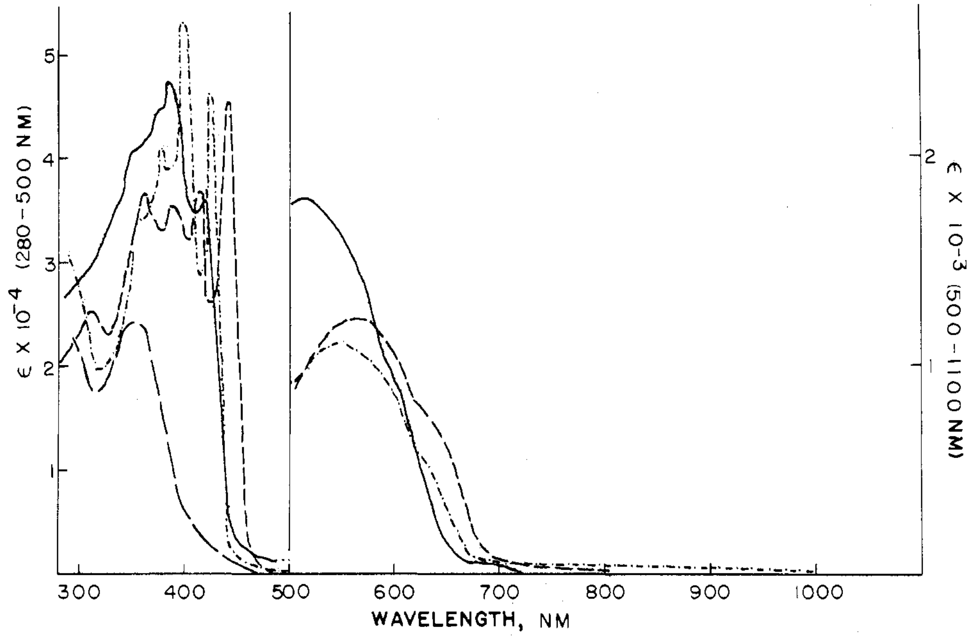

Figure 7. Visible spectra of hpH_2, hpCo, hpNi, and hpCu in 50:50 v/v DMSO-benzene (0.10 *F* TEAP): — — — —, hpH_2; ————, hpCo; — — — — — — —, hpNi; · — · — · —, hpCu.

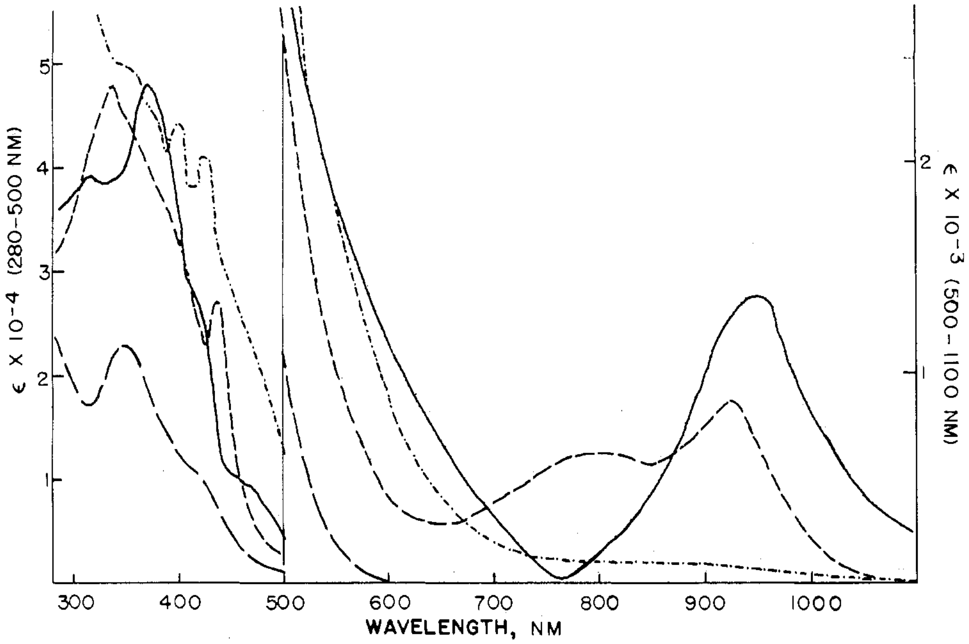

Figure 8. Visible spectra of hpH^-, $hpCo^-$, $hpNi^-$, and $hpCu^-$ in 50:50 v/v DMSO-benzene (0.10 *F* TEAP), obtained by bulk electrolysis at −1.40 V: — —, hpH^-; ————, hpCo; — — — — — —, hpNi; · — · — · —, $hpCu^-$.

reduction to Cu(I), with the electron in the second reduction step of hpCu residing in an orbital of primarily ligand character. (It should be pointed out that the epr data in themselves do not indicate whether the first and second reduction steps are metal and ligand or ligand and metal reduction steps.) The absence of hyperfine structure in the spectrum of the two-electron reduction product is not unusual. Similar observations have been reported for mononegative ions of certain metal and metal-free porphins and phthalocyanines.[22,23]

In the absence of the desired supportive epr data for establishing the nature of the reduced species of hpCo and hpNi and in order to reinforce further the electrochemical picture of the one- and two-electron reduction products of hpCu, it was decided to examine the polarographic behavior of the four hemiporphyrazines in the presence of benzoic acid, making use of the fact that proton addition to radical anions of aromatic hydrocarbons and related substances leads to profound changes in their voltammetric curves.[24] As expected, there was no effect of benzoic acid on the first reduction wave of hpCu, consistent with this step involving an orbital of primarily metal rather than ligand character. The second reduction step was affected, as expected on the basis of the initial electrochemical and

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epr data. The marked changes in the polarograms of hpH_2, hpCo, and hpNi in the presence of benzoic acid are indicative of the reduction steps of the cobalt and nickel hemiporphyrazines involving ligand-like molecular orbitals.

Finally, a look at the visible spectra of the parent hemiporphyrazines and their reduction products revealed the likelihood of a difference in the nature of the one-electron reduction product of hpCu from those of hpCo and hpNi. Whereas the three metal hemiporphyrazines originally showed rather similar spectra in this region, the spectrum of the one-electron reduction product of hpCu in the 300–1100-nm region is different from those of hpNi and hpCo, particularly in the 500–1100-nm region. (No definitive band assignments are available at this time.)

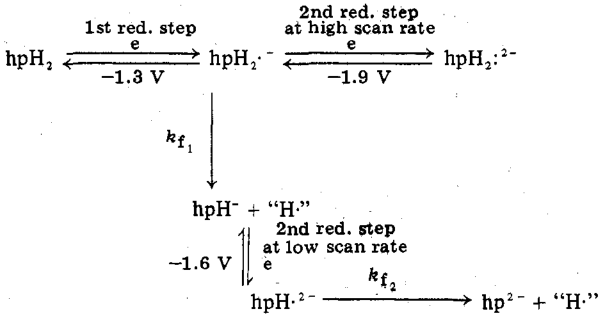
Interestingly the modification made in the fixed coordination sphere in going from phthalocyanine to hemiporphyrazine changes the nature of the reduction products of hpCo from those of the corresponding phthalocyanines; those of hpNi are similar. In the phthalocyanines, the cobalt compound undergoes a one-electron reduction involving a molecular orbital of primarily metal character, while the two-electron reduction product appears to involve a ligand-like orbital.[22] In the case of copper phthalocyanine, from magnetic susceptibility,[25] and epr and spectral examinations,[26] it was suggested that the first and second electrons go into orbitals of primarily ligand character. More recently, the two-electron reduction product has been described as having the unpaired electron in the ligand orbital $b_{1u}(\pi)$, but no statement was made concerning the possible nature of the first reduction product.

With regard to the final reduction products of the first two steps of hpH_2 at the dme and rpe, spectral studies at 300–700 nm leave no doubt that they are hpH^- for the first step and hp^{2-} for the second. This conclusion is based on the fact that identical spectra in the 300–700-nm region and identical polarograms were observed for solutions of hpH^- obtained chemically and electrolytically and for solutions of hp^{2-} similarly prepared.

Cyclic voltammetry at 600–2000 V/min has revealed that the first reduction step of hpH_2 involves a reversible electron-transfer step followed by an irreversible chemical step to give hpH^-. The chemical step involving the loss of a hydrogen atom is too rapid a process to be observed in slow-scan voltammetric methods. At high scan rates, the second electron-transfer step, now occurring at −1.9 V, is the reduction of $hpH_2\cdot^-$ before loss of a hydrogen atom. The loss of a hydrogen atom following reduction of hpH^- to $hpH\cdot^{2-}$, at −1.6 V, is slower than that following electron transfer to hpH_2.

For metal-free hemiporphyrazine, only the nature of the initial steps in its electrochemical reduction appear to be certain. (See Scheme I.)

Scheme I



In view of the fact that hemiporphyrazine is not oxidized before the solvent limit, the oxidation processes for hpCo and hpNi are ascribed to metal oxidations to Co(III) and Ni(III). Similar metal oxidations have been reported previously.[8,27–29]

Registry No. hpH_2, 343-44-2; hpCO, 21600-72-6; hpNi, 21600-71-5; hpCu, 17857-08-8; hpH^-, 36245-53-1; hp^{2-}, 12764-85-1; $hpCu^{2-}$, 36202-29-6; $hpCu^-$, 36245-55-3; hpHNa, 36245-56-4; $hpNa_2$, 17048-63-4; $hpCo^-$, 36245-58-6; $hpNi^-$, 36202-30-9; 1,3-diiminoisoindoline, 3468-11-9; 1,3-diiminoisoindoline + Me_4NOH, 36222-98-7; potassium 1,3-diiminoisoindoline, 36245-54-2; potassium 1,3-diiminoisoindoline + CF_3CO_2H, 36222-99-8.

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