Electrochemistry, Electron Paramagnetic Resonance, and Visible Spectra of Cobalt, Nickel, Copper, and Metal-Free Phthalocyanines in Dimethyl Sulfoxide

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Abstract: Half-wave potentials for tetrasulfonated divalent Co, Ni, Cu, and metal-free phthalocyanines were determined in dimethyl sulfoxide at rotating platinum and dropping mercury electrodes for both oxidation and reduction processes. Cyclic voltammetry and controlled-potential coulometry were used to establish the stabilities of the reduced species and the number of electrons involved in each step. Epr spectra of the Co and Cu starting materials, of the one-electron reduction products of the Ni and metal-free compounds, and of the two-electron reduction products of the Co and Cu species were obtained at 77 and 298°K. Electronic absorption spectra were obtained for the compounds and for their one- and, with the exception of Co, two-electron reduction products. For the Cu, Ni, and metal-free compounds the data show reduction to involve only the ligand. For Co, first-step reduction yields Co(I). The data for the second-step reduction are interpreted in terms of initial reduction to Co(0) and subsequent formation of a reactive hydride.

Reduction of Mn–Zn phthalocyanines (MPc) and the related porphyrins is fairly well established, reaction usually being carried out in THF with Li and Na as reducing agents.[1–4] Four distinct one-electron steps (five for CoPc) are observed. In terms of site of reduction for these complexes, *i.e.*, metal or ligand, the process offers considerable variety. Notably, an early report of a two-electron reduction product of CuPc with metallic potassium in liquid ammonia, with the central copper in the zerovalent state,[5] now appears best explained as electron transfer to the ligand. Chemical oxidation of the MPc complexes, with oxidants such as ceric ion, is quantitative, generally involving two one-electron steps.[6]

Electrochemical studies of porphyrins and of the related compounds, chlorophyll and vitamin B_{12}, have been reported both in water and, to some extent, in nonaqueous solvents. Vitamin B_{12} electrochemistry is limited to water solution and has been interpreted in terms of cobalt oxidation and reduction.[7–9] For the chlorophylls, studies in aqueous and nonaqueous solvents have emphasized the effects of the phytyl group, the carbocyclic ring, and the central magnesium.[10–13]

In protic solvents (water, methanol) reduction of porphyrins leads to formation of chlorins *via* the corresponding phlorins.[14] Addition of methanol to solutions of reduced porphyrins in N,N-dimethylformamide (DMF) instantly yields the phlorin, reaction continuing slowly to the chlorin with excess methanol.[1] In the case of iron(III) protoporphyrin (hemin) iron reduction was observed electrochemically in water and in ethanol, but at potentials less negative than those required for the porphyrin reduction.[15]

In aprotic, nonaqueous medium (butyronitrile), the oxidation of tetraphenylporphins and other porphyrins has been studied electrochemically,[16] the solutions generally showing two one-electron oxidation steps. Reduction has been studied polarographically in DMF and dimethyl sulfoxide (DMSO),[17,18] as many as four one-electron reduction waves being reported.

In view of the uniqueness of phthalocyanine as a ligand, of the biochemical relevance of the electrode behavior of its complexes, and of the reports of unusual oxidation states for several of its transition metal complexes, an electrochemical investigation of cobalt, nickel, copper, and metal-free phthalocyanines in aprotic, nonaqueous solvents was initiated. Because of solubility problems, the tetrasulfonated compounds (Figure 1) were selected for the present study.

Experimental Section

Materials. Preparation of tetraethylammonium perchlorate (TEAP) has been described earlier.[19] DMSO (Crown-Zellerbach, bulk) was purified by fractional distillation from CaH_2 and glass wool under vacuum (2–3 mm, *ca.* 50°), flushing the system well with nitrogen before distillation. All DMSO used was distilled twice in this manner, the second distillation either from CaH_2 or from powdered molecular sieves (Linde, size 4A), and stored under nitrogen. The water content in prepared background solutions (0.010 *N* TEAP) was determined by Karl Fischer titration and gas chromatography (20% Carbowax 20M on Fluoropak column) and found

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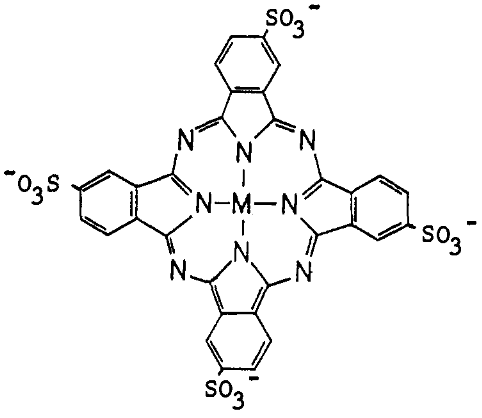

Figure 1. Tetrasulfonated metal phthalocyanine.

to be about 10^{-2} *M*. Spectroquality DMF (Baker) and Spectroquality methanol (Fisher) were used without further purification. 1,2-Dimethoxyethane (Matheson) was purified by distillation from CaH_2 under nitrogen.

The monosodium salt of 4-sulfophthalic acid (technical grade) was obtained, while available, from Aldrich Chemical Co. It was subsequently prepared by reaction of NaOH with aqueous 30% 4-sulfophthalic acid (Eastman Organic) and evaporation, the infrared spectra confirming the identity of the two compounds. The triammonium salt was prepared by addition of concentrated aqueous ammonia to the 30% solution of the acid and evaporation.

Metal Phthalocyanines. A highly purified sample of unsulfonated cobalt(II) phthalocyanine was obtained from Mr. Herbert K. Y. Lau of the University of Missouri. The metal derivatives of tetrasulfonated phthalocyanine were prepared according to the method described by Weber and Busch,[20] with only minor modifications. The solubility of the copper derivative, Na_4CuPTS, in various organic solvents was found to be as follows: insoluble in acetonitrile, propylene carbonate, ethyl acetate, nitroethane, acetone, and ethanol; slightly soluble in DMF and methanol; readily soluble in DMSO and water.

Metal-Free Phthalocyanine. Preparation of the metal-free compound, Na_4H_2PTS, was attempted by direct sulfonation of either metal-free phthalocyanine, H_2Pc, or phthalonitrile with HSO_3Cl, by reaction analogous to that used for preparation of the metal derivatives[20] but in the absence of metal salts, and by reaction of the triammonium salt of 4-sulfophthalic acid as above, using antimony in the place of ammonium molybdate as catalyst.[21] All attempts at direct sulfonation led to nitrile hydrolysis, as indicated by carbonyl bands in the ir spectra. Reaction of the monosodium salt of 4-sulfophthalic acid, with ammonium molybdate as catalyst, gave a blue-green product, but the yield was too low to isolate the phthalocyanine.

An adaptation of earlier procedures[20,21] was found most satisfactory. To a melt of urea (60 g) and antimony powder (1.5 g), heated in an oil bath to 195–200°, a mixture of the triammonium salt of 4-sulfophthalic acid (50 g) and antimony (0.5 g) was added. After 2 hr, urea (60 g) was added, and the temperature was maintained at 190–210° until the product solidified. Purification was done by alternate precipitation from 1 *N* HCl and 0.1 *N* NaOH with NaCl until the filtrates remained colorless (10–12 times). To obtain the final product, the concentration of NaOH was slowly reduced from 0.1 to about 0.02 *N* in successive precipitations, and absolute ethanol was used in place of NaCl to induce precipitation. The final precipitation was from pure 75–80% ethanol, several hours being required before solid particles could be observed. The sample was washed with absolute ethanol and ether and dried at 56° *in vacuo* over P_2O_5 to constant weight. Sensitivity of the rate of precipitation to sodium salts and the known association of sulfonated phthalocyanines in aqueous solution[21] suggest the small amount of impurity results from an adsorption or occlusion effect and is most probably a sodium compound. Impurity effects on the results were ruled out by studies of samples of widely varying purity.

Analysis. Metal analyses were carried out electrolytically. The metal-free and copper compounds were analyzed by oxidation with ceric solution, addition of excess ferrous solution, and back-titration with ceric to a ferroin end point.

Microanalyses were performed by Schwarzkopf Microanalytical Laboratory (C, H, N, S). Molecular weights were calculated on the basis of the ceric titrations, except in the cases of Na_4NiPTS and Na_4CoPTS, where the metal analyses were used.

Anal. Calcd for Na_4H_2PTS, $C_{32}H_{14}O_{12}N_8S_4Na_4$: mol wt, 923; C, 41.65; H, 1.53; N, 12.15; S, 13.90. Found: mol wt, 950; C, 40.38 ; H, 3.34; N, 11.99; S, 11.43. Calcd for $Na_4CuPTS \cdot 2H_2O$, $C_{32}H_{16}O_{14}N_8S_4Na_4Cu$: mol wt, 1020; C, 37.66; H, 1.58; N, 10.98; S, 12.56; Cu, 6.23. Found: mol wt, 1025; C, 37.59; H, 1.77; N, 11.12; S, 12.26; Cu, 6.16. Calcd for $Na_4NiPTS \cdot 2H_2O$, $C_{32}H_{16}O_{14}N_8S_4Na_4Ni$: mol wt, 1015; C, 37.85; H, 1.59; N, 11.04; S, 12.63; Ni, 5.78. Found: mol wt, 990; C, 37.45; H, 2.88; N, 10.95; S, 12.19; Ni, 5.94. Calcd for $Na_4CoPTS \cdot 2H_2O$, $C_{32}H_{16}O_{14}N_8S_4Na_4Co$: mol wt, 1016; C, 37.82; H, 1.59; N, 11.03; S, 12.62; Co, 5.80. Found: mol wt, 1010; C, 37.61; H, 2.35; N, 11.05; S, 11.72; Co, 5.85.

Voltammetry. The instrumentation and procedure used have been described previously.[19] With the exception of studies of temperature effects (25, 35, 45°) on the potentials (utilizing a constant-temperature water bath with a presaturator in the nitrogen stream), all studies were at room temperature (23–25°). A Sylvania 150-W projector spot lamp, placed close to the solution in the H-cell, was used to check for light effects. Scan rates used were generally 0.335 and 0.215 v/min, the slower rate used almost exclusively for studies at the rotating platinum electrode (rpe). The dropping mercury electrode (dme), on open circuit in DMSO, had characteristics between the extremes, 1.31 mg/sec, 5.45 sec, 30.0 cm, and 3.01 mg/sec, 2.45 sec, 68.4 cm.

Cyclic Voltammetry and Coulometry. The cyclic voltammetry instrumentation has been described elsewhere.[22] A stationary Pt disk electrode of area 0.22 cm² was used in these studies.

For controlled-potential coulometry a Wenking potentiostat (Brinkman Instruments) was used. Reductions were carried out over a mercury pool of area 16 cm², with the potential set at 0.2 v more cathodic than the corresponding half-wave potential. Solutions were about 1×10^{-3} *M*.

Electron Paramagnetic Resonance, Epr. Epr data were obtained on a Varian Model V-4500, X-band spectrometer with 100-kc field modulation. For studies at 77°K, solutions of 1–10 m*M* phthalocyanine in DMSO (0.100 *N* TEAP) were electrolytically reduced as above over a large Hg pool (32 cm²) and samples extracted and squirted into liquid nitrogen. The resulting frozen pellets were used for the studies. For work at 298°K, electrolyses were carried out with a Pt gauze electrode in the cavity and auxiliary and reference (sce) electrodes in two upper arms of the electrolysis tube. Diphenylpicrylhydrazyl (DPPH) was used as a reference.

Visible Spectra. A Cary Model 14 spectrophotometer was used for the studies, scanning at 25 Å/sec. Millimolar solutions were electrolyzed as above and transferred to a 1-mm cell, and a spacer was inserted to make the path length 0.12 mm, all under nitrogen. For calculation of the extinction coefficients of the reduced species, oxygen was bubbled through the cell, regenerating the parent phthalocyanine. From the absorbance, the concentration of the parent compound was calculated. It was assumed that the reduced species had the same concentration as that of the regenerated parent.

Results

Voltammetry. The electrochemical behavior of Na_4MPTS solutions in DMSO (0.100 *N* TEAP), within the solvent limitations, is shown in Figure 2. The large wave at −2.10 v has been attributed to Na^+.

The half-wave potentials observed are listed in Table I. In the study, particular attention was directed toward the first three reduction waves and toward the first oxidation wave of the Co compound, the other waves being too near the background for precise study. Half-wave potentials were unaffected by changes in the electrode, sce, column height, scan rate, and cell geometry (two- *vs.* three-compartment cells). Changes in the $E_{1/2}$ with temperature (25, 35, 45°) and subsequently on illumination with a spotlight were quite small (usu-

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Table I. Half-Wave Potentials^{a} for Na_4MPTS (DMSO, 0.100 N TEAP)

	$E_{1/2}$ vs. sce							
	Co		Ni		Cu		H_2	
	Dme	Rpe	Dme	Rpe	Dme	Rpe	Dme	Rpe
$E_{1/2}$	−0.547	...	−0.672	-0.682^{b}	−0.727	−0.735	−0.525	−0.530
Δ	0.065	...	0.075^{b}	0.078	0.065	0.074	0.072	0.076
$E_{1/2}$	−1.346	−1.355	−1.165	−1.171	−1.111	-1.113^{b}	−0.970	−0.980
Δ	0.065	0.065	0.082^{b}	0.084	0.071	0.072	0.072	0.082
$E_{1/2}$	...	...	−1.933	−1.925	−1.895	-1.88^{b}	−1.810	...
Δ	...	...	0.061	0.060	0.062^{c}	0.070^{c}	0.066	...
$E_{1/2}$	...	+0.455	...	...	...	...	...	...
Δ	...	0.084^{b}	...	...	...	...	...	...
$E_{1/2}$	...	$+1.09^{c,d}$	...	$+0.98^{c,d}$	...	+0.872	...	$+0.90^{c,d}$
Δ	...	0.10^{c}	...	0.10^{c}	...	0.070^{b}	...	0.080

^{a} All values ±0.010 except as indicated. $\Delta = |E_{3/4} - E_{1/4}|$. ^{b} ±0.015. ^{c} ±0.020. ^{d} Two-electron process.

ally less than 10 mv), the former showing the process to be diffusion controlled, the latter ruling out any light effects on the half-wave potentials. The three most probable contaminants in DMSO (dimethyl sulfide, dimethyl sulfone, and water) were tested for their effects and found to have none. Even addition of a small drop of water to the DMSO solution in the H-cell, making the water concentration well over 0.1 M, caused shifts of only about 10 mv.

Shifts in the $E_{1/2}$ with supporting electrolyte concentration were studied by comparison with those observed for analogous ferrocene solutions. Supporting electrolyte concentration changes alter both the liquid-junction potential between the DMSO (0.1 M TEAP) and the aqueous reference electrode (saturated KCl) solutions and the dissociation (activity) of the oxidized and reduced species.[23] At high ionic strengths the activity coefficient of ferricinium species, f_{ox}, is decreased relative to that of ferrocene, f_{red}, and shifts of the $E_{1/2}$ as a result of increased supporting electrolyte concentration, according to the expression below, should be in a negative direction. The potentials $E°$

$$E_{1/2} = E° + E_{lj} - 0.059 \log (f_{red}D_{ox}^{1/2})/(f_{ox}D_{red}^{1/2})$$

and E_{lj} are the standard potential for the couple oxidant–reductant and the liquid-junction potential, respectively; f's are the activity coefficients and D's the diffusion coefficients. The $E_{1/2}$ for the ferricinium–ferrocene couple in DMSO was +0.446 v vs. sce (slope 0.056) in 0.100 N TEAP and was shifted about 50 mv positive in 0.030 N and less than 10 mv negative in 0.130 N TEAP. For the sulfonated phthalocyanines shifts are expected in the opposite direction (positive) with increasing ionic strength due to the resultant decrease in the activity coefficient of the reduced species relative to that of the parent. In 0.130 N TEAP the potentials were shifted about 10 mv anodic and in 0.030 N TEAP, about 30 mv cathodic from the values in 0.100 N TEAP. Because the results are in the opposite direction of those observed for ferrocene, activity effects must outweigh liquid-junction potential changes.

Half-wave potentials were independent of concentration over the range 10^{-4}–10^{-3} M, with the exception of the first reduction wave for Na_4CoPTS solutions on Pt and the degradative oxidation (+1 v) of the Co, Ni, and metal-free compounds. At the rpe the first-step reduction of the cobalt compound was quite irreversible, showing marked adsorption effects at higher concentrations (1 mM) and considerable lack of reproducibility. Reduction of millimolar solutions led to apparent surface deposition, currents falling off to zero on the reverse (positive) scan. At low concentrations (0.07–0.4 mM) these effects were less pronounced and did not interfere with the second reduction wave. At these concentrations a typical $E_{1/2}$ for the first-step reduction would be −0.65 v with a slope of 0.18. All other shifts (degradative oxidation at the rpe) were observed only at concentrations of 10^{-3} M and greater and were always accompanied by increasingly irreversible slopes. Other than these two cases, no adsorption effects (prewaves) were noted.

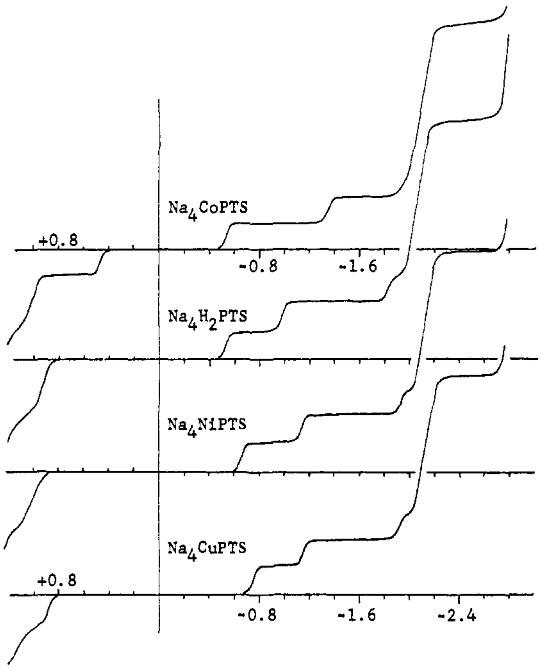

Figure 2. Voltammetry of Na_4MPTS in DMSO (0.100 N TEAP); potentials vs. sce.

All plots of limiting current vs. concentration at the rpe were linear, passing through the origin. By comparison of the limiting current of the extra anodic wave observed for Na_4CoPTS solutions (Figure 2), assigned to a Co(II)–Co(III) oxidation process, with those for the other oxidation–reduction waves, it was evident

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Table II. Electron Paramagnetic Resonance Data[a] for Na_4MPTS Solution in DMSO–0.100 *N* TEAP at 77°K

Na_4MPTS	g	Line width, gauss	$g_\parallel$	A_M	A_N	$g_\perp$	B_M	B_N
$H_2(-1)$	2.004	6	...	...	...	...	...	...
Ni (−1)	2.004	10	...	...	...	...	...	...
Cu	...	..	2.18	0.0207	...	2.05	0.002^b	0.0016^c
Cu (−2)	...	..	2.14	0.0212	0.0012^c	2.05	0.002^b	0.0017^c
Co	...	..	2.007	0.0097^c	...	2.26	0.005^b	...
Co (−2)	...	..	2.13	0.006^b	...	2.02	0.002^b	0.0017^c

[a] All values reproducible to 0.5% except as indicated. All coupling constants expressed in cm^{-1}. [b] ±0.001. [c] 0.0005.

that all waves involved one electron, except those for the Co, Ni, and H_2 oxidation at +1 v. For the Co and Ni compounds these oxidation waves were quite irreversible and too close to the background for accurate analysis. Taking the irreversibility and the background current into account, it could be concluded that each of these processes involved two electrons (Table I).

For the dme data, plots of limiting current *vs.* concentration at a given mercury column height were linear and passed through the origin. The same held true for plots of limiting current *vs.* the square root of the corrected Hg column height for a given concentration, a test for diffusion-controlled processes. Although the electrocapillary curve was not determined, from the heights of the Na^+ waves it could be concluded that a fourth phthalocyanine reduction step was included in this wave for the Cu, Ni, and H_2 compounds and two further steps were included for the Co compound. This is in agreement with earlier observations.[3,17]

Cyclic Voltammetry and Coulometry. Cyclic voltammetry data for the first two reduction steps and the first cobalt oxidation wave at scan rates between 1 and 25 v/min showed the oxidation–reduction products to be stable. For both reduction steps in solutions of the Cu, Ni, and metal-free compounds the separation of the half-peak potentials for cathodic and anodic scans was 0.06, except at the fastest scan rates, and peak currents for both scan directions were equal and proportional to concentration and to the square root of the scan rate. For the Co compound the separation of the half-peak potentials for the first reduction step showed the process to be irreversible. The second reduction wave was a reversible, diffusion-controlled process, yielding a stable product. In scanning the oxidation wave, if the first reduction wave was included, the anodic wave was distorted so as to seem to indicate decomposition of the Co(III) species. This was attributed to an adsorption process because the effect was only apparent at high scan rates and toward the end of a series of runs. When the oxidation wave alone was scanned, the data indicated a reversible, diffusion-controlled process with a stable product. The half-peak potentials agreed with the polarographic $E_{1/2}$ values to generally less than 10–20 mv.

Controlled-potential coulometry over a mercury pool showed both reduction waves for all compounds to be one-electron (±0.1) processes with the exception of the second reduction wave of the Co compound. Solutions of this compound were reduced at −0.8 v *vs.* sce until the current had fallen off to 1–2% of its initial value. The potential was then set at −1.5 v. At this potential the initial current was the same as that of the first-step reduction. The current fell off sharply, paralleling that of the first-step reduction, but stopped rather abruptly at somewhat less than 50% reduction. From this point the current decay was much slower. Prolonged electrolysis reduced the current somewhat, but was not successful in completing the reduction. After about 30 min at this potential, the odor of dimethyl sulfide coming from the electrolysis vessel became quite noticeable.

Electron Paramagnetic Resonance. Table II lists the values obtained from the spectra of the various species for g, $g_\parallel$, $g_\perp$, A_M, and B_M (the metal hyperfine interaction constants associated with $g_\parallel$ and $g_\perp$, respectively) and A_N and B_N (the observed nitrogen splitting on the corresponding metal hyperfine components). The spectra were analyzed according to the method of Sands,[24] from consideration of the first-order interaction only.

At room temperature, electrolysis of 1–5 m*M* solutions of Na_4H_2PTS in the cavity at potentials on the first reduction plateau (Figure 2) yielded a strong epr signal at $g = 2.00$ which increased with time. Subsequent electrolysis at −1.2 v (second plateau) caused the signal to decrease. When the current was stopped the peak began to increase. This would be the behavior expected from voltammetry and would represent reaction between the two-electron reduction product, in the cavity, and the starting material, diffusing into the region about the Pt gauze, giving the paramagnetic one-electron reduction product. No hyperfine could be resolved on this signal either at 298 or at 77°K.

For solutions of the metal derivatives, high concentrations (5–10 m*M*) were necessary. Solutions of the Ni compound at room temperature showed a very weak signal at $g = 2.00$ which was unaffected by electrolysis and probably resulted from an impurity, particularly in view of the high modulation and gain settings used in an attempt to observe the one-electron reduction product. No signal was observed at room temperature, but at 77°K a strong organic radical signal was observed for the reduced Ni solutions. The signal differed only slightly from that of the metal-free species, being somewhat broader and less symmetrical.

Reduction of solutions of the Cu complex in the cavity at potentials on the first plateau resulted in a decrease in the signal intensity, while subsequent reduction at −1.7 v (second plateau) caused the signal to increase again. The spectrum of the starting material at 298°K, along with that of the corresponding Co derivative, is shown in Figure 3.

The spectra of frozen solutions of Na_4CuPTS and Na_4CuPTS^{2-} are shown in Figure 4. The spectrum of the two-electron reduction product is even better resolved than that of the starting material. Neverthe-

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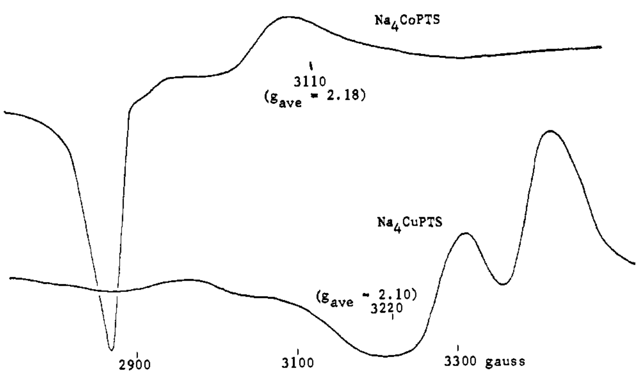

Figure 3. Epr spectra of Na$_4$CuPTS and Na$_4$CoPTS solutions in DMSO (0.100 *N* TEAP) at room temperature.

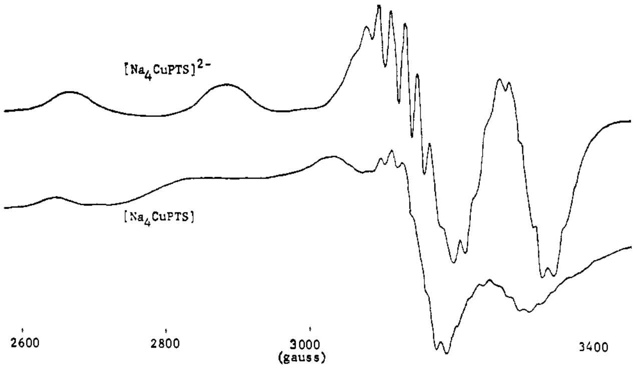

Figure 4. Epr spectra of Na$_4$CuPTS and [Na$_4$CuPTS]$^{2-}$ in DMSO (0.100 *N* TEAP) at 77°K.

less, the coupling constants (Table II) are very nearly the same, ruling out the possibility of reduction of the Cu(II) to Cu(0), since the lone electron in Cu(0) would be in a 4s orbital, strongly coupled to the metal. Using the techniques described by Sands[24] and by Kivelson and Neiman,[25] values of $g_{\parallel}$ and $g_{\perp}$ were determined, along with A_{Cu}, the copper hyperfine interaction constant. From the width of the perpendicular component, a value of B_{Cu} was estimated. A value of B_N could be calculated from the readily apparent nitrogen hyperfine on the perpendicular component. At higher instrument sensitivity settings, partial resolution of the parallel components was observed for the two-electron reduction product, from which an estimated value of A_N was calculated. From the relationship, $g_{av} = {}^1/_3(g_{\parallel} + 2g_{\perp})$, the difference between the spectrum at 298°K (Figure 3) and that at 77°K (Figure 4) can be interpreted in terms of partial tumbling of the phthalocyanine molecules at the higher temperature. The values of g_{av} have been noted on the spectra. Although numerous electrolyses were carried out, the one-electron reduction product always showed a very weak signal of the type shown in Figure 4, but this may well have been due to difficulties in the transfer technique. No other signals were observed from 1000 to 4500 gauss.

The spectrum of the Co compound at room temperature is shown in Figure 3 and, as in the case of the Cu compound, may be interpreted in terms of a superposition of the spectra of the fixed and of the tumbling (averaged) orientations of the molecule. On electrolysis in the cavity at potentials on the first oxidation plateau and on the first and second reduction plateaus (Figure 2), a decrease in signal strength was observed. The spectrum of the starting material at 77°K is shown in Figure 5 and has been analyzed in the same manner as that of the Cu compound (Co, $I = {}^7/_2$), although no nitrogen splittings were observed.[26] On prolonged reduction at -1.6 v, a purple product could be obtained and frozen in liquid nitrogen which gave the weak signal shown in Figure 5. This spectrum is that expected for a single, unpaired electron on a metal in an axially symmetrical environment, and the values in Table II have been interpreted in this manner, estimating values of A_{Co} and B_{Co} from the widths of the corresponding components. The partially resolved

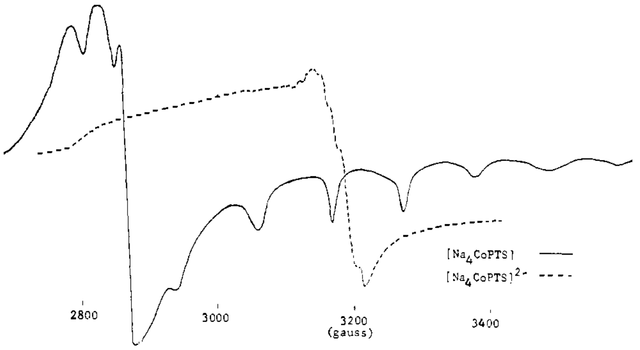

Figure 5. Epr spectra of Na$_4$CoPTS and [Na$_4$CoPTS]$^{2-}$ in DMSO (0.100 *N* TEAP) at 77°K.

hyperfine structure on the perpendicular component has been attributed to nitrogen and a corresponding value of B_N calculated. The signal for this two-electron reduction product was always about five times weaker than that of the starting material.

Visible Spectra. The spectra observed in DMF, methanol, and DMSO are very similar to those of the unsulfonated compounds in 1-chloronaphthalene.[27] The maxima have been listed in Table III. DMSO

Table III. Visible Spectra of Na$_4$MPTS in Various Solvents[a]

Solvent	Na$_4$MPTS	λ	Log ε	λ	λ	Log ε	λ	Log ε
DMSO	Co	663	5.11	...	600	4.51	332	4.84
	Ni	673	5.26	(644)	606	4.48	336	4.38
	Cu	677	5.44	(646)	609	4.63	350	4.77
	H_2	698	5.1	(640)	608	4.4	(364)	...
		668	5.1				342	4.7
DMF	Co	676	(5.3)	(645)	608	(4.5)	348	(4.6)
	Ni	671	5.26	(644)	604	4.48	348	4.34
	Cu	666	5.13	(645)	604	4.50	332	(4.6)
	H_2	698	...	(640)	608	...	346	...
		664	...					
MeOH	Co	656	5.11	...	593	4.54	328	4.52
	Ni	662	...	(636)	596	...	335	...
	Cu	666	...	(640)	602	...	345	...
	H_2	692	...	(638)	594	...	(360)	
		655	...				338	...
H_2O	Co	668	...	630	(604)	...	320	...
	Ni	(660)	...	622	...	...	334	...
	Cu	660	...	630	...	...	336	...
	H_2	(670)	...	630	...	...	332	...

[a] All wavelengths in millimicrons, with shoulders in parentheses.

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(25) D. Kivelson and R. Neiman, *J. Chem. Phys.*, 35, 149, 156 (1961).

(26) J. M. Assour, *J. Am. Chem. Soc.*, 87, 4701 (1965).

(27) J. S. Anderson, E. F. Bradbrook, A. H. Cook, and R. P. Linstead, *J. Chem. Soc.*, 1151 (1938).

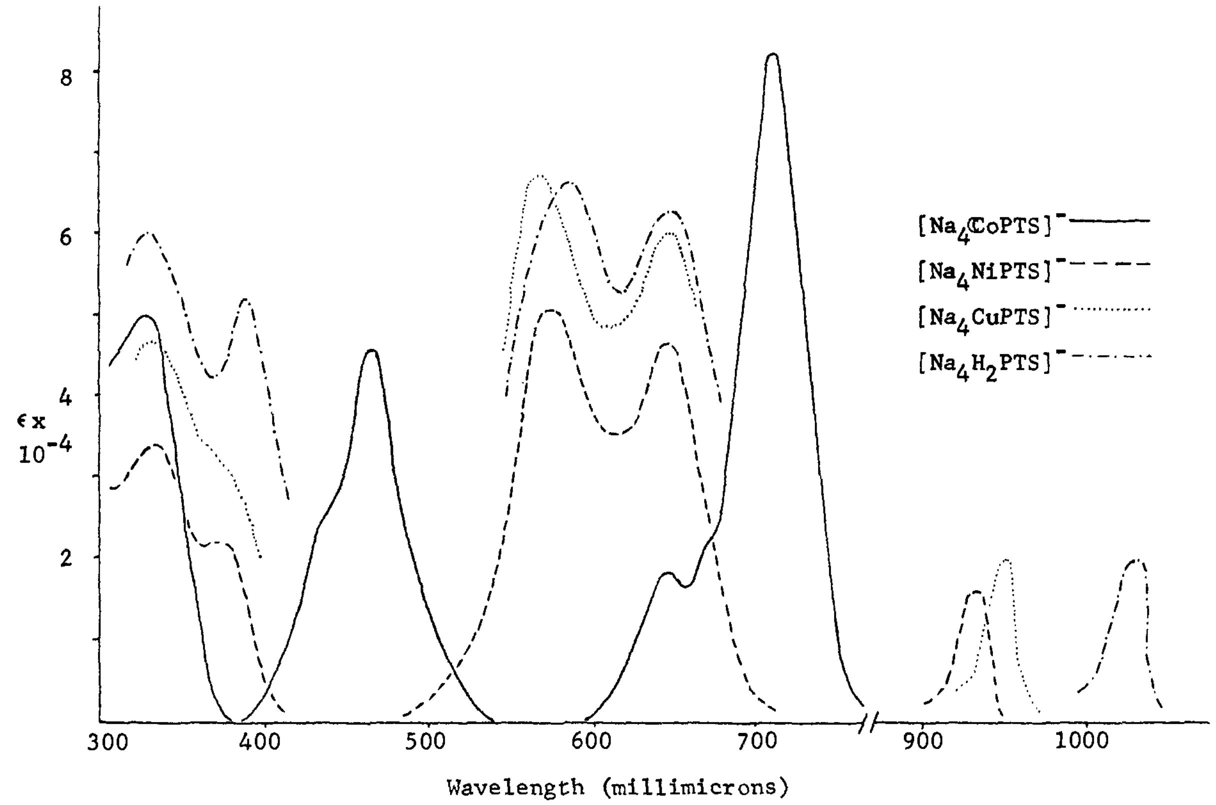

Figure 6. Electronic absorption spectra of $[Na_4MPTS]^-$ in DMSO (0.100 *N* TEAP).

solutions obeyed Beer's law over the accessible concentration range (10^{-6}–10^{-3} *M*). The low solubilities in methanol precluded accurate determination of the extinction coefficients. In DMF, furthermore, apparent slow decomposition of the Co compound was observed, the solutions turning yellow in the course of several days. Comparison of the maxima shows a red shift in the order, methanol, DMF (except for Co), DMSO. This shift, the high extinction coefficients, and the relative spectral independence of central metal are in agreement with the assignment of these electronic absorption bands to $\pi \rightarrow \pi^*$ transitions.[28]

In water, the sulfonated compounds show distinctly different spectra, generally attributed to association,[29] and the spectra of the unassociated species began to appear only at very low concentrations. At concentrations of 10^{-6}–10^{-7} *M* shoulders were observed in the case of the Cu, Ni, and H_2 compounds, showing decreased association. In the case of Co, this was observed at somewhat higher concentrations (10^{-4}–10^{-5} *M*). Using this spectral change to test 0.01 *M* solutions in DMSO, it was possible to rule out any significant association which might have affected interpretation of the results, notably epr.

The spectra of the one-electron reduction products are shown in Figure 6, plotting extinction coefficients *vs.* wavelength. Most striking in general are the lower extinction coefficients as compared with those of the starting solutions. These same results were reported, however, by Hush and Dodd[2] and may well be the result of the method and assumptions used in estimating the concentration. These coefficients and those obtained from the spectra of all reduced species should thus be regarded as estimates. The spectrum of the singly reduced Co solutions differs markedly from the corresponding Cu, Ni, and H_2 spectra, the low-energy band resembling that of the starting material but shifted to lower energy. One-step reduction of the unsulfonated CoPc with sodium metal in 1,2-dimethoxyethane proceeded smoothly, and a yellow solution with the same spectrum as that of the electrolytically reduced solutions was produced.

In the reduction of Cu, Ni, and metal-free solutions, a spectrum assigned to a decomposition product was frequently observed, particularly if the electrolysis time was long, with maxima at about 600 and 800–900 mμ. The reduced species spectra were also rapidly replaced by this decomposition product spectrum if the ir source was turned on, which, in the Cary Model 14, passes through the cell before passing through the monochromator. Heating the cell in warm water (*ca.* 80°) did not produce the same decomposition. This spectrum is strikingly similar to the spectrum reported by Closs and Closs[1] for reduction of ZnTPP, which they attributed to product protonation. No such spectrum was observed for the Co(I) solutions.

On regeneration with oxygen, and as a further species present in the reduced solutions, the metal-free compound showed a spectrum with only one peak in the 700-mμ region, a spectrum similar to those of the parent metalated compounds. This was also noted earlier[30] and most probably involves substitution of the central protons by sodium or tetraethylammonium ions, which would change the symmetry from D_{2h} to D_{4h} and explain the absence of the dual bands.

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[28] H. McConnell, *J. Chem. Phys.*, 20, 700 (1952).

[29] H. Kobayashi, Y. Torii, and N. Fukada, *Nippon Kagaku Zasshi*, 81, 694 (1960).

[30] A. V. Shablya and A. N. Terenin, *Opt. i Spektroskopiya*, 9, 533 (1960).

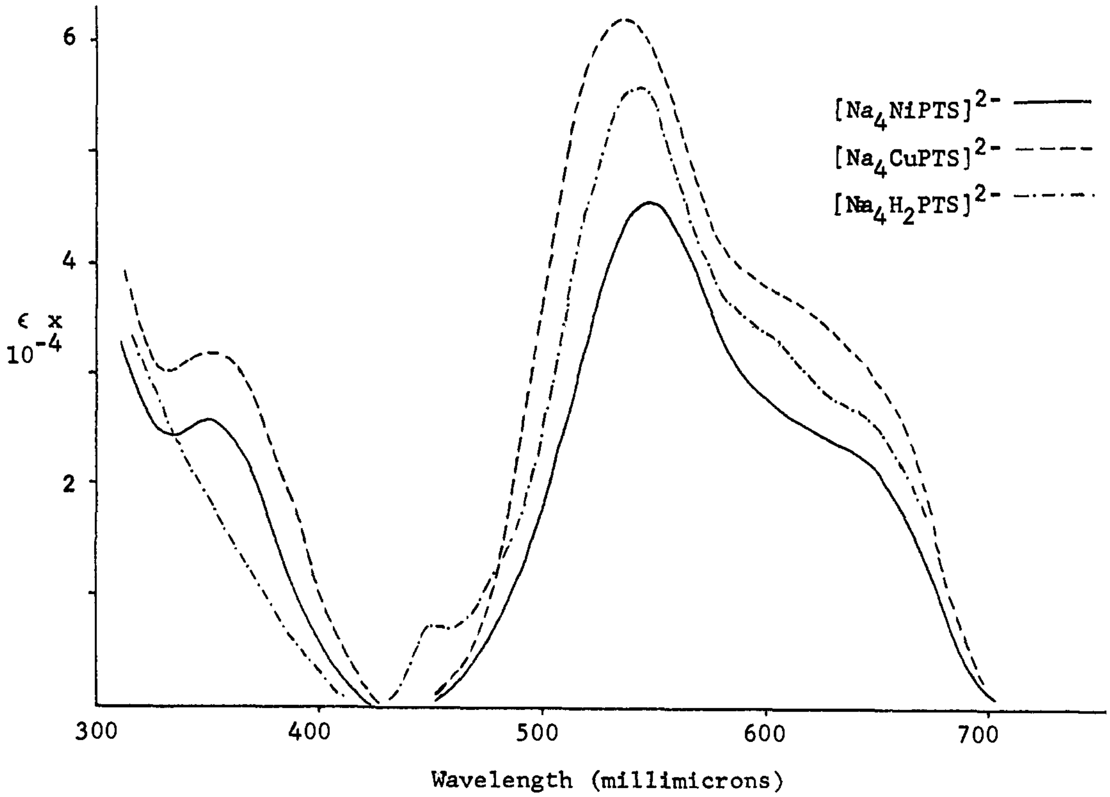

Figure 7. Electronic absorption spectra of $[Na_4MPTS]^{2-}$ in DMSO (0.100 *N* TEAP).

The spectra of the two-electron reduction products of the Cu, Ni, and H_2 compounds are shown in Figure 7. Just as was the case with the singly reduced species, these compounds were sensitive to the infrared source.

Although it was possible to obtain purple solutions (two-electron reduction) of both sulfonated and unsulfonated Co phthalocyanines by electrolytic and chemical means, respectively, it was not possible to obtain a reliable spectrum of these solutions. A small peak was noted at 780 and two at 430 and 540 mμ, but these may well be side-reaction products. The presence of water in the solvent and the highly sensitive nature of the reduction product preclude assignment of these weak bands to the Co two-electron reduction product.

Discussion

Ease of reduction (less negative potentials) decreases in the order H_2, Co, Ni, Cu, for the first reduction step. Subsequent to the first reduction wave, the order becomes H_2, Cu, Ni, Co. The change in order in the case of Co will be quite reasonable in the following discussion, in which first-step reduction of the cobalt compound is assigned to a Co(II)–Co(I) process. In the case of Cu and Ni, the difference is quite small but can be explained, using visible spectra and epr data, in terms of differing electronic configurations. These results show the same order of reduction found by others[18] for general porphyrins, with the exception of the first reduction wave for Co compounds (which was similarly interpreted), the ordering resulting from increasingly negative ring charge.[31] Ease of oxidation is in the order Co(II), Cu, H_2, Ni, Co(III), although the two-electron, irreversible waves of the last three derivatives rule out any definitive comparison. Because two-step oxidations are observed for the sulfonated Co and Cu phthalocyanines with ceric ion[6] and because both Cu and CoTPP exhibit two one-electron oxidation steps in butyronitrile on Pt,[16] it is most probable that these oxidation waves, in the cases of Co and Ni, appear to be two-electron, irreversible steps as a result of their proximity to the background wave rather than as a result of any intrinsic instability of the one-electron oxidation products. For H_2TPP, the difference between the successive half-wave potentials for the two one-electron oxidation waves is reported to be only 50 mv,[16] so it is not unreasonable that only one wave, somewhat irreversible, should be observed for the H_2 phthalocyanine. No observable two-step oxidation with ceric ion was reported for this sulfonated compound.[6]

The separation of the successive half-wave potentials can easily be shown to approximate the disproportionation energy of the chemical species stable in this potential region.[17] This separation has been listed in Table IV, noting the uncertainty of comparison where irreversible waves are involved. The disproportionation intervals fall generally into groups, the parent compounds having the highest stability, the two-electron reduction products next, and the one-electron products the lowest. The least stable species is the singly reduced Cu compound, a fact which is reflected in the change in order of ease of reduction in the second wave. While the order is the same for the Co species, the one-electron reduction product has a remarkably high stability. This has been used in the past as evidence for central metal reduction.[18] Since reduction to Co(I) would yield a d^8 configuration, in the square-planar phthalocyanine

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[31] M. Zerner and M. Gouterman, *Theoret. Chim. Acta*, 4, 44 (1966).

Table IV. Disproportionation Intervals for Na_4MPTS and Reduced Species[a] (DMSO, 0.100 *N* TEAP)

Species	$\Delta G/F$	TPP[17,18]	Etio[17]
Na_4H_2PTS	(1.43 v)	...	...
$Na_4H_2PTS^-$	0.445	0.42	0.43
$Na_4H_2PTS^{2-}$	0.840	0.86	0.87
Na_4CuPTS	1.60	...	...
Na_4CuPTS^-	0.384	0.48	0.51
Na_4CuPTS^{2-}	0.784	...	0.71
Na_4NiPTS	(1.65)	...	...
Na_4NiPTS^-	0.493	0.57	...
Na_4NiPTS^{2-}	0.768	...	...
Na_4CoPTS (III)	(0.64)	...	...
Na_4CoPTS (II)	1.002	...	...
Na_4CoPTS (I)	0.799	1.05	(0.53)[18]
Na_4CoPTS^{2-}	(0.75)	...	...

[a] Where some uncertainty exists in the half-wave potentials, generally as a result of irreversibility, the values above have been placed in parentheses.

complex an anomalously high stability is to be expected.

In electrochemical studies the existence of Co(I) in reductions of Co(II) and Co(III) complexes is fairly well established. Applying a liquid-junction potential correction of −0.32 v, obtained in the manner described earlier,[19] expectation values for the cobalt reduction potentials in aqueous solution may be calculated which compare favorably with values reported for similar complexes, within the limitations of the uncertainty introduced by the widely varied supporting electrolyte.[7–9]

Cyclic voltammetry shows all reduction products, and the first Co oxidation product to be stable, as expected from the disproportionation energies in Table IV. Controlled-potential coulometry confirms the one-electron nature of all of these reduction processes but casts some doubt on the stability of the second reduction product of the Co compound on the longer time scale involved in bulk electrolyses.

Epr data show conclusively that the one-electron reduction products of Ni and H_2 compounds involve ligand reduction. The broadened signal in the case of the Ni compound at 77°K relative to that of the H_2 species explains the failure to observe a spectrum at room temperature. No signal was observed for the two-electron reduction products, the compounds being reportedly diamagnetic.[3] For the Cu complex the starting material and the doubly reduced species have very similar spectra, assignable in both cases to Cu(II). No reliable spectrum was observed for the one-electron reduction product, although the species reportedly contains two unpaired electrons.[4] The data can best be explained in terms of a d^9 metal configuration and one unpaired electron in the ligand π system. The relaxation interaction between these two electrons would explain the lack of observation of a signal as well as the low stability of the species toward disproportionation, as noted earlier. The g values and coupling constants observed are in good agreement with those published from single-crystal studies of the unsulfonated compound.[32] For the Co compound, the spectrum of the starting material is very similar to spectra of the unsulfonated compound in H_2SO_4 and nitrogen-donor solvents, with the expected solvent dependence of the g values.[26] The spectrum of the two-electron reduction product is, however, of critical importance in characterizing the reduction product. From the shape of the spectrum, which is that of a lone electron on a metal in an axially symmetrical environment, the immediate implication is that a Co(0) species is present. This is further supported by the reversal of the values of $g_\parallel$ and $g_\perp$ relative to those in the Co(II) compound. The lone electron in Co(II) phthalocyanine has been shown to be in the d_{z^2} orbital,[26] above and below the molecular plane. In a Co(0) species (d^9), the electron would be in a $d_{x^2-y^2}$ orbital, directed toward the coordinating nitrogens. This is supported by the partially resolved hyperfine structure on the perpendicular component, which has been assigned to nitrogen splitting. These results will be discussed further in the light of all the data and an explanation proposed.

From the electronic absorption spectra (Figures 6 and 7), it is possible to assign conclusively the reduction of the Cu, Ni, and metal-free compounds to ligand reduction, all spectra being very similar. Since the electronic transition places an electron in an e_g orbital,[3,31] which has nodes at the central nitrogens, the transition results in an effective charge transfer to the periphery of the molecule. A decrease in central metal charge should result in a lowering of the energy of this transition. The spectrum of the first reduction product of the Co complex, assigned to reduction of Co(II) to Co(I), fits this interpretation perfectly. Furthermore, if the small peak noted at 780 mμ arises from the two-electron reduction product, the shift in the peak to lower energy would be that expected for further metal reduction. It is now possible to correlate all of the data from the various experimental approaches.

Conclusions

In the cases of the Cu, Ni, and H_2 compounds the results are quite unequivocal. Oxidation and reduction occur at the potentials listed in Table I, and all involve the ligand π system. This conclusion was reached on the basis of the following evidence.

1. The electrochemical behavior of all three is very much the same, disproportionation energies being very similar for analogous species. Trends in half-wave potentials and in disproportionation energies parallel those observed for other porphyrins.[17,18]

2. Epr data show both the Ni and H_2 one-electron reduction products to have a lone electron in the π system, the doubly reduced species showing no signal. Both the Cu(II) compound and the two-electron reduction product show a single electron in a square-planar environment, and the spectra are those expected for divalent Cu. No reliable signal was observed for the one-electron reduction product, but other reports show it to have two unpaired electrons.[4]

3. Electronic absorption spectra were the same for both reduced species of all three compounds.

Because oxidation and reduction involve only the ligand π orbitals and because the lowest lying empty orbital and the highest filled orbital have opposite symmetries relative to inversion,[3] the energy of the electronic transition at longest wavelength and the separation between the half-wave potentials for oxidation and for reduction (the disproportionation interval for the parent compounds), both expressed in kilocalories/mole,

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(32) S. E. Harrison and J. M. Assour, *J. Chem. Phys.*, **40**, 365 (1964).

should be equal. Using the Cu complex for the calculations, the peak at 677 mμ corresponds to 42 kcal/mole (1.83 ev). The disproportionation energy is 37 kcal/mole (1.60 ev). If a correlation between polarographic half-wave potentials and molecular orbital energy calculations[33] has any validity, this difference of 5 kcal/mole must be explained.

First-step reduction of these compounds places an electron in a doubly degenerate orbital (e_g). The second electron, however, yields a singlet state,[3] which can only be explained if the e_g orbital is split on addition of the first electron, most probably by a Jahn–Teller-type distortion.[34] This splitting would explain the visible bands in the spectra of the one-electron reduction products, which are split into a doublet. For the Cu compound the bands were observed at 650 and 580 mμ (44 and 49 kcal/mole, respectively). Only one band (53 kcal/mole) is observed for the doubly reduced species, since the lowest lying orbital resulting from the splitting of the original e_g orbital would now be filled. Because oxidation involves a nondegenerate orbital, no such effect is expected in this case. This splitting would then explain the difference between the spectral and electrochemical data, although the identity of the energy difference (5 kcal/mole) in both cases is most probably fortuitous.

In the case of Co, first-step reduction can be conclusively assigned to reduction to Co(I) as shown by its diamagnetism[3] and its visible spectrum. For the second reduction step, results are less definitive. The following explanation appears to be the only one which will explain all of the data. The Co(II) complex is reduced to a Co(I) species, which is subsequently reduced to a Co(0) phthalocyanine. This species slowly forms a hydride, perhaps in a light-catalyzed reaction, which reacts immediately, either with the solvent or with the small amount of water present, yielding either a Co(I) or Co(II) species.

A cycle of this type can be supported as follows. (1) The epr spectrum of the Co(0) species shows a reversal of the values of $g_{\parallel}$ and $g_{\perp}$ relative to those of the Co(II) compound. More significantly, the signal shows nitrogen splitting, but nothing assignable to proton (hydride) splitting, and is much weaker than the parent signal, Co(II). (2) The odor of dimethyl sulfide (DMS), shown by gas chromatography to be noticeable when present in concentrations of 10^{-3} M and greater, is discernible on electrolytic reduction of the Co(I) species. No such odor is apparent in electrolyses of the other compounds. This would result from a reaction between a cobalt hydride and DMSO, giving DMS, OH^-, and the Co(II) complex, which, with excess Co(0), would immediately yield Co(I).

This scheme would explain the low epr signal intensity, the failure, noted by others,[18] to obtain satisfactory reduction of the Co(I) solutions, the odor of DMS, and the failure to obtain a reliable visible spectrum. The slow reaction of Co(0) to give the hydride was postulated in order to explain the reversibility of the polarographic waves and the stability suggested by the disproportionation energy and by the cyclic voltammetry data. The possibility of a light effect in bulk electrolysis was proposed because epr spectra (frozen, concentrated, opaque solutions) but no reliable visible spectra (dilute, transparent) could be obtained.

It is on this evidence that the postulated reduction of $Na_4Co^{II}PTS$ to $Na_4Co^{I}PTS$ to, initially, $Na_4Co^{0}PTS$ stands. Definitive results, however, must come from studies in anhydrous systems, where Taube[3] reports successful reduction but no characterization (other than magnetic susceptibilities) of CoPc.

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(33) A. Streitwieser, Jr., "Molecular Orbital Theory for Organic Chemists," John Wiley and Sons, Inc., New York, N. Y., 1961, p 173.

(34) L. C. Snyder, *J. Phys. Chem.*, **66**, 2299 (1962).