

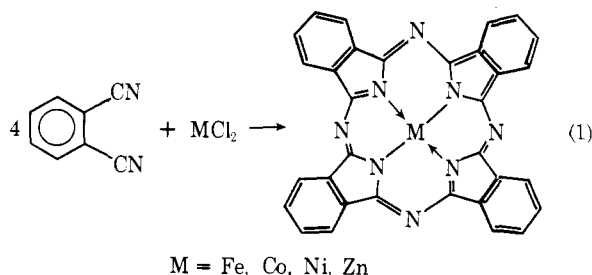
Large Metal Ion-Centered Template Reactions. Chemical and Spectral Studies of the "Superphthalocyanine" Dioxocyclopentakis(1-iminoisindolinato)uranium(VI) and Its Derivatives

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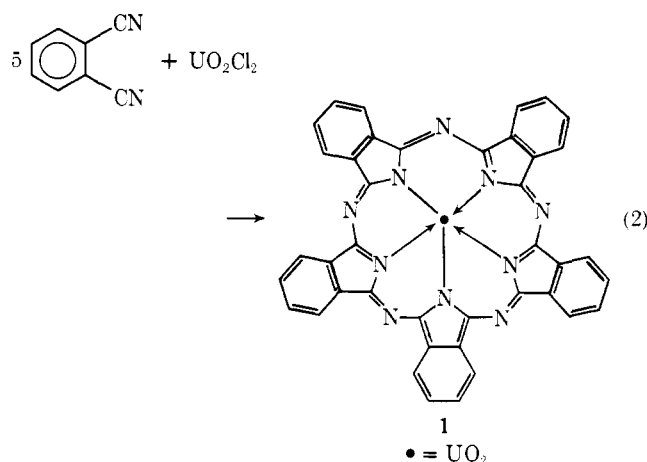
Abstract: This paper reports on chemical and spectral studies of the macrocyclic uranyl complexes dioxocyclopentakis(1-iminoisindolinato)uranium(VI), SPcUO_2 , and dioxocyclopentakis(1-imino-5-methylisindolinato)uranium(VI), $\text{Me}_5\text{SPcUO}_2$. These expanded, five-subunit analogues of phthalocyanines were synthesized in template reactions from uranyl salts and the corresponding phthalonitriles. The conditions for a high-yield synthesis are critical and include a polar solvent (e.g., dimethylformamide), high temperatures, and strict exclusion of water. Phthalocyanine, PcH_2 , is a side product of the reaction with the source of protons being the solvent. Attempts to displace the uranyl ion from SPcUO_2 with acids or other metal ions (M^{n+}) invariably result in macrocycle contraction to produce PcH_2 or PcM^{n-2} and phthalonitrile. ^1H NMR studies reveal the five-subunit macrocycle to be stereochemically dynamic. The analysis of ring current induced ^1H NMR shifts indicates considerably reduced π electron delocalization in SPcUO_2 compared to PcM derivatives. The electronic spectrum of SPcUO_2 exhibits strong absorption maxima at 4240 and 9140 Å. With the aid of Pariser-Parr-Pople SCF LCAO CI π electron molecular orbital calculations, the electronic structure of the macrocycle and the origin of the spectral transitions can be shown to be closely analogous to phthalocyanine systems. Many of the chemical and spectral properties of SPcUO_2 and $\text{Me}_5\text{SPcUO}_2$ reflect the severe buckling and strain within the macrocyclic ligand.

The application of transition metal ion "templates" to the construction of macrocyclic organic molecules is an area of synthetic chemistry which is rapidly growing in sophistication.^{2,3} It is clear that the presence of a metal ion can exert a profound control over the course of a number of types of condensation reactions, and can selectively promote the formation of otherwise inaccessible cyclic products in high yield. Though these results surely reflect the coordinative effects of the metal ion, it has not been clear to what degree it might be possible to alter the direction of these types of transformations by variation of the template. Since d-transition metal ions possess intrinsic limitations in coordination geometry and ionic radius, it has been our interest to explore the use of larger actinide ions in modifying template coordination chemistry. We recently demonstrated unequivocally⁴ that when the phthalocyanine (Pc) condensation^{2,5} (eq 1) is carried out in the presence of the

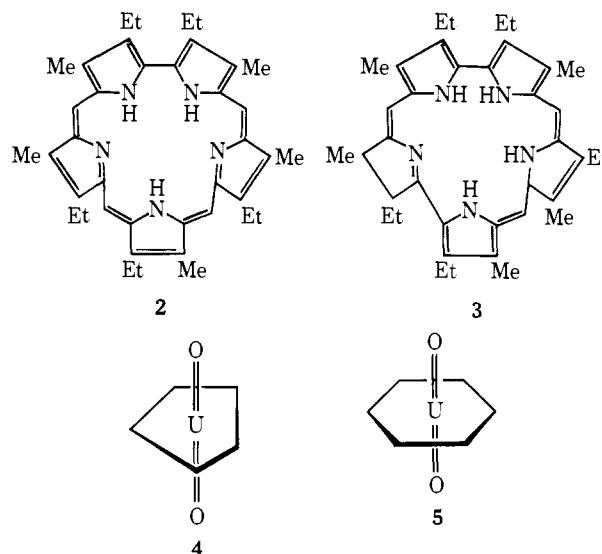


uranyl ion,^{4,6} a complex of an expanded five-subunit macrocycle, the "superphthalocyanine" ligand⁷ (SPc), **1**, results (eq 2). Such conjugated nitrogenous macrocycles with 22 π electron ($4n + 2$ aromatic⁸) inner rings are ordinarily not so readily accessible, and the syntheses of porphyrin analogues such as Woodward's sapphyrin, **2**,⁹ or Johnson's^{9b,10} norsapphyrin, **3**, require nontrivial [3 + 2] condensations of the appropriate polypyrroles.

The general tendency of the uranyl ion to achieve a pentagonal bipyramidal, **4**, or hexagonal bipyramidal, **5**, coordination geometry together with the long U-N contacts observed in **1** (ca. 2.5–2.6 Å as opposed to ca. 1.85–2.05 Å in most phthalocyanines^{5,11}) and in other uranyl complexes^{4,12} suggests



vehicles for expanded macrocycle fabrication. Thus, it has been of interest to ascertain to what extent the structural and chemical stability of **1** (and by inference its formation and



coordinative specificity) are promoted by the unique coordinative properties of the uranyl ion.¹³ In this contribution we describe chemical studies relating to the synthesis and reactions of uranyl superphthalocyanine and related complexes, as well as spectral investigations of molecular and electronic structure.

Experimental Section

All operations involving air-sensitive reagents were carried out under nitrogen in Schlenk ware or in a glove box with rigorous exclusion of oxygen and moisture. Where necessary, solvents were refluxed over the appropriate drying agent and were freshly distilled under nitrogen. *N,N*-Dimethylformamide (Burdick and Jackson "distilled in glass") was stored over molecular sieves, then vacuum distilled twice from BaO. It was handled under nitrogen at all times. Infrared spectra were recorded on a Perkin-Elmer 267 spectrophotometer, and UV-visible spectra on Cary 14 or Cary 17D instruments. Proton nuclear magnetic resonance spectra were recorded on Perkin-Elmer R20B (60 MHz, CW), Bruker HFX-90 (90 MHz, CW), or Varian CFT-20 (80 MHz, FT) instruments. Elemental analyses were performed by Micro-Tech Laboratories, Inc., Skokie, Ill., or by Miss H. Beck, Northwestern Analytical Services Laboratory. Mass spectra were recorded on C.E.C. 21-104 or H.-P. 5930 instruments by Dr. Doris Hung.

Synthesis of Dioxocyclopentakis(1-iminoisolidolinato)uranium(VI), SPcUO₂. I. SPcUO₂ Synthesis in Dimethylformamide (Modified Literature^{6a} Procedure). A. A mixture of 2.5 g (7.33 mmol) of anhydrous powdered uranyl chloride (BDH Ltd.), 14.0 g (109 mmol) of phthalonitrile (Pfaltz and Bauer, dried under high vacuum), and 1.1 mL of dry dimethylformamide (Burdick and Jackson) was heated under nitrogen with stirring at 170 °C. Within 80–90 min the tan mixture abruptly turned dark green. On cooling to room temperature, the reaction mixture solidified. The dark green solid was crushed, washed with ethanol, water, and acetone, then dried under vacuum to yield a mixture of SPcUO₂ and PcH₂ in a mole ratio of 1.9:1 (by electronic spectrophotometry). Soxhlet extraction of this material with benzene yielded 1.37 g (24%) of a dark blue, microcrystalline product which was ≥97% SPcUO₂ by spectrophotometry (≤3% PcH₂). Larger crystals can be grown by slow evaporation of 1,2,4-trichlorobenzene solutions. A slightly purer product can also be obtained by sublimation at 400 °C (10⁻³ mm); however, the yield is greatly reduced.

Anal. Calcd for (C₈H₄N₂)₅UO₂: C, 52.72; H, 2.22; N, 15.37. Found: C, 52.54; H, 2.16; N, 15.21.

Infrared spectrum (Nujol mull): 1505 ms, 1495 sh, 1460 m, 1410 m, 1370 w, 1330 s, 1280 m, 1180 vw, 1165 w, 1110 m, 1070 s, 1025 s, 1013 s, 940 w, 925 s, 897 w, 865 m, 765 m, 715 s, 700 s, 660 w, 625 w cm⁻¹.

Mass spectrum (70 eV, 260 °C): strong parent ion at *m/e* 910.

II. SPcUO₂ Synthesis in Dimethylformamide-*d*₇. The procedure in part I was carried out with 0.31 g (0.909 mmol) of anhydrous uranyl chloride, 1.17 g (9.14 mmol) of phthalonitrile, and 1.0 mL of dry dimethylformamide-*d*₇ (Wilmad, 99.5% D). Workup yielded 0.11 g of dark blue, microcrystalline solid, which infrared spectra indicated to be a mixture of SPcUO₂ and PcD₂ (ν_{N-D} 2490 cm⁻¹).^{5a} The electronic spectrum indicated an SPcUO₂:PcD₂ molar ratio of 2.27:1.0. The yield of SPcUO₂ was 11% based upon UO₂Cl₂.

III. Synthesis in *N,N*-Dimethylacetamide. The procedure described in part A was carried out with 0.79 g (2.32 mmol) of anhydrous uranyl chloride, 2.00 g (15.6 mmol) of phthalonitrile, and 1.0 mL of dry dimethylacetamide. Workup yielded 0.43 g of violet, microcrystalline solid which electronic spectra (as well as infrared) indicated to be a 0.13:1.0 molar mixture of SPcUO₂ and PcH₂. This corresponds to a 3.8% yield of SPcUO₂ based upon UO₂Cl₂.

IV. SPcUO₂ Synthesis with Uranyl Acetate. A mixture of 1.17 g (3.44 mmol) of anhydrous UO₂(OAc)₂(DMF)₂,¹⁴ 4.0 g (31.2 mmol) of phthalonitrile, and 0.52 mL of dry DMF was reacted as in part A. Workup yielded 0.15 g of blue-violet solid, which was shown to be a 9.5:1 (molar) mixture of SPcUO₂-PcH₂ by spectrophotometry. This corresponds to a 7.1% yield of SPcUO₂ based upon UO₂(OAc)₂(DMF)₂.

V. SPcUO₂ Synthesis with Uranyl Nitrate. As described in part I A 0.36 g (1.06 mmol) of anhydrous UO₂(NO₃)₂(DMF)₂,¹⁴ 0.60 g (4.68 mmol) of phthalonitrile, and 0.10 mL of DMF were reacted. The standard workup procedure gave 0.03 g of blue-violet solid, which was shown by UV-vis measurements to be a 1.7:1 (molar) mixture of

SPcUO₂ and PcH₂. The overall yield of SPcUO₂ was 3.7% based upon UO₂(NO₃)₂(DMF)₂.

Synthesis of Dioxocyclopentakis(1-imino-5-methylisolidolinato)uranium(VI), Me₅SPcUO₂. To 0.60 g (4.22 mmol) of 4-methylphthalonitrile (prepared from 3-aminotoluene by the literature procedure^{15,16}) were added 0.30 g (0.880 mmol) of anhydrous uranyl chloride and 0.30 mL of dry DMF. Reaction of this mixture under nitrogen for 40 min at 170 °C yielded a dark green solution. Solidification occurred on cooling to room temperature and the resulting solid was crushed and washed with water, then with a 4:1 acetone-water mixture. Finally, the product was extracted with three 25-mL portions of acetone and the filtered extracts were evaporated under vacuum. This procedure yielded 0.063 g (7.6% based upon 4-methylphthalonitrile) of Me₅SPcUO₂ as a dark green, microcrystalline powder. This compound is considerably more soluble than SPcUO₂ in organic solvents, which made purification difficult. It decomposes when sublimation is attempted.

Anal. Calcd for (C₉H₆N₂)₅UO₂: C, 55.12; H, 3.06; N, 14.29. Found: C, 56.58; H, 3.51; N, 14.23.

Infrared spectrum (Nujol mull): 1613 ms, 1512 ms, 1501 m, 1486 vw, 1398 m, 1327 s, 1309 ms, 1273 m, 1159 m, 1120 w, 1111 w, 1071 s, 1032 ms, 1014 m, 993 w, 931 s, 920 m, 883 w, 819 m, 798 vw, 768 vw, 759 w, 731 m, 714 s, 697 m, 689 w, 661 m, 635 w cm⁻¹.

Electronic spectrum (in 1-chloronaphthalene): 442 vs, 804 m, sh, 930 nm vs. Mass spectrum (70 eV, 250 °C): strong parent ion at *m/e* 980.

Representative Demetalation and Transmetalation Experiments.

I. Reactions of SPcUO₂ with Lewis Acids. A. To 4.0 mL of CF₃CO₂H was added 0.10 g (0.11 mmol) of SPcUO₂ and the mixture was brought to reflux (72 °C) for 60 min. After this time, the resulting dark blue suspension was poured into 50 g of ice, and the precipitate isolated by centrifugation. The violet-blue powder was washed with water and acetone, and then air dried to yield 0.020 g (35%) of α -PcH₂, identified by infrared⁵ and optical spectra. A similar result was obtained when the Lewis acid employed was CCl₃CO₂H. Operating at lower temperatures only decreased the rate of contraction.

B. Several additional experiments were conducted by stirring SPcUO₂ in chlorobenzene with aqueous acids (e.g., 6 N HCl, 25% HF) at 25 °C. In these cases the organic layer gradually faded in color and white solid formed at the interface between layers. The solid was identified as phthalic acid by melting point and infrared spectrum.

II. Transmetalation and Contraction Reactions of SPcUO₂. Anhydrous CuCl₂, CoCl₂, ZnCl₂, and ErCl₃ were prepared by the standard method¹⁷ of refluxing the hydrated salts with thionyl chloride. Anhydrous Zn(OAc)₂, Pb(OAc)₂, and SnCl₂ were prepared by refluxing the hydrates with acetic anhydride. Commercial bis(trifluoroacetylacetonato)copper(II) (PCR Inc.) was purified by vacuum sublimation. The anhydrous metal salts were handled under nitrogen at all times.

A. To 0.030 g (0.223 mmol) of anhydrous CuCl₂ dissolved in 2.0 mL of dry DMF was added 0.10 g (0.11 mmol) of SPcUO₂, and the mixture was heated under nitrogen for 3 h at 120 °C with stirring. After this time the solvent was removed in vacuo and the resulting solid was washed with water, acetone, and ether and then vacuum dried. The product consisted of 0.060 g of violet, microcrystalline powder, identified as PcCu by infrared and electronic spectra and by elemental analysis. The yield was 95% based on SPcUO₂.

B. Kinetic studies of the above reaction were performed in 1/300 DMF-1-chloronaphthalene at 75 ± 1 °C. The 1-chloronaphthalene had been stored over molecular sieves and then vacuum distilled from BaO. Concentrations were maintained at a level such that all reactants and products were in solution, i.e., 1.35 × 10⁻⁵ M SPcUO₂ and 7.44 × 10⁻⁵ M CuCl₂. The reaction mixture was vigorously stirred under nitrogen. Aliquots were periodically withdrawn (using a glass pipet to avoid trace Cu²⁺ contamination from the brass in the syringe fittings) and examined by electronic spectrophotometry.

C. Phthalonitrile formation in reaction A was quantitatively monitored by infrared spectrophotometry in the 2200-cm⁻¹ ($\nu_{C\equiv N}$) region. Spectra of diluted reaction mixture aliquots were recorded in matched CaF₂ infrared cells. Yields of phthalonitrile were determined using calibration solutions of known concentration, while electronic spectra were used to calculate the extent to which the SPcUO₂ contraction had progressed. At 15% conversion of SPcUO₂ to PcCu, 65% of the expected phthalonitrile was present; at 25% conversion, 38% of the expected phthalonitrile was present; and at 100% conversion, only 7%. Clearly the phthalonitrile was being consumed in some re-

Table I. Transmetalation Reactions of SPcUO₂ and Me₅SPcUO₂^a

Starting macrocycle	Metal salt	Solvent	Temp. °C	Time, h	Product(s)	Yield, %
SPoUO ₂	CuCl ₂	DMF	120	3	PcCu	95
SPcUO ₂	CuCl ₂	1-Pentanol	120	15	PcCu	87
SPcUO ₂	Cu(tfacac) ₂ ^b	DMF	123	13	PcCu	25
					SPcUO ₂	75
SPcUO ₂	Cu(tfacac) ₂ ^b	Toluene	195 ^c	10	PcCu	33
					SPcUO ₂	67
Me ₅ SPcUO ₂	CuCl ₂	DMF	75	47	Me ₄ PcCu	95
SPcUO ₂	CoCl ₂	Quinoline	120	1.5	PcCo ⁵	59
SPcUO ₂	ZnCl ₂	DMF	135	30	PcZn	45
SPcUO ₂	ZnCl ₂ ·4H ₂ O	DMF	135	30	PcH ₂	49
					PcZn	26
SPcUO ₂	NiSO ₄ ·6H ₂ O	DMF	140	50	PcNi ⁵	82
SPcUO ₂	SnCl ₂	DMF	120	2.5	PcSn ^{5,19}	82
SPcUO ₂	ErCl ₃	DMF	116	4	PcErCl ^{5a}	37

^a Procedure of Experimental Section, part IIA. Products were identified by spectral data given in the references cited and, where necessary, by elemental analysis. ^b tfacac = trifluoroacetylacetonato. ^c Sealed tube reaction.

action following SPcUO₂ contraction.

D. Experiments with other metal salts and solvents are summarized in Table I; the general procedure was similar to that of IIA.

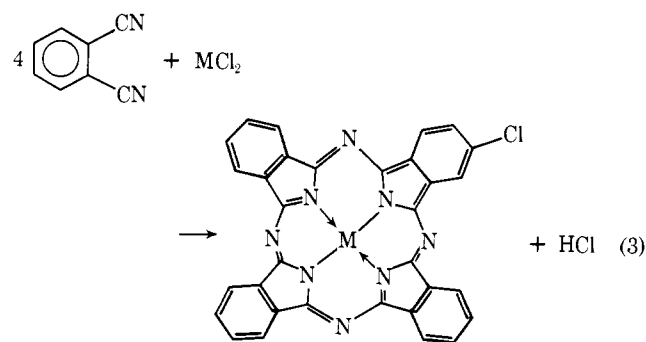
III. Reactions of Phthalonitrile Related to Contraction Studies. A. Dry phthalonitrile (4.0 g, 31.3 mmol) was heated under nitrogen with 1.0 mL of DMF for 2 h at 250 °C. After cooling to room temperature, the resulting solid was crushed and washed repeatedly with acetone to remove phthalonitrile as well as the thermal trimer²⁰ of phthalonitrile. What remained after washing was 0.020 g (0.6%) of a violet-blue powder, identified as PcH₂ by infrared and electronic spectra.

B. When the above reaction was carried out in 1.0 mL of DMF-*d*₇, the violet-blue powder isolated (again 0.020 g) was identified as PcD₂ from infrared spectra.⁵ In particular $\nu_{\text{N-H}}$ (3250–3300 cm⁻¹) was absent and $\nu_{\text{N-D}}$ was apparent at 2460 cm⁻¹.

Results

The Formation Reaction of SPcUO₂ and Homologues.

Phthalocyanine and its metal complexes have been extensively studied in academic and industrial laboratories.⁵ These efforts have led to the development and refinement of synthetic techniques and to a reasonably clear understanding of most chemical and physicochemical properties. Surprisingly, however, very little is known about the mechanism of the condensation reaction (eq 1). One of the most commonly employed syntheses of metal phthalocyanines involves heating phthalonitrile with a stoichiometric amount of the metal chloride at temperatures greater than ca. 200 °C in a solvent such as quinoline or trichlorobenzene. In the absence of basic solvents (e.g., quinoline) or additives such as urea, ring halogenation (eq 3) occurs.



The basic additives and/or their decomposition products are believed to function as halogen acceptors, thus minimizing ring attack. Whether these reactions involve free radicals is not known. Only in the case of 1,3-diiminoisoindoline condensations in protic solvents (e.g., amyl alcohol) have intermediates been identified. These appear to contain isoindoline func-

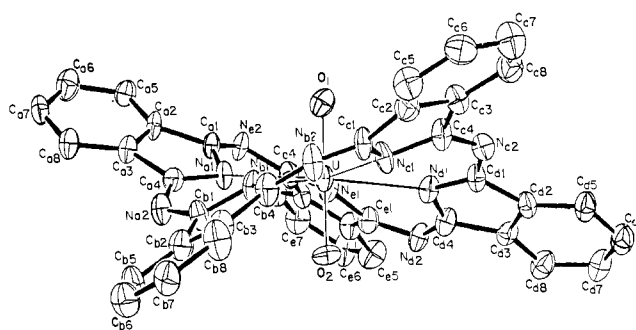
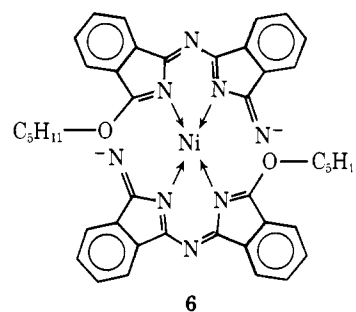


Figure 1. Perspective view of the structure of SPcUO₂ perpendicular to the O=U=O axis (from ref 4).

tionalties such as **6**;²¹ however, it is not clear whether such species have any relevance to standard synthetic conditions. Phthalocyanines are also commonly prepared from isoindolines and from phthalic anhydride and urea.⁵



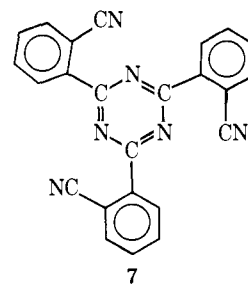
The reaction of anhydrous uranyl chloride with phthalonitrile in dry dimethylformamide produces the uranyl complex of the expanded phthalocyanine macrocycle SPcUO₂ as a dark blue, microcrystalline solid which is sparingly soluble in aromatic solvents and insoluble in others. X-ray diffraction studies⁴ reveal a pentagonal bipyramidal coordination geometry about uranium as schematized in eq 2 with only a 0.20 Å average deviation of each of the five coordinated nitrogen atoms from their unit-weighted least-squares mean plane. As can be best appreciated by viewing Figure 1, the remainder of the macrocycle is severely and irregularly buckled, and the normals to the isoindole mean planes make angles of -38.7 to +39.8° with the normal to the mean plane for the entire macrocycle. It will be seen that many of the properties of SPcUO₂ are explicable in terms of severe strain within the macrocycle.

The reaction conditions for a successful SPcUO₂ synthesis were found to be rather critical. The presence of large quantities of water in the reagents reduces the yield and promotes the formation of the side product, metal-free phthalocyanine (PcH₂). The yield of the condensation also falls when uranyl nitrate or acetate are substituted for the chloride, and no more than traces of 1 are produced in reactions with UO₂Br₂, UO₂F₂, or UO₂SO₄. The choice of solvent is also crucial and high-boiling amides (DMF, *N,N*-dimethylformamide) in which UO₂Cl₂ is appreciably soluble gave the highest yields. The standard PcM condensation procedure employing UO₂Cl₂, phthalic anhydride, and urea, with or without a molybdate catalyst,⁵ fails to produce the five-membered macrocycle.

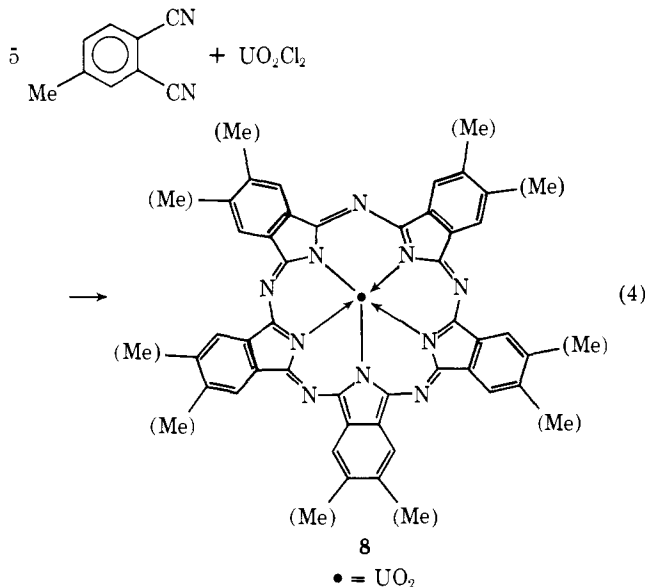
Several additional observations concerning the superphthalocyanine condensation are noteworthy. First, the analytical and mass spectral data as well as the x-ray diffraction study provide no evidence for ring chlorination during the synthesis of SPcUO₂. As written, reaction 2 must produce, stoichiometrically, either Cl₂ or 2Cl. The absence of SPc chlorination appears to be due to the halogen accepting (or halogen radical scavenging) power of DMF (vide infra) and to the relatively low reaction temperature. Though the abrupt commencement of the reaction (see Experimental Section) after what might be interpreted as an induction period suggests the possibility of a free-radical chain mechanism, attempts at initiation with dibenzoyl peroxide or azobisisobutyronitrile were unsuccessful. The rapid color change observed may simply reflect, instead, a final ring closure, after a number of preliminary steps, to form the intensely colored macrocycle. If the reaction is halted before completion, it is possible to isolate a yellow solid, analyzing approximately as (phthalonitrile)₂UO₂Cl₂. Infrared spectra reveal the presence of free and coordinated $\text{C}\equiv\text{N}$, and >C=N- functionalities.

The SPcUO₂ condensation reaction is invariably accompanied by the formation of the metal-free four-membered macrocycle, PcH₂. The ratio of SPcUO₂:PcH₂ depends on the reaction conditions (see Experimental Section). When the SPcUO₂ synthesis is carried out in DMF-*d*₇, the phthalocyanine is isolated as PcD₂, indicating that the hydrogen source is the solvent. Control experiments indicate that DMF alone does not promote phthalonitrile tetramerization at temperatures below ca. 240 °C, and even under these conditions the yield after several hours is less than 1%. When SPcUO₂ is heated under the condensation reaction conditions with DMF slow conversion to PcH₂ occurs; however, the yield (determined spectrophotometrically) is only 10–15% of that produced in the condensation reaction. These results strongly suggest that DMF (or its decomposition products CO and HN(CH₃)₂ at the reaction temperature)²² or the other solvents serve as scavengers for halogen. The resulting HCl then provides protons for the demetalation of SPcUO₂ (vide infra) to produce PcH₂ (or PcD₂). The presence of halogen was not detected (chemically or mass spectrometrically) in the PcH₂, nor in the unreacted phthalonitrile, isolated after the condensation was complete. The other major nonpolymeric organic product of the condensation was identified mass spectrometrically as the phthalonitrile thermal trimer, 2,4,6-tri(*o*-cyanophenyl)-1,3,5-triazene (7).²⁰ It also did not contain halogen.

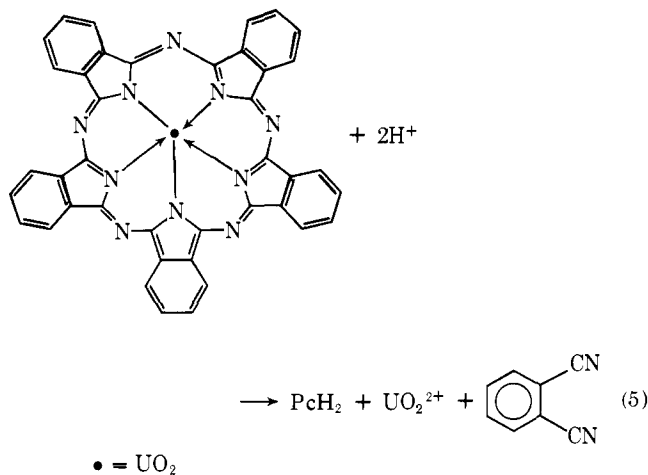
The use of substituted phthalonitriles in the uranyl-centered condensation was also investigated. It is possible to prepare the more soluble pentamethyl derivative, Me₅SPcUO₂, 8 (eq 4), although in somewhat lower yield than SPcUO₂. Not surprisingly, 270-MHz ¹H NMR studies (vide infra) indicate that 8 is a mixture of isomers. Curiously, when the condensation reaction is conducted using 1,2-dicyanobenzenes with electron-withdrawing groups (3,4,5,6-tetrachloro or 3,4,5,6-tetrafluoro) or greater steric congestion (3,6-dimethoxy) no five-subunit macrocycle can be detected. Mixed condensation



experiments involving various proportions of phthalonitrile and the above dinitriles yield only SPcUO₂.



The Chemistry of SPcUO₂. Demetalation and Transmetalation Reactions. It was of considerable interest to determine to what degree the integrity of the superphthalocyanine macrocycle depends on the presence of the uranyl ion. This question was approached by an investigation of the demetalation and transmetalation reactions of SPcUO₂. The reaction of SPcUO₂ with acids under conditions (e.g., heating in CCl₃CO₂H or CF₃CO₂H) which readily demetalate many phthalocyanine and porphyrin coordination complexes^{5,23} leads to an unusual contraction¹³ reaction, which is unprecedented in macrocycle chemistry (eq 5). Reactions at lower tempera-



ture only produce slower contraction. At no time was there spectrophotometric evidence for the free, five-subunit ligand. If the reaction is carried out in aqueous solution, considerable quantities of the phthalocyanine hydrolysis product, phthalic acid, are formed.

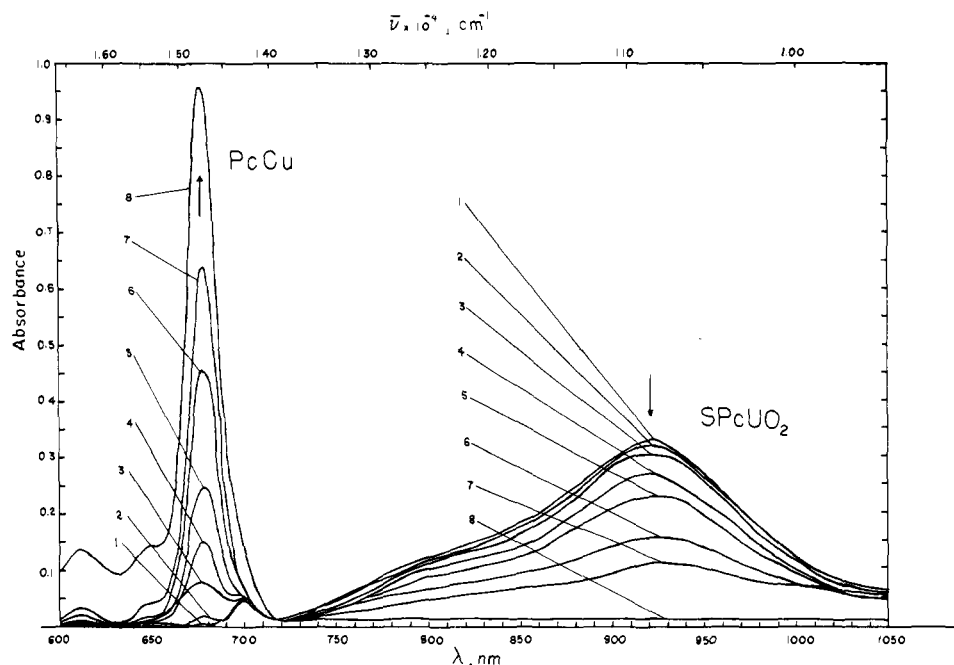
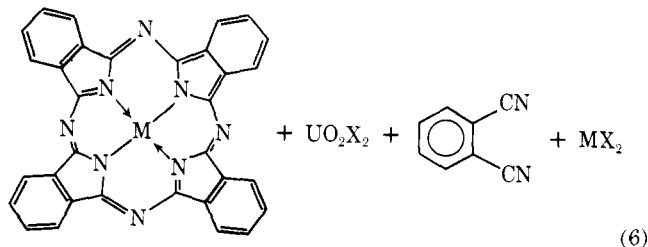
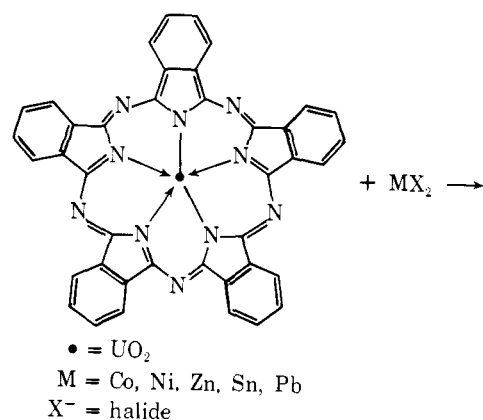


Figure 2. Spectrophotometric record of the reaction of SPcUO₂ with CuCl₂ in the solvent 300:1 1-chloronaphthalene-dimethylformamide at 75 °C.

Attempts to replace the uranyl ion in SPcUO₂ by other metal ions were also conducted. These experiments are summarized in Table I. Anhydrous transition metal salts such as CuCl₂, CoCl₂, and ZnCl₂, when dissolved in DMF, react with SPcUO₂ to produce the corresponding four-subunit transition metal complex in high yield (eq 6). Under the same conditions,



the larger Sn²⁺ and Pb²⁺ ions also induce SPc contraction along with the formation of PcSn and PcPb, respectively. Hydrated metal salts yield appreciable amounts of PcH₂ in cases where the corresponding PcM derivative is known to be proton sensitive. Anhydrous ThCl₄ in DMF causes decomposition of SPcUO₂ with no phthalocyanine products being formed. No reaction occurs with anhydrous BaCl₂, PdCl₂, or K₂PtCl₄. The methylated derivative, Me₅SPcUO₂, reacts with CuCl₂ in DMF to yield Me₄PcCu.¹⁸ The macrocycle contraction was studied in several solvents besides DMF. At 195

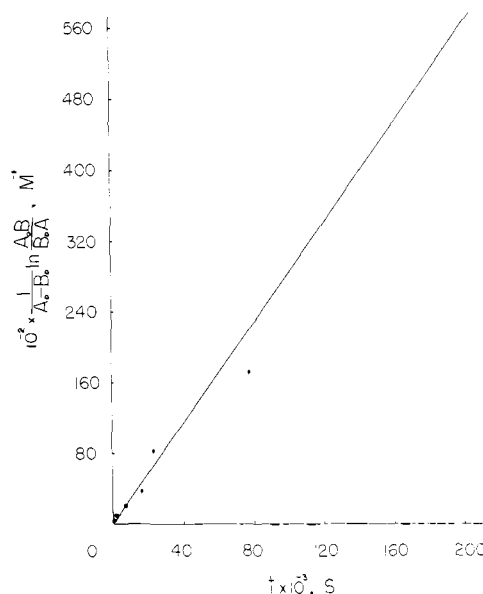


Figure 3. Kinetic plot of the reaction shown in Figure 2.

°C in toluene (sealed tube) or 208 °C in 1,2,3,4-tetrahydronaphthalene (reflux) the soluble metal complex bis(trifluoroacetylacetonato)copper(II) reacts with SPcUO₂ to produce considerable quantities (33% yield) of PcCu. Under the same conditions, the reaction with the insoluble CuCl₂ produces only traces of PcCu. In very polar solvents such as 1-pentanol at 120 °C, the reaction between CuCl₂ and SPcUO₂ (insoluble in this solvent) is complete in ca. 15 h, to produce PcCu in 87% yield.

The mechanistic features of the transmetalation/contraction reaction were investigated in most detail for the CuCl₂ system. As shown in Figure 2, the reaction proceeds cleanly and the yield of PcCu is essentially quantitative. Kinetically, the reaction rate at 75 ± 1 °C is first order in CuCl₂ and first order in SPcUO₂ (Figure 3) with $k = 0.28 \pm 0.06 \text{ L mol}^{-1} \text{ s}^{-1}$.²⁴ That the PcCu does not arise via metalation of initially formed PcH₂ was demonstrated kinetically by showing that CuCl₂ converted added PcH₂ to PcCu at a far slower rate than the

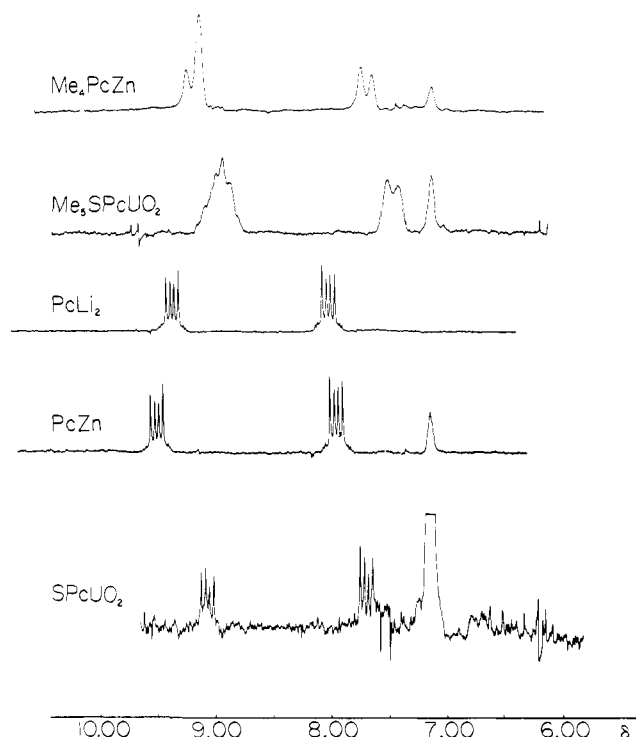


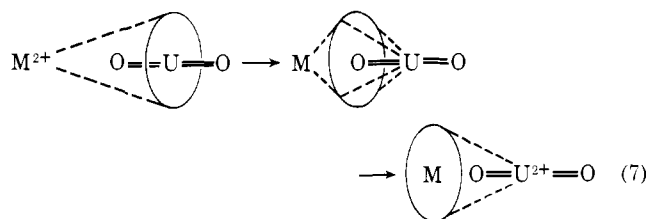
Figure 4. ^1H NMR spectra (FT, 80 MHz) of various macrocyclic complexes. The solvents are C_6D_6 (uranyl complexes), $\text{C}_6\text{D}_6 + 2\%$ $(\text{CD}_3)_2\text{SO}$ (zinc complexes), and $(\text{CD}_3)_2\text{CO}$ (lithium complex). Number of transients ranged from 400 (PcLi_2) to 8000 (SPcUO_2). The peak at $\delta \approx 7.15$ is due to $\text{C}_6\text{D}_5\text{H}$.

rate of SPcUO_2 contraction. The formation of phthalonitrile was monitored during the course of the reaction by infrared spectrophotometry. In the early stages of the contraction process, phthalonitrile formation extrapolates to stoichiometric quantities as dictated by eq 6. In later stages of the reaction, however, the phthalonitrile concentration decreases considerably. A plausible explanation for this disappearance is oligomerization to yield products such as the trimer, **7**.²⁰ Cyclization to form phthalocyanines was found to be slow under these conditions (see Experimental Section).

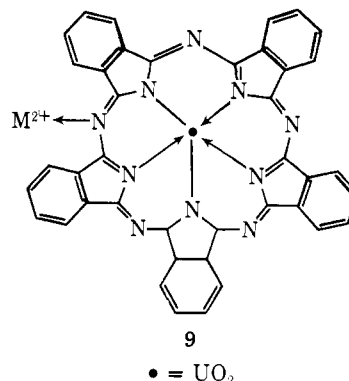
The tendency of the five-subunit SPc macrocycle to undergo contraction to the four-subunit Pc ligand appears to be a ubiquitous feature of the chemistry related to UO_2^{2+} displacement. This pattern is proof that the uranyl ion plays a significant role in stabilizing the SPc macrocycle. The reasons for the facile contraction appear to be severalfold. First as noted in our structural discussion,⁴ the SPc macrocycle appears to be significantly destabilized by internal strain. There is also spectroscopic evidence (vide infra) that the electronic conjugation of the π system is impaired (by the severe ring buckling) in SPc as compared to Pc. Also, though the radius of the central "hole" in SPc, 2.55 Å, is ideally suited for UO_2^{2+} incorporation, such distances are not generally expected to favor the formation of stable, planar conjugated SPcM complexes where M is a transition metal or main group ion and where there is good M-N overlap. For phthalocyanines with the metal in the plane of the ring, typical M-N distances are found in the range 1.83 Å (PcNi^{25a}), 1.934 (6) Å (PcCu^{26}), 1.938 (3) Å (PcMn^{27}), 1.980 (2) Å (PcZn^{28}), 1.93 (3) Å (PcPt^{29}), to 2.051 (3) Å (PcSnCl_2^{30}). Ions such as Sn^{2+} and Pb^{2+} , which are sufficiently large as to be forced over 1 Å out of the plane of the phthalocyanine ligand, possess M-N distances which are still considerably shorter than 2.55 Å, i.e., 2.25 Å (PcSn^{31}) and 2.21 Å (PcPb^{32}). Thus, a few metal ions will have sufficiently large ionic radii to overlap well with the N atoms of the SPc macrocycle. Furthermore, many ions of large ionic radius

adopt coordination polyhedra which are more compatible with the Pc ligand. For example, the Archimedean antiprism of eight coordination will favor two groups of four coplanar ligands, as approximated in PC_2U .³³ In summary, the contraction process appears to reflect both the strain in SPcUO_2 as well as the inherent instability of other SPcH_2 and SPcM species vis-à-vis the PcH_2 and PcM analogues.

The actual mechanism of the SPc contraction is open to speculation. A process involving rate-determining displacement of UO_2^{2+} to form an SPcM species (eq 7) which subsequently



contracts is compatible with the kinetic data and is analogous to mechanisms proposed for transmetalation processes in porphyrin systems.^{23,34} The limited mechanistic information which is available for phthalocyanine metalation^{35,36} and demetalation³⁷ reactions is in accord with this suggestion. Alternatively, the rate-determining step involves coordination of the attacking metal ion to an imino nitrogen on the SPcUO_2 periphery, **9**, followed by Lewis acid promoted ring opening.



There is spectrophotometric evidence in phthalocyanine chemistry for the formation of such adducts with strong Lewis acids (AlCl_3).³⁸ Furthermore, the addition of AlCl_3 to a solution of SPcUO_2 in chloronaphthalene at 0 °C induces an analogous 580-Å shift³⁸ of the 9140-Å maximum to lower energies.

Molecular and Electronic Structures of SPcUO_2 and $\text{Me}_5\text{SPcUO}_2$ in Solution. NMR Studies. The low solubility of SPcUO_2 and $\text{Me}_5\text{SPcUO}_2$ necessitated the use for NMR spectroscopy of either long-term CW time averaging, or more satisfactorily, Fourier transform techniques. Representative 80-MHz proton FT spectra are presented in Figure 4 and data are set out in Table I. Comparative results for several diamagnetic metal phthalocyanines are also shown. Except for the exact resonance positions, the spectral patterns observed for the four- and five-subunit complexes are rather similar. In view of the distorted structure of **1** (Figure 1) it is noteworthy that the magnetic nonequivalence of the various benzo and methyl protons is not evident. Assuming a nonplanar macrocycle structure similar to **1**, complex **8** can exist in four possible isomers, i.e., structures which differ by relative positioning of methyl groups, and three of these isomers can also exist in a number of conformers, i.e., structures rendered energetically and magnetically nonequivalent by virtue of the buckled character of the macrocycle and the accompanying nonequivalence of the isoindoline environments. That none of these species are observed in the proton spectra suggests either dy-

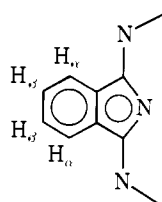
Table II. ^1H NMR Data for PcM and SPcM Derivatives^{a-c}

Compd	^1H NMR
PcZn ^d	9.50 (8 H, m), 7.94 (8 H, m)
(5-CH ₃) ₄ PcZn ^d	9.19 (8 H, d, $J = 8.8$ Hz), 7.69 (4 H, d, $J = 8.0$ Hz), 2.76 (12 H, s)
SPcUO ₂ (1)	9.06 (10 H, m), 7.68 (10 H, m)
(5-CH ₃) ₅ SPcUO ₂ (8)	8.96 (10 H, m), 7.46 (5 H, d, $J = 7.2$ Hz), 2.46 (15 H, s)
PcLi ₂ ^e	9.38 (8 H, m), 8.04 (8 H, m)

^a FT data in δ (ppm). ^b All data in C₆D₆ at 30 °C. ^c Key: s = singlet; d = doublet; m = multiplet. ^d 2% Me₂SO-*d*₆ added to enhance solubility. ^e In acetone-*d*₆.

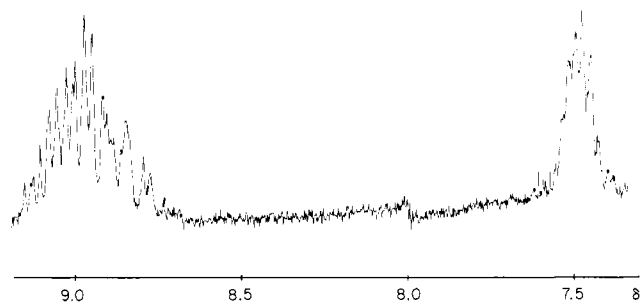
namic interchange of the isoindoline unit environments in **1** or accidental magnetic degeneracy. In **8** stereochemical non-rigidity should only average the conformers of a given isomer and not the isomers. This problem was next investigated by variable temperature studies of the more soluble system, **8**, at 270 MHz. The spectrum at -30 °C is shown in Figure 5. The pattern of the low-field multiplet is rather complex and not in accord with that predicted for a single conformer of a single isomer (five singlets and five doublets, $J_{\text{ortho}} \approx 7$ –10 Hz, of equal intensity). As the temperature is raised to 70 °C, various components of the low-field multiplet collapse, narrow, and change intensity in a complicated manner, suggesting that conformer interchange processes take place within several unequally populated isomers and with somewhat different energies of activation. These results argue strongly that the superphthalocyanine ligand in these uranyl complexes is conformationally dynamic.

The exact proton resonance positions in **1** and **8** were also of interest, especially in comparison to parameters for normal phthalocyanines. Substantial diamagnetic ring current shifts are a general characteristic of all cyclic $4n + 2\pi$ electron systems³⁹ and their magnitudes are a sensitive indication of changes in π electron delocalization. These shielding effects have been extensively studied in porphyrins,⁴⁰ where they are large, and to a lesser extent in phthalocyanines,⁴¹ where they are also large. Reference to Figure 4 and Table II reveals two significant trends. Not only are both the α and β benzo protons, **10**, less deshielded in the supermacrocycles SPcUO₂ and

**10**

Me₅SPcUO₂, but also the chemical shift difference between the AA'BB' multiplets is smaller in the five-subunit complexes. This result cannot be explained on the basis of the inductive effect of the hexavalent metal ion since the benzo protons are in all probability too far removed and, in addition, any inductive shift would be expected to be in the opposite direction.⁴⁰ It is thus necessary to quantitatively consider π electron shielding differences in SPc and Pc systems.

The nuclear magnetic shielding of protons in aromatic molecules can be divided into two major contributions.⁴² Local anisotropy shielding arises from the nonspherical shielding tensors of proximate carbon atoms and has an r^{-3} dependence.^{43,44} It is only recently that the importance of the local anisotropy contribution (at least 50% of the shift in most aromatic compounds) has been fully appreciated.⁴²⁻⁴⁴ Delocalized or ring current shielding arises from the magnetic anisotropy of the conjugated cyclic π electron system. It can be described

**Figure 5.** High-field (FT, 270 MHz) ^1H NMR spectrum of Me₅SPcUO₂ at -30 °C.

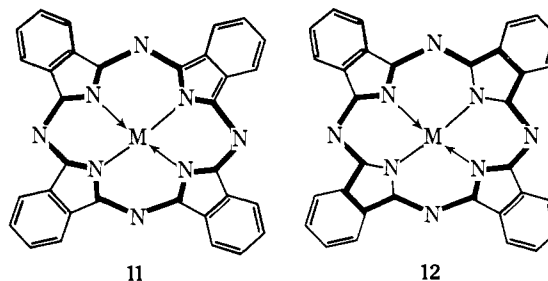
with reasonable accuracy in classical terms⁴⁵ as the magnetic induction arising from current loops comprised of circulating electrons.^{39,40,42} For aromatic annulenes the ring current shift for proton i can be expressed by⁴²

$$\sigma^{\text{H}_i} = C \sum_i \left\{ (I'/I) [(a_r + r_i)^2 + z^2]^{-1/2} \left[K + \frac{a_r^2 - r_i^2 - z^2}{(a_r - r_i)^2 + z^2} E \right] \right\} \quad (8)$$

where C is an empirical scaling constant, I'/I is the current relative to benzene, a_r is the radius of the loop, r_i is the distance from the ring center to proton i , z is the distance between proton i and the plane in which the current loop lies, and K and E are complete elliptic integrals of the first and second kind, respectively, with the argument k^2 given by

$$k^2 = 4a_r [(a_r + r)^2 + z^2]^{-1} \quad (9)$$

To identify the cause of shielding differences between the Pc and SPc macrocycles, it is first necessary to investigate shielding and the applicability of eq 8 in the Pc system. We assume that the chemical shifts of the phthalocyanine α and β benzo protons arise from three sources: local anisotropy effects, delocalized shielding from the isoindoline benzene ring, and delocalized shielding from the 18π electron octaaza [16]-annulene great ring. We also assume that differences in shifts induced by various diamagnetic metal ions are small; this assumption is supported by existing phthalocyanine (Table I) and metalloporphyrin⁴⁰ data. Nonmacrocyclic ortho-disubstituted aromatic model compounds such as phthalic anhydride and phthalate esters should provide reasonable estimates of local anisotropy and benzene ring current shielding in Pc (as well as SPc) macrocycles. If the foregoing approach is valid, it should then be possible to predict the ring current displacements (σ_α , σ_β) from the relationship of eq 8. For testing the applicability of this equation, r_i can be obtained from structural data²⁵⁻²⁹ and z from theoretical or empirical studies.⁴² The parameter a_r , the effective radius of the current loop, is calculated by assuming that the area circumscribed by the current loop (in this case structure **11**) is circular, i.e., the area

**11****12**

$= \pi a_r^2$. For completeness, we also consider several larger circular loops as well as loop **12**, which is similar to that used

Table III. Calculated and Experimental Ring Current Shielding Parameters^a for PcM and SPcM Compounds

Compd	Loop	$a_r, \text{\AA}$	I_i/I	Structure	$\sigma_\alpha/\sigma_\beta$		C^b	σ_α		σ_β	
					Calcd	Exptl		Calcd	Exptl	Calcd	Exptl
PcZn	11	2.77	4.69	Planar	1.61	1.97	0.605	1.72	1.89	1.07	0.96
PcZn	Circular	3.05	5.76	Planar	1.66	1.97	0.395	1.74	1.89	1.05	0.96
PcZn	12	3.17	5.85	Planar	1.66	1.97	0.359	1.74	1.89	1.05	0.96
PcZn	Circular	4.10	10.41	Planar	1.75	1.97	0.107	1.79	1.89	1.02	0.96
PcZn	Circular	5.10	16.12	Planar	1.66	1.97	0.0393	1.74	1.89	1.05	0.96
SPcUO ₂	13	3.39	7.15	Planar			0.605	3.36	1.46	2.08	0.70
SPcUO ₂	13	3.39	7.15	Buckled			0.605	2.86	1.46	1.58	0.70
SPcUO ₂	14	3.73	8.27	Planar			0.359	3.12	1.46	1.75	0.70
SPcUO ₂	14	3.73	8.27	Buckled			0.359	2.33	1.46	1.25	0.70

^a Shifts in parts per million from dibutyl phthalate. ^b Average of empirical scaling parameters for α and β sites.

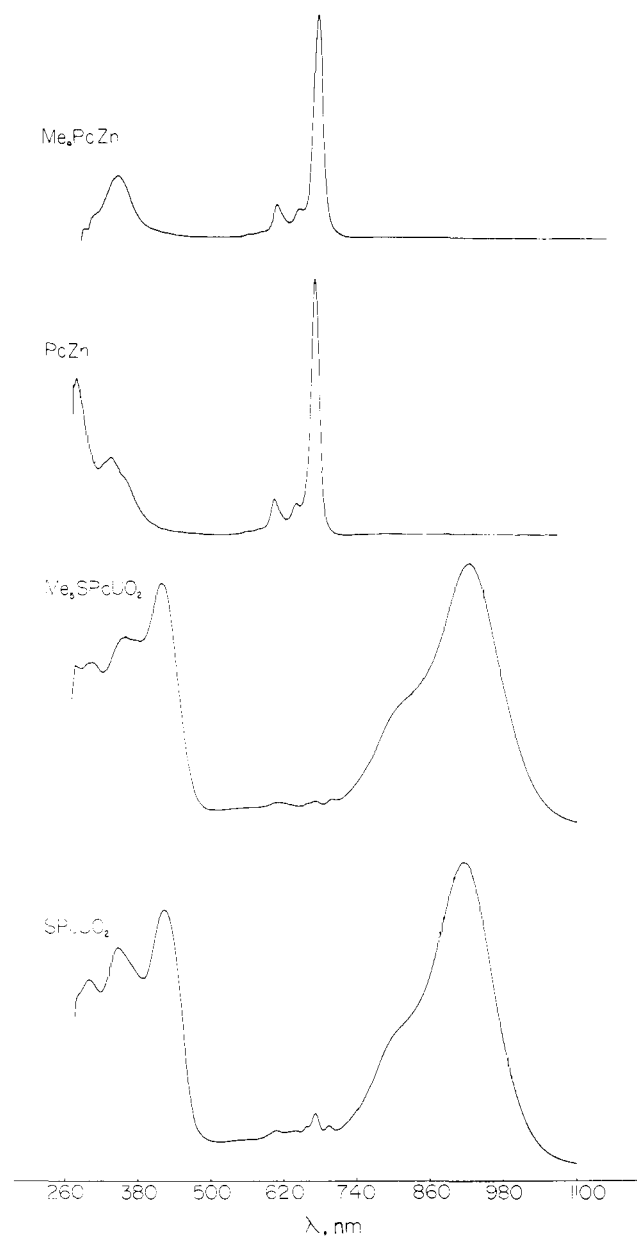
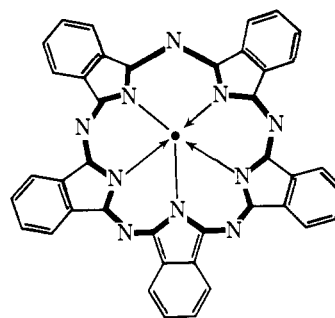
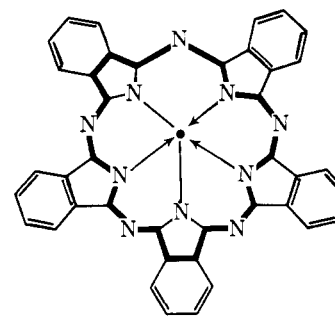


Figure 6. Electronic spectra of macrocyclic complexes in C₆H₆ (uranyl complexes) and C₆H₆ + 2% (CH₃)₂SO (zinc complexes). For the uranyl complexes, the very weak absorption at 6000–7000 Å is due to traces of PcH₂ or Me₄PcH₂.

in several porphyrin studies.⁴⁰ The term I_i/I is a measure of the current flow in the classical loop relative to benzene and is taken to be the ratio of the macrocycle loop circumference relative to that of benzene. The accuracy of the ring current

calculations and their dependence on a_r can best be gauged by comparing calculated and experimental shift ratios $\sigma_\alpha/\sigma_\beta$, which are independent of C . The results of these calculations are compared to the experimental data in Table III. It can be seen that the agreement is good, supporting the validity of eq 8 for describing ring currents effects in phthalocyanine-like macrocycles; this good agreement is comfortably insensitive to choice of a_r . The experimental shifts in the Pc system were next used to calculate C values for classical loop paths **11** and **12** (Table III). Then these C parameters were employed to calculate ring current shieldings in the SPc macrocycle under four sets of conditions, which offer the widest variation of applicable parameters. The shifts were calculated both for conjugative paths **13** and **14**, as well as for proton positions in as-

**13****14**

sumed planar and nonplanar⁴⁶ (i.e., the diffraction-determined structure⁴) versions of the SPc macrocycle. Results are summarized in Table III. Importantly, *any reasonable choice of parameters predicts a far larger delocalized (ring current) shift in the superphthalocyanine*. That this effect is not observed experimentally and that the Pc shifts are instead greater indicates that π electron delocalization, i.e., classically, the conductivity of the loop reflected in I_i/I is considerably decreased in the SPc system. Logically, the explanation for the decrease in electronic delocalization lies in the severe buckling of the SPc macrocycle and accompanying interference in overlap between atomic orbitals in the π system.

Electronic Structure of SPcUO₂. The Optical Spectrum. In

Table IV. Transition Energies and Oscillator Strengths for Pc and SPc Systems

	Calcd ^a				Exptl		
	Transition energy		Oscillator strength		Transition energy		Oscillator strength ^b
	eV	Å	Dipole length approx	Dipole velocity approx	eV	Å	
Pc	1.769	6989	1.02	0.270	1.843	6700 ^c	0.5 ^c (0.4 ^d)
	1.776	6950	1.01	0.269			
	3.726	3313	2.32	0.700	3.707	3330 ^c	1.2 ^d
	3.733	3307	2.29	0.693			
Me ₄ Pc					1.843	6700 ^e	
					3.610	3420 ^e	
					1.831	6743 ^c	
					3.551	3476 ^c	
SPc (planar)	1.486	8310	1.31	0.186			
	1.508	8185	1.21	0.189			
	3.610	3419	2.94	0.806			
	3.669	3365	2.94	0.797			
SPc (buckled)	1.411	8751	1.26	0.158	1.351	9140 ^f	0.4
	1.447	8531	0.981	0.178			
	3.425	3604	2.78	0.749	2.911	4240 ^f	0.9
	3.645	3387	3.00	0.794			
Me ₅ SPc					1.336	9240 ^f	
					2.946	4190 ^f	

^a PPP SCF LCAO CI calculations described in text. Calculated transitions are singlet-singlet. ^b Calculated by the approximation $d f = 4.33 \times 10^{-9} \int \epsilon d\bar{\nu} \approx 4.33 \times 10^{-9} \epsilon_{\max} \Delta\bar{\nu}_{1/2}$. ^c Zinc complex in benzene + 2% dimethyl sulfoxide. ^d From ref 48c. ^e Zinc complex in benzene. ^f Benzene solution.

addition to the characteristic magnetic shielding properties which $4n + 2 \pi$ electron aromatic annulenes exhibit, such systems also display distinctive optical spectra.⁴⁷ It was of interest to further investigate the electronic structure of the SPc ligand via the electronic spectrum, and to compare these results with those for the four-subunit analogue, Pc. The solution optical spectra of SPcUO₂ and Me₅SPcUO₂ are presented in Figure 6 along with those of PcZn and Me₄PcZn for comparison. Data are summarized in Table IV. The optical spectra of metal and metal-free phthalocyanines are now reasonably well understood⁴⁸ (much of the understanding has been transferred from exhaustive theoretical and experimental studies on porphyrins⁴⁹) and it is generally agreed that the intense absorption at ca. 6700 Å corresponds to a π - π^* transition polarized in the plane of the ring. This absorption represents, in a one-electron picture, an excitation from the highest occupied molecular orbital (a_{1u} in the D_{4h} point group) to the lowest unoccupied molecular orbital (e_g) and is completely analogous to the α (or Q) band of metalloporphyrins. The high-energy shoulder at ca. 6100 Å is believed to be vibronic in origin (0-1) and is analogous to the β band of metalloporphyrins. In the case of the metal-free ligand, PcH₂, the lower D_{2h} symmetry gives rise to splitting of the Q band into Q_x and Q_y components.^{48b} In the ultraviolet, metal and metal-free phthalocyanines exhibit an intense absorption at ca. 3400 Å which is a π - π^* transition also to the e_g level ($a_{2u} \rightarrow e_g$ in D_{4h}). This transition is analogous to the Soret (B) band of porphyrins. It should be noted that the Q and B bands are not strictly one-electron transitions, but are mixed by two-electron terms, i.e., configuration interaction. This mixing is probably not as extensive in phthalocyanines as in porphyrins.^{48,49} The 3400-Å phthalocyanine band is somewhat broader than porphyrin Soret transitions and this breadth is attributed to underlying n - π^* transitions involving the peripheral imino nitrogens.^{48,49b} The attachment of the four methyl groups in Me₄PcZn leads to slight shifts of +43 and +146 Å in the long- and short-wavelength absorptions, respectively (Table IV). The spectra of the five-subunit macrocycles are considerably different from those of the PcM derivatives (Figure 6). SPcUO₂ exhibits a strong, broad absorption at rather long wavelength,⁶ 9140 Å ($\epsilon 6.67 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$) with a pronounced shoulder at ca.

8100 Å, and a strong, short-wavelength transition at 4240 Å ($\epsilon 5.02 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$). Methyl substitution causes small displacements of +100 and -50 Å, respectively, in the above maxima. The appearance of the uranyl supermacrocycle electronic spectra is unlike any other uranyl complexes.⁵⁰ It will be seen that these unusual spectra can be most reasonably and consistently interpreted in terms of phthalocyanine-like, largely ligand-centered transitions.

The electronic structure of the SPc macrocycle and its relationship to the Pc macrocycle were examined by π electron molecular orbital calculations at the Pariser-Parr-Pople (PPP) LCAO SCF CI level of approximation.^{47b,51,52} Such calculations with configuration interaction included have provided accurate insight into the origin of porphyrin spectral transitions.^{49a} Furthermore, experience ensures that reasonably reliable semiempirical parametrization is available. For the present study, the parameters of McHugh, Gouterman, and Weiss⁵³ were employed, i.e., atomic valence state ionization potentials of 11.22 (carbon), 20.04 (central nitrogen), and 14.51 eV (imino nitrogen) together with atomic valence state electron affinities of 0.62 (carbon), 6.73 (central nitrogen), and 1.20 eV (imino nitrogen). Resonance integrals were taken to be -2.72 (β_{CN}) and -2.42 eV (β_{cc}).^{52b} Two-center electron repulsion integrals were computed by the method of Mataga and Nishimoto,⁵⁴ and configuration interaction procedures utilized the monoexcited model.⁵² Calculations were performed for planar Pc²⁻ and SPc²⁻ using standard phthalocyanine structural data,^{11,25-29} and also for buckled SPc²⁻ using the SPcUO₂ x-ray data.⁴ In the latter case resonance integrals were adjusted for reduced interaction in cases where the dihedral angle between overlapping $p\pi$ orbitals was not 0°. This was accomplished using the SPcUO₂ metrical data⁴ together with the relationship for β as a function of dihedral angle. θ , given by⁵⁵

$$\beta(\theta) = k\beta$$

where $k = 0.970 \cos \theta - 0.150 \cos \theta(1 - \cos \theta)$.

The PPP calculations for planar Pc²⁻ and SPc²⁻ reveal several noteworthy similarities. Both macrocycles have singly degenerate molecular orbitals as the two highest levels of occupation, and an essentially degenerate pair of orbitals as the

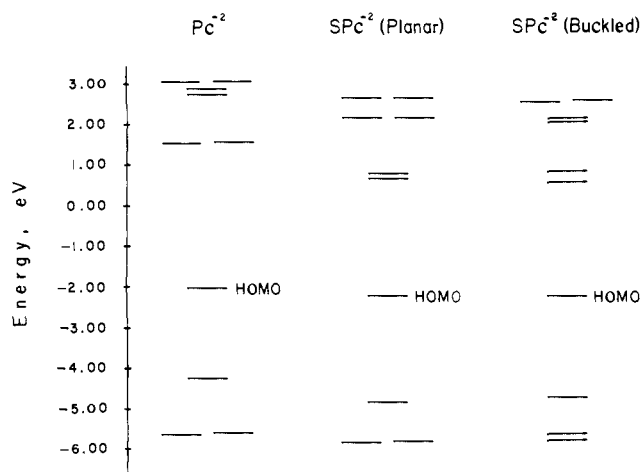


Figure 7. Partial molecular orbital energy level diagram for phthalocyanine and superphthalocyanine macrocycles (HOMO = highest occupied molecular orbital).

lowest unoccupied level.⁵⁶ This relationship is shown in Figure 7 and data are set out in Table IV. The analogous Pc and SPc molecular orbitals have similar compositions of atomic orbitals. As mentioned above, in a one-electron description the Q band in a phthalocyanine corresponds to a transition from the highest occupied molecular orbital to the doubly degenerate, lowest unoccupied molecular orbital. For Pc^{2-} the present PPP calculations reveal this transition to be at 6960 Å, which is in good agreement with experiment (6700 Å) and demonstrates the reliability of the parametrization. Turning now to the case of planar SPc^{2-} , the analogous highest occupied to lowest unoccupied MO transition is calculated to be at substantially longer wavelength, 8250 Å. This is in the correct direction but falls somewhat short of the experimental value of 9140 Å. Oscillator strengths for these transitions were calculated by both the dipole length and dipole velocity methods.^{49a,52b,57} As can be seen in Table IV, the long-wavelength Pc^{2-} and SPc^{2-} transitions are predicted to be rather intense and comparable in oscillator strength, as observed. Similarly, in the short-wavelength region, proceeding from Pc^{2-} to SPc^{2-} is calculated to displace the absorption maximum to longer wavelength, i.e., 3310 to 3390 Å, which is the direction observed. Again the oscillator strengths are large (the largest in both macrocycles) and comparable, as detected experimentally. These computational results reveal a marked congruence between the transitions giving rise to planar phthalocyanine and planar superphthalocyanine optical spectra. Further refinement of the molecular orbital calculations was next undertaken by simulating the buckled SPc^{2-} macrocycle with a planar SPc^{2-} having appropriately adjusted resonance integrals (vide supra). Since the PPP method is restricted to planar systems^{47b,51} (or simple deviations from planarity⁵⁸), and since β adjustment does not take into account changes in the σ bond framework and in the two-center repulsion integrals on buckling, this is admittedly a pragmatic, qualitative approach. It is found by this approach that the macrocycle distortion leads to slight energy level shifts and to an increased splitting of the nearly degenerate (in the planar structure) lowest unoccupied molecular orbitals (Figure 7). Consequently, two long-wavelength transitions are now anticipated at 8750 and 8531 Å, which is closer to the actual maximum at 9140 Å than calculated for the planar structure. The separation between the calculated bands may explain the experimentally observed shoulder at 8100 Å (Figure 6). Such an explanation is completely analogous to the Q band splitting observed on lowering phthalocyanine symmetry from PcM to PcH_2 .^{48b} In the short-wavelength region, buckled SPcUO_2 is predicted to

have transitions at 3600 and 3390 Å. The experimentally observed transitions at 4240, 3455, and 3000 Å may reflect both the predicted splitting of the Soret-like band (probably the former two) as well as $n-\pi^*$ ^{48,49b} and/or ligand-to-metal charge transfer transitions.⁵⁰

The molecular orbital calculations indicate that the total π electron energy⁵¹ for planar SPc^{2-} is -3376 eV and for buckled SPc^{2-} is -3374 eV. The observed destabilization on buckling is in accord with the previously discussed ring current results, which suggest impairment of π electron delocalization. However, since the calculated loss in stability represents the difference between two rather large numbers and since the computational adjustments to mimic buckling were only approximate, this result should be regarded as approximate at best.

Conclusions

It is apparent from the results of this investigation that the reported five-subunit analogues of phthalocyanine, SPc and Me_5SPc , are chemically rather fragile and that complexation by the uranyl ion plays a crucial role in the formation and stabilization of these macrocycles. Attempts to dislodge the uranyl ion from SPcUO_2 or $\text{Me}_5\text{SPcUO}_2$ invariably result in demetalation accompanied by ring contraction to produce the corresponding phthalocyanine or metallophthalocyanine species. The molecular structure of SPcUO_2 in the solid state is severely distorted from planarity, and NMR studies suggest a similar situation in solution. It appears that the inherent strain evidenced by such a molecular structure and the accompanying impairment of electronic delocalization, as detected in the NMR ring current analysis, lead to significant destabilization of the molecule with respect to phthalocyanine and metallophthalocyanine products. The electronic structure and the unusual optical spectrum associated with the SPc macrocycle are understandable in terms of what is known about phthalocyanine electronic structures and spectra. Again the effect of the ligand buckling is evident.

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References and Notes

- (1) (a) Fellow of the Alfred P. Sloan Foundation; (b) Camille and Henry Dreyfus Teacher-Scholar.
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Nitric Oxide Reactivity with Manganese Complexes Containing Linear Pentadentate Ligands

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Abstract: Manganese(II) and manganese(III) complexes incorporating linear pentadentate ligands derived from various salicylaldehydes and triamines have been allowed to react with nitric oxide. The extent of nitric oxide reactivity with the manganese(II) precursors is a function of both the substituent on the salicylaldehyde ring and the central nitrogen donor. Bulky groups on the central nitrogen donor and electron-donating substituents on the salicylaldehyde portion produce complexes which have little affinity for NO. For those manganese(II) complexes which react with NO, reduction to formally manganese(I) appears to occur and in several cases isolable materials of formula $[\text{MnL}(\text{NO})]^0$ are produced where L = pentadentate ligand. All the corresponding manganese(III) complexes, $[\text{MnLX}]^0$, where X = I^- , NO_2^- , and NCS^- , readily react in a nonreversible manner with NO to yield ESR-active solutions characteristic of manganese(II). Magnetic susceptibility measurements on these solutions suggest that the manganese(II) is high spin.

Introduction

The reactivity of nitric oxide with iron and manganese porphyrin complexes shows a pronounced ligand and metal oxidation state dependence.¹ The interaction of nitric oxide with a few ferric hemoproteins is reported to be accompanied by the transfer of an electron from NO to the ferric heme iron. Reducibility was demonstrated to be easier with hemoglobin

than myoglobin. Ferric cytochrome peroxidase and horseradish peroxidase were reported, however, to not be reduced by NO but instead formed low-spin iron(III) adducts. Nitric oxide, on the other hand, has been recently shown² to reversibly react with $\text{Fe}^{\text{III}}(\text{TPP})\text{Cl}$ to form diamagnetic $\text{Fe}^{\text{II}}(\text{TPP})(\text{Cl})(\text{NO})$ where TPP represents the tetraphenylporphyrinato dianionic ligand. Previous work³ by other researchers had formulated