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NORTHWESTERN UNIV EVANSTON IL DEPT OF CHEMISTRY  
SYNTHESIS AND CHARACTERIZATION OF OCTAALKYL METALLO AND METAL-F--ETC(U)  
MAY 81 E A CUELLAR, T J MARKS

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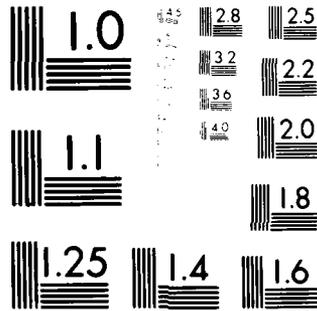
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Synthesis and Characterization of Octaalkyl Metallo and Metal-Free  
Phthalocyanines and Decaalkyl Uranyl Superphthalocyanines

Edward A. Cuellar and Tobin J. Marks

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have been characterized by a variety of chemical and physicochemical methods. Quantitative determination of the solubilities of substituted and unsubstituted phthalocyanine and superphthalocyanine complexes in both 1,2,4-trichlorobenzene and toluene demonstrate decreasing solubility in the order  $(4,5\text{-Bu}_2)_5\text{SPcUO}_2 > (4\text{-Me})_5\text{SPcUO}_2 > (4,5\text{-Me}_2)_5\text{SPcUO}_2 \sim \text{SPcUO}_2 > (4\text{-Me})_4\text{PcH}_2 > \text{Ni}(4,5\text{-Bu}_2)\text{Pc} > \text{Ni}(4,5\text{-Me}_2)_4\text{Pc} \sim \text{NiPc}$ . Attempts to displace the uranyl ion from  $(4,5\text{-R}_2)_5\text{SPcUO}_2$  with acids or  $\text{Cu}(\text{OAc})_2$  lead to the formation of  $(4,5\text{-R}_2)_4\text{PcH}_2$  or  $\text{Cu}(4,5\text{-R}_2)_4\text{Pc}$ , respectively.

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Department of Chemistry  
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SYNTHESIS AND CHARACTERIZATION OF OCTAALKYL METALLO AND METAL-FREE  
PHTHALOCYANINES AND DECAALKYL URANYL SUPERPHTHALOCYANINES.<sup>1</sup>

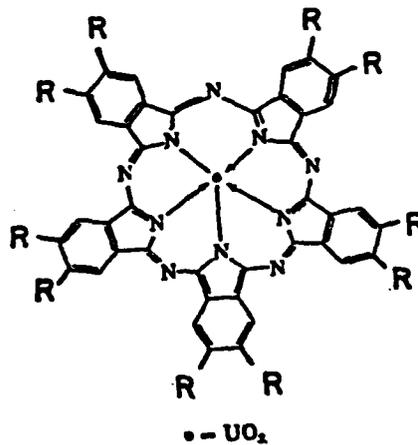
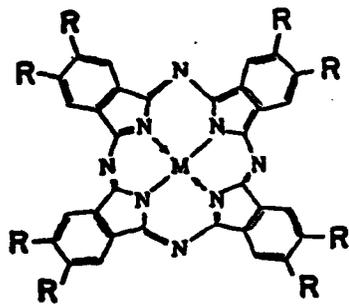
by Edward A. Cuellar and Tobin J. Marks\*

ABSTRACT

A straightforward, efficient, and generalizable synthesis of symmetrically substituted 2,3,9,10,16,17,23,24-octaalkyl phthalocyanines and 2,3,9,10,16,17,23,24,30,31-decaalkyl uranyl superphthalocyanines from *o*-dialkyl benzenes is described. For phthalocyanines, the approach is illustrated for methyl and *n*-butyl substituents, and both metal-free and nickel complexes are reported. Uranyl superphthalocyanines have been prepared with methyl and *n*-butyl substituents. The new complexes have been characterized by a variety of chemical and physicochemical methods. Quantitative determination of the solubilities of substituted and unsubstituted phthalocyanine and superphthalocyanine complexes in both 1,2,4-trichlorobenzene and toluene demonstrates decreasing solubility in the order  $(4,5\text{-Bu}_2)_5\text{SPcUO}_2 > (4\text{-Me})_5\text{SPcUO}_2 > (4,5\text{-Me}_2)_5\text{SPcUO}_2 > \text{SPcUO}_2 > (4\text{-Me})_4\text{PcH}_2 > \text{Ni}(4,5\text{-Bu}_2)\text{Pc} > \text{Ni}(4,5\text{-Me}_2)_4\text{Pc} \uparrow \text{NiPc}$ . Attempts to displace the uranyl ion from  $(4,5\text{-R}_2)_5\text{SPcUO}_2$  with acids or  $\text{Cu}(\text{OAc})_2$  lead to the formation of  $(4,5\text{-R}_2)_4\text{PcH}_2$  or  $\text{Cu}(4,5\text{-R}_2)_4\text{Pc}$ , respectively.

INTRODUCTION

Metallophthalocyanines (MPC, 1) and metal-free phthalocyanine (PCH<sub>2</sub>) comprise a remarkably robust and versatile class of chemical compounds.<sup>2-4</sup> They are of enormous technological importance for the manufacture of blue and green pigments.<sup>2,4,5</sup> Other areas of current interest include applications as catalysts,<sup>4,6</sup> electrocatalysts,<sup>2,7</sup> photoconductors,<sup>4,8</sup> photosensitizers,<sup>4,9</sup> electrode<sup>10</sup> and photo-



1 R = H, M = H<sub>2</sub>, metal (MPC)

2 R = CH<sub>3</sub>, M = H<sub>2</sub>,

metal (M(4,5-Me<sub>2</sub>)<sub>4</sub>Pc)

3 R = n-C<sub>4</sub>H<sub>9</sub>, M = H<sub>2</sub>,

metal (M(4,5-Bu<sub>2</sub>)<sub>4</sub>Pc)

4 R = H

5 R = CH<sub>3</sub>

6 R = n-C<sub>4</sub>H<sub>9</sub>

voltaic<sup>11,12</sup> materials, heme<sup>2,13</sup> and dismutase<sup>14</sup> models, peptide synthesis reagents,<sup>15</sup> modified supports for gas-solid chromatography,<sup>16</sup> and precursors for new low-dimensional mixed-valence materials.<sup>17,18</sup> Two areas of phthalocyanine chemistry are of interest in this Laboratory. The first area concerns the design of partially oxidized molecular<sup>17,19</sup> and macromolecular<sup>17,20</sup> solids with metal-like electrical properties. The second area involves large metal ion-centered template<sup>21</sup> reactions, such as that in which the uranyl ion serves as a framework for the selective condensation of phthalonitrile to produce the five-subunit uranyl "superphthalocyanine" (SPc), 4.<sup>22-24</sup> In both areas there is a need for efficient and flexible synthetic approaches to polyalkyl phthalocyanines and superphthalocyanines. For "molecular metals", alkyl-functionalized phthalocyanines would allow exploration of oxidation state and charge transport characteristics in systems with sequentially modified ionization potentials and donor-donor, donor-acceptor spatial relationships. In the "superphthalocyanine" studies, functionalization offers a route to probing the sensitivity of the cyclization process to substituent effects, and of modifying the chemical and spectral properties of the resulting metallomacrocycles. Needless to say, in both areas, general routes to alkyl functionalization would lead to more soluble complexes and would thus

facilitate crystallization, purification, and solution spectroscopy, as well as numerous other avenues of experimentation.

We report here a straightforward synthetic approach to 2,3,9,10,16-17,23,24-octaalkylphthalocyanines (2,3) and 2,3,9,10,16,17,23,24,30-31-decaalkyl uranyl superphthalocyanines (5,6), and some of the interesting properties of these new macrocycles.<sup>25</sup> Although we illustrate here with methyl and *n*-butyl substituents, the generality of the approach should be evident.

#### EXPERIMENTAL

Anhydrous uranyl chloride<sup>26</sup> was handled under an atmosphere of prepurified nitrogen by Schlenk methods<sup>27</sup> or in a Vacuum Atmospheres Corp. HE-43-2 "Dri-Lab" glove box fitted with a HE-193-1 "Dri-Train" atmosphere recirculating unit. Quinoline (Eastman Kodak Co.) and *N,N*-dimethylformamide (DMF, Mallinckrodt, Inc.) were predried over KOH, vacuum distilled from BaO, and stored over Davison 4A molecular sieves. Alternatively, the quinoline can be passed over silica gel and 4A molecular sieves immediately prior to use. The dry solvents were handled under prepurified nitrogen at all times. Routine <sup>1</sup>H NMR spectra were recorded on Perkin-Elmer R-20B (60 MHz, CW), Varian CFT-20 (80 MHz, FT) or JEOL FX-90Q (90 MHz, FT, double-precision) spectrometers. High-field <sup>1</sup>H NMR spectra were recorded on a Bruker HFX-270 (270 MHz, FT) at the High Field NMR Facility, Yale University. Infrared spectra were recorded on Perkin-Elmer 267 or 283 spectrometers as Nujol mulls or KBr pellets. Electronic spectra were recorded on a Cary 17D spectrophotometer. Mass spectra were obtained on a Kratos MS-50 mass spectrometer

at the Midwest Center for Mass Spectrometry, University of Nebraska. Elemental analyses were performed by Micro-Tech Laboratories, Inc., Skokie, IL, or by Miss H. Beck, Northwestern University Analytical Services Laboratory. Melting points are uncorrected.

Submilligram samples (0.03-0.7 mg) for extinction coefficient measurements were weighed on a Cahn ratio electrobalance, Model G. The samples were dissolved in 100-250 mL of solvent with heating and then allowed to cool. For the solubility measurements, a saturated solution was prepared as above, gravity filtered, and diluted. The concentration was found from the absorbance and extinction coefficient using Beer's law.

Synthesis. (A) 4,5-Dibromo-1,2-dibutylbenzene. A 2000 mL three-neck flask was fitted with a mechanical stirrer, a 500 mL dropping funnel, a thermometer, and a gas inlet connected to a water trap for removing evolved HBr. The flask was charged with 506 g (2.66 moles) of o-dibutylbenzene,<sup>28</sup> 500 mL of dry CH<sub>2</sub>Cl<sub>2</sub>, 18 g of iron filings, a spatula tip quantity of I<sub>2</sub>, and was then brought to 0°C in an ice-salt bath. A 290 mL (5.66 moles) quantity of bromine was then added via the dropping funnel at a rate to keep the temperature of the reaction mixture below 5°C. The addition requires approximately 4 h. The reaction mixture was then stirred at 0°C for an additional 18 h, and 6 h more at approximately 20°C. The reaction mixture was then poured into 1000 mL of aqueous 5% NaOH/sodium bisulfite. The organic fraction was isolated, washed with water (2 x 1000 mL), concentrated, and distilled. The fraction boiling from 128-154°C (0.025 mm), 638 g, was collected as a partially solidified oil. This material was recrystallized three times

from 800 mL of acetone at  $-10^{\circ}\text{C}$ , yielding 328 g of colorless needles. The combined filtrates from above were reduced in volume and cooled to  $-20^{\circ}\text{C}$ . Two additional recrystallizations of the material so obtained yielded an additional 97 g of product. Total yield 415 g (45%), mp  $34-35^{\circ}\text{C}$ .

Anal. Calcd for  $\text{C}_{14}\text{H}_{20}\text{Br}_2$ : C, 48.30; H, 5.79. Found: C, 48.19; H, 5.79.

Infrared spectrum (KBr pellet,  $\text{cm}^{-1}$ ): 2950vs, 2925vs, 2870s, 2855s, 1462s, 1378m, 1355m, 13212, 1296w, 1249w, 1196w, 1126m, 908m, 881m, 745w, 728w, 652m.

$^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  7.23 (s, 1H);  $\delta$  2.48 (t, 2H);  $\delta$  1.42 (m, 4H);  $\delta$  0.91 (m, 3H).

(B) 4,5-Dibutyl-1,2-dicyanobenzene. A 2000 mL three-neck flask was fitted with a mechanical stirrer and charged with 200 g (0.57 moles) of 4,5-dibromo-1,2-dibutylbenzene, 130 g (1.45 moles) of CuCN, and 1200 mL of DMF. The mixture was brought to reflux and kept there until the mixture began to turn dark green (ca. 55 min from reflux). The mixture was next cooled, poured into 1200 mL of aqueous 7.5%  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ , and extracted with hexane (2 x 1000 mL). The combined extracts were washed with water (2 x 1000 mL), dried over  $\text{Na}_2\text{SO}_4$ , reduced in volume, and cooled at  $-10^{\circ}\text{C}$  until product crystallization ceased (approximately 45 g), or green "clumps" began forming. Cooling at lower temperature caused impurities to precipitate. The supernatant was next filtered off and the hexane removed in vacuo, leaving 91 g of a greenish oil. Repeating the reaction as above with this oil yielded an additional 47 g

of product; a third reaction, an additional 13 g. The combined product, 105 g, was then recrystallized three times from pentane at  $-10^{\circ}\text{C}$ , yielding 69 g (50%) of large, colorless needles, mp  $51-52^{\circ}\text{C}$ . The purpose of relatively short reaction times and recycling incompletely reacted components is to prevent large amounts of the product from being converted into  $\text{Cu}(4,5\text{-Bu}_2)_4\text{Pc}$ , which is responsible for the blue color that forms after approximately 1 h of refluxing.

Anal. Calcd for  $\text{C}_{16}\text{H}_{20}\text{N}_2$ : C, 79.96; H, 8.39; N, 11.66. Found: C, 79.97; H, 8.41; N, 11.61.

Infrared spectrum (KBr pellet,  $\text{cm}^{-1}$ ): 2950vs, 2930vs, 2870vs, 2235s, 1598m, 1492m, 1467s, 1379m, 1246m, 1108m, 939m, 912m, 882m, 741m, 534m.

$^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  7.53 (s, 1H);  $\delta$  2.71 (t, 2H);  $\delta$  1.52 (m, 4H); 0.97 (m, 3H).

(C) 2,3,9,10,16,17,23,24-Octamethylphthalocyanine,  $(4,5\text{-Me}_2)_4\text{PcH}_2$ . Following the general procedure of Linstead *et al.*,<sup>29</sup> a 250 mL flask was charged with 10 g (64 mmol) of 4,5-dimethyl-1,2-dicyanobenzene,<sup>31</sup> 1.8 g (80 mmol) of sodium metal, 100 mL of 1-pentanol (dried over molecular sieves), and brought to reflux for 20 min. The hot mixture was next filtered in a Buchner funnel, leaving a purple solid which was washed with absolute ethanol. A suspension of this material in 80 mL of 5% aqueous HCl was refluxed for 15 min. The crude product was then collected by filtration, washed with water, methanol, hexane, and acetone. The resulting blue-green powder was dried under high vacuum for 4 h, yielding 2.0 g (20%) product. It can be made analytically pure by dissolving in concentrated  $\text{H}_2\text{SO}_4$  and filtering through a sintered-glass funnel into ice-water.

Anal. Calcd for  $(C_{10}H_8N_2)_4H_2$ : C, 76.65; H, 5.47; N, 17.88. Found: C, 77.04; H, 5.76; N, 17.72.

Infrared spectrum (Nujol mull,  $cm^{-1}$ ): 3285w, 1614w, 1500m, 1330w, 1312m, 1298w, 1183w, 1171w, 1138w, 1103s, 1028s, 1011s, 1000w, 987w, 880m, 840m, 830w, 782w, 758s, 730m, 708m, 699s, 685w.

(D) 2,3,9,10,16,17,23,24-Octabutylphthalocyanine, (4,5-Bu<sub>2</sub>)<sub>4</sub>PcH<sub>2</sub>.

The aforementioned procedure for the synthesis and purification of  $(4,5-Me_2)_4PcH_2$  was followed with 4,5-dibutyl-1,2-dicyanobenzene to produce the desired product in 38% yield.

Anal. Calcd for  $(C_{14}H_{20}N_2)_4H_2$ : C, 79.79; H, 8.58; N, 11.63. Found: C, 80.16; H, 8.41; N, 11.56.

Infrared spectrum (Nujol mull,  $cm^{-1}$ ): 3293m, 1617w, 1499m, 1348w, 1336w, 1320m, 1300w, 1170w, 1100s, 1006s, 932w, 899w, 875w, 848w, 840w, 749s, 714w, 701m.

<sup>1</sup>H NMR (toluene-d<sub>8</sub>, 100°C): δ9.47(2, 8H); δ3.13(t, 16H); δ1.57(m, 32H); δ1.07(t, 24H). The NH signal was not located.

(E) [2,3,9,10,16,17,23,24-Octamethylphthalocyaninato(2-)]nickel(II), Ni(4,5-Me<sub>2</sub>)<sub>4</sub>Pc.<sup>32</sup> A 100 mL one-neck flask was fitted with a magnetic stirring bar and charged with a finely ground mixture of 4,5-dimethyl-1,2-dicyanobenzene<sup>31</sup> (2.0 g, 12.8 mmol), NiCl<sub>2</sub>·6H<sub>2</sub>O (0.76 g, 3.2 mmol), and 5 mL of quinoline. The reaction mixture was stirred at 200-230°C for approximately 2.5 h, cooled, diluted with methanol, filtered, and then washed successively with more methanol, water, hexane, and acetone. Vacuum drying of the remaining dark blue-green powder for several hours left 2.2 g (57%) of product. The product can be further purified by

dissolving in  $\text{H}_2\text{SO}_4$  and filtering into ice-water. The complex can be sublimed at  $425^\circ\text{C}$  ( $10^{-3}$  torr) in low yield.

Anal. (sublimed sample) Calcd for  $(\text{C}_{10}\text{H}_8\text{N}_2)_4\text{Ni}$ : C, 70.30; H, 4.72; N, 16.40. Found: C, 70.17; H, 4.53; N, 16.36.

Infrared spectrum (Nujol mull,  $\text{cm}^{-1}$ ): 1625m, 1537s, 1470s, 1415s, 1355w, 1315s, 1240w, 1205w, 1180m, 1140w, 1105vs, 1045m, 1020w, 955w, 875s, 815w, 752s, 735m, 720m.

(F) [2,3,9,10,16,17,23,24-Octabutylphthalocyaninato(2-)]nickel(II),  $\text{Ni}(4,5\text{-Bu}_2)_4\text{Pc}$ . The aforementioned procedure for the synthesis and purification of  $\text{Ni}(4,5\text{-Me}_2)_4\text{Pc}$  was followed with 4,5-dibutyl-1,2-dicyanobenzene to produce the desired product in 26% yield. The complex decomposes upon attempted sublimation at  $425^\circ\text{C}$  ( $10^{-3}$  torr).

Anal. Calcd for  $(\text{C}_{14}\text{H}_{20}\text{N}_2)_4\text{Ni}$ : C, 75.36, H, 7.91; N, 10.98. Found: C, 75.10; H, 7.56; N, 11.10.

Infrared spectrum (Nujol mull,  $\text{cm}^{-1}$ ): 1615w, 1530m, 1498w, 1428m, 1349w, 1330w, 1300w, 1278w, 1250w, 1216w, 1168w, 1105s, 1071w, 1044w, 1007w, 960w, 938w, 900w, 882w, 878w, 831m, 752s, 741m, 730m, 638w.

$^1\text{H}$  NMR (toluene- $d_8$ ,  $100^\circ\text{C}$ ):  $\delta$ 9.39(s, 8H);  $\delta$ 3.13(t, 16H);  $\delta$ 1.57(m, 32H);  $\delta$ 1.07(m, 24H).

(G) [2,3,9,10,16,17,23,24,30,31-Decamethylsuperphthalocyaninato(2-)]-uranium(VI),  $(4,5\text{-Me}_2)_5\text{SPcUO}_2$ . In a glove box, a 100 mL two-neck flask fitted with a magnetic stirring bar was charged with 6.3 g (18 mmol) of anhydrous  $\text{UO}_2\text{Cl}_2$  and 15 g (96 mmol) of 4,5-dimethyl-1,2-dicyanobenzene<sup>31</sup> (sublimed). The flask was next removed to a fume hood and 3.0 mL of dry DMF was introduced by syringe under a vigorous nitrogen flush. The reac-

tion mixture was heated at 175°C with stirring for 45 min, at which point an additional 6 mL of DMF was introduced to suppress sublimation of the dinitrile. The solution was dark-green within 80 min, at which point the temperature was raised to 193°C. The reaction mixture turned blue-black within a few minutes, and the reaction was halted. The reaction mixture was next filtered hot, and the solid residue washed with methanol, water, and acetone, leaving 0.8 g of a dark blue solid. Soxhlet extraction of this material for 1 day with benzene yielded mostly unreacted dinitrile and other impurities. Extraction for another day with  $\text{CHCl}_3$  yielded 10 mg of a dark blue microcrystalline product which was < 1%  $(4,5\text{-Me}_2)_4\text{PcH}_2$  by spectrophotometry. Extraction for an additional 5 days with toluene yielded another 60 mg of product. The total yield of  $(4,5\text{-Me}_2)_5\text{SPcUO}_2$  was 70 mg (0.36%). Further extraction of the crude reaction mixture led to significant contamination of the product.

Anal. Calcd for  $(\text{C}_8\text{H}_8\text{N}_2)_5\text{UO}_2$ : C, 57.14; H, 3.84; N, 13.33. Found: C, 54.95; H, 4.25; N, 12.89.

Infrared spectrum (Nujol mull,  $\text{cm}^{-1}$ ): 1615w, 1508w, 1410w, 1315s, 1108w, 1060s, 1021w, 934s, 880w, 838w, 758w, 741m, 729m, 721m, 716m, 698m.

NMR (99.96%  $\text{C}_6\text{D}_5\text{Cl}^{33}$ ):  $\delta$  8.81(s, 10H), 2.60(s, 30H).

Mass spectrum: strong parent ion at m/e 1050.

(H) [2,3,9,10,16,17,23,24,30,31-Decabutylsuperphthalocyaninato(2-)]-uranium(VI),  $(4,5\text{-Bu}_2)_5\text{SPcUO}_2$ . A mixture of 10.1 g (42.0 mmol) of 4,5-dibutyl,2-dicyanobenzene, 2.8 g (8.2 mmole) of anhydrous  $\text{UO}_2\text{Cl}_2$ , and 9.8 mL of dry quinoline was heated under nitrogen with stirring at 170°C. The mixture turned deep green within 8 min. After 40 min, the

reaction mixture was allowed to cool, diluted with 75 mL of methanol, and filtered. The crude product was next washed with more methanol (2 x 25 mL), water (3 x 50 mL), and dried under high vacuum for 1.5 h, leaving 0.75 g of a fluffy, dark green powder. Electronic spectrophotometry indicated the ratio of  $(4,5\text{-Bu}_2)_5\text{SPcUO}_2:(4,5\text{-Bu}_2)_4\text{PcH}_2$  to be approximately 7:3. Soxhlet extraction of this material with pentane for 5 days yielded 0.30 g (2.5%) of a dark green microcrystalline powder. Larger crystals can be grown by slow evaporation of pentane or benzene solutions.

Anal. Calcd for  $(\text{C}_{14}\text{H}_{20}\text{N}_2)_5\text{UO}_2$ : C, 65.29; H, 6.85; N, 9.52. Found: C, 64.70; H, 6.30; N, 9.55.

Infrared spectrum (KBr pellet,  $\text{cm}^{-1}$ ): 2955s, 2935s, 2861m, 1505m, 1456m, 1405m, 1332s, 1319s, 1068vs, 933s, 720s.

$^1\text{H}$  NMR (toluene- $d_6$ ):  $\delta$ 9.13(s, 10H);  $\delta$ 2.86(t, 20H);  $\delta$ 1.50(m, 40H);  $\delta$ 0.97(m, 30H).

#### RESULTS AND DISCUSSION

Synthesis. Symmetrically substituted 2,3,9,10,16,17,23,24-uranyl octaalkylphthalocyanines and 2,3,9,10,16,17,23,24,30,31-decaalkylsuperphthalocyanines can be readily prepared from easily obtainable 4,5-dialkyl-1,2-dicyanobenzenes. The octaalkylated phthalocyanines may also be obtained by reacting the corresponding  $(4,5\text{-R}_2)_5\text{SPcUO}_2$  complexes with either acid (e.g.,  $\text{CH}_3\text{COOH}$  in chlorobenzene) to generate the metal-free complex or a metal salt (e.g.,  $\text{Cu}(\text{OAc})_2$  in DMF) to generate the metalated complex, analogous to the reactions of  $\text{SPcUO}_2$ .<sup>23</sup> These transformations are summarized in Scheme I. There is no evidence for the free five-membered ligand,  $(4,5\text{-R}_2)_5\text{SPcH}_2$ , or another metal derivative

thereof, in this chemistry. Complementary but different synthetic routes to other 2,3,9,10,16,17,23,24-octasubstituted phthalocyanines, where R = phenyl<sup>34</sup> or  $-\text{CH}_2-\text{O}-\text{R}'$ ,<sup>35</sup> have appeared recently.

NMR Studies. <sup>1</sup>H NMR data for the compounds prepared in the present study are compared to those of ZnPc, Zn(4-Me)<sub>4</sub>Pc, PcLi<sub>2</sub>, SPcUO<sub>2</sub>, (4-Me)<sub>5</sub>SPcUO<sub>2</sub>, and (4,5-CH<sub>2</sub>OC<sub>2</sub>H<sub>4</sub>OC<sub>2</sub>H<sub>5</sub>)<sub>4</sub>PcH<sub>2</sub> in Table I. In all cases, the benzo protons of a specific superphthalocyanine complex are shielded in relation to an analogous phthalocyanine complex. An analysis of the nuclear magnetic shielding in unsubstituted, planar phthalocyanines and superphthalocyanines in terms of diamagnetic ring current shifts predicts the opposite trend.<sup>23a</sup> Therefore, the smaller downfield ring current shift in the SPc ligand with respect to the Pc ligand is logically attributed<sup>23a</sup> to decreased  $\pi$  electron delocalization in the SPc macrocycle due to severe buckling<sup>22</sup> of the ring (Figure 1). This result suggests similar structures for the alkyl-substituted superphthalocyanines, although the <sup>1</sup>H resonance positions of (4,5-Bu<sub>2</sub>)<sub>5</sub>SPcUO<sub>2</sub> appear to be somewhat to lower field than expected from the <sup>1</sup>H resonance positions of the other Pc and SPc complexes containing electron donating substituents.

The severe buckling of the SPc ligand in SPcUO<sub>2</sub> (Figure 1) suggests that it may be conformationally dynamic.<sup>23a</sup> Unfortunately, we have been unable to provide further information with the decaalkyl superphthalocyanines. Increasing line broadening of the benzo resonance is observed at successively lower temperatures for a sample of (4,5-Bu<sub>2</sub>)<sub>5</sub>SPcUO<sub>2</sub> in toluene-d<sub>6</sub>. However, the slow-exchange limit

(assuming that this line broadening is due to a slowing dynamic interchange of the isoindoline environments) could not be reached at  $-90^{\circ}\text{C}/270\text{ MHz}$ .

Optical Spectra. Optical data for the complexes synthesized in this study are presented in Table II. Representative electronic spectra are shown in Figure 2. The unusual optical spectrum associated with the SPc macrocycle is understandable in terms of what is known about phthalocyanine<sup>36,37</sup> and porphyrin<sup>36,38</sup> electronic structures and spectra. The results of SCF CI molecular orbital calculations at the Pariser-Parr-Pople (PPP)  $\pi$ -electron level indicate that both planar  $\text{Pc}^{2-}$  and  $\text{SPc}^{2-}$  possess a singly degenerate highest occupied molecular orbital (HOMO) and an essentially doubly degenerate lowest unoccupied molecular orbital (LUMO).<sup>23a</sup> An intense, low-energy absorption is expected for both ligands corresponding to a  $\pi \rightarrow \pi^*$  transition analogous to the  $\alpha$  (or Q) band of metalloporphyrins.<sup>36,38</sup> The observation of two intense bands in  $\text{PcH}_2$  located at 665 and 698 nm (the weaker bands at 602 and 638 nm are believed to be vibronic in origin) and what appear to be two intense transitions in  $\text{SPcUO}_2$  located at 810 and 914 nm can then be explained by a lifting of the degeneracy of the LUMO due to a lowering of the molecular symmetry from  $D_{4h}$  and  $D_{5h}$ , respectively.<sup>23a,37b</sup> Similar conclusions apply to the  $\pi \rightarrow \pi^*$  Soret-like (or B) bands in the ultraviolet.<sup>23a</sup> It can be seen in Table II that a progressive shift of the visible absorption bands to lower energy occurs on increasing alkyl substitution and chain length; there is little effect of substituents on the ultraviolet transitions.

Solubility. A quantitative determination of the solubilities of the complexes in the present study are presented in Table II. It can be seen that the superphthalocyanines are substantially more soluble than the phthalocyanines. In each case, as might be expected, alkyl substitution increases the solubility, with the effect of n-butyl substitution being greater than of methyl. Particularly noteworthy also is the relatively high solubility of less symmetrical (4-Me)<sub>4</sub>PcH<sub>2</sub>, compared to (4,5-Me<sub>2</sub>)<sub>4</sub>PcH<sub>2</sub>, and (4,5-Bu<sub>2</sub>)<sub>4</sub>PcH<sub>2</sub>, in spite of the larger number of "solubilizing" groups present in the latter complexes. In accord with this trend, tetra-tert-butylphthalocyanine<sup>39</sup> is reported to be even more soluble, dissolving appreciably even in non-aromatic solvents. It is likely that the multiplicity of isomers present in the less symmetrical, tetrasubstituted phthalocyanines interferes with crystallization.

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Scheme I

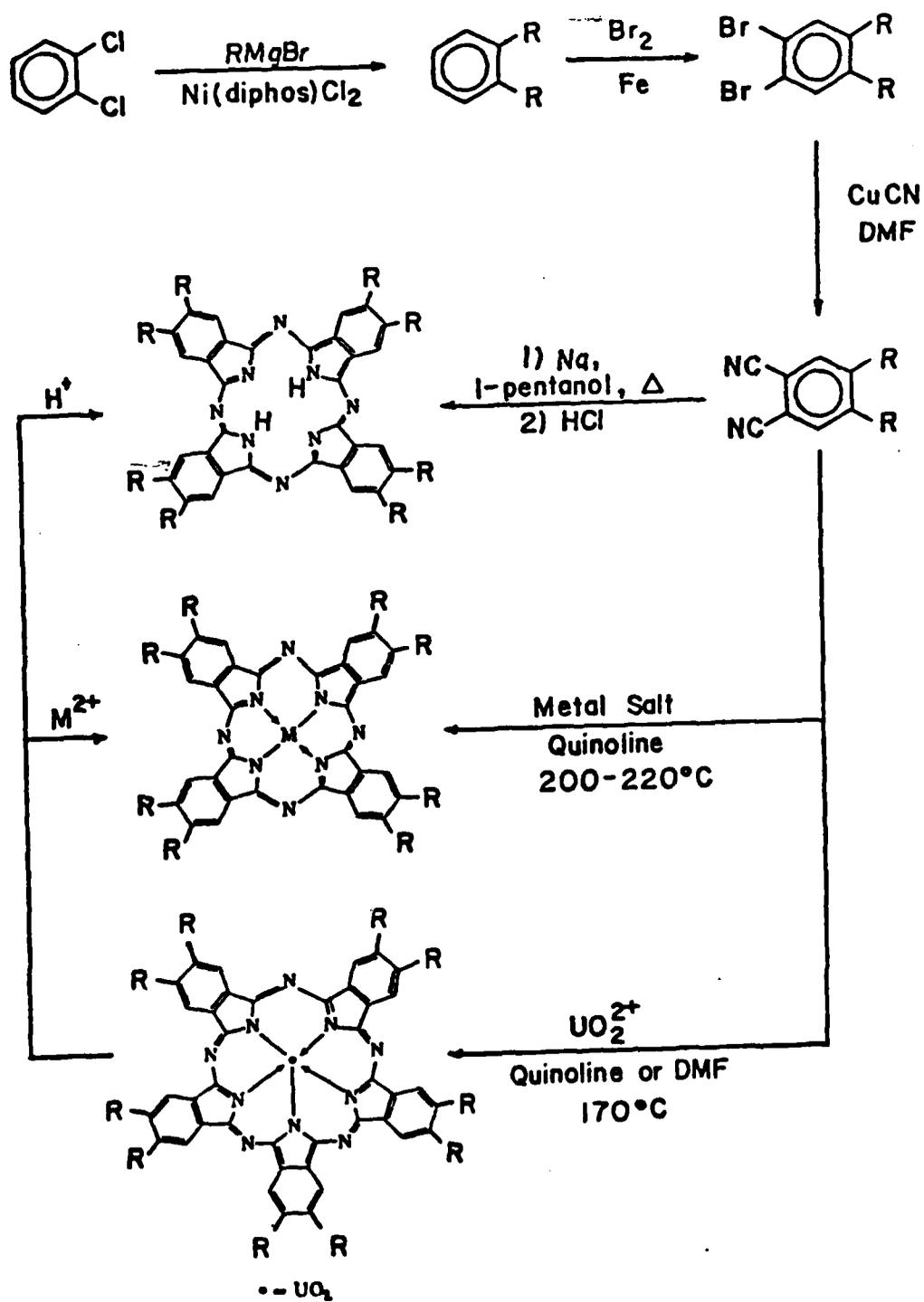


Table I.  $^1\text{H}$  NMR Data for MPC and SPcUO<sub>2</sub> Derivatives<sup>a</sup>

Compound	$^1\text{H}$ NMR
ZnPc <sup>b,c</sup>	9.50 (8H,m), 7.94 (8H,m)
Zn(4-Me) <sub>4</sub> Pc <sup>b,c</sup>	9.19 (8H,d, J=8.8 Hz), 7.69 (4H,d, J=80Hz), 2.76 (12H,s)
PcLi <sub>2</sub> <sup>b,d</sup>	9.38 (8H,m), 8.04 (8H,m)
94,5-Bu <sub>2</sub> )PcH <sub>2</sub> <sup>e,f</sup>	9.47 (8H,s), 3.13 (16H,t), 1.57 (32H,m), 1.07 (24h,t)
Ni(4,5-Bu <sub>2</sub> ) <sub>4</sub> Pc <sup>e</sup>	9.39 (8H,s), 3.13 (16H,t), 1.57 (32H,m), 1.07 (24H,m)
(4,5-CH <sub>2</sub> -O-C <sub>2</sub> H <sub>4</sub> -OC <sub>2</sub> H <sub>5</sub> ) <sub>4</sub> )PcH <sub>2</sub> <sup>f,g</sup>	8.95 (8H,s), 5.15 (16H,s), 3.9 (32H,s), 3.7 (16H,q), 1.35 (24H,t)
SPcUO <sub>2</sub> <sup>b,c</sup>	9.06 (10H,m), 7.68 (10H,m)
(4-Me) <sub>5</sub> SPcUO <sub>2</sub> <sup>b,c</sup>	8.96 (10H,m), 7.46 (5H,d, J=7.2 Hz), 2.46 (15H,s)
(4,5-Me <sub>2</sub> ) <sub>5</sub> SPcUO <sub>2</sub> <sup>h</sup>	8.81 (10H,s), 2.60 (30H,s)
(4,5-Bu <sub>2</sub> ) <sub>5</sub> SPcUO <sub>2</sub> <sup>i</sup>	9.13 (10H,s), 2.86 (20H,t), 1.50 (40H,m), 0.97 (30H,m)

<sup>a</sup>Key: s = singlet; d = doublet; t = triplet; q = quartet; m = multiplet

<sup>b</sup>From reference 23a.

<sup>c</sup>In benzene-d<sub>6</sub> at 30°C.

<sup>d</sup>In acetone-d<sub>6</sub>.

<sup>e</sup>In toluene-d<sub>8</sub> at 100°C.

<sup>f</sup>The NH signals could not be located.

<sup>g</sup>From reference 35, in CDCl<sub>3</sub>.

<sup>h</sup>In 100% chlorobenzene at 22°C.

<sup>i</sup>In toluene-d<sub>8</sub> at 22°C.

Table II. Electronic Spectra<sup>a</sup> and Solubilities of Some Phthalocyanine and Superphthalocyanine Complexes

Compound	Wavelength (nm)				Solubility <sup>b</sup>	
	$(\epsilon \times 10^{-4} \text{ M}^{-1} \text{ cm}^{-1})$					
PcH <sub>2</sub> <sup>c</sup>	602 (2.69)	638 <sup>d</sup> (4.17)	665 (15.1)	698 (16.2)		9.5x10 <sup>-6</sup>
(4-Me) <sub>4</sub> PcH <sub>2</sub> <sup>e, f</sup>	601	635	646	665	700	8.5x10 <sup>-4</sup> g
(4-Me) <sub>4</sub> PcH <sub>2</sub> <sup>f, h</sup>	596	632	642	659	696	2.7x10 <sup>-5</sup> g
(4,5-Me <sub>2</sub> ) <sub>4</sub> PcH <sub>2</sub> <sup>e</sup>	612	647	658	678	704	<1x10 <sup>-5</sup> g
(4,5-Bu <sub>2</sub> ) <sub>4</sub> PcH <sub>2</sub> <sup>e</sup>	609 (2.64)	641 (3.57)	653 (2.64)	673 (15.0)	708 (18.4)	6.8x10 <sup>-5</sup>
CuPc <sup>c</sup>	611 (3.63)	648 (3.24)	678 (21.9)			9.8x10 <sup>-6</sup>
NiPc <sup>c</sup>	603 (3.24)	643 (2.95)	671 (21.6)			.....
Ni(4,5-Me <sub>2</sub> ) <sub>4</sub> Pc <sup>e</sup>	607 (0.96)	644 (0.94)	674 (28.1)			1.5x10 <sup>-5</sup>
Ni(4,5-Bu <sub>2</sub> ) <sub>4</sub> Pc <sup>e</sup>	611 (4.11)	649 (3.82)	679 (24.2)			4.2x10 <sup>-5</sup>
Ni(4,5-Bu <sub>2</sub> ) <sub>4</sub> Pc <sup>h</sup>	607	645	675			8.8x10 <sup>-6</sup> i
SPcUO <sub>2</sub> <sup>j</sup>	424 (5.02)	810 <sup>k</sup>	914 (6.67)			1.4x10 <sup>-3</sup>
SPcUO <sub>2</sub> <sup>h</sup>	420 (5.41)	810 <sup>k</sup>	912 (6.67)			6.8x10 <sup>-5</sup>
(4-Me) <sub>5</sub> SPcUO <sub>2</sub> <sup>h</sup>	420	810 <sup>k</sup>	922			9.4x10 <sup>-4</sup> l
(4,5-Me <sub>2</sub> ) <sub>5</sub> SPcUO <sub>2</sub> <sup>m</sup>	422	820 <sup>k</sup>	935			n
(4,5-Bu <sub>2</sub> ) <sub>5</sub> SPcUO <sub>2</sub> <sup>e, o</sup>	419 (7.26)	820 <sup>k</sup>	939 (7.34)			9.0x10 <sup>-2</sup>
(4,5-Bu <sub>2</sub> ) <sub>5</sub> SPcUO <sub>2</sub> <sup>h, o</sup>	417 (6.90)	820 <sup>k</sup>	938 (6.98)			5.8x10 <sup>-2</sup>

Table II. Continued. Footnotes

<sup>a</sup>Only the visible region is treated in detail here. PCH<sub>2</sub>, CuPc, and NiPc exhibit absorptions in 1-chloronaphthalene at 350 ( $\epsilon = 5.50 \times 10^4 \text{M}^{-1}\text{cm}^{-1}$ ), 350 ( $\epsilon = 5.75 \times 10^4 \text{M}^{-1}\text{cm}^{-1}$ ), and 351 ( $3.72 \times 10^4 \text{M}^{-1}\text{cm}^{-1}$ ) nm, respectively (reference 40). (4-Me)<sub>4</sub>PCH<sub>2</sub> and (4,5-Bu<sub>2</sub>)<sub>4</sub>PCH<sub>2</sub> exhibit absorptions in 1,2,4-trichlorobenzene at 345 and 350 nm, respectively. The electronic spectra of phthalocyanines in the UV region is treated in detail in reference 39.

<sup>b</sup>Of a saturated solution at 25°C in moles/liter, where  $c = A/\epsilon l$ ,  $l = 1 \text{ cm}$ .

<sup>c</sup>Visible spectrum in 1-chloronaphthalene from reference 40. Solubility in 1,2,4-trichlorobenzene.

<sup>d</sup>This absorption is a doublet with maxima at 633 and 643 nm.

<sup>e</sup>In 1,2,4-trichlorobenzene.

<sup>f</sup>Reference 41.

<sup>g</sup>Assume  $\epsilon$  for lowest energy transition is the same as in PCH<sub>2</sub> ( $1.62 \times 10^5$ ).

<sup>h</sup>In toluene.

<sup>i</sup>Assume  $\epsilon(675)$  is the same as in 1,2,4-trichlorobenzene ( $2.42 \times 10^5$ ).

<sup>j</sup>Visible spectrum in 1-chloronaphthalene from reference 23a. Solubility in 1,2,4-trichlorobenzene.

<sup>k</sup>Shoulder, approximate position.

<sup>l</sup>Assume  $\epsilon(922)$  is the same as in SPcUO<sub>2</sub> ( $6.67 \times 10^4$ ).

<sup>m</sup>In 1-chloronaphthalene.

<sup>n</sup>Solubility not measured. Approximately equal to that of SPcUO<sub>2</sub>.

<sup>o</sup>Error in extinction coefficients  $\pm 7\%$ .

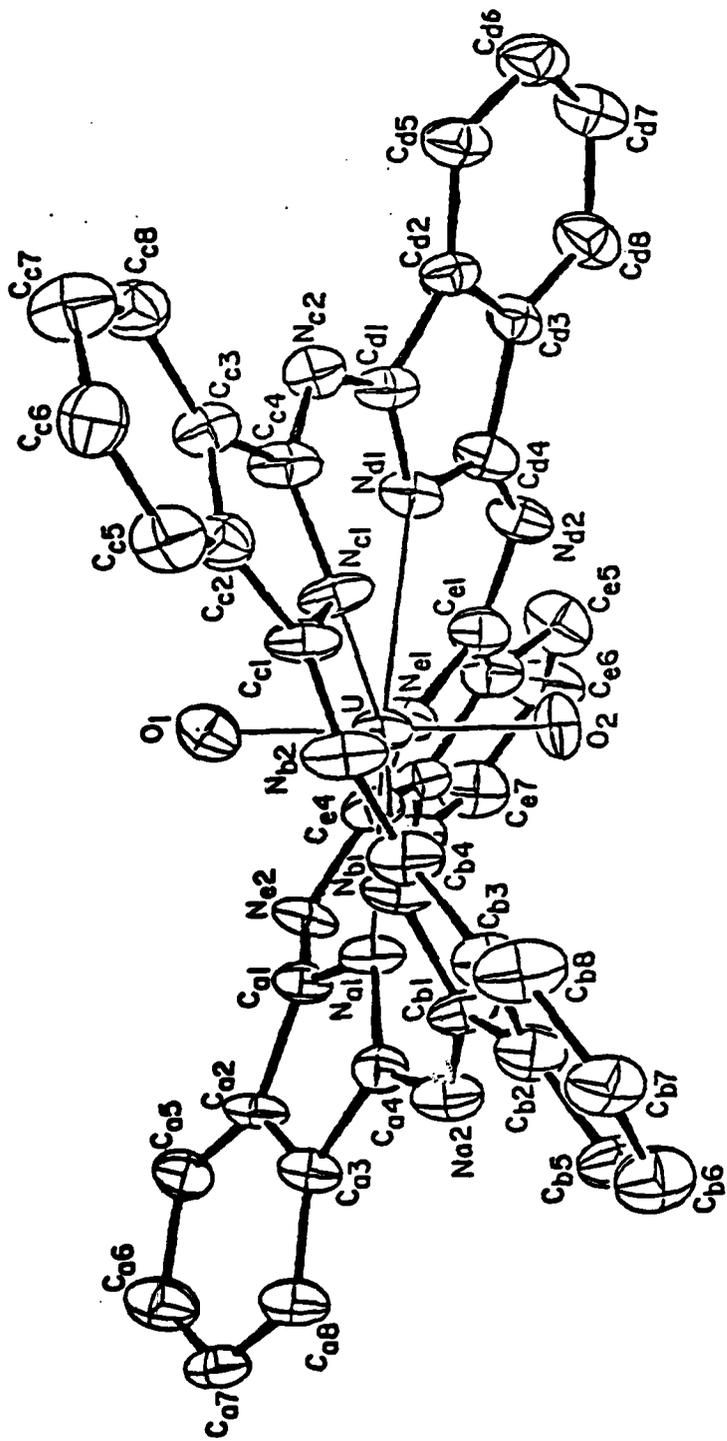
### Figure Captions

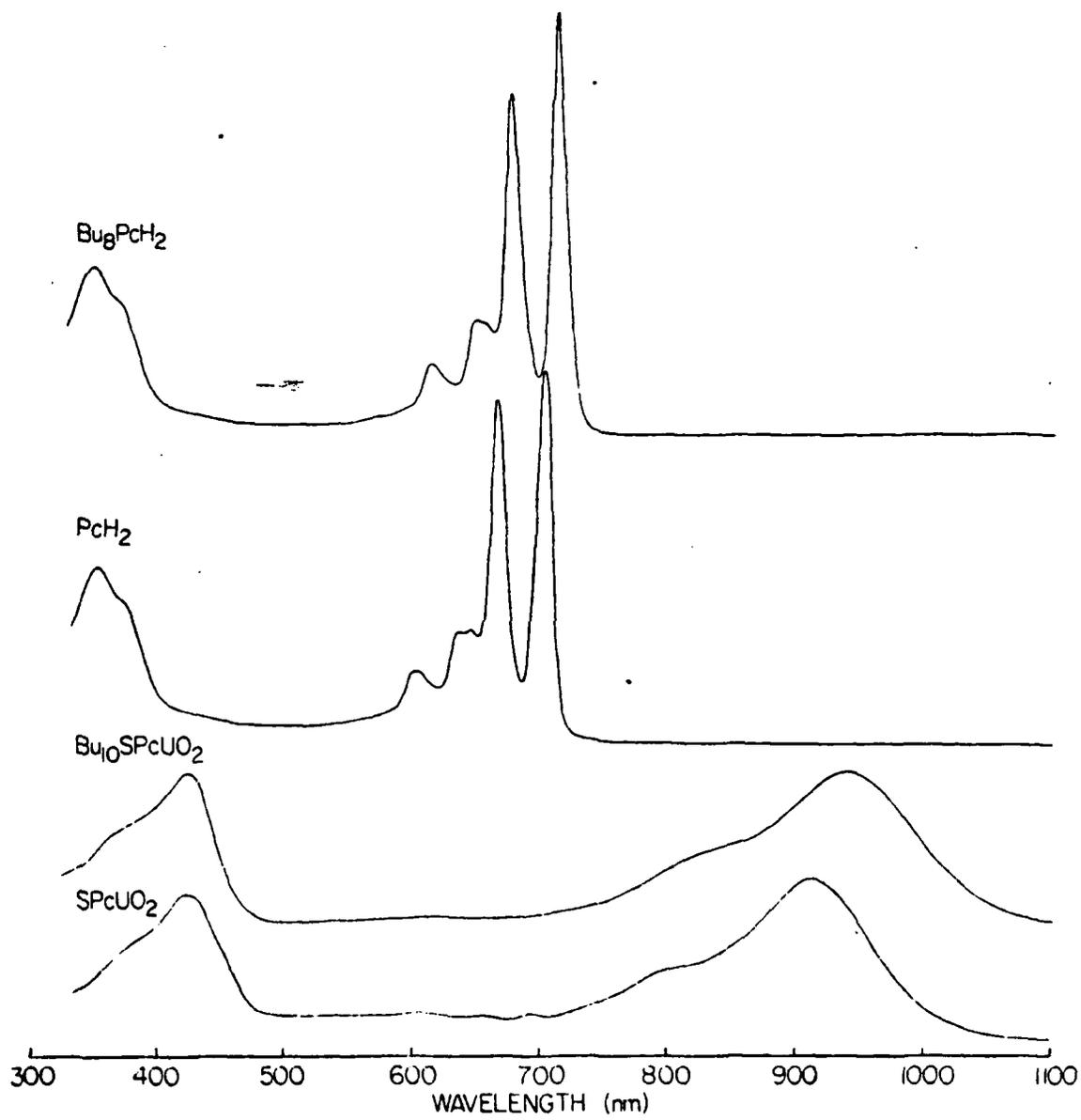
Figure 1. Perspective view of the structure of  $\text{SPcUO}_2$  perpendicular to the  $\text{O=U=O}$  axis. From reference 4.

Figure 2. Electronic spectra of phthalocyanine and uranyl superphthalocyanine complexes in 1-chloronaphthalene. For  $\text{SPcUO}_2$ , the very weak absorptions from 600-700 nm are due to traces of  $\text{PcH}_2$ .

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