Macrocycle Contraction Reactions of 5,35:14,19-Diimino-7,12:21,26:28,33-trinitrilopentabenzo[*c,h,m,r,w*][1,6,11,16,21]pentaazacyclopentacosinatodioxouranium(VI)

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Summary Displacement of the uranyl ion from 5,35:14,19-diimino-7,12:21,26:28,33-trinitrilopentabenzo[*c,h,m,r,w*][1,6,11,16,21]pentaazacyclopentacosinatodioxouranium(VI)† with a variety of metal ions is accompanied by ring contraction, yielding the corresponding metal phthalocyanine.

IT has recently been demonstrated[1] that a metal phthalocyanine[2] condensation reaction in the presence of uranyl ion can give a uranyl complex of the superphthalocyanine ligand, SPc, an expanded five-subunit[3] analogue of phthalocyanine. It is of great interest to determine to what degree the structural and chemical stability of the macrocyclic ligand (and thus its formation and selectivity) are influenced by the unusual co-ordinative properties of the uranyl ion. We now report a surprising ligand contraction process which is unprecedented in macrocycle co-ordination chemistry.[4]

The reaction of $SPcUO_2$ with various metal salts in dimethylformamide–1-chloronaphthalene at 60—130 °C results both in displacement of the uranyl ion and contraction of the ring system (Scheme). Products were identified by i.r., mass, and visible spectra, and by elemental analysis; yields of metal phthalocyanine (PcM) are essentially quantitative. An example of this reaction, monitored spectrophotometrically, is shown in the Figure. Under the same conditions, metallation of the free PcH_2 ligand is far slower. Reaction with trivalent metal salts, *e.g.* lanthanides, occurs to yield the corresponding PcMX compound. Likewise, reaction with finely dispersed active metals, *e,g.* Na, K in boiling mesitylene produces the corresponding metal phthalocyanine. Treatment of $SPcUO_2$ with aqueous

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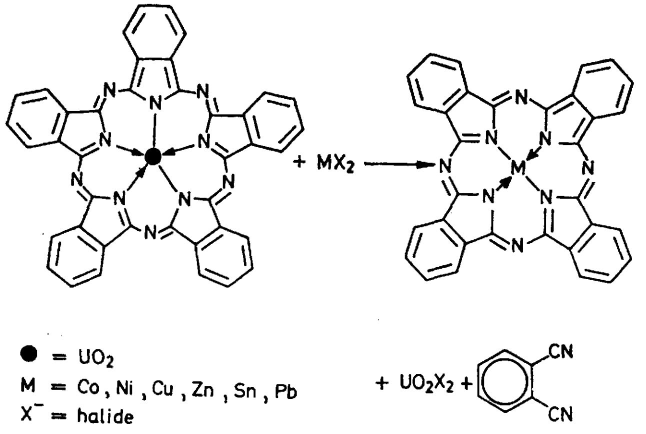
† Compound previously named as dioxocyclopentakis(2-iminoisoindolinato)uranium(VI).

and nonaqueous acids under a variety of conditions yields PcH_2.



SCHEME

The marked propensity for ring contraction indicates that the favourable pentagonal bipyramidal uranyl co-ordination geometry and optimum U–N bond distance [average = 2·524 (9) Å[1]] are important in stabilizing the superphthalocyanine ligand system. Though PcSn is severely distorted, with the relatively large Sn^{II} ion displaced 1·1 Å from the ring co-ordination plane (Sn–N = 2·25 Å),[4e] tin still fails to satisfy these requirements. Besides these criteria, steric strain in the five subunit ligand[1] may be an important driving force for contraction. Electronic factors within the ligand do not appear to be important, as indicated by our Hückel M.O.[5] calculations on the free $SPcH_2$ and PcH_2 ligands (minus the fused benzene rings). Within the accuracy of these calculations, the π energy of $SPcH_2$ is not significantly different from that of PcH_2[6] plus phthalonitrile.

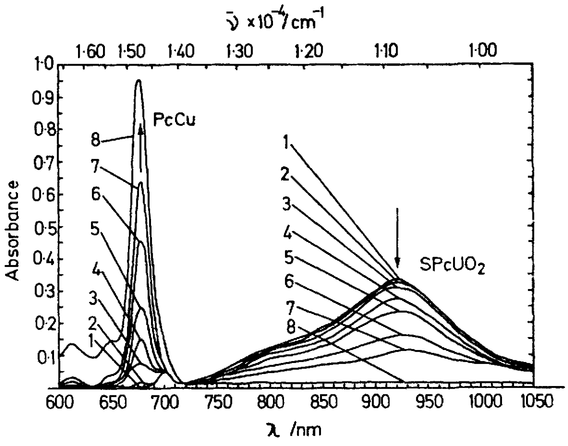


FIGURE. Spectrophotometric record of the reaction of $SPcUO_2$ with $CuCl_2$ in 200:1 1-chloronaphthalene–DMF at 75°C; observed second-order rate constant = 0·26 l mol^{-1} sec^{-1}.

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