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Reactions that Involve Collapse of the 'Superphthalocyanine' Dioxocyclopentakis(1-iminoisoindolinato)uranium(VI) to either Phthalocyanine or Metal Phthalocyanine

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Abstract

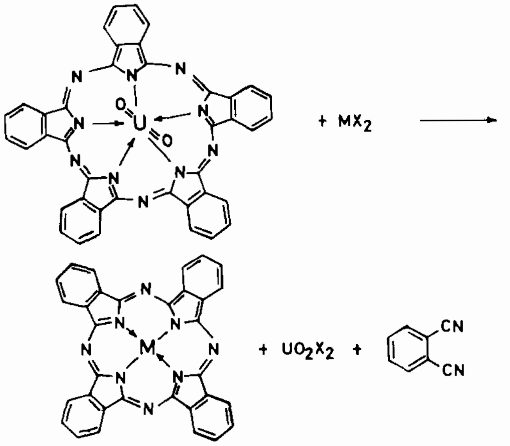
In this paper we report chemical and spectral studies on the reactions of dioxocyclopentakis(1-iminoisoindolinato)uranium(VI), $SPcUO_2$, with tri-n-butylphosphine ($P(^nB)_3$), DMF, thiophenol, 2-mercaptoethanol, $CuCl_2$, $FeCl_3$, $ZnCl_2$ and $Th(NO_3)_4 \cdot 6H_2O$. In all cases macrocycle contraction is found to result to produce H_2Pc or $PcMX_m$ (where M = Fe, Zn or Cu; X = no ligand, where M = U, X = $P(^nB)_3$, DMF or 2-mercaptoethanol, *m* is not established). Spectral evidence is found for these new U(IV) mono-phthalocyanine species. A mechanism for the formation of these PcU(IV) species is suggested. The mechanism involves the initial reduction of the $SPcUO_2$ complex by either $P(^nB)_3$, DMF or 2-mercaptoethanol.

The spectrum of a purple intermediate found in the $SPcUO_2$ reaction with $P(^nB)_3$ is presented and the nature of this complex is discussed.

Introduction

The preparation, structure and some properties of dioxocyclopentakis(1-iminoisoindolinato)uranium(VI) ($SPcUO_2$) have been described by T. J. Marks and coworkers [1–4]. They report that many of the properties of $SPcUO_2$ are explicable in terms of severe strain within the macrocycle. These workers [2, 3] have proposed the following reaction pathway for ring contraction in the presence of a number of metal halides MX_2 (M = Co, Ni, Zn, Sn and Pb; X^- = halide). The solvent systems used [3] were (1) 300:1 1-chloronaphthalene:dimethylformamide for kinetic studies, however, DMF seems to have been the preferred solvent for most of the quantitative work, though 1-pentanol, toluene and quinoline were also used.

We have recently initiated studies of metallomacrocyclic complexes with phosphine ligands and in the course of this work with $SPcUO_2$ and tri-n-butylphosphine ($P(^nB)_3$) we observed a purple intermediate complex in solution. We report here these studies and relate them to the work of T. J. Marks [1–4].



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Experimental

All experiments involving air-sensitive reagents were carried out under nitrogen atmospheres in Schlenk tubes with rigorous exclusion of oxygen and water. Solvents were refluxed over the appropriate drying agent and freshly distilled under nitrogen. UV visible spectra were recorded on a Perkin-Elmer Lambda 5G instrument.

Synthesis of Dioxocyclopentakis(1-iminoisoindolinato)uranium(VI) ($SPcUO_2$)

$SPcUO_2$ was synthesised according to literature methods [1, 3, 4] using $UO_2(OAc)_2(DMF)_2$ [5].

The final dark-blue $SPcUO_2$ contained a trace of metal-free phthalocyanine (PcH_2) (identified by electronic absorption spectra; Fig. 1). We note that Marks and Stojakovic [3] also found PcH_2 present in their synthesis.

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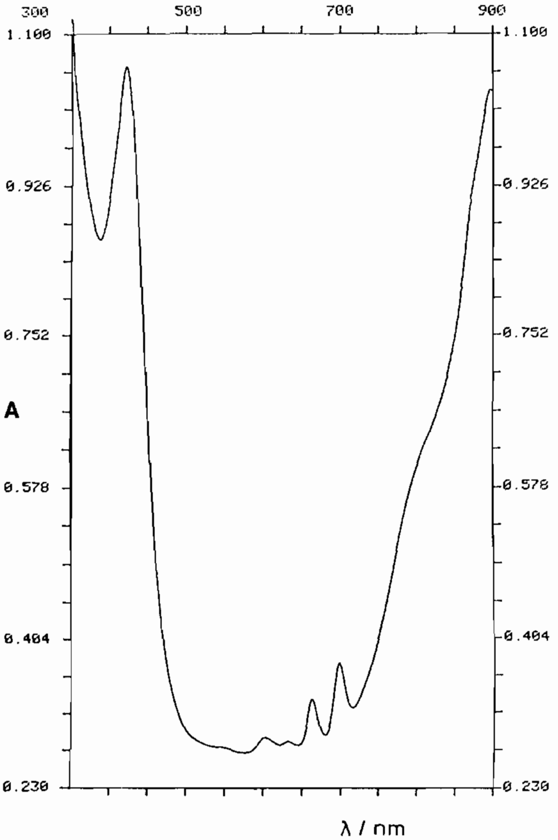


Fig. 1. Electronic absorption spectrum of $SPcUO_2$ in 1-chloronaphthalene.

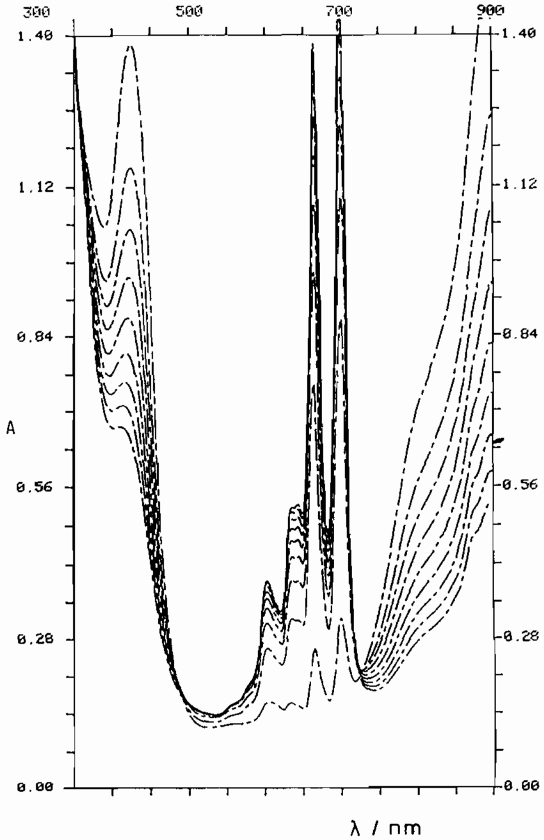


Fig. 2. Electronic absorption spectra of experiment 1 in Table I. Spectra were taken at times of 5, 95, 185, 275, 365, 455, 545, 635 and 725 min after mixing.

Demetalation and Transmetalation Experiments

(1) Reactions of tri-n-butylphosphine with $SPcUO_2$

All the reactions were carried out under nitrogen. 4 ml of a 1-chloronaphthalene solution of $SPcUO_2$ (conc. 2.20×10^{-4} M) were mixed with 1 ml of tri-n-butylphosphine ($P(^nB)_3$). The mixture was diluted with 5 ml of 1-chloronaphthalene to make the total volume 10 ml. 2.5 ml of this were quickly transferred to a cuvette. The course of the reaction was immediately followed by electronic absorption spectroscopy.

The reaction is observed to initiate by reduction of the visible spectrum of $SPcUO_2$ and the concomitant growth of bands at 665 nm and 698 nm due to metal-free phthalocyanine (Fig. 2). The reaction goes to completion within 12 h.

The same experiment was repeated with different mole-ratios of $P(^nB)_3$ to $SPcUO_2$ as set out in Table I and the resulting electronic absorption spectra are shown in Figs. 3–6. All reactions were at 293 K.

(2) Reaction of $SPcUO_2$ with dimethylformamide (DMF)

To 2 ml of a 1-chloronaphthalene containing $SPcUO_2$ (conc. 2.20×10^{-4} M) different amounts of DMF were added (see Fig. 7 caption for details). The reaction was followed by changes in the electronic absorption spectra. The spectra show evidence for the formation of H_2Pc and a second species which has a maximum absorption around 660 nm, that from the spectral shape we assign to a monophthalocyanine–U(IV) complex possibly with DMF ligated to the uranium atom.

(3) Reaction of $SPcUO_2$ with anhydrous $CuCl_2$

2 ml of an acetone solution saturated with anhydrous $CuCl_2$ was mixed with 4 ml of 1-chloronaphthalene containing $SPcUO_2$ (2.20×10^{-4} M) and the mixture was diluted with 4 ml of 1-chloronaphthalene to make the final volume 10 ml. This reaction was also monitored by electronic absorption spectroscopy. The bands due to $SPcUO_2$ immediately began to lose intensity and those of

CuPc, 611 nm, 648 nm and 678 nm began to grow (Fig. 8).

(4) Reaction of $SPcUO_2$ and anhydrous $FeCl_3$

This reaction was carried out by the method outlined for $CuCl_2$ above except that $FeCl_3$ was used instead of $CuCl_2$. Visible bands (Fig. 9) at 577 nm and 658 nm identify that FePc was amongst the products along with H_2Pc (bands at 665 nm, 698 nm) and at least one other material as seen by the bands at 722 nm, 820 nm, 840 nm and 860 nm.

(5) Reaction of $SPcUO_2$ and anhydrous $ZnCl_2$

This reaction was carried out by the method given for $CuCl_2$ above except that a saturated methanolic solution of $ZnCl_2$ was used instead of acetone and $CuCl_2$. The product found in the reaction identified from its absorption spectrum was ZnPc (Fig. 10) (bands at 611 nm, 649 nm and 680 nm).

(6) Reaction of $SPcUO_2$ and $Th(NO_3)_4 \cdot 6H_2O$

6 ml of an acetone solution saturated with thorium(IV) nitrate hexahydrate, was mixed with 4 ml of $SPcUO_2$ (2.20×10^{-4} M) in 1-chloronaphthalene. The reaction was studied using electronic absorption spectroscopy. The only product after 6 h was H_2Pc. So once again $SPcUO_2$ is seen to be broken down.

(7) Reactions of $SPcUO_2$ with thiophenol or 2-mercaptoethanol

6 ml of thiophenol were added to 4 ml of $SPcUO_2$ (2.20×10^{-4} M) in 1-chloronaphthalene and the reaction was monitored by electronic absorption spectroscopy. Only H_2Pc was found to be produced, thus again the $SPcUO_2$ is broken down.

In the case of 2-mercaptoethanol, 4 ml of this were added to a solution of 6 ml of $SPcUO_2$ (2.20×10^{-4} M) in 1-chloronaphthalene. The reaction was very slow, however, evidence for H_2Pc and another product possibly a monophthalocyanine U(IV) complex (band around 675 nm) (see Fig. 11) was found.

Results and Discussion

The reaction of $SPcUO_2$ and $P(^nB)_3$

The reaction of $P(^nB)_3$ with $SPcUO_2$ is clearly concentration-dependent (Table I and Figs. 3–6). From the Figures and comparing our results with those of other reactions reported by Marks [2, 3] it is obvious that at low volumes of $P(^nB)_3$ the $SPcUO_2$ decomposes to H_2Pc. As the concentration of $P(^nB)_3$ is increased (experiment No. 3 in Table I and Fig. 4), a purple intermediate which we designate as A is clearly seen in the reaction mixture. The bands associated with this species in the electronic absorption spectrum are at 500, 526, 560 and 595 nm, respectively (more clearly observed in Fig. 5), the strongest being that at 560 nm. Over a period of time, this purple species slowly fades. It is likely that this intermediate was present in the reactions at low concentrations of $P(^nB)_3$ (experiment 1, Table I), but was not visible to the eye (*i.e.* not present in high enough concentration). At higher concentrations of $P(^nB)_3$ (experiments 4 and 5, Table I) another species which we designate as **B** is observed. In Fig. 5 it can be seen that this species continues to develop at the expense of H_2Pc and species **A** and finally is the only species present (Fig. 6). The final solution colour is green. The electronic absorption spectrum of **B** (Fig. 6) has features in common with that reported by Guilard *et al.* [6] for $PcU(acac)_2$. From this and the fact that **B** grows at the expense of H_2Pc in our experiments (experiment 5, Table I and Fig. 5), we believe that **B** is a monophthalocyanine complex containing U(IV). Some $P(^nB)_3$ is likely to be ligated to the U(IV) in this monophthalocyanine complex. This complex is not air stable, in air it reverts to H_2Pc, presumably the U(IV) is reoxidised after the excess $P(^nB)_3$ is oxidised.

TABLE I. Reactions of $SPcUO_2$ with Tri-n-butylphosphine ($P(^nB)_3$) at 293 K

Experiment number	Volume of $P(^nB)_3$ (ml)	Total volume of 1-chloronaphthalene (ml) containing $SPcUO_2$ [a]	Time (h) for complete reaction	Intermediate product(s) observed[c]	Final products
1	1	9	12	H_2Pc	H_2Pc
2	2	8	5.5	H_2Pc, A (trace)	H_2Pc
3	4	6	3.5	H_2Pc + A	H_2Pc
4	6	4	0.5	H_2Pc + A + B	H_2Pc
5	9	1	6.5[b]	H_2Pc + A + B	B

[a] In all experiments the concentration of $SPcUO_2$ was 8.75×10^{-5} M. [b] This experiment was repeated several times as it was noted that a different end product appeared (see text). [c] A = purple intermediate, B = mono(PcU(IV) – $(P(^nB)_3)_m$ complex.

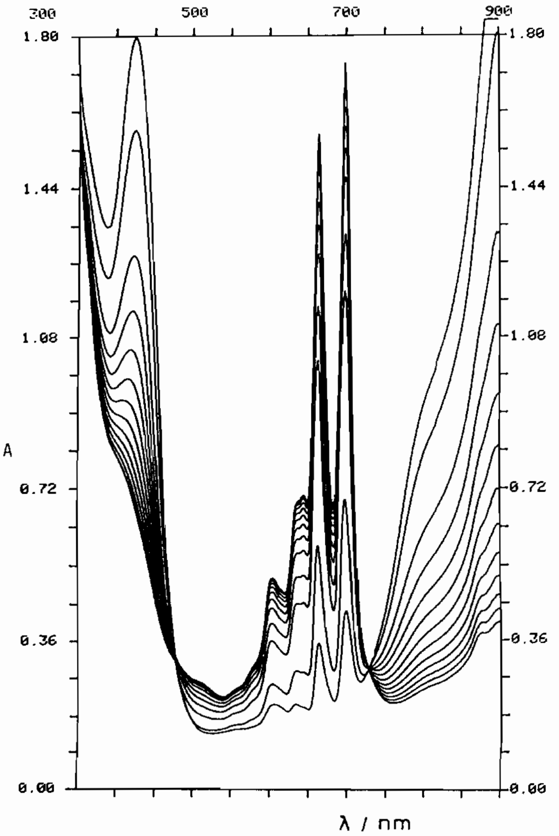


Fig. 3. Electronic absorption spectra of experiment 2 in Table I. Spectra were taken at times of 5, 10, 45, 75, 105, 135, 165, 195, 215, 245, 275, 305 and 335 min after mixing.

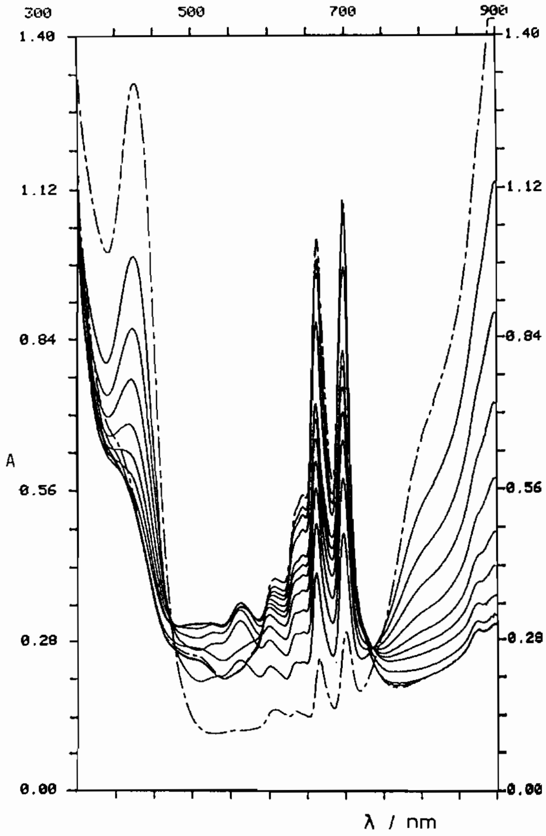


Fig. 4. Electronic absorption spectra of experiment 3 in Table I. The initial spectrum was almost directly after mixing and a separate experiment. The others were at times of 10, 15, 20, 25, 30, 35, 45, 75, 105, 135 and 195 min after mixing.

From these observations and the above discussion it is obvious that the $P(^nB)_3$ is acting as a reducing agent and is responsible for the production of U(IV) in these experiments.

The nature of the purple intermediate species remains to be fully elucidated, however, there are several possibilities:

(1) First if the $P(^nB)_3$ reduces the UO_2^{2+} in $SPcUO_2$ to UO_2^+, then the resulting $(SPcUO_2)^+$ complex would be a strong candidate.

(2) If the reduction of the UO_2^{2+} goes directly to U(IV), then the purple complex may involve either the SPc ligand and U^{4+} or the collapse of the SPc ligand to a U^{4+} Pc complex.

(3) Alternatively the purple species may involve partially reduced $SPcUO_2$ complex with $P(^nB)_3$ molecule(s) bound to the uranium atom.

(4) A variant of three in which the $SPcUO_2$ complex has lost an oxygen and this is replaced by bound $P(^nB)_3$ ligand(s).

We do not believe that the purple intermediate could be a demetallated SPc ring as such a species was not observed in the work of Marks [2, 3]. As the final end product of experiment 5 (Table I) is green, we do not believe that a U^{4+} monophthalocyanine complex could be responsible for the purple colour. Moreover, our purple complex shows no similarity in its visible spectrum to those of oxidised samples of $PcU(acac)_2$ [6].

The fact that the end complex **B** grew at the expense of H_2Pc (experiment 5, Table I and Fig. 6) shows that once the U^{4+} was generated in the solution, it is able to bind to the Pc ring. Guilard *et al.* [6] have recently described the synthesis of $PcU(acac)_2$ actinide and $PcTh(acac)_2$. These were claimed to be the first actinide monophthalocyanine complexes, so our complex **B**, when fully characterised, is another to be added to this class of compounds.

Reaction of $SPcUO_2$ with DMF

Figure 7 shows the spectra we obtained from reaction of various ratios of DMF with $SPcUO_2$ (ratios given in Figure Legends). These data show that DMF is able to activate the decomposition of the $SPcUO_2$ complex causing both demetallation and the formation of a monophthalocyanine uranium(IV)-$(DMF)_x$ complex (see Experimental Section). We

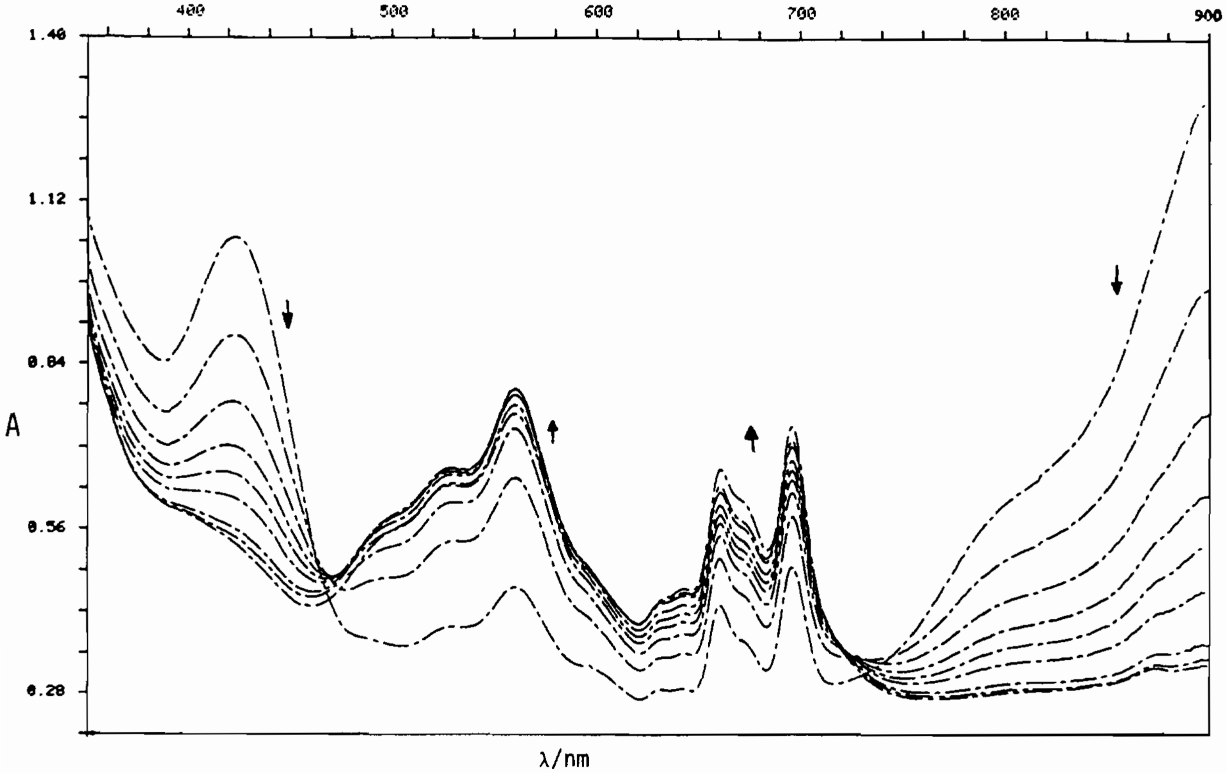


Fig. 5. Electronic absorption spectra of experiment 4 in Table I. The spectra were taken at times of ~0, 0.5, 1, 1.5, 2, 2.5, 5, 10 and 30 minutes after mixing. (It should be noted that this experiment was taken as ended while the intermediate purple species was still present, but before the final species of experiment 5 began to form.)

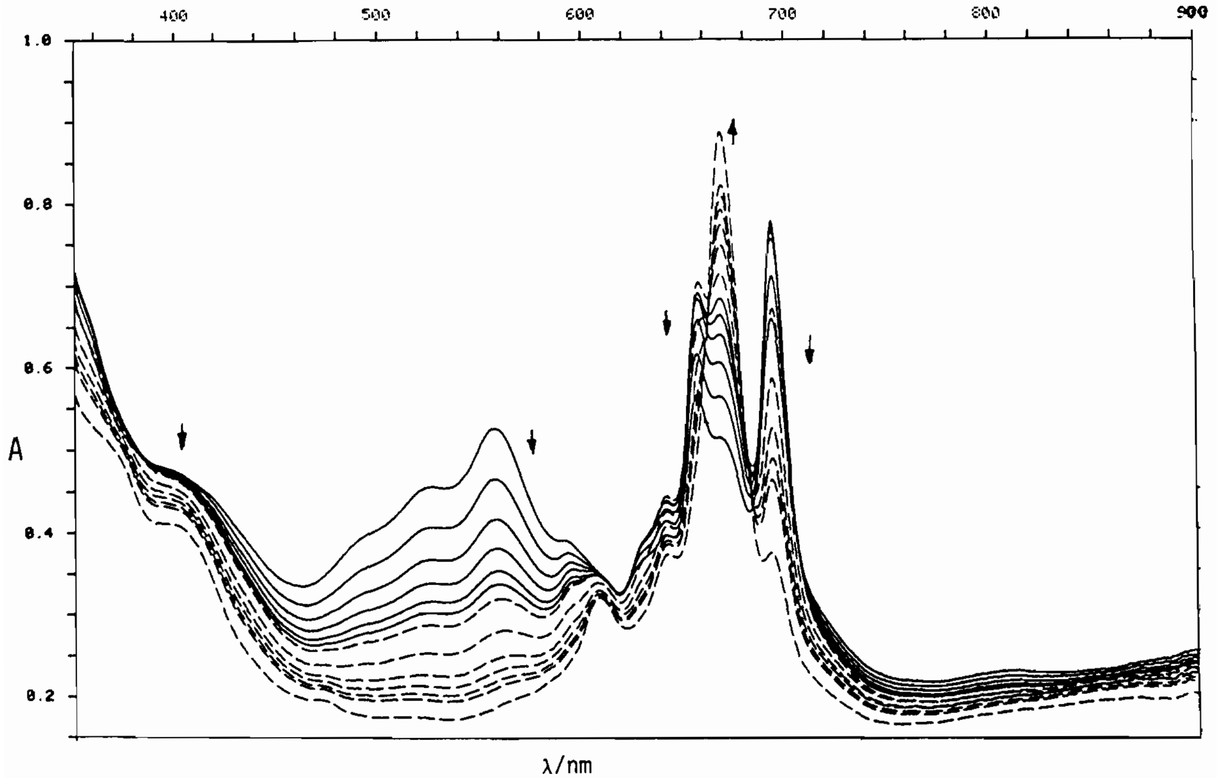


Fig. 6. Electronic absorption spectra of experiment 5 in Table I. The spectra were taken at times 15, 30, 45, 60, 75, 90, 110, 170, 230, 290, 350, 410 and 720 min after mixing.

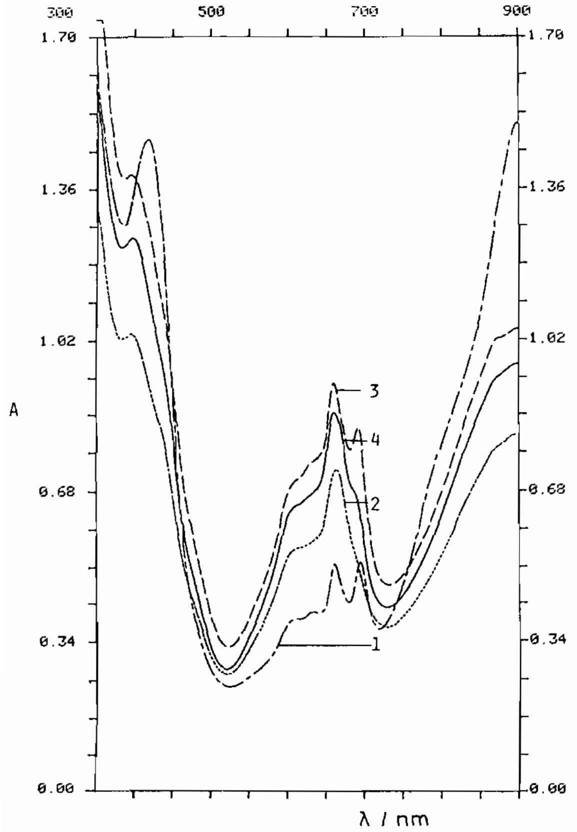


Fig. 7. Electronic absorption spectra containing 2 ml of $SPcUO_2$ (2.20×10^{-4} M) in 1-chloronaphthalene made up to a total of 5 ml by the following additions (numbers refer to spectra in Figure). (1) 2.5 ml 1-chloronaphthalene, 0.5 ml DMF. (2) 1.5 ml 1-chloronaphthalene, 1.5 ml DMF. (3) 0 ml 1-chloronaphthalene, 3 ml DMF. For spectrum (4) only 1 ml of $SPcUO_2$ (2.20×10^{-4} M) was used with 4 ml DMF.

tentatively assign a valence state of four to the uranium atom in this complex and suggest that the DMF acts as a reducing agent. We note that Marks [2,3] used DMF–1-chloronaphthalene mixtures in many of their reactions with metal salts and $SPcUO_2$, which is unfortunate in the light of our findings.

Although we found no evidence to suggest $SPcUO_2$ decomposes in 1-chloronaphthalene alone in our work, it might over very long time periods.

Reaction of $SPcUO_2$ with $CuCl_2$

Figure 8 shows the growth of peaks due to CuPc (see Experimental Section 3), when $SPcUO_2$ is reacted with $CuCl_2$ in 1-chloronaphthalene. This reaction, unlike those of Marks and Stojakovic [2,3] was carried out in the absence of DMF and still gives the result found by them [2,3] *i.e.* that CuPc is formed. From this work it appears that both DMF and $CuCl_2$ cause the $SPcUO_2$ molecule to break up and the SPc ring to contract to a Pc ring. From our results and those of Marks and Stojakovic [2,3] it appears that at low concentrations of DMF in 1-chloronaphthalene in the presence of $CuCl_2$, the end product is CuPc and not a Pc complex of U(IV) and DMF, such as that found in the preceding section. It should be noted that we found that acetone does not react with $SPcUO_2$.

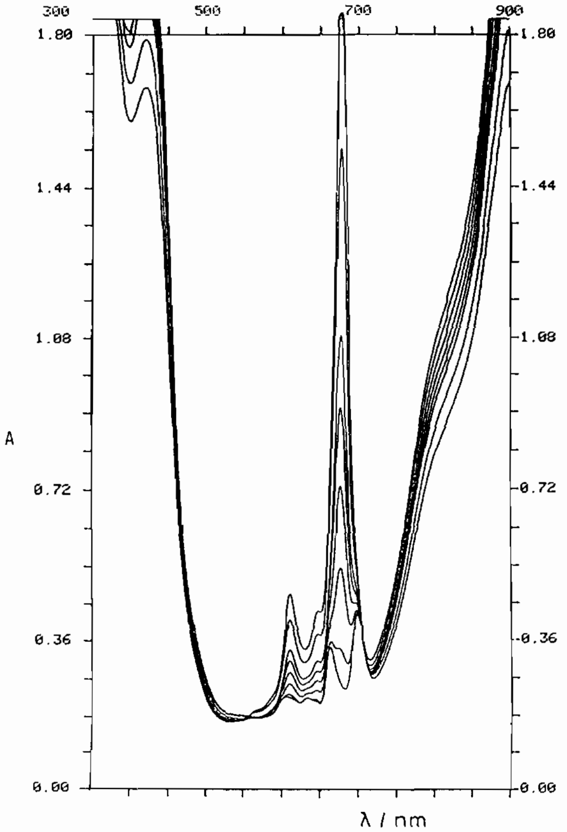


Fig. 8. Electronic absorption spectra of the reaction of $SPcUO_2$ with anhydrous $CuCl_2$ (conditions as in experimental part 3) at times of 5, 15, 35, 55, 75, 95, 155 and 215 min after mixing.

Reaction of $SPcUO_2$ with $FeCl_3$

Figure 9 provides evidence for the formation of FePc, H_2Pc and another species (see Section 4 of the Experimental on reactions). We offer no suggestions at this point on the nature of the other species.

Reaction of $SPcUO_2$ and $ZnCl_2$

In Fig. 10, ZnPc can be seen to be the only major species forming as the $SPcUO_2$ is destroyed. It should be noted that we found no evidence of methanol reacting with $SPcUO_2$.

Reaction of $SPcUO_2$ and $Th(NO_3)_4 \cdot 6H_2O$

The only product found in this reaction was H_2Pc. Unlike the findings of Marks and Stojakovic [3] with anhydrous $ThCl_4$ in DMF where no Pc products were found.

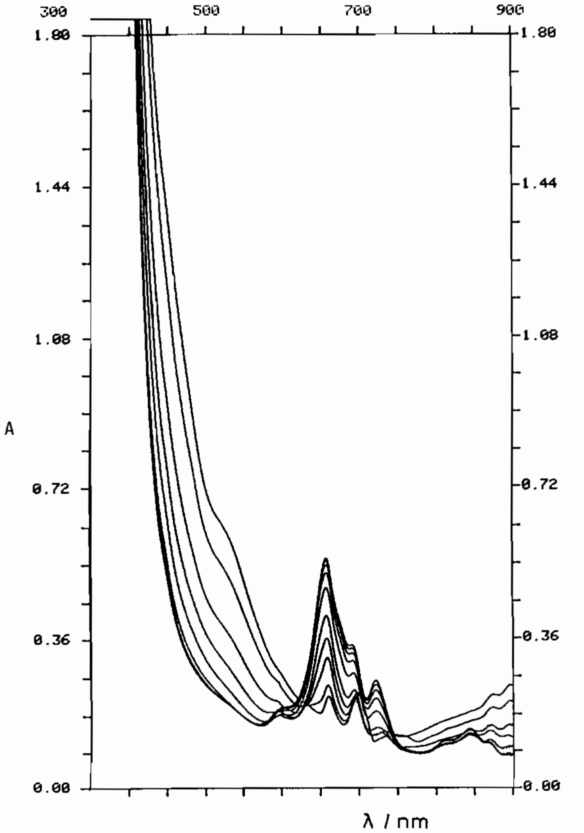


Fig. 9. Electronic absorption spectra of the reaction of $SPcUO_2$ and anhydrous $FeCl_3$ (for conditions see experimental parts 3 and 4) at times of 5, 10, 15, 20, 25, 40, 55, 70, 85 and 100 min after mixing.

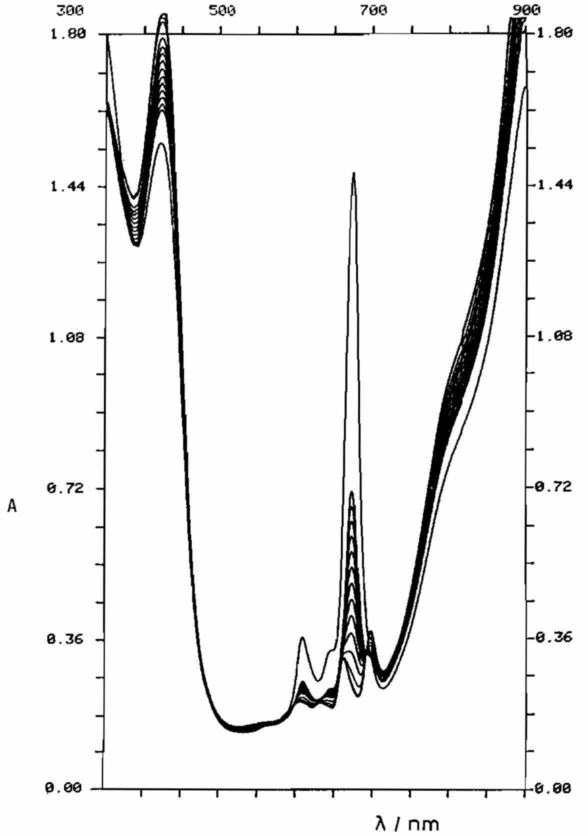


Fig. 10. Electronic absorption spectra of the reaction of $SPcUO_2$ and anhydrous $ZnCl_2$ (for conditions see experimental part 5) at times of 0.0, 1, 5, 10, 20, 50, 80, 110, 140, 170, 200, 230, 260, 290 and 720 min after mixing.

Reaction of $SPcUO_2$ with Thiophenol and 2-Mercaptoethanol

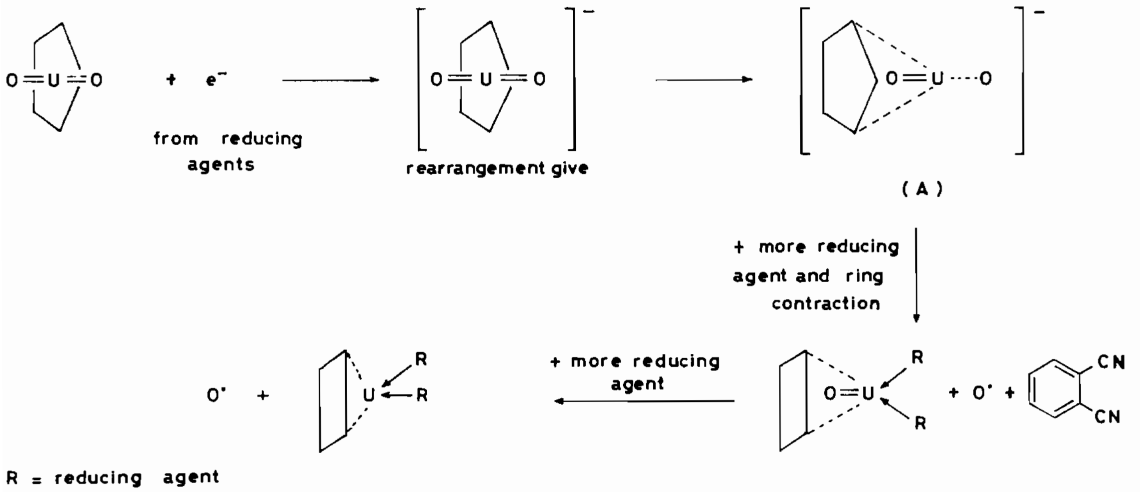
In the reaction of $SPcUO_2$ with thiophenol (excess), evidence for the breakdown of the former to H_2Pc was found. Thus thiophenol reacts with and/or complexes with UO_2^{2+} and concomitant with this reaction H_2Pc is formed.

When excess 2-mercaptoethanol reacts with $SPcUO_2$, both H_2Pc and a species that has an absorption band around 675 nm is formed (Fig. 11). The latter species we deduce is a monophthalocyanine U(IV) complex possibly containing 2-mercaptoethanol ligand(s). If our deductions are correct, then 2-mercaptoethanol reduces the UO_2^{2+} to U(IV) in this reaction. We have previously used 2-mercaptoethanol as a ligand in reaction with protoporphyrin(IX) iron(III) [7].

Conclusions

Marks and coworkers [1–4] have discussed the severe strain and buckling [3] of the macrocycle in $SPcUO_2$ and have speculated on the nature of the SPc contraction. They have proposed two possible mechanisms as being compatible with their kinetic data: the first is a process involving rate determining displacement of UO_2^{2+} to form an SPcM species, which then subsequently contracts [3]. The second involves metal ion attack at the imino nitrogen on the $SPcUO_2$ periphery followed by Lewis acid promoted ring opening. Our studies with $CuCl_2$, $FeCl_3$ and $ZnCl_3$ shed no further light on which of these two reactions may be correct.

However, the studies reported here using tri-n-butyl phosphine ($P(^nB)_3$), DMF and mercaptoethanol are interesting. In all three cases evidence is found for the end product being a U(IV) monophthalocyanine complex. So in all three cases the UO_2^{2+} was reduced to U(IV). In the case of the $P(^nB)_3$ reaction with $SPcUO_2$ a purple intermediate was found. (The nature of this intermediate was discussed above). These reactions allow a suggestion for a mechanism for the SPc contraction when a reducing agent is present which is similar to the first process of Marks [3] outlined above.



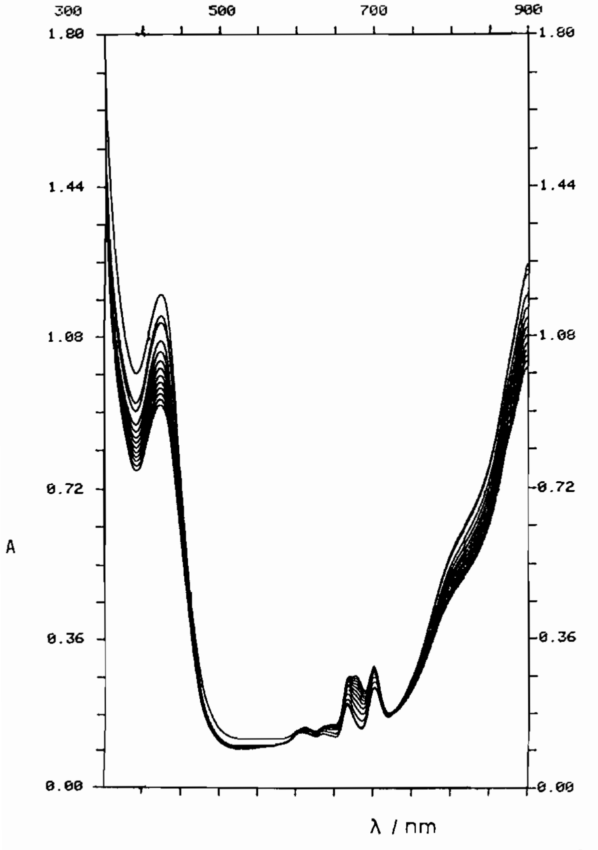


Fig. 11. Electronic absorption spectra of the reaction of $SPcUO_2$ and 2-mercaptoethanol (for conditions see experimental part 7) at times of 5, then each one an hour later successively.

First the $SPcUO_2$ is attacked somewhere on the complex periphery and an electron is injected, then rearrangement followed by further reduction and concomitant ring contraction takes place yielding the U(IV)phthalocyanine end complex bonded to an unknown number of ligand molecules. Species **A** would be the purple complex.

Acknowledgement

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