Tetrahedron Letters No. 31, pp 2637 - 2640, 1975. Pergamon Press. Printed in Great Britain.

NEW METALLOPORPHYRINS. THORIUM AND YTTRIUM COMPLEXES OF TETRAPHENYLPORPHIN.

Ching-Ping Wong and William DeW. Horrocks, Jr.*
The Grover Cleveland Chandlee Laboratory, Department of Chemistry
The Pennsylvania State University, University Park, Pa. 16802

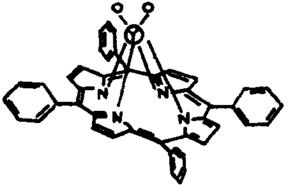
(Received in USA 8 May 1975; received in UK for publication 17 June 1975)

The availability of a wide variety of metalloporphyrins[1] provides the opportunity to introduce into heme proteins a spectrum of metals with interesting spectroscopic and chemical probe characteristics. Fruitful studies of proteins reconstituted with cobalt, manganese and other metal porphyrin complexes represent what is likely to be only the beginning of a significant and important area of research. With our recent synthesis of lanthanide porphyrin complexes[2] no more than a handful of metallic elements remain for which no porphyrin complex is known.[1] We report here the synthesis and characterization of *meso*tetraphenylporphin (TPP) complexes of thorium (IV) and yttrium (III). The former is the first example of a porphyrin complex of an actinide element while the latter, with the previously reported complexes of scandium (III)[3] and lanthanum (III),[2] completes the IIIB subgroup.

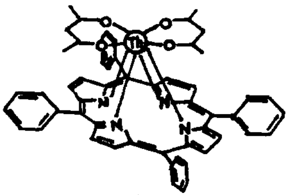
The syntheses were accomplished by a procedure similiar to that used for the lanthanide elements.[2] A 1,2,4-trichlorobenzene solution (75 ml) of TPP (1.0 g, 1.63×10^{-3} mol) and hydrated tris (2,4-pentanedionato)yttrium (2.0 g, 5.17×10^{-3} mol) was refluxed for 3 to 4 hrs (214°) after which time the solvent was removed under reduced pressure (∿200°). The product was purified by chromatography on neutral alumina and recrysta-lized from chloroform-methanol. *Anal.*[4] Calcd. for $Y(C_{44}H_{28}N_4)(C_5H_7O_2)$ C, 73.50; H, 4.37; N, 7.00; TPP; 76.5%; Found: C, 70.33; H, 4.13; N, 6.97; TPP, 75.0%. The mass spectrum (obtained on a MS9 spectrometer at 70 eV with a probe temperature of 400°) showed a parent ion at m/e 800 and a peak at m/e 701 consistent with the loss of an acetylacetonate fragment (acac, $C_5H_7O_2$) from the parent ion. As expected, the uv-visible spectrum, shown in Fig 1, closely resembles those of Cd(II)TPP[5] and the lanthanide complexes of TPP.[2] The complex is stable towards air and water in water-organic solvent mixtures. When treated with hydrogen chloride gas in organic solvent it is quantitatively converted into the green dication,[6] H_4TPP^{2+}. The proton nmr spectrum of Y(TPP)acac exhibits resonances (ppm from TMS) at -8.83 singlet (pyrrole); -8.13 multiplet (ortho); -7.78 multiplet (meta and para); -1.93 singlet (acac methyl) with integrated areas consistent with these assignments. The infrared spectrum shows stretching frequencies at 1510 and 1595 cm^{-1} in agreement with peaks reported by Buchler et al.[3] for a number of metalloporphyrin acac complexes. No peaks characteristic[3] of coordinated acetate (which could have been formed by pyrolosis during the course of high temperature synthesis) were observed, although minor peaks attributable to complexes of this ligand were observed in the mass spectrum.[7]

The thorium complex was synthesized and purified in a manner identical to that of Y(TPP)acac except that 2.0 g (3.18×10^{-3} mol) of *tetrakis*(2,4-pentanedionato)thorium (IV) was employed as the source of metal. *Anal.*[4] Calcd. for $Th(C_{44}H_{28}N_4)(C_5H_7O_2)_2$ C, 62.19; H, 4.03; N, 5.37; TPP, 58.7%; Found: C, 60.68, H, 4.12, N, 5.60; TPP, 58.8%. The uv-visible spectrum of $ThTPP(acac)_2$ is shown in Fig. 1. Like Y(TPP)acac it is stable to air and water. It reacts rapidly with hydrogen chloride to form H_4TPP^{2+}, but at a somewhat slower rate than the yttrium complex. The mass spectrum (conditions as for Y(TPP)acac) shows a parent peak at m/e 1042 to be expected for ThTPP $(acac)_2$ and a peak at m/e 943 attributable to the loss of an acac fragment. The proton nmr spectrum has peaks (ppm from TMS) at -8.87 singlet (pyrrole); -8.27 multiplet (ortho); -7.77 multiplet (meta and para); -4.13 singlet (acac-methine); -1.10 singlet (acac-methyl), with integrated areas consistent with these assignments for two acac and one TPP ligand per complex. Infrared absorptions at 1520 and 1595 cm^{-1} are consistent with coordinated acac ligands.[3]

In the absence of structural information we tentatively assign the yttrium complex the six-coordinate structure 1, and anticipate that the metal will be considerably out of the porphyrin plane. Again tentatively, we propose the structure of the thorium complex to involve eight-coordination as shown by 2. Of the twelve metalloporphyrin coordination types proposed by Buchler et al.[8] structures 1 and 2 correspond to types G and M, respectively. In



1



2

the solid state, structures involving dimerization through bridging acac ligands to achieve higher coordination numbers is by no means ruled out.

Among the useful applications we anticipate, the thorium complex reported here represents the heaviest metal for which a porphyrin complex is known, thorium complexes of naturally occurring porphyrin ligands would have obvious applications in the x-ray crystallography of biological macromolecules, provided the appropriate reconstitutions can be carried out.[9] Yttrium porphyrin complexes might be excellent fluorescent probes for studies of biological macromolecules.

Acknowledgements. This work was supported by the National Science Foundation through Grant GP 37577X. We thank Mr. R. F. Venteicher for helpful discussions.

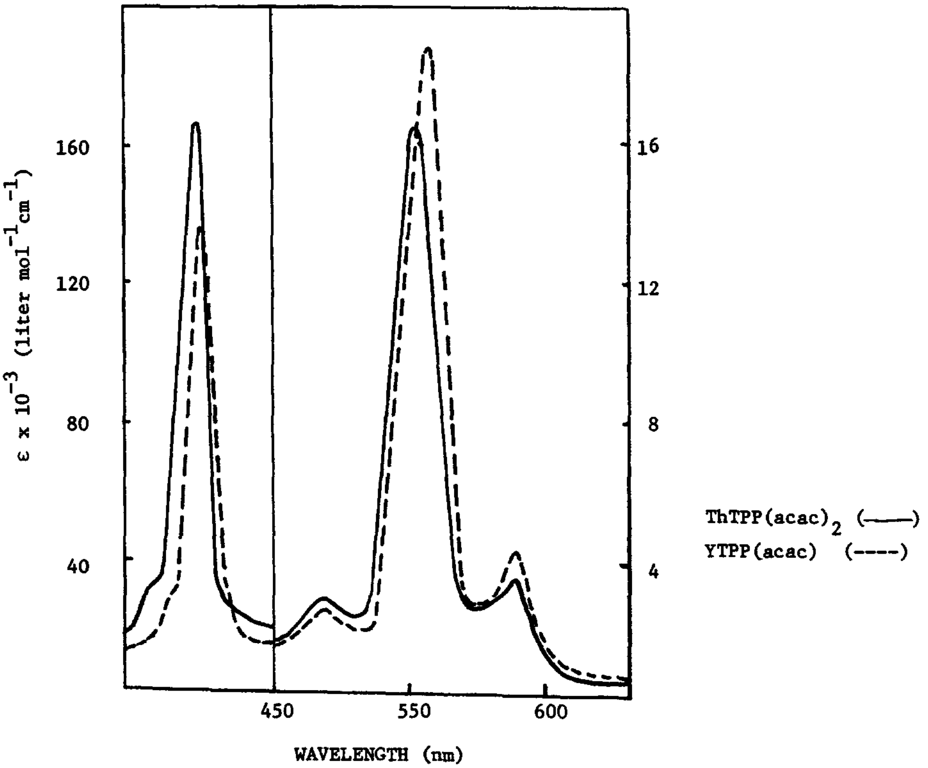


Figure 1. Electronic spectrum of 2,4-pentanedianato-meso-tetraphenylporphine-yttrium(III) and thorium (IV) in dimethyl sulphoxide at room temperature.

References

(1) See for instance D. Ostfeld and M. Tsutsui, *Accounts Chem. Res.*, 7, 52 (1974).

(2) C.-P. Wong, R. F. Venteicher, and W. DeW. Horrocks, Jr., *J. Amer. Chem. Soc.*, 96, 7149 (1974).

(3) J. W. Buchler, G. Eikelmann, L. Puppe, K. Rohbock, H. H. Schneehage, and D. Weck, *Justus Liebigs Ann. Chem.*, 745, 135 (1971).

(4) Elemental analyses were performed by Galbraith Laboratories, Inc., Knoxville, Tenn. TPP was determined spectrophotometrically as the H_4TPP^{2+} cation.

(5) G. D. Dorough, J. R. Miller, and F. M. Huenneken, *J. Amer. Chem. Soc.*, 73, 4315 (1951).

(6) A. Stone and E. B. Fleischer, *J. Amer. Chem. Soc.*, 90, 2735 (1968).

(7) These could easily have formed in the high temperature probe.

(8) J. W. Buchler, L. Puppe, K. Rohbock, and H. H. Schneehage, *Ann. N. Y. Acad. Sci.*, 206, 116 (1973).

(9) Our successful reconstitution of ytterbium(III) mesoporphyrin IX into apomyoglobin demonstrates that highly out-of-plane metalloporphyrins and derivatives of the bulky acetylacetonate are no obstacles to reconstitution. *Biochem. Biophys. Res. Comm.* (in press).