Inorganica Chimica Acta, 90 (1984) L73–L74

Synthesis and Characterization of Tin(II) Tetraphenylporphyrin

JOHN T. LANDRUM*

Department of Chemistry, Florida International University, Miami, Fla. 33199, U.S.A.

M. AMINI and J. J. ZUCKERMAN

Department of Chemistry, University of Oklahoma, Norman, Okla. 73019, U.S.A.

Received July 23, 1984

With the exception of the lead(II) porphyrin [1] little is known about the porphyrin complexes of the divalent group IVB elements. This is due principally to the difficulties in their preparation. The earliest solution evidence for a tin(II)–porphyrin association was obtained in the late 1960's [2]. We report here the first synthesis of a tin(II) porphyrin as an analytically pure, crystalline solid. A study [3] of the electrochemistry of the well-characterized tin(IV) and germanium(IV) porphyrins indicates that ring reduction occurs prior to reduction at the metal center. This is consistent with our own electrochemical measurements in which we observe no redox occuring between the ring-reduction waves and the ring-oxidation waves in the cyclic voltamogram of tin(IV) tetraphenylporphyrin. Attempts to prepare tin(II) porphyrins from tin(IV) porphyrins using the chemical reductant, $NaBH_4$ [4], and more recently in our laboratory the atom-transfer reductant $Cr(acac)_2$ have also been unsuccessful in producing the desired tin(II) porphyrin complex. Both reagents result in isolation of the tin(IV) chlorin. The barrier to reduction of tin(IV) porphyrins is perhaps best rationalized in terms of the large change in ionic radius of the tin ion upon reduction and the expected large out-of-plane distortion of the tin(IV) ion required prior to reduction to satisfy the Franck-Condon principle since tin(II) cannot be accommodated within the plane of the macrocycle. This kinetic stability of the 4+ valence state does not argue against a reasonable thermodynamic stability for the metalloid-porphyrin complex when the metalloid has a formally 2+ oxidation state. Synthesis of these complexes is, however, restricted to direct insertion of the metalloid as a 2+ ion.

Our synthesis of tin(II) tetraphenylporphyrin (SnTPP) takes advantage of the direct incorporation of tin(II) and the relative solubilities of $SnCl_2$ and the product. In a typical reaction, carried out in a Vacuum Atmospheres glove box, 500 mg of anhydrous $SnCl_2$ dissolved in 15–20 ml of hot THF were allowed to react with 500 mg of H_2TPP in the presence of 1–2 ml of dry pyridine. After a 5–10 min reflux the solution was cooled to room temperature and the crystalline product collected on a medium porosity sintered-glass frit in 70–75% yield.**

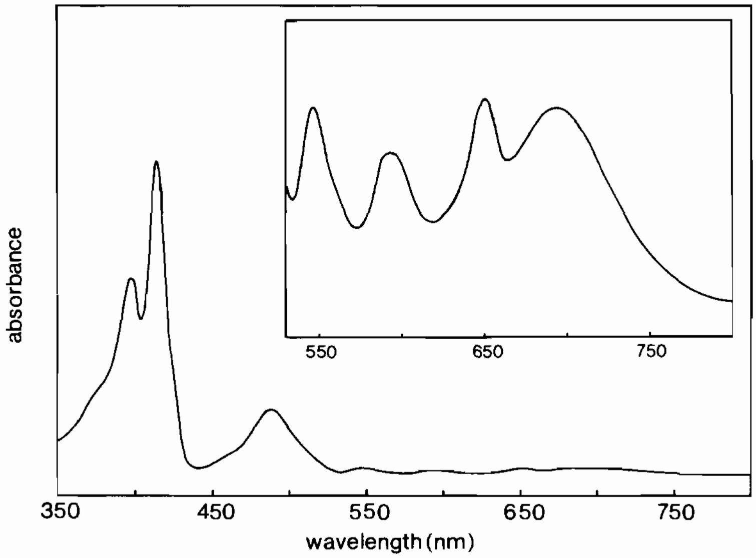

Fig. 1. Visible spectrum of SnTPP in THF.

---

*Author to whom correspondence should be addressed.

**Analysis performed by Galbraith Laboratories, Knoxville, Tenn. for $C_{44}H_{56}N_4Sn$: Calcd: C, 72.25; H, 3.86; N, 7.66%. Found: C, 72.12; H, 4.00; N, 7.49%.

0020-1693/84/$3.00

The tin(II) porphyrin is characterized as having a p-type hyperporphyrin spectrum[†] exhibiting 2 maxima in the Soret region in addition to several bands in the visible and near IR, Fig. 1, consistent with the earlier *in situ* preparation [5]. The assignment of the formal oxidation state of the tin ion is confirmed by the tin-119m Mössbauer spectrum of the solid which exhibits a typical large positive isomer shift, 2.96 ± 0.03 mms^{-1}, relative to SnO_2, characteristic of tin(II) [6]. The quadrupole splitting (1.19 ± 0.06 mms^{-1}) is well resolved and is consistent with the expectation of low axial symmetry at the tin coordination center.

Preliminary studies on the reactivity of SnTPP indicate that the pure compound is only slowly oxidized by molecular oxygen when dissolved in THF or benzene. No reaction was observed between SnTPP and the hydroxylic solvents H_2O and EtOH or with dimethylketone. The pure solid is stable in air for periods as long as 12 h, showing no sign of oxidation when subsequently returned to the glove box and dissolved in anaerobic solvents. Efforts to characterize further the reactivity of SnTPP are underway.

An analogous synthesis of the previously unknown germanium(II) TPP was attempted. The compound has yet to be isolated as an analytically pure solid, however, the product is air sensitive, undergoing oxidation to the germanium(IV) complex. Efforts to fully characterize the compound are now in progress.

Acknowledgements

Support for this work obtained from the National Science Foundation (NSF #PRM-8115166) and the donors of the Petroleum Research Fund (PRF #13247-GB3) is gratefully acknowledged by J. T. L.

References

1 a) A. Treibs, *Ann. Chem.*, *728*, 115 (1969).
b) G. D. Dorough, J. R. Miller and F. M. Huennekens, *J. Am. Chem. Soc.*, *73*, 4315 (1951).
2 B. F. Burnham and J. J. Zuckerman, *J. Am. Chem. Soc.*, *92*, 1547 (1970).
3 J.-H. Fuhrhop, K. Kadish and D. G. Davis, *J. Am. Chem. Soc.*, *95*, 5140 (1973).
4 D. G. Whitten, J. C. Yau and F. A. Carroll, *J. Am. Chem. Soc.*, *93*, 2291 (1970).
5 P. Sayer, M. Gouterman and C. R. Connel, *Acc. Chem. Res.*, *15*, 73 (1982).
6 J. J. Zuckerman, *Adv. Organomet. Chem.*, *9*, 21 (1970).

[†] Visible spectrum of SnTPP: wavelength-nm (extinction coefficient, L/mol cm): 397(6.4 × 10^4), 414(9.4 × 10^4), 488(2.2 × 10^4), 547(2.3 × 10^3), 592(1.9 × 10^3), 649(2.6 × 10^3), 692(2.2 × 10^3).