

THE REDOX PROPERTIES OF TIN(IV) - AND GERMANIUM(IV) -  
OCTAETHYL PORPHINATO - DIHYDROXIDES  
AS COMPARED TO OTHER METALLO - OCTAETHYLPORPHINS

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A three fold excess of a saturated methanol solution of N - bromosuccinimide was mixed with chloroform solutions of metal complexes of octaethylporphin (OEP)<sup>x</sup> ( $\sim 10^{-4}$  molar) with the following central ions : Mg<sup>2+</sup>, Ca<sup>2+</sup>, Al<sup>3+</sup>, Ga<sup>3+</sup>, In<sup>3+</sup>, Si<sup>4+</sup>, Ge<sup>4+</sup>, Sn<sup>4+</sup>, Pb<sup>2+</sup>, Sc<sup>3+</sup> xx, TiO<sup>2+</sup>, VO<sup>2+</sup>, Cr<sup>3+</sup>, Mn<sup>3+</sup>, Fe<sup>3+</sup>, Co<sup>2+</sup>, Ni<sup>2+</sup>, Cu<sup>2+</sup>, Ag<sup>2+</sup> and Zn<sup>2+</sup>.

OEP itself and its di-cation were treated identically. All compounds, with the exception of Sn(IV) - OEP - (OH)<sub>2</sub><sup>x</sup> and Ge(IV) - OEP - (OH)<sub>2</sub> were irreversibly oxidized to brown compounds with no absorption bands above 550 nm. The intermediacy of a broad absorbance between 800 and 900 nm (possibly a metallo isoporphyrin<sup>1</sup>) was often observed.

Sn(IV) - OEP - (OH)<sub>2</sub> and Ge(IV) - OEP - (OH)<sub>2</sub> were the only stable compounds under the conditions indicated; Si(IV) - OEP - (OH)<sub>2</sub><sup>2</sup> and Pb - OEP were not stable. We explain the unique inertness of the tin and germanium complexes by the strong positive electrostatic field which is exerted on the porphin ligand by the central ion. The different behavior of the silicon complex may be explained by assuming, that in this case the bonds of the central ion to the porphin - nitrogens as well as to the axial hydroxyl ions have a less ionic character than with the more metallic tin and germanium. The facts, that silicon prefers covalent bonds to oxygen, as in the silanols,

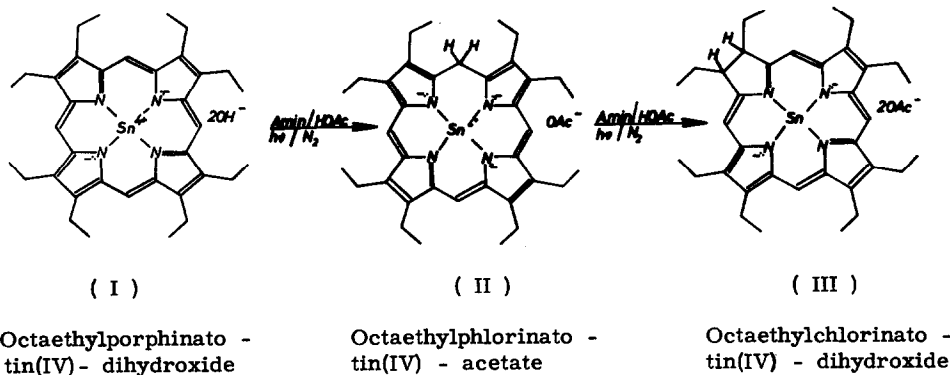
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<sup>x</sup> The following abbreviations are used : OEP = Octaethylporphin ; OEC = Octaethylchlorin ; M(IV) - OEP - (OH)<sub>2</sub> = Octaethylporphinato - metal(IV) - dihydroxides  
other metal complexes are described analogously ; "Amine" = N, N, N', N' - Tetramethyl - ethylenediamine ; OAc = acetate anion  
xx The procedure for synthesizing Sc(III)-OEP-(OH)<sub>2</sub> was kindly provided by Dr. J. Buchler

and that it usually has a coordination number of four, make it understandable that silicon does not pull as much electron density toward the central ion as tin and germanium do. The less ionized state of the silicon compound is somewhat substantiated by the high volatility of the trimethyl - siloxy derivatives <sup>2</sup> and the low extinction coefficient of the main absorption band [  $\lambda_{\max}$  408 nm (330,000)] as compared to Sn(IV) - OEP - (OH)<sub>2</sub> [ 406 nm (400,000) ] and Ge(IV) - OEP - (OH)<sub>2</sub> [404 nm (420,000)], whose extinction coefficients are very close to that of the OEP - di-cation [ 403 nm (400,000) ].

The assumed positive charge on the ligand in the tin and germanium complexes should on the other hand facilitate a reduction of, or any other nucleophilic addition to, the porphin macrocycle. This in fact has been reported <sup>3,4,5</sup>, and low potentials in polarographic reduction of tin(IV) - porphyrins <sup>6</sup> also support this view. Basing our procedure on the work of MAUZERALL <sup>7</sup>, we have developed a new photo-reduction of Sn(IV) - OEP - (OH)<sub>2</sub>. A solution of this compound in N,N,N',N' - Tetramethyl - ethylenediamine/acetic acid (1:1) was irradiated under nitrogen with a 1000 W incandescent lamp, giving Sn(IV) - OEC - (OH)<sub>2</sub> as determined by electronic spectra <sup>4</sup>. We used this mixture, rather than WHITTEN's reaction conditions (saturated SnCl<sub>2</sub> solutions with the free base OEP), because this reduction took place rather slowly and always produced a mixture of Sn(IV) - OEC - (OH)<sub>2</sub> and Sn(IV) - 1,2,3,4 - tetrahydro - OEP - (OH)<sub>2</sub>.

All the metal complexes mentioned at the beginning of this communication were tried in the photoreduction, and again positive results were only obtained with the tin and germanium complexes. The course of the photoreduction was also followed spectroscopically in the case of Sn(IV) - OEP - (OH)<sub>2</sub>; irradiation at -20° C under nitrogen produced a compound with a broad absorption peak at 785 nm and a narrow one at 440 nm (O.D. ratio approx. 1 : 3) together with Sn(IV) - OEC - (OAc)<sub>2</sub>. We think the first compound is Sn(IV) - octaethylphlorin - acetate (II), in analogy to reduction products already reported, e.g. by CLOSS and CLOSS <sup>8</sup>, WOODWARD<sup>9</sup>, MAUZERALL<sup>7</sup>, and INHOFFEN et al. <sup>10</sup>. On standing in the dark under nitrogen this metal-phlorin slowly and irreversibly decomposes to compounds with no characteristic spectrum,



except for a broad peak at 630 nm. With air it is immediately reoxidized to Sn(IV) - OEP - (OAc)<sub>2</sub>. On further irradiation with incandescent light at room temperature, or at -20° C under nitrogen, it is quantitatively converted to Sn(IV) - OEC - (OAc)<sub>2</sub> (III). No intermediate absorption peak between 450 and 800 nm was observed in the course of this reaction. We believe this to be good evidence for the direct light induced conversion of a phlorin into a chlorin. Hitherto, the intermediacy of a "porphomethene", absorbing at 500 nm, was always observed in photo-reductions of porphyrins <sup>6, 11</sup>. The unusual reactivity of the peripheric double bond adjacent to the methylene bridge, as compared to the opposite methine bridge in (II) may again be explained by the strong positive field induced by the central Sn<sup>4+</sup> - ion. WHITTEN'S conditions <sup>5</sup> were also found to produce some intermediate phlorin.

In order to confirm the structure ( III ) for the final product of the photoreduction we looked for a demetalation procedure for Sn(IV) - chlorins. EISNER'S method <sup>12</sup>, reduction with lithium in an amine at high temperatures, led only to OEP. Reaction of ( III ) with sodium borohydride in chloroform/ethanol/ammonia = 1:8:1 under nitrogen, and subsequent acidification with deoxygenated concentrated hydrochloric acid led to the desired OEC in an overall yield from Sn(IV) - OEP - (OH)<sub>2</sub> of about 20%. The low yield of the demetalation is probably due to some side reactions with sodium borohydride.

KENNEY <sup>13</sup> has reported that sodium borohydride reduces tin(IV) to tin(II) in phthalocyanine complexes. Analogously we presume that the same reduction takes place with Sn(IV) - OEC - (OH)<sub>2</sub> yielding Sn(II) - OEC, whose central ion can be easily replaced by two protons. We also tried Kenney's second reduction method with SnCl<sub>2</sub> in quinoline, but subsequent acidification of this reaction mixture did not yield any free chlorin or porphyrin base. Sn(IV) - OEP - (OH)<sub>2</sub> could be demetalized in 70% yield by the above sodium borohydride procedure, but no ammonia was needed as with the tin-chlorin. If air was not rigorously excluded, no demetalation was achieved. Neither the amine/acetic acid mixture with (I) or (III) used in this work, nor WHITTEN's saturated SnCl<sub>2</sub> solutions after chlorin formation yielded any free chlorins on acidification with concentrated hydrochloric acid under nitrogen, so that one may conclude that no Sn(II) - complex is formed under the conditions of the photo-reductions. Thus the unique qualities of tin(IV) - porphyrins seem not to relate to any special redox properties of the central ion as suggested by CORWIN <sup>3</sup> but rather the coordination properties of the Sn<sup>4+</sup> - cation.

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