

## Comparison of Back-Bonding in Osmium(II) versus Iron(II) Octaethylporphyrins via Resonance Raman Spectroscopy

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Received October 27, 1987

Resonance Raman spectra (RR) are compared for the carbonyl-pyridine [(CO)(py)], bis(pyridine) [(py)<sub>2</sub>], and bis(ammine) [(NH<sub>3</sub>)<sub>2</sub>] adducts of Os(II) and Fe(II) octaethylporphyrin (OEP). These complexes represent a series in which back-bonding from the metal to the porphyrin ring (equatorial back-bonding) is increased from a minimum (carbonyl-pyridine) to a maximum extent (bis(ammine)) through an intermediate value (bis(pyridine)). The frequency-shift patterns that are exhibited by the porphyrin skeletal modes indicate that only the  $\nu_{11}$  and  $\nu_4$  modes are reliable indicators of equatorial back-bonding and that  $\nu_{11}$  is the more reliable indicator of the two. Comparison of the shifts for the complexes of a given metal ion suggests that for both OsOEP(py)<sub>2</sub> and FeOEP(py)<sub>2</sub> approximately two-thirds of the back-donated electron density is directed toward the porphyrin ring while the other third is directed toward the axial pyridine ligands. Comparison of the shifts for the Os(II) versus Fe(II) complexes of a given adduct suggests that the absolute back-bonding capability of the former metal ion is 50% larger than that of the latter.

### Introduction

Metalloporphyrins that contain Ru(II) and Os(II) have attracted interest because of their unusual electronic properties and their analogy to the biologically important Fe(II) complexes.<sup>1-12</sup> The divalent heavy-metal systems exhibit optical spectra that are blue shifted relative to those of "normal" metalloporphyrins. This spectral characteristic has been attributed to back-donation of electron density from the filled  $d_x$  orbitals of the divalent metal ion into the empty  $e_g^*$  orbitals of the porphyrin macrocycle.<sup>7,8</sup> The electronic properties of low-spin iron(II) porphyrins are also influenced by this type of back-bonding although to a lesser extent than either the Ru(II) or Os(II) complexes. The extent of back-bonding to the porphyrin ring can be attenuated if  $\pi$ -acceptor ligands such as pyridine and/or carbon monoxide are axially ligated to the metal ion.<sup>10</sup> The interplay of axial versus equatorial back-bonding ultimately determines the charge distribution in the complex.

Certain vibrational frequencies of the porphyrin macrocycle are sensitive to the extent of back-bonding.<sup>13-15</sup> In the study reported herein, we exploit this sensitivity and use resonance Raman (RR) spectroscopy to compare the extent of back-bonding in a series of osmium(II) porphyrins with that present in the analogous Fe(II) systems. The complexes that are examined include M<sup>II</sup>OEP(CO)(py), M<sup>II</sup>OEP(py)<sub>2</sub>, and M<sup>II</sup>OEP(NH<sub>3</sub>)<sub>2</sub> (OEP = octaethylporphyrin; py = pyridine). The carbonyl-pyridine complexes are representative of systems in which equatorial back-bonding is expected to be minimal because the strong  $\pi$ -acceptor capabilities of CO direct most, if not all, of the available charge density toward this axial ligand.<sup>10</sup> On the other hand, both

axial and equatorial back-bonding pathways are expected to be active in the bis(pyridine) complexes because of the more comparable  $\pi$ -acceptor capabilities of the porphyrin and pyridine ligands.<sup>10,12</sup> For the bis(ammine) complexes, all of the back-bonding is equatorial. Together, the data for the carbonyl-pyridine and bis(ammine) adducts establish a scale for the evaluation of equatorial versus axial back-bonding in systems where both pathways are active.

### Experimental Section

The various Fe(II) and Os(II) complexes were prepared according to previously reported methods.<sup>7,8,16-18</sup> The identities of the compounds were confirmed via UV-vis absorption spectroscopy. All solvents were spectral grade and used without further purification with the exception of 2-picoline, which was distilled over calcium hydride prior to use.

The RR spectra were recorded with the optics in a 90° scattering configuration with instrumentation previously described.<sup>19</sup> Excitation wavelengths were provided by the discrete outputs of Ar ion (Coherent Innova 15UV) and Kr ion (Coherent K2000) lasers and a tunable dye (Coherent 590-03) laser utilizing Rhodamine 560 (Exciton Chemical Co.). The RR samples were either suspended in compressed pellets with a supporting medium of Na<sub>2</sub>SO<sub>4</sub> or KBr (2-3 mg of guest/100 mg of host) or dissolved in rigorously degassed benzene, methylene chloride, or 2-picoline (~0.1 or 1.0 mM for B- or Q-band excitation, respectively). The RR frequencies that were observed for solid versus solution samples were found to be within 2-3 cm<sup>-1</sup> of one another. Both FeOEP(NH<sub>3</sub>)<sub>2</sub> and OsOEP(NH<sub>3</sub>)<sub>2</sub> were found to undergo rapid oxidation when subjected to laser irradiation under ambient conditions. Oxidation was evident in the pellet samples even at the lowest usable laser powers. No oxidation was detected for these complexes in rigorously degassed solutions. The OsOEP(CO)(py) complex is also photolabile; therefore, minimal laser powers were used to obtain the RR spectra.

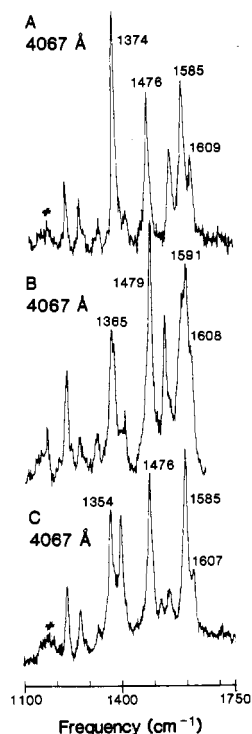
### Results and Discussion

The high-frequency regions of the B- and Q-state excitation RR spectra of OsOEP(CO)(py), OsOEP(py)<sub>2</sub>, and OsOEP(NH<sub>3</sub>)<sub>2</sub> are shown in Figures 1 and 2, respectively. The analogous RR spectra of Fe(OEP)(py)<sub>2</sub> and FeOEP(NH<sub>3</sub>)<sub>2</sub> are shown in Figures 3 and 4, respectively. The frequencies of a number of back-bonding and/or core-size sensitive RR bands for the various Os(II) and Fe(II) complexes are summarized in Table I. RR spectra of FeOEP(CO)(py) have been previously reported by Spaulding et al.<sup>20</sup> and the pertinent vibrational frequencies for this complex are also included in Table I.

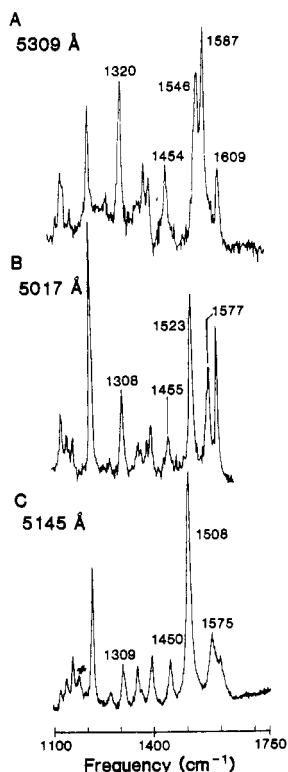
Comparison of the vibrational frequencies of the  $\nu_{10}$ ,  $\nu_2$ ,  $\nu_{19}$ , or  $\nu_3$  modes of the three Os(II) or the three Fe(II) complexes

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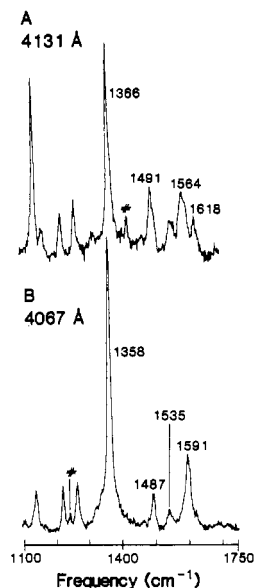


**Figure 1.** High-frequency region of the B-state excitation RR spectra of (A) OsOEP(CO)(py) in a benzene solution, (B) OsOEP(py)<sub>2</sub> in a Na<sub>2</sub>SO<sub>4</sub> pellet, and (C) OsOEP(NH<sub>3</sub>)<sub>2</sub> in a benzene solution. The symbol # indicates solvent peaks.

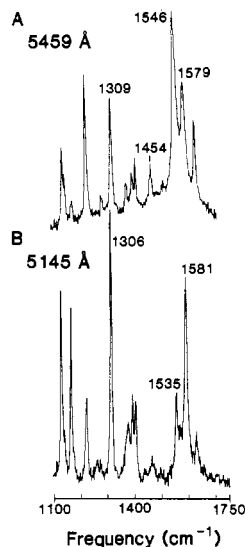


**Figure 2.** High-frequency region of the Q-state excitation RR spectra of (A) OsOEP(CO)(py) in a Na<sub>2</sub>SO<sub>4</sub> pellet, (B) OsOEP(py)<sub>2</sub> in a Na<sub>2</sub>SO<sub>4</sub> pellet, and (C) OsOEP(NH<sub>3</sub>)<sub>2</sub> in a benzene solution. The symbol # indicates solvent peaks.

reveals no obvious trends that can be correlated with charges in the axial ligands. For example,  $\nu_{10}$  occurs at essentially the same frequency for all three Os(II) complexes ( $\sim 1608$  cm<sup>-1</sup>). The frequencies of  $\nu_{10}$  for FeOEP(py)<sub>2</sub> and FeOEP(NH<sub>3</sub>)<sub>2</sub> are also nearly the same ( $\sim 1619$  cm<sup>-1</sup>); however, this mode is at a considerably higher frequency in FeOEP(CO)(py) (1636 cm<sup>-1</sup>).



**Figure 3.** High-frequency region of the B-state excitation RR spectra of (A) FeOEP(py)<sub>2</sub> in a methylene chloride solution and (B) FeOEP(NH<sub>3</sub>)<sub>2</sub> in a 2-picoline solution. The symbol # indicates solvent peaks.



**Figure 4.** High-frequency region of the Q-state excitation RR spectrum of (A) FeOEP(py)<sub>2</sub> in a methylene chloride solution and (B) FeOEP(NH<sub>3</sub>)<sub>2</sub> in a KBr pellet.

Other high-frequency porphyrin skeletal modes such as  $\nu_{28}$ ,  $\nu_{29}$ ,  $\nu_{20}$ , and  $\nu_{12}$  (not listed) also fail to exhibit shift patterns that can be correlated with changes in the axial ligands. Inasmuch as the extent of equatorial back-bonding must change along the series bis(ammine) to carbonyl-pyridine, the lack of systematic shift patterns for the above-mentioned modes ( $\nu_{10}$ ,  $\nu_2$ ,  $\nu_{19}$ ,  $\nu_3$ ,  $\nu_{28}$ ,  $\nu_{29}$ ,  $\nu_{20}$  and  $\nu_{12}$ ) indicates that they are not reliable indicators of equatorial back-bonding.

Unlike the other porphyrin skeletal vibrations, the  $\nu_{11}$  and  $\nu_4$  modes of both the Os(II) and Fe(II) complexes exhibit large, systematic shifts as the axial ligands are changed. The frequencies of the  $\nu_{11}$  vibrations of OsOEP(py)<sub>2</sub> and OsOEP(NH<sub>3</sub>)<sub>2</sub> are 23 and 40 cm<sup>-1</sup> lower, respectively, than that of OsOEP(CO)(py) while the frequencies of the  $\nu_4$  vibrations of the bis(pyridine) and bis(ammine) adducts are 9 and 20 cm<sup>-1</sup> lower, respectively, than that of OsOEP(CO)(py). Similarly, the frequencies of the  $\nu_{11}$  vibrations of FeOEP(py)<sub>2</sub> and FeOEP(NH<sub>3</sub>)<sub>2</sub> are downshifted 21 and 32 cm<sup>-1</sup>, respectively, from that of FeOEP(CO)(py) whereas the  $\nu_4$  vibrations of the bis(pyridine) and bis(ammine) complexes are downshifted 14 and 22 cm<sup>-1</sup>, respectively, from that of FeOEP(CO)(py). Both the magnitude and the direction of the

**Table I.** Resonance Raman Frequencies ( $\text{cm}^{-1}$ ) for the  $\text{M}^{\text{II}}\text{OEP}(\text{L})\text{L}'$  Complexes

mode <sup>a</sup>	OsOEP(L)L'				FeOEP(L)L'			
	$\nu_{\text{calcd}}^b$	L = CO; L' = py	L = L' = py	L = L' = NH <sub>3</sub>	$\nu_{\text{calcd}}^b$	L = CO; L' = py <sup>c</sup>	L = L' = py	L = L' = NH <sub>3</sub>
$\nu_{10}$ (B <sub>1g</sub> )	1614	1609	1608	1607	1633	1636	1618	1620
$\nu_2$ (A <sub>1g</sub> )	1582	1585	1591	1585	1593	1588	1584	1591
$\nu_{19}$ (A <sub>2g</sub> )	1564	1567	1577	1575	1587	1588	1579	1583
$\nu_{11}$ (B <sub>1g</sub> )	1556	1546	1523	1506	1565	1567	1546	1535
$\nu_3$ (A <sub>1g</sub> )	1486	1476	1479	1476	1504	1503	1491	1487
$\nu_4$ (A <sub>1g</sub> )	1375	1374	1365	1354	1379	1380	1366	1358

<sup>a</sup> Mode numbering and assignments follow ref 21. <sup>b</sup>  $\nu_{\text{calcd}} = K(A - d)$ , where  $K(A) = 415$  (5.94), 243 (8.56), 507.7 (5.13), 197 (9.95), 383 (5.93), and 80.73 (19.08) for  $\nu_{10}$ ,  $\nu_2$ ,  $\nu_{19}$ ,  $\nu_{11}$ ,  $\nu_3$ , and  $\nu_4$ . The parameters for  $\nu_{10}$ ,  $\nu_2$ ,  $\nu_{11}$ , and  $\nu_3$  are those reported for metallo-OEP complexes;<sup>22</sup> the parameters for  $\nu_{19}$  and  $\nu_4$  were calculated from the vibrational data reported in ref 20.  $d = 2.05$  Å for OsOEP(L)L', the average of the C<sub>1</sub>-N distances reported for RuOEP(py)<sub>2</sub><sup>23</sup> and RuOEP(CO)(py),<sup>24</sup> respectively;  $d = 2.004$  Å for FeOEP(L)L', the C<sub>1</sub>-N distance reported for (tetraphenylporphyrinato)(2-methylimidazole)iron.<sup>25</sup> <sup>c</sup> Taken from ref 20. The frequencies of  $\nu_2$  and  $\nu_{11}$  are not given in this reference; the frequency listed for  $\nu_{11}$  is that reported for Fe(mesoporphyrin)(CO)(py).<sup>17</sup>

shifts of the  $\nu_{11}$  and  $\nu_4$  modes are consistent with increased equatorial back-bonding along the series bis(amine) > bis(pyridine) > carbonyl-pyridine. The sensitivity of the  $\nu_4$  vibration to the extent of equatorial back-bonding is well established.<sup>13,14</sup> The back-bonding sensitivity of the  $\nu_{11}$  vibration has also been previously noted;<sup>13,14</sup> however, the results reported here suggest that this mode is in fact a better indicator of the extent of back-bonding to the porphyrin ring than is  $\nu_4$ .

In order to use the frequencies of the porphyrin skeletal modes as indicators of the relative extent of equatorial back-bonding in metalloporphyrins that contain metal ions of different ionic radius, it is necessary to account for the effects of porphyrin core size, C<sub>1</sub>-N, on the vibrational frequencies.<sup>14,22,26</sup> The ability to separate the effects of core size from the effects of back-bonding served as the starting point for the assessment by Spiro and co-workers of the relative extent of back-bonding in ruthenium(II) versus iron(II) porphyrins.<sup>10</sup> These workers found that the frequencies of the porphyrin skeletal modes of RuOEP(CO)(py) and RuOEP(CO)(CH<sub>3</sub>OH) fit reasonably well on the  $\nu$  versus C<sub>1</sub>-N plots despite the large back-bonding capability of the Ru(II) ion. This result indicates that the CO ligand effectively eliminates equatorial back-bonding in the Ru<sup>II</sup>OEP complexes and establishes the frequencies of the CO adducts as a reference point to which the vibrational data for other ruthenium porphyrin complexes can be compared.

The skeletal-mode frequencies that are expected for the Os(II) and Fe(II) OEP complexes on the basis of core size are listed in Table I along with the observed frequencies for the various complexes. Because structural data is not available for osmium(II) porphyrins, the value of C<sub>1</sub>-N for these systems was assumed to be the same as that of Ru<sup>II</sup> OEP complexes. The two different types of heavy-metal porphyrins are expected to have comparable core sizes.<sup>27</sup> The frequencies of  $\nu_{10}$ ,  $\nu_2$ ,  $\nu_{11}$ , and  $\nu_3$  were calculated by using the C<sub>1</sub>-N parameters obtained for metallo-OEP complexes by Oertling et al.<sup>22</sup> These workers did not report parameters for  $\nu_{19}$  and  $\nu_4$ . The frequencies of these modes were calculated from parameters obtained from a least squares fit of the metallo-OEP RR data reported in ref 20.

The observed frequencies of the various skeletal modes of FeOEP(CO)(py)<sup>20</sup> are essentially identical with those calculated on the basis of core size (Table I). The increasingly downshifted frequencies of the  $\nu_{11}$  and  $\nu_4$  modes of FeOEP(py)<sub>2</sub> and FeOEP(NH<sub>3</sub>)<sub>2</sub> relative to those of FeOEP(CO)(py) provide a measure of the increase in the extent of equatorial back-bonding. The shifts of both the  $\nu_{11}$  and  $\nu_4$  modes of FeOEP(NH<sub>3</sub>)<sub>2</sub> (32 and 21  $\text{cm}^{-1}$ , respectively) are approximately 1.5 times larger than the shifts

of these vibrations in FeOEP(py)<sub>2</sub> (22 and 14  $\text{cm}^{-1}$ , respectively). Both modes shifting by an identical factor only seems likely if the shifts are a linear function of the extent of equatorial back-bonding. If so, the porphyrin ligand of FeOEP(py)<sub>2</sub> is the recipient of two-thirds of the back-donated electron density while the two pyridine ligands share the other third of the back-donated density. This result is intuitively appealing because there are twice as many pyrrole as pyridine nitrogen atoms participating in back-bonding to the metal ion.

Comparison of the observed skeletal-mode frequencies of OsOEP(CO)(py) with those calculated on the basis of core size reveals that there are disparities for the  $\nu_{10}$  (5  $\text{cm}^{-1}$ ),  $\nu_{11}$  (10  $\text{cm}^{-1}$ ), and  $\nu_3$  (10  $\text{cm}^{-1}$ ) modes. On the other hand, the observed frequencies of  $\nu_2$ ,  $\nu_{19}$ , and  $\nu_4$  are in reasonable agreement with the calculated values. The disparity between the observed and calculated skeletal-mode frequencies of OsOEP(CO)(py) could indicate that osmium(II) porphyrins in general exhibit anomalous frequencies with respect to core size. This seems unlikely, however, considering that the frequencies of the skeletal modes of other metallo-OEP species that possess core sizes comparable to those of the Os<sup>II</sup> OEP complexes fit reasonably well on the  $\nu$  versus C<sub>1</sub> plots.<sup>10,26</sup> At this time, we are unable to provide an explanation that consistently accounts for the deviation of  $\nu_{10}$ ,  $\nu_{11}$ , and  $\nu_3$ , from the  $\nu$  versus C<sub>1</sub> plots.

A possible rationale for the disparity between the observed and calculated frequencies of  $\nu_{11}$  is that the back-bonding capability of Os(II) is sufficiently large that the CO ligand is not capable of accommodating all of the electron density that is available for back-donation. If so, equatorial as well as axial back-bonding pathways would be expected to be active in OsOEP(CO)(py). Equatorial back-bonding would lower the frequency of  $\nu_{11}$  from that calculated on the basis of core size. (It is not clear how  $\nu_{10}$  and  $\nu_3$  would be affected by equatorial back-bonding because these modes are not reliable back-bonding indicators.) As was noted,  $\nu_{11}$  is observed 10  $\text{cm}^{-1}$  lower than the calculated frequency. If the calculated rather than the observed frequency is used as the reference point, the  $\nu_{11}$  modes of OsOEP(py)<sub>2</sub> and OsOEP(NH<sub>3</sub>)<sub>2</sub> are downshifted by 33 and 50  $\text{cm}^{-1}$ , respectively, from the frequency observed for this vibration in OsOEP(CO)(py). These shifts would imply that the extent of equatorial back-bonding in OsOEP(NH<sub>3</sub>)<sub>2</sub> is 50% larger than that in OsOEP(py)<sub>2</sub>. This percentage is identical with that predicted for the relative extent of equatorial back-bonding in FeOEP(NH<sub>3</sub>)<sub>2</sub> versus FeOEP(py)<sub>2</sub>. The 33- and 50- $\text{cm}^{-1}$  shifts for the two Os(II) complexes compared with the 21- and 32- $\text{cm}^{-1}$  shifts for the two Fe(II) systems further suggest that the equatorial back-bonding in a given complex of the heavy metal is 50% larger than that in the analogous complex of the light metal.

Unlike the  $\nu_{11}$  mode, the  $\nu_4$  vibration of OsOEP(CO)(py) is observed at a frequency quite close to that calculated on the basis of core size. Regardless, the shift patterns that are observed for  $\nu_4$  suggest that the frequency of this mode of OsOEP(CO)(py) is lowered by back-bonding. In particular,  $\nu_4$  of OsOEP(py)<sub>2</sub> is 9  $\text{cm}^{-1}$  lower than  $\nu_4$  of OsOEP(CO)(py) whereas this mode of FeOEP(py)<sub>2</sub> is 14  $\text{cm}^{-1}$  lower than that of FeOEP(CO)(py). If the frequency of  $\nu_4$  of OsOEP(CO)(py) were not lowered by

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back-bonding, this result would imply that equatorial back-bonding in FeOEP(py)<sub>2</sub> is larger than that in OsOEP(py)<sub>2</sub>. This conclusion seems highly improbable. In addition,  $\nu_4$  of OsOEP(py)<sub>2</sub> is downshifted 9 cm<sup>-1</sup> from that of OsOEP(CO)(py) whereas  $\nu_4$  of OsOEP(NH<sub>3</sub>)<sub>2</sub> is downshifted 11 cm<sup>-1</sup> from that of OsOEP(py)<sub>2</sub>. The shifts for the analogous Fe complexes are 14 and 8 cm<sup>-1</sup>, respectively. The reversal in the ordering of the  $\nu_4$  shifts of the Os(II) versus Fe(II) complexes again suggests that the frequency of  $\nu_4$  is reduced by equatorial back-bonding. Collectively, these results suggest that the similarity between the observed and calculated frequencies of  $\nu_4$  for OsOEP(CO)(py) is fortuitous. This seems all the more likely considering that the frequency of the  $\nu_4$  mode of Ru(OEP)(CO)(py) is 1371 cm<sup>-1</sup>, which is lower than that of  $\nu_4$  of Os(OEP)(CO)(py) (1374 cm<sup>-1</sup>). It should also be noted that the correlation coefficient for the  $\nu$  versus C<sub>1</sub>-N plot of the  $\nu_4$  mode ( $r \sim 0.7$ ) of metallo-OEP complexes is much less

satisfying than those obtained for the other high-frequency skeletal modes ( $r \sim 0.95$ ). The poor correlation coefficient for the  $\nu_4$  mode is in large part due to the fact that metallo-OEP complexes with large core sizes deviate the most from the straight line generated by least-squares fitting of the data. Given this fact, the  $\nu_4$  mode is probably best used only as an indicator of the extent of equatorial back-bonding in different axial ligand adducts of a given metal ion. Thus, the  $\nu_{11}$  mode appears to be the most reliable indicator of the extent of equatorial back-bonding in metalloporphyrins in general.

**Acknowledgment.** This work was supported by Grant GM-36243 from the National Institute of General Medical Sciences.

**Registry No.** OsOEP(CO)(py), 51286-85-2; OsOEP(py)<sub>2</sub>, 51286-87-4; OsOEP(NH<sub>3</sub>)<sub>2</sub>, 72099-11-7; FeOEP(py)<sub>2</sub>, 19496-63-0; FeOEP(NH<sub>3</sub>)<sub>2</sub>, 61095-78-1.

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## Synthesis and Reactivity of $\sigma$ -Bonded Silicon Metalloporphyrins. Spectroscopic Characterization and Electrochemistry of (P)Si(R)<sub>2</sub>, (P)Si(R)X, and (P)SiX<sub>2</sub>, Where R = C<sub>6</sub>H<sub>5</sub> or CH<sub>3</sub> and X = OH<sup>-</sup> or ClO<sub>4</sub><sup>-</sup>

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Received May 4, 1987

The synthesis, characterization, and electrochemistry of several (OEP)Si(R)<sub>2</sub>, (OEP)Si(R)X, and (OEP)SiX<sub>2</sub> complexes are reported, where OEP is the dianion of octaethylporphyrin, R is C<sub>6</sub>H<sub>5</sub> or CH<sub>3</sub>, and X = ClO<sub>4</sub><sup>-</sup> or OH<sup>-</sup>. (OEP)Si(C<sub>6</sub>H<sub>5</sub>)<sub>2</sub> can be converted to (OEP)Si(C<sub>6</sub>H<sub>5</sub>)OH in CHCl<sub>3</sub> by irradiation with visible light in the absence of oxygen. Each Si(IV) complex undergoes a reversible electroreduction at the porphyrin  $\pi$  ring system. In contrast, the initial electrooxidations of these complexes are irreversible and the overall processes involve one or more coupled chemical reactions following electron transfer. (OEP)Si(C<sub>6</sub>H<sub>5</sub>)<sub>2</sub> can be converted to (OEP)Si(C<sub>6</sub>H<sub>5</sub>)OH after oxidation by one electron while further oxidation generates (OEP)Si(C<sub>6</sub>H<sub>5</sub>)ClO<sub>4</sub>. The latter compound can also be formed by reaction of (OEP)Si(C<sub>6</sub>H<sub>5</sub>)<sub>2</sub> with 2 equiv of HClO<sub>4</sub> in PhCN. (OEP)Si(CH<sub>3</sub>)<sub>2</sub> undergoes electrochemistry different from that of (OEP)Si(C<sub>6</sub>H<sub>5</sub>)<sub>2</sub> and gives (OEP)Si(CH<sub>3</sub>)ClO<sub>4</sub> and (OEP)Si(ClO<sub>4</sub>)<sub>2</sub> as successive electrooxidation products. An overall oxidation/reduction scheme for (OEP)Si(R)<sub>2</sub> is presented and compared to mechanisms for oxidation/reduction of (OEP)Si(R)X and (OEP)SiX<sub>2</sub>.

### Introduction

Non-transition-metal porphyrins with  $\sigma$ -bonded ligands have been reported for Ga, In, and Tl in group 13 and for Ge and Sn in group 14 of the periodic table.<sup>2</sup> Of these compounds, the synthesis and spectroscopic properties of  $\sigma$ -bonded germanium and tin dialkyl and diaryl porphyrins have been the most extensively studied.<sup>3-9</sup> Our laboratories have also recently completed a chemical and electrochemical investigation of (P)Ge(R)<sub>2</sub> and

(P)Ge(R)X, where P = the dianion of the tetraphenylporphyrin (TPP) or octaethylporphyrin (OEP), R = CH<sub>3</sub>, CH<sub>2</sub>C<sub>6</sub>H<sub>5</sub>, or C<sub>6</sub>H<sub>5</sub>, and X = Cl<sup>-</sup>, OH<sup>-</sup>, or ClO<sub>4</sub><sup>-</sup>.<sup>10</sup> This work is a continuation of our synthetic and electrochemical/spectroscopic studies on group 14 metalloporphyrins and reports the electrochemistry of (OEP)Si(R)<sub>2</sub>, (OEP)Si(R)OH, and (OEP)Si(OH)<sub>2</sub>, where R = C<sub>6</sub>H<sub>5</sub> or CH<sub>3</sub>. We also give preliminary data on the electrochemistry of (OEP)Si(C<sub>6</sub>H<sub>5</sub>)ClO<sub>4</sub>. No characterization of a dialkyl or diaryl  $\sigma$ -bonded silicon porphyrin has ever been reported nor has an electrochemical study of any silicon porphyrin ever been published. As will be shown in this paper, the electrochemistry of  $\sigma$ -bonded Si(IV) metalloporphyrins is similar to but not identical with that of the related  $\sigma$ -bonded Ge(IV) derivatives.

### Experimental Section

(OEP)Si(C<sub>6</sub>H<sub>5</sub>)<sub>2</sub> and (OEP)Si(CH<sub>3</sub>)<sub>2</sub> were synthesized by using the same method employed for preparation of dialkyl- and diarylgermanium porphyrins.<sup>10</sup> Characterization of each complex was achieved by <sup>1</sup>H NMR, IR, UV-visible spectroscopies, mass spectrometry, and elemental analysis. The (OEP)Si(R)<sub>2</sub> complexes are sensitive to both oxygen and visible light. Therefore, all electrochemical measurements were carried

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