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Communications

Electrochemistry of a Metalloporphyrin-Bridging Biferrocene Complex. Reactions of Fc–(OEP)Ge–Fc

Sir:

A number of biferrocene,[1] bridged-biferrocene,[2-8] and poly(vinylferrocene)[9,10] complexes have been synthesized and characterized in terms of their spectroscopic and electrochemical properties. The ferrocenyl, Fc, unit of Fc–Fc, Fc–X–Fc, or $[Fc(CH_2CH_2)]_n$, where X = a bridging group, is easily oxidized and thus provides a ready access to the study of mixed-valent iron compounds,[8] as well as models for understanding multiple-electron-transfer reactions at isolated reaction sites.[9]

The potential separation between the first and second oxidation of biferrocene type complexes provides a measurement of charge interaction between the two reaction sites.[11,12] This interaction is maximum for the case of biferrocenophane ($\Delta E_{1/2}$ = 590 mV) and biferrocene ($\Delta E_{1/2}$ = 350 mV)[3] but decreases for biferrocene containing one or more bridging atoms. For example, the $\Delta E_{1/2}$ value of 0.35 V for Fc–Fc is lowered to 0.17–0.20 V for Fc–X–Fc, where X = CH_2,[2,3] Se,[2] or $Si(CH_3)_2$,[13] and to 0.04 V for the complex where X = CH_2CH_2.[3] For the case of X = Hg, only a single overall process involving both ferrocenyl units is observed.[3] In many, but not all, cases, the separation in $E_{1/2}$ between the two oxidations of Fc–X–Fc parallels the intensity of an intervalent charge-transfer band that arises from electron transfer between the two sites in the mixed-valent singly oxidized complex.[7]

Two points are important in the generation of stable mixed-valence ferrocene complexes. The first involves the separation in $E_{1/2}$ between the two redox reactions while the second involves the actual potential for abstraction of the first and second electron from the complex. It is desired to have as facile an oxidation as possible, but for all previously investigated bridged-biferrocene complexes the initial oxidation did not differ substantially from $E_{1/2}$ of the simple ferrocene/ferrocenium couple.[11,12]

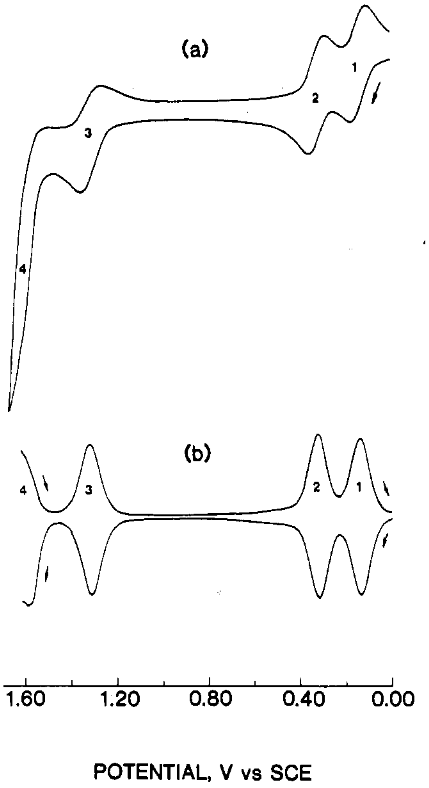

Figure 1. (a) Cyclic voltammogram (scan rate 0.10 V/s) and (b) differential pulse voltammogram (scan rate 4 mV/s, ΔE = 10 mV) of 1.4 × 10^{-3} M Fc–(OEP)Ge–Fc in CH_2Cl_2 containing 0.1 M TBAP.

In this communication we present the electrochemistry and spectroelectrochemistry of Fc–X–Fc, where X = (OEP)Ge. To our knowledge, this is the first example of bridged biferrocene where the singly oxidized biferrocene is significantly stabilized by a large bridging unit. Fc–(OEP)Ge–Fc was synthesized according to published methods.[14] Characterization was achieved by ^{1}H NMR, UV–visible, and IR spectroscopies.[15] Cyclic

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(15) UV–visible data (PhCN; λ, nm (ϵ, 10^{-4} M^{-1} cm^{-1})): 357 (2.98), 428 (3.50), 440 (14.1), 570 (0.58). IR data (CsI pellets; ν, cm^{-1}): 3080 (C–H Fc), 350 (Ge–C). ^{1}H NMR data ($CDCl_3$; δ multiplicity/intensity, assignment)): 10.14 (singlet/4, meso H), 4.15 (quartet/16, methylenic H), 1.96 (massive/34, methylic H and Fc H), 1.74 (multiplet/4, 3–4 Fc H), –2.33 (multiplet/4, 2–5 Fc H).

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Table I. Maximum Absorbance Wavelengths and Corresponding Molar Absorptivities of Neutral and Electrooxidized Fc-(OEP)Ge-Fc in CH_2Cl_2 Containing 0.1 M TBAP

electrode reacn[a]	absorbing species	λ_{max}, nm (ϵ, 10^{-4} cm^{-1} M^{-1})		
none	Fc-(OEP)Ge-Fc	439 (14.1)	569 (0.6)	
1e oxidn	$[Fc-(OEP)Ge-Fc]^+$	435 (8.0)	561 (0.6)	
2e oxidn	$[Fc-(OEP)Ge-Fc]^{2+}$	434 (5.9)	559 (0.9)	
3e oxidn	$[Fc-(OEP)Ge-ClO_4]^+$	408 (6.1)	537 (0.1)	578 (0.04)

[a] See Figure 1.

voltammetric and spectroelectrochemical measurements were carried out at a Pt electrode in dichloromethane (CH_2Cl_2) containing 0.1 M tetrabutylammonium perchlorate (TBAP).

Four reversible oxidations are observed at $E_{1/2}$ = 0.14, 0.32, 1.32, and 1.57 V in CH_2Cl_2 containing 0.1 M TBAP (see Figure 1). The difference between the third and fourth oxidations of Fc-(OEP)Ge-Fc is 0.25 V, which compares to an average separation of 0.29 ± 0.05 V for oxidation of various metalloporphyrins at the porphyrin π ring system.[16] The difference between the first and second oxidation of Fc-(OEP)Ge-Fc is 0.18 V in CH_2Cl_2, and this agrees with separations of 0.17-0.20 V between the two oxidations of $Fc-Si(CH_3)_2-Fc$,[13] Fc-Se-Fc,[2] and $Fc-CH_2-Fc$[2,3] in CH_2Cl_2 or CH_3CN. More importantly, however, the first oxidation of Fc-(OEP)Ge-Fc is shifted negatively by 0.350 V with respect to the Fc/Fc^+ couple in the same solvent. This is the most negatively shifted oxidation of any biferrocene complex and compares to potentials of -0.04 and +0.07 V vs. Fc/Fc^+ for the oxidation of Fc-X-Fc, where X = $Si(CH_3)$[13] and Se,[2] respectively.

Electronic absorption spectra of metalloporphyrins are directly influenced by both the axial ligands bound to the central metal and the charge on the porphyrin ring.[17] The electronic absorption spectrum of Fc-(OEP)Ge-Fc (Figure 2a) is typical of a σ-bonded $(OEP)Ge(R)_2$ complex. This spectrum is virtually identical with that of $C_6H_5-(OEP)Ge-C_6H_5$ (Figure 2b) but differs from that of $C_6H_5-(OEP)Ge-ClO_4$ (Figure 2c).

The spectral changes during the first two oxidations of Fc-(OEP)Ge-Fc are shown in Table I and may provide insights into the mechanism of stabilization of singly oxidized Fc-(OEP)Ge-Fc. Apparently, the oxidized ferrocenyl ligand becomes an electron acceptor. This electron-withdrawing effect of the ligand results in a blue shift of the Soret band.[17] The Soret band is further blue-shifted after the second oxidation which generates a second electron-acceptor Fc ligand. Thus, the large decrease in the Soret band intensity after both the first and the second oxidation of Fc-(OEP)Ge-Fc is attributed to a partial delocalization of charge on the a_{1u} and a_{2u} orbitals of the macrocycle. The absorbing species after abstraction of a third electron is assigned as $[Fc-(OEP)Ge-ClO_4]^+$, which results from cleavage of one Ge-Fc bond on the longer spectroelectrochemical time scale (2-5 min). The fourth oxidation is beyond the potential window of CH_2Cl_2, and no spectral changes could be monitored in the thin-layer cell.

In summary, Fc-(OEP)Ge-Fc is the most easily oxidized bridged biferrocene complex studied to date and the first bridged biferrocene complex where delocalization of charge on the bridge can be detected. These effects are attributed to the electron-donating ability of the porphyrin macrocycle which facilitates abstraction of the first and second electron from Fc-(OEP)Ge-Fc. Further stabilization and delocalization of charge on the oxidized species are expected to occur if electron-donating substituents are added to the porphyrin macrocycle, and an evaluation of these data should aid in quantitating the changes in spectra.

Finally, it is also significant to note that Fc-(OEP)Ge-Fc is unusually stable toward light and oxygen. This stability and ease of Fc-(OEP)Ge-Fc oxidation may have interesting properties in terms of the compound's ability to undergo intermolecular photocatalyzed electron-transfer reactions. This application is now under investigation.

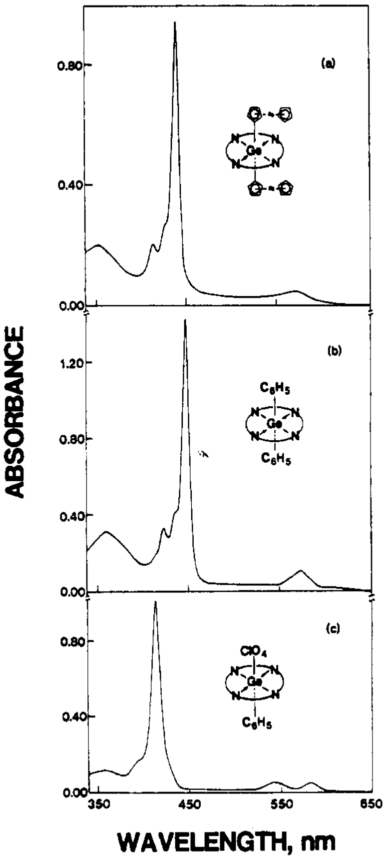

Figure 2. Electronic absorption spectra of (a) Fc-(OEP)Ge-Fc, (b) $C_6H_5-(OEP)Ge-C_6H_5$ and (c) $C_6H_5-(OEP)Ge-ClO_4$ in PhCN.

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Differences in the Band Electronic Structures of the Tetragonal and Orthorhombic Phases of the High-Temperature Superconductor $YBa_2Cu_3O_{7-y}$ (T_c > 90 K)

Sir:

Since the first report[1] of ambient-pressure superconductivity above 90 K in a multiphase sample of the Y-Ba-Cu-O system, a number of studies[2-11] have been carried out to identify the

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