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Communications

(μ-Nitrido)bis[(5,10,15,20-tetraphenylporphyrinato)iron](2+), an Iron(IV) Porphyrin π-Radical Cation

Sir:

Porphyrin radicals are crucial to a variety of biological redox processes. They are involved, for example, in the storage and transfer of oxidizing equivalents in the hydrperoxidases[1] and are believed to play a similar role in cytochrome P-450.[2] Dimeric chlorophyll radicals are the putative phototraps in photosynthesis.[3] We have previously examined a series of highly oxidized iron porphyrin complexes and shown that $(FeTPP)_2N^+$ contains iron(IV).[4,5] We wish to report that oxidation of this complex to the dication produces a stable iron(IV) porphyrin π-cation-radical complex, in which the rate of electron transfer between the two porphyrins of the dimer in the solid state is sensitive to the anion.

Oxidation of $(FeTPP)_2N$ (**1**)[6] with 1 equiv of phenoxathiin hexachloroantimonate,[7] phen$(SbCl_6)$, produces $[(FeTPP)_2N](SbCl_6)$ (**2**). This complex is analogous to the previously studied perchlorate salt[4] in that it contains iron(IV) and nonradical porphyrins.[8] Further oxidation of **2** with 1 equiv by weight of phen$(SbCl_6)$ in CH_2Cl_2 produces a greenish solution from which $[(FeTPP)_2N](SbCl_6)_2$ (**3**) can be isolated in yields of >80%. The bridged dimer remains intact, as demonstrated by the quantitative rereduction of **3** to **1** with $(C_2H_5)_4NI$. The infrared spectrum of **3** has a π-radical-cation band[8] at 1290 cm^{-1}, which is not present in **1** or **2**. The EPR spectrum for a 1:1 dichloromethane/1,1,2-trichloroethane solution of **3** at room temperature exhibits one feature at $g = 2.00$. The magnetic moment of **3** in the solid state is $2.0 \pm 0.3\ \mu_B$ from 7 to 300 K. These data indicate that **3** contains one unpaired electron, which could be either localized as a π-radical cation on one porphyrin of the dimer or delocalized over both. The Mössbauer spectrum of **3** at 133 K, as shown in Figure 1, allows this point to be answered. The two equal-area doublets[9] are consistent with a localized porphyrin radical. The spectra of **3** are virtually identical at 5, 206, and 280 K. Thus the radical is localized at all temperatures. Measurements of several independently prepared samples gave identical spectra.

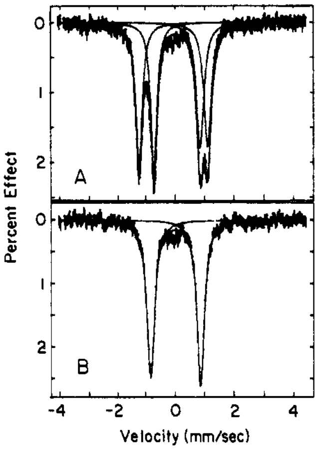

Figure 1. Mössbauer spectra at 133 K of (A) $[(FeTPP)_2N](SbCl_6)_2$ (**3**) and (B) $[(FeTPP)_2N](CF_3SO_3)_2$ (**4**).

The Mössbauer properties of **3** can be contrasted with those of $[(FeTPP)_2N](CF_3SO_3)_2$ (**4**).[10] **4** is similar to **3** in that it has a porphyrin π-radical-cation marker band at 1288 cm^{-1} and a room-temperature solution EPR spectrum (1:1 CH_2Cl_2/1,1,2-trichloroethane) with a single feature at $g = 2.00$. However, the Mössbauer spectrum of **4** (shown in Figure 1) consists of only one doublet[9] (with equal-area components) from 10 to 300 K. Hence, changing the counterion from $SbCl_6^-$ to $CF_3SO_3^-$ causes the mixed-valence porphyrin dimer to switch from localized to delocalized behavior on the Mössbauer time scale (10^{-7} s).

The EPR spectra of **3** and **4** in the solid state show some resolution of g values at 77 K but no discernible hyperfine. Simulations of the spectra indicate that **3** has g values of 2.000, 1.998, and 1.996 while **4** has g values of 2.004, 2.004, and 1.988. The frozen-glass spectra at 77 K do not show resolved g values, but the line shape indicates that $g_{\parallel} < g_{\perp}$, similar to the case for **4** in the solid state. This suggests that both of these complexes are delocalized in solution.

The visible spectrum of **4** is very similar to that of $Mg(OEP)^+$, a known a_{1u} radical.[11] Thin films of concentrated solutions are

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(4) Abbreviations: EPR, electron paramagnetic resonance; OEP, 2,3,7,8,12,13,17,18-octaethylporphyrinate(2−); phen, phenoxathiin; TPP, 5,10,15,20-tetraphenylporphyrinate(2−).

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(7) Gans, P.; Marchon, J.-C.; Reed, C. A.; Regnard, J.-R. *Nouv. J. Chim.* **1981**, *5*, 203–204.

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(9) At 126 K, the isomer shifts (vs. Fe foil) and the quadrupole splitting parameters derived from a least-squares fit of the spectra, in mm/s, are as follows: for $[(FeTPP)_2N]SbCl_6$, 0.01 and 1.94; for $[(FeTPP)_2N](SbCl_6)_2$, inner doublet, 0.07 and 1.48; for $[(FeTPP)_2N](SbCl_6)_2$, outer doublet, −0.04 and 2.21; for $[(FeTPP)_2N]CF_3SO_3$, and 0.04 and 2.06; for $[(FeTPP)_2N](CF_3SO_3)_2$, 0.00 and 1.68.

(10) This complex is prepared by reacting $(FeTPP)_2N$ in CH_2Cl_2 with I_2 in CH_2Cl_2 and $AgCF_3SO_3$ in toluene.

(11) Fajer, J.; Davis, M. S. In "The porphyrins"; Dolphin, D., Ed.; Academic Press: New York, 1979; Vol. 4, pp 197–256.

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necessary to obtain such spectra due to the sensitivity of dilute solutions of this compound to light and to trace impurities in the solvent. The lack of hyperfine in the EPR spectra is consistent with that expected for an a_{1u} porphyrin radical with meso substituents.[11,12]

The factors controlling the intradimer electron-transfer rate might include (1) anion coordination, (2) intermolecular interactions, or (3) lattice-induced site asymmetry. The first of these is unlikely, since the infrared spectrum of **4** as a Nujol mull does not show the resonances associated with triflate coordination in $Fe(TPP)CF_3SO_3$[13] and since it is doubtful that hexachloroantimonate is coordinated in **3**. The second factor is probably unimportant in these compounds since the EPR spectrum in frozen dilute glass is similar to **4** in the solid. X-ray powder diffraction patterns for **3** and **4** are qualitatively different. This suggests that differences in lattice asymmetry due to the different counterions may be influencing the electronic structure.

An interesting comparison may be made between **3** and **4** and analogous μ-oxo systems. $(FeTPP)_2O^+$ also has one unpaired electron in its π-system.[8,14] The Mössbauer spectrum of $[(FeTPP)_2O](ClO_4)$ consists of one doublet at 77 K.[14] We have obtained a Mössbauer spectrum of $[(FeTPP)_2O](SbCl_6)$ at 77 K, and it also consists of one doublet. Thus, the μ-oxo species do not exhibit the same sensitivity to counterion as the μ-nitrido complexes.

In conclusion, $(FeTPP)_2N^{2+}$ is an iron(IV) porphyrin π-cation-radical species. This is the only such synthetic complex to date that is stable indefinitely at room temperature. The counterion has a profound effect on the inter-porphyrin electron-transfer rate. The sensitivity of the electronic structure to such subtle changes illustrates the major influences that minor perturbations may have in related biological systems.

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Articles

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Redox Properties and Stability of Hydroxy Complexes of Protected Iron(III) and Iron(II) Porphyrins

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Efficient protection from μ-oxo dimer formation in hydroxy complexes of iron(III) tetraphenylporphyrin is provided by 12-carbon aliphatic hydrocarbon ("basket-handle") chains anchored through amide or ether linking in the ortho position of the phenyl groups in a cross-trans arrangement. Electrochemical reduction of the iron(III) hydroxo complexes in benzonitrile yields reversibly the corresponding stable iron(II) hydroxo complexes. The redox characteristics of the $Fe^{III}OH/Fe^{II}OH^-$ couple and the stability constants of both its members have been derived from cyclic voltammetry and thin-layer electrochemistry. They appear to be sensitive to variation of the molecular environment as offered by the presence of either amide or ether groups in the vicinity of the heme ring. The discussion of the data involves comparison with the corresponding chloro complexes, the characteristics of which have been determined in the same fashion.

Introduction

The description and rationalization of the physicochemical characteristics of the complexes of iron porphyrins with dioxygen and the various species resulting from its reduction are of essential importance for the understanding of the transport and activation properties of hemoproteins.[2] Regarding the hydroxyl ion, detailed studies have long been hampered by the conversion of the hydroxoiron(III) complexes into the corresponding μ-oxo dimer.[3] Previous investigation of the electrochemical reduction of the Fe^{III}–O–Fe^{III} complex in dimethylformamide indicated that it undergoes a $2e^- + H^+$ reduction cleavage, leading to $Fe^{II}OH$ and Fe^{II}.[4] μ-oxo dimerization thus appears to take place only at the Fe^{III} oxidation level. Recently however, a few examples of true iron(III) OH^- porphyrin complexes have been reported in the tetraphenylporphyrin series, μ-oxo dimerization being prevented, at least partially, by protecting structures anchored at various positions of the phenyl ring.[5] There are however no data so far

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