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In Situ Fe K-Edge X-ray Absorption Fine Structure of a Nitrosyl Adduct of Iron Phthalocyanine Irreversibly Adsorbed on a High Area Carbon Electrode in an Acidic Electrolyte

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Key aspects of the microenvironment surrounding the Fe center in the nitrosyl adduct of iron phthalocyanine, [Fe(Pc)(NO)], have been elucidated from the analysis of the Fe K-edge extended X-ray absorption fine structure (EXAFS) of the material adsorbed on the surface of a high area carbon electrode recorded in situ, in 0.5 M H_2SO_4. Statistical best fits to the EXAFS data place the Fe center in a five-coordinated square pyramidal configuration shifted away from the Pc plane toward the axially bound NO bent at an angle of ca. 40° with respect to the normal to the Pc plane. This environment is analogous to that of Fe in the nitrosyl adduct of crystalline [Fe(TPP)], where TPP = *meso*-tetraphenylporphyrinato(2–), determined from X-ray diffraction.

Introduction

A detailed characterization of the electronic and structural properties of nitrosyl adducts of iron porphyrins and phthalocyanines may be regarded as crucial to the further understanding of the role these materials play in such diverse areas as mammalian physiology,[1,2] sensor technology,[3,4] and electrocatalysis.[5] Although the structures of NO adducts of a variety of iron porphyrins have been known for quite some time,[6−8] no methods have yet been devised for producing crystals of the corresponding adduct of iron phthalocyanine, [Fe(Pc)(NO)], of sufficiently high quality for X-ray diffraction (XRD) analysis, since its synthesis was first described about four decades ago.[9]

The present work exploits the virtues of extended X-ray absorption fine structure (EXAFS) to elucidate the structure surrounding the iron center in [Fe(Pc)(NO)] irreversibly adsorbed on the surface of a high area carbon electrode in an acidic aqueous electrolyte. Strong support for the overall reliability of this methodology was obtained recently using, as a model system, [Fe(TMPP)(NO)], where TMPP = *meso*-tetramethoxyphenylporphyrinato(2−), prepared under otherwise very similar conditions.[10] As shown in that work, analysis of the Fe K-edge EXAFS for [Fe(TMPP)(NO)] recorded in situ, i.e., under potential control, in which the Fe center was constrained to reside in the porphyrin plane, yielded a bent Fe−NO moiety, as found for crystalline [Fe(TPP)(NO)] on the basis of XRD.[6] Best fits to the in situ EXAFS data for [Fe(Pc)(NO)] (also for [Fe(Pc)(NO)] in powder form recorded ex situ) reported herein, in which the Fe center was allowed to shift along an axis normal to the Pc plane, placed the metal away from the Pc plane toward the axially bound NO in a five-coordinated, square pyramidal configuration forming an Fe−N−O angle of 140°, as has

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been inferred from vibrational spectroscopy[11,12] and other empirical observations.[13,14]

Experimental Section

Iron phthalocyanine ([Fe(Pc)], Aldrich) was adsorbed on Ketjen Black (KB) high area carbon (EC600JD, 1360 m^2/g, Lion Corp., Japan) at nominally submonolayer coverages by mixing a solution of [Fe(Pc)] (20 mg)/methanol (50 mL) with KB (50 mg) dispersed in methanol (50 mL), as described elsewhere.[15] Following ultrasonic agitation for 1 h, the mixture was filtered (Whatman No. 2 paper) and subsequently washed with methanol until the filtrate became colorless. The wet powder was then collected, dried under vacuum, and finally stored in a nitrogen atmosphere at room temperature until further use.

The nitrosyl adduct of [Fe(Pc)], [Fe(Pc)(NO)], in crystalline form was prepared by methods specified elsewhere[16] and its Fe K-edge XAFS recorded in the transmission mode using a homogeneously dispersed specimen with μ ca. 0.1.

Electrodes for in situ X-ray absorption fine structure (XAFS) measurements were prepared by first mixing 2.3 mg of [Fe(Pc)]/KB with a Teflon suspension (T30B, DuPont, 5 mg mL^{-1}, 20 μL) in air, and then pressing the resulting paste firmly onto a 1.15×0.5 cm^2 hydrophobic carbon sheet (Eltech Corp.), which served as the current collector. A high area carbon sheet (ICET, Inc.) and a reversible hydrogen electrode in the same solution (RHE) were used as counter and reference electrodes, respectively.

In situ Fe K-edge XAFS were recorded in the fluorescence mode at the Stanford Synchrotron Radiation Laboratory (SSRL, beamline 4-3) at ring currents in the range 60−100 mA with a Si(220) double-crystal monochromator detuned to 50% at 7500 eV to reduce contributions due to higher harmonics, while maintaining a reasonable photon flux at the sample. All measurements were performed with the beam unfocused using a 13-element Ge detector to collect the fluorescent radiation. Details regarding the spectroelectrochemical cell and data acquisition have been given in previous papers[17,18] and will not be repeated here. In situ XAFS were recorded first for adsorbed [Fe(Pc)] in its various redox states in neat 0.5 M H_2SO_4 (Aldrich, 98%). Once this set of experiments was completed, an aliquot of 0.1 M $NaNO_2$ was injected directly into the cell to a final concentration of ca. 10 mM, to form the [Fe(Pc)(NO)] adduct, and after a few minutes, the solution was replaced with neat 0.5 M H_2SO_4 for subsequent electrochemical and in situ XAFS measurements. To improve the overall quality of the data, at least four sequential spectra for each of the species examined in situ were recorded, coadded, and then averaged prior to subsequent statistical analysis. The EXAFS oscillations were isolated by subtracting from the absorption and fluorescence data a smooth background using 4 splines for the non-NO-bound [Fe(Pc)] species and [Fe(TMPP)-(NO)], and 5 splines for the [Fe(Pc)(NO)] complexes. In situ EXAFS data were analyzed using XFIT[19] and FEFF 6.01[20] to calculate theoretical curves by multiple-scattering (MS) ab initio methods, following the procedure specified in ref 21. All constituent atoms of the macrocyclic rings (except hydrogens) were considered while refining the structures of the species investigated. Furthermore, bond distances and angles extracted from X-ray diffraction (XRD) data for [Fe(Pc)][22] were used as starting points for optimizing [Fe(Pc)] in its various redox states and also [Fe(Pc)(NO)], in which the N in NO was initially placed at a distance of 1.72 Å from the Fe center along an axis perpendicular to the plane of the Pc ring (*z*-axis, see below), and thus very close to the corresponding value found for [Fe(TPP)(NO)] from XRD. Oxygen atoms representing aqua (or hydroxo) ligands, bound to one or both axial positions of the macrocycles, were set at an initial distance of 2 Å along the *z*-axis. Unlike the approach followed in our previous work, the Fe center in the current investigation was allowed to move along the *z*-axis, so as to enable XRD structures of known nytrosyl Fe porphyrins to be statistically examined.[7] A similar approach was employed to fit in situ data reported earlier for [Fe(TMPP)(NO)] using metrical parameters derived from XRD for [Fe(TPP)(NO)].[6]

For practical reasons, the MS refinement calculations were restricted to paths with effective lengths of ≤ 6 and ≤ 8 Å for TMPP- and Pc-based species, respectively, with up to six legs, and an importance factor $\geq 2\%$ compared to the predominant path. The number of independent variables was reduced by imposing symmetry constraints, including ring planarity, and reasonable restraints for bond distances and angles based on XRD data for the closely related analogues, as necessary to increase the overdeterminancy, N_i/p, of the refinement to the values indicated in Tables 1 and 2.[7,23] Additional details of the fits can be found in the Supporting Information.

Results and Discussion

Electrochemistry. The cyclic voltammogram of [Fe(Pc)]/KB, recorded at 10 mV/s in 0.5 M H_2SO_4 (see insert in Figure 1a, solid line) in the same cell in which the in situ XAS measurements were performed, displayed two well-defined sets of redox processes at E_{av} $(=(E_+ - E_-)/2$, where E_j represents the peak potential observed during the scan in the direction j, either positive (+), or negative (−)) ca. 0.15 for peak I, and E_{av} ca. 0.65 V versus RHE for peak II, characteristic of adsorbed [Fe(Pc)] in this media.[24] As was the case for [Fe(TMPP)(NO)] prepared in situ,[10] formation of the NO adduct, under the conditions specified in the Experimental Section, led to the disappearance of the voltammetric features attributed to [Fe(Pc)] over the potential range indicated (see curve in dashed line, in the insert, Figure 1a).

X-ray Near Edge Structure (XANES). Marked differences were found in the Fe K-edge XANES region (7.10−7.20 keV) for the [Fe(Pc)]/KB electrode polarized at 0.40 V (A, insert Figure 1a) and 0.84 V (B, insert Figure 1a) versus

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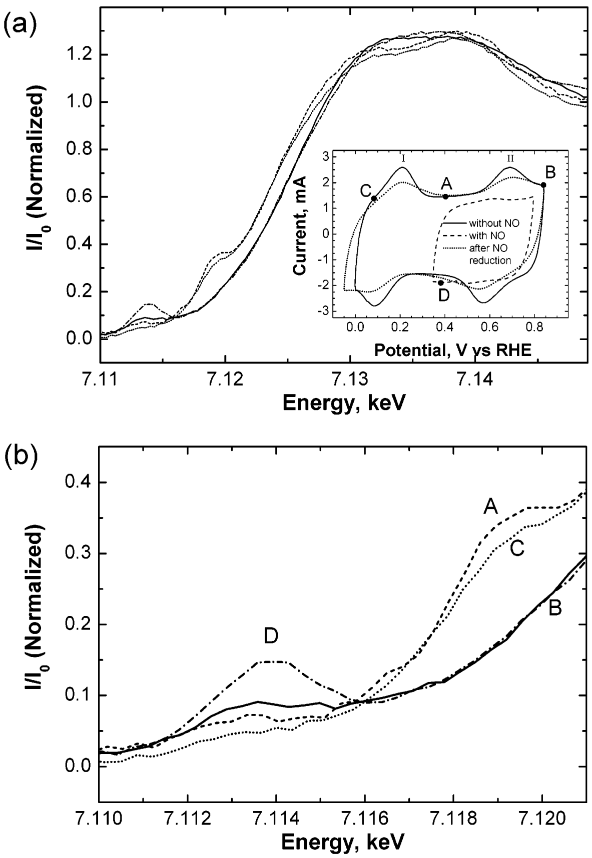

Figure 1. (a) In situ Fe K-edge XANES of [Fe(Pc)]/KB in 0.5 M H_2SO_4 recorded at 0.4 V (A, - - -), 0.84 V (B, —), and 0.08 V (C, • • •), and of [Fe(Pc)(NO)] at 0.38 V (D, — • — line). Insert: Cyclic voltammograms of [Fe(Pc)]/KB recorded at 10 mV/s in 0.5 M H_2SO_4 (—), after formation of the NO adduct (- - -), and after its subsequent reduction at −0.13 V (• • •). Solid circles (●) indicate potentials at which in situ Fe K-edge XAS spectra were recorded. (b) Expanded view of the 7110−7121 eV range.

RHE (see curves A and B, Figure 1b), i.e., before and after peak II, in general agreement with in situ data for [Fe(Pc)]/KB in the same electrolyte reported earlier by Ha et al.[24] In particular, oxidation of adsorbed [Fe(Pc)] led, in addition to a shift in the onset of the edge jump of ca. 1.2 eV toward higher energies, to the disappearance of an overlapping shoulder centered at 7.117 keV, and to the increase of a smaller feature centered at 7.114 keV. This behavior bears close resemblance to that found earlier for adsorbed [Fe(TMPP)$_2$O] and is attributed to a redox process localized primarily on the Fe center to yield [Fe^{III}(TMPP)].[18] On this basis, peak II (see insert Figure 1a) is ascribed to the oxidation of [Fe^{II}(Pc)] to yield a species formally represented as [Fe^{III}(Pc)]$^+$, as has already been suggested in the literature.[24]

In stark contrast with the spectral behavior found for peak II, only very small differences could be discerned between the Fe K-edge XANES of [Fe(Pc)] and those of its reduced form at 0.08 V versus RHE (C, insert Figure 1a), shown in dashed (curve A) and dotted lines (curve C) in Figure 1b, respectively. This finding, originally reported by Ha et al.,[15,24] is consistent with electron injection into a predominantly ring-based, as opposed to metal-based, orbital, to form [Fe^{II}-{Pc(3−)}]$^-$, where the notation emphasizes that the added electron is delocalized in the chelating ring. Although in harmony with conclusions drawn by Clack and Yandle on the basis of UV−vis spectra,[25] this assignment is at variance with information derived from electron paramagnetic resonance (EPR) of electrochemically generated solution phase species in organic solvents, which suggests that peak I involves the reduction of the Fe center to generate [Fe^I{Pc-(2−)}]$^-$.[26] Some evidence in support of a predominantly ring-based orbital being involved may be found in the work of Donohue et al.,[27] who examined the spectral properties of the reduced and oxidized products of β-substituted [Fe(TPP)]. On the basis of a combination of resonance Raman (ring specific) and EPR (metal-center specific), these authors surmised that cyano substituents on the porphyrin ring, such as in [Fe{TPP(CN)$_4$}]$^-$, force the extra electron to migrate from a metal-based (for [Fe(TPP)]) to a ring-based orbital. Moreover, the presence of electron withdrawing groups on the ring has been found to shift the half-wave potential of the neutral complex in *N*,*N*-dimethylformamide, $E_{1/2}$, to more positive potentials, e.g., from $E_{1/2} = -0.986$ V for [Fe(TPP)] to $E_{1/2} = -0.475$ V versus Ag/AgCl for [Fe{TPP(CN)$_4$}]. On this basis, and given the high electron withdrawing and delocalization ability of the benzo substituent groups, it is very likely that the extra electron in the reduced form of [Fe(Pc)], for which $E_{1/2} = -0.08$ V versus Ag/AgCl, resides mostly on the Pc ring.

The slight increase in the pre-edge feature at about 7113.5 eV observed for adsorbed [Fe(Pc)] (see Figure 1b) could in principle be ascribed to the formation of a dimeric, μ-oxo form of [Fe(Pc)];[16] however, it is doubtful this species would be stable under the highly acidic conditions used for these experiments. A more likely explanation for this enhanced pre-edge feature is a decrease in the symmetry around the Fe center induced by the axial binding of a single aqua (or hydroxo) ligand, as the best fit to the EXAFS data suggests (see Table 1).[16]

Formation of the [Fe(Pc)(NO)] adduct led to the emergence of a characteristic prominent peak in the pre-edge XANES region centered at about 7114 eV (see curve D in Figure 1). A similar feature has also been found in the Fe K-edge XANES spectra of NO adducts of heme proteins,[28,29] and also of [Fe(Pc)(NO)] in crystalline form.[16] This pre-edge feature is due to the dipole forbidden 1s → 3d electronic transition, which becomes allowed due to p−d orbital mixing, when the D_{4h} symmetry surrounding the Fe center is broken, such as, for example, in a five-coordinate complex, a six-coordinate complex incorporating different axial ligands, or a four-coordinate complex with the metal center displaced from the macrocyclic plane. The relatively larger intensities of the pre-edge features observed for axially bound NO complexes compared to other Fe$^{III/II}$ complexes in similar environments are due to strong π-back-bonding. At least two

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Table 1. Fe Center Site Dimensions in [Fe(Pc)] Neutral, Oxidized, and Reduced, Determined by MS XAFS Analyses[a]

param	[Fe(Pc)] XRD[22]	[Fe(Pc)]	[Fe(Pc)-(H_2O)$_2$]	[Fe(Pc)]$^+$	[Fe(Pc)-(H_2O)$_2$]$^+$	[Fe(Pc)(H_2O)]$^+$ or [Fe(Pc)(OH)]$^+$	[Fe(Pc)]$^-$	[Fe(Pc)-(H_2O)$_2$]$^-$	[Fe(Pc)(H_2O)]$^-$ or [Fe(Pc)(OH)]$^-$
R (%)		19.0	20.9	22.2	18.5	17.1	16.0	21.6	23.1
E_0 (eV)		7125.8	7124.9	7119.6	7122.6	1722.1	7127.5	7127.0	7125.5
S_0^2		0.90	0.90	1.23	1.04	1.05	0.96	0.91	0.78
Fe−N (Å)	1.927	1.94	1.93	1.95	1.95	1.98	1.94	1.92	1.92
Fe−O (Å)			2.24		2.03	2.01		2.18	2.23
σ_N (Å^2)		0.003	0.001	0.008	0.002	0.004	0.002	0.001	0.001
σ_O (Å^2)			0.007		0.001	0.001		0.009	0.006
Fe−ring (Å)	0	0	0	0	0	0.19	0	0	0.09
N_i/p		2.3	2.1	2.3	2.1	2.0	2.3	2.1	2.0

[a] Typical estimated errors were 0.02 Å for the Fe−L bond length.

formal electronic configurations can be envisaged for the nitrosyl adducts of iron porphyrin and iron phthalocyanine, involving in each case different oxidation states for the metal center, i.e., [Fe^{III}−NO^-] and [Fe^{II}−$NO^{\bullet}$]. Whereas the Mössbauer parameters reported by Taube[30] for the solvent-free adduct are compatible with [Fe^{II}−$NO^{\bullet}$], the position of the IR stretching band of the NO moiety at 1695 cm^{-1}, according to Ercolani et al.,[11] is more characteristic of [Fe^{III}−NO^-]. In fact, this latter configuration is supported by the XPS studies of Uchida et al.,[13,14] which yielded for the iron center, $S = {}^1/_2$. The position of the Fe K-edge of [Fe(Pc)(NO)] appears virtually identical to that of [Fe^{III}(Pc)]$^+$ (see Figure 1A,D) and would therefore support the "ferric" character of the metal center in the adduct as inferred from the IR data.

Extended X-ray Absorption Fine Structure (EXAFS). Parameters extracted from statistical best fits to the EXAFS spectra collected in situ for adsorbed [Fe(Pc)] in its three redox forms and for the corresponding [Fe(Pc)(NO)] adduct are given in Tables 1 and 2, respectively. Also included therein, for comparison, are bond lengths and angles for [Fe(Pc)(NO)] powder synthesized by the method specified in ref 16, as well as those for [Fe(Pc)],[22] [Fe(TPP)], and [Fe(TPP)(NO)] in crystalline forms obtained from XRD data,[6] of direct relevance to the present work.

[Fe(Pc)]. The Fe−N(Pc) distance obtained from the analysis of the EXAFS for [Fe(Pc)] (as well as other bond lengths and angles not listed in Table 1) compared very well with that obtained by XRD for [Fe(Pc)] crystals.[22] Addition of two oxygen atoms in the axial positions (specified as aqua ligand in the table) worsens somewhat the fit without altering significantly the Fe−N(Pc) distance; however, the resulting values for the Fe−O distance and also the corresponding Debye−Waller factor σ_O were rather large, 2.24 Å and 0.007 Å^2, respectively, and, thus, close to the upper limit for a bonding interaction.

[Fe(Pc)]$^+$. As shown in Table 1, the Fe−N(Pc) distance in [Fe(Pc)]$^+$ increased by ca. 0.02 Å compared to that in [Fe(Pc)], in qualitative agreement with the results of Kim et al.[15] based on MS single-shell EXAFS analysis of their in situ [Fe(Pc)]/KB data assuming a strict square-planar environment, i.e., without considering axially bound aqua (or hydroxo) ligands nor out of plane metal displacement. Although EXAFS is not particularly sensitive to out of plane distances, statistical refinements of data obtained for α-chlorohemin, a synthetic iron-protoporphyrin-IX compound, have been found to reproduce, albeit not quantitatively, the out of plane displacement found from XRD.[23] Indeed, the more refined analysis herein performed places the Fe center 0.19 Å away from the Pc plane toward a single coordinating oxygen (probably OH^-) at a distance of ca. 2.01 Å. This value is quite comparable to those found by XRD for the five coordinate [Fe(Pc)(Cl)] of 0.30 Å,[31] and [Fe(Pc)(I)] of 0.258 Å,[32] and also for [Fe^{III}(TPP)] halides, e.g., 0.39 Å for [Fe(TPP)(Cl)],[33] and 0.53 Å for [Fe(TPP)(I)].[34] It must be stressed that attempts to fit the data for [Fe(Pc)]$^+$ (as well as for [Fe(Pc)(NO)] and [Fe(TMPP)(NO)], see below) starting with the metal center in the macrocyclic plane lifted the Fe out of the plane.

[Fe(Pc)]$^-$. No changes in the geometry surrounding the metal center were observed upon reduction of [Fe(Pc)] to form [Fe(Pc)]$^-$ (see Table 1), consistent with delocalization of the extra charge in the ring, as the XANES data above would suggest. As was the case with [Fe(Pc)], addition of axial oxygen(s) does not improve the fits, and the bond distances and σ_O appeared too large to support an octahedral-type environment.

[Fe(Pc)(NO)] and [Fe(TMPP)(NO)]. Metrical parameters for [Fe(Pc)(NO)] were determined from the analysis of the Fe K-edge EXAFS recorded in situ using XRD structural data for [Fe(Pc)] as a model. As was stressed earlier, the in-plane Fe center geometries considered in our previous work[10] were relaxed to allow the Fe center to move freely about the axis normal to the molecular plane. This same approach was also implemented to re-examine the in situ data for [Fe(TMPP)(NO)] presented in our earlier communication and, thus, assess whether EXAFS can predict at least qualitatively the square pyramidal five-coordinated geometry expected for simple Fe porphyrin NO adducts. Indeed, as evidenced by the results obtained (see Table 2), the distance between the Fe and the porphyrin plane in [Fe(TMPP)(NO)] was found to be quite significant, ca. 0.32 Å, and larger than that reported for [Fe(TPP)(NO)] from XRD, 0.211 Å.[6] Such displacements are common among NO adducts of metal porphyrins and may be attributable, at least

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Table 2. Fe Center Site Dimensions in [Fe(TMPP)(NO)] and [Fe(Pc)(NO)] Adducts Determined by MS XAFS Analyses[a]

param	[Fe(TPP)(NO)] XRD[22]	[Fe(TMPP)(NO)] adsorbed, in situ	[Fe(TMPP)(NO)(O)] adsorbed, in situ	[Fe(Pc)(NO)] powder, ex situ	[Fe(Pc)(NO)] adsorbed, in situ	[Fe(Pc)(NO)(O)] adsorbed, in situ
R (%)		15.5	15.9	15.7	20.1	21.4
E_0 (eV)		7128.2	7128.6	7128.8	7126.6	7126.9
S_0^2		0.84	0.87	0.84	0.88	1.00
Fe−N(ring) (Å)	2.001	2.00	2.00	1.96	1.96	1.96
Fe−N(NO) (Å)	1.717	1.76	1.76	1.78	1.78	1.78
N−O (Å)	1.122	1.15	1.14	1.15	1.15	1.15
Fe−O (Å)			2.12			2.18
Fe−N−O (deg)	149	151	153	136	139	140
Fe−ring (Å)	0.211	0.32	0	0.48	0.47	0
N(NO)−N(ring) (Å)	2.77	2.87	2.67	2.95	2.95	2.65
$\sigma_{N(Pc)}$ (Å^2)		0.001	0.001	0.004	0.001	0.001
$\sigma_{N(NO)}$ (Å^2)		0.003	0.003	0.005	0.002	0.003
$\sigma_{O(NO)}$ (Å^2)		0.001	0.001	0.001	0.001	0.001
σ_O (Å^2)			0.012			0.004
N_i/p		2.2	1.9	1.7	1.7	1.5

[a] Typical estimated errors were 0.02 Å for the Fe−L bond length.

in part, to repulsions (nonbonding interactions) between the four nitrogen atoms in the macrocyclic ring, on one hand, and the nitrogen atom belonging to the NO ligand, on the other. According to Scheidt et al.[35,36] such repulsions are minimized by setting the distance between two nonbonded nitrogen atoms to be larger than ca. 2.8 Å.

Only very small changes in the predicted structure of [Fe(TMPP)(NO)] in situ were observed upon changing the site geometry from square pyramidal to octahedral, with the Fe in the plane of the porphyrin and an oxygen bound to the free axial position. In fact, the values for the Fe−N(ring) and the Fe−N(NO) distances of 2.00 and 1.76 Å are, within experimental error, the same as those found by XRD for [Fe(TPP)(NO)].[6] However, such an octahedral environment placed the N in NO at 2.67 Å with respect to N in the porphyrin ring and thus too close to N in N(P), and in addition, the Fe−O(axial) distances were rather long, lending strong support to Fe being in a square pyramidal five-coordinated microenvironment. As expected, the NO ligand for [Fe(TMPP)(NO)] was found to be tilted, with an Fe−N−O angle of ca. 151°, again similar to that in the [Fe(TPP)(NO)] adduct.[6]

On the basis of the success of this model approach, the same methodology was applied for optimizing the structure of [Fe(Pc)(NO)]. The starting parameters for this species in powder and adsorbed forms in situ were those of [Fe(Pc)] with N in NO along the *z*-axis at a distance of 1.72 Å. The overall geometry for both [Fe(Pc)(NO)] in powder form and adsorbed on the electrode recorded in situ was found to be very similar to that of [Fe(TPP)(NO)] (see Table 2), i.e., a square pyramidal five-coordinate structure with the NO forming an angle with respect to the *z*-axis, as has been proposed on the basis of other spectral evidence,[11,12] and on the $\{MNO\}^7$-type electronic structure.[37−40] In particular, the Fe−N(ring), Fe−N(NO) distances yielded values of 1.96 and 1.78 Å, respectively, and an Fe−N−O bond angle in the range 136−139°, which is well within the range found for a series of Fe^{II} porphyrin NO adducts, i.e., 138−152°,[7] with Debye−Waller factors characteristic of well-ordered shells. The results for [Fe(Pc)(NO)] adsorbed are also displayed in Figure 2, in which the statistical best fit (see solid line, upper panel) is compared to the experimental reduced $k^3\chi(k)$ EXAFS function (dashed line in this figure). Also given in panel b, Figure 2, are the corresponding experimental (dashed line) and best fit (solid line) FTs of the $k^3\chi(k)$ EXAFS function. Despite the relatively high noise, the magnitudes of the residuals (see lower curve in panel a) at low k are quite comparable to those found for fits of biological compounds.[21]

As shown in Table 2, the *R*-factors both for [Fe(Pc)(NO)] powder for [Fe(Pc)(NO)] adsorbed in situ were around 20%, and thus within the range in which fits are often regarded as good. Also within a reasonable range were the values of the Debye−Waller (DW) factors, 0.001−0.005 for coordinated atoms including O in NO. In the case of noncoordinated ligand atoms, such as outer carbons, values for DW factors of up to 0.006 were obtained (not shown in the table). EXAFS analyses of model compounds for biological materials such as heme-type systems are usually found to yield S_0^2 values of 0.9 or higher. The slightly lower values found for [Fe(Pc)(NO)] powder, i.e., 0.84, cannot at this time be satisfactorily explained, as no methods have as yet been devised for producing crystals of sufficiently high quality for XRD analysis. Despite these difficulties, and as noted above, the metrical parameters extracted from the EXAFS analysis of [Fe(Pc)(NO)] powder and adsorbed material recorded in situ do appear to provide a consistent and reasonable metal microenvironment, as evidenced by the quality of the fits obtained (see Table 2).

In direct analogy with the results found for [Fe(TMPP)(NO)], addition of a sixth ligand to the axial position opposite to NO without allowing metal center displacement from the

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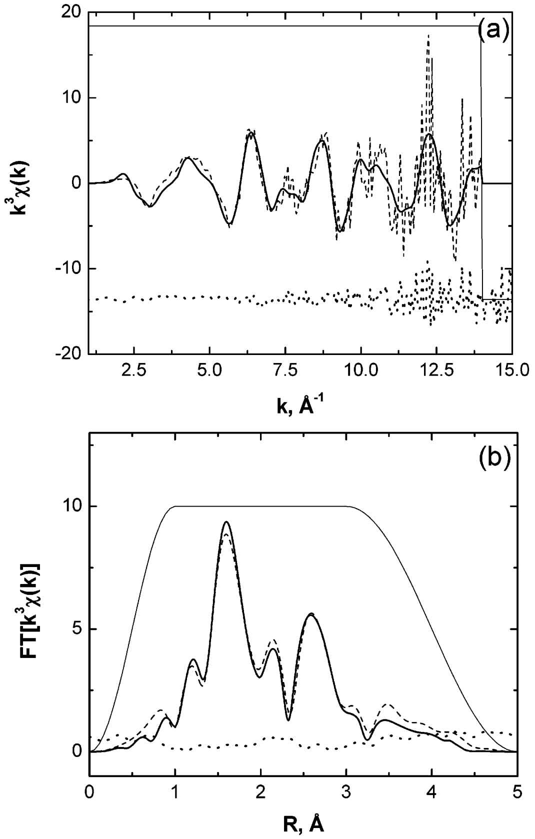

Figure 2. Plots of (a) $k^3\chi(k)$ vs k and (b) Fourier transform (FT) amplitude for [Fe(Pc)(NO)] adsorbed recorded in situ (- - -) and calculated from the refined five-coordinate geometry model (—, see text). The residuals in both panels are shown in dotted lines (• • •), and the window used for Fourier filtering is given as a thin solid line (—).

PC ring plane (see last column, Table 2) increased the *R*-factor, suggesting that the five-coordinate [Fe(Pc)(NO)] may better represent the adsorbed species. Furthermore, both the five- and six-coordinate structures yielded, within the errors of this analysis, identical values for the Fe−N−O angle, and also for the Fe−N(ring), Fe−N(NO), and N−O distances, and therefore a common Fe site microenvironment.

Other Observations. Once the in situ EXAFS experiments had been completed, the potential of the [Fe(Pc)(NO)]/KB electrode was scanned to −0.13 V versus RHE and back to 0.4 V in an attempt to reduce the adduct. Immediately thereafter, the potential was set at 0.36 V versus RHE and an in situ Fe K-edge XANES recorded. Although the XANES region was found to be very similar to that recorded for [Fe(Pc)], providing ample evidence that [Fe(Pc)(NO)] was reduced to yield, as intended, a nitrosyl free [Fe(Pc)], subsequent voltammetric data indicated a sizable reduction, ca. 50%, in the areas under peaks I and II (see insert, Figure 1), indicating that polarization to such negative potentials leads to the decomposition and/or desorption of the macrocycle.

Summary

Statistical analysis of the Fe K-edge EXAFS of an electrode incorporating [Fe(Pc)(NO)] adsorbed on a high area carbon recorded in situ in an acidic aqueous electrolyte revealed that the microenvironment surrounding the Fe center is very similar to that found for the better characterized nitrosyl adducts of Fe porphyrins. In particular, best fits to the data indicate that the Fe center in the adduct is present in a square pyramidal five-coordinate arrangement with the axially bound NO forming an angle of about 40° with respect to the normal to the Pc plane. The bent character of the NO ligand is also in agreement with information derived from IR spectroscopic data and other considerations.

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Supporting Information Available: Schematic diagram of the [Fe(Pc)(NO)] structural model, list of constraints and restraints used for EXAFS data analysis, and refined coordinates of the constituent atoms of the [Fe(Pc)(NO)] adduct. This material is available free of charge via the Internet at htpp://pubs.acs.org.

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