Investigation of solvation and solvent coordination effects in iron porphyrin nitrosyls by infrared spectroelectrochemistry and DFT calculations

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ABSTRACT: Visible and infrared spectroelectrochemistry of Fe(OEPone)(NO) (H₂OEPone = octaethylporphione) were examined in methylene chloride and THF. The visible spectra of Fe(OEPone)(NO) were similar in both solvents. Unlike other ferrous porphyrin nitrosyls, a six-coordinate complex was formed with THF as a ligand. This led to two nitrosyl bands in the infrared spectrum. The absorbance of these bands depended on the concentration of THF in the solution. Solvation and coordination effects on the carbonyl and nitrosyl bands were observed for both the nitrosyl and reduced-nitrosyl complexes. DFT calculations were carried out to interpret the spectral changes.

KEYWORDS: solvent coordination, iron porphyrin nitrosyl, infrared spectroelectrochemistry, DFT.

INTRODUCTION

Changes in the coordination geometry of iron-porphyrin complexes can have a significant impact on their properties and reactivities. Iron porphyrin dioxygen and carbon monoxide complexes are typically six coordinate if ligands are present [1]. Ferrous nitrosyl porphyrins, however, are generally five-coordinate, even in the presence of ligands. Ligation of nitrosyl complexes generally weakens both the nitrosyl and the bond of the *trans*-ligand [2], often leading to dissociation of the NO and the formation of a bis-ligated complex [3–7]. In ferrous guanylate cyclase (sGC), the formation of a nitrosyl complex leads to the loss of histidine ligation and the formation of a 5-coordinate nitrosyl complex [8, 9].

Yoshimura [10] examined the effect of solvation on the nitrosyl bond of the Fe(PPDME)(NO) complex (PPDME = protoporphyrin-dimethyl ester). The energy of the band varied over a narrow range for a variety of solvents between 1658 and 1684 cm⁻¹, with the most significant shift only being observed for the strongest coordinating solvents such as acetonitrile (1658 cm⁻¹) and DMSO (1660 cm⁻¹). Only a small shift was observed between CCl₄ (1684 cm⁻¹) [11] and THF (1673 cm⁻¹). The shifts in the nitrosyl band in the solvents studied were ascribed to solvation rather than coordination effects. Amines such as pyridine did yield bands for the five- and six-coordinate complexes. Nitrosyl bands for the six-coordinate amine complexes were observed between 1618 and 1643 cm⁻¹ [10]. Linear relationships were observed between the pK_a of the base and the ν_{NO} stretching frequencies, but different linear relationships were observed for imidazoles, pyridines and aliphatic amines. The largest shifts were observed for imidazole, with smaller shifts for pyridines, then aliphatic amines. The shifts varied from 30 cm⁻¹ for 3-chloropyridine (pK_a = 2.84) to 47 cm⁻¹ for 4-methylimidazole (pK_a = 7.52) and 4-dimethylaminopyridine (pK_a = 9.70).

The visible spectra of iron porphyrin nitrosyl complexes in the presence of nitrogenase bases were studied by Yoshimura and Ozaki [6]. Wyllie *et al.* [12] examined the crystal structures of five- and six-coordinate

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Fig. 1. Structure of octaethylporphione

iron(II) porphyrin nitrosyls. Six-coordinate Fe(TPP)(NO) complexes with 1-methylimidazole or 4-methylpiperidine led to a lengthening and weakening the Fe–N bond *trans* to the NO [3, 12–14]. In the six-coordinate complex, the spin density (0.8) was mostly localized on the NO group, while there was a lower spin density (0.5) for the five-coordinate complex [3]. The formation constants, *K*, for pyridines and amines with iron porphyrin nitrosyls were determined using voltammetry by Choi and Ryan [4] and Liu *et al.* [15]. The *K* values were found to be generally small. The formation constants for Fe(OEPone)(NO) and Fe(OEPdione)(NO) (OEPdione = 2,4-octaethylporphinedione) with pyridines were larger than Fe(OEP)(NO)/pyridine complexes.

The infrared spectroelectrochemistry of Fe(P)(NO) complexes where P = porphyrins or porphines has been examined in our laboratory, mostly in THF [16]. Upon further study, it was found that Fe(OEPone)(NO) (H₂OEPone = octaethylporphione, Fig. 1) was more complex than reported with evidence of solvent (THF) coordination, that was not observed for Fe(OEP)(NO).

EXPERIMENTAL

Materials and reagents

Tetrahydrofuran (THF) and methylene chloride (CH₂Cl₂) were purchased from Sigma–Aldrich Chemical Co. THF-*d*₈ and methylene chloride-*d*₂ were purchased from Cambridge Isotope Laboratories. The deuterated solvents were used for infrared spectroelectrochemical experiments. Octaethylporphione was purchased from Frontier Scientific, and iron was inserted and the nitrosyl complex synthesized by procedures in the literature [17, 18].

Equipment and procedures

The FTIR spectroelectrochemical cell was previously described [16]. The infrared spectra were obtained using 64 scans and 2 cm^{−1} resolution, recorded with a Thermo

Nicolet-FTIR spectrophotometer (Model 670 Nexus) with a MCT detector. The visible spectroelectrochemical experiments have been previously described [19]. UV-vis spectra were recorded on a HP 8452A diode array spectrophotometer. All solutions were prepared in a glove box under dinitrogen. For UV-vis spectra, a slow cyclic scan of the potential was used. For the FTIR, potentials were chosen to be sufficiently negative to insure complete electrolysis.

Computational methods

Electronic structure calculations were carried out with the Gaussian 09 suite of programs [20] using the procedures previously described [19], or, as noted, by the Gaussian 16 suite of programs [21]. Infrared frequencies were corrected with scale factors of 0.94 for m06, 0.96 for m06L and 1.0 for mpwvwn and bp86.

RESULTS AND DISCUSSION

Infrared spectroscopy of Fe(OEPone)(NO)

The infrared spectrum of Fe(OEPone)(NO) in methylene chloride was typical of other metalloporphyrin nitrosyls (Fig. 2). The ν_{NO} bands in methylene chloride and KBr were identical (Table 1). Similar results were also observed for Fe(OEP)(NO). The downshift for ¹⁵NO substitution for ¹⁴NO (*na* = normal abundance) in methylene chloride was also consistent with metalloporphyrin nitrosyls. The infrared spectrum for Fe(OEPone)(NO) in THF, however, was significantly different. The ν_{NO} band at 1680 cm^{−1} was still observed in THF, but a new band was also seen at 1658 cm^{−1} (Fig. 2).

Fig. 2. Infrared spectra of Fe(OEPone)(NO) in methylene chloride and THF. Fe(OEPone)(¹⁴NO): CH₂Cl₂ (red), THF (black); Fe(OEPone)(¹⁵NO): CH₂Cl₂ (blue), THF (green)

These bands have been previously observed, but the lower energy band was not attributed to be a nitrosyl vibration [16] because isotopic substitution was not done. In this work, it was found that both bands were sensitive to ^{15}NO substitution. The lower-energy nitrosyl band in THF was consistent with a six-coordinate iron porphyrin nitrosyl complex. For nitrogen ligands, two nitrosyl bands were observed in the infrared spectra of $\text{Fe}(\text{PPDME})(\text{NO})$ in the presence of nitrogen ligands; the first was due to the 5-coordinate ferrous nitrosyl complex and the second (with a downshift of 33 cm^{-1}) was due to the 6-coordinate complex. Ligation *trans*- to the nitrosyl ligand in iron porphyrin complexes is generally weak. For example, the equilibrium constant for the ligation of pyridine with $\text{Fe}(\text{OEP})(\text{NO})$ is about 0.3, which increased to 4.8 for $\text{Fe}(\text{OEPone})(\text{NO})$ [15].

Repeating the experiment with $\text{Fe}(\text{OEP})(\text{NO})$, only a single isotopically sensitive ^{15}NO band was observed in methylene chloride and THF. In addition, there was no significant difference in the ν_{NO} band between KBr pellets and THF. The infrared bands for ν_{CO} and ν_{NO} are summarized in Table 1. In addition to the downshift of the nitrosyl band, the ν_{CO} was upshifted by 5 cm^{-1} in THF as compared to methylene chloride. On the other hand, the ν_{NO} was the same in methylene chloride and the five-coordinate complex in THF (1681 cm^{-1}) (Table 1).

The appearance of the 1658 cm^{-1} band was found to be a function of the %THF in methylene chloride (Fig. S1). The band could be clearly observed at 60% THF or more, and the height of the band, relative to the 1680 cm^{-1} band increased as the %THF increased. A rough estimate of the percent 6-coordinate complex that was present was estimated by using the absorbance of the ν_{CO} band as a reference and assuming that the molar absorptivities of the ν_{CO} band of the 5- and 6-coordinates are the same. With these rough assumptions, 22% of the iron nitrosyl

species was 6-coordinate in 60% THF, increasing to 46% in pure THF. This would yield a K for the formation of the 6-coordinate THF complex to be 0.07 ± 0.02 .

Spectroelectrochemical reduction of $\text{Fe}(\text{OEPone})(\text{NO})$ in methylene chloride and THF

The visible spectroelectrochemistry of $\text{Fe}(\text{OEPone})(\text{NO})$ in methylene chloride is shown in Fig. S2. The Soret band shifted from 406 to 410 nm and decreased slightly in absorbance. In the longer wavelength region, the 625 nm band disappeared and two new bands at 532 and 612 nm appeared. Similar results were observed for the reduction of $\text{Fe}(\text{OEPone})(\text{NO})$ in THF (Fig. S3), with the Soret band shifting from 410 to 415 nm. The Q band for the nitrosyl complex was 618 nm, and for the reduced nitrosyl complex the bands were 535 and 607 nm.

The infrared spectroelectrochemical difference spectra of $\text{Fe}(\text{OEPone})(\text{NO})$ in methylene chloride is shown in Fig. 3. The general features show reduction of the carbonyl band at 1710 cm^{-1} and the nitrosyl band at 1681 cm^{-1} . The reduced nitrosyl band at 1440 cm^{-1} increased as the reduction proceeded. The carbonyl band was considerably downshifted by the reduction, as can be seen by the positive ΔA band at 1662 cm^{-1} . The inset in Fig. 3 shows the absorbance spectra for $\text{Fe}(\text{OEPone})(\text{NO})$ and $\text{Fe}(\text{OEPone})(\text{NO})^-$ between 1750 and 1600 cm^{-1} . The band at 1669 cm^{-1} for ν_{CO} can be seen (the overlap with the nitrosyl band caused a shift in the difference spectrum). This downshift was comparable to the ν_{CO} band shift that was observed for the formation of $\text{Fe}(\text{OEPone})^-$ in THF (1671 cm^{-1}) [16]. The infrared spectroelectrochemistry of $\text{Fe}(\text{OEPone})(^{15}\text{NO})$ was carried out (Fig. S4). The nitrosyl band was downshifted to 1647 cm^{-1} and the reduced nitrosyl band to 1410 cm^{-1} . These shifts were consistent with the isotopic substitution. As expected, the carbonyl

Table 1. Experimental and calculated infrared bands for CO and NO vibrations

Compound		Solvent	$\nu_{\text{CO}}, \text{ cm}^{-1}$	$\nu_{\text{NO}}, \text{ cm}^{-1}$
$\text{Fe}(\text{OEPone})(\text{NO})$	Experimental	CH_2Cl_2	1710	1681
	Experimental	THF	1715	1681
	Experimental	KBr	1715	1681
	DFT/m06	—	1720	1683
	DFT/m06L	—	1718	1702
	DFT/bp86	—	1701	1690
$\text{Fe}(\text{OEPone})(\text{THF})(\text{NO})$	Experimental	THF	1715	1658
	DFT/m06	—	1721	1683
	DFT/m06L	—	1713	1694
	DFT/bp86	—	1698	1672
$\text{Fe}(\text{OEPone})(\text{NO})^-$	Experimental	CH_2Cl_2	1669	1440
	Experimental	THF	1702	1440
	DFT/m06	—	1679	1538

Fig. 3. Difference infrared spectroelectrochemical spectra of Fe(OEPone)(NO) in CD_2Cl_2 . Red spectra: initial difference spectrum; green: intermediate spectra; blue: final spectrum. Inset: Absorbance spectrum of Fe(OEPone)(NO) (red); spectrum of Fe(OEPone)(NO) $^-$ (blue)

Fig. 4. Difference infrared spectroelectrochemical spectra of Fe(OEPone)(NO) in THF. Red spectra: initial difference spectrum; green: intermediate spectra; blue: final spectrum

bands for the nitrosyl and the reduced nitrosyl complexes were unchanged from the normal abundance spectra.

The infrared spectroelectrochemistry of Fe(OEPone)(NO) in THF is shown in Fig. 4. Both Fe–NO bands decreased as the reduction proceeded, but only one ν_{NO} (1440 cm^{-1}) was observed for the reduced nitrosyl product, which was a value typical of other reduced ferrous porphyrin nitrosyls [16], and Fe(OEPone)(NO) in methylene chloride. The downshift of the ν_{CO} band is significantly smaller (1715 to 1702 cm^{-1}) than the shift observed earlier in methylene chloride. The results were confirmed for Fe(OEPone)(^{15}NO) (Fig. S5) where the nitrosyl and the reduced nitrosyl bands were both downshifted as expected, and the carbonyl bands were at the same position as for the normal abundance

spectra. The small shift in the ν_{CO} band as compared to methylene chloride was probably due to solvation rather than coordination effects. This will be investigated in the next section. Voltammetric data showed no evidence for 6-coordinate complexes for the reduced nitrosyl complex, consistent with the fact that stronger ligands showed no evidence of coordination [4, 15].

DFT calculations

DFT calculations were carried out on the 5- and 6-coordinate Fe(OEPone)(NO) complexes and their reduction product. In general, the localized functionals such as m06L and bp86 predicted stronger Fe–THF interactions than m06 and mpwvwn. In fact, mpwvwn predicted no bond between iron and THF. For the other functionals, the Fe–O(THF) bond lengths from $2.489\text{ \AA}$ (bp86) to $2.569\text{ \AA}$ (m06) were calculated. These bond lengths were somewhat longer than the experimental Fe–O(THF) bond length in Fe(TPP)(THF) $_2$ of $2.351\text{ \AA}$ [22]. The calculated O–Fe–N bond angle in Fe(OEPone)(THF)(NO) was found to be 173° , with the deviation due to the known tilt of the Fe–NO group. The DFT calculations were consistent with a weak complexation of THF to the iron-nitrosyl complex.

The calculated ν_{NO} and ν_{CO} bands for Fe(OEPone)(NO) complexes are shown in Table 1. The m06 functional predicted the longest Fe–O(THF) bond and also predicted that THF coordination would not affect the ν_{NO} and ν_{CO} bands. As would be expected, a shorter Fe–O(THF) bond led to a greater downshift in the ν_{NO} band, dropping by 8 cm^{-1} for m06L to 18 cm^{-1} for bp86. These compare with the observed downshift of 23 cm^{-1} . The absolute values of the ν_{NO} and ν_{CO} energies followed trends which we have seen earlier. The bp86 functional predicts reasonably well the experimental values without a scale factor, but its energies are systematically low [23]. The m06 and m06L generally need a scale factor of 0.94 and 0.96, respectively, for these complexes. In this work, the bp86 predicted a small upshift in the ν_{CO} band upon forming the THF complex (as was observed), while the m06 functional showed no shift and the m06L functional predicted a downshift.

As was discussed earlier [3], the SOMO for Fe(OEPone)(NO)(THF) is mostly localized on the Fe–NO moiety (Fig. S6). By contrast, there was significant delocalization of the electron density in the five coordinate complex (Fig. S6). Similar results were observed by Praneeth *et al.* [3] for Fe(P)(NO) complexes with nitrogen ligands.

DFT calculations of Fe(OEPone)(NO)(THF) $^-$ showed a much weaker interaction between the Fe atom and THF than was observed for the nitrosyl complex. The Fe–O(THF) bond length increased from $2.530\text{ \AA}$ to $2.657\text{ \AA}$ (m06L), with an O–Fe–N bond angle of 176° . As discussed earlier, stronger ligands such as pyridine showed no evidence for coordination with the reduced

Fig. 5. HOMO orbitals for $\text{Fe}(\text{OEPone})(\text{NO})^-$ with THF solvation (a) and without solvation (b). Functional: m06. Gaussian 16

nitrosyl complex. Thus, both DFT calculations and experimental evidence showed that the reduced iron nitrosyl species was 5-coordinate. The most significant difference in the infrared spectra between $\text{Fe}(\text{OEPone})(\text{NO})^-$ in THF and methylene chloride is the carbonyl band. Only a small downshift was observed for ν_{CO} in THF solution (1715 to 1702 cm^{-1} , or 13 cm^{-1} downshift), while the ν_{CO} in methylene chloride decreased from 1710 to 1669 cm^{-1} (41 cm^{-1} downshift). The origin of this shift is not due to coordination differences, but rather due to solvation. Evidence for this can be seen in comparing the HOMO for $\text{Fe}(\text{OEPone})(\text{NO})^-$ with and without solvation (Fig. 5). Figure 5a shows the HOMO for THF-solvated $\text{Fe}(\text{OEPone})(\text{NO})^-$. The electron density was mostly on the Fe-NO moiety, with essentially no electron density on the carbonyl group. By contrast, Fig. 5b (for the unsolvated complex) showed an increased electron density on the carbonyl group, in an anti-bonding π^* orbital, weakening the C-O bond, consistent with a larger downshift in the poorly solvating methylene chloride. This has been observed before for $\text{Ni}(\text{OEPone})^-$ where

interactions between a strongly associated cation and the carbonyl group [24] downshifted the ν_{CO} band by increasing the electron density on the carbonyl group, and hence, the π^* orbital. The observed differences in the ν_{CO} between the two solvents can be best attributed to solvation rather than iron coordination effects.

CONCLUSIONS

Solvents can affect the spectral and redox properties of a complex by either solvation or coordination effects. Ferrous porphyrin nitrosyl complexes are often 5-coordinate, and 6-coordinate complexes are prone to the loss of NO and the formation of bis-ligand complexes. While $\text{Fe}(\text{OEP})(\text{NO})$ shows no evidence of coordination with THF, the porphyrinone analogue was able to form a 6-coordinate complex with THF. In this work, the combination of infrared spectroelectrochemistry and DFT calculations made it possible to identify changes that were primarily due to coordination or solvation. Solvent coordination by THF to the ferrous nitrosyl complex was the source of the significant downshift in the ν_{NO} band for $\text{Fe}(\text{OEPone})(\text{NO})$. For $\text{Fe}(\text{OEPone})(\text{NO})^-$, solvation was the source of the observed changes in the carbonyl band, with little evidence for the formation of a six-coordinate complex. This was consistent with previous studies where the reduced iron-nitrosyl complex was a much weaker Lewis acid. On the other hand, the solvation of the reduced Fe-nitrosyl moiety by THF drew electron density away from the π^* orbital between C and O, causing the ν_{CO} to downshift significantly less than was observed in a non-coordinating solvent such as methylene chloride.

Supporting information

Figures S1–S6 are given in the supplementary material. This material is available free of charge *via* the Internet at <http://www.worldscinet.com/jpp/jpp.shtml>.

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