



One Electron Makes Differences: From Heme {FeNO}⁷ to {FeNO}⁸

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Dedicated to Professor W. Robert Scheidt

Abstract: The first X-ray single-crystal structure of a {FeNO}⁸ porphyrin complex [Co(Cp)₂][Fe(TFPPBr₈)(NO)], and the structure of the {FeNO}⁷ precursor [Fe(TFPPBr₈)(NO)] are determined at 100 K. The two complexes are also characterized by FTIR and UV/Vis spectroscopy. [Fe(TFPPBr₈)(NO)][−] shows distinct structural features in contrast to a nitrosyl iron(II) porphyrinate on the Fe–N–O[−] moiety, which include a much more bent Fe–N–O[−] angle (122.4(3)°), considerably longer Fe–NO[−] (1.814(4)) and N–O[−] (1.194(5) Å) bond distances. These and the about 180 cm^{−1} downshift ν_{N–O} stretch (1540 cm^{−1}) can be understood by the covalently bonding nature between the iron(II) and the NO[−] ligand which possesses a two-electron-occupied π* orbital as a result of the reduction. The overall structural features of [Fe(TFPPBr₈)(NO)][−] and [Fe(TFPPBr₈)(NO)] suggest a low-spin state of the iron(II) atom at 100 K.

There has been considerable research interest over the past decades in the NO[−] ligand (nitroxyl anion)^[1] not only because of its biological significance,^[2] but also because of its relationship with NO (nitric oxide or nitrosyl)^[3] and HNO (nitroxyl or azanone).^[4,5] NO[−] is the one-electron-reduced form of NO. The important properties of NO in biology as a messenger and as an immune defense agent are significant in heme systems.^[6] NO[−] is also the deprotonated form of HNO. There is great interest in the coordination chemistry of HNO and NO[−] with hemes because of the role of these complexes as an important effector molecule in biology or as key intermediates in nitrite (NO₂[−]) and nitric oxide (NO) reducing enzymes.^[7,8]

NO[−] is highly reactive and has its own distinct chemistry. It is isoelectronic with dioxygen (O₂); both can exist in singlet or triplet electronic spin states. Triplet NO[−] reacts with O₂ to produce the ONOO[−] (peroxynitrite) at a nearly diffusion-controlled rate (2.7 × 10⁹ M^{−1} s^{−1}),^[9] rather singlet NO[−] does not.^[10] This is contrasted to NO which reacts with superoxide to produce the ONOO[−].^[11] It has also been suggested that ONOO[−] formation is observed when NO[−] is formed by the reduction of NO by ferrocyanochrome c.^[12]

Extensive studies,^[13] including Fe^{II,III} ligand vibration identifications by single-crystal nuclear resonance vibrational spectroscopy (NRVS),^[14,15] have been completed on ferro and ferric heme nitrosyl complexes which are labeled {FeNO}⁶ and {FeNO}⁷ in the Enemark–Feltham notation.^[16] However, limited success has been achieved in producing corresponding, one-electron-reduced {FeNO}⁸ complexes where NO[−] is formally bound to an iron(II) center. Several spectroelectrochemical studies on the reduction of ferrous heme-nitrosyl complexes to generate corresponding Fe^{II}–NO[−] species have been reported.^[17] The groundbreaking isolation of a solid powder of the five-coordinate [Fe^{II}(Porph)(NO[−])]^[18] by chemical reduction of the [Fe^{II}(Porph)(NO)] precursor was achieved by using the extremely electron-poor porphyrin H₂TFPPBr₈.^[19] Most recently, Lehnert and co-workers reported new reactivity data using a bis-picket fence porphyrin model system.^[20] Herein, we report the first structural determination of a {FeNO}⁸ porphyrin complex [Co(Cp)₂][Fe(TFPPBr₈)(NO)]. The characterization of the {FeNO}⁷ precursor [Fe(TFPPBr₈)(NO)] is also reported and the two species are compared.

To obtain single crystals of satisfactory quality for X-ray diffraction, different solvents have been tried in the reduction of [Fe(TFPPBr₈)(NO)]. Dichloromethane was first used because of its good solubility for the reactants. Three single-crystal specimens from different reactions have been measured; in each case the iron and axial ligand show two positionally and crystallographically independent disorders. Disorders were also found for the [Co(Cp)₂]⁺ cation and CH₂Cl₂ solvent molecules. These are given in the Supporting Information. Subsequently toluene is used to replace CH₂Cl₂ and decent single crystals were isolated. The crystal structure was determined at 100 K.^[21] The asymmetric unit contains one [Fe(TFPPBr₈)(NO)][−] porphyrin anion, one [Co(Cp)₂]⁺ cation, and toluene solvent molecules. All molecules including the [Co(Cp)₂]⁺ cation are ordered, except one partially occupied toluene molecule. The crystalline product was further confirmed by FTIR and UV/Vis spectroscopy. A common FTIR spectrometer with a pyroelectric detector (DTGS) showed a shoulder peak at the position of the N–O[−] stretch (Figures S5 and S6). Whereas the spectrometer with a liquid-nitrogen-cooled mercury–cadmium–telluride (MCT) detector afforded an unambiguous individual peak at 1540 cm^{−1}, which is first observed for an isolated sample. The comparison is shown in Figure 1. An important correlation between ν(N–O) of {FeNO}⁷ and {FeNO}⁸ systems has been given by Lehnert and co-workers.^[20] [Fe(TFPPBr₈)(NO)][−] and its precursor show the highest N–O stretches

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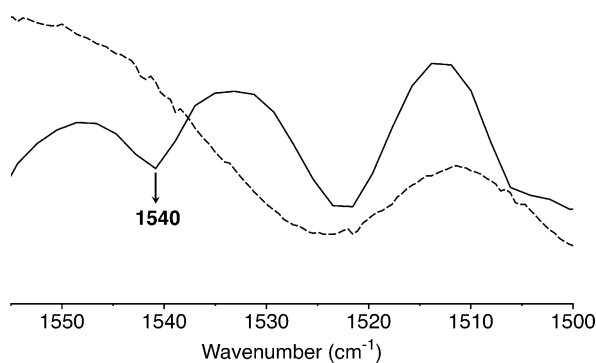


Figure 1. FTIR spectra of $[\text{Co}(\text{Cp})_2][\text{Fe}(\text{TFPPBr}_8)(\text{NO})]$. Only part of the spectrum is shown for clarity. Dashed and solid lines are for DTGS and MCT detectors, respectively.

among the analogs, which is ascribed to the electron-withdrawing peripheral groups.

An edge-on ORTEP drawing of $[\text{Co}(\text{Cp})_2][\text{Fe}(\text{TFPPBr}_8)(\text{NO})]$ is displayed in Figure 2. The NO^- ligand binds to the iron(II) atom in a distinctly bent fashion with the $\text{Fe}-\text{N}-\text{O}^-$ angle being $122.4(3)^\circ$, which is much smaller than 149° for the $\text{Fe}-\text{N}-\text{O}^-$ angles in $\{\text{FeNO}\}^7$ analogs.^[13,22] Interestingly, this angle is comparable to the $\text{Fe}-\text{O}-\text{O}$ angles ($118\text{--}132^\circ$) in the diamagnetic oxyheme complexes $[\text{Fe}(\text{TpivPP})(\text{R-Im})(\text{O}_2)]$ ($\text{R-Im} = 1\text{-MeIm}, 1\text{-EtIm}$ and 2-MeHIm),^[23] where the dioxygen ligand corresponds to a Pauling model with its singlet state.^[24] The $\text{Fe}-\text{NO}^-$ and $\text{N}-\text{O}^-$ bond distances are $1.814(4)$ and $1.194(5)$ Å, respectively; both appear longer than those in a $\{\text{FeNO}\}^7$ system. The $\text{Fe}-\text{NO}^-$ bond is almost normal to the porphyrin plane with a tilt angle of 1.8° . The dihedral angle between the $\text{Fe}-\text{N}-\text{O}$ plane and the closest $\text{Fe}-\text{N}_\text{p}$ vector (φ) is 37.3° (see Figure S3 in the Supporting Information). The porphyrin plane is strongly saddled. These structural features are consistent with the DFT predictions of a singlet state.^[19]

The $\{\text{FeNO}\}^7$ precursor of $[\text{Fe}(\text{TFPPBr}_8)(\text{NO})]$ is also structurally determined at 100 K. The asymmetric unit contains one $[\text{Fe}(\text{TFPPBr}_8)(\text{NO})]$ porphyrin complex and one

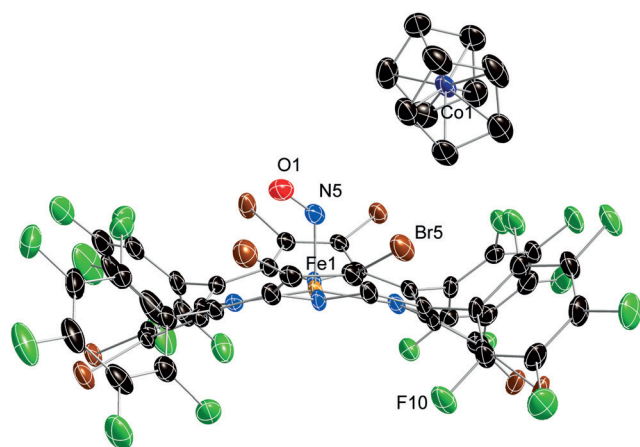


Figure 2. Thermal ellipsoid diagram of $[\text{Fe}(\text{TFPPBr}_8)(\text{NO})]$. Ellipsoids are drawn at the 50% probability level. Solvent molecules are not shown for reasons of clarity.

CH_2Cl_2 solvent molecule. An ORTEP drawing of the $[\text{Fe}(\text{TFPPBr}_8)(\text{NO})]$ structure is given in Figure 3 and an overlay diagram showing both $[\text{Fe}(\text{TFPPBr}_8)(\text{NO})]$ and $[\text{Fe}(\text{TFPPBr}_8)(\text{NO})]^-$ is given in Figure 4 for comparison. Similar to $[\text{Fe}(\text{TFPPBr}_8)(\text{NO})]^-$, the porphyrin core is strongly saddled, which suggests that it is the nature of the octabromo porphyrin derivatives that tend to show a saddled porphyrin core.^[25] The NO ligand binds to the iron in a bent fashion with the $\text{Fe}-\text{N}-\text{O}$ angle being $148.5(4)^\circ$. The $\text{Fe}-\text{NO}$ bond is $1.741(5)$ Å long and has a tilt angle of 5.0° . The average $\text{Fe}-\text{N}_\text{p}$ distance is $1.988(12)$ Å. The overall structural features are those expected for a low-spin $\{\text{FeNO}\}^7$ porphyrin complex.^[26]

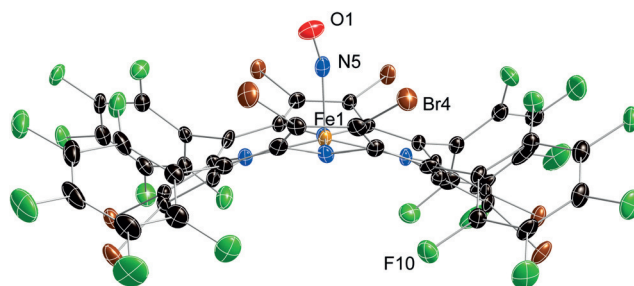


Figure 3. Thermal ellipsoid diagram of $[\text{Fe}(\text{TFPPBr}_8)(\text{NO})]$. Ellipsoids are drawn at the 50% probability level. Solvent molecules are not shown for reasons of clarity.

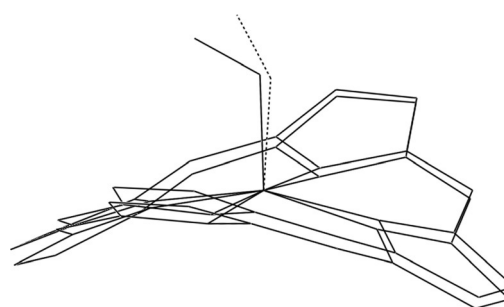


Figure 4. An overlay diagram showing the structures of $[\text{Fe}(\text{TFPPBr}_8)(\text{NO})]$ and $[\text{Fe}(\text{TFPPBr}_8)(\text{NO})]^-$. Only the 24-atom porphyrin cores are shown for clarity. The molecules can be seen to have nearly identical core conformations. But the $\text{Fe}-\text{N}-\text{O}$ moieties show distinct fashions.

Key structural parameters of $[\text{Fe}(\text{TFPPBr}_8)(\text{NO})]^-$, and the nitrosyl analogs of $[\text{Fe}(\text{TFPPBr}_8)(\text{NO})]$, $[\text{Fe}(\text{TPP})(\text{NO})]$, and $[\text{Fe}(\text{OEP})(\text{NO})]$ are given in Table 1; DFT predictions are also given for comparison. It is seen that the $\text{Fe}-\text{NO}^-$ axial bond ($1.814(4)$) is considerably longer than the $\text{Fe}-\text{NO}$ bond ($1.717\text{--}1.741$ Å). The shorter $\text{Fe}-\text{NO}$ bond suggests stronger π back bonding from iron $d\pi$ orbitals to the NO ligand. However, the one-electron reduction of NO resulted in a π^* orbital of NO^- occupied by two electrons, which strengthened the σ bonding to the iron d_{z^2} orbital, which accounts for the $\text{Fe}-\text{N}-\text{O}^-$ angle, which is more bent in the $[\text{Fe}(\text{TFPPBr}_8)(\text{NO})]^-$ anion by about 26° .^[13b] The higher electron density of the π^* orbital also results in a longer $\text{N}-\text{O}^-$ bond distance and a 180 cm^{-1} downshift of the $\nu_{\text{N-O}}$ stretch (Table 1). Similar drops of $\nu_{\text{N-O}}$ have been observed by the research groups of Ryan^[17b,c] and Lehnert.^[20]

Table 1: Selected Structural Parameters of {FeNO}⁸, {FeNO}⁷, and {CoNO}⁸ porphyrin complexes and related DFT predications.^[a]

Complexes	Method	M–N _{NO} ^[b]	N–O ^[b]	(M–N _p) _{av} ^[b]	M–N–O ^[c]	τ ^[c,d]	ν _{N–O} ^[e]	Ref.
{FeNO} ⁸ Structures and DFT Predications								
[Fe(TFPPBr ₈)(NO)] [–]	SC	1.814(4)	1.194(5)	1.972(11)	122.4(3)	1.8	1540	tw ^[g]
[Fe(TFPPBr ₈)(NO)] [–]	DFT	1.790	1.201		122.7		1547 ^[f]	[19]
[Fe(Porphine)(NO)] [–]	DFT	1.778	1.211		123.1		1530	[19]
[Fe(Porphine)(NO)] [–]	DFT	1.786	1.206	2.011	125		1533	[20]
Mb-HNO	XAFS	1.82(2)	1.24(1)	2.00(2)	131(6)		1385	[5a]
{FeNO} ⁷ Structures and DFT Predications								
[Fe(TFPPBr ₈)(NO)]	SC	1.741(5)	1.131(6)	1.988(12)	148.5(4)	5.0	1718	tw
[Fe(TPP)(NO)]	SC	1.717(7)	1.122(12)	2.001(3)	149.2(6)		1670	[22]
[Fe(OEP)(NO)]	SC	1.7307(7)	1.1677(11)	2.009(12)	142.74(8)	8.2	1673	[29]
[Fe(TFPPBr ₈)(NO)]	DFT	1.711	1.182		144.4		1726 ^[f]	[19]
{CoNO} ⁸ Structures								
[Co(TPPBr ₈ NO ₂)(NO)]	SC	1.827(21)	1.081(43)	1.945(28)	124.7(23)	1.9	1710	[30]
[Co(OEP)(NO)]	SC	1.8444(9)	1.1642(13)	1.984(8)	122.70(8)	2.2	1677	[31]
[Co(OEP)(NO)]	SC	1.844(2)	1.152(3)	1.985(9)	123.4(2)		1675	[32]
[Co(TPP)(NO)]	SC	1.8301(5)	1.1492(7)	1.9672(6)	123.39(5)	0.6	1681	[33]

[a] Estimated standard deviations are given in parentheses. [b] Value in angstroms. [c] Value in degrees. [d] The tilt of the Fe–NO vector from normal to the 24-atom mean plane. [e] Values in cm^{–1}. [f] Experimental value. [g] This Work.

24-atom mean planes of [Fe(TFPPBr₈)(NO)][–] and [Fe(TFPPBr₈)(NO)] are presented in Figure S3. The iron of [Fe(TFPPBr₈)(NO)][–] shows a two-fold smaller out-of-plane displacement ($\Delta_{24} = 0.19$ Å) than that of [Fe(TFPPBr₈)(NO)] (0.36 Å), which is in agreement with its shorter (Fe–N_p)_{av} bond distance and slightly larger (N_p–Fe–N_p)_{av} angle (89.9(8) vs. 89.0(3)°). The lower and upper extremes of metal displacements for a low-spin, five-coordinate nitrosyl iron(II) porphyrin complex are 0.19 and 0.36 Å.^[27]

In Table 1 structural parameters of several nitrosyl cobalt(II) porphyrinates are given. It is seen that {FeNO}⁸ and {CoNO}⁸ systems show a strong similarity in the geometry of the M–N–O moieties, suggesting the highly covalent nature of the triatomic M–N–O units. The M–N–O angles of the {CoNO}⁸ system are very similar to that of the {FeNO}⁸ system, the values of which are in a narrow range of 122–125°. In a {CoNO}⁸ complex, the low-spin d⁷ cobalt(II) atom and the nitrosyl molecule contribute each one electron to form the Co–NO σ bonding.^[28] This is compared to the same strong σ bonding of the Fe–NO[–] bond, where the two electrons originate from the π* orbital of the NO[–] ligand. However, different electron density populations are indicated by N–O bond stretches. [Fe(TFPPBr₈)(NO)][–] with its two-electron π* orbital shows the lowest ν_{N–O} (1540 cm^{–1}) of the three systems, in contrast to the about 140 cm^{–1} higher ν_{N–O} of the {CoNO}⁸ and {FeNO}⁷ complexes where only one electron occupies the π* orbital of the NO ligand.

In summary, we have synthesized and characterized the {FeNO}⁸ porphyrin complex [Fe(TFPPBr₈)(NO)][–] and its nitrosyl precursor [Fe(TFPPBr₈)(NO)] by single-crystal X-ray diffraction and FTIR and UV/Vis spectroscopy. The high-quality crystallographic study reveals distinct differences on the Fe–NO moieties between the two systems. Both species present structural characteristics belonging to a low-spin iron(II) porphyrin complex at 100 K. Physical characterizations including multi-temperature Mössbauer measurements

on [Fe(TFPPBr₈)(NO)] and [Co(Cp)₂][Fe(TFPPBr₈)(NO)] are in progress.

Experimental Section

Synthesis of [Fe(TFPPBr₈)(NO)]: [Fe(TFPPBr₈)Cl] (100 mg, 0.048 mmol) was dried in vacuum for 1 h in a Schlenk tube. Dichloromethane (ca. 10 mL) was transferred into the Schlenk tube by cannula and ethanethiol (ca. 4 mL) was added via syringe. The mixture was stirred under argon at ambient temperature. After 5 h, the reduction was completed (monitored by UV/Vis spectroscopy) and the solvent was evaporated by the pump. NO gas was bubbled in slowly through a solution of the residue in degassed dichloromethane (ca. 8 mL) for 5 minutes under an argon atmosphere. There is a dramatic color change from red to greenish yellow and the reaction was thought to be complete upon the disappearance of the red color. X-ray quality crystals were obtained by liquid diffusion using hexane as the non-solvent. UV/vis (CH₂Cl₂): λ_{max} = 430, 582 nm. IR (Nujol): ν(N–O) = 1718 cm^{–1}.

Synthesis of [Co(Cp)₂][Fe(TFPPBr₈)(NO)]: [Fe(TFPPBr₈)(NO)] (10 mg, 0.0059 mmol) and Co(C₅H₅)₂ (1 mg, 0.053 mmol) was dried in vacuum for 1 h in a Schlenk tube. Dichloromethane (ca. 5 mL) was transferred into the Schlenk tube by cannula. The mixture was then stirred for an hour under argon at ambient temperature. The product, which precipitated after the addition of 5 mL of cold hexane, was separated from the solution by filtration. The resulting solid was dissolved in toluene and hexane was then allowed to diffuse slowly into the solution. Crystals of X-ray quality were obtained several weeks later. UV/Vis (CH₂Cl₂): λ_{max} = 430, 582 nm. IR (KBr plates): ν(N–O) = 1540 cm^{–1}.

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- [18] Abbreviations: CH_2Cl_2 , dichloromethane; Cp, cyclopentadienyl; Porph, a generalized porphyrin dianion; TFPPBr₈, dianion of 2,3,7,8,12,13,17,18-octabromo-5,10,15,20-[tetrakis-(pentafluorophenyl)]porphyrin; TpivPP, dianion of $\alpha,\alpha,\alpha,\alpha$ -tetrakis(*o*-pivalamidophenyl)porphyrin; TPP, dianion of *meso*-tetraphenylporphyrin; OEP, dianion of octaethyl tetranitroporphyrins; TPPBr₄NO₂, dianion of 2-nitro-7,8,17,18-tetrabromo-5,10,15,20-tetraphenylporphyrin; 1-MeIm, 1-methylimidazole; 1-EtIm, 1-ethylimidazole; 2-MeHIm, 2-methylimidazole; N_{pp}, porphyrinato nitrogen.
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