Structure Elucidation **Hot Paper**

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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* $[Co(Cp)_2][Fe(TFPPBr_8)(NO)]$, *and the structure of the* $\{FeNO\}^7$ *precursor* $[Fe(TFPPBr_8)(NO)]$ *are determined at 100 K. The two complexes are also characterized by FTIR and UV/Vis spectroscopy.* $[Fe(TFPPBr_8)(NO)]^-$ *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* $\nu_{N\text{-}O}$ *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* $[Fe(TFPPBr_8)(NO)]^-$ *and* $[Fe(TFPPBr_8)(NO)]$ *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 (NO_2^-) and nitric oxide (NO) reducing enzymes.[7,8]

NO^- is highly reactive and has its own distinct chemistry. It is isoelectronic with dioxygen (O_2); both can exist in singlet or triplet electronic spin states. Triplet NO^- reacts with O_2 to produce the $ONOO^-$ (peroxynitrite) at a nearly diffusion-controlled rate ($2.7\times10^9\,M^{-1}s^{-1}$),[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 ferrocytochrome *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 $H_2TFPPBr_8$.[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 $[Co(Cp)_2][Fe(TFPPBr_8)(NO)]$. The characterization of the $\{FeNO\}^7$ precursor $[Fe(TFPPBr_8)(NO)]$ 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 $[Fe(TFPPBr_8)(NO)]$. 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 CH_2Cl_2 solvent molecules. These are given in the Supporting Information. Subsequently toluene is used to replace CH_2Cl_2 and decent single crystals were isolated. The crystal structure was determined at 100 K.[21] The asymmetric unit contains one $[Fe(TFPPBr_8)(NO)]^-$ 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] $[Fe(TFPPBr_8)(NO)]^-$ and its precursor show the highest N–O stretches

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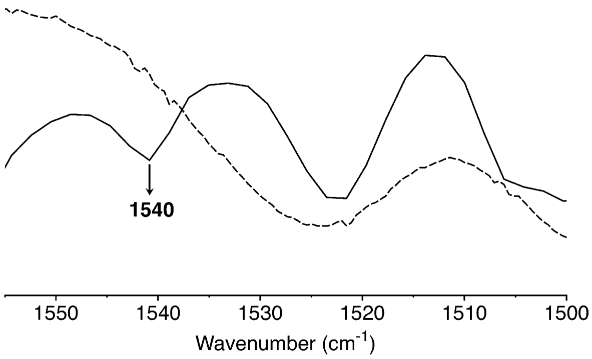

Figure 1. FTIR spectra of [Co(Cp)$_2$][Fe(TFPPBr$_8$)(NO)]. Only part of the spectrum is shown for clarity. Dashed and solid lines are for DTGS and MCT detectors, respectively.

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

An edge-on ORTEP drawing of [Co(Cp)$_2$][Fe(TFPPBr$_8$)(NO)] is displayed in Figure 2. The NO$^-$ ligand binds to the iron(II) atom in a distinctly bent fashion with the Fe–N–O$^-$ angle being 122.4(3)°, which is much smaller than 149° for the Fe–N–O angles in {FeNO}^{7} analogs.[13,22] Interestingly, this angle is comparable to the Fe–O–O angles (118–132°) in the diamagnetic oxyheme complexes [Fe(TpivPP)(R-Im)(O$_2$)] (R-Im = 1-MeIm, 1-EtIm and 2-MeHIm),[23] where the dioxygen ligand corresponds to a Pauling model with its singlet state.[24] The Fe–NO$^-$ and N–O$^-$ bond distances are 1.814(4) and 1.194(5) Å, respectively; both appear longer than those in a {FeNO}^{7} system. The Fe–NO$^-$ bond is almost normal to the porphyrin plane with a tilt angle of 1.8°. The dihedral angle between the Fe–N–O plane and the closest Fe–N$_p$ 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 {FeNO}^{7} precursor of [Fe(TFPPBr$_8$)(NO)] is also structurally determined at 100 K. The asymmetric unit contains one [Fe(TFPPBr$_8$)(NO)] porphyrin complex and one CH$_2$Cl$_2$ solvent molecule. An ORTEP drawing of the [Fe(TFPPBr$_8$)(NO)] structure is given in Figure 3 and an overlay diagram showing both [Fe(TFPPBr$_8$)(NO)] and [Fe(TFPPBr$_8$)(NO)]$^-$ is given in Figure 4 for comparison. Similar to [Fe(TFPPBr$_8$)(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 Fe–N–O angle being 148.5(4)°. The Fe–NO bond is 1.741(5) Å long and has a tilt angle of 5.0°. The average Fe–N$_p$ distance is 1.988(12) Å. The overall structural features are those expected for a low-spin {FeNO}^{7} porphyrin complex.[26]

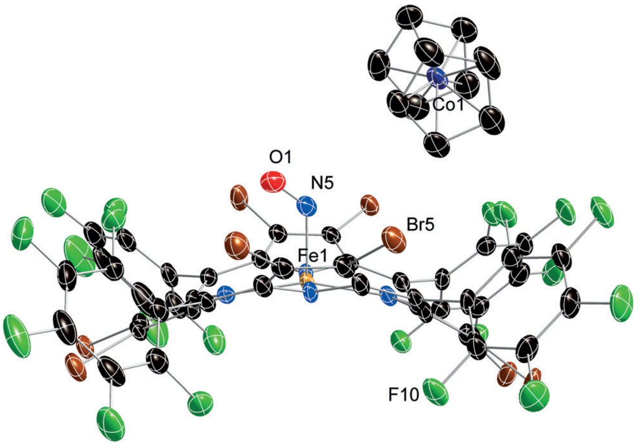

Figure 2. Thermal ellipsoid diagram of [Fe(TFPPBr$_8$)(NO)]. Ellipsoids are drawn at the 50% probability level. Solvent molecules are not shown for reasons of clarity.

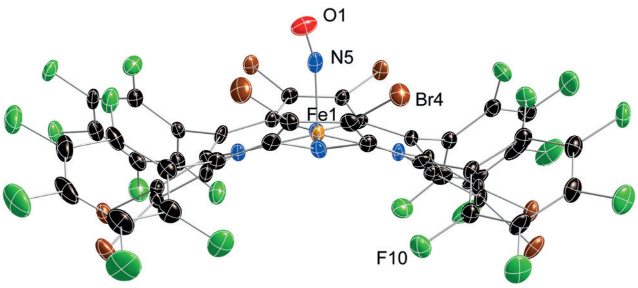

Figure 3. Thermal ellipsoid diagram of [Fe(TFPPBr$_8$)(NO)]. Ellipsoids are drawn at the 50% probability level. Solvent molecules are not shown for reasons of clarity.

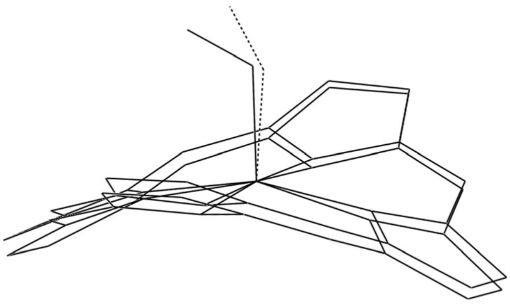

Figure 4. An overlay diagram showing the structures of [Fe(TFPPBr$_8$)(NO)] and [Fe(TFPPBr$_8$)(NO)]$^-$. Only the 24-atom porphyrin cores are shown for clarity. The molecules can be seen to have nearly identical core conformations. But the Fe–N–O moieties show distinct fashions.

Key structural parameters of [Fe(TFPPBr$_8$)(NO)]$^-$, and the nitrosyl analogs of [Fe(TFPPBr$_8$)(NO)], [Fe(TPP)(NO)], and [Fe(OEP)(NO)] are given in Table 1; DFT predictions are also given for comparison. It is seen that the Fe–NO$^-$ axial bond (1.814(4)) is considerably longer than the Fe–NO bond (1.717–1.741 Å). The shorter Fe–NO bond suggests stronger π back bonding from iron dπ 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 Fe–N–O$^-$ angle, which is more bent in the [Fe(TFPPBr$_8$)(NO)]$^-$ anion by about 26° .[13b] The higher electron density of the π^* orbital also results in a longer N–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]	$\nu_{N\text{-}O}$ [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					
$[Co(TPPBr_4NO_2)(NO)]$	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 $[Fe(TFPPBr_8)(NO)]^-$ and $[Fe(TFPPBr_8)(NO)]$ are presented in Figure S3. The iron of $[Fe(TFPPBr_8)(NO)]^-$ shows a two-fold smaller out-of-plane displacement ($\Delta_{24} = 0.19$ Å) than that of $[Fe(TFPPBr_8)(NO)]$ (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 d^7 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. $[Fe(TFPPBr_8)(NO)]^-$ with its two-electron π* orbital shows the lowest $\nu_{N\text{-}O}$ (1540 cm^{-1}) of the three systems, in contrast to the about 140 cm^{-1} higher $\nu_{N\text{-}O}$ 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 $[Fe(TFPPBr_8)(NO)]^-$ and its nitrosyl precursor $[Fe(TFPPBr_8)(NO)]$ 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 $[Fe(TFPPBr_8)(NO)]$ and $[Co(Cp)_2][Fe(TFPPBr_8)(NO)]$ are in progress.

Experimental Section

Synthesis of $[Fe(TFPPBr_8)(NO)]$: $[Fe(TFPPBr_8)Cl]$ (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 (CH_2Cl_2): $\lambda_{max} = 430$, 582 nm. IR (Nujor): ν(N-O) = 1718 cm^{-1}.

Synthesis of $[Co(Cp)_2][Fe(TFPPBr_8)(NO)]$: $[Fe(TFPPBr_8)(NO)]$ (10 mg, 0.0059 mmol) and $Co(C_5H_5)_2$ (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 (CH_2Cl_2): $\lambda_{max} = 430$, 582 nm. IR (KBr plates): ν(N–O) = 1540 cm^{-1}.

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[1] The chemical notation for nitroxyl (NO$^-$/HNO) is often used interchangeably, but here the term NO$^-$ denotes nitroxyl anion with the understanding that the molecule can exist as a protonated species as well.

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[18] Abbreviations: CH$_2$Cl$_2$, dichloromethane; Cp, cyclopentadienyl; Porph, a generalized porphyrin dianion; TFPPBr$_8$, 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 ltetranitroporphyrins; TPPBr$_4$NO$_2$, 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$_p$, porphyrinato nitrogen.

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