

Reactions of Nitric Oxide with a Low-Spin Fe(III) Center Ligated to a Tetradentate Dicarboxamide N₄ Ligand: Parallels between Heme and Non-heme Systems

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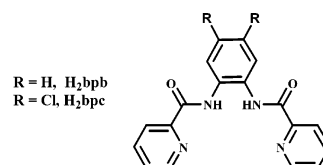
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Although transition metal complexes of nitric oxide (NO) have been studied for quite some time,¹ reactions of NO at the metal centers of designed complexes have drawn much attention in recent years. Such reactions are of fundamental chemical interest in relation to various important biological and environmental processes.² Lippard and co-workers have recently reported disproportionation of NO effected by tropocoronand (TC-5,5) complexes of bivalent manganese and iron.³ The iron complex [Fe(NO)(TC-5,5)], in the presence of excess NO, converts to a *metastable* nitrosyl–nitrito complex which decomposes to afford NO₂ and subsequent nitration of the aromatic ring.^{3b} Several (nitro)(nitrosyl)iron(III) complexes of general formula [Fe(Porph)(NO₂)(NO)], (where Porph is the dianion of tetraphenylporphyrin, octaethylporphyrin, tetra-*p*-methoxyphenylporphyrin, or picket fence porphyrin) have been synthesized via metal-assisted disproportionation of NO.⁴ A close scrutiny of the literature, however, reveals that no single complex exhibits all the reactions of NO noted with heme *and* non-heme systems. For example, in no case has nitration of the porphyrin ring been observed. At the same time, no non-heme iron complex with (nitro)-(nitrosyl) coordination has been structurally characterized in which the bound nitro group results from metal-assisted disproportionation of NO in the reaction mixture.⁵ Also, no metal nitrosyl by itself leads to ring nitration in solution in the presence of dioxygen. Herein we report an iron complex derived from a non-heme tetradentate planar N₄ ligand system that exhibits regular and reductive nitrosylation, formation of (nitrosyl)(nitro) species via disproportionation of NO, and ring nitration upon reaction with NO under slightly different conditions.

The dicarboxamide ligand H₂bpb, in its deprotonated form, can provide four nitrogen donor sites, two neutral N and two anionic carboxamido N. The negative charges on the carboxamido N are highly delocalized on the ligand frame; hence, it resembles the porphyrinato ligand to some extent. Indeed, chemistry parallel to iron-porphyrin complexes has been reported with the iron complexes of bpb²⁻ (and its ring-substituted derivatives) such as spin-state regulation⁶ and π -cation radical complex formation.⁷ To date, the reactions of the iron complexes of bpb²⁻ ligand with NO have not been explored. In this Communication, we report the syntheses and characterization of the iron nitrosyls [(bpb)Fe(NO)(NO₂)] (**1**) and [(bpb)Fe(NO)] (**2**) and a ring-nitrated complex [(bpb-NO₂)Fe(NO₃)-(DMF)] (**3**).

Although the high-spin Fe(III) complex (Et₄N)[(bpb)Fe(Cl)₂] did not afford any isolable nitrosyl, reaction of NO with the low-spin starting complex[(bpb)Fe(Py)₂]ClO₄ afforded **1** and **2** in different mixed solvent media. It is therefore evident that the spin state of the iron center of the precursor complex dictates its affinity toward NO. When a solution of [(bpb)Fe(Py)₂]ClO₄ in thoroughly degassed MeCN solution was kept in an atmosphere of purified NO⁸ at room



temperature for 12 h, microcrystalline [(bpb)Fe(NO)(NO₂)] (**1**) separated out from the reaction mixture in 80% yield. This diamagnetic compound displays ν_{NO} at 1919 cm⁻¹, ν_{CO} at 1634 cm⁻¹, and ν_{NO_2} at 1475, 1423, and 1312 cm⁻¹, respectively. The bound NO₂⁻ is presumably formed in the reaction mixture in the presence of excess NO via formation of an N–N-coupled, (NO)₂ adduct intermediate as suggested in the case of TpCu(NO) (Tp = sterically protected tris(pyrazolyl)borate)⁹ as well as [Fe(TPP)(NO)].¹⁰ In **1** (Figure 1), the iron center is ligated to four N atoms of the deprotonated bpb²⁻ ligand in the equatorial plane, while the NO and NO₂⁻ occupy the axial sites. The average Fe–N_{amide} distance (1.9113(18) Å) is shorter than the average Fe–N_{py} distance (2.0236(18) Å). The Fe–N(NO) bond distance (1.6847(19) Å) and the Fe–N–O angle (171.24 (17)°) are typical of {Fe–NO}⁶-type iron nitrosyls.¹¹

Interestingly, when a solution of [(bpb)Fe(Py)₂]ClO₄ in MeCN/MeOH (1:1 v/v) was stored under an atmosphere of NO, reductive nitrosylation afforded dark brown blocks of [(bpb)Fe(NO)] (**2**) in ~65% yield. This {Fe–NO}⁷-type nitrosyl has a *S* = 1/2 ground state (μ_{eff} = 1.75 μ_{B} at 298 K) and exhibits a rhombic electron paramagnetic resonance (EPR) spectrum with *g* values at 2.17, 1.99, and 1.96 (MeCN/MeOH glass, 100 K, Figure S1, Supporting Information). Complex **2** displays ν_{NO} at 1673 cm⁻¹, much like the other {Fe–NO}⁷-type nitrosyls reported so far.¹¹ Isolation of **2** clearly demonstrates that solvents used during the synthesis of iron nitrosyls play a crucial role. Even in the presence of excess NO, no disproportionation was observed during the synthesis of **2** in the presence of MeOH. As shown in Figure 2, the geometry around the iron center of **2** is distorted square pyramidal, and the axial position is occupied by NO. The Fe–N(NO) bond distance (1.7129(11) Å) and the Fe–N–O angle (144.74 (11)°) are typical of {Fe–NO}⁷-type iron nitrosyls.¹¹

Complex **1** is sparingly soluble in most common organic solvents, except for DMF and DMSO. When a solution of **1** in DMF/MeCN (1:3 v/v) was kept in the presence of dioxygen, the initial brown solution slowly changed into a dark green one. Diffusion of Et₂O into this solution afforded green blocks of [(bpb-NO₂)Fe(NO₃)-(DMF)] (**3**) in ~40% yield. The most important feature of the structure of **3** (Figure 3) is the presence of the nitro group on the benzene ring of the bpb²⁻ ligand. The oxygen atom of DMF and one of the oxygens of nitrate occupy the axial positions. Both the Fe–N_{amide} (average distance = 2.035(4) Å) and Fe–N_{py} (average distance = 2.142(4) Å) distances of **3** are comparable to those in the high-spin Fe(III) complex ((*n*-Bu)₄N)[Fe^{III}(bpb)(N₃)₂].^{7b}

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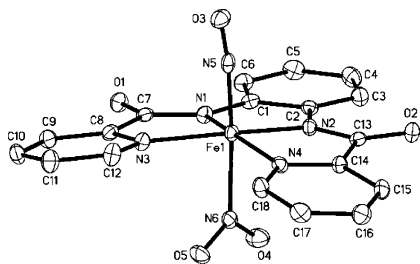


Figure 1. ORTEP diagram of [(bpb)Fe(NO)(NO₂)] (**1**), showing the atom labeling scheme. All H atoms have been omitted for clarity. Selected bond lengths [Å] and bond angles [°]: Fe–N1 1.9145(19), Fe–N2 1.9082(18), Fe–N3 2.0254(19), Fe–N4 2.0218(18), Fe–N5 1.6847(19), Fe–N6 2.0110(18), N5–O3 1.137(2), N6–O4 1.237(2), Fe–N5–O3 171.24(17).

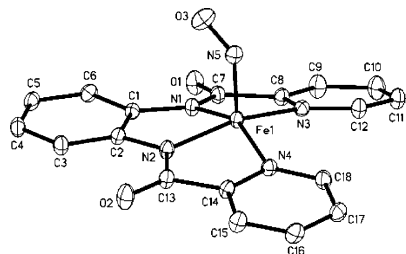


Figure 2. ORTEP diagram of [(bpb)Fe(NO)] (**2**), showing the atom labeling scheme. All H atoms have been omitted for clarity. Selected bond lengths [Å] and bond angles [°]: Fe–N1 1.8939(11), Fe–N2 1.8952(11), Fe–N3 2.0440(11), Fe–N4 2.0288(11), Fe–N5 1.7129(11), N5–O3 1.1818(15), Fe–N5–O3 144.74(11).

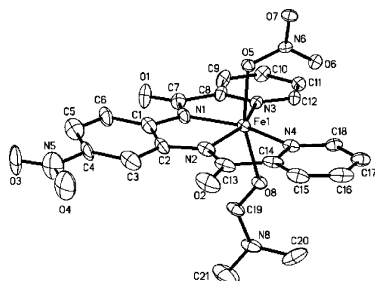
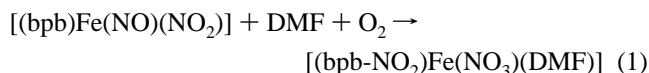


Figure 3. ORTEP diagram of [(bpb-NO₂)Fe(NO₃)(DMF)] (**3**), showing the atom labeling scheme. All H atoms have been omitted for clarity. Selected bond lengths [Å] and bond angles [°]: Fe–N1 2.037(4), Fe–N2 2.033(4), Fe–N3 2.131(4), Fe–N4 2.154(4), Fe–O5 2.049(3), Fe–O8 2.009(4), O5–Fe–O8 162.26(13).

During the transformation **1** → **3**, the dark green color is generated only in the presence of dioxygen, and the reaction goes according to eq 1. In the absence of dioxygen, the DMF/MeCN solution of **1** decomposed over time to give yellow gelatinous precipitate.



Ford and co-workers have recently reported that dilution of a toluene solution of [Fe(TPP)(NO)(NO₂)] decayed via NO dissociation to form [Fe(TPP)(NO₂)], which upon subsequent reaction with dioxygen forms [Fe(TPP)(NO₃)].¹² In the present case, dissolution of solid **1** in DMF/MeCN causes the dissociation of bound NO, which then reacts with dioxygen to provide NO₂, the species responsible for ring nitration.¹³ That NO₂ is the nitrating agent is proved by the fact that reaction of NO₂ gas with [(bpb)Fe(Py)(NO₂)] in DMF/MeCN (1:3 v/v) affords **3** within minutes. Dissociation of the bound NO₂[−] and its subsequent reaction with dioxygen (or NO₂) presumably produce NO₃[−] (which eventually binds Fe(III) via an O atom), much like the mechanism proposed for the formation of [Fe(TPP)(NO₃)].¹² Finally, DMF coordinates

to the Fe(III) center through its oxygen atom to produce **3**. Thus, **1** utilizes both of its axial ligands to afford **3** in the presence of dioxygen. To prove that the bound NO is responsible for ring nitration, we have repeated the reaction of **1** with dioxygen in DMF/MeCN in the presence of glutathione (GSH), a NO scavenger. In that experiment, no green color was generated even after 12 h, and *S*-nitroso glutathione (GSNO) was detected in the reaction mixture by HPLC.

Although conversion of **1** to **3** in the presence of dioxygen is slow (several hours) in the dark, the process can be made fast by exposing the reaction mixture to light (tungsten lamp, 100 W). This indicates that NO in **1** is photolabile.¹¹ Complex **3** can be readily synthesized in higher yield (~50%) via incubation of a solution of [(bpb)Fe(Py)₂]ClO₄ in DMF/MeCN (1:3 v/v) in the presence of a large excess of NO plus a small amount of dioxygen. The initial brown solution turns dark green within minutes. It is very possible that this reaction proceeds via the intermediacy of **1**. Indeed, the same brown reaction mixture turns green (formation of **3**) even faster upon illumination. Nitration of the bpb^{2−} ligand can be easily checked by isolating NO₂-bpbH₂ from **3** via mild acidification and measuring its mass spectrum. Both the EPR spectrum (*g* = 4.37) and the magnetic moment value (*μ*_{eff} = 6.01 *μ*_B at 298 K) of **3** clearly demonstrate the high-spin nature (*S* = 5/2) of the Fe(III) center.

In conclusion, we have synthesized both the {Fe–NO}⁶(nitrosyl)-(nitro) complex [(bpb)Fe(NO)(NO₂)] (**1**) and the {Fe–NO}⁷ complex [(bpb)Fe(NO)] (**2**) via regular and reductive nitrosylation in conjunction with NO disproportionation reactions. A ring-nitrated complex [(bpb-NO₂)Fe(NO₃)(DMF)] (**3**) has also been characterized. Although these reactions have been individually reported with different heme and non-heme systems, the Fe/bpb^{2−} system reported here is the first example in which all the reactions of NO are observed. These reactions underscore the parallels between heme and non-heme chemistry. The solvent plays a crucial role in these syntheses.

Supporting Information Available: Experimental details for the synthesis of **1–3**, X-band EPR spectrum of **2**, and X-ray crystallographic files, in CIF format. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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JA040015N