Inorganic Chemistry
Communication
pubs.acs.org/IC

An Exclusively Organometallic $\{FeNO\}^7$ Complex with Tetracarbene Ligation and a Linear FeNO Unit

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Supporting Information

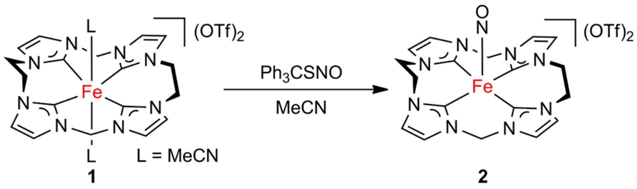
ABSTRACT: The iron(II) complex **1** of a macrocyclic tetracarbene binds NO to form a low-spin (S = $^1/_2$) $\{FeNO\}^7$ complex (**2**) with a linear FeNO unit and a short Fe–NO bond. IR, electron paramagnetic resonance, and Mössbauer spectroscopies as well as density functional theory calculations suggest some Fe^INO^+ character and reveal that the singly occupied molecular orbital of **2**, resulting from the σ-antibonding interaction of Fe d_{z^2} and the NO lone pair, is largely iron-based. Reduction yields a quite stable $\{FeNO\}^8$ species (**3**); both **2** and **3** feature very low Mössbauer isomer shifts (~0.0 mm·s^{-1}).

While long viewed only as a toxic environmental pollutant, nitric oxide (NO) is now known to serve many essential biological functions.[1] Its interaction with metallobiosites, in particular with heme and nonheme iron centers, plays a key role in this respect. Because of their high covalency, which usually hampers the assignment of oxidation states, iron-bound NO compounds are classified according to the Enemark–Feltham notation.[2] Nitrosylhemes and related $\{FeNO\}^7$ complexes with tetragonal metal-ion coordination, either six-coordinate (6C) octahedral or five-coordinate (5C) square-pyramidal, are generally S = $^1/_2$ species, while nonheme examples have been reported with either S = $^1/_2$ or $^3/_2$ ground state.[3,4] The vast majority of these $\{FeNO\}^7$ complexes have a bent FeNO unit with angles in the range 140–150°, resulting from the crucial σ interaction between the Fe d_{z^2} orbital and an NO π^* orbital. A few exceptions stand out because they feature quasi-linear $\{FeNO\}^7$ units, some of them 5C with S = $^1/_2$ and some of them four-coordinate (4C) pseudotetrahedral with S = $^3/_2$ ground state.[3,5,6] The electronic structure basis for this linear NO coordination has recently been elucidated in a series of density functional theory (DFT) studies.[7]

Most of the reported and structurally authenticated FeNO species are supported by nitrogen- or sulfur-donor ligands, likely because of the biological relevance of such a ligand environment. Apart from cyano complexes such as nitroprusside and $[Fe(CN)_4(NO)]^{2-}$,[5] organometallic FeNO complexes featuring Fe–C bonds are rare and are so far limited to N-confused porphyrin systems with a $\{N_3C\}$ donor set.[8] However, it has recently been shown that N-heterocyclic carbenes (NHCs) can stabilize key bioinorganic moieties, in some cases with unusual electronic structures or properties.[9−12] In particular, a macrocyclic tetracarbene scaffold L^{TC}, which is topologically reminiscent of tetrapyrrole macrocycles although electronically quite distinct,[13] has allowed isolation of an unprecedented organometallic oxoiron(IV) complex.[12] Here we present the synthesis, structure, spectroscopic properties, and DFT-based electronic structure description of an organometallic $\{FeNO\}^7$ complex with exclusive carbon-donor ligation provided by L^{TC}.

The new FeNO complex $[L^{TC}Fe(NO)](OTf)_2$ (**2**) can be synthesized by treating an acetonitrile (MeCN) solution of the iron(II) tetracarbene $[L^{TC}Fe(MeCN)_2](OTf)_2$ (**1**) with either gaseous NO or 1 equiv of trityl *S*-nitrosothiol (Scheme 1). Blue crystals suitable for X-ray diffraction could be obtained in 54% yield by the slow diffusion of Et_2O into a MeCN solution of **2** at −35 °C. Crystalline material is stable under light and air for several days, but a solution of **2** slowly turns yellow upon exposure to light and yields the starting material **1** or, under air, the corresponding μ-oxodiiron(III) complex $[(L^{TC}Fe)_2O)]^{4+}$.[12] Light sensitivity is typical for many FeNO complexes.[14]

Scheme 1. Formation of 2 via Reaction of the Iron(II) Complex 1 with the NO Precursor Trityl *S*-Nitrosothiol



Complex **2** crystallizes in the triclinic space group $P\bar{1}$. The iron center is found 5C in a roughly square-pyramidal environment (τ = 0.27),[15] with the tetracarbene macrocycle forming the basal plane and the NO ligand in the axial position (Figure 1). The iron atom is displaced by 0.41 Å out of the basal $\{C_4\}$ plane toward the

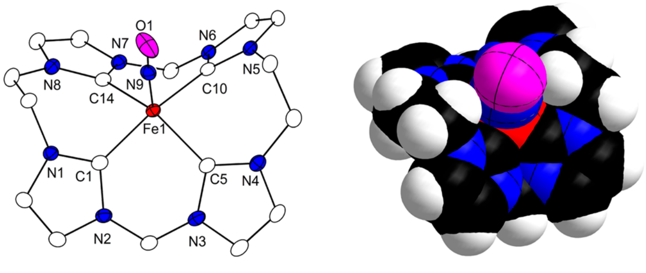


Figure 1. Molecular structure of the cation of **2** (left, 30% probability thermal ellipsoids; right, space-filling model). Anions and hydrogen atoms have been omitted for clarity.

Received: February 10, 2015
Published: March 18, 2015

DOI: 10.1021/acs.inorgchem.5b00301
Inorg. Chem. 2015, 54, 3096−3098

NO. The macrocycle is ruffled, and the C−Fe−C angles are relatively small (164.3° and 148.1°). Importantly, **2** is a rare example of an $\{FeNO\}^7$ complex that shows a quasi-linear Fe−N−O moiety (angle Fe1−N9−O1 176.9°). A space-filling model confirms that linearity is not imposed by steric constraints (Figure 1); hence, it should have its origin in the electronic structure. While the N−O bond length of 1.166(4) Å is in the typical range (1.15−1.18 Å), the Fe−NO bond [1.670(3) Å] is shorter than that in most reported $\{FeNO\}^7$ complexes. The latter value is actually close to the Fe−NO bond lengths of several $\{FeNO\}^6$ complexes (1.63−1.67 Å), which are usually described as having some nitrosonium (NO^+) character.[3]

A SQUID magnetic susceptibility measurement confirmed the low-spin state of **2**. The $\chi_M T$ value of 0.39 $cm^3 \cdot K \cdot mol^{-1}$ is almost constant in the range from 295 to 10 K and is close to the spin-only value expected for an $S = {}^1/_2$ system [0.375 $cm^3 \cdot K \cdot mol^{-1}$; see the Supporting Information (SI) for details]. The zero-field ^{57}Fe Mössbauer spectrum of the solid material, collected at 80 K, is depicted in Figure 2. Complex **2** shows a low isomer shift (IS), $\delta = -0.01$ $mm \cdot s^{-1}$, and a large quadrupole splitting, $\Delta E_Q = 2.36$ $mm \cdot s^{-1}$. These values reflect the strong equatorial donor strength of the macrocyclic tetracarbene, pronounced charge donation into the Fe 4s and $3d_{x^2-y^2}$ orbitals, and resulting oblate charge distribution around the iron nucleus. Large quadrupole splittings have been observed previously for ferrous and ferric complexes of L^{TC}.[12] Interestingly, the IS of **2** is similar to the one for the low-spin μ-oxoiron(III) dimer $[(L^{TC}Fe)_2O)]^{4+}$ ($\delta = 0.04$ $mm \cdot s^{-1}$), although the available Mössbauer data for these tetracarbene systems are still too limited for any firm correlation with the metal ion's oxidation state. Furthermore, the Mössbauer parameters of FeNO species are often unusual because of the highly covalent bonding, and a low IS may be caused by strong π-back-bonding ligands such as NO^+.[16]

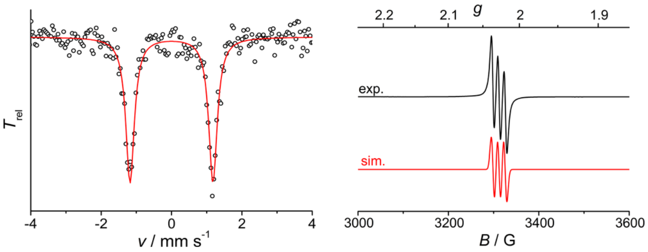


Figure 2. Left: Mössbauer spectrum of solid **2** recorded at 80 K. Right: X-band EPR spectra of **2** in a frozen MeCN solution at 220 K. The red line represents a simulation with parameters $g_{iso} = 2.027$ and $A(^{14}N_{NO}) = 38$ MHz and a Gaussian line broadening of 0.9 mT.

Most reported low-spin $\{FeNO\}^7$ compounds feature electron paramagnetic resonance (EPR) spectra with g values close to 2.0 and low g anisotropy. X-band EPR spectroscopy of a frozen MeCN solution of **2** at 159 K shows a rather broad and almost isotropic signal without resolved ^{14}N ($I = 1$) hyperfine splitting, which can be simulated with g values of 2.029, 2.014, and 1.996 ($g_{av} = 2.013$; Figure S8 in the SI). Temperature-dependent broadening was reported for other paramagnetic FeNO complexes, and a large anisotropy of the line width has been mentioned as a typical feature of 5C ($S = {}^1/_2$) $\{FeNO\}^7$ complexes with four equatorial nitrogen donors.[17,18] At 220 K, an isotropic triplet at $g_{iso} = 2.027$ with hyperfine coupling A ($^{14}N_{NO}$) = 13.4 G is observed for **2** (Figure 2).

The UV/vis/near-IR spectrum of **2** shows a prominent absorption around 350 nm, which is only slightly shifted, although less intense, in comparison with the characteristic $C^{NHC} \rightarrow$ Fe ligand-to-metal charge-transfer band of **1**. In addition, **2** features a broad band at 615 nm, which, on the basis of the DFT results, is assigned to a transition within the FeNO unit with largely NO → Fe character (see the SI). The IR spectrum of **2** in MeCN shows a ν_{N-O} absorption at 1742 cm^{-1} (1748 cm^{-1} for solid material), which is at higher energy than those for other low-spin $\{FeNO\}^7$ complexes (usually in the range 1600−1700 cm^{-1}).[3,19] The position of the ν_{N-O} band is sensitive to the oxidation and spin state of the iron center, and low-spin $\{FeNO\}^7$ generally shows lower NO stretching frequencies than high-spin $\{FeNO\}^7$ (1700−1850 cm^{-1}). On the other hand, linear FeNO groups have higher ν_{N-O} values than their bent analogues, in line with the relatively high frequency for the low-spin system **2**.[20]

Unrestricted DFT calculations (ORCA, BP86, def2-tzvp; see the SI for details) reproduce well the geometry of **2** determined crystallographically. In particular, they reproduce the linearity of the FeNO unit (exptl, 176.9°; calcd, 179.5°), the short Fe−NO bond (exptl, 1.670(3) Å; calcd, 1.661 Å), and the N−O distance (exptl, 1.166 Å; calcd, 1.168 Å). Furthermore, calculated spectroscopic features such as Mössbauer parameters (DFT: $\delta = -0.1$ $mm \cdot s^{-1}$ and $\Delta E_Q = 2.1$ $mm \cdot s^{-1}$) and IR frequencies (DFT: ν_{N-O} at 1795 cm^{-1} and ν_{Fe-NO} at 625 cm^{-1}; both unscaled) agree reasonably well with the experimental data, supporting the suitability of the DFT model. Figure 3 shows the molecular frontier orbitals and reveals that the singly occupied molecular orbital (SOMO) of **2** originates from σ donation of NO(σ^*) into Fe d_{z^2} and has predominantly iron character (53% Fe and 10% NO ligand). This is complemented by π-back-bonding from the occupied Fe d_{xz}/d_{yz} orbitals into NO(π^*); the bonding combination has approximately ${}^2/_3$ $L^{TC}Fe$ character with major L^{TC} contributions, whereas the corresponding antibonding orbital has mainly NO character (68%). The Fe $d_{x^2-y^2}$ orbital is destabilized and lifted even higher than the antibonding orbitals, resulting from Fe d_{xz}/d_{yz}−NO(π^*) interactions, which reflects the extreme in-plane σ-donor

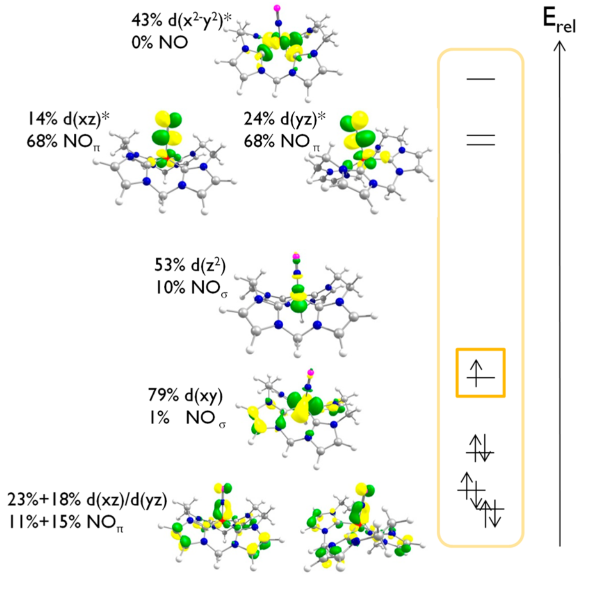


Figure 3. DFT-calculated molecular frontier orbitals (BP86 and def2-tzvp): majority (α) spin orbitals are shown (middle; contour value 0.05) with their dominating Fe d orbital and NO contributions (left) and the molecular orbital scheme according to E_{rel} (right).

strength of the tetracarbene macrocycle. Detailed DFT studies by Conradie and Ghosh have identified metal d_{z^2}/p_z mixing, which is enhanced upon pyramidalization in square-pyramidal $\{FeNO\}^7$ complexes, as a key factor that allows for linearity of the FeNO unit because it minimizes the repulsion between the Fe d_{z^2} orbital and the σ lone pair of NO.[7] The present experimental and DFT results are in accordance with that picture: as reflected by its shape, the SOMO of **2** indeed shows a significant admixture of Fe p_z character (8 and 13%; Table S4 in the SI), which is likely related to the pronounced pyramidalization at iron that results from the rather acute C−Fe−C angles. Taken together, the experimental data and DFT results are in line with the typical highly covalent bonding in the FeNO unit and, although assignment of the formal oxidation states in NO complexes is generally ambiguous, suggest considerable contribution from $Fe^{I}NO^{+}$ character.

Cyclic voltammetry of **2** in a MeCN solution shows a reversible reduction at −0.98 V versus the Cp_2Fe/Cp_2Fe^{+} couple to give the $\{FeNO\}^8$ species, which is at rather positive potential compared to heme nitrosyls (Figure 4).[19] During bulk electrochemical reduction, the blue solution of **2** turned green; the band at 340 nm increases, and a new shoulder around 380 nm arises (see Figure S3 in the SI). Chemical reduction of **2** with cobaltocene gave the same green species, which is quite stable even at room temperature. Its ν_{N-O} absorption is found at 1604 cm^{-1}, which is a moderate shift relative to **2** although in the range of literature-reported shifts of 100−250 cm^{-1} upon going from $\{FeNO\}^7$ to $\{FeNO\}^8$ species (see Figure S5 in the SI).[4,19] A Mössbauer spectrum of a frozen MeCN solution of reduced $[L^{TC}Fe(NO)]^{+}$ at 80 K shows that the IS δ = 0.01 $mm\cdot s^{-1}$ is almost identical with the one of **2**, although the quadrupole splitting ΔE_Q = 0.87 $mm\cdot s^{-1}$ is much smaller (Figure 4). Some Mössbauer-characterized $\{FeNO\}^8$ systems have shown a drastic increase in δ compared to their $\{FeNO\}^7$ precursors,[21] while negligible changes have been interpreted in terms of purely ligand-centered reduction.[18] However, the IS may depend on a subtle interplay of the π-back-bonding ability of the axial ligand, the metal−ligand bond lengths, etc. Efforts toward isolation of the unusual tetracarbene-ligated $\{FeNO\}^8$ complex and full elucidation of its geometric and electronic structure are in progress.

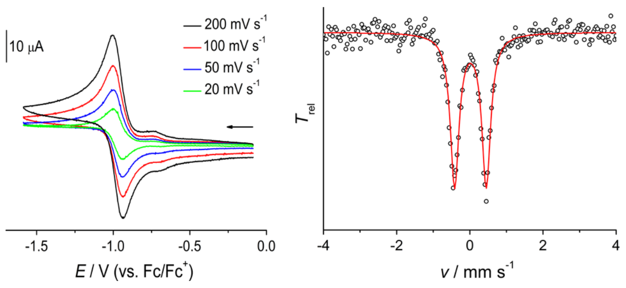


Figure 4. Left: cyclic voltammogram of **2** (c = 1.5 mM) in MeCN/0.1 M Bu_4NPF_6 versus Fc/Fc^{+} at various scan rates. Right: Mössbauer spectrum of the reduced $\{FeNO\}^8$ in MeCN recorded at 80 K.

In summary, **2** is an exclusively organometallic $\{FeNO\}^7$ complex that exhibits rather unusual structural and spectroscopic signatures, likely associated with some $Fe^{I}NO^{+}$ character. The quite high stability of its reduced form offers the prospect of isolating the corresponding $\{FeNO\}^8$ species.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Experimental details, additional spectroscopic and mass spectrometry data, crystallographic data in CIF format, and details of the DFT calculations. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

Support from the Fonds der Chemischen Industrie (Kekulé-Scholarship for C.K.) and the DFG (IRTG 1422 “Metal Sites in Biomolecules: Structures, Regulation and Mechanisms”) is gratefully acknowledged.

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