Iron Catalysis

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The Electronic Ground State of $[Fe(CO)_3(NO)]^-$: A Spectroscopic and Theoretical Study

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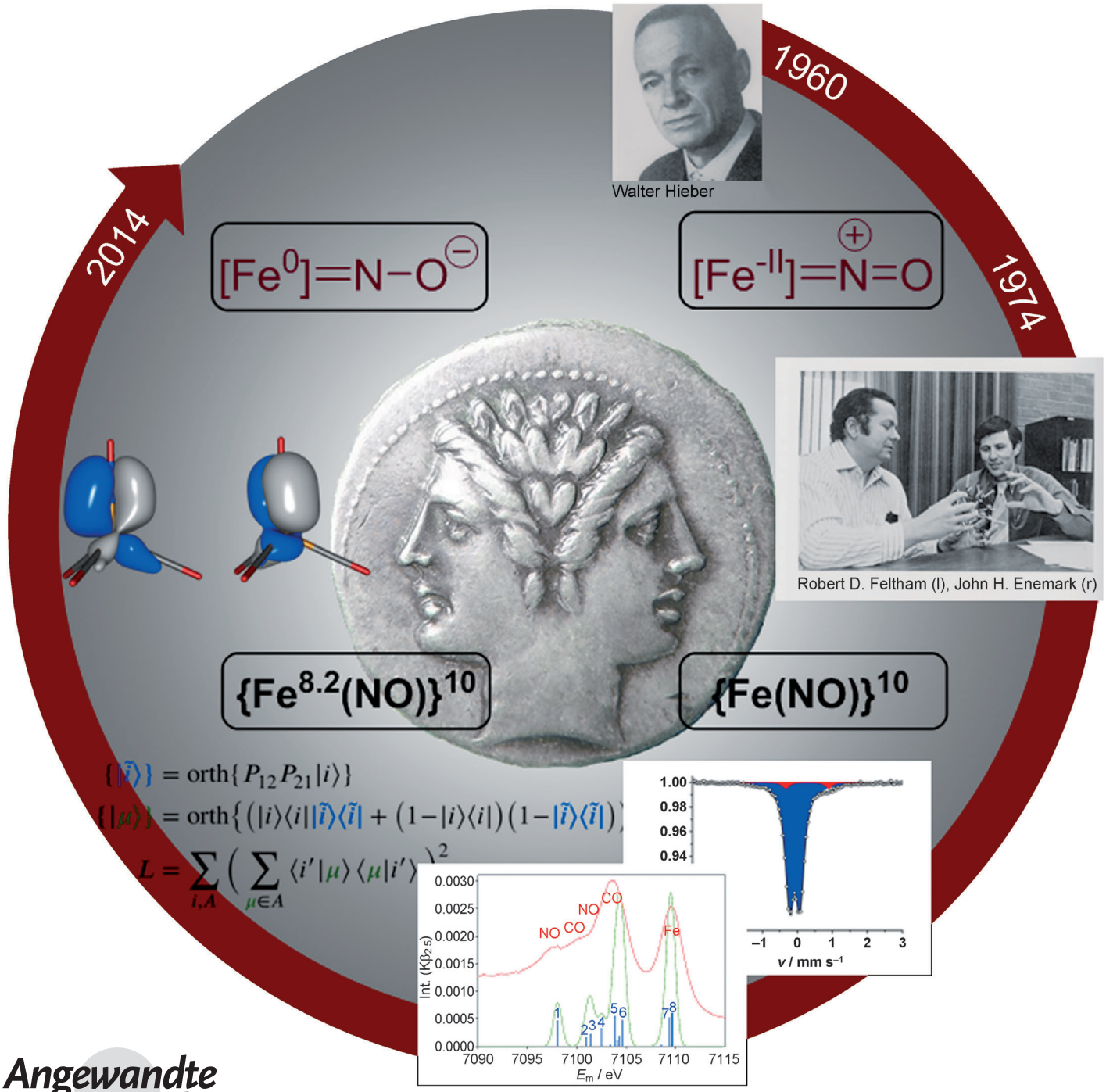

Abstract: *During the past 10 years iron-catalyzed reactions have become established in the field of organic synthesis. For example, the complex anion $[Fe(CO)_3(NO)]^-$, which was originally described by Hogsed and Hieber, shows catalytic activity in various organic reactions. This anion is commonly regarded as being isoelectronic with $[Fe(CO)_4]^{2-}$, which, however, shows poor catalytic activity. The spectroscopic and quantum chemical investigations presented herein reveal that the complex ferrate $[Fe(CO)_3(NO)]^-$ cannot be regarded as a Fe^{-II} species, but rather is predominantly a Fe^0 species, in which the metal is covalently bonded to NO^+ by two π-bonds. A metal–N σ-bond is not observed.*

Both Hieber and Beutner,[1] but also Hogsed,[2] reported the synthesis of the complex ferrate $[Fe(CO)_3(NO)]^-$ more than 50 years ago. Based on measurements of the magnetic susceptibility Hieber described this anion as diamagnetic.[1a] Subsequent IR-spectroscopic investigations and X-ray spectroscopy of different salts showed that the anion has C_{3V} symmetry and a linearly bound NO ligand.[3] Usually this bonding motif is interpreted as the NO ligand being a $[NO]^+$ ion.[4] Early on, however, it was recognized that a clear classification of the NO ligand might be problematic. Meanwhile, neutral or even anionic linear bound NO ligands have been described.[5] To circumvent the problems of classification in transition-metal NO complexes the Enemark–Feltham notation,[6] in which the number of d electrons for a fragment of the general form $\{M(NO)_n\}^m$ (n: number of bound NO ligands; m: number of accessible d electrons) is given thereby avoiding the oxidation-state assignment.

In the past few years we reported a variety of $[Fe(CO)_3(NO)]^-$-catalyzed reactions.[3,7] During these investigations we observed that the formal isoelectronic Collman reagent,[8] $Na_2[Fe(CO)_4]$, shows no activity in the same reactions. Apparently, the NO ligand plays a decisive role in these catalytic transformations. If the NO ligand is considered to be cationic, the iron in the complex ferrate $[Fe(CO)_3(NO)]^-$ should have an oxidation state of −II. However, two of the reported spectroscopic properties are not in line with this assignment:

a) a N–O bond length of 1.212 Å,[9] and
b) a NO signal in the IR spectrum at 1647 cm^{-1}.[10]

These properties indicate the NO ligand may not be cationic but in a reduced form. However, in the majority of cases reduced NO ligands are expected to be bound in a nonlinear fashion.

In light of these arguments we asked ourselves whether the application of modern spectroscopic (Mössbauer spectroscopy, EXAFS spectroscopy, XES spectroscopy) and theoretical methods (DFT, TDDFT, and CASSCF) could help to elucidate the electronic ground state of $[Fe(CO)_3(NO)]^-$ and the nature of the NO ligand. Herein we report the results of this study which led to a significant revision of the classically proposed ground-state structure of this complex ferrate. Despite the linear Fe-N-O bond, the NO ligand should be regarded as a $[NO]^-$ unit rather than a $[NO]^+$ moiety, and it is covalently attached by two Fe–N π bonds to a Fe^0 center.

We started our investigation with a validation of the unusual N–O distance[9] and of the small IR NO signal[10] using DFT methods and additional spectroscopic measurements. The BP86 functional[11] with the def-TZVP basis set[12] and COSMO[13] (Mössbauer parameters were used to generate calibration data using COSMO ($\varepsilon = 80$)) proved to be the method of choice.[14] Bond lengths and angles in $[Fe(CO)_3(NO)]^-$ were obtained that are in good agreement with experimental data derived from X-ray crystallography.[9] Furthermore, both EXAFS in solid phase and in solution (THF) were in good agreement with the Fe–C and Fe–N distances (Table 1).

Table 1: Comparison of experimental and computed structural parameters.

Bond	BP86/def-TZVP COSMO ($\varepsilon = 80$)	EXAFS[a] solid	EXAFS[a] solution	X-Ray[9]
Fe-C	1.776 Å	1.78	1.78	1.800(8) Å
Fe-N	1.661 Å	±0.02 Å	±0.02 Å	1.659(11) Å
C-O	1.175 Å			1.150(9) Å
N-O	1.200 Å			1.212(14) Å
C-Fe-N	116.4°			116.7(3)°
C-Fe-C	101.7...101.8°			101.4(3)°
Fe-N-O	180.0°			180.0°

[a] X-ray absorbing atom: Fe, backscattering neighboring atom: C/N; C and N are not distinguishable by EXAFS, average values for 3×C and 1×N were obtained.

These results support those from the X-ray analysis. The structures obtained were subsequently subjected to frequency analysis within the harmonic approximation (Table 2).

The IR frequencies of the complex anion with various cations were reported by Pannell.[10] Using the non-coordinating cation PPN^+ and crown-ether complexed cations (Na^+ and K^+) in a THF solution, two CO signals (1979, 1875 cm^{-1}) and a characteristic NO signal (1647 cm^{-1}) were observed.[10] The calculated IR frequencies are in good agreement with the experimental ones. The IR frequencies are shifted to lower wavenumbers with increasing polarity/dielectric constant of

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Table 2: Comparison of experimental and theoretical IR frequencies.

Parameter	$\tilde{\nu}$ [cm^{-1}]		
	CO	CO	NO
experimental[10]	1979	1875	1647
gas phase[a]	1953	1875	1681
COSMO ($\varepsilon = 7.36$)[a]	1950	1839	1631
COSMO ($\varepsilon = 80$)[a]	1949	1828	1613

[a] Calculated at the BP86/def-TZVP level of theory.

the solvent. The experimental and theoretical NO frequency differ by only 16 cm^{-1}. Calculations using higher spin multiplicities ($S = 1$ and 2) showed significantly deviating geometries and IR frequencies and will not be considered for in the following (for details see the Supporting Information). The originally reported data is in good agreement with the values reported herein. Hence, DFT is able to describe the properties of our complex anion correctly.

The K$\beta_{2,5}$ XES (valence-to-core(V2C) spectrum) can be calculated using the TD-DFT-level (BP86/def2-TZVP[15]/Fe:CP(PPP)[16]) and are again in good agreement with the experimental data (Figure 1 a). The K$\beta_{1,3}$ XES (core-to-core-(C2C) emission spectrum) provides information regarding the spin-state of the Fe atom. A comparison of the spectra obtained for $[Fe(CO)_3(NO)]^-$ and $[Fe_2(CO)_9]$ (Figure 1 b) shows no Kβ' satellites indicating a low-spin configuration for both complexes.[17] This result is in accordance with the measurement of the magnetic susceptibility of $[Fe(CO)_3(NO)]^-$ and confirms the diamagnetism.[1a] An isomer shift of $\delta = -0.07$ mm s^{-1} and a quadrupole splitting of $|\Delta E_Q| = 0.29$ mm s^{-1} were experimentally determined by Mössbauer spectroscopy (Figure 1 c). Literature Mössbauer spectra of different $[Fe(CO)_3(NO)]^-$ salts are in good agreement with the data obtained in this study.[18]

Neese and Ye used the calculation of Mössbauer parameters for the evaluation of the electronic structure of dinitrosyl iron complexes of the general type $\{Fe(NO)_2\}^{10}$.[19] In these cases a broken symmetry solution BS(4,4) in combination with the TPSSh functional was used for the successful reproduction of the experimental data. Therefore, it was concluded that the complex has a Fe^{+II} ($S = 2$) center with two antiferromagnetically coupled linear bound anionic NO ligands ($S = 1$).[19]

Based upon these results the Mössbauer parameters of the calculated $[Fe(CO)_3(NO)]^-$ structure (BP86/def-TZVP/COSMO(ε=80)) were calculated using BP86 (GGA), TPSS (*meta*-GGA),[20] TPSSh (*meta*-hybrid functional),[21] and B3LYP (hybrid functional)[22] (Table 3).

The CP(PPP) basis set[16] for iron and the def-TZVP basis set for all other atoms was used. All calculations were performed using ORCA 2.9.1[24] in combination with calibration data by Neese and co-workers.[23] Broken symmetry solution (BS(2,2)) converged to restricted Kohn–Sham solutions for the functionals BP86, TPSS, TPSSh, and B3LYP. The calculated energies showed no significant deviation. All attempts to assign the electronic structure based on the Mössbauer parameters using broken symmetry calculations by DFT, in analogy to the dinitrosyl iron complexes, were

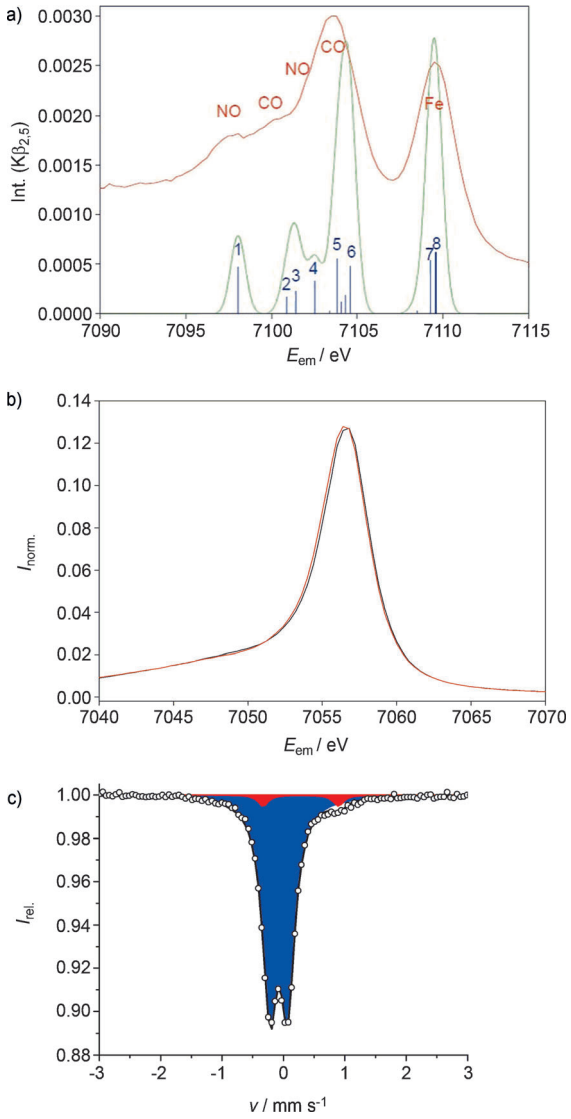

Figure 1. a) K$\beta_{2,5}$ XES (valence to core) of $[Fe(CO)_3NO]^-$. b) K$\beta_{1,3}$ XES (core-to-core emission) of $[Fe(CO)_3NO]^-$ (black) and $[Fe_2(CO)_9]$ (red). c) ^{57}Fe Mössbauer spectrum of $Bu_4N[Fe(CO)_3(NO)]$ ($T = 77$ K): blue: $Bu_4N[Fe(CO)_3(NO)]$, $\delta = -0.07$ mm s^{-1}, $|\Delta E_Q| = 0.29$ mm s^{-1}, relative intensity 96%; red: unidentified impurity, $\delta = 0.28$ mm s^{-1}, $|\Delta E_Q| = 1.23$ mm s^{-1}, relative intensity 4%.

Table 3: Comparison of computed and experimentally determined Mössbauer parameters.

Parameter	δ [mm s^{-1}][a]	ΔE_Q [mm s^{-1}][b]
Experimental	−0.07	+0.29
BP86	−0.21	+0.57
TPSS	−0.23	+0.56
TPSSh	−0.24	+0.63
B3LYP	−0.13	+0.71

[a] Single-point calculations were performed using the CP(PPP) basis set for Fe and the def-TZVP base set for C, N, and O. COSMO ($\varepsilon = 80$) at BP86/def-TZVP/COSMO(ε=80) structures. Calibration data were taken from Ref. [23]. [b] Quadrupole splitting.

unsuccessful. For closed-shell systems an assignment of oxidation states by DFT can be difficult or impossible.[25]

Despite these problems we performed additional attempts to extract a bonding picture from our qualitatively correct DFT wave function. Therefore we calculated intrinsic bond orbitals (IBOs)[26] in Molpro[27] and compared them to the orbitals derived from an analysis of the CASSCF wave function (Figure 2).

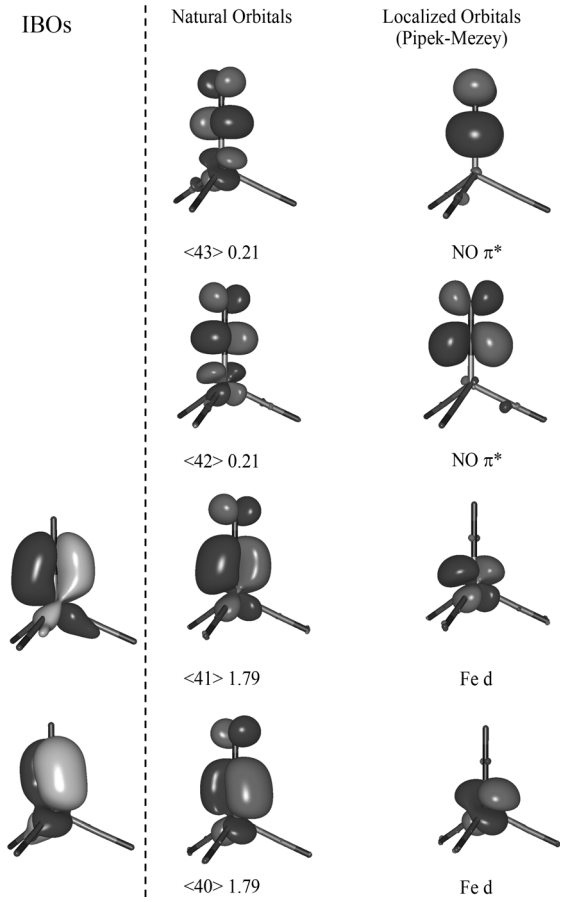

Figure 2. left: IBOs of the Fe–N bond based on BP86(DFT) calculations. Middle: Natural orbitals of the active space derived from CASSCF(4,4)/def2-QZVP[15] calculations and Right: the derived localized orbitals. Occupation numbers of natural orbitals are annotated. Isosurface = 0.05. Depicted using Gabedit.[30]

According to the IBO analysis, two covalent d–p π bonds are present between Fe–N (Figure 2). Instead of a σ bond between Fe–N a N-based lone pair is found. The electrons in the π bond are equally distributed and can be assigned to both Fe and N (for a detailed analysis see the Supporting Information). To verify this IBO-derived bonding picture, CASSCF calculations were performed, which are based on recently published investigations on complexes of the general type $\{Ni(NO)\}^{10}$ having C_{3V} symmetry and a linear-bound NO ligand,[28] with subsequent localization of the orbitals with the active space. This method was previously employed in the evaluation of Fe–NO complexes in higher oxidation states.[29] The CASSCF calculations were performed at the optimized DFT structure. The active space was limited to the two d orbitals at the Fe and the two NO π* orbitals (CASSCF-(4,4)) (Figure 2). After Pipek–Mezey localization,[31] two Fe d orbitals and two NO π* orbitals are identified that represent the bonding situation precisely (two covalent π-Fe–N bonds). This result shows that the IBO analysis can serve as a fast and reliable method for the interpretation of the bonding scenario. Such results might be of particular interest for the investigation of reaction mechanisms using DFT based methods.

Furthermore the analysis of the CASSCF wave-function composition indicates that the main configuration is about 52 % Fe^0 ($S=1$), which is antiferromagnetically coupled to an NO^- ($S=1$). This situation again reflects the covalent Fe–N π-bond character. Apart from this main configuration, about 19 % Fe^0 ($S=0$) and NO^- ($S=0$) and minor portions of Fe^{+I} ($S=1/2$) coupled to NO^{2-} ($S=1/2$) and Fe^{-I} ($S=1/2$) coupled to NO^0 ($S=1/2$) are present (Figure 3).

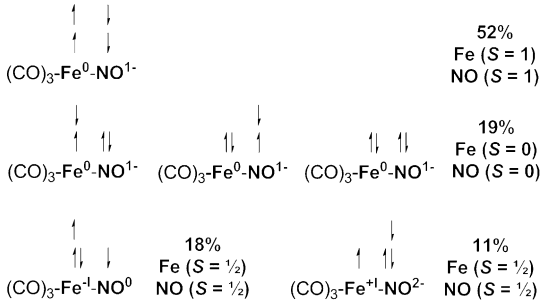

Figure 3. Composition of the CASSCF(4,4)/def2-QZVP[15] wave function based on localized orbitals and resulting oxidation states.

To follow the changes of the electronic configuration of the iron atom, as part of mechanistic investigations, the results presented above indicate that the assignment of oxidation states is problematic. At this point, we suggest to extend the existing Enemark–Feltham notation in a way that the NPA (natural population analysis)[32,33] derived metal-centered d-valence electron number, should be incorporated (Figure 4).

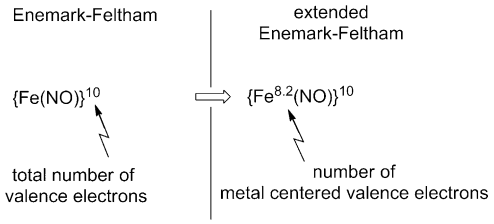

Figure 4. The extended Enemark–Feltham Notation.

Hence it is not necessary to assign an oxidation state but the changes of the electronic configuration at the metal can be followed. However, it is important to point out that an average valence electron number of 8.2 does not refer to an oxidation state of 0 but is rather a reflection of the presence of different resonance-stabilized modifications of the complex ferrate.

In summary, we were able to demonstrate that, in contrast to established opinion, the electronic ground-state configuration of $[Fe(CO)_3(NO)]^-$ is best described as a Fe^0 center that is bound by two covalent π bonds to a $[NO]^{1-}$ moiety. These results open the door toward a deeper understanding of existing and future applications of $Bu_4N[Fe(CO)_3(NO)]$ in metal catalysis.

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