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The electronic ground state of $[\text{Fe}(\text{CO})_3(\text{NO})]^-$: A spectroscopic and theoretical study

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Abstract. During the past 10 years Fe-catalyzed reactions have become established in the field of organic synthesis. For example, the complex anion $[\text{Fe}(\text{CO})_3(\text{NO})]^-$, which was originally described by Hogsed and Hieber, shows catalytic activity in various organic reactions. This anion is commonly regarded to be isoelectronic to $[\text{Fe}(\text{CO})_4]^{2-}$, which, however, shows poor catalytic activity. The spectroscopic and quantumchemical investigations presented here reveal that the complex ferrate $[\text{Fe}(\text{CO})_3(\text{NO})]^-$ can not be regarded as a Fe(-II)-species, but rather is predominantly a Fe(0) species, in which the metal is covalently bonded to NO⁻ via 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 $[\text{Fe}(\text{CO})_3(\text{NO})]^-$ 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 proved that the anion has C_{3v} symmetry and a linearly bound NO-ligand. demonstrated the C_{3v} -symmetry of the anion and the linear bound NO-ligand.^[3] Usually this bonding motif is interpreted as the NO-ligand being a $[\text{NO}]^+$.^[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] In order 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 $\{\text{M}(\text{NO})_n\}^m$ (n: number of bound NO-ligands; m: number of accessible d-electrons) is given thereby avoiding the oxidation state assignment.

Within the past years we reported a variety of $[\text{Fe}(\text{CO})_3(\text{NO})]^-$ -catalyzed reactions.^[3,7] During these investigations we observed that the formal isoelectronic Collman-reagent^[8], $\text{Na}_2[\text{Fe}(\text{CO})_4]$, 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 cationic the iron in the complex ferrate $[\text{Fe}(\text{CO})_3(\text{NO})]^-$ 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 distance 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 reduced. However, in the majority of cases reduced NO-ligands are expected to be bound in a non-linear 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 $[\text{Fe}(\text{CO})_3(\text{NO})]^-$ 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 $[\text{NO}]^-$ rather than a $[\text{NO}]^+$, and it is covalently attached via two Fe-N- π -bonds to a Fe(0)-center.

We started our investigation with a validation of the unusual N-O-bond 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 ($\epsilon = 80$)) proved to be the method of choice.^[14] Bond lengths and angles in $[\text{Fe}(\text{CO})_3(\text{NO})]^-$ 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-bond distances (Table 1)

Table 1. Comparison of experimental and computed structural parameters.

	BP86/def-TZVP COSMO ($\epsilon = 80$)	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 neighbour atom: C/N, C and N are not distinguishable by EXAFS, average values for 3x C and 1x N were obtained.^[15]

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author.

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

Table 2. Comparison of experimental and theoretical IR-frequencies.

ν (cm ⁻¹)	CO	CO	NO
experimental ^[10]	1979	1875	1647
gas phase ^a	1953	1875	1681
COSMO ($\epsilon = 7.36$) ^a	1950	1839	1631
COSMO ($\epsilon = 80$) ^a	1949	1828	1613

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

The IR-frequencies of the complex anion using various cations were reported by Pannell. 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 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 the following results (for details see ESI). 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^[16]/Fe:CP(PPP)^[17]) and are again in good agreement with the experimental data (Figure 1, spectrum (1)).

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 $[\text{Fe}(\text{CO})_3(\text{NO})]^-$ and $\text{Fe}_2(\text{CO})_9$ (Figure 1, spectrum (2)) shows no $K\beta'$ satellites indicating a low-spin configuration for both complexes.^[18] This is in accordance with the measurement of the magnetic susceptibility of $[\text{Fe}(\text{CO})_3(\text{NO})]^-$ 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 obtained via Mössbauer spectroscopy (Figure 1, spectrum (3)). Mössbauer spectra of different $[\text{Fe}(\text{CO})_3(\text{NO})]^-$ salts were previously published and are in good agreement with the data obtained in this study.^[19]

Neese and Ye used the calculation of Mössbauer parameters for the evaluation of the electronic structure of dinitrosyl iron complexes of the general type $\{\text{Fe}(\text{NO})_2\}^{10, [20]}$ 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 possesses a Fe^{+II} ($S = 2$) with two antiferromagnetically coupled linear bound anionic NO-ligands ($S = 1$).^[20]

Based upon these results the Mössbauer parameters of the calculated $[\text{Fe}(\text{CO})_3(\text{NO})]^-$ structure (BP86/def-TZVP/COSMO($\epsilon = 80$)) were calculated using BP86 (GGA), TPSS (meta-GGA),^[21] TPSSh (meta-hybrid functional)^[22] und B3LYP (hybrid functional)^[23] (Table 3).

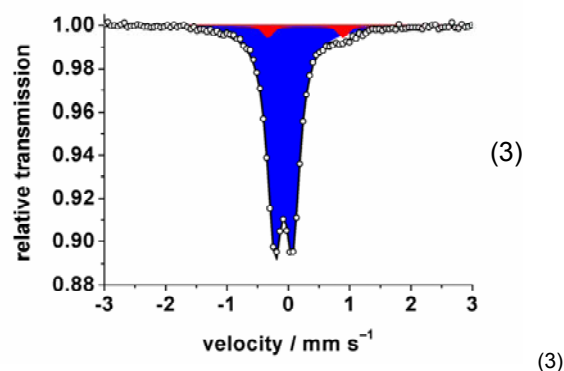
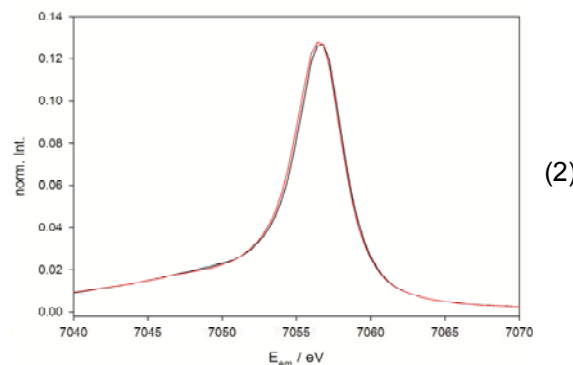
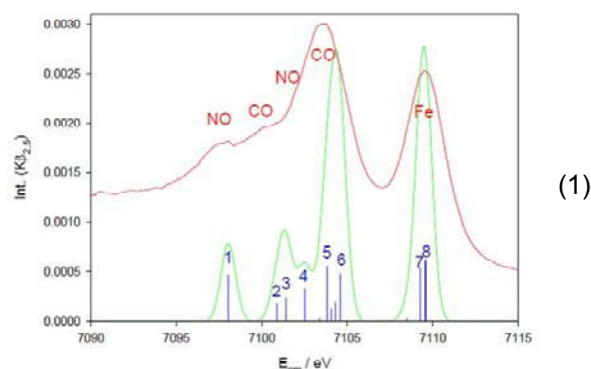


Figure 1. Spectrum (1): $K\beta_{2,5}$ XES (valence to core) of $[\text{Fe}(\text{CO})_3\text{NO}]^-$; Spectrum (2): $K\beta_{1,3}$ XES (core to core emission) of $[\text{Fe}(\text{CO})_3\text{NO}]^-$ (black) and $\text{Fe}_2(\text{CO})_9$ (red) (spectrum 2); and ⁵⁷Fe-Mössbauer-spectrum of $\text{Bu}_4\text{N}[\text{Fe}(\text{CO})_3(\text{NO})]$ ($T = 77$ K; Spectrum (3): a) $\text{Bu}_4\text{N}[\text{Fe}(\text{CO})_3(\text{NO})]$, $\delta = -0.07$ mm s⁻¹, $|\Delta E_Q| = 0.29$ mm s⁻¹, relative intensity 96%; b) not identified impurity, $\delta = 0.28$ mm s⁻¹, $|\Delta E_Q| = 1.23$ mm s⁻¹, relative intensity 4%. $\text{NBu}_4[\text{Fe}(\text{CO})_3(\text{NO})]$ in blue, impurity in red).

Tab. 3. Comparison of computed and experimentally determined Mössbauer-parameters.

	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

^aSingle-point calculations were performed using the CP(PPP) base set for Fe and the def-TZVP base set for C, N and O. COSMO ($\epsilon = 80$) at BP86/def-TZVP/COSMO($\epsilon = 80$) structures. Calibration data were taken from reference [24].

The CP(PPP) basis set^[17] for iron and the def-TZVP basis set for all other atoms was used. All calculations were performed using ORCA 2.9.1^[25] in combination with calibration data by Neese and coworkers.^[24] *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 via DFT, in analogy to the dinitrosyl iron complexes, were unsuccessful. For closed-shell systems an assignment of oxidation states by DFT can be difficult or impossible in this way.^[26]

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)^[27] in Molpro^[28] and compared them to the orbitals derived from an analysis of the CASSCF-wave function (Figure 2).

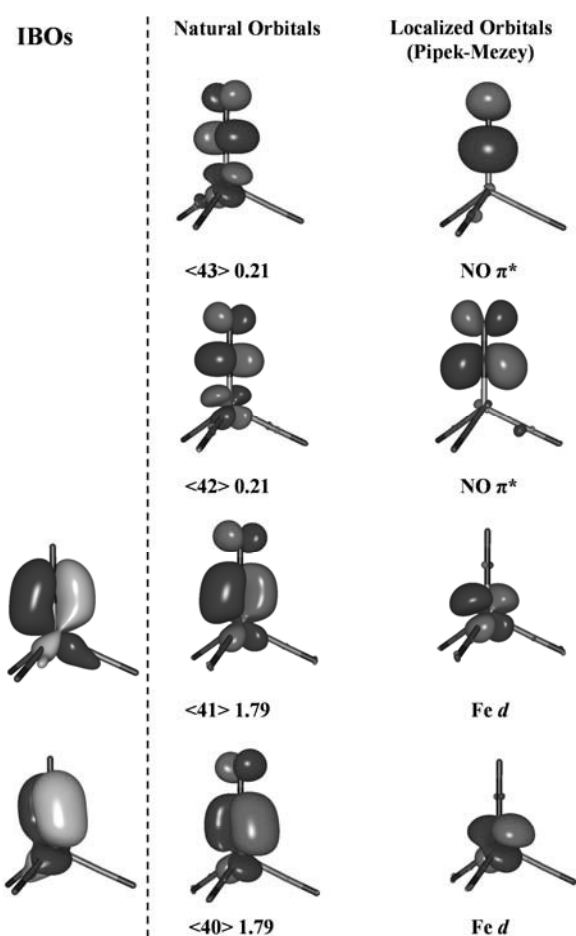


Figure 2. IBOs of the Fe-N based on BP86(DFT)-calculations (left). Natural orbitals of the active space derived from CASSCF(4,4)/def2-QZVP^[31] calculations (middle) and the derived localized orbitals (right). Occupation numbers of natural orbitals are annotated. Isosurface = 0.05. Depicted using Gabedit.^[32]

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 ESI). In order to verify this IBO-derived bonding picture, CASSCF calculations were performed, which are based on

recently published investigations on complexes of the general type $\{\text{Ni}(\text{NO})\}^{10}$ possessing C_{3v} -symmetry and a linear bound NO-ligand,^[29] 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.^[30] 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-Mezzey localisation^[33] 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. This result might be of particular interest for the investigation of reaction mechanisms using DFT based methods.

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

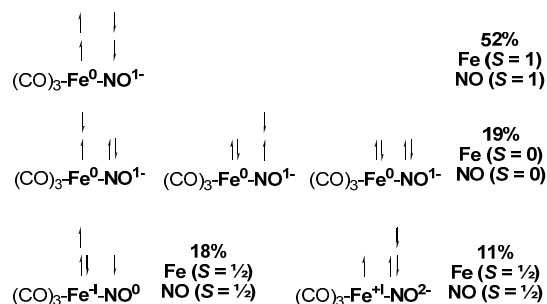


Figure 3. Composition of the CASSCF(4,4)/def2-QZVP^[31] wave function based on localized orbitals and resulting oxidation states.

In order to follow the changes of the electronic configuration of the iron atom, as part of a 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)^[34,35] derived metal-centered d-valence electron number, should be incorporated (Figure 4). Hence one does not need to assign an oxidation state but can follow the changes of the electronic configuration at the metal. 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.

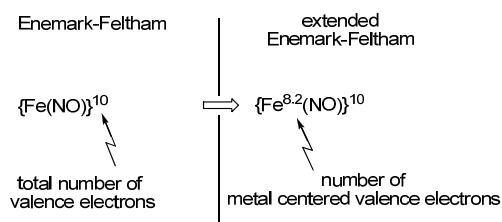


Figure 4. The extended Enemark-Feltham-Notation.

In summary, we were able to demonstrate that in contrast to the established opinion the electronic ground-state configuration of $[\text{Fe}(\text{CO})_3(\text{NO})]^-$ is best described as a Fe^0 that is bound via two covalent π -bonds to a $[\text{NO}]^{1-}$. These results open the door toward a deeper understanding of existing and future applications of $\text{Bu}_4\text{N}[\text{Fe}(\text{CO})_3(\text{NO})]$ in metal catalysis.

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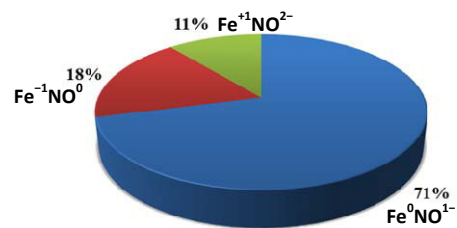
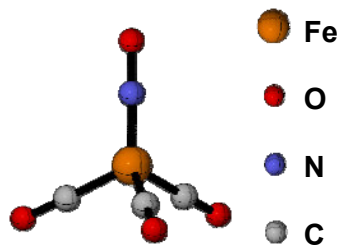
Keywords: Fe-catalysis · spectroscopy · ferrate · electronic structure · Enemark-Feltham notation

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- [35] It should be noted that this concept is not limited to NPA. Any other population analysis may be employed, e.g. IAOs.

Entry for the Table of Contents (Please choose one layout)

Fe catalysis

Johannes E. M. N. Klein, Burkhard Miehlich, Matthias Bauer, Marat M. Khusniyarov, Michael S. Holzwarth, Magdalena Milek, Gerald Knizia, Hans-Joachim Werner und Bernd Plietker*
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The electronic ground-state of $[\text{Fe}(\text{CO})_3(\text{NO})]^-$: A spectroscopic and theoretical study

Even more complex: Spectroscopic and quantumchemical investigations show that the complex ferrate $[\text{Fe}(\text{CO})_3(\text{NO})]^-$ should not be considered to be a Fe(-II)-species but rather a complex mixture of ferrates in different electronic states. In the majority of cases the metal is bound covalently via two π -bonds to a formal NO^- . A Fe-N- σ -bond is not observed.