Supporting Information

Identification of a Two-Coordinate Iron(I)–Oxalate Complex

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# Table of contents

S1. Experimental section  

S2. IR-FL-MALDI (-) mass spectrum assignment  

S3. Comparison of harmonic MP2 vs. B3LYP spectra  

S4. Isomer comparison \([\text{Fe}^{\text{III}}(\text{C}_2\text{O}_4)_2]^\text{−}\)  

S5. Isomer comparison \([\text{Fe}^{\text{II}}(\text{C}_2\text{O}_4)\text{CO}_2]^\text{−}\)  

S6. Isomer comparison \([\text{Fe}^{\text{I}}(\text{C}_2\text{O}_4)]^\text{−}\)  

S7. Band assignment  

S8. Natural population analysis (NPA) for the iron-oxalate complexes (energetically lowest-lying isomers)  

S9. Optimized Cartesian coordinates in Å of the energetically lowest-lying isomers of the studied iron-oxalate complexes.
S1. Experimental section

S1.1 IR-FL-MALDI

For IR-FL-MALDI measurements, an aqueous solution of iron(III) nitrate (c = 1.6 mmol L$^{-1}$) and oxalic acid (c = 3.2 mmol L$^{-1}$) dissolved in water/methanol (2:1, v/v) was used. The main components of the setup consist of a thin liquid μ-beam, an IR-laser (Photonic Industries, DP20-OPO) and a reflectron-type mass spectrometer. The liquid beam is injected into high vacuum via a 20 μm quartz nozzle generated by a HPLC pump. For injection of the samples into the liquid beam line a high-pressure valve is used. The IR-laser emits nanosecond pulses at a pulse repetition rate of 1 kHz with a pulse energy of 1mJ at a wavelength of 2900 nm. The light is focused onto the liquid using a CaF$_2$ lens with a focal length of 50 mm, generating a focus diameter of 56 μm and peak energy densities up to GW/cm$^2$. The IR-light excites the OH-stretch of the water molecules, heats up and then disperses the liquid beam, and in turn desolvates the ions. It displays a linear response between liquid phase ion concentration and gas phase ion signal over several orders of magnitude. This soft and sensitive MS approach allowed us to detect ionic species in different oxidation states.

More details on the experimental setup and the method are given in Ref. [1,3].

S1.2 Leipzig cyrogenic ion trap triple mass spectrometer

Nano-ionspray mass spectra and IRPD spectra were recorded using the Leipzig 6 K ion trap triple mass spectrometer described in detail elsewhere.[4,5] In brief, ions were transferred from a solution of iron(III) nitrate (c = 1.6 mmol L$^{-1}$) and oxalic acid (c = 3.2 mmol L$^{-1}$), dissolved in water/methanol (2:1, v/v), into the gas phase using a nanospray ion source. The ion beam was collimated and compressed in phase space in a He-buffer-gas filled radio frequency (RF) ion-guide, held at room temperature. Subsequently, the ions with m/z = 144, 188 and 232 were mass-selected by using a quadrupole mass filter and focused in a RF ring-electrode ion-trap. The trap was filled with deuterium (D$_2$) buffer gas at a temperature of 13 K. The trapped ions were thermalized and weakly bound ion-messenger complexes with D$_2$ are formed by many-body collisions.[6] Messenger-tagging ensures measuring an IRPD spectrum in the linear absorption regime and facilitates structural assignment based on a comparison to calculated vibrational spectra. Every 100 ms, all ions were extracted from the ion trap and focused into the center of the extraction region of an orthogonally mounted reflectron tandem mass spectrometer. IRPD spectra were obtained by irradiating the ions in the center of the extraction region with an IR laser pulse from a Nd:YAG laser (Continuum Surelight EX1) pumped OPO/OPA/AgGaSe$_2$ laser system (Laser Vision) operated at 10 Hz and with a bandwidth of approximately 3.5 cm$^{-1}$. IRPD spectra were recorded by continuously scanning the laser wavelength with a scan speed such that a TOF mass spectrum averaged over 20 laser shots was obtained every 2 cm$^{-1}$. Typically, three to four scans were measured and averaged to obtain an IRPD spectrum. The photodissociation cross-section $\sigma_{\text{IRPD}}$ was determined as described previously.[4,5]

S1.3 Computational details

Electronic structure calculations and vibrational frequency analysis were carried out with the Gaussian 16, rev C.01 program package[8] using the MP2 method[9] in combination with the def2-SVPD basis sets.[10] The simulated vibrational spectra were obtained from unscaled anharmonic vibrational frequencies and intensities, and convoluting the corresponding stick spectra with a Gaussian line shape function (12 cm$^{-1}$ full-width-at-half-maximum). QTAIM calculations[11] for determination of the Bader charge on Fe were performed at the DFT (B3LYP) level for the MP2-optimized structures by means of the ADF2019 software package.[12,13]
S2. IR-FL-MALDI (-) mass spectrum assignment

Table S1. Assignment of the dominant mass peaks shown in Figure 1c and 1d.

| m/z   | chemical formula                                                                 |
|-------|----------------------------------------------------------------------------------|
| 144   | [Fe^{III}(C_2O_4)]                                                              |
| 161   | [Fe^{III}(C_2O_4)(OH)]                                                           |
| 162   | [Fe^{III}(C_2O_4)(H_2O)]                                                         |
| 178   | [Fe^{III}(C_2O_4)(OH)_2]                                                          |
| 188   | [Fe^{III}(C_2O_4)(CO_2)]                                                         |
| 203   | Fe-containing ion                                                                |
| 212   | n-butyl benzenesulfonamide [M-H]                                                 |
| 224   | [Fe^{III}(C_2O_4)(CO_2)(H_2O)_2]                                                 |
| 232   | [Fe^{III}(C_2O_4)_3]                                                              |
S3. Comparison of harmonic MP2 vs. B3LYP spectra

The harmonic vibrational spectra calculated at the DFT (B3LYP) and the MP2 levels of theory agree well for the iron-oxalate complexes [Fe(III)(C₂O₄)₂] (Figure S5a) and [Fe(II)(C₂O₄)] (Figure S5c). However, for [Fe(II)(C₂O₄)CO₂]{ }the IR spectra of several isomers exhibit substantial differences (B3LYP vs. MP2). An example is shown in Figure S1. The comparison reveals significant differences in the absorption frequencies of the antisymmetric and the symmetric CO stretching vibrations of the single CO₂ moiety. As the comparison with the experimental IRPD spectrum indicates, the MP2 calculation overestimates the absorption frequencies of these bands. This overestimation is attributed to the slight difference in the geometry of the complexes optimized with the two different methods. As Figure S1 illustrates, the MP2 calculation predicts a planar geometry, with a dihedral angle between the intersecting planes of the oxalate and the CO₂ moieties of 0°. In contrast, in the B3LYP-optimized structure, the oxalate and CO₂ moieties are not co-planar, the dihedral angle being 28°.

**Figure S1.** Comparison between the unscaled harmonic vibrational spectra of [Fe(III)(C₂O₄)₂]: as calculated at the DFT (B3LYP) and at the MP2 levels of theory (the def2-SVPD basis sets were used in both cases). The minimum-energy structures of [Fe(II)(C₂O₄)CO₂] with \( M = 4 \), as identified at the two levels of theory, and the respective dihedral angles between the intersecting planes of the oxalate and CO₂ moieties are also shown.
Figure S2. Comparison of the IRPD spectra (red trace) of D$_2$-tagged [Fe$^{\text{III}}$(C$_2$O$_4$)$_2$]$^-$ to harmonic B3LYP (left) and MP2 (right) calculated spectra (scaled by 0.9928, the def2-SVPD basis sets were used in both cases) of the three energetically low-lying isomers with spin multiplicities 6, 4 and 2.

Table S2. ZPE-corrected relative energies (in kJ mol$^{-1}$) of the energetically low-lying isomers of [Fe$^{\text{III}}$(C$_2$O$_4$)$_2$]$^-$ with various spin multiplicities ($M$). The corresponding optimized structures are shown in Figure S2.
S5. Isomer comparison for $[\text{Fe}^{\text{III}}(\text{C}_2\text{O}_4)\text{CO}_2]^-$

**Figure S3.** Comparison of the IRPD spectra (blue trace) of $\text{D}_2$-tagged $[\text{Fe}^{\text{III}}(\text{C}_2\text{O}_4)\text{CO}_2]^-$ to harmonic B3LYP (left) and MP2 (right) calculated spectra (scaled by 0.9928, the def2-SVPD basis sets were used in both cases) of the energetically low-lying isomers with spin multiplicities 6, 4 and 2. Two fundamentally different orientations of the single CO$_2$ molecule with respect to the iron center are distinguished and the corresponding types of structures are labeled $[\text{Fe}^{\text{III}}(\text{C}_2\text{O}_4)-\text{CO}_2]$ and $[\text{Fe}^{\text{III}}(\text{C}_2\text{O}_4)-\text{O}_2\text{C}]$, resp.
Table S3. ZPE-corrected relative energies (in kJ mol\(^{-1}\)) of the energetically low-lying isomers of the type [Fe\(^{III}\)(C\(_2\)O\(_4\))\(-\)CO\(_2\)] and [Fe\(^{III}\)(C\(_2\)O\(_4\))CO\(_2\)] with various spin multiplicities (\(M\)). The corresponding structures are shown in Figure S3.

| Binding motif          | \(M\) | B3LYP/def2-SVPD | MP2/def2-SVPD |
|------------------------|-------|----------------|---------------|
| [Fe\(^{III}\)(C\(_2\)O\(_4\))\(-\)CO\(_2\)] | 2     | 87             | 230           |
|                        | 4     | 0              | 18            |
|                        | 6     | 44             | 0             |
|                        | 2     | 119            | 236           |
| [Fe\(^{III}\)(C\(_2\)O\(_4\))\(-\)O\(_2\)C\(_\)\)] | 4     | 117            | 13            |
|                        | 6     | 47             | 6             |
S6. Isomer comparison for [Fe⁰(C₂O₄)]⁻

Figure S4. Comparison of the IRPD spectra (green trace) of D₂-tagged [Fe⁰(C₂O₄)]⁻ to harmonic B3LYP (left) and MP2 (right) calculated spectra (scaled by 0.9928, the def2-SVPD basis sets were used in both cases) of the energetically low-lying isomers with spin multiplicities 2, 4 and 6. Two distinct binding motifs of the oxalate ligand are distinguished and the corresponding types of structures are labeled “end-on” and “side-on.”
Table S4. ZPE-corrected relative energies (in kJ mol\(^{-1}\)) of the energetically low-lying isomers of [Fe\(^{II}\)(C\(_2\)O\(_4\))] with various spin multiplicities (M). The corresponding structures are shown in Figure S4.

| Isomer | M  | B3LYP | MP2 |
|--------|----|-------|-----|
| side-on| 2  | 120   | 276 |
|        | 4  | 25    | 55  |
|        | 6  | 0     | 0   |
| end-on | 2  | 219   | 376 |
|        | 4  | 125   | 157 |
|        | 6  | 99    | 98  |
Figure S5. Comparison of the experimental IRPD spectra of D$_2$-tagged [Fe$^{	ext{III}}$(C$_2$O$_4$)$_2$] (a, red), [Fe$^{	ext{III}}$(C$_2$O$_4$)CO$_2$] (b, blue) and [Fe$^{	ext{II}}$(C$_2$O$_4$)] (c, green) with MP2-calculated anharmonic (top black, unscaled) and harmonic (bottom black, scaled by 0.9928, the def2-SVPD basis sets were used in both cases) vibrational spectra. The corresponding structures ($M = 6$) are also shown. Labels "#" denote combination bands, labels "**" denote overtones.
Table S5. Experimentally determined band positions, MP2-computed harmonic (scaled by 0.9928) and anharmonic (unscaled) vibrational frequencies, and band assignments of D$_2$-tagged iron complexes of the types [Fe$^{III}$($C_2O_4$)$_2$] (band labels a1-a5), [Fe$^{II}$($C_2O_4$)CO$_2$] (band labels b1-b3) and [Fe$^{I}$($C_2O_4$)] (band labels c1-c6). v: stretching vibration, δ: bending vibration, as: antisymmetric, s: symmetric

| Band | Experiment | Harmonic | Anharmonic | Assignment          |
|------|------------|----------|------------|---------------------|
| a1   | 1755       | 1773     | 1765       | $v^\text{as-s}_\text{CO}_2$ (oxalate) |
| a2   | 1252       | 1294     | 1269       | $v^\text{s}_\text{CO}_2$ (oxalate)     |
| a3   | 1103       | 1141     | 1114       | $v^\text{s-s}_\text{CO}_2$ (oxalate)   |
| a4   | 869        | 881      | 873        | $\delta_{\text{CO}_2}$ (oxalate)       |
| a5   | 802        | 804      | 808        | $\delta_{\text{CO}_2}$ (oxalate)       |
| b1   | 1798       | 1809     | 1797       | $v^\text{as}_\text{CO}_2$ (CO2)        |
| b2   | 1745       | not assigned | not assigned | not assigned |
| b3   | 1730       | 1755     | 1743       | $v^\text{as-s}_\text{CO}_2$ (oxalate)   |
| b4   | 1712       | 1732     | 1723       | $v^\text{s-as}_\text{CO}_2$ (oxalate)   |
| b5   | 1299       | 1335     | 1344       | $v^\text{s-s}_\text{CO}_2$ (oxalate)    |
| b6   | 1119       | 1194     | 1238       | $v^\text{s-s}_\text{CO}_2$ (oxalate)    |
| b7   | 872        | 876      | 865        | $\delta_{\text{CO}_2}$ (oxalate)       |
| b8   | 795        | 793      | 792        | $\delta_{\text{CO}_2}$ (oxalate)       |
| b9   | 724        | 766      | 762        | $\delta_{\text{CO}_2}$ (CO2)           |
| c1   | 1719       | 1744     | 1721       | $v^\text{s-s}_\text{CO}_2$ (oxalate)    |
| c2   | 1690       | 1715     | 1694       | $v^\text{s-as}_\text{CO}_2$ (oxalate)   |
| c3   | 1313       | 1354     | 1331       | $v^\text{s-s}_\text{CO}_2$ (oxalate)    |
| c4   | 1164       | 1213     | 1190       | $v^\text{s-s}_\text{CO}_2$ (oxalate)    |
| c5   | 860        | 878      | 861        | $\delta_{\text{CO}_2}$ (oxalate)       |
| c6   | 787        | 786      | 782        | $\delta_{\text{CO}_2}$ (oxalate)       |
S8. Natural population analysis (NPA) for the iron-oxalate complexes (energetically lowest-lying isomers)

Table S6. Natural charge on iron in the energetically lowest-lying isomers of [Fe$^{III}$(C$_2$O$_4$)$_2$]$^{-}$, [Fe$^{III}$(C$_2$O$_4$)CO$_2$]$^{-}$ and [Fe$^{III}$(C$_2$O$_4$)]$^{-}$, all with spin multiplicity of $M = 6$, as discussed in the main text. NPA were calculated via the NBO 6.0 software at the B3LYP/Zora scalar/TZ2P level of theory with the ADF2019 software package.$^{[12,13]}

| Complex             | Oxidation state | Natural charge |
|---------------------|-----------------|----------------|
| [Fe$^{III}$(C$_2$O$_4$)$_2$]$^{-}$ | 3               | 1.9            |
| [Fe$^{III}$(C$_2$O$_4$)CO$_2$]$^{-}$ | 2               | 1.4            |
| [Fe$^{III}$(C$_2$O$_4$)]$^{-}$, side-on isomer | 1               | 0.7            |
| [Fe$^{III}$(C$_2$O$_4$)]$^{-}$, end-on isomer | 1               | 0.7            |
S9. Optimized Cartesian coordinates in Å of the energetically lowest-lying isomers of the studied iron-oxalate complexes.

1. [Fe(III)(C₂O₄)₂], \( M = 6 \), MP2-optimized geometry (Fig. 2a and Fig. S5a)

|        |        |        |        |
|--------|--------|--------|--------|
| C      | -2.61319600 | -0.55639971 | 0.55607821 |
| C      | -2.61248200 | 0.55686168  | 0.55685419 |
| O      | -3.64401450 | 1.00923443 | 1.01008134 |
| O      | -1.38456650 | 0.92526029  | 0.92389380  |
| O      | -3.64527800 | -1.00950984 | -1.00774934 |
| O      | -1.38573000 | -0.92446232 | -0.92504281 |
| Fe     | 0.00000000  | 0.00000000  | 0.00108599  |
| C      | 2.61319600  | 0.55639971  | 0.55607821  |
| C      | 2.61248200  | 0.55686168  | 0.55685419  |
| O      | 3.64401450  | 1.00923443  | 1.01008134  |
| O      | 1.38456650  | 0.92526029  | 0.92389380  |
| O      | 3.64527800  | -1.00950984 | -1.00774934 |
| O      | 1.38573000  | -0.92446232 | -0.92504281 |

2. [Fe(II)(C₂O₄)CO₂], \( M = 6 \), MP2-optimized geometry (Fig. 2b and Fig. S5b)

|        |        |        |        |
|--------|--------|--------|--------|
| C      | -3.31728900 | -0.00037800 | 0.41702900 |
| O      | -2.45566200 | 0.00069200  | -0.54771700 |
| O      | -4.52538200 | -0.00040900 | 0.42198700  |
| Fe     | -0.52963200 | 0.00016600  | -0.17937700 |
| C      | 2.08937200  | -0.79164500 | 0.07776200  |
| C      | 2.08951500  | 0.79144400  | 0.07792200  |
| O      | 3.13750300  | 1.41193000  | 0.17828600  |
| O      | 0.89084500  | 1.33382300  | -0.03841800 |
| O      | 3.13720600  | -1.41236600 | 0.17816000  |
| O      | 0.89059500  | -1.33775000 | -0.03856000 |

3. [Fe(C₂O₄)]-, side-on isomer, \( M = 6 \), MP2-optimized geometry (Fig. 2c, top image and Fig. S5c)

|        |        |        |        |
|--------|--------|--------|--------|
| C      | 0.00000000 | 0.79008150 | 1.03243550 |
| C      | 0.00000000 | -0.79008150 | 1.03243550 |
| O      | 0.00000000 | -1.41332750 | 2.08895950 |
| O      | 0.00000000 | -1.32262350 | -0.16789150 |
| O      | 0.00000000 | 1.41332750 | 2.08895950 |
| O      | 0.00000000 | 1.32262350 | -0.16789150 |
| Fe     | 0.00000000 | 0.00000000 | -1.65870500 |

4. [Fe(C₂O₄)]-, end-on isomer, \( M = 6 \), MP2-optimized geometry (Fig. 2c, bottom image)

|        |        |        |        |
|--------|--------|--------|--------|
| C      | 0.45425600 | -0.0009313 | 0.00000000 |
| C      | 1.98918700 | -0.0015855 | 0.00000000 |
| O      | 2.49925750 | 0.0008931  | 1.14866400 |
| O      | 2.49925750 | 0.0008931  | -1.14866400 |
| O      | -0.21950330 | -1.10165594 | 0.00000000 |
| O      | -0.21944970 | 1.10152806 | 0.00000000 |
| Fe     | -1.96681400 | 0.0004254  | 0.00000000 |

13
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