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## **Supporting Information to**

# "Magnetostructural correlation in isolated trinuclear iron(III) oxo acetate complexes"

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**Figure S12: Top:** IR-MPD spectrum of  $[Fe_3O(OAc)_6]^+$  in the spectral range of 1000 – 3300 cm<sup>-1</sup>. Middle and Bottom: Calculated IR absorption spectra of geometry optimized  $[Fe_3O(OAc)_6]^+$  (S+1 = 16) without and with dispersion correction (Grimme D3).

**Figure S13: Top:** IR-MPD spectrum of  $[Fe_3O(OAc)_6(Py)_1]^+$  in the spectral range of 1000 – 3300 cm<sup>-1</sup>. **Middle and Bottom:** Calculated IR absorption spectra of geometry optimized  $[Fe_3O(OAc)_6]^+$  (S+1 = 16) without and with dispersion correction (Grimme D3).

**Figure S14: Top:** IR-MPD spectrum of  $[Fe_3O(OAc)_6(Py)_2]^+$  in the spectral range of 1000 - 3300 cm<sup>-1</sup>. **Middle and Bottom:** Calculated IR absorption spectra of geometry optimized  $[Fe_3O(OAc)_6]^+$  (S+1 = 16) without and with dispersion correction (Grimme D3).

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Table S4: Observed parent and fragment masses of [Fe<sub>3</sub>O(OAc)<sub>6</sub>(Py)<sub>1</sub>]<sup>+</sup>

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Figure S18: Isotopic substitution experiments

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**Figure S20:** Isotopic substitution experiments: The same as Fig. S18, but with a different decomposition of the experimental spectrum in **(a)**.

**Table S7:** Assignment of experimentally observed IR-MPD bands to calculated vibrational bands in [Fe<sub>3</sub>O(OAc)<sub>6</sub>(Py)<sub>n</sub>]<sup>+</sup>; n= 0, 1, 2, 3.

#### 1. Details on the ESI-MS and CID measurements (Bruker AmaZon SL)



**Figure S1:** Mass spectra of isolated  $[Fe_3O(OAc)_6]^+$  (top), its CID fragmentation mass spectra of (middle) and simulated mass peaks (FWHM = 0.4).



**Figure S2:** Mass spectra of isolated  $[Fe_3O(OAc)_6(Py)_1]^+$  (top), its CID fragmentation mass spectra of (middle) and simulated mass peaks (FWHM = 0.4).



**Figure S3:** Mass spectra of isolated  $[Fe_3O(OAc)_6(Py)_2]^+$  (top), its CID fragmentation mass spectra of (middle) and simulated mass peaks (FWHM = 0.4).



Figure S4: Mass spectra of isolated  $[Fe_3O(OAc)_6(Py)_3]^+$  (top), its CID fragmentation mass spectra of (middle) and simulated mass peaks (FWHM = 0.4).



**Figure S5:** Mass spectra of isolated  $[Fe_3O(OAc)_6(Py)_2]^+$  (top), its CID fragmentation (second), subsequent isolation of  $[Fe_3O(OAc)_6(Py)_1]^+$  (third), its CID fragmentation mass spectra (fourth) and simulated mass peaks (FWHM = 0.4) (bottom).

**Table S1:** Compilation of ESI-MS data on  $[Fe_3O(OAc)_6(Py)_n]^+$  (n = 1,2,3; OAc = CH<sub>3</sub>CO<sub>2</sub>). The indicated mass labels refer to the most abundant isotope peaks.

Species	m/z
[Fe <sub>3</sub> O(OAc) <sub>4</sub> ] <sup>+</sup>	420
[Fe <sub>3</sub> O(OAc) <sub>5</sub> ] <sup>+</sup>	479
[Fe <sub>3</sub> O(OAc) <sub>6</sub> ] <sup>+</sup>	538
[Fe <sub>3</sub> O(OAc) <sub>6</sub> (Py) <sub>1</sub> ] <sup>+</sup>	617
[Fe <sub>3</sub> O(OAc) <sub>6</sub> (Py) <sub>2</sub> ] <sup>+</sup>	696
[Fe <sub>3</sub> O(OAc) <sub>6</sub> (Py) <sub>3</sub> ] <sup>+</sup>	775



**Figure S6:** Mass spectra of isolated  $[Fe_3O(OAc)_6(Py)_3]^+$  (top), its CID fragmentation (second), subsequent isolation of  $[Fe_3O(OAc)_6(Py)_2]^+$  (third), its CID fragmentation mass spectra (fourth), isolation of  $[Fe_3O(OAc)_6(Py)_1]^+$  (fifth), its CID fragmentation mass spectra (sixth), isolation of  $[Fe_3O(OAc)_6]^+$  (seventh), its CID fragmentation mass spectra (eighth) and simulated mass peaks (FWHM = 0.4) (bottom).



**Figure S7**: **a)** IR-MPD spectrum of  $[Fe_3O(OAc)_6]^+$  in the spectral range of 1000 – 3300 cm<sup>-1</sup>. (**b-e**) Calculated IR absorption spectra of geometry optimized  $[Fe_3O(OAc)_6]^+$  in the four broken symmetry configurations 16-tet, DUU, UDU and UUD. The stick spectra (grey) were broadened with Gaussian envelope curves (FWHM = 7 cm<sup>-1</sup> (black) and 4 cm<sup>-1</sup> (green). The calculations were performed at the B3LYP / cc-pVTZ (H, C, N, O) and ecp-10-mdf (Fe) level of theory. The frequencies are scaled with 0.98. The insets show atomic distances (in Å) within the triangular Fe<sub>3</sub>O cores of [Fe<sub>3</sub>O(OAc)<sub>6</sub>]<sup>+</sup>.



**Figure S8: (a)** IR-MPD spectrum of  $[Fe_3O(OAc)_6Py_1]^+$  in the spectral range of 1000 – 3300 cm<sup>-1</sup>. Red curves indicate measurements at maximum photon flux while blue curves show spectra with attenuated pulse energies (~ 50%). (b-e) Calculated IR absorption spectra of geometry optimized  $[Fe_3O(OAc)_6Py_1]^+$  in the four broken symmetry configurations 16-tet, DUU, UDU and UUD. The stick spectra (grey) were broadened with Gaussian envelope curves (FWHM = 7 cm<sup>-1</sup> (black) and 4 cm<sup>-1</sup> (green). The calculations were performed at the B3LYP / cc-pVTZ (H, C, N, O) and ecp-10-mdf (Fe) level of theory. The frequencies are scaled with 0.98. The insets show atomic distances (in Å) within the triangular Fe<sub>3</sub>O cores of [Fe<sub>3</sub>O(OAc)<sub>6</sub>Py<sub>1</sub>]<sup>+</sup>.



**Figure S9: (a)** IR-MPD spectrum of  $[Fe_3O(OAc)_6Py_2]^+$  in the spectral range of 1000 – 3300 cm<sup>-1</sup>. Red curves indicate measurements at maximum photon flux while blue curves show spectra with attenuated pulse energies (~ 50%). (b-e) Calculated IR absorption spectra of geometry optimized  $[Fe_3O(OAc)_6Py_2]^+$  in the four broken symmetry configurations 16-tet, DUU, UDU and UUD. The stick spectra (grey) were broadened with Gaussian envelope curves (FWHM = 7 cm<sup>-1</sup> (black) and 4 cm<sup>-1</sup> (green). The calculations were performed at the B3LYP/ cc-pVTZ (H, C, N, O) and ecp-10-mdf (Fe) level of theory. The frequencies are scaled with 0.98. The insets show atomic distances (in Å) within the triangular Fe<sub>3</sub>O cores of  $[Fe_3O(OAc)_6Py_2]^+$ .



**Figure S10:** IR-MPD spectrum of  $[Fe_3O(OAc)_6Py_3]^+$  in the spectral range of  $1000 - 3300 \text{ cm}^{-1}$ . Red curves indicate measurements at maximum photon flux while blue curves show spectra with attenuated pulse energies (~ 50%). **b-e**) Calculated IR absorption spectra of geometry optimized  $[Fe_3O(OAc)_6Py_3]^+$  in the four broken symmetry configurations 16-tet, DUU, UDU and UUD. The stick spectra (grey) were broadened with Gaussian envelope curves (FWHM = 7 cm<sup>-1</sup> (black) and 4 cm<sup>-1</sup> (green). The calculations were performed at the B3LYP\_Gaussian / cc-pVTZ (H, C, N, O) and ecp-10-mdf (Fe) level of theory. The frequencies are scaled with 0.98. The insets show atomic distances (in Å) within the triangular Fe<sub>3</sub>O cores of [Fe<sub>3</sub>O(OAc)<sub>6</sub>Py<sub>3</sub>]<sup>+</sup>.



**Figure S11:** Relative energies of  $[Fe_3O(OAc)_6(Py)_n]^+$  (n = 0,1,2,3) as a function of the multiplicity. The geometry was fully optimized for each multiplicity. The calculations were performed at the B3LYP\_Gaussian / cc-pVTZ (H, C, N, O) and ecp-10-mdf (Fe) level of theory

**Table S2:** Calculated fragmentation free energies  $\Delta_{fr} G_n^0$  and fragmentation energies  $\Delta_{fr} E_n$  of  $[Fe_3O(OAc)_6(Py)_n]^+$  (n = 1,2,3). The multiplicity is S+1 = 16. The calculations were performed at the B3LYP/cc-pVTZ (H,C,N,O) and Stuttgart 1997 ECP (Fe) level of theory as implemented in the Gaussian 09 programm package. BSSE correction was performed using the conterpoise routine.

[Fe₃O(OAc)₀(Py)n]⁺	$\Delta_{fr} G^0_n$ /kJ/mol	$\Delta_{fr} G^0_n$ (BSSE corr.)/kJ/mol	$\Delta_{fr} E_n$ / kJ/mol	$\Delta_{fr} E_{n=1}$ (BSSE corr.) / kJ/mol
n = 3	28	19	90	81
n = 2	55	46	113	104
n = 1	82	73	136	127



**Figure S12: Top:** IR-MPD spectrum of  $[Fe_3O(OAc)_6]^+$  in the spectral range of 1000 – 3300 cm<sup>-1</sup>. Middle and Bottom: Calculated IR absorption spectra of geometry optimized  $[Fe_3O(OAc)_6]^+$  (S+1 = 16) without and with dispersion correction (Grimme D3). The calculations were performed at the B3LYP/ cc-pVTZ (H, C, N, O) and ecp-10-mdf (Fe) level of theory. The frequencies are scaled with 0.98.

Ref.: S. Grimme, J. Antony, S. Ehrlich and H. Krieg, J. Chem. Phys., 2010, 132, 154104.



**Figure S13: Top:** IR-MPD spectrum of  $[Fe_3O(OAc)_6(Py)_1]^+$  in the spectral range of 1000 - 3300 cm<sup>-1</sup>. Red curves indicate measurements at maximum photon flux while blue curves show spectra with attenuated pulse energies (~ 50%). **Middle and Bottom:** Calculated IR absorption spectra of geometry optimized  $[Fe_3O(OAc)_6]^+$  (S+1 = 16) without and with dispersion correction (Grimme D3). The calculations were performed at the B3LYP/ cc-pVTZ (H, C, N, O) and ecp-10-mdf (Fe) level of theory. The frequencies are scaled with 0.98.



**Figure S14: Top:** IR-MPD spectrum of  $[Fe_3O(OAc)_6(Py)_2]^+$  in the spectral range of 1000 – 3300 cm<sup>-1</sup>. Red curves indicate measurements at maximum photon flux while blue curves show spectra with attenuated pulse energies (~ 50%). **Middle and Bottom:** Calculated IR absorption spectra of geometry optimized  $[Fe_3O(OAc)_6]^+$  (S+1 = 16) without and with dispersion correction (Grimme D3). The calculations were performed at the B3LYP/ cc-pVTZ (H, C, N, O) and ecp-10-mdf (Fe) level of theory. The frequencies are scaled with 0.98.



**Figure S15:** Vibrational shifts of the CH<sub>3</sub> bending vibration frequency ( $\delta$ (CH<sub>3</sub>)) as well as the asymmetric carboxylic CO stretching vibration frequency (v(CO)) in [**Fe<sub>3</sub>O(OAc)<sub>6</sub>(Py)<sub>n</sub>**]<sup>+</sup> (n = 0,1,2,3). The calculations were performed at the B3LYP/cc-pVTZ (H, C, N, O) and ecp-10-mdf (Fe) level of theory with five unpaired electrons on each Fe center and a UUD (n = 0,1,3) or DUU (n = 2) symmetry configuration corresponding to the minimum structures. All frequencies are scaled with 0.98.



**Figure S16: Left:** Calculated binding energies  $\Delta_{fr} E_n$  and free binding energies  $\Delta_{fr} G_n^0$  of pyridine ligands in  $[Fe_3O(OAc)_6(Py)_n]^+$ (n = 1,2,3). The calculations were performed at the B3LYP\_Gaussian / cc pVTZ (H, C, N, O) and ecp-10-mdf (Fe) level of theory. **Right:**  $E_{com}^{50}$  values extracted from CID appearance curves (cf. Fig. 2).



**Figure S17:** Relaxed total energy of the coordinated pyridine torsion around the Fe-N axis in  $[Fe_3O(OAc)_6(Py)_1]^+$ . Calculation performed at B3LYP / cc-pVDZ (green) and cc-pVTZ (blue) (H, C, N, O) and ecp-10-mdf (Fe) level of theory. The given angle is that of the pyridine plane relative to the plane through all three Fe atoms.

#### 5. Monitored m/z values of IR-MPD spectra and of CID – appearance curves

Parent	Fragment 1	Fragment 2
[Fe₃O(OAc) <sub>6</sub> ]⁺	[Fe₃O(OAc)₅]⁺:	[Fe₃O(OAc)₄]⁺:
535.8	476.7	417.7
536.8	477.8	418.8
537.8	478.7	419.7
538.7	479.8	420.8
 553.7		

Table S3: Observed parent and fragment masses of [Fe<sub>3</sub>O(OAc)<sub>6</sub>]<sup>+</sup>

Table S4: Observed parent and fragment masses of [Fe<sub>3</sub>O(OAc)<sub>6</sub>(Py)<sub>1</sub>]<sup>+</sup>

Parent	Fragment
[Fe₃O(OAc) <sub>6</sub> (Py) <sub>1</sub> ] <sup>+</sup>	[Fe₃O(OAc) <sub>6</sub> ]⁺
614.8	535.8
615.8	536.8
616.8	537.8
617.7	538.7
618.9	553.7

Table S5: Observed parent and fragment masses of [Fe<sub>3</sub>O(OAc)<sub>6</sub>(Py)<sub>2</sub>]<sup>+</sup>:

Parent	Fragment 1	Fragment 2	
[Fe₃O(OAc) <sub>6</sub> (Py) <sub>2</sub> ]⁺	[Fe₃O(OAc) <sub>6</sub> (Py) <sub>1</sub> ]⁺	[Fe₃O(OAc) <sub>6</sub> ]⁺	
693.8	614.8	535.8	
694.9	615.8	536.8	
695.8	616.8	537.8	
696.8	617.7	538.7	
698.9	618.9	553.7	

Table S6:	Observed	parent and	fragment	masses of	[Fe₃O(OAd	:) <sub>6</sub> (Py) <sub>3</sub> ]⁺:
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Parent	Fragment 1	Fragment 2	Fragment 3
[Fe₃O(OAc) <sub>6</sub> (Py)₃]⁺	[Fe₃O(OAc) <sub>6</sub> (Py) <sub>2</sub> ]⁺	[Fe₃O(OAc) <sub>6</sub> (Py) <sub>1</sub> ]⁺	[Fe₃O(OAc) <sub>6</sub> ]⁺
772.9	693.8	614.8	535.8
773.9	694.9	615.8	536.8
775	695.8	616.8	537.8
776	696.8	617.7	538.7
	698.9	618.9	553.7



#### 6. Assignments of IR-MPD Bands and isotopic substitution experiments

**Figure S18:** Overview of the isotopic substitution experiments IR-MPD spectra of  $[Fe_3O(OAc)_6Py_3]^+$ ,  $[Fe_3O(OAcD_3)_6(PyD_5)_3]^+$ ,  $[Fe_3O(OAcD_3)_6Py_3]^+$ ,  $[Fe_3O(OAc)_6(PyD_5)_3]^+$  The red curves are recorded with enhanced photon flux. Note that the three sharp bands above 3000 cm<sup>-1</sup> in  $[Fe_3O(OAc)_6Py_3]^+$  vanish in  $[Fe_3O(OAc)_6(PyD_5)_3]^+$  while the three broad bands to the red persist in both cases. The two bottom graphs depict DFT calculations of  $[Fe_3O(OAc)_6(PyD_5)_3]^+$  (convoluted, second from bottom) and of all other isotopomers (sticks spectra, bottom graph) at the B3LYP / cc-pVTZ (H, C, N, O) and ecp-10-mdf (Fe) level of theory. These results fully support the assignments of the manuscript. For further interpretation refer to Fig.s S19 and S20, and to the discussion in the text of the paper.



**Figure S19:** Isotopic substitution experiments: **(a,b)** IR-MPD spectrum of  $[Fe_3O(OAc)_6Py_3]^+$  and  $[Fe_3O(OAcD_3)_6(PyD_5)_3]^+$  in the spectral range of 1500 – 1700cm<sup>-1</sup>, each with a fit of three gaussian functions and their sum. In graph **(b)** two additional gaussians are added to approximate a new band around 1660, presumably a combination band. **(c-d)** Calculated IR absorption spectra of geometry optimized  $[Fe_3O(OAc)_6]^+$  and  $[Fe_3O(OAcD_3)_6(PyD_5)_3]^+$  respectively. The stick spectra (blue, pink) were broadened with Gaussian envelope curves (FWHM = 14 cm<sup>-1</sup> (black). The calculations were performed at the B3LYP / cc-pVTZ (H, C, N, O) and ecp-10-mdf (Fe) level of theory. The frequencies are scaled with 0.986. Additional experimental bands at 1535 and 1659 cm<sup>-1</sup> and beyond are likely hot bands and combination bands, respectively.



**Figure S20:** Isotopic substitution experiments: The same as Fig. S18, but with an alternative decomposition of the experimental spectrum in (a). Obviously, the broad band consists of at least three contributions which cannot be determined unambiguously. In any case the experimental IR-MPD observations are well in line with DFT predictions for the linear IR absorptions when considering that mode specific fragmentation likely modulates the intensities in the IR-MPD experiment.

Table S7: Assignment of experimentally observed IR-MPD bands to calculated vibrational bands in  $[Fe_3O(OAc)_6(Py)_n]^+$ ; n= 0, 1, 2, 3. Calculations are on the B3LYP\_Gaussian/cc-pVTZ(H, C, N, O);ecp-10-mdf (Fe) level of theory. Predicted line strengths are indicated by s (strong), m (medium), and w (weak).

	calc. band	IR-MPD	Assignment
n=0	1357 w	-	γ(CH <sub>3</sub> ) <sub>OAc</sub>
	1411* s	1445	v <sub>s</sub> (COO) <sub>OAc</sub>
	1447 m	1490**	γ (CH <sub>3</sub> ) <sub>OAc</sub>
	1575* s	1574	vas(COO) <sub>OAc</sub>
	3002 w	-	v(CH) <sub>OAc</sub>
	3069 w	-	v(CH) <sub>OAc</sub>
	3115 w	-	v(CH) <sub>OAc</sub>
n=1	1213 w	-	δ(CH) <sub>Py</sub>
	1356 w	1360	γ (CH <sub>3</sub> ) <sub>OAc</sub>
	1413* s	1445	ν <sub>s</sub> (COO) <sub>OAc</sub> ν (CH <sub>3</sub> ) <sub>OAc</sub>
	1447 m	-	$\gamma$ (CH <sub>3</sub> ) <sub>OAC</sub>
	1587* s	1586	δ(CH) <sub>Pv</sub>
	3070 w	-	v(CH) <sub>OAc</sub>
	3110 w	-	v(CH) <sub>OAc</sub>
	3170 w	3090	v(CH) <sub>Py</sub>
n=2	1212 w	-	δ(CH) <sub>Py</sub>
	1353 w	1360	γ (CH <sub>3</sub> ) <sub>OAc</sub>
	1/16* c	1446	v <sub>s</sub> (COO) <sub>OAc</sub>
	1410 3	1440	γ (CH <sub>3</sub> ) <sub>OAc</sub>
	1448 m	-	γ (CH3) <sub>OAc</sub>
	1507* c	1507	vas(COO) <sub>OAc</sub>
	1337 3	1557	δ(CH) <sub>Py</sub>
	3069 m	2955 b	v(CH) <sub>OAc</sub>
	3108 m	3055 b	v(CH) <sub>OAc</sub>
	3170 w	3098	v(CH) <sub>Py</sub>
n=3	1213 w	1229	δ(CH) <sub>Py</sub>
	1351 w	1358	γ (CH <sub>3</sub> ) <sub>OAc</sub>
	1419* s	1454 b	v <sub>s</sub> (COO) <sub>OAc</sub>
			γ(CH <sub>3</sub> ) <sub>OAc</sub>
	1449 m	1493**	γ(CH <sub>3</sub> ) <sub>OAc</sub>
	1607* s	1613 b	Vas(COO) <sub>OAc</sub>
	-		δ(CH) <sub>Py</sub>
	3001 w	2880 b	V(CH <sub>3</sub> ) <sub>OAc</sub>
	3067 m	2948 b	v(CH <sub>3</sub> ) <sub>OAc</sub>
	3105 m	3050 b	V(CH <sub>3</sub> ) <sub>OAc</sub>
	3131 w	3085	v(CH) <sub>Py</sub>
	3149 W	310/	V(CH) <sub>Py</sub>
	3170 m	3124	V(CH) <sub>Py</sub>

\* Center of gravity of several near degenerate bands from multiple, equivalent chromophores.

\*\* unresolved shoulder; b indicates significant broadening