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Vibrational Blue Shift of coordinated N₂ in [Fe₃O(OAc)₆(N₂)_n]⁺: "Non Classical" Dinitrogen Complexes

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1. Mass Spectra



Figure S1: Cationic mass spectrum of a $[Fe_3O(OAc)_6(H_2O)_3]CIO_4$ acetonitrile solution a). Simulated isotopic pattern of $[Fe_3O(OAc)_6(L)_n]^+$ (n=0,1,2,3; L= H₂O, acetonitrile and acetic acid) b). For peak assignment refer to table S1.



Figure S2: Cationic mass spectrum of a $[Fe_3O(OAc)_6(H_2O)_3]ClO_4$ acetonitrile solution after collision induced dissociation and subsequent N₂ coordination to $[Fe_3O(OAc)_6]^+$ a). Simulated isotopic pattern of $[Fe_3O(OAc)_6(N_2)_n]^+$ (n=0,1,2,3) b). For peak assignment refer to table S1.

Species	m/z
[Fe ₃ O(OAc) ₆] ⁺	538
$\left[Fe_{3}O(OAc)_{6}(H_{2}O)_{1}\right]^{+}$	556
$\left[\operatorname{Fe_3O(OAc)_6(N_2)_1}\right]^+$	566
$\left[Fe_{3}O(OAc)_{6}(H_{2}O)_{2}\right]^{+}$	574
$[Fe_3O(OAc)_6(CH_3CN)_1]^+$	579
$\left[Fe_{3}O(OAc)_{6}(N_{2})_{2}\right]^{+}$	594
$[Fe_3O(OAc)_6(HOAc)_1]^+$	598
$\left[Fe_3O(OAc)_6(HOAc)_1(H_2O)_1\right]^+$	616
$\left[Fe_{3}O(OAc)_{6}(N_{2})_{3}\right]^{+}$	622

Table S1: Compilation of ESI-MS data on $[Fe_3O(OAc)_6(L)_n]^+$ (n=1,2,3; OAc=CH₃CO₂). The indicated mass labels refer to the most abundant isotope peaks.

2. Calculated N₂-binding Gibbs energies

 $\Delta \Delta_{bind} G_n^T = \Delta_f G^T ([\mathbf{Fe_3O}(\mathbf{OAc})_6 (\mathbf{N_2})_n]^*) + \Delta_f G^T (\mathbf{N_2}) - \Delta_f G^T ([\mathbf{Fe_3O}(\mathbf{OAc})_6 (\mathbf{N_2})_{n+1}]^*)$



Figure S3: Temperature dependence of N₂-binding Gibbs energies $(\Delta \Delta_{bind} G_n^T)$ of $[Fe_3O(OAc)_6(N_2)_n]^+$ (n=0,1,2,3). DFT calculations were performed at the B3LYP/cc-pVTZ (H, C, N, O) and Stuttgart 1997 ECP (Fe) level of theory.

3. Details of the DFT calculations



Figure S4: Left: IR-PD spectra of $[Fe_3O(OAc)_6(N_2)_n]^+$ (n=1,2,3) at 26 K (black and blue curves) and calculated IR absorption spectra of optimized $[Fe_3O(OAc)_6(N_2)_n]^+$ (n=1-3) (green curves) in the range of 1300–2500 cm⁻¹. The blue IR-PD spectrum shows the CO stretching band (recorded with highly attenuated laser power to avoid saturation effects). The calculations were performed at the B3LYP/cc pVTZ (H,C,N,O) and Stuttgart 1997 ECP (Fe) level of theory. The multiplicity is 16 and frequencies are unscaled. Calculated stick spectra were convoluted with a Gaussian envelope of FWHM = 7 cm⁻¹. Right: A zoom into the N₂ stretching vibration region. Calculated lines were convoluted with a Gaussian envelope of FWHM = 3.5 cm⁻¹. Insets show associated geometry optimized structures.



Figure S5: IR-PD spectra of $[Fe_3O(OAc)_6(N_2)_n]^+$ (n=1,2,3) at 26 K (black curves) and calculated IR absorption spectra of geometry optimized $[Fe_3O(OAc)_6(N_2)_n]^+$ (n=1,2,3) (green curves) in the range of 1300 – 2400 cm⁻¹. The calculations were performed at the PBEO /cc-pVTZ (H, C, N, O) and Stuttgart 1997 ECP (Fe) level of theory. The multiplicity is 16 and frequencies are scaled with 0.951 (0.946) above 2300 cm⁻¹ (below 2300 cm⁻¹). Calculated stick spectra were convoluted with a Gaussian envelope of FWHM = 7 cm⁻¹. The calculated intensities above 2300 cm⁻¹ were multiplied by a factor of 20 for clarity



Figure S6: Displacement vectors and vibrational frequencies of IR active asymmetric carboxylate stretching vibrations in $Fe_3O(OAc)_6(N_2)_n]^+$ (n = 0-3) The calculations were performed at the B3LYP/cc-pVTZ (H, C, N, O) and Stuttgart 1997 ECP (Fe) level of theory. The multiplicity is 16 and frequencies are scaled with 0.986



Figure S7: IR-PD spectra of $[Fe_3O(OAc)_6(N_2)_n]^+$ (n=1,2,3) at 26 K (black curves) and calculated IR absorption spectra of geometry optimized $[Fe_3O(OAc)_6(N_2)_n]^+$ (n=1,2,3) (green sticks and curves, FWHM = 7 cm⁻¹ assumed) in the range of the asymmetric carboxylate stretching vibration. The calculations were performed at the B3LYP/cc-pVTZ (H, C, N, O) and Stuttgart 1997 ECP (Fe) level of theory. The multiplicity is 16 and frequencies are scaled with 0.986.



Figure S8: Displacement vectors and vibrational frequencies of IR active N-N stretching vibrations in $Fe_3O(OAc)_6(N_2)_n]^+$. The calculations were performed at the B3LYP/cc-pVTZ (H, C, N, O) and Stuttgart 1997 ECP (Fe) level of theory. The multiplicity is 16 and frequencies are scaled with 0.951.

Table S2: Structural data of $[Fe_3O(OAc)_6(N_2)_n]^+$ (n=0,1,2,3) by DFT at B3LYP/cc-pVTZ (H, C, N, O) and Stuttgart 1997 ECP (Fe) level of theory. The multiplicity is 16. Note that the calculated N-N bond length of free N₂ is 1.091 Å.

	[Fe ₃ O(OAc) ₆] ⁺	$[Fe_3O(OAc)_6(N_2)_1]^+$	$\left[Fe_{3}O(OAc)_{6}(N_{2})_{2}\right]^{+}$	$\left[Fe_{3}O(OAc)_{6}(N_{2})_{3}\right]^{+}$
Fa O	1.892	1.884	1.880	1.905
distance / Å	1.893	1.913	1.909	1.905
distance / A	1.892	1.884	1.908	1.904
Fo Fo distance	3.271	3.298	3.270	3.300
re-redistance / Å	3.271	3.238	3.269	3.301
/ A	3.269	3.303	3.329	3.296
Fo N distance			2 176	2.501
re-N distance	-	2.451	2.470	2.497
/ A			2.476	2.499
				3.041
				3.038
			3.041	3.042
			3.042	3.042
		3.046	3.043	3.041
NN-O		3.046	3.044	3.040
distances/ Å	-	3.049		3.042
		3.046		3.043
			3.041	3.039
			3.043	3.039
			3.046	3.042
			3.046	3.039
			1 000	1.089
			1.089	1.089
N-N bond	_	1.089		
length/ Á			1.089	1.089



Figure S9: IR-PD spectra of $[Fe_3O(OAc)_6(N_2)_n]^+$ (n=1,2,3) at 26 K (black curves) and calculated IR absorption spectra of geometry optimized $[Fe_3O(OAc)_6(N_2)_n]^+$ (n=1,2,3) (green curves) in the range of $1300 - 2400 \text{ cm}^{-1}$. The calculations were performed at the B3P86/cc-pVTZ (H, C, N, O) and Stuttgart 1997 ECP (Fe) level of theory. The multiplicity is 16 and frequencies are scaled with 0.968 (0.949) above 2300 cm⁻¹ (below 2300 cm⁻¹). Calculated stick spectra were convoluted with a Gaussian envelope of FWHM = 7 cm⁻¹. The calculated intensities above 2300 cm⁻¹ were multiplied by a factor of 20 for clarity.



Figure S10: IR-PD spectra of $[Fe_3O(OAc)_6(N_2)_n]^+$ (n=1,2,3) at 26 K (black curves) and calculated IR absorption spectra of geometry optimized $[Fe_3O(OAc)_6(N_2)_n]^+$ (n=1,2,3) (green curves) in the range of 1300 – 2400 cm⁻¹. The calculations were performed at the TPSSh/cc-pVTZ (H, C, N, O) and Stuttgart 1997 ECP (Fe) level of theory. The multiplicity is 16 and frequencies are scaled with 0.989 (0.962) above 2300 cm⁻¹ (below 2300 cm⁻¹). Calculated stick spectra were convoluted with a Gaussian envelope of FWHM = 5 cm⁻¹. The calculated intensities above 2300 cm⁻¹ were multiplied by a factor of 20 for clarity.



Interaction:

Repulsion

Figure S11: Geometry optimized structure plots and NCI of $[Fe_3O(OAc)_6(N_2)_{1-3}]^+$ by DFT calculations at the B3LYP/cc-pVTZ (H, C, N, O) and Stuttgart 1997 ECP (Fe) level of theory. The atom colors are shown in grey scale for clarity.



Figure S12: Relative energies and vibrational frequencies of $[Fe_3O(OAc)_6(N_2)_1]^+$ as a function of the multiplicity. The geometry was fully



optimized for each multiplicity. The DFT calculations were performed at the

Figure 13: Left: $4\sigma^*$ and 5σ molecular orbitals of isolated N₂. Right: Selected molecular orbitals of **[Fe₃O(OAc)₆(N₂)_n]**⁺ involving the former $4\sigma^*(N_2)$ and $5\sigma(N_2)$ orbitals. The $4\sigma^*$ and 5σ MO's of the N₂ unit overlap with orbitals of the **[Fe₃O(OAc)₆]**⁺ unit. The $4\sigma^*$ electron density delocalizes into the whole complex, which leads to a slight increase of the bond order of the N₂ unit.



Figure 14: Calculated IR absorption spectra of geometry optimized $[Fe_3O(OAc)_6(N_2)_n]^+$ (n=1,2,3) in the range of 300 – 700 cm⁻¹. The calculations were performed at the B3LYP/ccpVTZ (H, C, N, O) and Stuttgart 1997 ECP (Fe) level of theory. The multiplicity is 16 and frequencies are scaled with 0.986. Calculated stick spectra were convoluted with a Gaussian envelope of FWHM = 5 cm⁻¹.

4. Details of the IR-PD spectra

4.1. Observed Masses

$[Fe_3O(OAc)_6(N_2)_1]^+$:

565.9 (Parent)

537.9 (Fragment)

$[Fe_3O(OAc)_6(N_2)_2]^+$:

593.9 (Parent)

565.9 (Fragment)

$[Fe_3O(OAc)_6(N_2)_3]^+$:

621.9 (Parent)

565.9 (Fragment)

593.9 (Fragment)



Figure S15: IR-MD spectra of $[Fe_3O(OAc)_6(N_2)_n]^+$ (n=1,2,3) at 26 K (black lines) and laser power curves (red lines).

5. XYZ Files of geometry optimized $[Fe_3O(OAc)_6(N_2)_n]^+$ (B3LYP)

5.1 [Fe₃O(OAc)₆]⁺

С	-7.53798	-17.72381	-2.90914
С	-8.72985	-17.80218	-2.00244
Н	-8.91205	-16.84205	-1.52765
Н	-8.51032	-18.52988	-1.21754
Н	-9.60439	-18.14589	-2.54733
С	-4.32323	-19.42052	-3.05628
С	-3.59747	-20.47165	-2.27040
Н	-2.64269	-20.66457	-2.76503
Н	-4.16266	-21.39971	-2.26220
Н	-3.39359	-20.12487	-1.26151
С	-5.63766	-13.94424	-4.83758
С	-6.12867	-12.53390	-4.70035
Н	-5.85303	-12.12362	-3.73326
Н	-7.21890	-12.54685	-4.76879
Н	-5.75060	-11.91842	-5.51222
С	-2.42159	-15.63289	-4.95488
С	-0.97452	-15.24321	-4.89779
Н	-0.37540	-16.14892	-5.01726
Н	-0.73354	-14.80228	-3.93480
Н	-0.72852	-14.56865	-5.71328
С	-7.48510	-17.24818	-7.53020
С	-8.68824	-17.09671	-8.41241
Н	-9.45600	-16.56174	-7.84873
Н	-9.09034	-18.07164	-8.67580
Н	-8.44653	-16.51791	-9.29876
С	-4.26086	-18.92548	-7.67513
С	-3.52751	-19.77875	-8.66682
Н	-2.46424	-19.75925	-8.42100
Н	-3.63412	-19.35720	-9.66485

Н	-3.88522	-20.80279	-8.63977
Fe	-4.86157	-16.48760	-3.43988
Fe	-6.15542	-18.80965	-5.34655
Fe	-4.81767	-16.15019	-6.69279
0	-5.27829	-17.14922	-5.15837
0	-6.61958	-16.90086	-2.61129
0	-7.50332	-18.49467	-3.91502
0	-4.15933	-18.20835	-2.72295
0	-5.04149	-19.79988	-4.03074
0	-5.46480	-14.62032	-3.77900
0	-5.44658	-14.39418	-6.00804
0	-3.00388	-15.91891	-3.86494
0	-2.97840	-15.68154	-6.09310
0	-7.47321	-18.21471	-6.70803
0	-6.55735	-16.39083	-7.63224
0	-4.99954	-19.49712	-6.81901
0	-4.08487	-17.67007	-7.73843



5.2 [Fe₃O(OAc)₆(N₂)₁]⁺:

С	-7.54966	-17.72287	-2.90713
С	-8.74707	-17.77991	-2.00441
н	-8.92455	-16.81126	-1.54526
н	-8.53622	-18.49599	-1.20665
н	-9.62223	-18.12451	-2.54771
С	-4.30408	-19.41870	-3.05071
С	-3.55311	-20.45967	-2.27304
н	-2.59342	-20.62489	-2.76807
н	-4.09536	-21.40125	-2.27052
н	-3.35739	-20.11557	-1.26151
С	-5.64550	-13.95817	-4.83529
С	-6.13072	-12.54551	-4.69746
н	-5.84217	-12.13304	-3.73497
н	-7.22174	-12.55521	-4.75155
н	-5.76049	-11.93373	-5.51559
С	-2.43288	-15.64266	-4.96525
С	-0.98764	-15.24486	-4.90796
н	-0.38300	-16.14565	-5.03587
н	-0.74737	-14.80903	-3.94252
н	-0.74759	-14.56295	-5.71919
С	-7.49721	-17.23369	-7.53487
С	-8.70827	-17.05785	-8.40334
Н	-9.44950	-16.48762	-7.83875
н	-9.14568	-18.02213	-8.64814
н	-8.45995	-16.49965	-9.30122
С	-4.25120	-18.93105	-7.68159
С	-3.48809	-19.78327	-8.65291
Н	-2.47973	-19.92770	-8.25870
Н	-3.39845	-19.27684	-9.61064
Н	-3.95677	-20.75618	-8.76592
Fe	-4.87544	-16.50910	-3.46097

Fe	-6.18784	-18.87439	-5.35567
Fe	-4.83389	-16.17453	-6.68102
0	-5.30104	-17.19049	-5.16509
0	-6.62433	-16.90947	-2.60805
0	-7.52001	-18.50145	-3.90640
0	-4.15290	-18.20610	-2.71476
0	-5.02727	-19.80716	-4.01650
0	-5.47802	-14.63573	-3.77707
0	-5.45411	-14.40828	-6.00508
0	-3.01510	-15.92837	-3.87587
0	-2.98774	-15.69788	-6.10400
0	-7.48672	-18.20811	-6.72391
0	-6.56301	-16.38436	-7.64116
0	-4.99250	-19.51045	-6.83302
0	-4.09078	-17.67529	-7.74988
Ν	-7.32900	-21.03112	-5.59175
N	-7.83876	-21.98821	-5.69543



5.3 [Fe₃O(OAc)₆(N₂)₂]⁺:

С	-7.54422	-17.71607	-2.92077
С	-8.73803	-17.77917	-2.01321
н	-8.91658	-16.81233	-1.55068
Н	-8.52199	-18.49682	-1.21831
н	-9.61439	-18.12484	-2.55393
С	-4.30245	-19.40901	-3.06457
С	-3.55660	-20.45059	-2.28218
н	-2.59595	-20.62010	-2.77380
н	-4.10180	-21.39047	-2.27898
н	-3.36297	-20.10473	-1.27085
С	-5.65684	-13.95017	-4.83094
С	-6.16501	-12.54553	-4.68361
н	-5.87599	-12.13268	-3.72137
Н	-7.25608	-12.57329	-4.72863
Н	-5.81134	-11.92288	-5.50083
С	-2.41981	-15.64744	-4.96061
С	-0.96765	-15.27332	-4.89452
н	-0.37716	-16.18482	-5.01179
н	-0.72789	-14.83611	-3.92953
н	-0.70882	-14.59954	-5.70674
С	-7.51200	-17.23050	-7.53545
С	-8.73894	-17.04852	-8.38166
н	-9.47344	-16.48976	-7.79727
н	-9.17603	-18.01183	-8.63106
н	-8.50942	-16.47862	-9.27716
С	-4.24077	-18.94319	-7.68310
С	-3.46288	-19.80630	-8.63434
н	-2.46141	-19.94892	-8.22246
н	-3.35726	-19.31091	-9.59619
н	-3.93144	-20.77959	-8.74495
Fe	-4.87605	-16.50604	-3.49432

Fe	-6.17501	-18.84786	-5.37015
Fe	-4.81524	-16.13586	-6.74163
0	-5.28996	-17.16550	-5.20569
0	-6.62059	-16.90053	-2.62401
0	-7.51579	-18.49194	-3.92181
0	-4.14961	-18.19640	-2.73080
0	-5.02303	-19.79715	-4.03202
0	-5.47774	-14.62812	-3.77578
0	-5.45890	-14.38976	-6.00290
0	-3.01028	-15.92182	-3.87368
0	-2.96872	-15.69337	-6.10191
0	-7.49177	-18.20975	-6.73160
0	-6.57821	-16.38352	-7.65453
0	-4.99257	-19.51648	-6.84065
0	-4.08146	-17.68879	-7.76362
Ν	-4.20786	-14.81072	-8.74301
Ν	-7.32769	-21.02648	-5.59184
Ν	-3.94130	-14.22706	-9.62339
N	-7.83770	-21.98450	-5.68595



5.4 [Fe₃O(OAc)₆(N₂)₃]⁺:

С	-7.55951	-17.71257	-2.92089
С	-8.76892	-17.76494	-2.03197
н	-8.94352	-16.79855	-1.56702
Н	-8.57618	-18.49092	-1.23873
н	-9.64075	-18.09591	-2.58907
С	-4.29233	-19.41947	-3.06403
С	-3.53371	-20.46893	-2.30313
н	-2.58587	-20.64198	-2.81769
н	-4.08405	-21.40584	-2.29234
н	-3.31540	-20.13057	-1.29433
С	-5.66951	-13.94121	-4.83187
С	-6.20125	-12.54310	-4.69715
н	-5.95145	-12.12810	-3.72508
н	-7.28934	-12.58398	-4.78339
н	-5.82669	-11.91384	-5.50014
С	-2.40534	-15.64994	-4.96920
С	-0.94622	-15.29766	-4.91863
н	-0.37054	-16.21115	-5.08355
н	-0.67959	-14.89714	-3.94500
н	-0.69550	-14.59868	-5.71219
С	-7.50544	-17.22680	-7.52306
С	-8.72791	-17.05277	-8.37779
н	-9.47478	-16.50927	-7.79482
н	-9.15031	-18.01968	-8.63869
н	-8.49849	-16.47289	-9.26683
С	-4.23898	-18.93702	-7.66600
С	-3.46546	-19.80008	-8.62126
н	-2.46294	-19.94541	-8.21296
н	-3.36216	-19.30337	-9.58266
н	-3.93620	-20.77234	-8.73190
Fe	-4.85784	-16.48017	-3.42680

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Fe	-6.16280	-18.82377	-5.35032
Fe	-4.81682	-16.13894	-6.70875
0	-5.27895	-17.14784	-5.16059
0	-6.63416	-16.90518	-2.61054
0	-7.52380	-18.49154	-3.91832
0	-4.13569	-18.21057	-2.72130
0	-5.02720	-19.80175	-4.02209
0	-5.48433	-14.60920	-3.77218
0	-5.45859	-14.38150	-6.00046
0	-2.98984	-15.91364	-3.87732
0	-2.96289	-15.68634	-6.10592
0	-7.48546	-18.20396	-6.71715
0	-6.57498	-16.37598	-7.63717
0	-4.98675	-19.51004	-6.82022
0	-4.08010	-17.68293	-7.74627
Ν	-4.30072	-15.60865	-1.15372
Ν	-4.21136	-14.81130	-8.73985
Ν	-7.32742	-21.02204	-5.59002
Ν	-4.05662	-15.22800	-0.16256
Ν	-3.94854	-14.23331	-9.62515
N	-7 83815	-21 97887	-5 69264



6. Molecular Orbital Diagram of N₂



Scheme S1: Simplified molecular orbital diagram of the N_2 molecule. s-p hybridization is included, but additional connection lines are omitted for clarity.

7. Experimental and Computational Methods

We utilized a customized Fourier Transform-Ion Cyclotron Resonance (FT-ICR)-mass spectrometer (Apex Ultra, Bruker Daltonics) equipped with a Electrospray Ionization (ESI) source (Apollo 2, Bruker). Sample solutions of Iron(III) oxo acetate perchlorate hydrate ([$Fe_3O(OAc)_6(H_2O)_3(CIO_4$)]), Sigma-Aldrich, cf. Scheme 1a) in acetonitrile at concentrations of 1 x 10⁻⁵ mol/I were used without further purification and continuously infused into the ESI source by a syringe pump at a flow rate of 2 µL min⁻¹. The ion source was set to positive electrospray ionization mode. Nitrogen was used as drying gas with a flow rate of 6.0 L min⁻¹ at 220°C. The solutions were sprayed at a nebulizer flow of 2.5 L min⁻¹ and the spray shield was held at 3.6 kV.

The ESI generated ions are injected into a cryogenic hexapole ion trap passing different ion lenses, a 90 degrees ion beam bender and a quadrupole mass filter. In Source Collision Induced Dissociation (CID) of the ESI generated $[Fe_3O(OAc)_6(L)_n]^+$ ions (L = H₂O and acetonitrile, n=1,2,3) enabled us to produce the under-coordinated species $[Fe_3O(OAc)_6]^+$. The ion trap is cooled by a closed cycle Helium cryostat and held at 26 K for the measurements. Buffer or reaction gas can be introduced both pulsed and continuously. In this work we used two continuous gas inlets. The pressure is first increased by N₂ gas from 1.7×10^{-7} mbar up to 3.0×10^{-7} mbar and subsequently increased with He gas up to 4.0×10^{-6} mbar to accomplish N₂ attachment as well as efficient trapping and cooling of the ions. Storage of the ions for a variable time (0-10 s) allows them to react with N₂ to yield $[Fe_3O(OAc)_6(N_2)_n]^+$. The product ions are guided by electrostatic lenses into the FT-ICR cell of the so-called "infinity" type¹. This cell is cooled at a temperature of about 10 K with a closed cycle Helium cryostat to prevent heating of the clusters by black body radiation. The cell is used for isolation and detection of the ions. It is coupled to a tunable IR laser ($\delta n = 0.9 \text{ cm}^{-1}$, $\delta t = 7 \text{ ns}$) to record InfraRed Photon Dissociation (IR-PD) spectra of isolated $[Fe_3O(OAc)_6(N_2)_n]^+.$

The laser is a KTP/KTA optical parametric oscillator/amplifier (OPO/A, LaserVision) system pumped by a pulsed 10 Hz injection seeded Nd^{3+} :YAG laser (Continuum, Powerlite DLS 8000). The OPA idler wave (\leq 10 mJ per pulse) can be used to record spectra within 2600–3900 cm¹. In this work we used the difference frequency (DF) between the OPA signal and idler waves generated in a AgGaSe₂ crystal (0.1 – 1.2 mJ per pulse). We recorded IR-PD spectra in the range of $1200 - 2400 \text{ cm}^{-1}$. Each trapped and isolated package of ions is irradiated by 10 - 15 laser pulses to yield a sufficient amount of fragment ions. The IR spectra were recorded as ion chromatograms while continuously scanning the IR frequency. An experimental IR-PD spectrum arises from a plot of the fragmentation efficiency as a function of laser frequency (ν). The IR-MPD yield $Y(\nu)$ is defined as:

$$Y(\nu) = \left(\frac{\sum_{i} I_{i}^{fr}(\nu)}{\sum_{i} I_{i}^{fr}(\nu) + \sum_{i} I_{i}^{p}(\nu)}\right)$$
(1)

The IR frequency was calibrated using a wave meter (821B-NIR, Bristol instruments), and we recorded laser power curves (cf. Fig. S12 in the ESI).

Optimized minimum energy structures, Gibbs energies and linear IR absorption spectra were calculated at the B3LYP^{2.3} level of theory using cc-pVTZ basis sets⁴ (C, H, N, O), and Stuttgart RSC 1997⁵ effective core potential (Fe) basis sets, respectively, as implemented in the Gaussian 09 program package⁶. Standard convergence criteria were applied. Basis set superposition errors (BSSE) were corrected using the Counterpoise routine^{7,8}. We present unrestricted DFT calculations with 15 unpaired alpha electrons yielding a spin multiplicity of 16 with other multiplicies (2 - 18) found significantly less stable (c.f. Fig. S9.). We scale calculated frequencies with two different scaling factors: One scaling factor (0.951) is specifically designed to elucidate N₂ stretching bands in $[Fe_3O(OAc)_6(N_2)_n]^+$. It scales calculated N₂ stretching frequencies such that a calculated free N₂ stretching vibration frequency matches the experimental value^{9,10} of 2330cm⁻¹. This approach conveniently reveals any effects of Fe-N₂ coordination on N₂ stretching frequencies. A second unspecific scaling factor (0.986) is applied for all other bands. It scales the calculated asymmetric carboxylate stretching vibration frequencies of $[Fe_3O(OAc)_6(N_2)_1]^+$ to match our own experimental value of 1587 cm⁻¹. Unscaled spectra are provided in the supplement (cf. Fig. S4). The usage of two different scaling factors for high and low frequency vibrations is validated by many theoretical studies¹¹⁻¹³. Especially frequencies calculated via DFT/B3LYP benefit from this method¹⁴.

A Natural Population Analysis (NPA) was performed with the NBO 5.9 program¹⁵. We elucidate weak interactions such as hydrogen bonds or van der Waals-interactions in geometry optimized structures using the non-covalent interaction (NCI) technique¹⁶. This

method and its application to intramolecular H-bonds has been described previously¹⁷⁻¹⁹. In short, the electron density ρ and its reduced gradient $s(\rho)$ of a molecule are topologically analyzed in regions of small electron density and small reduced gradient. Non-covalent interactions prevail in areas where $s(\rho)$ is close to zero (minima of electron density). Isosurfaces of the reduced gradient $s(\rho)$ in conjunction with a RGB-colour ranking scheme visualize non-covalent interactions. The RGB-colour indicates the sign of the second eigenvalue, λ_2 , of the Hessian matrix. Red corresponds to positive λ_2 , (repulsive areas, e.g. steric repulsion), blue to negative λ_2 (areas of favorable interactions, e.g. hydrogen bonds) and green to weak delocalized interactions (λ_2 is approximately zero). We use *Multiwfn*²⁰ in conjunction with *Visual Molecular Dynamics* VMD²¹ software to plot these isosurfaces.

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8. ¹⁵N₂ Experiments

Isotope labeling of the N₂ molecule serves to validate our assignment of the observed mass peaks to the N₂ complexes (cf. Table S3) as well as the assignment of the recorded IR-PD bands above 2200 cm⁻¹ to the N₂ stretching frequencies. Exchanging the ¹⁴N₂ reaction gas with ¹⁵N₂ enriched gas (99,999 %, Sigma-Aldrich) leads to expected shifts of N₂ associated mass peaks: +2 m/z per ¹⁴N₂ to ¹⁵N₂ exchange (cf. Fig. S14 and Table S3). Residual ¹⁴N₂ gas in the hexapole leads prominent peaks of mixed ¹⁴N₂/¹⁵N₂ species. Flushing the apparatus with ¹⁵N₂ enriched gas over a few hours suffices to observe exclusive ¹⁵N₂ complexes.

Table S3: Compilation of ESI-MS data on $[Fe_3O(OAc)_6(^XN_2)_n]^+$ (n=1,2,3; X = 14, 15; OAc=CH₃CO₂). The indicated mass labels refer to the most abundant isotope peaks.

Species	m/z
$[Fe_3O(OAc)_6]^+$	538
[Fe ₃ O(OAc) ₆ (¹⁴ N ₂) ₁] ⁺	566
[Fe ₃ O(OAc) ₆ (¹⁵ N ₂) ₁] ⁺	568
[Fe ₃ O(OAc) ₆ (¹⁴ N ₂) ₂] ⁺	594
$[Fe_3O(OAc)_6(^{14}N_2)_1(^{15}N_2)_1]^+$	596
[Fe ₃ O(OAc) ₆ (¹⁵ N ₂) ₂] ⁺	598
[Fe ₃ O(OAc) ₆ (¹⁴ N ₂) ₃] ⁺	622
$[Fe_3O(OAc)_6(^{14}N_2)_2(^{15}N_2)_1]^+$	624
[Fe ₃ O(OAc) ₆ (¹⁴ N ₂) ₂ (¹⁵ N ₂) ₂] ⁺	626
$[Fe_3O(OAc)_6(^{15}N_2)_3]^+$	628

The IR-PD spectrum of $[Fe_3O(OAc)_6(^{14}N_2)_1(^{15}N_2)_1]^+$ (cf. Fig. S16a) reveals two bands at 2268 cm⁻¹ and 2347 cm⁻¹. The ¹⁵N₂ stretching frequency decreases by 79 cm⁻¹ with respect to the frequency of ¹⁴N₂. Published Raman spectroscopy data^{1,II} on free ¹⁴N₂ ($v_0 = 2330$ cm⁻¹) and ¹⁵N₂ ($v_0 = 2252$ cm⁻¹) indicates a red shift of 78 cm⁻¹. Note, that mass scaling of the ¹⁴N₂ vibration frequency to ¹⁵N₂ yields a frequency of 2251 cm⁻¹.

Our value of 2268 cm⁻¹ for the ¹⁵N₂ stretching frequency in $[Fe_3O(OAc)_6(^{14}N_2)_1(^{15}N_2)_1]^+$ represents a blue shift of 16 cm⁻¹ with respect to 2252 cm⁻¹ (free ¹⁵N₂ vibration frequency by Raman spectroscopy) or a blue shift of 17 cm⁻¹ in respect to 2251 cm⁻¹ (free ¹⁵N₂ vibration frequency by mass scaling from ¹⁴N₂). The blue shift of ¹⁵N₂ in the complex is nearly identical with respect to the blue shift of ${}^{14}N_2$ frequency. Calculated linear IR spectra of $[Fe_3O(OAc)_6({}^{14}N_2)_1({}^{15}N_2)_1]^+$ (cf. Fig S16b) as well as $[Fe_3O(OAc)_6({}^{15}N_2)_2]^+$ and $[Fe_3O(OAc)_6({}^{14}N_2)_2]^+$ reveal a red shift of 79 cm⁻¹ with the given scaling factor of 0.951.



Figure S16: Cationic mass spectra of a $[Fe_3O(OAc)_6(H_2O)_3]CIO_4$ acetonitrile solution after collision induced dissociation and subsequent ¹⁴N₂ and/or ¹⁵N₂ coordination to $[Fe_3O(OAc)_6]^+$ The upper spectrum was measured directly after ¹⁵N₂ addition to the hexapole. The lower spectrum was measured after 3h of flushing with ¹⁵N₂ gas. For peak assignment refer to Table S3.



Figure S17: a: IR-PD spectrum of $[Fe_3O(OAc)_6({}^{14}N_2)_1({}^{15}N_2)_1]^+$ at 26 K. **b:** Calculated IR absorption spectrum of geometry optimized of $[Fe_3O(OAc)_6({}^{14}N_2)_1({}^{15}N_2)_1]^+$ **c:** Calculated IR absorption spectrum of geometry optimized of $[Fe_3O(OAc)_6({}^{14}N_2)_2]^+$ (blue) and $[Fe_3O(OAc)_6({}^{15}N_2)_2]^+$ (red). The calculations were performed at the B3LYP/cc-pVTZ (H, C, N, O) and Stuttgart 1997 ECP (Fe) level of theory. The multiplicity is 16 and frequencies are scaled with 0.951. Calculated stick spectra were convoluted with a Gaussian envelope of FWHM = 3.5 cm⁻¹. We obtain two values for the free ${}^{15}N_2$ vibration frequency: 2252 cm⁻¹ by Raman spectroscopy^{1,11} or 2251 cm⁻¹ by mass scaling of the ${}^{14}N_2$ frequency.

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