

A Comparative IRMPD and DFT Study of Fe^{3+} and UO_2^{2+} Complexation with N-Methylacetohydroxamic Acid

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I. Crystallographic data for [Fe(NMA)₃]·H₂O

Table S1. Crystal data for [Fe(NMA)₃]·H₂O.

CCDC	1538337
Formula	C ₉ H ₂₀ FeN ₃ O ₇
$D_{calc.}/\text{g cm}^{-3}$	1.509
μ/mm^{-1}	8.458
Formula Weight	338.13
Colour /Shape	clear dark red plates
Size/mm ³	0.15 × 0.12 × 0.02
T/K	100(2)
Crystal System	monoclinic
Space Group	$P2_1/n$
$a/\text{\AA}$	10.4087(6)
$b/\text{\AA}$	10.4063(6)
$c/\text{\AA}$	27.4839(15)
$\beta/^\circ$	91.156(3)
$V/\text{\AA}^3$	2976.3(3)
Z	8
Z'	2
Wavelength/ $\text{\AA}$	1.54178
Radiation type	CuK α
$\theta_{min} / \theta_{max} / ^\circ$	3.216 / 66.685
Measured / Independent / Used Reflections	30590 / 5184 / 4460
R_{int}	0.0544
Parameters	370
Restraints	16
Deepest Hole/Largest Peak	−0.282 / 0.648
GooF	1.034
wR_2 (all data)	0.1006
wR_2	0.0951
R_1 (all data)	0.0461
R_1	0.0375

Table S2. Fractional atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for $[\text{Fe}(\text{NMA})_3]\cdot\text{H}_2\text{O}$. U_{eq} is defined as 1/3 of the trace of the orthogonalized U_{ij} .

Atom	x	y	z	U_{eq}
Fe1	3486.3(4)	6594.9(4)	3424.8(2)	16.63(12)
O1	1561.2(18)	6714.2(18)	3435.9(7)	22.4(4)
O2	3165.6(16)	6140.2(18)	4117.0(7)	22.4(4)
O3	3778.8(18)	4727.1(17)	3302.9(7)	20.8(4)
O4	3510.1(19)	6529.8(17)	2685.6(7)	23.1(4)
O5	5370.1(18)	6911.5(17)	3567.2(7)	21.3(4)
O6	3587.0(18)	8529.8(17)	3403.5(7)	22.2(4)
N1	1145(5)	6230(11)	3869(2)	20.6(4)
N1B	1884(4)	5939(11)	4172(2)	20.6(4)
N2	3913(2)	4460(2)	2821.5(8)	21.6(5)
N3	5672(2)	8175(2)	3573.6(9)	23.8(5)
C1	−241(5)	6123(7)	3950(2)	20.6(4)
C1B	−347(5)	6252(7)	3841(2)	20.6(4)
C2	1971(4)	5919(13)	4212(3)	20.6(4)
C2B	1073(5)	6249(13)	3823(2)	20.6(4)
C3	1685(7)	5375(7)	4698(2)	20.6(4)
C3B	1464(6)	5356(7)	4625(2)	20.6(4)
C4	3898(3)	5228(3)	1978.7(10)	27.1(7)
C5	3769(2)	5407(2)	2511.5(9)	17.1(5)
C6	4249(3)	3136(3)	2714.6(12)	30.2(7)
C7	4905(3)	10397(3)	3449.3(13)	34.8(8)
C8	4732(2)	8990(2)	3484.6(9)	17.3(5)
C9	7016(3)	8485(3)	3678.9(13)	35.3(8)
Fe1A	1225.9(4)	7955.3(4)	5931.8(2)	16.25(12)
O1A	76.7(17)	7695.0(17)	5358.6(6)	18.6(4)
O2A	312.7(17)	9676.2(17)	5902.5(6)	20.2(4)
O3A	12.5(17)	6955.2(17)	6336.0(6)	19.2(4)
O4A	1916.6(18)	8363.7(18)	6610.0(7)	22.5(4)
O5A	2302.7(17)	6375.1(18)	5852.3(7)	21.1(4)
O6A	2804.0(18)	8684.1(18)	5601.1(7)	24.2(4)
N1A	−805(2)	8655(2)	5317.8(8)	19.3(5)

Atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> _{eq}
N2A	413(2)	6921(2)	6808.8(8)	22.1(5)
N3A	3460(2)	6645(2)	5649.9(9)	25.0(5)
C1A	−1796(3)	8444(3)	4945(1)	21.6(6)
C2A	−668(2)	9650(2)	5602.1(9)	14.4(5)
C3A	−1588(3)	10744(3)	5603.9(10)	24.9(6)
C4A	1913(3)	7665(3)	7440.4(11)	32.6(7)
C5A	1380(3)	7655(3)	6935.4(9)	19.1(6)
C6A	−270(3)	6020(3)	7121.0(11)	28.8(7)
C7A	4885(3)	8204(4)	5281.2(15)	47.7(10)
C8A	3672(3)	7831(3)	5522.3(10)	24.0(6)
C9A	4338(3)	5560(3)	5618.7(12)	34.6(8)
O7	7119(2)	4902(2)	3223.9(8)	33.1(5)
O8	2711.8(19)	2796(2)	3923.6(8)	27.4(5)

Table S3. Anisotropic displacement parameters ($\times 10^4$) for $[\text{Fe}(\text{NMA})_3]\cdot\text{H}_2\text{O}$. The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2} \times U_{11} + \dots + 2hka^* \times b^* \times U_{12}]$.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Fe1	14.6(2)	15.0(2)	20.4(2)	2.53(15)	3.35(16)	1.48(16)
O1	17.9(10)	23.9(10)	25.7(11)	2.6(8)	2.6(8)	1.0(8)
O2	18.7(10)	26.5(10)	22.1(10)	2.4(8)	3.3(8)	1.3(8)
O3	26(1)	18.4(9)	18.2(10)	2.3(7)	3.1(8)	0.4(8)
O4	27.7(11)	19.3(10)	22.4(10)	4.3(8)	2.3(8)	1.4(8)
O5	19.2(10)	16.0(9)	28.8(11)	4.5(7)	1.6(8)	2.8(8)
O6	17.8(10)	16.9(10)	31.9(11)	1.5(8)	0.6(8)	2.6(8)
N2	23.2(13)	20.8(12)	20.8(12)	-2.4(9)	4.0(9)	-0.5(10)
N3	22.4(12)	20.4(12)	28.5(13)	-2.8(9)	-1.6(10)	2.8(9)
C4	30.8(17)	29.3(16)	21.3(15)	-0.5(12)	2.4(12)	-12.9(13)
C5	13.1(13)	20.4(14)	17.9(14)	0.7(10)	1.2(10)	-4(1)
C6	36.2(19)	18.1(14)	36.6(18)	-3.2(12)	4.4(14)	0.0(13)
C7	33.8(18)	16.0(15)	55(2)	-2.9(13)	0.1(15)	-0.7(13)
C8	16.1(12)	15.7(12)	20.1(14)	-1.3(10)	1(1)	2.1(9)
C9	23.1(16)	34.8(18)	47(2)	-11.2(14)	-13.0(14)	1.8(14)
Fe1A	13.0(2)	20.1(2)	15.7(2)	1.87(15)	0.87(16)	2.28(16)
O1A	18.2(10)	17.0(9)	20.5(10)	-1.2(7)	-1.2(7)	7.7(8)
O2A	21.1(10)	19.0(9)	20.4(10)	-2.3(7)	-0.9(8)	2.6(8)
O3A	17.4(10)	24.5(10)	15.9(10)	-0.7(7)	1.8(7)	0.4(8)
O4A	19.1(10)	27.9(11)	20.3(10)	0.1(8)	0.0(8)	-1.1(8)
O5A	17(1)	23.8(10)	22.8(10)	3.6(8)	4.6(7)	4.4(8)
O6A	17.9(10)	26.1(10)	28.8(11)	8.4(8)	3.9(8)	1.4(8)
N1A	15.6(11)	20.5(11)	21.8(12)	3.2(9)	1.5(9)	3.3(9)
N2A	23.7(13)	24.4(12)	18.4(12)	-0.3(9)	5.2(10)	5.3(10)
N3A	18.7(13)	33.9(14)	22.6(13)	4.7(10)	5.1(10)	9.1(10)
C1A	16.6(14)	26.9(15)	21.3(15)	-0.6(11)	-3.3(11)	3.9(11)
C2A	15.5(13)	15.2(12)	12.7(13)	2.0(9)	4.7(10)	1.5(10)
C3A	26.6(16)	23.8(15)	24.3(15)	1.5(11)	1.5(12)	7.5(12)
C4A	30.2(17)	47(2)	20.3(16)	-1.5(13)	-0.1(12)	4.1(15)
C5A	17.0(14)	21.4(14)	18.9(14)	-3.5(11)	0.8(11)	6.0(11)
C6A	36.3(18)	26.0(15)	24.3(16)	2.8(12)	9.1(13)	0.8(13)
C7A	25.7(19)	59(2)	59(2)	35.3(19)	15.1(16)	8.3(17)

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
C8A	14.5(14)	32.5(17)	25.1(15)	13.5(12)	6.6(11)	7.6(12)
C9A	28.3(17)	39.7(18)	36.1(18)	8.1(14)	10.1(14)	20.8(14)
O7	34.8(13)	36.4(13)	28.2(12)	6.0(9)	5.5(9)	15(1)
O8	20.1(10)	26.8(11)	35.5(12)	11.8(9)	3.4(9)	−0.8(9)

Table S4. Bond lengths in Å for [Fe(NMA)₃] $\cdot$ H₂O.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
Fe1	O1	2.009(2)	Fe1A	O1A	1.977(2)
Fe1	O2	1.995(2)	Fe1A	O2A	2.028(2)
Fe1	O3	1.997(2)	Fe1A	O3A	1.992(2)
Fe1	O4	2.033(2)	Fe1A	O4A	2.029(2)
Fe1	O5	2.019(2)	Fe1A	O5A	2.005(2)
Fe1	O6	2.017(2)	Fe1A	O6A	2.040(2)
O1	N1	1.371(4)	O1A	N1A	1.359(3)
O1	C2B	1.284(4)	O2A	C2A	1.300(3)
O2	N1B	1.362(4)	O3A	N2A	1.357(3)
O2	C2	1.296(4)	O4A	C5A	1.294(3)
O3	N2	1.362(3)	O5A	N3A	1.366(3)
O4	C5	1.293(3)	O6A	C8A	1.288(3)
O5	N3	1.352(3)	N1A	C1A	1.456(3)
O6	C8	1.300(3)	N1A	C2A	1.304(3)
N1	C1	1.469(4)	N2A	C5A	1.305(4)
N1	C2	1.304(1)	N2A	C6A	1.465(4)
N1B	C2B	1.305(1)	N3A	C8A	1.303(4)
N1B	C3B	1.460(4)	N3A	C9A	1.456(4)
N2	C5	1.309(3)	C2A	C3A	1.487(4)
N2	C6	1.453(4)	C4A	C5A	1.484(4)
N3	C8	1.314(3)	C7A	C8A	1.489(4)
N3	C9	1.459(4)			
C1B	C2B	1.480(4)			
C2	C3	1.486(4)			
C4	C5	1.485(4)			
C7	C8	1.479(4)			

Table S5. Bond angles in ° for [Fe(NMA)₃].H₂O.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
O1	Fe1	O4	92.84(8)	C8	N3	O5	117.0(2)
O1	Fe1	O5	162.24(8)	C8	N3	C9	127.0(2)
O1	Fe1	O6	89.49(8)	O2	C2	N1	115.5(5)
O2	Fe1	O1	79.28(7)	O2	C2	C3	117.4(4)
O2	Fe1	O3	87.60(8)	N1	C2	C3	127.1(4)
O2	Fe1	O4	161.90(8)	O1	C2B	N1B	116.1(5)
O2	Fe1	O5	91.97(8)	O1	C2B	C1B	116.0(4)
O2	Fe1	O6	105.91(8)	N1B	C2B	C1B	127.5(4)
O3	Fe1	O1	102.61(8)	O4	C5	N2	117.5(2)
O3	Fe1	O4	78.17(7)	O4	C5	C4	120.1(2)
O3	Fe1	O5	92.33(8)	N2	C5	C4	122.4(2)
O3	Fe1	O6	163.46(8)	O6	C8	N3	118.1(2)
O5	Fe1	O4	99.66(8)	O6	C8	C7	117.8(2)
O6	Fe1	O4	90.15(8)	N3	C8	C7	124.1(3)
O6	Fe1	O5	77.99(7)	O1A	Fe1A	O2A	79.27(7)
N1	O1	Fe1	108.8(2)	O1A	Fe1A	O3A	89.57(8)
C2B	O1	Fe1	113.7(3)	O1A	Fe1A	O4A	163.32(8)
N1B	O2	Fe1	109.0(2)	O1A	Fe1A	O5A	97.55(7)
C2	O2	Fe1	114.5(3)	O1A	Fe1A	O6A	100.11(8)
N2	O3	Fe1	112.4(1)	O2A	Fe1A	O4A	90.49(8)
C5	O4	Fe1	114.0(2)	O2A	Fe1A	O6A	92.01(8)
N3	O5	Fe1	112.7(2)	O3A	Fe1A	O2A	100.45(8)
C8	O6	Fe1	114.3(2)	O3A	Fe1A	O4A	79.28(8)
O1	N1	C1	119.2(4)	O3A	Fe1A	O5A	89.68(8)
C2	N1	O1	120.3(4)	O3A	Fe1A	O6A	165.49(8)
C2	N1	C1	120.4(4)	O4A	Fe1A	O6A	93.32(8)
O2	N1B	C3B	118.0(4)	O5A	Fe1A	O2A	169.30(8)
C2B	N1B	O2	120.2(5)	O5A	Fe1A	O4A	94.79(8)
C2B	N1B	C3B	121.9(4)	O5A	Fe1A	O6A	78.42(8)
O3	N2	C6	114.8(2)	N1A	O1A	Fe1A	111.2(1)
C5	N2	O3	117.8(2)	C2A	O2A	Fe1A	111.6(2)
C5	N2	C6	127.4(2)	N2A	O3A	Fe1A	111.2(2)
O5	N3	C9	116.1(2)	C5A	O4A	Fe1A	111.5(2)

Atom	Atom	Atom	Angle/°
N3A	O5A	Fe1A	112.0(2)
C8A	O6A	Fe1A	113.1(2)
O1A	N1A	C1A	114.5(2)
C2A	N1A	O1A	118.0(2)
C2A	N1A	C1A	127.5(2)
O3A	N2A	C6A	115.7(2)
C5A	N2A	O3A	117.4(2)
C5A	N2A	C6A	126.8(2)
O5A	N3A	C9A	115.1(2)
C8A	N3A	O5A	117.4(2)

Atom	Atom	Atom	Angle/°
C8A	N3A	C9A	127.5(3)
O2A	C2A	N1A	118.2(2)
O2A	C2A	C3A	118.6(2)
N1A	C2A	C3A	123.2(2)
O4A	C5A	N2A	119.3(2)
O4A	C5A	C4A	119.0(3)
N2A	C5A	C4A	121.7(3)
O6A	C8A	N3A	119.0(2)
O6A	C8A	C7A	119.9(3)
N3A	C8A	C7A	121.1(3)

Table S6. Torsion angles in ° for [Fe(NMA)₃]·H₂O.

Atom	Atom	Atom	Atom	Angle/°
Fe1	O1	N1	C1	−175.5(7)
Fe1	O1	N1	C2	7.4(13)
Fe1	O1	C2B	N1B	9.0(14)
Fe1	O1	C2B	C1B	−177.1(7)
Fe1	O2	N1B	C2B	−10.7(13)
Fe1	O2	N1B	C3B	168.3(7)
Fe1	O2	C2	N1	−10.9(15)
Fe1	O2	C2	C3	170.5(8)
Fe1	O3	N2	C5	−3.6(3)
Fe1	O3	N2	C6	174.46(19)
Fe1	O4	C5	N2	3.4(3)
Fe1	O4	C5	C4	−176.29(19)
Fe1	O5	N3	C8	−0.6(3)
Fe1	O5	N3	C9	179.4(2)
Fe1	O6	C8	N3	−0.6(3)
Fe1	O6	C8	C7	176.8(2)
O1	N1	C2	O2	2.1(18)
O1	N1	C2	C3	−179.5(11)
O2	N1B	C2B	O1	1.4(18)
O2	N1B	C2B	C1B	−171.8(10)
O3	N2	C5	O4	0.1(4)
O3	N2	C5	C4	179.8(2)
O5	N3	C8	O6	0.8(4)
O5	N3	C8	C7	−176.3(3)
C1	N1	C2	O2	−175.0(10)
C1	N1	C2	C3	3(2)
C3B	N1B	C2B	O1	−177.7(10)
C3B	N1B	C2B	C1B	9(2)
C6	N2	C5	O4	−177.7(3)
C6	N2	C5	C4	2.0(4)
C9	N3	C8	O6	−179.2(3)
C9	N3	C8	C7	3.6(5)
Fe1A	O1A	N1A	C1A	−171.97(17)

Atom	Atom	Atom	Atom	Angle/°
Fe1A	O1A	N1A	C2A	9.1(3)
Fe1A	O2A	C2A	N1A	−10.4(3)
Fe1A	O2A	C2A	C3A	168.71(19)
Fe1A	O3A	N2A	C5A	8.9(3)
Fe1A	O3A	N2A	C6A	−169.09(18)
Fe1A	O4A	C5A	N2A	−7.8(3)
Fe1A	O4A	C5A	C4A	170.0(2)
Fe1A	O5A	N3A	C8A	−2.8(3)
Fe1A	O5A	N3A	C9A	175.1(2)
Fe1A	O6A	C8A	N3A	0.8(3)
Fe1A	O6A	C8A	C7A	179.8(3)
O1A	N1A	C2A	O2A	1.0(3)
O1A	N1A	C2A	C3A	−178.1(2)
O3A	N2A	C5A	O4A	−0.6(4)
O3A	N2A	C5A	C4A	−178.4(2)
O5A	N3A	C8A	O6A	1.4(4)
O5A	N3A	C8A	C7A	−177.6(3)
C1A	N1A	C2A	O2A	−177.7(2)
C1A	N1A	C2A	C3A	3.2(4)
C6A	N2A	C5A	O4A	177.1(2)
C6A	N2A	C5A	C4A	−0.7(4)
C9A	N3A	C8A	O6A	−176.2(3)
C9A	N3A	C8A	C7A	4.8(5)

Table S7. Hydrogen fractional atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for $[\text{Fe}(\text{NMA})_3]\cdot\text{H}_2\text{O}$. U_{eq} is defined as 1/3 of the trace of the orthogonalised U_{ij} .

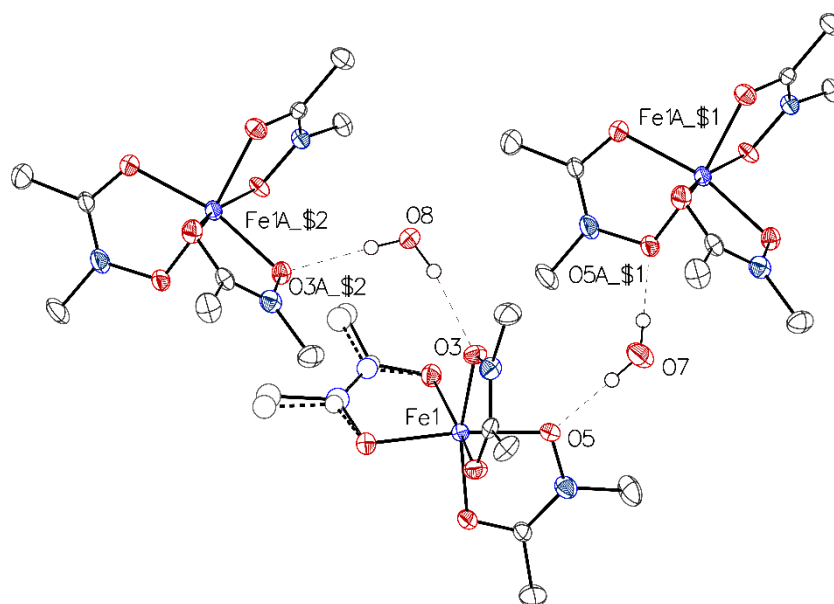
Atom	<i>x</i>	<i>y</i>	<i>z</i>	U_{eq}
H1A	−651.91	6955.69	3888.32	31
H1B	−383.69	5864.28	4287.82	31
H1C	−611.5	5477.16	3729.19	31
H1BA	−633.67	6997.29	4027.63	31
H1BB	−641.74	5461.64	3996.62	31
H1BC	−707.03	6300.52	3508.73	31
H3A	2489.8	5126.13	4863.74	31
H3B	1132.51	4618.86	4658.33	31
H3C	1244.8	6023.07	4892.76	31
H3BA	2005.58	4609.66	4701.93	31
H3BB	567.18	5079.74	4587.33	31
H3BC	1537.31	5985.27	4888.95	31
H4A	3592.14	6000.23	1808.32	41
H4B	3384.84	4486.27	1872.22	41
H4C	4802.59	5079.44	1903.78	41
H6A	5068.83	2922.92	2876.58	45
H6B	4328.03	3028.41	2362.22	45
H6C	3576.1	2563.27	2832.89	45
H7A	4789.34	10666.61	3109.65	52
H7B	5771.98	10627.07	3564.81	52
H7C	4269.12	10829.28	3650.15	52
H9A	7281.77	8092.73	3989.07	53
H9B	7117.35	9419.55	3700.08	53
H9C	7550.9	8150.74	3418.26	53
H1AA	−2336.83	7718.21	5039.11	32
H1AB	−1391.64	8253.77	4634.21	32
H1AC	−2326.04	9218.2	4910.85	32
H3AA	−1337.6	11378.59	5359.86	37
H3AB	−1576.21	11145.93	5926.48	37
H3AC	−2455.2	10429.03	5526.57	37
H4AA	2414.52	8451.08	7493.67	49

Atom	x	y	z	U_{eq}
H4AB	2468.77	6914.23	7490.1	49
H4AC	1207.14	7635.66	7670.8	49
H6AA	285.15	5283.16	7196.3	43
H6AB	-1052.59	5721.58	6951.71	43
H6AC	-500.88	6452.31	7423.75	43
H7AA	4991.21	9138.94	5298.64	72
H7AB	4846.53	7934.59	4939.62	72
H7AC	5614.42	7785	5446.79	72
H9AA	3905.24	4845.54	5450.91	52
H9AB	4602.09	5289.8	5947.29	52
H9AC	5097.01	5815.54	5436.97	52
H7D	6547.42	5485.19	3286.95	50
H7E	7293.26	4461.76	3486.27	50
H8A	3120.1	3369.3	3755.9	41
H8B	1892.63	2850.7	3857.54	41

Table S8. Hydrogen bond information for [Fe(NMA)₃] $\cdot$ H₂O.^a

D	H	A	$d(\text{D}-\text{H})/\text{\AA}$	$d(\text{H}\cdots\text{A})/\text{\AA}$	$d(\text{D}\cdots\text{A})/\text{\AA}$	$\text{D}-\text{H}\cdots\text{A}/^\circ$
O7	H7D	O5	0.87	2.08	2.941(3)	168.8
O7	H7E	O5A ¹	0.87	2.05	2.918(3)	173.3
O8	H8A	O3	0.87	2.01	2.874(3)	170.2
O8	H8B	O3A ²	0.87	2.05	2.922(3)	176.4

^a Symmetry transformations used to generate equivalent atoms: (1) $1 - x, 1 - y, 1 - z$; (2) $-x, 1 - y, 1 - z$.

**Figure S1.** ORTEP view of [Fe(NMA)₃] $\cdot$ H₂O showing the intermolecular hydrogen bonds. Hydrogen atoms not involved in hydrogen bonds have been omitted for clarity.**Table S9.** Atomic occupancies for all atoms that are not fully occupied in [Fe(NMA)₃] $\cdot$ H₂O.

Atom	Occupancy	Atom	Occupancy	Atom	Occupancy
N1	0.5	H1BA	0.5	H3B	0.5
N1B	0.5	H1BB	0.5	H3C	0.5
C1	0.5	H1BC	0.5	C3B	0.5
H1A	0.5	C2	0.5	H3BA	0.5
H1B	0.5	C2B	0.5	H3BB	0.5
H1C	0.5	C3	0.5	H3BC	0.5
C1B	0.5	H3A	0.5		

Table S10. Statistics on bond distances for iron(III) hydroxamate complexes. Structural data were retrieved from the CCDC database (May 2017 release).

Ref. code	Fe–O (Å)	N–O (Å)	C=O (Å)	C–N (Å)
Mean	1.986	1.374	1.277	1.317
Std. deviation	0.034	0.021	0.019	0.025
XUPVIP	2.017	1.351	1.285	1.363
XUPVIP	2.046	1.334	1.293	1.369
XUPVIP	2.048	1.504	1.125	1.356
BOPMUO01	1.99	1.368	1.296	1.32
BOPMUO01	1.974	1.378	1.282	1.323
BOPMUO01	2.011	1.381	1.272	1.316
BOSMOL	2.001	1.366	1.272	1.312
BOSMOL	2.005	1.374	1.27	1.315
BOSMOL10	2.002	1.365	1.274	1.317
BOSMOL10	2.004	1.375	1.271	1.319
BUHQUQ	1.971	1.39	1.261	1.326
BUHQUQ	1.992	1.387	1.287	1.318
BUHQUQ	1.967	1.379	1.271	1.325
CETWIH	1.963	1.368	1.271	1.316
COFDIK10	1.971	1.406	1.26	1.347
COFDIK10	1.979	1.414	1.291	1.355
COFDIK10	2.004	1.381	1.306	1.194
COLTUU	2.009	1.415	1.292	1.327
COLTUU	1.991	1.413	1.299	1.325
CUJHIY	1.982	1.412	1.285	1.335
CUJHIY	1.99	1.391	1.257	1.353
CUJHIY	2.000	1.373	1.355	1.293
CUJHIY	1.962	1.389	1.282	1.311
CUJHIY	2.023	1.393	1.317	1.303
CUJHIY	2.019	1.37	1.245	1.33
CUJHOE	1.994	1.381	1.272	1.332
CUJHOE	1.979	1.371	1.289	1.32
CUJHOE	1.993	1.375	1.292	1.323
DEWNAU	2.009	1.372	1.279	1.365
DEWNAU	2.014	1.363	1.266	1.368

Ref. code	Fe–O (Å)	N–O (Å)	C=O (Å)	C–N (Å)
DEWNAU	1.993	1.377	1.274	1.379
DEWNAU	2.01	1.345	1.298	1.365
DEWNAU	2.006	1.368	1.297	1.365
DEWNAU	2.004	1.364	1.284	1.363
DORFUM	2.064	1.346	1.278	1.38
DORGAT	2.015	1.354	1.286	1.381
DORGAT	2.012	1.355	1.274	1.378
DORGEX	2.01	1.356	1.282	1.374
DORGEX	2.029	1.359	1.281	1.372
DORGEX	2.002	1.36	1.28	1.366
DUPJON	1.956	1.363	1.278	1.321
DUPJON	1.95	1.378	1.274	1.33
DUPJON	1.98	1.388	1.271	1.307
EKOTAB	1.996	1.378	1.275	1.304
EKOTAB	1.986	1.373	1.28	1.306
EKOTAB	1.992	1.362	1.285	1.299
EKOTEF	1.959	1.372	1.269	1.314
EKOTEF	2.106	1.371	1.278	1.31
EKOTIJ	1.981	1.367	1.285	1.304
EKOTIJ	2.005	1.369	1.272	1.315
EKOTIJ	2.017	1.379	1.272	1.31
EKOTOP	2.006	1.377	1.273	1.311
EKOTOP	2.003	1.374	1.265	1.31
EKOTOP	1.996	1.375	1.26	1.326
EKOTUV	1.96	1.358	1.292	1.312
EKOTUV	2.000	1.372	1.291	1.312
EKOTUV	2.000	1.368	1.283	1.313
EKOVAD	1.973	1.364	1.282	1.312
EKOVAD	2.024	1.366	1.278	1.311
EKOVAD	1.963	1.372	1.286	1.3
FEBOAH	1.974	1.363	1.305	1.322
FEBOAH	1.978	1.39	1.271	1.311
FEBOAH	1.991	1.37	1.285	1.343
FEBOAH01	1.975	1.366	1.278	1.311

Ref. code	Fe–O (Å)	N–O (Å)	C=O (Å)	C–N (Å)
FEBOAH01	1.972	1.371	1.27	1.314
FEBOAH01	1.969	1.37	1.282	1.299
FEBOAH02	1.985	1.368	1.278	1.297
FEBOAH02	1.975	1.368	1.28	1.308
FEBOAH02	1.981	1.376	1.276	1.304
FEPSBC10	2.012	1.367	1.257	1.304
FEPSBC10	2.002	1.344	1.282	1.313
FERCRN10	1.996	1.371	1.309	1.314
FERCRN10	1.993	1.372	1.315	1.323
FERCRN10	1.955	1.397	1.26	1.331
FERCRN10	1.967	1.383	1.276	1.293
FERCRN10	1.969	1.394	1.286	1.273
FERCRN10	2.007	1.386	1.288	1.295
FERMAH11	1.967	1.364	1.269	1.329
FERMAH11	1.98	1.379	1.27	1.329
FERMAH11	1.994	1.372	1.254	1.319
FEROXE10	1.945	1.389	1.274	1.302
FEROXE10	1.938	1.379	1.271	1.314
FEROXE10	1.975	1.375	1.282	1.308
FERRID10	1.983	1.406	1.265	1.32
FERRID10	2.001	1.368	1.276	1.283
FERRID10	1.967	1.391	1.292	1.312
FTAFUS10	1.969	1.337	1.272	1.341
FTAFUS10	1.999	1.326	1.279	1.4
FTAFUS10	1.949	1.385	1.275	1.334
FUYVUS	1.811	1.405	1.291	1.305
IRADEK	1.967	1.317	1.227	1.269
IRADEK	1.983	1.301	1.296	1.271
IRADEK	1.977	1.331	1.272	1.248
IRADEK	1.996	1.378	1.292	1.303
IRADEK	1.987	1.384	1.32	1.303
IRADEK	1.964	1.309	1.244	1.31
IRADEK	1.988	1.357	1.256	1.304
IRADEK	1.969	1.33	1.191	1.327

Ref. code	Fe–O (Å)	N–O (Å)	C=O (Å)	C–N (Å)
JEP RAX	1.977	1.408	1.283	1.336
JEP RAX	1.962	1.359	1.256	1.299
JEP RAX	2.005	1.36	1.292	1.346
KAXHEW	2.056	1.424	1.304	1.299
NOKNUY	1.966	1.365	1.268	1.291
OCELOX	1.973	1.379	1.277	1.329
OCELOX	1.978	1.373	1.256	1.344
OCELOX	1.961	1.382	1.27	1.303
OFUYET	1.971	1.375	1.284	1.31
OFUYET	1.981	1.381	1.292	1.307
OFUYET	1.984	1.373	1.276	1.33
OJABUX	2.01	1.36	1.277	1.302
OJABUX	2.002	1.362	1.268	1.308
OJABUX	2.016	1.361	1.275	1.31
OY EYUN	2.002	1.376	1.284	1.289
OY EYUN	1.979	1.385	1.258	1.307
QOZDUE	1.974	1.371	1.258	1.318
QOZDUE	1.974	1.399	1.312	1.298
QOZDUE	1.964	1.364	1.298	1.298
QUXXOX	1.962	1.382	1.282	1.315
QUXXOX	1.982	1.378	1.283	1.304
QUXXOX	1.977	1.379	1.285	1.313
SEMKOM	1.971	1.342	1.276	1.299
SEMKOM	1.995	1.363	1.25	1.307
SEMKOM	1.913	1.359	1.275	1.292
SIPMEJ	1.989	1.386	1.282	1.315
SIPMEJ	1.968	1.37	1.268	1.328
SIPMEJ	1.989	1.385	1.272	1.322
SISSAO	1.973	1.386	1.27	1.322
SISSAO	1.966	1.382	1.267	1.326
SISSAO	1.971	1.383	1.268	1.323
SISSES	1.978	1.378	1.278	1.316
SISSES	1.975	1.375	1.277	1.31
SISSES	1.995	1.378	1.278	1.318

Ref. code	Fe–O (Å)	N–O (Å)	C=O (Å)	C–N (Å)
SUXREI	1.973	1.37	1.262	1.301
SUXREI	1.977	1.384	1.265	1.299
SUXREI	1.984	1.371	1.279	1.295
SUXREI	1.946	1.367	1.275	1.293
SUXREI	1.984	1.369	1.268	1.302
SUXREI	1.99	1.381	1.265	1.294
TEQKUV	1.99	1.382	1.287	1.313
TEQKUV	1.989	1.377	1.266	1.328
TEQKUV	1.964	1.382	1.291	1.289
TEQKUV	1.952	1.371	1.268	1.31
TEQKUV	1.975	1.389	1.29	1.331
TEQKUV	1.995	1.398	1.276	1.313
TEQKUV01	1.99	1.382	1.287	1.313
TEQKUV01	1.989	1.377	1.266	1.328
TEQKUV01	1.964	1.382	1.291	1.289
TEQKUV01	1.952	1.371	1.268	1.31
TEQKUV01	1.975	1.389	1.29	1.331
TEQKUV01	1.995	1.398	1.276	1.313
TOLSIX	1.818	1.356	1.27	1.338
TOLSOD	1.805	1.42	1.306	1.292
UDAWUS	1.988	1.359	1.275	1.292
UDAWUS	1.995	1.375	1.263	1.304
UDAWUS	1.978	1.37	1.263	1.309
UDAWUS	2.01	1.371	1.288	1.31
UDAWUS	1.948	1.371	1.273	1.309
UDAWUS	1.984	1.357	1.291	1.308
UDAXAZ	2.011	1.338	1.288	1.301
UDAXAZ	2.001	1.35	1.244	1.336
UDAXAZ	1.977	1.34	1.299	1.304
UMOVEY	1.965	1.36	1.276	1.351
UMOVEY	1.982	1.359	1.257	1.358
UNEVUE	1.961	1.376	1.29	1.294
UNEVUE	1.993	1.368	1.283	1.313
UNEVUE	1.982	1.389	1.272	1.31

Ref. code	Fe–O (Å)	N–O (Å)	C=O (Å)	C–N (Å)
UNEWAL	1.988	1.36	1.299	1.298
UNEWAL	1.986	1.407	1.279	1.304
UNEWAL	1.989	1.392	1.257	1.319
UNEWEP	1.983	1.366	1.27	1.316
UNEWEP	1.994	1.379	1.272	1.323
UNEWEP	1.975	1.377	1.272	1.297
VAYYEB	1.981	1.396	1.293	1.283
VEYFEL	1.965	1.363	1.282	1.29
VEYFIP	1.998	1.361	1.279	1.292
WAKXAH	2.013	1.37	1.267	1.355
WAKXAH	2.02	1.379	1.277	1.36
WAKXAH	2.038	1.382	1.277	1.399
YOFCAZ	1.923	1.365	1.269	1.307
YOLBOR	2.087	1.379	1.271	1.317
YOLBOR	1.955	1.364	1.273	1.312
YOLBUX	1.996	1.378	1.274	1.309
YOLBUX	1.988	1.373	1.287	1.305
YOLBUX	1.984	1.374	1.273	1.31
YOLBUX	1.985	1.37	1.276	1.306
YOLBUX	2.001	1.378	1.275	1.315
YOLBUX	1.999	1.382	1.278	1.308
HADWOB	2.057	1.414	1.285	1.314
HADWUH	2.023	1.407	1.296	1.314
HADWUH	2.031	1.411	1.279	1.309
HADWUH	2.044	1.419	1.282	1.32

II. Experimental Data for $[\text{Fe}(\text{NMA})_3] \cdot 0.6\text{H}_2\text{O}$

1. Thermogravimetric Analysis

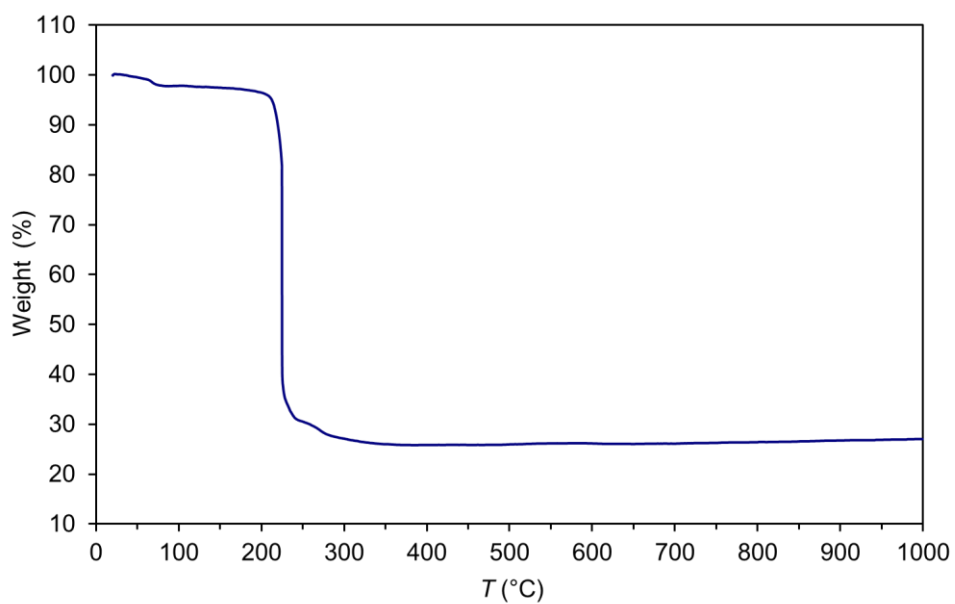


Figure S2. TGA curve for $[\text{Fe}(\text{NMA})_3] \cdot 0.6\text{H}_2\text{O}$ recorded under a N_2/O_2 gas flow.

2. FTIR Spectroscopy

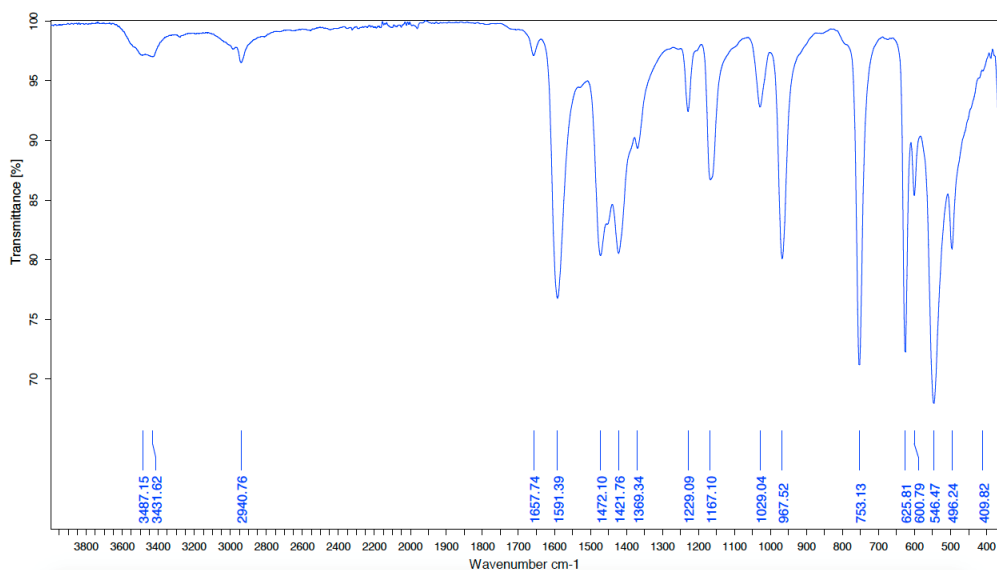


Figure S3. ATR-FTMIR spectrum of $[\text{Fe}(\text{NMA})_3] \cdot 0.6\text{H}_2\text{O}$.

3. (+)-ESI-MS Spectroscopy

A sample of $[\text{Fe}(\text{NMA})_3] \cdot 0.6\text{H}_2\text{O}$ was dissolved in 2.25 mL of methanol. The mass spectrum was subsequently recorded by electro-spray ionization of this solution (Figure S4).

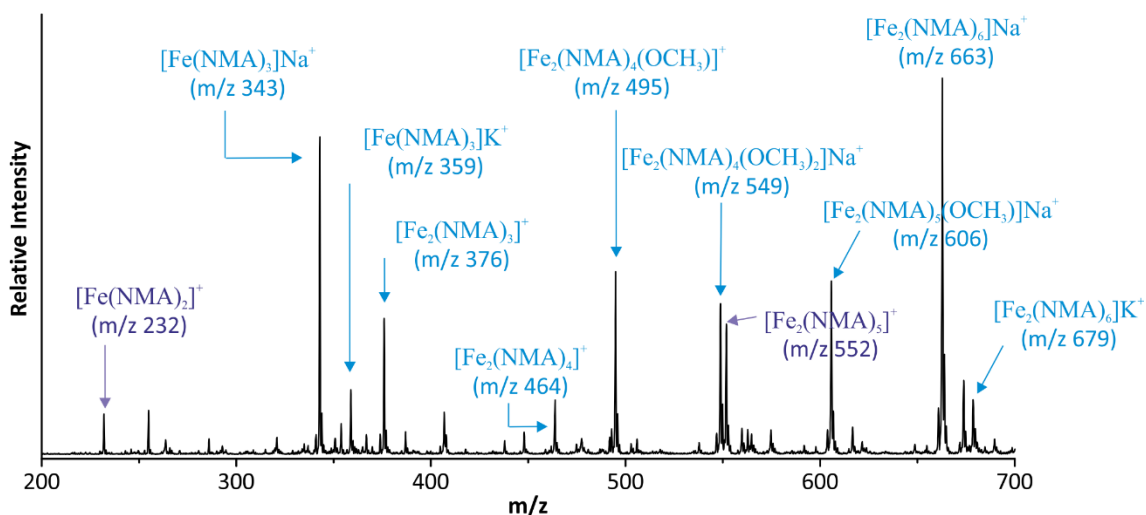


Figure S4. (+)-ESI-MS spectrum of $[\text{Fe}(\text{NMA})_3] \cdot 0.6\text{H}_2\text{O}$ in methanol.

4. Collision-Induced Dissociation of $[\text{Fe}_2(\text{NMA})_5]^+$

The collision-induced dissociation (CID) of the dinuclear $[\text{Fe}_2(\text{NMA})_5]^+$ cation leads to the elimination of one and two *N*-methylacetoxyhydroxamate radicals. The release of the first (NMA) $^{\bullet}$ radical requires a higher collision energy (1.54 eV) than the second one (1.33 eV) (Figure S5). CID experiments can furthermore provide the appearance energies (AE), which are related to the bond dissociation energies.¹ The evolution of the relative cross-section in dependence of the collision energy can be modelled by a sigmoidal function. The appearance energy can be determined from the linear extrapolation of the tangent at the inflexion point to the zero relative cross-section. Numerical values are reported in Figure S5. The collision-energy scale has to be calibrated. To that end, the appearance energies of a series of alkylpyridinium ions were measured and the derived values were calibrated to the theoretical bond dissociation energies of the given parent ions.¹

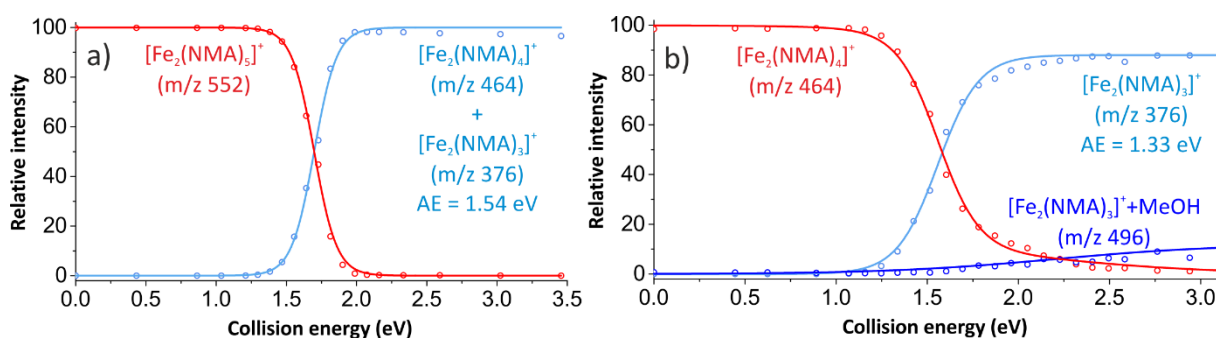


Figure S5. Collision induced dissociation of (a) $[\text{Fe}_2(\text{NMA})_5]^+$ and (b) $[\text{Fe}_2(\text{NMA})_4]^+$.

III. Experimental Data for $[\text{UO}_2(\text{NMA})_2(\text{H}_2\text{O})]$

1. FTIR Spectroscopy

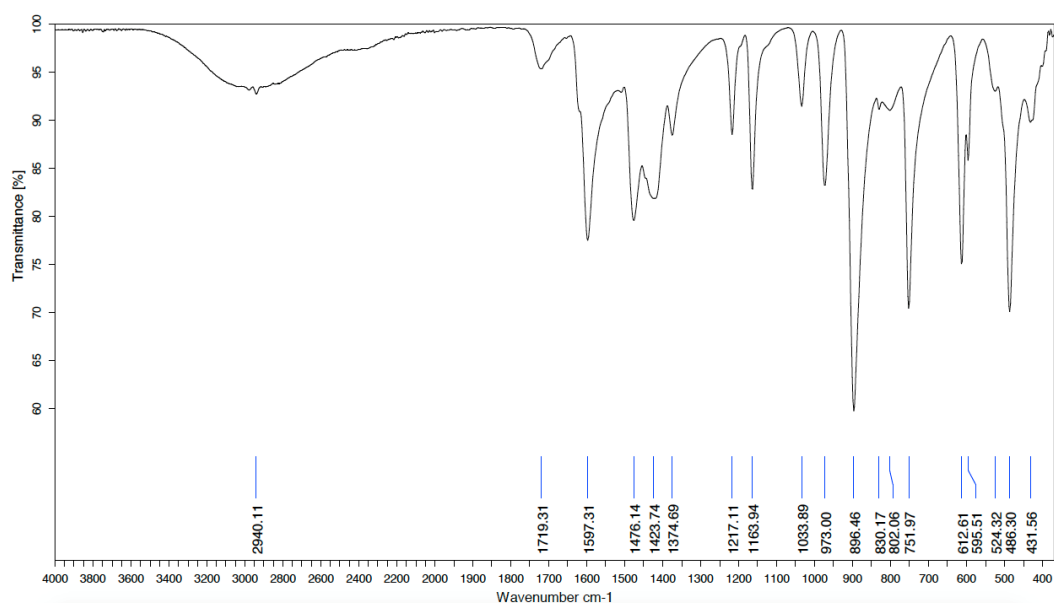


Figure S6. ATR-FTMIR spectrum of $[\text{UO}_2(\text{NMA})_2(\text{H}_2\text{O})]$.

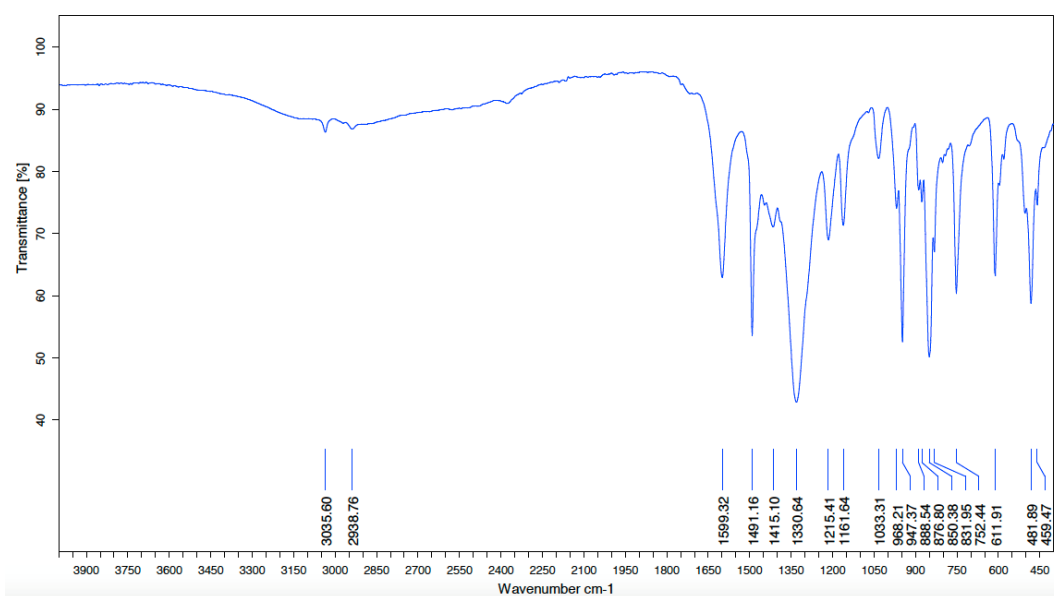


Figure S7. ATR-FTMIR spectrum of $[\text{U}^{18}\text{O}_2(\text{NMA})_2(\text{H}_2\text{O})]$.

2. (+)-ESI-MS Spectroscopy

A sample of $[\text{UO}_2(\text{NMA})_2(\text{H}_2\text{O})]$ was dissolved in 2.25 mL of methanol. The mass spectrum was subsequently recorded by electro-spray ionization of this solution (Figure S8 and Table S11).

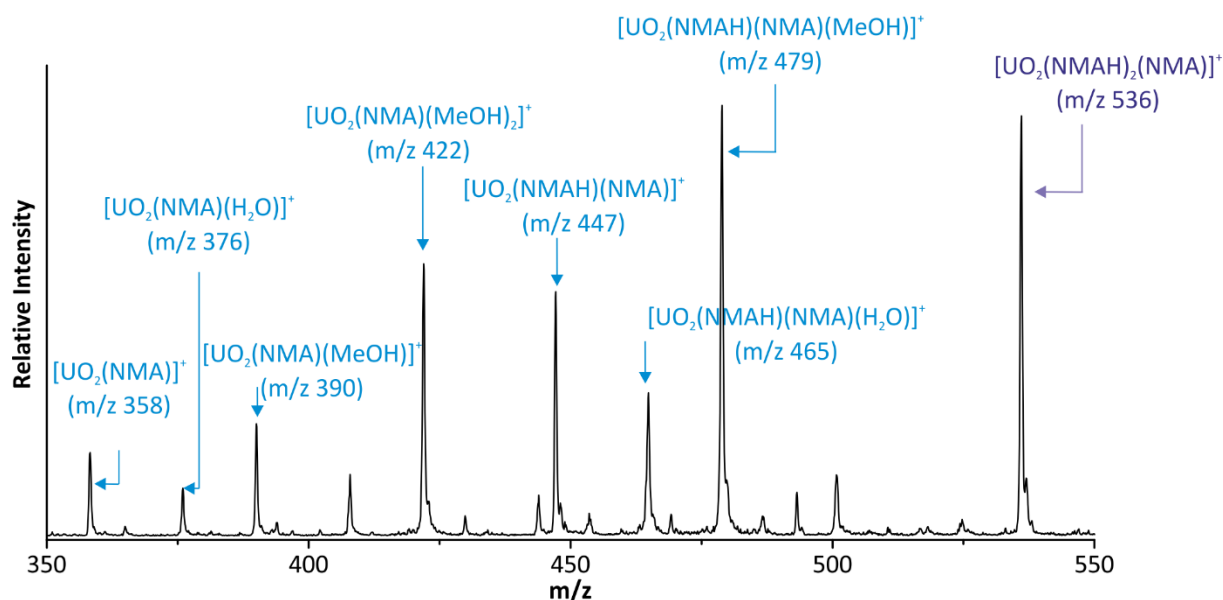


Figure S8. (+)-ESI-MS spectrum of $[\text{UO}_2(\text{NMA})_2(\text{H}_2\text{O})]$ in methanol.

Table S11. (+)-ESI-MS data for a methanolic solution of $[\text{UO}_2(\text{NMA})_2(\text{H}_2\text{O})]$.

<i>m/z</i> found	<i>m/z</i> calcd.	Assignment
358	358.0799	$[\text{UO}_2(\text{NMA})]^+$
376	376.0905	$[\text{UO}_2(\text{NMA})(\text{H}_2\text{O})]^+$
390	390.1061	$[\text{UO}_2(\text{NMA})(\text{CH}_3\text{OH})]^+$
422	422.1323	$[\text{UO}_2(\text{NMA})(\text{CH}_3\text{OH})_2]^+$
447	447.1276	$[\text{UO}_2(\text{NMA})(\text{NMAH})]^+$
465	465.1381	$[\text{UO}_2(\text{NMA})(\text{H}_2\text{O})(\text{NMAH})]^+$
479	479.1538	$[\text{UO}_2(\text{NMA})(\text{CH}_3\text{OH})(\text{NMAH})]^+$
536	536.1753	$[\text{UO}_2(\text{NMA})(\text{NMAH})_2]^+$

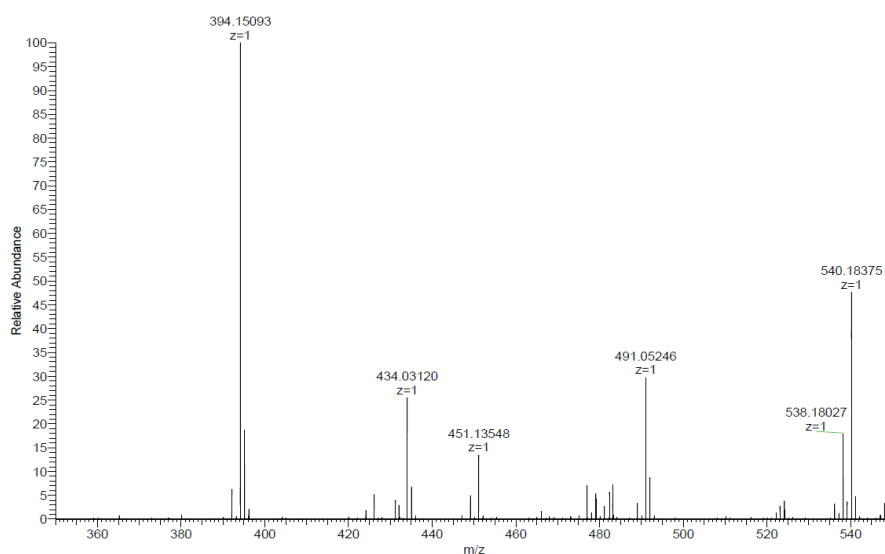


Figure S9. (+)-HR-ESI-MS spectrum of $[\text{U}^{18}\text{O}_2(\text{NMA})_2(\text{H}_2\text{O})]$ in methanol.

3. Collision-Induced Dissociation of $[\text{UO}_2(\text{NMA})(\text{NMAH})_2]^+$ and $[\text{U}^{18}\text{O}_2(\text{NMA})(\text{NMAH})_2]^+$

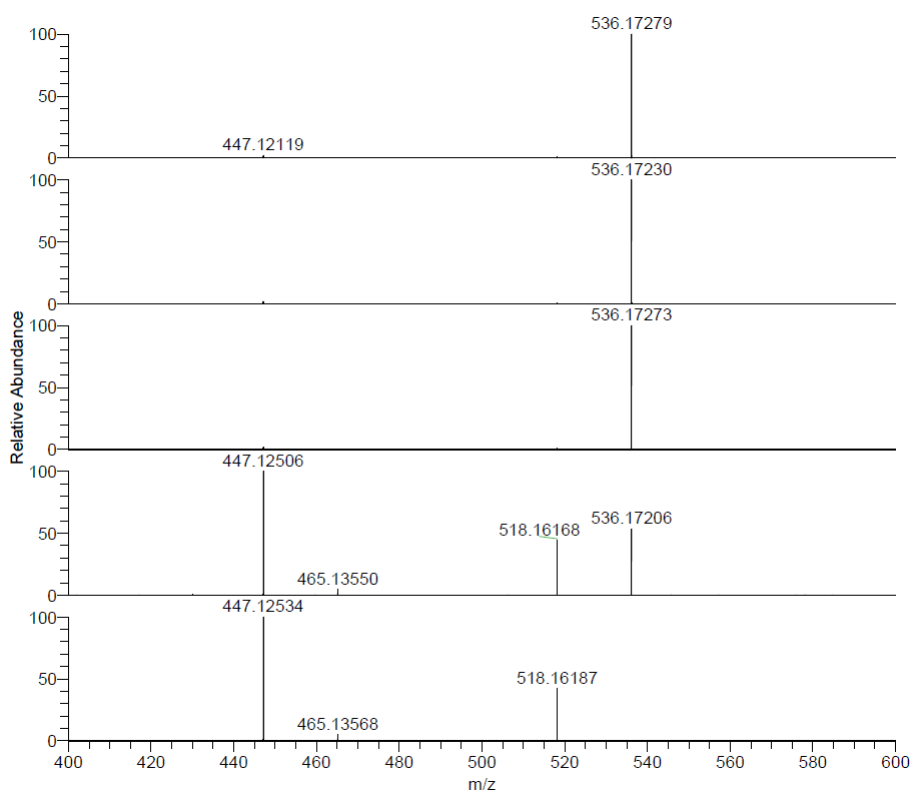


Figure S10. Collision-induced dissociation spectra of the selected $[\text{UO}_2(\text{NMA})(\text{NMAH})_2]^+$ ion ($m/z = 536.1728$) generated from $[\text{U}^{18}\text{O}_2(\text{NMA})_2(\text{H}_2\text{O})]$ dissolved in methanol for different normalized collision energies expressed in % (from top to bottom: 0, 5, 10, 11, 15). The peaks at $m/z = 518.1619$ and 447.1253 correspond to the loss of a molecule of water and NMAH, respectively.

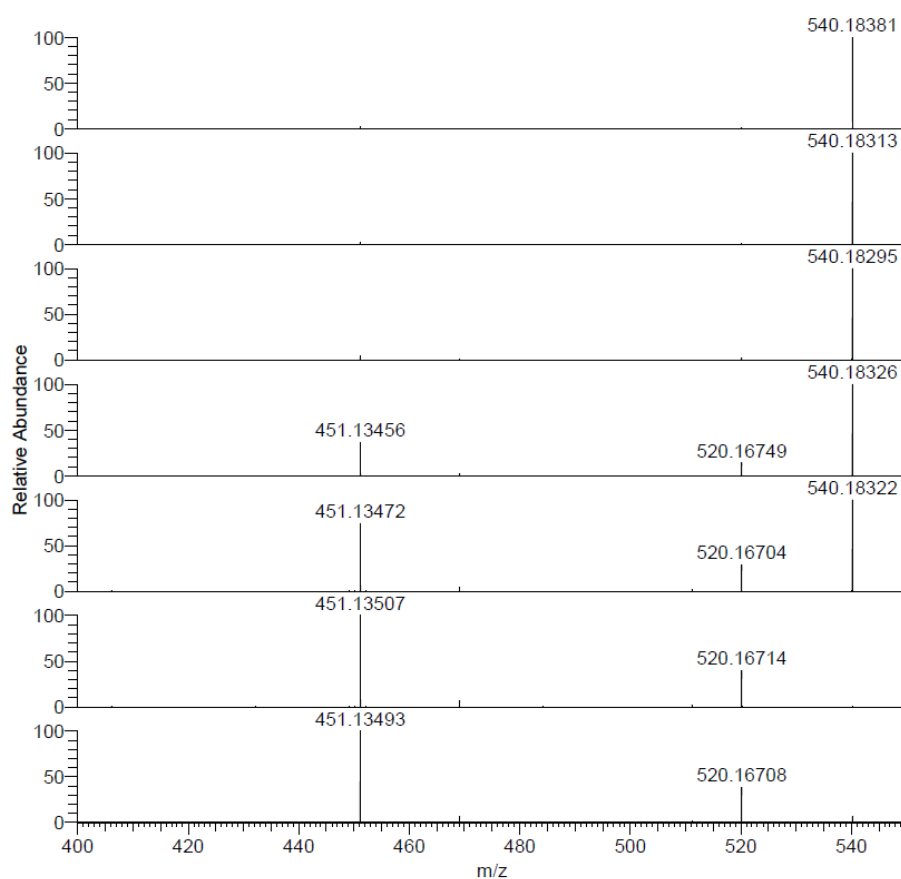


Figure S11. Collision-induced dissociation spectra of the selected $[\text{U}^{18}\text{O}_2(\text{NMA})(\text{NMAH})_2]^+$ ion ($m/z = 540.1838$) generated from $[\text{U}^{18}\text{O}_2(\text{NMA})_2(\text{H}_2\text{O})]$ dissolved in methanol for different normalized collision energies expressed in % (from top to bottom: 0, 5, 10, 11, 12, 15, 18). The peaks at $m/z = 520.1671$ and 451.1349 correspond to the loss of a molecule of a ^{18}O -labeled water (H_2^{18}O) and NMAH, respectively.

4. Collision-Induced Dissociation of $[\text{U}^{18}\text{O}_2(\text{NMA})(\text{NMAH})]^+$

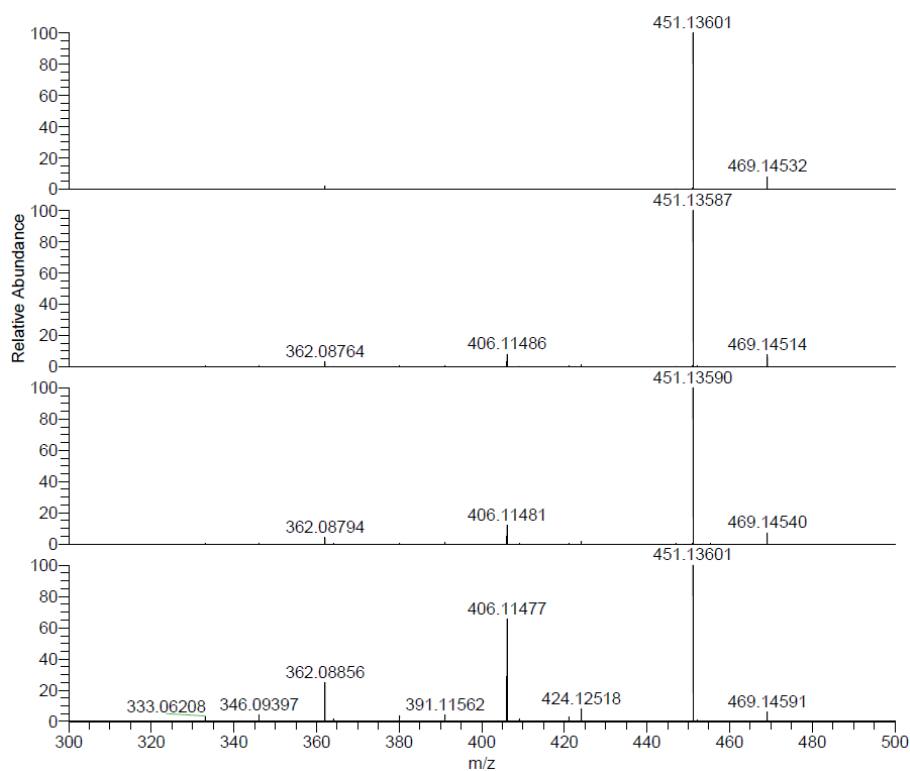


Figure S12. Collision-induced dissociation spectra of the selected $[\text{U}^{18}\text{O}_2(\text{NMA})(\text{NMAH})]^+$ ion ($m/z = 451.1360$) generated from $[\text{U}^{18}\text{O}_2(\text{NMA})_2(\text{H}_2\text{O})]$ dissolved in methanol for different normalized collision energies expressed in % (from top to bottom: 0, 9, 11, 12). The peaks at $m/z = 362.0886$ and 406.1148 correspond to the loss of a NMAH molecule and CH_3NO fragment, respectively.

5. Collision-Induced Dissociation of $[\text{U}^{18}\text{O}_2(\text{NMA})(\text{CH}_3\text{OH})]^+$

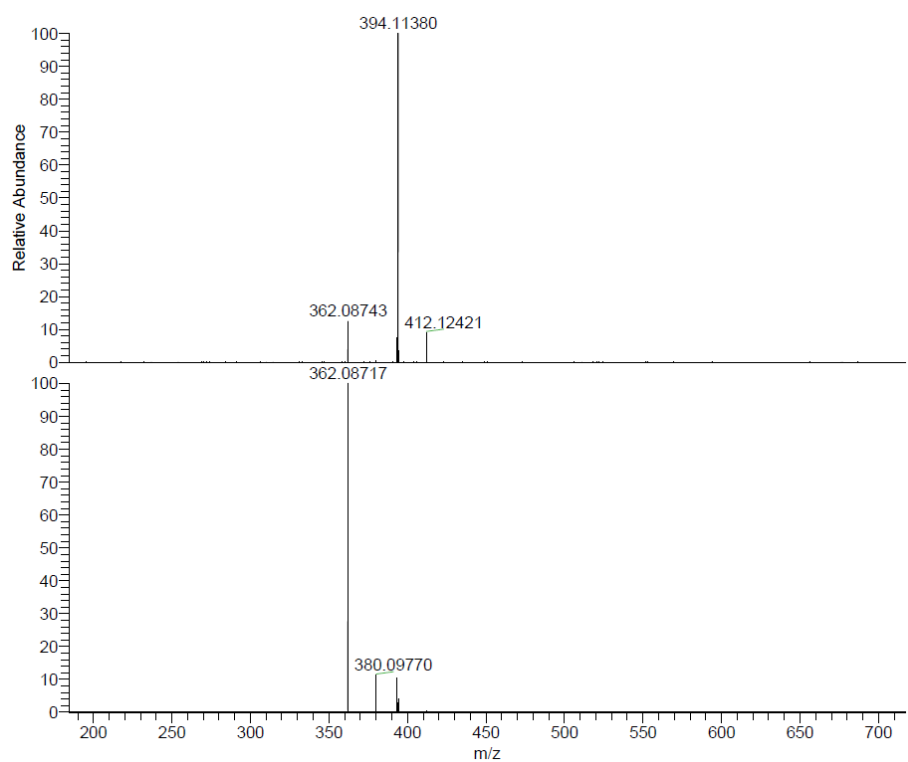


Figure S13. Collision-induced dissociation spectra of the selected $[\text{U}^{18}\text{O}_2(\text{NMA})(\text{CH}_3\text{OH})]^+$ ion ($m/z = 394.1138$) generated from $[\text{U}^{18}\text{O}_2(\text{NMA})_2(\text{H}_2\text{O})]$ dissolved in methanol for different normalized collision energies expressed in % (from top to bottom: 0, 11). The peak at $m/z = 362.0872$ corresponds to the loss of a molecule of methanol.

IV. Laser Power During IRMPD Measurements

The laser power at the CLIO facility (Centre Laser Infrarouge Orsay, Orsay, France) is subject to fluctuations over time. Thus, the wavenumber dependence of the laser power on the free-electron laser CLIO during the IRMPD measurements is reported in Figure S4.

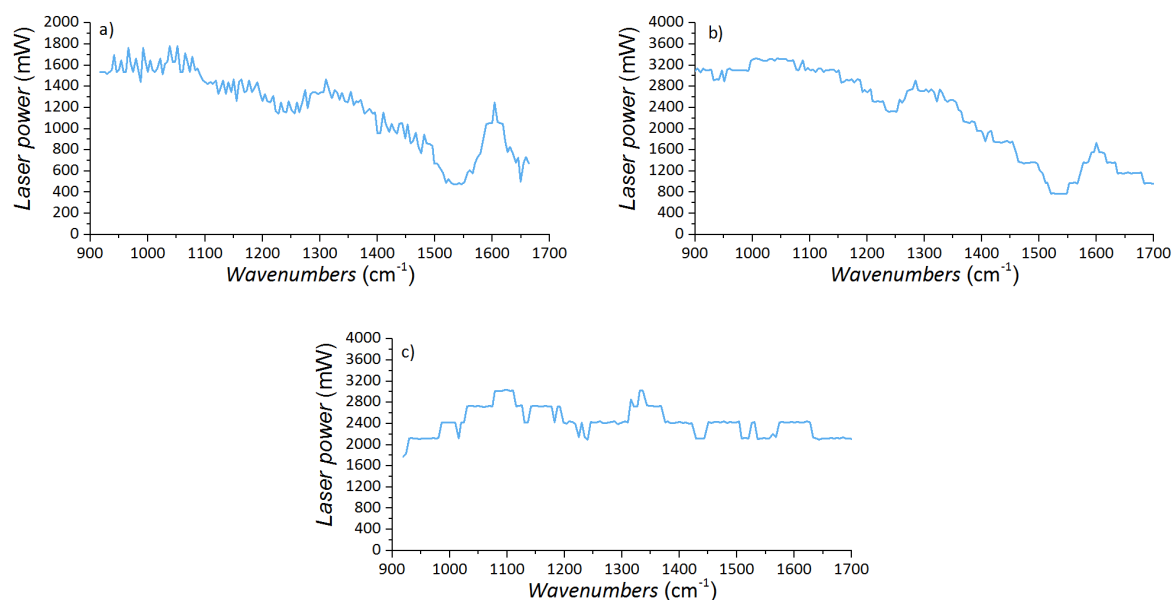


Figure S14. Wavenumber dependence of the laser power during the IRMPD measurements for the ions at $m/z = 552$ [Fe₂(NMA)₅]⁺ (a), $m/z = 536$ [UO₂(NMA)(NMAH)₂]⁺ (b), and $m/z = 518$ [UO(NMA)₃]⁺ (c).

V. Detailed Vibrational Attribution

All attributions are made by observing the displacement for each vibrational normal mode. Band assignment follows the classical nomenclature used in the literature. The out-of-plane label is defined as out of plane of the molecule. Symmetric and antisymmetric for CH₃ means that hydrogens of both carbon atoms vibrate in phase or not. The order of attribution reflects the importance of the contribution, *i.e.* the first attribution is the main contribution.

1. *N*-Methylacetohydroxamic Acid (NMAH) and its Conjugated Base (NMA⁻)

The structure of *N*-methylacetohydroxamic acid (NMAH) was optimized as a neutral molecule and the corresponding conjugated base (NMA⁻) as an anion of charge -1, in singlet spin state using the B3LYP method and cc-pVTZ basis set. In order to observe the changes upon the coordination of the hydroxamate moiety to a metal, the infrared spectra of the *cis* forms of *N*-methylacetohydroxamic acid (NMAH) and of its conjugated base (NMA⁻) were calculated by DFT. Overall, the calculated transition energies (Figure S15 and Table S12) and band assignments derived from normal-mode analysis (Figure S16) are both fully consistent with previously published theoretical investigations.² Moreover, there is also a good match between computed and experimentally-measured wavenumbers for pure NMAH, although FTMIR spectroscopy does not appear to be the most suitable method for establishing unambiguously the conformation adopted by the molecule in the neat oil.^{2c}

The important vibrational modes which are dominantly influenced by the coordination of the hydroxamate to a metal ion are the C=O and the N–O vibrations. The carbonyl stretch for the neutral ligand is found at 1656 cm⁻¹ and for the anion at 1634 cm⁻¹, in excellent agreement with the values computed by Yang et al. (1662 vs 1631 cm⁻¹) for the $\nu(\text{C=O}) + \delta(\text{CH}_3)$ combination band.^{2a} The magnitude of the red shift (22 cm⁻¹) undergone upon deprotonation of NMAH *in silico* is similar to the displacement measured in water (13 cm⁻¹),^{2a} and moreover compares favorably well also with the shifts reported for acetohydroxamic acid ($R^1 = \text{CH}_3$, $R^2 = \text{H}$) in aqueous media by Edwards et al. (46 cm⁻¹)³ and Yang et al. (29 cm⁻¹).^{2a}

The N–O stretching mode, which is combined with CH₃ rocking and C–C stretching vibrations is found at 957 cm⁻¹ for the neutral acid and at 930 cm⁻¹ for the anion. This band is less intense than the $\nu(\text{C=O})$ signal. Although slightly different combination modes were proposed by Yang et al. ($\nu_{\text{as}}(\text{N–O} + \text{C=O}) + \delta(\text{CH}_3)$ for NMAH and $\nu(\text{N–O}) + \delta(\text{CH}_3)$ for NMA⁻),^{2a} the reported wavenumbers (964 and 940 cm⁻¹ *in silico* vs 958 and 950 cm⁻¹ *in aquo*, respectively) are in excellent agreement with our findings. Most of the remaining bands in both NMAH and NMA⁻ spectra are related to the bending modes of the methyl groups.

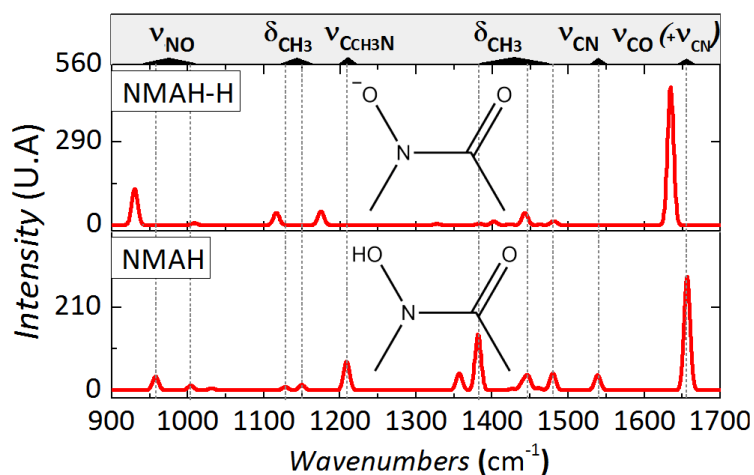


Figure S15. Infrared spectra calculated for *N*-methylacetohydroxamate (NMA^-) and *N*-methylacetohydroxamic acid (NMAH) at the B3LYP/cc-pVTZ level. A scaling factor of 0.98 was applied to all harmonic frequencies. The panel on the top shows the peak attribution derived from normal-mode analysis.

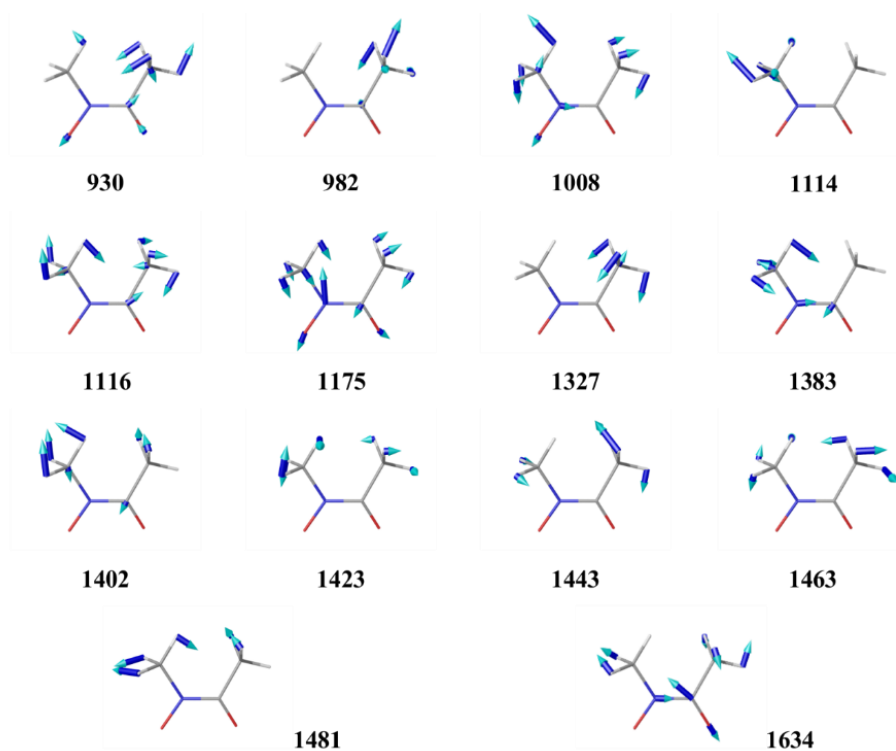


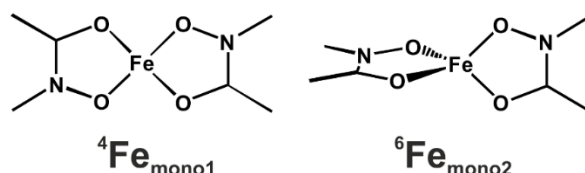
Figure S16. Representation of calculated displacement vectors of each vibrational normal mode of NMA^- . The arrows show the displacement vector for each atom (displacements of less than 0.1 Bohr are not shown).

Table S12. DFT-computed vibrational frequencies (cm^{-1}) and band assignments for NMAH and NMA^- .

NMAH	NMA^-	Attribution
957	930	Rocking CH_3 (-C) + N-O & C-C stretching + symmetric rocking
1004	1008	Rocking CH_3 (-N) + N-O & C-N stretching + anti-symmetric rocking
1031	982	Rocking out-of-plane CH_3 (-C)
1128	1114	Rocking out-of-plane CH_3 (-N)
1150	1116	Stretching CH_3 -C + symmetric rocking CH_3 + deformation OCNO
1209	1175	Stretching CH_3 -N
1357	1327	Umbrella CH_3 (-C)
1381	1383	Umbrella CH_3 (-N) + stretch CC and CN
1426	1402	Umbrella CH_3 (-N) + symmetric scissoring CH_3 (-C)
1440	1423	Twist CH_3 (-N) + symmetric twist
1447	1443	Scissoring CH_3 (-C) + anti-symmetric scissoring
1461	1463	Twist CH_3 (-C) + anti-symmetric twist
1479	1481	Scissoring CH_3 (-N) + symmetric scissoring
1538		C=N stretching
	1634	C=O + C=N stretching
1656		C=O stretching

2. Mononuclear Iron Complexes

For the mononuclear $[\text{Fe}(\text{NMA})_2]^+$ cation, DFT calculations were performed for a square planar (**Fe_{mono1}**) and a tetrahedral (**Fe_{mono2}**) coordination geometry (Scheme S1), while assuming +1 total charge in both cases. For **Fe_{mono1}** and **Fe_{mono2}**, quartet and sextet spin states were considered, respectively. B3LYP method and cc-pVTZ basis set (organic part) and SDD basis set and pseudo potential (Fe) were used for these calculations. Table S13 summarizes the computed vibrational frequencies and the corresponding band assignments.



Scheme S1

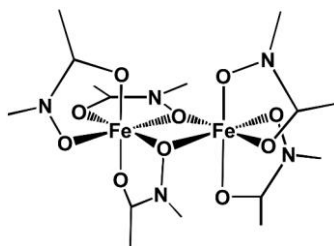
Table S13. DFT computed vibrational frequencies (cm^{-1}) and band assignments for the mono-iron complexes **Fe_{mono1}** and **Fe_{mono2}** of formula $[\text{Fe}(\text{NMA})_2]^+$.

Fe_{mono1}	Fe_{mono2}	Attribution
969 ; 973	970 ; 970	Rocking CH_3 (-C) + NO & CO stretch
1025 ; 1029	1025 ; 1027	Rocking CH_3 (-N) + NO & CN stretch
1054 ; 1055	1052 ; 1052	Rocking out-of-plane CH_3 (-C)
1139 ; 1139	1139 ; 1139	Rocking out-of-plane CH_3 (-N)
1184 ; 1186	1179 ; 1179	Stretching $\text{C}_{\text{CH}_3}\text{C}+$ Rocking CH_3 + deformation OCNO
1212 ; 1216	1213 ; 1216	Stretching $\text{C}_{\text{CH}_3}\text{N}$
1397 ; 1398	1396 ; 1397	Umbrella CH_3 (-C)
1418 ; 1420	1420 ; 1420	Scissoring CH_3 (-C) + stretching CO
1437 ; 1438	1437 ; 1437	Umbrella CH_3 (-N)
1453 ; 1453	1454 ; 1454	Twist CH_3 (-N)
1467 ; 1468	1463 ; 1464	Scissoring CH_3 (-N)
1471 ; 1471	1472 ; 1472	Twist CH_3 (-N)
1490 ; 1490	1490 ; 1490	Stretching CO
1603 ; 1606	1572 ; 1575	Stretching CN

These theoretical calculations enabled to propose a first assignment of some features occurring in the IRMPD spectrum of the dinuclear $[\text{Fe}_2(\text{NMA})_5]^+$ cluster ion. Accordingly, the experimental band observed at 976 cm^{-1} should correspond to the N–O stretching vibration, which is mixed with the C–O vibration and the deformation of the carbon-bound methyl group. The band at about 1183 cm^{-1} could correspond either to the stretching vibration of the C–N bond between the methyl group and the nitrogen atom or to methyl deformation vibrations. The bands at 1496 and 1605 cm^{-1} would correspond to the formal carbonyl vibration and the C–N stretching mode, respectively. Compared to the spectrum of NMA^- , the considerable red-shift of the C=O vibration ($\Delta\nu = 138 \text{ cm}^{-1}$) towards wavenumbers characteristic for double bonds is associated with delocalization of the non-bonding electrons from the nitrogen atom towards the carbonyl carbon atom and the π -electrons from the carbonyl function towards the iron center. This is also reflected in the Mulliken charge and spin distribution and can be visualized in the form of the resonance structures.

3. Dinuclear Iron Complexes

Fe_{di1} of formula $[\text{Fe}_2(\text{NMA})_5]^+$, possesses an octahedral geometry around each iron center (Scheme S2). The structure was optimized with a +1 total charge. For all calculations on di-iron complexes, a high spin state was considered ($S = 10/2$). B3LYP method and cc-pVTZ basis set (organic part) and SDD basis set and pseudo potential (Fe) were used for these calculations.



Scheme S2

Table S14. DFT computed vibrational frequencies (cm^{-1}) and band assignments for the di-iron complex **Fe_{di}** of formula $[\text{Fe}_2(\text{NMA})_5]^+$.

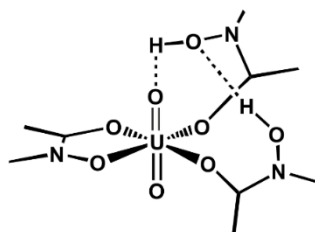
Frequency (cm^{-1})	Attribution
976–992	Rocking CH_3 (-C) + NO & CO stretch + symmetric rocking
1031–1033	Rocking CH_3 (-N) + NO stretch + anti-symmetric rocking
1041–1051	Rocking out-of-plane CH_3 (-C)
1136–1146	Rocking out-of-plane CH_3 (-N)
1179–1188	Symmetric Rocking CH_3 + stretching $\text{C}_{\text{CH}_3}\text{C}$ + deformation OCNO
1224–1232	Stretching $\text{C}_{\text{CH}_3}\text{N}$
1391–1395	Umbrella CH_3 (-C)
1436–1438	Umbrella CH_3 (-N)
1449–1453	Scissoring CH_3 (-C) + anti-symmetric scissoring
1456–1459	Twist CH_3 (-N) + symmetric twist
1473–1474	Scissoring CH_3 (-N) + symmetric scissoring
1475–1483	Twist CH_3 (-C) + anti-symmetric twist
1507–1519	Stretching CO
1570–1576	Stretching CN
1586–1605	Stretching CO & CN

4. Uranium Complexes

The characteristic IR active $\text{O}=\text{U}=\text{O}$ antisymmetric stretching mode (ν_{as}) is observed by IRMPD at 944 cm^{-1} for the $[\text{UO}_2(\text{NMA})(\text{NMAH})_2]^+$ cation. This vibration received particular attention in the literature because its frequency is directly related to the binding strength of the ligands to uranium.⁴ Lower wavenumbers reflect weaker and thus longer $\text{U}=\text{O}$ bonds, as a result of an increased electron density on the uranium atom donated by the equatorial ligands.⁵ For instance, this vibration is observed in the gas phase at 988 cm^{-1} for $[\text{UO}_2(\text{acetone})_4]^6$ and at 949 cm^{-1} for $[\text{UO}_2(\text{NO}_3)_3]^-$.⁷ Interestingly, the value of 944 cm^{-1} determined herein for $[\text{UO}_2(\text{NMA})(\text{NMAH})_2]^+$ in vacuum falls relatively close to the wavenumbers found by ATR-FTMIR for the crystalline $[\text{UO}_2(\text{NO}_3)_2(\text{H}_2\text{O})_2] \cdot 4\text{H}_2\text{O}$ salt ($\nu_{\text{as}} =$

941 cm^{-1} ; $\text{U}=\text{O} = 1.75(2) \text{ \AA}$) and the genuine $[\text{UO}_2(\text{NMA})(\text{NO}_3)(\text{H}_2\text{O})_2]$ complex ($\nu_{\text{as}} = 934 \text{ cm}^{-1}$; $\text{U}=\text{O} = 1.770(3) \text{ \AA}$).^{2c} In the latter species, the uranyl cation is five-coordinate and bound to a bidentate NMA^- ligand, a monodentate NO_3^- anion, and two water molecules. In spite of different coordination numbers, the similar ν_{as} values suggest equivalent equatorial ligand field strengths in both species as well as comparable $\text{U}=\text{O}$ distances (vide infra). In turn, the bischelated $[\text{UO}_2(\text{NMA})_2(\text{H}_2\text{O})]$ complex evidences in the crystal state a much stronger equatorial ligand field ($\nu_{\text{as}} = 896 \text{ cm}^{-1}$) resulting in a substantial elongation of the $\text{U}=\text{O}$ distance ($1.785(4) \text{ \AA}$).^{2c}

The model structure **U1** of $[\text{UO}_2(\text{NMA})(\text{NMAH})_2]^+$ has been optimized by imposing an octahedral geometry around uranium (Scheme S3) and a +1 total charge in singlet spin state. B3LYP method with cc-pVTZ basis set (organic part) and SDD basis set and pseudo potential (U) were used for these calculations. The calculated vibration energy for the $\text{O}=\text{U}=\text{O}$ antisymmetric stretching ($\nu_{\text{as}} = 933 \text{ cm}^{-1}$, Table S15) reproduced fairly well the experimental value of 944 cm^{-1} .



Scheme S3

Table S15. DFT computed vibrational frequencies (cm^{-1}) and band assignments for the uranium complex **U₁** of formula $[\text{UO}_2(\text{NMA})(\text{NMAH})_2]^+$.

Frequency (cm^{-1})	Attribution
933	O=U=O anti-symmetric stretching
968 ; 975 ; 979	Rocking CH_3 (-C) + NO & CO stretch + symmetric rocking
1024 ; 1030 ; 1036	Rocking CH_3 (-N) + NO stretch + anti-symmetric rocking
1043 ; 1044 ; 1047	Rocking out-of-plane CH_3 (-C)
1132 ; 1133 ; 1136	Rocking out-of-plane CH_3 (-N)
1150 ; 1164 ; 1173	Symmetric rocking CH_3 + deformation OCNO
1191 ; 1201 ; 1223	Stretching $\text{C}_{\text{CH}_3}\text{N}$
1380-1398	Umbrella CH_3 (-C)
1425-1434	Umbrella CH_3 (-N)
1437-1445	Scissoring CH_3 (-C)
1447 ; 1450 ; 1460	Twist CH_3 (-N) + symmetric twist
1468 ; 1469 ; 1469	Twist CH_3 (-C) + anti-symmetric twist
1475 ; 1506 ; 1513	CO stretch
1595	CN stretch
1609 ; 1631	CN & CO stretching

VI. Mulliken Charge Distributions

Computed Mulliken charges for NMAH, unbound NMA^- , and NMA^- ligand in the $\text{Fe}_{\text{mono}2}$ complex are collected in Table S16.

Table S16. Mulliken charge distribution in NMAH, NMA^- , and NMA^- ligand in the $\text{Fe}_{\text{mono}2}$ complex.

Atom	NMAH	NMA^-	$\text{Fe}_{\text{mono}2}$
N	0.07	0.17	0.15
C (-N)	-0.17	-0.16	-0.16
O (-N)	-0.30	-0.63	-0.48
C	0.22	0.12	0.44
C (-C)	-0.31	-0.32	-0.28
O (-C)	-0.39	-0.46	-0.48
H (-C-N)	0.09	0.02	0.12
H (-C-N)	0.11	0.04	0.14
H (-C-N)	0.10	0.04	0.14
H (-C-C)	0.13	0.07	0.15
H (-C-C)	0.10	0.06	0.14
H (-C-C)	0.11	0.06	0.14
H (-O)	0.23	--	--

In neutral NMAH, oxygen atoms are non-equivalent but both are negatively charged. There is only a slight positive charge on the nitrogen atom, and a more positive charge on the carbon atom. In deprotonated NMA^- , oxygens are also non-equivalent but both are negatively charged. In contrast with NMAH, there is a more positive charge on the nitrogen atom than on the carbon atom. This change reflects the existence of a mesomeric structure in which a positive charge is located on the nitrogen atom and one negative charge on each oxygen atom.

Upon iron complexation in $\text{Fe}_{\text{mono}2}$, both oxygens are almost equivalent and negatively charged. The carbon atom bears a higher positive charge, reflecting the existence of a mesomeric structure where it bears a formal positive charge and each oxygen a negative charge (simultaneously with a loss of double bond character of CO bond observed in IR spectra). The charge on the nitrogen atom is slightly lower than the one in NMA^- , reflecting a higher weight of the mesomeric structure with a CN double bond (simultaneously with increased CN frequencies upon complexation).

VII. Geometries

Table S17. Comparison of DFT-calculated bond distances (Å) for *N*-methylacetohydroxamic acid (NMAH), the free conjugated base NMA[−] and its iron(III) and uranium(VI) complexes [Fe(NMA)₂]⁺ (**Fe_{mono1}**), [Fe₂(NMA)₅]⁺ (**Fe_{di1}**), and [UO₂(NMA)(NMAH)₂]⁺ (**U₁**).

Bond (Å)	NMAH	NMA [−]	Fe_{mono1}	Fe_{di1}	U₁	
					NMA [−]	NMAH
M–O _N			1.82	1.94–2.06	2.25	
M–O _C			1.87		2.35	2.36 / 2.39
U=O					1.79 (H-bond side) 1.77 (opposite side)	
C=O	1.23	1.25	1.29	1.27	1.27	1.27 / 1.25
C–N	1.35	1.34	1.31	1.32	1.32	1.32 / 1.33
N–O	1.40	1.34	1.37	1.36–1.38	1.37	1.39 / 1.39
C–C _{Me}	1.51	1.54	1.49	1.50	1.50	1.50 / 1.50
N–C _{Me}	1.44	1.45	1.45	1.45	1.45	1.45 / 1.45
C–H	1.09	1.09	1.09	1.09	1.09	1.09 / 1.09
O–H	0.98					0.98 / 0.98

VIII. NBO Analysis

Results of the NBO analysis for both mononuclear **Fe_{mono2}** and **U₁** structures are reported in Table S18, while those corresponding to the dimeric iron complex (**Fe_{di1}**) are gathered in Table S19. In both tables, the bonds between the heavy (iron or uranium) and oxygen atoms are highlighted in red.

Table S18. NBO analysis for each oxygen atom bound to the metal center in **Fe_{mono2}** and **U₁**.

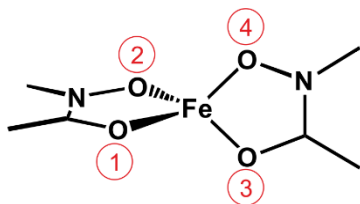
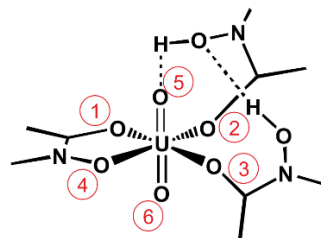
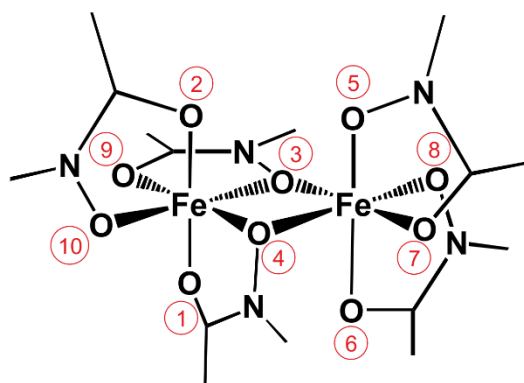
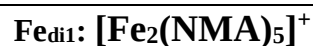
Fe _{mono2} : [Fe(NMA) ₂] ⁺				U ₁ : [UO ₂ (NMA)(NMAH) ₂] ⁺			
							
Atom	Type	Occupation	Composition	Atom	Type	Occupation	Composition
O1	O–Fe	0.96633	(86%O)14% <i>s</i> _O , 86% <i>p</i> _O , (14%Fe)15% <i>s</i> _{Fe} , 31% <i>p</i> _{Fe} , 54% <i>d</i> _{Fe}	O1	O–U	0.97479	(89%O)30% <i>s</i> _O , 70% <i>p</i> _O , (11%U)14% <i>s</i> _U , 18% <i>p</i> _U , 42% <i>d</i> _U , 26% <i>f</i> _U
	O–C	0.99326	(65%O)36% <i>s</i> _O , 64 <i>p</i> _O , (35%C)30% <i>s</i> _C , 70% <i>p</i> _C	O–C	0.99354	(65%O)33% <i>s</i> _O , 67% <i>p</i> _O , (35%C)31% <i>s</i> _C , 69% <i>p</i> _C	
	LP	0.96222	51% <i>s</i> _O , 49% <i>p</i> _O	O–C	0.97680	(80%O)0% <i>s</i> _O , 100% <i>p</i> _O , (20%C)0% <i>s</i> _C , 100% <i>p</i> _C	
	LP	0.81906	0% <i>s</i> _O , 100% <i>p</i> _O	LP	0.95336	37% <i>s</i> _O , 63% <i>p</i> _O	
O2	O–Fe	0.97703	(84%O)15% <i>s</i> _O , 85% <i>p</i> _O , (16%Fe)15% <i>s</i> _{Fe} , 19% <i>p</i> _{Fe} , 66% <i>d</i> _{Fe}	O2	O–C	0.99515	(65%O)37% <i>s</i> _O , 63% <i>p</i> _O , (35%C)31% <i>s</i> _C , 69% <i>p</i> _C
	O–Fe	0.94604	(86%O)0% <i>s</i> _O , 100% <i>p</i> _O , (14%Fe)0% <i>s</i> _{Fe} , 38% <i>p</i> _{Fe} , 62% <i>d</i> _{Fe}	O–C	0.96876	(80%O)3% <i>s</i> _O , 97 <i>p</i> _O , (20%C)0% <i>s</i> _C , 100% <i>p</i> _C	
	O–N	0.99158	(53%O)21% <i>s</i> _O , 79 <i>p</i> _O , (47%N)24% <i>s</i> _N , 76% <i>p</i> _N	LP	0.92654	16% <i>s</i> _O , 84% <i>p</i> _O	
	LP	0.96636	64% <i>s</i> _O , 36% <i>p</i> _O	LP	0.90665	45% <i>s</i> _O , 55% <i>p</i> _O	
O3	O–Fe	0.97703	(83%O)15% <i>s</i> _O , 85% <i>p</i> _O , (17%Fe)15% <i>s</i> _{Fe} , 19% <i>p</i> _{Fe} , 66% <i>d</i> _{Fe}	O3	O–U	0.97945	(91%O)38% <i>s</i> _O , 62% <i>p</i> _O , (9%U)11% <i>s</i> _U , 20% <i>p</i> _U , 38% <i>d</i> _U , 31% <i>f</i> _U
	O–Fe	0.94604	(86%O)0% <i>s</i> _O , 100% <i>p</i> _O , (14%Fe)0% <i>s</i> _{Fe} , 38% <i>p</i> _{Fe} , 62% <i>d</i> _{Fe}	O–C	0.99559	(65%O)37% <i>s</i> _O , 63% <i>p</i> _O , (35%C)32% <i>s</i> _C , 68% <i>p</i> _C	
	O _N	0.99158	(53%O)21% <i>s</i> _O , 79 <i>p</i> _O , (47%N)24% <i>s</i> _N , 76% <i>p</i> _N	O–C	0.97774	(79%O)0% <i>s</i> _O , 100% <i>p</i> _O , (21%C)0% <i>s</i> _C , 100% <i>p</i> _C	
	LP	0.96636	64% <i>s</i> _O , 36% <i>p</i> _O	LP	0.94073	25% <i>s</i> _O , 75% <i>p</i> _O	
O4	O–Fe	0.96633	(86%O)14% <i>s</i> _O , 86% <i>p</i> _O , (14%Fe)15% <i>s</i> _{Fe} , 31% <i>p</i> _{Fe} , 54% <i>d</i> _{Fe}	O4	O–U	0.98650	(87%O)37% <i>s</i> _O , 63% <i>p</i> _O , (13%U)14% <i>s</i> _U , 14% <i>p</i> _U , 40% <i>d</i> _U , 32% <i>f</i> _U
	O–C	0.99326	(65%O)36% <i>s</i> _O , 64 <i>p</i> _O , (35%C)30% <i>s</i> _C , 70% <i>p</i> _C	O–N	0.99159	(53%O)20% <i>s</i> _O , 80% <i>p</i> _O , (47%N)25% <i>s</i> _N , 75% <i>p</i> _N	
	LP	0.96222	51% <i>s</i> _O , 49% <i>p</i> _O	LP	0.95582	44% <i>s</i> _O , 56% <i>p</i> _O	
	LP	0.81906	0% <i>s</i> _O , 100% <i>p</i> _O	LP	0.90462	0% <i>s</i> _O , 100% <i>p</i> _O	
				O5	O–U	0.99358	(80%O)0% <i>s</i> _O , 100% <i>p</i> _O , (20%U)0% <i>s</i> _U , 1% <i>p</i> _U , 50% <i>d</i> _U , 49% <i>f</i> _U
				O–U	0.97561	(78%O)17% <i>s</i> _O , 83% <i>p</i> _O , (22%U)1% <i>s</i> _U , 1% <i>p</i> _U , 49% <i>d</i> _U , 49% <i>f</i> _U	
				O–U	0.96384	(80%O)10% <i>s</i> _O , 90% <i>p</i> _O , (20%U)2% <i>s</i> _U , 3% <i>p</i> _U , 46% <i>d</i> _U , 49% <i>f</i> _U	
				LP	0.93085	26% <i>s</i> _O , 74% <i>p</i> _O	
				O6	O–U	0.99308	(79%O)0% <i>s</i> _O , 100% <i>p</i> _O , (21%U)0% <i>s</i> _U , 1% <i>p</i> _U , 49% <i>d</i> _U , 50% <i>f</i> _U
				O–U	0.98836	(79%O)0% <i>s</i> _O , 100% <i>p</i> _O , (21%U)0% <i>s</i> _U , 4% <i>p</i> _U , 48% <i>d</i> _U , 48% <i>f</i> _U	
				O–U	0.94849	(76%O)24% <i>s</i> _O , 76% <i>p</i> _O , (24%U)3% <i>s</i> _U , 1% <i>p</i> _U , 47% <i>d</i> _U , 49% <i>f</i> _U	
				LP	0.92979	24% <i>s</i> _O , 76% <i>p</i> _O	

Table S19. NBO analysis for each oxygen atom bound to an iron center in the **Fe_{di1}** cation.

Atom	type	Occupation	Composition
O1	O-Fe	0.96516	(87%O) 20% _{sO} , 80% _{pO} , (13%Fe) 16% _{sFe} , 37% _{pFe} , 47% _{dFe}
	OC	0.99313	(65%O) 35% _{sO} , 65% _{pO} , (35%C) 32% _{sC} , 68% _{pC}
	LP	0.95974	36% _{sO} , 64% _{pO}
	LP	0.80445	0% _{sO} , 100% _{pO}
O2	O-Fe	0.96572	(87%O) 19% _{sO} , 81% _{pO} , (13%Fe) 16% _{sFe} , 38% _{pFe} , 46% _{dFe}
	OC	0.99376	(64%O) 35% _{sO} , 65% _{pO} , (36%C) 31% _{sC} , 69% _{pC}
	OC	0.96668	(76%O) 0% _{sO} , 100% _{pO} , (24%C) 0% _{sC} , 100% _{pC}
	LP	0.96536	46% _{sO} , 54% _{pO}
O3	O-Fe	0.96916	(89%O) 36% _{sO} , 64% _{pO} , (11%Fe) 15% _{sU} , 43% _{pFe} , 42% _{dFe}
	ON	0.99218	(55%O) 26% _{sO} , 74% _{pO} , (45%N) 24% _{sN} , 76% _{pN}
	ON	0.91883	(73%O) 14% _{sO} , 86% _{pO} , (27%N) 0% _{sN} , 100% _{pN}
	ON*	0.72188	(27%O) 14% _{sO} , 86% _{pO} , (73%N) 0% _{sN} , 100% _{pN}
O4	LP	0.90439	25% _{sO} , 75% _{pO}
	O-Fe	0.96956	(88%O) 21% _{sO} , 79% _{pO} , (12%Fe) 16% _{sFe} , 39% _{pFe} , 45% _{dFe}
	O-Fe	0.95053	(89%O) 15% _{sO} , 85% _{pO} , (11%Fe) 14% _{sFe} , 45% _{pFe} , 41% _{dFe}
	ON	0.99141	(53%O) 21% _{sO} , 79% _{pO} , (47%N) 25% _{sN} , 75% _{pN}
O5	LP	0.94907	44% _{sO} , 56% _{pO}
	O-Fe	0.97535	(85%O) 26% _{sO} , 74% _{pO} , (15%Fe) 16% _{sFe} , 39% _{pFe} , 45% _{dFe}
	O-Fe	0.95191	(85%O) 0% _{sO} , 100% _{pO} , (15%Fe) 0% _{sFe} , 21% _{pFe} , 79% _{dFe}
	ON	0.99099	(52%O) 20% _{sO} , 80% _{pO} , (48%N) 26% _{sN} , 74% _{pN}
O6	LP	0.96406	55% _{sO} , 45% _{pO}
	O-Fe	0.96650	(88%O) 22% _{sO} , 78% _{pO} , (12%Fe) 16% _{sFe} , 45% _{pFe} , 39% _{dFe}
	OC	0.99377	(65%O) 35% _{sO} , 65% _{pO} , (35%C) 32% _{sC} , 68% _{pC}
	OC	0.96972	(77%O) 0% _{sO} , 100% _{pO} , (23%C) 0% _{sC} , 100% _{pC}
O7	LP	0.96471	44% _{sO} , 56% _{pO}
	O-Fe	0.97291	(86%O) 20% _{sO} , 80% _{pO} , (14%Fe) 25% _{sFe} , 21% _{pFe} , 54% _{dFe}
	ON*	0.93932	(56%O) 0% _{sO} , 100% _{pO} , (44%N) 0% _{sN} , 100% _{pN}
	ON	0.63301	(44%O) 0% _{sO} , 100% _{pO} , (56%N) 0% _{sN} , 100% _{pN}
O8	OC	0.99360	(64%O) 35% _{sO} , 65% _{pO} , (36%C) 32% _{sC} , 68% _{pC}
	LP	0.96485	45% _{sO} , 55% _{pO}
	O-Fe	0.97763	(85%O) 25% _{sO} , 75% _{pO} , (15%Fe) 16% _{sFe} , 36% _{pFe} , 48% _{dFe}
	O-Fe	0.95690	(87%O) 0% _{sO} , 100% _{pO} , (13%Fe) 0% _{sFe} , 11% _{pFe} , 89% _{dFe}
O9	ON	0.99153	(52%O) 20% _{sO} , 80% _{pO} , (48%N) 25% _{sN} , 75% _{pN}
	LP	0.96733	55% _{sO} , 45% _{pO}
	O-Fe	0.96678	(86%O) 20% _{sO} , 80% _{pO} , (14%Fe) 18% _{sFe} , 39% _{pFe} , 43% _{dFe}
	OC	0.97034	(77%O) 0% _{sO} , 100% _{pO} , (23%C) 0% _{sC} , 100% _{pC}
O10	LP	0.96142	45% _{sO} , 55% _{pO}
	O-Fe	0.97637	(85%O) 25% _{sO} , 75% _{pO} , (15%U) 17% _{sFe} , 33% _{pFe} , 50% _{dFe}
	O-Fe	0.95301	(84%Fe) 0% _{sO} , 100% _{pO} , (16%U) 0% _{sFe} , 24% _{pFe} , 76% _{dFe}
	ON	0.99156	(52%O) 20% _{sO} , 80% _{pO} , (48%N) 26% _{sN} , 74% _{pN}
O10	LP	0.96596	55% _{sO} , 45% _{pO}

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