

Molecular Fe(III) Phosphonates: Synthesis, Structure, Magnetism and Mössbauer Studies

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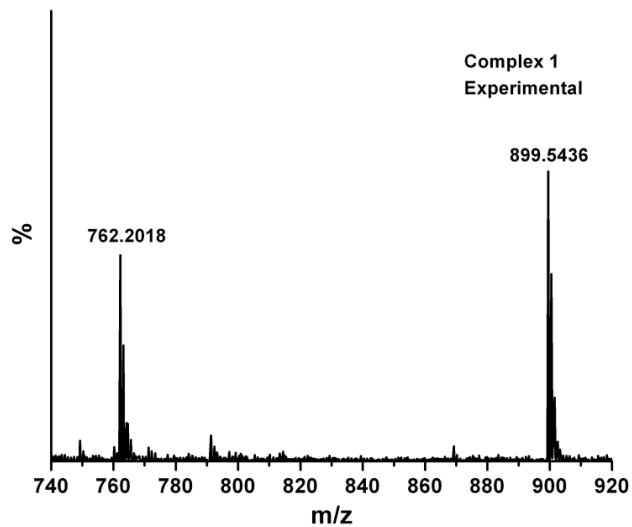


Figure S1: ESI-MS spectra of **1** (Experimental).

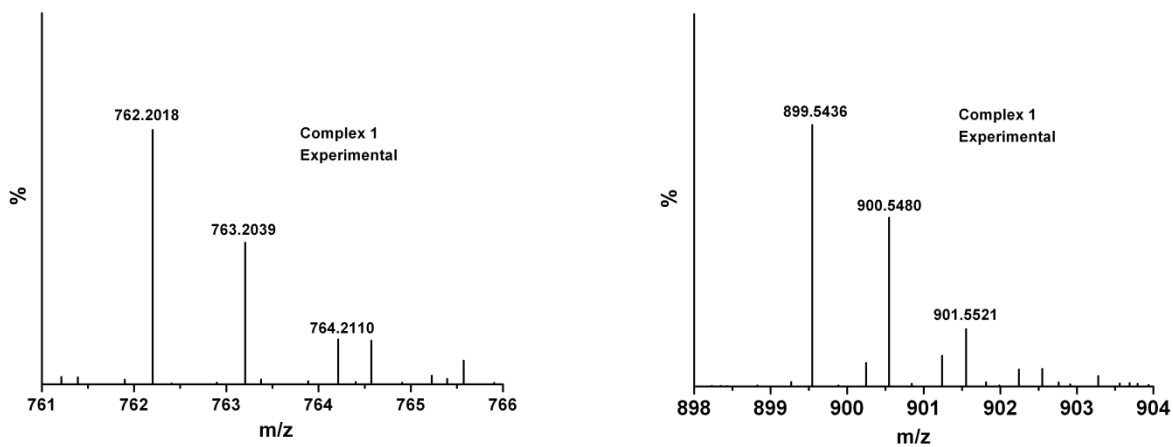


Figure S2: ESI-MS spectra of **1** (Experimental) isotopic distribution pattern

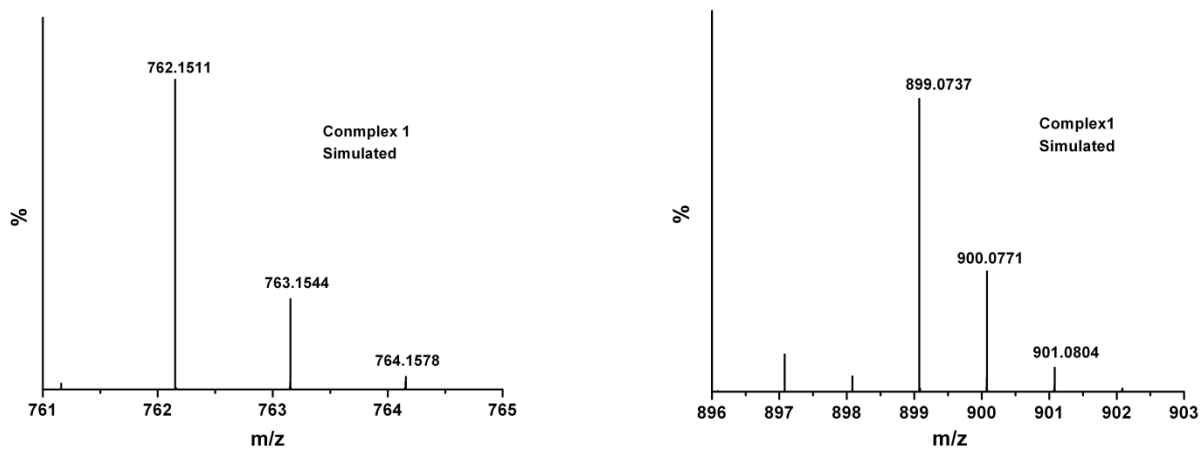


Figure S3: ESI-MS spectra of **1** (Simulated)

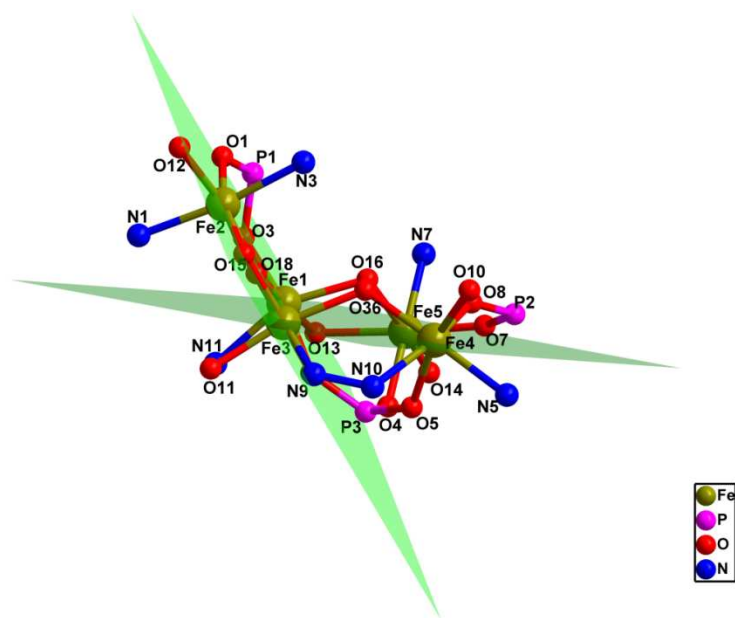


Figure S4: Mean plane of complex **2**

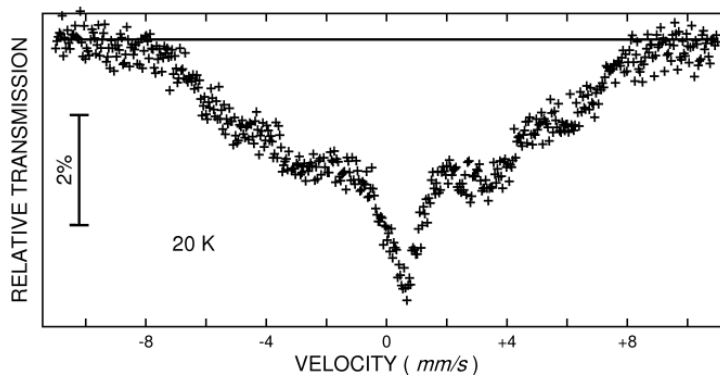


Figure S5: Mössbauer spectrum of compound **2** at 20 K.

Table S1. BVS calculation of compound **2**

Atoms name	Bond length	r_0	B	s	Assigned
Fe1-O18	1.866(5)	1.759	0.37	0.748	
Fe2-O18	1.914(5)	1.759	0.37	0.657	
Fe3-O18	1.950(5)	1.759	0.37	0.596	
				2.001	O ²⁻
Fe3-O36	1.992(4)	1.759	0.37	0.532	
Fe4-O36	1.962(5)	1.759	0.37	0.577	
				1.019	HO ⁻
Fe1-O16	2.008(5)	1.759	0.37	0.576	
Fe5-O16	1.963(4)	1.759	0.37	0.510	
				1.086	HO ⁻

Table S2: Coordination environment, τ (degree of trigonality) values for complex **1**

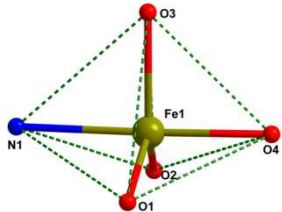
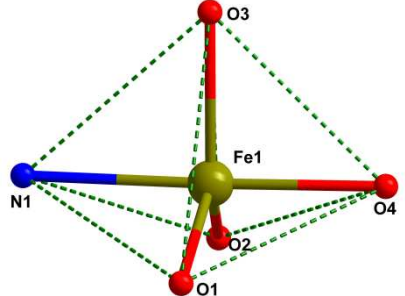
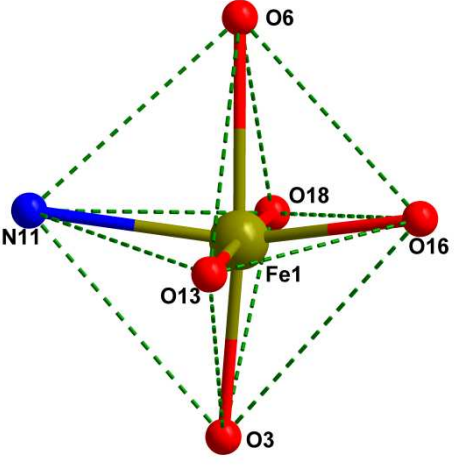
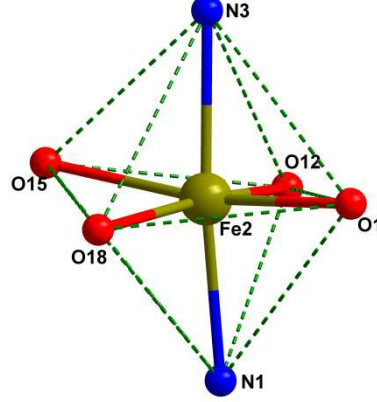
Coordination environment around metal ion	Atom Lable	Coordination Environment	Value of τ^{22}
 <p>Complex 1 : Distorted square pyramidal</p>	Fe(1)	1N 4O	0.88

Table S3: Coordination geometry, bond distances (Å) and bond angles(°) of complexes **1** and **2**

Coordination environment around metal ion	Bond lengths(Å)	Bond angles(°)
 <p>Complex 1 : Distorted square pyramidal</p>	Fe(1)-O(1) 1.856(3) Fe(1)-O(2) 1.900(3) Fe(1)-O(3) 1.945(3) Fe(1)-O(4) 1.956(3) Fe(1)-N(1) 2.093(4)	O(1)-Fe(1)-O(2) 124.26(15) O(1)-Fe(1)-O(3) 113.87(15) O(2)-Fe(1)-O(3) 121.31(14) O(1)-Fe(1)-O(4) 94.29(15) O(2)-Fe(1)-O(4) 93.40(13) O(3)-Fe(1)-O(4) 89.65(14) O(1)-Fe(1)-N(1) 85.10(16) O(2)-Fe(1)-N(1) 88.86(15) O(3)-Fe(1)-N(1) 88.47(15) O(4)-Fe(1)-N(1) 177.59(16)

 <p>Complex 2 : Distorted octahedral</p>	<p>Fe(1)-O(18) 1.866(5) Fe(1)-O(16) 1.963(4) Fe(1)-O(3) 1.979(5) Fe(1)-O(13) 2.030(5) Fe(1)-N(11) 2.102(6) Fe(1)-O(6) 2.206(5)</p>	<p>O(18)-Fe(1)-O(16) 101.9(2) O(18)-Fe(1)-O(3) 89.6(2) O(16)-Fe(1)-O(3) 104.1(2) O(18)-Fe(1)-O(13) 177.9(2) O(16)-Fe(1)-O(13) 76.64(19) O(3)-Fe(1)-O(13) 89.3(2) O(18)-Fe(1)-N(11) 98.8(2) O(16)-Fe(1)-N(11) 152.9(2) O(3)-Fe(1)-N(11) 93.3(2) O(13)-Fe(1)-N(11) 83.1(2) O(18)-Fe(1)-O(6) 78.01(19) O(16)-Fe(1)-O(6) 85.17(18) O(3)-Fe(1)-O(6) 165.92(19) O(13)-Fe(1)-O(6) 103.37(18) N(11)-Fe(1)-O(6) 82.2(2)</p>
 <p>Complex 2 : Distorted octahedral</p>	<p>Fe(2)-O(18) 1.914(5) Fe(2)-O(12) 1.967(5) Fe(2)-O(1) 1.986(5) Fe(2)-O(15) 2.044(5) Fe(2)-N(1) 2.079(5) Fe(2)-N(3) 2.122(6)</p>	<p>O(18)-Fe(2)-O(12) 166.0(2) O(18)-Fe(2)-O(1) 94.9(2) O(12)-Fe(2)-O(1) 97.1(2) O(18)-Fe(2)-O(15) 78.60(19) O(12)-Fe(2)-O(15) 91.0(2) O(1)-Fe(2)-O(15) 166.83(18) O(18)-Fe(2)-N(1) 90.0(2) O(12)-Fe(2)-N(1) 82.9(2) O(1)-Fe(2)-N(1) 90.2(2) O(15)-Fe(2)-N(1) 101.1(2) O(18)-Fe(2)-N(3) 97.8(2) O(12)-Fe(2)-N(3) 89.5(2) O(1)-Fe(2)-N(3) 89.1(2) O(15)-Fe(2)-N(3) 80.6(2) N(1)-Fe(2)-N(3) 172.1(2)</p>

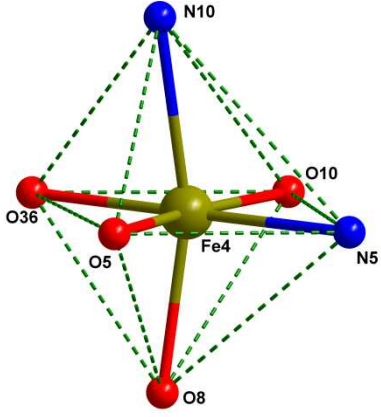
 <p>Complex 2 : Distorted octahedral</p>	<p>Fe(4)-O(10) 1.898(5) Fe(4)-O(36) 1.962(5) Fe(4)-O(8) 2.005(5) Fe(4)-O(5) 2.043(5) Fe(4)-N(5) 2.087(5) Fe(4)-N(10) 2.208(6)</p>	<p>O(10)-Fe(4)-O(36) 96.3(2) O(10)-Fe(4)-O(8) 97.0(2) O(36)-Fe(4)-O(8) 87.1(2) O(10)-Fe(4)-O(5) 166.6(2) O(36)-Fe(4)-O(5) 97.0(2) O(8)-Fe(4)-O(5) 85.43(19) O(10)-Fe(4)-N(5) 84.6(2) O(36)-Fe(4)-N(5) 179.0(2) O(8)-Fe(4)-N(5) 93.3(2) O(5)-Fe(4)-N(5) 82.1(2) O(10)-Fe(4)-N(10) 97.3(2) O(36)-Fe(4)-N(10) 83.0(2) O(8)-Fe(4)-N(10) 163.4(2) O(5)-Fe(4)-N(10) 82.6(2) N(5)-Fe(4)-N(10) 96.4(2)</p>
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Table S4. Bond lengths [\AA] found in **1**.

Fe(1)-O(1)	1.856(3)	P(1)-O(3)	1.543(4)
Fe(1)-O(2)	1.900(3)	P(1)-C(16)	1.820(5)
Fe(1)-O(3)	1.945(3)	O(2)-P(1)#2	1.523(3)
Fe(1)-O(4)#1	1.956(3)	O(1)-C(1)	1.349(6)
Fe(1)-N(1)	2.093(4)	O(4)-Fe(1)#2	1.956(3)
P(1)-O(4)	1.519(3)	N(1)-N(2)	1.344(6)
P(1)-O(2)#1	1.523(3)		

Table S5. Bond angles [$^\circ$] found in **1**.

O(1)-Fe(1)-O(2)	124.26(15)	O(4)-P(1)-O(3)	109.41(19)
O(1)-Fe(1)-O(3)	113.87(15)	O(2)#1-P(1)-O(3)	110.20(18)
O(2)-Fe(1)-O(3)	121.31(14)	O(4)-P(1)-C(16)	108.4(2)

O(1)-Fe(1)-O(4)#1	94.29(15)	O(2)#1-P(1)-C(16)	107.5(2)
O(2)-Fe(1)-O(4)#1	93.40(13)	O(3)-P(1)-C(16)	108.0(2)
O(3)-Fe(1)-O(4)#1	89.65(14)	P(1)#2-O(2)-Fe(1)	155.3(2)
O(1)-Fe(1)-N(1)	85.10(16)	P(1)-O(3)-Fe(1)	126.1(2)
O(2)-Fe(1)-N(1)	88.86(15)	C(1)-O(1)-Fe(1)	137.4(3)
O(3)-Fe(1)-N(1)	88.47(15)	P(1)-O(4)-Fe(1)#2	143.1(2)
O(4)#1-Fe(1)-N(1)	177.59(16)	N(2)-N(1)-C(7)	106.2(4)
O(4)-P(1)-O(2)#1	113.25(18)	N(2)-N(1)-Fe(1)	123.7(3)

Table S6. Bond lengths [\AA] found in **2**.

Fe(1)-O(18)	1.866(5)	Fe(4)-O(8)	2.005(5)
Fe(1)-O(16)	1.963(4)	Fe(4)-O(5)	2.043(5)
Fe(1)-O(3)	1.979(5)	Fe(4)-N(5)	2.087(5)
Fe(1)-O(13)	2.030(5)	Fe(4)-N(10)	2.208(6)
Fe(1)-N(11)	2.102(6)	Fe(5)-O(14)	1.910(5)
Fe(1)-O(6)	2.206(5)	Fe(5)-O(7)	1.964(5)
Fe(2)-O(18)	1.914(5)	Fe(5)-O(16)	2.008(5)
Fe(2)-O(12)	1.967(5)	Fe(5)-O(4)	2.053(5)
Fe(2)-O(1)	1.986(5)	Fe(5)-O(13)	2.083(4)
Fe(2)-O(15)	2.044(5)	Fe(5)-N(7)	2.116(6)
Fe(2)-N(1)	2.079(5)	P(1)-O(2)	1.492(5)
Fe(2)-N(3)	2.122(6)	P(1)-O(1)	1.520(5)
Fe(3)-O(11)	1.948(5)	P(1)-O(3)	1.524(5)
Fe(3)-O(18)	1.950(5)	P(2)-O(9)	1.499(5)
Fe(3)-O(36)	1.992(4)	P(2)-O(8)	1.510(5)
Fe(3)-O(15)	2.039(5)	P(2)-O(7)	1.520(5)
Fe(3)-N(9)	2.050(6)	P(3)-O(4)	1.498(5)
Fe(3)-O(6)	2.125(5)	P(3)-O(5)	1.516(5)
Fe(4)-O(10)	1.898(5)	P(3)-O(6)	1.534(5)
Fe(4)-O(36)	1.962(5)		

Table S7. Bond angles [°] found in **2**.

O(18)-Fe(1)-O(16)	101.9(2)	O(7)-Fe(5)-N(7)	88.9(2)
O(18)-Fe(1)-O(3)	89.6(2)	O(16)-Fe(5)-N(7)	88.2(2)
O(16)-Fe(1)-O(3)	104.1(2)	O(4)-Fe(5)-N(7)	179.8(2)
O(18)-Fe(1)-O(13)	177.9(2)	O(13)-Fe(5)-N(7)	95.4(2)
O(16)-Fe(1)-O(13)	76.64(19)	O(2)-P(1)-O(1)	112.3(3)
O(3)-Fe(1)-O(13)	89.3(2)	O(2)-P(1)-O(3)	115.7(3)
O(18)-Fe(1)-N(11)	98.8(2)	O(1)-P(1)-O(3)	113.7(3)
O(16)-Fe(1)-N(11)	152.9(2)	O(2)-P(1)-C(106)	108.1(3)
O(3)-Fe(1)-N(11)	93.3(2)	O(1)-P(1)-C(106)	104.5(3)
O(13)-Fe(1)-N(11)	83.1(2)	O(3)-P(1)-C(106)	101.1(3)
O(18)-Fe(1)-O(6)	78.01(19)	O(9)-P(2)-O(8)	116.8(3)
O(16)-Fe(1)-O(6)	85.17(18)	O(9)-P(2)-O(7)	112.9(3)
O(3)-Fe(1)-O(6)	165.92(19)	O(8)-P(2)-O(7)	113.4(3)
O(13)-Fe(1)-O(6)	103.37(18)	O(9)-P(2)-C(105)	106.0(3)
N(11)-Fe(1)-O(6)	82.2(2)	O(8)-P(2)-C(105)	101.4(3)
O(18)-Fe(2)-O(12)	166.0(2)	O(7)-P(2)-C(105)	104.4(3)
O(18)-Fe(2)-O(1)	94.9(2)	O(4)-P(3)-O(5)	116.2(3)
O(12)-Fe(2)-O(1)	97.1(2)	O(4)-P(3)-O(6)	113.0(3)
O(18)-Fe(2)-O(15)	78.60(19)	O(5)-P(3)-O(6)	112.7(3)
O(12)-Fe(2)-O(15)	91.0(2)	O(4)-P(3)-C(107)	106.9(3)
O(1)-Fe(2)-O(15)	166.83(18)	O(5)-P(3)-C(107)	102.1(3)
O(18)-Fe(2)-N(1)	90.0(2)	O(6)-P(3)-C(107)	104.4(3)
O(12)-Fe(2)-N(1)	82.9(2)	P(1)-O(1)-Fe(2)	126.0(3)
O(1)-Fe(2)-N(1)	90.2(2)	P(1)-O(3)-Fe(1)	121.8(3)
O(15)-Fe(2)-N(1)	101.1(2)	P(3)-O(4)-Fe(5)	128.9(3)
O(18)-Fe(2)-N(3)	97.8(2)	P(3)-O(5)-Fe(4)	132.0(3)
O(12)-Fe(2)-N(3)	89.5(2)	P(3)-O(6)-Fe(3)	133.0(3)
O(1)-Fe(2)-N(3)	89.1(2)	P(3)-O(6)-Fe(1)	121.1(3)
O(15)-Fe(2)-N(3)	80.6(2)	Fe(3)-O(6)-Fe(1)	92.63(18)
N(1)-Fe(2)-N(3)	172.1(2)	P(2)-O(7)-Fe(5)	140.5(3)
O(11)-Fe(3)-O(18)	93.7(2)	P(2)-O(8)-Fe(4)	142.5(3)
O(11)-Fe(3)-O(36)	168.9(2)	C(16)-O(10)-Fe(4)	134.8(5)
O(18)-Fe(3)-O(36)	96.07(19)	C(1)-O(11)-Fe(3)	123.5(4)
O(11)-Fe(3)-O(15)	91.18(19)	C(76)-O(12)-Fe(2)	127.8(4)

O(18)-Fe(3)-O(15)	77.92(19)	C(61)-O(13)-Fe(1)	125.7(4)
O(36)-Fe(3)-O(15)	96.01(19)	C(61)-O(13)-Fe(5)	134.5(4)
O(11)-Fe(3)-N(9)	87.5(2)	Fe(1)-O(13)-Fe(5)	99.0(2)
O(18)-Fe(3)-N(9)	178.6(2)	C(46)-O(14)-Fe(5)	125.8(4)
O(36)-Fe(3)-N(9)	82.7(2)	C(31)-O(15)-Fe(3)	129.3(4)
O(15)-Fe(3)-N(9)	102.8(2)	C(31)-O(15)-Fe(2)	123.3(4)
O(11)-Fe(3)-O(6)	89.58(19)	Fe(3)-O(15)-Fe(2)	97.8(2)
O(18)-Fe(3)-O(6)	78.31(19)	Fe(1)-O(16)-Fe(5)	103.9(2)
O(36)-Fe(3)-O(6)	87.22(19)	Fe(1)-O(18)-Fe(2)	142.8(3)
O(15)-Fe(3)-O(6)	156.21(18)	Fe(1)-O(18)-Fe(3)	110.4(2)
N(9)-Fe(3)-O(6)	101.0(2)	Fe(2)-O(18)-Fe(3)	105.5(2)
O(10)-Fe(4)-O(36)	96.3(2)	Fe(4)-O(36)-Fe(3)	122.0(2)
O(10)-Fe(4)-O(8)	97.0(2)	C(82)-N(1)-N(2)	106.8(6)
O(36)-Fe(4)-O(8)	87.1(2)	C(82)-N(1)-Fe(2)	130.6(5)
O(10)-Fe(4)-O(5)	166.6(2)	N(2)-N(1)-Fe(2)	122.6(5)
O(36)-Fe(4)-O(5)	97.0(2)	N(1)-N(2)-C(84)	111.1(6)
O(8)-Fe(4)-O(5)	85.43(19)	C(37)-N(3)-N(4)	107.3(6)
O(10)-Fe(4)-N(5)	84.6(2)	C(37)-N(3)-Fe(2)	127.4(5)
O(36)-Fe(4)-N(5)	179.0(2)	N(4)-N(3)-Fe(2)	125.4(5)
O(8)-Fe(4)-N(5)	93.3(2)	C(39)-N(4)-N(3)	110.2(6)
O(5)-Fe(4)-N(5)	82.1(2)	C(22)-N(5)-N(6)	107.0(6)
O(10)-Fe(4)-N(10)	97.3(2)	C(22)-N(5)-Fe(4)	129.9(5)
O(36)-Fe(4)-N(10)	83.0(2)	N(6)-N(5)-Fe(4)	122.5(4)
O(8)-Fe(4)-N(10)	163.4(2)	N(5)-N(6)-C(24)	111.1(6)
O(5)-Fe(4)-N(10)	82.6(2)	C(52)-N(7)-N(8)	106.5(6)
N(5)-Fe(4)-N(10)	96.4(2)	C(52)-N(7)-Fe(5)	121.3(5)
O(14)-Fe(5)-O(7)	96.3(2)	N(8)-N(7)-Fe(5)	129.7(5)
O(14)-Fe(5)-O(16)	167.0(2)	N(7)-N(8)-C(54)	110.4(6)
O(7)-Fe(5)-O(16)	94.3(2)	C(7)-N(9)-N(10)	108.9(6)
O(14)-Fe(5)-O(4)	95.3(2)	C(7)-N(9)-Fe(3)	125.3(5)
O(7)-Fe(5)-O(4)	90.95(19)	N(10)-N(9)-Fe(3)	124.3(4)
O(16)-Fe(5)-O(4)	92.0(2)	C(9)-N(10)-N(9)	106.7(5)
O(14)-Fe(5)-O(13)	95.5(2)	C(9)-N(10)-Fe(4)	137.8(5)
O(7)-Fe(5)-O(13)	167.7(2)	N(9)-N(10)-Fe(4)	114.4(4)
O(16)-Fe(5)-O(13)	74.46(18)	C(67)-N(11)-N(12)	107.0(6)

O(4)-Fe(5)-O(13)	84.70(18)	C(67)-N(11)-Fe(1)	126.8(5)
O(14)-Fe(5)-N(7)	84.5(2)	N(12)-N(11)-Fe(1)	124.9(5)