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New 3D metal–organic framework isomer containing trinuclear oxo-centered mixed valence iron

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Table of Contents

1. Supporting tables

Table S1 Crystal data and structure refinement of **2**.

Empirical formula	$C_{36}H_{18}Br_6Fe_3N_6O_{13}$
Space group	Pa-3
a (Å)	20.3708(6)
Refinement method	Full-matrix least-squares on F^2
Goodness-of-fit on F^2	1.058
Final R indices [I>4sigma(I)]	R1 = 0.0178, wR2 = 0.0449

* $R_1 = \Sigma||F_0|-|F_c|| / \Sigma|F_0|$, $wR_2 = [\Sigma(F_0^2 - F_c^2) / \Sigma w(F_0)^2]^{1/2}$

The Laue symmetry was determined to be m-3 in cubic crystal system for **2** and from the systematic absences noted the space group was shown unambiguously to be *P*a-3 for **2**. The sample crystal for **2** was significantly twinned, resulting in rather poor quality for higher angle data. Thus the integration was only carried out to 47 degrees two-theta. Since the overlap between twin domains was not too serious, the data were treated as if from a single crystal.

Table S2 Selected bond distances (Å) and angles (deg) for **2**.

Fe-O(5)	1.8962(4)	O(5)-Fe-N(2)	174.29(7)
Fe-O(1)	2.0309(19)	O(1)-Fe-N(2)	86.73(8)
Fe-O(3)#1	2.0523(19)	O(3)#1-Fe-N(2)	80.71(8)
Fe-O(2)#2	2.069(2)	O(2)#2-Fe-N(2)	82.84(8)
Fe-O(4)#3	2.1090(19)	O(4)#3-Fe-N(2)	85.75(8)
Fe-N(2)	2.229(2)	C(6)-O(1)-Fe	131.85(18)
Br(1)-C(4)	1.890(3)	C(6)-O(2)-Fe#4	129.09(18)
Br(2)-C(10)	1.887(3)	C(12)-O(3)-Fe#5	136.87(18)
O(1)-C(6)	1.261(3)	C(12)-O(4)-Fe#6	124.28(18)
O(2)-C(6)	1.263(3)	Fe#2-O(5)-Fe#4	119.90(1)
O(2)-Fe#4	2.069(2)	Fe#2-O(5)-Fe	119.90(1)
O(3)-C(12)	1.263(3)	Fe#4-O(5)-Fe	119.90(1)
O(3)-Fe#5	2.0523(19)	C(1)-N(1)-C(5)	116.9(3)
O(4)-C(12)	1.253(3)	C(7)-N(2)-C(11)	118.4(2)
O(4)-Fe#6	2.1091(19)	C(7)-N(2)-Fe	124.94(18)
O(5)-Fe#2	1.8961(4)	C(11)-N(2)-Fe	115.53(18)
O(5)-Fe#4	1.8962(4)	N(1)-C(1)-C(2)	124.0(3)
N(1)-C(1)	1.335(4)	C(1)-C(2)-C(3)	118.3(3)

N(1)-C(5)	1.337(4)	C(1)-C(2)-C(6)	122.3(3)
N(2)-C(7)	1.340(3)	C(3)-C(2)-C(6)	119.3(3)
N(2)-C(11)	1.341(4)	C(4)-C(3)-C(2)	118.0(3)
C(1)-C(2)	1.384(4)	C(3)-C(4)-C(5)	119.7(3)
C(2)-C(3)	1.391(4)	C(3)-C(4)-Br(1)	119.5(2)
C(2)-C(6)	1.496(4)	C(5)-C(4)-Br(1)	120.8(2)
C(3)-C(4)	1.377(4)	N(1)-C(5)-C(4)	122.9(3)
C(4)-C(5)	1.384(5)	O(1)-C(6)-O(2)	126.2(3)
C(7)-C(8)	1.393(4)	O(1)-C(6)-C(2)	116.5(2)
C(8)-C(9)	1.390(4)	O(2)-C(6)-C(2)	117.3(2)
C(8)-C(12)	1.508(4)	N(2)-C(7)-C(8)	122.8(3)
C(9)-C(10)	1.379(4)	C(9)-C(8)-C(7)	118.2(3)
C(10)-C(11)	1.381(4)	C(9)-C(8)-C(12)	119.8(2)
O(5)-Fe-O(1)	98.46(8)	C(7)-C(8)-C(12)	121.9(2)
O(5)-Fe-O(3)#1	94.03(8)	C(10)-C(9)-C(8)	118.7(3)
O(1)-Fe-O(3)#1	167.34(8)	C(11)-C10)-C(9)	119.7(3)
O(5)-Fe-O(2)#2	95.00(9)	C(11)-C10-Br(2)	118.4(2)
O(1)-Fe-O(2)#2	86.85(8)	C(9)-C(10)-Br(2)	121.8(2)
O(3)#1-Fe-O2#2	90.01(8)	N(2)-C11)-C(10)	122.1(3)
O(5)-Fe-O(4)#3	96.61(9)	O(4)-C(12)-O(3)	126.2(3)
O(1)-Fe-O(4)#3	89.62(8)	O(4)-C(12)-C(8)	118.7(2)
O(3)#1-Fe-O4#3	91.02(8)	O(3)-C(12)-C(8)	115.0(2)
O(2)#2-Fe-O4#3	168.23(8)		

Symmetry transformations used to generate equivalent atoms:
#1 -z+3/2,x-1/2,y #2 y+1/2,-z+1/2,-x+1
#3 -y+1,-z+1,-x+1 #4 -z+1,x-1/2,-y+1/2
#5 y+1/2,z,-x+3/2 #6 -z+1,-x+1,-y+1

2. Analytical supporting data

Table S3 Elemental Analyses performed by Galbraith Laboratory for complex **2**.

Element	Found	Calculated
Carbon	30.7%	31.0%
Iron	12.0%	12.0%
Hydrogen	0.88%	1.2%
Nitrogen	5.8%	6.0%

The elemental analysis result shows that the elemental content of the complex 2 is matching well with the chemical formula.

FT-IR

The results of the FT-IR analysis for **2** is shown in figure below. The peak at 1371 cm^{-1} corresponding to the C-O stretching. The peaks at 1551 cm^{-1} and 1610 cm^{-1} corresponding to the C-C stretching which is the carbon located on the BNA ring. The peak at 1287 cm^{-1} corresponding to the C-N stretching which is the C-N bond on the BNA ligand.

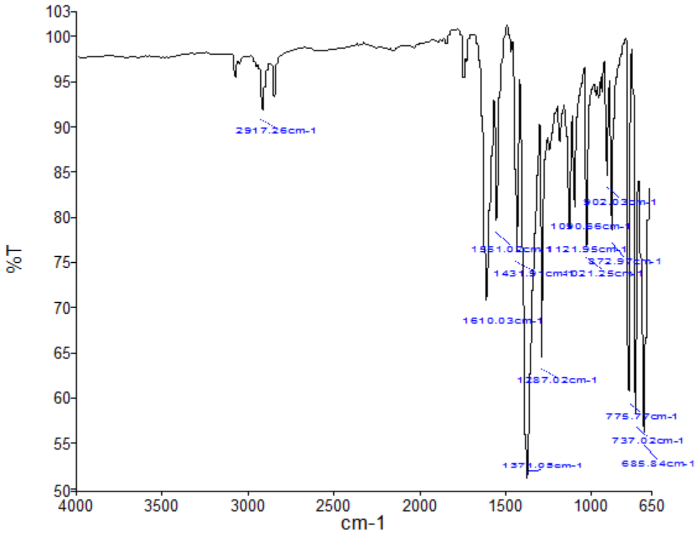

Figure S1 IR spectrum for complex **2**.

3. Summary of data

Summary of Data (CCDC 1870136)

Formula: $(C_{36} H_{18} Br_6 Fe_3 N_6 O_{13})_n$

Unit Cell Parameters: a 20.3708(6) b 20.3708(6) c 20.3708(6) Pa-3

Table S4 Crystal data and structure refinement for $Fe_3(BNA)_6O$.

Identification code	$Fe_3(BNA)_6O$
Empirical formula	$C_{36} H_{18} Br_6 Fe_3 N_6 O_{13}$
Formula weight	1389.57
Temperature	223(2) K

Wavelength	0.71073 A
Crystal system, space group	Cubic, Pa-3
Unit cell dimensions	a = 20.3708(6) A alpha = 90 deg.
	b = 20.3708(6) A beta = 90 deg.
	c = 20.3708(6) A gamma = 90 deg.
Volume	8453.3(4) A^3
Z, Calculated density	8, 2.184 Mg/m^3
Absorption coefficient	6.761 mm^-1
F(000)	5344
Crystal color and shape	black cube
Crystal size	0.15 x 0.15 x 0.15 mm
Theta range for data collection	1.73 to 23.51 deg.
Limiting indices	0<=h<=15, 0<=k<=16, 1<=l<=22
Reflections collected / unique	39304 / 2310 [R(int) = 0.0469]
Completeness to theta = 23.51	100.0 %
Absorption correction	Empirical
Max. and min. transmission	0.983 and 0.655
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	1696 / 0 / 193
Goodness-of-fit on F^2	1.058
Final R indices [I>4sigma(I)]	R1 = 0.0178, wR2 = 0.0449
R indices (all data)	R1 = 0.0267, wR2 = 0.0486
Largest diff. peak and hole	0.414 and -0.395 e.A^-3

Table S5 Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (A^2 x 10^3) for $Fe_3(BNA)_6O$.

	x	y	z	U(eq)
Fe	7171(1)	2628(1)	3670(1)	15(1)
Br(1)	4454(1)	3813(1)	5561(1)	36(1)
Br(2)	8694(1)	4785(1)	4708(1)	31(1)

O(1)	6213(1)	2717(1)	3933(1)	22(1)
O(2)	5645(1)	2231(1)	3120(1)	25(1)
O(3)	7642(1)	3596(1)	6825(1)	23(1)
O(4)	6859(1)	2899(1)	6485(1)	20(1)
O(5)	7060(1)	2060(1)	2940(1)	14(1)
N(1)	3913(1)	2439(2)	4176(2)	46(1)
N(2)	7402(1)	3256(1)	4535(1)	17(1)
C(1)	4481(2)	2337(2)	3865(2)	35(1)
C(2)	5070(1)	2622(1)	4045(1)	22(1)
C(3)	5073(2)	3050(1)	4577(1)	24(1)
C(4)	4485(2)	3181(2)	4883(2)	27(1)
C(5)	3921(2)	2864(2)	4677(2)	40(1)
C(6)	5692(1)	2508(1)	3672(1)	18(1)
C(7)	7254(1)	3107(1)	5159(1)	17(1)
C(8)	7528(1)	3435(1)	5692(1)	17(1)
C(9)	7980(1)	3932(1)	5568(1)	19(1)
C(10)	8113(1)	4097(1)	4926(1)	19(1)
C(11)	7818(1)	3753(1)	4422(1)	18(1)
C(12)	7326(1)	3288(1)	6389(1)	17(1)

U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

Table S6 Bond lengths [Å] and angles [deg] for $Fe_3(BNA)_6O$**.**

Fe-O(5)	1.8962(4)
Fe-O(1)	2.0309(19)
Fe-O(3)#1	2.0523(19)
Fe-O(2)#2	2.069(2)
Fe-O(4)#3	2.1090(19)
Fe-N(2)	2.229(2)
Br(1)-C(4)	1.890(3)

Br(2)-C(10)	1.887(3)
O(1)-C(6)	1.261(3)
O(2)-C(6)	1.263(3)
O(2)-Fe#4	2.069(2)
O(3)-C(12)	1.263(3)
O(3)-Fe#5	2.0523(19)
O(4)-C(12)	1.253(3)
O(4)-Fe#6	2.1091(19)
O(5)-Fe#2	1.8961(4)
O(5)-Fe#4	1.8962(4)
N(1)-C(1)	1.335(4)
N(1)-C(5)	1.337(4)
N(2)-C(7)	1.340(3)
N(2)-C(11)	1.341(4)
C(1)-C(2)	1.384(4)
C(2)-C(3)	1.391(4)
C(2)-C(6)	1.496(4)
C(3)-C(4)	1.377(4)
C(4)-C(5)	1.384(5)
C(7)-C(8)	1.393(4)
C(8)-C(9)	1.390(4)
C(8)-C(12)	1.508(4)
C(9)-C(10)	1.379(4)
C(10)-C(11)	1.381(4)
O(5)-Fe-O(1)	98.46(8)
O(5)-Fe-O(3)#1	94.03(8)
O(1)-Fe-O(3)#1	167.34(8)
O(5)-Fe-O(2)#2	95.00(9)
O(1)-Fe-O(2)#2	86.85(8)
O(3)#1-Fe-O(2)#2	90.01(8)
O(5)-Fe-O(4)#3	96.61(9)
O(1)-Fe-O(4)#3	89.62(8)

O(3)#1-Fe-O(4)#3	91.02(8)
O(2)#2-Fe-O(4)#3	168.23(8)
O(5)-Fe-N(2)	174.29(7)
O(1)-Fe-N(2)	86.73(8)
O(3)#1-Fe-N(2)	80.71(8)
O(2)#2-Fe-N(2)	82.84(8)
O(4)#3-Fe-N(2)	85.75(8)
C(6)-O(1)-Fe	131.85(18)
C(6)-O(2)-Fe#4	129.09(18)
C(12)-O(3)-Fe#5	136.87(18)
C(12)-O(4)-Fe#6	124.28(18)
Fe#2-O(5)-Fe#4	119.903(10)
Fe#2-O(5)-Fe	119.903(10)
Fe#4-O(5)-Fe	119.903(10)
C(1)-N(1)-C(5)	116.9(3)
C(7)-N(2)-C(11)	118.4(2)
C(7)-N(2)-Fe	124.94(18)
C(11)-N(2)-Fe	115.53(18)
N(1)-C(1)-C(2)	124.0(3)
C(1)-C(2)-C(3)	118.3(3)
C(1)-C(2)-C(6)	122.3(3)
C(3)-C(2)-C(6)	119.3(3)
C(4)-C(3)-C(2)	118.0(3)
C(3)-C(4)-C(5)	119.7(3)
C(3)-C(4)-Br(1)	119.5(2)
C(5)-C(4)-Br(1)	120.8(2)
N(1)-C(5)-C(4)	122.9(3)
O(1)-C(6)-O(2)	126.2(3)
O(1)-C(6)-C(2)	116.5(2)
O(2)-C(6)-C(2)	117.3(2)
N(2)-C(7)-C(8)	122.8(3)
C(9)-C(8)-C(7)	118.2(3)
C(9)-C(8)-C(12)	119.8(2)

C(7)-C(8)-C(12)	121.9(2)
C(10)-C(9)-C(8)	118.7(3)
C(11)-C(10)-C(9)	119.7(3)
C(11)-C(10)-Br(2)	118.4(2)
C(9)-C(10)-Br(2)	121.8(2)
N(2)-C(11)-C(10)	122.1(3)
O(4)-C(12)-O(3)	126.2(3)
O(4)-C(12)-C(8)	118.7(2)
O(3)-C(12)-C(8)	115.0(2)

Symmetry transformations used to generate equivalent atoms:

#1 -z+3/2,x-1/2,y   #2 y+1/2,-z+1/2,-x+1

#3 -y+1,-z+1,-x+1   #4 -z+1,x-1/2,-y+1/2

#5 y+1/2,z,-x+3/2   #6 -z+1,-x+1,-y+1

Table S7 Anisotropic displacement parameters (A^2 x 10^3) for $Fe_3(BNA)_6O$.

	U11	U22	U33	U23	U13	U12
Fe	14(1)	16(1)	15(1)	-1(1)	0(1)	0(1)
Br(1)	39(1)	37(1)	31(1)	-3(1)	9(1)	13(1)
Br(2)	32(1)	28(1)	32(1)	3(1)	3(1)	-13(1)
O(1)	16(1)	27(1)	24(1)	-6(1)	2(1)	1(1)
O(2)	18(1)	34(1)	24(1)	-7(1)	-1(1)	-3(1)
O(3)	28(1)	26(1)	13(1)	-2(1)	0(1)	-11(1)
O(4)	20(1)	21(1)	18(1)	0(1)	1(1)	-7(1)
O(5)	14(1)	14(1)	14(1)	-1(1)	-1(1)	1(1)
N(1)	25(2)	52(2)	63(2)	-13(2)	13(2)	-8(1)
N(2)	16(1)	20(1)	17(1)	-4(1)	0(1)	1(1)
C(1)	21(2)	38(2)	46(2)	-11(2)	7(2)	-5(2)
C(2)	24(2)	19(2)	24(2)	2(1)	6(1)	1(1)
C(3)	22(2)	23(2)	26(2)	6(1)	3(1)	3(1)

C(4)	29(2)	24(2)	27(2)	4(1)	10(1)	8(1)
C(5)	24(2)	45(2)	52(2)	-2(2)	16(2)	0(2)
C(6)	17(2)	15(1)	23(2)	4(1)	2(1)	2(1)
C(7)	16(2)	18(2)	18(2)	-2(1)	2(1)	-1(1)
C(8)	17(2)	18(2)	15(1)	-2(1)	1(1)	2(1)
C(9)	20(2)	20(2)	18(2)	-3(1)	-1(1)	-1(1)
C(10)	16(2)	18(2)	23(2)	0(1)	2(1)	-3(1)
C(11)	19(2)	19(2)	17(2)	2(1)	1(1)	2(1)
C(12)	19(2)	15(1)	17(2)	0(1)	1(1)	4(1)

The anisotropic displacement factor exponent takes the form:

-2 pi^2 [h^2 a*^2 U11 + ... + 2 h k a* b* U12]

Table S8 Hydrogen coordinates (x 10^4) and isotropic displacement parameters (A^2 x 10^3) for $Fe_3(BNA)_6O$.

	x	y	z	U(eq)
H(1)	4480	2053	3501	42
H(3)	5465	3245	4723	28
H(5)	3526	2951	4898	48
H(7)	6952	2768	5239	21
H(9)	8190	4151	5916	23
H(11)	7912	3871	3985	22

Table S9 Torsion angles [deg] for $Fe_3(BNA)_6O$.

O(5)-Fe-O(1)-C(6)	-4.9(3)
O(3)#1-Fe-O(1)-C(6)	-175.4(3)
O(2)#2-Fe-O(1)-C(6)	-99.5(2)

O(4)#3-Fe-O(1)-C(6)	91.7(3)
N(2)-Fe-O(1)-C(6)	177.5(3)
O(1)-Fe-O(5)-Fe#2	-135.76(16)
O(3)#1-Fe-O(5)-Fe#2	42.15(18)
O(2)#2-Fe-O(5)-Fe#2	-48.21(18)
O(4)#3-Fe-O(5)-Fe#2	133.65(16)
O(1)-Fe-O(5)-Fe#4	38.04(18)
O(3)#1-Fe-O(5)-Fe#4	-144.05(17)
O(2)#2-Fe-O(5)-Fe#4	125.59(17)
O(4)#3-Fe-O(5)-Fe#4	-52.56(18)
O(1)-Fe-N(2)-C(7)	59.6(2)
O(3)#1-Fe-N(2)-C(7)	-118.8(2)
O(2)#2-Fe-N(2)-C(7)	-27.6(2)
O(4)#3-Fe-N(2)-C(7)	149.5(2)
O(1)-Fe-N(2)-C(11)	-132.6(2)
O(3)#1-Fe-N(2)-C(11)	49.03(19)
O(2)#2-Fe-N(2)-C(11)	140.2(2)
O(4)#3-Fe-N(2)-C(11)	-42.69(19)
C(5)-N(1)-C(1)-C(2)	2.5(6)
N(1)-C(1)-C(2)-C(3)	-1.1(5)
N(1)-C(1)-C(2)-C(6)	-178.3(3)
C(1)-C(2)-C(3)-C(4)	-1.7(4)
C(6)-C(2)-C(3)-C(4)	175.6(3)
C(2)-C(3)-C(4)-C(5)	2.9(4)
C(2)-C(3)-C(4)-Br(1)	-174.9(2)
C(1)-N(1)-C(5)-C(4)	-1.2(6)
C(3)-C(4)-C(5)-N(1)	-1.5(5)
Br(1)-C(4)-C(5)-N(1)	176.3(3)
Fe-O(1)-C(6)-O(2)	-7.6(4)
Fe-O(1)-C(6)-Cf(2)	174.59(18)
Fe#4-O(2)-C(6)-O(1)	-12.9(4)
Fe#4-O(2)-C(6)-C(2)	164.92(18)
C(1)-C(2)-C(6)-O(1)	-170.3(3)

C(3)-C(2)-C(6)-O(1)	12.5(4)
C(1)-C(2)-C(6)-O(2)	11.6(4)
C(3)-C(2)-C(6)-O(2)	-165.6(3)
C(11)-N(2)-C(7)-C(8)	-1.9(4)
Fe-N(2)-C(7)-C(8)	165.6(2)
N(2)-C(7)-C(8)-C(9)	-0.7(4)
N(2)-C(7)-C(8)-C(12)	176.3(2)
C(7)-C(8)-C(9)-C(10)	2.9(4)
C(12)-C(8)-C(9)-C(10)	-174.2(3)
C(8)-C(9)-C(10)-C(11)	-2.5(4)
C(8)-C(9)-C(10)-Br(2)	177.6(2)
C(7)-N(2)-C(11)-C(10)	2.4(4)
Fe-N(2)-C(11)-C(10)	-166.2(2)
C(9)-C(10)-C(11)-N(2)	-0.2(4)
Br(2)-C(10)-C(11)-N(2)	179.7(2)
Fe#6-O(4)-C(12)-O(3)	15.6(4)
Fe#6-O(4)-C(12)-C(8)	-162.03(18)
Fe#5-O(3)-C(12)-O(4)	0.2(5)
Fe#5-O(3)-C(12)-C(8)	177.88(18)
C(9)-C(8)-C(12)-O(4)	171.0(3)
C(7)-C(8)-C(12)-O(4)	-6.0(4)
C(9)-C(8)-C(12)-O(3)	-6.8(4)
C(7)-C(8)-C(12)-O(3)	176.1(3)

Symmetry transformations used to generate equivalent atoms:

#1 -z+3/2,x-1/2,y   #2 y+1/2,-z+1/2,-x+1

#3 -y+1,-z+1,-x+1   #4 -z+1,x-1/2,-y+1/2

#5 y+1/2,z,-x+3/2   #6 -z+1,-x+1,-y+1