Supporting Information

Air oxidation-induced single-crystal-to-single-crystal transformation of a mixed-valence tetranuclear Fe(II)-Fe(III) complex

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Experimental Section

General: All chemicals and solvents used in this study were of reagent grade and used without further purification. *N*-(2-Pyridylmethyl)iminodiethanol (H_2pmide) was synthesized using a previously reported method.[1] Infrared spectra were recorded with a Thermo Fisher Scientific IR200 spectrophotometer (±1 cm^{-1}) using KBr disk. Elemental analyses were performed using the Fisons/Carlo Erba EA1108 instrument. Temperature-dependent magnetic susceptibilities were measured on a Quantum Design MPMS-5S superconducting quantum interference device magnetometer in an applied field of 5,000/10,000 Oe between 2 K and 300 K with a sweep mode of 2 K min^{-1}. Diamagnetic corrections were made by using Pascal's constants [756.46 (**1**) and 693.35 × 10^{-6} (**2**) emu/mol].[2] Susceptibility data of **1** and **2** were simulated with the PHI program package for magnetic models.[3] Zero-field Mössbauer spectra of **1** and **2** were recorded at 298 or 5 K using the Wissel MVT-1000 Mössbauer spectrometer with a ^{57}Co/Rh radiation source equipped with a closed-cycle He refrigerator cryostat in transmission mode. All spectra were calibrated using a standard α-Fe foil as a reference at room temperature. The Mössbauer parameters were obtained by a least-square fitting program (MossA) assuming the Lorentzian line shapes.[4]

X-ray Crystallographic Data Collection and Refinement. Single crystal diffraction data of **1** and **2** were collected on same crystal. The crystal data for **1** and **2** were coated with paratone-*N* oil and the diffraction data measured at 100(2) K with synchrotron radiation (λ = 0.65000 and 0.70000 Å) on an ADSC Quantum-210 detector at 2D SMC with a silicon (111) double crystal monochromator (DCM) at the Pohang Accelerator Laboratory, Korea, respectively. The ADSC Q210 ADX program[5] was used for data collection (detector distance is 63 mm, omega scan; Δω =

1°, exposure time is 1 sec per frame) and HKL3000sm (Ver. 703r)[6] was used for cell refinement, reduction and absorption correction. The crystal structures of **1** and **2** were solved by direct methods,[7] and refined by full-matrix least-squares refinement using the SHELXL-2014 computer program.[8] The positions of all non-hydrogen atoms were refined with anisotropic displacement factors. All hydrogen atoms were placed using a riding model, and their positions were constrained relative to their parent atoms using the appropriate HFIX command in SHELXL-2014, except the hydrogen atoms of water molecules. Even though the guest solvent molecules were found in the structure, those could not be well refined because of severe disorder. The final refinement was performed with modification of the structure factors for contribution of the disordered solvent electron densities using the SQUEEZE option of PLATON program.[9,10] The methanol molecules in **1** could be found by the residual peaks located in the space between the tetranuclear units. Unfortunately, they were disordered so badly that it could not be modeled. Thus, the Squeeze program was used to calculate the void space. As a result, total potential solvent area volume was 543.9 $Å^3$ (8.5% per unit cell volume). This could be corresponded to 8 methanol molecules (538.4 $Å^3$), based on the methanol volume as guest molecule (67.3 $Å^3$ per methanol). The formula of complex **1** was suggested from the results. The crystallographic data and the result of refinements of **1** and **2** are summarized in Table 1.

Preparation of $[(Hpmide)Fe^{II}(NCSe)_2Fe^{III}(pmide)]_2 \cdot 5CH_3OH$ (1)

A solution of KNCSe (0.116 g, 0.80 mmol) in MeOH (2 mL) was added to $FeSO_4 \cdot 7H_2O$ (0.112 g, 0.40 mmol) in MeOH (3 mL). The mixture was stirred for 20 min and filtered off the white precipitate (K_2SO_4). A solution of H_2pmide (0.084 g, 0.40 mmol) in MeOH (2 mL) was slowly

added into the filtered solution with stirring and the color became greenish-yellow. Yellow crystals of **1** were obtained by slow evaporation of yellow solution for several days and were collected by filtration and washed with MeOH. Yield: 122 mg (80%). IR (KBr, cm^{-1}): 3416, 3068, 2954, 2066, 1604, 1442, 1294, 1076, 897, 764. Anal Calcd for $C_{49}H_{78}N_{12}Fe_4O_{13}Se_4$: C, 37.19; H, 4.97; N, 10.62. Found: C, 36.88; H, 4.92; N, 10.77.

Preparation of $[(pmide)Fe^{III}(NCSe)Fe^{III}(pmide)]_2(NCSe)_2 \cdot 2H_2O$ (2)

1 was oxidized in air for several days. The complex became from yellowish to reddish. IR (KBr, cm^{-1}): 3430, 3066, 2922, 2059, 1605, 1442, 1293, 1068, 898, 772. Anal Calcd for $C_{44}H_{62}N_{12}Fe_4O_{11}Se_4$: C, 35.85; H, 4.24; N, 11.40. Found: C, 35.50; H, 3.94; N, 11.27.

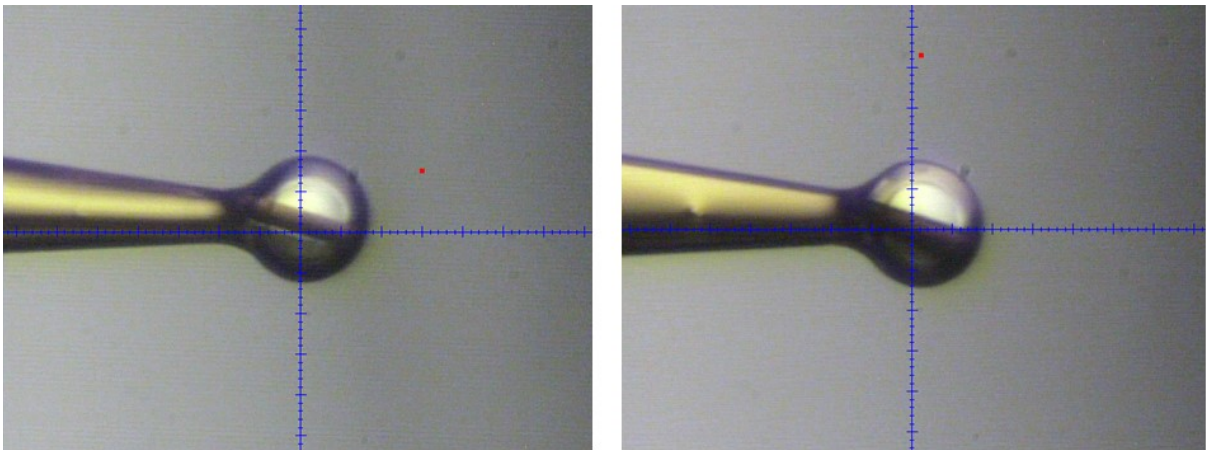

Fig. S1 Single crystal images of **1** in PAL at 100 K under N_2 (left) and its exposed one to air at room temperature (right).

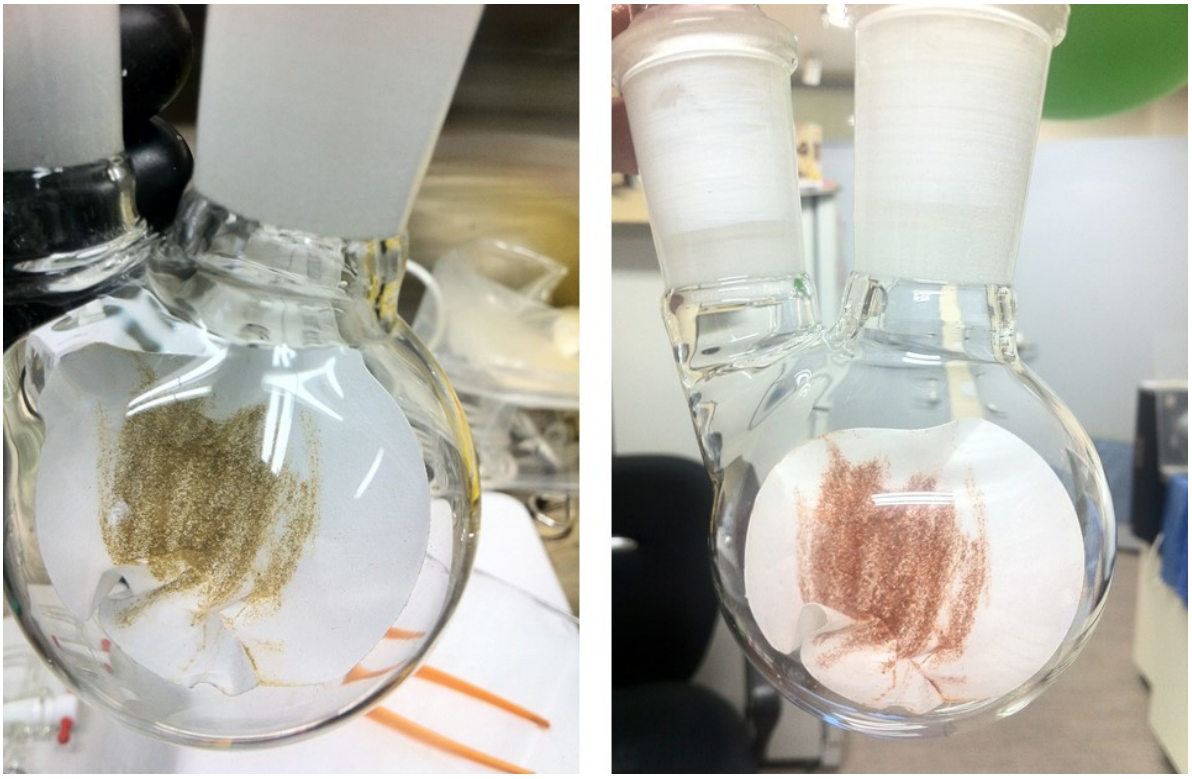

Fig. S2 Photographs of powder **1** scratched with a spatula in a glove box (left) and its exposed one to air (right) at room temperature.

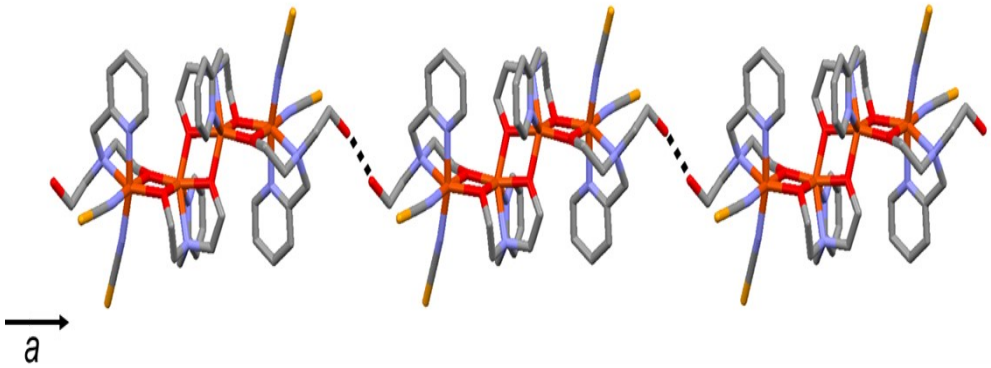

Fig. S3 Perspective view of **1**, showing the 1-D polymer. The hydrogen bonding interactions are indicated as a dashed line.

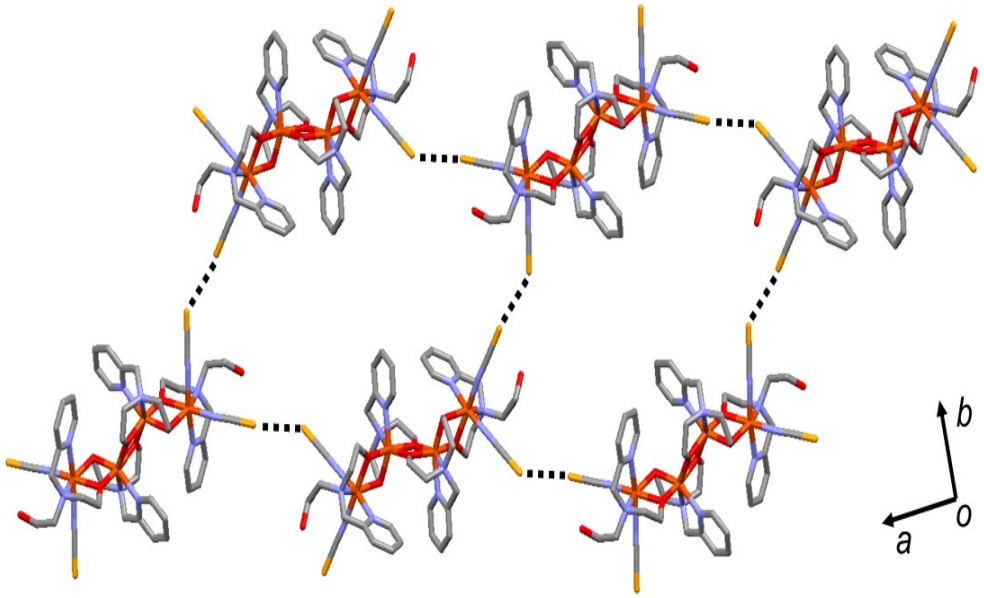

Fig. S4 Perspective view of **1**, showing the 2-D polymer. The selenium–selenium interactions are indicated as a dashed line.

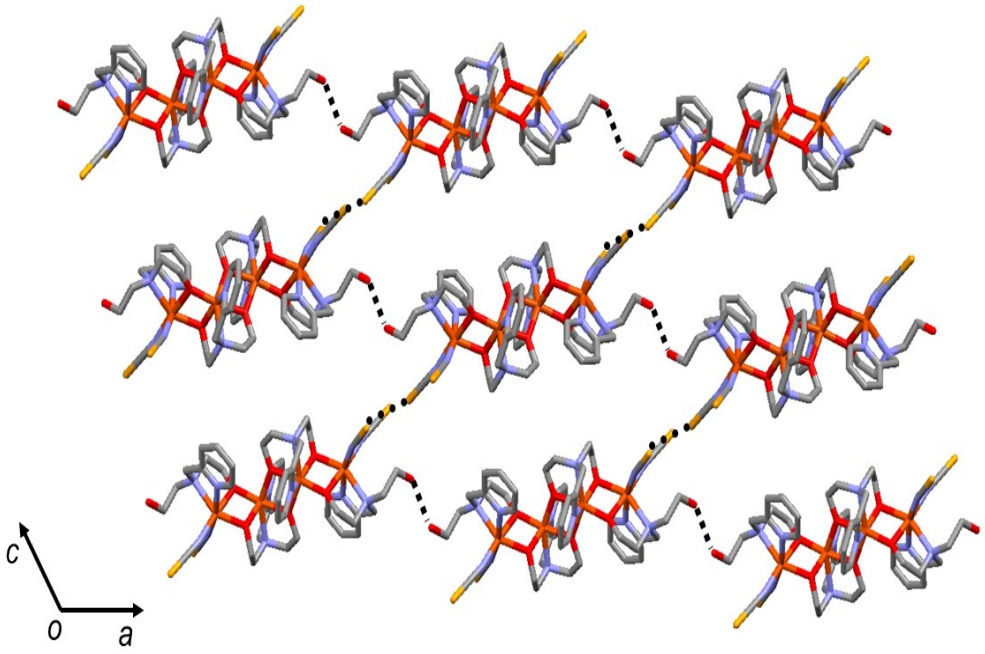

Fig. S5 Perspective view of **1**, showing the 3-D polymer. The hydrogen bonding interactions and the selenium-selenium interactions are indicated as ▪▪▪ and •••, respectively.

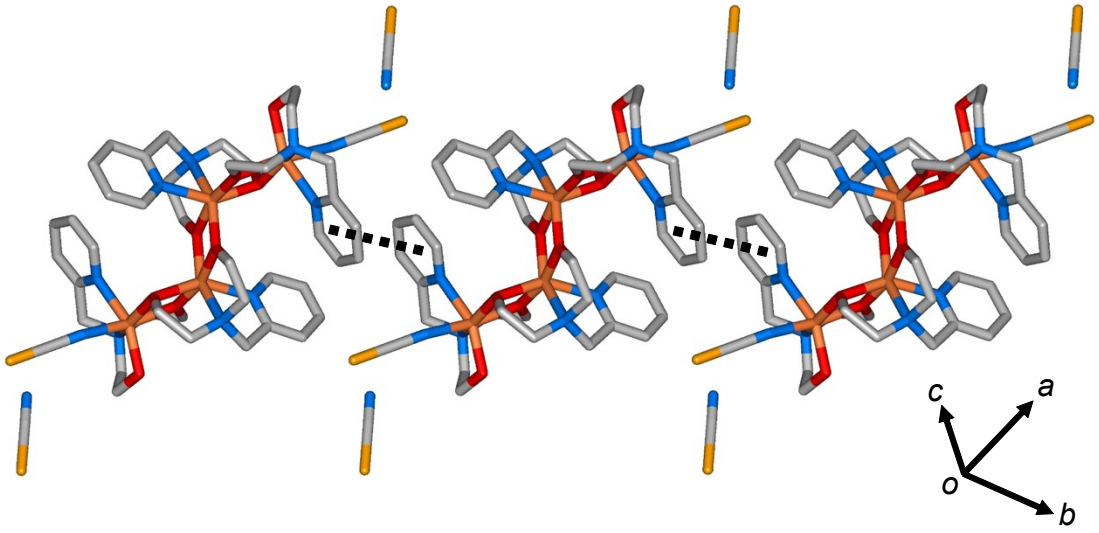

Fig. S6 Perspective view of **2**, showing the 1-D polymer. The offset π–π stacking interaction via pyridine groups leading to a polymer is indicated as a dashed line. The interplanar separation of the pyridine rings was 3.526(13)-3.556(14) Å (centroid···centroid, 4.240 Å), and the dihedral and offset angles between the pyridine rings were 0.0(7) and 30.6(3)°, respectively.

Table S1. Crystallographic data and structure refinement for **1** and **2**.

Compound	**1**	**2**
Empirical formula	$C_{49}H_{78}Fe_4N_{12}O_{13}Se_4$	$C_{44}H_{60}Fe_4N_{12}O_{10}Se_4$
Formula weight	1582.46	1456.28
Crystal system	Monoclinic	Monoclinic
Space group	*C*2/c	*C*2/c
a (Å)	18.912(4)	19.075(4)
b (Å)	17.656(4)	16.976(3)
c (Å)	20.462(4)	18.802(4)
β (°)	110.52(3)	108.26(3)
V (Å^3)	6399(3)	5782(2)
Z	4	4
d_{calc} (g cm^{-3})	1.643	1.673
λ (Å)	0.65000	0.70000
T (K)	100(2)	100(2)
μ (mm^{-1})	2.523	3.411
F(000)	3200	2912
Reflections collected	41155	21631
Independent reflections	11675	6569
Reflections with $I>2\sigma(I)$	9130	3277
Goodness-of-fit on F^2	1.054	0.998
R_1[a] (4σ data)	0.0411	0.0839
wR_2[b] (4σ data)	0.1141	0.2543
CCDC	2170049	2170050

[a] $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$.

[b] $wR_2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2]^{1/2}$.

Table S2. Bond lengths [Å] and angles [°] for **1**.

Fe(1)-O(1)	2.0961(14)	N(4)-C(17)	1.492(3)
Fe(1)-N(6)	2.1011(17)	N(5)-C(21)	1.160(3)
Fe(1)-O(4)	2.1100(14)	N(6)-C(22)	1.160(2)
Fe(1)-N(5)	2.1260(17)	O(1)-C(8)	1.413(2)
Fe(1)-N(1)	2.2029(17)	O(2)-C(10)	1.435(3)
Fe(1)-N(2)	2.2928(17)	O(3)-C(18)	1.416(2)
Fe(2)-O(1)	1.9107(14)	O(4)-C(20)	1.420(2)
Fe(2)-O(3)#1	1.9612(13)	C(1)-C(2)	1.387(3)
Fe(2)-O(4)	1.9674(13)	C(2)-C(3)	1.381(3)
Fe(2)-O(3)	2.0386(14)	C(3)-C(4)	1.391(3)
Fe(2)-N(3)	2.1554(17)	C(4)-C(5)	1.381(3)
Fe(2)-N(4)	2.2329(16)	C(5)-C(6)	1.506(3)
Se(1A)-C(21)	1.795(3)	C(7)-C(8)	1.520(3)
Se(1B)-C(21)	1.776(7)	C(9)-C(10)	1.527(3)
Se(2)-C(22)	1.7987(19)	C(11)-C(12)	1.385(3)
N(1)-C(5)	1.344(3)	C(12)-C(13)	1.383(3)
N(1)-C(1)	1.346(2)	C(13)-C(14)	1.391(3)
N(2)-C(6)	1.483(3)	C(14)-C(15)	1.389(3)
N(2)-C(9)	1.485(2)	C(15)-C(16)	1.502(3)
N(2)-C(7)	1.495(2)	C(17)-C(18)	1.528(3)
N(3)-C(11)	1.343(2)	C(19)-C(20)	1.527(3)
N(3)-C(15)	1.353(2)	C(23)-O(5)	1.423(3)
N(4)-C(16)	1.483(3)	C(24)-O(6)	1.372(5)
N(4)-C(19)	1.490(2)		

O(1)-Fe(1)-N(6)	175.79(6)	O(4)-Fe(1)-N(1)	91.20(6)
O(1)-Fe(1)-O(4)	73.86(5)	N(5)-Fe(1)-N(1)	165.25(7)
N(6)-Fe(1)-O(4)	102.92(6)	O(1)-Fe(1)-N(2)	79.67(6)
O(1)-Fe(1)-N(5)	87.60(6)	N(6)-Fe(1)-N(2)	104.13(7)
N(6)-Fe(1)-N(5)	90.54(7)	O(4)-Fe(1)-N(2)	149.57(5)
O(4)-Fe(1)-N(5)	103.20(6)	N(5)-Fe(1)-N(2)	90.25(6)
O(1)-Fe(1)-N(1)	93.41(6)	N(1)-Fe(1)-N(2)	75.48(6)
N(6)-Fe(1)-N(1)	89.35(7)	O(1)-Fe(2)-O(3)#1	96.92(6)

O(1)-Fe(2)-O(4)	81.32(6)	C(8)-O(1)-Fe(1)	112.96(11)
O(3)#1-Fe(2)-O(4)	112.31(6)	Fe(2)-O(1)-Fe(1)	103.54(6)
O(1)-Fe(2)-O(3)	169.10(6)	C(10)-O(2)-H(2A)	109.5
O(3)#1-Fe(2)-O(3)	73.41(6)	C(18)-O(3)-Fe(2)#1	131.99(11)
O(4)-Fe(2)-O(3)	97.49(6)	C(18)-O(3)-Fe(2)	121.37(10)
O(1)-Fe(2)-N(3)	90.82(6)	Fe(2)#1-O(3)-Fe(2)	106.58(6)
O(3)#1-Fe(2)-N(3)	97.87(6)	C(20)-O(4)-Fe(2)	114.72(11)
O(4)-Fe(2)-N(3)	149.46(6)	C(20)-O(4)-Fe(1)	120.92(11)
O(3)-Fe(2)-N(3)	95.44(6)	Fe(2)-O(4)-Fe(1)	101.10(6)
O(1)-Fe(2)-N(4)	112.99(6)	N(1)-C(1)-C(2)	122.4(2)
O(3)#1-Fe(2)-N(4)	149.09(6)	C(3)-C(2)-C(1)	118.9(2)
O(4)-Fe(2)-N(4)	81.03(6)	C(2)-C(3)-C(4)	118.70(19)
O(3)-Fe(2)-N(4)	77.34(6)	C(5)-C(4)-C(3)	119.3(2)
N(3)-Fe(2)-N(4)	74.99(6)	N(1)-C(5)-C(4)	122.22(18)
C(5)-N(1)-C(1)	118.44(17)	N(1)-C(5)-C(6)	116.36(17)
C(5)-N(1)-Fe(1)	115.82(12)	C(4)-C(5)-C(6)	121.39(18)
C(1)-N(1)-Fe(1)	125.63(14)	N(2)-C(6)-C(5)	111.15(16)
C(6)-N(2)-C(9)	110.14(15)	N(2)-C(7)-C(8)	111.64(15)
C(6)-N(2)-C(7)	110.21(15)	O(1)-C(8)-C(7)	108.41(16)
C(9)-N(2)-C(7)	109.31(15)	N(2)-C(9)-C(10)	115.05(16)
C(6)-N(2)-Fe(1)	105.39(11)	O(2)-C(10)-C(9)	112.72(17)
C(9)-N(2)-Fe(1)	117.53(12)	N(3)-C(11)-C(12)	122.36(19)
C(7)-N(2)-Fe(1)	103.99(11)	C(13)-C(12)-C(11)	118.5(2)
C(11)-N(3)-C(15)	119.19(17)	C(12)-C(13)-C(14)	119.74(19)
C(11)-N(3)-Fe(2)	124.07(14)	C(15)-C(14)-C(13)	118.71(19)
C(15)-N(3)-Fe(2)	116.64(13)	N(3)-C(15)-C(14)	121.48(18)
C(16)-N(4)-C(19)	113.24(14)	N(3)-C(15)-C(16)	114.83(17)
C(16)-N(4)-C(17)	109.17(16)	C(14)-C(15)-C(16)	123.69(18)
C(19)-N(4)-C(17)	112.64(15)	N(4)-C(16)-C(15)	108.49(15)
C(16)-N(4)-Fe(2)	106.32(12)	N(4)-C(17)-C(18)	111.31(15)
C(19)-N(4)-Fe(2)	106.48(12)	O(3)-C(18)-C(17)	107.78(15)
C(17)-N(4)-Fe(2)	108.68(10)	N(4)-C(19)-C(20)	109.64(14)
C(21)-N(5)-Fe(1)	168.56(16)	O(4)-C(20)-C(19)	109.82(15)
C(22)-N(6)-Fe(1)	170.39(17)	N(5)-C(21)-Se(1B)	172.7(3)
C(8)-O(1)-Fe(2)	142.91(12)	N(5)-C(21)-Se(1A)	176.9(2)

Se(1B)-C(21)-Se(1A)	10.4(3)	O(6)-C(24)-H(24B)#2	109.47(3)
N(6)-C(22)-Se(2)	177.44(18)	O(6)-C(24)-H(24C)#2	109.472(6)
O(6)-C(24)-H(24A)#2	109.473(7)	C(24)-O(6)-H(6)#2	109.472(8)

Symmetry transformations used to generate equivalent atoms: #1 -x-1/2, -y+1/2, -z; #2 -x+1, y, -z+1/2.

Table S3. Bond lengths [Å] and angles [°] for **2**.

Fe(1)-O(2)	1.890(6)	O(3)-C(18)	1.457(9)
Fe(1)-O(4)	1.985(6)	O(4)-C(20)	1.424(10)
Fe(1)-O(1)	2.035(5)	C(1)-C(2)	1.358(13)
Fe(1)-N(5)	2.069(7)	C(2)-C(3)	1.339(14)
Fe(1)-N(1)	2.163(7)	C(3)-C(4)	1.358(14)
Fe(1)-N(2)	2.186(8)	C(4)-C(5)	1.388(13)
Fe(2)-O(1)	1.940(5)	C(5)-C(6)	1.537(14)
Fe(2)-O(3)#1	1.942(5)	C(7)-C(8)	1.539(14)
Fe(2)-O(4)	1.994(5)	C(9)-C(10)	1.437(15)
Fe(2)-O(3)	2.010(5)	C(11)-C(12)	1.355(12)
Fe(2)-N(3)	2.136(7)	C(12)-C(13)	1.366(13)
Fe(2)-N(4)	2.229(7)	C(13)-C(14)	1.406(14)
Se(1)-C(21)	1.793(10)	C(14)-C(15)	1.362(12)
N(1)-C(5)	1.302(11)	C(15)-C(16)	1.510(12)
N(1)-C(1)	1.348(11)	C(17)-C(18)	1.508(12)
N(2)-C(6)	1.478(12)	C(19)-C(20)	1.539(13)
N(2)-C(9)	1.500(11)	Se(2)-C(23)	1.840(9)
N(2)-C(7)	1.505(12)	Se(2)-C(22)	1.863(9)
N(3)-C(15)	1.338(11)	N(6)-C(22)	1.166(9)
N(3)-C(11)	1.341(10)	C(22)-C(23)	2.03(3)
N(4)-C(19)	1.446(10)	C(23)-N(7)	1.177(9)
N(4)-C(16)	1.482(11)	O(5A)-O(5B)	1.08(3)
N(4)-C(17)	1.504(11)	Fe(1)-Fe(2)	3.148(2)
N(5)-C(21)	1.157(11)	Fe(2)-Fe(2)#1	3.159(2)
O(1)-C(8)	1.423(10)	Fe(1)-Fe(1)#1	8.650(3)
O(2)-C(10)	1.457(13)		

O(2)-Fe(1)-O(4)	113.7(3)	O(2)-Fe(1)-N(1)	149.9(3)
O(2)-Fe(1)-O(1)	97.2(3)	O(4)-Fe(1)-N(1)	96.1(2)
O(4)-Fe(1)-O(1)	74.3(2)	O(1)-Fe(1)-N(1)	94.9(2)
O(2)-Fe(1)-N(5)	89.7(3)	N(5)-Fe(1)-N(1)	82.6(3)
O(4)-Fe(1)-N(5)	96.0(3)	O(2)-Fe(1)-N(2)	81.1(3)
O(1)-Fe(1)-N(5)	169.7(3)	O(4)-Fe(1)-N(2)	150.6(2)

O(1)-Fe(1)-N(2)	78.9(2)	C(17)-N(4)-Fe(2)	106.8(4)
N(5)-Fe(1)-N(2)	109.8(3)	C(21)-N(5)-Fe(1)	164.3(8)
N(1)-Fe(1)-N(2)	74.3(3)	C(8)-O(1)-Fe(2)	139.2(5)
O(1)-Fe(2)-O(3)#1	96.3(2)	C(8)-O(1)-Fe(1)	115.7(5)
O(1)-Fe(2)-O(4)	76.2(2)	Fe(2)-O(1)-Fe(1)	104.8(2)
O(3)#1-Fe(2)-O(4)	110.6(2)	C(10)-O(2)-Fe(1)	109.7(6)
O(1)-Fe(2)-O(3)	165.5(2)	C(18)-O(3)-Fe(2)#1	133.4(4)
O(3)#1-Fe(2)-O(3)	74.0(2)	C(18)-O(3)-Fe(2)	120.4(4)
O(4)-Fe(2)-O(3)	97.0(2)	Fe(2)#1-O(3)-Fe(2)	106.0(2)
O(1)-Fe(2)-N(3)	92.4(2)	C(20)-O(4)-Fe(1)	122.2(4)
O(3)#1-Fe(2)-N(3)	99.5(2)	C(20)-O(4)-Fe(2)	112.7(5)
O(4)-Fe(2)-N(3)	148.7(2)	Fe(1)-O(4)-Fe(2)	104.7(2)
O(3)-Fe(2)-N(3)	99.6(2)	N(1)-C(1)-C(2)	121.9(9)
O(1)-Fe(2)-N(4)	111.9(2)	C(3)-C(2)-C(1)	119.8(10)
O(3)#1-Fe(2)-N(4)	151.6(2)	C(2)-C(3)-C(4)	118.7(10)
O(4)-Fe(2)-N(4)	80.9(2)	C(3)-C(4)-C(5)	119.6(10)
O(3)-Fe(2)-N(4)	79.0(2)	N(1)-C(5)-C(4)	121.4(9)
N(3)-Fe(2)-N(4)	76.5(3)	N(1)-C(5)-C(6)	115.4(8)
C(5)-N(1)-C(1)	118.4(8)	C(4)-C(5)-C(6)	123.2(9)
C(5)-N(1)-Fe(1)	117.0(6)	N(2)-C(6)-C(5)	106.7(8)
C(1)-N(1)-Fe(1)	124.5(6)	N(2)-C(7)-C(8)	106.0(8)
C(6)-N(2)-C(9)	111.0(8)	O(1)-C(8)-C(7)	108.2(7)
C(6)-N(2)-C(7)	110.1(8)	C(10)-C(9)-N(2)	108.5(9)
C(9)-N(2)-C(7)	111.6(8)	C(9)-C(10)-O(2)	110.5(8)
C(6)-N(2)-Fe(1)	107.8(6)	N(3)-C(11)-C(12)	122.2(9)
C(9)-N(2)-Fe(1)	106.9(6)	C(11)-C(12)-C(13)	118.8(9)
C(7)-N(2)-Fe(1)	109.3(5)	C(12)-C(13)-C(14)	119.5(8)
C(15)-N(3)-C(11)	119.6(7)	C(15)-C(14)-C(13)	118.3(9)
C(15)-N(3)-Fe(2)	116.8(5)	N(3)-C(15)-C(14)	121.5(8)
C(11)-N(3)-Fe(2)	123.5(6)	N(3)-C(15)-C(16)	115.5(7)
C(19)-N(4)-C(16)	114.3(6)	C(14)-C(15)-C(16)	122.9(8)
C(19)-N(4)-C(17)	114.7(7)	N(4)-C(16)-C(15)	110.6(6)
C(16)-N(4)-C(17)	107.6(7)	N(4)-C(17)-C(18)	112.4(7)
C(19)-N(4)-Fe(2)	106.6(5)	O(3)-C(18)-C(17)	107.8(6)
C(16)-N(4)-Fe(2)	106.3(5)	N(4)-C(19)-C(20)	110.4(6)

O(4)-C(20)-C(19)	108.6(7)	Se(2)-C(22)-C(23)	56.2(6)
N(5)-C(21)-Se(1)	179.7(10)	N(7)-C(23)-Se(2)	172(2)
C(23)-Se(2)-C(22)	66.4(11)	N(7)-C(23)-C(22)	126.5(18)
N(6)-C(22)-Se(2)	164(2)	Se(2)-C(23)-C(22)	57.3(6)
N(6)-C(22)-C(23)	139.5(19)		

Symmetry transformations used to generate equivalent atoms: #1 -x+1/2, -y+1/2, -z.

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