Supplementary Information for:

Expanded Redox Accessibility via Ligand Substitution in an Octahedral Fe_6Br_6 Cluster

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Experimental Section

General Considerations. Manipulations involving metal complexes were carried out using standard glove-box techniques under a dinitrogen atmosphere unless otherwise noted. Glassware was oven-dried for a minimum of 10 h and cooled in an evacuated antechamber prior to use in the dry box. Acetonitrile and diethyl ether was dried and deoxygenated on a Glass Contour System (SG Water USA, Nashua, NH) and stored over 4 Å molecular sieves (Strem) prior to use. Anhydrous DMF was purchased from Sigma Aldrich and degassed via three freeze-pump-thaw cycles prior to use. Water was purified using a Barnstead NANOpure Diamond Water Purifier. The compounds $(^{H}L)_2Fe_6$ and $[(^{H}L)_2Fe_6(NCMe)_6](PF_6)_4$ were prepared as described previously.[1] All other reagents were purchased from commercial vendors and used without further purification unless explicitly stated.

$(^{H}L)_2Fe_6Br_6$ (1). Solid $[Cp_2Fe](PF_6)$ (0.288 g, 0.869 mmol) was added to a stirred mixture of $(Bu_4N)Br$ (0.154 g, 0.478 mmol) and $(^{H}L)_2Fe_6$ (0.0800 g, 0.0724 mmol) in MeCN (15 mL). After stirring for 24 h, the resulting dark solid precipitate was collected on a medium-porosity fritted glass funnel. The residue was washed with successive aliquots of MeCN (5 × 8 mL) and Et_2O (3 × 8 mL), then dried under vacuum, to give **1** (0.102 g, 88%) as a dark brown powder. Anal. Calcd. for $C_{46}H_{48}Br_6Fe_6N_{12}$: C, 34.89; H, 3.05; N, 10.61%. Found: C, 34.95; H, 3.12; N, 10.61%.

Crystallization of 1. In air, a saturated aqueous solution (ca. 0.5 mL) of KBr was added to a Wako 4.970 mm thick 8 in. borosilicate NMR tube. A 1:1 mixture of MeCN/H_2O (ca. 0.5 mL) was then carefully layered on top of the KBr solution. A 2.6 mM solution (ca. 0.5 mL) of $[(^{H}L)_2Fe_6(NCMe)_6](PF_6)_4$ and $[Cp_2Fe](PF_6)$ in MeCN was carefully layered on top of the MeCN/H_2O mixture. Upon standing for 2 weeks, black plate-like crystals of **1** formed from the layering.

$(Ph_4P)_2[(^{H}L)_2Fe_6Br_6]\cdot 2DMF$ (2). A saturated solution of $(Ph_4P)Br$ in DMF (8 mL) was added to a solution of $[(^{H}L)_2Fe_6(NCMe)_6](PF_6)_4$ (0.072 g, 0.037 mmol) in DMF (8 mL). The resulting dark solution was allowed to stand. Over the course of 12 h, a dark amorphous solid precipitated from solution. Additionally, a few dark block-shaped crystals of **2** also formed from solution. Crystals of **2** have thus far only been obtained in this one isolated instance.

X-Ray Structure Determinations. Single crystals suitable for X-ray analysis were coated with deoxygenated Paratone-N oil and mounted on Kaptan loops. Data were collected at 100 K on an APEX II CCD or APEX II DUO single crystal diffractometer. Neither of the crystals showed significant decay during data collection. Raw data were integrated and corrected for Lorentz and polarization effects using Bruker APEX2 v. 2009.1.[2] Absorption corrections were applied using SADABS.[3] Space group assignments were determined by examination of systematic absences, E-statistics, and successive refinement of the structures. The program PLATON[4] was employed to confirm the absence of higher symmetry for any of the crystals. The positions of the heavy atoms were determined using direct methods using the program SHELXTL.[5] Subsequent cycles of least-squares refinement followed by difference Fourier syntheses revealed the positions of the remaining non-hydrogen atoms. Non-hydrogen atoms were refined with anisotropic displacement parameters, and hydrogen atoms were added in idealized positions.

Magnetic Susceptibility Measurements. Magnetic data for **1** were collected using a Quantum Design MPMS-5S SQUID magnetometer. Measurements for were obtained for a powder restrained in a polyethylene bag within a gelatin capsule. Dc magnetic susceptibility measurements were collected in the temperature range 5-300 K under an applied dc field of 1 T. All data were corrected for core diamagnetism of the sample, estimated using Pascal's constants, in addition to contributions from the sample holder.

Other Physical Measurements. Elemental analyses were performed by Complete Analysis Laboratories, Inc., Parsippany, New Jersey or Robertson Microlit Laboratories, Madison, New Jersey.

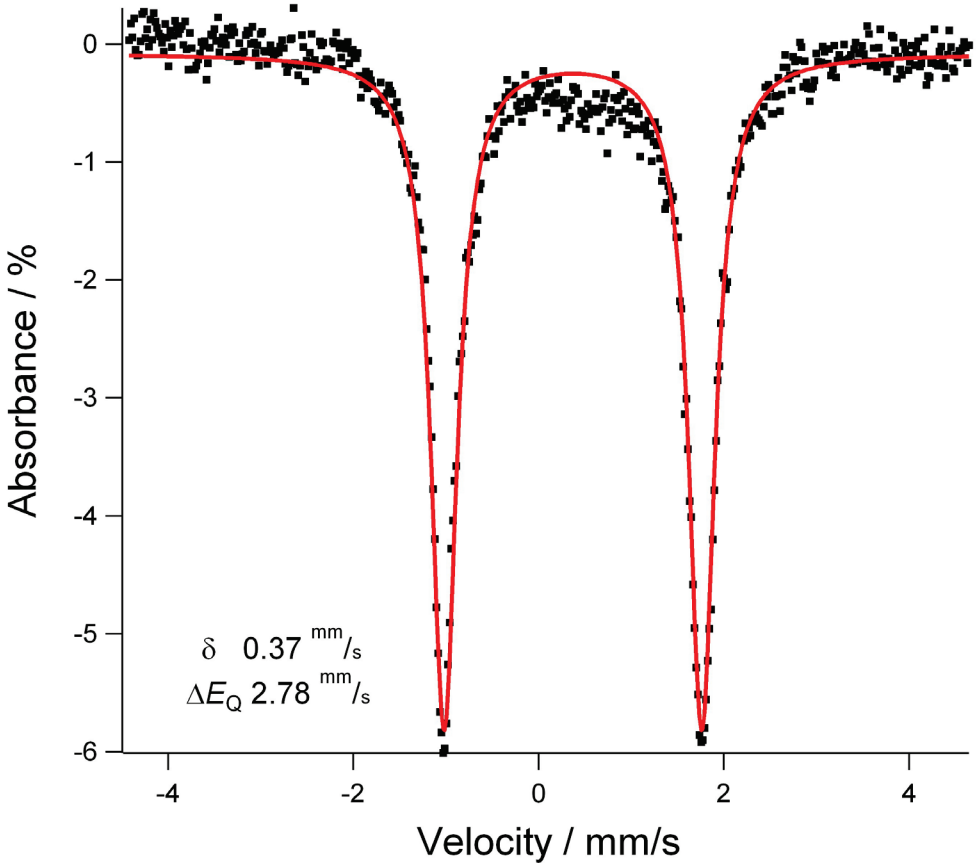

Fig. S1 Zero-field Mössbauer spectrum for **1**, collected at 100 K. Black squares correspond to experimental data, and red solid line corresponds to fit.

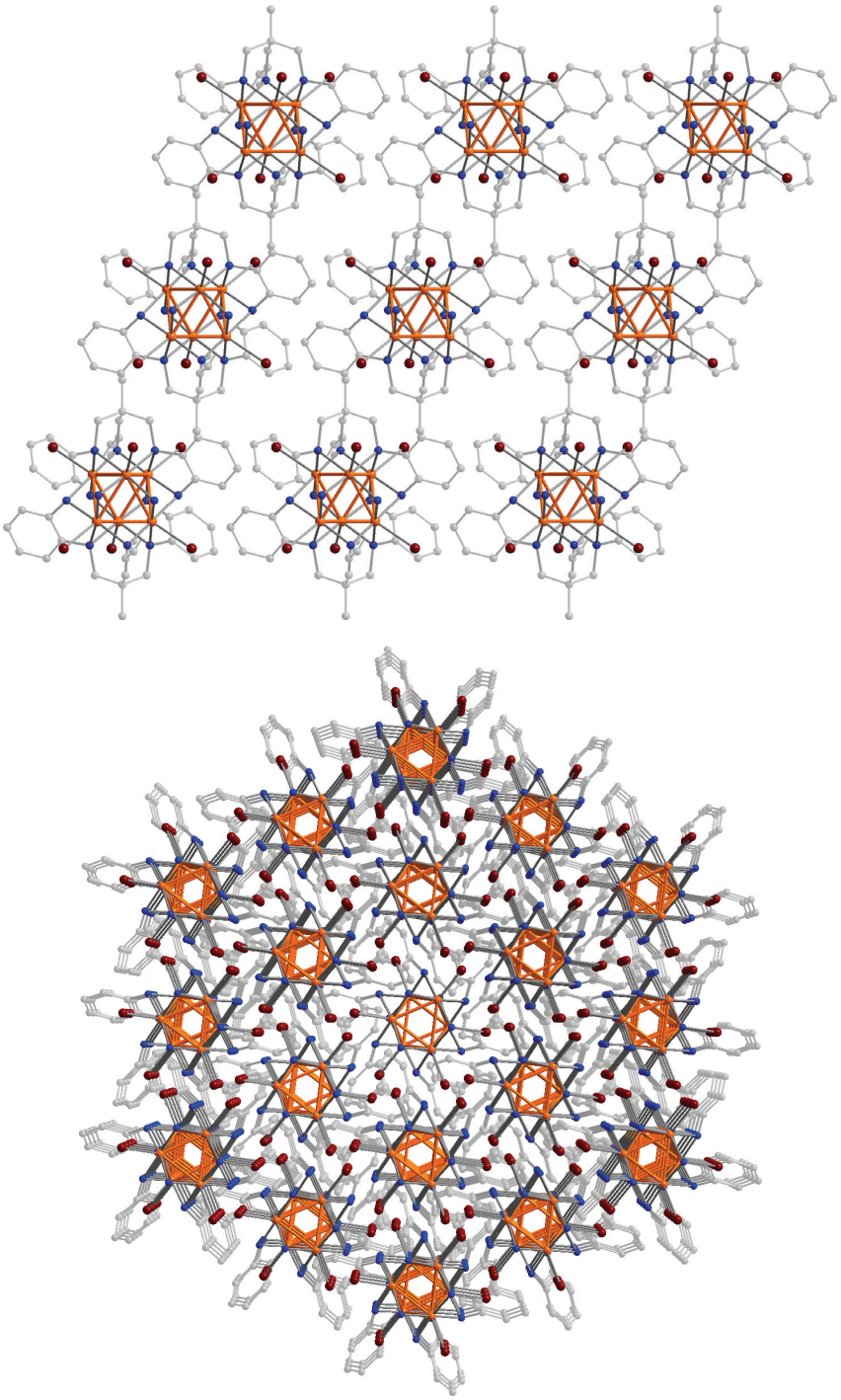

Fig. S2 Crystal packing diagram for **1**, as viewed along the *a* (upper) and *c* (lower) axes. Orange, maroon, gray, and blue ellipsoids represent Fe, Br, C, and N atoms, respectively; H atoms are omitted for clarity.

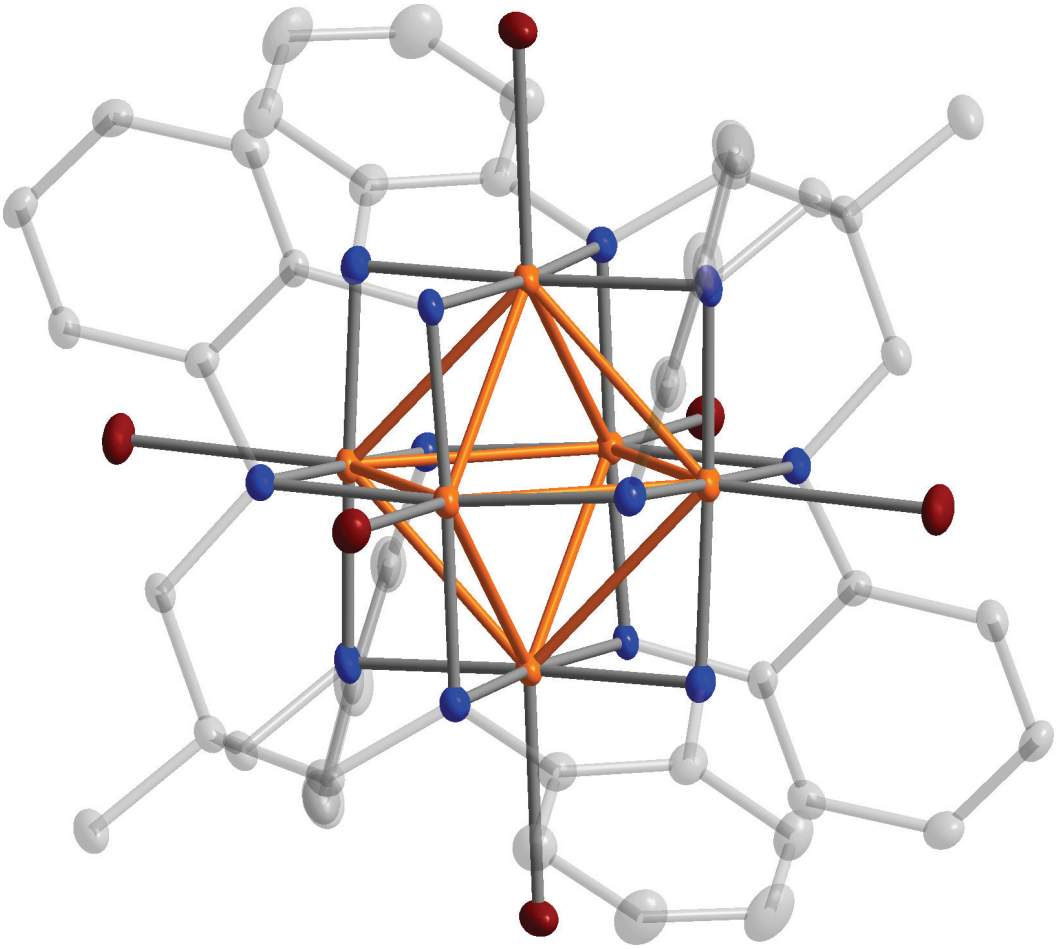

Fig. S2 Crystal structure of $[(^{H}L)_2Fe_6Br_6]^{2-}$, as observed in **2**. Orange, maroon, gray, and blue ellipsoids (50% probability level) represent Fe, Br, C, and N atoms, respectively; H atoms are omitted for clarity. Periphery of $[^{H}L]^{6-}$ ligand is shown transparent to aid visualization of the octahedral Fe_6 core.

Table S1 Selected Interatomic Distances (Å) for **1**.

C1—C2	1.516 (7)	Fe1—Fe1^{i}	2.6782 (17)
C2—C1^{i}	1.516 (7)	Fe1—Fe1^{ii}	2.6782 (17)
C2—C1^{ii}	1.516 (7)	Fe1—Fe1^{iii}	2.7478 (16)
C2—C3	1.531 (15)	Fe1—Fe1^{iv}	2.7478 (16)
C4—C5^{ii}	1.395 (9)	Fe1—N1^{ii}	1.973 (5)
C4—C9^{ii}	1.392 (9)	Fe1—N1	2.015 (5)
C5—C4^{i}	1.395 (9)	Fe1—N2	1.922 (6)
C5—C6	1.399 (9)	Fe1—N2^{iii}	1.972 (5)
C6—C7	1.398 (11)	N1—C1	1.476 (8)
C7—C8	1.391 (11)	N1—C5	1.443 (8)
C8—C9	1.381 (10)	N1—Fe1^{i}	1.973 (5)
C9—C4^{i}	1.392 (9)	N2—C4	1.413 (8)
Fe1—Br1	2.4454 (12)	N2—Fe1^{iv}	1.972 (5)

Symmetry code(s): (i) -*x*+*y*+1, -*x*+1, *z*; (ii) -*y*+1, *x*-*y*, *z*; (iii) *y*+1/3, -*x*+*y*+2/3, -*z*+2/3; (iv) *x*-*y*+1/3, *x*-1/3, -*z*+2/3.

Table S2 Selected Interatomic Angles (°) for **1**.

C1—C2	1.516 (7)	Br1—Fe1—Fe1^{i}	135.85 (4)	N1—Fe1—Fe1^{iii}	90.65 (15)
C2—C1^{i}	1.516 (7)	Br1—Fe1—Fe1^{ii}	138.14 (4)	N1^{ii}—Fe1—Fe1^{iv}	91.56 (15)
C2—C1^{ii}	1.516 (7)	Br1—Fe1—Fe1^{iii}	131.82 (4)	N1—Fe1—Fe1^{iv}	136.95 (15)
C2—C3	1.531 (15)	Br1—Fe1—Fe1^{iv}	133.89 (4)	N1^{ii}—Fe1—N1	95.1 (3)
C4—C5^{ii}	1.395 (9)	Fe1^{i}—Fe1—Fe1^{ii}	60.0	N2—Fe1—Br1	88.68 (16)
C4—C9^{ii}	1.392 (9)	Fe1^{i}—Fe1—Fe1^{iii}	60.83 (2)	N2^{iii}—Fe1—Br1	87.53 (16)
C5—C4^{i}	1.395 (9)	Fe1^{ii}—Fe1—Fe1^{iii}	90.0	N2—Fe1—Fe1^{i}	135.46 (16)
C5—C6	1.399 (9)	Fe1^{i}—Fe1—Fe1^{iv}	90.0	N2^{iii}—Fe1—Fe1^{i}	93.23 (16)
C6—C7	1.398 (11)	Fe1^{ii}—Fe1—Fe1^{iv}	60.83 (2)	N2—Fe1—Fe1^{ii}	87.60 (17)
C7—C8	1.391 (11)	Fe1^{iii}—Fe1—Fe1^{iv}	58.33 (4)	N2^{iii}—Fe1—Fe1^{ii}	134.01 (16)
C8—C9	1.381 (10)	N1^{ii}—Fe1—Br1	89.66 (15)	N2—Fe1—Fe1^{iii}	92.24 (17)
C9—C4^{i}	1.392 (9)	N1—Fe1—Br1	88.71 (15)	N2^{iii}—Fe1—Fe1^{iii}	44.38 (16)
Fe1—Br1	2.4454 (12)	N1^{ii}—Fe1—Fe1^{i}	94.32 (15)	N2—Fe1—Fe1^{iv}	45.85 (16)
N1—C1—C2	116.5 (6)	N1—Fe1—Fe1^{i}	47.14 (15)	N2^{iii}—Fe1—Fe1^{iv}	84.69 (17)
C1^{i}—C2—C1^{ii}	111.9 (4)	Fe1—Fe1^{i}	2.6782 (17)	N2—Fe1—N1^{ii}	83.3 (2)
C1^{i}—C2—C1	111.9 (4)	Fe1—Fe1^{ii}	2.6782 (17)	N2^{iii}—Fe1—N1^{ii}	171.6 (2)
C1^{ii}—C2—C1	111.9 (4)	Fe1—Fe1^{iii}	2.7478 (16)	N2—Fe1—N1	177.0 (2)
C1^{i}—C2—C3	106.9 (5)	Fe1—Fe1^{iv}	2.7478 (16)	N2^{iii}—Fe1—N1	92.7 (2)
C1^{ii}—C2—C3	106.9 (5)	Fe1—N1^{ii}	1.973 (5)	N2—Fe1—N2^{iii}	88.69 (4)
C1—C2—C3	106.9 (5)	Fe1—N1	2.015 (5)	C1—N1—Fe1^{i}	121.5 (4)
C5^{ii}—C4—N2	114.5 (6)	Fe1—N2	1.922 (6)	C1—N1—Fe1	117.1 (4)
C9^{ii}—C4—C5^{ii}	121.3 (6)	Fe1—N2^{iii}	1.972 (5)	C5—N1—C1	108.6 (5)
C9^{ii}—C4—N2	124.2 (6)	N1—C1	1.476 (8)	C5—N1—Fe1^{i}	109.0 (4)
C4^{i}—C5—C6	119.2 (6)	N1—C5	1.443 (8)	C5—N1—Fe1	114.6 (4)
C4^{i}—C5—N1	114.9 (6)	N1—Fe1^{i}	1.973 (5)	Fe1^{i}—N1—Fe1	84.4 (2)
C6—C5—N1	125.8 (6)	N2—C4	1.413 (8)	C4—N2—Fe1	111.6 (4)
C7—C6—C5	119.0 (7)	N2—Fe1^{iv}	1.972 (5)	C4—N2—Fe1^{iv}	119.6 (4)
C8—C7—C6	121.1 (7)	N1^{ii}—Fe1—Fe1^{ii}	48.49 (15)	Fe1—N2—Fe1^{iv}	89.8 (2)
C9—C8—C7	119.9 (7)	N1—Fe1—Fe1^{ii}	93.32 (15)		
C8—C9—C4^{i}	119.4 (7)	N1^{ii}—Fe1—Fe1^{iii}	138.29 (15)		

Symmetry code(s): (i) $-x+y+1, -x+1, z$; (ii) $-y+1, x-y, z$; (iii) $y+1/3, -x+y+2/3, -z+2/3$; (iv) $x-y+1/3, x-1/3, -z+2/3$.

Table S3 Selected Interatomic Distances (Å) for **2**.

Fe1—N4	1.930 (2)	C14—C15	1.384 (5)	N3—C31	1.434 (3)	N1S—C2S	1.397 (7)
Fe1—N6	1.979 (2)	C14—H14A	0.9500	N3—C5	1.478 (4)	P1—C61	1.786 (3)
Fe1—N1	1.987 (2)	C15—C16	1.386 (4)	N3—Fe2^{i}	1.992 (2)	P1—C71	1.793 (3)
Fe1—N2	2.017 (2)	C15—H15A	0.9500	N4—C16	1.408 (4)	P1—C51	1.796 (3)
Fe1—Br1	2.4908 (5)	C21—C26	1.400 (4)	N4—Fe3^{i}	1.978 (2)	P1—C41	1.799 (3)
Fe1—Fe3	2.7457 (6)	C21—C22	1.405 (4)	N4—H4B	0.9300	C41—C42	1.387 (5)
Fe1—Fe2^{i}	2.7486 (6)	C22—C23	1.386 (5)	N5—C26	1.410 (4)	C41—C46	1.400 (5)
Fe1—Fe3^{i}	2.7613 (6)	C22—H22A	0.9500	N5—H5C	0.9300	C42—C43	1.397 (5)
Fe1—Fe2	2.7683 (6)	C23—C24	1.390 (5)	N6—C36	1.408 (4)	C43—C44	1.377 (6)
Fe2—N6	1.936 (2)	C23—H23A	0.9500	N6—H6A	0.9300	C44—C45	1.382 (6)
Fe2—N5	1.981 (2)	C24—C25	1.396 (5)	C1—C2	1.548 (4)	C45—C46	1.391 (5)
Fe2—N3^{i}	1.992 (2)	C24—H24A	0.9500	C1—H1A	0.9800	C51—C52	1.401 (4)
Fe2—N1^{i}	2.013 (2)	C25—C26	1.390 (4)	C1—H1B	0.9800	C52—C53	1.384 (5)
Fe2—Br2	2.5171 (5)	C25—H25A	0.9500	C1—H1C	0.9800	C53—C54	1.380 (5)
Fe2—Fe1^{i}	2.7486 (6)	C31—C36^{i}	1.393 (4)	C2—C4	1.511 (4)	C54—C55	1.392 (5)
Fe2—Fe3^{i}	2.7587 (6)	C31—C32	1.398 (4)	C2—C3	1.511 (4)	C55—C56	1.393 (5)
Fe2—Fe3	2.7629 (6)	C32—C33	1.388 (4)	C2—C5	1.517 (4)	C61—C62	1.376 (5)
Fe3—N5	1.932 (2)	C32—H32A	0.9500	C3—H3A	0.9900	C61—C66	1.400 (5)
Fe3—N4^{i}	1.978 (2)	C33—C34^{i}	1.394 (4)	C3—H3B	0.9900	C62—C63	1.393 (5)
Fe3—N2	1.994 (2)	C33—H33A	0.9500	C4—H4A	0.9900	C63—C64	1.380 (6)
Fe3—N3	2.023 (2)	C34—C35	1.391 (4)	C4—H4C	0.9900	C64—C65	1.368 (5)
Fe3—Br3	2.5040 (5)	C34—C33^{i}	1.394 (4)	C5—H5A	0.9900	C65—C66	1.381 (5)
Fe3—Fe2^{i}	2.7587 (6)	C34—H34A	0.9500	C5—H5B	0.9900	C71—C72	1.390 (4)
Fe3—Fe1^{i}	2.7613 (6)	C35—C36	1.389 (4)	C11—C16	1.395 (4)	C71—C76	1.399 (4)
N1—C11	1.438 (4)	C35—H35A	0.9500	C11—C12	1.398 (4)	C72—C73	1.387 (4)
N1—C3	1.485 (4)	C36—C31^{i}	1.393 (4)	C12—C13	1.384 (5)	C73—C74	1.385 (4)
N1—Fe2^{i}	2.013 (2)	O1S—C1S	1.150 (8)	C12—H12A	0.9500	C74—C75	1.382 (5)
N2—C21	1.434 (4)	N1S—C1S	1.251 (7)	C13—C14	1.384 (5)	C75—C76	1.381 (5)
N2—C4	1.473 (4)	N1S—C3S	1.378 (6)	C13—H13A	0.9500		

Symmetry code(s): (i) -*x*+1, -*y*, -*z*.

Table S4 Selected Interatomic Angles (°) for **2**.

Fe1—N4	1.930 (2)	C14—C15	1.384 (5)
Fe1—N6	1.979 (2)	C14—H14A	0.9500
Fe1—N1	1.987 (2)	C15—C16	1.386 (4)
Fe1—N2	2.017 (2)	C15—H15A	0.9500
Fe1—Br1	2.4908 (5)	C21—C26	1.400 (4)
Fe1—Fe3	2.7457 (6)	C21—C22	1.405 (4)
Fe1—Fe2^{i}	2.7486 (6)	C22—C23	1.386 (5)
Fe1—Fe3^{i}	2.7613 (6)	C22—H22A	0.9500
Fe1—Fe2	2.7683 (6)	C23—C24	1.390 (5)
Fe2—N6	1.936 (2)	C23—H23A	0.9500
Fe2—N5	1.981 (2)	C24—C25	1.396 (5)
Fe2—N3^{i}	1.992 (2)	C24—H24A	0.9500
Fe2—N1^{i}	2.013 (2)	C25—C26	1.390 (4)
Fe2—Br2	2.5171 (5)	C25—H25A	0.9500
Fe2—Fe1^{i}	2.7486 (6)	C31—C36^{i}	1.393 (4)
Fe2—Fe3^{i}	2.7587 (6)	C31—C32	1.398 (4)
Fe2—Fe3	2.7629 (6)	C32—C33	1.388 (4)
Fe3—N5	1.932 (2)	C32—H32A	0.9500
Fe3—N4^{i}	1.978 (2)	C33—C34^{i}	1.394 (4)
Fe3—N2	1.994 (2)	C33—H33A	0.9500
Fe3—N3	2.023 (2)	C34—C35	1.391 (4)
Fe3—Br3	2.5040 (5)	C34—C33^{i}	1.394 (4)
Fe3—Fe2^{i}	2.7587 (6)	C34—H34A	0.9500
Fe3—Fe1^{i}	2.7613 (6)	C35—C36	1.389 (4)
N1—C11	1.438 (4)	C35—H35A	0.9500
N1—C3	1.485 (4)	C36—C31^{i}	1.393 (4)
N1—Fe2^{i}	2.013 (2)	O1S—C1S	1.150 (8)
N2—C21	1.434 (4)	N1S—C1S	1.251 (7)
N2—C4	1.473 (4)	N1S—C3S	1.378 (6)
N3—C31	1.434 (3)	N1S—C2S	1.397 (7)
N3—C5	1.478 (4)	P1—C61	1.786 (3)
N3—Fe2^{i}	1.992 (2)	P1—C71	1.793 (3)
N4—C16	1.408 (4)	P1—C51	1.796 (3)
N4—Fe3^{i}	1.978 (2)	P1—C41	1.799 (3)
N4—H4B	0.9300	C41—C42	1.387 (5)

N5—C26	1.410 (4)	C41—C46	1.400 (5)
N5—H5C	0.9300	C42—C43	1.397 (5)
N6—C36	1.408 (4)	C43—C44	1.377 (6)
N6—H6A	0.9300	C44—C45	1.382 (6)
C1—C2	1.548 (4)	C45—C46	1.391 (5)
C1—H1A	0.9800	C51—C52	1.401 (4)
C1—H1B	0.9800	C52—C53	1.384 (5)
C1—H1C	0.9800	C53—C54	1.380 (5)
C2—C4	1.511 (4)	C54—C55	1.392 (5)
C2—C3	1.511 (4)	C55—C56	1.393 (5)
C2—C5	1.517 (4)	C61—C62	1.376 (5)
C3—H3A	0.9900	C61—C66	1.400 (5)
C3—H3B	0.9900	C62—C63	1.393 (5)
C4—H4A	0.9900	C63—C64	1.380 (6)
C4—H4C	0.9900	C64—C65	1.368 (5)
C5—H5A	0.9900	C65—C66	1.381 (5)
C5—H5B	0.9900	C71—C72	1.390 (4)
C11—C16	1.395 (4)	C71—C76	1.399 (4)
C11—C12	1.398 (4)	C72—C73	1.387 (4)
C12—C13	1.384 (5)	C73—C74	1.385 (4)
C12—H12A	0.9500	C74—C75	1.382 (5)
C13—C14	1.384 (5)	C75—C76	1.381 (5)
C13—H13A	0.9500	C11—N1—C3	108.3 (2)
N4—Fe1—N6	89.77 (10)	C11—N1—Fe1	108.14 (18)
N4—Fe1—N1	83.04 (10)	C3—N1—Fe1	120.49 (19)
N6—Fe1—N1	172.68 (10)	C11—N1—Fe2^{i}	115.63 (18)
N4—Fe1—N2	177.55 (10)	C3—N1—Fe2^{i}	116.28 (17)
N6—Fe1—N2	91.58 (10)	Fe1—N1—Fe2^{i}	86.81 (10)
N1—Fe1—N2	95.55 (10)	C21—N2—C4	108.6 (2)
N4—Fe1—Br1	88.41 (7)	C21—N2—Fe3	108.51 (19)
N6—Fe1—Br1	88.88 (7)	C4—N2—Fe3	120.53 (18)
N1—Fe1—Br1	89.53 (7)	C21—N2—Fe1	115.09 (18)
N2—Fe1—Br1	89.58 (7)	C4—N2—Fe1	116.5 (2)
N4—Fe1—Fe3	135.51 (7)	Fe3—N2—Fe1	86.39 (9)
N6—Fe1—Fe3	92.67 (7)	C31—N3—C5	108.5 (2)
N1—Fe1—Fe3	93.43 (7)	C31—N3—Fe2^{i}	108.52 (18)
N2—Fe1—Fe3	46.46 (7)	C5—N3—Fe2^{i}	121.14 (19)

Br1—Fe1—Fe3	136.03 (2)	C31—N3—Fe3	114.92 (18)
N4—Fe1—Fe2^{i}	87.27 (7)	C5—N3—Fe3	115.75 (18)
N6—Fe1—Fe2^{i}	134.31 (7)	Fe2^{i}—N3—Fe3	86.81 (9)
N1—Fe1—Fe2^{i}	47.00 (7)	C16—N4—Fe1	110.66 (19)
N2—Fe1—Fe2^{i}	93.24 (7)	C16—N4—Fe3^{i}	120.05 (19)
Br1—Fe1—Fe2^{i}	136.52 (2)	Fe1—N4—Fe3^{i}	89.90 (10)
Fe3—Fe1—Fe2^{i}	60.277 (16)	C26—N5—Fe3	110.68 (19)
N4—Fe1—Fe3^{i}	45.75 (7)	C26—N5—Fe2	118.87 (18)
N6—Fe1—Fe3^{i}	86.13 (7)	Fe3—N5—Fe2	89.84 (10)
N1—Fe1—Fe3^{i}	89.82 (7)	C36—N6—Fe2	110.77 (18)
N2—Fe1—Fe3^{i}	136.39 (7)	C36—N6—Fe1	118.96 (19)
Br1—Fe1—Fe3^{i}	133.81 (2)	Fe2—N6—Fe1	90.00 (10)
Fe3—Fe1—Fe3^{i}	90.096 (18)	C4—C2—C3	113.0 (2)
Fe2^{i}—Fe1—Fe3^{i}	60.191 (15)	C4—C2—C5	112.7 (3)
N4—Fe1—Fe2	93.37 (7)	C3—C2—C5	112.1 (3)
N6—Fe1—Fe2	44.37 (7)	C4—C2—C1	105.9 (2)
N1—Fe1—Fe2	137.18 (7)	C3—C2—C1	106.2 (3)
N2—Fe1—Fe2	89.02 (7)	C5—C2—C1	106.3 (2)
Br1—Fe1—Fe2	133.15 (2)	N1—C3—C2	116.1 (2)
Fe3—Fe1—Fe2	60.140 (15)	N2—C4—C2	116.1 (2)
Fe2^{i}—Fe1—Fe2	90.303 (17)	N3—C5—C2	116.0 (2)
Fe3^{i}—Fe1—Fe2	59.853 (16)	C16—C11—C12	118.9 (3)
N6—Fe2—N5	90.29 (10)	C16—C11—N1	115.2 (3)
N6—Fe2—N3^{i}	82.85 (10)	C12—C11—N1	125.8 (3)
N5—Fe2—N3^{i}	173.07 (10)	C13—C12—C11	119.9 (3)
N6—Fe2—N1^{i}	177.60 (10)	C12—C13—C14	120.5 (3)
N5—Fe2—N1^{i}	91.75 (10)	C15—C14—C13	120.2 (3)
N3^{i}—Fe2—N1^{i}	95.08 (10)	C14—C15—C16	119.6 (3)
N6—Fe2—Br2	88.85 (7)	C15—C16—C11	120.8 (3)
N5—Fe2—Br2	88.44 (7)	C15—C16—N4	124.5 (3)
N3^{i}—Fe2—Br2	90.40 (7)	C11—C16—N4	114.7 (3)
N1^{i}—Fe2—Br2	89.96 (7)	C26—C21—C22	118.4 (3)
N6—Fe2—Fe1^{i}	134.95 (7)	C26—C21—N2	115.2 (3)
N5—Fe2—Fe1^{i}	92.42 (7)	C22—C21—N2	126.4 (3)
N3^{i}—Fe2—Fe1^{i}	93.15 (7)	C23—C22—C21	120.2 (3)
N1^{i}—Fe2—Fe1^{i}	46.20 (7)	C22—C23—C24	120.7 (3)
Br2—Fe2—Fe1^{i}	136.16 (2)	C23—C24—C25	119.8 (3)

N6—Fe2—Fe3^{i}	87.02 (7)	C26—C25—C24	119.4 (3)
N5—Fe2—Fe3^{i}	133.88 (7)	C25—C26—C21	121.3 (3)
N3^{i}—Fe2—Fe3^{i}	47.07 (7)	C25—C26—N5	123.8 (3)
N1^{i}—Fe2—Fe3^{i}	92.46 (7)	C21—C26—N5	114.9 (3)
Br2—Fe2—Fe3^{i}	137.44 (2)	C36^{i}—C31—C32	118.9 (3)
Fe1^{i}—Fe2—Fe3^{i}	59.810 (15)	C36^{i}—C31—N3	115.1 (2)
N6—Fe2—Fe3	93.10 (7)	C32—C31—N3	126.0 (3)
N5—Fe2—Fe3	44.36 (7)	C33—C32—C31	120.2 (3)
N3^{i}—Fe2—Fe3	136.72 (7)	C32—C33—C34^{i}	120.4 (3)
N1^{i}—Fe2—Fe3	89.23 (7)	C35—C34—C33^{i}	119.7 (3)
Br2—Fe2—Fe3	132.73 (2)	C36—C35—C34	119.8 (3)
Fe1^{i}—Fe2—Fe3	60.132 (15)	C35—C36—C31^{i}	121.0 (3)
Fe3^{i}—Fe2—Fe3	89.794 (18)	C35—C36—N6	124.0 (3)
N6—Fe2—Fe1	45.63 (7)	C31^{i}—C36—N6	115.0 (2)
N5—Fe2—Fe1	86.29 (7)	C1S—N1S—C3S	117.2 (7)
N3^{i}—Fe2—Fe1	89.61 (7)	C1S—N1S—C2S	122.9 (8)
N1^{i}—Fe2—Fe1	135.78 (7)	C3S—N1S—C2S	119.8 (6)
Br2—Fe2—Fe1	134.04 (2)	C61—P1—C71	109.47 (14)
Fe1^{i}—Fe2—Fe1	89.697 (17)	C61—P1—C51	108.56 (15)
Fe3^{i}—Fe2—Fe1	59.947 (16)	C71—P1—C51	107.26 (15)
Fe3—Fe2—Fe1	59.524 (15)	C61—P1—C41	106.82 (15)
N5—Fe3—N4^{i}	89.44 (10)	C71—P1—C41	112.66 (14)
N5—Fe3—N2	83.17 (10)	C51—P1—C41	112.00 (15)
N4^{i}—Fe3—N2	172.53 (10)	O1S—C1S—N1S	142.6 (11)
N5—Fe3—N3	177.67 (10)	C42—C41—C46	120.5 (3)
N4^{i}—Fe3—N3	91.92 (10)	C42—C41—P1	121.3 (3)
N2—Fe3—N3	95.44 (10)	C46—C41—P1	118.1 (3)
N5—Fe3—Br3	88.94 (7)	C41—C42—C43	119.5 (4)
N4^{i}—Fe3—Br3	87.89 (7)	C44—C43—C42	119.9 (4)
N2—Fe3—Br3	90.88 (7)	C43—C44—C45	120.7 (3)
N3—Fe3—Br3	89.22 (7)	C44—C45—C46	120.4 (4)
N5—Fe3—Fe1	87.87 (7)	C45—C46—C41	119.0 (4)
N4^{i}—Fe3—Fe1	133.94 (7)	C56—C51—C52	120.5 (3)
N2—Fe3—Fe1	47.15 (7)	C56—C51—P1	120.2 (2)
N3—Fe3—Fe1	92.54 (7)	C52—C51—P1	119.1 (3)
Br3—Fe3—Fe1	137.98 (2)	C53—C52—C51	119.3 (3)
N5—Fe3—Fe2^{i}	135.71 (7)	C54—C53—C52	120.7 (3)

N4^{i}—Fe3—Fe2^{i}	92.60 (7)	C53—C54—C55	120.0 (3)
N2—Fe3—Fe2^{i}	93.44 (8)	C54—C55—C56	120.3 (3)
N3—Fe3—Fe2^{i}	46.12 (7)	C55—C56—C51	119.1 (3)
Br3—Fe3—Fe2^{i}	135.34 (2)	C62—C61—C66	119.9 (3)
Fe1—Fe3—Fe2^{i}	59.913 (16)	C62—C61—P1	120.0 (3)
N5—Fe3—Fe1^{i}	93.12 (7)	C66—C61—P1	119.9 (3)
N4^{i}—Fe3—Fe1^{i}	44.35 (7)	C61—C62—C63	119.8 (4)
N2—Fe3—Fe1^{i}	136.88 (7)	C64—C63—C62	119.6 (4)
N3—Fe3—Fe1^{i}	89.17 (7)	C65—C64—C63	121.0 (4)
Br3—Fe3—Fe1^{i}	132.11 (2)	C64—C65—C66	119.7 (3)
Fe1—Fe3—Fe1^{i}	89.904 (18)	C65—C66—C61	119.9 (3)
Fe2^{i}—Fe3—Fe1^{i}	60.201 (15)	C72—C71—C76	120.1 (3)
N5—Fe3—Fe2	45.80 (7)	C72—C71—P1	120.1 (2)
N4^{i}—Fe3—Fe2	85.96 (7)	C76—C71—P1	119.7 (2)
N2—Fe3—Fe2	89.64 (7)	C73—C72—C71	119.6 (3)
N3—Fe3—Fe2	136.19 (7)	C74—C73—C72	120.1 (3)
Br3—Fe3—Fe2	134.28 (2)	C75—C74—C73	120.5 (3)
Fe1—Fe3—Fe2	60.336 (15)	C76—C75—C74	119.9 (3)
Fe2^{i}—Fe3—Fe2	90.206 (18)	C75—C76—C71	119.8 (3)
Fe1^{i}—Fe3—Fe2	59.677 (16)		

Symmetry code(s): (i) -*x*+1, -*y*, -*z*.

References.

(1) Q. Zhao, T. D. Harris and T. A. Betley, *submitted for publication.*
(2) *APEX2 v.2009*; Bruker Analytical X-Ray Systems, Inc: Madison, WI, 2009.
(3) Sheldrick, G. M. *SADABS, Version 2.03*; Bruker Analytical X-Ray Systems, Inc: Madison, WI, 2000.
(4) Spek, A. L. *PLATON, A Multipurpose Crystallographic Tool*; Utrecht University, Utrecht, The Netherlands, 2010.
(5) Sheldrick, G. M. *SHELXTL, Version 6.12*; Bruker Analytical X-Ray Systems, Inc: Madison, WI, 2000.