Electronic Supplementary Information

Cluster dynamics of heterometallic trinuclear clusters during ligand substitution, redox chemistry, and group transfer processes

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Experimental Methods

Materials and methods. All manipulations involving metal complexes were carried out using standard Schlenk line or glovebox techniques under a dinitrogen atmosphere. All glassware was oven-dried for a minimum of 8 h and cooled in an evacuated antechamber prior to use in a glovebox. Celite ® 545 (J. T. Baker) was dried in a Schlenk flask for 24 h under dynamic vacuum while heating to at least 150 °C prior to use in the drybox. Benzene, diethyl ether, hexanes, and tetrahydrofuran (THF) were 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 pentane and pyridine were purchased from Sigma Aldrich and stored over 4 Å molecular sieves prior to use. Benzene-d_6 and tetrahydrofuran-d_8 were purchased from Cambridge Isotope Laboratories and were degassed and stored over 4 Å molecular sieves prior to use. Non-halogenated solvents were typically tested with a standard purple solution of sodium benzophenone ketyl in THF in order to confirm effective oxygen and moisture removal. Ligand ($^{tbs}LH_6$),[1] ligand precursors,[1] ($^{tbs}LH_2$)Fe_2,[2] and (^{tbs}L)Fe_3(thf)[1] were synthesized as previously reported. $Fe_2(N(SiMe_3)_2)_4$,[3] $Zn(N(SiMe_3)_2)_2$,[3] $ZnCl_2py_2$,[4] KC_8,[5] PhN_3,[6] and $(3,5\text{-}CF_3)_2C_6H_3N_3$[7] were prepared following published methods. The adducts $Fe(N(SiMe_3)_2)_2(py)_2$ and $Zn(N(SiMe_3)_2)_2(py)$ were prepared by adding the appropriate number of equivalents of pyridine to the unsolvated precursors. All other reagents were purchased from commercial vendors and used without further purification unless explicitly stated.

Physical Measurements. All of the measurements for the metal complexes were made under anaerobic conditions unless explicitly stated. Elemental analysis of $[NBu_4][(^{tbs}L)Zn_3(\mu^3\text{–}Cl)]$ (**8**) was performed by Complete Analysis Laboratories, Inc., Parsippany, NJ. All other elemental analyses were performed in-house on a 2400 Series II CHNS/O Elemental Analyzer manufactured by Perkin Elmer, Inc. ^{1}H and ^{19}F NMR spectra were recorded on Varian Unity/Inova 500 or 600 MHz- spectrometers. Chemical shifts in ^{1}H NMR spectra were referenced to solvent residual resonances (C_6D_6, 7.16 ppm; THF-d_8, 3.58 and 1.73 ppm). Chemical shifts in ^{19}F NMR spectra were referenced to $BF_3(Oet_2)$ (–153 ppm) or fluorobenzene (–113 ppm).

Zero-Field ^{57}Fe Mössbauer Spectroscopy. ^{57}Fe Mössbauer spectra were measured with a constant acceleration spectrometer (SEE Co, Minneapolis, MN). Unless otherwise indicated, all ^{57}Fe Mössbauer spectra were recorded under zero applied field. Samples were prepared as Paratone-N mulls in a glovebox and frozen in liquid nitrogen prior to handling in air. Isomer shifts are quoted relative to α-Fe metal at room temperature. Data were processed, fitted, and analyzed using an in-house package for IGOR Pro 6 (Wavemetrics, Lake Oswego, OR) written by Evan R. King.

X-ray Fluorescence Spectroscopy. X-ray fluorescence analyses were recorded using an Olympus Delta Innov-X XRF analyzer with no additional filter (Olympus, NDT, Inc., Waltham, MA). Samples for the calibration curve were prepared by dissolving ferrocence and *bis*[4,4,4-trifluoro-1-(2-thienyl-1,3-butanedionato)]Zn·(TMEDA) in benzene, and then lyophilizing the solution to afford a homogenous mixture of solids. The areas of the Kα peaks for Fe and Zn were calculated by integration using IGOR Pro 6 (Wavemetrics, Lake Oswego, OR). Quantification was performed using the Kα peak area. Fe:Zn molar ratios in samples were determined from the peak area ratios using a linear fit to the calibration curve (Figure S13).

X-ray Diffraction Techniques. All structures were collected on a Bruker three-circle platform goniometer equipped with an Apex II CCD area detector and an Oxford cryostream cooling device at 100 K. Structures were obtained using radiation from a graphite fine-focus sealed tube Mo Kα

(0.71073 Å) source or synchrotron radiation (0.41328 Å) using the Advanced Photon Source (APS) at Argonne National Laboratory. Crystals were mounted on a cryoloop or glass fiber pin using Paratone-N oil. Data were collected as a series of φ and/or ω scans. Data were integrated using SAINT[8] and scaled with either a numerical or multi-scan absorption correction using SADABS.[8] The structures were solved by intrinsic phasing or direct methods using SHELXT/SHELXS[9] and refined against F^2 on all data by full matrix least squares with SHELXL[9] using the OLEX2 interface.[10] All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were placed at idealized positions and refined using a riding model. The isotropic displacement parameters of all hydrogen atoms were fixed to 1.2 times the atoms they are linked to (1.5 times for methyl groups). Unless otherwise indicated, all depictions of solid-state structures are displayed as 50% probability thermal ellipsoid plots. Further details on particular structures are noted in the X-Ray Diffraction Techniques section.

SQUID Magnetometry. Magnetic measurements were recorded using a Quantum Design MPMS-3 system. Samples used for magnetic characterization were prepared by carefully adding carefully weighed, finely crushed microcrystalline powder (ca. 25 mg) to the bottom of a low-paramagnetic impurity 500 MHz borosilicate NMR tube in an air-free, Argon-filled glovebox. An equal volume of n-eicosane was added to the tube (~30 mg); all weighing was performed using plastic anti-static spatulas. The NMR tube was then fitted with a gas-line adaptor, removed from the glovebox, and transferred to a Schlenk line. The tube was then flame sealed under vacuum, and the eicosane was melted using a 40-43 °C hot water bath. Upon cooling, the product-eicosane mixture formed a solid matrix. The sealed ampule was placed in a straw and suspended in the magnetometer. Dc magnetic susceptibility data were collected in the temperature range 1.8–300 K under applied fields of 0.1 and 0.5 T. Susceptibility data were corrected for the diamagnetic contribution of a blank sample consisting of eicosane, capsule and straw. The magnetic susceptibilities were adjusted for diamagnetic contributions using the constitutive corrections from Pascal's constants.[11] Dc susceptibility data and magnetization data were fitted using PHI.[12]

Synthesis.

(^{tbs}L)Fe_3(py) (2). *Method 1*: A solution of $^{tbs}LH_6$ (109 mg, 0.146 mmol) and $Fe(N(SiMe_3)_2)_2(py)_2$ (234 mg, 0.438 mmol) in benzene (2 mL) was heated to 120 °C for 3 days. The reaction mixture was lyophilized and extracted with diethyl ether; the remaining solid was identified as pure (^{tbs}L)Fe_3(py) following extraction in benzene, filtration through a glass wool plug, and lyophilization (29.2 mg). The diethyl ether fraction was filtered through a glass wool plug and concentrated, and crystallization was achieved at –33 °C to yield brown crystalline product (58.1 mg). The two fractions resulted in an overall yield of 87.3 mg of product (61%).

Method 2: To (^{tbs}L)Fe_3(thf) (115 mg, 0.117 mmol) in benzene (2 mL) was added a solution of pyridine (14.4 mg, 0.182 mmol) in benzene (2 mL). The reaction mixture was stirred at room temperature for 1 h, then concentrated *in vacuo* and crystallized from concentrated diethyl ether. Crystallization at –33 °C yielded 86.4 mg of product (74%) ^{1}H NMR (500 MHz, C_6D_6): δ 222.5, 113.7, 66.8, 55.7, 54.1, 49.3, 46.0, 43.9, 31.4, 26.2, 23.2, 3.3, 1.1, –1.1, –5.9, –17.0, –23.0, –53.0, –77.9, –95.5, –105.1, –197.9, –208.1. ^{57}Fe Mössbauer (90 K) (δ, $|\Delta E_Q|$ (mm/s)): component 1 (38%): 0.33, 1.84 (Γ = 0.18 mm/s); component 2 (28%): 0.55, 1.76 (Γ = 0.16 mm/s), component 3 (33%): 0.74, 1.39 (Γ = 0.29 mm/s). Calc. for $C_{47}H_{71}Fe_3N_7Si_3$: C, 57.26; H, 7.26; N, 9.94. Found: C, 57.61; H, 7.21; N, 10.09.

[Na(thf)][(^{tbs}L)Fe$_2$Na(thf)] (4). To a frozen solution of NaN(SiMe$_3$)$_2$ (166.7 mg, 0.909 mmol) in THF (3 mL) was added (^{tbs}LH$_2$)Fe$_2$ (387.8 mg, 0.454 mmol) in THF (3 mL). The reaction mixture was frozen to keep the layers separate, then thawed to allow slow diffusion of the layers, and stirred at room temperature over the course of 2 h. The volatile components of the reaction mixture were removed *in vacuo*, then washed with hexanes. The remaining solid was collected with THF and filtered through a glass wool plug. Removal of the volatile components from the filtrate *in vacuo* yielded 467.7 mg of dark brown solid (99%). It is noted that crystallization of **4** from ether solution at –33 °C yields a composition differing in the coordinated solvent; refer to the X-Ray Diffraction Techniques section. ^{1}H NMR (500 MHz, THF-d_8): δ 136.5, 89.8, 77.8, 48.7, 45.0, 41.3, 37.4, 31.2, 24.8, 23.8, 14.1, 7.3, 1.3, 0.9, –1.3, –3.6, –5.5, –9.1, –11.2, –15.3, –19.8, –34.6, –38.5, –39.2, –43.5, –44.2, –65.2, –73.4. ^{57}Fe Mössbauer (90 K) (δ, |ΔE$_Q$| (mm/s)): component 1 (50%): 0.54, 0.87 (Γ = 0.16 mm/s); component 2 (50%): 0.47, 1.51 (Γ = 0.16 mm/s). Calc. for C$_{50}$H$_{82}$Fe$_2$N$_6$Na$_2$O$_2$Si$_3$: C, 57.68; H, 7.94; N, 8.07. Found: C, 57.68; H, 7.90; N, 8.20.

(^{tbs}L)Fe$_2$Zn(thf) (5). To ZnCl$_2$ (19.2 mg, 0.14 mmol) frozen in THF (3 mL) was added (^{tbs}L)Fe$_2$Na$_2$(thf)$_2$ (**4**) (146.3 mg, 0.14 mmol) in THF (3 mL). The reaction mixture was frozen to keep the layers separate, then thawed to allow slow diffusion of the layers, and stirred at room temperature overnight. The volatile components of the reaction mixture were removed *in vacuo*, and the resulting dark brown solid was extracted in hexanes with drops of benzene. The dark brown extracts were filtered through a Celite plug, and maintenance of the filtrate at –33 °C yielded 117 mg of dark brown crystalline product (84%). ^{1}H NMR (600 MHz, C$_6$D$_6$): δ 143.0, 108.7, 45.3, 41.0, 27.4, 25.6. 23.7, 22.6, 19.1, 17.0, 14.1, 9.5, 8.3, 6.0, 5.4, 4.1, 3.8, 3.1, 1.8, 1.7, 1.6, 1.5, 1.2, 1.0, 1.0, 0.9, –0.6, –1.1, –2.0, –2.2, –5.4, –8.5, –10.4, –11.2, –15.4, –17.8, –23.8, –28.1, –41.4, –42.0, –54.3. ^{57}Fe Mössbauer (90 K) (δ, |ΔE$_Q$| (mm/s)): component 1 (50%): 0.6, 1.83; component 2 (50%): 0.84, 1.55. Calc. for C$_{46}$H$_{74}$Fe$_2$N$_6$Si$_3$Zn: C, 55.90; H, 7.55; N, 8.50. Found: C, 56.30; H, 7.89; N, 8.29. Fe/Zn ratio by XRF: 2.2:1.

(^{tbs}L)Fe$_2$Zn(py) (6). To ZnCl$_2$(py) (30.8 mg, 0.10 mmol) frozen in benzene (2 mL) was added (^{tbs}L)Fe$_2$Na$_2$(thf)$_2$ (99 mg, 0.095 mmol) in benzene (2 mL). The reaction mixture was frozen to keep the layers separate, then thawed to allow slow diffusion of the layers, and stirred at room temperature overnight. The volatile components of the reaction mixture were removed *in vacuo*, and the brown solids were extracted in diethyl ether. Filtration of the extracts through a Celite plug, and maintenance of the filtrate at –33 °C yielded 70.7 mg of dark brown crystalline product (75%). ^{1}H NMR (600 MHz, C$_6$D$_6$): δ 129.8, 97.8, 37.9, 27.3, 25.3, 24.9, 19.9, 19.7, 16.0, 14.2, 10.5, 4.3, 3.6, 3.3, 1.7, 1.6, 1.5, 1.2, 1.1, 1.0, 0.9, 0.1, –0.2, –0.6, –0.81, –0.84, –2.0, –3.0, –7.8, –10.9, –16.7, –21,9, –26.0, –36.0, –40.3. ^{57}Fe Mössbauer (90 K) (δ, |ΔE$_Q$| (mm/s)): component 1 (50%): 0.61, 1.68; component 2 (50%): 0.79, 1.63. Calc. for C$_{47}$H$_{71}$Fe$_2$N$_7$Si$_3$Zn: C, 56.71; H, 7.19; N, 9.85. Found: C, 57.09; H, 7.48; N, 9.78. Fe/Zn ratio by XRF: 2.1:1.

[NBu$_4$][(^{tbs}L)Fe$_3$(μ^3–Cl)] (7). To [NBu$_4$][Cl] (28.2 mg, 0.101 mmol) frozen in THF (2 mL) was added (^{tbs}L)Fe$_3$(thf) (**1**) (99.6 mg, 0.102 mmol) in THF (2 mL). The reaction mixture was frozen to keep the layers separate, then thawed to allow slow diffusion of the layers, and stirred at room temperature over the course of 3 hours. The volatile components of the reaction mixture were removed *in vacuo*, and the brown solids were extracted in diethyl ether. Filtration of the extracts through a Celite plug, and maintenance of the filtrate at -33 °C yielded 100.9 mg of dark brown crystals (>99%). ^{1}H NMR (500 MHz, C$_6$D$_6$): δ 184.7, 56.9, 36.1, 32.7, 31.1, 7.3, 5.8, 3.4, 3.1, 1.6, 1.1, 1.0, 0.7, 0.2, –36.9, –41.4. ^{57}Fe Mössbauer (90 K) (δ, |ΔE$_Q$| (mm/s)): 0.72, 1.31 (Γ = 0.24 mm/s). Calc. for C$_{58}$H$_{102}$ClFe$_3$N$_7$Si$_3$: C, 58.80; H, 8.68; N, 8.28. Found: C, 58.98; H, 8.60; N, 8.66.

[NBu_4][(^{tbs}L)Zn_3(μ^3–Cl)] (8). In a thick-walled bomb flask with a Teflon screw cap, $Zn(N(SiMe_3)_2)_2$(py) (464 mg, 1.0 mmol) and $^{tbs}LH_6$ (247.7 mg, 0.33 mmol) were combined in benzene (10 mL). The reaction mixture was heated to 110 °C for five hours. This solution was added to a vial containing [NBu_4][Cl] (93 mg, 0.33 mmol), and the resulting mixture stirred at room temperature overnight. A white precipitate formed which was filtered and washed with benzene. The remaining solid was Extracted in THF and filtered through a glass wool plug. The filtrate was layered with hexanes, and maintenance of the mixture at –33 °C yielded 287.2 mg of white crystalline product (71% yield). ^{1}H NMR (500 MHz, THF-d_8): δ 6.97 (d, 3H), 6.76 (d, 3H), 6.49 (t, 3H), 6.23 (t, 3H), 3.77 (br, s, 3H), 3.22 (t, 8H), 2.28 (d, 3H), 2.09 (d, 3H), 1.66 (m, 8H), 1.39 (m, 8H), 0.99 (t, 12H), 0.96 (s, 27H), –0.10 (s, 9H), –0.20 (s, 9H). Calc. for $C_{58}H_{102}ClN_7Si_3Zn_3$: C, 57.41; H, 8.47; N, 8.08. Found: C, 57.25; H, 8.47; N, 7.87.

[NBu_4][(^{tbs}L)Fe_nZn_{3-n}(μ^3–Cl)] (9; *n* = 1,2). To [NBu_4][Cl] (11 mg, 0.040 mmol) frozen in benzene (1 mL) was added (^{tbs}L)Fe_2Zn(thf) (**4**) (39.2 mg, 0.040 mmol) in benzene (1 mL). The reaction mixture was frozen to keep the layers separate, then thawed to allow slow diffusion of the layers, and stirred at room temperature overnight. The remaining solid was extracted in THF and filtered through a glass wool plug. The filtrate was layered with hexanes, and maintenance of the mixture at –33 °C yielded 33.6 mg of dark brown crystalline material (71%, based on recovery of mass). ^{1}H NMR (600 MHz, THF-d_8): δ 223.7, 220.9, 210.4, 191.1, 189.5, 130.7, 124.1, 122.0, 57.8, 50.4, 50.5, 48.3, 47.5, 42.7, 41.8, 39.9, 36.3, 36.2, 35.9, 33.2, 32.0, 31.3, 26.7, 26.6, 25.5, 21.5, 21.2, 16.1, 15.7, 13.7, 11.6, 10.9, 7.3, 7.1, 5.6, 5.5, 5.0, 2.7, 1.9, 1.3, 1.1, 1.0, 0.9, 0.8, 0.2, 0.0, –0.7, –1.5, –2.2, –3.1, –3.6, –5.3, –6.3, –7.5, –9.7, –11.1, –28.0, –29.2, –33.4, –37.7, –42.2, –43.6 – 59.7, –65.3. ^{57}Fe Mössbauer (90 K) (δ, $|\Delta E_Q|$ (mm/s)): 0.77, 1.13. Fe/Zn ratio by XRF: 2.1:1.

(^{tbs}L)Fe_2Zn(μ^3–NPh) (11). To phenyl azide (3.8 mg, 0.032 mmol) frozen in benzene (1 mL) was added a benzene solution (1 mL) of (^{tbs}L)Fe_2Zn(thf) (**5**) (30.1 mg, 0.030 mmol). The reaction mixture was frozen to keep the layers separate, then thawed to allow slow diffusion of the layers, and stirred at room temperature over the course of 1 h. The reaction mixture was lyophilized to yield 28.6 mg of dark brown powder, which represented a mixture of (^{tbs}L)Fe_3(μ^3–NPh) and (^{tbs}L)Fe_2Zn(μ^3–NPh) (95% mass recovery). Crystals suitable for X-ray diffraction were obtained from a saturated hexanes solution of **11** at –33 °C. Crude ^{57}Fe Mössbauer (90 K) (δ, $|\Delta E_Q|$ (mm/s)): 0.28, *2.31*.

(^{tbs}L)Fe_2Zn(μ^3–NPh)(py) (12). To phenyl azide (5.9 mg, 0.050 mmol) frozen in benzene (1 mL) was added (^{tbs}L)Fe_2Zn(py) (**6**) (41.5 mg, 0.042 mmol) in benzene (1 mL). The reaction mixture was frozen to keep the layers separate, then thawed to allow slow diffusion of the layers, and stirred at room temperature over the course of 1 hour. The reaction mixture was lyophilized, and then extracted in hexanes. Following filtration of the hexanes extracts through a glass wool plug, maintenance of the filtrate at –33 °C yielded 26.4 mg of dark brown crystalline product (58% yield). ^{1}H NMR (500 MHz, C_6D_6): δ 176.4, 110.7, 74.8, 54.6, 27.1, 25.6, 22.7, 21.3, 16.2, 14.5, 11.9, 9.7, 9.1, 8.5, 8.2, 7.8, 6.7, 4.4, 3.6, 2.5, 1.8, 1.4, 1.2, 1.0, 0.9, 0.3, –0.2, –1.9, –2.8, –3.6, –5.4, –7.4, –8.7, –14.6, –16.9, –21.6, –23.8. ^{57}Fe Mössbauer (90 K) (δ, $|\Delta E_Q|$ (mm/s)): component 1 (51%): 0.33, 1.80; component 2 (49%): 0.35, 2.76. Calc. for $C_{53}H_{76}Fe_2N_8Si_3Zn$: C, 58.59; H, 7.05; N, 10.31. Found: C, 58.40; H, 6.99; N, 10.33. Fe/Zn ratio by XRF: 2.1:1.

(^{tbs}L)Fe_3(μ^3–N(3,5-$C_6H_3(CF_3)_2$)) (13). To a frozen solution of 3,5-$(CF_3)_2C_6H_3N_3$ (27.6 mg, 0.11 mmol) in benzene (2 mL) was added (^{tbs}L)Fe_3(thf) (**1**) (100.1 mg, 0.10 mmol) in benzene (2 mL). The reaction mixture was frozen to keep the layers separate, then thawed to allow slow diffusion of the layers, and stirred at room temperature over the course of 1 h. The reaction mixture was

lyophilized and washed with cold pentane. Crystals were obtained upon cooling of the pentane wash to –33 °C. The remaining solid extracted in hexanes and filtered through a glass wool plug. Maintenance of the hexanes filtrate at –33 °C yielded a second crystalline crop. Crystals harvested from the two fractions gave an overall yield of 61.8 mg of product (53% yield). ^{1}H NMR (500 MHz, C_6D_6): δ 194.7, 60.1, 9.8, 8.0, 5.6, 3.0, 2.5, 1.9, –5.1, –5.5, –8.4, –21.7. ^{19}F NMR (500 MHz, C_6D_6): δ –69.4. ^{57}Fe Mössbauer (90 K) (δ, $|\Delta E_Q|$ (mm/s)): component 1 (33%): 0.37, 1.8; component 2 (33%): 0.38, 1.13; component 3 (33%): 0.45, 2.61. Calc. for $C_{50}H_{69}F_6Fe_3N_7Si_3$: C, 52.96; H, 6.13; N, 8.65. Found: C, 53.30; H, 6.28; N, 8.28.

(^{tbs}L)Fe$_2$Zn(μ^3–N(3,5-(CF$_3$)$_2$C$_6$H$_3$)). To a frozen solution of 3,5-$(CF_3)_2C_6H_3N_3$ (5.3 mg, 0.028 mmol) in benzene (1 mL) was added a benzene solution (1 mL) of (^{tbs}L)Fe$_2$Zn(thf) (**5**) (27.1 mg, 0.027 mmol). The reaction mixture was frozen to keep the layers separate, then thawed to allow slow diffusion of the layers, and stirred at room temperature over the course of 1 h. The reaction mixture was lyophilized to yield 27.6 mg of dark brown powder, which represented a mixture of (^{tbs}L)Fe$_3$(μ^3–N(3,5-$(CF_3)_2C_6H_3$)) and (^{tbs}L)Fe$_2$Zn(μ^3–N(3,5-$(CF_3)_2C_6H_3$)) (86% mass recovery).

(^{tbs}L)Fe$_2$Zn(μ^3–N(3,5-(CF$_3$)$_2$C$_6$H$_3$))(py) (14). To a frozen solution of 3,5-$(CF_3)_2C_6H_3N_3$ (12 mg, 0.047 mmol) in benzene (1 mL) was added crystalline **5** (47.7 mg, 0.048 mmol) in benzene (1 mL). The reaction mixture was frozen to keep the layers separate, then thawed to allow slow diffusion of the layers, and stirred at room temperature over the course of 1 h. The volatile components of the reaction mixture were removed *in vacuo*, and the resulting solid was extracted in hexanes with drops of benzene. The dark brown extracts were filtered through a Celite plug, and maintenance of the filtrate at –33 °C yielded 30 mg of dark brown crystalline product (51%). ^{1}H NMR (500 MHz, C_6D_6): δ 216.0, 197.4, 135.1, 64.1, 60.6, 50.3, 32.2, 31.3, 25.8, 24.8, 20.9, 18.8, 13.3, 10.8, 8.8, 6.7, 5.4, 2.4, 1.2, 0.9, –0.7, –1.9, –3.3, –5.3, –9.1, –11.1, –14.9, –15.8, –20.0, –21.6, –23.5, –24.4, –43.5, –45.4, –48.6. ^{19}F NMR (500 MHz, C_6D_6): δ –68.5, –71.2. ^{57}Fe Mössbauer (90 K) (δ, $|\Delta E_Q|$ (mm/s)): component 1 (55%): 0.33, 1.76; component 2 (45%): 0.40, 2.92. Calc. for $C_{55}H_{74}F_6Fe_2N_8Si_3Zn$: C, 54.03; H, 6.10; N, 9.17. Found: C, 54.21; H, 5.79; N, 8.85. Fe/Zn ratio by XRF: 2.1:1.

[CoCp$^*_2$][(^{tbs}L)Fe$_3$(μ^3–N(3,5-(CF$_3$)$_2$C$_6$H$_3$))] (15). To $CoCp^*_2$ (14.3 mg, 0.043 mmol) frozen in THF (1 mL) was added (^{tbs}L)Fe$_3$(μ^3–N(3,5-$C_6H_3(CF_3)_2$)) (**13**) (49.1 mg, 0.043 mmol) in THF (1 mL). The reaction mixture was frozen to keep the layers separate, then thawed to allow slow diffusion of the layers. The reaction mixture was stirred at room temperature, and the volatile components were removed *in vacuo* 1 h after thawing. The resulting solid was extracted in THF and filtered through a glass wool plug. Diffusion of hexanes into the filtrate solution at –33 °C yielded 44.8 mg of dark brown crystalline product (71%). ^{1}H NMR (500 MHz, THF-d_8): δ 56.1, 12.1, 9.7, 7.3, 7.0, 6.8, 5.8, 5.4, 2.2, 1.3, 1.0, 0.9, 0.4, –3.8, –10.1, –29.4, –55.9, –70.9. ^{19}F NMR (500 MHz, THF-d_8): δ –85.9. ^{57}Fe Mössbauer (90 K) (δ, $|\Delta E_Q|$ (mm/s)): component 1 (67%): 0.49, 1.82 (Γ = 0.35 mm/s); component 2 (33%): 0.59, 1.20 (Γ = 0.16 mm/s). Calc. for $C_{70}H_{99}CoF_6Fe_3N_7Si_3$: C, 57.46; H, 6.82; N, 6.70. Found: C, 57.19; H, 6.87; N, 7.02.

[(2,2,2-cryptand)K][(^{tbs}L)Fe$_2$Zn(μ^3–N(3,5-(CF$_3$)$_2$C$_6$H$_3$))] (16). To a frozen suspension of KC_8 (3.8 mg, 0.028 mmol) in THF (1 mL) was added a solution of crystalline (^{tbs}L)Fe$_2$Zn(μ^3–N(3,5-$C_6H_3(CF_3)_2$))(py) (**14**) (34.3 mg, 0.028 mmol) in THF (1 mL). The reaction mixture was frozen to keep the layers separate, then thawed to allow slow diffusion of the layers, and stirred at room temperature over the course of 1 h. The reaction mixture was filtered through Celite to a vial containing 2,2,2-cryptand (10.6 mg, 0.028 mmol), and the resulting mixture was stirred at room

temperature for 30 min. The volatile components of the reaction mixture were then removed *in vacuo*, and the resulting solid was extracted in diethyl ether. Filtration of the ethereal extracts, followed by maintenance of the filtrate at –33 °C yielded 30 mg of dark brown crystalline product (69% yield). ^{1}H NMR (500 MHz, THF-d_8): δ 237.7, 156.3, 126.9, 47.7, 45.9, 23.5, 20.8, 16.9, 14.8, 13.8, 10.3, 9.2, 7.0, 5.2, 2.6, 1.3, 0.9, –0.3, –1.2, –2.5, –2.8, –4.4, –5.6, –7.5, –9.4, –18.0, –19.2, –23.2, –41.8, –52.7. ^{19}F NMR (500 MHz, THF-d_8): δ –79.4. ^{57}Fe Mössbauer (90 K) (δ, $|\Delta E_Q|$ (mm/s)): component 1 (50%): 0.35, 1.73 (Γ = 0.29 mm/s); component 2 (%): 0.59, 3.01 (Γ = 0.20 mm/s). Calc. for $C_{68}H_{105}F_6Fe_2KN_9O_6Si_3Zn$: C, 52.39; H, 6.79; N, 8.09. Found: C, 52.24; H, 6.73; N, 8.51. Fe/Zn ratio by XRF: 1.9:1.

Reaction of [NBu$_4$][(^{tbs}L)Fe$_3$(μ^3–Cl)] (7) and [NBu$_4$][(^{tbs}L)Zn$_3$(μ^3–Cl)] (8). Crystalline [NBu$_4$][(^{tbs}L)Fe$_3$(μ^3–Cl)] (**7**) (10.1 mg, 0.00853 mmol) and [NBu$_4$][(^{tbs}L)Zn$_3$(μ^3–Cl)] (**8**) (10.3 mg, 0.00853 mmol) were separately dissolved in THF (0.2 mL) and combined in a J. Young NMR tube. Three 0.05 mL aliquots of THF were used to rinse the vials used in sample preparation, and the aliquots were added to the reaction mixture. ^{1}H NMR spectra collected within 1 h of sample preparation and after 24 h were identical. The sample was then subjected to heating at 40 °C for 24 h and then at 60 °C for 24 h; ^{1}H NMR spectra recorded after each heating period showed no change. Heating at 80 °C for 24 h resulted in formation of small quantities of the metal-atom redistribution product [NBu$_4$][(^{tbs}L)Fe$_n$Zn$_{3-n}$(μ^3–Cl)] (**9**). These ^{1}H NMR spectra are presented in Figure S21.

Reaction of (^{tbs}L)Fe$_2$Zn(thf) (5) and [NBu$_4$][(^{tbs}L)Fe$_3$(μ^3–Cl)] (7). Crystalline (^{tbs}L)Fe$_2$Zn(thf) (**5**) (10.2 mg, 0.0103 mmol) and [NBu$_4$][(^{tbs}L)Fe$_3$(μ^3–Cl)] (**7**) (12.2 mg, 0.0103 mmol) were separately dissolved in THF/C_6D_6 (25% v/v; 0.2 mL) and combined in a J. Young NMR tube. Three 0.05 mL aliquots of the solvent mixture were used to rinse the vials used in sample preparation, and the aliquots were added to the reaction mixture. ^{1}H NMR spectra were recorded after 4 h and 24 h of maintenance at room temperature, and after heating at 60 °C for 24 h. These spectra indicate that the metal-atom redistribution product [NBu$_4$][(^{tbs}L)Fe$_n$Zn$_{3-n}$(μ^3–Cl)] (**9**) was generated rapidly at room temperature after 4 h, with **5** and **7** being no longer observable. No further change was observed after heating at 60 °C for 24 h. These ^{1}H NMR spectra are presented in Figure S22.

Reaction of (^{tbs}L)Fe$_2$Zn(thf) (5) and [NBu$_4$][(^{tbs}L)Zn$_3$(μ^3–Cl)] (8). Crystalline (^{tbs}L)Fe$_2$Zn(thf) (**5**) (10.7 mg, 0.0108 mmol) and [NBu$_4$][(^{tbs}L)Zn$_3$(μ^3–Cl)] (**8**) (13.1 mg, 0.0108 mmol) were separately dissolved in THF/C_6D_6 (25% v/v; 0.2 mL) and combined in a J. Young NMR tube. Three 0.05 mL aliquots of the solvent mixture were used to rinse the vials used in sample preparation, and the aliquots were added to the reaction mixture. ^{1}H NMR spectra were recorded after 4 h and 24 h of maintenance at room temperature, and after heating at 60 °C for 24 h. These spectra indicate that the metal-atom redistribution product [NBu$_4$][(^{tbs}L)Fe$_n$Zn$_{3-n}$(μ^3–Cl)] (**9**) was generated slowly at room temperature, and the reaction mixture is predominantly composed of **5** and **8**. At elevated temperatures, conversion to **9** is increased, but **5** and **8** persist in solution. These ^{1}H NMR spectra are presented in Figure S23.

Reaction of (^{tbs}L)Fe$_2$Zn(thf) (5) with FeCl$_2$. A suspension of $FeCl_2$ (1.3 mg, 0.010 mmol) in THF (0.2 mL) was added to a solution of (^{tbs}L)Fe$_2$Zn(thf) (**5**) (10.1 mg; 0.0102 mmol) in THF (0.2 mL). Three 0.05 mL aliquots of THF were used to rinse the vials used in sample preparation, and the aliquots were added to the reaction mixture. ^{1}H NMR spectra were recorded after 4 h and 24 h of

maintenance at room temperature. These spectra indicate that metal-atom redistribution product [NBu_4][(^{tbs}L)Fe_nZn_{3-n}(μ^3–Cl)] (**9**) and tri-ferrous [NBu_4][(^{tbs}L)Fe_3(μ^3–Cl)] **7** were generated at room temperature, although small quantities of **5** remain present. Several unidentified resonances attributed to paramagnetic species are also present in the ^{1}H NMR spectra, and increase in intensity from 4 h to 24 h. Over this period, the color of the reaction mixture changed from dark brown to purple; this process was further accompanied by the deposition of a precipitate. These ^{1}H NMR spectra are presented in Figure S24.

Reaction of (^{tbs}L)Fe_2Zn(thf) (5) with $ZnCl_2$. A solution of $ZnCl_2$ (1.1 mg, 0.0081 mmol) in THF (0.2 mL) was added to a solution of (^{tbs}L)Fe_2Zn(thf) (**5**) (8.0 mg, 0.0081 mmol) in THF (0.2 mL). Three 0.05 mL aliquots of THF were used to rinse the vials used in sample preparation, and the aliquots were added to the reaction mixture. ^{1}H NMR spectra were recorded after 4 h and 24 h of maintenance at room temperature. These spectra indicate that no metal-scambling products were generated at room temperature, and **5** persisted in solution. However, the intensity of all resonances diminished noticeably after 24 h, and this was accompanied by a change in the color of the reaction mixture from dark brown to purple, although no precipitation was evident. These ^{1}H NMR spectra are presented in Figure S25.

Zero Field ^{57}Fe Mössbauer Spectroscopy

Table S1. ^{57}Fe Mössbauer Parameters for Selected Complexes

Compound		δ (mms/s)	$\|\Delta E_Q\|$ (mm/s)	%
(^{tbs}L)Fe$_3$(thf)[1]	(**1**)	0.37 0.46 0.88	1.99 1.52 1.29	36 36 28
(^{tbs}L)Fe$_3$(py)	(**2**)	0.33 0.55 0.74	1.84 1.76 1.39	38 28 33
[Na(thf)][(^{tbs}L)Fe$_2$Na(thf)]	(**4**)	0.47 0.54	1.51 0.87	50 50
(^{tbs}L)Fe$_2$Zn(thf)	(**5**)	0.60 0.84	1.83 1.55	50 50
(^{tbs}L)Fe$_2$Zn(py)	(**6**)	0.61 0.79	1.68 1.63	50 50
[NBu$_4$][(^{tbs}L)Fe$_3$(μ^3–Cl)]	(**7**)	0.72	1.31	100
[NBu$_4$][(^{tbs}L)Fe$_n$Zn$_{3-n}$(μ^3–Cl)]	(**9**)	0.77	1.13	100
(^{tbs}L)Fe$_3$(μ^3–NPh)[1b]	(**10**)	0.42 0.42	1.97 1.09	67 33
(^{tbs}L)Fe$_2$Zn(μ^3–NPh)	(**11**)	0.28	2.31	100
(^{tbs}L)Fe$_2$Zn(μ^3–NPh)(py)	(**12**)	0.33 0.35	1.80 2.76	51 49
(^{tbs}L)Fe$_3$(μ^3–N(3,5-(CF$_3$)$_2$C$_6$H$_3$))	(**13**)	0.37 0.38 0.45	1.80 1.13 2.61	33 33 33
(^{tbs}L)Fe$_2$Zn(μ^3– N(3,5-(CF$_3$)$_2$C$_6$H$_3$))(py)	(**14**)	0.33 0.40	1.76 2.92	55 45
[CoCp$^*_2$][(^{tbs}L)Fe$_3$(μ^3–N(3,5-(CF$_3$)$_2$C$_6$H$_3$))]	(**15**)	0.49 0.59	1.82 1.20	67 33
[2,2,2-crypt(K)][(^{tbs}L)Fe$_2$Zn(μ^3–N(3,5-(CF$_3$)$_2$C$_6$H$_3$))]	(**16**)	0.35 0.59	1.73 3.01	50 50

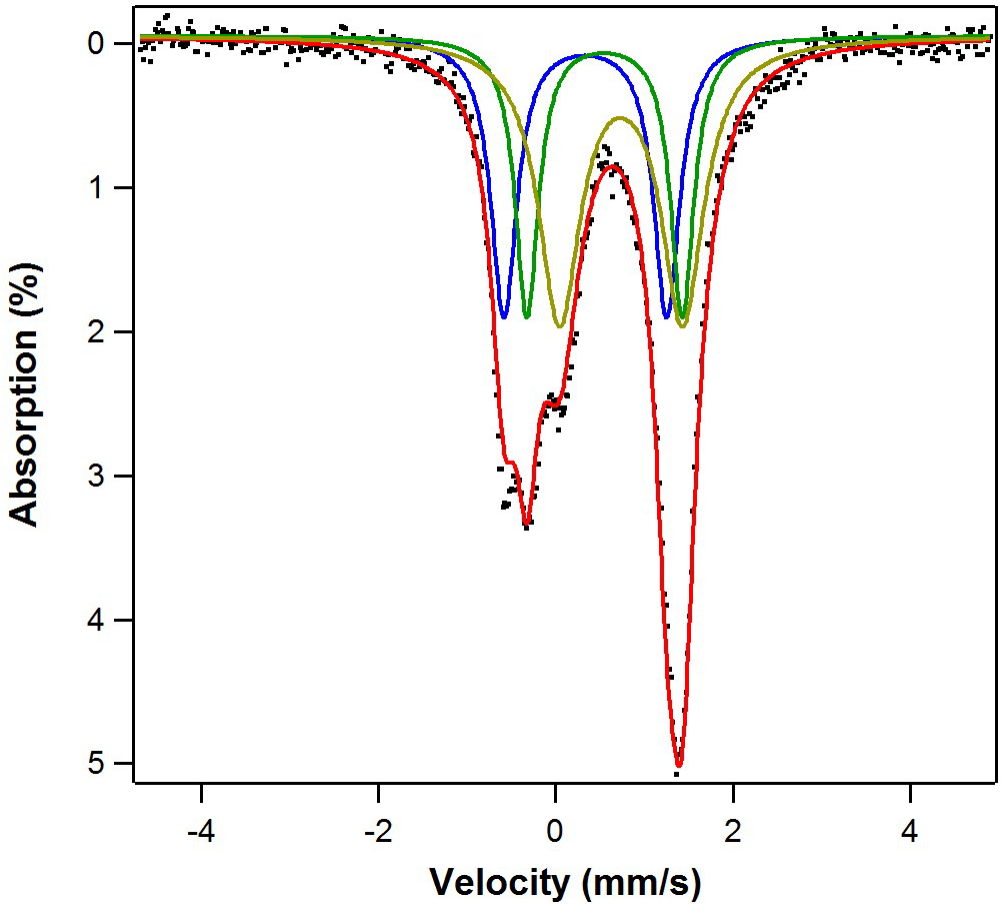

Figure S1. Zero-field ^{57}Fe Mössbauer spectrum of (^{tbs}L)Fe$_3$(py) (**2**) collected at 90 K. Simulation yields the following parameters: δ, $|\Delta E_Q|$ ($^{mm}/_s$) component 1 (blue, 38%) 0.33, 1.84 (Γ = 0.18 $^{mm}/_s$); component 2 (green, 28%) 0.55, 1.76 (Γ = 0.16 $^{mm}/_s$); component 3 (yellow, 33%) 0.74, 1.39 (Γ = 0.29 $^{mm}/_s$).

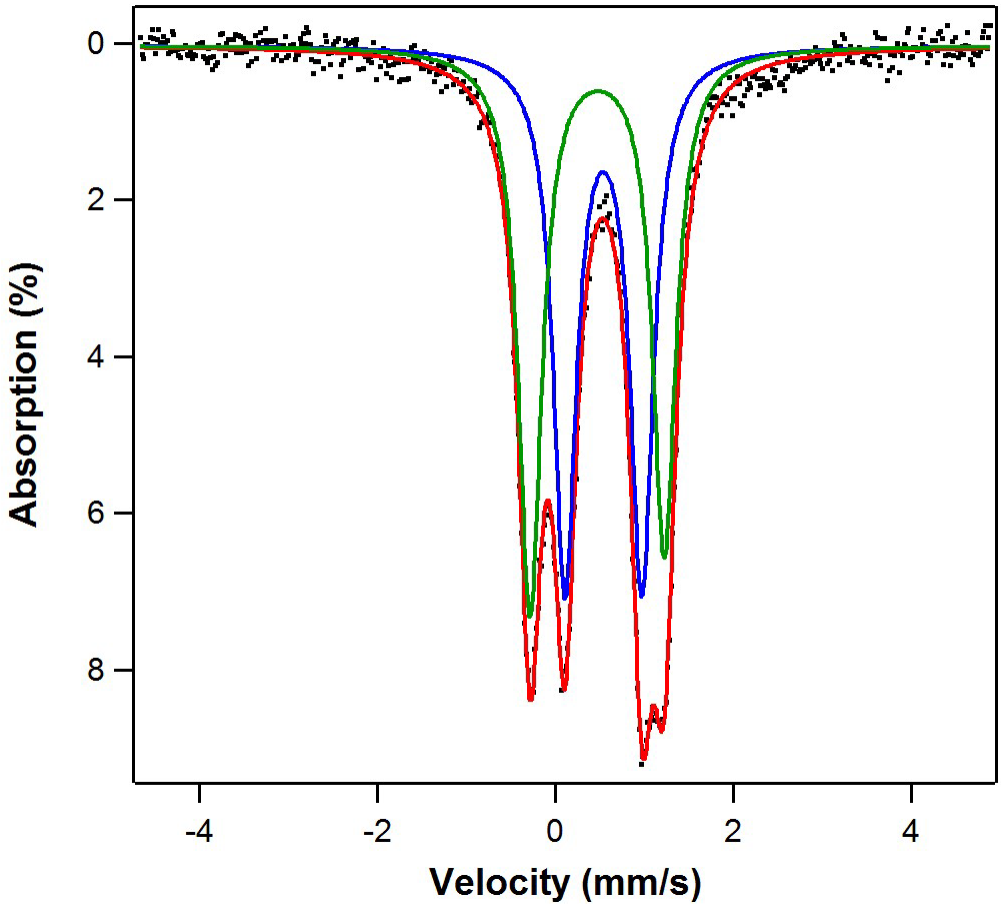

Figure S2. Zero-field ^{57}Fe Mössbauer spectrum of [Na(thf)][(^{tbs}L)Fe$_2$Na(thf)] (**4**) collected at 90 K. Simulation yields the following parameters: δ, $|\Delta E_Q|$ ($^{mm}/_s$) component 1 (blue, 50%) 0.54, *0.87* (Γ = 0.16 $^{mm}/_s$); component 2 (green, 50%) 0.47, *1.51* (Γ = 0.16 $^{mm}/_s$).

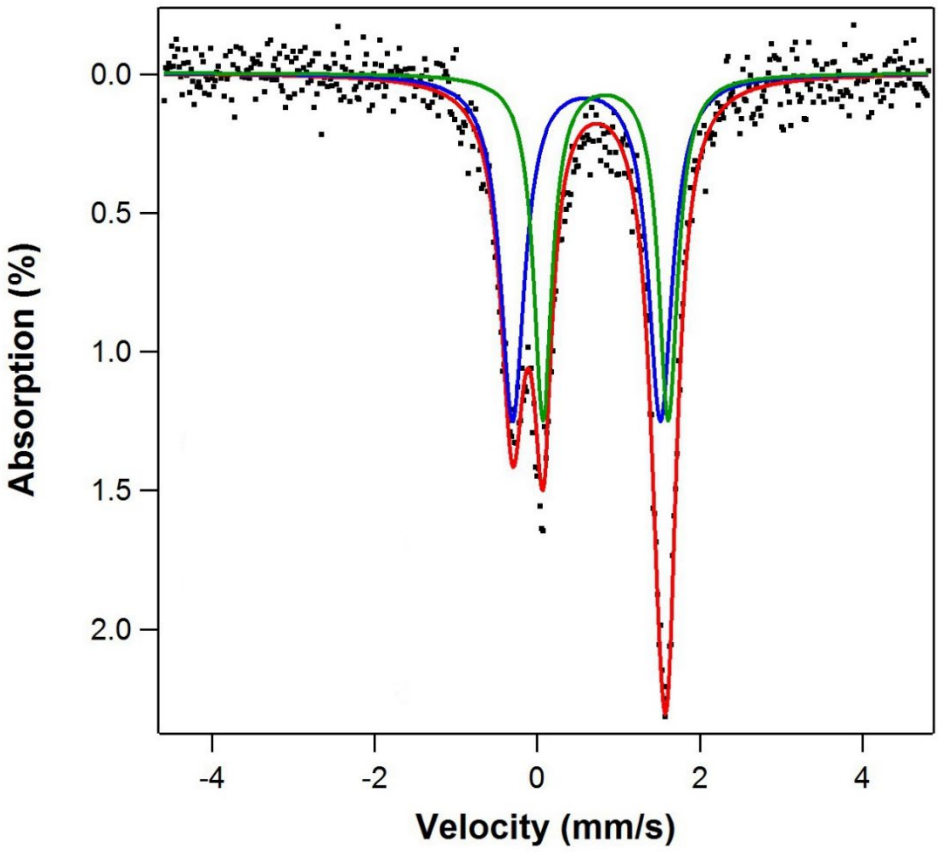

Figure S3. Zero-field ^{57}Fe Mössbauer spectrum of (^{tbs}L)Fe_2Zn(thf) (**5**) collected at 90 K. Simulation yields the following parameters: δ, $|\Delta E_Q|$ ($^{mm}/_{s}$) component 1 (blue, 50%) 0.60, *1.83* (Γ = 0.18 $^{mm}/_{s}$); component 2 (green, 50%) 0.84, *1.55* (Γ = 0.14 $^{mm}/_{s}$).

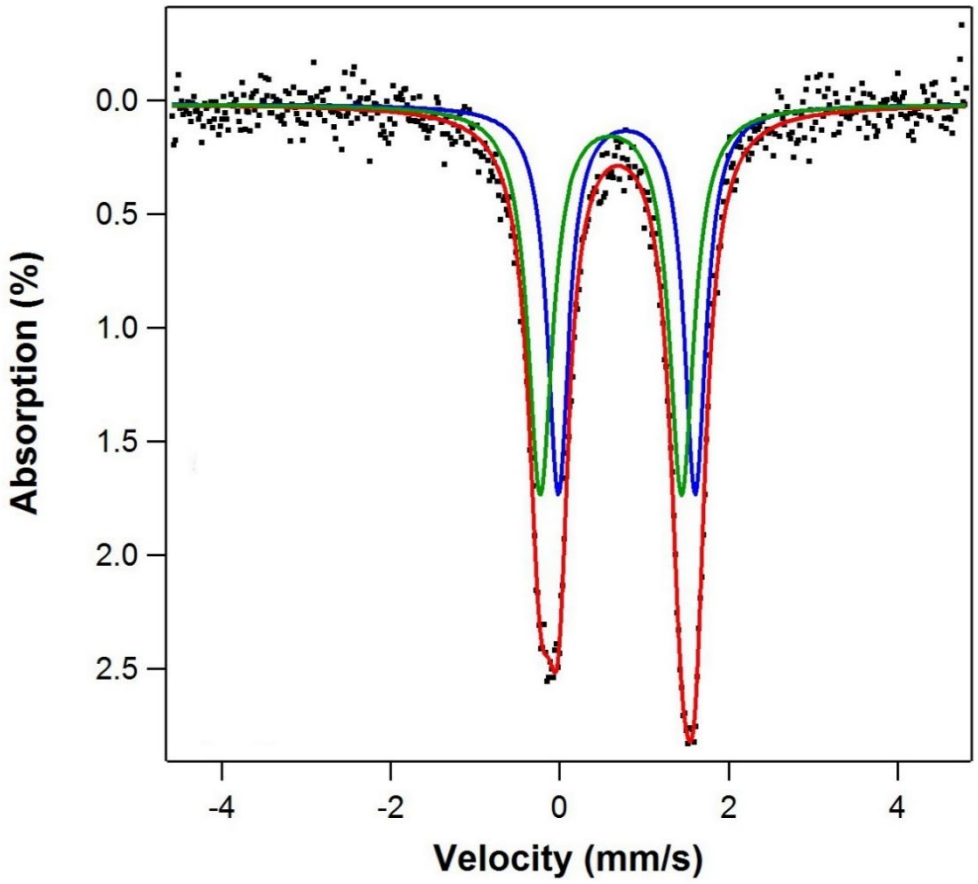

Figure S4. Zero-field ^{57}Fe Mössbauer spectrum of (^{tbs}L)Fe$_2$Zn(py) (**6**) collected at 90 K. Simulation yields the following parameters: δ, $|\Delta E_Q|$ ($^{mm}/_{s}$) component 1 (blue, 50%) 0.79, *1.63* (Γ = 0.16 $^{mm}/_{s}$); component 2 (green, 50%) 0.61, *1.68* (Γ = 0.18 $^{mm}/_{s}$).

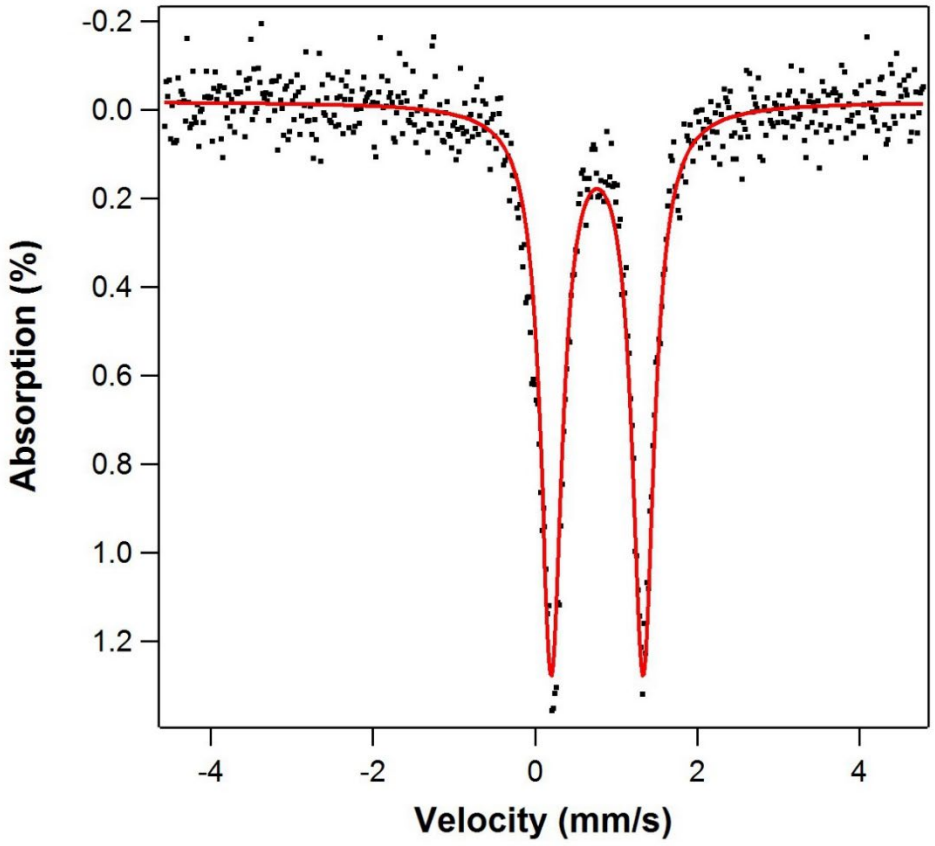

Figure S5. Zero-field ^{57}Fe Mössbauer spectrum of [NBu_4][(^{tbs}L)Fe$_n$Zn$_{3-n}$(μ^3–Cl)] (**9**) collected at 90 K. Simulation yields the following parameters: δ, $|\Delta E_Q|$ ($^{mm}/_s$) 0.77, *1.13* (Γ = 0.16 $^{mm}/_s$).

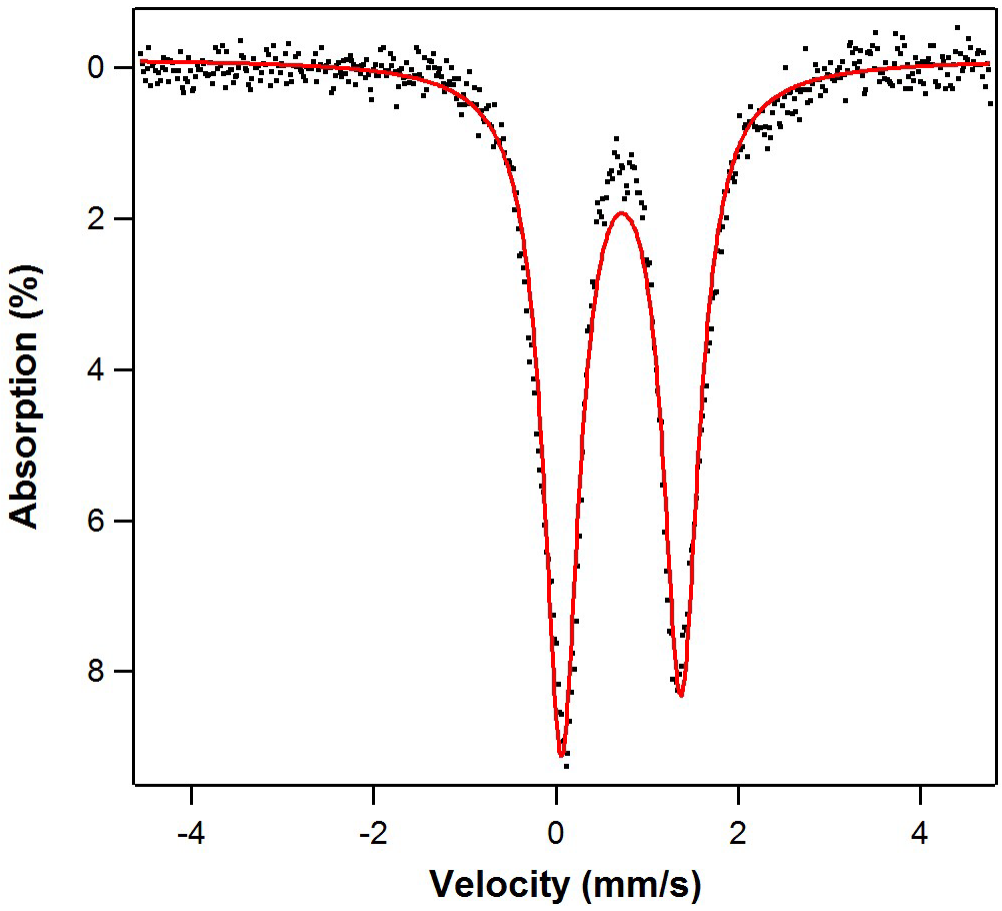

Figure S6. Zero-field ^{57}Fe Mössbauer spectrum of [NBu$_4$][(^{tbs}L)Fe$_3$(μ^3–Cl] (**7**) collected at 90 K. Simulation yields the following parameters: δ, |ΔE_Q| ($^{mm}/_s$) 0.72, *1.31* (Γ = 0.24 $^{mm}/_s$).

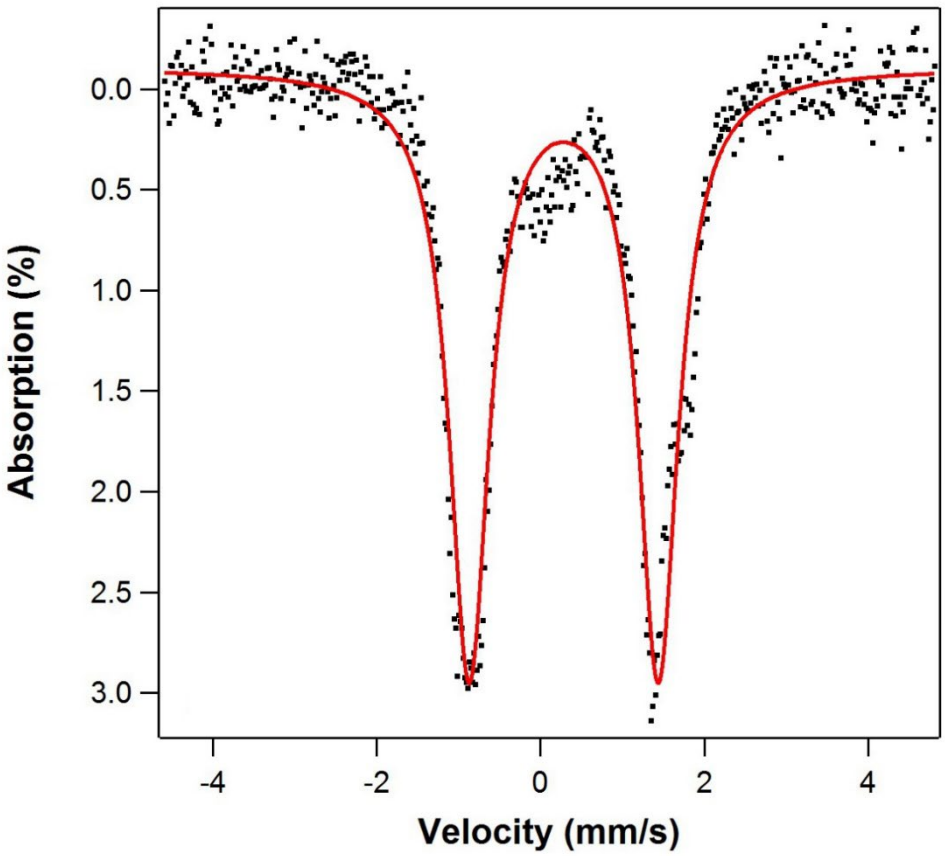

Figure S7. Zero-field ^{57}Fe Mössbauer spectrum of crude (^{tbs}L)$Fe_2Zn(\mu^3$–NPh) (**11**) collected at 90 K. Simulation yields the following parameters: δ, $|\Delta E_Q|$ ($^{mm}/_{s}$) 0.28, *2.31* (Γ = 0.30 $^{mm}/_{s}$).

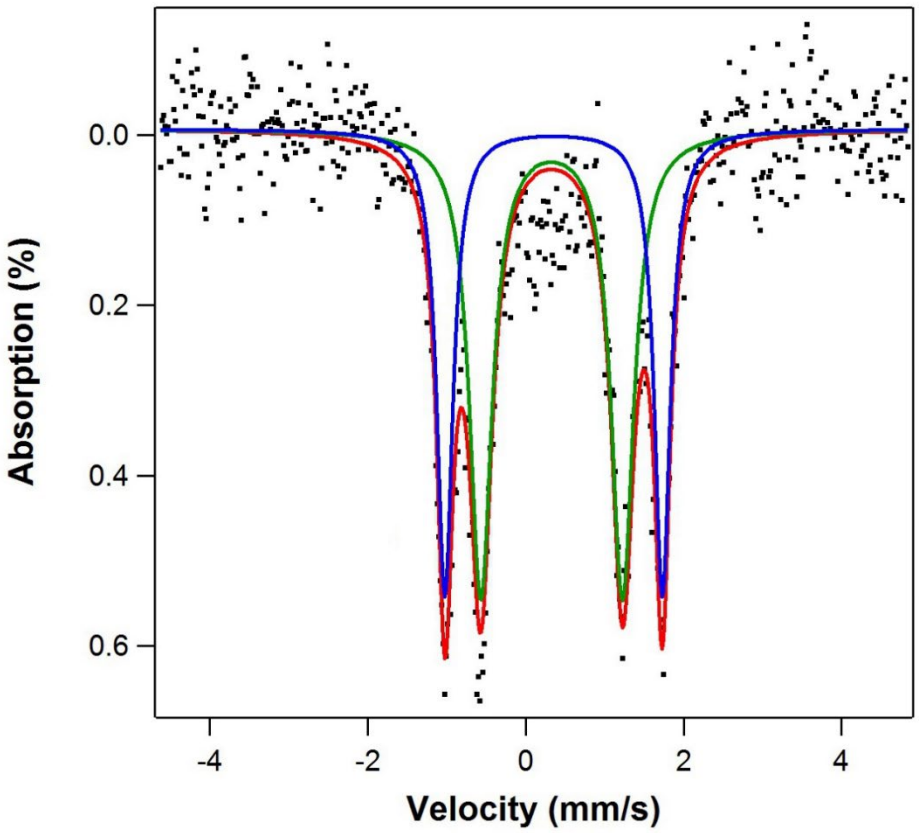

Figure S8. Zero-field ^{57}Fe Mössbauer Spectrum of (^{tbs}L)Fe$_2$Zn(μ^3–NPh)(py) (**12**) collected at 90 K. Simulation yields the following parameters: δ, |ΔE_Q| ($^{mm}/_s$) component 1 (blue, 49%) 0.35, *2.76* (Γ = 0.12 $^{mm}/_s$); component 2 (green, 51%) 0.33, *1.80* (Γ = 0.17 $^{mm}/_s$).

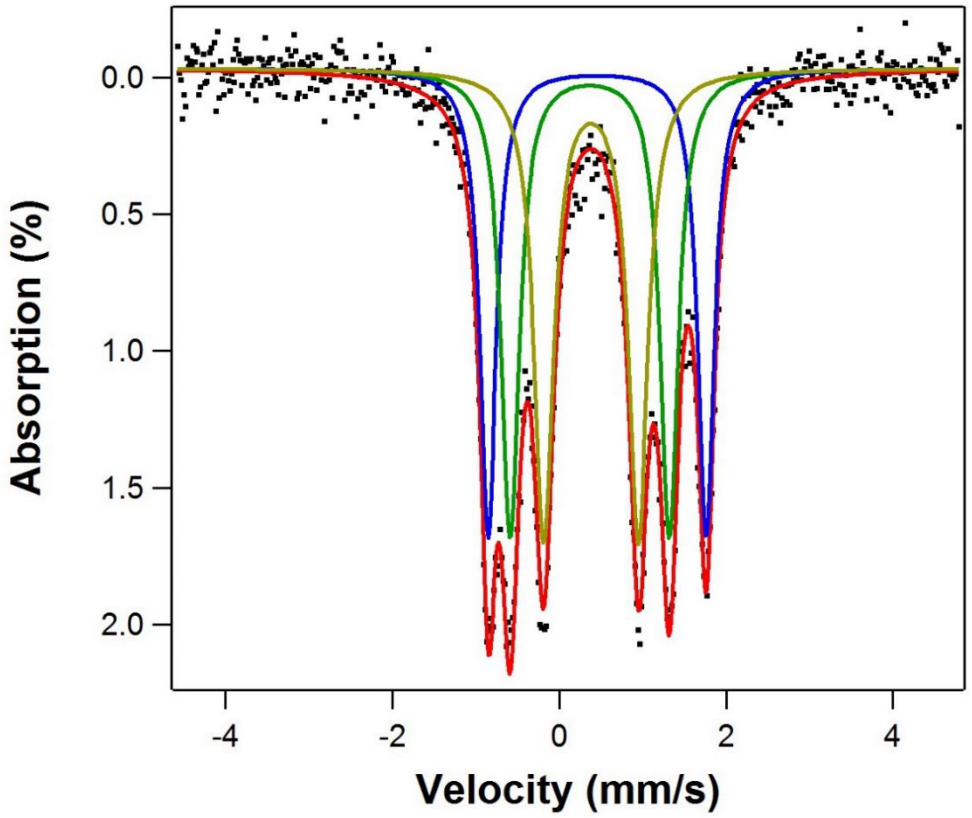

Figure S9. Zero-field ^{57}Fe Mössbauer Spectrum of (^{tbs}L)Fe$_3$(μ^3–N(3,5-(CF$_3$)$_2$C$_6$H$_3$)) (**13**) collected at 90 K. Simulation yields the following parameters: δ, |ΔE_Q| ($^{mm}/_s$) component 1 (blue, 33%) 0.45, *2.61* (Γ = 0.12 $^{mm}/_s$); component 2 (green, 33%) 0.37, *1.80* (Γ = 0.13 $^{mm}/_s$); component 3 (yellow, 34%) 0.38, *1.13* (Γ = 0.14 $^{mm}/_s$).

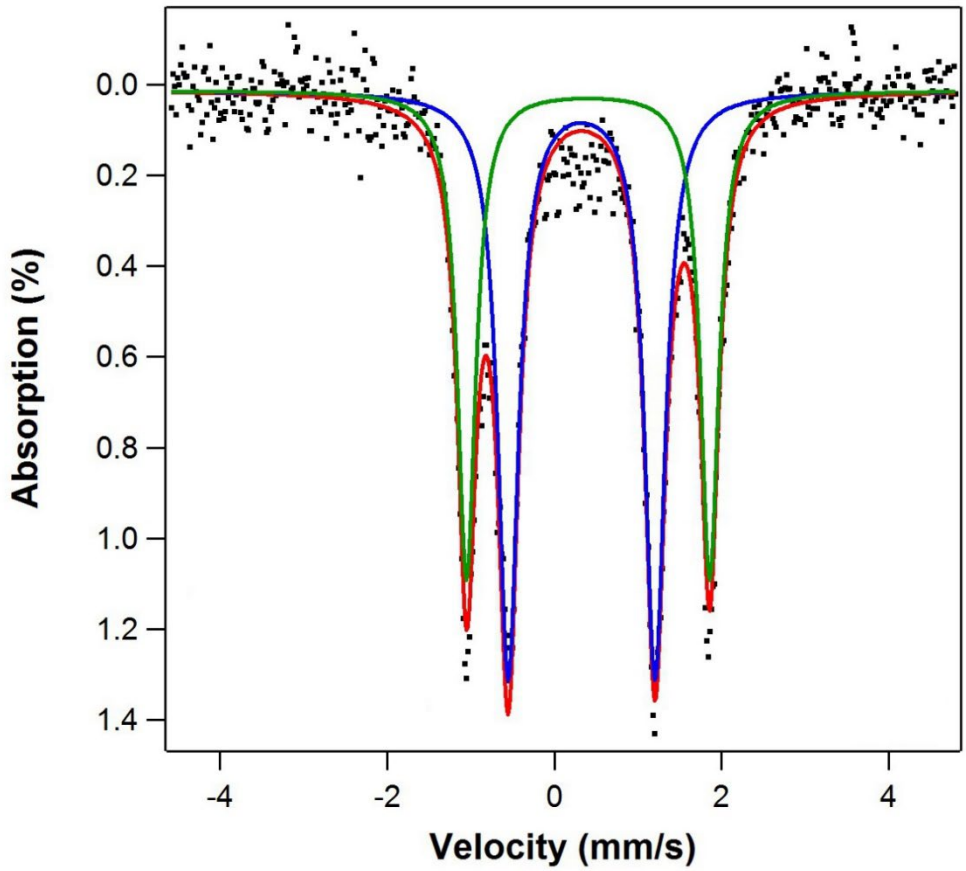

Figure S10. Zero-field ^{57}Fe Mössbauer Spectrum of (^{tbs}L)$Fe_2Zn(\mu^3$–N(3,5-$(CF_3)_2C_6H_3$))(py) (**14**) collected at 90 K. Simulation yields the following parameters: δ, $|\Delta E_Q|$ ($^{mm}/_s$) component 1 (green, 46%) 0.33, *1.76* (Γ = 0.15 $^{mm}/_s$); component 2 (blue, 54%) 0.40, *2.92* (Γ = 0.13 $^{mm}/_s$).

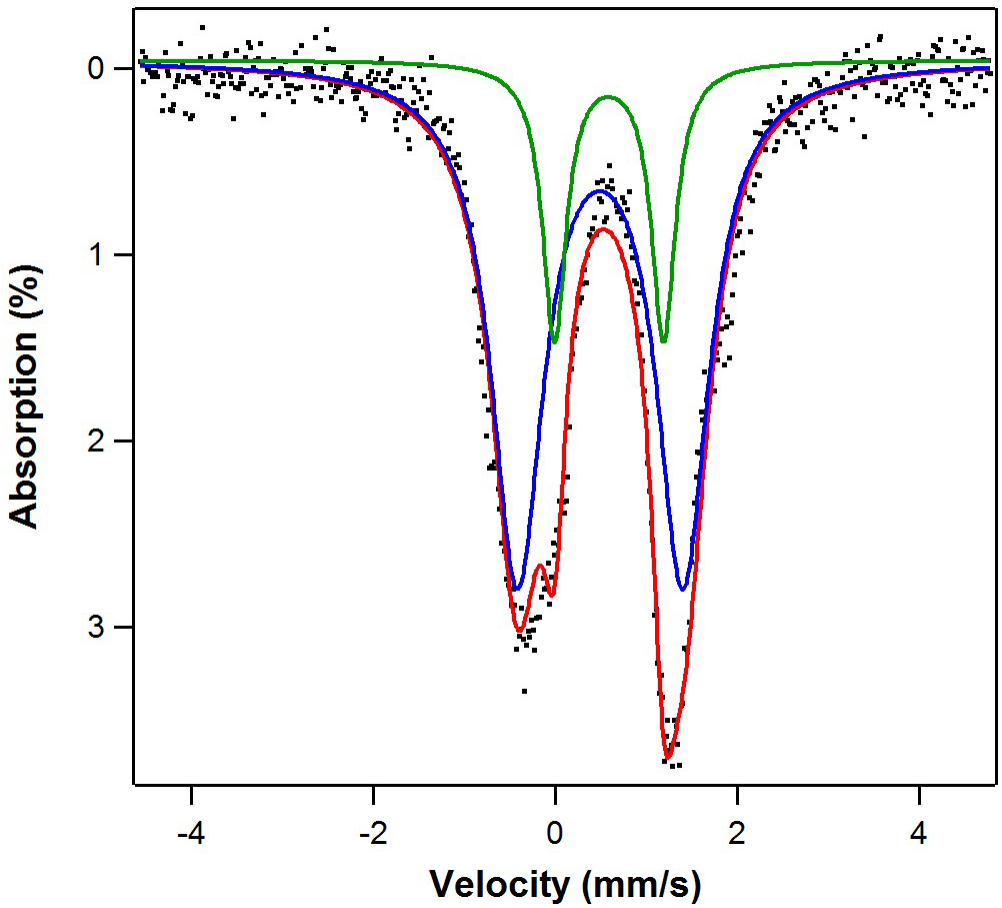

Figure S11. Zero-field ^{57}Fe Mössbauer Spectrum of [CoCp*$_2$][(^{tbs}L)Fe$_3$(μ^3–N(3,5-(CF$_3$)$_2$C$_6$H$_3$))] (**15**) collected at 90 K. Simulation yields the following parameters: δ, |ΔE_Q| ($^{mm}/_s$) component 1 (blue, 67%) 0.49, *1.82* (Γ = 0.35 $^{mm}/_s$); component 2 (green, 33%) 0.59, *1.20* (Γ = 0.16 $^{mm}/_s$).

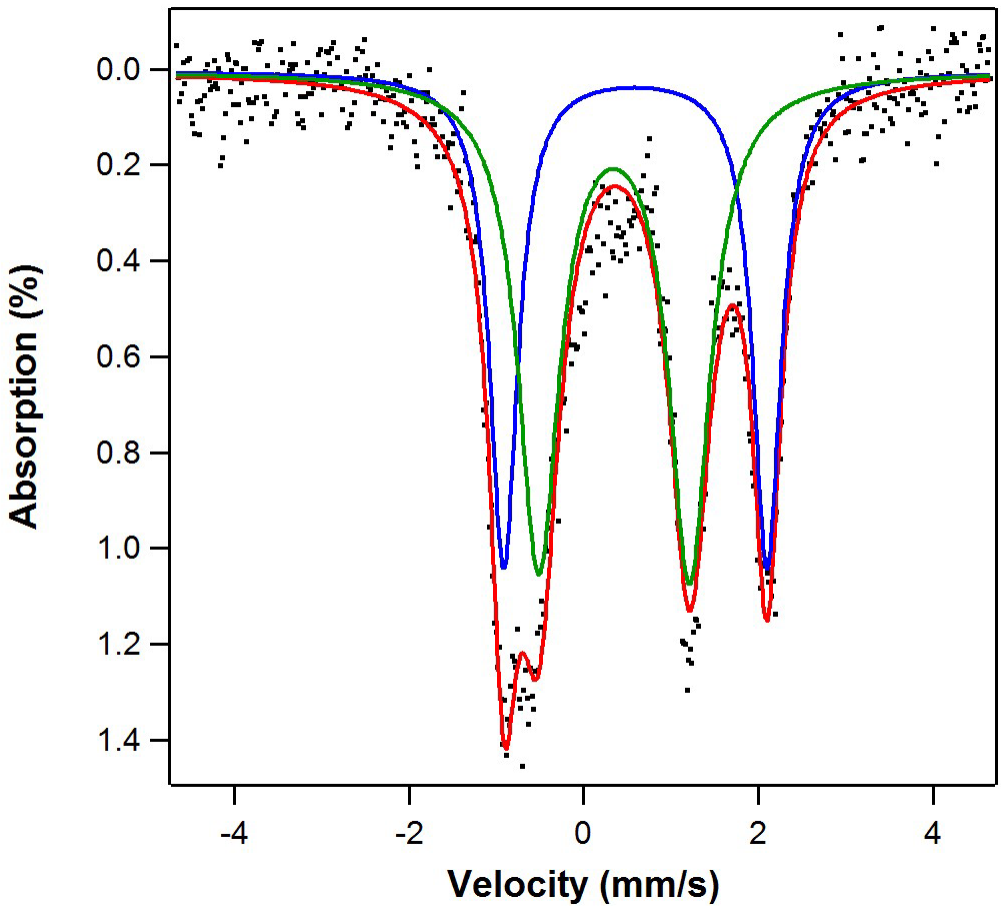

Figure S12. Zero-field ^{57}Fe Mössbauer Spectrum of [2,2,2-cryptand(K)][(^{tbs}L)Fe$_2$Zn(μ^3–N(3,5-(CF$_3$)$_2$C$_6$H$_3$))] (**16**) collected at 90 K. Simulation yields the following parameters: δ, |ΔE_Q| ($^{mm}/_s$) component 1 (green, 50%) 0.35, *1.73* (Γ = 0.29 $^{mm}/_s$); component 2 (blue, 50%) 0.59, *3.01* (Γ = 0.20 $^{mm}/_s$).

X-Ray Fluorescence Spectroscopy

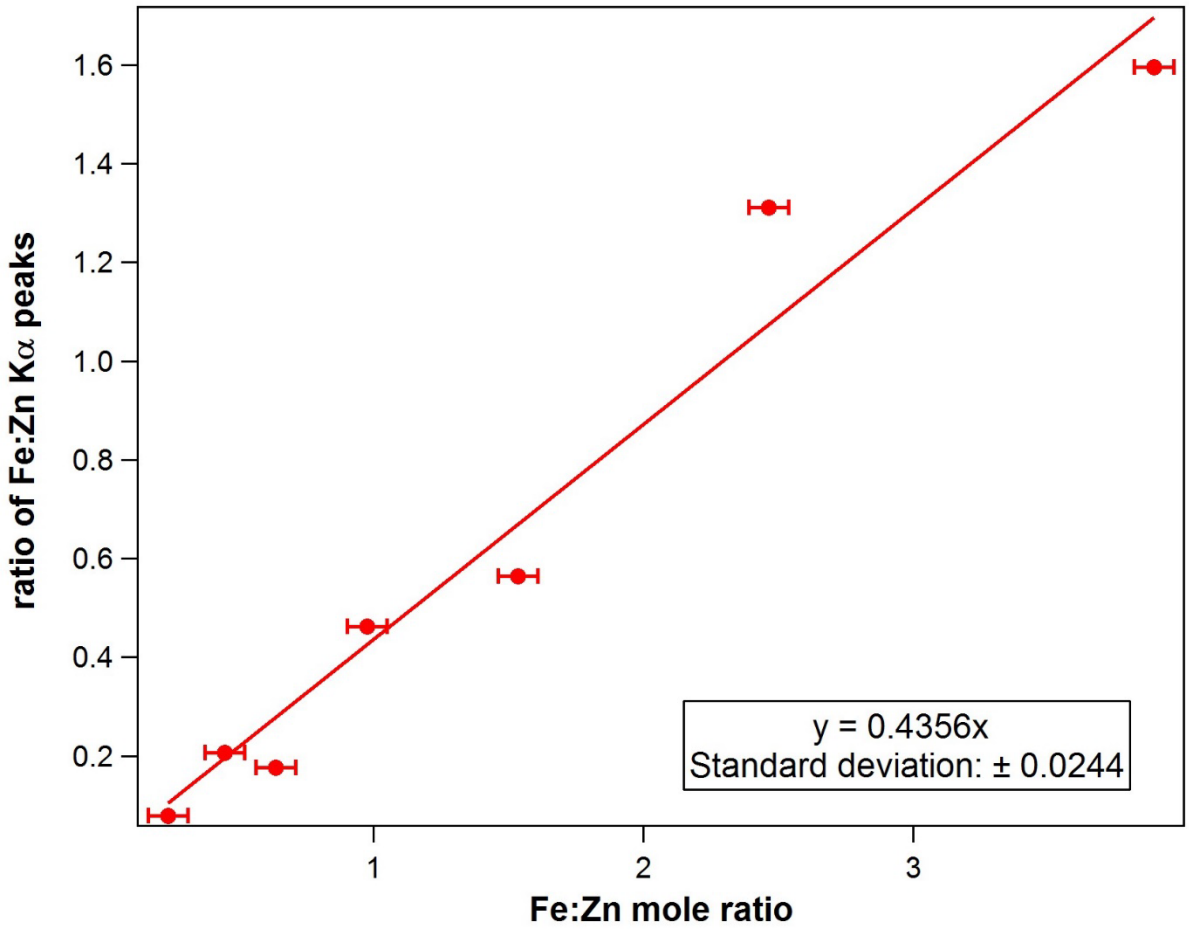

Figure S13. Solid-state X-ray fluorescence calibration curve obtained from homogeneous powder samples of ferrocene and bis[4,4,4-trifluoro-1-(2-thienyl-1,3-butanedionato)]zinc·(TMEDA).

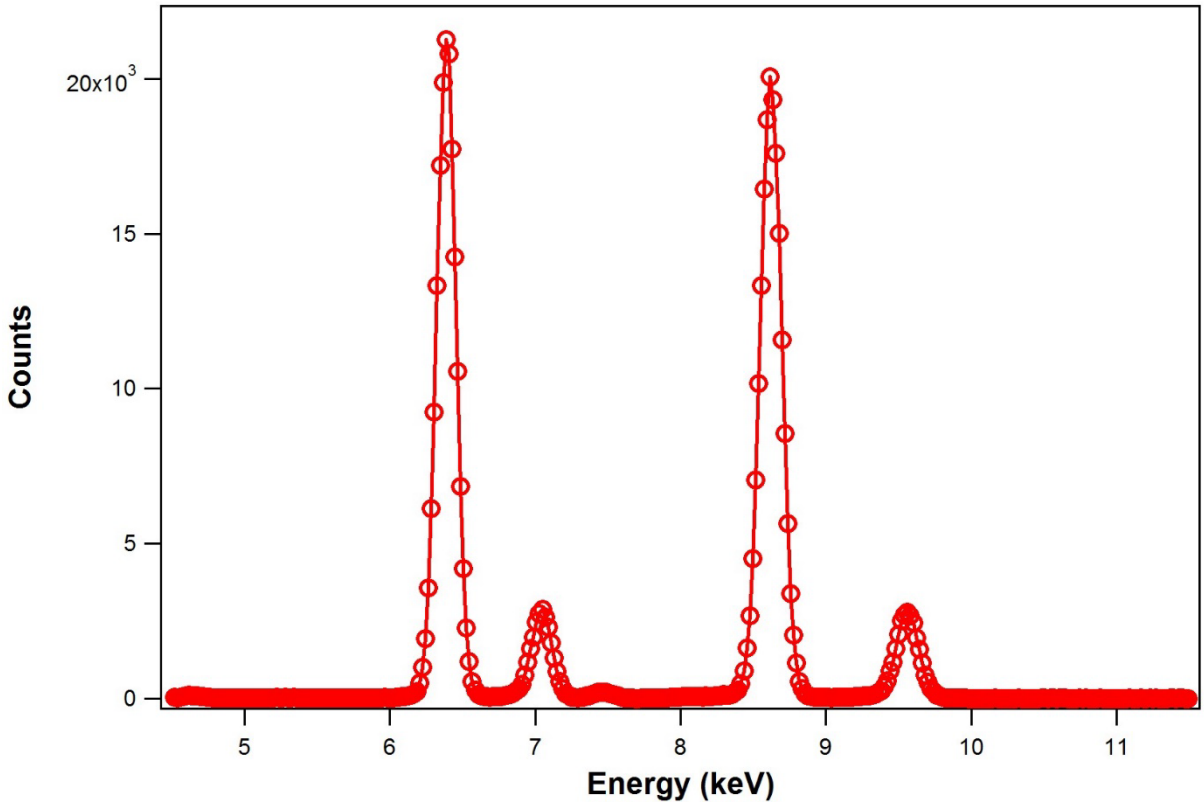

Figure S14. X-ray fluorescence spectrum of (^{tbs}L)Fe_2Zn(thf) (**5**).

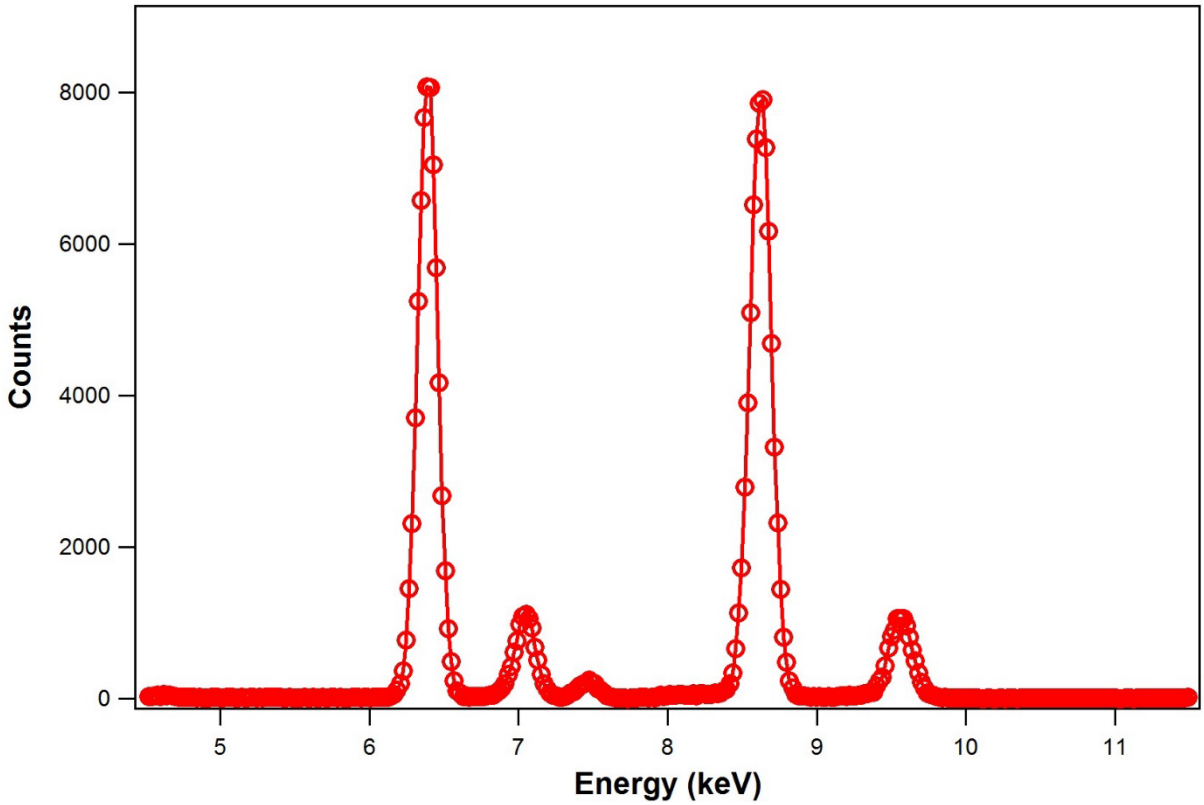

Figure S15. X-ray fluorescence spectrum of (^{tbs}L)Fe_2Zn(py) (**6**).

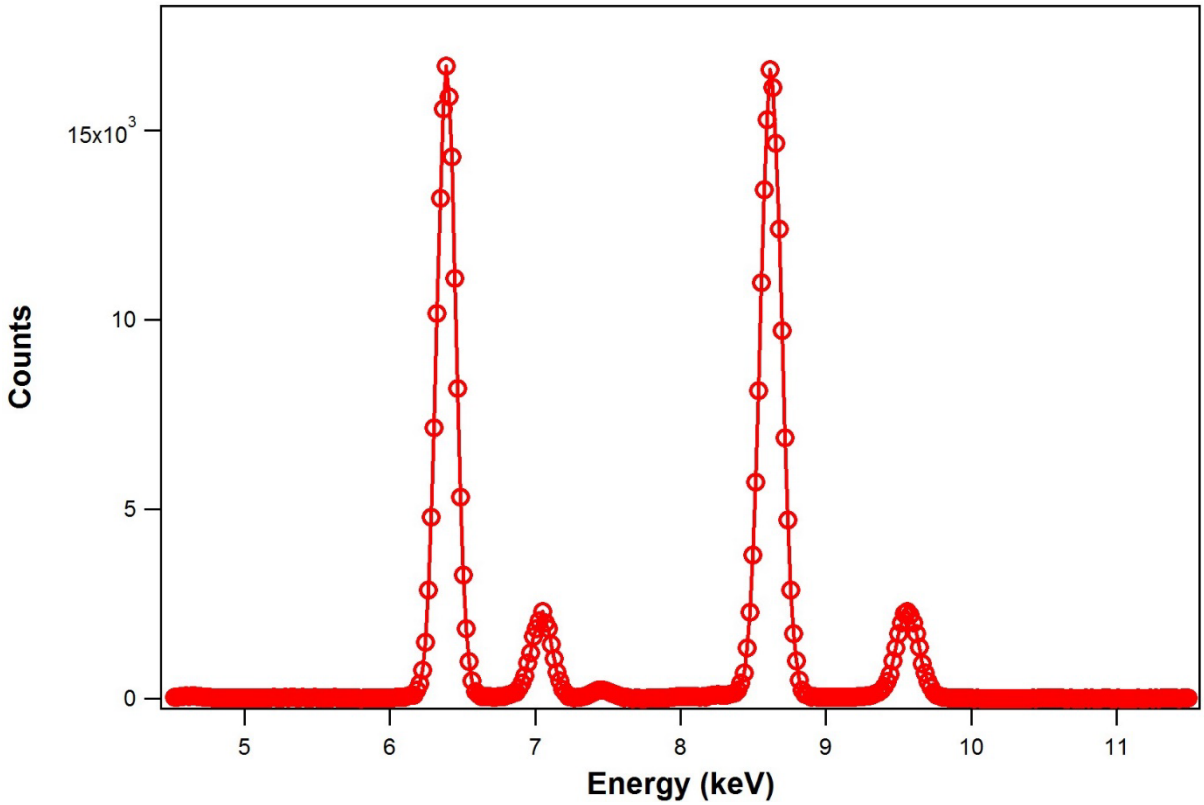

Figure S16. X-ray fluorescence spectrum of $[NBu_4][(^{tbs}L)Fe_nZn_{3-n}(\mu^3\text{–}Cl)]$ (**9**).

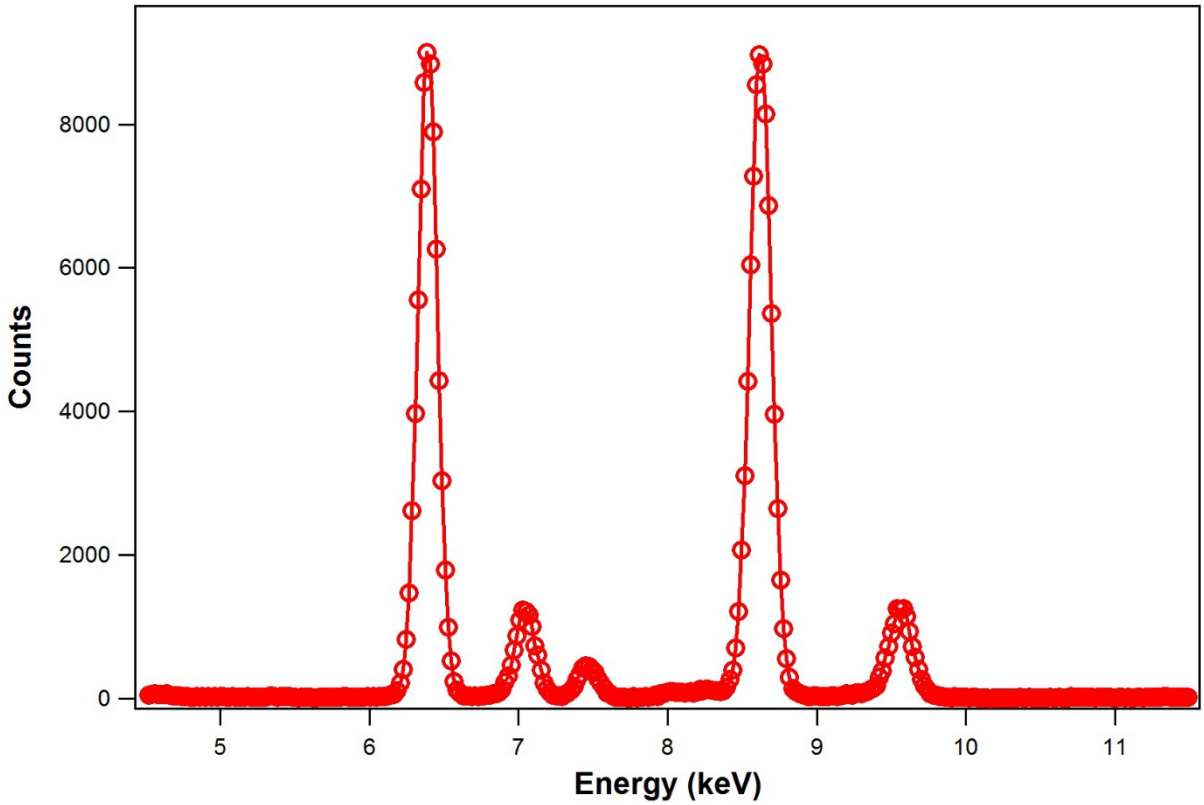

Figure S17. X-ray fluorescence spectrum of (^{tbs}L)$Fe_2Zn(\mu^3$–NPh)(py) (**12**).

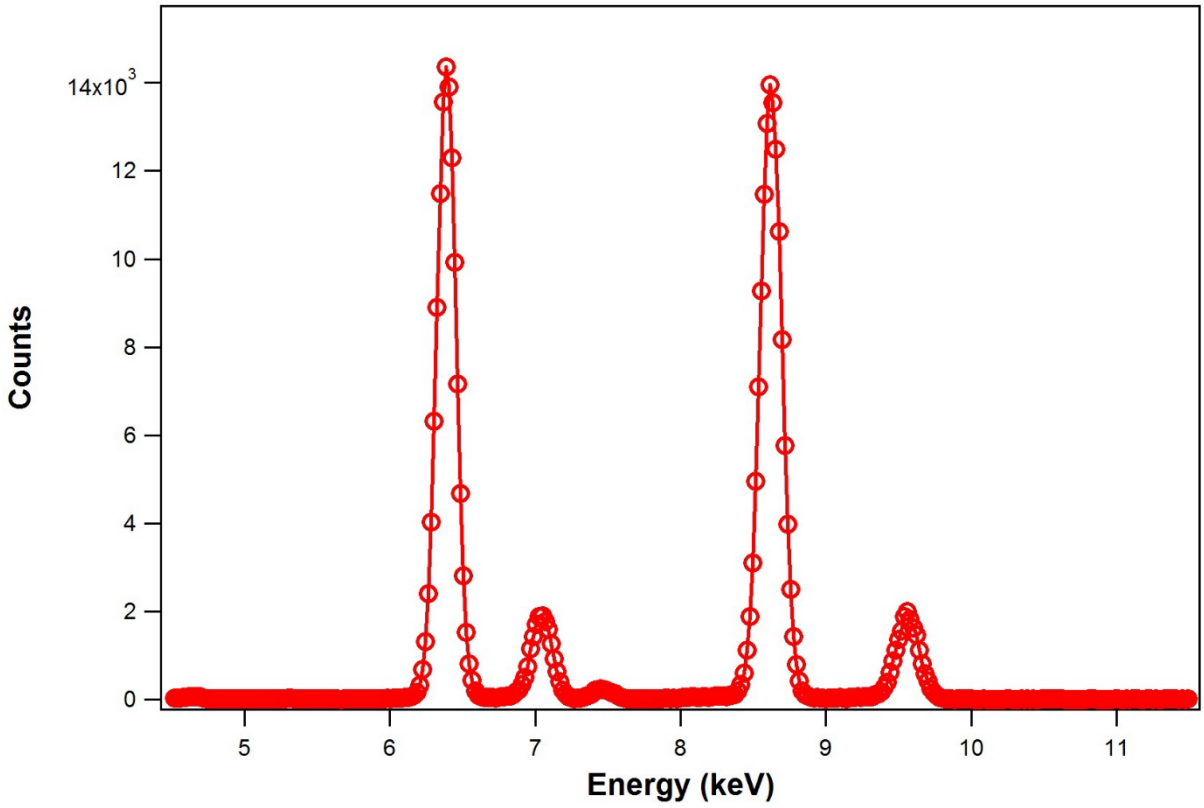

Figure S18. X-ray fluorescence spectrum of (^{tbs}L)$Fe_2Zn(\mu^3$–N(3,5-$(CF_3)_2C_6H_3$))(py) (**14**).

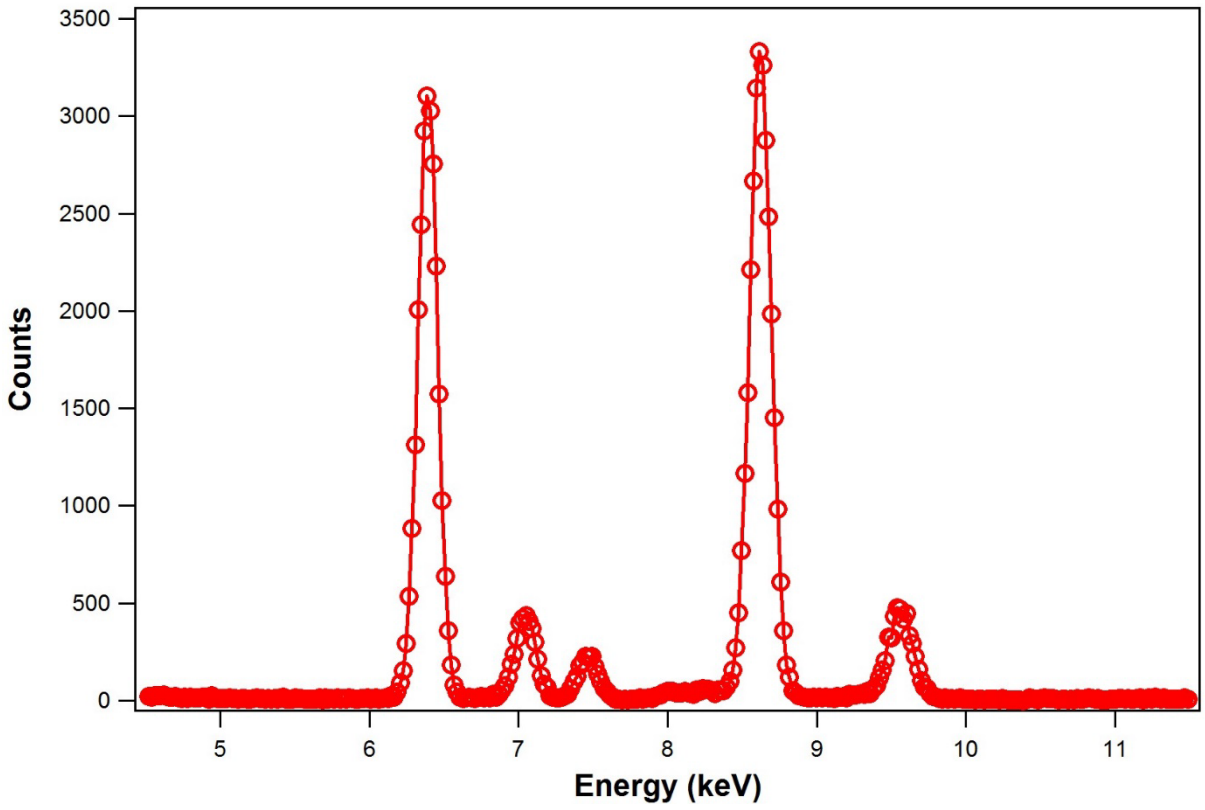

Figure S19. X-ray fluorescence spectrum of [2,2,2-cryptand(K)][(^{tbs}L)Fe_2Zn(μ^3–N(3,5-$(CF_3)_2C_6H_3$))] (**16**).

NMR Spectroscopy

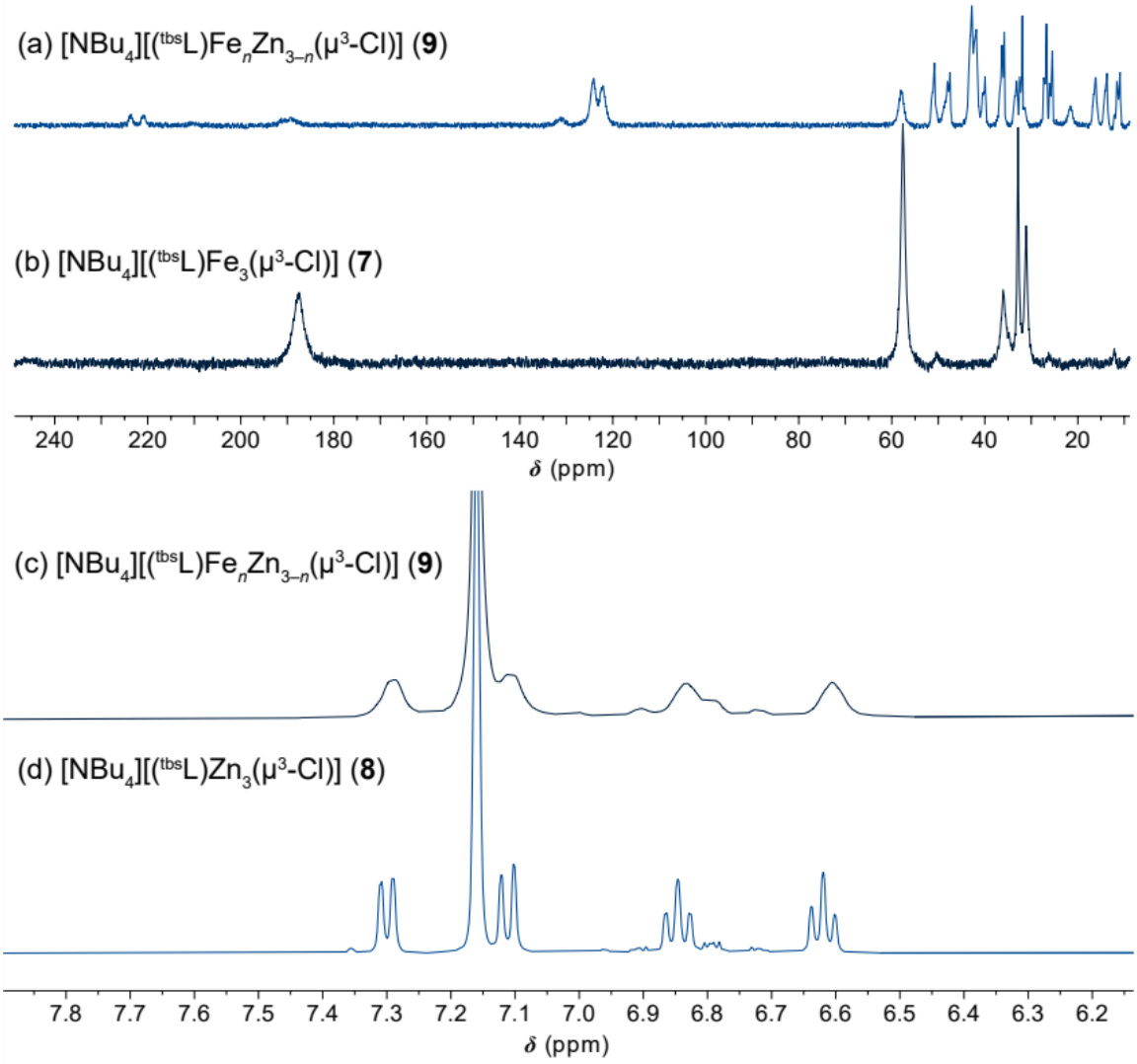

Figure S20. Comparison of ^{1}H NMR spectra of [NBu_4][(^{tbs}L)Fe_nZn_{3-n}(μ^3–Cl)] (**9**) with that of the analogous homometallic species [NBu_4][(^{tbs}L)Fe_3(μ^3–Cl)] (**7**) and [NBu_4][(^{tbs}L)Zn_3(μ^3–Cl)] (**8**). A portion of the paramagnetic window is shown for **9** (a) and **8** (b). The diamagnetic region has been removed from these spectra for clarity. The bottom figure shows an enlargement of the diamagnetic aromatic region of the spectra **9** (c) and **8** (d). The peaks highlighted in black in (a) and (c) correspond to the homometallic products which form upon anation of the hetero-metallic starting materials; the intense resonance at 7.16 ppm corresponds to the benzene solvent residual.

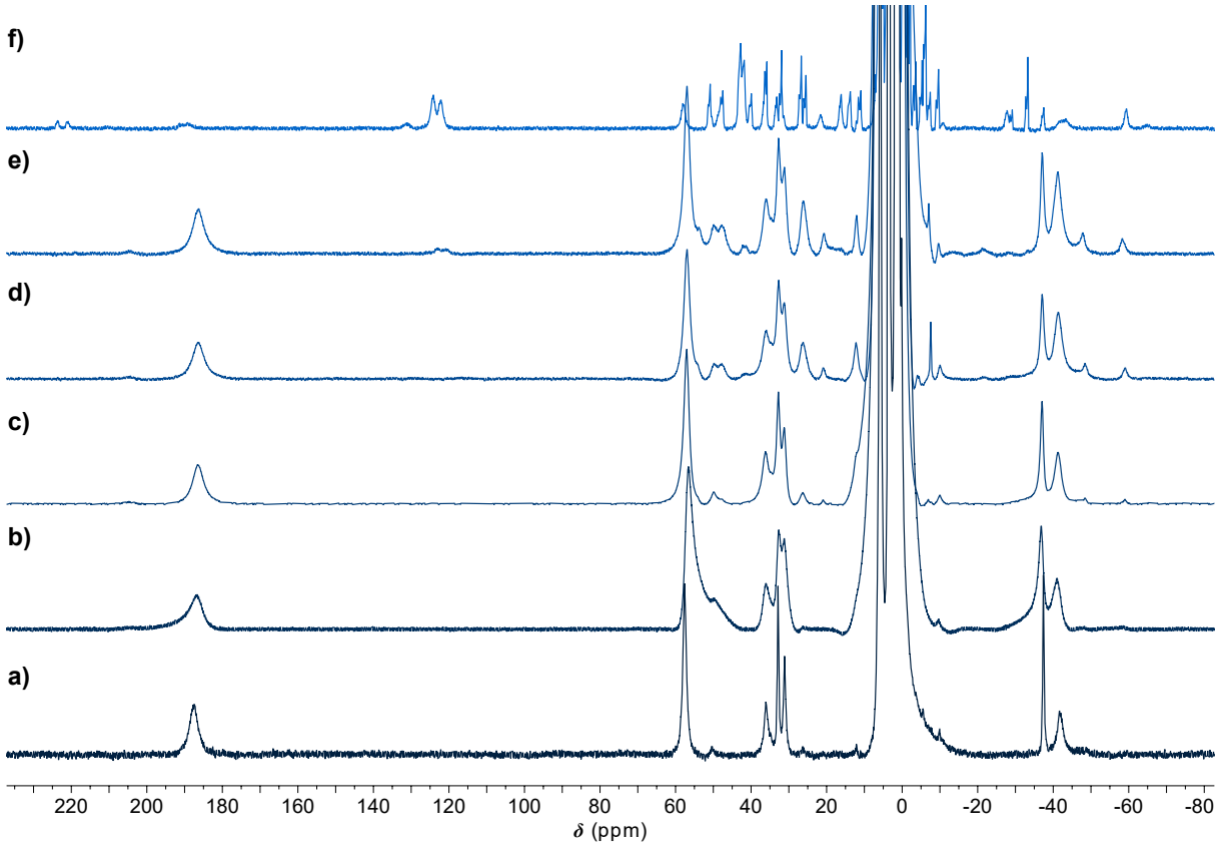

Figure S21. ^{1}H NMR spectra of a mixture of [NBu_4][(^{tbs}L)Fe_3(μ^3–Cl)] (**7**) and [NBu_4][(^{tbs}L)Zn_3(μ^3–Cl)] (**8**) subjected to heat in THF: (a) authentic **7**, (b) 24 h at room temperature, (c) 24 h at 40 ˚C, (d) 24 h at 60 ˚C, (e) 24 h at 80 ˚C, (f) authentic [NBu_4][(^{tbs}L)Fe_nZn_{3-n}(μ^3–Cl)] (**9**).

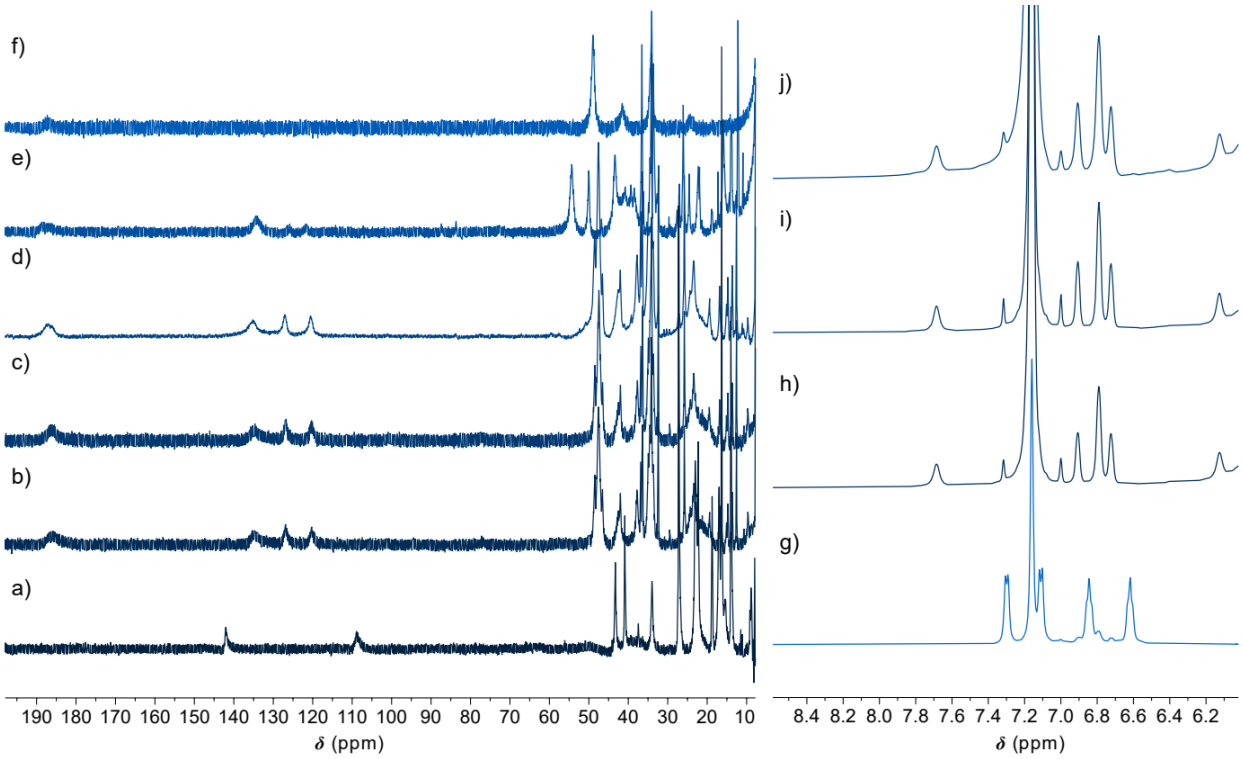

Figure S22 Left: ^{1}H NMR spectra of a) (^{tbs}L)Fe$_2$Zn(thf) (**5**), b) the reaction mixture formed from **5** and [NBu$_4$][(^{tbs}L)Fe$_3$(μ^3–Cl)] (**7**) after 4 h, c) after 24 h, d) after 24 h at 60 °C, e) [NBu$_4$][(^{tbs}L)Fe$_n$Zn$_{3-n}$(μ^3–Cl)] (**9**), and f) **7**, recorded in THF/C$_6$D$_6$ (25% v/v). Right: Magnification of aromatic regions of the same spectra for g) [NBu$_4$][(^{tbs}L)Zn$_3$(μ^3–Cl)] (**8**), h) the reaction mixture formed from **5** and **7** after 4 h, i) after 24 h, and j) after 24 h at 60 °C.

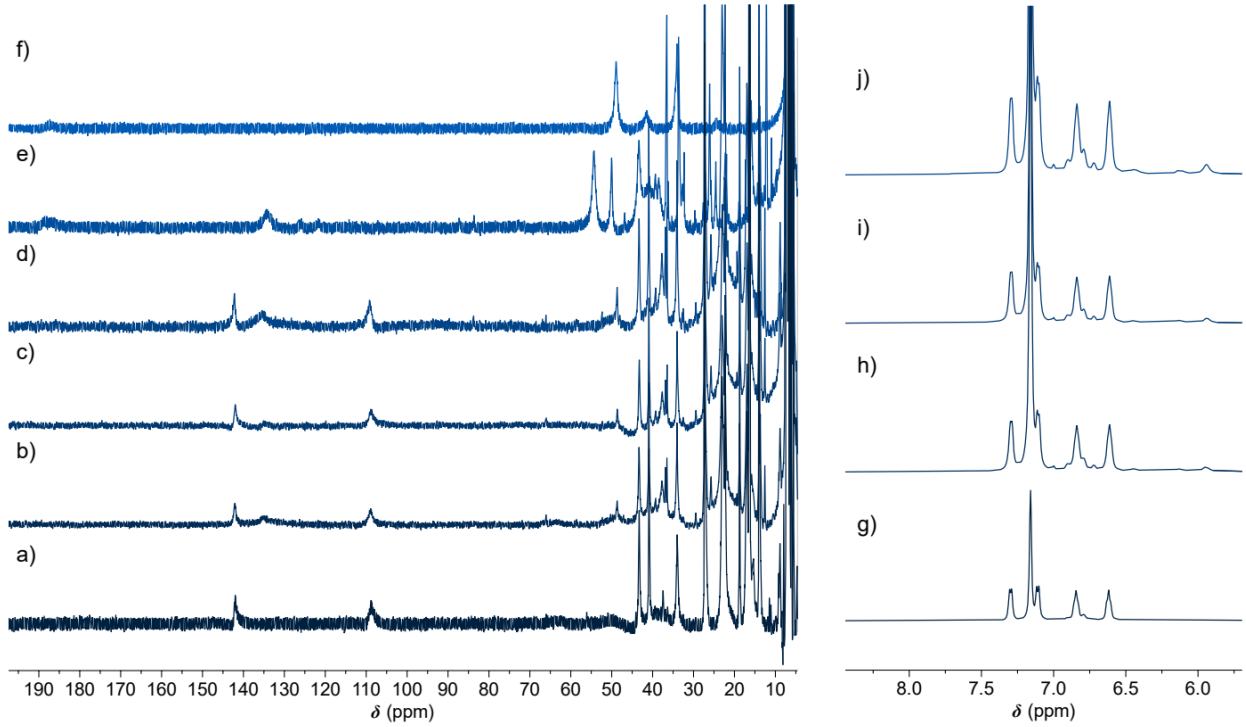

Figure S23. Left: ^{1}H NMR spectra of a) (^{tbs}L)Fe$_2$Zn(thf) (**5**), b) the reaction mixture formed from **5** and [NBu$_4$][(^{tbs}L)Zn$_3$(μ^3–Cl)] (**8**) after 4 h, c) after 24 h, d) after 24 h at 60 °C, e) [NBu$_4$][(^{tbs}L)Fe$_n$Zn$_{3-n}$(μ^3–Cl)] (**9**), and f) [NBu$_4$][(^{tbs}L)Fe$_3$(μ^3–Cl)] (**7**), recorded in THF/C$_6$D$_6$ (25% v/v). Right: Magnification of aromatic regions of the same spectra for g) **8**, h) the reaction mixture formed from **5** and **8** after 4 h, i) after 24 h, and j) after 24 h at 60 °C.

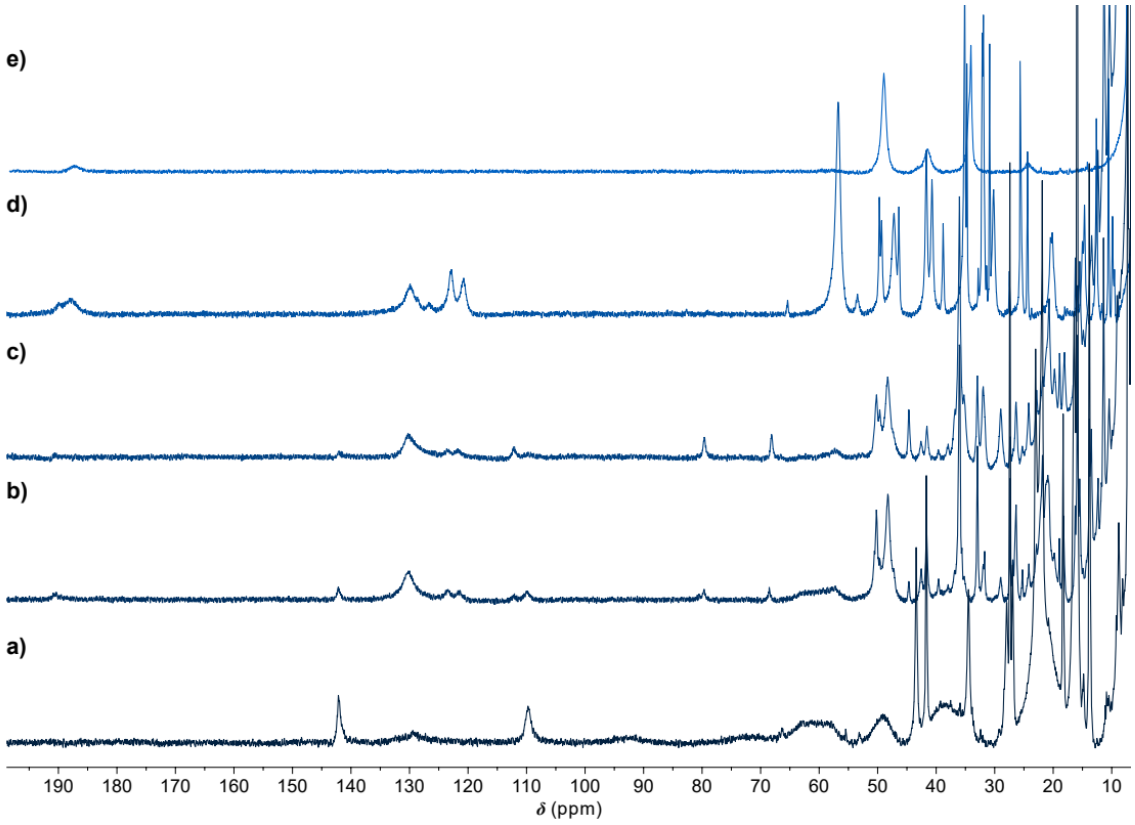

Figure S24. ^{1}H NMR spectra of a) (^{tbs}L)Fe$_2$Zn(thf) (**5**), b) the reaction mixture formed from **5** and $FeCl_2$ after 4 h, c) after 24 h, d) [NBu$_4$][(^{tbs}L)Fe$_n$Zn$_{3-n}$(μ^3–Cl)] (**9**), and e) [NBu$_4$][(^{tbs}L)Fe$_3$(μ^3–Cl)] (**7**), recorded in THF.

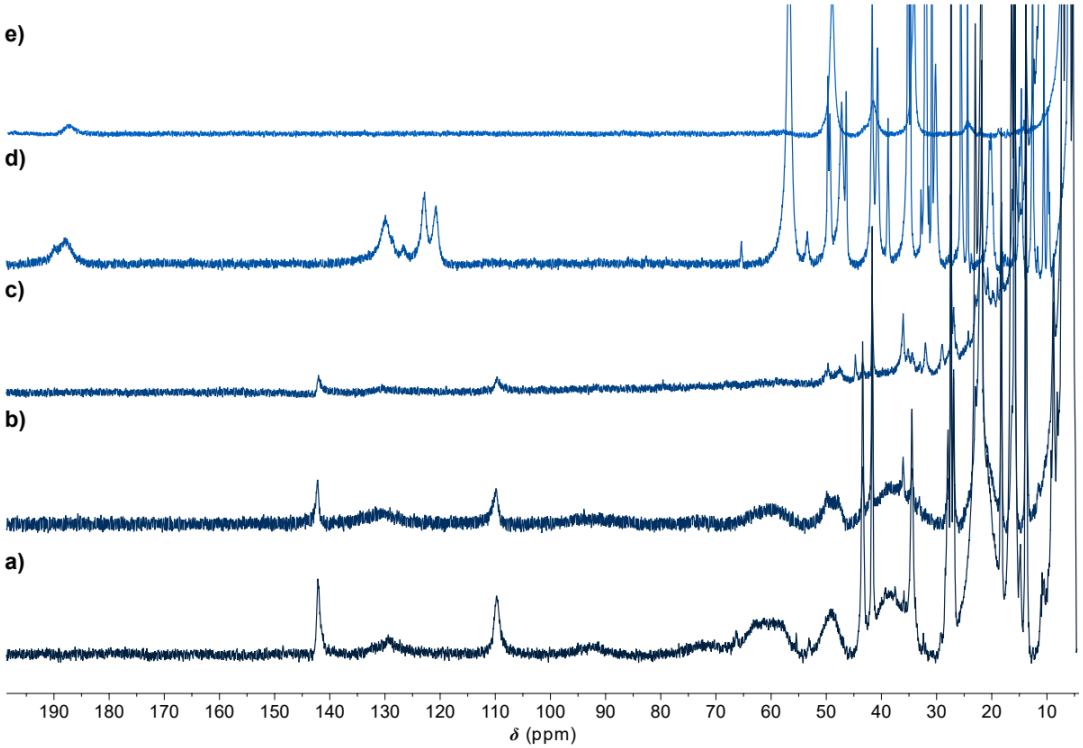

Figure S25. ^{1}H NMR spectra of a) (^{tbs}L)Fe$_2$Zn(thf) (**5**), b) the reaction mixture formed from **5** and $ZnCl_2$ after 4 h, c) after 24 h, d) [NBu$_4$][(^{tbs}L)Fe$_n$Zn$_{3-n}$(μ^3–Cl)] (**9**), and e) [NBu$_4$][(^{tbs}L)Fe$_3$(μ^3–Cl)] (**7**), recorded in THF.

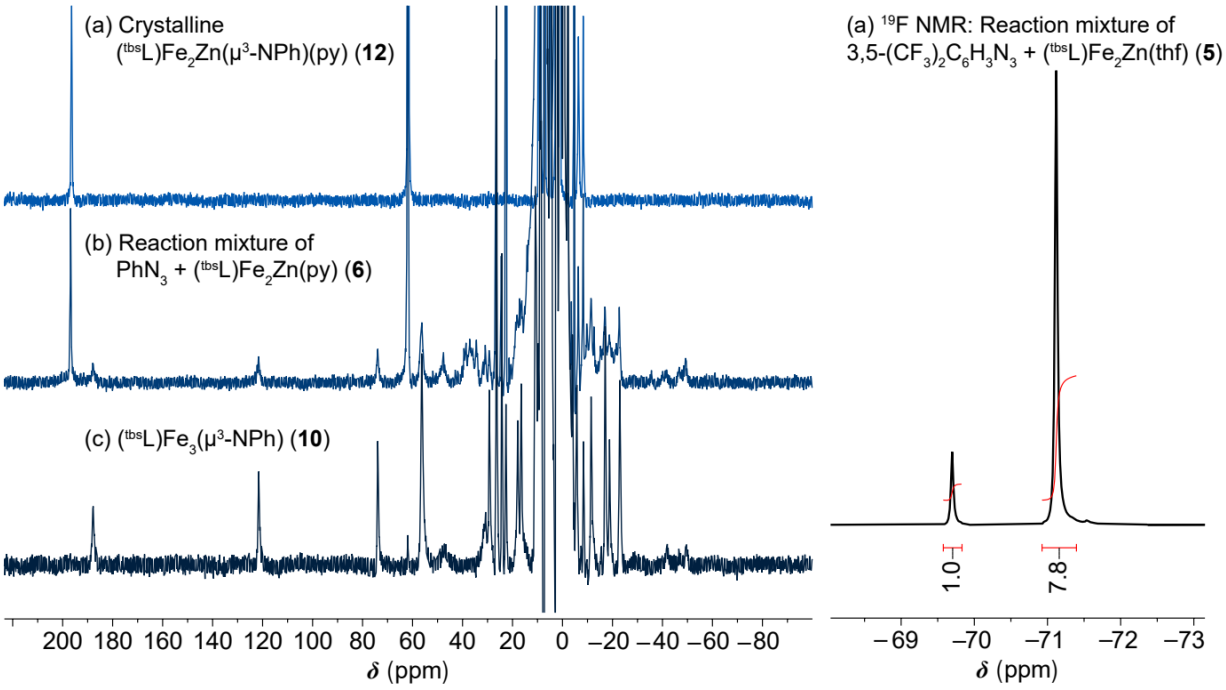

Figure S26. Comparison of ^{1}H NMR spectrum of (^{tbs}L)Fe$_3$(μ^3–NPh) (**10**) (c) with that of the crystalline mixed-metal product (^{tbs}L)Fe$_2$Zn(μ^3–NPh)(py) (**12**) (a) and the reaction mixture formed by treatment of (^{tbs}L)Fe$_2$Zn(py) (**6**) with phenyl azide (b). The right-hand figure (d) shows the integrated ^{19}F NMR spectrum of the products obtained via reaction of (^{tbs}L)Fe$_2$Zn(thf) (**5**) with 3,5-(CF$_3$)$_2$C$_6$H$_3$N$_3$. The smaller of the two peaks (–69.7 ppm) represents the triiron product (^{tbs}L)Fe$_3$(μ^3–N(3,5-(CF$_3$)$_2$C$_6$H$_3$)), while the larger peak (–71.1 ppm) represents the mixed-metal species (^{tbs}L)Fe$_2$Zn(μ^3–N(3,5-(CF$_3$)$_2$C$_6$H$_3$)), indicating a 7.8:1 ratio of products, with the diiron species dominating the mixture.

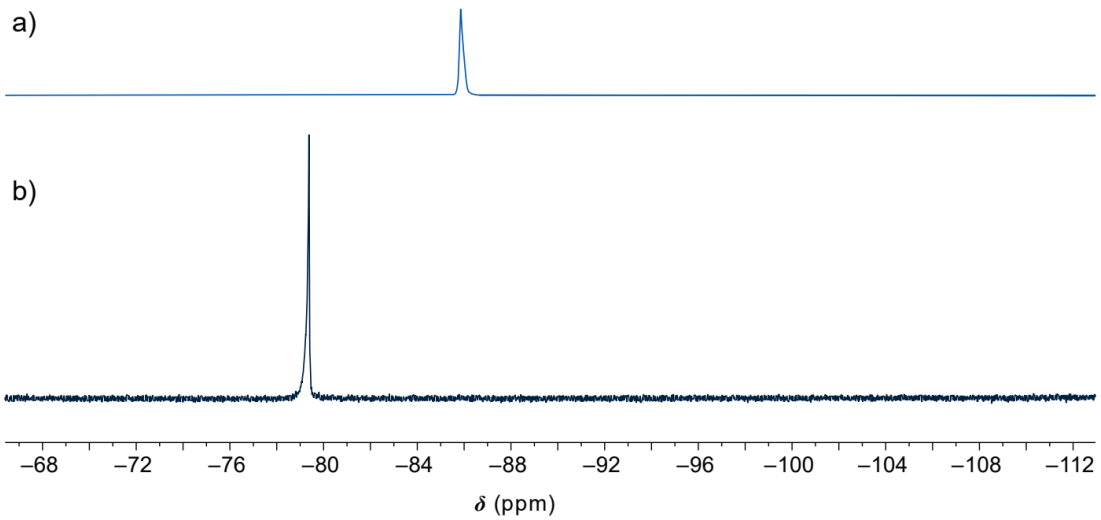

Figure S27. ^{19}F NMR spectra for [$CoCp^*_2$][(^{tbs}L)Fe_3(μ^3–N(3,5-$(CF_3)_2C_6H_3$))] (**15**) (a) and [2,2,2-cryptand(K)][(^{tbs}L)Fe_2Zn(μ^3–N(3,5-$(CF_3)_2C_6H_3$))] (**16**) (b).

SQUID Magnetometry

Dc susceptibility and magnetization data for **1** were simultaneously modeled according to a spin-Hamiltonian for three exchange-coupled spins in an equilateral arrangement ($J_1 = J_2 = J_3$): $\hat{H} = -2(J_1S_1S_2 + J_2S_1S_3 + J_3S_2S_3) + D\hat{S}_z^2 + E(\hat{S}_x^2+\hat{S}_y^2) + g\mu_B\hat{S}B$. The fit parameters are: J = +40(1) cm^{-1}, D = 20.0(9) cm^{-1}, $|E/D|$ = 0.082(7) cm^{-1}, and g = 1.92(1). Attempts to fit the data according to an isosceles ($J_1 = J_2 \neq J_3$) or to a scalene triangle ($J_1 \neq J_2 \neq J_3$) gave physically implausible values of the exchange coupling constants, zero-field splitting parameters, or both. A fit of the data according to a single "giant-spin" system using a spin-Hamiltonian of the form): $\hat{H} = D\hat{S}_z^2 + E(\hat{S}_x^2+\hat{S}_y^2) + g\mu_B\hat{S}B$ provided an inferior fit of the dc susceptibility data that did not reproduce the diminution of χ_MT at higher temperatures.

Attempts to fit the dc susceptibility and magnetization data for **5** were unsuccessful when considering either an exchange-coupled two spin system or a single S = 4 manifold. Inclusion of temperature independent paramagnetism or intermolecular interaction (zJ) terms did not provide physically reasonable fits. A likely explanation for this is the contamination of **5** with trace quantities of **1**. This possibility seems reasonable in light of the facile metal redistribution observed in complexes of this family; indeed, the presence of even trace quantities of **1**, which possesses a much larger value of χ_MT across the surveyed temperature range, will significantly impact attempts to fit the data. Nonetheless, the essential features of the dc susceptibility and magnetization data strongly indicate that **5** is an antiferromagnetically coupled system which populates high-spin states at higher temperatures.

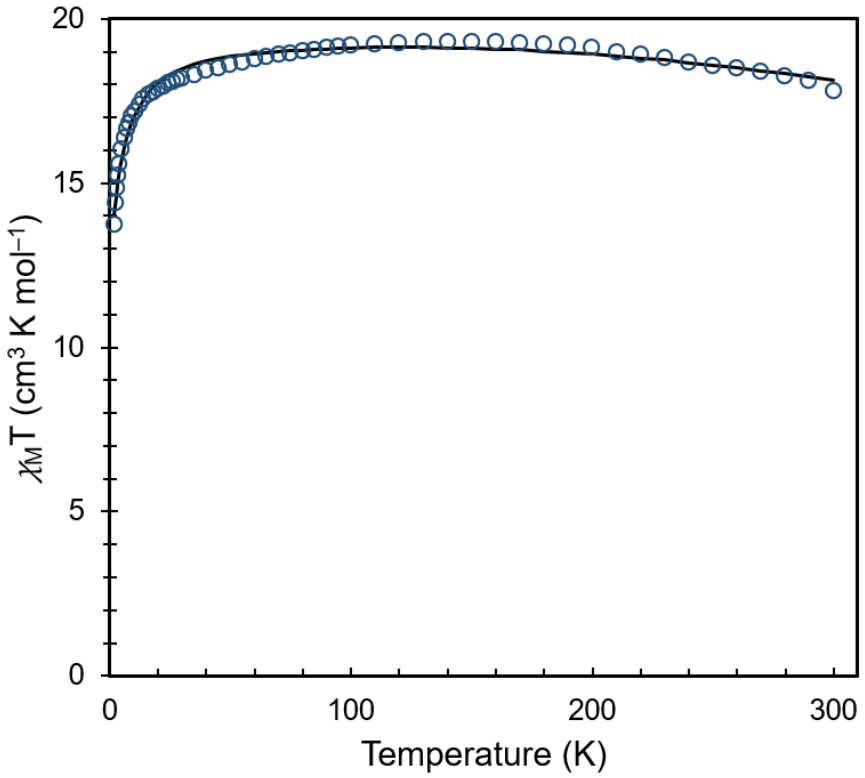

Figure S28. Plot of $\chi_M T$ for (^{tbs}L)Fe$_3$(thf) (**1**) over a temperature range of 1.8-300 K. Experimental data are denoted by open circles, and the fit is denoted by a black line.

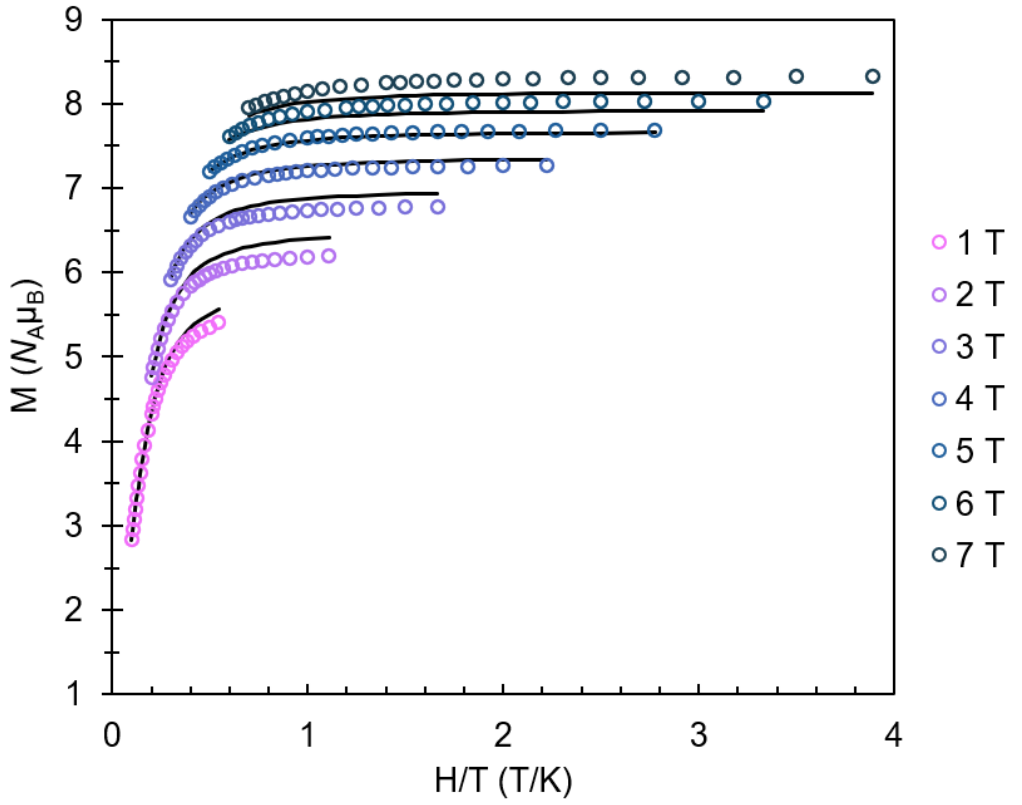

Figure S29. Plot of reduced magnetization for (^{tbs}L)Fe_3(thf) (**1**) over a temperature range of 1.8-10 K and an applied field range of 1.0-7.0 T. Experimental data are denoted by open circles, and the fit is denoted by a black line.

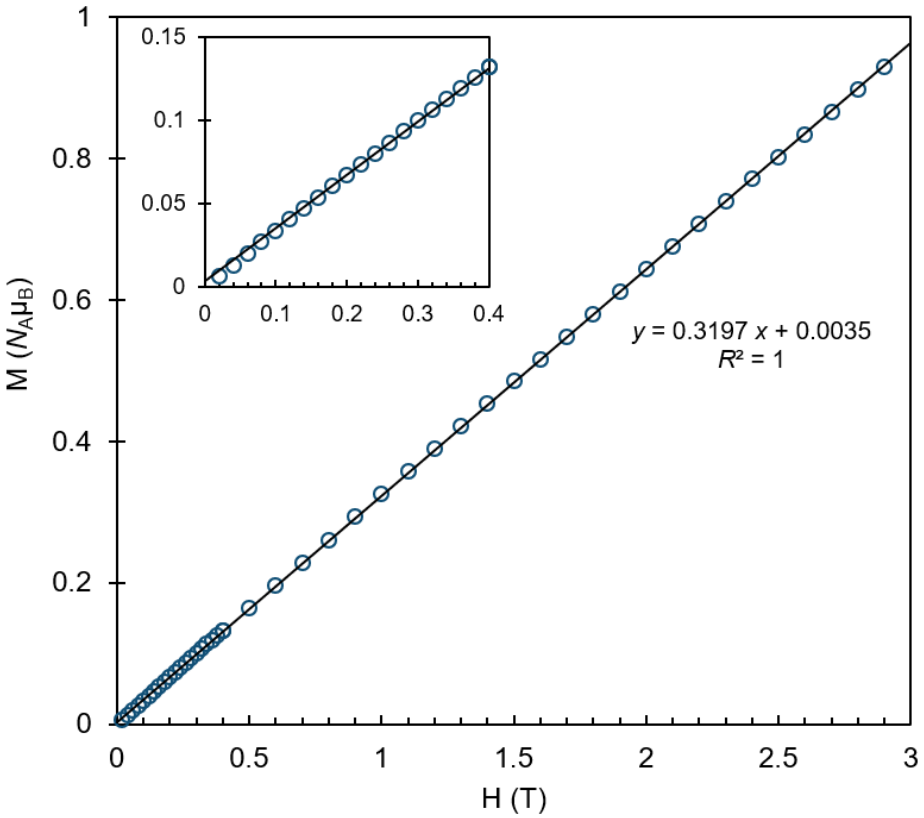

Figure S30. Plot of magnetization for (^{tbs}L)Fe$_3$(thf) (**1**) obtained at 100 K over an applied field of 0-3.0 T. Inset: expansion of low-field region. Linearity of the plot demonstrates the absence of ferromagnetic impurities.

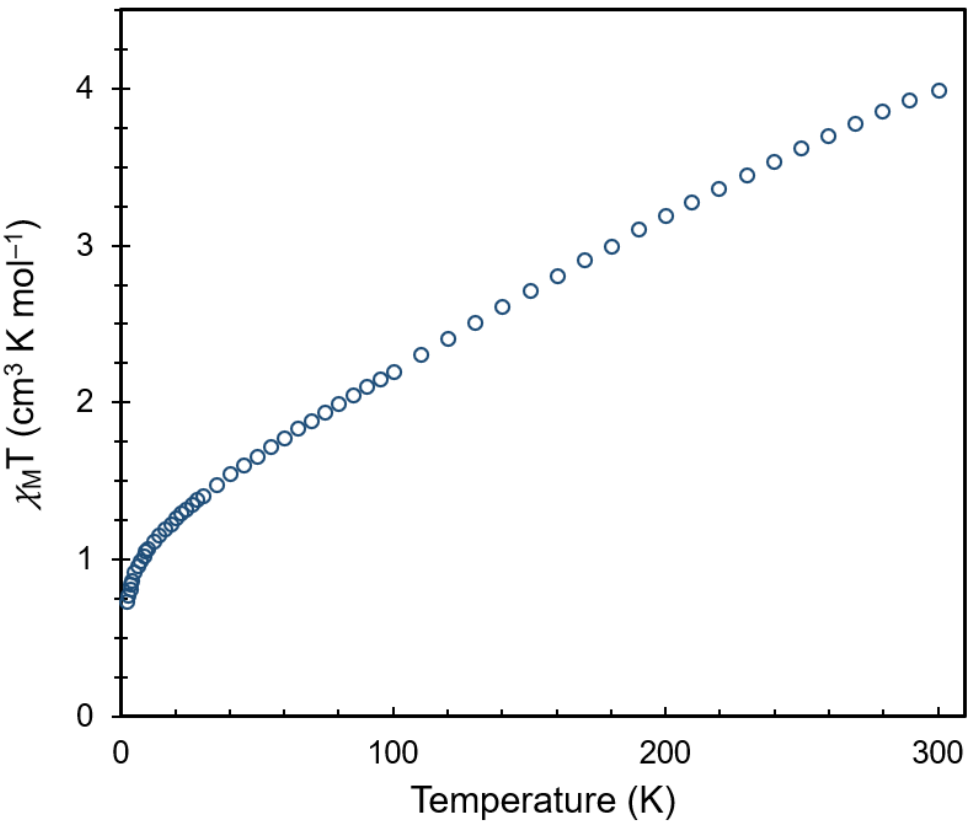

Figure S31. Plot of $\chi_M T$ data for (^{tbs}L)Fe$_2$Zn(thf) (**5**) over a temperature range of 1.8-300 K. Experimental data are denoted by open circles.

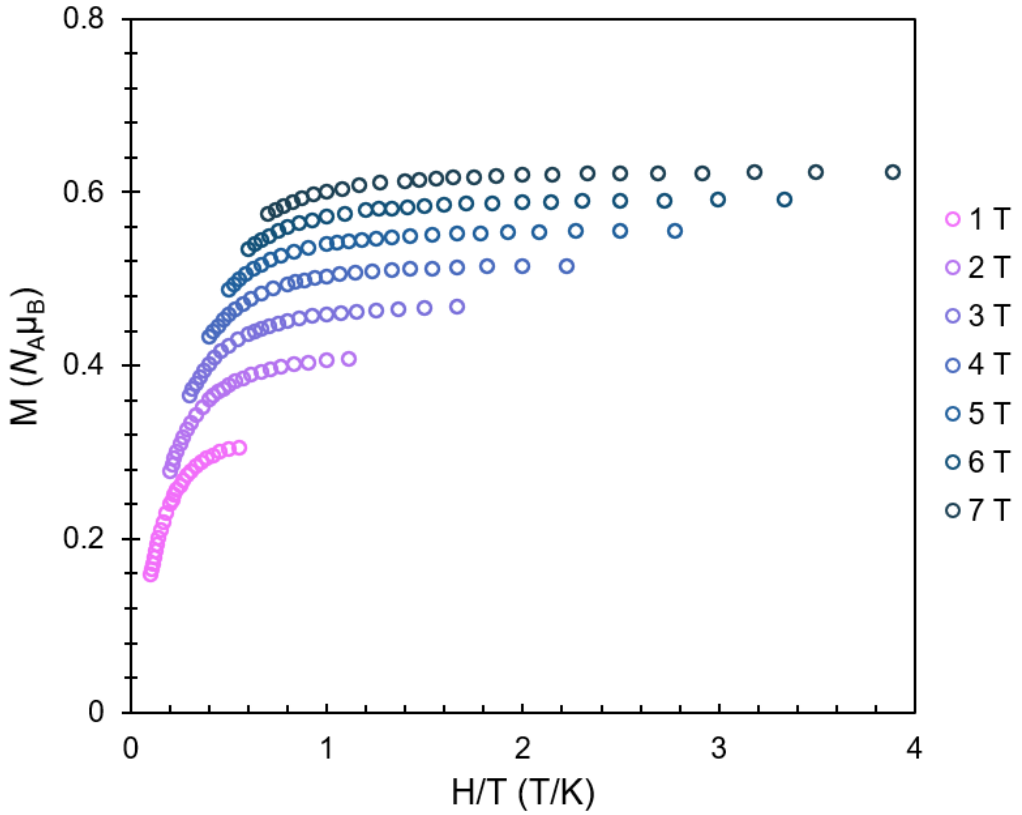

Figure S32. Plot of reduced magnetization for (^{tbs}L)Fe_2Zn(thf) (**5**) over a temperature range of 1.8-10 K and an applied field range of 1.0-7.0 T. Experimental data are denoted by open circles.

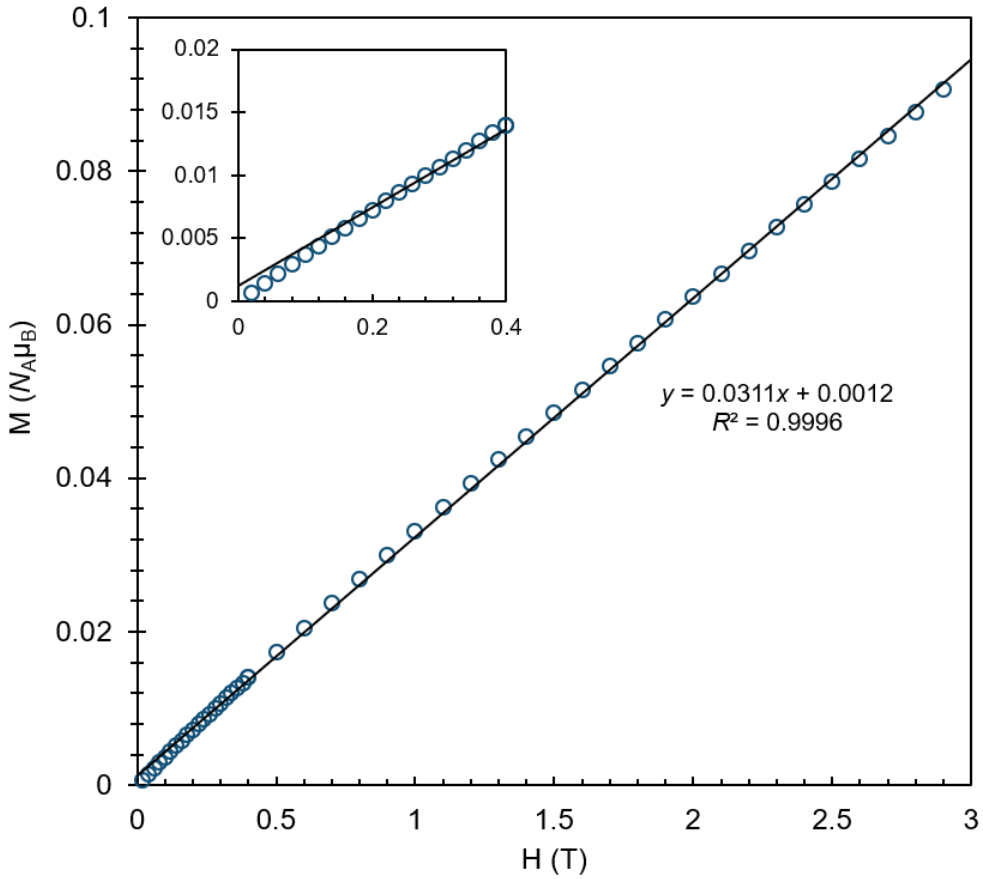

Figure S33. Plot of magnetization for (^{tbs}L)Fe_2Zn(thf) (**5**) obtained at 100 K over an applied field of 0-3.0 T. Inset: expansion of low-field region. Linearity of the plot demonstrates the absence of ferromagnetic impurities.

X-Ray Diffraction Techniques

All structures were collected on a Bruker three-circle platform goniometer equipped with an Apex II CCD area detector and an Oxford cryostream cooling device. Radiation was from a graphite fine focus sealed Mo Kα (0.71073 Å) source or synchrotron radiation as specified. Crystals were mounted on a cryoloop or glass fiber pin using Paratone-N oil. Structures were collected at 100 K. Data was collected as a series of φ and/or ω scans. Data was integrated using SAINT[8] and scaled with either a numerical or multi-scan absorption correction using SADABS[8]. The structures were solved by intrinsic phasing or direct methods using SHELXS-97[9] and refined against F^2 on all data by full matrix least squares with SHELXL-97[9]. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were placed at idealized positions and refined using a riding model. The isotropic displacement parameters of all hydrogen atoms were fixed to 1.2 times the atoms they are linked to (1.5 times for methyl groups). Further details on particular structures are noted below.

(^{tbs}L)Fe$_3$(py) (2). The structure was solved in the monoclinic space group $P2_1/c$ with four molecules per unit cell. The asymmetric unit was found to contain one molecule of **2** and approximately two molecules of disordered ether. Data was collected at APS using 0.41328 Å radiation. Seven reflections were omitted due to detector overflow.

[Na(thf)(OEt$_2$)][(^{tbs}L)Fe$_2$Na(OEt$_2$)] (4). The structure was solved in the triclinic space group $P\bar{1}$ with two molecules per unit cell. The asymmetric unit was found to contain one molecule of **4**. Data was collected using sealed-tube Mo radiation. The sodium ion that is contained with the ligand pocket is bound to one molecule of solvent (diethyl ether), which is disordered over two positions. The second sodium ion, which is coordinated to the ligand via arene interactions is bound to two solvent molecules. One of the solvents is disordered between diethyl ether and tetrahydrofuran. Two of the t-butyl dimethylsilyl groups are modeled with positional disorder. Note: crystallization conditions result in difference in solvation from powder material.

(^{tbs}L)Fe$_2$Zn(thf) (5). The structure was solved in the monoclinic space group $P2_1/n$ with four molecules per unit cell. The asymmetric unit was found to contain one molecule of (^{tbs}L)Fe$_2$Zn(thf) and one molecule of hexane. Data was collected at APS using 0.40659 Å radiation. Eight reflections were omitted due to detector overflow. Residual electron density from disordered solvent channels was removed using the SQUEEZE function in Platon.

(^{tbs}L)Fe$_2$Zn(py) (6). The structure was solved using the intrinsic phasing method in the triclinic space group $P\bar{1}$ with two molecules per unit cell. The asymmetric unit was found to contain one molecule of (^{tbs}L)Fe$_2$Zn(py) and half a molecule of hexane (located on a special position). Data was collected at APS using 0.40651 Å radiation. Eleven reflections were omitted due to detector overflow.

[NBu$_4$][(^{tbs}L)Fe$_n$Zn$_{3-n}$(μ^3–Cl)] (9). The structure was solved in the orthorhombic space group *Pbca* with eight molecules per unit cell. The asymmetric unit was found to contain one molecule of **9**. Data was collected using sealed-tube Mo radiation. Residual electron density from disordered solvent channels was removed using SQUEEZE function in Platon. Disorder was modeled in butyl group of the tetrabutylammonium counter ion. Occupancy of each metal site was restricted to 67% Fe and 33% Zn.

[NBu$_4$][(^{tbs}L)Fe$_3$(μ^3–Cl)] (7). The structure was solved in the orthorhombic space group *Pbca* with eight molecules per unit cell. The asymmetric unit was found to contain one molecule of **7**. Data was collected with sealed-tube Mo radiation. Residual electron density from disordered solvent channels was removed using the SQUEEZE function in Platon. Disorder was modeled in butyl group of the tetrabutylammonium counter ion.

[NBu$_4$][(^{tbs}L)Zn$_3$(μ^3–Cl)] (8). The structure was solved in the orthorhombic space group *Pbca* with 8 molecules per unit cell. The asymmetric unit was found to contain one molecule of **8**. Data was collected using sealed-tube Mo radiation. Residual electron density from disordered solvent channels was removed using the SQUEEZE function in Platon. Disorder was modeled in butyl group of the tetrabutylammonium counter ion.

(^{tbs}L)Fe$_2$Zn(μ^3–NPh) (11). The structure was solved in the monoclinic space group *C2/c* with eight molecules in the unit cell. The asymmetric unit was found to contain one molecule of **11**. Data was collected using sealed-tube Mo radiation. Residual electron density from disordered solvent channels was removed using the SQUEEZE function in Platon. Disorder was modeled in the orientation of one of the *tert*-butyldimethylsilyl groups of the ligand and in the orientation of the imido moiety. Occupancy of each metal site was restricted to 67% Fe and 33% Zn.

(^{tbs}L)Fe$_2$Zn((μ^3–NPh)(py) (12). The structure was solved in the triclinic space group *P–1* with 2 molecules per unit cell. The asymmetric unit was found to contain one molecule of **12**. Data was collected at APS using 0.40651 Å radiation. Residual electron density from disordered solvent channels was removed using the SQUEEZE function in Platon. Bad reflections were omitted due to detector overflow.

(^{tbs}L)Fe$_3$(μ^3–N(3,5-(CF$_3$)$_2$C$_6$H$_3$)) (13). The structure was solved in the monoclinic space group $P2_1/n$ with four molecules per unit cell. The asymmetric unit was found to contain one molecule of **13**. Data was collected using sealed-tube Mo radiation. There appears to be whole-molecule disorder, where the molecule is in two slightly different orientations. However, the occupancy of this second part of is so small that only metal atoms can be modeled. Additionally, disorder was modeled on one *tert*-butyldimethylsilyl group.

(^{tbs}L)Fe$_2$Zn(μ^3–N(3,5-(CF$_3$)$_2$C$_6$H$_3$))(py) (14). The structure was solved in the triclinic space group *P*–1 with two molecules per unit cell. The asymmetric unit was found to contain one molecule of **14**. Data was collected using sealed-tube Mo radiation. Residual electron density from disordered solvent channels was removed using the SQUEEZE function in Platon. One of the CF_3 groups was modeled with rotational disorder.

[CoCp*$_2$][(^{tbs}L)Fe$_3$(μ^3–N(3,5-(CF$_3$)$_2$C$_6$H$_3$))] (15). The structure was solved in the monoclinic space group $P2_1/n$ with four molecules per unit cell. The asymmetric unit was found to contain one molecule of **15** and one molecule of diethyl ether. Data was collected using sealed-tube Mo radiation. Residual electron density from disordered solvent channels was removed using the SQUEEZE function in Platon. Both CF_3 groups were modeled with rotational disorder.

[2,2,2-cryptand(K)][(^{tbs}L)Fe$_2$Zn(μ^3–N(3,5-(CF$_3$)$_2$C$_6$H$_3$))] (16). The structure was solved in the triclinic space group *P*–1 with four molecules per unit cell. The asymmetric unit was found to contain two molecules of **16** and several disordered diethyl ether solvent molecules. Data was collected at APS using 0.41328 Å radiation. Diethyl ether was modeled to fill the solvent voids in the structures, but has large ADPs due to large amounts of disorder. Occupancy of the metal sites was allowed to freely refine.

Table S2 X-ray diffraction experimental details

	(^{tbs}L)Fe$_3$(py) **(2)**	[Na(thf)(OEt$_2$)] [(^{tbs}L)Fe$_2$Na(OEt$_2$)] **(4·Et$_2$O)**	(^{tbs}L)Fe$_2$Zn(thf) **(5)**	(^{tbs}L)Fe$_2$Zn(py) **(6)**
Chemical formula	$C_{54}H_{88.50}Fe_3N_7O_{1.75}Si_3$	$C_{54}H_{94.97}Fe_2N_6Na_2O_3Si_3$	$C_{52}H_{88}Fe_2N_6OSi_3Zn$	$C_{50}H_{78}Fe_2N_7Si_3Zn$
FW	1115.63	1118.27	1074.62	1038.53
Crystal System	Monoclinic	Triclinic	Monoclinic	Triclinic
Space Group	*P*2$_1$/*c*	*P*–1	*P*2$_1$/*n*	*P*–1
Temperature (K)	100	100	100	100
***a* (Å)** ***b* (Å)** ***c* (Å)**	10.4451 (12) 27.261 (3) 21.186 (3)	11.040 (2) 14.175 (3) 21.290 (5)	10.3835 (18) 18.015 (2) 30.663 (7)	10.6298 (8) 11.1655 (9) 23.6682 (18)
α (°) ***β* (°)** **γ (°)**	90 102.166 (4) 90	106.479 (4) 93.058 (4) 106.770 (4)	90 91.703 (6) 90	98.248 (2) 101.941 (2) 101.506 (2)
***V* (Å^3)**	5897.2 (12)	3025.6 (11)	5733.3 (17)	2642.6 (4)
Z	4	2	4	2
Radiation type	Synchrotron λ = 0.41328 Å	Mo *K*α	Synchrotron λ = 0.40659 Å	Synchrotron λ = 0.40651 Å
μ (mm^{-1})	0.17	0.60	0.51	0.21
Crystal size (mm)	0.19 × 0.11 × 0.04	0.3 × 0.2 × 0.1	0.14 × 0.08 × 0.02	0.17 × 0.06 × 0.02
R*1[a]** ***wR*2[b]** ***S (GOOF)	0.042 0.107 1.04	0.040 0.093 1.01	0.059 0.148 1.02	0.044 0.111 1.09
Reflections	12080	11243	17045	8937

[a] $R1 = [\sum w(F_o - F_c)^2 / \sum w F_o^{\,2}]^{1/2}$

[b] $wR2 = [\sum[w(F_o^{\,2} - F_c^{\,2})^2] / \sum w (F_o^{\,2})^2]^{1/2}$ $w = 1/[\sigma^2(F_o^{\,2}) + (aP)^2 + bP]$, where $P = [\max(F_o^{\,2}, 0) + 2((F_c^{\,2})]/3$

Table S2. Continuation …

	[NBu$_4$][(^{tbs}L)Fe$_3$(Cl)] (7)	**[NBu$_4$][(^{tbs}L)Zn$_3$(Cl)] (8)**	**[NBu$_4$][(^{tbs}L)Fe$_{3-n}$Zn$_n$ (Cl)] (9)**	**(^{tbs}L)Fe$_{3-n}$Zn$_n$(NPh) (11)**
Chemical formula	$C_{57}H_{100}ClFe_3N_7Si_3$	$C_{58}H_{102}ClN_7Si_3Zn_3$	$C_{58}H_{102}ClFe_2N_7Si_3Zn$	$C_{48}H_{71}Fe_2N_7Si_3Zn$
FW	1170.70	1213.29	1194.25	1007.45
Crystal System	Orthorhombic	Orthorhombic	Orthorhombic	Monoclinic
Space Group	*Pbca*	*Pbca*	*Pbca*	*C*2/*c*
Temperature (K)	100	100	100	100
***a* (Å)** ***b* (Å)** ***c* (Å)**	26.839 (3) 19.358 (2) 27.601 (4)	27.1744 (9) 19.1482 (7) 27.5979 (10)	27.053 (4) 19.227 (3) 27.643 (4)	22.150 (4) 20.383 (3) 26.428 (4)
α (°) ***β* (°)** **γ (°)**	90 90 90	90 90 90	90 90 90	90 101.975 (3) 90
***V* (Å^3)**	14340 (3)	14360.3 (9)	14378 (4)	11672 (3)
Z	8	8	8	8
Radiation type	Mo *K*α	Mo *K*α	Mo *K*α	Mo *K*α
μ (mm^{-1})	0.72	1.12	0.85	0.99
Crystal size (mm)	0.40 × 0.30 × 0.20	0.40 × 0.39 × 0.38	0.33 × 0.26 × 0.16	0.30 × 0.20 × 0.10
R*1[a]** ***wR*2[b]** ***S (GOOF)	0.043 0.126 1.04	0.033 0.079 1.03	0.056 0.131 1.02	0.068 0.143 1.09
Reflections	13621	12718	12755	10413

[a] $R1 = [\sum w(F_o - F_c)^2 / \sum w F_o{}^2]^{1/2}$

[b] $wR2 = [\sum[w(F_o{}^2 - F_c{}^2)^2] / \sum w (F_o{}^2)^2]^{1/2}$ $w = 1/[\sigma^2(F_o{}^2) + (aP)^2 + bP]$, where $P = [\max(F_o{}^2, 0) + 2((F_c{}^2)]/3$

Table S2. Continuation …

	(^{tbs}L)Fe$_2$Zn(NPh)(py) **(12)**	(^{tbs}L)Fe$_3$(N(3,5-(CF$_3$)$_2$C$_6$H$_3$)) **(13)**	(^{tbs}L)Fe$_2$Zn(N(3,5-(CF$_3$)$_2$C$_6$H$_3$))(py) **(14)**
Chemical formula	$C_{53}H_{76}Fe_2N_8Si_3Zn$	$C_{50}H_{69}F_6Fe_3N_7Si_3$	$C_{55}H_{74}F_6Fe_2N_8Si_3Zn$
FW	1086.55	1133.94	1222.56
Crystal System	Triclinic	Monoclinic	Triclinic
Space Group	*P*–1	$P2_1/n$	*P*–1
Temperature (K)	100	100	100
***a* (Å)** ***b* (Å)** ***c* (Å)**	12.4239 (10) 14.2358 (12) 19.0442 (16)	15.1571 (7) 21.4890 (11) 16.3741 (8)	12.3372 (6) 14.5673 (7) 19.6915 (10)
α (°) ***β* (°)** **γ (°)**	109.6426 (17) 95.5642 (18) 102.0493 (18)	90 93.577 (1) 90	76.058 (1) 73.437 (1) 79.142 (1)
***V* (Å^3)**	3050.8 (4)	5322.8 (4)	3264.8 (3)
Z	2	4	2
Radiation type	Synchrotron, λ = 0.40651 Å	Mo *K*α	Mo *K*α
μ (mm^{-1})	0.19	0.94	0.91
Crystal size (mm)	0.30 × 0.15 × 0.10	0.14 × 0.14 × 0.06	0.45 × 0.26 × 0.22
R*1**[a] ***wR*2**[b] ***S (GOOF)	0.043 0.13 1.04	0.066 0.194 1.02	0.033 0.079 1.03
Reflections	10463	9399	11581

[a] $R1 = [\sum w(F_o - F_c)^2 / \sum w F_o^{\,2}]^{1/2}$

[b] $wR2 = [\sum[w(F_o^{\,2} - F_c^{\,2})^2] / \sum w (F_o^{\,2})^2]^{1/2}$ $w = 1/[\sigma^2(F_o^{\,2}) + (aP)^2 + bP]$, where $P = [\max(F_o^{\,2}, 0) + 2((F_c^{\,2})]/3$

Table S2. Continuation …

	[CoCp*$_2$][(^{tbs}L)Fe$_3$(N(3,5-(CF$_3$)$_2$C$_6$H$_3$))] **(15)**	**[2,2,2-crypt(K)][(^{tbs}L)Fe$_2$Zn(N(3,5-(CF$_3$)$_2$C$_6$H$_3$))]** **(16)**
Chemical formula	$C_{74}H_{109}CoF_6Fe_3N_7OSi_3$	$C_{50}H_{69}F_6Fe_2N_7Si_3Zn \cdot C_{18}H_{36}KN_2O_6 \cdot 2.63(C_4H_{10}O)$
FW	1533.57	1753.01
Crystal System	Monoclinic	Triclinic
Space Group	$P2_1/n$	$P\bar{1}$
Temperature (K)	100	100
***a* (Å)** ***b* (Å)** ***c* (Å)**	11.9733 (5) 26.2570 (9) 26.2043 (10)	15.4746 (7) 23.8238 (11) 27.1431 (13)
α (°) **β (°)** **γ (°)**	90 100.148 (1) 90	78.401 (1) 74.315 (1) 83.137 (1)
***V* (Å^3)**	8109.3 (5)	9414.8 (8)
Z	4	4
Radiation type	Mo *K*α	Synchrotron, λ = 0.41328 Å
μ (mm^{-1})	0.83	0.51
Crystal size (mm)	0.20 × 0.18 × 0.08	0.17 × 0.15 × 0.09
R*1[a]** ***wR*2[b]** ***S (GOOF)	0.070 0.183 1.02	0.055 0.154 1.03
Reflections	14337	37723

[a] $R1 = [\sum w(F_o - F_c)^2 / \sum w F_o^{\,2}]^{1/2}$

[b] $wR2 = [\sum[w(F_o^{\,2} - F_c^{\,2})^2] / \sum w (F_o^{\,2})^2]^{1/2}$ $w = 1/[\sigma^2(F_o^{\,2}) + (aP)^2 + bP]$, where $P = [\max(F_o^{\,2}, 0) + 2((F_c^{\,2})]/3$

Table S3. Selected bond metrics (Å) of trinuclear complexes

Bond	1	2	5	6
M1–M2	2.6128(6)	2.6502(7)	2.7354(9)	2.8141(7)
M1–M3	2.6119(5)	2.6306(7)	3.1629(9)	2.9792(6)
M2–M3	2.5061(5)	2.5422(5)	2.9399(6)	2.8939(6)
$M–M_{avg}$	2.5769(9)	2.608(1)	2.946(1)	2.896(1)

Table S4. Selected bond metrics of reaction products

Compound		M–M		M–Ligand	
$[NBu_4][(^{tbs}L)Fe_3(\mu^3–Cl)]$	(**7**)	Fe1–Fe2 Fe1–Fe3 Fe2–Fe3 $Fe–Fe_{avg}$	2.8061(8) 2.6813(6) 2.8281(8) 2.772(1)	Fe1–Cl Fe2–Cl Fe3–Cl $Fe–Cl_{avg}$	2.5579(8) 2.5177(8) 2.4785(7) 2.518(1)
$[NBu_4][(^{tbs}L)Zn_3(\mu^3–Cl)]$	(**8**)	Zn1–Zn2 Zn1–Zn3 Zn2–Zn3 $Zn–Zn_{avg}$	3.0176(8) 2.9444(8) 2.9942(8) 2.985(1)	Zn1–Cl Zn2–Cl Zn3–Cl $Zn–Cl_{avg}$	2.6173(8) 2.5016(7) 2.6209(8) 2.579(1)
$[NBu_4][(^{tbs}L)Fe_nZn_{3-n}(\mu^3–Cl)]$	(**9**)	M1–M2 M1–M3 M2–M3 $M–M_{avg}$	2.8674(9) 2.9830(8) 2.9860(8) 2.945(1)	M1–Cl M2–Cl M3–Cl $M–Cl_{avg}$	2.641(1) 2.568(1) 2.501(1) 2.570(1)
$(^{tbs}L)Fe_3(\mu^3–NPh)$[1b]	(**10**)	Fe1–Fe2 Fe1–Fe3 Fe2–Fe3 $Fe–Fe_{avg}$	2.549(1) 2.502(1) 2.539(1) 2.530(1)	$Fe1\text{-}N_{im}$ $Fe2–N_{im}$ $Fe3–N_{im}$ $Fe–N_{im\ avg}$	1.936(5) 1.944(5) 1.944(5) 1.941(9)
$(^{tbs}L)Fe_2Zn(\mu^3–NPh)$	(**11**)	M1–M2 M1–M3 M2–M3 $M–M_{avg}$	2.725(1) 2.678(1) 2.7010(9) 2.701(2)	$M1–N_{im}$ $M2–N_{im}$ $M3–N_{im}$ $M–N_{im\ avg}$	2.004(4) 2.060(4) 1.968(4) 2.011(7)
$(^{tbs}L)Fe_2Zn(\mu^3–NPh)(py)$	(**12**)	Fe1–Fe2 Fe1–Zn Fe2–Zn	2.4880(6) 3.2059(7) 2.7599(6)	$Fe1–N_{im}$ $Fe2–N_{im}$ $Zn–N_{im}$	1.917(2) 1.961(2) 2.077(3)
$(^{tbs}L)Fe_3(\mu^3–N(3,5\text{-}(CF_3)_2C_6H_3))$	(**13**)[a]	Fe1–Fe2 Fe1–Fe3 Fe2–Fe3 $Fe–Fe_{avg}$	2.457(2) 2.668(2) 2.520(2) 2.548(3)	$Fe1\text{-}N_{im}$ $Fe2–N_{im}$ $Fe3–N_{im}$ $Fe–N_{im\ avg}$	1.977(5) 1.931(5) 1.972(5) 1.960(9)
$(^{tbs}L)Fe_2Zn(\mu^3–N(3,5\text{-}(CF_3)_2C_6H_3))(py)$	(**14**)	Fe1–Fe2 Fe1–Zn Fe2–Zn	2.5008(6) 2.7806(4) 3.1982(6)	$Fe1–N_{im}$ $Fe2–N_{im}$ $Zn–N_{im}$	1.976(2) 1.932(2) 2.084(2)
$[CoCp^*_2][(^{tbs}L)Fe_3(\mu^3–N(3,5\text{-}(CF_3)_2C_6H_3))]$	(**15**)	Fe1–Fe2 Fe1–Fe3 Fe2–Fe3 $Fe–Fe_{avg}$	2.532(1) 2.632(1) 2.596(1) 2.587(1)	$Fe1\text{-}N_{im}$ $Fe2–N_{im}$ $Fe3–N_{im}$ $Fe–N_{im\ avg}$	1.953(5) 1.978(4) 1.996(4) 1.976(7)
$[2,2,2\text{-crypt}(K)][(^{tbs}L)Fe_2Zn(\mu^3–N(3,5\text{-}(CF_3)_2C_6H_3))]$	(**16**)[b]	M1–M2 M1–M3 M2–M3 $M–M_{avg}$	2.7085(7) 2.6751(8) 2.7843(6) 2.723(1)	$M1\text{-}N_{im}$ $M2–N_{im}$ $M3–N_{im}$ $M–N_{im\ avg}$	2.032(3) 2.035(3) 2.010(2) 2.026(5)

[a]Bond metrics reported for one part of the disorder model in **13**, which represents >90% occupancy.
[b] Bond metrics listed for only one of the two clusters in the asymmetric unit (see Table S17 for full bond metric details).

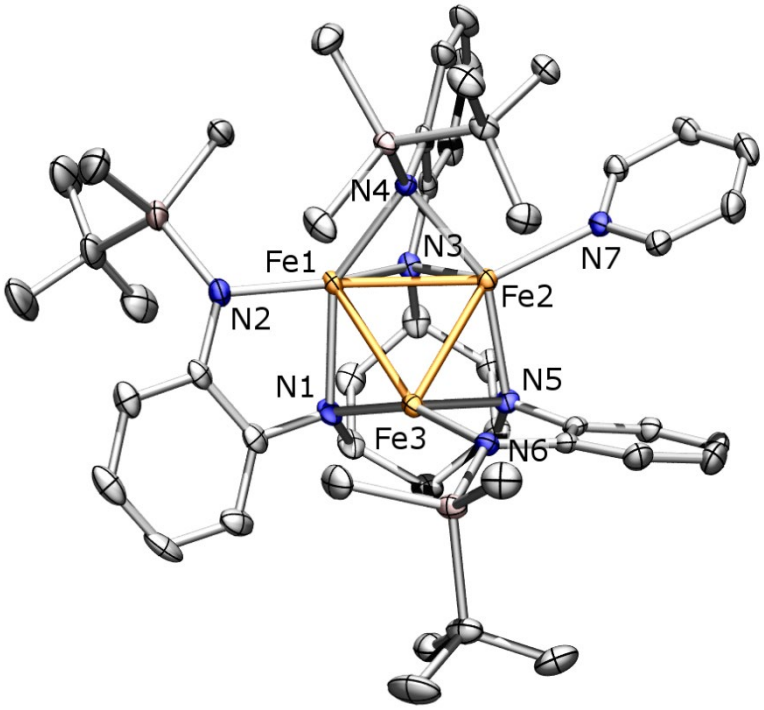

Figure S34. Solid state structure of (^{tbs}L)Fe_3(py) (**2**). Hydrogen atoms and ether solvent molecules have been omitted for clarity.

Table S5. Selected bond metrics for **2** (Å).

Fe1—Fe2	2.6502(7)	Fe2—N5	2.031(2)
Fe1—Fe3	2.6306(7)	Fe2—N4	2.120(2)
Fe2—Fe3	2.5422(5)	Fe2—N7	2.154(2)
Fe1—N2	1.966(2)	Fe2—N3	2.166(2)
Fe1—N3	2.030(2)	Fe3—N6	1.937(2)
Fe1—N1	2.115(2)	Fe3—N1	1.959(2)
Fe1—N4	2.134(2)	Fe3—N5	2.053(2)

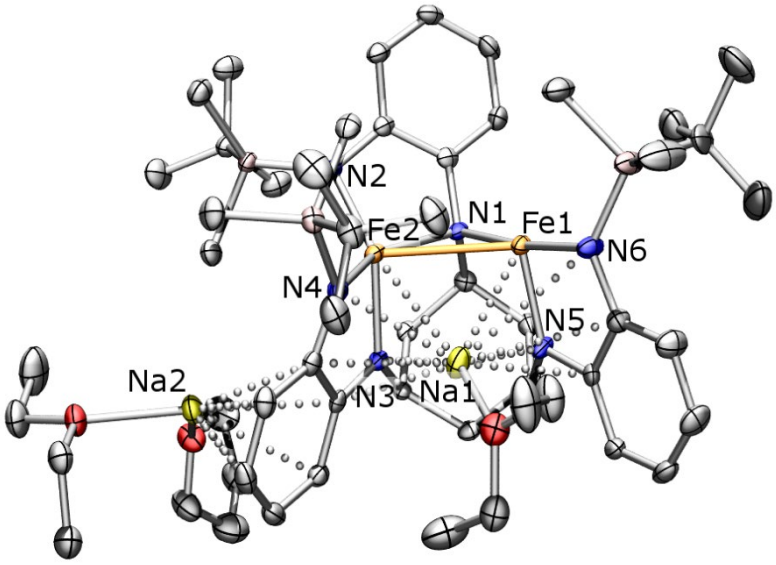

Figure S35. Solid state structure of [Na(thf)(OEt_2)][(^{tbs}L)Fe_2Na(OEt_2)] (**4**). Hydrogen atoms have been omitted for clarity. Only one part of the disorder is depicted for clarity.

Table S6. Selected bond metrics for **4** (Å).

Fe1—Fe2	2.8586(8)	Fe1—N5	1.939(2)
Fe1—Na1	2.997(1)	Fe2—N1	2.144(2)
Fe2—Na1	3.182(1)	Fe2—N4	2.058(2)
Fe1—N1	1.955(2)	Fe2—N2	1.991(2)
Fe1—N6	1.945(2)	Fe2—N3	1.999(2)

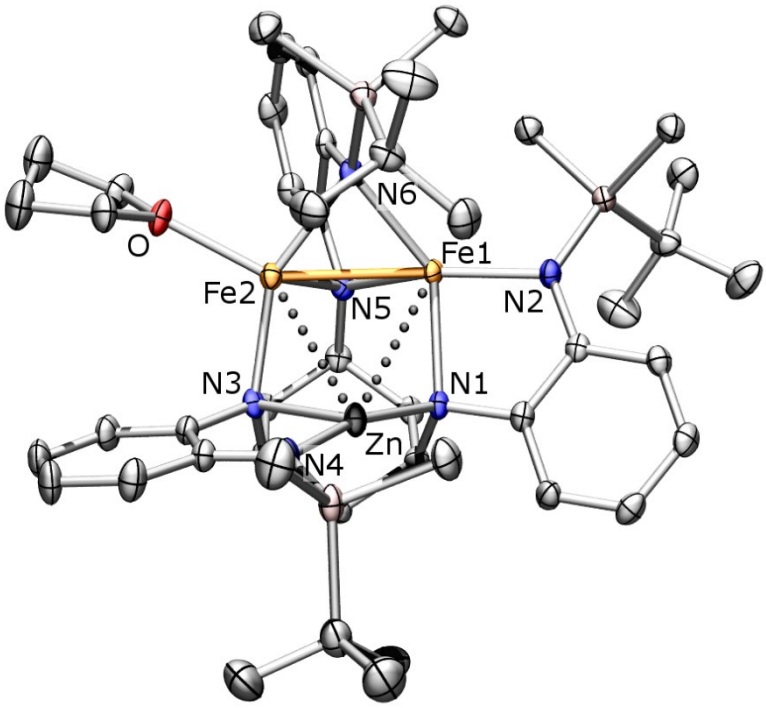

Figure S36. Solid state structure of (^{tbs}L)Fe_2Zn(thf) (**5**). Hydrogen atoms and hexane solvent molecule omitted for clarity.

Table S7. Selected bond metrics for **5** (Å).

Fe1—Fe2	2.7354(9)	Fe2—N3	2.007(2)
Zn—Fe1	3.1629(9)	Fe2—N5	2.09(3)
Zn—Fe2	2.9399(6)	Fe2—N6	2.098(2)
Fe1—N2	1.950(2)	Fe2—O	2.051(2)
Fe1—N5	2.030(2)	Zn—N4	1.885(3)
Fe1—N1	2.132(2)	Zn—N1	1.916(3)
Fe1—N6	2.142(2)	Zn—N3	2.049(2)

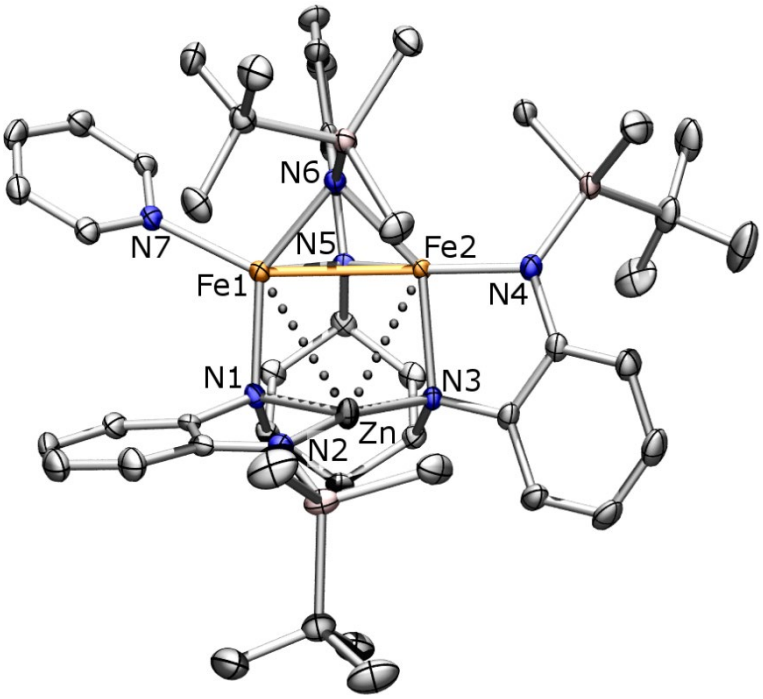

Figure S37. Solid state structure of (^{tbs}L)Fe_2Zn(py) (**6**). Hydrogen atoms and hexane solvent molecule omitted for clarity.

Table S8. Selected bond metrics for **6** (Å).

Fe1—Fe2	2.8141(7)	Fe2—N3	2.109(2)
Zn—Fe1	2.9792(6)	Fe2—N4	1.938(4)
Zn—Fe2	2.8939(6)	Fe2—N5	2.030(2)
Fe1—N1	2.021(2)	Fe2—N6	2.176(3)
Fe1—N6	2.079(2)	Zn—N2	1.881(2)
Fe1—N5	2.106(3)	Zn—N3	1.911(3)
Fe1—N7	2.113(3)	Zn—N1	2.024(3)

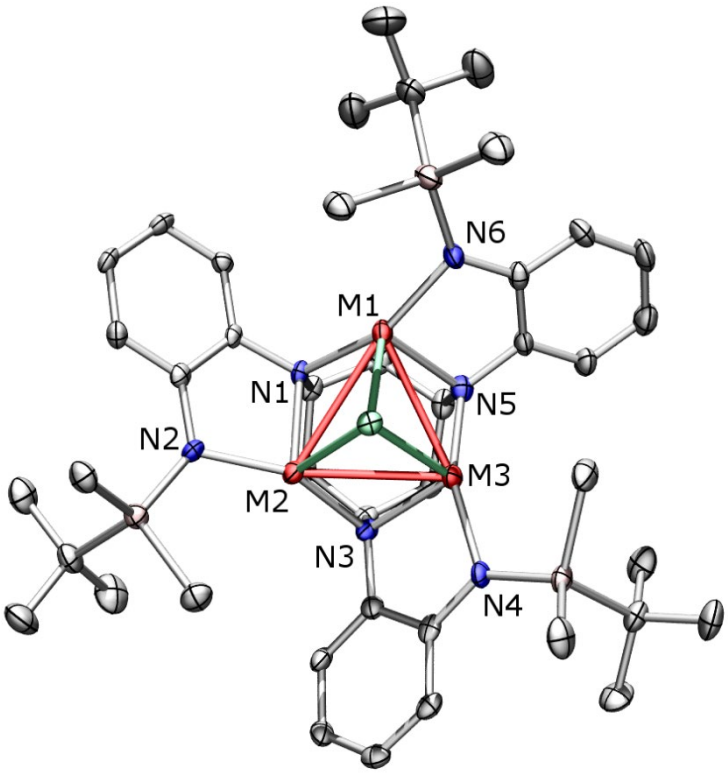

Figure S38. Solid state structure of $[NBu_4][(^{tbs}L)Fe_nZn_{3-n}(\mu^3\text{–}Cl)]$ (**9**). Hydrogen atoms and tetrabutylammonium counter ion have been omitted for clarity. Because each metal site is a mixture of Fe and Zn, the metal ions are depicted in red for generic metal M.

Table S9. Selected bond metrics for **9** (Å).

M1—M2	2.8674(9)	M2—N2	1.943(3)
M1—M3	2.9830(8)	M2—N3	1.973(3)
M2—M3	2.9860(9)	M2—N1	2.107(3)
M1—Cl1	2.641(1)	M3—N4	1.935(3)
M2—Cl1	2.568(1)	M3—N5	1.982(3)
M3—Cl1	2.501(1)	M3—N3	2.095(3)
M1—N6	1.921(3)	M—M_{avg}	2.945(1)
M1—N1	1.966(3)	M—Cl_{avg}	2.570(1)
M1—N5	2.076(3)		

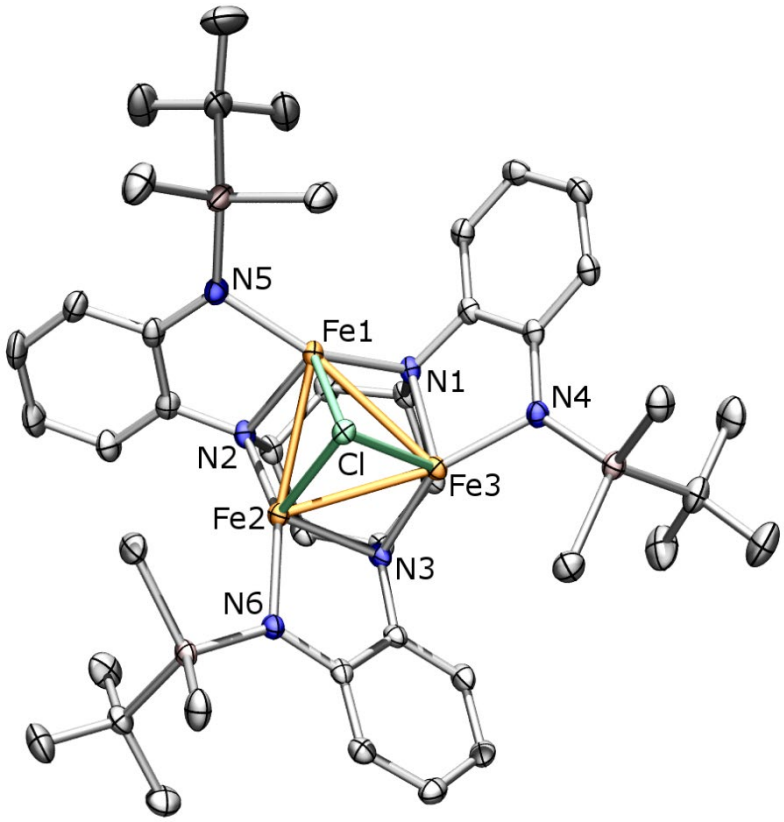

Figure S39. Solid state structure of $[NBu_4][(^{tbs}L)Fe_3(\mu^3\text{–}Cl)]$ (**7**). Hydrogen atoms and tetrabutylammonium counter ion have been omitted for clarity.

Table S10. Selected bond metrics for **7** (Å).

Fe1—Fe2	2.8061(8)	Fe2—N6	1.959(2)
Fe1—Fe3	2.6813(8)	Fe2—N2	1.989(3)
Fe2—Fe3	2.8281(8)	Fe2—N3	2.108(2)
Fe1—Cl1	2.5579(8)	Fe3—N4	1.961(3)
Fe2—Cl1	2.4785(7)	Fe3—N3	1.986(2)
Fe3—Cl1	2.5177(8)	Fe3—N1	2.112(2)
Fe1—N5	1.951(3)	$Fe—Fe_{avg}$	2.772(1)
Fe1—N1	1.988(2)	$Fe—Cl_{avg}$	2.518(1)
Fe1—N2	2.100(2)		

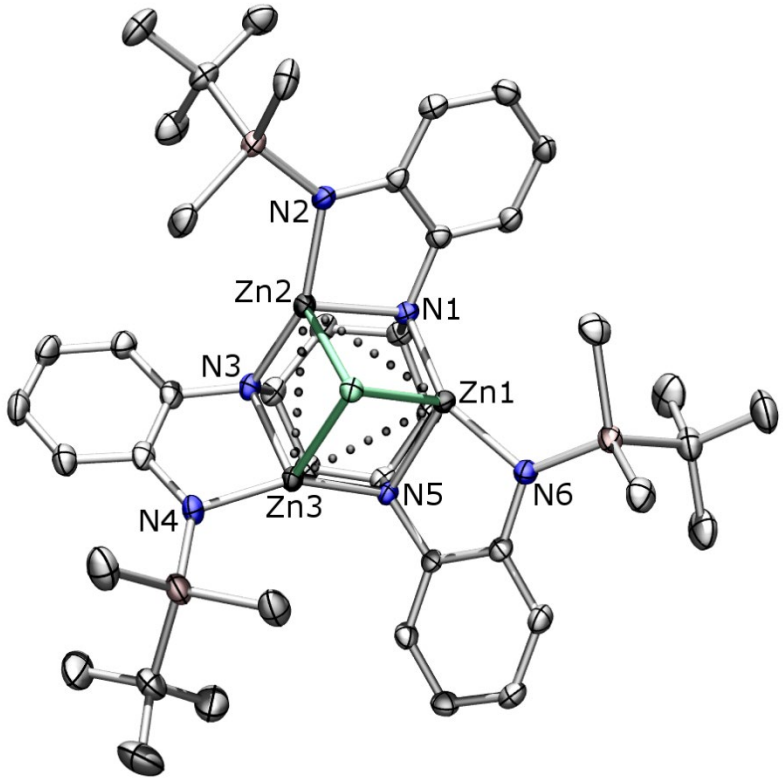

Figure S40. Solid state structure of $[NBu_4][(^{tbs}L)Zn_3(\mu^3\text{–}Cl)]$ (**8**). Hydrogen atoms and tetrabutylammonium chloride counter ion omitted for clarity.

Table S11. Selected bond metrics for **8** (Å).

Zn1—Zn2	3.0176(8)	Zn2—N1	2.058(2)
Zn1—Zn3	2.9444(8)	Zn2—N2	1.916(2)
Zn2—Zn3	2.9942(8)	Zn2—N3	1.962(2)
Zn1—Cl1	2.6173(8)	Zn3—N4	1.906(2)
Zn2—Cl1	2.5016(7)	Zn3—N5	1.949(2)
Zn3—Cl1	2.6209(8)	Zn3—N3	2.046(2)
Zn1—N6	1.910(2)	$Zn—Zn_{avg}$	2.985(1)
Zn1—N1	1.949(2)	$Zn—Cl_{avg}$	2.579(1)
Zn1—N5	2.062(2)		

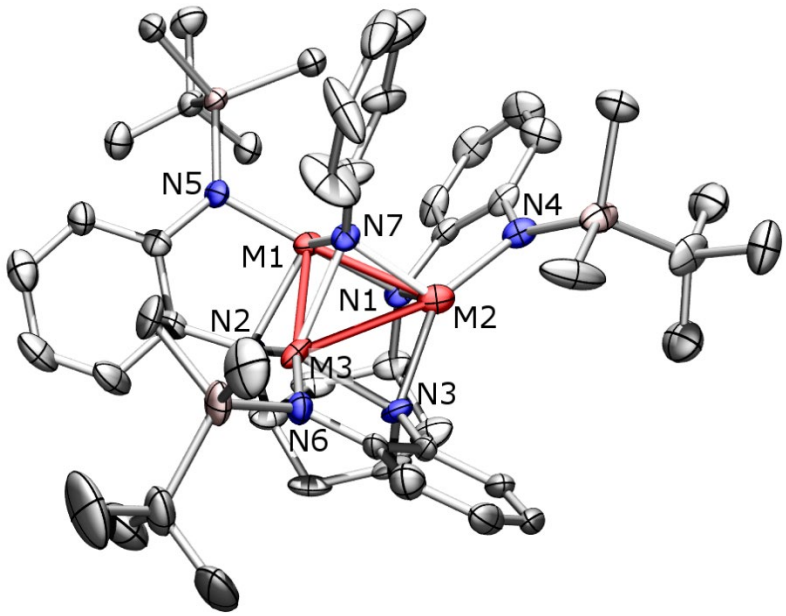

Figure S41. Solid state structure of (^{tbs}L)$Fe_2Zn(\mu^3$–NPh) (**11**). Hydrogen atoms have been omitted for clarity. Only one part of the disorder is depicted for clarity. Because each metal site is a mixture of Fe and Zn, the metal ions are depicted in red for generic metal M.

Table S12. Selected bond metrics for **11** (Å).

M1—M2	2.725(1)	M2—N1	2.056(4)
M1—M3	2.678(1)	M2—N3	1.995(4)
M2—M3	2.7010(9)	M2—N4	1.888(4)
M1—N7	2.004(4)	M3—N2	2.004(4)
M2—N7	2.060(4)	M3—N3	2.056(4)
M3—N7	1.968(4)	M3—N6	1.902(4)
M1—N5	1.893(5)	M—M_{avg}	2.701(2)
M1—N1	1.975(5)	M—$N7_{avg}$	2.011(7)
M1—N2	2.042(4)		

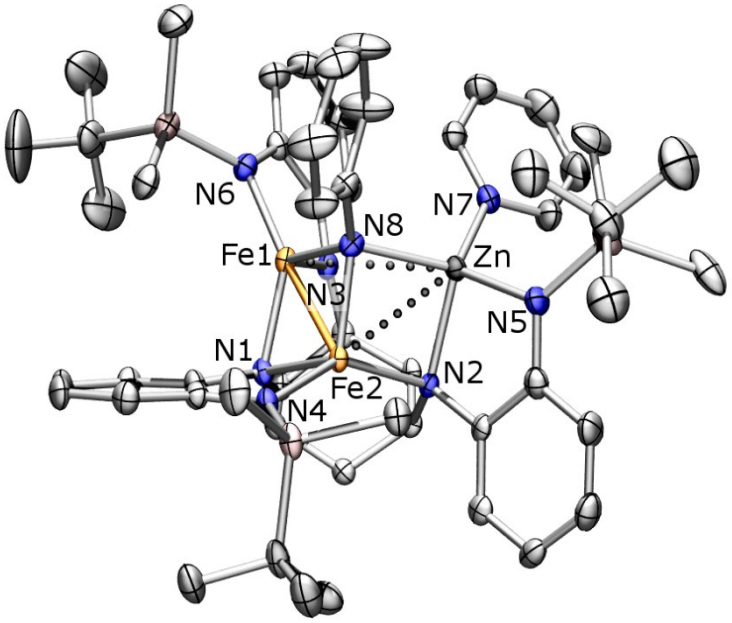

Figure S42. Solid state structure of (^{tbs}L)Fe_2Zn((μ^3–NPh)(py) (**12**). Hydrogen atoms have been omitted for clarity. Only one part of the disorder is depicted for clarity.

Table S13. Selected bond metrics for **12** (Å).

Fe1—Fe2	2.4880(6)	Fe1—N6	1.917(3)
Fe1—Zn	3.2059(7)	Fe2—N1	2.014(2)
Fe2—Zn	2.7599(6)	Fe2—N2	2.025(3)
Fe1—N8	1.917(2)	Fe2—N4	1.934(3)
Fe2—N8	1.961(2)	Zn—N2	2.083(2)
Zn—N8	2.077(3)	Zn—N5	1.957(3)
Fe1—N1	1.992(2)	Zn—N7	2.039(3)
Fe1—N3	1.924(3)		

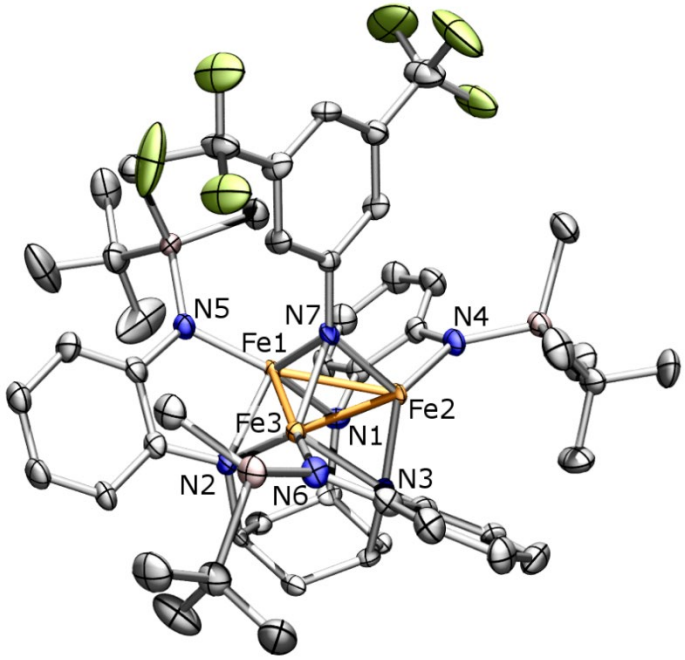

Figure S43. Solid state structure of (^{tbs}L)Fe_3(μ^3–N(3,5-$(CF_3)_2C_6H_3$)) (**13**). Hydrogen atoms have been omitted for clarity. Only one part of the disorder is depicted for clarity.

Table S14. Selected bond metrics for **13** (Å).[a]

Fe1—Fe2	2.457(2)	Fe2—N1	2.026(5)
Fe1—Fe3	2.668(2)	Fe2—N3	1.923(5)
Fe2—Fe3	2.520(2)	Fe2—N4	1.887(5)
Fe1—N7	1.977(5)	Fe3—N2	1.994(5)
Fe2—N7	1.931(5)	Fe3—N3	2.051(5)
Fe3—N7	1.972(5)	Fe3—N6	1.919(5)
Fe1—N1	2.020(5)	Fe—Fe_{avg}	2.548(3)
Fe1—N2	2.081(5)	Fe—$N7_{avg}$	1.960(9)
Fe1—N5	1.929(5)		

[a] Listed bond metrics are for the Fe centers with >90% occupancy

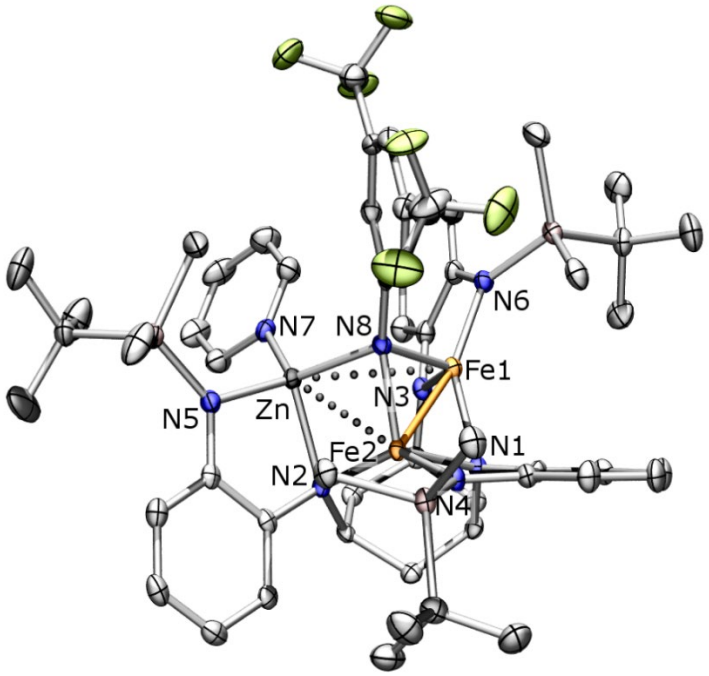

Figure S44. Solid state structure of (^{tbs}L)$Fe_2Zn(\mu^3$–N(3,5-$(CF_3)_2C_6H_3$))(py) (**14**). Hydrogen atoms have been omitted for clarity. Only one part of the disorder is depicted for clarity.

Table S15. Selected bond metrics for **14** (Å).

Fe1—Fe2	2.5008(6)	Fe1—N6	1.914(2)
Fe1—Zn	3.1982(6)	Fe2—N1	2.021(2)
Fe2—Zn	2.7806(4)	Fe2—N2	2.030(2)
Fe1—N8	1.932(2)	Fe2—N4	1.925(2)
Fe2—N8	1.976(2)	Zn—N2	2.089(2)
Zn—N8	2.084(2)	Zn—N5	1.959(2)
Fe1—N1	1.973(2)	Zn—N7	2.060(2)
Fe1—N3	1.922(2)		

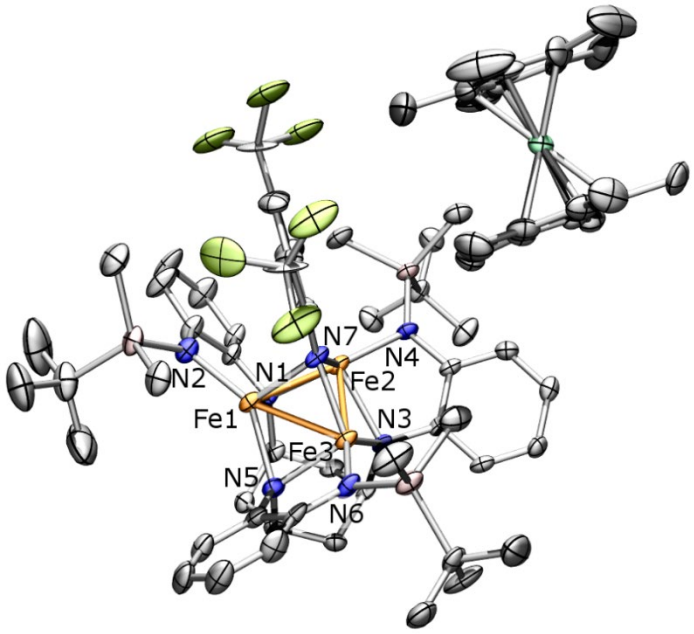

Figure S45. Solid state structure of $[CoCp^*_2][(^{tbs}L)Fe_3(\mu^3\text{–}N(3,5\text{-}(CF_3)_2C_6H_3))]$ (**15**). Hydrogen atoms have been omitted for clarity. Only one part of the disorder is depicted for clarity.

Table S16. Selected bond metrics for **15** (Å).

Fe1—Fe2	2.532(1)	Fe2—N1	2.002(5)
Fe1—Fe3	2.632(1)	Fe2—N3	2.065(4)
Fe2—Fe3	2.596(1)	Fe2—N4	1.933(5)
Fe1—N7	1.953(5)	Fe3—N3	2.010(4)
Fe2—N7	1.978(4)	Fe3—N5	2.076(5)
Fe3—N7	1.996(4)	Fe3—N6	1.953(5)
Fe1—N1	2.068(5)	Fe—Fe_{avg}	2.587(1)
Fe1—N2	1.957(4)	Fe—$N7_{avg}$	1.976(7)
Fe1—N5	2.013(4)		

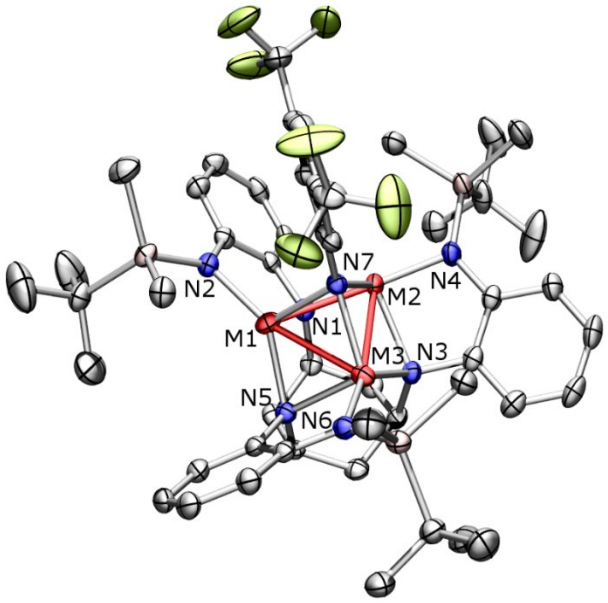

Figure S46. Solid state structure of [2,2,2-cryptand(K)][(^{tbs}L)$Fe_2Zn(\mu^3$–N(3,5-$(CF_3)_2C_6H_3$))] (**16**). Hydrogen atoms, disordered solvent molecules, and counter ion have been omitted for clarity. Only one cluster from the unit cell is depicted. Because each metal site is a mixture of Fe and Zn, the metal ions are depicted in red for generic metal M.

Table S17. Selected bond metrics for two clusters (A and B) in unit cell of **16** (Å).

$M1_A$—$M2_A$	2.7085(7)	$M1_B$—$M2_B$	2.7650(7)
$M1_A$—$M3_A$	2.6751(8)	$M1_B$—$M3_B$	2.6660(7)
$M2_A$—$M3_A$	2.7843(6)	$M2_B$—$M3_B$	2.6918(9)
$M1_A$—$N7_A$	2.032(3)	$M1_B$—$N7_B$	2.014(2)
$M2_A$—$N7_A$	2.035(3)	$M2_B$—$N7_B$	2.101(3)
$M3_A$—$N7_A$	2.010(2)	$M3_B$—$N7_B$	1.967(3)
$M1_A$—$N1_A$	2.062(3)	$M1_B$—$N1_B$	2.006(3)
$M1_A$—$N5_A$	1.974(2)	$M1_B$—$N5_B$	2.085(3)
$M1_A$—$N2_A$	1.923(3)	$M1_B$—$N2_B$	1.926(3)
$M2_A$—$N1_A$	2.015(3)	$M2_B$—$N1_B$	2.090(2)
$M2_A$—$N3_A$	2.104(2)	$M2_B$—$N3_B$	1.974(3)
$M2_A$—$N4_A$	1.939(3)	$M2_B$—$N4_B$	1.910(4)
$M3_A$—$N3_A$	2.008(3)	$M3_B$—$N3_B$	2.096(3)
$M3_A$—$N5_A$	2.104(3)	$M3_B$—$N5_B$	2.011(3)
$M3_A$—$N6_A$	1.935(3)	$M3_B$—$N6_B$	1.935(3)
M_A—M_{Aavg}	2.723(1)	M_B—M_{Bavg}	2.708(1)
M_A—$N7_{Aavg}$	2.026(5)	M_B—$N7_{Bavg}$	2.027(5)

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checkCIF/PLATON report

You have not supplied any structure factors. As a result the full set of tests cannot be run.

THIS REPORT IS FOR GUIDANCE ONLY. IF USED AS PART OF A REVIEW PROCEDURE FOR PUBLICATION, IT SHOULD NOT REPLACE THE EXPERTISE OF AN EXPERIENCED CRYSTALLOGRAPHIC REFEREE.

No syntax errors found. CIF dictionary Interpreting this report

Datablock: 2

Bond precision: C-C = 0.0041 A Wavelength=0.41328

Cell: a=10.4451(12) b=27.261(3) c=21.186(3)
alpha=90 beta=102.166(4) gamma=90
Temperature: 100 K

	Calculated	Reported
Volume	5897.1(13)	5897.2(12)
Space group	P 21/c	P 1 21/c 1
Hall group	-P 2ybc	-P 2ybc
Moiety formula	4(C47 H71 Fe3 N7 Si3), 7(C4 H10 O)	C47 H71 Fe3 N7 Si3, 1.75(C4 H10 O)
Sum formula	C216 H354 Fe12 N28 O7 Si12	C54 H88.50 Fe3 N7 O1.75 Si3
Mr	4462.55	1115.63
Dx,g cm-3	1.257	1.257
Z	1	4
Mu (mm-1)	0.194	0.165
F000	2382.0	2382.0
F000'	2384.23	
h,k,lmax		13,34,26
Nref		12080
Tmin,Tmax	0.978,0.993	0.673,0.744
Tmin'	0.969	

Correction method= # Reported T Limits: Tmin=0.673 Tmax=0.744
AbsCorr = MULTI-SCAN

Data completeness= Theta(max)= 14.997

R(reflections)= 0.0421(9217) wR2(reflections)= 0.1073(12080)

S = 1.042 Npar= 745

The following ALERTS were generated. Each ALERT has the format
test-name_ALERT_alert-type_alert-level.
Click on the hyperlinks for more details of the test.

Alert level C

```
PLAT042_ALERT_1_C Calc. and Reported MoietyFormula Strings  Differ     Please Check
             Calc: 4(C47 H71 Fe3 N7 Si3), 7(C4 H10 O)
             Rep.: C47 H71 Fe3 N7 Si3, 1.75(C4 H10 O)
```

Alert level G

```
ABSMU01_ALERT_1_G  Calculation of _exptl_absorpt_correction_mu
                not performed for this radiation type.
PLAT002_ALERT_2_G Number of Distance or Angle Restraints on AtSite         15 Note
PLAT003_ALERT_2_G Number of Uiso or Uij Restrained non-H Atoms ...         20 Report
PLAT045_ALERT_1_G Calculated and Reported Z Differ by a Factor ...      0.250 Check
PLAT092_ALERT_4_G Check: Wavelength Given is not Cu,Ga,Mo,Ag,In Ka    0.41328 Ang.
PLAT175_ALERT_4_G The CIF-Embedded .res File Contains SAME Records          3 Report
PLAT178_ALERT_4_G The CIF-Embedded .res File Contains SIMU Records          1 Report
PLAT302_ALERT_4_G Anion/Solvent/Minor-Residue Disorder (Resd  2  )        100% Note
PLAT302_ALERT_4_G Anion/Solvent/Minor-Residue Disorder (Resd  3  )        100% Note
PLAT302_ALERT_4_G Anion/Solvent/Minor-Residue Disorder (Resd  4  )        100% Note
PLAT302_ALERT_4_G Anion/Solvent/Minor-Residue Disorder (Resd  5  )        100% Note
PLAT304_ALERT_4_G Non-Integer Number of Atoms in ..... (Resd  2  )       7.58 Check
PLAT304_ALERT_4_G Non-Integer Number of Atoms in ..... (Resd  3  )       7.21 Check
PLAT304_ALERT_4_G Non-Integer Number of Atoms in ..... (Resd  4  )       7.42 Check
PLAT304_ALERT_4_G Non-Integer Number of Atoms in ..... (Resd  5  )       4.04 Check
PLAT720_ALERT_4_G Number of Unusual/Non-Standard Labels .........         23 Note
             H1SA    H1SB    H1SC    H2SA    H2SB    H3SA    H3SB    H4SA
             H4SB    H4SC    H5SA    H5SB    H5SC    H6SA    H6SB    H7SA
             H7SB    H8SA    H8SB    H8SC    H9SA    H9SB    H9SC
PLAT789_ALERT_4_G Atoms with Negative _atom_site_disorder_group  #         60 Check
PLAT790_ALERT_4_G Centre of Gravity not Within Unit Cell: Resd.  #          3 Note
             C4 H10 O
PLAT790_ALERT_4_G Centre of Gravity not Within Unit Cell: Resd.  #          5 Note
             C4 H10 O
PLAT822_ALERT_4_G CIF-embedded .res Contains Negative PART Numbers          4 Check
PLAT860_ALERT_3_G Number of Least-Squares Restraints .............       264 Note
PLAT883_ALERT_1_G No Info/Value for _atom_sites_solution_primary .    Please Do !
PLAT933_ALERT_2_G Number of HKL-OMIT Records in Embedded .res File          7 Note
              1  0  0,   0  1  1,   0  1  2,   0  2  0,  -1  1  1,   1  1  0,
             -1  0  2,
```

---

  0 **ALERT level A** = Most likely a serious problem - resolve or explain
  0 **ALERT level B** = A potentially serious problem, consider carefully
  1 **ALERT level C** = Check. Ensure it is not caused by an omission or oversight
 23 **ALERT level G** = General information/check it is not something unexpected

  4 ALERT type 1 CIF construction/syntax error, inconsistent or missing data
  3 ALERT type 2 Indicator that the structure model may be wrong or deficient
  1 ALERT type 3 Indicator that the structure quality may be low
 16 ALERT type 4 Improvement, methodology, query or suggestion
  0 ALERT type 5 Informative message, check

Datablock: 4

Bond precision: C-C = 0.0037 A Wavelength=0.71073

Cell: a=11.040(2) b=14.175(3) c=21.290(5)
alpha=106.479(4) beta=93.058(4) gamma=106.770(4)
Temperature: 100 K

	Calculated	Reported
Volume	3025.6(11)	3025.6(11)
Space group	P -1	P -1
Hall group	-P 1	-P 1
Moiety formula	C46 H75.24 Fe2 N6 Na O Si3, C8 H19.72 Na O2	C54 H94.963 Fe2 N6 Na2 O3 Si3
Sum formula	C54 H94.96 Fe2 N6 Na2 O3 Si3	C54 H94.96 Fe2 N6 Na2 O3 Si3
Mr	1118.27	1118.27
Dx,g cm-3	1.227	1.227
Z	2	2
Mu (mm-1)	0.597	0.597
F000	1201.9	1202.0
F000'	1204.20	
h,k,lmax		13,17,25
Nref		11243
Tmin,Tmax	0.867,0.942	0.696,0.745
Tmin'	0.836	

Correction method= # Reported T Limits: Tmin=0.696 Tmax=0.745
AbsCorr = MULTI-SCAN

Data completeness= Theta(max)= 25.709

R(reflections)= 0.0396(8448) wR2(reflections)= 0.0926(11243)

S = 1.015 Npar= 728

The following ALERTS were generated. Each ALERT has the format
test-name_ALERT_alert-type_alert-level.
Click on the hyperlinks for more details of the test.

Alert level C

PLAT042_ALERT_1_C Calc. and Reported MoietyFormula Strings Differ Please Check
Calc: C46 H75.24 Fe2 N6 Na O Si3, C8 H19.72 Na O2
Rep.: C54 H94.963 Fe2 N6 Na2 O3 Si3

```
PLAT094_ALERT_2_C Ratio of Maximum / Minimum Residual Density ....       2.33 Report
PLAT220_ALERT_2_C NonSolvent   Resd 1  C   Ueq(max)/Ueq(min) Range       3.9 Ratio
PLAT222_ALERT_3_C NonSolvent Resd 1  H   Uiso(max)/Uiso(min) Range       5.0 Ratio
PLAT230_ALERT_2_C Hirshfeld Test Diff for    Si2      --C25      .       5.3 s.u.
```

Alert level G

```
PLAT002_ALERT_2_G Number of Distance or Angle Restraints on AtSite         8 Note
PLAT154_ALERT_1_G The s.u.'s on the Cell Angles are Equal ..(Note)      0.004 Degree
PLAT171_ALERT_4_G The CIF-Embedded .res File Contains EADP Records        21 Report
PLAT175_ALERT_4_G The CIF-Embedded .res File Contains SAME Records         1 Report
PLAT180_ALERT_4_G Check Cell Rounding: # of Values Ending with 0 =         3 Note
PLAT230_ALERT_2_G Hirshfeld Test Diff for    C43      --C44      .       7.7 s.u.
PLAT232_ALERT_2_G Hirshfeld Test Diff (M-X)  Na2      --O3A      .       6.9 s.u.
PLAT301_ALERT_3_G Main Residue  Disorder ..............(Resd  1  )       27% Note
PLAT302_ALERT_4_G Anion/Solvent/Minor-Residue Disorder (Resd  2  )       45% Note
PLAT304_ALERT_4_G Non-Integer Number of Atoms in ..... (Resd  1  )    134.24 Check
PLAT304_ALERT_4_G Non-Integer Number of Atoms in ..... (Resd  2  )     30.72 Check
PLAT412_ALERT_2_G Short Intra XH3 .. XHn     H13C     ..H40E     .      1.90 Ang.
                                                     x,y,z  =     1_555 Check
PLAT412_ALERT_2_G Short Intra XH3 .. XHn     H14C     ..H17A     .      1.95 Ang.
                                                     x,y,z  =     1_555 Check
PLAT764_ALERT_4_G Overcomplete CIF Bond List Detected (Rep/Expd) .      1.13 Ratio
PLAT811_ALERT_5_G No ADDSYM Analysis: Too Many Excluded Atoms ....         ! Info
PLAT860_ALERT_3_G Number of Least-Squares Restraints .............         6 Note
PLAT883_ALERT_1_G No Info/Value for _atom_sites_solution_primary .    Please Do !
PLAT941_ALERT_3_G Average HKL Measurement Multiplicity ...........       2.3 Low
```

```
   0 ALERT level A = Most likely a serious problem - resolve or explain
   0 ALERT level B = A potentially serious problem, consider carefully
   5 ALERT level C = Check. Ensure it is not caused by an omission or oversight
  18 ALERT level G = General information/check it is not something unexpected

   3 ALERT type 1 CIF construction/syntax error, inconsistent or missing data
   8 ALERT type 2 Indicator that the structure model may be wrong or deficient
   4 ALERT type 3 Indicator that the structure quality may be low
   7 ALERT type 4 Improvement, methodology, query or suggestion
   1 ALERT type 5 Informative message, check
```

Datablock: 5

```
Bond precision:   C-C = 0.0047 A          Wavelength=0.40659

Cell:             a=10.3835(18)     b=18.015(2)        c=30.663(7)
                  alpha=90          beta=91.703(6)     gamma=90
Temperature:      100 K
```

	Calculated	Reported
Volume	5733.3(18)	5733.3(17)
Space group	P 21/n	P 1 21/n 1
Hall group	-P 2yn	-P 2yn
Moiety formula	C46 H74 Fe2 N6 O Si3 Zn, C6 H14 [+ solvent]	C46 H74 Fe2 N6 O Si3 Zn, C6 H14
Sum formula	C52 H88 Fe2 N6 O Si3 Zn [+ solvent]	C52 H88 Fe2 N6 O Si3 Zn
Mr	1074.64	1074.62
Dx,g cm-3	1.245	1.245
Z	4	4
Mu (mm-1)	0.226	0.507
F000	2296.0	2296.0
F000'	2298.39	
h,k,lmax		14,25,43
Nref		17045
Tmin,Tmax	0.952,0.990	0.628,0.719
Tmin'	0.931	

Correction method= # Reported T Limits: Tmin=0.628 Tmax=0.719
AbsCorr = MULTI-SCAN

Data completeness= Theta(max)= 16.741

R(reflections)= 0.0593(10447) wR2(reflections)= 0.1480(17045)

S = 1.015 Npar= 603

The following ALERTS were generated. Each ALERT has the format
test-name_ALERT_alert-type_alert-level.
Click on the hyperlinks for more details of the test.

Alert level C

RINTA01_ALERT_3_C The value of Rint is greater than 0.12
Rint given 0.120

Alert level G

ABSMU01_ALERT_1_G Calculation of _exptl_absorpt_correction_mu not performed for this radiation type.
PLAT020_ALERT_3_G The Value of Rint is Greater Than 0.12 ..... 0.120 Report
PLAT051_ALERT_1_G Mu(calc) and Mu(CIF) Ratio Differs from 1.0 by . 55.34 %
PLAT092_ALERT_4_G Check: Wavelength Given is not Cu,Ga,Mo,Ag,In Ka 0.40659 Ang.
PLAT605_ALERT_4_G Largest Solvent Accessible VOID in the Structure 202 A**3
PLAT794_ALERT_5_G Tentative Bond Valency for Zn1 (II) . 1.64 Info
PLAT869_ALERT_4_G ALERTS Related to the Use of SQUEEZE Suppressed ! Info
PLAT883_ALERT_1_G No Info/Value for _atom_sites_solution_primary . Please Do !

```
PLAT933_ALERT_2_G Number of HKL-OMIT Records in Embedded .res File          5 Note
                1  2  2,   2  3  2,   0  5  3,   0  3  2,   0  6  4,
PLAT941_ALERT_3_G Average HKL Measurement Multiplicity ...........        4.5 Low
PLAT984_ALERT_1_G The Fe-f'=    0.2886 Deviates from the B&C-Value     0.1938 Check
PLAT984_ALERT_1_G The Si-f'=    0.0522 Deviates from the B&C-Value     0.0258 Check
PLAT984_ALERT_1_G The Zn-f'=    0.3242 Deviates from the B&C-Value     0.2556 Check
PLAT985_ALERT_1_G The Fe-f"=    0.5448 Deviates from the B&C-Value     0.2969 Check
PLAT985_ALERT_1_G The Si-f"=    0.0431 Deviates from the B&C-Value     0.0221 Check
PLAT985_ALERT_1_G The Zn-f"=    0.9375 Deviates from the B&C-Value     0.5209 Check
```

```
   0 ALERT level A = Most likely a serious problem - resolve or explain
   0 ALERT level B = A potentially serious problem, consider carefully
   1 ALERT level C = Check. Ensure it is not caused by an omission or oversight
  16 ALERT level G = General information/check it is not something unexpected

   9 ALERT type 1 CIF construction/syntax error, inconsistent or missing data
   1 ALERT type 2 Indicator that the structure model may be wrong or deficient
   3 ALERT type 3 Indicator that the structure quality may be low
   3 ALERT type 4 Improvement, methodology, query or suggestion
   1 ALERT type 5 Informative message, check
```

Datablock: 6

Bond precision: C-C = 0.0056 A Wavelength=0.40651

Cell: a=10.6298(8) b=11.1655(9) c=23.6682(18)
alpha=98.248(2) beta=101.941(2) gamma=101.506(2)

Temperature: 100 K

	Calculated	Reported
Volume	2642.6(4)	2642.6(4)
Space group	P -1	P -1
Hall group	-P 1	-P 1
Moiety formula	C47 H71 Fe2 N7 Si3 Zn, 0.5(C6 H14)	C47 H71 Fe2 N7 Si3 Zn, C3 H7
Sum formula	C50 H78 Fe2 N7 Si3 Zn	C50 H78 Fe2 N7 Si3 Zn
Mr	1038.55	1038.53
Dx,g cm-3	1.305	1.305
Z	2	2
Mu (mm-1)	0.244	0.213
F000	1102.0	1102.0
F000'	1103.19	
h,k,lmax		12,13,28
Nref		8937
Tmin,Tmax	0.985,0.996	0.633,0.744
Tmin'	0.964	

Correction method= # Reported T Limits: Tmin=0.633 Tmax=0.744
AbsCorr = MULTI-SCAN

Data completeness= Theta(max)= 14.031

R(reflections)= 0.0441(7925) wR2(reflections)= 0.1106(8937)

S = 1.094 Npar= 584

The following ALERTS were generated. Each ALERT has the format
test-name_ALERT_alert-type_alert-level.
Click on the hyperlinks for more details of the test.

Alert level A

PLAT051_ALERT_1_A Mu(calc) and Mu(CIF) Ratio Differs from 1.0 by . 14.58 %

Author Response: Structure collected with synhcrotron radiation; difference in Mu(calc) from Shelx program and checkcif due to rounding errors in f', f'', and mu values.

Alert level B

PLAT029_ALERT_3_B _diffrn_measured_fraction_theta_full value Low . 0.950 Why?

Author Response: Structure collected with fixed chi geometry at synchrotron source; hardware limit prevents >95% completeness.

Alert level C

PLAT042_ALERT_1_C Calc. and Reported MoietyFormula Strings Differ Please Check
Calc: C47 H71 Fe2 N7 Si3 Zn, 0.5(C6 H14)
Rep.: C47 H71 Fe2 N7 Si3 Zn, C3 H7
PLAT094_ALERT_2_C Ratio of Maximum / Minimum Residual Density .... 2.05 Report
PLAT232_ALERT_2_C Hirshfeld Test Diff (M-X) Fe2 --N5 . 5.6 s.u.

Alert level G

ABSMU01_ALERT_1_G Calculation of _exptl_absorpt_correction_mu
not performed for this radiation type.
PLAT083_ALERT_2_G SHELXL Second Parameter in WGHT Unusually Large 7.03 Why ?
PLAT092_ALERT_4_G Check: Wavelength Given is not Cu,Ga,Mo,Ag,In Ka 0.40651 Ang.
PLAT154_ALERT_1_G The s.u.'s on the Cell Angles are Equal ..(Note) 0.002 Degree
PLAT794_ALERT_5_G Tentative Bond Valency for Zn1 (II) . 1.68 Info
PLAT883_ALERT_1_G No Info/Value for _atom_sites_solution_primary . Please Do !
PLAT933_ALERT_2_G Number of HKL-OMIT Records in Embedded .res File 11 Note
0 0 2, 0 2 1, -1 2 2, -1 -1 3, -1 1 5, -1 -3 1,
-1 0 4, -1 -4 3, -1 -3 3, -2 0 7, -1 -4 2,

1 **ALERT level A** = Most likely a serious problem - resolve or explain
1 **ALERT level B** = A potentially serious problem, consider carefully
3 **ALERT level C** = Check. Ensure it is not caused by an omission or oversight
7 **ALERT level G** = General information/check it is not something unexpected

5 ALERT type 1 CIF construction/syntax error, inconsistent or missing data
4 ALERT type 2 Indicator that the structure model may be wrong or deficient
1 ALERT type 3 Indicator that the structure quality may be low
1 ALERT type 4 Improvement, methodology, query or suggestion
1 ALERT type 5 Informative message, check

Datablock: 7

Bond precision: C-C = 0.0045 A Wavelength=0.71073

Cell: a=26.839(3) b=19.358(2) c=27.601(4)
alpha=90 beta=90 gamma=90
Temperature: 100 K

	Calculated	Reported
Volume	14340(3)	14340(3)
Space group	P b c a	P b c a
Hall group	-P 2ac 2ab	-P 2ac 2ab
Moiety formula	C42 H66 Cl Fe3 N6 Si3, C15 H34 N [+ solvent]	C42 H66 Cl Fe3 N6 Si3, C15 H34 N
Sum formula	C57 H100 Cl Fe3 N7 Si3 [+ solvent]	C57 H100 Cl Fe3 N7 Si3
Mr	1170.71	1170.70
Dx,g cm-3	1.084	1.085
Z	8	8
Mu (mm-1)	0.722	0.722
F000	5024.0	5024.0
F000'	5036.37	
h,k,lmax		32,23,33
Nref		13621
Tmin,Tmax	0.771,0.866	0.645,0.745
Tmin'	0.749	

Correction method= # Reported T Limits: Tmin=0.645 Tmax=0.745
AbsCorr = MULTI-SCAN

Data completeness= Theta(max)= 25.694

R(reflections)= 0.0426(11027)

wR2(reflections)= 0.1258(13621)

S = 1.040 Npar= 661

The following ALERTS were generated. Each ALERT has the format
test-name_ALERT_alert-type_alert-level.
Click on the hyperlinks for more details of the test.

Alert level B

PLAT094_ALERT_2_B Ratio of Maximum / Minimum Residual Density .... 6.63 Report

Author Response: Remaining residual density is located next to a disordered butyl group on the tetrabutyl ammonium counterion. The large Q peak is accounted for by a failure of the disorder modeling to successfully fit all of the remaining electron density.

PLAT097_ALERT_2_B Large Reported Max. (Positive) Residual Density 3.04 eA-3

Author Response: Remaining residual density is located next to a disordered butyl group on the tetrabutyl ammonium counterion. The large Q peak is accounted for by a failure of the disorder modeling to successfully fit all of the remaining electron density.

Alert level C

DIFMX02_ALERT_1_C The maximum difference density is > 0.1*ZMAX*0.75
The relevant atom site should be identified.
PLAT220_ALERT_2_C NonSolvent Resd 1 C Ueq(max)/Ueq(min) Range 3.7 Ratio
PLAT222_ALERT_3_C NonSolvent Resd 1 H Uiso(max)/Uiso(min) Range 4.3 Ratio

---

Alert level G

PLAT083_ALERT_2_G SHELXL Second Parameter in WGHT Unusually Large 31.70 Why ?
PLAT171_ALERT_4_G The CIF-Embedded .res File Contains EADP Records 1 Report
PLAT232_ALERT_2_G Hirshfeld Test Diff (M-X) Fe1 --Cl1 . 6.2 s.u.
PLAT232_ALERT_2_G Hirshfeld Test Diff (M-X) Fe2 --Cl1 . 6.0 s.u.
PLAT232_ALERT_2_G Hirshfeld Test Diff (M-X) Fe3 --Cl1 . 7.2 s.u.
PLAT302_ALERT_4_G Anion/Solvent/Minor-Residue Disorder (Resd 2) 13% Note
PLAT410_ALERT_2_G Short Intra H...H Contact H43B ..H55C . 1.84 Ang.
x,y,z = 1_555 Check

Author Response: H43B and H55C are on the tetrabutyl ammonium counterion. H55C is on the butyl group which has been modeled for disorder. The short interatomic distance is a result of this modeling.

```
PLAT410_ALERT_2_G Short Intra H...H Contact  H44B     ..H54A     .       2.02 Ang.
                                                     x,y,z  =      1_555 Check
```

Author Response: H43B and H55C are on the tetrabutyl ammonium counterion. H55C is on the butyl group which has been modeled for disorder. The short interatomic distance is a result of this modeling.

```
PLAT410_ALERT_2_G Short Intra H...H Contact  H44B     ..H54D     .       2.09 Ang.
                                                     x,y,z  =      1_555 Check
```

Author Response: H43B and H55C are on the tetrabutyl ammonium counterion. H55C is on the butyl group which has been modeled for disorder. The short interatomic distance is a result of this modeling.

```
PLAT606_ALERT_4_G Solvent Accessible VOID(S) in Structure ........          ! Info
PLAT720_ALERT_4_G Number of Unusual/Non-Standard Labels ..........          3 Note
             C0AA    H0AA    H0AB
PLAT869_ALERT_4_G ALERTS Related to the Use of SQUEEZE  Suppressed          ! Info
PLAT883_ALERT_1_G No Info/Value for _atom_sites_solution_primary .     Please Do !
```

```
   0 ALERT level A = Most likely a serious problem - resolve or explain
   2 ALERT level B = A potentially serious problem, consider carefully
   3 ALERT level C = Check. Ensure it is not caused by an omission or oversight
  13 ALERT level G = General information/check it is not something unexpected

   2 ALERT type 1 CIF construction/syntax error, inconsistent or missing data
  10 ALERT type 2 Indicator that the structure model may be wrong or deficient
   1 ALERT type 3 Indicator that the structure quality may be low
   5 ALERT type 4 Improvement, methodology, query or suggestion
   0 ALERT type 5 Informative message, check
```

Datablock: 8

```
Bond precision:   C-C = 0.0038 A          Wavelength=0.71073

Cell:             a=27.1744(9)     b=19.1482(7)     c=27.5979(10)
                  alpha=90         beta=90          gamma=90
Temperature:      100 K
```

	Calculated	Reported
Volume	14360.3(9)	14360.3(9)
Space group	P b c a	P b c a
Hall group	-P 2ac 2ab	-P 2ac 2ab
Moiety formula	C42 H66 Cl N6 Si3 Zn3, C16 H36 N [+ solvent]	C42 H66 Cl N6 Si3 Zn3, C16 H36 N
Sum formula	C58 H102 Cl N7 Si3 Zn3 [+ solvent]	C58 H102 Cl N7 Si3 Zn3
Mr	1213.36	1213.29
Dx,g cm-3	1.122	1.122
Z	8	8
Mu (mm-1)	1.117	1.117
F000	5184.0	5184.0
F000'	5194.86	
h,k,lmax		32,22,32
Nref		12718
Tmin,Tmax	0.646,0.654	0.680,0.745
Tmin'	0.633	

Correction method= # Reported T Limits: Tmin=0.680 Tmax=0.745
AbsCorr = MULTI-SCAN

Data completeness= Theta(max)= 25.056

R(reflections)= 0.0332(9744) wR2(reflections)= 0.0791(12718)

S = 1.028 Npar= 676

The following ALERTS were generated. Each ALERT has the format
test-name_ALERT_alert-type_alert-level.
Click on the hyperlinks for more details of the test.

Alert level C

PLAT220_ALERT_2_C NonSolvent Resd 1 C Ueq(max)/Ueq(min) Range 3.9 Ratio
PLAT222_ALERT_3_C NonSolvent Resd 1 H Uiso(max)/Uiso(min) Range 4.1 Ratio
PLAT223_ALERT_4_C Solv./Anion Resd 2 H Ueq(max)/Ueq(min) Range 4.1 Ratio
PLAT250_ALERT_2_C Large U3/U1 Ratio for Average U(i,j) Tensor .... 2.2 Note

---

Alert level G

PLAT083_ALERT_2_G SHELXL Second Parameter in WGHT Unusually Large 9.88 Why ?
PLAT171_ALERT_4_G The CIF-Embedded .res File Contains EADP Records 2 Report
PLAT232_ALERT_2_G Hirshfeld Test Diff (M-X) Zn01 --Cl1 . 12.3 s.u.
PLAT232_ALERT_2_G Hirshfeld Test Diff (M-X) Zn02 --Cl1 . 12.0 s.u.
PLAT232_ALERT_2_G Hirshfeld Test Diff (M-X) Zn03 --Cl1 . 13.3 s.u.
PLAT302_ALERT_4_G Anion/Solvent/Minor-Residue Disorder (Resd 2) 12% Note

```
PLAT410_ALERT_2_G Short Intra H...H Contact  H47B     ..H56C     .       1.97 Ang.
                                                    x,y,z  =      1_555 Check
PLAT413_ALERT_2_G Short Inter XH3 .. XHn     H40C     ..H57D     .       1.98 Ang.
                                               1-x,1-y,1-z  =      5_666 Check
```

Author Response: H57D is located on a disordered butyl group on the tetrabutyl ammonium counterion. Modeling of this disorder results in unusually short interatomic distances in some cases.

```
PLAT606_ALERT_4_G Solvent Accessible VOID(S) in Structure ........          ! Info
PLAT720_ALERT_4_G Number of Unusual/Non-Standard Labels ..........          3 Note
             Zn01    Zn02    Zn03
PLAT794_ALERT_5_G Tentative Bond Valency for Zn01      (II)      .       1.73 Info
PLAT794_ALERT_5_G Tentative Bond Valency for Zn02      (II)      .       1.77 Info
PLAT794_ALERT_5_G Tentative Bond Valency for Zn03      (II)      .       1.75 Info
PLAT869_ALERT_4_G ALERTS Related to the Use of SQUEEZE  Suppressed          ! Info
PLAT883_ALERT_1_G No Info/Value for _atom_sites_solution_primary .     Please Do !
```

```
   0 ALERT level A = Most likely a serious problem - resolve or explain
   0 ALERT level B = A potentially serious problem, consider carefully
   4 ALERT level C = Check. Ensure it is not caused by an omission or oversight
  15 ALERT level G = General information/check it is not something unexpected

   1 ALERT type 1 CIF construction/syntax error, inconsistent or missing data
   8 ALERT type 2 Indicator that the structure model may be wrong or deficient
   1 ALERT type 3 Indicator that the structure quality may be low
   6 ALERT type 4 Improvement, methodology, query or suggestion
   3 ALERT type 5 Informative message, check
```

Datablock: 9

```
Bond precision:   C-C = 0.0062 A           Wavelength=0.71073

Cell:               a=27.053(4)      b=19.227(3)      c=27.643(4)
                    alpha=90         beta=90          gamma=90
Temperature:        100 K
```

	Calculated	Reported
Volume	14379(4)	14378(4)
Space group	P b c a	P b c a
Hall group	-P 2ac 2ab	-P 2ac 2ab
Moiety formula	C42 H66 Cl Fe2 N6 Si3 Zn, C16 H36 N [+ solvent]	C42 H66 Cl Fe2 N6 Si3 Zn1, C16 H36 N
Sum formula	C58 H102 Cl Fe2 N7 Si3 Zn [+ solvent]	C58 H102 Cl Fe2 N7 Si3 Zn
Mr	1194.28	1194.25
Dx,g cm-3	1.103	1.103
Z	8	8
Mu (mm-1)	0.852	0.852
F000	5120.0	5120.0
F000'	5131.87	
h,k,lmax		32,22,32
Nref		12755
Tmin,Tmax	0.767,0.873	0.626,0.745
Tmin'	0.755	

Correction method= # Reported T Limits: Tmin=0.626 Tmax=0.745
AbsCorr = MULTI-SCAN

Data completeness= Theta(max)= 25.103

R(reflections)= 0.0563(8699) wR2(reflections)= 0.1307(12755)

S = 1.021 Npar= 670

The following ALERTS were generated. Each ALERT has the format
test-name_ALERT_alert-type_alert-level.
Click on the hyperlinks for more details of the test.

Alert level C

RINTA01_ALERT_3_C The value of Rint is greater than 0.12
Rint given 0.151
PLAT220_ALERT_2_C NonSolvent Resd 1 C Ueq(max)/Ueq(min) Range 4.2 Ratio
PLAT222_ALERT_3_C NonSolvent Resd 1 H Uiso(max)/Uiso(min) Range 4.6 Ratio
PLAT341_ALERT_3_C Low Bond Precision on C-C Bonds ..... 0.00619 Ang.

Alert level G

PLAT020_ALERT_3_G The Value of Rint is Greater Than 0.12 ..... 0.151 Report
PLAT042_ALERT_1_G Calc. and Reported MoietyFormula Strings Differ Please Check
Calc: C42 H66 Cl Fe2 N6 Si3 Zn, C16 H36 N
Rep.: C42 H66 Cl Fe2 N6 Si3 Zn1, C16 H36 N
PLAT083_ALERT_2_G SHELXL Second Parameter in WGHT Unusually Large 22.96 Why ?
PLAT168_ALERT_4_G The CIF-Embedded .res File Contains EXYZ Records 3 Report

```
PLAT171_ALERT_4_G The CIF-Embedded .res File Contains EADP Records          5 Report
PLAT232_ALERT_2_G Hirshfeld Test Diff (M-X)  Zn1      --Cl1      .       21.0 s.u.
PLAT232_ALERT_2_G Hirshfeld Test Diff (M-X)  Zn2      --Cl1      .       22.5 s.u.
PLAT232_ALERT_2_G Hirshfeld Test Diff (M-X)  Zn3      --Cl1      .        7.5 s.u.
PLAT232_ALERT_2_G Hirshfeld Test Diff (M-X)  Fe1A     --Cl1      .       21.0 s.u.
PLAT232_ALERT_2_G Hirshfeld Test Diff (M-X)  Fe2A     --Cl1      .       22.5 s.u.
PLAT232_ALERT_2_G Hirshfeld Test Diff (M-X)  Fe3A     --Cl1      .        7.5 s.u.
PLAT300_ALERT_4_G Atom Site Occupancy of Zn1        Constrained at     0.3333 Check
PLAT300_ALERT_4_G Atom Site Occupancy of Zn2        Constrained at     0.3333 Check
PLAT300_ALERT_4_G Atom Site Occupancy of Zn3        Constrained at     0.3333 Check
PLAT300_ALERT_4_G Atom Site Occupancy of Fe1A       Constrained at     0.6667 Check
PLAT300_ALERT_4_G Atom Site Occupancy of Fe2A       Constrained at     0.6667 Check
PLAT300_ALERT_4_G Atom Site Occupancy of Fe3A       Constrained at     0.6667 Check
PLAT301_ALERT_3_G Main Residue  Disorder .............(Resd  1  )         5% Note
PLAT302_ALERT_4_G Anion/Solvent/Minor-Residue Disorder (Resd  2  )        12% Note
PLAT410_ALERT_2_G Short Intra H...H Contact  H51A     ..H56B     .       1.99 Ang.
                                                    x,y,z  =      1_555 Check
PLAT606_ALERT_4_G Solvent Accessible VOID(S) in Structure ........          ! Info
PLAT720_ALERT_4_G Number of Unusual/Non-Standard Labels ..........         10 Note
              C1AA    C3AA    H3AA    H3AB    C0AA    H0AA    C2AA    H2AA
              H2AB    H2AC
PLAT869_ALERT_4_G ALERTS Related to the Use of SQUEEZE  Suppressed          ! Info
PLAT883_ALERT_1_G No Info/Value for _atom_sites_solution_primary .     Please Do !
```

```
   0 ALERT level A = Most likely a serious problem - resolve or explain
   0 ALERT level B = A potentially serious problem, consider carefully
   4 ALERT level C = Check. Ensure it is not caused by an omission or oversight
  24 ALERT level G = General information/check it is not something unexpected

   2 ALERT type 1 CIF construction/syntax error, inconsistent or missing data
   9 ALERT type 2 Indicator that the structure model may be wrong or deficient
   5 ALERT type 3 Indicator that the structure quality may be low
  12 ALERT type 4 Improvement, methodology, query or suggestion
   0 ALERT type 5 Informative message, check
```

Datablock: 11

```
Bond precision:   C-C = 0.0082 A           Wavelength=0.71073

Cell:             a=22.150(4)     b=20.383(3)          c=26.428(4)
                  alpha=90        beta=101.975(3)      gamma=90
Temperature:      100 K
```

	Calculated	Reported
Volume	11672(3)	11672(3)
Space group	C 2/c	C 1 2/c 1
Hall group	-C 2yc	-C 2yc
Moiety formula	C48 H71 Fe2 N7 Si3 Zn [+ solvent]	C48 H71 Fe2 N7 Si3 Zn, 1[C6H14]
Sum formula	C48 H71 Fe2 N7 Si3 Zn [+ solvent]	C54 H85 Fe2 N7 Si3 Zn
Mr	1007.48	1093.62
Dx,g cm-3	1.147	1.245
Z	8	8
Mu (mm-1)	0.994	0.999
F000	4256.0	4656.0
F000'	4266.50	
h,k,lmax		26,24,31
Nref		10413
Tmin,Tmax	0.787,0.905	0.647,0.745
Tmin'	0.741	

Correction method= # Reported T Limits: Tmin=0.647 Tmax=0.745
AbsCorr = MULTI-SCAN

Data completeness= Theta(max)= 25.158

R(reflections)= 0.0681(7862) wR2(reflections)= 0.1430(10413)

S = 1.090 Npar= 568

The following ALERTS were generated. Each ALERT has the format
test-name_ALERT_alert-type_alert-level.
Click on the hyperlinks for more details of the test.

Alert level C

PLAT213_ALERT_2_C Atom C45 has ADP max/min Ratio ..... 3.4 prolat
PLAT213_ALERT_2_C Atom C5A has ADP max/min Ratio ..... 3.4 prolat
PLAT220_ALERT_2_C NonSolvent Resd 1 C Ueq(max)/Ueq(min) Range 4.1 Ratio
PLAT234_ALERT_4_C Large Hirshfeld Difference C45 --C46 . 0.21 Ang.
PLAT241_ALERT_2_C High 'MainMol' Ueq as Compared to Neighbors of C14 Check
PLAT242_ALERT_2_C Low 'MainMol' Ueq as Compared to Neighbors of C27 Check
PLAT341_ALERT_3_C Low Bond Precision on C-C Bonds ..... 0.0082 Ang.

Alert level G

FORMU01_ALERT_2_G There is a discrepancy between the atom counts in the
_chemical_formula_sum and the formula from the _atom_site* data.
Atom count from _chemical_formula_sum:C54 H85 Fe2 N7 Si3 Zn1
Atom count from the _atom_site data: C48 H71. Fe2. N7 Si3 Zn1.0049

```
CELLZ01_ALERT_1_G Difference between formula and atom_site contents detected.
CELLZ01_ALERT_1_G ALERT: Large difference may be due to a
           symmetry error - see SYMMG tests
          From the CIF: _cell_formula_units_Z    8
          From the CIF: _chemical_formula_sum  C54 H85 Fe2 N7 Si3 Zn
          TEST: Compare cell contents of formula and atom_site data

          atom    Z*formula  cif sites diff
          C        432.00    384.00   48.00
          H        680.00    568.00  112.00
          Fe        16.00     16.00   -0.00
          N         56.00     56.00    0.00
          Si        24.00     24.00    0.00
          Zn         8.00      8.00    0.00
PLAT003_ALERT_2_G Number of Uiso or Uij Restrained non-H Atoms ...          2 Report
PLAT041_ALERT_1_G Calc. and Reported SumFormula    Strings  Differ     Please Check
             Calc: C48 H71 Fe2 N7 Si3 Zn
             Rep.: C54 H85 Fe2 N7 Si3 Zn
PLAT042_ALERT_1_G Calc. and Reported MoietyFormula Strings  Differ     Please Check
             Calc: C48 H71 Fe2 N7 Si3 Zn
             Rep.: C48 H71 Fe2 N7 Si3 Zn, 1[C6H14]
PLAT083_ALERT_2_G SHELXL Second Parameter in WGHT  Unusually Large     126.69 Why ?
PLAT168_ALERT_4_G The CIF-Embedded .res File Contains EXYZ Records          5 Report
PLAT171_ALERT_4_G The CIF-Embedded .res File Contains EADP Records         14 Report
PLAT186_ALERT_4_G The CIF-Embedded .res File Contains ISOR Records          1 Report
PLAT232_ALERT_2_G Hirshfeld Test Diff (M-X)  Zn1      --N7       .        8.0 s.u.
PLAT232_ALERT_2_G Hirshfeld Test Diff (M-X)  Zn2      --N7       .        6.0 s.u.
PLAT232_ALERT_2_G Hirshfeld Test Diff (M-X)  Fe1      --N7       .        8.0 s.u.
PLAT232_ALERT_2_G Hirshfeld Test Diff (M-X)  Fe2      --N7       .        6.0 s.u.
PLAT300_ALERT_4_G Atom Site Occupancy of Zn1        Constrained at     0.3333 Check
PLAT300_ALERT_4_G Atom Site Occupancy of Zn2        Constrained at     0.3333 Check
PLAT300_ALERT_4_G Atom Site Occupancy of Zn3        Constrained at     0.3333 Check
PLAT300_ALERT_4_G Atom Site Occupancy of Fe1        Constrained at     0.6667 Check
PLAT300_ALERT_4_G Atom Site Occupancy of Fe2        Constrained at     0.6667 Check
PLAT300_ALERT_4_G Atom Site Occupancy of Fe3        Constrained at     0.6667 Check
PLAT301_ALERT_3_G Main Residue  Disorder .............(Resd  1  )        23% Note
PLAT411_ALERT_2_G Short Inter H...H Contact  H22      ..H1A      .       2.09 Ang.
                                          1-x,y,1/2-z  =      2_655 Check
PLAT412_ALERT_2_G Short Intra XH3 .. XHn     H9       ..H13B     .       2.13 Ang.
                                          x,y,z  =      1_555 Check
PLAT412_ALERT_2_G Short Intra XH3 .. XHn     H9       ..H13B     .       2.13 Ang.
                                          x,y,z  =      1_555 Check
PLAT412_ALERT_2_G Short Intra XH3 .. XHn     H38A     ..H48      .       2.08 Ang.
                                          x,y,z  =      1_555 Check
PLAT606_ALERT_4_G Solvent Accessible VOID(S) in Structure ........          ! Info
PLAT720_ALERT_4_G Number of Unusual/Non-Standard Labels ..........          2 Note
             H4AA    H6AA
PLAT860_ALERT_3_G Number of Least-Squares Restraints .............         12 Note
PLAT868_ALERT_4_G ALERTS Due to the Use of _smtbx_masks Suppressed          ! Info
PLAT883_ALERT_1_G No Info/Value for _atom_sites_solution_primary .     Please Do !
```

---

0 **ALERT level A** = Most likely a serious problem - resolve or explain
0 **ALERT level B** = A potentially serious problem, consider carefully
7 **ALERT level C** = Check. Ensure it is not caused by an omission or oversight
30 **ALERT level G** = General information/check it is not something unexpected

```
   5 ALERT type 1 CIF construction/syntax error, inconsistent or missing data
  16 ALERT type 2 Indicator that the structure model may be wrong or deficient
   3 ALERT type 3 Indicator that the structure quality may be low
  13 ALERT type 4 Improvement, methodology, query or suggestion
   0 ALERT type 5 Informative message, check
```

Datablock: 12

Bond precision: C-C = 0.0053 A Wavelength=0.40651

Cell: a=12.4239(10) b=14.2358(12) c=19.0442(16)
alpha=109.6426(17) beta=95.5642(18) gamma=102.0493(18)
Temperature: 100 K

	Calculated	Reported
Volume	3050.8(4)	3050.8(4)
Space group	P -1	P -1
Hall group	-P 1	-P 1
Moiety formula	C53 H76 Fe2 N8 Si3 Zn [+ solvent]	C53 H76 Fe2 N8 Si3 Zn, 0.75[C6H14]
Sum formula	C53 H76 Fe2 N8 Si3 Zn [+ solvent]	C57.50 H86.50 Fe2 N8 Si3 Zn
Mr	1086.58	1151.18
Dx,g cm-3	1.183	1.253
Z	2	2
Mu (mm-1)	0.213	0.186
F000	1148.0	1223.0
F000'	1149.17	
h,k,lmax		14,16,22
Nref		10455
Tmin,Tmax	0.967,0.982	0.670,0.744
Tmin'	0.946	

Correction method= # Reported T Limits: Tmin=0.670 Tmax=0.744
AbsCorr = MULTI-SCAN

Data completeness= Theta(max)= 14.015

R(reflections)= 0.0426(8583) wR2(reflections)= 0.1294(10455)

S = 1.035 Npar= 646

The following ALERTS were generated. Each ALERT has the format
test-name_ALERT_alert-type_alert-level.
Click on the hyperlinks for more details of the test.

Alert level C

```
PLAT029_ALERT_3_C _diffrn_measured_fraction_theta_full value Low .      0.968 Why?
PLAT220_ALERT_2_C NonSolvent   Resd 1  C   Ueq(max)/Ueq(min) Range        5.3 Ratio
PLAT222_ALERT_3_C NonSolvent Resd 1  H   Uiso(max)/Uiso(min) Range        6.6 Ratio
PLAT242_ALERT_2_C Low    'MainMol' Ueq as Compared to Neighbors of        C39 Check
```

Alert level G

```
FORMU01_ALERT_2_G  There is a discrepancy between the atom counts in the
           _chemical_formula_sum and the formula from the _atom_site* data.
           Atom count from _chemical_formula_sum:C57.5 H86.5 Fe2 N8 Si3 Zn1
           Atom count from the _atom_site data:  C53 H76 Fe2 N8 Si3 Zn1
ABSMU01_ALERT_1_G  Calculation of _exptl_absorpt_correction_mu
             not performed for this radiation type.
CELLZ01_ALERT_1_G Difference between formula and atom_site contents detected.
CELLZ01_ALERT_1_G ALERT: Large difference may be due to a
           symmetry error - see SYMMG tests
          From the CIF: _cell_formula_units_Z    2
          From the CIF: _chemical_formula_sum  C57.50 H86.50 Fe2 N8 Si3 Zn
          TEST: Compare cell contents of formula and atom_site data

          atom    Z*formula  cif sites diff
          C        115.00    106.00    9.00
          H        173.00    152.00   21.00
          Fe         4.00      4.00    0.00
          N         16.00     16.00    0.00
          Si         6.00      6.00    0.00
          Zn         2.00      2.00    0.00
PLAT002_ALERT_2_G Number of Distance or Angle Restraints on AtSite          4 Note
PLAT041_ALERT_1_G Calc. and Reported SumFormula    Strings  Differ     Please Check
             Calc: C53 H76 Fe2 N8 Si3 Zn
             Rep.: C57.50 H86.50 Fe2 N8 Si3 Zn
PLAT042_ALERT_1_G Calc. and Reported MoietyFormula Strings  Differ     Please Check
             Calc: C53 H76 Fe2 N8 Si3 Zn
             Rep.: C53 H76 Fe2 N8 Si3 Zn, 0.75[C6H14]
PLAT092_ALERT_4_G Check: Wavelength Given is not Cu,Ga,Mo,Ag,In Ka    0.40651 Ang.
PLAT171_ALERT_4_G The CIF-Embedded .res File Contains EADP Records          7 Report
PLAT176_ALERT_4_G The CIF-Embedded .res File Contains SADI Records          2 Report
PLAT191_ALERT_3_G A Non-default SADI Restraint Value has been used     0.0010 Report
PLAT191_ALERT_3_G A Non-default SADI Restraint Value has been used     0.0010 Report
PLAT301_ALERT_3_G Main Residue  Disorder ..............(Resd  1  )        10% Note
PLAT412_ALERT_2_G Short Intra XH3 .. XHn     H21      ..H28F     .       2.09 Ang.
                                                    x,y,z  =      1_555 Check
PLAT606_ALERT_4_G Solvent Accessible VOID(S) in Structure ........          ! Info
PLAT860_ALERT_3_G Number of Least-Squares Restraints .............          4 Note
PLAT868_ALERT_4_G ALERTS Due to the Use of _smtbx_masks Suppressed          ! Info
PLAT883_ALERT_1_G No Info/Value for _atom_sites_solution_primary .     Please Do !
PLAT933_ALERT_2_G Number of HKL-OMIT Records in Embedded .res File         28 Note
              -2  1  0,  -2  1  1,  -2  2  0,  -2  2  1,  -1  0  2,  -1  0  3,
              -1  0  5,  -1  2  0,   0 -2  2,   0 -2  3,   0 -1  3,   0 -1  4,
               0  0  3,   0  1  2,   1 -3  1,   1 -2  2,   1 -1  3,   1  0  1,
               1  1  0,   1  1  1,   1  2  1,   2 -3  4,   2 -2  1,   2 -2  4,
```

2 -1 1, 2 -1 2, 2 0 3, 2 1 3,

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0 **ALERT level A** = Most likely a serious problem - resolve or explain
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4 **ALERT level C** = Check. Ensure it is not caused by an omission or oversight
19 **ALERT level G** = General information/check it is not something unexpected

6 ALERT type 1 CIF construction/syntax error, inconsistent or missing data
6 ALERT type 2 Indicator that the structure model may be wrong or deficient
6 ALERT type 3 Indicator that the structure quality may be low
5 ALERT type 4 Improvement, methodology, query or suggestion
0 ALERT type 5 Informative message, check

Datablock: 13

Bond precision: C-C = 0.0085 A Wavelength=0.71073

Cell: a=15.1571(7) b=21.4890(11) c=16.3741(8)
alpha=90 beta=93.577(1) gamma=90
Temperature: 100 K

	Calculated	Reported
Volume	5322.8(5)	5322.8(4)
Space group	P 21/n	P 1 21/n 1
Hall group	-P 2yn	-P 2yn
Moiety formula	C50 H69 F6 Fe3 N7 Si3	C50 H69 F6 Fe2.741 N7 Si3, 0.086(Fe3)
Sum formula	C50 H69 F6 Fe3 N7 Si3	C50 H69 F6 Fe3 N7 Si3
Mr	1133.95	1133.94
Dx,g cm-3	1.415	1.415
Z	4	4
Mu (mm-1)	0.937	0.937
F000	2368.0	2368.0
F000'	2373.92	
h,k,lmax		18,25,19
Nref		9399
Tmin,Tmax	0.873,0.942	0.635,0.745
Tmin'	0.873	

Correction method= # Reported T Limits: Tmin=0.635 Tmax=0.745
AbsCorr = MULTI-SCAN

Data completeness= Theta(max)= 25.115

R(reflections)= 0.0664(6425) wR2(reflections)= 0.1942(9399)

S = 1.018 Npar= 648

The following ALERTS were generated. Each ALERT has the format
test-name_ALERT_alert-type_alert-level.
Click on the hyperlinks for more details of the test.

Alert level C

```
PLAT042_ALERT_1_C Calc. and Reported MoietyFormula Strings  Differ     Please Check
             Calc: C50 H69 F6 Fe3 N7 Si3
             Rep.: C50 H69 F6 Fe2.741 N7 Si3, 0.086(Fe3)
PLAT213_ALERT_2_C Atom F5              has ADP max/min Ratio .....        3.2 prolat
PLAT213_ALERT_2_C Atom C30             has ADP max/min Ratio .....        3.3 prolat
PLAT213_ALERT_2_C Atom C3A             has ADP max/min Ratio .....        3.3 prolat
PLAT220_ALERT_2_C NonSolvent   Resd 1  C   Ueq(max)/Ueq(min) Range        4.6 Ratio
PLAT222_ALERT_3_C NonSolvent Resd 1  H   Uiso(max)/Uiso(min) Range        5.8 Ratio
PLAT230_ALERT_2_C Hirshfeld Test Diff for    F1       --C49      .        6.8 s.u.
PLAT230_ALERT_2_C Hirshfeld Test Diff for    F3       --C49      .        5.2 s.u.
PLAT341_ALERT_3_C Low Bond Precision on  C-C Bonds ...............    0.00853 Ang.
```

Alert level G

```
PLAT002_ALERT_2_G Number of Distance or Angle Restraints on AtSite          8 Note
PLAT003_ALERT_2_G Number of Uiso or Uij Restrained non-H Atoms ...          8 Report
PLAT083_ALERT_2_G SHELXL Second Parameter in WGHT  Unusually Large      21.24 Why ?
PLAT168_ALERT_4_G The CIF-Embedded .res File Contains EXYZ Records          1 Report
PLAT171_ALERT_4_G The CIF-Embedded .res File Contains EADP Records          9 Report
PLAT175_ALERT_4_G The CIF-Embedded .res File Contains SAME Records          1 Report
PLAT177_ALERT_4_G The CIF-Embedded .res File Contains DELU Records          2 Report
PLAT178_ALERT_4_G The CIF-Embedded .res File Contains SIMU Records          2 Report
PLAT232_ALERT_2_G Hirshfeld Test Diff (M-X)  Fe1      --N3       .        5.5 s.u.
PLAT232_ALERT_2_G Hirshfeld Test Diff (M-X)  Fe2      --N3       .        5.5 s.u.
PLAT232_ALERT_2_G Hirshfeld Test Diff (M-X)  Fe2      --N5       .        6.0 s.u.
PLAT232_ALERT_2_G Hirshfeld Test Diff (M-X)  Fe3A     --N5       .        6.0 s.u.
PLAT242_ALERT_2_G Low    'MainMol' Ueq as Compared to Neighbors of        C49 Check
PLAT242_ALERT_2_G Low    'MainMol' Ueq as Compared to Neighbors of        C50 Check
PLAT301_ALERT_3_G Main Residue  Disorder ..............(Resd  1  )        10% Note
PLAT720_ALERT_4_G Number of Unusual/Non-Standard Labels ..........          9 Note
             H3AA    H3AB    H3AC    H4AA    H4AB    H4AC    H5AA    H5AB
             H5AC
PLAT860_ALERT_3_G Number of Least-Squares Restraints .............         54 Note
PLAT883_ALERT_1_G No Info/Value for _atom_sites_solution_primary .     Please Do !
PLAT941_ALERT_3_G Average HKL Measurement Multiplicity ...........        3.1 Low
```

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19 **ALERT level G** = General information/check it is not something unexpected

2 ALERT type 1 CIF construction/syntax error, inconsistent or missing data

```
 15 ALERT type 2 Indicator that the structure model may be wrong or deficient
  5 ALERT type 3 Indicator that the structure quality may be low
  6 ALERT type 4 Improvement, methodology, query or suggestion
  0 ALERT type 5 Informative message, check
```

Datablock: 14

Bond precision: C-C = 0.0036 A Wavelength=0.71073

Cell: a=12.3372(6) b=14.5673(7) c=19.6915(10)
alpha=76.058(1) beta=73.437(1) gamma=79.142(1)
Temperature: 100 K

	Calculated	Reported
Volume	3264.8(3)	3264.8(3)
Space group	P -1	P -1
Hall group	-P 1	-P 1
Moiety formula	C55 H74 F5.93 Fe2 N8 Si3 Zn, 0.065(F) [+ solvent]	C55 H74 F6 Fe2 N8 Si3 Zn, 1.5[C6H6]
Sum formula	C55 H74 F6 Fe2 N8 Si3 Zn [+ solvent]	C64 H83 F6 Fe2 N8 Si3 Zn
Mr	1222.53	1339.72
Dx,g cm-3	1.244	1.363
Z	2	2
Mu (mm-1)	0.914	0.920
F000	1275.9	1402.0
F000'	1278.80	
h,k,lmax		14,17,23
Nref		11581
Tmin,Tmax	0.750,0.817	0.690,0.745
Tmin'	0.661	

Correction method= # Reported T Limits: Tmin=0.690 Tmax=0.745
AbsCorr = MULTI-SCAN

Data completeness= Theta(max)= 25.065

R(reflections)= 0.0327(9245) wR2(reflections)= 0.0791(11581)

S = 1.026 Npar= 712

The following ALERTS were generated. Each ALERT has the format
test-name_ALERT_alert-type_alert-level.
Click on the hyperlinks for more details of the test.

Alert level C

```
PLAT220_ALERT_2_C NonSolvent   Resd 1  C   Ueq(max)/Ueq(min) Range        3.9 Ratio
PLAT222_ALERT_3_C NonSolvent Resd 1  H   Uiso(max)/Uiso(min) Range        4.9 Ratio
PLAT230_ALERT_2_C Hirshfeld Test Diff for    Si3      --C38      .        6.3 s.u.
PLAT242_ALERT_2_C Low    'MainMol' Ueq as Compared to Neighbors of        C15 Check
```

Alert level G

```
FORMU01_ALERT_2_G  There is a discrepancy between the atom counts in the
           _chemical_formula_sum and the formula from the _atom_site* data.
           Atom count from _chemical_formula_sum:C64 H83 F6 Fe2 N8 Si3 Zn1
           Atom count from the _atom_site data:  C55 H74 F6.001999 Fe2 N8 Si3 Zn1
CELLZ01_ALERT_1_G Difference between formula and atom_site contents detected.
CELLZ01_ALERT_1_G ALERT: Large difference may be due to a
           symmetry error - see SYMMG tests
           From the CIF: _cell_formula_units_Z    2
           From the CIF: _chemical_formula_sum  C64 H83 F6 Fe2 N8 Si3 Zn
           TEST: Compare cell contents of formula and atom_site data

           atom    Z*formula  cif sites diff
           C        128.00    110.00   18.00
           H        166.00    148.00   18.00
           F         12.00     11.99    0.01
           Fe         4.00      4.00    0.00
           N         16.00     16.00    0.00
           Si         6.00      6.00    0.00
           Zn         2.00      2.00    0.00
PLAT041_ALERT_1_G Calc. and Reported SumFormula    Strings  Differ     Please Check
              Calc: C55 H74 F6 Fe2 N8 Si3 Zn
              Rep.: C64 H83 F6 Fe2 N8 Si3 Zn
PLAT042_ALERT_1_G Calc. and Reported MoietyFormula Strings  Differ     Please Check
              Calc: C55 H74 F5.93 Fe2 N8 Si3 Zn, 0.065(F)
              Rep.: C55 H74 F6 Fe2 N8 Si3 Zn, 1.5[C6H6]
PLAT154_ALERT_1_G The s.u.'s on the Cell Angles are Equal ..(Note)      0.001 Degree
PLAT171_ALERT_4_G The CIF-Embedded .res File Contains EADP Records          3 Report
PLAT230_ALERT_2_G Hirshfeld Test Diff for    F1       --C54      .        7.7 s.u.
PLAT230_ALERT_2_G Hirshfeld Test Diff for    F3       --C54      .        6.3 s.u.
PLAT242_ALERT_2_G Low    'MainMol' Ueq as Compared to Neighbors of        C55 Check
PLAT301_ALERT_3_G Main Residue  Disorder .............(Resd  1  )         4% Note
PLAT302_ALERT_4_G Anion/Solvent/Minor-Residue Disorder (Resd  2  )       100% Note
PLAT304_ALERT_4_G Non-Integer Number of Atoms in ..... (Resd  1  )    148.93 Check
PLAT304_ALERT_4_G Non-Integer Number of Atoms in ..... (Resd  2  )      0.06 Check
PLAT432_ALERT_2_G Short Inter X...Y Contact  F1       ..C34      .       2.95 Ang.
                                                  -1+x,y,z  =     1_455 Check
PLAT432_ALERT_2_G Short Inter X...Y Contact  F3A      ..C54      .       1.74 Ang.
                                                    x,y,z  =      1_555 Check
PLAT432_ALERT_2_G Short Inter X...Y Contact  F3A      ..C52      .       2.46 Ang.
                                                    x,y,z  =      1_555 Check
PLAT606_ALERT_4_G Solvent Accessible VOID(S) in Structure ........          ! Info
PLAT720_ALERT_4_G Number of Unusual/Non-Standard Labels ..........          3 Note
              F0AA    F1AA    F2AA
PLAT860_ALERT_3_G Number of Least-Squares Restraints .............          1 Note
```

```
PLAT868_ALERT_4_G ALERTS Due to the Use of _smtbx_masks Suppressed          ! Info
PLAT883_ALERT_1_G No Info/Value for _atom_sites_solution_primary .     Please Do !
PLAT941_ALERT_3_G Average HKL Measurement Multiplicity ...........        3.1 Low
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   4 **ALERT level C** = Check. Ensure it is not caused by an omission or oversight
  23 **ALERT level G** = General information/check it is not something unexpected

   6 ALERT type 1 CIF construction/syntax error, inconsistent or missing data
  10 ALERT type 2 Indicator that the structure model may be wrong or deficient
   4 ALERT type 3 Indicator that the structure quality may be low
   7 ALERT type 4 Improvement, methodology, query or suggestion
   0 ALERT type 5 Informative message, check

Datablock: 15

Bond precision: C-C = 0.0089 A Wavelength=0.71073

Cell:	a=11.9733(5)	b=26.2570(9)	c=26.2043(10)
	alpha=90	beta=100.148(1)	gamma=90
Temperature:	100 K		

	Calculated	Reported
Volume	8109.3(5)	8109.3(5)
Space group	P 21/n	P 1 21/n 1
Hall group	-P 2yn	-P 2yn
Moiety formula	C50 H69 F6 Fe3 N7 Si3, C20 H30 Co, C4 H10 O [+ solvent]	C50 H69 F6 Fe3 N7 Si3, C20 H30 Co, C4 H10 O, 1[C4H8O]
Sum formula	C74 H109 Co F6 Fe3 N7 O Si3 [+ solvent]	C78 H117 Co F6 Fe3 N7 O2 Si3
Mr	1537.44	1609.53
Dx,g cm-3	1.259	1.318
Z	4	4
Mu (mm-1)	0.829	0.833
F000	3244.0	3404.0
F000'	3251.56	
h,k,lmax		14,31,31
Nref		14337
Tmin,Tmax	0.847,0.936	0.683,0.745
Tmin'	0.847	

Correction method= # Reported T Limits: Tmin=0.683 Tmax=0.745
AbsCorr = MULTI-SCAN

Data completeness= Theta(max)= 25.089

R(reflections)= 0.0691(8091) wR2(reflections)= 0.1765(14337)

S = 1.026 Npar= 878

The following ALERTS were generated. Each ALERT has the format
test-name_ALERT_alert-type_alert-level.
Click on the hyperlinks for more details of the test.

Alert level C

PLAT220_ALERT_2_C NonSolvent Resd 1 C Ueq(max)/Ueq(min) Range 5.0 Ratio
PLAT222_ALERT_3_C NonSolvent Resd 1 H Uiso(max)/Uiso(min) Range 5.9 Ratio
PLAT234_ALERT_4_C Large Hirshfeld Difference C54 --C55 . 0.18 Ang.
PLAT242_ALERT_2_C Low 'MainMol' Ueq as Compared to Neighbors of C15 Check
PLAT242_ALERT_2_C Low 'MainMol' Ueq as Compared to Neighbors of C27 Check
PLAT250_ALERT_2_C Large U3/U1 Ratio for Average U(i,j) Tensor .... 2.1 Note
PLAT260_ALERT_2_C Large Average Ueq of Residue Including O1 0.117 Check
PLAT341_ALERT_3_C Low Bond Precision on C-C Bonds ..... 0.0089 Ang.
PLAT360_ALERT_2_C Short C(sp3)-C(sp3) Bond C71 - C72 . 1.42 Ang.

Alert level G

FORMU01_ALERT_2_G There is a discrepancy between the atom counts in the
_chemical_formula_sum and the formula from the _atom_site* data.
Atom count from _chemical_formula_sum:C78 H117 Co1 F6 Fe3 N7 O2 Si3
Atom count from the _atom_site data: C74 H109 Co1 F6 Fe3 N7 O1 Si3
CELLZ01_ALERT_1_G Difference between formula and atom_site contents detected.
CELLZ01_ALERT_1_G ALERT: Large difference may be due to a
symmetry error - see SYMMG tests
From the CIF: _cell_formula_units_Z 4
From the CIF: _chemical_formula_sum C78 H117 Co F6 Fe3 N7 O2 Si3
TEST: Compare cell contents of formula and atom_site data

atom	Z*formula	cif sites	diff
C	312.00	296.00	16.00
H	468.00	436.00	32.00
Co	4.00	4.00	0.00
F	24.00	24.00	0.00
Fe	12.00	12.00	0.00
N	28.00	28.00	0.00
O	8.00	4.00	4.00
Si	12.00	12.00	0.00

PLAT002_ALERT_2_G Number of Distance or Angle Restraints on AtSite 14 Note
PLAT041_ALERT_1_G Calc. and Reported SumFormula Strings Differ Please Check
Calc: C74 H109 Co F6 Fe3 N7 O Si3
Rep.: C78 H117 Co F6 Fe3 N7 O2 Si3
PLAT042_ALERT_1_G Calc. and Reported MoietyFormula Strings Differ Please Check
Calc: C50 H69 F6 Fe3 N7 Si3, C20 H30 Co, C4 H10 O
Rep.: C50 H69 F6 Fe3 N7 Si3, C20 H30 Co, C4 H10 O, 1[C4H8O]
PLAT083_ALERT_2_G SHELXL Second Parameter in WGHT Unusually Large 14.44 Why ?
PLAT171_ALERT_4_G The CIF-Embedded .res File Contains EADP Records 4 Report
PLAT176_ALERT_4_G The CIF-Embedded .res File Contains SADI Records 4 Report

```
PLAT187_ALERT_4_G The CIF-Embedded .res File Contains RIGU Records          2 Report
PLAT190_ALERT_3_G A Non-default RIGU Restraint Value for First Par     0.0050 Report
PLAT190_ALERT_3_G A Non-default RIGU Restraint Value for SecondPar     0.0050 Report
PLAT190_ALERT_3_G A Non-default RIGU Restraint Value for First Par     0.0010 Report
PLAT190_ALERT_3_G A Non-default RIGU Restraint Value for SecondPar     0.0010 Report
PLAT230_ALERT_2_G Hirshfeld Test Diff for    F6       --C49      .        7.7 s.u.
PLAT230_ALERT_2_G Hirshfeld Test Diff for    F4A      --C49      .        6.5 s.u.
PLAT230_ALERT_2_G Hirshfeld Test Diff for    F5A      --C49      .        9.0 s.u.
PLAT242_ALERT_2_G Low    'MainMol' Ueq as Compared to Neighbors of        C49 Check
PLAT301_ALERT_3_G Main Residue  Disorder ..............(Resd  1  )         9% Note
PLAT380_ALERT_4_G Incorrectly? Oriented X(sp2)-Methyl Moiety .....        C59 Check
PLAT606_ALERT_4_G Solvent Accessible VOID(S) in Structure ........          ! Info
PLAT720_ALERT_4_G Number of Unusual/Non-Standard Labels ..........         26 Note
              Ha      Hb      Hc      Hd      He      Hf      Hg      Hh
              Hi      Hj      Hk      Hl      Hm      Hn      Ho      Hp
              Hq      Hr      Hs      Ht      Hu      Hv      Hw      Hx
              Hy      Hz
PLAT794_ALERT_5_G Tentative Bond Valency for Co1       (III)     .       3.31 Info
PLAT860_ALERT_3_G Number of Least-Squares Restraints .............        117 Note
PLAT868_ALERT_4_G ALERTS Due to the Use of _smtbx_masks Suppressed          ! Info
PLAT883_ALERT_1_G No Info/Value for _atom_sites_solution_primary .     Please Do !
PLAT941_ALERT_3_G Average HKL Measurement Multiplicity ...........        4.3 Low
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   5 ALERT type 1 CIF construction/syntax error, inconsistent or missing data
  13 ALERT type 2 Indicator that the structure model may be wrong or deficient
   9 ALERT type 3 Indicator that the structure quality may be low
   8 ALERT type 4 Improvement, methodology, query or suggestion
   1 ALERT type 5 Informative message, check

Datablock: 16

Bond precision: C-C = 0.0062 A Wavelength=0.41328

Cell: a=15.4746(7) b=23.8238(11) c=27.1431(13)
       alpha=78.401(1) beta=74.315(1) gamma=83.137(1)
Temperature: 100 K

	Calculated	Reported
Volume	9414.8(8)	9414.8(8)
Space group	P -1	P -1
Hall group	-P 1	-P 1
Moiety formula	C50 H69 F6 Fe2 N7 Si3 Zn, C18 H36 K N2 O6, 2.625(C4 H10 O)	C50 H69 F6 Fe2.01 N7 Si3 Zn0.99, C18 H36 K N2 O6, 2.625(C4 H10
Sum formula	C78.50 H131.25 F6 Fe2 K N9 O8.63 Si3 Zn	C78.50 H131.25 F6 Fe2.01 K N9 O8.62 Si3 Zn0.99
Mr	1753.54	1753.51
Dx,g cm-3	1.237	1.237
Z	4	4
Mu (mm-1)	0.168	0.168
F000	3724.8	3725.0
F000'	3727.58	
h,k,lmax		19,29,33
Nref		37723
Tmin,Tmax	0.972,0.985	0.909,1.014
Tmin'	0.972	

Correction method= # Reported T Limits: Tmin=0.909 Tmax=1.014
AbsCorr = MULTI-SCAN

Data completeness= Theta(max)= 14.987

R(reflections)= 0.0548(27581) wR2(reflections)= 0.1539(37723)

S = 1.026 Npar= 2087

The following ALERTS were generated. Each ALERT has the format
test-name_ALERT_alert-type_alert-level.
Click on the hyperlinks for more details of the test.

Alert level C

RINTA01_ALERT_3_C The value of Rint is greater than 0.12
Rint given 0.124
PLAT029_ALERT_3_C _diffrn_measured_fraction_theta_full value Low . 0.979 Why?
PLAT041_ALERT_1_C Calc. and Reported SumFormula Strings Differ Please Check
Calc: C78.50 H131.25 F6 Fe2 K N9 O8.63 Si3 Zn
Rep.: C78.50 H131.25 F6 Fe2.01 K N9 O8.62 Si3 Zn0.99
PLAT042_ALERT_1_C Calc. and Reported MoietyFormula Strings Differ Please Check
Calc: C50 H69 F6 Fe2 N7 Si3 Zn, C18 H36 K N2 O6, 2.625(C4 H10 O)
Rep.: C50 H69 F6 Fe2.01 N7 Si3 Zn0.99, C18 H36 K N2 O6, 2.625(C4 H
PLAT077_ALERT_4_C Unitcell Contains Non-integer Number of Atoms .. Please Check
PLAT213_ALERT_2_C Atom F4 has ADP max/min Ratio ..... 3.2 prolat
PLAT213_ALERT_2_C Atom F4A has ADP max/min Ratio ..... 3.2 prolat
PLAT223_ALERT_4_C Solv./Anion Resd 2 H Ueq(max)/Ueq(min) Range 4.1 Ratio

```
PLAT241_ALERT_2_C High   'MainMol' Ueq as Compared to Neighbors of      C125 Check
PLAT241_ALERT_2_C High   'MainMol' Ueq as Compared to Neighbors of      C126 Check
PLAT242_ALERT_2_C Low    'MainMol' Ueq as Compared to Neighbors of       C66 Check
PLAT244_ALERT_4_C Low    'Solvent' Ueq as Compared to Neighbors of       O13 Check
PLAT244_ALERT_4_C Low    'Solvent' Ueq as Compared to Neighbors of       O14 Check
PLAT260_ALERT_2_C Large Average Ueq of Residue Including      O13      0.150 Check
PLAT260_ALERT_2_C Large Average Ueq of Residue Including      O14      0.112 Check
PLAT260_ALERT_2_C Large Average Ueq of Residue Including      O16      0.200 Check
PLAT260_ALERT_2_C Large Average Ueq of Residue Including      O17      0.185 Check
PLAT260_ALERT_2_C Large Average Ueq of Residue Including     O16A      0.200 Check
PLAT260_ALERT_2_C Large Average Ueq of Residue Including      O18      0.130 Check
PLAT260_ALERT_2_C Large Average Ueq of Residue Including     O18A      0.130 Check
PLAT341_ALERT_3_C Low Bond Precision on  C-C Bonds ...............    0.00621 Ang.
```

Alert level G

```
ABSMU01_ALERT_1_G  Calculation of _exptl_absorpt_correction_mu
                not performed for this radiation type.
PLAT002_ALERT_2_G Number of Distance or Angle Restraints on AtSite        43 Note
PLAT003_ALERT_2_G Number of Uiso or Uij Restrained non-H Atoms ...        28 Report
PLAT012_ALERT_1_G N.O.K.   _shelx_res_checksum Found in CIF ......     Please Check
PLAT020_ALERT_3_G The Value of Rint is Greater Than 0.12 .........      0.124 Report
PLAT068_ALERT_1_G Reported F000 Differs from Calcd (or Missing)...     Please Check
PLAT083_ALERT_2_G SHELXL Second Parameter in WGHT  Unusually Large      14.64 Why ?
PLAT092_ALERT_4_G Check: Wavelength Given is not Cu,Ga,Mo,Ag,In Ka    0.41328 Ang.
PLAT154_ALERT_1_G The s.u.'s on the Cell Angles are Equal ..(Note)      0.001 Degree
PLAT168_ALERT_4_G The CIF-Embedded .res File Contains EXYZ Records         7 Report
PLAT171_ALERT_4_G The CIF-Embedded .res File Contains EADP Records        25 Report
PLAT175_ALERT_4_G The CIF-Embedded .res File Contains SAME Records         6 Report
PLAT177_ALERT_4_G The CIF-Embedded .res File Contains DELU Records         4 Report
PLAT178_ALERT_4_G The CIF-Embedded .res File Contains SIMU Records         4 Report
PLAT187_ALERT_4_G The CIF-Embedded .res File Contains RIGU Records         1 Report
PLAT188_ALERT_3_G A Non-default SIMU Restraint Value has been used     0.0100 Report
PLAT188_ALERT_3_G A Non-default SIMU Restraint Value has been used     0.0100 Report
PLAT188_ALERT_3_G A Non-default SIMU Restraint Value has been used     0.0100 Report
PLAT188_ALERT_3_G A Non-default SIMU Restraint Value has been used     0.0100 Report
PLAT192_ALERT_3_G A Non-default DELU Restraint Value for First Par     0.0050 Report
PLAT192_ALERT_3_G A Non-default DELU Restraint Value for SecondPar     0.0050 Report
PLAT192_ALERT_3_G A Non-default DELU Restraint Value for First Par     0.0050 Report
PLAT192_ALERT_3_G A Non-default DELU Restraint Value for SecondPar     0.0050 Report
PLAT192_ALERT_3_G A Non-default DELU Restraint Value for First Par     0.0050 Report
PLAT192_ALERT_3_G A Non-default DELU Restraint Value for SecondPar     0.0050 Report
PLAT192_ALERT_3_G A Non-default DELU Restraint Value for First Par     0.0050 Report
PLAT192_ALERT_3_G A Non-default DELU Restraint Value for SecondPar     0.0050 Report
PLAT242_ALERT_2_G Low    'MainMol' Ueq as Compared to Neighbors of       C49 Check
PLAT242_ALERT_2_G Low    'MainMol' Ueq as Compared to Neighbors of      C100 Check
PLAT242_ALERT_2_G Low    'MainMol' Ueq as Compared to Neighbors of      C101 Check
PLAT300_ALERT_4_G Atom Site Occupancy of Zn1        Constrained at       0.33 Check
PLAT300_ALERT_4_G Atom Site Occupancy of Zn2        Constrained at       0.33 Check
PLAT300_ALERT_4_G Atom Site Occupancy of Zn3        Constrained at       0.33 Check
PLAT300_ALERT_4_G Atom Site Occupancy of Fe1        Constrained at       0.67 Check
PLAT300_ALERT_4_G Atom Site Occupancy of Fe2        Constrained at       0.67 Check
PLAT300_ALERT_4_G Atom Site Occupancy of Fe3        Constrained at       0.67 Check
PLAT300_ALERT_4_G Atom Site Occupancy of Zn4        Constrained at       0.33 Check
PLAT300_ALERT_4_G Atom Site Occupancy of Zn5        Constrained at       0.33 Check
PLAT300_ALERT_4_G Atom Site Occupancy of Zn6        Constrained at       0.33 Check
PLAT300_ALERT_4_G Atom Site Occupancy of Fe4        Constrained at       0.67 Check
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PLAT300_ALERT_4_G Atom Site Occupancy of Fe5        Constrained at       0.67 Check
PLAT300_ALERT_4_G Atom Site Occupancy of Fe6        Constrained at       0.67 Check
PLAT300_ALERT_4_G Atom Site Occupancy of O17        Constrained at        0.5 Check
PLAT300_ALERT_4_G Atom Site Occupancy of C155       Constrained at        0.5 Check
PLAT300_ALERT_4_G Atom Site Occupancy of C156       Constrained at        0.5 Check
PLAT300_ALERT_4_G Atom Site Occupancy of C157       Constrained at        0.5 Check
PLAT300_ALERT_4_G Atom Site Occupancy of C158       Constrained at        0.5 Check
PLAT300_ALERT_4_G Atom Site Occupancy of H15G       Constrained at        0.5 Check
PLAT300_ALERT_4_G Atom Site Occupancy of H15H       Constrained at        0.5 Check
PLAT300_ALERT_4_G Atom Site Occupancy of H15I       Constrained at        0.5 Check
PLAT300_ALERT_4_G Atom Site Occupancy of H15J       Constrained at        0.5 Check
PLAT300_ALERT_4_G Atom Site Occupancy of H15K       Constrained at        0.5 Check
PLAT300_ALERT_4_G Atom Site Occupancy of H15L       Constrained at        0.5 Check
PLAT300_ALERT_4_G Atom Site Occupancy of H15M       Constrained at        0.5 Check
PLAT300_ALERT_4_G Atom Site Occupancy of H15N       Constrained at        0.5 Check
PLAT300_ALERT_4_G Atom Site Occupancy of H15O       Constrained at        0.5 Check
PLAT300_ALERT_4_G Atom Site Occupancy of H15P       Constrained at        0.5 Check
PLAT301_ALERT_3_G Main Residue  Disorder .............(Resd  1  )         10% Note
PLAT302_ALERT_4_G Anion/Solvent/Minor-Residue Disorder (Resd  2  )          4% Note
PLAT302_ALERT_4_G Anion/Solvent/Minor-Residue Disorder (Resd  7  )        100% Note
PLAT302_ALERT_4_G Anion/Solvent/Minor-Residue Disorder (Resd  8  )        100% Note
PLAT302_ALERT_4_G Anion/Solvent/Minor-Residue Disorder (Resd  9  )        100% Note
PLAT302_ALERT_4_G Anion/Solvent/Minor-Residue Disorder (Resd 10  )        100% Note
PLAT302_ALERT_4_G Anion/Solvent/Minor-Residue Disorder (Resd 11  )        100% Note
PLAT302_ALERT_4_G Anion/Solvent/Minor-Residue Disorder (Resd 12  )        100% Note
PLAT302_ALERT_4_G Anion/Solvent/Minor-Residue Disorder (Resd 13  )        100% Note
PLAT304_ALERT_4_G Non-Integer Number of Atoms in ..... (Resd  7  )       9.06 Check
PLAT304_ALERT_4_G Non-Integer Number of Atoms in ..... (Resd  8  )      10.83 Check
PLAT304_ALERT_4_G Non-Integer Number of Atoms in ..... (Resd  9  )       7.50 Check
PLAT304_ALERT_4_G Non-Integer Number of Atoms in ..... (Resd 10  )       5.94 Check
PLAT304_ALERT_4_G Non-Integer Number of Atoms in ..... (Resd 11  )       4.17 Check
PLAT304_ALERT_4_G Non-Integer Number of Atoms in ..... (Resd 12  )       3.85 Check
PLAT304_ALERT_4_G Non-Integer Number of Atoms in ..... (Resd 13  )       7.39 Check
PLAT398_ALERT_2_G Deviating  C-O-C   Angle From 120 for O13      .      109.3 Degree
PLAT398_ALERT_2_G Deviating  C-O-C   Angle From 120 for O17      .      141.3 Degree
PLAT411_ALERT_2_G Short Inter H...H Contact  H2B      ..H15V     .       2.10 Ang.
                                           1-x,1-y,-z  =      2_665 Check
PLAT413_ALERT_2_G Short Inter XH3 .. XHn     H13V     ..H1IB     .       1.79 Ang.
                                           1-x,1-y,1-z  =      2_666 Check
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Author Response: H atoms are located on a disordered solvent molecule. Modeling of this disorder results in unusually short interatomic distances in some cases.

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PLAT432_ALERT_2_G Short Inter X...Y Contact  O13      ..C159     .       2.62 Ang.
                                           1-x,1-y,1-z  =      2_666 Check
PLAT432_ALERT_2_G Short Inter X...Y Contact  C139     ..C159     .       3.18 Ang.
                                           1-x,1-y,1-z  =      2_666 Check
PLAT720_ALERT_4_G Number of Unusual/Non-Standard Labels .........         32 Note
              Ha      H1AA    H1AB    H1AC    H1BA    H1BB    H1CA    H1CB
              H1DA    H1DB    H1DC    H1EA    H1EB    H1EC    H1FA    H1FB
              H1GA    H1GB    H1HA    H1HB    H1HC    Hb      H1IA    H1IB
              H1IC    H1JA    H1JB    H1KA    H1KB    H1LA    H1LB    H1LC
PLAT789_ALERT_4_G Atoms with Negative _atom_site_disorder_group  #         45 Check
PLAT822_ALERT_4_G CIF-embedded .res Contains Negative PART Numbers          3 Check
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PLAT860_ALERT_3_G Number of Least-Squares Restraints .............        365 Note
PLAT933_ALERT_2_G Number of HKL-OMIT Records in Embedded .res File         40 Note
               -2 -5  1,  -2  0  1,  -2  0  2,  -2  1  1,  -1 -1  2,  -1  0  2,
               -1  2  1,  -1  2  2,  -1  3  1,  -1  3  2,   0 -3  3,   0 -2  1,
                0 -1  4,   0  1  4,   0  3  4,   1  1  4,   1  2  3,   1  2  8,
                1  3  0,   2  0  1,   2  3  2,   2  3  4,   2  4  3,   2  5  1,
                3  2  0,   3  5  7,   1  0  0,  -1  1  0,   0  1  0,   1  1  0,
                0  2  0,   0 -1  1,   1 -1 -1,  -1  0  1,   0  0  1,   1  0  1,
                0  1  1,   1  1  1,   0  0  2,   0  1  2,
```

```
   0 ALERT level A = Most likely a serious problem - resolve or explain
   0 ALERT level B = A potentially serious problem, consider carefully
  21 ALERT level C = Check. Ensure it is not caused by an omission or oversight
  84 ALERT level G = General information/check it is not something unexpected

   6 ALERT type 1 CIF construction/syntax error, inconsistent or missing data
  25 ALERT type 2 Indicator that the structure model may be wrong or deficient
  18 ALERT type 3 Indicator that the structure quality may be low
  56 ALERT type 4 Improvement, methodology, query or suggestion
   0 ALERT type 5 Informative message, check
```

It is advisable to attempt to resolve as many as possible of the alerts in all categories. Often the minor alerts point to easily fixed oversights, errors and omissions in your CIF or refinement strategy, so attention to these fine details can be worthwhile. In order to resolve some of the more serious problems it may be necessary to carry out additional measurements or structure refinements. However, the purpose of your study may justify the reported deviations and the more serious of these should normally be commented upon in the discussion or experimental section of a paper or in the "special_details" fields of the CIF. checkCIF was carefully designed to identify outliers and unusual parameters, but every test has its limitations and alerts that are not important in a particular case may appear. Conversely, the absence of alerts does not guarantee there are no aspects of the results needing attention. It is up to the individual to critically assess their own results and, if necessary, seek expert advice.

Publication of your CIF in IUCr journals

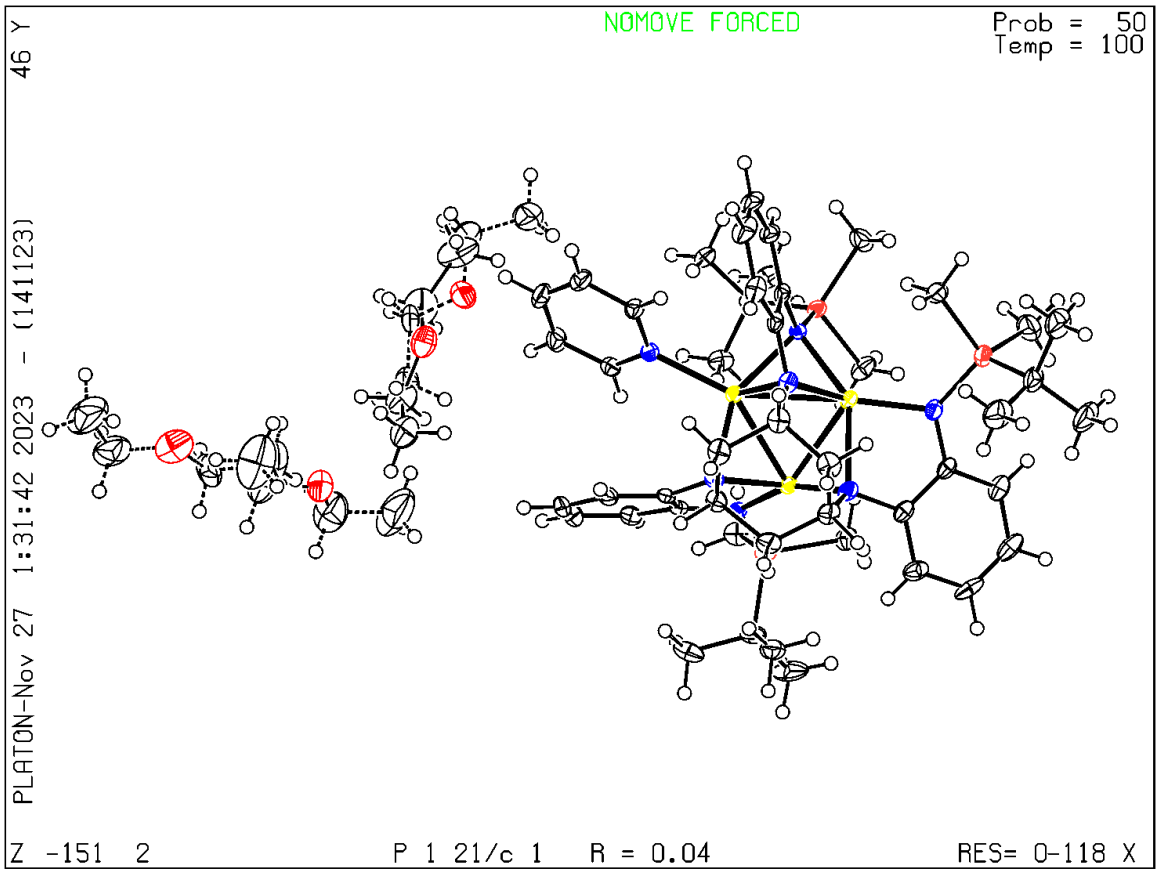
A basic structural check has been run on your CIF. These basic checks will be run on all CIFs submitted for publication in IUCr journals (*Acta Crystallographica*, *Journal of Applied Crystallography*, *Journal of Synchrotron Radiation*); however, if you intend to submit to *Acta Crystallographica Section C* or *E* or *IUCrData*, you should make sure that full publication checks are run on the final version of your CIF prior to submission.

Publication of your CIF in other journals

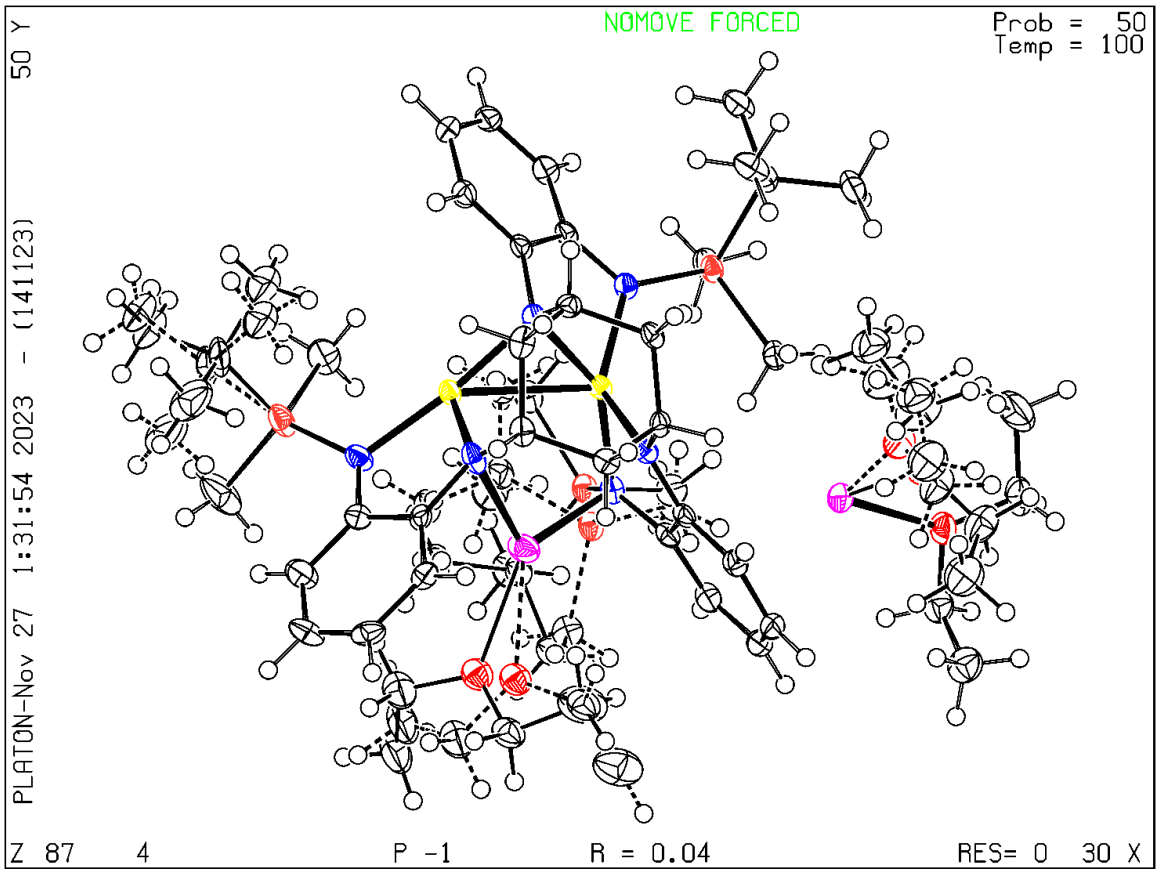
Please refer to the *Notes for Authors* of the relevant journal for any special instructions relating to CIF submission.

PLATON version of 14/11/2023; check.def file version of 14/09/2023

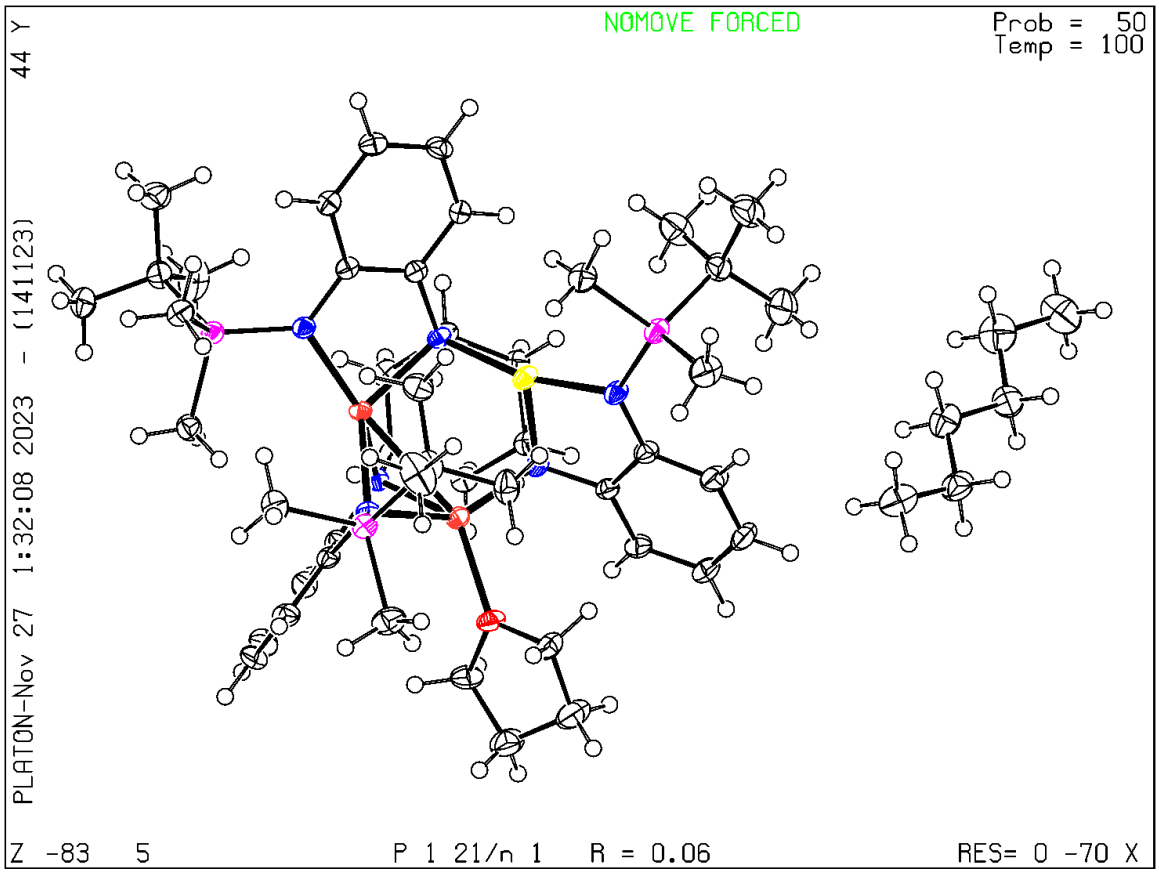
Datablock 2 - ellipsoid plot



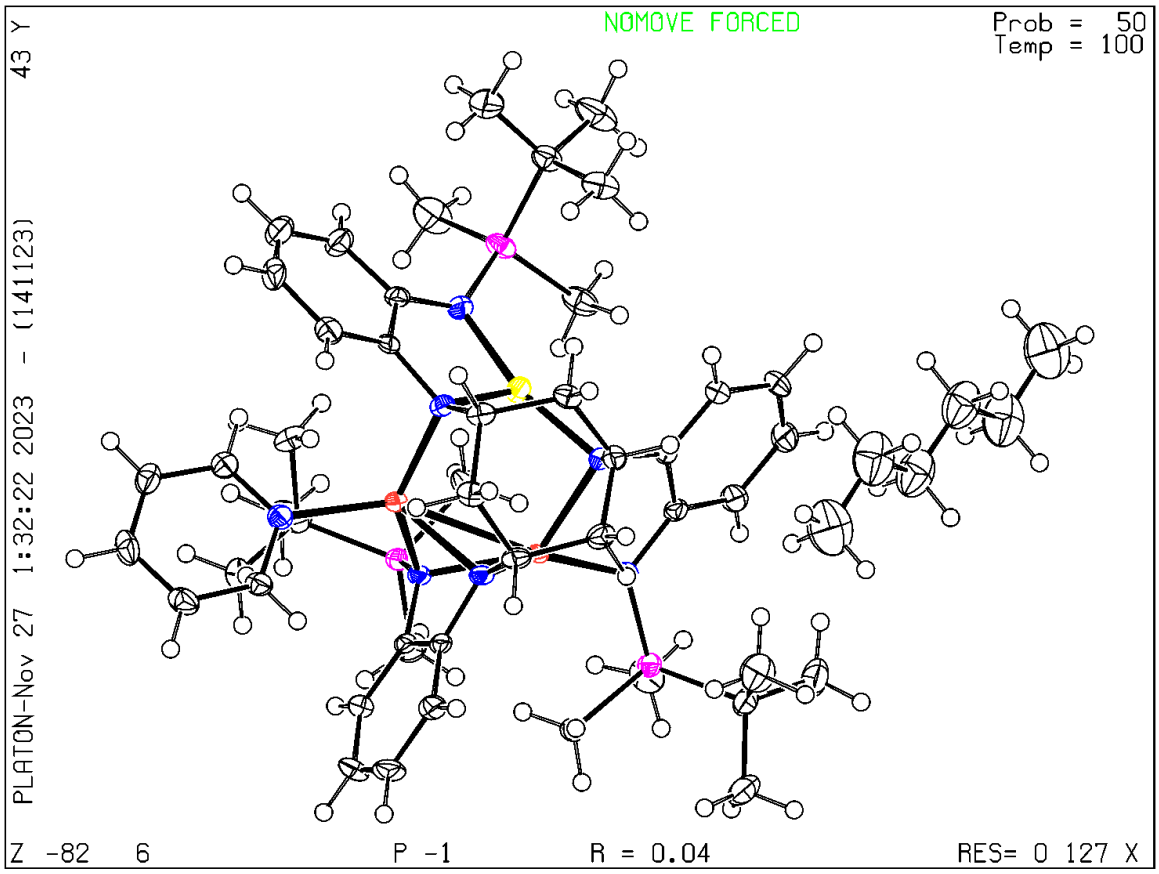
Datablock 4 - ellipsoid plot



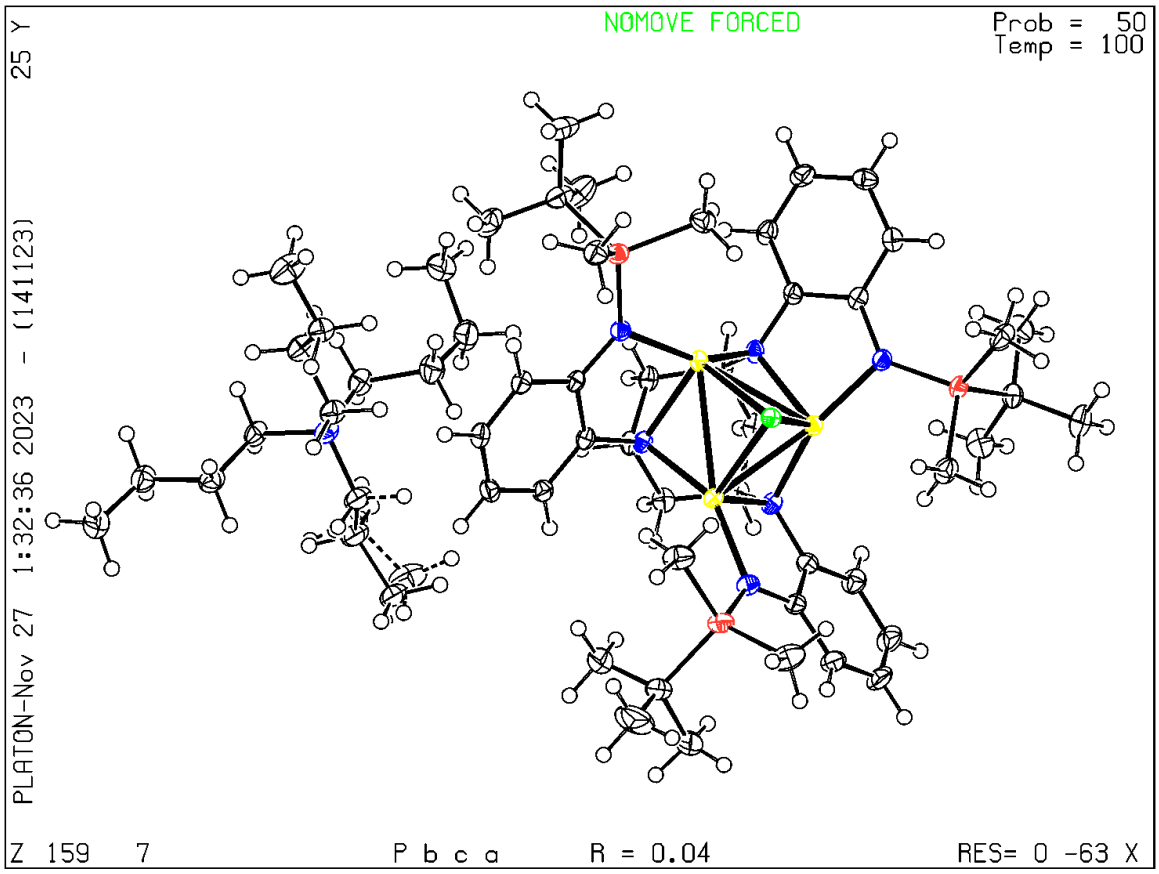
Datablock 5 - ellipsoid plot



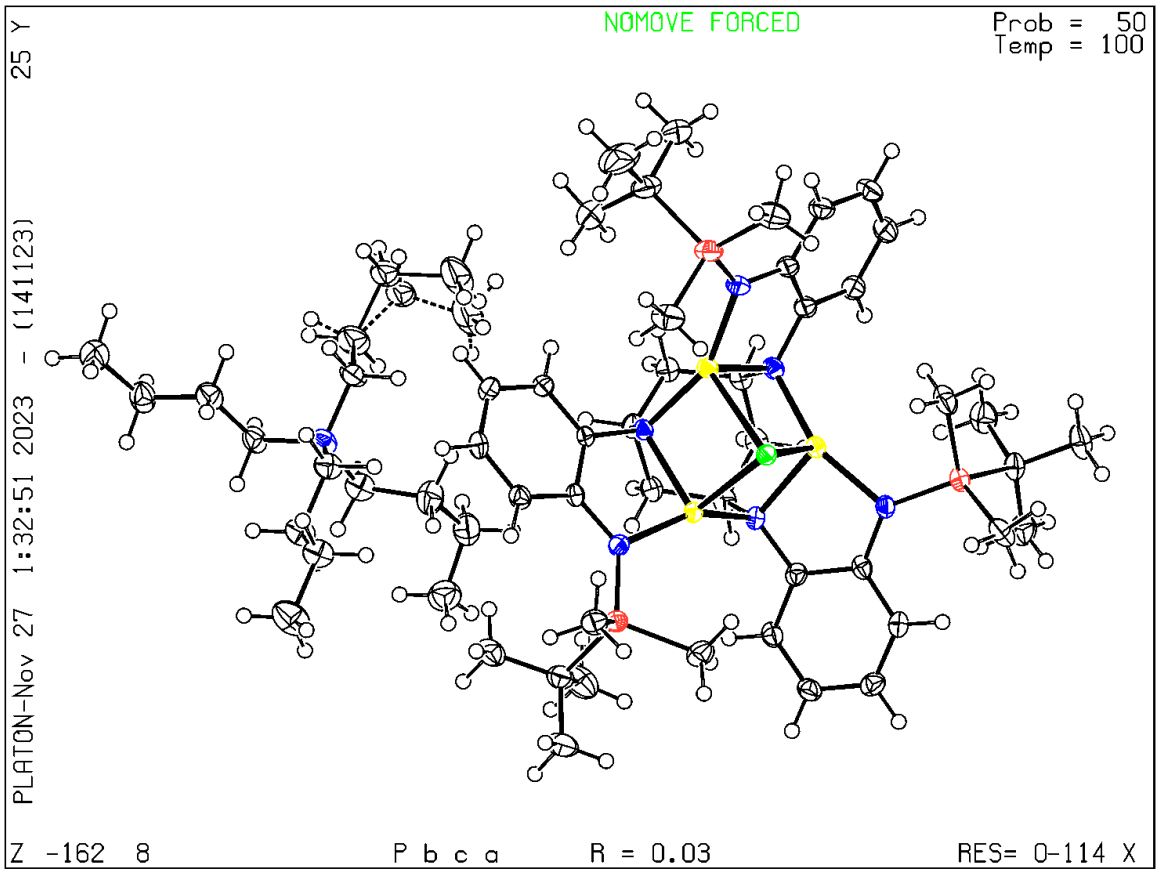
Datablock 6 - ellipsoid plot



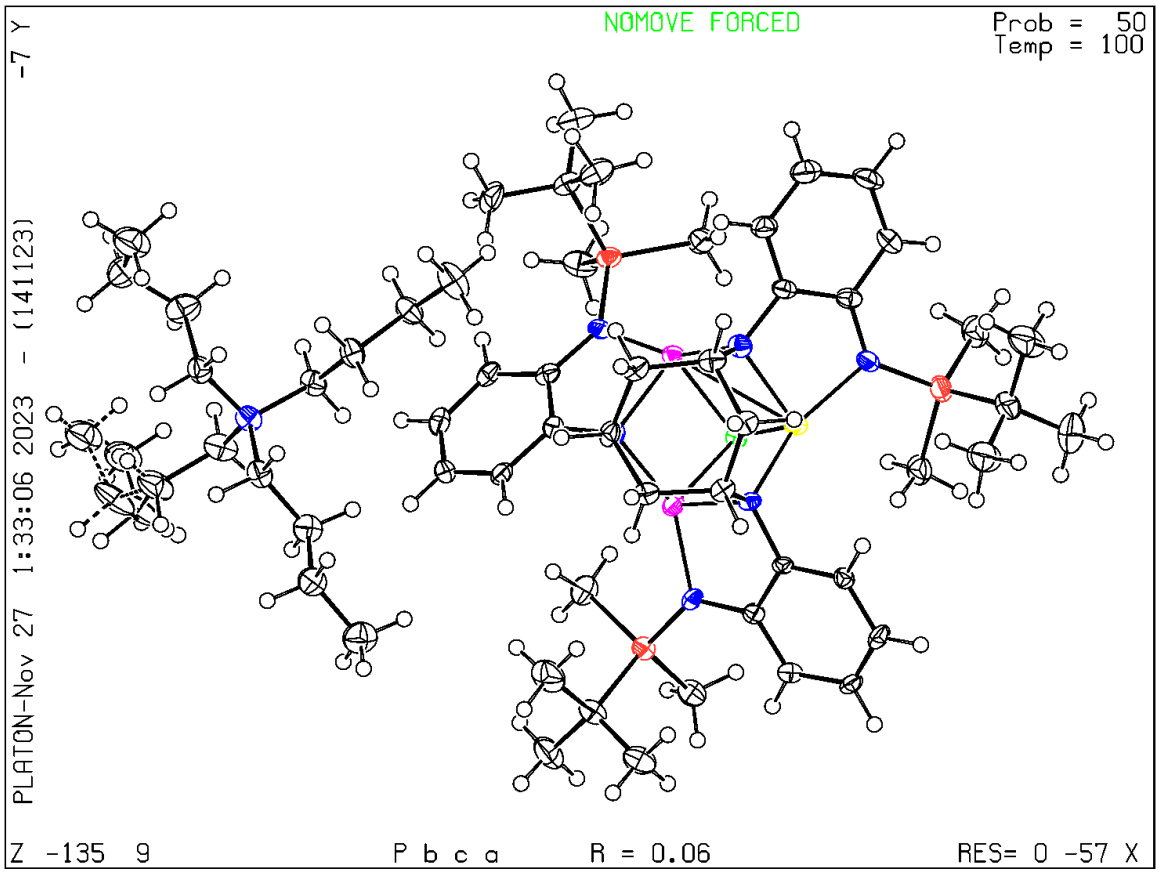
Datablock 7 - ellipsoid plot



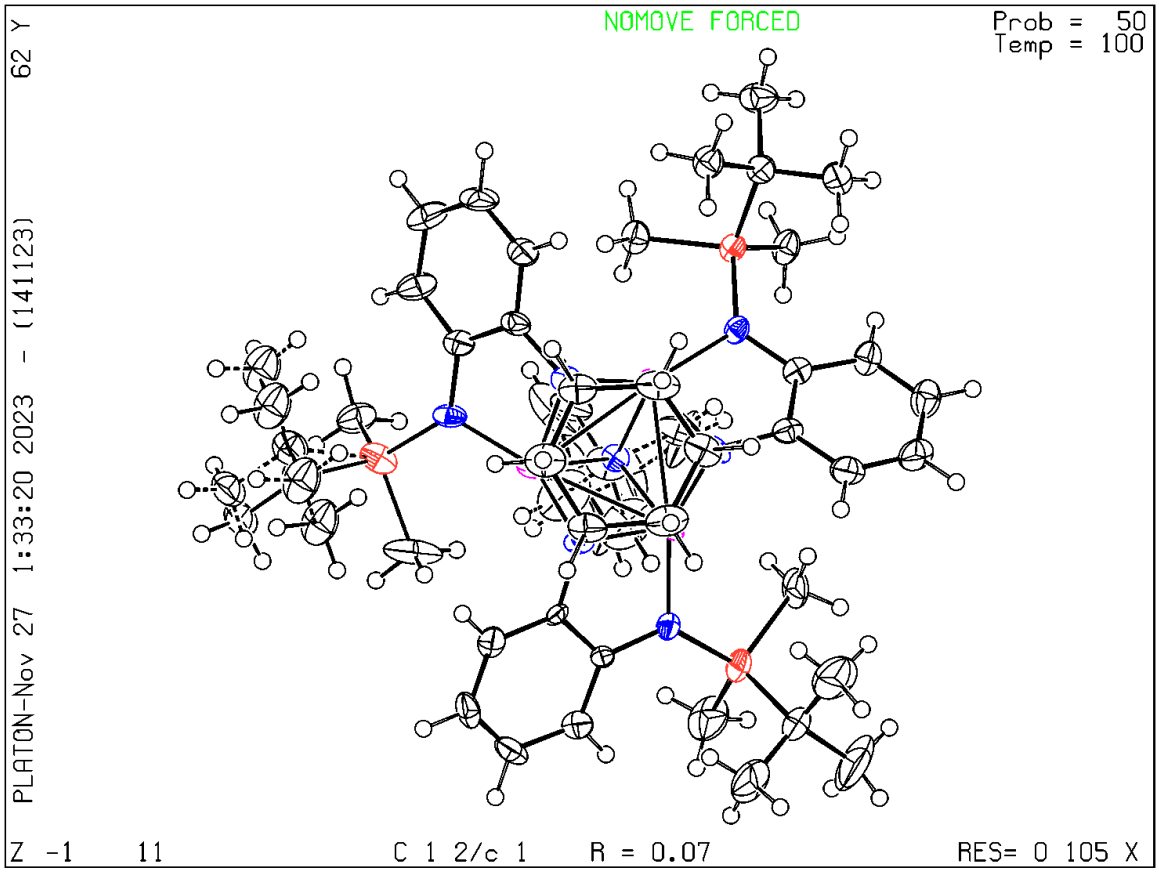
Datablock 8 - ellipsoid plot



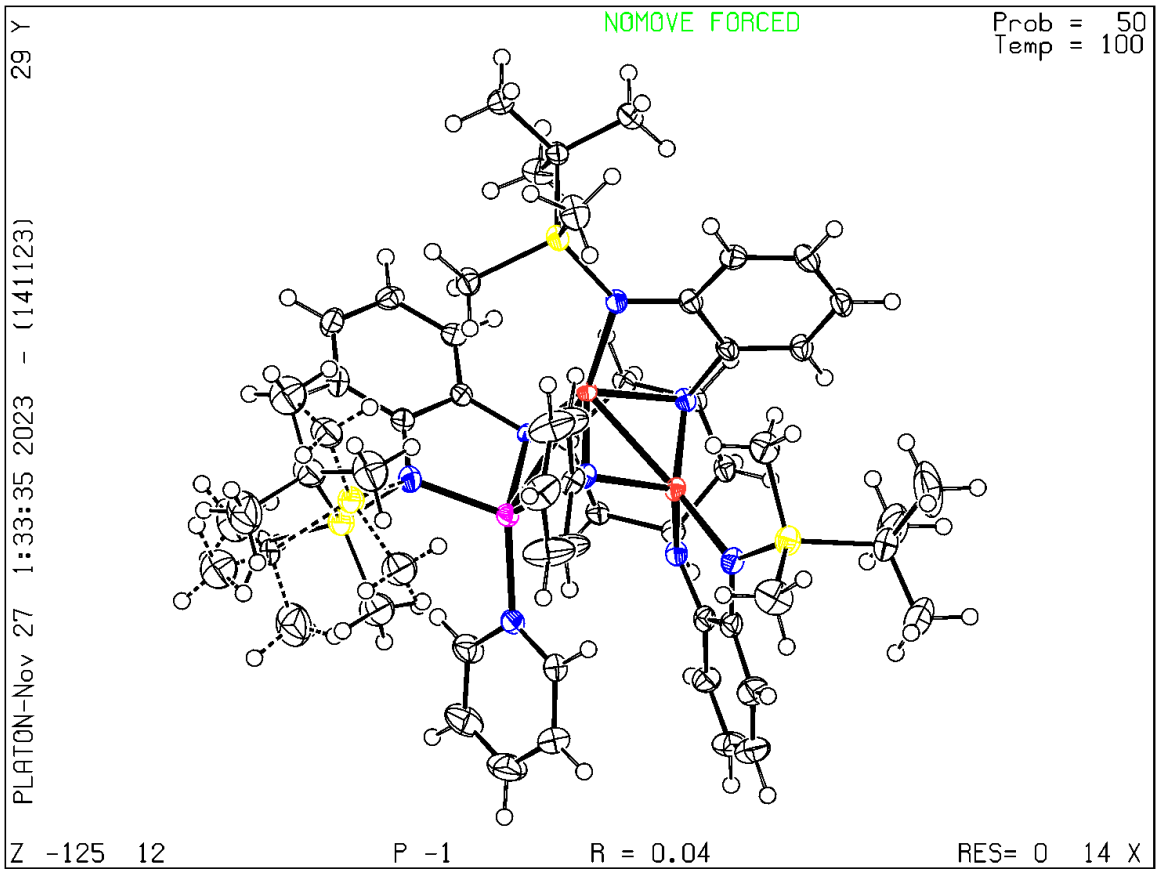
Datablock 9 - ellipsoid plot



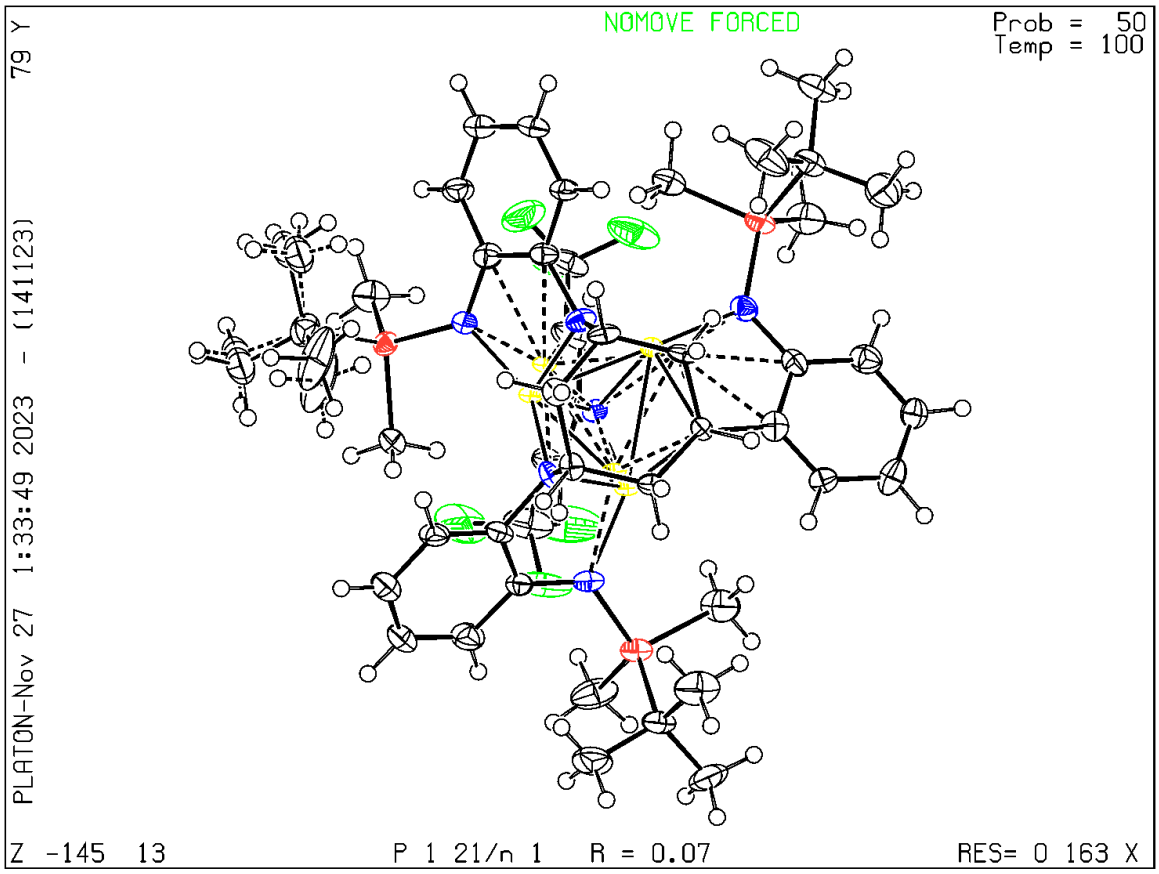
Datablock 11 - ellipsoid plot



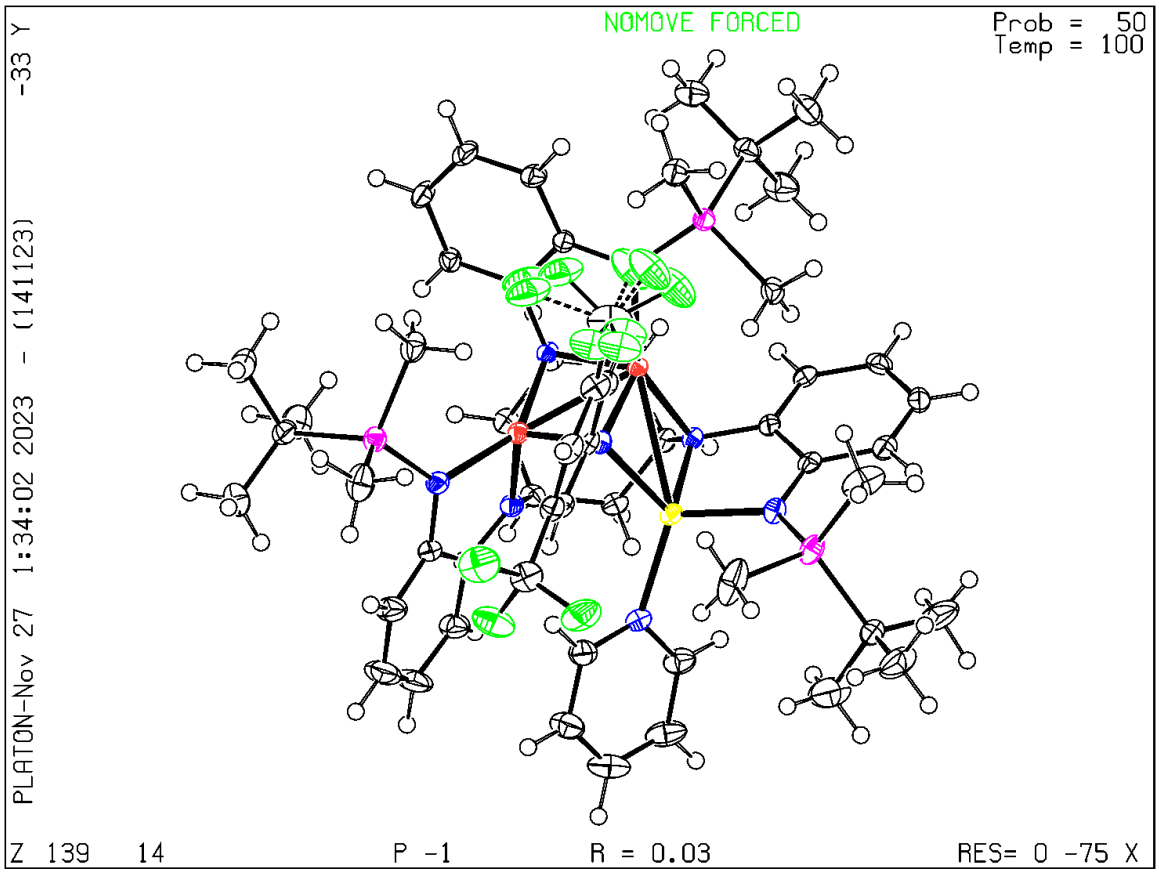
Datablock 12 - ellipsoid plot



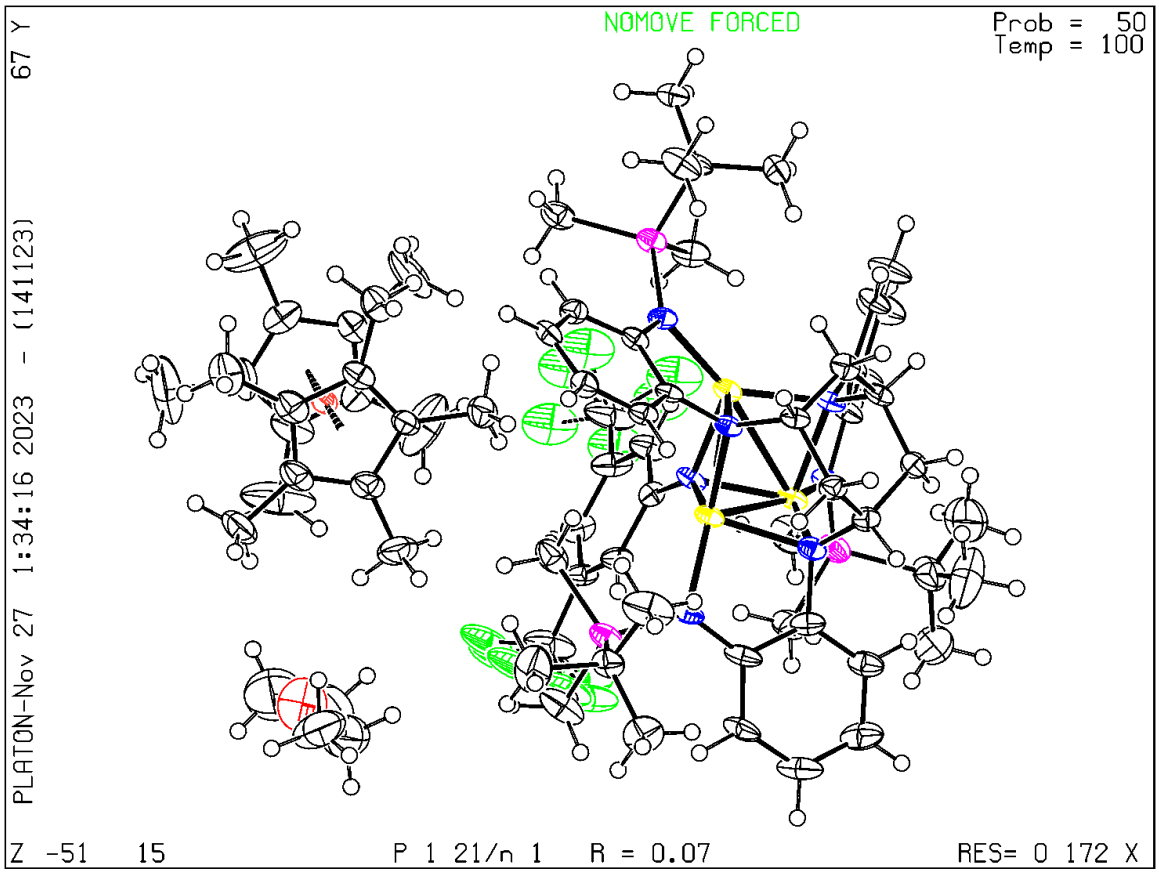
Datablock 13 - ellipsoid plot



Datablock 14 - ellipsoid plot



Datablock 15 - ellipsoid plot



Datablock 16 - ellipsoid plot