Supplementary Material for:

Properties of Square-Pyramidal Alkyl-Thiolate Fe^{III}-Complexes, Including an Analogue of the Unmodified Form of Nitrile Hydratase

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Supplementary Tables:

Experimental Section

General Methods. All reactions were performed under an atmosphere of dinitrogen in a glove box or using standard Schlenk techniques, or using a custom–made solution cell equipped with a threaded glass connector sized to fit a dip probe. Reagents purchased from commercial vendors were of the highest purity available and used without further purification. The carboxamide ligand N,N'-1,2-ethane–diylbis(2-mercapto-2-methyl-propanamide) ($S_2^{Me2}N_2^{amide}$–H_4) was synthesized as previously described.[34] Toluene, tetrahydrofuran (THF), diethyl ether (Et_2O), and acetonitrile (MeCN) were rigorously degassed and purified using solvent purification columns housed in a custom stainless steel cabinet, dispensed via a stainless steel schlenk-line (GlassContour). Methanol (MeOH) and ethanol (EtOH) were distilled from magnesium methoxide or ethoxide and degassed prior to use. Methylene chloride (DCM) was distilled from CaH_2 and degassed prior to use. DMF was distilled from 4 Å molecular sieves and degassed prior to use. ^{1}H NMR spectra were recorded on Bruker AV 301, Bruker AV 500, or Bruker DRX 499 FT-NMR spectrometers and are referenced to an external standard of TMS (paramagnetic compounds) or to residual protio-solvent (diamagnetic compounds). Chemical shifts are reported in ppm and coupling constants (*J*) are in Hz. EPR spectra were recorded on a Bruker EPX CW-EPR spectrometer operating at X-band frequency at 7 K. EPR spectra were fit using the program EasySpin for Matlab. IR spectra were recorded on a Perkin-Elmer 1700 FT-IR spectrometer as KBr pellets. Cyclic voltammograms were recorded in MeCN, MeOH, or DMF (100 –900 mM $Bu^n_4N(PF_6)$ solutions) on a PAR 273 potentiostat utilizing a glassy carbon working electrode, platinum auxiliary electrode, and an SCE reference electrode. Magnetic

moments (solution state) were obtained using the Evans' method as modified for super-conducting solenoids.[35,36] Temperatures were obtained using Van Geet's method.[37] Solid state magnetic measurements were obtained with polycrystalline samples in gel-caps using a Quantum Design MPMS S5 SQUID magnetometer. Ambient temperature electronic absorption spectra were recorded on a Hewlett-Packard Model 8450 spectrometer, interfaced to an IBM PC. Low temperature electronic absorption spectra were recorded using a Varian Cary 50 spectrophotometer equipped with a fiber optic cable connected to a "dip" ATR probe (C-technologies), with a custom–built two-neck solution sample holder equipped with a threaded glass connector (sized to fit the dip probe). Elemental Analyses were performed by Galbraith Labs (Knoxville, TN), Atlantic Microlabs (Norcross, GA) or Canadian Microanalytical Service Ltd. (Delta, BC). 3-methyl-3mercapto-2-butanone was synthesized as previously described.[21]

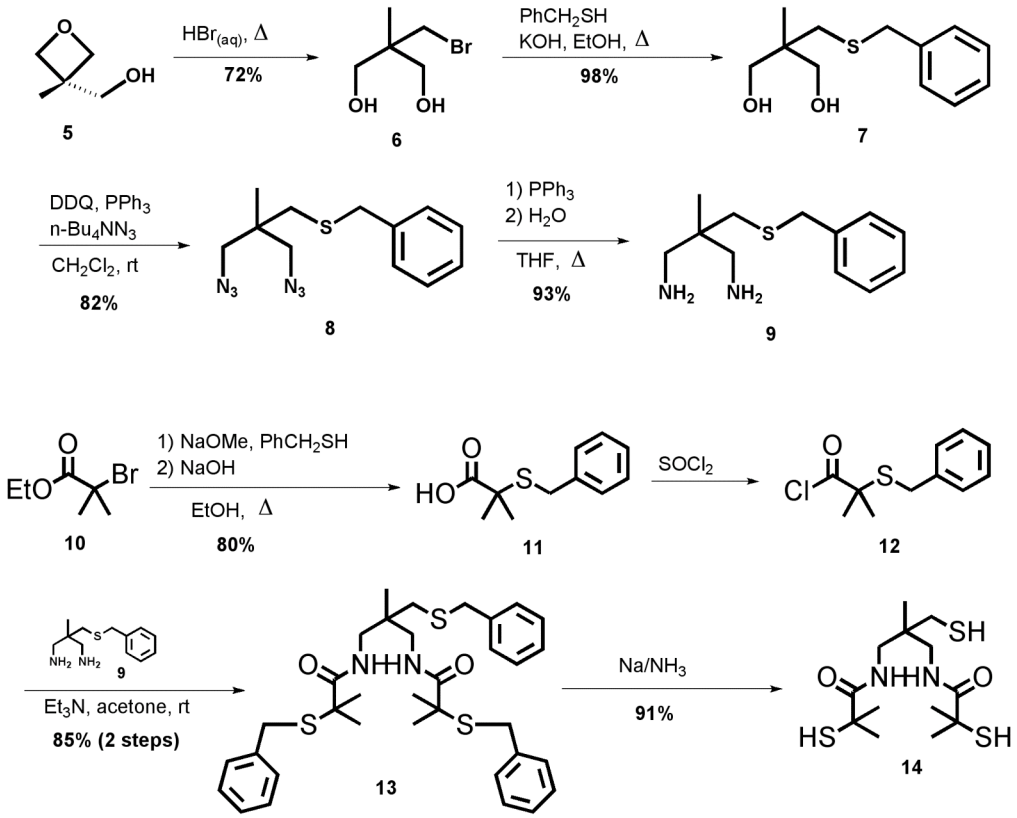
Synthesis of $[Fe^{III}(tame–N_3)S_2{}^{Me2})](PF_6)$•BzCN (1). Two equivalents of 3-methyl-3-mercapto-2-butanone (1.17 g, 10 mmol) were combined with two equiv. of NaOMe, one equiv of 1,1,1–tris(aminomethyl)ethane (tame)[40] (0.59 g, 5 mmol) and one equiv of anhydrous $FeCl_2$ (0.64 g, 5 mmol) in 50 mL of MeOH. Oxidation with Cp_2FePF_6 (0.66 g, 5 mmol), followed by filtration, solvent removal under vacuum, Et_2O extraction to remove Cp_2Fe, and recrystallization from $PhCN/Et_2O$, afforded 1.24 g (41 % yield) of **1**. Electronic absorption (MeCN): λ_{max} (ε): 400 (3380), 540 (1300) nm. IR (KBr pellet) $\nu(cm^{-1})$: 1618 (C=N). $E_{1/2}$ (MeCN) = -650 mV vs SCE. Solution magnetic moment (299 K; MeOH) μ_{eff} = 3.74 BM. EPR (Me-THF, 7 K): g_1 = 4.88, g_2 = 2.60, g_3 = 1.71. ESI-MS calcd for $[FeC_{13}H_{21}N_2O_2S_3]^{2-}$: 389.4, found 389.3. Anal. calcd. for $C_{15}H_{29}FeN_3S_2PF_6$: C, 34.89; H, 5.66; N, 8.14. Found: C, 34.82; H, 5.79; N, 8.04.

Synthesis of Dimeric $(NMe_4)_2[Fe^{III}(Et–N_2)S_2^{Me2})]_2$•2MeOH (2). N,N'-1,2-Ethanediylbis[2-mercapto-2-methyl-propanamide] (400 mg, 1.513 mmol) was dissolved in ~ 10 ml MeOH, and NaOH (242 mg, 6.052 mmol), dissolved in 10 mL of MeOH was then added. Once all of the NaOH was dissolved, the deprotonated ligand was added to a solution consisting of NMe_4FeCl_4 (411 mg, 1.513 mmol) dissolved in MeOH (~15 mL). After stirring for 3 h, the solvent was removed from the intensely colored brown solution, the residue was washed with Et_2O, and then redissolved MeOH/Et_2O (1:1; ~ 60 mL), and filtered to remove insoluble impurities. After removal of the solvent under vacuum, the residue was then dissolved in 10 mL of MeOH, and layered with Et_2O (110 mL) and cooled to - 35 °C for several days. After the mother liquid was decanted, the remaining black crystalline solid (440 mg, 0.52 mmol, 69% yield) was washed by suspending it several times in Et_2O and dried under high vacuum. Electronic absorption (MeOH): λ_{max} (ε): 208 (38000), 301 (16400), 420 (5700), 465 (6000) nm; (MeCN): λ_{max} (ε): 306 (7500), 497 (3000) nm. IR (KBr pellet) ν(cm^{-1}): 1550 (C=O), 1583 (C=O). $E_{1/2}$ (MeCN) = -1.13 V vs SCE. Solution magnetic moment (304 K; MeOH) μ_{eff} = 4.01 BM. EPR (MeOH/EtOH glass (9:1), 7 K): $g_{\perp}$ = 4.35, $g_{||}$ = 2.00. ESI-MS calcd for $[FeC_{13}H_{21}N_2O_2S_3]^{2-}$: 389.4, found 389.3. Anal. calcd. for $C_{28}H_{56}N_6Fe_2O_4S_4$ • 3 MeOH: C, 42.46; H, 7.82; N, 9.58. Found: C, 42.09; H, 7.65; N, 9.51.

Synthesis of Monomeric $(Me_4N)[Fe^{III}(Et–N_2)S_2^{Me2})(Py)]$•2MeOH (3). In the glove box, **2** (140 mg, 0.1657 mmol) was dissolved in 15 mL of a 2:1 MeOH/pyridine mixture. The solution was layered with 100 mL of Et_2O and placed in a -35 °C refrigerator. After standing for several days at -35 °C, the mother liquor was decanted and the remaining brown crystals (0.090 g, 0.1687 mmol, 51% yield) were washed by suspending them several times in Et_2O and dried under high vacuum. Electronic absorption (pyridine): λ_{max} (ε): 309 (8000), 415 (2600), 494

(4800) nm. IR (KBr pellet) ν(cm^{-1}): 1576 (C=O). $E_{1/2}$ (pyridine) = -1.34 V vs SCE. Solution magnetic moment (304 K; MeOH) μ_{eff} = 3.72 BM. EPR (MeOH/EtOH glass (9:1), 7 K): $g_{\perp}$ = 4.45, $g_{||}$ = 1.97. ESI-MS calcd for $[FeC_{13}H_{21}N_2O_2S_3]^{2-}$: 389.4, found 389.3. Anal. Calcd for $C_{19}H_{33}N_4FeO_2S_2$ • 1/2 MeOH: C, 48.24; H, 7.27; N, 11.54. Found: C, 47.87; H, 7.15; N, 11.82.

Synthesis of 2-bromomethyl-2-methyl-propane-1,3-diol (6). To a stirred solution of (3-Methyl-oxetan-3-yl)-methanol (**5**, 17.0 mL, 170.4 mmol; Scheme 2) at ambient temperature was added HBr (25.1 mL of a 48% w/w solution in H_2O, 221.8 mmol). The reaction mixture was allowed to reflux overnight. Upon cooling to 4 °C, a white precipitate was obtained, which was washed with cold hexanes, filtered and dried to yield **6** (22.5 g, 122.9 mmol, 72%). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 3.70 (s, 4H), 3.58 (s, 2H), 2.23 (bs, 2H), 0.95 (s, 3H).



Synthesis of 2-benzylsulfanylmethyl-2-methyl-propane-1,3-diol (7). To a degassed ethanolic solution of benzyl mercaptan (14.0 mL, 119.2 mmol) was added KOH (6.7 g, 119.0 mmol) followed by **6** (21.8 g, 119.0 mmol; Scheme 2). The reaction mixture was refluxed for 20 h. The reaction mixture was concentrated, and suspended in acetone. KBr was filtered off, and acetone was removed *in vacuo*. The resulting solid was washed with water and cold hexanes to yield **7** (26.4 g, 116.7 mmol, 98%) as a white crystalline solid. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.36-7.27 (m, 5H), 3.76 (s, 2H), 3.58 (m, 4H), 2.63 (s, 2H), 2.06 (bs, 2H), 0.85 (s, 3H). ^{13}C NMR($CDCl_3$): δ 138.72, 129.10, 128.74, 127.31, 69.47, 40.67, 37.94, 36.83, 19.12. ESI-MS calcd for $[C_{12}H_{18}SO_2 + Na]^+$: 249.3, found 249.1.

Synthesis of (3-azido-2-azidomethyl-2-methyl-propylsulfanylmethyl)-benzene (8). To a stirred solution of PPh_3 (338 mg, 1.3 mmol) and 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) (390 mg, 1.72 mmol) in dry CH_2Cl_2 (5 mL) at ambient temperature was added tetra-*n*-butylammonium azide (488 mg, 1.72 mmol). After 5 min, **7** (194 mg, 858 μmol; Scheme 2) was added. The reaction mixture was allowed to stir overnight at ambient temperature. Solvent was evaporated under *vacuo*. The residue was purified by silica gel column chromatography (hexanes/ethyl acetate, 4:1, v/v) to yield **8** (194 mg, 703 μmol, 82%) as an orange oil. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.36-7.30 (m, 5H), 3.74 (s, 2H), 3.29 (dd, J = 12.0, 3.9 Hz, 4H), 2.45 (s, 2H), 0.99 (s, 3H). ^{13}C NMR ($CDCl_3$): δ 138.16, 129.07, 128.72, 127.38, 57.01, 40.69, 38.15, 37.91, 20.63.

Synthesis of 2-benzylsulfanylmethyl-2-methyl-propane-1,3-diamine (9). To a stirred solution of **8** (1.0 g, 3.6 mmol; Scheme 2) in THF (20 mL) at ambient temperature was added triphenylphosphine (1.9 g, 7.2 mmol). The reaction mixture was heated at 60 °C overnight. After 12 h, H_2O was added in excess and the reaction was stirred at 60 °C for an additional 3 h.

THF was removed under rotary evaporation. The aqueous solution was acidified with 1M HCl (5 mL) and extracted (3 x 5 mL) with Et_2O to separate the $Ph_3P{=}O$ from the amine. The acidified aqueous layer was washed with 1M KOH (5 mL) and extracted (3 x 5 mL) with Et_2O. The combined organic layers were washed with H_2O and brine (5 mL each), dried over Na_2SO_4, and concentrated *in vacuo*. The combined organic layers were washed with H_2O and brine (3 mL each), dried over Na_2SO_4, and concentrated *in vacuo*. The combined organic extract was concentrated to yield the product **9** (773 mg, 3.5 mmol, 93%) as a clear, colorless oil. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.34-7.32 (m, 5H), 3.72 (s, 2H), 2.62-2.53 (m, 4H), 2.46 (s, 2H), 1.29 (bs, 4H), 0.88 (s, 3H). ESI-MS calcd for $[C_{12}H_{20}N_2S + H]^+$: 225.3, found 225.1.

Synthesis of 2-benzylsulfanyl-2-methyl propionic acid (11). To a stirred solution of ethyl 2-bromo-2-methyl propionate (**10**, 15.0 mL, 102.5 mmol; Scheme 2) in EtOH (340 mL) was added NaOMe (5.5 g, 102.5 mmol) followed by benzyl mercaptan (12.0 mL, 102.2 mmol). After stirring at 90 °C for 3.5 h, NaOH (5.3 g, 133.3 mmol) was added. The reaction mixture was heated at 90 °C for an additional 5 h. The solution was filtered, and the solid recovered was washed with the minimum amount of EtOH. The solid was dissolved in H_2O (25 mL), and concentrated HCl was added dropwise until the solution reached pH=2. After filtration, the solid was dried *in vacuo* overnight to afford **11** (17.3 g, 81.2, 80%) as a white powder. ^{1}H NMR ($CDCl_3$, 301 MHz): δ 7.35-7.32 (m, 5H), 3.93 (s, 2H), 1.60 (s, 6H). ^{13}C NMR ($CDCl_3$): δ 180.74, 137.13, 129.31, 128.71, 127.34, 47.69, 35.05, 25.51. ESI-MS calcd for $[C_{11}H_{14}O_2S + Na]^+$: 233.3, found 233.0.

Synthesis of Benzyl-protected (Tame–N_2S_3) (13). To a stirred solution of 2-benzylsulfanyl-2-methyl propionic acid (**11**, 3.1 g, 14.7 mmol; Scheme 2), placed in an ambient temperature H_2O bath, was added thionyl chloride (5.4 mL, 73.5 mmol). After 30 min, the excess thionyl chloride

was removed under *vacuo*. The crude acid chloride derivative, 2-benzylsulfanyl-2-methyl-propionyl chloride **(12)**, was used immediately in the next step without further purification.

To a stirred solution of 2-benzylsulfanyl-2-methyl-propionyl chloride **(12**; Scheme 2**)** (3.4 g, 14.7 mmol) in acetone (25 mL) at ambient temperature was added **9** (1.7 g, 7.4 mmol) followed by Et_3N (6.1 mL, 44.1 mmol). After stirring for 6 h, saturated aqueous NH_4Cl (20 mL) was added. The aqueous layer was extracted (3 x 20 mL) with Et_2O. The combined organic layers were washed with H_2O and brine (20 mL each), dried over Na_2SO_4, and concentrated *in vacuo* to yield **13** (3.8 g, 6.3 mmol, 85% (2 steps); Scheme 2) as a light yellow oil. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.53 (m, 2H), 7.32-7.23 (m, 15H), 3.77 (s, 4H), 3.71 (s, 2H), 3.20 (dd, *J* = 13.8, 7.8 Hz, 2H), 2.80 (dd, *J* = 14.0, 6.0 Hz, 2H), 2.37 (s, 2H), 1.58 (s, 6H), 1.54 (s, 6H), 0.92 (s, 3H). ^{13}C NMR ($CDCl_3$): δ 175.36, 138.17, 137.35, 129.15, 128.99, 128.78, 128.73, 127.35, 127.29, 50.18, 44.43, 40.93, 37.87, 34.93, 27.19, 26.74, 20.87. ESI-MS calcd for $[C_{34}H_{44}N_2O_2S_3 + H]^+$: 609.9, found 609.3.

Synthesis of Tame–$(NH)_2(SH)_3$ (14). To a stirred solution of liquid ammonia (~50 mL), sodium metal (200 mg) was added to afford an intense blue solution. To this blue solution was added 1 mL aliquots of a solution of **13** (2.0 g, 3.3 mmol) dissolved in diethyl ether (5 mL). Additional sodium was periodically added in small proportions to maintain the deep blue color of the solution. The completion of the reaction was assumed once the solution maintained its deep blue color for more than 30 min. The reaction was then quenched with NH_4Cl (200 mg), and the remaining liquid ammonia was evaporated under a stream of N_2. The resulting solid was dissolved in MeOH (15 mL), and conc. HCl was then added until the solution reached pH=2. The solution was then concentrated *in vacuo*, redissolved in CH_3CN (15 mL), then filtered, and the MeCN solvent evaporated under reduced pressure. The product was extracted from the

brown paste by stirring with Et_2O, and the undesirable solids were then removed by filtration. After concentration of the Et_2O solvent *in vacuo*, the resulting light yellow paste was triturated with hexanes, the solution decanted, and the remaining oily liquid dried under *vacuo* to yield **14** (1.0 g, 3.0 mmol, 91%) as a clear oil. ^{1}H NMR ($CDCl_3$): δ 7.59 (m, 2H), 3.28 (dd, J = 14.0, 6.9 Hz, 2H), 3.01 (dd, J = 14.0, 6.6 Hz, 2H), 2.43 (d, 2H), 2.35 (bs, 1H), 1.73 (bs, 2H), 1.65 (s, 12H), 0.97 (s, 3H) (Figures S–1 and S–2). IR (KBr pellet) ν(cm^{-1}): 3343 (N-H), 2544 (S-H), 1658 (C=O) (Figure S–3). ESI-MS calcd for $[C_{13}H_{26}N_2O_2S_3 + H]^+$: 339.6, found 339.3 (Figure S–4). Anal. calcd. for $C_{13}H_{26}N_2O_2S_3$: C, 46.1; H, 7.7; N, 8.3, found: C, 47.6; H, 7.8; N, 8.1.

Synthesis of $(NMe_4)_2[Fe^{III}(tame–N_2S)S_2^{Me2})]$•MeCN (15). To a stirred solution of **14** (230 mg, 0.7 mmol) and NaOMe (160 mg, 3.0 mmol) in MeOH (7 mL) at -35 °C was added a pre-cooled (-35 °C) methanolic solution (5 mL) of $FeCl_3$ (100 mg, 0.6 mmol). The resulting red orange solution was stirred for 30 min and NMe_4Cl (130 mg, 1.2 mmol) was added. The reaction mixture was allowed to stir overnight at ambient temperature. The solution was concentrated to dryness, dissolved in MeCN, filtered over a bed of celite and concentrated to a minimum amount of MeCN (~2 mL). X-ray quality dark orange crystals (205 mg, 0.4 mmol, 52%) were grown from slow diffusion of diethyl ether (20 ml) into MeCN (2 mL) at –35 °C.

$(NEt_4)_2[Fe^{III}(tame–N_2S)S_2^{Me2})]$•$3H_2O$ (15a). To a stirred solution of **14** (100 mg, 0.3 mmol) in DMF (1 mL) at -35 °C was added dropwise a pre-cooled (-35 °C) solution of $(Et_4N)(FeCl_4)$ (97 mg, 0.3 mmol) in "wet" DMF (1 mL). A pre-cooled (-35 °C) solution of NaH (71 mg of a 60% dispersion in mineral oil, 1.8 mmol) in DMF (1 mL) was added followed by a pre-cooled (-35 °C) DMF (1 mL) solution of Et_4NCl (49 mg, 0.3 mmol). The resulting reaction mixture was allowed to stir overnight at ambient temperature. Diethyl ether (50 mL) was added to the solution resulting in the immediate precipitation of a red orange solid. The solid was dissolved

in MeCN and filtered. The solution was concentrated to a minimum amount of MeCN (~2 mL), layered with 10 mL of Et_2O, and cooled to -35 °C overnight to afford **15a** (130 mg, 0.2 mmol, 68%) as a red orange crystalline solid. IR (KBr pellet) $\nu(cm^{-1})$: 1559 (C=O). Electronic absorption (CH_3CN): λ_{max} (ε) = 330 (8860), 433 (2570), 471 (3250) nm; (MeOH): λ_{max} (ε) = 323 (10400), 424 (2630), 479 (2560) nm; (H_2O): λ_{max} (ε) = 319 (10380), 420 (3190), 473 (2930) nm. Solution magnetic moment (298 K; MeOH) μ_{eff} = 3.99 BM. EPR (MeOH/EtOH glass (9:1), 7 K): g_1 = 4.60, g_2 = 3.40, g_3 = 1.97. ESI-MS calcd for $[FeC_{13}H_{21}N_2O_2S_3]^{2-}$: 389.4, found 389.3. Anal. calcd. for $FeC_{29}H_{61}N_4O_2S_3$: C, 53.6; H, 9.5; N, 8.6. Found: C, 53.6; H, 9.7; N, 8.5.

Synthesis of $[Fe^{II}((tame–N_3)S_2^{Me2})(CO)]$•MeCN (16). Two equivalents of 3-methyl-3-mercapto-2-butanone (1.17 g, 10 mmol) were combined with 1,1,1–Tris(aminomethyl)ethane (0.59 g, 5 mmol) and $FeCl_2$ (0.64 g, 5 mmol), in 30 mL MeOH. Carbon monoxide was then bubbled through the resulting reaction mixture for 30 min, the solution filtered, evaporated to dryness, and the solid redissolved in ~ 20 mL MeCN, and placed in a freezer overnight to afford 0.4 g (18% yield) of **16**•MeCN, as red plates. Electronic absorption (MeCN): λ_{max} (ε) = 349 (2730) nm. IR (KBr pellet) $\nu(cm^{-1})$: 1895 (CO), 1602 (C=N). Anal. calcd. for $C_{18}H_{32}FeN_4OS_2$: C, 49.00; H, 7.30; N, 12.70. Found: C, 48.67; H, 7.42; N, 12.69.

Synthesis of $[Fe^{III}(tame–N_3S_2^{Me2})(NO)](PF_6)$ (18). On a high-vacuum line, 1.15 equivalents (in a calibrated 50 mL bulb) of NO $_{(g)}$ was added to a frozen degassed MeCN solution (10 mL) of **1** (2.57g, 5 mmol). The resulting solution was allowed to warm to ambient temperature and then layered with ether to afford 0.63 g (23 % yield) of **18**•MeCN, as orange plates. Electronic absorption (MeCN): λ_{max} (ε) = 490 (400) nm. IR (KBr pellet) $\nu(cm^{-1})$: 1866

(NO), 1622 (C=N). Anal. calcd. for $C_{17}H_{32}FeN_5OS_2PF_6$: C, 34.70; H, 5.49; N, 11.92. Found: C, 34.61; H, 5.55; N, 11.83.

Synthesis of $(Et_4N)_2[Fe^{III}(Tame–N_2S_2(SO_2)]$ (20). To a stirred solution of **15a** (100 mg, 0.3 mmol) in DMF (1 mL) at -35 °C was added dropwise a pre-cooled (-35 °C) solution of $(Et_4N)(FeCl_4)$ (97 mg, 0.3 mmol) in DMF (1 mL). A pre-cooled (-35 °C) solution of NaH (71 mg of a 60% dispersion in mineral oil, 1.8 mmol) in DMF (1 mL) was added followed by a pre-cooled (-35 °C) DMF (1 mL) solution of Et_4NCl (49 mg, 0.3 mmol). The resulting reaction mixture was allowed to stir overnight at ambient temperature. Diethyl ether (50 mL) was added to the solution resulting in the immediate precipitation of a red orange solid. The solid was dissolved in MeCN and filtered. The solution was concentrated to a minimum amount of MeCN (~2 mL), layered with 10 mL of Et_2O, and cooled to -35 °C overnight to afford **20** (130 mg, 0.2 mmol, 68%) as a red orange crystalline solid. IR (KBr pellet) $\nu(cm^{-1})$: 1559 (C=O), 1035 (S-O). Electronic absorption (CH_3CN): λ_{max} (ε) = 330 (8860), 433 (2570), 471 (3250) nm; (MeOH): λ_{max} (ε) = 323 (10400), 424 (2630), 479 (2560) nm; (H_2O): λ_{max} (ε) = 319 (10380), 420 (3190), 473 (2930) nm. EPR (MeOH/EtOH glass (9:1), 7 K): g_1 = 3.74, g_2 = 2.02. ESI-MS calcd for $[FeC_{13}H_{21}N_2O_2S_3]^{2-}$: 389.4, found 389.3. Anal. calcd. for $FeC_{29}H_{61}N_4O_2S_3$: C, 53.6; H, 9.5; N, 8.6. Found: C, 53.6; H, 9.7; N, 8.5.

X-ray Crystallographic Structure Determination. Red crystal prisms of **1** (0.13 x 0.06 x 0.06 mm) and **2** (0.25 x 0.18 x 0.09 mm) were each mounted on a glass capillary with oil. Data for both was collected at -112 °C. The crystal-to-detector distance was set to 27 mm for both **1** and **2**, and the exposure time was 60 seconds per degree for **1** and 20 seconds per degree for **2** for all sets, each with a scan width of 1°. The data collection

for **1** was 85.8% complete to 25° in ϑ, and for **2** 93.5% complete to 20.80° in ϑ . A total of 82543 partial and complete reflections were collected covering the indices, h = -16 to 16, k = -18 to 18, l = -16 to 16 for **1**, and 46010 partial and complete reflections covering the indices, h = -15 to 15, k = -11 to 11, l = -22 to 22 for **2**. For **1**, 48000 reflections were symmetry independent, and for **2**, 4412 reflections were symmetry independent. The R_{int} = 0.0250 indicated that the data for **1** was brilliant, while the R_{int} = 0.0765 for **2** indicated that the quality of data was fair (average quality 0.07). Indexing and unit cell refinement indicated an orthorhombic P lattice for **1**, and monoclinic P lattice for **2**. The space group for **1** was found to be P nma (No.62), and that of **2** was found to be $P\,2_1/c$ (No. 14) based on systematic absences

A brownish crystal prism of **3** (0.10 x 0.12 x 0.17 mm), and orange prism of **15** (0.48 × 0.12 × 0.12 mm) was mounted on a glass capillary with oil. Data for each was collected at –143°C. The crystal-to-detector distance was set to 30 mm and exposure time was 40 seconds per degree for **3** for all sets, and 30 seconds per degree for **15** for all sets with a scan width of 0.7° for **3** and 1.3° for **15**. The data collection for **3** was 93.7% complete to 24.79° in ϑ, and 99.5% complete to 25° in ϑ for **15**. A total of 91440 partial and complete reflections were collected covering the indices, h = -10 to 10, k = -13 to 13, l = -30 to 30 for **3**, and 53920 partial and complete reflections, covering the indices, h = -24 to 24, k = -20 to 20, l = -28 to 28 for **15**. 8596 reflections were symmetry independent for **3**, and 7568 reflections were symmetry independent for **15**. the R_{int} = 0.0603 indicated that the data was good for **3**, and that of **15** (R_{int} = 0.0457) indicated that the data was of better than average quality (average quality 0.07). Indexing and unit cell

refinement indicated a monoclinic P lattice for **3**, and an orthorhombic P lattice for **15**. The space group was found to be *P* $2_1/c$ (No. 14) for **3**, and P*bca* (No.61) for **15**.

A black crystal prism 0.24 x 0.18 x 0.3 mm of **4** was mounted on a glass capillary in epoxy. Data was collected at 20 ˚C. The crystal-to-detector distance was set to 27 mm and exposure time was 60 seconds per degree for all sets with a scan width of 1.5º. The data collection was 94.4% complete to 26.35º in ϑ. A total of 28235 partial and complete reflections were collected covering the indices, h = -27 to 24, k = -14 to 12, l = -18 to 18. 3490 reflections were symmetry independent and the R_{int} = 0.1224 indicated that the quality of data was acceptable, although the average value is smaller (0.07). Indexing and unit cell refinement indicated a monoclinic P lattice. The space group was found to be *P* $2_1/c$ (No. 14). Analysis of the normalized structure factors indicated a centric cell favoring above symmetry.

A red plate of **16** (0.24 × 0.23 × 0.09 mm), and orange plate of **18** (0.25 × 0.20 × 0.13 mm) was mounted on a glass capillary in epoxy. Data was collected at –112 ºC. The crystal-to-detector distance was set to 27 mm and exposure time was 10 seconds per degree for **16**, and 15 seconds per degree for **18**, for all data sets, with a scan width of 1.0º for **16** and 2.4º for **18**. The data collection for **16** and **18** was 92.7%, and 95.2% complete, respectively, to 30.5º in ϑ for each. A total of 33204 partial and complete reflections for **16**, and 46749 partial and complete reflections for **18**, were collected covering the indices, h = -13 to 14, k = -14 to 15, l = -17 to 17 for **16**, and h = -16 to 16, k = -21 to 23, l = -19 to 19 for **18**. 6233 reflections for **16**, and 7487 reflections for **18**, were symmetry independent. The R_{int} = 0.0588 for **16**, and that for **18** (R_{int} = 0.0668), indicated that the data was of better than average quality for both (average quality 0.07).

Indexing and unit cell refinement indicated a triclinic P lattice for **16**, and monoclinic P lattice for **18**. The space group for **16** was found to be *P*1 bar (No.2), and that for **18** was found to be $P\ 2_1/c$ (No. 14).

A purple plate 0.34 × 0.30 × 0.20 mm of **19** was mounted on a glass capillary in epoxy. Data was collected at –112ºC. The crystal-to-detector distance was set to 27 mm and exposure time was 30 seconds per degree for all sets with a scan width of 1.0º. The data collection was 97.5% complete to 30.5º in ϑ. A total of 52433 partial and complete reflections were collected covering the indices, h = -18 to 18, k = -17 to 17, l = -21 to 21. 7859 reflections were symmetry independent and the R_{int} = 0.051 indicated that the data was of better than average quality (average quality 0.07). Indexing and unit cell refinement indicated a orthorhombic P lattice. The space group was found to be $P\ 2_12_12_1$ (No. 19).

A red prism size 0.31 × 0.24 × 0.12 mm of **20** was mounted on a glass capillary with oil. Data was collected at –143ºC. The crystal-to-detector distance was set to 30 mm and exposure time was 50 seconds per degree for all sets with a scan width of 1.4º. The data collection was 98.5% complete to 25º in ϑ. A total of 117076 partial and complete reflections were collected covering the indices, h = -14 to 14, k = -22 to 23, l = -27 to 27. 8809 reflections were symmetry independent and the R_{int} = 0.0973 indicated that the data was of slightly less than average quality (average quality 0.07). Indexing and unit cell refinement indicated a monoclinic P lattice. The space group was found to be $P\ 2_1/c$ (No. 14).

The data for **1**–**4**, **16**, **18**–**19**, and **20**, was integrated and scaled using Denzo-hkl-SCALEPACK, while that for **15**, was integrated and scaled using hkl-2000. With the

exception of **2**, and **18**, an absorption correction was performed using SORTAV for all structures. Solution by direct methods (SIR-2004 for **15**, SIR97 for **1**, and **20**, and SIR92 for **2–16**, and **18–19**) produced a complete heavy atom phasing model consistent with each of the proposed structures. All non-hydrogen atoms were refined anisotropically by full-matrix least-squares methods, while all hydrogen atoms were refined using a riding model. All hydrogen atoms for **19** were located by fourier synthesis except those on N(3), C(10), C(11), C(12), C(14), C(17) and C(18). All hydrogen atoms for **18** were located by fourier synthesis except those on C(16) which were placed with idealized methyl geometery. With structure **2,** the **H**-O-C-H torsion angle, involving the methanol solvate -OH hydrogens, was refined by adding two extra parameters, one for each methanol. The methanol solvate C(21)-O(4) of **3** was found to be disordered with a smaller than full occupancy (74(1)%). The other methanol solvate of **3** was found to to be present in close to full site occupancy (98.2(8)%). The asymmetric unit of structure **4** was found to contain 1.5 cobalt anions and 1.5 tetraethyl ammonium cations; Co(2) and N(5) were each found on special positions. For structure **20**, S(3) and C(7) were disordered over two positions (77.8(5)% : 22.2(5)%) involving S(4) and C(32)). Crystal data for **1–4**, **15–16**, **18–19**, and **20**, is presented in Table 1. Selected bond distances and angles are assembled in Tables 2 and 4.

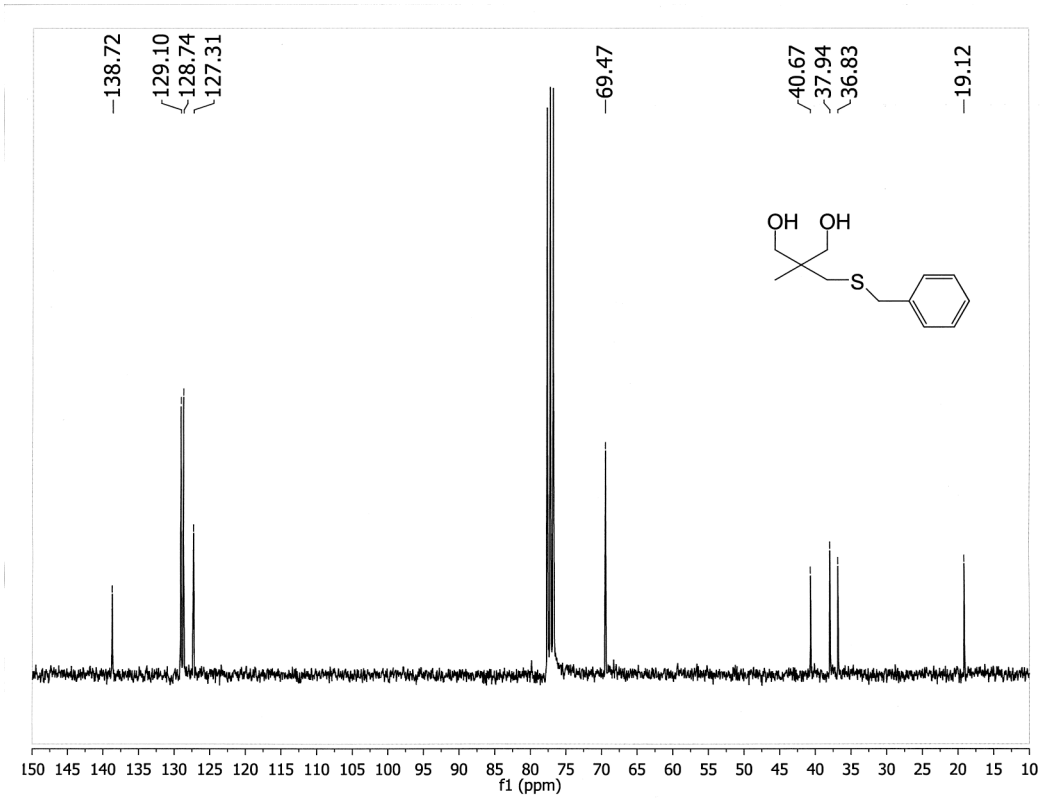


Figure S–1. ^{13}C NMR($CDCl_3$) of 2-benzylsulfanylmethyl-2-methyl-propane-1,3-diol (**7**).

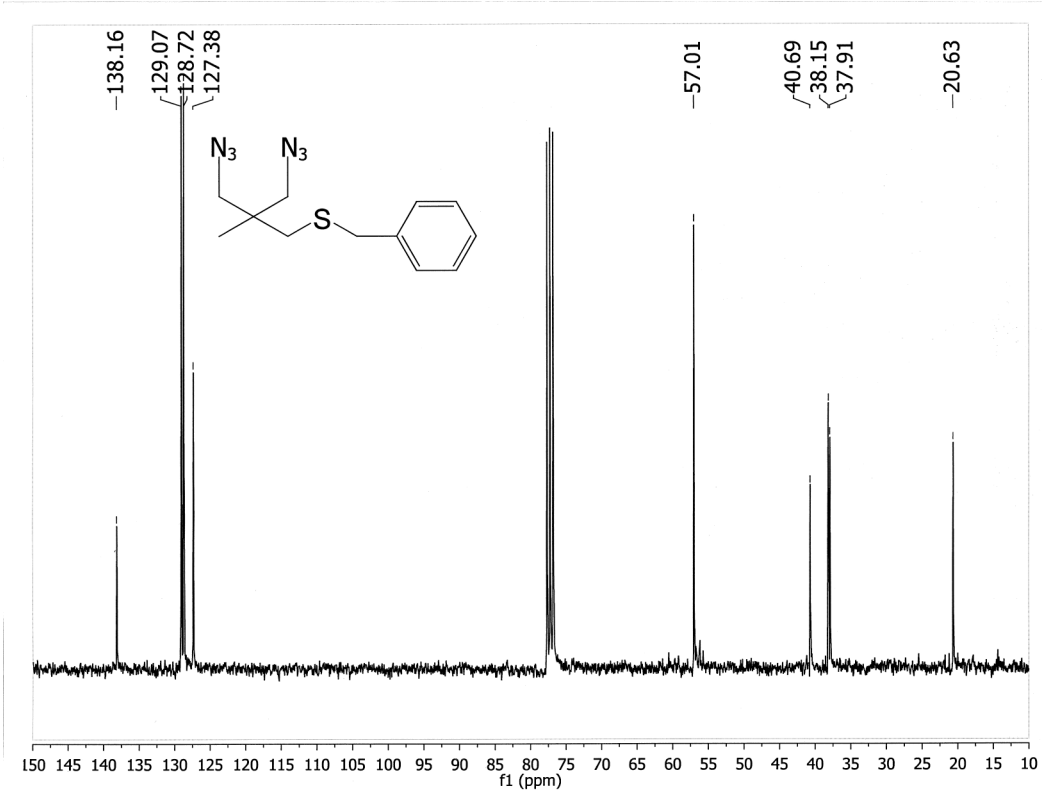


Figure S–2. ^{13}C NMR($CDCl_3$) of (3-azido-2-azidomethyl-2-methyl-propylsulfanylmethyl)-benzene (**8**).

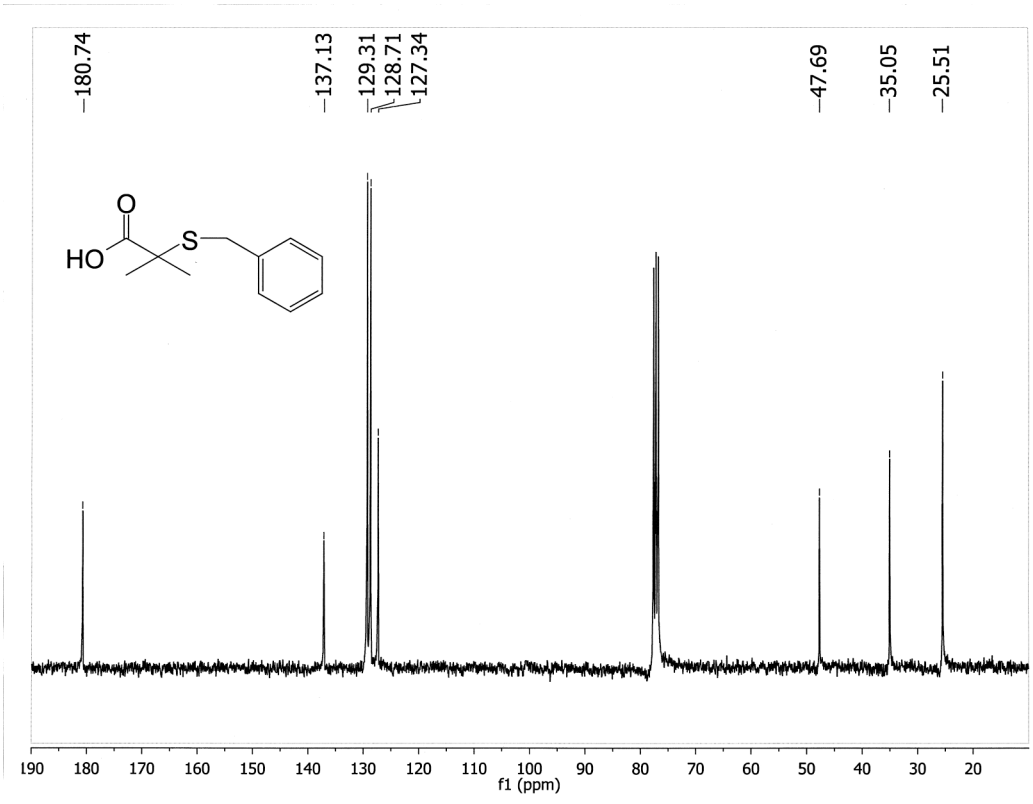


Figure S–3. ^{13}C NMR($CDCl_3$) of 2-benzylsulfanyl-2-methyl propionic acid (**11**).

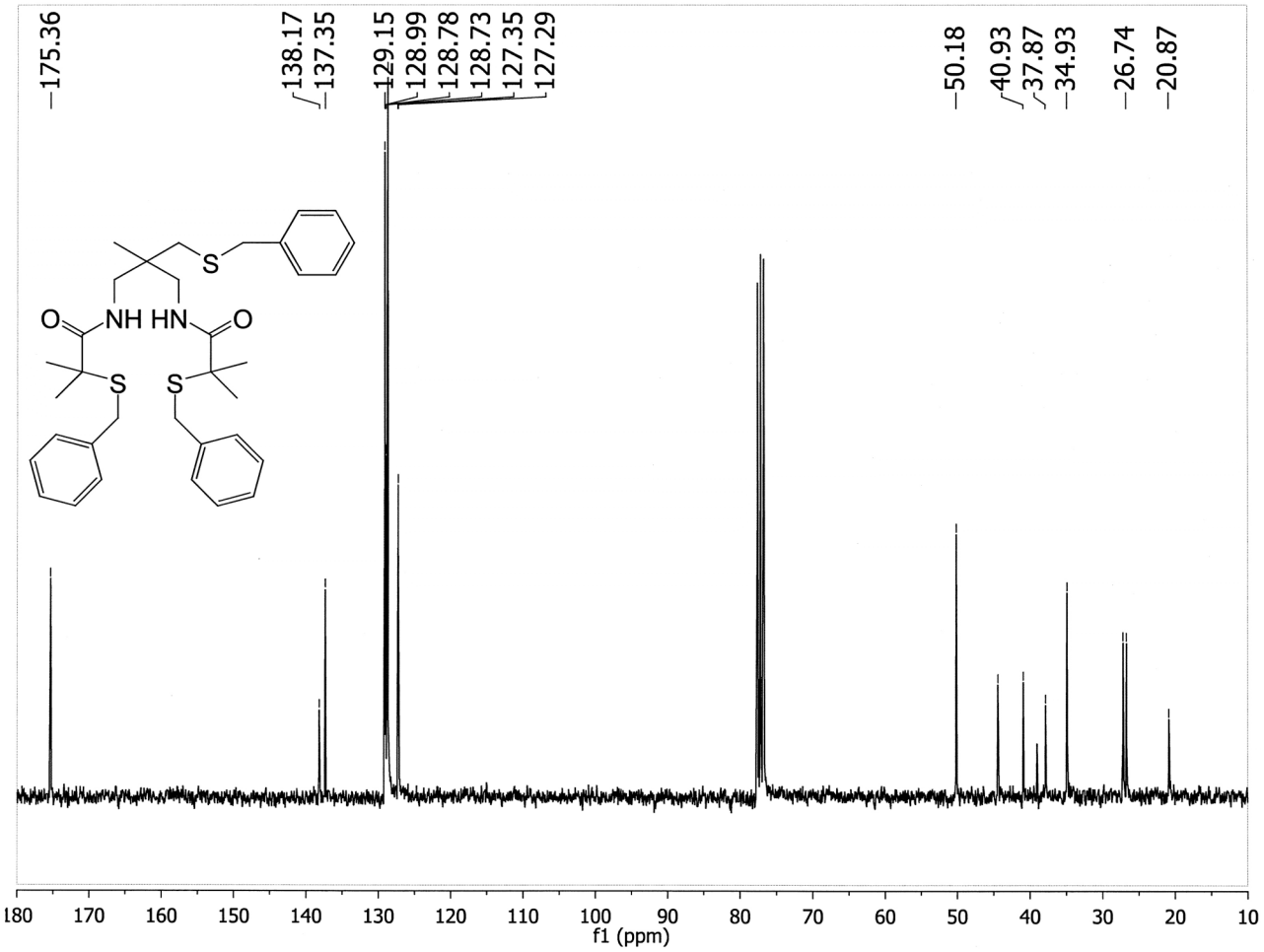


Figure S–4a. ^{13}C NMR($CDCl_3$) of benzyl-protected (Tame–N_2S_3) (**13**)

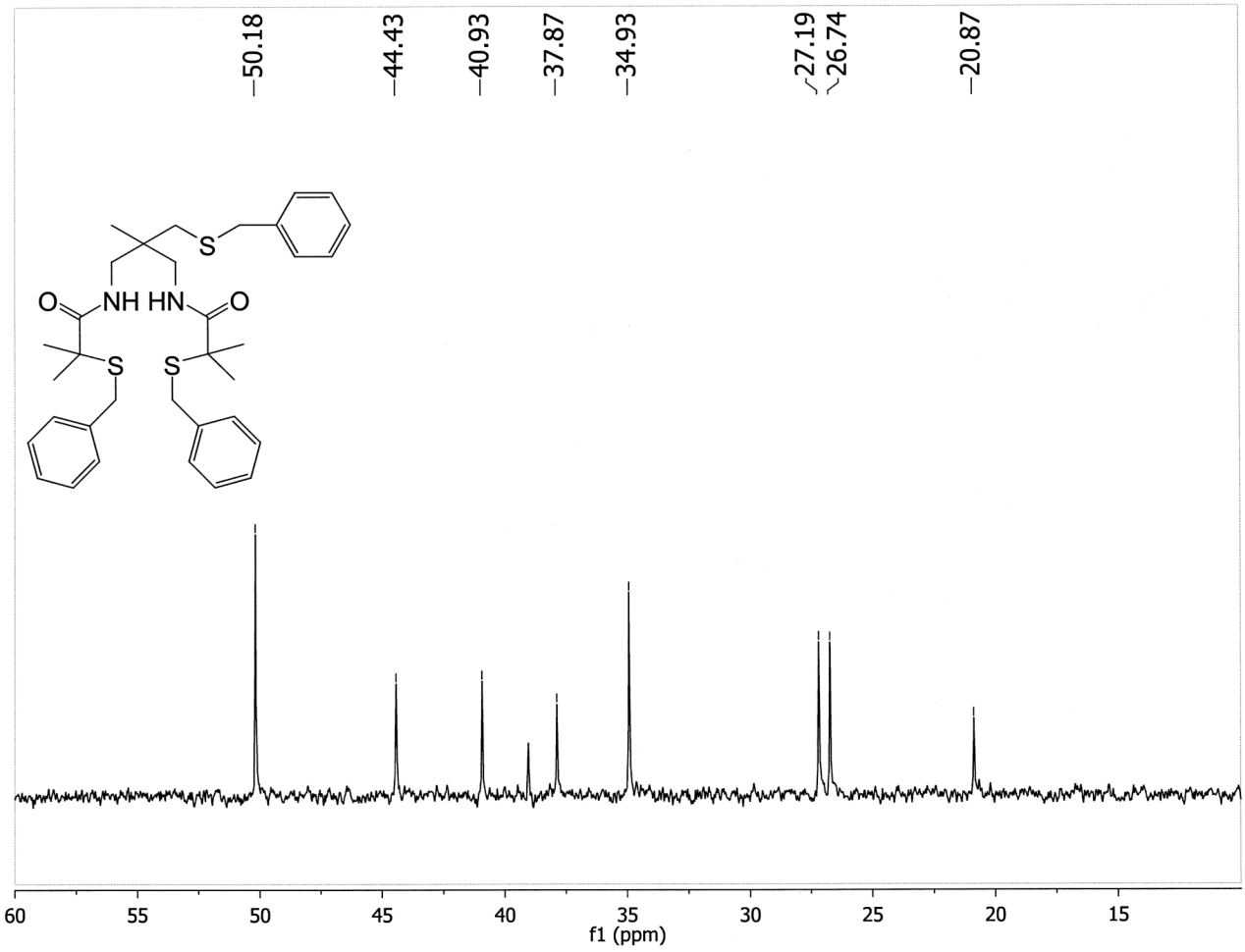


Figure S–4b. ^{13}C NMR($CDCl_3$) of benzyl-protected (Tame–N_2S_3) (**13**)

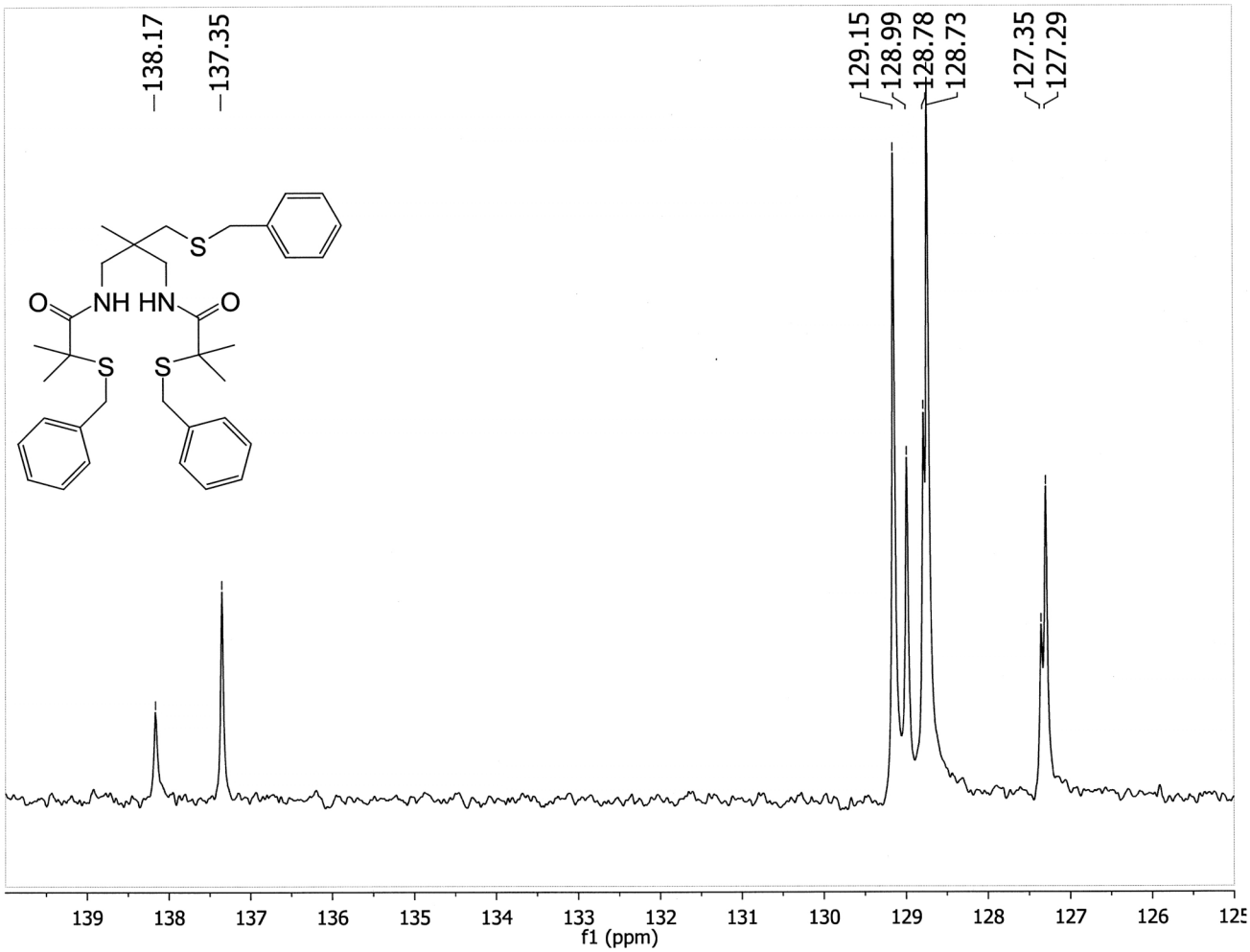


Figure S–4c. ^{13}C NMR($CDCl_3$) of benzyl-protected (Tame–N_2S_3) (**13**)

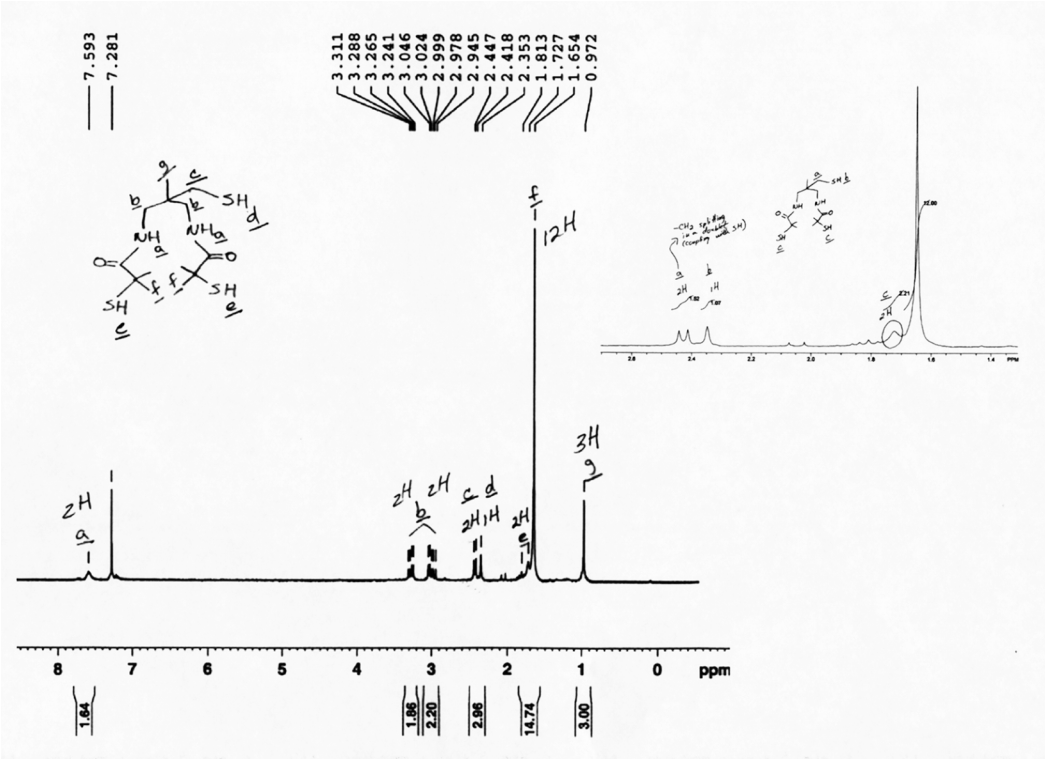


Figure S–5. ^{1}H NMR of tame–$(NH)_2(SH)_3$ (**14**) ligand in $CDCl_3$.

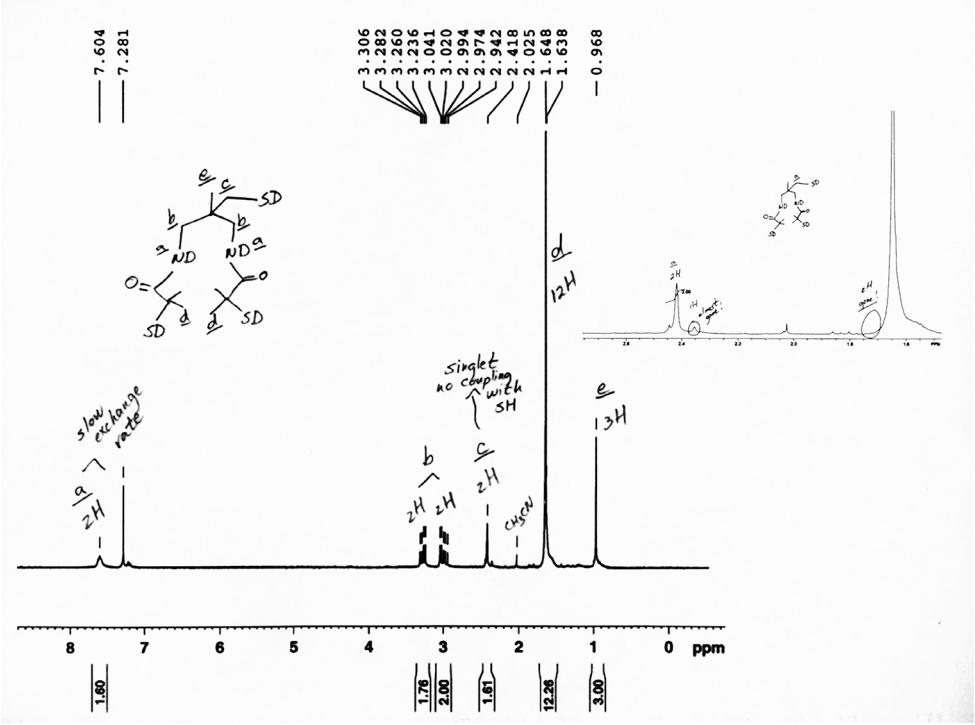


Figure S–6. ^{1}H NMR of deuterated tame–$(ND)_2(SD)_3$ (**14**) ligand in $CDCl_3$.

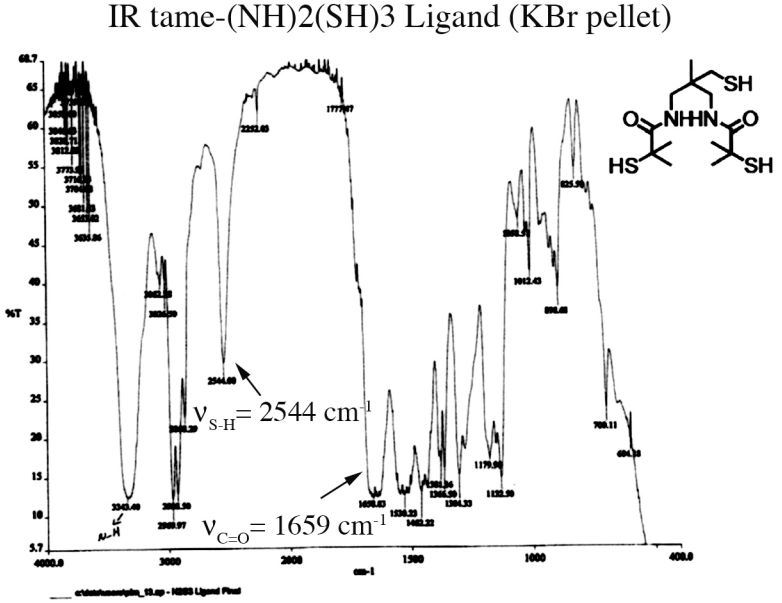


Figure S–7. IR spectrum of tame–$(NH)_2(SH)_3$ (**14**) ligand, showing the ν_{SH} and $\nu_{C=O}$ stretches at 2544 cm^{-1} and 1659 cm^{-1}, respectively.

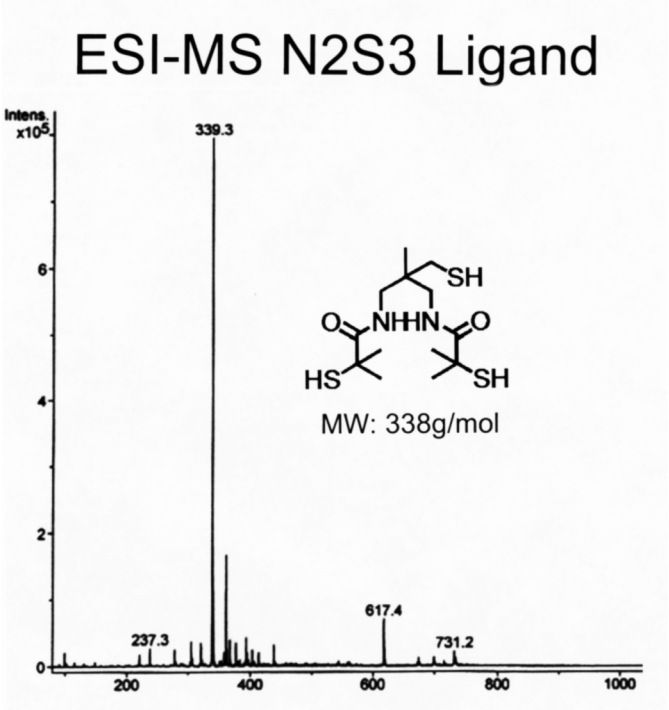


Figure S–8. ESI mass spec of tame–$(NH)_2(SH)_3$ (**14**) ligand**.**

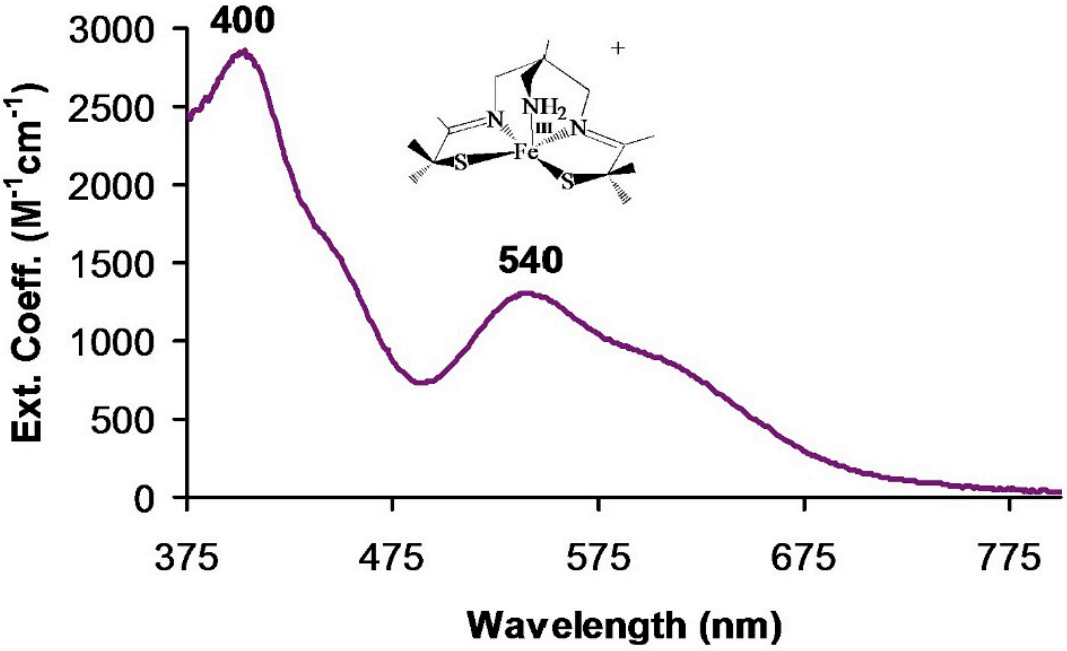


Figure S–9. Electronic absorption spectrum of $[Fe^{III}((tame–N_3)S_2^{Me2})](PF_6)$•BzCN (**1**) in MeCN at ambient temperature.

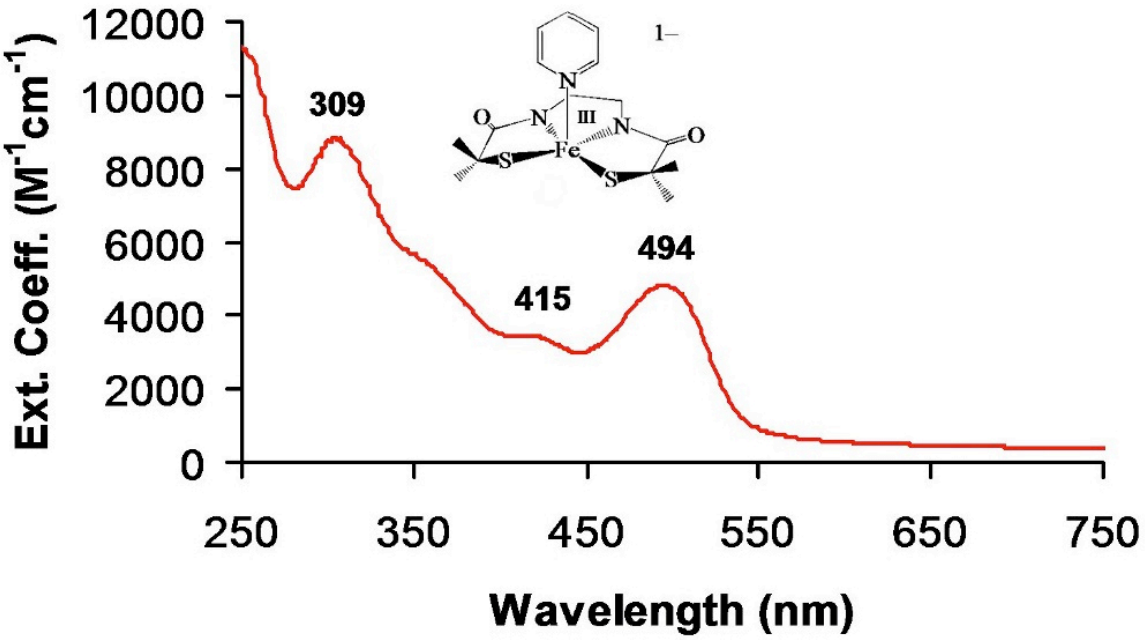


Figure S–10. Electronic absorption spectrum of pyridine-bound $(Me_4N)[Fe^{III}((Et–N_2)S_2^{Me2})(Py)]$•2MeOH (**3**) in pyridine at ambient temperature.

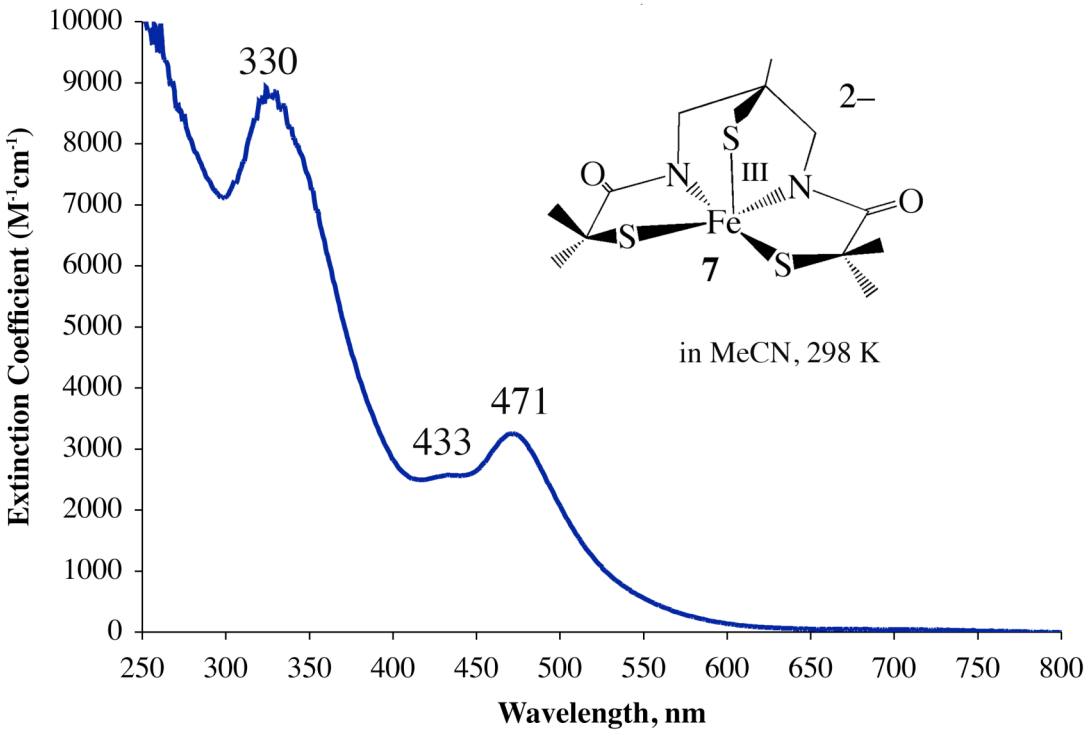


Figure S–11. Electronic absorption spectrum of red tris-thiolate ligated $(NMe_4)_2[Fe^{III}((tame–N_2S)S_2{}^{Me2})]$•MeCN (**15**) in MeCN at ambient temperature.

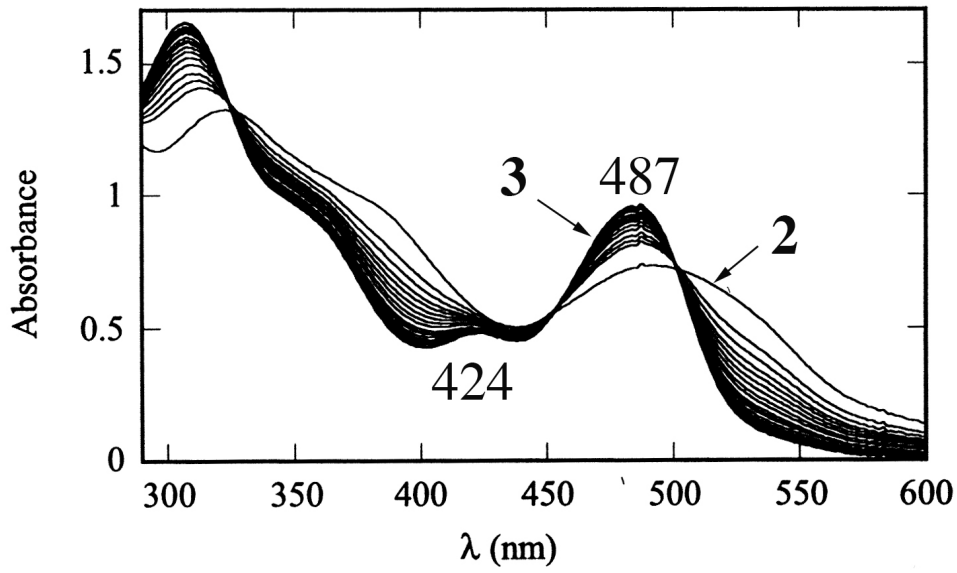


Figure S–12. Conversion of dimeric $[Fe^{III}((Et–N_2)S_2{}^{Me2})]_2{}^{2–}$ (**2**) to monomeric $[Fe^{III}((Et–N_2)S_2{}^{Me2})(Py)]^{1–}$ (**3**) via the addition of 1-6 equiv pyridine in CH_2Cl_2 at ambient temperature

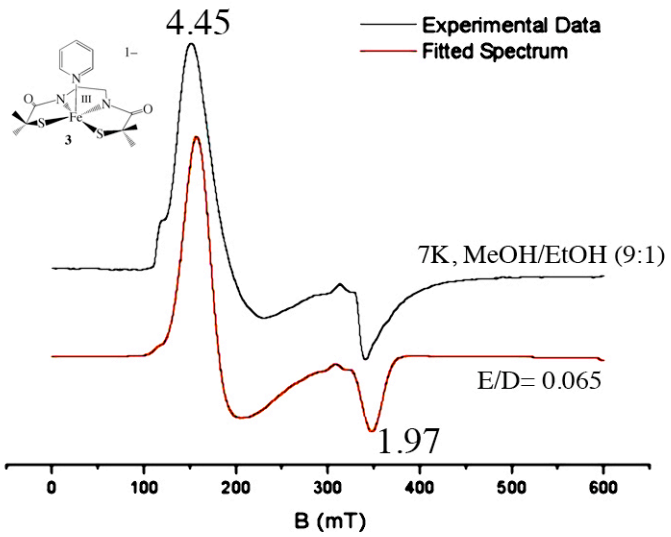


Figure S–13. Low temperature (7 K) X-band EPR spectrum (black) of $(Me_4N)[Fe^{III}((Et–N_2)S_2{}^{Me2})(Py)]$•2MeOH (**3**) in MeOH/EtOH (9:1) glass, fitted (red) to E/D= 0.065.

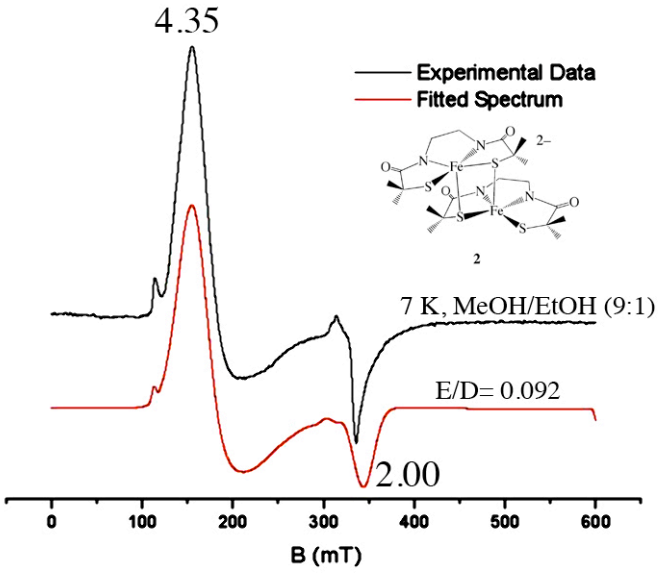


Figure S–14. Low temperature (7 K) X-band EPR spectrum (black) of dimeric $(NMe_4)_2[Fe^{III}((Et–N_2)S_2{}^{Me2})]_2$•2MeOH (**2**) in MeOH:EtOH (9:1) glass fitted (red) to E/D = 0.092.

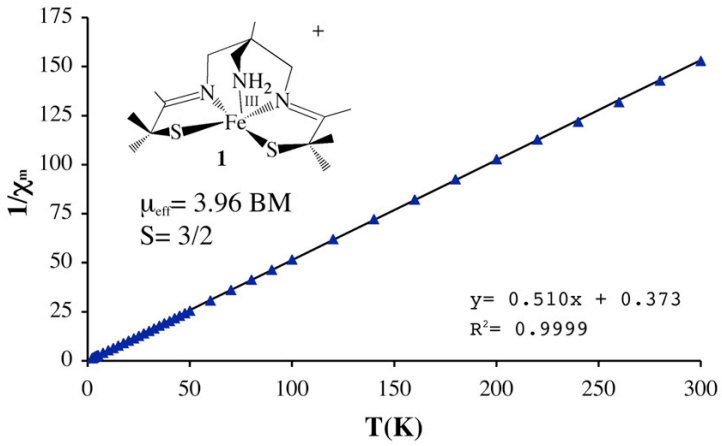


Figure S–15. Inverse molar magnetic susceptibility ($1/\chi_m$) vs. temperature (T) plot for monomeric [Fe^{III}((tame–N_3)S_2^{Me2})](PF_6)•BzCN (**1**) fit to an S= 3/2 spin–state.

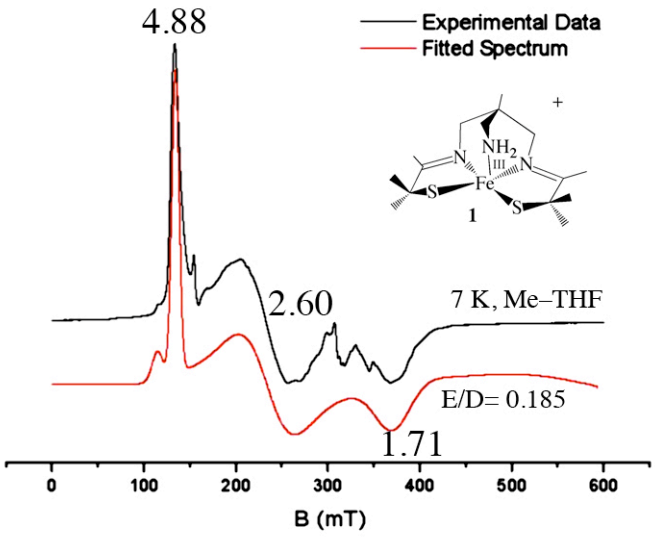


Figure S–16. Low temperature (7 K) X-band EPR spectrum (black) of [Fe^{III}((tame–N_3)S_2^{Me2})](PF_6)•BzCN (**1**) in Me-THF glass, fitted (red) to E/D= 0.185.

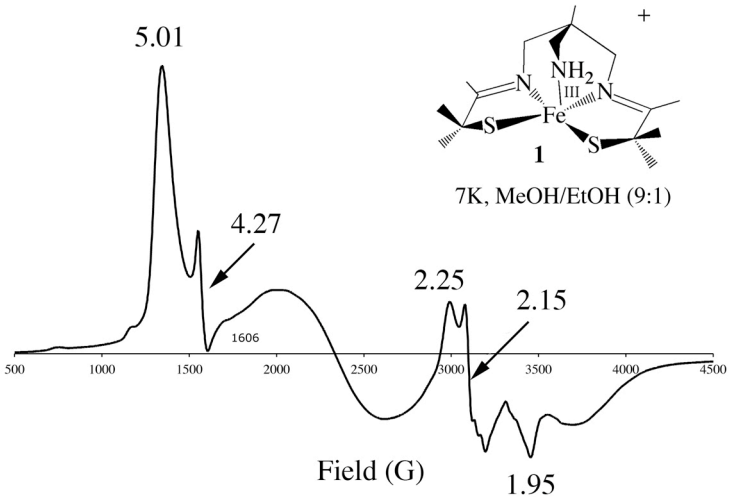


Figure S–17. Low temperature (7 K) X-band EPR spectrum of $[Fe^{III}((tame–N_3)S_2^{Me2})](PF_6)$•BzCN (**1**) in MeOH/EtOH (9:1) coordinating solvent displaying a mixture of S=1/2 and S= 3/2 spin-states.

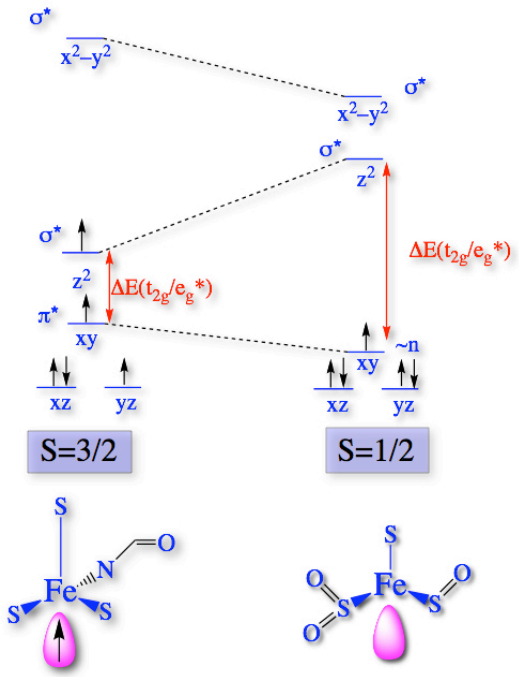


Figure S–18. d-orbital splitting diagram showing how the spin-state influences the Lewis acidity of the vacant apical site, and depends on the parameter ΔE. π-bonding in the xy plane shrinks ΔE favoring an S= 3/2 state. Oxygenation of the equatorial sulfurs would cause a spin-state change by diminishing the Fe–S π-interaction, increasing metal ion Lewis acidity, and consequently decreasing in the apical Fe–S bond length.

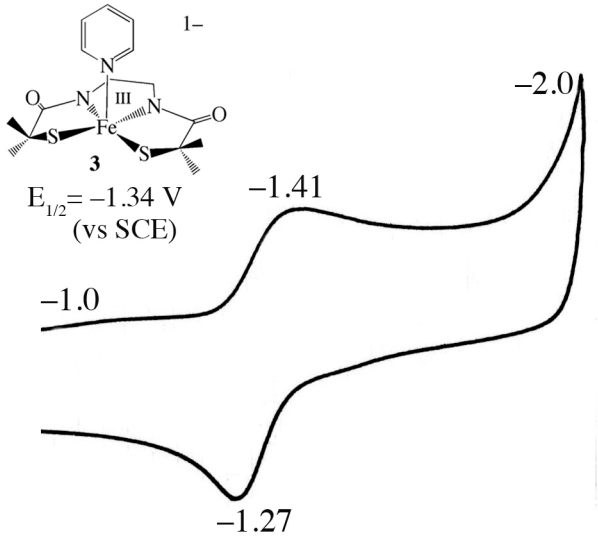


Figure S–19. Cyclic voltammogram of $(Me_4N)[Fe^{III}((Et–N_2)S_2{}^{Me2})(Py)]$•2MeOH (**3**) in pyridine at 298 K (0.1 M $(Bu_4N)PF_6$, glassy carbon electrode, 150 mV/sec scan rate). Peak potentials versus SCE indicated.

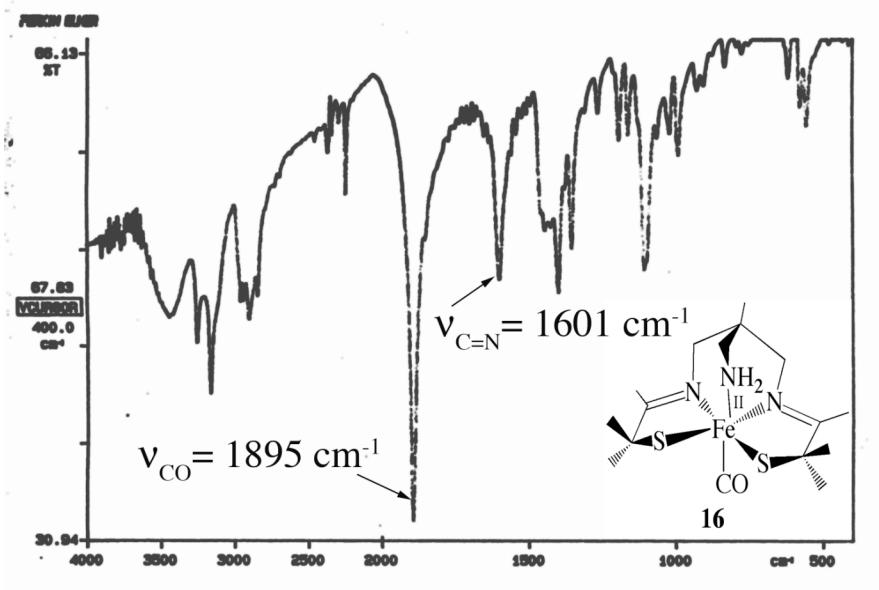


Figure S–20. Vibrational (IR) spectrum of $[Fe^{II}((tame–N_3)S_2{}^{Me2})(CO)]$•MeCN (**16**) (KBr pellet) showing the ν_{CO} and $\nu_{C=N}$ stretches.

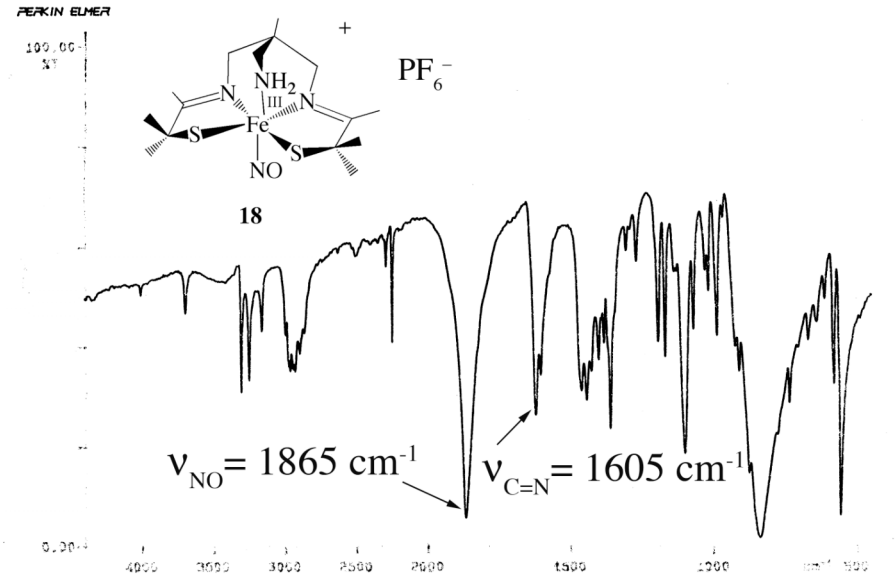


Figure S–21. Vibrational (IR) spectrum of [Fe^{III}((tame–N_3)S_2^{Me2})(NO)](PF_6)•MeCN (**18**) (KBr pellet) showing the ν_{NO} and $\nu_{C=N}$ stretches.

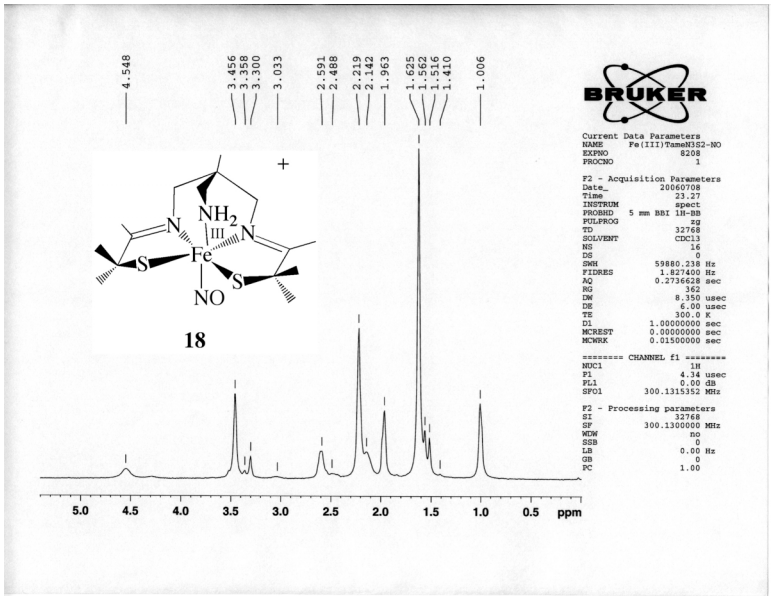


Figure S–22. Diamagnetic ^{1}H-NMR of [Fe^{III}((tame–N_3)S_2^{Me2})(NO)](PF_6)•MeCN (**18**).

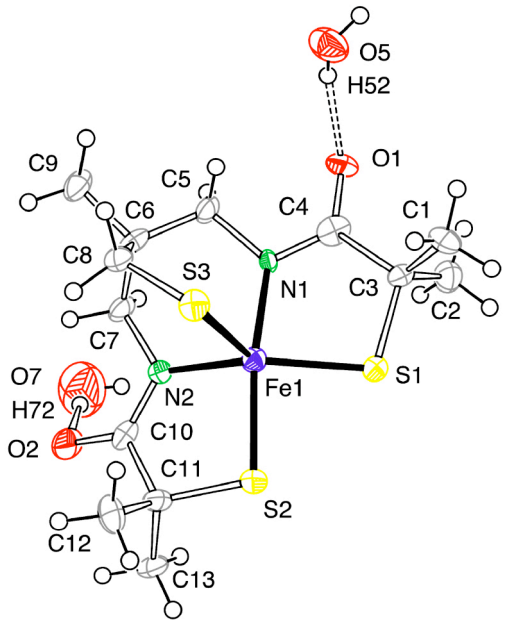


Figure S–23. ORTEP diagram of tris-thiolate ligated $[Fe^{III}(tame–N_2SS_2^{Me2})]^{2–}$ •$3H_2O$ (**15•3H$_2$O)** showing one of the two dianionic iron complexes contained in the unit cell, and three H–bonded co-crystallized H_2O's with H-bonding metrical parameters of: O(1)•••H(52)(H_2O)= 2.010 Å; O(1)-H(52)-O(5)= 163.3°; O(2)•••H(72)(H_2O)= 2.049 Å; O(2)-H(72)-O(7)= 176.1°; O(3)•••H(61)(H_2O)= 1.998 Å; O(3)-H(61)-O(6)= 169.0°).

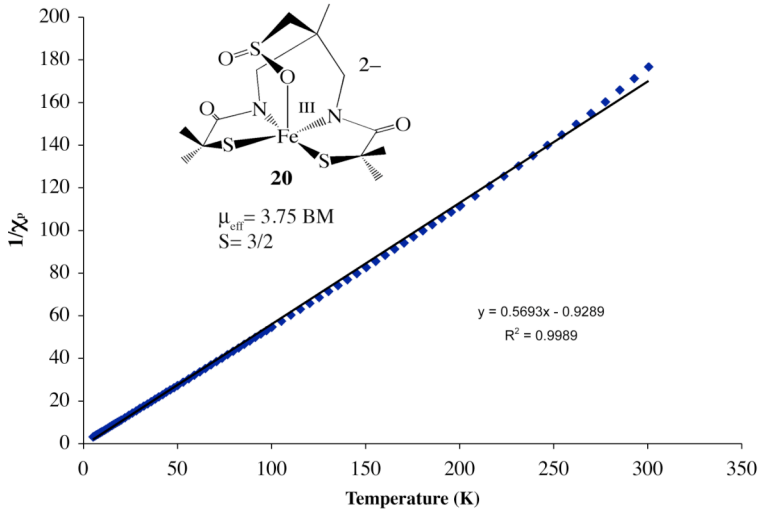


Figure S–24. Inverse molar magnetic susceptibility ($1/\chi_m$) vs. temperature (T) plot for $(Et_4N)_2[Fe^{III(}(tame\text{-}N_2SO_2)S_2^{Me2})]$ (**20**) fit to an S= 3/2 spin–state.

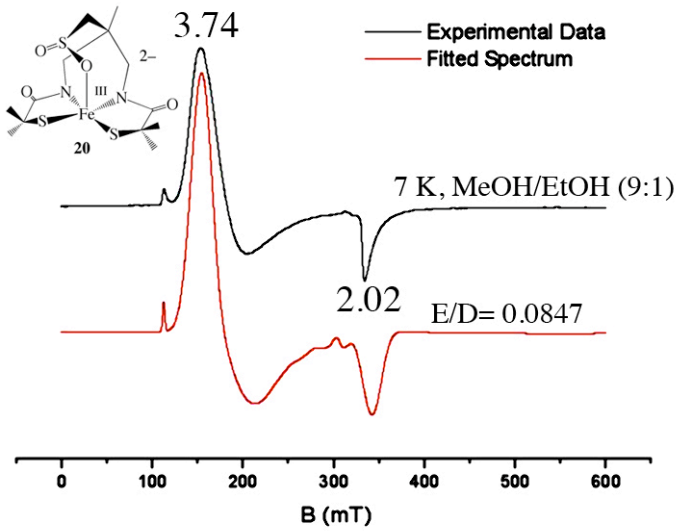


Figure S-25. Low temperature (7 K) X-band EPR spectrum (black) of $(Et_4N)_2[Fe^{III}(tame\text{-}N_2SO_2)S_2{}^{Me2})]$ (**20**) in 9:1 MeOH/EtOH glass, fitted (red) to E/D= 0.085.

Table 1. Crystal Data, Intensity Collection,[a] and Structure Refinement Parameters for $[Fe^{III}(tame–N_3)S_2{}^{Me2})](PF_6)$•BzCN (**1**), $(NMe_4)_2[Fe^{III}(Et–N_2S_2{}^{Me2})]_2$•2MeOH (**2**), $(Me_4N)[Fe^{III}(N_2–Et)S_2{}^{Me2})(Py)]$•2MeOH (**3**), $(NMe_4)_2[Fe^{III}(tame–N_2S)S_2{}^{Me2})]$•MeCN (**15**), $[Fe^{II}(tame–N_3)S_2{}^{Me2})(CO)]$•MeCN (**16**), $[Fe^{III}(tame–N_3)S_2{}^{Me2})(NO)](PF_6)$•MeCN (**18**), and $[Fe^{III}((tame–N_3)S_2{}^{Me2})(MeCN)](PF_6)$•MeCN(**19**), and $(NEt_4)_2[Fe^{III}(tame–N_2SO_2)S_2{}^{Me2})]$•MeCN (**20**).

	1	**2**	**3**	**15**	**16**	**18**	**19**	**20**
formula	$C_{22}H_{34}F_6N_4PS_2$	$Fe_2C_{30}H_{64}N_6O_6S_4$	$FeC_{21}H_{40}N_4O_4S_2$	$FeC_{23}H_{48}N_5O_2S_3$	$FeC_{18}H_{32}N_4OS_2$	$FeC_{17}H_{32}N_5F_6OPS_2$	$FeC_{19}H_{41}F_6N_5PS_2$	$FeC_{31}H_{64}N_5O_4S_3$
MW	619.47	844.81	524.76	578.69	440.45	587.42	604.51	722.90
T, K	161(2)	161(2)	130(2)	130(2)	161(2)	161(2)	161(2)	130(2)
unit cell	orthorhombic	monoclinic	monoclinic	orthorhombic	triclinic	monoclinic	orthorhombic	monoclinic
a, Å	13.4465(3)	15.6210(5)	9.0629(3)	18.6780(3)	9.8660(2)	11.8332(4)	13.1206(3)	11.1840(4)
b, Å	14.8447(4)	11.8659(6)	11.0976(3)	15.0370(3)	10.6971(2)	16.5201(6)	13.6458(2)	17.9000(6)
c, Å	13.7368(4)	22.8715(10)	26.0129(9)	21.9230(5)	12.0377(3)	13.3947(3)	14.9657(4)	20.8980(7)
α, deg	90	90	90	90	69.978(1)	90	90	90
β, deg	90	92.556(2)	93.499(2)	90	75.412(1)	106.785(2)	90	112.903(1)
γ, deg	90	90	90	90	68.508(1)	90	90	90
V, $Å^3$	2741.99(12)	4235.2(3)	2611.4(1)	6157.3(2)	1098.97(4)	2506.91(1)	2679.5(1)	3853.8(2)
Z	4	4	4	8	2	4	4	4
d(calc), g/cm^3	1.501	1.325	1.335	1.249	1.331	1.556	1.499	1.246
space group	*P*nma	$P2_1/c$	$P2_1/c$	*P*bca	P1(bar)	$P2_1/c$	$P2_12_12_1$	$P2_1/c$
R	0.0732[b]	0.0923[b]	0.0446[b]	0.0426[b]	0.0446[b]	0.0503[b]	0.0534[b]	0.0647[b]
R_w	0.2017[c]	0.2514[c]	0.1047[c]	0.1095[c]	0.1256[c]	0.1508[c]	0.1691[c]	0.2015[c]
GOF	0.965	1.021	0.935	0.940	1.09	1.06	1.036	0.960

[a] Mo Ko(α,-) (λ = 0.71073 Å) radiation; graphite monochromator; -90 ºC. [b] $R = \Sigma \, ||F_o| - |F_c|| \, / \, \Sigma \, |F_o|$. [c] $R_w = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$; $w = 1/[\sigma^2(F_o^2) + (0.1155P)^2 + 10.6657P]$, where $P = [F_o^2 + 2F_c^2]/3$ and $x = 0.1155$ (**1**), 0.1138 (**2**), 0.0481 (**3**), 0.0591 (**15**), 0.0703 (**16**), 0.0792 (**18**), 0.1061 (**19**), 0.0906 (**20**); and $y = 10.6657$ (**1**), 0.000 (**2**, **3**, **15**, **16**, **19**, **20**), 0.310 (**18**).

Table S–2. Selected bond distances (Å) and bond angles (deg) for Five-Coordinate $[Fe^{III}(tame–N_3)S_2{}^{Me2})](PF_6)$•BzCN (**1**), $(NMe_4)_2[Fe^{III}(Et–N_2)S_2{}^{Me2})]_2$•2MeOH (**2**), $(Me_4N)[Fe^{III}(Et–N_2)S_2{}^{Me2})(Py)]$•2MeOH (**3**), $(NMe_4)_2[Fe^{III}((tame–N_2S)S_2{}^{Me2})]$•MeCN (**15**) and $(NEt_4)_2[Fe^{III}((tame–N_2SO_2)S_2{}^{Me2})]$•MeCN (**20**).

	1	**2**	**3**	**15**	**20**
Fe-S(1)	2.189(1)	2.251(2)	2.216(1)	2.2171(7)	2.225(1)
Fe-S(2)	2.189(1)	2.199(2)	2.204(1)	2.2219(6)	2.222(1)
Fe-S(3)	N/A	2.4464(18)	N/A	2.4058(7)	N/A
Fe-N(1)	1.999(4)	1.915(5)	1.920(3)	1.9572(18)	1.941(4)
Fe-N(2)	1.999(4)	1.900(4)	1.898(3)	1.9573(18)	1.942(4)
Fe-N(3)	2.132(6)	N/A	2.167(3)	N/A	N/A
Fe-O(3)	N/A	N/A	N/A	N/A	2.025(3)
N(1)-C(#)	1.291(6)	1.325(8)	1.332(4)	1.337(3)	1.352(7)
C(#)-O(1)	N/A	1.261(7)	1.251(4)	1.259(3)	1.249(6)
N(2)-C(#)	1.291(6)	1.318(8)	1.342(4)	1.337(3)	1.340(6)
C(#)-O(2)	N/A	1.245(7)	1.250(4)	1.252(3)	1.255(5)
S(3)-O(3)	N/A	N/A	N/A	N/A	1.511(3)
S(3)-O(4)	N/A	N/A	N/A	N/A	1.498(4)
S(1)-Fe-S(2)	89.55(8)	94.93(6)	94.83(4)	86.91(2)	87.23(5)
S(2)-Fe-N(1)	163.42(13)	153.82(18)	153.77(9)	161.81(6)	154.6(1)
S(1)-Fe-N(2)	163.42(13)	154.47(18)	159.22(9)	151.92(6)	164.3(1)
N(1)-Fe-N(2)	97.0(2)	83.5(2)	82.91(12)	95.12(7)	93.7(2)
S(1)-Fe-S(3)	N/A	99.14(6)	N/A	117.19(2)	N/A
S(2)-Fe-S(3)	N/A	92.85(6)	N/A	109.72(3)	N/A
S(1)-Fe-N(3)	110.96(12)	N/A	100.86(8)	N/A	N/A
S(2)-Fe-N(3)	110.96(12)	N/A	102.87(8)	N/A	N/A
S(1)-Fe-O(3)	N/A	N/A	N/A	N/A	101.8(1)
S(2)-Fe-O(3)	N/A	N/A	N/A	N/A	107.9(1)
τ-value	0.0	0.011	0.090	0.165	0.162

Table S–3. Selected Bond Distances (Å) and Angles (deg) for oxidized $[Fe^{III}(tame–N_3)S_2{}^{Me2})]^+$ (**1**), $[Fe^{III}(tame–N_3)S_2{}^{Me2})(NO)]^+$ (**18**), and $[Fe^{III}(N_3(tame)S_2{}^{Me2})(MeCN)]^+$ (**19**). And reduced $[Fe^{II}(tame–N_3)S_2{}^{Me2})(CO)]$ (**16**).

	1	**16**	**18**	**19**
Fe-S(1)	2.1887(14)	2.2790(4)	2.2582(6)	2.1884(12)
Fe-S(2)	2.1886(14)	2.2782(4)	2.2504(6)	2.1852(12)
Fe-N(1)	1.999(4)	1.9876(12)	1.9996(18)	2.012(3)
Fe-N(2)	1.999(4)	1.9947(13)	2.0035(17)	2.002(4)
Fe-N(3)	2.132(6)	2.0663(13)	2.0324(17)	2.188(3)
Fe-X	N/A	1.7281(17)[&]	1.6359(18)[@]	2.63[#]
X–Y	N/A	1.155(2)[&]	1.144(2)[@]	1.159(7)[#]
N(1)-C(#)	1.291(6)	1.2831(19)	1.288(3)	1.276(5)
N(2)-C(#)	1.291(6)	1.2862(19)	1.286(3)	1.287(5)
S(1)-Fe-S(2)	89.55(8)	92.612(16)	89.27(2)	91.38(4)
N(1)-Fe-N(2)	97.0(2)	100.43(5)	101.64(7)	97.91(12)
N(3)-Fe-X	N/A	174.60(6)[&]	174.29(8)[@]	153.4
S(1)-Fe-N(3)	110.96(12)	92.91(4)	89.45(5)	105.22(10)
S(2)-Fe-N(3)	110.96(12)	93.07(3)	91.08(5)	105.99(10)

[&]X= C(16); Y= O(1); C(16)–O(1); [@] X= N(4); Y= O(1); N(4)–O(1); [#] X= N(4); Y= C(16); N(4)–C((16)–C(17)

Table S–4. Crystal data and structure refinement for [Fe(III)(tame–N_3)S_2^{Me2})](${PF_6}$)•BzCN (**1**).

Empirical formula	C22 H34 F6 Fe N4 P S2
Formula weight	619.47
Temperature	161(2) K
Wavelength	0.71073 A
Crystal description/color	prism / red
Crystal system, space group	Orthorhombic, Pnma
Unit cell dimensions	a = 13.4460(3)A alpha = 90 deg. b = 14.8450(4)A beta = 90 deg. c = 13.7370(4)A gamma = 90 deg.
Volume	2741.99(12) A^3
Z, Calculated density	4, 1.501 Mg/m^3
Absorption coefficient	0.821 mm^-1
F(000)	1284
Crystal size	0.13 x 0.06 x 0.06 mm
Reflections for indexing	259
Theta range for data collection	2.97 to 25.68 deg.
Index ranges	-16<=h<=16, 18<=k<=18, -16<=l<=16
Reflections collected/unique	4800 / 2604 [R(int) = 0.0250]
Completeness to theta	25.00 95.8%
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.953 and 0.901
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	2604 / 7 / 187
Goodness-of-fit on F^2	S = 0.965
S = root(sum(w*D*D)/(n-p)), where D = (Fo*Fo - Fc*Fc)	
Final R indices [I>2sigma(I)]	*R1 = 0.0732, wR2 = 0.1901
R indices (all data)	R1 = 0.0896, *wR2 = 0.2017
R1 = sum||Fo|-|Fc||/sum|Fo|, wR2=root(sum(w*D*D)/sum(w*Fo*Fo)), where D = (Fo*Fo - Fc*Fc)	
Weighting scheme	calc w=1/[\s^2(Fo^2)+(0.1155P)^2 +10.6657P] where P=(Fo^2 + 2Fc^2)/3
Largest diff. peak and hole	1.426 and -0.853 e.A^-3

Table S–5. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (A^2 x 10^3) for [Fe(III)(tame–N_3)S_2^{Me2})](PF_6)•BzCN (**1**). U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

	x	y	z	U(eq)
Fe(1)	3909(1)	7500	2175(1)	30(1)
S(1)	4608(1)	6462(1)	1274(1)	44(1)
P(1)	5000	0	5000	49(1)
F(1)	4469(4)	813(4)	5483(7)	162(4)
F(2)	5559(6)	633(4)	4265(4)	134(3)
F(3)	5879(5)	187(4)	5710(5)	133(3)
N(1)	3049(3)	6491(3)	2644(3)	34(1)
N(2)	4517(4)	7500	3608(4)	37(1)
N(3)	3160(7)	2500	6066(7)	92(3)
C(1)	3239(5)	5269(5)	521(4)	58(2)
C(2)	4445(5)	4680(4)	1763(6)	62(2)
C(3)	3789(4)	5479(4)	1468(4)	42(1)
C(4)	3064(4)	5690(3)	2279(4)	39(1)
C(5)	2377(5)	4958(4)	2595(5)	54(2)
C(6)	2396(4)	6651(4)	3475(4)	43(1)
C(7)	2664(5)	7500	4035(6)	39(2)
C(8)	3752(5)	7500	4386(5)	37(2)
C(9)	2004(7)	7500	4975(6)	50(2)
C(10)	2561(6)	2500	4279(7)	74(3)
C(11)	3264(7)	2500	3539(6)	78(3)
C(12)	2881(8)	2500	2599(8)	119(6)
C(13)	1878(7)	2500	2352(7)	78(3)
C(14)	1215(9)	2500	3129(7)	98(4)
C(15)	1544(7)	2500	4086(8)	88(4)
C(16)	2887(8)	2500	5245(9)	76(3)

Table S–6. Bond lengths [A] and angles [deg] for [Fe(III)(tame–N_3)S_2^{Me2})](PF_6)•BzCN (**1**).

Fe(1)-N(1)	1.999(4)
Fe(1)-N(1)#1	1.999(4)
Fe(1)-N(2)	2.132(6)
Fe(1)-S(1)#1	2.1886(14)
Fe(1)-S(1)	2.1887(14)
S(1)-C(3)	1.848(5)
P(1)-F(1)	1.551(5)
P(1)-F(1)#2	1.551(5)
P(1)-F(3)#2	1.558(5)
P(1)-F(3)	1.558(5)
P(1)-F(2)	1.571(6)
P(1)-F(2)#2	1.571(6)
N(1)-C(4)	1.291(6)
N(1)-C(6)	1.460(6)
N(2)-C(8)	1.484(9)
N(2)-H(2E)	0.9200
N(2)-H(2D)	0.9200
N(3)-C(16)	1.186(14)
C(1)-C(3)	1.527(8)
C(1)-H(1A)	0.9800
C(1)-H(1B)	0.9800
C(1)-H(1C)	0.9800
C(2)-C(3)	1.533(8)
C(2)-H(2A)	0.9800
C(2)-H(2B)	0.9800
C(2)-H(2C)	0.9800
C(3)-C(4)	1.513(7)
C(4)-C(5)	1.490(7)
C(5)-H(5A)	0.9800
C(5)-H(5B)	0.9800
C(5)-H(5C)	0.9800
C(6)-C(7)	1.520(7)
C(6)-H(6A)	0.9900
C(6)-H(6B)	0.9900
C(7)-C(6)#1	1.520(7)
C(7)-C(8)	1.539(10)
C(7)-C(9)	1.568(10)
C(8)-H(8A)	0.9900
C(8)-H(8B)	0.9900
C(9)-H(9A)	0.9800
C(9)-H(9B)	0.9800
C(9)-H(9C)	0.9800
C(10)-C(11)	1.388(13)

C(10)-C(15)	1.393(12)
C(10)-C(16)	1.397(15)
C(11)-C(12)	1.390(14)
C(11)-H(11)	0.9500
C(12)-C(13)	1.391(14)
C(12)-H(12)	0.9500
C(13)-C(14)	1.391(14)
C(13)-H(13)	0.9500
C(14)-C(15)	1.387(15)
C(14)-H(14)	0.9500
C(15)-H(15)	0.9500
N(1)-Fe(1)-N(1)#1	97.0(2)
N(1)-Fe(1)-N(2)	85.62(16)
N(1)#1-Fe(1)-N(2)	85.62(16)
N(1)-Fe(1)-S(1)#1	163.42(13)
N(1)#1-Fe(1)-S(1)#1	84.44(12)
N(2)-Fe(1)-S(1)#1	110.96(12)
N(1)-Fe(1)-S(1)	84.44(12)
N(1)#1-Fe(1)-S(1)	163.42(13)
N(2)-Fe(1)-S(1)	110.96(12)
S(1)#1-Fe(1)-S(1)	89.55(8)
C(3)-S(1)-Fe(1)	102.64(17)
F(1)-P(1)-F(1)#2	179.999(1)
F(1)-P(1)-F(3)#2	93.2(4)
F(1)#2-P(1)-F(3)#2	86.8(4)
F(1)-P(1)-F(3)	86.8(4)
F(1)#2-P(1)-F(3)	93.2(4)
F(3)#2-P(1)-F(3)	179.998(1)
F(1)-P(1)-F(2)	91.7(4)
F(1)#2-P(1)-F(2)	88.3(4)
F(3)#2-P(1)-F(2)	93.9(4)
F(3)-P(1)-F(2)	86.1(4)
F(1)-P(1)-F(2)#2	88.3(4)
F(1)#2-P(1)-F(2)#2	91.7(4)
F(3)#2-P(1)-F(2)#2	86.1(4)
F(3)-P(1)-F(2)#2	93.9(4)
F(2)-P(1)-F(2)#2	179.999(1)
C(4)-N(1)-C(6)	117.6(4)
C(4)-N(1)-Fe(1)	123.8(3)
C(6)-N(1)-Fe(1)	118.6(3)
C(8)-N(2)-Fe(1)	113.5(4)
C(8)-N(2)-H(2E)	108.9
Fe(1)-N(2)-H(2E)	108.9
C(8)-N(2)-H(2D)	108.9
Fe(1)-N(2)-H(2D)	108.9
H(2E)-N(2)-H(2D)	107.7
C(3)-C(1)-H(1A)	109.5
C(3)-C(1)-H(1B)	109.5

H(1A)-C(1)-H(1B)	109.5
C(3)-C(1)-H(1C)	109.5
H(1A)-C(1)-H(1C)	109.5
H(1B)-C(1)-H(1C)	109.5
C(3)-C(2)-H(2A)	109.5
C(3)-C(2)-H(2B)	109.5
H(2A)-C(2)-H(2B)	109.5
C(3)-C(2)-H(2C)	109.5
H(2A)-C(2)-H(2C)	109.5
H(2B)-C(2)-H(2C)	109.5
C(4)-C(3)-C(1)	110.9(4)
C(4)-C(3)-C(2)	109.7(5)
C(1)-C(3)-C(2)	110.3(5)
C(4)-C(3)-S(1)	109.1(3)
C(1)-C(3)-S(1)	109.0(4)
C(2)-C(3)-S(1)	107.8(4)
N(1)-C(4)-C(5)	123.3(5)
N(1)-C(4)-C(3)	119.1(4)
C(5)-C(4)-C(3)	117.5(5)
C(4)-C(5)-H(5A)	109.5
C(4)-C(5)-H(5B)	109.5
H(5A)-C(5)-H(5B)	109.5
C(4)-C(5)-H(5C)	109.5
H(5A)-C(5)-H(5C)	109.5
H(5B)-C(5)-H(5C)	109.5
N(1)-C(6)-C(7)	112.8(4)
N(1)-C(6)-H(6A)	109.0
C(7)-C(6)-H(6A)	109.0
N(1)-C(6)-H(6B)	109.0
C(7)-C(6)-H(6B)	109.0
H(6A)-C(6)-H(6B)	107.8
C(6)-C(7)-C(6)#1	112.0(7)
C(6)-C(7)-C(8)	112.6(4)
C(6)#1-C(7)-C(8)	112.6(4)
C(6)-C(7)-C(9)	106.4(4)
C(6)#1-C(7)-C(9)	106.4(4)
C(8)-C(7)-C(9)	106.2(6)
N(2)-C(8)-C(7)	115.6(6)
N(2)-C(8)-H(8A)	108.4
C(7)-C(8)-H(8A)	108.4
N(2)-C(8)-H(8B)	108.4
C(7)-C(8)-H(8B)	108.4
H(8A)-C(8)-H(8B)	107.4
C(7)-C(9)-H(9A)	109.5
C(7)-C(9)-H(9B)	109.5
H(9A)-C(9)-H(9B)	109.5
C(7)-C(9)-H(9C)	109.5
H(9A)-C(9)-H(9C)	109.5

H(9B)-C(9)-H(9C)	109.5
C(11)-C(10)-C(15)	121.9(10)
C(11)-C(10)-C(16)	118.8(9)
C(15)-C(10)-C(16)	119.3(9)
C(10)-C(11)-C(12)	115.4(11)
C(10)-C(11)-H(11)	122.3
C(12)-C(11)-H(11)	122.3
C(11)-C(12)-C(13)	125.9(11)
C(11)-C(12)-H(12)	117.1
C(13)-C(12)-H(12)	117.1
C(14)-C(13)-C(12)	115.8(11)
C(14)-C(13)-H(13)	122.1
C(12)-C(13)-H(13)	122.1
C(15)-C(14)-C(13)	121.5(11)
C(15)-C(14)-H(14)	119.3
C(13)-C(14)-H(14)	119.3
C(14)-C(15)-C(10)	119.6(10)
C(14)-C(15)-H(15)	120.2
C(10)-C(15)-H(15)	120.2
N(3)-C(16)-C(10)	179.7(12)

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

Table S–7. Anisotropic displacement parameters (A^2 x 10^3) for [Fe(III)(tame–N_3)S_2^{Me2})](PF_6)•BzCN (**1**). The anisotropic displacement factor exponent takes the form: -2 pi^2 [h^2 a*^2 U11 + ... + 2 h k a* b* U12]

	U11	U22	U33	U23	U13	U12
Fe(1)	26(1)	31(1)	33(1)	0	3(1)	0
S(1)	38(1)	42(1)	51(1)	-12(1)	15(1)	-5(1)
P(1)	42(1)	42(1)	65(1)	-16(1)	-1(1)	-3(1)
F(1)	97(4)	83(4)	306(11)	-96(5)	62(5)	-19(3)
F(2)	200(6)	108(4)	94(4)	-27(3)	34(4)	-91(5)
F(3)	134(5)	119(5)	146(5)	-1(4)	-70(4)	-58(4)
N(1)	30(2)	35(2)	38(2)	0(2)	4(2)	-4(2)
N(2)	33(3)	35(3)	43(3)	0	-7(3)	0
N(3)	66(6)	145(10)	64(6)	0	1(5)	0
C(1)	65(4)	57(4)	53(3)	-15(3)	3(3)	-8(3)
C(2)	54(4)	46(3)	87(5)	0(3)	17(3)	4(3)
C(3)	40(3)	35(3)	51(3)	-11(2)	7(2)	-4(2)
C(4)	29(2)	40(3)	48(3)	-6(2)	-1(2)	-5(2)
C(5)	52(3)	37(3)	74(4)	-10(3)	18(3)	-14(3)
C(6)	38(3)	40(3)	50(3)	-7(2)	13(2)	-8(2)
C(7)	41(4)	28(3)	47(4)	0	11(3)	0
C(8)	49(4)	32(3)	32(3)	0	-3(3)	0
C(9)	64(5)	40(4)	47(5)	0	21(4)	0
C(10)	92(8)	51(5)	78(7)	0	0(6)	0
C(11)	69(7)	65(6)	99(8)	0	-14(6)	0
C(12)	153(14)	51(6)	153(13)	0	-97(12)	0
C(13)	112(9)	65(6)	57(6)	0	-9(6)	0
C(14)	112(10)	93(9)	88(9)	0	49(8)	0
C(15)	62(7)	120(10)	82(8)	0	14(6)	0
C(16)	67(6)	97(8)	65(7)	0	4(5)	0

Table S–8. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (A^2 x 10^3) for [Fe(III)(tame–N_3)S_2^{Me2})](PF_6)•BzCN (**1**).

	x	y	z	U(eq)
H(2E)	4914	7000	3682	45
H(2D)	4914	8000	3682	45
H(1A)	2834	4726	607	70
H(1B)	3723	5170	-1	70
H(1C)	2808	5778	350	70
H(2A)	4038	4135	1807	75
H(2B)	4751	4803	2397	75
H(2C)	4967	4593	1274	75
H(5A)	1711	5208	2701	65
H(5B)	2622	4692	3202	65
H(5C)	2346	4493	2089	65
H(6A)	2432	6128	3920	51
H(6B)	1702	6701	3241	51
H(8A)	3856	8038	4800	45
H(8B)	3856	6962	4800	45
H(9A)	2150	8039	5362	75
H(9B)	2149	6961	5361	75
H(9C)	1300	7501	4790	75
H(11)	3959	2500	3667	93
H(12)	3347	2500	2079	143
H(13)	1660	2500	1694	94
H(14)	520	2500	3002	118
H(15)	1079	2500	4607	106

Table S–9. Crystal data and structure refinement for $(NMe_4)_2[Fe(III)(Et\text{–}N_2S_2^{Me2})]_2 \bullet 2MeOH$ (**2**).

Empirical formula	C30 H64 Fe2 N6 O6 S4
Formula weight	844.81
Temperature	161(2) K
Wavelength	0.71070 A
Crystal description/color	prism / red
Crystal system, space group	Monoclinic, P 21/c
Unit cell dimensions	a = 15.6210(5)A alpha = 90 deg. b = 11.8659(6)A beta = 92.556(2) deg. c = 22.8715(10)A gamma = 90 deg.
Volume	4235.2(3) A^3
Z, Calculated density	4, 1.325 Mg/m^3
Absorption coefficient	0.926 mm^-1
F(000)	1800
Crystal size	0.18 x 0.13 x 0.10 mm
Reflections for indexing	812
Theta range for data collection	1.93 to 30.02 deg.
Index ranges	-20<=h<=20, -15<=k<=16, -31<=l<=31
Reflections collected / unique	19609 / 11435 [R(int) = 0.1148]
Completeness to theta = 25.00	98.0%
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.9131 and 0.8510
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	11435 / 1 / 453
Goodness-of-fit on F^2	S = 1.021
S = root(sum(w*D*D)/(n-p)), where D = (Fo*Fo - Fc*Fc)	
Final R indices [I>2sigma(I)]	*R1 = 0.0923, wR2 = 0.2132
R indices (all data)	R1 = 0.1908, *wR2 = 0.2514
R1 = sum||Fo|-|Fc||/sum|Fo|, wR2= root(sum(w*D*D)/sum(w*Fo*Fo)), where D = (Fo*Fo - Fc*Fc)	
Weighting scheme	calc w=1/[\s^2(Fo^2)+(0.1138P)^2 +0.0000P] where P=(Fo^2 + 2Fc^2)/3
Largest diff. peak and hole	1.557 and -0.793 e.A^-3

Table S–10. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (A^2 x 10^3) for $(NMe_4)_2[Fe(III)(Et–N_2S_2^{Me2})]_2 \bullet 2MeOH$ (**2**). U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

	x	y	z	U(eq)
C(1)	7292(5)	4372(7)	6043(3)	49(2)
C(2)	8666(4)	3466(7)	5764(3)	47(2)
C(3)	7748(4)	3253(6)	5954(3)	36(1)
C(4)	7193(4)	2583(6)	5501(3)	35(1)
C(5)	5955(4)	1409(7)	5342(3)	46(2)
C(6)	5140(4)	1418(8)	5689(3)	48(2)
C(7)	4756(4)	1273(6)	6687(3)	37(2)
C(8)	5038(4)	1151(6)	7334(3)	37(2)
C(9)	5040(4)	-108(6)	7489(3)	38(2)
C(10)	4425(4)	1797(7)	7725(3)	45(2)
C(11)	7625(4)	-2412(6)	6344(3)	42(2)
C(12)	6315(4)	-1532(6)	5866(3)	40(2)
C(13)	7220(4)	-1311(5)	6122(3)	32(1)
C(14)	7810(4)	-813(5)	5676(3)	31(1)
C(15)	9017(4)	392(6)	5507(3)	36(1)
C(16)	9813(4)	490(6)	5912(3)	38(2)
C(17)	10166(4)	950(6)	6910(3)	34(1)
C(18)	9879(4)	1190(6)	7521(3)	33(1)
C(19)	9916(4)	2454(6)	7610(3)	36(1)
C(20)	10467(4)	613(7)	7982(3)	45(2)
C(21)	7991(5)	-7025(8)	8642(4)	63(2)
C(22)	7368(4)	-5540(6)	8023(3)	39(2)
C(23)	7625(4)	-5225(7)	9079(3)	41(2)
C(24)	6497(4)	-6489(7)	8731(3)	43(2)
C(25)	7058(4)	-1745(6)	9312(3)	43(2)
C(26)	8113(4)	-294(7)	9116(3)	48(2)
C(27)	6947(5)	-657(7)	8410(3)	51(2)
C(28)	8084(5)	-2026(7)	8558(3)	49(2)
C(29)	5218(6)	981(11)	9465(5)	97(4)
C(30)	9672(5)	-2089(9)	10426(4)	71(3)
Fe(1)	6565(1)	1488(1)	6535(1)	29(1)
Fe(2)	8370(1)	632(1)	6645(1)	27(1)
N(1)	6636(3)	1882(5)	5727(2)	33(1)
N(2)	5388(3)	1255(5)	6324(2)	33(1)
N(3)	8321(3)	11(5)	5864(2)	30(1)
N(4)	9556(3)	801(4)	6506(2)	27(1)
N(5)	7361(3)	-6074(5)	8619(2)	37(1)
N(6)	7558(3)	-1183(5)	8850(2)	36(1)

O(1)	7243(3)	2832(5)	4967(2)	48(1)
O(2)	3985(3)	1346(5)	6530(2)	46(1)
O(3)	7823(3)	-1268(4)	5186(2)	37(1)
O(4)	10947(3)	904(4)	6816(2)	43(1)
O(5)	6048(4)	674(7)	9527(3)	90(2)
O(6)	9155(4)	-2341(6)	9936(2)	65(2)
S(1)	7760(1)	2534(1)	6672(1)	31(1)
S(2)	6132(1)	1734(2)	7428(1)	35(1)
S(3)	7167(1)	-371(1)	6767(1)	30(1)
S(4)	8778(1)	665(2)	7583(1)	33(1)

Table S–11. Bond lengths [A] and angles [deg] for $(NMe_4)_2[Fe(III)(Et–N_2S_2^{Me2})]_2 \bullet 2MeOH$ (**2**).

C(1)-C(3)	1.524(10)
C(1)-H(1A)	0.9800
C(1)-H(1B)	0.9800
C(1)-H(1C)	0.9800
C(2)-C(3)	1.538(9)
C(2)-H(2A)	0.9800
C(2)-H(2B)	0.9800
C(2)-H(2C)	0.9800
C(3)-C(4)	1.541(9)
C(3)-S(1)	1.850(7)
C(4)-O(1)	1.261(7)
C(4)-N(1)	1.325(8)
C(5)-N(1)	1.463(8)
C(5)-C(6)	1.531(9)
C(5)-H(5A)	0.9900
C(5)-H(5B)	0.9900
C(6)-N(2)	1.498(8)
C(6)-H(6A)	0.9900
C(6)-H(6B)	0.9900
C(7)-O(2)	1.245(7)
C(7)-N(2)	1.318(8)
C(7)-C(8)	1.531(9)
C(8)-C(9)	1.535(10)
C(8)-C(10)	1.543(9)
C(8)-S(2)	1.847(6)
C(9)-H(9A)	0.9800
C(9)-H(9B)	0.9800
C(9)-H(9C)	0.9800
C(10)-H(10A)	0.9800
C(10)-H(10B)	0.9800
C(10)-H(10C)	0.9800
C(11)-C(13)	1.528(9)
C(11)-H(11A)	0.9800
C(11)-H(11B)	0.9800
C(11)-H(11C)	0.9800
C(12)-C(13)	1.528(8)
C(12)-H(12A)	0.9800
C(12)-H(12B)	0.9800
C(12)-H(12C)	0.9800
C(13)-C(14)	1.525(8)
C(13)-S(3)	1.853(6)
C(14)-O(3)	1.244(7)
C(14)-N(3)	1.323(8)
C(15)-N(3)	1.460(7)

C(15)-C(16)	1.522(8)
C(15)-H(15A)	0.9900
C(15)-H(15B)	0.9900
C(16)-N(4)	1.481(7)
C(16)-H(16A)	0.9900
C(16)-H(16B)	0.9900
C(17)-O(4)	1.249(7)
C(17)-N(4)	1.309(7)
C(17)-C(18)	1.515(9)
C(18)-C(19)	1.515(9)
C(18)-C(20)	1.528(9)
C(18)-S(4)	1.841(6)
C(19)-H(19A)	0.9800
C(19)-H(19B)	0.9800
C(19)-H(19C)	0.9800
C(20)-H(20A)	0.9800
C(20)-H(20B)	0.9800
C(20)-H(20C)	0.9800
C(21)-N(5)	1.496(9)
C(21)-H(21A)	0.9800
C(21)-H(21B)	0.9800
C(21)-H(21C)	0.9800
C(22)-N(5)	1.504(8)
C(22)-H(22A)	0.9800
C(22)-H(22B)	0.9800
C(22)-H(22C)	0.9800
C(23)-N(5)	1.502(8)
C(23)-H(23A)	0.9800
C(23)-H(23B)	0.9800
C(23)-H(23C)	0.9800
C(24)-N(5)	1.470(8)
C(24)-H(24A)	0.9800
C(24)-H(24B)	0.9800
C(24)-H(24C)	0.9800
C(25)-N(6)	1.500(8)
C(25)-H(25A)	0.9800
C(25)-H(25B)	0.9800
C(25)-H(25C)	0.9800
C(26)-N(6)	1.479(9)
C(26)-H(26A)	0.9800
C(26)-H(26B)	0.9800
C(26)-H(26C)	0.9800
C(27)-N(6)	1.492(8)
C(27)-H(27A)	0.9800
C(27)-H(27B)	0.9800
C(27)-H(27C)	0.9800
C(28)-N(6)	1.472(9)
C(28)-H(28A)	0.9800

C(28)-H(28B)	0.9800
C(28)-H(28C)	0.9800
C(29)-O(5)	1.349(11)
C(29)-H(29A)	0.9800
C(29)-H(29B)	0.9800
C(29)-H(29C)	0.9800
C(30)-O(6)	1.385(9)
C(30)-H(30A)	0.9800
C(30)-H(30B)	0.9800
C(30)-H(30C)	0.9800
Fe(1)-N(2)	1.900(4)
Fe(1)-N(1)	1.915(5)
Fe(1)-S(2)	2.1993(17)
Fe(1)-S(1)	2.2513(17)
Fe(1)-S(3)	2.4464(18)
Fe(2)-N(4)	1.904(4)
Fe(2)-N(3)	1.930(5)
Fe(2)-S(4)	2.2104(16)
Fe(2)-S(3)	2.2520(16)
Fe(2)-S(1)	2.4513(18)
O(5)-H(5)	1.0100
O(6)-H(6)	1.0100
C(3)-C(1)-H(1A)	109.5
C(3)-C(1)-H(1B)	109.5
H(1A)-C(1)-H(1B)	109.5
C(3)-C(1)-H(1C)	109.5
H(1A)-C(1)-H(1C)	109.5
H(1B)-C(1)-H(1C)	109.5
C(3)-C(2)-H(2A)	109.5
C(3)-C(2)-H(2B)	109.5
H(2A)-C(2)-H(2B)	109.5
C(3)-C(2)-H(2C)	109.5
H(2A)-C(2)-H(2C)	109.5
H(2B)-C(2)-H(2C)	109.5
C(1)-C(3)-C(2)	110.0(6)
C(1)-C(3)-C(4)	106.7(5)
C(2)-C(3)-C(4)	113.5(5)
C(1)-C(3)-S(1)	105.6(4)
C(2)-C(3)-S(1)	110.7(5)
C(4)-C(3)-S(1)	110.0(5)
O(1)-C(4)-N(1)	126.4(6)
O(1)-C(4)-C(3)	118.2(6)
N(1)-C(4)-C(3)	114.9(5)
N(1)-C(5)-C(6)	106.5(5)
N(1)-C(5)-H(5A)	110.4
C(6)-C(5)-H(5A)	110.4
N(1)-C(5)-H(5B)	110.4
C(6)-C(5)-H(5B)	110.4

H(5A)-C(5)-H(5B)	108.6
N(2)-C(6)-C(5)	108.4(5)
N(2)-C(6)-H(6A)	110.0
C(5)-C(6)-H(6A)	110.0
N(2)-C(6)-H(6B)	110.0
C(5)-C(6)-H(6B)	110.0
H(6A)-C(6)-H(6B)	108.4
O(2)-C(7)-N(2)	124.2(6)
O(2)-C(7)-C(8)	121.2(6)
N(2)-C(7)-C(8)	114.6(5)
C(7)-C(8)-C(9)	108.3(6)
C(7)-C(8)-C(10)	110.8(5)
C(9)-C(8)-C(10)	110.1(5)
C(7)-C(8)-S(2)	107.5(4)
C(9)-C(8)-S(2)	110.2(4)
C(10)-C(8)-S(2)	109.9(5)
C(8)-C(9)-H(9A)	109.5
C(8)-C(9)-H(9B)	109.5
H(9A)-C(9)-H(9B)	109.5
C(8)-C(9)-H(9C)	109.5
H(9A)-C(9)-H(9C)	109.5
H(9B)-C(9)-H(9C)	109.5
C(8)-C(10)-H(10A)	109.5
C(8)-C(10)-H(10B)	109.5
H(10A)-C(10)-H(10B)	109.5
C(8)-C(10)-H(10C)	109.5
H(10A)-C(10)-H(10C)	109.5
H(10B)-C(10)-H(10C)	109.5
C(13)-C(11)-H(11A)	109.5
C(13)-C(11)-H(11B)	109.5
H(11A)-C(11)-H(11B)	109.5
C(13)-C(11)-H(11C)	109.5
H(11A)-C(11)-H(11C)	109.5
H(11B)-C(11)-H(11C)	109.5
C(13)-C(12)-H(12A)	109.5
C(13)-C(12)-H(12B)	109.5
H(12A)-C(12)-H(12B)	109.5
C(13)-C(12)-H(12C)	109.5
H(12A)-C(12)-H(12C)	109.5
H(12B)-C(12)-H(12C)	109.5
C(14)-C(13)-C(11)	107.4(5)
C(14)-C(13)-C(12)	112.7(5)
C(11)-C(13)-C(12)	110.1(6)
C(14)-C(13)-S(3)	110.4(4)
C(11)-C(13)-S(3)	106.5(4)
C(12)-C(13)-S(3)	109.5(4)
O(3)-C(14)-N(3)	125.5(6)
O(3)-C(14)-C(13)	118.0(6)

N(3)-C(14)-C(13)	116.3(5)
N(3)-C(15)-C(16)	106.9(5)
N(3)-C(15)-H(15A)	110.3
C(16)-C(15)-H(15A)	110.3
N(3)-C(15)-H(15B)	110.3
C(16)-C(15)-H(15B)	110.3
H(15A)-C(15)-H(15B)	108.6
N(4)-C(16)-C(15)	109.3(5)
N(4)-C(16)-H(16A)	109.8
C(15)-C(16)-H(16A)	109.8
N(4)-C(16)-H(16B)	109.8
C(15)-C(16)-H(16B)	109.8
H(16A)-C(16)-H(16B)	108.3
O(4)-C(17)-N(4)	124.0(6)
O(4)-C(17)-C(18)	119.9(5)
N(4)-C(17)-C(18)	116.1(5)
C(19)-C(18)-C(17)	107.4(5)
C(19)-C(18)-C(20)	109.5(5)
C(17)-C(18)-C(20)	111.0(5)
C(19)-C(18)-S(4)	110.8(4)
C(17)-C(18)-S(4)	108.8(4)
C(20)-C(18)-S(4)	109.3(5)
C(18)-C(19)-H(19A)	109.5
C(18)-C(19)-H(19B)	109.5
H(19A)-C(19)-H(19B)	109.5
C(18)-C(19)-H(19C)	109.5
H(19A)-C(19)-H(19C)	109.5
H(19B)-C(19)-H(19C)	109.5
C(18)-C(20)-H(20A)	109.5
C(18)-C(20)-H(20B)	109.5
H(20A)-C(20)-H(20B)	109.5
C(18)-C(20)-H(20C)	109.5
H(20A)-C(20)-H(20C)	109.5
H(20B)-C(20)-H(20C)	109.5
N(5)-C(21)-H(21A)	109.5
N(5)-C(21)-H(21B)	109.5
H(21A)-C(21)-H(21B)	109.5
N(5)-C(21)-H(21C)	109.5
H(21A)-C(21)-H(21C)	109.5
H(21B)-C(21)-H(21C)	109.5
N(5)-C(22)-H(22A)	109.5
N(5)-C(22)-H(22B)	109.5
H(22A)-C(22)-H(22B)	109.5
N(5)-C(22)-H(22C)	109.5
H(22A)-C(22)-H(22C)	109.5
H(22B)-C(22)-H(22C)	109.5
N(5)-C(23)-H(23A)	109.5
N(5)-C(23)-H(23B)	109.5

H(23A)-C(23)-H(23B)	109.5
N(5)-C(23)-H(23C)	109.5
H(23A)-C(23)-H(23C)	109.5
H(23B)-C(23)-H(23C)	109.5
N(5)-C(24)-H(24A)	109.5
N(5)-C(24)-H(24B)	109.5
H(24A)-C(24)-H(24B)	109.5
N(5)-C(24)-H(24C)	109.5
H(24A)-C(24)-H(24C)	109.5
H(24B)-C(24)-H(24C)	109.5
N(6)-C(25)-H(25A)	109.5
N(6)-C(25)-H(25B)	109.5
H(25A)-C(25)-H(25B)	109.5
N(6)-C(25)-H(25C)	109.5
H(25A)-C(25)-H(25C)	109.5
H(25B)-C(25)-H(25C)	109.5
N(6)-C(26)-H(26A)	109.5
N(6)-C(26)-H(26B)	109.5
H(26A)-C(26)-H(26B)	109.5
N(6)-C(26)-H(26C)	109.5
H(26A)-C(26)-H(26C)	109.5
H(26B)-C(26)-H(26C)	109.5
N(6)-C(27)-H(27A)	109.5
N(6)-C(27)-H(27B)	109.5
H(27A)-C(27)-H(27B)	109.5
N(6)-C(27)-H(27C)	109.5
H(27A)-C(27)-H(27C)	109.5
H(27B)-C(27)-H(27C)	109.5
N(6)-C(28)-H(28A)	109.5
N(6)-C(28)-H(28B)	109.5
H(28A)-C(28)-H(28B)	109.5
N(6)-C(28)-H(28C)	109.5
H(28A)-C(28)-H(28C)	109.5
H(28B)-C(28)-H(28C)	109.5
O(5)-C(29)-H(29A)	109.5
O(5)-C(29)-H(29B)	109.5
H(29A)-C(29)-H(29B)	109.5
O(5)-C(29)-H(29C)	109.5
H(29A)-C(29)-H(29C)	109.5
H(29B)-C(29)-H(29C)	109.5
O(6)-C(30)-H(30A)	109.5
O(6)-C(30)-H(30B)	109.5
H(30A)-C(30)-H(30B)	109.5
O(6)-C(30)-H(30C)	109.5
H(30A)-C(30)-H(30C)	109.5
H(30B)-C(30)-H(30C)	109.5
N(2)-Fe(1)-N(1)	83.5(2)
N(2)-Fe(1)-S(2)	85.43(16)

N(1)-Fe(1)-S(2)	153.82(18)
N(2)-Fe(1)-S(1)	154.47(18)
N(1)-Fe(1)-S(1)	85.20(15)
S(2)-Fe(1)-S(1)	94.93(6)
N(2)-Fe(1)-S(3)	106.34(18)
N(1)-Fe(1)-S(3)	113.02(18)
S(2)-Fe(1)-S(3)	92.85(6)
S(1)-Fe(1)-S(3)	99.14(6)
N(4)-Fe(2)-N(3)	83.36(19)
N(4)-Fe(2)-S(4)	85.35(15)
N(3)-Fe(2)-S(4)	154.43(17)
N(4)-Fe(2)-S(3)	154.12(17)
N(3)-Fe(2)-S(3)	85.06(15)
S(4)-Fe(2)-S(3)	95.50(6)
N(4)-Fe(2)-S(1)	106.81(16)
N(3)-Fe(2)-S(1)	112.04(17)
S(4)-Fe(2)-S(1)	93.18(6)
S(3)-Fe(2)-S(1)	98.98(6)
C(4)-N(1)-C(5)	118.6(5)
C(4)-N(1)-Fe(1)	126.6(4)
C(5)-N(1)-Fe(1)	114.5(4)
C(7)-N(2)-C(6)	116.1(5)
C(7)-N(2)-Fe(1)	125.5(4)
C(6)-N(2)-Fe(1)	115.7(4)
C(14)-N(3)-C(15)	120.0(5)
C(14)-N(3)-Fe(2)	125.6(4)
C(15)-N(3)-Fe(2)	113.6(4)
C(17)-N(4)-C(16)	117.5(5)
C(17)-N(4)-Fe(2)	125.5(4)
C(16)-N(4)-Fe(2)	115.6(4)
C(24)-N(5)-C(21)	110.3(6)
C(24)-N(5)-C(23)	109.1(5)
C(21)-N(5)-C(23)	108.8(5)
C(24)-N(5)-C(22)	110.1(5)
C(21)-N(5)-C(22)	108.7(5)
C(23)-N(5)-C(22)	109.9(6)
C(28)-N(6)-C(26)	110.0(5)
C(28)-N(6)-C(27)	109.4(5)
C(26)-N(6)-C(27)	109.0(6)
C(28)-N(6)-C(25)	109.6(6)
C(26)-N(6)-C(25)	109.9(5)
C(27)-N(6)-C(25)	108.9(5)
C(29)-O(5)-H(5)	109.5
C(30)-O(6)-H(6)	109.5
C(3)-S(1)-Fe(1)	98.9(2)
C(3)-S(1)-Fe(2)	113.0(2)
Fe(1)-S(1)-Fe(2)	79.04(6)
C(8)-S(2)-Fe(1)	99.4(2)

C(13)-S(3)-Fe(2)	98.80(19)
C(13)-S(3)-Fe(1)	113.7(2)
Fe(2)-S(3)-Fe(1)	79.13(6)
C(18)-S(4)-Fe(2)	99.32(19)

Table S–12. Anisotropic displacement parameters (A^2 x 10^3) for $(NMe_4)_2[Fe(III)(Et\text{–}N_2S_2^{Me2})]_2 \cdot 2MeOH$ (**2**). The anisotropic displacement factor exponent takes the form: -2 pi^2 [h^2 a*^2 U11 + ... + 2 h k a* b* U12]

	U11	U22	U33	U23	U13	U12
C(1)	74(5)	37(5)	36(4)	-1(3)	-4(3)	2(4)
C(2)	48(4)	53(5)	39(4)	3(4)	-2(3)	-10(3)
C(3)	46(4)	26(4)	38(3)	-7(3)	2(3)	-5(3)
C(4)	46(4)	33(4)	26(3)	-2(3)	1(2)	8(3)
C(5)	51(4)	63(6)	24(3)	-7(3)	1(3)	-10(4)
C(6)	31(3)	72(6)	39(4)	11(4)	-9(3)	-4(3)
C(7)	39(4)	28(4)	44(4)	2(3)	-3(3)	7(3)
C(8)	33(3)	43(4)	35(3)	-2(3)	5(3)	-3(3)
C(9)	41(3)	36(4)	36(3)	-1(3)	3(3)	0(3)
C(10)	46(4)	45(5)	46(4)	-14(4)	14(3)	2(3)
C(11)	61(4)	23(4)	43(4)	8(3)	10(3)	3(3)
C(12)	39(3)	40(4)	39(3)	-12(3)	2(3)	-8(3)
C(13)	40(3)	25(3)	31(3)	2(3)	5(2)	-4(2)
C(14)	36(3)	26(3)	32(3)	1(3)	-1(2)	7(2)
C(15)	45(4)	34(4)	29(3)	-3(3)	9(3)	-13(3)
C(16)	35(3)	44(4)	36(3)	-7(3)	13(3)	-3(3)
C(17)	34(3)	29(4)	39(3)	2(3)	2(3)	-2(3)
C(18)	33(3)	38(4)	29(3)	-3(3)	0(2)	-4(3)
C(19)	48(4)	24(3)	36(3)	3(3)	1(3)	-5(3)
C(20)	51(4)	39(4)	44(4)	-1(3)	-10(3)	0(3)
C(21)	80(6)	50(6)	58(5)	4(4)	10(4)	28(4)
C(22)	43(4)	40(4)	33(3)	3(3)	5(3)	-5(3)
C(23)	44(4)	48(5)	29(3)	-14(3)	-6(3)	2(3)
C(24)	58(4)	47(5)	25(3)	-10(3)	6(3)	-13(3)
C(25)	51(4)	39(4)	39(3)	8(3)	5(3)	-1(3)
C(26)	56(4)	45(5)	42(4)	1(3)	-1(3)	-8(3)
C(27)	59(4)	55(5)	37(4)	14(4)	-5(3)	8(4)
C(28)	60(5)	40(5)	48(4)	-8(4)	0(3)	7(3)
C(29)	78(7)	93(10)	120(9)	-29(8)	-4(6)	-5(6)
C(30)	81(6)	67(7)	64(5)	-5(5)	-4(5)	-23(5)
Fe(1)	31(1)	30(1)	26(1)	-3(1)	0(1)	0(1)
Fe(2)	30(1)	27(1)	26(1)	-2(1)	3(1)	-2(1)
N(1)	34(3)	34(3)	32(3)	-5(2)	1(2)	-5(2)
N(2)	25(2)	36(3)	37(3)	1(2)	-6(2)	-2(2)
N(3)	29(2)	36(3)	25(2)	1(2)	5(2)	-6(2)
N(4)	26(2)	26(3)	30(2)	-6(2)	6(2)	-5(2)
N(5)	45(3)	35(3)	31(3)	-9(2)	3(2)	5(2)
N(6)	42(3)	38(3)	27(2)	2(2)	2(2)	4(2)

O(1)	52(3)	60(4)	31(2)	-5(2)	3(2)	-14(2)
O(2)	30(2)	58(4)	49(3)	10(3)	-1(2)	-3(2)
O(3)	50(3)	36(3)	25(2)	-5(2)	0(2)	-5(2)
O(4)	27(2)	49(3)	51(3)	-4(2)	-2(2)	0(2)
O(5)	86(5)	71(5)	114(6)	-38(5)	1(4)	12(4)
O(6)	70(4)	70(4)	54(3)	18(3)	3(3)	-12(3)
S(1)	35(1)	27(1)	31(1)	-3(1)	-1(1)	-1(1)
S(2)	40(1)	36(1)	28(1)	-7(1)	3(1)	-4(1)
S(3)	32(1)	25(1)	32(1)	-2(1)	4(1)	-4(1)
S(4)	38(1)	36(1)	27(1)	1(1)	2(1)	-5(1)

Table S–13. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (A^2 x 10^3) for $(NMe_4)_2[Fe(III)(Et\text{–}N_2S_2^{Me2})]_2 \bullet 2MeOH$ (**2**).

	x	y	z	U(eq)
H(1A)	7289	4811	5680	74
H(1B)	7593	4795	6358	74
H(1C)	6701	4229	6150	74
H(2A)	8647	3859	5387	70
H(2B)	8963	2744	5726	70
H(2C)	8974	3930	6059	70
H(5A)	6100	629	5228	51
H(5B)	5875	1869	4983	51
H(6A)	4837	2146	5632	53
H(6B)	4751	806	5551	53
H(9A)	4467	-422	7407	57
H(9B)	5200	-202	7905	57
H(9C)	5454	-503	7253	57
H(10A)	3860	1439	7702	67
H(10B)	4375	2580	7592	67
H(10C)	4653	1781	8132	67
H(11A)	7716	-2913	6012	63
H(11B)	7243	-2778	6614	63
H(11C)	8176	-2250	6548	63
H(12A)	6344	-2024	5524	59
H(12B)	6046	-816	5749	59
H(12C)	5974	-1898	6162	59
H(15A)	8874	1132	5328	39
H(15B)	9114	-156	5191	39
H(16A)	10123	-238	5927	42
H(16B)	10201	1072	5762	42
H(19A)	10492	2728	7534	54
H(19B)	9781	2635	8013	54
H(19C)	9498	2819	7339	54
H(20A)	11052	899	7954	68
H(20B)	10462	-203	7914	68
H(20C)	10264	772	8373	68
H(21A)	8003	-7369	9032	94
H(21B)	8562	-6738	8562	94
H(21C)	7819	-7591	8348	94
H(22A)	7019	-4853	8018	58
H(22B)	7131	-6069	7729	58
H(22C)	7958	-5349	7932	58
H(23A)	7210	-4604	9072	61
H(23B)	8194	-4930	9001	61

H(23C)	7641	-5586	9465	61
H(24A)	6106	-5849	8761	65
H(24B)	6514	-6914	9099	65
H(24C)	6297	-6981	8410	65
H(25A)	6681	-1192	9488	64
H(25B)	7454	-2055	9615	64
H(25C)	6712	-2356	9136	64
H(26A)	7760	252	9318	72
H(26B)	8420	90	8809	72
H(26C)	8527	-636	9398	72
H(27A)	6566	-140	8609	76
H(27B)	6606	-1246	8211	76
H(27C)	7268	-238	8122	76
H(28A)	8448	-2421	8852	74
H(28B)	8444	-1649	8278	74
H(28C)	7708	-2570	8351	74
H(29A)	5030	1292	9835	146
H(29B)	4868	321	9358	146
H(29C)	5151	1553	9158	146
H(30A)	9575	-1306	10543	106
H(30B)	10275	-2187	10335	106
H(30C)	9533	-2594	10747	106
H(5)	6382	1280	9748	136
H(6)	8765	-2990	10027	97

Table S-14. Crystal data and structure refinement for (NMe_4) $[Fe^{III}(Et\text{-}N_2)S_2^{Me2})(Py)]\bullet 2MeOH$ (**3**).

Empirical formula	C20.73 H39.90 Fe N4 O3.72 S2
Formula weight	524.76
Temperature	130(2) K
Wavelength	0.71070 A
Crystal description/color	prism / brown
Crystal system, space group	Monoclinic, P 21/c
Unit cell dimensions	a = 9.0629(3)A alpha = 90 deg. b = 11.0976(3)A beta = 93.4992(18)deg. c = 26.0129(9)A gamma = 90 deg.
Volume	2611.41(14) A^3
Z, Calculated density	4, 1.335 Mg/m^3
Absorption coefficient	0.768 mm^-1
F(000)	1120.2
Crystal size	0.17 x 0.12 x 0.10 mm
Reflections for indexing	170
Theta range for data collection	2.00 to 24.79 deg.
Index ranges	0<=h<=10, -13<=k<=13, -30<=l<=30
Reflections collected / unique	8560 / 4427 [R(int) = 0.0619]
Completeness to theta = 25.00	98.5%
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.9271 and 0.8805
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	4427 / 0 / 304
Goodness-of-fit on F^2	S = 0.935
S = root(sum(w*D*D)/(n-p)), where D = (Fo*Fo - Fc*Fc)	
Final R indices [I>2sigma(I)]	*R1 = 0.0446, wR2 = 0.0934
R indices (all data)	R1 = 0.0899, *wR2 = 0.1047
*Report these R factors.	
R1 = sum||Fo|-|Fc||/sum|Fo|, wR2= root(sum(w*D*D)/sum(w*Fo*Fo)), where D = (Fo*Fo - Fc*Fc)	
Weighting scheme	calc w=1/[\s^2(Fo^2)+(0.0481P)^2 +0.0000P] where P=(Fo^2 + 2Fc^2)/3
Extinction coefficient	0.0051(9)
Largest diff. peak and hole	0.514 and -0.314 e.A^-3

Table S–15. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (A^2 x 10^3) for $(NMe_4)[Fe^{III}(Et–N_2)S_2^{Me2})(Py)]•2MeOH$ (**3**). U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

	x	y	z	U(eq)
C(1)	8293(4)	1306(4)	5907(2)	43(1)
C(2)	7105(5)	3308(3)	6039(2)	45(1)
C(3)	6878(4)	1949(3)	6033(1)	31(1)
C(4)	5658(4)	1655(3)	5624(1)	31(1)
C(5)	3218(4)	836(3)	5411(1)	31(1)
C(6)	2247(4)	-71(3)	5674(1)	35(1)
C(7)	1499(4)	-475(3)	6526(1)	33(1)
C(8)	1642(4)	-190(3)	7102(1)	31(1)
C(9)	491(4)	758(3)	7217(2)	40(1)
C(10)	1412(4)	-1322(3)	7424(2)	43(1)
C(11)	1869(4)	3290(3)	6222(1)	36(1)
C(12)	1227(4)	4410(3)	6251(2)	39(1)
C(13)	1746(4)	5195(3)	6626(2)	38(1)
C(14)	2893(4)	4840(3)	6960(2)	37(1)
C(15)	3504(4)	3719(3)	6904(1)	34(1)
C(16)	4751(4)	-2436(3)	6599(2)	46(1)
C(17)	7330(4)	-1954(3)	6788(2)	41(1)
C(18)	6267(5)	-1759(3)	5908(2)	47(1)
C(19)	6646(5)	-3756(3)	6293(2)	51(1)
C(20)	85(7)	6953(5)	5243(2)	89(2)
C(21)	3759(14)	-5050(8)	5189(4)	157(5)
N(1)	4417(3)	1167(2)	5788(1)	30(1)
N(2)	2296(3)	204(2)	6224(1)	29(1)
N(3)	3003(3)	2931(2)	6539(1)	31(1)
N(4)	6244(3)	-2473(2)	6398(1)	35(1)
O(1)	5854(3)	1894(2)	5163(1)	42(1)
O(2)	636(3)	-1293(2)	6368(1)	44(1)
O(3)	-230(4)	6934(3)	5728(1)	73(1)
O(4)	3718(8)	-3890(5)	5426(2)	117(3)
S(1)	6322(1)	1468(1)	6676(1)	33(1)
S(2)	3519(1)	415(1)	7259(1)	32(1)
Fe(1)	3950(1)	1145(1)	6490(1)	29(1)

Table S–16. Bond lengths [A] and angles [deg] for $(NMe_4)[Fe^{III}(Et–N_2)S_2^{Me2})(Py)]•2MeOH$ (**3**).

C(1)-C(3)	1.521(5)
C(1)-H(1A)	0.9800
C(1)-H(1B)	0.9800
C(1)-H(1C)	0.9800
C(2)-C(3)	1.522(5)
C(2)-H(2A)	0.9800
C(2)-H(2B)	0.9800
C(2)-H(2C)	0.9800
C(3)-C(4)	1.523(5)
C(3)-S(1)	1.854(4)
C(4)-O(1)	1.250(4)
C(4)-N(1)	1.342(4)
C(5)-N(1)	1.466(4)
C(5)-C(6)	1.526(5)
C(5)-H(5A)	0.9900
C(5)-H(5B)	0.9900
C(6)-N(2)	1.462(4)
C(6)-H(6A)	0.9900
C(6)-H(6B)	0.9900
C(7)-O(2)	1.251(4)
C(7)-N(2)	1.332(4)
C(7)-C(8)	1.529(5)
C(8)-C(9)	1.525(5)
C(8)-C(10)	1.532(5)
C(8)-S(2)	1.851(3)
C(9)-H(9A)	0.9800
C(9)-H(9B)	0.9800
C(9)-H(9C)	0.9800
C(10)-H(10A)	0.9800
C(10)-H(10B)	0.9800
C(10)-H(10C)	0.9800
C(11)-N(3)	1.338(4)
C(11)-C(12)	1.377(5)
C(11)-H(11)	0.9500
C(12)-C(13)	1.370(5)
C(12)-H(12)	0.9500
C(13)-C(14)	1.372(5)
C(13)-H(13)	0.9500
C(14)-C(15)	1.374(5)
C(14)-H(14)	0.9500
C(15)-N(3)	1.348(4)
C(15)-H(15)	0.9500
C(16)-N(4)	1.480(5)

C(16)-H(16A)	0.9800
C(16)-H(16B)	0.9800
C(16)-H(16C)	0.9800
C(17)-N(4)	1.486(4)
C(17)-H(17A)	0.9800
C(17)-H(17B)	0.9800
C(17)-H(17C)	0.9800
C(18)-N(4)	1.501(4)
C(18)-H(18A)	0.9800
C(18)-H(18B)	0.9800
C(18)-H(18C)	0.9800
C(19)-N(4)	1.499(4)
C(19)-H(19A)	0.9800
C(19)-H(19B)	0.9800
C(19)-H(19C)	0.9800
C(20)-O(3)	1.309(6)
C(20)-H(20A)	0.9800
C(20)-H(20B)	0.9800
C(20)-H(20C)	0.9800
C(21)-O(4)	1.429(10)
C(21)-H(21A)	0.9800
C(21)-H(21B)	0.9800
C(21)-H(21C)	0.9800
N(1)-Fe(1)	1.898(3)
N(2)-Fe(1)	1.920(3)
N(3)-Fe(1)	2.167(3)
O(3)-H(3)	0.8400
O(4)-H(4)	0.8400
S(1)-Fe(1)	2.2037(10)
S(2)-Fe(1)	2.2162(11)
C(3)-C(1)-H(1A)	109.5
C(3)-C(1)-H(1B)	109.5
H(1A)-C(1)-H(1B)	109.5
C(3)-C(1)-H(1C)	109.5
H(1A)-C(1)-H(1C)	109.5
H(1B)-C(1)-H(1C)	109.5
C(3)-C(2)-H(2A)	109.5
C(3)-C(2)-H(2B)	109.5
H(2A)-C(2)-H(2B)	109.5
C(3)-C(2)-H(2C)	109.5
H(2A)-C(2)-H(2C)	109.5
H(2B)-C(2)-H(2C)	109.5
C(1)-C(3)-C(2)	110.5(3)
C(1)-C(3)-C(4)	109.5(3)
C(2)-C(3)-C(4)	108.1(3)
C(1)-C(3)-S(1)	109.8(2)
C(2)-C(3)-S(1)	108.7(3)
C(4)-C(3)-S(1)	110.1(2)

O(1)-C(4)-N(1)	124.2(3)
O(1)-C(4)-C(3)	119.1(3)
N(1)-C(4)-C(3)	116.7(3)
N(1)-C(5)-C(6)	106.8(3)
N(1)-C(5)-H(5A)	110.4
C(6)-C(5)-H(5A)	110.4
N(1)-C(5)-H(5B)	110.4
C(6)-C(5)-H(5B)	110.4
H(5A)-C(5)-H(5B)	108.6
N(2)-C(6)-C(5)	108.5(3)
N(2)-C(6)-H(6A)	110.0
C(5)-C(6)-H(6A)	110.0
N(2)-C(6)-H(6B)	110.0
C(5)-C(6)-H(6B)	110.0
H(6A)-C(6)-H(6B)	108.4
O(2)-C(7)-N(2)	124.6(3)
O(2)-C(7)-C(8)	119.1(3)
N(2)-C(7)-C(8)	116.3(3)
C(9)-C(8)-C(7)	108.5(3)
C(9)-C(8)-C(10)	109.9(3)
C(7)-C(8)-C(10)	111.1(3)
C(9)-C(8)-S(2)	109.7(2)
C(7)-C(8)-S(2)	108.3(2)
C(10)-C(8)-S(2)	109.3(2)
C(8)-C(9)-H(9A)	109.5
C(8)-C(9)-H(9B)	109.5
H(9A)-C(9)-H(9B)	109.5
C(8)-C(9)-H(9C)	109.5
H(9A)-C(9)-H(9C)	109.5
H(9B)-C(9)-H(9C)	109.5
C(8)-C(10)-H(10A)	109.5
C(8)-C(10)-H(10B)	109.5
H(10A)-C(10)-H(10B)	109.5
C(8)-C(10)-H(10C)	109.5
H(10A)-C(10)-H(10C)	109.5
H(10B)-C(10)-H(10C)	109.5
N(3)-C(11)-C(12)	123.1(3)
N(3)-C(11)-H(11)	118.5
C(12)-C(11)-H(11)	118.5
C(13)-C(12)-C(11)	119.0(4)
C(13)-C(12)-H(12)	120.5
C(11)-C(12)-H(12)	120.5
C(12)-C(13)-C(14)	118.9(4)
C(12)-C(13)-H(13)	120.6
C(14)-C(13)-H(13)	120.6
C(13)-C(14)-C(15)	119.1(4)
C(13)-C(14)-H(14)	120.4
C(15)-C(14)-H(14)	120.4

N(3)-C(15)-C(14)	122.8(3)
N(3)-C(15)-H(15)	118.6
C(14)-C(15)-H(15)	118.6
N(4)-C(16)-H(16A)	109.5
N(4)-C(16)-H(16B)	109.5
H(16A)-C(16)-H(16B)	109.5
N(4)-C(16)-H(16C)	109.5
H(16A)-C(16)-H(16C)	109.5
H(16B)-C(16)-H(16C)	109.5
N(4)-C(17)-H(17A)	109.5
N(4)-C(17)-H(17B)	109.5
H(17A)-C(17)-H(17B)	109.5
N(4)-C(17)-H(17C)	109.5
H(17A)-C(17)-H(17C)	109.5
H(17B)-C(17)-H(17C)	109.5
N(4)-C(18)-H(18A)	109.5
N(4)-C(18)-H(18B)	109.5
H(18A)-C(18)-H(18B)	109.5
N(4)-C(18)-H(18C)	109.5
H(18A)-C(18)-H(18C)	109.5
H(18B)-C(18)-H(18C)	109.5
N(4)-C(19)-H(19A)	109.5
N(4)-C(19)-H(19B)	109.5
H(19A)-C(19)-H(19B)	109.5
N(4)-C(19)-H(19C)	109.5
H(19A)-C(19)-H(19C)	109.5
H(19B)-C(19)-H(19C)	109.5
O(3)-C(20)-H(20A)	109.5
O(3)-C(20)-H(20B)	109.5
H(20A)-C(20)-H(20B)	109.5
O(3)-C(20)-H(20C)	109.5
H(20A)-C(20)-H(20C)	109.5
H(20B)-C(20)-H(20C)	109.5
O(4)-C(21)-H(21A)	109.5
O(4)-C(21)-H(21B)	109.5
H(21A)-C(21)-H(21B)	109.5
O(4)-C(21)-H(21C)	109.5
H(21A)-C(21)-H(21C)	109.5
H(21B)-C(21)-H(21C)	109.5
C(4)-N(1)-C(5)	119.3(3)
C(4)-N(1)-Fe(1)	123.5(2)
C(5)-N(1)-Fe(1)	116.1(2)
C(7)-N(2)-C(6)	118.2(3)
C(7)-N(2)-Fe(1)	122.4(2)
C(6)-N(2)-Fe(1)	116.2(2)
C(11)-N(3)-C(15)	117.0(3)
C(11)-N(3)-Fe(1)	121.8(2)
C(15)-N(3)-Fe(1)	121.1(2)

C(16)-N(4)-C(17)	109.3(3)
C(16)-N(4)-C(19)	109.2(3)
C(17)-N(4)-C(19)	109.5(3)
C(16)-N(4)-C(18)	110.2(3)
C(17)-N(4)-C(18)	109.4(3)
C(19)-N(4)-C(18)	109.3(3)
C(20)-O(3)-H(3)	109.5
C(21)-O(4)-H(4)	109.5
C(3)-S(1)-Fe(1)	99.40(12)
C(8)-S(2)-Fe(1)	98.22(11)
N(1)-Fe(1)-N(2)	82.91(12)
N(1)-Fe(1)-N(3)	99.06(11)
N(2)-Fe(1)-N(3)	102.43(11)
N(1)-Fe(1)-S(1)	86.44(9)
N(2)-Fe(1)-S(1)	153.77(9)
N(3)-Fe(1)-S(1)	102.87(8)
N(1)-Fe(1)-S(2)	159.22(9)
N(2)-Fe(1)-S(2)	87.06(9)
N(3)-Fe(1)-S(2)	100.86(8)
S(1)-Fe(1)-S(2)	94.83(4)

Table S–17. Anisotropic displacement parameters (A^2 x 10^3) for $(NMe_4)[Fe^{III}(Et\text{–}N_2)S_2^{Me2})(Py)]\bullet 2MeOH$ (**3**). The anisotropic displacement factor exponent takes the form: -2 pi^2 [h^2a*^2 U11 + ... + 2 h k a* b* U12]

	U11	U22	U33	U23	U13	U12
C(1)	38(2)	51(3)	40(3)	7(2)	8(2)	-1(2)
C(2)	61(3)	36(2)	37(3)	1(2)	-6(2)	-13(2)
C(3)	33(2)	29(2)	29(2)	-1(2)	3(2)	-7(2)
C(4)	40(2)	25(2)	27(2)	-1(2)	7(2)	2(2)
C(5)	36(2)	33(2)	25(2)	0(2)	2(2)	-2(2)
C(6)	35(2)	38(2)	33(2)	-5(2)	0(2)	-6(2)
C(7)	33(2)	31(2)	35(2)	-3(2)	0(2)	2(2)
C(8)	36(2)	31(2)	24(2)	1(2)	3(2)	-5(2)
C(9)	41(2)	44(2)	35(2)	-1(2)	6(2)	2(2)
C(10)	47(2)	41(2)	41(3)	9(2)	0(2)	-6(2)
C(11)	41(2)	35(2)	30(2)	-1(2)	-2(2)	-2(2)
C(12)	37(2)	40(2)	40(3)	3(2)	0(2)	0(2)
C(13)	42(2)	29(2)	43(3)	3(2)	7(2)	1(2)
C(14)	45(2)	29(2)	38(3)	-3(2)	5(2)	-5(2)
C(15)	34(2)	37(2)	32(2)	1(2)	3(2)	-5(2)
C(16)	45(2)	33(2)	59(3)	2(2)	4(2)	-3(2)
C(17)	44(2)	38(2)	41(3)	2(2)	-3(2)	-4(2)
C(18)	68(3)	38(2)	35(3)	4(2)	5(2)	7(2)
C(19)	78(3)	33(2)	41(3)	0(2)	2(2)	13(2)
C(20)	122(5)	80(4)	67(4)	-9(3)	12(4)	-10(4)
C(21)	271(14)	79(6)	112(9)	21(6)	-58(8)	-22(8)
N(1)	34(2)	32(2)	25(2)	0(1)	0(1)	-2(1)
N(2)	33(2)	28(2)	26(2)	3(1)	1(1)	-2(1)
N(3)	35(2)	29(2)	29(2)	1(1)	0(1)	-3(1)
N(4)	47(2)	26(2)	32(2)	0(1)	1(2)	2(1)
O(1)	48(2)	47(2)	34(2)	1(1)	4(1)	-10(1)
O(2)	48(2)	44(2)	40(2)	-8(1)	4(1)	-18(1)
O(3)	121(3)	50(2)	48(2)	-12(2)	11(2)	-20(2)
O(4)	211(8)	72(4)	62(4)	13(3)	-35(4)	-57(4)
S(1)	35(1)	35(1)	30(1)	1(1)	-1(1)	-1(1)
S(2)	36(1)	32(1)	27(1)	0(1)	0(1)	-1(1)
Fe(1)	34(1)	26(1)	27(1)	-1(1)	0(1)	-1(1)

Table S–18. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (A^2 x 10^3) for $(NMe_4)[Fe^{III}(Et–N_2)S_2^{Me2})(Py)]•2MeOH$ (**3**).

	x	y	z	U(eq)
H(1A)	8116	435	5891	65
H(1B)	9071	1480	6175	65
H(1C)	8605	1589	5574	65
H(2A)	6181	3708	6117	67
H(2B)	7401	3573	5701	67
H(2C)	7881	3518	6303	67
H(5A)	3625	471	5102	38
H(5B)	2635	1557	5303	38
H(6A)	1217	-18	5526	42
H(6B)	2612	-899	5620	42
H(9A)	702	1506	7036	60
H(9B)	525	912	7589	60
H(9C)	-495	466	7102	60
H(10A)	2139	-1935	7341	65
H(10B)	412	-1636	7346	65
H(10C)	1537	-1120	7791	65
H(11)	1490	2746	5965	43
H(12)	434	4635	6014	47
H(13)	1320	5972	6654	45
H(14)	3260	5363	7228	45
H(15)	4314	3488	7131	41
H(16A)	4494	-1600	6677	69
H(16B)	4742	-2921	6913	69
H(16C)	4028	-2760	6339	69
H(17A)	7060	-1119	6860	62
H(17B)	8319	-1975	6656	62
H(17C)	7327	-2428	7106	62
H(18A)	6053	-912	5979	70
H(18B)	5517	-2076	5656	70
H(18C)	7245	-1824	5770	70
H(19A)	6630	-4225	6612	76
H(19B)	7639	-3786	6164	76
H(19C)	5933	-4096	6034	76
H(20A)	-220	7727	5090	134
H(20B)	-443	6298	5058	134
H(20C)	1152	6847	5219	134
H(21A)	4030	-5659	5451	235
H(21B)	4492	-5048	4927	235
H(21C)	2783	-5240	5026	235
H(3)	239	7484	5888	109
H(4)	3082	-3459	5265	175

Table S–19. Crystal data and structure refinement for $(NMe_4)_2[Fe(III)(N_2S–tame)S_2^{Me2})]•MeCN$ (**15**).

Empirical formula	C23 H48 Fe N5 O2 S3
Formula weight	578.69
Temperature	130(2) K
Wavelength	0.71073 A
Crystal description/color	prism / orange
Crystal system, space group	Orthorhombic, P b c a
Unit cell dimensions	a = 18.6780(3)A alpha = 90 deg.
	b = 15.0370(3)A beta = 90 deg.
	c = 21.9230(5)A gamma = 90 deg.
Volume	6157.3(2) A^3
Z, Calculated density	8, 1.249 Mg/m^3
Absorption coefficient	0.720 mm^-1
F(000)	2488
Crystal size	0.48 x 0.12 x 0.12 mm
Reflections for indexing	1025
Theta range for data collection	3.06 to 28.34 deg.
Index ranges	-24<=h<=24, -20<=k<=20, -28<=l<=28
Reflections collected / unique	14120 / 7568 [R(int) = 0.0457]
Completeness to theta	= 25.00 99.5%
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.9185 and 0.7237
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	7568 / 0 / 321
Goodness-of-fit on F^2	S = 0.940
S = root(sum(w*D*D)/(n-p)), where D = (Fo*Fo - Fc*Fc)	
Final R indices [I>2sigma(I)]	*R1 = 0.0426, wR2 = 0.0964
R indices (all data)	R1 = 0.0835, *wR2 = 0.1095
*Report these R factors.	R1 = sum||Fo|-|Fc||/sum|Fo|,
wR2= root(sum(w*D*D)/sum(w*Fo*Fo)), where D = (Fo*Fo - Fc*Fc)	
Weighting scheme calcw=1/[\s^2^(Fo^2^)+(0.0591P)^2^+0.0000P]	
where P=(Fo^2^+2Fc^2^)/3	
Largest diff. peak and hole	0.427 and -0.437 e.A^-3

Table S–20. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (A^2 x 10^3) for $(NMe_4)_2[Fe(III)(N_2S–tame)S_2^{Me2})]$•MeCN (**15**). U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

	x	y	z	U(eq)
Fe(1)	1793(1)	117(1)	3162(1)	26(1)
S(1)	1979(1)	-412(1)	2231(1)	29(1)
S(2)	2702(1)	-730(1)	3461(1)	32(1)
S(3)	715(1)	-344(1)	3673(1)	36(1)
O(5)	645(1)	1549(1)	1895(1)	34(1)
O(8)	2564(1)	990(1)	4807(1)	37(1)
N(1)	1233(1)	1035(1)	2746(1)	30(1)
N(2)	2056(1)	868(1)	3855(1)	28(1)
N(3)	3467(1)	1831(2)	1102(1)	44(1)
N(4)	1325(1)	3632(1)	1225(1)	30(1)
N(5)	3670(1)	1983(1)	2860(1)	29(1)
C(1)	1331(1)	218(1)	1785(1)	29(1)
C(2)	1055(1)	1004(1)	2156(1)	28(1)
C(3)	813(1)	1680(2)	3092(1)	40(1)
C(4)	868(1)	1593(1)	3773(1)	30(1)
C(5)	1642(1)	1676(1)	3984(1)	33(1)
C(6)	2466(1)	583(1)	4316(1)	29(1)
C(7)	2822(1)	-331(2)	4242(1)	31(1)
C(8)	678(1)	-367(2)	1636(1)	40(1)
C(9)	1680(1)	531(2)	1193(1)	38(1)
C(10)	514(1)	739(2)	4023(1)	45(1)
C(11)	463(1)	2397(2)	4040(1)	38(1)
C(12)	2442(1)	-963(2)	4683(1)	41(1)
C(13)	3616(1)	-260(2)	4400(1)	41(1)
C(14)	3620(1)	2185(2)	664(1)	39(1)
C(15)	3816(1)	2647(2)	102(1)	53(1)
C(16)	2011(1)	3129(2)	1171(1)	36(1)
C(17)	1095(1)	3672(2)	1875(1)	37(1)
C(18)	760(1)	3165(2)	863(1)	36(1)
C(19)	1427(1)	4559(2)	986(1)	41(1)
C(20)	2926(1)	2134(2)	2632(1)	35(1)
C(21)	3902(1)	1058(1)	2694(1)	39(1)
C(22)	3689(1)	2101(2)	3532(1)	41(1)
C(23)	4168(1)	2641(1)	2576(1)	33(1)

Table S–21. Bond lengths [A] and angles [deg] for $(NMe_4)_2[Fe(III)(N_2S–tame)S_2^{Me2})]\bullet MeCN$ (**15**).

Fe(1)-N(1)	1.9572(18)
Fe(1)-N(2)	1.9573(18)
Fe(1)-S(1)	2.2171(7)
Fe(1)-S(2)	2.2219(6)
Fe(1)-S(3)	2.4058(7)
S(1)-C(1)	1.822(2)
S(2)-C(7)	1.830(2)
S(3)-C(10)	1.839(2)
O(5)-C(2)	1.259(3)
O(8)-C(6)	1.252(3)
N(1)-C(2)	1.337(3)
N(1)-C(3)	1.460(3)
N(2)-C(6)	1.337(3)
N(2)-C(5)	1.468(3)
N(3)-C(14)	1.134(3)
N(4)-C(17)	1.489(3)
N(4)-C(16)	1.493(3)
N(4)-C(18)	1.496(3)
N(4)-C(19)	1.502(3)
N(5)-C(22)	1.485(3)
N(5)-C(23)	1.494(3)
N(5)-C(20)	1.494(3)
N(5)-C(21)	1.502(3)
C(1)-C(2)	1.524(3)
C(1)-C(9)	1.526(3)
C(1)-C(8)	1.539(3)
C(3)-C(4)	1.502(3)
C(3)-H(3A)	0.9900
C(3)-H(3B)	0.9900
C(4)-C(5)	1.521(3)
C(4)-C(11)	1.542(3)
C(4)-C(10)	1.545(3)
C(5)-H(5A)	0.9900
C(5)-H(5B)	0.9900
C(6)-C(7)	1.535(3)
C(7)-C(13)	1.527(3)
C(7)-C(12)	1.530(3)
C(8)-H(8A)	0.9800
C(8)-H(8B)	0.9800
C(8)-H(8C)	0.9800
C(9)-H(9A)	0.9800
C(9)-H(9B)	0.9800
C(9)-H(9C)	0.9800

C(10)-H(10A)	0.9900
C(10)-H(10B)	0.9900
C(11)-H(11A)	0.9800
C(11)-H(11B)	0.9800
C(11)-H(11C)	0.9800
C(12)-H(12A)	0.9800
C(12)-H(12B)	0.9800
C(12)-H(12C)	0.9800
C(13)-H(13A)	0.9800
C(13)-H(13B)	0.9800
C(13)-H(13C)	0.9800
C(14)-C(15)	1.460(4)
C(15)-H(15A)	0.9800
C(15)-H(15B)	0.9800
C(15)-H(15C)	0.9800
C(16)-H(16A)	0.9800
C(16)-H(16B)	0.9800
C(16)-H(16C)	0.9800
C(17)-H(17A)	0.9800
C(17)-H(17B)	0.9800
C(17)-H(17C)	0.9800
C(18)-H(18A)	0.9800
C(18)-H(18B)	0.9800
C(18)-H(18C)	0.9800
C(19)-H(19A)	0.9800
C(19)-H(19B)	0.9800
C(19)-H(19C)	0.9800
C(20)-H(20A)	0.9800
C(20)-H(20B)	0.9800
C(20)-H(20C)	0.9800
C(21)-H(21A)	0.9800
C(21)-H(21B)	0.9800
C(21)-H(21C)	0.9800
C(22)-H(22A)	0.9800
C(22)-H(22B)	0.9800
C(22)-H(22C)	0.9800
C(23)-H(23A)	0.9800
C(23)-H(23B)	0.9800
C(23)-H(23C)	0.9800
N(1)-Fe(1)-N(2)	95.12(7)
N(1)-Fe(1)-S(1)	84.71(6)
N(2)-Fe(1)-S(1)	151.92(6)
N(1)-Fe(1)-S(2)	161.81(6)

Table S–21 (cont). Bond lengths [A] and angles [deg] for $(NMe_4)_2[Fe^{III}(tame\text{–}N_2S_3)]\bullet MeCN$ (**15**).

N(2)-Fe(1)-S(2)	84.78(6)
S(1)-Fe(1)-S(2)	86.91(2)
N(1)-Fe(1)-S(3)	88.48(6)
N(2)-Fe(1)-S(3)	90.85(6)
S(1)-Fe(1)-S(3)	117.19(2)
S(2)-Fe(1)-S(3)	109.72(3)
C(1)-S(1)-Fe(1)	101.75(7)
C(7)-S(2)-Fe(1)	100.46(7)
C(10)-S(3)-Fe(1)	96.33(8)
C(2)-N(1)-C(3)	113.10(18)
C(2)-N(1)-Fe(1)	124.01(14)
C(3)-N(1)-Fe(1)	120.86(15)
C(6)-N(2)-C(5)	114.92(19)
C(6)-N(2)-Fe(1)	123.13(15)
C(5)-N(2)-Fe(1)	119.59(14)
C(17)-N(4)-C(16)	110.15(18)
C(17)-N(4)-C(18)	108.90(18)
C(16)-N(4)-C(18)	109.06(17)
C(17)-N(4)-C(19)	109.41(18)
C(16)-N(4)-C(19)	109.40(18)
C(18)-N(4)-C(19)	109.91(19)
C(22)-N(5)-C(23)	108.63(18)
C(22)-N(5)-C(20)	109.71(18)
C(23)-N(5)-C(20)	109.80(17)
C(22)-N(5)-C(21)	110.07(18)
C(23)-N(5)-C(21)	109.48(17)
C(20)-N(5)-C(21)	109.13(17)
C(2)-C(1)-C(9)	111.02(18)
C(2)-C(1)-C(8)	106.74(18)
C(9)-C(1)-C(8)	109.6(2)
C(2)-C(1)-S(1)	109.96(16)
C(9)-C(1)-S(1)	109.44(16)
C(8)-C(1)-S(1)	110.07(15)
O(5)-C(2)-N(1)	124.6(2)
O(5)-C(2)-C(1)	117.9(2)
N(1)-C(2)-C(1)	117.32(19)
N(1)-C(3)-C(4)	114.98(19)
N(1)-C(3)-H(3A)	108.5
C(4)-C(3)-H(3A)	108.5
N(1)-C(3)-H(3B)	108.5
C(4)-C(3)-H(3B)	108.5
H(3A)-C(3)-H(3B)	107.5
C(3)-C(4)-C(5)	111.1(2)
C(3)-C(4)-C(11)	105.95(19)

Table S–21 (cont). Bond lengths [A] and angles [deg] for $(NMe_4)_2[Fe^{III}(tame–N_2S_3)]\bullet MeCN$ (**15**).

C(5)-C(4)-C(11)	106.72(18)
C(3)-C(4)-C(10)	113.2(2)
C(5)-C(4)-C(10)	111.6(2)
C(11)-C(4)-C(10)	107.84(19)
N(2)-C(5)-C(4)	112.03(18)
N(2)-C(5)-H(5A)	109.2
C(4)-C(5)-H(5A)	109.2
N(2)-C(5)-H(5B)	109.2
C(4)-C(5)-H(5B)	109.2
H(5A)-C(5)-H(5B)	107.9
O(8)-C(6)-N(2)	125.3(2)
O(8)-C(6)-C(7)	117.7(2)
N(2)-C(6)-C(7)	117.0(2)
C(13)-C(7)-C(12)	110.5(2)
C(13)-C(7)-C(6)	109.55(19)
C(12)-C(7)-C(6)	106.77(19)
C(13)-C(7)-S(2)	110.74(17)
C(12)-C(7)-S(2)	109.32(16)
C(6)-C(7)-S(2)	109.84(16)
C(1)-C(8)-H(8A)	109.5
C(1)-C(8)-H(8B)	109.5
H(8A)-C(8)-H(8B)	109.5
C(1)-C(8)-H(8C)	109.5
H(8A)-C(8)-H(8C)	109.5
H(8B)-C(8)-H(8C)	109.5
C(1)-C(9)-H(9A)	109.5
C(1)-C(9)-H(9B)	109.5
H(9A)-C(9)-H(9B)	109.5
C(1)-C(9)-H(9C)	109.5
H(9A)-C(9)-H(9C)	109.5
H(9B)-C(9)-H(9C)	109.5
C(4)-C(10)-S(3)	120.04(17)
C(4)-C(10)-H(10A)	107.3
S(3)-C(10)-H(10A)	107.3
C(4)-C(10)-H(10B)	107.3
S(3)-C(10)-H(10B)	107.3
H(10A)-C(10)-H(10B)	106.9
C(4)-C(11)-H(11A)	109.5
C(4)-C(11)-H(11B)	109.5
H(11A)-C(11)-H(11B)	109.5
C(4)-C(11)-H(11C)	109.5
H(11A)-C(11)-H(11C)	109.5
H(11B)-C(11)-H(11C)	109.5
C(7)-C(12)-H(12A)	109.5
C(7)-C(12)-H(12B)	109.5

Table S–21 (cont). Bond lengths [A] and angles [deg] for $(NMe_4)_2[Fe^{III}(tame–N_2S_3)]$•MeCN (**15**).

H(12A)-C(12)-H(12B)	109.5
C(7)-C(12)-H(12C)	109.5
H(12A)-C(12)-H(12C)	109.5
H(12B)-C(12)-H(12C)	109.5
C(7)-C(13)-H(13A)	109.5
C(7)-C(13)-H(13B)	109.5
H(13A)-C(13)-H(13B)	109.5
C(7)-C(13)-H(13C)	109.5
H(13A)-C(13)-H(13C)	109.5
H(13B)-C(13)-H(13C)	109.5
N(3)-C(14)-C(15)	179.6(3)
C(14)-C(15)-H(15A)	109.5
C(14)-C(15)-H(15B)	109.5
H(15A)-C(15)-H(15B)	109.5
C(14)-C(15)-H(15C)	109.5
H(15A)-C(15)-H(15C)	109.5
H(15B)-C(15)-H(15C)	109.5
N(4)-C(16)-H(16A)	109.5
N(4)-C(16)-H(16B)	109.5
H(16A)-C(16)-H(16B)	109.5
N(4)-C(16)-H(16C)	109.5
H(16A)-C(16)-H(16C)	109.5
H(16B)-C(16)-H(16C)	109.5
N(4)-C(17)-H(17A)	109.5
N(4)-C(17)-H(17B)	109.5
H(17A)-C(17)-H(17B)	109.5
N(4)-C(17)-H(17C)	109.5
H(17A)-C(17)-H(17C)	109.5
H(17B)-C(17)-H(17C)	109.5
N(4)-C(18)-H(18A)	109.5
N(4)-C(18)-H(18B)	109.5
H(18A)-C(18)-H(18B)	109.5
N(4)-C(18)-H(18C)	109.5
H(18A)-C(18)-H(18C)	109.5
H(18B)-C(18)-H(18C)	109.5
N(4)-C(19)-H(19A)	109.5
N(4)-C(19)-H(19B)	109.5
H(19A)-C(19)-H(19B)	109.5
N(4)-C(19)-H(19C)	109.5
H(19A)-C(19)-H(19C)	109.5
H(19B)-C(19)-H(19C)	109.5
N(5)-C(20)-H(20A)	109.5
N(5)-C(20)-H(20B)	109.5
H(20A)-C(20)-H(20B)	109.5
N(5)-C(20)-H(20C)	109.5

Table S–21 (cont). Bond lengths [A] and angles [deg] for $(NMe_4)_2[Fe^{III}(tame–N_2S_3)]\bullet MeCN$ (**15**).

H(20A)-C(20)-H(20C)	109.5
H(20B)-C(20)-H(20C)	109.5
N(5)-C(21)-H(21A)	109.5
N(5)-C(21)-H(21B)	109.5
H(21A)-C(21)-H(21B)	109.5
N(5)-C(21)-H(21C)	109.5
H(21A)-C(21)-H(21C)	109.5
H(21B)-C(21)-H(21C)	109.5
N(5)-C(22)-H(22A)	109.5
N(5)-C(22)-H(22B)	109.5
H(22A)-C(22)-H(22B)	109.5
N(5)-C(22)-H(22C)	109.5
H(22A)-C(22)-H(22C)	109.5
H(22B)-C(22)-H(22C)	109.5
N(5)-C(23)-H(23A)	109.5
N(5)-C(23)-H(23B)	109.5
H(23A)-C(23)-H(23B)	109.5
N(5)-C(23)-H(23C)	109.5
H(23A)-C(23)-H(23C)	109.5
H(23B)-C(23)-H(23C)	109.5

Table S–22. Anisotropic displacement parameters (A^2 x 10^3) for $(NMe_4)_2$[Fe(III)(N_2S–tame)S_2^{Me2})]•MeCN (**15**). The anisotropic displacement factor exponent takes the form: -2 pi^2 [h^2 a*^2 U11 + ... + 2 h k a* b* U12]

	U11	U22	U33	U23	U13	U12
Fe(1)	28(1)	28(1)	22(1)	-1(1)	1(1)	-1(1)
S(1)	34(1)	32(1)	22(1)	-1(1)	0(1)	4(1)
S(2)	38(1)	32(1)	24(1)	-2(1)	-2(1)	6(1)
S(3)	34(1)	37(1)	38(1)	-5(1)	7(1)	-8(1)
O(5)	38(1)	36(1)	27(1)	1(1)	-4(1)	7(1)
O(8)	42(1)	42(1)	26(1)	-6(1)	-7(1)	4(1)
N(1)	32(1)	30(1)	26(1)	-4(1)	-1(1)	4(1)
N(2)	28(1)	30(1)	27(1)	-2(1)	0(1)	0(1)
N(3)	44(1)	53(1)	35(1)	0(1)	-1(1)	-1(1)
N(4)	31(1)	31(1)	28(1)	1(1)	-1(1)	1(1)
N(5)	31(1)	29(1)	28(1)	1(1)	3(1)	0(1)
C(1)	35(1)	31(1)	22(1)	-1(1)	1(1)	2(1)
C(2)	25(1)	31(1)	28(1)	-1(1)	0(1)	-2(1)
C(3)	47(2)	45(1)	28(2)	-8(1)	-4(1)	15(1)
C(4)	28(1)	35(1)	27(1)	-6(1)	0(1)	3(1)
C(5)	31(1)	32(1)	35(2)	-6(1)	0(1)	3(1)
C(6)	29(1)	34(1)	24(1)	0(1)	5(1)	-3(1)
C(7)	38(1)	33(1)	23(1)	-2(1)	-2(1)	4(1)
C(8)	37(1)	37(1)	45(2)	-4(1)	-12(1)	-1(1)
C(9)	49(2)	42(1)	24(1)	2(1)	2(1)	7(1)
C(10)	40(1)	46(1)	51(2)	-12(1)	15(1)	-8(1)
C(11)	33(1)	44(1)	36(2)	-10(1)	-1(1)	7(1)
C(12)	59(2)	37(1)	27(2)	4(1)	-2(1)	1(1)
C(13)	42(2)	45(1)	36(2)	-4(1)	-8(1)	10(1)
C(14)	32(1)	46(1)	40(2)	-3(1)	-6(1)	4(1)
C(15)	41(2)	70(2)	47(2)	18(1)	-7(1)	1(1)
C(16)	33(1)	36(1)	38(2)	-4(1)	-1(1)	5(1)
C(17)	42(1)	43(1)	26(1)	-2(1)	4(1)	-3(1)
C(18)	35(1)	44(1)	29(1)	-6(1)	-4(1)	2(1)
C(19)	44(2)	32(1)	48(2)	11(1)	8(1)	4(1)
C(20)	28(1)	38(1)	40(2)	1(1)	1(1)	0(1)
C(21)	39(1)	30(1)	48(2)	-1(1)	3(1)	3(1)
C(22)	49(2)	47(1)	27(2)	0(1)	4(1)	-6(1)
C(23)	32(1)	31(1)	35(2)	2(1)	3(1)	-1(1)

Table S–23. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (A^2 x 10^3) for $(NMe_4)_2$[Fe(III)(N_2S–tame)S_2^{Me2})]•MeCN (**15**).

	x	y	z	U(eq)
H(3A)	304	1617	2974	48
H(3B)	968	2285	2975	48
H(5A)	1868	2187	3775	39
H(5B)	1650	1794	4428	39
H(8A)	353	-42	1365	48
H(8B)	427	-519	2015	48
H(8C)	838	-914	1434	48
H(9A)	1338	895	962	46
H(9B)	1819	14	949	46
H(9C)	2105	887	1288	46
H(10A)	-11	826	4000	55
H(10B)	638	695	4460	55
H(11A)	-17	2427	3860	45
H(11B)	725	2945	3946	45
H(11C)	422	2330	4483	45
H(12A)	2489	-737	5100	49
H(12B)	2659	-1554	4656	49
H(12C)	1934	-1001	4575	49
H(13A)	3670	18	4802	49
H(13B)	3859	103	4093	49
H(13C)	3828	-856	4408	49
H(15A)	3406	2993	-45	63
H(15B)	3953	2210	-209	63
H(15C)	4219	3047	182	63
H(16A)	2379	3419	1421	43
H(16B)	2165	3122	744	43
H(16C)	1941	2518	1314	43
H(17A)	649	4014	1907	44
H(17B)	1468	3962	2118	44
H(17C)	1015	3068	2028	44
H(18A)	315	3509	877	43
H(18B)	676	2572	1035	43
H(18C)	918	3106	439	43
H(19A)	965	4866	976	50
H(19B)	1627	4532	573	50
H(19C)	1757	4883	1254	50
H(20A)	2773	2739	2736	42
H(20B)	2601	1705	2822	42
H(20C)	2915	2058	2188	42

H(21A)	3581	626	2887	47
H(21B)	4392	959	2837	47
H(21C)	3883	985	2250	47
H(22A)	3549	2711	3635	49
H(22B)	4175	1988	3681	49
H(22C)	3356	1682	3724	49
H(23A)	4023	3245	2693	39
H(23B)	4149	2583	2131	39
H(23C)	4657	2529	2718	39

Table S-24. Crystal data and structure refinement for [Fe(II)(tame–N_3)S_2^{Me2})(CO)]•MeCN (**16**).

Compound	C16 H29 Fe N3 O S2 * CH3CN
Empirical formula	C18 H32 Fe N4 O S2
Formula weight	440.45
Temperature	161(2) K
Wavelength	0.71070 A
Crystal description/color	plate/red
Crystal system, space group	Triclinic, P -1 (No. 2)
Unit cell dimensions	a = 9.8660(2) A alpha = 69.9776(14) deg.
	b = 10.6971(2) A beta = 75.4115(13) deg.
	c = 12.0377(3) A gamma = 68.5081(15) deg.
Volume	1098.97(4) A^3
Z, Calculated density	2, 1.331 Mg/m^3
Absorption coefficient	0.890 mm^-1
F(000)	468
Crystal size	0.24 x 0.23 x 0.09 mm
Reflections for indexing	220
Theta range for data collection	2.13 to 30.51 deg.
Index ranges	-13<=h<=14, -14<=k<=15, -17<=l<=17
Reflections collected / unique	33204 / 6233 [R(int) = 0.0335]
Completeness to 2theta = 30.51	92.7%
Absorption correction	Scalepack
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	6233 / 0 / 235
Goodness-of-fit on F^2	1.090
Final R indices [I>2sigma(I)]	*R1 = 0.0446, wR2 = 0.1136
R indices (all data)	R1 = 0.0668, *wR2 = 0.1256
*Report these R factors	
Weighting scheme	calc w=1/[\s^2^(Fo^2^)+ (0.0703P)^2^+0.0000P]
	where P=(Fo^2^+2Fc^2^)/3
Largest diff. peak and hole	0.690 and -0.857 e.A^-3

Table S-25. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (A^2 x 10^3) for [Fe(II)(tame–N_3)S_2^{Me2})(CO)]•MeCN (**16**). U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

	x	y	z	U(eq)
C(1)	4227(3)	-783(3)	-2380(2)	33(1)
C(2)	4688(3)	-2243(3)	-3759(2)	34(1)
C(3)	3484(2)	-1352(2)	-3000(2)	21(1)
C(4)	2582(2)	-2224(2)	-2078(2)	19(1)
C(5)	3404(3)	-3643(2)	-1331(2)	28(1)
C(6)	-2615(3)	3729(2)	-2258(2)	29(1)
C(7)	-4067(2)	3581(2)	-3624(2)	30(1)
C(8)	-2765(2)	2783(2)	-2911(2)	20(1)
C(9)	-3005(2)	1463(2)	-2014(2)	20(1)
C(10)	-4497(3)	1582(2)	-1256(2)	30(1)
C(11)	330(2)	-2692(2)	-1164(2)	21(1)
C(12)	-2264(2)	-999(2)	-1154(2)	20(1)
C(13)	-1069(2)	-2063(2)	-2889(2)	21(1)
C(14)	-1188(2)	-2284(2)	-1533(2)	19(1)
C(15)	-1804(3)	-3513(2)	-874(2)	28(1)
C(16)	515(2)	941(2)	-1952(2)	23(1)
C(17)	1769(3)	3835(3)	-4176(2)	39(1)
C(18)	1898(3)	4130(3)	-3125(2)	34(1)
Fe(1)	74(1)	169(1)	-2799(1)	15(1)
O(1)	826(2)	1436(2)	-1370(2)	40(1)
S(1)	2276(1)	98(1)	-4002(1)	19(1)
S(2)	-1096(1)	2294(1)	-3971(1)	19(1)
N(1)	1172(2)	-1755(2)	-1944(2)	17(1)
N(2)	-1951(2)	299(2)	-1912(1)	17(1)
N(3)	-466(2)	-909(2)	-3672(1)	16(1)
N(4)	2009(3)	4368(3)	-2311(3)	57(1)

Table S-26. Bond lengths [A] and angles [deg] for [Fe(II)(tame–N_3)S_2^{Me2})(CO)]•MeCN (**16**).

C(1)-C(3)	1.543(3)
C(1)-H(1A)	0.9436
C(1)-H(1B)	0.9647
C(1)-H(1C)	0.9489
C(2)-C(3)	1.541(3)
C(2)-H(2A)	0.9296
C(2)-H(2B)	0.9326
C(2)-H(2C)	1.0046
C(3)-C(4)	1.515(3)
C(3)-S(1)	1.835(2)
C(4)-N(1)	1.282(3)
C(4)-C(5)	1.518(3)
C(5)-H(5A)	0.8992
C(5)-H(5B)	1.0058
C(5)-H(5C)	0.9630
C(6)-C(8)	1.542(3)
C(6)-H(6A)	0.9278
C(6)-H(6B)	0.9793
C(6)-H(6C)	0.9920
C(7)-C(8)	1.538(3)
C(7)-H(7A)	0.9329
C(7)-H(7B)	0.9483
C(7)-H(7C)	0.9762
C(8)-C(9)	1.513(3)
C(8)-S(2)	1.838(2)
C(9)-N(2)	1.287(3)
C(9)-C(10)	1.511(3)
C(10)-H(10A)	0.9507
C(10)-H(10B)	0.9647
C(10)-H(10C)	0.9550
C(11)-N(1)	1.466(3)
C(11)-C(14)	1.535(3)
C(11)-H(11A)	0.9521
C(11)-H(11B)	0.9555
C(12)-N(2)	1.470(3)
C(12)-C(14)	1.530(3)
C(12)-H(12A)	0.9544
C(12)-H(12B)	0.9798
C(13)-N(3)	1.491(3)
C(13)-C(14)	1.547(3)

C(13)-H(13A)	1.0015
C(13)-H(13B)	0.9482
C(14)-C(15)	1.535(3)
C(15)-H(15A)	0.9547
C(15)-H(15B)	0.9438
C(15)-H(15C)	1.0123
C(16)-O(1)	1.160(3)
C(16)-Fe(1)	1.725(2)
C(17)-C(18)	1.450(4)
C(17)-H(17A)	1.0100
C(17)-H(17B)	1.0100
C(17)-H(17C)	1.0100
C(18)-N(4)	1.133(4)
Fe(1)-N(1)	1.9866(16)
Fe(1)-N(2)	1.9933(17)
Fe(1)-N(3)	2.0680(17)
Fe(1)-S(2)	2.2777(5)
Fe(1)-S(1)	2.2790(6)
N(3)-H(3N)	1.0101
N(3)-H(3NB)	1.0100
C(3)-C(1)-H(1A)	108.7
C(3)-C(1)-H(1B)	108.2
H(1A)-C(1)-H(1B)	109.3
C(3)-C(1)-H(1C)	108.9
H(1A)-C(1)-H(1C)	112.0
H(1B)-C(1)-H(1C)	109.6
C(3)-C(2)-H(2A)	109.3
C(3)-C(2)-H(2B)	109.4
H(2A)-C(2)-H(2B)	114.8
C(3)-C(2)-H(2C)	106.0
H(2A)-C(2)-H(2C)	108.0
H(2B)-C(2)-H(2C)	109.0
C(4)-C(3)-C(2)	110.33(19)
C(4)-C(3)-C(1)	110.29(18)
C(2)-C(3)-C(1)	108.69(19)
C(4)-C(3)-S(1)	109.14(14)
C(2)-C(3)-S(1)	108.12(15)
C(1)-C(3)-S(1)	110.25(15)
N(1)-C(4)-C(3)	120.14(18)
N(1)-C(4)-C(5)	122.1(2)
C(3)-C(4)-C(5)	117.76(18)
C(4)-C(5)-H(5A)	110.0
C(4)-C(5)-H(5B)	106.9
H(5A)-C(5)-H(5B)	111.4
C(4)-C(5)-H(5C)	108.0
H(5A)-C(5)-H(5C)	114.1
H(5B)-C(5)-H(5C)	106.1
C(8)-C(6)-H(6A)	111.9

C(8)-C(6)-H(6B)	110.7
H(6A)-C(6)-H(6B)	110.8
C(8)-C(6)-H(6C)	109.8
H(6A)-C(6)-H(6C)	108.4
H(6B)-C(6)-H(6C)	105.0
C(8)-C(7)-H(7A)	107.8
C(8)-C(7)-H(7B)	108.6
H(7A)-C(7)-H(7B)	112.7
C(8)-C(7)-H(7C)	107.0
H(7A)-C(7)-H(7C)	110.5
H(7B)-C(7)-H(7C)	110.2
C(9)-C(8)-C(7)	110.25(19)
C(9)-C(8)-C(6)	109.86(17)
C(7)-C(8)-C(6)	109.32(18)
C(9)-C(8)-S(2)	108.62(13)
C(7)-C(8)-S(2)	107.88(15)
C(6)-C(8)-S(2)	110.89(16)
N(2)-C(9)-C(10)	122.6(2)
N(2)-C(9)-C(8)	119.88(19)
C(10)-C(9)-C(8)	117.52(17)
C(9)-C(10)-H(10A)	108.3
C(9)-C(10)-H(10B)	108.5
H(10A)-C(10)-H(10B)	109.4
C(9)-C(10)-H(10C)	109.0
H(10A)-C(10)-H(10C)	111.4
H(10B)-C(10)-H(10C)	110.1
N(1)-C(11)-C(14)	111.86(16)
N(1)-C(11)-H(11A)	112.3
C(14)-C(11)-H(11A)	105.0
N(1)-C(11)-H(11B)	111.1
C(14)-C(11)-H(11B)	105.8
H(11A)-C(11)-H(11B)	110.4
N(2)-C(12)-C(14)	112.08(16)
N(2)-C(12)-H(12A)	110.0
C(14)-C(12)-H(12A)	108.3
N(2)-C(12)-H(12B)	109.7
C(14)-C(12)-H(12B)	108.4
H(12A)-C(12)-H(12B)	108.3
N(3)-C(13)-C(14)	114.75(17)
N(3)-C(13)-H(13A)	110.0
C(14)-C(13)-H(13A)	106.1
N(3)-C(13)-H(13B)	112.1
C(14)-C(13)-H(13B)	107.5
H(13A)-C(13)-H(13B)	105.8
C(12)-C(14)-C(11)	111.68(18)
C(12)-C(14)-C(15)	107.55(18)
C(11)-C(14)-C(15)	107.18(17)
C(12)-C(14)-C(13)	111.26(16)

C(11)-C(14)-C(13)	111.40(17)
C(15)-C(14)-C(13)	107.51(18)
C(14)-C(15)-H(15A)	111.6
C(14)-C(15)-H(15B)	112.6
H(15A)-C(15)-H(15B)	111.2
C(14)-C(15)-H(15C)	110.2
H(15A)-C(15)-H(15C)	105.5
H(15B)-C(15)-H(15C)	105.3
O(1)-C(16)-Fe(1)	178.71(19)
C(18)-C(17)-H(17A)	109.5
C(18)-C(17)-H(17B)	109.5
H(17A)-C(17)-H(17B)	109.5
C(18)-C(17)-H(17C)	109.5
H(17A)-C(17)-H(17C)	109.5
H(17B)-C(17)-H(17C)	109.5
N(4)-C(18)-C(17)	179.3(3)
C(16)-Fe(1)-N(1)	93.59(8)
C(16)-Fe(1)-N(2)	94.93(9)
N(1)-Fe(1)-N(2)	100.47(7)
C(16)-Fe(1)-N(3)	174.65(9)
N(1)-Fe(1)-N(3)	82.06(7)
N(2)-Fe(1)-N(3)	82.85(7)
C(16)-Fe(1)-S(2)	91.53(7)
N(1)-Fe(1)-S(2)	173.55(5)
N(2)-Fe(1)-S(2)	82.97(5)
N(3)-Fe(1)-S(2)	93.03(5)
C(16)-Fe(1)-S(1)	89.74(8)
N(1)-Fe(1)-S(1)	83.48(5)
N(2)-Fe(1)-S(1)	173.65(5)
N(3)-Fe(1)-S(1)	92.86(5)
S(2)-Fe(1)-S(1)	92.63(2)
C(3)-S(1)-Fe(1)	99.03(7)
C(8)-S(2)-Fe(1)	98.96(7)
C(4)-N(1)-C(11)	118.80(17)
C(4)-N(1)-Fe(1)	122.79(15)
C(11)-N(1)-Fe(1)	118.37(12)
C(9)-N(2)-C(12)	118.87(18)
C(9)-N(2)-Fe(1)	122.69(15)
C(12)-N(2)-Fe(1)	118.38(12)
C(13)-N(3)-Fe(1)	115.87(12)
C(13)-N(3)-H(3N)	108.3
Fe(1)-N(3)-H(3N)	108.3
C(13)-N(3)-H(3NB)	108.3
Fe(1)-N(3)-H(3NB)	108.4
H(3N)-N(3)-H(3NB)	107.4

Table S-27. Anisotropic displacement parameters (A^2 x 10^3) for [Fe(II)(tame–N_3)S_2^{Me2})(CO)]•MeCN (**16**). The anisotropic displacement factor exponent takes the form: -2 pi^2 [h^2 a*^2 U11 + ... + 2 h k a* b* U12]

	U11	U22	U33	U23	U13	U12
C(1)	27(1)	32(1)	43(1)	-6(1)	-14(1)	10(1)
C(2)	23(1)	29(1)	37(1)	-8(1)	1(1)	1(1)
C(3)	14(1)	23(1)	25(1)	-6(1)	-5(1)	-3(1)
C(4)	19(1)	21(1)	20(1)	-7(1)	-7(1)	-4(1)
C(5)	22(1)	23(1)	34(1)	-3(1)	-9(1)	-1(1)
C(6)	30(1)	23(1)	33(1)	-15(1)	-2(1)	-3(1)
C(7)	21(1)	29(1)	32(1)	-5(1)	-6(1)	-1(1)
C(8)	17(1)	18(1)	22(1)	-7(1)	-1(1)	-2(1)
C(9)	18(1)	22(1)	20(1)	-8(1)	-2(1)	-5(1)
C(10)	23(1)	28(1)	32(1)	-8(1)	5(1)	-5(1)
C(11)	21(1)	19(1)	19(1)	-1(1)	-5(1)	-4(1)
C(12)	19(1)	22(1)	17(1)	-2(1)	-1(1)	-8(1)
C(13)	26(1)	19(1)	21(1)	-4(1)	-4(1)	-11(1)
C(14)	19(1)	17(1)	20(1)	-2(1)	-3(1)	-7(1)
C(15)	28(1)	23(1)	30(1)	1(1)	-3(1)	-13(1)
C(16)	21(1)	22(1)	24(1)	-8(1)	-4(1)	-3(1)
C(17)	48(2)	36(1)	41(2)	-9(1)	-9(1)	-21(1)
C(18)	26(1)	31(1)	46(2)	-15(1)	-4(1)	-8(1)
Fe(1)	14(1)	15(1)	16(1)	-5(1)	-3(1)	-4(1)
O(1)	44(1)	42(1)	45(1)	-26(1)	-17(1)	-9(1)
S(1)	16(1)	21(1)	21(1)	-4(1)	-2(1)	-6(1)
S(2)	19(1)	15(1)	19(1)	-4(1)	-1(1)	-4(1)
N(1)	17(1)	17(1)	18(1)	-5(1)	-5(1)	-5(1)
N(2)	17(1)	18(1)	16(1)	-6(1)	-2(1)	-5(1)
N(3)	16(1)	16(1)	16(1)	-3(1)	-2(1)	-5(1)
N(4)	60(2)	64(2)	58(2)	-34(2)	-7(1)	-18(1)

Table S-28. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (A^2 x 10^3) for [Fe(II)(tame N_3)S_2^{Me2})(CO)]•MeCN (**16**).

	x	y	z	U(eq)
H(1A)	4823	-1545	-1857	50
H(1B)	3466	-205	-1925	50
H(1C)	4781	-237	-2972	50
H(2A)	5278	-3013	-3260	51
H(2B)	5192	-1679	-4355	51
H(2C)	4158	-2593	-4142	51
H(5A)	4380	-3810	-1558	43
H(5B)	3059	-4355	-1455	43
H(5C)	3085	-3663	-502	43
H(6A)	-3444	3974	-1711	43
H(6B)	-2405	4564	-2832	43
H(6C)	-1750	3237	-1825	43
H(7A)	-4909	3848	-3088	45
H(7B)	-4146	2991	-4024	45
H(7C)	-3844	4403	-4204	45
H(10A)	-5093	2532	-1469	45
H(10B)	-4369	1303	-428	45
H(10C)	-4920	982	-1389	45
H(11A)	800	-3633	-1198	23
H(11B)	143	-2647	-358	23
H(12A)	-2200	-1128	-342	22
H(12B)	-3264	-940	-1200	22
H(13A)	-2089	-1867	-3042	23
H(13B)	-512	-2932	-3050	23
H(15A)	-1945	-3677	-28	42
H(15B)	-1226	-4337	-1097	42
H(15C)	-2813	-3291	-1085	42
H(17A)	1796	4669	-4893	59
H(17B)	806	3638	-4051	59
H(17C)	2613	2992	-4318	59
H(3N)	-1216	-219	-4206	18
H(3NB)	444	-1316	-4203	18

Table S-29. Crystal data and structure refinement [Fe(III)(tame—N_3)S_2^{Me2})(NO)](PF_6)•MeCN (**18**).

Compound	C15 H29 Fe N4 O S2^+^ PF6 *C2H3N
Empirical formula	C17 H32 F6 Fe N5 O P S2
Formula weight	587.42
Temperature	161(2) K
Wavelength	0.71070 A
Crystal description/color	plate/orange
Crystal system, space group	Monoclinic, P 21/c (No. 14)
Unit cell dimensions	a = 11.8332(4) A alpha = 90 deg.
	b = 16.5201(6) A beta = 106.7848(18) deg.
	c = 13.3947(3) A gamma = 90 deg.
Volume	2506.91(14) A^3
Z, Calculated density	4, 1.556 Mg/m^3
Absorption coefficient	0.897 mm^-1
F(000)	1216
Crystal size	0.25 x 0.20 x 0.13 mm
Reflections for indexing	1416
Theta range for data collection	2.18 to 30.49 deg.
Index ranges	-16<=h<=16, -21<=k<=23, -19<=l<=19
Reflections collected / unique	46749 / 7487 [R(int) = 0.0668]
Completeness to 2theta = 30.49	95.2%
Absorption correction	None
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	7487 / 0 / 298
Goodness-of-fit on F^2	1.057
Final R indices [I>2sigma(I)]	*R1 = 0.0503, wR2 = 0.1324
R indices (all data)	R1 = 0.0794, *wR2 = 0.1508
*Report these R factors	
Weighting scheme calc w=1/[\s^2^(Fo^2^)+(0.0792P)^2^+0.3100P] where P=(Fo^2^+2Fc^2^)/3	
Largest diff. peak and hole	0.757 and -0.991 e.A^-3

Table S-30. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (A^2 x 10^3) for [Fe(III)(tame—N_3)S_2^{Me2})(NO)](PF_6)•MeCN (**18**). U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

	x	y	z	U(eq)
C(1)	9644(2)	2166(2)	6259(2)	33(1)
C(2)	8871(3)	1078(2)	4926(2)	37(1)
C(3)	8554(2)	1847(2)	5427(2)	27(1)
C(4)	8069(2)	2490(2)	4604(2)	25(1)
C(5)	8917(2)	2913(2)	4136(2)	37(1)
C(6)	2302(3)	1483(2)	5237(2)	41(1)
C(7)	3041(3)	641(2)	3987(2)	36(1)
C(8)	3266(2)	1400(2)	4671(2)	26(1)
C(9)	3275(2)	2131(2)	3986(2)	24(1)
C(10)	2103(2)	2443(2)	3317(2)	35(1)
C(11)	6498(2)	3349(2)	3654(2)	27(1)
C(12)	4287(2)	3166(2)	3334(2)	24(1)
C(13)	5516(2)	3802(1)	5010(2)	25(1)
C(14)	5377(2)	3686(1)	3841(2)	23(1)
C(15)	5158(3)	4525(2)	3322(2)	30(1)
C(16)	2637(3)	1191(2)	1205(3)	44(1)
C(17)	1579(3)	699(2)	1054(3)	56(1)
Fe(1)	5813(1)	2003(1)	4841(1)	19(1)
F(1)	8695(2)	4265(1)	5909(1)	52(1)
F(2)	7722(2)	4186(1)	7128(2)	52(1)
F(3)	9716(2)	4283(2)	7619(2)	62(1)
F(4)	8605(2)	5336(2)	7866(2)	68(1)
F(5)	7590(2)	5317(1)	6141(2)	50(1)
F(6)	9575(2)	5416(1)	6636(2)	59(1)
N(1)	6959(2)	2659(1)	4336(2)	22(1)
N(2)	4264(2)	2438(1)	3963(1)	21(1)
N(3)	5744(2)	3037(1)	5643(2)	23(1)
N(4)	5860(2)	1229(1)	4092(2)	25(1)
N(5)	3472(3)	1571(2)	1348(3)	61(1)
P(1)	8656(1)	4803(1)	6897(1)	36(1)
S(1)	7442(1)	1623(1)	6108(1)	25(1)
S(2)	4694(1)	1349(1)	5684(1)	26(1)
O(1)	5902(2)	705(1)	3550(2)	48(1)

Table S-31. Bond lengths [A] and angles [deg] for [Fe(III)(tame–N_3)S_2^{Me2})(NO)](PF_6)•MeCN (**18**).

C(1)-C(3)	1.534(3)
C(1)-H(1A)	1.0768
C(1)-H(1B)	0.9150
C(1)-H(1C)	0.9437
C(2)-C(3)	1.534(4)
C(2)-H(2A)	0.9301
C(2)-H(2B)	0.8721
C(2)-H(2C)	0.9089
C(3)-C(4)	1.519(4)
C(3)-S(1)	1.841(3)
C(4)-N(1)	1.288(3)
C(4)-C(5)	1.501(4)
C(5)-H(5A)	0.9291
C(5)-H(5B)	1.0752
C(5)-H(5C)	1.0234
C(6)-C(8)	1.548(4)
C(6)-H(6A)	1.0314
C(6)-H(6B)	0.9155
C(6)-H(6C)	0.9594
C(7)-C(8)	1.531(4)
C(7)-H(7A)	1.0309
C(7)-H(7B)	1.0774
C(7)-H(7C)	0.8245
C(8)-C(9)	1.519(3)
C(8)-S(2)	1.838(3)
C(9)-N(2)	1.283(3)
C(9)-C(10)	1.507(3)
C(10)-H(10A)	1.0242
C(10)-H(10B)	0.9147
C(10)-H(10C)	0.8763
C(11)-N(1)	1.464(3)
C(11)-C(14)	1.525(3)
C(11)-H(11A)	0.9242
C(11)-H(11B)	0.9636
C(12)-N(2)	1.473(3)
C(12)-C(14)	1.535(3)
C(12)-H(12A)	0.9570
C(12)-H(12B)	0.9204
C(13)-N(3)	1.504(3)
C(13)-C(14)	1.538(3)

C(13)-H(13A)	0.9372
C(13)-H(13B)	0.8508
C(14)-C(15)	1.539(3)
C(15)-H(15A)	0.9761
C(15)-H(15B)	0.9461
C(15)-H(15C)	0.9764
C(16)-N(5)	1.139(4)
C(16)-C(17)	1.457(5)
C(17)-H(17A)	1.0100
C(17)-H(17B)	1.0100
C(17)-H(17C)	1.0100
Fe(1)-N(4)	1.636(2)
Fe(1)-N(1)	2.000(2)
Fe(1)-N(2)	2.0044(19)
Fe(1)-N(3)	2.032(2)
Fe(1)-S(2)	2.2499(7)
Fe(1)-S(1)	2.2586(7)
F(1)-P(1)	1.6057(18)
F(2)-P(1)	1.597(2)
F(3)-P(1)	1.596(2)
F(4)-P(1)	1.584(2)
F(5)-P(1)	1.612(2)
F(6)-P(1)	1.596(2)
N(3)-H(3A)	0.8861
N(3)-H(3B)	0.8548
N(4)-O(1)	1.140(3)
C(3)-C(1)-H(1A)	107.4
C(3)-C(1)-H(1B)	112.4
H(1A)-C(1)-H(1B)	106.1
C(3)-C(1)-H(1C)	110.7
H(1A)-C(1)-H(1C)	110.5
H(1B)-C(1)-H(1C)	109.6
C(3)-C(2)-H(2A)	113.5
C(3)-C(2)-H(2B)	110.6
H(2A)-C(2)-H(2B)	106.4
C(3)-C(2)-H(2C)	114.2
H(2A)-C(2)-H(2C)	109.9
H(2B)-C(2)-H(2C)	101.2
C(4)-C(3)-C(2)	110.5(2)
C(4)-C(3)-C(1)	110.4(2)
C(2)-C(3)-C(1)	110.0(2)
C(4)-C(3)-S(1)	109.02(17)
C(2)-C(3)-S(1)	110.53(19)
C(1)-C(3)-S(1)	106.35(17)
N(1)-C(4)-C(5)	122.2(2)
N(1)-C(4)-C(3)	119.7(2)

C(5)-C(4)-C(3)	118.1(2)
C(4)-C(5)-H(5A)	114.0
C(4)-C(5)-H(5B)	110.1
H(5A)-C(5)-H(5B)	103.6
C(4)-C(5)-H(5C)	106.2
H(5A)-C(5)-H(5C)	106.0
H(5B)-C(5)-H(5C)	117.1
C(8)-C(6)-H(6A)	108.2
C(8)-C(6)-H(6B)	108.6
H(6A)-C(6)-H(6B)	113.3
C(8)-C(6)-H(6C)	108.6
H(6A)-C(6)-H(6C)	117.4
H(6B)-C(6)-H(6C)	100.2
C(8)-C(7)-H(7A)	112.9
C(8)-C(7)-H(7B)	105.2
H(7A)-C(7)-H(7B)	108.6
C(8)-C(7)-H(7C)	111.5
H(7A)-C(7)-H(7C)	116.8
H(7B)-C(7)-H(7C)	100.4
C(9)-C(8)-C(7)	108.7(2)
C(9)-C(8)-C(6)	111.1(2)
C(7)-C(8)-C(6)	109.9(2)
C(9)-C(8)-S(2)	108.52(16)
C(7)-C(8)-S(2)	111.60(18)
C(6)-C(8)-S(2)	107.04(18)
N(2)-C(9)-C(10)	122.7(2)
N(2)-C(9)-C(8)	119.6(2)
C(10)-C(9)-C(8)	117.7(2)
C(9)-C(10)-H(10A)	104.5
C(9)-C(10)-H(10B)	107.3
H(10A)-C(10)-H(10B)	111.7
C(9)-C(10)-H(10C)	107.5
H(10A)-C(10)-H(10C)	115.1
H(10B)-C(10)-H(10C)	110.2
N(1)-C(11)-C(14)	111.51(19)
N(1)-C(11)-H(11A)	117.6
C(14)-C(11)-H(11A)	107.6
N(1)-C(11)-H(11B)	104.9
C(14)-C(11)-H(11B)	119.6
H(11A)-C(11)-H(11B)	95.2
N(2)-C(12)-C(14)	110.87(19)
N(2)-C(12)-H(12A)	106.4
C(14)-C(12)-H(12A)	109.1
N(2)-C(12)-H(12B)	108.0
C(14)-C(12)-H(12B)	102.3
H(12A)-C(12)-H(12B)	120.0
N(3)-C(13)-C(14)	114.74(19)

N(3)-C(13)-H(13A)	103.0
C(14)-C(13)-H(13A)	113.7
N(3)-C(13)-H(13B)	115.8
C(14)-C(13)-H(13B)	107.2
H(13A)-C(13)-H(13B)	101.7
C(11)-C(14)-C(12)	112.5(2)
C(11)-C(14)-C(13)	111.7(2)
C(12)-C(14)-C(13)	110.4(2)
C(11)-C(14)-C(15)	107.2(2)
C(12)-C(14)-C(15)	107.1(2)
C(13)-C(14)-C(15)	107.58(19)
C(14)-C(15)-H(15A)	110.3
C(14)-C(15)-H(15B)	110.0
H(15A)-C(15)-H(15B)	110.6
C(14)-C(15)-H(15C)	108.6
H(15A)-C(15)-H(15C)	101.2
H(15B)-C(15)-H(15C)	115.8
N(5)-C(16)-C(17)	178.4(4)
C(16)-C(17)-H(17A)	109.5
C(16)-C(17)-H(17B)	109.5
H(17A)-C(17)-H(17B)	109.5
C(16)-C(17)-H(17C)	109.5
H(17A)-C(17)-H(17C)	109.5
H(17B)-C(17)-H(17C)	109.5
N(4)-Fe(1)-N(1)	94.05(9
N(4)-Fe(1)-N(2)	96.18(9)
N(1)-Fe(1)-N(2)	101.66(8)
N(4)-Fe(1)-N(3)	174.21(9)
N(1)-Fe(1)-N(3)	81.84(8)
N(2)-Fe(1)-N(3)	80.74(8)
N(4)-Fe(1)-S(2)	93.48(8)
N(1)-Fe(1)-S(2)	170.03(6)
N(2)-Fe(1)-S(2)	83.99(6)
N(3)-Fe(1)-S(2)	91.08(6)
N(4)-Fe(1)-S(1)	94.06(8)
N(1)-Fe(1)-S(1)	83.69(6)
N(2)-Fe(1)-S(1)	168.05(6)
N(3)-Fe(1)-S(1)	89.56(6)
S(2)-Fe(1)-S(1)	89.28(2)
C(4)-N(1)-C(11)	120.6(2)
C(4)-N(1)-Fe(1)	121.60(17)
C(11)-N(1)-Fe(1)	117.77(16)
C(9)-N(2)-C(12)	120.3(2)
C(9)-N(2)-Fe(1)	122.02(17)
C(12)-N(2)-Fe(1)	117.59(15)
C(13)-N(3)-Fe(1)	115.87(14)
C(13)-N(3)-H(3A)	110.6

Fe(1)-N(3)-H(3A)	110.1
C(13)-N(3)-H(3B)	104.0
Fe(1)-N(3)-H(3B)	105.4
H(3A)-N(3)-H(3B)	110.5
O(1)-N(4)-Fe(1)	178.0(2)
F(4)-P(1)-F(3)	90.66(13)
F(4)-P(1)-F(6)	90.91(12)
F(3)-P(1)-F(6)	90.53(13)
F(4)-P(1)-F(2)	90.19(12)
F(3)-P(1)-F(2)	90.29(12)
F(6)-P(1)-F(2)	178.63(11)
F(4)-P(1)-F(1)	179.47(13)
F(3)-P(1)-F(1)	89.84(11)
F(6)-P(1)-F(1)	89.27(12)
F(2)-P(1)-F(1)	89.63(11)
F(4)-P(1)-F(5)	90.78(13)
F(3)-P(1)-F(5)	178.55(11)
F(6)-P(1)-F(5)	89.27(12)
F(2)-P(1)-F(5)	89.88(11)
F(1)-P(1)-F(5)	88.72(10)
C(3)-S(1)-Fe(1)	98.54(8)
C(8)-S(2)-Fe(1)	98.99(8)

Table S-32. Anisotropic displacement parameters (A^2 x 10^3) for [Fe(III)(tame–N_3)S_2^{Me2})(NO)](PF_6)•MeCN (**18**). The anisotropic displacement factor exponent takes the form: -2 pi^2 [h^2 a*^2 U11 + ... + 2 h k a* b* U12]

	U11	U22	U33	U23	U13	U12
C(1)	18(1)	43(2)	32(1)	-2(1)	-1(1)	-1(1)
C(2)	27(1)	43(2)	40(1)	-8(1)	6(1)	6(1)
C(3)	17(1)	36(1)	26(1)	-2(1)	4(1)	2(1)
C(4)	22(1)	31(1)	22(1)	-5(1)	7(1)	-2(1)
C(5)	23(1)	56(2)	32(1)	2(1)	10(1)	-2(1)
C(6)	25(1)	55(2)	44(2)	6(1)	14(1)	-6(1)
C(7)	33(1)	31(1)	37(1)	-1(1)	1(1)	-7(1)
C(8)	18(1)	31(1)	28(1)	4(1)	4(1)	-1(1)
C(9)	19(1)	28(1)	22(1)	-3(1)	2(1)	1(1)
C(10)	21(1)	38(2)	40(1)	7(1)	-1(1)	2(1)
C(11)	26(1)	30(1)	27(1)	7(1)	10(1)	2(1)
C(12)	24(1)	25(1)	22(1)	1(1)	2(1)	0(1)
C(13)	29(1)	22(1)	22(1)	-1(1)	4(1)	1(1)
C(14)	24(1)	22(1)	22(1)	0(1)	6(1)	-1(1)
C(15)	35(1)	24(1)	29(1)	2(1)	7(1)	0(1)
C(16)	44(2)	39(2)	55(2)	0(1)	24(2)	6(1)
C(17)	42(2)	74(3)	54(2)	-16(2)	17(2)	-11(2)
Fe(1)	17(1)	22(1)	17(1)	-1(1)	2(1)	0(1)
F(1)	61(1)	56(1)	36(1)	-12(1)	12(1)	10(1)
F(2)	43(1)	64(1)	48(1)	-1(1)	10(1)	-17(1)
F(3)	39(1)	94(2)	44(1)	10(1)	-1(1)	9(1)
F(4)	74(2)	82(2)	52(1)	-36(1)	28(1)	-20(1)
F(5)	38(1)	52(1)	59(1)	2(1)	11(1)	9(1)
F(6)	47(1)	71(1)	62(1)	-4(1)	19(1)	-22(1)
N(1)	21(1)	24(1)	20(1)	-1(1)	4(1)	-2(1)
N(2)	20(1)	24(1)	18(1)	1(1)	4(1)	2(1)
N(3)	24(1)	27(1)	17(1)	-1(1)	4(1)	0(1)
N(4)	21(1)	27(1)	24(1)	-4(1)	2(1)	-1(1)
N(5)	57(2)	43(2)	97(3)	-4(2)	44(2)	-4(2)
P(1)	30(1)	45(1)	32(1)	-9(1)	7(1)	-4(1)
S(1)	20(1)	32(1)	21(1)	2(1)	1(1)	2(1)
S(2)	23(1)	31(1)	22(1)	5(1)	4(1)	-3(1)
O(1)	43(1)	48(1)	54(1)	-29(1)	14(1)	-5(1)

Table S-33. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (A^2 x 10^3) for [Fe(III)(tame—N_3)S_2^{Me2})(NO)](PF_6)•MeCN (**18**).

	x	y	z	U(eq)
H(1A)	9900	1713	6859	50
H(1B)	10278	2235	6006	50
H(1C)	9472	2660	6540	50
H(2A)	9197	673	5405	56
H(2B)	9390	1185	4596	56
H(2C)	8269	873	4402	56
H(5A)	9601	2621	4181	55
H(5B)	9236	3459	4561	55
H(5C)	8493	2971	3357	55
H(6A)	2372	2051	5569	61
H(6B)	1582	1388	4766	61
H(6C)	2354	1026	5690	61
H(7A)	3603	593	3528	54
H(7B)	2152	706	3486	54
H(7C)	2966	236	4322	54
H(10A)	1534	1968	3271	53
H(10B)	2192	2569	2679	53
H(10C)	1934	2879	3618	53
H(11A)	7002	3779	3668	30
H(11B)	6483	3169	2966	30
H(12A)	4331	2979	2670	27
H(12B)	3677	3498	3374	27
H(13A)	4843	4014	5150	28
H(13B)	6014	4181	5224	28
H(15A)	5827	4882	3623	45
H(15B)	4454	4750	3402	45
H(15C)	5196	4476	2606	45
H(17A)	1786	182	1471	84
H(17B)	1247	563	290	84
H(17C)	972	1010	1296	84
H(3A)	5227	2983	6003	25
H(3B)	6440	3101	6054	25

Table S-34. Crystal data and structure refinement for [Fe(III)((tame–N_3)S_2^{Me2})(MeCN)](PF_6)•MeCN (**19**).

Compound	C15 H29 Fe N5 S2^+^ PF6^-^ *2CH3CN
Empirical formula	C19 H41 F6 Fe N5 P S2
Formula weight	604.51
Temperature	161(2) K
Wavelength	0.71070 A
Crystal system, space group	Orthorhombic, P 21 21 21 (No. 19)
Unit cell dimensions	a = 13.1206(3) A alpha = 90 deg.
	b = 13.6458(2) A beta = 90 deg.
	c = 14.9657(4) A gamma = 90 deg.
Volume	2679.48(10) A^3
Z, Calculated density	4, 1.499 Mg/m^3
Reflections used for indexing	821
Absorption coefficient	0.838 mm^-1
F(000)	1268
Crystal description / color	plate / purple
Crystal size	0.34 x 0.30 x 0.20 mm
Theta range for data collection	2.06 to 30.47 deg.
Index ranges	-18<=h<=18, -17<=k<=17, -21<=l<=21
Reflections collected / unique	52433 / 7859 [R(int) = 0.051]
Completeness to 2theta = 30.47	97.5%
Absorption correction	SCALEPACK
Max. and min. transmission	0.8503 and 0.7637
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	7859 / 0 / 309
Goodness-of-fit on F^2	1.036
Final R indices [I>4sigma(I)]	*R1 = 0.0534, wR2 = 0.1534
R indices (all data)	R1 = 0.0876, *wR2 = 0.1691
*Report these R factors	
Weighting scheme	calc w=1/[\s^2^(Fo^2^)+(0.1061P)^2^+0.0000P] where P=(Fo^2^+2Fc^2^)/3
Absolute structure parameter	0.31(2)
Largest diff. peak and hole	0.660 and -0.841 e.A^-3

Table S-35. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (A^2 x 10^3) for [Fe(III)((tame—N_3)S_2^{Me2})(MeCN)](PF_6)•MeCN (**19**). U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

	x	y	z	U(eq)
C(1)	9302(4)	4333(3)	10385(3)	37(1)
C(2)	7960(3)	3171(3)	9835(3)	36(1)
C(3)	8954(3)	3713(3)	9600(2)	25(1)
C(4)	9779(3)	2980(3)	9361(3)	25(1)
C(5)	10135(3)	2316(3)	10088(3)	32(1)
C(6)	8977(4)	4297(3)	4768(3)	36(1)
C(7)	7678(3)	3132(3)	5431(3)	37(1)
C(8)	8705(3)	3667(3)	5580(3)	29(1)
C(9)	9530(3)	2925(3)	5759(3)	27(1)
C(10)	9864(3)	2274(3)	5010(3)	36(1)
C(11)	10954(3)	2276(3)	8351(3)	28(1)
C(12)	10853(3)	2262(3)	6661(3)	33(1)
C(13)	11492(3)	2525(2)	7473(3)	25(1)
C(14)	11852(3)	3589(3)	7456(3)	30(1)
C(15)	12457(3)	1890(3)	7433(3)	31(1)
C(16)	7506(3)	1692(3)	7640(3)	44(1)
C(17)	6657(4)	1012(4)	7668(4)	62(2)
C(18)	5325(5)	3484(5)	7496(4)	69(2)
C(19)	5858(7)	4385(5)	7714(5)	92(2)
F(1)	12031(2)	5458(2)	9099(2)	54(1)
F(2)	13417(2)	4484(2)	9213(2)	53(1)
F(3)	11906(3)	5516(2)	10594(2)	56(1)
F(4)	11954(2)	4055(2)	9874(2)	60(1)
F(5)	13378(2)	5938(2)	9924(3)	70(1)
F(6)	13296(3)	4537(2)	10709(2)	62(1)
N(2)	10092(2)	2927(2)	8554(2)	21(1)
N(3)	9959(2)	2906(2)	6538(2)	25(1)
N(1)	11009(2)	4337(2)	7483(2)	27(1)
N(4)	8161(3)	2265(3)	7648(3)	55(1)
N(5)	4924(6)	2753(6)	7368(5)	115(3)
P(1)	12666(1)	5000(1)	9903(1)	34(1)
S(1)	8721(1)	4528(1)	8640(1)	28(1)
S(2)	8571(1)	4490(1)	6554(1)	30(1)
Fe(1)	9472(1)	3723(1)	7562(1)	27(1)

Table S-36. Bond lengths [A] and angles [deg] for [Fe(III)((tameN_3)S_2^{Me2})(MeCN)](PF_6)•MeCN (**19**).

C(1)-C(3)	1.518(5)
C(1)-H(1A)	1.0183
C(1)-H(1B)	1.0720
C(1)-H(1C)	1.0708
C(2)-C(3)	1.540(5)
C(2)-H(2A)	1.0357
C(2)-H(2B)	0.9971
C(2)-H(2C)	1.0105
C(3)-C(4)	1.516(5)
C(3)-S(1)	1.844(4)
C(4)-N(2)	1.278(5)
C(4)-C(5)	1.492(5)
C(5)-H(5A)	0.9594
C(5)-H(5B)	1.0135
C(5)-H(5C)	0.9859
C(6)-C(8)	1.530(6)
C(6)-H(6A)	1.0616
C(6)-H(6B)	0.9049
C(6)-H(6C)	1.0778
C(7)-C(8)	1.549(6)
C(7)-H(7A)	1.0456
C(7)-H(7B)	0.9640
C(7)-H(7C)	1.0160
C(8)-C(9)	1.506(5)
C(8)-S(2)	1.849(4)
C(9)-N(3)	1.295(5)
C(9)-C(10)	1.495(6)
C(10)-H(10A)	1.0100
C(10)-H(10B)	1.0100
C(10)-H(10C)	1.0100
C(11)-N(2)	1.469(4)
C(11)-C(13)	1.531(5)
C(11)-H(11A)	1.0100
C(11)-H(11B)	1.0100
C(12)-N(3)	1.478(5)
C(12)-C(13)	1.518(6)
C(12)-H(12A)	1.0100
C(12)-H(12B)	1.0100
C(13)-C(14)	1.528(5)
C(13)-C(15)	1.535(4)
C(14)-N(1)	1.505(4)
C(14)-H(14A)	1.0100
C(14)-H(14B)	1.0100
C(15)-H(15A)	1.0708

C(15)-H(15B)	1.0094
C(15)-H(15C)	1.0104
C(16)-N(4)	1.161(6)
C(16)-C(17)	1.450(7)
C(17)-H(17A)	1.0100
C(17)-H(17B)	1.0100
C(17)-H(17C)	1.0100
C(18)-N(5)	1.143(9)
C(18)-C(19)	1.452(9)
C(19)-H(19A)	1.0100
C(19)-H(19B)	1.0100
C(19)-H(19C)	1.0100
F(1)-P(1)	1.590(3)
F(2)-P(1)	1.591(3)
F(3)-P(1)	1.600(3)
F(4)-P(1)	1.593(3)
F(5)-P(1)	1.586(3)
F(6)-P(1)	1.594(3)
N(1)-Fe(1)	2.011(3)
N(3)-Fe(1)	2.000(3)
N(1)-Fe(1)	2.186(3)
N(1)-H(3A)	0.9599
N(1)-H(3B)	0.9603
S(1)-Fe(1)	2.1866(11)
S(2)-Fe(1)	2.1835(11)
C(3)-C(1)-H(1A)	104.7
C(3)-C(1)-H(1B)	115.3
H(1A)-C(1)-H(1B)	91.7
C(3)-C(1)-H(1C)	113.5
H(1A)-C(1)-H(1C)	127.5
H(1B)-C(1)-H(1C)	102.5
C(3)-C(2)-H(2A)	108.6
C(3)-C(2)-H(2B)	110.9
H(2A)-C(2)-H(2B)	98.8
C(3)-C(2)-H(2C)	123.0
H(2A)-C(2)-H(2C)	107.3
H(2B)-C(2)-H(2C)	105.6
C(4)-C(3)-C(1)	109.7(3)
C(4)-C(3)-C(2)	110.0(3)
C(1)-C(3)-C(2)	110.2(3)
C(4)-C(3)-S(1)	109.4(2)
C(1)-C(3)-S(1)	108.4(3)
C(2)-C(3)-S(1)	109.0(3)
N(1)-C(4)-C(5)	123.7(4)
N(1)-C(4)-C(3)	119.4(3)
C(5)-C(4)-C(3)	116.8(3)
C(4)-C(5)-H(5A)	108.4
C(4)-C(5)-H(5B)	106.0

H(5A)-C(5)-H(5B)	112.6
C(4)-C(5)-H(5C)	114.2
H(5A)-C(5)-H(5C)	97.4
H(5B)-C(5)-H(5C)	118.0
C(8)-C(6)-H(6A)	123.0
C(8)-C(6)-H(6B)	113.2
H(6A)-C(6)-H(6B)	89.9
C(8)-C(6)-H(6C)	115.1
H(6A)-C(6)-H(6C)	103.5
H(6B)-C(6)-H(6C)	109.1
C(8)-C(7)-H(7A)	95.6
C(8)-C(7)-H(7B)	100.3
H(7A)-C(7)-H(7B)	134.0
C(8)-C(7)-H(7C)	101.8
H(7A)-C(7)-H(7C)	103.3
H(7B)-C(7)-H(7C)	115.0
C(9)-C(8)-C(6)	110.6(3)
C(9)-C(8)-C(7)	109.5(3)
C(6)-C(8)-C(7)	110.7(3)
C(9)-C(8)-S(2)	109.7(3)
C(6)-C(8)-S(2)	107.9(3)
C(7)-C(8)-S(2)	108.4(3)
N(3)-C(9)-C(10)	122.4(4)
N(3)-C(9)-C(8)	119.0(3)
C(10)-C(9)-C(8)	118.5(3)
C(9)-C(10)-H(10A)	109.5
C(9)-C(10)-H(10B)	109.5
H(10A)-C(10)-H(10B)	109.5
C(9)-C(10)-H(10C)	109.5
H(10A)-C(10)-H(10C)	109.5
H(10B)-C(10)-H(10C)	109.5
N(1)-C(11)-C(13)	113.4(3)
N(1)-C(11)-H(11A)	108.9
C(13)-C(11)-H(11A)	108.9
N(1)-C(11)-H(11B)	108.9
C(13)-C(11)-H(11B)	108.9
H(11A)-C(11)-H(11B)	107.7
N(3)-C(12)-C(13)	113.4(3)
N(3)-C(12)-H(12A)	108.9
C(13)-C(12)-H(12A)	108.9
N(3)-C(12)-H(12B)	108.9
C(13)-C(12)-H(12B)	108.9
H(12A)-C(12)-H(12B)	107.7
C(12)-C(13)-C(14)	112.5(3)
C(12)-C(13)-C(11)	112.3(3)
C(14)-C(13)-C(11)	111.5(3)
C(12)-C(13)-C(15)	106.9(3)
C(14)-C(13)-C(15)	106.3(3)

C(11)-C(13)-C(15)	106.8(3)
N(1)-C(14)-C(13)	114.6(3)
N(1)-C(14)-H(14A)	108.6
C(13)-C(14)-H(14A)	108.6
N(1)-C(14)-H(14B)	108.6
C(13)-C(14)-H(14B)	108.6
H(14A)-C(14)-H(14B)	107.6
C(13)-C(15)-H(15A)	108.7
C(13)-C(15)-H(15B)	112.5
H(15A)-C(15)-H(15B)	114.6
C(13)-C(15)-H(15C)	120.0
H(15A)-C(15)-H(15C)	92.3
H(15B)-C(15)-H(15C)	107.4
N(4)-C(16)-C(17)	176.7(5)
C(16)-C(17)-H(17A)	109.5
C(16)-C(17)-H(17B)	109.5
H(17A)-C(17)-H(17B)	109.5
C(16)-C(17)-H(17C)	109.5
H(17A)-C(17)-H(17C)	109.5
H(17B)-C(17)-H(17C)	109.5
N(5)-C(18)-C(19)	176.2(8)
C(18)-C(19)-H(19A)	109.5
C(18)-C(19)-H(19B)	109.5
H(19A)-C(19)-H(19B)	109.5
C(18)-C(19)-H(19C)	109.5
H(19A)-C(19)-H(19C)	109.5
H(19B)-C(19)-H(19C)	109.5
C(4)-N(1)-C(11)	118.5(3)
C(4)-N(1)-Fe(1)	122.5(3)
C(11)-N(1)-Fe(1)	119.1(2)
C(9)-N(3)-C(12)	118.0(3)
C(9)-N(3)-Fe(1)	122.7(3)
C(12)-N(3)-Fe(1)	119.3(3)
C(14)-N(1)-Fe(1)	114.8(2)
C(14)-N(1)-H(3A)	106.5
Fe(1)-N(1)-H(3A)	109.4
C(14)-N(1)-H(3B)	107.1
Fe(1)-N(1)-H(3B)	109.4
H(3A)-N(1)-H(3B)	109.5
F(5)-P(1)-F(1)	90.38(19)
F(5)-P(1)-F(2)	90.29(19)
F(1)-P(1)-F(2)	90.47(16)
F(5)-P(1)-F(4)	179.5(2)
F(1)-P(1)-F(4)	89.47(18)
F(2)-P(1)-F(4)	89.25(17)
F(5)-P(1)-F(6)	89.9(2)
F(1)-P(1)-F(6)	179.68(19)
F(2)-P(1)-F(6)	89.65(17)

F(4)-P(1)-F(6)	90.24(19)
F(5)-P(1)-F(3)	89.92(18)
F(1)-P(1)-F(3)	89.45(17)
F(2)-P(1)-F(3)	179.78(17)
F(4)-P(1)-F(3)	90.54(18)
F(6)-P(1)-F(3)	90.43(17)
C(3)-S(1)-Fe(1)	101.36(12)
C(8)-S(2)-Fe(1)	101.64(13)
N(3)-Fe(1)-N(2)	97.76(11)
N(3)-Fe(1)-S(2)	84.91(10)
N(1)-Fe(1)-S(2)	170.97(9)
N(3)-Fe(1)-S(1)	171.66(10)
N(1)-Fe(1)-S(1)	84.80(9)
S(2)-Fe(1)-S(1)	91.40(4)
N(3)-Fe(1)-N(1)	82.97(12)
N(1)-Fe(1)-N(1)	82.72(12)
S(2)-Fe(1)-N(1)	106.21(9)
S(1)-Fe(1)-N(1)	105.26(9)

Table S-37. Anisotropic displacement parameters (A^2 x 10^3) for [Fe(III)((tame–N_3)S_2^{Me2})(MeCN)](PF_6)•MeCN (**19**). The anisotropic displacement factor exponent takes the form: -2 pi^2 [h^2 a*^2 U11 + ... + 2 h k a* b* U12]

	U11	U22	U33	U23	U13	U12
C(1)	46(3)	36(2)	28(2)	-2(2)	3(2)	2(2)
C(2)	28(2)	38(2)	43(2)	9(2)	9(2)	4(2)
C(3)	24(2)	27(2)	25(2)	3(2)	6(1)	2(2)
C(4)	26(2)	18(2)	30(2)	3(1)	-1(2)	-4(1)
C(5)	36(2)	33(2)	28(2)	7(2)	4(2)	9(2)
C(6)	43(2)	39(2)	26(2)	1(2)	-1(2)	1(2)
C(7)	34(2)	38(2)	39(2)	-5(2)	-10(2)	-2(2)
C(8)	39(2)	24(2)	25(2)	-2(1)	-3(2)	9(2)
C(9)	28(2)	23(2)	29(2)	3(1)	-1(2)	-2(2)
C(10)	40(2)	37(2)	31(2)	-11(2)	-10(2)	2(2)
C(11)	24(2)	28(2)	32(2)	13(2)	3(2)	10(2)
C(12)	35(2)	34(2)	31(2)	-5(2)	-2(2)	11(2)
C(13)	23(2)	30(2)	23(2)	3(2)	2(2)	11(1)
C(14)	23(2)	33(2)	33(2)	-3(2)	2(2)	-1(1)
C(15)	25(2)	41(2)	27(2)	-1(2)	0(2)	11(1)
C(16)	41(3)	43(2)	49(3)	5(2)	0(2)	1(2)
C(17)	62(3)	57(3)	69(4)	-9(3)	7(3)	-8(3)
C(18)	62(3)	97(4)	47(3)	-3(3)	-11(3)	-11(3)
C(19)	108(6)	99(5)	69(5)	-12(4)	-7(4)	-17(5)
F(1)	59(2)	63(2)	40(2)	4(1)	-14(1)	17(2)
F(2)	51(2)	58(2)	49(2)	-6(1)	-5(1)	13(1)
F(3)	70(2)	57(2)	40(2)	-14(1)	-3(2)	14(2)
F(4)	57(2)	36(1)	88(2)	-9(2)	3(2)	-13(1)
F(5)	50(2)	34(2)	126(3)	-7(2)	-14(2)	-9(1)
F(6)	74(2)	69(2)	44(2)	-6(2)	-27(2)	26(2)
N(2)	24(2)	17(2)	23(2)	-2(1)	3(1)	0(1)
N(3)	27(2)	23(2)	25(2)	-1(1)	1(1)	1(1)
N(1)	37(2)	23(1)	21(1)	4(1)	-2(1)	4(1)
N(4)	43(2)	70(3)	52(3)	6(2)	2(2)	2(2)
N(5)	96(5)	153(6)	94(5)	-11(5)	-10(4)	-54(5)
P(1)	40(1)	26(1)	35(1)	-4(1)	-12(1)	-2(1)
S(1)	32(1)	24(1)	26(1)	2(1)	4(1)	8(1)
S(2)	35(1)	26(1)	28(1)	-3(1)	-6(1)	8(1)
Fe(1)	33(1)	25(1)	22(1)	-1(1)	-2(1)	10(1)

Table S-38. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (A^2 x 10^3) for [Fe(III)((tame–N_3)S_2^{Me2})(MeCN)](PF_6)•MeCN (**19**).

	x	y	z	U(eq)
H(1A)	9059	3961	10935	55
H(1B)	8823	4946	10541	55
H(1C)	10029	4672	10284	55
H(2A)	7389	3685	9928	54
H(2B)	7677	2831	9300	54
H(2C)	7908	2682	10340	54
H(5A)	10814	2504	10253	48
H(5B)	9630	2398	10595	48
H(5C)	10295	1645	9888	48
H(6A)	9203	3995	4145	54
H(6B)	9591	4594	4818	54
H(6C)	8413	4835	4585	54
H(7A)	7316	3722	5118	56
H(7B)	7599	2814	6002	56
H(7C)	7849	2677	4915	56
H(10A)	10419	1820	5228	54
H(10B)	10133	2688	4503	54
H(10C)	9265	1874	4794	54
H(11A)	10698	1579	8321	31
H(11B)	11464	2316	8855	31
H(12A)	11296	2300	6110	36
H(12B)	10611	1563	6724	36
H(14A)	12317	3702	7984	33
H(14B)	12267	3698	6896	33
H(15A)	12867	1973	8047	46
H(15B)	12874	2016	6878	46
H(15C)	12406	1156	7510	46
H(17A)	6500	841	8309	94
H(17B)	6842	397	7329	94
H(17C)	6040	1326	7384	94
H(19A)	5346	4928	7810	138
H(19B)	6328	4567	7205	138
H(19C)	6270	4288	8276	138
H(3A)	11133	4739	7998	30
H(3B)	11068	4728	6952	30

Table S–39. Crystal data and structure refinement for $(Me_4N)_2[Fe^{III}(tame–N_2S)S_2^{Me2})]\bullet 3H_2O$. (**15a**)

Empirical formula	C42 H96 Fe2 N8 O7 S6
Formula weight	1129.33
Temperature	130(2) K
Wavelength	0.71070 A
Crystal description/color	block / dark red
Crystal system, space group	Monoclinic, P 21/a (No.14)
Unit cell dimensions	a = 18.8870(12)A alpha = 90 deg. b = 10.8610(8)A beta = 101.867(3) deg. c = 29.7740(17)A gamma = 90 deg.
Volume	5977.1(7) A^3
Z, Calculated density	4, 1.255 Mg/m^3
Absorption coefficient	0.743 mm^-1
F(000)	2432
Crystal size	0.19 x 0.14 x 0.12 mm
Reflections for indexing	209
Theta range for data collection	3.01 to 22.72 deg.
Index ranges	-20<=h<=20, -11<=k<=11, -31<=l<=31
Reflections collected / unique	13626 / 7318 [R(int) = 0.1177]
Completeness to theta	= 22.72 85.5%
Absorption correction	HKL-Scalepack
Max. and min. transmission	0.9162 and 0.8717
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	7318 / 9 / 630
Goodness-of-fit on F^2	S = 0.910
S = root(sum(w*D*D)/(n-p)), where D = (Fo*Fo - Fc*Fc)	
Final R indices [I>2sigma(I)]	*R1 = 0.0588, wR2 = 0.0907
R indices (all data)	R1 = 0.1373, *wR2 = 0.1088
*Report these R factors.	
R1 = sum||Fo|-|Fc||/sum|Fo|, wR2= root(sum(w*D*D)/sum(w*Fo*Fo)), where D = (Fo*Fo - Fc*Fc)	
Weighting scheme	calc w=1/[\s^2^(Fo^2^)+(0.0110P)^2^+0.0000P] where P=(Fo^2^+2Fc^2^)/3
Largest diff. peak and hole	0.695 and -0.467 e.A^-3

Table S–40. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (A^2 x 10^3) for $(Me_4N)_2[Fe^{III}(tame–N_2S)S_2^{Me2})]\bullet 2H_2O$ (**15a**). U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

	x	y	z	U(eq)
C(1)	4948(3)	5705(6)	1041(2)	40(2)
C(2)	4189(3)	5985(6)	260(2)	37(2)
C(3)	4173(3)	5748(5)	763(2)	25(2)
C(4)	3773(3)	6783(7)	946(2)	27(2)
C(5)	2935(3)	7531(5)	1371(2)	27(2)
C(6)	2372(3)	7171(6)	1638(2)	24(2)
C(7)	1738(3)	6499(6)	1330(2)	27(2)
C(8)	2664(3)	6402(6)	2072(2)	30(2)
C(9)	2061(3)	8380(6)	1793(2)	36(2)
C(10)	1400(4)	4384(6)	1245(2)	25(2)
C(11)	1630(3)	3032(6)	1263(2)	27(2)
C(12)	1690(3)	2595(6)	1756(2)	37(2)
C(13)	1060(3)	2264(6)	939(2)	33(2)
C(14)	735(3)	2136(6)	4868(2)	35(2)
C(15)	-33(3)	1992(6)	4076(2)	30(2)
C(16)	735(3)	1935(6)	4363(2)	24(2)
C(17)	1156(3)	2967(6)	4187(2)	23(2)
C(18)	1885(3)	3683(6)	3699(2)	29(2)
C(19)	2372(3)	3294(6)	3364(2)	19(2)
C(20)	1961(3)	2600(6)	2942(2)	31(2)
C(21)	3015(3)	2552(6)	3611(2)	27(2)
C(22)	2670(3)	4489(5)	3196(2)	32(2)
C(23)	3236(3)	398(6)	3565(2)	22(2)
C(24)	2995(3)	-925(6)	3598(2)	22(2)
C(25)	2791(3)	-1407(6)	3097(2)	34(2)
C(26)	3597(3)	-1728(6)	3873(2)	38(2)
C(27)	3733(5)	-378(9)	-59(3)	105(4)
C(28)	3160(4)	1707(7)	-48(2)	60(2)
C(29)	3983(4)	935(7)	634(2)	70(3)
C(30)	2816(4)	82(8)	370(3)	93(3)
C(31)	5070(3)	1053(6)	2541(2)	34(2)
C(32)	4607(3)	2554(6)	1941(2)	41(2)
C(33)	4300(3)	2701(6)	2701(2)	43(2)
C(34)	3793(3)	1041(6)	2165(2)	49(2)
C(35)	2816(3)	1181(6)	5334(2)	37(2)
C(36)	3681(3)	923(6)	4827(2)	41(2)
C(37)	4027(3)	2102(6)	5535(2)	35(2)

C(38)	3121(4)	2949(6)	4905(2)	44(2)
C(39)	841(3)	7213(6)	2872(2)	40(2)
C(40)	273(3)	8834(5)	2359(2)	29(2)
C(41)	124(4)	8779(6)	3154(2)	50(2)
C(42)	-462(3)	7244(6)	2612(2)	29(2)
N(1)	3208(2)	6489(4)	1133(2)	18(1)
N(2)	1919(2)	5222(5)	1245(2)	25(1)
N(3)	1642(2)	2645(4)	3939(2)	22(1)
N(4)	2815(2)	1262(5)	3699(2)	22(1)
N(5)	3450(3)	630(5)	211(2)	32(2)
N(6)	4437(3)	1833(5)	2336(2)	25(1)
N(7)	3413(3)	1804(5)	5148(2)	23(1)
N(8)	185(3)	8019(5)	2748(2)	25(1)
O(1)	4008(2)	7878(4)	932(1)	30(1)
O(2)	753(2)	4616(4)	1257(2)	42(1)
O(3)	1000(2)	4062(4)	4259(1)	27(1)
O(4)	3795(2)	595(4)	3417(1)	32(1)
O(5)	4885(3)	8989(5)	1690(1)	47(1)
O(6)	140(2)	5420(4)	3558(2)	37(1)
O(7)	183(4)	6318(7)	546(2)	108(2)
S(1)	3733(1)	4281(2)	819(1)	32(1)
S(2)	2517(1)	2892(2)	1109(1)	28(1)
S(3)	3302(1)	5145(2)	2037(1)	28(1)
S(4)	1125(1)	445(2)	4279(1)	29(1)
S(5)	2196(1)	-1010(2)	3854(1)	28(1)
S(6)	1328(1)	1362(2)	3008(1)	29(1)
Fe(1)	2924(1)	4796(1)	1228(1)	23(1)
Fe(2)	1840(1)	937(1)	3797(1)	23(1)

Table S–41. Bond lengths [A] and angles [deg] for $(Me_4N)_2[Fe^{III}(tame–N_2S)S_2^{Me2})]\bullet 3H_2O$. (**15a**)

C(1)-C(3)	1.528(8)
C(1)-H(1A)	0.9800
C(1)-H(1B)	0.9800
C(1)-H(1C)	0.9800
C(2)-C(3)	1.525(8)
C(2)-H(2A)	0.9800
C(2)-H(2B)	0.9800
C(2)-H(2C)	0.9800
C(3)-C(4)	1.517(8)
C(3)-S(1)	1.821(6)
C(4)-O(1)	1.273(7)
C(4)-N(1)	1.341(7)
C(5)-N(1)	1.482(6)
C(5)-C(6)	1.504(7)
C(5)-H(5A)	0.9900
C(5)-H(5B)	0.9900
C(6)-C(7)	1.535(7)
C(6)-C(8)	1.544(8)
C(6)-C(9)	1.547(7)
C(7)-N(2)	1.464(7)
C(7)-H(7A)	0.9900
C(7)-H(7B)	0.9900
C(8)-S(3)	1.838(6)
C(8)-H(8A)	0.9900
C(8)-H(8B)	0.9900
C(9)-H(9A)	0.9800
C(9)-H(9B)	0.9800
C(9)-H(9C)	0.9800
C(10)-O(2)	1.254(6)
C(10)-N(2)	1.338(7)
C(10)-C(11)	1.530(8)
C(11)-C(12)	1.524(7)
C(11)-C(13)	1.536(7)
C(11)-S(2)	1.834(6)
C(12)-H(12A)	0.9800
C(12)-H(12B)	0.9800
C(12)-H(12C)	0.9800
C(13)-H(13A)	0.9800
C(13)-H(13B)	0.9800
C(13)-H(13C)	0.9800
C(14)-C(16)	1.519(7)
C(14)-H(14A)	0.9800
C(14)-H(14B)	0.9800

C(14)-H(14C)	0.9800
C(15)-C(16)	1.525(7)
C(15)-H(15A)	0.9800
C(15)-H(15B)	0.9800
C(15)-H(15C)	0.9800
C(16)-C(17)	1.529(8)
C(16)-S(4)	1.816(6)
C(17)-O(3)	1.254(7)
C(17)-N(3)	1.337(7)
C(18)-N(3)	1.459(6)
C(18)-C(19)	1.548(7)
C(18)-H(18A)	0.9900
C(18)-H(18B)	0.9900
C(19)-C(21)	1.515(7)
C(19)-C(20)	1.533(7)
C(19)-C(22)	1.538(7)
C(20)-S(6)	1.837(6)
C(20)-H(20A)	0.9900
C(20)-H(20B)	0.9900
C(21)-N(4)	1.489(7)
C(21)-H(21A)	0.9900
C(21)-H(21B)	0.9900
C(22)-H(22A)	0.9800
C(22)-H(22B)	0.9800
C(22)-H(22C)	0.9800
C(23)-O(4)	1.245(6)
C(23)-N(4)	1.342(7)
C(23)-C(24)	1.516(8)
C(24)-C(26)	1.529(7)
C(24)-C(25)	1.553(7)
C(24)-S(5)	1.828(5)
C(25)-H(25A)	0.9800
C(25)-H(25B)	0.9800
C(25)-H(25C)	0.9800
C(26)-H(26A)	0.9800
C(26)-H(26B)	0.9800
C(26)-H(26C)	0.9800
C(27)-N(5)	1.518(8)
C(27)-H(27A)	0.9800
C(27)-H(27B)	0.9800
C(27)-H(27C)	0.9800
C(28)-N(5)	1.445(7)
C(28)-H(28A)	0.9800
C(28)-H(28B)	0.9800
C(28)-H(28C)	0.9800
C(29)-N(5)	1.480(7)
C(29)-H(29A)	0.9800
C(29)-H(29B)	0.9800

C(29)-H(29C)	0.9800
C(30)-N(5)	1.499(8)
C(30)-H(30A)	0.9800
C(30)-H(30B)	0.9800
C(30)-H(30C)	0.9800
C(31)-N(6)	1.489(7)
C(31)-H(31A)	0.9800
C(31)-H(31B)	0.9800
C(31)-H(31C)	0.9800
C(32)-N(6)	1.502(7)
C(32)-H(32A)	0.9800
C(32)-H(32B)	0.9800
C(32)-H(32C)	0.9800
C(33)-N(6)	1.499(7)
C(33)-H(33A)	0.9800
C(33)-H(33B)	0.9800
C(33)-H(33C)	0.9800
C(34)-N(6)	1.492(7)
C(34)-H(34A)	0.9800
C(34)-H(34B)	0.9800
C(34)-H(34C)	0.9800
C(35)-N(7)	1.514(6)
C(35)-H(35A)	0.9800
C(35)-H(35B)	0.9800
C(35)-H(35C)	0.9800
C(36)-N(7)	1.511(6)
C(36)-H(36A)	0.9800
C(36)-H(36B)	0.9800
C(36)-H(36C)	0.9800
C(37)-N(7)	1.493(6)
C(37)-H(37A)	0.9800
C(37)-H(37B)	0.9800
C(37)-H(37C)	0.9800
C(38)-N(7)	1.486(7)
C(38)-H(38A)	0.9800
C(38)-H(38B)	0.9800
C(38)-H(38C)	0.9800
C(39)-N(8)	1.499(7)
C(39)-H(39A)	0.9800
C(39)-H(39B)	0.9800
C(39)-H(39C)	0.9800
C(40)-N(8)	1.494(6)
C(40)-H(40A)	0.9800
C(40)-H(40B)	0.9800
C(40)-H(40C)	0.9800
C(41)-N(8)	1.487(7)
C(41)-H(41A)	0.9800
C(41)-H(41B)	0.9800

C(41)-H(41C)	0.9800
C(42)-N(8)	1.471(6)
C(42)-H(42A)	0.9800
C(42)-H(42B)	0.9800
C(42)-H(42C)	0.9800
N(1)-Fe(1)	1.952(5)
N(2)-Fe(1)	1.964(4)
N(3)-Fe(2)	1.956(5)
N(4)-Fe(2)	1.956(5)
O(5)-H(51)	0.800(5)
O(5)-H(52)	0.799(5)
O(6)-H(61)	0.800(5)
O(6)-H(62)	0.800(5)
O(7)-H(71)	0.802(5)
O(7)-H(72)	0.803(5)
S(1)-Fe(1)	2.2122(15)
S(2)-Fe(1)	2.2085(19)
S(3)-Fe(1)	2.3980(17)
S(4)-Fe(2)	2.2284(15)
S(5)-Fe(2)	2.2141(19)
S(6)-Fe(2)	2.3931(18
C(3)-C(1)-H(1A)	109.5
C(3)-C(1)-H(1B)	109.5
H(1A)-C(1)-H(1B)	109.5
C(3)-C(1)-H(1C)	109.5
H(1A)-C(1)-H(1C)	109.5
H(1B)-C(1)-H(1C)	109.5
C(3)-C(2)-H(2A)	109.5
C(3)-C(2)-H(2B)	109.5
H(2A)-C(2)-H(2B)	109.5
C(3)-C(2)-H(2C)	109.5
H(2A)-C(2)-H(2C)	109.5
H(2B)-C(2)-H(2C)	109.5
C(4)-C(3)-C(2)	109.9(5)
C(4)-C(3)-C(1)	108.7(5)
C(2)-C(3)-C(1)	109.1(5)
C(4)-C(3)-S(1)	110.2(4)
C(2)-C(3)-S(1)	109.9(4)
C(1)-C(3)-S(1)	109.1(4)
O(1)-C(4)-N(1)	123.2(6)
O(1)-C(4)-C(3)	118.6(6)
N(1)-C(4)-C(3)	118.1(6)
N(1)-C(5)-C(6)	114.0(5)
N(1)-C(5)-H(5A)	108.7
C(6)-C(5)-H(5A)	108.7
N(1)-C(5)-H(5B)	108.7
C(6)-C(5)-H(5B)	108.7
H(5A)-C(5)-H(5B)	107.6

C(5)-C(6)-C(7)	111.0(5)
C(5)-C(6)-C(8)	114.4(5)
C(7)-C(6)-C(8)	110.1(5)
C(5)-C(6)-C(9)	106.9(5)
C(7)-C(6)-C(9)	106.5(5)
C(8)-C(6)-C(9)	107.6(5)
N(2)-C(7)-C(6)	111.9(5)
N(2)-C(7)-H(7A)	109.2
C(6)-C(7)-H(7A)	109.2
N(2)-C(7)-H(7B)	109.2
C(6)-C(7)-H(7B)	109.2
H(7A)-C(7)-H(7B)	107.9
C(6)-C(8)-S(3)	118.6(4)
C(6)-C(8)-H(8A)	107.7
S(3)-C(8)-H(8A)	107.7
C(6)-C(8)-H(8B)	107.7
S(3)-C(8)-H(8B)	107.7
H(8A)-C(8)-H(8B)	107.1
C(6)-C(9)-H(9A)	109.5
C(6)-C(9)-H(9B)	109.5
H(9A)-C(9)-H(9B)	109.5
C(6)-C(9)-H(9C)	109.5
H(9A)-C(9)-H(9C)	109.5
H(9B)-C(9)-H(9C)	109.5
O(2)-C(10)-N(2)	125.6(6)
O(2)-C(10)-C(11)	117.6(6)
N(2)-C(10)-C(11)	116.7(6)
C(12)-C(11)-C(10)	107.3(5)
C(12)-C(11)-C(13)	109.9(5)
C(10)-C(11)-C(13)	110.0(5)
C(12)-C(11)-S(2)	109.0(4)
C(10)-C(11)-S(2)	109.8(4)
C(13)-C(11)-S(2)	110.8(4)
C(11)-C(12)-H(12A)	109.5
C(11)-C(12)-H(12B)	109.5
H(12A)-C(12)-H(12B)	109.5
C(11)-C(12)-H(12C)	109.5
H(12A)-C(12)-H(12C)	109.5
H(12B)-C(12)-H(12C)	109.5
C(11)-C(13)-H(13A)	109.5
C(11)-C(13)-H(13B)	109.5
H(13A)-C(13)-H(13B)	109.5
C(11)-C(13)-H(13C)	109.5
H(13A)-C(13)-H(13C)	109.5
H(13B)-C(13)-H(13C)	109.5
C(16)-C(14)-H(14A)	109.5
C(16)-C(14)-H(14B)	109.5
H(14A)-C(14)-H(14B)	109.5

C(16)-C(14)-H(14C)	109.5
H(14A)-C(14)-H(14C)	109.5
H(14B)-C(14)-H(14C)	109.5
C(16)-C(15)-H(15A)	109.5
C(16)-C(15)-H(15B)	109.5
H(15A)-C(15)-H(15B)	109.5
C(16)-C(15)-H(15C)	109.5
H(15A)-C(15)-H(15C)	109.5
H(15B)-C(15)-H(15C)	109.5
C(14)-C(16)-C(15)	110.8(5)
C(14)-C(16)-C(17)	109.8(5)
C(15)-C(16)-C(17)	106.2(5)
C(14)-C(16)-S(4)	110.3(4)
C(15)-C(16)-S(4)	109.0(4)
C(17)-C(16)-S(4)	110.6(4)
O(3)-C(17)-N(3)	123.7(6)
O(3)-C(17)-C(16)	118.7(5)
N(3)-C(17)-C(16)	117.5(6)
N(3)-C(18)-C(19)	113.2(5)
N(3)-C(18)-H(18A)	108.9
C(19)-C(18)-H(18A)	108.9
N(3)-C(18)-H(18B)	108.9
C(19)-C(18)-H(18B)	108.9
H(18A)-C(18)-H(18B)	107.8
C(21)-C(19)-C(20)	110.9(5)
C(21)-C(19)-C(22)	107.2(5)
C(20)-C(19)-C(22)	107.8(5)
C(21)-C(19)-C(18)	110.8(5)
C(20)-C(19)-C(18)	113.2(5)
C(22)-C(19)-C(18)	106.5(5)
C(19)-C(20)-S(6)	120.2(4)
C(19)-C(20)-H(20A)	107.3
S(6)-C(20)-H(20A)	107.3
C(19)-C(20)-H(20B)	107.3
S(6)-C(20)-H(20B)	107.3
H(20A)-C(20)-H(20B)	106.9
N(4)-C(21)-C(19)	112.3(5)
N(4)-C(21)-H(21A)	109.1
C(19)-C(21)-H(21A)	109.1
N(4)-C(21)-H(21B)	109.1
C(19)-C(21)-H(21B)	109.1
H(21A)-C(21)-H(21B)	107.9
C(19)-C(22)-H(22A)	109.5
C(19)-C(22)-H(22B)	109.5
H(22A)-C(22)-H(22B)	109.5
C(19)-C(22)-H(22C)	109.5
H(22A)-C(22)-H(22C)	109.5
H(22B)-C(22)-H(22C)	109.5

O(4)-C(23)-N(4)	125.6(6)
O(4)-C(23)-C(24)	118.2(6)
N(4)-C(23)-C(24)	116.2(5)
C(23)-C(24)-C(26)	112.0(5)
C(23)-C(24)-C(25)	106.1(5)
C(26)-C(24)-C(25)	109.4(5)
C(23)-C(24)-S(5)	111.0(4)
C(26)-C(24)-S(5)	109.6(4)
C(25)-C(24)-S(5)	108.6(4)
C(24)-C(25)-H(25A)	109.5
C(24)-C(25)-H(25B)	109.5
H(25A)-C(25)-H(25B)	109.5
C(24)-C(25)-H(25C)	109.5
H(25A)-C(25)-H(25C)	109.5
H(25B)-C(25)-H(25C)	109.5
C(24)-C(26)-H(26A)	109.5
C(24)-C(26)-H(26B)	109.5
H(26A)-C(26)-H(26B)	109.5
C(24)-C(26)-H(26C)	109.5
H(26A)-C(26)-H(26C)	109.5
H(26B)-C(26)-H(26C)	109.5
N(5)-C(27)-H(27A)	109.5
N(5)-C(27)-H(27B)	109.5
H(27A)-C(27)-H(27B)	109.5
N(5)-C(27)-H(27C)	109.5
H(27A)-C(27)-H(27C)	109.5
H(27B)-C(27)-H(27C)	109.5
N(5)-C(28)-H(28A)	109.5
N(5)-C(28)-H(28B)	109.5
H(28A)-C(28)-H(28B)	109.5
N(5)-C(28)-H(28C)	109.5
H(28A)-C(28)-H(28C)	109.5
H(28B)-C(28)-H(28C)	109.5
N(5)-C(29)-H(29A)	109.5
N(5)-C(29)-H(29B)	109.5
H(29A)-C(29)-H(29B)	109.5
N(5)-C(29)-H(29C)	109.5
H(29A)-C(29)-H(29C)	109.5
H(29B)-C(29)-H(29C)	109.5
N(5)-C(30)-H(30A)	109.5
N(5)-C(30)-H(30B)	109.5
H(30A)-C(30)-H(30B)	109.5
N(5)-C(30)-H(30C)	109.5
H(30A)-C(30)-H(30C)	109.5
H(30B)-C(30)-H(30C)	109.5
N(6)-C(31)-H(31A)	109.5
N(6)-C(31)-H(31B)	109.5
H(31A)-C(31)-H(31B)	109.5

N(6)-C(31)-H(31C)	109.5
H(31A)-C(31)-H(31C)	109.5
H(31B)-C(31)-H(31C)	109.5
N(6)-C(32)-H(32A)	109.5
N(6)-C(32)-H(32B)	109.5
H(32A)-C(32)-H(32B)	109.5
N(6)-C(32)-H(32C)	109.5
H(32A)-C(32)-H(32C)	109.5
H(32B)-C(32)-H(32C)	109.5
N(6)-C(33)-H(33A)	109.5
N(6)-C(33)-H(33B)	109.5
H(33A)-C(33)-H(33B)	109.5
N(6)-C(33)-H(33C)	109.5
H(33A)-C(33)-H(33C)	109.5
H(33B)-C(33)-H(33C)	109.5
N(6)-C(34)-H(34A)	109.5
N(6)-C(34)-H(34B)	109.5
H(34A)-C(34)-H(34B)	109.5
N(6)-C(34)-H(34C)	109.5
H(34A)-C(34)-H(34C)	109.5
H(34B)-C(34)-H(34C)	109.5
N(7)-C(35)-H(35A)	109.5
N(7)-C(35)-H(35B)	109.5
H(35A)-C(35)-H(35B)	109.5
N(7)-C(35)-H(35C)	109.5
H(35A)-C(35)-H(35C)	109.5
H(35B)-C(35)-H(35C)	109.5
N(7)-C(36)-H(36A)	109.5
N(7)-C(36)-H(36B)	109.5
H(36A)-C(36)-H(36B)	109.5
N(7)-C(36)-H(36C)	109.5
H(36A)-C(36)-H(36C)	109.5
H(36B)-C(36)-H(36C)	109.5
N(7)-C(37)-H(37A)	109.5
N(7)-C(37)-H(37B)	109.5
H(37A)-C(37)-H(37B)	109.5
N(7)-C(37)-H(37C)	109.5
H(37A)-C(37)-H(37C)	109.5
H(37B)-C(37)-H(37C)	109.5
N(7)-C(38)-H(38A)	109.5
N(7)-C(38)-H(38B)	109.5
H(38A)-C(38)-H(38B)	109.5
N(7)-C(38)-H(38C)	109.5
H(38A)-C(38)-H(38C)	109.5
H(38B)-C(38)-H(38C)	109.5
N(8)-C(39)-H(39A)	109.5
N(8)-C(39)-H(39B)	109.5
H(39A)-C(39)-H(39B)	109.5

N(8)-C(39)-H(39C)	109.5
H(39A)-C(39)-H(39C)	109.5
H(39B)-C(39)-H(39C)	109.5
N(8)-C(40)-H(40A)	109.5
N(8)-C(40)-H(40B)	109.5
H(40A)-C(40)-H(40B)	109.5
N(8)-C(40)-H(40C)	109.5
H(40A)-C(40)-H(40C)	109.5
H(40B)-C(40)-H(40C)	109.5
N(8)-C(41)-H(41A)	109.5
N(8)-C(41)-H(41B)	109.5
H(41A)-C(41)-H(41B)	109.5
N(8)-C(41)-H(41C)	109.5
H(41A)-C(41)-H(41C)	109.5
H(41B)-C(41)-H(41C)	109.5
N(8)-C(42)-H(42A)	109.5
N(8)-C(42)-H(42B)	109.5
H(42A)-C(42)-H(42B)	109.5
N(8)-C(42)-H(42C)	109.5
H(42A)-C(42)-H(42C)	109.5
H(42B)-C(42)-H(42C)	109.5
C(4)-N(1)-C(5)	113.7(5)
C(4)-N(1)-Fe(1)	123.3(4)
C(5)-N(1)-Fe(1)	121.2(3)
C(10)-N(2)-C(7)	116.5(5)
C(10)-N(2)-Fe(1)	123.5(4)
C(7)-N(2)-Fe(1)	119.3(4)
C(17)-N(3)-C(18)	112.9(5)
C(17)-N(3)-Fe(2)	123.4(4)
C(18)-N(3)-Fe(2)	122.2(3)
C(23)-N(4)-C(21)	114.8(5)
C(23)-N(4)-Fe(2)	123.4(4)
C(21)-N(4)-Fe(2)	118.5(4)
C(28)-N(5)-C(29)	112.9(6)
C(28)-N(5)-C(30)	104.5(5)
C(29)-N(5)-C(30)	105.5(5)
C(28)-N(5)-C(27)	116.0(5)
C(29)-N(5)-C(27)	111.1(6)
C(30)-N(5)-C(27)	105.8(6)
C(31)-N(6)-C(34)	109.9(5)
C(31)-N(6)-C(33)	107.8(5)
C(34)-N(6)-C(33)	111.1(5)
C(31)-N(6)-C(32)	109.5(4)
C(34)-N(6)-C(32)	108.9(5)
C(33)-N(6)-C(32)	109.6(5)
C(38)-N(7)-C(37)	110.2(5)
C(38)-N(7)-C(36)	111.2(4)
C(37)-N(7)-C(36)	108.5(4)

C(38)-N(7)-C(35)	108.8(4)
C(37)-N(7)-C(35)	109.4(4)
C(36)-N(7)-C(35)	108.7(5)
C(42)-N(8)-C(41)	110.0(4)
C(42)-N(8)-C(40)	110.1(4)
C(41)-N(8)-C(40)	109.9(5)
C(42)-N(8)-C(39)	109.3(5)
C(41)-N(8)-C(39)	108.9(5)
C(40)-N(8)-C(39)	108.6(4)
H(51)-O(5)-H(52)	105.3(9)
H(61)-O(6)-H(62)	105.1(9)
H(71)-O(7)-H(72)	104.8(9)
C(3)-S(1)-Fe(1)	102.09(19)
C(11)-S(2)-Fe(1)	100.8(2)
C(8)-S(3)-Fe(1)	96.45(19)
C(16)-S(4)-Fe(2)	101.04(18)
C(24)-S(5)-Fe(2)	100.6(2)
C(20)-S(6)-Fe(2)	96.1(2)
N(1)-Fe(1)-N(2)	94.4(2)
N(1)-Fe(1)-S(2)	162.90(14)
N(2)-Fe(1)-S(2)	85.33(17)
N(1)-Fe(1)-S(1)	85.30(14)
N(2)-Fe(1)-S(1)	148.72(14)
S(2)-Fe(1)-S(1)	86.12(6)
N(1)-Fe(1)-S(3)	87.79(14)
N(2)-Fe(1)-S(3)	91.50(14)
S(2)-Fe(1)-S(3)	109.32(7)
S(1)-Fe(1)-S(3)	119.69(7)
N(4)-Fe(2)-N(3)	95.1(2)
N(4)-Fe(2)-S(5)	84.46(16)
N(3)-Fe(2)-S(5)	163.26(14)
N(4)-Fe(2)-S(4)	148.53(14)
N(3)-Fe(2)-S(4)	85.41(14)
S(5)-Fe(2)-S(4)	86.35(6)
N(4)-Fe(2)-S(6)	91.27(14)
N(3)-Fe(2)-S(6)	88.41(14)
S(5)-Fe(2)-S(6)	108.32(7)
S(4)-Fe(2)-S(6)	120.17(7)

Symmetry transformations used to generate equivalent atoms:

Table S-42. Anisotropic displacement parameters (A^2 x 10^3) for $(Me_4N)_2[Fe^{III}(tame\text{—}N_2S)S_2^{Me2})]\bullet 3H_2O$ (**15a**). The anisotropic displacement factor exponent takes the form: -2 pi^2 [h^2 a*^2 U11 + ... + 2 h k a* b* U12]

	U11	U22	U33	U23	U13	U12
C(1)	24(4)	38(5)	58(5)	-14(4)	8(4)	-13(4)
C(2)	41(4)	35(5)	38(4)	2(4)	18(4)	2(4)
C(3)	29(4)	21(5)	27(4)	-6(3)	8(4)	-2(3)
C(4)	26(4)	26(5)	22(4)	9(4)	-11(3)	12(4)
C(5)	33(4)	18(4)	32(4)	-1(3)	15(4)	6(4)
C(6)	29(4)	18(4)	21(4)	-6(3)	-4(3)	9(3)
C(7)	25(4)	20(5)	36(4)	-9(4)	6(3)	6(4)
C(8)	28(4)	30(5)	33(4)	-15(4)	7(3)	-5(4)
C(9)	26(4)	45(5)	37(4)	-21(4)	3(4)	3(4)
C(10)	27(5)	26(5)	19(4)	-4(3)	1(3)	10(4)
C(11)	33(4)	16(4)	32(4)	0(3)	8(3)	-4(4)
C(12)	37(4)	52(6)	27(4)	4(4)	16(4)	-1(4)
C(13)	35(4)	22(5)	43(4)	-16(4)	9(4)	-6(4)
C(14)	42(4)	23(5)	45(5)	-7(4)	20(4)	3(4)
C(15)	22(4)	25(5)	44(4)	5(3)	10(4)	2(3)
C(16)	23(4)	29(5)	20(4)	4(3)	3(3)	0(4)
C(17)	23(4)	20(5)	27(4)	3(4)	7(4)	1(4)
C(18)	35(4)	17(4)	35(4)	2(3)	9(4)	16(4)
C(19)	18(4)	22(4)	20(4)	3(3)	11(3)	-2(3)
C(20)	33(4)	30(5)	30(4)	8(4)	9(3)	1(4)
C(21)	29(4)	25(5)	29(4)	-5(3)	14(3)	-1(4)
C(22)	45(4)	27(5)	30(4)	5(3)	21(4)	2(4)
C(23)	14(4)	25(5)	26(4)	7(3)	-1(3)	2(4)
C(24)	15(4)	23(5)	29(4)	-5(3)	8(3)	-3(3)
C(25)	37(4)	37(5)	29(4)	-12(4)	13(4)	-5(4)
C(26)	39(5)	29(5)	47(5)	10(4)	10(4)	9(4)
C(27)	118(8)	128(10)	56(6)	-25(6)	-16(6)	65(7)
C(28)	88(6)	41(6)	34(5)	13(4)	-26(4)	-13(5)
C(29)	102(7)	41(6)	45(5)	7(4)	-34(5)	1(5)
C(30)	101(8)	73(8)	100(7)	43(6)	6(6)	12(6)
C(31)	40(4)	19(4)	39(4)	-5(4)	-3(4)	13(4)
C(32)	47(5)	46(5)	33(4)	18(4)	17(4)	10(4)
C(33)	51(5)	48(6)	33(4)	8(4)	15(4)	9(4)
C(34)	29(4)	55(6)	58(5)	6(4)	1(4)	-7(4)
C(35)	27(4)	30(5)	55(5)	8(4)	13(4)	-3(4)
C(36)	48(5)	44(5)	35(4)	-16(4)	18(4)	-4(4)
C(37)	39(4)	37(5)	22(4)	-2(4)	-8(4)	-2(4)
C(38)	63(5)	37(5)	28(4)	16(4)	-2(4)	4(4)

C(39)	22(4)	42(5)	53(5)	10(4)	1(4)	-6(4)
C(40)	30(4)	21(4)	37(4)	6(4)	11(3)	-6(4)
C(41)	73(6)	42(6)	38(5)	-20(4)	19(4)	-20(5)
C(42)	26(4)	23(5)	38(4)	-5(3)	4(3)	-9(4)
N(1)	17(3)	16(3)	24(3)	3(3)	12(3)	2(3)
N(2)	22(3)	23(4)	33(3)	-6(3)	10(3)	-2(3)
N(3)	22(3)	19(4)	28(3)	4(3)	10(3)	-5(3)
N(4)	23(3)	18(4)	21(3)	7(3)	-2(3)	-5(3)
N(5)	39(4)	36(4)	27(3)	8(3)	18(3)	13(3)
N(6)	24(3)	22(4)	30(3)	1(3)	8(3)	3(3)
N(7)	25(3)	17(4)	22(3)	1(3)	-5(3)	5(3)
N(8)	20(3)	24(4)	31(3)	-4(3)	8(3)	-1(3)
O(1)	32(3)	21(3)	38(3)	3(2)	7(2)	-9(2)
O(2)	21(3)	36(3)	69(3)	-13(3)	11(3)	5(2)
O(3)	28(3)	18(3)	36(3)	0(2)	10(2)	0(2)
O(4)	23(3)	24(3)	52(3)	3(2)	14(2)	-1(2)
O(5)	52(4)	54(4)	35(3)	0(3)	12(3)	-21(3)
O(6)	27(3)	41(4)	43(3)	9(2)	8(3)	3(3)
O(7)	126(6)	118(7)	87(6)	11(4)	40(5)	3(5)
S(1)	36(1)	22(1)	44(1)	-5(1)	22(1)	-3(1)
S(2)	29(1)	21(1)	36(1)	-2(1)	12(1)	-2(1)
S(3)	28(1)	31(1)	25(1)	1(1)	4(1)	1(1)
S(4)	30(1)	25(1)	35(1)	2(1)	16(1)	2(1)
S(5)	33(1)	22(1)	33(1)	-1(1)	16(1)	-1(1)
S(6)	33(1)	28(1)	24(1)	-3(1)	3(1)	-5(1)
Fe(1)	24(1)	21(1)	24(1)	1(1)	7(1)	1(1)
Fe(2)	24(1)	22(1)	22(1)	-1(1)	7(1)	0(1)

Table S—43. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (A^2 x 10^3) for $(Me_4N)_2[Fe^{III}(tame—N_2S)S_2^{Me2})]\bullet 3H_2O$ (**15a**).

	x	y	z	U(eq)
H(1A)	5180	6506	1024	61
H(1B)	5220	5068	915	61
H(1C)	4943	5514	1362	61
H(2A)	3693	6067	83	55
H(2B)	4428	5294	140	55
H(2C)	4458	6745	234	55
H(5A)	2726	8158	1140	32
H(5B)	3348	7915	1584	32
H(7A)	1315	6510	1479	32
H(7B)	1602	6939	1034	32
H(8A)	2244	6043	2176	36
H(8B)	2904	6975	2316	36
H(9A)	2456	8882	1966	55
H(9B)	1718	8186	1989	55
H(9C)	1812	8838	1523	55
H(12A)	2070	3062	1959	56
H(12B)	1811	1716	1777	56
H(12C)	1227	2725	1849	56
H(13A)	1206	1397	957	49
H(13B)	1018	2559	623	49
H(13C)	591	2347	1029	49
H(14A)	1234	2142	5043	53
H(14B)	466	1470	4979	53
H(14C)	504	2926	4907	53
H(15A)	-251	2786	4124	44
H(15B)	-322	1324	4168	44
H(15C)	-18	1901	3750	44
H(18A)	2157	4263	3928	35
H(18B)	1457	4125	3525	35
H(20A)	2325	2244	2783	37
H(20B)	1685	3219	2731	37
H(21A)	3391	2543	3423	32
H(21B)	3223	2956	3907	32
H(22A)	3025	4856	3447	48
H(22B)	2272	5070	3095	48
H(22C)	2904	4303	2939	48
H(25A)	2394	-910	2923	50
H(25B)	2637	-2269	3098	50
H(25C)	3212	-1347	2953	50
H(26A)	4019	-1706	3729	57

H(26B)	3424	-2578	3879	57
H(26C)	3732	-1414	4188	57
H(27A)	3341	-671	-304	158
H(27B)	3915	-1063	147	158
H(27C)	4126	-50	-194	158
H(28A)	3534	2077	-189	90
H(28B)	3004	2305	159	90
H(28C)	2745	1469	-288	90
H(29A)	4439	1192	553	105
H(29B)	4069	209	833	105
H(29C)	3795	1607	796	105
H(30A)	2594	708	534	140
H(30B)	2980	-611	576	140
H(30C)	2459	-209	105	140
H(31A)	4961	591	2801	51
H(31B)	5493	1578	2646	51
H(31C)	5171	476	2309	51
H(32A)	4750	1988	1719	61
H(32B)	5005	3127	2055	61
H(32C)	4178	3019	1792	61
H(33A)	3904	3260	2570	64
H(33B)	4739	3181	2818	64
H(33C)	4168	2231	2952	64
H(34A)	3919	405	1961	73
H(34B)	3398	1548	1995	73
H(34C)	3639	649	2425	73
H(35A)	3007	441	5505	55
H(35B)	2422	951	5079	55
H(35C)	2632	1749	5539	55
H(36A)	4076	1308	4710	61
H(36B)	3284	722	4570	61
H(36C)	3856	168	4993	61
H(37A)	4401	2550	5417	52
H(37B)	4232	1338	5682	52
H(37C)	3852	2615	5760	52
H(38A)	2936	3490	5117	67
H(38B)	2728	2739	4646	67
H(38C)	3507	3372	4790	67
H(39A)	777	6638	3114	60
H(39B)	1269	7725	2981	60
H(39C)	905	6750	2600	60
H(40A)	306	8328	2092	44
H(40B)	715	9324	2449	44
H(40C)	-145	9385	2281	44
H(41A)	-293	9331	3073	75
H(41B)	565	9268	3249	75
H(41C)	59	8240	3406	75
H(42A)	-425	6767	2339	44

H(42B)	-894	7767	2544	44
H(42C)	-499	6681	2864	44
H(51)	5180(20)	9390(50)	1598(15)	50
H(52)	4590(20)	8810(60)	1466(10)	50
H(61)	380(20)	4950(40)	3732(17)	50
H(62)	-269(8)	5220(50)	3552(19)	50
H(71)	430(30)	6290(50)	360(14)	50
H(72)	350(30)	5820(50)	736(16)	50

Table S–44. Crystal data and structure refinement for $(Et_4N)_2[Fe^{III}(tame–N_2SO_2)S_2^{Me2})]$•MeCN (**20**).

Empirical formula	C31 H64 Fe N5 O4 S3
Formula weight	722.90
Temperature	130(2) K
Wavelength	0.71073 A
Crystal description/color	prism / red
Crystal system, space group	Monoclinic, P 21/c
Unit cell dimensions	a = 11.1840(4)A alpha = 90 deg.
	b = 17.9000(6)A beta = 112.9030(14) deg.
	c = 20.8980(7)A gamma = 90 deg.
Volume	3853.8(2) A^3
Z, Calculated density	4, 1.246 Mg/m^3
Absorption coefficient	0.593 mm^-1
F(000)	1564
Crystal size	0.31 x 0.24 x 0.12 mm
Reflections for indexing	749
Theta range for data collection	2.12 to 28.40 deg.
Index ranges	-14<=h<=14, -22<=k<=23, -27<=l<=27
Reflections collected / unique	16700 / 8809 [R(int) = 0.0973]
Completeness to theta = 25.00	98.5%
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.9323 and 0.8376
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	8809 / 6 / 430
Goodness-of-fit on F^2	S = 0.960
S = root(sum(w*D*D)/(n-p)), where D = (Fo*Fo - Fc*Fc)	
Final R indices [I>2sigma(I)]	*R1 = 0.0627, wR2 = 0.1428
R indices (all data)	R1 = 0.1827, *wR2 = 0.2015
*Report these R factors.	
R1 = sum||Fo|-|Fc||/sum|Fo|, wR2= root(sum(w*D*D)/sum(w*Fo*Fo)), where D = (Fo*Fo - Fc*Fc)	
Weighting scheme	calc w=1/[\s^2^(Fo^2^)+(0.0906P)^2^+0.0000P] where P=(Fo^2^+2Fc^2^)/3
Largest diff. peak and hole	0.563 and -0.465 e.A^-3

Table S—45. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (A^2 x 10^3) for $(Et_4N)_2[Fe^{III}(tame—N_2SO_2)S_2^{Me2})]$•MeCN (**20**). U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

	x	y	z	U(eq)
Fe(1)	4284(1)	2685(1)	2545(1)	45(1)
S(1)	6212(1)	3112(1)	2638(1)	52(1)
S(2)	3961(1)	2346(1)	1468(1)	49(1)
S(3)	2087(2)	3639(1)	2654(1)	52(1)
S(4)	3004(7)	3878(4)	3083(3)	51(2)
O(1)	6805(4)	2752(2)	4579(2)	69(1)
O(2)	1233(3)	1232(2)	1782(2)	54(1)
O(3)	3292(3)	3645(2)	2493(2)	50(1)
O(4)	1823(4)	4427(2)	2801(2)	64(1)
N(1)	5042(4)	2592(2)	3550(2)	50(1)
N(2)	2810(4)	2051(2)	2442(2)	47(1)
N(3)	6548(4)	62(2)	3921(2)	48(1)
N(4)	7603(4)	1322(2)	1319(2)	46(1)
N(5)	7923(6)	5086(3)	1135(3)	85(2)
C(1)	8382(5)	3091(4)	3861(3)	69(2)
C(2)	6757(6)	4119(3)	3706(3)	65(2)
C(3)	6941(5)	3289(3)	3572(3)	54(1)
C(4)	6254(5)	2837(3)	3937(3)	57(1)
C(5)	4340(5)	2294(3)	3959(3)	62(1)
C(6)	2882(5)	2398(3)	3621(3)	54(1)
C(7)	2631(8)	3251(5)	3528(4)	53(2)
C(8)	2336(6)	2109(3)	4152(3)	67(2)
C(9)	2318(5)	1900(3)	2995(3)	56(1)
C(10)	2121(5)	1692(3)	1850(3)	46(1)
C(11)	2372(5)	1901(3)	1208(2)	46(1)
C(12)	1312(5)	2461(3)	797(3)	53(1)
C(13)	2307(5)	1225(3)	764(3)	54(1)
C(14)	7041(6)	861(3)	4067(3)	67(2)
C(15)	7868(6)	1043(3)	4824(3)	75(2)
C(16)	5824(6)	-32(3)	3138(3)	65(2)
C(17)	4681(5)	472(3)	2820(3)	67(2)
C(18)	5668(5)	-95(3)	4305(3)	64(2)
C(19)	5070(6)	-877(3)	4180(3)	63(2)
C(20)	7670(6)	-496(3)	4155(3)	69(2)
C(21)	8777(5)	-303(3)	3940(3)	69(2)
C(22)	6347(5)	906(4)	1165(3)	69(2)
C(23)	5364(6)	977(4)	463(3)	81(2)
C(24)	8566(5)	1138(3)	2049(3)	62(1)
C(25)	8224(7)	1416(4)	2623(3)	82(2)

C(26)	7313(5)	2163(3)	1238(3)	62(2)
C(27)	8434(6)	2675(3)	1446(3)	77(2)
C(28)	8222(5)	1106(3)	812(3)	60(1)
C(29)	8366(6)	286(3)	724(3)	66(2)
C(30)	8277(6)	4883(3)	1702(4)	63(2)
C(31)	8701(5)	4641(3)	2406(3)	63(2)
C(32)	2140(20)	3132(15)	3280(14)	38(7)

Table S–46. Bond lengths [A] and angles [deg] for $(Et_4N)_2[Fe^{III}(tame\text{-}N_2SO_2)S_2^{Me2})]\bullet MeCN$ **(20).**

Fe(1)-N(1)	1.941(4)
Fe(1)-N(2)	1.942(4)
Fe(1)-O(3)	2.025(3)
Fe(1)-S(2)	2.2219(14)
Fe(1)-S(1)	2.2246(15)
S(1)-C(3)	1.828(5)
S(2)-C(11)	1.826(5)
S(3)-S(4)	1.150(7)
S(3)-O(4)	1.498(4)
S(3)-O(3)	1.511(3)
S(3)-C(7)	1.823(8)
S(4)-O(3)	1.452(6)
S(4)-O(4)	1.566(7)
S(4)-C(32)	1.79(3)
O(1)-C(4)	1.249(6)
O(2)-C(10)	1.255(5)
N(1)-C(4)	1.352(7)
N(1)-C(5)	1.468(6)
N(2)-C(10)	1.340(6)
N(2)-C(9)	1.486(6)
N(3)-C(18)	1.519(6)
N(3)-C(14)	1.520(7)
N(3)-C(20)	1.527(6)
N(3)-C(16)	1.527(6)
N(4)-C(22)	1.510(6)
N(4)-C(24)	1.522(6)
N(4)-C(28)	1.524(6)
N(4)-C(26)	1.534(7)
N(5)-C(30)	1.152(7)
C(1)-C(3)	1.526(7)
C(1)-H(1A)	0.9800
C(1)-H(1B)	0.9800
C(1)-H(1C)	0.9800
C(2)-C(3)	1.540(7)
C(2)-H(2A)	0.9800
C(2)-H(2B)	0.9800
C(2)-H(2C)	0.9800
C(3)-C(4)	1.511(7)
C(5)-C(6)	1.516(7)
C(5)-H(5A)	0.9900
C(5)-H(5B)	0.9900
C(6)-C(9)	1.504(7)
C(6)-C(8)	1.550(6)

C(6)-C(7)	1.551(9)
C(6)-C(32)	1.57(3)
C(7)-H(7A)	0.9900
C(7)-H(7B)	0.9900
C(8)-H(8A)	0.9800
C(8)-H(8B)	0.9800
C(8)-H(8C)	0.9800
C(9)-H(9A)	0.9900
C(9)-H(9B)	0.9900
C(10)-C(11)	1.521(6)
C(11)-C(13)	1.510(6)
C(11)-C(12)	1.535(7)
C(12)-H(12A)	0.9800
C(12)-H(12B)	0.9800
C(12)-H(12C)	0.9800
C(13)-H(13A)	0.9800
C(13)-H(13B)	0.9800
C(13)-H(13C)	0.9800
C(14)-C(15)	1.525(7)
C(14)-H(14A)	0.9900
C(14)-H(14B)	0.9900
C(15)-H(15A)	0.9800
C(15)-H(15B)	0.9800
C(15)-H(15C)	0.9800
C(16)-C(17)	1.492(7)
C(16)-H(16A)	0.9900
C(16)-H(16B)	0.9900
C(17)-H(17A)	0.9800
C(17)-H(17B)	0.9800
C(17)-H(17C)	0.9800
C(18)-C(19)	1.529(7)
C(18)-H(18A)	0.9900
C(18)-H(18B)	0.9900
C(19)-H(19A)	0.9800
C(19)-H(19B)	0.9800
C(19)-H(19C)	0.9800
C(20)-C(21)	1.512(7)
C(20)-H(20A)	0.9900
C(20)-H(20B)	0.9900
C(21)-H(21A)	0.9800
C(21)-H(21B)	0.9800
C(21)-H(21C)	0.9800
C(22)-C(23)	1.456(8)
C(22)-H(22A)	0.9900
C(22)-H(22B)	0.9900
C(23)-H(23A)	0.9800
C(23)-H(23B)	0.9800
C(23)-H(23C)	0.9800

C(24)-C(25)	1.481(7)
C(24)-H(24A)	0.9900
C(24)-H(24B)	0.9900
C(25)-H(25A)	0.9800
C(25)-H(25B)	0.9800
C(25)-H(25C)	0.9800
C(26)-C(27)	1.475(8)
C(26)-H(26A)	0.9900
C(26)-H(26B)	0.9900
C(27)-H(27A)	0.9800
C(27)-H(27B)	0.9800
C(27)-H(27C)	0.9800
C(28)-C(29)	1.497(7)
C(28)-H(28A)	0.9900
C(28)-H(28B)	0.9900
C(29)-H(29A)	0.9800
C(29)-H(29B)	0.9800
C(29)-H(29C)	0.9800
C(30)-C(31)	1.426(8)
C(31)-H(31A)	0.9800
C(31)-H(31B)	0.9800
C(31)-H(31C)	0.9800
C(32)-H(32A)	0.9900
C(32)-H(32B)	0.9900
N(1)-Fe(1)-N(2)	93.72(17)
N(1)-Fe(1)-O(3)	97.52(15)
N(2)-Fe(1)-O(3)	93.80(15)
N(1)-Fe(1)-S(2)	154.56(13)
N(2)-Fe(1)-S(2)	86.09(12)
O(3)-Fe(1)-S(2)	107.88(10)
N(1)-Fe(1)-S(1)	86.26(13)
N(2)-Fe(1)-S(1)	164.26(13)
O(3)-Fe(1)-S(1)	101.82(10)
S(2)-Fe(1)-S(1)	87.23(5)
C(3)-S(1)-Fe(1)	99.58(18)
C(11)-S(2)-Fe(1)	100.14(15)
S(4)-S(3)-O(4)	71.2(3)
S(4)-S(3)-O(3)	64.5(3)
O(4)-S(3)-O(3)	107.7(2)
S(4)-S(3)-C(7)	60.8(4)
O(4)-S(3)-C(7)	99.7(3)
O(3)-S(3)-C(7)	104.3(3)
S(3)-S(4)-O(3)	69.9(4)
S(3)-S(4)-O(4)	64.8(3)
O(3)-S(4)-O(4)	107.1(4)
S(3)-S(4)-C(32)	60.3(9)
O(3)-S(4)-C(32)	107.4(10)
O(4)-S(4)-C(32)	95.9(9)

S(4)-O(3)-S(3)	45.6(3)
S(4)-O(3)-Fe(1)	119.7(3)
S(3)-O(3)-Fe(1)	119.95(19)
C(4)-N(1)-C(5)	114.1(4)
C(4)-N(1)-Fe(1)	122.2(3)
C(5)-N(1)-Fe(1)	123.6(3)
C(10)-N(2)-C(9)	112.2(4)
C(10)-N(2)-Fe(1)	122.7(3)
C(9)-N(2)-Fe(1)	125.1(3)
C(18)-N(3)-C(14)	109.1(4)
C(18)-N(3)-C(20)	109.3(4)
C(14)-N(3)-C(20)	111.2(4)
C(18)-N(3)-C(16)	111.3(4)
C(14)-N(3)-C(16)	108.5(4)
C(20)-N(3)-C(16)	107.4(4)
C(22)-N(4)-C(24)	110.1(4)
C(22)-N(4)-C(28)	111.2(4)
C(24)-N(4)-C(28)	107.8(4)
C(22)-N(4)-C(26)	108.7(4)
C(24)-N(4)-C(26)	111.1(4)
C(28)-N(4)-C(26)	107.8(4)
C(3)-C(1)-H(1A)	109.5
C(3)-C(1)-H(1B)	109.5
H(1A)-C(1)-H(1B)	109.5
C(3)-C(1)-H(1C)	109.5
H(1A)-C(1)-H(1C)	109.5
H(1B)-C(1)-H(1C)	109.5
C(3)-C(2)-H(2A)	109.5
C(3)-C(2)-H(2B)	109.5
H(2A)-C(2)-H(2B)	109.5
C(3)-C(2)-H(2C)	109.5
H(2A)-C(2)-H(2C)	109.5
H(2B)-C(2)-H(2C)	109.5
C(4)-C(3)-C(1)	110.0(4)
C(4)-C(3)-C(2)	107.2(4)
C(1)-C(3)-C(2)	110.3(5)
C(4)-C(3)-S(1)	110.0(4)
C(1)-C(3)-S(1)	110.2(4)
C(2)-C(3)-S(1)	109.0(4)
O(1)-C(4)-N(1)	124.4(5)
O(1)-C(4)-C(3)	118.1(5)
N(1)-C(4)-C(3)	117.4(4)
N(1)-C(5)-C(6)	114.0(4)
N(1)-C(5)-H(5A)	108.8
C(6)-C(5)-H(5A)	108.8
N(1)-C(5)-H(5B)	108.8
C(6)-C(5)-H(5B)	108.8
H(5A)-C(5)-H(5B)	107.7

C(9)-C(6)-C(5)	110.1(4)
C(9)-C(6)-C(8)	106.0(4)
C(5)-C(6)-C(8)	106.1(4)
C(9)-C(6)-C(7)	118.7(5)
C(5)-C(6)-C(7)	106.8(5)
C(8)-C(6)-C(7)	108.5(5)
C(9)-C(6)-C(32)	97.6(10)
C(5)-C(6)-C(32)	126.7(10)
C(8)-C(6)-C(32)	108.6(11)
C(6)-C(7)-S(3)	118.3(5)
C(6)-C(7)-H(7A)	107.7
S(3)-C(7)-H(7A)	107.7
C(6)-C(7)-H(7B)	107.7
S(3)-C(7)-H(7B)	107.7
H(7A)-C(7)-H(7B)	107.1
C(6)-C(8)-H(8A)	109.5
C(6)-C(8)-H(8B)	109.5
H(8A)-C(8)-H(8B)	109.5
C(6)-C(8)-H(8C)	109.5
H(8A)-C(8)-H(8C)	109.5
H(8B)-C(8)-H(8C)	109.5
N(2)-C(9)-C(6)	114.3(4)
N(2)-C(9)-H(9A)	108.7
C(6)-C(9)-H(9A)	108.7
N(2)-C(9)-H(9B)	108.7
C(6)-C(9)-H(9B)	108.7
H(9A)-C(9)-H(9B)	107.6
O(2)-C(10)-N(2)	124.4(4)
O(2)-C(10)-C(11)	118.1(4)
N(2)-C(10)-C(11)	117.3(4)
C(13)-C(11)-C(10)	111.3(4)
C(13)-C(11)-C(12)	109.8(4)
C(10)-C(11)-C(12)	106.7(4)
C(13)-C(11)-S(2)	109.9(3)
C(10)-C(11)-S(2)	109.7(3)
C(12)-C(11)-S(2)	109.4(3)
C(11)-C(12)-H(12A)	109.5
C(11)-C(12)-H(12B)	109.5
H(12A)-C(12)-H(12B)	109.5
C(11)-C(12)-H(12C)	109.5
H(12A)-C(12)-H(12C)	109.5
H(12B)-C(12)-H(12C)	109.5
C(11)-C(13)-H(13A)	109.5
C(11)-C(13)-H(13B)	109.5
H(13A)-C(13)-H(13B)	109.5
C(11)-C(13)-H(13C)	109.5
H(13A)-C(13)-H(13C)	109.5
H(13B)-C(13)-H(13C)	109.5

N(3)-C(14)-C(15)	115.8(5)
N(3)-C(14)-H(14A)	108.3
C(15)-C(14)-H(14A)	108.3
N(3)-C(14)-H(14B)	108.3
C(15)-C(14)-H(14B)	108.3
H(14A)-C(14)-H(14B)	107.4
C(14)-C(15)-H(15A)	109.5
C(14)-C(15)-H(15B)	109.5
H(15A)-C(15)-H(15B)	109.5
C(14)-C(15)-H(15C)	109.5
H(15A)-C(15)-H(15C)	109.5
H(15B)-C(15)-H(15C)	109.5
C(17)-C(16)-N(3)	114.6(4)
C(17)-C(16)-H(16A)	108.6
N(3)-C(16)-H(16A)	108.6
C(17)-C(16)-H(16B)	108.6
N(3)-C(16)-H(16B)	108.6
H(16A)-C(16)-H(16B)	107.6
C(16)-C(17)-H(17A)	109.5
C(16)-C(17)-H(17B)	109.5
H(17A)-C(17)-H(17B)	109.5
C(16)-C(17)-H(17C)	109.5
H(17A)-C(17)-H(17C)	109.5
H(17B)-C(17)-H(17C)	109.5
N(3)-C(18)-C(19)	114.1(4)
N(3)-C(18)-H(18A)	108.7
C(19)-C(18)-H(18A)	108.7
N(3)-C(18)-H(18B)	108.7
C(19)-C(18)-H(18B)	108.7
H(18A)-C(18)-H(18B)	107.6
C(18)-C(19)-H(19A)	109.5
C(18)-C(19)-H(19B)	109.5
H(19A)-C(19)-H(19B)	109.5
C(18)-C(19)-H(19C)	109.5
H(19A)-C(19)-H(19C)	109.5
H(19B)-C(19)-H(19C)	109.5
C(21)-C(20)-N(3)	114.9(5)
C(21)-C(20)-H(20A)	108.5
N(3)-C(20)-H(20A)	108.5
C(21)-C(20)-H(20B)	108.5
N(3)-C(20)-H(20B)	108.5
H(20A)-C(20)-H(20B)	107.5
C(20)-C(21)-H(21A)	109.5
C(20)-C(21)-H(21B)	109.5
H(21A)-C(21)-H(21B)	109.5
C(20)-C(21)-H(21C)	109.5
H(21A)-C(21)-H(21C)	109.5
H(21B)-C(21)-H(21C)	109.5

C(23)-C(22)-N(4)	116.6(5)
C(23)-C(22)-H(22A)	108.1
N(4)-C(22)-H(22A)	108.1
C(23)-C(22)-H(22B)	108.1
N(4)-C(22)-H(22B)	108.1
H(22A)-C(22)-H(22B)	107.3
C(22)-C(23)-H(23A)	109.5
C(22)-C(23)-H(23B)	109.5
H(23A)-C(23)-H(23B)	109.5
C(22)-C(23)-H(23C)	109.5
H(23A)-C(23)-H(23C)	109.5
H(23B)-C(23)-H(23C)	109.5
C(25)-C(24)-N(4)	115.7(5)
C(25)-C(24)-H(24A)	108.4
N(4)-C(24)-H(24A)	108.4
C(25)-C(24)-H(24B)	108.4
N(4)-C(24)-H(24B)	108.4
H(24A)-C(24)-H(24B)	107.4
C(24)-C(25)-H(25A)	109.5
C(24)-C(25)-H(25B)	109.5
H(25A)-C(25)-H(25B)	109.5
C(24)-C(25)-H(25C)	109.5
H(25A)-C(25)-H(25C)	109.5
H(25B)-C(25)-H(25C)	109.5
C(27)-C(26)-N(4)	117.2(5)
C(27)-C(26)-H(26A)	108.0
N(4)-C(26)-H(26A)	108.0
C(27)-C(26)-H(26B)	108.0
N(4)-C(26)-H(26B)	108.0
H(26A)-C(26)-H(26B)	107.2
C(26)-C(27)-H(27A)	109.5
C(26)-C(27)-H(27B)	109.5
H(27A)-C(27)-H(27B)	109.5
C(26)-C(27)-H(27C)	109.5
H(27A)-C(27)-H(27C)	109.5
H(27B)-C(27)-H(27C)	109.5
C(29)-C(28)-N(4)	115.7(4)
C(29)-C(28)-H(28A)	108.3
N(4)-C(28)-H(28A)	108.3
C(29)-C(28)-H(28B)	108.3
N(4)-C(28)-H(28B)	108.3
H(28A)-C(28)-H(28B)	107.4
C(28)-C(29)-H(29A)	109.5
C(28)-C(29)-H(29B)	109.5
H(29A)-C(29)-H(29B)	109.5
C(28)-C(29)-H(29C)	109.5
H(29A)-C(29)-H(29C)	109.5
H(29B)-C(29)-H(29C)	109.5

N(5)-C(30)-C(31)	179.1(7)
C(30)-C(31)-H(31A)	109.5
C(30)-C(31)-H(31B)	109.5
H(31A)-C(31)-H(31B)	109.5
C(30)-C(31)-H(31C)	109.5
H(31A)-C(31)-H(31C)	109.5
H(31B)-C(31)-H(31C)	109.5
C(6)-C(32)-S(4)	119.4(16)
C(6)-C(32)-H(32A)	107.5
S(4)-C(32)-H(32A)	107.5
C(6)-C(32)-H(32B)	107.5
S(4)-C(32)-H(32B)	107.5
H(32A)-C(32)-H(32B)	107.0

Symmetry transformations used to generate equivalent atoms:

Table S–47. Anisotropic displacement parameters (A^2 x 10^3) for $(Et_4N)_2[Fe^{III}(tame–N_2SO_2)S_2^{Me2})]\bullet MeCN$ **(20).** The anisotropic displacement factor exponent takes the form: -2 pi^2 [h^2 a*^2 U11 + ... + 2 h k a* b* U12]

	U11	U22	U33	U23	U13	U12
Fe(1)	48(1)	44(1)	43(1)	0(1)	18(1)	1(1)
S(1)	50(1)	57(1)	50(1)	-7(1)	19(1)	-3(1)
S(2)	50(1)	55(1)	46(1)	-4(1)	22(1)	-7(1)
S(3)	55(1)	49(1)	55(1)	0(1)	24(1)	4(1)
S(4)	55(5)	50(4)	47(4)	1(3)	19(4)	6(3)
O(1)	77(3)	74(3)	45(2)	-2(2)	11(2)	-4(2)
O(2)	57(2)	57(2)	51(2)	2(2)	23(2)	-11(2)
O(3)	54(2)	46(2)	57(2)	5(2)	30(2)	6(2)
O(4)	77(3)	49(2)	74(2)	4(2)	39(2)	16(2)
N(1)	50(2)	48(3)	46(2)	-1(2)	14(2)	2(2)
N(2)	55(3)	47(2)	42(2)	-2(2)	21(2)	-4(2)
N(3)	53(2)	47(3)	43(2)	-4(2)	18(2)	6(2)
N(4)	49(2)	46(3)	47(2)	-5(2)	23(2)	-4(2)
N(5)	101(4)	76(4)	78(4)	-14(3)	35(3)	1(3)
C(1)	63(4)	72(4)	63(4)	-5(3)	15(3)	-3(3)
C(2)	79(4)	61(4)	49(3)	-5(3)	18(3)	-4(3)
C(3)	49(3)	49(3)	52(3)	0(2)	8(2)	5(3)
C(4)	62(3)	57(4)	47(3)	-2(3)	17(3)	5(3)
C(5)	61(3)	69(4)	54(3)	6(3)	21(3)	-6(3)
C(6)	68(3)	50(3)	50(3)	-1(2)	31(3)	1(3)
C(7)	55(5)	57(5)	42(5)	-11(4)	16(4)	0(4)
C(8)	83(4)	76(4)	51(3)	5(3)	37(3)	0(3)
C(9)	60(3)	67(4)	45(3)	-3(3)	25(3)	-12(3)
C(10)	45(3)	41(3)	55(3)	2(2)	23(2)	-3(2)
C(11)	51(3)	45(3)	44(3)	-2(2)	19(2)	-5(2)
C(12)	52(3)	61(4)	48(3)	2(2)	21(2)	-3(3)
C(13)	56(3)	53(3)	57(3)	-8(3)	25(3)	-7(3)
C(14)	76(4)	62(4)	58(4)	4(3)	22(3)	4(3)
C(15)	97(5)	64(4)	54(4)	-7(3)	19(3)	-4(4)
C(16)	76(4)	66(4)	48(3)	-6(3)	20(3)	0(3)
C(17)	61(4)	79(4)	52(3)	-3(3)	14(3)	11(3)
C(18)	71(4)	68(4)	55(3)	-3(3)	27(3)	-1(3)
C(19)	74(4)	61(4)	65(4)	-8(3)	41(3)	-3(3)
C(20)	71(4)	61(4)	71(4)	1(3)	25(3)	13(3)
C(21)	55(3)	71(4)	70(4)	3(3)	13(3)	14(3)
C(22)	55(3)	72(4)	82(4)	-13(3)	30(3)	-3(3)
C(23)	51(3)	95(5)	91(5)	-13(4)	22(3)	1(3)
C(24)	74(4)	58(4)	50(3)	3(3)	21(3)	-2(3)
C(25)	116(5)	84(5)	56(4)	7(3)	42(4)	19(4)

C(26)	66(4)	67(4)	50(3)	-2(3)	20(3)	2(3)
C(27)	97(5)	62(4)	77(4)	3(3)	38(4)	-7(4)
C(28)	57(3)	69(4)	56(3)	-9(3)	25(3)	1(3)
C(29)	61(4)	70(4)	69(4)	-14(3)	29(3)	3(3)
C(30)	69(4)	55(4)	70(4)	-18(3)	32(3)	-5(3)
C(31)	56(3)	68(4)	65(4)	-15(3)	23(3)	-5(3)
C(32)	39(9)	36(9)	36(9)	2(6)	10(6)	-2(6)

Table S—48. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (A^2 x 10^3) for $(Et_4N)_2[Fe^{III}(tame—N_2SO_2)S_2^{Me2})]$•MeCN (**20**).

	x	y	z	U(eq)
H(1A)	8785	3245	4349	83
H(1B)	8804	3352	3592	83
H(1C)	8482	2551	3827	83
H(2A)	7092	4212	4207	78
H(2B)	5831	4245	3498	78
H(2C)	7230	4430	3496	78
H(5A)	4668	2544	4419	74
H(5B)	4532	1754	4039	74
H(7A)	3444	3510	3818	63
H(7B)	1974	3380	3718	63
H(8A)	1387	2146	3951	80
H(8B)	2684	2411	4576	80
H(8C)	2591	1586	4265	80
H(9A)	2513	1374	3147	67
H(9B)	1363	1959	2797	67
H(12A)	463	2216	636	64
H(12B)	1476	2642	395	64
H(12C)	1321	2884	1096	64
H(13A)	1466	977	643	65
H(13B)	3005	877	1023	65
H(13C)	2409	1382	339	65
H(14A)	6283	1201	3906	80
H(14B)	7558	968	3786	80
H(15A)	8148	1565	4861	90
H(15B)	8632	716	4990	90
H(15C)	7356	964	5106	90
H(16A)	6438	60	2910	77
H(16B)	5525	-556	3041	77
H(17A)	4219	342	2329	80
H(17B)	4978	991	2858	80
H(17C)	4096	413	3065	80
H(18A)	4959	279	4160	77
H(18B)	6173	-29	4809	77
H(19A)	4642	-968	4503	75
H(19B)	5754	-1249	4257	75
H(19C)	4431	-914	3701	75
H(20A)	8015	-534	4668	82
H(20B)	7327	-993	3964	82
H(21A)	9395	-719	4056	83

H(21B)	9216	148	4186	83
H(21C)	8436	-213	3438	83
H(22A)	6553	369	1259	82
H(22B)	5966	1080	1494	82
H(23A)	4647	632	403	97
H(23B)	5747	855	127	97
H(23C)	5035	1490	387	97
H(24A)	8663	588	2091	74
H(24B)	9422	1348	2107	74
H(25A)	8875	1245	3068	99
H(25B)	7369	1223	2568	99
H(25C)	8201	1963	2615	99
H(26A)	6761	2262	745	74
H(26B)	6794	2291	1514	74
H(27A)	8125	3192	1372	92
H(27B)	8942	2573	1165	92
H(27C)	8979	2599	1938	92
H(28A)	7692	1322	352	72
H(28B)	9092	1339	970	72
H(29A)	8865	206	435	79
H(29B)	7505	58	500	79
H(29C)	8822	55	1180	79
H(31A)	8127	4243	2441	76
H(31B)	8675	5062	2700	76
H(31C)	9591	4451	2561	76
H(32A)	1742	3334	3592	46
H(32B)	1418	2988	2842	46

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