Supporting Information

Synthesis, structure, and reactivity of Fe^{II}-NH_3 and Fe^{III}-NH_3 complexes bearing a tripodal sulfonamido ligand.

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General Methods

All reagents were purchased from commercial sources and used as received, unless otherwise noted. Solvents were sparged with argon and dried over columns containing Q-5 and molecular sieves. Sodium hydride (NaH) as a 30% dispersion in mineral oil was filtered with a medium porosity glass frit and washed 5 times each with pentane and Et_2O. Solid NaH was dried under a vacuum and stored under an inert atmosphere. Ferrocenium tetrafluoroborate ($[FeCp_2]BF_4$) was prepared according to literature procedures.[1] H_3MST and $[Ga^{III}MST]$ were synthesized according to previous reports.[2,3] Elemental analyses were performed on a Perkin-Elmer 2400 CHNS analyzer. The syntheses of metal complexes were conducted in a Vacuum Atmospheres, Co. drybox under an argon atmosphere. Electronic absorbance spectra were recorded with a Cary 50 and Agilent spectrophotometer using a 1.00 cm quartz cuvette. Fourier transform infrared spectra were collected on a Varian 800 Scimitar Series FTIR spectrometer. ^1H NMR and ^{13}C NMR spectra were recorded on a Bruker DRX500 spectrometer and referenced to residual solvent. Cyclic voltammetric experiments were conducted using a CHI600C electrochemical analyzer. A 2.0 mm glassy carbon electrode was used as the working electrode, with Pt wire as the counter electrode. A ferrocenium/ferrocene couple ($[FeCp_2]^{+/0}$) was used as an internal reference to monitor the reference electrode (Ag^+/Ag). Gas chromatography-mass spectrometry (GC-MS) was performed on a Thermo Trace MS+ GC-MS operated in electrospray mode. Perpendicular-mode or parallel-mode electron paramagnetic resonance (EPR) spectra were collected using a Bruker EMX spectrometer at 77 K with liquid nitrogen or at 10 K with liquid helium, respectively.

Complex Synthesis

Preparation of $Na[Fe^{II}MST]$. A solution of H_3MST (300 mg, 0.43 mmol) dissolved in 6 mL of anhydrous DMA was treated with solid NaH (31 mg, 1.3 mmol). The mixture was stirred until gas evolution ceased. $Fe(OAc)_2$ (75 mg, 0.43 mmol) was added to the solution, after which the pale yellow mixture was stirred for two h. The mixture was filtered to remove NaOAc. The filtrate was concentrated under vacuum to ca. 1 mL and triturated with Et_2O (10 mL) until a solid began to form. Pentane (20 mL) was added to complete the precipitation of a pale yellow solid, which was collected on a porous-glass fritted funnel. The solid was washed with THF (5 mL) and Et_2O (5 mL) to yield a white solid and was dried under vacuum to give 250 mg of product (76 %). Anal. Calc (found) for $Na[Fe^{II}MST]\cdot DMA$; $C_{37}H_{54}FeN_5NaO_7S_3$: C, 51.92 (51.48); H, 6.36 (6.69); N, 8.18 (8.35); X-band EPR (1:1 THF:DMA, parallel-mode, 10K) $g = 9.1$.

Preparation of $Na[Fe^{II}MST(NH_3)]$. A suspension of $Na[Fe^{II}MST]$ (56 mg, 0.073 mmol) in 2 mL of anhydrous THF was treated with a 0.5 M NH_3 solution in THF (260 µL, 0.13 mmol). The suspended $Na[Fe^{II}MST]$ immediately dissolved, forming a clear and faintly yellow solution. After 15 min, the solution was layered under pentane, and clear colorless crystals were obtained after 24 h. The solid was washed with pentane and dried under vacuum to afford 34 mg (50%) pure crystalline product. Anal. Calc (found) for $Na[Fe^{II}MST(NH_3)]\cdot 2$ THF; $C_{41}H_{64}FeN_5NaO_8S_3$: C, 50.95 (50.92); H, 6.94 (6.87); N, 7.53 (7.07); FTIR (Nujol, cm^{-1}) ν(NH) 3408, 3382; X-band EPR (1:1 THF:DMA, parallel-mode, 10K) $g = 9.4$.

Preparation of $[Fe^{III}MST(NH_3)]$. A solution of $Na[Fe^{II}MST(NH_3)]$ (49 mg, 0.063 mmol) in 3 mL of anhydrous THF was treated with ferrocenium tetrafluoroborate ($[FeCp_2]BF_4$) (17 mg, 0.063 mmol). After stirring for two h, the red-brown solution was filtered to remove insoluble solids. The filtrate was layered under pentane to form red-brown crystals over 24 h. The solid was washed with pentane and dried under vacuum to afford 32 mg (62 %) of crystalline product. Tropylium tetrafluoroborate ($C_7H_7BF_4$) can also be used for the oxidation. Note: Although reactivity of $[Fe^{III}MST(NH_3)]$ was assessed with crystals grown from THF, the best quality XRD crystal structure was obtained from a concentrated benzene solution of the complex. Anal. Calc (found) for $[Fe^{III}MST(NH_3)]\cdot 0.75$ THF; $C_{33}H_{48}N_5O_6S_3Fe$: C, 52.93 (52.53); H, 6.66 (6.80); N, 8.57 (8.32); λ_{max} (THF, nm (ε, $M^{-1}cm^{-1}$)) 398 (8000); FTIR (Nujol, cm^{-1}) ν(NH) 3349, (1:1 DCM:THF, cm^{-1}) ν(NH) 3339, 3309; X-band EPR (1:1 DCM:THF, perpendicular-mode, 77K) $g = 5.59, 1.99$.

Direct Preparation of $[Fe^{III}MST(NH_3)]$ from $Na[Fe^{II}MST]$. A suspension of $Na[Fe^{II}MST]$ (51 mg, 0.067 mmol) in 3 mL of anhydrous THF was treated with a 0.5 M NH_3 solution in THF (210 µL, 0.105 mmol). The suspended $Na[Fe^{II}MST]$ immediately dissolved, forming a clear and colorless solution. After stirring for 15 min, $[FeCp_2]BF_4$

(18 mg, 0.067 mmol) was added to the reaction, and the resulting red-brown solution was allowed to stir for 1.5 h. The solution was filtered to remove insoluble solids, and the filtrate was layered under pentane, forming red-brown crystals over 24 h. The solid was washed with pentane and dried under vacuum to afford 34 mg (63 %) of crystalline product. Tropylium tetrafluoroborate can also be used for the oxidation.

Preparation of [Ga^{III}MST(NH$_3$)]: A solution of Ga^{III}MST (83 mg, 0.12 mmol) in 2 mL of anhydrous DCM was treated with a 0.5 M NH$_3$ solution in THF (300 µL, 0.15 mmol). The clear, colorless solution became turbid upon NH$_3$ addition. The mixture stirred for 4 h, followed by filtration with a fine-fritted glass funnel. The filtrate was collected in a test tube and layered with Et$_2$O and pentane, resulting in colorless hexagonal rods over the next 24 h. The collected crystals were washed with Et$_2$O and dried to yield 49 mg (53 %) crystalline material. Anal. Calc (found) for [Ga^{III}MST(NH$_3$)]•0.75CH$_2$Cl$_2$•0.25C$_4$H$_8$O; $C_{34.75}H_{51.5}Cl_{1.5}GaN_5O_{6.25}S_3$: C, 48.62 (48.59); H, 6.05 (5.85); N, 8.16 (8.23). ^{1}H NMR (500MHz, CDCl$_3$, ppm): 2.29 (s, 9H), 2.70 (s, 18H), 2.82 (br t, 6H), 2.98 (br t, 6H), 4.75 (s, 3N*H*), 6.94 (s, 6H). ^{13}C NMR (125 MHz, 298K, CDCl$_3$, ppm): 21.0, 23.3, 41.3, 55.4, 132.0, 134.4, 139.7, 141.7. FTIR (KBr, selected bands, cm^{-1}) ν(NH): 3339, 3261; 2972, 2921, 2866, 1604, 1565, 1467, 1384, 1289, 1185, 1137, 1072, 947, 810, 750, 655.

Reactivity of [Fe^{III}MST(NH$_3$)] with base

In a typical reaction, a 0.12 mM solution of [Fe^{III}MST(NH$_3$)] in THF was prepared and added to a 1.0 cm quartz cuvette. One equivalent of base (triethylamine, pyrrolidine, 2-phenyl-1,1,3,3-tetramethylguanidine, 1,8-Diazabicyclo[5.4.0]undec-7-ene [DBU], or 1,5,7-triazobicyclo[4.4.0]dec-5-ene [TBD]) was injected *via* gastight syringe. The reactions were monitored at 298 K with electronic absorption spectroscopy. If necessary, additional equivalents of base were added to evaluate the stoichiometry of deprotonation.

EPR Studies of the Deprotonation/Protonation of [Fe^{III}MST(NH$_3$)]

A 9.8 mM solution of [Fe^{III}MST(NH$_3$)] in 1:1 DCM:THF was prepared in an EPR tube. An EPR spectrum of the frozen glass solution was obtained in perpendicular mode at 77 K, after which the solution was thawed. A substoichiometric amount of TBD in 1:1

DCM:THF was injected *via* gastight syringe, and the solution was mixed in the tube for 10 min. A new spectrum at 77 K was obtained, and the solution was thawed again. An equivalent of triethylammonium tetrafluoroborate ($HNEt_3BF_4$) in 1:1 DCM:THF was injected, and the solution was mixed in the tube for 10 min. A final EPR spectrum at 77 K was obtained of the solution.

UV/Vis Studies of the Deprotonation/Protonation of [$Fe^{III}MST(NH_3)$]

A 0.12 mM solution of [$Fe^{III}MST(NH_3)$] in THF was prepared and added to a 1.0 cm quartz cuvette. One equivalent of TBD was injected *via* gastight syringe, and the reaction was monitored at 298 K with electronic absorption spectroscopy. When the spectrum stabilized, an equivalent of $HNEt_3BF_4$ was added, and the protonation reaction was monitored.

Deprotonated [$Fe^{III}MST(NH_3)$] in the presence of substrates

A solution of 5.8 mM [$Fe^{III}MST(NH_3)$] in THF was treated with one equivalent of NaHMDS in THF at 298 K, causing an immediate color change to light orange. After 10 min, 0.5 equiv. of substrate (diphenylhydrazine [DPH], 9,10-dihydroanthracene [DHA], or 1 equiv. 2,6-*t*-butyl-*p*-cresol [BHT]) was added. The reactions stirred for several h, after which pentane was added to precipitate the complex. The reaction mixtures were filtered, and the filtrate solvent was removed *in vacuo*. Residues from the DPH and DHA reactions were dissolved in $CDCl_3$ and analyzed by ^1H NMR. Residues from the BHT reactions were dissolved in Et_2O and DCM and analyzed with GC-MS.

Crystallography

Structure of Na[Fe^{II}MST(NH$_3$)].

A colorless crystal of approximate dimensions 0.17 x 0.32 x 0.33 mm was mounted on a glass fiber and transferred to a Bruker SMART APEX II diffractometer. The APEX2[4] program package was used to determine the unit-cell parameters and for data collection (20 sec/frame scan time for a sphere of diffraction data). The raw frame data was processed using SAINT[5] and SADABS[6] to yield the reflection data file. Subsequent calculations were carried out using the SHELXTL[7] program. The diffraction symmetry was 2/*m* and the systematic absences were consistent with the monoclinic space groups *Cc* and *C*2/*c*. It was later determined that space group *C*2/*c* was correct.

The structure was solved by direct methods and refined on F^2 by full-matrix least-squares techniques. The analytical scattering factors[8] for neutral atoms were used throughout the analysis. Hydrogen atoms H(5B), H(5C) and H(5D) were located from a difference-Fourier map and refined (x,y,z and U_{iso}) with d(N-H) fixed at 0.95Å. The remaining hydrogen atoms were included using a riding model. The molecule was located on an inversion center (Z = 4). There were three molecules of THF solvent present per dimeric formula-unit. One of the THF molecules was located on a 2-fold rotation axis. Carbon atom C(36) was disordered and included using multiple components with partial site-occupancy-factors.

At convergence, wR2 = 0.0886 and Goof = 1.045 for 583 variables refined against 10993 data (0.77Å), R1 = 0.0323 for those 9617 data with $I > 2.0\sigma(I)$.

Structure of [Fe^{III}MST(NH$_3$)].

A red crystal of approximate dimensions 0.134 x 0.178 x 0.294 mm was mounted on a glass fiber and transferred to a Bruker SMART APEX II diffractometer. The APEX2[9] program package was used to determine the unit-cell parameters and for data collection (20 sec/frame scan time for a sphere of diffraction data). The raw frame data was processed using SAINT[5] and SADABS[6] to yield the reflection data file. Subsequent calculations were carried out using the SHELXTL[10] program. The systematic absences were consistent with the hexagonal space groups $P6_3$ and $P6_3/m$. The chiral space group $P6_3$ was assigned and later determined to be correct.

The structure was solved by direct methods and refined on F^2 by full-matrix least-squares techniques. The analytical scattering factors[8] for neutral atoms were used throughout the analysis. The molecule was located on a three-fold rotation axis. Hydrogen atoms were included using a riding model.

At convergence, wR2 = 0.0616 and Goof = 1.067 for 149 variables refined against 3279 data (0.75Å), R1 = 0.0221 for those 3176 data with $I > 2.0\sigma(I)$. The absolute structure was assigned by refinement of the Flack[11] parameter.

There were several high residuals present in the final difference-Fourier map. It was not possible to determine the nature of the residuals although it was probable from the crystallization method that a benzene solvent molecule was present. The SQUEEZE routine in the PLATON[12] program package was used to account for the electrons in the solvent accessible voids.

Structure of [$Ga^{III}MST(NH_3)$].

A colorless crystal of approximate dimensions 0.144 x 0.250 x 0.290 mm was mounted on a glass fiber and transferred to a Bruker SMART APEX II diffractometer. The APEX2[9] program package was used to determine the unit-cell parameters and for data collection (20 sec/frame scan time for a sphere of diffraction data). The raw frame data was processed using SAINT[5] and SADABS[6] to yield the reflection data file. Subsequent calculations were carried out using the SHELXTL[7] program. The systematic absences were consistent with the hexagonal space groups $P6_3$ and $P6_3/m$. The chiral space group $P6_3$ was assigned and later determined to be correct.

The structure was solved by direct methods and refined on F^2 by full-matrix least-squares techniques.[10] The analytical scattering factors[8] for neutral atoms were used throughout the analysis. The molecule was located on a three-fold rotation axis. Hydrogen atom H(3) was located from a difference-Fourier map and refined (x,y,z and U_{iso}) The remaining hydrogen atoms were included using a riding model.

At convergence, wR2 = 0.0520 and Goof = 1.058 for 152 variables refined against 2920 data (0.78Å), R1 = 0.0186 for those 2869 data with $I > 2.0\sigma(I)$. The absolute structure was assigned by refinement of the Flack[11] parameter.

There were several high residuals present in the final difference-Fourier map. It was not possible to determine the nature of the residuals although it was probable that diethylether and/or pentane solvents were present. The SQUEEZE routine in the PLATON[12] program package was used to account for the electrons in the solvent accessible voids.

Definitions:

$wR2 = [\Sigma[w(F_o^2-F_c^2)^2] / \Sigma[w(F_o^2)^2]]^{1/2}$

$R1 = \Sigma||F_o|-|F_c|| / \Sigma|F_o|$

$Goof = S = [\Sigma[w(F_o^2-F_c^2)^2] / (n-p)]^{1/2}$ where n is the number of reflections and p is the total number of parameters refined.

Table S1 Crystal data and structure refinement for 2 Na[Fe^{II}MST(NH$_3$)] • 3 THF.

Empirical formula	$C_{74}H_{112}Fe_2N_{10}Na_2O_{14}S_6 \cdot 3(C_4H_8O)$	
Formula weight	1932.09	
Temperature	88(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	*C*2/*c*	
Unit cell dimensions	a = 23.5685(19) Å	α = 90°.
	b = 19.6966(16) Å	β = 109.8619(9)°
	c = 21.9611(18) Å	γ = 90°.
Volume	9588.3(13) Å^3	
Z	4	
Density (calculated)	1.338 Mg/m^3	
Absorption coefficient	0.510 mm^{-1}	
F(000)	4112	
Crystal color	colorless	
Crystal size	0.33 x 0.32 x 0.17 mm^3	
Theta range for data collection	1.84 to 27.49°	
Index ranges	$-30 \le h \le 30$, $-25 \le k \le 25$, $-28 \le l \le 28$	
Reflections collected	51099	
Independent reflections	10993 [R(int) = 0.0332]	
Completeness to theta = 25.50°	100.0 %	
Absorption correction	Numerical	
Max. and min. transmission	0.9183 and 0.8481	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	10993 / 3 / 583	
Goodness-of-fit on F^2	1.045	
Final R indices [I>2sigma(I) = 9617 data]	R1 = 0.0323, wR2 = 0.0850	
R indices (all data, 0.77 Å)	R1 = 0.0381, wR2 = 0.0886	
Largest diff. peak and hole	0.598 and -0.441 e.Å^{-3}	
CCDC deposition number	971643	

Table S2 Crystal data and structure refinement for [$Fe^{III}MST(NH_3)$].

Empirical formula	$C_{33} H_{48} Fe N_5 O_6 S_3$	
Formula weight	762.79	
Temperature	88(2) K	
Wavelength	0.71073 Å	
Crystal system	Hexagonal	
Space group	$P6_3$	
Unit cell dimensions	a = 13.6656(9) Å	α= 90°.
	b = 13.6656(9) Å	β = 90°.
	c = 12.2841(8) Å	γ= 120°.
Volume	1986.7(3) $Å^3$	
Z	2	
Density (calculated)	1.275 Mg/m^3	
Absorption coefficient	0.583 mm^{-1}	
F(000)	806	
Crystal color	red	
Crystal size	0.294 x 0.178 x 0.134 mm^3	
Theta range for data collection	1.721 to 28.278°	
Index ranges	$-18 \le h \le 18$, $-18 \le k \le 18$, $-16 \le l \le 16$	
Reflections collected	23645	
Independent reflections	3279 [R(int) = 0.0246]	
Completeness to theta = 25.242°	99.9 %	
Absorption correction	Numerical	
Max. and min. transmission	0.9721 and 0.8556	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	3279 / 1 / 149	
Goodness-of-fit on F^2	1.067	
Final R indices [I>2sigma(I) = 3176 data]	R1 = 0.0221, wR2 = 0.0611	
R indices (all data, 0.75Å)	R1 = 0.0233, wR2 = 0.0616	
Absolute structure parameter	0.025(4)	
Largest diff. peak and hole	0.316 and -0.256 $e.Å^{-3}$	
CCDC deposition number	971644	

Table S3 Crystal data and structure refinement for [Ga^{III}MST(NH_3)]

Empirical formula	C_{33} H_{48} Ga N_5 O_6 S_3	
Formula weight	776.66	
Temperature	143(2) K	
Wavelength	0.71073 Å	
Crystal system	Hexagonal	
Space group	$P6_3$	
Unit cell dimensions	a = 13.6450(9) Å	α = 90°.
	b = 13.6450(9) Å	β = 90°.
	c = 12.2882(8) Å	γ = 120°.
Volume	1981.4(3) $Å^3$	
Z	2	
Density (calculated)	1.302 Mg/m^3	
Absorption coefficient	0.898 mm^{-1}	
F(000)	816	
Crystal color	colorless	
Crystal size	0.290 x 0.250 x 0.144 mm^3	
Theta range for data collection	1.723 to 27.089°	
Index ranges	$-17 \leq h \leq 17$, $-17 \leq k \leq 17$, $-15 \leq l \leq 15$	
Reflections collected	22408	
Independent reflections	2920 [R(int) = 0.0228]	
Completeness to theta = 25.242°	99.9 %	
Absorption correction	Numerical	
Max. and min. transmission	0.8914 and 0.7934	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	2920 / 1 / 152	
Goodness-of-fit on F^2	1.058	
Final R indices [I>2sigma(I) = 2869 data]	R1 = 0.0186, wR2 = 0.0518	
R indices (all data, 0.74Å)	R1 = 0.0190, wR2 = 0.0520	
Absolute structure parameter	0.017(3)	
Largest diff. peak and hole	0.257 and -0.163 e.$Å^{-3}$	
CCDC deposition number	971645	

Table S4 Selected bond distances (Å) and angles (˚) for Na[Fe^{II}MST(NH_3)]

Fe1—N5	2.145(1)
Fe1—N1	2.224(1)
Fe1—N2	2.104(1)
Fe1—N3	2.098(1)
Fe1—N4	2.096(1)
N5···O1	2.810(24)
N5···O3	2.914(24)
N5···O5	2.918(24)
N4—Fe1—N3	106.71(5)
N4—Fe1—N2	122.35(5)
N3—Fe1—N2	119.96(5)
N4—Fe1—N5	100.67(5)
N3—Fe1—N5	103.41(5)
N2—Fe1—N5	99.46(5)
N4—Fe1—N1	80.17(5)
N3—Fe1—N1	78.44(5)
N2—Fe1—N1	78.20(5)
N5—Fe1—N1	177.58(5)

Table S5 Selected bond distances (Å) and angles (˚) for [Fe^{III}MST(NH_3)] and [Ga^{III}MST(NH_3)]

	Fe^{III}	**Ga^{III}**
M1–N1	2.295(3)	2.259(4)
M1–N2	1.979(2)	1.946(1)
M1–N3	2.080(3)	2.015(3)
N3···O1	2.881(15)	2.837(15)
N2–M1–N2	117.33(3)	118.17(2)
N2–M1–N3	99.51(5)	97.84(5)
N2–M1–N1	80.49(5)	82.16(5)
N3–M1–N1	180.00(1)	180.00(1)

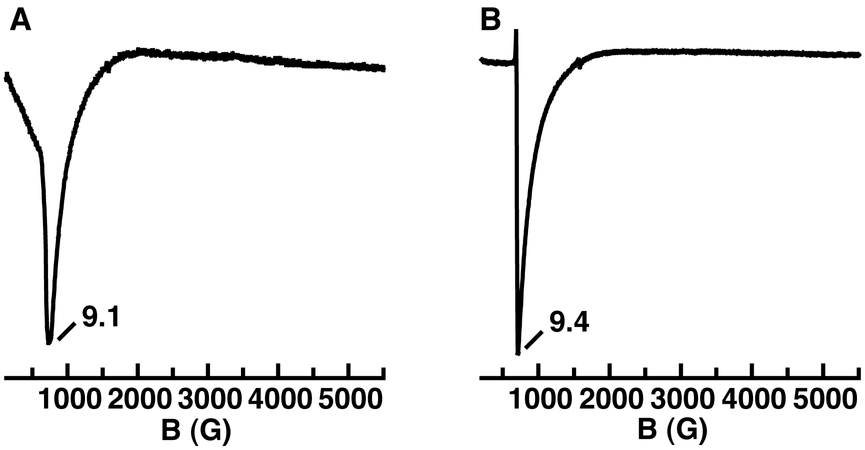

Fig. S1 Parallel-mode X-band EPR spectra of Na[Fe^{II}MST] (**A**) and Na[Fe^{II}MST(NH$_3$)] (**B**), each collected as a frozen glass in 1:1 DMA:THF at 10 K.

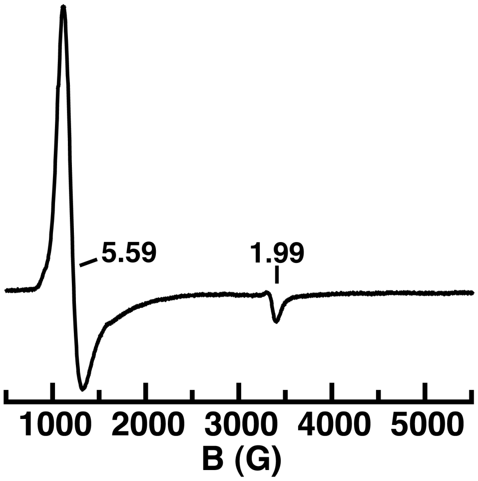

Fig. S2 Perpendicular-mode X-band EPR spectrum of 9.8 mM Fe^{III}MST(NH$_3$) collected as a frozen glass in 1:1 DCM:THF at 77K.

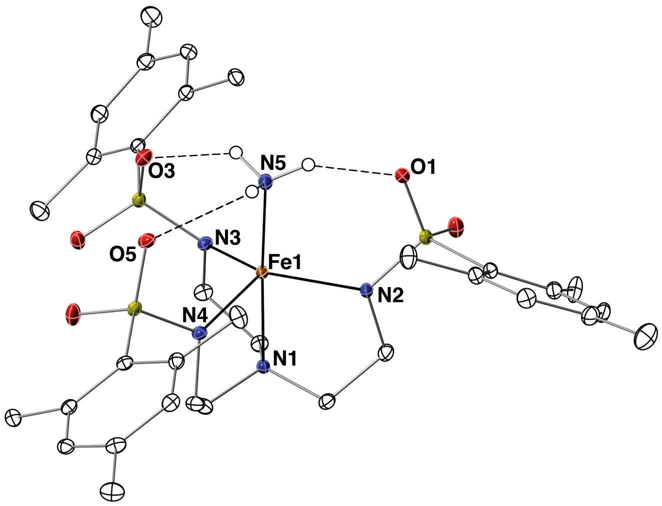

Fig. S3 Thermal ellipsoid diagram depicting the molecular structure of [Fe^{II}MST(NH$_3$)]$^-$. Ellipsoids are drawn at the 50% probability level, and for clarity only the ammine hydrogen atoms are shown.

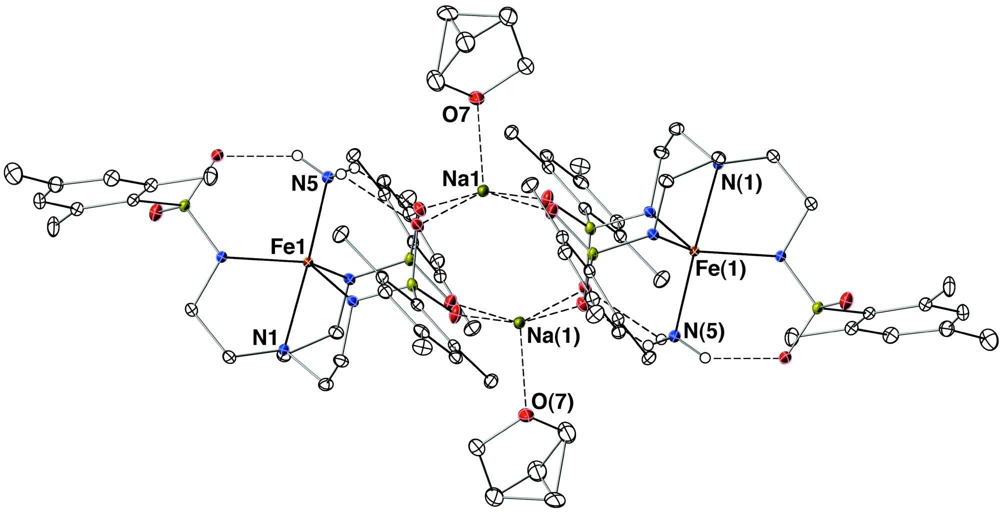

Fig. S4 Thermal ellipsoid diagram depicting the dimeric molecular structure of $[Na[Fe^{II}MST(NH_3)] \bullet THF]_2$. Ellipsoids are drawn at the 50% probability level, and for clarity only the ammine hydrogen atoms are shown.

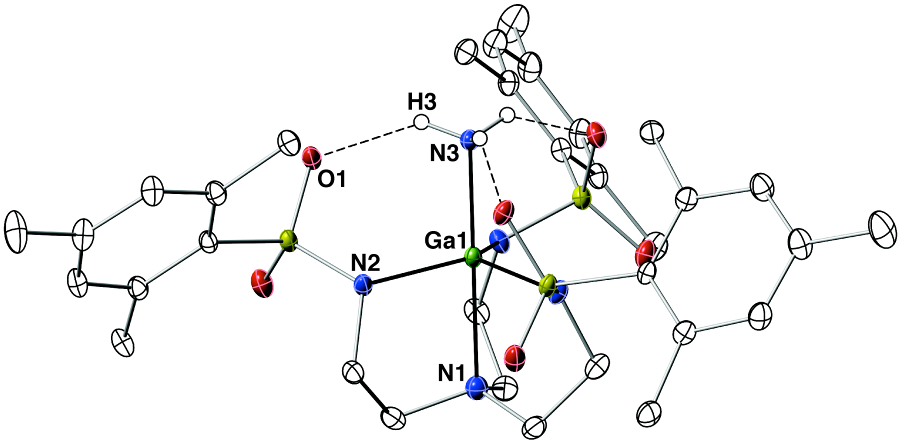

Fig. S5 Thermal ellipsoid diagram depicting the molecular structure of $[Ga^{III}MST(NH_3)]$. Ellipsoids are drawn at the 50% probability level, and for clarity only the ammine hydrogen atoms are shown.

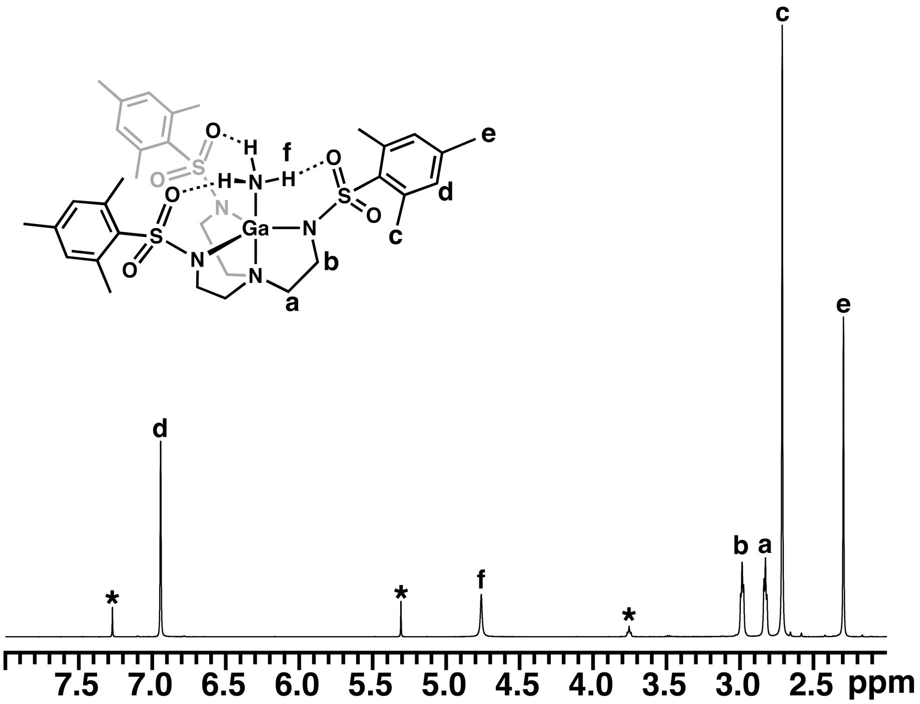

Fig. S6 ^{1}H NMR spectrum of [Ga^{III}MST(NH$_3$)] in CDCl$_3$ at 298 K. Asterisks denote residual solvent peaks.

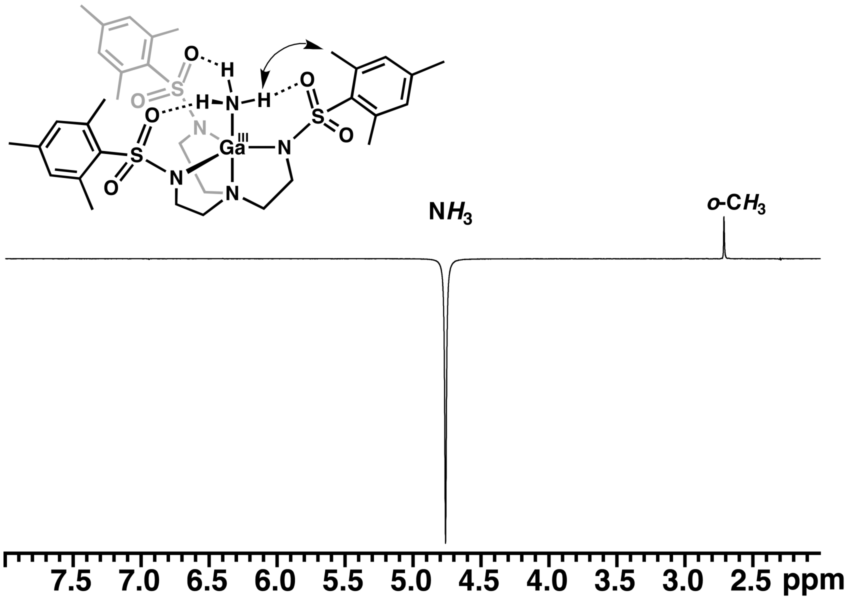

Fig. S7 ^{1}H gNOE NMR spectrum of [Fe^{III}MST(NH$_3$)] in CDCl$_3$ at 298 K with indicated NOE interactions. Irradiation frequency was set to 500.2224075 MHz.

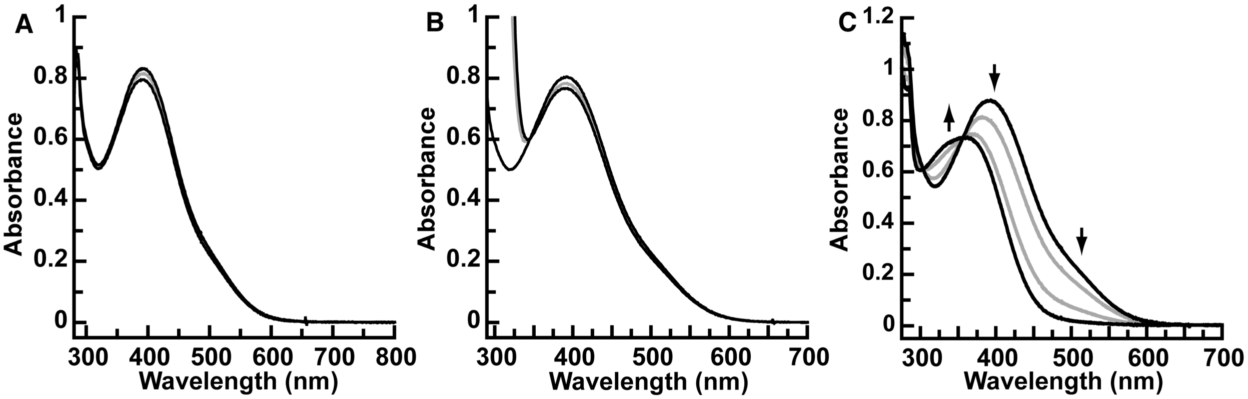

Fig. S8 Electronic absorption spectra of [Fe^{III}MST(NH$_3$)] treated with an excess of pyrrolidine (**A**) 2-phenyl-1,1,3,3-tetramethylguanidine (**B**) or 1,8-diazabicyclo[5.4.0]undec-7-ene (**C**). Spectra were collected in DMSO at 298 K.

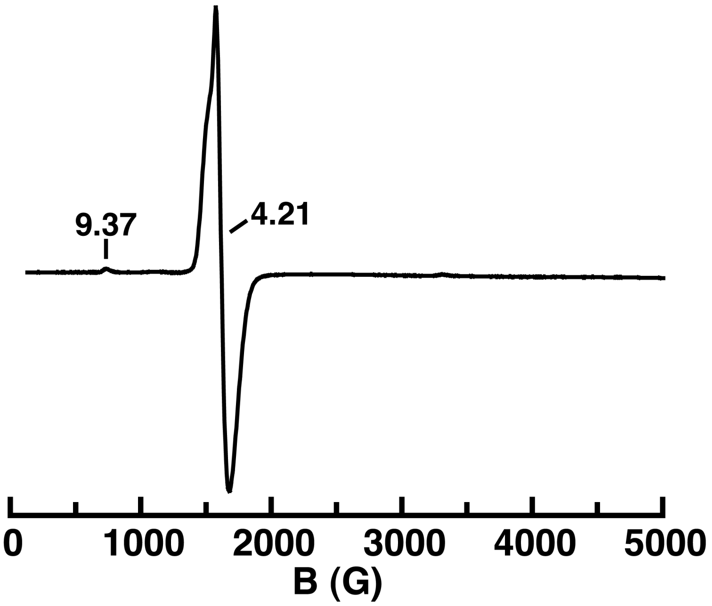

Fig. S9 Perpendicular-mode X-band EPR spectrum of 9.8 mM [Fe^{III}MST(NH$_3$)] after treatment with TBD, collected as a frozen glass in 1:1 DCM:THF at 77K.

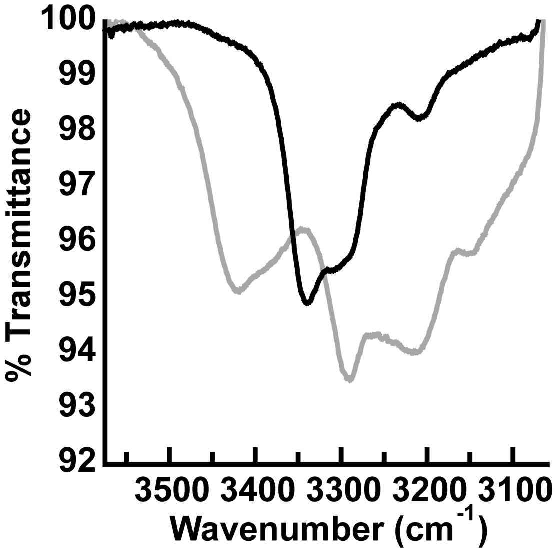

Fig. S10 Solution FTIR spectra of 9.8 mM [Fe^{III}MST(NH$_3$)] before (black line) and after (gray line) treatment with TBD. Spectra collected in 1:1 DCM:THF at 298 K. Note: ν(NH) peaks at 3289, 3213, and 3153 cm^{-1} for the gray line are from TBD.

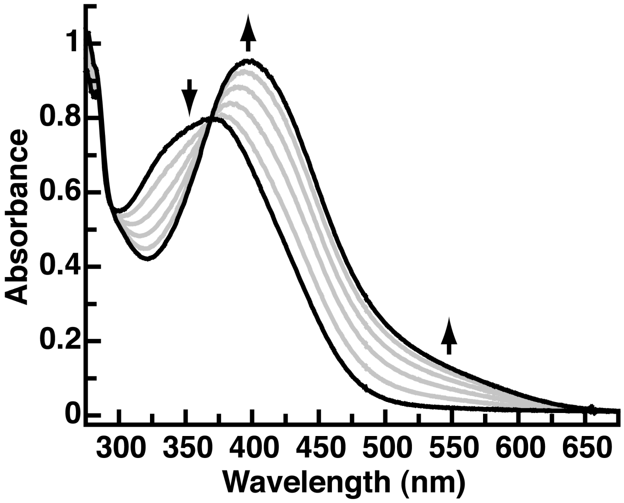

Fig. S11 Electronic absorption spectrum of [Fe^{III}MST(NH$_2$)]$^-$ in THF treated with HNEt$_3$BF$_4$ at 298 K.

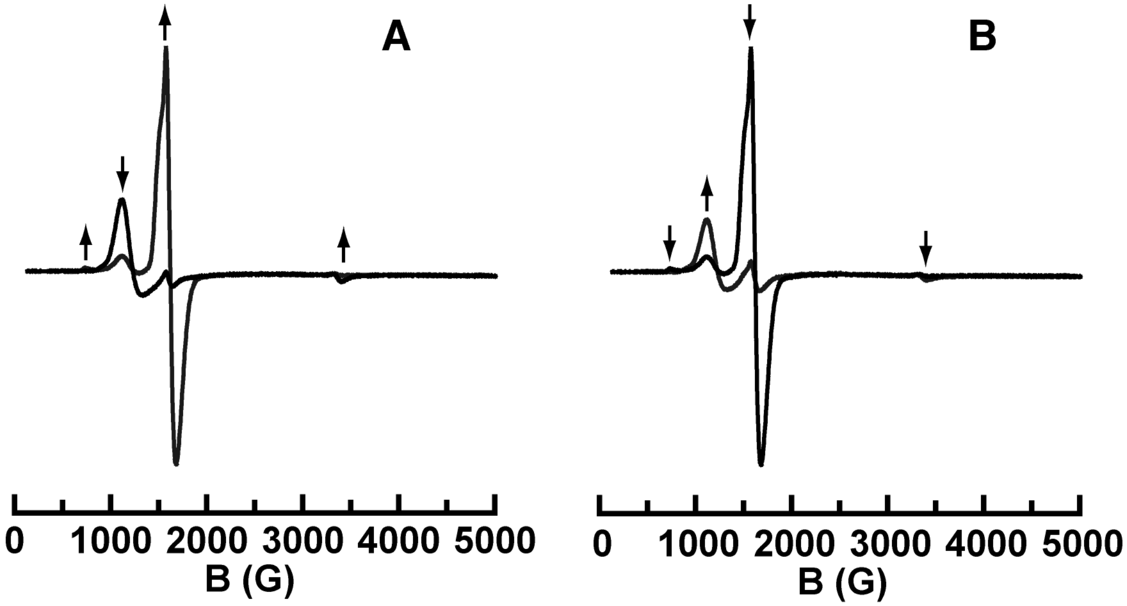

Fig. S12 Perpendicular-mode X-band EPR spectra of 9.8 mM [Fe^{III}MST(NH$_3$)] before and after addition of TBD (**A**) and regeneration of the [Fe^{III}MST(NH$_3$)] signal after the addition of HNEt$_3$BF$_4$ (**B**). The sample was collected as a frozen glass in 1:1 DCM:THF at 77 K.

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