

## Supporting Information

### *Investigations of Iron–Ammine and Amido Complexes within a C<sub>3</sub>-Symmetrical Phosphinic Amide Tripodal Ligand*

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#### **X-ray crystallography.**

**Table S1.** Selected Structural Parameters for {K[Fe<sup>II</sup>poat]}<sub>2</sub>·3THF, {K[Fe<sup>III</sup>poat]<sub>2</sub>}[BF<sub>4</sub>], K(crypt)[Fe<sup>II</sup>poat(NH<sub>3</sub>)], [Fe<sup>III</sup>poat(NH<sub>3</sub>)], and K[Fe<sup>III</sup>poat(NHtol)].

**Table S2.** Selected distances and angles for {K[Fe<sup>II</sup>poat]}<sub>2</sub>·3THF, {K[Fe<sup>III</sup>poat]<sub>2</sub>}[BF<sub>4</sub>], K(crypt)[Fe<sup>II</sup>poat(NH<sub>3</sub>)], [Fe<sup>III</sup>poat(NH<sub>3</sub>)], and K[Fe<sup>III</sup>poat(NHtol)].

**Figure S1.** EPR spectra of [Fe<sup>II</sup>poat]<sup>-</sup> and K(crypt)[Fe<sup>II</sup>poat(NH<sub>3</sub>)].

**Figure S2.** CV of [Fe<sup>II</sup>poat]<sup>-</sup> in DCM.

**Figure S3.** electronic absorption and EPR spectra of {K[Fe<sup>III</sup>poat]<sub>2</sub>}<sup>+</sup> and [Fe<sup>III</sup>poat(NH<sub>3</sub>)].

**Figure S4.** CV of Na[Fe<sup>II</sup>MST(NH<sub>3</sub>)] in DCM:THF.

**Figure S5.** Thermal ellipsoid plot of two [Fe<sup>III</sup>poat(NH<sub>3</sub>)] molecules in asymmetric unit.

**Figure S6.** UV-vis and EPR spectra after addition of DBU to [Fe<sup>III</sup>poat(NH<sub>3</sub>)].

**Figure S7.** Thermal ellipsoid plot of {K[Fe<sup>III</sup>poat(NHtol)]}<sub>2</sub>.

#### **References.**

## X-ray crystallography.

**Structure of  $\{\text{K}[\text{Fe}^{\text{II}}\text{poat}]\}_2 \cdot 3\text{THF}$ .** A yellow crystal of approximate dimensions 0.543 x 0.385 x 0.250 mm was mounted on a glass fiber and transferred to a Bruker SMART APEX II diffractometer. The APEX2<sup>1</sup> program package was used to determine the unit-cell parameters and for data collection (5 sec/frame scan time for a sphere of diffraction data). The raw frame data was processed using SAINT<sup>2</sup> and SADABS<sup>3</sup> to yield the reflection data file. Subsequent calculations were carried out using the SHELXTL<sup>4</sup> program. The systematic absences were consistent with the hexagonal space groups  $R3c$  and  $R\bar{3}c$ . The non-centrosymmetric space group  $R\bar{3}c$  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<sup>5</sup> for neutral atoms were used throughout the analysis. Hydrogen atoms were included using a riding model.

Least-squares analysis yielded  $wR2 = 0.1256$  and  $\text{Goof} = 1.029$  for 185 variables refined against 4029 data (0.78 Å),  $R1 = 0.0504$  for those 2771 data with  $I > 2.0\sigma(I)$ .

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 diethyl ether solvent was present. The SQUEEZE<sup>6</sup> routine in the PLATON<sup>7</sup> program package was used to account for the electrons in the solvent accessible voids.

**Structure of  $\{\text{K}[\text{Fe}^{\text{III}}\text{poat}]\}_2 [\text{BF}_4]$ .** A red crystal of approximate dimensions 0.269 x 0.398 x 0.413 mm was mounted on a glass fiber and transferred to a Bruker SMART APEX II diffractometer. The APEX2<sup>1</sup> program package was used to determine the unit-cell parameters and for data collection (15 sec/frame scan time for a sphere of diffraction data). The raw frame data was processed using SAINT<sup>2</sup> and SADABS<sup>3</sup> to yield the reflection data file. Subsequent calculations were carried out using the SHELXTL<sup>4</sup> program. There were no

systematic absences nor any diffraction symmetry other than the Friedel condition. The centrosymmetric triclinic space group  $P\bar{1}$  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<sup>5</sup> for neutral atoms were used throughout the analysis. Hydrogen atoms were included using a riding model.

Least-squares analysis yielded  $wR2 = 0.3166$  and  $Goof = 1.018$  for 964 variables refined against 17424 data ( $0.80\text{\AA}$ ),  $R1 = 0.1076$  for those 12798 data with  $I > 2.0\sigma(I)$ .

Several atoms were disordered and included using multiple components with partial site-occupancy-factors. 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 acetonitrile solvent was present. The SQUEEZE<sup>6</sup> routine in the PLATON<sup>7</sup> program package was used to account for the electrons in the solvent accessible voids.

**Structure of  $K(\text{crypt})[\text{Fe}^{\text{II}}\text{poat}(\text{NH}_3)]$ .** A yellow crystal of approximate dimensions  $0.393 \times 0.391 \times 0.178$  mm was mounted on a glass fiber and transferred to a Bruker SMART APEX II diffractometer. The APEX2<sup>1</sup> 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<sup>2</sup> and SADABS<sup>3</sup> to yield the reflection data file. Subsequent calculations were carried out using the SHELXTL<sup>4</sup> program. There were no systematic absences nor any diffraction symmetry other than the Friedel condition. The centrosymmetric triclinic space group  $P\bar{1}$  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<sup>5</sup> for neutral atoms were used throughout the analysis. Hydrogen atoms on ammonia ligand (N5) were located from a difference-Fourier map and refined ( $x,y,z$  and  $U_{\text{iso}}$ ). The remaining

hydrogen atoms were included using a riding model. There were two molecules of dichloromethane solvent present. One solvent molecule was disordered and included using multiple components with partial site-occupancy-factors.

Least-squares analysis yielded  $wR2 = 0.0943$  and  $Goof = 1.023$  for 804 variables refined against 14722 data ( $0.78 \text{ \AA}$ ),  $R1 = 0.0365$  for those 13000 data with  $I > 2.0\sigma(I)$ .

**Structure of  $[\text{Fe}^{\text{III}}\text{poat}(\text{NH}_3)]$ .** A violet crystal of approximate dimensions  $0.222 \times 0.254 \times 0.307 \text{ mm}$  was mounted on a glass fiber and transferred to a Bruker SMART APEX II diffractometer. The APEX2<sup>1</sup> 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<sup>2</sup> and SADABS<sup>3</sup> to yield the reflection data file. The systematic absences were consistent with the trigonal space groups  $P3$  and  $P\bar{3}$ . The noncentrosymmetric space group  $P3$  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<sup>4</sup>. The analytical scattering factors<sup>5</sup> for neutral atoms were used throughout the analysis. Hydrogen atoms H(5) and H(10) were located from a difference-Fourier map and refined ( $x,y,z$  and  $U_{\text{iso}}$ ). The remaining hydrogen atoms were included using a riding model. There were two molecules of the formula-unit present. Each molecule was located on a three-fold rotation axis. There was one-half molecule of tetrahydrofuran solvent per formula-unit. The solvent was located on a three-fold rotation axis and was disordered. Hydrogen atoms associated with the disordered solvent were not included in the refinement.

Least-squares analysis yielded  $wR2 = 0.0630$  and  $Goof = 1.050$  for 347 variables refined against 7144 data ( $0.73 \text{ \AA}$ ),  $R1 = 0.0237$  for those 7061 data with  $I > 2.0\sigma(I)$ . The absolute structure was assigned by refinement of the Flack parameter<sup>8</sup>.

**Structure of K[Fe<sup>III</sup>poat](NH<sub>4</sub>l)].** A black crystal of approximate dimensions 0.186 x 0.223 x 0.323 mm was mounted in a cryoloop and transferred to a Bruker SMART APEX II diffractometer. The APEX2<sup>1</sup> program package was used to determine the unit-cell parameters and for data collection (25 sec/frame scan time for a sphere of diffraction data). The raw frame data was processed using SAINT<sup>2</sup> and SADABS<sup>3</sup> to yield the reflection data file. Subsequent calculations were carried out using the SHELXTL<sup>4</sup> program. The diffraction symmetry was *mmm* and the systematic absences were consistent with the orthorhombic space group *P*2<sub>1</sub>2<sub>1</sub>2<sub>1</sub> that was later determined to be correct.

The structure was solved by direct methods and refined on F<sup>2</sup> by full-matrix least-squares techniques. The analytical scattering factors<sup>5</sup> for neutral atoms were used throughout the analysis. The amide hydrogen atoms (H5) were located from a difference-Fourier map and refined (x,y,z and U<sub>iso</sub>) with fixed length. The remaining hydrogen atoms were included using a riding model. Disordered atoms were included as isotropic atoms using multiple components with partial site-occupancy factors.

Least-squares analysis yielded wR2 = 0.0994 and Goof = 1.036 for 550 variables refined against 12304 data (0.75 Å), R1 = 0.0426 for those 10451 data with I > 2.0σ(I). The structure was refined as a two-component twin. The absolute structure was assigned by refinement of the Flack<sup>8</sup> 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 dichloromethane was present. The SQUEEZE<sup>6</sup> routine in the PLATON<sup>7</sup> program package was used to account for the electrons in the solvent accessible voids.

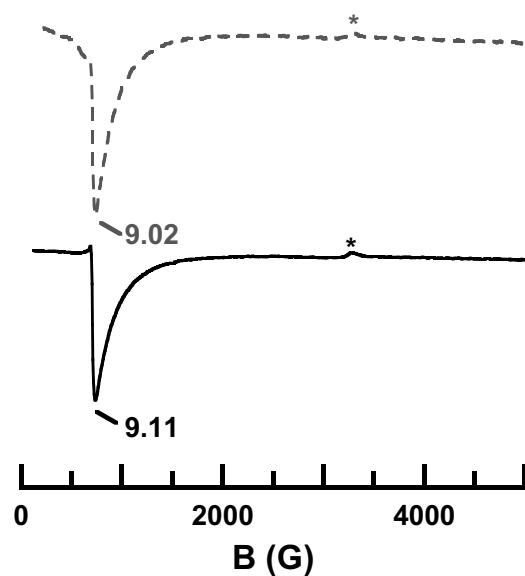
**Table S1.** Crystallographic and Structural Refinement Parameters.

Complexes	{K[Fe <sup>II</sup> poat]} <sub>2</sub> ·3THF	{K[Fe <sup>III</sup> poat] <sub>2</sub> }[BF <sub>4</sub> ]	K(crypt)[Fe <sup>II</sup> poat(NH <sub>3</sub> )]	[Fe <sup>III</sup> poat(NH <sub>3</sub> )]	K[Fe <sup>III</sup> poat(NHto)]
Formula	C <sub>96</sub> H <sub>108</sub> Fe <sub>2</sub> K <sub>2</sub> N <sub>8</sub> O <sub>9</sub> P <sub>6</sub>	C <sub>84</sub> H <sub>84</sub> Fe <sub>2</sub> N <sub>8</sub> O <sub>6</sub> P <sub>6</sub> · KBF <sub>4</sub>	C <sub>60</sub> H <sub>79</sub> FeKN <sub>7</sub> O <sub>9</sub> P <sub>3</sub> · 2(CH <sub>2</sub> Cl <sub>2</sub> )	C <sub>42</sub> H <sub>45</sub> FeN <sub>5</sub> O <sub>3</sub> P <sub>3</sub> · ½(C <sub>4</sub> H <sub>8</sub> O)	C <sub>49</sub> H <sub>49</sub> FeKN <sub>5</sub> O <sub>3</sub> P <sub>3</sub>
fw	1893.62	1725.02	1402.03	852.64	943.79
T (K)	133(2)	88(2)	133(2)	88(2)	133(2)
Crystal Space	Trigonal R $\bar{3}c$	Triclinic P $\bar{1}$	Triclinic P $\bar{1}$	Trigonal P3	Orthorhombic P2 <sub>1</sub> 2 <sub>1</sub>
a (Å)	14.8465(13)	14.409(2)	14.6635(7)	17.2520(6)	14.8454(10)
b (Å)	14.8465(13)	16.274(2)	14.8610(7)	17.2520(6)	17.4775(11)
c (Å)	85.868(8)	18.382(3)	18.8343(9)	8.2626(3)	19.4608(13)
α (°)	90	93.3944(19)	101.9506(7)	90	90
β (°)	90	90.1241(18)	98.9294(7)	90	90
γ (°)	120	95.9266(17)	118.7866(7)	120	90
V (Å <sup>3</sup> )	16391(3)	4279.9(11)	3359.9(3)	2129.74(17)	5049.3(6)
Z	6	2	2	2	4
δ <sub>calcd</sub>	1.151	1.339	1.386	1.330	1.242
Indep. re-	4029	17424	14722	7144	12304
GOF on	1.029	1.018	1.023	1.050	1.036
R1	0.0504	0.1076	0.0365	0.0237	0.0426
wR2	0.1256	0.3166	0.0943	0.0630	0.0994
CCDC#	2053480	2053482	2053479	2053478	2053481

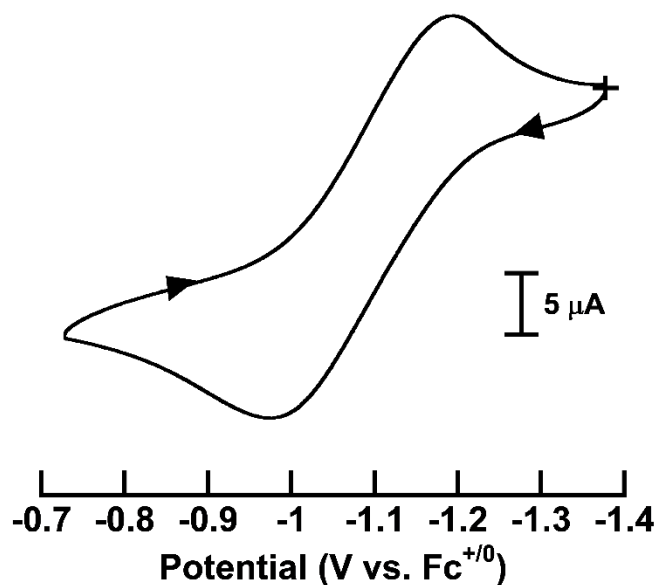
**Table S2.** Selected distances (Å) and angles (°) for  $K_2[Fe^{II}poat]_2 \cdot 3THF$ ,  $K[Fe^{III}poat]_2(BF_4)$ ,  $K(crypt)[Fe^{II}poat(NH_3)]$ ,  $[Fe^{III}poat(NH_3)]$ , and  $[Fe^{III}poat(NHtol)]^-$  complexes.

Complexes	$\{K[Fe^{II}poat]\}_2 \cdot 3THF$	$\{K[Fe^{III}poat]_2\}(BF_4)$	$K(crypt)[Fe^{II}poat(NH_3)]$	$[Fe^{III}poat(NH_3)]^a$	$K[Fe^{III}poat(NHtol)]$
	<i>Distances (Å)</i>				
Fe1–N1	2.127(4)	2.336(5)	2.220(1)	2.220 (4)	2.401(3)
Fe1–N2	1.994(2)	1.972(5)	2.112(1)	1.998(3)	2.030(3)
Fe1–N3	-	1.999(5)	2.110(1)	-	2.004(3)
Fe1–N4	-	2.004(5)	2.104(1)	-	2.040(3)
Fe1–N5	-	-	2.143(2)	2.060(4)	1.950(3)
Fe1–O2	-	2.235(5)	-	-	-
Fe1–O3	-	2.323(4)	-	-	-
N5...O1	-	-	2.884(2)	2.774(3)	-
N5...O2	-	-	2.921(2)	-	-
N5...O3	-	-	2.988(2)	-	-
K1...O1	2.651(2)	2.645(5)	-	-	2.547(3)
K1...O2	2.750(2)	2.637(4)	-	-	2.539(3)
K1...O3	-	2.592(4)	-	-	2.589(3)
K1...O4	-	2.546(5)	-	-	-
K1...O5	-	2.642(5)	-	-	-
K1...O6	-	2.665(5)	-	-	-
	<i>Angles (°)</i>				
N1–Fe1–N2	83.62(7)	78.0(2)	79.83(5)	81.10(7)	75.98(11)
N1–Fe1–N3	-	78.2(2)	80.26(5)	-	77.80(11)
N1–Fe1–N4	-	75.1(2)	79.92(5)	-	77.35(11)
N1–Fe1–N5	-	-	177.74(6)	180.0	168.79(12)
N2–Fe1–N2	118.78(3)	-	-	117.65(4)	-
N2–Fe1–N3	-	110.1(2)	120.30(6)	-	114.72(13)
N2–Fe1–N4	-	119.6(2)	115.67(6)	-	116.78(14)
N2–Fe1–N5	-	-	97.95(6)	98.91(7)	96.58(13)
N3–Fe1–N4	-	113.6(2)	115.17(5)	-	113.85(12)
N3–Fe1–N5	-	-	101.31(6)	-	113.19(13)
N4–Fe1–N5	-	-	100.77(6)	-	99.15(12)
O2–Fe1–O3	-	78.26(15)	-	-	-

a. Bond distances and angles are shown in average

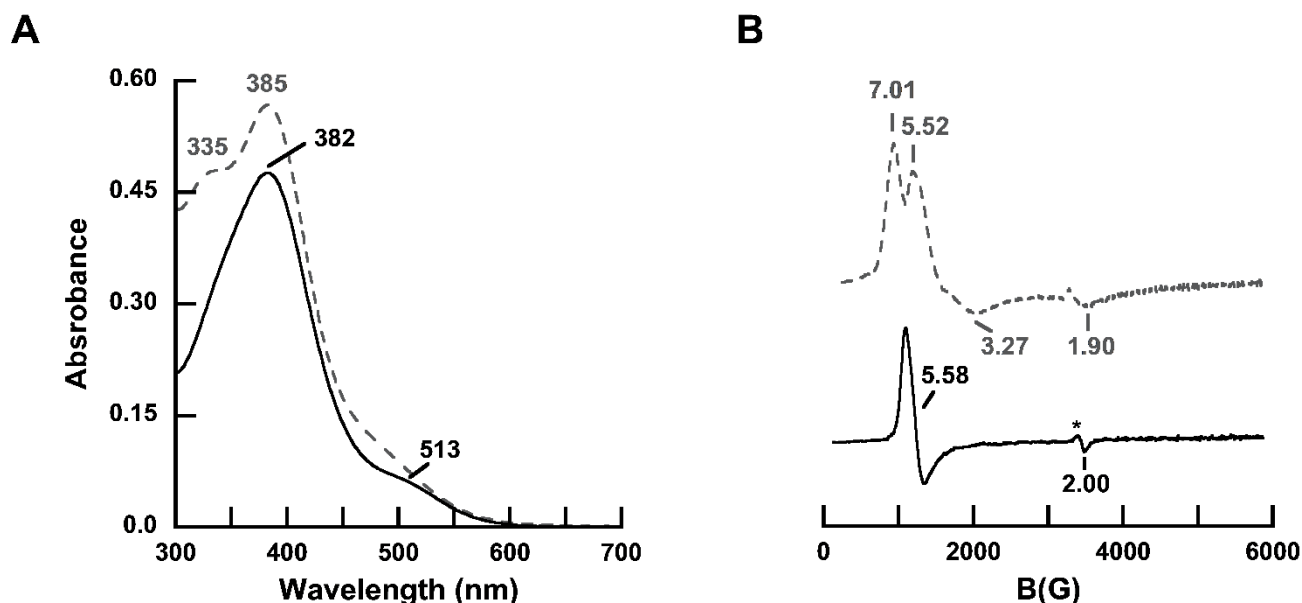


**Figure S1.** EPR spectra of  $[\text{Fe}^{\text{II}}\text{poat}]^-$  (dash line) and  $\text{K}(\text{crypt})[\text{Fe}^{\text{II}}\text{poat}(\text{NH}_3)]$  (solid line) measured in dimethyl formamide (DMF) : tetrahydrofuran (THF) (II-mode, 10K)

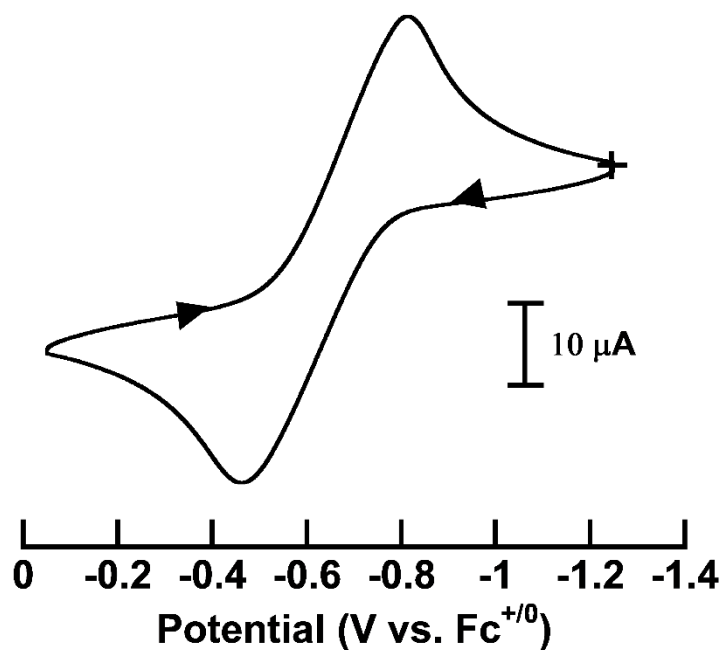


**Figure S2.** CV of 5 mM  $[\text{Fe}^{\text{II}}\text{poat}]^-$  measured in DCM. The measurement was done with 100 mV/s scan rate using 100 mM tetrabutylammonium hexafluorophosphate ( $\text{TBAPF}_6$ ) as electrolyte, glassy carbon electrode as working electrode, platinum wire as counter electrode, silver wire as reference electrode, and  $[\text{Fe}^{\text{III/I}}\text{Cp}_2]^{+/0}$  couple as internal standard.

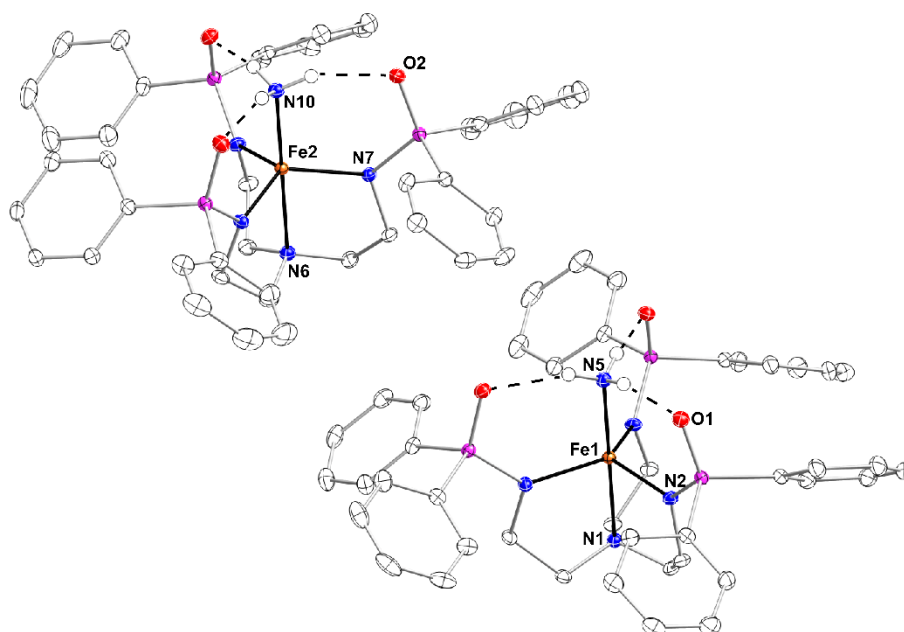




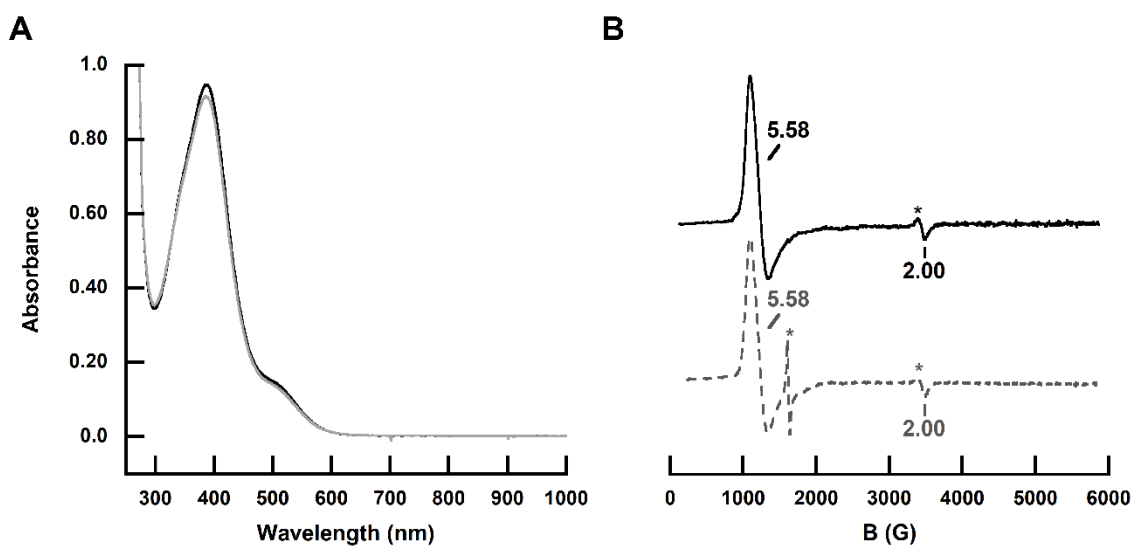
**Figure S3.** (A) electronic absorption spectra of  $\{K[Fe^{III}poat]_2\}^+$  (dash line) in acetonitrile (MeCN) and  $[Fe^{III}poat(NH_3)]$  (solid line) in dichloromethane (DCM). Both Spectra were measured as 0.1 mM solution at room temperature. (B) EPR spectra of  $\{K[Fe^{III}poat]_2\}^+$  (dash line) in MeCN and  $[Fe^{III}poat(NH_3)]$  (solid line) in DCM:THF ( $\perp$ -mode, 77K). Asterisks in panel B indicate signals from small amounts of impurities.



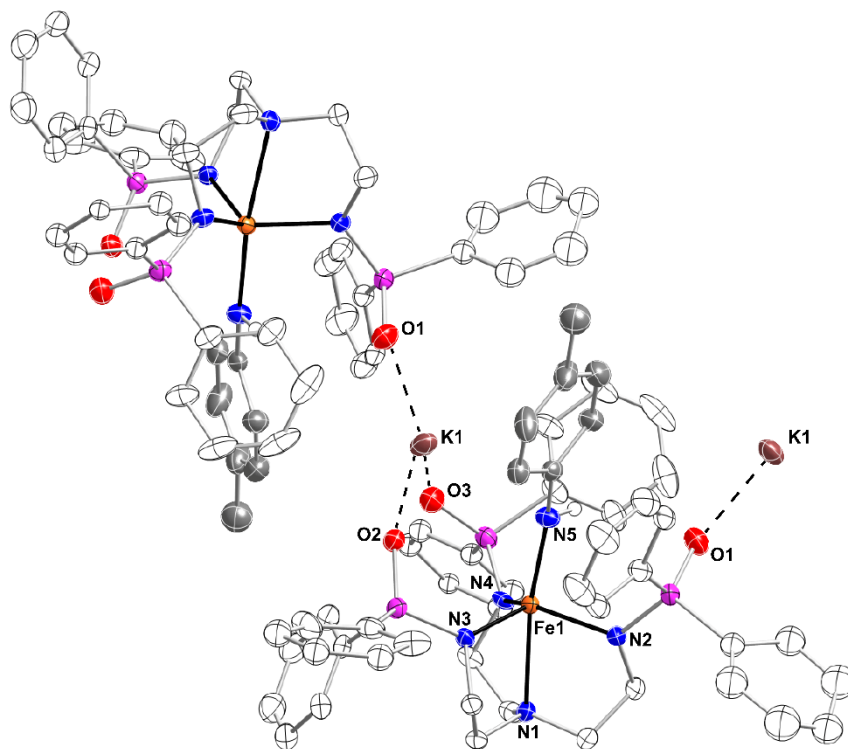
**Figure S4.** CV of 5 mM  $Na[Fe^{II}MST(NH_3)]$  measured in DCM:THF. The measurement was done with 100 mV/s scan rate using 100 mM tetrabutylammonium hexafluorophosphate ( $TBAPF_6$ ) as electrolyte, glassy carbon electrode as working electrode, platinum wire as counter electrode, silver wire as reference electrode, and  $[Fe^{III/II}Cp_2]^{+/0}$  couple as internal standard.



**Figure S5.** Thermal ellipsoid plots of two  $[\text{Fe}^{\text{II}}\text{poat}(\text{NH}_3)]$  molecules present in asymmetric unit determined by XRD methods. Only hydrogen atoms on  $\text{NH}_3$  are shown; solvent molecules are omitted for clarity. Ellipsoids are drawn at the 50% probability.



**Figure S6.** (A) electronic absorption spectra of  $[\text{Fe}^{\text{III}}\text{poat}(\text{NH}_3)]$  (black) and after addition of DBU (grey) in DCM. Both Spectra were measured as 0.2 mM solution at room temperature. (B) EPR spectra of  $[\text{Fe}^{\text{III}}\text{poat}(\text{NH}_3)]$  (black) and after addition of DBU (dash grey) in DCM:THF ( $L$ -mode, 77K). Asterisks in panel B indicate signals from small amounts of impurities.



**Figure S7.** Thermal ellipsoid plots of  $\{K[Fe^{III}poat(NHtol)]\}_2$  determined by XRD methods. Only the hydrogen atom on amido ligand is shown. Carbon atoms on the amide ligand are highlighted in grey to distinguish from the other carbon atoms. Ellipsoids are drawn at the 50% probability. Only one orientation of the disordered molecule is shown.

## References

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