

## Supporting Information

### Stepwise Assembly of Heterobimetallic Complexes: Synthesis, Structure, and Physical Properties.

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## Crystallography

**Structure of  $\{K[Fe^{III}poat(OH)]\}_2$ .** An orange crystal of approximate dimensions 0.293 x 0.313 x 0.363 mm was mounted in a cryoloop and transferred to a Bruker SMART APEX II diffractometer system. 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 package. The diffraction symmetry was  $2/m$  and the systematic absences were consistent with the monoclinic space group  $P2_1/c$  that was 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 atom H(1) was located from a difference-Fourier map and refined ( $x,y,z$  and  $U_{iso}$ ) with  $d(O-H) = 0.85\text{\AA}$ . The remaining hydrogen atoms were included using a riding model. The molecule was located about an inversion center. Least-squares analysis yielded  $wR2 = 0.0813$  and  $Goof = 1.063$  for 499 variables refined against 10756 data ( $0.73\text{\AA}$ ),  $R1 = 0.0294$  for those 9510 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 diethylether solvent was present. The SQUEEZE<sup>6a</sup> routine in the PLATON<sup>6b</sup> program package was used to account for the electrons in the solvent accessible voids.

**Structure of  $[(TMTACN)Zn^{II}-(\mu-OH)-Fe^{III}poat]OTf$ .** A yellow crystal of approximate dimensions 0.247 x 0.208 x 0.152 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 (30 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. The hydroxide hydrogen atoms (H1 and H8) were located from a difference-Fourier map and refined ( $x,y,z$  and  $U_{iso}$ ). The remaining hydrogen atoms were included using a riding model. There were two molecules of the formula-unit present ( $Z = 4$ ). Disordered atoms were included as isotropic atoms using multiple components with partial site-occupancy factors.

Least-squares analysis yielded  $wR2 = 0.1138$  and  $Goof = 1.016$  for 1341 variables refined against 32345 data ( $0.70\text{\AA}$ ),  $R1 = 0.0504$  for those 24496 data with  $I > 2.0\sigma(I)$ .

**Structure of  $[(TMTACN)Cu^{II}-(\mu-OH)-Fe^{III}poat]OTf$ .** A yellow crystal of approximate dimensions 0.276 x 0.189 x 0.131 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 (90 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. The hydroxide hydrogen atoms (H1 and H8) were located from a difference-Fourier map and refined ( $x,y,z$  and  $U_{iso}$ ). The remaining hydrogen atoms were included using a riding model. There were two molecules of the formula-unit present ( $Z = 4$ ). Disordered atoms were included as isotropic atoms using multiple components with partial site-occupancy factors.

Least-squares analysis yielded  $wR2 = 0.0899$  and  $Goof = 1.026$  for 1396 variables refined against 31356 data (0.70 Å),  $R1 = 0.0355$  for those 25498 data with  $I > 2.0\sigma(I)$ .

**Structure of [(TMTACN)Ni<sup>II</sup>-( $\mu$ -OH)-Fe<sup>III</sup>poat]OTf.** An orange crystal of approximate dimensions 0.258 x 0.099 x 0.086 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 (180 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 groups  $Pbcm$  and  $Pca2_1$ . It was later determined that space group  $Pca2_1$  was 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. The hydroxide hydrogen atoms (H1 and H8) were located from a difference-Fourier map and refined ( $x,y,z$  and  $U_{iso}$ ) with fixed length. The remaining hydrogen atoms were included using a riding model. There were two molecules of the formula-unit present ( $Z = 4$ ). Disordered atoms were included as isotropic atoms using multiple components with partial site-occupancy factors.

Least-squares analysis yielded  $wR2 = 0.0988$  and  $Goof = 1.010$  for 1356 variables refined against 27950 data (0.74 Å),  $R1 = 0.0532$  for those 21063 data with  $I > 2.0\sigma(I)$ . The structure was refined as a two-component twin. The absolute structure was assigned by refinement of the Flack<sup>7</sup> parameter.

## Data Analysis of EPR Measurements

The simulation software *SpinCount* diagonalizes the electronic terms of the spin Hamiltonian

$$H = J\mathbf{S}_1 \cdot \mathbf{S}_2 + H_1 + H_2 \quad (1)$$

with

$$H_i = \beta \mathbf{S}_i \cdot \mathbf{g}_i \cdot \mathbf{B} + \mathbf{S}_i \cdot \mathbf{D}_i \cdot \mathbf{S}_i \quad i = 1, 2$$

and

$$\mathbf{S}_i \cdot \mathbf{D}_i \cdot \mathbf{S}_i = D_i[\mathbf{S}_{xi}^2 - \mathbf{S}_i(\mathbf{S}_i + 1)/3 + (E/D)_i(\mathbf{S}_{xi}^2 - \mathbf{S}_{yi}^2)] \quad i = 1, 2$$

where the parameters have the usual definitions,<sup>8</sup> and performs least-squares fitting of simulations to the spectra. The spin  $\mathbf{S}_i$  refers to individual Fe<sup>III</sup> ( $S = 5/2$ ) or M<sup>II</sup> sites depending on the M<sup>II</sup> ion incorporated into the complex.  $\mathbf{D}_i$  is assumed coaxial with  $\mathbf{g}_i$  unless specified.<sup>9</sup>

**Table S1.** Crystallographic data for  $K[Fe^{III}poat(OH)]$  and  $[(TMTACN)M^{II}-(\mu-OH)-Fe^{III}poat]OTf$  complexes ( $M^{II} = Zn, Cu, Ni$ )

	$\{K[Fe^{III}poat(OH)]\}_2$	$[(TMTACN)Zn^{II}-(\mu-OH)-Fe^{III}poat]OTf$	$[(TMTACN)Cu^{II}-(\mu-OH)-Fe^{III}poat]OTf$	$[(TMTACN)Ni^{II}-(\mu-OH)-Fe^{III}poat]OTf$
Formula	$C_{84}H_{86}Fe_2K_2N_8O_8P_6$	$C_{52}H_{64}F_3FeN_7O_7P_3S$	$C_{52}H_{64}CuF_3FeN_7O_7P_3S$	$C_{52}H_{64}F_3FeN_7NiO_7P_3S$
fw	1711.32	1202.29	1200.46	1195.63
T (K)	88(2)	88(2)	133(2)	93(2)
Crystal system	Monoclinic	Triclinic	Triclinic	Orthorhombic
Space group	$P2_1/c$	$P\bar{1}$	$P\bar{1}$	$Pca2_1$
a (Å)	15.8093(12)	14.8745(7)	14.8537(13)	21.3910(9)
b (Å)	14.4288(11)	17.1815(8)	17.1335(15)	17.3399(8)
c (Å)	19.8831(15)	21.4499(10)	21.4044(19)	29.1742(13)
$\alpha$ (°)	90	89.3968(8)	90.9050(15)	90
$\beta$ (°)	111.1598(9)	89.9334(8)	91.3032(14)	90
$\gamma$ (°)	90	81.8418(8)	98.1532(14)	90
Z	2	4	4	8
V (Å <sup>3</sup> )	4229.7(6)	5426.1(4)	5389.9(8)	10821.2(8)
$\delta_{calc}$ (mg/m <sup>3</sup> )	1.344	1.472	1.479	1.468
Independent reflections	10756	32345	31356	27950
R1	0.0294	0.0504	0.0355	0.0532
wR2	0.0813	0.1138	0.0899	0.0988
Goof	1.063	1.016	1.026	1.010
CCDC#	2072600	2072601	2072602	2072603

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

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

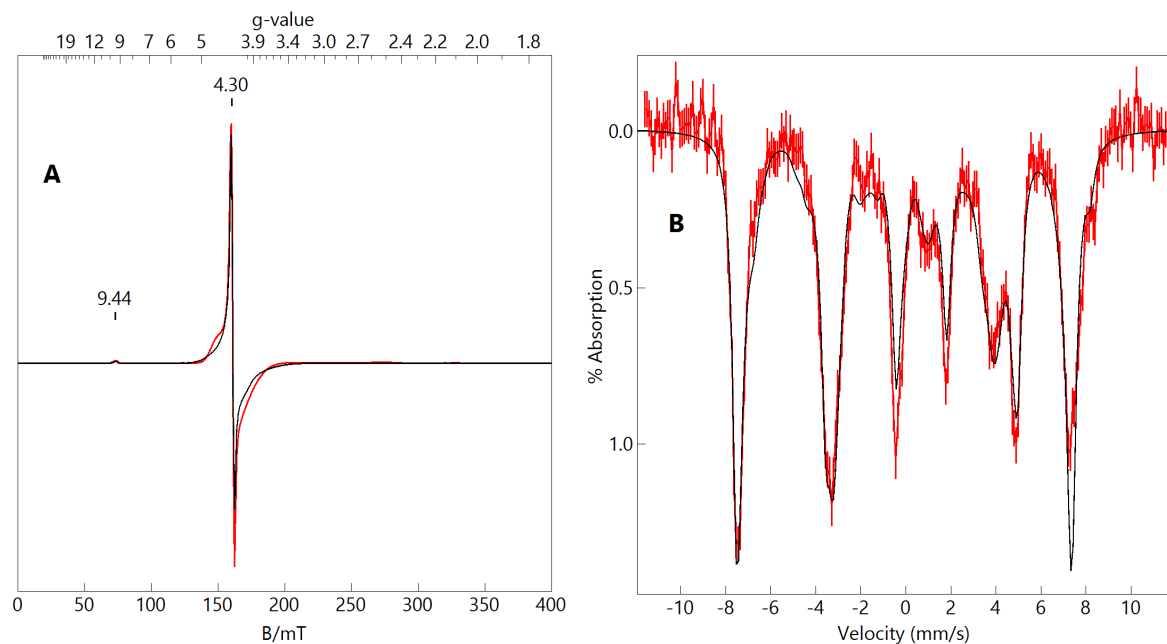
Goof =  $S = [\Sigma[w(F_o^2 - F_c^2)^2] / (n-p)]^{1/2}$  where n is the number of reflections and p is the total number of parameters refined.

The thermal ellipsoid plot is shown at the 50% probability level.

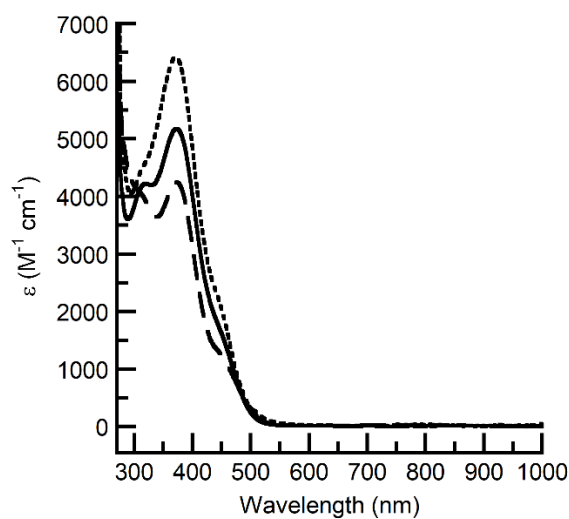
**Table S2.** Selected Metrical Parameters for  $\{\text{K}[\text{Fe}^{\text{III}}\text{poat}(\text{OH})]\}_2$ .

	Bond Lengths (Å)
Fe1–N1	2.373(1)
Fe1–N2	2.026(1)
Fe1–N3	2.004(1)
Fe1–N4	2.003(1)
Fe1–O1	1.896(1)
K1–O1	2.759(1)
K1–O2	2.665(1)
K1'–O1	2.870(1)
K1'–O3	2.656(1)
K1'–O4	2.655(1)
$d[\text{Fe1–N}_{\text{eq}}]$	0.425
	Angles (°)
O1–Fe1–N1	175.84(4)
N2–Fe1–N3	114.67(5)
N3–Fe1–N4	113.33(4)
N2–Fe1–N4	118.96(5)
Fe1–O1–K1	135.95(5)
Fe1–O1–K1'	121.22(4)
$\tau_5^a$	0.948

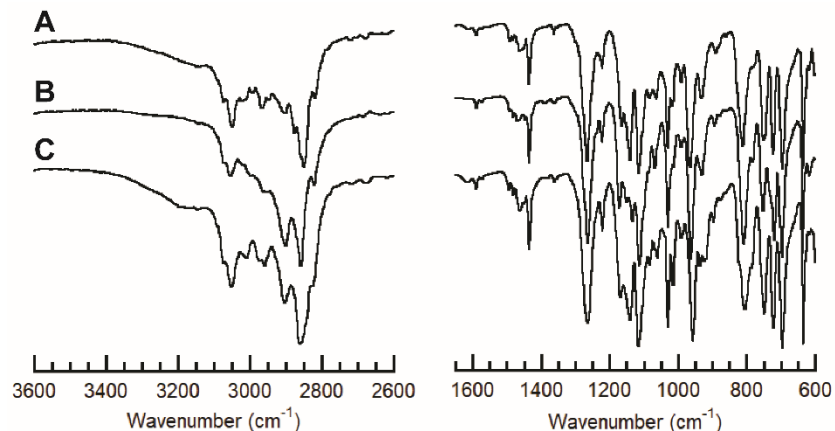
<sup>a</sup>Trigonality structural parameter,  $\tau_5 = (\beta - a)/60^\circ$ .  $\beta$  is the largest bond angle observed, and  $a$  is the second largest bond angle observed.



**Figure S1.** EPR (A) and Mössbauer (B) spectra of 1.6mM (K18c6)[ $^{57}\text{Fe}^{\text{III}}\text{poat}(\text{OH})$ ] in 1:1 DMF:THF (red plots). Experimental parameters: (A) microwaves, 0.2 mW at 9.645 GHz; temperature, 12 K; (B) magnetic field 45 mT parallel to  $\gamma$ -ray direction, temperature, 4.2 K. The black lines are simulation for:  $S = 5/2$ ,  $D = 1 \text{ cm}^{-1}$ ,  $E/D = 0.27$ ,  $A_{\text{Fe}} = (-20, -19, -19) \text{ T}$ ,  $\delta = 0.32 \text{ mm/s}$ ,  $\Delta E_{\text{Q}} = 0.92 \text{ mm/s}$ ,  $\eta = 0.9$ .



**Figure S2.** Full electronic absorbance spectra for (A)  $[\text{Zn}^{\text{II}}(\text{OH})\text{Fe}^{\text{III}}]^+$  (black solid line), (B)  $[\text{Cu}^{\text{II}}(\text{OH})\text{Fe}^{\text{III}}]^+$  (black dashed line), and (C)  $[\text{Ni}^{\text{II}}(\text{OH})\text{Fe}^{\text{III}}]^+$  (black dotted line) complexes. Absorbance measurements were performed on a 0.10 mM  $\text{CH}_2\text{Cl}_2$  solution at room temperature.



**Figure S3.** FTIR spectra for  $[\text{Zn}^{\text{II}}(\text{OH})\text{Fe}^{\text{III}}]^+$  (A),  $[\text{Cu}^{\text{II}}(\text{OH})\text{Fe}^{\text{III}}]^+$  (B), and  $[\text{Ni}^{\text{II}}(\text{OH})\text{Fe}^{\text{III}}]^+$  (C).

## References

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