# **Supporting Information**

## Preorganized assembly of three iron(II) or manganese(II) βdiketiminate complexes using a cyclophane ligand

Gary L. Guillet,<sup>*a*</sup> Forrest T. Sloane,<sup>*a*</sup> David M. Ermert,<sup>*a*</sup> Matthew W. Calkins,<sup>*b*</sup> Marcus K. Peprah,<sup>*b*</sup> Elisabeth S. Knowles,<sup>*b*</sup> Erik Čižmár,<sup>*c*</sup> Khalil A. Abboud,<sup>*a*</sup> Mark W. Meisel,<sup>*b,c*</sup> and Leslie J. Murray\*<sup>*a*</sup>

 <sup>a</sup> University of Florida, Department of Chemistry, Center for Catalysis, Gainesville, FL 32611-7200, USA. Tel: +001 352-392-0564; E-mail:murray@chem.ufl.edu
<sup>b</sup> Department of Physics and the National High Magnetic Field Laboratory, University of Florida, Gainesville, Florida 32611-8440, United States
<sup>c</sup> Institute of Physics, Faculty of Science, P.J. Šafárik University, 041 54 Košice, Slovakia

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## **General Considerations**

All reactions were performed under dry, air free conditions using standard Schlenk techniques or in an Innovative Technologies glovebox unless otherwise noted. Solvents were either purchased anhydrous and used as received (Sigma-Aldrich) or extracted from an Innovative Technologies solvent purification system. Anhydrous MnBr<sub>2</sub> and FeBr<sub>2</sub> were purchased from Sigma-Aldrich, washed with diethyl ether, and dried under reduced pressure overnight prior to use. NMR spectra were recorded on either a 500 MHz Inova or 300 MHz Mercury spectrophotometer with the spectra referenced to the residual protonated solvent signal, 7.27 ppm for  $CDCl_3-d_1$  and 3.58 for THF- $d_8$ . Deuterated solvents were purchased from Cambridge Isotope Labs and dried by standard methods as described elsewhere.<sup>1</sup> Infrared spectra were recorded as solids on a Bruker Vertex 80v FTIR using a Pike GladiATR stage. UV/VIS spectra were recorded on a Varian Cary 50 UV/VIS spectrophotometer using screw-top quartz cuvettes with a 1 cm path-length. Cyclic voltammetry was performed under a nitrogen atmosphere using a standard three electrode setup. Electrodes were purchased from either BASi, Inc. or CH Instruments, Inc. Potential sweeps were controlled by a Princeton Applied Research Versastat II potentiostat. EPR measurements were recorded on a Bruker Elexsys E580 with a Bruker 4116DM resonator. Data was collected in the field from 50 to 7050 G with the following parameters for (1): temperature = 5 K, power = 6.30x  $10^{-2}$  mW, frequency = 9.629 GHz, modulation frequency = 100.00 kHz, modulation amplitude = 10.00 G, and gain = 60 dB and for (2): temperature = 5 K, power =  $6.30 \times 10^{-2} \text{ mW}$ , frequency = 9.622 GHz, modulation frequency = 100.00 kHz, modulation amplitude = 10.00 G, and gain = 60 dB. Elemental analyses were performed by Complete Analysis Laboratories, Inc (Parsippany, NJ). 1,3,5-trisaminomethyl-2,4,6-triethylbenzene was synthesized according to a previous report.<sup>2</sup> All other reagents were purchased from Sigma-Aldrich and used without further purification.

## X-Ray Crystallography

X-Ray Intensity data were collected at 100 K on a Bruker DUO diffractometer using MoK $\alpha$  radiation ( $\lambda = 0.71073$  Å) or CuK $\alpha$  radiation ( $\lambda = 1.54178$  Å) from an ImuS power source, and an APEXII CCD area detector. Raw data frames were read by the SAINT<sup>3</sup> program and integrated using 3D profiling algorithms. The resulting data were reduced to produce hkl reflections and their intensities and estimated standard deviations. The data were corrected for Lorentz and polarization effects and numerical absorption corrections were applied based on indexed and measured faces. The structures were solved and refined in SHELXTL6.1, using full-matrix least-squares refinement.<sup>4</sup> The non-H atoms were refined with anisotropic thermal parameters and all of the H atoms were calculated in idealized positions and refined riding on their parent atoms unless otherwise stated.

 $(H_3L)$ The asymmetric unit consists of a half molecule (located on a 2-fold rotation axis) and a dichloromethane solvent molecule. The amino protons are disordered. Protons H1 and H2 are obtained from a Difference Fourier map and refined with 50% occupancy factors. Proton H3 was also obtained from a Difference Fourier map and refined with 50% occupancy. It is disordered against its symmetry equivalent position on the N3 related by the 2-fold rotation axis. In the final cycle of refinement, 5244 reflections (of which 4362 are observed with I >  $2\sigma(I)$ ) were used to refine 276 parameters and the resulting  $R_1$ ,  $wR_2$  and S (goodness of fit) were 3.78%, 10.73% and 1.072, respectively. The refinement was carried out by minimizing the  $wR_2$  function using

 $F^2$  rather than F values.  $R_1$  is calculated to provide a reference to the conventional R value but its function is not minimized.

(1) The core is partially disordered. Specifically, atoms Fe3 and Br3 are refined against the minor part of Fe3' and Br3'. Their site occupation factors refined to 0.981(1) and 0.019(1) for the major and minor parts, respectively. In the final cycle of refinement, 14157 reflections (of which 10123 are observed with I >  $2\sigma(I)$ ) were used to refine 721 parameters and the resulting R<sub>1</sub>, wR<sub>2</sub> and S (goodness of fit) were 2.96%, 6.67% and 0.917, respectively. The refinement was carried out by minimizing the wR<sub>2</sub> function using F<sup>2</sup> rather than F values. R<sub>1</sub> is calculated to provide a reference to the conventional R value but its function is not minimized.

(2) The asymmetric unit consists of the Mn3 complex and three toluene solvent molecules. The Mn/Br core is disordered where in one part, Mn1, Mn2, Br1 and Br2 form a diamond geometry and Br3 coordinated only to Mn3, and in the second part, all Mn and Br atoms form two fused diamond geometries with Mn1' and Br2 common to both. The refined site occupation factors for both parts of the disorder are 0.943(1) and 0.057(1), for the major and minor parts respectively. In the final cycle of refinement, 97347 reflections (of which 11233 are observed with I >  $2\sigma(I)$ ) were used to refine 764 parameters and the resulting R<sub>1</sub>, wR<sub>2</sub> and S (goodness of fit) were 2.77%, 6.69% and 0.968, respectively. The refinement was carried out by minimizing the wR<sub>2</sub> function using F<sup>2</sup> rather than F values. R<sub>1</sub> is calculated to provide a reference to the conventional R value but its function is not minimized.

## Synthesis of H<sub>3</sub>L

2,4-pentanedione-2,2-(ethylene glycol) monoketal was synthesized according to a previous literature report.<sup>5</sup> Distillation of the product mixture yielded a fraction containing a 6.0:1 mixture of the monoketal to the diketal, determined by integration of <sup>1</sup>H-NMR peaks. This mixture was used without further purification, though it has been observed that to maximize yield, this starting material should be as pure as possible with respect to the monoketal. The monoketal (12.03 g mixture, 68.79 mmol of monoketal) was dissolved along with 1,3,5-trisaminomethyl-2,4,6-triethylbenzene (13.30 g, 53.33 mmol) in methanol (500 mL) and stirred at reflux under N<sub>2</sub> for two days. The pure product was isolated as an off-white powder by filtration and dried overnight under vacuum (12.56 g, 68% yield). An x-ray quality crystal was grown by evaporation of a saturated dichloromethane solution. <sup>1</sup>H-NMR (CDCl<sub>3</sub> 299 MHz,)  $\delta$ : 10.50 (br. s., 3 H), 4.62 (s, 3 H), 4.28 (s, 12 H), 2.52 (q, 12 H), 2.04 (s, 18 H), 1.09 (t, 18 H). <sup>13</sup>C-NMR (CDCl<sub>3</sub>, 126 MHz)  $\delta$ : 159.73, 142.20, 133.16, 93.53, 45.08, 22.65, 19.99, 16.01. (+) ESI-MS ([M+H]<sup>+</sup>) m/z calcd. for C<sub>45</sub>H<sub>67</sub>N<sub>6</sub>: 691.5422, found: 691.5434. Anal. calcd. for C<sub>45</sub>H<sub>66</sub>N<sub>6</sub>: C, 78.21; H, 9.63; N, 12.16. Found: C, 78.49; H, 10.01; N, 12.16. IR (cm<sup>-1</sup>) 1618, 1550, 1485, 1433, 1367, 1275, 1230, 1026, 773, 723.

## Synthesis of Fe<sub>3</sub>Br<sub>3</sub>L (1)

A solution of benzylpotassium (549 mg, 4.10 mmol ) in 12 mL of THF at  $-90^{\circ}$ C was added dropwise to a solution of H<sub>3</sub>L (900 mg, 1.30 mmol) in 15 mL of THF at  $-90^{\circ}$ C over a period of 30 minutes. The solution turned dark purple and was stirred for 12 hours. The solvent was removed under reduced pressure and anhydrous FeBr<sub>2</sub> (900 mg, 4.17 mmol) was added to the residue. Toluene (55 mL) was added and the reaction was stirred for 1 hour at room temperature and then overnight at 80°C to afford a deep red solution. After cooling, the solution was filtered to remove residual benzyl potassium and precipitated KBr. The filtrate volume was reduced to approximately 40 mL, filtered, and cooled to  $-40^{\circ}$ C for a period of two days which resulted in the formation of crystalline Fe<sub>3</sub>Br<sub>3</sub>L as red/brown crystals that were x-ray quality. A second crop of crystals was obtained by repeating the toluene crystallization procedure (761 mg, 53% yield). Anal. calcd. for C<sub>45</sub>H<sub>63</sub>N<sub>6</sub>Br<sub>3</sub>Fe<sub>3</sub>: C, 49.35; H, 5.80; N, 7.67. Found: C, 49.30; H, 5.84; N, 7.61.

## Synthesis of Mn<sub>3</sub>Br<sub>3</sub>L (2)

A solution of benzylpotassium (117.0 mg, 0.898 mmol) in 5 ml of THF was added dropwise to a solution of  $H_3L$  (200 mg, 0.290 mmol) in 10 ml THF at -90°C over 30 minutes, warmed to room temperature, and stirred for 1 hour. The resulting dark purple solution was added dropwise to a slurry of MnBr<sub>2</sub> (193.6 mg, 0.898 mmol) in 5 ml of THF at -90 °C over 15 minutes. The reaction was warmed to room temperature and stirred overnight. The following day the reaction was observed to be a light yellow mixture. The reaction was filtered and the solvent removed under reduced pressure to yield a dark yellow residue, which was extracted in 18 ml of toluene at 90°C for two days. The resulting yellow mixture was cooled to room temperature and filtered. The residue was extracted a second time with toluene at 90°C for two days, both extracts combined, and the solvent removed under reduced pressure to yield. Anal. calcd. for C<sub>45</sub>H<sub>63</sub>N<sub>6</sub>Br<sub>3</sub>Mn<sub>3</sub>: C, 49.47; H, 5.81; N, 7.69. Found: C, 49.52; H, 5.75; N, 7.74.

#### **Magnetometry Data Analysis**

The Hamiltonian,  $\mathcal{H}$ , for the magnetic trimer can be written as

$$\mathcal{H} = -2 J_{12} \overrightarrow{S_1} \cdot \overrightarrow{S_2} - 2 J_{13} \overrightarrow{S_1} \cdot \overrightarrow{S_3} - 2 J_{23} \overrightarrow{S_2} \cdot \overrightarrow{S_3} + D S_i^2 + \overrightarrow{B} \cdot \overleftarrow{g_i} \cdot \overrightarrow{S_i}, \qquad (S1)$$

where the superexchange pathways, i.e.  $J_{ij}$  terms, are sketched in Scheme S1, and the zero-field splitting term, D, is considered to be the same for all three spins,  $S_i$ , B is the external magnetic field, and the g-tensor for each spin is assumed to be isotropic and identical for all spins. The assumptions restricting the D and g values were motivated by an attempt to use a minimum set of simulation parameters. In addition, initially, each  $J_{ij}$  term was assumed to be equal, and using our own algorithms written for MATLAB and supplemented with EasySpin<sup>6</sup> routines, the magnetic data could not be reasonably simulated with these initial assumptions. Consequently, variation of the  $J_{ij}$  terms was introduced such that  $J_{12} = J$  and  $J_{13} = J_{23} = J'$ , as sketched in the inset to Figure 2. An iterative process was used to arrive at the results, since the modeling of both the low-field, temperature-dependent magnetic susceptibility, Figure 2, and the isothermal, fielddependent magnetization, Figure S9, constrain the values of the parameters. As explained in the text of the paper, given the aforementioned assumptions, the data for 2 could be reasonably simulated, while the data for 1 required a finite value for D. As explained in the text of the paper, given the aforementioned assumptions, the data for 1 required a finite value for D. On the other hand, the data for 2 could be reasonably simulated, but a small D term, which was needed to model the EPR data, was subsequently included when re-simulated. Ultimately, the simulations provide qualitative insight about the microscopic magnetic interactions, and additional experiments are required to quantitatively understand the magnetic response. For example, highfield, high-frequency EPR studies on single crystal samples could provide information about the g-tensor and zero-field terms for each spin in each trimer, while magnetization studies performed

in fields capable of achieving saturation would further constrain the simulations (Figure S10). These potential investigations are beyond the scope of the present report.

#### Re-protonation of K<sub>3</sub>L by acetonitrile

A solution of benzylpotassium (15.1 mg .116 mmol) in 2ml of THF was added dropwise to a solution of  $H_3L$  (25.0 mg, .036 mmol) in 3ml of THF to yield a dark purple solution. The solvent was removed under reduced pressure to yield  $K_3L$  as a dark red/purple powder. <sup>1</sup>H-NMR of  $K_3L$  was recorded in  $d_8$ -THF. 12 equivalents of acetonitrile was added to the NMR sample resulting in the immediate precipitation of a white powder. <sup>1</sup>H-NMR of the reaction (Figure S14) after the addition of acetonitrile shows free ligand is present in solution. The white powder was collected and dried under reduced pressure. IR spectra of this solid is consistent with that of free ligand.



Scheme S1. Scheme of the notation used in Equation S1.



**Figure S1** <sup>1</sup>H-NMR (top) and <sup>13</sup>C-NMR (bottom) for  $H_3L$  in CDCl<sub>3</sub>.



**Figure S2**. <sup>1</sup>H-NMR of  $K_3L$  in  $d_8$ -THF.



**Figure S3**. <sup>1</sup>H-NMR of Fe<sub>3</sub>Br<sub>3</sub>L in  $d_8$ -THF. <sup>1</sup>H-NMR spectra of the corresponding Mn<sub>3</sub>Br<sub>3</sub>L compound did not display any discernible information and is not shown here.



**Figure S4** Infrared spectrum of crystalline H<sub>3</sub>L.



**Figure S5** Infrared spectra of crystalline 1 (*i*) and 2 (*ii*).



Figure S6 UV//VIS spectrum of the putative  $K_3L$  formed by combination of  $H_3L$  with three equivalents of benzylpotassium in THF.



Figure S7 UV/VIS spectrum of the 1 (top) at a concentration of  $1.18 \times 10^{-4}$  M and 2 (bottom) at a concentration of  $5.072 \times 10^{-4}$  M in THF.



Figure S8 (Top) Depictions of bond angles within interior of 1 and 2. Atoms represented by highest occupancy positions. All bond angle values are approximate. (Bottom) View down z-axis of  $H_3L$ , 1, and 2. Atoms represented as 90% probability ellipsoids.



**Figure S9** Isothermal, field-dependent magnetization data for 1 (●) and 2 (■) collected at 5 K and the corresponding simulations (black lines) generated using the inset parameters.



Figure S10Simulated isothermal field-dependent magnetization plots for  $1 (\bullet)$  and  $2 (\blacksquare)$  at<br/>5 K.



**Figure S11** X-band EPR spectra of Fe<sub>3</sub>Br<sub>3</sub>L at 5 K in 2-methyltetrahydrofuran.



**Figure S12** X-band EPR spectra of  $Mn_3Br_3L$  at 5 K in 2-methyltetrahydrofuran over the entire field-sweep and an expanded view of the region between 250-2500 G. The simulation uses g = 2.02, D = +0.6 cm<sup>-1</sup>, and A (hyperfine tensor) = 250 MHz, for a combination of the  $S_{\text{trimer}} = 3/2$  ground state and the  $S_{\text{trimer}} = 5/2$  first excited states at 5 K.



Figure S13 Cyclic voltammograms for 1 (Top) and 2 (Bottom) at room temperature collected in 0.1 M tetrabutylammonium hexafluorophosphate THF solution. Data for 1 were collected at scan rate of 100 mV/s and 2 at 200 mV/s. Working electrode: 1 mm Pt button for 1 and 2 mm Pt button for 2; reference electrode: Ag/AgNO<sub>3</sub> in MeCN; auxillary electrode: Pt wire.



**Figure S14** <sup>1</sup>H-NMR of  $K_3L$  in  $d_8$ -THF treated with 12 equivalents of acetonitrile. Treatment of  $K_3L$  solution with acetonitrile results in formation of a white precipitate and free ligand is observed by <sup>1</sup>H-NMR (shown above). Likewise, a precipitate is observed upon treatment of  $K_3L$  solution with dichloromethane and free ligand is observed in the <sup>1</sup>H-NMR.

Identification Code	gui7 ( $H_3L$ )	ylee37 ( <b>1</b> )	murr1 ( <b>2</b> )
Empirical Formula	$C_{47}H_{70}C_{14}N_6$	$C_{66}H_{87}Br_3Fe_3N_6$	$C_{66}H_{87}Br_3Mn_3N_6$
Formula Weight	860.89	1371.70	1368.97
Temperature	100(2) K	100(2) K	100(2) K
Wavelength	0.71073 Å	0.71073 Å	0.71073 Å
Crystal System	Monoclinic	Triclinic	Triclinic
Space Group	C2/c	P-1	P-1
Unit Cell Dimensions	a = 18.8053(15) Å	a = 11.8711(12) Å	a = 11.9019(4)  Å
	b = 13.8571(11) Å	b = 15.8346(16) Å	b = 15.8453(5)  Å
	c = 18.1615(14)  Å	c = 16.9540(17) Å	c = 17.0528(5)) Å
	$\alpha = 90^{\circ}$	$\alpha = 90.828(2)^{\circ}$	$\alpha = 90.492(2)^{\circ}$
	β= 105.249(2)°	$\beta = 96.343(2)^{\circ}$	$\beta = 96.339(2)^{\circ}$
	$\gamma = 90^{\circ}$	$\gamma = 102.824(2)^{\circ}$	$\gamma = 102.919(2)^{\circ}$
Volume	4566.0(6) Å <sup>3</sup>	3085.9(5) Å <sup>3</sup>	3113.56(17) Å <sup>3</sup>
Z	4	2	2
Density (calc.)	$1.252 \text{ Mg/m}^3$	$1.476 \text{ Mg/m}^3$	$1.460 \text{ Mg/m}^3$
Absorption Coefficient	$0.299 \text{ mm}^{-1}$	$2.683 \text{ mm}^{-1}$	$2.569 \text{ mm}^{-1}$
F(000)	1848	1416	1410
Crystal Size	$0.27 \text{ x } 0.19 \text{ x } 0.16 \text{ mm}^3$	$0.20 \ge 0.12 \ge 0.09 \text{ mm}^3$	$0.34 \ge 0.13 \ge 0.05 \text{ mm}^3$
Theta Range for data collection	1.85 to 27.49°	1.75 to 27.50°	1.75 to 27.50°
Index Ranges	$\begin{array}{ c c c } -24 \leq h \leq 23, -18 \leq k \leq 16, \\ -23 \leq l \leq 23 \end{array}$	$-15 \le h \le 15, -20 \le k \le 20, \\ -21 \le 1 \le 22$	$-15 \le h \le 15, -20 \le k \le 20, \\ -21 \le 1 \le 22$
Reflections Collected	24501	52627	97347
Independent Reflections	5244 [R(int) = 0.0161]	14157 [R(int) = 0.0430]	14301 [R(int) = 0.0623]
Completeness to theta	99.8 % (to 27.49°)	99.9 % (to 27.50°)	100.0 % (to 27.50°)
Absorption correction	Numerical	Numerical	Integration
Max. and min. transmission	0.9551 and 0.9250	0.8001 and 0.6132	0.8823 and 0.4799
Refinement Method	Full-matrix least-squares on F <sup>2</sup>	Full-matrix least-squares on F <sup>2</sup>	Full-matrix least-squares on F <sup>2</sup>
Data/ restraints/ parameters	5244/0/276	14157/0/721	14301/0/764
Goodness-of-fit on F <sup>2</sup>	1.072	0.917	0.968
Final R indices [I >	R1 = 0.0378, wR2 =	R1 = 0.0296, wR2 =	R1 = 0.0277, wR2 =
2sigma(I)]	0.1073 [4362]	0.0667 [10123]	0.0669 [11233]
R indices (all data)	R1 = 0.0456, wR2 = 0.1128	R1 = 0.0514, wR2 = 0.0710	R1 = 0.0409, wR2 = 0.0699
Largest difference peak and hole	0.439 and -0.420 e Å <sup>-3</sup>	0.969 and -1.021 e Å <sup>-3</sup>	0.532 and -0.729 e Å <sup>-3</sup>

**Table S1**Crystal Data and structure refinement

 $R1 = \sum (||F_0| - |F_c||) \ / \ \sum |F_0|$ 

$$\begin{split} & wR2 = [\sum[w(F_0{}^2 - F_c{}^2)^2] \ / \ \sum[w(F_0{}^2)^2]]^{1/2} \\ & S = [\sum[w(F_0{}^2 - F_c{}^2)^2] \ / \ (n-p)]^{1/2} \\ & w = 1/0[\sigma^2(F_0{}^2) + (m^*p)^2 + n^*p], \ p = [max(F_0{}^2, 0) + 2^* \ F_c{}^2]/3, \ m \ \& \ n \ are \ constants. \end{split}$$

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