

# Preorganized assembly of three iron(II) or manganese(II) $\beta$ -diketiminate complexes using a cyclophane ligand†

Cite this: *Chem. Commun.*, 2013, **49**, 6635

Received 7th May 2013,  
Accepted 6th June 2013

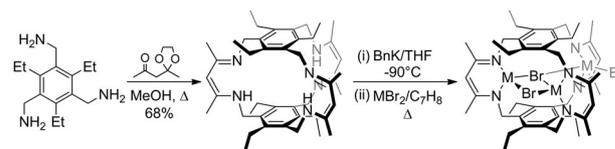
DOI: 10.1039/c3cc43395a

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**A trinucleating cyclophane bearing three  $\beta$ -diketimine arms, and the corresponding iron(II) and manganese(II) complexes have been synthesized and characterized. The three metal ions are oriented towards the internal void space, and are coordinated by a  $N_2Br_2$  donor set, in which a unique combination of  $\mu^3$ ,  $\mu$ , and terminal coordination modes are observed for the halide donors.**

$\beta$ -Diketiminates have been used extensively in inorganic and organometallic chemistry owing to their ability to support low-coordinate metal centres in a wide range of oxidation states.<sup>1</sup> Monometallic complexes of this ligand frequently assemble into clusters as synthesized (*e.g.*, halide-bridged dimers) or upon reaction with small molecule substrates.<sup>2</sup> Recently, alkali cations have been reported as essential for reactivity; however, it remains unclear if the main-group cation is structural or if its effect is an electronic one.<sup>3</sup> Given the broad applicability of this donor set to organometallic and bioinorganic chemistry, and the prevalence of multimetallic assemblies in their chemistry, we sought to synthesize complexes in which metal-diketiminate units were preorganized *by design* with sufficient steric protection to maintain low coordination numbers. To that end, the synthesis and characterization of a tris( $\beta$ -diketimine) cyclophane, and its bromide-bridged triiron(II) and trimanganese(II) complexes, are reported here. These complexes were targeted because of the prominent role of multi-iron and -manganese clusters in biological chemistry (*e.g.*, FeMoco and OEC clusters, respectively), which is a similar inspiration for other researchers.<sup>4</sup>



Scheme 1

Reaction of 1,3,5-tris(aminomethyl)-2,4,6-triethylbenzene<sup>5</sup> with the ethylene glycol monoketal derivative of 2,4-pentanedione<sup>6</sup> in a 2:3 ratio in refluxing methanol led to the precipitation of  $H_3L$  in 68% yield (Scheme 1). This yield is comparable to those of other  $C_3$ -symmetrical aza-cyclophanes, and arises from the preferred orientation of the primary amines to one molecular face in the triamine starting material.<sup>7</sup> The molecular structure of  $H_3L$  is consistent with ligand design; the ketimine N-atoms in  $H_3L$  are oriented towards the interior of the molecule, and the two aromatic rings of the ligand are almost parallel (dihedral angle =  $5.03(3)^\circ$ ). A minor distortion in two ketimine arms of  $H_3L$  lowers the symmetry in the solid state from the idealized  $D_{3h}$  geometry to  $C_{2v}$ ; however, solution  $^1H$ - and  $^{13}C$ -NMR spectra are consistent with an averaged  $D_{3h}$  structure at room temperature (Fig. S1, ESI†).  $H_3L$  is the first instance of the controlled preassembly of three of these units, and complements prior work on dinucleating bis( $\beta$ -diketimine) ligands.<sup>6,8</sup>

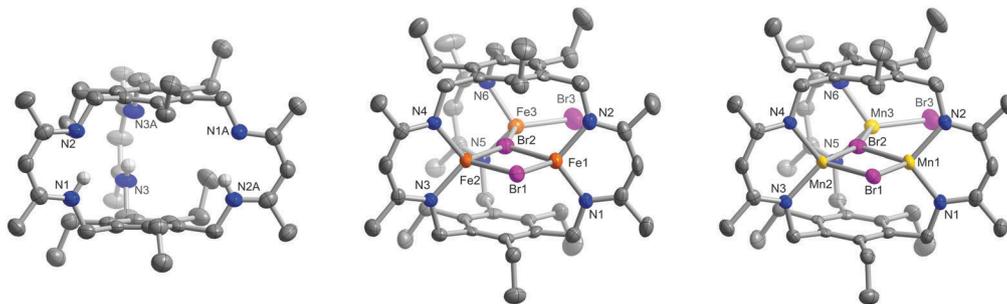
Upon reacting  $H_3L$  with benzylpotassium, the solution changes from pale yellow to orange-purple with a new broad absorption band centred at  $\sim 310$  nm (Fig. S5, ESI†). Addition of either excess  $FeBr_2$  or  $MnBr_2$  to  $K_3L$  generated *in situ* affords deep red or yellow-orange solutions of  $Fe_3Br_3L$  (**1**) or  $Mn_3Br_3L$  (**2**), respectively (Scheme 1). In the solid-state structures of **1** and **2** determined from single crystals grown from toluene, each halide donor adopts a distinct coordination mode (*i.e.*, terminal,  $\mu^2$ , and  $\mu^3$ ). To our knowledge, this combination has not been previously observed in any trimetallic complex (Fig. 1). More importantly,  $H_3L$  functions as expected by directing at least one of the halide-occupied coordination sites on each metal centre towards the interior cavity. Here, we have demonstrated that

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† Electronic supplementary information (ESI) available: Full experimental procedures, spectroscopic data, cyclic voltammetry, and crystallographic data. CCDC 923619–923621. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c3cc43395a



**Fig. 1** Solid-state structures of  $H_3L$  (left), **1** (middle), and **2** (right) collected at 100 K.  $H_3L$  preorganizes the metal binding sites to orient the frontier orbitals of the metal centres towards the central cavity (left). C, N, H, Br, Fe, and Mn are represented as grey, blue, white, pink, orange, and yellow spheres, respectively. Hydrogen atoms and solvents of crystallization are omitted for clarity. Atoms represented by 90% probability ellipsoids. For  $H_3L$ , symmetry transformations were used to generate equivalent atoms (A):  $1 - x, y, 0.5 - z$ .

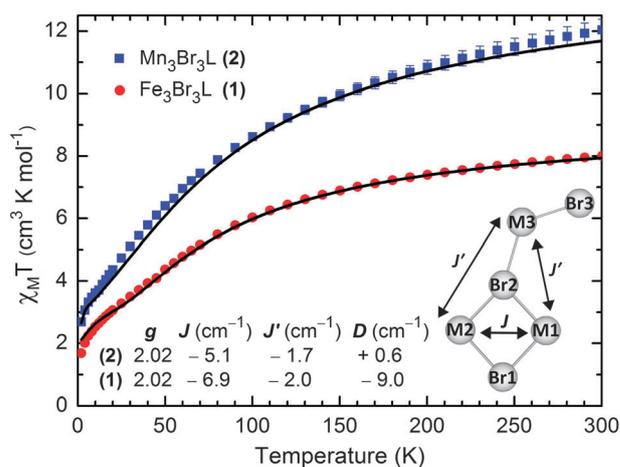
molecular receptor design can be readily applied to the rational synthesis of metal clusters, with the metal cluster protected within the organic shell of the ligand. The orientation of the diketiminate arms and the cavity size of  $H_3L$  perform the function of the bulky aryl-substituents in monometallic complexes, while allowing interactions between the metal centres.

Each metal ion in **1** and **2** is coordinated by an  $N_2Br_2$  donor set in either a distorted tetrahedral (*viz.* Mn1, Mn2, and Fe1 with  $\tau_4 = 0.90$ – $0.92$ ) or trigonal pyramidal geometry (*viz.* Mn3, Fe2, and Fe3 with  $\tau_4 = 0.80$ – $0.85$ ).<sup>9</sup> The cations lie out of the NCCC plane of the  $\beta$ -diketiminato arm, which is comparable to the deviations from planarity observed in halide-bridged dimers of sterically-encumbered metal  $\beta$ -diketiminates.<sup>10</sup> Thus, the deviations suggest that there is a balance between the steric constraints imposed by the internal cavity and the ethyl substituents, and the electronic demands of the metal centres (*e.g.*, N...N distance in the  $\beta$ -diketiminato chelate).<sup>11</sup> Other bond metrics and angles are similar to those observed in other di( $\mu$ -bromo)diiron(II) or dimanganese(II) complexes.<sup>12</sup>

Independent of the coordination modes of the three halide donors, the planar  $\mu^3$ -bromide is an unusual motif in iron(II) and manganese(II) chemistry. For Mn(II), halides are typically out of the plane of the three metal centers<sup>13</sup> whereas the  $Mn_3Br$  core is planar in **2** (distance of Br2 above M1, M2, M3 plane: (**1**) 0.0014(3) Å; (**2**) 0.0060(9) Å). No ferrous clusters containing this motif could be found in the Cambridge Structure Database (Version 5.33, November 2011) and the only comparable complex contains an HBr molecule coordinated to three iron centres in a porphyrin-linked dicarboxylate ligand.<sup>14</sup> Although the ionic radius of bromide is larger than the centroid-to-centroid distance in  $H_3L$ , two factors potentially contribute to the increase in the cavity volume to accommodate the central halide. First, metal binding leads to a lengthening of the N...N distance in each arm as observed in monometallic complexes employing diketiminato ligands,<sup>11</sup> increasing the cavity volume. Second, the dihedral angle between the two aromatic rings increases from 5.09 Å in  $H_3L$  to 6.09 Å and 6.14 Å in **1** and **2** respectively, expanding the cavity opening adjacent to M1 and M3. Consequently, the central  $\mu^3$ -bromide in both the trimanganese and triiron complexes lies off-centre of the two aromatic rings, positioned slightly towards the M1 and M2, and is typically close to both triethylbenzene rings of the cyclophane with halide-to-centroid distances of  $\sim 3.08$  Å (Fig. S8, ESI<sup>†</sup>). This distance is the shortest crystallographically reported value between a bromide and any

aromatic ring.<sup>15</sup> This result suggests that these types of complexes can function as selective anion receptors through the careful interplay between steric demands of the cavity interior and the ethyl substituents, the coordination preferences of the selected metal ions, and size of the halide.

To elucidate the electronic interactions between the metal ions in **1** and **2**, temperature-dependent magnetic susceptibility measurements (Fig. 2) and isothermal (5 K) magnetization studies up to 70 kG (Fig. S9, ESI<sup>†</sup>) were performed. Although the molecular structures of **1** and **2** would suggest a scalene triangle with three inequivalent magnetic superexchange constants, the variables of the Hamiltonian, defined in the ESI<sup>†</sup> were restricted in order to avoid over-parameterization. Using our own algorithms operating within EasySpin,<sup>16</sup> the magnetic data for **2** ( $S_{Mn} = 5/2$ ) were initially modelled without including a zero-field splitting,  $D$ , term. However, simulations of **1** ( $S_{Fe} = 2$ ) required a finite  $D$  value, consistent with the observed anisotropy for the lithium adduct of a  $\beta$ -diketiminatoiron(II) dichloride complex.<sup>17</sup> Overall, the simulations suggest antiferromagnetic interactions in both systems, with the trimers possessing ground state spin values of 2 for **1** and 3/2 for **2**. A definitive understanding of the



**Fig. 2** Temperature-dependent magnetic susceptibility plot for **1** (red circles) and **2** (blue squares) in a 100 G field. (inset) Diagram indicates magnetic superexchange coupling interactions and table provides values used to generate the black lines.

magnetism of both of these trimers requires high-field experiments, which are described in the ESI† but are beyond the scope of this report. The EPR analysis of **1** is consistent with a high-spin ferrous complex; that is, **1** is EPR silent in perpendicular mode at 5 K (Fig. S11, ESI†). Contrastingly, the EPR data and analysis for **2** constrained the *g*-value and indicated the need for a small *D* contribution (Fig. S12, ESI†). The values of these parameters were then fixed when the magnetic data of **2** were re-simulated to yield the results shown in Fig. 2. The reductive and oxidative waves are irreversible in the cyclic voltammograms recorded in THF for both complexes, which is counter to our expectation that the macrobicyclic should stabilize the complex to redox cycling by limiting the degrees of freedom for the cluster. Given the distorted coordination environments of the metal ions in **1** and **2**, structural changes may occur upon oxidation or reduction, which contribute to the observed irreversibility; however, we cannot exclude possible effects arising from chemical changes under our experimental conditions (Fig. S13, ESI†). Attempts to measure voltammograms in dichloromethane or acetonitrile were unsuccessful as both **1** and **2** undergo re-protonation and demetallation in these solvents (Fig. S14, ESI†). We observe a similar solvent-sensitivity for other trinuclear complexes currently under investigation in our group.<sup>18</sup> This result was unexpected given prior reports in which monometallic  $\beta$ -diketiminato complexes are stable in these solvents,<sup>19</sup> but might arise from an increase in the second and third  $pK_a$  values for  $H_3L$  as compared to the  $pK_a$  of an isolated  $\beta$ -diketimine. Such changes in the  $pK_a$  values have been reported previously for other macrobicyclics.<sup>20</sup>

In summary, we report a novel tris( $\beta$ -diketimine) ligand and its corresponding triiron(II) and trimanganese(II) complexes. The ligand preorganizes the assembly of the trimetallic clusters with frontier orbitals of each metal centre oriented towards the central cavity. Simulations of the magnetic susceptibility data suggest antiferromagnetic superexchange between the metal ions of both clusters, and future magnetic experiments can be designed to address these aspects. More immediately, ongoing work is focused on the reactivity of these and similar complexes.

This work was funded by the University of Florida, the Fulbright Commission of the Slovak Republic (MWM), the Slovak Agency for Support of Research and Development APVV-0132-11, and the National Science Foundation awards: CHE-0821346, CHE-1048604, DMR-1202033 (MWM), and DMR-1157490 (NHMFL). The authors acknowledge Joseph Zadrozny for helpful discussions, and Umar Twahir and Prof. Alex Angerhofer for help collecting EPR data.

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