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# "Squaring the Circle": Molecular Squares and Rectangles from Chelate-Induced Structural Transformations of Known $Fe_{10}$ and New $Fe_{12}$ Ferric Wheels

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Single-strand molecular wheels[1] of paramagnetic 3d metals are of growing interest for reasons such as their high symmetry, which makes them good model systems for the study of one-dimensional magnetism,[2] magnetic anisotropy, and quantum effects such as coherent tunneling of the Néel vector.[3] As a result, a growing number of $M_x$ ($x \geq 8$) molecular wheels are being studied. There are, however, relatively few other 3d $M_x$ loop-like closed topologies[4] when compared to those containing diamagnetic 4d and 5d metals such as Pd, Pt, Au, etc., or metal−metal-bonded $M_2$ repeating units.[4] These span a variety of metals and ligands and have resulted in a wide range of loop and multi-loop structures, from squares, rectangles, boxes, etc., to complicated three-dimensional polyhedra.[5] In addition to their inherent properties, such species are also potential building blocks for molecular nanodevices.[6] Analogous access to a greater range of loop-like closed topologies for paramagnetic 3d metals would offer benefits to a variety of spectroscopic, electrochemical, magnetic, and host−guest binding studies. For this reason, we are developing the currently unexplored reactivity chemistry of 3d metal wheels, the prototype of which was the planar "ferric wheel" $[Fe_{10}(OMe)_{20}(O_2CR)_{10}]$ (**1**).[7] In this paper, we report a new, diolate-containing class of ferric wheel $[Fe_{12}(pd)_{12}(O_2CEt)_{12}]$ (**2**), and that N-based chelates can convert molecular wheels **1** and **2** into molecular squares and rectangles.

The reaction of $[Fe_3O(O_2CEt)_6(H_2O)_3]^+$ with an excess of 1,3-propanediol ($pdH_2$) in MeCN followed by addition of $Et_2O$ gave yellow-green needles of $[Fe_{12}(pd)_{12}(O_2CEt)_{12}]$ (**2**) in 75% yield. Its structure[8] (Figure 1) comprises 12 $Fe^{III}$ atoms linked via $EtCO_2^-$ and $pd^{2-}$ bridges to form a puckered wheel of crystallographic $S_6$ symmetry, with each $\eta^2{:}\eta^2{:}\mu_3$-$pd^{2-}$ group bridging three adjacent octahedral Fe atoms. There are two symmetry-distinct Fe···Fe pairs, with identical bridges but differing slightly in metric parameters: (A) av Fe−O = 2.001 Å, av Fe−O−Fe = 99.57°; (B) av Fe−O = 2.022 Å, av Fe−O−Fe 97.45°. Complex **2** is a member of the general $[Fe_x(OR)_{2x}(O_2CR)_x]$ family of ferric wheels, of which **1** and $[Fe_{12}(OMe)_{24}(O_2CC(OH)Ph_2)_{12}]$[9a] are the $\{x = 10\}$ and $\{x = 12\}$ members, respectively; complex **2** is a $\{x = 12, (OR)_2 = pd^{2-}\}$ member, the first of a new class with diolate bridges. With $NO_3^-$ ions, it has elsewhere been shown that $pd^{2-}$ gives $[Fe_{18}(O_2CPh)_6(pd)_{12}(pdH)_{12}(NO_3)_6](NO_3)_6$.[9b]

In the absence of any significant previous reactivity studies of the ferric wheel family, other than carboxylate substitution,[10] we have initiated a study of their reactions with heteroaromatic chelates such as 2,2′-bipyridine (bpy) and 2,2′:6′,2″-terpyridine (tpy). We wondered if such relatively inflexible chelates might affect wheel curvature and/or three-dimensional shape and thus lead to new types of wheel-related products. Indeed, reaction of **2** in MeCN with 4 equiv each of tpy and $NaClO_4$ gave, on addition of $Et_2O$, yellow prisms of $[Fe_{12}O_4(pd)_8(O_2CEt)_4(tpy)_8](ClO_4)_8$ (**3**) as **3**·10MeCN in 10% nonoptimized yield. A higher-yield procedure (~90% based on Fe) was subsequently developed from the reaction of $Fe(ClO_4)_3 \cdot 6H_2O$ with 1 equiv of tpy and a large excess of $pdH_2$ in MeCN. The $[Fe_{12}]^{8+}$ cation[8] of **3** (Figure 2) is a molecular square comprising alternating $\{Fe_2(\mu\text{-}O)(tpy)_2\}^{4+}$ "side" and $\{Fe(\eta^2{:}\eta^2{:}\mu_3\text{-}pd)_2(\eta^2\text{-}O_2CEt)\}^{2-}$ "corner" subunits linked by $pd^{2-}$ O atoms. As for **2**, the $[Fe_{12}]^{8+}$ square is not planar, and the Fe−Fe distances fall into two ranges: 3.506−3.551 Å in the $\{Fe_2(\mu\text{-}O)(tpy)_2\}^{4+}$ subunits, and 3.135−3.162 Å between the latter and the $\{Fe(O_2CEt)(pd)_2\}^{2-}$ subunits. The Fe−$O^{2-}$−Fe and Fe−O(pd)−Fe ranges are 161.19−168.10 and 103.31−109.22°, respectively.

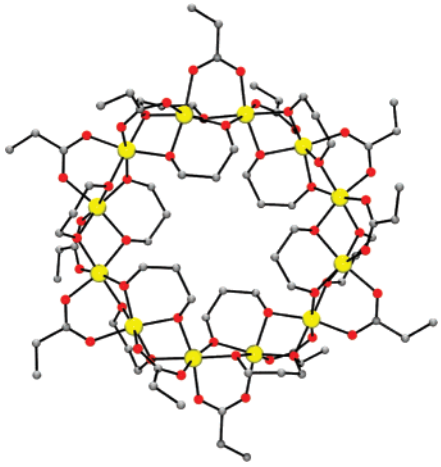

***Figure 1.*** The structure of the $Fe_{12}$ ferric wheel **2**. Hydrogen atoms have been omitted for clarity. Color scheme: $Fe^{III}$ yellow, O red, C gray.

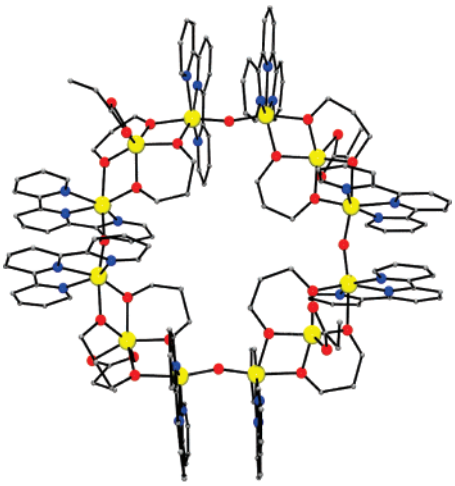

***Figure 2.*** The structure of the $[Fe_{12}]^{8+}$ cation of **3**. Hydrogen atoms have been omitted for clarity. Color scheme: $Fe^{III}$ yellow, O red, N blue, C gray.

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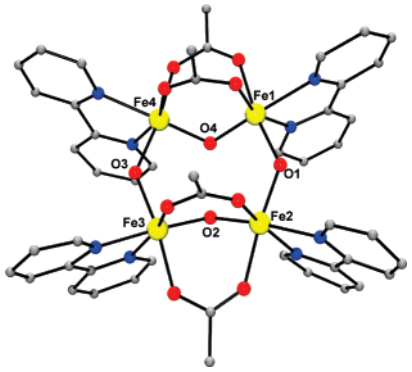


***Figure 3.*** The structure of the cation of **4**. Hydrogen atoms are omitted for clarity. Color scheme: $Fe^{III}$ yellow, O red, N blue, C gray.

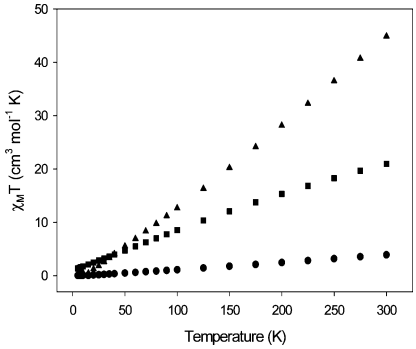


***Figure 4.*** Plot of $\chi_M T$ versus $T$ for complexes **1** (■), **3** (▲), and **4** (●).

Similarly, reaction of **1** (R = Me) in MeCN with 4 equiv each of bpy and $NaClO_4$ gave, on addition of $Et_2O$, green crystals of $[Fe_4O(OH)_3(O_2CMe)_4(bpy)_4](ClO_4)_3$ (**4**) in 30% yield. The structure[8] of the cation of **4** (Figure 3) is similar to the 1,10-phenanthroline derivative[11] and consists of a planar $Fe^{III}_4$ rectangle (Fe1···Fe4 = 3.207 Å, Fe2···Fe3 3.293 Å, Fe1···Fe2 = 3.674 Å, and Fe3···Fe4 = 3.698 Å); the Fe−Fe−Fe angles are in the range of 89.30−91.08°. Three sides are bridged by $OH^-$ (O1, O2, O3) and one by $O^{2-}$ (O4) ions (confirmed by bond valence sum calculations; see Supporting Information) and the short sides each also by two $\eta^1$:$\eta^1$:$\mu$-$MeCO_2^-$ groups. There is an intramolecular hydrogen bond (O2···O4 = 2.523 Å) with the H atom asymmetrically located since Fe−O4 bonds (av 1.856 Å) are shorter than Fe−O2 ones (av 1.926 Å), showing that O4 retains its $O^{2-}$ character.

Solid-state magnetic susceptibility ($\chi_M$) data were collected on vacuum-dried, microcrystalline samples of complexes **2**−**4** in the 5.0−300 K range and in a 0.1 T magnetic field. In all cases, $\chi_M T$ decreases steadily with decreasing temperature from 20.96 (**2**), 44.87 (**3**), and 3.90 (**4**) $cm^3\ mol^{-1}$ K at 300 K to 1.35 (**2**), 0.40 (**3**), and 0.03 (**4**) $cm^3\ mol^{-1}$ K at 5.0 K (Figure 4). These indicate $S = 0$ ground states, as expected for antiferromagnetic exchange interactions between even-membered loops of $Fe^{III}$ atoms.

Theoretical calculations were performed on **2**−**4** using the ZILSH method[12] to probe the strength of their exchange constants $J_{ij}$ ($\mathscr{H} = -2J\hat{S}_i\cdot\hat{S}_j$ convention). For **2**, the two exchange constants were $J = -20.5\ cm^{-1}$ and $J' = -13.3\ cm^{-1}$ for the A and B $Fe_2$ pairs, respectively. For **3**, {$Fe_2(\mu$-O)} and {$Fe(\mu$-pd)$_2$} $J$ values were in the ranges of $-124.6$ to $-152.6\ cm^{-1}$ and $-32.1$ to $-49.8\ cm^{-1}$, respectively. For **4**, $J_{14} = -69.0\ cm^{-1}$, $J_{12} = -27.0\ cm^{-1}$, $J_{34} = -32.4\ cm^{-1}$, and $J_{23} = -22.8\ cm^{-1}$ (the subscripts refer to the atom labels); these were refined by fits to the magnetic susceptibility data using a genetic algorithm method described elsewhere,[12] which gave $J_{14} = -63.3\ cm^{-1}$, $J_{12} = -25.2\ cm^{-1}$, $J_{34} = -26.6\ cm^{-1}$, $J_{23} = -19.8\ cm^{-1}$, and $g = 1.97$, with TIP fixed at $600 \times 10^{-6}\ cm^3\ K\ mol^{-1}$. The fit is shown in the Supporting Information. As expected, the oxide-bridged pair (Fe1···Fe4) is much more strongly antiferromagnetically coupled than the $OH^-$-bridged pairs.[13] The Fe1···Fe2 and Fe3···Fe4 couplings are similar, as expected, and $J_{23}$ is weaker, again as expected on the basis of the smaller Fe2−O−Fe3 angle (117.5°) versus ∼135° for Fe1−O−Fe2 and Fe3−O−Fe4.[14−16] For all the compounds, the signs and relative magnitudes are consistent with established magnetostructural correlations.[12−16]

In summary, the incorporation of inflexible bpy and tpy chelates into ferric wheel chemistry has led to products retaining a single-strand loop structure and possessing square or rectangular topologies. Of the products **3** and **4**, $Fe_{12}$ complex **3** more closely resembles its $Fe_{12}$ starting material **2**, which can be rationalized as due to the bidentate, chelating $pd^{2-}$ being more able to resist structural disruption by the added chelate than can $MeO^-$ wheel **1**. In fact, **3** can be conveniently related to **2** as being the result of clipping eight tpy groups onto **2** and causing, as a consequence of the loss of the bridging carboxylate groups at these positions, formation of the near-linear Fe−O−Fe sides of a square topology. This suggests that many other interesting loop structures of various size and shape await discovery in 3d M/O chemistry by appropriate choice of the combination of bridging and chelating ligands. Further studies along these lines are in progress.

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**Supporting Information Available:** Crystallographic details in CIF format for **2**−**4**, additional structural figures, magnetic susceptibility fit for **4**, and Fe and O bond valence sums. This material is available free of charge via the Internet at http://pubs.acs.org.

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