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Carboxylate free μ -oxo bridged ferric wheel with a record exchange coupling†

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A novel oxo-bridged, carboxylate free ‘ferric wheel’ was isolated with the molecular formula $[\text{Fe}_8^{\text{III}}(\mu\text{-O})_4(\text{L}^{2-})_8]$ (1**). Magnetic susceptibility measurements suggest that the $\text{Fe}(\text{III})$ ions are coupled anti-ferromagnetically and magnetic data modelling yields $J_1 = -26.4 \text{ cm}^{-1}$, $J_2 = -170 \text{ cm}^{-1}$ which are rationalized by DFT calculation. The exchange value for **1** of -170 cm^{-1} (Fe-O(oxo)-Fe) is the largest exchange value known compared to any homometallic or heterometallic wheel reported to date.**

An aesthetically pleasing “ferric wheel” (Fe_{10}) was first structurally characterized by Lippard and co-workers in 1990.¹ Following this, pioneering work by various research groups led to the isolation of a variety of homo- and heterometallic wheels (odd and even numbers) whose nuclearity range from 6 to 84.² These molecular wheel complexes gained much attention recently as they are proposed as excellent candidates for Quantum Information Processing (QIP).³ This proposal has been tested and verified in linked heterometallic Cr_7Ni wheels recently, and the results reported by Winpenny and co-workers appear to be very promising for QIP in molecules.⁴ Not only that, but these entities are also suitable candidates to probe quantum behaviour such as quantum tunnelling of Neel vectors⁵ and spin frustration effects.⁶ The strength of exchange interactions between the metal centres in the wheels (iron,⁷ chromium,⁸ and vanadium^{2a,9}) reported to date span between -11 and -25 cm^{-1} , which needs to be increased significantly to develop molecular based devices.^{1b,2d,10} The likely reason for these small exchange values is the countercomplementarity effect of the carboxylate bridges in the wheel architectures.¹¹ Ideally, to increase the intramolecular exchange interaction,

these peripheral carboxylate ligands need to be replaced or removed completely. But, more than 95% of the wheel structures reported in the literature are decorated by carboxylate bridges and synthesizing a carboxylate free transition metal ion wheel is a daunting task, and extremely rare in the literature.^{2c,7,10d,12} With the aim of developing a synthetic strategy to produce carboxylate free ferric wheels, we have employed a Schiff base ligand (2-methoxy-6-[(*E*)-2'-hydroxymethylphenyliminomethyl]-phenol; $\text{C}_{15}\text{H}_{15}\text{NO}_3$; H_2L) whose coordination capability has been probed meagrely.¹³ In this communication, we report an octanuclear, oxo-bridged, carboxylate free wheel complex with the molecular formula of $[\text{Fe}_8(\mu\text{-O})_4(\text{L}^{2-})_8]$ (**1**). To the best of our knowledge, this is the first reported oxo-bridged ferric wheel using a Schiff base ligand exclusively, and it is registered with the largest exchange interaction (-170 cm^{-1}) known compared to any wheel architecture reported to date (*vide infra*).

One equivalent of the deprotonated Schiff base ligand (L^{2-}) reacts with one equivalent of iron(III) nitrate hydrate in methanol and crystallization in dimethylformamide (DMF) yielded red brown single crystals which were suitable for X-ray diffraction (see ESI† for the detailed experimental procedure and Fig. S1† for the structure of the ligand). The X-ray structure solution reveals the molecular formula is $[\text{Fe}_8(\mu\text{-O})_4(\text{L}^{2-})_8]$ (**1**) (Fig. 1 and S2†). Complex **1** crystallized in a monoclinic $P2_1/n$ space group (Table S1 of ESI†). In complex **1**, there is no crystallographically imposed (inversion) symmetry present in the molecule, and the asymmetric unit contains the entire molecule. All the iron atoms are in a trivalent oxidation state as confirmed by bond valence sum (BVS) calculations¹⁴ (Table S2†). The $\text{Fe}(\text{III})$ atoms are found to lie in the same plane and are arranged in each corner of an octagon. Out of four potential coordination sites (phenoxo oxygen, imino nitrogen, alkoxy and methoxy) of L^{2-} only three are utilized for coordination and the methoxy sites of all the eight ligands in **1** remain free.

There are two types of bridging environments found in complex **1**; each of the iron atoms is doubly bridged to the neighbouring iron atom *via* an alkoxy arm of the Schiff base ligand (average $\angle\text{Fe-O(alkoxy)-Fe} = 104^\circ(5)$), thus forming a

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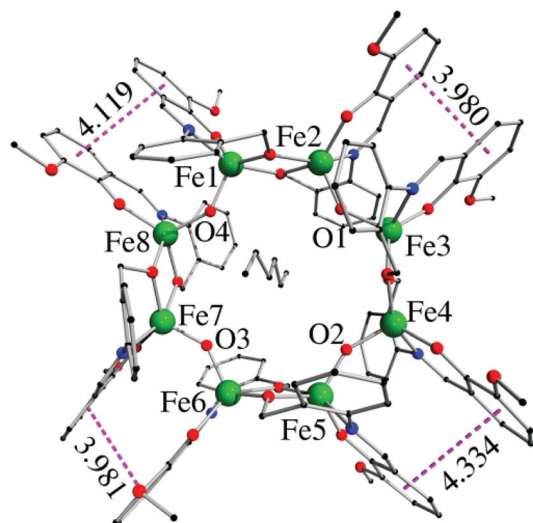


Fig. 1 (A) Crystal structure of complex **1**, a view perpendicular to the Fe8 plane.

dimeric unit. This dimeric unit is bridged to the other dimeric units exclusively through single μ -oxo ligands with an average Fe–O–Fe angle of $142^\circ(8)$.

The valency of these oxo groups is determined with BVS calculations¹⁴ (Table S3[†]), which are consistent and satisfy the charge balance requirement in **1**. Each of the iron(III) ions are surrounded by $\{O_4N\}$ atoms and exhibit distorted square pyramidal geometry. Moreover, five coordinate Fe(III) complexes are rare as Fe(III) ions generally exhibit octahedral geometry as seen in all the previously reported ferric wheels. For all the iron atoms, the axial positions are occupied by an oxo group (O1, O2, O3 and O4) which have the shortest Fe–O(oxo) bond lengths (average Fe–O(oxo) = 1.797 (3) Å) among the other bond lengths in complex **1**.

The observed bond lengths are consistent with other reported Fe(III)-oxo complexes.¹⁵ In complex **1**, The Fe–N (imino) bond lengths (average Fe–N = 2.114 (4) Å) are observed to be the longest compared to the remaining Fe–O (phenoxo and alkoxo) lengths. The selected bond lengths and bond angles for **1** are given in Table S4.[†]

A detailed structural analysis of **1** evidently shows that the phenyl ring on the imino-nitrogen of each L^{2-} (bound to iron atom) is arranged in an alternate fashion, in such a way that four of them lie above and below the central Fe₈ plane. This structural arrangement leaves a cavity in the middle, which is large enough to accommodate a guest molecule (hexane) inside it (see Fig. 1 and S3[†]). Additional stability in **1** is gained through displaced π – π stacking interactions between the vanillin rings of L^{2-} on one dimeric unit to the adjacent dimeric unit (see Fig. 1). This is likely to be the reason why complex **1** can be isolated without any carboxylate supports around the rim of the ferric wheel.

A temperature dependent direct current (dc) magnetic susceptibility measurement was performed on a polycrystalline

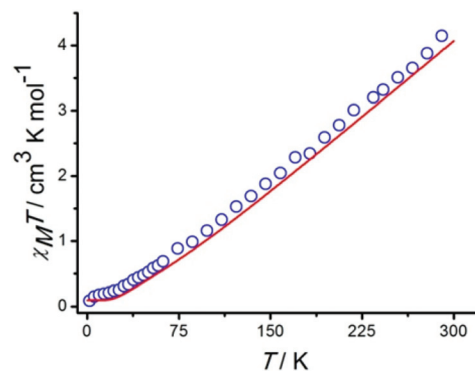


Fig. 2 Temperature dependent magnetic susceptibility measurement performed on polycrystalline sample of **1** at $B = 1$ T. The red solid curve represents simulated data using the parameters mentioned in the main text.

sample of **1** in a 1.0 Tesla external magnetic field (Fig. 2). The observed room temperature (RT) $\chi_M T$ value of $4.26 \text{ cm}^3 \text{ K mol}^{-1}$ is significantly lower than the expected value ($35 \text{ cm}^3 \text{ K mol}^{-1}$) for eight magnetically diluted Fe(III) high spin ions with an average g -value of 2.0.

The majority of the reported ferric wheels have lower than expected $\chi_M T$ values due to minor or no population of all of the excited energy levels at RT even with weak exchange.^{1b,2d,10c–e,12e} Upon decreasing the temperature the $\chi_M T$ value of **1** steadily decreases and reaches a value close to zero at 2.0 K. This scenario confirms that in **1** predominantly antiferromagnetic interactions exist which leads to a diamagnetic ground state.

A field dependent magnetization measurement was performed on a polycrystalline sample of **1** measured at various temperatures between 2–10 K (Fig. S4[†]). Even at low temperatures and high magnetic fields the magnetization of **1** only reaches $0.1 N\mu_B$. The origin of this small magnetic moment is due to a tiny amount of paramagnetic impurities (*vide infra*) and the contribution of **1** to the magnetization is virtually zero under high field and low temperature conditions (Fig. S4[†]). This unambiguously confirms a singlet ground state associated with complex **1**.

To probe the strength of exchange interaction between the Fe(III) ions, we have employed two different J values to simulate the magnetic data ($\chi_M T(T)$ and $M(H)$) and the Hamiltonian employed is given below.

$$\hat{H} = -J_1(\hat{s}_1 \cdot \hat{s}_2 + \hat{s}_3 \cdot \hat{s}_4 + \hat{s}_5 \cdot \hat{s}_6 + \hat{s}_7 \cdot \hat{s}_8) - J_2(\hat{s}_2 \cdot \hat{s}_3 + \hat{s}_4 \cdot \hat{s}_5 + \hat{s}_6 \cdot \hat{s}_7 + \hat{s}_8 \cdot \hat{s}_1) + g\mu_B B \sum_{i=1,8} \hat{s}_i$$

The spin and point group (C_4) symmetries have been exploited to evaluate all of the energy eigenvalues.¹⁶ For the spectroscopic splitting factor, $g = 2$ is assumed. Due to the very strong antiferromagnetic exchange, and thus a large gap to excited states with $S > 0$, the magnetization stays at virtually zero for low temperatures.

The experimental magnetization (Fig. S4[†]), corresponds to 0.021% impurity spins with $S = 5/2$ per Fe_8 molecule. Adding the contributions of **1** with $J_1 = -26.4 \text{ cm}^{-1}$ and $J_2 = -170 \text{ cm}^{-1}$ as well as the impurity spins yields the red susceptibility curve in Fig. 2 (see also Fig. S5[†]), which corresponds with the experimental data perfectly. The J values employed to simulate the experimental magnetic data were obtained from DFT calculations as discussed in the following section.

In order to better understand the electronic and exchange structure of the complex **1**, DFT calculations were performed (Fig. 3). Based on the crystal structures, two unique exchange interactions (J_1 and J_2) are modelled between the Fe^{3+} ions, through the two μ -alkoxo bridges as J_1 and single μ -oxo bridge as J_2 . The DFT J values have been estimated using Noodleman's broken symmetry method (see ESI for computational details, Fig. S6 and Table S5[†]). The calculated J values are found to be antiferromagnetic in nature ($J_1 = -25.4 \text{ cm}^{-1}$ and $J_2 = -183.1 \text{ cm}^{-1}$) and these values clearly demonstrate that the exchange interaction through the single μ -oxo bridge is more than seven times stronger than through the double bridge. We have also employed a $4J$ model (see Fig. S7[†]) for **1** and the extracted J values ($J_1 = -27.4$, $J_2 = -183.1$, $J_3 = -23.3$, $J_4 = -200.9 \text{ cm}^{-1}$) are in reasonable agreement with the $2J$ model. The presence of two non-identical bridges (such as carboxylate and oxo) between the metal centers, either adds to or counter balances the exchange effect. The existence of a countercomplementarity effect shown by the carboxylate in a dinuclear Cu(II) complex *i.e.* replacing the carboxylate ligand with other ligands or removal of carboxylate, reveals the realistic strength of the antiferromagnetic exchange interaction exerted by the oxo bridge in such complexes. The L^{2-} ligand employed has significant influence in stabilizing the carboxylate free system in **1**, which facilitates the strongest exchange between the Fe(III) ions through the oxo-bridge.¹¹ These computed parameters of **1** reproduce the experimental magnetic data reasonably well (Fig. S4 and S5[†]). Further J values were computed from dinuclear models (see Fig. S8[†] for the dimeric model employed; $J_1 = -26.4 \text{ cm}^{-1}$ and $J_2 = -170 \text{ cm}^{-1}$) and from diamagnetic models,¹⁷ such as $\{\text{Fe}_2\text{Ga}_6\}$ (-187 cm^{-1}). Presence of similar J_2 value, in both models employed offers confidence in the estimated spin Hamiltonian parameters.

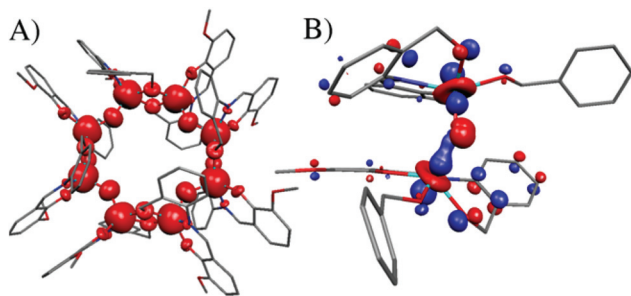


Fig. 3 (A) Computed High Spin (HS) spin density plot for **1**. (B) Superimposed d_{z^2} orbitals of the Fe(III) ions in a dimeric J_2 model.

The extracted exchange interaction values are consistent with the magneto-structural correlations developed on complexes related to complex **1**.^{15b,18}

To understand the variation in the magnitude of the computed J values, MO analysis has been performed. The net J values have contributions from the J_{AF} (between non-orthogonal orbitals) and J_{F} (between orthogonal orbitals) parts and can be well understood by computing overlap integrals between the singly occupied magnetic orbitals (SOMOs). The different interactions between the magnetic orbitals obtained from computed overlap integral values of dimer models are depicted in Fig. S9 and S10[†] (see ESI for computed overlap integral values, Tables S6 and S7[†]). For the J_2 interaction, the d_{z^2} orbitals are found to lie along the μ -oxo bridge leading to a significant $d_{z^2}|p_z|d_{z^2}$ overlap and hence very large exchange interactions (see Fig. 3B). Apart from this, the computed non-zero overlap (see Tables S8 and S9[†] and related discussion in ESI[†]) between non-orthogonal magnetic orbital pairs obtained from the corresponding orbital transformation (COT)¹⁹ further adds support for the existence of a strong J_2 antiferromagnetic interaction in **1**. For the J_1 interaction, on the other hand, the σ -type orbitals are orthogonal and only weak overlap between the SOMOs is detected leading to a moderate AF interaction.

The computed spin density plot for the high spin state is shown in Fig. 3A. The spin density values on the iron atom are calculated to be <4.4 which implies that the magnetic orbitals are centered on the iron atom with non-negligible spin densities delocalized on the ligand atoms.²⁰ The shorter Fe-O(oxo) distance results in the increased spin density on the bridging oxygen atoms (0.66) compared to alkoxo oxygen atoms (0.25; 0.25) reflecting again the stronger and weaker exchange couplings computed for this pair. Overall, the computed J_s values are in excellent agreement with the spin Hamiltonian parameters derived from magnetic data modelling.

Often Fe(II) and Fe(III) mixed valent systems are known to exhibit double exchange interactions.²¹ Hence, to infer whether other redox states of the iron ion are accessible in **1** we performed cyclic voltammetry (CV) studies in dichloromethane (stability of the complex **1** in solution confirmed by UV-Vis studies, Fig. S11[†]) using glassy carbon as the working electrode, platinum wire as a counter electrode, and Ag/Ag^+ as a reference electrode in the presence of tetrabutylammonium perchlorate as a supporting electrolyte. The cyclic voltammogram obtained for complex **1** is shown in Fig. S12[†] and clearly shows that there are two reversible one electron reductions. The two metal based redox processes (Fig. S12[†]) are assigned as $\text{Fe}_8^{\text{III}}/\text{Fe}_7^{\text{III}}\text{Fe}^{\text{II}}$ and $\text{Fe}_7^{\text{III}}\text{Fe}^{\text{II}}/\text{Fe}_6^{\text{III}}\text{Fe}_2^{\text{II}}$ redox processes, which are centered at -1.058 V and -1.369 V respectively. The preliminary result obtained from cyclic voltammetry appears promising for isolation of mixed valent species, which is currently underway in our laboratory.

To conclude, we have reported the synthesis of an octanuclear, un-supported (by the absence of metal ions such as alkali or transition metal ions at the center of the wheel) and unprecedented oxo bridged "ferric wheel" using exclusively a Schiff base ligand, which is extremely scarce in the literature.

The temperature dependent magnetic susceptibility data of **1** demonstrates the existence of antiferromagnetic interactions between the iron(III) centres. The exchange values are computed through DFT calculations and the computed SH parameters reproduces the experimental magnetic data excellently. The J_2 value found for complex **1** is the largest value reported for any ferric wheel or other wheels reported in the literature. The origin of the larger exchange along the μ -oxo bridge compared to the alkoxo bridge is rationalized based on theoretical calculations. The preliminary study reveals that the π - π interaction of the ligands can be exploited to uncover a new generation of carboxylate free wheel complexes, a synthetic method distinctly different from other existing methods.^{7a,8} An attempt to isolate the mixed valent species of **1** either chemically or electrochemically, to bring an overall ground state $S = 1/2$ in the system is currently in progress.

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