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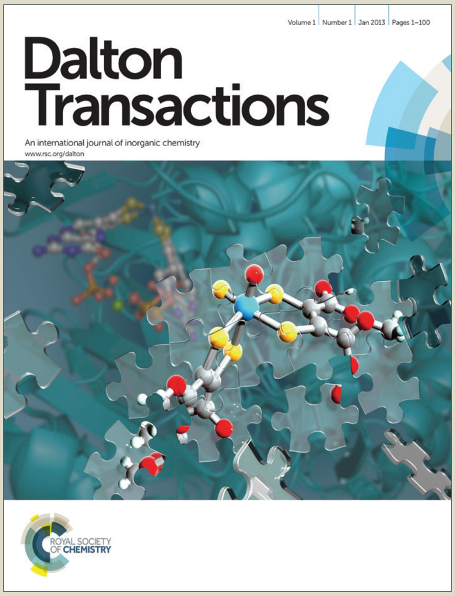

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COMMUNICATION

Carboxylate Free μ-Oxo Bridged Ferric Wheel with a Record Exchange Coupling

Received 00th January 20xx,
Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

www.rsc.org/

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

An aesthetically pleasing "ferric wheel" (Fe_{10}) is first structurally characterized by Lippard and co-workers in 1990.[1] Followed by this, pioneering work by various research groups led to the isolation of variety of homo and heterometallic wheels (odd and even numbers) whose nuclearity ranging 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, these entities are suitable candidates to probe quantum behaviour such as quantum tunnelling of Neel vectors[5] 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 to -25 cm^{-1} which needs to be increased significantly to develop molecular based devices.[1b, 2d, 10] The likely reason for this small exchange value is due to the countercomplementarity effect of the carboxylate bridges in 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 decorated by carboxylate bridges and synthesizing carboxylate free transition metal ion wheel is daunting task which are extremely rare in the literature.[2c, 7, 10d, 12] With the aim of developing synthetic strategy to reveal carboxylate free ferric wheels, we have employed a Schiff base ligand (2-methoxy-6-[(E)-2'-hydroxymethylphenyliminomethyl]-phenol; $C_{15}H_{15}NO_3$; 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 $[Fe_8(\mu\text{-}O)_4(L^{2-})_8]$ (**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*).

When one equivalent of deprotonated Schiff base ligand (L^{2-}) reacts with same equivalent of iron(III) nitrate hydrate in methanol and crystallization in dimethylformamide (DMF) yielded red brown single crystals which is suitable for X-ray diffraction (see ESI for detailed experimental procedure and Fig S1 for structure of ligand). X-ray structure solution reveals the molecular formula as $[Fe_8(\mu\text{-}O)_4(L^{2-})_8]$ (**1**) (Fig 1 and Fig S2). Complex **1** crystallized in a monoclinic *P2₁/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 trivalent oxidation state confirmed by bond valence sum (BVS) calculations[14] (Table S2). The Fe(III) atoms are found to lie in the same plane and arranged in each corners of an octagon. Out of four potential coordination sites (phenoxo oxygen, imino nitrogen, alkoxy and methoxy) of L^{2-} only three of them are utilized for coordination and the methoxy site in all the eight ligand in **1** remains 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 alkoxy arm of Schiff base ligand (average ∠Fe-O(alkoxo)-Fe = 104°(5)), thus forms a dimeric unit. This dimeric unit is bridged to the other dimeric units

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Electronic Supplementary Information (ESI) available: Synthetic procedure and supporting magnetic data along with the complete computation details are listed. CCDC number: 1045923. See DOI: 10.1039/x0xx00000x

exclusively through a single μ-oxo ligand with an average Fe-O-Fe angle of 142°(8).

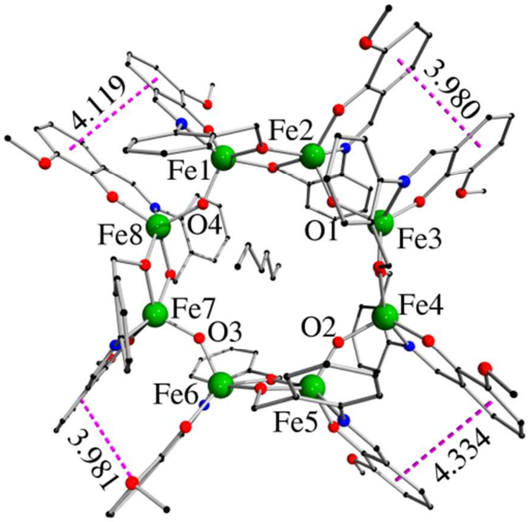

Fig 1. A) Crystal structure of complex **1** a view perpendicular to the Fe8 plane.

The valency of these oxo groups is determined with BVS calculations[14] (Table S3), which are consistent and satisfy the charge balance requirement in **1**. Each of the iron(III) ion is surrounded by {O_4N} atoms and exhibits distorted square pyramidal geometry. Moreover, five coordinate Fe(III) complexes are rare as Fe(III) generally exhibit octahedral geometry as seen in all the reported ferric wheels. In all the iron atoms the axial position is occupied by an oxo group (O1, O2, O3 and O4) which has the shortest Fe-O(oxo) bond length (average Fe-O(oxo) = 1.797 (3) Å) among the other bond lengths in complex **1**.

The observed bond lengths are consistent with the 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) arranged in an alternate fashion in such a way that four of them lie above and below the central Fe_8 plane. This structural arrangement leaves a cavity in the middle, which is large enough to accommodate a guest molecule (hexane) in it (see Fig 1 and Fig S**3**). Besides, additional stability in **1** is gained through displaced π-π staking interaction between the vanillin rings of L^{2-} on one dimeric unit to the adjacent dimeric unit (see Fig 1). This could be the likely reason why complex **1** can be isolated without any carboxylate support around the rim of ferric wheel.

Temperature dependent direct current (dc) magnetic susceptibility measurement was performed on polycrystalline sample of **1** at 1.0 Tesla external magnetic field (Fig 2). The observed room temperature (RT) $\chi_M T$ value of 4.26 $cm^3\ K\ mol^{-1}$ is significantly lower than the expected value (35 $cm^3\ K\ mol^{-1}$) for eight magnetically diluted Fe(III) high spin ions with an average g-value of 2.0.

The majority of the reported ferric wheels show lower than the expected $\chi_M T$ value due to minor or no population of all 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 close to zero at 2.0 K. This scenario confirms that in **1** predominantly antiferromagnetic interactions exist which leads to a diamagnetic ground state.

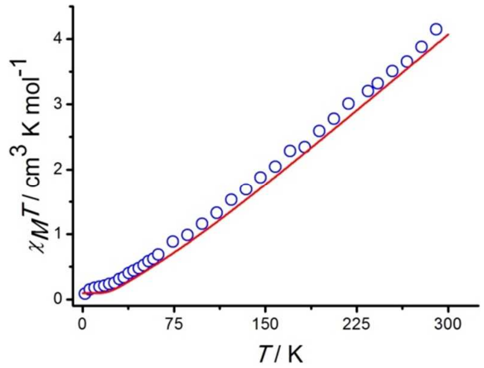

Fig 2. Temperature dependent magnetic susceptibility measurement performed on polycrystalline sample of **1** at *B=1* T. Red solid curve represents simulated data using the parameters mentioned in the main text.

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** reaches only 0.1 $N\mu_B$. The origin of this small magnetic moment is due to tiny amount of paramagnetic impurities (*vide infra*) and the contribution of **1** to the magnetization is virtually zero under high field and low temperature condition (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.

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

Spin and point group (C_4) symmetries have been exploited to evaluate all 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 virtually zero for low temperatures.

The experimental magnetization (Fig S4), correspond to 0.021% impurity spins with S = 5/2 per Fe_8 molecule. Adding the contributions of **1** with J_1=-26.4 cm^{-1} and J_2=-170 cm^{-1} as well as the impurity spins yields the red susceptibility curve in

Fig 2 (see also Fig S5), which meets the experimental data perfectly. The *J values* employed to simulate 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 Fe^{3+} ions, through 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 cm^{-1} and J_2=-183.1 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 4*J*'s model (See Fig S7) in **1** and the extracted *J* values (J_1=-27.4, J_2=-183.1, J_3=-23.3, J_4=-200.9 cm^{-1}) are in reasonable agreement with two *J*'s model. Presence of two non-identical bridges (such as carboxylate and oxo) between the metal centers, either add or counter balances the exchange effect. The existence of countercomplementarity effect shown by the carboxylate in a dinuclear Cu(II) complex ie replacing the carboxylate ligand by other ligands or removal of carboxylate reveals the realistic strength of antiferromagnetic exchange interaction exerted by the oxo bridge in such complexes. The L^{2-} ligand employed possess significant influence in stabilizing carboxylate free system in **1** which facilitates the strongest exchange between the Fe(III) ions through oxo-bridge.[11] These computed parameters on **1** reproduces the experimental magnetic data reasonably well (Fig S4 and S5). Further *J* values obtained from dinulcear model structures (See Fig S8 for the structure of model dimers; J_1=-26.4 cm^{-1} and J_2=-170 cm^{-1}) and also diamagnetic model structures [17] such as {Fe_2Ga_6} yield similar J_2 (-187 cm^{-1}) value and thus offer confidence on the estimated spin Hamiltonian parameters. The extracted exchange interaction values are consistent with the magneto-structural correlations developed on complexes related to complex **1**.[15b, 18]

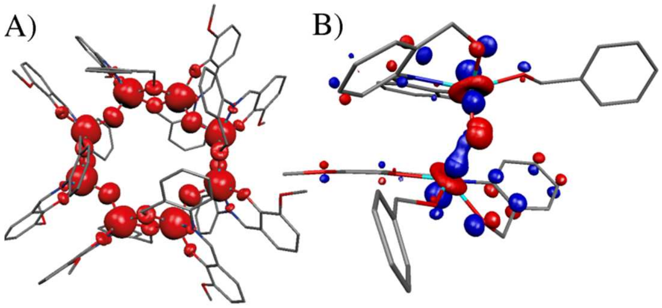

Fig 3. A) Computed High Spin (HS) spin density plot for **1.** B) Superimposed d_z^2 orbitals of Fe(III) ions in dimeric J_2 model.

To understand the variation in the magnitude of computed *J* values, MO analysis has been performed. The net *J* values have contributions from 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 magnetic orbitals obtained from computed overlap integral values of dimer models are depicted in Figures 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 interaction (see Fig 3B). Apart from this, the computed non-zero overlap (See Tables S8, S9 and related discussion in ESI) between non-orthogonal magnetic orbital pairs obtained from corresponding orbital transformation (COT)[19] further adds support for the existence of 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 iron atom are calculated to be <4.4 and this 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 bridging oxygen atoms (0.66) compared to alkoxo oxygen atoms (0.25;0.25) reflecting again stronger and weaker exchange coupling computed for this pair. Overall, the computed *J*s are in excellent agreement with spin Hamiltonian parameters derived from magnetic data modelling.

Often Fe(II) and Fe(III) mixed valent systems are known to exhibit double exchange interaction.[21] Hence, to infer whether other redox states of iron ion is 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 a working electrode, platinum wire as a counter electrode, 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, which clearly shows that there are two reversible one electron reductions. The two metal based redox processes (Fig S12) are assigned as $Fe^{III}_8/Fe^{III}_7Fe^{II}$ and $Fe^{III}_7Fe^{II}/Fe^{III}_6Fe^{II}_2$ 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 an octanuclear, un-supported (absence of metal ions such as alkali or transition metal ion at the center of the wheel) and unprecedented oxo bridged "ferric wheel" using exclusively Schiff base ligand which is extremely scarce in the literature. Temperature dependent magnetic susceptibility data of **1** demonstrates the existence of antiferromagnetic interaction between the iron (III) centres. The exchange values are computed through DFT calculations and are estimated by simulating the magnetic susceptibility data. The J_2 value found for complex **1** is the largest value reported for any ferric wheels or other wheels reported in the literature. The origin of largest exchange along the μ-oxo bridge compared to the alkoxo bridge is rationalized based on theoretical calculations. Preliminary study reveals that the π-π interaction of the ligands can be exploited to uncover new generation of carboxylate free wheel complexes, a synthetic method distinctly different from other existing methods.[7a, 8] Attempt to isolate the mixed valent species of **1** either by chemically or electrochemically to bring overall ground state S = ½ in the system is currently in progress.

Acknowledgement

MS likes to acknowledge DST (SR/S1/IC-32/2011), DST nanomission (SR/NM/NS-1119/2011), BRNS (2012/20/37C/12/BRNS), and IIT Bombay for finacial support. GR would like to acknowledge DST, INSA and DST Nanomission for funding. JS acknowledges financial support by the German Science Foundation (DFG SCHN 615/20-1). TR acknowledges CSIR for financial support.

Notes and references

Detailed experimental procedure for synthesis of **1** is given in ESI. The Schiff base ligands were synthesized as per the reported method in the literature.[13c, d]. CCDC number: 1045923.

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