

Synthesis and Magnetism of a Linked Iron (III) Wheel System

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Polymetallic rings have been put forward as potential candidates for use in quantum computing as qubits – the equivalent of a bit in conventional computing¹. The two qubit gate is another necessary component of a quantum computer. This would consist of two qubits linked together with an interaction between them¹. This project is part of investigations into linking polymetallic wheels with magnetic interaction between them. Here we present the structure and magnetism of a molecule composed of two octametallic Iron (III) rings linked by biphenol.

We looked at a previously known example of a polymetallic cycle: $\text{Fe}_8(\text{OH})_4(\text{OPh})_8(\text{piv})_{12}$ [1]². This is made by reaction of $\text{Fe}_3\text{O}(\text{piv})_6(\text{H}_2\text{O})_3$ piv [where $\text{Hpiv} = (\text{CH}_3)_3\text{CCO}_2\text{H}$] in excess phenol solution. We hoped to link such wheels by replacing phenol groups with biphenols. This was achieved by reaction of $\text{Fe}_3\text{O}(\text{piv})_6(\text{H}_2\text{O})_3$ piv with phenol and biphenol in dichloromethane. X ray diffraction of crystals obtained from this reaction gave the structure of the molecule $\text{Fe}_{16}(\text{OH})_8(\text{OPh})_8(\text{OPhPhO})_4(\text{piv})_{24} \cdot 2\text{H}_2\text{O}$ [2] which is pictured in figure 2 below.

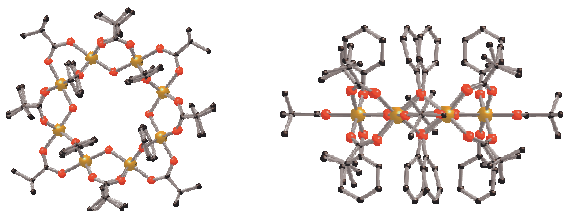


Figure 1: top and side views of [1], $\text{Fe}_8(\text{OH})_4(\text{OPh})_8(\text{piv})_{12}$. Fe = orange, O = red, C = black. Hydrogen atoms are not shown for clarity.

Each ring contains eight Iron (III) centres with the bridging between them alternating between two bridging pivalates and a hydroxide, and one pivalate, a biphenol and a phenol. The four biphenols link the two wheels together. A guest water molecule sits in each cavity.

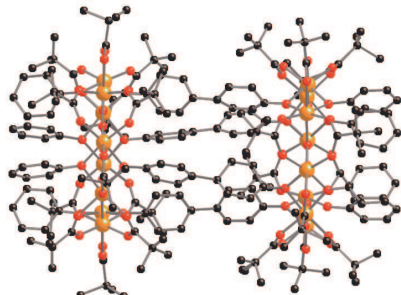


Figure 2: $\text{Fe}_{16}(\text{OH})_8(\text{OPh})_8(\text{OPhPhO})_4(\text{piv})_{24} \cdot 2\text{H}_2\text{O}$, compound [2]. Fe = orange, O = red, C = black. Hydrogen atoms are not shown for clarity. All the aromatic rings in the biphenols are disordered between two sites

Magnetic studies of the single wheel $\text{Fe}_8(\text{OH})_4(\text{OPh})_8(\text{piv})_{12}$ have been published previously³. Antiferromagnetic coupling in the wheel leads to a ground state spin of zero. Magnetic susceptibility measurements were carried out for the linked wheels and measurements for [1] were also recorded for comparison.

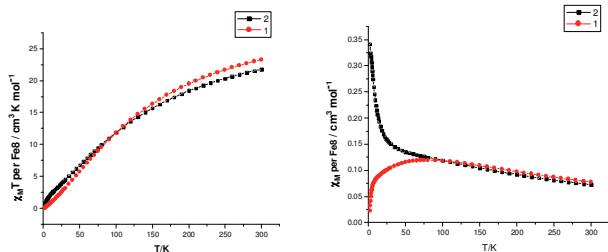


Figure 3 (left): Graph of magnetic susceptibility \times temperature against temperature for compounds [1] and [2].
Figure 4 (right): Graph of magnetic susceptibility against temperature for compounds [1] and [2]

Results for [2] have been halved so that they correspond to values per Fe_8 wheel. The $\chi_M T$ against T graph (figure 3) shows antiferromagnetic behaviour with the low temperature behaviour tending towards zero and the room temperature value of being lower than the calculated value for eight non-interacting iron (III) centres. The χ_M against temperature plot (figure 4) shows similar behaviour for both compounds at higher temperatures with a dramatic divergence at low temperature. Magnetisation against field studies (figure 5) show the linked system rising much quicker, with magnetisation of the sample occurring as soon as a field is applied.

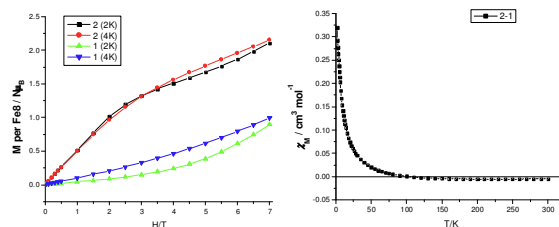


Figure 5 (left): A graph of magnetisation against magnetic field for compounds [1] and [2] at 2K and 4K.
Figure 6 (right): A graph showing the difference in magnetic susceptibility against temperature for compounds [1] and [2].

These results could imply ferromagnetic coupling within each ring and an interaction between the rings which lowers the energy gap between the ground state and the lowest lying excited state. However simulations carried out on a simplified model of this cannot replicate the observed behaviour. It is also possible that there are paramagnetic impurities, which would be consistent with the instantaneous magnetisation. However the experiment was carried out on crystalline material with good elemental analysis. Measurements must be repeated on a new sample before this can be ruled out. There is also the possibility that the linking biphenols have semiquinone character.

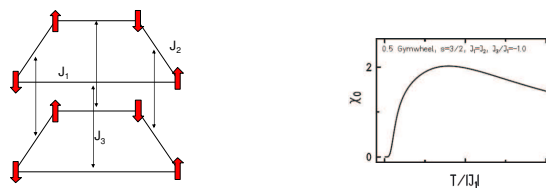


Figure 7 (left): The simplified model used to simulate the magnetic data obtained for compound [2].
Figure 8 (right): Simulated magnetic susceptibility graph for the model of [2] with ferromagnetic interaction between rings



Figure 9 (left): Simulated magnetic susceptibility graph for the model of [2] with antiferromagnetic interaction between rings.
Figure 10 (right): The best fit found for the magnetic data of [2] simulated with a designed energy level system which was not based on a molecular model.

Further work ensues on trying to make a soluble analogue of the linked ring system and analogues with chromium and vanadium, the single wheel versions of which have been isolated.

References

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