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COMMUNICATION

An octahedral tetrachlorido Fe(II) complex with aminopyrazinium ligands from a serendipitous redox synthesis exhibiting magnetic exchange through non-covalent 3-D architectures

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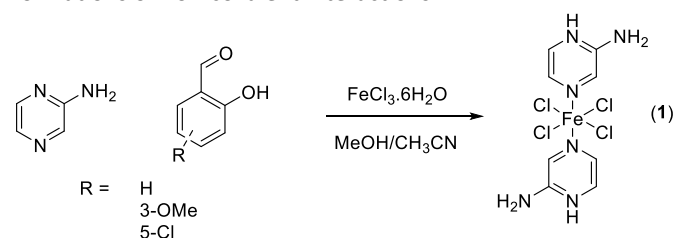
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An air stable, neutral Fe(II) complex with four equatorial chlorido ligands has been stabilised through a serendipitous redox process and *in situ* ligand protonation. A three dimensional non-covalent network composed of halogen bonding and π - π stacking propagates magnetic exchange interactions through the lattice. The electronic structure has been investigated using DFT.

Supramolecular chemistry has become a fascinating area of research that relies on self-assembly of small molecules to produce a material that is greater than the sum of its parts. The importance of understanding these phenomena underpin our very existence with biological processes such as DNA assembly¹ and protein folding^{2,3} being dominated by non-covalent interactions. From its humble beginnings, the field has been recognised with two Nobel prizes: the first for the field of supramolecular chemistry in 1987 and the second for its application in molecular machines in 2016. Applications in a plethora of useful areas, ranging from gas separation and biological mimics to magnetic materials and modern day electronics have now been developed.⁴⁻⁹ There are a number of interactions to consider, such as hydrogen and halogen bonding and π - π stacking, when attempting to make an interesting supramolecular material. This is where serendipity can aid the synthetic chemist. There are many examples of chemical syntheses undergoing redox processes wherein the oxidation state of the starting metal ion is different to the product through changes of ligands to the metal or changes in the

coordinated ligand itself.¹⁰⁻¹² Such changes in metal properties can lead to new magnetic and crystal packing phenomenon. Many interactions can be planned; however many routes to functional supramolecular systems, particularly those based in the area of magnetism, rely on serendipity to form new and novel clusters and assemblies that display interesting magnetic phenomena.¹³⁻¹⁹ Historically, many single molecule magnets used covalent linkers that facilitated the interactions between magnetic ions.²⁰⁻²² In recent years, many examples of magnetic interactions propagated through non-covalent interactions such as π - π stacking and/or hydrogen bonding have shown a new way to merge supramolecular chemistry with magnetism and electronic effects.²³⁻²⁸

Here we present a *pseudo* octahedral mononuclear iron(II) complex, [Fe(HL)₂Cl₄], **1**, where L = 2-aminopyrazine, consisting of four chloride ligands in the equatorial positions and two 2-aminopyrazinium ligands in the axial positions. The 2-aminopyrazinium ligands undergo an *in situ* protonation on the non-ligated pyrazine nitrogen to balance the charge of the Fe(II) centre, Scheme 1. This leads to the presence of both an aromatic amine proton and a primary amine proton for the formations of non-covalent interactions.

Scheme 1: Synthesis of **1**.

We believe the Fe(III) chloride used in the synthesis is reduced to Fe(II), while the salicylaldehyde is oxidised to salicylic acid. Several synthetic experiments were undertaken to elucidate the nature of this redox pathway. Firstly, the reaction was

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performed in the absence of salicylaldehyde yielding no formation of complex **1**. Secondly, a range of variously substituted salicylaldehydes were utilised to investigate the effects of electron donating *versus* electron withdrawing groups on the oxidation pathway to form complex **1**. In all cases, complex **1** was successfully synthesised. However, the yield varied depending on the substituent used, (3-OMe – 9.9 mg, Sal – 35.3 mg, 5-Cl – 67.5mg). This we believe is due to the change in electron density at the aldehyde carbonyl moiety and therefore it's susceptibility to oxidation. Lastly, to test the range of aldehyde oxidations possible, the reaction was repeated with propionaldehyde, 61.7 mg, phenylacetaldehyde, 11.5 mg, and benzaldehyde, 25.7 mg. This also resulted in formation of complex **1** with the yield being affected by the steric bulk around the carbonyl with propionaldehyde yielding the most and phenylacetaldehyde yielding the least. The oxidation of the aldehyde to the carboxylic acid is most likely the rate-determining step as it produces both the metal ion for complexation and removes the aldehyde so formation of the Schiff base condensate with the aminopyrazinium does not occur. UV-Vis analysis shows the decrease of the salicylaldehyde peaks associated with the oxidation to salicylic acid (Fig S1).^{29,30}

Complex **1** crystallises in the triclinic space group P-1 and the unit cell consists of two half-occupancy cations. There is a centre of inversion around the central Fe atom; as a result, there are only three distinct iron-ligand distances, Figure 1. The bond lengths are indicative of a high spin (HS), $S = 2$, Fe(II) ion. A continuous shape analysis, where the geometry (ignoring symmetry) of the given complex is compared to an idealised geometry, was carried out, using the program SHAPE 2.0,³¹ on the immediate coordination sphere of complex **1**. This generates an $S(Oc)$ of 0.295, inferring the complex is almost perfectly octahedral in shape, ($S(Oc) = 0$).

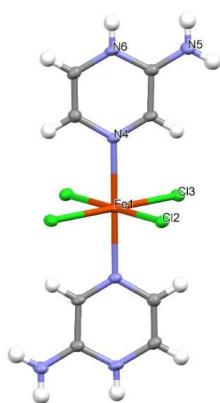


Figure 1: Crystal structure of complex **1** at 150 K. Ellipsoids at 50% probability. Selected bonds (Å) and angles (°) Fe1-Cl2 2.4899(6), Fe1-Cl3 2.4458(6), Fe1-N4 2.2076(19), N4-Fe1-Cl2 91.45(5), N4-Fe1-Cl3 90.16(5), Cl3-Fe1-Cl2 91.62(2).

The discrepancies in the Fe-Cl bond lengths can be attributed to the manifestation of a weak Jahn-Teller distortion as the asymmetric orbital population occurs in the t_{2g} orbital set. These have been noted many times in HS Fe(II) complexes and can directly affect their magnetic properties.^{32–34} A number of non-

covalent interactions link the monomeric complex **1** into a supramolecular network. Halogen bonding persists in several patterns in this network. One motif persists between Cl2 and Cl3' of one complex ion with the N6 (pyrazine) and N5 (amine) of the neighbouring complex above and below resulting in a halogen bonding 1-D chain. The distances are in line with a halogen bond, N6-Cl3' 3.258(3) Å, N5-Cl2 3.269(2) Å. This 1-D chain is then further linked into a 2-D sheet by halogen bonding between Cl2 and Cl2' of one chain with the N5 amine nitrogen of the neighbouring parallel chains, with a bond length of 3.173(2) Å. This results in a halogen bonded 2-D sheet, Fig 2. Further to the halogen-bonding present in the lattice, π - π stacking aids not only in the formation of the 1-D chain but also in linking the 2-D sheets to one another to form a full 3-D non-covalently linked assembly. The π - π stacking that reinforces the 1-D chain manifests as a displaced stacking motif within the lattice with the edge of the π -system overlapping, with a distance of 3.346(5) Å. The π - π stacking that links the 2-D sheets together manifests as a sandwich-type stacking where the π -systems of the aminopyrazinium ligand are completely overlapped with a distance between the rings of 3.379(5) Å (calculated from one centroid of the aminopyrazinium ring to the centroid of the opposing aminopyrazinium ring), Fig S2/S3. The presence of these non-covalent interactions in a three-dimensional lattice paired with a magnetic ion such as HS Fe(II) can lead to interesting magnetic properties. Therefore, a full study was undertaken to investigate the magnetic properties of this assembly.

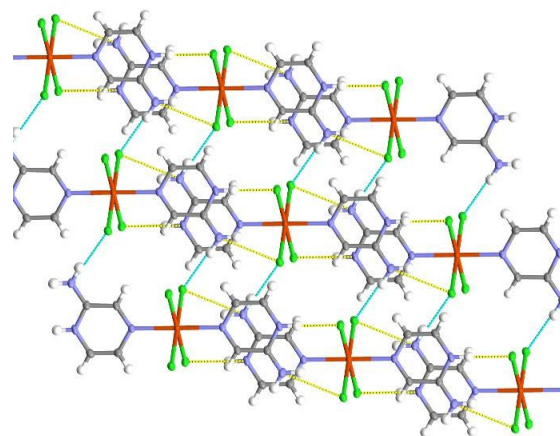


Figure 2: Packing structure of complex **1** at 150 K. Halogen bonds between the N6-Cl3' and N5-Cl2 in yellow forming a 1-D chain in the lattice. Halogen bonds between N5-Cl2/Cl2' in blue forming a 2-D sheet.

Variable temperature magnetic susceptibility, isothermal magnetisation curves and AC magnetic susceptibility were carried out on a polycrystalline sample of **1** in an eicosane matrix using a Quantum Design MPMS SQUID XL-7 magnetometer between 300 and 2 K. The magnetic susceptibility data, Fig 3, is in agreement with an $S = 2$, HS Fe(II), 5T state. At 300 K the susceptibility is $3.55 \text{ cm}^3 \text{ mol}^{-1} \text{ K}$, indicating a g value of approximately 2.1. This value stays constant until *ca.* 100 K where a small decrease in the susceptibility is

observed. This is due to weak antiferromagnetic coupling facilitated by the non-covalent interactions found in the lattice. The sharp decrease in susceptibility from *ca.* 40 K can be attributed to the large zero field splitting. Isothermal magnetisation measurements were then performed to probe the possibility of remnant magnetisation. While no hysteresis is observed, the values for magnetisation even at 7 T and 2 K are well below the expected values for HS Fe(II), Fig 3 inset. This indicates the presence of a non-zero anisotropy within the system with the value of *ca.* 2.9 μ_B being in line with the value of 2.4 μ_B observed in the Fe(II) SIM by Sitzmann *et al.*³⁵ The susceptibility and magnetisation data were simultaneously fitted using the program PHI³⁶ using Eq. 1 with the mean field correction, zj' , to model the non-covalent exchange interaction.

$$\hat{H}=D\left[\hat{S}_z^2-\frac{S(S+1)}{3}\right]+\mu_B g\hat{S}B \quad (\text{Eq 1})$$

This yields parameters $g = 2.138$, $|D| = 9.74 \text{ cm}^{-1}$, $zj' = -0.12 \text{ cm}^{-1}$ and $R = 0.00025$. Although the value for D is moderately high compared to other first row transition metal complexes that exhibit some degree of slow relaxation under an applied DC field,^{37,38} complex **1** shows no out of phase signal in the AC susceptibility to indicate slow relaxation, Fig. S4. This may be a clue to the sign of D , which can be somewhat ambiguous when fitting magnetic data using PHI. Therefore, the lack of a signal in the dynamic measurement when the magnitude of D is in line with other Fe(II) SIM complexes point towards a positive anisotropy.

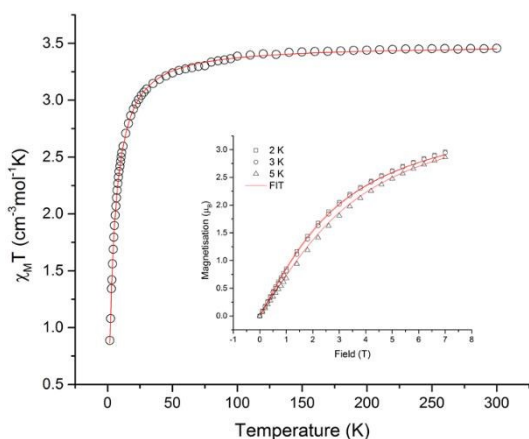


Figure 3: Variable temperature magnetic susceptibility for complex **1** carried out between 300 and 2 K in a 0.1 T applied DC field. (Red line is fit to Eq. 1). Inset: Isothermal magnetisation curves with fit to Eq 1 exhibiting no saturation even at seven tesla.

While the overall magnetic effects observed in complex **1** yield no promise for data storage, it does reinforce a novel route for magnetic exchange, which can be further tailored through ligand design. The relationship between the electronic structure present in complex **1** and the physical properties observed were further investigated through a computational study. Density functional theory (DFT) calculations using the ω B97X-D functional³⁹ and Stuttgart-Bonn basis set and pseudopotentials^{40,41} were performed for **1** in the gas phase and

in aqueous solution using the polarisable continuum model (PCM).^{42–44} The gas phase calculations reveal the C_i symmetry of the molecule is a saddle-point and that breaking the molecular symmetry with different Fe – N bond lengths (1.99 Å and 2.26 Å) gives a lower energy minimum. The frontier molecular orbitals are delocalised across the metal centre, chloride ions and pyrazine moieties, indicating strong interactions between the ligands and the metal centre (see figure S5). The calculated spin densities are given in Figure 4 for the symmetric and non-symmetric geometries of **1**. The calculated spin density and frontier molecular orbitals lie on both the chloride ligands and pyrazine rings, which participate in the non-covalent interactions resulting in orbital interactions propagating magnetic exchange. Upon symmetry breaking, the spin-density is removed from the pyrazine moiety with the longest Fe – N bond, but remains delocalised over the rest of the molecule. The geometry of **1** obtained using the PCM solvent model is a minimum within C_i symmetry, with no lower energy symmetry-broken solution found. Quantitatively correct bond dissociation energies (BDEs) are notoriously difficult for DFT along a dissociation coordinate, but comparison of the bound and bond-broken energies give reliable estimates of BDEs.⁴⁵ Optimised geometries of the fragments are given in the supporting information, Fig S6. Removal of one chloride anion requires 2.3 kcal mol⁻¹, while removal of a protonated pyrazine requires 12.1 kcal mol⁻¹.

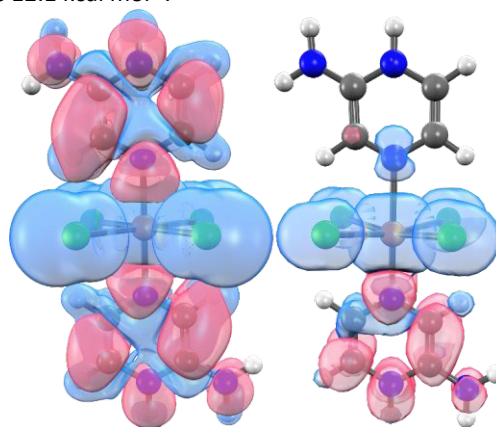


Figure 4: Spin densities for the symmetric (left) and symmetry-broken (right) geometries calculated using DFT. Regions coloured in blue correspond to positive spin density; pink to negative spin density. An isovalue of 0.02 au was used.

In conclusion, we have presented an example of an equatorial tetrachlorido Fe(II) species, where a formally tetra anionic Fe ion is charge balanced with two cationic aminopyrazinium ligands, derived from an *in situ* redox complexation in aerobic conditions. An interwoven, three-dimensional non-covalent framework utilising halogen bonding and π - π stacking persists in the lattice and propagates magnetic interactions in an antiferromagnetic manner between the $S = 2$ ions. This result brings an important aspect to *in situ* Schiff base synthesis and coordination as the rate of the formation of the imine is far slower than the rate of the redox process resulting in complex **1**.

There are no conflicts of interest to declare

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