Filling the Gap in Extended Metal Atom Chains: Ferromagnetic Interactions in a Tetrairon(II) String Supported by Oligo-α-pyridylamido Ligands

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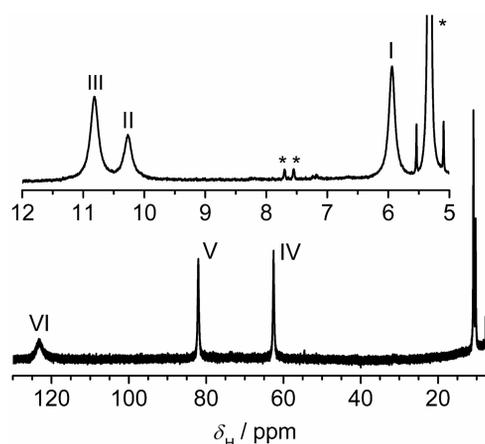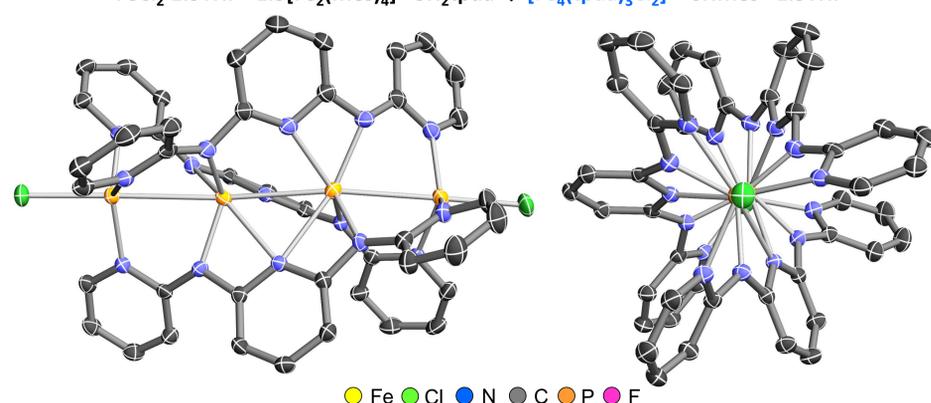
Introduction

Extended Metal Atom Chains (EMACs) consist in arrays of metal ions, wrapped together by oligo-α-pyridylamido, or related ligands.[1-3] The arrangement of the donor atoms often promotes the formation of metal-metal bonds.[1] EMACs have attracted renewed interest after some of us reported that the pentachromium(II) complex [Cr5(tpda)4Cl2] (H2tpda = N^2,N^6-di(pyridin-2-yl)pyridine-2,6-diamine) shows a directionally-bistable magnetic moment at low temperature (S = 2 ground state).[4] **Homometallic iron-based EMACs** are particularly appealing synthetic targets, owing to the **large spin and magnetic anisotropy of high-spin iron(II)** ions. They have proved very elusive, most likely as a consequence of the high tendency of Fe^{2+} toward oxidation and hydrolysis.[5] Here, in **strictly anaerobic and anhydrous conditions**, refluxing [Fe2(Mes)4] (HMes = mesitylene), Fe4Cl8·6THF and H2tpda in toluene, we isolated crystals of **the first homometallic iron(II)-based EMAC supported by oligo-α-pyridylamido ligands**: the tetrairon(II) complex **[Fe4(tpda)3Cl2] (1)**.[6]

Concept

In an EMAC, the metal ions are enforced in an almost perfectly axial coordination environment. Moreover, molecules with high-spin iron(II) ions can exhibit well-isolated high-spin states even at room temperature. **We contend that the electronic features of EMACs are potentially suitable for SMM behaviour.** The key to success in the synthesis of **1** was utilizing [Fe2(Mes)4] as the main iron(II) source and deprotonating agent for the ligand molecules.

NMR Spectroscopy
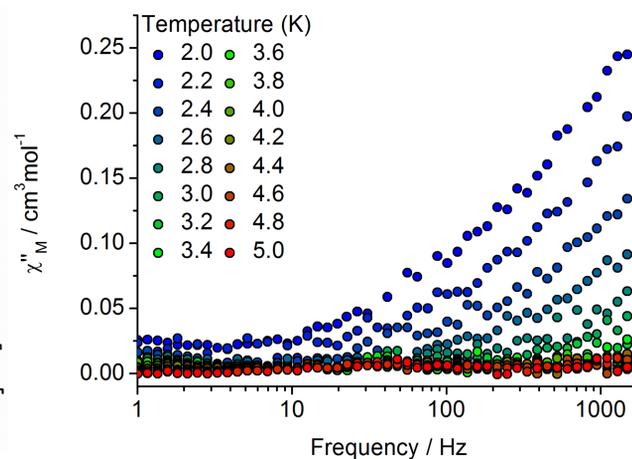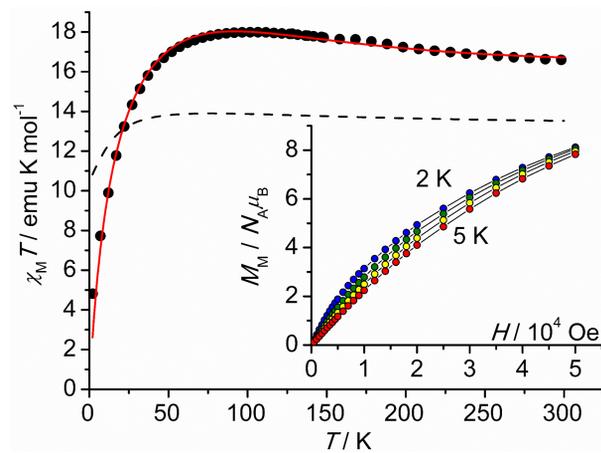
FeCl2·1.5THF +1.5[Fe2(Mes)4] +3H2tpda → [Fe4(tpda)3Cl2] + 6HMes +1.5THF

Fe ⬤ Cl ⬤ N ⬤ C ⬤ P ⬤ F ⬤

¹H NMR spectrum of **1** in CD2Cl2 showed six well-resolved singlets covering a range of chemical shift exceeding 100 ppm, indicating strong interaction with paramagnetic centers in the complex. Both the number of observed resonances and their intensity ratio require that only 6 of the 11 hydrogen atoms in each ligand's molecule are chemically inequivalent. This indicates that the unsymmetric binding of the ligands is averaged out in solution, so that the helical structure achieves its maximum possible symmetry (D_3) over NMR timescale.[6]
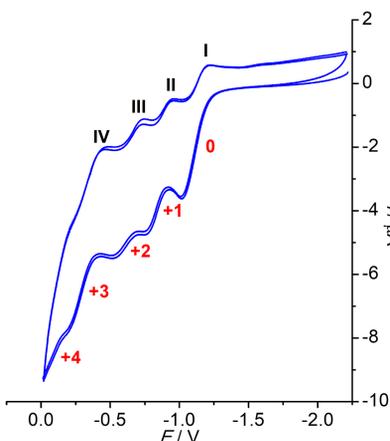
Magnetic studies

Susceptibility curve ($\chi_M T$ vs T, χ_M is the molar magnetic susceptibility) of a microcrystalline sample of **1**·2.6CH2Cl2·0.84Et2O measured at 1 kOe (main panel) and **magnetization curves** recorded from 2.0 to 5.0 K (inset). The dashed line shows the magnetic response of four anisotropic noninteracting iron(II) ions with all ligand field parameters held fixed at the values resulting from angular overlap model (AOM) calculations. The trend of $\chi_M T$ is in accordance with DFT calculations that described the system as two ferromagnetic Fe2 dimers, weakly antiferromagnetically coupled with each other. The solid red line arises from the best-fit parameters ($J\widehat{S}_i \cdot \widehat{S}_j$ convention): $J = -21.4(4)$ cm^{-1}, $J_{eff}/g_{av}^2 = 0.345(7)$ cm^{-1} and TIP = 2.1(2) × 10^{-3} emu mol^{-1} (J_{eff} = interdimer interaction in the mean-field approximation, g_{av} = average g factor of the Fe2 unit, TIP = temperature-independent paramagnetism).

Out-of-phase component of the molar magnetic susceptibility (χ_M'') was detected in the optimal field value of 2.0 kOe. We scanned isothermal χ_M'' vs ν between 2.0 and 5.0 K (ν is the frequency of the 3 Oe oscillating magnetic field). **The results reveal the onset of slow relaxation of the magnetization below 2.8 K.** Since no maximum in the curves could be detected in the available frequency range, the characteristic relaxation time ($\tau_0 = 2.6(2.1) \times 10^{-7}$ s) and the energy barrier ($U_{eff}/k_B = 10.1(1.3)$ K) where roughly extracted using the equation $\ln(\chi_M''/\chi_M') = \ln(\omega\tau_0) + U_{eff}/k_B T$ ($\omega = 2\pi\nu$ and χ_M' is the in-phase component of χ_M), instead of the (generalized) Debye model.[7,8] This SMM behaviour is principally due to the terminal iron(II) ions, which have an unquenched orbital momentum (due to their coordination geometry, close to trigonal-pyramidal), and provide the largely dominant anisotropic contribution. Consequently, each Fe2 dimer has a huge easy-axis anisotropy, with a calculated susceptibility (at 2 K and 1 kOe) 25 times higher along the chain axis than orthogonal to it.[6]
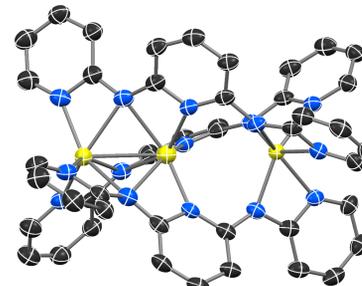
Electrochemistry

The CV curve for **1** in CH2Cl2 (tetrabutylammonium chloride as base electrolyte) is here shown. The electrochemistry of the complex consists in four quasi-reversible, diffusion-controlled redox processes, observed in a potential window of only 0.8 V. The large separations between two consecutive peaks correspond to rather large comproportionation constants.[9,10] This indicates high thermodynamic stability of each redox form toward disproportionation, suggesting the possibility of isolating mixed-valence compounds from CH2Cl2 solution.[11]

Oxidised Mixed Valent Compounds

The one-electron oxidised compound **[Fe3(tpda)3]PF6 (2)** was isolated by reacting **1** with FcPF6 (1 equiv) in CH2Cl2 solution (Fc = ferrocene). The two short-distance iron ions are both Fe^{2+} while the farthest one is the oxidized metal center (Fe^{3+}).

UV-vis-NIR spectrum of **2** is similar to that of **1** but is characterized by a significative broad band around 700-750 nm, which is assigned to a charge-transfer process, typical of **mixed-valent compounds**, in which the electronic interaction mechanism know as *double-exchange*, generally provides a source of ferromagnetic coupling between ions in different oxidation states.[12-14]

[Fe4(tpda)3Cl2] + FcPF6 → [Fe3(tpda)3]PF6 + FeCl2 + Fc

Conclusions

The wide class of EMACs supported by oligo-α-pyridylamido ligands, known since five decades, **was finally extended to include homometallic iron derivatives**. **[Fe4(tpda)3Cl2]** proved sufficiently stable to be characterized by spectroscopic, electrochemical and magnetic techniques. Because of the unquenched orbital momentum of the terminal iron(II) ions, spin-orbit interaction produces a large easy-axis anisotropy along their idealized trigonal axis, which is almost collinear with the chain axis. DFT studies are in accordance with magnetic measurements and describe the molecule as two ferromagnetic Fe2 pairs weakly antiferromagnetically coupled with each other. In spite of antiferromagnetic interdimer coupling, slow magnetic relaxation was detected at low temperatures, with an estimated energy barrier of only 10 K.

References

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