Extended Metal Atom Chains (EMACs) as magnetic nanostructures: synthesis and magnetic behavior of the first iron(II) based EMAC

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EMACs constitute a wide class of polynuclear metal complexes containing three to eleven metal centers lined up in a string by a helical array of deprotonated oligo-α-pyridylamine (or related) ligands.[1] In these materials, which may be homo- or heterometallic, homo- or heterovalent, the arrangement of donor atoms often promotes the formation of metal-metal bonds.[2] EMACs were consequently investigated as analogues of macroscopic wires in molecular electronics.[3] Recently these systems have attracted renewed interest after Cr_3 and Cr_5 EMACs showed slow relaxation of the magnetization, a phenomenon that is typical of single molecule magnets (SMMs) and is potentially useful for magnetic storage.
Homometallic Fe-based EMACs are particularly appealing synthetic targets in molecular magnetism owing to the large spin and magnetic anisotropy of high-spin iron(II).[4] In addition, metal-metal bonds in low-valent polyiron species may afford strong ferromagnetic interactions, with thermally-persistent high-spin states even at room temperature.[5] A well-isolated S = 6 state was indeed theoretically predicted for a hypothetical triiron(II) EMAC assembled using an Hdpa-related ligand.[6] Curiously, although iron(II) was incorporated into heterometallic trinuclear EMACs, homometallic iron(II) strings have never been isolated (Sundberg and co-workers have isolated the dimeric species $[Fe_2(Mes)_2(dpa)_2]$ and $[Fe_2Cl(dpa)_3]$, that cannot be considered true EMACs).[7] So far, homometallic Fe-based EMACs have proved very elusive most likely as a consequence of the high tendency of iron(II) toward oxidation and hydrolysis.
We demonstrate that homometallic iron(II) EMACs are indeed accessible synthetic targets. In rigorously anhydrous and anaerobic conditions, we were able to isolated in pure form and characterize the first homometallic iron(II)-based EMAC, namely $[Fe_4(tpda)_3Cl_2]$ (**1**) (see Figure), were H_2tpda = N^2, N^6-di(2-pyridyl)-2,6-diaminopyridine. All synthetic operation were performed under inert controlled and purified N_2 atmosphere, inside an MBraun UniLAB dry-box. The key point was the use of dimesityliron, $[Fe_2(Mes)_4]$ (**2**), both as a deprotonating agent and as a metal source.[8] Infact, the Mes^- ion is a sufficiently strong base to deprotonate the H_2tpda molecules, forming mesitylene as the only by-product of the reaction.[9] This elusive string complex was reproducibly isolated as **1**·2.60CH_2Cl_2·0.84Et_2O by first refluxing **2** with $FeCl_2$·1.5THF (0.5 equivs) and H_2tpda (2 equivs) in toluene under strict exclusion of oxygen and moisture.[10] The orange precipitate thus formed was extracted with CH_2Cl_2 and the product crystallized by vapour diffusion of Et_2O, affording large dark-red prisms in 25-30% yield. A single-crystal X-ray diffraction study at 115 K evidenced that **1**·2.60CH_2Cl_2·0.84Et_2O contains tetrairon(II) string-like complexes wrapped by three doubly-deprotonated *all-syn* H_2tpda ligands and capped at their termini by two chloride ions. Regarding the magnetic characterization of **1**, the four iron ions in the complex form two ferromagnetic pairs, among which we found a weak antiferromagnetic interaction, in accordance with DFT calculations.

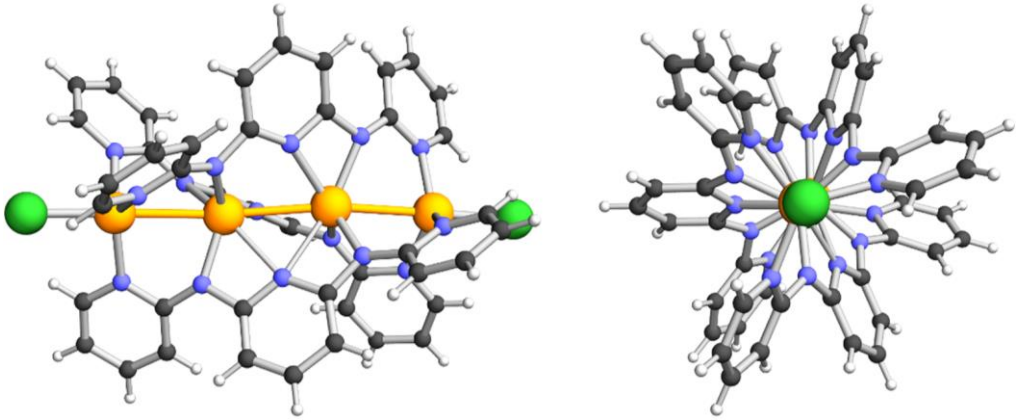

Figure: Molecular structure of **1**, viewed approximately normal to the metal axis (left) and along it (right).

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