181

Tetrairon(II) Extended Metal Atom Chains as Single-Molecule Magnets

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Abstract

Iron-based extended metal atom chains (EMACs) are potentially high-spin molecules with axial magnetic anisotropy and thus candidate single-molecule magnets (SMMs). We herein compare the tetrairon(II), halide-capped complexes $[Fe_4(tpda)_3Cl_2]$[1] (**1Cl**) and $[Fe_4(tpda)_3Br_2]$ (**1Br**), obtained by reacting $Fe_4Cl_8(thf)_6$, or $FeBr_2(thf)_2$, with $[Fe_2(Mes)_4]$ and N^2,N^6-di(pyridin-2-yl)pyridine-2,6-diamine (H_2tpda) in toluene, under strictly anhydrous and anaerobic conditions (HMes = mesitylene).[2] Detailed structural, electrochemical and Mössbauer data are presented along with direct-current (DC) and alternating-current (AC) magnetic characterizations. DC measurements revealed similar static magnetic properties for the two derivatives, with $\chi_M T$ at room temperature above that for independent spin carriers, but much lower at low temperature. The electronic structure of the iron(II) ions in each derivative was explored by *ab-initio* (CASSCF-NEVPT2-SO) calculations, which showed that the main magnetic axis of all metals is directed close to the axis of the chain. The outer metals, Fe1 and Fe4, have an easy-axis magnetic anisotropy (D = −11 to −19 cm^{-1}, $|E/D|$ = 0.05-0.18), while the internal metals, Fe2 and Fe3, possess weaker hard-axis anisotropy (D = 8-10 cm^{-1}, $|E/D|$ = 0.06-0.21). These single-ion parameters were held constant in the fitting of DC magnetic data, which revealed ferromagnetic Fe1-Fe2 and Fe3-Fe4 interactions and antiferromagnetic Fe2-Fe3 coupling. The competition between super-exchange interactions and the large, noncollinear anisotropies at metal sites results in a weakly magnetic non-Kramers doublet ground state. This explains the SMM behavior displayed by both derivatives in the AC susceptibility data, with slow magnetic relaxation in **1Br** being observable even in zero static field.

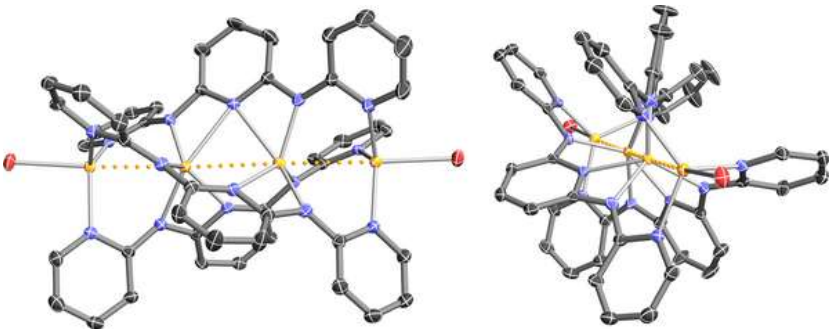

Figure 1. Molecular structure of **1Br**.

[1] A. Nicolini *et al.*, *Inorg. Chem.*, **2018**, *57*, 5438-5448. [2] A. Nicolini *et al.*, *Dalton Trans.*, **2021**, Advance Article, DOI: 10.1039/d1dt01007g.