# Encapsulation of a hexairon SMM by a tridecadentate N-based ligand

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The new tridecadentate proligand H_6L (**Fig. 1**, left) was designed and synthesized with the idea of using its dipyridylamine-like branches to assemble new Extended Metal Atom Chains (EMACs) [1,2]. To this aim, H_6L was refluxed with 1.6 molar equivalents of $[Fe_2(Mes)_4]$ in toluene for 3 h in strictly anaerobic and anhydrous conditions (HMes = mesitylene). After work-up, beautiful X-ray quality crystals of complex $[Fe_6O_2(OH)(H_3L)L]$ (**1**) were obtained from THF/Et_2O in substantial (48%) yield. The formula and structure of **1** were inferred by combined use of EA, ESI-MS, and X-ray crystallography. The complex (**Fig. 1**, right) crystallizes in a trigonal space group and contains two crystallographically-equivalent tripodal ligands that entrap an Fe/O core. The latter is severely disordered by rotation around the trigonal axis and was modelled as a central $Fe_5(\mu_5\text{-}O)$ cluster *plus* a sixth, half-occupancy Fe center (Fe3) residing in the *tren*-like aliphatic pockets of the tripodal ligands. Significantly, the shortest Fe−Fe distances in the central pentairon unit (2.629(2) Å) are suggestive of Fe-Fe bonds. Two additional O atoms, O2 and O2^{III}, lie on opposite sides of the $Fe_5(\mu_5\text{-}O)$ moiety and are at hydrogen-bond distance from pyridine N atoms. Based on Bond Valence Sum (BVS) analysis, the structure of the Fe/O core was then modelled as $[Fe(\mu_3\text{-}O)Fe_5(\mu_5\text{-}O)(\mu\text{-}OH)]$. BVS calculations, charge-balance considerations, and Mössbauer spectra suggest that **1** is a valence-delocalized $Fe_4^{II}Fe_2^{III}$ species. DC magnetometry establishes a room temperature χT value of 27.4 cm^3 K mol^{-1}, which is well above the Curie constant for noninteracting, valence-localized centers (C = 22.6 cm^3 K mol^{-1} for 4 high-spin Fe^{2+} ions with g = 2.15 and 2 high-spin Fe^{3+} ions with g = 2.00). The χT product increases slightly with cooling, reaching a maximum of ~30 cm^3 K mol^{-1} at ~25 K. These results indicate predominant ferromagnetic interactions in **1**, which shows slow magnetic relaxation detectable even in zero field (U_{eff}/k_B= 49 K, τ_0 = 4·10^{-10} s).
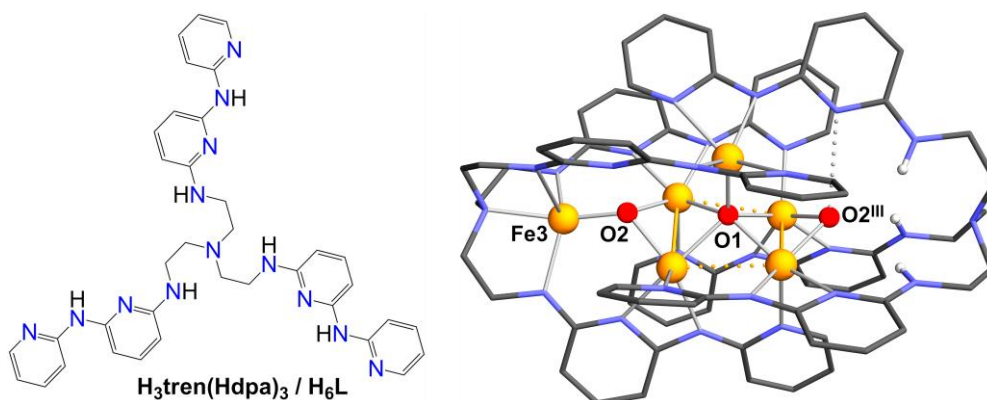
Figure 1: Structures of H_6L (left) and **1** (right; color code: orange, Fe; red, O; blue, N; dark grey, C; light grey, H). Potential OH···N$_{py}$ interaction is highlighted with light grey dots.

References:

[1] J. F. Berry, Extended Metal Atom Chains. In *Multiple Bonds Between Metal Atoms*, Cotton, F. A. *et al.*, Eds.; Springer Science and Business Media: New York, USA, 669-706 (2005).
[2] A. Nicolini *et al.*, Dalton Trans. 50, 7571 (2021)