Pentadecadentate Chelating Ligands as Building Blocks for an {Fe_6} Cage with 12 *Exo*-coordinated Sodium Cations

Geoffrey J. T. Cooper, Hamera Abbas, Paul Kögerler, De-Liang Long and Leroy Cronin *

Department of Chemistry, The University of Glasgow, University Avenue, Glasgow, G12 8QQ, UK
and Ames Laboratory, Iowa State University, Ames, IA 50010, USA

E-mail: L.Cronin@chem.gla.ac.uk

Supplementary Material

Synthesis of *cis,cis*-1,3,5-cyclohexanetriamine-*N,N,N',N',N'',N''*-hexaacetic acid (H_6**L**)

A solution of *cis*-TACH · 3 HCl (2.96 g, 12.4 mmol) and sodium hydrogencarbonate (3.38 g, 26.2 mmol) in water was slowly added by peristaltic pump over 5 hours to a refluxing aqueous solution of chloroacetic acid (14.06 g, 149.0 mmol) and sodium hydrogencarbonate (25.00 g, 298.0 mmol) under nitrogen. The reaction mixture was kept at reflux for a further 36 hours and then reduced to dryness to give an off-white paste. This was dissolved in minimum water at 70°C and ethanol was added to the point of precipitation. Concentrated HCl (~50 ml) was added, whereupon a cloudy white precipitate was observed. This was stirred for 1 hour and then collected and dried. The solid was recrystallised from a water/ethanol mixture to give a *mono*-sodium salt of H_5**L** in 55% yield. $C_{18}H_{26}N_3Na_1O_{12}$ (H_5**L**.Na): calcd. C, 43.29; H, 5.25; N, 8.41; found: C, 43.24; H, 5.73; N, 8.34. IR (saphire anvil) ν/cm^{-1}: 2959w, 2359m, 2340m, 1729s, 1613s, 1390m, 1326m, 1213s, 1049w, 997w, 959w, 893m, 842m. ^{1}H NMR (400 MHz, D_2O) δ = 3.23 (12H, s), 2.73 (3H, t, J = 10.9), 2.01 (3H, d, J = 11.2), 1.22 (3H, q, J = 11.8). ^{13}C NMR (400 MHz, D_2O) δ = 170.58 (C_q), 59.89 (CH_2), 54.67 (CH), 27.21 (CH_2).

Synthesis of $Na_{12}[Fe_6(O)_3(CO_3)_6(L)_2] \cdot 36\ H_2O$ (1)

A 5ml aqueous solution of H_5**L**.Na (100 mg, 0.199 mmol) was adjusted to pH 7.5 by the addition of saturated sodium hydrogencarbonate solution. Solid iron (III) chloride hexahydrate (54 mg, 0.199 mmol) was added and the mixture was sonicated to produce a clear orange solution. The pH was further raised to 8.5, to give a yellow-green solution. This was allowed to stand for 1 hour after which time it was filtered carefully through glass wool. Green needles of **1** suitable for single crystal x-ray diffraction were obtained in a yield of 35%, by slow diffusion of ethanol into this solution over 8-10 days. $C_{42}H_{72}Fe_6N_6Na_{12}O_{60}$ (Na_{12}**1a** ·$15H_2O$ vacuum dried): calcd. C, 22.60; H, 3.25; N, 3.76; Na, 12.36; found: C, 22.53; H, 3.19; N, 3.72; Na, 11.6. UV/vis (KBr): λ_{max}/nm (Abs) 474 (1.71), 512 (1.52), 632 (1.34). IR (KBr) ν/cm^{-1}: 3314br, 2937w, 2677.68w, 2359m, 1608s, 1479s, 1341s, 1154m, 1068m, 918m, 839m, 722s.

Magnetic susceptibility data for 1

Magnetic susceptibility data for **1** was obtained at 0.1 Tesla using a Quantum Design MPMS-5 SQUID magnetometer (see Figure S1). Susceptibility data were corrected for diamagnetic contributions using χ_{dia}(**1**) = -1.27×10^{-3} emu mol^{-1}. Susceptibility data indicated a presence of 4 % mononuclear Fe(III) complexes. The spin Hamiltonian $\mathbf{H} = -J\mathbf{S}_A \cdot \mathbf{S}_B + \mu_B g(\mathbf{S}_A + \mathbf{S}_B)H$ was used and yields the expression $\chi_{mol}T = (2N_A g^2 \mu_B{}^2/k)(e^x + 5e^{3x} + 14e^{6x} + 30e^{10x} + 55e^{15x})/(1 + 3e^x + 5e^{3x} + 7e^{6x} + 9e^{10x} + 11e^{15x})$ ($x = J/kT$) for $S_A = S_B = 5/2$.

Crystal Structure of 1

The cif file has also been submitted to the CSD database reference code: CCDC 239962