Strict Self-assembly of [Fe(cyclam)]$^{3+}$ and [Hydrogenbis(1,1′-ferrocenedicarboxylate)]$^{3-}$ into a Novel Mixed-valent One-dimensional Polymer containing an Fe^{III}N$_4$O$_2$ Chromophore

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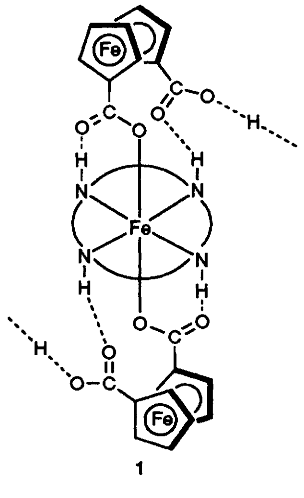
trans-[Fe^{III}(cyclam)][{Fc(CO$_2$)$_2$}$_2$H], **1**, (cyclam = 1,4,8,11-tetraazacyclotetradecane; [Fc(CO$_2$)$_2$]$^{2-}$ = 1,1′-ferrocenedicarboxylate) strictly self-assembles *via* Fe^{III}–carboxylate covalent bonds and hydrogenbiscarboxylate hydrogen bonds to form a one-dimensional polymer that contains the first crystallographically characterized Fe^{III}N$_4$O$_2$ chromopore.

Crystal engineering of solids through strict self-assembly[1] of complementary neutral molecules and/or ions represents an attractive route to molecular materials with novel solid-state properties.[2] Indeed, coordination polymerisation,[3] hydrogen bonding[4] and π–π interactions[5] have all been exploited to engineer one-, two- and three-dimensional crystalline solids with novel structural features. Macrocyclic metal complexes[6] and salts of macrocyclic cations[7] are also capable of directing and sustaining supramolecular structures. Here we report the results of an attempt to prepare the cyclam salt of 1,1′-ferrocenedicarboxylic acid, Fc(CO$_2$H)$_2$, which serendipitously afforded a novel mixed-valence one-dimensional polymer **1** in good yield.

1 was obtained as a mixture of microcrystalline and large black crystals from a 1:3 molar ratio of cyclam and Fc(CO$_2$H)$_2$ reacted in acetonitrile–ethanol in the presence of light and oxygen. Single crystals† suitable for X-ray crystallography were obtained directly from the reaction mixture. An ORTEP view of a portion of the polymeric chain of **1** is shown in Fig. 1 and reveals that the crystal structure of **1** consists of monomeric units of *trans*-[Fe^{III}(cyclam)][{Fc(CO$_2$)$_2$}$_2$H] linked into a one-dimensional polymeric chain in which the symmetrical hydrogenbisdicarboxylate [O$_2$CFcCO$_2$···H···O$_2$CFcCO$_2$; O···O = 2.482(10) Å] moiety is the bridging unit. That the polymer possesses no net charge implies that the iron centre in the cyclam cavity is in a formal +3 oxidation state and that the iron centres in 1,1′-ferrocenedicarboxylic acid units remain in a formal +2 oxidation state. The coordination geometry around the proposed Fe^{II} centres does not show any significant deviation from that of Fc(CO$_2$H)$_2$.[8] The Fe–N and Fe–O(CO) distances in the macrocylic units are 2.014(7) and 1.925(5) Å, respectively. There are no relevant structural studies on Fe^{III}N$_4$O$_2$ coordination complexes available for comparison since Fe^{III}N$_4$X$_2$(X = O, CN) complexes where the equatorial nitrogen donors are part of a saturated ligand system tend to undergo oxidative dehydrogenation.[9] The only octahedral (Fe^{III}N$_6$) saturated macrocyclic amine complex[10] that has been X-ray structurally characterised is that of 6,13-diamino-6,13-dimethyl-1,4,8,11-tetraazacyclotetradecane, L. The complex Fe^{III}L exhibits equatorial Fe–N distances of 1.951(4) and 1.967(5) Å and axial Fe–N distances of 1.985(4) Å. That carboxylate moieties rarely function as monodentate ligands and the chemistry of iron(III) carboxylates is complex[11] mean that the Fe–O(CO) distance observed in **1** is not directly comparable to those in other iron(III) complexes. Fe–O(CO) distances observed in iron(III) complexes vary between 2.200(4) and 1.898(4) Å depending upon their spin state, ligand environment, coordination geometry and coordination mode of the carboxylate group.[12] The room-temperature effective magnetic moment supports the presence of low-spin Fe^{III} centres in **1** (μ = 2.95 μ_B or 1.86 per mole) with no significant interaction between the ferrocenyl and cyclam iron centres. Ferrocene derivatives bearing electron withdrawing groups, such as Fc(CO$_2$H)$_2$ are known to be photolabile.[13] Hence, the formation of **1** presumably involves photo-liberation of free Fe^{II} from 1,1′-ferrocene-



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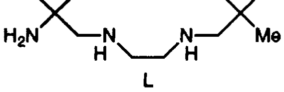

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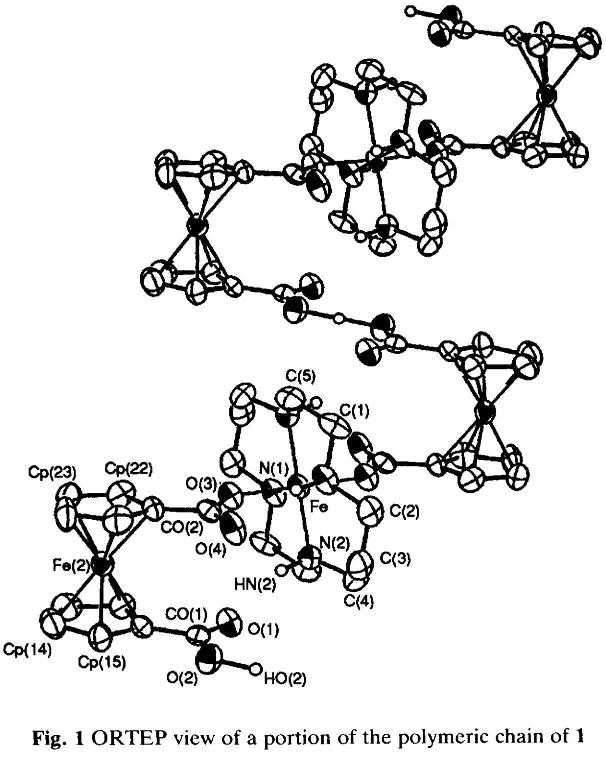

Fig. 1 ORTEP view of a portion of the polymeric chain of **1**

dicarboxylic acid, complexation by cyclam and oxidation to Fe^{III}.[14] Fe^{III} has low affinity for saturated nitrogen donors[15] and requires special conditions[16] or ligand environments for its formation.[10] Though insoluble in most solvents, **1** appears indefinitely stable in the solid state. The absence of oxidative dehydrogenation of cyclam in [Fe(cyclam)]$^{3+}$ may be due to the presence of *trans*-axial carboxylates and the low solubility. carboxylates and the low solubility.

As an organometallic-macrocyclic coordination polymer with mixed-valent iron moieties **1** is unprecedented. However, it is perhaps of greater interest that the cyclam ligand adapts the stable *trans*-III configuration[17] and the hydrogen atoms on the secondary amines are hydrogen bonded to the carbonyl oxygen atoms [N(2)···O(1), 2.830(9) and N(1)···O(4), 2.813(9) Å]. Such anchoring of coordinated ligands through intramolecular hydrogen bonding to redox active metal centres is an important aspect of biological systems[18] and has been proposed in the [Ni(cyclam)]$^{+}$ catalysed electrochemical reduction of CO_2 to CO[19] and the [Fe(cyclam)]$^{2+}$ catalysed epoxidation of olefins.[20] In principle, the hydrogenbis(dicarboxylate) group in **1** can be replaced by any other isofunctional bridging group and any [M(cyclam)]$^{n+}$ complex that would prefer octahedral coordination could be incorporated into the polymer. **1** is therefore a possible prototype for a much wider range of crystal engineered one-dimensional polymers.

We thank the NSERC, Canada, for financial support and Saint Mary's University for provision of the X-ray diffractometer.

Received, 26th July 1994; Com. 4/04598J

Footnote

† *Crystal data*: [Fe(cyclam)][Fe{$C_5H_4(CO_2)_2$}$_2$H]·EtOH, monoclinic, space group $P2_1/n$; a = 12.531(3), b = 11.0230(20), c = 15.333(3) Å, β = 113.322(20)°, U = 1944.8(9) Å^3; Z = 2; D_c = 1.35 Mg m^{-3}; μ = 8.1 cm^{-1}; crystal dimensions: 0.6 × 0.6 × 0.6 mm; 2008 reflections with $I > 2.5\sigma(I)$ converged at R = 0.062 and R_w = 0.066. One disordered ethanol molecule per monomeric unit was located *via* difference Fourier map inspection and refined. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Information for Authors, Issue No. 1.

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