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Synthesis and structural characterisation of the novel iron helicate $[Fe_2(\mu\text{-}L)_4(\mu\text{-}Cl)_2][FeCl_4]_2$ and metalla-macrocycle $[Fe_2(\mu\text{-}L)_2(THF)_4Cl_2][FeCl_4]_2$ {L = *N*,*N*′-di(*n*-butylcarbamoyl)pyridine-2,6-dicarboxamide}

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The reactions of a new disubstituted pyridine with $FeCl_2$ have been studied resulting in the formation of two novel structures: a quadruply-stranded iron helicate and a metalla-macrocycle.

There is great current interest in developing strategies for the synthesis of complex molecular architectures with novel properties. During the last few years supramolecular and coordination chemistry have provided important advances in this direction. By using metal centres and carefully designed ligands a large number of novel architectures such as cages,[1] catenanes,[2] rotaxanes[3] and helicates[4] have been prepared.

As part of our efforts to understand the self-assembly process of metal complexes with functionalised ligands[5] we have recently synthesised a series of molecules with several potential coordinating sites and a *pocket* for supramolecular binding (by H-bonding interactions). Here we report the synthesis of one such ligand, *N*,*N*′-di(*n*-butylcarbamoyl)pyridine-2,6-dicarboxamide (L) (see Fig. 1) and the products resulting from its reaction with iron(II) chloride. Depending on the ligand-to-iron ratio and the solvent used in this reaction the novel quadruply-stranded helicate $[Fe_2(\mu\text{-}L)_4(\mu\text{-}Cl)_2][FeCl_4]_2$ (**1**) and the metalla-macrocycle $[Fe_2(\mu\text{-}L)_2(THF)_4Cl_2][FeCl_4]_2$ (**2**) can be prepared.

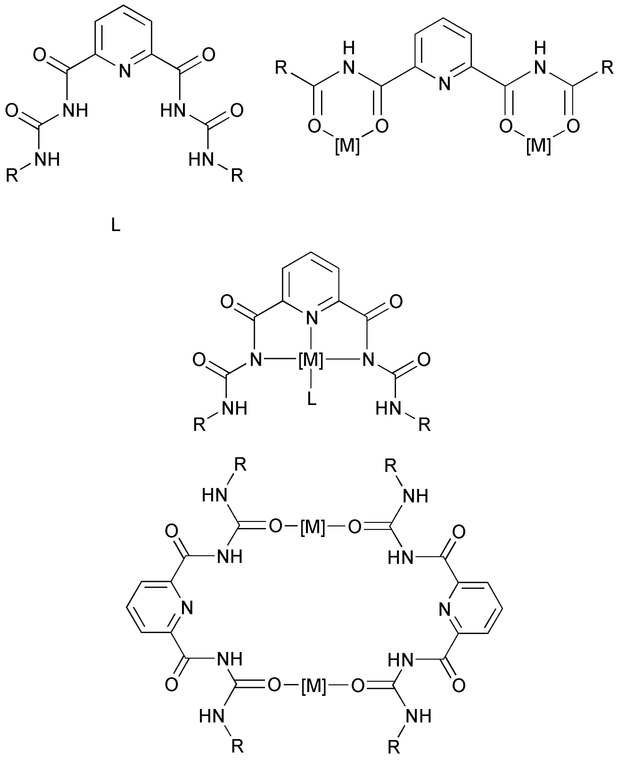

Fig. 1 Schematic representation of ligand L and its potential coordination sites.

Ligand L was prepared by reacting 2,6-pyridinedicarbonyldichloride with a two-fold excess of butylurea in dichloromethane. The resulting product was washed with water and recrystallised from a dichloromethane/diethyl ether mixture giving pure L in 76 % yield. The product was successfully characterised by ^{1}H-NMR, IR, FAB$^+$ mass spectrometry and elemental analyses. † This ligand has several potential coordinating sites and a wide range of potential metal complexes can be envisaged (see some examples in Fig. 1).[6,7] In order to explore some of these possibilities the reactivity of L with $FeCl_2$ was studied and the results obtained are herein reported.

When a CH_2Cl_2 solution containing two equivalents of L was reacted with $FeCl_2$ and $FeCl_3$ (one equivalent of each) for 12 hours a yellow product was isolated and, on the basis of spectroscopic and structural analyses, formulated as $[Fe_2(\mu\text{-}L)_4(\mu\text{-}Cl)_2][FeCl_4]_2$ (**1**). ‡ The role of $FeCl_3$ in this reaction is as a chloride abstractor (consequently forming an iron(II) dimer and $[FeCl_4]^-$ counterions). The IR spectrum of this product shows two clear C=O stretches, one at 1703 cm^{-1} (very close to the stretch observed in the free ligand) and a second one shifted to 1661 cm^{-1}, suggesting an interaction between one of the carbonyl groups and a metal centre. A strong band at 381 cm^{-1} indicates the presence of $[FeCl_4]^-$. FAB$^+$ mass spectrometry suggested the formation of a dimetallic species with at least three ligands (an intense peak at *m*/*z* 1270 consistent with a core formulation of $[Fe_2L_3]^+$ was observed). The unambiguous characterisation of this product as dimer **1** was only possible thanks to a crystallographic study. The X-ray structure determination revealed the complex dication in **1** to comprise four independent L ligands (A, B, C and D) which bridge *via* their urea oxygen atoms between equatorial and axial sites on adjacent Cl_2 bridged Fe^{II} octahedra to create a quadruply-stranded helicate (Fig. 2). Although several doubly and triply-stranded helicates have been reported,[4] quadruply-stranded helical assemblies are still rare.[8] The geometry at each of the two unique iron centres is slightly distorted octahedral with *cis* angles in the range 83.6(2) to 95.8(2)° and *trans* angles between 169.8(2) and 179.4(2)°. The Fe–O distances are unexceptional, ranging between 2.090(6) and 2.139(6) Å, and show no distinct pattern *vis-a-vis* their *cis*/*trans* relationship to the bridging chlorides, which are themselves essentially symmetric [2.493(2) and 2.516(3) Å to Cl(1), and 2.487(2) and 2.500(3) Å to Cl(2)]. The central Fe_2Cl_2 ring is planar to within 0.02 Å, although the two octahedra have their axes inclined by *ca.* 11° to each other. This distortion is possibly a consequence of the adoption by the O,O′ ligand of an essentially planar geometry for the $\{(H)NC(=O)N(H)C(=O)\}_2\text{-}2,6\text{-}C_5H_3N$ portion in all four cases (coplanar to within 0.37, 0.15, 0.22 and 0.26 Å for A, B, C and D respectively) which produces a common "bite" for the pairs of oxygen donor atoms of between 5.81 and 5.91 Å. The planarity adopted by the ligand could, in part, be a con-

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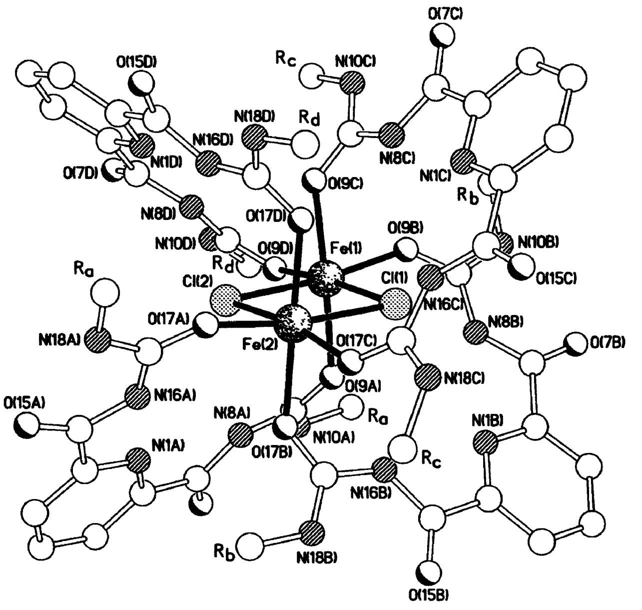

Fig. 2 The molecular structure of the dication in **1**. Selected bond lengths (Å): Fe(1)–Cl(1) 2.493(2), Fe(1)–Cl(2) 2.500(3), Fe(1)–O(9A) 2.127(6), Fe(1)–O(9B) 2.124(7), Fe(1)–O(9C) 2.090(6), Fe(1)–O(9D) 2.097(6), Fe(2)–Cl(1) 2.516(3), Fe(2)–Cl(2) 2.487(2), Fe(2)–O(17A) 2.108(7), Fe(2)–O(17B) 2.139(6), Fe(2)–O(17C) 2.095(6), Fe(2)–O(17D) 2.118(6). The transannular Fe ··· Fe separation is 3.558(2) Å.

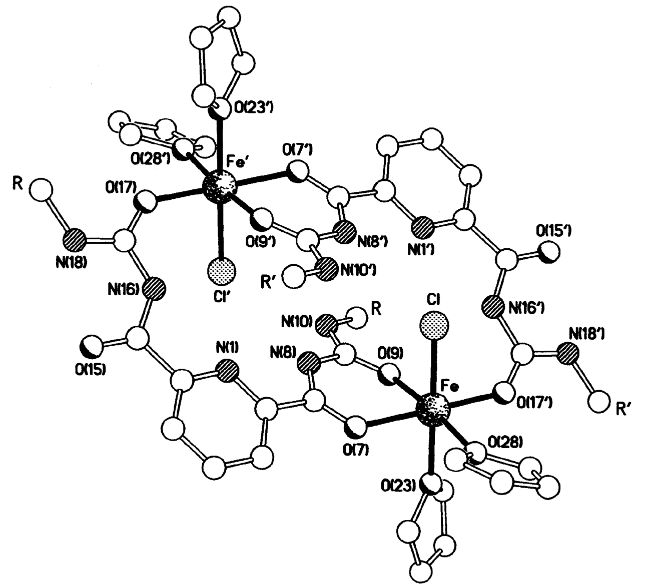

Fig. 3 The molecular structure of the dication in **2**. Selected bond lengths (Å): Fe–Cl 2.461(3), Fe–O(7) 2.105(5), Fe–O(9) 2.092(6), Fe–O(17′) 2.088(6), Fe–O(23) 2.140(6), Fe–O(28) 2.110(6). The transannular Fe ··· Fe separation is 7.716(2) Å.

sequence of intra-ligand N–H ··· N and N–H ··· O interactions and bond delocalisation. The Fe–Cl distances in the anionic fragment of this dimer range between 2.159(4) and 2.187(4) Å which is consistent with the distances previously reported for the $[FeCl_4]^-$ anion.[9] There are no cation ··· anion interactions of note.

After establishing the structure of **1** it was of interest to explore the possibility of preparing a macrocycle (instead of the helix-like structure of **1**) by using a 1 : 1 ratio of ligand to $FeCl_2$. This could potentially generate a metallo-host with H-bonding sites for inclusion of potential guests. When one equivalent of L in THF was reacted with a mixture of $FeCl_2$ and $FeCl_3$ (one equivalent of each) for three hours the new dimer $[Fe_2(\mu\text{-}L)_2(THF)_4Cl_2][FeCl_4]_2$ (**2**) was obtained in high yield.§ The IR spectrum of this yellow–orange crystalline material shows C=O stretches at 1703 and 1663 cm^{-1} and the characteristic band for $[FeCl_4]^-$ at 383 cm^{-1}. The FAB^+ mass spectrum showed an intense peak at *m*/*z* 1051 which was later assigned to a dimeric species $[Fe_2(L)_2(THF)_2Cl_2]^+$. Crystals suitable for X-ray crystallography were obtained from a mixture of THF and hexane.

The single crystal structure determination shows that in **2** the ligand (L) adopts a distinctly different coordination mode than in **1**, being both chelating and binucleating. The ligand utilises adjacent carbonyl oxygen atoms in one arm of the ligand (chelating) and only the urea oxygen atom of the other arm to bridge to an adjacent iron centre (Fig. 3). The complex is centrosymmetric, and the geometry at each iron(II) centre is distorted octahedral having axial Cl and THF ligands, the equatorial sites being occupied by the chelating and bridging L ligand oxygen atoms and the oxygen atom of a second coordinated THF molecule. Compared with **1**, distortions from octahedral geometry are here larger, with *cis* angles in the range 80.8(2) to 95.8(2)°, the most acute angle being associated with the bite of the chelating O,O′ portion of the tridentate ligand. The Fe–O coordination distances are unexceptional, but interestingly the terminal Fe–Cl distance of 2.461(3) Å is only very slightly shorter than those to the bridging chlorides in **1**. In contrast to the planar conformations seen in **1**, here the $\{(H)NC(=O)N(H)C(=O)\}_2\text{-}2,6\text{-}C_5H_3N$ portion of the now tridentate O,O′,O″ ligand adopts a twisted geometry with the two (H)NC(=O)N(H)C(=O) moieties (which are coplanar to within 0.10 Å) being rotated by *ca.* 30° in opposite senses out of the plane of the central pyridyl ring. The six-membered chelate ring is folded about the O(7) ··· O(9) vector such that N(8) lies 0.69 Å out of the equatorial coordination plane (which is coplanar to within 0.06 Å) in the direction of the chloride. Once again the Fe–Cl distances of the anionic fragment of this complex [ranging between 2.182(4) and 2.195(5) Å] are consistent with the distances previously found in the $[FeCl_4]^-$ anion.[9] There are no noteworthy cation ··· anion interactions.

In order to establish the nature of the iron centres the magnetic *momenta* of the complexes were measured using a magnetic susceptibility balance and found to be 10.5 and 10.7 μ_B for **1** and **2** (at 295 K) respectively. Both these values are in good agreement with the calculated value of 10.8 μ_B corresponding to a complex with two high-spin iron(III) centres (S = 5/2) and two high-spin iron(II) centres (S = 2). This is consistent with the assemblies **1** and **2** formed by two $[FeCl_4]^-$ counterions and two Fe(II) centres coordinated to the weak-field ligand L.

In conclusion, we have demonstrated that the new species L is a very versatile ligand which can be used to build a novel quadruply-stranded helicate (**1**) and a metal-containing macrocycle (**2**). We are currently exploring the possibility of using the coordination versatility of this ligand to prepare a wider range of metal-containing assemblies.

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Notes and references

† Selected data for ligand L: yield 2.68 g (76%) (Found: C, 56.11; H, 6.80; N, 19.12. $C_{17}H_{25}N_5O_4$ requires: C, 56.19; H, 6.93; N, 19.27%). ν_{max}/cm^{-1} 3324 (NH), 1693 (vs and broad, CO), 1550 (CN). ^1H-NMR δ_H ($CDCl_3$): 0.9 (t, 6H, $^3J_{HH}$ 7.3), 1.4 (m, 4H), 1.53 (m, 4H), 3.3 (dt, 4H, $^3J_{HH}$ 5.7, $^3J_{HH}$ 6.9), 8.1 (t, 1H, $^3J_{HH}$ 7.8), 8.4 (d, 2H, $^3J_{HH}$ 7.8), 8.5 (t, 2H, $^3J_{HH}$ 5.7 Hz), 10.7 (s, 2H). $FAB\text{-}MS^+$ *m*/*z* 364 $[M + H]^+$.

‡ Selected data for compound **1**: yield 230 mg (79%) (Found: C, 41.18; H, 5.19; N, 13.35. $[C_{68}H_{100}N_{20}O_{16}Cl_2Fe_2][FeCl_4]_2\cdot C_4H_8O$ requires: C, 41.11; H, 5.17; N, 13.32%). ν_{max}/cm^{-1} 3298 (NH), 1703 (CO), 1661 (CO), 1563 (CN), 381 ($FeCl_4^-$). $FAB\text{-}MS^+$: *m*/*z* 1270 $\{[M - L - 2FeCl_4]^+\}$, 907 $\{[M - 2L - 2FeCl_4]^+\}$. μ_{eff} = 10.5 μ_B. Crystal data: $[C_{68}H_{100}N_{20}O_{16}Cl_2Fe_2][FeCl_4]_2\cdot C_4H_8O$, M = 2103.7, triclinic, $P\bar{1}$ (no. 2), a = 15.229(1), b = 17.919(2), c = 19.795(2) Å, α = 74.64(1), β = 72.61(1), γ = 86.63(1)°, V = 4969.8(9) $Å^3$, Z = 2, D_c = 1.406 g cm^{-3}, μ(Mo-Kα) = 0.91 mm^{-1}, T = 293 K, light green prismatic needles; 12793 independent measured reflections, F^2 refinement, R_1 = 0.0688, wR_2 = 0.153,

6824 independent observed reflections [$|F_o| > 4\sigma(|F_o|)$, $2\theta \le 45°$], 1208 parameters. The disorder present in one of the $FeCl_4^-$ was modelled as two overlying orientations whose occupancies (60 : 40) were determined by refinement and then rounded to the nearest 5%.

§ Selected data for compound **2**: yield 188 mg (84%) (Found: C, 34.28; H, 4.75; N, 8.20. $[C_{42}H_{70}N_{10}O_{12}Cl_2Fe_2][FeCl_4]_2$ requires: C, 33.97; H, 4.75; N, 9.43%). ν_{max}/cm^{-1} 3306 (NH), 2960 (C–H), 2934 (C–H), 2873 (C–H), 1703 (CO), 1663 (CO), 1563 (CN), 383 ($FeCl_4^-$). FAB-MS$^+$: *m*/*z* 1051 {[M − 2THF]$^+$}, 945 {[M − 3THF − Cl]$^+$}. $\mu_{eff} = 10.7\ \mu_B$. Crystal data: $[C_{50}H_{82}N_{10}O_{12}Cl_2Fe_2][FeCl_4]_2\cdot 1.5C_4H_8O$, $M = 1701.3$, monoclinic, $P2_1/n$ (no. 14), $a = 10.166(1)$, $b = 18.797(2)$, $c = 22.468(2)$ Å, $\beta = 102.41(1)°$, $V = 4192.9(9)$ Å^3, $Z = 2$ (C_i symmetry), $D_c = 1.348$ g cm^{-3}, μ(Mo-Kα) = 1.05 mm^{-1}, $T = 293$ K, orange–brown prismatic needles; 7278 independent measured reflections, F^2 refinement, $R_1 = 0.074$, $wR_2 = 0.159$, 3037 independent observed absorption corrected reflections [$|F_o| > 4\sigma(|F_o|)$, $2\theta \le 50°$], 482 parameters. The disorder present in one of the *n*-butyl side-arms and the included THF solvent molecules was in each case modelled as two overlying orientations whose occupancies (55 : 45 and 50 : 25 respectively) were determined by refinement and then rounded to the nearest 5%. CCDC reference numbers 172862 and 172863. See http://www.rsc.org/suppdata/dt/b2/b200191h/ for crystallographic data in CIF or other electronic format.

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