A new twist in anion binding: metallo-helicate hosts for anionic guests

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The condensation of 5-chlorocarbonyl-2,2'-bipyridine with a variety of rigid aromatic diamines, L, gave a series of new bisamido-2,2'-bipyridine based ligands (L = 4.4'-methylenediamine, L1; L = 1,1-bis(4aminophenyl)cyclohexane, L2; L = 1,1-bis(4-amino-3,5-dimethylphenyl)cyclohexane, L3) capable of forming dinuclear triple helicate complexes on coordination to Fe(II). The reaction of various Fe(II) salts with L1–L3 gave: {[Fe₂(L1)₃](BF₄)₄, 1; [Fe₂(L1)₃](ClO₄)₄, 2; [Fe₂(L1)₃]Cl₄, 3; [Fe₂(L1)₃](SO₄)₂, 4; [Fe₂(L2)₃](BF₄)₄, **5**; [Fe₂(L2)₃]Cl₄, **6**; [Fe₂(L3)₃](BF₄)₄; **7**; [Fe₂(L3)₃]Cl₄, **8**; and [Fe₂(L3)₃](SO₄)₂, **9**, as determined by UV-Vis, IR and ¹H NMR spectroscopy, electrospray mass spectrometry (ESMS) and elemental analyses. A UV-Vis complexometric titration experiment between L3 and $Fe(BF_{4})_2$ established conclusively a $[Fe_2(L3)_3]^{4+}$ product species. ¹H NMR spectroscopy showed that the complexes exist as both rac-(helical) and meso-(non-helical) isomers in DMSO-d6 solution at 298 K. L1-L3 were designed such that following complexation, six amide hydrogen atoms would line an inter-strand intrahelical cavity of sufficient size to facilitate the binding of guest species within it. Indeed, ESMS studies showed characteristic peaks typical of complex-anion species in solution. Furthermore, ¹H NMR titration experiments showed that anions bind within the intrahelical cavity as titration of 1, 5 and 7 with Bu₄NCl showed significant downfield shifts in the amide and bipyridyl H⁶ proton resonances to yield a species of 1 : 2 host to guest stoichiometry. Moreover, addition of Bu₄NCl to 1, 5 and 7 shifted the rac-/meso-species distribution from 1 : 2 in favour of the meso- to 100% in favour of the rac-isomer, showing that Cl⁻ ions favour the formation of the triple helicate species in DMSO-d6 solution.

Introduction

There is considerable current interest in the development of molecular and supramolecular systems that have the ability to bind, identify, and signal the presence of negatively charged ions.¹ The motivation behind such studies is the recognition that anions enjoy an important role in biology, medicine, and the environment.² In the field of supramolecular chemistry, anion receptors typically rely on hydrogen bonding as the dominant force driving their interaction with anions. Ideally, a number of judiciously placed hydrogen bond donors will maximise binding to a specific anionic species. Numerous studies involving the selfassembly of various metallo-helicates have been conducted over the last 20 years.³ Whilst anions may template their synthesis and in some instances have been structurally identified as being bound by these species,⁴ they have not, to the best of our knowledge, been specifically designed to act as anion receptors. Nevertheless, Rice and co-workers have recently reported dinuclear triple helicate complexes, $[M_2L_3]$, of pyridyl-thiazole ligands appended peripherally with amide functionalities that, upon metal coordination, form 'pockets' capable of binding anions at each end of the helicate.⁵ Similarly, Janiak et al.⁶ and Williams et al.⁷ have observed anion binding behaviour within 'clefts' formed by mononuclear $[FeL_3]^{2+}$ complexes where L is either 5,5'-diamido-2,2'-bipyridine or 5,5'-amino-acido-2,2'-bipyridine functionalised ligands, respectively. Moreover, Beer *et al.* have shown that $[Ru(5,5'-diamido-2,2'-bipyridine)_3]^{2+}$ and related species are capable of binding anions.⁸ However, these systems all employ exo-receptors and, to the best of our knowledge, no metallo-helicate system has employed inter-strand (intrahelical) receptors to specifically bind anions.

Consequently, we designed three new amide-based bisbipyridine ligands, L1–L3, with the intention of forming $[M_2L_3]$ complexes upon their coordination to Fe(II) and, in doing so, generating an inter-strand (intrahelical) cavity of sufficient size to bind anionic guests, Fig. 1. The [M₂L₃] complexes pre-organise six amide groups around a cavity that is reminiscent of the hexa-amide cryptand ligands exploited with great effect in anion binding by Bowman-James et al.9 The amide groups also provide a convenient ¹H NMR spectroscopic handle by which to probe the contents of the cavity. Furthermore, employment of Fe(II) as the template in the formation of $[Fe_2L_3]^{4+}$ complexes introduces a positive charge into the ligand scaffold, increasing the electrostatic contribution to prospective anion binding. Low spin, diamagnetic Fe(II) also provides an effective means of introducing helical chirality into the host molecule without greatly perturbing any ¹H NMR spectroscopic investigations, and serves as a useful UV-Vis marker for complex formation as bipyridine-Fe(II) compounds are intensely coloured. We report here the synthesis of L1-L3 and detail the formation of [Fe2L3]4+ host complexes by UV-Vis, IR and ¹H NMR spectroscopy and ESMS and include details on their ability to bind anionic guests within their cavities.

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Fig. 1 Structure of the ligands **L1–L3** from the current study with the labelling scheme used for ¹H NMR spectroscopy shown on **L1** (top), and a molecular model of a prospective $[Fe_2(L1)_3]^{4+}$ complex showing the six amide hydrogen atoms lining the intrahelical cavity (bottom).

Experimental

Materials and methods

5-Methyl-2,2'-bipyridine was prepared by the traditional Kröhnke procedure from 2-acetylpyridine and methacrolein following an adapted procedure according to Balzani et al.¹⁰ The method of Fletcher et al. was followed in the synthesis of 2,2'-bipyridine-5-carboxylic acid and 5-chlorocarbonyl-2,2'bipyridine was prepared from it in situ following reaction with an excess of thionyl chloride under an Ar atmosphere.¹¹ 1.1-Bis(4-amino-3.5-dimethylphenyl)cyclohexane and 1.1-bis(4aminophenyl)cyclohexane were prepared following the method of Hunter.¹² The syntheses of L1-L3 were performed in dry CH₂Cl₂ solution under an Ar atmosphere. Standard chemicals and solvents were of reagent grade and purchased from Aldrich, Merck, Riedel de Haën, Fluka or local solvent suppliers and used as received. Dichloromethane was dried before use by distillation from calcium hydride. Chemical analyses were performed at the Microanalytical Laboratories, University College Dublin, Ireland. ¹H NMR spectra were acquired on a Bruker DPX 400 machine and referenced to the residual proton shifts in the internal deuterated solvent. UV-Vis spectra were carried out using a Cary 300 UV-Vis spectrophotometer in spectroscopic grade CH₃CN or MeOH operating between 200-800 nm. IR spectra were recorded as KBr pellets on a Mattson Genesis II FTIR in the 4000–400 cm⁻¹ region. Mass spectra were recorded on a Micromass LCT electrospray instrument.

Synthesis of *N*,*N*'-bis(2,2'-bipyridyl-5-yl)carbonyl-4,4'-methylenediamine (L1). A CH₂Cl₂ solution containing 4,4'-methylenediamine (0.093 g, 0.45 mmol) and 0.9 ml triethylamine (6.6 mmol) was added dropwise to a CH₂Cl₂ solution of 5chlorocarbonyl-2,2'-bipyridine (0.2 g, 1.0 mmol) at room temperature. The reaction mixture was heated at reflux for 15 h and filtered to retrieve a brown solid that was washed with CH₂Cl₂ and hot EtOH. Yield 71%. Found C, 67.0; H, 4.3; N, 12.7%. C₃₅H₂₆N₆O₂·CH₂Cl₂ requires C, 66.8; H, 4.4, N, 13.0%. $\delta_{\rm H}$ (400 MHz; DMSO-d6): 3.93 (2H, s, CH₂), 7.25 (4H, d, *J* = 8.2 Hz, H^{8/8'}), 7.52 (2H, ddd, *J* = 7.5, 4.9 and 1.4 Hz, H^{5'}), 7.73 (4H, d, *J* = 8.2 Hz, H^{7/7'}), 8.00 (2H, ddd, *J* = 7.6, 7.5, 1.4 Hz, H^{4'}), 8.50 (6H, m, H^{3/3'/4}), 8.74 (2H, d, *J* = 4.1 Hz, H^{6'}), 9.20 (2H, s, H⁶), 10.51 (2H, s, NH). ν_{max} /cm⁻¹ (KBr): 3333 (br, N–H), 1528 (N–H), 1646 (C=O).

Synthesis of N, N'-bis(2,2'-bipyridyl-5-yl)carbonyl-1,1-bis(4aminophenyl)cyclohexane (L2). L2 was prepared by an analogous procedure to L1 by employing 1,1-bis(4-aminophenyl)cyclohexane (0.121 g, 0.45 mmol) as the diamine precursor and filtered after 15 h reflux. The filtrate was subsequently washed with 20 mL of water (\times 4) and dried over anhydrous MgSO₄. The residue obtained after the removal of solvent under reduced pressure was taken into MeCN, sonicated and filtered to give an off-white powder in 53% yield. Found C, 74.9; H, 5.1; N, 14.3%. C₄₀H₃₄N₆O₂·MeCN requires C, 75.1; H, 5.5; N, 14.6%. $\delta_{\rm H}$ (400 MHz; DMSO-d6): 1.49 (6H, br, cyclohex-H), 2.29 (4H, br, cyclohex-H), 7.33 (4H, d, J = 8.5 Hz, $H^{8/8'}$), 7.53 (2H, ddd, J =7.5, 4.9 and 1.5 Hz, $H^{5'}$), 7.70 (4H, d, J = 8.5 Hz, $H^{7/7'}$), 8.00 (2H, ddd, J = 7.6, 7.5, 1.5 Hz, $H^{4'}$), 8.48 (6H, m, $H^{3/3'/4}$), 8.75 (2H, d, J = 4.5 Hz, H^{6'}), 9.20 (2H, s, H⁶), 10.46 (2H, s, NH). $v_{\text{max}}/\text{cm}^{-1}$ (KBr): 3314 (br, N–H), 1522 (N–H), 1648 (C=O).

Synthesis of N,N'-bis(2,2'-bipyridyl-5-yl)carbonyl-1,1-bis(4amino-3,5-di-methylphenyl)cyclohexane (L3). L3 was prepared by an analogous procedure to L1 by employing 1,1-bis(4-amino-3,5-dimethylphenyl)cyclohexane (0.146 g, 0.45 mmol) as the diamine precursor and filtered after 15 h reflux. The filtrate was subsequently washed with 20 mL water (\times 4) and dried over anhydrous MgSO₄. The residue obtained after the removal of solvent under reduced pressure was recrystallised from MeOH to give a cream crystalline solid in 50% yield. Found C, 75.0; H, 6.2; N, 11.5% C₄₄H₄₂N₆O₂.CH₃OH requires C, 75.2, H, 6.4; N, 11.7%. $\delta_{\rm H}$ (400 MHz; DMSO-d6): 1.50 (6H, br, cyclohex-H), 2.19 (12H, s, Me), 2.30 (4H, br, cyclohex-H), 7.12 (4H, s, H^{8/8'}), 7.53 $(2H, ddd, J = 7.5, 4.5 and 1.5 Hz, H^{5'}), 8.00 (2H, ddd, J = 7.7, 1.5)$ 7.5, 1.5 Hz, $H^{4'}$), 8.50 (6H, m, $H^{3/3'/4}$), 8.75 (2H, d, J = 4.5 Hz, H^{6'}), 9.24 (2H, s, H⁶), 9.92 (2H, s, NH). v_{max}/cm⁻¹ (KBr): 3262 (br, N-H), 1510 (N-H), 1649 (C=O).

Synthesis of $[Fe_2(L1)_3](BF_4)_4$, 1, $[Fe_2(L1)_3](CIO_4)_4$, 2, $[Fe_2(L1)_3]Cl_4$, 3, $[Fe_2(L2)_3](BF_4)_4$, 5 and $[Fe_2(L2)_3]Cl_4$, 6. To a stirred suspension of either L1 (0.1 g, 0.18 mmol) or L2 (0.1 g, 0.16 mmol) in MeOH (80 mL) a methanolic solution of $Fe(X)_2$ ·6H₂O (0.12 mmol) $[X = BF_4^{-1}$ 1 and 5; CIO_4^{-2} ; CI^{-3} and 6] was added dropwise. The resultant deep purple mixture was heated at reflux temperature for 22 h and allowed to cool. A deep purple precipitate was filtered off directly for 1–3, washed with MeOH and ether and recrystallised from MeOH or MeCN. For 5 and 6 the solution was filtered and the deep purple filtrate evaporated to dryness

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under reduced pressure. The residue was dissolved in MeCN from which a purple microcrystalline powder was retrieved by filtration after a few days following the slow diffusion of ether into the MeCN solution.

Analytical data for 1. Yield 51%. Found C, 58.4; H, 3.7; N, 11.7%. [Fe₂(L1)₃](BF₄)₄ requires C, 58.7; H, 3.7; N, 11.7%. $\delta_{\rm H}$ (400 MHz; DMSO-d6): 3.71 (2H, d, J = 14.5 Hz, meso-CH₂), 3.77 (2H, d, J = 14.5 Hz, meso-CH₂), 3.80 (2H, s, rac-CH₂), 7.11 (4H, d, J = 8.5 Hz, rac-H^{8/8}), 7.15 (8H, d, J = 8.5 Hz, meso-H^{8/8'}), 7.41 (4H, d_{obs}, J = 5.5 Hz, meso-H^{5'}), 7.45 (2H, d_{obs}, J = 5.5 Hz, meso-H^{5'}), 7.45 (2H, d_{obs}, J = 5.5 Hz, rac-H^{5'}), 7.53 (4H, d, J = 8.5 Hz, meso-H⁴), 7.58 (14H, m, meso-+ rac-H^{17/7'}, rac-H⁴), 7.86 (2H, s, rac-H⁶), 8.00 (4H, s, meso-H⁶), 8.28 (6H, m, meso- + rac-H^{3'}), 8.69 (4H, d, J = 8.5 Hz, meso-H³), 8.73 (2H, d, J = 8.5 Hz, rac-H³), 9.00 (12H, m, meso- + rac-H^{4'/6'}), 10.67 (2H, s, rac-NH), 10.77 (4H, s, meso-NH). λ_{max}/nm , (MeCN:MeOH): 350 sh (19,556 M⁻¹ cm⁻¹), 546 (6,357 M⁻¹ cm⁻¹). ν_{max}/cm^{-1} (KBr): 3416 (br, N–H), 1539 (N–H), 1656 (C=O), 1055 (br, BF₄⁻). MS (ESI): m/z 449.86 [1 – (4 × BF₄⁻)]⁴⁺.

Analytical data for 2. Yield 46%. Found C, 57.0; H, 3.5; N, 11.3%. [Fe₂(L1)₃](ClO₄)₄·MeOH requires C, 57.1; H, 3.7; N, 11.3%. $\delta_{\rm H}$ (400 MHz; DMSO-d6): 3.73 (2H, d, J = 14.5 Hz, meso-CH₂), 3.76 (2H, d, J = 14.5 Hz, meso-CH₂), 3.81 (2H, s, rac-CH₂), 7.09 (4H, d, J = 8.5 Hz, rac-H^{8/8}'), 7.15 (8H, d, J = 8.5 Hz, meso-H^{8/8}'), 7.43 (4H, d_{obs}, J = 5.5 Hz, meso-H⁵'), 7.45 (2H, d_{obs}, J = 5.5 Hz, meso-H⁵'), 7.45 (2H, d_{obs}, J = 5.5 Hz, rac-H⁵'), 7.55 (4H, d, J = 8.5 Hz, meso-H⁴), 7.60 (14H, m, meso- + rac-H^{17/7}, rac-H⁴), 7.84 (2H, s, rac-H⁶), 8.03 (4H, s, meso-H⁶), 8.26 (6H, m, meso- + rac-H³'), 8.70 (4H, d, J = 8.5 Hz, meso-H⁶), 8.26 (6H, m, d, J = 8.5 Hz, rac-H³), 9.01 (12H, m, meso- + rac-H^{4'/6'}), 10.65 (2H, s, rac-NH), 10.75 (4H, s, meso-NH). λ_{max}/nm , (MeCN:MeOH): 350 sh (19,061 M⁻¹ cm⁻¹), 545 (6,204 M⁻¹ cm⁻¹). ν_{max}/cm^{-1} (KBr): 3409 (br, N–H), 1535 (N–H), 1650 (C=O), 1092 (br, ClO₄⁻), 624 (ClO₄⁻). MS (ESI): m/z 449.50 [**2** – (4 × ClO₄⁻)]⁴⁺.

Analytical data for 3. Yield 61%. Found C, 62.4; H, 4.5; N, 11.8%. [Fe₂(L1)₃]Cl₄·5MeOH requires C, 62.9; H, 4.7; N, 12.0%. $\delta_{\rm H}$ (400 MHz; DMSO-d6): 3.69 (6H, s, *rac*-CH₂), 6.98 (12H, d, J = 8.5 Hz, *rac*-H^{8/8'}), 7.32 (6H, d_{obs}, J = 5.5 Hz, *rac*-H^{5'}), 7.55 (6H, dd_{obs}, J = 5.5, 2.5 Hz, *rac*-H^{4'}), 7.61 (12H, d, J = 8.5 Hz, *rac*-H^{7/7'}), 8.22 (6H, s, *rac*-H⁶), 8.51 (6H, d, J = 7.5 Hz, *rac*-H^{6'}), 8.91 (18H, m, *rac*-H^{3/3'/4}), 11.05 (6H, s, *rac*-NH). $\lambda_{\rm max}/\rm{nm}$, (MeCN:MeOH): 350 sh (19,227 M⁻¹ cm⁻¹), 543 (4,898 M⁻¹ cm⁻¹). $v_{\rm max}/\rm{cm}^{-1}$ (KBr): 3433 (br, N–H), 1533 (N–H), 1670 (C=O). MS (ESI): *m/z* 653.07 [**3**·(MeOH)₄ – (3 × Cl⁻)]³⁺; 934.66 [**3** – (2 × Cl⁻)]²⁺.

Analytical data for 5. Yield 40%. Found C, 61.1; H, 4.1; N, 11.5%. [Fe₂(L2)₃](BF₄)₄·3MeCN requires C, 61.1; H, 4.5; N, 11.8%. $\delta_{\rm H}$ (400 MHz; DMSO-d6): 1.45 (18H, br, cyclohex-H), 2.26 (12H, br, cyclohex-H), 7.20 (4H, d, J = 8.5 Hz, rac-H^{s'}), 7.23 (8H, d, J = 8.5 Hz, meso-H^{8.8'}), 7.44 (4H, d_{obs}, J = 6.5 Hz, meso-H^{s'}), 7.48 (2H, d_{obs}, J = 6.5 Hz, rac-H^{s'}), 7.54 (18H, m, meso- + rac-H^{7/7'/4'}), 7.69 (2H, s, rac-H^{6'}), 7.89 (4H, s, meso-H⁶), 8.30 (6H, m, meso- + rac-H^{3'}), 8.77 (6H, m, meso- + rac-H³), 9.01 (12H, m, meso- + rac-H^{4/6'}), 10.67 (2H, s, rac-NH), 10.77 (4H, s, meso-NH). λ_{max}/nm , (MeOH): 350 sh (24,390 M⁻¹ cm⁻¹), 545 (6,398 M⁻¹ cm⁻¹). ν_{max}/cm^{-1} (KBr): 3434 (br, N–H), 1522 (N–H), 1663 (C=O), 1083 (br, BF₄⁻). MS (ESI): m/z 500.99 [5 – (4 × BF₄⁻)]⁴⁺.

Analytical data for 6. Yield 53%. Found C, 67.0; H, 4.9; N, 13.0%. [Fe₂(L2)₃]Cl₄·3MeCN requires C, 67.5; H, 4.99; N, 13.1%. $\delta_{\rm H}$ (400 MHz; DMSO-d6): 1.41 (18H, br, cyclohex-H), 2.30 (12H, br, cyclohex-H), 7.20 (12H, d, J = 7.5 Hz, rac-H^{8/8'}), 7.35 (6H, m, rac-H^{5'}), 7.54 (18H, d, J = 7.5 Hz, rac-H^{7/7'/4'}), 8.12 (6H, s, rac-H⁶), 8.23 (6H, br, rac-H^{6'}), 8.54 (6H, d, J = 8.5 Hz, rac-H⁴), 8.86 (6H, d_{obs}, J = 7.5 Hz, rac-H^{3'}), 8.90 (6H, d, J = 8.5 Hz, rac-H³), 10.92 (6H, s, rac-NH). $\lambda_{\rm max}/\rm{nm}$, (MeCN): 350 sh (24,217 M⁻¹ cm⁻¹), 544 (4,939 M⁻¹ cm⁻¹). $v_{\rm max}/\rm{cm^{-1}}$ (KBr): 3431 (br, N–H), 1532 (N–H), 1672 (C=O). MS (ESI): m/z 500.93 [6 – (4 × Cl⁻)]⁴⁺, 721.18 [6·(MeOH)₄ – (3 × Cl⁻)]³⁺.

Synthesis of $[Fe_2(L1)_3](SO_4)_2$, 4, and $[Fe_2(L3)_3](SO_4)_2$, 9. An aqueous solution of $FeSO_4 \cdot 6H_2O(0.12 \text{ mmol})$ was added dropwise to a stirred methanolic suspension of L1 (0.1 g, 0.18 mmol) (4) (or solution of L3, 9) and the reaction mixture heated at reflux for 22 h (4), or stirred at room temperature for *ca*. 5 h (9). After allowing the solution to cool, it was filtered and the filtrate evaporated to dryness under reduced pressure. The residue was dissolved in MeOH and a purple powder retrieved by filtration after a few days following the slow diffusion of ether into the MeOH solution.

Analytical data for 4. Yield 42%. Found C, 62.5; H, 4.0; N, 12.0%. [Fe₂(L1)₃](SO₄)₂·2MeOH requires C, 62.5; H, 4.2; N, 12.3%. $\delta_{\rm H}$ (400 MHz; DMSO-d6): 3.69 (2H, d, J = 14.1 Hz, meso-CH₂), 3.74 (2H, d, J = 14.1 Hz, meso-CH₂), 3.77 (2H, s, rac-CH₂), 7.08 (4H, d, J = 8.0 Hz, rac-H^{8/8}'), 7.14 (8H, d, J = 8.0 Hz, meso-H^{8,8}'), 7.38 (4H, d_{obs}, J = 5.0 Hz, meso-H⁵'), 7.41 (2H, d_{obs}, J = 5.0 Hz, meso-H⁴), 7.61 (14H, m, meso- + rac-H^{7/7/4}'), 7.95 (2H, s, rac-H⁶), 8.11 (4H, s, meso-H⁶), 8.28 (6H, m, meso- + rac-H³'), 8.47 (4H, d, J = 8.5 Hz, meso-H³'), 8.53 (2H, d, J = 8.5 Hz, rac-H³), 8.96 (12H, m, meso- + rac-H^{4/6}'), 10.77 (2H, s, rac-NH), 10.89 (4H, s, meso-NH). $\lambda_{\rm max}/{\rm nm}$ (MeOH): 350 sh (12,833 M⁻¹ cm⁻¹), 546 (3,053 M⁻¹ cm⁻¹). $v_{\rm max}/{\rm cm^{-1}}$ (KBr): 3432 (br, N–H), 1535 (N–H), 1664 (C=O), 1132 (br, SO₄^{2–}). MS (ESI): m/z 578.24 [4-(MeOH)₄ – (2 × SO₄^{2–})]⁴⁺.

Analytical data for 9. Yield 26%. Found C, 66.1; H, 5.52; N, 10.0%. [Fe₂(L3)₃](SO₄)₂·2MeOH requires C, 66.3; H, 5.6; N, 10.4%. $\delta_{\rm H}$ (400 MHz; DMSO-d6): signals are broad with many overlapping resonances, which renders the identification and assignment impossible. $\nu_{\rm max}/\rm{cm}^{-1}$ (KBr): 3430 (br, N–H), 1535 (N–H), 1668 (C=O), 1128 (br, SO₄²⁻). MS (ESI): *m/z* 575.06 [9·(MeOH)₄ – (2 × SO₄²⁻)]⁴⁺.

Synthesis of $[Fe_2(L3)_3](BF_4)_4$, 7, and $[Fe_2(L3)_3]Cl_4$, 8. A methanolic solution of $Fe(X)_2$ (0.097 mmol) (X = BF_4^- , 7; Cl⁻, 8) was added dropwise to a stirred methanolic solution of L3 (0.1 g, 0.15 mmol). The solution became deep purple and was allowed to stir at room temperature for *ca*. 5 h. It was then filtered and reduced to dryness. The resulting powder was taken up in dichloromethane and sonicated for 5 min, filtered and washed with dichloromethane.

Analytical data for 7. Yield 51%. Found C, 60.0; H, 5.8, N, 8.8%. [Fe₂(L3)₃](BF₄)₄·10MeOH requires C, 60.1; H, 5.9; N, 8.9%. $\delta_{\rm H}$ (400 MHz; DMSO-d6): signals are broad with many overlapping resonances, which renders the identification and as signment impossible. $\lambda_{\rm max}$ /nm, (MeCN): 350 sh (13,379 M⁻¹ cm⁻¹), 544 (10,099 M⁻¹ cm⁻¹). $\nu_{\rm max}$ /cm⁻¹ (KBr): 3419 (br, N–H), 1523

(N–H), 1655 (C=O), 1059 (br, BF₄⁻). MS (ESI): m/z 542.93 [7- $(4 \times BF_4^-)$]⁴⁺.

Analytical data for 8. Yield 49%. Found C, 66.4; H, 5.9; N, 10.1%; [Fe₂(L3)₃]Cl₄·5MeOH requires C, 66.5; H, 5.9; N, 10.2%. $\delta_{\rm H}$ (400 MHz; DMSO-d6): 1.44 (18H, br, cyclohex-H), 1.78 (36H, s, Me), 2.19 (12H, br, cyclohex-H), 7.12 (12H, d, J = 7.5 Hz, rac-H^{8.8'}), 7.36 (6H, br, rac-H^{5'}), 7.54 (18H, d, J = 7.5 Hz, rac-H^{6'}), 8.45 (6H, s, rac-H^{6'}), 8.95 (18H, br, rac-H^{3/3'/4}), 10.40 (6H, s, rac-NH). $\lambda_{\rm max}$ /nm, (MeOH): 350 sh (13,284 M⁻¹ cm⁻¹), 542 (6,036 M⁻¹ cm⁻¹). $\nu_{\rm max}$ /cm⁻¹ (KBr): 3425 (br, N–H), 1530 (N–H), 1671 (C=O). MS (ESI): *m*/*z* 542.9 [8-(4 × Cl⁻)]⁴⁺, 777.25 [8·(MeOH)₄ – (3 × Cl⁻)]³⁺.

UV-Vis spectrophotometric complexiometric titration of L3 with $Fe(BF_4)_2{\cdot}6H_2O$

Sequential 10 μ L aliquots of a Fe(BF₄)₂·6H₂O stock solution (MeOH, 5.2 × 10⁻⁴ M) were added to a methanolic solution of L3 (5.8 × 10⁻⁵ M) at room temperature and the UV-Vis spectrum recorded after each addition such that no more than 10% additional volume was added in total.

1H NMR titration experiments of 1, 5 and 7 with Bu₄NX (X = Cl⁻, F⁻, Br⁻, HSO₄⁻)

DMSO-d6 solutions of Bu_4NX (0.064 M) were added in 10 µL aliquots to DMSO-d6 solutions of either $[Fe_2(L1)_3](BF_4)_4$, **1**, $[Fe_2(L2)_3](BF_4)_4$, **5** or $[Fe_2(L3)_3](BF_4)_4$, **7**, (5.4 mM) and the ¹H NMR spectrum of the resultant solution recorded. This was repeated until no changes were noted within the spectra.

Molecular mechanics modelling studies

Molecular mechanics calculations on $[Fe_2(L1)_3]^{4+}$ and $[Fe_2(L1)_3Cl_2]^{2+}$ were undertaken with Hyperchem Version 7.52. Molecular mechanics calculations were carried out using MM+ with the Polak–Ribiere algorithm of Hyperchem. The target configuration was arranged roughly by eye and the energy minimised at an RMS gradient of 0.01. Molecular dynamics was also used (simulated heating to 3000 K) to ensure that the true energy minima had been reached. Guided by the ESMS, UV-Vis and ¹H NMR spectroscopic data the modelling studies were limited to dinuclear species of general formula $[Fe_2L_3]^{4+}$ of *rac*- and *meso*-configuration. The lowest energy structures for *rac*- $[Fe_2(L1)_3]^{4+}$ and *rac*- $[Fe_2(L1)_3Cl_2]^{2+}$ minimised to 146.0 and 140.7 kJ mol⁻¹, respectively, and are shown in Fig. 1 and 5, whereas *meso*- $[Fe_2(L1)_3]^{4+}$ minimised to 164.0 kJ mol⁻¹.

Results and discussion

Ligand design strategy, synthesis and characterisation

Armed with the knowledge that flexible polypyridyl ligands readily coordinate to Fe(II) to form multinuclear helicate complexes,¹³ we set about designing new ligand types such that upon the formation of a helicate an intrahelical cavity of sufficient size to bind guest species within it would be formed. A more rigid spacer separating coordination sites would therefore be required to maintain the integrity of the cavity and to prevent the ligand strands from filling the void between them. Furthermore, by incorporating amide functionalities within the ligand strands prospective binding of anions within the cavity would be assisted and easily monitored through ¹H NMR spectroscopy. These design criteria were met by **L1–L3** and molecular modelling studies supported their ability to prospectively form dinuclear $[Fe_2L_3]^{4+}$ complexes potentially capable of accommodating anions within their cavity, Fig. 1. From this modelling study a cavity bound by $[Fe('bipy')_3]$ head groups separated by *ca*. 18.9 Å (Fe–Fe distance) and ligand sides with *ca*. 8.9 Å separation between each central methylene spacers was identified. This compares with *ca*. 11.3 Å M–M separations and *ca*. 7.3 Å methylene–methylene distances in the smaller metallohelicate complexes based on ligands with pyridylimino head groups and diphenylmethane spacers.^{3f,g}

The amide-based ligands L1-L3 were readily synthesised via the condensation of 5-chlorocarbonyl-2,2'-bipyridine with either 4,4'-methylenediamine, L1, 1,1-bis(4-aminophenyl)cyclohexane, L2, or 1,1-bis(4-amino-3,5-dimethylphenyl)cyclohexane, L3, in dichloromethane solution. L1 and L2 were isolated as poorly soluble pale brown and off-white solids, respectively, whereas L3 was isolated as a cream coloured solid which, as a result of its greater substitution, was fully soluble in common laboratory solvents. Each ligand was characterised through elemental analyses, ¹H NMR and IR spectroscopy, which were fully consistent with their proposed structures. Of particular note within the ¹H NMR spectra of L1-L3 are the characteristic singlet resonances due to the amide protons at δ 10.51, 10.46 and 9.92, and H⁶-bipyridine protons at δ 9.20, 9.20 and 9.24, respectively, along with the readily identifiable resonances from the remainder of the ligand backbone, Table 1. The ca. 0.6 ppm shift within the NH resonance on moving from L1 to L3 arises from the increased substitution on the ligand framework and reflects the influence this has upon the basicity of the NH proton. Similarly, within the IR spectra of L1-L3 broad amide N-H stretches are evident between ca. 3200-3400 cm⁻¹ along with the amide C=O stretch at *ca*. 1650 cm⁻¹.

[Fe₂(L)₃]⁴⁺ host complex formation and characterisation

The formation of the $[Fe_2L_3]^{4+}$ host complexes **1–9** was straightforward and simply involved the treatment of aqueous or methanolic solutions of the appropriate Fe(II) salt with either a methanolic suspension of **L1** or **L2** or solution of **L3**. Deep purple coloured solids were obtained in each case following work-up and fully characterised by elemental analyses, ESMS, IR, UV-Vis and ¹H NMR spectroscopy. The elemental data are consistent with the

Table 1	Selected	¹ H NMR	data for	L1-L3 an	id 1–6 and 84
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Ligand/Complex	$\delta~\mathrm{H^6}~(rac\text{-}/meso\text{-})$	δ NH (rac-/meso-)	
L1	9.20	10.51	
$[Fe_2(L1)_3](BF_4)_4$ 1	(7.86/8.00)	(10.67/10.77)	
$[Fe_2(L1)_3](ClO_4)_4$ 2	(7.84/8.03)	(10.65/10.75)	
$[Fe_2(L1)_3]Cl_4$ 3	8.22	11.05	
$[Fe_2(L1)_3](SO_4)_2$ 4	(7.95/8.11)	(10.77/10.89)	
L2	9.20	10.46	
$[Fe_2(L2)_3](BF_4)_4$ 5	(7.69/7.89)	(10.67/10.77)	
$[Fe_2(L2)_3]Cl_4 6$	8.12	10.92	
L3	9.24	9.92	
$[Fe_{2}(L_{3})_{2}]Cl_{4} 8$	8.45	10.40	

formation of dinuclear species of general formula [Fe₂L₃]⁴⁺ and this composition was further confirmed by ESMS. Indeed, ESMS of each complex apart from 3 displayed peaks characteristic of $[Fe_2L_3]^{4+}$ ions in solution with those of 4 and 9 also indicating the association of four MeOH molecules with these ions. Interestingly, the chloride containing complexes 3, 6 and 8 show peaks attributable to ${[Fe_2L_3Cl] \cdot MeOH_4}^{3+}$ ions, with **3** also displaying peaks for $[Fe_2(L1)_3Cl_2]^{2+}$ ions in solution. This observation is consistent with the chloride ion being more tightly associated with the complex ions and possibly indicates that they are encapsulated within the inter-strand cavity under these conditions. ESMS did not show peaks attributable to more highly charged species that might be associated with $[Fe_4L_6]^{8+}$ or related complexes being present in solution, or the presence of other compounds (e.g. circular helicates) with variable $\{M_x : L_y\}^{n+}$ stoichiometry. Unfortunately, all attempts to grow single crystals suitable for X-ray diffraction studies only yielded small, weakly diffracting crystals from which no workable data could be obtained.

UV-Vis spectroscopy of 1–9

Deep purple coloured solutions were obtained on reacting L1– L3 with Fe(II) solutions in 3 : 2 stoichiometry, whose UV-Vis spectra are dominated by three characteristic bands at *ca*. 300, 350 and 540 nm, indicative of the formation of *tris*-(2,2'-bipy)Fe(II) type complexes.¹⁴ The former band may be assigned to the π -- π^* transitions of the 2,2'-bipy moieties, whilst the latter two are characteristic of [Fe(2,2'-bipy)₃]²⁺ complexes and are due to MLCT from the 3d atomic orbital to the two lowest vacant π^* molecular orbitals of the ligand. The peak at 540 nm is red-shifted compared to that of [Fe(2,2'-bipy)₃]²⁺ (500 nm)¹⁴ due to the electron withdrawing nature of the amide group.

To better ascertain the nature of the species in solution, we undertook a complexometric titration study to follow the course of complex formation,¹⁵ tracking any changes that occurred *via* UV-Vis spectroscopy. Solutions of L3 were employed for the titration due to the poor solubility of L1 and L2 at appropriate concentrations. To this end, sequential addition of a $Fe(BF_4)_2$ stock solution to L3 resulted in the growth of two new bands at

350 (sh) and 540 nm, the red-shift of the 290 nm band to 300 nm and the hypochromic red-shift of the 242 nm band to 247 nm due to the formation of the complex species, Fig. 2. The presence of three well defined isosbestic points at 230, 256 and 296 nm suggests the presence of two predominant absorbing species in solution, the uncoordinated ligand and complex species. By plotting the growth of the 543 nm band as function of the [Fe(II)] : [L3] concentration (Fig. 2, inset), it is clear that no further change in the intensity of this band occurs following the addition of ~0.67 equivalents of Fe(II), consistent with the formation of a [Fe₂(L3)₃]⁴⁺ species in solution.

¹H NMR spectroscopy of 1–9

We can anticipate three species being present in solution for $[Fe_2L_3]$ complexes: the *rac*-isomers, Λ,Λ and Δ,Δ , in which both complex units possess the same configuration and give rise to triple helicate structures, or the corresponding *meso*-form, Λ,Δ , where each complex unit has opposite configuration (*meso*-cate).¹⁶ The ¹H NMR spectra for **1–6** and **8** are well resolved whereas those for **7** and **9**, which incorporate the bulky **L3** ligand, are broadened possibly indicating the presence of some fluxional behaviour.¹⁷ Each resonance within **1–9** has shifted to some degree in comparison to those of the free ligands consistent with Fe(II) coordination, Table 1.

The spectra of complexes incorporating L1 are particularly informative as the CH₂ protons of the spacer permit easier assignment of the resonances to either of the *rac-* or *meso*isomers. For the *rac-*form these protons are equivalent and a single resonance is observed whereas in the *meso-*form they are diastereotopic and give rise to two doublets. A mixture of the *rac-* and *meso-*isomers with an approximate 1 : 2 abundance is clearly evident within the spectra of 1, 2 and 4 with a singlet resonance at *ca.* 3.80 ppm (*rac-*) and two doublets at *ca.* 3.70 and 3.77 ppm, respectively. This mixture of isomers is also evident in the other resonances of the ligand backbone and particularly so in the amide-NH and bipyridine proton H⁶, as they too clearly split with 1 : 2 abundance, Fig. 3. Complex 5, which incorporates the cyclohexane substituted ligand L2, also displays the *rac/meso*



Fig. 2 UV-Vis spectra resulting from the titration of L3 with Fe(BF₄)₂·6H₂O in MeOH. The inset shows the change in the absorption band at $\lambda = 543$ nm as a function of Fe(II) : L3 concentration.



Fig. 3 ¹H NMR spectra of **L1** (bottom), $[Fe_2(L1)_3](BF_4)_4$, **1** (middle), and **1** following the titration of five equivalents NBu₄Cl (top) in DMSO-d6. For the sake of clarity only the *meso-* and *rac-*NH resonances are labelled on the spectra of **1**. Note the 1 : 2 abundance of the *rac-* and *meso-* isomers within the spectrum of **1**. Dashed lines track changes in NH and H⁶ resonances.

mix of isomers in 1 : 2 proportion under these conditions. It is interesting to note that each of these complexes, 1, 2, 4 and 5, contain counteranions with tetrahedral geometry, BF_4^- (1 and 5), CIO_4^- (2) and SO_4^{2-} (4), suggesting that anion geometry might play a role in determining which species, *rac-* or *meso-*, predominates in solution.

This latter observation is in marked contrast to the situation in 3, 6 and 8, which contain the spherical Cl^{-} as the counteranion. The spectra for these complexes are consistent with the sole presence of the rac-isomer in solution i.e. 100% triple helicate. This dramatic effect is seen across the ligand series, 3 (L1), 6 (L2) and 8 (L3), but is particularly striking for complex 8 as the spectra for the related complexes 7 and 9, which contain L3 but BF_4^- and SO_4^{2-} counteranions, respectively, are broad and featureless indicative of some underlying fluxional process. We suggest that the Cl⁻ ions are bound within the intrahelical cavity and interact more strongly with the amide and bipyridyl H⁶ protons through hydrogen bonding than the other anions. These interactions favour the formation of the helicate species, as they possibly optimise the hydrogen bonding between them, and 'lock' the complexes into this conformation.18 This is fully consistent with the observation that the resonances for these protons in 3, 6 and 8 are further downfield, indicative of stronger hydrogen bonding than the corresponding resonances for the rac-isomers in 1, 2, 4 and 5, Table 1. This is also supported by the ESMS data for 3, 6 and 8 which showed peaks assignable to complex species containing Cl⁻ ions, perhaps indicating that they are trapped within the intrahelical cavity.

Titration of 1, 5 and 7 with anions as followed by ¹H NMR spectroscopy

The ability of hosts 1, 5 and 7 to bind anions was investigated by monitoring the changes in the ¹H NMR spectra of DMSO-d6 solutions of each host upon addition of F^- , Cl^- , Br^- and HSO_4^- (as their tetrabutylammonium salts).¹⁹ These hosts were chosen for the titration study for solubility reasons and because ESMS and ¹H NMR data suggest that the BF₄⁻ counteranions are only weakly interacting with the host molecule.²⁰ The addition of Br- or HSO₄to 1, 5 or 7 afforded only minor changes in the ¹H NMR spectra and we concluded that very weak, if any, binding of these anions occurred. The addition of F⁻ produced slight downfield shifts (ca. 0.03 ppm) within the amide proton resonance but after about 1.5 equivalents the signals broadened considerably. We have seen similar effects within naphthalimide based anion sensors, which is often accompanied by deprotonation of the amide.^{1g,j} Subsequent additions of F- caused further broadening in all resonances until such time that the solution changed in colour from purple to orange consistent with complex decomposition.²¹ The addition of Cl⁻, however, produced significant changes within the spectra, Fig. 3. The amide and bipyridyl H⁶ proton resonances gradually shifted downfield by ca. 0.30 and 0.25 ppm, respectively, indicative of hydrogen bonding of the anion to the receptor. Furthermore, peaks attributable to the presence of both the rac- and mesoisomers within the receptor species coalesce to yield only the racisomer in solution, Fig. 3.

Several conclusions may be drawn from this titration study: (i) the free ligand L3 (and presumably L1 and L2) only interacts very weakly with any anion;19 (ii) of the anions tested, only the spherical Cl- ion elicited a significant response suggesting that the host molecules are selective for this ion; (iii) both the amide and bipyridyl H⁶ protons are equally affected by the presence of Cl⁻ ions suggesting that they are buried deep within the pocket created by the ligand strands; (iv) by plotting the change in shift of the NH and bipyridyl H⁶ proton resonances for meso-1 as a function of added Cl-, it is evident that after the addition of around two equivalents of Cl- ion no further major changes occur which is consistent with strong binding and the formation of a 1:2 host-toguest complex, Fig. 4; (v) addition of Cl⁻ ions causes the complexes to adopt the helical conformation, which is consistent with that observed within the ¹H NMR spectra of the 'legitimate' chloride complexes 3, 6 and 8.



Fig. 4 Changes in the chemical shift of the amide NH and bipyridine H⁶ protons within *meso-***1** upon addition of NBu₄Cl in DMSO-d6.

Conclusion

We have successfully designed and synthesised three new bisamido-2,2'-bipyridine ligands L1–L3 and shown them to be capable of forming dinuclear triple helicate $[Fe_2L_3]^{4+}$ complexes, 1–9, on coordination to Fe(II). ¹H NMR spectroscopy showed that the complexes exist as both *rac*-(helical) and *meso*-(nonhelical) isomers in DMSO-d6 solution at 298 K, although in the presence of Cl⁻ ions the *rac*-isomer is favoured. Coordination of L1–L3 to Fe(II) was such that six amide hydrogen atoms were preorganised to line an intrahelical cavity of sufficient size to enable the accommodation of guest species within it. Indeed, ¹H NMR titration experiments demonstrated that Cl⁻ anions bind within the intrahelical cavity as titration of 1, 5 and 7 with Bu₄NCl showed significant downfield shifts in the amide and bipyridyl H⁶ proton resonances to yield a species of 1 : 2 host-to-guest stoichiometry.

Based on these observations we can propose a likely structure for the 1 : 2 host-to-guest complex formed following the addition of Cl⁻ ions to 1, 5 and 7. It is clearly a helical complex in which two Cl⁻ ions bind within an intrahelical cavity through hydrogen bonding with the amide and bipyridyl H⁶ protons. Molecular modelling followed by geometry optimisation gave the structure as shown in Fig. 5, which is consistent with these conclusions. We believe this to be the first report detailing the synthesis of metallo-helicate complexes designed specifically to bind anions within an intrahelical cavity. We are currently extending this work to incorporate other metal ions in conjunction with L1–L3 to see whether these species might act as potential luminescent or redox



Fig. 5 Molecular model of the triple helical $[Fe_2(L1)_3(Cl)_2]^{2+}$ complex showing the proposed mode of binding of two chloride ions shown in space-filling mode within the intrahelical cavity.

sensors for anions. We will report the results of this work when they come to hand.

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- 17 The origin of this fluxional behaviour may lie with the rate associated with the *rac-/meso*-interconversion in the complexes containing the more bulky ligand L3. It may also lie with ligand dissociation and solvolysis combined with the effects of associated Fe(II) spin-state equilibria experienced by the products that arise from dissociation and solvolysis. The presence of Cl⁻ ions clearly suppresses these phenomena. See also ref. 21.
- 18 A similar effect was noted by Raymond and co-workers^{16a} when working with metallo-helicate complexes of bishydroxypyridinone

ligands. They showed that the helicate–mesocate equilibrium in $[Al_2L_3]$ complexes could be shifted in favour of the helicate when a solvent molecule (H₂O) is contained within the intrahelical cavity and interacts with the host through hydrogen bonding.

- 19 To test whether the amide group within this ligand framework was itself capable of interacting with anions, we first undertook a ¹H NMR titration study of L3 with Bu₄NCl. L3 was chosen, as it was sufficiently soluble at relevant concentrations compared to L1 and L2. The sequential addition of Bu₄NCl to L3 in DMSO-d6 solution of up to six equivalents resulted in the very slight gradual downfield shift of the amide proton resonance by *ca*. 0.03 ppm consistent with very weak, if any, binding of the Cl⁻ ion with the amide.
- 20 If the anions are to interact with the host molecules **1**, **5** and **7** then they must successfully compete with BF_4^- , although we conclude that it is only very weakly interacting with the host molecules in the first place. Irrespective of this, the anions F^- , CI^- , Br^- and HSO_4^- are better hydrogen bond acceptors than BF_4^- and we would anticipate them to successfully displace it from the cavity if it were there.
- 21 It should be noted, however, that of the anions tested only Fcaused this colour change and response. Given the stability associated with [Fe(bipy)₃]²⁺ complexes this observation was initially surprising. However, solvolyses of [Fe(bipy)₃]²⁺ complexes readily occurs in nonaqueous solvents such as DMF and DMSO as employed here (see, A. M. Josceanu and P. Moore, J. Chem. Soc., Dalton Trans., 1998, 369). The colour changes most probably arise from a combination of ligand deprotonation, ligand dissociation, solvolysis and subsequent generation of intermediate solvated species followed by F- coordination to the Fe(II) centre which may be accompanied by oxidation to Fe(III). Indeed, treating DMSO solutions of [Fe(bipy)₃]²⁺ with a five-fold excess of Bu₄NF leads to solution discolouration similar to that observed here. The [Fe(bipy)₃]²⁺ solution was unaffected upon the addition of the other anions tested (*i. e.* Bu_4NX where $X = Cl^-$, Br^- and HSO_4^-). To the best of our knowledge this observation is without precedent in the literature and will be the subject of further investigation.