DALTON
FULL PAPER

Synthesis of two covalently linked bis(2,2′:6′,2″-terpyridine) (terpy) chelating ligands with different length spacers, comparison of the crystal structures of their mononuclear nickel(II) complexes, and kinetic and mechanistic studies of the reaction of one ligand with $[Fe(terpy)_2]^{2+}$

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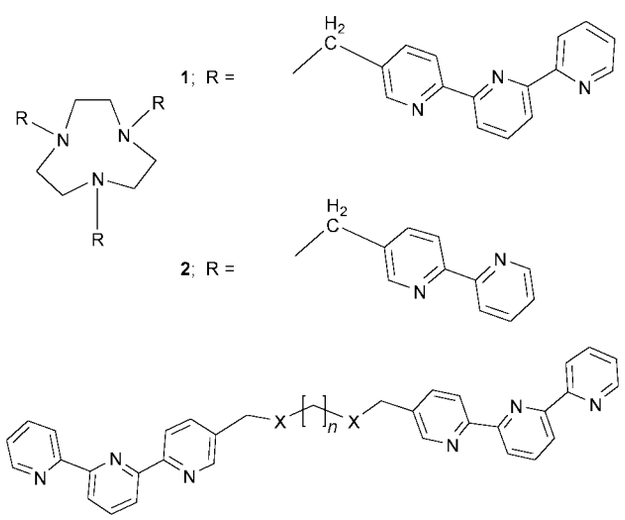
Two new covalently linked bis(2,2′:6′,2″-terpyridine)-chelating hexadentate ligands, 1,3-bis(2,2′:6′,2″-terpyridyl-5-ylmethylsulfanyl)propane (L^1), and 1,4-bis(2,2′:6′,2″-terpyridyl-5-ylmethylsulfanyl)butane (L^2), and their six-coordinate mononuclear metal complexes $[ML][PF_6]_2$ (M = Fe and Ni; L = L^1 and L^2) have been prepared and characterised. The X-ray structures of $[NiL](PF_6)_2$ (L = L^1 and L^2) have been compared to establish that L^2 has the optimum length of linker to give the least strained mononuclear complex. The marked stability of $[ML]^{2+}$ is demonstrated by kinetic studies that show that one equivalent of L^1 is capable of substituting both 2,2′:6′,2″-terpyridine (terpy) ligands of $[Fe(terpy)_2]^{2+}$ to give $[FeL^1]^{2+}$ in a two stage kinetic process.

There is considerable current interest in the co-ordination and supramolecular chemistry of 2,2′:6′,2″-terpyridine and its derivatives.[1–4] Recently we reported the reaction of 5-bromomethyl-2,2′:6′,2″-terpyridine (three equivalents) with 1,4,7-triazacyclononane (1 equivalent), in the presence of triethylamine, to give the potentially nonadentate ligand tris(2,2′:6′,2″-terpyridyl-5-ylmethyl)-1,4,7-triazacyclononane, **1**, that is suitable for co-ordination to large metal ions that prefer a high co-ordination number.[5,6] For example, **1** was found to give a europium(III) complex $[Eu(\mathbf{1})H](PF_6)_4$ that is highly luminescent in acetonitrile solution, and which is consistent with co-ordination of all nine *N*-atoms of the three pendent terpyridyl groups. Earlier we showed that an analogous tris(2,2′-bipyridyl-5-yl-methyl)-derivative of 1,4,7-triazacyclononane, **2**, is capable of forming M(II) complexes of the type $[M(\mathbf{2})H]^{3+}$ (M = Fe, Co, Ni, Cu, Zn, Ru) in which all three pendent bipyridine groups co-ordinate simultaneously, and without significant distortion of the ligand or of the octahedral complexes that form.[5,7] The considerable extra donor strength of **2** in $[Fe(\mathbf{2})]^{2+}$ compared with bipy in $[Fe(bipy)_3]^{2+}$ (bipy = 2,2′-bipyridine) was demonstrated recently by means of a detailed kinetic and mechanistic investigation.[8]

In a search for even more powerful ligands, in this study we used molecular modelling to explore the ease of co-ordination to iron(II) of covalently linked bis(2,2′:6′,2″-terpyridine) ligands of type **3** [*n* = 2–4; X = O, S, NR (R = H, Me)]. Based on the predictions from molecular modelling, ligands **3** (*n* = 3,4; X = S) were prepared, and the complexes they form with nickel(II) and iron(II) investigated.



3; X = S; L^1, *n* = 3; L^2, *n* = 4

Results and discussion

Molecular modelling of $[Fe(\mathbf{3})]^{2+}$ was carried out using both molecular mechanics (MM+) and molecular dynamics as described previously.[9] At the start of the modelling, the two terpyridine groups of **3** were placed in their normal meridional positions about the iron. The results of the modelling calculations clearly demonstrated that the short link (*n* = 2) ligand would only form a mononuclear bis(2,2′:6′,2″-terpyridine) complex by significant bowing of the normally planar terpyridine groups, and with some distortion of the normally regular octahedral geometry of the complex. However, the ligands with the longer (*n* = 3, 4) carbon chains were found to be suitable. They gave complexes in which each of the two terpyridines were nearly planar, and with the planes of the two terpyridine groups at angles of *ca.* 85° (*n* = 3) and 89° (*n* = 4) to each other, that is very close to the idealised angle of 90°. The point of attachment of the linking groups to the terpyridine was also investigated by molecular modelling. Both the 4- and 5-linked positions were found to be suitable, with the latter giving the slightly lower strain energy. Linking at the 6-position was found to be unsuitable for mononuclear complexation.

Ligands **3** with X = S were chosen for study so as to avoid complications from protonation of the anchoring X atoms (as found for **1** and **2**),[6,7] and because thiolates are very good nucleophiles for the synthetic route shown in Scheme 1. The new ligands L^1 (*n* = 3) and L^2 (*n* = 4) were obtained in good

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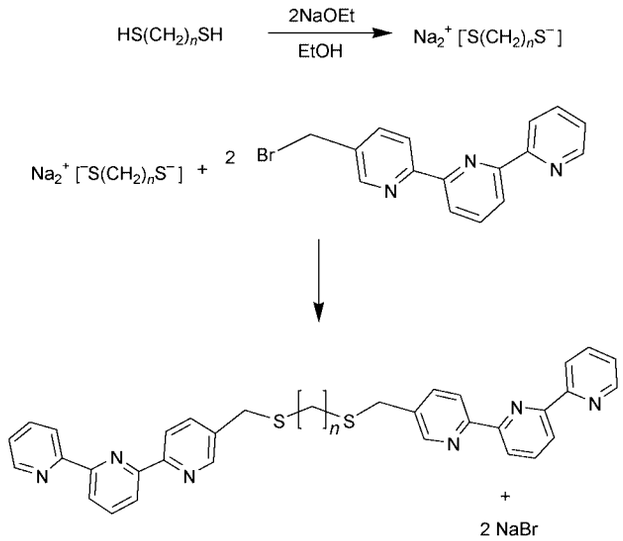


3 (n = 3,4)

Scheme 1

yield and characterised by proton and ^{13}C NMR, mass spectra and elemental analyses. Methanolic solutions of each ligand were reacted in a 1:1 molar ratio with either Ni(II) or Fe(II), and complexes of the type $[ML](PF_6)_2$ isolated in good yield (M = Ni, Fe; L = L^1, L^2) by addition of an excess of a strong solution of NH_4PF_6.

For ligands of type **3** it was anticipated that two modes of co-ordination might occur. Either both terpyridine arms would co-ordinate to a single metal to give a mononuclear complex, or the two terpyridines would bind to different metals to give di- or poly-nuclear species analogous to those reported previously.[2] Formation of polynuclear complexes is expected to be more likely as the length (n) of the linking carbon chain increases. The ^1H and ^{13}C NMR spectra of the diamagnetic, purple and inert $[FeL^1]^{2+}$, where the ligand has the shorter linking chain length, showed that the symmetry observed for the free ligand is maintained on co-ordination, with three aliphatic and 15 aromatic carbon resonances present. This is as expected for a mononuclear rather than either a dimeric or polynuclear complex, and there is no evidence for the formation of any species of higher nuclearity in this case. However, although the analogous NMR spectra of $[FeL^2]^{2+}$ also showed that a mononuclear complex is dominantly formed, additional resonances close to those of the major species indicated that small amounts (5–10% based on NMR integrals) of as yet unidentified oligomeric species are also produced in this case. The FAB mass spectra of the recrystallised major products showed parent ions at m/z values corresponding to $\{[ML]PF_6\}^+$ (L = L^1, L^2; M = Fe, Ni), which also confirmed that mononuclear complexes are formed.

To establish the co-ordination modes conclusively, and to investigate the degree of distortion in the complexes, crystals of $[NiL](PF_6)_2$ (L = L^1 and L^2) suitable for X-ray analysis were grown by slow diffusion of diethyl ether vapour into an acetonitrile solution of each complex. The structures of the cations are shown in Figs. 1 and 2, and establish that both ligands form a mononuclear complex, with minimal distortion of the octahedral geometry about the nickel. The Ni–N bond distances (Tables 1 and 2) are very similar to those reported for $[Ni(terpy)_2]^{2+}$ ion (Ni–N(terminal) av. 2.12 and Ni–N(central) av. 2.01 Å), as are the average *trans* N–Ni–N bond angles of 156.9° (terminal *N*) and 175.9° (central N).[10]

Visible spectra of $[FeL]^{2+}$ (L = L^1, L^2) are very similar to that of $[Fe(terpy)_2]^{2+}$ as expected (λ_{max} in the range 552–553 nm for all three complexes), but there is a small but sufficient difference in the UV spectra (ligand bands; Fig. 3) which enabled the kinetics and mechanism of reaction (1) to be examined spectrophotometrically.

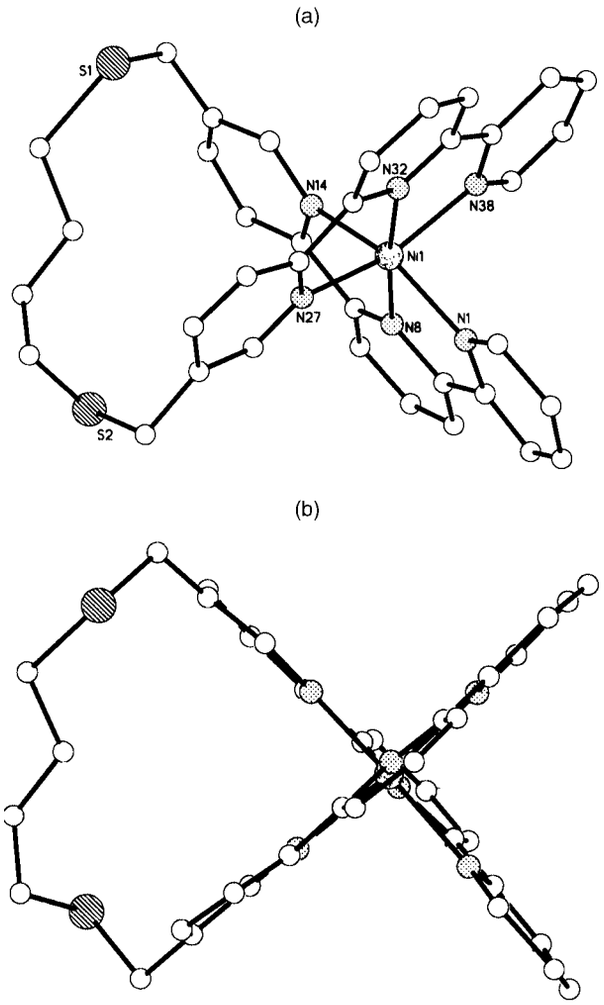


Fig. 1 Two views of $[NiL^2]^{2+}$ ion. In (b) the terpyridines are shown to be almost planar, and the angle between the two mean terpyridine planes is *ca*. 89°.

$$[Fe(terpy)_2]^{2+} + L^1 \underset{k_a}{\overset{k_f}{\rightleftharpoons}} [FeL^1]^{2+} + 2(terpy) \qquad (1)$$

Equimolar amounts of $[Fe(terpy)_2]^{2+}$ and L^1 (5×10^{-5} mol dm^{-3}) in acetonitrile solution were placed in a tightly stoppered 1 cm pathlength quartz cuvette, in the thermostatted cell holder of a Jasco spectrophotometer set at 48.4 °C. Spectra were recorded between 290 and 650 nm every 20 minutes for 17 h until reaction (1) is complete. The observation of the kinetics of this reaction (Fig. 4) demonstrates the extra donor strength of L^1 compared with two moles of 2,2′:6′,2″-terpyridine (terpy), which is as expected on the basis of the chelate effect. During the first 2–3 h reaction (1) is first-order, and proceeds with isosbestic points at 293 and 326 nm. At longer times the initially observed isosbestic points are no longer maintained, and are observed to drift slowly to longer wavelengths. The multiwavelength absorbance–time data were fitted to a consecutive first-order equation,[11] and gave rate constants at 48.4 °C of $(3.4 \pm 0.1) \times 10^{-2}$ and $(5.9 \pm 0.1) \times 10^{-3}$ min^{-1}. This is consistent with the mechanism shown in eqn. (2)–(4):

$$[Fe(terpy)_2]^{2+} \xrightarrow{k_1} [Fe(terpy)]^{2+} + terpy \qquad (2)$$

$$[Fe(terpy)]^{2+} + L^1 \xrightarrow{rapid} [Fe(terpy)L^1]^{2+} \qquad (3)$$

$$[Fe(terpy)L^1]^{2+} \xrightarrow{k_2} [FeL^1]^{2+} + terpy \qquad (4)$$

Table 1 Selected bond lengths (Å) and angles (°) for $[NiL^2]^{2+}$

Ni1–N14	2.089(10)	Ni1–N27	2.137(9)	Ni1–N32	1.969(10)
Ni1–N8	2.005(12)	Ni1–N38	2.099(10)	Ni1–N1	2.114(10)
N14–Ni1–N1	155.0(5)	N27–Ni1–N38	157.2(5)	N32–Ni1–N8	174.0(2)
N14–Ni1–N27	91.91(17)	N1–Ni1–N27	93.1(4)	N1–Ni1–N38	92.22(18)
N14–Ni1–N38	92.6(4)	N32–Ni1–N14	106.1(4)	N32–Ni1–N38	78.9(4)
N32–Ni1–N1	98.9(4)	N32–Ni1–N27	78.4(4)		

Table 2 Selected bond lengths (Å) and angles (°) for $[NiL^1]^{2+}$

Ni1–N14	2.103(2)	Ni1–N8	2.003(2)	Ni1–N1	2.112(2)
N14–Ni1–N1	155.19(7)	N8–Ni1–N8A	171.60(10)	N8A–Ni1–N14	108.42(7)
N14–Ni1–N8	77.79(7)	N8–Ni1–N1A	96.24(7)	N8–Ni1–N1	77.95(7)
N1A–Ni1–N1	93.88(9)	N14A–Ni1–N14	88.90(10)	N14–Ni1–N1A	93.85(7)

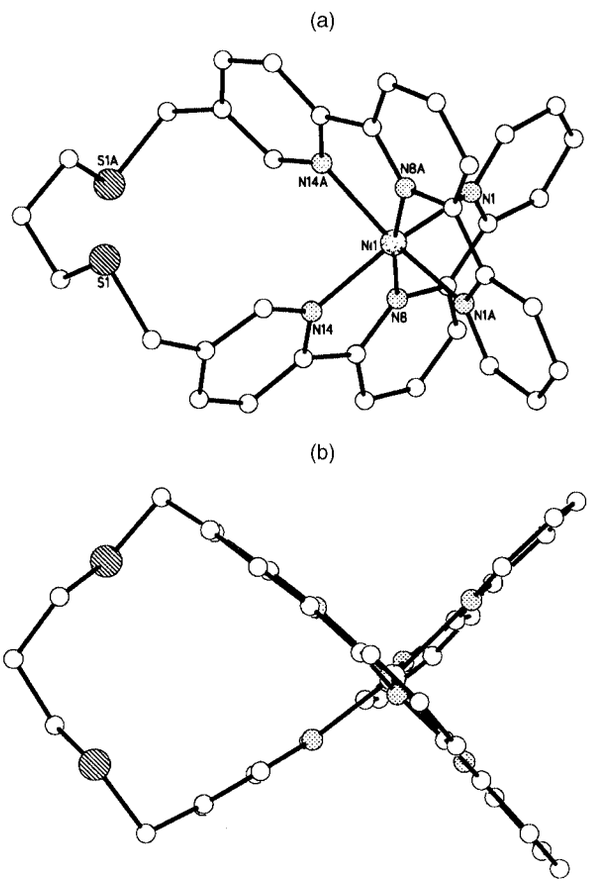


Fig. 2 Two views of $[NiL^1]^{2+}$ ion. In (b) the terpyridines are shown to be slightly bowed, and the angle between the two mean terpyridine planes is *ca.* 85°.

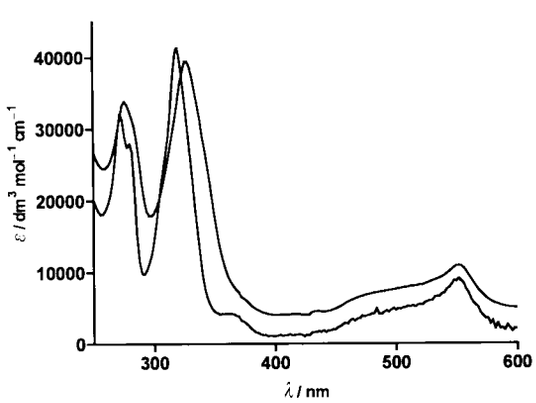


Fig. 3 Comparison of the UV-visible spectra of $[Fe(terpy)_2]^{2+}$ (lower trace at 550 nm) and $[FeL^1]^{2+}$ (upper trace) in methanol at 25 °C.

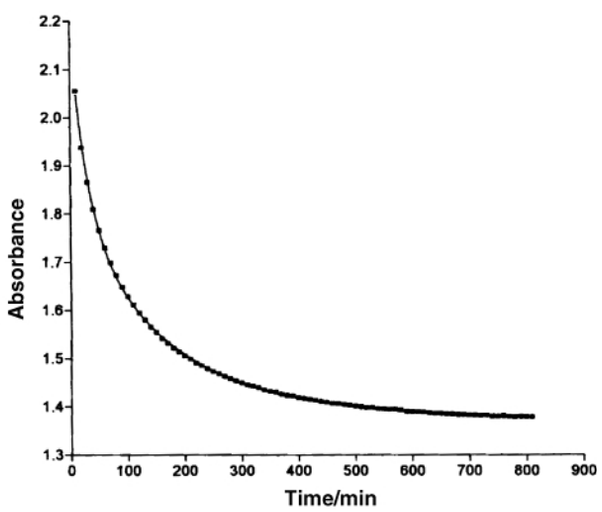


Fig. 4 Absorbance–time trace recorded at 318 nm for the reaction between $[Fe(terpy)_2]^{2+}$ and L^1 (both 5×10^{-5} mol dm^{-3}) in MeCN at 48.4 °C (eqn. (2)–(4)). Recorded data (squares) were fitted to the equation for a consecutive first-order equation using nonlinear least-squares (solid line).

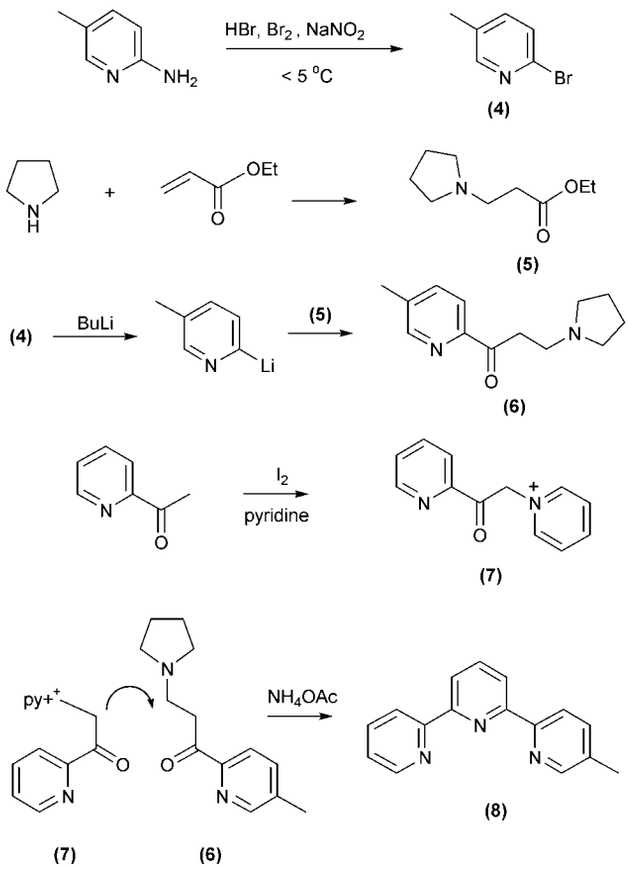
The intermediate $[Fe(terpy)L^1]^{2+}$ is most likely a species in which only one of the two terpy arms of L^1 is co-ordinated, and final ring closure involving loss of the second terpy (rate constant k_2) is slower than the rate of loss of the first terpy (rate constant k_1). Further studies are needed to establish this postulated mechanism with certainty. Since k_1 and k_2 differ by only a factor of *ca.* 5.8 at 48.4 °C, isolation of the intermediate will be difficult, and so far has not been attempted.

We conclude that the new ligands L^1 and L^2 have the correct geometry to form very stable mononuclear complexes with transition metal ions. Since the overall stability constant for $[Fe(terpy)_2]^{2+}$, β_2 is $10^{20.9}$, K_1 for $[FeL]^{2+}$ ($L = L^1$ and L^2) must be significantly larger than this. This is entirely consistent with the chelate effect, and is further confirmation that the complexes formed with these linked terpy ligands are relatively strain free.

Experimental

Materials and methods

All reagents were the best commercially available, and were not purified further. FTNMR spectra were recorded with Bruker spectrometers operating at proton frequencies of either 250, 300 or 400 MHz, mass spectra with a Micromass Autospec spectrometer, and visible spectra with a Jasco V-570 UV/VIS/NIR spectrophotometer. CHN combustion analyses were obtained with a Leeman Laboratories CE 440 elemental analyser.



Scheme 2

Synthesis of 5-methyl-2,2′:6′,2″-terpyridine. The synthetic method is outlined in Scheme 2. It is similar to the literature method reported for the synthesis of 2,2′:6′,2″-terpyridine,[12] but starting with 2-bromo-5-methylpyridine in place of 2-bromopyridine. 2-Bromo-5-methylpyridine (**4**) is available commercially (Aldrich), or may be prepared from 2-amino-5-methylpyridine following a literature method.[13]

Synthesis of 1-oxo-1-[2-{5-methyl}pyridyl]-3-[N-pyrollidino]-propane, oxalate salt (6)·$(CO_2H)_2$. *N*-Butyllithium (23 cm^3 of 1.6 mol dm^{-3} solution in hexane, 36.8 mmol) was added to dry, deoxygenated THF (60 cm^3) at −78 °C under N_2. Keeping the temperature at −78 °C, a solution of 2-bromo-5-methylpyridine (5.95 g, 34.6 mmol) in THF (30 cm^3) was added dropwise. The reaction mixture became orange-brown, and was stirred for a further 15 min after the addition was complete. A solution of ethyl-β-pyrollidinopropionate (**5**) (6.86 g, 40.1 mmol; prepared as described)[12] in THF (30 cm^3) was added dropwise, again keeping the temperature at −78 °C. After addition, the mixture was stirred for 1 h at −78 °C and then allowed to warm up slowly to room temperature. HCl (50 cm^3, 2 mol dm^{-3}) was added, and most of the THF was removed with a rotary evaporator. The aqueous solution was basified with NaOH, whereupon a brown oil separated which was extracted with ether (3 × 50 cm^3). The combined ethereal extracts were dried over anhydrous $MgSO_4$, filtered, and the solvent removed by evaporation. The residual brown oil was dissolved in acetone (50 cm^3), and a solution of oxalic acid (5 g) in acetone (50 cm^3) was added. On cooling, a white solid precipitated which was collected by filtration and recrystallised from acetone–water (4:1) at −20 °C. Yield 5.1 g, 50%. Mass spectrum (EI) *m*/*z* 218 (Calc. for $[C_{13}H_{19}N_2O]^+$, 218). δ_H (250 MHz; $(CD_3)_2SO$) 8.69 (s, 1H), 7.99 (m, 2H), 3.74 (t, 2H), 3.55 (t, 2H), 3.40 (m, 4H), 2.40 (s, 3H), 1.92 (m, 4H).

Synthesis of pyridacyl pyridinium iodide (7). 2-Acetylpyridine (6.05 g, 50 mmol) was added dropwise to a stirred solution of iodine (12.69 g, 50 mmol) in dry pyridine (60 cm^3). The mixture was heated under reflux for 1 h, then allowed to cool slowly to room temperature. The reaction flask was then cooled further in ice, to give a thick black precipitate. The precipitate was collected by filtration and washed with ether–ethanol (9:1; 50 cm^3). The black solid was redissolved in boiling methanol (200 cm^3) to which a little activated charcoal was added. After refluxing for 5 min, the black mixture was filtered hot through a Celite pad to give a clear yellow solution. On cooling, golden yellow crystals precipitated which were collected by filtration and dried. Yield 9.8 g, 60%.

Synthesis of 5-methyl-2,2′:6′,2″-terpyridine (8). A mixture of **6** (3.06 g, 10 mmol), **7** (3.26 g, 10 mmol) and ammonium acetate (4 g, a large excess) in methanol–water (2:1, 100 cm^3) was heated at reflux overnight to give a clear, dark brown solution and a white precipitate of ammonium oxalate. The solution was filtered, and the filtrate was concentrated with a rotary evaporator until a precipitate appeared; the flask was then chilled in an ice bath. The product was collected as an off-white crystalline solid, and washed thoroughly with water. Further purification may be affected by recrystallisation from ethanol–water (1:1). The compound was dried in air (70 °C). Yield 1.14 g (46%). Mass spectrum (CI/NH_3) *m*/*z* 248 (Calc. for MH^+, 248). δ_H (250 MHz; solvent $CDCl_3$) 8.70 (d, 1H), 8.61 (d, 1H), 8.52 (s, 1H), 8.50 (d, 1H), 8.41 (d, 2H), 7.94 (t, 1H), 7.85 (t, 1H), 7.66 (d, 1H), 7.33 (m, 1H), 2.42 (s, 3H). δ_C (100.62 MHz; solvent $CDCl_3$) 156.2, 155.4, 155.1, 153.6, 149.5, 149.0, 137.7, 137.3, 136.7, 133.1, 123.6, 121.0, 120.6 (2C), 120.5, 18.3. Found: C, 77.4; H, 5.25, N. 16.8. $C_{16}H_{13}N_3$ requires C, 77.7; H, 5.30; N, 17.0%.

Synthesis of 5-bromomethyl-2,2′:6′,2″-terpyridine. 5-Methyl-2,2′:6′,2″-terpyridine (494 mg, 2.0 mmol) and *N*-bromosuccinimide (356 mg, 2.0 mmol) were refluxed in CCl_4 (50 cm^3) under N_2 with irradiation by a 500 W sun lamp placed close to the flask, and until reaction had occurred (about 1 h). Completion of the reaction could be determined by the disappearance of *N*-bromosuccinimide (which is denser than CCl_4) and its replacement by succinimide (which floats on top of the solvent). The succinimide was filtered off, the solvent evaporated and the residue recrystallised from diethyl ether. Yield 354 mg, 54%. δ_H (250 MHz; $CDCl_3$) 8.70 (d, 2H), 8.59 (d, 2H), 8.45 (m, 2H), 7.96 (t, 1H), 7.86 (t, 2H), 7.39 (m, 1H), 4.55 (s, 2H). δ_C (62.9 MHz; $CDCl_3$; relative populations in parentheses) 156.0 (2), 155.2 (1), 149.1 (2), 149.0 (1), 137.9 (1), 137.4 (1), 136.9 (1), 133.6 (1), 123.7 (1), 121.1 (3), 29.6 (1). Mass spectrum (CI/NH_3): *m*/*z* 326/328 (Calc. for MH^+ (^{79}Br and ^{81}Br), 326/328).

Synthesis of L^1. Propane-1,3-dithiol (83 mg, 0.765 mmol) was added to a stirred solution of sodium ethoxide (104 mg, 1.53 mmol) in absolute ethanol (10 cm^3). After stirring at room temperature under N_2, an ethanolic solution of 5-bromomethyl-2,2′:6′,2″-terpyridine (500 mg, 1.53 mmol) was added, and the mixture was heated at reflux under N_2 overnight. After cooling, the solvent was evaporated, the product was extracted with dichloromethane, and the NaBr residue was filtered off. The filtrate was evaporated to leave L^1 as a white solid, which was recrystallised from ethanol and dried *in vacuo* (yield 217 mg, 47%). δ_H (250 MHz; $CDCl_3$): 1.82 (q, 1H), 2.40 (t, 2H), 3.73 (s, 2H), 7.32 (ddd, 1H), 7.83 (m, 2H), 7.94 (t, 1H), 8.41 (m, 2H), 8.58 (m, 3H), 8.68 (dd, 1H). δ_C (62.9 MHz; $CDCl_3$): 28.53, 30.12, 33.30, 120.89, 120.92, 120.98, 121.11, 123.71, 134.21, 136.80, 137.20, 137.85, 149.10, 149.24, 155.04, 155.15, 155.33, 156.16. FAB MS: *m*/*z* 599 $(M)^+$. Found: C, 69.2; H, 5.10; N. 13.8. Required for $C_{35}H_{30}N_6S_2·0.5H_2O$: C, 69.2; H, 5.14; N, 13.8%.

The ligand L^2 was prepared using the analogous procedure with butane-1,4-dithiol instead of propane-1,3-dithiol (yield

45%). δ_H (250 MHz; $CDCl_3$) 1.66 (m, 2H), 2.42 (t, 2H), 3.74 (s, 2H), 7.29 (ddd, 1H), 7.85 (m, 2H), 7.96 (t, 1H), 8.41 (m, 2H), 8.57 (m, 3H), 8.67 (dd, 1H). δ_C (62.9 MHz; $CDCl_3$): 27.98, 30.79, 33.20, 120.88, 120.92, 120.96, 121.11, 123.71, 134.21, 136.80, 137.20, 137.86, 149.10, 149.26, 155.08, 155.10, 155.34, 156.18. FAB MS: *m*/*z* 613 $(M)^+$. Found: C, 70.4; H, 5.24; N, 13.7. Required for $C_{36}H_{32}N_6S_2$: C, 70.6; H, 5.26; N, 13.7%.

Synthesis of $[FeL^1](PF_6)_2$. A solution of $Fe(BF_4)_2 \cdot 6H_2O$ (29 mg, 0.0859 mmol) in argon scrubbed methanol (30 cm^3) was added dropwise to a warm solution of $L^1 \cdot 0.5H_2O$ (50 mg, 0.0823 mmol) in methanol, and the mixture was heated at reflux under argon for 30 min. After cooling the complex was precipitated from solution as a dark purple solid by the addition of excess methanolic NH_4PF_6, collected by filtration, washed with diethyl ether and dried *in vacuo* (yield 41 mg, 50%). FAB MS (NBA): *m*/*z* 799 $[FeL^1PF_6]^+$ and 654 $[Fe(L^1 - H)]^+$. Found: C, 42.2; H, 3.8; N, 8.1. $C_{35}H_{30}F_{12}FeN_6P_2S_2 \cdot 3H_2O$ requires C, 42.1; H, 3.6; N, 8.4%. δ_C (62.9 MHz; CD_3CN; populations 2C unless specified): 29.11, 31.08 (1C), 33.08, 123.77, 124.07, 124.27, 124.43, 128.17, 138.97, 139.50, 139.56, 141.85, 153.63, 155.48, 156.46, 158.95, 160.98, 161.29.

Synthesis of $[FeL^2](PF_6)_2$ was as described for $[FeL^1](PF_6)_2$, starting with $L^2 \cdot H_2O$ (100 mg, 0.159 mmol) and giving $[FeL^2][PF_6]_2 \cdot H_2O$ (84.9 mg, 54%). FAB MS (NBA): *m*/*z* 813 $(FeL^2PF_6)^+$, 668 $[Fe(L^2 - H)]^+$. Found: C, 44.2; H, 3.33; N, 8.57. $C_{36}H_{32}F_{12}FeN_6P_2S_2 \cdot H_2O$ requires C, 44.3; H, 3.51; N, 8.61%. δ_C (62.9 MHz; CD_3CN) 29.77, 31.37, 33.97, 124.25, 124.35, 124.39, 124.69, 128.21, 138.91, 139.56, 140.42, 142.68, 153.52, 153.65, 157.06, 158.87, 160.84, 161.22.

Synthesis of $[NiL](PF_6)_2$ (L = L^1 and L^2). The complexes were obtained from $Ni(OCOCH_3)_2 \cdot 4H_2O$ using a similar procedure to that described for the Fe(II) complexes. For $[NiL^1][PF_6]_2$; FAB MS (NBA): *m*/*z* 801 $[NiL^1PF_6]^+$, 656 $[Ni(L^1 - H)]^+$. Found: C, 43.0; H, 3.10, N, 8.50. $C_{35}H_{30}F_{12}N_6NiP_2S_2 \cdot 2H_2O$ requires C, 42.8; H, 3.48, N. 8.55%. For $[NiL^2](PF_6)_2$; FAB MS (NBA): *m*/*z* 815 $[NiL^2PF_6]^+$, 670 $[Ni(L^2 - H)]^+$. Found: C, 43.6; H, 2.94; N, 8.33. $C_{36}H_{32}F_{12}N_6NiP_2S_2 \cdot 2H_2O$ requires C, 43.4; H, 3.64; N, 8.43%.

Crystal structure analyses

Crystals of the Ni(II) complexes suitable for X-ray crystallography were grown by slow diffusion of diethyl ether vapour into an acetonitrile solution (L^1 complex) or acetonitrile–ethanol (2:1) solution (L^2 complex). Data were collected with a Siemens SMART three-circle system with CCD area detector.[14] Temperature maintained with an Oxford Cryosystem Cryostream Cooler.[15] $\lambda = 0.71073$ Å. Maximum θ 24.00°. Absorption correction by psi-scan; no crystal decay. The structures were solved by direct methods using SHELXS (TREF) with additional light atoms found by Fourier methods. Anisotropic displacement parameters were used for all non-H atoms (apart from minor F positions). Hydrogen atoms were added at calculated positions and refined using a riding model (apart from the lattice EtOH). The weighting scheme was calc $w = 1/[\sigma^2(F_o^2) + (aP)^2 + bP]$ where $P = (F_o^2 + 2F_c^2)/3$; for L^1, $a = 0.0690$, $b = 0$; for L^2, $a = 0.0859$, $b = 1.9161$. Refinement used SHELXL 96.[16]

For the L^1 complex, the cation and both anions lie on two-fold axes. One PF_6 has an alternative minor position for the fluorine atoms in one equatorial plane.

For the L^2 complex, the PF_6 groups were found to be severely disordered with minor positions for four atoms in each (and indications that more complex modelling might be possible). Additionally, one acetonitrile and a 0.25 occupancy EtOH were located; the C–C and C–O distances of the EtOH were restrained. The absolute structure of the individual crystal chosen was checked by refinement of a delta-f″ multiplier. Absolute structure parameter $x = 0.49(4)$, indicated that the crystal chosen was a racemic twin.

Crystal data for $[NiL^1](PF_6)_2 \cdot 2CH_3CN$. $C_{35}H_{30}F_{12}N_6NiP_2S_2 \cdot 2MeCN$ (deep red blocks) $M = 1029.51$, monoclinic, space group $C2/c$, $a = 12.414(5)$, $b = 26.007(5)$, $c = 13.372(5)$ Å, $\beta = 99.644(4)°$, $U = 4255.9(5)$ $Å^3$, $T = 200(2)$ K, $Z = 4$, μ(Mo-Kα) = 0.724 mm^{-1}. 12791 reflections measured, 4992 unique; R(int) = 0.0276. Final $R1$[for 3700 reflections with $I > 2\sigma(I)$] = 0.0397, $wR2 = 0.1134$.

Crystal data for $[NiL^2](PF_6)_2 \cdot CH_3CN \cdot 0.25EtOH$. Crystals (golden-yellow plates) $C_{36}H_{32}F_{12}N_6NiP_2S_2 \cdot MeCN \cdot 0.25EtOH$, $M = 1014.0$, orthorhombic, space group $Pna2_1$, $a = 26.815(2)$, $b = 11.289(1)$, $c = 14.976(1)$ Å, $U = 4533.47(11)$ $Å^3$, $T = 200(2)$ K, $Z = 4$, μ(Mo-Kα) = 0.678 mm^{-1}. 19958 reflections measured, 7019 unique; R(int) = 0.0541. $S = 1.057$, $R1$ [for 3998 reflections with $I > 2\sigma(I)$] = 0.0606, $wR2 = 0.1826$.

CCDC reference number 186/1794.

See http://www.rsc.org/suppdata/dt/a9/a907543g/ for crystallographic files in .cif format.

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