

# A convenient high yield synthesis of 2,2':6',2'':6'',2''':6''',2''':6''',2''':6''',2''':6''''-sexipyridine and helical transition-metal complexes of substituted sexipyridines

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The compound 2,2':6',2'':6'',2''':6''',2''':6''',2''':6''',2''':6''''-sexipyridine (spy) has been synthesised in high yield by the coupling of 6-bromo-2,2':6',2'':6'',2''':6''',2''':6''',2''':6''',2''':6''''-terpyridine with a nickel(0) reagent, followed by demetallation of the resultant double-helical  $[\text{Ni}_2(\text{spy})_2]^{4+}$  complex with KCN. In order to probe the effects of substitution of spy upon helication processes, the substituted compounds 4',4''-bis(methylsulfanyl)-2,2':6',2'':6'',2''':6''',2''':6''',2''':6''',2''':6''''-sexipyridine (msspy), 4',4''-diphenyl-2,2':6',2'':6'',2''':6''',2''':6''',2''':6''',2''':6''''-sexipyridine (pspy) and 4',4''-bis(4-*tert*-butylphenyl)-2,2':6',2'':6'',2''':6''',2''':6''',2''':6''',2''':6''''-sexipyridine (tbspy) were also prepared and studied. The reaction of each of these compounds with transition-metal ions capable of adopting an octahedral geometry results in the self-assembly of dinuclear double-helical complexes of the type  $[\text{M}_2\text{L}_2]^{4+}$  [M = iron(II), cobalt(II), nickel(II), copper(II), zinc(II), cadmium(II) or mercury(II); L = spy, msspy, pspy or tbspy]; the double-helical topology of the zinc complex of pspy was confirmed by a crystal-structure analysis of the salt  $[\text{Zn}_2(\text{pspy})_2] \cdot [\text{PF}_6]_4 \cdot 2\text{MeCN} \cdot 2\text{H}_2\text{O}$  [space group  $P4_22_12$ ,  $a = 15.518(2)$ ,  $c = 18.443(1)$  Å,  $R = 0.0638$ ,  $R' = 0.0735$ ].

Self-assembly processes have attracted considerable recent interest and those in which the assembly is directed by a metal–ligand interaction have proved to be particularly versatile and facile.<sup>1,2</sup> We and others<sup>3</sup> have investigated the structural requirements of ligands which give rise to helical co-ordination compounds, and have demonstrated that the oligopyridines are of particular utility for the assembly of multiple-helical species.<sup>4,5</sup> Our interest lies in the development of the co-ordination chemistry of the higher oligopyridines as the organic components of helical supramolecular systems. In this paper we describe facile routes for the preparation of 2,2':6',2'':6'',2''':6''',2''':6''',2''':6''',2''':6''''-sexipyridine (spy) and a number of its derivatives and report a comparative study of the co-ordination behaviour of the various sexipyridines with a range of metal ions possessing differing electronically imposed preferences for their co-ordination geometries. The synthesis of spy has previously been reported.<sup>6</sup>

## Experimental

Infrared spectra were recorded on Perkin-Elmer 1710, Philips PU9624 or Mattson Genesis Fourier-transform spectrophotometers with samples in compressed KBr discs. Proton NMR spectra were recorded on Brüker WM250, AM400 or Varian Gemini 300 MHz spectrometers. Fast atom bombardment (FAB) and electron-impact (EI) mass spectra were recorded on Kratos MS-50, MS-890, VG 70–250 or MS-902 spectrometers; for FAB or FIB spectra the sample was loaded using acetonitrile as a solvent and 3-nitrobenzyl alcohol as supporting matrix. Time of flight (MALDI) spectra were recorded using a PerSeptive Biosystems Voyager-RP Biospectrometry workstation. Electrochemical measurements were performed with an Amel model 553 potentiostat connected to an Amel model 567 function generator and an Amel model 560/A interface or an Eco Chemie Autolab PGSTAT 20 system using a platinum bead or glassy carbon working and auxiliary electrodes with an Ag–AgCl electrode as reference. The experiments were conducted using purified acetonitrile as solvent and freshly recrystallised 0.1 mol dm<sup>-3</sup>  $[\text{Bu}^n_4\text{N}][\text{BF}_4]$  or  $[\text{Bu}^n_4\text{N}][\text{PF}_6]$

as supporting electrolyte; ferrocene (Fc) was added at the end of each experiment as an internal reference. The compounds [2'-oxo-2'-(2''-pyridyl)ethyl]pyridinium iodide,<sup>7</sup> 2-bromo-6-(3'-dimethylammonio-1'-oxopropyl)pyridine chloride,<sup>8</sup> 6,6'-diacetyl-2,2'-bipyridine,<sup>9</sup> 3,3-bis(methylsulfanyl)-1-pyridylprop-2-enone,<sup>10</sup> 2-acetyl-6-bromopyridine,<sup>9</sup> 1-(6-bromo-2-pyridyl)-3-phenylprop-2-enone,<sup>11</sup> 4',4''-bis(methylsulfanyl)-2,2':6',2'':6'',2''':6''',2''':6''',2''':6''',2''':6''''-sexipyridine (msspy),<sup>12</sup> 4',4''-bis(4-*tert*-butylphenyl)-2,2':6',2'':6'',2''':6''',2''':6''',2''':6''',2''':6''''-sexipyridine (tbspy)<sup>13</sup> and  $[\text{NiCl}_2(\text{PPh}_3)_2]$ <sup>14</sup> were prepared according to published procedures. All other chemicals were used as supplied.

## Preparations

**6-Bromo-2,2':6',2'':6'',2''':6''',2''':6''',2''':6''',2''':6''''-terpyridine (btpy).** 2-Bromo-6-(3'-dimethylammonio-1'-oxopropyl)pyridine chloride (1.01 g, 3.44 mmol), [2'-oxo-2'-(2''-pyridyl)ethyl]pyridinium iodide (1.12 g, 3.40 mmol) and ammonium acetate (4.0 g) were heated to reflux in methanol (30 cm<sup>3</sup>) for 4 h after which time a flaky solid had precipitated. The reaction mixture was cooled and the off-white precipitate was collected by filtration and washed with cold ethanol to give btpy (0.690 g, 64%) (Found: C, 57.5; H, 3.1; N, 13.1. Calc. for C<sub>15</sub>H<sub>10</sub>BrN<sub>3</sub>: C, 57.7; H, 3.2; N, 13.4%). Mass spectrum (EI):  $m/z$  311/313 ( $M^+$ ) and 232 ( $M^+ - \text{Br}$ ). <sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>): δ 7.36 (1 H, tdd, H<sup>5'</sup>), 7.54 (1 H, dd, H<sup>5</sup>), 7.75 (1 H, t, H<sup>4</sup>), 7.88 (1 H, tdd, H<sup>4'</sup>), 7.98 (1 H, t, H<sup>4</sup>), 8.40 (1 H, dd, H<sup>3</sup>), 8.49 (1 H, dd, H<sup>5</sup>), 8.59 (1 H, dd, H<sup>3'</sup>), 8.61 (1 H, dd, H<sup>3</sup>) and 8.69 (1 H, ddd, H<sup>6</sup>).

**6-Bromo-4'-phenyl-2,2':6',2'':6'',2''':6''',2''':6''',2''':6''',2''':6''''-terpyridine (btpy).** 1-(6-Bromo-2-pyridyl)-3-phenylprop-2-enone (5.3 g, 18.5 mmol), [2'-oxo-2'-(2''-pyridyl)ethyl]pyridinium iodide (6.0 g, 18.4 mmol) and ammonium acetate (15 g) were heated to reflux in ethanol (40 cm<sup>3</sup>) for 12 h after which time golden yellow crystals had precipitated. The product was collected by filtration and recrystallised from chloroform to give yellow blocks of btpy (4.5 g, 63%). Mass spectrum (EI):  $m/z$  387/389 ( $M^+$ ) and 308 ( $M^+ - \text{Br}$ ). <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ 7.35 (1 H, dd, H<sup>5'</sup>), 7.50 (4 H, m, H<sup>5</sup>, <sup>m, p</sup>), 7.72 (1 H, t, H<sup>4</sup>), 7.87 (3 H, m, H<sup>4'</sup>, <sup>o</sup>), 8.61 (1 H,

dd, H<sup>3''</sup>), 8.63 (1 H, dd, H<sup>3</sup>), 8.68 (1 H, d, H<sup>3'/5'</sup>), 8.72 (1 H, d, H<sup>6''</sup>) and 8.74 (1 H, d, H<sup>5'/3'</sup>).

**2,2':6',2'':6'',2''':6''',2'''' :6'''' :6''''-Sexipyridine (spy).** A solution of [Ni(H<sub>2</sub>O)<sub>6</sub>]Cl<sub>2</sub> (1.81 g, 7.6 mmol) and PPh<sub>3</sub> (8.00 g, 30.5 mmol) in deoxygenated *N,N*-dimethylformamide (dmf) (30 cm<sup>3</sup>) was stirred at room temperature under an atmosphere of dry N<sub>2</sub> for 20 min, after which period the blue reaction mixture was treated with zinc dust (0.50 g, 7.6 mmol) to produce a deep red suspension. After a further 30 min, a solution of btpy (1.19 g, 3.8 mmol) in dmf (10 cm<sup>3</sup>) was added and the mixture was stirred for 16 h to give a very dark green slurry. As much of the solvent as possible was removed *in vacuo*, the sticky green residue boiled with water (100 cm<sup>3</sup>) and the resultant mixture filtered. The pale green filtrate was warmed slightly and KCN (4.0 g) was added, after which it was heated to reflux for 1 h (**CARE**: some HCN is evolved during this process) to give a turbid white suspension. This was filtered from the hot solution and washed with water (2 × 10 cm<sup>3</sup>). The solid was dried, collected and purified by Soxhlet extraction with acetone–methanol–acetonitrile (3:2:1) for 4 h, after which 2,2':6',2'':6'',2''':6''',2'''' :6'''' :6''''-sexipyridine remained in the thimble as a white solid (0.42 g, 48%), m.p. > 250 °C (Found: C, 76.9; H, 4.25; N, 18.4. C<sub>30</sub>H<sub>20</sub>N<sub>6</sub> requires C, 77.6; H, 4.3; N, 18.1%). Mass spectrum (EI): *m/z* 464 (M<sup>+</sup>), 386 (M<sup>+</sup> – py), 309 (M<sup>+</sup> – 2py) and 232 (M<sup>+</sup> – 3py). IR (KBr): 1578m, 1563s, 1428s, 1271m, 1110w, 1076m, 992m, 773s, 657m and 637m cm<sup>-1</sup>.

**6,6'-Bis(1-oxo-3-phenylprop-2-enyl)-2,2'-bipyridine.** A solution of 6,6'-diacetyl-2,2'-bipyridine (0.20 g, 0.90 mmol) and benzaldehyde (1.0 cm<sup>3</sup>, excess) in propan-2-ol (10 cm<sup>3</sup>) containing diethylamine (1 cm<sup>3</sup>) was heated at reflux for 16 h. After cooling, the yellow precipitate was filtered off and recrystallised from ethanol (0.25 g, 67%), m.p. 233–235 °C (sublimes). <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ 7.46 (3 H, m, H<sup>m, p</sup>), 7.77 (2 H, m, H<sup>o</sup>), 8.02 (1 H, d, *J* 16, H<sup>a</sup>), 8.12 (1 H, t, H<sup>a</sup>), 8.28 (1 H, d, H<sup>3/5</sup>), 8.45 (1 H, d, *J* 16 Hz, H<sup>b</sup>) and 8.82 (1 H, d, H<sup>3/5</sup>). IR (KBr): 1671vs, 1609vs, 1576s, 1450m, 1341s, 1271m, 1224s, 1099m, 1039s, 999m, 809m, 760s, 694m and 680m cm<sup>-1</sup>.

**4',4''-Diphenyl-2,2':6',2'':6'',2''':6''',2'''' :6'''' :6''''-sexipyridine (pspy).** *Method 1.* A solution of [Ni(PPh<sub>3</sub>)<sub>2</sub>]Cl<sub>2</sub> (0.66 g, 1 mmol) and PPh<sub>3</sub> (0.60 g, 2.3 mmol) in deoxygenated dmf (10 cm<sup>3</sup>) was stirred at room temperature under an atmosphere of dry dinitrogen for 20 min. Zinc dust (0.13 g, 2 mmol) was added to the blue solution to give a deep red suspension. After 30 min a solution of btpy (0.390 g, 1 mmol) in dry dmf (5 cm<sup>3</sup>) was added and the mixture stirred for 16 h. The solvent was then removed *in vacuo* and the sticky brown residue boiled with water (25 cm<sup>3</sup>). The mixture was filtered and KCN (1.0 g) added to the pale green filtrate. This mixture was heated at reflux for 1 h (**CARE**: some HCN is produced during this process) to give a white suspension which was filtered from the hot solution and washed with water (2 × 10 cm<sup>3</sup>). After drying, the solid was recrystallised from toluene to give pspy as a colourless solid (0.70 g, 23%), m.p. > 250 °C (Found: C, 80.6; H, 4.8; N, 13.4. C<sub>42</sub>H<sub>28</sub>N<sub>6</sub> requires C, 81.8; H, 4.6; N, 13.6%). Mass spectrum (EI): *m/z* 617 (M + H<sup>+</sup>), 464 (M<sup>+</sup> – 2Ph). <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ 7.36 (1 H, m, H<sup>5A</sup>), 7.55 (4 H, m, H<sup>5C, m, p</sup>), 7.95 (3 H, m, H<sup>o, 4A</sup>), 8.10 (1 H, t, H<sup>4C</sup>), 8.75 (4 H, m, H<sup>6A, 3A, 3B/5B, 3C</sup>) and 8.95 (1 H, d, H<sup>5B/3B</sup>). IR (KBr): 1600m, 1570s, 1474s, 1268m, 1095w, 1076m, 855m, 722s, 667m and 524m cm<sup>-1</sup>.

*Method 2.* 6,6'-Bis(1-oxo-3-phenylprop-2-enyl)-2,2'-bipyridine (0.25 g, 0.60 mmol) and [2'-oxo-2'-(2'-pyridyl)ethyl]pyridinium iodide (0.40 g, 1.20 mmol) were heated at reflux in ethanol (20 cm<sup>3</sup>) containing anhydrous ammonium acetate (0.50 g, excess) for 16 h. After cooling, the pale green precipitate was isolated and washed with ethanol. Recrystallisation from chloroform–ethanol afforded pspy as a colourless solid (0.24 g, 65%).

**[Fe<sub>2</sub>(spy)<sub>2</sub>][BF<sub>4</sub>]<sub>4</sub>.** A suspension of spy (0.02 g, 43 mmol) and [Fe(H<sub>2</sub>O)<sub>6</sub>][BF<sub>4</sub>]<sub>2</sub> (0.015 g, 43 mmol) in methanol (20 cm<sup>3</sup>) was heated to reflux for 2 h to give a clear purple solution. A solution of [NH<sub>4</sub>][BF<sub>4</sub>] in methanol was added to the hot solution which deposited a fine purple crystalline precipitate on cooling. This was filtered off and recrystallised by the diffusion of diethyl ether vapour into an acetonitrile solution to yield purple needles of [Fe<sub>2</sub>(spy)<sub>2</sub>][BF<sub>4</sub>]<sub>4</sub> (0.015 g, 50%) (Found: C, 49.0; H, 2.7; N, 11.7. C<sub>60</sub>H<sub>40</sub>B<sub>4</sub>F<sub>16</sub>Fe<sub>2</sub>N<sub>12</sub> requires C, 51.9; H, 2.9; N, 12.1%). Mass spectrum (FAB): *m/z* 1302 {[Fe<sub>2</sub>(spy)<sub>2</sub>][BF<sub>4</sub>]<sub>3</sub>}<sup>+</sup>, 1215 {[Fe<sub>2</sub>(spy)<sub>2</sub>][BF<sub>4</sub>]<sub>2</sub>}<sup>+</sup>, 1127 {[Fe<sub>2</sub>(spy)<sub>2</sub>][BF<sub>4</sub>]}<sup>+</sup>, 1041 [Fe<sub>2</sub>(spy)<sub>2</sub>]<sup>+</sup> and 520 [Fe(spy)]<sup>+</sup>. <sup>1</sup>H NMR (CD<sub>3</sub>CN): δ –16, 5, 14, 38, 52, 54, 57, 64, 79 and 171.

**General method for [M<sub>2</sub>(spy)<sub>2</sub>][PF<sub>6</sub>]<sub>4</sub> (M = Co, Ni, Zn or Hg).** As described above for [Fe<sub>2</sub>(spy)<sub>2</sub>][BF<sub>4</sub>]<sub>4</sub>, with spy (0.020 g, 43 mmol) and 43 mmol of the appropriate metal acetate and precipitated with ammonium hexafluorophosphate.

**[Co<sub>2</sub>(spy)<sub>2</sub>][PF<sub>6</sub>]<sub>4</sub>.** Dark orange crystals (0.025 g, 70%) (Found: C, 42.1; H, 2.7; N, 9.9. C<sub>60</sub>H<sub>40</sub>Co<sub>2</sub>F<sub>24</sub>N<sub>12</sub>P<sub>4</sub> requires C, 44.3; H, 2.5; N, 10.3%). Mass spectrum (FAB): *m/z* 1483 {[Co<sub>2</sub>(spy)<sub>2</sub>][PF<sub>6</sub>]<sub>3</sub>}<sup>+</sup>, 1337 {[Co<sub>2</sub>(spy)<sub>2</sub>][PF<sub>6</sub>]<sub>2</sub>}<sup>+</sup>, 1192 {[Co<sub>2</sub>(spy)<sub>2</sub>][PF<sub>6</sub>]}<sup>+</sup>, 1046 [Co<sub>2</sub>(spy)<sub>2</sub>]<sup>+</sup> and 523 [Co(spy)]<sup>+</sup>. <sup>1</sup>H NMR (CD<sub>3</sub>CN): δ –24, –18, 13, 34, 41, 49, 68, 127, 146 and 268.

**[Ni<sub>2</sub>(spy)<sub>2</sub>][PF<sub>6</sub>]<sub>4</sub>.** Pale green solid (0.025 g, 70%) (Found: C, 43.0; H, 2.6; N, 9.7. C<sub>60</sub>H<sub>40</sub>F<sub>24</sub>N<sub>12</sub>Ni<sub>2</sub>P<sub>4</sub> requires C, 44.3; H, 2.5; N, 10.3%). Mass spectrum (FAB): *m/z* 1480 {[Ni<sub>2</sub>(spy)<sub>2</sub>][PF<sub>6</sub>]<sub>3</sub>}<sup>+</sup>, 1335 {[Ni<sub>2</sub>(spy)<sub>2</sub>][PF<sub>6</sub>]<sub>2</sub>}<sup>+</sup>, 1190 {[Ni<sub>2</sub>(spy)<sub>2</sub>][PF<sub>6</sub>]}<sup>+</sup>, 1045 [Ni<sub>2</sub>(spy)<sub>2</sub>]<sup>+</sup>, 668 {[Ni(spy)]-PF<sub>6</sub>]}<sup>+</sup> and 523 [Ni(spy)]<sup>+</sup>.

**[Zn<sub>2</sub>(spy)<sub>2</sub>][PF<sub>6</sub>]<sub>4</sub>.** Off-white solid (0.025 g, 70%) (Found: C, 43.2; H, 2.4; N, 9.8. C<sub>60</sub>H<sub>40</sub>F<sub>24</sub>N<sub>12</sub>P<sub>4</sub>Zn<sub>2</sub> requires C, 43.9; H, 2.5; N, 10.2%). Mass spectrum (FAB): *m/z* 1492 {[Zn<sub>2</sub>(spy)<sub>2</sub>][PF<sub>6</sub>]<sub>3</sub>}<sup>+</sup>, 1347 {[Zn<sub>2</sub>(spy)<sub>2</sub>][PF<sub>6</sub>]<sub>2</sub>}<sup>+</sup>, 1202 {[Zn<sub>2</sub>(spy)<sub>2</sub>][PF<sub>6</sub>]}<sup>+</sup> and 527 [Zn(spy)]<sup>+</sup>. <sup>1</sup>H NMR (CD<sub>3</sub>CN): δ 6.92 (2 H, m, H<sup>6A, 5C</sup>), 7.15 (1 H, ddd, H<sup>5A</sup>), 7.71 (1 H, t, H<sup>4C</sup>), 8.00 (1 H, t, H<sup>4A</sup>), 8.25 (1 H, dd, H<sup>3C</sup>), 8.35 (1 H, m, H<sup>3A</sup>) and 8.60 (3 H, m, H<sup>3B, 4B, 5B</sup>).

**[Hg<sub>2</sub>(spy)<sub>2</sub>][PF<sub>6</sub>]<sub>4</sub>.** Off-white solid (0.025 g, 60%) (Found: C, 37.7; H, 2.4; N, 8.5. C<sub>60</sub>H<sub>40</sub>F<sub>24</sub>Hg<sub>2</sub>N<sub>12</sub>P<sub>4</sub> requires C, 37.7; H, 2.1; N, 8.8%). Mass spectrum (FAB): *m/z* 1765 {[Hg<sub>2</sub>(spy)<sub>2</sub>][PF<sub>6</sub>]<sub>3</sub>}<sup>+</sup>, 1620 {[Hg<sub>2</sub>(spy)<sub>2</sub>][PF<sub>6</sub>]<sub>2</sub>}<sup>+</sup>, 1457 {[Hg<sub>2</sub>(spy)<sub>2</sub>][PF<sub>6</sub>]}<sup>+</sup>, 1130 [Hg<sub>2</sub>(spy)<sub>2</sub>]<sup>+</sup> and 665 [Hg(spy)]<sup>+</sup>. <sup>1</sup>H NMR (CD<sub>3</sub>CN): δ 7.01 (1 H, m, H<sup>5C</sup>), 7.21 (1 H, m, H<sup>6A</sup>), 7.27 (1 H, m, H<sup>5A</sup>), 7.87 (1 H, t, H<sup>4C</sup>), 8.02 (1 H, td, H<sup>4A</sup>), 8.23 (1 H, dd, H<sup>3C</sup>), 8.34 (1 H, d, H<sup>3A</sup>) and 8.60 (3 H, m, H<sup>3B, 4B, 5B</sup>).

**General method for [M<sub>2</sub>L<sub>2</sub>][PF<sub>6</sub>]<sub>4</sub> (M = Fe, Co, Ni, Zn, Cd or Hg; L = msspy, pspy or tbspy).** A suspension of L (0.025 g, 45 mmol) and a stoichiometric amount of the appropriate metal acetate (or FeCl<sub>2</sub> in the case of M = Fe) in methanol (10 cm<sup>3</sup>) was heated to reflux for 2 h. Addition of ammonium hexafluorophosphate precipitated the complexes, which were filtered off and recrystallised by the diffusion of diethyl ether vapour into an acetonitrile solution of the complex.

**[Fe<sub>2</sub>(msspy)<sub>2</sub>][PF<sub>6</sub>]<sub>4</sub>.** Purple needles (0.020 g, 60%) (Found: C, 41.2; H, 2.6; N, 9.1. C<sub>64</sub>H<sub>48</sub>F<sub>24</sub>Fe<sub>2</sub>N<sub>12</sub>P<sub>4</sub>S<sub>4</sub> requires C, 42.6; H, 2.7; N, 9.3%). Mass spectrum (FAB): *m/z* 1657 {[Fe<sub>2</sub>(msspy)<sub>2</sub> – 3H][PF<sub>6</sub>]<sub>3</sub>}<sup>+</sup>, 1512 {[Fe<sub>2</sub>(msspy)<sub>2</sub> – 3H][PF<sub>6</sub>]<sub>2</sub>}<sup>+</sup>, 1368 {[Fe<sub>2</sub>(msspy)<sub>2</sub> – 2H][PF<sub>6</sub>]}<sup>+</sup>. <sup>1</sup>H NMR (CD<sub>3</sub>CN): δ 11, 18, 41, 56, 57, 67, 80 and 178.

**[Co<sub>2</sub>(msspy)<sub>2</sub>][PF<sub>6</sub>]<sub>4</sub>.** Dark orange solid (0.020 g, 60%) (Found: C, 40.1; H, 2.4; N, 9.0. C<sub>64</sub>H<sub>48</sub>Co<sub>2</sub>F<sub>24</sub>N<sub>12</sub>P<sub>4</sub>S<sub>4</sub> requires C, 36.7; H, 2.3; N, 8.0%). Mass spectrum (FAB): *m/z* 1663 {[Co<sub>2</sub>(msspy)<sub>2</sub> – 3H][PF<sub>6</sub>]<sub>3</sub>}<sup>+</sup>, 1519 {[Co<sub>2</sub>(msspy)<sub>2</sub> – 2H][PF<sub>6</sub>]<sub>2</sub>}<sup>+</sup>, 1374 {[Co<sub>2</sub>(msspy)<sub>2</sub> – 2H][PF<sub>6</sub>]}<sup>+</sup> and 1231 [Co<sub>2</sub>(msspy)<sub>2</sub>]<sup>+</sup>. <sup>1</sup>H NMR (CD<sub>3</sub>CN): δ –33, –18, 14, 23, 41, 43, 68, 131 and 151.

[Ni<sub>2</sub>(msspy)<sub>2</sub>][PF<sub>6</sub>]<sub>4</sub>. Pale green solid (0.020 g, 55%) (Found: C, 41.9; H, 2.6; N, 9.0. C<sub>64</sub>H<sub>48</sub>F<sub>24</sub>N<sub>12</sub>Ni<sub>2</sub>P<sub>4</sub>S<sub>4</sub> requires C, 42.5; H, 2.7; N, 9.3%). Mass spectrum (FAB): *m/z* 1665 {[Ni<sub>2</sub>(msspy)<sub>2</sub>][PF<sub>6</sub>]<sub>3</sub>}<sup>+</sup>, 1520 {[Ni<sub>2</sub>(msspy)<sub>2</sub>][PF<sub>6</sub>]<sub>2</sub>}<sup>+</sup> and 1357 {[Ni<sub>2</sub>(msspy)<sub>2</sub>][PF<sub>6</sub>]}<sup>+</sup>.

[Zn<sub>2</sub>(msspy)<sub>2</sub>][PF<sub>6</sub>]<sub>4</sub>. Off-white solid (0.020 g, 60%) (Found: C, 42.9; H, 2.4; N, 8.9. C<sub>64</sub>H<sub>48</sub>F<sub>24</sub>N<sub>12</sub>P<sub>4</sub>S<sub>4</sub>Zn<sub>2</sub> requires C, 42.1; H, 2.6; N, 9.2%). Mass spectrum (FAB): *m/z* 1697 {[Zn<sub>2</sub>(msspy)<sub>2</sub>][PF<sub>6</sub>]<sub>3</sub>}<sup>+</sup>, 1535 {[Zn<sub>2</sub>(msspy)<sub>2</sub>][PF<sub>6</sub>]<sub>2</sub>}<sup>+</sup>, 1388 {[Zn<sub>2</sub>(msspy)<sub>2</sub>][PF<sub>6</sub>]}<sup>+</sup> and 628 [Zn(msspy)]<sup>+</sup>.

[Cd<sub>2</sub>(msspy)<sub>2</sub>][PF<sub>6</sub>]<sub>4</sub>. Off-white solid (0.020 g, 60%) (Found: C, 37.8; H, 2.4; N, 8.1. C<sub>64</sub>H<sub>48</sub>Cd<sub>2</sub>F<sub>24</sub>N<sub>12</sub>P<sub>4</sub>S<sub>4</sub> requires C, 40.0; H, 2.5; N, 8.7%). Mass spectrum (FAB): *m/z* 1795 {[Cd<sub>2</sub>(msspy)<sub>2</sub>][PF<sub>6</sub>]<sub>3</sub>}<sup>+</sup>, 1630 {[Cd<sub>2</sub>(msspy)<sub>2</sub>][PF<sub>6</sub>]<sub>2</sub>][F]}<sup>+</sup>, 815 {[Cd(msspy)][PF<sub>6</sub>]}<sup>+</sup> and 669 [Cd(msspy)]<sup>+</sup>.

[Hg<sub>2</sub>(msspy)<sub>2</sub>][PF<sub>6</sub>]<sub>4</sub>. Off-white solid (0.020 g, 55%) (Found: C, 37.0; H, 2.4; N, 8.1. C<sub>64</sub>H<sub>48</sub>F<sub>24</sub>Hg<sub>2</sub>N<sub>12</sub>P<sub>4</sub>S<sub>4</sub> requires C, 36.7; H, 2.3; N, 8.0%).

[Fe<sub>2</sub>(pspy)<sub>2</sub>][PF<sub>6</sub>]<sub>4</sub>. Dark purple crystals (0.015 g, 55%) (Found: C, 57.6; H, 4.2; N, 9.7. C<sub>84</sub>H<sub>56</sub>F<sub>24</sub>Fe<sub>2</sub>N<sub>12</sub>P<sub>4</sub> requires C, 59.6; H, 3.3; N, 9.9%). Mass spectrum (FAB): *m/z* 1781 {[Fe<sub>2</sub>(pspy)<sub>2</sub>][PF<sub>6</sub>]<sub>3</sub>}<sup>+</sup>, 1635 {[Fe<sub>2</sub>(pspy)<sub>2</sub>][PF<sub>6</sub>]<sub>2</sub>}<sup>+</sup>, 1490 {[Fe<sub>2</sub>(pspy)<sub>2</sub>][PF<sub>6</sub>]}<sup>+</sup> and 672 [Fe(psps)]<sup>+</sup>. <sup>1</sup>H NMR (CD<sub>3</sub>CN): δ 4, 5, 6, 9, 15, 32, 48, 49, 51, 58, 72 and 155.

[Co<sub>2</sub>(pspy)<sub>2</sub>][PF<sub>6</sub>]<sub>4</sub>. Orange crystals (0.010 g, 32%) (Found: C, 51.3; H, 3.6; N, 8.4. C<sub>84</sub>H<sub>56</sub>Co<sub>2</sub>F<sub>24</sub>N<sub>12</sub>P<sub>4</sub> requires C, 52.2; H, 2.9; N, 8.7%). Mass spectrum (FAB): *m/z* 1786 {[Co<sub>2</sub>(pspy)<sub>2</sub>][PF<sub>6</sub>]<sub>3</sub>}<sup>+</sup>, 1641 {[Co<sub>2</sub>(pspy)<sub>2</sub>][PF<sub>6</sub>]<sub>2</sub>}<sup>+</sup>, 1496 {[Co<sub>2</sub>(pspy)<sub>2</sub>][PF<sub>6</sub>]}<sup>+</sup> and 695 [Co(psps)]<sup>+</sup>. <sup>1</sup>H NMR (CD<sub>3</sub>CN): δ -33, -18, 14, 17, 19, 24, 28, 33, 41, 43, 48, 55, 68, 131, 149 and 268.

[Ni<sub>2</sub>(pspy)<sub>2</sub>][PF<sub>6</sub>]<sub>4</sub>. Green solid (0.010 g, 32%) (Found: C, 41.9; H, 2.6; N, 9.0. C<sub>84</sub>H<sub>56</sub>F<sub>24</sub>N<sub>12</sub>Ni<sub>2</sub>P<sub>4</sub> requires C, 42.5; H, 2.7; N, 9.3%). Mass spectrum (FAB): *m/z* 1786 {[Ni<sub>2</sub>(pspy)<sub>2</sub>][PF<sub>6</sub>]<sub>3</sub>}<sup>+</sup>, 1641 {[Ni<sub>2</sub>(pspy)<sub>2</sub>][PF<sub>6</sub>]<sub>2</sub>}<sup>+</sup>, 1496 {[Ni<sub>2</sub>(pspy)<sub>2</sub>][PF<sub>6</sub>]}<sup>+</sup> and 695 [Ni(psps)]<sup>+</sup>.

[Zn<sub>2</sub>(pspy)<sub>2</sub>][PF<sub>6</sub>]<sub>4</sub>. Off-white solid (0.023 g, 73%). Mass spectrum (TOF): *m/z* 1508 {[Zn<sub>2</sub>(pspy)<sub>2</sub>][PF<sub>6</sub>]}<sup>+</sup>, 1362 [Zn<sub>2</sub>(pspy)<sub>2</sub>]<sup>+</sup>, 1297 [Zn(psps)]<sup>+</sup> and 681 [Zn(psps)]<sup>+</sup>.

[Cd<sub>2</sub>(pspy)<sub>2</sub>][PF<sub>6</sub>]<sub>4</sub>. Off-white solid (0.019 g, 58%) (Found: C, 49.2; H, 2.9; N, 8.2. C<sub>84</sub>H<sub>56</sub>Cd<sub>2</sub>F<sub>24</sub>N<sub>12</sub>P<sub>4</sub> requires C, 49.5; H, 2.8; N, 8.2%). Mass spectrum (TOF): *m/z* 1344 [Cd(psps)]<sup>+</sup> and 728 [Cd(psps)]<sup>+</sup>.

[Hg<sub>2</sub>(pspy)<sub>2</sub>][PF<sub>6</sub>]<sub>4</sub>. Off-white solid (0.028 g, 80%). Mass spectrum (TOF): *m/z* 2068 {[Hg<sub>2</sub>(psps)][PF<sub>6</sub>]<sub>3</sub>}<sup>+</sup>, 1778 {[Cd<sub>2</sub>(pspy)<sub>2</sub>][PF<sub>6</sub>]}<sup>+</sup>, 1432 [Cd(psps)]<sup>+</sup> and 816 [Cd(psps)]<sup>+</sup>.

[Fe<sub>2</sub>(tbspy)<sub>2</sub>][PF<sub>6</sub>]<sub>4</sub>. Dark red needles (0.030 g, 70%) (Found: C, 51.9; H, 3.3; N, 9.0. C<sub>100</sub>H<sub>88</sub>F<sub>24</sub>Fe<sub>2</sub>N<sub>12</sub>P<sub>4</sub> requires C, 51.9; H, 2.9; N, 8.7%). Mass spectrum (TOF): *m/z* 1130 {[Fe<sub>2</sub>(tbspy)<sub>2</sub>][PF<sub>6</sub>]<sub>2</sub>}<sup>+</sup>, 929 {[Fe(tbspy)][PF<sub>6</sub>]}<sup>+</sup> and 784 [Fe(tbspy)]<sup>+</sup>. <sup>1</sup>H NMR (CD<sub>3</sub>CN): δ 2, 5, 6, 7, 9, 15, 48, 49, 60 and 122.

[Co<sub>2</sub>(tbspy)<sub>2</sub>][PF<sub>6</sub>]<sub>4</sub>. Red needles (0.037 g, 86%) (Found: C, 55.4; H, 4.0; N, 8.2. C<sub>100</sub>H<sub>88</sub>Co<sub>2</sub>F<sub>24</sub>N<sub>12</sub>P<sub>4</sub> requires C, 55.7; H, 4.1; N, 7.8%). Mass spectrum (TOF): *m/z* 1574 [Co<sub>2</sub>(tbspy)<sub>2</sub>]<sup>+</sup>, 1517 [Co(tbspy)]<sup>+</sup> and 787 [Co(tbspy)]<sup>+</sup>. <sup>1</sup>H NMR (CD<sub>3</sub>CN): δ -19, 8, 13, 18, 28, 41, 47, 69, 131 and 150.

[Ni<sub>2</sub>(tbspy)<sub>2</sub>][PF<sub>6</sub>]<sub>4</sub>. Pale green needles (0.032 g, 74%) (Found: C, 55.4; H, 4.2; N, 7.7. C<sub>100</sub>H<sub>88</sub>F<sub>24</sub>N<sub>12</sub>Ni<sub>2</sub>P<sub>4</sub> requires C, 55.7; H, 4.1; N, 7.8%). Mass spectrum (TOF): *m/z* 1573 {[Ni<sub>2</sub>(tbspy)<sub>2</sub>][F]}<sup>+</sup>, 932 {[Ni(tbspy)][PF<sub>6</sub>]}<sup>+</sup>, 864 {[Ni(tbspy)][F]}<sup>+</sup> and 787 [Ni(tbspy)]<sup>+</sup>. <sup>1</sup>H NMR (CD<sub>3</sub>CN): δ 2, 7, 11, 14, 44, 60, 63, 66, 75 and 122.

[Zn<sub>2</sub>(tbspy)<sub>2</sub>][PF<sub>6</sub>]<sub>4</sub>. Cream needles (0.035 g, 74%) (Found: C, 54.3; H, 4.1; N, 7.7. C<sub>100</sub>H<sub>88</sub>F<sub>24</sub>N<sub>12</sub>P<sub>4</sub>Zn<sub>2</sub> requires C, 55.4; H, 4.1; N, 7.8%). Mass spectrum (TOF): *m/z* 1685 {[Zn<sub>2</sub>(tbspy)<sub>2</sub>][PF<sub>6</sub>][F]}<sup>+</sup>, 1540 {[Zn(tbspy)<sub>2</sub>][F]}<sup>+</sup>, 1293 {[Zn<sub>2</sub>(tbspy)][PF<sub>6</sub>]<sub>3</sub>}<sup>+</sup>, 1148 {[Zn<sub>2</sub>(tbspy)][PF<sub>6</sub>]}<sup>+</sup> and 938 [Zn(tbspy)][PF<sub>6</sub>]<sup>+</sup>.

[Cd<sub>2</sub>(tbspy)<sub>2</sub>][PF<sub>6</sub>]<sub>4</sub>. Cream solid (0.039 g, 69%) (Found: C, 53.0; H, 3.9; N, 7.3. C<sub>100</sub>H<sub>88</sub>Cd<sub>2</sub>F<sub>24</sub>N<sub>12</sub>P<sub>4</sub> requires C, 53.1; H, 3.9; N, 7.4%). Mass spectrum (TOF): *m/z* 2260 [Cd<sub>2</sub>(tbspy)<sub>2</sub>]<sup>+</sup>, 1568 [Cd(tbspy)<sub>2</sub>]<sup>+</sup> and 840 [Cd(tbspy)]<sup>+</sup>.

[Hg<sub>2</sub>(tbspy)<sub>2</sub>][PF<sub>6</sub>]<sub>4</sub>. Cream solid (0.032 g, 53%). Mass spectrum (TOF): *m/z* 1765 {[Hg<sub>2</sub>(tbspy)<sub>2</sub>][PF<sub>6</sub>]<sub>3</sub>}<sup>+</sup>, 1620 {[Hg<sub>2</sub>(tbspy)<sub>2</sub>][PF<sub>6</sub>]<sub>2</sub>}<sup>+</sup>, 1475 {[Hg<sub>2</sub>(tbspy)<sub>2</sub>][PF<sub>6</sub>]}<sup>+</sup>, 1120 [Hg<sub>2</sub>(tbspy)<sub>2</sub>]<sup>+</sup> and 665 [Hg(tbspy)]<sup>+</sup>.

#### Crystal-structure determination of [Zn<sub>2</sub>(pspy)<sub>2</sub>][PF<sub>6</sub>]<sub>4</sub>·2MeCN·2H<sub>2</sub>O

Pale yellow blocks of the compound were obtained from the diffusion of diethyl ether vapour into an acetonitrile solution.

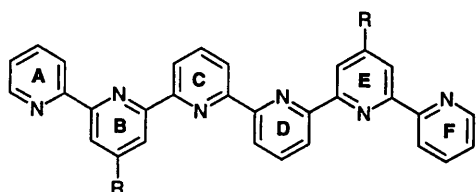
**Crystal data.** C<sub>88</sub>H<sub>66</sub>F<sub>24</sub>N<sub>14</sub>O<sub>2</sub>P<sub>4</sub>Zn<sub>2</sub>, yellow block, crystal size 0.12 × 0.18 × 0.35 mm, *M* = 2062.20, tetragonal, space group *P*4<sub>2</sub>2<sub>1</sub>2, *a* = 15.518(2), *c* = 18.443(1) Å, *U* = 4442 Å<sup>3</sup>, *F*(000) = 2088, *Z* = 2, *D*<sub>c</sub> = 1.542 g cm<sup>-3</sup>, μ(Cu-Kα) = 23.0 cm<sup>-1</sup>.

**Data collection and refinement.** The crystal selected for X-ray structure determination was stuck onto a glass fibre with oil and cooled to 223 K using an Oxford Cryostream low-temperature device. Unit-cell parameters were determined by the least-squares method using 20 carefully centred independent reflections. Data collection was carried out at 223 K on a four-circle Enraf-Nonius CAD4 diffractometer using monochromatised Cu-Kα radiation (λ = 1.541 80 Å). The ω-2θ technique was used to measure 5146 reflections in the range 5 ≤ 2θ ≤ 155°. Three standard reflections monitored every hour during data collection showed a rather high intensity loss of 25% which was corrected for during data reduction. This decay was attributed to solvent loss which could be slowed down but not completely stopped by cooling the sample. The 2810 unique data with *I* ≥ 3σ(*I*) were used to solve and refine the structure. The usual corrections were applied. The absorption correction was determined by ψ scans (maximum, minimum transmission 1.00, 0.76).

**Structural analysis and refinement.** The structure was solved by direct methods using the program SIR 92.<sup>15</sup> Anisotropic least-squares refinement on *F* was carried out on all non-hydrogen atoms except those of the acetonitrile and water solvent molecules using the program CRYSTALS.<sup>16</sup> The hydrogen atoms are in calculated positions with a fixed distance of 1.0 Å. Scattering factors were taken from ref. 17. The structure is built up around the special position 0,0,0 of the tetragonal space group *P*4<sub>2</sub>2<sub>1</sub>2. As the pspy is achiral and the synthesis is expected to yield a racemic mixture of *P* and *M* helicates, the chiral space group *P*4<sub>2</sub>2<sub>1</sub>2 is somewhat surprising. This could be the result of (1) a spontaneous separation of the racemic pair during the crystallisation process or (2) a twinning of the crystal used for the data collection. Refinement of the Flack enantiomorph parameter<sup>18</sup> led to a value of 0.48(6) causing a slight drop of the *R* value. This suggests that the second possibility is correct. As the metal centres in the dinuclear cation are generated by a centre of symmetry the contributions of the metals to anomalous scattering sum to zero. Therefore, information about the chirality can only be obtained from the anomalous dispersion of the heteroatoms P, O, N and F. Acetonitrile and water molecules are located in the cavities between the complex cations and are disordered. The PF<sub>6</sub> anions are also disordered and have been refined using restraints for bond lengths, angles and thermal parameters. A Chebyshev polynomial weighting scheme was applied. The final *R* values were 0.0638 and 0.0735 and the final Fourier-difference maps were featureless with no peaks greater than 0.80 e Å<sup>-3</sup>. Selected bond lengths and angles within the co-ordination spheres of the zinc atoms are presented in Table 1.

**Table 1** Bond lengths (Å) and angles (°) in the co-ordination sphere of the zinc atoms in the complex  $[\text{Zn}_2(\text{pspy})_2][\text{PF}_6]_4 \cdot 2\text{MeCN} \cdot 2\text{H}_2\text{O}$

Zn(1)–N(1)	2.210(4)	Zn(1)–N(3)	2.223(4)
Zn(1)–N(2)	2.064(4)		
N(1)–Zn(1)–N(1')	97.9(2)	N(1)–Zn(1)–N(3')	87.6(2)
N(1)–Zn(1)–N(2)	76.0(2)	N(2)–Zn(1)–N(3)	75.9(2)
N(1)–Zn(1)–N(2')	94.1(2)	N(2)–Zn(1)–N(3')	114.2(2)
N(2)–Zn(1)–N(2')	165.1(3)	N(3)–Zn(1)–N(3')	100.7(2)
N(1)–Zn(1)–N(3)	151.7(2)		



	R
spy	H
pspy	Ph
msspy	MeS
tbspy	4-Bu <sup>t</sup> C <sub>6</sub> H <sub>4</sub>

Atomic coordinates, thermal parameters, and bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1996, Issue 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 186/229.

## Discussion

### Synthesis of spy, pspy, msspy and tbspy

Although spy was first described in 1938,<sup>19</sup> the development of the co-ordination chemistry of this compound has been hindered by the lack of suitable high-yielding synthetic routes. Synthetic strategies involving Ullmann couplings of 6-bromo-2,2':6',2''-terpyridine or mixtures of 6,6'-dibromo-2,2'-bipyridine and 6-bromo-2,2'-bipyridine, the oxidative oligomerisation of pyridine by iron(III) chloride or the oxidative dimerisation of 2,2':6',2''-terpyridine (tpty) by iron(III) chloride were all investigated by Burstall<sup>19</sup> and found to be low yielding or inconvenient. More recently, we have shown that spy may be prepared by a Krohnke<sup>7</sup> pyridine synthesis, involving the reaction of 6,6'-bis(1-pyridinioacetyl)-2,2'-bipyridine diiodide with 2-[1-oxo-3'-(1''-pyrrolidino)propyl]pyridinium oxalate in the presence of ammonium acetate.<sup>20,21</sup> This effectively results in the generation of the B and the E rings (introducing a simple nomenclature in which the rings are labelled sequentially along the chain, beginning with A) and gives a crude product which may be recrystallised to give spy in 16% yield. This multi-stage synthesis is more convenient than those developed by Burstall,<sup>19</sup> but is still relatively inefficient, and hence general methods for the preparation of spy and its B,E-ring 4',4'''-diaryl-substituted derivatives were developed. Parallel studies by Potts and co-workers<sup>10,12</sup> have resulted in methods for the preparation of alkylsulfanyl-substituted derivatives of spy, and we have recently described approaches to C,D-ring<sup>22</sup> and other B,E-ring functionalised derivatives.<sup>13,23</sup>

We have previously used nickel(0) reagents for the symmetrical coupling of 6-halogeno-2,2'-bipyridines in the preparation of 2,2':6',2''-6''',2'''-quaterpyridine<sup>24</sup> and other

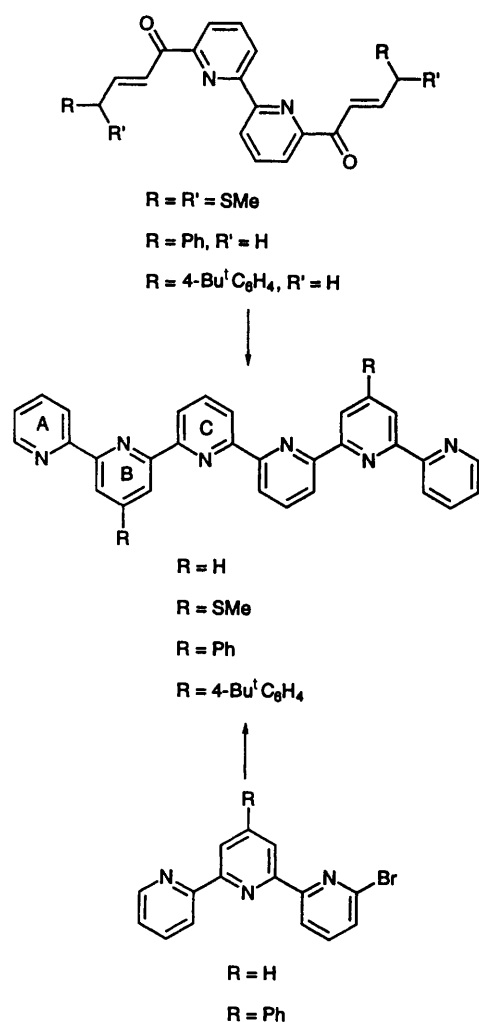
oligopyridines<sup>25–28</sup> and this methodology has now been employed for the preparation of spy.<sup>6</sup> The reaction of  $[\text{Ni}(\text{H}_2\text{O})_6]\text{Cl}_2$  or  $[\text{NiCl}_2(\text{PPh}_3)_2]$  with excess triphenylphosphine in degassed dmf followed by treatment with zinc dust gives a red suspension of  $[\text{Ni}(\text{PPh}_3)_n]$  ( $n = 3$  or 4) which is an effective *catalyst* for the coupling of haloarenes, with the zinc acting as the reducing agent and the nickel only being required in *catalytic* amounts.<sup>29</sup> In reactions involving the coupling of halopyridines to give oligopyridines which are effective metal chelators, it is necessary for *stoichiometric* amounts of nickel to be used, as the product oligopyridines co-ordinate to the nickel(II) preventing subsequent reduction by the zinc to regenerate the active nickel(0) species.<sup>24</sup> Although not a true template reaction,<sup>30</sup> the approach has advantages in terms of the ease of isolation of the desired product as the metal complex; at its simplest it is merely necessary to precipitate the nickel(II) complex as an appropriate salt.

The symmetrical coupling of 6-bromo-2,2':6',2''-terpyridine (btpty) by nickel(0) appeared to be a promising route to spy. The intermediate btpty is readily prepared in 64% yield from 2-bromo-6-(3'-dimethylammonio-1'-oxopropyl)pyridine chloride and [2'-oxo-2''-(2''-pyridyl)ethyl]pyridinium iodide in the presence of ammonium acetate. The <sup>1</sup>H NMR spectrum of a solution of 6-bromo-2,2':6',2''-terpyridine is entirely in accord with the proposed structure, and the assignments given in the Experimental section have been made on the basis of a double quantum filtered correlation spectroscopy experiment.

The addition of a dmf solution of btpty to a suspension of the nickel(0) reagent in dmf gives, after several hours of stirring at room temperature under dinitrogen, a viscous dark green slurry of nickel(II) complexes and unreacted zinc dust. The dmf is removed *in vacuo* to give a dark green pasty mass, which partially redissolves in water. Filtration effectively removes unreacted zinc dust and the bulk of the PPh<sub>3</sub> and gives a pale green aqueous filtrate. Treatment of the aqueous filtrate with  $[\text{NH}_4][\text{PF}_6]$  results in the precipitation of the pale green salt  $[\text{Ni}_2(\text{spy})_2][\text{PF}_6]_4$ . The FAB mass spectrum of this salt exhibits ions at  $m/z$  1480  $\{\text{Ni}_2(\text{spy})_2(\text{PF}_6)_3\}$ , 1335  $\{\text{Ni}_2(\text{spy})_2(\text{PF}_6)_2\}$ , 1190  $\{\text{Ni}_2(\text{spy})_2(\text{PF}_6)\}$ , 1045  $\{\text{Ni}_2(\text{spy})_2\}$ , 668  $\{\text{Ni}(\text{spy})(\text{PF}_6)\}$  and 523  $\{\text{Ni}(\text{spy})\}$  which are fully in accord with the dinuclear structure, and the complex is identical in all respects with that obtained unambiguously by the reaction of nickel(II) acetate with an authentic sample of spy.

In order to obtain unco-ordinated spy, rather than its nickel(II) complex, it is more convenient *not* to isolate the hexafluorophosphate salt. The best yields of spy were obtained if the pale green aqueous filtrate was immediately treated with an excess of potassium cyanide. This resulted in the formation of an off-white suspension of spy in a yellow solution containing  $[\text{Ni}(\text{CN})_4]^{2-}$ . The sexipyridine was filtered off and then purified by Soxhlet extraction [acetone–methanol–acetonitrile (3:2:1)] to give spy as a white solid in ~50% yield. This material is identical in all respects to that previously obtained.<sup>20,21</sup> The free spy may also be obtained from the isolated salt,  $[\text{Ni}_2(\text{spy})_2][\text{PF}_6]_4$ , by treatment of an aqueous acetonitrile solution with KCN, although yields are slightly lower and the method offers no significant advantages. The overall process is presented in Scheme 1. Alternative demetallation procedures with  $\text{Na}_4(\text{edta})$  [edta = (ethane-1,2-diyl)dinitrilo]tetraacetate or CO were unsuccessful.

In order to probe the effects of substituents upon the co-ordination behaviour of spy we also prepared a number of substituted derivatives. We concentrate here upon the effect of B and E ring substitution and the ligands 4',4'''-bis(methylsulfanyl)-2,2':6',2''-6''',2'''-6''''',2''''-6''''',2''''-sexipyridine (msspy)<sup>12</sup> and 4',4'''-bis(4-*tert*-butylphenyl)-2,2':6',2''-6''',2'''-6''''',2''''-sexipyridine (tbspy)<sup>13</sup> were prepared by the literature methods. We also prepared 4',4'''-diphenyl-2,2':6',2''-6''',2'''-6''''',2''''-sexipyridine (pspy) by the nickel(0) coupling of 6-bromo-4'-phenyl-2,2':6',2''-terpyridine, btpty



**Scheme 1** Alternative synthetic strategies for spy derivatives

(Scheme 1) and from the enone resulting from the condensation of benzaldehyde with 6,6'-diacetyl-2,2'-bipyridine.

In the first route all of the pyridine rings of the product are present in the bptpy precursor. The required intermediate bptpy was readily prepared by Krohnke methodology.<sup>7</sup> The reaction of 2-acetyl-6-bromopyridine with benzaldehyde in aqueous methanolic KOH gives the pale yellow enone 1-(6-bromo-2-pyridyl)-3-phenylprop-2-enone in high yield.<sup>11</sup> Subsequent reaction with [2'-oxo-2'-(2''-pyridyl)ethyl]pyridinium iodide in the presence of ammonium acetate resulted in the formation of bptpy as a white solid in 63% yield. The <sup>1</sup>H NMR spectrum of a solution of this compound was compatible with the structure, and the EI mass spectrum exhibited parent ions at *m/z* 389/387. The coupling of bptpy with nickel(0) proceeded in exactly the same manner as that of btpy, and after demetallation of the nickel(II) complexes with cyanide, pspy was obtained as a white solid in 23% yield. The <sup>1</sup>H NMR spectrum of a solution of this compound was fully compatible with the structure, and the EI mass spectrum exhibited a parent ion at *m/z* 617.

The second route involves the generation of the B and E rings with the incorporation of the C and D rings in a 2,2'-bipyridine unit. The condensation of 6,6'-diacetyl-2,2'-bipyridine with benzaldehyde in propan-2-ol in the presence of base gave the enone 6,6'-bis(1-oxo-3-phenylprop-2-enyl)-2,2'-bipyridine as a yellow crystalline solid in 67% yield. The reaction of this compound with [2'-oxo-2'-(2''-pyridyl)ethyl]pyridinium iodide and ammonium acetate in ethanolic solution yielded pspy in 65% yield. The product from this reaction was identical in all respects to that obtained from the nickel-coupling of bptpy. The

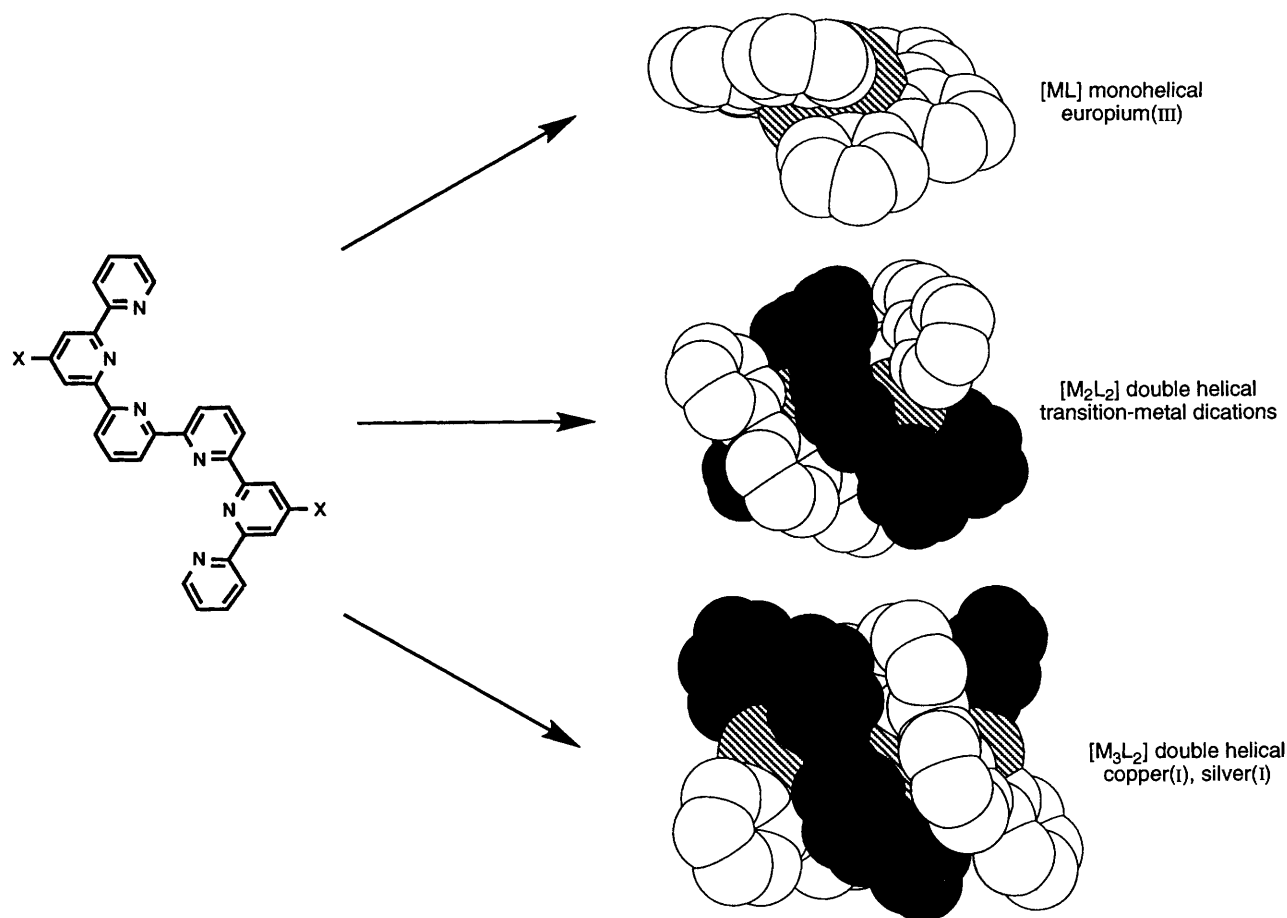
higher yields obtained in the second route are, in part, offset by the inconvenience of preparing the 6,6'-diacetyl-2,2'-bipyridine precursor.

### Transition-metal complexes

We have previously shown that spy forms double-helical dinuclear complexes  $[\text{M}_2(\text{spy})_2]^{4+}$  with a variety of divalent transition-metal ions which bind to a terdentate tpy functionality of each of two spy ligands,<sup>20,21</sup> although other nuclearities and topologies are possible (Scheme 2).<sup>31</sup> Independent studies with 4',4'''-alkylsulfanyl derivatives support these results and a structural analysis of  $[\text{Cu}_2(\text{msspy})_2][\text{PF}_6]_4$  also confirms the double-helical structure in this case.<sup>32</sup> This bonding mode is likely to be favoured by any suitably sized metal ion which can adopt a pseudo-octahedral six-co-ordinate geometry. We now describe a systematic study of the co-ordination behaviour of a variety of metal ions with the four ligands spy, msspy, pspy and tbspy.

The reaction of spy with  $[\text{Fe}(\text{H}_2\text{O})_6][\text{BF}_4]_2$  yields a deep purple solid for which microanalysis indicates a formulation  $\{\text{FeL}(\text{BF}_4)\}_n$ . The mass spectrum of this purple product exhibited intense peaks assigned to  $\{\text{Fe}_2(\text{spy})_2(\text{BF}_4)_3\}$ ,  $\{\text{Fe}_2(\text{spy})_2(\text{BF}_4)_2\}$ ,  $\{\text{Fe}_2(\text{spy})_2(\text{BF}_4)\}$  and  $\{\text{Fe}_2(\text{spy})_2\}$  strongly supporting the formulation of this compound as the double-helical species  $[\text{Fe}_2(\text{spy})_2][\text{BF}_4]_4$ . Modelling studies indicate that with spy ligands in which the only rotational freedom is about the interannular C–C bonds between  $\text{sp}^2$  hybridised centres, the dinuclear  $[\text{M}_2\text{L}_2]$  structure with six-co-ordinate metal centres must be double-helical (Scheme 2); no open face-to-face structures are possible. Similar red or purple complexes were isolated as the crystalline hexafluorophosphate salts  $[\text{Fe}_2\text{L}_2][\text{PF}_6]_4$  from analogous reactions with the ligands msspy, pspy and tbspy. In each case, mass spectrometric and microanalytical data were fully in accord with the formulation of the products as dinuclear double-helical species. It is interesting that although  $[\text{Fe}(\text{tpy})_2]^{2+}$  salts are low spin and diamagnetic, all of the complexes with spy ligands are paramagnetic and have paramagnetically shifted <sup>1</sup>H NMR spectra with peaks as far down field as  $\delta + 178$ . In general, the <sup>1</sup>H NMR spectra of the complexes were quite variable and complete assignment is not possible. A unique resonance at  $\delta - 16$  observed in the spectrum of  $[\text{Fe}_2(\text{spy})_2][\text{BF}_4]_4$  can, however, be assigned to  $\text{H}^{4\text{B}}$  which is only present with this ligand. The <sup>1</sup>H NMR spectrum of a CD<sub>3</sub>CN solution of  $[\text{Fe}_2(\text{spy})_2][\text{BF}_4]_4$  is presented in Fig. 1. For each of the iron complexes, the most down-field resonance is assigned to  $\text{H}^{6\text{A}}$  (the proton which is closest to the paramagnetic centre). The variation in this resonance reflects the dependence of the magnetic properties upon the precise geometry and metal–ligand interactions. However, in each case an appropriate number of proton environments consistent with the proposed structure was observed. In particular, only a single ligand environment was observed, which was symmetrical about the interannular bond between the C and D rings. The change to the high-spin iron(II) centre is associated with the introduction of substituents in the 6 position of the tpy ligand and the resultant distortion from local  $D_{2d}$  symmetry. Similar effects are observed in the complex  $[\text{Fe}(\text{dptpy})_2][\text{PF}_6]_2$  (dptpy = 4,6-diphenyl-2,2':6',2''-terpyridine).<sup>33</sup>

We have previously briefly described the electrochemical behaviour of  $[\text{Fe}_2(\text{spy})_2]^{2+}$  salts in which two reversible or quasi-reversible iron(II)–iron(III) processes are observed at +0.96 V and +1.11 V *vs.*  $\text{Fc}^+/\text{Fc}$  demonstrating a metal–metal interaction in the complex.<sup>20</sup> In contrast, acetonitrile solutions of  $[\text{Fe}_2(\text{pspy})_2][\text{PF}_6]_4$  exhibited only very broad and unresolved processes in their cyclic voltammetry. However, solutions of  $[\text{Fe}_2(\text{msspy})_2][\text{PF}_6]_4$  in acetonitrile exhibit two fully reversible oxidation waves at +0.83 and +0.96 V (*vs.*  $\text{Fc}^+/\text{Fc}$ ). The shifting to less positive potential in comparison to the



Scheme 2 Possible consequences of co-ordination of spy derivatives to metal ions

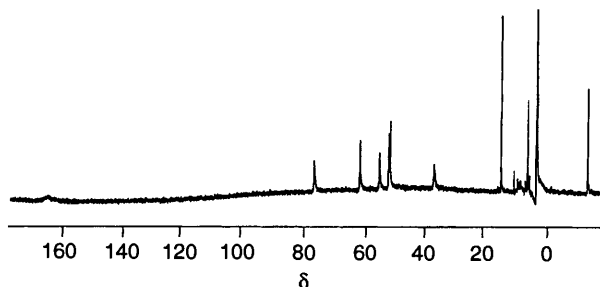


Fig. 1 Proton NMR spectrum of a  $\text{CD}_3\text{CN}$  solution of  $[\text{Fe}_2(\text{spy})_2][\text{BF}_4]_4$

spy complex indicates the greater stabilisation of iron(III) in msspy as a consequence of the electron-donating properties of the methylsulfanyl substituent. The reductive cyclic voltammogram of  $[\text{Fe}_2(\text{msspy})_2][\text{PF}_6]_4$  also exhibits four fully reversible waves at  $-1.19$ ,  $-1.38$ ,  $-1.65$  and  $-1.85$  V (*vs.*  $\text{Fc}-\text{Fc}^+$ ). The close similarity between these values and those for  $[\text{Fe}_2(\text{spy})_2][\text{BF}_4]_4$  ( $-1.17$ ,  $-1.37$ ,  $-1.67$  and  $-1.88$  V) indicates that the methylsulfanyl substituents have no significant effect on these ligand reductive processes. Interestingly, the complex  $[\text{Fe}_2(\text{tbspy})_2][\text{PF}_6]_4$  exhibited no metal-centred processes in its cyclic voltammogram, but four fully reversible waves at  $-1.12$ ,  $-1.30$ ,  $-1.62$  and  $-1.78$  V (*vs.*  $\text{Fc}-\text{Fc}^+$ ). We have no explanation for this anomalous behaviour with the tbspy ligand, although we note that similar results are obtained at glassy carbon and platinum electrodes.

The reaction of spy, pspy, msspy or tbspy with  $\text{Co}(\text{O}_2\text{CMe})_2$  in methanol yielded orange solutions, from which orange or red crystalline hexafluorophosphate salts could be precipitated by the addition of a methanolic solution of  $[\text{NH}_4][\text{PF}_6]$ . In each case, mass spectrometry exhibited ions assigned to the species  $\{\text{Co}_2(\text{L})_2(\text{PF}_6)_3\}$ ,  $\{\text{Co}_2(\text{L})_2(\text{PF}_6)_2\}$ ,  $\{\text{Co}_2(\text{L})_2(\text{PF}_6)\}$  and

$\{\text{Co}_2(\text{L})_2\}$  fully consistent with the formulation of the products as the dinuclear double-helical complexes  $[\text{Co}_2(\text{L})_2][\text{PF}_6]_4$ . Further evidence for the stoichiometry of the complexes was provided by elemental analyses which indicated a 1:1 Co to L ratio. These complexes are all paramagnetic and the  $^1\text{H}$  NMR spectra are paramagnetically shifted with resonances between  $\delta -30$  and  $+280$ . However, the number of resonances observed indicated that the solution species possessed a single ligand environment symmetrical about the interannular bond between the C and D rings.

A solution of  $[\text{Co}_2(\text{spy})_2][\text{PF}_6]_4$  in acetonitrile exhibited two fully reversible cobalt(II)–cobalt(III) processes at  $+0.44$  and  $+0.77$  V and four ligand-based reversible reductions at  $-0.91$ ,  $-1.07$ ,  $-1.97$  and  $-2.19$  V (*vs.*  $\text{Fc}-\text{Fc}^+$ ). The large difference between the two cobalt(II)–cobalt(III) potentials (0.33 V) suggests significant metal–metal interactions are occurring. Thus,  $[\text{Co}_2(\text{spy})_2]^{4+}$  acts as a dimetallic species with communicating metal centres and not as two independent  $[\text{Co}(\text{tpy})_2]^{2+}$  units. The cyclic voltammogram of an acetonitrile solution of  $[\text{Co}_2(\text{msspy})_2][\text{PF}_6]_4$  was generally similar and exhibited reversible processes at  $+0.64$  and  $+1.04$  V and four reductive processes at  $-0.96$ ,  $-1.12$ ,  $-1.92$  and  $-2.11$  V.<sup>32</sup> In contrast to the situation with iron, the incorporation of the methylsulfanyl substituents has resulted in a stabilisation of the cobalt(II) state relative to cobalt(III). We have noted similar effects in simple  $\text{Xtpy}$  ( $\text{X} = \text{Cl}$ ,  $\text{Me}_2\text{N}$ , *etc.*) complexes. As in the spy complex there is a strong metal–metal interaction as shown by the large potential difference (0.39 V) between the two metal-centred processes. The cyclic voltammogram of  $[\text{Co}_2(\text{pspy})_2][\text{PF}_6]_4$  exhibited cobalt(II)–cobalt(III) processes at  $+0.64$  and  $+0.95$  V and ligand-centred reduction processes at  $-0.78$ ,  $-0.97$ ,  $-1.47$  and  $-2.01$  V (*vs.*  $\text{Fc}-\text{Fc}^+$ ). Once again, the large potential separation between the two cobalt(II)–cobalt(III) processes (0.31 V) indicates a significant interaction

between the two metal centres. As with the iron complex, the *tbspy* ligand resulted in rather different electrochemical behaviour and no metal-centred redox processes were observed up to +1.5 V for  $[\text{Co}_2(\text{tbspy})_2][\text{PF}_6]_4^+$  (*vs.*  $\text{Fc}-\text{Fc}^+$ ) whilst to negative potentials only an absorption spike at -0.98 V was observed.

The addition of a methanolic solution of ammonium hexafluorophosphate to a solution of *spy* and nickel(II) acetate in methanol resulted in the precipitation of a pale green solid from which green needle-like crystals were obtained after recrystallisation. Similar green to blue products were obtained with the ligands *msspy*, *pspy* and *tbspy*. In the case of *spy*, the same complex was also formed in the coupling of 6-bromo-2,2':6',2''-bipyridine with a nickel(0) reagent. In each case, mass spectrometry showed major ions assigned to  $\{\text{Ni}_2(\text{L})_2(\text{PF}_6)_3\}$ ,  $\{\text{Ni}_2(\text{L})_2(\text{PF}_6)_2\}$ ,  $\{\text{Ni}_2(\text{L})_2(\text{PF}_6)\}$  and  $\{\text{Ni}_2(\text{L})_2\}$ . In combination with microanalytical data, these results strongly suggest that these compounds should also be formulated as dinuclear double-helical  $[\text{Ni}_2(\text{L})_2][\text{PF}_6]_4$  species. Although the complexes were paramagnetic and the  $^1\text{H}$  NMR spectra were both shifted and extremely broad, the number of resonances suggested that only a single highly symmetrical solution species was present.

The electrochemical behaviour of  $[\text{Ni}_2(\text{spy})_2][\text{PF}_6]_4$  is complex,<sup>20</sup> whereas  $[\text{Ni}_2(\text{msspy})_2][\text{PF}_6]_4$  exhibits no processes to positive potential and three reversible ligand-centred reduction processes at -1.40, -1.63 and -1.91 V (*vs.*  $\text{Fc}-\text{Fc}^+$ ). The cyclic voltammogram of an acetonitrile solution of  $[\text{Ni}_2(\text{pspy})_2][\text{PF}_6]_4$  exhibited just four reversible processes at -0.65, -1.00, -1.65 and -1.95 V (*vs.*  $\text{Fc}-\text{Fc}^+$ ). Similarly,  $[\text{Ni}_2(\text{tbspy})_2][\text{PF}_6]_4$  exhibited just three reversible reductive processes at -0.86, -1.21 and -1.45 V.

In conclusion, the presence of substituents on the *spy* ligands does not alter their ability to form dinuclear double-helical complexes with six-co-ordinate transition-metal ions. However, the presence of such substituents has a profound influence on the metal-ligand and metal-metal interactions. In particular, we note that the 4-*tert*-butylphenyl substituent, which we introduced as a solubilising group, has an unexpected effect upon the electrochemical behaviour of the complexes. Furthermore, the influence of substituents is not always easy to predict.

### Complexes with Group 12 metals

The studies described above establish the versatile character of the *spy* ligand in forming dinuclear double-helicates with first-row transition-metal ions. We also wished to probe the role of the metal centre, in particular its size, in helicate self-assembly. Unfortunately, although self-assembly is an excellent methodology when dealing with divalent first-row transition-metal ions which are kinetically labile, it is not usually applicable to the formation of the analogous second- and third-row transition-metal complexes, as a result of the kinetic inertness of such metal centres. However, the Group 12 metal ions undergo reasonably rapid ligand exchange reactions and we decided to make a systematic investigation of their behaviour with *spy* and its substituted derivatives.

The reaction of zinc(II) acetate with 1 equivalent of *spy* in methanol afforded a clear solution from which an off-white precipitate was produced upon addition of methanolic  $[\text{NH}_4][\text{PF}_6]$ . Off-white solids were also obtained from analogous reactions with *msspy*, *pspy* and *tbspy*. In each case, the FAB or TOF mass spectrum exhibited peaks assigned to  $\{\text{Zn}_2(\text{L})_2(\text{PF}_6)_3\}$ ,  $\{\text{Zn}_2(\text{L})_2(\text{PF}_6)_2\}$  and  $\{\text{Zn}_2(\text{L})(\text{PF}_6)\}$ . Microanalysis indicated a formulation  $\{\text{Zn}(\text{L})(\text{PF}_6)_2\}$  for each of these compounds. The divalent Group 12 metal ions possess a  $d^{10}$  electronic configuration and have no electronic (ligand-field) preference for a particular geometry. We cannot *a priori* assume that the zinc will be six-co-ordinate in these complexes and hence the assignment of a dinuclear double-helical structure is

less certain than with the first-row transition-metal ions discussed above. We return to this topic shortly.

Suspensions of *spy*, *msspy*, *pspy* or *tbspy* in methanol reacted with 1 equivalent of cadmium(II) acetate to form clear solutions from which off-white solids were precipitated upon the addition of methanolic ammonium hexafluorophosphate. Microanalysis indicated 1:1 metal to ligand ratios and the FAB or TOF mass spectra of the recrystallised products usually exhibited ions assigned to dinuclear  $\{\text{Cd}_2(\text{L})_2\}$  species, although these were absent from the TOF spectrum of the *pspy* complex.

The addition of a methanolic solution of ammonium hexafluorophosphate to a solution of *spy* and mercury(II) acetate afforded an off-white solid. Similar solids were obtained with *msspy*, *pspy* and *tbspy*. Once again, elemental analysis showed the complex to contain an equivalent number of ligands to metal ions whilst FAB or TOF mass spectrometry exhibited peaks assigned to  $\{\text{Hg}_2(\text{L})_2\}$  species.

Accordingly, with the Group 12 metal ions we have a series of complexes with each member of the triad and with a range of substituted ligands. What are these species?

The unambiguous entry to the series comes with the cadmium complexes, where we have previously shown that a dinuclear double-helical species  $[\text{Cd}_2(\text{spy})_2][\text{PF}_6]_4$  is present in both the solid state and in solution.<sup>20,21</sup> The  $^1\text{H}$  NMR spectra of  $\text{CD}_3\text{CN}$  solutions of the four cadmium complexes are listed in Table 2 and those of  $[\text{Cd}_2(\text{spy})_2][\text{PF}_6]_4$  and  $[\text{Cd}_2(\text{tbspy})_2][\text{PF}_6]_4$  are presented in Fig. 2. The first feature of note is that in each case a single set of resonances is obtained and that the ligands are symmetrical about the  $\text{C}_{\text{ring}}-\text{D}_{\text{ring}}$  interannular bond. When a substituent is present, only a single environment for it is observed. The similarity between the spectra of the known double-helical complex with *spy* is such that we can unambiguously assign dinuclear double-helical structures to all of these cadmium complexes.

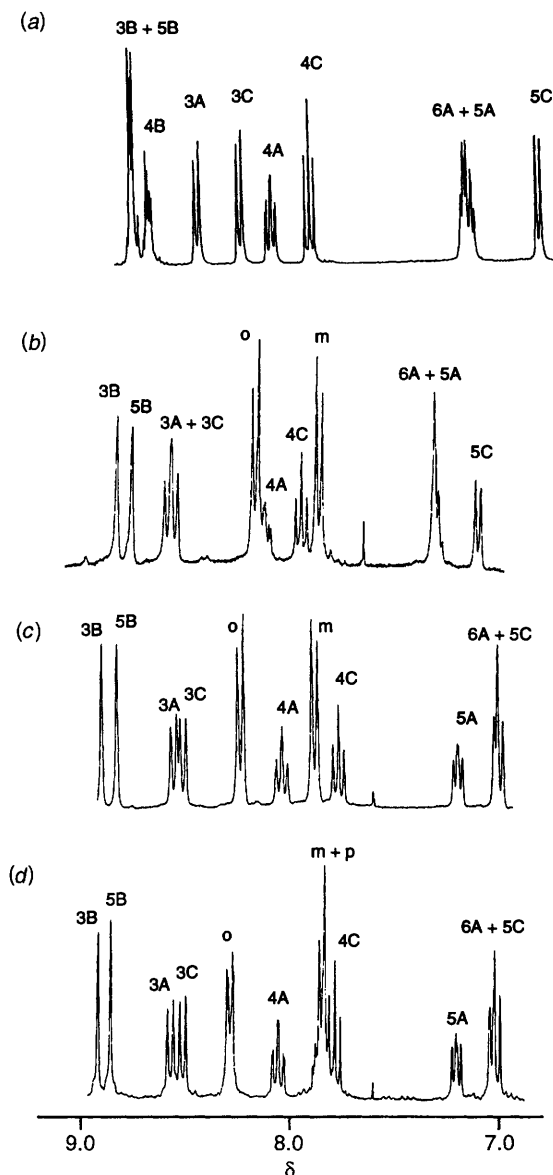
The  $^1\text{H}$  NMR spectra of solutions of the mercury(II) complexes are extremely similar to those of the corresponding cadmium complexes. The only significant changes occur in the shifts of  $\text{H}^{5\text{C}}$ , which is the resonance which will be most sensitive to changes in the twisting about the interannular bond between the C and D rings as the ligand is divided into the two tridentate *tpy* metal-binding domains. On the basis of the mass spectrometry and the  $^1\text{H}$  NMR spectra we can confidently assign the mercury(II) complexes as dinuclear double-helical complexes containing two six-co-ordinate mercury(II) centres.

There is a similar general resemblance between the  $^1\text{H}$  NMR spectra of the zinc complexes and their cadmium analogues, although there are rather more variations. In the cadmium complexes the highest field aromatic resonance is assigned to  $\text{H}^{5\text{C}}$  with  $\text{H}^{6\text{A}}$  and  $\text{H}^{5\text{A}}$  overlapping and lying to slightly lower field. In the zinc complexes,  $\text{H}^{6\text{A}}$  and  $\text{H}^{5\text{C}}$  are overlapping and to highest field with  $\text{H}^{5\text{A}}$  lying slightly down-field. Although cadmium(II) and mercury(II) are essentially the same size, zinc(II) is substantially smaller. It is not surprising, therefore, that  $\text{H}^{6\text{A}}$  which is closest to the metal centre experiences a different environment in the zinc complexes. The overall symmetry of the spectra is consistent with the formation of dinuclear double-helical complexes containing two six-co-ordinate zinc centres, but there are enough differences to leave some ambiguity. In Fig. 2 a series of spectra relating the structurally characterised complex  $[\text{Cd}_2(\text{spy})_2][\text{PF}_6]_4$  to the derivatives  $[\text{Cd}_2(\text{tbspy})_2][\text{PF}_6]_4$ ,  $[\text{Zn}_2(\text{tbspy})_2][\text{PF}_6]_4$  and  $[\text{Zn}_2(\text{pspy})_2][\text{PF}_6]_4$  is presented. Assuming that  $[\text{Zn}_2(\text{pspy})_2][\text{PF}_6]_4$  is a dinuclear double helix, so are all of the other zinc(II) complexes.

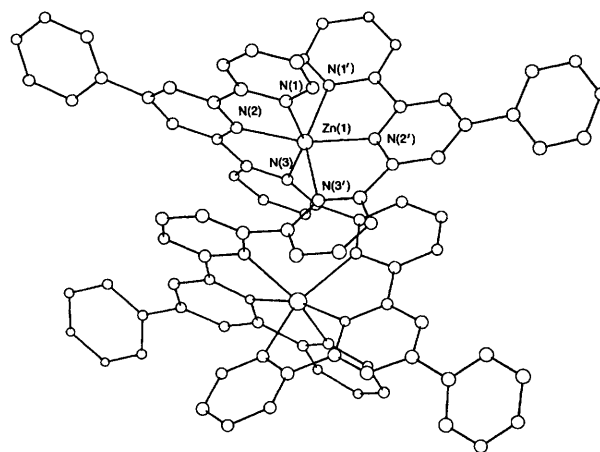
In order to confirm the solid-state formulation of the zinc complexes as double-helical species we have determined the crystal and molecular structure of the complex  $[\text{Zn}_2(\text{pspy})_2][\text{PF}_6]_4 \cdot 2\text{H}_2\text{O} \cdot 2\text{MeCN}$ . The structure of one of the two enantiomeric cations is presented in Fig. 3. The gross structure confirms our double-helical formulation for the zinc complexes of substituted *spy* ligands. Bond lengths and angles within the

**Table 2** Proton NMR data for CD<sub>3</sub>CN solutions of the Group 12 complexes

Complex	$\delta(^1\text{H})$													o	m	R	
	6A	5A	4A	3A	3B	4B	5B	5C	4C	3C							
[Zn <sub>2</sub> (spy) <sub>2</sub> ][PF <sub>6</sub> ] <sub>4</sub>	6.92	7.15	8.00	8.35	8.60	8.60	8.60	6.92	7.71	8.25							
[Zn <sub>2</sub> (msspy) <sub>2</sub> ][PF <sub>6</sub> ] <sub>4</sub>	6.97	7.17	7.96	8.35	8.31/8.24		8.24/8.31	6.90	7.80	8.35							2.93
[Zn <sub>2</sub> (pspy) <sub>2</sub> ][PF <sub>6</sub> ] <sub>4</sub>	7.03	7.20	8.04	8.54	8.81/8.88		8.81/8.88	7.01	7.77	8.48				8.25	7.83		7.83
[Zn <sub>2</sub> (tbspy) <sub>2</sub> ][PF <sub>6</sub> ] <sub>4</sub>	7.00	7.18	8.02	8.51	8.81/8.88		8.81/8.88	6.98	7.76	8.49				8.23	7.87		1.50
[Cd <sub>2</sub> (spy) <sub>2</sub> ][PF <sub>6</sub> ] <sub>4</sub>	7.22	7.22	8.05	8.37	8.80	8.65	8.80	6.92	7.89	8.18							
[Cd <sub>2</sub> (msspy) <sub>2</sub> ][PF <sub>6</sub> ] <sub>4</sub>	7.21	7.21	8.00	8.33	8.17/8.22		8.22/8.17	7.03	7.90	8.37							2.96
[Cd <sub>2</sub> (pspy) <sub>2</sub> ][PF <sub>6</sub> ] <sub>4</sub>	7.23	7.23	8.03	8.48	8.62/8.72		8.62/8.72	7.05	7.85	8.45				8.08	7.71		7.71
[Cd <sub>2</sub> (tbspy) <sub>2</sub> ][PF <sub>6</sub> ] <sub>4</sub>	7.25	7.25	8.09	8.51	8.70/8.77		8.70/8.77	7.04	7.90	8.51				8.09	7.81		1.50
[Hg <sub>2</sub> (spy) <sub>2</sub> ][PF <sub>6</sub> ] <sub>4</sub>	7.21	7.27	8.02	8.34	8.60	8.60	8.60	7.01	7.87	8.23							
[Hg <sub>2</sub> (msspy) <sub>2</sub> ][PF <sub>6</sub> ] <sub>4</sub>	7.25	7.25	7.94	8.24	8.08/8.22		8.22/8.08	7.30	7.87	8.32							2.94
[Hg <sub>2</sub> (pspy) <sub>2</sub> ][PF <sub>6</sub> ] <sub>4</sub>	7.30	7.30	8.01	8.53	8.62/8.74		8.62/8.74	7.30	7.83	8.45				8.06	7.67		7.67
[Hg <sub>2</sub> (tbspy) <sub>2</sub> ][PF <sub>6</sub> ] <sub>4</sub>	7.28	7.28	8.02	8.50	8.65/8.76		8.65/8.76	7.28	7.81	8.45				8.07	7.74		1.47

**Fig. 2** Proton NMR spectra of CD<sub>3</sub>CN solutions of (a) [Cd<sub>2</sub>(spy)<sub>2</sub>][PF<sub>6</sub>]<sub>4</sub>, (b) [Cd<sub>2</sub>(tbspy)<sub>2</sub>][PF<sub>6</sub>]<sub>4</sub>, (c) [Zn<sub>2</sub>(tbspy)<sub>2</sub>][PF<sub>6</sub>]<sub>4</sub> and (d) [Zn<sub>2</sub>(pspy)<sub>2</sub>][PF<sub>6</sub>]<sub>4</sub>

co-ordination sphere of the zinc are presented in Table 1. Each zinc is co-ordinated to three nitrogen atoms of a tpy unit of each of two ligands. The zinc–nitrogen distances of 2.064–2.223 Å are typical for zinc oligopyridine complexes.<sup>34</sup> The double-helical structure is achieved by a twisting of 68.6° about the

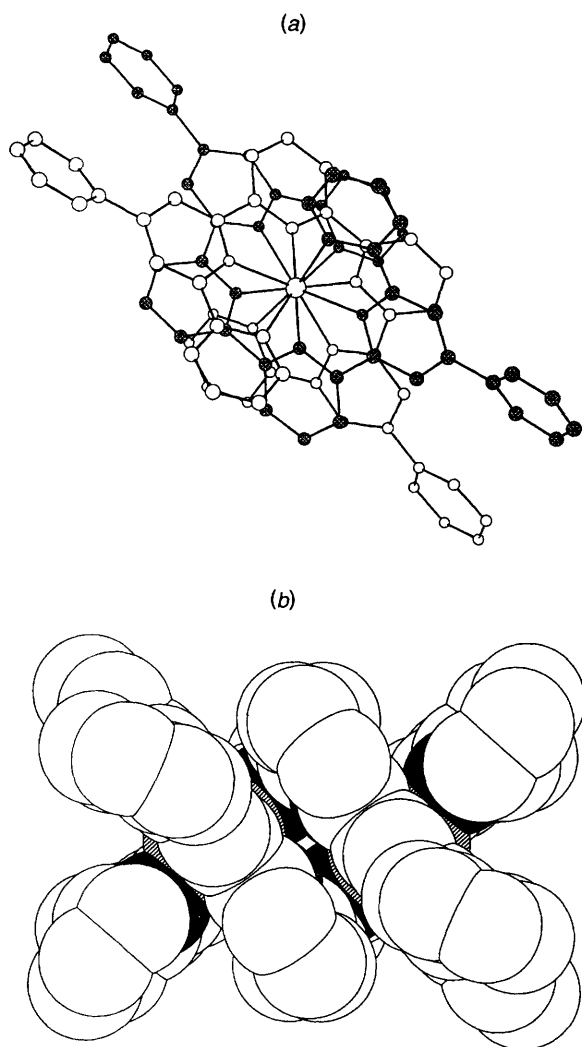
**Fig. 3** View of one of the enantiomeric [Zn<sub>2</sub>(pspy)<sub>2</sub>]<sup>4+</sup> cations present in the lattice of [Zn<sub>2</sub>(pspy)<sub>2</sub>][PF<sub>6</sub>]<sub>4</sub>·2MeCN·2H<sub>2</sub>O showing the numbering scheme adopted for the nitrogen and zinc atoms. Hydrogen atoms have been omitted for clarity

interannular bond connecting rings C and D; the other directly linked rings are close to co-planar (A–B, 7.0°; B–C, 4.3°). The pendant phenyl rings are twisted at an angle of 30.3° with respect to the directly bonded ring B, as observed in a range of other 4'-substituted 2,2':6',2''-terpyridine ligands.<sup>35</sup> A view along the Zn...Zn axis is presented in Fig. 4(a), together with a space-filling representation to emphasise the helical structure in Fig. 4(b). There are no interactions between the pendant phenyl groups, which have centroid–centroid contacts of over 9 Å. However, there is a noticeable  $\pi$ -stacking interaction between ring B of one ligand strand with ring C of the other strand; the shortest centroid–atom contacts are of the order 3.4 Å indicating a significant stacking. The Zn...Zn distance is 4.714 Å, which is significantly longer than the 4.33 Å observed in a related complex with a septipyridine ligand. The structural characterisation of this key complex establishes the double-helical nature of the remaining zinc complexes.

The electrochemical behaviour of these Group 12 complexes has proved to be of some interest. The cyclic voltammogram of [Zn<sub>2</sub>(spy)<sub>2</sub>][PF<sub>6</sub>]<sub>4</sub> in acetonitrile showed only fully reversible reduction waves at –1.41, –1.54, –1.78 and –1.99 V (*vs.* Fc–Fc<sup>+</sup>). The absence of any metal oxidation processes was not surprising since Zn<sup>2+</sup> resides in the very stable t<sub>2g</sub><sup>6</sup>e<sub>g</sub><sup>4</sup> configuration upon co-ordination to a strong-field ligand. Similar results are observed for the other zinc complexes. The remarkable similarity between the reduction potentials infers that the substituents are not having a significant effect on the ligand manifold.

The oxidative cyclic voltammogram of [Cd<sub>2</sub>(spy)<sub>2</sub>][PF<sub>6</sub>]<sub>4</sub> showed no metal-based redox processes as expected. The





**Fig. 4** Views of the  $[\text{Zn}_2(\text{pspy})_2]^{4+}$  cation (a) along the  $\text{Zn} \cdots \text{Zn}$  axis and (b) a space-filling representation to emphasise the helical character. The two ligand strands have been differently shaded

reductive cycle showed the usual four ligand-based reversible reductive processes at  $-1.44$ ,  $-1.60$ ,  $-1.90$  and  $-2.01$  V (vs.  $\text{Fc-Fc}^+$ ). Of interest, however, is the presence of an asymmetric reductive wave at  $-0.72$  V which increases in intensity with increasing scans of the reductive cycle of the voltammogram with a concomitant change in the four reversible waves. Since there are no oxidative processes the appearance of the absorption spike suggests that a ligand-centred ligand radical complex is being electrogenerated. A similar situation was observed for  $[\text{Cd}_2(\text{tbspy})_2][\text{PF}_6]_4$ . In the case of  $[\text{Cd}_2(\text{pspy})_2][\text{PF}_6]_4$ , an acetonitrile solution of the complex showed only two reversible reductive processes.

In contrast to the analogous zinc and cadmium complexes, the cyclic voltammogram of the mercury complexes showed none of the usual ligand reductions only asymmetric absorption spikes. These are undoubtedly ligand-based reductions with the probable subsequent ejection of metal and concomitant liberation of free ligand.

## Conclusion

We have established that the incorporation of substituents onto rings B and E of a spy ligand does not effect the formation of dinuclear double-helical complexes with first-row transition-metal ions, although significant changes in the metal-ligand and metal-metal interactions are observed in the electrochemical behaviour. For the first time, we have established the role of metal ion size within a triad and established that all of the

Group 12 metal ions form double-helical complexes with a range of spy ligands. We are currently further investigating the electrochemical properties of these complexes.

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