Dinuclear Double Helicates incorporating a 1,3-Phenylene Spacer; the Crystal and Molecular Structure of Diacetato-$1\kappa^2O$-,$2\kappa^2O$-bis[μ-1,3-bis(4-methylthio-2,2'-bipyridin-6-yl)benzene-$1\kappa^2N,N'$:$2\kappa^2N'',N'''$]dinickel Bis(hexafluorophosphate)†

Edwin C. Constable,*[a] **Michael J. Hannon**[a] and **Derek A. Tocher***[b]
[a] *Cambridge Centre for Molecular Recognition, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW, UK*
[b] *Department of Chemistry, University College London, 20 Gordon St., London WC1H 0AJ, UK*

Linking two bipyridine units by a 1,3-phenylene spacer has provided a novel class of ligand which promotes the spontaneous self-assembly of double helicates upon reaction with transition-metal ions. Interaction with copper(I) or silver(I) resulted in dinuclear double-helical complexes with the metal ions occupying pseudo-tetrahedral co-ordination sites. Reaction with cobalt(II) or nickel(II) acetates gave similar dinuclear double-helical structures with a didentate acetate ligand completing the co-ordination sphere of each metal to give a pseudo-octahedral geometry. The crystal structure of $[Ni_2L^2{}_2(O_2CMe)_2][PF_6]_2$ [L^2 = 1,3-bis(4-methylthio-2,2'-bipyridin-6-yl)benzene] has been determined. The two metal centres are separated by 5.875 Å. In contrast to the helicates formed by the linear oligopyridines, no significant π-stacking interactions are observed between pyridine moieties on the helical strands.

There has been much recent interest in the self-assembly of supramolecular species.[1] We and others have used the preferred co-ordination numbers and geometries of transition-metal ions to control the assembly of oligopyridine ligand strands to give complexes with helical topologies.[2] Much of this work has utilised the established co-ordination chemistry of the lower oligopyridines 2,2'-bipyridine (bipy) and 2,2':6',2''-terpyridine (terpy). Linking these subunits directly [to give the higher oligopyridines 2,2':6',2'':6'',2''':6''',2''''-quinquepyridine (qpy) and 2,2':6',2'':6'',2''':6''',2'''':6'''',2'''''-sexipyridine] or with aliphatic spacers results in ligands which assemble double helicates upon reaction with appropriate transition-metal ions. We are interested in using the properties of metal ions to control the interannular twisting between aromatic groups on ligand strands as a method of helicate formation. The higher oligopyridines may form mononuclear monohelical or dinuclear double-helical complexes, and the balance between the two structures may be subtle and finely controlled. The placing of a phenylene link into the ligand strand prevents the formation of mononuclear complexes whilst maintaining the wide variety of metal ions that may be used to induce helication. Phenylene spacers have not previously been used for helicate formation. They have the advantage that the concepts and lessons learnt in oligopyridine chemistry may be applied without the introduction of the greater degree of rotational freedom produced by sp^3 centres. Williams and co-workers[3] have reported the formation of mononuclear copper complexes with a ligand in which bipy groups are linked by a 2,2'-biphenylene spacer.

In this paper we report the preparation of ligands in which two bipy groups are linked by a 1,3-phenylene spacer and demonstrate the formation of a range of dinuclear double-helical complexes. A preliminary report of this work has appeared.[4]

Experimental

Infrared spectra were recorded on a Perkin Elmer 1710 or Philips PU9624 Fourier-transform spectrophotometer, with the samples in compressed KBr discs. Proton NMR spectra were recorded on a Brüker WM250 spectrometer. Fast atom bombardment (FAB) and electron-impact (EI) mass spectra were recorded on a Kratos MS-50 spectrometer, with 3-nitrobenzyl alcohol as matrix for the FAB spectra. Electrochemical measurements were performed using an AMEL model 553 potentiostat, model 567 function generator and model 721 integrator connected to an X-Y recorder *via* an AMEL model 560/A interface. A conventional three-electrode configuration was used, with platinum-bead working and auxiliary electrodes and an Ag–AgCl reference. Acetonitrile, freshly distilled from CaH_2 and then P_4O_{10}, was used as solvent in all cases. The base electrolyte was 0.1 mol dm^{-3} $[NBu^n{}_4][BF_4]$, recrystallised from ethanol–water and rigorously dried. Potentials are quoted *vs.* the ferrocene–ferrocenium couple (0.0 V), and all potentials were referenced to internal ferrocene added at the end of each experiment. 1,3-Diacetylbenzene, potassium *tert*-butoxide and other reagents were used as supplied; *N*-[2-oxo-2-(2-pyridyl)-ethyl]pyridinium iodide[5] and 3,3-bis(methylthio)-1-(2-pyridyl)-prop-2-en-1-one[6] were prepared according to published procedures.

Preparations.—1,3-*Bis*(3-*dimethylammonio*-1-*oxopropyl*)-*benzene dichloride*. A mixture of dimethylammonium chloride (2.4 g, 30 mmol), paraformaldehyde (5.0 g, 0.17 mol) and 1,3-diacetylbenzene (2.4 g, 6.2 mmol) was heated to reflux in ethanol (30 cm^3) containing three drops of concentrated hydrochloric acid for 4 h. After this period a further portion of paraformaldehyde (1.0 g) was added and the heating continued for 4 h. Upon cooling the reaction mixture the salt precipitated as a white solid (1.72 g, 79%). IR (KBr): 3419s, 3057m, 2800–2400(br)m, 1684s, 1601m, 1469m, 1413m, 1389m, 1344m, 1252m, 1203s, 1074m, 1036w, 998w, 963w, 789m, 754w and 678w cm^{-1}. Mass spectrum (FAB): m/z 277 (P + H). ^{1}H NMR

---

† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1993, Issue 1, pp. xxiii–xxviii.

(CD_3OD): δ 8.70 (1 H, s, H^a), 8.35 (2 H, d, H^b), 7.75 (1 H, t, H^c), 3.75, 3.60 (8 H, AB, CH_2CH_2) and 3.0 (12 H, s, CH_3).

1,3-*Bis*(2,2′-*bipyridin*-6-*yl*)*benzene* (L^1). *Method* 1. 1,3-Bis(3-dimethylammonio-1-oxopropyl)benzene dichloride (0.72 g, 2.05 mmol), *N*-[2-oxo-2-(2-pyridyl)ethyl]pyridinium iodide (1.09 g, 4.17 mmol) and ammonium acetate (7.4 g) were heated to reflux in glacial acetic acid for 4 h. On cooling a black precipitate formed and was filtered off, dissolved in chloroform and purified by chromatography on a silica column by elution with chloroform–diethyl ether (1 : 1) to give the required compound (0.24 g, 30%) as a white or very pale yellow solid. Recrystallisation from methanol gave the analytically pure ligand (Found: C, 78.7; H, 4.9; N, 13.6. Calc. for $C_{26}H_{18}N_4\cdot0.5MeOH$: C, 79.1; H, 5.0; N, 13.9%). IR (KBr): 1580s, 1561s, 1464m, 1423s, 1384m and 770vs cm^{-1}. Mass spectrum (EI): *m*/*z* 386 (*P*), 308 (*P* − py) and 231 (*P* − 2py).

Method 2. A solution of $NiCl_2\cdot6H_2O$ (2.29 g, 10 mmol) and 1,3-bis(4-methylthio-2,2′-bipyridin-6-yl)benzene (0.23 g, 0.48 mmol) in ethanol (50 cm^3) was stirred under nitrogen in an ice-bath and a solution of $Na[BH_4]$ (1.0 g, 26 mmol) in 40% aqueous sodium hydroxide (10 cm^3) was added slowly over 4 h. The mixture was then heated to reflux for 24 h, after which it was filtered hot through Celite. The Celite was washed with hot ethanol (3 × 15 cm^3) and the khaki coloured filtrates were combined and taken to dryness. The off-white solid was washed with water to give the required product (0.11 g, 60%) identical in all respects to that prepared by method 1.

1,3-*Bis*(4-*methylthio*-2,2′-*bipyridin*-6-*yl*)*benzene* (L^2). 3,3-Bis(methylthio)-1-(2-pyridyl)prop-2-en-1-one (14.0 g, 61.6 mmol) was added to a suspension of 1,3-diacetylbenzene (5.0 g, 30 mmol) and potassium *tert*-butoxide (14.0 g, 126 mmol) in tetrahydrofuran (thf) (200 cm^3) and the mixture stirred at room temperature under an atmosphere of dinitrogen for 4 h. After this period the flask was fitted with an air condensor, acetic acid (50 cm^3) and ammonium acetate (10.0 g) were added and the mixture was boiled for 3 h. After cooling the reaction mixture was treated with water (100 cm^3) and the solid recrystallised from EtOH–dimethylformamide (dmf) in the presence of activated charcoal to yield the required product (8.6 g, 60%) (Found: C, 69.8; H, 4.7; N, 11.6. Calc. for $C_{28}H_{22}N_4S_2$: C, 70.2; H, 4.7; N, 11.7%). IR (KBr): 1573s, 1563s, 1538s, 1473w, 1438w, 1393m, 1373w, 1082m and 792s cm^{-1}. Mass spectrum (FAB): *m*/*z* 479 (*P* + H).

$[Ni_2L^1_2(O_2CMe)_2][PF_6]_2$. The salt $Ni(O_2CMe)_2\cdot4H_2O$ (0.039 g, 0.16 mmol) and L^1 (0.06 g, 0.16 mmol) were heated to reflux in methanol (10 cm^3) for 4 h. The resulting clear lime-green solution was then treated whilst hot with methanolic $[NH_4][PF_6]$. On cooling green crystals of $[Ni_2L^1_2(O_2CMe)_2][PF_6]_2$ separated (0.074 g, 73%). IR (KBr): 1606m, 1596m, 1576m, 1563m, 1533m, 1489w, 1464s, 1455s, 1446s, 1429w, 848vs, 776s and 559s cm^{-1}. Mass spectrum (FAB): *m*/*z* 443 $[NiL^1]$, 503 $[NiL^1(O_2CMe)]$, 830 $[NiL^1_2]$, 889 $[Ni_2L^1_2]$, 1093 $[Ni_2L^1_2(O_2CMe)(PF_6)]$ and 1153 $[Ni_2L^1_2(O_2CMe)_2(PF_6)]$ (Found: C, 50.9; H, 3.4; N, 8.4. Calc. for $C_{56}H_{42}F_{12}N_8Ni_2O_4P_2\cdot H_2O$: C, 51.0; H, 3.3; N, 8.5%).

$[Ni_2L^2_2(O_2CMe)_2][PF_6]_2$. The salt $Ni(O_2CMe)_2\cdot4H_2O$ (0.026 g, 0.1 mmol) and L^2 (0.05 g, 0.1 mmol) were heated to reflux in methanol (10 cm^3) for 5 h. The resulting clear emerald-green solution was then treated whilst hot with methanolic $[NH_4][PF_6]$. On cooling emerald-green crystals of $[Ni_2L^2_2(O_2CMe)_2][PF_6]_2$ separated (0.061 g, 79%). IR (KBr): 1606w, 1587s, 1573s, 1532s, 1487m, 1451m, 1410w, 846vs, 788m and 558s cm^{-1}. Mass spectrum (FAB): *m*/*z* 535 $[NiL^2]$, 593 $[NiL^2(O_2CMe)]$, 1191 $[Ni_2L^2_2(O_2CMe)_2]$ and 1337 $[Ni_2L^2_2(O_2CMe)_2(PF_6)]$ (Found: C, 47.3; H, 3.5; N, 7.1. Calc. for $C_{60}H_{50}F_{12}N_8Ni_2O_4P_2S_4\cdot2H_2O$: C, 47.4; H, 3.6; N, 7.4%).

$[Co_2L^1_2(O_2CMe)_2][PF_6]_2$. The salt $Co(O_2CMe)_2\cdot4H_2O$ (0.039 g, 0.16 mmol) and L^1 (0.06 g, 0.16 mmol) were heated to reflux in methanol (10 cm^3) for 4 h. The resulting clear red solution was treated with methanolic $[NH_4][PF_6]$ and cooled to give orange crystals of $[Co_2L^1_2(O_2CMe)_2][PF_6]_2$ (0.067 g, 67%). IR (KBr): 1595s, 1562m, 1539s, 1488s, 1465s, 1446s, 848vs, 778s and 559s cm^{-1}. Mass spectrum (FAB): *m*/*z* 444 $[CoL^1]$, 504 $[CoL^1(O_2CMe)]$, 829 $[CoL^1_2]$, 890 $[Co_2L^1_2]$, 1009 $[Co_2L^1_2(O_2CMe)_2]$, 1095 $[Co_2L^1_2(O_2CMe)(PF_6)]$ and 1153 $[Co_2L^1_2(O_2CMe)_2(PF_6)]$ (Found: C, 49.1; H, 3.1; N, 7.9. Calc. for $C_{56}H_{42}Co_2F_{12}N_8O_4P_2\cdot2H_2O$: C, 50.4; H, 3.4; N, 8.4%).

$[Co_2L^2_2(O_2CMe)_2][PF_6]_2$. The salt $Co(O_2CMe)_2\cdot4H_2O$ (0.026 g, 0.1 mmol) and L^2 (0.05 g, 0.1 mmol) were heated to reflux in methanol (10 cm^3) for 6 h. The resulting orange solution was filtered and the filtrate treated with methanolic $[NH_4][PF_6]$. On cooling orange crystals of $[Co_2L^2_2(O_2CMe)_2][PF_6]_2$ separated (0.062 g, 80%). IR (KBr): 1606w, 1586s, 1573s, 1531m, 1485w, 1450m, 1410w, 844vs, 789m and 558s cm^{-1}. Mass spectrum (FAB): *m*/*z* 536 $[CoL^2]$, 595 $[CoL^2(O_2CMe)]$, 1016 $[CoL^2_2]$, 1105 $[Co_2L^2_2]$ and 1337 $[Co_2L^2_2(O_2CMe)_2(PF_6)]$ (Found: C, 46.7; H, 3.5; N, 7.4. Calc. for $C_{60}H_{50}Co_2F_{12}N_8O_4P_2S_4\cdot3H_2O$: C, 46.9; H, 3.6; N, 7.3%).

$[Ag_2L^1_2][PF_6]_2$. The salt $Ag(O_2CMe)$ (0.022 g, 0.13 mmol) and L^1 (0.05 g, 0.13 mmol) were heated to reflux in methanol (10 cm^3) for 7 h. The resulting colourless solution was treated with methanolic $[NH_4][PF_6]$ and the white precipitate filtered off and recrystallised from acetonitrile by the slow diffusion of ether to yield colourless blocks of $[Ag_2L^1_2][PF_6]_2$ (0.058 g, 69%). IR (KBr): 1600m, 1574s, 1472s, 1446s, 1427m, 844vs, 774s and 559s cm^{-1}. Mass spectrum (FAB): *m*/*z* 493 $[AgL^1]$, 601 $[Ag_2L^1]$, 879 $[AgL^1_2]$, 989 $[Ag_2L^1_2]$ and 1133 $[Ag_2L^1_2(PF_6)]$ (Found: C, 48.6; H, 2.6; N, 9.0. Calc. for $C_{52}H_{36}Ag_2F_{12}N_8P_2$: C, 48.8; H, 2.8; N, 8.8%).

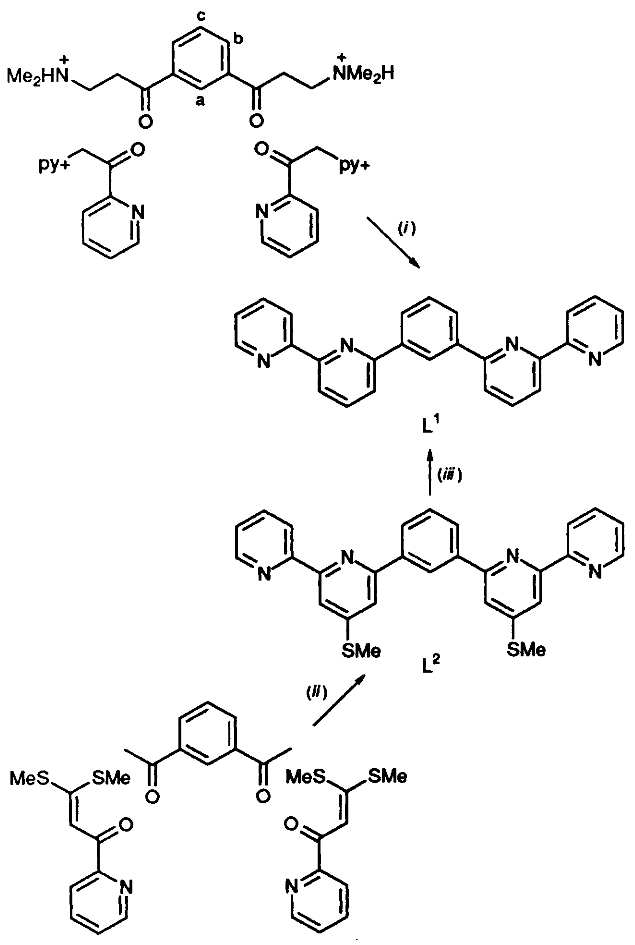
$[Ag_2L^2_2][BF_4]_2$. The salt $Ag(O_2CMe)$ (0.009 g, 0.055 mmol) and L^2 (0.025 g, 0.055 mmol) were heated to reflux in methanol (10 cm^3) for 6 h and the resulting colourless solution treated with methanolic $[NH_4][BF_4]$. The white precipitate was collected and recrystallised from acetonitrile by slow diffusion of ether to yield pale yellow crystals of $[Ag_2L^2_2][BF_4]_2$ (0.027 g, 77%). IR (KBr): 1579s, 1566s, 1537s, 1479m, 1444m, 1400m, 1058s, 792s and 686m cm^{-1}. Mass spectrum (FAB): *m*/*z* 585 $[AgL^2]$, 693 $[Ag_2L^2]$, 1064 $[AgL^2_2]$ and 1259 $[Ag_2L^2_2(BF_4)]$ (Found: C, 45.8; H, 3.0; N, 7.7. Calc. for $C_{56}H_{44}Ag_2F_{12}N_8P_2S_4$: C, 46.0; H, 3.0; N, 7.7%).

$[Cu_2L^1_2][PF_6]_2$. *Method* 1. The salt $[Cu(MeCN)_4][PF_6]$ (0.05 g, 0.13 mmol) and L^1 (0.052 g, 0.13 mmol) were heated to reflux in acetonitrile (10 cm^3) for 4 h. The resulting red solution was taken to dryness and the red solid washed with a small amount of cold methanol. Recrystallisation from acetonitrile by slow diffusion of ether yielded deep red blocks of $[Cu_2L^1_2][PF_6]_2$ (0.06 g, 76%). IR (KBr): 1593s, 1586s, 1563s, 1472m, 1445s, 1385s, 844vs, 772s and 558s cm^{-1}. Mass spectrum (FAB): *m*/*z* 449 $[CuL^1]$, 836 $[CuL^1_2]$, 900 $[Cu_2L^1_2]$ and 1046 $[Cu_2L^1_2(PF_6)]$ (Found: C, 50.2; H, 3.0; N, 8.8. Calc. for $C_{52}H_{36}Cu_2F_{12}N_8P_2\cdot3H_2O$: C, 50.2; H, 3.3; N, 9.0%).

Method 2. The salt $Cu(O_2CMe)_2\cdot H_2O$ (0.026 g, 0.125 mmol) and L^1 (0.05 g, 0.125 mmol) were heated to reflux in methanol (10 cm^3) for 8 h and the red solution treated with methanolic $[NH_4][PF_6]$ to give a deep red precipitate of $[Cu_2L^1_2][PF_6]_2$ (0.031 g, 40%).

$[Cu_2L^2_2][PF_6]_2$. *Method* 1. The salt $[Cu(MeCN)_4][PF_6]$ (0.023 g, 0.063 mmol) and L^2 (0.03 g, 0.063 mmol) were heated to reflux in degassed methanol (10 cm^3) under dinitrogen for 6 h. The resulting red solution was cooled to −10 °C and the deep red precipitate collected. Recrystallisation from acetonitrile by slow diffusion of ether yielded dark red crystals of $[Cu_2L^2_2][PF_6]_2$ (0.034 g, 79%). IR (KBr): 1584s, 1532m, 1470w, 1440w, 1400w, 844vs, 789s and 559s cm^{-1}. Mass spectrum (FAB): *m*/*z* 541 $[CuL^2]$, 605 $[Cu_2L^2]$, 1086 $[Cu_2L^2_2]$ and 1229 $[Cu_2L^2_2(PF_6)]$ (Found: C, 53.2; H, 3.4; N, 8.9. Calc. for $C_{56}H_{44}Cu_2F_{12}N_8P_2S_4$: C, 53.5; H, 3.5; N, 8.9%).

Method 2. The salt $Cu(O_2CMe)_2\cdot H_2O$ (0.025 g, 0.125 mol) and L^2 (0.06 g, 0.125 mmol) were heated to reflux in methanol (10 cm^3) for 7 h. The dark green solution rapidly turned red. The red solution was treated with methanolic $[NH_4][PF_6]$ to give a deep red precipitate of $[Cu_2L^2_2][PF_6]_2$ (0.073 g, 85%).



Scheme 1 (*i*) $[NH_4][O_2CMe]$; (*ii*) base then $[NH_4][O_2CMe]$; (*iii*) Ni^{II}, $Na[BH_4]$

Crystal Structure Determination of $[Ni_2L^2_2(O_2CMe)_2][PF_6]_2$.—Suitable single crystals of the complex were obtained by slow cooling of a hot methanol solution.

Crystal data. $C_{60}H_{50}F_{12}N_8Ni_2O_4P_2S_4$, $M = 1482.69$, monoclinic, space group $C2/c$, $a = 16.157(5)$, $b = 23.640(7)$, $c = 18.806(3)$ Å, $\beta = 97.66(2)°$, $U = 7119$ Å^3, $Z = 4$, D_m not measured, $D_c = 1.38$ g cm^{-3}, $F(000) = 3024$, Mo-Kα radiation ($\lambda = 0.710\,73$ Å), μ(Mo-Kα) = 7.63 cm^{-1}.

Data collection and processing. A suitable green crystal of size 0.65 × 0.3 × 0.3 mm was mounted on a glass fibre and all geometric and intensity data were obtained using an automated four-circle diffractometer (Nicolet R3m/V). The lattice vectors were identified by application of the automatic indexing routine of the diffractometer to the positions of 24 reflections ($14 \leqslant 2\theta \leqslant 27°$) taken from a rotation photograph and centred by the diffractometer. The ω–2θ technique was used to measure 6611 reflections (6210 unique) in the range $5 \leqslant 2\theta \leqslant 50°$. Three standard reflections were remeasured every 97 scans and showed no significant loss in intensity during the data collection. The data were corrected for Lorentz and polarisation effects and an empirical absorption correction applied. There were 3616 unique data with $I \geqslant 3.0\sigma(I)$. The data were solved in the monoclinic space group $C2/c$.

Structure analysis and refinement. The structure was solved by direct methods and developed using alternating cycles of least-squares refinement and Fourier-difference syntheses. All non-hydrogen atoms were refined anisotropically. The hydrogen atoms were placed in idealised positions with C–H distances of 0.96 Å and a fixed U_{iso} of 0.08 Å^2. The final cycle of least-squares refinement included 417 parameters for 3616 variables and did not shift any parameter by more than 0.001 times its standard deviation. The last cycle gave $R = 0.0773$, $R' = 0.0793$, $\omega^{-1} = \sigma^2(F) + 0.0005F^2$. The final Fourier difference map was featureless with no peaks greater than 1.1 e Å^{-3}. Structure solution used SHELXTL-PLUS on a MicroVax II computer.[7]

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom coordinates, thermal parameters and remaining bond lengths and angles.

Results and Discussion

We have previously demonstrated that when 2,2′:6′,2″:6″,2‴:6‴,2⁗-quinquepyridine (qpy) forms helicates it may be regarded as presenting bipy and terpy metal-binding domains to different metals.[2] We considered that the replacement of the central pyridine ring of qpy by a 1,3-phenylene group would result in a ligand L^1 which could form helicates by presenting two bipy metal-binding domains. To test this model the new ligands L^1 and L^2 were prepared by Kröhnke[5] or Potts[6,8] methodologies respectively (Scheme 1). Both synthetic strategies involve the generation of the pyridine rings adjacent to the central 1,3-phenylene spacer, with the intermediacy of a 1,5-dicarbonyl compound, and subsequent ring closure with ammonium acetate. The substituted ligand L^2 may be prepared in yields of ≈60% by the reaction of 1,3-diacetylbenzene with 3,3-bis(methylthio)-1-(2-pyridyl)prop-2-en-1-one[6] in the presence of base, followed by treatment with ammonium acetate in glacial acetic acid. The Kröhnke route to L^1 consists of the synthesis of the Mannich salt of 1,3-diacetylbenzene by reaction with dimethylammonium chloride and paraformaldehyde, and subsequent reaction with *N*-[2-oxo-2-(2-pyridyl)ethyl]pyridinium iodide[5] and ammonium acetate in glacial acetic acid. This reaction is less satisfactory with yields of ≈30% and we have found the dethiomethylation[6,8] of L^2 is a more reliable route for the preparation of L^1. The conversion of L^2 into L^1 in 60% yield is achieved by reaction with a nickel boride reagent generated *in situ* from the reaction of nickel(II) chloride with alkaline sodium tetrahydroborate.[6,8]

The ^{1}H NMR spectra of solutions of the ligands L^1 and L^2 in CD_3SOCD_3 are presented in Figs. 1(*a*) and 1(*b*), together with their assignments (Table 1). The spectra are very similar to that of the related ligand qpy [Fig. 1(*c*)]. In solution the molecules are symmetrical about the central phenylene spacer. Whilst we have been unable to obtain any X-ray-quality crystals of the free ligands it seems likely that in the solid state they will exhibit a transoid geometry about the interannular C–C bond of each of the bipy moieties.[2] The solubility properties of these new ligands are worthy of note. The substituted ligand L^2 exhibits similar solubility properties to those of qpy and its derivatives, being soluble in chloroform, dichloromethane, toluene and Me_2SO but only sparingly soluble in alcoholic solvents. On the other hand, L^1 is readily soluble in ethanol and methanol. Indeed, this unexpectedly high solubility in alcoholic solvents resulted in our failure to isolate L^1 from Kröhnke syntheses for a considerable period of time. We are unable to provide an explanation for this observation, but suggest that it may reflect the adoption of a solid-state structure by L^1 in which there are few coplanar stacking interactions.

Whereas qpy may exhibit a mononucleating near-planar bonding mode, this is not possible for the new ligands L^1 and L^2. Steric interactions between the H^a of the phenylene ring and a metal ion co-ordinated to the two bipy domains are expected to twist the ligand away from planarity such that, *in extremis*, only one bipy domain can interact with the metal (Scheme 2). The twisting between chelating subunits is an essential requirement for helication.[2] An alternative to the twisting would be an activation of the ligand and insertion of a metal into the C–H bond in a cyclometallation process (Scheme 2).[9] Although such reactivity was one of our hopes when we designed these ligands, we have not yet unambiguously observed the formation of cyclometallates.

We initially investigated the reactions of the ligands L^1 and L^2 with copper(I) and silver(I). These metal ions frequently

Table 1 Proton NMR data for free ligands and their complexes

Compound	$H^{3'}$	$H^{4'}$	$H^{5'}$	$H^{6'}$	$H^{3/5\,a}$	H^{4}	$H^{5/3\,a}$	H^{a}	H^{b}	H^{c}	Other
$L^{1\,b}$	8.66	8.02	7.51	8.74	8.22	8.10	8.41	9.07	8.35	7.72	
$L^{2\,b}$	8.65	8.01	7.51	8.74	8.01	—	8.23	9.04	8.36	7.70	SCH_3 2.71
qpy[b,c]	8.69	8.04	7.51	8.73	8.51	8.19	8.73				$H^{3''}$ 8.73;[c] $H^{4''}$ 8.24[c]
$[Cu_2L^1{}_2]^{2+\,d}$	7.98	7.80	6.98	7.65	7.55	7.95	7.95	9.60	7.40	7.10	
$[Cu_2L^2{}_2]^{2+\,d}$	8.00	7.82	7.05	7.64	7.26	—	7.70	9.56	7.36	7.05	SCH_3 2.79
$[Ag_2L^1{}_2]^{2+\,d}$	7.87	7.81	7.05	7.65	7.48	7.95	7.88	9.70	7.52	7.28	
$[Ag_2L^2{}_2]^{2+\,d}$	7.93	7.87	7.06	7.67	7.14	—	7.63	9.69	7.52	7.23	SCH_3 2.76
$[H_2qpy]^{2+\,c,d}$	8.75	8.75	8.10	8.90	8.45	8.40	9.0				$H^{3''}$ 9.0,[c] $H^{4''}$ 8.35[c]
$[H_2L^1]^{2+\,d}$	8.75	8.75	8.10	8.90	8.45	8.30	8.35	9.00	8.50	7.85	
$[H_2L^2]^{2+\,d}$	8.65	8.65	8.00	8.90	8.00	—	7.90	9.15	8.15	7.60	SCH_3 2.75

[a] Ambiguity in the assignment of the resonances for H^3 and H^5 of these rings. [b] In CD_3SOCD_3. [c] For qpy the numbering is consistent with that used for L^1 and L^2 rather than the conventional numbering scheme. The unique central ring is indicated by the $H^{3''}$ and $H^{4''}$ entries in the table. [d] In CD_3CN.

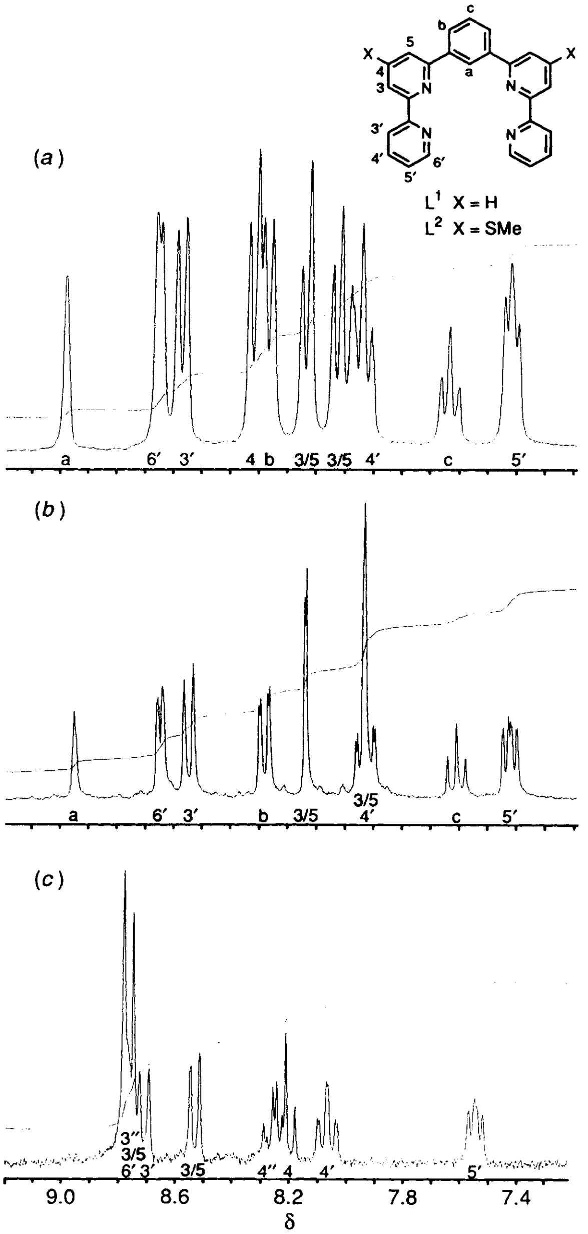
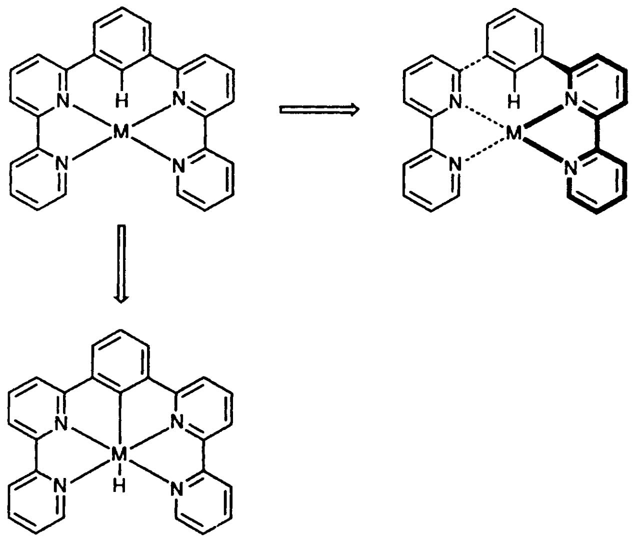
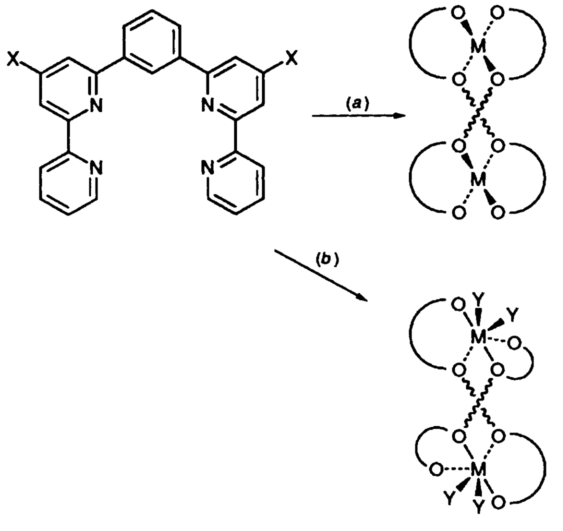


Fig. 1 Proton NMR spectra of CD_3SOCD_3 solutions of (*a*) L^1, (*b*) L^2 and (*c*) qpy showing the assignments



Scheme 2 Possible consequences of L^1 or L^2 interacting with transition-metal ions



Scheme 3 Representation of the assembly of dinuclear double-helical complexes of L^1-type ligands with two tetrahedral (*a*) and two octahedral (*b*) metal centres

adopt near-tetrahedral four-co-ordinate environments, and molecular modelling studies indicated that they could occupy the two N_4-donor metal binding sites resulting from a double-helical array of the two ligands (Scheme 3). The reaction of the ligands with copper(II) acetate in methanol or with $[Cu(MeCN)_4]^+$ salts in methanol or acetonitrile gives rise to red-brown solutions, from which similar ESR-silent, diamagnetic, red-brown hexafluorophosphate or tetrafluoroborate

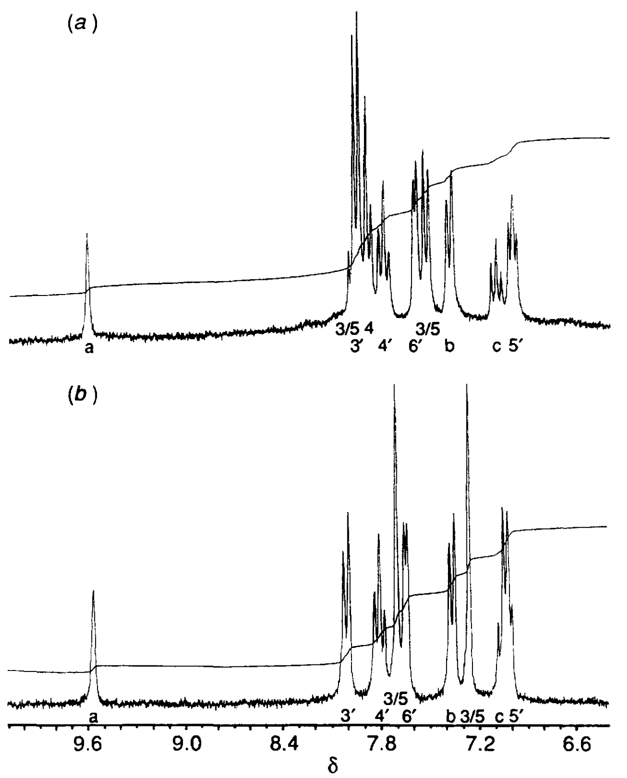


Fig. 2 Proton NMR spectra of CD_3CN solutions of (*a*) $[Cu_2L^1_2][PF_6]_2$ and (*b*) $[Cu_2L^2_2][PF_6]_2$ showing the assignments

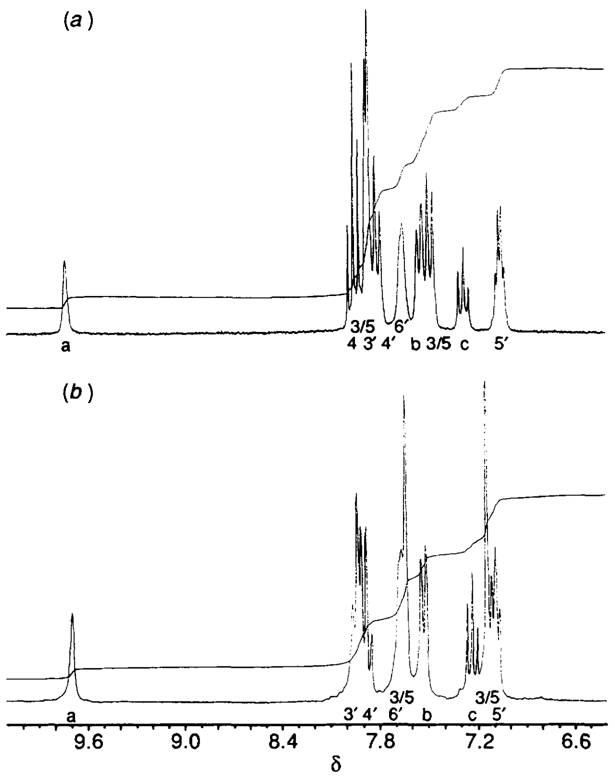


Fig. 3 Proton NMR spectra of CD_3CN solutions of (*a*) $[Ag_2L^1_2][PF_6]_2$ and (*b*) $[Ag_2L^2_2][PF_6]_2$ showing the assignments

salts may be precipitated. Microanalysis of the products indicates the stoichiometries $CuL^1(X)$ or $CuL^2(X)$ ($X = PF_6$ or BF_4) to be appropriate. The FAB mass spectrum of $CuL^1(PF_6)$ exhibits peaks at *m*/*z* 449 $[CuL^1]$, 836 $[CuL^1_2]$, 900 $[Cu_2L^1_2]$ and 1046 $[Cu_2L^1_2(PF_6)]$, whilst that of $CuL^2(PF_6)$ similarly shows peaks for $[CuL^2]$, $[Cu_2L^2]$, $[Cu_2L^2_2]$ and $[Cu_2L^2_2(PF_6)]$. These data are strongly suggestive of a dinuclear structure, and the natural consequence of such a stoichiometry with a rigid ligand such as L^1 or L^2 is the adoption of a double-helical array.[2] The stability of copper(I) in such an environment is well documented and has been used by ourselves and others to control the formation of inorganic helicates.[2,10]

The complexes exhibit well resolved ^1H NMR spectra in CD_3CN solution with the ligands being symmetrical about the central benzene ring [Fig. 2(*a*) and 2(*b*)]. The spectra are similar for the complexes obtained with both L^1 and L^2, indicating that the substituent has little effect on the structural properties of the resultant complexes. The most striking feature of the spectra is the downfield shift of the peak assigned to H^a at δ 9.6. This formation of similar structures regardless of the substitution of the ligand is in accord with our work on qpy systems where we have demonstrated near-identical structures for the double-helical cations formed from the interaction of nickel(II) with variously substituted qpy ligands.[2,11]

The complexes are electrochemically active and their cyclic voltammograms exhibit a single near-reversible coincident oxidation of both metal centres (+0.16 and +0.12 V *vs.* ferrocene–ferrocenium for complexes with L^1 and L^2 respectively). A mixed-valence copper(I)–copper(II) complex is not observed. The oxidation potentials are very similar for the complexes with L^1 and L^2 indicating that the substituents have little effect on their metal-binding properties. These potentials are consistent with those we have previously described for copper(I) centres in N_4 donor environments in double-helical dicopper complexes of 2,2′:6′,2″:6″,2‴-quaterpyridine (qtpy) (+0.05 V)[10] and qpy ligands (+0.12 to +0.18 V depending on the substituent).[11,12] This provides some additional support for our formulation of these complexes as helicates. At negative potentials (≈ −1.0 V) the complex undergoes a demetallation reaction and copper(0) is deposited on the electrode. Introducing the phenylene spacer increases the stability of the helix with respect to direct linkage of the bipy subunits; the complex cation $[Cu_2(qtpy)_2]^{2+}$ undergoes a similar degradative process at −0.42 V.[10] This stabilisation is probably partially due to the additional flexibility allowing the bipy subunits to approach the tetrahedral geometry favoured on valence shell electron pair repulsion (VSEPR) grounds, stabilising the metal centre, and partially to the greater distance between the metal centres.

Upon warming the ligands L^1 or L^2 with silver(I) acetate in methanol, straw coloured solutions are obtained from which white hexafluorophosphate, tetrafluoroborate, perchlorate or tetraphenylborate salts may be precipitated. The complexes exhibit peaks corresponding to M_2L_2X and M_2L_2 ($L = L^1$ or L^2; $X = PF_6$, BF_4, ClO_4 or BPh_4) in their FAB mass spectra and their analyses indicate that a formulation ML(X) is appropriate. The $[Ag(qpy)]^+$ cation is mononuclear in the solid state, but does exhibit very weak dinuclear peaks in its FAB mass spectrum, although the silver complexes of substituted quinquepyridines exhibit no such peaks. The dinuclear peaks obtained with L^1 and L^2 are very intense and provide strong evidence for a dinuclear double-helical structure. The ^1H NMR spectra of these silver complexes closely resemble those of the analogous copper(I) complexes with a high degree of symmetry and a downfield H^a peak at δ 9.7 [Fig. 3(*a*) and 3(*b*)].

The cyclic voltammograms of the silver complexes of L^1 and L^2 do not exhibit any oxidative waves, and acetone solutions of the complexes are resistant to oxidation by persulfate. This is in contrast to the ready oxidation of $[Ag(bipy)_2]^+$ to silver(II),[13] but is in accord with the observation that the silver complex of qtpy was resistant to persulfate ($S_2O_8^{2-}$) oxidation.[14] We have recently shown the latter complex to possess a double-helical structure[10] and believe that the resistance to oxidation in the complexes of L^1, L^2 and qtpy, despite the bis(bipy) N_4 environment, may be due to the more rigid nature of the helix in comparison to the flexible donor set offered by two independent 2,2′-bipyridines.

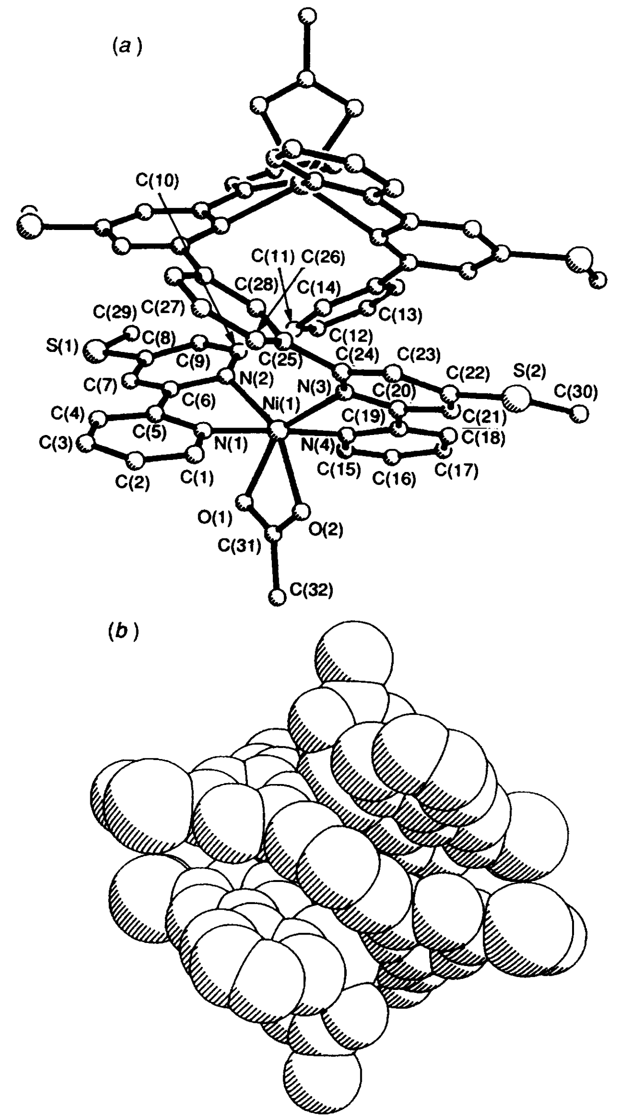


Fig. 4 (*a*) Crystal and molecular structure of one of the two enantiomers of the cation present in $[Ni_2L^2{}_2(O_2CMe)_2][PF_6]_2$ showing the numbering scheme adopted. Hydrogen atoms have been omitted for clarity. (*b*) A space-filling representation of the same cation emphasising the double-helical character

These data are strongly supportive of a dinuclear double-helical structure with the silver ions in a pseudo-tetrahedral N_4 environment similar to that of $[Ag_2(qtpy)_2]^{2+}$ (qtpy may be regarded as two 2,2′-bipyridine subunits linked directly rather than *via* an aryl spacer). Unfortunately all crystals that we have been able to obtain of the copper(I) or silver(I) complexes with a range of counter ions have proved to be twinned or unsuitable for X-ray analysis. In the absence of such data we suggest that these complexes are double helical, with each metal occupying an N_4 metal-binding domain within a double-helical ligand array.

Nickel(II) acetate reacts with L^1 or L^2 in methanol to give emerald-green solutions from which paramagnetic, green crystals precipitate upon the addition of a methanolic solution of $[NH_4][PF_6]$. The FAB mass spectra of these green complexes exhibit peaks corresponding to $[Ni_2L_2]$, $[Ni_2L_2(O_2CMe)(PF_6)]$ and $[Ni_2L_2(O_2CMe)_2(PF_6)]$. Analysis suggests a formulation $NiL(O_2CMe)(PF_6)$. Reactions with metal : ligand stoichiometries of 1 : 1, 1 : 2, 2 : 1 and 3 : 2 all give the same green products.

The electrochemical behaviour of solutions of the two complexes in acetonitrile is unremarkable. No oxidation processes are detected but three reversible reductions, which are probably ligand based, are observed for each complex.

The nature of the solution species has also been investigated by ^1H NMR spectroscopy. The complexes are paramagnetic in the solid state and in acetonitrile solution and the ^1H NMR spectrum of an acetonitrile solution is paramagnetically shifted but reasonably well resolved although no coupling is measurable. We have not, thus, been able fully to assign the spectra, but the number of environments suggests that the solution species are symmetrical about the central benzene ring and (more importantly) that there is only one solution species. In the light of these electrochemical and NMR data it seems likely that the helical structure is maintained in solution. We suggest that these complexes are double helical, with each metal occupying an N_4 metal-binding domain within a double-helical ligand array; the metals are six-co-ordinate with a didentate acetate completing the co-ordination sphere at each centre. A determination of the solution magnetic moment by the Evans method gave μ_{eff} 4.3 ± 0.3 for the binuclear formulation. Apart from ligand n–π^* and π–π^* transitions and charge-transfer bands, the only other feature in the electronic spectrum of acetonitrile solutions of $[Ni_2L_2(O_2CMe)_2][PF_6]_2$ is a single d–d transition (578 nm, ε 33 for L^1 and 576 nm, ε 53 dm^3 mol^{-1} cm^{-1} for L^2).

In order to confirm the dinuclear double-helical nature of the $[Ni_2L_2(O_2CMe)_2]^{2+}$ cations we have determined the crystal structure of a complex of L^2. A crystal of the $[Ni_2L^2{}_2(O_2CMe)_2][PF_6]_2$ which slowly precipitated after the addition of methanolic $[NH_4][PF_6]$ to the green solution obtained from the reaction of L^2 with nickel(II) acetate proved to be suitable for X-ray analysis. The structure of one of the two enantiomers of the cation present in the unit cell is shown in Fig. 4(*a*), together with a space-filling representation in Fig. 4(*b*); atomic coordinates and selected bond lengths and angles are given in Tables 2 and 3. The cation is a double helix with each nickel(II) centre co-ordinating to a bipy subunit from each of two different ligands. The remaining co-ordination sites are occupied by a didentate acetate group to give a pseudo-octahedral geometry at the metal centre. The ligand has two principal twists about the interannular bonds between the central 1,3-phenylene spacer and the bipy groups (38 and 35°). Smaller twistings within the bipy groups are observed (13.9 and 14.9°). The Ni–N [2.014(7)–2.154(5) Å] and Ni–O [2.085(7)–2.148(6) Å] distances are unremarkable. Each bipy–Ni interaction is associated with a typical 'bite angle' of 79 ± 0.5°.[13] There are no significant interactions between the cations and the hexafluorophosphate anions.

In contrast to many of the other double helices that we have studied, there are no short face-to-face π-stacking interactions between pyridine rings on the two strands.[2] The closest contacts between aromatic rings are of 3.79 and 3.67 Å between the terminal rings of one ligand and the central phenylene ring of the other ligand. However, these rings are not coplanar and the interplanar angles for the two interactions are 28.1 and 24.7° respectively. Such interactions are not observed in the double-helical $[Ag_2(qtpy)_2]^{2+}$ ion[10] and this raises doubts about the importance of these interactions in the stabilisation of the helical motif. These interactions may provide an overall energetic stabilisation but it is apparent that the matching of the donor properties of a ligand with the acceptor properties of the metal ion is one of the principal features of helication. In this case interaction between H^a and a metal ion co-ordinated to one bipy unit forces the ligand to dinucleate. To satisfy the six-co-ordinate octahedral geometric preference the nickel(II) centre must interact with four more donor atoms. Two of these are provided by a didentate bipy domain from a second ligand molecule. The ligands are unable to twist sufficiently to allow a third ligand to fill the co-ordination sphere to give a triple helix and in this case a didentate acetate occupies the remaining co-ordination sites. The Ni ··· Ni distance is 5.87(1) Å and there are no metal–metal interactions. The helix is more extended than that formed from nickel(II) and qpy (Ni ··· Ni 4.45 Å). This is a direct result of the increased flexibility afforded by the

Table 2 Atomic coordinates (× 10^4) for $[Ni_2L^2_2(O_2CMe)_2][PF_6]_2$

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
Ni(1)	3179(1)	2231(1)	2120(1)	C(18)	3061(7)	1059(4)	3770(5)
S(1)	4301(2)	1415(2)	−906(1)	C(19)	3187(5)	1508(3)	3346(4)
S(2)	3773(2)	2927(1)	5509(1)	C(20)	3526(5)	2060(3)	3650(4)
N(1)	3228(4)	2953(3)	1557(3)	C(21)	3539(5)	2175(4)	4379(4)
N(2)	3968(4)	1981(3)	1344(3)	C(22)	3797(5)	2704(4)	4628(4)
N(3)	3786(4)	2429(3)	3182(3)	C(23)	4094(5)	3074(4)	4149(4)
N(4)	3061(4)	1480(3)	2625(3)	C(24)	4099(5)	2927(3)	3446(4)
C(1)	2946(6)	3456(4)	1739(5)	C(25)	4538(5)	3275(3)	2961(4)
C(2)	2891(7)	3905(5)	1265(7)	C(26)	4551(6)	3871(4)	2960(5)
C(3)	3108(8)	3832(5)	590(7)	C(27)	5000	4138(6)	2500
C(4)	3395(6)	3316(4)	409(5)	C(28)	5000	3003(5)	2500
C(5)	3447(5)	2879(3)	893(4)	C(29)	4564(9)	698(6)	−840(6)
C(6)	3771(5)	2317(4)	757(4)	C(30)	3547(7)	2309(5)	5974(4)
C(7)	3878(5)	2135(4)	74(4)	O(1)	2066(4)	2033(3)	1407(3)
C(8)	4207(6)	1614(5)	−26(4)	O(2)	2035(4)	2460(3)	2434(3)
C(9)	4452(5)	1279(4)	570(4)	C(31)	1655(6)	2238(5)	1879(5)
C(10)	4325(5)	1476(4)	1245(4)	C(32)	738(7)	2193(6)	1797(6)
C(11)	4665(5)	1142(4)	1888(4)	P(1)	7702(2)	4576(2)	744(2)
C(12)	4667(6)	561(4)	1902(5)	F(1)	8333(6)	4543(4)	1438(4)
C(13)	5000	271(6)	2500	F(2)	8401(7)	4797(6)	342(6)
C(14)	5000	1433(5)	2500	F(3)	7934(9)	3988(4)	533(5)
C(15)	2779(6)	1015(4)	2321(5)	F(4)	7158(7)	4653(5)	3(5)
C(16)	2623(9)	541(5)	2702(6)	F(5)	7559(10)	5198(4)	928(5)
C(17)	2768(10)	554(5)	3440(6)	F(6)	7031(9)	4389(7)	1156(7)

Table 3 Selected bond lengths (Å) and angles (°) in the co-ordination sphere of the cation in $[Ni_2L^2_2(O_2CMe)_2][PF_6]_2$

Ni(1)–N(1)	2.014(7)	Ni(1)–N(2)	2.146(6)
Ni(1)–N(3)	2.154(5)	Ni(1)–N(4)	2.036(7)
Ni(1)–O(1)	2.148(6)	Ni(1)–O(2)	2.085(7)
N(1)–Ni(1)–N(2)	78.9(3)	N(1)–Ni(1)–N(3)	105.0(3)
N(2)–Ni(1)–N(3)	116.8(2)	N(1)–Ni(1)–N(4)	175.4(3)
N(2)–Ni(1)–N(4)	100.2(3)	N(3)–Ni(1)–N(4)	79.4(2)
N(1)–Ni(1)–O(1)	86.8(3)	N(2)–Ni(1)–O(1)	92.2(2)
N(3)–Ni(1)–O(1)	150.0(2)	N(4)–Ni(1)–O(1)	88.7(2)
N(1)–Ni(1)–O(2)	91.6(3)	N(2)–Ni(1)–O(2)	153.4(2)
N(3)–Ni(1)–O(2)	89.6(2)	N(4)–Ni(1)–O(2)	87.3(3)
O(1)–Ni(1)–O(2)	62.2(2)	N(1)–Ni(1)–C(31)	90.4(3)
N(2)–Ni(1)–C(31)	123.4(3)	N(3)–Ni(1)–C(31)	119.6(3)
N(4)–Ni(1)–C(31)	86.4(3)	O(1)–Ni(1)–C(31)	31.3(3)
O(2)–Ni(1)–C(31)	30.9(3)		

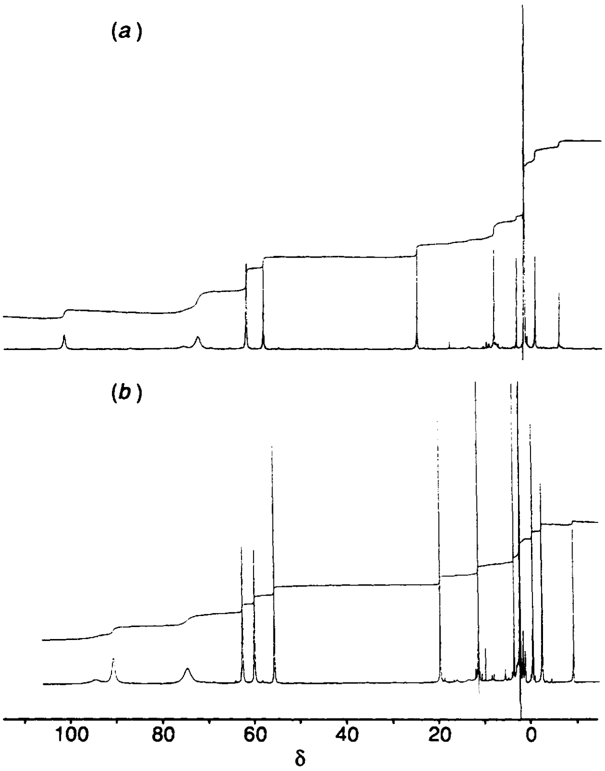


Fig. 5 Proton NMR spectra of CD_3CN solutions of (*a*) $[Co_2L^1_2(O_2CMe)_2][PF_6]_2$ and (*b*) $[Co_2L^2_2(O_2CMe)_2][PF_6]_2$

introduction of a non-co-ordinated spacer group and allows an additional level of control in the design of helicates.

We have also investigated the reactions of cobalt(II) acetate with L^1 and L^2. Upon warming cobalt(II) acetate and the ligands in methanol, orange solutions are obtained from which paramagnetic, orange, crystalline material precipitates on the addition of $[NH_4][PF_6]$. Unfortunately, these crystals invariably contain pockets of solvent rendering them unsuitable for X-ray analysis. The infrared spectra of these complexes are identical to those of the analogous nickel(II) complexes suggesting that they are isostructural and also contain dinuclear double-helical cations. Microanalysis is compatible with this assignment, suggesting a formulation $CoL(O_2CMe)(PF_6)$ (L = L^1 or L^2). The FAB mass spectra show a strong CoL peak and much weaker peaks corresponding to $[CoL_2]$, $[Co_2L_2]$, $[Co_2L_2(O_2CMe)_2]$, $[Co_2L_2(O_2CMe)(PF_6)]$ and $[Co_2L_2(O_2CMe)_2(PF_6)]$ (L = L^1 or L^2). The ^1H NMR spectra of acetonitrile solutions of these complexes are paramagnetically shifted, but sharp and well resolved [Fig. 5(*a*) and 5(*b*)] and indicate the presence of only one solution species of high symmetry. The cyclic voltammogram shows no oxidative peaks.

The similarity in behaviour of L^1 and L^2 to qpy led us to investigate further analogies. We have previously shown that although qpy forms double helicates with cationic transition-metal ions, protonation is not sufficient to cause the required interannular twisting to give non-planar conformations (although it is sufficient to give the cisoid conformation of the terminal bipy domains).[15] The addition of HPF_6 to a methanolic solution of L^1 results in the immediate formation of a white precipitate. The ligand L^2 dissolves in dilute aqueous HCl to give a colourless solution from which a white precipitate is obtained upon the addition of $[NH_4][PF_6]$. Analysis indicates that the formulation $[H_2L][PF_6]_2$ (L = L^1 or L^2) is appropriate. Both salts give similar ^1H NMR spectra and their

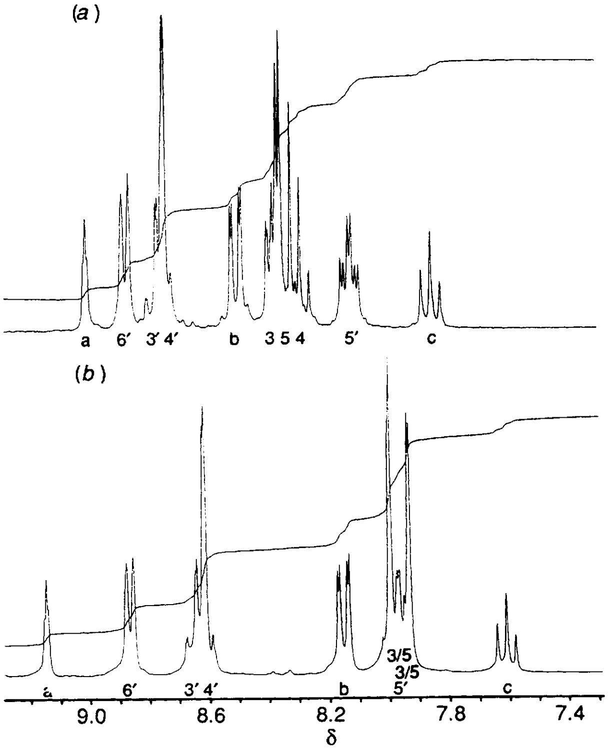


Fig. 6 Proton NMR spectra of CD_3CN solutions of (*a*) $[H_2L^1][PF_6]_2$ and (*b*) $[H_2L^2][PF_6]_2$ showing the assignments

infrared spectra exhibit aromatic stretching modes and a stretch at ≈845 cm^{-1} (indicative of a PF_6^- counter ion). The FAB mass spectra exhibit peaks corresponding to HL and $H_2L(PF_6)$. The ^1H NMR spectra show a high degree of symmetry and only exhibit ten peaks. These data are all consistent with the formation of the doubly protonated cations $[H_2L^1]^{2+}$ and $[H_2L^2]^{2+}$. The absence of any 2:2 peaks in their mass spectra suggests that protonation is not sufficient to induce helication with these ligands. This is fully in accord with our findings for qpy.[15] Indeed, it seems likely that the ligands L^1 and L^2 give similar structures to that obtained with qpy with the two bipy subunits each co-ordinated to a proton. The ^1H NMR spectrum of $[H_2L^1][PF_6]_2$ in CD_3CN solution bears a close resemblance to that of $[H_2qpy][PF_6]_2$ in the same solvent [Fig. 6(*a*) and 6(*b*)]. All the signals corresponding to the pyridine rings are at identical shifts with the exception of that of H^5 (which may be due to the difference between having a phenyl or 2-pyridyl group in the 6 position).

We have recently extended this work to a 3,3′-biphenylene spacer the dinuclear double-helical nickel(II) complex of which has a metal–metal distance of 7.76 Å.[16] We are currently utilising these concepts of matching donor and acceptor properties to assemble novel mononuclear building blocks for supramolecular chemistry.[11,15,16,17]

Acknowledgements

We thank Ciba-Geigy for support (to M. J. H.), the SERC for funds towards the purchase of a diffractometer (D. A. T.) and the Royal Society and Isaac Newton Trust for grants towards the cost of spectrometers (E. C. C.).

References

1 J.-M. Lehn, in *Perspectives in Coordination Chemistry*, eds. A. F. Williams, C. Floriani and A. Merbach, VCH, Weinheim, 1992, p. 447.
2 E. C. Constable, *Tetrahedron*, 1992, **48**, 10013 and refs. therein.
3 E. Müller, C. Piguet, G. Bernardinelli and A. F. Williams, *Inorg. Chem.*, 1988, **27**, 849.
4 E. C. Constable, M. J. Hannon and D. A. Tocher, *Angew. Chem., Int. Ed. Engl.*, 1992, **31**, 230; *Angew. Chem.*, 1992, **104**, 218.
5 F. Kröhnke, *Synthesis*, 1976, 1.
6 K. T. Potts, P. Ralli, G. Theodoridis and P. Winslow, *Org. Synth.*, 1985, **64**, 478; K. T. Potts, M. J. Cipullo, P. Ralli and G. Theodoridis, *J. Org. Chem.*, 1982, **47**, 3027.
7 G. M. Sheldrick, SHELXTL-PLUS, University of Göttingen, 1986.
8 K. T. Potts, *Bull. Soc. Chim. Belg.*, 1990, **99**, 741.
9 E. C. Constable, *Polyhedron*, 1984, **3**, 1037.
10 E. C. Constable, M. J. Hannon, A. Martin, P. R. Raithby and D. A. Tocher, *Polyhedron*, 1992, **11**, 2967.
11 E. C. Constable, M. D. Ward, M. G. B. Drew and G. A. Forsyth, *Polyhedron*, 1989, **8**, 2551; E. C. Constable, M. G. B. Drew, J. V. Walker and P. D. Wood, in the press.
12 E. C. Constable, M. G. B. Drew and M. D. Ward, *J. Chem. Soc., Chem. Commun.*, 1987, 1600; M. Barley, E. C. Constable, S. Corr, R. C. S. McQueen, J. C. Nutkins, M. D. Ward and M. G. B. Drew, *J. Chem. Soc., Dalton Trans.*, 1988, 2655.
13 E. C. Constable, *Adv. Inorg. Chem.*, 1989, **34**, 1.
14 E. C. Constable, *Adv. Inorg. Chem. Radiochem.*, 1987, **30**, 69.
15 E. C. Constable, S. M. Elder, J. V. Walker, P. D. Wood and D. A. Tocher, *J. Chem. Soc., Chem. Commun.*, 1992, 229.
16 E. C. Constable, M. J. Hannon, A. J. Martin and P. R. Raithby, unpublished work.
17 E. C. Constable, M. J. Hannon, A. M. W. Cargill Thompson, D. A. Tocher and J. V. Walker, *Supramol. Chem.*, in the press; E. C. Constable and A. M. W. Cargill Thompson, *J. Chem. Soc., Dalton Trans.*, 1992, 3467; E. C. Constable and A. M. W. Cargill Thompson, *J. Chem. Soc., Dalton Trans.*, 1992, 2947; E. C. Constable, A. M. W. Cargill Thompson and D. A. Tocher, *New J. Chem.*, 1992, **16**, 855; E. C. Constable and A. M. W. Cargill Thompson, *J. Chem. Soc., Chem. Commun.*, 1992, 617; E. C. Constable, A. M. W. Cargill Thompson and D. A. Tocher, *Supramolecular Chemistry*, eds. V. Balzani and L. De Cola, Klewer Academic Press, Dordrecht, 1992, p. 219.

Received 21*st January* 1993; *Paper* 3/00401E