Metallosupramolecular Assembly of Dinuclear Double Helicates incorporating a Biphenyl-3,3′-diyl Spacer; Molecular Structure of Bis{3,3′-bis[4-(methylsulfanyl)-2,2′-bipyridin-6-yl]biphenyl-κ^2N,N':κ^2N'',N''']}dicopper(I) Hexafluorophosphate†

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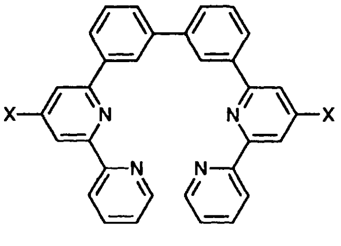
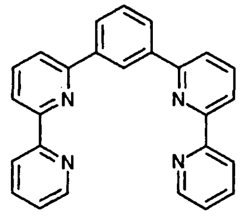
Linking two 2,2′-bipyridine metal-binding domains by a biphenyl-3,3′-diyl spacer provided a new type of helicand, 3,3′-bis[4-(methylsulfanyl)-2,2′-bipyridin-6-yl]biphenyl (L), which has been shown to form dinuclear double-helical complexes with a range of transition-metal ions. The copper(I) complex $[Cu_2L_2][PF_6]_2$ has been structurally characterised [orthorhombic, space group *Pba*2, $a = 23.023(5)$, $b = 23.206(5)$, $c = 12.224(2)$ Å, $Z = 4$, $wR_2 = 0.259$ for all data]. These complexes show increased intermetallic separations with respect to analogous complexes formed with ligands in which the metal-binding domains are directly linked or are connected by a 1,3-phenylene spacer. This provides an additional level of control in the deliberate design of molecules containing helical motifs. Stacking interactions do not appear to be of importance in the stabilisation of these helical structures. The biphenyl spacer does not appear to be sufficiently flexible to permit the formation of triple-helical complexes.

We and others have been interested in the use of the specific geometric co-ordination preferences of metal ions to control the spontaneous self-assembly of supramolecular architectures. We have been particularly interested in understanding the coding principles which control this metallosupramolecular chemistry.[1] Much work in this area has centred around the formation of molecules containing helical motifs[2] and the co-ordination of suitable transition-metal ions to the linear oligopyridines may lead to the formation of polynuclear double-helical cations.[2,3] Alternatively, mononuclear species may also be formed and this has permitted the controlled assembly of heterodinuclear species using 2,2′:6′,2″:6″,2‴:6‴,2⁗-quinquepyridine.[2,4] We recently reported the synthesis and co-ordination chemistry of compound L^1 in which a 1,3-phenylene spacer has been incorporated between didentate metal-binding 2,2′-bipyridine domains.[5] The 1,3-phenylene spacer prevents the formation of mononuclear species in which all of the donor atoms interact with one metal centre. We now report the expansion of this approach to systems with greater separations between the metal-binding domains, and specifically the incorporation of biphenyl spacers. Williams and co-workers[6] have previously reported the formation of mononuclear copper complexes from compounds containing a biphenyl-2,2′-diyl spacer, and we considered that related ligands with a different substitution pattern at the biphenyl might be more suited to helication. We now describe the synthesis and co-ordination chemistry of 3,3′-bis[4-(methylsulfanyl)-2,2′-bipyridin-6-yl]biphenyl (L) which contains two 2,2′-bipyridine metal-binding domains linked by a biphenyl-3,3′-diyl spacer group. It forms dinuclear double-helical complexes with a range of transition-metal ions. The introduction of this spacer group leads to large intermetallic separations.



L X = SMe
L^2 X = H



L^1

Experimental

Infrared spectra were recorded on a Perkin-Elmer 1710 Fourier-transform spectrophotometer, with the samples in compressed KBr discs, proton NMR spectra on Brüker WM250 and AM400 spectrometers using standard Brüker software. Fast-atom bombardment (FAB), fast-ion bombardment (FIB) and electron-impact (EI) mass spectra were recorded on a Kratos MS-50 spectrometer, with 3-nitrobenzyl alcohol as matrix for the FAB and FIB 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. Aceonitrile, freshly distilled from CaH_2 and then P_2O_5, was used as solvent in all cases. The base electrolyte was 0.1 mol dm^{-3} [NBu^n_4][BF_4], recrystallised from ethanol–

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† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1994, Issue 1, pp. xxiii–xxviii.

water and rigorously dried. Potentials are quoted *vs.* ferrocene–ferrocenium couple (0.0 V), and all potentials were referenced to internal ferrocene added at the end of each experiment.

The complex $[NiCl_2(PPh_3)_2]$ [7] and 3,3-bis(methylsulfanyl)-1-(2-pyridyl)prop-2-en-1-one [8] were prepared according to literature methods. Ammonium acetate was dried over P_2O_5, and tetrahydrofuran (thf) was distilled over sodium–benzophenone prior to use. Zinc dust was washed with successive portions of dilute hydrochloric acid, distilled water, ethanol, acetone and diethyl ether prior to use to remove the oxide layer. Tetraethylammonium iodide, 1-acetyl-3-bromobenzene, potassium *tert*-butoxide, triphenylphosphine and other reagents were used as supplied (Aldrich).

Preparations.—3,3′-*Diacetylbiphenyl.* The complex $[NiCl_2(PPh_3)_2]$ (1.635 g, 2.5 mmol), $[NEt_4]I$ (0.645 g, 2.5 mmol) and zinc dust (2.455 g, 40 mmol) were placed in a Schlenk tube together with a magnetic stirrer bar. The tube was sealed (with a suba-seal) and repeatedly evacuated and flushed with argon. Degassed thf (20 cm^3) was added *via* a syringe and the mixture stirred under argon at 50 °C. After a few minutes the solution turned red indicating formation of the catalytic nickel(0) species. Stirring was continued for 30 min after which time 1-acetyl-3-bromobenzene (5 g, 3.32 cm^3, 25 mmol) was added (*via* a syringe) and the mixture stirred at 50 °C for 24 h. The mixture was filtered through Celite to remove any solid zinc and nickel species and the Celite washed well with acetone. The washings were combined and taken to dryness. The solid residue was recrystallised from ethanol to give white crystals of 3,3′-diacetylbiphenyl (2.24 g, 75%). IR (KBr): 1685s, 1596m, 1470w, 1403m, 1354m, 1274m, 1257s, 963w, 794m, 696m and 590m cm^{-1}. Mass spectrum: (EI) *m/z* 238 (*M*), 223 (*M* − Me), 195 (*M* − MeCO) and 152 (*M* − 2MeCO); (positive ion FAB) *m/z* 239 (*M* + H). ^1H NMR ($CDCl_3$): δ 8.19 (1 H, s), 7.95 (1 H, d, *J* = 7.8), 7.80 (1 H, d, *J* = 7.8), 7.56 (1 H, t, *J* = 7.8 Hz) and 2.67 (3 H, s).

3,3′-*Bis*[4-(*methylsulfanyl*)-2,2′-*bipyridin*-6-*yl*]*biphenyl*, L. 3,3-Bis(methylsulfanyl)-1-(2-pyridyl)prop-2-en-1-one (4.6 g, 20.4 mmol) was added to a suspension of 3,3′-diacetylbiphenyl (2.42 g, 9.2 mmol) and potassium *tert*-butoxide (4.6 g, excess) in thf (30 cm^3) and the mixture stirred at room temperature under an atmosphere of dinitrogen for 6 h. After this period the flask was fitted with an air condenser, acetic acid (15 cm^3) and ammonium acetate (6.3 g, excess) were added and the mixture heated under reflux for 8 h. After cooling, the reaction mixture was treated with water (100 cm^3). The solid formed was filtered off and recrystallised from EtOH–dimethylformamide (dmf) in the presence of activated charcoal to yield L (2.65 g, 47%) (Found: C, 71.3; H, 4.6; N, 9.3. Calc. for $C_{34}H_{26}N_4S_2 \cdot 0.75C_2H_4O_2$: C, 71.1; H, 4.8; N, 9.3%). IR (KBr): 1576s, 1562s, 1541s, 1474m, 1430w, 1397m and 792 s cm^{-1}. ^1H NMR ($CDCl_3$): δ 8.76 (1 H, d, *J* = 4.8, $H^{6'}$), 8.71 (1 H, d, *J* = 7.9, $H^{3'}$), 8.48 (1 H, s, H_a), 8.34 (1 H, s, $H^{3/5}$), 8.19 (1 H, dd, *J* = 7.8, H_b), 7.89 (1 H, td, *J* = 7.7, 1.7, $H^{4'}$), 7.83 (1 H, d, *J* = 7.2, H_d), 7.74 (1 H, d, *J* = 1.2, $H^{3/5}$), 7.72 (1 H, t, *J* = 7.7, H_c), 7.38 (1 H, ddd, *J* = 7.5, 4.8, 1.1, $H^{5'}$), 2.72 (3 H, s, SCH_3); (CD_3SOCD_3) δ 8.72 (1 H, d, *J* = 4.5, $H^{6'}$), 8.59 (1 H, d, *J* = 7.8, $H^{3'}$), 8.57 (1 H, s, H_a), 8.31 (1 H, d, *J* = 7.7, $H_{b/d}$), 8.22 (1 H, d, *J* = 1.2, $H^{3/5}$), 8.02 (1 H, d, *J* = 1.2, $H^{3/5}$), 7.94 (1 H, td, *J* = 7.7, 1.6, $H^{4'}$), 7.92 (1 H, d, *J* = 7.8, $H_{d/b}$), 7.69 (1 H, t, *J* = 7.7, H_c), 7.49 (1 H, dd, *J* = 7.4, 4.8 Hz, $H^{5'}$) and 2.70 (3 H, s, SCH_3). Mass spectrum: (EI) *m/z* 554 (*M*), 539 (*M* − Me), 507 (*M* − SMe) and 478 (*M* − C_5H_5N); (positive-ion FAB) *m/z* 555 (*M* + H).

$[Cu_2L_2][PF_6]_2$. *Method* 1. The salt $[Cu(MeCN)_4][PF_6]$ (0.014 g, 0.038 mmol) and L (0.020 g, 0.036 mmol) were heated to reflux in degassed methanol (15 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 diethyl ether vapour yielded dark red crystals of $[Cu_2L_2][PF_6]_2$ (0.024 g, 87%).

Method 2. The salt $Cu(O_2CMe)_2 \cdot H_2O$ (0.007 g, 0.036 mmol) and L (0.020 g, 0.036 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 an excess of methanolic $[NH_4][PF_6]$ to give a deep red precipitate of $[Cu_2L_2][PF_6]_2$ (0.018 g, 65%) (Found: C, 53.4; H, 3.5; N, 7.2. Calc. for $C_{68}H_{52}Cu_2F_{12}N_8P_2S_4$: C, 53.5; H, 3.4; N, 7.3%). IR (KBr): 1585s, 1533m, 1488w, 1440w, 1407w, 844vs, 788s and 559s cm^{-1}. Mass spectrum (FAB): *m/z* 617 (CuL), 682 (Cu_2L), 1236 (Cu_2L_2) and 1381 $[Cu_2L_2(PF_6)]$. UV/VIS (MeCN): 513 (ε = 3200), 380 (sh), 320 (sh) and 255 nm (ε = 120 000 dm^3 mol^{-1} cm^{-1}). ^1H NMR (CD_3CN): δ 8.19* (1 H, s, H_a), 7.73* (1 H, d, $H^{3'}$), 7.62* (2 H, m, $H^{4',6'}$), 7.40* (2 H, m, $H^{3/5}$, $H_{b/d}$), 7.30* (1 H, s, $H^{3/5}$), 7.21 (1 H, t, *J* = 7.6, H_c), 7.05 (1 H, d, *J* = 7.5 Hz, $H_{b/d}$), 6.89* (1 H, m, $H^{5'}$) and 2.72 (3 H, s, SCH_3) [asterisked peaks broadened at room temperature (250 and 400 MHz)].

$[Ag_2L_2][PF_6]_2$. The salt $Ag(O_2CMe)$ (0.006 g, 0.036 mmol) and L (0.020g, 0.036 mmol) were heated to reflux in methanol (15 cm^3) for 7 h and the resulting colourless solution treated with an excess of methanolic $[NH_4][PF_6]$. A white precipitate formed instantly, and was filtered off and recrystallised from acetonitrile by the slow diffusion of diethyl ether vapour to yield colourless crystals of $[Ag_2L_2][PF_6]_2$ (0.026 g, 69%) (Found: C, 50.8; H, 3.4; N, 7.1. Calc. for $C_{68}H_{52}Ag_2F_{12}N_8P_2S_4$: C, 50.6; H, 3.2; N, 6.9%). IR (KBr): 1597w, 1580s, 1569s, 1538m, 1479m, 1438w, 1404w, 842vs, 788s and 558s cm^{-1}. ^1H NMR (CD_3CN): δ 8.60 (1 H, s, H_a), 7.65 (2 H, m, $H^{3',4'}$), 7.51 (1 H, d, *J* = 4.8, $H^{6'}$), 7.47 (1 H, d, *J* = 8.0, $H_{b/d}$), 7.40 (1 H, s, $H^{3/5}$), 7.27 (1 H, s, $H^{3/5}$), 7.22 (1 H, t, *J* = 8.0, H_c), 7.06 (1 H, d, *J* = 8.0 Hz, $H_{b/d}$, H_c), 6.92 (1 H, m, $H^{5'}$) and 2.72 (3 H, s, SCH_3). Mass spectrum (FAB): *m/z* 663 (AgL), 772 (Ag_2L), 1218 (AgL_2) and 1472 $[Ag_2L_2(PF_6)]$.

$[Ni_2L_2(O_2CMe)_2][PF_6]_2$. The salt $Ni(O_2CMe)_2 \cdot 4H_2O$ (0.010 g, 0.040 mmol) and L (0.022 g, 0.040 mmol) were heated to reflux in methanol (10 cm^3) for 7 h. The resulting clear emerald-green solution was then treated whilst hot with methanolic $[NH_4][PF_6]$. On cooling emerald-green crystals of $[Ni_2L_2(O_2CMe)_2][PF_6]_2$ separated (0.018 g, 55%) (Found: C, 51.1; H, 3.5; N, 6.5. Calc. for $C_{72}H_{58}F_{12}N_8Ni_2O_4P_2S_4 \cdot 3H_2O$: C, 51.2; H, 3.8; N, 6.6%). IR (KBr): 1589s, 1574s, 1533s, 1486m, 1455m, 1408w, 844vs, 789m and 559m cm^{-1}. Mass spectrum (FAB): *m/z* 613 (NiL), 672 $[NiL(O_2CMe)]$, 1167 (NiL_2), 1225 (Ni_2L_2), 1285 $[Ni_2L_2(O_2CMe)]$, 1345 $[Ni_2L_2(O_2CMe)_2]$, 1428 $[Ni_2L_2(O_2CMe)(PF_6)]$ and 1489 $[Ni_2L_2(O_2CMe)_2(PF_6)]$.

$[Co_2L_2(O_2CMe)_2][PF_6]_2$. The salt $Co(O_2CMe)_2 \cdot 4H_2O$ (0.011 g, 0.045 mmol) and L (0.025 g, 0.045 mmol) were heated to reflux in methanol (10 cm^3) for 8 h. The resulting orange solution was filtered and the filtrate treated with methanolic $[NH_4][PF_6]$. On cooling orange crystals of $[Co_2L_2(O_2CMe)_2][PF_6]_2$ separated (0.025 g, 68%). IR (KBr): 1589s, 1574s, 1533m, 1485m, 1441m, 1408w, 845vs, 790m and 559s cm^{-1}. Mass spectrum (FIB): *m/z* 613 (CoL), 672 $[CoL(O_2CMe)]$, 1167 (CoL_2), 1226 (Co_2L_2), 1430 $[Co_2L_2(O_2CMe)(PF_6)]$ and 1489 $[Co_2L_2(O_2CMe)_2(PF_6)]$.

Structure Determination of $[Cu_2L_2][PF_6]_2$.—*Crystal data.* *M* = 1526.44, orthorhombic, space group *Pba*2, *a* = 23.023(5), *b* = 23.206(5), *c* = 12.224(2) Å, *Z* = 4, *U* = 6531(2) $Å^3$, *F*(000) = 3104, D_c = 1.552 g cm^{-3}, λ(Mo-Kα) = 0.710 73 Å, crystal size 0.32 × 0.38 × 0.41 mm, *T* = 153 K, μ(Mo-Kα) = 9.12 cm^{-1}.

Data collection and refinement. Data were collected on a Stoe four-circle diffractometer equipped with an Oxford Cryostream cooling apparatus using the ω–θ scan mode ($7.0 \leqslant 2\theta \leqslant 45.0°$) with graphite-monochromated Mo-Kα radiation. Of 8460 reflections collected, 7857 were unique (R_{int} = 0.025). No absorption correction was applied because of crystal decomposition at the end of the data collection. Three standard reflections showed a 36% decomposition during the data collection; this was corrected for during data reduction. The structure was solved by a combination of direct methods and Fourier-difference techniques (Viglen Vig IV/25 personal computer, SHELXTL PLUS[9] and SHELX 93[10]) and refined using blocked full-matrix least-squares analysis on F_o^2 with all non-hydrogen atoms assigned anisotropic displacement parameters. The hydrogen atoms were placed in idealised positions and allowed to ride on the relevant carbon atoms; displacements for the hydrogens were refined at a value of 1.2 times that of the carbon atom to which they were attached. The weighting scheme $w^{-1} = [\sigma^2(F_o^2) + (0.1515P)^2 + 24.09P]$ where $P = (\max.\ F_o^2 + 2F_c^2)/3$ was introduced in the final cycles of refinement. The converged residuals were $R_1 = 0.069$ for 6432 $F_o > 4\sigma(F_o)$ and $wR_2 = 0.259$ for all data, goodness of fit = 1.159. The Flack parameter x refined to 0.00(3) indicating that the absolute configuration was correct. The largest peak and hole in the final difference map were +2.415 (close to the F atoms in the PF_6 anions) and −0.915 e Å^{-3}. Final atomic coordinates for non-hydrogen atoms and relevant bond lengths and angles are presented in Tables 2 and 3.

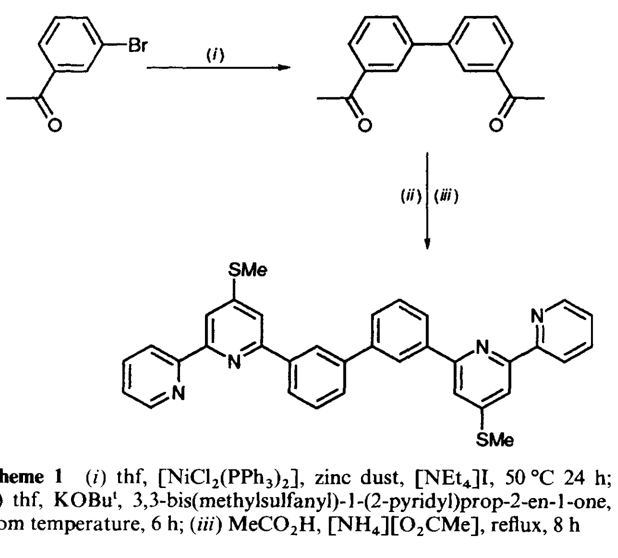
Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom coordinates, thermal parameters and remaining bond lengths and angles.

Results and Discussion

The approach used to synthesise the ligand 3,3′-bis[4-(methylsulfanyl)-2,2′-bipyridin-6-yl]biphenyl (L) is outlined in Scheme 1. The first step involves the coupling of 3-bromoacetophenone with a system catalytic in a nickel(0) species using an extension of the methodology developed by Iyoda *et al.*[11] The active catalyst is generated by zinc-dust reduction of a thf solution of $[NiCl_2(PPh_3)_2]$ in the presence of $[NEt_4]I$. The principal advantage of this methodology is that the acetyl group is not reduced under the mild conditions used. The reaction proceeds to give 3,3′-diacetylbiphenyl in 75% isolated yield as a white crystalline solid which was fully characterised.

In the second step of the synthesis two new pyridine rings are generated using Potts methodology.[8] The bis(enolate) of 3,3′-diacetylbiphenyl is generated *in situ* by reaction with potassium *tert*-butoxide and then treated with 3,3-bis(methylsulfanyl)-1-(2-pyridyl)prop-2-en-1-one to give a 1,5-dicarbonyl compound. The latter species was not isolated, but is treated immediately with ammonium acetate to give the new pyridine rings. The ligand L was obtained in approximately 50% yield as a white solid.

We also considered an alternative synthetic strategy in which the ring-synthesis step is performed first, to give 6-(3-bromophenyl)-4′-methylsulfanyl-2,2′-bipyridine which could then be coupled using the nickel(0) methodology. This synthetic route was rejected for several reasons. Performing the coupling reaction as the second step would be likely to give rise to a nickel(II) complex of L [as we have previously reported in the syntheses of 2,2′:6′,2″:6″,2‴-quaterpyridine (qtpy) and 2,2′:6′,2″:6″,2‴:6‴,2⁗:6⁗,2⁗′-sexipyridine[12] by nickel(0) methodology] and would require a stoichiometric (rather than a catalytic) amount of the nickel coupling reagent. More significantly, a cyanide demetallation step would then be required to yield free L from the metal complex and competing reactions at the MeS group might be observed. Furthermore, the successful coupling of halogenoaryl species containing RS (R = alkyl) substituents has not to our knowledge been achieved by nickel(0) methodology.



Scheme 1 (*i*) thf, $[NiCl_2(PPh_3)_2]$, zinc dust, $[NEt_4]I$, 50 °C 24 h; (*ii*) thf, $KOBu^t$, 3,3-bis(methylsulfanyl)-1-(2-pyridyl)prop-2-en-1-one, room temperature, 6 h; (*iii*) $MeCO_2H$, $[NH_4][O_2CMe]$, reflux, 8 h

The compound L has been characterised by ^1H NMR and infrared spectroscopies and by positive-ion FAB and EI mass spectrometry. The ^1H NMR data for L in CD_3SOCD_3 solution are presented in Table 1 along with those for the related compound 1,3-bis(2,2′-bipyridin-6-yl)benzene (L^1).[5] The spectra are very similar, which strongly suggests that the two compounds adopt similar configurations in solution. The infrared spectrum of L is also almost identical to that of L^1.[5] The mass spectra are unremarkable; a strong $M + 1$ peak is observed at m/z 555 in the positive-ion FAB spectrum and fragmentation peaks corresponding to the loss of pyridyl rings and of the MeS substituents in the EI spectrum.

The parent compound 3,3′-bis(2,2′-bipyridin-6-yl)biphenyl L^2 may be prepared by Kröhnke methodology[13,14] or the MeS substituents may be removed from L using a nickel tetrahydroborate catalyst[5,15] to yield L^2 the co-ordination chemistry of which we have shown to be completely analogous to that reported herein for L.[13]

Some of the potential co-ordination modes that might be adopted by L are depicted in Fig. 1. It was anticipated that metal ions possessing a preference for a four-co-ordinate tetrahedral geometry would direct the assembly of a double helicate in which each of two ligand molecules would present a didentate 2,2′-bipyridine metal-binding domain to the metal ion. The remaining didentate domain of each ligand would then co-ordinate to a second tetrahedral metal centre. The inevitable consequence is the adoption of a dinuclear double-helical structure analogous to that observed in the copper(I) and silver(I) complexes of qtpy[2,3] and proposed for the complexes of

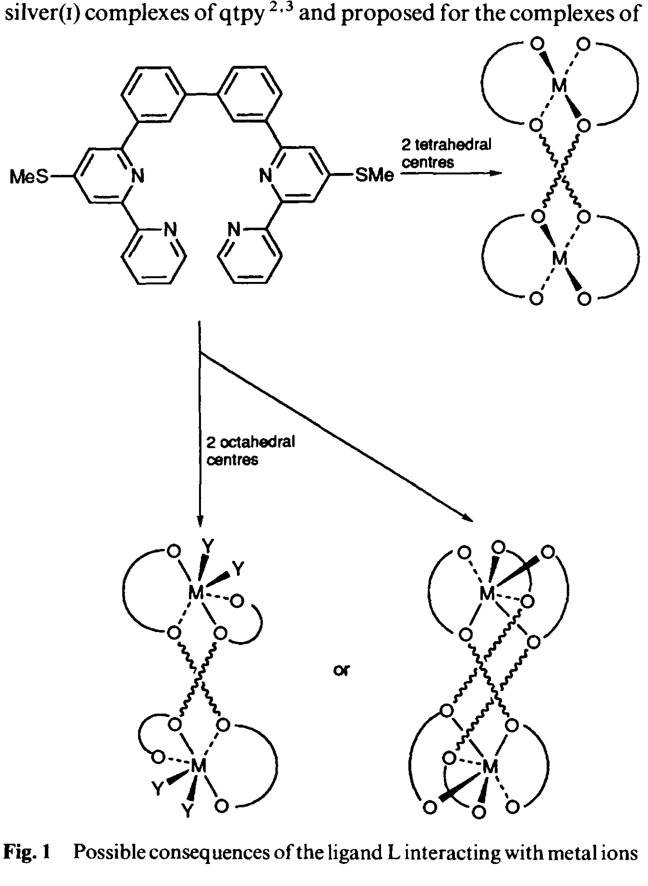


Fig. 1 Possible consequences of the ligand L interacting with metal ions

Table 1 Proton NMR chemical shift data (δ) for free compounds L and L^1 in CD_3SOCD_3 solution and their diamagnetic silver(I) and copper(I) complexes in CD_3CN solution

	$H^{3'}$	$H^{4'}$	$H^{5'}$	$H^{6'}$	$H^{3/5}$[a]	$H^{5/3}$[a]	H_a	H_b	H_c	H_d	SCH_3
L^1	8.65	8.01	7.51	8.74	8.01	8.23	9.04	8.36	7.70		2.72
L	8.59	7.94	7.49	8.72	8.02	8.22	8.57	8.31[b]	7.69	7.92[b]	2.70
$[Cu_2L^1{}_2]^{2+}$	8.00	7.82	7.05	7.64	7.26	7.70	9.56	7.36	7.05		2.79
$[Cu_2L_2]^{2+}$	7.73	7.62	6.89	7.62	7.30	7.40	8.19	7.40[b]	7.21	7.05[b]	2.72
$[Ag_2L^1{}_2]^{2+}$	7.93	7.87	7.06	7.67	7.14	7.63	9.69	7.52	7.23		2.76
$[Ag_2L_2]^{2+}$	7.65	7.65	6.92	7.51	7.27	7.40	8.60	7.47[b]	7.22	7.06[b]	2.72

[a] Ambiguity in the assignment of the resonances for H^3 and H^5 of these rings. [b] Ambiguity in the assignment of the resonances.

Table 2 Atomic coordinates (× 10^4) for non-hydrogen atoms in $[Cu_2L_2][PF_6]_2$

Atom	*x*	*y*	*z*
Cu(1)	3 541(1)	−16(1)	8 059(2)
Cu(2)	2 489(1)	2 440(1)	8 787(2)
S(1)	694(2)	−534(2)	8 842(4)
S(2)	5 204(1)	3 008(2)	10 232(4)
S(1′)	5 973(2)	1 537(2)	7 602(4)
S(2′)	233(2)	1 169(2)	6 320(4)
N(11)	3 472(5)	−362(4)	9 540(9)
C(12)	3 932(6)	−418(6)	10 214(11)
C(13)	3 866(6)	−640(6)	11 220(13)
C(14)	3 303(8)	−794(7)	11 596(14)
C(15)	2 841(7)	−718(7)	10 943(12)
C(16)	2 933(6)	−489(5)	9 892(11)
N(21)	2 581(4)	−81(4)	8 187(10)
C(22)	2 435(6)	−369(5)	9 097(11)
C(23)	1 871(6)	−525(6)	9 351(12)
C(24)	1 436(6)	−404(6)	8 601(13)
C(25)	1 576(6)	−131(6)	7 649(12)
C(26)	2 160(6)	36(5)	7 467(11)
C(27)	653(7)	−660(8)	10 309(15)
C(31)	2 704(5)	830(5)	6 612(11)
C(32)	2 302(5)	401(6)	6 508(11)
C(33)	2 002(6)	341(6)	5 516(11)
C(34)	2 125(6)	723(6)	4 641(12)
C(35)	2 524(6)	1 163(6)	4 774(11)
C(36)	2 838(6)	1 211(6)	5 782(12)
C(41)	3 371(5)	1 869(5)	7 056(10)
C(42)	3 254(5)	1 669(5)	5 968(11)
C(43)	3 575(6)	1 933(6)	5 087(13)
C(44)	3 995(6)	2 372(6)	5 347(13)
C(45)	4 076(6)	2 555(6)	6 411(11)
C(46)	3 770(6)	2 298(5)	7 279(12)
N(51)	3 401(4)	2 427(4)	9 119(8)
C(52)	3 861(6)	2 473(5)	8 414(11)
C(53)	4 402(5)	2 653(5)	8 769(13)
C(54)	4 490(5)	2 792(5)	9 868(12)
C(55)	4 041(5)	2 749(5)	10 613(12)
C(56)	3 491(5)	2 571(5)	10 178(11)
C(57)	5 162(6)	3 136(7)	11 672(14)
N(61)	2 453(4)	2 534(4)	10 413(10)
C(62)	2 976(6)	2 536(6)	10 897(12)
C(63)	3 027(6)	2 503(6)	12 079(11)
C(64)	2 524(6)	2 463(5)	12 708(12)
C(65)	1 997(6)	2 463(6)	12 162(11)
C(66)	1 968(6)	2 509(6)	11 017(12)
N(11′)	3 801(4)	−35(5)	6 522(9)
C(12′)	3 510(6)	−341(6)	5 740(12)
C(13′)	3 606(7)	−269(7)	4 667(12)
C(14′)	4 038(7)	127(6)	4 342(12)
C(15′)	4 344(6)	441(6)	5 114(11)
C(16′)	4 210(5)	356(5)	6 219(11)
N(21′)	4 219(4)	679(4)	8 086(9)
C(22′)	4 495(6)	666(5)	7 108(11)
C(23′)	5 017(5)	933(5)	6 935(11)
C(24′)	5 302(5)	1 218(5)	7 816(12)
C(25′)	4 994(5)	1 249(5)	8 818(12)
C(26′)	4 458(5)	971(5)	8 914(12)
C(27′)	6 169(6)	1 808(6)	8 964(13)
C(31′)	3 531(5)	963(5)	9 910(10)
C(32′)	4 120(6)	1 000(5)	9 954(10)
C(33′)	4 389(6)	1 076(6)	10 798(11)
C(34′)	4 054(6)	1 102(6)	11 913(12)
C(35′)	3 446(6)	1 051(6)	11 844(11)
C(36′)	3 178(6)	989(5)	10 820(13)
C(41′)	2 312(5)	1 200(5)	9 740(10)
C(42′)	2 534(5)	962(6)	10 681(11)
C(43′)	2 145(6)	726(6)	11 455(11)
C(44′)	1 560(5)	619(6)	11 245(12)
C(45′)	1 340(5)	950(5)	10 286(11)
C(46′)	1 711(5)	1 200(5)	9 515(10)
N(51′)	1 828(4)	1 893(4)	8 036(9)
C(52′)	1 507(5)	1 457(5)	8 474(12)
C(53′)	1 023(5)	1 243(5)	7 935(11)
C(54′)	843(5)	1 466(6)	6 951(12)
C(55′)	1 180(5)	1 922(5)	6 502(11)
C(56′)	1 650(5)	2 119(5)	7 063(10)
C(57′)	194(7)	1 520(8)	5 036(14)
N(61′)	2 376(4)	2 857(4)	7 388(9)
C(62′)	2 013(5)	2 616(5)	6 632(11)
C(63′)	1 968(5)	2 808(5)	5 582(10)
C(64′)	2 302(6)	3 287(6)	5 266(12)
C(65′)	2 686(6)	3 518(6)	5 984(12)
C(66′)	2 703(6)	3 301(6)	7 073(12)
P(1)	8 559(2)	959(2)	3 294(3)
F(1)	7 886(4)	855(6)	3 567(9)
F(2)	8 386(5)	1 129(5)	2 077(8)
F(3)	8 614(5)	309(4)	2 930(10)
F(4)	8 740(4)	802(4)	4 533(7)
F(5)	8 468(6)	1 610(4)	3 675(10)
F(6)	9 212(4)	1 077(6)	3 005(9)
P(2)	4 446(2)	−1 760(2)	3 586(3)
F(7)	5 096(3)	−1 994(4)	3 464(8)
F(8)	4 366(4)	−1 833(3)	2 288(7)
F(9)	4 214(3)	−2 408(3)	3 771(8)
F(10)	4 534(4)	−1 687(4)	4 897(8)
F(11)	4 682(4)	−1 115(3)	3 419(7)
F(12)	3 791(3)	−1 532(3)	3 686(8)

the same metal ions with L^1.[5] With metal ions possessing a preference for an octahedral geometry a related structure should be obtained with two additional donors completing the co-ordination sphere of each metal ion. This has previously been observed[5] in the structurally characterised cation $[(MeCO_2)NiL^1{}_2Ni(O_2CMe)]^{2+}$. As an alternative, three ligand molecules might wrap around two metal ions, each presenting a 2,2′-bipyridyl binding subunit to each metal centre and forming a dinuclear cation possessing a triple-helical geometry.[16]

The reaction of a solution of L with $[Cu(MeCN)_4][PF_6]$ in degassed methanol gave a deep red solution from which a dark red hexafluorophosphate salt was precipitated upon cooling. This same product was obtained when L and copper(II) acetate were heated in methanol and then the red-brown solution was treated with an excess of methanolic $[NH_4][PF_6]$. The infrared spectrum of the complex shows aromatic stretching modes and also peaks corresponding to the hexafluorophosphate counter ion and is very similar[5] to that of $[Cu_2L^1{}_2][PF_6]_2$. Partial

Table 3 Selected bond lengths (Å) and bond angles (°) for $[Cu_2L_2][PF_6]_2$

Cu(1)–N(11′)	1.973(11)	Cu(1)–N(11)	1.986(11)
Cu(1)–N(21)	2.219(10)	Cu(1)–N(21′)	2.245(9)
Cu(2)–N(61′)	1.982(11)	Cu(2)–N(61)	2.001(12)
Cu(2)–N(51)	2.140(10)	Cu(2)–N(51′)	2.185(10)
N(11′)–Cu(1)–N(11)	152.0(3)	N(11′)–Cu(1)–N(21)	111.6(3)
N(11)–Cu(1)–N(21)	80.2(4)	N(11′)–Cu(1)–N(21′)	79.5(4)
N(11)–Cu(1)–N(21′)	109.4(3)	N(21)–Cu(1)–N(21′)	137.7(3)
N(61′)–Cu(2)–N(61)	143.0(3)	N(61′)–Cu(2)–N(51)	107.4(3)
N(61)–Cu(2)–N(51)	81.6(4)	N(61′)–Cu(2)–N(51′)	80.2(4)
N(61)–Cu(2)–N(51′)	116.9(3)	N(51)–Cu(2)–N(51′)	139.0(3)

microanalytical data are consistent with a formulation $CuL(PF_6)$ and the FAB mass spectrum shows peaks (with the correct isotopomer distributions) corresponding to CuL (*m*/*z* 617), Cu_2L (682), Cu_2L_2 (1236) and $Cu_2L_2(PF_6)$ (1381). The electronic spectrum of an acetonitrile solution of the complex shows a broad absorption centred at 513 ($\varepsilon = 3200$) and a shoulder at about 380 nm ($\varepsilon \approx 5000$ dm^3 mol^{-1} cm^{-1}). These data are similar to those previously reported[5] for the $[Cu_2L^1{}_2]^{2+}$ cation and are fully consistent with a double-helical formulation, $[Cu_2L_2][PF_6]_2$.

Recrystallisation of the red salt from acetonitrile by slow diffusion of diethyl ether vapour afforded red crystals of the complex which proved to be suitable for X-ray analysis and the structure of one of the two enantiomers of the cation present in the lattice is shown in Fig. 2(*a*). The cation is indeed a dinuclear double helix, and a space-filling representation emphasising this architecture is presented in Fig. 2(*b*). Each of the two copper atoms is co-ordinated to a didentate domain from each ligand strand to give a pseudo-tetrahedral site. The Cu–N bond lengths [1.973(11)–2.245(9) Å] and the bite angles to the bipyridyl subunits [79.5(4)–81.6(4)°] are unremarkable and are generally similar to those observed in the double-helical cation $[Cu_2(qtpy)_2]^{2+}$.[3] The pyridine rings within the 2,2′-bipyridine subunits are not fully coplanar (interplanar angles of 6.3, 20.0, 13.5 and 21.5°), but the major twists within the ligand strands are found to be between the 2,2′-bipyridine units and the biphenyl-3,3′-diyl spacer groups (36.4, 31.3, 26.2 and 31.5°) and within the biphenyl-3,3′-diyl units (25.5 and 32.9°). In contrast to our observations with previous systems, intramolecular π-stacking interactions do not appear to play a significant role in the stabilisation of helical structure in the solid state. Rings 2 and 4′ (rings numbered according to the nitrogen atoms they contain) are approximately coplanar with a centroid–centroid distance of 3.8 Å which may indicate a weak π–π interaction; all of the other rings are separated with intercentroid distances greater than 4 Å. The two copper(I) ions are separated by 6.26 Å, which is approximately twice the intermetallic distance of 3.17 Å observed[3] in the cation $[Cu_2(qtpy)_2]^{2+}$. This observation supports our earlier suggestions that the incorporation of specifically designed space groups may be used to control the intermetallic distance within a multinuclear double helix, and also to control the overall length of the helical structure. In contrast to the smaller helicates which have been previously structurally characterised,[2,3] each ligand strand twists through a complete helical turn in this cation. There are no significant intermolecular cation–cation or –anion interactions.

The electrochemical behaviour of an acetonitrile solution of this copper complex has been investigated by cyclic voltammetry. The compound exhibits a single reversible oxidation at +0.11 V (*vs.* ferrocene–ferrocenium) corresponding to the simultaneous oxidation of both redox centres. A stable mixed-valence copper(I)–copper(II) complex is not observed with this ligand system. The cyclic voltammetric behaviour of the complex is independent of scan rate. An irreversible reduction process is observed at −1.95 V as copper metal plates out on the electrode. The oxidation potential compares closely with the value of the copper(I) complex of L^1 (+0.12 V)[5] and further supports our suggestion of a similar arrangement of the donor set about the metal centres in the latter complex. The reversible nature of the two-electron oxidative wave confirms the stability of the double-helical structure and may usefully be contrasted with the behaviour[3] of the complex $[Cu_2(qtpy)_2][PF_6]_2$ in the same solvent. In this latter complex the oxidation occurs at a similar potential (+0.05 V), but is, however, irreversible as it is followed by breakdown of the double-helical structure to give a mononuclear copper(II) species.

The aromatic region of the room-temperature 250 MHz ^1H NMR spectrum of a solution of a crystalline sample of the complex in CD_3CN solution is shown in Fig. 3(*a*). The spectrum is slightly broadened, and at 400 MHz the broadening is increased. This broadening reflects fluxional behaviour resulting from the flexible nature of the helix with the larger spacer group. It seems likely that the fluxional behaviour is a 'ring-wobbling' motion of the phenyl spacer rings which lie over the co-ordinated pyridine rings on the other strand of the helical structure. Similar processes have been described in related complexes bearing non-co-ordinated pyridyl or phenyl residues.[5] We have not made a detailed variable-temperature study of the spectroscopic behaviour of this complex. A single MeS resonance is observed at δ 2.72 indicating that in solution the two ligands are equivalent on the NMR time-scale. The aromatic region of the spectrum only exhibits ten resonances, again confirming the equivalence of the two ligands. The spectrum has been assigned with the aid of decoupling experiments, and the assignments are shown in Fig. 3(*a*) and the data are included in Table 1.

In general, silver(I) and copper(I) centres behave similarly in their interactions with helicating ligands. The reaction of silver(I) acetate with a solution of L in methanol gave a colourless solution from which a white salt was precipitated upon treatment with methanolic $[NH_4][PF_6]$. The FAB mass spectrum of this salt shows peaks with the correct isotopomer distributions corresponding to AgL, Ag_2L, AgL_2 and $Ag_2L_2(PF_6)$ suggesting a dinuclear structure. Partial microanalytical data confirm a formulation $AgL(PF_6)$. The infrared spectrum of the salt exhibits ligand stretches and peaks corresponding to the hexafluorophosphate counter ion. Other than those peaks corresponding to counter ion stretches, the infrared spectra of this salt and of the complex[5] $[Ag_2L^1{}_2][BF_4]_2$ are virtually identical. The 250 MHz ^1H NMR spectrum at room temperature [Fig. 3(*b*)] is less broad than that of the copper(I) species but still shows an increased broadening when recorded at 400 MHz. The spectrum has been assigned with the help of 400 MHz ^1H NMR correlation spectroscopy (COSY) (Fig. 4) and the resulting assignments are presented in Fig. 3(*b*) and Table 1. The chemical shifts of the proton resonances are generally similar to those of the dicopper(I) complex (Table 1), implying a similar dinuclear double-helical solution structure.

Solutions of the complex are resistant to persulfate oxidation and the cyclic voltammogram of a solution of the complex in acetonitrile shows no Ag^I–Ag^{II} or ligand oxidative processes. This may be usefully compared with the behaviour of dinuclear double-helical cation $[Ag_2(qtpy)_2]^{2+}$ and the related cation $[Ag_2L^1{}_2]^{2+}$ which are similarly resistant to oxidation; the cation $[Ag(bipy)_2]^+$ (bipy = 2,2′-bipyridine) is readily oxidised to a silver(II) species. It appears that the increased flexibility afforded by the biphenyl-3,3′-diyl spacer is not accompanied by a destabilisation of the helical array. These data are all consistent with a dinuclear double-helical geometry for $[Ag_2L_2]^{2+}$ cation which is strictly analogous to the structurally characterised dicopper(I) complex.

Heating nickel(II) acetate with compound L in methanol gave a green solution from which green crystals precipitated on the addition of an excess of methanolic $[NH_4][PF_6]$. Partial microanalytical data for the green crystals are consistent with a formulation $NiL(O_2CMe)$ and the FAB mass spectrum shows

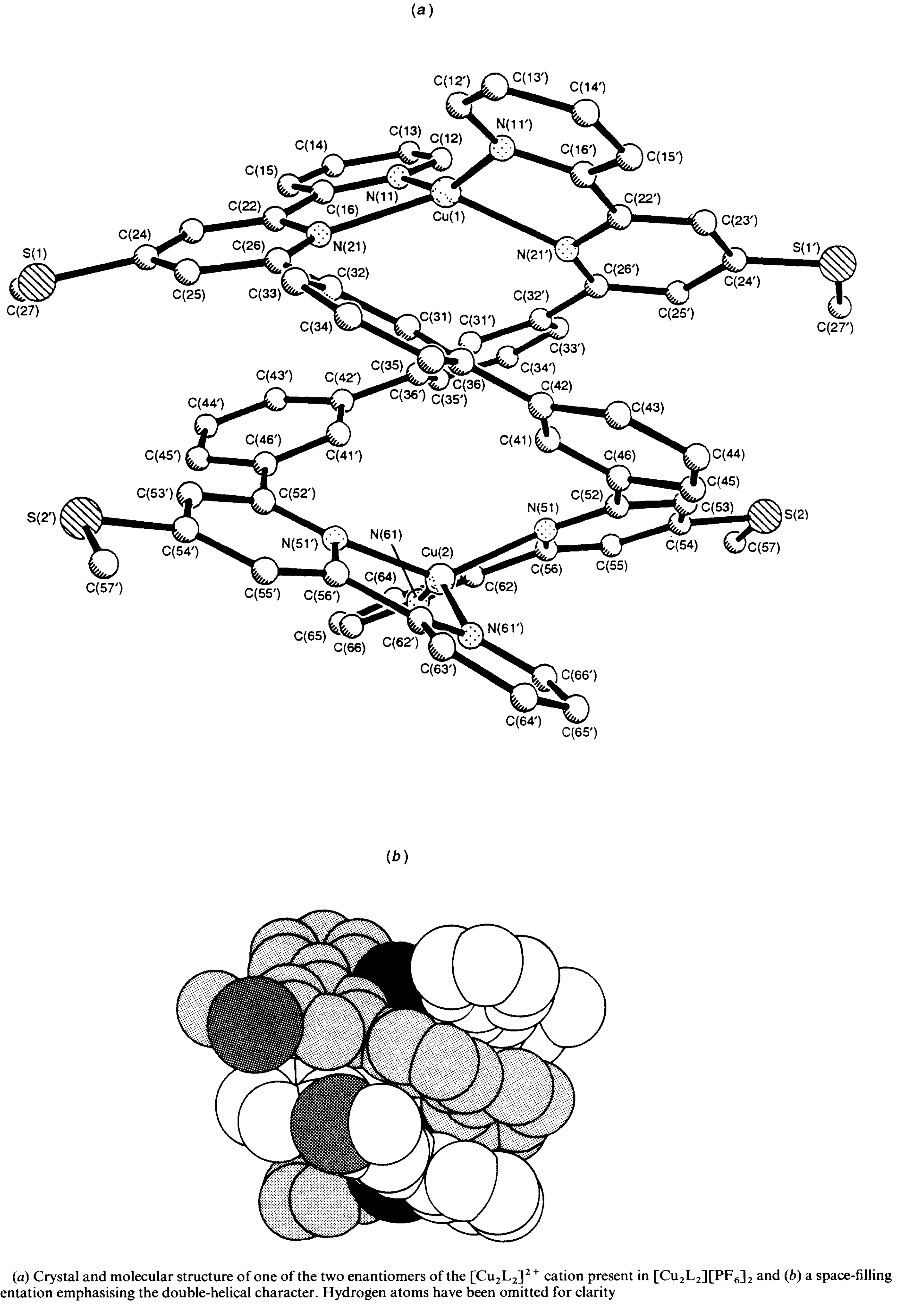


Fig. 2 (*a*) Crystal and molecular structure of one of the two enantiomers of the $[Cu_2L_2]^{2+}$ cation present in $[Cu_2L_2][PF_6]_2$ and (*b*) a space-filling representation emphasising the double-helical character. Hydrogen atoms have been omitted for clarity

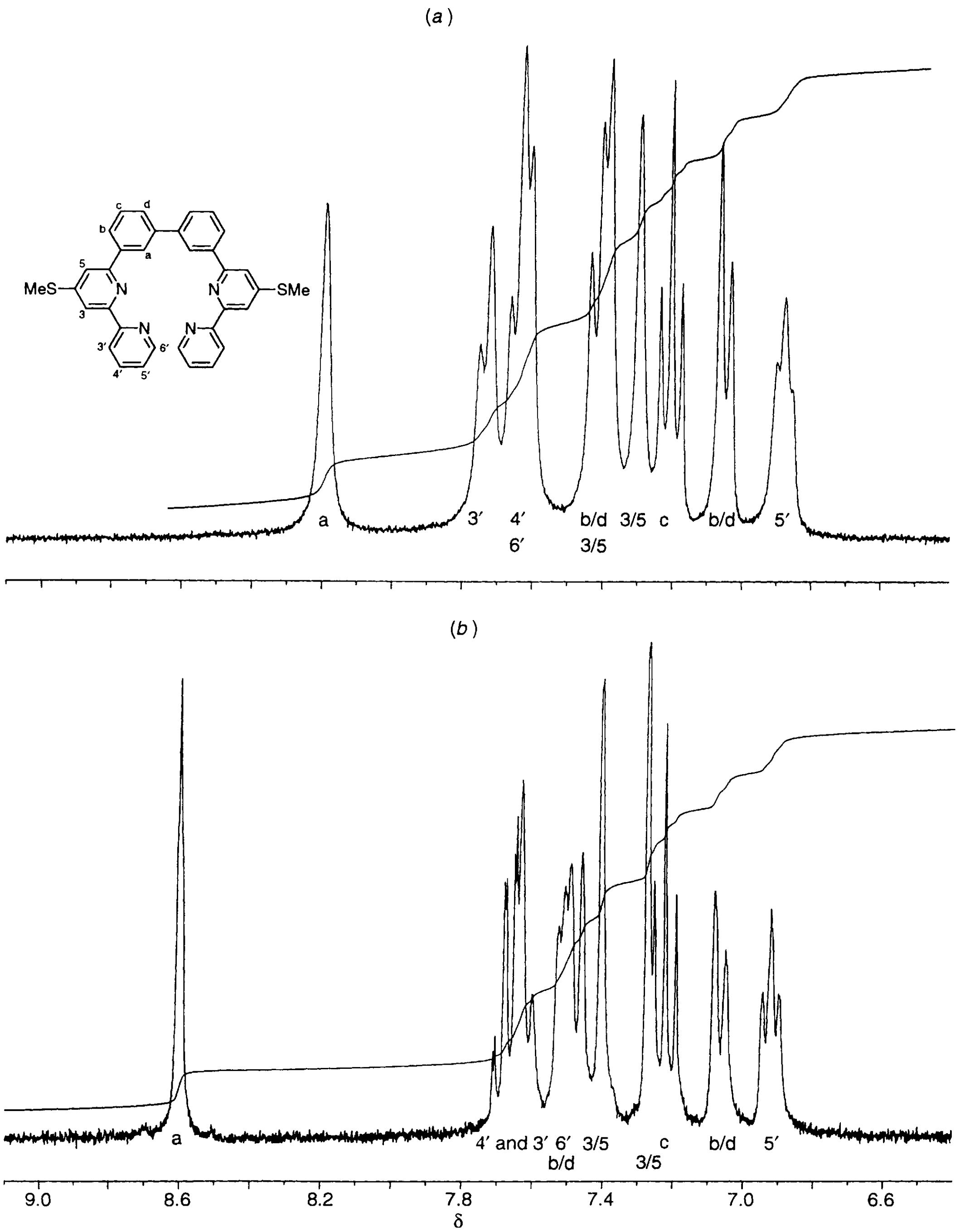


Fig. 3 Aromatic region of the 250 MHz ^1H NMR spectrum of CD_3CN solutions of (*a*) $[Cu_2L_2][PF_6]_2$ and (*b*) $[Ag_2L_2][PF_6]_2$

peaks, with the correct isotopomer distributions, corresponding to NiL, $NiL(O_2CMe)$, NiL_2, Ni_2L_2, $Ni_2L_2(O_2CMe)$, $Ni_2L_2(O_2CMe)_2$, $Ni_2L_2(O_2CMe)(PF_6)$ and $Ni_2L_2(O_2CMe)_2(PF_6)$. These data are consistent with a formulation $[(MeCO_2)NiL_2Ni(O_2CMe)][PF_6]_2$. No higher-mass peaks are observed, suggesting that the larger and more flexible biphenyl-3,3′-diyl spacer is not sufficiently flexible to permit the formation of triple-helical complexes. The infrared spectrum shows peaks due to the ligand and to the hexafluorophosphate counter ion and is virtually identical to that of the structurally characterised complex $[(MeCO_2)NiL^1{}_2Ni(O_2CMe)][PF_6]_2$.

X-Ray crystallographic data on one of the green crystals have been collected and a representation of the preliminary structure is presented in Fig. 5. Unfortunately one of the counter ions is highly disordered and we have been unable to obtain a definitive solution. Repeated attempts to grow better crystals with a variety of counter ions have been unsuccessful, and we are not optimistic that we will be able to obtain a fully refined structure. Nevertheless, this preliminary structure confirms the double-helical nature of the cation $[(MeCO_2)NiL_2Ni(O_2CMe)]^{2+}$. The structure is generally similar to that previously reported for the $[(MeCO_2)NiL^1{}_2Ni(O_2CMe)]^{2+}$ cation[5] with each metal centre co-ordinated to a 2,2′-bipyridine domain from each ligand and the co-ordination sphere completed by a didentate acetate ion. As anticipated, the replacement of the 1,3-phenylene spacer with the biphenyl-3,3′-diyl spacer increases the pitch of the helix and the two metal centres are separated by around 7.7 Å {*cf.* Ni–Ni 5.87(1) Å in the $[(MeCO_2)NiL^1{}_2Ni(O_2CMe)]^{2+}$ cation[5]}.

The 250 MHz ^1H NMR spectrum of the (paramagnetic) dinickel(II) complex in CD_3CN solution has been recorded and is shown in Fig. 6(*a*). The spectrum shows the high degree of

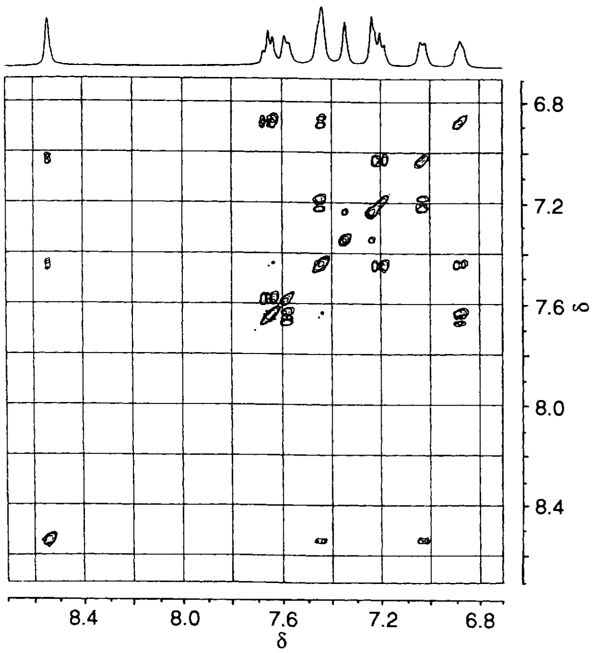


Fig. 4 The 400 MHz ^{1}H NMR COSY spectrum of a CD_3CN solution of $[Ag_2L_2][PF_6]_2$

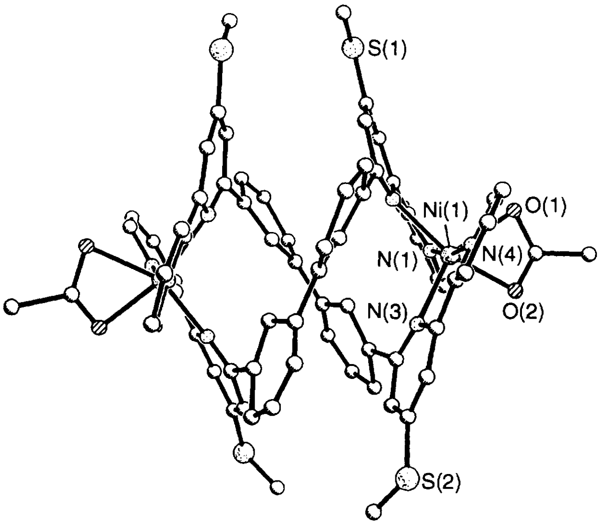


Fig. 5 Structure of one of the enantiomers of the $[(MeCO_2)NiL_2Ni(O_2CMe)]^{2+}$ cation

symmetry in the complex and very clearly indicates the presence of only one solution species. The number of resonances shows that the ligand L is symmetrical about the central biphenyl-3,3′-diyl unit on the NMR time-scale. The spectrum is superficially very similar to that of $[(MeCO_2)NiL^1{}_2Ni(O_2CMe)][PF_6]_2$ suggesting that the double-helical structure is also maintained in solution. The cyclic voltammogram of an acetonitrile solution of the complex shows no Ni^{II}–Ni^{III} redox processes and a variety of ligand-centred reductions.

The reaction of methanolic solutions of nickel(II) acetate with L in methanol in the ratio 2 : 3 and in a variety of other ratios has also been examined. In each case the only complexes isolated contained the $[(MeCO_2)NiL_2Ni(O_2CMe)]^{2+}$ cation. Attempts to prepare a dinuclear triple-helical complex from the interactions of L with alternative nickel(II) starting materials (perchlorate, nitrate or sulfate) were also unsuccessful. This suggests that the biphenyl-3,3′-diyl spacer is not sufficiently flexible to permit the formation of triple-helical cations and, instead, promotes the formation of double helicates. Molecular modelling studies support this view.

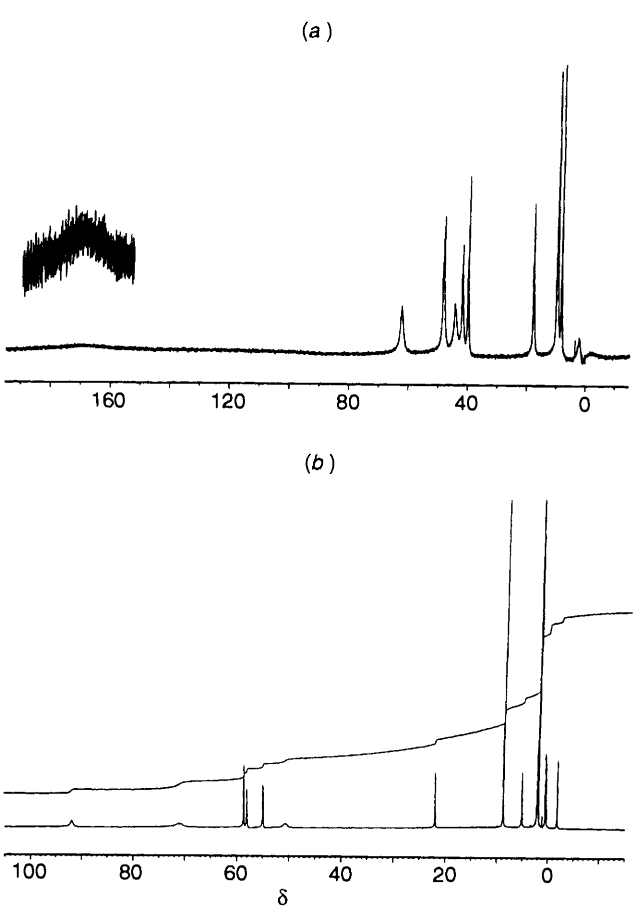


Fig. 6 The 250 MHz ^{1}H NMR spectra of CD_3CN solutions of (*a*) $[(MeCO_2)NiL_2Ni(O_2CMe)][PF_6]_2$ and (*b*) $[(MeCO_2)CoL_2Co(O_2CMe)][PF_6]_2$

The reaction of cobalt(II) acetate with L in methanol gave an orange solution from which an orange salt was precipitated by the addition of methanolic $[NH_4][PF_6]$. The FIB mass spectrum of this shows peaks corresponding to CoL, $CoL(O_2CMe)$, CoL_2, Co_2L_2, $Co_2L_2(O_2CMe)(PF_6)$ and $Co_2L_2(O_2CMe)_2(PF_6)$ suggesting a dinuclear formulation. The infrared and ^{1}H NMR spectroscopic data [Fig. 6(*b*)] for this salt are very similar to those[5] of $[(MeCO_2)CoL^1{}_2Co(O_2CMe)][PF_6]_2$ and it seems likely that the orange product is $[(MeCO_2)CoL_2Co(O_2CMe)][PF_6]_2$ and possesses a similar double-helical structure. The infrared spectrum is almost identical to that of the nickel(II) complex $[(MeCO_2)NiL_2Ni(O_2CMe)][PF_6]_2$ lending further support for a dinuclear double-helical structure. It has not proved possible to obtain material suitable for X-ray analysis to confirm this proposal. This cyclic voltammogram of an acetonitrile solution of the complex shows no Co^{II}–Co^{III} redox processes and a variety of ligand-centred reductions.

The introduction of a biphenyl-3,3′-diyl spacer between two 2,2′-bipyridine metal-binding domains yields a compound which forms double helicates of predictable structure with a variety of transition-metal ions. Neither mononuclear nor triple-helical complexes are observed. The introduction of this elongated spacer group leads both to large intermetallic distances within the helical array and to an increase in length of the overall assembly along the helical axis. This, combined with our earlier work on compounds in which 2,2′-bipyridine domains are linked directly or with a 1,3-phenylene spacer, emphasises the ability to design helicates with precise structural properties. We are currently investigating the structural and electrochemical effects of substituents on the co-ordination behaviour of such helicating compounds.

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