Copper(I) and Silver(I) Homometallic Complexes of New Bis(2,2'-bipyridine) Ligands

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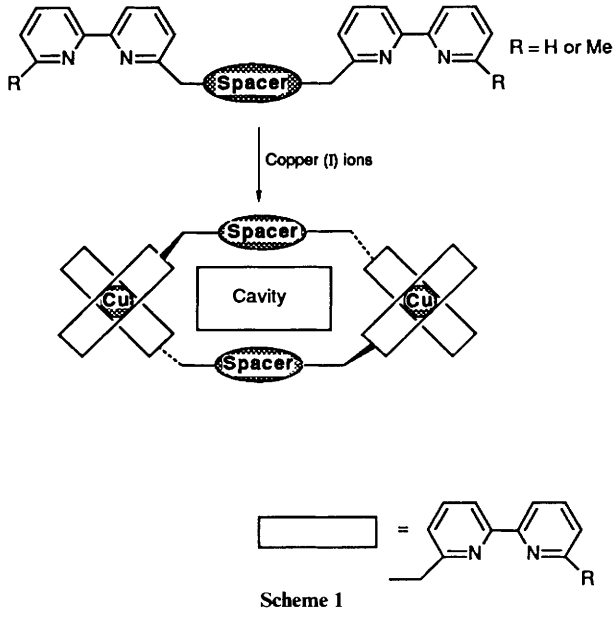
New ligand systems containing two 2,2'-bipyridin-6-ylmethyl moieties linked *via* 1,4,10,13-tetraoxa-7,16-diazacyclooctadecane, 1,4,10,13-tetrathia-7,16-diazacyclooctadecane, 4,4'-bipyridinediium, *N,N',N''*-tritosyldiethylenetriamine and toluene-*p*-sulfonamide spacer units have been prepared. A variety of homometallic copper(I) complexes have been isolated and fast atom bombardment mass spectrometry investigations suggest most of the complexes to be of general formula $[Cu_2L_2][PF_6]_2$. Solution ^1H NMR spectra of these species imply the existence of additional complex components of 1 : 1 L:copper(I) ratio. A variety of mono- and bi-metallic silver(I) complexes were also isolated with these ligands.

The self-assembly of well defined supramolecular structures from their component species is of considerable current interest.[1] Lehn and co-workers[2] have designed linear polybipyridyl ligands that spontaneously undergo self-organisation in the presence of copper(I) ions to form double-stranded helicates. Similar helical entities have been constructed by Constable and co-workers,[3] using oligopyridines and a variety of transition metals such as copper(I),[3a] copper(II),[3b] cobalt(II),[3c] cadmium(II),[3d] zinc(II)[3e] and silver(I).[3e] In each case the preferred geometry of the metal ion influences the precise nature of the helix produced. Sauvage and co-workers[4] have designed and prepared a synthon containing two 1,10-phenanthroline units which has been used to self-assemble a helical species with copper(I) ions and subsequently shown to undergo cyclisation reactions to produce the exotic trefoil knot.

We were interested in utilising this copper(I) self-assembly process for the potential construction of new macrocyclic host systems. Acyclic ligands that consist of two 2,2'-bipyridine moieties linked by a spacer unit may complex with copper(I) cations in a [2 + 2] manner to form helical products and at the same time create a chiral cavity designed subsequently to include a chiral guest (Scheme 1). This paper describes our initial efforts towards this goal through the preparation of a variety of new bis(2,2'-bipyridine) ligands containing diaza crown ether, diaza crown thia ether, 4,4'-bipyridinediium, *N,N',N''*-tritosyldiethylenetriamine, and toluene-*p*-sulfonamide linkages and their copper(I) and silver(I) co-ordination chemistry.



Scheme 1

Results and Discussion

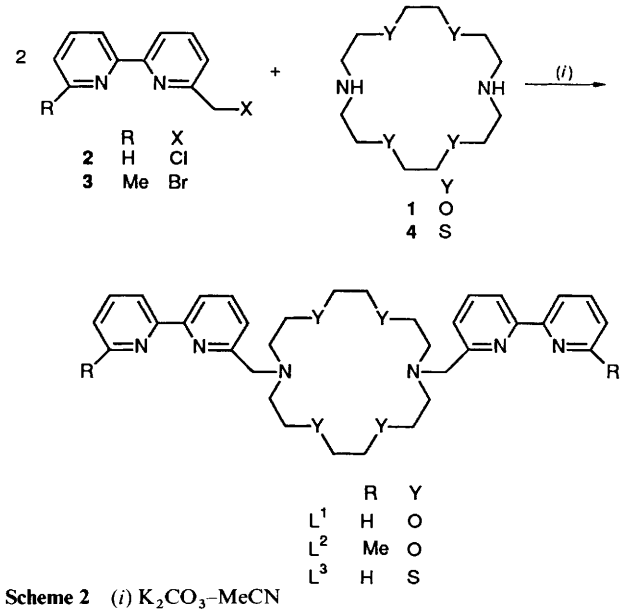
Ligand Syntheses.—The reaction of diaza-18-crown-6 (1,4,10,13-tetraoxa-7,16-diazacyclooctadecane) **1** with 2 equivalents of 6-chloromethyl-2,2'-bipyridine **2**[5] in acetonitrile in the presence of potassium carbonate gave, after column chromatography on alumina and recrystallisation from acetonitrile, L^1 in 80% yield. Analogous synthetic procedures were used to prepare L^2 and L^3 in 77 and 75% yields respectively using 2 equivalents of 6-bromomethyl-6'-methyl-2,2'-bipyridine **3**[6] and **1**, and diaza tetrathia crown ether **4** and 2 equivalents of **2**, Scheme 2.

4,4'-Bipyridine **5** was added to an acetonitrile solution of 2 equivalents of **3** and the resulting mixture refluxed for 48 h to give on cooling a yellow-green precipitate. The solid was collected, dissolved in water and treated with ammonium hexafluorophosphate to produce the dicationic ligand L^4 in 86% yield (Scheme 3).

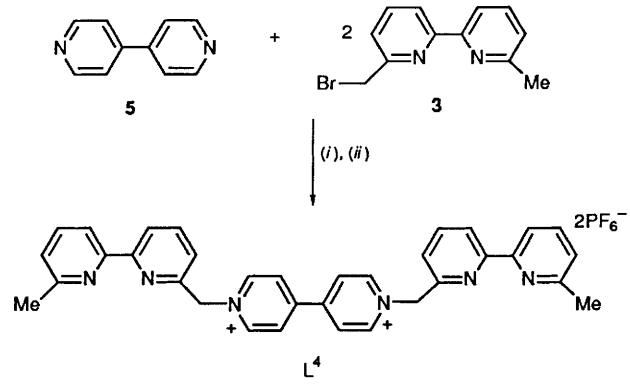
The reaction of 2 equivalents of compound **2** with the disodium salt of *N,N',N''*-tritosyldiethylenetriamine **6**[7] in dimethylformamide (dmf) at 70 °C gave, after column chromatographic purification on silica gel using CH_2Cl_2–MeOH (98:2) as eluent, the ligand L^5 as a pale yellow oil. Addition of acetonitrile and subsequent trituration over several hours produced L^5 as a white solid in *ca.* 50% yield (Scheme 4).

The tosylamide sodium salt **7** and 2 equivalents of compound **2** were dissolved in ethanol and heated to reflux for 5 h. The resulting crude product was purified by column chromatography on alumina using CH_2Cl_2–MeOH (99:1) as eluent, and recrystallisation from acetonitrile gave ligand L^6 in 56% yield as pale yellow crystals (Scheme 5).

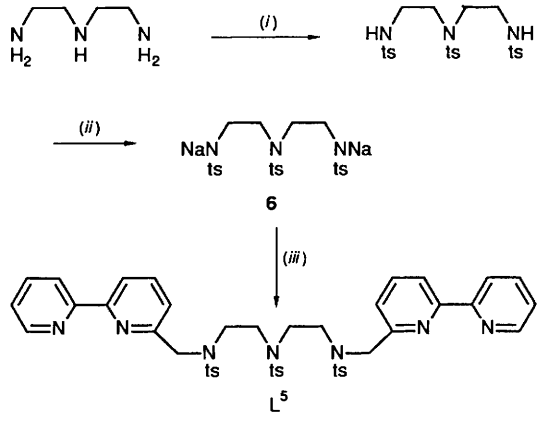
All of these new ligands were characterised using ^1H and ^{13}C NMR, mass spectrometry and elemental analysis (see Experimental section).



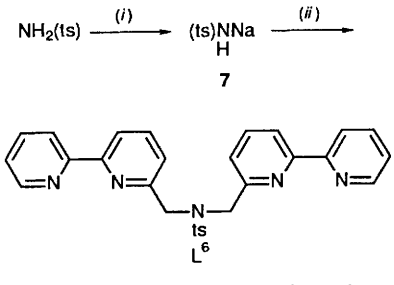
Scheme 2 (*i*) K_2CO_3–MeCN



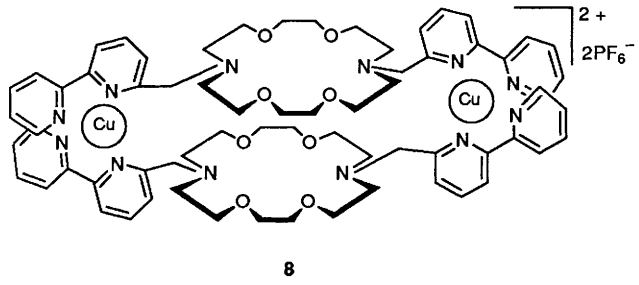
Scheme 3 (*i*) MeCN; (*ii*) NH_4PF_6–water



Scheme 4 ts = Tosyl. (*i*) 3 Tosyl chloride, pyridine; (*ii*) Na–MeOH; (*iii*) 2 equivalents of **2**, dmf, 70 °C



Scheme 5 (*i*) Na–MeOH; (*ii*) 2 equivalents of **2**, EtOH



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Copper(I) Complexation Studies.—With macrocyclic ligands L^{1-3}. A general procedure for the copper(I) complexation was employed for each ligand. For example, to L^1 dissolved in acetonitrile was added an acetonitrile solution of tetrakis(acetonitrile)copper(I) hexafluorophosphate.[8] A deep red homogeneous solution immediately formed whose UV/VIS spectrum revealed a characteristic metal-to-ligand charge-transfer (m.l.c.t.) band at 445 nm, and upon addition of diethyl ether a red precipitate was collected and dried. The fast atom bombardment (FAB) mass spectrum of the red product revealed a peak at *m/z* 1468 which corresponds to the cationic fragment $[Cu_2L^1{}_2(PF_6)]^+$. This experimental observation is consistent with the desired [2 + 2] helical species **8**. A signal at *m/z* 661 was also present which may be assigned to a [1 + 1] $[CuL^1]^+$ moiety or the doubly charged cation of the [2 + 2] complex $[Cu_2L^1{}_2]^{2+}$. It was not possible to measure the peak spacings because the FAB mass spectrum was at low resolution. Elemental analysis indicated that the red product contained the ligand L^1 and copper(I) in a 1:1 ratio, but obviously this does not discriminate between the existence of [1 + 1] and [2 + 2] complexes.

The ^1H NMR spectrum recorded in CD_3CN was surprisingly found to exhibit very broad featureless absorptions suggesting either a mixture of copper(I)-complexed species undergoing rapid exchange on the NMR time-scale or the presence of copper(II) paramagnetic impurities. A careful ^1H NMR titration experiment in the same solvent under nitrogen and in the absence of water produced similar results. After the addition of 0.5 equivalent of $[Cu(MeCN)_4]PF_6$ to a CD_3CN solution of L^1 the resonances of all the aza crown ether, methylenebipyridyl and bipyridyl (4,4′, 5,5′, 6,6′) protons became broad. A noteworthy exception were the bipyridyl 3,3′ protons which remained as a pair of doublets. The methylene protons adjacent to the bipyridyl moiety had moved upfield by *ca.* 0.1 ppm. The progressive addition of 0.5 equivalent increments of $[Cu(MeCN)_4]PF_6$ up to 2.5 equivalents resulted in these methylenebipyridyl protons becoming broader and broader and the ligand aza crown ether and bipyridyl protons began to show complicated broad multiplets. Analogous titration experiments were carried out in CD_2Cl_2 and although precipitation problems were encountered similar broad-peak spectra were obtained.

Proton NMR spectra were also recorded in CD_3CN–CD_2Cl_2 (1:1) at low temperatures. It was noteworthy that at −43 °C an AB system for the methylene protons adjacent to the bipyridyl group was observed. As Lehn and co-workers [2] discussed, in the formation of the kinetically inert double-stranded copper(I) helicate complexes produced from oligobipyridyl ligands, this AB absorption pattern is indicative of the formation of an inflexible species in which the methylene protons exist in different chemical environments and is therefore evidence for the existence of the [2 + 2] double helicate. However, relative ^1H NMR integration revealed this AB pattern accounted for only *ca.* 60% of all species in solution implying the presence of more than one type of solution copper(I) complex. Models were used to suggest their possible solution structures (Fig. 1). The complexes in Fig. 1(*a*) and 1(*b*) are both distinct isomeric [2 + 2] species, the former being of a helical nature. The

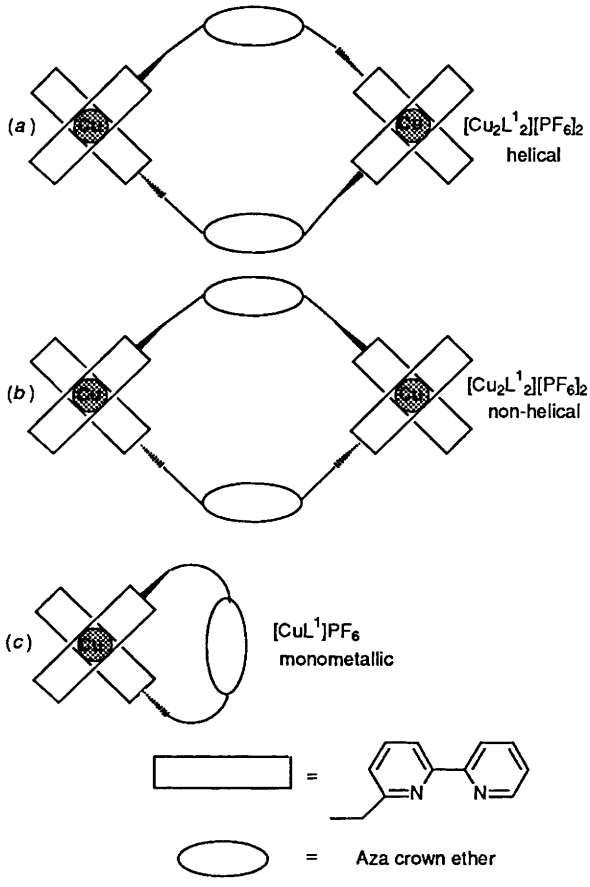

Fig. 1 Schematic representation of the possible forms of the copper(I) complexes of the ligand L^1

effective twelve-atom linkage between the 2,2′-bipyridyl ligating sites is flexible and may allow both of these types of complex to co-exist in solution. Also they are only interchangeable as a result of a copper(I) decomplexation–recomplexation process. In the template copper(I) synthesis of the trefoil knot, Sauvage and co-workers[4,9] observed similar isomeric types of complexes derived from ligands containing two 1,10-phenanthroline binding sites, with only one leading to the formation of the desired product. The mononuclear [1 + 1] complex [Fig. 1(*c*)] could also be present in solution since models imply the aza crown ether spacer unit is flexible enough to enable L^1 to wrap around a single copper(I) cation.

Ligand L^2 was synthesised with the intention of the extra methyl group in the 6′ position of the 2,2′-bipyridyl moiety conferring interlocking stabilisation of the target [2 + 2] complex. Nonetheless, although complexation with copper(I) afforded a deep red solid exhibiting molecular ions at *m*/*z* 1523 $\{[Cu_2L^2_2(PF_6)]^+\}$ and 689 $([CuL^2]^+)$ in the FAB mass spectrum, and elemental analysis consistent with 1:1 L^2:Cu, the room- and low-temperature ^1H NMR spectra were very similar to those obtained with copper(I) complexes of L^1. Therefore it must be concluded that the more sterically demanding aza crown ether spacer unit, compared to Lehn's simple CH_2OCH_2 ether linkage,[2] destabilises the respective [2 + 2] helicate complexes to such an extent that a proportion spontaneously decomplex in solution to produce an equilibrium mixture of helical and non-helical complexes.

The copper(I) complex of L^3 was isolated as a pale orange solid and elemental analysis suggested two copper(I) cations to one of the ligand. The solid was insoluble in acetonitrile and halogenated solvents and had limited solubility in pyridine. The ^1H NMR spectrum in C_5D_5N could be totally assigned to a single solution species (see Experimental section). The methylene protons adjacent to the 2,2′-bipyridyl group

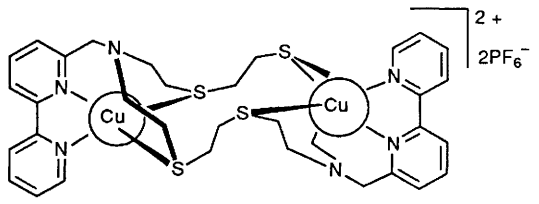

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Table 1 Mass spectral (FAB) and elemental analytical data for copper(I) complexes of acyclic ligands L^{4-6}

Complex of ligand	Molecular ions	Elemental analysis[a] (%)
L^4	—	C 39.3 (39.0)[b]
		H 3.3 (3.2)[b]
		N 7.5 (8.2)[b]
L^5	2077 ([2 + 2])[c]	C 50.5 (50.8)
	968 ([1 + 1])[c]	H 4.1 (4.3)
		N 8.8 (8.8)
L^6	1286 ([2 + 2])[c]	C 48.1 (48.6)
	570 ([1 + 1])[c]	H 3.5 (3.5)
		N 9.4 (9.8)

[a] Values in parentheses correspond to those calculated for a 1:1 ligand:copper(I) complex. [b] Calculated for dihydrate complex. [c] [2 + 2] refers to $[Cu_2L_2(PF_6)]^+$, [1 + 1] to $[CuL]^+$ molecular cations.

appeared as a singlet and so the complex was not helical. Taking these experimental results into consideration and the fact that sulfur binding sites are well known strongly to co-ordinate copper(I) cations,[10] a likely structure for this complex $[Cu_2L^3][PF_6]_2$ is **9** in which each copper(I) cation is co-ordinated to the 2,2′-bipyridyl moiety and two sulfur donor atoms.

With acyclic ligands L^{4-6}. Analogous copper(I) complexation procedures were used with all three acyclic ligands and respective deep red solid products isolated. The results of FAB mass spectral investigations and elemental analyses are shown in Table 1. Presumably as a consequence of the highly charged nature of the predicted complex $[Cu_2L^4_2][PF_6]_6$, FAB mass spectrometery proved uninformative. However, molecular ions corresponding to $[Cu_2L_2(PF_6)]^+$ and $[CuL]^+$ where L = L^5 or L^6 were observed and analyses of each of the three complexes suggest a 1:1 ligand to copper(I) ratio.

The respective ^1H NMR spectra of each isolated copper(I)-containing red complex exhibited similar observations to those previously described for L^1 and L^2. For example the ^1H NMR spectrum of the product resulting from L^5 (Fig. 2) in CD_3CN was found to be far more complicated than would have been expected for the solution existence of the [2 + 2] helical complex alone. As Fig. 2 illustrates, there are many more signals in the aromatic region than observed for the free ligand L^5 and also three absorptions (δ 2.39, 2.43 and 2.51) that can be assigned to the methyl groups of the toluene-*p*-sulfonyl units of the ligand, when only two would be predicted. No clear AB pattern in the expected region of the spectrum is observed; a broad signal at δ 4.30 is evident the integral of which is insufficient to account for all the methylene protons adjacent to the bipyridyl moieties. Low-temperature ^1H NMR studies were thwarted by solubility problems.

The product from L^4 and $[Cu(MeCN)_4]PF_6$ showed a sharp AB pattern (δ 3.55 and 4.68) accounting for *ca.* 45% of the complexed species in solution, possibly assignable to the [2 + 2] helical product. The remaining *ca.* 55% of the species were observed as multiplet and broad absorptions which did not change on variation of temperature.

Although the absorptions of the ^1H NMR spectrum in CD_3CN of the copper(I) complex of L^6 were very broad and

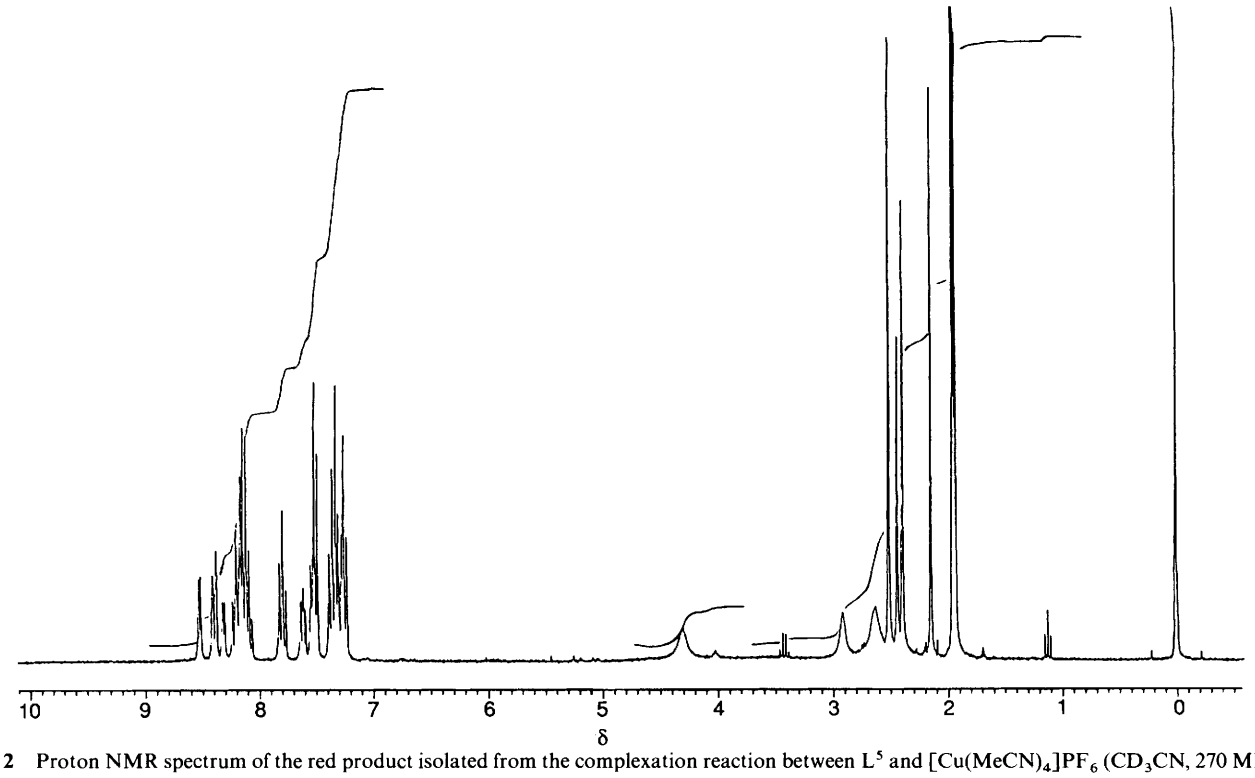

Fig. 2 Proton NMR spectrum of the red product isolated from the complexation reaction between L^5 and $[Cu(MeCN)_4]PF_6$ (CD_3CN, 270 MHz)

totally unassignable, the spectrum in $(CD_3)_2CO$ revealed an AB system centred at δ 3.49 and 4.59. However, relative integration suggested this helical species accounted for only *ca.* 15% of the total solution products. The major components were represented by a series of broad signals which were invariant to temperature implying, once again, the existence of other non-helical complexed solution species.

Silver(I) *Complexation Studies.—With macrocyclic ligands* L^1 *and* L^3. The addition of silver trifluorosulfonate (triflate) to acetonitrile solutions of L^1 and L^3 led to the isolation of bimetallic silver(I) complexes of general formula $[Ag_2L][CF_3SO_3]_2$ in 84 and 80% respective yields. The FAB mass spectra, elemental analyses and ^1H NMR spectra all support the $L:2Ag^+$ stoichiometry, suggesting a similar solution structure to that observed with copper(I) cations and L^3, in which each silver(I) cation co-ordinates to the 2,2′-bipyridyl moiety and two oxygen (L^1) or two sulfur (L^3) donor atoms.

With acyclic ligands L^5 *and* L^6. Ligands L^5 and L^6 were found to form monometallic silver(I) complexes $[AgL][CF_3SO_3]$ (L = L^5 or L^6) in 69 and 60% respective yields. Elemental analysis, FAB mass and ^1H NMR spectra were all consistent with this formulation. For example, the ^1H NMR spectrum of $[AgL^5][CF_3SO_3]$ is very similar to that recorded for the free ligand L^1 in CD_3CN, with proton resonances shifted downfield on co-ordination of the silver(I) cation. The methylene protons adjacent to the 2,2′-bipyridyl unit appear as a singlet (δ 4.13) and not as an AB system. Thus for silver(I) complexation only the [1 + 1] mononuclear complex is produced which markedly contrasts with the previously discussed results of copper(I) complexation with the same ligands. It is noteworthy that the formation constant for $[Ag(bipy)_2]^+$ (bipy = 2,2′-bipyridine) has been reported to be approximately one-half[11] that for $[Cu(bipy)_2]^+$, and related oligopyridine ligands did not produce silver(I) helicates but formed mononuclear near-planar complexes.[12]

Conclusion

Six new ligand systems containing 2,2′-bipyridyl moieties linked *via* diaza crown ether, diaza crown thia ether, 4,4′-bipyridinediium, *N*,*N*′,*N*″-tritosyldiethylenetriamine and toluene-*p*-sulfonamide spacer units have been prepared with the objective of producing copper(I) self-assembled [2 + 2] helical complexes that contain chiral spacer cavities. Although on copper(I) complexation with L^1, L^2 and L^{4-6} in every case FAB mass spectrometry displayed evidence for these target complex species, the respective ^1H NMR spectra revealed the additional existence of a variety of non-helical components in solution. These results are in stark contrast to Lehn's findings with the ether ($-CH_2OCH_2-$) linked 2,2′-bipyridyl oligomers, which form very stable kinetically inert helicates with copper(I) cations. Possibly the more sterically demanding and flexible spacer units employed here may destabilise the respective [2 + 2] helicate complexes to such an extent that a proportion spontaneously decomplex in solution to produce an equilibrium mixture of helical and non-helical complex species.

In comparison to the above, silver(I) was found to form bimetallic complexes with L^1 and L^3 and monometallic complexes with L^5 and L^6; no evidence for [2 + 2] helical complex formation was ever detected.[13]

The co-ordination chemistry of L^1–L^6 with other transition metals and in the case of L^1 and L^2 with Group 1, 2 metal cations is currently in progress.

Experimental

Instrumentation.—Melting points were recorded on a Gallenkamp apparatus in open capillaries and are uncorrected. Mass spectra (electron impact and fast atom bombardment) were obtained on a Kratos MS80 RF instrument and also at the Kodak Analytical Laboratories, Harrow and the SERC mass spectrometry service at University College Swansea. Infrared spectra were recorded on a Perkin-Elmer 297 instrument (4000–600 cm^{-1}). Solid samples were run in the form of KBr discs and liquid samples neat between NaCl plates. Nuclear magnetic resonance spectra were obtained on JEOL FX90Q, GX270 and Bruker WH400 (University of Warwick) instruments using tetramethylsilane as an internal standard. Electrochemical

measurements were carried out using an E. G. & G. Princeton Applied Research 362 scanning potentiostat. Elemental analyses were performed at the University of Birmingham and at the Kodak Analytical Laboratories, Harrow.

Solvent and Reagent Pre-treatment.—Where necessary, solvents were purified prior to use and stored under nitrogen. Acetonitrile was pre-dried over class 4A molecular sieves (4–8 mesh) and then distilled from calcium hydride, carbon tetrachloride was pre-dried over calcium hydride and distilled immediately prior to use. Diethyl ether was pre-dried over sodium wire and distilled from sodium immediately prior to use, and dimethylformamide was dried overnight over activated class 3A molecular sieves. Ethanol was distilled under nitrogen from sodium ethoxide, methanol was distilled from $CaSO_4$ and stored over class 4A sieves and tetrahydrofuran and toluene were distilled from sodium using benzophenone as an indicator.

Unless stated to the contrary, commercial grade chemicals were used without further purification. The following compounds were prepared according to literature procedures: 6-chloromethyl-2,2′-bipyridine **2**,[5] *N,N′,N″*-tritosyldiethylenetriamine,[7] 6-bromomethyl-6′-methyl-2,2′-bipyridine **3**[6] and tetrakis(acetonitrile)copper(I) hexafluorophosphate.[8]

Syntheses.—7,16-*Bis*(2,2′-*bipyridin*-6-*ylmethyl*)-1,4,10,13-*tetraoxa*-7,16-*diazacyclooctadecane* (L^1). Diaza-18-crown-6 **1** (0.58 g, 2.21 mmol) was dissolved in acetonitrile (40 cm^3), potassium carbonate (4.84 g, 35.0 mmol) was added and the mixture heated to reflux under nitrogen. Then a solution of 6-chloromethyl-2,2′-bipyridine **2** (1.00 g, 4.89 mmol) in acetonitrile was added dropwise with stirring and the resultant mixture heated at reflux for 22 h. After cooling to room temperature the insoluble material was filtered off and washed with acetonitrile (2 × 50 cm^3). The solvent was removed from the filtrate to give an orange residue which was chromatographed on alumina using dichloromethane–methanol (99:1) as eluent. A pale yellow band was collected and removal of the solvent gave an oil. Addition of acetonitrile (5 cm^3) and vigorous stirring gave a precipitate. The mixture was heated to reflux to dissolve the solid which, on cooling, afforded small pale yellow crystals of L^1 (1.06 g, 80%), m.p. 83–85 °C. Mass spectrum (FAB): *m/z* 599, $[M + H]^+$; 429, $[M - CH_2(bipy) + H]^+$; and 170, $[(bipy)CH_2 + H]^+$. IR: 3050 (aromatic CH stretch), 2860/2800 (aliphatic CH stretch), 1580/1560 (C=C/C=N ring stretch) and 1120/1060 cm^{-1} (CH_2OCH_2 stretch). NMR ($CDCl_3$): ^1H (270 MHz), δ 2.95 (8 H, t, ^3J = 5.9, NCH_2CH_2O), 3.64 (8 H, s, $NCH_2CH_2OCH_2$), 3.69 (8 H, t, ^3J = 5.9, NCH_2CH_2O), 3.96 [4 H, s, $(bipy)CH_2$], 7.29 (2 H, d, ^3J 7.5, d, ^3J = 4.0, d, ^4J = 2.0, $H^{5'}$ of bipy), 7.56 (2 H, d, ^3J = 7.7, H^5 of bipy), 7.77 (2 H, t, ^3J = 7.9, H^4 of bipy), 7.80 (2 H, t, ^3J = 1.8, $H^{4'}$ of bipy), 8.23 (2 H, d, ^3J = 7.9, H^3 of bipy), 8.40 (2 H, d, ^3J = 7.9, $H^{3'}$ of bipy) and 8.67 (2 H, d, ^3J = 4.0 Hz, $H^{6'}$ of bipy); ^{13}C (22.5 MHz), δ 54.43 (NCH_2CH_2O), 61.75 [$(bipy)CH_2N$], 70.10 and 70.79 ($NCH_2CH_2OCH_2$), 119.07, 121.12, 122.91, 123.43, 136.73, 137.15, 149.08, 155.20, 156.46 and 159.81 (aromatic C) (Found: C, 68.0; H, 7.0; N, 14.0. Calc. for $C_{34}H_{42}N_6O_4$: C, 68.2; H. 7.1; N, 14.0%).

7,16-*Bis*(6′-*methyl*-2,2′-*bipyridin*-6-*ylmethyl*)-1,4,10,13-*tetraoxa*-7,16-*diazacyclooctadecane* (L^2). This compound was prepared following the method for L^1 using compound **1** (0.20 g, 0.76 mmol), potassium carbonate (1.67 g, 16.9 mmol), 6-bromomethyl-6′-methyl-2,2′-bipyridine **3** (0.44 g, 1.68 mmol) and a reaction time of 9 h. The product was recrystallised from hot acetonitrile to give small yellow crystals of L^4 (0.37 g, 77%), m.p. 88–89 °C. Mass spectrum (FAB): *m/z* 627, $[M + H]^+$; 443, $[M - CH_3C_{10}H_6N_2CH_2]^+$; and 184, $[CH_3C_{10}H_6N_2CH_2 + H]^+$. IR: 3070 (aromatic CH stretch), 2950/2880/2840 (aliphatic CH stretch), 1580 (C=C/C=N ring stretch) and 1140–1050 cm^{-1} (CH_2OCH_2 stretch). NMR ($CDCl_3$): ^1H (270 MHz), δ 2.63 (6 H, s, bipy CH_3), 2.94 (8 H, t, ^3J = 5.5, NCH_2CH_2O), 3.63 (8 H, s, $NCH_2CH_2OCH_2$), 3.68 (8 H, t, ^3J = 5.5, NCH_2CH_2O), 3.95 [4 H, s, $(bipy)CH_2$], 7.15 (2 H, d, ^3J = 7.5, $H^{5'}$ of bipy), 7.53 (2 H, d, ^3J = 7.0, H^5 of bipy), 7.68 (2 H, t, ^3J = 7.5, $H^{4'}$ of bipy), 7.75 (2 H, t, ^3J = 8.0, H^4 of bipy), 8.18 (2 H, d, ^3J = 7.5, $H^{3'}$ of bipy) and 8.24 (2 H, d, ^3J = 8.0 Hz, H^3 of bipy); ^{13}C (22.5 MHz), δ 24.65 (bipy CH_3), 54.37 (NCH_2CH_2O), 61.71 [$(bipy)CH_2$], 70.07 and 70.75 ($NCH_2CH_2OCH_2$), 118.13, 119.14, 122.71, 122.97, 136.89, 137.09, 155.88, 157.73 and 159.62 (aromatic C) (Found: C, 68.9; H, 7.4; N, 13.6. Calc. for $C_{36}H_{46}N_6O_4$: C, 69.0; H, 7.4; N, 13.4%).

7,16-*Bis*(2,2′-*bipyridin*-6-*ylmethyl*)-1,4,10,13-*tetrathia*-7,16-*diazacyclooctadecane* (L^3). This compound was prepared following the method for L^1 using salt **7** (0.52 g, 1.59 mmol), in place of **1**, 6-chloromethyl-2,2′-bipyridine **2** (0.72 g, 3.52 mmol) and a reflux time of 6 d. The product was eluted from the alumina chromatographic column using dichloromethane–methanol (99.5:0.5) and was isolated as pale yellow crystals after recrystallisation (0.79 g, 75%), m.p. 118–120 °C. Mass spectrum (FAB): *m/z* 663, $[M + H]^+$; and 495, $[(bipy)CH_2 + 2H]^+$. IR: 3040 (aromatic CH stretch), 2950/2900/2820 (aliphatic CH stretch) and 1580/1560 cm^{-1} (C=C/C=N ring stretch). NMR: ^1H ($CDCl_3$, 270 MHz), δ 2.75–2.87 (24 H, m, $NCH_2CH_2SCH_2$), 3.92 [4 H, s, $(bipy)CH_2$]), 7.29 (2 H, d, ^3J = 7.5, d, ^3J = 4.8, d, ^4J = 1.1, $H^{5'}$ of bipy), 7.51 (2 H, d, ^3J = 7.7, H^5 of bipy), 7.81 (2 H, t, ^3J = 7.7, d, ^4J = 1.7, $H^{4'}$ of bipy), 7.81 (2 H, t, ^3J = 7.7, H^4 of bipy), 8.27 (2 H, d, ^3J = 7.7, H^3 of bipy), 8.39 (2 H, d, ^3J = 7.9, $H^{3'}$ of bipy) and 8.67 (2 H, d, ^3J = 4.8, d, ^4J = 1.8, d, ^5J = 0.9, $H^{6'}$ of bipy); (CD_3CN, 270 MHz), δ 2.73–2.81 (24 H, m, $NCH_2CH_2SCH_2$), 3.86 [4 H, s, $(bipy)CH_2$], 7.36 (2 H, d, ^3J = 7.5, d, ^3J = 4.8, $H^{5'}$ of bipy), 7.53 (2 H, d, ^3J = 7.7, H^5 of bipy), 7.85 (2 H, t, ^3J = 7.5, d, ^4J = 1.8, $H^{4'}$ of bipy), 8.28 (2 H, d, ^3J = 7.9, H^3 of bipy), 8.41 (2 H, d, ^3J = 7.9, $H^{3'}$ of bipy) and 8.64 (2 H, d, ^3J = 4.0 Hz, $H^{6'}$ of bipy); ^{13}C ($CDCl_3$, 22.5 MHz), δ 30.60 and 32.74 ($NCH_2CH_2SCH_2$), 54.30 (NCH_2CH_2), 60.54 [$(bipy)CH_2N$], 119.36, 121.09, 122.91, 123.52, 136.76, 137.31, 149.12, 155.39, 156.27 and 158.68 (aromatic C) (Found: C, 61.6; H, 6.4; N, 13.0. Calc. for $C_{34}H_{42}N_6S_4$: C, 61.6; H, 6.4; N, 12.7%).

N,N′-*Bis*(6′-*methyl*-2,2′-*bipyridin*-6-*ylmethyl*)-4,4′-*bipyridinediium bis*(*hexafluorophosphate*) (L^4). 6-Bromomethyl-6′-methyl-2,2′-bipyridine **3** (0.20 g, 0.76 mmol) and 4,4′-bipyridine **5** (54 mg, 0.35 mmol) were heated at reflux in acetonitrile (20 cm^3) for 48 h. After cooling to room temperature, the pale yellow-green precipitate was filtered off, washed with dichloromethane (2 × 10 cm^3) and dried under vacuum. The solid was then dissolved in water (10 cm^3) with warming and a saturated aqueous solution of ammonium hexafluorophosphate added dropwise until precipitation no longer occurred. The precipitate was filtered off, washed with water (3 × 5 cm^3) and dried under vacuum over silica gel to afford a white powder of L^4 (0.24 g, 86%), m.p. >230 °C (decomp.). Mass spectrum (FAB): *m/z* 667, $[M - PF_6]^+$; and 522, $[M - 2PF_6]^+$. IR: 3140/3080 (aromatic CH stretch), 2920 (aliphatic CH stretch), 1640/1590/1575 (C=C/C=N ring stretch) and 804 cm^{-1} (br, PF_6^-). NMR (CD_3CN): ^1H (270 MHz), δ 2.55 (6 H, s, bipy CH_3), 6.01 [4 H, s, $(bipy)CH_2N$], 7.24 (2 H, d, ^3J = 7.7, $H^{5'}$ of bipy), 7.65 (2 H, d, ^3J = 7.7, H^5 of bipy), 7.68 (2 H, t, ^3J = 7.7, $H^{4'}$ of bipy), 7.91 (2 H, d, ^3J = 7.9, $H^{3'}$ of bipy), 8.03 (2 H, t, ^3J = 7.9, H^4 of bipy), 8.45 (2 H, d, ^3J = 8.0, H^3 of bipy), 8.49 (4 H, d, ^3J = 7.0, H^3 of 4,4′-bipy) and 9.14 (4 H, d, ^3J = 7.0 Hz, H^2 of 4,4′-bipy); ^{13}C (67.8 MHz), δ 24.66 (bipy CH_3), 65.95 [$(bipy)CH_2N$], 118.89, 122.00, 124.06, 124.93, 127.98, 138.42, 139.94, 147.80, 151.47, 151.98, 155.05, 157.37 and 159.30 (aromatic C) (Found: C, 50.6; H, 4.0; N, 10.6. Calc. for $C_{34}H_{30}F_{12}N_6P_2$: C, 50.3; H, 3.7, N, 10.3%).

N,N″-*Bis*(2,2′-*bipyridin*-6-*ylmethyl*)-N,N′,N″-*tri*(*toluene*-p-*sulfonyl*)*diethylenetriamine* (L^5). Sodium metal (0.15 g) was dissolved in cold anhydrous methanol (40 cm^3) with stirring under nitrogen. To this was added *N,N′,N″*-tritosyldiethylenetriamine (1.23 g) and the solution heated to reflux for 1.5 h. After cooling to room temperature the solvent was removed under reduced pressure and the sodium salt dried under vacuum

for 1 h. The disodium salt (0.80 g, 1.13 mmol) was dissolved in dry dimethylformamide (50 cm^3) and heated to 70 °C under nitrogen with stirring. To this was added dropwise a solution of 6-chloromethyl-2,2′-bipyridine **2** (0.59 g, 2.88 mmol) in dimethylformamide (10 cm^3) and the resultant solution heated at 70 °C for 4 h. After cooling to room temperature the solvent was removed under reduced pressure. The residue was taken up in water (50 cm^3), extracted with dichloromethane (3 × 100 cm^3) and the combined organic layers washed with water (4 × 500 cm^3), dried (Na_2SO_4), filtered and the solvent removed under reduced pressure. The yellow oil was then chromatographed on silica gel using dichloromethane–methanol (98.2) as eluent and a pale yellow band collected. Removal of the solvent gave a pale yellow oil which, on stirring in acetonitrile (5 cm^3), became a white solid. This was filtered off and dried under vacuum to give the product L^5 (0.58 g, 50%), m.p. 162–164 °C. Mass spectrum (FAB): *m/z* 902, $[M + H^+]^+$; and 746, $[M - ts]^+$. IR: 2950/2910 (aliphatic CH stretch), 1600/1580/ 1560 (C=C/C=N ring stretch) and 1340/1150 cm^{-1} (SO_2N stretch). NMR: ^1H ($CDCl_3$, 270 MHz), δ 2.26 [3 H, s, CH_3 of N′(ts)], 2.28 [6 H, s, CH_3 of N(ts)], 3.15 [4 H, m, (bipy)CH_2NCH_2], 3.51 [4 H, m, (bipy)$CH_2NCH_2CH_2$], 4.55 [4 H, s, (bipy)CH_2], 6.97 [2 H, d, ^3J = 7.9 Hz, H^3 of N′(ts)], 7.13 [4 H, d, ^3J = 8.1, H^3 of N(ts)], 7.27 (2 H, d, ^3J = 7.5, d, ^3J = 4.9, d, ^3J = 1.3, $H^{5'}$ of bipy), 7.27 (2 H, d, ^3J = 8.0, H^5 of bipy), 7.32 [2 H, d, ^3J = 8.1, H^2 of N (ts)], 7.64 [4 H, d, ^3J = 8.2, H^2 of N(ts)], 7.70 (2 H, t, ^3J = 7.5, d, ^4J = 1.9, $H^{4'}$ of bipy), 7.75 (2 H, t, ^3J = 7.7, H^4 of bipy), 8.14 (2 H, d, ^3J = 7.9, d, ^3J = 7.9, d, ^4J = 0.9, $H^{3'}$ of bipy), 8.30 (2 H, d, ^3J = 7.9, H^3 of bipy) and 8.65 (2 H, d, ^3J = 4.8, d, ^4J = 1.8 Hz, $H^{6'}$ of bipy); (CD_3CN, 270 MHz), δ 2.25 [6 H, s, CH_3 of N(ts)], 2.27 [3 H, s, CH_3 of N′(ts)], 3.12 [4 H, m, (bipy)CH_2NCH_2], 3.41 [4 H, m, (bipy)$CH_2NCH_2CH_2$], 4.50 [4 H, s, (bipy)CH_2], 7.10 [2 H, d, ^3J = 7.9, H^3 of N′(ts)], 7.17 [4 H, d, ^3J = 8.1, H^3 of N(ts)], 7.29 [2 H, ^3J = 8.1, H^2 of N′(ts), tentative], 7.33 (2 H, d, ^3J = 4.8, d, ^3J = 1.1, $H^{5'}$ of bipy), 7.33 (2 H, d, ^3J = 8.2, H^5 of bipy, tentative), 7.57 [4 H, d, ^3J = 8.2, H^2 of N(ts)], 7.71 (2 H, t, ^3J = 7.5, d, ^4J = 1.8, $H^{4'}$ of bipy), 7.79 (2 H, t, ^3J = 7.7, H^4 of bipy), 8.01 (2 H, d, ^3J = 7.9, d, $H^{3'}$ of bipy), 8.25 (2 H, d, ^3J = 8.1, H^3 of bipy) and 8.61 (2 H, d, ^3J = 4.8, d, ^4J = 1.8, d, ^4J = 0.9 Hz, $H^{6'}$ of bipy); ^{13}C ($CDCl_3$, 22.5 MHz), δ 21.36 (CH_3 of ts), 48.51 and 49.00 (NCH_2CH_2N), 54.50 [(bipy)CH_2N], 119.79, 121.25, 122.78, 123.72, 127.01, 127.27, 129.61, 135.00, 136.24, 136.79, 137.64, 143.30, 143.39, 148.95 and 155.65 (aromatic C) (Found: C, 62.4; H, 5.6; N, 10.6. Calc. for $C_{47}H_{47}N_7O_6S_3$: C, 62.6; H, 5.3; N, 10.9%).

N,N-*Bis*(2,2′-*bipyridin*-6-*ylmethyl*)*toluene*-p-*sulfonamide* (L^6). Sodium metal (0.45 g, 19.6 mmol) was dissolved in cold anhydrous methanol (40 cm^3) with stirring under nitrogen. Toluene-*p*-sulfonamide (3.35 g, 19.6 mmol) was added and the solution heated to reflux for 1 h. After cooling, the solvent was removed under reduced pressure and the white solid dried under vacuum for 1 h. To a boiling solution of toluene-*p*-sulfonamide sodium salt (0.39 g, 2.0 mmol) in dry ethanol (35 cm^3) under nitrogen was added dropwise a solution of 6-chloromethyl-2,2′-bipyridine **2** (0.60 g, 2.9 mmol) in ethanol (20 cm^3) with stirring. The solution was then heated at reflux for 5 h. After cooling to room temperature the solvent was removed under reduced pressure, the residue taken up in chloroform (25 cm^3) and washed with water (3 × 25 cm^3). The organic layer was dried (Na_2SO_4), filtered and the solvent removed under reduced pressure. The yellow oil was then chromatographed on alumina using dichloromethane–methanol (99:1) as eluent. A pale yellow band was collected. After removal of the solvent the oil was stirred in acetonitrile (10 cm^3) to produce a white precipitate which was recrystallised from hot acetonitrile to afford small yellow crystals of L^6 (0.42 g, 56%), m.p. 118–120 °C. Mass spectrum (FAB): *m/z* 508, $[M + H]^+$; 352, $[M - ts]^+$. IR: 3040 (aromatic CH stretch), 1595/1585 (C=C/C=N ring stretch) and 1320/1150 cm^{-1} (SO_2N). NMR ($CDCl_3$): ^1H (270 MHz), δ 2.27 (3 H, s, CH_3 of ts), 4.48 [4 H, s, (bipy)CH_2], 7.12 (2 H, d, ^3J = 8.1, H^3 of ts), 7.24 (2 H, d, ^3J = 7.5, d, ^3J = 4.8, d, ^4J = 1.3, $H^{5'}$ of bipy), 7.36 (2 H, d, ^3J = 7.7, d, ^4J = 0.8, H^5 of bipy), 7.65 (2 H, t, ^3J = 7.7, d, ^4J = 1.9, $H^{4'}$ of bipy), 7.67 (2 H, d, ^3J = 8.2, H^2 of ts), 7.68 (2 H, t, ^3J = 7.9, H^4 of bipy), 8.12 (2 H, d, ^3J = 8.1, t, ^4J = 1.1, $H^{3'}$ of bipy), 8.17 (2 H, d, ^3J = 7.9, d, ^4J = 0.9, H^3 of bipy) and 8.61 (2 H, d, ^3J = 4.8 Hz, $H^{6'}$ of bipy); ^{13}C (22.5 MHz), δ 21.33 (CH_3 of ts), 53.75 [(bipy)CH_2N], 119.49, 121.06, 122.62, 123.53, 127.20, 129.41, 136.53, 137.31, 143.10, 148.95, 155.33 and 155.75 (aromatic C) (Found: C, 68.5; H, 5.1; N, 14.1. Calc. for $C_{29}H_{25}N_5O_2S$: C, 68.6; H, 5.0; N, 13.8%).

Copper(I) *Complexation Experiments*.—The general method of the copper(I) complexation experiments was as follows. To a solution of the ligand L (0.09 mmol) in dry acetonitrile (2 cm^3) under nitrogen in a Schlenk tube was added by syringe a solution of tetrakis(acetonitrile)copper(I) hexafluorophosphate (0.105 mmol) in acetonitrile (2 cm^3). The mixture immediately became deep red and after stirring at room temperature for 1 h the volume of the solvent was reduced *in vacuo* to ≈2 cm^3. Addition of diethyl ether (10 cm^3) precipitated the product which was filtered off, washed with diethyl ether (2 × 2 cm^3) and dried *in vacuo*.

With L^1. The complex was recrystallised from acetonitrile. Mass spectrum (FAB): *m/z* 1468, $[Cu_2L^1{}_2(PF_6)]^+$; and 661, $[CuL^1]^+$ (Found: C, 50.4; H, 5.5; N, 10.1. Calc. for $C_{34}H_{42}CuF_6N_6O_4P$: C, 50.6; H, 5.2; N, 10.4%).

With L^2. This complex was recrystallised from acetonitrile. Mass spectrum (FAB): *m/z* 1523 $[Cu_2L^2{}_2(PF_6)]^+$; and 689, $[CuL^2]^+$ (Found: C, 51.5; H, 5.3; N, 10.3. Calc. for $C_{36}H_{46}CuF_6N_6O_4P$: C, 51.8; H, 5.5; N, 10.1%).

With L^3. Following the general method the complexation of ligand L^3 (100 mg, 0.151 mmol) and tetrakis(acetonitrile)-copper(I) hexafluorophosphate (124 mg, 0.332 mmol) was undertaken. The orange precipitate deposited was filtered off, washed with acetonitrile (2 × 5 cm^3) and dried under vacuum to give the complex $[Cu_2L^3][PF_6]_2$ (115 mg, 71%). Mass spectrum (FAB): no significant signals observed as the complex was involatile. NMR (C_5D_5N): ^1H (400 MHz), δ 2.90–2.99 (24 H, m, $NCH_2CH_2SCH_2$), 4.03 [4 H, s, (bipy)CH_2], 7.32 (2 H, d, ^3J = 7.2, d, ^3J = 5.3, $H^{5'}$ of bipy), 7.66 (2 H, d, ^3J = 7.6, H^5 of bipy), 7.84 (2 H, t, ^3J = 7.8, d, ^4J = 1.7, $H^{4'}$ of bipy), 7.87 (2 H, t, ^3J = 7.8, H^4 of bipy), 8.59 (2 H, d, ^3J = 7.8, $H^{3'}$ of bipy), 8.69 (2 H, d, ^3J = 8.0, H^3 of bipy) and 8.84 (2 H, d, ^3J = 4.5 Hz, $H^{6'}$ of bipy); ^{13}C (100.6 MHz), δ 31.00 and 33.13 ($NCH_2CH_2SCH_2$), 54.40 [(bipy)CH_2NCH_2], 60.52 [(bipy)CH_2], 119.68, 121.34, 124.33, 134.97, 137.23, 137.79, 149.33, 155.25, 156.13 and 159.42 (aromatic C) (Found: C, 37.9; H, 3.9; N, 7.7. Calc. for $C_{34}H_{42}Cu_2F_{12}N_6P_2S_4$: C, 37.8; H, 3.9; N, 7.8%).

With L^4. Following the general method a red hygroscopic compound was isolated and recrystallised from acetonitrile. Mass spectrum (FAB): no significant signals observed (Found: C, 39.3; H, 3.3; N, 7.5. Calc. for $C_{68}H_{60}Cu_2F_{36}N_{12}P_6{\cdot}2H_2O$: C, 39.0; H, 3.2; N, 8.2%).

With L^5. Following the general procedure a red product was isolated. Mass spectral and elemental analytical data are in Table 1.

With L^6. A deep red complex was isolated using the general procedure. Mass spectral and elemental data are in Table 1.

Silver(I) *Complexation Experiments*.—A general procedure for the silver(I) complexations was used throughout as follows. To a suspension of the ligand L (0.1 mmol) in dry acetonitrile (5 cm^3) under nitrogen in a Schlenk tube was added by syringe a solution of silver(I) triflate (0.12 mmol) in acetonitrile (3 cm^3). Typically all the material had dissolved after stirring in the dark at room temperature for 1 h. The volume of the solvent was reduced to ≈2 cm^3 and diethyl ether added to precipitate the product. This was filtered off, washed with diethyl ether and recrystallised from acetonitrile.

$[Ag_2L^1][CF_3SO_3]_2$. Yield 84%. Mass spectrum (FAB): *m/z*

964, $[Ag_2L^1(CF_3SO_3)]^+$; and 708, $[AgL^1]^+$. IR: 3070 (aromatic CH stretch), 2880 (aliphatic CH stretch), 1590/1580 (C=C/C=N ring stretch) and 1270/1160 cm^{-1} ($CF_3SO_3^-$). NMR (CD_3CN): ^1H (270 MHz), δ 2.87–3.34 [24 H, m, (bipy)CH_2NCH_2-CH_2OCH_2], 4.06 [4 H, s, (bipy)CH_2], 7.37 (2 H, br, $H^{5'}$ of bipy), 7.64 (2 H, d, ^3J = 7.5, H^5 of bipy), 7.88 (2 H, t, br, $H^{4'}$ of bipy), 8.01 (2 H, t, ^3J = 7.7, H^4 of bipy), 8.15 (2 H, d, ^3J = 7.7, $H^{3'}$ of bipy), 8.21 (2 H, d, ^3J = 8.1 Hz, H^3 of bipy) and 8.38 (2 H, br, $H^{6'}$ of bipy); ^{13}C (67.8 MHz), δ 57.36, 64.16, 69.43 and 70.04 [(bipy)$CH_2NCH_2CH_2OCH_2$], 122.19, 123.38, 125.97, 139.20, 139.96, 150.86, 152.32, 154.67 and 160.20 (aromatic C).

$[Ag_2L^3][CF_3SO_3]_2$. Yield 80%. Mass spectrum (FAB): *m/z* 1027, $[Ag_2L^3(CF_3SO_3)]^+$; 877, $[Ag_2L^3]^+$; 771, $[AgL^3]^+$. IR: 3110/3060 (aromatic CH stretch), 2940/2830 (aliphatic CH stretch), 1595/1565 (C=C/C=N ring stretch) and 1260/1150 cm^{-1} ($CF_3SO_3^-$). NMR (CD_3CN): ^1H (270 MHz), δ 2.83–2.93 [24 H, m, (bipy)$CH_2NCH_2CH_2SCH_2$], 3.86 [4 H, s, (bipy)CH_2], 7.51 (2 H, d, ^3J = 7.7, H^5 of bipy), 7.70 (2 H, br, $H^{5'}$ of bipy), 8.03 (2 H, t, ^3J = 7.7, H^4 of bipy), 8.13 (2 H, br, $H^{4'}$ of bipy), 8.18 (2 H, d, ^3J = 8.1 Hz, H^3 of bipy), 8.34 (2 H, d, br, $H^{3'}$ of bipy) and 8.85 (2 H, br, $H^{6'}$ of bipy); ^{13}C (22.5 MHz), δ 33.13, 34.37, 54.17 and 60.35 [(bipy)$CH_2NCH_2CH_2SCH_2$], 122.51, 124.37, 126.42, 127.10 and 140.88 (aromatic C) (Found: C, 36.9; H, 3.7; N, 7.4. Calc. for $C_{36}H_{42}Ag_2F_6N_6O_6S_6$: C, 36.7; H, 3.6; N, 7.1%).

$[AgL^5][CF_3SO_3]$. Yield 69%. Mass spectrum (FAB): *m/z* $[AgL^5]^+$. IR: 3070 (aromatic CH stretch), 2940 (aliphatic CH stretch), 1600/1580 (C=C/C–N ring stretch) and 1270/1180 cm^{-1} ($CF_3SO_3^-$). NMR (CD_3CN): ^1H (270 MHz), δ 2.19–2.60 [8 H, m, (bipy)$CH_2NCH_2CH_2$], 2.43 [3 H, s, CH_3 of N′(ts)], 2.48 [6 H, s, CH_3 of N′(ts)], 4.13 [4 H, s, (bipy)CH_2], 7.22 [4 H, d, ^3J = 8.1, H^3 of N(ts)], 7.36 [2 H, d, ^3J = 8.4, H^3 of N′(ts)], 7.40 [4 H, d, ^3J = 8.4, H^2 of N(ts)], 7.51 [2 H, d, ^3J = 8.2, H^2 of N′(ts)], 7.58 (2 H, d, ^3J = 7.1, d, ^3J = 4.9, d, ^4J = 2.4, $H^{5'}$ of bipy), 7.80–8.12 (10 H, m, H of bipy) and 8.68 (2 H, d, ^3J = 5.0, t, ^4J = 1.1 Hz, $H^{6'}$ of bipy); ^{13}C (22.5 MHz), δ 21.59 and 21.78 (CH_3 of ts), 49.91 and 50.36 [(bipy)$CH_2NCH_2CH_2$], 58.59 [(bipy)CH_2], 123.29, 124.17, 126.97, 127.94, 128.37, 130.87, 131.03, 135.32, 140.46, 141.41, 145.27, 151.92, 152.49 and 157.92 (aromatic C) (Found: C, 49.5; H, 4.3; N, 8.2. Calc. for $C_{48}H_{47}AgF_3N_7O_9S_4$: C, 49.7; H, 4.1; N, 8.5%).

$[AgL^6][CF_3SO_3]$. Yield 60%. Mass spectrum (FAB): *m/z* 615, $[AgL^6]^+$. IR: 3060 (aromatic CH stretch), 2930 (aliphatic CH stretch), 1600/1580/1565 (C=C/C=N ring stretch) and 1260/1160 cm^{-1} ($CF_3SO_3^-$). NMR (CD_3CN): ^1H (270 MHz), δ 2.35 (3 H, s, CH_3 of ts), 4.70 [4 H, s, (bipy)CH_2], 7.22 (2 H, d, ^3J = 7.9, H^3 of ts), 7.53 (4 H, d, ^3J = 8.2, H^5 of bipy, H^2 of ts), 7.63 (2 H, d, ^3J = 7.5, d, ^3J = 5.0, d, ^4J = 1.1, $H^{5'}$ of bipy), 8.20 (2 H, t, ^3J = 7.9, H^4 of bipy), 8.12 (2 H, t, ^3J = 7.7, d, ^4J = 1.8, $H^{4'}$ of bipy), 8.21 (2 H, d, ^3J = 8.1, H^3 of bipy), 8.30 (2 H, d, ^3J = 8.2, t, ^4J = 1.1, $H^{3'}$ of bipy) and 8.69 (2 H, d, ^3J = 4.9, d, ^4J = 1.7, d, ^5J = 0.9 Hz, $H^{6'}$ of bipy); ^{13}C (67.8 MHz), δ 21.54 (CH_3 of ts), 53.59 [(bipy)CH_2], 123.16, 124.27, 126.81, 127.29, 128.08, 130.80, 137.85, 140.40, 141.03, 145.29, 152.25, 152.52, 152.79 and 156.77 (aromatic C) (Found: C, 47.0; H, 3.5; N, 9.4. Calc. for $C_{30}H_{25}AgF_3N_5O_5S_2$: C, 47.1; H, 3.3; N, 9.2%).

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