Directed one-pot syntheses of enantiopure dinuclear silver(I) and copper(I) metallo-supramolecular double helicates

Jacqueline Hamblin, Laura J. Childs, Nathaniel W. Alcock and Michael J. Hannon *

Centre for Supramolecular and Macromolecular Chemistry, Department of Chemistry, University of Warwick, Gibbet Hill Road, Coventry, UK CV4 7AL. E-mail: M.J.Hannon@warwick.ac.uk

Enantiopure dinuclear silver(I) double helicates were prepared in simple one-pot reactions from commercially available starting materials and the pure complexes isolated as the hexafluorophosphate salts. The $(R),(+)$ and $(S),(-)$ enantiomers of 1,1′-binaphthalene-2,2′-diamine were used as spacer groups and reacted with pyridine-2-carbaldehyde to form chiral didentate imine ligands. These chiral ligands predetermine the chirality of the helicates: the R spacer gives a P helicate and the S spacer an M helicate. The dinuclear double helical structures are confirmed by single crystal X-ray analysis and their persistence in solution is supported by inter-strand NOE data. Enantiopure copper(I) dinuclear species were also prepared by similar one-pot procedures and analysed by ^{1}H NMR, mass spectrometry and circular dichroism.

Introduction

The supramolecular synthetic approach permits the design of arrays with complex molecular architectures whose dimensions are greater than those found in traditional covalent based chemistry.[1,2] This ability to control architecture at the molecular level is important as it offers a potential route to systematically encode the properties of a molecule or material; indeed this is a common theme in biological systems.[3] Double-helical molecular architectures have been influential in the development of supramolecular chemistry, providing a forum for establishing construction principles and retaining a unique fascination because life itself is encoded within double-helical DNA arrays.[4]

The molecular encoding required to generate metallo-helical arrays is now reasonably well established[4] and requires ligands which contain two or more discrete metal binding sites either linked directly or *via* a spacer unit. On metal coordination the position of the link or nature of the spacer must prevent mononucleation (thereby promoting the formation of a multinuclear array). The spacer must also give rise to a twisting in the ligand strand which will result in the formation of a helical (*rac-*) array rather than an alternative (*meso-*) metallo-cyclophane structure. The helical chirality is a direct result of the twisting in the ligand strands and controlling the twisting offers the opportunity to control the chirality.

We are interested in synthetic routes to prepare sophisticated supramolecular architectures quickly and simply and to this end have employed imine-based ligands, prepared readily from commercial amines and aldehydes.[5–10] Freed from the constraints of extensive ligand synthetic procedures, we have been systematically exploring how ligand design can address the challenge not only of defining the supramolecular architecture or superstructure but also of defining the precise topography or conformation of this superstructure. For example, we have illustrated how spacer groups can be used to control the directionality of ligand strands within a helical array[7] and to give distinct (major and minor) helical grooves.[8] While these features are reminiscent of features observed in B-DNA, B-DNA is found as a single helical enantiomer. Herein we explore whether defined helicity may also be imparted within our synthetic

imine-based helicates, and describe a system in which enantiopure P and M helicates can be prepared by mixing commercial reagents.

Inducing metallo-helicate chirality requires introduction of chirality into the structure of the organic ligand. Chirality in organic chemistry is most frequently associated with tetrahedral carbon atoms bearing four non-equivalent substituents and such groups have been the focus for most studies of chiral induction in helicates.[11,12] Induction of helical chirality has followed two strategies: (i) Chiral groups may be attached to the metal binding units, with the extent of chiral induction depending on the proximity of the chiral unit to the metal[13,14] (*e.g.* for pyridines, substituents at the 6 position are much more effective than at the 4 position).[15] (ii) More effectively, helicity may be induced by imparting the chirality into the spacer unit(s) between the metal binding units.[16] This relays the chirality directly into the heart of the helical array and is consequently our preferred strategy.

In addition to tetra-substituted sp^3 centres, organic chiral species may also result from twisting about bonds and restriction to rotation (atropisomerism). For example, Scott and co-workers have recently reported the implications of chiral biarylamines on ligand and catalyst design.[17] In these biarylamine units the rotation around the 1,1′ axis is restricted by the presence of two methyl groups in the 2,2′ position of the rings thereby imparting chirality. Other examples of this type of chiral species include 2,2′-substituted 1,1′-binaphthalenes which have been widely explored for chiral catalysis. Given that twisting in the ligand strand is a helicate design requirement and that there is a direct link between the strand twisting and the chirality of the helicate, units of this type seemed to us ideally suited to control helicate chirality. For our chiral spacer unit, we chose to use a binaphthalene unit. Herein we now report the use of the commercially available $(R),(+)$ and $(S),(-)$ enantiomers of 1,1′-binaphthalene-2,2′-diamine to prepare two pyridylimine-based dinuclear double helicates in which the chirality at the metal centres is predetermined by the chirality of the ligands. Racemic 1,1′-binaphthalene-2,2′-diamine has been used as a ligand producing racemic mononuclear complexes[18–21] and some mononuclear complexes incorporating the enantiopure form have also been

reported.[22–24] A helical infinite polymer based on terpyridine substituted binaphthalene units has recently been reported.[25]

Results and discussion

Silver(I) complexes

Ethanolic solutions containing two equivalents of pyridine-2-carbaldehyde were treated with ethanolic suspensions of one equivalent of *R*- or *S*-binaphthalene-diamine and heated under reflux to afford clear pale yellow solutions. These solutions were treated directly with one equivalent of silver(I) acetate to afford yellow solutions from which yellow solids precipitated on treatment with ethanolic ammonium hexafluorophosphate. The complexes were isolated by filtration. Attempts to isolate the free ligands (see Fig. 1) in both cases were unsuccessful, however
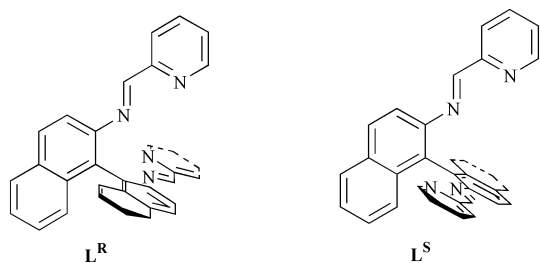

Fig. 1 The L^R and L^S ligands.

these one-pot procedures produced clean complexes with further purification required only for X-ray analysis.

The infrared spectra of these salts exhibit peaks corresponding to aromatic stretches in addition to weak imine stretches at 1615 cm^{-1}. Partial microanalytical data of the complexes indicate a formulation $\{AgL(PF_6)\}_n$ ($L = C_{32}H_{22}N_4$). Positive ion FAB mass spectra for both compounds display peaks (with the correct isotopic distributions) corresponding to $\{AgL\}$, $\{AgL_2\}$, $\{Ag_2L_2\}$ and $\{Ag_2L_2PF_6\}$ indicating complexes with the desired dinuclear formulation. No peaks corresponding to higher aggregates (*e.g.* trimers *etc.*) are observed.

Crystallographic investigations. X-Ray quality crystals of both complexes were obtained from nitromethane solutions by slow diffusion of diethyl ether for the L^R complex and benzene for the L^S complex. The X-ray structural analyses confirm that the solid state structures of the two complexes are dinuclear double helicates. The crystal structures demonstrate that, as anticipated, the chiral twisting of the binaphthalene can be used to control the helicity of the array. The coordination of two L^R ligands around two silver(I) tetrahedral ions results in the formation of a *P* (right-handed)[4] double helix and that the coordination of two L^S ligands around two silver(I) tetrahedral ions similarly results in the formation of an *M* (left-handed) double helix (Fig. 2). (For the L^S enantiomer, two very similar but crystallographically distinct cations are present in the solid state structure.)

Each silver(I) centre is four-coordinate pseudo-tetrahedral, bound to two pyridylimine units, each of which is approximately planar (pyridyl–imine torsion angles in the range 3–11°). The naphthalene units are twisted with respect to the imine group (torsion angles in the range 38–44°) and a more dramatic twisting is observed between the naphthalene rings which are almost perpendicular to each other (torsion angles in the range 70–78°). The combination of these twistings gives rise to the formation of the double helical structure, the chirality of the helical arrays being prescribed by the chiral twist inherent in the binaphthalene unit. The two silver(I) centres within the helical dications are separated by 3.61–3.78 Å. Within the helical arrays each pyridyl is stacked on top of a naphthalene unit. Such extensive face–face π-stacking interactions are also observed in polypyridyl helicates[4] and presumably contribute to the stabilisation of the structure. Although the conditions used to prepare the helicates were quite vigorous, the chirality of the spacer groups and in consequence the ligands is preserved (steric hindrance in the binaphthalene units results in a relatively high activation energy for inversion of configuration).

Solution structure. The ^1H NMR chemical shift data and coupling constants for the two complexes in CD$_3$CN solution are identical. This is consistent with formation of two enanti-
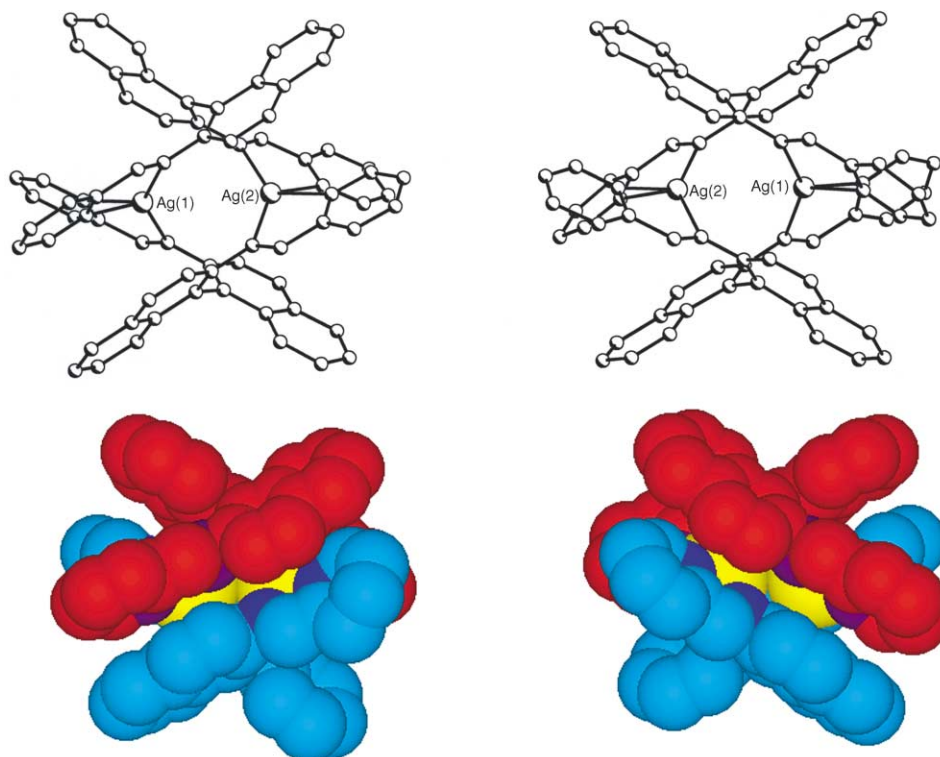

Fig. 2 The X-ray crystal structures of the silver(I) complexes of the L^R and L^S ligands confirming a solid state double helical structure for both complexes (the hydrogen atoms are omitted for clarity). Left hand side $Ag_2L^R_2{}^{2+}$. Right hand side $Ag_2L^S_2{}^{2+}$

omers of the same compound. The spectra also indicate that the complexes are symmetrical on the NMR timescale. The pyridyl resonances can be readily assigned from their distinctive splitting patterns and the binaphthyl resonances were fully assigned from COSY and NOE experiments. The imine resonances at δ 8.77 exist as doublets displaying distinctive coupling to the silver(I) ion with $^3J_{Ag-H}$ = 9.0 Hz and this confirms coordination to the metal. We have previously reported that ^{1}H NMR spectra in deuterated dichloromethane of silver(I) imine complexes show multiple resonances if more than one solution species is present[8] (e.g. if a helicate and a non-helical dimer structure are in equilibrium). The ^{1}H NMR of these complexes even at low temperature show no such splitting indicating only one solution species.

Electrospray mass spectra of acetonitrile solutions of the two enantiomers are dominated by two peaks corresponding to $\{Ag_2L_2\}^{2+}$ and $\{Ag_2L_2PF_6\}^+$, indicating that a dinuclear formulation is retained in solution. Peaks corresponding to species of higher nuclearity are not observed. ^{1}H NMR nuclear overhauser enhancements (NOEs) are observed between the resonances corresponding to H_{9bi} and H_{imine} and between those corresponding to H_{6py} and H_{6bi} (see Fig. 5 for numbering scheme). The structure of the ligands means that these NOEs must arise from inter-strand through-space contacts and indeed in the solid state structures there are corresponding close inter-strand contacts. This indicates that the solution structure is similar to that observed in the solid state.

Addition of racemic mixtures of chiral anions or chiral shift reagents did not reveal changes that conclusively confirm the chiral nature of the solution species; Addition of the chiral anion tris(tetrachlorobenzenediolato)phosphate (TRIS-PHAT)[26] to the solution of the complexes did lead to some broadening of some signals but these did not resolve conclusively into two diastereoisomers. However treatment of equimolar CD$_3$OD solutions of the L^R and L^S silver(I) complexes with equal aliquots of enantiopure-sodium antimonyl-L-tartrate led to different observed chemical shifts for the resonances of the two cations with a particularly dramatic difference between the two cations observed for the naphthyl resonances H_{3bi} and H_{4bi} adjacent to the imine functionality. This confirms the enantiomeric nature of the cationic species in the two solutions. Addition of the antimonyl tartrate solution to the two enantiomeric cations causes changes in chemical shift to all cation resonances with the most dramatic shifts on addition being observed (for both cations) for the resonances corresponding to H_{imine}, H_{3py} and H_{3bi}. From these shifts it seems likely that the antimonyl tartrate anion binds to the cations either along the strand backbone in the region defined by H_{3py}/H_{imine}/H_{3bi} or across the groove of the helix from the H_{3py}/H_{imine} region of one strand to the naphthyl region of the other strand. On mixing the two solutions of the two enantiomeric cations containing antimonyl-L-tartrate two distinct sets of resonances were retained and no new resonances arose confirming the expected integrity of the helical species towards diastereoisomer formation arising from ligand exchange.

The circular dichroism spectra of the two complexes in solution were recorded in acetonitrile solution. Equal and opposite signals are observed for each species in solution. This is also consistent with the two enantiomeric structures being retained in solution, not just in the solid state (Fig. 3).

Copper(I) complexes

The formation of the two corresponding copper(I) complexes was achieved by similar one pot methods. Ethanolic solutions containing two equivalents of pyridine-2-carbaldehyde were treated with ethanolic suspensions of one equivalent of R- or S-binaphthalene-diamine and heated under reflux to afford clear pale yellow solutions. These solutions were treated directly with one equivalent of [Cu(MeCN)$_4$][PF$_6$] (suspended in ethanol) to
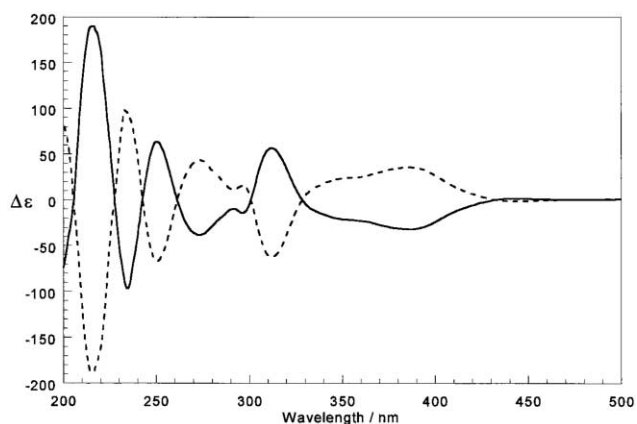
Fig. 3 The circular dichroism spectra for the L^R and L^S silver(I) complexes in acetonitrile solution. (The unbroken line corresponds to the L^R silver(I) complex and the dotted line to the L^S silver(I) complex).

afford green solutions containing green-grey precipitates. Heating was maintained for a further 16 hours and the resulting green-grey solid collected by vacuum filtration. Both the green colour of the precipitate and broad signals in the ^{1}H NMR spectra of the compounds indicated the presence of copper(II) species. In order to isolate the desired copper(I) species the solids were dissolved in acetonitrile and the resulting red solution heated to reflux for 24 hours. Red precipitates were isolated by the concentration of the solutions *in vacuo* and treatment with diethyl ether.

Partial microanalytical data for the complexes indicate a formulation $\{CuL(PF_6)\}_n$. Positive ion electrospray ionisation and FAB mass spectra for the L^R complexes show peaks (with the correct isotopic distributions) corresponding to $\{CuL\}$, $\{CuL_2\}$, $\{Cu_2L_2\}$ and $\{Cu_2L_2PF_6\}$. For the L^S complex only peaks for $\{CuL\}$ and $\{Cu_2L_2PF_6\}$ species are observed in electrospray but the FAB mass spectrum is similar to that of the L^R complexes. In all the mass spectra no peaks corresponding to higher aggregates (*e.g.* trimers *etc.*) are observed. This indicates the complexes are again of dimeric dinuclear formulation. The ^{1}H NMR spectra for the two copper(I) complexes in acetonitrile are again identical to each other (as expected for enantiomers). Complete assignment of the ^{1}H NMR spectra was accomplished through a combination of COSY and NOE experiments. Weak NOE signals were also observed between H_{9bi}–H_{imine} and H_{6bi}–H_{6py}. This is consistent with the maintenance of a double helical conformation in solution similar to that observed for the silver(I) helicates. An additional weak NOE is observed between H_{9bi} and H_{6py} indicating that the shorter metal–ligand bond lengths in the copper complexes may lead to small changes in the relative positions of the spacer units over the pyridyl rings. The copper(I) complexes are unstable in most common organic solvents and over time convert to green solutions indicating oxidation to the copper(II) species. As a result crystals suitable for X-ray analysis were not obtained. Circular dichroism spectra of the two complexes were recorded in acetonitrile. Equal and opposite signals are again observed for each enantiomer in solution (Fig. 4).

Conclusion

We have shown that enantiopure helicates may readily be prepared in one-pot reactions from commercial reagents by using the spacer group to induce and control the chirality of the array. The two enantiomers formed are $P\Delta\Delta$ L^R double helicates and $M\Lambda\Lambda$ L^S double helicates and inter-strand NOE data imply that these same structures are retained in solution.

We are currently examining further the use of spacer chirality to control the chirality of metallo-supramolecular arrays and the effect of the chirality on the properties.
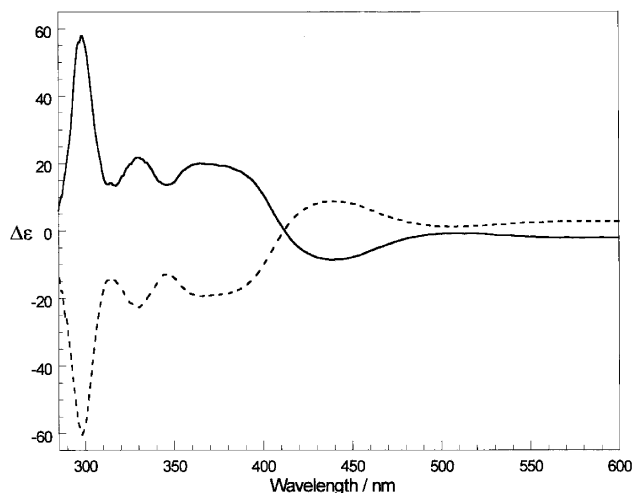
Fig. 4 The circular dichroism spectra for the L^R and L^S copper(I) complexes in acetonitrile solution. (The unbroken line corresponds to the L^S copper(I) complex and the dotted line to the L^R copper(I) complex).

Experimental

General

All starting materials were purchased from Aldrich and used without further purification. NMR spectra (see Fig. 5 for the numbering scheme used) were recorded on Bruker DPX300 and DRX500 instruments using standard Bruker software. ESI mass spectra were recorded on a Micromass Quatro (II) (low resolution triple quadrupole mass spectrometer) at the EPSRC National Mass Spectrometry Service Centre, Swansea. FAB mass spectra were recorded by the Warwick mass spectrometry service on a Micromass Autospec spectrometer using 3-nitrobenzyl alcohol as matrix. Microanalyses were conducted on a Leeman Labs CE44 CHN analyser by the University of Warwick Analytical service. Infrared spectra were recorded on a Bruker Vector 220 instrument fitted with an ATR Golden Gate. Circular dichroism spectra were recorded using a Jasco J-715 spectropolarimeter.
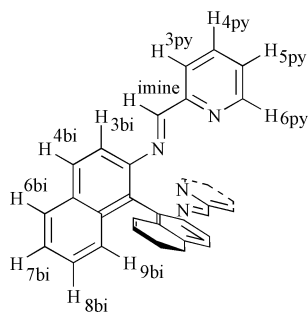

Fig. 5 The numbering scheme used for the protons in the ligand.

Syntheses

L^S-[Ag$_2$(C$_{32}$H$_{22}$N$_4$)$_2$][PF$_6$]$_2$. Pyridine-2-carbaldehyde (0.17 cm^3, 1.76 mmol) was dissolved in ethanol (3 cm^3) and heated with a suspension of $(S),(-)$-1,1′-binaphthalene-2,2′-diamine (0.25 g, 0.89 mmol) in ethanol (3 cm^3) to 79 °C for 18 hours. A suspension of silver(I) acetate (0.15 g, 0.89 mmol) in ethanol (3 cm^3) was then added and heating maintained for a further 18 hours. The reaction mixture was then filtered through Celite and ethanolic ammonium hexafluorophosphate added. The yellow precipitate was collected by vacuum filtration (0.35 g, 55%) (Found: C, 51.9; H, 3.0; N, 7.7. [Ag$_2$(C$_{32}$H$_{22}$N$_4$)$_2$][PF$_6$]$_2$·2.5H$_2$O requires C, 52.1; H, 3.3; N, 7.6%). ^{1}H (300 MHz; CD$_3$CN): δ 8.77 [4 H, d, J(H$_{imine}$–Ag) 9.0 Hz, H$_{imine}$], 8.14 [4 H, td, J(H$_{4py}$–

H$_{3py}$) 7.7, (H$_{4py}$–H$_{5py}$) 7.7 Hz, H$_{4py}$], 7.92 [4 H, d, J(H$_{4py}$–H$_{3py}$) 7.7 Hz, H$_{3py}$], 7.54 [4 H, d, J(H$_{6bi}$–H$_{7bi}$) 8.1 Hz, H$_{6bi}$], 7.41 [4 H, ddd, J(H$_{5py}$–H$_{4py}$) 7.7, (H$_{5py}$–H$_{6py}$) 4.7 Hz, H$_{5py}$], 7.37 [4 H, d, J(H$_{3bi}$–H$_{4bi}$) 8.9 Hz, H$_{3bi}$], 7.32 [4 H, ddd, J(H$_{7bi}$–H$_{6bi}$) 8.1, (H$_{7bi}$–H$_{8bi}$) 6.8 Hz, H$_{7bi}$], 7.15 [4 H, ddd, J(H$_{8bi}$–H$_{9bi}$) 8.3, (H$_{8bi}$–H$_{7bi}$) 6.8 Hz, H$_{8bi}$], 7.07 [4 H, d, J(H$_{4bi}$–H$_{3bi}$) 8.9 Hz, H$_{4bi}$], 6.78 [4 H, dd, J(H$_{9bi}$–H$_{8bi}$) 8.3 Hz, H$_{9bi}$], 6.72 [4 H, dd, J(H$_{6py}$–H$_{5py}$) 4.7 Hz, H$_{6py}$]. ^{13}C(75.5 MHz; CD$_3$CN): δ 162.2 (C$_{imine}$), 149.5 (C$_{6py}$), 147.8 (C$_{4°}$), 144.2 (C$_{4°}$), 139.0 (C$_{4py}$), 132.5 (C$_{4°}$), 132.2 (C$_{4°}$), 130.6 (C$_{4bi}$), 128.9 (C$_{3py}$), 128.5 (C$_{6bi}$), 128.0 (C$_{5py}$), 127.3 (C$_{8bi}$), 126.1 (C$_{7bi}$), 125.7 (C$_{4°}$), 125.0 (C$_{9bi}$), 118.6 (C$_{3bi}$). Positive-ion FAB, m/z 1286 ([Ag$_2$(C$_{32}$H$_{22}$N$_4$)$_2$][PF$_6$]$^+$, 93%), 1140 ([Ag$_2$(C$_{32}$H$_{22}$N$_4$)$_2$]$^+$, 90%), 571 ([Ag(C$_{32}$H$_{22}$N$_4$)]$^+$, 53%). Positive-ion ESI, m/z 1285 ([Ag$_2$(C$_{32}$H$_{22}$N$_4$)$_2$][PF$_6$]$^+$), 1033 ([Ag(C$_{32}$H$_{22}$N$_4$)$_2$]$^+$), 571 ([Ag$_2$(C$_{32}$H$_{22}$N$_4$)$_2$]$^{2+}$). ν_{max}/cm^{-1} 3050–2800w, 1615w, 1587m, 1568m, 1439m, 1305m, 1204m, 1006m, 837s, 776m, 750m, 692m, 672m, 651m, 633m, 585s, 556s, 527m, 511m. λ_{max}/nm (MeCN) 229 (ε/mol^{-1} dm^{-3} cm^{-1} 1.6 × 10^5), 279 (1.0 × 10^5), 322 (4.0 × 10^4), 360 (3.0 × 10^4).

L^R-[Ag$_2$(C$_{32}$H$_{22}$N$_4$)$_2$][PF$_6$]$_2$. Preparation as for the $(S),(-)$ silver(I) salt except for the use of the $(R),(+)$-1,1′-binaphthalene-2,2′-diamine spacer group, yield (0.40 g, 63%) (Found: C, 51.4; H, 3.1; N, 7.4. [Ag$_2$(C$_{32}$H$_{22}$N$_4$)$_2$][PF$_6$]$_2$·3.5H$_2$O requires C, 51.5; H, 3.4; N, 7.5%). ^{1}H (300 MHz; CD$_3$CN): δ 8.77 [4 H, d, J(H$_{imine}$–Ag) 9.0 Hz, H$_{imine}$], 8.14 [4 H, td, J(H$_{4py}$–H$_{3py}$) 7.7, (H$_{4py}$–H$_{5py}$) 7.7 Hz, H$_{4py}$], 7.92 [4 H, d, J(H$_{4py}$–H$_{3py}$) 7.7 Hz, H$_{3py}$], 7.54 [4 H, d, J(H$_{6bi}$–H$_{7bi}$) 8.1 Hz, H$_{6bi}$], 7.41 [4 H, ddd, J(H$_{5py}$–H$_{4py}$) 7.7, (H$_{5py}$–H$_{6py}$) 4.7 Hz, H$_{5py}$], 7.37 [4 H, d, J(H$_{3bi}$–H$_{4bi}$) 8.9 Hz, H$_{3bi}$], 7.32 [4 H, ddd, J(H$_{7bi}$–H$_{6bi}$) 8.1, (H$_{7bi}$–H$_{8bi}$) 6.8 Hz, H$_{7bi}$], 7.15 [4 H, ddd, J(H$_{8bi}$–H$_{9bi}$) 8.3, (H$_{8bi}$–H$_{7bi}$) 6.8 Hz, H$_{8bi}$], 7.07 [4 H, d, J(H$_{4bi}$–H$_{3bi}$) 8.9 Hz, H$_{4bi}$], 6.78 [4 H, dd, J(H$_{9bi}$–H$_{8bi}$) 8.3 Hz, H$_{9bi}$], 6.72 [4 H, dd, J(H$_{6py}$–H$_{5py}$) 4.7 Hz, H$_{6py}$]. ^{13}C(75.5 MHz; CD$_3$CN): δ 162.2 (C$_{imine}$), 149.5 (C$_{6py}$), 147.8 (C$_{4°}$), 144.2 (C$_{4°}$), 139.0 (C$_{4py}$), 132.5 (C$_{4°}$), 132.2 (C$_{4°}$), 130.6 (C$_{4bi}$), 128.9 (C$_{3py}$), 128.5 (C$_{6bi}$), 128.0 (C$_{5py}$), 127.3 (C$_{8bi}$), 126.1 (C$_{7bi}$), 125.7 (C$_{4°}$), 125.0 (C$_{9bi}$), 118.6 (C$_{3bi}$). Positive-ion FAB, m/z 1285 ([Ag$_2$(C$_{32}$H$_{22}$N$_4$)$_2$][PF$_6$]$^+$, 93%), 1140 ([Ag$_2$(C$_{32}$H$_{22}$N$_4$)$_2$]$^+$, 90%), 571 ([Ag(C$_{32}$H$_{22}$N$_4$)]$^+$, 53%). Positive-ion ESI, m/z 1285 ([Ag$_2$(C$_{32}$H$_{22}$N$_4$)$_2$][PF$_6$]$^+$), 1033 ([Ag(C$_{32}$H$_{22}$N$_4$)$_2$]$^+$), 571 ([Ag$_2$(C$_{32}$H$_{22}$N$_4$)$_2$]$^{2+}$). ν_{max}/cm^{-1} 3050–2800w, 1615w, 1567m, 1568w, 1504m, 1439m, 1304m, 1204m, 1005m, 831s, 777s, 757s, 747s, 739s, 693m, 673m, 651m, 651m, 632m, 621w, 555s, 523w, 509w. λ_{max}/nm (MeCN) 229 (ε/mol^{-1} dm^{-3} cm^{-1} 1.6 × 10^5), 279 (1.0 × 10^5), 322 (4.0 × 10^4), 360 (3.0 × 10^4).

L^R-[Cu$_2$(C$_{32}$H$_{22}$N$_4$)$_2$][PF$_6$]$_2$. Pyridine-2-carbaldehyde (0.17 cm^3, 1.76 mmol) was dissolved in ethanol (3 cm^3) and heated with a suspension of $(R),(+)$-1,1′-binaphthalene-2,2′-diamine (0.25 g, 0.89 mmol) in ethanol (3 cm^3). The reaction was heated to 80 °C for 16 hours. A suspension of copper(I) tetrakis-(acetonitrile) hexafluorophosphate (0.33 g, 0.89 mmol) in ethanol (3 cm^3) was then added and heating continued for a further 16 hours. The resulting green-grey solid was collected, dissolved in acetonitrile (100 cm^3) and the red solution heated to reflux for 24 hours. The solution was then concentrated *in vacuo* and treated with diethyl ether (10 cm^3). The resulting red-brown solid was collected by vacuum filtration (0.27 g, 45%) (Found: C, 57.3; H, 3.3; N, 8.4. [Cu$_2$(C$_{32}$H$_{22}$N$_4$)$_2$][PF$_6$]$_2$·0.3H$_2$O requires C, 57.0; H, 3.3; N, 8.3%). ^{1}H(300 MHz; CD$_3$CN): δ 8.89 [4 H, s, H$_{imine}$], 7.84 [8 H, m, J(H$_{4py}$–H$_{3py}$) 7.7, (H$_{4py}$–H$_{5py}$) 8.7 Hz, 4H$_{4py}$/H$_{3py}$], 7.59 [4 H, d, J(H$_{3bi}$–H$_{4bi}$) 8.9 Hz, H$_{3bi}$], 7.41 [4 H, d, J(H$_{6bi}$–H$_{7bi}$) 8.1 Hz, H$_{6bi}$], 7.31 [4 H, d, J(H$_{4bi}$–H$_{3bi}$) 8.9 Hz, H$_{4bi}$], 7.28 [4 H, ddd, J(H$_{7bi}$–H$_{6bi}$) 8.1, (H$_{7bi}$–H$_{8bi}$) 6.9 Hz, H$_{7bi}$], 7.16 [4 H, ddd, J(H$_{8bi}$–H$_{9bi}$) 8.5, (H$_{8bi}$–H$_{7bi}$) 6.9 Hz, H$_{8bi}$], 6.84 [4 H, ddd, J(H$_{5py}$–H$_{4py}$) 8.7, (H$_{5py}$–H$_{6py}$) 4.8 Hz, H$_{5py}$], 6.72 [4 H, d, J(H$_{9bi}$–H$_{8bi}$) 8.5 Hz, H$_{9bi}$], 5.60 [4 H, d, J(H$_{6py}$–H$_{5py}$) 4.8 Hz, H$_{6py}$]. ^{13}C(75.5 MHz; CD$_3$CN): δ 162.4 (C$_{imine}$), 149.0 (C$_{4°}$), 146.2 (C$_{6py}$), 144.0 (C$_{4°}$), 137.5 (C$_{3py}$), 133.0 (C$_{4°}$), 130.2 (C$_{4bi}$),

Table 1 Crystallographic data and structural refinements for the L^R and L^S silver(I) double helicates

Complex	L^R silver(I) helix	L^S silver(I) helix
Empirical formula	$C_{65.50}H_{48.50}Ag_2F_{12}N_{9.50}O_3P_2$	$C_{147.50}H_{107}Ag_4F_{24}N_{16}P_4$
Formula weight	1522.32	3114.85
Temperature/K	180(2)	180(2)
Crystal system	$P3_1$	$P2_1$
Space group	Trigonal	Monoclinic
a/Å	14.38840(10)	13.1740(2)
b/Å	14.38840(10)	32.1983(2)
c/Å	27.22160(10)	17.9687(3)
α/°	90	90
β/°	90	108.6280(10)
γ/°	120	90
V/Å^3, Z	4880.55(5), 3	7222.67(17), 2
μ/mm^{-1}	0.739	0.664
Crystal size/mm	$0.4 \times 0.4 \times 0.2$	$0.36 \times 0.36 \times 0.2$
Reflections collected	31885	46496
Independent reflections	15474 ($R_{int} = 0.0266$)	31159 ($R_{int} = 0.0766$)
Data/restraints/parameters	15474/1/869	31159/1/1706
Goodness-of-fit on F^2	0.958	0.900
Final R indices[$I > 2\sigma(I)$]	$R1 = 0.0370$, $wR2 = 0.0749$	$R1 = 0.0662$, $wR2 = 0.1182$
R indices (all data)	$R1 = 0.0593$, $wR2 = 0.0820$	$R1 = 0.2412$, $wR2 = 0.1700$
Largest difference peak, hole/ e Å^{-3}	0.506, −0.402	0.566, −0.477
Absolute structure parameter	−0.010(14)	0.01(2)

128.5 (C_{6bi}), 128.0 (C_{5py}), 127.5 (C_{8bi}), 127.3 (C_{4py}), 126.0 (C_{7bi}), 124.8 (C_{9bi}), 119.6 (C_{3bi}). Positive-ion ESI, m/z 1197 ([Cu$_2$-($C_{32}H_{22}N_4)_2$][PF$_6$]$^+$), 1094 ([Cu$_2$($C_{32}H_{22}N_4)_2$][CH$_3$CN]$^+$), 1052 ([Cu$_2$($C_{32}H_{22}N_4)_2$]$^+$), 989 ([Cu($C_{32}H_{22}N_4)_2$]$^+$), 525 ([Cu(C_{32}-H$_{22}N_4$)]$^+$). Positive-ion FAB, m/z 1197 ([Cu$_2$($C_{32}H_{22}N_4)_2$]-[PF$_6$]$^+$), 1052 ([Cu$_2$($C_{32}H_{22}N_4)_2$]$^+$), 525 ([Cu$_2$($C_{32}H_{22}N_4)_2$]$^{2+}$). ν_{max}/cm^{-1} 3050–3070w, 1581m, 1557w, 1505w, 1471w, 1302w, 1268w, 1204w, 1157w, 1102w, 1011w, 969w, 901w, 830s, 749m, 693w, 673w, 612w, 584w. λ_{max}/nm (MeCN) 227 (ε/mol^{-1} dm^{-3} cm^{-1} 1.5 × 10^5), 281 (7.0 × 10^4), 324 (4.0 × 10^4), 374 (2.0 × 10^4), 518 (3.5 × 10^3).

L^S-[Cu$_2$($C_{32}H_{22}N_4)_2$][PF$_6$]$_2$. Preparation as for the (*R*),(+) copper(I) salt except for the use of (*S*),(−)-1,1′-binaphthalene-2,2′-diamine, yield (0.32 g, 53%) (Found: C, 55.9; H, 3.3; N, 8.1. [Cu$_2$($C_{32}H_{22}N_4)_2$][PF$_6$]$_2$·2H$_2$O requires C, 55.8; H, 3.5; N, 8.1%). ^{1}H(300 MHz; CD$_3$CN): δ 8.89 [4 H, s, H$_{imine}$], 7.84 [8 H, m, J(H$_{4py}$–H$_{3py}$) 7.7, (H$_{4py}$–H$_{5py}$) 8.7 Hz, 4H$_{4py}$/H$_{3py}$], 7.59 [4 H, d, J(H$_{3bi}$–H$_{4bi}$) 8.9 Hz, H$_{3bi}$], 7.41 [4 H, d, J(H$_{6bi}$–H$_{7bi}$) 8.1 Hz, H$_{6bi}$], 7.31 [4 H, d, J(H$_{4bi}$–H$_{3bi}$) 8.9 Hz, H$_{4bi}$], 7.28 [4 H, ddd, J(H$_{7bi}$–H$_{6bi}$) 8.1, (H$_{7bi}$–H$_{8bi}$) 6.9 Hz, H$_{7bi}$], 7.16 [4 H, ddd, J(H$_{8bi}$–H$_{9bi}$) 8.5, (H$_{8bi}$–H$_{7bi}$) 6.9 Hz, H$_{8bi}$], 6.84 [4 H, ddd, J(H$_{5py}$–H$_{4py}$) 8.7, (H$_{5py}$–H$_{6py}$) 4.8 Hz, H$_{5py}$], 6.72 [4 H, d, J(H$_{9bi}$–H$_{8bi}$) 8.5 Hz, H$_{9bi}$], 5.60 [4 H, d, J(H$_{6py}$–H$_{5py}$) 4.8 Hz, H$_{6py}$]. ^{13}C(75.5 MHz; CD$_3$CN): δ 162.4 (C$_{imine}$), 149.0 (C$_{4°}$), 146.2 (C$_{6py}$), 144.0 (C$_{4°}$), 137.5 (C$_{3py}$), 133.0 (C$_{4°}$), 130.2 (C$_{4bi}$), 128.5 (C$_{6bi}$), 128.0 (C$_{5py}$), 127.5 (C$_{8bi}$), 127.3 (C$_{4py}$), 126.0 (C$_{7bi}$), 124.8 (C$_{9bi}$), 119.6 (C$_{3bi}$). Positive-ion ESI, m/z 1197 ([Cu$_2$($C_{32}H_{22}$-N$_4)_2$][PF$_6$]$^+$), 525 ([Cu($C_{32}H_{22}N_4)$]$^+$). Positive-ion FAB, m/z 1197 ([Cu($C_{32}H_{22}N_4)_2$][PF$_6$]$^+$), 1052 ([Cu$_2$($C_{32}H_{22}N_4)_2$]$^+$), 525 ([Cu$_2$-($C_{32}H_{22}N_4)_2$]$^{2+}$). ν_{max}/cm^{-1} 3050–3070w, 1581m, 1557w, 1505w, 1471w, 1302w, 1268w, 1204w, 1157w, 1102w, 1011w, 969w, 901w, 830s, 780m, 766m, 747m, 692w, 634w, 557w. λ_{max}/nm (MeCN) 227 (ε/mol^{-1} dm^{-3} cm^{-1} 1.5 × 10^5), 281 (7.0 × 10^4), 324 (4.0 × 10^4), 374 (2.0 × 10^4), 518 (3.5 × 10^3).

X-Ray crystallography

Suitable crystals of L^S-[Ag$_2$($C_{32}H_{22}N_4)_2$][PF$_6$]$_2$ were grown from nitromethane–benzene and L^R-[Ag$_2$($C_{32}H_{22}N_4)_2$][PF$_6$]$_2$ from nitromethane–diethyl ether. Crystallographic data are collected in Table 1. Data were measured on a Siemens SMART[27] three-circle system with CCD area detector using the oil-mounting method at 180(2) K (maintained with the Oxford Cryosystems Cryostream Cooler).[28] Absorption correction by ψ-scan. The structures were solved by direct methods using SHELXS[29] (TREF).

CCDC reference numbers 166445 and 166446.

See http://www.rsc.org/suppdata/dt/b1/b106987j/ for crystal-lographic data in CIF or other electronic format.

References

1 J.-M. Lehn, *Supramolecular Chemistry–Concepts and Perspectives*, VCH, Weinheim, 1995.
2 D. Philp and J. F. Stoddart, *Angew. Chem., Int. Ed. Engl.*, 1996, **35**, 1155.
3 C. Branden and J. Tooze, *Introduction to Protein Structure*, Garland Publishing, New York, 2nd edn., 1999.
4 E. C. Constable, *Prog. Inorg. Chem.*, 1994, **42**, 67; C. Piguet, G. Bernardinelli and G. Hopfgartner, *Chem. Rev.*, 1997, **97**, 2005; M. Albrecht, *J. Inclusion Phenom. Macrocyclic Chem.*, 2000, **36**, 127; A. F. Williams, *Pure Appl. Chem.*, 1996, **68**, 1285.
5 M. J. Hannon, C. L. Painting, J. Hamblin, A. Jackson and W. Errington, *Chem. Commun.*, 1997, 1807.
6 L. J. Childs, N. W. Alcock and M. J. Hannon, *Angew. Chem., Int. Ed.*, 2001, **40**, 1079.
7 M. J. Hannon, S. Bunce, A. J. Clarke and N. W. Alcock, *Angew. Chem., Int. Ed.*, 1999, **38**, 1277.
8 M. J. Hannon, C. L. Painting and N. W. Alcock, *Chem. Commun.*, 1999, 2023.
9 M. J. Hannon, I. Meistermann, C. J. Isaac, C. Blomme, J. Aldrich-Wright and A. Rodger, *Chem. Commun.*, 2001, 1078.
10 M. J. Hannon, V. Moreno, M. J. Prieto, E. Moldrheim, E. Sletten, I. Meistermann, C. J. Isaac, K. J. Sanders and A. Rodger, *Angew. Chem., Int. Ed.*, 2001, **40**, 879.
11 G. Baum, E. C. Constable, D. Fenske, C. E. Housecroft and T. Kulke, *Chem. Commun.*, 1998, 195; W. Zarges, J. Hall, J.-M. Lehn and C. Bolm, *Helv. Chim. Acta*, 1991, **74**, 1843.
12 P. K. Bowyer, K. A. Porter, A. D. Rae, A. C. Willis and S. B. Wild, *Chem. Commun.*, 1998, 1153.
13 C. Provent, E. Rivara-Minten, S. Hewage, G. Brunner and A. F. Williams, *Chem. Eur. J.*, 1999, **5**, 3487.
14 E. C. Constable, T. Kulke, M. Neuberger and M. Zehnder, *Chem. Commun.*, 1997, 489.
15 G. Baum, E. C. Constable, D. Fenske, C. E. Housecroft, T. Kulke, M. Neuberger and M. Zehnder, *J. Chem. Soc., Dalton Trans.*, 2000, 945.
16 U. Knof and A. Von Zelewsky, *Angew. Chem., Int. Ed.*, 1999, **38**, 302.
17 C. J. Sanders, K. M. Gillespie, D. Bell and P. Scott, *J. Am. Chem. Soc.*, 2000, **122**, 7132.

18 W.-K. Wong, J.-X. Gao and W.-T. Wong, *Polyhedron*, 1993, **12**, 2063.

19 W.-K. Wong, J.-X. Gao, W.-T. Wong, W. C. Cheng and C.-M. Che, *J. Organomet. Chem.*, 1994, **471**, 277.

20 A. Nishinaga, T. Tsutsui, H. Moriyama, T. Wazaki, T. Mashino and Y. Fugii, *J. Mol. Catal.*, 1993, **83**, 117.

21 T.-C. Cheung, T.-F. Lai and C.-M. Che, *Polyhedron*, 1994, **13**, 2073.

22 S. Miyano, M. Nawa, A. Mori and H. Hashimoto, *Bull. Chem. Soc. Jpn.*, 1984, **57**, 2171.

23 J.-H. Lin, C.-M. Che, T.-F. Lai, C.-K. Poon and Y. X. Cui, *J. Chem. Soc., Chem. Commun.*, 1991, 468.

24 H. Sakiyama, H. Okawa, N. Oguni, T. Katsuki and R. Irie, *Bull. Chem. Soc. Jpn.*, 1992, **65**, 606.

25 M. Kimura, M. Sano, T. Muto, K. Hanabusa and H. Shirai, *Macromolecules*, 1999, **32**, 7951.

26 J. Lacour, C. Ginglinger, F. Favarger and S. Torche-Haldimann, *Chem. Commun.*, 1997, 2285; J. Lacour, S. Barchéchath, J. J. Jodry and C. Ginglinger, *Tetrahedron Lett.*, 1998, **39**, 567.

27 SMART User's Manual, Siemens Industrial Automation Inc, Madison, WI, 1994.

28 J. Cosier and A. M. Glazer, *J. Appl. Crystallogr.*, 1986, **19**, 105.

29 G. M. Sheldrick, *Acta Crystallogr., Sect. A*, 1990, **46**, 467.