# Spacer Control of Directionality in Supramolecular Helicates Using an Inexpensive Approach**

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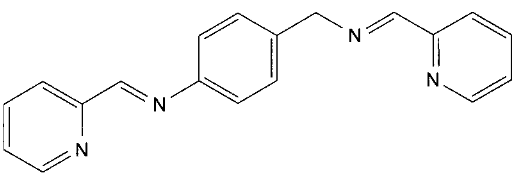
The double-helical structure has provided an important forum for the evolution of metallo-supramolecular construction principles.[1] Their application in other systems has led to a plethora of supramolecular architectures such as boxes,[1–3] grids,[4] and cylinders.[5] While the basic features of the design necessary to assemble a double helix are now fairly well established,[1] challenges in defining the precise topology or conformation of the helical superstructure remain. If a nonsymmetrical ligand is used for helicate formation, the issue of controlling the relative orientations (or directions) of the ligands within the helical superstructure arises. This issue is important because selectively orienting substituents on the outside of a helix is desirable in order to control the assembly of helicates into larger supramolecular arrays (we have previously used this principle to control the aggregation of supramolecular boxes[2]) or to relay the chiral information inherent in the helix to an extra-helical site.

Constable et al. have shown that by careful positioning of bulky substituents on the back of a ligand, double helices of an exclusive head-to-head or head-to-tail ligand orientation can be assembled.[6] However, such interactions seem to represent a relatively small energy term and may be relieved by a flattening of the helical pitch resulting in a mix of head-to-head and head-to-tail helices in solution, for all but the most bulky substituents.[6] An alternative approach is to use different donor sets to control the assembly: Piguet et al.[7] and Albrecht and Fröhlich[8] have used ligands containing two different binding units to form directional triple helices.

We reasoned that an alternative approach might be to introduce asymmetry into a spacer placed between the metal-binding domains. Since this introduces the asymmetry directly within the helical array rather than at the periphery, it seems likely to provide a greater energetic stabilization for one orientation over the other. An additional advantage is that the extra-helical sites are left vacant for subsequent incorporation of functional substituents.

We have recently described an inexpensive and simple imine-based approach to supramolecular architecture which has the advantage that it allows us to generate ligands which can act as supramolecular building blocks rapidly in high yields from commercial materials.[9] Applying this imine approach, we prepared the ligand **L** to investigate the effect of incorporating an asymmetric spacer. The ligand contains two binding domains separated by a methylenephenylene spacer. The two binding domains are sterically prevented from binding to the same metal center and so the ligand is constrained to act as a dinucleating ligand. As illustrated in Figure 1, a head-to-tail configuration is anticipated when **L** reacts with tetrahedral metal ions; a head-to-head configuration would result in a very small dihedral angle between the two 'head' binding units (almost square planar rather than tetrahedral) and the two phenyl rings would also be placed unacceptably close. Ligand **L** is prepared in 77% yield by mixing ethanolic solutions containing two equivalents of 2-pyridinecarbaldehyde and one equivalent of 4-aminobenzylamine. Reaction of **L** with silver(I) acetate in methanol yields a colorless solution from which a white solid is obtained on treatment with $[NH_4][PF_6]$. Mass spectrometry (FAB) shows peaks corresponding to $\{Ag_2L_2(PF_6)\}^+$ and $\{Ag_2L_2\}^+$ consistent with formation of a dimeric species of formula $[Ag_2L_2][PF_6]_2$. Such a formulation is consistent with either a helix or the alternative box structure (Figure 2) and also with either a head-to-tail (HT) or head-to-head (HH) configuration of the ligands (Figure 1). The $^1$H NMR spectra of the compound in $CD_2Cl_2$ recorded at both room temperature and low temperature (193 K) confirm the presence of a unique molecular species, which from consideration of the ligand geometry we anticipated to contain a helical arrangement.[10]



**L**

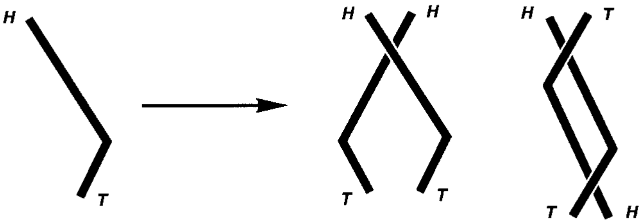


Figure 1. Schematic illustration of the formation of head-to-head and head-to-tail structures.

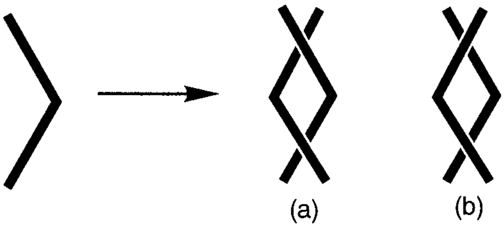


Figure 2. Schematic illustration of the formation of (a) helical or (b) bridging nonhelical (box) structures.

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The imine proton resonances show coupling to Ag at both 298 K and 193 K confirming the coordination of the silver ion. The magnitude of the Ag–imine coupling is unaffected by temperature. The $^{109}$Ag NMR spectrum reveals the presence of a single silver resonance at $\delta = 533$. This observation indicates that the solution species is indeed the head-to-tail isomer (the head-to-head isomer should contain two non-equivalent silver centers; it is possible that the peak might represent two coincident signals, though unlikely given the different nature of the HH and TT environments).

Recrystallization of the compound from acetonitrile by diffusion of diethyl ether afforded X-ray quality crystals and we have determined the crystal structure to confirm the molecular structure.[11] The structure of the cation (Figure 3) is indeed a head-to-tail helix, containing each silver(I) ion in a pseudo-tetrahedral coordination geometry bound to the pyridyl–phenylimine donor unit of one ligand and the pyridyl–methylimine unit of the other. The two ligands wrap around the metal–metal axis giving rise to the helical structure, both enantiomers of which are present. The phenyl ring is approximately coplanar with the adjacent pyridylimine unit as expected for maximum conjugation; the helical twisting of the ligand is restricted by the design to the methylene group.

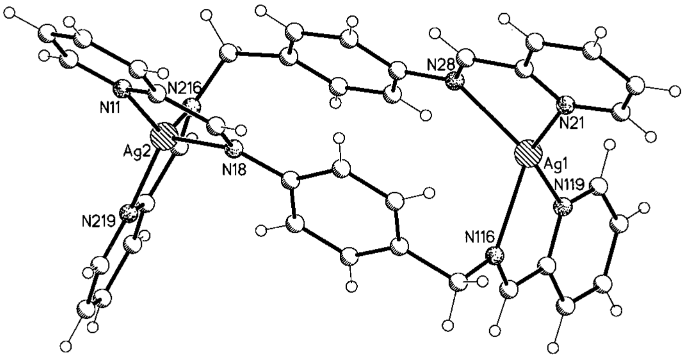

Figure 3. View of the cation $[Ag_2L_2]^{2+}$.

We have shown that by careful selection of spacer unit between ligand binding sites the directionality of a helicate may be controlled. We are currently extending our studies to apply this principle within more sophisticated supramolecular arrays and are also investigating incorporation of directional helicates within larger supramolecular arrays.

## *Experimental Section*

**L**: 2-Pyridinecarbaldehyde (1.6 mL, 16.8 mmol) and 4-aminobenzylamine (0.9 mL, 8.0 mmol) were stirred in ethanol (25 mL) for 12 h. The orange solution was concentrated under reduced pressure and cooled in ice. An off-white solid precipitated (1.85 g, 77 %) and was collected by filtration and dried over $P_2O_5$. $^1$H NMR ($CDCl_3$): $\delta = 8.68$ (1H, d, $J = 5.6$ Hz; $H_6$), 8.64 (1H, d, $J = 5.6$ Hz; $H_6$), 8.60 (1H, s; $H_{im}$), 8.50 (1H, s; $H_{im}$), 8.18 (1H, d, $J = 7.6$ Hz; $H_3$), 8.07 (1H, d, $J = 7.6$ Hz; $H_3$), 7.80 (1H, t, $J = 7.6$ Hz; $H_4$), 7.76 (1H, t, $J = 7.6$ Hz; $H_4$), 7.40–7.20 (6H, m; $H_{Ph}$ $H_5$ $H_5$), 4.76 (2H, s; $CH_2$); MS (EI): $m/z$: 300 [$M^+$].

$[Ag_2\mathbf{L}_2][PF_6]_2$: Ligand **L** (0.045 g, 0.15 mmol) and Ag(OAc). (0.025 g, 0.15 mmol) were stirred in methanol (25 mL) for 2 h. The solution was treated with methanolic $[NH_4][PF_6]$ (excess) to yield a pale yellow product (0.056 g, 68 %) which was isolated by filtration. $^1$H NMR[10] ($CD_2Cl_2$): $\delta = 8.79$ (1H, d, $J = 6.4$ Hz; $H_{im}$), 8.66 (1H, d, $J = 7.4$ Hz; $H_{im}$), 8.62 (1H, d, $J = 4.9$ Hz; $H_6$), 8.53 (1H, d, $J = 4.9$ Hz; $H_6$), 8.08 (1H, t, $J = 7.6$ Hz; $H_4$), 8.02 (1H, t, $J = 7.6$ Hz; $H_4$), 7.96 (1H, d, $J = 7.8$ Hz; $H_3$), 7.78 (1H, d, $J = 7.8$ Hz; $H_3$), 7.64–7.54 (2H, m; $H_5$ $H_5$) 7.07 (2H, d, $J = 7.8$ Hz; $H_{Ph}$), 6.92 (2H, d, $J = 7.8$ Hz; $H_{Ph}$), 4.77 (2H, s; $CH_2$); MS (FAB): $m/z$: 961 $[Ag_2\mathbf{L}_2(PF_6)]$ and 816 $[Ag_2\mathbf{L}_2]$.

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[10] Although the (diastereotopic) $CH_2$ resonance broadens at lower temperature we see no significant broadening of any other resonances at low temperature and no new peaks appear in the spectrum. This is consistent with the presence of only one solution species (albeit in two exchanging enantiomeric forms).

[11] a) Crystal structure data for $C_{19}H_{16}N_4AgPF_6 \cdot 1.5\,C_2H_3N$, $M_r = 614.78$, triclinic, space group $P\bar{1}$, $a = 13.1320(10)$, $b = 15.1807(5)$, $c = 15.4680(10)$ Å, $\alpha = 105.268(5)$, $\beta = 105.745(5)$, $\gamma = 113.796(5)°$, $V = 2460.2(3)$ Å$^3$, $T = 180(2)$ K, $\lambda = 0.71073$ Å, $Z = 4$, $\rho_{calcd} = 1.660$ Mg m$^{-3}$, $F(000) = 1228$. $\mu(Mo_{K\alpha}) = 0.952$ mm$^{-1}$. Crystal character: golden-yellow blocks. Crystal dimensions 0.3 × 0.3 × 0.3 mm, data Collected with a Siemens SMART three-circle system with CCD area detector. The crystal was held at 180(2) K with an Oxford Cryosystem Cryostream Cooler; $\theta_{max} = 28.44°$. A total of 14820 reflections were measured, 10802 unique [$R_{int} = 0.0175$]. Absorption correction by Psi-scan. Weighting scheme $w = 1/[\sigma^2(F_o^2) + (0.0383\,P)^2]$, where $P = (F_o^2 + 2F_c^2)/3$. Goodness-of-fit on $F^2$ was 0.936, $R1$ [for 7511 reflections with $I > 2\sigma(I)$] = 0.0340, $wR2 = 0.0833$. Data/restraints/parameters 10802/0/643. Largest difference Fourier peak and hole 0.841 and $-0.482$ e Å$^{-3}$. Refinement used SHELXL 96 (G. M. Sheldrick, **1996**). b) Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Center as supplementary publication no. CCDC-102733. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).