Diastereoselective formation of disilver(I) double helicates with chiral 2,2′ : 6′,2″ : 6″,2‴-quaterpyridines

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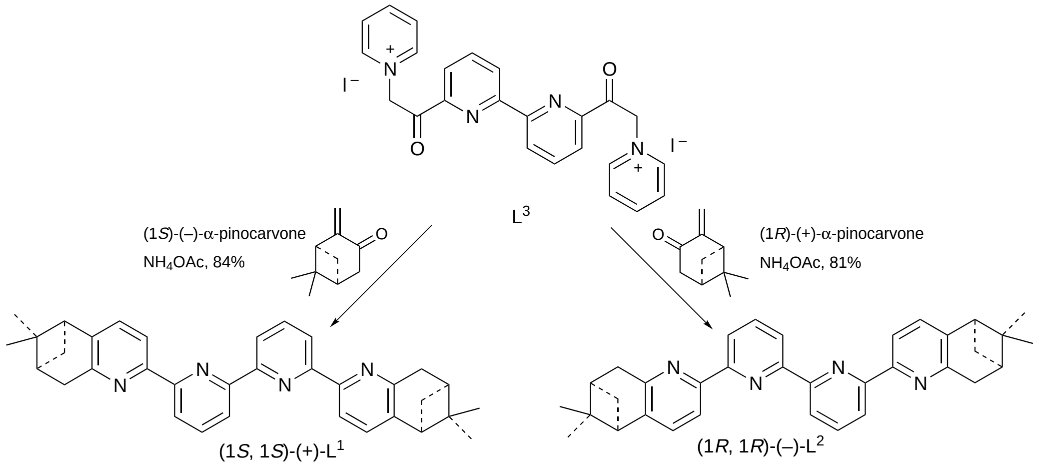
Chiral 2,2′:6′,2″ : 6″,2‴-quaterpyridines bearing fused chiral groups in the 5,6- and 5‴,6‴-positions are prepared; these ligands preferentially form *P* or *M* dinuclear double helicates upon coordination to silver(I), one of which has been structurally characterised.

Oligopyridines and oligopyridine metal-binding domains are a recurrent feature in metallosupramolecular chemistry[1] and it is now well established that the higher oligopyridines can give multiple-helical transition-metal complexes.[2] Although preorganised chiral ligands bearing multiple oligopyridine domains have been previously studied[3,4] we have recently shown that the right- or left-handed chirality of the helix may also be controlled in true self-assembly processes by the use of chiral oligopyridines and have demonstrated that modest diastereomeric excesses (de, 75%) of the *P* or *M* double helicates are formed upon reaction of enantiomerically pure chiral 2,2′:6′,2″-terpyridines with copper(I).[5] Here, we show that acceptably high de values may be obtained by (*i*) varying the metal, (*ii*) increasing the number of donor atoms and (*iii*) increasing the number of chiral sites in the ligands.

2,2′ : 6′,2″:6″,2‴-Quaterpyridines react with silver(I) salts to give dinuclear double helicates.[6,7] A pair of enantiomeric 2,2′:6′,2″:6″,2‴-quaterpyridines (1*S*, 1*S*)-(+)-L^1 and (1*R*, 1*R*)-(−)-L^2 were prepared enantioselectively from (1*S*)-(−) or (1*R*)-(+) pinocarvone[8] by reaction with salt L^3 (ref. 9) and ammonium acetate in a mixture of acetic acid and acetic anhydride in near quantitative yield as white crystalline solids (Scheme 1).† The ligands were fully characterised and exhibited spectroscopic properties closely resembling those of analogous lower homologues first reported by von Zelewsky and co-workers.[10]

The reaction of L^1 or L^2 with silver(I) acetate in methanol followed by precipitation with ammonium hexafluorophosphate gave cream coloured precipitates of $[Ag_2L^1_2][PF_6]_2$ or $[Ag_2L^2_2][PF_6]_2$ as established by elemental analysis and mass spectrometry [*m*/*z* 1358 ($M^+ - PF_6$)] in 85–90% yield.‡ In principle, each ligand could give a pair of diastereomeric double helicates, for example L^1 could give *P*-$[Ag_2\{(1S,\ 1S)\text{-}L^1)\}_2]^{2+}$ or *M*-$[Ag_2\{(1S,\ 1S)\text{-}L^1\}_2]^{2+}$. Unlike the case investigated earlier[5] the use of the symmetrically substituted ligands L^1 and L^2 eliminates any additional complications from head–tail isomerism. The ^{1}H NMR spectrum of CD_3CN solutions of the crude precipitates revealed a 0.024 : 1.00 ratio of diastereomers in each case [Fig. 1(*a*)]. This corresponds to a 95.3% de of one of the two diastereomers. A single recrystallisation from acetonitrile yielded good quality crystals which ^{1}H NMR spectroscopy revealed to contain only the major diastereomer. Circular dichroism spectroscopy confirmed that the compounds prepared from L^1 and L^2 possessed equal and opposite chiroptical properties [Fig. 1(*b*)] as expected for an enantiomeric pair of (*S**,*S**,*S**,*S**)-P* and (*R**,*R**,*R**,*R**)-*M** helicates. After a single recrystallisation, a de of 100% has been obtained. The only question remaining was to determine which of the two helical conformations (*P* or *M*) was favoured in each case. In related systems, a large positive CD absorption at *ca.* 320 nm is characteristic of a *P* helicate, whereas a negative mode is seen for *M*-helicates.[10] On this basis, we propose *P*-$[Ag_2\{(1S,\ 1S)\text{-}L^1\}_2]^{2+}$ and *M*-$[Ag_2\{(1R,\ 1R)\text{-}L^2\}_2]^{2+}$ structures. Molecular modelling gave equivocal results and we have determined the X-ray structure of $[Ag_2\{(1S,\ 1S)\text{-}L^1\}_2]$-$[PF_6]_2$.§

Initial attempts to determine the structure revealed a very large unit cell [U = 49 245(9) Å^3] and the structure was only solved using data from an area detector. The structure of the cation present in $[Ag_2\{(1S,\ 1S)\text{-}L^1\}_2][PF_6]_2$ is presented in Fig. 2(*a*). The double-helical geometry is confirmed and the double helix is revealed unambiguously to possess a *P* conformation [most easily seen in the space-filling representation in Fig. 2(*b*)]. The Ag–N distances [2.245(6), 2.343(6) Å] are unremarkable and closely resemble those in the parent 2,2′:6′,2″ : 6″,2‴-quaterpyridine complex (2.223–2.409 Å).[6,7] The Ag···Ag distance within the cation of 3.230(2) Å is slightly longer than observed in the parent 2,2′ : 6′,2″ : 6″,2‴-quaterpyr-



Scheme 1

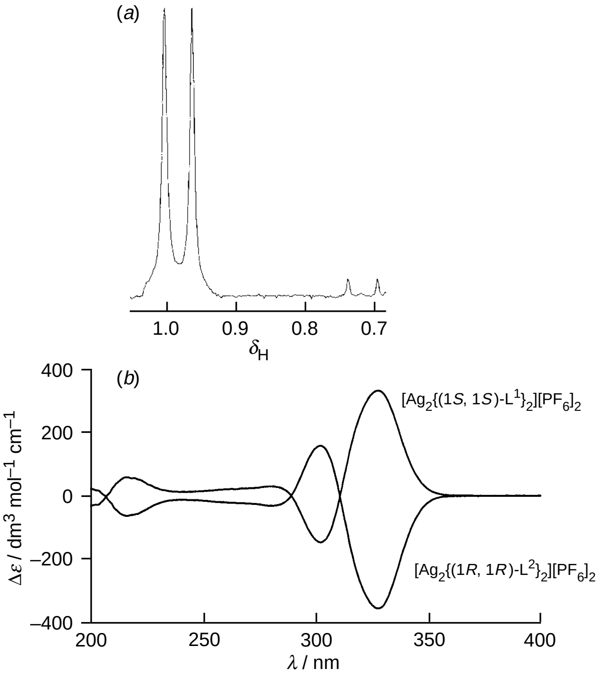


Fig. 1 (*a*) Part of the ^{1}H NMR spectrum of a CD_3CN solution showing H^{7PB} of the crude product $[Ag_2\{(1R,\ 1R)\text{-}L^2\}_2][PF_6]_2$ showing the 95% de of one of the two diastereomers and (*b*) the CD spectra of the diastereomerically pure products obtained from the recrystallisation of $[Ag_2\{(1S,\ 1S)\text{-}L^1\}_2][PF_6]_2$ and $[Ag_2\{(1R,\ 1R)\text{-}L^2\}_2][PF_6]_2$

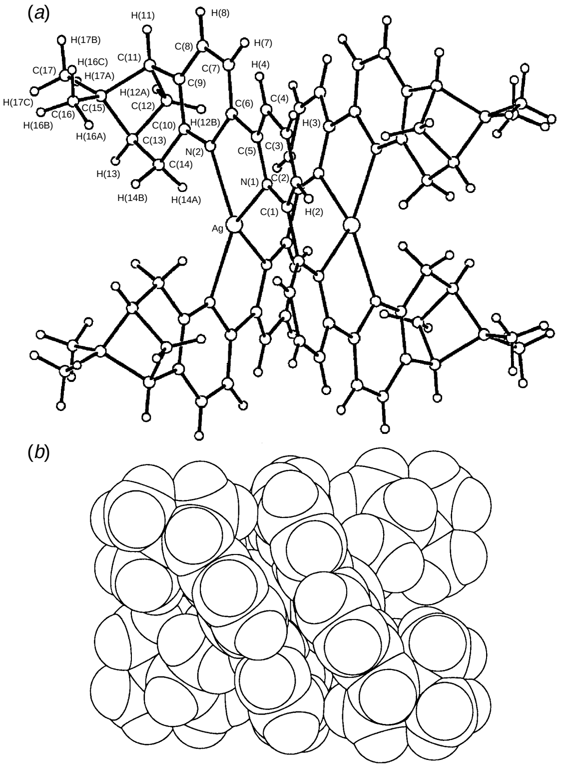


Fig. 2 Crystal and molecular structures of (*a*) the double-helical cation with *P* chirality in the lattice of *P*-$[Ag_2\{(1S,\ 1S)\text{-}\mathbf{1}\}_2][PF_6]_2$ showing the numbering scheme and adopted and (*b*) a space-filling representation of the same cation

idine complex [3.107(2) Å][6,7] which presumably represents the repulsion between the fused chiral substituents. The principal twisting within the ligand occurs between the two central rings (41.4°) although a significant twist of 17.4° occurs between the outer rings (*cf.* 45–47 and 13.0–13.5° in the 2,2′ : 6′,2″ : 6″,2‴-quaterpyridine complex).[6,7] Interestingly, the (*S*,*S*,*S*,*S*)-*P* and (*R*,*R*,*R*,*R*)-*M* preference that is shown is opposite to the (*S*,*S*)-*M* and (*R*,*R*)-*P* preferences shown with monofunctionalised 2,2′:6′,2″-terpyridines.

In conclusion, we have demonstrated that 2,2′ : 6′,2″ : 6″,2‴-quaterpyridines bearing two fused chiral substituents give high diastereomeric excesses of *P* or *M* helicates upon reaction with silver(I). We are currently probing the origin of the diastereoselectivity and attempting to increase the selectivity further.

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Footnotes and References

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† *Selected data* for **1** and **2**: mp. > 250 °C. MS (MALDI TOF): *m*/*z* 499 (M^+). IR (KBr): ν/cm^{-1} 2919, 1563, 1431, 1421, 807. $[\alpha]^D_{21}$ +66.8° (**1**), −63.0° (**2**). ^{1}H NMR ($CDCl_3$): δ 0.69 (3 H, s, H^{6PA}), 1.33 (2 H, d, *J* 9.3 Hz, H^{7PB}), 1.43 (3 H, s, H^{6PB}), 2.41 (2 H, m, H^{5P}), 2.72 (2 H, m, H^{7PA}), 2.83 (2 H, t, *J* 5.9, 5.4 Hz, H^{1P}), 3.21 (4 H, d, *J* 2.4 Hz, H^{4P}), 7.38 (2 H, d, *J* 7.8 Hz, H^4), 8.42 (2 H, dd, *J* 7.8, 1.0 Hz, $H^{3'}$), 7.94 (2 H, t, *J* 7.8 Hz, $H^{4'}$), 8.31 (2 H, 2, *J* 7.8 Hz, H^3), 8.62 (2 H, dd, *J* 7.8, 1.0 Hz, $H^{5'}$):^{13}C NMR ($CDCl_3$): δ 21.35, 26.09, 31.98, 36.74, 39.58, 40.29, 46.54, 117.97, 120.40, 120.64, 133.75, 137.61, 142.27, 153.71, 155.46, 155.88, 156.35.

‡ *Selected spectroscopic data* for the major diastereomer of $[Ag_2L^1{}_2][PF_6]_2$ or $[Ag_2L^2{}_2][PF_6]_2$: mp. > 250 °C, MALDI TOF mass spectrum: *m*/*z* 1358 ($M^+ - PF_6$), 1105 ($[AgL^2]^+$), 606 ($[AgL]^+$), 499 (L^+). IR (KBr): ν/cm^{-1} 2926, 1564, 1432, 1422, 833, 560. $[\alpha]^D_{21}$ +1128.3° (**1**), −1132.4° (**2**). ^{1}H NMR ($CDCl_3$): δ 0.36 (3 H, s, H^{6PA}), 0.98 (2 H, d, *J* 9.8 Hz, H^{7PB}), 1.30 (3 H, s, H^{6PB}), 1.65 (2 H, dd, *J* 2.9, 17.6 Hz, H^{4PB}), 1.94 (2 H, m, H^{5P}), 2.63 (2 H, dd, *J* 2.0, 17.6 Hz, H^{4PA}), 2.66 (2 H, m, H^{7PA}), 2.85 (2 H, t, *J* 5.9, 5.4 Hz, H^{1P}), 7.47 (2 H, d, *J* 7.8 Hz, H^4), 7.7 (2 H, d, *J* 7.3, 1.0 Hz, $H^{3'}$), 7.96 (2 H, t, *J* 7.8 Hz, $H^{4'}$), 7.66 (2 H, 2, *J* 7.8 Hz, H^3), 8.06 (2 H, d, *J* 7.4 Hz, $H^{5'}$).

§ *Crystal data* for $[Ag_2L^1{}_2][PF_6]_2\cdot 0.33H_2O$: colourless crystal, $C_{68}H_{62}Ag_2F_{12}N_8O_{0.33}P_2$, M = 1502.27, cubic, space group $F432$, a = 36.654(4) Å, U = 49 245 (9) Å^3, Z = 24, D_c = 1.216 g cm^{-3}, $F(000)$ = 18 256, λ = 0.71073 Å, μ(Mo-Kα) 0.582 mm^{-1}. Intensity data were collected on a Stoe IPDS diffractometer (1.84 < θ < 125.10°) at 200 K; of 40 542 reflections measured, 3672 independent reflections were used in the structure solution. The structure was solved by direct methods using SHELXS-86[11] and refined using SHELXL-93[12] to give final R and wR_2 values of 0.0713 and 0.2169 for 2577 observed reflections with $I \geqslant 2\sigma(I)$ respectively (all data values: R 0.0956 and wR_2 0.2403). The absolute structure parameter was 0.01(9). CCDC 182/582.

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