A metallo-supramolecular double-helix containing a major and a minor groove

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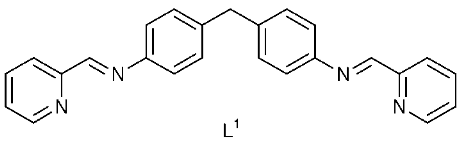
Received (in Basel, Switzerland) 19th July 1999, Accepted 8th September 1999

Control of the microarchitecture in a metallo-supramolecular double-helical array results from inter-strand edge–face π-stacking interactions which pull the ligand strands together thereby creating two distinct helical grooves (major and minor).

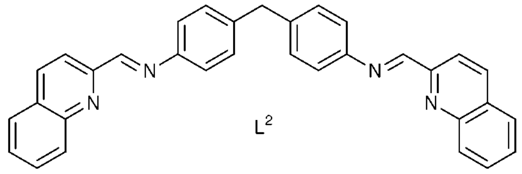
Double-helical molecular architectures retain a unique fascination because life itself is encoded within double-helical DNA arrays. The assembly of synthetic double-helical architectures through metallo-supramolecular design has been an area of intense activity and the construction principles necessary to assemble a double-helix are now fairly well established.[1] However challenges in defining the precise topography or conformation of the helical superstructure remain. To this end, we have recently illustrated how careful selection of the spacer group used to separate the metal-binding domains can be used to control the directionality of ligand strands within a helix.[2] We wish now to report a system, based on our inexpensive and readily-prepared imine ligands,[2,3] in which π-stacking interactions between the spacer groups control the microarchitecture of the helix and give rise to a double-helix containing major and minor grooves reminiscent of B-DNA.

The two distinct grooves in B-DNA arise from the positions through which the sugar–phosphate backbones are connected to the purine and pyrimidine bases; the two strands are not arranged along the vector of the cohesive forces (hydrogen bonds) which hold the helix together but both displaced to one side. This contrasts with the situation found in most synthetic metallo-helicates. The metal binding units usually form an integral part of the ligand backbone.[1] The inherent coordination preferences of the metal ions used in the assembly process (most commonly octahedral or tetrahedral) position these binding units (and hence the ligand strands) symmetrically on opposite sides of the helix. This leads to two equivalent grooves. Achieving distinct grooves within metallo-helicate architectures of this type would therefore appear to require ligand strands that are predisposed to associate on one side of the helical axis.

We have recently described triple-helical complexes formed from the reaction of ligand L^1 with octahedral metal ions.[3] In these triple-helical architectures, inter-strand face–edge π-stacking interactions (aromatic C–H···π)[4] are observed between the phenylene rings of the diarylmethane spacer-groups. Such secondary inter-strand interactions might provide a suitable tool for controlling the spatial orientation of ligand strands in a double-helicate superstructure and we have therefore examined the effect of interacting ligands of this type with tetrahedral metal ions.



L^1



L^2

Ligand L^2 is prepared in 93% yield by mixing ethanolic solutions containing 2 equivalents of 2-quinolinecarbaldehyde and 1 equivalent of 4,4′-methylenedianiline. Reaction of L^2 with silver(I) acetate in methanol yields a pale-yellow solution from which a yellow solid is obtained on treatment with $[NH_4][PF_6]$.[5] Mass spectrometry (FAB and ESI) is consistent with the formation of a dimeric species of formula $[Ag_2(L^1)_2][PF_6]_2$. Recrystallisation of the compound from acetonitrile by benzene diffusion afforded X-ray quality crystals and we have determined the X-ray crystal structure to examine the molecular conformation.[6]

The structure reveals a dimeric $[Ag_2(L^2)_2]^{2+}$ cation (Fig. 1). Each silver(I) centre occupies a four-coordinate pseudo-

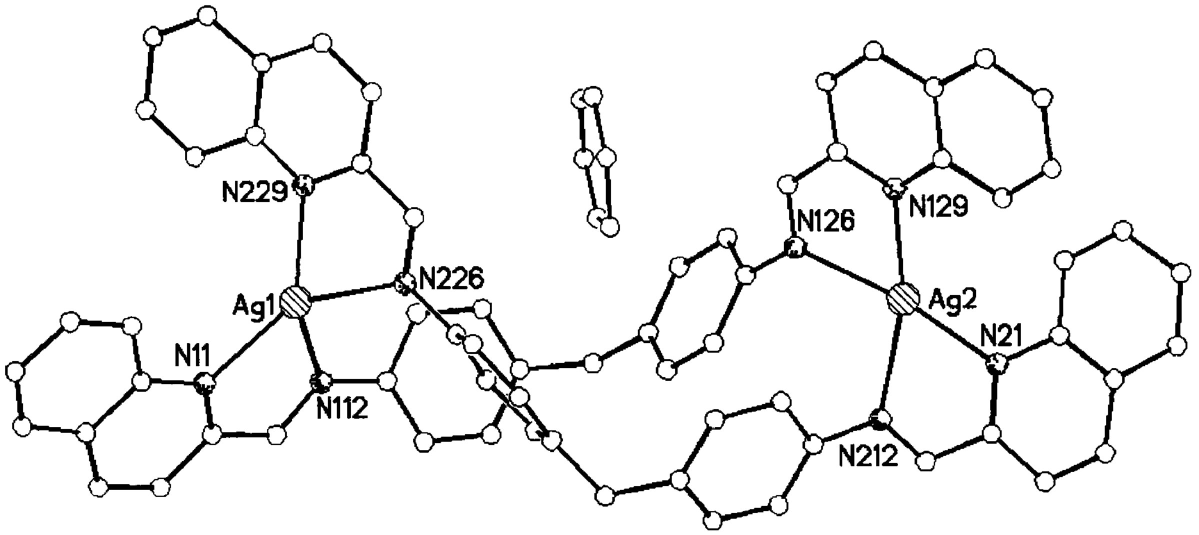


Fig. 1 View of the cation $[Ag_2(L^2)_2]^{2+}$.

tetrahedral environment bound to two pyridylimine units, one from each ligand. The two ligands wrap around the metal–metal axis giving rise to a double-helical structure, both enantiomers of which are observed. The phenyl rings of the diarylmethane spacer, which separates the metal binding units, are face–edge π-stacked[4] with those on the adjacent ligand strand (centroid–centroid: 5.1 and 5.2Å). To achieve this the two ligand strands are pulled together on one side of the helical axis and this leads inevitably to the presence of two distinct grooves (major and minor). The solid state structure reveals a benzene solvent molecule located in the larger (major) groove, however no specific interactions (face–face or face–edge π–π) are identifiable between this benzene and the walls of the groove.

While the solid state structure reveals this sophisticated helical microarchitecture, the solution behaviour is more complicated.[5] Electrospray mass spectrometry reveals the presence only of dinuclear $\{M_2L_2\}$ species. There are two possible basic configurations for such a species. The two ligand strands may either wrap around the metal–metal axis (*rac*-isomer) giving rise to a double-helix or one may pass above the metal–metal axis while the other passes beneath (*meso*-isomer) giving a non-helical metallo-cyclophane.[2,7] The room temperature ^{1}H NMR spectrum of an acetonitrile solution of the silver(I) complex reveals a single set of proton resonances. However on cooling (233 K, 400 MHz) the resonances broaden, indicating some form of fluxional behaviour. The spectrum in dichloromethane solution is broadened at room temperature, and at low temperature (193 K, 400 MHz) reveals two discrete solution species. The (non-diastereotopic) CH_2 protons permit assignment of these species. For the *rac*- (helical) isomer the protons are equivalent and a single resonance is observed while in the *meso*-isomer the structure of the metallo-macrocycle renders them inequivalent and two doublets result. The equilibrium between these species is temperature dependent with the percentage of helical isomer present increasing with decreasing temperature, indicating that this isomer is favoured enthalpically.[8] Two phenyl resonances are observed for the helix; four would be expected in a frozen-out π-stacked configuration. In view of the weak nature of π-stacking interactions it is perhaps unsurprising that this is not observed and it is unclear whether in solution the helical isomer does contain two distinct grooves or whether it has relaxed into a more conventional double-helicate structure with equivalent grooves. The absence of significant upfield shifts for either of the phenyl resonances might support the latter.

We have shown that secondary interactions between the spacer units may be used to control the superstructure of a helical array in the solid state. We are currently extending our studies to examine further routes for controlling the precise microarchitecture of supramolecular arrays.

We are grateful to the Nuffield Foundation (Awards to newly appointed science lecturers, M. J. H.) and the EPSRC (C. L. P.) for support, the EPSRC and Siemens Analytical Instruments for grants in support of the diffractometer and the Swansea National Mass Spectrometry Centre for recording the mass spectra.

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4 For examples of such interactions, see E.-I. Kim, S. Paliwal and C. S. Wilcox, *J. Am. Chem. Soc.*, 1998, **120**, 11192; Y. Umezawa, S. Tsuboyama, K. Honda, J. Uzawa and M. Nishio, *Bull. Chem. Soc. Jpn.*, 1998, **71**, 1207; M. Nishio, Y. Umezawa, M. Hirota and Y. Takeuchi, *Tetrahedron*, 1995, **51**, 8665; C. A. Hunter, *Chem. Soc. Rev.*, 1994, **23**, 101 and references therein.

5 *Selected data* for $[Ag_2(L^2)_2][PF_6]_2$: MS (FAB): *m/z* 585 $\{Ag(L^2)\}$, 1061 $\{Ag(L^2)_2\}$, 1168 $\{Ag_2(L^2)_2\}$, 1313 $\{Ag_2(L^2)_2(PF_6)\}$. MS (ESI): *m/z* 584 $\{Ag_2(L^2)_2\}^{2+}$, 1313 $\{Ag_2(L^2)_2(PF_6)\}^+$ (Found: C, 52.7; H, 3.3; N, 7.5. Calc. for $Ag_2C_{66}H_{48}N_8P_2F_{12}\cdot 2H_2O$: C, 53.0; H, 3.5; N, 7.5%). ^{1}H NMR (CD_3CN, 250 MHz, 298 K): δ 9.31 (2H, s, H^i), 8.78 (2H, d, J 8.1 Hz, $H^{3/4}$), 8.18 (2H, d, J 8.1 Hz, $H^{3/4}$), 8.13 (2H, d, J 8.0 Hz, $H^{5/8}$), 8.00 (2H, d, J 8.1 Hz, $H^{5/8}$), 7.70 (4H, m, $H^{6,7}$), 7.51 (4H, d, J 8.4 Hz, Ph), 7.23 (4H, d, J 8.4 Hz, Ph), 3.89 (2H, s, CH_2).

^{1}H NMR (CD_2Cl_2, 400 MHz, 183 K): δ 9.30 (3H, d, J 6.4 Hz, H^i *rac*), 9.24 (2H, d, J 6.9 Hz, H^i *meso*), 8.72 (5H, m, $H^{3/4}$ *rac* + *meso*), 8.14 (5H, m, $H^{3/4}$ *rac* + *meso*), 8.06 (5H, m, $H^{5/8}$ *rac* + *meso*), 7.94 (2H, d, J 8.0 Hz, $H^{5/8}$ *meso*), 7.90 (3H, d, J 8.0 Hz, $H^{5/8}$ *rac*), 7.65 (10H, m, $H^{6,7}$ *rac* + *meso*), 7.55 (3H, d, J 8.4 Hz, Ph *rac*), 7.43 (2H, d, J 8.4 Hz, Ph *meso*), 7.29 (3H, d, J 8.4 Hz, Ph *rac*), 7.13 (2H, d, J 8.4 Hz, Ph *meso*), 3.80 (3H, s, CH_2 *rac*), 3.86 (1H, d, J 9.8 Hz, CH_2 *meso*), 3.75 (1H, d, J 9.8 Hz, CH_2 *meso*).

6 *Crystal data* for $C_{45.5}H_{36.75}AgF_6N_{4.25}P$: M = 895.88, triclinic, space group $P\bar{1}$, a = 13.351(3), b = 15.931(3), c = 20.478(3) Å , α = 86.741(5), β = 83.700(5), γ = 73.329(5)°, U = 4145.8(14) Å^3 (by least squares refinement on 5622 reflection positions), Z = 4, μ(Mo-Kα) = 0.589 mm^{-1}, 16667 reflections measured on a Bruker AXS SMART system, 10674 unique (R_{int} = 0.0539). T = 180(2) K. Absorption correction by Ψ-scans; minimum and maximum transmission factors: 0.73; 0.93. The lattice contains three fully occupied (as shown by test refinement) but highly mobile benzene molecules and one acetonitrile molecule (50% occupancy). Goodness-of-fit was 0.997, $R1$[for 5837 reflections with $I > 2\sigma(I)$] = 0.0744, $wR2$ = 0.2093. Refinement used SHELXTL (G. M. Sheldrick, 1997). CCDC 182/1403. See http://www.rsc.org/suppdata/cc/1999/2023/ for crystallographic files in .cif format.

7 Such *meso*- and *rac*-systems have also been observed by other workers. See, for example: A. Bilyk, M. M. Harding, P. Turner and T. W. Hambley, *J. Chem. Soc., Dalton Trans.*, 1994, 2783; C. O. Dietrich-Buchecker, J. F. Nierengarten, J. P. Sauvage, N. Armaroli, V. Balzani and L. DeCola, *J. Am. Chem. Soc.*, 1993, **115**, 11237.

8 The temperature range over which the resonances of the two isomers are distinct is insufficient for accurate determination of thermodynamic parameters. Simple modelling reveals that the box conformation cannot accommodate inter-strand π-stacking interactions. If maintained in solution, the face–edge π-stacking interactions may contribute to the enthalpic preference for the helix and the concomitant restrictions on the free rotation of the phenyl rings in the helix might contribute to the entropic preference for the *meso*-isomer.

Communication 9/05795A