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Dinuclear double helicates with a twist: synthesis, structure and supramolecular entanglement in [M_2L_2] metallo-helices {M = Co(II), Cu(II), H_2L = bis(*N*-salicylidene-4,4′-diaminodiphenyl)methane}†

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Self-assembly of the tetradentate ligand bis(*N*-salicylidene-4,4′-diaminodiphenyl)methane, (H_2L), around Co(II) and Cu(II) gives rise to the dinuclear double helicates [Co_2L_2]·1.7CH_2Cl_2·0.6H_2O, (**1**) and [Cu_2L_2]·CH_2Cl_2 (**2**), which have been characterised by a single crystal X-ray diffraction study. Complexes **1** and **2** are structurally similar with two four coordinate metal centres in slightly distorted tetrahedral geometries in **1** and severely distorted tetrahedral geometry in **2**. The different geometric preferences of Co(II) (tetrahedral) and Cu(II) (square planar) contort the ligands such that extended planarity is absent in **1** whilst present in **2**. This distortion results in a tighter helical twist in **1** compared with **2**, which consequently has a larger metal–metal separation. Complexes **1** and **2** each exhibit three-dimensional supramolecular entanglement brought about by elaborate inter-molecular $\pi\cdots\pi$ (face-to-face) and C–H$\cdots\pi$ interactions.

It is well established that self-assembly processes may generate well-defined architectures in a spontaneous and directed manner.[1] This requires ligands to be tailored for the recognition of the intrinsic stereochemical properties of a particular metal ion. Control over ligand properties such as donor density, type and number as well as the spacer group separating coordination sites has led to a wide variety of resultant structural motifs such as grids,[2] boxes,[3] cylinders[4] and helicates.[5] The helicate architecture is one of the most investigated and therefore best understood of these edifices.[5–7] Nevertheless, predicting the outcome of self-assembly processes is difficult and dependent upon numerous factors, such as the nature of the coordination site, the structure of the bridging ligand, the metal's geometric preferences and weaker non-covalent interactions, which all influence the resultant architecture.[1] In addition, until recently the ligands employed in helicate synthesis have been dominated by benzimidazole[6] or polypyridyl[7] types and this usually necessitates exhaustive multi-step synthetic routes to construct the ligands. This time-consuming approach has been a major limiting factor in the search for improved structural control. Recently, a move toward the employment of more synthetically amenable Schiff's-base ligand types has occurred and this has increased knowledge of the self-assembly process greatly.[8–11] Within these studies it has been proposed that weak *intra-molecular* (inter-strand) face-to-face and edge-to-face $\pi\cdots\pi$ interactions between the aromatic rings of these ligands gives rise to helicate formation and the resultant solid-state structures.[9–11] Herein we report the synthesis and structural characterisation of Co(II) and Cu(II) dinuclear double helicates with the *N*,*O*-bis-bidentate Schiff's-base ligand, bis(*N*-salicylidene-4,4′-diaminodiphenyl)methane (H_2L), and compare and contrast our findings with those recently reported by Yoshida,[9] Hannon,[10] and Chun-ying[11] who employed the related ligand sets, H_2L^1, L^2 and L^4, and L^3, respectively, Fig. 1.

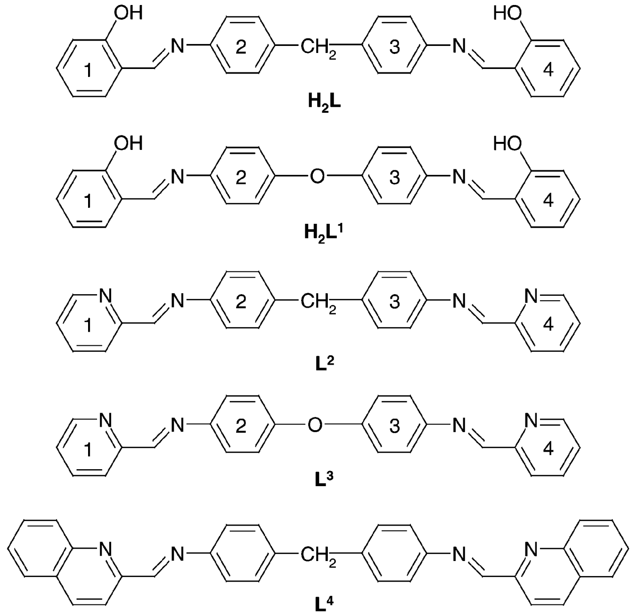

Fig. 1 Structures of the ligand employed in the current study H_2L, and those of related ligand sets H_2L^1, L^2, L^3 and L^4. Numbering scheme used to denote the aromatic rings of the ligands (see text).

Counter to previous assertions relating to these ligand types, we propose here that *intermolecular* interactions between the ligands are of more importance in determining the nature and the solid-state architectures of these helicate types.

Experimental

Materials and methods

^{1}H NMR spectra were recorded on a Bruker Avance DPX 400 FT spectrometer using TMS as an internal standard. Electrospray mass spectra were carried out on a Shimadzu Micromass

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† Electronic supplementary information (ESI) available: selected distances and angles for $\pi\cdots\pi$ and CH$\cdots\pi$ interactions in **1** and **2**. See http://www.rsc.org/suppdata/dt/b1/b102028p/

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LCT. Starting materials were purchased from Aldrich. Chemical analyses: C,H,N were performed at the Chemistry Department, Open University, Milton Keynes, UK. All solvents were of reagent grade and used without further purification.

Synthesis of bis(*N*-salicylidene-4,4′-diaminodiphenyl)methane, H_2L

H_2L was prepared as described elsewhere.[9a] Found: C, 79.6; H, 5.0; N, 6.9%. $C_{27}H_{22}N_2O_2$ requires C, 79.8; H, 5.46; N, 6.9%. ν_{max}/cm^{-1} (KBr) 1617s (C=N), 1595, 1563 (ArOH); δ_H (400 MHz; $CDCl_3$): 13.28 (bs, 2H, OH) 8.65 (s, 2H, imine), 7.41 (m, 4H), 7.26 (m, 8H), 7.04 (d, 2H), 6.96 (t, 2H), 4.07 (s, 2H, CH_2). MS (ESI): *m*/*z* 407 $[H_2L]^+$.

Synthesis of 1 and 2

Complexes **1** and **2** were synthesised in similar fashion employing either cobalt(II) acetate tetrahydrate in **1** and copper(II) acetate monohydrate in **2**. The following preparation of **1** is representative.

A methanolic solution of cobalt(II) acetate tetrahydrate (0.25 g, 1 mmol) was added with stirring to a dichloromethane solution of H_2L (0.4 g, 1 mmol). An orange colour developed immediately, the solution was filtered and allowed to evaporate slowly in air. Deep red crystals of **1** (dark brown-black for **2**) suitable for single crystal X-ray diffraction were isolated directly from solution after a few days. As the crystals slowly deteriorated on standing, presumably due to loss of solvent, samples for microanalyses were first dried *in vacuo.*

$[Co_2L_2]$ (1). Yield 80%. Found: C, 69.8; H, 4.0; N, 5.9%. $Co_2C_{54}H_{40}N_4O_4$ requires: C, 69.98; H, 4.35; N, 6.05%. ν_{max}/cm^{-1} (Nujol) 1600s, 1579vs, 1529s, 1504s, 1350sh, 1300m, 1160m, 1147s, 1120sh, 995w, 750m and 700m. μ_{eff} (293 K) = 4.59 μ_B per Co. MS (ESI): *m*/*z* 927 $[Co_2L_2]^+$, 464 $[Co_2L_2]^{2+}$.

$[Cu_2L_2]$ (2). Yield 76%. Found: C, 69.1; H, 4.1; N, 5.9%. $Cu_2C_{54}H_{40}N_4O_4$ requires: C, 69.29; H, 4.31; N, 5.99%. ν_{max}/cm^{-1} (Nujol) 1603s, 1587vs, 1531s, 1504s, 1355sh, 1310m, 1160m, 1145s, 1123sh, 995w, 755m and 705m. μ_{eff} (293 K) = 1.83 μ_B per Cu. MS (ESI): *m*/*z* 937 $[Cu_2L_2]^+$, 469 $[Cu_2L_2]^{2+}$.

Crystallographic measurements on 1 and 2

Crystal data and experimental details are summarised in Table 1. Data for **1** were collected on a Bruker SMART diffractometer with graphite monochromated Mo-Kα radiation and Lorentz and polarisation corrections were applied. An empirical absorption correction was applied using SADABS.[12] Data for **2** were collected using a Siemens P4 four circle diffractometer with graphite monochromated Mo-Kα radiation and Lorentz and polarisation corrections were applied. An empirical absorption correction was applied using ψ scans. The XSCANS[13] and SHELXTLPC[14] packages were used for data collection, reduction, structure solution and refinement.

CCDC reference numbers 152492 and 152493.

See http://www.rsc.org/suppdata/dt/b1/b102028p/ for crystallographic data in CIF or other electronic format.

Results and discussion

Synthesis and characterisation

The bis-bidentate ligand H_2L was synthesised by the standard Schiff's-base condensation in ethanol of two equivalents of salicylaldehyde with one equivalent of 4,4′-diaminodiphenylmethane following reported procedures.[9a] Treatment of a CH_2Cl_2–MeOH solution (10:1) of H_2L with an equivalent of either $Co(OAc)_2 \cdot 4H_2O$ or $Cu(OAc)_2 \cdot H_2O$ gave, upon slow evaporation, crystalline samples whose microanalyses were consistent with the formation of $[M_nL_n]$ species. The IR spectrum of H_2L displays a sharp peak characteristic of the C=N bond at 1617 cm^{-1}, which upon complexation of Co(II) or Cu(II) shifts to lower frequency (*ca.* 1585 cm^{-1}), and is consistent with coordination to the imino nitrogen. ESMS on CH_2Cl_2 solutions of **1** and **2** found predominant peaks centred at *m*/*z* 927 and 937 respectively, which are consistent with the presence of $[M_2L_2]^+$ in solution and the existence of either an achiral molecular box or a dinuclear double helix. The room temperature magnetic moments of **1** and **2** are 4.59 μ_B and 1.83 μ_B, respectively. The magnitude of the moment in **1** is characteristic of a tetrahedrally disposed Co(II) ion in which the $^4A_2$ ground state has acquired some orbital angular momentum through mixing in of the excited $^4T_2$ state by spin–orbit coupling, and that for **2** is consistent with that expected for a Cu(II) ion in a distorted tetrahedral field.[15]

Table 1 Crystallographic details for **1** and **2**

	1·1.7CH$_2$Cl$_2$·0.6H$_2$O	**2**·2CH$_2$Cl$_2$
Chemical formula	$C_{55.7}H_{43.6}Cl_{3.4}Co_2$-$N_4O_{4.6}$	$C_{56}H_{44}Cl_4Cu_2N_4O_4$
Formula weight	1080.73	1105.83
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1/c$	$C2/c$
μ(Mo-Kα)/cm^{-1}	9.36	11.73
a/Å	17.9545(9)	16.695(3)
b/Å	15.5789(8)	14.676(3)
c/Å	18.3432(9)	19.573(4)
β/°	109.913(1)	97.14(2)
V/Å^3	4824.0(4)	4759(2)
Z	4	4
T/K	153(2)	153(2)
R_{int}	0.1296	0.0000
R, $wR2$ [$I > 2\sigma(I)$]	0.0512, 0.1257	0.0712, 0.1151
R, $wR2$ (all data)	0.0982, 0.1559	0.1612, 0.1499
Reflections: collected/independent	92148/8536	2031/1103

Table 2 Selected bond lengths (Å) and angles (°) for **1**

Co1–O1B	1.898(3)	Co1–O1A	1.901(3)
Co1–N8A	1.990(3)	Co1–N8B	1.999(3)
Co2–O29A	1.899(3)	Co2–O29B	1.909(3)
Co2–N22B	1.998(3)	Co2–N22A	2.007(3)
O1B–Co1–O1A	119.5(1)	O1B–Co1–N8A	118.2(1)
O1A–Co1–N8A	95.0(1)	O1B–Co1–N8B	95.3(1)
O1A–Co1–N8B	123.0(1)	N8A–Co1–N8B	106.9(1)
O29A–Co2–O29B	109.7(1)	O29A–Co2–N22B	128.4(1)
O29B–Co2–N22B	94.6(1)	O29A–Co2–N22A	94.3(1)
O29B–Co2–N22A	128.5(1)	N22B–Co2–N22A	105.2(1)

Crystal structure of 1

The atomic numbering scheme and atom connectivity for **1** is shown in Fig. 2(a). The asymmetric unit of **1** contains two unique Co atoms, two ligands and disordered solvent that has been modelled as a mixture of CH_2Cl_2 and H_2O. The Co atoms have distorted tetrahedral coordination environments with a Co ··· Co separation of 11.58 Å, Table 2. The dihedral angles for the two coordination chromophores are 83.4° and 72.6° for Co(1) and Co(2), respectively. Dihedral angles of 0° and 90° would be expected for planar and pseudo-tetrahedral geometries, respectively. The ligands wrap around the metal centres such that a helical structure is formed with a twist defined by the torsion angles Co1–N8A–N22A–Co2 and Co1–N8B–N22B–Co2 of 145.6° and 139.7°, respectively. The difference in torsion angle for the two ligands A and B is probably a consequence of the different intra-and inter-molecular interactions experienced by each ligand. This also gives the helical structure a major and minor groove,[10c] as exemplified by the distance C5A–C25B (10.05 Å) being *ca.* 4 Å shorter than C5B–C25A (14.12 Å). We also note close intramolecular (inter-strand)

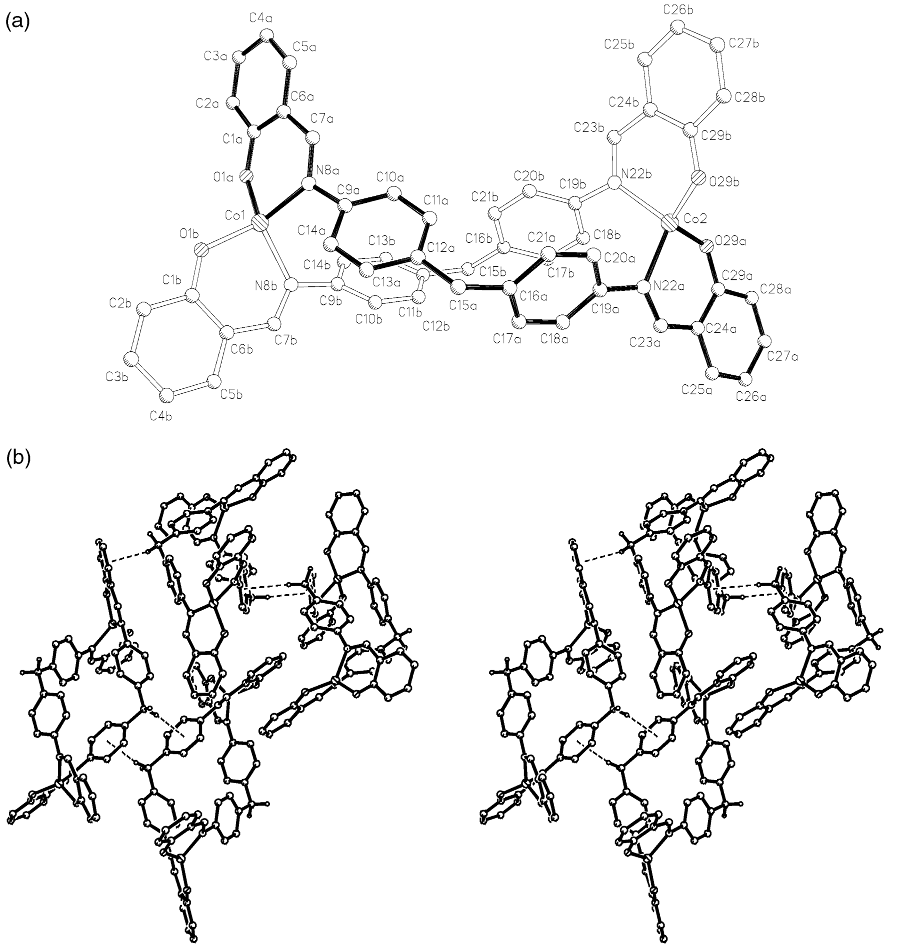

Fig. 2 (a) Molecular structure and atomic numbering scheme of **1**. Solid bonds (ligand A) and hollow bonds (ligand B). H-atoms and solvent molecules of crystallisation removed for clarity. (b) Stereo illustration showing intermolecular interactions in **1**.

contacts between the aromatic rings 2A and 2B and the 3A and 3B rings of 3.5–3.9 Å, although they are not strictly co-planar (mean plane angles of 24.1° and 25.2° between 2A and 2B rings, and 3A and 3B rings, respectively). These interactions are probably a consequence of the constraints imposed upon the ligands on coordination to the cobalt centres. Furthermore, it is also noteworthy that rings 1 and 2 (3 and 4), are not co-planar with each other: angles between the mean planes for 1 and 2 are 50.8° and 43.2° for ligand strands A and B, respectively (angles between mean planes for 3 and 4 are 52.1° and 52.0° for ligand strands A and B, respectively). This ligand distortion probably derives from the steric constraints imposed by the tetrahedrally disposed Co(II) centres.

The helical complexes pack together through a combination of several intermolecular interactions, (see electronic supplementary information).† Firstly, face-to-face $\pi\cdots\pi$ (3.5–3.8 Å) interactions occur between aromatic rings 1A and 4B of an adjacent molecule. Secondly, C–H$\pi\cdots\pi$ (3.7–3.9 Å) interactions occur between the C15A methylene proton (H15A) *via* a self-complementary C-H$\cdots\pi$ interaction with aromatic ring 3 from an adjacent molecule, Fig. 2(b). Similarly, the C15B methylene proton (H15C) is involved in an intermolecular C–H$\cdots\pi$ interaction with an adjacent ring 1. These interactions combine to form an entangled three-dimensional supramolecular network. This arrangement creates cavities within the lattice in which the disordered solvent molecules are located.

Crystal structure of 2

The atomic numbering scheme and atom connectivity for **2** is shown in Fig. 3(a). The asymmetric unit of **2** contains one Cu

Table 3 Selected bond lengths (Å) and angles (°) for **2**

Cu1–O29A	1.880(9)	Cu1–N8	1.96(1)
Cu1–O1	1.902(8)	Cu1–N22A	1.97(1)
O29–Cu1–O1A	94.1(4)	O29–Cu1–N8A	144.6(3)
O1–Cu1–N8	92.7(4)	O29A–Cu1–N22A	94.6(4)
O1–Cu1–N22A	145.6(3)	N8–Cu1–N22A	99.2(5)

Symmetry code: A = $-x, y, -z - 0.5$.

atom, one ligand and a CH_2Cl_2 solvent molecule. The Cu$\cdots$Cu separation is 11.87 Å and the ligands wrap around the two copper centres forming a double helix with a helical twist of 159.2°, as defined by the Cu1–N8–N22–Cu1A dihedral angle. This is a significantly larger twist than in **1** and is probably a consequence of a large distortion about the copper centre, Table 3. The dihedral angle for the coordination chromophore about Cu(1) is 48.3°. As in **1**, there are a large number of intra- and inter-molecular face-to-face $\pi\cdots\pi$ (3.5–3.8 Å) and edge-to-face C–H$\cdots\pi$ (3.7–3.9 Å) interactions between the aromatic rings, (see electronic supplementary information).† However, the intramolecular (inter-strand) interactions are probably a consequence of coordination to the copper centre and its distortion. This distortion promotes a more coplanar orientation of ring 1 with ring 2 within the same ligand strand (angle between mean planes is 14.2°), whilst that between rings 3 and 4 is quite removed from planarity at 46.6°. The co-planarity between ring 1 and ring 2 results in an extended intermolecular $\pi\cdots\pi$ interaction which is reinforced by C–H$\cdots\pi$ interactions between the methylene bridge to ring 1 of an adjacent molecule and forms an extended methylene C–H$\cdots\pi/\pi\cdots\pi$ chain,

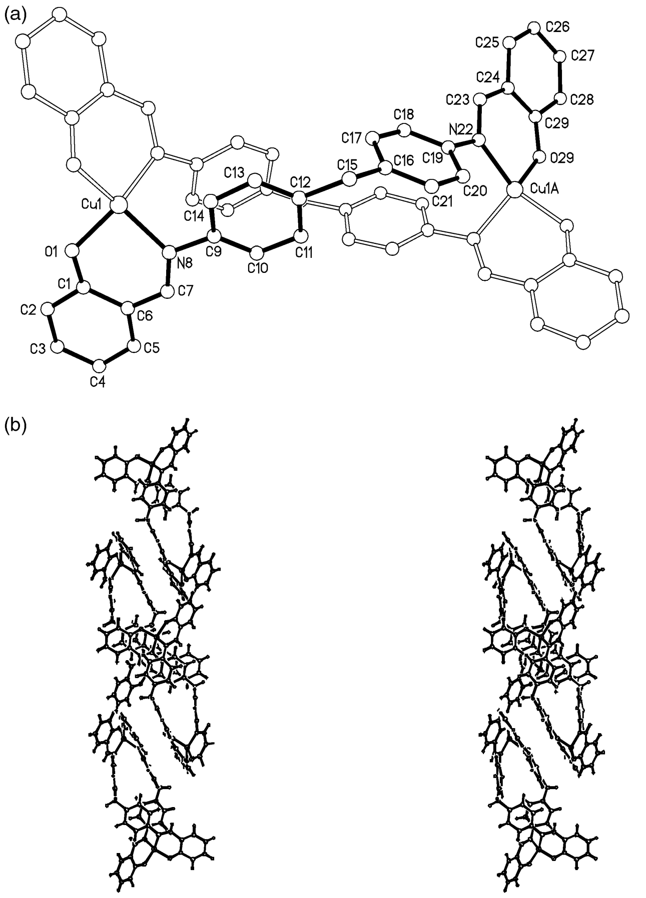

Fig. 3 (a) Molecular structure and atomic numbering scheme of **2**. H-atoms and solvent molecules of crystallisation removed for clarity. (b) Stereo illustration showing intermolecular interactions in **2**.

Fig. 3(b). The chains form a three dimensional network *via* edge-to-face C–H $\cdots\pi$ interactions. The combination of these interactions creates cavities into which the CH_2Cl_2 solvent molecules are incorporated.

Discussion

The rigid nature of H_2L predisposes it to coordinate to two metals and conceptually to form either a coordination polymer, an achiral molecular box or, as in the present case, a chiral helix. It is clear therefore that if a helicate is to form, a compromise must be made between the geometrical preference of the metal and the conformational preference of the ligand.[5] In this respect, the structure of **1** probably represents a better match between both the metal and ligand coordination preferences. In **2** however, juxtaposition between the metal and ligand preferences results in a severe distortion about the metal centre toward tetrahedral geometry. An obvious further consequence of these distortions and subsequent metal geometries is the disparate nature of both the intra- and inter-molecular interactions ($\pi\cdots\pi$, CH $\cdots\pi$) experienced by **1** and **2**.

These structural observations are broadly in agreement with those put forward by Yoshida and co-workers who examined the behaviour of the related ether-based ligand H_2L^1 on coordination to Cu(II) (**3**).[9b] Although fewer ligand–ligand interactions are evident in **3** (*cf.* **1** and **2**), a comparison of the Cu(II) coordination in this complex shows it to be similar to that of **2**. The dihedral angle for the coordination chromophore about the Cu(II) centres is 45°, with a Cu $\cdots$ Cu separation of 11.98 Å and a helical twist of 134°. The absence of the methylene group in **3** accounts for the difference in the helical twist and the elongation of the Cu $\cdots$ Cu distance compared with those found in **2**.[16] Yoshida states that the helical structure in the solid-state derives from the intramolecular (inter-strand) $\pi\cdots\pi$ and CH $\cdots\pi$ interactions in **3**, and supports this by observing that there are few intermolecular interactions in the complex. This conclusion was supported by both Chun-ying,[11] who stated that steric effects are not as important as $\pi\cdots\pi$ interactions (although they did not state the nature of these), and broadly by Hannon.[10] We believe that whilst the intramolecular interactions may be a contributing factor in determining the structure of these related helicates, they are not the driving force: they are most likely present as a consequence of binding to the metal centres *i.e.* coordination of the ligands to the metal ensures their close proximity. In support of this we also note that Chun-ying and co-workers reported the structure of an achiral dimeric silver(I) molecular box of L^3 with composition $[Ag_2L^3{}_2](BF_4)_2$ (**4**). From this structure we observe that the disposition of the silver ion is pseudo-tetrahedral and extended ligand planarity is evident between aromatic rings 3 and 4 (dihedral angle of 3° between their mean planes). Intermolecular face-to-face $\pi\cdots\pi$ stacking between rings 3 and 4 (and pyridyl ring 1) with those from adjacent molecules promotes the formation of a two-dimensional sheet. Thus, it would appear that these interactions occur at the expense of any intramolecular (inter-strand) associations and thus negate the formation of a prospective double helicate in the solid-state. Moreover, Hannon and co-workers[10c] have shown that $[Ag_2L^4{}_2](PF_6)_2$ (**5**) forms a helicate with a major and minor groove in a similar fashion to **1**. They ascribe this unusual topology to the presence of intramolecular inter-strand edge-to-face $\pi\cdots\pi$ stacking which is observed in the solid-state. Notably however, ^{1}H NMR studies gave no evidence for these interactions being maintained in solution, as this may have been expected if the interactions were significant, and has been observed by others.[9a,b] We believe that the irregular nature of **5** results from the extensive intermolecular face-to-face and edge-to-face $\pi\cdots\pi$ stacking that exists. Indeed, we note that these contacts give rise to an intricately interwoven two-dimensional sheet which significantly includes each aromatic ring interacting intermolecularly with at least one other. These interactions would obviously have a more profound influence upon the structure of the helicate than any intramolecular ones.

We propose therefore, that the nature of the helical structures derived from these Schiff-base ligands (**1**–**5**) are dependent upon the metal coordination environment and its distortion (as dictated by the metal's coordination preference), in combination with the large number of intermolecular interactions experienced by them, rather than any intramolecular (inter-strand) interactions. There are a number of structural features that suggest this is likely in **1** and **2** and also in **3**, **4** and **5**: i) only one of the rings in **1** (none in **2**) could be said to be participating in such an intramolecular (inter-strand) interaction. Even so, the relative orientations of the rings deviate significantly from co-planarity by *ca.* 25° making even this tentative. This distortion is such that face-to-face $\pi\cdots\pi$ interactions are weakened, whilst not being sufficient enough to enhance edge-to-face interactions; ii) the coordination environment of the metal centres is distorted tetrahedral. Ideally, maximum intramolecular (inter-strand) interaction between the bridging ligands would be realised by a planar geometry about the metal centre as this would optimise either face-to-face or edge-to-face $\pi\cdots\pi$ interactions. Therefore distortion from planar geometry should be less favoured; iii) each ring in **1**–**5** interacts intermolecularly with two or three rings from adjacent units and therefore these are probably more significant in determining the solid state structure of the complexes, and iv) the large variation in helical pitch *i.e.* 138–160° would suggest that any intramolecular (inter-strand) interaction is very weak and their presence is therefore subject to other variables (metal coordination geometry, intermolecular interactions *etc.*) and most probably arises because of these.

Furthermore, it would appear from the structures of **1** and **2** and those of **4** and **5** that these types of molecule will endeavour to optimise intermolecular interactions over intramolecular ones, even at the expense of helicate formation (in **4**). This clearly has implications for the design of new inorganic materials.[17] It seems to us that, although the coordination preferences of the metal centres and those of the ligand can be relied upon in the self-assembly of molecular species, the effects of the non-coordinating atoms far from the coordination sites are much less certain. Furthermore, even weak intermolecular interactions have a profound influence upon the resultant solid-state structure. We are currently examining a number related ligands in an attempt to rationalise the effect that changing the bridging group has upon the 3-D structure in these types of materials. We are also examining the role that the crystallising solvent plays upon determining and defining the nature of the products formed. This work is on going.

Acknowledgements

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