

Triple helicates and planar dimers arising from silver(I) coordination to directly linked bis-pyridylimine ligands

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Silver(I) coordination is investigated for three ligands of the pyridine-azine class, in which two pyridylimine binding units are linked directly through the imine nitrogen atoms. ¹H NMR, X-ray analysis and ESI mass spectrometry indicate the presence of a range of metallo-supramolecular architectures in solution for all three ligands. X-Ray analysis confirms the solid state structures for a dinuclear triple helicate containing five-coordinate silver centres and a dinuclear dimer in which the silver ions are three-coordinate with long range stabilising interactions to trifluoromethanesulfonate counter-ions. A tetranuclear grid-like array is also implied as a component of the solution library. The five-coordinate silver(I) ions in the triple helicate result in a hetero-ligand system with two ligands oriented in a head-to-tail fashion. This is distinct from the triple helicates formed with octahedral metals such as an iron(II) triple helicate also crystallographically characterised herein.

Introduction

The design of complex molecular architectures is an important goal as it offers a route to encode the properties of materials at the molecular level. Supramolecular synthesis¹ has emerged as a powerful tool for such design and arrays assembled through metal–ligand interactions have played a key role. Initial work focused predominantly on design of discrete architectures such as helicates, knots and boxes.^{2,3} More recently it has been recognised that libraries of architectures (either virtual or real) are *also* attractive targets,⁴ since the library equilibria can be responsive to external agents (such as anions, solvents, guests or temperature) imparting molecular level sensing or switching functions. Design of such libraries requires systems for which two or more different supramolecular architectures are close in energy. For metallo-assembled arrays this is most likely to occur for metals without strong coordination preferences (such as d¹⁰ systems).⁵

We are interested in synthetic routes that will allow sophisticated metallo-supramolecular architectures to be constructed quickly and simply from commercial reagents and to this end have been developing simple imine systems. Using this approach we have designed helicate and cyclophane systems from bis-pyridylimine ligands and explored routes to encode additional information into the array such as strand directionality, groove size and chirality (all through the use of spacer units).^{6,7} We have also demonstrated that the molecular shape or architecture may be used to encode the molecular function in such systems, through design of cylindrical agents that recognize the major groove of DNA.⁸

The simplest bis-pyridylimine ligand system is 2-pyridinealdazine (**L**²) (Fig. 1) in which the two pyridylimine binding units are linked directly (no spacer unit) through the imine nitrogen atoms. Our interest in this ligand was stimulated by the analogy between its donor set and that of the 3,6-di(2'-pyridyl)pyridazine (**dppn**) system which Osborn and Youinou⁹ showed to form 2 × 2 grid arrays with tetrahedral metal ions and which Lehn has so elegantly extended to create higher order *N* × *N* grid arrays.¹⁰ In contrast to **dppn** with its rigid central ring, **L**² has the freedom to rotate about the central N–N bond.

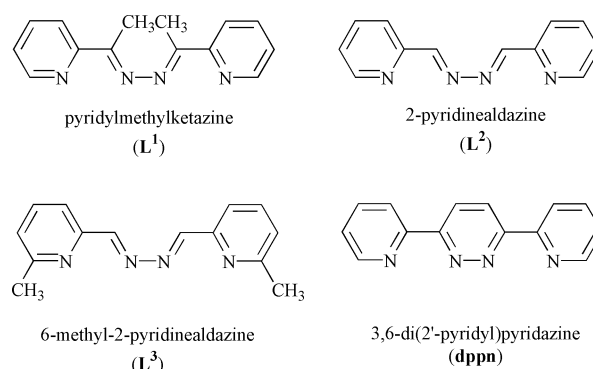


Fig. 1 Ligands **L**¹, **L**², **L**³ and **dppn**.

Since the linearity and planarity of **dppn** are central to grid formation, such twisting might both disfavour grid formation and permit formation of other architectures. The twisting is expected to be enhanced in the ketazine analogue (**L**¹) and consequently the coordination of this ligand has also been explored together with a further analogue (**L**³) in which a methyl group is introduced at the 6-position of the pyridine (with the aim of slowing down any rapid exchange processes in the NMR). We wish now to report the effects of interacting these ligands with silver(I). Preliminary studies with copper(I) do imply an analogous chemistry but are complicated by the very facile oxidation of the cuprous products to give the much studied^{11–13} cupric salts.

The coordination chemistry of **L**² was first described by Stratton and Busch in papers in 1958 and 1960 and their studies are of particular historic importance to the field of metallo-supramolecular chemistry and in particular to helicate formation.¹³ These workers described the coordination of **L**² to octahedral transition metal ions to form complexes with the formula [M₂(**L**²)₃]⁴⁺ (M = Co, Fe and Ni)^{13–15} and recognized that the species must consist of three strands wrapped around two metals in a spiral fashion. Their studies thus represent the first recognized (if perhaps not deliberately designed)¹⁶ triple helicates. The helical complexes were shown to undergo

exchange reactions on heating or standing to form mononuclear complexes $[M(L^2)_2]^{2+}$ in which the ligand twists to coordinate as a tridentate with a non-coordinated imine residue; Stratton and Busch proposed the term “flexidentate” to describe the coordination behaviour of the ligand.¹³ No crystal structures of these early triple helicates have been reported to date, however in 1974 Sheldrick *et al.* reported the X-ray crystal structure of the dinuclear triple helical cobalt complex formed from the pyridylmethylketazine ligand (L^1)¹⁷ and more recently Thompson and co-workers have crystallographically characterised similar structures with picolinamide azine.¹⁸

Results and discussion

In the course of our studies we fortuitously obtained crystals of the hexafluorophosphate salt of Stratton and Busch’s original iron(II) complex¹³ (Fig. 2). Since the unsubstituted triple

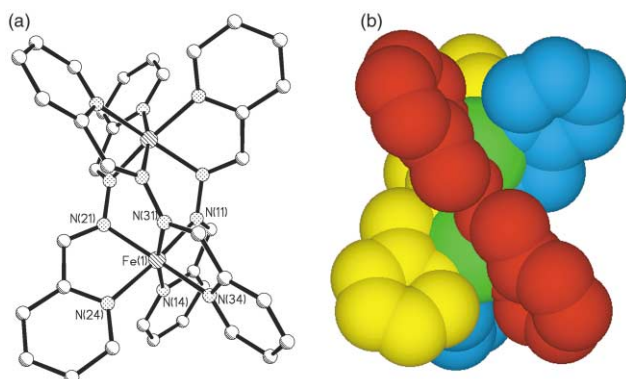


Fig. 2 X-Ray crystal structure for the iron(II) complex of L^2 together with a colour space filling representation, emphasising the triple helical nature of the complex cation. Hydrogen atoms have been omitted for clarity.

helicates proposed with L^2 have not previously been crystallographically characterised we have undertaken a structural determination both to investigate the twisting about the N–N bonds that must be inherent in the structure and because the supramolecular architecture adopted with this octahedral metal might prove of relevance or contrast to those obtained with silver(I). Entirely as predicted¹³ the structure is a dinuclear triple-helicate with each ligand bound as a bis didentate to two different iron centres. However, closer examination reveals some interesting features that are important for the structures of the silver complexes that are the focus of this work.

Each iron(II) centre binds to three ligand strands thereby attaining a pseudo-octahedral coordination geometry. The two iron centres are separated by 3.498(2) Å. The bond lengths to the imine groups (1.93 Å) are slightly shorter than those to the pyridine units (1.98 Å). This may be a consequence of the helical structure but could also imply more effective σ donation or π back donation.

The pyridylimine units are essentially planar (dihedral angles¹⁹ py–imine 4 and 7°) and the helical twist is achieved primarily by twisting about the central N–N bond (dihedral angles 57 and 63°). This twisting is less dramatic than that observed in the cobalt complex of L^1 (84–93°)¹⁷ consistent with the absence of the steric effects introduced in that ligand by the methyl groups. There are no significant π – π interactions between the pyridyl rings either within or without the helicates however other supramolecular interactions are present in the structure: The stability of the red triple helical $[Fe_2(L^2)_3]^{4+}$ cation (with respect to conversion to the blue mononuclear complex $[Fe(L^2)_2]^{2+}$) appears to be enhanced in nitromethane as reflected by our ability to grow crystals from this solvent by slow diffusion of diethyl ether over a period of days. Consistent with this, four molecules of the nitromethane solvent per helical

cation are incorporated into the crystal lattice and these solvent molecules appear to play an important role in the supramolecular stabilisation of the acidic imine CH protons; each imine CH proton forms a short CH \cdots X interaction,²⁰ with four of the protons forming contacts to the oxygens of nitromethane solvent molecules (CH \cdots O 2.33, 2.48 and 2.52 Å) and the remaining two protons forming contacts with fluorines from hexafluorophosphate counter-ions (CH \cdots F 2.14 Å).²¹

Despite the extensive coordination studies that have been undertaken on this series of ligands^{11–15,17,18,22–31} the focus to date has remained on the coordination to octahedral dications. We were intrigued to see what type of architectures these ligand systems might support with monocations such as silver(I).

Silver(I) complexes of L^1

Coordination of L^1 to silver(I) was achieved by stirring one equivalent of L^1 with one equivalent of silver(I) acetate in methanol for 48 hours. The resulting yellow solution was filtered through Celite and treated with methanolic ammonium hexafluorophosphate. A yellow precipitate formed and was collected by vacuum filtration. Partial microanalytical data indicated that the chemistry might be complicated; for the experiment carried out on two separate occasions, two different results were obtained. On the first occasion the data appeared to be consistent with the formulation $[Ag_n(L^1)_n][PF_6]_n$ however on the second occasion the data was consistent with the formulation $[Ag_2(L^1)_3][PF_6]_2$. The experiment was repeated with a 2 : 3 ratio and consistently compounds analysing as $[Ag_2(L^1)_3][PF_6]_2$ were obtained.

Crystallographic investigation. The solid of the hexafluorophosphate salt from the 1 : 1 experimental ratio was redissolved in acetonitrile and diethyl ether diffused into the solution to yield crystals suitable for X-ray analysis. Despite the initial 1 : 1 ratio, the solid state structure revealed the complex of 2 : 3 stoichiometry to have crystallised.

The structure is again a dinuclear triple helix (Fig. 3) but the

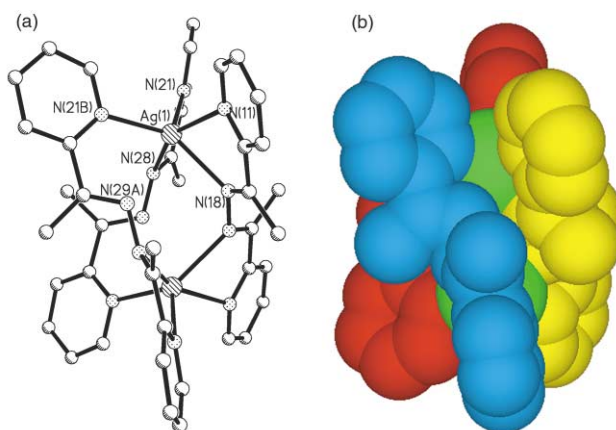


Fig. 3 X-Ray crystal structure for the silver(I) complex of L^1 together with a colour space filling representation, emphasising the triple helical nature of the complex cation. Hydrogen atoms have been omitted for clarity.

structure is distinct from that of the iron(II) complex of L^2 , containing the silver(I) centres in an unusual five-coordinate distorted trigonal bipyramidal environment. One ligand uses all four donor atoms to coordinate as a bis didentate ligand to the two metal centres. However, the other two ligands use only three donors and coordinate as a didentate to one metal and a monodentate to the other with a non-coordinated imine residue acting as a spacer unit between the binding sites. These two hypodentate³ ligands are arranged in a head-to-tail^{2,7} (anti-parallel) fashion and consequently both metal centres are presented with five donors. The structure is thus distinct from that

observed in the $[\text{Fe}_2(\text{L}^2)_3]^{4+}$ cation, where all three strands are equivalent and non-directional.

Triple helicates containing directional ligands have been reported previously,^{32,33} though not crystallographically characterised. For a system with three directional strands, two conformations are possible,³³ either all three strands may be orientated in the same direction (head-to-head) or one strand may be orientated in the opposite direction to the other two. The system herein is different, since directionality is only induced into the strands by the coordination preference of the silver(I) ion. In effect the silver coordination results in a hetero-strand helicate, with two directional ligand strands orientated head-to-tail and a third non-directional strand completing the array. This is quite remarkable and illustrates the power exerted by metal coordination preferences in helicate design and structure.

The $\text{M} \cdots \text{M}$ distance (4.48 Å) is substantially longer than that in the iron(II) helix, consistent with the presence of an imino spacer in two of the ligand strands. The didentate pyridylimine units are essentially planar (pyridyl-imine dihedral angles 10, 20°). Ag–N bond lengths are in the range 2.32–2.49 Å (with the shortest bonds being formed by the monodentate pyridyls) and bond lengths to both imine and pyridine units are similar. Helical twisting in the bis-didentate strand is predominantly about the central N–N bond (108°) while in the hypodentate strands the twisting is more dramatic, occurring about the central N–N bond (109°) and between the non-coordinated imine and the pyridine (40°). The twistings about the central N–N bonds are greater than in the iron(II) complex of L^2 , consistent with the steric effects of the ketimine methyl groups in L^1 .

The individual helicates stack into infinite chains stabilised by face-to-face π -stacking interactions, (Fig. 4) between the

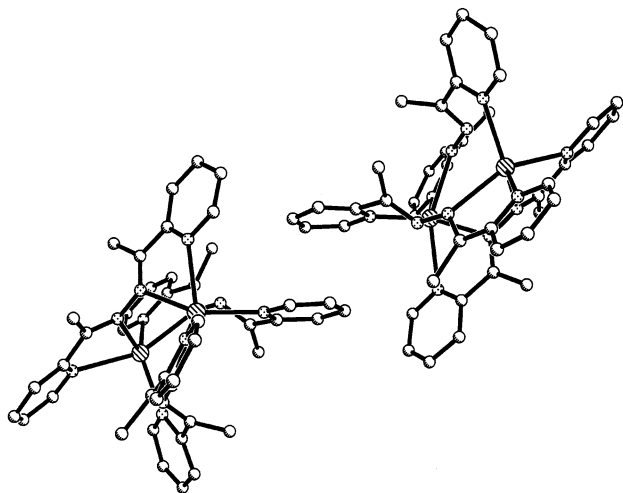


Fig. 4 Stacking between the silver(I) triple helicates.

monodentate pyridyl rings (from the hypodentate ligands) at the ends of the helices (centroid–centroid 3.7 Å). The interaction is associated with two concomitant face–edge ($\text{CH} \cdots \pi$) stacking interactions from the edge of the monodentate pyridyl to the face of a pyridyl from the bis-didentate strand (centroid–centroid 5.1 and 5.0 Å; $\text{CH} \cdots \text{centroid}$ 2.88 and 3.34 Å). Short $\text{CH} \cdots \text{F}$ distances²⁰ are observed between the methyl groups and the hexafluorophosphate anions.

Solution structures. ^1H NMR spectra at both 1 : 1 and 2 : 3 coordination ratios were recorded in deuterated dichloromethane solutions. Two different spectra were obtained. With a 2 : 3 ratio the resonance for H_6 occurs at δ 8.66 ppm, H_3 and H_4 overlap to give a multiplet at δ 7.96 ppm, H_5 appears at δ 7.52 ppm and a singlet for the methyl group is observed at δ 2.25

Table 1 Species observed (m/z) in the electrospray mass spectra for silver(I) coordination experiments with L^1

Species	Dichloromethane–methanol		Acetonitrile	
	1 : 1	2 : 3	1 : 1	2 : 3
$[\text{M}_4(\text{L}^1)_4][\text{PF}_6]_3^+$	—	—	1819	—
$[\text{M}_3(\text{L}^1)_3][\text{PF}_6]_2^+$	1329	—	1329	—
$[\text{M}_2(\text{L}^1)_2][\text{PF}_6]^+$	—	—	1075	1075
$[\text{M}_2(\text{L}^1)_3]^{2+}$	—	465	—	—
$[\text{M}_2(\text{L}^1)_2][\text{PF}_6]^+$	837	837	837	837
$[\text{M}_2(\text{L}^1)_2]^+$	691	—	—	691
$[\text{M}(\text{L}^1)_2]^+$	585	585	585	583
$[\text{M}(\text{L}^1)]^+$	346	346	346	346
$[\text{M}(\text{L}^1)][\text{MeCN}]^+$	—	—	—	388

ppm. The ^1H NMR spectrum at a 1 : 1 ratio however shows a distinct triplet of doublets for H_4 at δ 8.12 ppm and a doublet of triplets for H_3 at δ 7.98 ppm. The H_6 resonance is observed at δ 8.79 ppm, H_5 at δ 7.66 ppm and the methyl protons at δ 2.47 ppm. These results indicate the formation of two different solution species for the two ratios. For both samples, dilution studies revealed no change in the peak distributions indicating that the different sets of peaks observed in these NMR experiments do not result from concentration effects. When the NMR samples for the two experiments were mixed the spectrum observed did not, however, display two distinct sets of peaks. Instead a single set of peaks was evident. This suggests that, even in a non-coordinating solvent like dichloromethane, the solution species are in rapid exchange on the NMR timescale. NMR experiments run at low temperatures (183 K) did not resolve distinct species but merely led to peak broadening. Given the proposed rapid exchange it is unsurprising that no ligand asymmetry is observed for the $[\text{M}_2\text{L}_3]^{2+}$ cation by NMR.

To probe further the solution species present, we examined the solutions by positive ion ESI mass spectrometry. Mass spectra were obtained for both mixing ratios in both acetonitrile and dichloromethane–methanol mixtures. The peaks observed in each case are presented in Table 1.

In acetonitrile at a 1 : 1 ratio, peaks corresponding to the dinuclear triple helicates were observed alongside peaks for dinuclear dimers and species of higher order such as trimers and tetramers (presumably triangles and grids). This indicates an equilibrium in solution between a number of different architectures and supports the observed formation of triple helicates in the crystalline state from a 1 : 1 reaction ratio of ligand to silver(I) ions. The 2 : 3 ratio in acetonitrile shows M_2L_3 peaks with only peaks corresponding to lower species that could result from the break-up of M_2L_3 . ESI studies in dichloromethane at 1 : 1 ratio indicate that dimeric and trimeric species are present in solution while for the 2 : 3 ratio, peaks corresponding to the dinuclear triple helix are observed.

These combined NMR and ESI-MS studies indicate that coordination of L^1 to silver(I) leads to the formation of a library of architectures in solution, the ratios of which may be influenced by both the ratio of silver(I) to ligand introduced into the reaction and the type of solvent used. Having established possible structural motifs formed with L^1 , we turned to L^2 in which the ligand is not expected to be subject to quite such dramatic twisting.

Silver(I) complexes of L^2

Following on from the observations with L^1 , the coordination of L^2 to silver(I) was also performed in both 1 : 1 and 2 : 3 ratios. In contrast to the results for L^1 the partial microanalytical data for the products of both combinations of ligand to silver in these experiments were consistent with the formulation $\{\text{Ag}(\text{L}^2)\text{X}\}_n$ where X is the hexafluorophosphate or trifluoromethanesulfonate counter-ion as appropriate.

Crystallographic investigation. Crystallisation of the material obtained from the 1 : 1 reaction of L^2 with silver(I) trifluoromethanesulfonate from acetonitrile by the slow diffusion of diethyl ether afforded crystals suitable for X-ray characterisation.

A planar dinuclear M_2L_2 cation is obtained (Fig. 5). Silver(I)

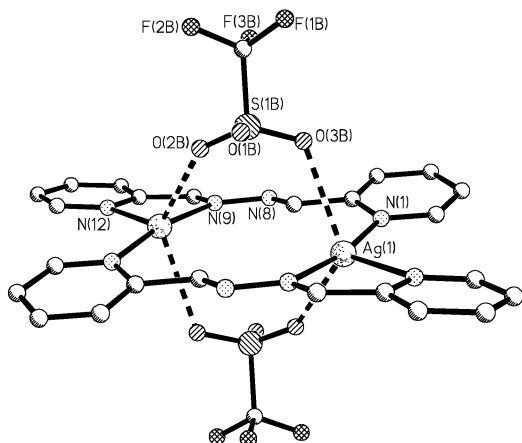


Fig. 5 Crystal structure of the dimeric silver(I) complex of L^2 with trifluoromethanesulfonate counter-ion. Hydrogen atoms have been omitted for clarity.

complexes of di-imine ligands are usually associated with an N_4 pseudo-tetrahedral coordination geometry.^{5–7} However, although this ligand system is able to support triple helicate formation it is unable to wrap sufficiently about a metal–metal axis to support double helicate formation which would be required to afford a tetrahedral geometry in a dinuclear 2 : 2 formulation.⁷ Instead, in this complex, the silver(I) ions in the dimer are supported in a relatively unusual three-coordinate distorted T-shaped geometry. Both ligands coordinate in a hypodentate fashion acting as a didentate ligand to one silver(I) centre and binding through a monodentate pyridyl residue to the other, much in the same way as two of the strands in the triple helical 2 : 3 complex of L^1 . The silver(I) ions are also associated with long-range interactions to the oxygen atoms of the trifluoromethanesulfonate counter-ions (2.82 and 2.79 Å) which are situated above and below the planar complex. These long interactions may help to offset the formally low coordination number. The non-coordinated imine units act as spacers between the binding sites and the Ag...Ag separation (4.95 Å) reflects this spacing. The ligands are essentially planar with only small twists observed (dihedral angle of 5° between the didentate pyridyl and imine; dihedral angle of 15° between the monodentate pyridyl and adjacent imine; N–N dihedral angle of 5°).

The planar units stack in the solid-state (Fig. 6) to form

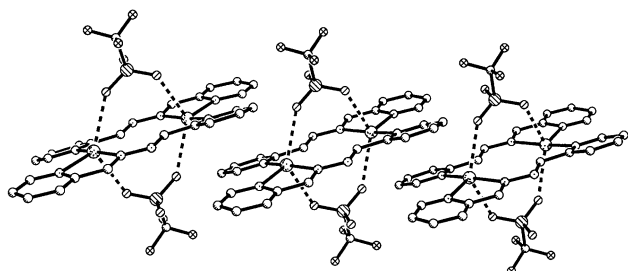


Fig. 6 Face-to-face π -stacking interactions between silver(I) dinuclear dimers of L^2 .

extended chains with two face–face π -stacking interactions (centroid–centroid 3.90 Å) formed by each end of the dimer with its neighbour. As in the iron(II) complex, the acidic CH protons on the imine form CH...X interactions, this time

with an anion bound to an adjacent $M_2L_2X_2$ unit, the interaction occurring with the oxygen which is not engaged in bonding to silver centres (CH...O 2.43 Å). These interactions link the chains into a three dimensional network.

Solution structures. Although soluble in acetonitrile, the hexafluorophosphate complexes prepared in both 1 : 1 and 2 : 3 ratios proved to be insoluble in dichloromethane. Varying the counter-ion (BF_4 , CF_3SO_3) did not afford dichloromethane solubility, therefore solution studies were restricted to acetonitrile. No significant differences were observed in the 1H NMR studies for the solids obtained for the 1 : 1 or 2 : 3 ratios with hexafluorophosphate as counter-ion. Positive ion ESI mass spectrometry for the two ratios indicated a range of solution species (see Table 2). In addition the mass spectrum for the coordination of L^2 to silver(I) with trifluoromethanesulfonate counter-ion similarly revealed the presence of a number of architectures in solution. Once again low temperature (183 K) NMR studies failed to freeze out multiple species. The solution behaviour appears analogous to that with L^1 and supports the presence of a library of species.

Silver complexes of L^3

Coordination of this ligand to silver(I) was similarly carried out with 1 : 1 and 2 : 3 ratios of silver(I) to L^3 and the complexes isolated as the hexafluorophosphate salts. As with L^2 , dichloromethane soluble salts were not obtained. Partial microanalytical data for both coordination reactions are consistent with the formulation $[Ag_n(L^3)_n][PF_6]_n$. For the coordination of L^2 this formulation results in a planar dinuclear dimer. For complexes of L^3 with silver(I), however, the two methyl groups on the 6-position of the pyridine ring might distort the system from planarity and potentially favour higher coordination arrays. However, despite our best efforts we were unable to obtain X-ray quality crystals of this complex.

Solution structures. The 1H NMR in deuterated acetonitrile of the solids obtained from the 2 : 3 and 1 : 1 mixing ratios showed virtually identical spectra. The peaks observed in these spectra may represent an average of signals corresponding to a number of solution species, however, once again NMR experiments at low temperatures (183 K) showed only broadening of the original signals. While this broadening may represent the initial stages of the peaks splitting into more than one set of signals it is more likely that it is due to increasing viscosity of the solutions. The addition of methyl groups to the 6-position of the pyridyl ring usually has a dramatic effect on slowing the kinetics of exchange in such systems.^{6,7} The failure to freeze out multiple species in these systems probably reflects very fast exchange kinetics. Positive ion mass spectrometry again revealed a range of dimers, dinuclear triple helicates, trimers and tetramers for both mixing ratios as with L^1 and L^2 .

Conclusion

The library of species observed in the silver(I) complexes arise from the multiple competing interactions present in these systems (M–L, ligand twisting, π – π , CH– π , CH...X). We have recently also observed such “frustration” in the silver(I) complexes of a thiomethyl substituted terpyridine,⁵ and proposed it as a method of library design. The primary frustration in this system is between the requirements of the metal which prefers a tetrahedral coordination geometry and the ligand which is unable to readily afford this except in an (entropically disfavoured) M_4L_4 grid arrangement.³⁴ (Moreover this requires a planar *cis* arrangement of the ligand about the N–N bond which may also be disfavoured). Indeed in this system we not only have a metal with a potentially variable geometry but a “flexidentate” ligand too: Both silver(I) crystal structures contain ligands bound only through three of their donors. This

Table 2 Solution species observed (m/z) for the coordination of L^2 to silver(I), observed by ESI mass spectrometry

Species	1 : 1 [X = PF ₆]	2 : 3 [X = PF ₆]	1 : 1 [X = CF ₃ SO ₃]
[M ₄ (L ²) ₄][X] ₃ ⁺	1708	—	—
[M ₃ (L ²) ₃][X] ₂ ⁺	1243	1243	1253
[M ₂ (L ²) ₂][X] ⁺	991	991	—
[M ₂ (L ²) ₂][X] ⁺	781	781	785
[M ₂ (L ²) ₂][F] ⁺	655	—	—
[M(L ²) ₂] ⁺	528	528	528
[M(L ²)][MeCN] ⁺	358	358	358
[M(L ²)] ⁺	319	319	319

coordination flexibility permits the formation of a range of different architectures of similar energy and in solution there is evidence for dimers and triple helicates (presumably similar to those crystallographically characterised) as well as trimers (possibly of circular helicate configuration) and tetramers (which may be similar to the grids of Youinou⁹ containing approximately planar ligands or if the ligand is twisted may be interwoven grid systems^{35,36} that are in effect circular helicates).⁴ Substituents, solvents or anions may be able to influence the relative stability of different components (and thus the library equilibria). For example the methyl groups in L^1 presumably disfavour the planar structure observed in the solid state for L^2 and consequently the triple helix crystallises preferentially for that complex. However, since exchange in solution appears to be very rapid we have been unable to probe this further by NMR.

Experimental

General

All starting materials were purchased from Aldrich and used without further purification. NMR spectra were recorded on Brüker ACF 250, DPX 300, and 400 instruments using standard Brüker software. Electrospray ionisation (ESI) analyses were performed on a Micromass Quattro (II) in positive ionisation mode. Samples were loop injected into a stream of water–methanol (1 : 1). Nebulisation was pneumatically assisted by a flow of nitrogen through a sheath around the capillary. Capillary (ionising) voltage +3.5 kV; source voltage 20 V. ESI analyses were recorded at the EPSRC National Mass Spectrometry Service Centre, Swansea. Microanalyses were conducted on a Leeman Labs CE44 CHN analyser by the University of Warwick Analytical Service.

L^1 , L^2 and L^3 were prepared according to procedures reported by Stratton and Busch. The [Fe₂(L²)₃]⁴⁺ cation was prepared according to the procedure reported by Stratton and Busch and precipitated as the hexafluorophosphate salt by anion metathesis with NH₄PF₆.^{13,14}

Silver(I) + L^1 , 2 : 3 ratio, PF₆ salt

L^1 (0.051 g, 0.214 mmol) and silver acetate (0.024 g, 0.145 mmol), were stirred in methanol (30 cm³) for 48 hours, filtered through Celite and treated with methanolic ammonium hexafluorophosphate. The resulting yellow precipitate was collected by vacuum filtration (0.057 g, 65%). (Found: C, 41.0; H, 3.4; N, 13.5; [Ag₂(C₁₄H₁₄N₄)₃][PF₆]₂ requires C, 41.3; H, 3.5; N, 13.8%). δ_H (250 MHz; CD₂Cl₂): 8.66 [1 H, dt, $J = 4.9, 1.5$ Hz, H₆], 7.96 [2 H, m, H₃ and H₄], 7.52 [1 H, m, $J = 6.1, 4.9, 2.9$ Hz, H₅], 2.25 [3 H, s, CH₃]. δ_H (400 MHz; CD₃CN): 8.79 [1 H, ddd, $J = 5.0, 1.8, 0.9$ Hz, H₆], 8.06 [1 H, td, $J = 8.0, 1.8$ Hz, H₄], 7.90 [1 H, dt, $J = 8.0, 0.9$ Hz, H₃], 7.66 [1 H, ddd, $J = 8.0, 5.0, 1.2$ Hz, H₅], 2.24 [3 H, s, CH₃]. Positive-ion ESI, (CH₂Cl₂–CH₃OH), m/z 837 ([Ag₂(L¹)₂][PF₆]⁺), 585 ([Ag(L¹)₂]⁺), 465 ([Ag₂(L¹)₃]²⁺), 346 ([Ag(L¹)]⁺), 239 ([L¹][H]⁺). Positive-ion ESI, (Crystals used for X-ray analysis CH₃CN), m/z 1075 ([Ag₂(L¹)₃][PF₆]⁺), 837 ([Ag₂(L¹)₂][PF₆]⁺), 691 ([Ag₂(L¹)₂]⁺), 583 ([Ag(L¹)₂]⁺), 388 ([Ag(L¹)][MeCN]⁺), 346 ([Ag(L¹)]⁺), 239 ([L¹][H]⁺).

Silver(I) + L^1 , 1 : 1 ratio, PF₆ salt

L^1 (0.055 g, 0.229 mmol) and silver acetate (0.038 g, 0.229 mmol) were stirred in methanol (30 cm³) for 48 hours, filtered through Celite and treated with methanolic ammonium hexafluorophosphate. The resulting yellow precipitate was collected by vacuum filtration (0.064 g, 56%). (Found: C, 40.3; H, 3.4; N, 13.2; [Ag₂(C₁₄H₁₄N₄)₃][PF₆]₂·H₂O requires C, 40.7; H, 3.6; N, 13.6%). (Found: C, 34.9; H, 3.2; N, 11.4; [Ag₂(C₁₄H₁₄N₄)₃][PF₆]₂ requires C, 34.2; H, 2.9; N, 11.4%). δ_H (250 MHz; CD₂Cl₂): 8.79 [1 H, ddd, $J = 5.0, 1.8, 0.9$ Hz, H₆], 8.12 [1 H, td, $J = 7.9, 1.8$ Hz, H₄], 7.98 [1 H, dt, $J = 7.9, 0.9$ Hz, H₃], 7.66 [1 H, ddd, $J = 7.9, 5.0, 1.0$ Hz, H₅], 2.47 [3 H, s, CH₃]. δ_H (400 MHz; CD₃CN): 8.79 [1 H, ddd, $J = 5.0, 1.8, 0.9$ Hz, H₆], 8.06 [1 H, td, $J = 8.0, 1.8$ Hz, H₄], 7.90 [1 H, dt, $J = 8.0, 0.9$ Hz, H₃], 7.66 [1 H, ddd, $J = 8.0, 5.0, 1.2$ Hz, H₅], 2.24 [3 H, s, CH₃]. Positive-ion ESI, (CH₂Cl₂–CH₃OH), m/z 1329 ([Ag₃(L¹)₃][PF₆]₂⁺), 837 ([Ag₂(L¹)₂][PF₆]⁺), 691 ([Ag₂(L¹)₂]⁺), 585 ([Ag(L¹)₂]⁺), 346 ([Ag(L¹)]⁺), 239 ([L¹][H]⁺). Positive-ion ESI, (CH₃CN), m/z 1819 ([Ag₄(L¹)₄][PF₆]₃⁺), 1329 ([Ag₃(L¹)₃][PF₆]₂⁺), 1075 ([Ag₂(L¹)₂][PF₆]⁺), 837 ([Ag₂(L¹)₂][PF₆]⁺), 585 ([Ag(L¹)₂]⁺), 346 ([Ag(L¹)]⁺).

Silver(I) + L^2 , 2 : 3 ratio, PF₆ salt

L^2 (0.05 g, 0.24 mmol) and silver acetate (0.03 g, 0.16 mmol) were stirred in methanol (30 cm³) for 10 minutes, filtered through Celite and treated with methanolic ammonium hexafluorophosphate. The resulting yellow–orange precipitate was collected by vacuum filtration (0.06 g, 54%). (Found: C, 30.7; H, 2.2; N, 11.6; [Ag₂(L²)₂][PF₆]₂·H₂O requires C, 30.7; H, 2.2; N, 11.6%). δ_H (400 MHz; CD₃CN): 8.79 [1 H, s, H₁], 8.72 [1 H, dt, $J = 4.9, 1.5, 0.9$ Hz, H₆], 8.00 [2 H, m, H₃ and H₄], 7.63 [1 H, ddd, $J = 7.3, 4.9, 1.2$ Hz, H₅]. Positive-ion ESI, (CH₃CN), m/z 1243 ([Ag₃(L²)₃][PF₆]₂⁺), 991 ([Ag₂(L²)₂][PF₆]⁺), 781 ([Ag₂(L²)₂][PF₆]⁺), 527 ([Ag(L²)₂]⁺), 445 ([Ag₂(L²)][F]⁺), 358 ([Ag(L²)][CH₃CN]⁺), 319 ([Ag(L²)]⁺).

Silver(I) + L^2 , 1 : 1 ratio, PF₆ salt

L^2 (0.05 g, 0.24 mmol) and silver acetate (0.04 g, 0.24 mmol) were stirred in methanol (30 cm³) for 10 minutes, filtered through Celite and treated with methanolic ammonium hexafluorophosphate. The resulting yellow–orange precipitate was collected by vacuum filtration (0.08 g, 73%). (Found: C, 30.5; H, 2.2; N, 11.7; [Ag₂(C₁₂H₁₀N₄)₂][PF₆]₂·H₂O requires C, 30.7; H, 2.2; N, 11.6%). δ_H (400 MHz; CD₃CN): 8.73 [1 H, s, H₁], 8.72 [1 H, d, $J = 4.9, 1.5$ Hz, H₆], 8.05 [1 H, td, $J = 7.9, 1.5$ Hz, H₄], 7.97 [1 H, br d, $J = 7.9$ Hz, H₃], 7.66 [1 H, ddd, $J = 7.3, 4.9, 1.8$ Hz, H₅]. Positive-ion ESI, (CH₃CN), m/z 1708 ([Ag₄(L²)₄][PF₆]₃⁺), 1243 ([Ag₃(L²)₃][PF₆]₂⁺), 991 ([Ag₂(L²)₂][PF₆]⁺), 781 ([Ag₂(L²)₂][PF₆]⁺), 655 ([Ag₂(L²)₂][F]⁺), 528 ([Ag(L²)₂]⁺), 358 ([Ag(L²)][MeCN]⁺), 319 ([Ag(L²)]⁺), 211 ([L²][H]⁺).

[Ag₂(L²)₂][CF₃SO₃]₂

L^2 (0.03 g, 0.14 mmol) was dissolved in ethanol (5 cm³) and added to a solution of silver(I) trifluoromethanesulfonate (0.037 g, 0.14 mmol) in acetone (5 cm³). A yellow precipitate formed which was collected by filtration through cotton wool (0.035 g, 52%). The product was dissolved in acetonitrile

Table 3 Crystallographic data and structural refinements

Complex	[Fe ₂ (L ²) ₃][PF ₆] ₄ ·4MeNO ₂	[Ag ₂ (L ¹) ₃][PF ₆] ₂	[Ag ₂ (L ²) ₂][CF ₃ SO ₃] ₂
Empirical formula	C ₄₀ H ₄₂ F ₂₄ Fe ₂ N ₁₆ O ₈ P ₄	C ₄₂ H ₄₂ Ag ₂ F ₁₂ N ₁₂ P ₂	C ₁₃ H ₁₀ AgF ₃ N ₄ O ₃ S
Formula weight	1566.41	1220.56	467.18
Crystal system	Orthorhombic	Monoclinic	Monoclinic
Space group	<i>Fdd2</i>	<i>C2/c</i>	<i>P2(1)/c</i>
<i>a</i> /Å	22.74680(10)	12.813(2)	8.9563(5)
<i>b</i> /Å	41.1307(7)	23.504(2)	19.8349(10)
<i>c</i> /Å	13.0308(2)	16.140(2)	9.3583(5)
β /°	90	92.878(5)	107.48(10)
Volume/Å ³ , <i>Z</i>	12191.5(3), 8	4854.3(11), 4	1585.71(15), 4
Absorption coefficient/mm ⁻¹	0.716	0.964	1.458
Reflections collected	15169	14565	9277
Independent reflections	5165 (<i>R</i> _{int} = 0.0924)	5689 (<i>R</i> _{int} = 0.0270)	3697 (<i>R</i> _{int} = 0.0216)
Data/restraints/parameters	5165/40/448	5689/0/336	3697/0/227
Goodness-of-fit-on <i>F</i> ²	1.198	1.027	0.944
Final <i>R</i> indices [<i>I</i> > 2σ(<i>I</i>)]	<i>R</i> 1 = 0.0809, <i>wR</i> 2 = 0.1547	<i>R</i> 1 = 0.0413, <i>wR</i> 2 = 0.0962	<i>R</i> 1 = 0.0223, <i>wR</i> 2 = 0.0506
<i>R</i> indices (all data)	<i>R</i> 1 = 0.1109, <i>wR</i> 2 = 0.1739	<i>R</i> 1 = 0.0650, <i>wR</i> 2 = 0.1059	<i>R</i> 1 = 0.0311, <i>wR</i> 2 = 0.0529

Table 4 Metal ion to nitrogen atom bond lengths for the three crystal structures

Complex	Metal ion number	Nitrogen donor number	Distance/Å
[Fe ₂ (L ²) ₃][PF ₆] ₄ ·4MeNO ₂	Fe1	N11	1.928(6)
		N21	1.932(7)
		N24	1.981(7)
		N31	1.930(7)
		N14	1.978(7)
		N34	1.982(7)
[Ag ₂ (L ¹) ₃][PF ₆] ₂	Ag1A	N212	2.315(3)
		N18A	2.377(3)
		N21A	2.356(3)
		N28A	2.485(3)
		N11A	2.460(3)
		N29	3.428(3)
[Ag ₂ (L ²) ₂][CF ₃ SO ₃] ₂	Ag1	N1	2.2255(16)
		N12#1	2.4564(16)
		N9#1	2.2710(15)

(2 cm³) and on slow diffusion of diethyl ether X-ray quality crystals formed. (Found: C, 32.5; H, 2.1; N, 11.5; [Ag₂(C₁₂-H₁₀N₄)₂][CF₃SO₃]₂·H₂O requires C, 32.8; H, 2.3; N, 11.8%). δ_H (300 MHz; CD₃CN): 8.81 [1 H, s, H₁], 8.75 [1 H, dt, *J* = 4.9, 0.9 Hz, H₆], 8.05 [1 H, td, *J* = 7.9, 0.9 Hz, H₄], 8.00 [1 H, dt, *J* = 7.9, 1.8 Hz, H₃], 7.63 [1 H, ddd, *J* = 7.0, 4.9, 1.8 Hz, H₅]. Positive-ion ESI, (CH₃CN), *m/z* 1253 ([Ag₃(L²)₃][CF₃SO₃]₂), 785 ([Ag₂(L²)₂][CF₃SO₃]₂), 528 ([Ag(L²)₂]⁺), 358 ([Ag(L²)][MeCN]⁺) 319 ([Ag(L²)]⁺).

Silver(I) + L³, 1 : 1 ratio, PF₆ salt

L³ (0.05 g, 0.21 mmol) and silver acetate (0.035 g, 0.21 mmol), were stirred in methanol (30 cm³) for 1 hour, filtered through Celite and treated with methanolic ammonium hexafluorophosphate. The resulting yellow precipitate was collected by vacuum filtration (0.113 g, 91%). Found: C, 33.7; H, 2.9; N, 11.1; [Ag_n(C₁₄H₁₄N₄)_n][PF₆]_n·0.5H₂O requires C, 33.6; H, 3.0; N, 11.2%). δ_H (250 MHz; CD₃CN): 8.79 [1H, s, H₁], 7.96 [1H, t, *J* = 7.6 Hz, H₄], 7.84 [1H, d, *J* = 7.6 Hz, H₃], 7.53 [1H, d, *J* = 7.6 Hz, H₅], 2.60 [3H, s, H_{Me}]. Positive-ion ESI, (CH₃CN), *m/z* 1819 ([Ag₄(L³)₄][PF₆]₃), 1330 ([Ag₃(L³)₃][PF₆]₂), 1221 ([Ag₂(L³)₂][PF₆]₂), 1075 ([Ag₂(L³)₃][PF₆]₂), 837 ([Ag₂(L³)₂][PF₆]₂), 691 ([Ag₂(L³)₂]⁺), 583 ([Ag(L³)₂]⁺), 345 ([Ag(L³)][MeCN]⁺), 345 ([Ag(L³)]⁺), 239 ([L³][H]⁺).

Silver(I) + L³, 2 : 3 ratio, PF₆ salt

L³ (0.03 g, 0.13 mmol) and silver(I) acetate (0.016 g, 0.08 mmol), were heated under reflux in methanol (30 cm³) for 1 hour, filtered through Celite and treated with methanolic ammonium hexafluorophosphate. The resulting yellow precipitate was collected by vacuum filtration (0.05 g, 68%). (Found:

C, 33.8; H, 2.9; N, 10.9; [Ag_n(C₁₄H₁₄N₄)_n][PF₆]_n·H₂O requires C, 33.6; H, 3.0; N, 11.2%). δ_H (300 MHz; CD₃CN): 8.80 [1 H, s, H₁], 7.95 [1 H, t, *J* = 7.7 Hz, H₄], 7.84 [1 H, d, *J* = 7.7 Hz, H₃], 7.53 [1 H, d, *J* = 7.7 Hz, H₅], 2.60 [3 H, s, H_{Me}]. Positive-ion ESI, (CH₃CN), *m/z* 1330 ([Ag₃(L³)₃][PF₆]₂), 1075 ([Ag₂(L³)₃][PF₆]₂), 837 ([Ag₂(L³)₂][PF₆]₂), 691 ([Ag₂(L³)₂]⁺), 583 ([Ag(L³)₂]⁺), 473 ([Ag(L³)][F]⁺), 386 ([Ag(L³)][MeCN]⁺), 345 ([Ag(L³)]⁺), 239 ([L³][H]⁺).

X-Ray crystallography

Crystallographic data are collected in Table 3 with selected bond lengths in Table 4. Data were measured on a Siemens SMART³⁷ three-circle system with CCD area detector using the oil-mounting method at 180(2) K (maintained with the Oxford Cryosystems Cryostream Cooler).³⁸ Absorption correction by psi-scan. Mo-Kα radiation (λ = 0.71069 Å) was used. The structures were solved by direct methods using SHELXS.³⁹

[Fe₂(L²)₃][PF₆]₄. Suitable crystals were obtained by the slow diffusion of diethyl ether into nitromethane. The crystals were weakly scattering, which (with the solvent disorder) accounts for the relatively high *R*-factor. The PF₆ groups were restrained to octahedral geometry. Two nitromethane solvent molecules were located, one of which was partly disordered. In addition, a highly disordered solvent was included, modeled as four part-occupancy carbon atoms.

[Ag₂(L¹)₃][PF₆]₂. Suitable crystals were obtained by the slow diffusion of diethyl ether into acetonitrile. Refinement showed that *C2/c* was the correct space group, with the cation on an inversion centre and both PF₆ groups on two-fold axes. The fluorine atoms of the PF₆ groups have high thermal parameters

and one PF₆ is disordered about the two-fold axis (refined occupancies 0.68(1) and 0.34).

[Ag₂(L²)₂][CF₃SO₃]₂. Suitable crystals were obtained by the slow diffusion of diethyl ether into acetonitrile. This gave no difficulties in refinement; an extinction parameter was included.

CCDC reference numbers 173888–173890.

See <http://www.rsc.org/suppdata/dt/b1/b110137b/> for crystallographic data in CIF or other electronic format.

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