

Metallo-supramolecular libraries: triangles, polymers and double-helicates assembled by copper(I) coordination to directly linked bis-pyridylimine ligands

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Copper(I) coordination is investigated for three pyridine-azine ligands, in which two pyridylimine binding units are linked directly through the imine nitrogen atoms. Substituents on the imine units of the ligands influence the metallo-supramolecular architecture adopted. X-Ray analysis confirms the solid state structures for a dinuclear double-helicate, a trinuclear circular-helicate and a polymeric array. In each structure the copper(I) centre is four-coordinate. In acetone solution a library of architectures is observed. For the unsubstituted and methyl substituted ligands dinuclear (double-helical) and trinuclear (circular helical) structures dominate. With phenyl substituents only the double-helical species is present in solution. The work casts further light on the use of multiple competing interactions ('frustration') to design libraries of supramolecular architectures.

Introduction

The ability to design and construct complex molecular architectures offers a route to encode the properties of materials at the molecular level. A wide variety of such architectures have been designed by supramolecular approaches¹ and metal-ligand interactions, in particular, have proved to be powerful construction tools.² Discrete architectures, such as helicates, knots and boxes,² are attractive targets, but libraries of architectures (either virtual or real) are *also* of considerable interest,³⁻⁵ 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.

We have been focusing on simple pyridyl-imine metallo-supramolecular systems with the goal of constructing discrete architectures or libraries of architectures quickly and simply from commercial reagents.^{5,6} In this context we recently described the silver(I) chemistry of a series of ligands in which the two pyridylimine binding units are linked directly (no spacer unit) through the imine nitrogen atoms.⁵ A library of species of varying nuclearity were observed in solution. We structurally characterised a dinuclear triple-helicate ($\text{Ag}_2\text{L}_3^{2+}$) and a planar dimer ($\text{Ag}_2\text{L}_2^{2+}$) and proposed that trinuclear circular-helicates ($\text{Ag}_3\text{L}_3^{3+}$) and tetranuclear grid-like ($\text{Ag}_4\text{L}_4^{4+}$) species were also components in solution. The library of species observed arises from the multiple competing interactions present in these systems (M-L, ligand twisting, π - π , CH- π , CH...X). We are interested in such chemical "frustration"⁴ as a method of library design.⁵ For metallo-assembled arrays the dominant interactions are usually the metal-ligand interactions and any structure adopted must satisfy the requirements of the metal ion. Thus frustration is most likely to occur for metals without strong coordination preferences (such as d^{10} systems) in which the metal requirements can be met in various different ways. Consequently silver(I) is ideal for preparing diverse libraries. Indeed in the structurally characterised triple-helicate the silver(I) centre was five coordinate, while in the dimer it was three coordinate.⁵

To facilitate effective design of supramolecular libraries, we wished to gain a deeper understanding of the competing interactions involved and how they can influence the system. Our

strategy to achieve this is to systematically change one of the interactions and to examine the effect of this on the system. This should afford information not only about the interaction which is varied but also the relative influences of the other interactions. Herein we examine the effect of changing the metal-ligand interactions, by switching from silver(I) to copper(I). Although copper(I), as silver(I), is d^{10} its complexes exhibit a strong preference for a tetrahedral coordination geometry. We report the copper(I) chemistry of the ligand systems L^1 , L^2 and L^3 (Fig. 1). The chemistry is complicated by facile redox reactions between cuprous species and the much studied^{7,8} cupric salts in some solvents but we have been able to structurally characterise a dinuclear double-helicate, a trinuclear circular-helicate and a polymeric array and describe these structures and the associated solution chemistry. In each structure the copper(I) centre is four coordinate.

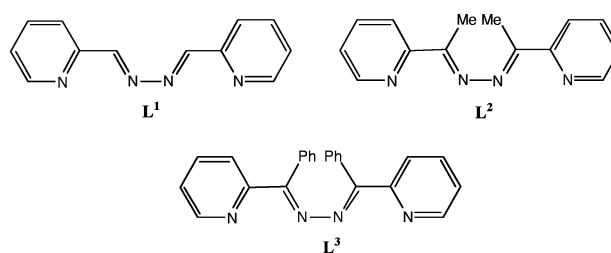


Fig. 1 Ligands L^1 , L^2 and L^3 .

Results

Reaction of one equivalent of L^1 , L^2 or L^3 (Fig. 1) with one equivalent of copper(II) acetate monohydrate in methanol resulted in the formation of red-brown solutions from which copper(I) salts of stoichiometry $[\text{Cu}_n(\text{L}^1)]_n[\text{PF}_6]_n$ **1**, $[\text{Cu}_3(\text{L}^2)]_3[\text{PF}_6]_3$ **2** or $[\text{Cu}_2(\text{L}^3)]_2[\text{PF}_6]_2$ **3**, respectively, were precipitated upon addition of a methanolic solution of ammonium hexafluorophosphate. The same compounds could be prepared from $[\text{Cu}(\text{MeCN})_4][\text{PF}_6]$ and the ligand in methanol. The use of other copper(II) salts led to the cupric species.

X-Ray quality crystals of **1** and **2** were obtained from acetonitrile solutions by slow diffusion of diethyl ether, and those of **3** from a methanolic solution by slow evaporation of

the solvent at 4 °C. Determination of the crystal structures of these compounds reveal a variety of different structural motifs:

Solid-state structures of the copper(I) complexes

[Cu_n(L¹)_n][PF₆]_n 1. The crystallographic analysis of **1** shows that its structure is an infinite coordination polymer with the copper(I) centers positioned along two parallel planes (Fig. 2). The Cu ··· Cu inter-metallic separations are 5.09 and 5.13 Å. Each ligand binds as a bis-bidentate to two different copper centers; Each copper(I) center binds to two pyridylimine units from two distinct ligands to give a pseudo-tetrahedral environment. The copper(I) centers disposed along the same plane have the same configurations but each plane differs in configuration. Thus, down the chain, the copper(I) centres alternate in configuration in a $\Lambda\Lambda\Delta\Delta$ fashion giving an achiral polymer chain.

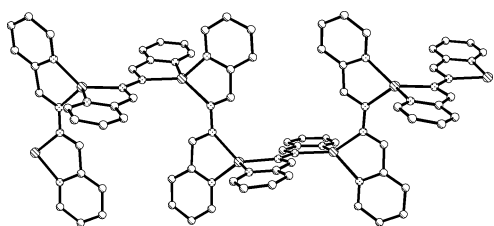


Fig. 2 Structure of the cationic polymeric chains in **1**. Hydrogens are omitted for clarity.

There are two crystallographically independent copper(I) centers and both are four-coordinate pseudo-tetrahedral. Each pyridylimine unit is approximately planar (pyridyl–imine dihedral angles⁹ in the range 4.1–8.2°). The Cu–N bond lengths (2.00–2.06 Å) and bond angles (79.6–81.6°) are unremarkable. The two pyridylimine units within each ligand are approximately coplanar (dihedral angles⁹ 2.9 and 5.9°) and the orientation about the central N–N bond is *trans*. Such an orientation is also seen in the structure of the free ligand¹⁰ and minimises proton–proton interactions while maintaining conjugation.

Perhaps surprisingly, there are no significant face-face π – π interactions between the pyridyl rings/imines either within or without the chains. The anions reside between the chains and make short contacts to the pyridyl and imine protons in the chains (average of 2.1 contacts per F in the range C–H ··· F 2.43–2.91 Å).¹¹ The asymmetric unit also contains three non-coordinated acetonitrile solvent molecules which form short contacts to the imine and aromatic protons of the ligand units (C–H ··· N 2.53–2.96 Å).

[Cu₃(L²)₃][PF₆]₃ 2. The X-ray crystal structure of compound **2** reveals the complex to be a trimer and possess a trinuclear circular helical architecture (Fig. 3).¹² Each copper(I) ion is once again coordinated to four nitrogen atoms, provided by the pyridylimine groups of two distinct ligands. However, instead of a polymeric structure with planar ligands, a cyclic trimer results. The pyridylimine units are essentially planar (dihedral angles⁹ in the range 1.8–6.2°) however there is substantial twisting about the central N–N bonds (dihedral angles⁹ 81–101°). Consistent with this intra-ligand twisting, the inter-metallic separation of the copper(I) ions (4.45–4.53 Å) is shorter than that observed in the polymer **1**. Cu–N bond lengths (1.98–2.05 Å) and bond angles (79.9–80.3°) are similar to those observed in the polymeric structure **1**.

The pyridyl rings define cavities, above and below the plane of the metal centres. One cavity of each trimer contains a hexafluorophosphate anion, while the other cavity contains part of a diethyl ether solvent molecule (Fig. 4). The anion in the cavity forms short contacts to the pyridyl and methyl protons. Anion encapsulation by cationic supramolecular arrays has been noted in a number of systems.¹³ The trinuclear circular helicate is chiral and the structure contains equal amounts of the two

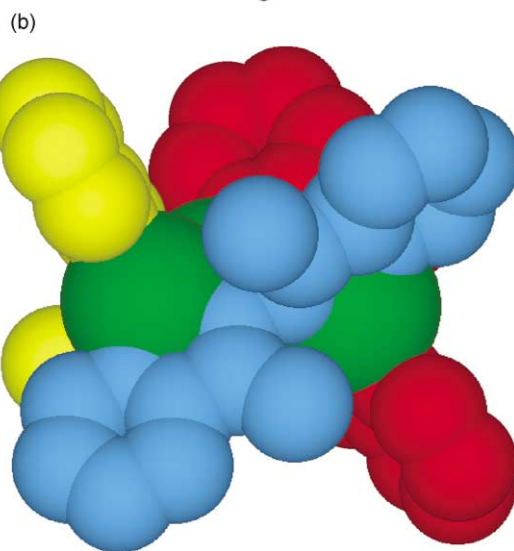
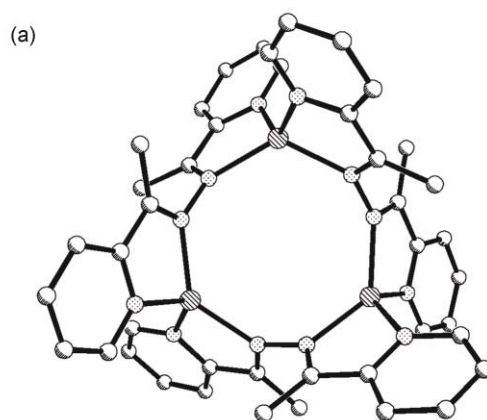


Fig. 3 Crystal structure of the trinuclear cation in **2**. (a) Top view showing the coordination sphere of the copper(I) centres. (b) Space-filling side view with the three ligands coloured separately, emphasising the ligand twisting and the cavities formed by the pyridyl rings. Hydrogens are omitted for clarity.

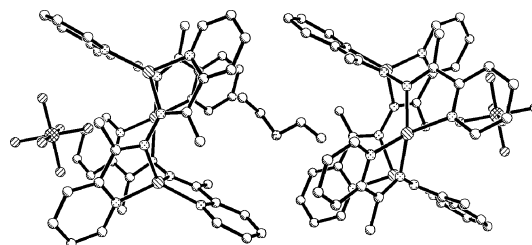


Fig. 4 View of two trinuclear cations in **2**, illustrating the inclusion of anions and solvent in the cavities. Hydrogens are omitted for clarity.

enantiomers. The remaining anions and a non-coordinated acetonitrile molecule are packed around the trimeric arrays and again form short contacts to the pyridyl and methyl protons.

While octahedral metals usually give triple-helical structures with these ligands,⁷ recently an unexpected solid-state trinuclear circular helicate was formed from the reaction of L¹ with Ni(SCN)₂.¹⁴ The coordination sphere of the octahedral metals is completed by coordinated thiocyanates and consequently that circular structure does not contain cavities above and below the plane of the metals. The inter-metallic separations (average 4.95 Å) are greater than those observed in this copper(I) structure.

[Cu₂(L³)₂][PF₆]₂ 3. The X-ray crystal structure of **3** reveals the cation to have a dinuclear double-helical structure (Fig. 5). Each copper(I) centre again occupies a four-coordinate pseudo-tetrahedral coordination geometry bound to two pyridylimine

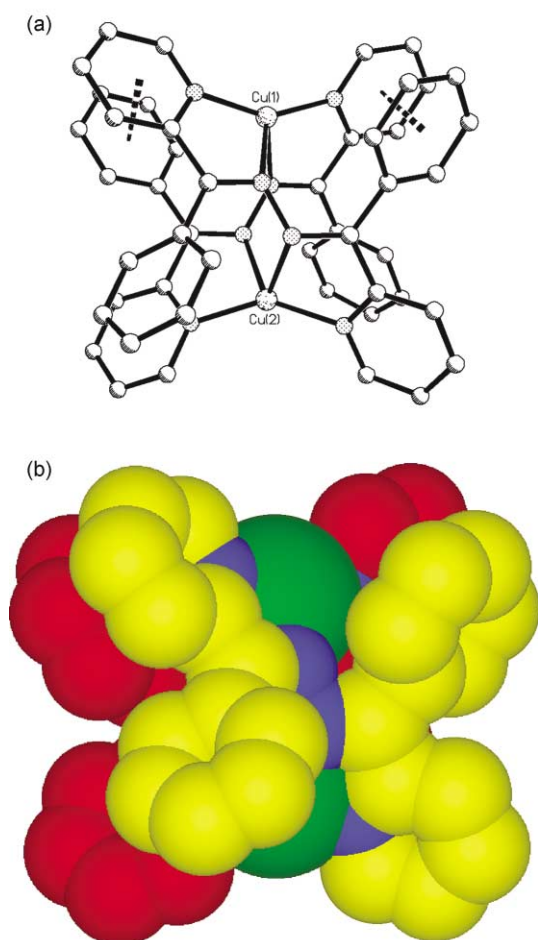


Fig. 5 The structure of the double-helical cation in **3**. (a) A view illustrating the metal coordination geometry and emphasising the two intra-helical π -stacking interactions (b) A space-filling representation with the two ligands coloured separately, emphasising the helical nature and the twisting of the ligand. Hydrogens are omitted for clarity.

units. The twisting of the ligand strand (essential for helicate formation) takes place primarily about the central N–N bond (dihedral angle 47°), but also within the pyridylimine units (dihedral angles 10° , 26°). In this structure the bonds to the imino nitrogens (2.179(3), 2.174(3) Å) are significantly longer than those to the pyridyl nitrogens (1.947(3), 1.950(3) Å). The phenyl units twist about the aryl-imine bond (41° , 56°) to allow them to lie approximately co-planar with the pyridyl rings on the adjacent strand. Two of the phenyl rings are π -stacked above the pyridyl rings on the adjacent strand in a typical coplanar offset arrangement (centroid \cdots centroid 3.79 Å). Within the confines of this copper(I) helicate structure, the ligand is insufficiently flexible to permit all four phenyl rings to engage in idealised intra-helicate face–face π -stacking interactions; The remaining two phenyl rings are approximately coplanar with pyridyl rings from the adjacent strand but substantially displaced (centroid–centroid 4.7 Å). Nevertheless these rings do make short inter-ring contacts at ~ 3.5 Å and these probably represent additional weak stacking interactions. The two copper(I) centres are separated by 4.33 Å, the shortest intermetallic separation of the three structures reported herein and consistent with the degree of twisting about the central N–N bond.

Outwith the helix, all four pyridyl rings form face–face π -stacking interactions (centroid–centroid 3.56 Å) with pyridyl groups from adjacent helices, linking the helicates into a three dimensional array (Fig. 6). There are also face–edge π -interactions (CH \cdots π) between phenyl rings on adjacent helicates (CH \cdots centroid 3.1 Å; centroid \cdots centroid 5.1 Å). The anions are packed about the helical cations and there are no

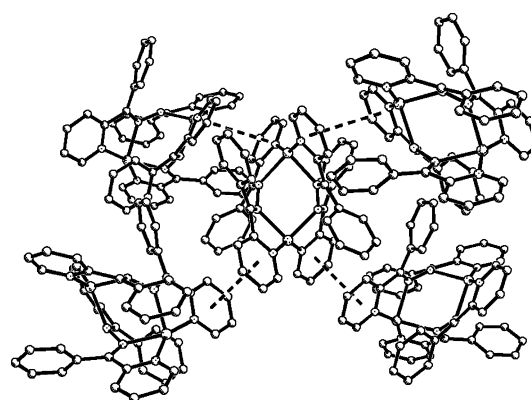


Fig. 6 The packing of the cations in **3**. Hydrogens are omitted for clarity

short contacts from the anions to the metal centres, although there are a considerable number of short F \cdots HC contacts. The crystals are spontaneously resolved and a single enantiomer is present in the crystal structure. Some double-helical silver(I) complexes of L^2 have recently been reported; in each case the double helical array is supported by coordinated anions,¹⁵ in contrast to this copper(I) structure.

Solution structures of the copper(I) complexes

The ^1H NMR spectra of all three copper(I) complexes in deuterated acetonitrile solution are broad. Although they sharpen slightly as the temperature is reduced, they remain broad within the temperature range of the solvent. (Fluxional behaviour is common in acetonitrile solution for copper(I) systems and this is reflected in dramatically lower stability constants for copper(I) bipyridines and pyridylimines in acetonitrile than in other solvents.) The spectra in deuterated acetone solutions are more informative. For complex $[\text{Cu}_n(L^1)_n][\text{PF}_6]_n$ **1**, the ^1H NMR spectrum at room temperature displays five resonance signals corresponding to the imine and pyridine protons in L^1 , indicating a high degree of symmetry in the complex. The signal associated to the pyridine-H 3 proton is considerably broadened, suggesting a fluxional process(es) on the NMR timescale. At low temperature (193 K) the ^1H NMR spectrum of **1** is sharp and well-resolved (confirming that the complex is diamagnetic and that trace cupric ions are not causing the broadening) and reveals ten resonances (two for each proton), all of equally intensity. This could be explained either by a single solution species in which the ligand is unsymmetrical or (more probably) by the presence of two different solution species. To examine this further we recorded ESI and FAB mass spectra. Ions observed in ESI-MS are generally thought to reflect those present in solution. The electrospray mass spectra from acetone solution were uninformative because the samples did not fly well. However, in acetonitrile, peaks corresponding to dimeric and trimeric species were clearly observed together with some weak peaks for tetrameric species (presumably grids). Although the relationship between the ions present in solution and those seen in FAB-MS is less clear (FAB is a secondary ionisation technique from samples mounted in a matrix) the FAB-MS spectrum similarly shows peaks (with the correct isotopic distribution) corresponding to a tetramer, trimer and dimer. The peaks observed could be fragments of a high mass polymeric species, but the two sets of peaks observed in the NMR data (coupled with the solid-state and solution results discussed herein and previously⁵) seems more consistent with an equilibrium in solution between a number of different architectures of which a dimer and a trimer are the two dominant species and are present in a 3 : 2 ratio (giving ligand NMR signals of equal intensity).

^1H NMR spectra for the complex $[\text{Cu}_3(L^2)_3][\text{PF}_6]_3$ **2**, in acetone solution, show some similarities to those of **1**, revealing two

dominant solution species. In contrast to **1**, both species are observed in the room temperature spectrum. At room temperature, the ratio is 3 : 1 and this ratio does not alter significantly when the temperature is lowered to 193 K. Again the sample did not fly in ESI-MS from acetone solution. From acetonitrile solution only dimeric species could be unambiguously observed. FAB studies revealed peaks corresponding to dimers and trimers. The data is again consistent with an equilibrium in solution between a number of different architectures of which two are dominant in acetone solution (a dimer and a trimer).

The ^1H NMR spectrum of the complex $[\text{Cu}_2(\text{L}^3)_2][\text{PF}_6]_2$ **3** in acetone solution shows the presence of a single solution species (within the detection limits of NMR) at both room temperature and low temperature (193 K). At room temperature, the pyridine resonances are sharp but those corresponding to the phenyl groups are broad. On cooling the phenyls sharpen to five sharp resonances. We ascribe this to a ring spinning process which freezes out at low temperature and fixes the phenyls above the pyridine rings, as in the crystal structure, thereby rendering all five phenyl protons inequivalent. In contrast to the other complexes, it did prove possible to record an ESI mass spectrum for this complex from an acetone–methanol mixed solution. Peaks corresponding only to dimer are observed both in ESI-MS and FAB-MS. These data support a dinuclear structure for the complex and the natural consequence of such a stoichiometry, with a rigid binucleating ligand and copper(I) ions preferring a tetrahedral geometry, is the adoption of a double helical array as seen in the X-ray crystal structure.

Structure of the silver(I) hexafluorophosphate complex of L^1

The structure of the copper(I) hexafluorophosphate complex of L^1 contrasts with the structure of the silver(I) trifluoromethanesulfonate complex of L^1 that we have previously reported. With silver(I) a planar dimer, rather than a polymer, was observed (shown schematically in Fig. 7).⁵ The ligand did not make use of its full denticity but instead bound through only three donors and the silver(I) centres occupied a three-coordinate distorted trigonal planar environment. However this structural difference could be due to the different metal or to the different anion or to both. In particular the trifluoromethanesulfonate anion used to crystallise the silver complex might be playing an important role in stabilising the low coordination number (there are long contacts (~ 2.8 Å) to oxygen atoms of the trifluoromethanesulfonate anions).⁵ To allow direct comparison of the effects of the metals we have determined the structure of the silver(I) L^1 complex with hexafluorophosphate anions.

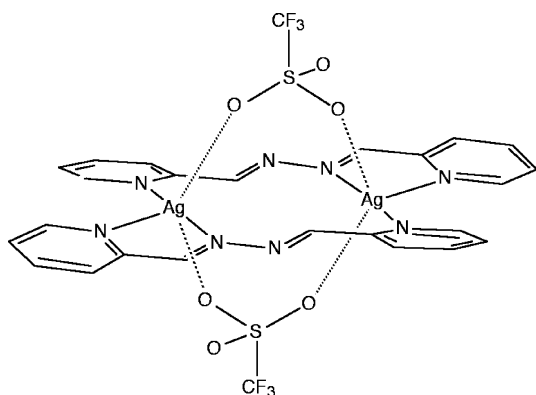


Fig. 7 Schematic of the structure⁵ of the silver(I) complex of L^1 with trifluoromethanesulfonate as anion.

Recrystallisation of the hexafluorophosphate salt from acetonitrile by the slow diffusion of diethylether afforded suitable pale yellow crystals. The crystal structure is complicated by a very unusual form of disorder, involving the pyridine rings

and the silver(I) centres. It appears that planar dimeric $[\text{Ag}_2(\text{L}^1)_2]^{2+}$ cations are again formed (Fig. 8) but are aligned in the mirror planes so that the positioning of the ligands around the silver ions is identical to their positioning adjoining the void outside the cation (Fig. 8(a)). Thus, in any one layer the vacant positions and those occupied by Ag alternate but, because the main inter-layer interactions involve face–face π – π stacking (centroid \cdots centroid 3.76 Å), the next layer may have its silver atoms in the same (Fig. 8(b)) or slipped (Fig. 8(c)) positions. Thus satisfactory refinement was only possible with two alternative sets of Ag positions, each with half occupancy, and two coincident pyridine orientations which differ only in that the pyridine nitrogen and the carbon adjacent to the site of the ring substitution change functions when the Ag atoms are in the alternative positions. This disorder is illustrated in Fig. 8 and the dimeric structure is similar to and consistent with that observed in the trifluoromethanesulfonate salt. However, because of this unusual disorder it is not possible from the crystallography to exclude the possibility that some (or all) of the layers are not layers of dimers but instead polymeric structures as illustrated for one of the layers in Fig. 8(d). Surprisingly therefore, a good quality crystal structure fails to resolve the molecular identity of the species.

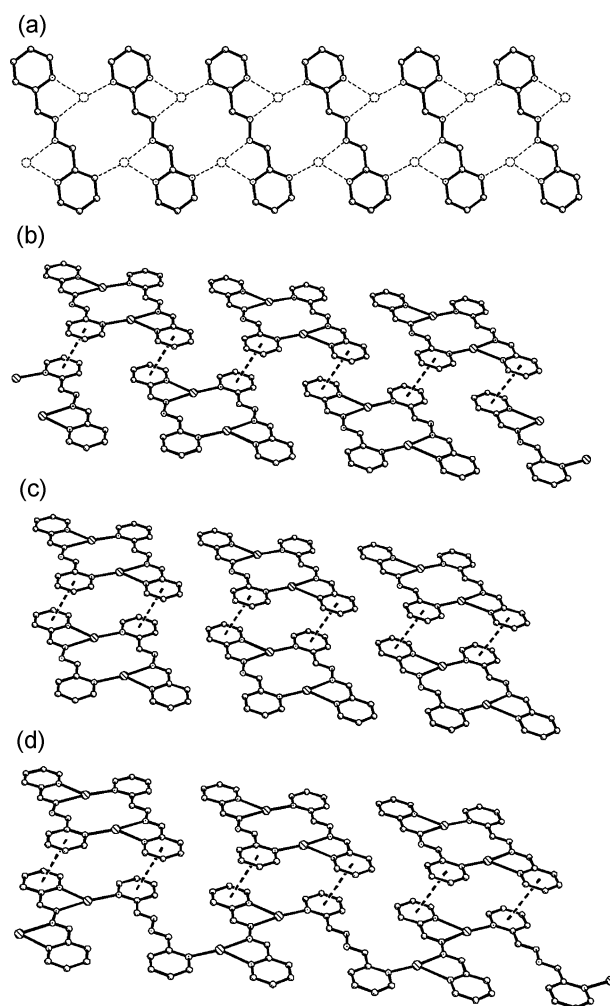


Fig. 8 The structure and relative positioning of the cations in **4**: (a) illustrating the disorder with each silver at half occupancy, (b) dimers stacked with layers in a slipped configuration, (c) dimers stacked with layers in the same position, (d) a layer of dimers stacked with a polymeric layer. Hydrogens are omitted for clarity.

In both possible structures, each silver(I) centre is bound to one didentate pyridylimine and a monodentate pyridine from another ligand. As in the trifluoromethanesulfonate salt, the ligand is planar but does not avail itself of its full denticity. The

silver ions make short contacts to hexafluorophosphate counterions located above and below all the silver sites (Fig. 9. $\text{Ag} \cdots \text{F}$ 2.74 Å) and these anion contacts may contribute to stabilisation of the low formal coordination number. The hexafluorophosphate anions are located between the planes (above and below the disordered silver sites) and make a number of additional short contacts to imino and pyridine protons (18 $\text{F} \cdots \text{H}$ contacts in the range 2.6–2.8 Å per anion).

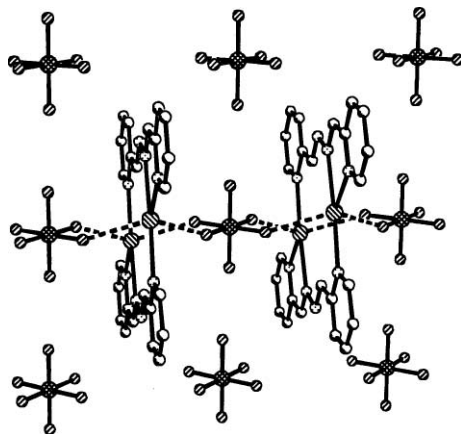


Fig. 9 The interaction and positioning of the anions in **4**. Hydrogens are omitted for clarity.

A very recent report has described the structure of a silver(I) tetrafluoroborate complex of this ligand.¹⁵ The complex has a polymeric structure in which each ligand uses its full donor set and binds as a planar bis-bidentate to silver(I) centres which are in a quite distorted tetrahedral environment. In this respect that structure has some superficial similarity to $[\text{Cu}_n(\text{L}^1)]_n[\text{PF}_6]_n$, however it differs in that the metal centres within a strand are homochiral giving an isotactic polymer which coils to give a helical structure. This complex is reported to have very poor solubility and consequently crystals were prepared by layering separate solutions of ligand and silver salt. In our hands both the trifluoromethanesulfonate and hexafluorophosphate salts which we have structurally characterised have good solubility in donor solvents (such as acetonitrile and nitromethane) and we have prepared analogous tetrafluoroborate salts which have similar solubility. The solubility of the hexafluorophosphate salt would be consistent with the molecular structure being a dinuclear box rather than a polymer. Nevertheless it is clear that under certain crystallisation conditions (solvent and/or anion) a polymeric array may be an alternative structure.

Discussion

The results reported herein give us a greater insight into the forces acting in these systems and which are the basis of the frustration that leads to these libraries of supramolecular architectures in solution:

As anticipated, the metal–ligand interactions dominate. Thus each structure observed with copper(I) satisfies the pseudo-tetrahedral N_4 geometric preference of the copper centre(s). By contrast the silver(I) ion exhibits greater coordination flexibility and a more diverse range of architectures result. The coordination flexibility associated with silver(I) makes it the metal of choice for such a frustration approach to library design. However the less flexible requirements of copper(I) ions do not prevent them from also being used in library design.

In all the solid state structures of the copper(I) and silver(I) complexes of the unsubstituted L^1 the ligand adopts a planar conformation. Only with octahedral metals is there any significant twisting about the N–N bond and these triple helical complexes are unstable and over time form mononuclear bis-ligand complexes in which the ligand acts as a tridentate ligand

regaining an approximately planar conformation.^{5,7} It therefore seems probable that the extended conjugation afforded by ligand planarity is a significant energy term in determining the solid state structure. The planar conformation should also be effective at maximising face–face π -interactions although intriguingly these are not observed in the copper(I) structure described herein implying that, even when employed in concert, they represent a relative weak contribution to the overall competition of forces. For copper(I), which has a strong preference for tetrahedral coordination, the combination of the tetrahedral metal requirements and the ligand planarity can only be truly satisfied by a tetranuclear grid arrangement or a polymeric structure in the solid state. The ligand and metal programming includes no rational control of tacticity and the $\Lambda\Lambda\Lambda$ polymeric structure observed is one of many possibilities, the selection of which is presumably controlled by inter-strand interactions, interactions with the anions and packing considerations. For silver(I) the preference for tetrahedral coordination is less marked and for this ligand donor system planar dinuclear complexes containing three-coordinate metal centres compete energetically in the solid state. This lower coordination geometry preference is seen even in the recently reported polymeric tetrafluoroborate structure¹⁵ in which the tetrahedral geometry at the silver is highly distorted to accommodate intra-strand π -interactions.

In solution, the rigid planarity of the ligand seems less important as an energy term and a library of species is observed. For copper(I), tetrahedral coordination is satisfied through formation of (double-helical) dimers and (circular helical) trimers. Such low nuclearity species are presumably favoured on entropy grounds. As we have previously described⁵ a more diverse library is seen with silver(I): dimers (planar; possibly also double-helicates), trimers, tetramers and triple-helices. It is clearly the greater flexibility in silver(I) coordination number that gives rise to this greater diversity confirming the power of using silver(I) in this ‘frustration’ approach.

The introduction of substituents at the imino carbons dramatically changes the energetic balance in these systems. Not only do the substituents have the potential to engage in additional interactions (e.g. π – π or $\text{CH} \cdots \pi$) but they force ligand twisting about the central N–N bond and thus remove planar conjugation as an important energy term and replace it by a barrier to planarity (although the free ligands can potentially adopt planar conformations in a *trans* conformation about the N–N bond, this is not compatible with metal coordination). The ligand twisting facilitates the formation of discrete (rather than polymeric) arrays in the solid state and so with copper(I) a trinuclear circular helicate is observed with methyl substituents and a dinuclear double-helicate with phenyl substituents.

For L^3 the phenyl rings drive the system solely to a double-helical structure (in both the solid state and solution). The capacity for additional face–face π -stacking supramolecular interactions introduced by the phenyl substituents presumably contribute significantly to the stability of (and favour the formation of) the double-helical structure. Moreover, the steric crowding introduced by the phenyl rings will disfavour cyclic trimers and tetramers.

The double-helical motif induces distortions to the pseudo-tetrahedral bis-pyridylimine coordination geometry (as reflected in the bond lengths in **3**) because of the constraints inherent in the connectivity of the ligands and the absence of a spacer group between the binding units. These distortions are relieved in part in the trinuclear circular-helicate structure and consequently this is the solid-state structure observed for L^2 . The higher order trinuclear structure will, however, be entropically disfavoured; consequently both dinuclear double-helicates and trinuclear circular helicates are observed in solution for the copper(I) complexes of L^1 and L^2 . In this system, the methyl groups are unable to form $\text{CH} \cdots \pi$ interactions within the

discrete or polymeric supramolecular architectures, although we have shown in other systems that such interactions can dramatically influence the architecture adopted.⁶

Conclusions

We have demonstrated that the directly linked bis-pyridylimine systems can support a range of different architectures including polymers, double-helices, planar dimers, triple-helices, trinuclear circular-helices and tetramers. The precise architectural composition of the library is dependent on the choice of metal ion, substituent, solvent and anion and arises from the competition of multiple interactions.

We have shown that copper(I), like silver(I), can be used to assemble such libraries of metallo-supramolecular architectures. However copper(I) is associated with a strong preference for a four-coordinate pseudo-tetrahedral coordination geometry and this requirement dominates and overwhelms other competing interactions. Thus, only architectures that satisfy this requirement are present in the solution library. Silver(I) is more flexible in the coordination number, donor type and geometry adopted and consequently can support a more diverse library of solution architectures.

The results have implications for the selection of metals when designing libraries which respond to external stimuli: Copper(I) prefers an N₄ bis-pyridylimine coordination and the metal centre does not interact directly with the anions. By contrast silver(I) can form long contacts with the anions and this can stabilise lower formal coordination numbers. Consequently silver(I) is more likely to give libraries which are responsive to anions, although more subtle interactions (e.g. CH...X) will also be important.

Even when the metal has a strong N₄ tetrahedral coordination preference, as copper(I), then reaction with a bis-pyridylimine ligand could potentially give an infinite library of species of formula [M_nL_n]ⁿ⁺. Many of these species will satisfy the donor requirements of the metal. It is thus other considerations which determine the structure. Higher nuclearity structures will usually be more flexible and consequently the metal coordination environment will be less subject to the constraints inherent in the ligand. This is illustrated by the difference in bond lengths in the double-helical dimer and the circular-helical trimer. However, entropy will usually favour structures of low nuclearity. For the copper(I) complexes of these ligands this is the primary source of competition (frustration) and for the L¹ and L² complexes a mixture of dimer and trimer is obtained in solution. When these effects are finely balanced, other supramolecular interactions can contribute to the competition and dramatically affect the energetic balance. Thus phenyl substituents introduce both additional π -stacking and steric crowding effects and this is sufficient to drive the system to just the dimeric species. Ligand planarity effects are important but more so in the solid state than in solution as illustrated by the polymeric solid-state structure for the copper(I) complex of L¹ which is a mixture of dimer and trimer in solution. Similarly ligand twisting (induced by the methyl and phenyl substituents) ensures discrete rather than polymeric structures for the copper(I) complexes of L² and L³.

We are currently applying the design principles established using this simple system within a range of other systems.

Experimental

General

All starting materials were purchased from Aldrich and used without further purification. Infrared spectra were recorded with a Perkin Elmer Paragon 1000 FTIR spectrometer from KBr pellets. NMR spectra were recorded on Bruker DPX 400 and DRX 500 instruments using standard Bruker software.

Electrospray Ionisation (ESI) analyses were performed by the EPSRC National Mass Spectrometry Service Centre, Swansea on a Micromass Quatro (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. FAB mass spectra were recorded by the Warwick mass spectrometry service on a Micromass Autospec spectrometer using 3-nitrobenzyl alcohol as matrix. Microanalyses were conducted on a Leeman Labs CE44 CHN analyser by the University of Warwick Analytical Service.

Syntheses

L¹, L² and L³ were prepared according to previously described procedures.⁷ [Ag_n(L¹)_n][PF₆]_n was prepared as previously described.⁵

Complex 1. L¹ (0.042 g, 0.2 mmol) and copper(II) acetate monohydrate (0.04 g, 0.2 mmol) were stirred in methanol (20 mL) for 30 min, filtered through Celite and treated with methanolic ammonium hexafluorophosphate. Dark red crystals appeared within a few min (0.062 g, 74%). The product was filtered off, washed three times with small amounts of cold methanol, and finally dried *in vacuo* over P₄O₁₀. Anal. Calc. for [Cu_n(C₁₂H₁₀N₄)_n][PF₆]_n: C, 34.4; H, 2.4; N, 13.4%. Found: C, 34.5; H, 2.5; N, 13.2%. Mass spectrum (FAB): *m/z* 1529 [Cu₄(L¹)₄(PF₆)₃], 1384 [Cu₄(L¹)₄(PF₆)₂], 1111 [Cu₃(L¹)₃(PF₆)₂], 966 [Cu₃(L¹)₃(PF₆)], 693 [Cu₂(L¹)₂(PF₆)], 546 [Cu₂(L¹)₂], 483 [Cu(L¹)], 273 [Cu(L¹)]. Positive-ion ESI (MeCN): *m/z* 1529 ([Cu₄(L¹)₄(PF₆)₃]⁺), 1111 ([Cu₃(L¹)₃(PF₆)₂]⁺), 903 ([Cu₂(L¹)₂(PF₆)₂]⁺), 773 ([Cu₂(L¹)₂(PF₆)(MeCN)₂]⁺), 693 ([Cu₂(L¹)₂(PF₆)₂]⁺), [Cu₄(L¹)₄(PF₆)₂]²⁺, 565 ([Cu₂(L¹)₂F]⁺), 483 ([Cu(L¹)₂]⁺), [Cu₃(L¹)₃(PF₆)₂]²⁺, 314 ([Cu(L¹)(MeCN)]⁺), 273 ([Cu_n(L¹)_n]ⁿ⁺; n = 1–4), 211 ([LH]⁺). ¹H NMR ((CD₃)₂CO, 400 MHz, 300 K): δ 9.26 (1H, s, H_{imine}), 8.68 (1H, d, *J* = 4.5 Hz, H⁶), 8.06 (1H, br t, H³), 7.81 (2H, m, H⁴, H⁵). ¹H NMR ((CD₃)₂CO, 500 MHz, 193 K): δ 9.45 (1H, s, H_{imine} S2), 9.35 (1H, s, H_{imine} S1), 8.79 (2H, br s, H⁶ S1, H⁶ S2), 8.38 (1H, t, *J* = 7.8 Hz, H⁴ S2), 8.32 (1H, d, *J* = 7.8 Hz, H³ S1), 7.90 (1H, t, *J* = 6.2 Hz, H⁵ S1), 7.81 (1H, t, *J* = 6.2 Hz, H⁵ S2), 7.74 (1H, t, *J* = 7.8 Hz, H⁴ S1), 7.26 (1H, d, *J* = 7.8 Hz, H³ S2). UV-Vis (Me₂CO): 330 (56000), 346 (41000) and 470 (ϵ = 12000 dm³ mol⁻¹ cm⁻¹) nm. Selected IR data (KBr, cm⁻¹): 1618m, 1587m, 1560w, 1474m, 1441m, 1306w, 1258w, 1215m, 1160w, 1105w, 1016w, 839vs, 771m, 558s, 508w. Red crystals suitable for X-ray analysis were grown by slow diffusion of diethyl ether into a solution of complex in acetonitrile.

Complex 2. L² (0.047 g, 0.2 mmol) and copper(II) acetate monohydrate (0.04, 0.2 mmol) were stirred in methanol (15 mL) for 20 min. The dark green solution rapidly turned red. The red solution was filtered and the filtrate treated with methanolic ammonium hexafluorophosphate. On cooling a deep red precipitate formed. This was collected by vacuum filtration, washed with a small amount of cold methanol and dried *in vacuo* under P₄O₁₀ (0.042 g, 47%). Anal. Calc. for [Cu₃(C₁₄H₁₄N₄)₃][PF₆]₃·CH₃OH: C, 37.6; H, 3.4; N, 12.2%. Found: C, 37.7; H, 3.2; N, 11.9%. Mass spectrum (FAB): *m/z* 1195 [Cu₃(L²)₃(PF₆)₂], 1050 [Cu₃(L²)₃(PF₆)], 747 [Cu₂(L²)₂(PF₆)], 603 [Cu₂(L²)₂], 365 [Cu₂(L²)], 301 [Cu(L²)]. Positive-ion ESI (MeCN): *m/z* 747 ([Cu₂(L²)₂(PF₆)]⁺), 603 ([Cu₂(L²)(L²-H)]⁺), 383 ([Cu(L²)(MeCN)₂]⁺), 342 ([Cu(L²)(MeCN)]⁺), 301 ([Cu_n(L²)_n]ⁿ⁺; n = 1, 2), 239 ([LH]⁺). ¹H NMR ((CD₃)₂CO, 400 MHz, 300 K): δ 8.97 (1H, d, *J* = 5.0 Hz, H⁶ S2), δ 8.96 (3H, d, *J* = 5.1 Hz, H⁶ S1), 8.28 (6H, m, H³, H⁴ S1), 8.25 (2H, m, H³, H⁴ S2), 7.91 (3H, ddd, *J* = 7.3, 5.2, 1.5 Hz, H⁵ S1), 7.87 (1H, ddd, *J* = 7.0, 4.9, 1.2 Hz, H⁵ S2), 2.64 (3H, s, CH₃ S2), 2.46 (9H, s, CH₃ S1). ¹H NMR ((CD₃)₂CO, 500 MHz, 193 K): δ 9.19 (1H, d, *J* = 4.8 Hz, H⁶ S2), δ 8.96 (3H, d, *J* = 4.8 Hz, H⁶ S1), 8.34 (3H, t,

Table 1 Crystallographic data for complexes 1–4 and details of refinement

Complex	1	2	3	4
Empirical formula	Cu ₂ (C ₁₂ H ₁₀ N ₄) ₂ (PF ₆) ₂ ·(C ₂ H ₃ N) ₃	Cu ₃ (C ₁₄ H ₁₄ N ₄) ₃ (PF ₆) ₃ ·(C ₂ H ₃ N) ₂ (C ₄ H ₁₀ O) _{0.5}	Cu ₂ (C ₂₄ H ₁₈ N ₄) ₂ (PF ₆) ₂ ·(CH ₄ O) _{0.5} (H ₂ O) _{0.5}	Ag(C ₁₂ H ₁₀ N ₄)(PF ₆)
Formula weight	960.66	1459.57	1166.90	463.08
Temperature/K	180(2)	180(2)	180(2)	180(2)
Crystal system	Orthorhombic	Triclinic	Trigonal	Monoclinic
Space group	<i>Pna</i> 2 ₁	<i>P</i> $\bar{1}$	<i>P</i> 3 ₂ 21	<i>C</i> 2/ <i>m</i>
<i>a</i> /Å	15.491(2)	12.3610(15)	16.9903(10)	16.8803(7)
<i>b</i> /Å	15.0327(19)	12.6347(13)	16.9903(10)	6.7726(3)
<i>c</i> /Å	16.746(2)	21.7155(13)	14.7009(15)	6.4436(2)
<i>a</i> /°	90	97.193(10)	90	90
<i>β</i> /°	90	102.657(11)	90	99.215(2)
<i>γ</i> /°	90	110.031(11)	120	90
<i>U</i> /Å ³	3899.6(9)	3033.8(5)	3675.2(5)	727.15(5)
<i>Z</i>	4	2	3	2
<i>D_c</i> /g cm ⁻³	1.636	1.598	1.582	2.115
<i>μ</i> /mm ⁻¹	1.270	1.224	1.026	1.568
Reflections collected	17801	14388	23499	2356
Independent reflections (<i>R</i> _{int})	5040 (0.1829)	9321 (0.0843)	6016 (0.0581)	962 (0.0888)
Parameters	507	786	351	74
Goodness-of-fit on <i>F</i> ²	1.049	0.943	1.061	0.943
Final <i>R</i> indices [<i>I</i> > 2σ(<i>I</i>)]	<i>R</i> ₁ = 0.0742 <i>wR</i> ₂ = 0.1044	<i>R</i> ₁ = 0.0751 <i>wR</i> ₂ = 0.1280	<i>R</i> ₁ = 0.0487 <i>wR</i> ₂ = 0.1145	<i>R</i> ₁ = 0.0750 <i>wR</i> ₂ = 0.170
(all data)	<i>R</i> ₁ = 0.1901 <i>wR</i> ₂ = 0.1417	<i>R</i> ₁ = 0.1933 <i>wR</i> ₂ = 0.1717	<i>R</i> ₁ = 0.0780 <i>wR</i> ₂ = 0.1328	<i>R</i> ₁ = 0.1115 <i>wR</i> ₂ = 0.1800

J = 7.5, H⁴ S1), 8.28 (3H, d, *J* = 7.5 Hz, H³ S1), 8.24 (2H, m, H³, H⁴ S2), 7.95 (4H, m, H⁵ S1, H⁵ S2), 2.73 (3H, s, CH₃ S2), 2.47 (9H, s, CH₃ S1). UV–Vis (Me₂CO): 328 (48000), 380sh (22000) and 470sh (ε = 9000 dm³ mol⁻¹ cm⁻¹) nm. Selected IR data (KBr, cm⁻¹): 3414w, 2926m, 2854w, 1601m, 1570sh, 1474w, 1441m, 1376w, 1328w, 1258w, 1167w, 1052w, 1027w, 841vs, 776s, 741w, 558s. X-Ray quality, red crystals were obtained from a saturated acetonitrile solution by slow diffusion of diethyl ether.

Complex 3. L³ (0.091 g, 0.25 mmol) and copper(II) acetate monohydrate (0.050 g, 0.25 mmol) were stirred in methanol (20 mL) for 30 min and the solution then treated with methanolic ammonium hexafluorophosphate. Slow evaporation of the solvent at 4 °C yielded red needles of compound **3** (0.078 g, 55%). Anal. Calc. for [Cu₂(C₂₄H₁₈N₄)₂][PF₆]₂: C, 50.5; H, 3.2; N, 9.8%. Found: C, 50.2; H, 3.2; N, 9.7%. Mass spectrum (FAB): *m/z* 997 [Cu₂(L³)₂(PF₆)], 852 [Cu₂(L³)₂], 425 [Cu(L³)]. Positive-ion ESI (MeOH–acetone): *m/z* 997 ([Cu₂(L³)₂(PF₆)⁺), 787 ([Cu(L³)₂]⁺), 425 ([Cu₂(L³)₂]²⁺, [Cu₂(L³)₂]⁺), 363 ([LH]⁺). ¹H NMR ((CD₃)₂CO, 400 MHz, 300 K): δ 8.34 (1H, d, *J* = 5.0 Hz, H⁶), 8.24 (1H, td, *J* = 7.9, 1.8 Hz, H⁴), 7.83 (1H, ddd, *J* = 7.9, 5.0, 1.2 Hz, H⁵), 7.71 (1H, d, *J* = 8.0 Hz, H³), 7.59 (1H, t, *J* = 7.5 Hz, H_{para}), 7.31 (4H, br, 2H_{meta}, 2H_{ortho}). ¹H NMR ((CD₃)₂CO, 500 MHz, 193 K): δ 8.28 (1H, t, *J* = 7.8 Hz, H⁴), 8.21 (1H, d, *J* = 4.7 Hz, H⁶), 7.98 (1H, d, *J* = 7.5 Hz, H_{ortho}), 7.83 (1H, dd, *J* = 7.9, 4.9 Hz, H⁵), 7.74 (1H, d, *J* = 7.9 Hz, H³), 7.56 (1H, t, *J* = 7.2 Hz, H_{para}), 7.47 (1H, t, *J* = 7.5 Hz, H_{meta}), 7.0 (2H, m, H_{ortho}, H_{para}). Selected IR data (KBr, cm⁻¹): 3441w, 3086w, 1636m, 1597m, 1570w, 1543m, 1492w, 1466m, 1441s, 1335s, 1311w, 1256m, 1165w, 1106w, 1022w, 1000w, 970w, 838vs, 795m, 773m, 739m, 702s, 660m, 558s.

X-Ray crystallography

Crystallographic data are collected in Table 1 with selected bond lengths and angles in Table 2. Data were measured at 180 K with a Siemens-SMART-CCD diffractometer¹⁶ equipped with an Oxford Cryosystem Cryostream Cooler.¹⁷ Refinements used SHELXTL.¹⁸ The structures were solved by direct methods with additional light atoms found by Fourier methods. Hydrogen atoms were added at calculated positions and refined using a riding model with freely rotation methyl groups. Anisotropic displacement parameters were used for all

Table 2 Selected bond lengths (Å) and bond angles (°) for complexes 1–4

	Metal center	M–N _{pyridyl}	M–N _{imine}	Bite angle
Complex 1	Cu1	2.005(13)	2.014(10)	81.6(5)
		2.035(11)	2.019(11)	81.3(4)
Complex 2	Cu1	2.003(11)	2.064(11)	80.7(5)
		2.016(12)	2.006(12)	79.6(5)
Complex 3	Cu1	1.986(8)	2.048(8)	80.3(3)
		1.996(8)	2.039(7)	80.7(3)
		2.023(7)	2.025(8)	80.3(3)
Complex 4	Ag1	2.024(8)	2.031(7)	80.0(3)
		1.994(7)	2.020(6)	80.3(3)
Complex 3	Cu2	2.016(8)	2.015(8)	79.9(3)
		1.946(3)	2.179(3)	80.08(13)
Complex 4	Ag1	1.949(3)	2.174(3)	80.05(12)
		2.462(7)	2.377(7)	70.1(2)
		2.205(6)		

non-H atoms; H-atoms were given isotropic displacement parameters equal to 1.2 (or 1.5 for methyl hydrogen atoms) times the equivalent isotropic displacement parameter of the atom to which the H-atom is attached.

For **1**, systematic absences indicated either space group *Pna*2₁ or *Pnam* (non-standard setting of *Pnma*). The former was chosen on the basis of intensity statistics and shown to be correct by successful refinement. There are three acetonitrile solvent molecules in the asymmetric unit. The absolute structure of the individual crystal chosen was checked by refinement of a delta-*f*^o multiplier, absolute structure parameter *χ* = 0.02(3). Floating origin constraints were generated automatically.

For **2**, the data shows no systematic absences. The structure was solved in space group *P*1 and the centre of inversion then located and the solution converted to *P* $\bar{1}$, which was shown to be correct by successful refinement. The unit cell contains two cyclic trimers of opposite configuration and six PF₆ counter ions some of which are disordered. There are additionally four molecules of acetonitrile solvent in the unit cell. In the face-to-face cavity between two trimers, diffuse electron density was modelled as a disordered diethyl ether molecule with partial occupancy.

For **3**, systematic absences and Laue symmetry indicated either space group *P*3₂21 or *P*3₁21; the latter was chosen and shown to be correct by successful refinement and the value of the Flack parameter (absolute structure parameter

$\chi = -0.009(16)$). The asymmetric unit includes a water molecule and a methanol solvent. The copper and phosphorus atoms and the solvent water and methanol lie on two-fold axis special positions. There is disorder in one of the PF₆ counter ions. The solvent molecules were modelled with 0.5 occupancy.

For **4**, the diffraction pattern showed strong diffuse rings corresponding to a doubling of the *c*-axis, but diffuse peaks in the rings suggested a possible doubling of *a* and *b* as well. However, the structure was solved and refined using only the ordered sub-cell. The systematic absences indicated either space group *C2/m*, *C2* or *Cm*. *Cm* was initially chosen for structure solution, but the presence of a centre of inversion allowed conversion to *C2/m* which was shown to be correct by successful refinement. The silver ion and ligand are in a mirror plane (position 4i) with the Ag ions disordered between two positions (given half occupancy). The ambiguity in the identity of N1/C1 and N5/C5 was modelled by placing a half N and a half CH at each position. The PF₆ ion has *2/m* symmetry (position 2a).

CCDC reference numbers 197156–197159.

See <http://www.rsc.org/suppdata/dt/b2/b211005a/> for crystallographic data in CIF or other electronic format.

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