

Supramolecular Circular Helicates Formed by Destabilisation of Supramolecular Dimers

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Abstract: The effect of changes in the angles at the connection points of linear/circular helicates is explored as a route to control the nuclearity and architecture of metallo-supramolecular arrays. This effect is probed by changing the geometry of the metal centre used to assemble bis-pyridylimine ligands that contain a 1,3-bis(amino-methyl) benzene spacer group. Tetrahedral metal ions favour linear dimers,

whereas octahedral nickel(II) predominantly gives a triangular circular helicate. Five-coordinate copper(II) falls in the middle of these extremes and results in the formation of solvent-depen-

dent mixtures of dimer and trimer. The trinuclear, triangular, circular helicate structures, which result from coordination to copper(II) and nickel(II), are structurally characterised by X-ray crystallography and reveal that the units can aggregate into hexagonal arrays that contain anion-filled tube-like channels in the solid state.

Keywords: circular helicates •
dinuclear double helicates •
N ligands • pyridylimine ligands •
supramolecular chemistry

Introduction

The supramolecular synthetic approach permits the design of arrays with complex molecular architectures whose dimensions are greater than those found in traditional covalent-based chemistry.^[1,2] This ability to control architecture at the molecular level is important because it offers a potential route to systematically encode the properties of a molecule or material; indeed this is a common theme in biological systems.^[3] Double-helical molecular architectures have been influential in the development of supramolecular chemistry by providing a forum for establishing construction principles and retain a unique fascination because life itself is encoded within double-helical DNA arrays.^[4-6] Dimeric M_2L_2 systems (helicates and boxes)^[7,8] and tetrameric M_4L_4 systems (squares and tetrahedra)^[9-11] are well established supramolecular architectures, whereas in contrast the assembly of triangular M_3L_3 arrays has received little attention. The triangle represents an important architectural element because of the many polyhedra that are based on this unit. The trinuclear trimer or triangle also represents the lowest possible nuclearity of circular helicates. Circular helicates are related to conventional (linear) helicates in that ligands wrap around metal centres, however, the metals are located

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in a cyclic (rather than linear) arrangement.^[7,8,12–19] In nature cyclic motifs occur in plasmid DNA and elsewhere.^[3]

In some systems, a mixture of different circular helicates may be formed in solution, which leads to a real or virtual library of structures. These oligomeric circular or linear structures (of different nuclearity) will generally possess similar metal coordination. Consequently, it can be weaker energetic contributions, such as inter- or intra-strand interactions,^[13,18] solvent interactions or anion binding,^[15,19] that determine which structure dominates. There have been several elegant studies that use anions to influence the structure formed, notably, those of Lehn and co-workers, who used different anions to select between tetra, penta and hexa nuclear stoichiometry.^[15,19] and Dunbar and co-workers (tetramer/pentamer).^[9] We have explored the use of inter- and intra-strand interactions to switch between a linear dinuclear helicate and a circular trinuclear helicate.^[18] Previous approaches focused on those weaker interactions, whereas an alternative approach that has not previously been explored would be to change the geometry at the metal centre. As this geometry change will directly affect the angles at the connection points of a circular helicate, this could be a powerful alternative approach to controlling the nuclearity and is the subject of the study described herein.

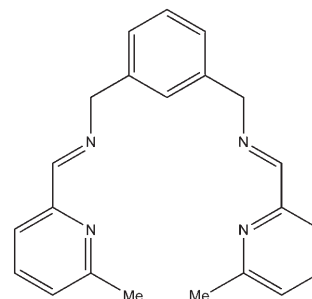
Our previous studies into the design of sophisticated supramolecular architectures has built on an imine-based strategy that allows such arrays to be assembled quickly and easily in simple mixing reactions.^[20–26] Freed from the constraints of extensive ligand synthetic procedures, we have systematically explored how ligand design can address the challenge, not only of defining the supramolecular architecture or superstructure, but also of defining the precise topography or conformation of this superstructure. For example, we have illustrated how spacer groups can be used to control the directionality of ligand strands within a helical array and also give distinct (major and minor) helical grooves.^[22] We have also explored the use of secondary events to aggregate such architectures.^[26]

Herein we describe a pyridylimine ligand system that can support dinuclear double helicates and circular helicates with copper(I) and silver(I) in which the average nuclearity of the library is solvent dependent and affected by anions. When the metal coordination geometry is changed to octahedral, the system is perturbed and produces predominantly trinuclear circular helicates (or triangles). In the solid state secondary interactions lead to hexagonal arrays that contain large channels.

Results and Discussion

Ligand **L** was prepared by the condensation of 6-methylpyridine-2-carboxaldehyde (2 equiv) with 1,3-bis(aminomethyl)benzene. 1,3-Phenylene spacers have been successfully employed in polypyridine chemistry to form robust double helicates with tetrahedral and octahedral metal cations^[27] and these helicates have been cyclised to give high yields of mo-

lecular trefoil knots.^[28] Most recently that spacer has been incorporated into bis-diketonate ligands, which enables the formation of triple and quadruple helicates with lanthanide ions.^[29] The 1,3-phenylene unit imparts twisting to the ligand strand, which is essential for helicate formation.



The 1,3-bis(methylene)phenylene spacer employed herein contains two additional methylene units in the spacer and these are expected to impart greater flexibility into the ligand. Despite the increased flexibility, the spacer will prevent both pyridylimine units from binding to the same metal centre and thereby promote the formation of multinuclear arrays.

Coordination to tetrahedral monocations: Reaction of this bis-pyridylimine ligand with metals that prefer a four-coordinate tetrahedral geometry (such as copper(I) and silver(I)) is expected to give complex cations of stoichiometry $[M_nL_n]^{n+}$.

Silver(I) complex formation was achieved by mixing **L** (1 equiv) with silver(I) acetate (1 equiv) in methanol. Addition of methanolic ammonium hexafluorophosphate or tetrafluoroborate afforded a white solid. The copper(I) complex was prepared by mixing **L** (1 equiv) with $[Cu(CH_3CN)_4][BF_4]$ (1 equiv) in methanol to give a red solution from which a red solid precipitated on cooling. The infrared spectra of these copper(I) and silver(I) complexes show absorptions that correspond to the coordinated ligand and the counterion. Partial microanalytical data were consistent with the formulation $[M_n(L)_n][X]_n$ (X = counterion) and the FAB mass spectra had signals (with the correct isotopic distributions) that corresponded to $[M_2L_2X]$, $[M_2L_2]$ and $[ML]$, which suggested a dinuclear formulation. Signals that corresponded to higher nuclearity complexes were not observed. For an $[M_2L_2]^{2+}$ cation, there are two possible conformations, a *rac* (helical) isomer in which both metal centres have the same configuration or a *meso* (box) isomer in which the two metals have opposite configurations.^[7,18,30]

The room temperature 400 MHz 1H NMR spectrum of the copper(I) complex in acetonitrile shows a single set of resonances. However, the resonance that corresponds to the CH_2 groups of the spacer unit is considerably broadened. As the temperature is increased the broad CH_2 resonance sharpens to give a singlet. As the temperature is reduced, the resonance splits into two doublets, which are both sharp

by 253 K (see the Supporting Information). Splitting of the CH₂ unit would be consistent with either the *rac* (helical) isomer (diastereotopic CH₂ protons) or the *meso* (box) isomer (two conformationally different protons, one pointing out of the box and the other pointing inwards). The fluxional process that renders the protons equivalent could involve ligand dissociation from one or both metal ions, or involve intramolecular torsion. The signals coalesce at 308 K and at this temperature we estimate that the rate of interconversion is 490 s⁻¹ and the barrier to inversion is 67 kJ mol⁻¹. At 233 K, small resonances that correspond to a second minor solution component can be discerned in the baseline.

The behaviour of the silver(I) complex in acetonitrile is similar (see the Supporting Information). At room temperature the CH₂ signal is broadened (though less so than in the copper(I) complex) and as the temperature is lowered the signal starts to split into two doublets. However, coalescence occurs at a lower temperature (≈250 K) than in the copper(I) complex and the two doublets remain somewhat broadened at 233 K. However, at this temperature traces of a second minor species can again be observed in the baseline. The imine signal appears as a singlet at room temperature, but as the temperature is lowered the silver(I)–imine coupling (7.9 Hz) is resolved. The absence of a silver–imine coupling at room temperature in acetonitrile is not unusual and is consistent with rapid on–off dissociation of the ligand in this solvent.^[22,26,30]

Electrospray mass spectra of these silver(I) and copper(I) complexes in acetonitrile revealed dominant signals that corresponded to dinuclear species ([M₂L₂]²⁺ and [M₂L₂(X)₂]⁺; X = BF₄ or PF₆). No higher nuclearity peaks were observed and this implied that the major and minor species in solution in acetonitrile were dinuclear species (the *rac* and *meso* isomers).

To further probe the solution behaviour, ¹H NMR spectra of the copper(I) complex were recorded in acetone and dichloromethane. Dissociative processes observed in acetonitrile are often slower in these solvents.^[18,30] At room temperature in both solvents, the CH₂ groups of the dominant solution species appeared as two sharp doublets. However, in both solvents more than one species was present in solution. In acetone, three distinct imine resonances and three methyl resonances were observed. The resonances of the principal species indicated that this comprised approximately 80% of the material in solution. This species is symmetrical about the central spacer and the two halves of the ligand are equivalent. Within experimental error, the other two imine signals integrate to the same magnitude (as do the two methyl resonances). It is unclear whether this represents a single minor species in solution in which the ligand is non-symmetrical or whether two minor species in solution are present in equal quantities. Both CH₂ groups associated with these species in solution appear as two doublets. COSY cross peaks allow the connectivity of imine and CH₂ resonances to be established, however, the weak and overlapping nature of the other peaks meant that neither COSY

nor NOE experiments were able to establish whether the minor component in solution is one or two species. Some other very small peaks could be discerned in the baseline, which implied that further species were present in acetone in very small amounts. For the major component in solution, an NOE was observed between the Me group and one of the CH₂ protons; this must represent an interstrand NOE.

Addition of the chiral anion tetrabutylammonium tris(tetrachlorobenzenediolato) phosphate (Λ-trisphat)^[31] perturbed the solution equilibrium to enhance the amount of the minor component(s). The two sets of resonances for the minor component(s) both increased, but no significant splitting of resonances was observed.

Electrospray mass spectra of the copper(I) complex in acetone revealed dominant signals that correspond to dinuclear species ([Cu₂L₂]²⁺ and [Cu₂L₂(BF₄)₂]⁺). However, a weaker peak that corresponds to [Cu₃L₃(BF₄)]²⁺ was observed together with an even weaker signal that corresponds to [Cu₄L₄(BF₄)]³⁺. Addition of trisphat causes a small increase in the amount of the trinuclear signal. This data implies the presence in solution of not only a dinuclear array (*rac* or *meso* or both), but also of small amounts of circular helicates with a nuclearity of three and four.

The ¹H NMR spectra of solutions of the complex in dichloromethane reveal the presence of four different imine resonances (and four corresponding pairs of CH₂ doublets) in a ratio of 65:15:15:5, together with some further weak resonances in the baseline whose presence is too small to accurately quantify. As in acetone, the weak and overlapping nature of the other peaks meant that neither COSY nor NOE experiments were able to establish whether the two imine resonances that each correspond to 15% of the species present in solution represent one or two species. Upon titration of the chiral trisphat anion into the solution, a number of shifts were induced, which indicated that the anion binds to the metal complexes. Although some new resonances appear and others disappear, the combination of anion-induced shifts in the position of the resonance and the effects of the anion on the solution equilibria between the solution species complicates detailed analysis and no information could be gleaned about the nature (*meso* or *rac*) of the species in solution.

Electrospray mass spectra of the complex in dichloromethane revealed signals that corresponded to four [Cu_nL_n]ⁿ⁺ species with a nuclearity of *n* = 2 to 5. Of these peaks, those that are dominant again correspond to dinuclear species ([Cu₂L₂]²⁺ and [Cu₂L₂(BF₄)₂]⁺) with weaker signals that correspond to [Cu₃L₃(BF₄)]²⁺ and [Cu₄L₄(BF₄)]³⁺ and a very weak signal that corresponds to [Cu₅L₅(BF₄)₂]³⁺. This was consistent with the four species observed in solution by NMR spectroscopy and implied a library of double and circular helicates (nuclearity 2–5) in dichloromethane. Electrospray mass spectra of the complex in a mixture of dichloromethane/methanol revealed signals that corresponded to [Cu_nL_n]ⁿ⁺ species with a nuclearity of *n* = 2 to 4, in which the percentage of the *n* = 3 and *n* = 4 species was higher than that in acetone.

The results imply that for the copper(I) complexes the $[M_2L_2]^{2+}$ cation is the dominant species in solution, although smaller amounts of other (circular) architectures are present. Unfortunately, despite numerous attempts, neither the copper(I) nor the silver(I) complexes have afforded material that was suitable for X-ray analysis.

Dications: Whereas the interaction of tetrahedral metal complexes with **L** primarily gives dimeric species, we reasoned that the different geometries of higher metal coordination numbers (5 or 6) might change the selection of the architecture obtained. In particular, moving from tetrahedral to octahedral geometries will affect the relative spatial distributions of the ligands and this effect might be mechanically relayed through the ligand backbone to cause a change in nuclearity (Figure 1). To explore this effect, we have examined the copper(II) and nickel(II) complexes of this ligand.

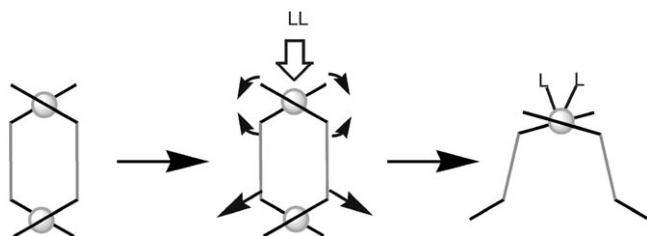


Figure 1. Destabilisation of dinuclear dimers on moving from tetrahedral to octahedral metal cations.

Commonly, reaction of a helicating ligand with an octahedral dication leads to the formation of a triple-stranded helicate. For example, the groups of Lehn and Williams have described bipyridyl and benzimidazole ligand systems with which a double helicate is formed with copper(I), whereas with metals such as nickel(II) or cobalt(II) a triple-stranded helicate resulted.^[32] Indeed we have described triple helicates by interacting five- and six-coordinate metals with other bis-pyridylimine systems^[21,25] and also reported systems in which both double- and triple-stranded helicates can be formed.^[18,21,24,30] However, in other cases the ligand is insufficiently flexible for three such ligands to wrap about the metal–metal axis, and double helicates that contain vacant coordination sites are formed with octahedral metal ions. A prime example of this is the ligand in which two bipyridine units are connected by a 1,3-phenylene spacer, which gives double helicates with both tetrahedral and octahedral metal ions.^[27] Similarly, ligand system **L** is insufficiently flexible for three ligands to wrap around two metals to form triple helicates.

Coordination of **L to copper(II):** Coordination of **L** to copper(II) was achieved by briefly stirring the ligand (1 equiv) with copper(II) acetate (1 equiv) monohydrate in a 1:1 solution of methanol/ethanol in an ice bath. Following treatment of the solution with ammonium hexafluorophosphate, a

green crystalline precipitate was collected by vacuum filtration. Prolonged stirring led to reduction of the copper centre and the formation of the red copper(I) complex. Similarly attempts to recrystallise the complex from acetonitrile also led to rapid reduction to the red copper(I) complex. Partial microanalytical data for the green copper(II) complex were consistent with the formulation $[Cu_n(L)_n(C_2H_3O_2)]_n[PF_6]_n$. The crystalline material that precipitated from solution proved to be suitable for X-ray crystallography and the structure revealed a trinuclear cation with a triangular circular helicate architecture (Figure 2).

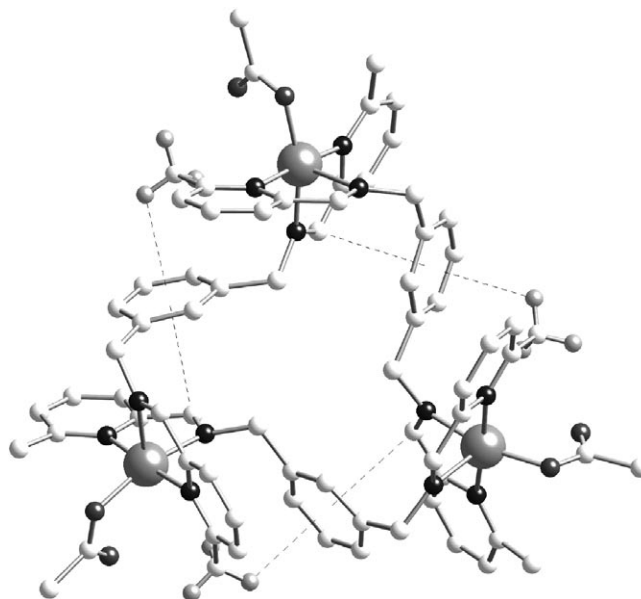


Figure 2. The structure of the trinuclear circular-helical cation in the complex $[Cu_3(L)_3(OAc)_3][PF_6]_3$. For clarity, hydrogens are omitted except for those on the methyl groups, which are included to illustrate the $CH\cdots\pi$ interactions.

The copper(II) ions in the structure adopt a five-coordinate geometry (distorted square pyramidal) bound to two pyridyl–imine binding sites and with the remaining coordination site filled by an acetate molecule bound through one oxygen atom (Cu–O 1.942(6) Å; the second acetate oxygen is located 2.87 Å from the copper centre). The axial coordination site of this pseudo-square pyramidal coordination environment is occupied by an imine nitrogen, and the bond length from the metal to this axial nitrogen is significantly longer (2.217(7) Å) than those to the other imine nitrogen (2.022(6) Å) and pyridine nitrogen atoms (2.070(7) and 2.062(7) Å). The copper(II) centres are separated by 8.89 Å and the ligands are wrapped around the copper–copper vectors, which gives rise to the circular helicate structure. The ligands are not wrapped symmetrically about these vectors and consequently the upper and lower triangular faces of this trinuclear circular helicate are not identical (see Figure S3 in the Supporting Information). However, in contrast to other systems that we have described,^[13,18] this asymmet-

ric wrapping does not lead to substantial bending or arcing of the helicate to give a bowl-shape configuration and the structure instead remains relatively flat and resembles a triangular disc. Within the circular-helicate structure, inter-strand non-covalent interactions were also observed. The central phenylene ring of each strand is face-to-face π stacked with an imine unit from another strand ($C\cdots$ centroid = 3.41 Å) and the same phenylene forms a $CH\cdots\pi$ contact with a methyl group ($H\cdots$ centroid = 3.02 Å) from the third strand.

Anions are located in the cavities of both triangular faces of the circular helicate (Figure 3). The anion located at the upper face is very disordered and, consistent with this,

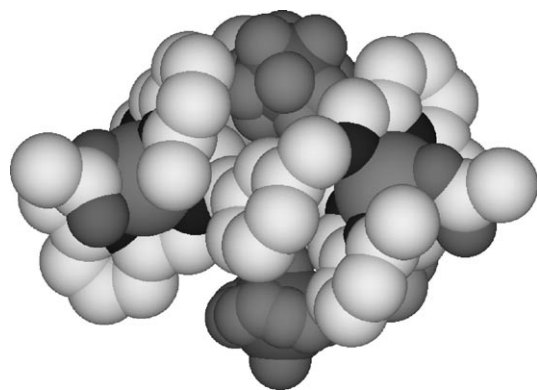


Figure 3. Location of anions within the upper and lower cavities of the trinuclear circular-helical cations in the complex $[Cu_3(L)_3(OAc)_3][PF_6]_3$. Hydrogens are omitted for clarity. Both anions exhibit disorder and the disordered positions are shown.

makes no significant $CH\cdots F$ contacts. Instead it resides in the triangular cavity created by the faces of the pyridyl rings and adjacent imine units. We have previously observed similar anion binding in a triangular cavity formed from a pyridylketazine ligand.^[24] In contrast, the anion in the lower cavity is only disordered about one axis. The fluorine atom on this axis, which projects into the cavity of the circular helicate, forms three short $F\cdots HC$ contacts to the three imino protons ($CH\cdots F = 2.68$ Å) that may serve to locate the anion.^[33]

The circular helicates pack together through face-to-face π - π interactions in which pairs of face-to-face (imine-pyridyl) π - π interactions link the pyridylimine units on the upper faces ($C_{\text{imine}}\cdots$ centroid_{pyridine} = 3.83 Å, $C_{\text{imine}}\cdots C_3 = 3.54$ Å) (see Figure S4 in the Supporting Information) and these interactions link the circular helicates together into a hexagonal array (Figure 4). The helicity of the circular helicates alternates around the hexagonal unit. The hexagons are linked together by further inter-circular helicate face-to-face π - π interactions between the remaining pyridyl rings (those on the more open, "lower", triangular faces of the circular helicates; centroid \cdots centroid = 3.74 Å, centroid $\cdots C_3 = 3.38$ Å); a large hexagonal tube-like channel approximately 1.2 nm in

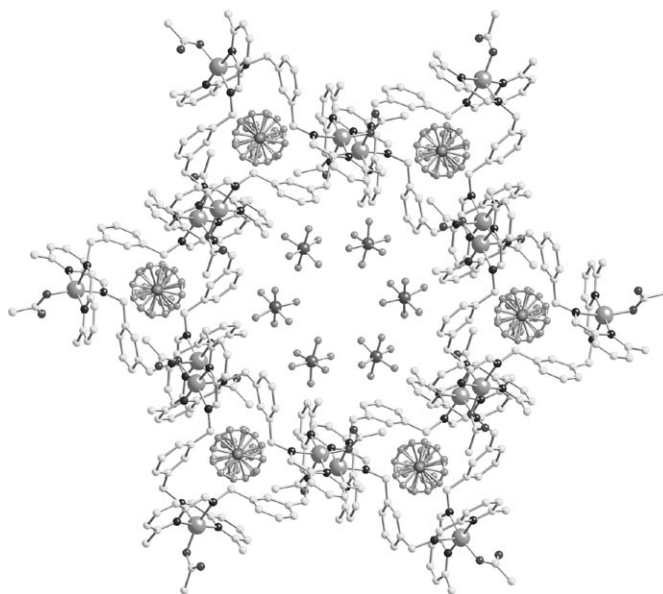


Figure 4. Packing of the trinuclear circular-helical cations and the hexafluorophosphate anions in the complex $[Cu_3(L)_3(OAc)_3][PF_6]_3$. Hydrogens are omitted for clarity.

diameter is created in which the remaining hexafluorophosphate anions reside together with some disordered solvent.

It is intriguing to compare the structure that is formed with that of the bowl-shaped triangles which we have recently described.^[13,18] In that system the bowl shape disfavoured planar packing, and as a consequence, a tetrahedral ball structure was created, in the centre of which hexafluorophosphate anions were bound. In this case, the more planar nature of the triangular circular helicate facilitated planar packing and this led to a hexagonal array, again with a cavity in which anions are located. The assembly of an anion-filled tube-like channel from readily prepared pyridylimine helicates has precedent from the packing of arch-shaped double helicates,^[26a] although the hexagonal channel formed herein is substantially larger.

ESI mass spectrometry was used to probe whether or not this trinuclear architecture was retained in solution. Analysis of methanolic solutions of the complexes revealed the presence of two solution species. From a solution in methanol, the spectrum showed signals that corresponded to trinuclear and dinuclear species, which indicated that there was an equilibrium between dimeric and trimeric species in solution (Figure 5, bottom). From a solution in acetonitrile, the spectrum also revealed dimer and trimer signals, however, in this solvent the dimer was the dominant species (Figure 5, top).

These results indicated that the architectures formed were solvent dependent and suggested that, whereas the trimer was favoured by the incorporation of the five-coordinate metal ion, the effect was not sufficient to promote total transformation to the trimer in solution. Next we turned to an octahedral metal centre, nickel(II).

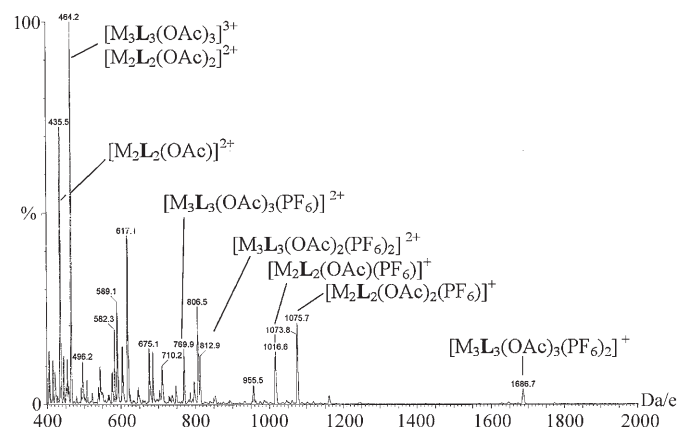
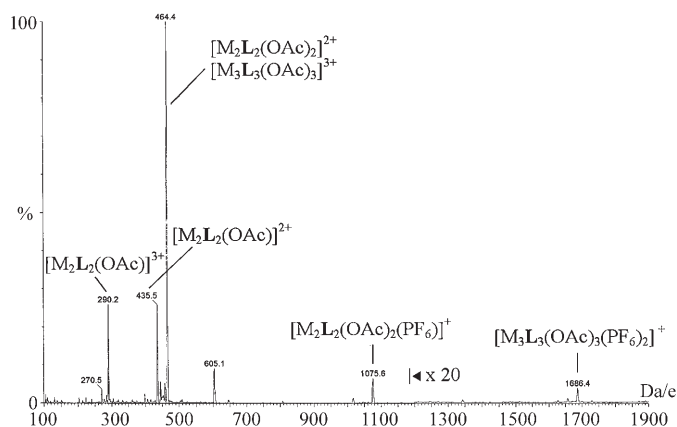


Figure 5. Electrospray mass spectra of $[\text{Cu}_3(\text{L})_3(\text{OAc})_3][\text{PF}_6]_3$ in acetonitrile (top) and methanol (bottom).

Coordination of L to nickel(II): Coordination of L to nickel(II) was achieved by stirring the ligand (1 equiv) with a solution of nickel(II) acetate in ethanol for one hour, followed by a brief period of sonication and then treatment with ammonium hexafluorophosphate in ethanol, which led to the formation of a green precipitate. The mixture was left to stand in air for 24 h during which time emerald-green crystals formed that proved to be suitable for X-ray analysis. Partial microanalytical data for the compound were consistent with a formulation of $[\text{Ni}_n(\text{L})_n(\text{OAc})_n][\text{PF}_6]_n$ and X-ray analysis again revealed that the structure was a triangular circular helicate (Figure 6).

The nickel(II) ions in the structure adopt a six-coordinate pseudo-octahedral geometry (distorted square pyramidal) bound to two pyridyl-imine binding sites and a didentate acetate molecule ($\text{Ni}-\text{O}=2.09\text{--}2.15\text{ \AA}$). The metal-ligand bond lengths to the imine nitrogen atoms ($2.03\text{--}2.08\text{ \AA}$) are shorter than those to the pyridine nitrogen atoms ($2.13\text{--}2.18\text{ \AA}$), as commonly observed in such pyridylimine systems.^[21] The nickel(II) centres are separated by 8.89 to 8.94 \AA and the ligands are wrapped around the nickel...nickel vectors, which gives rise to the circular helicate structure. The central phenylene ring of each strand is face-to-face π stacked with an imine unit from another strand

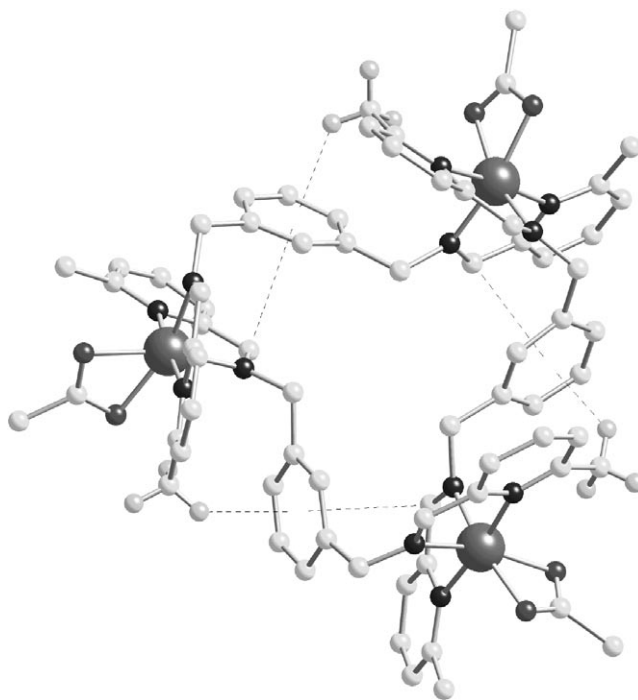


Figure 6. The structure of the trinuclear circular-helical cation in the complex $[\text{Ni}_3(\text{L})_3(\text{OAc})_3][\text{PF}_6]_3$ (crystallised from ethanol). For clarity, hydrogens are omitted except those on the methyl groups, which are included to illustrate the $\text{CH}\cdots\pi$ interactions.

($C_{\text{imine}}\cdots\text{centroid}=3.39\text{--}3.43\text{ \AA}$) and the same phenylene forms a $\text{CH}\cdots\pi$ contact with a methyl group ($\text{H}\cdots\text{centroid}=2.84\text{--}2.92\text{ \AA}$) from the third strand. The dimensions and structure of this nickel(II) circular helicate in the solid state are remarkably similar to those in the copper(II) complex (Figure 7), in part because the copper(II) centres adopted a square pyramidal coordination geometry. Although the

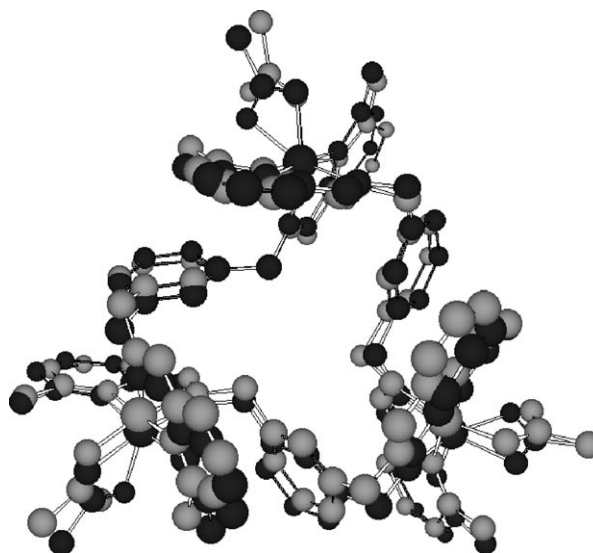


Figure 7. Overlay of the structures of the trinuclear circular-helical cations in the complexes $[\text{Cu}_3(\text{L})_3(\text{OAc})_3][\text{PF}_6]_3$ (light) and $[\text{Ni}_3(\text{L})_3(\text{OAc})_3][\text{PF}_6]_3$ (crystallised from ethanol) (dark).

change from square pyramidal (copper(II)) to octahedral (nickel(II)) coordination is accompanied by some alterations in the metal–ligand bond lengths, these are small (<10%) and do not dramatically affect the orientations or positioning of the ligand strands with respect to one another.

The asymmetric wrapping of the ligand about the lines that join the metal centres again leads to distinct upper and lower faces of the triangular helicates and the anions are again located in the cavities of both (see Figure S9 in the Supporting Information). The anion located in the upper face, in the triangular cavity created by the faces of the pyridyl rings and adjacent imine units, is disordered about a P–F axis, with the fluorine pointing into the cavity from the axis that forms a short CH⋯F (2.23 Å) contact to a CH₂ proton on one of the ligand strands. For the anion located in the lower cavity, the fluorine atom that projects into the cavity forms three short F⋯HC contacts to the three imino protons (CH⋯F=2.61–2.69 Å), as observed for the corresponding anion in the copper(II) complex, with further short contacts to protons also formed by the adjacent fluorine atoms.

These nickel(II) circular helicates pack together in a hexagonal array to give channels in which the remaining anions and solvent are located (Figure 8). However the packing is

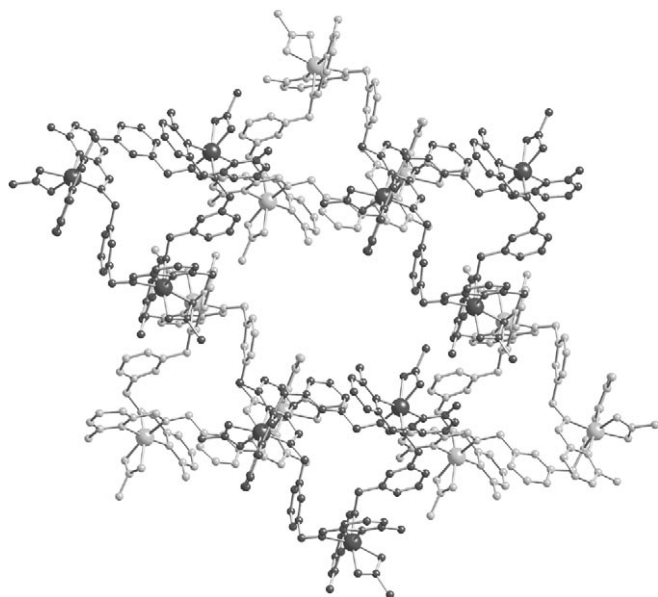


Figure 8. Packing of the trinuclear circular-helical cations in the complex $[\text{Ni}_3(\text{L})_3(\text{OAc})_3][\text{PF}_6]_3$ (crystallised from ethanol). Alternate circular helicates are shaded differently to illustrate their packing and hydrogens are omitted for clarity.

different from that in the copper(II) complex in that six circular helicates are arranged in an elongated hexagon rather than in a regular hexagon (see Figure S15 in the Supporting Information). The circular helicates are linked by π – π interactions between pyridyls located on the upper triangular faces (centroid⋯centroid=3.99 Å) and between pyridyls located on the lower faces (centroid⋯centroid=3.97 Å), but

the π stacking is less extensive than in the copper(II) structure. The helicity of the circular helicates alternates around the elongated hexagonal unit (see Figure S13 in the Supporting Information).

We were also able to obtain crystals of two further species, which include the same Ni cation. In both cases diffraction was very weak and only partial refinement was possible. However, the preliminary structures that were revealed are of interest to compare with the $[\text{Ni}_3(\text{L})_3(\text{OAc})_3][\text{PF}_6]_3$ structure crystallised from ethanol. The first modification was obtained by diffusion of diethyl ether into a solution of the same complex in acetonitrile. It was possible to identify a trigonal unit cell and obtain a preliminary solution of the structure. The cation structure is a trimeric circular helicate, which is almost identical to that crystallised from ethanol. Once again two of the anions are located in the upper and lower cavities of the cation, however, the packing of these circular helicates is more similar to that of the copper(II) circular helicates, with the circular helicates packed around regular tube-like hexagonal channels (diameter \approx 1.2 nm) in which the remaining anions and solvent reside (Figure 9).

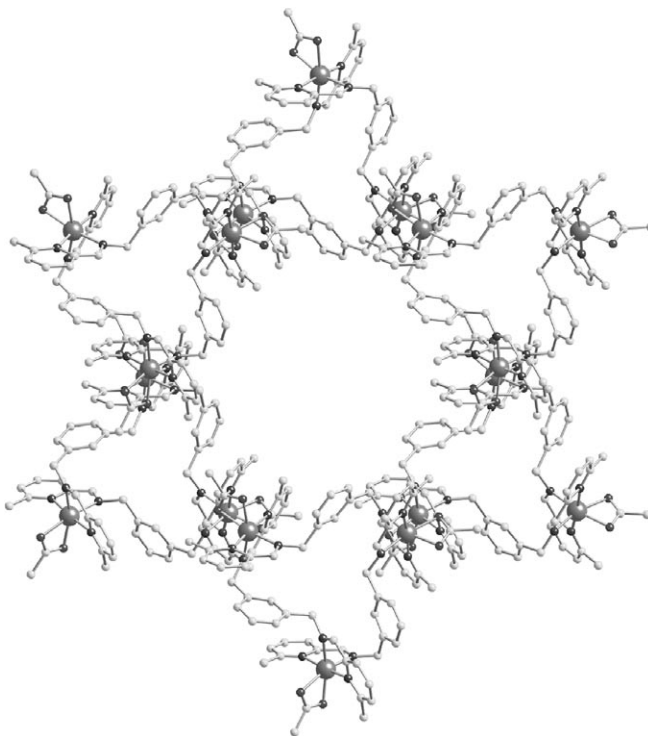


Figure 9. Packing of the trinuclear circular-helical cations in the complex $[\text{Ni}_3(\text{L})_3(\text{OAc})_3][\text{PF}_6]_3$ (crystallised from acetonitrile/diethyl ether). Hydrogens are omitted for clarity.

The hexagonal arrays are formed through π – π interactions between pyridine rings on the upper surfaces of the triangles, but the structure differs from the copper(II) structure in that each nickel(II) circular helicate in the hexagonal array has the same helicity. The circular helicates in the hexagonal array located above and below have the opposite

helicity, which renders the structure achiral (see Figure S14 in the Supporting Information).

We were also able to obtain crystals of the corresponding tetrafluoroborate salt of this nickel(II) complex for which the structure solution was complicated by solvent and anion disorder. The X-ray data confirmed that the structure of the cation in this salt is again a trinuclear circular helicate, which is similar to that observed for the hexafluorophosphate salt.

ESI spectrometry was again used to probe the solution structure of the nickel(II) complex and whether or not the trinuclear architecture was retained in solution. Analysis of solutions of the complexes in acetonitrile (Figure 10, top) re-

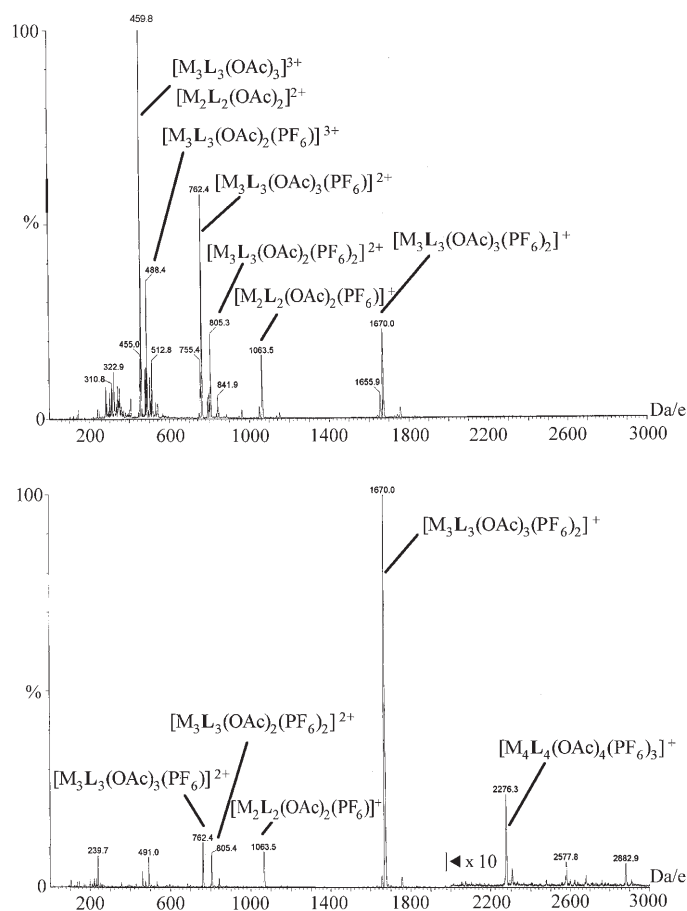


Figure 10. Electrospray mass spectra of $[\text{Ni}_3(\text{L})_3(\text{OAc})_3][\text{PF}_6]_3$ in acetonitrile (top) and methanol (bottom).

vealed the principal component to be the trimer, with just a small amount of dimer present. Although this again indicates an equilibrium between the dimeric and trimeric species, it is clear that the incorporation of the octahedral metal centre has significantly perturbed the equilibrium to favour the trimer in this solvent. The ESI mass spectrum for the sample in methanol (Figure 10, bottom) showed trimeric species to be by far the dominant species in solution with only peaks of very low intensity that correspond to the dimeric species. These results indicate that the dimer is indeed

more effectively destabilised by the incorporation of the six-coordinate metal ion, and that the triangle now occurs as the dominant species in solution (in both solvents).

Interestingly, in the ESI mass spectrum in methanol, very small amounts of a higher order (tetramer) structure are observed and an even weaker signal at m/z 2883 might tentatively be assigned to the pentanuclear complex. Although the dimer has been destabilised and the trimer is strongly favoured, other nuclearity circular helicates would satisfy the metal coordination environment requirements and may be present in small amounts. The observation of a peak at m/z 2578, which possibly corresponds to the dication of an apparently nonanuclear array, may indicate that the triangular structures can aggregate in solution as observed in the solid state.

Conclusion

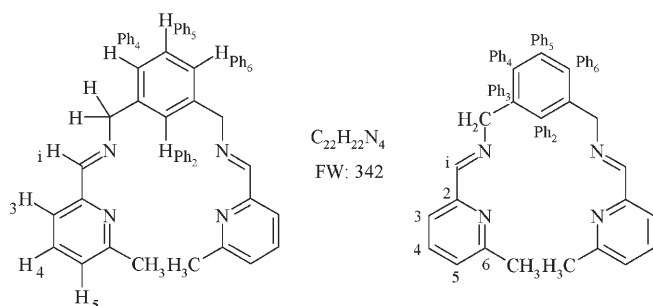
As anticipated, changes in the geometry of the metal (and thus the angles at the connection points) can indeed be used to affect the nuclearity of a supramolecular helicate system. For the tetrahedral metal ions, dimers are the dominant species (with circular helicates of differing nuclearity also present in solution as minor species). When the coordination sphere is expanded to octahedral geometry, the dimer is destabilised and the trimeric circular helicate becomes the dominant species. Copper(II) lies in between. It commonly adopts five-coordinate geometries with diimine type ligands. In the structurally characterised copper(II) trimeric circular helicate, the copper(II) centre adopts a square-based pyramidal geometry and consequently the structure of the trimer is not markedly different from that of the trimer formed with octahedral nickel(II). However, in solution copper(II) and nickel(II) are significantly different, with a substantial dimer component for copper(II), whereas trimers are dominant for nickel(II). This is probably a reflection of the more flexible geometry of five-coordinate systems (square-based pyramid, trigonal bipyramid and intermediate geometries are possible), that must allow the extra (acetate) ligand to be accommodated in the dimer structure with less dramatic destabilisation effects.

We have demonstrated that changes in the metal geometry can directly affect the angles at the connection points of a circular helicate and thus its nuclearity. This offers a powerful alternative approach to controlling the nuclearity of circular helicate arrays and is certainly a complementary approach to the previous studies in which the size of an anion guest was used to determine the nuclearity.

Experimental Section

General: All starting materials were purchased from Aldrich and used without further purification. NMR spectra were recorded by using Bruker ACF250, DPX300, DPX400 and DRX500 instruments with standard Bruker software. ESI mass spectra for the silver(I) and copper(I)

complexes were recorded by using a Micromass Quatro (II) (low resolution triple quadrupole mass spectrometer) at the EPSRC National Mass Spectrometry Service Centre, Swansea. ESI mass spectra for $[\text{Cu}_3(\text{L})_3(\text{OAc})_3][\text{PF}_6]_3$ and $[\text{Ni}_3(\text{L})_3(\text{OAc})_3][\text{PF}_6]_3$ were recorded at the Laboratoire de Spectrométrie de Masse Bio-Organique (LSMBO) in Strasbourg with a low cone voltage (5–10 Volts) by using a Quattro II ESI triple quadrupole mass spectrometer (Waters, MA). CI and FAB mass spectra were recorded by the Warwick mass spectrometry service by using a Micromass Autospec spectrometer with 3-nitrobenzyl alcohol as the matrix for the FAB experiments. Microanalyses were conducted by using a Leeman Labs CE44 CHN analyser by the University of Warwick Analytical service. IR spectra were recorded either as compressed pellets by using a Bruker Vector 220 instrument fitted with ATR Golden Gate or with the samples compressed in KBr discs by using a Perkin–Elmer Paragon 1000 instrument. UV/Vis measurements were obtained by using a PU 8720 scanning spectrometer or a Jasco V-550 spectrophotometer.



Ligand L ($\text{C}_{22}\text{H}_{22}\text{N}_4$): 6-Methylpyridine-2-carboxaldehyde (2.00 g, 16.51 mmol) and 1,3-bis(aminomethyl)benzene, (1.11 mL, 8.25 mmol) were stirred in diethyl ether (25 mL) over anhydrous magnesium sulfate for 2 h. The orange solution was then filtered and concentrated under reduced pressure. An orange solid crystallised from the solution over 14 h in air and was collected by vacuum filtration and washed with ice-cold ethanol (2.57 g, 92%). $^1\text{H NMR}$ (250 MHz, CDCl_3 , 298 K): δ = 8.56 (s, 2H; H_1), 7.95 (d, J = 7.6 Hz, 2H; H_3), 7.70 (t, J = 7.6 Hz, 2H; H_4), 7.48–7.37 (m, 4H; $\text{H}_{\text{Ph}2-5}$), 7.28 (d, J = 7.6 Hz, 2H; H_5), 5.25 (s, 4H; CH_2), 2.98 ppm (s, 6H; CH_3); $^{13}\text{C NMR}$ (75.6 MHz, CDCl_3 , 298 K): δ = 163.6 (C_1), 158.5 ($\text{C}_{2/6/\text{Ph}3}$), 154.3 ($\text{C}_{2/6/\text{Ph}5}$), 139.4 ($\text{C}_{2/6/\text{Ph}5}$), 129.2 ($\text{C}_{\text{Ph}2/\text{Ph}4/\text{Ph}5}$), 128.5 ($\text{C}_{\text{Ph}2/\text{Ph}4/\text{Ph}5}$), 127.4 ($\text{C}_{\text{Ph}2/\text{Ph}4/\text{Ph}5}$), 124.9 (C_3), 118.9 (C_3), 65.3 (C_{CH_2}), 24.7 ppm (C_{CH_3}); EI MS (+ve): m/z (%): 343 (50) [M^+], 236 (60) [$\text{M}^+ - \text{C}_6\text{H}_4\text{N}_2$], 221 (100) [$\text{M}^+ - \text{C}_7\text{H}_7\text{N}_2$]; CI MS (+ve): m/z (%): 343 (100) [$\text{M} + \text{H}^+$]; HRMS (+ve CI): m/z : calcd: 343.1923 [$\text{M} + \text{H}^+$]; found: 343.1923 [$\text{M} + \text{H}^+$]; IR (KBr): $\tilde{\nu}$ = 3062 (m), 3001 (m), 2954 (m), 2910 (w), 2868 (m), 2809 (w), 2018 (w), 1806 (w), 1651 (s), 1606 (w), 1590 (s), 1574 (s), 1491 (w), 1464 (s), 1441 (w), 1412 (m), 1374 (w), 1352 (m), 1327 (m), 1303 (w), 1268 (w), 1254 (w), 1222 (w), 1166 (w), 1086 (m), 1056 (w), 1043 (m), 995 (m), 984 (m), 905 (w), 884 (w), 803 (s), 793 (s), 774 (s), 746 (w), 736 (m), 694 (m), 650 (m), 621 (w), 577 (w), 546 (w), 494 cm^{-1} (w).

$[\text{Cu}_2(\text{L})_2][\text{BF}_4]_2$: Ligand **L** (0.03 g, 0.088 mmol) and $[\text{Cu}(\text{CH}_3\text{CN})_4][\text{BF}_4]$ (0.03 g, 0.095 mmol) were stirred in methanol (40 mL) under nitrogen for 14 h. The resulting red solution was concentrated in vacuo and diethyl ether (3 mL) was added. The solution was cooled in an ice bath and the resulting red solid collected by vacuum filtration (0.015 g, 34%). $^1\text{H NMR}$ (400 MHz, CD_3CN , 233 K): δ = 8.63 (s, 4H; H_1), 7.87 (t, J = 7.9 Hz, 4H; H_4), 7.64 (d, J = 7.9 Hz, 4H; H_3), 7.32 (d, J = 7.9 Hz, 4H; H_5), 7.00 (s, 2H; $\text{H}_{\text{Ph}2}$), 6.96 (t, J = 6.9 Hz, 2H; $\text{H}_{\text{Ph}5}$), 6.87 (d, J = 6.9 Hz, 4H; $\text{H}_{\text{Ph}4}$), 4.52 (d, J = 13.3 Hz, 4H; CH_2), 4.22 (d, J = 13.3 Hz, 4H; CH_2), 2.08 ppm (s, 12H; CH_3); FAB MS (+ve): m/z : 899 [$[\text{Cu}_2(\text{L})_2(\text{BF}_4)]^+$], 812 [$[\text{Cu}_2(\text{L})_2]^+$], 405 [$[\text{Cu}(\text{L})]^+$]; ESI MS (+ve, CH_3CN): m/z (%): 897.4 (20) [$[\text{Cu}_2(\text{L})_2(\text{BF}_4)]^+$], 406.2 (100) [$[\text{Cu}_2(\text{L})_2]^{2+}$]; ESI MS (+ve, acetone): m/z (%): 897.2 (20) [$[\text{Cu}_2(\text{L})_2(\text{BF}_4)]^+$], 652.2 (1) [$[\text{Cu}_3(\text{L})_3(\text{BF}_4)^{3+}$], 570.1 (1) [$[\text{Cu}_4(\text{L})_4(\text{BF}_4)^{3+}$], 406.3 (100) [$[\text{Cu}_2(\text{L})_2]^{2+}$]; ESI MS (+ve, CH_2Cl_2): m/z (%): 897.4 (45) [$[\text{Cu}_2(\text{L})_2(\text{BF}_4)]^+$], 734.6 (4) [$[\text{Cu}_3(\text{L})_3(\text{BF}_4)^{3+}$], 652.3 (25)

[$[\text{Cu}_3(\text{L})_3(\text{BF}_4)^{3+}$], 570.0 (15) [$[\text{Cu}_4(\text{L})_4(\text{BF}_4)^{3+}$], 406.0 (100) [$[\text{Cu}_n(\text{L})_n]^{n+}$]; IR (KBr): $\tilde{\nu}$ = 2800–3050 (w), 1624 (m), 1590 (m), 1464 (m), 1383 (m), 1257 (m), 1124 (m), 1084 (s), 1029 (m), 797 (m), 736 (w), 712 (w), 533 (w), 521 (w), 486 cm^{-1} (w); UV/Vis (CH_3CN): λ_{max} (ϵ) = 490 nm (3000); elemental analysis calcd (%) for $[\text{Cu}_2(\text{C}_{22}\text{H}_{22}\text{N}_4)_2][\text{BF}_4]_2 \cdot 1\text{H}_2\text{O}$: C 52.7, H 4.6, N 11.2; found: C 52.6, H 4.37, N 10.9.

$[\text{Cu}_2(\text{L})_2][\text{PF}_6]_2$: was prepared by an analogous route starting from $[\text{Cu}(\text{CH}_3\text{CN})_4][\text{PF}_6]$.

$[\text{Ag}_2(\text{L})_2][\text{PF}_6]_2$: Care was taken throughout this procedure to exclude light. Ligand **L** (0.03 g, 0.088 mmol) and silver acetate (0.015 g, 0.088 mmol) were heated to reflux for 1 h in methanol (30 mL). The resulting clear solution was then filtered through Celite and treated with ammonium hexafluorophosphate (excess) in methanol. The resulting white precipitate was collected by vacuum filtration (0.025 g, 48%). $^1\text{H NMR}$ (250 MHz, CD_3CN , 298 K): δ = 8.57 (s, 4H; H_1), 7.95 (t, J = 7.8 Hz, 4H; H_4), 7.60 (d, J = 7.8 Hz, 4H; H_3), 7.43 (d, J = 7.8 Hz, 4H; H_5), 7.25 (s, 2H; $\text{H}_{\text{Ph}2}$), 7.06 (s, 6H; $\text{H}_{\text{Ph}4/\text{Ph}5}$), 4.37 (s, 8H; CH_2), 2.03 ppm (s, 12H; CH_3); MS (+ve FAB): m/z : 1045 [$[\text{Ag}_2(\text{L})_2(\text{PF}_6)]^+$], 900 [$[\text{Ag}_2(\text{L})_2]^+$], 791 [$[\text{Ag}(\text{L})_2]^+$], 593 [$[\text{Ag}(\text{L})(\text{PF}_6)]^+$], 559 [$[\text{Ag}_2(\text{L})]^+$], 451 [$[\text{Ag}(\text{L})]^+$]; ESI MS (+ve, CH_3CN): m/z (%): 1045.2 (35) [$[\text{Ag}_2(\text{L})_2(\text{PF}_6)]^+$], 793.5 (25) [$[\text{Ag}(\text{L})_2]^+$], 450.3 (100) [$[\text{Ag}_2(\text{L})_2]^{2+}$]; IR (KBr): $\tilde{\nu}$ = 2914 (w), 1645 (m), 1593 (m), 1459 (m), 1383 (w), 1328 (w), 1257 (w), 1212 (w), 1165 (m), 1095 (m), 1050 (w), 1004 (w), 839 (s), 793 (m), 732 (w), 655 (w), 557 cm^{-1} ; elemental analysis calcd (%) for $[\text{Ag}_2(\text{C}_{22}\text{H}_{22}\text{N}_4)_2][\text{PF}_6]_2 \cdot 1.33\text{CHCl}_3$: C 40.3, H 3.4, N 8.3; found: C 40.3, H 3.1, N 8.1.

The analogous tetrafluoroborate salt $[\text{Ag}_2(\text{L})_2][\text{BF}_4]_2$ was prepared in a similar fashion by treating the clear solution with ammonium tetrafluoroborate.

$[\text{Cu}_3(\text{L})_3(\text{OAc})_3][\text{PF}_6]_3$: Ligand **L** (0.05 g, 0.146 mmol) in a solution of methanol/ethanol (1:1, 7.5 mL) was added to a stirred solution of copper acetate monohydrate (0.029 g, 0.146 mmol) also in a solution of methanol/ethanol (1:1, 7.5 mL) under nitrogen in an ice/water bath. The green solution was then treated with ammonium hexafluorophosphate (excess) in methanol. The product was collected by vacuum filtration and washed with ice-cold diethyl ether (5 mL) to give a green precipitate (0.047 g, 57%). ESI MS (+ve, methanol): m/z (%): 1686.7 (5) [$[\text{Cu}_3(\text{L})_3(\text{OAc})_3(\text{PF}_6)_2]^+$], 1075.7 (22) [$[\text{Cu}_2(\text{L})_2(\text{OAc})_2(\text{PF}_6)]^+$], 1016.6 (15) [$[\text{Cu}_2(\text{L})_2(\text{OAc})(\text{PF}_6)]^+$], 812.9 (13) [$[\text{Cu}_3(\text{L})_3(\text{OAc})_2(\text{PF}_6)^{2+}$], 769.9 (15) [$[\text{Cu}_3(\text{L})_3(\text{OAc})_3(\text{PF}_6)^{2+}$], 464.2 (100) [$[\text{Cu}_2(\text{L})_2(\text{OAc})_2]^{2+}$ or [$[\text{Cu}_3(\text{L})_3(\text{OAc})_3]^{3+}$], 435.5 (74) [$[\text{Cu}_2(\text{L})_2(\text{OAc})_2]^{2+}$]; ESI MS (+ve, CH_3CN): m/z (%): 1686.4 (1) [$[\text{Cu}_3(\text{L})_3(\text{OAc})_3(\text{PF}_6)_2]^{2+}$], 1075.6 (6) [$[\text{Cu}_2(\text{L})_2(\text{OAc})_2(\text{PF}_6)]^+$], 464.4 (100) [$[\text{Cu}_2(\text{L})_2(\text{OAc})_2]^{2+}$ or [$[\text{Cu}_3(\text{L})_3(\text{OAc})_3]^{3+}$], 435.5 (26) [$[\text{Cu}_2(\text{L})_2(\text{OAc})_2]^{2+}$], 290.2 (26) [$[\text{Cu}_2(\text{L})_2(\text{OAc})_2]^{2+}$]; IR (solid): $\tilde{\nu}$ = 2850–3100 (w), 1652 (w), 1601 (m), 1575 (w), 1538 (w), 1464 (m), 1442 (m), 1418 (w), 1378 (m), 1326 (m), 1257 (m), 1224 (m), 1171 (m), 1013 (w), 831 (s), 791 (m), 739 (m), 704 (m), 667 (m), 621 cm^{-1} (w); elemental analysis calcd (%) for $[\text{Cu}_3(\text{L})_3(\text{OAc})_3][\text{PF}_6]_3 \cdot 3\text{H}_2\text{O}$: C 45.9, H 4.3, N 8.9; found: C 45.7, H 4.0, N 8.6.

$[\text{Ni}_3(\text{L})_3(\text{OAc})_3][\text{PF}_6]_3$: Ligand **L** (0.50 g, 1.59 mmol) and nickel(II) acetate (0.40 g, 1.59 mmol) were stirred in ethanol (30 mL) for 1 h, sonicated for 5 min, and treated with ammonium hexafluorophosphate (excess) in ethanol. A green precipitate formed immediately. After 24 h green crystals formed that were collected for X-Ray analysis by manual separation before the bulk precipitate was collected by vacuum filtration (0.56 g, 63%). ESI MS (+ve, methanol): m/z (%): 2276.3 (3) [$[\text{Ni}_4(\text{L})_4(\text{OAc})_4(\text{PF}_6)_3]^+$], 1670.0 (100) [$[\text{Ni}_3(\text{L})_3(\text{OAc})_3(\text{PF}_6)_2]^+$], 1063.5 (14) [$[\text{Ni}_2(\text{L})_2(\text{OAc})_2(\text{PF}_6)]^+$], 805.4 (13) [$[\text{Ni}_3(\text{L})_3(\text{OAc})_2(\text{PF}_6)^{2+}$], 762.4 (17) [$[\text{Ni}_3(\text{L})_3(\text{OAc})_3(\text{PF}_6)^{2+}$]; ESI MS (+ve, CH_3CN): m/z (%): 1670.0 (24) [$[\text{Ni}_3(\text{L})_3(\text{OAc})_3(\text{PF}_6)_2]^+$], 1063.5 (16) [$[\text{Ni}_2(\text{L})_2(\text{OAc})_2(\text{PF}_6)]^+$], 805.3 (23) [$[\text{Ni}_3(\text{L})_3(\text{OAc})_2(\text{PF}_6)^{2+}$], 762.4 (60) [$[\text{Ni}_3(\text{L})_3(\text{OAc})_3(\text{PF}_6)^{2+}$], 488.4 (35%) [$[\text{Ni}_3(\text{L})_3(\text{OAc})_3(\text{PF}_6)^{3+}$], 459.8 (100) [$[\text{Ni}_3(\text{L})_3(\text{OAc})_3]^{3+}$ or [$[\text{Ni}_2(\text{L})_2(\text{OAc})_2]^{2+}$]; IR (solid): $\tilde{\nu}$ = 3100–3500 (w), 1652 (m), 1601 (m), 1538 (m), 1456 (m), 1418 (w), 1393 (w), 1327 (w), 1256 (m), 1223 (w), 1171 (w), 1107 (w), 1059 (w), 1007 (m), 946 (w), 830 (s), 788 (s), 740 (m), 702 (w), 680 (m), 665 (m), 625 cm^{-1} (w); elemental analysis calcd (%) for $[\text{Ni}_3(\text{L})_3][\text{OAc}]_3[\text{PF}_6]_3 \cdot 3\text{H}_2\text{O}$: C 46.3, H 4.4, N 9.0; found: C 46.1, H, 4.0, N 8.8.

$[\text{Ni}_3(\text{L})_3(\text{OAc})_3][\text{BF}_4]_3$ was prepared by an analogous route, in which ammonium tetrafluoroborate was added in place of ammonium hexafluorophosphate.

X-ray crystallographic structural characterisations: For all of the crystals, data were collected by using a Siemens SMART three-circle system equipped with CCD area detector^[34] in which crystals were held at 240 or 293 K by using an Oxford Cryosystems Cryostream Cooler.^[35] Absorption corrections were made by using Psi-scan data. Refinements used SHELXTL.^[36] The appropriate space group was identified by satisfactory refinement. The structures were solved by direct methods with additional light atoms found by Fourier methods. Hydrogen atoms were added at calculated positions and refined by using a riding model with freely rotating methyl groups. Anisotropic displacement parameters were used for all non-hydrogen atoms; hydrogen 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 hydrogen atom is attached (Table 1). CCDC-648994 and -648995 con-

Table 1. Crystallographic data and details of refinement for $[\text{Cu}_3(\text{L})_3(\text{OAc})_3][\text{PF}_6]_3$ and $[\text{Ni}_3(\text{L})_3(\text{OAc})_3][\text{PF}_6]_3$.

Complex	$[\text{Cu}_3(\text{L})_3(\text{OAc})_3][\text{PF}_6]_3$	$[\text{Ni}_3(\text{L})_3(\text{OAc})_3][\text{PF}_6]_3$
formula	$\text{C}_{75}\text{H}_{75}\text{Cu}_3\text{F}_{18}\text{N}_{12}\text{O}_{7.5}\text{P}_3$	$\text{C}_{76}\text{H}_{75}\text{F}_{18}\text{N}_{12}\text{Ni}_3\text{O}_{7.5}\text{P}_3$
M_r	1853.97	1887.52
T [K]	293(2)	240(2)
crystal system	trigonal	triclinic
space group	$P\bar{3}$	$P\bar{1}$
a [Å]	19.8197(4)	16.46920(10)
b [Å]	19.8197(4)	19.2438(3)
c [Å]	14.9925(4)	20.7328(3)
α [°]	90.00	102.5900(10)
β [°]	90.00	91.9340(10)
γ [°]	120.00	113.5150(10)
μ [Å ³]	5100.3(2)	5826.55(13)
Z	2	2
crystal size [mm]	0.4 × 0.3 × 0.2	0.5 × 0.3 × 0.3
ρ_{calcd} [g cm ⁻³]	1.207	1.076
μ [mm ⁻¹]	0.747	0.593
reflns collected	25 911	20 165
independent reflns	5972 ($R_{\text{int}} = 0.1020$)	12 343 ($R_{\text{int}} = 0.0314$)
data	5972	12 343
restraints	58	46
parameters	439	1097
final R indices	$R_1 = 0.0962$	$R_1 = 0.1014$ (for 7545
$[I > 2\sigma(I)]$	$wR_2 = 0.2448$	reflns)
		$wR_2 = 0.2965$
R indices (all data)	$R_1 = 0.1887$	$R_1 = 0.1511$
	$wR_2 = 0.3085$	$wR_2 = 0.3204$
GOF on F^2	1.044	1.850

tain the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

CCDC-648995, $[\text{Cu}_3(\text{L})_3(\text{OAc})_3][\text{PF}_6]_3$: Green crystals were obtained from a solution in methanol. The crystals decompose on cooling to 180 K and data was collected at 293 K to circumvent this. The trimer and two hexafluorophosphate anions are located on position 2d with threefold symmetry. Another hexafluorophosphate anion is at position 1a (low occupancy) with the remaining group in a general position. The channels (see Results and Discussion) also contain highly disordered partially occupied solvent molecules.

CCDC-648994, $[\text{Ni}_3(\text{L})_3(\text{OAc})_3][\text{PF}_6]_3$: Green diamond-shaped crystals were grown from a solution in ethanol. The crystals decay at low temperature (180 K) and data was collected at 240 K to circumvent this. The crystals diffracted very weakly beyond $2\theta = 40^\circ$. The asymmetric unit contains several ethanol molecules that are all highly disordered and with

partial occupancy; one PF_6 has four disordered F atoms and all the anions have very high thermal parameters. The high R_1 value is readily understandable in view of the weak diffraction and disorder.

$[\text{Ni}_3(\text{L})_3(\text{OAc})_3][\text{PF}_6]_3$: Green crystals (0.6 × 0.38 × 0.35 mm) were also obtained from a solution in acetonitrile by the slow diffusion of diethyl ether. Diffraction data were extremely weak (no diffraction beyond $2\theta = 40^\circ$). However it was possible to identify a trigonal unit cell with $a = 19.467(1)$, $c = 32.403(1)$ Å (hexagonal axes) and obtain a structure solution in space group P-3c1, although this could not be refined below $R = 0.125$.

$[\text{Ni}_3(\text{L})_3(\text{OAc})_3][\text{BF}_4]_3$: Green prisms with dimensions of 0.5 × 0.16 × 0.16 mm were obtained. Diffraction data proved to be extremely weak (no diffraction beyond $2\theta = 40^\circ$). However, it was possible to identify a trigonal unit cell with $a = 38.179(1)$, $c = 14.6052(8)$ Å (hexagonal axes), and obtain a preliminary structure solution in space group P3. This structure showed the presence of seven trimer cations (of the same form as that of the PF_6 salt) in the unit cell, with the asymmetric unit containing one trimer set on a three-fold axis, which was relatively well-defined, and two in general positions. The unit cell also contained a considerable number of highly disordered solvent molecules as well as the anions. The disorder and the weak data meant that it was not possible to refine the structure fully.

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