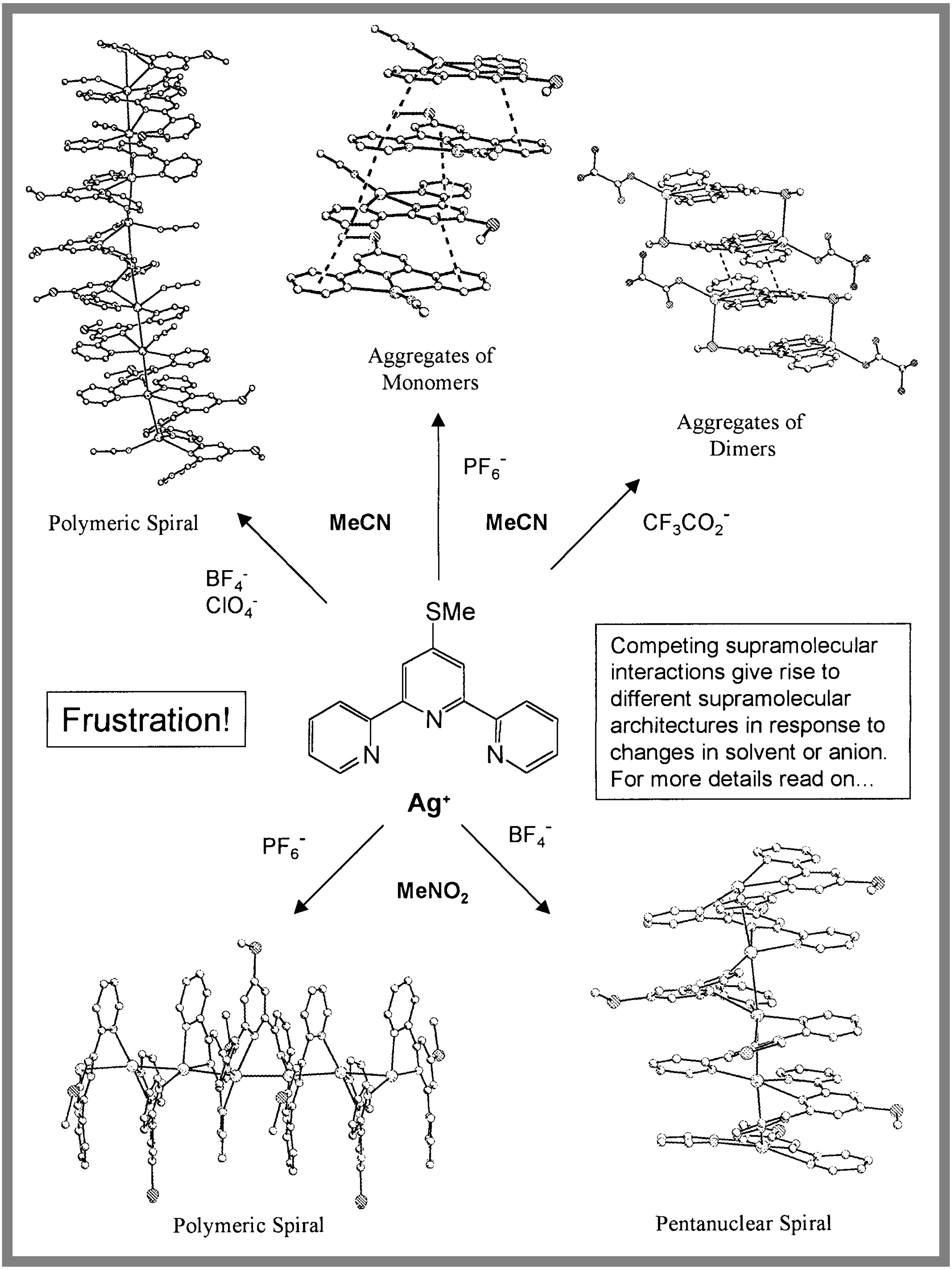

Competing supramolecular interactions give rise to different supramolecular architectures in response to changes in solvent or anion. For more details read on...

Competing Supramolecular Interactions Give a New Twist to Terpyridyl Chemistry: Anion- and Solvent-Induced Formation of Spiral Arrays in Silver(I) Complexes of a Simple Terpyridine

Michael J. Hannon,* Claire L. Painting, Edward A. Plummer, Laura J. Childs, and Nathaniel W. Alcock*[a]

Abstract: Multiple competing molecular interactions (metal – ligand, π-stacking and hydrogen-bonding) in the silver(I) complexes of 4′-thiomethyl-2,2′:6′,2″-terpyridine give rise to a range of different molecular architectures, in which the metal – ligand coordination requirements are satisfied in quite different ways. Polynuclear supramolecular spirals, aggregated mononuclear and aggregated dinuclear units are all structurally characterised. The metallo-supramolecular architecture obtained displays a remarkable dependence both on the choice of non-coordinated anion and the type of solvent used (coordinating or non-coordinating). The anion dependence is particularly surprising, since the anions are not integrated into the centre of the supramolecular structure. The solution behaviour is also solvent and anion dependent, with aggregation of planar mononuclear cations observed in acetonitrile, but oligonuclear spiral species implicated in nitromethane. The extraordinarily variable geometries of these systems suggest that they provide a novel example of the "frustration" principle, in which opposing tendencies cannot simultaneously be satisfied and identify an alternative approach to the design of metallo-supramolecular systems whose structure is responsive to external agents.

Keywords: helical structures · N ligands · noncovalent interactions · silver · supramolecular chemistry

Introduction

The design of complex molecular architectures is an important goal for synthetic chemistry as it provides the opportunity to control or encode the properties of a material at the molecular level. Supramolecular chemists[1] and crystal engineers[2] have made considerable progress towards this goal by using noncovalent interactions such as hydrogen bonding and π-stacking interactions. Notable contributions have also resulted from the use of metal – ligand interactions to generate sophisticated molecular architectures[3] and discrete helices, knots and boxes have been reported as well as polymeric solid-state cavity-containing arrays.[2] In such metallo-supramolecular species, the large energies associated with metal – ligand bond formation usually overwhelm the effects of weaker supramolecular interactions and the *global* architecture is primarily dictated by the metal – ligand interactions, that is, by 1) the coordination requirements of the metal ions, 2) the donor sets afforded by the ligands and 3) the relative spatial dispositions of the metal-binding sites.[1] Consequently the role of weaker supramolecular interactions is restricted to influencing the precise *microarchitecture* of the metallo-supramolecular array.[4]

However, recently metallo-supramolecular systems have been described in which anions play an important role in structure determination, through being integrated into the molecular architecture.[5, 6] The most striking examples are perhaps the "circular double helicates" described by Lehn in which the choice of anion dictates the selection of a square, pentagonal or hexagonal architecture from a "virtual combinatorial library" of many possible structures.[5] In the Lehn system, flexible linkers connect the metal-binding domains and a range of structures of different nuclearity are possible, all of which afford similar metal – ligand coordination environments. The weaker noncovalent interactions between anion and cation are thus able to influence which architecture is adopted.

We describe herein a different type of system in which multiple competing molecular interactions (metal – ligand, π-stacking and hydrogen-bonding) give rise to a range of different molecular architectures, but in which the metal – ligand coordination requirements are satisfied in quite different ways. The metallo-supramolecular architectures obtained

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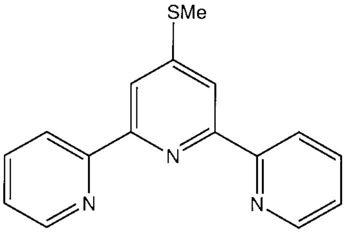
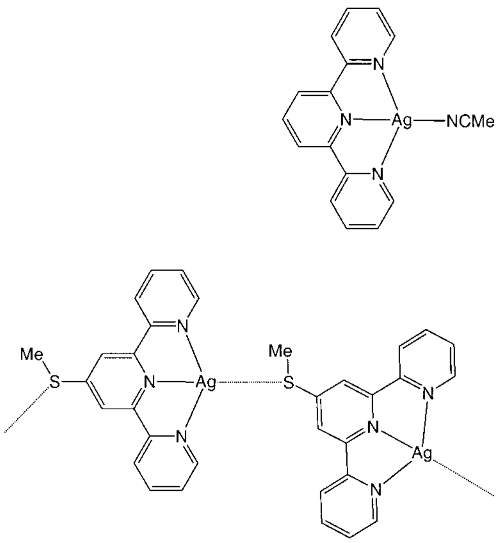
display a remarkable dependence both on the choice of non-coordinated anion and the type of solvent used (coordinating or non-coordinating). The anion dependence[7] is quite distinct from that observed in the circular helicates and particularly striking, since the anions are not integrated into the centre of the supramolecular structure. Furthermore, the extraordinarily variable geometries of these systems suggest that they provide a novel example of the "frustration" principle, in which opposing tendencies cannot simultaneously be satisfied (originally proposed for parallel and antiparallel magnetic interactions).[8]

Our studies arose from our interest in the development of second-generation supramolecular arrays in which discrete supramolecular entities are further assembled into larger arrays of defined architecture.[9, 10] We recently reported the controlled aggregation of supramolecular boxes to give a polymeric array of boxes,[9a] achieved through linking polypyridyl boxes[9b] together through the coordination of a silver(I) centre to a thioether group attached to the outside of the box array. On examining related literature we were surprised to find that, outside of macrocyclic chemistry, structurally characterised silver(I)–thioether interactions were rare[11] and indeed that no previous reports of silver(I)–arylthioether interactions had appeared.[12] To investigate further the efficacy of this interaction and assess its application for assembling large supramolecular arrays, we chose to investigate the coordination behaviour of silver(I) to the simple ligand 4′-thiomethyl-2,2′:6′,2″-terpyridine (L).



The chemistry of the unsubstituted parent ligand 2,2′:6′,2″-terpyridine (tpy) has been the subject of numerous studies, stimulated by the excellent chelating properties of the ligand and the exciting photophysical properties of metal–polypyridyl compexes.[13] The tpy ligand most commonly acts as a planar tridentate ligand and in a handful of examples acts as a didentate ligand with a non-coordinated residue.[14] While silver(I) terpyridyl complexes have received less attention than those of many other d-block metal ions, in the presence of a donor solvent, such as acetonitrile, tpy forms simple, monocationic, planar, four-coordinate, silver(I) complexes of 1:1 stoichiometry such as $[Ag(tpy)(MeCN)]^+$ (Scheme 1, top).[15]

We envisaged that adding a thiomethyl group to the 4′-position of tpy would result in cyclic oligomers or linear polymers (shown schematically in Scheme 1, bottom) through coordination of the thioether group from an adjacent molecule to the silver centre. Instead, to our considerable surprise, most of the resulting complexes contain spiral chains of silver ions coordinated by the tpy nitrogen atoms, but not involving Ag···S interactions.



Scheme 1. Top: The planar $[Ag(tpy)(MeCN)]^+$ ion. Bottom: Potential aggregation motifs formed through Ag···S interactions.

Results

The ligand L was prepared according to the procedure of Potts.[17] Complex formation was achieved by warming solutions of the ligand with silver(I) acetate in methanol. Treatment with solutions of suitable anions afforded white precipitates of stoichiometry $\{AgL(X)\}$ ($X = PF_6$; ClO_4; BF_4; CF_3CO_2). The FAB mass spectra of the four salts are similar and reveal a dominant peak corresponding to $[Ag(L)]^+$ together with some weak peaks corresponding to higher aggregates.

Structural characterisation of the solids crystallised from acetonitrile: Crystals of all four salts were obtained from acetonitrile and their structures determined.

ClO_4 salt: Recrystallisation of the perchlorate salt from acetonitrile by the slow diffusion of benzene yielded colourless crystals that proved suitable for X-ray analysis.

The solid-state structure of this perchlorate salt (Figure 1) contains neither the planar $\{AgL\}^+$ units found for the unsubstituted ligand nor the expected Ag···S interactions. Instead the structure of the cation is a spiral polymer of stoichiometry $[Ag_5L_5(MeCN)_3]_n^{5n+}$, in which every terpyridyl ligand bridges two silver(I) centres. There are five distinct silver centres with coordination numbers of three or four. In addition these centres have short silver···silver contacts (3.03–3.15 Å). Such silver···silver interactions are a common feature in silver coordination compounds.[15a, 18] The silver atoms define a shallow helical spiral about the axis of the array with small displacements from the mean spiral axis (in the range 0.30 to 0.59 Å). Each of the five silver atoms has a subtly different environment. Within the Ag_5 subunit a total of three acetonitrile molecules are involved in the coordination and in one of the tpy ligands the same N atom bridges between two silver ions. The environments can be described in terms of three- and four-coordinate Ag, but other Ag–N

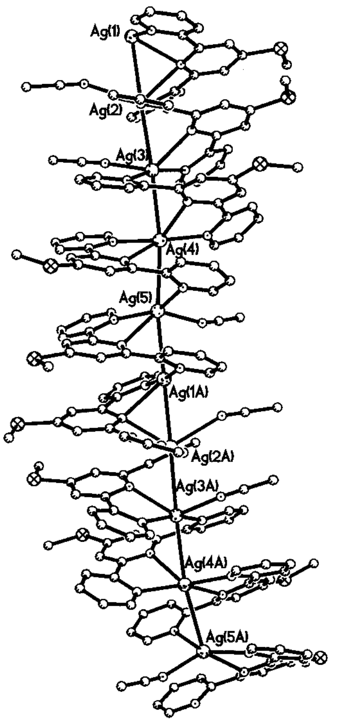


Figure 1. Crystal and molecular structure of the $[Ag_5L_5(MeCN)_3]_n^{5n+}$ ion in the compound $[Ag_5L_5(MeCN)_3]_n[ClO_4]_{5n}$ crystallised from acetonitrile.

contacts are only just longer than those notionally considered to be bonding, as seen in Table 1.

All the terpyridyl ligands bridge two metal centres, but their precise coordination modes vary; they are either bis-didentates with a bridging central pyridyl bound to both silver centres or they are didentate to one silver centre and monodentate to the other. As would be expected for such modes the ligands are twisted about the interannular bonds with torsion angles in the range of 13–51°. Very extensive face–face π–π stacking[19] is found within the spiral chain (centroid–centroid distances 3.54–3.85 Å); all three pyridyl rings π stack with the three rings of the ligand both above and below (for all but one pair of ligands, between which there are only two stacking interactions). Three of the five silver(I) centres are also coordinated to acetonitrile molecules.

Table 1. Bond lengths in the spiral $[Ag_5(L)_5(MeCN)_3]_n[ClO_4]_{5n}$.

	Coordination number	L bond range [Å]	MeCN bond [Å]	Longer interaction [Å]
Ag1	3	2.215–2.512		Ag–L 2.693
Ag2	3	2.280–2.540		Ag–L 2.730; Ag–MeCN 2.639
Ag3	4	2.331–2.478	2.434	Ag–L 2.721
Ag4	4	2.242–2.486		
Ag5	4	2.274–2.536	2.329	Ag–L 2.886

The infinite spiral chains have a pitch of 31 Å. Alternate chains have opposite chirality and the crystals contains both enantiomers in equal numbers. The chains are packed together in a grid (Figure 2) leaving large inter-chain voids that contain the perchlorate anions (there are no short contacts from the perchlorate anions to the silver centres). For each Ag_5 repeat, the lattice contains two additional acetonitrile solvent molecules together with a benzene solvent molecule (which forms a face–edge (CH···π) π stack to the edge of one of the pyridyl rings in the spiral; centroid-centroid 4.8 Å).

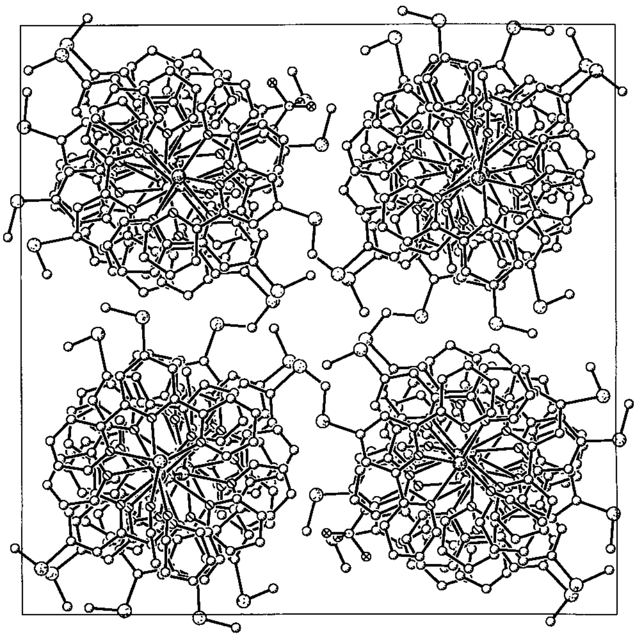


Figure 2. Packing of the $[Ag_5L_5(MeCN)_3]_n^{5n+}$ spiral ions in $[Ag_5L_5(MeCN)_3]_n[ClO_4]_{5n}$.

BF_4 salt: The tetrafluoroborate salt was also crystallised from acetonitrile by the slow diffusion of benzene. The structure is very similar to that of the perchlorate salt (although less well defined because of anion and solvent disorder) and contains infinite cationic molecular spirals of stoichiometry $[Ag_5L_5(MeCN)_3]_n^{5n+}$ with silver(I) centres bridged by the terpyridyl ligands (Figure 3). The coordination patterns of the five independent silver atoms are identical to those in the perchlorate salt. The chains are again packed in a grid surrounded by anions and solvent.[20] Thus this slightly smaller tetrahedral anion (approx 90% of the size by volume compared to perchlorate) gives an infinite spiral structure very similar to that observed with perchlorate.

PF_6 salt: Recrystallisation of the hexafluorophosphate salt from acetonitrile by the diffusion of diethyl ether also afforded material suitable for X-ray analysis; this time the X-ray crystal structure reveals simple mononuclear cations of formula $[AgL(MeCN)]^+$ (similar to those observed for the unsubstituted ligand), which contain silver(I) centres in a four-coordinate pseudo-square-planar coordination environment, bound to a tridentate terpyridyl and a monodentate acetonitrile ligand (Figure 4). The terpyridyl ligands are essentially planar (interannular torsion angles: 3.8 and 4.7°). Neither short Ag···Ag nor short Ag···S interactions are present. In the solid state, the planar cations are stacked, with double-ring face–face π–π interactions with the molecules both above and below (centroid–centroid 3.66–3.68 Å). In addition a

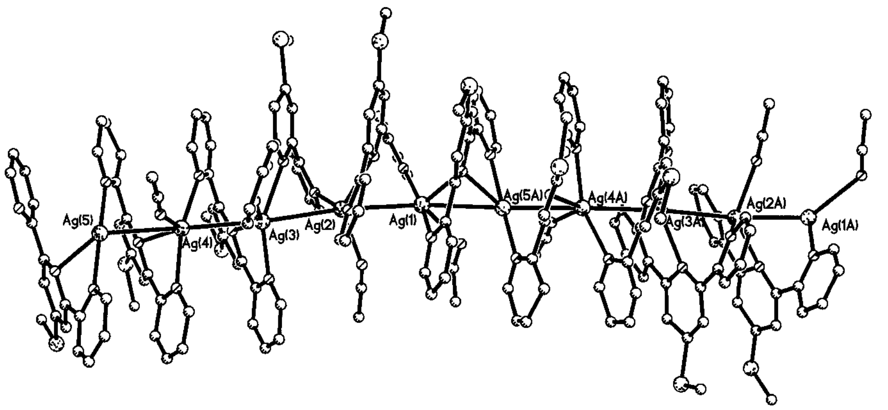


Figure 3. Crystal and molecular structure of the $[Ag_5L_5(MeCN)_3]_n^{5n+}$ ion in the compound $[Ag_5L_5(MeCN)_3]_n[BF_4]_{5n}$ crystallised from acetonitrile.

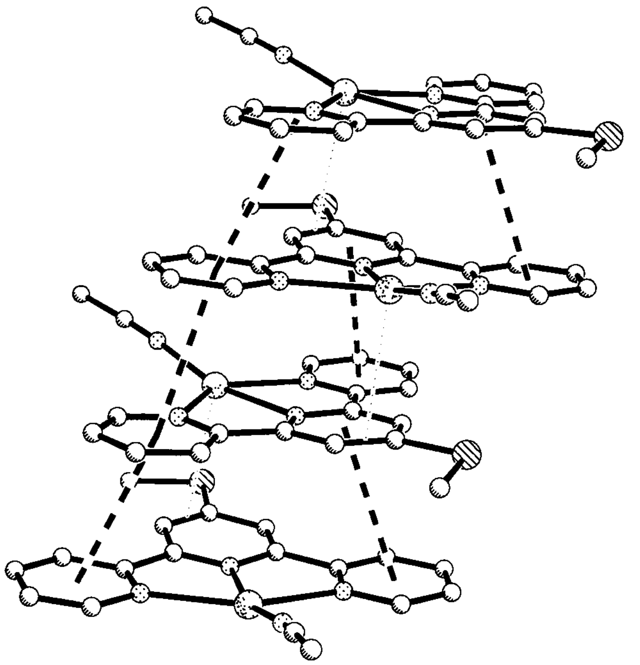


Figure 4. Crystal and molecular structure of the $[AgL(MeCN)]^+$ ions in the compound $[AgL(MeCN)][PF_6]$ crystallised from acetonitrile.

short contact is observed between the silver ion and the π system of the complex towards which it is displaced. As is usual for silver⋯π interactions, η^2 rather than η^6 coordination is implied; however, the observed shortest Ag⋯C distance (3.27 Å) is towards the long end of the range proposed for such interactions (indeed Munakata has proposed a cut-off value of 3 Å),[21] and it is unclear whether this distance represents a significant bonding interaction.

The π–π stacking links the planar cations into chains (Figure 5) that are separated by the hexafluorophosphate counterions and non-coordinated acetonitrile solvent molecules (one per cation).

CF_3CO_2 salt: The trifluoroacetate salt of the complex crystallised on treatment of the reaction mixture with ammonium trifluoroacetate. These crystals were also recrystallised from acetonitrile by the slow diffusion of diethyl ether; both sets of crystals are identical. They show a third structural type for this system: here silver–terpyridyl units are linked by Ag–S bonds, as envisaged at the outset of this study. Rather than leading to the formation of a polymer, the Ag⋯S interactions result in the dimeric structure illustrated in Figure 6.

The silver(I) centre is coordinated to a tridentate terpyridyl unit with a monodentate trifluoroacetate anion completing a planar environment. The thiomethyl substituent on an adjacent terpyridyl ligand is coordinated in an axial position giving a pseudo-square-pyramidal coordination environment. The Ag–S distance (2.7798(13) Å) is comparable with (and slightly shorter than) those that we have previously observed in the silver complex of 4-thiomethyl-6-(4-pyridyl)-2,2′-bipyridine (2.94–2.96 Å).[9a] The dimer is also supported by a face–face π-stacking interaction between the central pyridyl rings of the ligands (centroid–centroid 3.46 Å). The dimers aggregate into a polymeric chain (Figure 7) supported by two face–face π-stacking interactions between each dimer (centroid–centroid 3.80 Å). This interdimer link is also associated

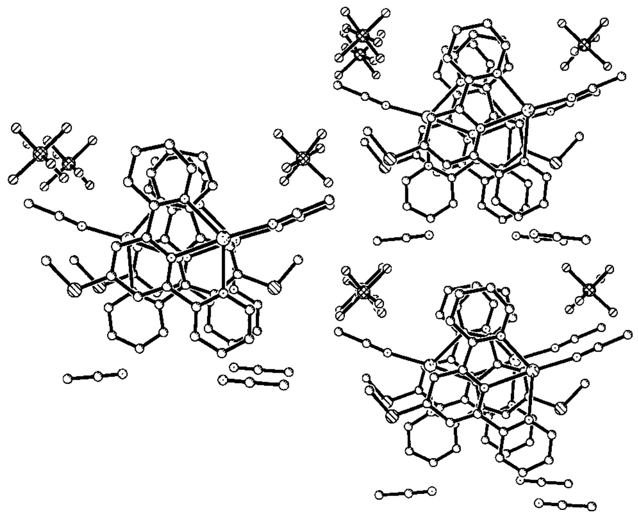


Figure 5. Packing of the $[AgL(MeCN)]^+$ ion chains in $[AgL(MeCN)][PF_6]$.

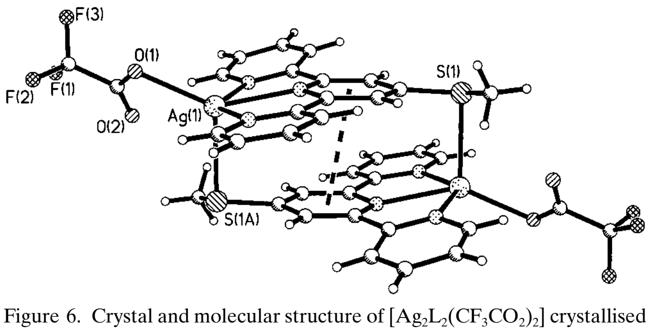


Figure 6. Crystal and molecular structure of $[Ag_2L_2(CF_3CO_2)_2]$ crystallised from acetonitrile or methanol.

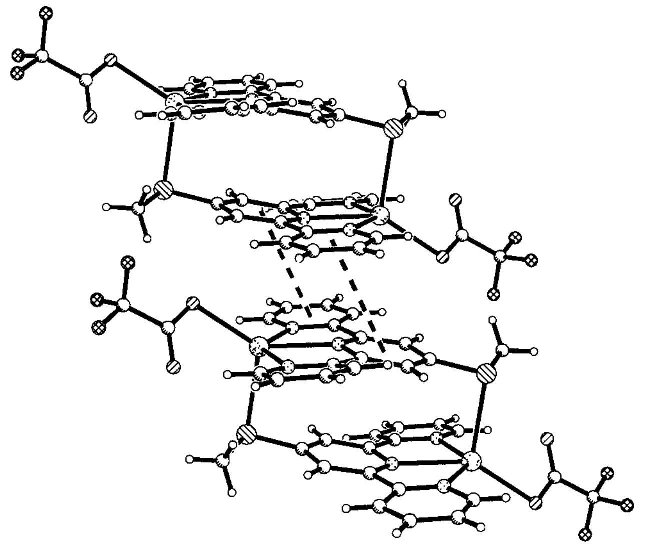


Figure 7. The π–π stacking of the $[Ag_2L_2(CF_3CO_2)_2]$ units to form chains.

with a long Ag···π interaction (shortest Ag···C distance 3.42 Å) opposite the axially coordinated thiomethyl group. It is unclear whether this contributes to the bonding.[21] The chains of dimers pack together in a co-parallel fashion.

Structural characterisation of the solids crystallised from nitromethane: Suitable crystals of the hexafluorophosphate and tetrafluoroborate salts were also obtained from nitromethane.

PF_6 salt: The hexafluorophosphate salt was recrystallised from nitromethane by diffusion of benzene. In contrast to the mononuclear structure obtained from acetonitrile, an infinite spiral motif of stoichiometry $\{Ag_nL_n\}^{n+}$ is obtained from nitromethane (Figure 8). However, the structure contrasts with the other spirals as the asymmetric unit contains only one AgL group; the spiral is formed by its repetition along the fourfold axis. Each terpyridyl ligand bridges between two silver(I) centres coordinating as a didentate ligand to one centre and a monodentate to the next. The ligands twist about the interpyridine links to afford the spiral environment (interannular torsion angles: 20 and 26°) rendering the didentate unit nonplanar. Each silver(I) centre is three-coordinate and there are no coordinated solvent molecules. The silver(I) centres are separated with Ag···Ag distances of 2.72 Å (with the chains containing either one or another alternative but equivalent sets of Ag positions). There is extensive face–face π–π stacking within the spiral array with each ligand forming a pair of π stacks (centroid–centroid 3.47–3.69 Å) to both of the adjacent ligands. The pitch of the helix is 10.82 Å and, as seen in the earlier spirals, the silver chain itself describes a shallow helical spiral within the centre of the array, with the silver(I) atoms displaced 0.19 Å from the mean axis. The packing of the chains is similar to those of the other spirals with a gridlike arrangement of chains, between which the anions are packed.

BF_4 salt: The tetrafluoroborate salt was recrystallised from nitromethane by diffusion of diethyl ether. Although prepared with a 1:1 stoichiometry, the material that crystallised contained spiral pentanuclear cations of stoichiometry $[Ag_5L_6]^{5+}$ (Figure 9). In this unit, the two terminal ligands coordinate in a conventional tridentate fashion to a single silver(I) centre, while the other four ligands bridge two metal centres, acting as a didentate ligand to one silver and a monodentate to the other. Thus three of the silver centres form four bonds (2.27–2.52 Å), while the two others have only three bonds which are significantly shorter, 2.19-2.38 Å; all the N atoms of the terpyridine ligand are coordinated and none are multidentate. The terminal ligands are close to planarity (interannular torsion angles: 9.7, 10.6°; 9.0, 9.9°), while the other ligands twist about the interannular bonds to afford the spiral structure (torsion angles: 11–33°). The two terminal silver(I) centres at the ends of the pentanuclear array are four-coordinate, bound to one tridentate ligand and one monodentate. The adjacent centres are three-coordinate bound to a didentate ligand and a monodentate one, while the central silver(I) is four coordinate bound to two didentate bridging ligands. Intermetallic Ag–Ag distances are in the range 3.01–3.09 Å. The silver chain again describes a shallow helical spiral within the centre of the array, with the silver(I)

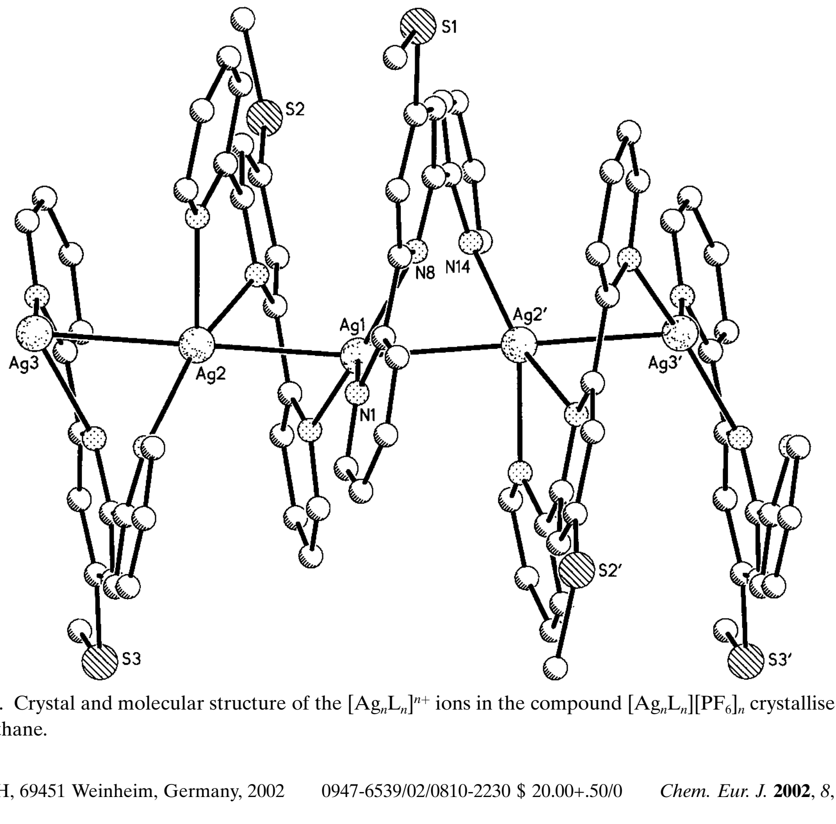


Figure 8. Crystal and molecular structure of the $[Ag_nL_n]^{n+}$ ions in the compound $[Ag_nL_n][PF_6]_n$ crystallised from nitromethane.

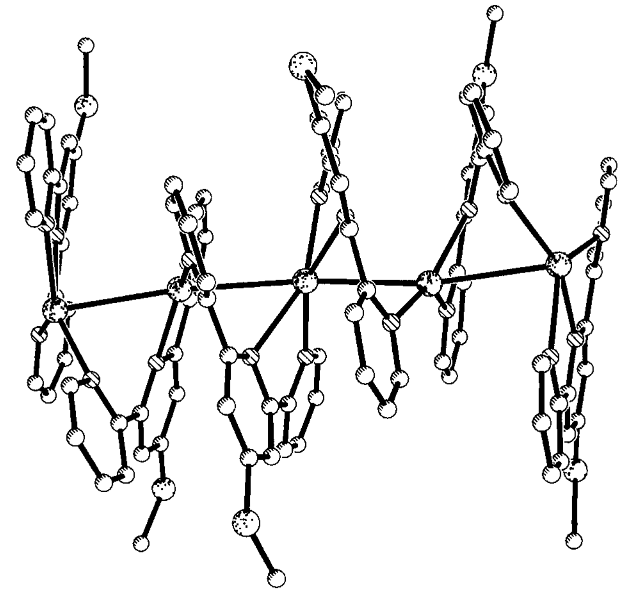


Figure 9. Crystal and molecular structure of the $[Ag_5L_6]^{5+}$ spiral cations in the compound $[Ag_5L_6][BF_4]_5$ crystallised from nitromethane.

atoms displaced 0.38 Å from the mean axis. Within the pentanuclear unit each ligand forms a pair of π-stacking interactions with both adjacent ligands.

The pentanuclear units associate through a pair of face–face π-stacking interactions (centroid–centroid 3.58 and 3.60 Å) with other units of the same helicity to form an infinite spiral structure (Figure 10). This infinite array superficially resembles the other spiral structures, but has a slip or displacement every five metals. The inter-unit Ag–Ag distance is 3.68 Å, only slightly longer than the intra-unit separation. The resulting spiral chains are again packed into a gridlike array between which the counterions and solvent (one nitromethane per silver centre) reside. However, in contrast to the other spiral structures, neighbouring spiral units have the same helicity and the crystal contains spontaneously resolved domains of alternate helicity.

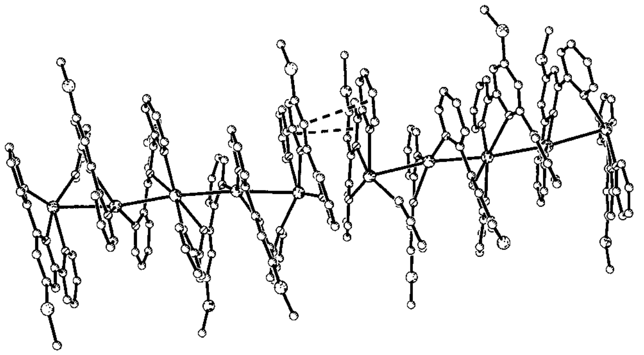


Figure 10. Packing of the $[Ag_5L_6]^{5+}$ ions to afford an infinite spiral chain.

Discussion

Structures obtained from solutions of the salts in acetonitrile: The infinite spiral chain motif observed in the structures of the perchlorate and tetrafluoroborate salts is most remarkable and was quite unexpected. The formation of such infinite polymeric spiral chain structures is unprecedented in terpyridine chemistry. Indeed any systems containing bridging terpyridyl ligands are rare.[15, 22, 16] With copper(I), several *dimetallic* double-helical $[M_2(Rtpy)_2]^{2+}$ complexes of substituted terpyridines (Rtpy) have been reported.[22] In each case the ligand bears one or more substituents in the 6-position(s) of the ligand, which are required to stabilise the metal centre towards oxidation, but which must also serve to destabilise a planar terdentate ligand configuration.[23] Previous work by Constable et al. has indicated that such dimetallic double-helical $[M_2(Rtpy)_2]^{2+}$ complexes may also be formed with silver(I) in solvents other than acetonitrile. Indeed for ligands bearing bulky substituents in the 6-position two such disilver(I) double-helical complexes have been crystallised from acetone solution.[15b,c] However, from acetonitrile solution only crystals containing mononuclear $[Ag(Rtpy)(MeCN)]^+$ ions were obtained.[15] There is one previous example of a bridging terpyridine ligand which does not bear substituents at the 6-position; a helical cation of 3:4 stoichiometry, $[Ag_3(tpy)_4]^{3+}$, which (despite its stoichiometry) was reported to crystallise from an acetonitrile solution of 1:1 stoichiometry.[16] This trication contains two bridging tpy ligands and cocrystallises along with simple $[Ag(tpy)(MeCN)]^+$ ions. Perhaps significantly this trinuclear complex was also obtained as the perchlorate complex; solutions of the hexafluorophosphate salt in acetonitrile give crystals only of the monomeric $[Ag(tpy)(MeCN)]^+$ ion.

Having stumbled across this unexpected spiral structure we investigated whether this remarkable spiral structural motif was observed for all complexes of this ligand (L) with silver(I), or whether alternate motifs containing, for example, the desired Ag···S interactions might also be observed with other anions. The similarity of the tetrafluoroborate and the perchlorate salts, both infinite spiral chains, led us to examine whether anion shape might be crucial factor. Consequently we next prepared and crystallised the analogous hexafluorophosphate salt.

The difference in structure between the perchlorate and hexafluorophosphate salts is dramatic, despite the fact that neither anion coordinates to the metal or is encapsulated within a cavity in the complex. The hexafluorophosphate salt contains the mononuclear $[AgL(MeCN)]^+$ ions commonly found for silver(I) terpyridyl complexes. Intriguingly, however, these units stack through π–π and Ag···π interactions to form infinite chains. Although these chains do not contain bridging terpyridyl units, and consequently do not exhibit the spiral structure, they nevertheless form infinite chains which pack into a grid like array and thus show some superficial similarity to the structure of the perchlorate complex.

To try to rationalise the effect of the anions we examined the weak interactions between the anions and the cation chains. For the perchlorate salt, the perchlorate groups make a number of short O···H–C contacts[24] in the range 2.1–3.0 Å to the methyl groups of the acetonitrile molecules and thiomethyl moieties, and also to the pyridine ring protons (on average each perchlorate makes 1.8 O···H contacts at less than 2.5 Å, 6.0 contacts at less than 2.7 Å and 12.8 contacts at less than 3.0 Å).[25] Such C–H···O interactions may contribute to the stabilisation of the solid-state structure.

The tetrafluoroborate salt contains a number of short F$\cdots$H contacts in the range of 2.2–3.0 Å. The number and distribution (by distance) of these close contacts mimics those of the O$\cdots$H contacts observed in the perchlorate structure, but the extensive disorder of the anions makes any further analysis impossible.

For the hexafluorophosphate salt, short F$\cdots$H–C contacts[24] in the range of 2.3–3.0 Å are formed, predominantly between the anions and the methyl groups on the acetonitrile and thiomethyl groups. As might be anticipated, more short contacts are observed per anion for this hexafluorophosphate salt than the perchlorate salt. (Each hexafluorophosphate makes three F$\cdots$H–C contacts at less than 2.5 Å, eight contacts at less than 2.7 Å and 18 contacts at less than 3.0 Å. However if these numbers are corrected to allow for the higher number of potential hydrogen-bond acceptors on the hexafluorophosphate anion—six rather than four—the pattern of contacts per acceptor is very similar to that observed for the perchlorate salt).

Clearly the anion does play a role in the determination of the solid-state structure and it seems quite likely that the number and position of the potential hydrogen-bond acceptors may be an important influence. However, using these to control the architecture of the cation chain in a systematic and predictable fashion would be a considerable challenge. The anion influence does imply that there must be little energetic difference between the spiral structure and the stacked mononuclear units. This is perhaps surprising given the different number of donors available to the silver centre in the two structures (3.6 per metal in the spirals and four per metal in the stack of monomers). This implies that the presence of Ag$\cdots$Ag interactions (one per metal) in the spiral compensates for the lower number of donors and makes a significant contribution to the bonding. The secondary interactions within the two chain types are similar: the spiral structures are associated with extensive $\pi-\pi$ stacking (2.8 per ligand), while the stack of mononuclear units also contains a series of π-stacking interactions (two per ligand) together with (long) Ag$\cdots\pi$ interactions (one per metal).

Although we prepared the trifluoroacetate salt to examine the effect of introducing a very differently shaped anion, the structure is fundamentally different to the others, since this anion coordinates to the metal. Consequently no information about anion shape effects can be gleaned from this structure. Nevertheless the structure is particularly interesting in its own right, since it contains the Ag$\cdots$S interactions envisaged at the outset of the study. Only in this isolated case do we observe these silver–thioether interactions, and even then they are associated with a concomitant π-stacking interaction. Supramolecular crystal engineering by its nature relies on the balance between a series of weak intermolecular interactions, and it appears that, unlike many metal-ligand interactions, these silver–thioether interactions are insufficiently strong to automatically overwhelm other interactions and dictate the solid-state structure. While the Ag$\cdots$S interaction does have potential for control and ordering aggregation,[9a, 12] it appears to be weak and thus may be overwhelmed by competing interactions.

The Ag$\cdots$S interaction (with its associated $\pi-\pi$ interaction) gives rise to dimers which then further associate into chains through additional $\pi-\pi$ interactions. The chains are packed in a grid arrangement and consequently there is again some similarity to the motifs observed in the other structures. Short C–H$\cdots$F interactions do not appear to play a significant role (F$\cdots$H; only four below 3.0 Å, all of which are in the range 2.7–2.9 Å); this is consistent with the less polarised nature of the hydrogen-bond acceptors in this anion. Some short C–H$\cdots$O interactions are observed within and between the chains, most notably within the dimeric unit from the non-coordinated oxygens to the thioalkyl groups above or below them (O$\cdots$H; 2.59 Å).

The range of structures obtained from acetonitrile for a simple 1:1 Ag/L stoichiometry is quite remarkable (and at first sight bewildering), yet in fact they all contain ordered cationic infinite chain motifs that run through the crystal domain. The precise type of chain motif obtained is dependent on the anions which are packed around (or in the case of trifluoroacetate, incorporated into) the infinite chains.

Structures obtained from solutions of the salts in nitromethane: In three of the above structures acetonitrile acts as a coordinating ligand, and presumably contributes significantly to the coordination of the silver(I) centres. To examine the effect of removing this coordinating unit we also attempted to crystallise the salts from a non-coordinating solvent. Nitromethane was selected as being such a solvent, but one in which the complexes nevertheless retained a reasonable level of solubility. In particular, we anticipated that mononuclear $\{AgL(solvent)\}^+$ species were unlikely to be stabilised by nitromethane. However, the spiral structures observed for the tetrafluoroborate and perchlorate salts from acetonitrile, also incorporate coordinated acetonitrile solvent molecules (three per five silver(I) centres); if a spiral motif were to be retained in the absence of the acetonitrile ligands, some structural rearrangement would be required. We were able to crystallise two of the salts from nitromethane and have investigated their structures. In both cases spiral arrays are obtained.

The hexafluorophosphate salt crystallises as an infinite spiral motif of stoichiometry $\{Ag_nL_n\}^{n+}$. This contrasts with the stack of planar mononuclear units obtained from acetonitrile. Each terpyridyl ligand bridges between two silver(I) centres and there are no additional coordinated solvent molecules. In the absence of coordinated solvents, the formal number of donors per metal (i.e., three) is lower than observed in the other chains. All the silver ions have the same geometry, with three bonds to pyridyl nitrogen atoms (2.222–2.377 Å); all the tpy-N atoms are coordinated and none are multidentate. The intermetallic Ag–Ag distance within the spiral is 2.72 Å, significantly shorter (~10%) than in the other spirals obtained from acetonitrile; this may indicate that the enhanced silver–silver interactions offset the lower formal coordination number at the metal. Although there is substantial $\pi-\pi$ stacking (two stacks per ligand) it is less extensive than in the acetonitrile spirals; this is a consequence of the absence of solvent co-ligands, with the terpyridyl ligands being required to wrap more symmetrically around the metal–metal axis. This more symmetric local distribution also leads to a much reduced helical pitch (10.82 Å).

The hexafluorophosphate anions reside in the channels between the chains and make a number of short F$\cdots$H–C contacts in the range 2.3–3.0 Å from the hexafluorophosphate groups to the methyl groups of the thiomethyl moieties and also to the pyridine ring protons (each hexafluorophosphate makes four F$\cdots$H contacts at less than 2.5 Å, seven contacts at less than 2.7 Å and twelve contacts at less than 3.0 Å). At contacts of <2.5 Å and <2.7 Å these numbers are very similar to those for the mononuclear planar hexafluorophosphate complex crystallised from acetonitrile, but the interactions are less extensive above 2.7 Å in this spiral.

Given the propensity of the tetrahedral anions to induce spiral formation in acetonitrile, from nitromethane one might anticipate a very similar structure for the tetrafluoroborate salt to the spiral observed for the hexafluorophosphate salt. However from a 1:1 Ag/L solution, a complex of stoichiometry $[Ag_5L_6]^{5+}$ crystallised that contains spiral pentanuclear cations. The metals are encapsulated within a spiral array with an average number of donors per metal of 3.6. This number is the same as that observed in the spirals obtained from acetonitrile, and (perhaps consequently) the intermetallic Ag–Ag distances (3.01–3.09 Å) observed are similar to those in the acetonitrile spirals (rather than to the shorter distances in the hexafluorophosphate spiral from nitromethane). Three of the silver centres form four bonds to the pyridine moieties (2.27–2.52 Å), while the two others have only three bonds, which are significantly shorter, 2.19-2.38 Å; all the tpy-N atoms are coordinated and none are multidentate. The pentanuclear units associate with other units of the same helicity through a pair of face–face π-stacking interactions to give rise to a third class of infinite spiral structure. This infinite array superficially resembles the other spiral structures, but has a slip or displacement every five metals.

Presumably the formation of this 5:6 stoichiometry structure is driven by the metal centres seeking to increase the number of coordinated donors, although the fact that this 5:6 stoichiometry complex is not obtained with hexafluorophosphate indicates that additional anion effects must contribute to the selection of structural array. Short F$\cdots$H–C contacts are observed in the range 2.2–3.0 Å from the tetrafluoroborate groups to the methyl groups of the nitromethane and thiomethyl moieties and also to the pyridine ring protons (on average each tetrafluoroborate has 2.2 F$\cdots$H contacts <2.5 Å; 8.4 contacts <2.7 Å; 12.8 contacts <3.0 Å). This pattern of contacts is similar to those for the perchlorate and tetrafluoroborate spirals crystallised from acetonitrile, although once again, using such a pattern to deliberately control or induce a structural type or stoichiometry would be challenging. The crystallisation of a helical 3:4 stoichiometry cation from a 1:1 solution of tpy with silver(I) perchlorate in acetonitrile[20] is presumably driven by similar anion contact effects.

Solution studies: The anion and solvent dependence of the solid-state structure is quite remarkable and we were intrigued to investigate whether this was reflected in the solution behaviour of these complexes.

Solution studies in acetonitrile: The ^{1}H NMR spectra of the tetrafluoroborate, perchlorate and hexafluorophosphate salts in CD_3CN are identical and reveal a single set of five aromatic and one aliphatic resonances. This indicates either a single solution species or multiple rapidly-exchanging species (rapid on/off kinetics are common for silver(I) complexes). The electrospray mass spectra[27] of these three salts in acetonitrile solution are analogous and exhibit a main peak corresponding to $[AgL^+]$ together with a slightly weaker peak corresponding to $[AgL(MeCN)^+]$, consistent with a solution species $[AgL(MeCN)]^+$. Weaker peaks are also observed that correspond to $[Ag_2L_2X^+]$ (X = anion) together with some weak peaks corresponding to higher aggregates. For these three salts it seems most likely that the predominant species is the $[AgL(MeCN)]^+$ ion (as observed in the crystal structure of the hexafluorophosphate salt). The ^{1}H NMR spectra of these complexes are concentration dependent with small, but reproducible downfield shifts on dilution observed for all the aromatic signals (the effect is greater for the resonances corresponding to H6′, H3 and H3′ than for H4 and H5). The resonance corresponding to the SMe protons is not significantly affected by dilution implying that any effects do not arise from aggregation caused by coordination of the thiomethyl group (at least at these concentrations; 1–10 mM). We speculate that the observed changes reflect concentration dependent aggregation through a combination of $\pi\cdots\pi$, Ag$\cdots$Ag or Ag$\cdots\pi$ interactions (perhaps in a similar fashion to the crystal structure of the hexafluorophosphate salt), with ring current effects causing the upfield shifts at increased concentration. Such aggregation effects are well known for planar platinum(II) terpyridyl complexes $[Pt(tpy)X]^{n+}$ in both the solid state and solution.[26] The observed shifts are not consistent with a simple decomplexation equilibrium; from the chemical shifts of the free ligand, a mix of upfield and downfield shifts would be expected.

The ^{1}H NMR spectrum of the trifluoroacetate salt in CD_3CN is at first sight almost identical to those of the hexafluorophosphate, perchlorate and tetrafluoroborate salts, revealing a single set of resonances, whose precise chemical shifts vary slightly with concentration (again the effect being greater for H6′, H3 and H3′ than for H4 and H5). However, analysis of the complexes at identical concentrations, reveals that the aromatic resonances are all shifted slightly downfield in the trifluoroacetate salt. Addition of one equivalent of ammonium trifluoroacetate to a solution of the tetrafluoroborate salt in CD_3CN resulted in similar small downfield shifts, while a second equivalent caused no further significant changes. This implies that the trifluoroacetate group competes effectively with the acetonitrile solvent for the fourth coordination site on the planar $[AgL(X)]^{n+}$ complex and that for this salt the predominant solution species is $[AgL(CF_3CO_2)]$. This is supported by the observation of a peak in the electrospray mass spectrum corresponding to $[AgL(CF_3CO_2)^+]$ in addition to the main peak which corresponds to $[AgL^+]$. This is also consistent with crystallisation of $[\{AgL(CF_3CO_2)\}_n]$ rather than $[\{AgL(MeCN)\}_n][\{CF_3CO_2\}_n]$ from acetonitrile. Although, no change in chemical shift is observed for the anion in the ^{19}F NMR spectrum (relative to $[NH_4][CF_3CO_2]$), this may simply reflect the remote nature of the CF_3 group from the silver centre. As with the other salts, the resonance corresponding to the SMe protons is not significantly affected by concentration, implying that solution aggregation is similarly through $\pi - \pi$, Ag···Ag or Ag···π interactions.

Solution studies in nitromethane: In solution, as in the solid state, we anticipated that nitromethane was less likely to stabilise mononuclear $\{AgL(solvent)\}^+$ species and consequently alternate structural motifs might predominate.

The ^1H NMR spectra of the tetrafluoroborate, perchlorate and hexafluorophosphate salts in nitromethane are indeed dramatically different from those observed in acetonitrile; the resonance corresponding to H5 is observed upfield at $\delta \sim 7.2$ and the other pyridyl resonances are bunched between $\delta = 7.8 - 8.2$. These spectra bear a striking resemblance to those obtained for the double-helical silver(I) and copper(I) complexes of 2,2′:6′,2″: 6′,2‴-quaterpyridine (qtpy) in acetonitrile.[28] (The ^1H NMR spectra of double-helical dinuclear complexes of qtpy are quite different from those of planar mononuclear qtpy complexes.[28]) The ^1H NMR spectra of the silver(I) terpyridyl complexes in nitromethane seem therefore to imply that alternate helical structure(s) may be present in this solvent.

The tetrafluoroborate and hexafluorophosphate salts both exhibit good solubility in this solvent. However, in both cases the spectra are considerably broadened throughout the concentration range studied (2–6 mM) and the spectra are concentration dependent with the resonance corresponding to H6 showing the most dramatic changes in chemical shift ($\Delta\delta \sim 0.1$ ppm over this concentration range). While the spectra of the two salts are similar in pattern, the chemical shifts of the resonances are not identical (even allowing for the concentration dependence); this implies anion, as well as concentration, dependence. Spectra of both concentrated and dilute samples of the tetrafluoroborate salt have been recorded at low temperature (255 K), but in both cases the spectra remain considerably broadened. The perchlorate salt exhibits spectra similar to those of the tetrafluoroborate and hexafluorophosphate salts; however, its lower solubility in this solvent prevented accurate concentration-dependent measurements. A dilute sample of the trifluoroacetate salt exhibited sharp resonances with a pattern more similar to that obtained in acetonitrile, but poor solubility prevented further investigation.

These results imply the presence of multiple rapidly exchanging solution species in nitromethane, with the composition of the mixture being sensitive to concentration and also to the choice of counterion.[29] For the perchlorate, tetrafluoroborate and hexafluorophosphate anions, the chemical shifts are consistent with the presence of one or more multinuclear helical/spiral species, rather than merely the mononuclear cations.[29, 30] The chemical shifts of the trifluoroacetate salt are consistent with retention of a planar mononuclear conformation, presumably with the anion coordinated in the fourth coordination site. This is perhaps unsurprising given that for this salt, even in acetonitrile, the solvent does not appear to a coordinate.

Conclusion

We have shown that infinite helical spiral arrays and aggregated monomers or dimers may all be prepared in simple silver(I) terpyridyl systems. The first reports of terpyridyl chemistry appeared in the 1930s and included a description of a silver(I) terpyridyl complex;[31] it is perhaps remarkable that, despite the attention that the coordination chemistry of this ligand has subsequently received,[13] its chemistry still retains the capacity to surprise.

It remains to consider why these particular Ag–tpy complexes take up such remarkable structures. The silver–ligand interaction must dominate energetically, needing to be satisfied in any potential structure. With other polypyridyl ligands such as 2,2′-bipyridine and 2,2′:6,2″:6″,2‴-quaterpyridine, silver(I) is most commonly associated with four-coordinate N_4 coordination in which the four donors arranged in a pseudo-tetrahedral fashion. However, the tpy ligand system does not readily accommodate such an environment. It is the combination of this inability of the ligand to sustain a pseudo-tetrahedral N_4 geometry and the range of potential interactions ($Ag{-}N_{py}$, $Ag{-}N_{MeCN}$, Ag–S, Ag···Ag, Ag···π, π···π, C–H···X) that leads directly to the structural diversity.

The planar mononuclear tpy coordination motif [AgL(X)] exhibited in the trifluoroacetate salt and the hexafluorophosphate salt from acetonitrile, permits a coordination number of four to be achieved but the spatial distribution of donors about the metal is unsatisfactory. By contrast the spiral structural motif, permits a more efficient distribution of the donors about the metal centre, but the silver(I) centres are associated with less than 4 nitrogen donors. The combination of additional Ag···Ag interactions and tpy-tpy π···π interactions overcomes this donor deficit and thus underpins the formation of the spiral chains. The spiral formed on crystallisation of the hexafluorophosphate salt from nitromethane has the lowest formal coordination number (3) but this is offset by closer Ag···Ag contacts. The tetrafluoroborate salt from nitromethane has three distinct coordination environments (3 or 4 coordinate) while the perchlorate salt from acetonitrile is even more complex with five different silver environments (also 3 or 4 coordinate). In all these systems, the ligands spiral around the silver chain to improve the silver coordination. To achieve the best π-π stacking of the ligand rings, the silver atoms are pulled slightly away from the linear Ag···Ag···Ag axis, leading to the spiraling silver chains characteristic of all these systems.

The extreme variation in environment suggests that to achieve ideal coordination geometry, the silver ions and the ligands are subject to conflicting forces, which cannot simultaneously be satisfied. Such a situation (and indeed the resulting spirals) bring to mind the effects of 'Frustration'. In its original application to the orientation of magnetic spins, energy terms simultaneously favouring parallel and antiparallel spins result in spiralling spin vectors, often incommensurate with the crystallographic repeat.[8] The concept has been applied to more specifically chemical systems in aligned polymer helices which attempt simultaneously to have the same and opposite chirality.[32] We suggest that the present systems demonstrate the same principle, in a still more directly chemical application. No simple geometry satisfies both the silver and the tpy requirements simultaneously, leading to the existence of a whole series of reasonable but not ideal coordinations. The result is that the silver ions take up a variety of subtly variable geometries, which lead to the diversity of structures.

This "chemical frustration" has led to a set of unusual spiral molecular architectures not anticipated for this simple ligand system. It points to an alternative approach to the design of metallo-supramolecular systems whose structure is responsive to external agents (such as anions)—the types of systems Lehn describes as "virtual combinatorial libraries".[5] Such a "frustration" approach is most likely to be effective with metals (such as silver(I)) that do not have a strong geometric coordination preference.

The distribution of the short C–H···X contacts to the anions indicates that the choice of anion (and its number and spatial distribution of hydrogen-bond acceptors) can be used to control the supramolecular architecture formed, even when the anion is not encapsulated within the supramolecular structure. To achieve this, the system must have a number of potential structures of very similar energy, the selection of which may be tipped by interactions of small energy (indeed this is intrinsic to Lehn's concept). However, with current knowledge, prediction of potential structures and of how they might be selected by a given anion (or solvent) is not yet feasible. For such a system, guidelines for architecture control are most likely to arise through experimental observation.

The effects are not restricted to the solid state. In acetonitrile, planar mononuclear species are formed. For non-coordinating anions, acetonitrile completes the coordination sphere. There appears to be a preference for coordination of trifluoroacetate over acetonitrile, and this may represent an electrostatic effect. The planar cations stack in solution to form higher aggregates at millimolar concentrations. However, in nitromethane, it appears that, for non-coordinating anions, an exchanging mixture of helical spiral oligomers is formed.[25] The average molecular weight and polydispersity for such a system is expected to be concentration dependent, and indeed concentration dependence is observed in the ^{1}H NMR spectra. Anion effects may also play a role in this solvent.

Dinuclear double-helical silver(I) complexes have previously been described for tpy ligands substituted at the 6-position and crystallised from acetone, and it was proposed that this was the structure formed by the unsubstituted tpy ligand in non-coordinating solvents too.[15b] Our study indicates that the silver(I) chemistry of terpyridyl ligands that do not bear substituents in the 6-position(s) is more complex and that the structure in non-coordinating solvents is not a simple dinuclear double helicate, but that oligomeric spirals are formed (of which the dinuclear double helicate is a low nuclearity example). Substituents in the 6-position sterically prevent the terpyridyl from engaging in the formation of trinuclear or higher oligomers and consequently drive the systems to give dinuclear double helices. Our rationalisation of the extraordinary geometries of these systems also leads to the suggestion that similar spiral motifs might well appear in the silver complexes of larger unsubstituted or thiosubstituted poly(pyridyl) ligands.

Experimental Section

4′-Thiomethyl-2,2′:6′,2′-terpyridine (L) was prepared by the literature method of Potts.[17]

Silver(I) complexes of L: Silver(I) acetate (0.0181 g, 0.11 mmol) and L (0.0302 g, 0.11 mmol) were heated to reflux in methanol (15 cm^3) for 2 hours. The resulting colourless solution was filtered through cotton wool to remove trace impurities and the filtrate treated with an excess of a saturated methanolic solution of the appropriate anion.

Tetrafluoroborate salt: Treatment with ammonium tetrafluoroborate (excess). On leaving the solution to stand, a white precipitate was formed and isolated by filtration (0.0356 g, 68 %). IR (KBr): $\tilde{\nu} = 1635$ (w), 1585 (s), 1562 (m), 1538 (m), 1469 (m), 1434 (w), 1407 (m), 1326 (w), 1245 (w), 1060 (s), 867 (w), 825 (w), 786 (s), 740 (w), 682 (w), 655 (w), 574 (w), 520 cm^{-1} (w); ^{1}H NMR (CD_3CN, 250 MHz, 3.5 mM, 298 K): $\delta = 8.57$ (d, J(H,H) = 4.0 Hz, 2H; H6), 8.28 (d, J(H,H) = 7.75 Hz, 2H; H3), 8.03 (s, 2H; H3′), 7.99 (td, J(H,H) = 7.6, 1.8 Hz, 2H; H4), 7.51 (ddd, J(H,H) = 7.6, 5.0, 1.2 Hz, 2H; H5), 2.71 (s, 3H; SMe); ^{1}H NMR (CD_3NO_2, 250 MHz, 5.9 mM, 298 K): $\delta = 8.13$ (d, J(H,H) = 7.1 Hz, 2H, H3), 8.03–7.88 (m, 6H; H6, H3′, H4), 7.24 (br, 2H; H5), 2.71 (s, 3H; SMe): MS (+ve FAB): m/z: 386 [AgL], 494 $[Ag_2L]$, 667 $[AgL_2]$, 773 $[Ag_2L_2]$, 861 $[Ag_2L_2(BF_4)]$, 1336 $[Ag_3L_3(BF_4)_2]$, 1530 $[Ag_4L_3(BF_4)_3]$, 1809 $[Ag_4L_4(BF_4)_3]$, 2003 $[Ag_5L_4(BF_4)_4]$; MS (ESI; MeCN): m/z (%): 386 (100) $[AgL^+]$, 427 (30) $[AgL(MeCN)^+]$, 665 (35) $[AgL_2^+]$, 759 (1) $[AgL_2(BF_4)^+]$, 861 (1) $[Ag_2L_2(BF_4)^+]$, 1140 (1) $[Ag_2L_3(BF_4)^+]$, 1226 (1) $[Ag_2L_2(BF_4)_2^+]$, 1335 (1) $[Ag_3L_3(BF_4)_2^+]$, 1614 (1) $[Ag_4L_3(BF_4)_4^+]$, 1809 (1) $[Ag_5L_3(BF_4)_5^+]$; elemental analysis calcd (%) for $AgC_{16}H_{13}N_3SBF_4 \cdot H_2O$: C 39.1, H 3.1, N 8.5; found: C 39.1, H 3.1, N 8.8.

Hexafluorophosphate salt: Treatment with ammonium hexafluorophosphate. On leaving the solution to stand, a white precipitate was formed and isolated by filtration (0.0429 g, 79 %). IR (KBr): $\tilde{\nu} = 1585$ (s), 1562 (m), 1538 (w), 1473 (m), 1434 (w), 1411 (m), 1330 (w), 1249 (w), 1160 (w), 1126 (m), 1014 (w), 995 (w), 836 (s), 786 (s), 740 (m), 682 (m), 682 (w), 655 (w), 624 (w), 559 cm^{-1} (s); ^{1}H NMR (CD_3CN, 250 MHz, 3.5 mM, 298 K): $\delta = 8.57$ (d, J(H,H) = 4.0 Hz, 2H; H6), 8.28 (d, J(H,H) = 7.76 Hz, 2H; H3), 8.03 (s, 2H; H3′), 7.99 (td, J(H,H) = 7.7, 1.8 Hz, 2H; H4), 7.51 (ddd, J(H,H) = 7.6, 4.9, 1.2 Hz, 2H; H5), 2.71 (s, 3H; SMe); ^{1}H NMR (CD_3NO_2, 300 MHz, 5.9 mM, 298 K): $\delta = 8.13$ (d, J(H,H) = 7.0 Hz, 2H; H3), 8.05–7.90 (m, 6H; H6, H3′, H4), 7.24 (br, 2H; H5). 2.71 (s, 3H; SMe); MS (+ve FAB): m/z: 386 [AgL], 494 $[Ag_2L]$, 667 $[AgL_2]$, 919 $[Ag_2L_2(PF_6)]$; MS (ESI; MeCN): m/z (%): 386 (70) $[AgL^+]$, 427 (30) $[AgL(MeCN)^+]$, 537 (1) $[AgL(PF_6)^+]$, 576 (1) $[AgL(MeCN)(PF_6)^+]$, 667 (40) $[AgL_2^+]$, 817 (1) $[Ag_2L_2(MeCN)^+]$, 919 (5) $[Ag_2L_2(PF_6)^+]$, 1000 (1) $[Ag_2L_2(MeCN)_2(PF_6)^+]$, 1198 (1) $[Ag_2L_2(PF_6)^+]$, 1452 (1) $[Ag_3L_3(PF_6)_2^+]$, 1731 (1) $[Ag_3L_4(PF_6)_2^+]$; elemental analysis calcd (%) for $AgC_{16}H_{13}N_3SPF_6$: C 36.1, H 2.5, N 7.9; found: C 36.4, H 2.6, N 7.8.

Trifluoroacetate salt: Treatment with ammonium trifluoroacetate. On leaving the solution to stand, yellow crystals precipitated and were isolated by filtration (0.0831 g, 77 %). IR (KBr): $\tilde{\nu} = 1662$ (s), 1585 (m), 1562 (m), 1542 (w), 1469 (m), 1434 (w), 1403 (m), 1326 (w), 1292 (w), 1199 (s), 1180 (s), 1122 (s), 998 (w), 964 (w), 821 (m), 786 (s), 721 (m), 682 (w), 655 (w), 624 (w), 574 cm^{-1} (m); ^{1}H NMR (CD_3CN, 250 MHz, 3.5 mM, 298 K): $\delta = 8.61$ (d, J(H,H) = 4.25 Hz, 2H; H6), 8.30 (d, J(H,H) = 8.0 Hz, 2H; H3), 8.04 (s, 2H; H3′), 8.02 (t, J(H,H) = 7.5 Hz, 2H; H4), 7.54 (dd, J(H,H) = 7.6, 1.8 Hz, 2H; H5), 2.71 (s, 3H; SMe); ^{1}H NMR (CD_3NO_2, 300 MHz, 298 K): $\delta = 8.11$ (d, J(H,H) = 4.5 Hz,2H; H6), 8.06 (d, J(H,H) = 8.4 Hz, 2H; H3), 7.85 (m, 4H; H3′, H4), 7.25 (ddd, J(H,H) = 7.9, 5.2, 1.1 Hz, 2H; H5), 2.71 (s, 3H; SMe); MS (+ve FAB): m/z: 386 [AgL], 667 $[AgL_2]$, 773 $[Ag_2L_2]$, 887 $[Ag_2L_2(CF_3CO_2)]$; MS (ESI; MeCN): m/z (%): 237 (5) $[AgL(MeCN)_2^{2+}]$, 386 (100) $[AgL^+]$, 427 (30) $[AgL(MeCN)^+]$, 506 (10) $[AgL(CF_3CO_2)^+]$, 667 (40) $[AgL_2^+]$, 887 (25) $[Ag_2L_2(CF_3CO_2)^+]$, 1108 (1) $[Ag_3L_2(CF_3CO_2)_2^+]$, 1223 (1) $[Ag_3L_2(CF_3CO_2)_3^+]$, 1385 (1) $[Ag_3L_3(CF_3CO_2)_2^+]$; elemental analysis calcd (%) for $Ag_2C_{36}H_{26}N_6S_2O_4F_6 \cdot 0.5\,H_2O$: C 42.8, H 2.7, N 8.3; found: C 42.8, H 2.6, N 8.0.

Perchlorate salt: Treatment with sodium perchlorate. On leaving the solution to stand, a white precipitate was formed and isolated by filtration

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(0.0375 g, 72 %). IR (KBr): 1578 (m), 1561 (s), 1540 (w), 1464 (w), 1393 (m), 1384 (s), 1147 (s), 1122 (s), 1077 (s), 1005 (w), 785 (s),730 (w), 680 (w), 667 (w), 637 (w), 630 (w), 624 (m), 575 cm^{-1} (m); ^{1}H NMR (CD_3CN, 250 MHz, 3.5 mM, 298 K): $\delta = 8.57$ (d, J(H,H) = 4.01 Hz, 2H; H6), 8.28 (d, J(H,H) = 7.78 Hz, 2H; H3), 8.03 (s, 2H; H3′), 7.99 (td, J(H,H) = 7.6, 1.8 Hz, 2H; H4), 7.51 (ddd, J(H,H) = 7.6, 5.0, 1.2 Hz, 2H; H5), 2.71 (s, 3H; SMe); ^{1}H NMR (CD_3NO_2, 300 MHz, 298 K): $\delta = 8.14$ (br d, J(H,H) = 6.9 Hz,2H; H3), 7.97 (br m, 6H; H6, H3′, H4), 7.24 (br, 2H; H5). 2.71 (s, 3H; SMe); MS (ESI; MeCN): m/z (%): 386 (100) [AgL^+], 429 (45) [$AgL(MeCN)^+$], 667 (20) [$AgL_2{}^+$], 873 (2) [$Ag_2L_2(ClO_4)^+$], 1152 (1) [$Ag_2L_3(ClO_4)^+$], 1359 (1) [$Ag_3L_3(ClO_4)_2{}^+$]; elemental analysis calcd (%) for $AgC_{16}H_{13}N_3SClO_4 \cdot 0.5H_2O$: C 38.8, H 2.8, N 8.5; found: C 38.7, H 2.6, N 8.3.

X-ray crystallographic structural characterisations: For all crystals, data were collected with a Siemens SMART three-circle system with CCD area detector. A summary of the crystallographic data can be found in Table 2. Specific details of the refinement were as follows:

$[\{Ag_5L_5(MeCN)_3\}_n][ClO_4]_{5n}$: Crystals were obtained from acetonitrile by the slow diffusion of benzene. Systematic absences indicated the space group *Pbca*. As well as three molecules of MeCN coordinated to Ag, the asymmetric unit contained lattice solvent comprising one C_6H_6, two 100 % occupancy MeCN and an additional highly disordered group modelled as two partial occupancy MeCN molecules.

$[\{Ag_5L_5(MeCN)_3\}_n][BF_4]_{5n}$: Crystals were obtained from acetonitrile by the slow diffusion of benzene. Both the crystal finally used and a previous one showed a very rapid fall-off in diffraction intensity at higher angle, attributed to the anion disorder. The borofluoride anions were very severely disordered and could not be completely modelled. Three full-occupancy and two half-occupancy anions were modelled as rigid bodies, with three further part-occupancy fluorine atoms. All residual peaks were in the region containing the disordered anions, but the largest peak was only 0.66 e Å^{-3} and no further complete anions could be located; this region probably also contains some disordered solvent. The terminal methyl groups (projecting into the anion region) were found to have high thermal motion and the S–Me distances were restrained to be equal. Anisotropic displacement parameters were used for all non-hydrogen atoms, apart from low occupancy anion atoms and the most mobile S–Me group (C519). The absolute structure of the individual crystal chosen was checked by refinement of a delta-f″ multiplier. Absolute structure parameter $x = 0.11(5)$. A merohedral twinning parameter was refined (value 0.190(1); inclusion of this parameter gave a substantial improvement in the R values.)

$[AgL(MeCN)][PF_6]$: Crystals were obtained from acetonitrile by the slow diffusion of diethyl ether. Systematic absences indicated either space group *Cc* or *C*2/*c*. The former was chosen on the basis of intensity statistics and the apparent value of Z, and was shown to be correct by successful refinement. The absolute structure of the individual crystal chosen was checked by refinement of a delta-f″ multiplier. Absolute structure parameter $x = 0.06(5)$. Floating origin constraints were generated automatically.

$[Ag_2L_2(CF_3CO_2)_2]$: Crystals were obtained from methanol on leaving the solution to stand. No solution or refinement problems were encountered. A second sample recrystallised from acetonitrile (by slow diffusion of diethyl ether) rather than from MeOH proved to have an identical unit cell and structure.

$[Ag_nL_n][PF_6]_n$: Crystals were obtained from nitromethane by the slow diffusion of benzene. The Ag atom was found to be disordered between two positions about 0.9 Å apart, so that the shortest Ag–Ag chain interactions are between two Ag atoms of the same type. The absolute structure of the individual crystal chosen was checked by refinement of a delta-f″ multiplier. Absolute structure parameter $x = 0.00(9)$. Floating origin constraints were generated automatically. Extinction coefficient 0.00026(9).

$[Ag_5L_6][BF_4]_5$: Crystals were obtained from nitromethane by the slow diffusion of diethyl ether. Systematic absences indicated space group *C*222$_1$, but the structure was solved by direct methods in space group *C*2 with additional symmetry later identified and added. One thiomethyl group was disordered between two positions. The asymmetric unit contained five molecules of nitromethane, one of which lay on a special position and one of which was modelled at 50 % occupancy; one residual peak was modelled as the oxygen of a 25 % occupancy water molecule. The BF_4 counterions were also partly disordered with two at half occupancy (one close to a symmetry element); the B–F and F–F distances were restrained in anion 4. The absolute structure of the individual crystal chosen was checked by refinement of a delta-f″ multiplier and it was found to show racemic twinning with absolute structure parameter $x = 0.67(3)$.

CCDC 167628–167633 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB21EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk).

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Table 2. Crystallographic data.

	$[\{Ag_5L_5(MeCN)_3\}_n][ClO_4]_{5n}$	$[\{Ag_5L_5(MeCN)_3\}_n][BF_4]_{5n}$	$[AgL(MeCN)][PF_6]$	$[Ag_2L_2(CF_3CO_2)_2]$	$[Ag_nL_n][PF_6]_n$	$[Ag_5L_6][BF_4]_5$
formula	$Ag_5C_{86}Cl_5H_{74}N_{18}O_{20}S_5 \cdot 2CH_3CN \cdot C_6H_6 \cdot xCH_3CN$	$Ag_5B_5C_{86}F_{20}H_{74}N_{18}S_5 \cdot xCH_3CN$	$AgC_{18}F_6H_{16}N_4PS \cdot CH_3CN$	$AgC_{18}F_6H_{13}N_3O_2S$	$AgC_{16}F_6H_{13}N_3PS$	$Ag_5B_5C_{96}F_{20}H_{78}N_{18}S_6 \cdot 4CH_3NO_2$
M_r	$n(2712.69 + x41.05)$	$n(2492.86 + x41.05)$n	614.30	500.24	n532.19	2893.70
crystal system	orthorhombic	tetragonal	monoclinic	triclinic	tetragonal	orthorhombic
a [Å]	25.0558(4)	26.346(2)	11.901(2)	8.266(3)	26.3004(3)	28.7382(4)
b [Å]	28.5128(4)	26.346(2)	27.314(4)	8.696(3)	26.3004(3)	26.83560(10)
c [Å]	30.83410(10)	30.516(4)	7.2602(10)	13.027(5)	10.8198(2)	31.2778(5)
α [°]	90	90	90	80.319(5)	90	90
β [°]	90	90	96.825(4)	84.767(5)	90	90
γ [°]	90	90	90	76.677(5)	90	90
V [Å^3]	22028.2(5)	21182(4)	2343.3(6)	896.9(6)	7484.17(18)	24121.6(5)
T [K]	180(2)	180(2)	185(2)	185(2)	180(2)	180(2)
space group	*Pbca*	$I\bar{4}$	*Cc*	$P\bar{1}$	$I4_1cd$	$C222_1$
Z	8	8	4	2	16	8
crystal size [mm]	0.2 × 0.2 × 0.1	0.85 × 0.12 × 0.15	0.5 × 0.1 × 0.06	0.6 × 0.08 × 0.06	0.58 × 0.14 × 0.14	0.6 × 0.1 × 0.1
data/parameters	17253/1381	18560/1198	2824/310	3930/254	2927/263	29493/1484
$R(F)$ [$I > 2\sigma(I)$]	0.0869	0.0635	0.0445	0.0372	0.0600	0.0595
$wR(F^2)$ (all data)	0.1735	0.1884	0.0969	0.0821	0.1723	0.1691
goof (F^2)	1.084	1.121	0.891	0.887	1.069	1.064

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