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Supramolecular design of one-dimensional coordination polymers based on silver(I) complexes of aromatic nitrogen-donor ligands

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Contents

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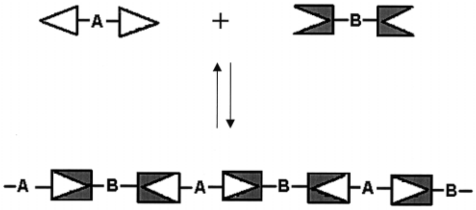
Abstract

This review discusses the design and structure of coordination polymers derived from Ag(I) with N-donor ligands and their role in the investigation of weak non-covalent interactions in the solid state. These forces include arene–arene, metal–anion, metal–arene and metal–metal interactions. The main purpose of this review is to classify and discuss the supramolecular forces which define the overall observed structure (topology, geometry and packing arrangement) of coordination polymers by comparison of a series of structurally related compounds when one parameter of the multi-component system (choice of anion, ligand or solvent) is varied. Design criteria for one-dimensional polymers are given and discussed with respect to the fundamental importance of these compounds for understanding and further development of supramolecular synthetic strategies.

Keywords: Crystal engineering; Coordination polymers; Silver(I) compounds; Supramolecular chemistry

1. Introduction

Supramolecular polymer chemistry is a branch of modern science which is developing through the combination of polymer chemistry with supramolecular chemistry [1,2]. The supramolecular polymer is generated by self-assembly of complementary monomeric compounds (Scheme 1). Constituents of the chain are



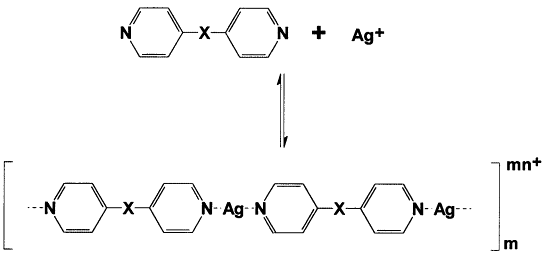
Scheme 1. Reversible association of complimentary molecular blocks leading to the formation of a polymeric supermolecule.

linked through reversible connections enabling the polymer to grow, shorten, rearrange and adapt, this class of compounds is defined as 'dynamic combinatorial materials' [2] and is currently drawing a great deal of attention [3].

The first aim of supramolecular polymer chemistry is to allow *predictable control* over the polymer structure or, more precisely, over the packing arrangement of the polymeric entities in the solid state and also the structure of the infinite array itself. The principles and strategy for the engineering of these polymers are based on two general concepts: *supramolecular interactions* and *supramolecular synthons* introduced by Desiraju in 1995 [4].

In order to establish general principles, researchers often exploit a simple system, allowing modelling and the study of phenomena which are superimposed upon a more complicated, multi-component system. Thus, one-dimensional (1D) chain-like complexes, being the simplest topological type of coordination array, represent a good starting point to model and investigate infinite, polymeric compounds to develop strategies for engineering supramolecular polymers. The relative simplicity of the 1D chain allows us to classify all types of non-covalent contacts between each polymeric supermolecule. For example, models of structural effects and interactions in diamondoid frameworks [5] involve viewing the 3D framework as a number of connected 1D arrays (1D infinite helices or aromatic stacks) and then interpreting the changes in these 1D units. These examples of the controlled engineering of 3D polymers stress the necessity for precise understanding of the design principles for 1D coordination polymers before one can start to rationalise solid-state structures with higher dimensionality.

In this review our main focus is on the coordination polymers constructed from bipyridyl ligands bound to Ag(I) metal cations (Scheme 2). Coordination polymers based on Ag(I) cations are attracting a great deal attention [3] primarily perhaps because they are readily available. Indeed, due to the high lability of the Ag-donor atom bond [6] the process of coordination polymer formation is totally reversible, and the resulting Ag(I) coordination polymers can generally be crystallised allowing investigation by single-crystal X-ray diffraction. The coordination sphere of Ag(I) is similarly very flexible and can adopt coordination numbers between two and six and various geometries from linear through trigonal to tetrahedral, trigonal pyramidal and octahedral [7]. The structural flexibility of these complexes is essential for



Scheme 2. Reversible metal–ligand interactions binding molecular components within a polymeric coordination array. Spacer **X** can be linear, angular or a flexible linker between pyridyl donor units.

the investigation of non-covalent interactions, as even weak intermolecular forces significantly affect the geometry and topology of the Ag(I) coordination polymers in the solid state. The supramolecular interactions defining the structures of these complexes are surveyed in Section 2.

2. Supramolecular interactions in coordination polymers

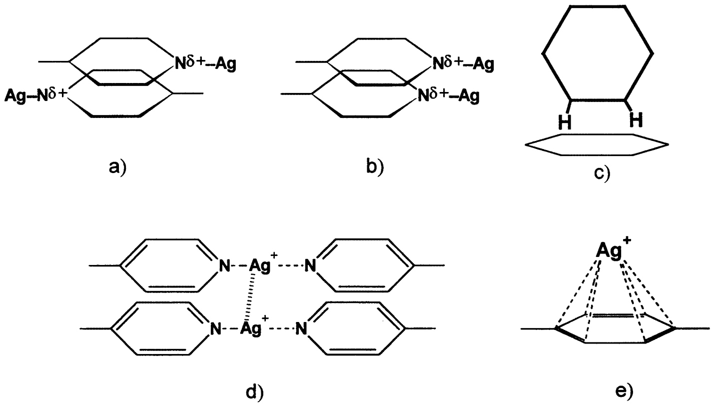
2.1. Metal–ligand interactions

The main synthon within polymers which is provided by a reversible interaction between Ag(I) and N-donor pyridyl ligands (Scheme 2). The nature of this interaction is predominantly donation of the pyridyl lone electron pair to the metal cation and its energy is comparable with that of a strong hydrogen bond (for example, 47.0(5) kJ mol^{-1} for Ag(I) [6]). The Ag(I) cation usually prefers a linear, two coordinate, coordination geometry with nitrogen donors [6], thus encouraging the formation of 1D polymers when Ag(I) salts react with a bridging bis-monodentate ligand (Scheme 2). Like hydrogen bonds in organic supermolecules, the metal cation–donor nitrogen synthon may be considered as a 'supramolecular cement' [4] in coordination polymers in that it binds molecular units into an infinite chain giving a nanoscopic species of higher order, in terms of supramolecular hierarchy [8] — a supramolecular array.

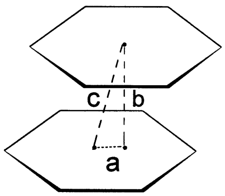
2.2. π–π Interactions

A coordination polymer designed from a bipyridyl ligand unavoidably contains aromatic groups in its structure. Even simple aromatic rings (for example, pyridyl or phenyl) may be involved in attractive contacts with each other; this interaction according to the Hunter–Sanders model exists due to an electrostatic attraction of aromatic π-electrons to a positively charged ring σ-frame (Scheme 3a–c) [9]. The energy of 'face-to-face' and 'face-to-edge' contacts based on experiments in solution can be estimated (in approximation of the energy as an additive function of number of π-electrons) as 4.0(2) [10] and 2.5(3) [11a] or 1.4(8) kJ mol^{-1} [11b] per six-membered aromatic cycle, respectively. High-precision ionisation measurements in the gas phase give much higher energies for the interaction of two benzene molecules, 10.0 ± 1.6 kJ mol^{-1} [12], which is in good agreement with the calculated value, 9.6 kJ mol^{-1} [13]. However, the same method of calculation performed for benzene dimers in solution indicates that the optimal gas phase interaction is considerably damped by solvent competition and entropic effects [13] so that in the solution the energy of phenyl–phenyl interactions is about 4 kJ mol^{-1} [13]. This is consistent with the energy per six-membered aromatic cycle deduced from the experimental data obtained in solution for larger aromatic systems [10,11a]. This energy depends significantly on the nature of the substituents on the aromatic ring [9,10,14] and even on the polarity of the solvent [15].

A recently published critical account on π–π-stacking in metal complexes with aromatic nitrogen-containing ligands is particularly relevant to coordination polymer construction [16]. Based on the geometrical analysis of structures of metal complexes extracted from the Cambridge Structural Database (CSD) the most favourable geometry for two interacting pyridyl donors has been postulated with centroid–centroid separation (distance *c*, Scheme 4) of 3.80 Å and offset distance (distance *a*, Scheme 4) of 1.30 Å [16]. Metal coordination to the donor atom of the heterocycle induces electron withdrawal from the aromatic ring thus increasing the electrostatic component of any intermolecular π–π interaction. As a result the 'head-to-tail' (Scheme 3a) orientation of stacked pyridyls is energetically more favourable than the 'head-to-head' one (Scheme 3b) as supported by numerous examples of coordination compounds [16]. It appears that geometric characteristics of stacked quinolyl donors are very similar to those observed for pyridyl groups suggesting that the general principles summarised in Ref. [16] will apply for most heteroaromatic ligands.



Scheme 3. Schematic representation of weak supramolecular contacts. Face-to-face aromatic interaction of pyridyl rings; two possible orientations: (a) 'head-to-tail' and (b) 'head-to-head'; (c) edge-to-face aromatic interaction; (d) metal–metal interactions occurring between two adjacent chains; (e) interaction of Ag(I)–η^6 cation with π-electrons of aromatic system.



Scheme 4. Geometric characteristics for two stacked aromatic rings: a = offset distance of centroids; b = plane-to-plane separation; c = centroid–centroid separation.

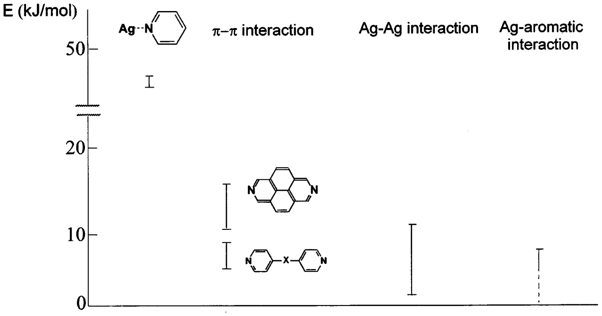
2.3. Metal–metal interactions

Some d^{10} metal cations [i.e. Au(I), Ag(I), Cu(I)] show a tendency to form metal–metal bonds (Scheme 3d) [17]. In the case of Ag(I) and Cu(I) the attractive character of this supramolecular contact has been debated and its energy, strongly dependent on ligand type, has been only roughly estimated as 5(7) kJ mol^{-1} [17,18]. However, examples of Ag–Ag contacts, which are unsupported by bridging ligands, show that this interaction may have a considerable influence on the orientation of coordination complexes in the crystalline state [19].

2.4. Metal–π interactions

Many transition metal cations can accept π-electrons from unsaturated organic molecules and, thus, form very stable organometallic molecules. The Ag(I) cation is known to form comparatively weak interactions with aromatic molecules; hence, measurements of association constants of Ag(I) with simple aromatic hydrocarbons lead to a conclusion that the broader a conjugated electronic system the stronger Ag(I)–π interaction [20]. With polycyclic aromatic molecules Ag(I) salts give polymeric complexes via a Ag–C(sp^2) bond [21]. There are about 130 examples of Ag–η^1 and Ag–η^2 arene bonding found in the CSD with a mean Ag–arene distance of 2.82 Å [22]. Structural statistics on long-range Ag–η^6 interactions are less reliable (Scheme 3e), but it occurs often in coordination polymers with nitrogen-donor ligands [23,24]. Despite the long-range interaction and its relative weakness, Ag–η^6 contacts with arenes have been documented in the solid state, including the first example of an arene–Ag sandwich compound [22]; the same work summarises structural statistics for metal–η^6 species reports a range of Ag–centroid distances of 2.89–3.37 Å [22].

The interaction between Ag(I) and donor-substituted naphthalene has been reported to be of comparable energy (Scheme 5) to the conformational interconver-



Scheme 5. Diagram showing overlapping of energetic ranges of supramolecular interactions, which cause interference of the non-covalent forces in the solid state.

sion (8.66 kJ mol^{-1}) of a so-called 'clip'-receptor based on diphenylglycouril molecule and able to bind Ag(I) cations between two aromatic cavity walls [25], according to a recent work, the energy of an Ag(I)–aromatic interaction might even be larger [26]. It would be expected that smaller or more electron-poor aromatic molecules would less readily donate π-electrons to Ag(I) and thus form weaker contacts. It is also logical that interactions between weakly coordinating anions and Ag(I) will affect the strength of any Ag–aromatic interaction. The observation that strongly coordinating anions (SO_4^{2-}, $PhCO_2^-$, $MeCO_2^-$) completely diminish the metal–aromatic interaction [25] is important, and therefore should be taken into consideration when Ag(I)–aromatic interactions are used during polymer construction.

2.5. Coulombic interactions

It is important to note that each metal cation brings a positive charge into the polymeric array. This charge can be delocalised due to ligand donor atom coordination and/or partially neutralised via a coordinating anion, and in the case of non-bonding anions such as PF_6^-, BF_4^- this charge may lead to a significant Coulombic repulsion between adjacent supermolecules. Being the main repulsive force within the polymeric structure, these electrostatic interactions between cations effectively counteract all the other contacts, which are usually attractive, as shown below.

2.6. Anion bridging

Anions, which have the ability to act in a polydentate manner (e.g. NO_3^-, SO_4^{2-}, $MeCO_2^-$) often link several cations together [27]. The energy of anion coordination in supramolecular structures can vary over a wide range and its influence is difficult to predict. Even a weak bridging interaction can distort a polymeric structure significantly when compared with an analogous structure formed in the presence of a non-bonded anion. Thus, anion-bridging interactions can play a significant role in long-range structural order.

Most information about the supramolecular interactions discussed above were obtained from studies of discrete molecular models designed to correlate specific 'insulated' supramolecular interaction. In a supramolecular array these intermolecular contacts interfere so that the overall structure is a compromise between interactions of different energy and nature (Scheme 5) [4]. To exploit the combined interfering effects between different types of interaction when one endeavours supramolecular design is a critical challenge in crystal engineering. We shall illustrate in the following sections how the synthons and their combinations can be applied for the construction of 1D chain-like coordination polymers.

3. Design of polymeric arrays

3.1. Topology of 1D Ag(I) polymers

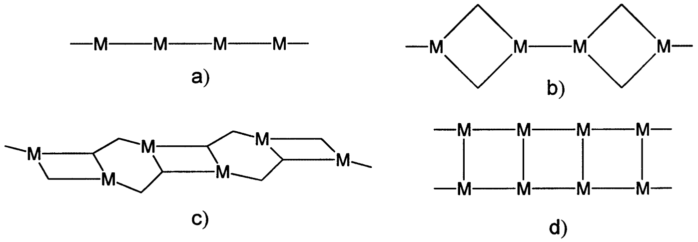
The idea of topological equivalence, a useful tool in description of coordination networks [3a], can be used to classify 1D polymers according to the connectivity of their constituents.

3.1.1. Simple chains

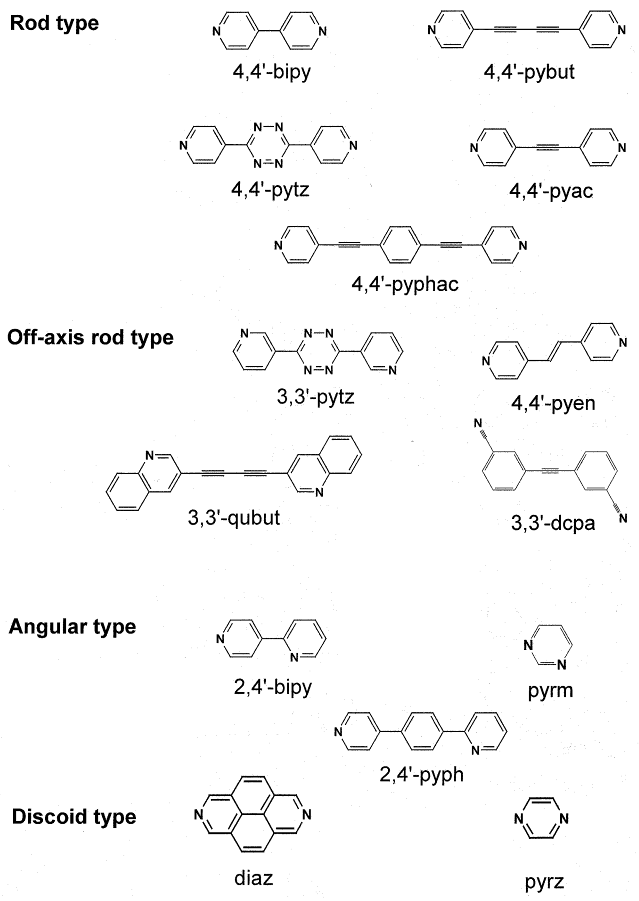
Most 1D polymeric complexes have the simplest topology of a single-strand chain (Scheme 6a), particularly when a two-coordinate metal interacts with a bidentate ligand (Scheme 7). Ligands tending to form single chains usually have linear (pyrazine [28], quinoxaline [29], diazapyrene [23,30], 4,4′-bipyridine [28e,31], 3,6-bis{4′-pyridyl}tetrazine [32], diphenazine [33]), angular (2,4′-bipyridine [34]) or ‘off-axis rod’ (1,2-bis{2′-pyridyl}ethylene [35], 1,4-bis{2′-pyridyl}butadiyne [36]) geometry, where donor groups are linked by a rigid spacer (Scheme 7). Polydentate ligands are also able to form single 1D chains when they chelate Ag(I) centres; in this case Ag(I) cations within the chain will adopt trigonal [37] or tetrahedral geometries [38].

3.1.2. Loops and chains

This topological type, which may be represented as a sequence of alternating rods and loops (Scheme 6b), is much rarer [39] and is usually formed by a bidentate ligand which has a flexible spacer (X = CH_2CH_2, $CH_2C_6H_4CH_2$, Scheme 2) between the donor groups [39a,b], or a ligand with ‘off-axis rod’ geometry [40]. A three-coordinate metal centre is also clearly required [39,40]. We have found that the anion type, as well as properties of solvent, significantly influence the chain topology [40]. Thus, the reaction between 3,3′-pytz (Scheme 7) and Ag(I) is dependent on the coordinative ability of anion and forms ‘loops and rods’ with weakly coordinating anion PF_6^- (Fig. 1) or single zigzag chains with the comparatively coordinating anion $CF_3SO_3^-$ (Fig. 2). The influence of solvent of crystallisation is similar to the influence of the anion: more-coordinating MeCN leads to a single-strand zigzag



Scheme 6. Topological types of 1D polymers: (a) chain; (b) sequence of loops and rods; (c) sequence of fused rings; and (d) ladder type. Lines joining metals represent bidentate bipyridyl ligands with general formula Py–X–Py, where X is a spacer group.



Scheme 7. Some ligands applied for the syntheses of the polymers discussed in this review.

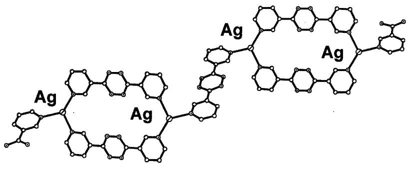


Fig. 1. Molecular structure of the $\{[Ag_2(3,3'\text{-pytz})_3]^+_\infty$ cationic chain with ‘loops and rods’ topology.

chain $\{[Ag(3,3'\text{-pytz})(MeCN)_2]PF_6(MeCN)\}_\infty$ (Fig. 3), whereas using less-coordinating $MeNO_2$ gives a compound $\{[Ag_2(3,3'\text{-pytz})_3](PF_6)_2(MeNO_2)_4\}_\infty$ with a more complex topology (Fig. 1). Alternatively, loops may be constructed from a number of metal cations and rigid angular ligands [39c].

3.1.3. Fused loops

The tridentate ligand, 1,3,5-tris(pyrazolyl)benzene (tpb), and the mixed donor tetradentate ligand, 4-thiomethyl-6-(4-pyridyl)-2,2′-bipyridine (tmpb), form binuclear metallacycles $[Ag(tpb)]_2^{2+}$ and $[Ag(tmpb)]_2^{2+}$, respectively, bearing an *exo*-dentate peripheral binding site [41]. The metallacycles assemble into 1D polymeric chains (Fig. 4) giving rise to another topological type, which can be depicted as a row of fused loops (Scheme 6c). The tetradentate mixed N,P-donor ligand 3,6-bis(-diphenylphosphino)pyridazine (3,6-dpp) can also form an infinite sequence of loops $\{Ag_2(3,6\text{-dpp})(MeCN)_2](ClO_4)_2\}_\infty$ where Ag(I) cations adopt a trigonal geometry coordinated by two donor atoms of the ligand and one MeCN solvent molecule [42] (Fig. 5). The presence of the soft phosphine-donor encourages Ag–Ag contacts

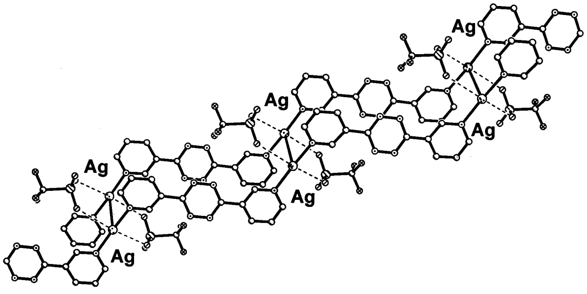


Fig. 2. Aggregation of the $\{[Ag(3,3'\text{-pytz})]^+\}_\infty$ cationic chains into parallel pairs; anions weakly coordinate and bridge adjacent chains.

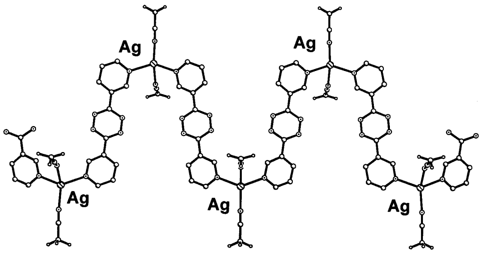


Fig. 3. Molecular structure of the $\{[Ag(3,3'\text{-pytz})(MeCN)_2]^+\}_\infty$ cationic chain with ‘rectangular wave’ geometry. Two MeCN solvent molecules coordinate each Ag(I) centre.

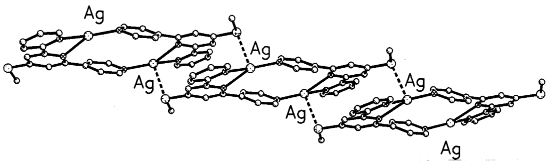


Fig. 4. Aggregation of the $[Ag(tmpb)]_2^{2+}$ binuclear metallacycles into infinite chain.

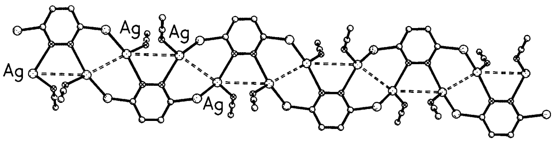


Fig. 5. Molecular structure of the $\{[Ag_2(3,6\text{-dpp})(MeCN)_2]^+\}_\infty$ cationic chain. Phenyl groups are omitted for clarity.

resulting in the infinite sequence of interacting Ag(I) cations within the ribbon-like coordination polymer [42]. Deprotonated sulphanilaminopyrimidine (sap) combined with Ag(I) salts results in an infinite electroneutral array of fused loops $\{[Ag(sap\text{-}H)]\}_\infty$ with discrete pairs of interacting Ag···Ag centres [43].

Various structural isomers of bis(2-pyridylsulphanylmethyl)benzene (psb) were reacted with $AgNO_3$ in order to study the influence of the donor groups on the complex structure [44]. The authors found that *para*-psb leads to a discrete cyclic binuclear complex [Ag(*para*-psb)(NO_3)]$_2$, whereas *meta*- and *ortho*-isomers both lead to polymeric species consisting of fused metallacycles where the Ag(I) centres adopt a distorted tetrahedral and trigonal bipyramidal geometries, respectively.

A four-coordinate metal cation combined with an *exo*-bidentate ligand often leads to the formation of ladder-like 1D polymers (Scheme 6d) [28d,45]. There are only two examples of the ladder complex in the literature when Ag(I) is coordinated to a rigid linear ligand such as 1,2-bispyridylethyne (4,4′-pyac) [45a] or pyrazine (pyrz) [28d]. In both complexes the Ag(I) centres have a distorted tetrahedral geometry completed by coordination of a sidearm terminating ligand in complex $\{[Ag_2(4,4'\text{-pyac})_5](BF_4)_2\}_\infty$ [45a] (Fig. 6) or an anion in complex $\{[Ag_2(pyrz)_3(CF_3SO_3)_2]\}_\infty$ [28d] (Fig. 7). In the latter example the ladder topology is sustained by the coordinating $CF_3SO_3^-$ anion and when a non-coordinating anion PF_6^- is used a single-strand linear chain is observed [28d].

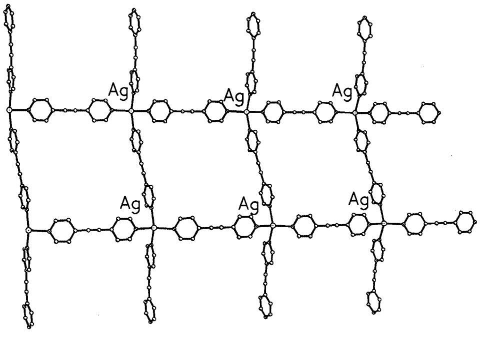


Fig. 6. Molecular structure of the $\{[Ag_2(4,4'\text{-pyac})_5]^{2+}\}_\infty$ cationic chain.

3.1.4. Interwoven strands

The flexible tetradentate ligand 1,6-bis(4-pyridyl)-2,5-diazahexane (1,6-bpd) is representative of a group of ambidentate *endo*-chelating/*exo*-bridging ligands for which the N-donors of the flexible saturated spacer chelate Ag(I) cations which are coordinated additionally by two pyridyl donors belonging to independent ligands [46] (Fig. 8). The chain $\{[Ag(1,6\text{-bpd})](NO_3)\}_\infty$ formed relates to the topological type (Scheme 6c), and hence may be interpreted in terms of two interwoven strands [46]. It is interesting to note that 5,5′-dicyano-2,2′-bipyridine (5,5′-dcbp), which has a rigid chelating spacer and is a geometrical analogue of 1,6-bispyridyl-2,5-diazahexane, forms a single-strand chain $\{[Ag(5,5'\text{-dcbp})(NO_3)]\}_\infty$ (Fig. 9) with a helical conformation where only one nitrile-donor of each ligand is involved in polymeric propagation while the other nitrile remains uncoordinated [47].

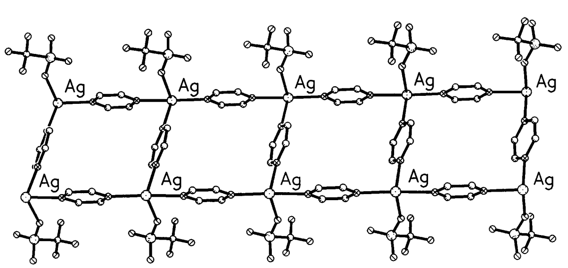


Fig. 7. Molecular structure of the $\{[Ag_2(pyrz)_3(CF_3SO_3)_2]\}_\infty$ chain.

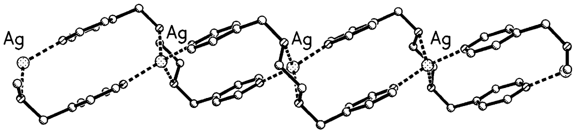


Fig. 8. Molecular structure of the $\{[Ag(1,6\text{-bpd})]^+\}_\infty$ cationic chain.

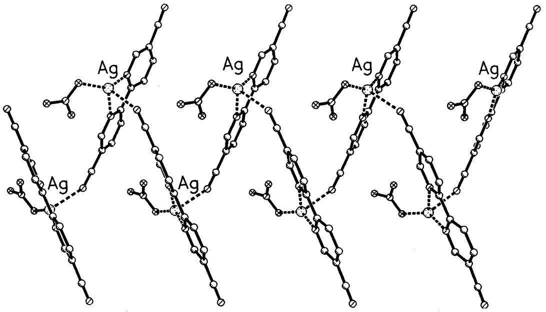


Fig. 9. Molecular structure of the $\{[Ag(5,5'\text{-dcbp})(NO_3)]\}_\infty$ chain.

3.1.5. Chains with pendant groups

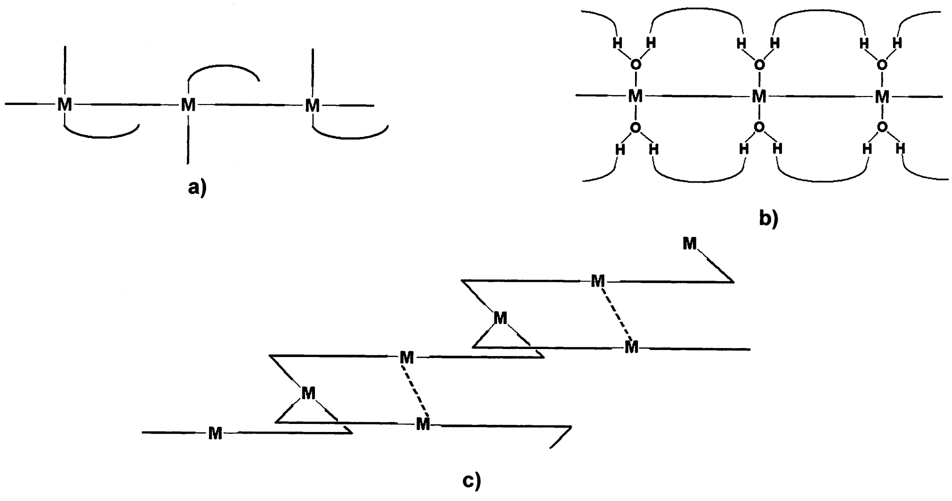
Metal cations within the backbone of a chain having vacant coordination sites can coordinate lateral groups, such as solvent, terminating ligand molecules and anions (Scheme 8a and b) [28d,45a,48]. The flexible coordination sphere of Ag(I) cations leads to a tendency to coordinate such pendant groups. For example, we have recently synthesised an interesting example of a complex $\{[Ag_3(2,4'\text{-pyph})_4](PF_6)_3(MeCN)_3\}_\infty$ where two- and three-coordinate Ag(I) cations alternate along the polymeric chains. Each three-coordinate Ag(I) centre has a pendant arm, which comprises a ligand–Ag–ligand fragment (Scheme 8c) [49].

Alternatively, a peripheral functional group on the ligand molecule can provide an 'anchor' for binding of a pendant. The structure of the polymeric complex of 4,4′-dipyridylsulphide (dps) with $AgNO_3$ demonstrates that the sulphur atoms, spacing pyridyl donors and thus lying within the chain, coordinate to a pendant Ag(I) cation terminated by nitrate groups [50]. The resulting polymer $\{[Ag_3(dps)_2(NO_3)_3(H_2O)_2]\}_\infty$ comprises an infinite zigzag chain $\{[Ag_2(dps)_2]^{+2}\}_\infty$ and pendant groups $[Ag(NO_3)_3]$ coordinated to sulphur atoms.

There are several reports of coordination polymers 'functionalised' with lateral groups able to participate in hydrogen bonding. These groups may be either hydrogen bond donors, as amino groups in the complex $\{[Ag(2\text{-aminopyrimidine})(TolSO_3)]\}_\infty$ [51a], or hydrogen bond acceptors, as carboxylate groups in $\{NH_4[Ag(nicotinate)_2](H_2O)\}_\infty$ [51b].

3.1.6. Other structural types

Careful ligand design allows the construction of 1D polymers with a fascinating complexity such as metallatubules 52a and polyrotaxanes [52b,52c]. It is interesting



Scheme 8. Schematic representation of functionalised 1D polymers bearing: (a) terminating ligand molecules; (b) lateral solvent molecules; and (c) pendant arms.

to note that the polymeric chain can be either threaded through the cavity of a macrocyclic host [52b] or the 1D polymer with a tubular topology can itself encapsulate a neutral guest molecules [52c] giving rise in both cases to polymeric pseudo-rotaxane — remarkable examples of infinite supermolecules based on Ag(I) cations.

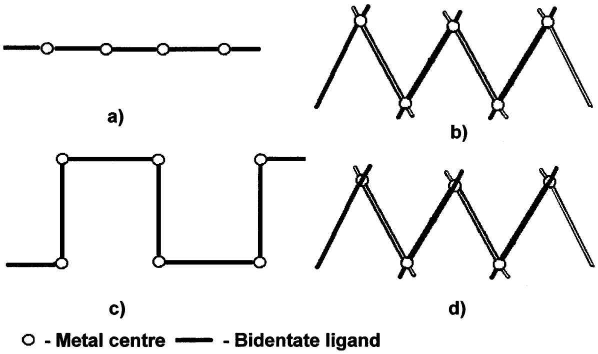
The topology observed in network polymers is predominantly a function of the geometry of the polydentate ligand, and the coordination properties of the metal centre, and the choice of anion and solvent. This allows Ag–N coordination bonds to be used reliably for the construction of supramolecular networks when monomeric building blocks are represented by simple geometric models. However, other structural properties of the polymers, such as the chain geometry and packing arrangement, are affected by a number of interfering supramolecular forces weaker than the 'supramolecular cement' that forms the chain. In order to demonstrate clearly how these weak non-covalent interactions tune the geometry and arrangement of the complexes, we have restricted the scope of the following parts of the review to the coordination polymers with the chain topology shown in Scheme 6a.

3.2. Chain geometry

Despite their overall simplicity the single-chain geometry of 1D polymers may be varied from a straight line to a helix (Scheme 9) depending upon the ligand, metal centre, solvent and anion. The shape of the polymer is therefore programmed by its constructing blocks. The character of the spacer between the donating units of the ligand (Scheme 7) provides the diversity for the organic constructing blocks and, thus, enables it to be programmed.

3.2.1. Linear and zigzag chains

An example where the chain geometry is directly dependent on the functionality of ligand is the case of the two structural isomers 4,4′-pytz and 3,3′-pytz (Scheme



Scheme 9. Geometrical diversity of coordination chains: (a) linear; (b) zigzag; (c) rectangular; and (d) helical geometries.

7) which are different only in the arrangement of the N-donor lone pairs. The first ligand is a linear linker, the second one is an example of an 'off-axis rod' that joins two metal centres. As a result of the ligand geometry, 4,4′-pytz tends to form linear chains, $\{[\mathrm{Ag}(4,4'\text{-pytz})]\mathrm{BF}_4\}_\infty$, when treated with Ag(I) salts (Fig. 10) [32] and the isomeric 3,3′-pytz gives zigzag shaped complexes, $\{[\mathrm{Ag}(3,3'\text{-pytz})]\mathrm{BF}_4\}_\infty$, under the same conditions (Fig. 11) [40]. There are many other examples in the literature where both linear and non-linear isomers of one organic ligand have been employed giving linear or zigzag polymers, respectively; for example Ag(I) complexes of 1,4-(4′-bispyridyl)butadiyne [23] and 1,4-(2′-bispyridyl)butadiyne [36], pyrazine [28] and pyrimidine [39c], 4,4′-bipyridine [23,31] and 2,4′-bipyridine [34] (Scheme 10) may be considered as pairs of isomers of 1D coordination arrays (if anions and solvent guest-molecules are ignored), where isomerism of the polycationic supermolecule is caused by the isomerism of the organic building components.

In addition to the ligand and the metal, the anion can also be important in influencing the chain geometry. Complexes with the disc-shaped ligand 2,7-diazapyrene (diaz) (Scheme 7) clearly demonstrate the way that a strongly coordinating

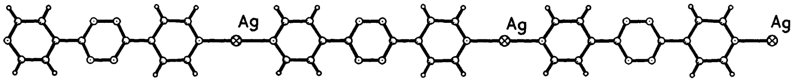


Fig. 10. Molecular structure of the $\{[\mathrm{Ag}(4,4'\text{-pytz})]^+\}_\infty$ cationic chain.

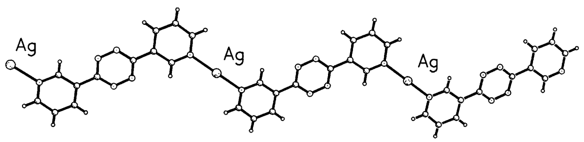
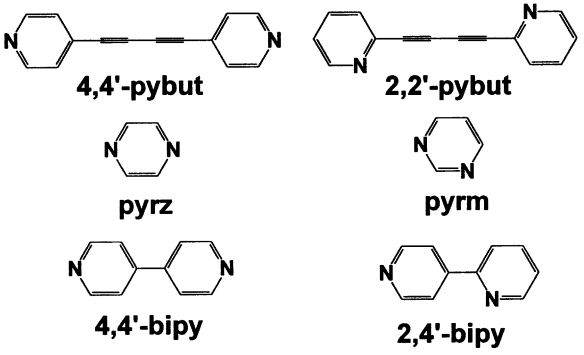


Fig. 11. Molecular structure of the $\{[\mathrm{Ag}(3,3'\text{-pytz})]^+\}_\infty$ cationic chain.



Scheme 10. Pairs of structural isomers of bidentate ligands.

anion can change the overall geometry of 1D polymers. The non-bonding BF_4^- anion in the complex $\{[Ag(diaz)]BF_4\}_\infty$ does not interfere with the ligand coordination and, therefore, does not distort the linear geometry of the Ag(I) cation allowing the formation of the precisely linear (N–Ag–N = 180°) chains (Fig. 12) [30]. In contrast, in the complex $\{[Ag(diaz)NO_3]\}_\infty$ each anion interacts with a metal centre in a bidentate fashion and causes the chains to undulate with an N–Ag–N with angle of 144.2(2)° (Fig. 13) [23]. The same tendency has been observed in 1D complexes of pyrazine where weakly coordinating BF_4^-, PF_6^- and NO_3^- anions do not disrupt the linearity of the cationic chains [28a], as NO_2^- chelating the Ag(I) centres and thus resulting in a zigzag polymer [28e]. Coordination of solvent can similarly influence the coordination polymer providing a wide geometric diversity of chains [28d,40].

The rectangular wave is an alternative non-linear geometry for coordination polymers (Scheme 9c). This type of the chain shape arises when non-linear ligands with asymmetric donating units are placed in a *syn*-conformation at the metal cation (Fig. 3) [35,40,49,53] (the issue of ligand placement will be discussed in Section 4). In the case of a very flexible spacer ($X = CH_2CH_2CH_2$) the polymer may undulate smoothly giving the chain a sinusoidal shape (Fig. 14) [3a,52c,54].

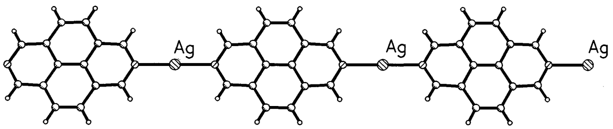


Fig. 12. Molecular structure of the $\{[Ag(diaz)]^+\}_\infty$ cationic chain.

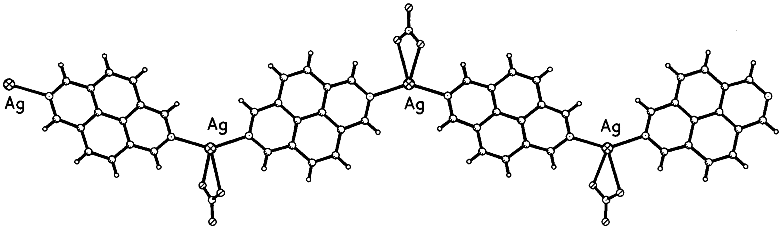


Fig. 13. Molecular structure of the $\{[Ag(diaz)(NO_3)]\}_\infty$ chain.

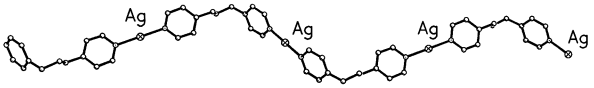


Fig. 14. Molecular structure of the $\{[Ag(PyCH_2CH_2CH_2Py)]^+\}_\infty$ cationic chain with 'sinusoidal' geometry.

3.2.2. Helical chains

In theory any non-linear chain can exist in a helical conformation (Scheme 9d). There are many examples of single-stranded helices based on coordination polymers [34,47,55]. Often the chain helicity is not noticeable because of a rather flat conformation, but some non-linear ligands, in *cisoid* conformation, form a distinctive pitch within a 'sheer' helix (Fig. 15) [55a,56]. Infinite helices can be constructed from bis-bidentate chelating ligands [55b,57], chelating ligands with lateral binding sites [47] or non-chelating polydentate ligands [38a,55a,56].

An interesting example of a coordination polymer with a controllable helicity has been reported recently for Ag(I) complexes of 2,2′-bispyridylketone [38b]. This potentially tetradentate ligand exhibits three coordination modes with Ag(I) cations: bis-chelating, mono chelating mono-bridging and bis-bridging (Scheme 11). It was demonstrated in Refs. [38b,58a] that anions such as NO_3^-, NO_2^- and ClO_3^- bind strongly to the metal centres resulting in the bis-bridging mode of the ligand (Scheme 11c) and leading to a chain with a pronounced helical pitch. In contrast, the non-binding PF_6^- [38b] and BF_4^- [58b] anions allow the ligand to adopt the bis-chelating mode (Scheme 11a) giving a chain with a flatter conformation. The ClO_4^- anion, which can be considered to have an intermediate coordinating ability to Ag(I), gives a complex with an intermediate, mono-chelating mono-bridging mode of binding (Scheme 11b) [38b].

A rigid discoid ligand pyridazine (prdz) readily forms helical polymers when treated with various Ag(I) salts [56a]. It was found [56a] that the size of the helical pitch in the twofold helix $\{[Ag(prdz)(X)]\}_\infty$ is controlled by the type of the anion and can be increased from 3.68 Å ($X = NO_3^-$ anion) to 5.40 Å ($X = CF_3SO_3^-$

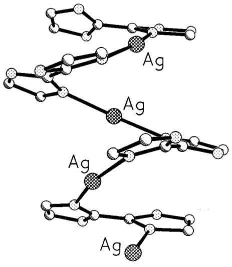
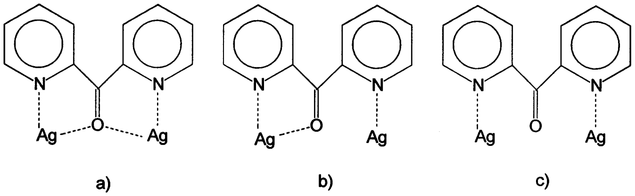


Fig. 15. Molecular structure of the $\{[Ag(bisimidazole)]NO_3\}_\infty$ helical chain.



Scheme 11. Coordination modes of bis(2-pyridyl)ketone with Ag(I) cations within polymeric helices [30].

anion). Although in the case of non-coordinating BF_4^- anion the polymer switches to a fourfold helical mode $\{[Ag(prdz)_2](BF_4)\}_\infty$ with a pitch of 11.17 Å [56a].

The more flexible ligand 3,3′-oxybispyridine (obp) has recently been found to form a polycationic twofold helical motif, $\{[Ag(obp)](X)\}_\infty$, regardless of the nature of the anion [56b]. Structural studies of a series of the complexes $\{[Ag(obp)](X)\}_\infty$ with a number of different anions allowed the authors to observe a direct dependence of the helical pitch on the size of the anion. Thus the shortest repeating unit of the helix was found in the complex $\{[Ag(obp)](NO_3)\}_\infty$ anion and the longest one in the complex $\{[Ag(obp)](PF_6)\}_\infty$ anion [56b].

An interesting example of a double helix, $\{[Ag(bis(4\text{-}pyridyl)propane)](CF_3SO_3)\}_\infty$, has been reported [52c]. This flexible ligand possessing a significant degree of the conformational freedom allows the right-handed and the left-handed strands to intertwine together and form a helix resembling the double helix of DNA. The intertwined strands are interacting via Ag–Ag contacts (Ag–Ag distance 3.089 Å) [52c].

The possibility to assemble coordination arrays into a triple infinite helix has been demonstrated when 3-aminomethylpyridine (3-amp) was used as a ligand [59]. The triple helices $\{[Ag(3\text{-}amp)](ClO_4)\}_\infty$ 'communicate' in the crystalline state due to a network of hydrogen bonds between ligand molecules mediated by ClO_4^- anions. It is worth noting that neither 2-amp nor 4-amp gave a helical array when reacted with $AgClO_4$ but rather gave chains with a zigzag geometry [59].

Although most helical structures that have been reported are crystallised as racemic mixtures, the possibility of stereoselective synthesis of a coordination helix has been demonstrated and can be controlled by using a chiral ligand [57b,60].

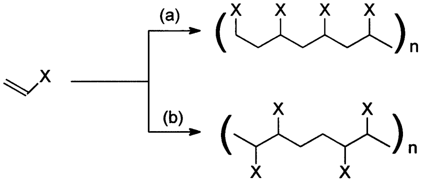
The examples given above illustrate the strategy of constructing various types of 1D coordination polymers simply by using the coordinative properties of the metal cation and anion and by exploiting ligand geometry.

3.3. Toposelective ligand placement in polymers: sequence isomerism in polycationic arrays

The definition of isomerism implies identical chemical composition for the two isomers. However, for coordination polymers the notion 'isomer' is not strictly defined and the reported examples of 'supramolecular isomerism' [61] do not meet the formal criteria of identical molecular formulae. The strict definition of isomers makes comparison of highly related chains difficult and therefore in Section 3.3 and Section 3.4 we will consider the structural features of only the polycationic backbones of coordination polymers and ignore anions and solvent molecules. Thus, we will describe any complexes with polycationic backbones composed from the same ligand molecules and the same metal centres with the same metal/ligand ratio 'isomers'.

There are several sorts of isomerism for covalent polymers. The most common is sequence isomerism [62] (Scheme 12) where the monomer units are incorporated into the chain in a specific order. Despite the large variety of coordination polymers, sequence isomerism has not been described for these compounds previously. Asymmetric ligands (for example, angular type, Scheme 7) which have two or more coordination sites with different ability to interact with a metal centre can potentially combine with transition metal cations to give the arrangement ABABAB ('head-to-tail') or AABBAA ('head-to-head') due to their asymmetry. More often asymmetric ligands are arranged in ABABAB sequence within the coordination chain which results in a polymer where all metal centres are identical [34,37a,37b,47,51a,59] and the repeating unit consists of one metal centre and one ligand molecule.

We have recently found that the rigid angular ligand 2,4′-pyph is a rare example exhibiting both types of orientation within the 1D array. The coordination inequivalence of the nitrogen donors 2,4′-pyph has been demonstrated clearly by the reaction of the ligand with Cu(II) salts. With both $Cu(OAc)_2$ and $Cu(NO_3)_2$ the ligand coordinates to the donor atom of the 4-pyridyl ring to give discrete molecular complexes [49] due to the 2-pyridyl donor being more sterically crowded than the 4-pyridyl unit. Reaction of 2,4′-pyph with $AgPF_6$, however, gives a 1D polymer $\{[Ag(2,4'\text{-pyph})](PF_6)MeCN\}_\infty$ consisting of single chains (Fig. 16). The geometry of all the Ag(I) cations is linear: each ion links together two 4-pyridyl (Ag2) or two 2-pyridyl (Ag1) rings, so that the ligand always has a 'head-to-head' orientation. The analogous reaction with $AgNO_3$ affords the product $\{[Ag(2,4'\text{-pyph})NO_3]\}_\infty$ which also has a polymeric structure, where the Ag(I) cations



Scheme 12. Two possible placements of asymmetric monomeric units within a covalent polymer: (a) 'head-to-tail' and (b) 'head-to-head'.

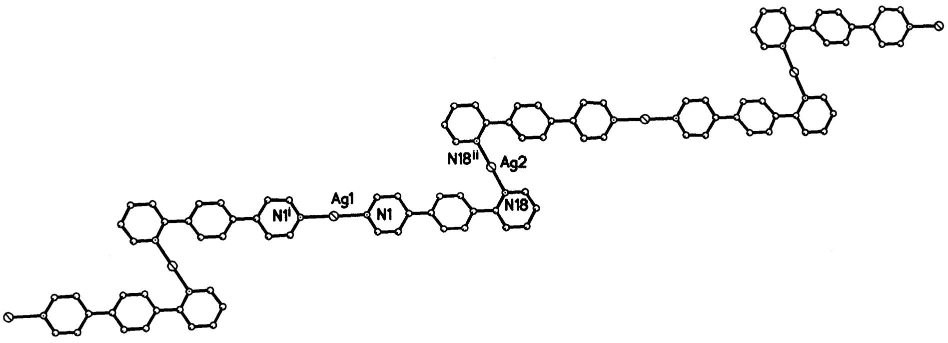


Fig. 16. Molecular structure of the $\{[Ag(2,4'\text{-pyph})]^+\}_\infty$ cationic chain with 'head-to-head' arrangement of the ligand.

organise the ligand molecules in a different orientation (Fig. 17) with the ligands 'head-to-tail' because each Ag(I) ion links the 4-pyridyl of one ligand and the 4-pyridyl of another. As a result, all metal centres are crystallographically identical and have a distorted trigonal geometry, with the NO_3^- anion playing the role of the third ligand. It is clear that the NO_3^- anions, having a larger affinity for silver centres than PF_6^-, interferes significantly in product formation.

It has been reported recently that the geometric analogue of 2,4′-pyph, 2,4′-bipyridyl (2,4′-bipy, Scheme 7) gives chain polymers with $AgNO_3$ and $AgClO_4$ [34]. In both complexes $\{[Ag(2,4'\text{-bipy})(NO_3)]\}_\infty$ and $\{[Ag(2,4'\text{-bipy})](ClO_4)\}_\infty$ the anions are coordinated to Ag(I) via their oxygen atoms. As a result, the authors isolated coordination polymers with only 'head-to-tail' ligand placement (Fig. 18). These observations support the hypothesis that the binding of Ag(I) by anions inhibit the formation of the 2-pyridyl-Ag-2-pyridyl junction ('head-to-head' orientation).

A possible explanation for such anion influence might be found in the mechanism of polymer formation. Unfortunately, the area of dynamic studies of coordination polymer formation is so far undeveloped. However, it is reasonable to assume that the macromolecular species are formed from monomeric or oligomeric coordination units, which are present in solution, and, therefore, the structure of these discrete,

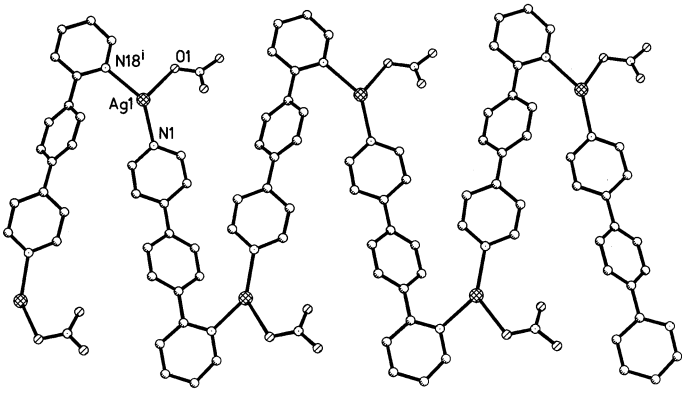


Fig. 17. Molecular structure of the $\{[Ag(2,4'\text{-pyph})(NO_3)]\}_\infty$ chain with 'head-to-tail' arrangement of the ligand.

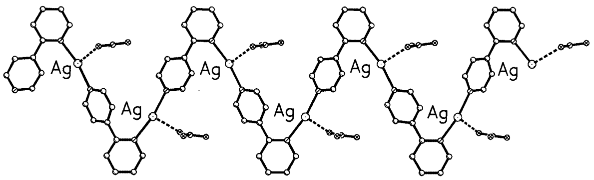
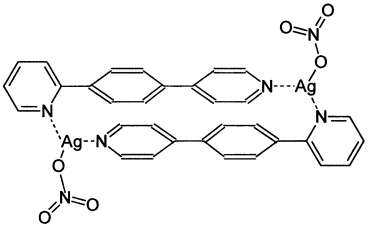


Fig. 18. Molecular structure of the $\{[Ag(2,4'\text{-bipy})(NO_3)]\}_\infty$ chain.

solution-based, units should define the structural sequence of the polymer. Mass-spectrometry analysis of a reaction mixture of 2,4′-pyph with $AgNO_3$ revealed the presence of $[Ag(2,4'\text{-pyph})(NO_3)]_2$ species in solution; it is likely, that this binuclear unit has a cyclic structure where Ag(I) adopts trigonal geometry similar to that observed in complex $\{[Ag(2,4'\text{-pyph})NO_3]\}_\infty$ (Scheme 13). Such binuclear helicates have been isolated recently when 2,4′-pyph reacts with $Zn(NO_3)_2$ and $Cd(NO_3)_2$ giving complexes $[Zn(NO_3)_2(2,4'\text{-pyph})]_2$ (Fig. 19) and $\{[Cd(NO_3)_2(2,4'\text{-pyph})]_2\}_\infty$, respectively [63], and showing the tendency of this ligand to form such units for transition-metal nitrates. The dimeric unit $[Ag(2,4'\text{-pyph})(NO_3)]_2$ represents a likely precursor of the polymers as the ligands are pre-organised in a ‘head-to-tail’ orientation and, therefore, would lead to the ‘head-to-tail’ polymer arrangement (Scheme 14). In the case of the PF_6^- anion the complex solution contains species of monomeric composition, such as [Ag(2,4′-pyph)MeCN] (Scheme 15), as shown by



Scheme 13. Proposed structure of the binuclear complex $[Ag(2,4'\text{-pyph})(NO_3)]_2$.

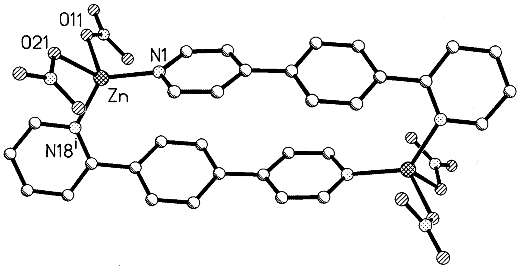
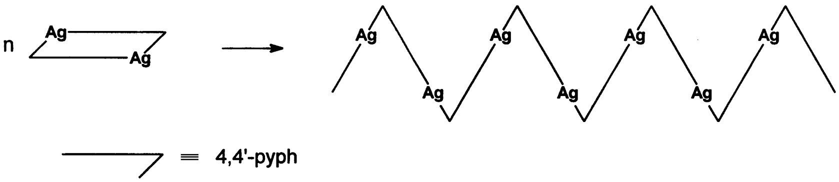
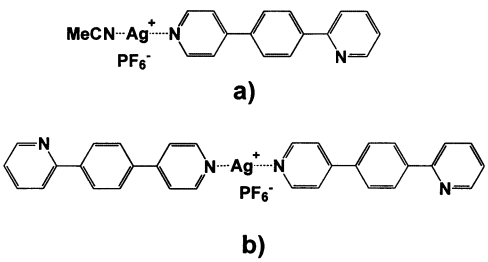


Fig. 19. Molecular structure of the $[Zn(2,4'\text{-pyph})(NO_3)_2]_2$ binuclear complex.



Scheme 14. Schematic representation of complex $\{[Ag(2,4'\text{-pyph})(NO_3)]\}_\infty$.



Scheme 15. Proposed structures of the mononuclear precursors of the 'head-to-head' $\{[Ag(2,4'\text{-pyph})]^+]_\infty$ cationic chain.

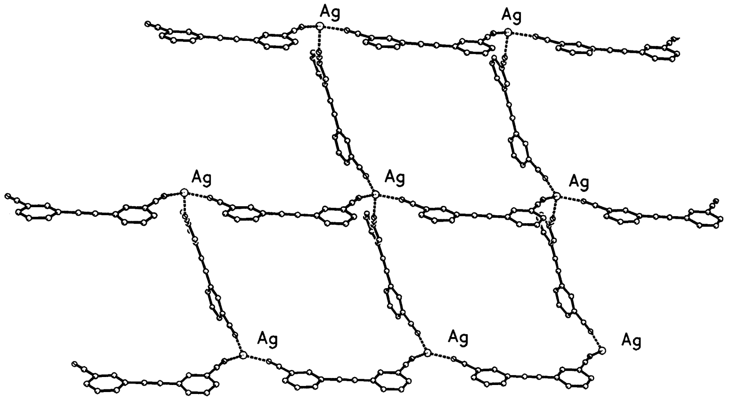


Fig. 20. Molecular structure of the $\{[Ag(3,3'\text{-dcpa})_2]^+\}_\infty$ cationic sheet where 3,3′-dcpa adopts *cisoid*-conformation.

mass spectroscopy, which might be considered a constructing block during the 'head-to-head' chain growth.

3.4. Conformational isomerism

Non-linear ligands, like 3,3′-pytz (Scheme 7) are of particular interest owing to their potential to generate both *cisoid* or *transoid* isomers and, hence in the latter case, act as 'off-axis-rods'. The *transoid* conformation is more common for bipyridyl ligands in 1D polymers [36,37,38a,48b,57a]. This can be explained by the requirements of crystalline packing where the *transoid* conformation allows the polymer to have an elongated shape and, therefore, to pack tightly in the solid state. However, there are complexes in which the less-preferable *cisoid* conformation is stabilised, for example, by intramolecular Ag–Ag interactions [55a]. The bidentate ligand 3,3′-di(cyanophenyl)acetylene (3,3′-dcpa) has been reported in both conformations [64], such that *cisoid*-3,3′-dcpa is found in $\{[Ag(3,3'\text{-dcpa})_2](XF_6)_2\}_\infty$ (X = P, As, Sb) (Fig. 20) and *transoid*-3,3′-dcpa is found in {[Ag(3,3′-

dcpa)(CF_3SO_3)]$C_6H_6\}_\infty$ [64] (Fig. 21). 3,3′-Pytz adopts both *cisoid* and *transoid* conformations when bridging Ag(I) centres [40]. Whereas the *cisoid* isomer forms double bridges, the *transoid* isomer generates single bridges (Fig. 1) [40].

Alkyl linkers ($X = CH_2CH_2$) give ligands such as 1,2-di(4-pyridyl)ethane (4,4′-pyeth) more conformational freedom which has been exploited for design of supramolecular complexes with $Co(NO_3)_2$ [61]. Hennigar et al. [61] have succeeded in the synthesis of isomeric polynuclear complexes {[Co(4,4′-pyeth)$_{1.5}$(NO_3)$_2$]-MeCN}$_\infty$ and {[Co(4,4′-pyeth)$_{1.5}$(NO_3)$_2$]$CHCl_3\}_\infty$ differing in the conformation of 1,2-(4-bispyridyl)-ethane. Nevertheless, this flexible ligand has exclusively an *anti*-conformation within the main bodies of the infinite chains in both isomers (this is the equivalent of the *transoid* conformation of a ligand with a rigid spacer). A similar effect has been observed when the same ligand has only an *anti*-conformation in the backbone of a polymer. However, when it is attached to the chain as a pendant arm it can adopt various conformations [48a]. More flexible bipyridyl ligands with a spacer-containing heteroatoms ($X = SCH_2C_6H_4CH_2S$, SC_6F_4S) are able to tune the distance and angle between donors over a wide range [65]: thus, the former ligand, 1,4-bis(2-pyridylsulphenylmethyl)benzene (1,4-bpsb), gives chains {[Co(1,4-bpsb)(NO_3)$_2$]}$_\infty$ with $Co(NO_3)_2$ in which the donor nitrogen atoms are arranged pointed in an *anti*-fashion [65a]. Recently, the conformational flexibility of saturated six-membered rings has been employed as a spacer for supramolecular design [24,38a]. In the case of polymeric Ag(I) complexes the spacer of ligand *N*,*N*′-bis(2-pyridylmethyl)piperazine (2,2′-bppz) adopts a chair-conformation (an analogue of the *transoid* conformation) giving rise to a 1D complex {[Ag(2,2′-bppz)](NO_3)(EtOH)}$_\infty$ (Fig. 22), whereas the ligand with boat-conformation (Cu(II), Co(II), Cd(II) and Mn(II) complexes) leads to discrete species [38a]. So, *transoid*, *anti* and chair-conformations dominate in the supramolecular structures, perhaps as a consequence of close packing; and it is not yet clear how they can be changed to the *cisoid*- and *syn*-form, respectively, by using the current understanding of supramolecular interactions.

When the donating pyridyl unit in the ligand is unsymmetrically substituted (such as, 2- or 3-substituted pyridyl or quinolyl groups) the possibility of *syn*/*anti* ligand

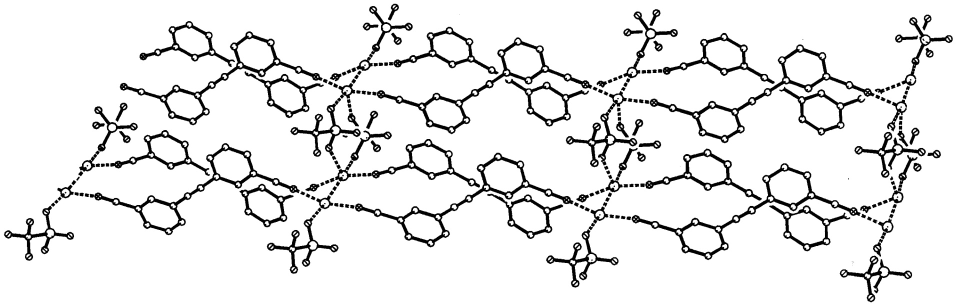


Fig. 21. Molecular structure of the {[Ag(3,3′-dcpa)(CF_3SO_3)]}$_\infty$ chain where 3,3′-dcpa adopts *transoid*-conformation.

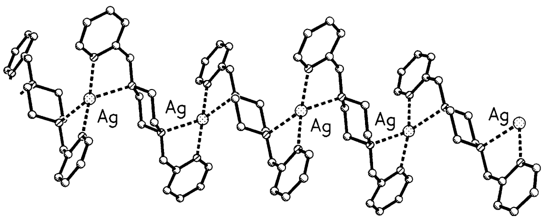
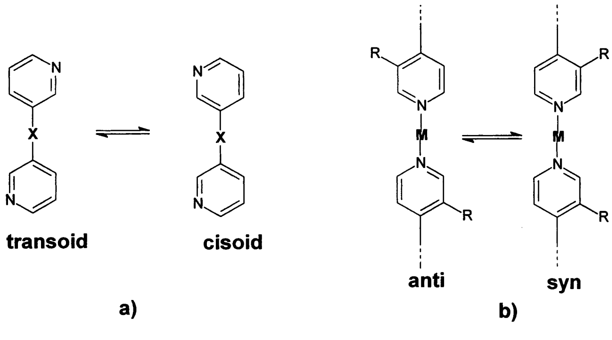


Fig. 22. Molecular structure of the $\{[Ag(2,2'\text{-bppz})]^{+}\}_{\infty}$ cationic chain.

placement relative to the metal centre arises (Scheme 16). This sort of conformational isomerism is related to the *cisoid*/*transoid* type discussed above affecting the chain geometry in a similar manner, but takes place only in coordination compounds and can be called coordination conformational isomerism.

Once again *anti*-orientation of the donor units about the metal centre may be considered as preferable for the close packing of the chains. However, there are several examples of *syn*-chains reported in the literature. In the case of simple rigid ligands such as quinoxaline (qxl) and 2-aminopyrimidine (ampm) it is possible to identify the non-covalent interactions stabilising the *syn*-conformation. Thus in complex $\{[Ag(ampm)(TolSO_3)]\}_{\infty}$ the *syn*-conformation of the chains is sustained by hydrogen bonds between the ligand and the anion [51a]; in the complex $\{[Ag(qxl)](ClO_4)\}_{\infty}$ the *syn*-conformation maximises the interchain aromatic interactions [29]. Examples when one ligand can form a chain with either *syn*- or *anti*-conformation dependent on the conditions of crystallisation are rare. The polydentate ligand *N*-(3-pyridyl)sulphanilamine (psa) yields two types of polymorphic crystals with composition $\{[Ag(psa\text{-}H)]\}_{\infty}$ when reacted with Ag(I) salts [66]. Both polymorphs consist of infinite chains with identical connectivity and a linear geometry of Ag(I). They differ only in relative orientation of the asymmetric ligands about the Ag(I) centres. The α-polymorph $\{[Ag(psa\text{-}H)]\}_{\infty}$ is the main product and its chains adopt *anti*-conformation. The β-polymorph crystallised poorly has chains in *syn*-conformation. Detailed structural analysis of the structures revealed that the



Scheme 16. (a) *cisoid* and *transoid* conformation of ligands. (b) *syn* and *anti*-ligand placement at linear two-coordinate metal centre.

anti-conformation is stabilised by interchain hydrogen bonds, whereas the *syn*-conformation is stabilised by weaker and less directional Ag–aromatic and aromatic π–π-interactions [66]. This interesting example shows that the conformation of the coordination polymer is controlled by competing intermolecular non-covalent interactions.

We have successfully synthesised both possible coordination chain conformers when the ligand 3,3′-qubut with quinolyl donors has been used (Scheme 7). $AgNO_3$ and $AgBF_4$ react with 3,3′-qubut to give the isostructural compounds $\{[Ag(3,3'\text{-qubut})NO_3(MeCN)]\}_\infty$ and $\{[Ag(3,3'\text{-qubut})]BF_4\}_\infty$, respectively, with the *transoid* arrangement of ligands (Fig. 23). Zigzag-like chains in the complexes are tightly packed forming an infinite 2D stack in which the NO_3^- and BF_4^- anions are accommodated between the layers (Fig. 24). In contrast, the orientation of the quinolyls in the complex $\{[Ag(3,3'\text{-qubut})MeCN](PF_6)MeCN\}_\infty$ is completely different (Fig. 25). The *anti* placement of the donor units allows the chain to form deep undulations, which are then overlaid on each other to give large infinite channels accommodating free PF_6^- anions and solvent molecules (Fig. 26) [49].

Related structures have been reported earlier [35] for polymeric complexes of 1,2-(3-bispyridyl)-ethene (3-pyen): the ligand has a *syn*-arrangement at the Ag(I) cations in the complex $\{[Ag(3\text{-pyen})]ClO_4\}_\infty$ [35] and an *anti*-arrangement in $\{[Cu(3\text{-pyen})]PF_6\}_\infty$ [35]. It was noted that Ag(I) and Cu(I) have an almost identical coordination geometry (N–M–N is about 169°) in both complexes but the

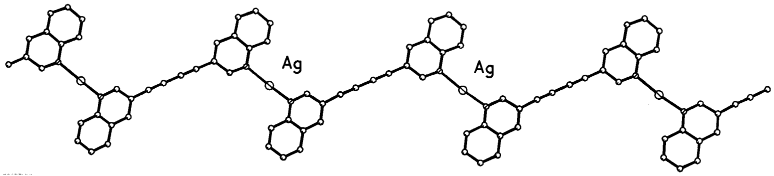


Fig. 23. Molecular structure of the $\{[Ag(3,3'\text{-qubut})]^+\}_\infty$ cationic chain exhibiting an *anti*-arrangement of the ligand.

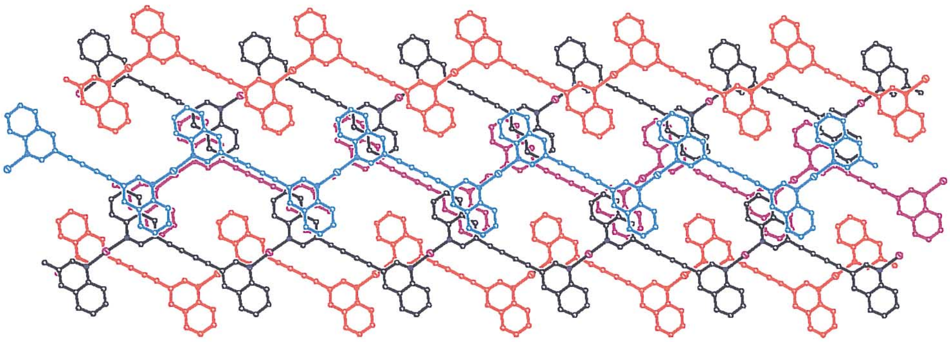


Fig. 24. Packing of the $\{[Ag(3,3'\text{-qubut})]^+\}_\infty$ cationic chains in complex $\{[Ag(3,3'\text{-qubut})]BF_4\}_\infty$; anions are omitted for clarity.

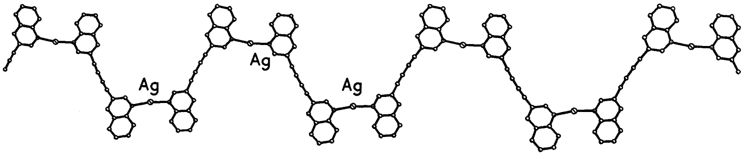


Fig. 25. Molecular structure of the $\{[Ag(3,3'\text{-qubut})]^+\}_\infty$ cationic chain exhibiting a *syn*-arrangement of the ligand.

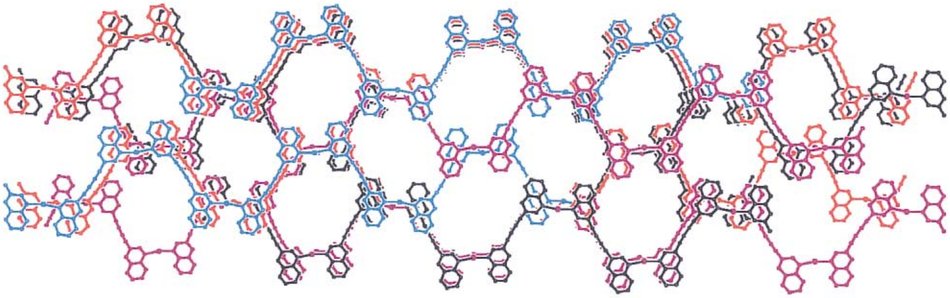


Fig. 26. Packing of the $\{[Ag(3,3'\text{-qubut})]^+\}_\infty$ cationic chains in complex $\{[Ag(3,3'\text{-qubut})MeCN](PF_6)\text{-}MeCN\}_\infty$; anions and solvent molecules are omitted for clarity.

assumption that the chain structure is affected by the non-coordinating anions is potentially not valid in this case [35] since the polymers are constructed from chemically different metal centres.

An investigation of anion influence on the coordination properties of the non-linear nitrile donor ligand, 3,3′-di(cyanophenyl)acetylene, (3,3′-dcpa), revealed the formation of an eightfold 3D adamantoid framework $\{[Ag(3,3'\text{-dcpa})_2](ClO_4)(H_2O)\}_\infty$ with $AgClO_4$ where the *transoid* form of the ligand gives rise to close packing of coordination polymers via aromatic stacking [64] (Fig. 27). Meanwhile, $AgPF_6$ and the same ligand form a 2D structure $\{[Ag(3,3'\text{-dcpa})_2](PF_6)\}_\infty$ with channels that accommodate PF_6^- anions as a result of the ligand adopting a *cisoid* conformation (Fig. 28). The difference in structures can be attributed to the influence of the size of the non-bonded anions (molecular volumes (V_m) for ClO_4^- and PF_6^- are 47 and 54 Å^3, respectively [67]), as both complexes were synthesised in similar conditions (CH_2Cl_2–MeCN, room temperature). We believe that the same sort of effect occurs in the 1D complexes of 3,3′-qubut; both BF_4^- and NO_3^- anions are relatively small ($V_m[BF_4^-] = 38$; $V_m[NO_3^-] = 34$ Å^3 [67]) and can be located in the space between infinite stacks of the ligand (Fig. 24); the more bulky PF_6^- anion requires more space and, therefore, causes the rearrangement of the chains resulting in the different structure with large channels (Fig. 26). It should be noted that the larger anion does not lead to a change in the ligand conformation itself as it does in the case of the binitrile donor 3,3′-dcpa [64]. Polymeric complexes with such a broad π-electronic system as observed in

$\{[Ag(3,3'\text{-qubut})]BF_4\}_\infty$ and $\{[Ag(3,3'\text{-qubut})MeCN](PF_6)MeCN\}_\infty$ cannot tolerate the loss, or decrease, of aromatic interactions caused by the *cisoid* ligand conformation. As a result, the anion size in coordination polymers of 3,3′-qubut tunes the ligand placement at Ag(I) rather than the conformation of the ligand itself, leading to anion-controlled coordination conformational isomerism of the polycationic array.

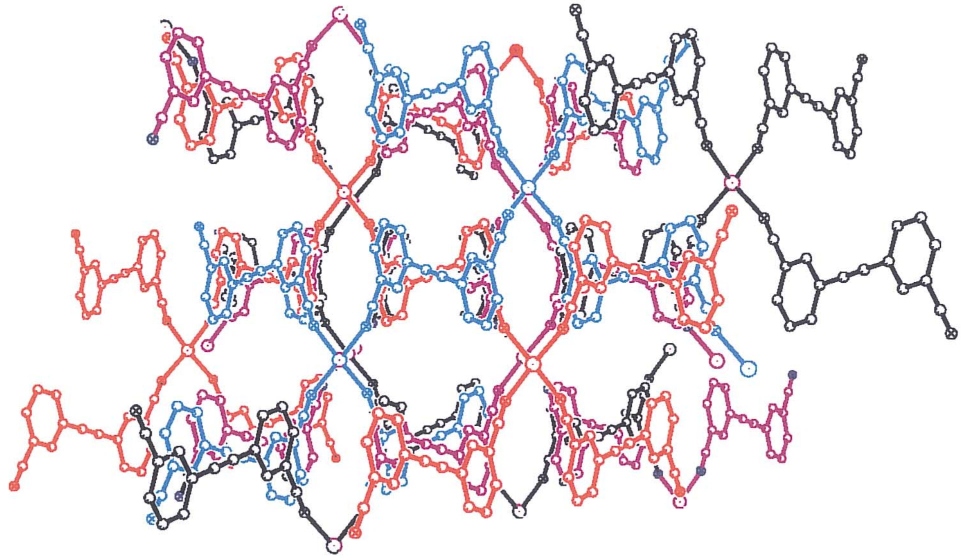


Fig. 27. Packing of the $\{[Ag(3,3'\text{-dcpa})_2]^+\}_\infty$ eightfold interpenetrating diamondoid frameworks in complex $\{[Ag(3,3'\text{-dcpa})_2](ClO_4)\}_\infty$.

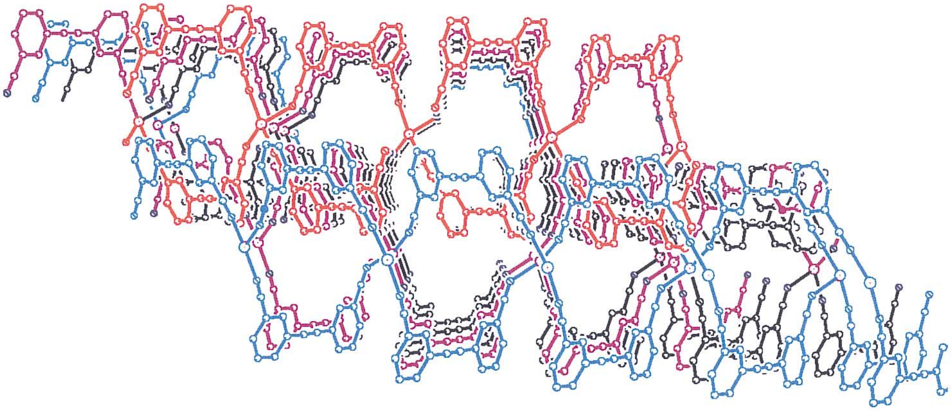


Fig. 28. Packing of the $\{[Ag(3,3'\text{-dcpa})_2]^+\}_\infty$ sheets in complex $\{[Ag(3,3'\text{-dcpa})_2](PF_6)\}_\infty$.

Our studies on the anion control of the geometry of 3,3′-pytz polymeric complexes demonstrate similar conformational behaviour of 3,3′-pytz as 3,3′-qubut [40]. This indicates a general mechanism for influence of anionic size on the complex geometry regardless of the nature of the donor unit (quinolyl or pyridyl) and spacer (butadiyne or tetrazine).

4. The arrangement of chains in the solid state

The packing of molecules in the solid state has a crucial effect on their properties. The type of packing arrangement is usually governed by weak supramolecular interactions, some of which have already been mentioned in Section 2. Strong interference between the interactions gives control over crystalline packing particularly difficult in coordination polymers, but, once again, the simplicity of 1D entities in conjunction with crystallographic analysis of a series of polymeric analogues enable us to recognise the influence of the supramolecular interactions and understand their features.

4.1. Long-range order

The anion effect on the long-range order of chains is perhaps the clearest example. In particular, replacement of the weakly coordinating BF_6^- and PF_6^- anions by more strongly coordinating NO_3^- anions has a profound effect upon network geometry.

In contrast with the linear chain complexes $\{[Ag(4,4'\text{-pytz})]PF_6(MeCN)\}_\infty$ and $\{[Ag(4,4'\text{-pytz})]BF_4(MeCN)\}_\infty$ (Fig. 10) the complex formed between $AgNO_3$ and 4,4′-pytz forms $\{[Ag(4,4'\text{-pytz})]NO_3\}_\infty$ which has a topology termed a helical staircase structure [32]. The structure of the complex comprises Ag(I) ions each coordinated to two 4,4′-pytz ligands in a linear arrangement to give linear chains of alternating Ag(I) ions and bipyridyl ligands. Each silver ion also exhibits a weak interaction with two NO_3^- ions [Ag···O = 2.787(2) Å] which adopt positions perpendicular to the pyridyl–Ag–pyridyl axis so as to give the Ag(I) centre a pseudo-square planar geometry (Fig. 29). These NO_3^- ions bridge adjacent Ag–bipyridyl chains through two of their oxygen atoms so that each silver chain is related to the

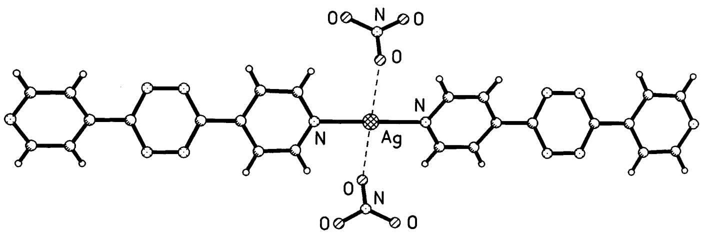


Fig. 29. Coordination geometry of Ag(I) in complex $\{[Ag(4,4'\text{-pytz})(NO_3)]\}_\infty$.

next by a 60° rotation and a step of 5.18 Å, generating a helical staircase motif (Fig. 30). Thus, it can be seen that the 3D structure is controlled via the Ag–ONO_2 interactions. The points at which the chains cross, which one may consider the centre of the helix, correspond to pyridyl units of the overlapping 4,4′-pytz ligands (Fig. 30).

The structure of $\{[Ag(4,4'\text{-bipy})]NO_3\}_\infty$ reveals a different structural motif with orthogonal linear chains linked via Ag···Ag contacts (Fig. 31) [31]. This contrasts with both the structure of $\{[Ag(4,4'\text{-bipy})]BF_4(MeCN)(H_2O)\}_\infty$ [23] (Fig. 32) and with the other structural motifs that we have observed with other complexes of $AgNO_3$ and linear bipyridyl ligands. The unique structural features of $\{[Ag(4,4'\text{-bipy})]NO_3\}_\infty$ are a result of a combination of two non-conflicting interchain interactions. Coplanar pyridyl rings stack (plane-to-plane separation 3.522 Å) and are twisted by 90° with respect to each other (which allows an effective charge separation) and the Ag(I) cations form short Ag···Ag contacts (2.970 Å). This structure is perhaps a consequence of the specific geometry of 4,4′-bipy which fits these particular packing arrangements of chains. The range of different structural motifs observed with these Ag–bipyridyl complexes emphasises the subtle effects that ligand functionality and anion structure can exert upon long-range order in these structures.

It should be emphasised that in case of the ligands based on pyridyl donors the examples of 1D complexes with complicated packing arrangements such as

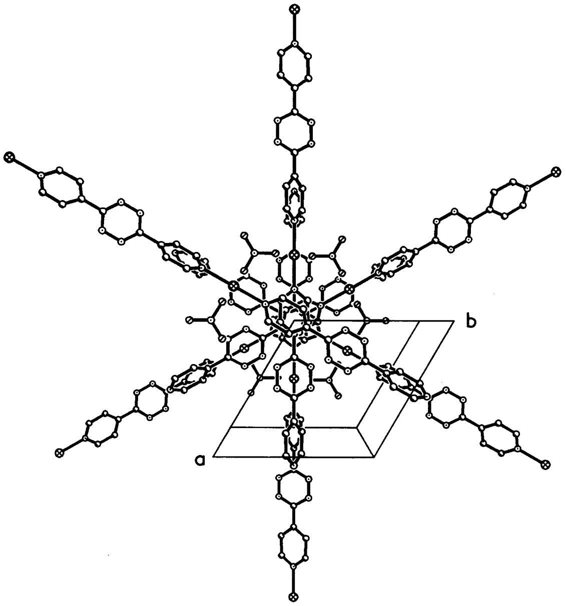


Fig. 30. ‘Helical staircase’ motif of chains placement in complex $\{[Ag(4,4'\text{-pytz})(NO_3)]\}_\infty$ (view along *c* crystallographic axis).

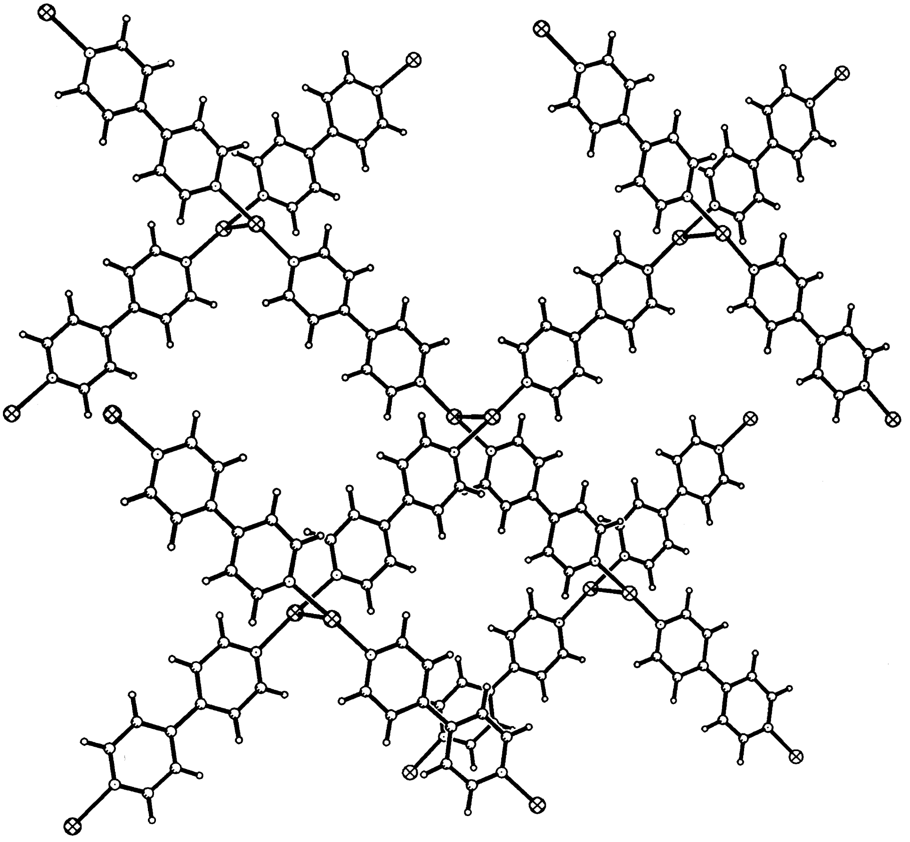


Fig. 31. Packing of the $\{[Ag(4,4'\text{-bipy})]^+\}_\infty$ cationic chains in complex $\{[Ag(4,4'\text{-bipy})](NO_3)\}_\infty$.

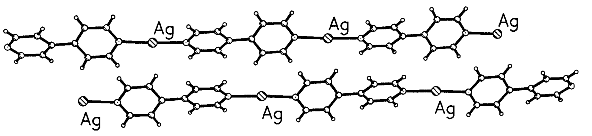


Fig. 32. Parallel packing of the $\{[Ag(4,4'\text{-bipy})]^+\}_\infty$ cationic chains in complex $\{[Ag(4,4'\text{-bipy})](BF_4)(MeCN)(H_2O)\}_\infty$.

$\{[Ag(4,4'\text{-pytz})]NO_3\}_\infty$ and $\{[Ag(4,4'\text{-bipy})]NO_3\}_\infty$ are the exception rather than the rule. The most common type of chain orientation is stacking where in chains are placed in a parallel fashion; there are relatively few different options for chain placement.

4.2. Chain stacking: pairs, ladders and sheets

The discoid aromatic molecule diaz (Scheme 7) has 16 electrons in its delocolised π-system with a maximum of π-electronic density between the donor units. Aromatic molecules with such structures tend to form associates via face-to-face stacking [68] that allows maximisation of attractive π–π-interactions with energies of about 15 kJ mol^{-1} (if the energy is considered as an additive function of the number of π-electrons; see Section 2). The crystal structure of the free ligand (Fig. 33) shows this contact with a plane–plane separation between parallel molecules of 3.450(2) Å and the centre of the molecules offset by a distance of 1.570(2) Å. It is interesting to note that in structures of smaller aromatic systems other types of aromatic interactions predominate: for example, the structure of crystalline benzene reveals edge-to-face contacts as a structure defining force [69]. But for larger aromatic species overlaying in a face-to-face fashion is the main structural pattern, which remains unchanged even when a metal cation is coordinated directly to a $C(sp^2)$ in the aromatic ring [21]. The structure of the complex $\{[Ag(diaz)]BF_4\}_\infty$ exhibits infinite stacks of the ligand with a plane-to-plane separation of 3.380(5) Å (Fig. 34) [30]. The stacks are arranged in a parallel fashion due to interactions with the Ag(I) cations; these contrasts with the 'herringbone' motif observed in the case of the free ligand (Fig. 33). The shortening of the interplanar distance is another result of Ag(I) coordination: as the transition-metal cation is a σ-acceptor and π-donor, the ligand molecule is polarised, increasing the electrostatic attraction of adjacent aromatic species [9]. The strong influence of π–π interactions in the

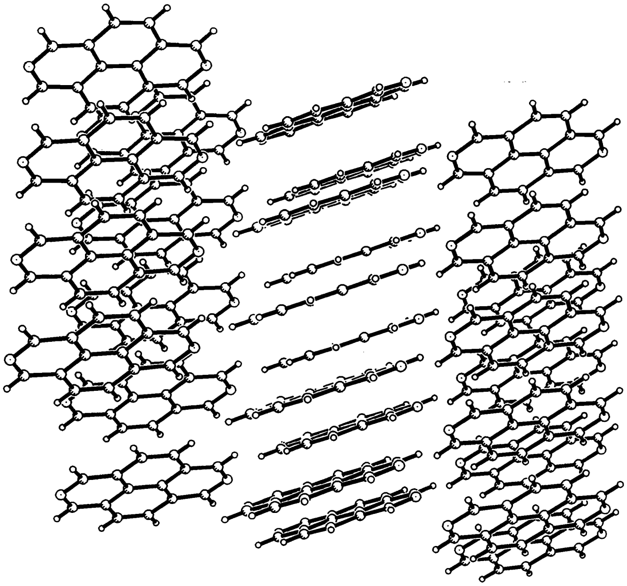


Fig. 33. Crystal structure of ligand diaz.

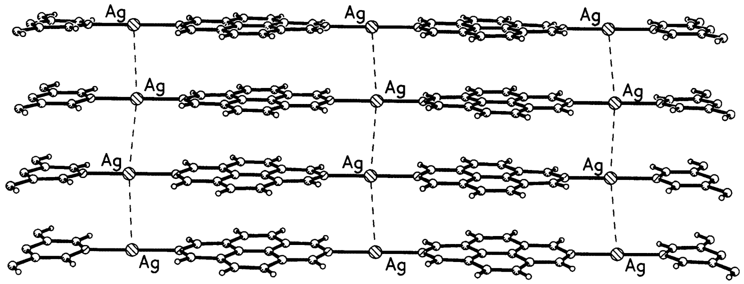
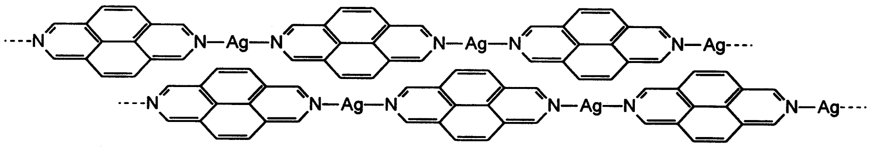


Fig. 34. Packing of the $\{[Ag(diaz)]^{+}\}_{\infty}$ cationic chains in complex $\{[Ag(diaz)(BF_4)]\}_{\infty}$.



Scheme 17. Theoretical 'shifted' placement of chains in complex in $\{[Ag(diaz)]BF_4\}_{\infty}$.

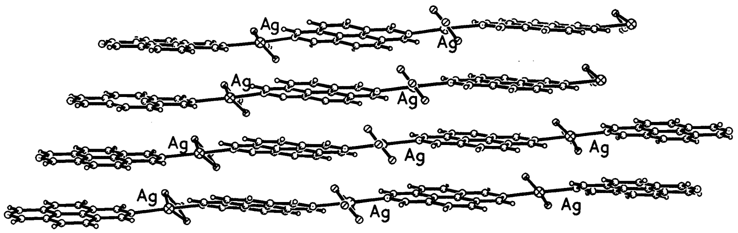


Fig. 35. Packing of the chains in complex $\{[Ag(diaz)(NO_3)]\}_{\infty}$.

complex discourages the alternative 'shifted' arrangement (Scheme 17) as a weaker metal–aromatic contact does not compensate for the loss of the strong facial interaction occurring in the case of the observed 'non-shifted' structure (Fig. 34). So, the ligand–ligand interaction forces Ag(I) cations to approach each other, but does not encourage the formation of Ag–Ag bonds [Ag–Ag distance in $\{[Ag(diaz)]BF_4\}_{\infty}$ is 3.640(3) Å] because of the ligand offset placement (1.351 Å) which is a requirement for effective charge distribution on the aromatic molecules and, therefore, a common feature for the aromatic–aromatic contact [9,16]. The approach of cationic centres in this way should be considered as a cause of repulsion between chains due to the Coulombic interaction counteracting the aromatic stacking [17]. The NO_3^- anion partially neutralises the positive charge at Ag(I) in $\{[Ag(diaz)NO_3]\}_{\infty}$ (Fig. 35) and makes the interchain distance 0.04 Å shorter than in $\{[Ag(diaz)]BF_4\}_{\infty}$ (Fig. 34) where each Ag(I) brings a single, non-compensated, positive charge to the coordination array.

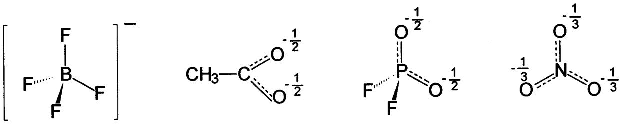
Packing of polymeric complexes of other discoid ligands such as quinoxaline [29] and diphenazine [33] resemble structures of the complexes of diaz: the ligand molecules lying in adjacent chains are involved in face-to-face aromatic interactions (plane-to-plane separation is 3.46 and 3.36 Å, respectively).

Some examples relevant to our research were reported for 1D complexes of the smallest aromatic bidentate pyridyl-type ligand pyrazine (pyrz). Both complexes $\{[Ag(pyrz)](PF_6)_{0.5}(OH)_{0.5}\}_\infty$ [28d] and $\{[Ag(pyrz)]BF_4\}_\infty$ [28b] with non-coordinating anions exhibit the same structural motif as the complex $\{[Ag(diaz)]BF_4\}_\infty$. In both complexes, $\{[Ag(pyrz)](PF_6)_{0.5}(OH)_{0.5}\}_\infty$ and $\{[Ag(pyrz)]BF_4\}_\infty$, the ligand molecules are involved in aromatic intermolecular interactions (plane-to-plane separation 3.56 and 3.66 Å, respectively) but the chains are not sufficiently close for Ag···Ag interactions to be adopted (Ag···Ag separations are 3.57 and 4.28 Å, respectively). The influence of more coordinating NO_3^- anion is essentially the same as observed for diaz complexes: weakly coordinating NO_3^- distorts the linear geometry of Ag(I) centres and allows adjacent chains to be closer [28a] (Ag···Ag distance 3.560 Å, plane-to-plane separation 3.436 Å). It can also be deduced that pyrazine molecules, with a relatively small aromatic π-electronic system, can tolerate the complete loss of aromatic interactions if it is compensated by another supramolecular contact. For example, in the 1D complex $\{[Ag(pyrz)(NO_2)]\}_\infty$ no aromatic interactions are observed between chains rather the chain arrangement is defined by moderate Ag···Ag interactions [Ag···Ag distance 3.2168(3) Å] [28e].

Using a rod-like ligand, as opposed to the disc-shaped diaz, gives new options for the arrangement of the chains. The ligand 4,4′-pybut (Scheme 7) is a structural isomer of diaz and has the same number of π-electrons in its delocalised system but an alternative distribution of the electronic density within the molecule. π-Electrons at the sp-hybridised carbons of the diyne linker are unlikely to play a significant part in interchain interactions and in the case of 4,4′-pybut aromatic interactions are no longer a dominating force, with its energy at least halved compared with the discoid species diaz (Scheme 5). This makes the arrangement of the chains sensitive to other supramolecular contacts, such as metal–metal and metal–anion interactions.

We have synthesised four complexes of 4,4′-pybut with Ag(I) salts under similar conditions [23]. All the complexes are 1D polymers comprising linear chains placed in a parallel fashion. Anion variation in the complex helps to reveal the role of anion in determining the overall interactions between the chains. Thus, we have used three different types of anions: weakly coordinating anion BF_4^-, strongly coordinating anions $MeCO_2^-$ and $PF_2O_2^-$ (with approximately half of the negative charge on each oxygen atom) and a moderately coordinating anion NO_3^- (with one-third of the negative charge on each oxygen atom) (Scheme 18). The complexes $\{[Ag(4,4'\text{-pybut})]BF_4(MeCN)\}_\infty$ and $\{[Ag(4,4'\text{-pybut})]NO_3(MeCN)\}_\infty$ form chains that are shifted relative to each other (Fig. 36) so that the shortest Ag–Ag distance is 7.147(2) and 7.079(3) Å, respectively. This type of placement is a result of coulombic repulsion between Ag(I) centres, and in this case the repulsion cannot be compensated for by strong face-to-face ligand stacking as it is in case of $\{[Ag(diaz)]BF_4\}_\infty$. Nevertheless, the aromatic groups in {[Ag(4,4′-pybut)]BF_4(MeCN)$\}_\infty$ are involved in facial interactions in a 'head-to-tail' fashion (Scheme 3b) (plane-to-plane separation 3.536 Å). This results in the binding of the chains into a 2D sheet with equal interchain distances (Fig. 37). It should be noted that the simplest bipyridyl ligand 4,4′-bipy gives the complex {[Ag(4,4′-bipy)]BF_4(MeCN)(H_2O)$\}_\infty$ [23] with essentially the same packing motif, where the cationic repulsion is minimised with the same type of 'head-to-tail' aromatic pairing (Fig. 32). {[Ag(4,4′-bipy)]$NO_2\}_\infty$, in which the NO_2^- anion coordinates at a similar distance (Ag···O distance 2.667 Å) [28e] as the NO_3^- anion in {[Ag(pybut)]$NO_3\}_\infty$ (Ag···O distance 2.687 Å), adopts the same chain as observed for {[Ag(4,4′-bipy)](BF_4)(H_2O)$\}_\infty$ ('head-to-tail' stacking of pyridyl rings, plane-to-plane separation 3.383 Å) as would be expected considering the charge compensation afforded by the anionic interaction.

In the complexes {[Ag(4,4′-pybut)(PO_2F_2)](MeCN)$\}_\infty$ and {[Ag(4,4′-pybut)($MeCO_2$)](MeCN)$\}_\infty$ the anions are coordinating and weakly bridge adjacent Ag(I) centres, thus reducing the effective positive charge at each individual Ag(I), allowing the cations to approach more closely and, therefore, to form Ag–Ag



Scheme 18. Qualitative description of anions with different negative charge distributions used for synthesis Ag(I) complexes with 4,4′-pybut.

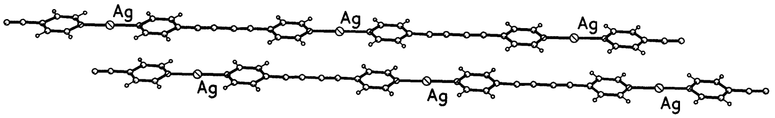


Fig. 36. Packing of the {[Ag(4,4′-pybut)]$^+\}_\infty$ cationic chains in complex {[Ag(4,4′-pybut)]BF_4(MeCN)$\}_\infty$.

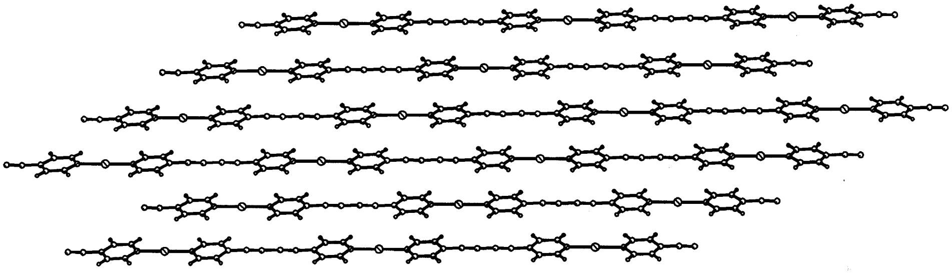


Fig. 37. Extended packing diagram of the {[Ag(4,4′-pybut)]$^+\}_\infty$ cationic chains in complex {[Ag(4,4′-pybut)]BF_4(MeCN)$\}_\infty$.

interactions with distances of 3.193 and 3.137 Å, respectively. Two supramolecular forces Ag···Ag and aromatic π–π-interactions in a 'head-to-head' fashion, bind two adjacent chains together to afford infinite 'ladders' (Fig. 38).

The interaction between a cation and the π-electronic system of a ligand may also be one of the driving forces of supramolecular structure formation, as mentioned in Section 2. The ligand 4,4′-pyphac can be considered as an elongated version of 4,4′-pybut (Scheme 7) in which the *p*-phenylene group separates the two triple C–C bonds and provides the maximum potential for aromatic based interactions at the midpoint of the ligand. When Ag(I) has no contact with an anion, 4,4′-pyphac gives a different motif of chain stacking in comparison with $\{[Ag(4,4'\text{-pybut})]BF_4(MeCN)\}_\infty$ and $\{[Ag(4,4'\text{-bipy})]BF_4(MeCN)(H_2O)\}_\infty$. The chains in the complex $\{[Ag(4,4'\text{-pyphac})]PF_6(MeCN)\}_\infty$ are significantly shifted with respect to each other (shortest Ag···Ag distance = 5.177(3) Å; Fig. 39), which can again be considered as an effect of the electrostatic repulsion. A precise analysis of the structure of $\{[Ag(4,4'\text{-pyphac})]PF_6(MeCN)\}_\infty$ reveals only one type of attractive interaction between chains, the Ag–phenylene contact with a Ag-plane distance of 3.273(3) Å which thus defines the overall packing arrangement [23].

In summary, the precise structural analysis of the series of structurally related compounds enables us to demonstrate the full set of supramolecular interactions occurring in pyridyl complexes of Ag(I) which has been applied for the design of 1D coordination polymers. A coordination polymer with any dimensionality and topology can be regarded as a combination of 1D arrays placed and linked in a certain order. Therefore, as the principles of chain construction are understood and all types of interchain interactions are revealed, one will be able to perform engineering of coordination entities of higher order.

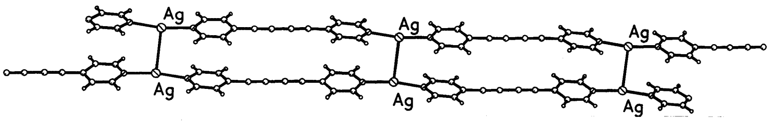


Fig. 38. Packing of the $\{[Ag(4,4'\text{-pybut})]^+\}_\infty$ cationic chains in complex $\{[Ag(4,4'\text{-pybut})]PO_2F_2\text{-}(MeCN)\}_\infty$.

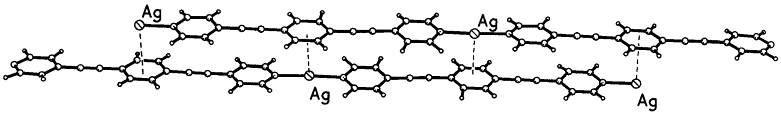


Fig. 39. Packing of the $\{[Ag(4,4'\text{-pyphac})]^+\}_\infty$ cationic chains in complex $\{[Ag(4,4'\text{-pyphac})](PF_6)\text{-}(MeCN)\}_\infty$.

5. Conclusions and perspectives

Supramolecular chemistry is currently in the middle of an avalanche-like process of experimental data accumulation and the extensive studies (especially, in the area of coordination supermolecules) and within the last decade has produced hundreds of new supramolecular compounds. The next level of the development of this modern branch of chemistry will be based upon the classification of the experimental material. One main goal of this classification is in establishing correlations between supramolecular interactions and structural characteristics of complexes. In this review, using our knowledge of 1D-coordination polymers, we have made a preliminary attempt at this kind of analysis, when each structural feature of the polymer is attributed to an individual non-covalent interaction or combination of several interactions. It should be emphasised that this classification is necessary for outlining the rules of supramolecular chemistry for controlled solid-state design and the application of this science in related areas in material science and chemical biology [70].

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