Silver Complexes of Azobenzene and Derivatives

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Contents

Abstract

Thirty four silver(I) complexes of azobenzene and derivatives have been synthesised, only two of which have been previously published.

The azobenzene derivatives used are 2-bromo, 3-bromo, 4-bromo, 3,4'-dibromo, 2,4'-dibromo, 3-nitro, 4-dimethylamino, 4-methoxy, 2,6-dimethyl-4'-chloro, 2,6,2',6'-tetramethyl and 2,2'-ethyleneazobenzene. 2,2'- and 4,4'-azobispyridine were also used along with diphenyltriazine. Six different silver(I) salts were used to make the complexes; they are tetrafluoroborate, hexafluorophosphate, perchlorate, nitrate, triflate and trifluoroacetate.

All of the complexes were analysed using X-ray crystallography.

In the complexes with azobenzene the anion was the most crucial factor in determining the resulting structure, as five different molecular topologies were seen with each change of anion. The 2-bromoazobenzene containing complexes continue this trend giving similar topologies to the azobenzene containing complexes. Once we come to the 3-bromo and 4-bromoazobenzene, we get a different molecular topology for the hexafluorophosphate containing complexes when compared to the original azobenzene containing complex, but we see a very similar structure for the perchlorate containing complexes. This would suggest that the coordinating anions give more predictable structures than the non-coordinating anions. The trend continues with both the 3,4'-dibromo and 2,4'-dibromoazobenzene complexes with triflate being structurally similar to the previous triflate containing complexes. The trend is reinforced further with 3-nitro and 4-methoxyazobenzene showing similar structures to the previously discussed complexes. The complex containing 4-dimethylaminoazobenzene can be disregarded, as the ligand has become protonated and therefore is unlike all the previously described results. When we come to the sterically hindered ligands 2,6-dimethyl-4'-chloroazobenzene the first three complexes show the same molecular topology of a silver atom bound to two ligands with a coordinating anion, however once we come to a tridentate coordinating anion triflate a 1-D metallopolymer is observed. This breaks the trend, as the structures are similar regardless of the change in anion. A similar effect is seen in 2,6,2',6'-tetramethylazobenzene with both structures standing alone as no complexes with a similar molecular topology were observed. This effect is again noted in the complexes containing 2,2'-ethyleneazobenzene. The complexes all form a similar structure regardless of the anion used. As expected the 2,2'- and 4,4'-azobispyridine along with diphenyltriazine do not follow the trend observed earlier with the non-sterically hindered ligands as they can coordinate through additional nitrogen atoms in the aromatic ring or in the case of diphenyltriazine an additional nitrogen atom in the triazine group.

Chapter One

Introduction

Introduction

Supramolecular chemistry is a relatively new and exciting branch of chemistry. It is the "chemistry of molecular assemblies and of the intermolecular bond" as defined by Nobel Prize winner Jean-Marie Lehn. [1] Supramolecular chemistry is also well known as "chemistry beyond the molecule". It uses weak non-covalent interactions such as π-π stacking, cation-π interactions, hydrogen bonding (H-bonds), coordination bonds (ion-dipole interactions) and Van der Waals forces etc. [1] These are relatively weak interactions with enthalpies of 0-50, 5-80, 4-120, 50-200 and <5 $kJmol^{-1}$, respectively. [1] In comparison ionic and covalent bonds are much stronger. Although these intermolecular bonds are weak, when many of them are present in the same assembly a very stable structure can be produced. One of the best examples of this is DNA where the large number of π-π stacking interactions and H-bonds (2 between AT and 3 between CG) create a very stable structure. [2]

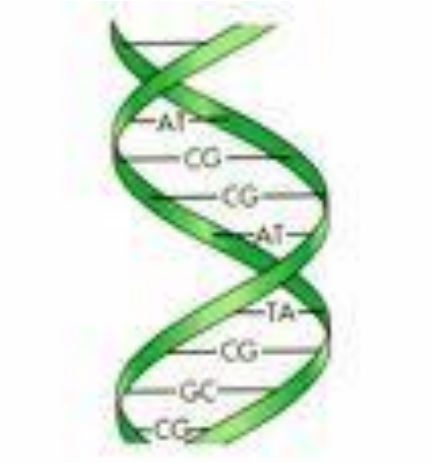

Fig (1) - The double helix of DNA showing H-bonds.

Fig (1) shows the structure of DNA in which the H-bonds hold together the two strands of the helix and cause DNA to have a relatively high melting point (50-60^{o}C) depending on the GC content of the DNA. [3] While this picture does not show the π-π stacking interactions, the A, T, C and G are aromatic and stack on top of each other.

Some important concepts in supramolecular chemistry are self recognition and self assembly. In organic chemistry the goal is often to build molecules from available precursors. However there is a loss of material with each new step; even high yielding reactions over several steps give a relatively low yield. In supramolecular chemistry the molecules that are combined have the ability to "recognise" each other and form a bond accordingly; this is called self recognition. [1] Self assembly is the spontaneous reaction of several components leading to the final structure. Due to the weakness of the bonds involved in supramolecular chemistry the bonds can form reversibly which means that the structure can cycle through many different compositions until the most stable structure is reached. [1]

The term metallosupramolecular chemistry was first coined in the 90's by Constable, to describe the metal directed self assembly of organised structures. [4] Metallosupramolecular chemistry uses metal atoms and organic molecules (ligands) to build structures. In the 90's Robson introduced the node and spacer concept. [5] Generally the metal atoms act as nodes while the ligands act as spacers to bridge the metal atoms; although the reverse is also possible.

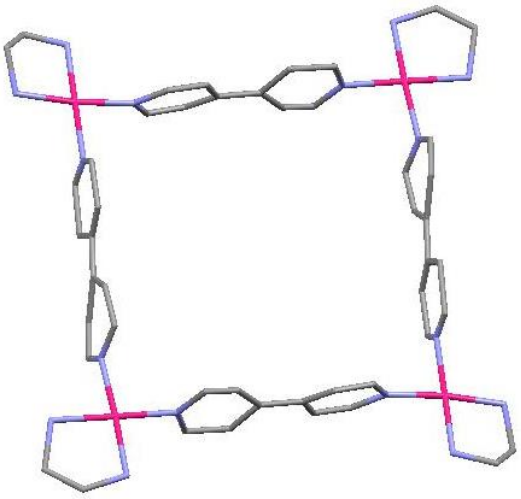

Fig (2) - A molecular square, the Pd atom acts as a node and the 4,4'-bipyridine acts as a spacer . [6] The hydrogen atoms have been omitted for clarity.

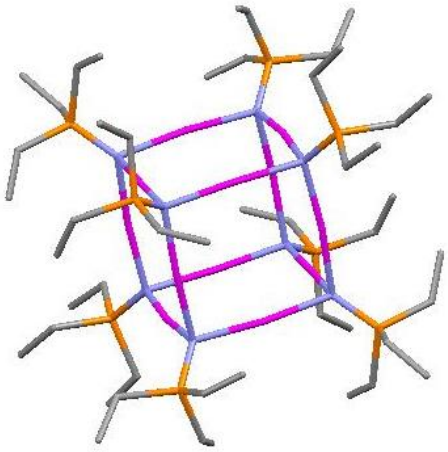

Fig (3) - A molecular cube, the Ag atom acts as a spacer and $NPEt_3$ acts as the node. [7] The hydrogen atoms have been omitted for clarity.

Depending on the geometries of these nodes and spacers, many different structures can be produced. In the above examples the Pd-amine node is square planar and the 4,4'-bipyridine spacer is linear so a molecular square is formed. In the other example the Ag spacer is linear and the $NPEt_3$ node acts as a corner unit so a molecular cube is formed. Another example is a diamondoid network as seen in Fig (4) which may be produced if a tetrahedral node and linear spacer are used and vice versa.

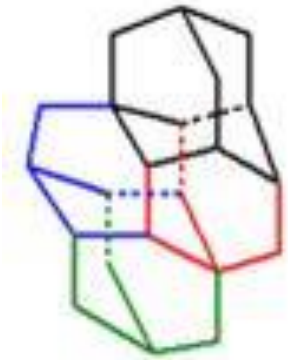

Fig (4) - A diamondoid network.

This is analogous to the way children build structures out of mechano, or lego, which is why metallosupramolecular chemistry is often described as molecular mechano. Generally it is quite easy to form a metallosupramolecular complex as the method involved is simply that the metal atoms are mixed with the ligand(s). If this is done in the right ratio and with the correct solvent system, there is usually an outcome determined by the geometries of the metal atom and the ligand.

Silver(I) is used extensively in metallosupramolecular studies due to its promiscuity in coordination number and geometry; for example silver(I) can adopt a coordination number of between 2 and 6. The geometry of silver is most commonly linear/bent when two coordinate, trigonal when three coordinate and tetrahedral when four coordinate.

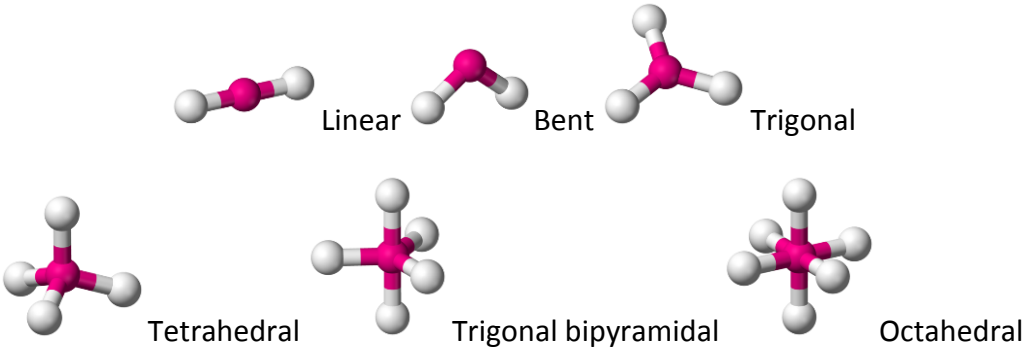

Fig (5) - Some common geometries adopted by silver

Silver(I) interacts strongly with nitrogen containing groups such as amine, amide, azo and nitrogen containing heterocycles. Silver(I) also interacts strongly with various donor atoms such as oxygen, phosphorous and sulphur, however, the silver-nitrogen interaction is stronger than others. Some of the most popular nitrogen containing ligands for metallosupramolecular chemistry are pyridines and analogues. Some of these are 2,2'-bipyridine [9] along with the 3,3'- and 4,4'- isomers, and also 2,2'-bipyrimidine [10] along with the 4,4'- and 5,5'- isomers.

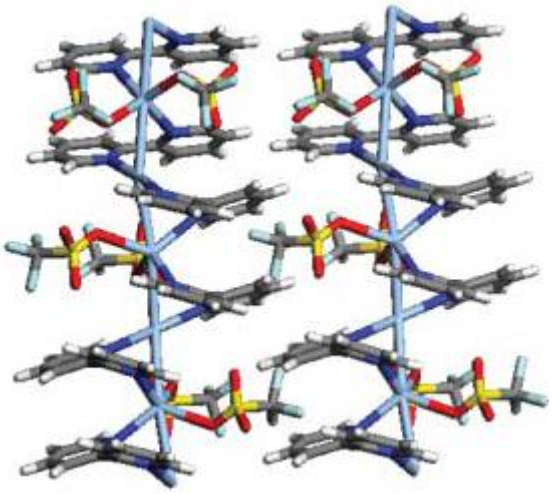

Fig (6) - This figure shows 2,2'-bipyridine ligands bridged by a silver atoms which are also linked to a triflate anion. This figure shows the binding ability of silver(I) to nitrogen atoms.

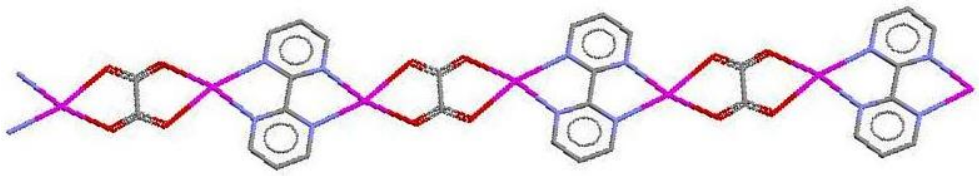

Fig (7) – This figure shows a 2,2'-bipyrimidine ligand linked to a tetrahedral silver atom which is also coordinated to an oxalate anion. This figure also shows the ability of silver(I) to coordinate to nitrogen and oxygen atoms. The hydrogen atoms have been omitted for clarity.

Azobenzene is a molecule consisting of two benzene rings bridged by a nitrogen-nitrogen double bond as shown in Fig (8).

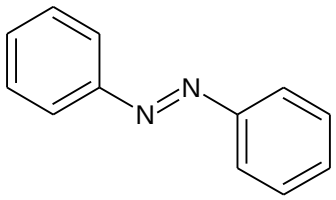

Fig (8) - Azobenzene

Azobenzene has six different coordination modes.

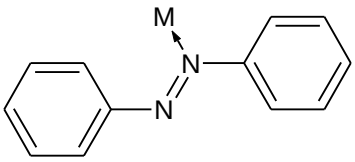

Fig (9) - Monodentate

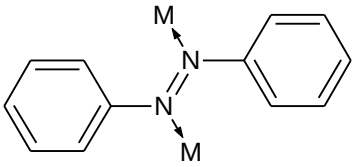

Fig (10) - Trans bridging bidentate

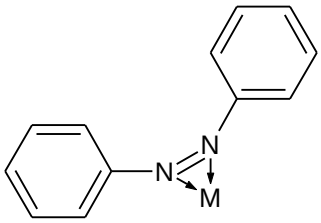

Fig (11) - Chelating bidentate

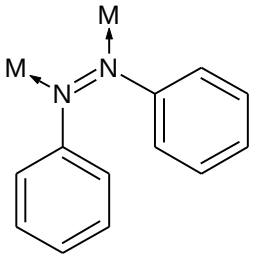

Fig (12) - Cis bridging bidentate

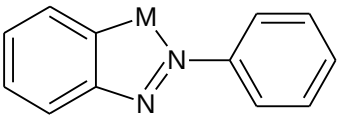

Fig (13) - Singly orthometallated

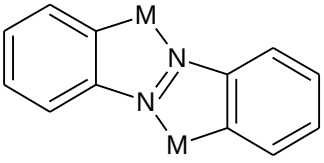

Fig (14) - Doubly orthometallated

Azobenzene was first synthesised in 1856, [11] by reducing nitrobenzene with iron filings in the presence of acetic acid. In the modern synthetic method, zinc with base takes the place of iron with acetic acid. [12]

The chemistry of azobenzene is well known due to the bright colours of many of the substituted azobenzenes, which leads to their use in the dye industry.

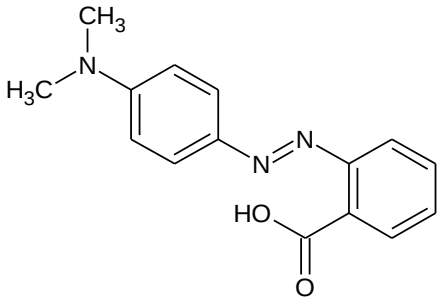

Fig (15) - Methyl red.

Fig (15) shows the dye methyl red, which is used as a pH indicator due to its obvious colour change to red when exposed to acidic conditions. [13] The vivid colours produced by azo dyes is due to the conjugation between the benzene rings, azo group and generally an electron withdrawing group (EWG) or electron donating group (EDG). In the case of aniline yellow the amine group acts an EDG.

Another reason the chemistry of azobenzene is so well studied is the ease of synthesis of substituted azobenzenes using an azo coupling reaction. Azo coupling involves a diazonium salt and another aromatic compound. [13]

One of the interesting properties of azobenzene and derivatives is the ability to isomerise the nitrogen-nitrogen double bond in the presence of UV light. Azobenzene and derivatives are generally found in the trans form as this lowers the steric clash between the bulky benzene rings. There is also an electronic effect as the cis form is not as conjugated as the trans form; both of these effects lead to the trans isomer being favoured by roughly 84 $kJmol^{-1}$. [14] Azobenzene has also been incorporated into crown ether type molecules to try to control conformational changes within the molecule. It has been found that when the azobenzene crown ether molecule was isomerised it lost the ability of binding Na^{+} ions. [15]

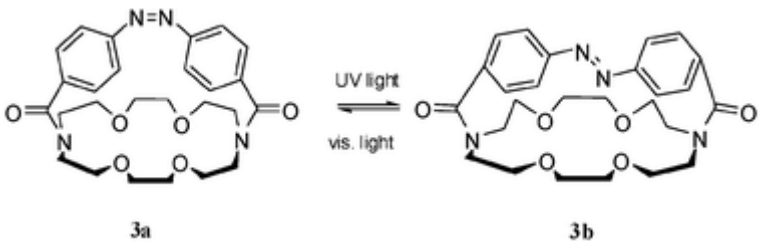

Fig (16) - Azobenzene crown ether undergoing photoisomerisation.

Fig (16) shows the azobenzene crown ether undergoing a conformational change due to isomerism. Isomerisation drastically changes the space in the crown ether unit, which is responsible for binding cations.

Azobenzene and derivatives have been coordinated to various transition metals such as Ru, [16] Ir [17] and Pd. [18] It has also been coordinated to Mg [19] and some lanthanides including Sm, [20] Yb, [21] Nd, Dy and Tm. [22]

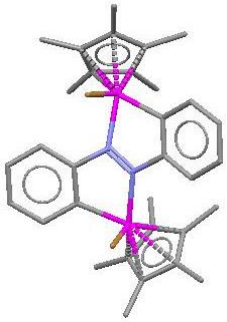

Fig (17) - Shows a doubly cyclometallated azobenzene bound to two Ir atoms that are in turn bound to a cyclopentadienyl anion and a bromide ion. The hydrogen atoms have been omitted for clarity.

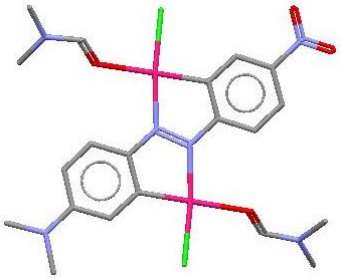

Fig (18) - Shows a doubly cyclometallated substituted azobenzene bound to two Pd atoms that are also bound to DMF and a chloride ion. The hydrogen atoms have been omitted for clarity.

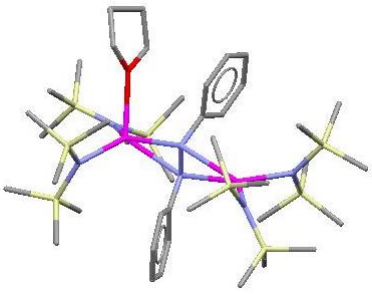

Fig (19) - Shows a reduced azobenzene coordinated to two Sm atoms which are then bound to two $(Me_3Si)_2N^-$ ions. The hydrogen atoms have been omitted for clarity.

Due to the ability of azobenzene and derivatives to be isomerised, these molecules, when incorporated into metallosupramolecular devices, can cause a functional change.

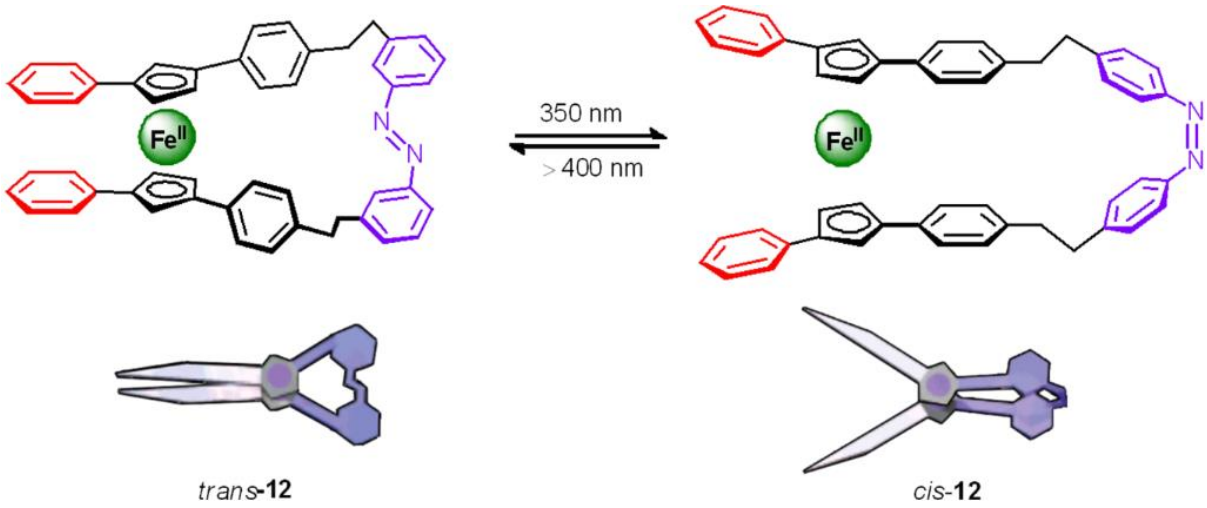

Fig (20) - Azo scissors opening and closing.

Fig (20) shows a substituted azobenzene that has been complexed with an iron atom. When the complex is exposed to different wavelengths of light the azo group isomerises and the "scissors" can be opened or closed. [23]

A similar effect has also been seen in a silver complex of a substituted azobenzene.

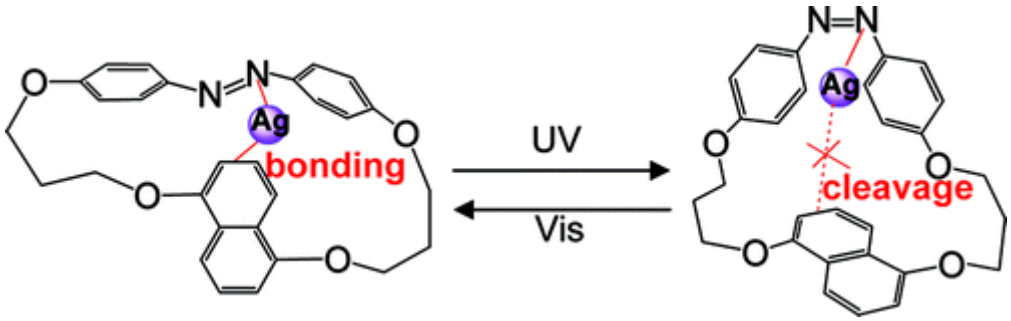

Fig (21) - Substituted azobenzene undergoing photoisomerisation.

Fig (21) shows a substituted azobenzene that has been complexed with a silver atom. When the complex is exposed to different wavelengths of light the azo group isomerises and the conformation of the molecule changes breaking the cation-π interaction between the silver atom and the naphthalene ring. [24]

From these examples and countless others, we see that the chemistry of azobenzene-metal complexes is varied. Some metals cause reduction of the nitrogen-nitrogen double bond or orthometallation while others simply form complexes of varying dimensions. Azobenzene-metal complexes have dimensions varying from discrete to 3-D metallopolymers.

To date only one azobenzene-silver complex has been reported in the literature; [25] this complex is a zigzag 1-D metallopolymer.

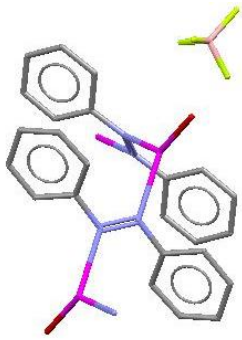

Fig (22) - Shows part of the zigzag structure of the complex. The azobenzene molecule is bridged by silver atoms with one coordinated water molecule per silver. The hydrogen atoms have been omitted for clarity.

Aim

The aim of this project is to systematically study silver complexes of azobenzene and derivatives. The possible binding modes of the silver to nitrogen bond will be investigated along with any other silver to heteroatom bonds and any other interactions; for example π-π stacking or cation-π interactions etc. This is the first study to systematically study these complexes. This will be carried out using X-ray crystallography on the crystalline complexes produced.

This study will look into what effect a change in the substituent/s within azobenzene will have on the binding mode of the silver to nitrogen bond, be they electronic or steric effects.

Other heterocyclic aromatic rings connected via an azo group will be synthesised to see what effect nitrogen containing aromatic systems have on the coordination mode.

Chapter Two

Discussion

Discussion

1.1 complexes of azobenzene

With silver(I) tetrafluoroborate (1.10)

The asymmetric unit of 1.10 contains one silver atom, one water molecule, two half molecules of azobenzene and a tetrafluoroborate anion. The crystal structure solves in the space group P-1 with R_1= 0.0181. This is the same complex, albeit with a much better refinement, as the previously reported structure.[25] This complex was made by mixing one equivalent of ligand with two and a half equivalents of silver salt; the ratio in the complex is one to one i.e. [ML].

Fig (1) shows the distorted trigonal planar geometry which Ag1 adopts; the ideal bond angle of a trigonal plane is 120˚. The bond angles around the silver atom are 97.64(5)˚ N1-Ag1-N2, 119.78(6)˚ O1-Ag1-N1 and 141.68(6)˚ O1-Ag1-N2. Fig (1) also shows the two half molecules of azobenzene coordinating to the silver atom. The nitrogen-nitrogen bond lengths of the azobenzene molecules are 1.253(3) (N1-N1A) and 1.257(3) Å (N2-N2A). These bond distances are similar to the nitrogen-nitrogen bond length (1.257(17) Å)[26] of crystalline azobenzene. These bond distances are the same as in the previously reported structure.[25] It is also shown in Fig (1) that the aromatic rings of the azobenzene molecules are not in the plane of the azo group; they have been rotated out of the plane of the azo group by 38.5(3) (N1A-N1-C1-C2) and 35.0(2)˚ (N2A-N2-C10-C11). Also shown in Fig (1) is the non-coordinating tetrafluoroborate anion.

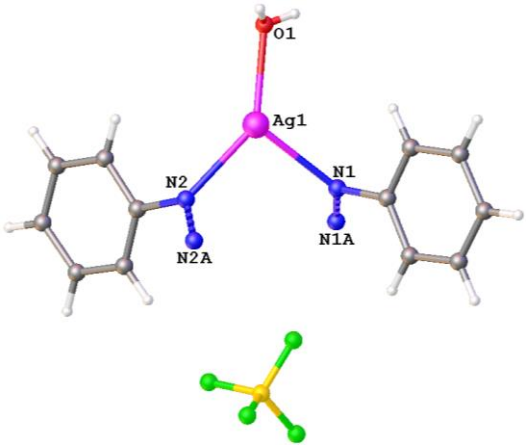

Fig (1) - The asymmetric unit of 1.10. Relevant bond lengths (Å) are Ag1-N1 2.3696(16), Ag1-N2 2.2939(16), Ag1-O1 2.2334(16), N1-N1A 1.253(3) and N2-N2A 1.257(3). Relevant bond angles (˚) are N1-Ag1-N2 97.64(5), O1-Ag1-N1 119.78(6) and O1-Ag1-N2 141.68(6). Relevant torsion angles (˚) are N1A-N1-C1-C2 38.5(3) and N2A-N2-C10-C11 35.0(2).

Due to the symmetry of the complex the azobenzene molecules have coplanar aromatic rings as seen in Fig (2). The structure of the complex is a 1-D zigzag metallopolymer with the

azobenzene molecules alternating in their conformation. Fig (2) also shows the azobenzene bridging distances, which are 5.531(1) and 5.370(1) Å in length. These distances are the same as those for the previously reported structure.[25]

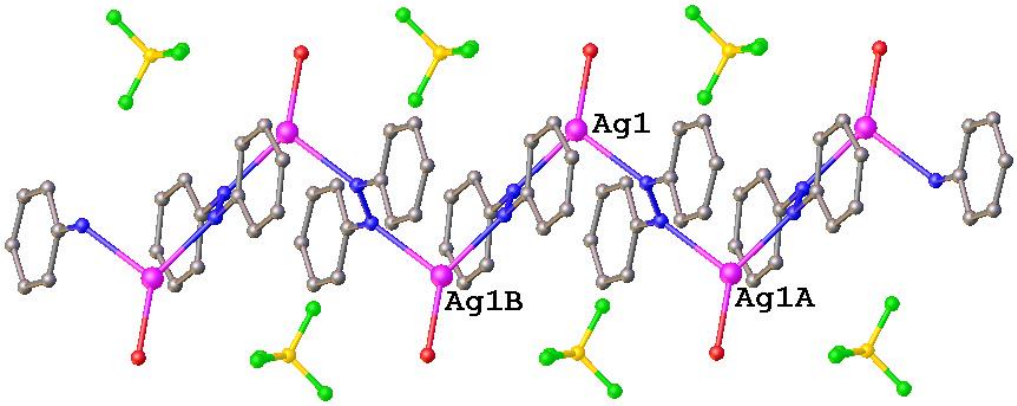

Fig (2) - View of a short strand of the polymer 1.10. The hydrogen atoms have been omitted for clarity. Relevant interatomic distances (Å) are Ag1-Ag1A 5.531(1) and Ag1-Ag1B 5.370(1).

In Fig (3), it is shown how the strands of the polymer are ordered by hydrogen bonds. The hydrogen bonds between the water molecule and the tetrafluoroborate anions form a six membered ring in a chair like conformation. The lengths of the hydrogen bonds are 2.11(2) (H1-F4), 1.99(2) Å (H2-F2A).

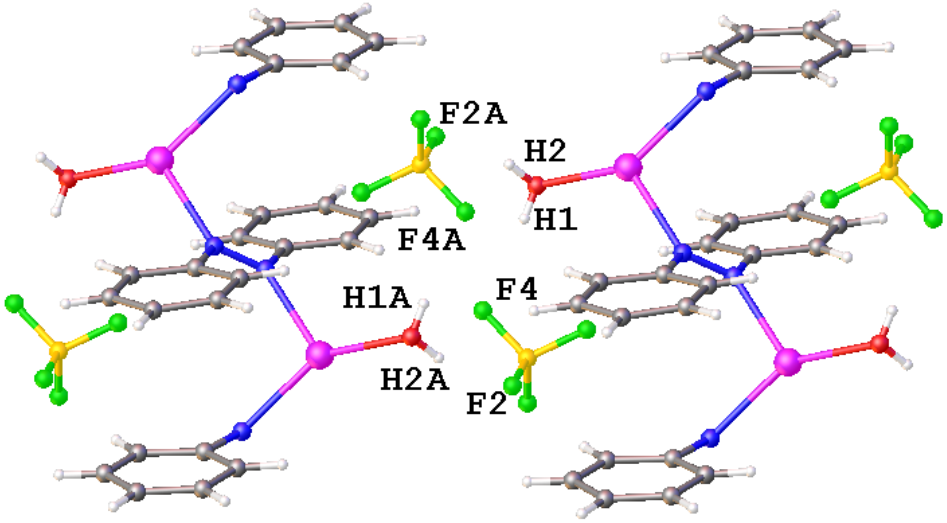

Fig (3) - View of the hydrogen bonding in 1.10. Relevant hydrogen bond lengths (Å) are H1-F4 2.11(2) and H2-F2A 1.99(2).

To summarise, the complex is a 1-D metallopolymer in which the silver atoms adopt a distorted trigonal planar geometry. There are two different types of azobenzene molecule in the complex; both of which are bridging bidentate. The tetrafluoroborate anion does not coordinate; however, it does create a six membered ring of hydrogen bonds in a chair like conformation.

With silver(I) hexafluorophosphate (1.11)

In the asymmetric unit of complex 1.11, there are one and a half silver atoms, one full azobenzene molecule and three half molecules, a full hexafluorophosphate anion and a half anion. The crystal structure solves in the space group P-1 with R_1= 0.0478. This complex was made by mixing one equivalent of ligand with two and a half equivalents of silver salt but produces a complex with a ratio of three to five i.e. $[M_3L_5]$.

The silver atom (Ag1) adopts a slightly distorted trigonal planar geometry with the three angles closely matching the ideal bond angle of 120˚; the angles are 110.72(15) (N1-Ag1-N2), 114.9(4) (N1-Ag1-N3) and 126.95(13)˚ (N2-Ag1-N3) as seen in Fig (4). The silver atom (Ag2) adopts a perfect linear geometry since it lies on a centre of inversion. Fig (4) also shows the three half azobenzene molecules coordinating to Ag1; they coordinate in a bidentate fashion. The nitrogen-nitrogen bond lengths of the bidentate azobenzene molecules are all shorter than the same bond length (1.257(17) Å)[26] in crystallised azobenzene; these bond lengths are 1.249(10) (N1-N1A), 1.253(7) (N2-N2A) and 1.251(7)Å (N3-N3A). These nitrogen-nitrogen bond lengths are all comparable to those in the previously reported structure,[25] that is 1.253(3) and 1.257(3) Å in length. There is also a monodentate azobenzene molecule coordinated to Ag2; the nitrogen-nitrogen bond length is 1.26(2) Å (N4-N5). In Fig (4) it is also shown that the hexafluorophosphate anions do not coordinate to the silver atoms; instead they occupy the pores in the honeycomb of the polymeric phase and the space between the polymeric and the discrete phase. One of the hexafluorophosphate anions is only half an anion to balance the charge due to the half-occupancy silver atom (Ag2).

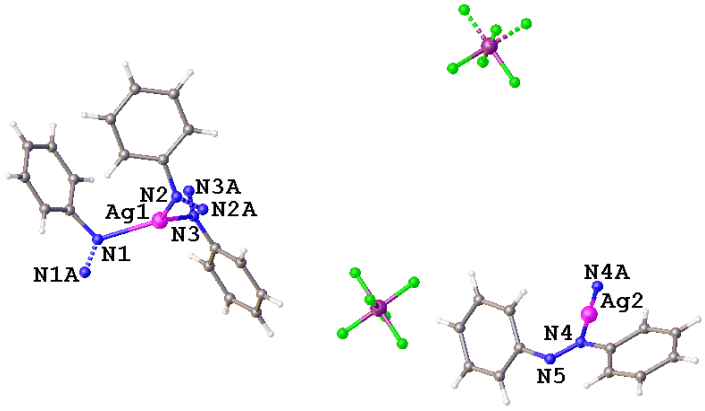

Fig (4) - The asymmetric unit of 1.11. Relevant bond lengths (Å) are Ag1-N1 2.296(5), Ag1-N2 2.291(4), Ag1-N3 2.288(3), N1-N1A 1.249(10), N2-N2A 1.253(7), N3-N3A 1.251(7) Ag2-N4 2.14(2) and N4-N5 1.26(2). Relevant bond angles (˚) are N1-Ag1-N2 110.72(15), N1-Ag1-N3 114.9(4), N2-Ag1-N3 126.95(13) and N4-Ag1-N4A 180.00(0).

Fig (5) shows the discrete component of complex 1.11. The azobenzene molecules coordinate in a monodentate fashion to the linear silver atom. The aromatic rings of the azobenzene molecules are not in the plane of the azo group; the rings N4/N4A are out of

the plane by only 2.2(13)˚ while the rings N5/N5A are out of the plane by 56.6(15)˚. The aromatic rings within one azobenzene molecule are not coplanar which is due to the steric interactions between the hydrogen atoms of the opposing aromatic ring; the angle between them is 55.5(4)˚.

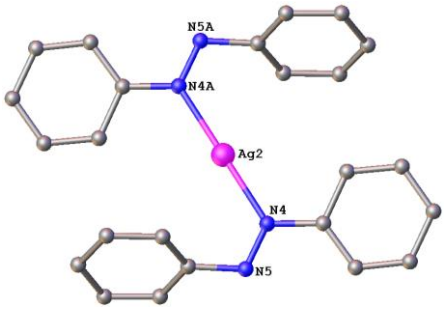

Fig (5) - View of the discrete component of the complex 1.11. The hydrogen atoms have been omitted for clarity. A relevant bond length (Å) is N4-N4A 4.29(4). Relevant torsion angles (˚) are N5-N4-C30-C31 2.2(13), N4-N5-C40-C41 56.6(15) and RingN4-RingN5 55.5(4).

Fig (6) shows the polymeric component of complex 1.11; the azobenzene molecules coordinate to the silver atom in a bidentate fashion. The azobenzene bridging distances between silver atoms are 5.385(1) (Ag1-Ag1A), 5.449(1) (Ag1A-Ag1B) and 5.396(1) Å (Ag1B-Ag1C). The pore of the honeycomb structure of the polymeric phase has dimensions, which vary between 9.041(1) and 11.175(1) Å. In Fig (6) it is also shown that the aromatic rings of azobenzene are rotated out of the plane of the azo group by 45.8(8) (N1A-N1-C1-C2), 44.7(6) (N2A-N2-C10-C11) and 53.0(6)˚ (N3A-N3-C20-C21). Due to the symmetry of the complex the aromatic rings of the azobenzene molecules are all coplanar.

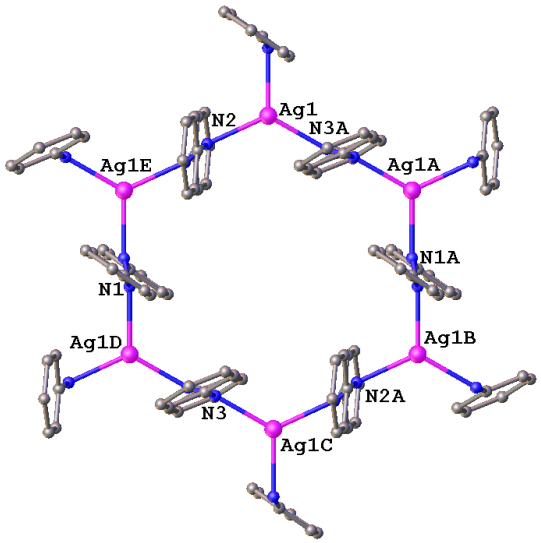

Fig (6) - View of the polymeric component of the complex 1.11. The hydrogen atoms have been omitted for clarity. Relevant bond lengths (Å) are N1-N1A 9.794(9), N2-N2A 9.285(7), N3-N3A 9.041(7), Ag1-Ag1A 5.385(1), Ag1A-Ag1B 5.449(1), Ag1B-Ag1C 5.396(1), Ag1-Ag1C

10.410(1), Ag1A-Ag1D 10.847(1) and Ag1B-Ag1E 11.175(1). Relevant torsion angles (˚) are N1A-N1-C1-C2 45.8(8), N2A-N2-C10-C11 44.7(6) and N3A-N3-C20-C21 53.0(6).

Fig (7) shows the honeycomb structure of the polymeric phase.

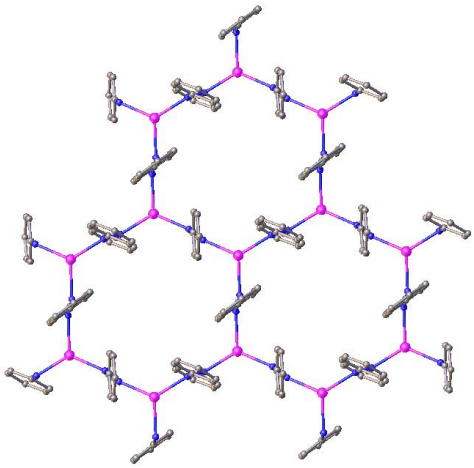

Fig (7) - View of the honeycomb structure the polymeric component adopts. The hydrogen atoms have been omitted for clarity.

The hexafluorophosphate anion sits in the pore of the polymeric component as shown in Fig (8). The hexafluorophosphate anion acts as a template, which allows the honeycomb structure of the complex to form; this is known as the templation effect.

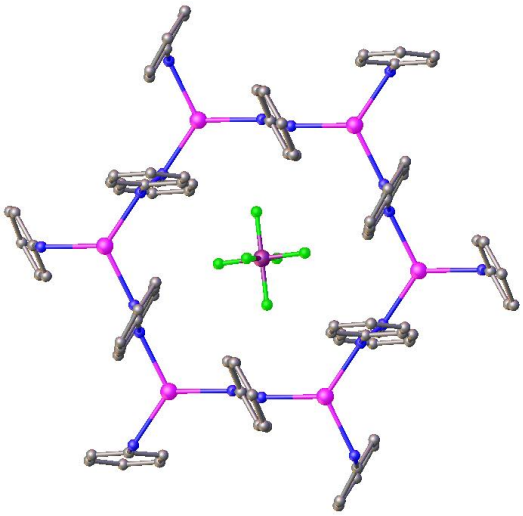

Fig (8) - A bird's-eye view of the hexafluorophosphate anion sitting in the pore of the complex 1.11. The hydrogen atoms have been omitted for clarity.

A view of the hexafluorophosphate anion sitting in the pore of the polymeric phase is shown in Fig (9).

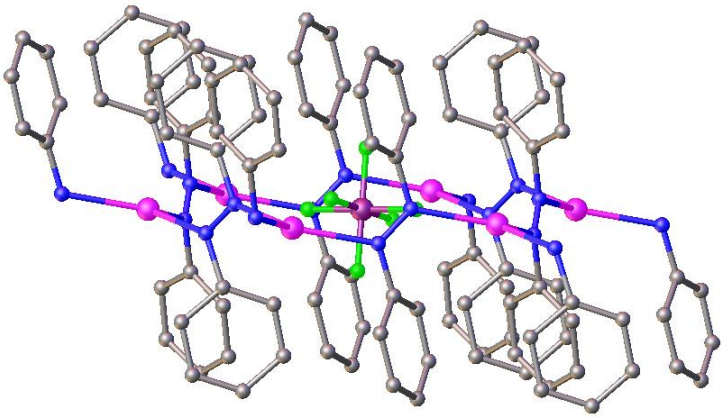

Fig (9) - A side-on view of the hexafluorophosphate anion sitting in the pore of the complex 1.11. The hydrogen atoms have been omitted for clarity.

To summarise, there are two different phases that the complex adopts; a polymeric phase and a discrete phase. The polymeric phase is 2-D in nature and resembles a honeycomb. In the discrete phase the silver atom is half-occupancy. The hexafluorophosphate anions do not coordinate to the silver atoms; instead the half-occupancy anion sits in the pore created by the honeycomb structure of the polymeric phase, while the full-occupancy anion sits in between the polymeric phase and the discrete phase. The azobenzene molecules in the polymeric phase bridge the silver atoms in a bidentate fashion. The azobenzene molecules in the discrete phase coordinate in a monodentate fashion to the silver atom.

<u>With silver(I) perchlorate (1.12)</u>

The complex of azobenzene and silver perchlorate has one silver atom, one and a half azobenzene molecules and a perchlorate anion in the asymmetric unit. The crystal structure solves in the triclinic space group P-1 with R_1= 0.0228. This complex was prepared using a ratio of one equivalent of ligand to two and a half equivalents of silver salt; the resulting ratio in the complex is two to three i.e. $[M_2L_3]$.

Fig (10) shows that the silver atom has a distorted tetrahedral configuration with three bond angles slightly higher than the ideal tetrahedral angle of 109˚; these are N1-Ag1-N3 (119.12(10)), N1-Ag1-O1 (114.88(11)) and N1-Ag1-O2A (123.84(12)). The three bond angles lower than 109˚ are N3-Ag1-O1 (92.56(11)), N3-Ag1-O2A (99.25(12)) and O1-Ag1-O2A (101.52(14)). The bond length of N1-N2 is 1.258(4) Å while the bond length of N3-N3A is 1.259(6) Å. These are the same as the nitrogen-nitrogen bond length, 1.257(17) Å,[26] of crystalline azobenzene. Fig (10) also shows the torsional angles between the azo groups and the benzene rings; all three of the aromatic rings of azobenzene have been rotated out of the plane of the azo group slightly. The ring attached to N1 has been rotated out of the plane by 5.10(5)˚ while the ring of N2 has come out of the plane by 37.30(5)˚ and the ring of N3 is 40.60(5)˚ out of the plane. In Fig (10), it is shown that the aromatic rings of the monodentate azobenzene molecule are not coplanar with an angle between them of 35.05(13)˚. Also shown in Fig (10) is the bridging bidentate perchlorate anion.

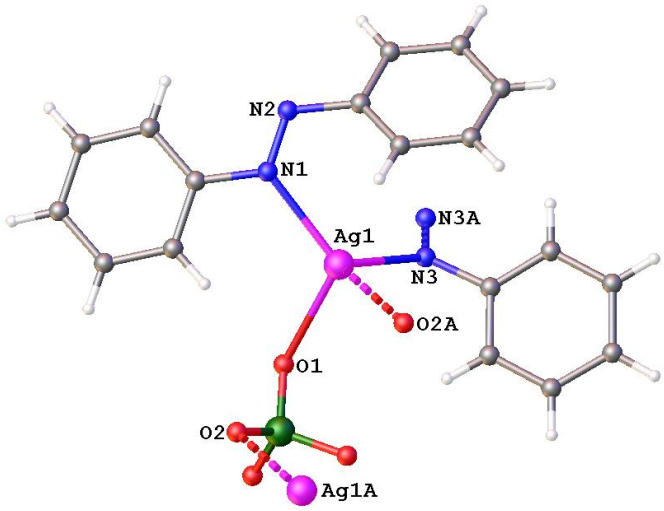

Fig (10) - The asymmetric unit of 1.12. Relevant bond lengths (Å) are Ag1-N1 2.314(3), Ag1-N3 2.329(3), Ag1-O1 2.515(4), Ag1-O2A 2.507(4), N1-N2 1.258(4) and N3-N3A 1.259(6). Relevant bond angles (˚) are N1-Ag1-N3 119.12(10), N1-Ag1-O1 114.88(11), N1-Ag1-O2A 123.84(12), N3-Ag1-O1 92.56(11), N3-Ag1-O2A 99.25(12) and O1-Ag1-O2A 101.52(14). Relevant torsion angles (˚) are N1-N2-C10-C11 37.30(5), N2-N1-C1-C2 5.10(5), N3A-N3-C20-C21 40.60(5) and RingN1-RingN2 35.05(13).

Due to the symmetry in the complex, the bidentate azobenzene molecule has coplanar aromatic rings as seen in Fig (11). The complex is a 1-D metallopolymer with a distance between the silver atoms bridged by the perchlorate anions (Ag1-Ag1A) of 5.074(1) Å while the distance between the azobenzene bridged silver atoms (Ag1-Ag1B) is 5.490(1) Å. The distance between the azobenzene bridged silver atoms is comparable to the previously reported structure,[25] that has distances of 5.531(1) and 5.370(1) Å.

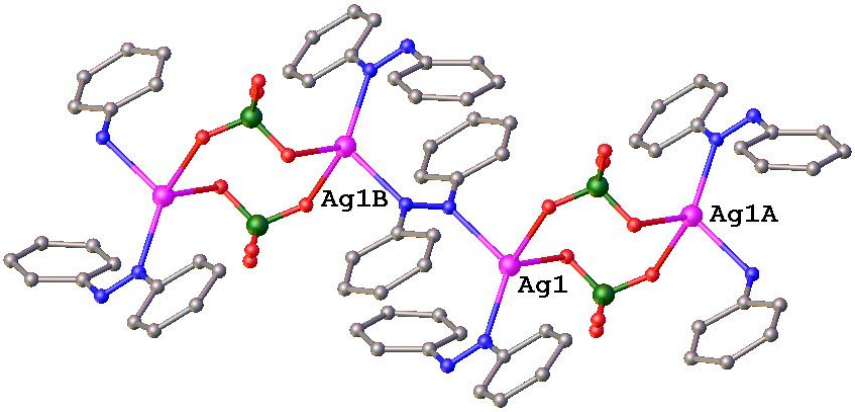

Fig (11) - View of a short strand of the polymer 1.12. The hydrogen atoms have been omitted for clarity. Relevant interatomic distances (Å) are Ag1-Ag1A 5.0740(1) and Ag1-Ag1B 5.490(1).

In Fig (12) it is shown how the strands of the complex are organised by the hydrogen bonding between 04-H5A and O4-H14A; the hydrogen bond lengths of these two

interactions are 2.58(2) and 2.65(2) Å respectively. There is also an intra-strand interaction between O3-H21, this interaction is the cause of the torsional angle between N3A-N3-C20-C21, which is 40.30(6)˚; the length of the aforementioned hydrogen bond is 2.52(2) Å.

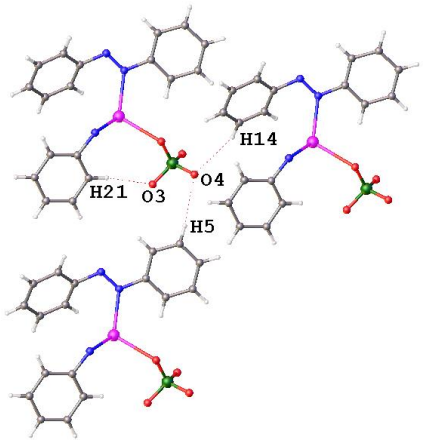

Fig (12) - View of the intra- and inter-strand hydrogen bonding in 1.12. Relevant hydrogen bond lengths (Å) are O3-H21 2.52(2), O4-H5 2.58(2) and 04-H14 2.65(2).

To summarise, the structure of the complex is a 1-D metallopolymer with the silver atoms adopting a distorted tetrahedral configuration. There are two different types of azobenzene in the complex, one of which is bidentate and bridges two silver atoms, while the other is monodentate. Two oxygen atoms (O1 and O2) of the perchlorate anion bridge the silver atoms in the complex; this leads to an eight membered ring in a chair like conformation.

With silver(I) triflate (1.13)

The asymmetric unit of the complex between azobenzene and silver triflate contains one silver atom, a half molecule of azobenzene and a triflate anion. The crystal structure solves in the space group P-1 with R_1= 0.0518. This complex was produced by using one equivalent of ligand to two and a half equivalents of silver salt but the resulting complex has a ratio of two to one i.e. [M_2L]; this approximately matches the ratio used in the preparation of the complex.

Fig (13) shows the geometry of the silver atom; there are three angles above the ideal tetrahedral angle of 109˚ and three angles below the tetrahedral angle. These are N1-Ag1-O1 102.8(6), N1-Ag1-O2A 125.3(6), N1-Ag1-O3A 130.1(6), O1-Ag1-O2A 98.4(6), O1-Ag1-O3A 95.1(6) and 02A-Ag1-O3A 96.8(5)˚. It is also shown in Fig(13) that the nitrogen-nitrogen bond length of the azobenzene molecule is 1.270(4) Å which is longer than the same bond length in crystallised azobenzene (1.257(17) Å).[26] The nitrogen-nitrogen bond length of azobenzene in the complex 1.11 is also longer than the same bond length in the previously reported structure,[25] which are 1.253(3) and 1.257(3) Å. The aromatic ring of the azobenzene molecule is rotated out of the plane of the azo group by 44.10(12)˚. Fig (13) also shows that the triflate anion is tridentate with each oxygen atom coordinated to a silver atom. The triflate anion also adopts a staggered conformation; this is the lowest energy

conformation that the triflate anion can adopt as it minimises the eclipsing interactions between the oxygen and fluorine atoms.

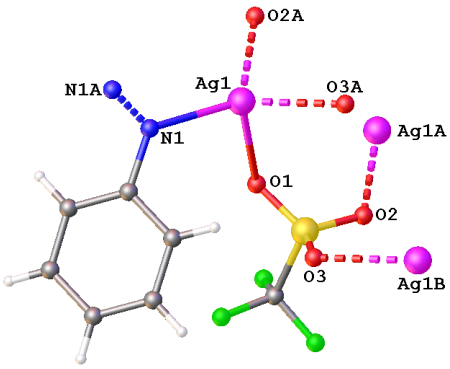

Fig (13) - The asymmetric unit of 1.13. Relevant bond lengths (Å) are Ag1-N1 2.287(17), Ag1-O1 2.423(15), Ag1-O2A 2.346(15), Ag1-O3A 2.361(15) and N1-N1A 1.270(4). Relevant bond angles (˚) are N1-Ag1-O1 102.8(6), N1-Ag1-O2A 125.3(6), N1-Ag1-O3A 130.1(6), O1-Ag1-O2A 98.4(6), O1-Ag1-O3A 95.1(6) and 02A-Ag1-O3A 96.8(5). A relevant torsion angle (˚) is N1A-N1-C1-C2 44.10(12).

In Fig (14) it is shown how the 2-D structure of the metallopolymer is arranged; the bidentate azobenzene molecules bridging the silver atoms expand the polymer in one direction while the tridentate triflate anions coordinate to the silver atoms and extend at a 90˚ angle to the azobenzene molecules. The distance between Ag1 and Ag1A (5.375(1) Å), which are the azobenzene bridging silver atoms, is comparable to the previously reported structure.[25]

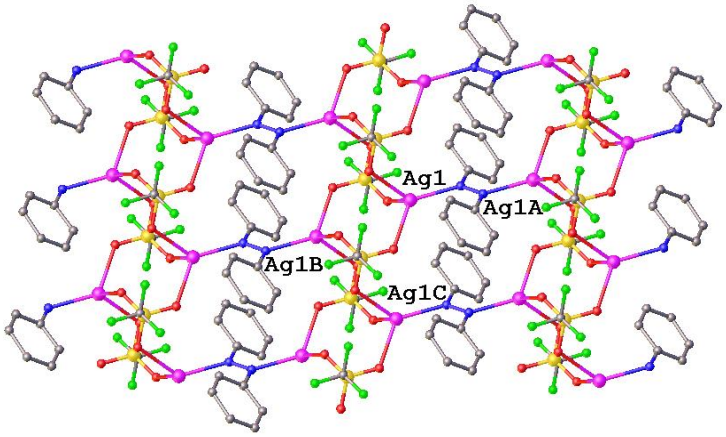

Fig (14) - View of a section of the 2-D metallopolymer 1.13. The hydrogen atoms have been omitted for clarity. Relevant interatomic distances (Å) are Ag1-Ag1A 5.375(1), Ag1-Ag1B 4.680(1) and Ag1-Ag1C 5.138(1).

Fig (15) shows how the tridenate triflate anions form a series of fused eight membered rings in a chair like conformation.

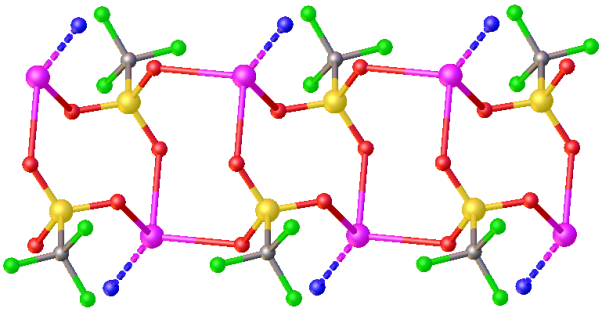

Fig (15) - View of a section of the structure showing the fused eight membered rings of complex 1.13. The azobenzene molecules have been omitted for clarity.

In Fig (16) the weak interactions that act between the different strands can be seen. The fluorine atoms of the triflate anion line the upper and bottom layer of the complex. These fluorine atoms interact to order the complex; the distance between F3 and F3A is 2.94(2) Å. These are considered relatively strong fluorine-fluorine interactions with the accepted distance range being 2.8 to 3.6 Å.[27]

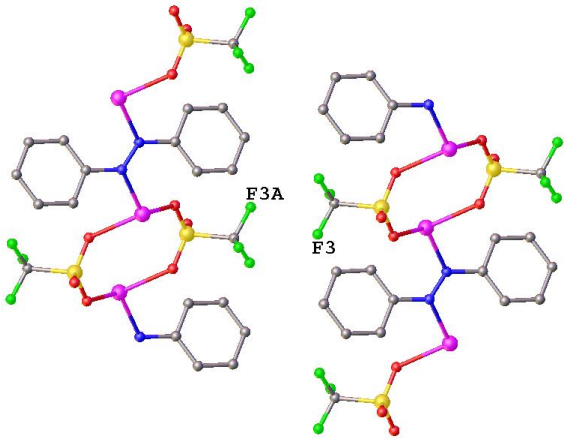

Fig (16) - View of the fluorine-fluorine interactions that take place between the sheets of polymer 1.13. The hydrogen atoms have been omitted for clarity. A relevant interatomic distance (Å) is F3-F3A 2.94(2).

To summarise, this structure is 2-D in nature with the silver atom in a distorted tetrahedral geometry. The azobenzene molecule in the complex bridges the silver atoms in a bidentate fashion around a crystallographic centre of inversion. The triflate anions in the complex are all tridentate with all the oxygen atoms coordinated to a silver atom.

<u>With silver(I) trifluoroacetate (1.14)</u>

In the asymmetric unit of complex 1.14, there is one molecule of azobenzene, two silver atoms and two trifluoroacetate anions. The crystal structure solves in the space group P-1 with R_1= 0.0326. This complex was prepared using a ratio of one equivalent of ligand to two and a half equivalents of silver salt but the complex itself has a ratio of two to one i.e. [M_2L]; this approximately matches the ratio used to prepare the complex.

Ag1 has an unusual five-coordinate geometry as seen in Fig (17) with none of the bond angles matching the ideal angles of a trigonal bipyramid, the three bond angles closest to their ideal angle are 103.11(7) (N1-Ag1-O1), 122.59(7) (N1-Ag1-O3) and 121.16(7)˚ (O1-Ag1-O3); these three angles should match up with 120˚. The other angles are 76.61(5) (N1-Ag1-Ag2) and 121.25(7)˚ (N1-Ag1-O3A) which should be 90˚ and 154.14(4)˚ (Ag2-Ag1-O3A) which should be 180˚. Overall the τ_5 index [31] is 0.53 which indicates an intermediate geometry between a trigonal bipyramid and a square pyramid. There is a strong silver-silver bond between Ag1-Ag2 (2.9294(3) Å). Silver-silver bonds are variable in nature and can range up to 3.102 Å.[28] Fig (17) also shows the unusual four-coordinate geometry around Ag2; three of the bond angles are close to the ideal bond angles of the square planar geometry. The angles around the four coordinate silver atom are 79.04(4) (Ag1-Ag2-O2), 81.59(5) (Ag1-Ag2-O4), 78.20(7) (O2-Ag2-O2A), 124.59(7) (O4-Ag2-O2A), 130.56(5) (Ag1-Ag2-O2A) and 156.78(6)˚ (O2-Ag2-O4). Overall the τ_4 index [32] is 0.52 which indicates an intermediate geometry between a tetrahedron and a square plane. Fig (17) also shows the azobenzene coordinating to the silver atom in a monodentate fashion. The nitrogen-nitrogen bond is 1.252(3) Å in length which is slightly shorter than the same bond length (1.257(17) Å)[26] for crystallised azobenzene and is almost identical to the nitrogen-nitrogen bond lengths of the previously reported structure.[25] The aromatic rings of the azobenzene molecule have been rotated out of the plane of the azo group by 30.90(4)˚ for the ring attached to N1 and 25.80(3)˚ for the ring attached to N2; also the rings are not coplanar with an angle between them of 6.00(18)˚. There is some disorder in the orientation of one of the CF_3 groups.

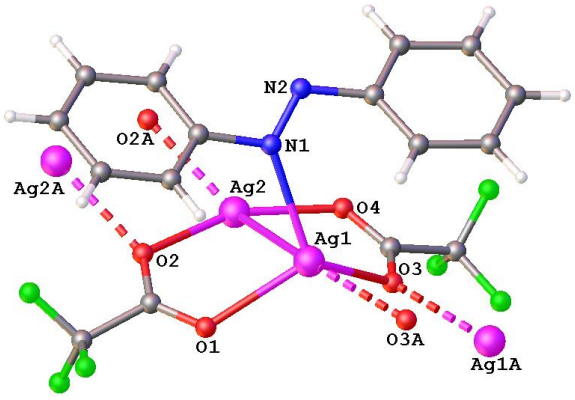

Fig (17) - The asymmetric unit of 1.14. The disorder around the CF_3 group accociated with O1/O2 has been omitted for clarity. Relevant bond lengths (Å) are Ag1-Ag2 2.9294(3), Ag1-N1 2.389(2) Ag1-O1 2.320(2) Ag1-O3 2.3498(18) Ag1-O3A 2.4527(16) Ag2-O2 2.2706(19) Ag2-O4 2.1889(19), Ag2-O2A 2.4096(17), O3-Ag1A 2.4096(17), O2-Ag2A 2.4096(17) and N1-N2 1.252(3). Relevant bond angles (˚) are N1-Ag1-Ag2 76.61(5), N1-Ag1-O1 103.11(7), N1-Ag1-O3 122.59(7), N1-Ag1-O3A 121.25(7), Ag2-Ag1-O1 79.47(5), Ag2-Ag1-O3 77.63(4), Ag2-Ag1-O3A 154.14(4), O1-Ag1-O3 121.16(7), O1-Ag1-O3A 110.90(6), O3-Ag1-O3A 76.80(6), Ag1-Ag2-O2 79.04(4), Ag1-Ag2-O4 81.59(5), Ag1-Ag2-O2A 130.56(5), O2-Ag2-O4 156.78(6), O2-Ag2-O2A 78.20(7) and O4-Ag2-O2A 124.59(7). Relevant torsion angles (˚) are N2-N1-C1-C2 30.90(4), N1-N2-C10-C11 25.80(3) and RingN1-RingN2 6.00(18).

In Fig (18) it is shown that the metallopolymer 1.14 is 1-D in nature with the azobenzene molecules coming off alternating sides of the surface of the polymer chain. The complex has a head-head/tail-tail like structure with Ag1 and Ag1A forming a square and Ag2 and Ag2A forming another square. The silver-silver distances of 3.764(1) and 3.633(1) Å give the distances between the opposite corners of the squares, each of which is positioned about a centre of inversion.

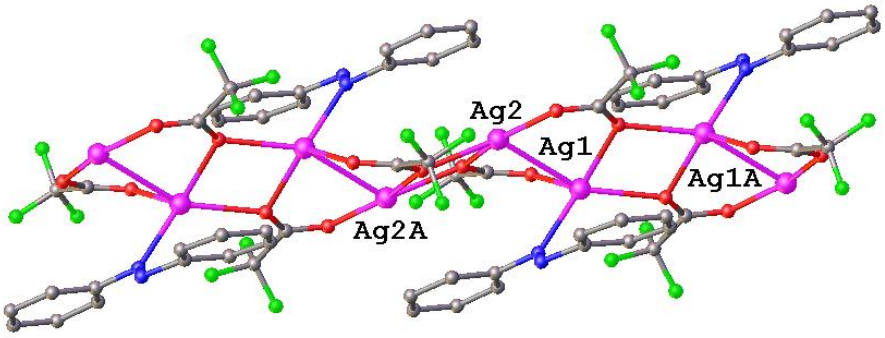

Fig (18) - View of a short strand of the polymer 1.14. The hydrogen atoms have been omitted for clarity. Relevant interatomic distances (Å) are Ag1-Ag1A 3.764(1) and Ag2-Ag2A 3.633(1).

Fig (19) shows how the monodentate and bidentate oxygen atoms of the trifluoroacetate anions form a series of fused four and five membered rings; this configuration resembles a hopscotch court.

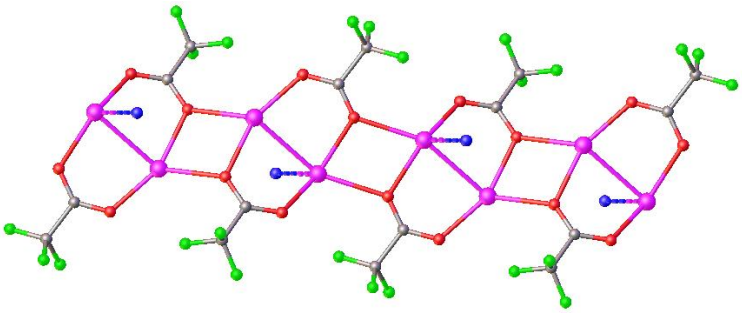

Fig (19) - View of a section of the structure showing the fused four and five membered rings in the hopscotch court configuration. The azobenzene molecules have been omitted for clarity.

The strands of the metallopolymer 1.14 orientate in the crystal via weak fluorine-fluorine interactions as shown in Fig (20). The trifluoroacetate anions have the CF_3 groups extending on the sides of the strands, which weakly interact with each other through the fluorine atoms; the length of these interactions are 3.04(2) and 3.18(2) Å. These fluorine-fluorine interactions have a moderate strength; fluorine-fluorine interactions usually fall between 2.8 and 3.6 Å.[27]

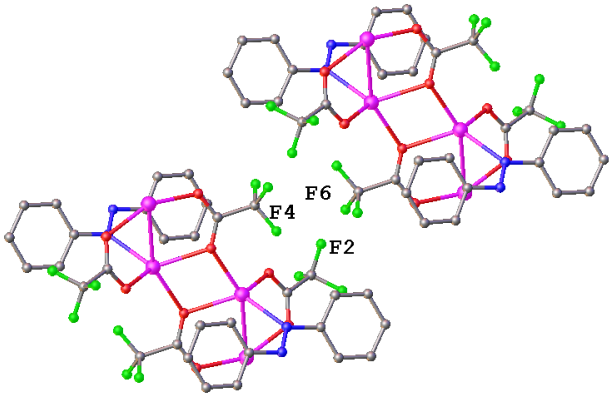

Fig (20) - View of how the strands of the polymer 1.14 are orientated relative to each other. The hydrogen atoms have been omitted for clarity. Relevant interatomic distances (Å) are F2-F6 3.04(2) and F4-F6 3.18(2).

To summarise, the structure of the complex is 1-D in nature with two different types of silver atom, one of which is arranged in an unusual five coordinate geometry with a τ_5 index [31] of 0.53; while the other has an unusual four coordinate geometry with τ_4 index [32] of 0.52. These τ indices indicate geometries roughly half way between a trigonal bipyramid/square pyramid and a tetrahedron/square plane respectively. The trifluoroacetate anions are tridentate with one oxygen atom bonding in a monodentate fashion to a silver atom, while the other oxygen atom coordinates to two silver atoms and is therefore bidentate. This arrangement between the silver atoms and the trifluoroacetate anions forms a series of fused four and five membered rings, which somewhat resembles a hopscotch court. The azobenzene molecule is monodentate in this complex and simply juts out from the surface of the polymer.

From all the above examples, it is shown that azobenzene is a versatile ligand for metallosupramolecular chemistry. The above complexes show a variety of molecular topologies in which azobenzene adopts two different binding modes either monodentate or bridging bidentate. It would seem that the anion plays the largest role in determining the structure of the complex with the non-coordinating tetrafluoroborate anion forming a zigzagging 1-D chain, while the other non-coordinating anion (hexafluorophosphate) templates the formation of a honeycomb-like lattice. The perchlorate anion structure forms a linear 1-D chain, which alternates between bridging perchlorate anions and bridging azobenzene molecules. The triflate anion on the other hand forms a 2-D sheet, which alternates between bridging triflate anions, which also form a series of fused eight membered rings, and bridging azobenzene molecules. Lastly the structure with the trifluoroacetate anion forms a linear head-head/tail-tail 1-D chain with the azobenzene molecules jutting out from the top and bottom of the structure.

2.1 complexes of 2-bromoazobenzene

With silver(I) triflate (2.10)

In the asymmetric unit of 2.10 there is half a molecule of 2-bromoazobenzene, a silver atom and a triflate anion. The crystal structure solves in the space group P-1 with R_1= 0.0513. This complex was made by mixing one equivalent of ligand with three equivalents of silver salt; the ratio in the complex is two to one i.e. [M_2L].

Fig (21) shows the seesaw geometry of the silver atom; the angles around the silver atom do not match the angles of a tetrahedron or a square plane. The τ_4 index [30] of the silver atom is 0.71 indicating that the geometry of the silver atom is closer to a tetrahedron than a square plane. The angles that most closely match the ideal tetrahedral angle of 109˚ are 118.16(18) (N1-Ag1-O3A) and 104.28(16)˚ (O1-Ag1-O2A). The 2-bromoazobenzene molecule is bidentate and bridges two silver atoms. The bromine atom of the 2-bromoazobenzene molecule has half-occupancy due to the centre of inversion in the middle of the azo group. The aromatic ring of the 2-bromoazobenzene molecule is rotated out of the plane of the azo group by 41.20(9)˚. Fig (21) also shows that the triflate anion is tridentate with each oxygen atom coordinated to a silver atom. The CF_3 group is staggered in relation to the SO_3 group, as this conformation is the lowest in energy because the eclipsing interactions are minimised. This asymmetric unit is very similar to the asymmetric unit of 1.13 as seen in Fig (13).

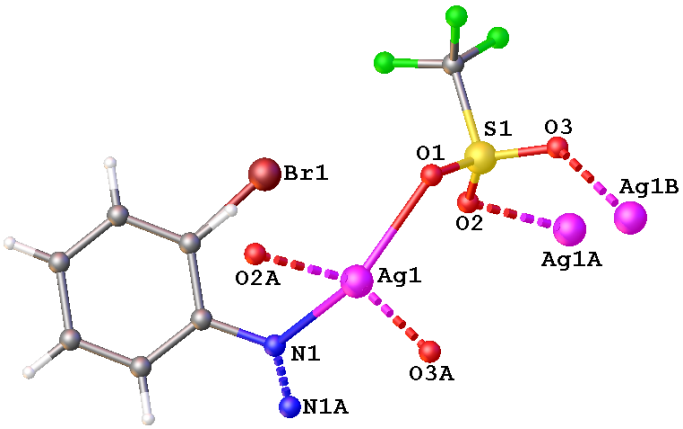

Fig (21) - The asymmetric unit of 2.10. Relevant bond lengths (Å) are Ag1-N1 2.345(5), Ag1-O1 2.335(5), Ag1-O2A 2.441(5), Ag1-O3A 2.361(6) and N1-N1A 1.277(10). Relevant bond angles (˚) are N1-Ag1-O1 141.53(17), N1-Ag1-O2A 90.41(17), N1-Ag1-O3A 118.16(18), O1-Ag1-O2A 104.28(16), O1-Ag1-O3A 95.45(18) and O2A-Ag1-O3A 97.05(19). A relevant torsion angle (˚) is N1A-N1-C1-C2 41.20(9).

The 2-D structure of the metallopolymer 2.10 can be seen in Fig (22); this structure is similar to the metallopolymer 1.13. There are some differences between the two structures due to the different geometry of the silver atom. The distance between Ag1 and Ag1A is 5.513(1) Å; this is the distance at which the 2-bromoazobenzene molecule bridges the silver atoms. This

distance is shorter that the azobenzene bridging distances of the previously reported structure.[25] This is unexpected due to the increased steric bulk due to the bromine atom in the 2-position. However this distance is longer than the azobenzene bridging distance (5.375(1) Å) in the complex 1.13 to which it is analogous; this is expected due to the increased steric bulk of the bromine atom. It is also shown in Fig (22) that the aromatic rings of the 2-bromoazobenzene molecule are coplanar due to the symmetry of the complex.

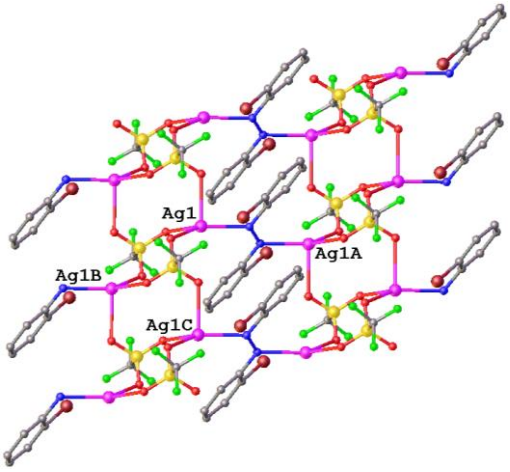

Fig (22) - View of a section of the 2-D metallopolymer 2.10. The hydrogen atoms have been omitted for clarity. Relevant interatomic distances (Å) are Ag1-Ag1A 5.513(1), Ag1-Ag1B 5.126(1) and Ag1-Ag1C 5.439(1).

Fig (23) shows how the tridenate triflate anions form a series of fused eight membered rings in a chair like conformation. This configuration is very similar to the configuration of the triflate anions in the metallopolymer 1.13.

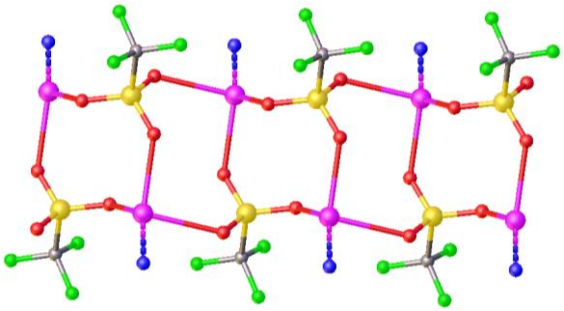

Fig (23) - View of a section of the structure showing the fused eight membered rings of complex 2.10. The azobenzene molecules have been omitted for clarity.

The weak interactions that act between the different strands are seen in Fig (24). The fluorine atoms of the triflate anion line the upper and bottom layer of the complex. These fluorine atoms interact to order the complex; the distance between F1 and F1A is 3.00(2) Å. These are considered relatively strong fluorine-fluorine interactions with the distance range being 2.8 to 3.6 Å.[27] There is also a bromine-fluorine interaction with a distance of 2.95(2) Å (Br1-F2); this is a fairly typical bromine-fluorine distance.[29]

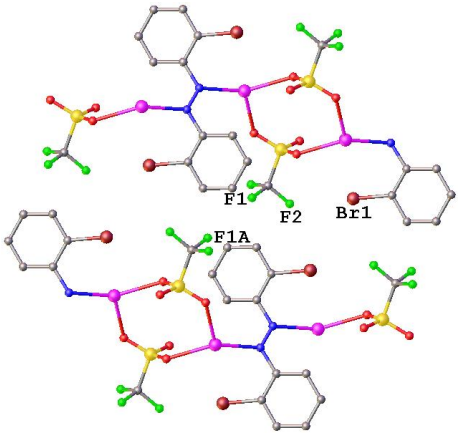

Fig (24) - View of the fluorine-fluorine/fluorine-bromine interactions that take place within and between the sheets of polymer 2.10. The hydrogen atoms have been omitted for clarity. Relevant interatomic distances (Å) are Br1-F2 2.95(2) and F1-F1A 3.00(2).

To summarise the structure of this complex is a 2-D metallopolymer with the silver atom arranged in a distorted tetrahedral geometry; the τ_4 index [30] is 0.71. The triflate anions are tridentate with each oxygen atom coordinating to a silver atom; this configuration forms a series of fused eight membered rings. The 2-bromoazobenzene molecule bridges the silver atoms in a bidentate fashion with each aromatic ring having a half-occupancy bromine atom due to the symmetry of the complex.

With silver(I) trifluroacetate (2.11)

In the asymmetric unit of 2.11 there are two silver atoms, two trifluoroacetate anions and a 2-bromoazobenzene molecule. The crystal structure solves in the space group $P2_1/c$ with R_1= 0.0395. This complex was made by mixing one equivalent of ligand with three equivalents of silver salt but the ratio in the complex is two to one i.e. $[M_2L]$.

The geometry of the two silver atoms is shown in Fig (25); the four-coordinate silver atom has a slightly distorted square planar geometry while the five-coordinate silver atom has a distorted square pyramidal geometry. All the angles around the four-coordinate silver atom are similar to the ideal angles of a square planar geometry, which are 90 and 180˚. These angles are 82.93(9) (Ag1-Ag2-O2), 83.46(10) (Ag1-Ag2-O3), 81.07(12) (O1A-Ag2-O2) and 112.74(13) (O1A-Ag2-O3) which should match 90˚ and 163.76(8) (Ag1-Ag2-O1A) and 165.08(13) (O2-Ag2-O3) which should match 180˚. The angles around the five-coordinate silver atom should match the ideal angles of a square pyramid, which are 90˚ and 180˚; they however do not. The τ_5 index [31] of the five coordinate silver atom is 0.25, which confirms that the geometry of the silver atom is closer to a square pyramid than a trigonal bipyramid. There is a strong silver-silver bond between Ag1-Ag2 (2.9190(6) Å). Silver-silver bonds are variable in nature and can range up to 3.102 Å.[28] Fig (25) shows that the 2-bromoazobenzene molecule is monodentate with the nitrogen atom associated with the bromine atom coordinating to the silver atom. The aromatic rings of the 2-

bromoazobenzene molecule are almost coplanar with an angle of only 1.42(17)˚ between them. The aromatic rings come out of the plane of the azo group by 28.6(5) (N1-N2-C10-C11) and 33.0(7)˚ (N2-N1-C10-C11). It is also shown in Fig (25) that one of the trifluoroacetate anions is bidentate while the other is tetradentate. There is some disorder in one of the CF_3 groups. This asymmetric unit is similar to the asymmetric unit of 1.14 except for one key difference; the trifluoroacetate anions of 1.14 are both tridentate, as seen in Fig (17), while they are bidentate and tetradentate in 2.11.

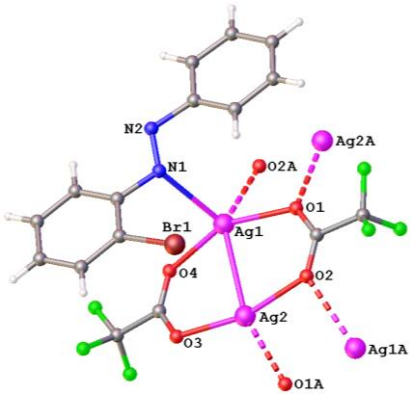

Fig (25) - The asymmetric unit of 2.11. Relevant bond lengths (Å) are Ag1-Ag2 2.9190(6), Ag1-N1 2.510(4), Ag1-O1 2.282(3), Ag1-O2A 2.593(3), Ag1-O4 2.258(3), Ag2-O2 2.246(3), Ag2-O3 2.202(3), Ag2-O1A 2.535(4), Ag1A-O2 2.593(3), Ag2A-O1 2.535(4) and N1-N2 1.249(6). Relevant bond angles (˚) are O1-Ag1-Ag2 79.92(9), O1-Ag1-N1 112.73(13), O1-Ag1-O2A 79.14(11), O1-Ag1-O4 154.26(13), N1-Ag1-Ag2 122.44(11), N1-Ag1-O4 90.56(13), N1-Ag1-O2A 97.98(13), Ag2-Ag1-O2A 139.16(8) O4-Ag1-O2A 109.45(12), O4-Ag1-Ag2 78.23(10), Ag1-Ag2-O2 82.93(9), Ag1-Ag2-O3 83.46(10), Ag1-Ag2-O1A 163.76(8), O1A-Ag2-O2 81.07(12), O1A-Ag2-O3 112.74(13) and O2-Ag2-O3 165.08(13). Relevant torsion angles (˚) are N1-N2-C10-C11 28.6(5), N2-N1-C10-C11 33.0(7) and RingN1-RingN2 1.42(17).

Fig (26) shows the 1-D structure of the metallopolymer 2.11; this structure is similar to Fig (18) of the metallopolymer 1.14. Again the key difference between the two structures is the denticity of the trifluoroacetate anions and also the structure of 2.11 has a head-tail type of structure while 1.14 has a head-head/tail-tail arrangment. Due to the symmetry of the complex there is only one type of square between the fused pentagons; the distance between Ag1-Ag1A is 3.674(1) Å. The distances between the squares of the metallopolymer 1.14 are 3.764(1) and 3.633(1) Å.

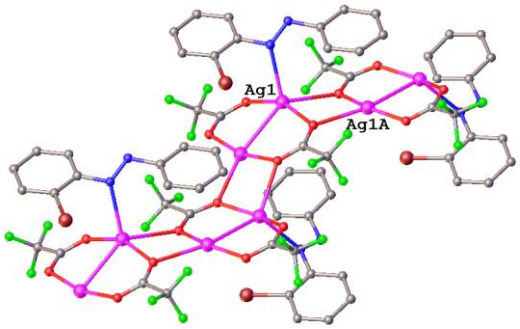

Fig (26) - View of a short strand of the polymer 2.11. The hydrogen atoms have been omitted for clarity. A relevant interatomic distance (Å) is Ag1-Ag1A 3.674(1).

The monodentate and bidentate oxygen atoms of the trifluoroacetate anions form a series of fused four and five membered rings as seen in Fig (27); this configuration resembles a hopscotch court. This is much the same as seen in Fig (19) of 1.14 except for the head-tail rather than head-head/tail-tail arrangement.

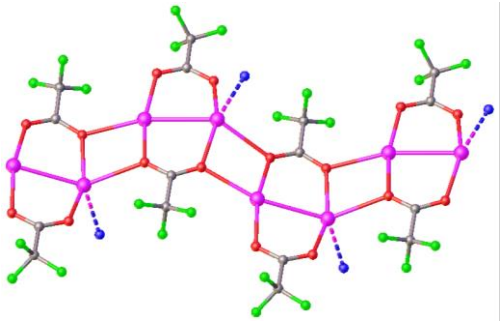

Fig (27) - View of a section of the structure showing the fused four and five membered rings in the hopscotch court configuration. The azobenzene molecules have been omitted for clarity.

Fig (28) shows how the strands of the complex are orientated relative to each other.

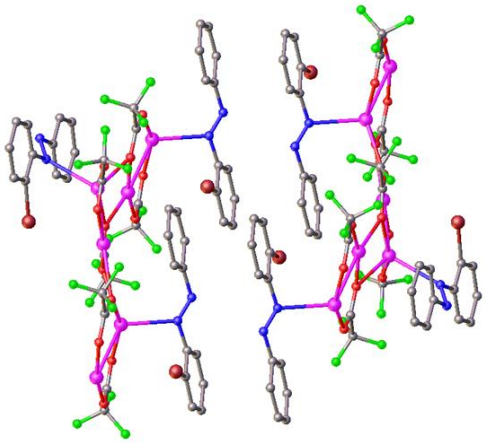

Fig (28) - View of how the strands of the polymer 2.11 are orientated relative to each other. The hydrogen atoms have been omitted for clarity.

It can be seen in Fig (29) that another weak interaction orders the strands of the structure; these weak interactions are fluorine-fluorine interactions. The distances of these interactions are 2.98(2) (F1-F4A) and 3.37(2) Å (F2-F4A); these interactions are considered to be of moderate strength.[27]

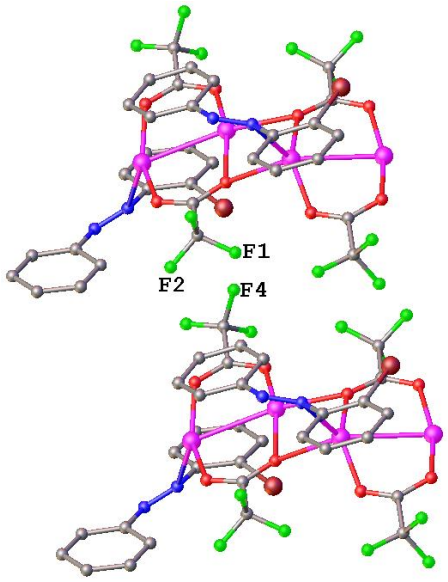

Fig (29) - View of how the strands of the polymer 2.11 are orientated relative to each other. The hydrogen atoms have been omitted for clarity. Relevant interatomic distances (Å) are F1-F4A 2.98(2) and F2-F4 3.37(2).

To summarise, the structure of this complex is a 1-D metallopolymer with two different types of silver atom one of which has a slightly distorted square planar geometry while the other has a distorted square pyramidal geometry with a τ_5 index [31] of 0.25. There are two different types of trifluoroacetate anion, one of which is bidentate while the other is tetradentate. These trifluoroacetate anions form a series of fused four and five membered rings with a head-tail type linkage. The 2-bromoazobenzene molecule is monodentate and is coordinated to the silver atom through the nitrogen atom associated with the bromine atom. The 2-bromoazobenzene molecule juts from the surface of the polymer in an alternating fashion.

The structures with 2-bromoazobenzene provide more evidence that the most important factor contributing to the differences between the structures are due to the effects of the anion. Both of the complexes made using 2-bromoazobenzene adopt a very similar structure to those made using the same anion and azobenzene. For example, the complex made with 2-bromoazobenzene and triflate forms a 2-D sheet with alternating bridging triflate molecules in a fused eight membered ring conformation and a bridging ligand, which is the same topology as the azobenzene structure. The complex prepared with 2-bromoazobenzene and trifluoroacetate forms a linear 1-D chain although with a head-tail rather than a head-head/tail-tail structure, which is seen in the azobenzene structure.

3.1 complexes of 3-bromoazobenzene

With silver(I) hexafluorophosphate (3.10)

The asymmetric unit of 3.10 contains two silver atoms, two hexafluorophosphate anions and four 3-bromoazobenzene molecules. The crystal structure solves in the space group $P2_1/n$ with an R_1= 0.0465. This complex was made by mixing one equivalent of ligand with three equivalents of silver salt; the ratio in the complex is one to two i.e. $[ML_2]$.

The silver atoms have a distorted linear geometry as seen in Fig (30); the angles between the coordinating nitrogen atoms are 164.91(18) (N1-Ag1-N3) and 177.65(17)˚ (N5-Ag2-N7). The 3-bromoazobenzene molecules are coordinated in a monodentate fashion through the nitrogen atom associated with the brominated aromatic ring. The reason the brominated aromatic rings are *trans* to each other is due to a noncrystallographic pseudocentre of inversion which minimises the dipole moment of the complex. None of the aromatic rings are coplanar with a range of angles between 31.9(2)-99.0(2)˚. The aromatic rings are also not in the plane of the azo group; the torsion angles range between 8.8(8)-61.6(7)˚. Fig (30) also shows that the hexafluorophosphate anions do not coordinate to the silver atoms and instead sit in between the layers of the complex.

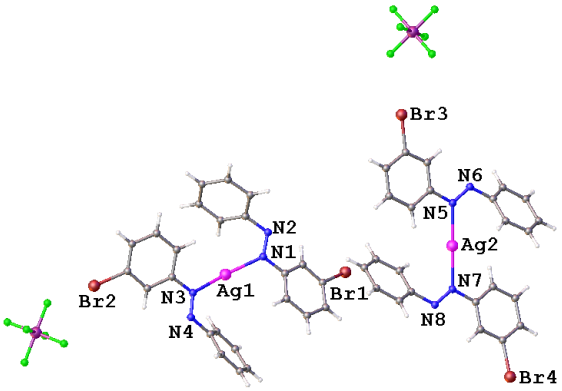

Fig (30) - The asymmetric unit of 3.10. Relevant bond lengths (Å) are Ag1-N1 2.201(5), Ag1-N3 2.206(5), Ag2-N5 2.208(4), Ag2-N7 2.210(4), N1-N2 1.253(6), N3-N4 1.251(6), N5-N6 1.259(6) and N7-N8 1.244(6). Relevant bond angles (˚) are N1-Ag1-N3 164.91(18) and N5-Ag2-N7 177.65(17). Relevant torsion angles (˚) are N1-N2-C10-C11 46.2(6), N2-N1-C1-C2 25.9(7), N3-N4-C30-C31 42.0(6), N4-N3-C20-C21 18.8(7), N5-N6-C50-C51 41.1(5), N6-N5-C40-C41 8.8(8), N7-N8-C70-C71 14.6(5), N8-N7-C60-C61 61.6(7), RingN1-RingN2 99.0(2), RingN3-RingN4 68.2(2), RingN5-RingN6 40.0(2), RingN7-RingN8 31.9(2).

It is shown in Fig (31) how the hexafluorophosphate anions occupy the space between the layers of the discrete molecules.

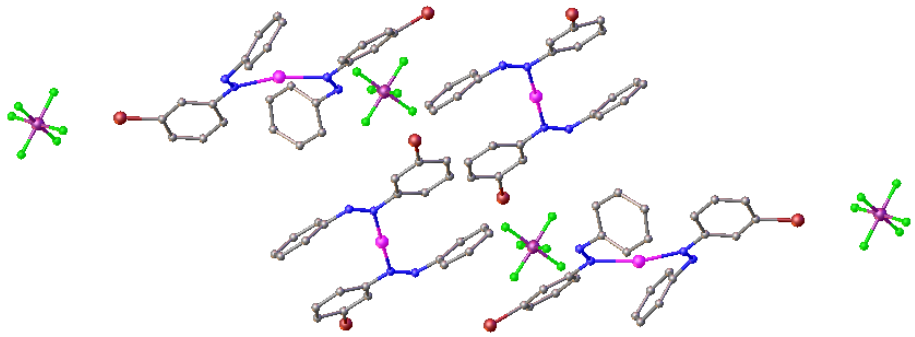

Fig (31) - View of how the discrete molecules are orientated relative to each other. The hydrogen atoms have been omitted for clarity.

To summarise, the structure of this complex is a discrete assembly with two silver atoms that have a distorted linear geometry. The hexafluorophosphate anion sits between the layers of the complex. The 3-bromoazobenzene molecule is monodentate and coordinates to the silver atom through the nitrogen atom associated with the brominated aromatic ring.

With silver(I) perchlorate (3.11)

The complex of 3-bromoazobenzene and silver perchlorate has one silver atom, one and a half 3-bromoazobenzene molecules and a perchlorate anion in the asymmetric unit. The crystal structure solves in the triclinic space group P-1 with R_1= 0.0504. This complex was made by mixing one equivalent of ligand with three equivalents of silver salt; the ratio in the complex is two to three i.e. $[M_2L_3]$.

Fig (32) shows that the silver atom has a distorted tetrahedral geometry; the angles around the silver atom are 116.19(18) (N1-Ag1-N3), 108.94(19) (N1-Ag1-O1), 121.2(2) (N1-Ag1-O2A), 104.89(19) (N3-Ag1-O1), 98.03(18) (N3-Ag1-O2A) and 105.90(18) Å (O1-Ag1-O2A). None of these angles match exactly the ideal tetrahedral angle of 109˚; however the angle between N1-Ag1-O1 comes very close (108.94(19)˚) as do two other angles which are 104.89(19) (N3-Ag1-O1) and 105.90(18)˚ (O1-Ag1-O2A). The bond length of N1-N2 is 1.274(7) while N3-N3A is 1.254(10) Å. These bond lengths are longer and shorter respectively than the bond lengths between the nitrogen atoms of the azo group in the complex 1.12. Complex 1.12 is structurally identical to this complex except that azobenzene rather than 3-bromoazobenzene is coordinated to the silver atom. The nitrogen-nitrogen bond lengths of the complex 3.11 are longer than the nitrogen-nitrogen bond lengths of the previously reported structure,[25] which are 1.253(3) and 1.257(3) Å. Fig (32) also shows the torsional angles between the aromatic rings and the azo group; these angles are 34.3(6) (N1-N2-C10-C11), 16.1(9) (N2-N1-C1-C2) and 43.3(9)˚ (N3A-N3-C20-C21). The aromatic rings of the monodentate 3-bromoazobenzene molecule are not coplanar and have an angle between them of 25.6(3)˚. Also shown in Fig (32) is the bridging bidentate perchlorate anion.

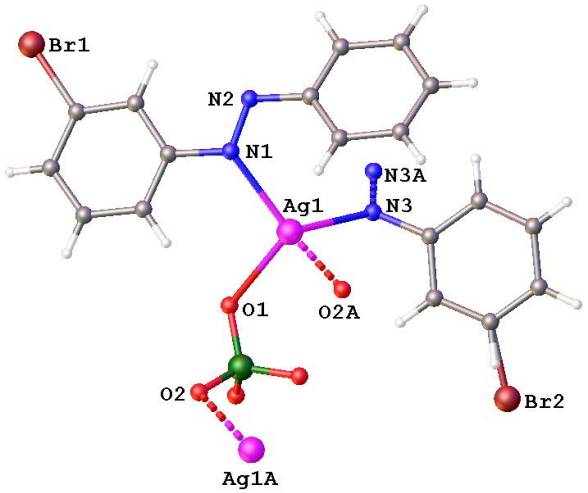

Fig (32) - The asymmetric unit of 3.11. Relevant bond lengths (Å) are Ag1-N1 2.321(5), Ag1-N3 2.376(5), Ag1-O1 2.498(6), Ag1-O2A 2.498(6), N1-N2 1.274(7) and N3-N3A 1.254(10). Relevant bond angles (˚) are N1-Ag1-N3 116.19(18), N1-Ag1-O1 108.94(19), N1-Ag1-O2A 121.2(2), N3-Ag1-O1 104.89(19), N3-Ag1-O2A 98.03(18) and O1-Ag1-O2A 105.90(18). Relevant torsion angles (˚) are N1-N2-C10-C11 34.3(6), N2-N1-C1-C2 16.1(9), N3A-N3-C20-C21 43.3(9) and RingN1-RingN2 25.6(3).

Due to the symmetry in the complex, the bidentate 3-bromoazobenzene molecule has coplanar aromatic rings as seen in Fig (33). The perchlorate bridging distance in this complex is 5.227(1) Å (Ag1-Ag1A) while the azo group bridging distance is 5.533(1) Å (Ag1-Ag1B). These distances are similar to the analogous complex 1.12, which has distances of 5.074(1) and 5.490(1) Å respectively.

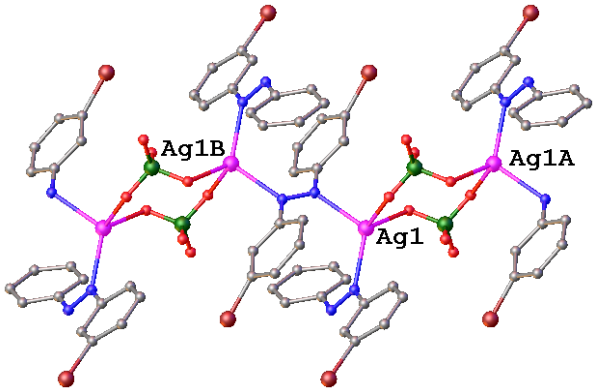

Fig (33) - View of a short strand of the polymer 3.11. The hydrogen atoms have been omitted for clarity. The bromine atoms of the bridging ligands have half occupancy. Relevant interatomic distances (Å) are Ag1-Ag1A 5.227(1) and Ag1-Ag1B 5.533(1).

The strands of the complex 3.11 are organised by hydrogen bonding interactions as shown in Fig (34). There is one inter-strand hydrogen bond (O4-H24A), which is 2.45(2) Å in length. There are four intra-strand hydrogen bonds that range from 2.49(2) to 2.64(2) Å.

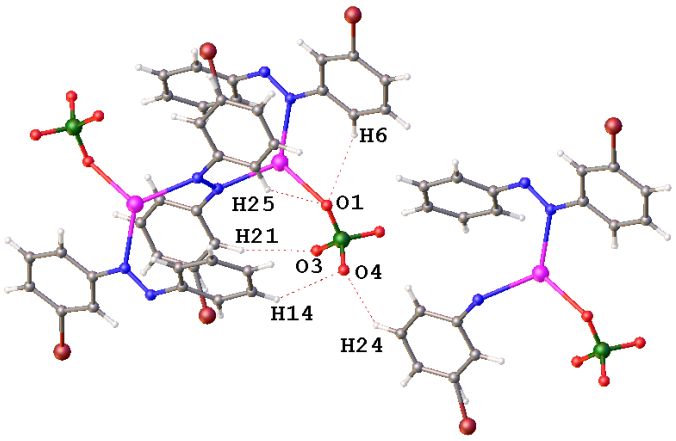

Fig (34) - View of the intra- and inter-strand hydrogen bonding in 3.11. Relevant hydrogen bond lengths (Å) are O1-H6 2.64(2), O1-H25 2.49(2), O3-H21 2.62(2), O4-H14 2.60(2) and O4-H24 2.45(2).

To summarise, the structure of this complex is a 1-D metallopolymer with the silver atom in a distorted tetrahedral geometry. There are two different types of 3-bromoazobenzene in the complex, one of which is bidentate and bridges two silver atoms, while the other is monodentate. The bidentate 3-bromoazobenzene molecule has two half-occupancy bromine atoms. Two oxygen atoms (O1 and O2) of the perchlorate anion bridge the silver atoms in the complex; this leads to an eight membered ring in a chair like conformation. This structure is analogous to the metallopolymer 1.12; this has the same tetrahedral geometry around the silver atom, the same bridging perchlorate anions/azo group and a monodentate ligand.

The structure with the hexafluorophosphate anion shows a different molecular topology to the structure with azobenzene; in this case the structure is discrete. On the other hand, the structure with perchlorate shows the same molecular topology as the structure with azobenzene; it has a 1-D linear structure with alternating bridging perchlorate and azo groups. This would suggest that the coordinating anions control the structure of the complex.

4.1 complexes of 4-bromoazobenzene

<u>With silver(I) hexafluorophosphate (4.10)</u>

The asymmetric unit of 4.10 contains two half-occupancy silver atoms, a hexafluorophosphate anion and two 4-bromoazobenzene molecules. The crystal structure solves in the space group P-1 with R_1= 0.1461. This complex was made by mixing one equivalent of ligand with three equivalents of silver salt but the ratio in the complex is one to two i.e. [ML_2].

The half-occupancy silver atoms seen in Fig (35) adopt perfect linear geometries as they lie on centres of inversion. The 4-bromoazobenzene molecules are monodentate and

coordinated to the silver atoms through the nitrogen atom associated with the brominated aromatic ring. The aromatic rings are not coplanar with angles between them of 21.5(1) (RingN1-RingN2) and 43.7(1)˚ (RingN3-RingN4). The aromatic rings are also not in the plane of the azo group; the torsion angles range between 5.6(17)-44.9(15)˚. Fig (35) also shows that the hexafluorophosphate anion is not coordinated to the silver atom and instead occupies the space between the layers of the complex. The asymmetric unit of 4.10 is very similar to the asymmetric unit of 3.10; except that 4.10 has only half the amount of atoms contained within the asymmetric unit. The geometry of the silver atoms is also different with the silver atoms of 3.10 not adopting a perfect linear angle of 180˚, due to the fact that the silver atoms do not lie on crystallographic centres of inversion.

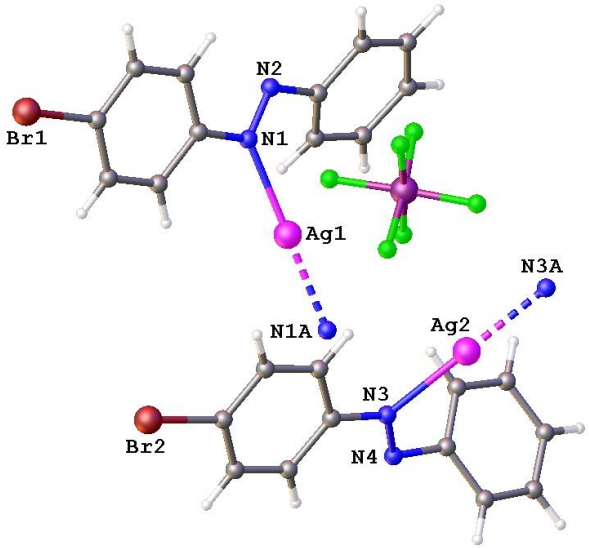

Fig (35) - The asymmetric unit of 4.10. Relevant bond lengths (Å) are Ag1-N1 2.218(10), Ag2-N3 2.206(9), N1-N2 1.267(14) and N3-N4 1.253(14). Relevant torsion angles (˚) are N1-N2-C10-C11 37.4(18), N2-N1-C1-C2 18.6(11), N3-N4-C30-C31 44.9(15), N4-N3-C20-C21 5.6(17), RingN1-RingN2 21.5(1) and RingN3-RingN4 43.7(1).

The hexafluorophosphate anions occupy the space between the layers of the discrete molecules as shown in Fig (36). The brominated aromatic rings are *trans* to each other due to the fact that there is a crystallographic centre of inversion at the silver atoms which minimises the dipole moment of the complex.

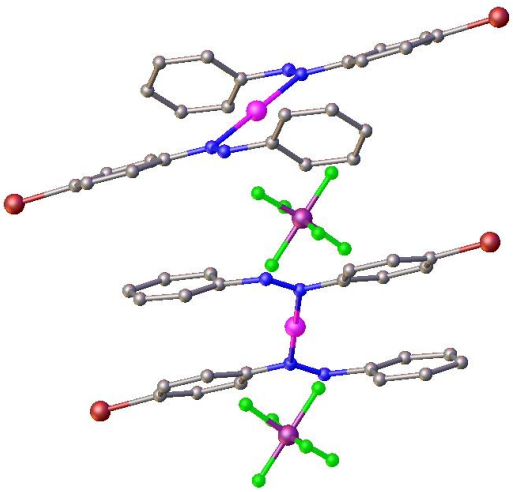

Fig (36) - View of how the discrete units of 4.10 orientate towards each other. The hydrogen atoms have been omitted for clarity.

To summarise, the structure of this complex is a discrete assembly with two half-occupancy silver atoms that have a perfect linear geometry due to the fact that they lie on centres of inversion. The hexafluorophosphate anion sits between the layers of the complex. The 4-bromoazobenzene molecule is monodentate and coordinates to the silver atom through the nitrogen atom associated with the brominated aromatic ring.

<u>With silver(I) perchlorate (4.11)</u>

The complex of 4-bromoazobenzene and silver perchlorate has one silver atom, one and a half 4-bromoazobenzene molecules and a perchlorate anion in the asymmetric unit. The crystal structure solves in the triclinic space group P-1 with R_1= 0.0344. This complex was made by mixing one equivalent of ligand with three equivalents of silver salt; the ratio in the complex is two to three i.e. $[M_2L_3]$.

The silver atom adopts a distorted tetrahedral geometry with none of the angles matching the ideal tetrahedral angle of 109˚; this is shown in Fig (37), although N3-Ag1-O2A comes close with an angle of 108.91(13)˚. The other angles around the silver atom range from 80.61(12)˚ for O1-Ag1-O2A to 131.46(12)˚ for N1-Ag1-O1. The bond length of N1-N2 is 1.260(5) while N3-N3A is 1.259(7) Å. These bond lengths are the same length as the nitrogen-nitrogen bonds in the complex 1.12, to which it is analogous. The bonds lengths in the complex are also shorter and longer respectively than the nitrogen-nitrogen bond lengths in the complex 3.11, to which it is also analogous and which has lengths of 1.274(7) and 1.254(10) Å. Fig (37) also shows the torsion angles between the aromatic rings and the azo group; these angles are 38.0(6) (N1-N2-C10-C11), 40.3(5) (N3A-N3-C20-C21) and the almost coplanar 1.9(5)˚ (N2-N1-C1-C2). The ring associated with N1 and the ring associated with N2 are not coplanar with an angle between them of 37.24(16)˚. Also shown in Fig (37) is the bridging bidentate perchlorate anion.

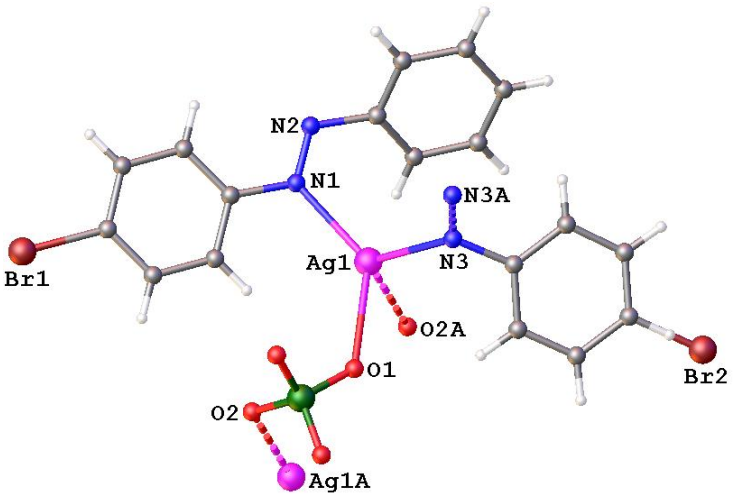

Fig (37) - The asymmetric unit of 4.11. Relevant bond lengths (Å) are Ag1-N1 2.312(4), Ag1-N3 2.342(4), Ag1-O1 2.500(3), Ag1-O2A 2.461(3), N1-N2 1.260(5) and N3-N3A 1.259(7). Relevant bond angles (˚) are N1-Ag1-N3 119.45(13), N1-Ag1-O1 131.46(12), N1-Ag1-O2A 117.08(12), N3-Ag1-O1 91.76(12), N3-Ag1-O2A 108.91(13) and O1-Ag1-O2A 80.61(12). Relevant torsion angles (˚) are N1-N2-C10-C11 38.0(6), N2-N1-C1-C2 1.9(5), N3A-N3-C20-C21 40.3(5) and RingN1-RingN2 37.24(16).

Due to the symmetry in the complex, the bidentate 4-bromoazobenzene molecule has coplanar aromatic rings as seen in Fig (38). This complex has a perchlorate bridging distance of 4.978(1) Å and an azo group bridging distance of 5.493(1) Å. The related distances in the analogous complex 1.12 are similar with distances of 5.074(1) and 5.490(1) Å, respectively. These distances are also similar to the other analogous complex 3.11, which has slightly longer distances of 5.227(1) and 5.533(1) Å, respectively. The bridging distance of 4.11 is in between the azo group bridging distances of the previously reported structure,[25] which are 5.531(1) and 5.370(1) Å.

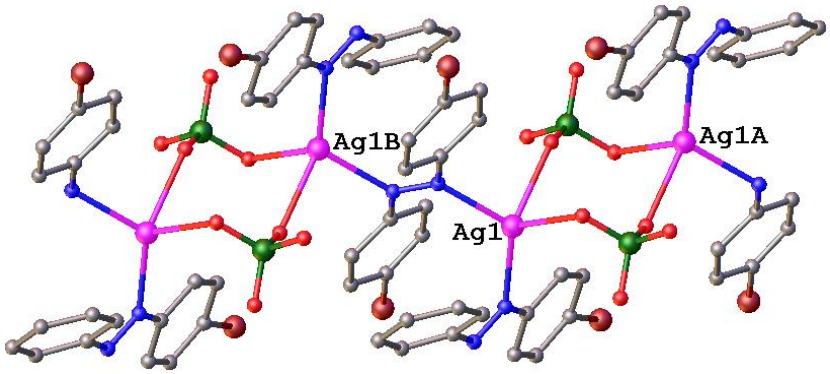

Fig (38) - View of a short strand of the polymer 4.11. The hydrogen atoms have been omitted for clarity. The bromine atoms of the bidentate ligands have half occupancy. Relevant interatomic distances (Å) are Ag1-Ag1A 4.978(1) and Ag1-Ag1B 5.493(1).

Fig (39) shows how the strands of the compex are orientated relative to each other with hydrogen bonds. There is an intra-strand hydrogen bond, which has a distance of 2.56(2) Å (O4-H21). There is also an inter-strand hydrogen bond, which has a distance of 2.45(2) Å (O3-H5A).

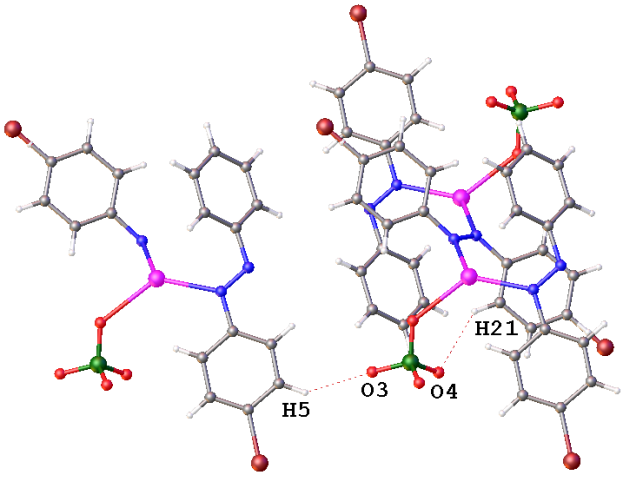

Fig (39) - View of the intra- and inter-strand hydrogen bonding in 4.11. Relevant hydrogen bond lengths (Å) are O3-H5 2.45(2) and O4-H21 2.56(2).

To summarise, the structure of this complex is a 1-D metallopolymer with the silver atom in a distorted tetrahedral geometry. There are two different types of 4-bromoazobenzene in the complex, one of which is bidentate and bridges two silver atoms, while the other is monodentate. The bidentate 4-bromoazobenzene molecule has two half-occupancy bromine atoms. Two oxygen atoms (O1 and O2) of the perchlorate anion bridge the silver atoms in the complex; this leads to an eight membered ring in a chair like conformation. This structure is analogous to the metallopolymers 1.12 and 3.11, which have the same tetrahedral geometry around the silver atom, the same bridging perchlorate anions/azo group and a monodentate ligand.

The structure with the hexafluorophosphate ion shows the same molecular topology to the structure with 3-bromoazobenzene; in this case the structure is discrete. However, the structure is different from the structure with azobenzene. On the other hand the structure with perchlorate shows the same molecular topology as the structure with azobenzene and 3-bromoazobenzene; it has a 1-D linear structure with alternating bridging perchlorate and azo groups. Both of these results show that the anion has the biggest influence on the structure of the complexes.

5.1 complexes of 3,4'-dibromoazobenzene

With silver(I) triflate (5.10)

The complex of 3,4'-dibromoazobenzene and silver triflate has one silver atom, one 3,4'-dibromoazobenzene molecule and a triflate anion in the asymmetric unit. The crystal structure solves in the monoclinic space group $P2_1/c$ with an R1= 0.0191. This complex was made by mixing one equivalent of ligand with two equivalents of silver salt; the ratio in the complex is one to one i.e. [ML].

Fig (40) shows that the silver atom has a distorted tetrahedral geometry with none of the angles matching the perfect tetrahedral angle of 109˚. The angles around the silver atom that most closely match the perfect tetrahedral angle are 104.55(5) (O1-Ag1-O3A), 117.81(6) (N1-Ag1-O1) and 119.48(6)˚ (N1-Ag1-O2A). The 3,4'-dibromoazobenzene molecule is monodentate; the complexes 1.13 and 2.10 have a similar asymmetric unit, however they only have a half molecule of their respective ligand which in turn causes the ligand to be bridging bidentate. The aromatic rings of 3,4'-dibromoazobenzene are rotated out of the plane of the azo group by 44.0(3) (N1-N2-C10-C11) and 2.5(2)˚ (N2-N1-C1-C2); the aromatic rings are also not coplanar with an angle between them of 42.69(7)˚. Also shown in Fig (40) is the triflate anion, which is tridentate with each oxygen atom coordinated to a silver atom. The CF_3 group is staggered in relation to the SO_3 group due to this conformation being the lowest in energy because the eclipsing interactions are minimised.

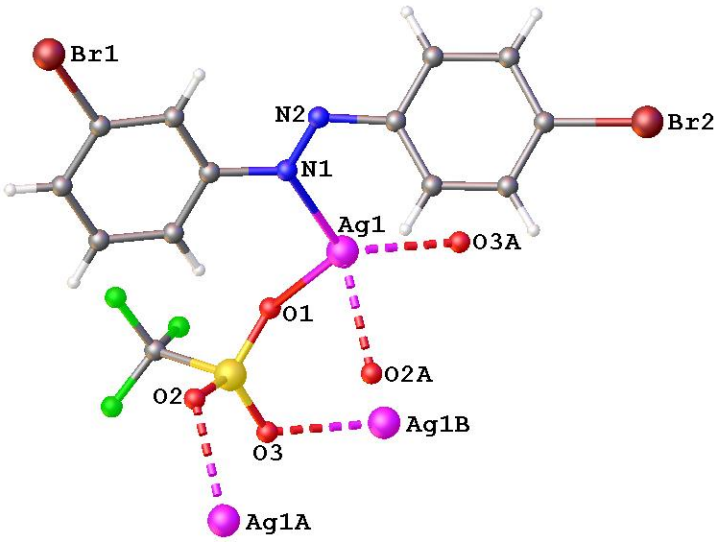

Fig (40) - The asymmetric unit of 5.10. Relevant bond lengths (Å) are Ag1-N1 2.3057(18), Ag1-O1 2.3887(16), Ag1-O2A 2.4524(17), Ag1-O3A 2.3714(15) and N1-N2 1.258(2). Relevant bond angles (˚) are N1-Ag1-O1 117.81(6), N1-Ag1-O2A 119.48(6), N1-Ag1-O3A 127.78(6), O1-Ag1-O2A 87.26(6), O1-Ag1-O3A 104.55(5) and O2A-Ag1-O3A 90.08(5). Relevant torsion angles (˚) are N1-N2-C10-C11 44.0(3), N2-N1-C1-C2 2.5(2) and RingN1-RingN2 42.69(7).

The 1-D nature of the metallopolymer 5.10 is seen in Fig (41). This is again similar to the structures 1.13 and 2.10 however due to the steric effects of the bromine atoms the polymer does not extend through the azo group. The distance between Ag1 and Ag1A is 5.069(1) Å while the distance between Ag1 and Ag1B is 4.764(1) Å.

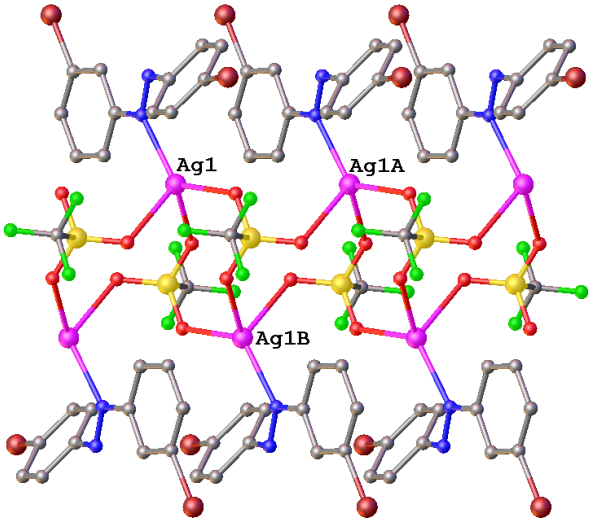

Fig (41) - View of a short strand of the polymer 5.10. The hydrogen atoms have been omitted for clarity. Relevant interatomic distances are Ag1-Ag1A 5.069(1) and Ag1-Ag1B 4.764(1) Å.

Fig (42) shows how the tridentate triflate anions form a series of fused eight membered rings in a chair like conformation. This configuration is very similar to the configuration of the triflate anions in the metallopolymers 1.13 and 2.10.

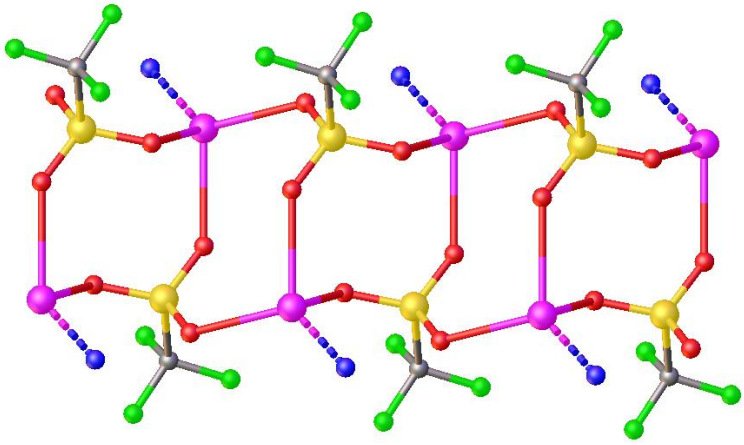

Fig (42) - View of a section of the structure showing the fused eight membered rings of complex 5.10. The azobenzene molecules have been omitted for clarity.

It can be seen in Fig (43) how the weak interactions act between the different strands. The bromine atoms of different aromatic rings interact with each other; this interaction has a length of 3.63(2) Å (Br1-Br2). This is a typical length for a bromine-bromine interaction.[30]

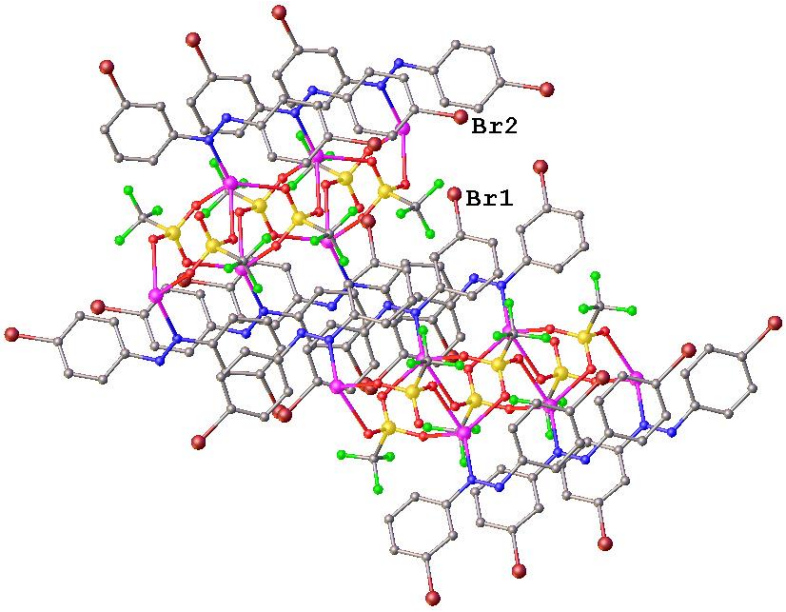

Fig (43) - View of the bromine-bromine interactions that take place within and between the strands of polymer 5.10. The hydrogen atoms have been omitted for clarity. A relevant interatomic distance (Å) is Br1-Br2 3.63(2).

To summarise, the complex is a 1-D metallopolymer in which the silver atom has a distorted tetrahedral geometry. The triflate anions are tridentate with each oxygen atom coordinated to a silver atom. The 3,4'-dibromoazobenzene molecule is monodentate and is coordinated through the nitrogen atom associated with the bromine atom in the 3-position.

The structure with 3,4'-dibromoazobenzene forms a very similar structure to the corresponding azobenzene/2-bromoazobenzene structures. Due to the fact that the ligand is unsymmetrical there can be no centre of inversion in the middle of the azo group, therefore the resulting structure forms a 1-D linear metallopolymer through the fused eight membered rings. Again, the anion seems to be the biggest contributing factor in determining the resulting structure.

6.1 complexes of 2,4'-dibromoazobenzene

<u>With silver(I) triflate (6.10)</u>

The complex of 2,4'-dibromoazobenzene and silver triflate has one silver atom, one 2,4'-dibromoazobenzene molecule and a triflate anion in the asymmetric unit. The crystal structure solves in the monoclinic space group $P2_1/c$ with an R_1= 0.0453. This complex was made by mixing one equivalent of ligand with two equivalents of silver salt; the ratio in the complex is one to one i.e. [ML].

Fig (44) shows that the silver atom has a distorted tetrahedral geometry with none of the angles matching the perfect tetrahedral angle of 109˚. The angle around the silver atom that most closely matches the perfect tetrahedral angle is 103.83(16) (O1-Ag1-O3A). The 2,4'-dibromoazobenzene molecule is monodentate; the complexes 1.13 and 2.10 have a similar asymmetric unit, however they only have a half molecule of their respective ligand which in turn causes the ligand to be bridging bidentate. The complex 5.10 is extremely similar to this complex and differs only slightly in the unit cell constants and which nitrogen atom is coordinated to the silver atom. The aromatic rings of 2,4'-dibromoazobenzene are rotated out of the plane of the azo group by 19.1(5) (N1-N2-C10-C11) and 10.2(9)˚ (N2-N1-C1-C2); the aromatic rings are also not coplanar with an angle between them of 32.5(2)˚. Also shown in Fig (44) is the triflate anion, which is tridentate with each oxygen atom coordinated to a silver atom. The CF_3 group is again staggered in relation to the SO_3 group.

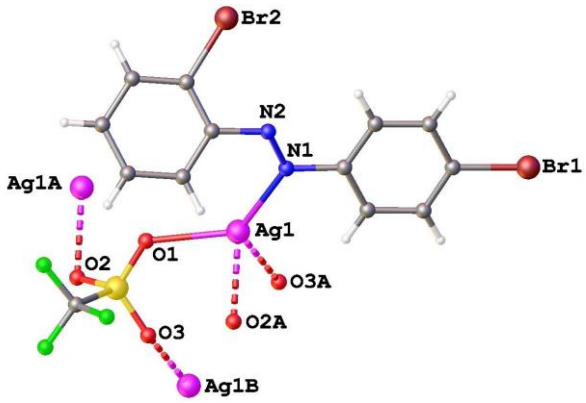

Fig (44) - The asymmetric unit of 6.10. Relevant bond lengths (Å) are Ag1-N1 2.294(5), Ag1-O1 2.346(4), Ag1-O2A 2.494(5), Ag1-O3A 2.387(5) and N1-N2 1.253(7). Relevant bond angles (˚) are N1-Ag1-O1 131.95(18), N1-Ag1-O2A 115.60(17), N1-Ag1-O3A 120.55(18), O1-Ag1-O2A 86.44(15), O1-Ag1-O3A 103.83(16) and O2A-Ag1-O3A 81.11(17). Relevant torsion angles (˚) are N1-N2-C10-C11 19.1(5), N2-N1-C1-C2 10.2(9) and RingN1-RingN2 32.5(2).

The 1-D nature of the metallopolymer 6.10 is seen in Fig (45). This is again similar to the structures 1.13 and 2.10 however due to the steric effects of the bromine atoms the polymer cannot extend through the azo group. It is also almost identical to 5.10 except that the silver atom is coordinated to a nitrogen atom attached to an aromatic ring with the bromine atom in the 4-position rather than the 3-position. The distance between Ag1 and Ag1A is 4.999(1) Å while the distance between Ag1 and Ag1B is 4.911(1) Å.

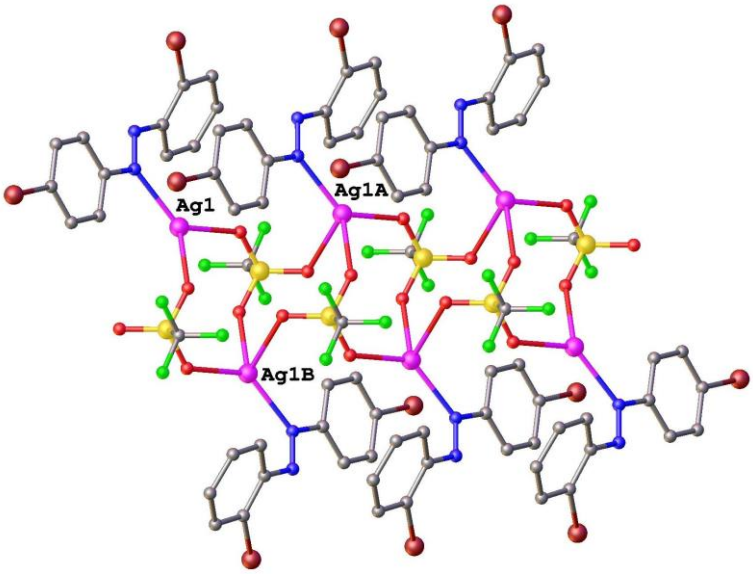

Fig (45) - View of a short strand of the polymer 6.10. The hydrogen atoms have been omitted for clarity. Relevant interatomic distances (Å) are Ag1-Ag1A 4.999(1) and Ag1-Ag1B 4.911(1).

Fig (46) shows how the tridentate triflate anions form a series of fused eight membered rings in a chair like conformation. This configuration is very similar to the configuration of the triflate anions in the metallopolymers 1.13 and 2.10. Again it is essentially identical to the complex in 5.10.

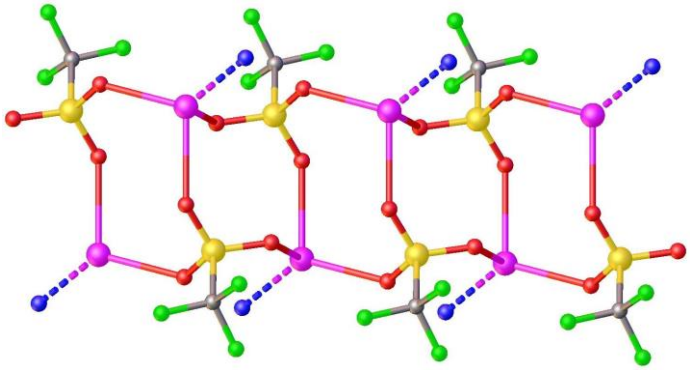

Fig (46) - View of a section of the structure showing the fused eight membered rings of complex 6.10. The azobenzene molecules have been omitted for clarity.

It can be seen in Fig (47) how the weak interactions act between the different strands. The bromine atoms of different aromatic rings interact with each other; this interaction has a length of 3.69(2) Å (Br1-Br2). This is a typical length for a bromine-bromine interaction.[30]

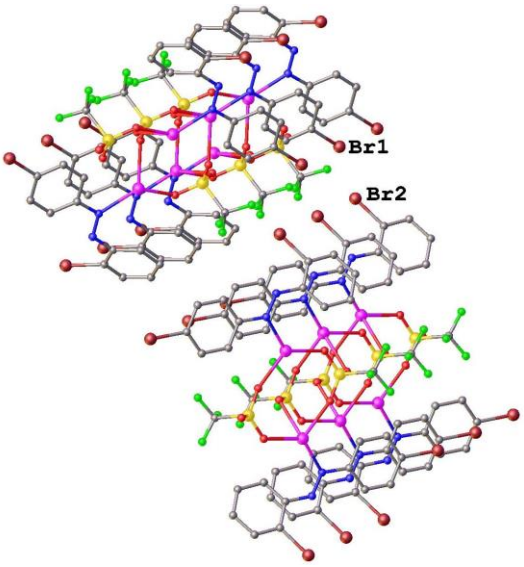

Fig (47) - View of the bromine-bromine interactions that take place within and between the strands of polymer 6.10. The hydrogen atoms have been omitted for clarity. A relevant interatomic distance (Å) is Br1-Br2 3.69(2).

To summarise, the complex is a 1-D metallopolymer in which the silver atom has a distorted tetrahedral geometry. The triflate anions are tridentate with each oxygen atom coordinated to a silver atom. The 2,4'-dibromoazobenzene molecule is monodentate and is coordinated through the nitrogen atom associated with the bromine atom in the 4-position.

The structure with 2,4'-dibromoazobenzene forms a very similar structure to the corresponding azobenzene/2-bromoazobenzene structures. Due to the fact that the ligand is unsymmetrical there can be no centre of inversion in the middle of the azo group; therefore the resulting structure forms a 1-D linear structure through the fused eight membered rings. The complex is very similar to complex 5.10 and only differs in the distances, angles and unit cell constants. Another difference is that the silver atom is coordinated to a nitrogen atom bound to an aromatic ring with a different substitution pattern; in this case it is the 4-position rather than the 3-position. Again, the anion seems to be the biggest contributing factor in determining the resulting structure.

7.1 complexes of 3-nitroazobenzene

<u>With silver(I) triflate (7.10)</u>

The complex of 3-nitroazobenzene and silver triflate has one silver atom, one 3-nitroazobenzene molecule and a triflate anion in the asymmetric unit. The crystal structure solves in the monoclinic space group $P2_1/n$ with R_1= 0.0270. This complex was made by mixing one equivalent of ligand with three equivalents of silver salt but the ratio in the complex is one to one i.e. [ML].

The geometry of the silver atom is tetrahedral in nature; this is shown in Fig (48); three of the angles are similar to the ideal tetrahedral angle of 109˚. The other three angles are much more acute with the lowest angle being 85.80(5)˚. The 3-nitroazobenzene molecule is monodentate with the nitrogen atom associated with the substituted aromatic ring coordinated to the silver atom. The aromatic rings of the ligand are rotated out of the plane of the azo group by 36.6(2) and 0.4(2)˚ for the unsubstituted and the substituted aromatic rings respectively. The aromatic rings are not coplanar and have a torsion angle between them of 42.42(8)˚. Fig (48) also shows that the triflate anion is tridentate with each oxygen atom coordinated to a silver atom. Again, there are no eclipsing interactions between the oxygen atoms of the SO_3 group and the fluorine atoms of the CF_3 group. This asymmetric unit is very similar to the asymmetric unit of complexes 1.13, 2.10, 5.10 and 6.10, which are shown in figures 13, 21, 40 and 44 respectively.

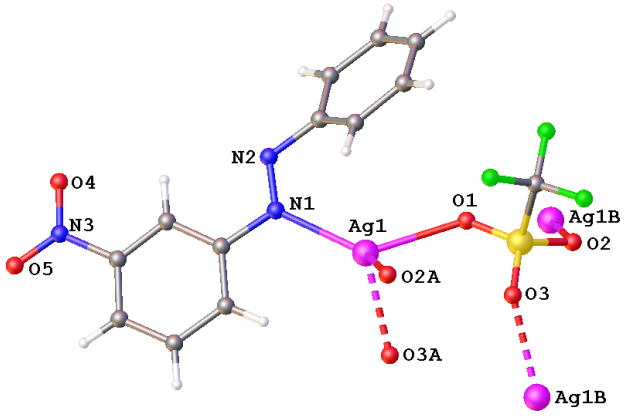

Fig (48) - The asymmetric unit of 7.10. Relevant bond lengths (Å) are Ag1-N1 2.2906(19), Ag1-O1 2.3706(16), Ag1-O2A 2.4618(17), Ag1-O3A 2.3795(16) and N1-N2 1.259(3). Relevant bond angles (˚) are N1-Ag1-O1 132.14(6), N1-Ag1-O2A 120.37(6), N1-Ag1-O3A 123.52(6), O1-Ag1-O2A 88.80(5), O1-Ag1-O3A 93.16(5) and O2A-Ag1-O3A 85.80(5). Relevant torsion angles (˚) are N1-N2-C10-C11 36.6(2), N2-N1-C1-C2 0.4(2) and RingN1-RingN2 42.42(8).

Fig (49) shows how the polymer is 1-D in nature. This structure is most similar to the complexes 5.10 and 6.10 which are also 1-D linear metallopolymers; however this structure also shows some similarities to the polymeric phases of the complexes 1.13 and 2.10. Complexes 1.13 and 2.10 are 2-D metallopolymers with half-occupancy substitutents. The distances between Ag1 and Ag1A is 5.044(1) Å, while the distance between Ag1 and Ag1B is 5.058(1) Å. These distances are shorter and longer respectively than the same distances in 5.10. The corresponding distances are both shorter in 6.10. The distances in 5.10 are 5.069(1) and 4.764(1) Å while in 6.10 they are 4.999(1) and 4.911(1) Å.

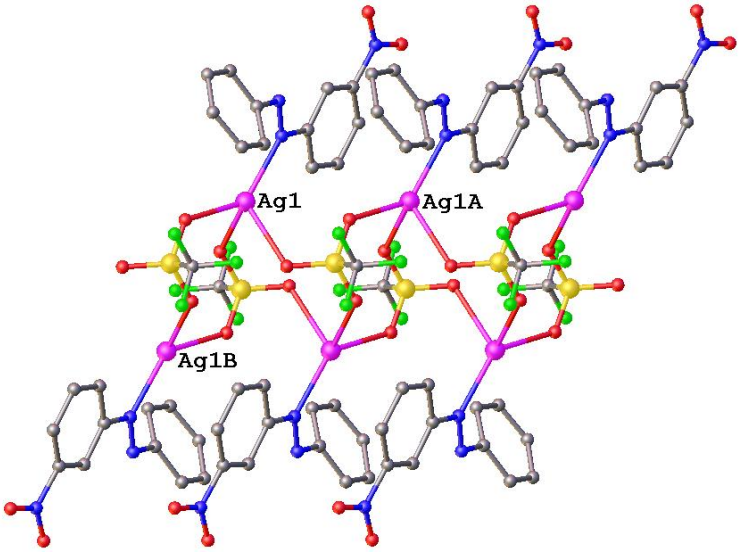

Fig (49) - View of a short strand of the polymer 7.10. The hydrogen atoms have been omitted for clarity. Relevant interatomic distances (Å) are Ag1-Ag1A 5.044(1) and Ag1-Ag1B 5.058(1).

Fig (50) shows how the tridentate triflate anions form a series of fused eight membered rings in a chair like conformation. This configuration is very similar to the configuration of the triflate anions in the metallopolymers 1.13, 2.10, 5.10 and 6.10.

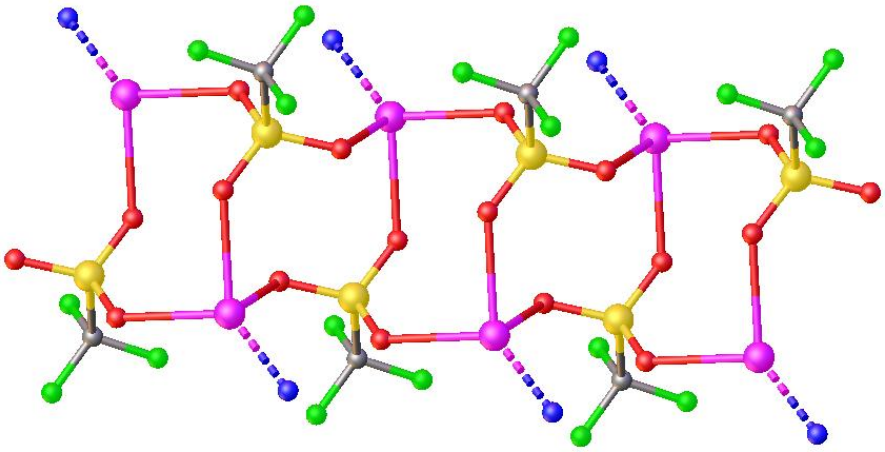

Fig (50) - View of a section of the structure showing the fused eight membered rings of complex 7.10. The 3-nitroazobenzene molecules have been omitted for clarity.

There is a hydrogen bond between O4 and H2; this weak interaction helps to organise the strands of the structure as seen in Fig (51).

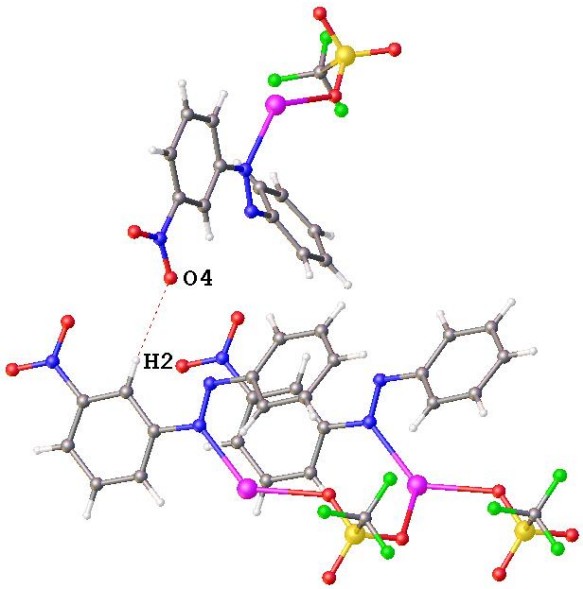

Fig (51) - View of the inter-strand hydrogen bonding in 7.10. A relevant hydrogen bond length (Å) is O4-H2 2.58(2).

Fig (52) shows the fluorine-fluorine interaction between F1 and F1A; fluorine-fluorine interactions are very weak interactions. However, the interaction between F1 and F1A can be considered very strong for this type of interaction.[27]

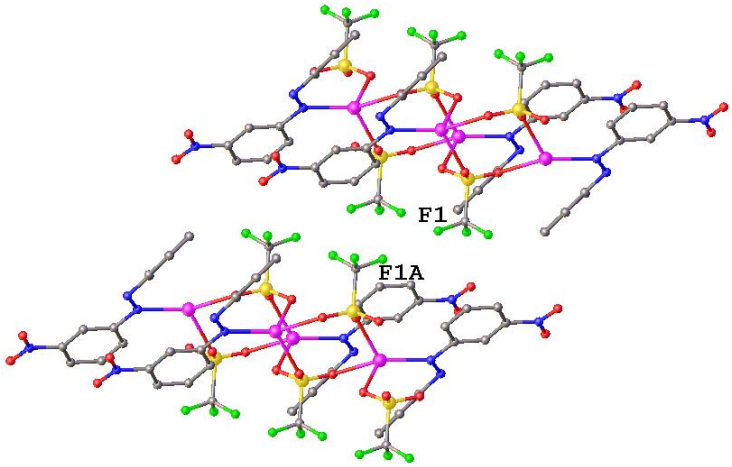

Fig (52) - View of how the strands of the polymer 7.10 are orientated relative to each other. The hydrogen atoms have been omitted for clarity. A relevant interatomic distance (Å) is F1-F1A 2.67(2).

To summarise, the complex is a 1-D metallopolymer in which the silver atom has a distorted tetrahedral geometry. The triflate anions are tridentate with each oxygen atom coordinated to a silver atom. The 3-nitroazobenzene molecule is monodentate and is coordinated through the nitrogen atom associated with the nitro group in the 3-position. The 3-nitroazobenzene molecule does not act in a bridging bidentate mode like complexes 1.13 and 2.10. It does however resemble 5.10 and 6.10 closely.

The structure with 3-nitroazobenzene forms an analogous structure to complexes 5.10 and 6.10 which contain 3,4'-dibromoazobenzene and 2,4'-dibromoazobenzene, respectively. The bromine atoms increase the steric bulk and make it impossible for the second nitrogen atom of the azo groups to coordinate to the silver atom; a similar effect is seen in the complex 7.10. The anion appears to have the largest effect on the resulting structure as an almost identical molecular topology has been seen to occur when silver triflate has been used.

8.1 complexes of 4-dimethylaminoazobenzene

With silver(I) triflate (8.10)

The complex of 4-dimethylaminoazobenzene and silver triflate has one silver atom, one protonated 4-dimethylaminoazobenzene molecule and two triflate anions in the asymmetric unit. The crystal structure solves in the orthorhombic space group Pbca with R_1= 0.0862. This complex was made by mixing one equivalent of ligand with three equivalents of silver salt.

Fig (53) shows how the silver atom adopts a tetrahedral geometry; the ideal angle of a tetrahedron is 109˚. Four of the angles around the silver atom are similar to 109˚; the two angles which are dissimilar are 95.71(18) (O4-Ag1-O3A) and 119.27(19)˚ (O1-Ag1-O4). The 4-dimethylaminoazobenzene molecule does not coordinate to the silver atom; however, there is a hydrogen bond that binds the ligand to the chain of anions, which will be shown in a later figure. The aromatic rings are almost in the same plane as the azo group with angles of only 6.8(6) (N1-N2-C10-C11) and 2.3(11)˚ (N2-N1-C1-C2). The aromatic rings are almost coplanar to each other with a small angle of only 2.9(2)˚ between them. It is also shown in Fig (53) that the triflate anions form a chain in which the anions are bidentate. The CF_3 group is again in the anti conformation in relation to the SO_3 group. This molecular topology has not been observed in any of the previous complexes, as none of the other ligands have been protonated. The fact that this ligand has become protonated is not surprising however, as it is a very common indicator for acid-base reactions.

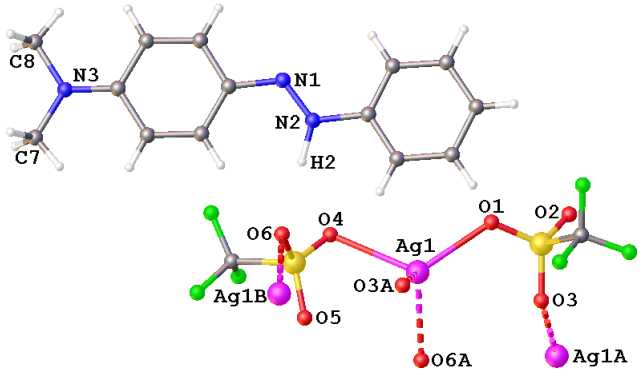

Fig (53) - The asymmetric unit of 8.10. Relevant bond lengths (Å) are N1-N2 1.279(8), N2-H2 0.88(7), Ag1-O1 2.286(5), Ag1-O4 2.454(5), Ag1-O3A 2.369(5) and Ag1-O6A 2.430(5). Relevant bond angles (˚) are O1-Ag1-O4 119.27(19), O1-Ag1-O3A 112.6(2), O1-Ag1-O6A

113.99(18), O4-Ag1-O3A 95.71(18), O4-Ag1-O6A 108.40(18) and O3A-Ag1-O6A 104.53(18). Relevant torsion angles (˚) are N1-N2-C10-C11 6.8(6), N2-N1-C1-C2 2.3(11) and RingN1-RingN2 2.9(2).

The 1-D nature of the salt 8.10 in shown in Fig (54). The chain of triflate anions forms a series of linked eight membered rings; there is a silver-silver interatomic distance of 4.988(1) Å.

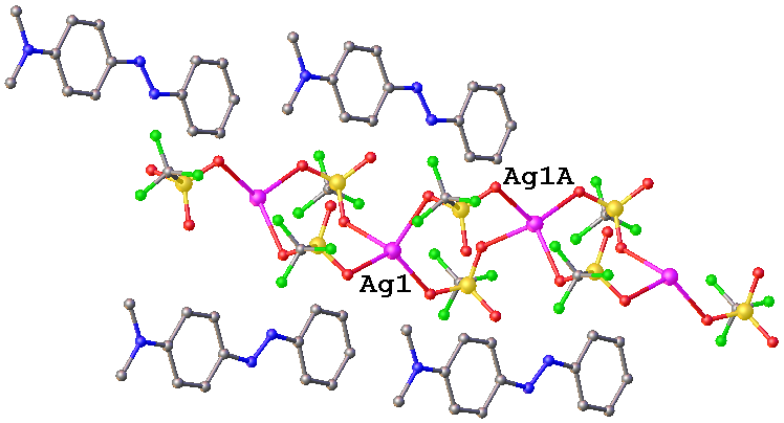

Fig (54) - View of a short strand of the polymer 8.10. The hydrogen atoms have been omitted for clarity. A relevant interatomic distance (Å) is 4.988(1).

The weak interactions that hold the 4-dimethylaminoazobenzene molecule in place are shown in Fig (55). There is the hydrogen bond that was alluded to in the discussion of Fig (53); this hydrogen bond has a length of 2.15(2) Å.

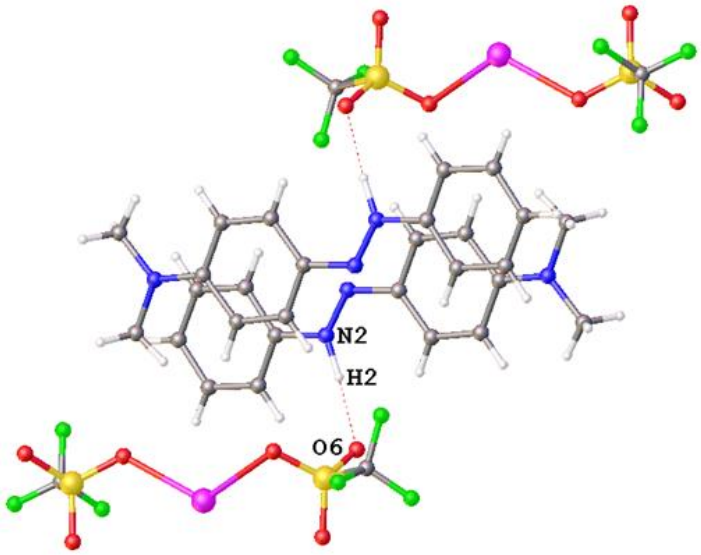

Fig (55) - View of one of the hydrogen bond in 8.10. A relevant interatomic distance (Å) is H2-O6 2.15(2).

It can be seen in Fig (56) how other weak interactions help to order the packing. There are two types of interaction shown; hydrogen bonds between the fluorine atoms and hydrogen

atoms and also fluorine-fluorine interactions. The fluorine-fluorine interactions have a distance of 2.78(2) (F2-F5) and 2.87(2) (F3-F6) Å. These fluorine-fluorine interactions are considered to be of moderate strength. [27]

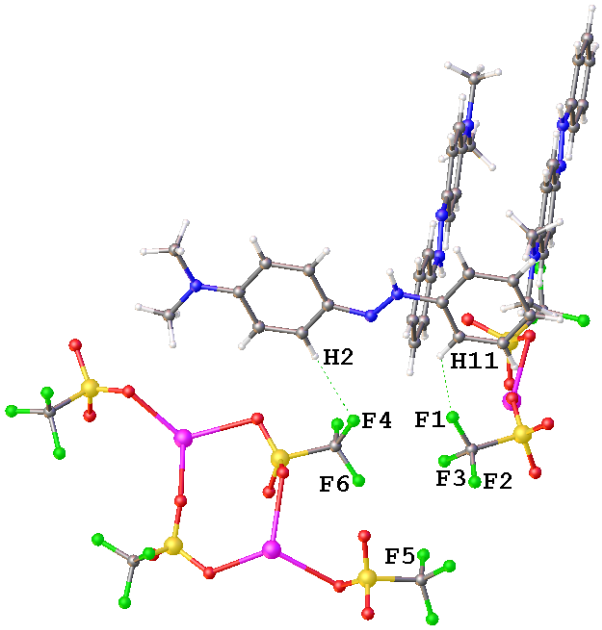

Fig (56) - View of the other hydrogen bonds and fluorine-fluorine interactions in 8.10. Relevant interatomic distances (Å) are F1-H11 2.54(2), F4-H2 2.41(2), F2-F5 2.78(2) and F3-F6 2.87(2).

To summarise, this complex is a 1-D metallopolymer with the silver atom adopting a tetrahedral geometry. The triflate anions are bidentate and form a chain of linked eight membered rings. The 4-dimethylaminoazobenzene molecule has become protonated and it is this proton which hydrogen bonds to an oxygen atom of the triflate anion.

This structure has a molecular topology not seen in any of the previous complexes due to the protonation of the ligand. This hydrogen atom changes the electronic and steric environment around the nitrogen atoms; this makes it impossible for either of the nitrogen atoms to coordinate to the silver atom.

9.1 complexes of 4-methoxyazobenzene

<u>With silver(I) tetrafluoroborate (9.10)</u>

The complex of 4-methoxyazobenzene and silver tetrafluoroborate has one silver atom, two 4-methoxyazobenzene molecules and a tetrafluoroborate anion in the asymmetric unit. The crystal structure solves in the triclinic space group P-1 with R_1= 0.0344. This complex was made by mixing one equivalent of ligand with three equivalents of silver salt but the ratio in the complex is one to two i.e. [ML_2].

It is shown in Fig (57) that the silver atom adopts a slightly bent geometry; this slight deviation from a perfect linear geometry, 161.96(7)˚ rather than 180˚, is due to a very weak interaction between the silver atom and the tetrafluoroborate anion. The 4-methoxyazobenzene molecules are monodentate with the nitrogen atom associated with the substituted aromatic ring coordinated to the silver atom. The 4-methoxyazobenzene molecules are coordinated to the silver in a *trans* manner, due to a noncrystallographic pseudocentre of inversion which minimises the dipole moment of the complex. The aromatic rings are not coplanar with the azo group with the highest angle of 63.8(3)˚ (N1-N2-C10-C11) and the lowest angle of 4.1(2)˚ (N4-N3-C20-C21); the aromatic rings are also not coplanar with each other. Fig (57) also shows that the tetrafluoroborate anion is not coordinating to the silver atom. A very weak interaction perturbs the ideal linear geometry between the silver atoms and the coordinating ligands. There is some disorder in the tetrafluoroborate anion, the boron atom spins around with one of the fluorine atoms acting as an axle. This asymmetric unit is quite similar to the asymmetric unit of complexes 3.10 and 4.10. Both of these structures have a similar geometry of the silver atom, a similar coordination of the ligands and a non-coordinating anion; the anion in these cases is hexafluorophosphate.

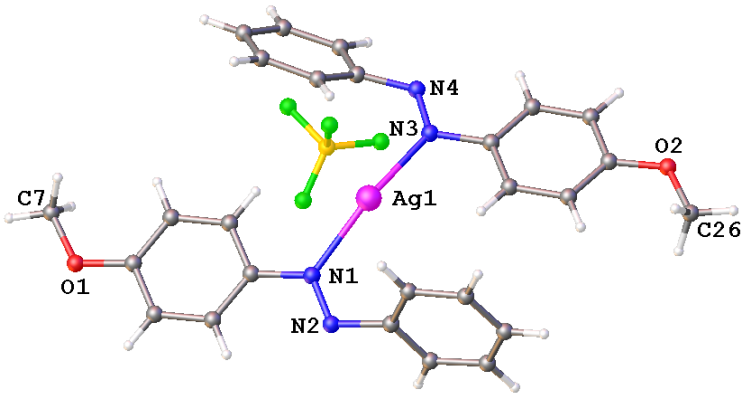

Fig (57) - The asymmetric unit of 9.10. Relevant bond lengths (Å) are Ag1-N1 2.2018(19), Ag1-N3 2.2016(18), N1-N2 1.256(3), N3-N4 1.265(2) and N1-N3 4.349(3). A relevant bond angle (˚) is N1-Ag1-N3 161.96(7). Relevant torsion angles (˚) are N1-N2-C10-C11 63.8(3), N2-N1-C1-C2 9.6(4), N3-N4-C30-C31 36.7(3), N4-N3-C20-C21 4.1(2), RingN1-RingN2 72.68(8) and RingN3-RingN4 33.80(8).

The tetrafluoroborate anion sits above the silver atom weakly interacting with it as seen in Fig (58).

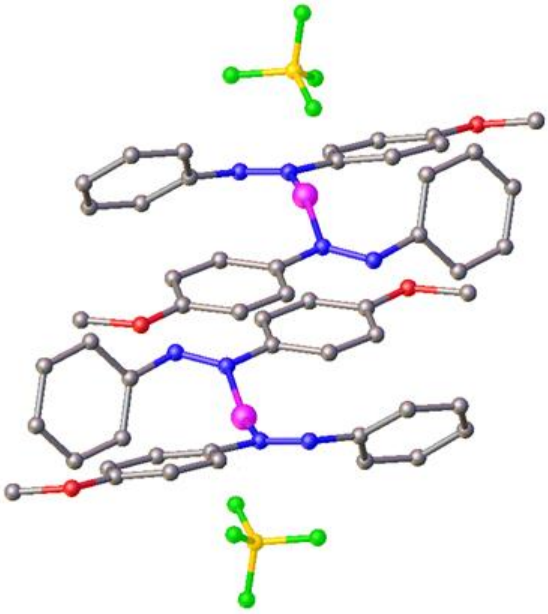

Fig (58) - View of how the discrete units of 9.10 are orientated to each other. The hydrogen atoms have been omitted for clarity.

To summarise, the structure of this complex is a discrete assembly with the silver atom adopting a slightly bent geometry; this is due to a weak interaction with the non-coordinating tetrafluoroborate anion. The 4-methoxyazobenzene molecules are coordinated to the silver atom in a monodentate fashion and coordinate to the silver atom via the nitrogen atom associated with the substituted aromatic ring. This structure bears similarities to the complexes 3.10 and 4.10, albeit with a different anion.

With silver(I) perchlorate (9.11)

The complex of 4-methoxyazobenzene and silver perchlorate has one silver atom, one and a half 4-methoxyazobenzene molecules and a perchlorate anion in the asymmetric unit. The crystal structure solves in the triclinic space group P-1 with R_1= 0.0559. This complex was made by mixing one equivalent of ligand with three equivalents of silver salt; the ratio in the complex is two to three i.e. $[M_2L_3]$.

It is shown in Fig (59) how the silver atom of 8.11 adopts a tetrahedral geometry with three of the bond angles above and three below the ideal tetrahedral angle of 109˚. The higher angles are N1-Ag1-N3 (121.88(14)), N1-Ag1-O3 (127.67(13)) and N1-Ag1-O4A (115.40(14)); the three lower angles are N3-Ag1-O3 (98.03(13)), N3-Ag1-O4A (93.03(13)) and O3-Ag1-O4A (92.41(13)). Fig (59) also shows that one of the 4-methoxyazobenzene molecules binds to the silver atom in a monodentate fashion while the half-occupancy molecule is bridging bidentate. The aromatic rings of the 4-methoxyazobenzene molecule are all out of the plane of the azo group; the full-occupancy substituted ring has a torsion angle of 3.8(7)˚, the half-

occupancy ring has a torsion angle of 41.6(7)˚ and the unsubstituted ring has a torsion angle of 37.0(5)˚. The aromatic rings of the full ligand are not coplanar and have a torsion angle of 35.16(18)˚. Due to the centre of inversion half way between the azo group of the half molecule of ligand the aromatic rings are coplanar. Also shown in Fig (59) is the bridging bidentate perchlorate anion. This asymmetric unit is essentially the same as in complexes 1.12, 3.11 and 4.11; it has a similar geometry of the silver atom and the same coordination mode in the ligands. The nitrogen-nitrogen bond lengths in this complex are 1.264(5) and 1.257(7) Å for N1-N2 and N3-N3A respectively; these bond lengths are in the same range as the nitrogen-nitrogen bond lengths found in the analogous structures.

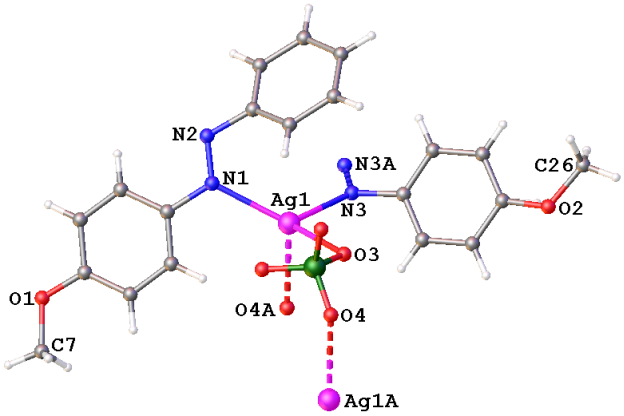

Fig (59) - The asymmetric unit of 9.11. Relevant bond lengths (Å) are N1-Ag1 2.302(4), N3-Ag1 2.335(4), O3-Ag1 2.479(4), O4A-Ag1 2.505(4), N1-N2 1.264(5) and N3-N3A 1.257(7). Relevant bond angles (˚) are N1-Ag1-N3 121.88(14), N1-Ag1-O3 127.67(13), N1-Ag1-O4A 115.40(14), N3-Ag1-O3 98.03(13), N3-Ag1-O4A 93.03(13) and O3-Ag1-O4A 92.41(13). Relevant torsion angles (˚) are N1-N2-C10-C11 37.0(5), N2-N1-C1-C2 3.8(7), N3A-N3-C20-C21 41.6(7) and RingN1-RingN2 35.16(18).

Fig (60) shows a short strand of the polymer, it is a 1-D metallopolymer with the same molecular topology as 1.12, 3.11 and 4.11. The perchlorate bridging distance in 9.11 is 5.339(1) Å while the azo group bridging distance is 5.483(1). These distances are all in the same range as 1.12, 3.11 and 4.11; the distances are in these complexes are 5.074(1) and 5.490(1), 5.227(1) and 5.533(1), 4.978(1) and 5.493(1) Å. The azo group bridging distance in the previously reported structure [25] are 5.531(1) and 5.370(1) Å; the azo group bridging distance of 9.11 is in between these two distances.

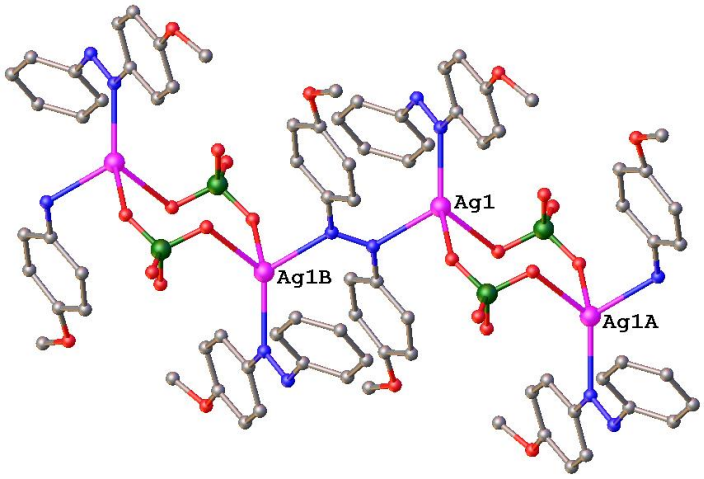

Fig (60) - View of a short strand of the polymer 9.11. The methoxy group of the bridging ligands have half occupancy. The hydrogen atoms have been omitted for clarity. Relevant interatomic distances (Å) are Ag1-Ag1A 5.337(1) and Ag1-Ag1B 5.483(1).

There is an intra-strand hydrogen bond in the complex, which can be seen in Fig (61); the hydrogen bond between O4 and H25 is the reason for the torsion angle between the half-occupancy substituted ring and the azo group.

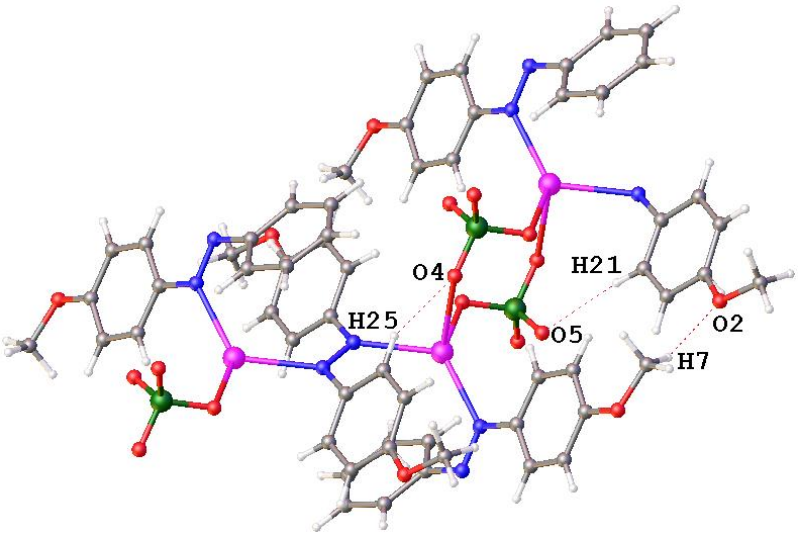

Fig (61) - View of the intra-strand hydrogen bonding in 8.11. Relevant hydrogen bond lengths (Å) are O2- H7 2.38(2), O4-H25 2.41(2) and O5-H21 2.57(2).

There is also an inter-strand hydrogen bond in the complex as seen in Fig (62); these hydrogen bonds order the strands of the complex.

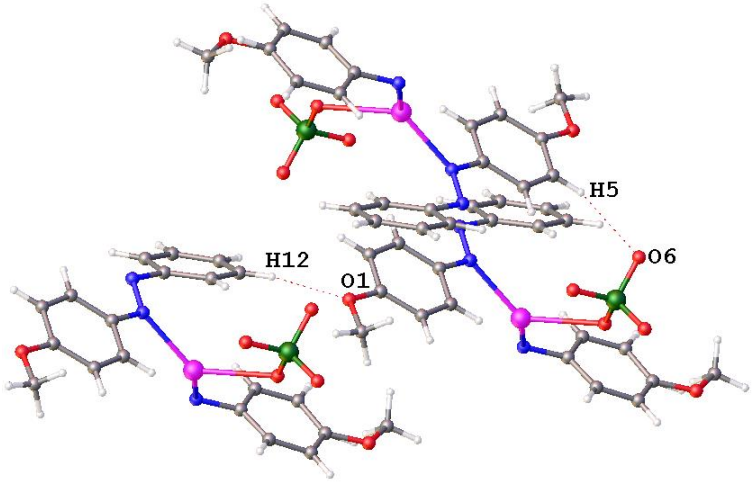

Fig (62) - View of the inter-strand hydrogen bonding in 9.11. Relevant hydrogen bond lengths (Å) are O6-H5 2.58(2) and O1-H12 2.42(2).

To summarise, the structure of this complex is a 1-D metallopolymer with the silver atom adopting a slightly disordered tetrahedral geometry. In the complex there is a full molecule of 4-methoxyazobenzene that is monodentate and a 4-methoxyazobenzene molecule consisting of two halves which have half-occupancy methoxy groups and is bridging bidentate. The perchlorate anion bridges the silver atoms of the complex, which leads to a chain of fused eight membered rings in a chair like conformation. This structure is analogous to the metallopolymers 1.12, 3.11 and 4.11; metallopolymer 9.11 has a similar tetrahedral geometry around the silver atom, the same bridging perchlorate anions/azo group and a monodentate ligand.

<u>With silver(I) triflate (9.12)</u>

The complex of 4-methoxyazobenzene and silver triflate has one silver atom, one 4-methoxyazobenzene molecule and a triflate anion in the asymmetric unit. The crystal structure solves in the monoclinic space group $P2_1/n$ with R_1= 0.0691. This complex was made by mixing one equivalent of ligand with three equivalents of silver salt; the ratio in the complex is one to one i.e. [ML].

Fig (63) shows the distorted tetrahedral nature of the silver atom in which two of the bond lengths are similar to the ideal tetrahedral angle of 109˚. These angles are 107.30(18) (N1-Ag1-O2) and 109.92(15)˚ (O2-Ag1-O4A); two of the other four angles are higher than the ideal and two are lower. The 4-methoxyazobenzene molecule is monodentate with the nitrogen atom associated with the substituted aromatic ring coordinated to the silver atom. The aromatic rings rotate out of the plane of the azo group slightly in one instance, which is 9.0(6) for N2-N1-C1-C2, and much more for the unsubstituted aromatic ring, which is 34.6(9) N1-N2-C10-C11. The aromatic rings are not coplanar; they have a torsion angle between them of 24.4(2)˚. Fig (63) also shows the manner in which the triflate anions coordinate to the silver atom; the triflate anions are tridentate with each oxygen atom binding to a silver

atom. The CF_3 group of the triflate anion is in an anti conformation relative to the SO_3 group. This asymmetric unit is most similar to the asymmetric unit of complexes 5.10, 6.10 and 7.10 as seen in figures 40, 44 and 48, respectively; it also has similarities to complexes 1.13 and 2.10 as seen in figures 13 and 21, respectively. The latter two complexes are 2-D metallopolymers with only half a ligand in the asymmetric unit.

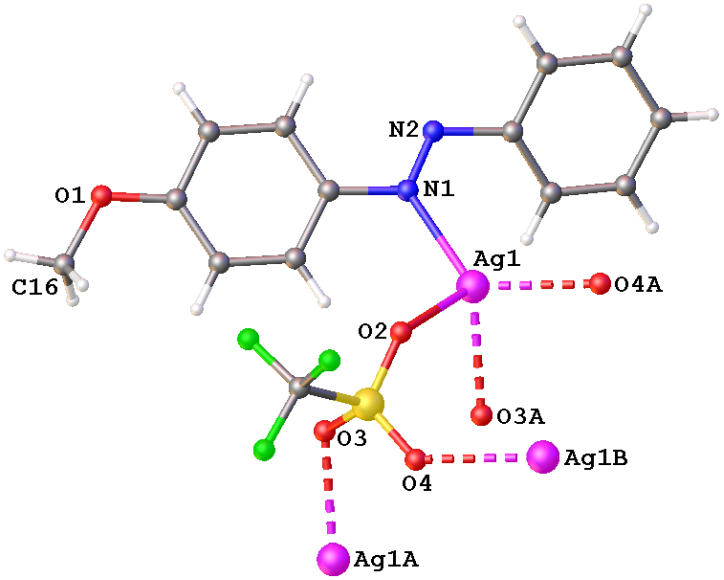

Fig (63) - The asymmetric unit of 9.12. Relevant bond lengths (Å) are N1-Ag1 2.296(5), O2-Ag1 2.451(4), O3A-Ag1 2.404(4), O4A-Ag1 2.366(4) and N1-N2 1.247(7). Relevant bond angles (˚) are N1-Ag1-O2 107.30(18), N1-Ag1-O3A 131.47(17), N1-Ag1-O4A 125.50(18), O2-Ag1-O3A 84.18(15), O2-Ag1-O4A 109.92(15) and O3A-Ag1-O4A 90.80(16). Relevant torsion angles (˚) are N1-N2-C10-C11 34.6(9), N2-N1-C1-C2 9.0(6) and RingN1-RingN2 24.4(2).

It can be seen in Fig (64) that the complex is a 1-D metallopolymer. The complexes 5.10, 6.10 and 7.10 are also 1-D metallopolymers with the same molecular topology as 9.12. The distance between Ag1 and Ag1A is 5.081(1) Å and the distance between Ag1 and Ag1B is 4.643(1) Å. These distances are within the same range as the related distances in previous structures; the same distances in 5.10 are 5.069(1) and 4.764(1) Å, the distances in 6.10 are 5.044(1) and 5.058(1) Å and in 7.10 they are 5.044(1) and 5.058(1) Å.

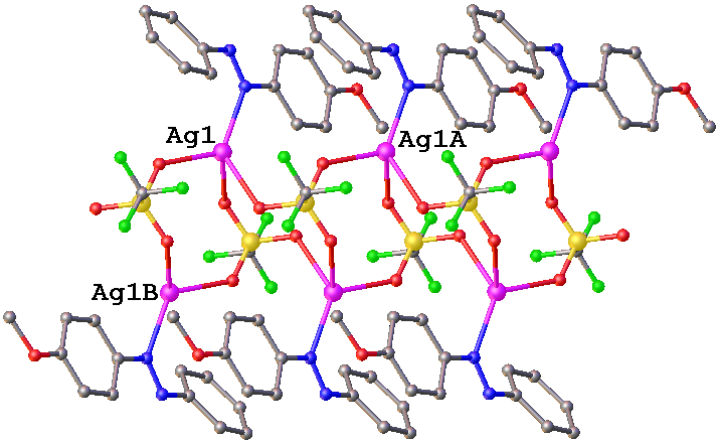

Fig (64) - View of a short strand of the polymer 9.12. The hydrogen atoms have been omitted for clarity. Relevant interatomic distances (Å) are Ag1-Ag1A 5.081(1) and Ag1-Ag1B 4.643(1).

Fig (65) shows how the tridentate triflate anions form a series of fused eight membered rings in a chair like conformation.

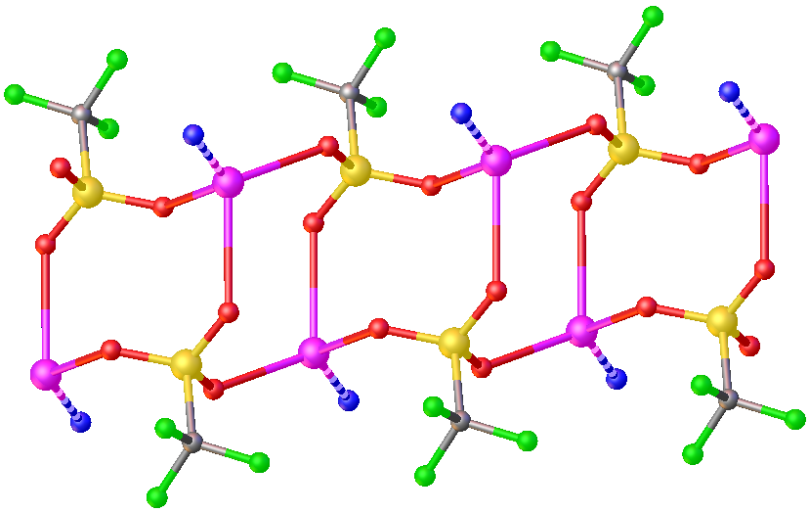

Fig (65) - View of a section of the structure showing the fused eight membered rings of complex 8.12. The 4-methoxyazobenzene molecules have been omitted for clarity.

Fig (66) shows the weak interactions that organise the strands of the complex; there is an inter-strand hydrogen bond and a fluorine-fluorine interaction. The fluorine-fluorine interaction has a distance of 2.88(2) Å; this interaction would be considered to be of moderate strength.[27]

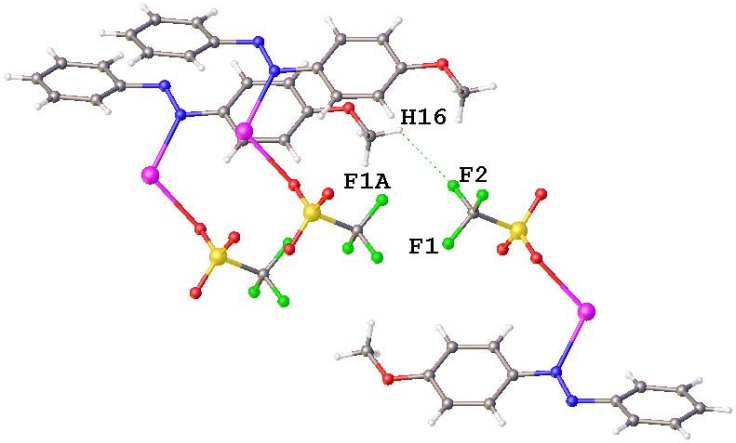

Fig (66) - View of the inter-strand hydrogen bonding and fluorine-fluorine interactions in 9.12. A relevant hydrogen bond length (Å) is F2-H16 2.57(2). A relevant interatomic distance (Å) is F1-F1A 2.88(2).

To summarise, the structure of this complex is a 1-D metallopolymer in which the silver atom adopts a distorted tetrahedral geometry. The 4-methoxyazobenzene molecule is monodentate and binds to the silver atom via the nitrogen atom associated with the substituted aromatic ring. The triflate anions are all tridentate with each oxygen atom bound to a silver atom; this leads to the chain of linked eight membered rings. This structure is most similar to the complexes 5.10, 6.10 and 7.10 as they are all 1-D in nature with the exact same molecular topology. This complex is also similar to the complexes 1.13 and 2.10; however these two complexes are 2-D due to 1.13 having no substituents on the aromatic rings and 2.10 having the two half-occupancy bromine atoms in the 2-position.

<u>With silver(I) trifluoroacetate (9.13)</u>

The complex of 4-methoxyazobenzene and silver trifluoroacetate has four silver atoms, one 4-methoxyazobenzene molecule and four trifluoroacetate anions in the asymmetric unit. The crystal structure solves in the monoclinic space group $P2_1/c$ with R_1= 0.0495. This complex was made by mixing one equivalent of ligand with three equivalents of silver salt but the ratio in the complex is four to one i.e. $[M_4L]$.

The silver atoms in the metallopolymer coordinated to the 4-methoxyazobenzene molecule have an unusual four coordinate geometry as shown in Fig (67). The τ_4 index [32] of the silver atoms Ag1 and Ag2 are 0.44 and 0.43 respectively. These τ_4 indices indicate an intermediate geometry between a square planar and a tetrahedral geometry; 0.44 and 0.43 indicate that the geometry is slightly closer to square planar. There are silver-silver bonds between Ag1 and Ag1A as well as Ag2 and Ag2A; these silver-silver bonds are considered to be strong.[28] Fig (67) also shows that the 4-methoxyazobenzene molecule is coordinated in a monodentate fashion. In this complex the nitrogen atom that is not associated with the substituted aromatic ring is binding to the silver atom; this has not been observed in any of the previous structures. This anomaly is likely to be due to the oxygen of the methoxy group

weakly interacting with the silver atom of the chain of trifluoroacetate anions; there are also two hydrogen bonds, which will be shown in a later figure. The aromatic rings of the ligand are slightly rotated out of the plane of the azo group; ringN1 by 11.1(9)˚ and ringN2 by 18.6(6)˚. The aromatic rings are also not coplanar with a torsion angle between them of 11.2(2)˚. The trifluoroacetate anions of this complex are unusually found in two different types of structure. There are the anions that are associated with the ligand and then there are the anions, which form a chain; this topology has not been observed in any of the previous structures. The trifluoroacetate anion associated with the 4-methoxyazobenzene molecules is tridentate while the other anion which is also part of the coordination polymer is bidentate. The trifluoroacetate anions in the chain and not part of the coordination complex are tridentate.

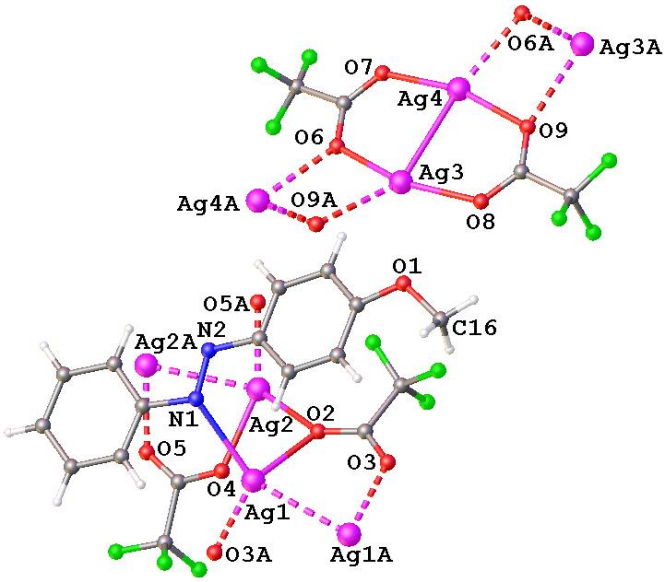

Fig (67) - The asymmetric unit of 9.13. Relevant bond lengths (Å) are N1-Ag1 2.508(6), O2-Ag1 2.247(5), O3A-Ag1 2.205(5), O2-Ag2 2.474(5), O4-Ag2 2.240(5), O5A-Ag2 2.183(5), N1-N2 1.255(8) Ag1-Ag1A 2.9371(11) and Ag2-Ag2A 2.9495(11). Relevant bond angles (˚) are N1-Ag1-O2 91.81(19), N1-Ag1-O3A 111.23(19), N1-Ag1-Ag1A 141.67(13), O2-Ag1-O3A 156.9(2), O2-Ag1-Ag1A 79,48(12), O3A-Ag1-Ag1A 80.97(13), O2-Ag2-O4 78.95(16), O2-Ag2-O5A 110.55(18), O2-Ag2-Ag2A 145.96(11), O4-Ag1-O5A 153.6(2), O4-Ag2-Ag2A 79.49(13) and O5A-Ag2-Ag2A 79.88(14). Relevant torsion angles (˚) are N1-N2-C10-C11 18.6(6), N2-N1-C1-C2 11.1(9) and RingN1-RingN2 11.2(2).

It is shown in Fig (68) how the coordination complex part of 9.13 forms a 1-D linear polymer, which has a head-head/tail-tail arrangement. The chain consists of two five membered rings fused together which then coordinate to each other via the oxygen atoms of the trifluoroacetate anions; the chain alternates between the fused five membered ring structure which bears the 4-methoxyazobenzene ligand and then one without the ligand. This structure bears no real similarity to any of the other structures that contain the trifluoroacetate anion.

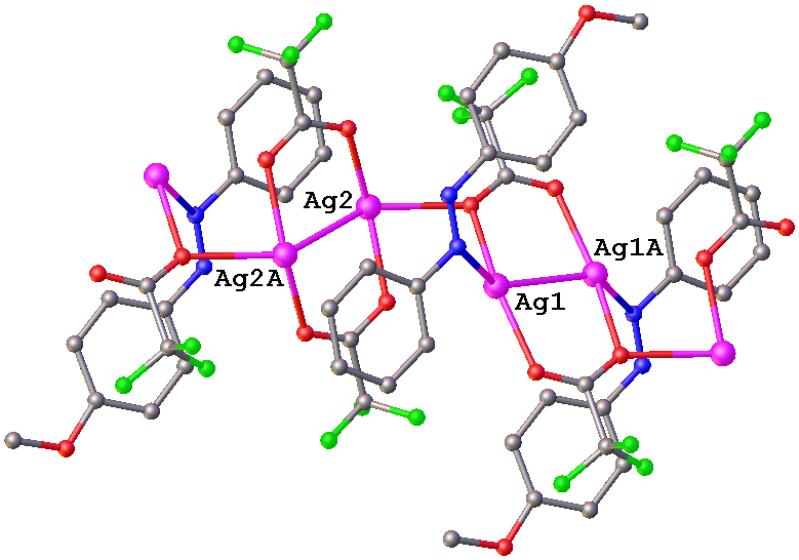

Fig (68) - View of a short strand of the polymer 9.13. The hydrogen atoms have been omitted for clarity. Relevant interatomic distances (Å) are Ag1-Ag2 3.4862(8), Ag1-Ag1A 2.937(1) and Ag2-Ag2A 2.950(1).

Fig (69) shows more clearly the head-head/tail-tail arrangement in the structure and the way in which the structure alternates.

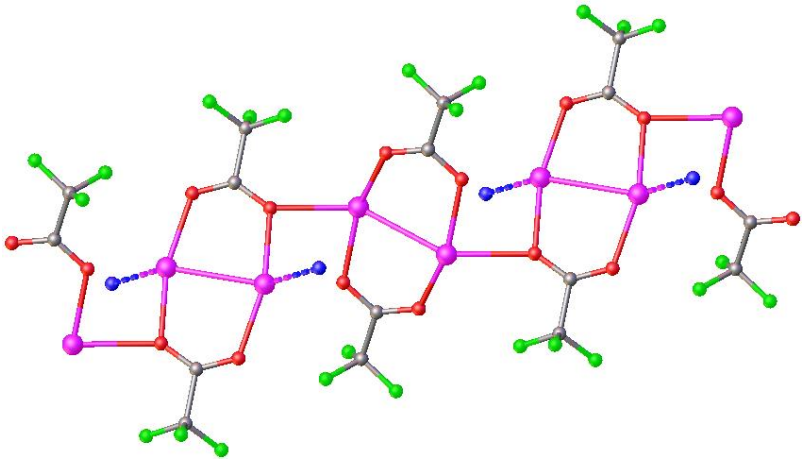

Fig (69) - View of a section of the structure 9.13 showing a series of fused five membered rings, which are linked. The 4-methoxyazobenzene molecules have been omitted for clarity.

Fig (70) shows the hydrogen bonds that were alluded to in the discussion of Fig (67). These hydrogen bonds influence which nitrogen atom binds to the silver atom. In all previous structures, including a structure with this same ligand, the nitrogen atom associated with the substituted aromatic ring has bound to the silver atom.

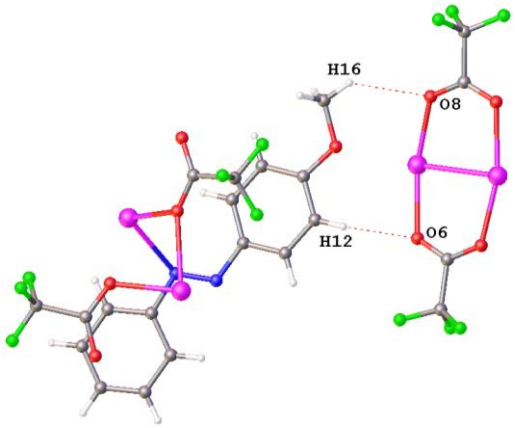

Fig (70) - View of the inter-strand hydrogen bonding in 9.13. Relevant hydrogen bond lengths (Å) are O6-H12 2.56(2) and O8-H16 2.59(2).

To summarise, the complex 9.13 is a 1-D linear metallopolymer with four different silver atoms two of which are in the actual coordination complex and have unusual four coordinate geometries with τ_4 index [32] of 0.44 and 0.43. The τ_4 index indicates a geometry half way between square planar and tetrahedral, with these two indices indicating that the geometries are closer to square planar. The other two silver atoms are in the chain of trifluoroacetate anions. There are also four trifluoroacetate anions in the asymmetric unit three of which are tridentate and one is bidentate. The coordination complex has one anion that is tridentate while the other anion is bidentate; the two anions in the chain are both tridentate. The 4-methoxyazobenzene molecule is monodentate and the nitrogen atom associated with the unsubstituted aromatic ring is coordinated to the silver atom. This type of coordination is not seen in any of the previous structures and is due to a weak interaction with the oxygen atom of the methoxy group and two hydrogen bonds.

Due to the non-coordinating nature of the tetrafluoroborate anion complex 9.10 has a similar molecular topology to some of the other complexes with non-coordinating anions namely 3.10 and 4.10, which both have hexafluorophosphate anions. The structure made using silver perchlorate has an identical molecular topology to the previous structures that were also made using this silver salt. The complex containing the triflate anions is identical to three of the five complexes that have triflate anions in the asymmetric unit and it bears large similarities to the other two structures. This would suggest that the anion with which the complex is made has the biggest contributing factor to the resulting molecular topology of the structure. Anomalously the complex 8.13 bears no real similarities to the previous complexes prepared with trifluoroacetate anions. Another anomalous feature of this complex is that the nitrogen atom associated with the unsubstituted aromatic ring coordinates to the silver atom; this has not been observed in any of the previous structures. Both of these effects are due to the methoxy group in the 4-position weakly interacting with one of the silver atoms in the chain of anions. There are also two hydrogen bonds, which increase the strength of this interaction.

10.1 complexes of 2,6-dimethyl-4'-chloroazobenzene

With silver(I) tetrafluoroborate (10.10)

The complex of 2,6-dimethyl-4'-chloroazobenzene and silver tetrafluoroborate has one silver atom, two 2,6-dimethyl-4'-chloroazobenzene molecules and one tetrafluoroborate anion in the asymmetric unit. The crystal structure solves in the monoclinic space group $P2_1/n$ with R_1= 0.0399. This complex was made by mixing one equivalent of ligand with three equivalents of silver salt; the ratio in the complex is one to two i.e. $[ML_2]$.

It can be seen in Fig (71) that the silver atom adopts a distorted T-shaped geometry; the ideal angles of a T-shaped geometry are 180 and 90˚. The angles around the silver atom roughly match the ideal angles, these are 159.45(14) (N1-Ag1-N3), 102.74(12) (N1-Ag1-F1) and 96.69(12)˚ (N3-Ag1-F1). The 2,6-dimethyl-4'-chloroazobenzene molecules are both monodentate with the nitrogen atoms associated with the chlorine containing aromatic ring coordinating to the silver atom. Unsurprisingly the aromatic rings containing the two methyl groups are almost orthogonal to the plane of the azo group and the other aromatic ring; this is due to the steric bulk associated with the two methyl groups. The aromatic rings associated with the chlorine atoms are almost coplanar with the azo group with torsion angles of only 6.9(4) and 18.7(4)˚ between them. Fig (71) also shows one of the fluorine atoms of the tetrafluoroborate anion coordinating to the silver atom; this is the cause of the 159.45(14)˚ angle between N1, Ag1 and N3.

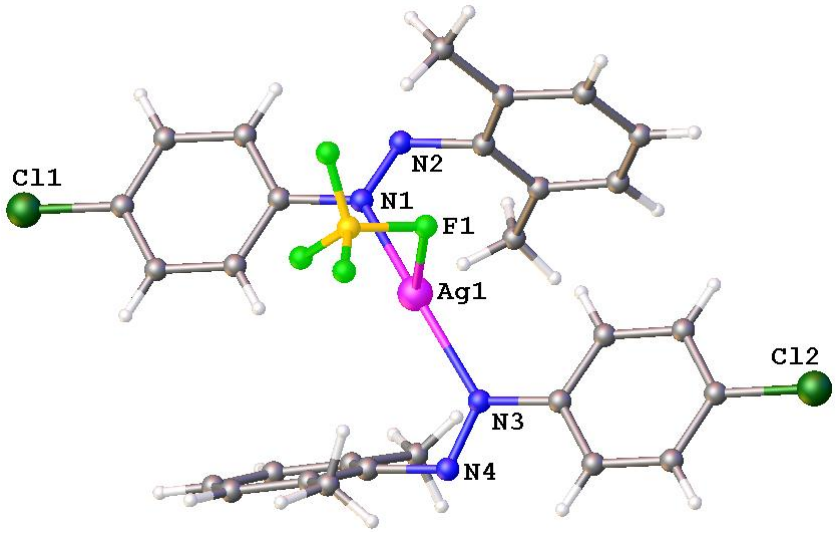

Fig (71) - The asymmetric unit of 10.10. Relevant bond lengths (Å) are N1-N2 1.255(4), N3-N4 1.264(4), Ag1-N1 2.194(4), Ag1-N3 2.185(4) and Ag1-F1 2.541(3). Relevant bond angles (˚) are N1-Ag1-N3 159.45(14), N1-Ag1-F1 102.74(12) and N3-Ag1-F1 96.69(12). Relevant torsion angles (˚) are N1-N2-C10-C11 79.7(5), N2-N1-C1-C2 6.9(4), RingN1-RingN2 74.86(15), N3-N4-C30-C31 78.7(6), N4-N3-C20-C21 18.7(4) and RingN3-RingN4 57.89(15).

Fig (72) shows the hydrogen bonding interactions that order the discrete molecules of the structure.

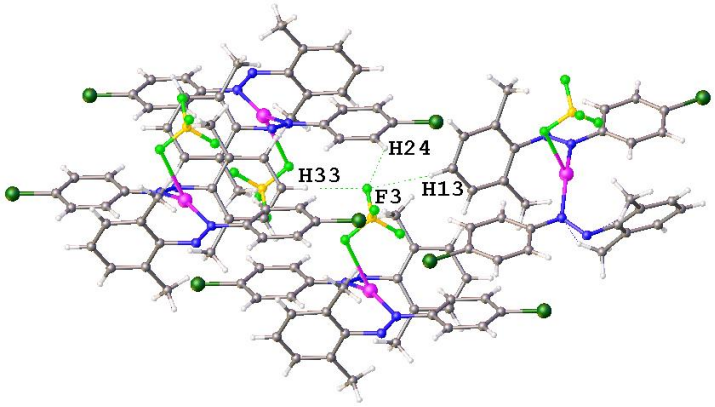

Fig (72) - View of the hydrogen bonding in 10.10. Relevant interatomic distances (Å) are F3-H13 2.622(3), F3-H24 2.437(3) and F3-H33 2.570(3).

Fig (73) shows another weak interaction that occurs between the discrete units of the complex. There is a chlorine-chlorine interaction between Cl1 and Cl2, which has a distance of 3.49(2) Å; this is a typical value for this type of interaction.[33]

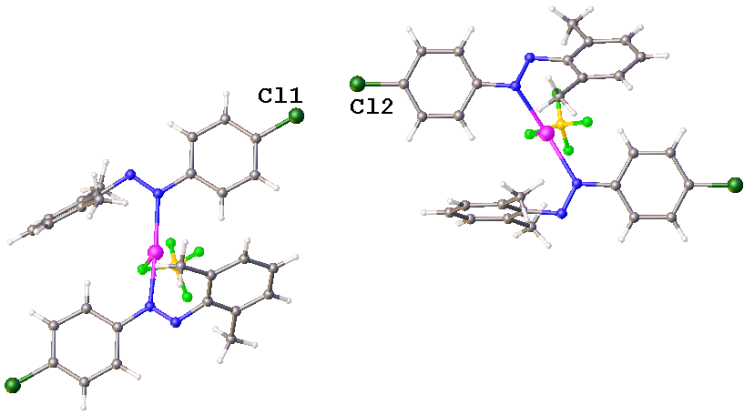

Fig (73) - View of the chlorine-chlorine interactions in 10.10. A relevant interatomic distance (Å) is Cl1-Cl2 3.49(2).

With silver(I) hexafluorophosphate (10.11)

The complex of 2,6-dimethyl-4'-chloroazobenzene and silver hexafluorophosphate has one silver atom, two 2,6-dimethyl-4'-chloroazobenzene molecules and one hexafluorophosphate anion in the asymmetric unit. The crystal structure solves in the monoclinic space group $P2_1/n$ with R_1= 0.0406. This complex was made by mixing one equivalent of ligand with three equivalents of silver salt; the ratio in the complex is one to two i.e. $[ML_2]$.

Fig (74) shows the linear nature of the silver atom; the angle between N1, Ag1 and N3 should be 180˚; however there is a weak interaction between the silver atom and the hexafluorophosphate anion. This weak interaction leads to an angle of 164.30(11)˚. The 2,6-dimethyl-4'-chloroazobenzene molecules are both monodentate and are both coordinating to the silver atom via the nitrogen atom associated with the aromatic rings containing

chlorine atoms. The steric interactions between the methyl groups and the nitrogen atom coordinated to the silver atom lead to the aromatic rings with the methyl groups becoming almost orthogonal. The aromatic rings associated with the chlorine atoms are almost coplanar with torsion angles of only 1.5(3) and 10.7(5)˚. Also shown in Fig (74) is the non-coordinating hexaflourophosphate anion, which is weakly interacting with the silver atom.

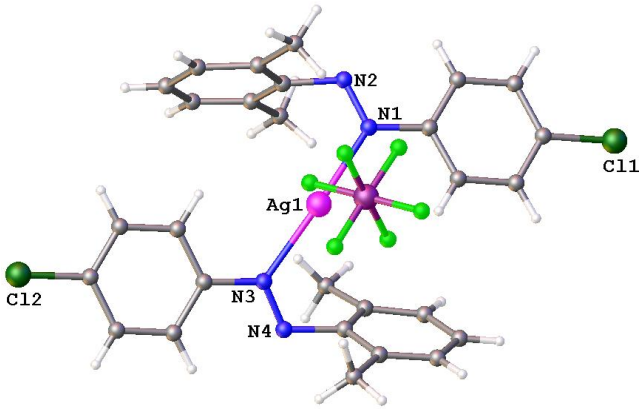

Fig (74) - The asymmetric unit of 10.11. Relevant bond lengths (Å) are N1-N2 1.258(4), N3-N4 1.252(4), Ag1-N1 2.213(3) and Ag1-N3 2.208(3). A relevant bond angle (˚) is N1-Ag1-N3 164.30(11). Relevant torsion angles (˚) are N1-N2-C10-C11 78.1(4), N2-N1-C1-C1 1.5(3), RingN1-RingN2 86.75(14), N3-N4-C30-C31 72.9(4), N4-N3-C20-C21 10.7(5) and RingN3-RingN4 63.31(13).

It is shown in Fig (75) that while the hexafluorophosphate anion is not coordinating to the silver atom it still has a large influence on the structure via hydrogen bonds. The shortest hydrogen bond is 2.38(2) Å (F1-H13) while the longest is 2.64(2) Å (F6-H37).

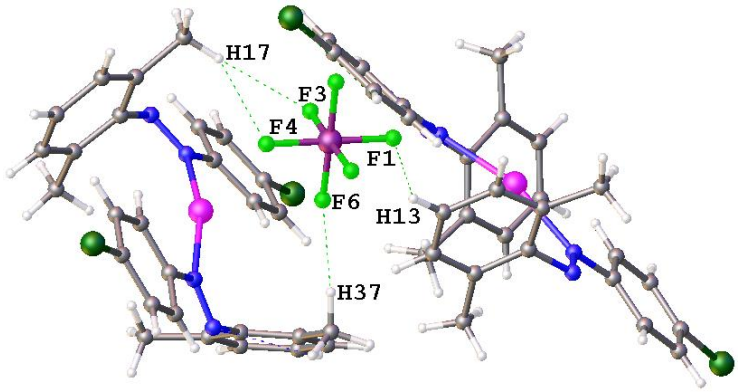

Fig (75) - View of the hydrogen bonding in 10.11. Relevant interatomic distances (Å) are F1-H13 2.38(2), F3-H17 2.58(2), F4-H17 2.61(2) and F6-H37 2.64(2).

Fig (76) shows some more hydrogen bonds that occur between the hexafluorophosphate anion and the hydrogen atoms of the ligand. The shortest hydrogen bond is 2.40(2) Å (F2-H25) while the longest is 2.58(2) Å (F5-H16).

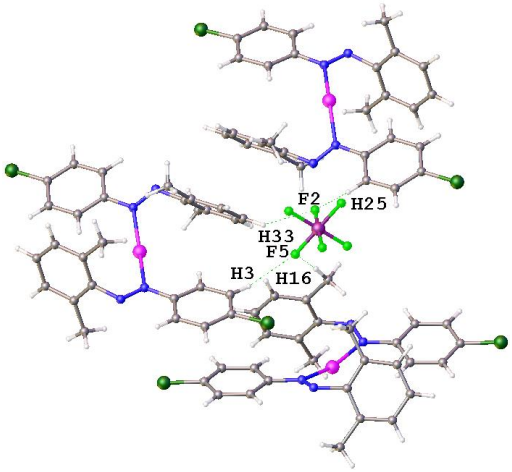

Fig (76) - View of more hydrogen bonding in 10.11. Relevant interatomic distances (Å) are F2-H25 2.40(2), F2-H33 2.57(2), F5-H3 2.51(2) and F5-H16 2.58(2).

With silver(I) perchlorate (10.12)

The complex of 2,6-dimethyl-4'-chloroazobenzene and silver perchlorate has one silver atom, two 2,6-dimethyl-4'-chloroazobenzene molecules and one perchlorate anion in the asymmetric unit. The crystal structure solves in the monoclinic space group $P2_1/n$ with R_1= 0.0394. This complex was made by mixing one equivalent of ligand with three equivalents of silver salt; the ratio in the complex is one to two i.e. [ML_2].

It is shown in Fig (77) that the silver atom has a T-shaped geometry; with none of the angles matching the ideal angles, which are 180 and 90˚. The angles around the silver atom are within range of the ideal angles, these are 157.21(11) (N1-Ag1-N3), 105.12(11) (N1-Ag1-O1) and 96.47(11)˚ (N3-Ag1-O1). The 2,6-dimethyl-4'-chloroazobenzene molecules are both monodentate with the nitrogen atoms associated with the chlorine containing aromatic ring coordinating to the silver atom. The steric clash between the methyl groups and the nitrogen atom coordinated to the silver atom leads to the methyl group containing aromatic rings being almost orthogonal to the plane of the azo group and the other aromatic ring. The aromatic rings containing the chlorine atoms are almost coplanar to the azo group with torsion angles between them of 8.6(5) and 16.7(5)˚. Fig (77) also shows the perchlorate anion coordinating to the silver atom via an oxygen atom, which causes the 157.21(11)˚ angle between N1, Ag1 and N3.

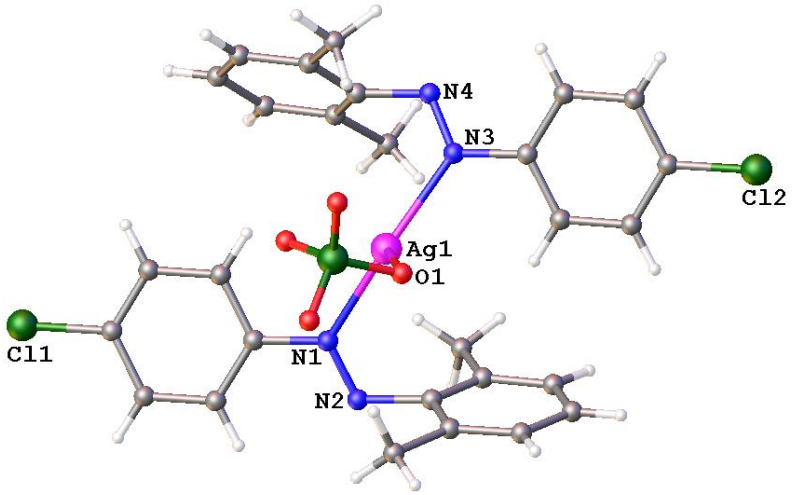

Fig (77) - The asymmetric unit of 10.12. Relevant bond lengths (Å) are N1-N2 1.260(4), N3-N4 1.252(4), Ag1-N1 2.211(3), Ag1-N3 2.210(3) and Ag1-O1 2.534(3). Relevant bond angles (˚) are N1-Ag1-N3 157.21(11), N1-Ag1-O1 105.12(11) and N3-Ag1-O1 96.47(11). Relevant torsion angles (˚) are N1-N2-C10-C11 80.1(5), N2-N1-C1-C2 8.6(5), RingN1-RingN2 73.92(13), N3-N4-C30-C31 71.9(4), N4-N3-C20-C21 16.7(5) and RingN3-RingN4 58.05(13).

Fig (78) shows the chlorine-chlorine interaction which exists between the discrete units of the complex. This chlorine-chlorine interaction has a distance of 3.5056(16) Å. This chlorine-chlorine interaction is relatively weak as chlorine-chlorine interactions range from 3.317 to 3.574 Å.[33]

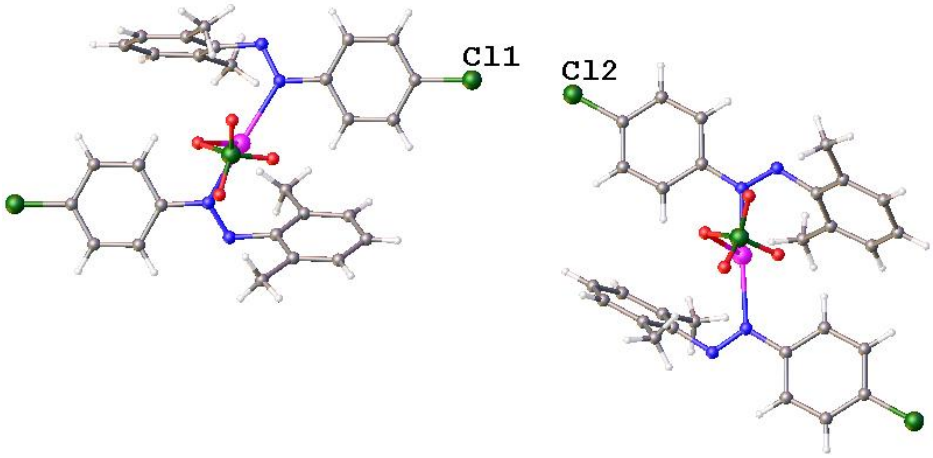

Fig (78) - View of the chlorine-chlorine interactions that take place within 10.12. A relevant interatomic distance (Å) is Cl1-Cl2 3.51(2).

Some more weak interactions which order the discrete units of the complex are shown in Fig (79). These are 2.48(2) (O3-H22) and 2.61(2) Å (O3-H33) in length.

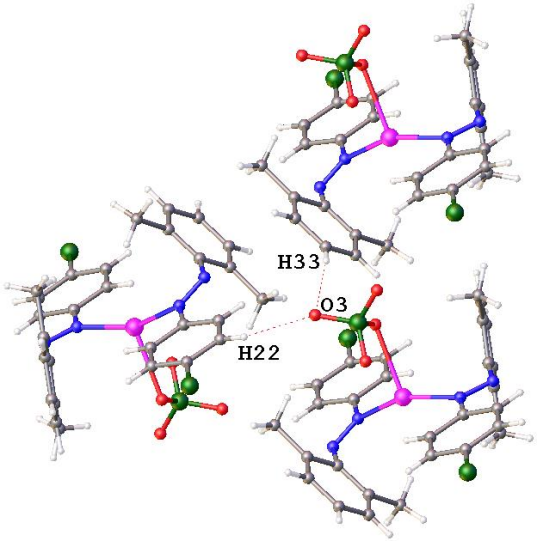

Fig (79) - View of the hydrogen bonding in 10.12. Relevant interatomic distances (Å) are O3-H22 2.48(2) and O3-H33 2.61(2).

With silver(I) triflate (10.13)

The complex of 2,6-dimethyl-4'-chloroazobenzene and silver triflate has two silver atoms, one 2,6-dimethyl-4'-chloroazobenzene molecule, two triflate anions and a water molecule in the asymmetric unit. The crystal structure solves in the triclinic space group P-1 with R_1= 0.0375. This complex was made by mixing one equivalent of ligand with three equivalents of silver salt; the ratio in the complex is two to one i.e. [M_2L].

The silver atom (Ag1) adopts a distorted square pyramidal geometry with the angles not closely matching the ideal of 180 and 90˚ as is seen in Fig (80). The τ_5 index [31] is 0.52 indicating an intermediate geometry between square pyramidal and a trigonal bipyramid. The other silver atom (Ag2) is found in a trigonal planar geometry with the angle between N1, Ag2 and O7 matching the perfect trigonal planar angle of 120˚ (120.00(14)˚). The other two angles do not closely match the ideal angle; these are 138.32(13) (N1-Ag2-O2) and 84.69(13)˚ (O2-Ag1-O7). The 2,6-dimethyl-4'-chloroazobenzene molecule is bidentate coordinating to the silver atoms via the nitrogen atom associated with the aromatic ring containing the chlorine atom and through one of the bonds of the aromatic ring containing the methyl groups. As expected the aromatic rings are almost orthogonal to each other with a torsion angle between them of 83.51(16)˚. The aromatic rings are not coplanar with the azo group with the aromatic ring containing the methyl groups having a torsion angle of 60.4(4)˚ and the aromatic ring containing the chlorine having a torsion angle of 17.8(4)˚. In Fig (80) it is also shown how there are two types of triflate anion; one of which is tridentate and coordinated through all the oxygen atoms while the other is bidentate and only coordinated through two oxygen atoms. The denticity of the triflate anions creates an unusual arrangement in the complex, which will be shown better in a later figure. Both of the triflate anions have their CF_3 groups staggered in relation to their SO_3.

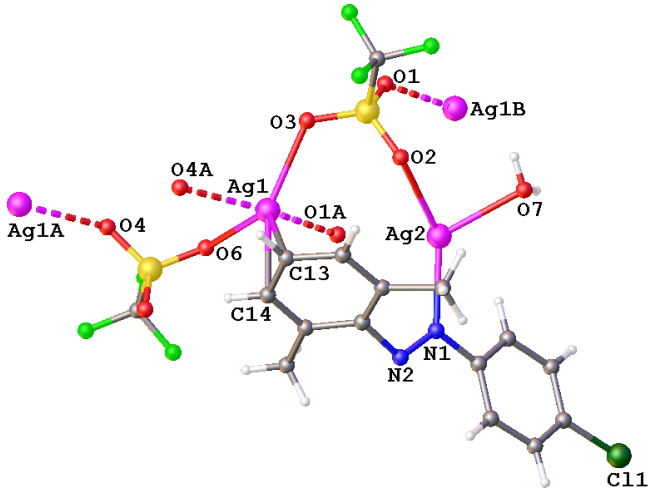

Fig (80) - The asymmetric unit of 10.13. Relevant bond lengths (Å) are N1-N2 1.256(5), Ag1-O3 2.370(3), Ag1-O6 2.469(3), Ag1-O1A 2.457(3), Ag1-O4A 2.459(3), Ag1-C13 2.664(5), Ag1-C14 2.449(5), Ag2-N1 2.261(4), Ag2-O2 2.439(3) and Ag1-O7 2.320(4). Relevant bond angles (˚) are O3-Ag1-O6 132.56(12), O3-Ag1-O1A 93.05(12), O3-Ag1-O4A 93.78(11), O3-Ag1-C13 100.6(14), O3-Ag1-C14 131.30(15), O6-Ag1-O1A 79.72(11), O6-Ag1-O4A 84.67(11), O6-Ag1-C13 125.35(13), O6-Ag1-C14 95.91(14), O1A-Ag1-O4A 163.58(11), O1A-Ag1-C13 113.84(14), O1A-Ag1-C14 101.37(14), O4A-Ag1-C13 79.49(14), O4A-Ag1-C14 85.19(15), C13-Ag1-C14 31.29(14), N1-Ag2-O2 138.32(13), N1-Ag2-O7 120.00(14) and O2-Ag1-O7 84.69(13). Relevant torsion angles (˚) are N1-N2-C10-C11 60.4(4), N2-N1-C1-C2 17.8(4) and RingN1-RingN2 83.51(16).

Fig (81) shows the 1-D nature of the metallopolymer 10.13. The polymer extends through the unusual arrangement of the triflate anions with the ligands covering the top and bottom of the chain.

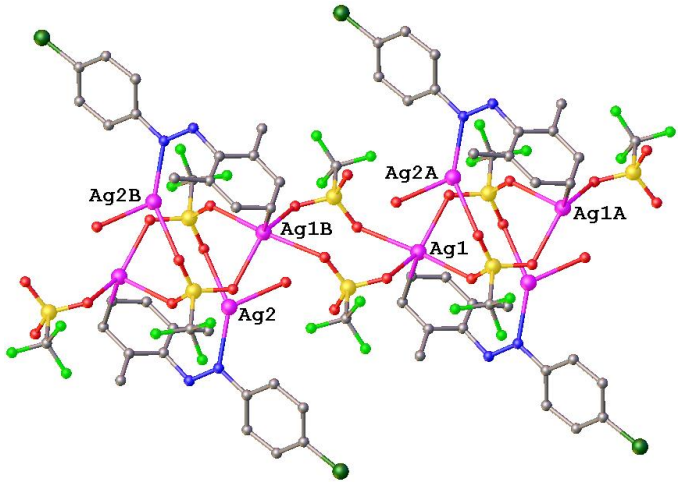

Fig (81) - View of a short strand of the polymer 10.13. Relevant interatomic distances (Å) are Ag1-Ag1A 5.706(1), Ag1-Ag1B 5.947(1), Ag2-Ag2A 9.724(1) and Ag2-Ag2B 5.469(1).

Fig (82) is the figure alluded to in the discussion of Fig (80) which shows the arrangement of the triflate anions. The anions form a chain of linked eight membered rings that alternate between tridentate and bidentate triflate anions.

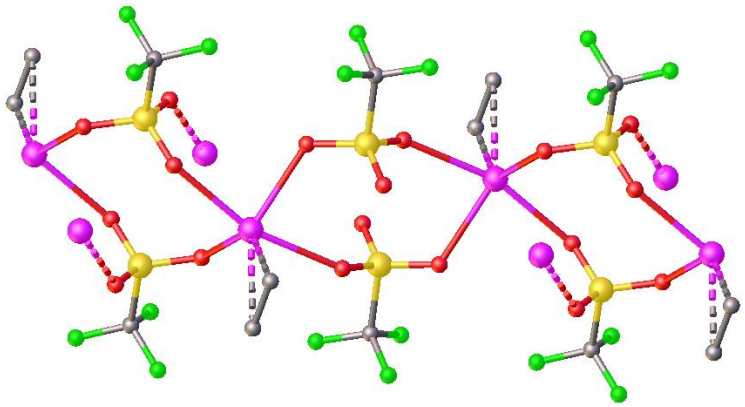

Fig (82) - View of a section of the structure showing the chain of eight membered rings. The azobenzene molecules have been omitted for clarity.

It is shown in Fig (83) how the intra-strand hydrogen bonding orders the structure. The hydrogen bonding between the hydrogen atoms of the water molecule and the oxygen atoms of the triflate anions explains why the bidentate anion does not coordinate in a tridentate fashion. These hydrogen bonds are 2.00(2) (O5-H7B) and 2.17(2) Å (O6-H7A) in length.

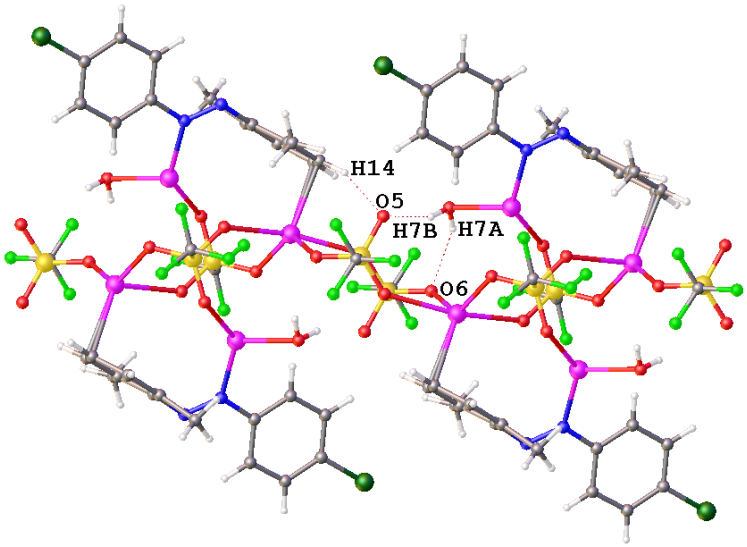

Fig (83) - View of the inter-strand hydrogen bonding in 10.13. O5-H14 2.63(2), O5-H7B 2.00(2) and O6-H7A 2.17(2).

To summarise, the structure of the complex is 1-D in nature with two different types of silver atom, one of which is in a distorted square pyramid geometry while the other is in a trigonal planar geometry. There are two different types of triflate anion; one is tridentate and the other is bidentate. The triflate anions form an unusual arrangement of linked eight

membered rings which alternate between a tridentate and bidentate coordination mode. This arrangement extends the polymer in one direction with the 2,6-dimethyl-4'-chloroazobenzene molecules lining the top and bottom of the complex. The 2,6-dimethyl-4'-chloroazobenzene molecules are bidentate and coordinate through a nitrogen atom associated with the chlorine containing aromatic ring and the aromatic ring containing the methyl groups.

The first three structures of the four show essentially the same molecular topology except in 10.11, which has the hexafluorophosphate anion that does not coordinate to the silver atom. This shows that for the first three structures the ligand has the biggest effect on the overall structure of the complex as the anion was changed three times with very little variation in the molecular topology. This changes when silver triflate is used; the triflate anion has an enormous effect on the molecular topology as the structure changes from discrete to 1-D as the triflate anion coordinates through more than one of the oxygen atoms.

11.1 complexes of 2,6,2',6'-tetramethylazobenzene

With silver(I) perchlorate (11.10)

The complex of 2,6,2',6'-tetramethylazobenzene and silver perchlorate has two silver atoms, one 2,6,2',6'-tetramethylazobenzene molecule and two perchlorate anions in the asymmetric unit. The crystal structure solves in the monoclinic space group $P2_1/n$ with R_1= 0.0222. This complex was made by mixing one equivalent of ligand with three equivalents of silver salt; the ratio in the complex is two to one i.e. $[M_2L]$.

There are two different types of silver atom in the asymmetric unit (Fig (84)), one of which is linear and the other has a slightly distorted trigonal planar geometry. Fig (84) also shows that the 2,6,2',6'-tetramethylazobenzene adopts a bridging bidentate coordination mode. Due to the steric interactions between the four methyl groups and the coordinated silver atoms the aromatic rings are almost orthogonal to the plane of the azo group with an angle between them of 69.9(2) and 66.7(3)˚ for the ring associated with N1 and N2 respectively. The aromatic rings are nearly coplanar with an angle between them of 11.35(7)˚, this small angle is due to the perchlorate anion. One of the perchlorate anions is coordinated to Ag2 in a monodentate fashion while the other is non-coordinating.

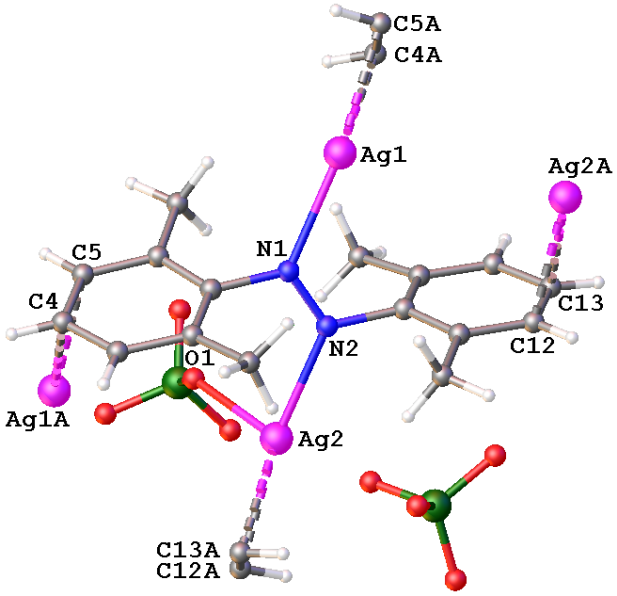

Fig (84) - The asymmetric unit of 11.10. Relevant bond lengths (Å) are N1-Ag1 2.3498(17), N2-Ag2 2.3021(18), O1-Ag2 2.419(2), C4A-Ag1 2.610(2), C5A-Ag1 2.489(2), C12A-Ag2 2.421(2) and C13A-Ag2 2.525(2). Relevant bond angles (˚) are N1-Ag1-C4A 126.90)(7), N1-Ag1-C5A 157.78(7), C4A-Ag1-C5A 31.72(7), N2-Ag2-O1 91.87(7), N2-Ag2-C12A 162.94(8), N2-Ag2-C13A 132.06(7), C12A-Ag2-C13A 32.79(8), O1-Ag2-C12A 104.39(8) and O1-Ag2-C13A 122.78(8). Relevant torsion angles (˚) are N1-N2-C10-C11 69.9(2), N2-N1-C1-C2 66.7(3) and RingN1-RingN2 11.35(7).

Fig (85) shows the 1-D nature of the metallopolymer, the polymer extends through the azo group and the aromatic rings. This topology resembles rectangles linked through the corners. The rectangles have dimensions of 4.132(1) (Ag1-Ag2) and 5.345(1) Å (C1-C10).

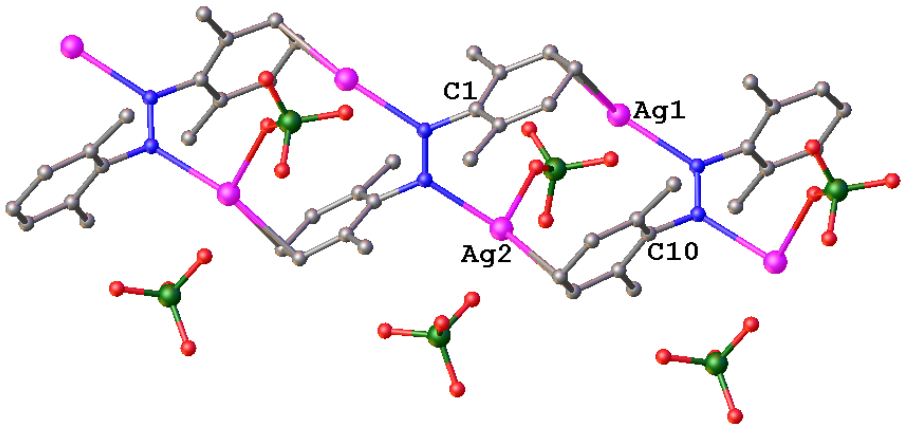

Fig (85) - View of a short strand of the polymer 11.10. The hydrogen atoms have been omitted for clarity. Relevant interatomic distances (Å) are Ag1-Ag2 4.132(1) and C1-C10 5.345(1).

The hydrogen bonds between the oxygen atoms of the perchlorate anion and the hydrogen atoms of the ligand order the strands of the complex as shown in Fig (86). The longest

hydrogen bond is 2.65(2) Å while the shortest is 2.35(2) Å. The hydrogen bond between O4 and H7 is the reason the aromatic rings are not coplanar.

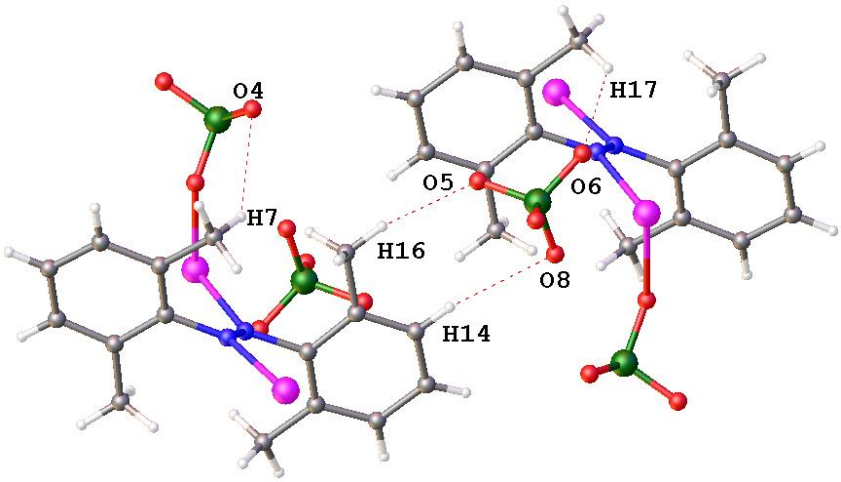

Fig (86) - View of the intra- and inter-strand hydrogen bonding in 11.10. Relevant hydrogen bond lengths (Å) are O4-H7 2.65(2), O5-H16 2.35(2), O8-H14 2.65(2) and O6-H17 2.51(2).

To summarise the structure of the complex is a 1-D metallopolymer with the two different types of silver atoms adopting a linear and a Y-shape respectively. The 2,6,2',6'-tetramethylazobenzene is bridging tetradentate with both the nitrogen atoms coordinated to the silver atoms. One of the bonds of the aromatic ring is also coordinated to a silver atom. One of the perchlorate anions is coordinated to a silver atom in a monodentate fashion while the other perchlorate anion is non-coordinating. This structure resembles the complex 10.13 slightly as it coordinates to the silver atoms via a bond in the aromatic ring.

<u>With silver(I) trifluoroacetate (11.11)</u>

The complex of 2,6,2',6'-tetramethylazobenzene and silver trifluoroacetate has two silver atoms, two half molecules of 2,6,2',6'-tetramethylazobenzene and two trifluoroacetate anions in the asymmetric unit. The crystal structure solves in the triclinic space group P-1 with an R_1= 0.0393. This complex was made by mixing one equivalent of ligand with three equivalents of silver salt; the ratio in the complex is two to one i.e. $[M_2L]$.

There are two types of silver atoms in complex 11.11 as seen in Fig (87), one of which is square planar while the other is a distorted trigonal bipyramid. The square planar silver atom has angles that are very close to the ideal angles of 90 and 120˚. The angles of the square planar silver atom are 169.6(6) (O2-Ag2-O3), 158.8(3) (Ag1-Ag2-O2A), 87.1(4) (Ag1-Ag2-O2), 83.5(4) (Ag1-Ag2-O3), 169.6(6) and 73.6(5) (O2-Ag2-O2A), 116.3(5) (O3-Ag2-O2A). The angles of the trigonal bipyramidal silver atom are slightly distorted with only a few of the angles matching the ideal angles of 90, 120 and 180˚. Fig (87) also shows how the half molecules of 2,6,2',6'-tetramethylazobenzene coordinate to Ag1 in a bridging bidentate fashion. As the methyl groups sterically clash with the nitrogen atoms coordinated to the silver atoms the aromatic rings are quite orthogonal to the plane of the azo group. The

torsional angle between the azo group and the aromatic rings are 59.0(2) and 63.0(2)˚ for the ring associated with N1 and N2 respectively. The trifluoroacetate anions form a pair of five membered rings; there is a strong silver-silver bond in the fused five membered rings which is 2.983(2) Å in length.[28]

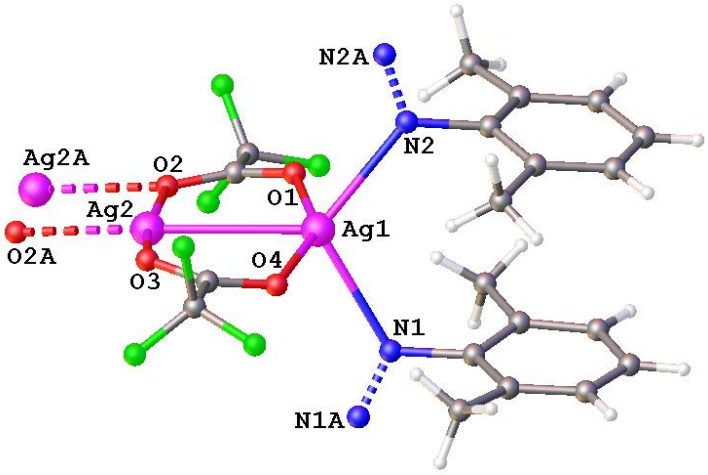

Fig (87) - The asymmetric unit of 11.11. Relevant bond lengths (Å) are N1-Ag1 2.496(14), N2-Ag1 2.456(15), O1-Ag1 2.293(13), O4-Ag1 2.259(12), Ag1-Ag2 2.983(2), O2-Ag2 2.204(14), O3-Ag2 2.159(14), O2A-Ag2 2.602(14), N1-N1A 1.28(3) and N2-N2A 1.24(3). Relevant bond angles (˚) are N1-Ag1-N2 86.0(5), N1-Ag1-O1 105.8, N1-Ag1-O4 88.3(5), N1-Ag1-Ag2 118.9(3), O1-Ag1-O4 151.2(5), N2-Ag1-O1 86.6(5), N2-Ag1-O4 112.8(5), O1-Ag1-Ag2 73.8(3), O4-Ag1-Ag2 77.4(3), N2-Ag1-Ag2 129.6(3), O2-Ag2-O2A 73.6(5), O2-Ag2-O3 169.6(6), O3-Ag2-O2A 116.3(5), Ag1-Ag2-O2A 158.8(3), Ag1-Ag2-O2 87.1(4) and Ag1-Ag2-O3 83.5(4). Relevant torsion angles (˚) are N1A-N1-C1-C2 59.0(2) and N2A-N2-C10-C11 63.0(2).

Fig (88) shows that complex 11.11 is a 2-D metallopolymer which extends through the azo groups of the ligand and through the anion. This structure resembles a hexagon in with four equal sides and another two equal sides. The polymer extends through the anions via the fused five membered rings which becoming fused again to form a four membered ring. The pore in the middle of the unsymmetrical hexagon has dimensions of 13.180(1) (Ag1A-Ag1B) and 11.070(1) Å (Ag2A-Ag2B). The azo group side of the hexagon has a distance of 5.678(1) Å while the anion side has a distance of 8.836(1) Å.

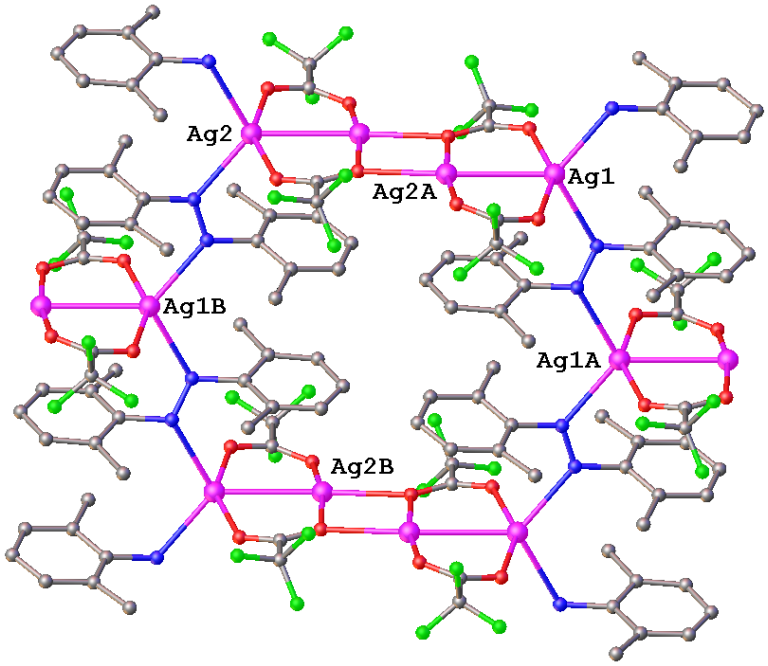

Fig (88) - View of a section of the structure 11.11 showing how the structure forms a hexagonal structure. The hydrogen atoms have been omitted for clarity. Relevant interatomic distances (Å) are Ag1-Ag1A 5.678(1), Ag1A-Ag1B 13.180(1), Ag1-Ag2 8.836(1) and Ag2A-Ag2B 11.070(1).

It is seen in Fig (89) how the structure forms a honeycomb structure.

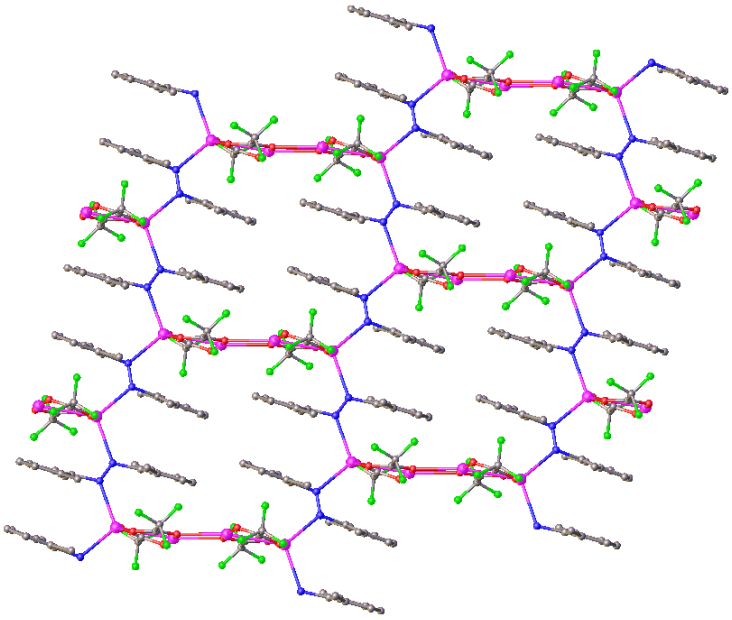

Fig (89) - Another view of the structure 11.11 showing how the structure forms a series of linked hexagons. The hydrogen atoms have been omitted for clarity.

Fig (90) shows how weak fluorine-fluorine interactions work to organise the sheets of the metallopolymer 11.11. The fluorine-fluorine interaction in this complex is considered to be

of median strength; this interaction has a distance of 2.90(2) Å; fluorine-fluorine interactions usually fall between 2.8 and 3.6 Å.[27]

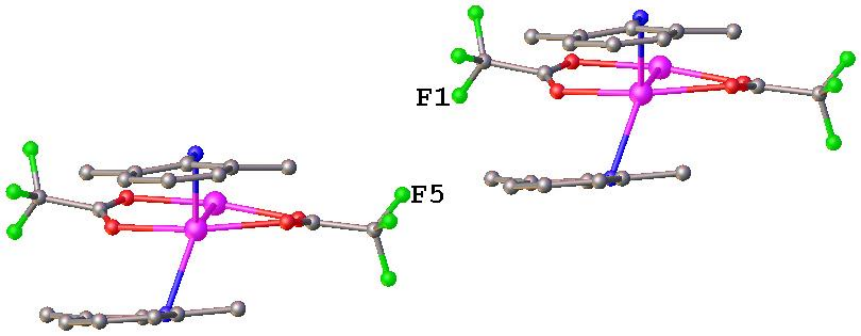

Fig (90) - View of the fluorine-fluorine interactions in 11.11. A relevant interatomic distance (Å) is F1-F5 2.90(2). The hydrogen atoms have been omitted for clarity.

To summarise, the structure of the complex is a 2-D metallopolymer in which there are two different types of silver atom. One of the silver atoms has a square planar geometry while the other has a trigonal bipyramidal geometry. The trifluoroacetate anions arrange to form fused five membered rings, which connect to form a four membered ring. This arrangement of anions creates two sides of the hexagonal structure that the complex adopts; the other four sides of the hexagon are created by the ligand bridging the silver atoms. The 2,6,2',6'-tetramethylazobenzene binds to the silver atom as two half molecules which leads to the aromatic rings being coplanar to each other.

The two above examples with 2,6,2',6'-tetramethylazobenzene show that in this case the ligand has the biggest impact on what sort of molecular topology is formed. The examples above do not have a similar structure to any of the other complexes, except for the structure 10.13, which slightly resembles 11.10. This is due to the steric interactions between the four methyl groups and the nitrogen atoms coordinated to the silver atoms.

12.1 complexes of 2,2'-ethyleneazobenzene

<u>With silver(I) tetrafluoroborate (12.10)</u>

The complex of 2,2'-ethyleneazobenzene and silver tetrafluoroborate has one silver atom, two 2,2'-ethyleneazobenzene molecules and one tetrafluoroborate anion in the asymmetric unit. The crystal structure solves in the triclinic space group P-1 with R_1= 0.0229. This complex was made by mixing one equivalent of ligand with three equivalents of silver salt; the ratio in the complex is one to two i.e. [ML_2].

Fig (91) shows how the silver atom adopts a trigonal planar geometry, which has ideal bond angles of 120˚. The bond angles around the silver atom are very close to 120˚ with angles of 111.25(5) (N1-Ag1-N3), 123.13(5) (N1-Ag1-N4) and 125.06(5) (N3-Ag1-N4). The asymmetric unit also contains two molecules of 2,2'-ethyleneazobenzene. One molecule of 2,2'-ethyleneazobenzene is monodentate and the other is bridging bidentate. However the

ethylene group forces the conformation of the azo group to be *cis*, as opposed to *trans*, causing this bridging mode to adopt a different conformation that is not seen in any of the previous complexes. The ethylene group forces the aromatic rings out of the coplanar geometry, which is seen in molecules containing azo groups without other groups linking the aromatic rings together. The torsion angles are found to be between 66.69(17) and 72.9(2)˚ for the azo groups and the aromatic rings. It is also shown in Fig (91) that there is a non-coordinating tetrafluoroborate anion, which is weakly interacting with the silver atom.

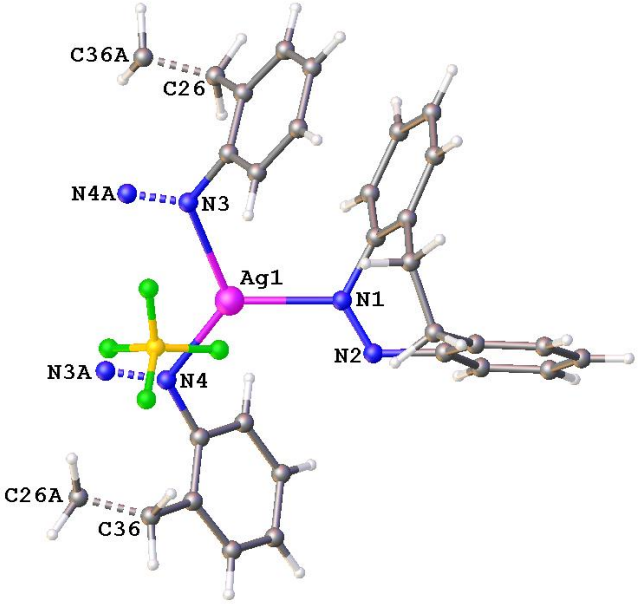

Fig (91) - The asymmetric unit of 12.10. Relevant bond lengths (Å) are Ag1-N1 2.2640(14), Ag1-N3 2.3458(14), Ag1-N4 2.2822(13), N1-N2 1.246(2) and N3-N4A 1.2513(18). Relevant bond angles (˚) are N1-Ag1-N3 111.25(5), N1-Ag1-N4 123.13(5) and N3-Ag1-N4 125.06(5). Relevant torsion angles (˚) are N1-N2-C10-C11 72.9(2), N2-N1-C1-C2 68.76(18), N3-N4-C30-C31 66.69(17) and N4-N3-C20-C21 72.5(2).

In Fig (92), it is shown how the complex is a discrete assembly consisting of four 2,2'-ethyleneazobenzene molecules two of which are monodentate while the other two are found to be bridging bidentate in a *cis* conformation. There are two silver atoms and two tetrafluoroborate anions. This arrangement forms a hexagon that has a distance between the silver atoms of 3.384(1) Å.

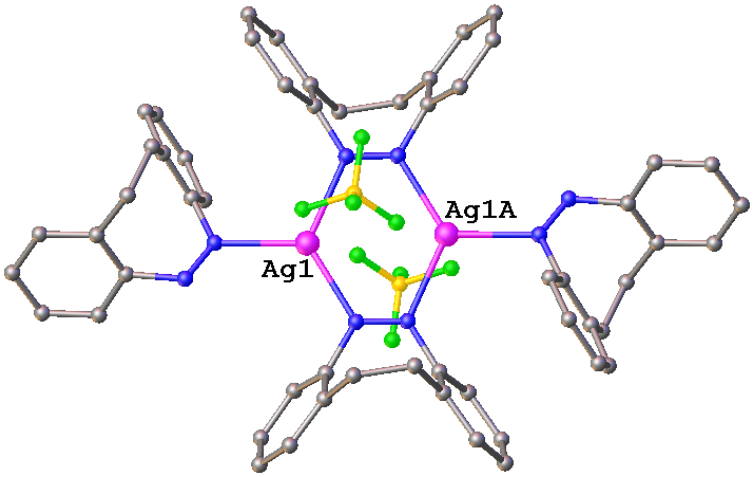

Fig (92) - View showing how 12.10 forms a discrete structure. The hydrogen atoms have been omitted for clarity. A relevant interatomic distance (Å) is Ag1-Ag1A 3.384(1).

While the tetrafluoroborate anion is not coordinating to the silver atom it still plays a role in ordering the structure as seen in Fig (93). There are five hydrogen bonds between the anion and the hydrogen atoms of the ligands the shortest of them is 2.44(2) Å (F2-H4) and the longest is 2.64(2) Å (F3-H26).

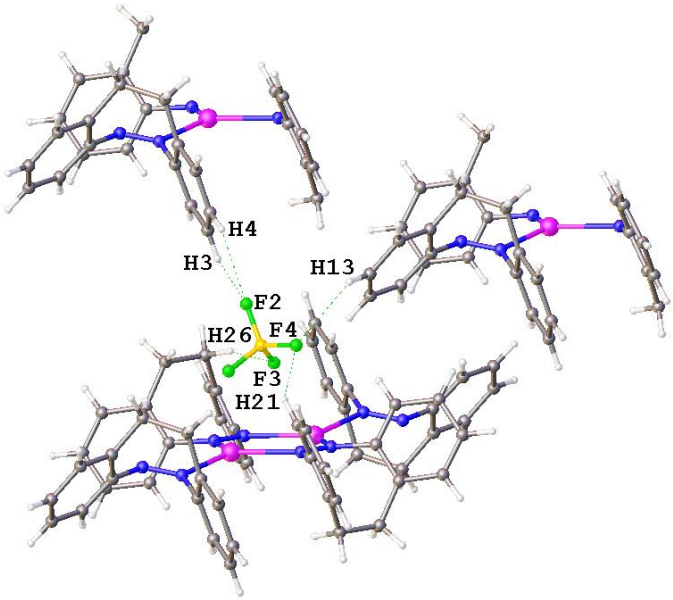

Fig (93) - View of the hydrogen bonding in 12.10. Relevant hydrogen bond lengths (Å) are F2-H3 2.62(2), F2-H4 2.44(2), F3-H26 2.64(2), F4-H13 2.58(2) and F4-H21 2.52(2).

To summarise, the complex is a discrete assembly in which the silver atom adopts a trigonal planar geometry closely matching the idealised angles. There are two different types of 2,2'-ethyleneazobenzene molecule one of which is monodentate while the other is bridging bidentate in a *cis* conformation due to the ethylene bridge. The tetrafluoroborate anion is non-coordinating; it does form hydrogen bonds to order the structure.

With silver(I) perchlorate (12.11)

The complex of 2,2'-ethyleneazobenzene and silver perchlorate has one silver atom, two 2,2'-ethyleneazobenzene molecules and one perchlorate anion in the asymmetric unit. The crystal structure solves in the triclinic space group P-1 with R_1= 0.0245. This complex was made by mixing one equivalent of ligand with three equivalents of silver salt; the ratio in the complex is one to two i.e. [ML_2].

Fig (94) shows the silver atom in a highly distorted and unusual trigonal bipyramidal geometry due to the silver-silver bond. The silver atom has a τ_5 index [31] of 0.71; this indicates a geometry that is intermediate between a square pyramid and a trigonal bipyramid but is closer to a trigonal bipyramid. The ideal angles of a trigonal bipyramid are 120 and 90˚; the silver atom has some angles that are close to the ideal however a few of the angles are very acute these are 63.46(4) (N3-Ag1-Ag1A) and 63.22(4)˚ (N4-Ag1-Ag1A). There are two 2,2'-ethyleneazobenzene molecules in the asymmetric unit. These 2,2'-ethyleneazobenzene molecules are monodentate and bridging bidentate respectively; the bridging bidentate molecules are bridging in a *cis* configuration due to the ethylene group in the 2-position between the rings. This bridging mode has not been observed in any of the previous complexes except the complexes that contain a 2,2'-ethyleneazobenzene molecule. Due to this ethylene group the molecule is rigidly held in the *cis* conformation leading to the aromatic rings and the azo group not being coplanar. The torsion angles are 65.3(2) to 74.7(2)˚ between the aromatic rings and the azo group. The perchlorate anion is coordinated to the silver atom in a monodentate fashion, as shown in Fig (94).

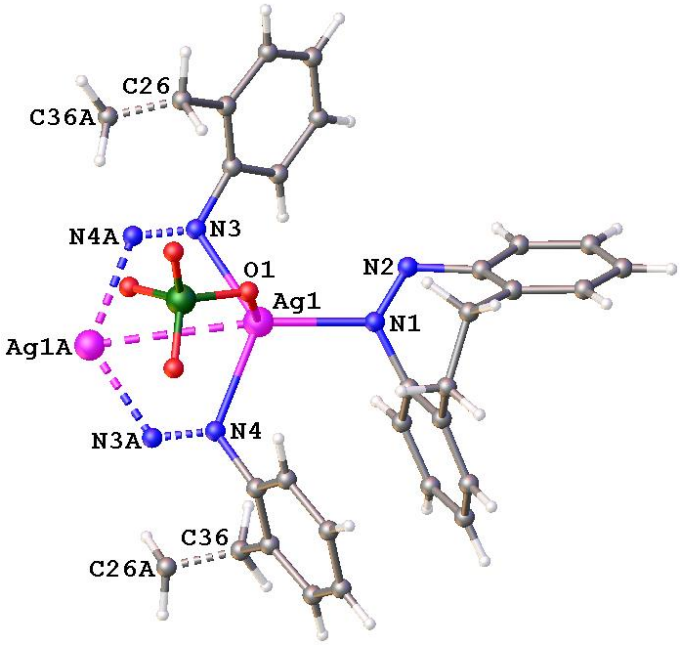

Fig (94) - The asymmetric unit of 12.11. Relevant bond lengths (Å) are Ag1-Ag1A 3.335(1), Ag1-N1 2.2678(16), Ag1-N3 2.2942(14), Ag1-N4 2.3559(14), Ag1-O1 2.5616(16), N1-N2 1.251(2) and N3-N4A 1.250(2). Relevant bond angles (˚) are N1-Ag1-Ag1A 169.29(4), N1-

Ag1-N3 121.30(5), N1-Ag1-N4 111.37(5), N1-Ag1-O1 96.13(5), N3-Ag1-Ag1A 63.46(4), N3-Ag1-N4 126.68(5), N3-Ag1-O1 94.82(5), N4-Ag1-Ag1A 63.22(4), N4-Ag1-O1 87.04(5) and O1-Ag1-Ag1A 92.87(4). Relevant torsion angles (˚) are N1-N2-C10-C11 65.3(2), N2-N1-C1-C2 74.7(2), N3-N4-C30-C31 71.4(2) and N4-N3-C20-C21 65.9(2).

In Fig (95), it is shown that the complex forms a discrete assembly in which four 2,2'-ethyleneazobenzene molecules are bound to two silver atoms to which there are also two perchlorate anions. The ligands are found in two different conformations; two of which are monodentate and the other two are bridging bidentate. The arrangement of ligands and silver atoms forms a structure, which has two trapezia fused together. This arrangement is formed rather than a hexagon due to the silver-silver bond that has a length of 3.335(1) Å, which is a weak silver-silver bond.[28]

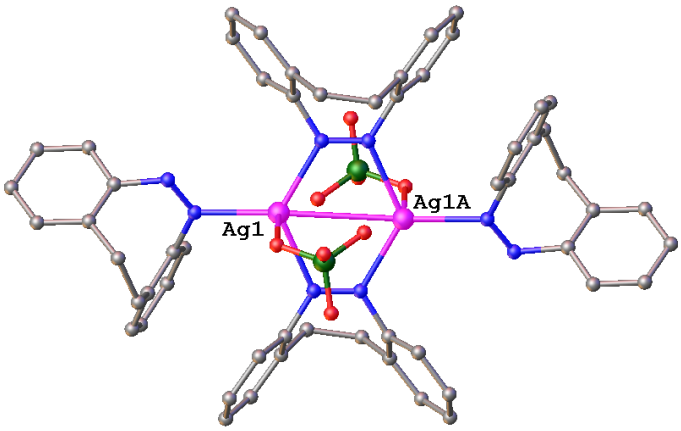

Fig (95) - View showing how 12.11 forms a discrete structure. The hydrogen atoms have been omitted for clarity. A relevant interatomic distance (Å) is Ag1-Ag1A 3.335(1).

The perchlorate anion is instrumental in ordering the discrete units of the structure as seen in Fig (96). These hydrogen bonds have a length of 2.64(2) (O2-H3) and 2.49(2) Å (O2-H4).

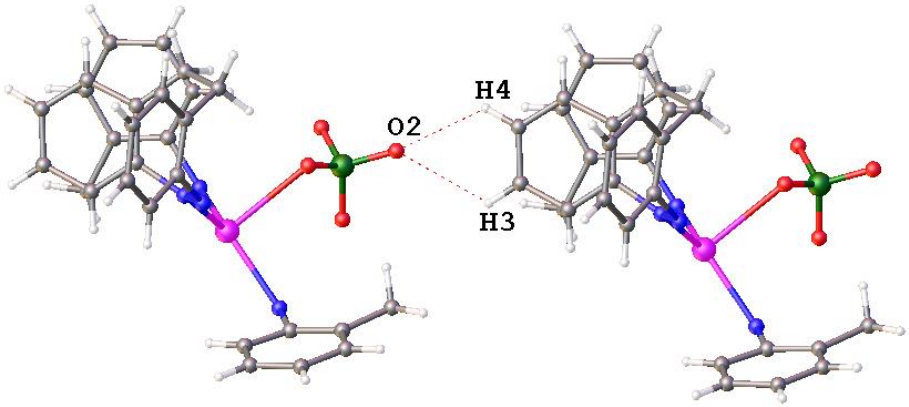

Fig (96) - View of the hydrogen bonding in 12.11. Relevant hydrogen bond lengths (Å) are O2-H3 2.64(2) and O2-H4 2.49(2).

Fig (97) shows the other hydrogen bonds that order the discrete units of the complex. These hydrogen bonds have lengths of 2.65(2) (O3-H36), 2.64(2) (O4-H13) and 2.57(2) Å (O4-H31).

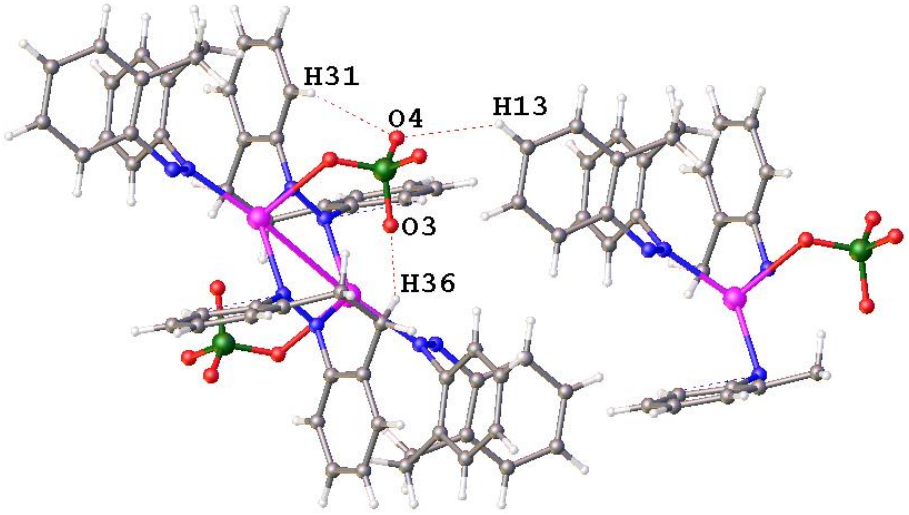

Fig (97) - View of more hydrogen bonding in 12.11. Relevant hydrogen bond lengths (Å) are O3-H36 2.65(2), O4-H13 2.64(2) and O4-H31 2.57(2).

To summarise, the complex is a discrete assembly in which the silver atom adopts a distorted trigonal bipyramidal geometry, which has a τ_5 index [31] of 0.71. This value indicates an intermediate geometry between a square pyramid and a trigonal bipyramid; however, it has a geometry closer to a trigonal bipyramid. There are two different types of 2,2'-ethyleneazobenzene molecule one of which is monodentate while the other is bridging bidentate in a *cis* conformation due to the ethylene bridge. The perchlorate anion is coordinating in a monodentate fashion.

<u>With silver(I) nitrate (12.12)</u>

The complex of 2,2'-ethyleneazobenzene and silver nitrate has one silver atom, two 2,2'-ethyleneazobenzene molecules and one nitrate anion in the asymmetric unit. The crystal structure solves in the monoclinic space group $P2_1/c$ with R_1= 0.0389. This complex was made by mixing one equivalent of ligand with three equivalents of silver salt; the ratio in the complex is one to two i.e. $[ML_2]$.

Fig (98) shows that the silver atom has a distorted trigonal pyramidal geometry; the ideal bond lengths of this geometry are 120 and 90˚. The silver atom has a τ_4 index [32] of 0.79, which indicates an intermediate geometry between tetrahedral and square planar but closer to a tetrahedral geometry. The three angles between the nitrogen atoms and the silver atoms are close to the ideal angle of 120˚; these are 123.67(9) (N1-Ag1-N3), 106.97(9) (N1-Ag1-N4) and 124.72(9)˚ (N3-Ag1-N4). There are two 2,2'-ethyleneazobenzene molecules in the asymmetric unit; one is monodentate and the other is bridging bidentate in a *cis* configuration. This ethylene group is the cause of the azo group and the aromatic rings not

being coplanar; these torsion angles fall between 68.8(4) and 72.5(4)˚. The nitrate anion is coordinated to the silver atom in a monodentate fashion, as seen in Fig (98).

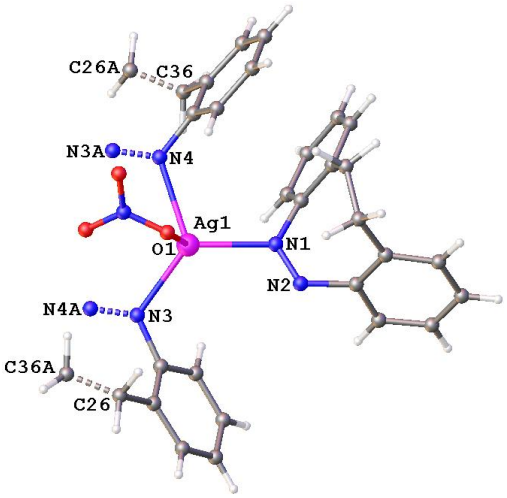

Fig (98) - The asymmetric unit of 12.12. Relevant bond lengths (Å) are Ag1-N1 2.276(3), Ag1-N3 2.288(3), Ag1-N4 2.388(3), Ag1-O1 2.489(3), N1-N2 1.260 and N3-N4A 1.254(4). Relevant bond angles (˚) are N1-Ag1-N3 123.67(9), N1-Ag1-N4 106.97(9), N1-Ag1-O1 108.71(10), N3-Ag1-N4 124.72(9), N3-Ag1-O1 99.61(10) and N4-Ag1-O1 82.18(9). Relevant torsion angles (˚) are N1-N2-C10-C11 72.5(4), N2-N1-C1-C2 68.8(4), N3-N4-C30-C31 70.3(4) and N4-N3-C20-C21 68.9(4).

In Fig (99), it is shown how a discrete assembly is formed with four 2,2'-ethyleneazobenzene molecules, two of which are monodentate while the other two are bridging bidentate in a *cis* configuration. There are two silver atoms and two nitrate anions. This assembles into a hexagonal shape with the silver atoms having a distance between them of 3.421(1) Å.

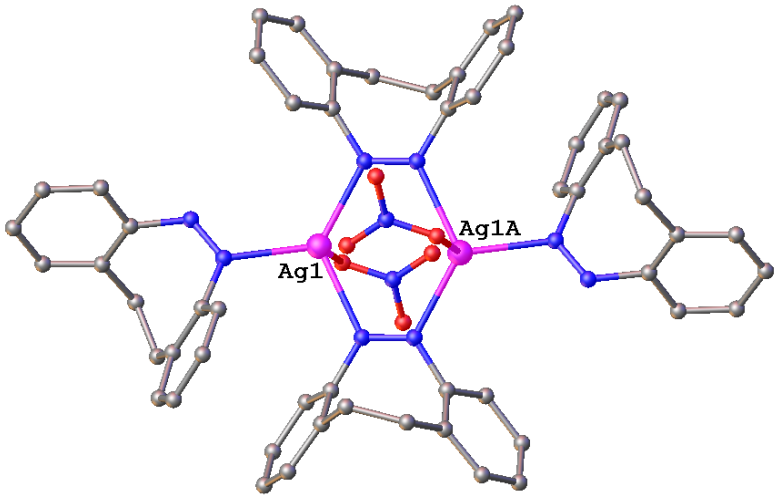

Fig (99) - View showing how 12.12 forms a discrete structure. The hydrogen atoms have been omitted for clarity. A relevant interatomic distance is Ag1-Ag1A 3.421(1).

There is only one hydrogen bond, which orders the structure; this is between O2-H2 and has a length of 2.63(2) Å as seen in Fig (100). This hydrogen bond is responsible for the nitrate anion being roughly in the same plane as the silver-nitrogen bonds.

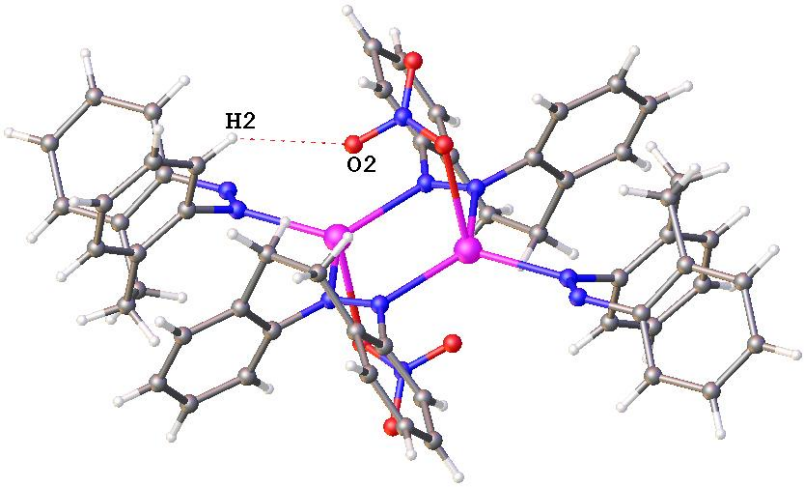

Fig (100) - View of the hydrogen bonding in 12.12. A relevant hydrogen bond length (Å) is O2-H2 2.63(2).

To summarise, the complex is a discrete assembly in which the silver atom adopts a distorted trigonal pyramidal geometry with a τ_4 index [32] of 0.79. This value shows that the silver atom has geometry between a tetrahedron and a square plane, the geometry, in this case is closer to a tetrahedron. The 2,2'-ethyleneazobenzene molecule is found in two different configurations one of which is monodentate while the other is bridging bidentate which is also found in a *cis* conformation. The nitrate anion is monodentate and coordinates to the silver atom via an oxygen atom.

<u>With silver(I) triflate in toluene (12.13)</u>

The complex of 2,2'-ethyleneazobenzene and silver triflate has one silver atom, one 2,2'-ethyleneazobenzene molecule, one triflate anion, one toluene molecule and a water molecule in the asymmetric unit. The crystal structure solves in the triclinic space group P-1 with R_1= 0.0256. This complex was made by mixing one equivalent of ligand with three equivalents of silver salt the ratio in the complex is one to one i.e. [ML].

It is shown in Fig (101) that the silver atoms have a distorted tetrahedral geometry, which has a τ_4 index [32] of 0.85. This value indicates an intermediate geometry between a tetrahedron and a square plane. The value of 0.85 indicates the geometry is closer to a tetrahedron. There is only one 2,2'-ethyleneazobenzene molecule in the asymmetric unit and it has a bridging bidentate coordination mode in a *cis* conformation. The *cis* conformation is observed in this complex due to the ethylene group in the 2-position of the molecule; this causes the azo group of the molecule to be rigidly locked in place. This is also the cause of the torsion angles between the azo group and the aromatic rings; these angles are 69.65(19) and 75.7(2)˚. Fig (101) also shows the non-coordinating triflate anion along

with the coordinating water and toluene molecule. The toluene molecule is coordinated to the silver atom through one of the bonds of the aromatic ring. This is the first complex made in which the triflate anion is non-coordinating.

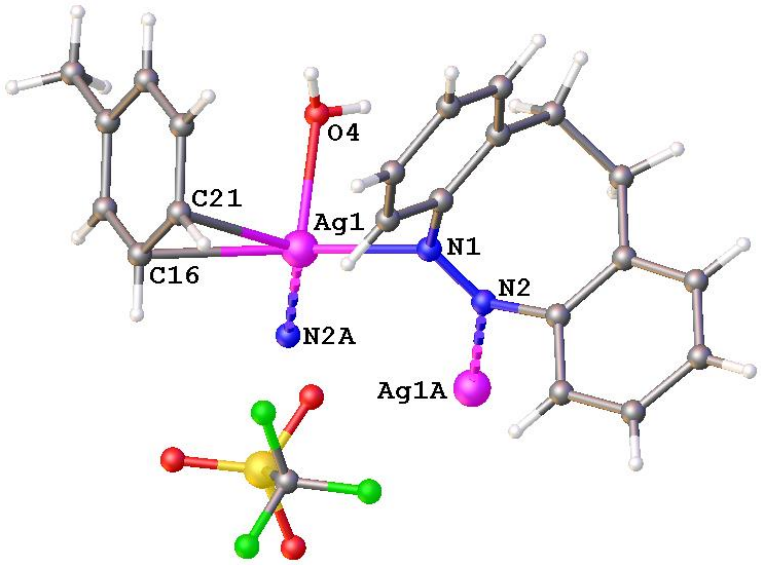

Fig (101) - The asymmetric unit of 12.13. Relevant bond lengths (Å) are Ag1-N1 2.3770(15), Ag1-N2A 2.3658(15), Ag1-O4 2.3939(17), Ag1-C16 2.614(2), Ag1-C21 2.616(2) and N1-N2 1.247(2). Relevant bond angles (˚) are N1-Ag1-N2A 118.56(5), N1-Ag1-O4 97.07(6), N1-Ag1-C16 135.51(6), N1-Ag1-C21 107.66(6), N2A-Ag1-O4 99.77(6), N2A-Ag1-C16 95.86(6), N2A-Ag1-C21 126.48(6), O4-Ag1-C16 104.29(6), O4-Ag1-C21 99.83(7) and C16-Ag1-C21 30.88(6). Relevant torsion angles (˚) are N1-N2-C10-C11 69.65(19) and N2-N1-C1-C2 75.7(2).

Fig (102) shows the discrete assembly of complex 12.13; there are two 2,2'-ethyleneazobenzene molecules both of which are bridging bidentate. These 2,2'-ethyleneazobenzene molecules make four corners of the hexagonal assembly while the two silver atoms make the other two corners; the interatomic distance between the silver atoms is 3.6626(3) Å. The water molecules are perpendicular to the plane of the hexagon and alternate with one up and one down. The triflate anions sit above the pore of the hexagon while the toluene molecules are coordinated to the silver atoms in a way that causes the methyl group to point in the direction of the ethylene bridge of the ligand. The toluene molecule also blocks a coordination site making it impossible for any further 2,2'-ethyleneazobenzene molecules to coordinate.

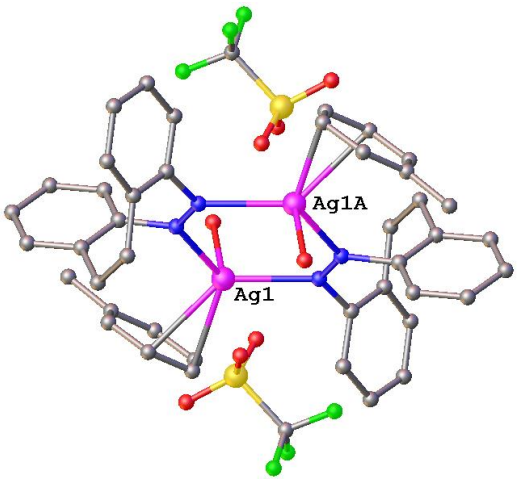

Fig (102) - View showing how 12.13 forms a discrete structure. The hydrogen atoms have been omitted for clarity. A relevant interatomic distance (Å) is 3.663(1).

Even though the triflate anion does not coordinate to the silver atoms it plays a part in ordering the structure through hydrogen bonding as seen in Fig (103). There are four hydrogen bonds one from O1 which has a length of 2.01(2) Å and three from O2 which have lengths of 2.58(2), 2.62(2) and 2.64(2) Å respectively.

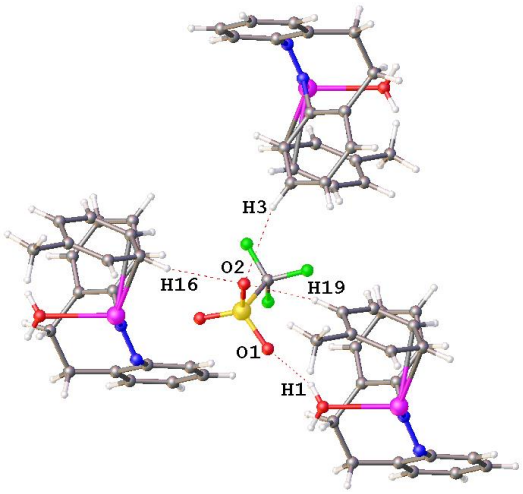

Fig (103) - View of the hydrogen bonding in 12.13. Relevant hydrogen bond lengths (Å) are O1-H1 2.01(2), O2-H3 2.58(2), O2-H16 2.61(2) and O2-H19 2.64(2).

To summarise, the complex is a discrete assembly in which the silver atom has a distorted tetrahedral geometry with a τ_4 index [32] of 0.85. This value indicates an intermediate geometry between tetrahedral and square planar it is closer to a tetrahedral geometry. The 2,2'-ethyleneazobenzene molecule is bridging bidentate with a *cis* conformation due to the ethylene group forcing the azo group to adopt a *cis* conformation. The triflate anions order the structure through hydrogen bonding and simply sit above the pore formed by the hexagonal assembly formed by the silver atoms and the ligand. There are also coordinating

water and toluene molecules. The toluene molecule blocks one of the possible coordination sites so there is no monodentate 2,2'-ethyleneazobenzene molecules in the complex.

With silver(I) triflate in benzene (12.14)

The complex of 2,2'-ethyleneazobenzene and silver triflate has one silver atom, two 2,2'-ethyleneazobenzene molecules, one triflate anion and half a molecule of benzene in the asymmetric unit. The crystal structure solves in the monoclinic space group $P2_1/n$ with R_1= 0.0315. This complex was made by mixing one equivalent of ligand with three equivalents of silver salt; the ratio in the complex is one to two i.e. $[ML_2]$.

It is shown in Fig (104) that the silver atom has a trigonal pyramidal geometry which is distorted somewhat. The silver atom has a τ_4 index [32] of 0.83 indicating an intermediate geometry between a tetrahedron and a square plane; in this case the geometry of the silver atom is closer to tetrahedral. There are two types of 2,2'-ethyleneazobenzene molecule in a monodentate and a bidentate binding modes. The bidentate 2,2'-ethyleneazobenzene molecule is bridging in a *cis* conformation due to the ethylene group which rigidly holds this conformation. This ethylene group is also the reason for the aromatic rings and the azo group not being coplanar. The torsion angles in the monodentate ligand are 63.4(2) and 71.9(3)˚ while the torsion angles for the bidentate ligand are 61.8(2) and 76.9(3)˚. Fig (104) also shows the triflate anion coordinating in a monodentate fashion and the non-coordinating half benzene molecule. The CF_3 and SO_3 groups are staggered in relation to each other to minimise the eclipsing interactions.

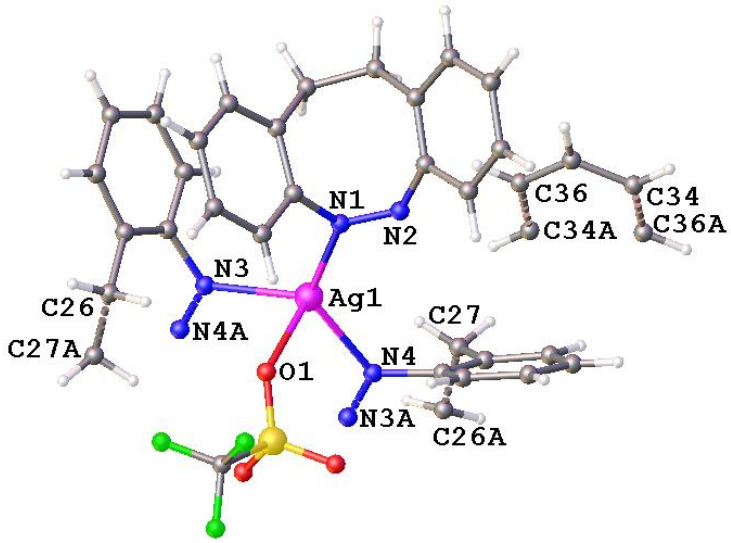

Fig (104) - The asymmetric unit of 12.14. Relevant bond lengths (Å) are Ag1-N1 2.2675(18), Ag1-N3 2.3031(18), Ag1-N4 2.2796(17), Ag1-O1 2.5188(18), N1-N2 1.253(3) and N3-N4A 1.256(2). Relevant bond angles (˚) are N1-Ag1-N3 116.15(6), N1-Ag1-N4 126.05(7), N1-Ag1-O1 91.09(7), N3-Ag1-N4 117.37(6), N3-Ag1-O1 89.46(7) and N4-Ag1-O1 94.86(6). Relevant torsion angles (˚) are N1-N2-C10-C11 63.4(2), N2-N1-C1-C2 71.9(3), N3-N4-C30-C31 61.8(2) and N4-N3-C20-C21 76.9(3).

Fig (105) shows how the silver atoms and the ligands assemble into a discrete assembly. The arrangement of ligands and silver atoms create a hexagon, above which the monodentate triflate anions are found. The hexagon is constructed by the bridging bidentate 2,2'-ethyleneazobenzene molecules, which form four corners and the silver atoms forming another two corners. The distance between the two silver atoms is 3.607(1) Å.

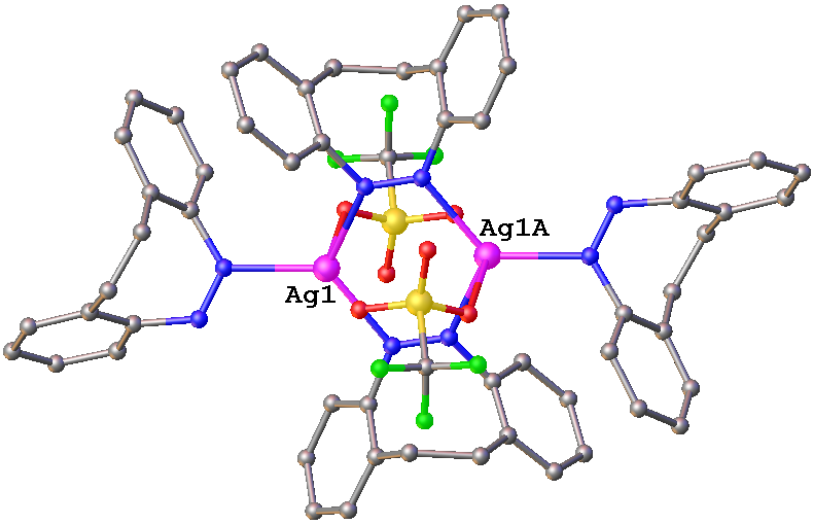

Fig (105) - View showing how 12.14 forms a discrete structure. The hydrogen atoms and benzene molecules have been omitted for clarity. A relevant interatomic distance (Å) is 3.607(1).

The triflate anion forms two hydrogen bonds to order the structure as shown in Fig (106). These hydrogen bonds have lengths of 2.52(2) (O1-H2) and 2.41(2) Å (O3-H30).

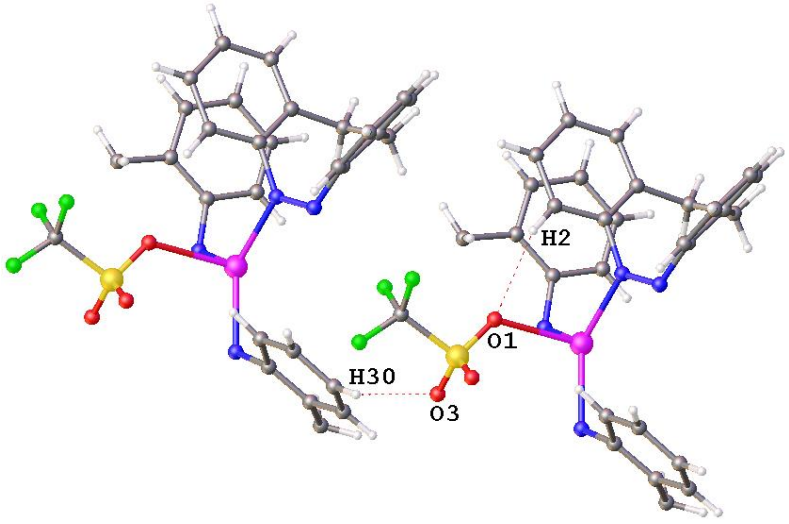

Fig (106) - View of the hydrogen bonding in 12.14. Relevant hydrogen bond lengths (Å) are O1-H2 2.52(2) and O3-H30 2.41(2).

To summarise, the structure is a discrete assembly with the silver atoms adopting a trigonal pyramidal geometry with a τ_4 index [32] of 0.83. This value indicates an intermediate geometry

between tetrahedral and square planar, which is closer to a tetrahedral geometry. There are two types of 2,2'-ethyleneazobenzene molecule one of which is monodentate and another which is bridging bidentate. The bridging bidentate ligand is found to have a *cis* configuration due to rigidly being held in a *cis* configuration by the bridging ethylene group. The triflate anions are monodentate and bound to the silver atoms via an oxygen atom. The triflate anion also forms hydrogen bonds to help order the complex. The benzene molecules simply sit in the pores between the discrete units of the complex.

With silver(I) trifluoroacetate (12.15)

The complex of 2,2'-ethyleneazobenzene and silver trifluoroacetate has two silver atoms, two 2,2'-ethyleneazobenzene molecules, two trifluoroacetate anions and a disordered toluene molecule in the asymmetric unit. The crystal structure solves in the triclinic space group P-1 with R_1= 0.0647. This complex was made by mixing one equivalent of ligand with three equivalents of silver salt; the ratio in the complex is one to one i.e. [ML].

It is shown in Fig (107) that there are two types of silver atom; one silver atom has a distorted octahedral geometry (Ag2) due to the silver-silver bonds. An ideal octahedron has angles of 180 and 90˚; the angles around the silver atom in 12.15 are much more acute than they should be. The other silver atom has a square pyramidal geometry (Ag1) again due to the silver-silver bonds; the τ_5 index [31] of this silver atom is 0.04, which strongly indicates a square pyramidal rather than a trigonal bipyramidal geometry. The 2,2'-ethyleneazobenzene molecules adopt two different binding modes, these are monodentate and bridging bidentate. The bridging bidentate 2,2'-ethyleneazobenzene molecules are in a *cis* conformation due to the bridging ethylene group in the 2-position keeping the molecule rigidly in the *cis* conformation. The azo groups and the aromatic rings are not coplanar as the ethylene group forces them out of the plane relative to each other; the torsion angles of the aromatic rings and the azo group are between 61.1(7) and 74.7(9)˚. Fig (107) also shows the trifluoroacetate anions binding to the silver atoms in a bridging bidentate fashion; this causes them to form two fused five membered rings. There is some disorder in the orientation of one of the CF_3 groups. There is also a toluene molecule, which is disordered in an unusual way; this disorder is caused by two toluene molecules becoming superimposed on top of one another.

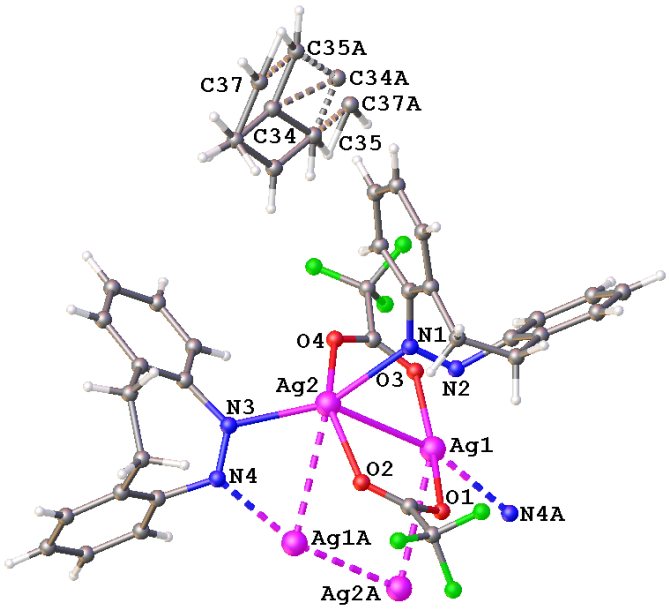

Fig (107) - The asymmetric unit of 12.15. Relevant bond lengths (Å) are Ag1-Ag2 3.029(1), Ag1-Ag2A 3.324(1), Ag1-N4A 2.439(5), Ag1-O1 2.263(5), Ag1-O3 2.211(5), Ag2-N1 2.446(5), Ag2-N3 2.348(5), Ag2-O2 2.366(5), Ag2-O4 2.312(5), N1-N2 1.254(7) and N3-N4 1.247(7). Relevant bond angles (˚) are O1-Ag1-Ag2 84.61(11), O1-Ag1-Ag2A 62.74(14), O1-Ag1-O3 163.73(17), O1-Ag1-N4A 78.92(16), O3-Ag1-Ag2 82.49(11), O3-Ag1-Ag2A 129.51(15), O3-Ag1-N4A 115.51(16), N4A-Ag1-Ag2 161.33(12), N4A-Ag1-Ag2A 62.26(12), Ag2-Ag1-Ag2A 103.057(19), O2-Ag1-O4 153.32(16), O2-Ag2-N1 87.74(18), O2-Ag2-N3 94.78(16), O2-Ag2-Ag1 76.45(10), O2-Ag2-Ag1A 55.67(12), O4-Ag2-N1 82.92(19), O4-Ag2-N3 107.35(17), O4-Ag2-Ag1 77.03(12), O4-Ag2-Ag1A 120.17(15), N1-Ag2-N3 144.26(18), N1-Ag2-Ag1 75.68(12), N1-Ag2-Ag1A 138.48(13), N3-Ag2-Ag1 139.52(13), N3-Ag2-Ag1A 66.06(13) and Ag1-Ag2-Ag1A 76.943(19). Relevant torsion angles (˚) are N1-N2-C10-C11 74.7(9), N2-N1-C1-C2 65.8(7), N3-N4-C30-C31 61.1(7) and N4-N3-C20-C21 69.6(9).

Fig (108) shows the discrete assembly that is formed from four 2,2'-ethyleneazobenzene molecules and four silver atoms along with four trifluoroacetate anions. A square is formed by the silver atoms, which have only two different silver-silver bond lengths due to a crystallographic centre of inversion; these distances are 3.029(1) (Ag1-Ag2) and 3.324(1) Å (Ag1-Ag2A). These bond lengths indicate that these are quite weak silver-silver bonds. [28] The diagonal distances of the square are 3.959(1) (Ag1-Ag1A) and 4.977(1) Å (Ag2-Ag2A) in length. The bridging 2,2'-ethyleneazobenzene molecules form trapezoids while the trifluoroacetate anions form fused five membered rings this leads to a highly unusual assembly of four five membered rings and three four membered rings.

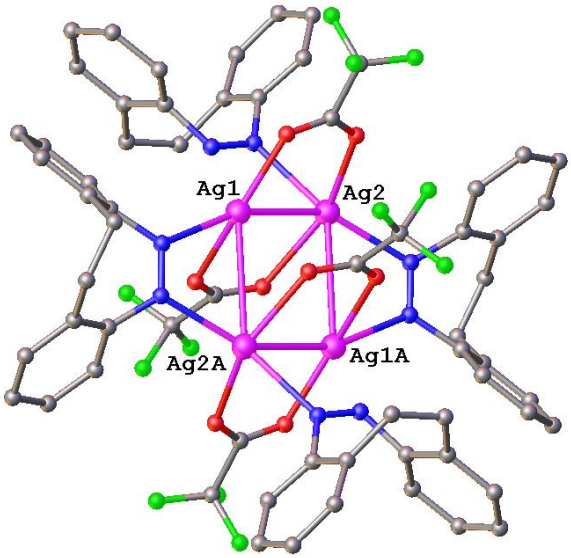

Fig (108) - View showing how 12.15 forms a discrete structure. The toluene molecule and hydrogen atoms have been omitted for clarity. Relevant interatomic distances (Å) are Ag1-Ag2 3.029(1), Ag1-Ag2A 3.324(1), Ag1-Ag1A 3.959(1) and Ag2-Ag2A 4.977(1).

As the trifluoroacetate anions point outwards from the complex they can form hydrogen bonds and fluorine-fluorine interactions as seen in Fig (109). The fluorine-fluorine interactions in this complex are considered quite strong [27] with distances of 2.93(2) (F3-F5) and 2.96(2) Å (F5-F6A).

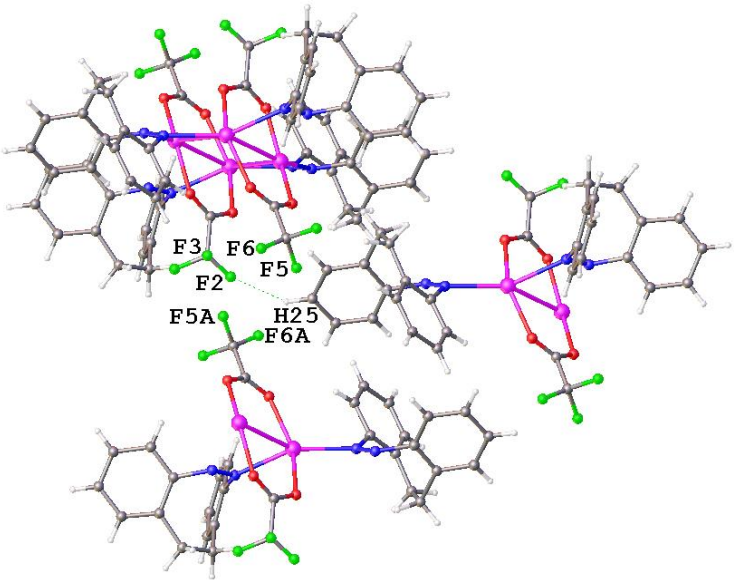

Fig (109) - View of the hydrogen bonding and fluorine-fluorine interactions in 11.15. Relevant interatomic distances (Å) are F2-H25 2.60(2), F3-F5 2.93(2) and F5-F6A 2.96(2).

To summarise, the structure of the complex is a discrete assembly with two different types of silver atom; a square pyramidal (Ag1) and a distorted octahedral (Ag2). The five-coordinate silver atom has a τ_5 index [31] of 0.04 strongly indicating a square pyramidal

geometry. The trifluoroacetate anions are bridging bidentate and coordinate to the silver atoms via oxygen atoms. There are two types of 2,2'-ethyleneazobenzene molecules one of which is monodentate while the other is bridging bidentate; the bridging bidentate ligand is in a *cis* conformation due to the bridging ethylene group in the 2-position. Overall the discrete assembly forms a square of silver atoms in an unusual arrangement with the trifluoroacetate anions forming fused five membered rings and the bidentate 2,2'-ethyleneazobenzene molecules forming four membered rings.

The structures with 2,2'-ethyleneazobenzene molecules have roughly the same molecular topology especially the structures 12.10, 12.11, 12.12 and 12.14; these complexes have less complicated anions except for 12.14. The four aforementioned structures all have similar asymmetric units except for 12.11 and 12.14, which has a silver-silver bond and a half molecule of benzene in the asymmetric unit respectively. This would indicate that it is the ligand rather than the anion that has the greater impact on the resulting structure. 12.13 is unusual as the solvent plays a role in determining the structure of the complex. The toluene molecule coordinates to the silver molecule via a bond in the aromatic ring and blocks off a potential coordination site for the 2,2'-ethyleneazobenzene molecules. There is also a water molecule that coordinates to the silver atom and blocks the site that the anion would usually bind to. 12.15 is unusual in this series as the anion plays the most important role in determining the structure of the complex. The trifluoroacetate anions cause the silver atoms to form a square upon which the 2,2'-ethyleneazobenzene molecules coordinate in either a monodentate or bidentate fashion.

13.1 complexes of 2,2'-azobispyridine

With silver(I) triflate (13.10)

The complex of 2,2'-azobispyridine and silver triflate has one silver atom, two half molecules of 2,2'-azobispyridine and one triflate anion in the asymmetric unit. The crystal structure solves in the monoclinic space group $P2_1/n$ with R_1= 0.0204. This complex was made by mixing one equivalent of ligand with two equivalents of silver salt; the ratio in the complex is one to one i.e. [ML].

The silver atom of complex 13.10 has an unusual four coordinate geometry, as seen in Fig (110), in which the silver atom is coordinated to the nitrogen atoms of the azo group and the nitrogen atom in the pyridine ring. The τ_4 index [32] is 0.49, which indicates an intermediate geometry between tetrahedron and a square plane. Two of the angles are very acute (52.77(5) and 68.80(5)˚) while two of the other angles are similar to the ideal angle of a square plane (116.95(5) and 124.38(5)˚); the other two angles are quite obtuse (133.87(5) and 157.47(6)˚). Fig (110) also shows the two half molecules of 2,2'-azobispyridine which are bridging tetradentate with the azo group and the nitrogen of the pyridine ring coordinating to the silver atom. The pyridine rings are almost coplanar due to the azo group and the pyridine ring coordinating to the same silver atom; the torsion angles are 5.0(3)˚ for the ring

containing N1 and 10.6(3)˚ for the ring containing N3. The triflate anion is non-coordinating and has a staggered conformation that lowers the energy, as there are no eclipsing interactions.

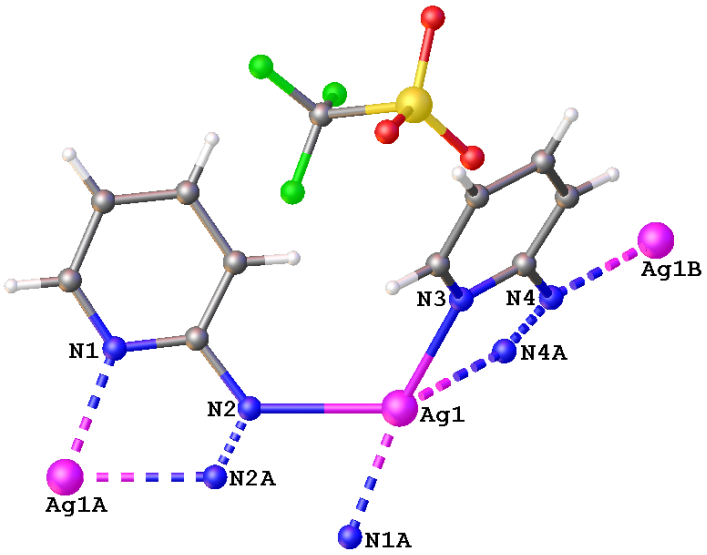

Fig (110) - The asymmetric unit of 13.10. Relevant bond lengths (Å) are N1-Ag1A 2.2440(15), N2-Ag1 2.4305(15), N3-Ag1 2.2527(16), N4-Ag1B 2.4054(14), N2-N2A 1.255(3) and N4-N4A 1.255(3). Relevant bond angles (˚) are N2-Ag1-N1A 68.80(5), N2-Ag1-N3 116.95(5), N2-Ag1-N4A 133.87(5), N3-Ag1-N4A 52.77(5), N3-Ag1-N1A 157.47(6) and N1A-Ag1-N4A 124.38(5). Relevant torsion angles (˚) are N2A-N2-C1-N1 5.0(3) and N4A-N4-C10-N3 10.6(3).

Fig (111) shows the 1-D nature of the metallopolymer; the seesaw nature of the four coordinate silver atom can be seen much better in this figure. The tetradentate nature of the 2,2'-azobispyridine molecule is also much more evident in the polymeric structure. Due to the chelate effect this structure forms five membered chelate rings which are particularly stable.

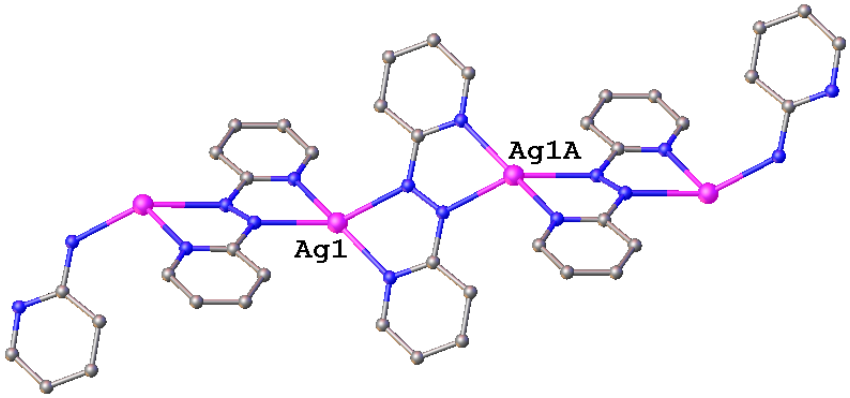

Fig (111) - View of a short strand of the polymer 13.10. The hydrogen atoms have been omitted for clarity. A relevant interatomic distance (Å) is Ag1-Ag1A 5.495(1).

It is shown in Fig (112) how the inter-strand hydrogen bonds organise the strands of the metallopolymer 13.10. The non-coordinating triflate anion may not coordinate to the silver atom; however, it has a large impact in organising the structure. All of the oxygen atoms have hydrogen bonding interactions; the longest hydrogen bond is 2.60(2) Å, while the shortest is 2.50(2) Å.

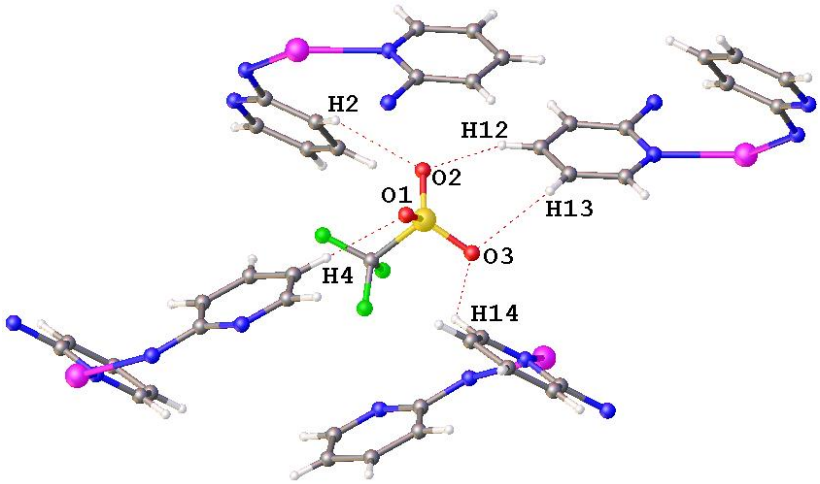

Fig (112) - View of the inter-strand hydrogen bonding between oxygen in 13.10. Relevant hydrogen bond lengths (Å) are O1-H4 2.50(2), O2-H2 2.59(2), O2-H12 2.55(2), O3-H13 2.50(2) and O3-H14 2.60(2).

Fig (113) shows the other hydrogen bonds that act to further order the complex. The hydrogen bond lengths are 2.60(2) and 2.55(2) Å.

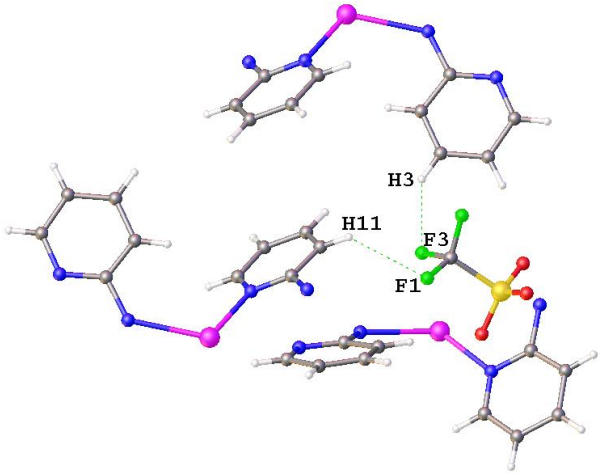

Fig (113) - View of the inter-strand hydrogen bonding between fluorine in 13.10. Relevant hydrogen bond lengths (Å) are F1-H11 2.60(2) and F3-H3 2.55(2).

To summarise, the structure of the complex is a 1-D metallopolymer in which the silver atom has a seesaw like geometry with a τ_4 index [32] of 0.49, this indicates an intermediate geometry between a tetrahedron and a square plane. The triflate anion is non-coordinating; however, it has several hydrogen bonding interactions between oxygen/fluorine and

hydrogen. The 2,2'-azobispyridine ligand is tetradentate with all the nitrogen atoms in the ligand cooridinated to the silver atoms.

The structure with 2,2'-azobispyridine forms a chain of five membered chelate rings. This effect has a much greater effect on the structure than the effect from the anion that has been observed in the previous complexes.

14.1 complexes of 4,4'-azobispyridine

With silver(I) trifluoroacetate (14.10)

The complex of 4,4'-azobispyridine and silver trifluoroacetate has one silver atom, one molecule of 4,4'-azobispyridine, one trifluoroacetate anion and a water molecule in the asymmetric unit. The crystal structure solves in the triclinic space group P-1 with R_1= 0.0533. This complex was made by mixing one equivalent of ligand with two equivalents of silver salt; the ratio in the complex is one to one i.e. [ML].

The silver atom has a highly distorted trigonal planar geometry; which is an almost perfect T-shape as can be seen in Fig (114). The angles around the silver atom are 170.35(17) (N1-Ag1-N4), 100.45(12) (N1-Ag1-Ag1A) and 88.45(12)˚ (N4-Ag1-Ag1A). Fig (114) also shows the 4,4'-azobispyridine which is bridging bidentate through the nitrogen atoms of the pyridine rings. The pyridine rings are rotated out of the plane of the azo group by only 16.5(7) and 13.2(9)˚ for the pyridine ring containing N1 and N4 respectively. The pyridine rings are almost coplanar with an angle of only 5.21(19)˚ between them. The trifluoroacetate anion is non-coordinating and has a disordered CF_3 group and a disordered CO_2 group. It can also be seen in Fig (114) that there is a non-coordinating water molecule.

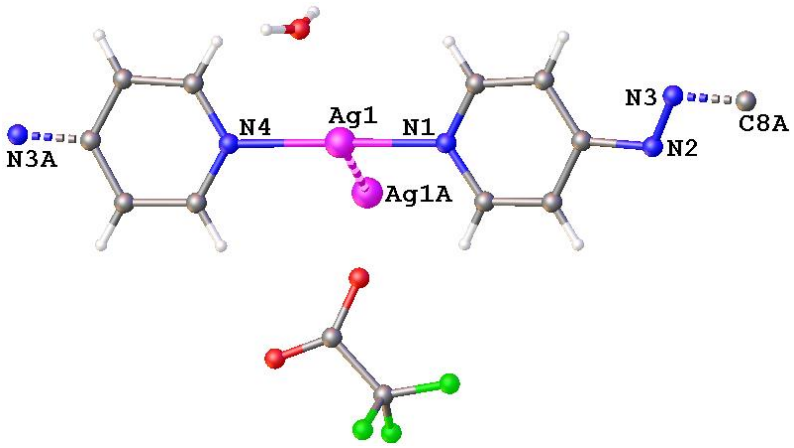

Fig (114) - The asymmetric unit of 14.10. Relevant bond lengths (Å) are N1-Ag1 2.179(4), N4-Ag1 2.182(5), Ag1-Ag1A 3.198(1). and N2-N3 1.195(8). Relevant bond angles (˚) are N1-Ag1-N4 170.35(17), N1-Ag1-Ag1A 100.45(12) and N4-Ag1-Ag1A 88.45(12). Relevant torsion angles (˚) are N2-N3-C8-C9 16.5(7), N3-N2-C1-C2 13.2(9) and RingN1-RingN2 5.21(19).

Fig (115) shows the 1-D ladder-like structure of the complex; the bidentate 4,4'-azobispyridine ligands bridge the T-shaped silver atoms.

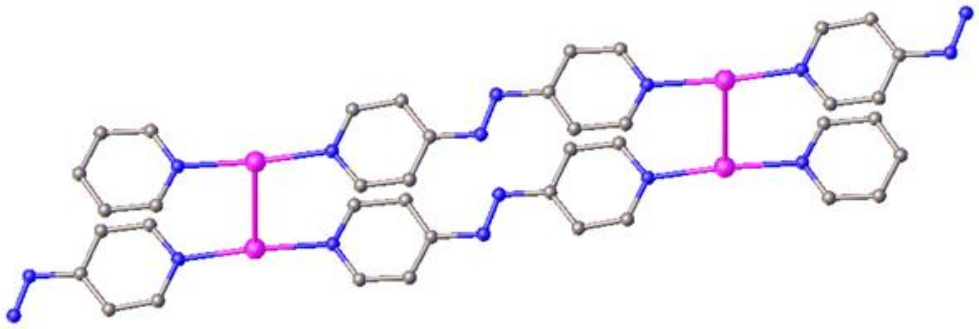

Fig (115) - View of a short strand of the polymer 14.10. The hydrogen atoms have been omitted for clarity.

It is shown in Fig (116) how inter-strand hydrogen bonds order the strands of the complex. The trifluoroacetate anions and the water molecules do not coordinate to the silver atom, yet they still have a role in ordering the structure. The longest hydrogen bond is 2.61(2) Å, while the shortest hydrogen bond is 1.61(2) Å.

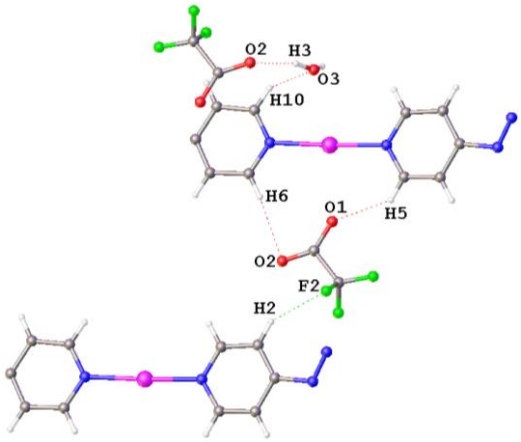

Fig (116) - View of the hydrogen bonding in 14.10. Relevant hydrogen bond lengths (Å) are O1-H5 2.51(2), O2-H6 2.38(2), O3-H10 2.61(2), O2-H3 1.61(2) and F2-H2 2.59(2).

To summarise, the structure is a 1-D metallopolymer in which the silver atom adopts a T-shaped geometry. The trifluoroacetate anion does not coordinate to the silver atom, neither does the water molecule; however they order the complex with hydrogen bonding. The 4,4'-azobispyridine ligand is bridging bidentate through the nitrogen atoms of the pyridine rings.

The structure with 4,4'-azobispyridine forms a chain of linked rectangles. Similarly to the complex 13.10 the anion does not have the greatest effect on the structure; rather the nitrogen atoms of the pyridine rings seem to be the most important factor that determines this particular structure.

15.1 complexes of diphenyltriazine

With silver(I) perchlorate (15.10)

The complex of diphenyltriazine and silver perchlorate has one silver atom and one diphenyltriazine molecule in the asymmetric unit; no perchlorate anions are found in the asymmetric unit. The crystal structure solves in the monoclinic space group C2/c with an R_1= 0.0460. This complex was made by mixing one equivalent of ligand with one equivalent of silver salt; the ratio in the complex is one to one i.e. [ML].

Fig (117) shows how the silver atom adopts a T-shaped geometry. The bond angles around the silver atom are very close to 90˚ with angles of 83.81(10) (Ag1A-Ag1-N1) and 83.99(10); the other angle is 167.77(14) (N1-Ag1-N3). The asymmetric unit also contains a molecule of diphenyltriazine. When the structure is grown it is chelating bidentate. The torsion angles are found to be 3.3(7) and 0.2(7)˚ for the azo groups and the aromatic rings, which indicates it is very close to planar. There is also a silver-silver bond which has a length of 2.6814(18) Å; this is very strong silver-silver bond. Silver-silver bonds are variable in nature and can range up to 3.102 Å.[28] This complex has been synthesised previously.[34] However X-ray crystallography was performed at room temperature, whereas this complex was done at 138K. This gave an R_1 of 0.0460 as opposed to the original 0.0470.

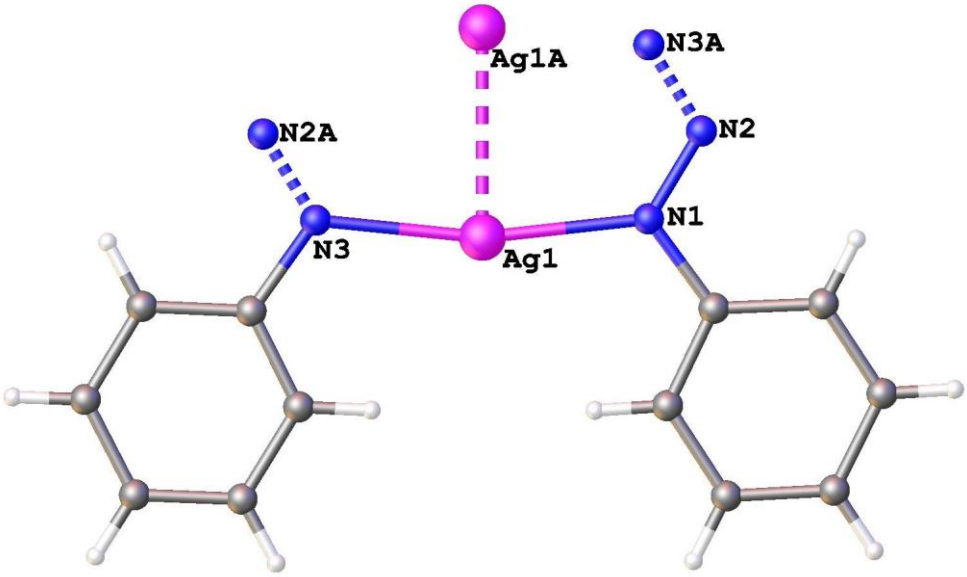

Fig (117) - The asymmetric unit of 15.10. Relevant bond lengths (Å) are Ag1-N1 2.139(4), Ag1-N3 2.147(4), N1-N2 1.312(5), N3-N2A 1.292(5) and Ag1-Ag1A 2.681(1). Relevant bond angles (˚) are N1-Ag1-N3 167.77(14), Ag1A-Ag1-N1 83.81(10), Ag1A-Ag1-N3 83.99(10) and N1-N2-N3A 117.5(4). Relevant torsion angles (˚) are N2-N1-C1-C2 3.3(7) and N2A-N3-C10-C11 0.2(7).

In Fig (118), it is shown how the complex is a discrete assembly consisting of two diphenyltriazine molecules both of which are chelating bidentate. There are two silver atoms, which have a very short silver-silver bond between them.

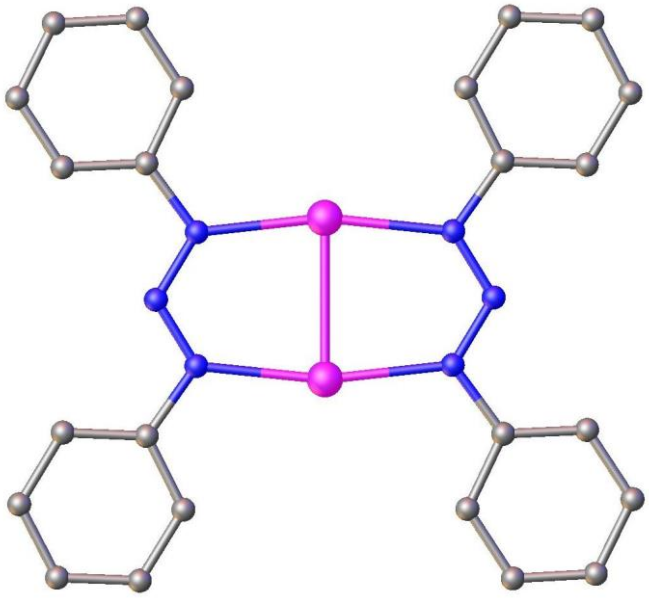

Fig (118) - View showing how 15.10 forms a discrete structure. The hydrogen atoms have been omitted for clarity.

In Fig (119), we see how the complex is planar. The aromatic rings are only 0.2(7) and 3.3(7) Å out of the plane respectively.

Fig (119) - View showing how 15.10 is almost perfectly planar. The hydrogen atoms have been omitted for clarity.

Fig (120) shows how the discrete units arrange into a herringbone configuration. This is commonly seen with planar molecules.[35]

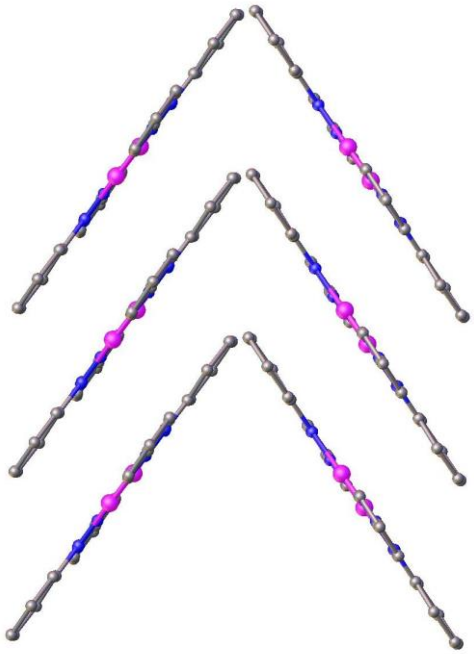

Fig (120) - View showing how the discrete units of 15.10 form a herringbone pattern.

To summarise, the structure is discrete with the silver atoms adopting a T-shaped geometry. There are no anions in the structure as one of the nitrogen atoms carries a negative charge so a neutral species is formed. The diphenyltriazine ligand is chelating bidentate through the two nitrogen atoms closest to the aromatic rings.

This structure has no similarities to any other structures, as the triazine group behaves in a *cis* fashion and it has no need of an anion to balance the charge, unlike the complexes 12.10-15.

16.1 other ligands

Several other ligands were used in attempts to make crystals suitable for X-ray analysis. However, no crystals were produced or the crystals were of a quality/size that made them unsuitable for X-ray crystallography. The ligands were azoxybenzene, 3,3'-azobispyridine, 4-methoxy-4'-nitroazobenzene, 4-dimethylamino-4'-nitroazobenzene and 4,4'-dicarboxyazobenzene. These ligands were tried using the method stated in the next chapter with the silver salts tetrafluoroborate, hexafluorophosphate, perchlorate, nitrate, triflate and trifluoroacetate. These silver salts were used in ratios varying from 1:1, 1:2, 1:3 and 2:1.

Chapter Three

Conclusion

Conclusion

Previously there has only been one silver(I) complex of azobenzene reported. Due to the ability of azobenzene to bind to silver atoms through a variety of binding modes it should be an interesting molecule for further research. Azobenzene is also relatively easy to derivatise as there are several methods for their synthesis including diazocoupling and the Mill's reaction. This leads to a huge variety of possible complexes. Another useful property of azobenzene and derivatives is the ability of the nitrogen-nitrogen double bond to photoisomerise leading to possible functionality in their complexes.

This thesis has described thirty four different silver(I)-azobenzene complexes, only two of which have been previously published.

As this research progressed some interesting trends were discovered. Simple unsubstituted, mono- and di- substituted azobenzene derivatives generally formed the same molecular topology with the same anion, especially if that anion was coordinating. The generally non-coordinating anions tetrafluoroborate and hexafluororphosphate were more unpredictable in their effects on molecular topology, as they were unable to bind to the silver atoms to influence the structure. This trend was not seen in the sterically hindered azobenzene derivatives 2,6,2',6'-tetramethyl and 2,6-dimethyl-4'-chloroazobenzene. These ligands had unpredictable structures that seemed to be influenced by the anion differently as the methyl groups in the 2- and 6- positions rotated the aromatic ring out of the plane of the azo group; often so much so that it was orthogonal to the plane of the azo group. Such trends were not observed when 2,2'-ethyleneazobenzene was used, with all the resulting complexes having very similar molecular topologies regardless of the nature of the anion used. This observation was due to the ethylene group forcing the azo group to be in a *cis* conformation, which then behaved in a different manner to the ligands with a *trans* conformation. As predicted the ligands containing additional nitrogen atoms such as 2,2'- and 4,4'-azobispyridine along with diphenyltriazine do not follow the trend observed earlier, as they can coordinate through additional nitrogen atoms in the aromatic ring or in the case of diphenyltriazine an additional nitrogen atom in the triazine group.

Chapter Four

Experimental

Experimental

3.1 Preparation of ligands

All ligands used in the project were available within the department and used as is, except for those discussed below.

3.11-13 General preparation of the azobispyridines

The azobispyridines were synthesised by using a literature method.[35] 3g (32mmol) of the corresponding amino pyridine was added to 50ml of H_2O in a 250ml round bottom flask and stirred in an ice bath. To this solution 150ml of 15% sodium hypochlorite solution was added dropwise over half an hour. The solution turned from colourless to red for the 2- isomer and orange for the 3- and 4- isomers. The solutions were extracted with dichloromethane and the organic phases were dried over anhydrous sodium sulphate. The organic phases were concentrated under vacuum to give red crystals for the 2- isomer, and orange powders for the 3- and the 4- isomers. The yield of 2,2'-azobispyridine was 1.01g or 34.4% with a melting point of 73˚C. The literature melting point is 81˚C. [36] The yield for 3,3'-azobispyridine was 1.10g or 36.6% with a melting point of 132˚C. The literature melting point is 141˚C. [37] The yield for 4,4'-azobispyridine was 1.31g or 44.4% with a melting point of 103˚C. The literature melting point is 107˚C. [38]

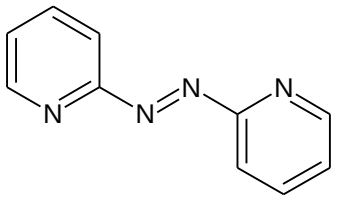

Fig (1) - 2,2'-Azobispyridine.

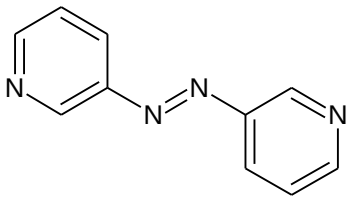

Fig (2) - 3,3'-Azobispyridine.

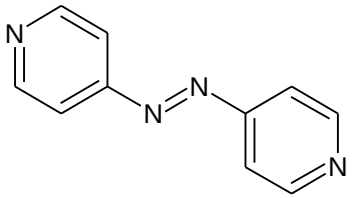

Fig (3) - 4,4'-Azobispyridine.

3.14 Preparation of diphenyltriazine

Diphenyltriazine was synthesised from a literature procedure. [39] 7ml of concentrated hydrochloric acid was added to a mixture of 25ml of H_2O and 5ml (54mmol) of aniline in a 250ml round bottom flask. The mixture was stirred in an ice bath while 20g of crushed ice was added to the mixture and a solution of 1.5g of sodium nitrite in 5ml of H_2O was added over ten minutes. The mixture was stirred for half an hour and a solution of 7g of sodium acetate in 15ml of H_2O was added over a period of five minutes. Immediately a yellow precipitate was formed. As the stirring continued, the yellow precipitate turned brown. The precipitate was stirred for an hour with the temperature not exceeding 20˚C. The precipitate was filtered, washed with cold H_2O and allowed to dry. The brown precipitate was then recrystallised from petroleum ether to give bright yellow flakes. The yield was 2.09g or 39.3% with a melting point of 92˚C. The literature melting point is 97˚C. [39]

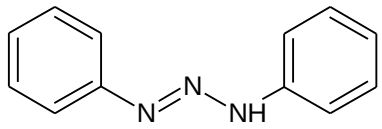

Fig (4) - Diphenyltriazine.

3.15 Preparation of 4-nitro-nitrosobenzene

4-Nitro-nitrososbenzene was synthesised according to a literature procedure. [40] 15g of oxone was added to 150ml of H_2O in a 250ml round bottom flask. This solution was stirred in an ice bath and once the solution was under 5˚C, 3g of 4-nitroaniline (22mmol) was added. The mixture was stirred for 48 hours during which time a yellow precipitate resulted. After 48 hours the solution was filtered off giving a yellow solid. The yellow solid was recrystallised from methanol to give yellow plates. The yield was 2.47g or 73.7% with a melting point of 118˚C. The literature melting point was 127˚C. [40]

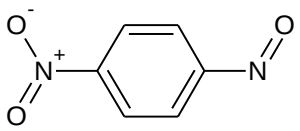

Fig (5) - 4-Nitro-nitrosobenzene.

3.16 Preparation of 4-methoxy-4'-nitroazobenzene

4-Methoxy-4'-nitroazobenzene was synthesised by adopting a literature method.[41] 1g of 4-nitro-nitrosobenzene (7mmol) was added to a solution of 1g of 4-nitroanisidine (8mmol) in glacial acetic acid; the mixture was stirred at room temperature for 24 hours. Once the acidic media was neutralised by adding potassium carbonate, the solution was extracted with dichloromethane, dried over anhydrous sodium sulphate, filtered and concentrated.

This gave a dark orange solid, which was recrystallised from ethyl acetate. The yield was 1.55g or 85.8% with a melting point of 148˚C. The literature melting point is 154˚C. [42]

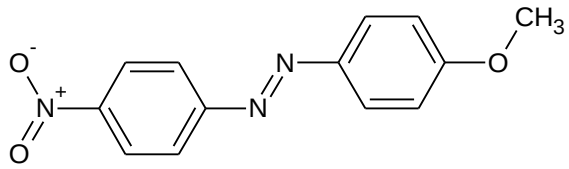

Fig (6) - 4-Methoxy-4'-nitroazobenzene.

3.17 Preparation of 4-dimethylamino-4'-nitroazobenzene

4-Dimethylamino-4'-nitroazobenzene was synthesised by adopting a literature method.[43] 1g of 4-nitroaniline (7mmol) was added to a mixture of 25ml of concentrated hydrochloric acid and 25ml of acetonitrile in a 250ml round bottom flask. This mixture was stirred in an ice bath until the temperature was below 5˚C. A solution containing 0.6g of sodium nitrite in 10ml of H_2O was added over 10 minutes. Once the addition was complete, the mixture was stirred for half an hour in the ice bath. After this a solution containing 1.1ml of 4-dimethylaniline (9mmol) in 25 ml of concentrated hydrochloric acid and 25ml of acetonitrile was added to the flask over 10 minutes. The solution was stirred for a further two hours and then the acid was neutralised by adding potassium carbonate. After this neutralisation the solution was extracted with dichloromethane, dried over anhydrous sodium sulphate, filtered and concentrated. This gave a dark purple solid, which was recrystallised from ethyl acetate. The yield was 1.53g or 80.8% with a melting point of 223˚C. The literarture melting point is 230˚C. [44]

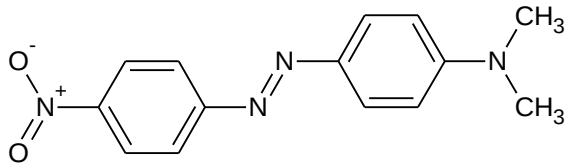

Fig (7) - 4-Dimethylamino-4'-nitroazobenzene.

3.18 Preparation of 4,4'-azodibenzoic acid

4,4'-Azodibenzoic acid was synthesised by using an adopted literature method.[45] 3g of 4-nitrobenzoic acid (18mmol) was added to 50ml of a 40M solution of sodium hydroxide in a 250ml round bottom flask; this mixture was heated to 70˚C. 30g of glucose was added to 50ml of H_2O in another 250ml round bottom flask, which was also heated to ensure complete dissolution of the glucose. This glucose solution was added dropwise over an hour to the initial solution; a bright yellow precipitate was formed, which turned brown as more glucose solution was added. This final solution had O_2 bubbled through it overnight; the resulting precipitate was filtered and washed with H_2O. The precipitate was then dissolved in hot water and acidified with acetic acid until a pink precipitate was formed. The pink solid

was dissolved in an ammonium acetate solution then filtered; the solution was acidified with acetic acid then hydrochloric acid. The pink solid was filtered and washed with H_2O then diethyl ether. The yield was 2.16g or 88.8% with a melting point of >300˚C. The literature melting point is >300˚C. [46]

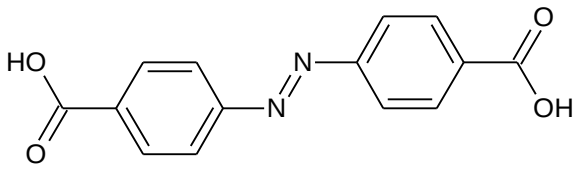

Fig (8) - 4,4'-Azodibenzoic acid.

3.2 Preparation of complexes

Most complexes were prepared by mixing 1ml of a ligand/toluene solution with 1ml of silver salt/acetone solution. This was carried out in a 10ml vial, which was then covered with parafilm. Slow evaporation of the solvent over a period of time afforded crystals suitable for X-ray structure analysis. The ratio of ligand:silver salt used was approximately 1:2.5 to begin with. If the crystals needed to be resynthesised the ratio of ligand:silver salt observed in the crystals was used. Benzene was used in place of toluene if a toluene molecule was found in the unit cell of the crystals produced; this method yielded the complex 12.13.

One complex (14.10) was produced using a layering technique in which 3ml of an acetone/silver salt solution was carefully layered on top of a ligand/toluene solution with a micropipette. This was carried out in a 20ml vial; crystals were formed at the boundary of the layers. The ratio of ligand:silver salt used was approximately 1:2.5.

Crystallography

Tables 1-12 list the crystallographic data for the thirty four complexes that were synthesised. Two diffractometers were used to obtain this data. They were a Bruker-Nonius APEX II and an Agilent Supernova. The Agilent Supernova was only used to collect the data for two complexes: 11.11 and 15.10. The data for the crystal structures reported were collected using monochromatic Mo Kα (λ=0.71073Å) radiation. Selected bond lengths and angles, as well as atomic coordinates, anisotropic displacement factors and hydrogen atom coordinates are available on request from the Department of Chemistry, University of Canterbury.

All structures had intensities corrected for Lorentz and polarisation effects and for absorption using SADABS. All structures were solved using direct methods using SHELXS and refined on F^2 using all data by full matrix least squares procedures using SHELXS-97.

Table 1: Crystal data

Identification code	**1.10** (3rg1)	**1.11** (3rg17)	**1.12** (3rg3)
Empirical formula	C12 H12 Ag B F4 N2 O	C30 H25 Ag1.50 F9 N5 P1.50	C18 H15 Ag Cl N3 O4
Formula weight	394.92	834.82	480.65
Temperature	108(2) K	114(2) K	111(2) K
Wavelength	0.71073 Å	0.71073 Å	0.71073 Å
Crystal system	Triclinic	Triclinic	Triclinic
Space group	P-1	P-1	P-1
Unit cell dimensions	a = 7.6147(3) Å	a = 9.1657(2) Å	a = 9.4872(5) Å
	b = 9.8431(4) Å	b = 9.3544(2) Å	b = 9.7437(5) Å
	c = 10.1436(4) Å	c = 20.4368(5) Å	c = 10.8304(6) Å
	α= 72.423(2)°	α= 88.0360(10)°	α= 83.415(3)°
	β= 68.607(2)°	β= 80.3370(10)°	β= 79.420(3)°
	γ = 88.297(2)°	γ = 62.2130(10)°	γ = 65.893(3)°
Volume	672.08(5) $Å^3$	1526.25(6) $Å^3$	897.43(8) $Å^3$
Z	2	2	2
Density (calculated)	1.951 Mg/m^3	1.817 Mg/m^3	1.779 Mg/m^3
Absorption coefficient	1.544 mm^{-1}	1.137 mm^{-1}	1.302 mm^{-1}
F(000)	388	828	480
Crystal size	0.58 x 0.19 x 0.16 mm^3	0.34 x 0.29 x 0.14 mm^3	0.62 x 0.43 x 0.20 mm^3
Theta range for data collection	2.88 to 25.63°	2.55 to 27.50°	2.82 to 27.49°
Index ranges	-9<=h<=9, -11<=k<=11, -12<=l<=12	-11<=h<=11, -12<=k<=12, -26<=l<=26	12<=h<=12, -12<=k<=12, -14<=l<=14
Reflections collected	13374	34927	19679
Independent reflections	2542 [R(int) = 0.0274]	6994 [R(int) = 0.0315]	4104 [R(int) = 0.0393]
Completeness to theta	99.8 %	99.9 %	99.8 %
Absorption correction	Semi-empirical from equivalents	Semi-empirical from equivalents	Semi-empirical from equivalents
Max. and min. transmission	1.000 and 0.712	0.8570 and 0.6985	0.7807 and 0.4990
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data / restraints / parameters	2542 / 0 / 198	6994 / 0 / 611	4104 / 0 / 244
Goodness-of-fit on F^2	1.068	2.072	1.121
Final R indices [I>2sigma(I)]	R1 = 0.0181, wR2 = 0.0437	R1 = 0.0478, wR2 = 0.1420	R1 = 0.0435, wR2 = 0.1211
R indices (all data)	R1 = 0.0198, wR2 = 0.0448	R1 = 0.0530, wR2 = 0.1443	R1 = 0.0465, wR2 = 0.1241
Largest diff. peak and hole	0.821 and -0.361 $e.Å^{-3}$	2.733 and -0.708 $e.Å^{-3}$	1.886 and -1.485 $e.Å^{-3}$

Table 2: Crystal data

Identification code	**1.13** (3rg7)	**1.14** (3rg53)	**2.10** (3rg25)
Empirical formula	C14 H10 Ag2 F6 N2 O6 S2	C8 H5 Ag F3 N O2	C14 H9 Ag2 Br F6 N2 O6 S2
Formula weight	696.10	312.00	775.00
Temperature	112(2)K	116(2)K	114(2)K
Wavelength	0.71073 Å	0.71073 Å	0.71073 Å
Crystal system	Triclinic	Triclinic	Triclinic
Space group	P-1	P-1	P-1
Unit cell dimensions	a = 5.1382(4) Å	a = 8.6188(3) Å	a = 5.4393(2) Å
	b = 9.2339(7) Å	b = 10.5628(3) Å	b = 9.5563(4) Å
	c = 11.5479(9) Å	c = 11.0371(3) Å	c = 11.1701(5) Å
	α= 101.772(5)°	α= 80.6760(10)°	α= 75.835(2)°
	β= 100.180(5)°	β= 81.430(2)°	β= 79.516(3)°
	γ = 99.341(5)°	γ = 71.734(2)°	γ = 76.490(2)°
Volume	516.62(7) $Å^3$	936.38(5) $Å^3$	542.57(4) $Å^3$
Z	1	4	1
Density (calculated)	2.237 Mg/m^3	2.213 Mg/m^3	2.372 Mg/m^3
Absorption coefficient	2.186 mm^{-1}	2.176 mm^{-1}	3.925 mm^{-1}
F(000)	336	600	370
Crystal size	0.25 x 0.23 x 0.01 mm^3	0.35 x 0.16 x 0.10 mm^3	0.72 x 0.41 x 0.13 mm^3
Theta range for data collection	2.58 to 26.59°	2.60 to 27.50°	3.23 to 27.50°
Index ranges	-6<=h<=6, -11<=k<=11, -14<=l<=14	-11<=h<=11, -13<=k<=13, -14<=l<=14	-7<=h<=7, -12<=k<=12, -14<=l<=14
Reflections collected	9487	19096	11169
Independent reflections	2138 [R(int) = 0.0625]	4269 [R(int) = 0.0297]	2480 [R(int) = 0.0343]
Completeness to theta	98.5%	99.1%	99.6%
Absorption correction	Semi-empirical from equivalents	Semi-empirical from equivalents	Semi-empirical from equivalents
Max. and min. transmission	0.9785 and 0.6110	0.8118 and 0.5164	0.6294 and 0.1644
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data / restraints / parameters	2138 / 0 / 145	4269 / 0 / 298	2480 / 0 / 154
Goodness-of-fit on F^2	1.068	1.096	1.176
Final R indices [I>2sigma(I)]	R1 = 0.0518, wR2 = 0.1174	R1 = 0.0265, wR2 = 0.0533	R1 = 0.0513, wR2 = 0.1302
R indices (all data)	R1 = 0.0838, wR2 = 0.1344	R1 = 0.0320, wR2 = 0.0560	R1 = 0.0573, wR2 = 0.1333
Largest diff. peak and hole	2.451 and -1.350 $e.Å^{-3}$	0.662 and -0.540 $e.Å^{-3}$	2.054 and -0.933 $e.Å^{-3}$

Table 3: Crystal data

Identification code	**2.11** (3rg47)	**3.10** (3rg5)	**3.11** (3rg20)
Empirical formula	C16 H9 Ag2 Br F6 N2 O4	C32 H24 Ag1.33 Br2.67 F8 N5.33 P1.33	C9 H6.75 Ag0.50 Br0.75 Cl0.50 N1.50 O2
Formula weight	702.90	1033.45	299.50
Temperature	117(2)K	110(2)K	115(2)K
Wavelength	0.71073 Å	0.71073 Å	0.71073 Å
Crystal system	Monoclinic	Monoclinic	Triclinic
Space group	P2(1)/c	P2(1)/n	P-1
Unit cell dimensions	a = 9.3556(6) Å	a = 10.5610(4) Å	a = 9.3244(3) Å
	b = 9.7048(6) Å	b = 32.6328(15) Å	b = 9.6658(3) Å
	c = 22.0667(14) Å	c = 16.3043(7) Å	c = 12.4726(4) Å
	α= 90°	α= 90°	α= 76.291(2)°
	β= 97.596(4)°	β= 108.205(2).	β= 81.859(2)°
	γ = 90°	γ = 90°	γ = 69.546(2)°
Volume	1985.9(2) $Å^3$	5337.8(4) $Å^3$	1021.11(6) $Å^3$
Z	4	6	4
Density (calculated)	2.351 Mg/m^3	1.929 Mg/m^3	1.948 Mg/m^3
Absorption coefficient	4.066 mm^{-1}	3.873 mm^{-1}	4.082 mm^{-1}
F(000)	1336	3008	582
Crystal size	0.21 x 0.20 x 0.06 mm^3	0.35 x 0.17 x 0.10 mm^3	0.40 x 0.35 x 0.14 mm^3
Theta range for data collection	2.20 to 27.50°	1.25 to 27.50°	2.30 to 27.50°
Index ranges	12<=h<=11, -12<=k<=12, -28<=l<=28	-13<=h<=13, -42<=k<=42, -21<=l<=21	-12<=h<=12, -12<=k<=12, -16<=l<=16
Reflections collected	25383	125378	22069
Independent reflections	4553 [R(int) = 0.0841]	12261 [R(int) = 0.0989]	4669 [R(int) = 0.0388]
Completeness to theta	99.8%	99.9%	99.8 %
Absorption correction	Semi-empirical from equivalents	Semi-empirical from equivalents	Semi-empirical from equivalents
Max. and min. transmission	0.7925 and 0.4822	0.6980 and 0.3442	1.000 and 0.744
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data / restraints / parameters	4553 / 0 / 308	12261 / 0 / 685	4669 / 0 / 262
Goodness-of-fit on F^2	0.829	1.056	1.118
Final R indices [I>2sigma(I)]	R1 = 0.0395, wR2 = 0.0721	R1 = 0.0463, wR2 = 0.1247	R1 = 0.0504, wR2 = 0.1145
R indices (all data)	R1 = 0.0836, wR2 = 0.0813	R1 = 0.0792, wR2 = 0.1313	R1 = 0.0729, wR2 = 0.1200
Largest diff. peak and hole	1.133 and -1.147 e.$Å^{-3}$	1.113 and -0.927 e.$Å^{-3}$	0.933 and -1.054 e.$Å^{-3}$

Table 4: Crystal data

Identification code	**4.10** (3rg9)	**4.11** (3rg16)	**5.10** (3rg31)
Empirical formula	C12 H9 Ag0.50 Br F3 N2 P0.50	C18 H13.50 Ag Br1.50 Cl N3 O4	C13 H8 Ag Br2 F3 N2 O3 S
Formula weight	387.54	599.00	596.96
Temperature	112(2)K	115(2)K	115(2)K
Wavelength	0.71073 Å	0.71073 Å	0.71073 Å
Crystal system	Triclinic	Triclinic	Monoclinic
Space group	P-1	P-1	P2(1)/c
Unit cell dimensions	a = 11.1941(13) Å	a = 9.6138(4) Å	a = 5.06920(10) Å
	b = 11.4092(13) Å	b = 10.9540(8) Å	b = 18.3772(4) Å
	c = 12.6103(14) Å	c = 11.3704(5) Å	c = 18.0458(4) Å
	α= 115.312(7)°	α= 110.423(3)°.	α= 90°
	β= 90.552(7)°	β= 111.608(2)°.	β= 94.5150(10)°
	γ = 114.624(7)°	γ = 98.750(3)°.	γ = 90°
Volume	1288.5(3) $Å^3$	987.69(9) $Å^3$	1675.89(6) $Å^3$
Z	4	2	4
Density (calculated)	1.998 Mg/m^3	2.014 Mg/m^3	2.366 Mg/m^3
Absorption coefficient	4.012 mm^{-1}	4.220 mm^{-1}	6.143 mm^{-1}
F(000)	742	582	1136
Crystal size	0.29 x 0.27 x 0.19 mm^3	0.66 x 0.47 x 0.17 mm^3	0.57 x 0.12 x 0.10 mm^3
Theta range for data collection	2.11 to 27.50°	2.63 to 26.41°	3.17 to 27.50°
Index ranges	-14<=h<=14, -14<=k<=14, -16<=l<=16	-11<=h<=12, -13<=k<=13, -14<=l<=13	-6<=h<=6, -23<=k<=23, -23<=l<=23
Reflections collected	26407	10107	36969
Independent reflections	5905 [R(int) = 0.0613]	4005 [R(int) = 0.0288]	3858 [R(int) = 0.0365]
Completeness to theta	99.7%	98.8 %	99.9%
Absorption correction	Semi-empirical from equivalents	Semi-empirical from equivalents	Semi-empirical from equivalents
Max. and min. transmission	0.5161 and 0.3892	0.5340 and 0.1671	0.5786 and 0.1275
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data / restraints / parameters	5905 / 0 / 348	4005 / 0 / 262	3858 / 0 / 226
Goodness-of-fit on F^2	1.749	1.054	0.963
Final R indices [I>2sigma(I)]	R1 = 0.1461, wR2 = 0.3883	R1 = 0.0344, wR2 = 0.0993	R1 = 0.0191, wR2 = 0.0414
R indices (all data)	R1 = 0.1664, wR2 = 0.4061	R1 = 0.0423, wR2 = 0.1035	R1 = 0.0326, wR2 = 0.0440
Largest diff. peak and hole	11.359 and -1.263 $e.Å^{-3}$	0.936 and -1.107 $e.Å^{-3}$	0.430 and -0.383 $e.Å^{-3}$

Table 5: Crystal data

Identification code	**6.10** (3rg86)	**7.10** (3rg45)	**8.10** (3rg60)
Empirical formula	C13 H8 Ag Br2 F3 N2 O3 S	C13 H9 Ag F3 N3 O5 S	C16 H16 Ag F6 N3 O6 S2
Formula weight	596.96	484.16	632.31
Temperature	113(2)K	117(2)K	113(2)K
Wavelength	0.71073 Å	0.71073 Å	0.71073 Å
Crystal system	Monoclinic	Monoclinic	Orthorhombic
Space group	P2(1)/c	P 21/n	P bca
Unit cell dimensions	a = 4.9989(3) Å	a = 10.2114(5) Å	a = 9.5845(4) Å
	b = 16.8559(10) Å	b = 5.0443(3) Å	b = 20.6610(10) Å
	c = 19.9213(12) Å	c = 30.6297(14) Å	c = 22.1402(11) Å
	α= 90°	α= 90°	α= 90°
	β= 94.996(4)°	β= 92.341(3)°	β= 90°
	γ = 90°	γ = 90°	γ = 90°
Volume	1672.21(17) $Å^3$	1576.40(14) $Å^3$	4384.3(4) $Å^3$
Z	4	4	8
Density (calculated)	2.371 Mg/m^3	2.040 Mg/m^3	1.916 Mg/m^3
Absorption coefficient	6.157 mm^{-1}	1.478 mm^{-1}	1.201 mm^{-1}
F(000)	1136	952	2512
Crystal size	0.40 x 0.05 x 0.05 mm^3	0.66 x 0.12 x 0.10 mm^3	0.26 x 0.14 x 0.02 mm^3
Theta range for data collection	3.17 to 27.50°	2.66 to 27.50°	2.81 to 27.50°
Index ranges	-6<=h<=6, -21<=k<=21, -25<=l<=25	-13<=h<=13, -6<=k<=6, -39<=l<=39	-12<=h<=12, -26<=k<=26, -28<=l<=28
Reflections collected	36267	19560	80446
Independent reflections	3836 [R(int) = 0.1072]	3636 [R(int) = 0.0419]	5038 [R(int) = 0.2030]
Completeness to theta	99.9%	99.9%	99.9%
Absorption correction	Semi-empirical from equivalents	Semi-empirical from equivalents	Semi-empirical from equivalents
Max. and min. transmission	0.7483 and 0.1921	0.8663 and 0.4422	0.9764 and 0.7454
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data / restraints / parameters	3836 / 0 / 226	3636 / 0 / 235	5038 / 0 / 313
Goodness-of-fit on F^2	0.939	0.926	1.094
Final R indices [I>2sigma(I)]	R1 = 0.0453, wR2 = 0.1038	R1 = 0.0270, wR2 = 0.0466	R1 = 0.0862, wR2 = 0.1608
R indices (all data)	R1 = 0.0863, wR2 = 0.1156	R1 = 0.0419, wR2 = 0.0494	R1 = 0.1601, wR2 = 0.1856
Largest diff. peak and hole	1.763 and -1.272 $e.Å^{-3}$	0.376 and -0.514 $e.Å^{-3}$	0.537 and -0.789 $e.Å^{-3}$

Table 6: Crystal data

Identification code	**9.10** (3rg54)	**9.11** (3rg55)	**9.12** (3rg51)
Empirical formula	C13 H12 Ag0.50 B0.50 F2 N2 O	C9.75 H9 Ag0.50 Cl0.50 N1.50 O2.75	C14 H12 Ag F3 N2 O4 S
Formula weight	309.59	262.84	469.19
Temperature	116(2)K	115(2)K	113(2)K
Wavelength	0.71073 Å	0.71073 Å	0.71073 Å
Crystal system	Triclinic	Triclinic	Monoclinic
Space group	P-1	P-1	P2(1)/n
Unit cell dimensions	a = 9.5230(3) Å	a = 9.6040(4) Å	a = 11.1459(7) Å
	b = 10.6779(4) Å	b = 10.8511(8) Å	b = 5.0813(3) Å
	c = 13.7040(5) Å	c = 11.5980(5) Å	c = 28.5723(17) Å
	α= 104.227(2)°	α= 106.972(4)°	α= 90°.
	β= 110.268(2)°	β= 111.419(3)°	β= 96.706(4)°.
	γ = 93.170(2)°	γ = 101.109(4)°	γ = 90°.
Volume	1251.92(8) $Å^3$	1013.58(10) $Å^3$	1607.14(17) $Å^3$
Z	4	4	4
Density (calculated)	1.643 Mg/m^3	1.722 Mg/m^3	1.939 Mg/m^3
Absorption coefficient	0.867 mm^{-1}	1.166 mm^{-1}	1.440 mm^{-1}
F(000)	624	528	928
Crystal size	0.30 x 0.20 x 0.07 mm^3	0.29 x 0.20 x 0.03 mm^3	0.60 x 0.10 x 0.05 mm^3
Theta range for data collection	2.81 to 27.50°	2.61 to 27.49°	2.66 to 27.50°
Index ranges	-12<=h<=12, -13<=k<=13, -17<=l<=17	-12<=h<=12, -14<=k<=14, -15<=l<=15	-13<=h<=14, -6<=k<=6, -37<=l<=36
Reflections collected	27655	19863	28135
Independent reflections	5733 [R(int) = 0.0540]	4589 [R(int) = 0.0689]	3672 [R(int) = 0.0942]
Completeness to theta	99.8 %	98.6%	99.2%
Absorption correction	Semi-empirical from equivalents	Semi-empirical from equivalents	Semi-empirical from equivalents
Max. and min. transmission	0.9418 and 0.7809	0.9658 and 0.7285	0.9315 and 0.4788
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data / restraints / parameters	5733 / 0 / 373	4589 / 0 / 282	3672 / 0 / 228
Goodness-of-fit on F^2	0.879	1.074	1.114
Final R indices [I>2sigma(I)]	R1 = 0.0344, wR2 = 0.0536	R1 = 0.0553, wR2 = 0.0977	R1 = 0.0668, wR2 = 0.1266
R indices (all data)	R1 = 0.0552, wR2 = 0.0579	R1 = 0.0814, wR2 = 0.1091	R1 = 0.0949, wR2 = 0.1370
Largest diff. peak and hole	0.501 and -0.490 $e.Å^{-3}$	0.555 and -0.973 $e.Å^{-3}$	0.783 and -1.041 $e.Å^{-3}$

Table 7: Crystal data

Identification code	**9.13** (3rg56)	**10.10** (3rg12)	**10.11** (3rg14)
Empirical formula	C10.50 H6 Ag2 F6 N O4.50	C28 H26 Ag B Cl2 F4 N4	C28 H26 Ag Cl2 F6 N4 P
Formula weight	547.90	684.11	742.27
Temperature	118(2)K	113(2)K	114(2)K
Wavelength	0.71073 Å	0.71073 Å	0.71073 Å
Crystal system	Monoclinic	Monoclinic	Monoclinic
Space group	P2(1)/c	P2(1)/n	P2(1)/n
Unit cell dimensions	a = 10.7948(4) Å	a = 9.207(6) Å	a = 9.4628(3) Å
	b = 23.4312(8) Å	b = 18.474(14) Å	b = 18.3165(5) Å
	c = 11.3841(3) Å	c = 17.028(12) Å	c = 17.3838(5) Å
	α= 90°	α= 90°	α= 90°
	β= 94.674(2)°	β= 96.11°	β= 94.130(2)°
	γ = 90°	γ = 90°	γ = 90°
Volume	2869.86(16) $Å^3$	2880(4) $Å^3$	3005.23(15) $Å^3$
Z	8	4	4
Density (calculated)	2.536 Mg/m^3	1.578 Mg/m^3	1.641 Mg/m^3
Absorption coefficient	2.821 mm^{-1}	0.937 mm^{-1}	0.965 mm^{-1}
F(000)	2080	1376	1488
Crystal size	0.44 x 0.29 x 0.24 mm^3	0.18 x 0.08 x 0.02 mm^3	0.36 x 0.20 x 0.08 mm^3
Theta range for data collection	2.50 to 27.50°	1.63 to 26.49°	2.60 to 26.40°
Index ranges	-14<=h<=14, -30<=k<=30, -14<=l<=14	-11<=h<=11, -23<=k<=23, -21<=l<=21	-11<=h<=11, -22<=k<=22, -21<=l<=21
Reflections collected	63053	59471	36378
Independent reflections	6585 [R(int) = 0.0411]	5939 [R(int) = 0.2209]	6134 [R(int) = 0.0464]
Completeness to theta	99.9 %	99.5%	99.5 %
Absorption correction	Semi-empirical from equivalents	Semi-empirical from equivalents	Semi-empirical from equivalents
Max. and min. transmission	0.5509 and 0.3700	0.9815 and 0.8495	0.9268 and 0.7226
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data / restraints / parameters	6585 / 0 / 434	5939 / 0 / 365	6134 / 0 / 383
Goodness-of-fit on F^2	1.354	0.665	1.059
Final R indices [I>2sigma(I)]	R1 = 0.0495, wR2 = 0.1016	R1 = 0.0399, wR2 = 0.0393	R1 = 0.0406, wR2 = 0.0967
R indices (all data)	R1 = 0.0575, wR2 = 0.1034	R1 = 0.1513, wR2 = 0.0535	R1 = 0.0619, wR2 = 0.1088
Largest diff. peak and hole	1.326 and -0.950 $e.Å^{-3}$	0.345 and -0.397 $e.Å^{-3}$	1.364 and -0.601 $e.Å^{-3}$

Table 8: Crystal data

Identification code	**10.12** (3rg11)	**10.13** (3rg13)	**11.10** (3rg24)
Empirical formula	C28 H26 Ag Cl3 N4 O4	C16 H15 Ag2 C21 F6 N2 O7 S2	C16 H18 Ag2 Cl2 N2 O8
Formula weight	696.75	776.60	652.96
Temperature	113(2)K	113(2)K	113(2)K
Wavelength	0.71073 Å	0.71073 Å	0.71073 Å
Crystal system	Monoclinic	Triclinic	Monoclinic
Space group	P2(1)/n	P-1	P 21/n
Unit cell dimensions	a = 9.2328(3) Å	a = 10.866(3) Å	a = 10.2050(3) Å
	b = 18.4682(7) Å	b = 11.390(3) Å	b = 15.1442(4) Å
	c = 17.0940(6) Å	c = 11.754(3) Å	c = 13.2216(3) Å
	α= 90°	α= 92.925(16)°	α= 90°
	β= 95.658(2)°	β= 115.004(14)°	β= 108.8410(10)°
	γ = 90°	γ = 104.260(15)°	γ = 90°
Volume	2900.55(18) $Å^3$	1257.7(6) $Å^3$	1933.87(9) $Å^3$
Z	4	2	4
Density (calculated)	1.596 Mg/m^3	2.051 Mg/m^3	2.243 Mg/m^3
Absorption coefficient	1.012 mm^{-1}	1.913 mm^{-1}	2.352 mm^{-1}
F(000)	1408	756	1280
Crystal size	0.55 x 0.36 x 0.03 mm^3	0.20 x 0.15 x 0.05 mm^3	0.29 x 0.11 x 0.08 mm^3
Theta range for data collection	1.63 to 26.45°	3.05 to 26.91°	2.21 to 27.50°
Index ranges	-11<=h<=11, -23<=k<=23, -21<=l<=21	-13<=h<=13, -14<=k<=14, -14<=l<=14	-13<=h<=13, -19<=k<=19, -17<=l<=17
Reflections collected	38045	25421	42765
Independent reflections	5971 [R(int) = 0.1018]	5173 [R(int) = 0.0782]	4431 [R(int) = 0.0335]
Completeness to theta	99.8%	95.1%	99.9%
Absorption correction	Semi-empirical from equivalents	Semi-empirical from equivalents	Semi-empirical from equivalents
Max. and min. transmission	0.9703 and 0.6059	0.9104 and 0.7009	0.8342 and 0.5487
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data / restraints / parameters	5971 / 0 / 365	5173 / 4 / 333	4431 / 0 / 283
Goodness-of-fit on F^2	0.837	0.995	1.048
Final R indices [I>2sigma(I)]	R1 = 0.0394, wR2 = 0.0684	R1 = 0.0375, wR2 = 0.0714	R1 = 0.0222, wR2 = 0.0542
R indices (all data)	R1 = 0.0985, wR2 = 0.0803	R1 = 0.0759, wR2 = 0.0827	R1 = 0.0285, wR2 = 0.0558
Largest diff. peak and hole	0.613 and -0.668 $e.Å^{-3}$	0.952 and -0.493 $e.Å^{-3}$	1.167 and -0.469 $e.Å^{-3}$

Table 9: Crystal data

Identification code	**11.11** (3rg88)	**12.10** (3rg30)	**12.11** (3rg27)
Empirical formula	C10 H9 Ag F3 N O2	C28 H24 Ag B F4 N4	C28 H24 Ag Cl N4 O4
Formula weight	340.05	611.20	623.84
Temperature	120(2)K	115(2)K	114(2)K
Wavelength	0.71073 Å	0.71073 Å	0.71073 Å
Crystal system	Triclinic	Triclinic	Triclinic
Space group	P-1	P-1	P-1
Unit cell dimensions	a = 10.4326(4) Å	a = 11.1061(3) Å	a = 11.0931(3) Å
	b = 11.0911(4) Å	b = 11.6378(3) Å	b = 11.7917(4) Å
	c = 11.8969(4) Å	c = 11.9620(3) Å	c = 11.8989(3) Å
	α= 93.115(3)°	α= 73.3990(10)°	α= 74.245(2)°
	β= 113.039(4)°	β= 64.6030(10)°	β= 64.7830(10)°
	γ = 114.294(4)°	γ = 68.3860(10)°	γ = 68.356(2)°
Volume	1115.90(7) $Å^3$	1283.37(6) $Å^3$	1296.68(7) $Å^3$
Z	4	2	2
Density (calculated)	2.024 Mg/m^3	1.582 Mg/m^3	1.598 Mg/m^3
Absorption coefficient	1.835 mm^{-1}	0.840 mm^{-1}	0.923 mm^{-1}
F(000)	664	616	632
Crystal size	0.66 x 0.07 x 0.05 mm^3	0.47 x 0.34 x 0.15 mm^3	0.46 x 0.19 x 0.12 mm^3
Theta range for data collection	2.64 to 27.50°	3.23 to 27.50°	2.85 to 27.50°
Index ranges	-13<=h<=13, -14<=k<=14, -15<=l<=15	-14<=h<=14, -15<=k<=15, -15<=l<=15	-14<=h<=14, -15<=k<=15, -15<=l<=15
Reflections collected	27631	29336	29624
Independent reflections	5124 [R(int) = 0.0325]	5893 [R(int) = 0.0307]	5953 [R(int) = 0.0330]
Completeness to theta	99.7 %	99.8%	99.9%
Absorption correction	Semi-empirical from equivalents	Semi-empirical from equivalents	Semi-empirical from equivalents
Max. and min. transmission	0.9138 and 0.3772	0.8844 and 0.6937	0.8973 and 0.6762
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data / restraints / parameters	5124 / 0 / 311	5893 / 0 / 343	5953 / 0 / 343
Goodness-of-fit on F^2	1.258	1.050	1.070
Final R indices [I>2sigma(I)]	R1 = 0.0393, wR2 = 0.1037	R1 = 0.0229, wR2 = 0.0599	R1 = 0.0245, wR2 = 0.0593
R indices (all data)	R1 = 0.0415, wR2 = 0.1047	R1 = 0.0260, wR2 = 0.0612	R1 = 0.0298, wR2 = 0.0609
Largest diff. peak and hole	1.586 and -0.746 $e.Å^{-3}$	0.375 and -0.369 $e.Å^{-3}$	0.598 and -0.568 $e.Å^{-3}$

Table 10: Crystal data

Identification code	**12.12** (3rg29)	**12.13** (3rg42)	**12.14** (3rg49)
Empirical formula	C56 H48 Ag2 N10 O6	C22 H22 Ag F3 N2 O4 S	C32 H27 Ag F3 N4 O3 S
Formula weight	1172.79	575.34	712.50
Temperature	114(2)K	113(2)K	118(2)K
Wavelength	0.71073 Å	0.71073 Å	0.71073 Å
Crystal system	Monoclinic	Triclinic	Monoclinic
Space group	P2(1)/c	P-1	P2(1)/n
Unit cell dimensions	a = 10.7387(4) Å	a = 9.4077(3) Å	a = 10.4174(4) Å
	b = 20.9327(8) Å	b = 11.5631(3) Å	b = 21.2037(7) Å
	c = 12.0975(4) Å	c = 11.9315(3) Å	c = 14.0379(5) Å
	α= 90°	α= 118.1470(10)°	α= 90°
	β= 115.873(2)°	β= 93.140(2)°	β= 106.439(2)°
	γ = 90°	γ = 96.277(2)°	γ = 90°
Volume	2446.81(15) $Å^3$	1129.17(5) $Å^3$	2974.04(18) $Å^3$
Z	2	2	4
Density (calculated)	1.592 Mg/m^3	1.692 Mg/m^3	1.591 Mg/m^3
Absorption coefficient	0.865 mm^{-1}	1.042 mm^{-1}	0.808 mm^{-1}
F(000)	1192	580	1444
Crystal size	0.47 x 0.14 x 0.03 mm^3	0.52 x 0.21 x 0.12 mm^3	0.32 x 0.25 x 0.10 mm^3
Theta range for data collection	2.88 to 27.50°	2.75 to 27.50°	2.86 to 27.50°
Index ranges	-13<=h<=13, -27<=k<=27, -15<=l<=1	-12<=h<=12, -15<=k<=15, -15<=l<=15	-13<=h<=13, -27<=k<=27, -18<=l<=18
Reflections collected	44445	25891	63271
Independent reflections	5605 [R(int) = 0.0998]	5195 [R(int) = 0.0381]	6833 [R(int) = 0.0611]
Completeness to theta	99.9%	99.9%	99.9%
Absorption correction	Semi-empirical from equivalents	Semi-empirical from equivalents	Semi-empirical from equivalents
Max. and min. transmission	0.9745 and 0.6866	0.8852 and 0.6133	0.9236 and 0.7821
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data / restraints / parameters	5605 / 0 / 334	5195 / 0 / 307	6833 / 0 / 397
Goodness-of-fit on F^2	0.812	0.996	0.926
Final R indices [I>2sigma(I)]	R1 = 0.0389, wR2 = 0.0640	R1 = 0.0256, wR2 = 0.0571	R1 = 0.0315, wR2 = 0.0658
R indices (all data)	R1 = 0.0832, wR2 = 0.0714	R1 = 0.0256, wR2 = 0.0571	R1 = 0.0482, wR2 = 0.0704
Largest diff. peak and hole	0.519 and -0.989 $e.Å^{-3}$	0.451 and -0.344 $e.Å^{-3}$	0.520 and -0.730 $e.Å^{-3}$

Table 11: Crystal data

Identification code	**12.15** (3rg57)	**13.10** (3rg35)	**14.10** (3rg48)
Empirical formula	C17.75 H14 Ag F3 N2 O2	C11 H8 Ag F3 N4 O3 S	C12 H9.50 Ag F3 N4 O2.50
Formula weight	452.18	441.14	414.61
Temperature	117(2)K	114(2)K	116(2)K
Wavelength	0.71073 Å	0.71073 Å	0.71073 Å
Crystal system	Triclinic	Monoclinic	Triclinic
Space group	P-1	P 21/n	P-1
Unit cell dimensions	a = 11.9781(5) Å	a = 10.5848(3) Å	a = 7.1236(5) Å
	b = 12.6820(6) Å	b = 10.3505(3) Å	b = 9.7099(6) Å
	c = 12.9615(7) Å	c = 13.5210(4) Å	c = 11.5056(7) Å
	α= 93.276(3)°	α= 90°	α= 69.923(4)°
	β= 106.211(3)°	β= 94.7650(10)°	β= 87.478(4)°
	γ = 114.325(3)°	γ = 90°	γ = 77.709(4)°
Volume	1689.13(14) $Å^3$	1476.21(7) $Å^3$	729.98(8) $Å^3$
Z	4	4	2
Density (calculated)	1.778 Mg/m^3	1.985 Mg/m^3	1.886 Mg/m^3
Absorption coefficient	1.239 mm^{-1}	1.559 mm^{-1}	1.430 mm^{-1}
F(000)	898	864	407
Crystal size	0.60 x 0.05 x 0.02 mm^3	0.53 x 0.48 x 0.20 mm^3	0.21 x 0.16 x 0.04 mm^3
Theta range for data collection	2.98 to 27.50°	2.55 to 27.50°	3.31 to 27.50°
Index ranges	-15<=h<=15, -16<=k<=16, -16<=l<=16	-13<=h<=13, -13<=k<=13, -17<=l<=17	-9<=h<=9, -12<=k<=12, -14<=l<=14
Reflections collected	31855	32043	9689
Independent reflections	7649 [R(int) = 0.0905]	3395 [R(int) = 0.0241]	3327 [R(int) = 0.0434]
Completeness to theta	98.5%	99.9%	99.2%
Absorption correction	Semi-empirical from equivalents	Semi-empirical from equivalents	Semi-empirical from equivalents
Max. and min. transmission	0.9756 and 0.5236	0.7456 and 0.4921	0.9450 and 0.7534
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data / restraints / parameters	7649 / 0 / 492	3395 / 0 / 208	3327 / 0 / 254
Goodness-of-fit on F^2	1.026	1.038	0.954
Final R indices [I>2sigma(I)]	R1 = 0.0647, wR2 = 0.1158	R1 = 0.0204, wR2 = 0.0531	R1 = 0.0533, wR2 = 0.1311
R indices (all data)	R1 = 0.1168, wR2 = 0.1357	R1 = 0.0241, wR2 = 0.0550	R1 = 0.0891, wR2 = 0.1446
Largest diff. peak and hole	0.775 and -0.725 $e.Å^{-3}$	0.634 and -0.314 $e.Å^{-3}$	1.323 and -0.842 $e.Å^{-3}$

Table 12: Crystal data

Identification code	**15.10** (3rg91)		
Empirical formula	C12 H10 Ag N3		
Formula weight	304.10		
Temperature	120(2)K		
Wavelength	0.71073 Å		
Crystal system	Monoclinic		
Space group	C 2/c		
Unit cell dimensions	a = 25.842(3) Å		
	b = 5.4709(6) Å		
	c = 16.6757(18) Å		
	α= 90°		
	β= 117.562(14)°		
	γ = 90°		
Volume	2090.0(4) $Å^3$		
Z	8		
Density (calculated)	1.933 Mg/m^3		
Absorption coefficient	1.900 mm^{-1}		
F(000)	1200		
Crystal size	0.23 x 0.05 x 0.05 mm^3		
Theta range for data collection	3.34 to 27.50°		
Index ranges	-33<=h<=25, -7<=k<=5, -18<=l<=21		
Reflections collected	4734		
Independent reflections	2317 [R(int) = 0.0429]		
Completeness to theta	97.1 %		
Absorption correction	Semi-empirical from equivalents		
Max. and min. transmission	1.0000 and 0.9217		
Refinement method	Full-matrix least-squares on F^2		
Data / restraints / parameters	2317 / 0 / 145		
Goodness-of-fit on F^2	1.050		
Final R indices [I>2sigma(I)]	R1 = 0.0460, wR2 = 0.0835		
R indices (all data)	R1 = 0.0707, wR2 = 0.0952		
Largest diff. peak and hole	0.884 and -0.589 $e.Å^{-3}$		

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