X-Ray Crystal Structures of Discrete and Polymeric Chiral Silver Complexes of Monoterpenoid Alkenes.

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Abstract

X-Ray crystal structures are reported for five silver(I) complexes of four monoterpenoid alkenes. Discrete mononuclear complexes of the chiral alkenes (1S)-(-)-α-pinene and (1S)-(-)-β-pinene with silver perchlorate and silver hexafluorophosphate are described. The achiral diene γ-terpinene forms a discrete mononuclear adduct with silver hexafluorophosphate and a two-dimensional polymeric network structure with silver triflate. The chiral diene (R)-(+)-limonene forms a one-dimensional chiral coordination polymer with silver hexafluorophosphate. In all structures the silver atom is η^2-bonded to the carbon-carbon bond(s) of the monoterpene with slightly longer bond distances to the more substituted carbon of the alkene moiety.

*Keywords:* Silver / Alkene / Crystal structure / Bridging ligands / Self-assembly

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1. Introduction

The use of combinations of organic ligands and metal ion precursors for the controlled self-assembly of metallosupramolecular species have been the subject of much work in recent years [1]. Most commonly, this involves the use of bridging nitrogen-containing heterocyclic ligands with transition metal reactants to form various zero-, one-, two- or three-dimensional assemblies with diverse molecular architectures [2]. Of the many metals used, silver(I) salts have proved particularly popular in recent years [3]. Bridging ligands containing other donor atoms, such as oxygen and phosphorus, have also been used for this purpose. Recently, we have identified the silver-alkene interaction as a new metallosupramolecular synthon [4]. Alkenes have long been known to complex silver ions [5], a phenomenon commonly exploited in the chromatographic separation of alkenes [6]. However, the use of dienes (or polyenes) as bridging moieties for supramolecular assembly has not been previously investigated.

Coordination polymers are currently considered to offer considerable potential as functional constructs in the topical area of material science [7]. One such application is in the field of non-linear optics [8], wherein an important requirement for second-order non-linear optical properties is that the material be non-centrosymmetric. We believe that the simplest way to access non-centrosymmetric coordination polymers is to use chiral bridging ligands as synthons [9]. Within this context, we now report an extension of our recent use of achiral dienes as building blocks in silver metallosupramolecular chemistry [4] to the use of naturally occurring chiral alkenes and dienes as reactants for the construction of discrete and polymeric chiral assemblies. For this purpose we have chosen the readily available monoterpenoid alkenes (**1**) and (**2**) and dienes (**3**) and (**4**) as the organic reactants.

(1)　　　　**(2)**　　　　**(3)**　　　　**(4)**
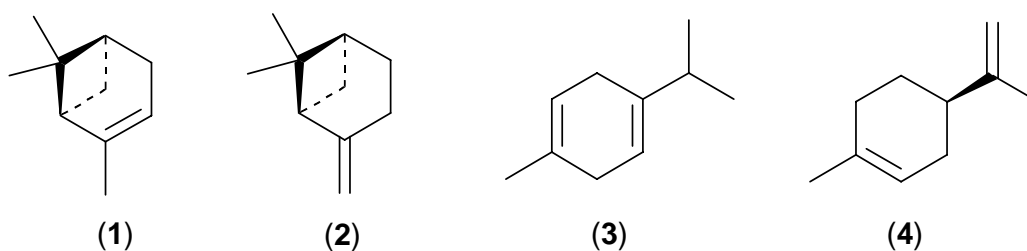
2. Results and Discussion

As a first step in this project we examined the reactions of the simple monoterpenoid alkenes (1S)-(-)-α-pinene (**1**) and (1S)-(-)-β-pinene (**2**) with a variety of silver(I) salts. From such exploratory experiments two crystalline adducts (**5**) and (**6**) were obtained by reactions of silver perchlorate with excess **1** and silver hexafluorophosphate with excess **2**, in the presence of dichloromethane as a cosolvent.   The complex (**5**) crystallizes in the orthorhombic space group $P2_12_12_1$ and consists of two molecules of **1** bound to a silver atom that is also coordinated to an oxygen atom of the perchlorate counterion (Fig. 1). The silver atom has trigonal geometry with silver-carbon bond distances in the range 2.402(4) – 2.515(4) Å. The distances to the more highly substituted carbons (C2 and C12) are longer than those to the less substituted (C3 and C13) carbons of the double bonds. Not unexpectedly, in both molecules of the monoterpene the silver atom coordinates to the face of the double bond that is *anti* to the bulky gem-dimethyl bridge. Thus, (1S)-(-)-α-pinene (**1**) readily forms a discrete 2:1 L:M complex in which the silver atom coordinates to the endocyclic double bond of the monoterpene.

[Figure 1 here]

The complex (**6**) crystallizes in the same space group and also has a L_2M stoichiometry. In this case the silver atom has a more linear geometry due to the much weaker interaction with the more weakly coordinating hexafluorophosphate counterion (Fig. 2). The silver-carbon distances are in the range 2.296(3) – 2.581(2) Å and, once again, the distances to the more substituted carbons (C2 and C12) are longer than those to the exocyclic methylene carbons (C10 and C20). The silver atoms complex to the less hindered face of the double bond, in both the coordinated molecules of **2**. These two structures serve to show that chiral, discrete silver complexes can readily be prepared in which the silver atom coordinates to either an endocyclic double bond (as in **5**) or an exocyclic double bond (as in **6**).

[Figure 2 here]

In order to extend this synthetic approach from discrete mononuclear complexes to multinuclear coordination polymers of higher dimensionality, the organic ligand needs to act

in a bridging mode. As we have shown recently, this requires the use of dienes as bridging ligands between silver centres [4]. Thus, the two readily available monoterpenoid dienes γ-terpinene, (**3**), and (R)-(+)-limonene, (**4**), were investigated as potential bridging ligands for silver-based coordination polymers. The achiral diene **3** was reacted with several silver salts and the product from reaction with silver hexafluorophosphate was found to form a discrete mononuclear complex (**7**). This compound crystallizes in the centrosymmetric monoclinic space group C2/c, with the asymmetric unit containing a molecule of γ-terpinene, half a silver atom and half a hexafluorophosphate counterion both of which lie on a two-fold rotation axis. Thus, the actual structure is a discrete L_2M complex similar to **6** (Fig. 3) and also has approximately linear coordination of the two double bonds to the silver which interacts only weakly with the counterion. The most surprising feature of this structure is that the silver coordinates to the more hindered of the two double bonds within the monoterpene. This is presumably because it is the more electron rich due to the greater electron donating ability of the isopropyl substituent compared to the methyl group. This electronic effect apparently overrides the steric effects. As with the other structures, the bond from the silver atom to the less substituted carbon of the double bond is shorter than the other.

[Figure 3 here]

Reaction of γ-terpinene with silver(I) triflate furnished a product (**8**) as thin, unstable plates, most of which were highly twinned. After many attempts a data set was extracted from one of several collections which was sufficient to reveal the structure to be a two-dimensional coordination polymer, albeit achiral. Figure 4 shows the contents of the asymmetric unit, which contains one molecule of γ-terpinene and two silver atoms bridged by two bidentate triflate anions with a silver-silver separation that is probably non-bonding [10]. Thus, this compound has LM_2 stoichiometry. The monoterpenoid diene acts as a bridge between two disilver units by coordinating through each of the two carbon-carbon double bonds from opposite faces of the central cyclohexadiene ring, thereby extending the structure into polymeric chains that propogate along the *b* axis. These chains are further crosslinked by the third oxygen of one of the triflates which binds to both silver of a disilver unit in the adjacent chain to result in a complex two-dimensional network structure (Fig. 5).

[Figures 4 and 5 here]

Having demonstrated that monoterpenoid dienes can be used for the formation of silver coordination polymers we proceeded to attempt to prepare a chiral variant. Pleasingly, the reaction of (R)-(+)-limonene, (**4**), with silver hexafluorophosphate did indeed result in the self-assembly of a one-dimensional chiral silver coordination polymer. This compound (**9**) crystallizes in space group $P2_12_12_1$ with a molecule of **4**, a silver atom with a coordinated water molecule and a hexafluorophosphate anion in the asymmetric unit (Fig. 6). In the extended structure (Fig. 7) the limonene is found to act as a bridging ligand with coordination to both the terminal vinyl group and the endocyclic double bond. Thus, the resulting coordination polymer has resulted from the faithful self-assembly of limonene bridges in a regularly arranged fashion. In our experience [2c], unsymmetrical bridging ligands of this type with similar, but different, binding domains tend to discombobulate the self-assembly process and produce mixtures of isomeric structures with different orientations of the bridge in the polymeric chain. In the extended structure of **9**, the presence of the coordinated water molecule results in a distorted trigonal coordination environment for the silver atom. The hexfluorophosphate anion has only a very weak association with the silver atom but is hydrogen bonded to the coordinated water molecule. Once again the silver atoms form shorter bonds to the less substituted carbons of each double bond.

[Figures 6 and 7 here]

3. Conclusion

In this study, we have shown that monoterpenoid alkenes are useful synthons for the formation of chiral metallosupramolecular assemblies. X-Ray crystal structures have been determined for discrete L_2M complexes of the two isomeric chiral pinenes and of γ-terpinene, while coordination polymers have been structurally characterized containing the bridging dienes γ-terpinene and (R)-(+)-limonene.

4. Experimental

The complexes were prepared, as described elsewhere [11], by reaction of the appropriate silver(I) salt with an excess of the liquid monoterpene, with addition of a small amount of dichloromethane to assist solubilization of the silver salt, if necessary. The products were obtained in moderate yields and often displayed low melting points and were hygroscopic and prone to decomposition; as a result successful combustion analyses were not obtained.

X-Ray Crystallography

The crystal data and details of the data collections and refinements for the five structures are listed in Table 1. Measurements were made with a SMART CCD area detector using graphite-monochromatized Mo Kα (λ = 0.71073Å) radiation. The structures were solved by direct methods using SHELXS [12] and refined on F^2 using all data by full-matrix least-squares procedures with SHELXL-97 [13]. All non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atoms were included in calculated positions with isotropic displacement parameters 1.2 times the isotropic equivalent of their carrier atoms. In the refinement of compounds 5 and **6** the positions of the olefinic hydrogen atoms were refined in order to check for any pyramidalization of the coordinated carbon atoms; none was found. The functions minimised were Σw (F_o^2 - F_c^2), with w = [$\sigma^2(F_o^2)$ + aP^2 + bP]$^{-1}$, where P = [max(F_o)^2 + 2F_c^2]/3. The refined Flack parameters [14] for the chiral compounds **5**, **6** and **9** were 0.05(3), 0.05(2) and 0.20(4) which confirm the absolute configurations and reveal a small racemic twin component in the structure of **9**. Full tables of atom coordinates, thermal parameters, and bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre. CCDC 287362 - 287366 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (internat.) + 44-1223/336-033; Email: deposit@ccdc.cam.ac.uk].

[Table 1 here]

Acknowledgement

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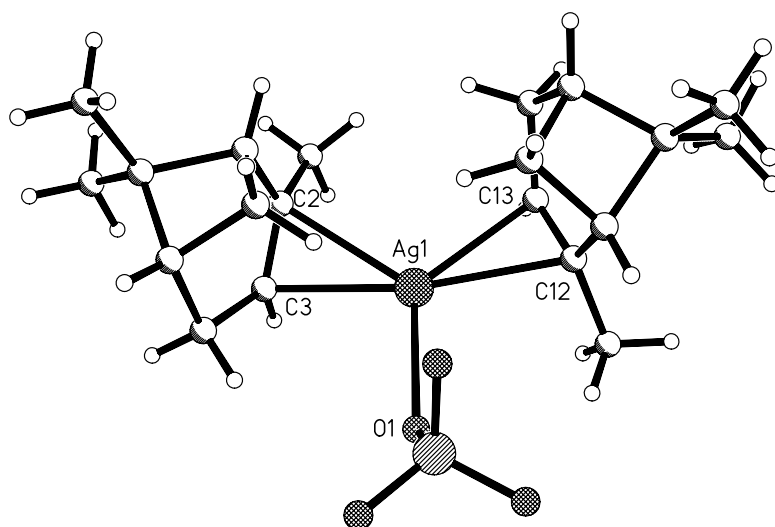
Fig. 1 Perspective view of the X-ray crystal structure of **5** formed from (1S)-(-)-α-pinene. Selected interatomic distances (Å): Ag1-C2 2.515(4), Ag1-C3 2.402(5), Ag1-C12 2.500(4), Ag1-C13 2.402(4), Ag1-O1 2.397(3).
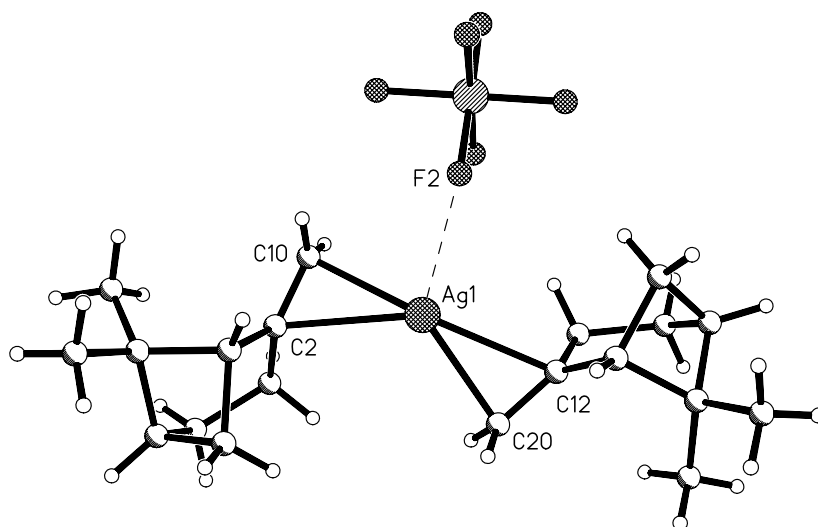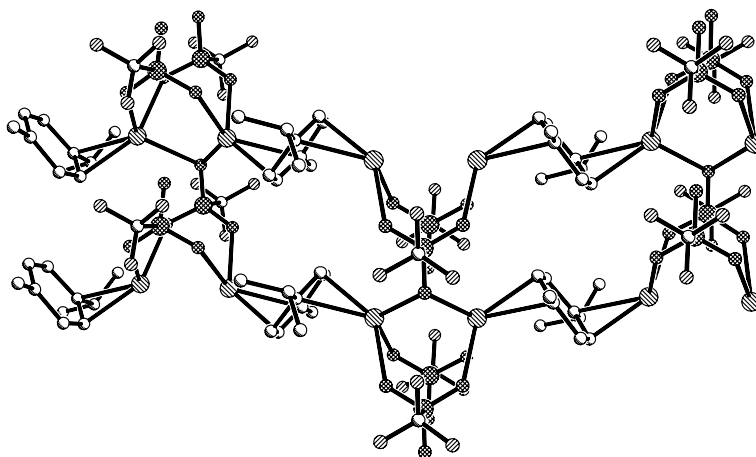

Fig. 2 Perspective view of the X-ray crystal structure of **6** formed from (1S)-(-)-β-pinene. Selected interatomic distances (Å): Ag1-C2 2.581(2), Ag1-C10 2.303(3), Ag1-C12 2.513(2), Ag1-C20 2.296(3), Ag1-F2 2.686(2).
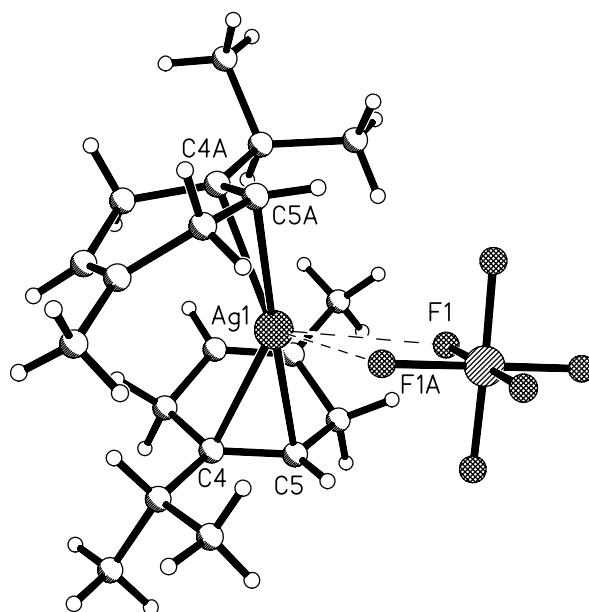
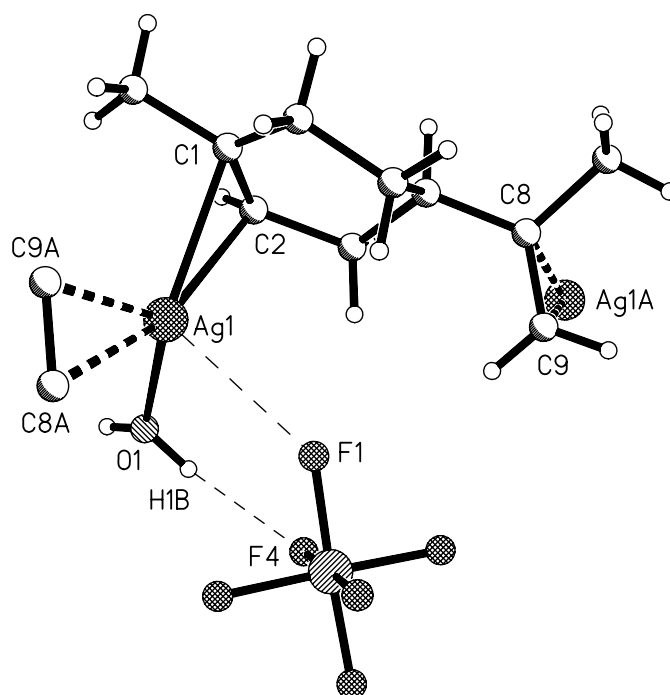**Fig. 3** Perspective view of the X-ray crystal structure of **7** formed from γ-terpinene. Selected interatomic distances (Å): Ag1-C4 2.437(2), Ag1-C5 2.369(2), Ag1-F1 2.699(2).
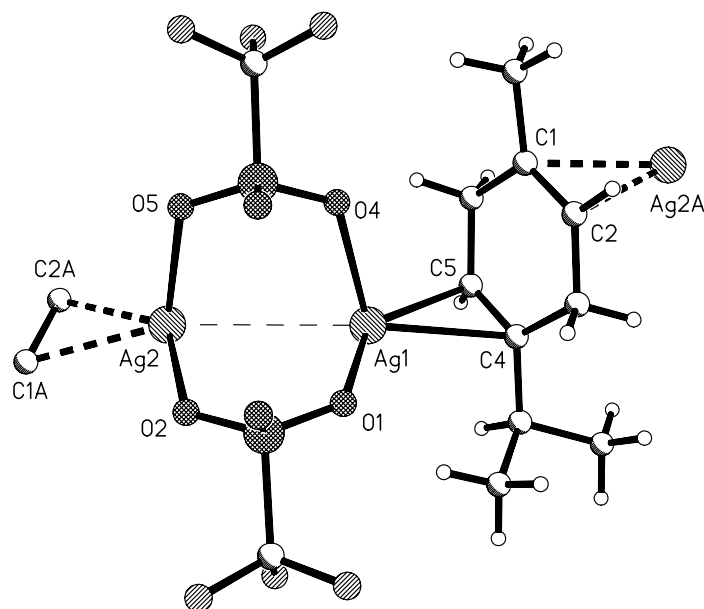

Fig. 4 Perspective view of the asymmetric unit in the X-ray crystal structure of **8**. Selected interatomic distances (Å): Ag1-C4 2.579(15), Ag1-C5 2.365(14), Ag2A-C1 2.536(15), Ag2A-C2 2.391(13), Ag1-O1 2.377(11), Ag1-O4 2.460(11), Ag2-O2 2.424(10), Ag2-O5 2.394(10), Ag1-Ag2 3.286(2).

Fig. 5 Perspective view of the extended two-dimensional polymeric structure of **8**. Hydrogen atoms have been omitted for clarity.

Fig. 6 Perspective view of the asymmetric unit in the X-ray crystal structure of **9**. Selected interatomic distances (Å): Ag1-C1 2.531(4), Ag1-C2 2.401(4), Ag1A-C8 2.548(4), Ag1A-C9 2.331(4), Ag1-O1 2.305(4), Ag1-F1 2.752(3), H1B-F4 2.09(2).
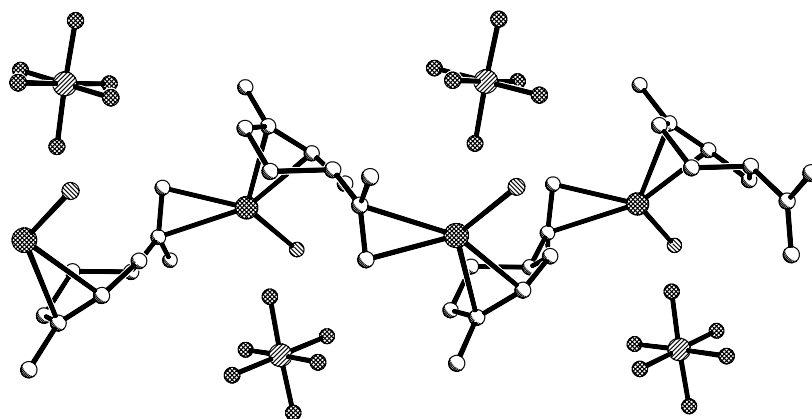
Fig. 7 Perspective view of the extended one-dimensional polymeric structure of **9**. Hydrogen atoms have been omitted for clarity.

Table 1. Crystal Data and X-ray Experimental Details for **5** – **9**.

Compound	**5**	**6**	**7**	**8**	**9**
Empirical formula	$C_{20}H_{32}AgClO_4$	$C_{20}H_{32}AgF_6P$	$C_{20}H_{32}AgF_6P$	$C_{12}H_{16}Ag_2F_6O_6S_2$	$C_{10}H_{18}AgF_6OP$
Formula weight	479.78	525.30	525.30	650.11	407.08
Temperature (K)	163(2)	163(2)	163(2)	163(2)	163(2)
Crystal system	Orthorhombic	Orthorhombic	Monoclinic	Monoclinic	Orthorhombic
Space group	$P2_12_12_1$	$P2_12_12_1$	$C2/c$	$P2_1/c$	$P2_12_12_1$
Unit cell: a (Å)	9.4056(16)	8.6396(11)	15.388(2)	5.0818(15)	7.5615(9)
b (Å)	10.7762(18)	9.3979(11)	9.9028(13)	17.211(5)	10.4903(13)
c (Å)	21.297(4)	26.820(3)	14.980(2)	21.123(6)	17.558(2)
α (°)	90	90	90	90	90
β (°)	90	90	98.969(2)	91.109(3)	90
γ (°)	90	90	90	90	90
Volume($Å^3$)	2158.6(6)	2177.6(5)	2254.8(5)	1847.1(9)	1392.8(3)
Z	4	4	4	4	4
Calc. density (Mg/m^3)	1.476	1.602	1.547	2.338	1.941
Abs. coeff. (mm^{-1})	1.078	1.052	1.016	2.433	1.619
F(000)	992	1072	1072	1264	808
Crystal size (mm)	0.22 x 0.08 x 0.04	0.39 x 0.25 x 0.03	0.64 x 0.19 x 0.08	0.51 x 0.31 x 0.04	0.34 x 0.31 x 0.26
Theta range (°)	1.91 to 25.04	2.30 to 26.42	2.45 to 25.04	1.93 to 25.05	2.26 to 26.42
Data collected	22605	25939	12697	15979	10595
Unique data [R(int)]	3801 [0.0810]	4444 [0.0304]	1989 [0.0198]	3231 [0.0390]	2834 [0.0289]
Obs. data [$I>2\sigma(I)$]	2793	3832	1888	3122	2620
Parameters	243	265	129	253	174
wR_2 (all data)	0.0552	0.0599	0.0451	0.2219	0.0774
R_1 [$I>2\sigma(I)$]	0.0366	0.0245	0.0165	0.0916	0.0294

Graphical Abstract

X-Ray Crystal Structures of Discrete and Polymeric Chiral Silver Complexes of Monoterpenoid Alkenes.

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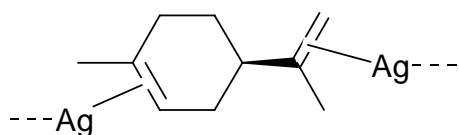
X-Ray crystal structures are reported for five silver(I) complexes of four naturally occurring monoterpenes, including discrete mononuclear species and coordination polymers.