



The influence of alkane spacer of bis(diphenylphosphino)alkanes on the nuclearity of silver(I): Syntheses and structures of P,P'-bridged clusters and coordination polymers involving dithiophosphates

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ABSTRACT

The effect of the length of alkane spacer in diphosphines on the nuclearity of Ag(I) complexes containing dialkyl dithiophosphates (dtp) ligands has been investigated. 1,1-Bis(diphenylphosphino)methane (dppm) yielded tetranuclear $[\text{Ag}_4(\text{dppm})_2\{\text{S}_2\text{P}(\text{OEt})_2\}_4]$ (**1**), $[\text{Ag}_4(\text{dppm})_2\{\text{S}_2\text{P}(\text{O}^i\text{Pr})_2\}_4]$ (**3**), trinuclear $[\text{Ag}_3(\text{dppm})_3\{\text{S}_2\text{P}(\text{OEt})_2\}_2](\text{PF}_6)$ (**2**), and a dinuclear $[\text{Ag}_2(\text{dppm})_2\{\text{S}_2\text{P}(\text{O}^i\text{Pr})_2\}](\text{PF}_6)$ (**4**). The increase in spacer length from one methylene in dppm to two in 1,2-bis(diphenylphosphino)ethane (dppe) resulted in the formation of polymeric, $[\text{Ag}(\text{dppe})\{\text{S}_2\text{P}(\text{OR})_2\}]_\infty$ (R = Et, **5a** and **5a'**; ⁱPr, **5b**), and $[\text{Ag}_4(\mu_3\text{-Cl})(\text{dppe})_{1.5}\{\text{S}_2\text{P}(\text{OR})_2\}_3]_\infty$ (R = Et, **6a**; ⁱPr, **6b**). Compounds **5a**, **5b**, **6a** and **6b** were reported earlier [C.W. Liu, B.-J. Liaw, L.-S. Liou, J.-C. Wang, Chem. Commun. (2005) 1983]. Further increase in the chain length to four methylene units in 1,4-bis(diphenylphosphino)butane (dppb) yielded dppb-bridged polymers, $[\text{Ag}(\text{dppb})\{\text{S}_2\text{P}(\text{OEt})_2\}]_\infty$ (**7**) and $[\text{Ag}_2(\text{dppb})\{\text{S}_2\text{P}(\text{OEt})_2\}_2]_\infty$ (**8**). In all the polynuclear compounds, diphosphines acted as P,P'-bridging ligands, while the dtp ligands (S,S'-donors) adopted varieties of coordination patterns: S,S'-chelating (**5**, **7**), S,S'-bridging (**4**), bimetallic-triconnective, $\mu_2:\eta^2,\eta^1$ (**1**, **3**, **8**), bimetallic-diconnective, $\mu_2:\eta^2$ (**2**, **3**) and trimetallic-triconnective, $\mu_3:\eta^2,\eta^1$ (**6**). Some of the complexes exhibit argentophilicity with Ag...Ag distances in the range, 2.918–3.360 Å. Concomitant bridging of two silver atoms either by dppm and dtp ligands (**1**, **3** and **4**) or two dtp ligands (**8**) lead to close silver-silver contacts. The diphosphines (dppe and dppb) with longer spacer appeared to favor 1D or 2D polymers due to the flexibility of the spacer within the diphosphine unit by adopting *anti* conformation as opposed to *syn* conformation of the dppm linker is revealed in complexes.

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1. Introduction

The study of silver–silver short contact in complexes, less than twice of van der Waal's radii of silver atom (3.40 Å), has invited attention of several research groups in the recent years [2–8], as such interaction has led to generate interesting electrical conducting properties [9,10]. The sulfur donor ligands have played an important role in the formation of such interactions due to their ability to bring two or more metals in close contact in view of angular flexibility at sulfur donor atoms [2–16]. Furthermore, silver–sulfur interactions are more covalent in nature due to the soft–soft acid–base interactions, and such interactions enhance the argentophilic character of silver atoms.

Dialkyl dithiophosphates $\{(\text{RO})_2\text{PS}_2\}$.dtp, a class of ligand having two sulfur donor atoms, are known to form a variety of metal complexes with bite angle of ca. 75° exhibiting different

coordination modes [12–15,17,18]. The study of metal–dtp interactions has another perspective because of several applications of these ligands and their complexes as fungicides, pesticides, vulcanization accelerators, floating agents for mineral ores, additives to lubricant oils, and solvent extraction reagents for metals [19–22]. However, there are only limited studies on silver–dtp chemistry [12–15,17,18].

In this paper, formation of the complexes of Ag(I) with dialkyl dithiophosphates in the presence of a series of diphosphines with different spacer lengths and the influence of the spacer length in the diphosphine on the nuclearity of silver(I) complexes have been described. Some of the complexes disclose short silver–silver contacts. Structural characterization reveal the formation of tetranuclear, $[\text{Ag}_4(\text{dppm})_2\{\text{S}_2\text{P}(\text{OEt})_2\}_4]$ (**1**), and $[\text{Ag}_4(\text{dppm})_2\{\text{S}_2\text{P}(\text{O}^i\text{Pr})_2\}_4]$ (**3**), trinuclear, $[\text{Ag}_3(\text{dppm})_3\{\text{S}_2\text{P}(\text{OEt})_2\}_2](\text{PF}_6)$ (**2**), and dinuclear $[\text{Ag}_2(\text{dppm})_2\{\text{S}_2\text{P}(\text{O}^i\text{Pr})_2\}](\text{PF}_6)$ (**4**) complexes in the presence of dppm with the shortest spacer. On the other hand, 1D $[\text{Ag}(\text{dppe})\{\text{S}_2\text{P}(\text{OR})_2\}]_\infty$ (R = Et, **5a** and **5a'**; ⁱPr, **5b**), $[\text{Ag}(\text{dppb})\{\text{S}_2\text{P}(\text{OEt})_2\}]_\infty$ (**7**), and $[\text{Ag}_2(\text{dppb})\{\text{S}_2\text{P}(\text{OEt})_2\}_2]_\infty$ (**8**),

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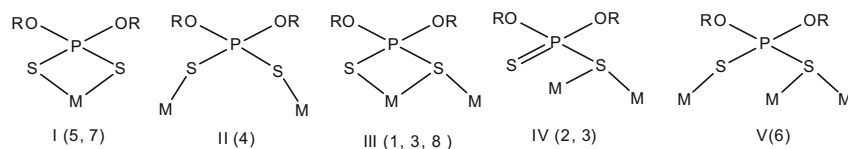


Chart 1.

and 2D honeycomb-shaped $[[Ag_4(\mu_3\text{-Cl})(dppe)_{1.5}(S_2P(OR)_2)_3]_\infty$ (R = Et, **6a**; ⁱPr, **6b**) polymers are obtained in the presence of dppe and dppb with longer spacer in the diphosphine backbone. A part of this work has been communicated earlier containing the description of **5a**, **5b**, **6a** and **6b** [1]. The dtp ligands exhibited various bonding modes in the complexes **1–8** as depicted in Chart 1.

2. Results and discussion

2.1. Synthesis

Simple stirring of Ag(I), dppm and dtp sources in 1:1:1 ratio at RT in acetonitrile produces $[Ag_4(dppm)_2(S_2P(OEt)_2)_4]$ (**1**) and $[Ag_3(dppm)_3(S_2P(OEt)_2)_2](PF_6)$ (**2**) in 76% and 7% yield, respectively. On the other hand, the same reaction in dichloromethane results in $[Ag_4(dppm)_2(S_2P(O^iPr)_2)_4]$ (**3**) in 75% yield. However, the change in the molar ratio of Ag(I), dppm, and dtp sources to 2:2:1 in dichloromethane yields $[Ag_2(dppm)_2(S_2P(O^iPr)_2)](PF_6)$ (**4**). Again, mixing of Ag(I), dppe and dtp (R = Et) sources in 1:1:2.1 ratio produced 1D polymeric $[Ag(dppe)\{S_2P(OEt)_2\}]_\infty$, **5a** and 2D honeycomb-shaped $[Ag_4(\mu_3\text{-Cl})(dppe)_{1.5}(S_2P(OEt)_2)_3]_\infty$ (**6a**) in 63% and 6% yield, respectively [1]. We have recently isolated **5a'**, a polymorph of **5a**, when single crystal were grown from acetone instead of dichloromethane. The similar reaction with isopropyl homolog of dtp results in $[Ag(dppe)\{S_2P(O^iPr)_2\}]_\infty$ (**5b**) and $[Ag_4(\mu_3\text{-Cl})(dppe)_{1.5}(S_2P(O^iPr)_2)_3]_\infty$ (**6b**) in 71% and 9% yield, respectively [1]. When the bridging diphosphine ligand is changed from dppm to dppb having a longer spacer, and the reaction conditions which produces **3** are maintained, a 1D polymeric $[Ag(dppb)\{S_2P(OEt)_2\}]_\infty$ (**7**) in 73% yield is obtained. On the other hand, a mixing of Ag(I), dppb and dtp sources in 2:1:2 ratio in dichloromethane gives rise to 1D chain of $[Ag_2(dppb)\{S_2P(OEt)_2\}]_\infty$ (**8**). In this regard, it is highly worthy to

be noted that silver clusters with formula $[Ag_4(\mu\text{-dppm})_2(S_2P(OEt)_2)_3]^+$ could be achieved by the reaction of $Ag(CH_3CN)_4X$ (where X = BF₄, PF₆), dppm, and dtp ligands in a ratio

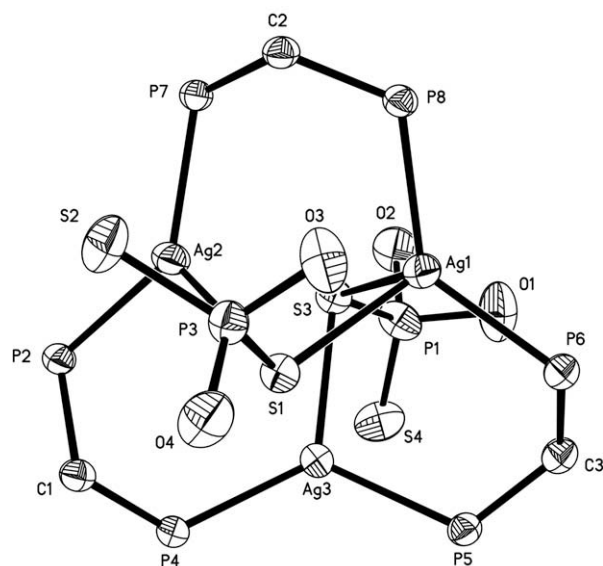


Fig. 2. Thermal ellipsoid drawing (30% probability) of **2** (phenyl and ethyl groups were omitted for clarity).

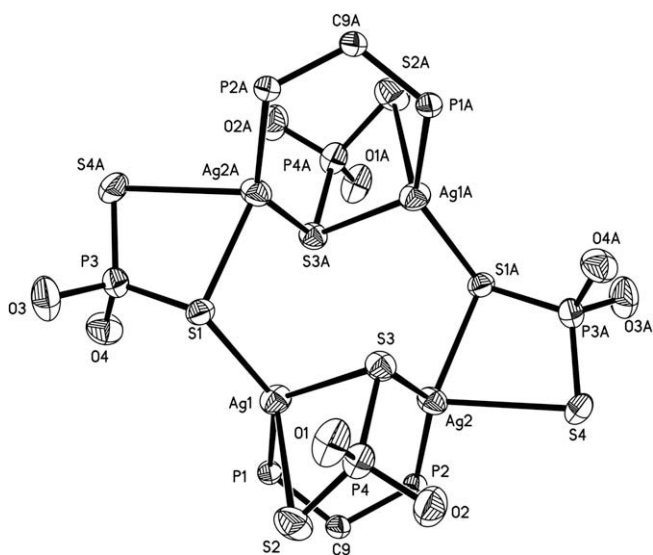


Fig. 1. Thermal ellipsoid drawing (30% probability) of **1** (phenyl and ethyl groups were omitted for clarity).

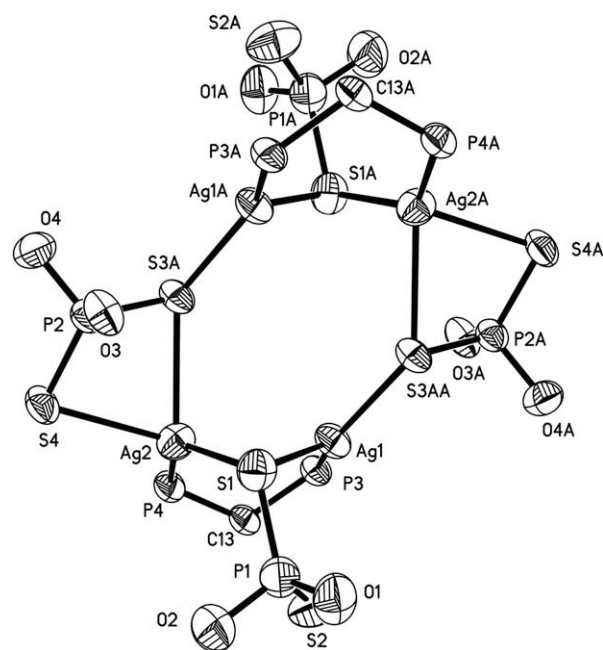


Fig. 3. Thermal ellipsoid drawing (30% probability) of **3** (phenyl and isopropyl groups were omitted for clarity).

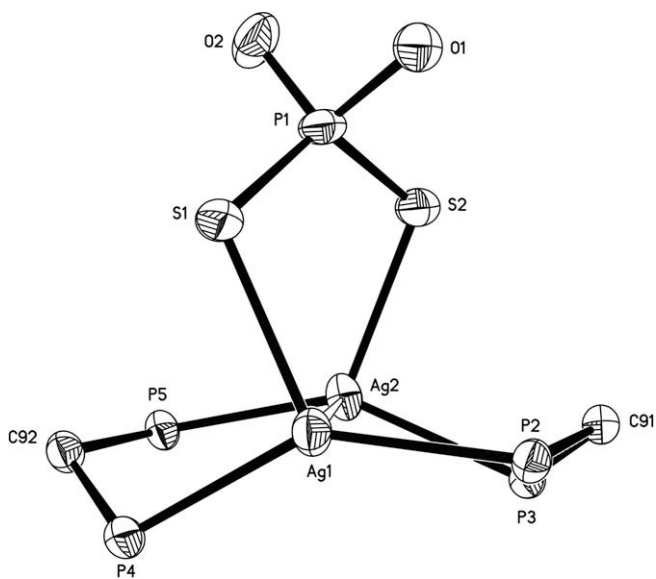


Fig. 4. Thermal ellipsoid drawing (30% probability) of **4** (phenyl and isopropyl groups were omitted for clarity).

of 4:2:3 in CH_2Cl_2 solution at ambient temperature in $\sim 75\%$ yield [23].

2.2. Structural studies

2.2.1. Structure of clusters, 1–4

Clusters **1–3** crystallize in the $P2_1/n$ (monoclinic), $Pbca$ and $Pna2_1$ (orthorhombic), respectively, whereas the dinuclear **4** crystallizes in the monoclinic space group $P2_1/c$. Figs. 1–4 depict the structures of compounds **1–4** and the selected metric data are given in Table 1. The tetranuclear cluster **1** contains a crystallographically imposed center of symmetry (Fig. 1). Besides four Ag atoms, it is composed of two P,P'-bridging dppm ligands with averaged Ag–P lengths of 2.405 Å, and four dtp ligands which bind to the Ag atoms via both chelating and bridging fashion by the sulfur atoms ($\mu_2:\eta^2,\eta^1$; mode III). It is interesting to point out that the eight-membered ring formed by Ag_4S_4 core remains in chair conformation. All Ag–S distances alternating in length across the ring are in the range, 2.514(1)–2.736(1) Å, and the terminal Ag–S distances are longer, 2.902(1)–2.935(1) Å. The lengthening of terminal distances may be due to the lower S–Ag–S bite angle (ca. 73°), and a strain imposed by the bridging requirement. There are two different Ag...Ag distances observed in **1**: two short at 3.1698(5) Å, and two long at 4.125(5) Å. The longer distances are between the silver atoms bridged only by sulfur atom of a dtp whereas the simultaneous bridging of two Ag by S atom from a dtp and P,P'-bridging dppm ligand shortens the silver–silver distances ($\text{Ag}1 \cdots \text{Ag}2$ and $\text{Ag}1\text{A} \cdots \text{Ag}2\text{A}$). The observed Ag...Ag distance of 3.17 Å, is less than twice of van der Waal's radii of Ag, 3.40 Å, and this is comparable to the average Ag...Ag distances 3.13 and 3.14 Å in $[\text{Ag}_4(\text{SPh})_4(\text{PPh}_3)_4]$ [24] and $[\text{Ag}_2(\text{sac})_2(\text{MeCN})_2]$ (sacH = 1,1-dioxo-1,2-benzothiazol-3-one) [25], respectively. Overall each silver atom is coordinated by a P and three S atoms in a distorted tetrahedral geometry.

The cation of trinuclear cluster **2** contains three silver atoms bridged by three dppm units to form a 12-membered ring, and further each of the two 'dtp' ligands binds to two Ag atoms via μ_2 -S from opposite sides of the metallacycle (Fig. 2). This results in two Ag atoms with distorted trigonal planar geometry {ca. 103 – 136° , Ag(2); ca. 110 – 126° , Ag(3)}, and a Ag atom in distorted tetrahedral geometry (ca. 104 – 132°) and leaves each dtp ligand with

Table 1
Bond lengths (Å) and angles ($^\circ$) for compounds **1–4**, **5a'**, **7**, and **8**.

1^a			
Ag(1)–P(1)	2.408(1)	Ag(2)–P(2)	2.401(1)
Ag(1)–S(1)	2.517(1)	Ag(2)–S(1A)	2.647(1)
Ag(1)–S(2)	2.902(1)	Ag(2)–S(3)	2.514(1)
Ag(1)–S(3)	2.736(1)	Ag(2)–S(4)	2.935(1)
Ag(1)···Ag(2)	3.1698(5)	Ag(1)···Ag(2A)	4.125(5)
P(1)–Ag(1)–S(1)	139.05(3)	S(3)–Ag(1)–S(2)	73.83(3)
P(1)–Ag(1)–S(2)	87.28(4)	Ag(1)–S(1)–Ag(2A)	106.01(3)
S(1)–Ag(1)–S(2)	109.05(4)	Ag(2)–S(3)–Ag(1)	74.15(3)
S(1)–Ag(1)–S(3)	87.66(3)		
2			
Ag(1)–P(6)	2.495(1)	Ag(3)–P(5)	2.508(1)
Ag(1)–P(8)	2.493(1)	Ag(1)–S(1)	2.678(1)
Ag(2)–P(2)	2.441(1)	Ag(1)–S(3)	2.747(1)
Ag(2)–P(3)	2.427(1)	Ag(2)–S(1)	2.676(1)
Ag(3)–P(4)	2.476(1)	Ag(3)–S(3)	2.608(1)
P(8)–Ag(1)–P(6)	132.21(4)	P(8)–Ag(1)–S(3)	104.29(3)
P(6)–Ag(1)–S(3)	108.62(3)	P(2)–Ag(2)–S(1)	102.91(4)
P(6)–Ag(1)–S(1)	106.85(4)	P(7)–Ag(2)–S(1)	120.37(4)
P(8)–Ag(1)–S(1)	110.52(3)	P(7)–Ag(2)–P(2)	136.32(4)
S(1)–Ag(1)–S(3)	83.46(3)	Ag(2)–S(1)–Ag(1)	87.62(3)
3^b			
Ag(1)–P(3)	2.413(3)	Ag(2)–S(1)	2.518(3)
Ag(2)–P(4)	2.406(3)	Ag(2)–S(3)	2.811(3)
Ag(1)–S(3A)	2.500(2)	Ag(1)···Ag(2)	3.063(1)
Ag(1)–S(1)	2.660(3)	Ag(1)···Ag(2A)	4.914(2)
Ag(2)–S(4)	2.728(3)		
P(1)–Ag(1)–S(1)	131.40(9)	S(1)–Ag(2)–S(4)	112.76(1)
P(3)–Ag(1)–S(3A)	133.21(9)	S(1)–Ag(2)–S(3)	95.54(9)
P(4)–Ag(2)–S(1)	132.22(1)	S(4)–Ag(2)–S(3)	73.38(8)
P(4)–Ag(2)–S(3A)	95.54(9)	Ag(2)–S(1)–Ag(1)	72.46(8)
P(4)–Ag(2)–S(4)	107.43(9)	Ag(1A)–S(3)–Ag(2)	135.36(1)
S(3A)–Ag(1)–S(1)	94.76(9)		
4			
Ag(1)–P(2)	2.442(2)	Ag(2)–P(3)	2.521(2)
Ag(1)–P(4)	2.498(2)	Ag(2)–P(5)	2.428(2)
Ag(1)–S(1)	2.589(2)	Ag(1)···Ag(2)	2.918(1)
Ag(2)–S(2)	2.575(2)		
P(2)–Ag(1)–P(4)	143.82(6)	P(4)–Ag(1)–S(1)	95.27(6)
P(2)–Ag(1)–S(1)	120.81(6)	P(1)–S(1)–Ag(1)	110.23(10)
P(5)–Ag(2)–S(2)	122.35(7)	P(5)–Ag(2)–P(3)	145.05(6)
P(3)–Ag(2)–S(2)	92.50(6)		
5a'			
Ag(1)–P(2)	2.4774(12)	Ag(1)–S(2)	2.7038(16)
Ag(1)–P(3)	2.4615(12)	Ag(1)–S(1)	2.6641(16)
P(2)–Ag(1)–S(1)	112.64(5)	P(3)–Ag(1)–S(2)	113.06(6)
P(2)–Ag(1)–S(2)	108.48(6)	S(2)–Ag(1)–S(1)	77.21(6)
P(3)–Ag(1)–S(1)	114.95(5)	P(2)–Ag(1)–P(3)	121.74(4)
7			
Ag(1)–P(2)	2.489(2)	Ag(1)–S(2)	2.681(2)
Ag(1)–P(3)	2.470(2)	Ag(1)–S(1)	2.697(2)
P(2)–Ag(1)–S(1)	115.92(8)	P(3)–Ag(1)–S(2)	122.31(7)
P(2)–Ag(1)–S(2)	109.53(8)	P(2)–Ag(1)–P(3)	112.62(7)
P(3)–Ag(1)–S(1)	115.87(8)	S(2)–Ag(1)–S(1)	76.10(8)
8^c			
Ag(1A)–P(2A)	2.425(1)	Ag(1A)–S(2A)	2.694(1)
Ag(1A)–S(1A)	2.530(1)	S(1A)–Ag(1B)	2.964(1)
Ag(1A)–S(1AA)	2.964(1)	Ag(1A)···Ag(1B)	3.360(1)
P(2)–Ag(1)–S(1)	134.77(2)		
P(2A)–Ag(1A)–S(2A)	119.56(2)	S(2A)–Ag(1A)–S(1AA)	73.49(2)
P(2A)–Ag(1A)–S(1AA)	104.10(2)	S(1A)–Ag(1A)–S(1AA)	105.04(2)
S(1A)–Ag(1A)–S(2A)	101.54(2)	Ag(1A)–S(1A)–Ag(1B)	74.96(2)

Symmetry transformations used to generate equivalent atoms: ^aA: $-x+2, -y, -z+1$; ^bA: $-x+1, -y, -z+1$; ^cA: $-x, -y+2, -z+1$; B: $-x+1, -y+2, -z+1$.

one dangling S atom. P–Ag–P angles are the largest around the metal centers as usual. The coordination mode for the dtp ligands is bimetallic–biconnective ($\mu_2:\eta^2$, mode IV). The average Ag...Ag distance of 3.8 Å, is much longer than that reported (3.3 Å) in $[\text{Ag}_3(\text{dppm})_3[\text{SC}(\text{O})\text{R}]_2](\text{ClO}_4)$ (R = Me, Ph) [26]. Although S(1) bridges Ag(2) and Ag(1) atoms almost symmetrically, S(3) bridges

Ag(1) and Ag(3) unsymmetrically with Ag(3)–S(3) being the shortest among all Ag–S distances [2.608(1)–2.747(1) Å]. The averaged Ag–P distance is 2.473 Å, which is not unusual.

The cluster **3**, with isopropoxyl groups in the dtp ligand, exhibits different structural characteristics in comparison to those revealed in **1** (Fig. 3). Two sorts of connection patterns for the dtp ligands, bridging–chelating (mode III) and bridging–dangling (mode IV), are identified in **3**, whereas only the mode III is displayed for the dtp ligands in **1**. The Ag–S distances lie in the range, 2.500(2)–2.811(3) Å; the longest bond is formed by the bridging S atom of dtp ligand which adopts mode III. Similar to **1**, cluster **3** also exhibits Ag–S distances alternating in length across the eight-membered ring formed by the Ag₄S₄ core. All Ag–P distances are similar to those observed in **1**. Two different Ag··Ag distances are present in **3**: two short [3.0630(12) Å] and two long [4.914(2) Å]; the distances between silver atoms bridged by a sulfur atom only are longer. Thus the simultaneous bridging of Ag··Ag by both a S atom from dtp and P,P′-bridging ligand shortens the silver–silver distance in the same way as in **1**. The cluster **3** reveals two three-coordinated Ag atoms with angles in the range, ca. 95–133°, and two four-coordinated Ag atoms with angles in the range, 73–132°; the lowest angle represents the bite angle (S–Ag–S) of the chelating dtp ligand.

The cation of dimer **4** consists of two Ag atoms bridged by two dppm and a dtp ligand adopting mode II, and thus each trigonally coordinated Ag has a P₂S coordination environment (Fig. 4). The Ag··Ag distance, 2.918(1) Å, is the shortest among all the

compounds under discussion. The Ag–S and Ag–P distances are comparable to those observed in other clusters **1–3**. The P–Ag–P angle is the largest, and S–Ag–P, the smallest angle; with geometry around each Ag atom in distorted T-shaped.

2.2.2. Structure of polymers, **5–8**

The increase in spacer length of diphosphine from –CH₂– in dppm to –(CH₂)₂– in dppe induces more flexibility in terms of possible bonding modes of the PPh₂ units as the P,P′-bridging ligand which leads to form polymeric 1D chains (**5a**, **5a′** and **5b**), and 2D honeycomb-shaped layers (**6a–b**) instead of oligomeric cluster compounds viz. **1–4** [1]. A newly isolated, polymeric **5a′**, a polymorph of **5a**, exhibits the same bonding patterns as those reported for **5a** [1]. Each silver atom bonded to one dtp ligand in chelating manner (mode I) is connected to two Ag atoms with dppe as the bridge to form a 1D chain. The S(1)–Ag(1)–S(2) bite angle in **5a′** (77.21°) is comparable to that in **5a** (76.97°). Both Ag–P [2.4615(12), 2.4774(12) Å] and Ag–S [2.6641(16), 2.7038(16) Å] distances in **5a′** are in normal range for a four-coordinated silver(I) center [27,28]. The linker, dppe, adopts *anti* conformation while connecting silver atoms and this trend continues to favor 1D zigzag chain rather than ring formation. Besides, the chelating dtp ligands are arranged in an alternating up and down fashion along the zigzag chain. Similar polymeric chain [Ag(dppe)(S₂PPh₂)] involving dppe and a dtp ligand was reported by Fenske and co-workers [29]. The characteristics of iso-structural polymers **6a** and **6b** were described in the previous communication [1].

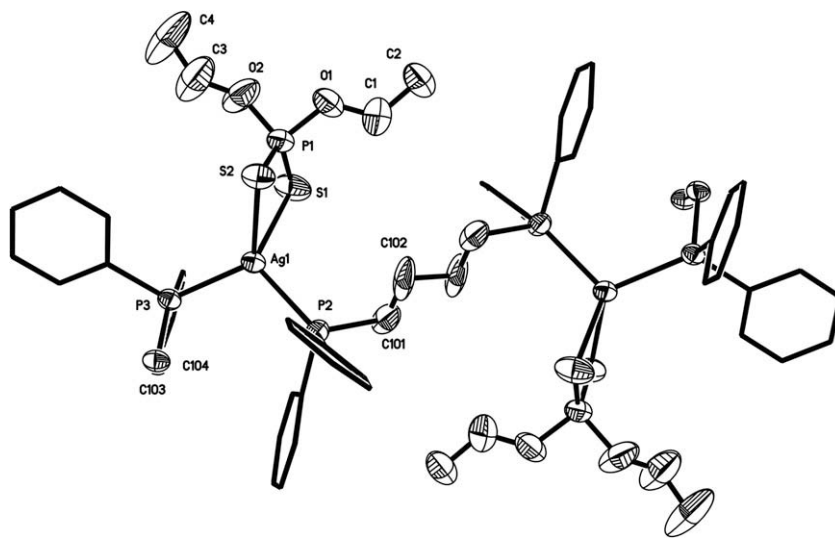


Fig. 5. Thermal ellipsoid drawing (30% probability) of **7**.

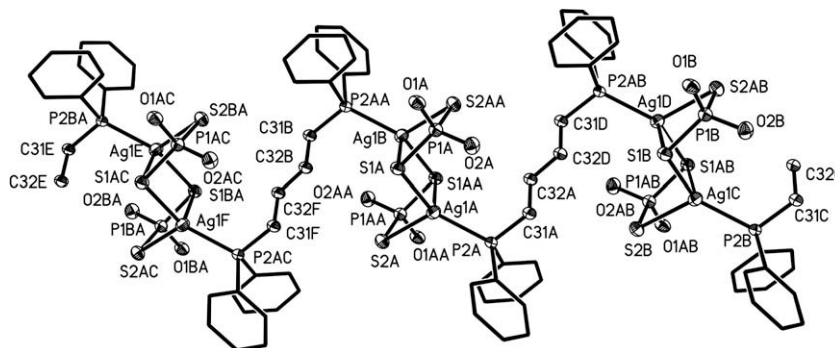
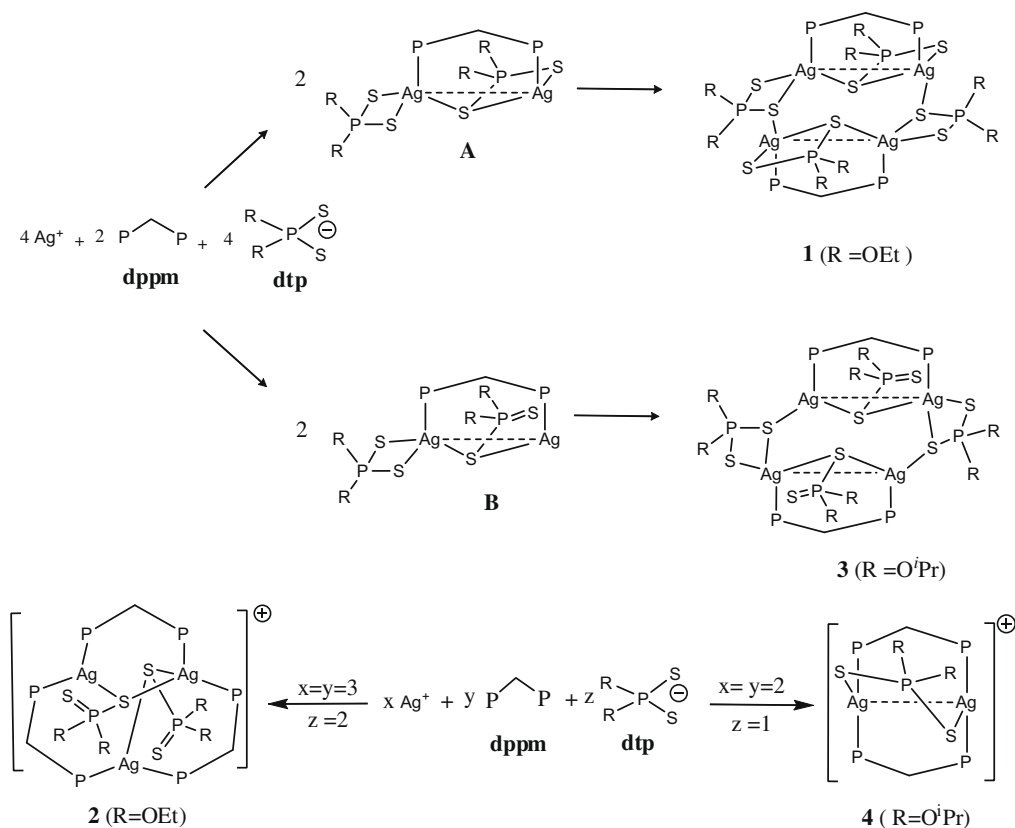


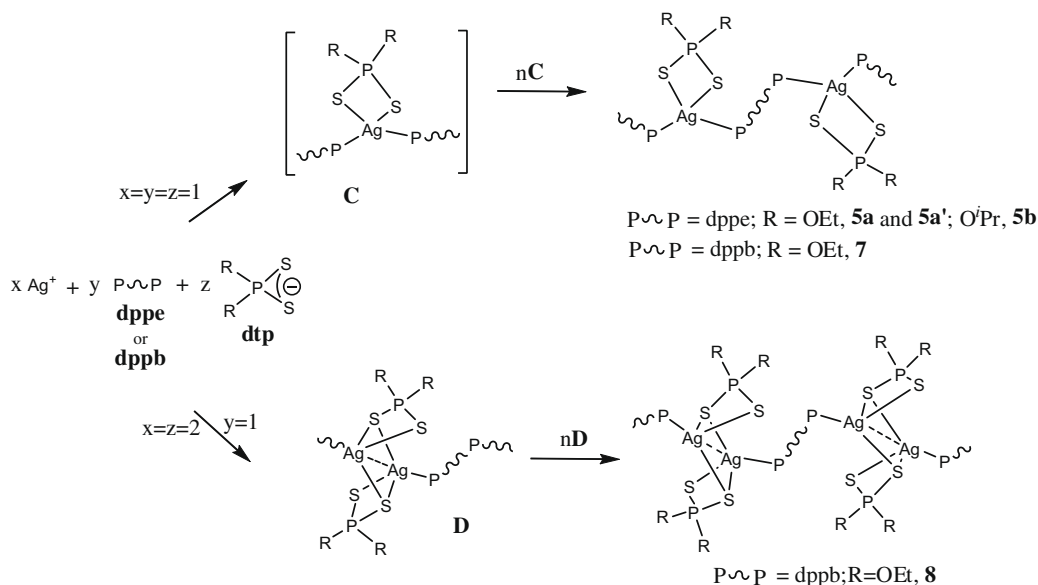
Fig. 6. Thermal ellipsoid drawing (30% probability) of **8**. Ethyl groups were omitted for clarity.



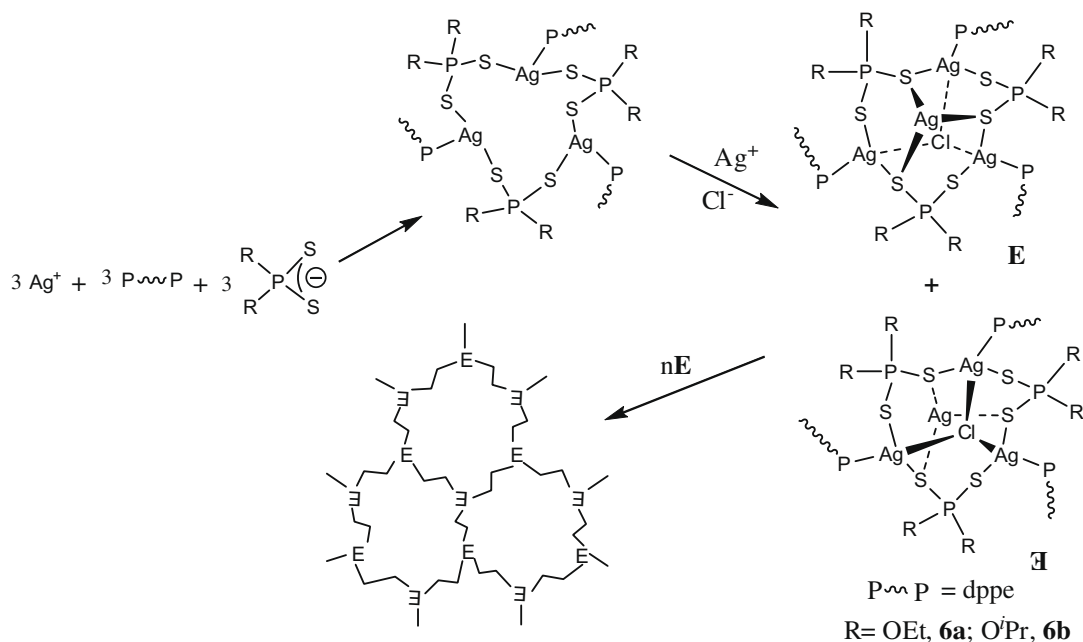
Scheme 1.

The increase in chain length of diphosphine from $-(\text{CH}_2)_2-$ in dppe to $-(\text{CH}_2)_4-$ in dppb, produces two types of polymers depending on the molar ratio used; a zigzag chain, **7** (Fig. 5), in which dppb bridges two $\text{Ag}(\text{dtp})$ units having a similar bonding pattern that observed in dppe polymer **5a**, **5a'** and $[\text{Cu}(\text{dppe})\{\text{S}_2\text{P}(\text{OR})_2\}]_\infty$ [30], and the other zigzag chain **8** in which the dppb ligands bridge dimeric $\text{Ag}_2(\text{dtp})_2$ units (Fig. 6). In polymer **7**, Ag–P and Ag–S bond lengths are similar to that in polymer **5a'**, and angles around silver

vary in the range, ca. 76 – 122° with the smallest angle being the bite angle of chelating dtp. The P–Ag–P bond angle in **7** is similar to that in **5a'**, and thus Ag atoms have distorted tetrahedral geometry. In polymer **8**, two PS_2 fragments, each from a dtp, and two Ag atoms form a fused eight-membered tricyclic ring which remains in chair form; however the central Ag_2S_2 core is a perfect parallelogram with Ag–S distances of $2.530(1)$ and $2.964(1)$ Å. Also the angles in Ag_2S_2 core are comparable to similar cores observed in the



Scheme 2.



Scheme 3.

literature [31]. The Ag...Ag distance of 3.360(1) Å is longer than that in **4**. The geometry around each Ag atom in **8** is distorted tetrahedral, similar to those in polymers **5** and **7**.

2.3. NMR spectroscopy

The ^1H NMR data of compounds **1–8** show peaks attributed to ethyl and isopropyl groups of dtp, as well as methylene and phenyl groups of dppm, dppe and dppb in their characteristic regions as listed in the Section 4. In ^{31}P NMR spectroscopy, dtp ligands show upfield coordination shifts ($\Delta\delta = \delta_{\text{complex}} - \delta_{\text{ligand}(\text{S}2\text{P})}$), which lie in the range, ca. -4 to -9 ppm. The high field shift might be caused by the electromeric effect of both alkoxy groups and S donors attached to the P atom which would have resulted in net shielding of P nucleus in the complexes. The PPh_2 groups of diphosphines show one broad signal in low field region relative to the free ligands with coordination shifts ($\Delta\delta = \delta_{\text{complex}} - \delta_{\text{ligand}(\text{Ph}2\text{P})}$), in the range, ca. 14–26 ppm. The dimer **4** exhibits the highest shift while the cluster **3** shows the lowest. The broad signals suggest possibilities of either more than one species co-existed in solution, which was confirmed from the isolation of some minor products (**2** and **6**) from the reaction mixtures of **1** and **5**, respectively, or the intrinsic lability of Ag–P bond. However, the exact nature is not well understood.

2.4. Rationalization of the reaction pathway

Although several possible binding modes of dtp ligands favor a variety of species being existed in solution in equilibrium, the structural characterization of species **1–8** prompts us to rationalize their formation pathways in order to get a better understanding of these types of ligands for further research. Schemes 1–3 depict a rationale of the formation of the complexes. The formation of **1** and **3** involve the reaction of Ag^+ , dtp and dppm in 2:2:1 ratio which may yield a dimeric intermediate A or B and further dimerization of them results in **1** and **3**, respectively. It is noted that the ratio of reactants used in these two reactions was 1:1:1. Although, we could not isolate any by-product from reaction mixture of **3**; however, cluster **2** is obtained as the minor product from the reaction mixture of **1**, by the reaction of three Ag^+ ions with three

dppm and two dtp ligands. Three dppm bridge three silver ions in *syn* manner to form a 12-membered ring and further two dtp ligands bridge these silver ions. The formation of dimer **4** involves the reaction of two Ag^+ ions with two dppm and one dtp ligand, which is the same as the mixing ratio of reactants. In all these complexes, the dppm ligand which acted as P,P'-bridge and remained in *syn* conformation, favored the formation of clusters (**1–4**) instead of polymeric compounds.

In the formation process of the polymers, which involves either dppe or dppb as the P,P'-bridging ligand, presumably a Ag(I) is chelated by a dtp to form a neutral species $\{\text{Ag}(\text{dtp})\}$, being coordinatively unsaturated, get polymerized with the help of either dppe or dppb as the linker to produce **5a**, **5a'**, or **7**, respectively (Scheme 2). The ratio of the Ag(I), dtp and dppe (or dppb) present in the polymers is 1:1:1, same as the mixing ratio of the reactants. However to rationalize the formation of **8**, it is assumed that two Ag^+ and two dtp ligands combined to yield $\text{Ag}_2(\text{dtp})_2$ which is further connected to dppb to form the repeating unit D of the polymer **8**. The molar ratio of Ag:dtp:dppb (2:2:1) in **8**, leads us to postulate that use of lower amount of dppb might favor the formation of $\text{Ag}_2(\text{dtp})_2$ species, followed by bridging by dppb. The P,P'-bridging ligands, dppe and dppb, remained in *anti* conformation in **5a**, **5a'**, **7** and **8** which facilitated the formation of the polymer species.

The formation of **6a**, the honeycomb-shaped network, is unusual in which three dtp ligands assembled to bridge three Ag atoms which generates a 12-membered metallacycle, and each of the Ag atoms is further bonded to one P atom of dppe with the second P atom remained dangling. Coordination of one more Ag(I) to three S atoms of three bridging dtp ligands, and abstraction of a Cl^- , presumably from the solvent CH_2Cl_2 , by three Ag atoms might lead to produce the repeating unit E (Scheme 3). This repeating unit led to the formation of 2D layer **6a** which was obtained as the minor product from the reaction mixture of polymer **5a**.

3. Conclusions

Diphosphines adopted P,P'-bridging mode in silver(I)-dtp chemistry; the shorter alkane spacer in dppm favors complexes with low nuclearity, the longer spacer as in dppe or dppb favors 1D and/or 2D polymers. The difference is attributed to the higher flexibility

of alkane spacers in dppe or dppb, which adopted *anti* conformation in the complexes vs. *syn* conformation adopted by dppm. The dtp exhibited several coordination modes in the complexes and it demonstrates larger angular flexibility on sulfur atom which can tune itself to local environments for a given metal center. That two silver atoms are concomitantly bridged by both phosphorus and sulfur donors of the dppm and dtp ligands led to short silver-silver contacts thus enhancing argentophilicity in cluster **1**, **3**, and **4**. On the other hand, polymeric **8** also showed short Ag...Ag contacts as they were bridged by two S from two dtp ligands.

4. Experimental

4.1. Materials and instruments

All the reactions were performed in oven-dried Schlenk glassware by using standard inert-atmosphere techniques. Solvents were purified following standard method prior to use. $\text{Ag}(\text{CH}_3\text{CN})_4(\text{PF}_6)$ [32], $\text{Ag}_2(\mu\text{-dppm})_2(\text{CH}_3\text{CN})_2(\text{PF}_6)_2$ [33], $\text{Ag}_2(\mu\text{-dppe})_2(\text{CH}_3\text{CN})_2(\text{PF}_6)_2$ [34], $\text{Ag}_2(\mu\text{-dppb})_2(\text{PF}_6)_2$ [35] and the ammonium dialkylidithiophosphates [36] were either procured or prepared according to the literature methods. Compounds **5a–b** and **6a–b** were reported previously [1]. All other reagents obtained from commercial sources, were used as received. NMR spectra were recorded on a Bruker Advance-300 FT spectrometer which operates on 300 MHz for ^1H NMR and on 121.49 MHz for ^{31}P NMR. The $^{31}\text{P}\{^1\text{H}\}$ NMR spectrometer is referenced externally against 85% H_3PO_4 . The elemental analyses (C, H, S) were done using a Perkin–Elmer 2400 Analyzer.

4.2. Syntheses

4.2.1. $[\text{Ag}_4(\text{dppm})_2\{\text{S}_2\text{P}(\text{OEt})_2\}_4]$ (**1**), and $[\text{Ag}_3(\text{dppm})_3\{\text{S}_2\text{P}(\text{OEt})_2\}_2](\text{PF}_6)$ (**2**)

Acetonitrile (30 mL) was added to a flask containing $\text{Ag}_2(\text{dppm})_2(\text{CH}_3\text{CN})_2(\text{PF}_6)_2$ (0.29 g, 0.2 mmol) and $\text{NH}_4[\text{S}_2\text{P}(\text{OEt})_2]$ (0.09 g, 0.4 mmol). It was stirred for 24 h at ambient temperature, and then filtered to remove any solid remained there. The filtrate was allowed to evaporate at room temperature, until white solid was obtained. The white solid was re-dissolved in CH_3OH (20 mL) and crystals of **2** were formed in 7% yield. After separation of the crystals of **2**, the filtrate was evaporated using rotavapor, and the solids obtained were re-dissolved in chloroform (20 mL) and layered with hexane (10 mL) which afforded crystalline material of **1**. Compound **2** was washed well with CHCl_3 to remove any traces of **1**.

Compound **1**: Yield: 76% (0.30 g). Anal. Calc. for $\text{C}_{66}\text{H}_{84}\text{Ag}_4\text{O}_8\text{S}_8\text{P}_8$: C, 40.84; H, 4.36; S, 13.21. Found: C, 40.76; H, 4.54; S, 13.05%. ^1H NMR (CDCl_3): δ 1.18 (m, 24H, CH_3), 3.39 (s, br; 4H, CH_2 of dppm), 4.07 (m, 16H, CH_2), 7.02–7.42 (m, 40H, Ph); $^{31}\text{P}\{^1\text{H}\}$ NMR (CDCl_3): δ 108.21 {s, $\text{P}(\text{OEt})_2$ }, 1.00 (br s, PPh_2). $\Delta\delta = \delta_{\text{Complex}} - \delta_{\text{Ligand}(\text{S}_2\text{P})} = -6.59$ ppm; $\Delta\delta = \delta_{\text{Complex}} - \delta_{\text{Ligand}(\text{PPh}_2)} = 20.5$ ppm.

Compound **2**: Yield: 7% (0.02 g). Anal. Calc. for $\text{C}_{83}\text{H}_{86}\text{Ag}_3\text{O}_4\text{S}_4\text{P}_9\text{F}_6 \cdot \text{CHCl}_3$: C, 47.78; H, 4.15; S, 6.07. Found: C, 47.76; H, 4.54; S, 6.05%. ^1H NMR (CDCl_3): δ 1.13 (m, 12H, CH_3), 3.56 (br s, 6H, CH_2 , dppm), 3.86 (m, 8H, CH_2), 7.05–7.37 (m, 60H, Ph); $^{31}\text{P}\{^1\text{H}\}$ NMR (CDCl_3): δ 106.03 {s, $\text{P}(\text{OEt})_2$ }, -0.20 (br s, PPh_2). $\Delta\delta = \delta_{\text{Complex}} - \delta_{\text{Ligand}(\text{S}_2\text{P})} = -8.77$ ppm; $\Delta\delta = \delta_{\text{Complex}} - \delta_{\text{Ligand}(\text{PPh}_2)} = 19.30$ ppm.

4.2.2. $[\text{Ag}_4(\text{dppm})_2\{\text{S}_2\text{P}(\text{O}^i\text{Pr})_2\}_4]$ (**3**)

It was prepared by the method as used for **1**, except using dichloromethane as solvent and $\text{NH}_4[\text{S}_2\text{P}(\text{O}^i\text{Pr})_2]$ as ligand. After isolation, **3** were subjected to thorough washing with CH_3OH to remove any species analogous to **2**. Yield: 75% (0.18 g). Anal. Calc.

for $\text{C}_{74}\text{H}_{100}\text{Ag}_4\text{O}_8\text{S}_8\text{P}_8 \cdot \text{CH}_3\text{OH}$: C, 43.20; H, 5.03; S, 12.30. Found: C, 43.15; H, 5.01; S, 12.01%. ^1H NMR (CDCl_3): δ 1.23 (m, 24H, CH_3), 3.07 (br s, 4H, CH_2 of dppm), 4.75 (m, 8H, CH), 7.08–7.43 (m, 40H, Ph). $^{31}\text{P}\{^1\text{H}\}$ NMR (CDCl_3): δ 106.75 {s, $\text{P}(\text{O}^i\text{Pr})_2$ }, -5.75 (br s, PPh_2). $\Delta\delta = \delta_{\text{Complex}} - \delta_{\text{Ligand}(\text{S}_2\text{P})} = -4.63$ ppm; $\Delta\delta = \delta_{\text{Complex}} - \delta_{\text{Ligand}(\text{PPh}_2)} = 13.75$ ppm.

4.2.3. $[\text{Ag}_2(\text{dppm})_2\{\text{S}_2\text{P}(\text{O}^i\text{Pr})_2\}](\text{PF}_6)$ (**4**)

Dichloromethane (30 mL) was added to a 100 mL flask containing $[\text{Ag}(\text{CH}_3\text{CN})_4](\text{PF}_6)$ (0.30 g, 0.72 mmol), dppm (0.27 g, 0.72 mmol) and $\text{NH}_4[\text{S}_2\text{P}(\text{O}^i\text{Pr})_2]$ (0.08 g, 0.36 mmol). The solution mixture was stirred for 24 h at ambient temperature and filtered to remove any solid. The filtrate was then washed with water and the dichloromethane extract was allowed to evaporate to get a white solid. This solid was re-dissolved in dichloromethane and layered with hexane which afforded crystalline material of **4**. Yield: 68% (0.16 g). Anal. Calc. for $\text{C}_{56}\text{H}_{58}\text{Ag}_2\text{O}_2\text{S}_2\text{P}_6\text{F}_6$: C, 50.09; H, 4.35; S, 4.78. Found: C, 49.98; H, 4.57; S, 4.83%. ^1H NMR (CDCl_3): δ 1.16 (m, 6H, CH_3), 3.60 (br s, 4H, CH_2 of dppm), 4.58 (br s, 1H, CH), 7.00–7.65 (m, 40H, PPh). $^{31}\text{P}\{^1\text{H}\}$ NMR (CDCl_3): δ 102.17 {s, $\text{P}(\text{O}^i\text{Pr})_2$ }, 6.62 (br, PPh_2). $\Delta\delta = \delta_{\text{Complex}} - \delta_{\text{Ligand}(\text{S}_2\text{P})} = -9.21$ ppm; $\Delta\delta = \delta_{\text{Complex}} - \delta_{\text{Ligand}(\text{PPh}_2)} = 26.12$ ppm.

4.2.4. $[\text{Ag}(\text{dppe})\{\text{S}_2\text{P}(\text{OEt})_2\}]_\infty$ (**5a'**)

The compound was prepared in a similar procedure described in case of **5a**. $[\text{Ag}_2(\text{dppe})_2(\text{CH}_3\text{CN})_2](\text{PF}_6)_2$ (0.50 g, 3.60 mmol) and $\text{NH}_4[\text{S}_2\text{P}(\text{OEt})_2]$ (0.15 g, 7.20 mmol) were taken in a 100 mL flask and 50 mL of CH_2Cl_2 was added and stirred for 24 h at ambient temperature. After this it was filtered to remove the solid formed and the dichloromethane solution was washed with 2×50 mL of water. The organic layer was dried over MgSO_4 and evaporated to dryness to get a white solid. The solid was washed by MeOH using sonication to get compound **5a** or **5a'**. Crystals of **5a'** were obtained from slow evaporation of acetone solution of this solid whereas crystals of **5a** could be obtained by diffusing hexane into dichloromethane solution of the isolated solid. Thus **5a** and **5a'** are polymorph. Yield: 63% (0.32 g). Anal. Calc. for $\text{C}_{30}\text{H}_{34}\text{AgO}_2\text{S}_2\text{P}_3$: C, 52.10; H, 4.95; S, 9.27. Found: C, 52.40; H, 5.00; S, 9.17%. ^1H NMR (CDCl_3): δ 1.13 (m, 6H, CH_3), 2.44 (br s, 4H, CH_2 of dppm), 3.93 (m, 4H, CH_2), 7.08–7.79 (m, 40H, Ph). $^{31}\text{P}\{^1\text{H}\}$ NMR (CDCl_3): δ 105.78 {s, $\text{P}(\text{O}^i\text{Pr})_2$ }, 2.87 (br, PPh_2). $\Delta\delta = \delta_{\text{Complex}} - \delta_{\text{Ligand}(\text{S}_2\text{P})} = 9.02$ ppm; $\Delta\delta = \delta_{\text{Complex}} - \delta_{\text{Ligand}(\text{PPh}_2)} = 17.07$ ppm.

4.2.5. $[\text{Ag}(\text{dppb})\{\text{S}_2\text{P}(\text{OEt})_2\}]_\infty$ (**7**)

The method is the same as for **1**, except using dichloromethane as solvent with $[\text{Ag}_2(\text{dppb})_2(\text{CH}_3\text{CN})_2](\text{PF}_6)_2$ as starting material. Crystals were grown from $\text{CH}_2\text{Cl}_2/\text{C}_2\text{H}_5\text{OH}$ mixed solvent. Yield: 73% (0.21 g). Anal. Calc. for $\text{C}_{32}\text{H}_{38}\text{AgO}_2\text{S}_2\text{P}_3 \cdot 1/2\text{CH}_2\text{Cl}_2$: C, 51.22; H, 5.16; S, 8.42. Found: C, 50.58; H, 5.16; S, 8.07%. ^1H NMR (CDCl_3): δ 1.28 (m, 6H, CH_3), 1.75 (br s, 4H, CH_2 of dppb), 2.15 (br s, 4H, CH_2 of dppb), 4.06 (m, 4H, CH_2), 7.24–7.78 (m, 20H, Ph). $^{31}\text{P}\{^1\text{H}\}$ NMR (CDCl_3): δ 105.96 {m, $\text{P}(\text{OEt})_2$ }, 0.33 (m, PPh_2). $\Delta\delta = \delta_{\text{Complex}} - \delta_{\text{Ligand}(\text{S}_2\text{P})} = -8.82$ ppm; $\Delta\delta = \delta_{\text{Complex}} - \delta_{\text{Ligand}(\text{PPh}_2)} = 19.83$ ppm.

4.2.6. $[\text{Ag}_2(\text{dppb})\{\text{S}_2\text{P}(\text{OEt})_2\}]_\infty$ (**8**)

It was prepared by the same method as for **4** by reacting $[\text{Ag}(\text{CH}_3\text{CN})_4](\text{PF}_6)$, dppb and $\text{NH}_4[\text{S}_2\text{P}(\text{OEt})_2]$ in 2:1:2 molar ratio. Yield: 68% (0.25 g). Anal. Calc. for $\text{C}_{36}\text{H}_{48}\text{Ag}_2\text{O}_4\text{S}_4\text{P}_4$: C, 42.70; H, 4.78; S, 12.67. Found: C, 43.15; H, 4.93; S, 12.36%. ^1H NMR (CDCl_3): δ 1.20 (m, 12H, CH_3), 1.58 (br s, 4H, CH_2 of dppb), 2.07 (br s, 4H, CH_2 of dppb), 4.00 (m, 4H, CH), 7.20–7.53 (m, 20H, PPh). $^{31}\text{P}\{^1\text{H}\}$ NMR (CDCl_3): δ 107.53 {s, $\text{P}(\text{OEt})_2$ }, 1.02 (br s, PPh_2). $\Delta\delta = \delta_{\text{Complex}} - \delta_{\text{Ligand}(\text{S}_2\text{P})} = -7.30$ ppm; $\Delta\delta = \delta_{\text{Complex}} - \delta_{\text{Ligand}(\text{PPh}_2)} = 20.52$ ppm.

Table 2Crystallographic data for compounds **1–4**, **5a'**, **7** and **8**.

	1	2	3	4	5a'	7 · CH₂Cl₂ · C₂H₅OH	8
Formula	C ₃₃ H ₄₂ Ag ₂ O ₄ S ₄ P ₄	C ₈₃ H ₈₆ Ag ₃ O ₄ S ₄ P ₉ F ₆	C ₇₄ H ₁₀₀ Ag ₄ O ₈ S ₈ P ₈	C ₅₆ H ₅₈ Ag ₂ F ₆ O ₂ P ₆ S ₂	C ₃₀ H ₃₄ AgO ₂ P ₃ S ₂	C ₃₅ H ₄₆ AgCl ₂ O ₃ P ₃ S ₂	C ₁₈ H ₂₄ AgO ₂ P ₂ S ₂
Formula weight	970.53	1992.10	2053.26	1342.70	691.47	850.52	506.30
Crystal system	Monoclinic	Orthorhombic	Orthorhombic	Monoclinic	Triclinic	Triclinic	Triclinic
space group	<i>P</i> 2 ₁ / <i>n</i>	<i>P</i> na2 ₁	<i>P</i> bca	<i>P</i> 2 ₁ / <i>c</i>	<i>P</i> $\bar{1}$	<i>P</i> $\bar{1}$	<i>P</i> $\bar{1}$
<i>a</i> (Å)	14.1504(11)	32.2003(16)	17.2672(17)	10.4045(13)	11.1168(17)	12.4844(17)	9.6616(13)
<i>b</i> (Å)	17.8787(13)	18.5101(9)	22.7228(17)	36.563(5)	11.640(2)	13.410(3)	10.5348(14)
<i>c</i> (Å)	16.4680(10)	14.5405(7)	23.462(2)	16.043(2)	13.4236(12)	14.4970(18)	11.5849(16)
α (°)	90	90	90	90	99.904(11)	102.387(10)	67.726(2)
β (°)	90.700(6)	90	90	105.644(3)	91.219(11)	107.825(9)	86.002(3)
γ (°)	90	90	90	90	106.036(15)	109.245(13)	86.095(3)
<i>V</i> (Å ³)	4165.9(5)	8666.6(7)	9205.5(14)	5877.2(13)	1640.2(4)	2042.7(5)	1087.4(3)
<i>Z</i>	4	4	4	4	2	2	2
ρ_{calc} (g cm ⁻³)	1.547	1.527	1.482	1.517	1.400	1.383	1.546
λ (Mo K α) (Å)	0.71073	0.71073	0.71073	0.71073	0.71073	0.71073	0.71073
μ (mm ⁻¹)	1.053	0.994	1.206	0.960	0.913	0.875	1.275
<i>T</i> (K)	298(2)	298(2)	293(2)	298(2)	293(2)	293(2)	298(2)
<i>R</i> 1 ^a	0.0358	0.0365	0.0659	0.0682	0.0470	0.0585	0.0241
<i>wR</i> 2 ^b	0.0936	0.0916	0.1473	0.1572	0.1165	0.1513	0.0600

^a $R1 = \sum |F_o| - |F_c| / \sum |F_o|$.^b $wR2 = [\sum (w(F_o^2 - F_c^2))^2] / [\sum (w(F_o^2))^2]^{1/2}$.

4.3. X-ray crystallography

The crystal structures of **1–4**, **5a'**, **7**, and **8** were obtained by single crystal X-ray diffraction technique. Crystals were mounted on the tips of glass fibers with epoxy resin. Data for compounds **3**, **5a'**, and **7** were collected at 298 K on a Siemens P4 diffractometer equipped with Mo K α radiation ($\lambda = 0.71073$ Å). The data were collected using 2θ - ω scan technique. Crystal data for compounds **1**, **2**, **4**, and **8** were collected at 293 K on a Siemens SMART CCD diffractometer. Data were measured with ω scans of 0.3° per frame for 90 s. Cell parameters were retrieved with SMART software [37] and refined with SAINT software on all observed reflection ($I > 10\sigma(I)$). Data reduction was performed with SAINT [38], which corrects for Lorentz and polarization effects. An empirical absorption correction was applied for all compounds. The structure was solved by the use of direct methods, and refinement was performed by the least-squares methods on F^2 with the SHELXL-97 package [39], incorporated in SHELXTL/PC V5.10 [40]. Selected crystal data for the compounds are summarized in Table 2. Compounds **5a** and **5a'**, with a different unit cell, are polymorphs. Structures of **5a**, **6a**, and **6b** (CCDC 254826–254828) were reported in the previous communication [1].

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Appendix A. Supplementary material

CCDC 293322, 293323, 293324, 293325, 293326, 293327, and 293328 contain the supplementary crystallographic data for compounds **1**, **2**, **3**, **4**, **5a'**, **7**, and **8**. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jorganchem.2009.02.017.

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