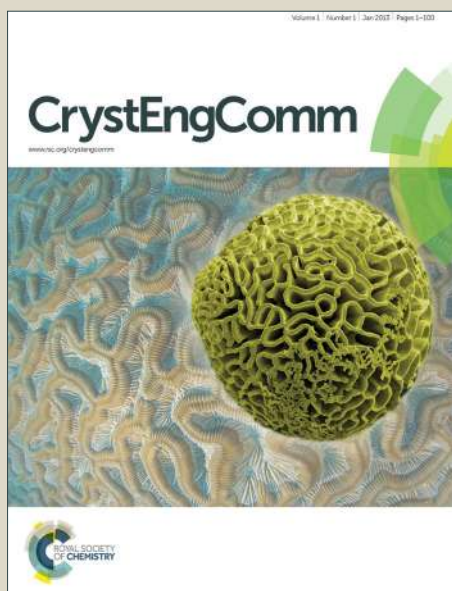


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## Hemilabile silver(I) complexes containing pyridyl chalcogenolate (S, Se) ligands and their utility as molecular precursors for silver chalcogenide

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A series of silver triphenylphosphine complexes containing pyridyl chalcogenolate (S, Se) ligands has been synthesized by employing  $[\text{AgCl}(\text{PPh}_3)_3]$  and  $[\text{Ag}_2(\mu\text{-Cl})_2(\text{PPh}_3)_4]$ . The complexes  $[\text{Ag}(\text{S-4-pyH}_{0.5})_2(\text{PPh}_3)_2]$  (**1**) and  $[\text{Ag}_2(\mu\text{-S-4-py})_2(\text{PPh}_3)_4]$  (**2**) were obtained by the reactions of  $[\text{Ag}_2(\mu\text{-Cl})_2(\text{PPh}_3)_4]$  with 4-pySH in the presence of  $\text{Et}_3\text{N}$  and  $\text{NaOH}$ , respectively. The former has a hydrogen bonded chain like structure, while the latter possesses discrete binuclear structure. The **2** on heating in methanol afforded a two-dimensional coordination polymer  $[\text{Ag}_2(\mu\text{-S-4-py})_2(\text{PPh}_3)_2]_n$  (**3**). The reaction of  $[\text{Ag}_2(\mu\text{-Cl})_2(\text{PPh}_3)_4]$  with  $\text{NaSe-4-py}$  gave  $[\text{Ag}_3(\mu\text{-Se-4-py})_3(\text{PPh}_3)_4]$  (**4**) as a primary product together with a minor mononuclear complex,  $[\text{Ag}(\text{Se-4-py})(\text{PPh}_3)_3]$  (**5**). The latter could be obtained in excellent yield under the same conditions utilising  $[\text{AgCl}(\text{PPh}_3)_3]$  as the starting material. The complex **5** on recrystallization afforded **4**. The reaction of  $[\text{AgCl}(\text{PPh}_3)_3]$  with  $\text{NaS-2-py}$  yielded  $[\text{Ag}(\text{S-2-py})(\text{PPh}_3)_3]$  (**6**). Complexes (**2** – **6**) on refluxing in chloroform gave insoluble polymeric complexes of composition  $[\text{Ag}(\text{Epy})]_n$  (**7**) (Epy = 4-pyS (**7a**), 4-pySe (**7b**), 2-pyS (**7c**)) which on thermolysis yielded  $\text{Ag}_2\text{E}$  (E = S, Se). The molecular structures of these complexes (**1** – **6**) have been established unambiguously by single crystal X-ray diffraction analyses. Non-bonding interactions in the molecular structures have been discussed.

### Introduction

Coordination and organometallic compounds with direct metal-chalcogen bond constitute an important class of molecules and find applications in diverse areas encompassing catalysis, biology and materials science.<sup>1</sup> These complexes provide knowledge of a wide range of structural diversity with the electron rich chalcogen donors which can coordinate up to four soft metal centres generating several novel structural motifs.<sup>2</sup> The soft nature of coinage (M = Ag(I) and Au(I)) metal ions having high affinity towards ligands containing chalcogen donor centres are suitable for this purpose.<sup>3</sup> These ions in closed shell  $d^{10}$  electronic configuration often exhibit metallophilic (M...M) interaction which can influence the self-assembly process.<sup>4</sup> The Ag(I) can have varying coordination numbers with flexible geometries which make it very interesting metal node to study its versatile coordination chemistry.<sup>5</sup> Organic ligands containing pyridyl-N donor along with S or Se donor can either chelate or bridge between two metal centres to generate either multinuclear complexes or

coordination polymeric networks.<sup>6</sup> N-heterocyclic thiolate complexes of coinage metals are fairly well investigated,<sup>6,7</sup> however, the heavier chalcogenolate (Se or Te) complexes received attention only recently.<sup>8</sup> The hexanuclear  $[\text{Ag}(\text{SeC}_4\text{H}(\text{Me-4,6})_2\text{N}_2)]_6$  has been successfully employed as a molecular precursor for the synthesis of monodispersed  $\text{Ag}_2\text{Se}$  nano-particles.<sup>8</sup> Of late solution phase pyrolytic methods have emerged as a successful strategy to prepare metal chalcogenide nano-materials.<sup>8,9</sup> The homoleptic silver chalcogenolate complexes are polymeric and are insoluble in common organic solvents thus limiting their utility as precursors for the preparation of silver-chalcogenides.

The complexes derived from Ag-P coordination bond have been investigated thoroughly.<sup>10</sup> The phosphine complexes have been isolated as low nuclearity complexes with reasonable solubility in organic solvents. Organic ligands having phosphine moiety together with relatively harder N-donor or with softer S or Se donors provide the scope of generating hemi-labile complexes.<sup>11</sup> 4-Mercapto pyridine often coordinates to Ag(I) only through S-donor while the pyridyl-N remain either protonated or uncoordinated. Tong and co-workers reported two coordination polymers of composition  $[\text{Ag}_3(\mu\text{-Cl})_3(\mu_3\text{-S-4-pyH})_2]$  and  $[\text{Ag}_2(\mu_3\text{-S-4-pyH})(\mu\text{-Cl})\text{Cl}]$  where the pyridyl-Ns are protonated. For the latter, a two-dimensional sheet-like structure is generated by  $\mu_3$ -bridging and  $\mu_2$ -bridging coordination of S and Cl, respectively.<sup>12</sup> Similarly in  $[\text{Ag}(\text{S-2-pyH})_2(\text{PPh}_3)_2](\text{NO}_3)$ , the pyridyl-Ns are

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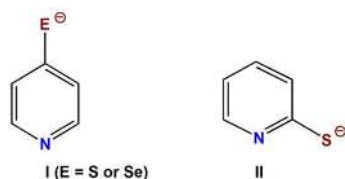
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protonated, thus unable to form any Ag-N coordination bond.<sup>13</sup>

The pyridyl chalcogenolate ligands with softer chalcogen donor (S/Se/Te) and relatively harder donor-N have been used to induce hemilability in the complexes. Moreover, the Ag-P coordination bond also provides hemilabile nature which can easily be formed or cleaved. In view of the above, we have explored the chemistry of pyridylchalcogenolate (**I** and **II** in Scheme 1) complexes of silver containing triphenylphosphine as an auxiliary ligand and examined their structural diversity and inter-conversion. The suitability of silver chalcogenolate complexes as molecular precursors for the synthesis of silver sulfide or selenide material has been evaluated.



Scheme 1: The structures of the pyridyl chalcogenolate ligands used in this study

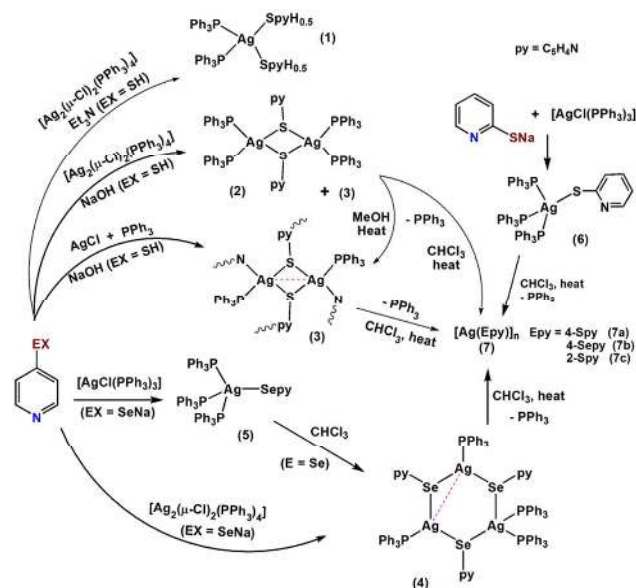
## Results and Discussion

### Synthesis and spectroscopy

Synthesis of various silver(I) chalcogenolate complexes are depicted in Scheme 2. All the complexes were synthesized at room temperature, except  $[\text{Ag}_2(\mu\text{-S-4-py})_2(\text{PPh}_3)_4]$  (**2**) and  $[\text{Ag}_2(\mu\text{-S-4-py})_2(\text{PPh}_3)_2]$  (**3**) which were obtained under hot (70 °C) reaction conditions. The reaction of  $[\text{Ag}_2(\mu\text{-Cl})_2(\text{PPh}_3)_4]$  with 4-mercapto pyridine in the presence of triethylamine gave  $[\text{Ag}(\text{S-4-pyH}_{0.5})_2(\text{PPh}_3)_2]$  (**1**). Treatment of  $[\text{Ag}_2(\mu\text{-Cl})_2(\text{PPh}_3)_4]$  with 4-pyENA afforded a binuclear complex,  $[\text{Ag}_2(\mu\text{-S-4-py})_2(\text{PPh}_3)_4]$  (**2**), a two-dimensional coordination polymer  $[\text{Ag}_2(\mu\text{-S-4-py})_2(\text{PPh}_3)_2]$  (**3**) and a trinuclear complex  $[\text{Ag}_3(\mu\text{-Se-4-py})_3(\text{PPh}_3)_4]$  (**4**) depending on the nature of chalcogenolate atom and reaction conditions. The **4** was accompanied with a small amount of a mononuclear complex  $[\text{Ag}(\text{Se-4-py})(\text{PPh}_3)_3]$  (**5**) which could be isolated in excellent yield by a reaction between  $[\text{AgCl}(\text{PPh}_3)_3]$  and 4-pySeNa. Attempt to isolate the selenium analogue of **2** was, however, unsuccessful. It is likely that the dissociation of one  $\text{PPh}_3$  ligand from **5** in solution may result in the selenium analogue of the binuclear complex **2**, but our efforts to detect it either in solution or in the solid state were futile. This could possibly be due to the difference in the nucleophilicity of sulfur and selenium. The later being stronger nucleophile, tends to stabilize phosphine deficient **4** rather than analogue of **2**. When the crystals of **5** were left in a  $\text{CHCl}_3$  solution for a few days, crystals of **4** were separated out. When the chloroform solution of **4** or **5** was heated for an hour, cream yellow precipitate of  $[\text{Ag}(\text{Se-4-py})]_n$  (**7b**) was formed. Similarly, when **2**, **3** and **6** were refluxed in chloroform for an hour, cream coloured precipitate of  $[\text{Ag}(\text{S-4-py})]_n$  (**7a**) and yellow precipitate of  $[\text{Ag}(\text{S-2-py})]_n$  (**7c**) were obtained. The **7c** has been reported earlier. Depending on the preparative method different structural forms like a metastable layered

polymer with graphite like array of silver ions,<sup>6a</sup> one dimensional chain structure<sup>6b</sup> and hexanuclear  $\text{Ag}_6\text{S}_6$  core<sup>14</sup> have been obtained. The latter structural form is also isolated with substituted 2-pyridylthiolate group,  $(\text{RC}_5\text{H}_3\text{N})\text{S}$ , ( $\text{R} = 3\text{-Bu}^t\text{Me}_2\text{Si}$ ,<sup>15</sup>  $3\text{-CF}_3$ ,<sup>16</sup>  $3\text{-CO}_2\text{H}$ <sup>17</sup>).

The  $^1\text{H}$  NMR spectra of these complexes exhibited expected resonances. The  $^{31}\text{P}$  NMR spectrum of  $[\text{Ag}(\text{S-4-pyH}_{0.5})_2(\text{PPh}_3)_2]$  (**1**) displayed a resonance due to free  $\text{PPh}_3$  indicating dissociation of the complex in solution. The  $^{31}\text{P}$  NMR spectra of **2** – **6** showed single resonances. The  $^{31}\text{P}$  NMR spectrum of **4**, despite of two different types of  $\text{PPh}_3$  ligands, exhibited only a single resonance indicative of a dynamic behaviour.



Scheme 2: Schematic depiction of synthetic protocol and inter-conversion of complexes

### Crystallography

The molecular structures of  $[\text{Ag}(\text{S-4-pyH}_{0.5})_2(\text{PPh}_3)_2]$  (**1**),  $[\text{Ag}_2(\mu\text{-S-4-py})_2(\text{PPh}_3)_4]$  (**2**),  $[\text{Ag}_2(\mu\text{-S-4-py})_2(\text{PPh}_3)_n]$  (**3**),  $[\text{Ag}_3(\mu\text{-Se-4-py})_3(\text{PPh}_3)_4]$  (**4**),  $[\text{Ag}(\text{Se-4-py})(\text{PPh}_3)_3]$  (**5**) and  $[\text{Ag}(\text{S-2-py})(\text{PPh}_3)_3]$  (**6**) were established unambiguously by single crystal X-ray diffraction analyses. Selected inter-atomic parameters are listed in Tables 1 – 5.

The asymmetric unit of  $[\text{Ag}(\text{S-4-pyH}_{0.5})_2(\text{PPh}_3)_2]$  (**1**) contains half of a molecule. The silver(I) adopts a distorted tetrahedral configuration defined by two  $\text{PPh}_3$  and two S atoms from S-4-py. The Ag-P (2.4663(6) Å) and Ag-S (2.5943(6) Å) distances are in conformity with those reported in  $[\text{Ag}_2\text{Cl}_2(\mu\text{-S-2-pyH})_2(\text{PPh}_3)_2]$  (Ag-P = 2.435(1) Å; Ag-S = 2.583(1), 2.721(1) Å),<sup>18</sup>  $[\text{Ag}_3(\mu_4\text{-S-4-py})(\mu_4\text{-NCS})_2]_n$  (Ag-S = 2.480, 2.501, 2.611 Å)<sup>19</sup> and  $[\text{Ag}(\text{S-2-pyH})_2(\text{PPh}_3)_2](\text{NO}_3)$  (Ag-P = 2.463(1), 2.503(1); Ag-S = 2.632(1), 2.602(1) Å).<sup>20</sup> The S-Ag-S angle (91.71(3)°) in **1** has reduced while the P-Ag-P angle (126.97(3)°) has opened up from the corresponding angles in  $[\text{Ag}(\text{S-2-pyH})_2(\text{PPh}_3)_2](\text{NO}_3)$  (S-Ag-S = 99.5(1)°; P-Ag-P = 118.0(1)°).<sup>21</sup> To maintain the charge balance, each pyridyl-N is protonated. The occupancy of the proton on each nitrogen atom is 0.5 constituting one

proton in each mononuclear complex. The shorter distance between two protonated pyridyl-Ns from neighbouring molecules (2.656 Å), suggests that there is hydrogen bonding between two neighbouring molecules and thus it creates an infinite chain of hydrogen bonded network passing along  $a$ -axis (Fig 1a). There are weak C-H $\cdots$ S (3.673 Å) (on the  $bc$  plane) (Fig 1b) and C-H $\cdots$  $\pi$  (3.501 Å, phenyl ring of PPh<sub>3</sub>) (Fig 1c) intermolecular interactions between two parallel chains.

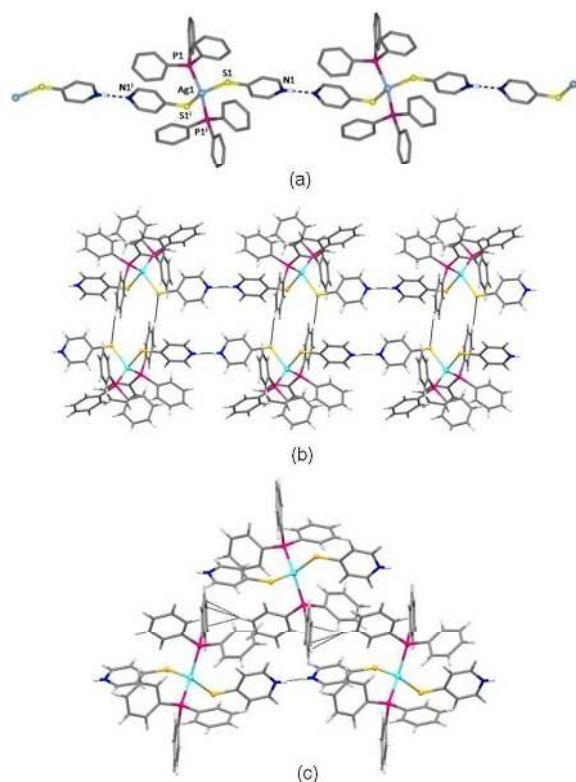


Figure 1: (a) one dimensional hydrogen bonded network structure of [Ag(S-4-pyH<sub>0.5</sub>)<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub>] (**1**) (Inter-atomic parameters Ag1-P1 = 2.4663(6) Å, Ag1-S1 = 2.5943(6) Å; P1-Ag1-P1 = 126.97(3)°, P1-Ag1-S1 = 115.48(2)°, P1-Ag1-S1 = 101.05(2)°, S1-Ag1-S1 = 91.71(3)°); Symmetry operator: <sup>i</sup> = 2-x, y, 1/2-z; (b) intermolecular C-H $\cdots$ S interaction and (c) intermolecular C-H $\cdots$  $\pi$  interactions between two parallel chains in **1**.

There are two halves of the binuclear complex [Ag<sub>2</sub>( $\mu$ -S-4-py)<sub>2</sub>(PPh<sub>3</sub>)<sub>4</sub>] (**2**) in the asymmetric unit. The interatomic parameters in the two molecules differ slightly from each other (Table 1). Each silver atom acquires distorted tetrahedral configuration defined by P<sub>2</sub>S<sub>2</sub> core. The two silver atoms are held together by bridging thiolate ligand to give a distorted rhombohedral Ag<sub>2</sub>S<sub>2</sub> core as one of two sulfur atoms in both the Ag<sub>2</sub>S<sub>2</sub> core is disordered over two positions (Fig 2). The Ag-P (av. 2.48(4) Å and Ag-S (2.513(14) – 2.691(13) Å) are well in agreement with those reported in silver thiolate complexes *e.g.* for [Ag<sub>2</sub>( $\mu$ -S-2-pyH)<sub>2</sub>X<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub>] (X = Cl, Br) (Ag-S = 2.583(1) – 2.721(1) Å).<sup>18</sup> The Ag $\cdots$ Ag distances in two molecules (3.981 and 4.071 Å) are longer than the sum of van der Waals radii of two silver atoms (3.44 Å); indicative of the absence of any argentophilic interactions. The pyridyl-N atoms are not coordinated to any metal centre. Although, there is no parallel

stacking of phenyl rings of PPh<sub>3</sub>, the distance between the carbon atoms of two phenyl rings are in the range of 3.58 – 3.74 Å indicating C-H $\cdots$ C( $\pi$ ) interaction. Apart from this weak interaction, there are no other noticeable significant intermolecular interactions.

Table 1: Selected bond lengths (Å) and angles (°) for **2**.

Ag1-P1	2.488(4)	Ag2-P3	2.486(4)
Ag1-P2	2.473(4)	Ag2-P4	2.474(4)
Ag1-S1 <sup>i</sup>	2.513(14)	Ag2-S3	2.63(5)
Ag1-S1	2.665(13)	Ag2-S3 <sup>ii</sup>	2.56(3)
Ag1-S2	2.65(2)	Ag2-S4	2.538(14)
Ag1-S2 <sup>i</sup>	2.62(2)	Ag2-S4 <sup>ii</sup>	2.691(13)
Ag1 $\cdots$ Ag1 <sup>i</sup>	3.981	Ag2 $\cdots$ Ag2 <sup>ii</sup>	4.071
P1-Ag1-P2	121.24(13)	P3-Ag2-P4	120.59(13)
P1-Ag1-S1	122.7(3)	P3-Ag2-S3	118.7(8)
P1-Ag1-S1 <sup>i</sup>	103.0(3)	P3-Ag2-S3 <sup>ii</sup>	107.9(8)
P1-Ag1-S2	104.4(4)	P3-Ag2-S4	100.9(3)
P1-Ag1-S2 <sup>i</sup>	117.1(4)	P3-Ag2-S4 <sup>ii</sup>	118.3(3)
P2-Ag1-S1	103.4(4)	P4-Ag2-S3	109.7(9)
P2-Ag1-S1 <sup>i</sup>	120.9(4)	P4-Ag2-S3 <sup>ii</sup>	119.4(8)
P2-Ag1-S2	119.6(3)	P4-Ag2-S4	122.0(3)
P2-Ag1-S2 <sup>i</sup>	106.4(3)	P4-Ag2-S4 <sup>ii</sup>	106.5(3)
Ag1-S1-Ag1 <sup>i</sup>	100.4(3)	Ag2-S3-Ag2 <sup>ii</sup>	103.3(4)
Ag1-S2-Ag1 <sup>i</sup>	98.1(3)	Ag2-S4-Ag2 <sup>ii</sup>	102.2(3)

Symmetry operators: <sup>i</sup> = -x-1, -y, z; <sup>ii</sup> = -x, 1-y, z

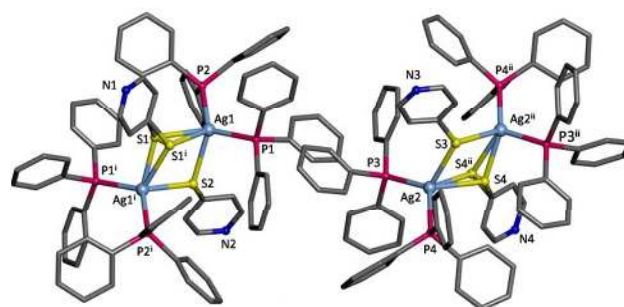


Figure 2: Molecular structure of [Ag<sub>2</sub>( $\mu$ -Spy-4)<sub>2</sub>(PPh<sub>3</sub>)<sub>4</sub>] (**2**). The symmetry operators are: <sup>i</sup> = -1-x, -y, z; <sup>ii</sup> = -x, 1-y, z.

In the asymmetric unit of [Ag<sub>2</sub>( $\mu$ -S-4-py)<sub>2</sub>(PPh<sub>3</sub>)<sub>4</sub>]<sub>n</sub> (**3**), there are two PPh<sub>3</sub>, two S-4-py and two Ag(I) atoms. Each S atom coordinates to two silver atoms and it forms an Ag<sub>2</sub>S<sub>2</sub> rhombohedral ring similar to the one noted in **2**. Each silver atom acquires distorted tetrahedral configuration defined by PNS<sub>2</sub> core. The Ag $\cdots$ Ag distances in the two Ag<sub>2</sub>S<sub>2</sub> rings (2.966 and 3.419 Å) are shorter than the sum of van der Waals radii of two silver atoms (3.44 Å) indicating strong argentophilic interaction in one ring while the absence of the same in the other ring. The planes of two types of Ag<sub>2</sub>S<sub>2</sub> rhombohedra orient at an angle of 12.4° with each other. The Ag-S, Ag-P distances found in **3** are in the similar range as found in **2**. Unlike in the case of **2**, the pyridyl-N of the mercaptopyrindine ligand coordinates to silver atom resulting in the formation of two dimensional network structure (Fig 3, see ESI also).

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Considering the centroids of the  $\text{Ag}_2\text{S}_2$  rings as node, the structure of this coordination polymer can be approximated as (4, 4) connected network. There are weak C-H $\cdots$ C( $\pi$ ) interaction between the phenyl rings of  $\text{PPh}_3$  and the existence of weak C-H $\cdots$ S interactions was also noted (see ESI).

Table 2: Selected bond lengths (Å) and angles (°) for **3**

Ag1-S1	2.713(2)	Ag2-S2	2.5347(19)
Ag1-S1 <sup>i</sup>	2.5615(19)	Ag2-S2 <sup>ii</sup>	2.654(2)
Ag1-P1	2.4421(18)	Ag2-P2	2.4414(18)
Ag1-N2 <sup>iii</sup>	2.369(7)	Ag2-N1	2.330(6)
Ag1 $\cdots$ Ag1 <sup>i</sup>	2.9657(10)	Ag2 $\cdots$ Ag2 <sup>iii</sup>	3.420
P1-Ag1-S1	99.65(6)	S2-Ag2-S2 <sup>ii</sup>	97.58(6)
P1-Ag1-S1 <sup>i</sup>	125.73(6)	P2-Ag2-S2	127.49(6)
S1-Ag1-S1 <sup>i</sup>	111.65(5)	P2-Ag2-S2 <sup>ii</sup>	102.97(6)
N2 <sup>iii</sup> -Ag1-P1	114.02(18)	N1-Ag2-S2 <sup>ii</sup>	107.33(19)
N2 <sup>iii</sup> -Ag1-S1	107.95(19)	N1-Ag2-S2	104.40(17)
N2 <sup>iii</sup> -Ag1-S1 <sup>i</sup>	97.39(19)	N1-Ag2-P2	114.29(17)
Ag1-S1-Ag1 <sup>i</sup>	68.35(5)	Ag2-S2-Ag2 <sup>ii</sup>	82.42(6)

Symmetry operators: <sup>i</sup> = 1-x, 1-y, 1-z; <sup>ii</sup> = -x, 1-y, 2-z; <sup>iii</sup> = 1-x, 1-y, 2-z.

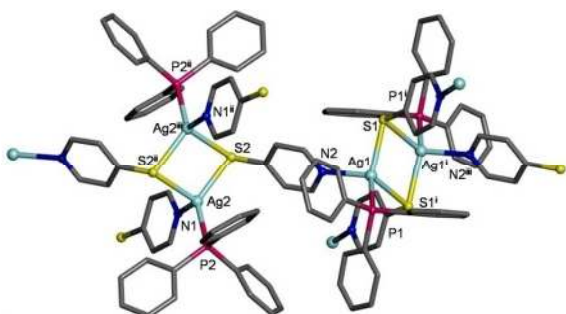


Figure 3: Part of the network structure of **3**. The symmetry operators are: <sup>i</sup> = 1-x, 1-y, 1-z; <sup>ii</sup> = -x, 1-y, 2-z; <sup>iii</sup> = 1-x, 1-y, 2-z.

The complex  $[\text{Ag}_3(\mu\text{-Se-4-py})_3(\text{PPh}_3)_4]$  (**4**) crystallizes with a water and a methanol molecules. The complex represents an interesting example of neutral trinuclear silver-selenolate complex. The asymmetric unit comprises of one molecule of trinuclear complex  $[\text{Ag}_3(\mu\text{-Se-4-py})_3(\text{PPh}_3)_4]$  (**4**) in which Se atoms of three Se-4-py ligands hold three Ag(I) atoms so as to form a six-membered  $\text{Ag}_3\text{Se}_3$  ring in twist-boat conformation. Ag1 in the  $\text{Ag}_3\text{Se}_3$  ring adopts a distorted tetrahedral geometry defined by two P atoms and two  $\mu\text{-Se}$  atoms; whereas each of Ag2 and Ag3 are coordinated by two  $\mu\text{-Se}$  atoms of Se-4-py and one P atom of  $\text{PPh}_3$  resulting in flattened pyramidal coordination sphere. The pyridyl-N does not coordinate to the metal atom. Recently, we have isolated palladium and platinum complexes of Se-4-py of composition  $[\text{MCl}(\text{Se-4-py})(\text{PEt}_3)_3]$  in which pyridyl selenolate ligand bridges metal atoms through both the Se and N centres generating 18-membered metallocyclic ring.<sup>1f</sup> The Ag $\cdots$ Ag separation (3.27 Å) involving three coordinated silver atoms (Ag2 and Ag3) is shorter than the sum of the van der Waal radii of two silver atoms (3.44 Å) suggesting the existence of argentophilic interaction (Fig 4); whereas the other two distances (Ag1 $\cdots$ Ag2 = 4.343, Ag1 $\cdots$ Ag3 = 4.369 Å) are longer. The Ag1-Se distances

are longer than those associated with Ag2 and Ag3 centres. The distances for the latter two can be compared with those reported in homoleptic complexes,  $[\text{Ag}\{\text{SeC}_5\text{H}_3(\text{SiMe}_3\text{-6})\text{N}\}]_6$  (Ag-Se = 2.5943(14) – 2.6044(13) Å)<sup>21</sup>  $[\text{Ag}\{\text{SeC}_4\text{H}(\text{Me-4,6})\text{N}_2\}]_6$  (2.5337(10) – 2.6158(11)Å).<sup>8</sup>

Table 3: Selected bond lengths (Å) and angles (°) for **4**.

Ag1-Se1	2.7236(10)	Ag1-P1	2.483(2)
Ag1-Se3	2.7156(11)	Ag1-P2	2.5164(19)
Ag2-Se1	2.5952(11)	Ag2-P3	2.440(2)
Ag2-Se2	2.5921(10)	Ag3-P4	2.473(2)
Ag3-Se2	2.6777(10)	Ag2 $\cdots$ Ag3	3.2689(9)
Ag3-Se3	2.5642(10)		
Se1-Ag1-Se3	84.28(3)	P4-Ag3-Se3	129.18(6)
P2-Ag1-Se1	104.15(5)	Se1-Ag2-Ag3	101.20(3)
P2-Ag1-Se3	114.97(6)	Se2-Ag2-Ag3	52.85(2)
P1-Ag1-Se1	121.74(6)	Se1-Ag2-Se2	109.88(4)
P1-Ag1-Se3	111.90(6)	P3-Ag2-Ag3	118.56(6)
P1-Ag1-P2	115.97(7)	P3-Ag2-Se1	126.35(6)
Se2-Ag3-Ag2	50.49(2)	P3-Ag2-Se2	122.44(6)
Se3-Ag3-Ag2	69.73(3)	Ag1-Se1-Ag2	109.47(4)
Se3-Ag3-Se2	117.41(3)	Ag2-Se2-Ag3	76.66(3)
P4-Ag3-Ag2	152.75(6)	Ag1-Se3-Ag3	111.66(4)
P4-Ag3-Se2	113.20(6)		

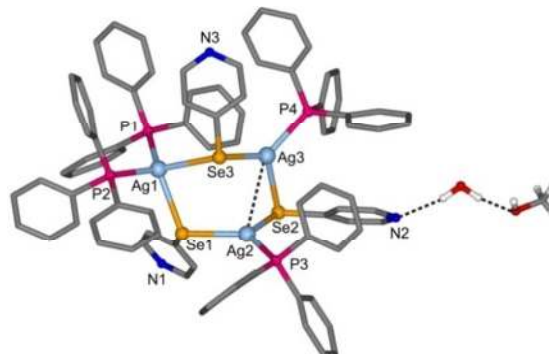


Figure 4: Molecular structure of  $[\text{Ag}_3(\mu\text{-Se-4-py})_3(\text{PPh}_3)_4]$  (**4**). Lattice methanol and water molecules exert hydrogen bonding with one of the pyridyl-N. Argentophilic interaction is present between Ag2 and Ag3.

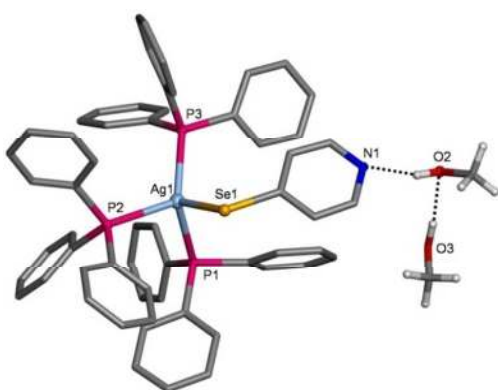
The N2 in **4** exerts hydrogen bonding interaction with the lattice water molecule which on the other side is bonded to N1 of another complex molecule and methanol via the same interaction. In this way, it produces a ring like arrangement consisting of two molecules of trinuclear complex  $[\text{Ag}_3(\mu\text{-Se-4-py})_3(\text{PPh}_3)_4]$  and two lattice water molecules. In addition, the C-atoms of the phenyl rings of  $\text{PPh}_3$  also exert weak  $\pi\cdots\pi$  interaction between them.

The complex  $[\text{Ag}(\text{Se-4-py})(\text{PPh}_3)_3]$  (**5**) crystallizes with two molecules of methanol. The asymmetric unit contains one molecule of the mononuclear complex together with two methanol molecules as lattice solvents. The metal atom acquires a distorted tetrahedral geometry. There are three P atoms and one Se atom in the coordination sphere of silver. All the three Ag-P distances (2.6158(17), 2.574(2), 2.543(2) Å) are distinctly different but are within the expected range reported

for silver triphenylphosphine complexes. The Ag-Se distance (2.6871(11) Å) can be compared with the Ag-Se distances found in  $[\text{Ag}_2(\mu\text{-SeCOPh})_2(\text{PPh}_3)_3]$  (Ag-Se = 2.623, 2.635, 2.727, 2.79 Å)<sup>22</sup>. The pyridyl-N exerts hydrogen bonding interaction with methanol (N-O = 2.751 Å and N-H-O angle = 175.35°) which is again connected to other methanol molecule via the same interaction (O-O = 2.755 Å and N-H-O angle = 177.53°) (Fig 5).

Table 4: Selected Bond lengths and angles (°) for **5**·2MeOH.

Ag1-P1	2.6158(17)	Ag1-P3	2.543(2)
Ag1-P2	2.574(2)	Ag1-Se1	2.6871(11)
P1-Ag1-Se1	109.47(5)	P1-Ag1-P2	102.61(6)
P2-Ag1-Se1	97.18(5)	P1-Ag1-P3	114.08(6)
P3-Ag1-Se1	113.19(5)	P2-Ag1-P3	118.61(7)

Figure 5: Molecular structure of  $[\text{Ag}(\text{Se-4-py})(\text{PPh}_3)_3] \cdot 2\text{MeOH}$  (**5**·2MeOH).Table 5: Selected bond lengths (Å) and angles (°) for **6**·MeOH.

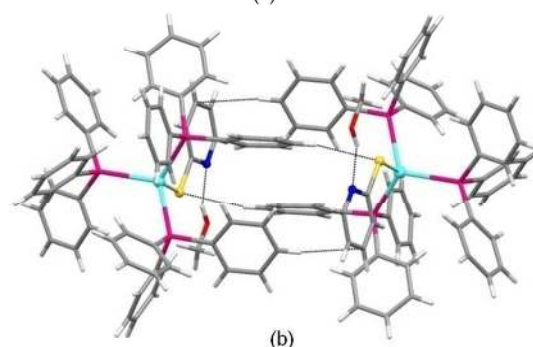
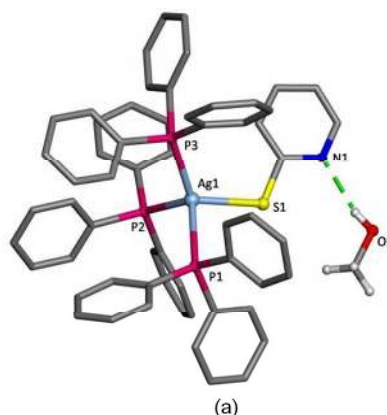
Ag1-P1	2.6515(17)	Ag1-P3	2.6093(17)
Ag1-P2	2.5513(15)	Ag1-S1	2.5309(19)
S1-Ag1-P1	97.49(6)	P1-Ag1-P2	112.02(5)
S1-Ag1-P2	118.37(7)	P1-Ag1-P3	111.25(6)
S1-Ag1-P3	105.26(8)	P2-Ag1-P3	111.54(5)

The complex  $[\text{Ag}(\text{S-2-py})(\text{PPh}_3)_3]$  (**6**) crystallizes with a methanol molecule in the lattice. The complex is isostructural to **5** (Fig 6a). The Ag-P distances (2.6515(17), 2.5513(15), 2.6093(17) Å) are slightly longer than the Ag-P distances observed in **1** and **2** but are in the acceptable range of Ag-P distance. The Ag-S distance (2.531(19) Å) is comparable with the Ag-S distances found in **1** – **3**. The pyridyl-N exerts hydrogen bonding interaction with one methanol molecule (N-O = 2.919 Å and N-H-O angle = 146.85°). In addition, there are a few weak intermolecular interactions like C-H...C( $\pi$ ) and C-H...S (Fig 6b) which hold the molecules together in the crystal lattice.

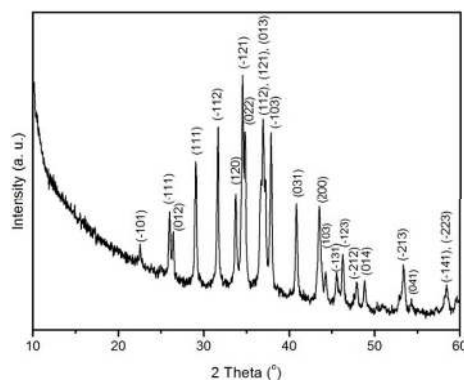
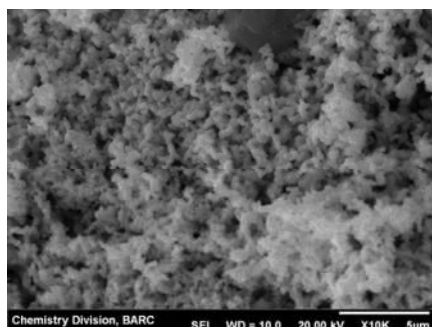
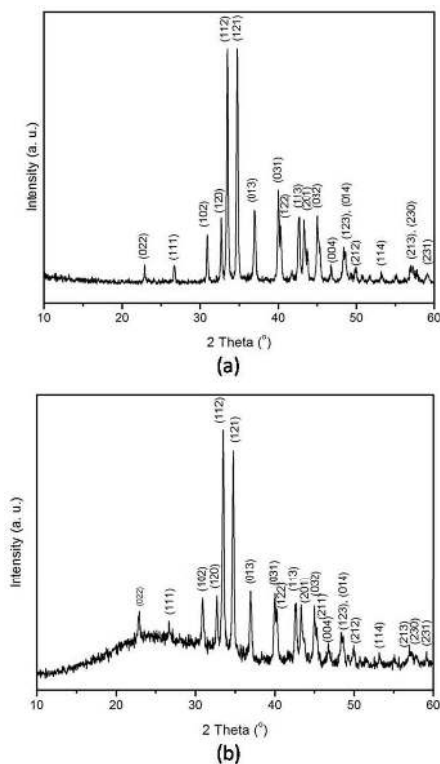
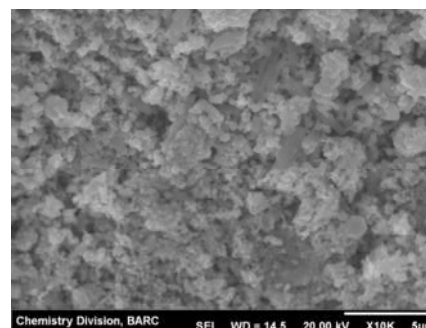
### Thermal Studies

Thermogravimetric analyses of these complexes have been carried out to understand their decomposition pattern so that

they can be used as molecular precursors for the synthesis silver chalcogenide nano-crystals. The TG patterns (see ESI) revealed that these complexes decompose in the temperature range 220 °C to 300 °C either in a single step or in an ill-defined two steps. Except complexes **1**, **3** and **6**, the remaining complexes on decomposition resulted into the formation of  $\text{Ag}_2\text{E}$  (E = S or Se) as inferred from the TG weight loss. The observed weight loss in the former three complexes was however not consistent with the formation of silver sulfide.

Figure 6: (a) Molecular structure of  $[\text{Ag}(\text{S-2-py})(\text{PPh}_3)_3] \cdot \text{MeOH}$  (**6**·MeOH). Methanol molecule present in the lattice exerts hydrogen bonding with the pyridyl-N. (b) Intermolecular C-H...S and C-H...C( $\pi$ ) interactions.

The complex **2** underwent two-step decomposition, the first being elimination of four  $\text{PPh}_3$  while the second step involved release of  $\text{pyS}$  and  $\text{S}$ , leading to the formation of  $\text{Ag}_2\text{S}$ . Thermolysis of **2** and **7a** were carried out in hexadecylamine and in a furnace at 270 °C respectively. In both cases the monoclinic phase of  $\text{Ag}_2\text{S}$  was obtained as was confirmed by PXRD data (JCPDS file no 14-0072) (Fig 7 and see ESI) and EDX analysis [64.87/35.13 Ag/S ratio]. The SEM image showed that the particles are agglomerated (Fig 8). The complexes **4** and **5** showed single step decomposition while **7b** showed ill-defined two step decomposition. In all the cases  $\text{Ag}_2\text{Se}$  was formed. Thermolysis of **4**, **5**, **7a** and **7b** were carried out either in a furnace (250 °C) or in coordinating solvents like hexadecylamine (HDA) or trioctylphosphine oxide (TOPO) at 270 °C. In all the cases the orthorhombic phase of  $\text{Ag}_2\text{Se}$  was formed as characterized by PXRD data (JCPDS file no 24-1041)

Figure 7: PXRD pattern of  $\text{Ag}_2\text{S}$  obtained from thermolysis of **2** in hexadecylamine.Figure 8: SEM image of  $\text{Ag}_2\text{S}$  obtained from thermolysis of **2** in hexadecylamine.Figure 9: The PXRD pattern of the  $\text{Ag}_2\text{Se}$  obtained by (a) solid state pyrolysis and (b) thermolysis of **7b** in hexadecylamine at 270°C for 1 h.Figure 10: SEM image of  $\text{Ag}_2\text{Se}$  obtained from thermolysis of **7b** in hexadecylamine.

(Fig 9) and EDX [67.7:32.2 Ag/Se ratio]. The SEM image showed that the particles are agglomerated (Fig 10). The characterization data of  $\text{Ag}_2\text{Se}$  obtained by thermolysis of **4** and **5** are given in ESI.

## Experimental

### Materials and Method

Mercaptopyrindines,  $\text{NaBH}_4$ ,  $\text{Et}_3\text{N}$  and common solvents were purchased from commercial sources and were used without further purification. The compounds 4,4'-dipyridyl diselenide ( $4,4'\text{-py}_2\text{Se}_2$ )<sup>23</sup>,  $[\text{Ag}_2(\mu\text{-Cl})_2(\text{PPh}_3)_4]$ <sup>24</sup> and  $[\text{AgCl}(\text{PPh}_3)_3]$ <sup>25</sup> were synthesized according to literature methods. Sodium 4-pyridyl selenolate was prepared *in-situ* by reduction of 4,4'-dipyridyl diselenide by  $\text{NaBH}_4$  in methanol under an argon atmosphere.

Elemental Analyses were carried out on a Thermo-Fischer Flash EA1112 elemental analyzer. The  $^1\text{H}$  and  $^{31}\text{P}\{^1\text{H}\}$  NMR spectra were recorded on a Bruker Avance-II spectrometer operating at 300 and 121.5 MHz, respectively. Chemical shifts are relative to the internal chloroform peak ( $\delta$  7.26 ppm relative to TMS) for  $^1\text{H}$  NMR spectra and external 85%  $\text{H}_3\text{PO}_4$  for  $^{31}\text{P}\{^1\text{H}\}$  NMR spectra. X-ray powder diffraction patterns were acquired on Philips PW-1820 and Bruker D8 advance powder diffractometer using  $\text{CuK}\alpha$  radiation. Thermogravimetric analyses (TGA) were carried out on a Nitzsch STA 409 PC-Luxx TG-DTA instrument, which was calibrated with  $\text{CaC}_2\text{O}_4 \cdot \text{H}_2\text{O}$ . The TG curves were acquired with a heating rate of 5 °C/min under a constant flow of argon gas. SEM and EDX measurements were carried out with Mirero Inc. AIS2100 and Oxford INCA E350 instruments respectively.

### Synthesis of $[\text{Ag}(\text{S-4-pyH}_{0.5})_2(\text{PPh}_3)_2]$ (**1**)

To a methanolic solution (20 mL) of 4-mercaptopyridine (45 mg, 0.4 mmol) containing triethylamine (40 mg, 0.05 mL), an acetonitrile suspension (20 mL) of  $[\text{Ag}_2(\mu\text{-Cl})_2(\text{PPh}_3)_4]$  (135 mg, 0.1 mmol) was added at room temperature with vigorous stirring which was continued for 2 hr. A clear yellow solution was formed which upon slow evaporation over a period of two days gave block-shaped greenish yellow crystals. The crystalline solid was filtered, washed with methanol and dried under vacuum (yield 125 mg, 73%), m.p. 225 °C (decomp.). Analysis calcd for  $\text{C}_{46}\text{H}_{39}\text{AgN}_2\text{P}_2\text{S}_2 \cdot \text{C}$ , C, 64.71; H, 4.60; N, 3.28%.

Found: C, 64.99; H, 4.55; N, 3.28%.  $^1\text{H}$  NMR (dms $o$ - $d_6$ )  $\delta$ : 7.17 – 7.25 (m), 7.39 (br, PPh $_3$  + H-3,5, pyS); 7.61 (d, 6.3 Hz, H-2,6, pyS).  $^{31}\text{P}\{^1\text{H}\}$  NMR (dms $o$ - $d_6$ )  $\delta$ : 25.8; -5.1 (PPh $_3$ ).

#### Synthesis of $[\text{Ag}_2(\mu\text{-S-4-py})_2(\text{PPh}_3)_4]$ (**2**) and $[\text{Ag}_2(\mu\text{-S-4-py})_2(\text{PPh}_3)]_n$ (**3**)

To a methanolic solution (20 mL) of sodium 4-pyridylthiolate, obtained from 4-mercaptopyridine (22 mg, 0.2 mmol) in methanol and aqueous NaOH (0.1 N, 2 mL  $\approx$  0.2 mmol), an acetonitrile suspension (20 mL) of  $[\text{Ag}_2(\mu\text{-Cl})_2(\text{PPh}_3)_4]$  (135 mg, 0.1 mmol) was added with stirring. The contents were heated at 70 °C for an hour till a cream turbidity appeared. After cooling to room temperature, the contents were filtered through a G-3 filtering unit and the filtrate on slow evaporation afforded colourless crystals (yield 70 mg, 47%); m.p. 168 °C. Analysis calcd for  $\text{C}_{82}\text{H}_{68}\text{Ag}_2\text{N}_2\text{P}_4\text{S}_2$ : C, 66.31; H, 4.61%; found: C, 66.61, H, 4.64%.  $^1\text{H}$  NMR (CDCl $_3$ )  $\delta$ : 6.93 (d, 5.7 Hz, H-3,5, pyS); 7.21 – 7.33 (m, PPh $_3$ ); 7.50 (d, 5.7 Hz, H-2,6, pyS).  $^{31}\text{P}\{^1\text{H}\}$  NMR (CDCl $_3$ )  $\delta$ : 2.8 ppm.

The precipitate was collected, washed and dried (yield 50 mg, 52%); m.p. 258 °C (dcomp.). Analysis calculated for  $\text{C}_{46}\text{H}_{38}\text{Ag}_2\text{N}_2\text{P}_2\text{S}_2$ : C, 57.31; H, 3.99; N, 2.92%; found: C, 56.57; H, 3.93; N, 2.98.  $^1\text{H}$  NMR (CDCl $_3$ )  $\delta$ : 7.50 (d, 6 Hz, H-3,5, pyS); 7.2 – 7.32 (m, PPh $_3$ ); 6.93 (d, 5.7 Hz, H-2,6, pyS).  $^{31}\text{P}\{^1\text{H}\}$  NMR (CDCl $_3$ )  $\delta$ : 5.15 ppm. The solid powder thus obtained was refluxed in methanol-acetonitrile (1:1 v/v) mixture for an hour and the hot mixture was filtered. Diffraction quality single crystals of  $[\text{Ag}_2(\mu\text{-S-4-py})_2(\text{PPh}_3)]_n$  were obtained on slow evaporation.

The complex **3** can alternatively be synthesized by direct reaction of AgCl, PPh $_3$  and NaS-4-py. AgCl (140 mg, 1 mmol) and PPh $_3$  (262 mg, 1 mmol) were stirred in methanol (20 mL) and heated at 70 °C. Stirring was continued for one hour and then sodium 4-pyridylthiolate, obtained from 4-mercaptopyridine (111 mg, 1 mmol) in methanol and aqueous NaOH (0.1 N, 10 mL  $\approx$  1 mmol), was added and the mixture was brought to reflux for another hour. White precipitate was filtered off and the filtrate on slow evaporation gave block shaped single crystals. Yield: 140 mg, 29% (based on single crystals).

#### Synthesis of $[\text{Ag}_3(\mu\text{-Se-4-py})_3(\text{PPh}_3)_4]$ (**4**)

To a methanolic solution (60 mL) of NaSe-4-py, prepared by reduction of 4,4'-dipyridyl diselenide (314 mg, 1 mmol) by NaBH $_4$  (75 mg, 2 mmol) in methanol in a Schlenk flask under an argon atmosphere, an acetonitrile suspension (60 mL) of  $[\text{Ag}_2(\mu\text{-Cl})_2(\text{PPh}_3)_4]$  (1.35 g, 1 mmol) was added with stirring which was continued for 1 hr at room temperature. The contents were filtered and the filtrate on slow evaporation gave block-shaped colourless crystals (yield 860 mg, 69%); m.p. 110 °C. Analysis calcd. for  $\text{C}_{87}\text{H}_{72}\text{Ag}_3\text{N}_3\text{P}_4\text{Se}_3$ : C, 56.66; H, 3.94%; found: C, 56.30, H, 3.94%.  $^1\text{H}$  NMR (CDCl $_3$ )  $\delta$ : 7.01 (br, H-3,5, pySe); 7.20 – 7.30 (br, PPh $_3$ ); 7.45 (br, H-2,6; pySe).  $^{31}\text{P}\{^1\text{H}\}$  NMR (CDCl $_3$ )  $\delta$ : 2.2 ppm.

The mother liquor after separating crystals of **4** was evaporated under vacuum and the residue was recrystallized from methanol to give colourless crystals of  $[\text{Ag}(\text{Se-4-}$

$\text{py})(\text{PPh}_3)_3]$  (**5**) (yield 110 mg). The characterization data are similar to the one described below.

#### Synthesis of $[\text{Ag}(\text{Se-4-py})(\text{PPh}_3)_3]$ (**5**)

To a methanolic solution of NaSe-4-py, prepared from 4-py $_2$ Se $_2$  (32 mg, 0.1 mmol) and NaBH $_4$  (8 mg, 0.2 mmol) in methanol (10 mL) under argon, was added an acetonitrile suspension (10 mL) of  $[\text{AgCl}(\text{PPh}_3)_3]$  (185 mg, 0.2 mmol) with stirring which was continued for 1 hr at room temperature. The contents were filtered through a G-3 filtering unit and the clear filtrate on slow evaporation gave colourless crystals of  $[\text{Ag}(\text{Se-4-py})(\text{PPh}_3)_3]$  (yield 180 mg, 86%), m.p. 104 °C. Analysis calcd. for  $\text{C}_{59}\text{H}_{49}\text{AgNP}_3\text{Se}$ : C, 67.37, H, 4.70%; found: C, 67.19, H, 4.67%.  $^1\text{H}$  NMR (CDCl $_3$ )  $\delta$ : 7.06 (br, H-3,5, Sepy); 7.24 – 7.32 (m, PPh $_3$ ); 7.47 (d, 4.8 Hz, H-2,6, Sepy).  $^{31}\text{P}\{^1\text{H}\}$  NMR (CDCl $_3$ )  $\delta$ : - 0.5 ppm.

#### Synthesis of $[\text{Ag}(\text{S-2-py})(\text{PPh}_3)_3]$ (**6**)

To a methanolic solution of 2-mercaptopyridine (22 mg, 0.2 mmol) an aqueous solution of NaOH (0.1N, 2 mL  $\approx$  0.2 mmol) was added and stirred for 30 min. To this solution, an acetonitrile (20 mL) suspension of  $[\text{AgCl}(\text{PPh}_3)_3]$  (185 mg, 0.2 mmol) was added at room temperature with stirring which was continued for 1 hr. The contents were filtered and the filtrate on slow evaporation afforded colourless crystals of  $[\text{Ag}(\text{S-2-py})(\text{PPh}_3)_3]$  (yield 140 mg, 70 %); m.p. 90 °C. Analysis calcd for  $\text{C}_{59}\text{H}_{49}\text{AgNP}_3\text{S}$ : C, 70.52; H, 4.91%; found: C, 70.56; H, 5.05%.  $^1\text{H}$  NMR (CDCl $_3$ )  $\delta$ : 6.60 (t, 6.3 Hz, pyS); 7.18 (t, 6.9 Hz, pyS); 7.24 – 7.35 (m, PPh $_3$ ); 7.67 (m, pyS).  $^{31}\text{P}\{^1\text{H}\}$  NMR (CDCl $_3$ )  $\delta$ : 0.0 ppm.

#### Synthesis of $[\text{Ag}(\text{Epy})]_n$ (**7**)

When the complexes **2** – **6** were refluxed in chloroform, cream coloured precipitates were obtained which after filtration and washing with chloroform gave nearly quantitative yield of  $[\text{Ag}(\text{Epy})]_n$ .

$[\text{Ag}(\text{S-4-py})]_n$  (**7a**): m. p. 186 °C (decomp). Analysis calcd for  $\text{C}_5\text{H}_4\text{AgNS}$ : C, 27.54; H, 1.85%; found: C, 26.31; H, 1.95%.

$[\text{Ag}(\text{Se-4-py})]_n$  (**7b**): m. p. 206 °C (decomp). Analysis calcd for  $\text{C}_5\text{H}_4\text{AgNSe}$ : C, 22.67; H, 1.52%; found: C, 22.62; H, 1.54%.

$[\text{Ag}(\text{S-2-py})]_n^{6a,b}$  (**7c**): m. p. 246 °C (decomp). Analysis calcd for  $\text{C}_5\text{H}_4\text{AgNS}$ : C, 27.54; H, 1.85%; found: C, 28.33; H, 1.89%.

#### Preparation of $\text{Ag}_2\text{S}$ or $\text{Ag}_2\text{Se}$ by thermal decomposition

In a typical synthetic method, a suspension of  $[\text{Ag}(\text{Sepy})]_n$  (**7b**, 100 mg) in 2 ml toluene was injected rapidly to a preheated (270°C) hexadecylamine (3 g) in a three-necked flask with vigorous stirring under an argon atmosphere. The temperature was maintained for an hour and the contents were cooled down to 50 °C, 10 ml hexane was added. The black residue was separated by centrifugation, washed with hexane and dried under vacuum. Similarly, decomposition of **2**, **4**, **5**, **7a** was also carried out either in hexadecylamine or in trioctylphosphine oxide under similar condition.



Table 6: Crystallographic and structural refinement data for **1** – **6**

Compounds	<b>1</b>	<b>2</b>	<b>3</b>	<b>4</b>	<b>5</b>	<b>6</b>
CCDC No.	1056425	1056426	1056427	1056428	1056429	1056425
Formula	C <sub>46</sub> H <sub>39</sub> AgN <sub>2</sub> P <sub>2</sub> S <sub>2</sub>	C <sub>82</sub> H <sub>68</sub> Ag <sub>2</sub> N <sub>2</sub> P <sub>4</sub> S <sub>2</sub>	C <sub>46</sub> H <sub>38</sub> Ag <sub>2</sub> N <sub>2</sub> P <sub>2</sub> S <sub>2</sub>	C <sub>88</sub> H <sub>79</sub> Ag <sub>3</sub> N <sub>3</sub> O <sub>2</sub> P <sub>4</sub>	C <sub>61</sub> H <sub>57</sub> AgNO <sub>2</sub> P <sub>3</sub> Se	C <sub>60</sub> H <sub>53</sub> AgNOP <sub>3</sub> S
<i>M</i>	853.72	1485.12	960.58	1894.91	1115.81	1036.87
<i>T</i> (K)	103(2)	293(2)	293(2)	293(2)	293(2)	293(2)
$\lambda$ (Å)	0.71073	1.5418	1.5418	1.5418	1.5418	1.5418
Crystal syst.	Orthorhombic	Tetragonal	Triclinic	triclinic	Triclinic	Triclinic
Space group	<i>Pbcn</i>	<i>I4<sub>1</sub></i>	<i>P</i> $\bar{1}$	<i>P</i> $\bar{1}$	<i>P</i> $\bar{1}$	<i>P</i> $\bar{1}$
<i>a</i> (Å)	14.7874(4)	20.4449(5)	9.9533(6)	14.6363(6)	12.2175(10)	11.4611(6)
<i>b</i> (Å)	17.9105(5)	20.4449(5)	14.2851(6)	16.8676(5)	13.7065(10)	12.6240(7)
<i>c</i> (Å)	14.6394(4)	34.6253(9)	15.2400(10)	19.0727(10)	17.1985(15)	19.6133(13)
$\alpha$ (°)	90	90	93.498(4)	97.323(3)	87.407(7)	85.935(5)
$\beta$ (°)	90	90	90.926(5)	112.344(4)	86.817(7)	74.285(5)
$\gamma$ (°)	90	90	103.226(4)	94.429(3)	69.329(7)	71.483(5)
Volume (Å <sup>3</sup> )	3877.24(18)	14473.2(8)	2104.5(2)	4278.9(3)	2689.5(4)	2589.9(3)
<i>Z</i>	4	8	2	2	2	2
<i>D</i> <sub>calcd</sub> (g cm <sup>-3</sup> )	1.463	1.363	1.516	1.471	1.378	1.330
$\mu$ (mm <sup>-1</sup> )	0.747	6.059	9.371	7.979	4.956	4.689
Reflns col.	75465	7691	13083	28724	17132	16270
Ind. Reflns.	6198	4710	7805	15959	9975	9535
<i>R</i> <sub>int</sub>	0.0811	0.0641	0.0767	0.0712	0.0693	0.0745
Goof on F <sup>2</sup>	1.079	1.036	1.003	0.990	1.003	1.077
Final <i>R</i> [ <i>I</i> > 2 $\sigma$ ] <sup>a</sup>	0.0401	0.0888	0.0796	0.0691	0.0802	0.0844
<i>R</i> <sub>1</sub>						
<i>wR</i> <sub>2</sub> <sup>b</sup>	0.0768	0.2519	0.2154	0.1868	0.2005	0.2321

$$^a R_1 = \sum ||F_o| - |F_c|| / \sum |F_o|, ^b wR_2 = [\sum w(F_o^2 - F_c^2)^2 / \sum w(F_o^2)^2]^{1/2}$$

### X-ray Crystallography

Intensity data for **1** was collected at 103 K on a Bruker Apex-II (Mo K $\alpha$  = 0.71073 Å). Intensity data for **2** – **6** were collected at room temperature (293 K) on a Agilent SuperNova microfocuss X-ray source (CuK $\alpha$ ,  $\lambda$  = 1.5418 Å) radiation. Empirical absorption corrections were applied to the data using CrysAlis program<sup>26</sup>. The structures were solved by charge flipping algorithm using Olex2 program<sup>27</sup> and refined using least squares minimization in ShelXL<sup>28</sup> refinement package. The non-hydrogen atoms were refined anisotropically. The hydrogen atoms were added at their geometric locations and refined isotropically. Crystallographic and structure determination data (CCDC No. 1056425 – 1056430) are listed in Table 6.

### Conclusions

A series of hemilabile silver(I) chalcogenolate complexes containing triphenylphosphine have been isolated and structurally characterized. We have demonstrated that by subtle changes in reaction conditions a variety of silver complexes can be synthesized which can be converted to a thermodynamically stable insoluble [Ag(Epy)]<sub>n</sub> via stepwise release of triphenylphosphine ligands. The silver centres in multinuclear complexes deficient in PPh<sub>3</sub> have propensity to exhibit argentophilic interactions (e.g. in **3** and **4**) while silver centres rich in PPh<sub>3</sub> lack such interaction (e.g. in **2** and **4**). Except for **3**, the relatively stronger donor pyridyl-N could not

form any Ag-N coordination bond in the competition with relatively softer donors (P, S, Se) to soft metal Ag(I). The occurrence of Ag-N coordination of mercatopyridine in **3** resulted in the formation of two dimensional (4,4) connected network. Except for **4**, all the Ag(I) centres are four coordinated with distorted tetrahedral geometry. Thermal decomposition studies of several complexes produced Ag<sub>2</sub>S or Ag<sub>2</sub>Se endorsing their suitability as versatile molecular precursors.

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## TOC graphic

