A 2D honeycomb-shaped network based on a starburst cluster: $[Ag_4(\mu_3\text{-}Cl)(PPh_2(CH_2)_2PPh_2)_{1.5}\{S_2P(OR)_2\}_3]$ (R = Et, Pr^i)

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The first 2D metal–organic framework utilizing $PPh_2(CH_2)_2PPh_2$ (dppe) units as the linkers and tetranuclear silver clusters, $[Ag_4(\mu_3\text{-}Cl)\{S_2P(OR)_2\}_3]$, as the network nodes in the formation of the honeycomb-shaped layer structure is reported.

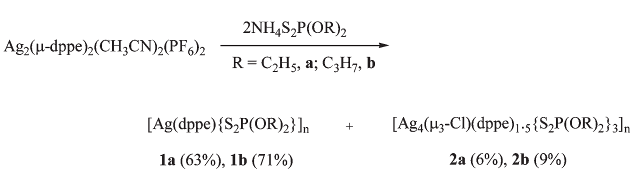
Coordination polymers exhibiting 2D honeycomb-shaped or hexagonal networks, structural analogues of graphite, normally consist of metals in trigonal planar coordination as network nodes and rigid organic molecules having O- or N-donating groups as linkers.[1] Rarely has a linker possessing a P-donor bridging group exhibited 2D hexagonal layer structures. Among the known examples are $[\{Au(\mu\text{-}PPh_2(CH_2)_4PPh_2)_{1.5}\}_n]^{n+}$ and $[\{Ag(CN\text{-}t\text{Bu})(\mu\text{-}PPh_2(CH_2)_4PPh_2)_{1.5}\}_n]^{n+}$, each containing a fused 42-membered ring, $[Au_6(\mu\text{-}PC_4P)_6]$[2] and $[Ag_6(\mu\text{-}PC_4P)_6]$[3] respectively. A related, puckered sheet network which indeed is the extremely distorted honeycomb layer structure, $\{Ag(O_2CCF_3)(\mu\text{-}PPh_2(CH_2)_6PPh_2)_{1.5}\}_n$,[4] consists of a fused 54-membered $\{Ag_6(\mu\text{-}PC_6P)_6\}$ ring. Another 2D network of large 72-atom rings containing 18 silver atoms and 12 bulky triphosphines, 1,3,5-tris(diphenylphosphinyl)-benzene (L), was characterized by James and coworkers.[5] In this molecule the network nodes are trigonal-planar silver centers bonded to three L units, and are connected by six Ag_2L_2 groups which have a 12-membered ring structure. All four examples mentioned above have a common structural motif: P-donor bridging ligands and metal corners. Alternatively, the large organic linkers that have a well-defined triangular shape such as 1,3,5-benzenetricarboxylate,[6] tri(4-pyridyl)triazine[7] and their derivatives[8] can form hexagonal macrocycles with metal connectors. In these cases, nodes are located at either the centers of the organic linkers or metals. Surprisingly, never has the metal cluster acting as the trigonal node and the diphosphine unit as the linker been present simultaneously to form a 2D honeycomb-shaped network. Herein we present the first 2D hexagonal network utilizing diphosphine units as the linkers and tetranuclear silver clusters as the network nodes. This star-shaped tetranuclear unit, $[Ag_4(\mu_3\text{-}Cl)(PPh_2(CH_2)_2PPh_2)_{1.5}\{S_2P(OR)_2\}_3]$, can also be delineated as the inorganic counterpart of the starburst molecule (or three-fold symmetric tritopic ligand).

This group has been interested in the synthesis of metal clusters containing both 1,1-dithiolate and diphosphine ligands for several years. Discrete copper and silver clusters with nuclearities ranging from four to nine were isolated by using dppm as auxiliary ligands.[9] In addition several new connecting patterns for the dithiolato ligands were identified. However, when the dppe unit is utilized as the auxiliary ligand in the cluster synthesis, instead of the formation of discrete clusters, the polymeric species are isolated.

The reaction of $Ag_2(\mu\text{-dppe})_2(CH_3CN)_2(PF_6)_2$ with $NH_4S_2P(OR)_2$ (R = Et, Pr^i) in CH_2Cl_2 at ambient temperature for 48 hours produces two types of coordination polymers, $[Ag(\mu\text{-dppe})\{S_2P(OR)_2\}]_n$, **1**, and $[Ag_4(\mu_3\text{-}Cl)(dppe)_{1.5}\{S_2P(OR)_2\}_3]_n$, **2** (Scheme 1). Both ^1H and ^{31}P NMR studies of **1** suggest that the repeating unit of $Ag(dppe)[S_2P(OR)_2]$ is present in solution.† Besides, two principal peaks whose structures correspond to the intact molecule and the intact molecule containing an additional silver ion to form the adduct ion, $[\{Ag\}\{Ag(dppe)(S_2P(OR)_2)\}]^+$, respectively, are observed in the FAB mass spectrum. Compounds **2** do not dissolve in any organic solvents; therefore, the characterization relies primarily on X-ray structure determination.

As seen in Fig. 1, the complex **1a** forms a polymeric chain structure in the solid state. Each silver(I) center is coordinated by two P atoms from two different dppe units and two S atoms of the dithiophosphato (dtp) ligand in a distorted tetrahedral AgP_2S_2 coordination. Both Ag–P and Ag–S distances in **1a** are not unusual for the four-coordinated silver(I) center.[9,10] The diphosphine ligand, dppe, adopts the *anti* conformation in bridging between silver(I) centers and this continues to favor 1D zigzag chain rather than ring formation. Besides, the dtp ligands which chelate to silver(I) centers are arranged in an alternating up and down fashion along the zigzag chain.

In the crystal structure of **2a**, four silver atoms, each located at the vertex of a pyramid, are held together with three, face-capped dithiophosphato ligands in a trimetallic triconnective coordination pattern[11] and one face-capped chloride ion derived from CH_2Cl_2, to form a tetranuclear unit (Fig. 2), in which a threefold axis parallel to the *c* axis passes through the Ag(1) and Cl(1) atoms. The geometry of the Ag_4 unit is much distorted from a regular tetrahedron which is evident from two kinds of Ag–Ag distances, 3.222 and 3.972 Å, and the angle of Ag(2)–Ag(1)–Ag(2A), 76.10(4)°. In addition, the Ag_4S_6 framework in **2a** is also different from the adamantane-like $\{M_4S_6\}$ polyhedron, the most frequently observed species in copper- and silver-thiolate chemistry.[12] The Ag(1) atom located at the apex of the pyramid is coordinated



Scheme 1

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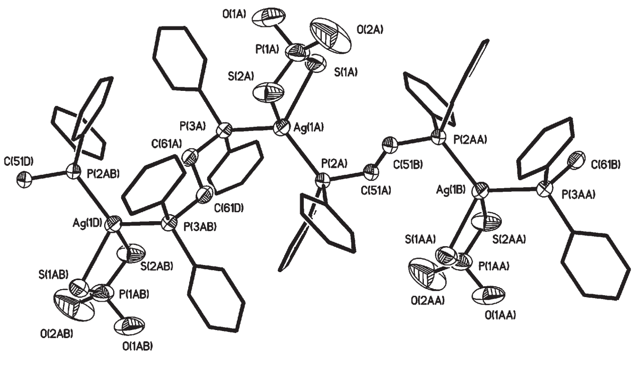

Fig. 1 A view of the 1D zigzag chain structure of **1a**. The ethyl groups are omitted for clarity. Selected bond lengths [Å] and angles [°]: Ag(1)–P(2) 2.474(1), Ag(1)–P(3) 2.479(1), Ag(1)–S(1) 2.640(1), Ag(1)–S(2) 2.720(1), S(1)–P(1) 1.958(2), S(2)–P(1) 1.978(2), P(2)–Ag(1)–P(3) 112.44(4), P(2)–Ag(1)–S(1) 114.86(5), P(3)–Ag(1)–S(1) 122.51(5), P(2)–Ag(1)–S(2) 114.27(4), P(3)–Ag(1)–S(2) 110.73(4), S(1)–Ag(1)–S(2) 76.97(5).

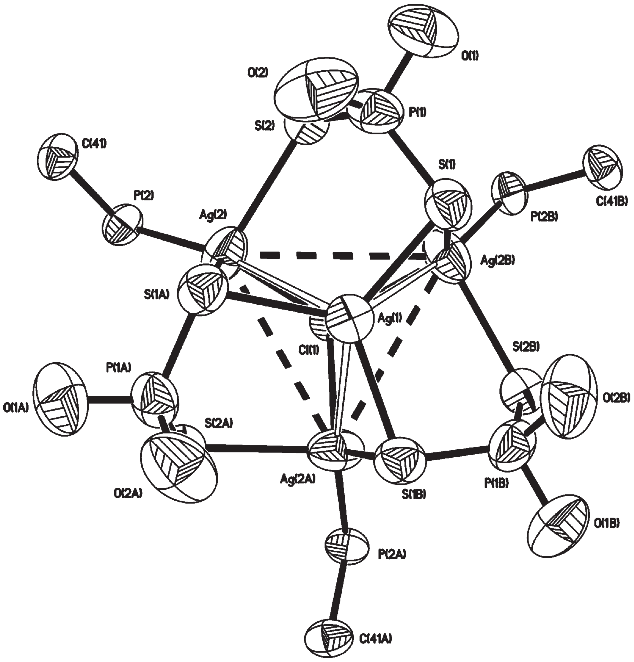

Fig. 2 Thermal ellipsoid drawing (40% probability level) of tetranuclear unit, [$Ag_4(\mu_3\text{-}Cl)(dppe)_{1.5}\{S_2P(OEt)_2\}_3$] (**2a**) with atom-numbering scheme. The ethyl groups and phenyl rings are omitted for clarity. Selected bond lengths [Å] and angles [°]: Ag(1)–S(1) 2.498(3), Ag(1)–Ag(2) 3.222(1), Ag(2)–P(2) 2.440(3), Ag(2)–S(1A) 2.598(3), Ag(2)–Cl(1) 2.616(2), Ag(2)–S(2) 2.753(3), S(1)···S(2), Ag(2)···Ag(2A) 3.972, S(1)–P(1) 2.013(4), S(2)–P(1) 1.941(5), P(1)–O(1) 1.547(10), P(1)–O(2) 1.597(11); Ag(2)–Cl(1)–Ag(2A) 98.79(11), Ag(2)–Ag(1)–Ag(2A) 76.10(4), S(1)–Ag(1)–S(1A) 119.37(2), S(2)–Ag(2)–P(2) 105.42(10), S(2)–Ag(2)–Cl(1) 92.87(3), S(2)–Ag(2)–S(1A) 99.93(11), S(1A)–Ag(2)–P(2) 122.14(9), P(2)–Ag(2)–Cl(1) 111.35(11), S(1A)–Ag(2)–Cl(1) 118.35(11), S(2)–P(1)–S(1) 117.95(18), O(1)–P(1)–O(2) 99.2(7).

by three sulfur atoms from three dtp ligands. The Ag(1)–S(1) distance of 2.498(3) Å and the S(1)–Ag(1)–S(1A) angle of 119.37(2)°, slightly deviating from 120°, indicate that the Ag(1) atom is not exactly located in the same plane defined by three sulfur atoms. The Ag(2) atoms, which form the base of the pyramid and are generated symmetrically by the C_3 axis, are each tetragonally coordinated by two sulfur atoms and one chlorine atom with the phosphorus atom from half of the dppe unit occupying the fourth coordination site. *Thus taking into consideration three protruded dppe units out of the Ag_4 cluster, the starburst molecule, [$Ag_4(\mu_3\text{-}Cl)(dppe)_{1.5}\{S_2P(OR)_2\}_3$], is generated.* The four-coordinated silver center is much distorted from the normal tetrahedral and the angles around it range from 92.87(3)–122.14(9)°. The Ag(2)–S distances, 2.598(3) and 2.753(3) Å, are within the reported values[9,10] and the bond length between the Ag(2) atom and the μ_3-Cl is 2.616(2) Å. The angle of Ag(2)–Cl–Ag(2A) is 98.79(11)°.

The six [$Ag_4(\mu_3\text{-}Cl)\{S_2P(OR)_2\}_3$] units are linked together by six dppe ligands in an alternating up and down fashion with respect to μ_3-Cl (or Ag1) ion to form an approximately honeycomb-shaped macrocycle as shown in Fig. 3a. Thus a total of 24 silver atoms are revealed within the macrocycle. Six of the phenyl groups of the dppe units point towards the center of the ring and the transannular H···H distance between phenyl groups on the macrocycle is ~10.325 Å (10.628 Å for **2b**). The 42-atom ring structure propagates along two dimensions, resulting in the formation of two-dimensional (2D) infinite layers (Fig. 3b). The 2D layers stack along the *c* axis with a mean interlayer separation of ~10.7 Å (~11 Å for **2b**). These 2D layers are arranged in the crystal in an *ABCABC* fashion, resembling cubic close-packed layers,[13] such that the macrocyclic cavity does not form extended channels perpendicular to the 2D network. The void volume of the crystal is estimated by PLATON[14] to be ~45% (~37% for **2b**) of the total volume and is surprisingly not filled with any solvent molecules. That no guest molecule is present in the crystal studies is supported by some residual electron density, 1.499 e A^{-3}, located in the vicinity of the Ag(I) atom from the final difference Fourier map.

It is worthwhile noting that the 2D honeycomb-shaped layers revealed in **2** represent *the first example which utilizes the tetranuclear silver unit, [$Ag_4(\mu_3\text{-}Cl)(PPh_2(CH_2)_2PPh_2)_{1.5}\{S_2P(OR)_2\}_3$], as the trigonal secondary building block[15] with regard to the disposition of the dppe groups.* The close example of **2** is the one developed by Kim and coworkers[16] who created a rigid chiral organic molecule with a carboxylic group at one end and a pyridal group at the other to serve the dual function of forming the oxo-bridged trinuclear metal carboxylate units, [$Zn_3(\mu_3\text{-}O)(O_2CR)_6]^{2-}$ (HO_2CR: D-tartaric acid), which then behave as a secondary building block in the formation of the hexagonal framework for the use of enantioselective separation and catalysis.

Obviously, the stripping of chloride ions from CH_2Cl_2 provides the source for the capping chlorine atom in the formation of starburst clusters, which in turn propagate to form a 2D layer structure. Whether the 1D zigzag chain will transform into the 2D layer in the presence of chloride ion in solution is not known; however, it has been reported that the mononuclear nickel-thiolate complex with CH_2Cl_2 affords the linear pentanuclear nickel cluster of which the terminal Ni(II) center is further bound by a chloride ion derived from CH_2Cl_2.[17] Work toward the synthesis of honeycomb-shaped layer structures with larger hexagonal rings by using dppb ($PPh_2(CH_2)_4PPh_2$) or dpph ($PPh_2(CH_2)_6PPh_2$) units as the linker is currently underway.

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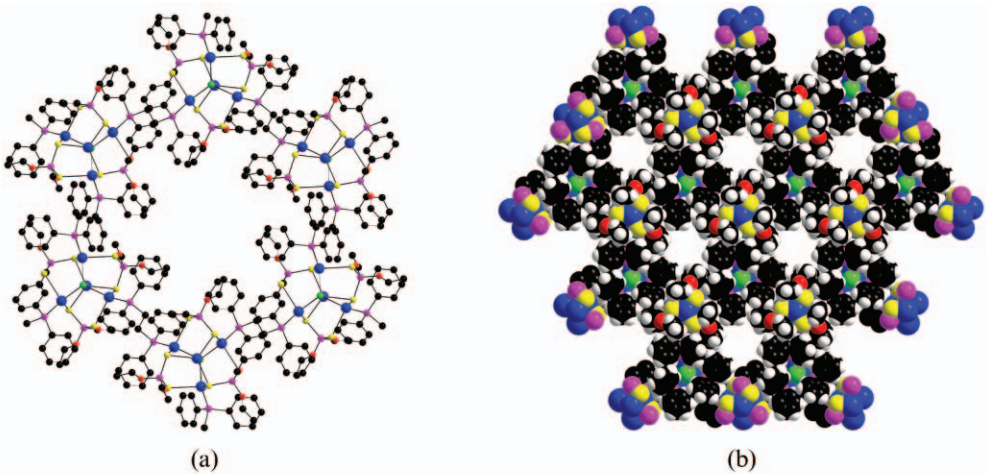

Fig. 3 a) The single honeycomb-shaped ring in **2a**. Ag: blue, Cl: green, S: yellow, P: pink, O: red, C: black; b) The 2D extended network of **2a** shown as a space-filling model.

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Notes and references

† **1a** : ^{1}H NMR (CD_2Cl_2): δ = 1.13 (d, 6H, CH_2CH_3), 2.44 (t, 4H, CH_2), 3.93 (m, 4H, CH_2CH_3), 7.08–7.79 (m, 20H). ^{31}P NMR (CD_2Cl_2): δ = 105.78(s), 2.87(br). Positive- ion FAB-MS (Found/Calcd): *m/z*: 799.1 (799.3) [(M + Ag)$^+$], 692.8 (691.5) [M$^+$]. Anal. Calcd for $AgP_3O_2S_2C_{30}H_{34}$: C, 52.10; S, 9.27; H, 4.95. Found: C, 51.40; S, 9.17; H, 5.00; **1b** : ^{1}H NMR (CD_2Cl_2): δ = 1.17 (d, 12H, $CH(CH_3)_2$), 2.46 (t, 4H, CH_2), 3.97 (m, 2H, $CH(CH_3)_2$), 7.15–7.77 (m, 20H). ^{31}P NMR (CD_2Cl_2): δ = 102.94(s), 3.87(br). Positive- ion FAB-MS (Found/Calcd): *m/z*: 827.1 (827.4) [(M + Ag)$^+$], 719.2 (719.5) [M$^+$]. Anal. Calcd for $AgP_3O_2S_2C_{32}H_{38}$: C, 53.43; S, 8.92; H, 5.28. Found: C, 52.91; S, 8.31; H, 5.22; **2a** : Anal. Calcd for $Ag_4Cl\ P_6S_6O_6C_{51}H_{66}$: C, 37.80; S, 11.87; H, 4.10. Found: C, 39.14; S, 11.46; H, 4.32; **2b** : Anal. Calcd for $Ag_4Cl\ P_6S_6O_6C_{57}H_{78}$: C, 40.16; S, 11.28; H, 4.61. Found: C, 38.42; S, 10.87; H, 4.73%. Crystal data for **1a**: $C_{30}H_{34}AgO_2P_3S_2$, triclinic, space group $P\bar{1}$, a = 11.954(2) Å, b = 12.985(2), c = 13.116(2) Å, α = 61.926(3), β = 77.409(3), γ = 68.296(3)°, V = 10923(2) Å^3, Z = 2, ρ_{calcd} 1.378 g cm^{-3}, Mo Kα radiation (λ = 0.71073), ω scan, T = 298 K, μ = 0.898 mm^{-1}, 7845 measured reflections, 5606 independent reflections (R_{int} = 0.0251), 5055 with $I > 2\sigma(I)$, Lorentzian, and empirical absorption correction were made, 343 parameters, R values for reflections with $I > 2\sigma(I)$: R_1 = 0.0428, wR_2 = 0.1070. **2a**: $C_{51}H_{66}Ag_4ClO_6P_6S_6$, trigonal, space group $R\bar{3}$, a = 19.778(2) Å, c = 32.244(4) Å, V = 10923(2) Å^3, Z = 6, ρ_{calcd} 1.478 g cm^{-3}, $2\theta_{max}$ = 45.00, Mo Kα radiation (λ = 0.71073), ω scan, T = 293 K, μ = 1.439 mm^{-1}, 3830 measured reflections, 3123 independent reflections (R_{int} = 0.0408), 2099 with $I > 2\sigma(I)$, 223 parameters, R values for reflections with $I > 2\sigma(I)$: R_1 = 0.0617, wR_2 = 0.1591. **2b**: $C_{57}H_{78}Ag_4ClO_6P_6S_6$, trigonal, space group $R\bar{3}$, a = 19.865(2) Å, c = 33.169(4) Å, V = 11336(2) Å^3, Z = 6, ρ_{calcd} 1.498 g cm^{-3}, $2\theta_{max}$ = 50.10, Mo Kα radiation (λ = 0.71073), ω scan, T = 298 K, μ = 1.390 mm^{-1}, 10226 measured reflections, 4412 independent reflections (R_{int} = 0.0546), 2415 with $I > 2\sigma(I)$, Lorentzian, and empirical absorption correction were made, 243 parameters, R values for reflections with $I > 2\sigma(I)$: R_1 = 0.0690, wR_2 = 0.1297. All three structures were solved by the use of direct methods, and refinement was performed by the least-squares method on F^2 with the SHELXL-97 package incorporated in SHELXTL/PC V5.10. H-atoms were added. Crystallographic data reported in this paper have been deposited with the Cambridge Crystallographic Data Center, CCDC 254826–254828 (**1a**, **2a**, and **2b**). See http://www.rsc.org/suppdata/cc/b4/b419474h/ for crystallographic data in .cif or other electronic format.

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