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Tetrahedral-Shaped Anions as a Template in the Synthesis of High-Nuclearity Silver(I) Dithiophosphate Clusters

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Ⓢ *Supporting Information*

ABSTRACT: Novel Ag_{32} clusters, $[Ag_{16}(EO_4)\{S_2P(OEt)_2\}_{12}]_2(PF_6)_4$ (E = S, **1**; Se, **2**) and $[Ag_{16}(MO_4)\{S_2P(OEt)_2\}_{12}]_2(PF_6)_4$ (M = Cr, **3**; Mo, **4**), were prepared in situ from the addition of a tetrahedral-shaped anion as a template to the pentanuclear extended chain $[Ag_5\{S_2P(OEt)_2\}_4]_n(PF_6)_n$.

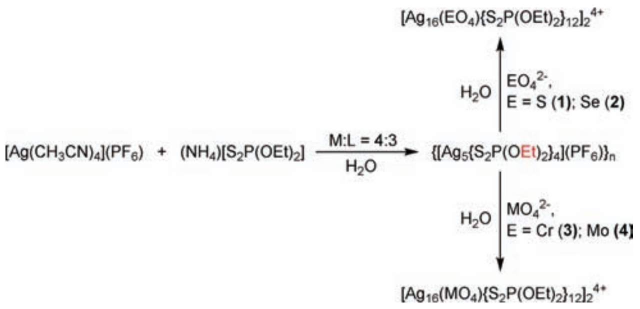
The application of anions as a template for the formation of molecular ensembles continues to blossom. Following some early notable works in the formation of tetrameric mercuracarboranes[1] and pentameric circular helicates[2] templated by halides, a series of interlocked catenanes and rotaxanes templated around chloride[3] and sulfate[4] anions have been developed in recent years by Beer et al.

The anion-template approach can also be applied to the synthesis of large silver alkynyl clusters. It started with the incorporation of spherical halides (F^-, Cl^-, and Br^-) to form Ag_{14} rhombohedral cages,[5] followed by a Ag_{17} cluster with a triangular carbonate,[6] a Ag_{22} cluster with a tetrahedral chromate,[7] and Ag_{40} clusters with encapsulated polyoxometalates such as $V_{10}O_{28}^{6-}$ and $Mo_6O_{22}^{8-}$.[8] Intriguingly, even larger silver alkynyl clusters, $[Ag_{60}(Mo_6O_{22})_2(C{\equiv}C^tBu)_{38}](CF_3SO_3)_6$, can be formed with a double template.[9] Contrarily, the synthesis of large Ag−S clusters has not been very successful via the anion-template approach even though Fenske and his co-workers reported a broad spectrum of silver sulfide clusters stabilized by tertiary phosphine ligands.[10] Access to these clusters is achievable by the reactions of simple silver salts with $S(SiMe_3)_2$ or $RSSiMe_3$ followed by the addition of tertiary phosphines.[11]

We have demonstrated that elemental anions such as halides and hydrides, which are spherical, can be a template in the synthesis of octanuclear silver dithiolato clusters from a pentanuclear extended chain polymer, $[Ag_5\{S_2P(OEt)_2\}_4]_n^{n+}$.[12] In the pursuit of nanometer-sized Ag−S cluster synthesis, a logical extension is to utilize tetrahedral-shaped anions, which are much larger in volume than halides,[13] as the directing agent with the aim that a high-nuclearity silver thiolate cluster can be isolated. Herein we report that both tetrahedral oxo and chromate (molybdate) anions can be successfully accommodated at the center of a Ag_{16} cluster, a distorted tetracapped icosahedron, which dimerizes to become a Ag_{32} cluster in the solid state.

Novel Ag_{32} clusters, $[Ag_{16}(EO_4)\{S_2P(OEt)_2\}_{12}]_2^{4+}$ (E=S, **1**; Se, **2**) and $[Ag_{16}(MO_4)\{S_2P(OEt)_2\}_{12}]_2^{4+}$ (M=Cr, **3**; Mo, **4**), were prepared in situ from the addition of an anionic template to a one-dimensional polymeric species in aqueous solution (Scheme 1).[14] The reaction of $[Ag(CH_3CN)_4]PF_6$ and $NH_4[S_2P(OEt)_2]$ in deionized water led to the formation of $[Ag_5\{S_2P(OEt)_2\}_4]_n^{n+}$, a one-dimensional chain, which can be further transformed into a Ag_{32} cluster in the presence of a tetrahedral-shaped anion such as sulfate, selenate, chromate, or molybdate. A single resonance around 104 ppm was identified in the $^{31}P\{^1H\}$ NMR spectrum, and a set of ethyl resonances was also detected in the ^1H NMR spectrum for compounds **1**−**4**, the chemical shifts for which indeed display little differences from their precursors. The presence of the selenate anion in **2** was further confirmed by the $^{77}Se\{^1H\}$ NMR spectrum.

Scheme 1. Pathway for the Formation of Ag_{32} Clusters 1−4



Cationic clusters **1**−**4** characterized by single-crystal X-ray analyses revealed that all four Ag_{32} frameworks have a similar structural motif that contains two Ag_{16} units, each being surrounded by 12 dithiophosphate (dtp) ligands. They are related by a crystallographic inversion center, and each Ag_{16} unit entraps one tetrahedral anion at its center (Figure 1a).[15] A total of 12 Ag^I atoms (Ag1−Ag12) constitute a distorted icosahedral cage with four outer Ag^I atoms (Ag13−Ag16) as capping atoms. Argentophilic interactions appear not to be significant because the adjacent Ag···Ag distances are quite long.[16] The Ag−S bond distances within the Ag_{16} unit are in the range of 2.323(5)−2.949(8) Å, and the dtp ligands display various coordination modes. Most of the S atoms in clusters **1**−**3** are doubly bridging (μ_2) except two S atoms: S11, in a monodentate fashion, and S5, in a triply bridging mode (μ_3) (Figure 1a−c). In **4**, all S atoms but S3 and S5, which are triply bridging, connect to two Ag atoms (Figure 1d). A trifurcated S atom of the dtp ligand has been observed in $[Ag_4(\mu\text{-dppm})_2\{S_2P(OEt)_2\}_3]^+$,[17a] and the long Ag−S bond, 2.949(8) Å, lies within the reported limit of 2.967(2) Å.[17b] The distorted tetracapped icosahedral silver framework dimerizes in the solid state via intermolecular Ag−S contacts, averaging 2.90(4) Å. Intriguingly, each $Ag_{16}S_{24}$ skeleton

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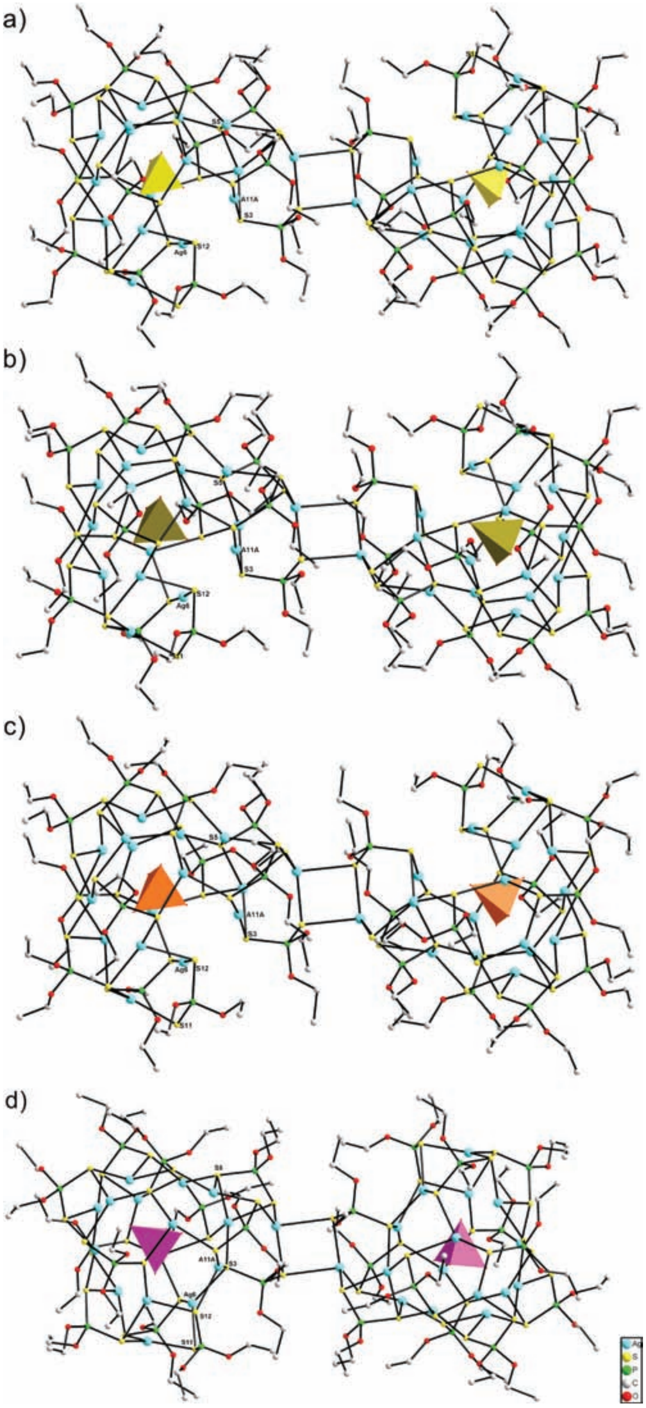

Figure 1. Molecular structures of the cationic parts of compounds (a) **1**, (b) **2**, (c) **3**, and (d) **4** with the templated anion highlighted as a tetrahedron.

in compounds **1**−**3** reveals a small aperture around O27 (Figure 1a); however, this aperture is sealed in compound **4** by the formation of two Ag−S bonds: Ag11−S12 and Ag6−S3 (Figure 1d). In order to hold the cationic cluster together, hexafluorophosphate anions play a role and are located in the space between clusters to balance the compound charge.

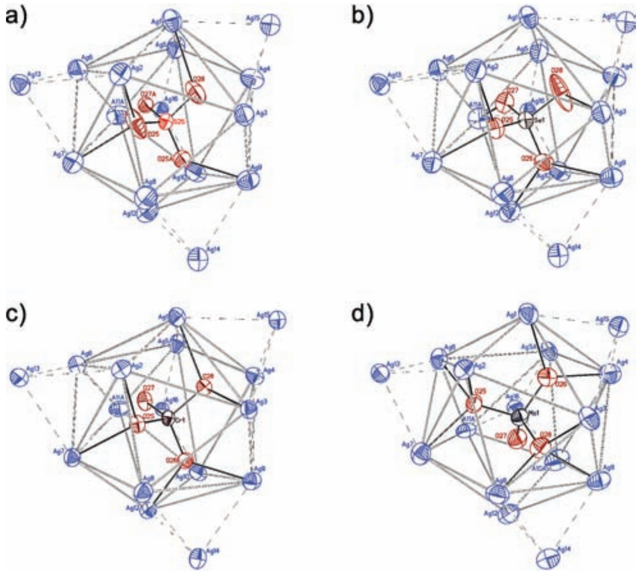

Figure 2. Core structures of (a) **1**, (b) **2**, (c) **3**, and (d) **4** (30% thermal ellipsoid).

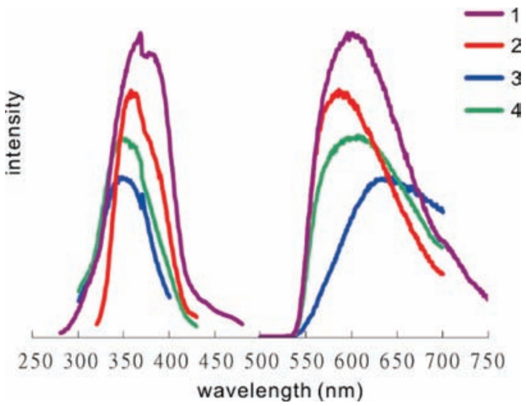

Figure 3. Excitation (left) and emission (right) spectra of compounds **1**−**4**, which were measured at 77 K in CH_3CN glass.

O atoms of the encapsulated anion display significant interactions with the surrounding Ag atoms because of their high affinity for O donor ligands. The Ag−O distances range from 2.395(5) to 2.595(8) Å, and the tetrahedral anion exhibits a $\mu_4;\eta^2,\eta^1,\eta^1$ bridging mode in **1**, a $\mu_6;\eta^2,\eta^2,\eta^1,\eta^1$ mode in **2**, a $\mu_6;\eta^2,\eta^2,\eta^2$ mode in **3**, and a $\mu_8;\eta^3,\eta^3,\eta^2$ mode in **4** (Figure 2). One of the O atoms of the tetrahedral oxyanions in clusters **1**, **3**, and **4** remains pendant. The tetrahedral oxyanion has almost the same orientation inside the silver cages of compounds **1**−**3** but is significantly different for MoO_4^{2-} in **4** (Figure 1). The number of Ag atoms to which the encapsulated anion is connected is not proportional to their volume, of which MoO_4^{2-} (68.6 Å^3) is the largest of the series.[13] Nonetheless, the expected templating effect is observed; that is, increasing the volume of the templating anion from spherical to tetrahedral shape enlarges the nuclearity of the surrounding Ag atoms.

Clusters **1**−**4** exhibit an orange emission both in the solid state and in solution under UV irradiation at 77 K. Structureless emissions centered at 598, 585, 625, and 605 nm are observed for **1**−**4**, respectively, and they are depicted in Figure 3. No significant shift for the emission band was observed in the degassed CH_3CN frozen glass. It appears that the emission origin is not directly associated with the encapsulated tetrahedral oxoanion but is likely from S → Ag charge transfer (LMCT).[18]

In summary, this work clearly demonstrates that, in the presence of tetrahedral-shaped anions, the nuclearity of silver clusters can be increased to 16 and dimerization via intermolecular Ag−S bonds yields Ag_{32} clusters that exhibit photoluminescence at 77 K. Our interest in template synthesis is ongoing and will likely lead us to pursue polyoxometalates as the anionic templates in the cluster assembly.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information. X-ray crystallographic files in CIF format (CCDC 796890−796893) for compounds **1**−**4**. This material is available free of charge via the Internet at http://pubs.acs.org.

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(14) Synthesis of **1**. $[Ag(CH_3CN)_4](PF_6)$ (0.4 g, 0.959 mmol) and $(NH_4)[S_2P(OEt)_2]$ (0.146 g, 0.719 mmol) were added in deionized water (30 mL) under sonication for 1 min and then continually stirred at 5 °C for 30 min under nitrogen to give a white suspension, to which $(NH_4)_2SO_4$ (0.007 g, 0.060 mmol) was added with stirring. After 2.5 h, a light-yellow suspension was obtained, and the precipitates were collected by filtration. These were dissolved in chloroform (30 mL), and the filtrate was evaporated to dryness to get a light-yellow solid **1**. Yield: 0.397 g (76.49%). Mp: 125 °C. Elem anal. Calcd for $C_{96}H_{240}Ag_{32}F_{24}O_{56}P_{28}S_{50}$: C, 13.30; H, 2.79. Found: C, 13.41; H, 2.72. $^{31}P\{^1H\}$ NMR (121.49 MHz, chloroform-*d*): 104.7. ^1H NMR (300.13 MHz, chloroform-*d*): 4.31 (m, 96H, CH_2), 1.42 (t, 144H, CH_3). The synthesis is general to compounds **2**−**4** by replacing $(NH_4)_2SO_4$ with Na_2SeO_4, K_2CrO_4, and Na_2MoO_4, respectively. Synthesis of **2**. Yield: 79.00% (0.166 g). Mp: 132 °C. Elem anal. Calcd for $C_{96}H_{240}Ag_{32}Se_2F_{24}O_{56}P_{28}S_{48}$: C, 13.16; H, 2.76. Found: C, 13.07; H, 3.11. $^{31}P\{^1H\}$ NMR (121.49 MHz, chloroform-*d*): 104.4. $^{77}Se\{^1H\}$ NMR (57.24 MHz, chloroform-*d*): 1054 (SeO_4^{2-}). ^1H NMR (300.13 MHz, chloroform-*d*): 4.31 (m, 96H, CH_2), 1.41 (t, 144H, CH_3). Synthesis of **3**. Yield: 46.95% (0.245 g). Mp: 81 °C. Elem anal. Calcd for $C_{96}H_{240}Ag_{32}Cr_2F_{24}O_{56}P_{28}S_{48}$: C, 13.24; H, 2.78. Found: C, 13.58; H, 2.64. $^{31}P\{^1H\}$ NMR (121.49 MHz, chloroform-*d*): 103.8. ^1H NMR (300.13 MHz, chloroform-*d*): 4.25 (m, 96H, CH_2), 1.42 (t, 144H, CH_3). Synthesis of **4**. Yield: 43.39% (0.229 g). Mp: 103 °C. Elem anal. Calcd for $C_{96}H_{240}Ag_{32}Mo_2F_{24}O_{56}P_{28}S_{48}$: C, 13.11; H, 2.75. Found: C, 12.78; H, 2.53. $^{31}P\{^1H\}$ NMR (121.49 MHz, chloroform-*d*): 103.9. ^1H NMR (300.13 MHz, chloroform-*d*): 4.24 (m, 96H, CH_2), 1.41 (t, 144H, CH_3).

(15) Single crystals suitable for X-ray diffraction were grown from acetone. Crystal data for **1**: $C_{96}H_{240}Ag_{32}F_{24}O_{56}P_{28}S_{50}$, fw = 8668.88 g mol^{-1}, triclinic, a=15.7461(14) Å, b=19.5259(18) Å, c=22.880(2) Å, α= 90.118(2)°, β = 94.861(2)°, γ = 109.468(2)°, V = 6605.1(10) $Å^3$, T = 296(2) K, space group $P\bar{1}$, Z = 1, μ(Mo Kα) = 2.948 mm^{-1}, 77 116 reflections measured, 32 924 independent reflections (R_{int}=0.058), 1250 parameters, R1=0.0550, wR2(F^2)=0.1326 [$I > 2\sigma(I)$]. The goodness of fit on F^2 was 0.974. Crystal data for **2**: $C_{96}H_{240}Ag_{32}Se_2F_{24}O_{56}P_{28}S_{48}$, fw = 8762.68 g mol^{-1}, triclinic, a = 15.7616(12) Å, b = 19.5255(13) Å, c = 22.9058(17) Å, α = 90.164(2)°, β = 94.972(2)°, γ = 109.426(2)°, V = 6619.2(8) $Å^3$, T = 296(2) K, space group $P\bar{1}$, Z = 1, μ(Mo Kα) = 3.201 mm^{-1}, 39 321 reflections measured, 23 125 independent reflections (R_{int}=0.032), 1312 parameters, R1=0.0565, wR2(F^2)=0.1586 [$I > 2\sigma(I)$]. The goodness of fit on F^2 was 1.023. Crystal data for **3**: $C_{96}H_{240}Ag_{32}Cr_2F_{24}O_{56}P_{28}S_{48}$, fw = 8708.76 g mol^{-1}, triclinic, a = 15.6196(10) Å, b = 19.3825(14) Å, c = 22.8341(16) Å, α = 90.814(2)°, β = 93.693(2)°, γ = 107.904(2)°, V = 6560.3(8) $Å^3$, T = 296(2) K, space group $P\bar{1}$, Z = 1, μ(Mo Kα) = 3.030 mm^{-1}, 43 109 reflections measured, 26 252 independent reflections (R_{int} = 0.026), 1280 parameters, R1 = 0.0463, wR2(F^2) = 0.1330 [$I > 2\sigma(I)$]. The goodness of fit on F^2 was 1.046. Crystal data for **4**: $C_{102}H_{252}Ag_{32}Mo_2F_{24}O_{58}P_{28}S_{48}\cdot 2(CH_3)_2CO$, fw=8912.80 g mol^{-1}, triclinic, a=15.6227(15) Å, b=15.7332(14) Å, c= 28.605(3) Å, α = 99.661(2)°, β = 90.995(2)°, γ = 95.522(2)°, V = 6895.2(11) $Å^3$, T = 253(2) K, space group $P\bar{1}$, Z = 1, μ(Mo Kα) = 2.897 mm^{-1}, 40 484 reflections measured, 24 021 independent reflections (R_{int}=0.023), 1329 parameters, R1=0.0643, wR2(F^2)=0.1875 [$I > 2\sigma(I)$]. The goodness of fit on F^2 was 1.028.

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