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## TRIGONAL PYRAMIDAL OXYANIONS AS STRUCTURE-DIRECTING TEMPLATES FOR THE SYNTHESIS OF SILVER DITHIOLATE CLUSTERS

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Trigonal pyramidal oxyanions,  $\text{EO}_3^{2-}$  (E = S, Se, Te), were utilized as a template in the formation of  $\text{Ag}_{16}$  clusters, which dimerize via intermolecular Ag—S bonds to form a  $\text{Ag}_{32}$  cluster stabilized by 1,1-dithiolate ligands. Structural elucidations on  $[\text{Ag}_{16}(\text{EO}_3)\{\text{S}_2\text{P}(\text{OEt})_2\}_{12}]^{2+}$  in comparison with tetrahedral oxyanion-centered  $\text{Ag}_{16}$  clusters previously characterized from this group clearly suggest that the lone-pair electrons on chalcogen center has a structure-directing effect.

**Keywords:** silver(I) clusters, anion template, template effect, dithiophosphate ligand, trigonal pyramidal oxyanions.

### INTRODUCTION

High-nuclearity silver clusters have been extensively investigated due to their wide variety of applications and structural diversities [ 1 ]. A well-documented approach to prepare giant silver clusters is the aggregation of multiple components. A number of nanometer-sized, sulfido silver clusters such as  $[\text{Ag}_{123}\text{S}_{35}(\text{S}^t\text{Bu})_{50}]$ ,  $[\text{Ag}_{344}\text{S}_{124}(\text{S}^t\text{Bu})_{96}]$ ,  $[\text{Ag}_{352}\text{S}_{128}(\text{S}^t\text{C}_5\text{H}_{11})_{96}]$ , and  $[\text{Ag}_{490}\text{S}_{188}(\text{S}^t\text{C}_5\text{H}_{11})_{114}]$  stabilized by thiolate ligands, have been reported by Fenske *et al.* by mixing silver salts,  $\text{S}(\text{SiMe}_3)_2$ , and thiols [ 2 ]. In addition, some mega silver clusters can be generated by the method of anion-template synthesis. A variety of templates have been successfully incorporated into silver-alkynyl cages such as a spherical halide in rhombohedral  $\text{Ag}_{14}$  cages  $[\text{Ag}_{14}(\text{C} \equiv \text{C}^t\text{Bu})_{12}\text{X}]^+$  (X = F, Cl, Br) [ 3 ], a triangular carbonate in  $[\text{Ag}_{19}(\text{C} \equiv \text{C}^t\text{Bu})_{14}(\text{CO}_3)]^+$  [ 4 ], a tetrahedral oxyanion in  $[\text{Ag}_{22}(\text{C} \equiv \text{C}^t\text{Bu})_{18}(\text{CrO}_4)]^{2+}$  [ 5 ], and a polyoxometalate in the fabrication of  $\text{Ag}_{40}$  clusters [ 6 ]. Astonishingly two  $\text{Mo}_6\text{O}_{22}^{8-}$  species can be simultaneously accommodated in one giant silver alkynyl cluster of  $\text{Ag}_{60}$  by taking advantages of oxophilic character of silver atoms [ 7 ]. Recently a  $\text{W}_6\text{O}_{21}^{6-}$  core, which is the isomerization product of Lindqvist-type  $\text{W}_6\text{O}_{19}^{2-}$  anion, has been accommodated in the  $[\text{Ag}_{34}(\text{S}^t\text{Bu})_{26}(\text{CF}_3\text{COO})]^{7+}$  shell to assemble a luminescent 1D chain [ 8 ].

We have demonstrated that an extended 1D chain polymer,  $[\text{Ag}_5\{\text{S}_2\text{P}(\text{OEt})_2\}_4]_n^{n+}$ , can be assembled into octanuclear silver clusters  $[\text{Ag}_8(\text{X})\{\text{S}_2\text{P}(\text{OEt})_2\}_6]^+$  (X = F<sup>-</sup>, Cl<sup>-</sup>, and H<sup>-</sup>) [ 9 ], by encapsulation of a spherical template such as halide and hydride ions. Tetrahedral oxyanions such as sulfate, selenate, chromate, and molybdate are also utilized as a template to form  $\text{Ag}_{16}$  clusters, which dimerize to become  $\text{Ag}_{32}$  clusters,  $[\text{Ag}_{16}(\text{EO}_4)\{\text{S}_2\text{P}(\text{OEt})_2\}_{12}]_2(\text{PF}_6)_4$  (E = S, Se, Cr, Mo) [ 10 ]. The volume of encapsulating anions seems to play a crucial role in the determination of silver cluster nuclearities.

In pursuit of nanometer-sized silver-dithiolato clusters via the applications of anion-templated synthetic methodology, we shift the target to divalent, trigonal pyramidal oxyanions ( $\text{EO}_3^{2-}$ , E = S, Se, Te) for the following two reasons. First, in sharp contrast to the broad studies of tetrahedral oxyanions manifested in the supramolecular chemistry [11], relatively few reports regarding the receptors for pyramidal oxyanions were known. As a result, few supramolecules templated by an  $\text{EO}_3^{2-}$  anion have been characterized structurally except in the field of polyoxometalates [12] and a urea-functionalized sulfite-binding capsule [13]. Thus it is not surprising that none of silver chalcogenolate clusters encapsulating an  $\text{EO}_3^{2-}$  anion at the cluster center is known. Second, due to the lone-pair electrons possessed by  $\text{E}^{4+}$  cations, which can induce second-order Jahn-Teller distortive effects to fabricate the non-centrosymmetric materials [14], it will be of great interest to see whether the presence or absence of stereochemical activity for the lone pair of electrons at chalcogen atom will influence the cluster nuclearity or not. Herein a new series of dithiolato-protective  $\text{Ag}_{32}$  clusters are fabricated from which both the template effect of trigonal pyramidal-shaped oxyanions and the structure-directing effect on the stereochemically active lone pair of electrons on chalcogen center are nicely demonstrated.

### EXPERIMENTAL

**Synthesis of 1.** Deionized water (30 mL) was added to a Schlenk flask containing  $[\text{Ag}(\text{CH}_3\text{CN})_4]\text{PF}_6$  (0.547 g, 1.31 mmol) and  $\text{NH}_4[\text{S}_2\text{P}(\text{OEt})_2]$  (0.200 g, 0.98 mmol) and continually stirred for 30 minutes at ambient temperature under nitrogen atmosphere to generate white suspension, followed by  $\text{Na}_2\text{SO}_3$  (0.010 g, 0.08 mmol), was added in situ and kept stirring. After 1 hour, gray-white precipitate was formed and washed with deionized water to obtained gray-white powder. Yield: 0.28 g (79.07 %). Mp: 117 °C. Anal. Calcd for  $\text{C}_{96}\text{H}_{240}\text{Ag}_{32}\text{F}_{24}\text{O}_{54}\text{P}_{28}\text{S}_{50}$ : C, 13.35; H, 2.80. Found: C, 13.15; H, 2.85.  $^{31}\text{P}\{^1\text{H}\}$  NMR (121.49 MHz, acetone- $d_6$ ): 104.6.  $^1\text{H}$  NMR (300.13 MHz, acetone- $d_6$ ): 4.32 (m, 96H,  $\text{CH}_2$ ), 1.42 (t, 144H,  $\text{CH}_3$ ). ESI-MS ( $m/z$ ): calcd for  $[\text{Ag}_{16}(\text{SO}_3)\{\text{S}_2\text{P}(\text{OEt})_2\}_{12}]^{2+}$  2014.3; found: 2014.2.

The synthesis is general to compounds **2** and **3** by replacing  $\text{Na}_2\text{SO}_3$  with  $\text{Na}_2\text{SeO}_3$  and  $\text{Na}_2\text{TeO}_3$ , respectively.

**2.** Yield: 0.29 g (72.67 %). Mp: 120 °C. Anal. Calcd for  $\text{C}_{96}\text{H}_{240}\text{Ag}_{32}\text{F}_{24}\text{O}_{54}\text{P}_{28}\text{S}_{48}\text{Se}_2$ : C, 13.21; H, 2.77. Found: C, 12.92; H, 2.60.  $^{31}\text{P}\{^1\text{H}\}$  NMR (121.49 MHz, acetone- $d_6$ ): 104.6.  $^{77}\text{Se}\{^1\text{H}\}$  NMR (57.24 MHz, acetone- $d_6$ ): 1286 ( $\text{SeO}_3^{2-}$ ).  $^1\text{H}$  NMR (300.13 MHz, acetone- $d_6$ ): 4.32 (m, 96H,  $\text{CH}_2$ ), 1.42 (t, 144H,  $\text{CH}_3$ ). ESI-MS ( $m/z$ ): calcd for  $[\text{Ag}_{16}(\text{SeO}_3)\{\text{S}_2\text{P}(\text{OEt})_2\}_{12}]^{2+}$  2037.8; found: 2036.9.

**3.** Yield: 0.27 g (75.00 %). Mp: 119 °C. Anal. Calcd for  $\text{C}_{96}\text{H}_{240}\text{Ag}_{32}\text{Te}_2\text{F}_{24}\text{O}_{54}\text{P}_{28}\text{S}_{48}$ : C, 13.06; H, 2.74. Found: C, 13.07; H, 3.11.  $^{31}\text{P}\{^1\text{H}\}$  NMR (121.49 MHz, acetone- $d_6$ ): 104.7.  $^{125}\text{Te}\{^1\text{H}\}$  NMR (94.69 MHz, acetone- $d_6$ ): 1756 ( $\text{TeO}_3^{2-}$ ).  $^1\text{H}$  NMR (300.13 MHz, acetone- $d_6$ ): 4.32 (m, 96H,  $\text{CH}_2$ ), 1.42 (t, 144H,  $\text{CH}_3$ ). ESI-MS ( $m/z$ ): calcd for  $[\text{Ag}_{16}(\text{TeO}_3)\{\text{S}_2\text{P}(\text{OEt})_2\}_{12}]^{2+}$  2062.1; found: 2061.1.

**Crystal data for 1.**  $\text{C}_{96}\text{H}_{240}\text{Ag}_{32}\text{F}_{24}\text{O}_{54}\text{P}_{28}\text{S}_{50}$ ,  $M_r = 8636.88$ , triclinic,  $P(-)1$ ,  $a = 15.830(2)$  Å,  $b = 19.608(3)$  Å,  $c = 22.928(3)$  Å,  $89.743(3)^\circ$ ,  $\alpha = 89.743(3)^\circ$ ,  $\beta = 85.426(3)^\circ$ ,  $\gamma = 70.640(3)^\circ$ ,  $V = 6691.0(16)$  Å<sup>3</sup>,  $Z = 1$ ,  $\rho = 2.143$  g·cm<sup>-3</sup>,  $\mu = 2.909$  mm<sup>-1</sup>,  $F(000) = 4188$ , GOOF = 1.049. A total of 38704 reflections were collected, 23137 of which were unique ( $R_{\text{int}} = 0.0534$ ).  $R_1(wR_2) = 0.0624(0.1726)$  for 1279 parameters and 13454 reflections ( $I > 2\sigma(I)$ ).

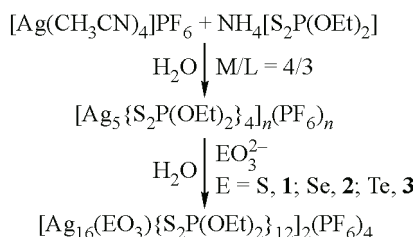
**2.**  $\text{C}_{96}\text{H}_{240}\text{Ag}_{32}\text{F}_{24}\text{O}_{54}\text{P}_{28}\text{S}_{50}$ ,  $M_r = 8730.68$ , triclinic,  $P(-)1$ ,  $a = 15.7513(19)$  Å,  $b = 19.498(2)$  Å,  $c = 22.923(3)$  Å,  $\alpha = 90.038(2)^\circ$ ,  $\beta = 94.841(2)^\circ$ ,  $\gamma = 109.456(2)^\circ$ ,  $V = 6611.1(14)$  Å<sup>3</sup>,  $Z = 1$ ,  $\rho = 2.193$  g·cm<sup>-3</sup>,  $\mu = 3.204$  mm<sup>-1</sup>,  $F(000) = 4224$ , GOOF = 1.024. A total of 61110 reflections were collected, 23282 of which were unique ( $R_{\text{int}} = 0.0431$ ).  $R_1(wR_2) = 0.0576(0.1417)$  for 1256 parameters and 15133 reflections ( $I > 2\sigma(I)$ ).

**3.**  $\text{C}_{96}\text{H}_{240}\text{Ag}_{32}\text{Te}_2\text{F}_{24}\text{O}_{54}\text{P}_{28}\text{S}_{48}$ ,  $M_r = 8827.96$ , triclinic,  $P(-)1$ ,  $a = 15.7918(4)$  Å,  $b = 19.5286(5)$  Å,  $c = 22.9037(6)$  Å,  $\alpha = 89.7580(10)^\circ$ ,  $\beta = 84.7250(10)^\circ$ ,  $\gamma = 70.1620(10)^\circ$ ,  $V = 6613.3(3)$  Å<sup>3</sup>,  $Z = 1$ ,  $\rho = 2.217$  g·cm<sup>-3</sup>,  $\mu = 3.144$  mm<sup>-1</sup>,  $F(000) = 4260$ , GOOF = 1.017. A total of 57414 reflections were collected, 22624 of which were unique ( $R_{\text{int}} = 0.0419$ ).  $R_1(wR_2) = 0.0574(0.1315)$  for 1291 parameters and 12652 reflections ( $I > 2\sigma(I)$ ).

The intensity data were collected on Bruker APEX-II CCD with graphite-monochromated  $\text{MoK}\alpha$  radiation ( $\lambda = 0.71073 \text{ \AA}$ ). Direct methods were used to solve the structure and to locate the heavy atoms using the SHELXTL-97 program package. The remaining atoms were found from successive full-matrix least-squares refinements on  $F^2$  and Fourier syntheses. All non-hydrogen atoms were refined anisotropically. The Ag2, Ag5 atoms in **1**, and Ag2 atom in **2** and **3** was disordered over two positions in a 1:1 ratio, respectively. CIF file containing complete information on the studied structure was deposited with CCDC, deposition number 926526—926528 (**1—3**), and is freely available upon request from the following web site: [www.ccdc.cam.ac.uk/data\\_request/cifCCDC](http://www.ccdc.cam.ac.uk/data_request/cifCCDC).

## RESULTS AND DISCUSSION

Following our recent report on the synthesis of  $\text{Ag}_{32}$  clusters which were fabricated via the combination of cationic one-dimensional chain polymer with an anionic template in aqueous solution at ambient temperature, a reaction mixture containing sixteen equiv. of  $[\text{Ag}(\text{CH}_3\text{CN})_4]\text{PF}_6$  and twelve equiv. of  $\text{NH}_4[\text{S}_2\text{P}(\text{OEt})_2]$  yields polymeric species,  $[\text{Ag}_5\{\text{S}_2\text{P}(\text{OEt})_2\}_4]_n^{n+}$ , from which the addition of one equiv. of pyramidal-shaped anion ( $\text{SO}_3^{2-}$ ,  $\text{SeO}_3^{2-}$ , and  $\text{TeO}_3^{2-}$ ) as the template produces  $[\text{Ag}_{16}(\text{EO}_3)\{\text{S}_2\text{P}(\text{OEt})_2\}_{12}]_2^{4+}$  ( $\text{E} = \text{S}$ , **1**;  $\text{Se}$ , **2**;  $\text{Te}$ , **3**) in over 70 % yield (Scheme 1). Similar to the previously characterized  $\text{Ag}_{32}$  clusters [10], the  $^{31}\text{P}\{^1\text{H}\}$  NMR spectra of all three compounds **1—3** at ambient temperature featured a single resonance centered at 104 ppm, and only a set of ethyl resonances was depicted in the  $^1\text{H}$  NMR spectrum. These data suggest that all dithiophosphate ligands are equivalent in solution at the NMR timescale. The selenium atom of central selenite in **2** is detected explicitly by  $^{77}\text{Se}$  NMR spectroscopy with a resonance frequency at  $\delta = 1286$  ppm. Furthermore a chemical shift at  $\delta = 1756$  ppm in the  $^{125}\text{Te}$  NMR spectrum authenticates the presence of tellurite anion in compound **3**. The cluster composition is also determined by ESI mass spectrometry analyses. A prominent band in the mass range at  $m/z$  2014.2, 2036.9, and 2061.1 observed at the positive electrospray ionization mass spectrum (ESI-MS) of compounds **1—3**, respectively, can be formulated as  $[\text{Ag}_{16}(\text{EO}_3)\{\text{S}_2\text{P}(\text{OEt})_2\}_{12}]_2^{2+}$  ( $M_{\text{calc}} = 2014.1, 2037.1, \text{ and } 2062.1$  for dicationic species). Thus only the molecular ion peak corresponding to half of the cluster was detected. This implies the dimeric structure composed of two  $\text{Ag}_{16}$  clusters is labile in the gas phase.



Scheme 1. Pathway for the Formation of  $\text{Ag}_{32}$  Clusters **1—3**

The crystal structure analysis reveals that complexes **1—3** all contain a  $\text{Ag}_{32}$  framework of  $[\text{Ag}_{16}(\text{EO}_3)\{\text{S}_2\text{P}(\text{OEt})_2\}_{12}]_2^{4+}$  (Fig. 1 and Fig. S1). The centrosymmetric  $\text{Ag}_{32}$  core is composed of two  $\text{Ag}_{16}$  cluster units linked by edge-sharing, two  $\{\text{AgS}_4\}$  tetrahedra. The  $\text{Ag}_{16}$  fragment is built by a distorted icosahedral cage ( $\text{Ag}1\text{—Ag}12$ ) and four face-capping  $\text{Ag}^1$  ions ( $\text{Ag}13\text{—Ag}16$ ). Twelve diethyl dithiophosphate (dtp) ligands surround the  $\text{Ag}_{16}$  fragment and a trigonal pyramidal  $\text{EO}_3^{2-}$  anion is located at the center of the  $\text{Ag}_{16}$  cage. The pyramidal-shaped template in **1—3** has almost the same orientation inside the silver cages, and each O atom of an  $\text{EO}_3^{2-}$  anion aims directly to the silver capping atom (Fig. 2). Astonishingly the silver framework in cluster cation,  $[\text{Ag}_{16}(\text{EO}_3)\{\text{S}_2\text{P}(\text{OEt})_2\}_{12}]_2^{4+}$ , is very similar to that of  $[\text{Ag}_{16}(\text{SO}_4)\{\text{S}_2\text{P}(\text{OEt})_2\}_{12}]_2^{4+}$ , **4**, reported by our group [10]. The main differences between **1—3** and **4** are the central unit of  $\text{Ag}_{16}$  core. The central fragment in **4** is a tetrahedron

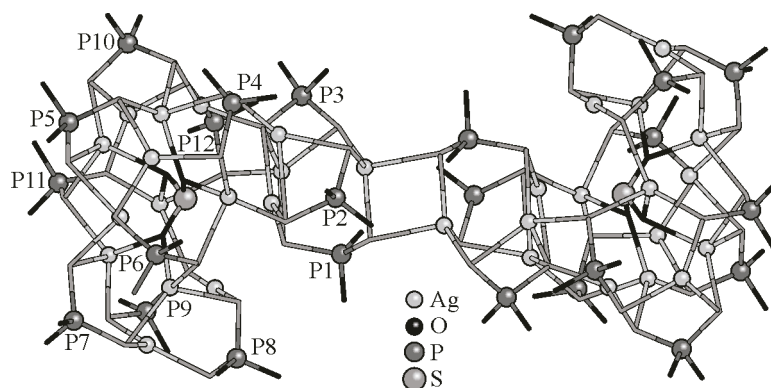


Fig. 1. Structure of  $[\text{Ag}_{16}(\text{SO}_3)\{\text{S}_2\text{P}(\text{OEt})_2\}_{12}]_2^{4+}$ . The ethyl groups are omitted for clarity

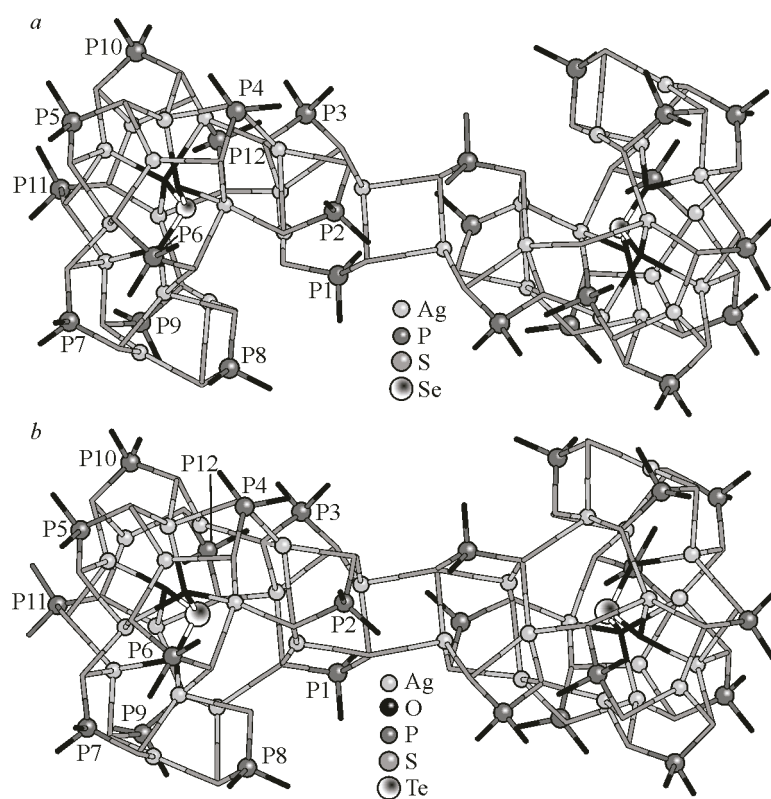


Fig. S1. Structure of  $[\text{Ag}_{16}(\text{SeO}_3)\{\text{S}_2\text{P}(\text{OEt})_2\}_{12}]_2^{4+}$  **2** (a) and  $[\text{Ag}_{16}(\text{TeO}_3)\{\text{S}_2\text{P}(\text{OEt})_2\}_{12}]_2^{4+}$  **3** (b). The ethyl groups are omitted for clarity

composed of a sulfate anion whereas that of **1**–**3** exist a trigonal pyramidal anion (e.g.,  $\text{SO}_3^{2-}$ ,  $\text{SeO}_3^{2-}$ ,  $\text{TeO}_3^{2-}$ ) (Fig. 3). Though the template anion  $\text{SO}_4^{2-}$  in **4** is replaced by a  $\text{SO}_3^{2-}$  group in **1**, surprisingly the silver skeleton of  $\text{Ag}_{16}$  is very much the same. Presumably  $\text{EO}_3^{2-}$  has a stereochemically active lone pair of electrons which occupy on the top of trigonal pyramidal to keep the interior space of an  $\text{Ag}_{12}$  icosahedron from collapsing. This assumption is further confirmed by the distance of two sulphur atoms of the encapsulated species in the  $\text{Ag}_{32}$  cluster. It is 15.679(4) Å in **1** which is shorter than that in **4**, 16.194(3) Å, because the volume of the lone pair electron is smaller than that of an oxygen atom. Such a structural directing effect exhibited by lone-pair electrons may eventually impede the isolation

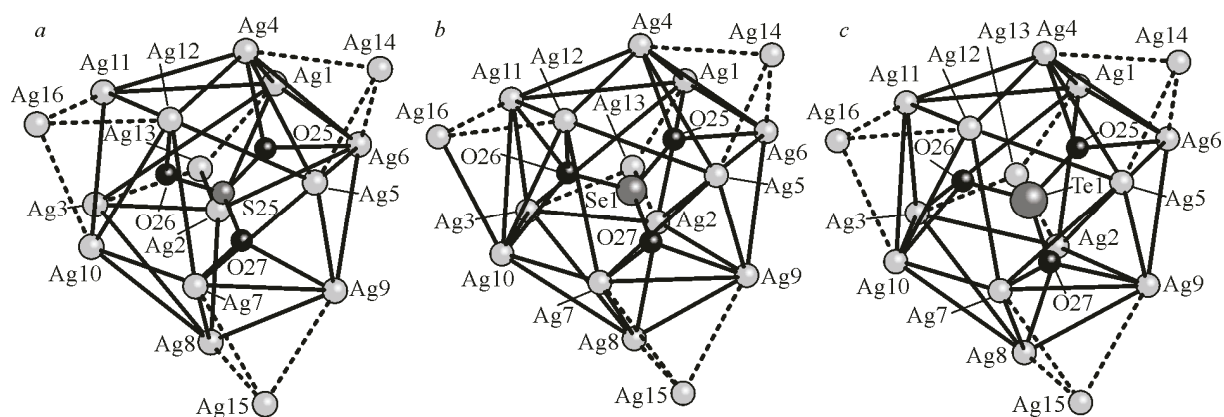


Fig. 2. The distorted icosahedral framework with four capping atom (linked with dotted lines) of **1** (a), **2** (b), **3** (c)

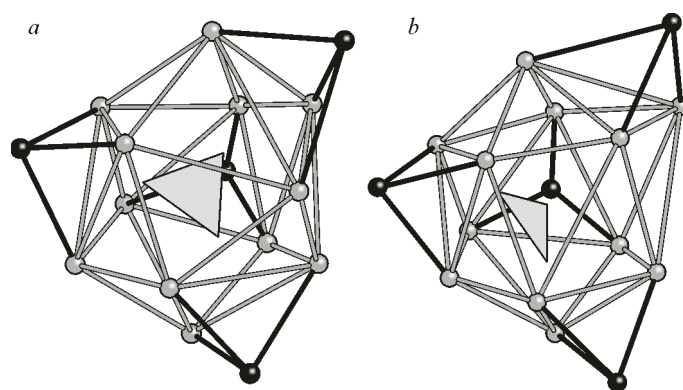
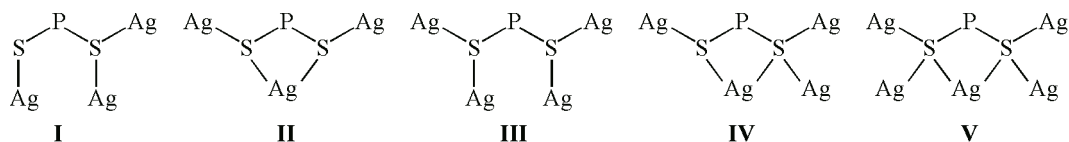


Fig. 3.  $\text{SO}_4^{2-}@Ag_{16}$  skeleton (a),  $\text{SeO}_4^{2-}@Ag_{16}$  skeleton (b) (cyan: silver at icosahedron; violet: capping silver; template anion was represented as a polyhedron)

of  $Ag_{16}$  clusters containing  $\text{CO}_3^{2-}$  or  $\text{NO}_3^-$  as the template due to its planar geometry and much smaller volume.

It is expected that the E—O bond lengths of templated-anion in **1**—**3** increase with ionic radius of E (S—O: 1.46(1)—1.49(1) Å; Se—O: 1.62(1)—1.652(8) Å; Te—O: 1.80(1)—1.813(9) Å). The templated-anions display variable coordination modes ( $\mu_6$ :  $\eta^2, \eta^2, \eta^2$  bridging mode in **1**,  $\mu_7$ :  $\eta^2, \eta^3, \eta^2$  in **2**, and  $\mu_7$ :  $\eta^3, \eta^2, \eta^2$  in **3**) and flexible bond angles to adapt voids of the  $Ag_{16}$  cage. (Fig. 2). The Ag—O bond lengths vary from 2.368(9) Å to 2.696(6) Å.



Scheme 2. Five coordination patterns of dtp ligands in compounds **1**—**3**

The dtp ligands exhibit five coordination patterns (**I**: trimetallic triconnective; **II**: trimetallic tetraconnective; **III**: tetrametallic tetraconnective; **IV**: tetrametallic pentaconnective; **V**: pentametallic hexaconnective) [ 15 ] in compounds **1**—**3** (Scheme 2) and twelve dtp ligands displayed three different coordination modes in compounds **1** and **2**, and four coordination modes in **3**. Most dtp ligands adopt mode **III** to bridge silver atoms except few ligands such as P8 with mode **I** fashion in **1**, whereas it dis-



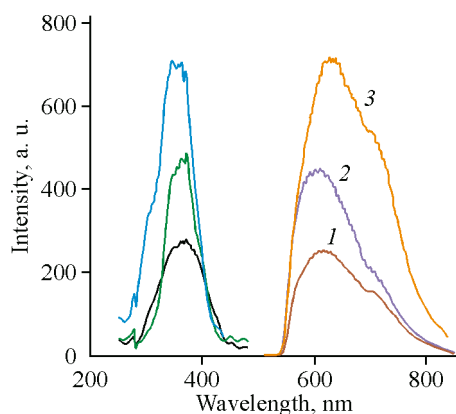


Fig. 4. Excitation (a) and emission (b) spectra of compounds **1**–**3** at 77 K in CH<sub>3</sub>CN glass

Table 1  
Photophysical data for [Ag<sub>16</sub>(EO<sub>3</sub>){S<sub>2</sub>P(OEt)<sub>2</sub>}<sub>12</sub>]<sub>2</sub>(PF<sub>6</sub>)<sub>4</sub> (E = S, **1**;  
Se, **2**; Te, **3**)

Compound	State (77 K)	$\lambda_{\text{ex}}$ , nm	$\lambda_{\text{em}}$ , nm	$\lambda_{\text{abs}}$ , nm ( $\epsilon/\text{dm}^3 \cdot \text{mol}^{-1} \cdot \text{cm}^{-1}$ )	$\tau$ , $\mu\text{s}$
<b>1</b>	CH <sub>3</sub> CN	360	614	371 (33,000)	1.1, 0.4
	solid	365	628		
<b>2</b>	CH <sub>3</sub> CN	357	606	371 (33,000)	6.5, 0.8
	solid	369	627		
<b>3</b>	CH <sub>3</sub> CN	353	628	361 (54,000)	2.5, 0.7
	solid	355	625		

plays mode **II** in **2** and **3**. Both P2 and P3 in **1**–**3** display mode **IV** fasion, and P1 in **3** displays mode **V** fasion (Fig. S1). The Ag–S bond distances within the Ag<sub>16</sub> unit are in the range of 2.432(3)–3.051(3) Å. The dimerization of two Ag<sub>16</sub> units is due to the formation of Ag<sub>13</sub>–S1 bond with a distance of 2.864(3) Å in **1**, 2.934(3) Å in **2**, and 3.057(3) Å in **3**.

All three compounds displayed orange luminescence at 77 K under UV-irradiation in both solid and solution state (Fig. 4). The absorption spectra of **1**–**3** in acetonitrile show bands in the UV region around 361 ~ 371 nm with molar extinction coefficients in the range of  $3.3 \times 10^4 \sim 5.4 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$  (Table 1). The emission bands with microsecond lifetime ( $\tau$ ) centered at 614, 606, and 628 nm for **1**–**3**, respectively, in CH<sub>3</sub>CN at 77 K are structureless and exhibit a slight shift of ~20 nm of the emission maximum in the solid state. Due to the great similarity in emission peak profiles and emission maxima, it appears that the emission origin of the spin-forbidden triplet state is not directly associated with the encapsulated pyramidal oxoanion but is likely from S → Ag charge transfer (LMCT) [ 16 ].

## CONCLUSIONS

In summary, high-nuclearity silver clusters encapsulating trigonal pyramidal-shaped templates have been characterized. Their Ag<sub>16</sub> core structure was almost the same as those containing a tetrahedral-shaped anion template. This clearly suggests that the presence of stereochemically active lone pair electrons of EO<sub>3</sub><sup>2-</sup> anion has a structure directing effect. Intriguingly, compound **3** is the first example of high-nuclearity silver cluster containing a tellurite anion. Work toward to incorporate a polyoxometalate anion into the silver cage stabilized by dithiolates is continuing.

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## REFERENCES

- (a) Gimeno M.C., Laguna A. In *Comprehensive Coordination Chemistry II, Vol. 6* (Eds.: J.A. McCleverty, T.J. Meyer) – Elsevier, Oxford, 2004. – P. 911 – 990. (b) Fuhr O., Dehnen S., Fenske D. // *Chem. Soc. Rev.* – 2013. – **42**. – P. 1871.
- (a) Fenske D., Persau C., Dehnen S., Anson C.E. // *Angew. Chem. Int. Ed.* – 2004. – **43**. – P. 305. (b) Fenske D., Anson C.E., Eichh fer A., Fuhr O., Ingendoh A., Persau C., Richert C. // *Angew. Chem. Int. Ed.* – 2005. – **44**. – P. 5242. (c) Anson C.E., Eichh fer A., Issac I., Fenske D., Fuhr O., Sevillano P., Persau C., Stalke D., Zhang J. // *Angew. Chem. Int. Ed.* – 2008. – **47**. – P. 1326.
- (a) Rais D., Yau J., Mingos D.M.P., Vilar R., White A.J.P., Williams D.J. // *Angew. Chem. Int. Ed.* – 2001. – **40**. – P. 3463. (b) Rais D., Mingos D.M.P., Vilar R., White A.J.P., Williams D.J. // *J. Organomet. Chem.* – 2002. – **652**. – P. 87.
- Bian S.-D., Jia J.-H., Wang Q.-M. // *J. Amer. Chem. Soc.* – 2009. – **131**. – P. 3422.

5. *Bian S.-D., Wu H.-B., Wang Q.-M.* // *Angew. Chem. Int. Ed.* – 2009. – **48**. – P. 5363.
6. *Gao G.-G., Cheng P.-S., Mak T.C.W.* // *J. Amer. Chem. Soc.* – 2009. – **131**. – P. 18257.
7. *Qiao J., Shi K., Wang Q.-M.* // *Angew. Chem. Int. Ed.* – 2010. – **49**. – P. 1765.
8. *Zhou K., Qin C., Li H.-B., Yan L.-K., Wang X.-L., Shan G.-G., Su Z.-M., Xu C., Wang X.-L.* // *Chem. Commun.* – 2012. – **48**. – P. 5844.
9. *Liu C.W., Chang H.-W., Fang C.-S., Sarkar B., Wang J.-C.* // *Chem. Commun.* – 2010. – **46**. – P. 4571.
10. *Liao J.-H., Chang H.-W., You H.-C., Fang C.-S., Liu C. W.* // *Inorg. Chem.* – 2011. – **50**. – P. 2070.
11. *Katayev E.A., Ustynyuk Y.A., Sessler J.L.* // *Coord. Chem. Rev.* – 2006. – **250**. – P. 3004.
12. (a) *Fay N., Bond A.M., Baffert C., Boas J.F., Pilbrow J.R., Long D.-L., Cronin L.* // *Inorg. Chem.* – 2007. – **46**. – P. 3502. (b) *Yan J., Long D.-L., Cronin L.* // *Angew. Chem. Int. Ed.* – 2010. – **49**. – P. 4117. (c) *Yan J., Long D.-L., Wilson E.F., Cronin L.* // *Angew. Chem. Int. Ed.* – 2009. – **48**. – P. 4376. (d) *Miras H.N., Chillas G.I., Cronin L., Kabanos T.A.* // *Eur. J. Inorg. Chem.* – 2013. – P. 1620.
13. (a) *Custelcean R., Remy P., Bonnesen P.V., Jiang D., Moyer B.A.* // *Angew. Chem. Int. Ed.* – 2008. – **47**. – P. 1866. (b) *Rajbanshi A., Custelcean R.* // *Supramol. Chem.* – 2011. – **23**. – P. 1.
14. (a) *Lee D.W., Bak D., Kim S.B., Kim J., Ok K.M.* // *Inorg. Chem.* – 2012. – **51**. – P. 7844. (b) *Nguyen S.D., Halasyamani P.S.* // *Inorg. Chem.* – 2013. – **52**. – P. 2637.
15. *Haiduc I.* // *Polyhedron.* – 1995. – **14**. – P. 3389.
16. (a) *Liu C.W., Chang H.-W., Liao P.-K., Fang C.-S., Saillard J.-Y., Kahlal S.* // *J. Clust. Sci.* – 2011. – **22**. – P. 381. (b) *Van Zyl W.E.* // *Comments Inorg. Chem.* – 2010. – **31**. – P. 13. (c) *Liao J.-H., Latouche C., Li B., Kahlal S., Saillard J.-Y., Liu C.W.* // *Inorg. Chem.* – 2014. – **53**. – P. 2260. (d) *Li Y.-J., Latouche C., Kahlal S., Liao J.-H., Dhayal R.S., Saillard J.-Y., Liu C.W.* // *Inorg. Chem.* – 2012. – **51**. – P. 7439.