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The solvent-induced isomerization of silver thiolate clusters with symmetry transformation

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A novel ligand-stabilized Ag12 nanocluster was synthesized as a model cluster to investigate the solvent-induced isomerization of Ag12 clusters. The other two novel Ag12 clusters as well as their related symmetry transformations were successfully obtained through the above solvent-induced isomerization process.

Increasing attention has been drawn to ligand-stabilized metal nanoclusters in recent decades because of their intriguing structures and broad applications in photoluminescence, catalysis, biosensing and bioimaging.^{1,2} Most of the works in this topic mainly focus on the transition metals, especially noble metals, such as Au, Ag, Pd etc.³ Among them, ligandstabilized Ag(I) nanoclusters persist in attracting interest since their fascinating structures and rich physicochemical properties.⁴ In general, these Ag(I) nanoclusters can be obtained from the self-assembly process between the ligands including alkynyl, thiolate or organophosphorus compounds and the Ag(I) salts with different anions.⁵ Through adjusting the central template anions, auxiliary ligands or reaction conditions, numerous ligand-stabilized Ag(I) nanoclusters with different cores can be synthesized.⁶ The current study about the ligand-stabilized Ag(I) clusters primarily focuses on the construction of their novel diverse structures and physicochemical properties, $^{7}% ^{2}$ while it remains insufficient for investigating the isomerization of the ligand-stabilized Ag(I) clusters under external stimuli.

Isomerization is a fundamental transformation in nature, and it plays a significantly important role in various biological processes.⁸ The isomerization has attracted much attention in synthetic chemistry and supramolecular chemistry since the different arrangements of the same number of atoms would

generate different physicochemical properties and chemical reactivities.9 However, the isomerization of the metal core of the metal nanoclusters remains a significant challenge because the small changes in the assembly process can lead to a significant change of the metal numbers in the metal nanoclusters.¹⁰ To date, there have been a few reports about the isomerization of the ligand-stabilized metal nanoclusters, much less the isomerization of Ag(I) nanoclusters. The reported examples about the isomerization of the Ag(I) nanoclusters primarily based on the ligand-change method, which employs the different ligands to obtain different Ag(I) nanoclusters with the same nuclearity.¹¹ However, the symmetry of these Ag(I) cluster isomers generally almost keeps no change. Therefore, it represents a tough job for the design and synthesis of Ag(I) clusters that can exhibit the isomerization with symmetry transformations upon mild outside stimuli, such as solvent change.

The exchange reaction of coordinated solvent molecules is one kind of fundamental reactions in the coordination chemistry.¹² In such coordination systems, the exchange of the coordinated solvent molecules can make a remarkable change on the structure.¹³ As illustrated in Scheme 1, the coordinated solvent molecules on the nanocluster A not only stabilize the metal cluster but also generate the interactions with the neighbor atoms to reach a certain symmetry of the cluster. Therefore, the change of the coordinated solvent molecules may afford an isomer nanocluster B with a similar structure but a different symmetry. In this regard, we prepared an Ag12 with nanocluster an octadecahedron geometry, $Ag_{12}(Tab)_6(TFA)_{12}(H_2O)_2 \cdot 4CH_3CN$ (TFA = trifluoroacetate, Tab = 4-(trimethylammonio)benzenethiolate¹⁴) (Ag12a), as a model cluster to explore the solvent-induced isomerization or rather the symmetry transformation of the silver nanoclusters (Table S1,ESI+). Ag12a can be readily converted to the other two novel Ag12 nanocluster, Ag12(Tab)6(TFA)12.2DMF (Ag12b) and Ag₁₂(Tab)₆(TFA)₁₀(CH₃CN)₂·2TFA (Ag12c), which show lower symmetry, through changing the coordinated solvent molecules. The main structures of Ag12b and Ag12c are similar to that of Ag12a, but some symmetry elements in the structure of Ag12a got disappeared in the transformation

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process. Remarkably, the transformation from **Ag12a** to **Ag12b** and **Ag12c** can be realized by simply changing the solvents at room temperature, thus exhibiting the solvent-induced isomerization of the silver nanoclusters.



Scheme 1 The solvent-induced nanocluster isomerization with symmetry transformation. The purple and yellow balls stand for the different solvent molecules while the blue ball stands for the coordinated ligands.

The model nanocluster Ag12a was synthesized at room temperature according to the reaction of Tab and silver(I) salt in DMF, CH₃CN and H₂O mixed solvent system. Colorless block crystals of Ag12a were then obtained through the diffusion method. Ag12a crystallizes in the orthorhombic space group Pbca and its kernel is stabilized by 6 Tab, 12 TFA and 2 water molecules (Fig. 1 and Fig. S1, ESI⁺). As shown in Fig. 1c, the essence of Ag12a is an Ag12 skeleton welded by argentophilic interactions formed a regular hollow octadecahedron with Ag...Ag contacts being 2.943(6)-3.269(7) Å. The six Tab ligands supporting the Ag12 skeleton adopt a quadruple coordination mode, or more precisely, the ligands adopt a μ_4 - η^1 : η^1 : η^1 : η^1 : η^1 ligation mode where the Ag-S bond distances are in the range of 2.451(13)-2.620(13) Å (Fig. S1b, ESI⁺). The twelve TFA ligands can be classified into three groups: two of them adopting a μ_3 - η^2 : η^1 ligation mode, six adopting a μ_2 - η^1 : η^1 ligation mode and the other four adopting a $\mu_2\text{-}\eta^1\text{:}\eta^1$ ligation mode with Ag-O distances being 2.257(5)-2.867 Å (Fig. S1c, ESI⁺). The coordinated water molecules adopting a μ_2 ligation mode bridge the two adjacent Ag atoms and get fixed by Hbonding interactions between TFA anions and H_2O molecules. There are two H₂O molecules coordinated with the silver in the vertex of the core structure, thus producing a change to be exchanged by other molecules. The weak interactions between the coordinated H_2O molecules and the TFA anions are contributed to the certain kernel geometry with D_{2h} symmetry.

The structure analysis of **Ag12a** encourages us to adjust the nanocluster structure based on the classic hard-soft-acid-base (HSAB) theory.¹⁵ If the hardness of the solvent molecule was adjusted, competition between the solvent, TFA and Tab could influence the whole structure rather than partial distortion. Based on the above consideration, the solvent system was changed to the mixture solvent of CH₃OH and DMF, and a new Ag12 isomer, **Ag12b**, was obtained. It crystallizes in monoclinic space group *C*2/*c* and its kernel is stabilized by 6 Tab and 12 TFA (Fig. S2, ESI†). Compared to that of **Ag12a**, the core of **Ag12b** is a distorted hollow octadecahedron structure with Ag…Ag contacts being 2.990(6)-3.364(7) Å and the symcenter is the only symmetry element (Fig. 2). There is no coordinated

solvent in Ag12b except two dissociative DMF molecules, which could be due to the big size 12/10/39/appropriate coordination capability of DMF. The silver atoms are coordinated with solvent and TFA in Ag12a but are coordinated with TFA anion only in Ag12b, so the distance between Ag4 and Ag6 is stretched to 4.017 Å. However, the distance between Ag4 and Ag3 is shortened to 3.311(7) Å. The six Tab ligands protecting the silver skeleton adopt the μ_4 - $\eta^1{:}\eta^1{:}\eta^1{:}\eta^1$ ligation mode with Ag-S bonds being 2.464(12)-2.672(13) Å (Fig. S2b, ESI⁺). Finally, the distance between Ag3 and Ag6 reaches 3.962 Å which is longer than that between these two Ag atoms in Ag12a (Ag-Ag bond length is 3.100(14) Å). The coordinated twelve TFA anions are arranged in two types of coordination modes: four of them are coordinated in the vertex of the cluster (μ_1 - η^1 : η^0 mode) with Ag-O distances being 2.205(5)-2.265(5) Å and remaining eight TFA anions adopt a μ_2 - η^1 : η^1 mode with Ag-O distances being 2.265(5)-2.579(5) Å (Fig. S2c, ESI⁺). It is worth noting that the slight change of the coordinated solvent molecules plays a crucial role in the assembly process of the silver clusters.



Fig. 1 (a) and (b) View of the crystal structures of **Ag12a** along with two orthogonal directions. Free solvent molecules and H atoms are omitted for clarity. (c) and (d) View of the Ag12 kernel in a polyhedron mode. Color codes: green, Ag; yellow, S; red, O; blue, N; grey, C; sky blue, F.

The above experimental results confirmed that the solvent strategy could influence the assembly process greatly and silver nanocluster isomers could be formed when the different solvents were chosen. A one-step strategy originated from the above results was used again: the silver salts and thiolate ligands were dissolved in CH₃CN. After five days, some colorless block crystals can be observed by the diffusion of Et₂O into the mixture. The following X-ray analysis reveals that another new Ag12 isomer, **Ag12c**, crystallizes in the monoclinic space group $P2_1/n$ and its kernel is stabilized by 6 Tab and 10 TFA (Fig. S3, ESI⁺). **Ag12c** has a hollow distorted cuboctahedron structure constructed by sparse argentophilic interactions with Ag···Ag contacts being 2.916(12)-3.418 Å (Fig. 2), whose symmetry is totally different from those of **Ag12a**

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and **Ag12b**. The six Tab ligands supporting the Ag12 skeleton adopt the same quadruple coordination mode with the Ag-S distances being 2.478(3)-2.583(3) Å (Fig. S3b, ESI⁺). Ten TFA anions which protect the silver skeleton as well adopt two types of coordination modes: two adopting the μ_1 - η^1 : η^0 ligation mode and eight adopting the μ_2 - η^1 : η^1 ligation mode with the Ag-O bonds being 2.232(4)-2.551(2) Å (Fig. S3c, ESI⁺). In particular, the two coordinated CH₃CN molecules which exhibit strong coordination ability, protect the vertex of the silver kernel and occupy the place supposed to TFA anions. Notably, only a small amount of Ag atoms are coordinated by the CH₃CN molecules in each silver cluster, but the structure and symmetry of the entire isomer were affected prodigiously.



Fig. 2 The ball-stick representation of $Ag_{12}S_6$ core (left, color code: Ag, green; S, yellow) and view of the corresponding Ag12 kernels in a polyhedron mode with different symmetry.

We are curious about the solvent effect and the three Ag12 isomers inspire us to investigate the isomerization of them by similar methods. To dissolve 20 mg crystals of Ag12a into 2mL CH₃OH and DMF mixed solvent and recrystallize it through the diffusion process, about 5 mg block crystals of Ag12b can be obtained. The structure of the crystals can be confirmed by single-crystal X-ray analysis. We successfully realized the isomerization between Ag12a and Ag12b. If we dissolved the crystals of Ag12a into DMF, CH₃CN, water and recrystallized it through the similar diffusion process, the crystals of Ag12a and Ag12c can also be realized. The following experiments indicated that the three Ag12 isomers can be readily transformed into each other in the related solvent systems.

The powder X-ray diffraction analysis was also employed to confirm the reversible configuration transformation between **Ag12a**, **Ag12b** and **Ag12c**. The experimental PXRD patterns of **Ag12a** can match its calculated patterns very well (Fig. S4, ESI[†]), which demonstrated the high purity of its bulk sample. After dissolving crystals of **Ag12a** into DMF and recrystallizing it through the diffusion process, the new PXRD patterns presented a structural change from **Ag12a** to **Ag12b**, which can meet those derived from the single crystal data (Fig. S5b[†]).

A similar procedure was applied to transform Ag12a dinto Ag12c if the solvent was changed to CH3CN⁰ (Fig. (SGC, CESPF)). When Ag12b was re-crystallized in CH₃CN, pure Ag12c crystals were afforded (Fig. S6d⁺). When the re-generated Ag12c was re-crystallized in DMF, its PXRD patterns could be recovered to those of Ag12b, thus implying that Ag12b can readily isomerize into Ag12c reversibly (Fig. S5c⁺). The PXRD patterns of Ag12c could also correspond to the changes of those of Ag12a (Fig. S4, ESI⁺) and Ag12b (Fig. S5, ESI⁺), thus further confirming the isomerization of Ag12a, Ag12b and Ag12c.



Fig. 3 View of the crystal structures of **Ag12a**, **Ag12b** and **Ag12c**. Anions, free solvent molecules and H atoms are omitted for clarity. Color codes: green, Ag; yellow, S; red, O; blue, N; grey, C; sky blue, F.

Although the crucial role of solvent molecules in the isomerization can be illustrated through the detailed structural analysis, more insight into the assembly process of the nanoclusters in solution still needs obtained. The mother liquors in the isomerization experiments were examined by using electrospray ionization mass spectrometry (ESI-MS) (Fig. S7-S11⁺). The Ag12c solution (obtained from dissolving Ag12a in CH₃CN) had a major fragment at m/z = 662.96corresponding to $[Ag_4(Tab)_4(TFA)_2]^{2+}$ (Fig. S7⁺). However, the Ag12b solution (obtained from dissolving Ag12a in DMF) showed more characteristic fragments like [Ag₄(Tab)₃(TFA)₂]²⁺, $[Ag_4(Tab)_3(TFA)_2(DMF)_2]^{2+}$ (Ag₅(Tab)₄(TFA)₃)²⁺, and $(Ag_6(Tab)_4(TFA)_4)^{2+}$ (Fig. S8⁺). The much heavier fragments $[Ag_7(Tab)_4(TFA)_5]^{2+}$ and $[Ag_8(Tab)_4(TFA)_6]^{2+}$ were observed in the Ag12a solution in H₂O/CH₃CN/DMF (Fig. S9⁺) compared to the previous two isomers.9a A meaningful result was the DMF-containing fragment pronounced signal of $[Ag_4(Tab)_3(TFA)_2(DMF)_2]^{2+}$ (m/z = 652.46) (Fig. S8-S9⁺) or $[Ag_{6}(Tab)_{4}(TFA)_{3}(DMF)_{2}]^{2+}$ (m/z = 873.35) (Fig. S10⁺) which indicated that the DMF molecules might coordinate with silver atoms in Ag12a, Ag12b and Ag12c during the assembly process but were substituted by TFA anions ultimately. The

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isomerism between Ag12b and Ag12c was also monitored by ESI-MS (Fig. S10-S11⁺), thus confirming the solvent effects.

In conclusion, a novel Ag12 cluster, Ag12a, was synthesized to explore the isomerization process of Ag12 cluster isomers. Through adjusting the solvent systems in the synthetic reactions, another two Ag12 isomers, Ag12b and Ag12c were successfully obtained. In particular, these three Ag12 isomers can be converted into each other by changing the solvent systems. The isomerization of the Ag12 isomers can be also confirmed by PXRD. Furthermore, the mechanism of the isomerization processes of Ag12 cluster isomers can be illustrated through the detailed structural analysis. This work offers not only new insight into the isomerization of the metal thiolate nanoclusters but also a new entry to synthesize novel metal thiolate nanoclusters. In addition, this work also extends the multi-dimensional Ag cluster-based frameworks through enriching the Ag cluster second building units with different symmetries.

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Conflicts of interest

There are no conflicts to declare.

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Graphic Contents Entry

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The solvent-induced isomerizations of Ag12 clusters with symmetry transformations were realized

by changing the coordinated solvent molecules at room temperature.

Figure for Graphic Contents Entry

