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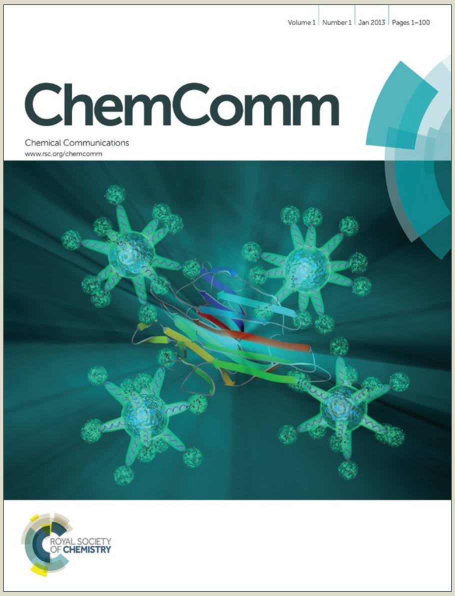

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ARTICLE TYPE

Organic Anion Template: a 24-Nuclearity Silver Cluster Encapsulating a Squarate Dimer

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The first silver cluster encapsulating an organic anion — squarate dianion has been synthesized. Two $C_4O_4^{2-}$ anions arranged in a staggered sandwich type are confined in the Ag_{24} cage. The incorporation of squarate anions into the silver alkynyl system leads to the red shift of absorption of the cluster in comparison to silver squarate.

High-nuclearity silver clusters have attracted much interest because of their structural diversity and intriguing physical and chemical properties.[1] Anion templating approach has been proved to be a convenient synthetic method for the preparation of high-nuclearity silver clusters.[2-6] A lot of inorganic anions, such as halides,[2] chromate,[3,4a] sulfate,[3] carbonate,[4b] molybdate[4a] and polyoxometalates[5-6] have been used for the syntheses of silver clusters. In contrast, organic anion templation has never been observed in such compounds. The use of organic anions as templates has several advantages: i) there are many types of organic anions and the sizes or shapes are much different from inorganic anions; ii) an organic anion may have flexibility; iii) the unique electronic properties of the organic anion could affect the chemical and physical performance of the cluster.

Based on above considerations, we extend the research work by using an organic anion — squarate dianion as the template in the synthesis of silver cluster. Squarate is planar with delocalized π-electrons[7] and has been used as templates for the assembly of polyoxothiometalates.[8] It is expected that the incorporation of planar squarates as templates could induce the formation of new silver clusters, and further, the π-delocalization cyclic organic center may interplay with silver ions, thus profoundly affect the properties of the cluster.

Such a synthetic strategy led to the isolation of a 24-nuclearity silver cage encapsulating an unprecedented squarate dimer, namely, $[(C_4O_4^{2-})_2@Ag_{24}(CF_3CO_2)_4(C{\equiv}C^tBu)_{16}]{\bullet}2CH_3CN$ (**1**•$2CH_3CN$). Two $C_4O_4^{2-}$ ions adopt a staggered sandwich configuration and are confined in the silver cage with a very short centroid-centroid spacing (3.098 Å). To the best of our knowledge, cluster **1** represents the first silver cluster encapsulating an organic anion as a template. The two repulsive squarate anions have never been found in such proximity. Moreover, the incorporation of squarates into the silver alkynyl system led to the E_g value of **1** dramatically red shift to visible light region compared with those values of the precursors. Herein, we report the synthesis and characterization of the unique silver cluster.

A methanol mixture of squaric acid and $[Me_4N]OH$ was added to the solution of $AgC{\equiv}C^tBu$ with $AgCF_3CO_2$ in acetonitrile led to the formation of a white suspension, which turned to clear after dppm (bis(diphenylphosphino)methane) was added. The solution was solvothermally treated to give **1** as yellow block crystals. It is noted that although dppm was not incorporated in cluster **1**, the reaction led to only precipitation in the absence of dppm. Because the insoluble precursor mixture could be decomposed to soluble species in the presence of dppm, it is proposed that dppm is helpful for the formation of certain intermediates by chelating the silver ions.

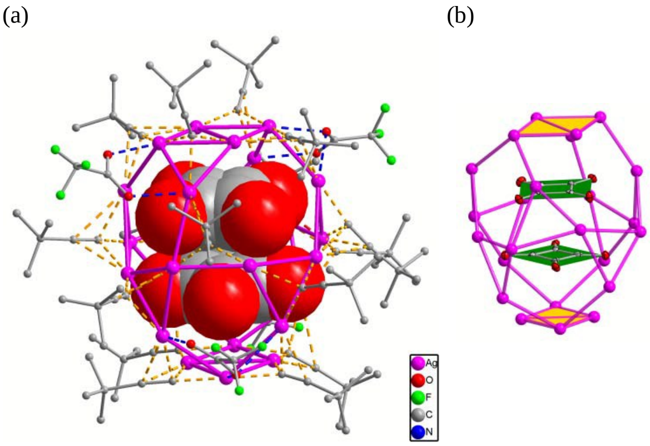


Fig. 1 (a) The molecular structure of cluster **1**. The encapsulated squarate anions are shown in space-filling mode. Hydrogen atoms have been omitted for clarity. (b) Illustration of silver skeleton with templating anions.

The composition of **1** was supported by elemental analysis. An IR band at 2011 cm^{-1} confirmed the presence of the C≡C group in **1**; the band at 1658 cm^{-1} was assigned to the trifluoroacetate ligand; and the band at 1496 cm^{-1} was due to the squarate dianion (Fig. S1).[9] The presence of the squarate anions were further confirmed by the solid-state ^{13}C NMR spectrum (Fig. S2). The peaks around 204.4 ppm for **1** were assigned to the carbon atoms of squarates, which were comparable with the solution ^{13}C NMR values of 195.1 and 203.9 ppm for squaric acid and potassium squarate, respectively.[10]

Single crystal X-ray structural analysis revealed that **1** consists of 24 silver atoms bridged by 16 alkynyl ligands and four trifluoroacetate ligands with a squarate dimer encapsulated (Fig. 1). The shape of the silver skeleton could be roughly described as a drum, which 16 silver atoms construct the drum body, and two groups of four silver atoms each acts as the upper and lower drum rims, respectively. Two $C_4O_4^{2-}$ ions locate inside the cavity of drum and arrange in staggered sandwich type (Fig. 2). The C-C bond lengths in the cycle are in the range of 1.442-1.480 Å, which are nearly identical. The C=O distances (1.253-1.269 Å) are significantly longer than those in saturated ketones (1.200 Å).[7] All these parameters reflect squarate is a π-delocalization cycle. The two squarates together with the upper and the lower rims are nearly parallel to each other, as reflected by the mean deviations from each planes and the dihedral angles of the four parallel planes (Tab. S2 and Fig. S3). Each squarate anion is coordinated to ten silver atoms by oxygen atoms, adopting μ_2 and μ_3 modes (Scheme 1). The Ag-O distances fall in the range of 2.417-2.846 Å (Tab. S3). Such high coordination numbers have never been observed in the metal complexes of squarate.[7] The silver cage is further consolidated by 16 peripheral alkynyl ligands adopting μ_3 bridging modes and four trifluoroacetate ligands adopting μ_2 and μ_3 bridging modes.

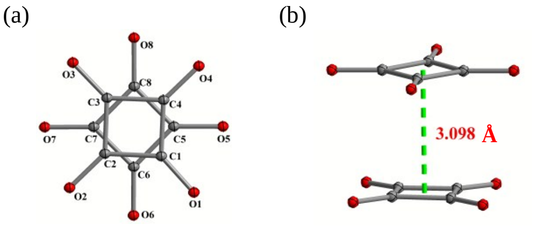
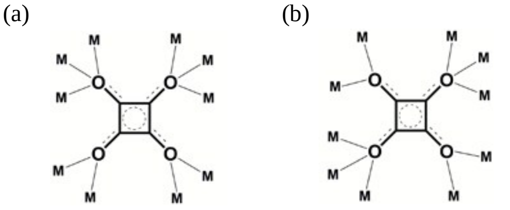


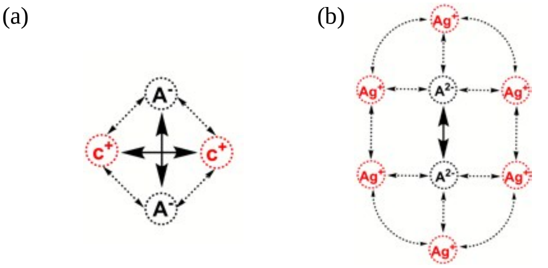
Fig. 2 The staggered sandwich of double-deck squarate dianion (D_{4d} symmetry): (a) View from the top; (b) View from the side.



Scheme 1. The coordination modes of two squarate anions in **1**.

The squarate molecule with π-delocalization cycle adopts D_{4h} symmetric geometry. In cluster **1**, two squarates stack with staggered arrangement giving a nearly D_{4d} symmetry. The double-deck squarate dimer prefers to adopt staggered arrangement rather than eclipsed conformation because it could reduce the repulsion from negatively charged O atoms of two ions, and further, it also provides efficient space for a maximum coordination of O atoms to Ag atoms. In the metal carbonyl dimers, such as $M_2(CO)_{10}$ (M = Mn, Re), it has also been confirmed that staggered conformation is energetically favorable compared to the eclipsed conformation.[11]

Two or more ions as co-templates have been observed in silver clusters but they are generally separating and no interactions among templating ions.[5,12] In the present case, the central distance of the two $C_4O_4^{2-}$ ions is being 3.098 Å, which is suggestive of the existence of strong π…π stacking interaciton between them. A structure search of interplanar π separations between squares in CSD database showed their centroid-centroid distances fall within the range of 3.243-3.847 Å.[13] For example, infinite interplanar π separations between $[HC_4O_4]^-$ anions have been observed in alkali hydrogen squarate salts with centroid-centroid spacings in the range of 3.466-3.601 Å.[14] The $[HC_4O_4]^-$ anions are connected *via* O-H$^-$…O$^-$ interactions and the shortening effect of intermolecular anions is arising from attractive neighboring anion-cation [A^-…C^+] interactions as shown in Scheme 2a.[14] In our case, the separation between two squarate dianions is even shorter. Besides the π…π attraction between two electron delocalization organic cycles, large number of interactions such as the anion-cation [Ag^+…A^{2-}] electrostatic attraction and the argentophilic Ag…Ag interaction (around 3 Å) (Scheme 2b) also make contribution to the stability of the cluster.



Scheme 2. A schematic representation of the interactions between ions (a): $(anion)_2(cation)_2$[14] and (b): $(A^{2-})_2$@(silver cage). (Dashed arrows correspond to attraction, solid arrows correspond to repulsion. **C**: cation; **A**: anion; Ag: silver.)

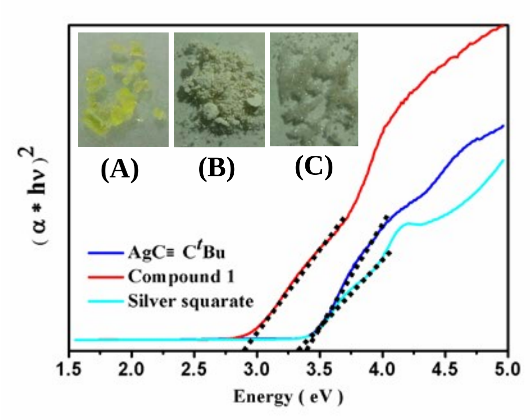


Fig. 3 The solid UV-vis diffuse reflectance spectra. Insert pictures : **A** (**1**, yellow solid), **B** (AgC≡C^{t}Bu, white powder) and **C** (silver squarate, colorless microcrystals).

The solid UV-Vis diffuse reflectance spectrum showed the optical energy gap of **1** is 2.83 eV. In comparison, the optical energy gaps of AgC≡C^{t}Bu and silver squarate are 3.32 eV and 3.33 eV, respectively (Fig. 3). These are consistent with the colors of the compounds: AgC≡C^{t}Bu and silver squarate are colorless, whereas **1** is bright yellow. It is noted that the silver clusters such as $[Ag_{19}(C{\equiv}C^tBu)_{16}(CO_3)]BF_4$[4b] and $[Ag_{21}(C{\equiv}C^tBu)_{18}(SO_4)]BF_4$[3] with inorganic anions CO_3^{2-}, SO_4^{2-} as templates are also colorless, and their energy gaps are 3.53 eV and 3.51 eV, respectively (Fig. S4).The incorporation of squarate anions into the silver alkynyl system led to dramatically red shift of absorption to visible light region. It is plausible that the two delocalizated squarate anions were confined in the silver cage, causing strong π…π interaction between two organic cycles and consequently led to the reduction of the HOMO-LUMO gap. Besides this, the interactions between the templating squarate and silver shell may also lower the optical energy gap.

Conclusions

In summary, we have synthesized and structurally characterized a drum-like cluster enclosing a squarate dimer. The two repulsive $C_4O_4^{2-}$ anions are confined in the silver cage with a very short central distance being 3.098 Å. The incorporating of squarate into the silver alkynyl system also leads to the absorption of **1** is dramatically red shifted in comparison to silver squarate. The result shows the feasibility of using organic anion as a template, which expands a large area of templation ions. The interaction between organic templates and inorganic components will profoundly affect the properties of the clusters, thus opens up a new direction for the syntheses of new silver clusters with excellent properties.

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Notes and references

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‡ Synthesis of **1**: 0.057 g (0.3 mmol) $AgC{\equiv}C^tBu$ was dissolved in an acetonitrile solution (5 mL) of $AgCF_3CO_2$ (0.132 g, 0.6 mmol) under ultrasonication. To the resulted solution 0.1 mL CH_3OH of squaric acid and $[Me_4N]OH$ (1:1, 0.1 mol/L) was added under ultrasonication. The solution became cloudy, and was changed into clear after bis(diphenylphosphino)methane (0.061 g, 0.16 mmol) was added. The solution color changed from pale yellow to yellow when 0.1 mL CH_3OH of $[Me_4N]OH$ (0.1 mol/L) was added, and the solution was sealed in a vial that was heated and kept at 70 ^{o}C for 20 h. After the solution was cooled down to room temperature, it was filtered. Slow evaporation of the yellow filtrate afforded **1** as yellow crystals after one week. Yield: 90.4 % (0.021 g, based on squaric acid). Elemental analysis (%) calcd for $C_{112}H_{144}O_{16}F_{12}Ag_{24}$: C 29.48, H 3.18; found: C 29.56, H.2.96; IR (KBr, ν/cm^{-1}): 2011 (C≡C), 1658 (vs, C=O in the tfa ligand); 1496 (vs, C=O in the squarate).

¶Crystal data for **1**•$2CH_3CN$, $[C_{116}H_{150}O_{16}N_2F_{12}Ag_{24}]$, *monoclinic*, $P2_1/n$, a = 23.5527(7) Å, b = 20.9694(8) Å, c = 29.3460(9) Å, β = 95.231(3) °, V = 14433.2(8) Å^3, Z = 4, T = 173 K, 68602 reflections measured, 28306 unique (R_{int} = 0.0437), final R_1 = 0.0489, wR_2 = 0.0860 for 28306 observed reflections [$I > 2\sigma(I)$]. Intensity data of **1** were collected on an Oxford Gemini S Ultra system (Mo, Kα source) at 173 K. Absorption corrections were applied by using the program CrysAlis (multi-scan). The structure was solved by direct methods, and non-hydrogen atoms were refined anisotropically by least-squares on F^2 using the SHELXTL program.

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