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Citation	Inorganic Chemistry. 2023, 62(24), p. 9291-9294
Version Type	AM
URL	https://hdl.handle.net/11094/92439
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Note	

Silver(I) Sulfide Clusters Protected by Rhodium(III) Metalloligands with 3-Aminopropanethiolate

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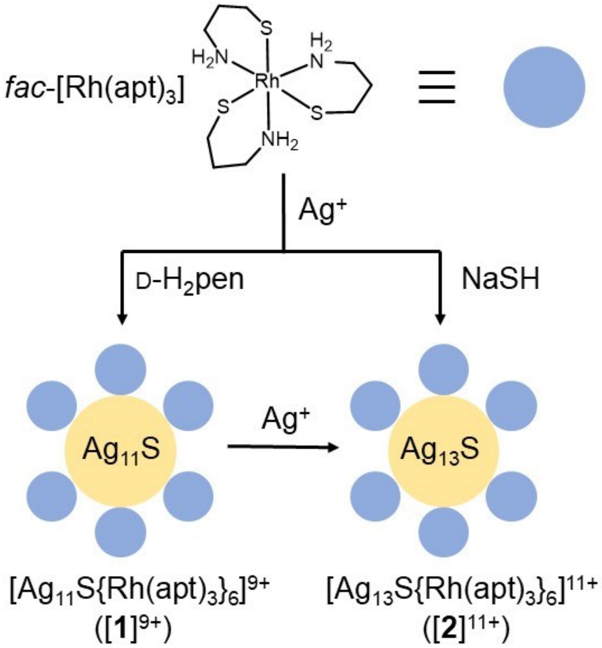
ABSTRACT: The two homochiral Ag^IRh^{III} nanoclusters, Δ_6/Λ_6-$[Ag_{11}S\{Rh(apt)_3\}_6]^{9+}$ ($[\mathbf{1}]^{9+}$) and Δ_6/Λ_6-$[Ag_{13}S\{Rh(apt)_3\}_6]^{11+}$ ($[\mathbf{2}]^{11+}$), in which $Ag_{11}S$ and $Ag_{13}S$ cluster cores, respectively, are protected by *fac*-$[Rh(apt)_3]$ metalloligands, were newly synthesized from *fac*-$[Rh(apt)_3]$ (Hapt = 3-aminopropanethiol) and Ag^+ in water in combination with sulfide sources. While $[\mathbf{1}]^{9+}$ was produced by using D-penicillamine as a sulfide source, the use of HS^- as a sulfide source afforded $[\mathbf{2}]^{11+}$ without causing any precipitation of Ag_2S. Cluster $[\mathbf{1}]^{9+}$ was convertible to $[\mathbf{2}]^{11+}$ via the reaction with Ag^+, which led to a turn-on-type switch in photoluminescence from nonemissive $[\mathbf{1}]^{9+}$ to emissive $[\mathbf{2}]^{11+}$.

In recent years, structurally precise silver(I) sulfide clusters have received increasing attention because of their structural diversity, intriguing electronic structure, and low-energy photoluminescence.[1] To date, considerable efforts have been made to regulate the size and shape of silver(I) sulfide cluster cores, which play a critical role in the emission characteristics of the overall clusters, by changing the reactants and conditions. The choice of suitable protecting ligands, typically S- or P-donating organic ligands, has been known to be the most effective approach to control silver(I) sulfide cluster structures.[1,2] In some cases, the introduction of a coligand such as chloride contributes to the rigidity of clusters to endow better luminescent properties.[3] Some templating anions, such as nitrate, trifluoracetate, and polyoxometalate, have been known to provide structural diversity to silver(I) sulfide clusters.[4] The sulfide sources employed in the reactions are also important to regulate the cluster growth. While silylated sulfides,[1a,5] tertiary thiols,[6] disulfides,[7] CS_2,[8] triphenylphosphine sulfides,[3,9] and thioketones[10] have been used as sulfide sources to prepare silver(I) sulfide clusters, the use of Na_2S and NaSH has rarely been attempted due to the high reactivity of S^{2-}, which produces nonprecise Ag_2S nanoparticles.

Previously, we reported that the water-soluble $Ag^{I}_{46}Rh^{III}_{14}$ 60-nuclear nanocluster $[Ag_{46}S_{13}\{Rh(aet)_3\}_{14}]^{20+}$ (Haet = 2-aminoethanethiol) with an $Ag_{46}S_{13}$ core is produced from Ag^+ in combination with *fac*-$[Rh(aet)_3]$ and D-penicillamine (D-H_2pen), which act as a protecting S-donating metalloligand and a sulfide source, respectively.[11] The corresponding $Ag^{I}_{46}Ir^{III}_{14}$ cluster $[Ag_{46}S_{13}\{Ir(aet)_3\}_{14}]^{20+}$, which is highly emissive, has also been synthesized by using *fac*-$[Ir(aet)_3]$ instead of *fac*-$[Rh(aet)_3]$.[12] In this work, we report on the use of *fac*-$[Rh(apt)_3]$ (Hapt = 3-aminopropanethiol) for creating analogous $Ag^{I}Rh^{III}$ nanoclusters. We expected that *fac*-$[Rh(apt)_3]$ would also serve as an effective S-donating metalloligand that can protect a silver(I) sulfide cluster core to form novel $Ag^{I}Rh^{III}$ clusters with different nuclearity due to the presence of the six-membered N,S-chelate rings in *fac*-[Rh(apt)$_3$] that are larger and more flexible than the five-membered rings in *fac*-[Rh(aet)$_3$].[13] Indeed, the reaction of Ag^+ and *fac*-[Rh(apt)$_3$] in the presence of D-H$_2$pen afforded the $Ag^{I}_{11}Rh^{III}_{6}$ nanocluster $[Ag_{11}S\{Rh(apt)_3\}_6]^{9+}$ ($[\mathbf{1}]^{9+}$), rather than an $Ag^{I}_{46}Rh^{III}_{14}$ nanocluster (Scheme 1). In addition, the use of NaSH in the reaction as a sulfide source, instead of D-H$_2$pen, led to the production of the $Ag^{I}_{13}Rh^{III}_{6}$ nanocluster $[Ag_{13}S\{Rh(apt)_3\}_6]^{11+}$ ($[\mathbf{2}]^{11+}$). To our knowledge, $[\mathbf{2}]^{11+}$ is the first structurally precise nanoclusters with a silver(I) sulfide core prepared by using NaSH as a sulfide source. The structural conversion from $[\mathbf{1}]^{9+}$ to $[\mathbf{2}]^{11+}$, which switches the photoluminescence of the clusters, as well as the homochiral nature of $[\mathbf{1}]^{9+}$ and $[\mathbf{2}]^{11+}$, which is different from the heterochiral nature of $[Ag_{46}S_{13}\{Ir(aet)_3\}_{14}]^{20+}$, is also reported.



Scheme 1. Synthetic routes of silver(I) sulfide clusters protected by *fac*-[Rh(apt)$_3$].

The previously reported $[Ag_{46}S_{13}\{Rh(aet)_3\}_{14}]^{20+}$ was prepared from the reaction of *fac*-$[Rh(aet)_3]$, D-H_2pen, and Ag^+ in a 1:1:3.3 ratio in water. Thus, we initially carried out a similar reaction using *fac*-$[Rh(apt)_3]$ instead of *fac*-$[Rh(aet)_3]$. Upon heating at 50 °C for 24 h, the reaction solution gradually turned from yellow to orange in color. From this reaction solution, an orange compound ([**1**]$(NO_3)_9$·nH_2O), which is soluble in water, was isolated as a crystalline solid by adding excess $NaNO_3$. The presence of Rh and Ag atoms in [**1**]$(NO_3)_9$·nH_2O was confirmed by X-ray fluorescence spectroscopy. In the IR spectrum, [**1**]$(NO_3)_9$·nH_2O showed a broad band due to *fac*-$[Rh(apt)_3]$ at 1588 cm^{-1}, in addition to a sharp band due to NO_3^- at 1345 cm^{-1} (Fig. S1). However, no IR band due to COO^- was observed for [**1**]$(NO_3)_9$·nH_2O, indicating the absence of D-H_2pen in the product. The ^1H NMR spectrum of [**1**]$(NO_3)_9$·nH_2O in D_2O gave a single set of sharp signals at δ 1.94-3.05 ppm, which is assignable to apt methylene protons (Fig. S2). This spectral feature suggests that $[\mathbf{1}]^{9+}$ has a highly symmetrical structure. In the absorption spectrum in water, no visible band was observed for [**1**]$(NO_3)_9$·nH_2O (Fig. S3), while it has been shown that $[Ag_{46}S_{13}\{Rh(aet)_3\}_{14}](NO_3)_{20}$·n$H_2O$ gives a characteristic visible band at approximately 520 nm, which arises from S-to-Ag charge transfer in the silver(I) sulfide cluster core.[11]

From single-crystal X-ray analysis of [**1**]$(NO_3)_9$·nH_2O, it was evident that $[\mathbf{1}]^{9+}$ is a new 17-nuclear $Ag^I_{11}Rh^{III}_6$ nanocluster of $[Ag_{11}S\{Rh(apt)_3\}_6]^{9+}$ with an S^{2-} ion at the center (Fig. S4). However, the coordination environments of Ag^I centers remained unclear in this structural analysis due to their high disorder. Precise X-ray structural analysis for $[\mathbf{1}]^{9+}$ was achieved using its tetrafluoroborate salt ([**1**]$(BF_4)_9$·nH_2O). As shown in Fig. 1a, an S^{2-} ion is located at the center of the structure, and it is bound by two two-coordinate Ag^I atoms, two three-coordinate Ag^I atoms, and one four-coordinate Ag^I atom to form an $[Ag_5S]^{3+}$ cluster core (av. Ag- S^{2-} = 2.46 Å) that is covered by six *fac*-[Rh(apt)$_3$] units through Ag-S coordination bonds (av. Ag-S$_{\text{thiolato}}$ = 2.54 Å) (Fig. S5). In [**1**]$^{9+}$, the outer six *fac*-[Rh(apt)$_3$] units are linked by six additional Ag$^{\text{I}}$ atoms through coordination bonds (av. Ag-S$_{\text{thiolato}}$ = 2.56 Å), completing the spherical 17-nuclear Ag$^{\text{I}}_{11}$Rh$^{\text{III}}_{6}$ structure in [Ag$_{11}$S{Rh(apt)$_3$}$_6$]$^{9+}$ with a diameter of ca. 15.6 Å. There exist a total of 14 Ag···Ag interactions (av. 3.04 Å) in [**1**]$^{9+}$,[14] which appear to sustain its cluster structure. Each *fac*-[Rh(apt)$_3$] unit in [**1**]$^{9+}$ acts as a metalloligand that coordinates to three or four Ag$^{\text{I}}$ atoms in a chelate-bridging mode using its three thiolato S atoms (Fig. S6). This coordination mode is different from that of *fac*-[Rh(aet)$_3$] found in [Ag$_{46}$S$_{13}${Rh(aet)$_3$}$_{14}$]$^{20+}$, which adopts a μ_3- or μ_4-bridging mode. The S-Rh-S angles in *fac*-[Rh(apt)$_3$] with six-membered N,S-chelate rings, which are smaller than those in *fac*-[Rh(aet)$_3$] with five-membered N,S-chelate rings, are suitable for adopting a chelating coordination mode, thus leading to the protection of a smaller [Ag$_5$S]$^{3+}$ core to construct the Ag$^{\text{I}}_{11}$Rh$^{\text{III}}_{6}$ structure in [**1**]$^{9+}$. While Δ and Λ configurations are possible for *fac*-[Rh(apt)$_3$], the six [Rh(apt)$_3$] units in [**1**]$^{9+}$ have the same configuration, forming the homochiral Δ_6 and Λ_6 isomers. In the crystal packing structure, the homochiral Δ_6- and Λ_6-[**1**]$^{9+}$ cations are arranged in parallel to form homochiral Δ_n and Λ_n layers, respectively, which are alternately stacked to form the racemic compound (Fig. S7).

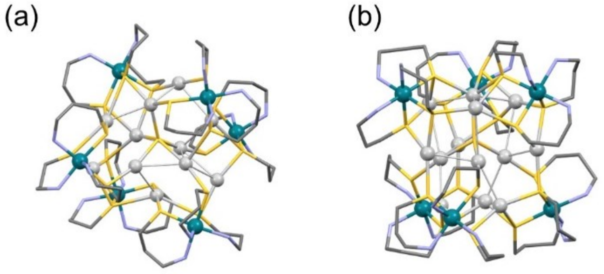


Figure 1. Molecular structures of (a) [**1**]$(BF_4)_9 \cdot nH_2O$ and (b) [**2**]$(BF_4)_{11} \cdot nH_2O$. Anions and solvent molecules are omitted for clarity. Metal elements are shown in ball model. Color codes: Rh: blue–green; Ag: gray; S: yellow; N: pale blue; C: dark gray.

It is well known that the direct mixing of Ag^+ with S^{2-} or SH^- in water results in the immediate precipitation of Ag_2S even in the presence of common protecting ligands owing to its exceptionally low solubility ($pK_{sp} = 53.6$).[15] However, treatment of an aqueous mixture of *fac*-[Rh(apt)$_3$] and $AgBF_4$ with NaSH in a Ag^+:S^{2-} ratio of ca. 3:1 gave a clear dark brown solution without causing any precipitation. From the reaction solution, dark yellow block crystals ([**2**]$(BF_4)_{11} \cdot nH_2O$) were isolated by adding $NaBF_4$.[16] While [**2**]$(BF_4)_{11} \cdot nH_2O$ showed an absorption spectrum similar to the spectrum of [**1**]$(NO_3)_9 \cdot nH_2O$ in water (Fig. S3), its ^{1}H NMR spectral feature in D_2O was different (Fig. S2). In addition, X-ray fluorescence analysis suggested that [**2**]$(BF_4)_{11} \cdot nH_2O$ contains more Ag atoms than [**1**]$(NO_3)_9 \cdot nH_2O$, while the content of Rh atoms in [**2**]$(BF_4)_{11} \cdot nH_2O$ is the same. Consistent with this, single-crystal X-ray analysis revealed that [**2**]$^{11+}$ contains 13 Ag^I atoms and 6 *fac*-[Rh(apt)$_3$] units, in addition to an S^{2-} ion.

As shown in Fig. 1b, the overall molecular structure of [**2**]$^{11+}$ resembles that of [**1**]$^{9+}$, having an S^{2-} ion at the center. However, the number and arrangement of Ag^I atoms that are surrounded by 6 *fac*-[Rh(apt)$_3$] units are different. That is, the central S^{2-} ion in [**2**]$^{11+}$ is bound by one four-coordinate and three two-coordinate Ag^I atoms (av. Ag-S^{2-} = 2.45 Å), forming an $[Ag_4S]^{2+}$ core, rather than the $[Ag_5S]^{3+}$ core in [**1**]$^{9+}$ (Fig. S8). While the core in [**2**]$^{11+}$ is bound by six *fac*-[Rh(apt)$_3$] units through Ag-S bonds (av. Ag-$S_{thiolato}$ = 2.56 Å), as in the case of [**1**]$^{9+}$, the six units are linked by nine Ag^I atoms that are disordered (av. Ag-$S_{thiolato}$ = 2.56 Å), rather than six Ag^I atoms, completing a spherical 19-nuclear $Ag^I_{13}Rh^{III}_6$ structure in $[Ag_{13}S\{Rh(apt)_3\}_6]^{11+}$ with a diameter of ca. 15.8 Å. Unlike the C_1 symmetric structure in [**1**]$^{9+}$, the structure in [**2**]$^{11+}$

belongs to a C_3 point group with a crystallographic 3-fold axis on the four-coordinate Ag^I and S^{2-} centers (Fig. S8). There are 12 Ag···Ag interactions with an average distance of 2.97 Å in $[\mathbf{2}]^{11+}$. The average distance is shorter than that in $[\mathbf{1}]^{9+}$ (3.04 Å), suggestive of the more rigid cluster structure in $[\mathbf{2}]^{11+}$ compared with the structure in $[\mathbf{1}]^{9+}$. The six *fac*-$[Rh(apt)_3]$ units in $[\mathbf{2}]^{11+}$, each of which binds to four Ag^I atoms in a chelate-bridging mode (Fig. S6), adopt the same chiral configuration to form the racemic compound consisting of the Δ_6 and Λ_6 isomers. The packing structure in $[\mathbf{2}](BF_4)_{11}$ is similar to that in $[\mathbf{1}](NO_3)_9$, in which the homochiral Δ_n and Λ_n layers are alternately arranged in the crystal (Fig. S7). Here, it should be noted that the previously reported $[Ag_{46}S_{13}\{Rh(aet)_3\}_{14}]^{20+}$ has a heterochiral structure, in which twelve *fac*-$[Rh(aet)_3]$ units in the equatorial site have the $(\Delta\Lambda)_6$ meso configuration, with the two *fac*-$[Rh(aet)_3]$ units at the apical site being disordered to have the Δ and Λ configurations.[11] Thus, this is a unique metal cluster system that shows the homochiral assembly of metalloligands on a silver(I) sulfide cluster surface.

Since $[\mathbf{1}]^{9+}$ and $[\mathbf{2}]^{11+}$ have a similar molecular shape to each other with different numbers of Ag^I atoms (Ag_{11} vs. Ag_{13}), we investigated whether $[\mathbf{1}]^{9+}$ is convertible to $[\mathbf{2}]^{11+}$ via the addition of $AgNO_3$. ^1H NMR monitoring showed that $[\mathbf{1}]^{9+}$ is fully converted to $[\mathbf{2}]^{11+}$ upon adding two equiv of $AgNO_3$ (Fig. S9).[17] It is likely that external Ag^+ ions are incorporated into $[\mathbf{1}]^{9+}$ from the interstices among *fac*-$[Rh(apt)_3]$ units, followed by the core rearrangement from $[Ag_5S]^{3+}$ to $[Ag_4S]^{2+}$, leading to the structural conversion from $[\mathbf{1}]^{9+}$ to $[\mathbf{2}]^{11+}$. This is the first example of a structural transformation of structurally precise silver(I) sulfide clusters caused by the insertion of Ag^I ions; reports on the transformation of this class of clusters have been limited to the ligand exchange reaction in an alkynyl silver(I) sulfide cluster [9] and H_2S capture by a thiolato silver(I) complex,[18] although many structurally precise silver(I) sulfide clusters have been synthesized to date. Notably, [**2**]$^{11+}$ exhibits an emission band at 678 nm at 77 K, while [**1**]$^{9+}$ is nonemissive (Fig. 2). Thus, the structural transformation from [**1**]$^{9+}$ to [**2**]$^{11+}$ led to a turn-on-type switch in photoluminescence of the clusters.[19] The emission band for [**2**]$^{11+}$ is assignable to the S^{2-}-to-Ag^{I} ^{3}LMCT that is perturbed by Ag···Ag interactions, based on the broad nature of the emission band, together with the large Stokes shift (222 nm).[12] We assume that the presence of Ag···Ag interactions in [**2**]$^{11+}$ that are stronger than those in [**1**]$^{9+}$ contributes to the photoluminescent characteristics of [**2**]$^{11+}$.[14]

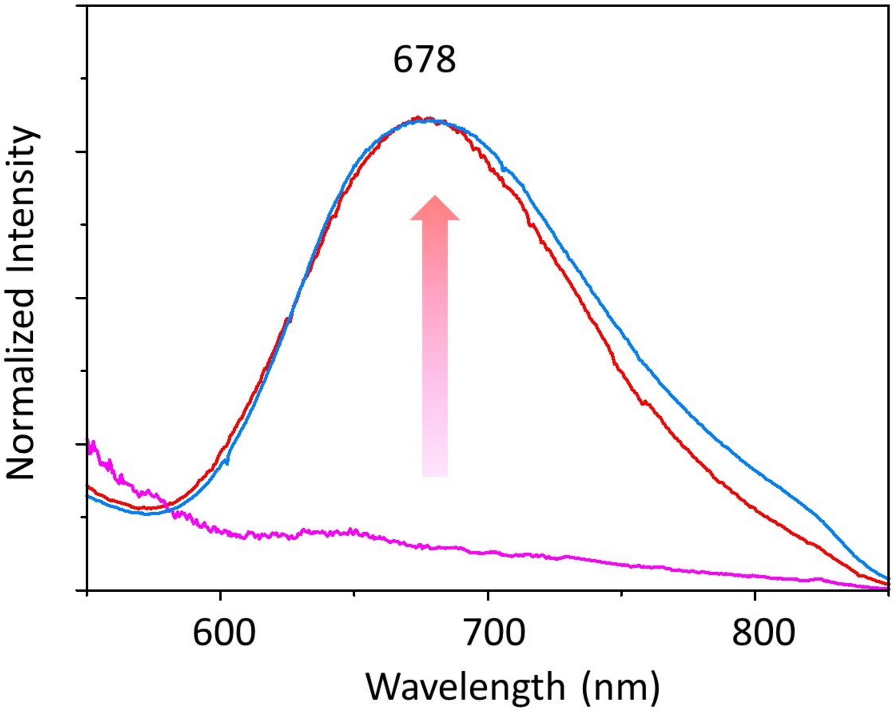


Figure 2. Luminescence spectra in a water/ethanol (9:1) glassy matrix at 77 K. (pink) [**1**]$(NO_3)_9 \cdot nH_2O$, (blue) [**2**]$(BF_4)_{11} \cdot nH_2O$, and (red) the reaction mixture containing [**1**]$(NO_3)_9 \cdot nH_2O$ and 2 equiv of Ag^+.

In conclusion, we showed that *fac*-[Rh(apt)$_3$] with six-membered N,S-chelate rings acts as a metalloligand that protects a silver(I) sulfide core, similar to *fac*-[Rh(aet)$_3$] with five-membered rings. However, *fac*-[Rh(apt)$_3$] was found to protect a smaller silver(I) sulfide core to produce the $Ag^{I}_{11}Rh^{III}_{6}$ nanocluster of [**1**]$^{9+}$ when D-H$_2$pen was used as a sulfide source. Remarkably, the use of HS^{-} as a sulfide source did not cause any Ag$_2$S precipitation but afforded the $Ag^{I}_{13}Rh^{III}_{6}$ nanocluster of [**2**]$^{11+}$, indicative of the potential control of silver(I) sulfide cores as well as the utility of *fac*-[Rh(apt)$_3$] as a metalloligand that prevents the precipitation of Ag$_2$S. Note that [**1**]$^{9+}$ and [**2**]$^{11+}$ are both homochiral due to the homochiral self-sorting[20] of *fac*-[Rh(apt)$_3$] on an silver(I) sulfide core, unlike the case for the *fac*-[Rh(aet)$_3$] system. Another remarkable finding in this study is the structural transformation from [**1**]$^{9+}$ to [**2**]$^{11+}$ via the insertion of Ag^{+}, which leads to a turn-on-type switch in photoluminescence. These results should contribute to the further development of metal cluster chemistry, not limited to silver(I) sulfide clusters.

ASSOCIATED CONTENT

Data Availability Statement

The data underlying this study are available in the published article and its supporting information.

Supporting Information.

The Supporting Information is available free of charge. Experimental information, spectroscopic data, and X-ray crystal structural data (PDF).

Accession Codes

CCDC 2258156-2258159 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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Author Contributions

ZLG and KN performed the syntheses and characterization of silver sulfide clusters; NY and ZLG wrote the draft; TK edited the manuscript and conceived the project. All authors have given approval to the final version of the manuscript.

Notes

There are no conflicts to declare.

ACKNOWLEDGMENTS

This work was supported by a Grant-in-Aid for JSPS Fellows (Grant No. 21J11148), JSPS KAKENHI (Grant No. 19K05496), and Proterial Materials Science Foundation. The synchrotron radiation experiments were performed at the BL02B1 beamline of SPring-8 with the approval of the Japan Synchrotron Radiation Research Institute (JASRI) (Proposal Nos. 2020A0603 and 2021A1242).

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16. As a preliminary result, a very small amount of orange plate crystals, Δ_{10}/Λ_{10}-$[Ag_{31}S_7\{Rh(apt)_3\}_{10}](BF_4)_{15}(SiF_6)$ ([**3**]$(BF_4)_{15}(SiF_6)$), was obtained, together with the major product [**2**]$(BF_4)_{11}$, when the Ag^+:S^{2-} ratio was changed to ca. 3:2 with the addition of a mixture of $NaBF_4$ and Na_2SiF_6 to the reaction solution. The X-ray fluorescence analysis revealed that [**3**]$(BF_4)_{15}(SiF_6)$ contains Rh and Ag atoms in a ca. 1:3 ratio, and its structure was determined by single-crystal X-ray analysis (Fig. S10).

17. The addition of one equiv of D-H_2pen to an aqueous solution of $[\mathbf{2}]^{11+}$ gave $[\mathbf{1}]^{9+}$ together with unidentified species (Fig. S11).

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SYNOPSIS

New homochiral $Ag^{I}Rh^{III}$ nanoclusters, Δ_6/Λ_6-$[Ag_{11}S\{Rh(apt)_3\}_6]^{9+}$ and Δ_6/Λ_6-$[Ag_{13}S\{Rh(apt)_3\}_6]^{11+}$ (Hapt = 3-aminopropanethiol), which are produced from *fac*-$[Rh(apt)_3]$ and Ag^+ dependent on the sulfide source (penicillamine vs. NaSH), are reported.