

Triple-Decker $\text{Au}_3\text{-Ag-Au}_3\text{-Ag-Au}_3$ Ion Cluster Enclosed in a Self-Assembled Cage**

Takafumi Osuga, Takashi Murase, and Makoto Fujita*

Soft d^{10} metal ions (M), such as Au^{I} and Ag^{I} , show metal-lophilicity and form $\text{M}\cdots\text{M}$ interactions despite their electrostatic repulsion.^[1] Although there are many examples of one-dimensional arrays of these metal ions both in solution and in the solid state,^[2] three-dimensionally controlled ionic clusters of these metals have seldom been synthesized.^[3] We recently prepared a $[3 \times 3] \text{Au}^{\text{I}}$ cluster,^[4] which consists of three layers of planar Au^{I} complex **2a**, in the confined cavity of self-assembled cage **1a** (Figure 1). Here, we report that trinuclear

prepared, even in the solid state. Thus, the adjustable, box-shaped cavity of **1**^[6] is useful, not only for limiting the cluster numbers, but also for stabilizing weakly associated metal ion clusters that cannot exist without the help of the cage.

To synthesize the triple-decker ion cluster, we went through several practical and theoretical experiments (Scheme 1). A one-step accumulation of all the components (three **2**^[7] and two Ag^{I} ions) within empty cage **1a** (route a) is the simplest approach, but it is not realistically possible because empty cage **1a** is unstable in the absence of template guests. Construction of the $[3 \times 3] \text{Au}^{\text{I}}$ ion cluster followed by the uptake of silver ions into the layers (route b) seemed to be a feasible stepwise approach, because cage **1a**, which accommodates the $[3 \times 3] \text{Au}^{\text{I}}$ ion cluster (**2a**)₃ has previously been synthesized.^[4] However, the $[3 \times 3]$ cluster of **2a** was not able to take up Ag^{I} ions, presumably owing to the insufficient ability of **2a** to act as a donor. We thought that replacing **2a** with electron rich **2b**^[8] would be highly promising for Ag^{I} ion uptake, but unfortunately, the **1a**·(**2b**)₃ complex was not obtained from the component parts, presumably because the triple layered stack of electron rich **2b** is repulsive and unfavorable.

In our attempt to synthesize inclusion complex **1a**·(**2b**)₃ from the components, we unexpectedly observed the self-assembly of inclusion complex **1a**·(**2b**·**3**·**2b**), in which electron-deficient ligand **3** was sandwiched between electron-rich **2b**, as the major product.^[6a,c] Finally, we found that this unusual inclusion complex, **1a**·(**2b**·**3**·**2b**), was a suitable precursor for the target triple-decker complex (route c). When **1a**·(**2b**·**3**·**2b**) was treated with additional **2b** (1 equiv) and AgNO_3 (2 equiv) at 40 °C for 12 h, we observed the smooth replacement of guest **3** with **2b**, accompanied by Ag^{I} ion uptake to form the **2b**· Ag^{I} ·**2b**· Ag^{I} ·**2b** triple-decker ion cluster accommodated within **1a** (Figure 2a).

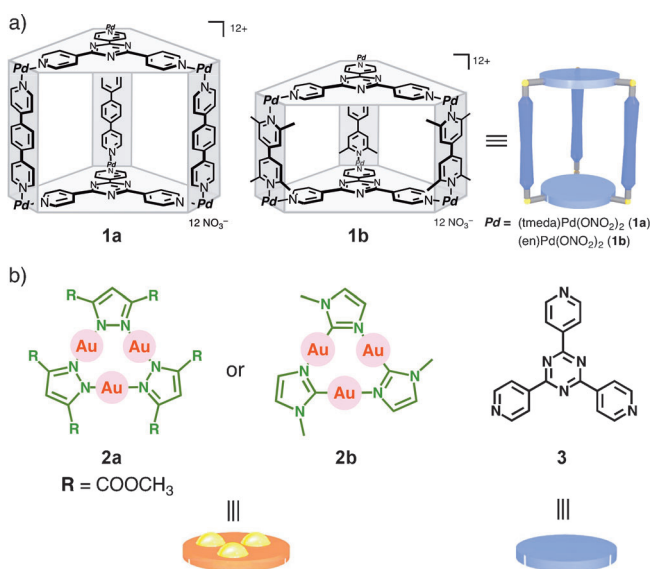
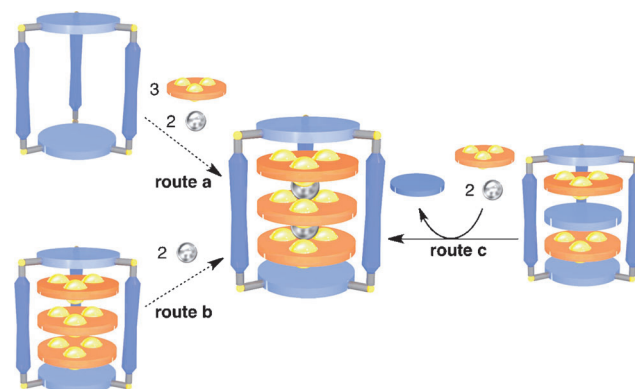


Figure 1. a) Self-assembled box-shaped cage **1**. b) Accumulated trinuclear Au^{I} complexes **2** and panel ligand **3**.

Au^{I} complex **2b** takes up silver ions to form an unprecedented triple-decker ion cluster ($\text{Au}_3\text{-Ag-Au}_3$) in the cage. There is only one example of a double-decker sandwich cluster, $\text{Au}_3\text{-Ag-Au}_3$, prepared by the co-crystallization of a Au^{I} trinuclear complex with a silver ion.^[5] However, this structure is only observable in the solid state, and high or infinite multi-decker clusters have never been



Scheme 1. Three routes to the synthesis of the Au^{I} - Ag^{I} triple-decker ion cluster within cage **1a**. Only route c was successful.

[*] T. Osuga, Dr. T. Murase, Prof. Dr. M. Fujita
Department of Applied Chemistry, School of Engineering
The University of Tokyo
7-3-1 Hongo, Bunkyo-ku, Tokyo 113-8656 (Japan)
E-mail: mfujita@appchem.t.u-tokyo.ac.jp

[**] This work was supported by a CREST (Core Research for Evolution Science and Technology) project from the Japan Science and Technology Agency (JST).

Supporting information for this article is available on the WWW under <http://dx.doi.org/10.1002/anie.201207619>.

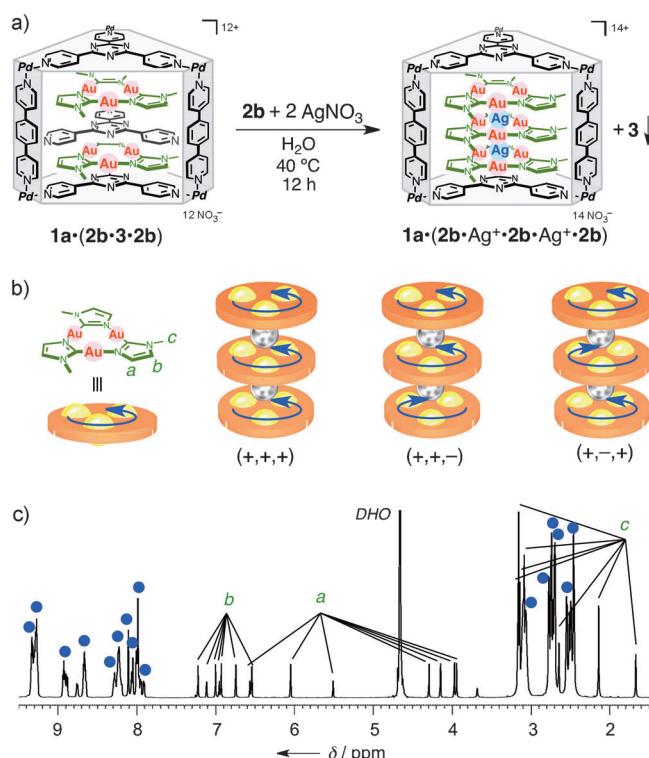


Figure 2. a) Formation of triple-decker cluster **1a·(2b·Ag⁺·2b·Ag⁺·2b)**. b) Three stacking modes of the guests. c) The ¹H NMR spectrum (500 MHz, 310 K) of **1a·(2b·Ag⁺·2b·Ag⁺·2b)** in D₂O; blue circles indicate signals from cage **1a**.

Because of its *C*_{3h} symmetry, **2b** can orient either clockwise (+) or counterclockwise (−), resulting in (+,+,+), (+,+,-), and (+,-,+) diastereomers for inclusion complex **1a·(2b·Ag⁺·2b·Ag⁺·2b)** (Figure 2b). In NMR spectra, both the (+,+,+) and (+,-,+) isomers show two sets of **2b** signals in a 2:1 ratio, whereas the (+,+,-) isomer exhibits three sets in a 1:1:1 ratio. Given the formation of a statistical distribution of the three isomers, (+,+,+)/(+,+,-)/(+,-,+) = 1:2:1, seven sets of **2b** signals should be observed in total, in a 2:2:2:2:2:1:1 ratio. In fact, the ¹H NMR spectrum clearly revealed seven sets of signals for H_a, H_b, and H_c of guest **2b** in the expected 2:2:2:2:2:1:1 integral ratio (Figure 2c), which strongly supports the formation of the triple-decker complex. A diffusion-ordered NMR spectroscopy (DOSY) experiment suggested that all of the signals derived from the three diastereomers showed the same diffusion constant (*D* = 1.4 × 10^{−10} m² s^{−1}).

The triple-decker **2b·Ag⁺·2b·Ag⁺·2b** structure was unambiguously determined by single-crystal X-ray analysis (Figure 3a). Pale yellow crystals were obtained by slow evaporation of an aqueous solution of ion cluster **1a·(2b·Ag⁺·2b·Ag⁺·2b)**. Within cage **1a**, Au^I complexes **2b** were disordered around the vertical axis, which indicates the almost free rotation of complex **2b**. The Au⋯Ag distances ranged from 2.694 to 2.823 Å,^[9] revealing Au^I–Ag^I interactions.^[10] The Au₃–Ag–Au₃–Ag–Au₃ alignment of trinuclear Au^I complexes **2b** and Ag^I ions is only available in the box-shaped cage. This hetero metal ion cluster was specific to Ag^I ions as a consequence of the effective Au⋯Ag interactions.

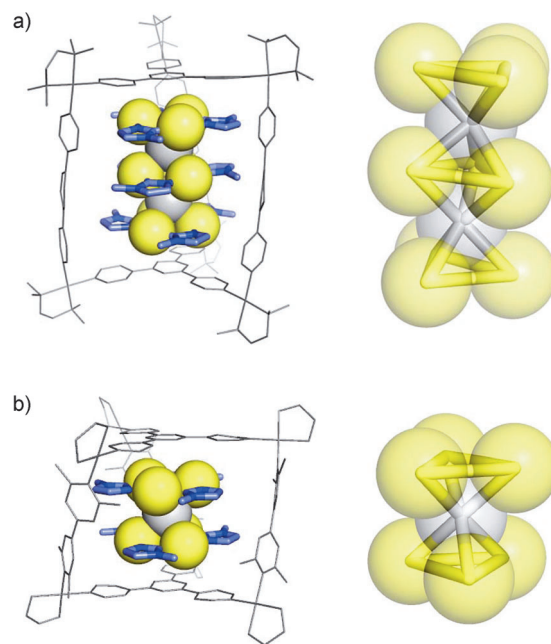


Figure 3. X-ray crystal structures of a) triple-decker ion cluster **1a·(2b·Ag⁺·2b·Ag⁺·2b)** and b) double-decker ion cluster **1b·(2b·Ag⁺·2b)**. The Au^I–Ag^I ion arrays are highlighted on the right.

For comparison, double-decker ion cluster **2b·Ag⁺·2b** was prepared within cage **1b** by treating [3 × 2] Au^I cluster complex **1b·(2b)₂**^[4] with one equivalent of Ag^I ions. The double-decker structure of **1b·(2b·Ag⁺·2b)** was also clearly determined by X-ray single crystal analysis (Figure 3b).^[11] The alignment of the metal ions is basically the same as that in the [Au₃–Ag–Au₃]_n infinite chain that forms as crystals from a Au^I trinuclear complex and silver ions.^[5]

Before Ag^I ion insertion, the [3 × 2] Au^I ion cluster **1b·(2b)₂** showed a strong absorption at around 415 nm (*ε* = 3000 M^{−1} cm^{−1}) because of charge transfer from electron rich **2b** to the electron deficient triazine ligand of **1b**. After Ag^I insertion, however, only weak CT bands (shoulder) were observed for **1a·(2b·Ag⁺·2b·Ag⁺·2b)** and **1b·(2b·Ag⁺·2b)** at around 355 nm because the electron density of **2b** significantly decreased and the charge transfer was diminished. As the HOMO levels of the Ag^I ion-inserted double or triple decker clusters are lower than that of [3 × 2] Au^I ion cluster (**2a**)₂, the CT bands were blue shifted (Figure 4).^[6a,12]

In conclusion, we successfully synthesized Au₃–Ag–Au₃ and Au₃–Ag–Au₃–Ag–Au₃ multi-decker, discrete ion clusters within a self-assembled coordination cage. Unlike the [Au₃–Ag–Au₃]_n infinite chain complex that forms only in the solid state, our multi-decker complexes are stable in aqueous solution because they are tightly encapsulated by the box-shaped cage. Moreover, the cage enabled the formation of a Au₃–Ag–Au₃–Ag–Au₃ triple-decker complex that could never be synthesized without the help of the cage. As the cage height can be systematically elongated, the family of box-shaped cages is a potential platform for the preparation of large multi-decker clusters.^[13] The method may be applied to other hetero metal ion clusters and will thus open the door to the solution chemistry of various multi-decker metal complexes in solution.

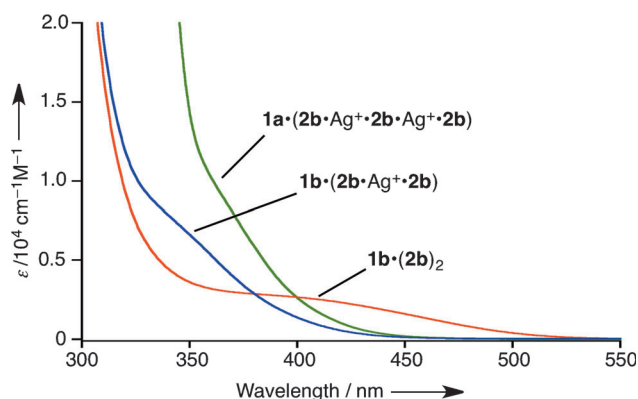


Figure 4. UV/Vis spectra (RT, 1.0 mm) of ion clusters **1b·(2b)₂**, **1b·(2b·Ag⁺·2b)** and **1a·(2b·Ag⁺·2b·Ag⁺·2b)** in H₂O.

Experimental Section

Preparation of precursor complex 1a·(2b·3·2b): Trinuclear Au^I complex **2b** (16.8 mg, 0.020 mmol), triazine panel ligand **3** (9.38 mg, 0.030 mmol), pillared ligand (1,4-di(pyridin-4-yl)benzene, 8.65 mg, 0.030 mmol) and (tmeda)Pd(ONO₂)₂ (17.4 mg, 0.060 mmol; tmeda = tetramethylethylenediamine) were mixed in water (1.0 mL) at 60 °C for 12 h. After filtration of the yellow solution, the ¹H NMR spectrum revealed the quantitative formation of complex **1a·(2b·3·2b)**. Two sets of signals were observed for cage **1a** and guest **2b**, indicating the presence of two stacking modes of **2b** with inserted panel ligand **3**. ¹³C NMR and 2D NMR were also measured (see the Supporting Information).

Synthesis of triple-decker ion cluster 1a·(2b·Ag⁺·2b·Ag⁺·2b): AgNO₃ (10.20 mg, 0.060 mmol) and trinuclear Au^I complex **2b** (33.36 mg, 0.040 mmol) were added to an aqueous solution of precursor complex **1a·(2b·3·2b)** (53.8 mg, 0.010 mmol). The suspended mixture was stirred at 40 °C for 12 h. After filtration of the resulting yellow solution, ¹H NMR analysis revealed quantitative guest exchange to form triple-decker ion cluster **1a·(2b·Ag⁺·2b·Ag⁺·2b)**.

Crystal data of 1a·(2b·Ag⁺·2b·Ag⁺·2b): Triclinic Space group *P* $\bar{1}$, *T* = 90(2) K, *a* = 19.4231(18), *b* = 26.329(2), *c* = 26.344(2) Å, *α* = 72.8860(10), *β* = 77.3130(10), *γ* = 77.2690(10)°, *V* = 12.385(2) Å³, *Z* = 2, *ρ*_{calcd} = 1.402 Mg m⁻³, *F*(000) = 4977, reflections collected/unique 130323/49353 (*R*_{int} = 0.0418). The structure was solved by direct methods (SHELXL-97) and refined by full-matrix least-squares methods (SHELXL-97) on *F*² with 1813 parameters. *R*₁ = 0.0818 (*I* > 2σ(*I*)), *wR*₂ = 0.2373. GOF 1.124, CCDC 894585 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Crystal data of 1b·(2b·Ag⁺·2b): Hexagonal Space group *P*321, *T* = 90(2) K, *a* = *b* = 20.533(2), *c* = 54.547(11) Å, *V* = 19915(5) Å³, *Z* = 2, *ρ*_{calcd} = 1.676 Mg m⁻³, *F*(000) = 9678, reflections collected/unique 169214/21042 (*R*_{int} = 0.0533). The structure was solved by direct methods (SHELXL-97) and refined by full-matrix least-squares methods (SHELXL-97) on *F*² with 1626 parameters. *R*₁ = 0.0873 (*I* > 2σ(*I*)), *wR*₂ = 0.2245. GOF 1.126, CCDC 866863 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. For full experimental details, characterizations, and crystallographic analysis, see the Supporting Information.

Received: September 20, 2012

Published online: October 26, 2012

Keywords: cluster compounds · gold · host-guest systems · multi-decker · silver

- [1] For selected reviews, see: a) P. Pyykkö, *Chem. Rev.* **1997**, *97*, 597–636; b) C.-M. Che, S.-W. Lai, *Coord. Chem. Rev.* **2005**, *249*, 1296–1309; c) H. Schmidbaur, A. Schier, *Chem. Soc. Rev.* **2008**, *37*, 1931–1951; d) H. Schmidbaur, A. Schier, *Chem. Soc. Rev.* **2012**, *41*, 370–412.
- [2] a) M. J. Katz, K. Sakai, D. B. Leznoff, *Chem. Soc. Rev.* **2008**, *37*, 1884–1895; b) O. Crespo in *Modern Supramolecular Gold Chemistry: Gold-Metal Interactions and Applications* (Ed.: A. Laguna), Wiley-VCH, Weinheim, **2008**, pp. 65–129.
- [3] a) B. K. Teo, K. Keating, *J. Am. Chem. Soc.* **1984**, *106*, 2224–2226; b) O. Crespo, M. C. Gimeno, P. G. Jones, A. Laguna, M. D. Villacampa, *Angew. Chem.* **1997**, *109*, 1025–1027; *Angew. Chem. Int. Ed. Engl.* **1997**, *36*, 993–995.
- [4] T. Osuga, T. Murase, K. Ono, Y. Yamauchi, M. Fujita, *J. Am. Chem. Soc.* **2010**, *132*, 15553–15555.
- [5] a) A. Burini, J. P. Fackler, Jr., R. Galassi, B. R. Pietroni, R. J. Staples, *Chem. Commun.* **1998**, 95–96; b) A. Burini, R. Bravi, J. P. Fackler, Jr., R. Galassi, T. A. Grant, M. A. Omary, B. R. Pietroni, R. J. Staples, *Inorg. Chem.* **2000**, *39*, 3158–3165.
- [6] a) M. Yoshizawa, J. Nakagawa, K. Kumazawa, M. Nagao, M. Kawano, T. Ozeki, M. Fujita, *Angew. Chem.* **2005**, *117*, 1844–1847; *Angew. Chem. Int. Ed.* **2005**, *44*, 1810–1813; b) M. Yoshizawa, K. Ono, K. Kumazawa, T. Kato, M. Fujita, *J. Am. Chem. Soc.* **2005**, *127*, 10800–10801; c) K. Ono, M. Yoshizawa, T. Kato, K. Watanabe, M. Fujita, *Angew. Chem.* **2007**, *119*, 1835–1838; *Angew. Chem. Int. Ed.* **2007**, *46*, 1803–1806; d) K. Ono, M. Yoshizawa, T. Kato, M. Fujita, *Chem. Commun.* **2008**, 2328–2330.
- [7] a) F. Bonati, A. Burini, B. R. Pietroni, *J. Organomet. Chem.* **1989**, *375*, 147–160; b) G. Yang, R. G. Raptis, *Inorg. Chem.* **2003**, *42*, 261–263; for reviews of cyclic trinuclear Au^I complexes, see: c) A. A. Mohamed, J. P. Fackler, Jr., *Comments Inorg. Chem.* **2003**, *24*, 253–280; d) H. E. Abdou, A. A. Mohamed, J. P. Fackler, Jr., in *Gold Chemistry: Applications and Future Directions in the Life Science* (Ed.: F. Mohr), Wiley-VCH, Weinheim, **2008**, pp. 1–45.
- [8] a) L. E. Sansores, R. Salcedo, A. Martínez, N. Mireles, *THEO-CHEM* **2006**, *763*, 7–11; b) S. M. Tekarli, T. R. Cundari, M. A. Omary, *J. Am. Chem. Soc.* **2008**, *130*, 1669–1675.
- [9] In this study, we discussed the molecular geometry of the largest portion of disordered molecules. The Au···Ag distances are close to those observed in an infinite (Au₃–Ag–Au₃)_n crystalline chain (2.731–2.922 Å), see ref. [5a].
- [10] These Au···Ag distances are less than the sum of the van der Waals radii (3.4 Å); see: a) A. Bondi, *J. Phys. Chem.* **1964**, *68*, 441–451; for Au···Ag interactions, see: b) V. J. Catalano, A. L. Moor, *Inorg. Chem.* **2005**, *44*, 6558–6566; c) A. A. Mohamed, A. Burini, J. P. Fackler, Jr., *J. Am. Chem. Soc.* **2005**, *127*, 5012–5013.
- [11] The Au···Ag distances ranged from 2.774 to 2.818 Å.
- [12] Au^I–Ag^I ion clusters were not emissive, as cage **1** strongly absorbs light with λ < 350 nm and host–guest interactions can also efficiently quench guest emission; see: a) J. K. Klosterman, M. Iwamura, T. Tahara, M. Fujita, *J. Am. Chem. Soc.* **2009**, *131*, 9478–9479; b) K. Ono, J. K. Klosterman, M. Yoshizawa, K. Sekiguchi, T. Tahara, M. Fujita, *J. Am. Chem. Soc.* **2009**, *131*, 12526–12527.
- [13] a) J. K. Klosterman, Y. Yamauchi, M. Fujita, *Chem. Soc. Rev.* **2009**, *38*, 1714–1725; b) Y. Yamauchi, M. Yoshizawa, M. Akita, M. Fujita, *J. Am. Chem. Soc.* **2010**, *132*, 960–966.