Metal Ion Clusters

Triple-Decker Au₃–Ag–Au₃–Ag–Au₃ Ion Cluster Enclosed in a Self-Assembled Cage**

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Soft d^{10} metal ions (M), such as Au^I and Ag^I, show metal-lophilicity and form M···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 $[3 \times 3]$ Au^I_9 cluster,[4] which consists of three layers of planar Au^I_3 complex **2a**, in the confined cavity of self-assembled cage **1a** (Figure 1). Here, we report that trinuclear
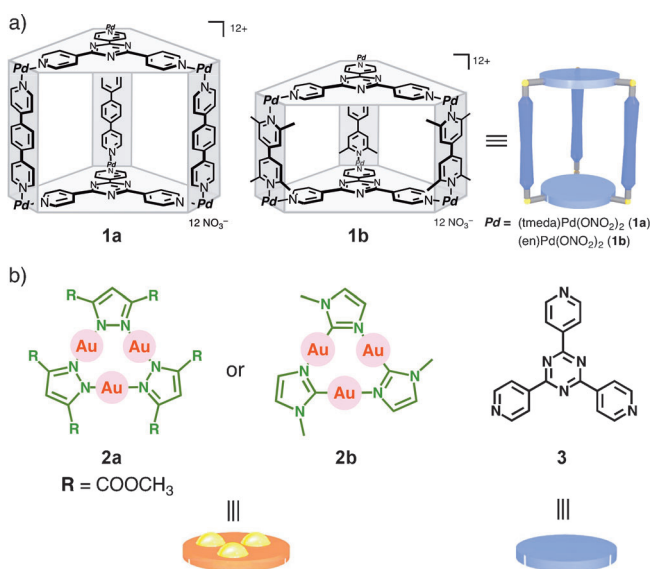

Figure 1. a) Self-assembled box-shaped cage **1**. b) Accumulated trinu-clear Au^I complexes **2** and panel ligand **3**.

Au^I_3 complex **2b** takes up silver ions to form an unprecedented triple-decker ion cluster (Au_3–Ag–Au_3–Ag–Au_3) in the cage. There is only one example of a double-decker sandwich cluster, Au_3–Ag–Au_3, prepared by the co-crystal-lization of a Au^I trinuclear complex with a silver ion.[5] However, this structure is only observable in the solid state, and higher or infinite multi-decker clusters have never been
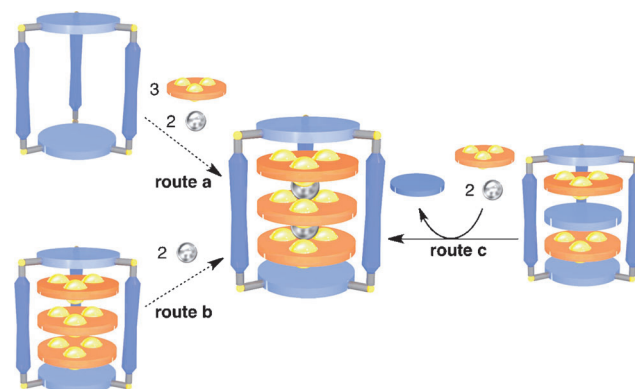
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prepared, even in the solid state. Thus, the adjustable, box-shaped cavity of **1**[6] is useful, not only for limiting the cluster numbers, but also for stabilizing weakly associated metal ion clusters that cannot exist without the help of the cage.

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 $[3 \times 3]$ Au^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 $[3 \times 3]$ Au^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 elec-tron-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 ion uptake to form the **2b·Ag⁺·2b·Ag⁺·2b** triple-decker ion cluster accommodated within **1a** (Figure 2a).

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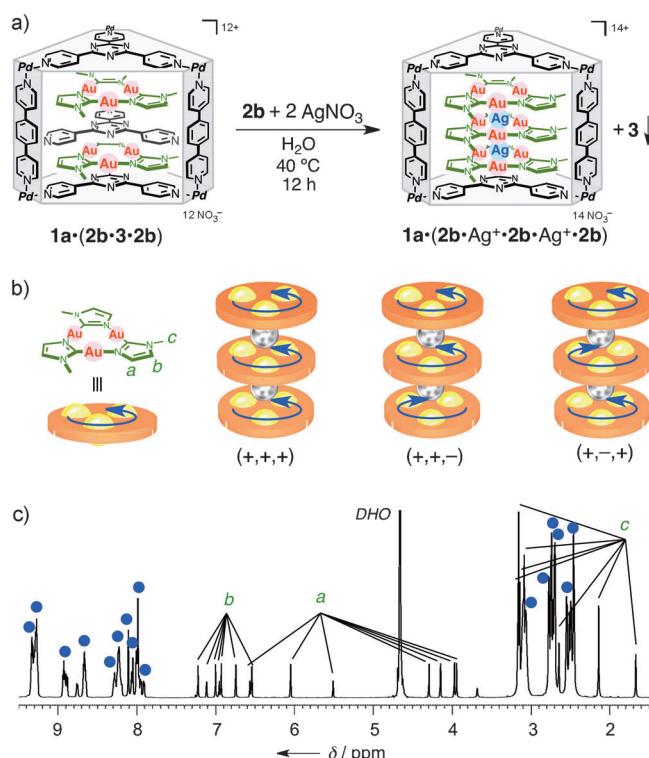
Figure 2. a) Formation of triple-decker cluster 1a·(2b·Ag⁺·2b·Ag⁺·2b). b) Three stacking modes of the guests. c) The ¹H NMR spectrum (500 MHz, 310 K) of 1a·(2b·Ag⁺·2b·Ag⁺·2b) in D₂O; blue circles indicate signals from cage 1a.

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 ($D = 1.4 \times 10^{-10}$ m²s⁻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**, Auᴵ 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 Auᴵ–Agᴵ interactions.[10] The Au₃–Ag–Au₃–Ag–Au₃ alignment of trinuclear Auᴵ complexes **2b** and Agᴵ ions is only available in the box-shaped cage. This hetero metal ion cluster was specific to Agᴵ ions as a consequence of the effective Au···Ag interactions.
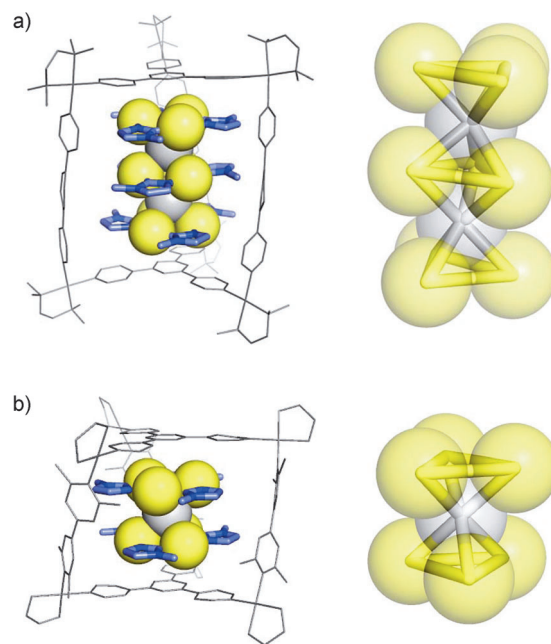

Figure 3. X-ray crystal structures of a) triple-decker ion cluster 1a·(2b·Ag⁺·2b·Ag⁺·2b) and b) double-decker ion cluster 1b·(2b·Ag⁺·2b). The Auᴵ–Agᴵ ion arrays are highlighted on the right.

For comparison, double-decker ion cluster **2b**·Ag⁺·**2b** was prepared within cage **1b** by treating [3×2] Auᴵ cluster complex **1b**·(**2b**)₂[4] with one equivalent of Agᴵ 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 Auᴵ trinuclear complex and silver ions.[5]

Before Agᴵ ion insertion, the [3×2] Auᴵ ion cluster **1b**·(**2b**)₂ showed a strong absorption at around 415 nm ($\varepsilon = 3000$ м⁻¹cm⁻¹) because of charge transfer from electron rich **2b** to the electron deficient triazine ligand of **1b**. After Agᴵ 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 Agᴵ ion-inserted double or triple decker clusters are lower than that of [3×2] Auᴵ 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.
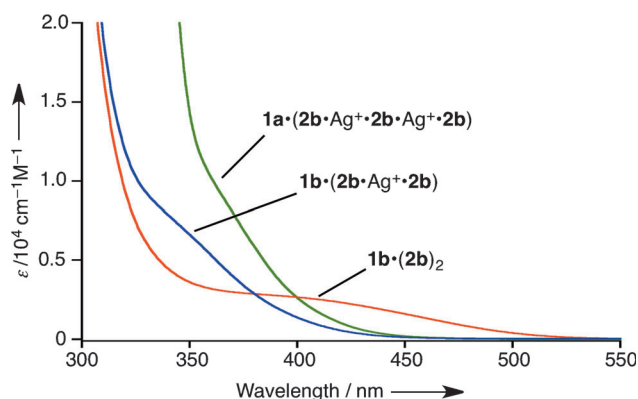
Figure 4. UV/Vis spectra (RT, 1.0 mM) of ion clusters **1b**·(**2b**)₂, **1b**·(**2b**·Ag⁺·**2b**) and **1a**·(**2b**·Ag⁺·**2b**·Ag⁺·**2b**) in H₂O.

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 ^{1}H 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**. ^{13}C 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, ^{1}H 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, $\alpha = 72.8860(10)$, $\beta = 77.3130(10)$, $\gamma = 77.2690(10)°$, $V = 12385(2)$ Å³, $Z = 2$, $\rho_{calcd} = 1.402$ Mg m^{-3}, $F(000) = 4977$, reflections collected/unique 130323/49353 ($R_{int} = 0.0418$). The structure was solved by direct methods (SHELXS-97) and refined by fill-matrix least-squares methods (SHELXL-97) on F^2 with 1813 parameters. $R_1 = 0.0818$ ($I > 2\sigma(I)$), $wR_2 = 0.2373$. 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 $P321$, $T = 90(2)$ K, $a = b = 20.533(2)$, $c = 54.547(11)$ Å, $V = 19915(5)$ Å³, $Z = 2$, $\rho_{calcd} = 1.676$ Mg m^{-3}, $F(000) = 9678$, reflections collected/unique 169214/21042 ($R_{int} = 0.0533$). The structure was solved by direct methods (SHELXS-97) and refined by fill-matrix least-squares methods (SHELXL-97) on F^2 with 1626 parameters. $R_1 = 0.0873$ ($I > 2\sigma(I)$), $wR_2 = 0.2245$. 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.

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