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VIP Supramolecular Chemistry

Au_{36} Crown: A Macrocyclization Directed by Metal–Metal Bonding Interactions**

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Large-ring molecules have excited chemists for over 40 years since the discovery of crown ethers in 1967.[1] The pioneering work of Nobel laureates Pedersen,[1] Lehn,[2] and Cram[3] on crown ethers, cryptands, and spherands has led to the development of the field of supramolecular chemistry, in which large-ring systems play a fundamental role in the search for novel functional materials and devices.[4–7] With the challenge of constructing large ring molecules, self-assembly has been recognized as a promising alternative to conventional organic synthesis. In particular, metal-directed self-assembly approaches have led to the synthesis of numerous functional metal-containing rings, for example, metal–organic (coordination bonding) macrocycles[8–11] and large cyclic aggregates bearing cluster units with metals bridged by small groups (X) (M−X−M type bonding).[12–14] However, the construction of large-ring aggregates containing continuous metal–metal bonds (M−M type)[15] or bonding interactions (M···M type)[16] remains a challenge.

$Au^I\cdots Au^I$ bonding interactions, which have similar strengths to hydrogen bonds, have emerged as structural motifs in the design of supramolecular aggregates with unusual properties.[17] Although there are numerous small rings with continuous $Au^I\cdots Au^I$ bonding interactions, for example Au_3 (triangle), Au_4 (square), Au_5 (pentagon), and Au_6 (hexagon), in the gold ring family,[18] only very recently was the self-assembly of a chiral Au_{16} ring, constructed by unique metal–metal bonding interactions from achiral molecular units, reported by us.[19] Herein, we present the spontaneous hierarchical hetero-chiral self-assembly of a crown-like Au_{36} ring, the largest member of the gold ring family to date, directed by strong $Au^I\cdots Au^I$ bonding interactions from achiral components.[20]

Addition of [Au(tht)Cl] (tht = tetrahydrothiophene) in dichloromethane to a solution of 0.5 molar equivalents of **1** in ethanol at room temperature (Scheme 1) resulted in the formation of a red precipitate. Evaporation of the solvent from the reaction mixture, followed by flash chromatography of the residue with chloroform as eluent, gave a pale-yellow solution. Slow diffusion of diethyl ether vapor into this dilute solution over several days gave a yellow cubic crystalline product whose structure was subseqently confirmed to be that of an Au_6 cluster (monomer **I**) by X-ray crystallography (see Table S1 in the Supporting Information). A dramatic color change from pale yellow to dark red occurred upon concentration of the dilute solution. Crystallization by layering methanol onto this red solution gave the title compound as dark-red crystals (the hexamer $\mathbf{I}_6$) in 75% yield. The ^1H NMR spectrum of $\mathbf{I}_6$ reveals it to be monomeric (**I**) in dilute solution (in $CDCl_3$) as the proton resonances of the methylene groups split into two pairs of doublets at $\delta = 6.3$ and 4.4 ppm ($PhCH_2$), and $\delta = 5.6$ and 4.6 ppm ($FcCH_2$), respectively. Correlation signals from the ^1H-^1H COSY spectrum indicate that the two protons in each of the two different methylene groups are in different environments. Both these findings suggest a highly asymmetric structure of the product, which is consistent with the crystal structure of the monomer **I**. X-ray crystallography of a dark-red crystal of $\mathbf{I}_6$ showed it to contain a supramolecular Au_{36} ring consisting of six Au_6 monomers joined by strong $Au^I\cdots Au^I$ interactions (see Table S2 in the Supporting Information). The hexameric structure was further confirmed by MALDI-TOF mass spectrometry, which showed signals for the monomer ($\mathbf{I}+1$, m/z 3227.6), dimer ($\mathbf{I}_2+1$, m/z 6460.8), and trimer ($\mathbf{I}_3+1$, m/z 9697.5).

The formation of the Au_{36} ring involves an $Au^I\cdots Au^I$ bonding interaction directed self-assembly (Scheme 1). In a first step, three bidentate dithiocarbamate units coordinate to six Au^I centers in a head-to-tail cyclic manner to form a three-bladed propeller-shaped monomer with D_3 symmetry. The chirality of these tris-bidentate octahedral complexes allows us to define the two different helical monomers formed as Δ-

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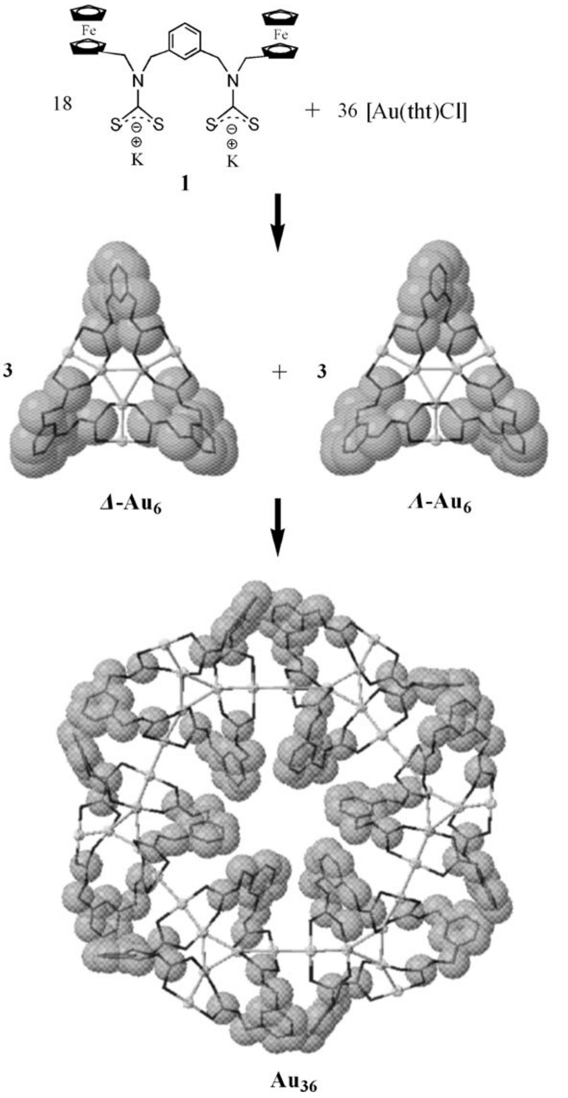

Scheme 1. Self-assembly process leading to the Au_{36} ring. All the hydrogen atoms and ferrocenylmethyl ($FcCH_2$) substituents in Δ-Au_6, Λ-Au_6, and Au_{36} have been omitted for clarity. The 36 gold(I) centers are presented in a ball-and-stick fashion and the carbon atoms are presented in both a capped-stick backbone and a space-filling shadow.

Au_6 and Λ-Au_6,[21] which are formed in equimolar amounts. Three alternating Δ-Au_6 and Λ-Au_6 units then crystallize into a racemic cyclic hexamer to afford the giant Au_{36} ring in a process driven by an increase of the monomer concentration.

As illustrated in Figure 1 a, the Au_{36} ring consists of three alternating Δ-Au_6 and Λ-Au_6 monomers with strong inter-monomer $Au^I \cdots Au^I$ bonding interactions (average: 2.890 Å). The result is a crown of gold atoms with a diameter of 2.25 nm and a perimeter of 6.88 nm that is analogous to Pedersen's [18]crown-6,[1] with three monomers above and three below the mean plane of the 36 gold atoms (Figure 1 b). The six Au^I centers in each monomer are coplanar (mean deviations of less than 0.06 Å) and are linked by three end-to-end bridging dithiocarbamate ligands directed by the linear coordination of the Au^I center to two sulfur atoms above and below the plane in an alternating fashion. The aromatic rings in the ligands are oriented in the same direction as the plane containing the six gold atoms, with dihedral angles ranging from 58.4° to 68.6°, as a result of the steric influence imposed by the ferrocenylmethyl substituents. These six gold atoms form two homocentric parallel equilateral gold triangles with outer sides averaging 7.84 Å and inner sides averaging 3.05 Å (Figure 1 c, top). This bonding situation is in contrast to the reported trigonal-planar structure of $[Au_6(o\text{-}CH_3C_6H_4CS_2)_6]$, which has a maximum number of close interatom contacts[22] (Figure 1 c, bottom). According to recent theoretical studies,[23] Au_6 prefers a trigonal-planar structure due to relativistic effects. The average dithiocarbamate-bridged $Au^I \cdots Au^I$ separation is 2.77 Å, which is consistent with those found in other related dithiocarbamate-bridged compounds.[19]

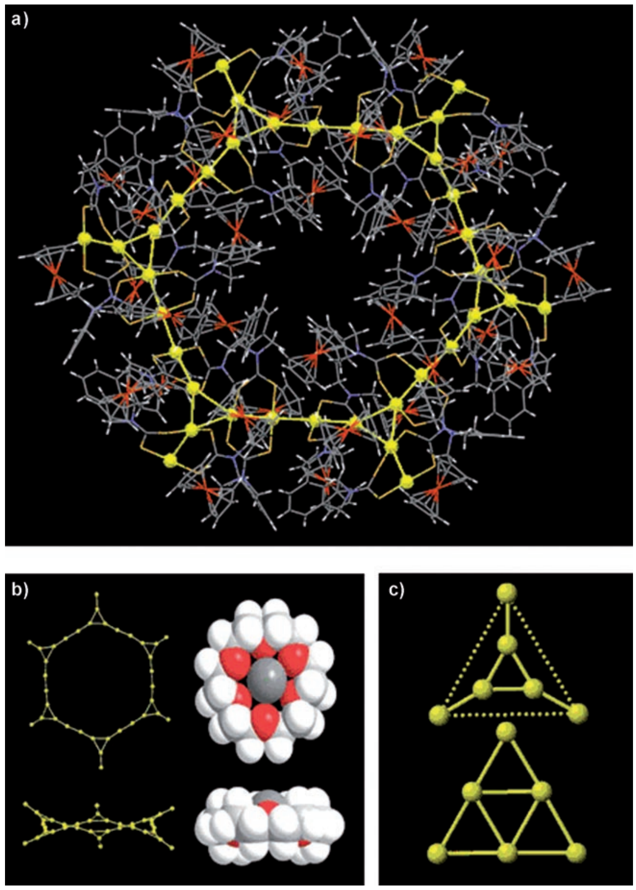

Figure 1. a) Crystal structure of Au_{36} viewed along the *b* axis. All solvent molecules have been omitted for clarity. The 36 gold(I) centers are presented in a ball and stick fashion. b) Perspective views of the Au_{36} backbone (left) and its resemblance to the structure of $K^+ \subset$([18]crown-6) (right). c) The two different trigonal-planar patterns of the Au_6 clusters. Top: intermediate number of close atom–atom contacts. Bottom: maximum number of close atom–atom contacts.[22,23]

The self-assembly process was further probed by UV/Vis absorption studies. Thus, dissolution of the Au_{36} compound in dichloromethane under dilute conditions ($\leq 10^{-5}$ M) gives rise to a yellow solution with absorption bands at $\lambda = 280$ ($\varepsilon = 86145$), 342 sh (23270), and 440 nm (10135 $M^{-1}cm^{-1}$; Figure 2 a), which were assigned to absorptions typical of the Au_6

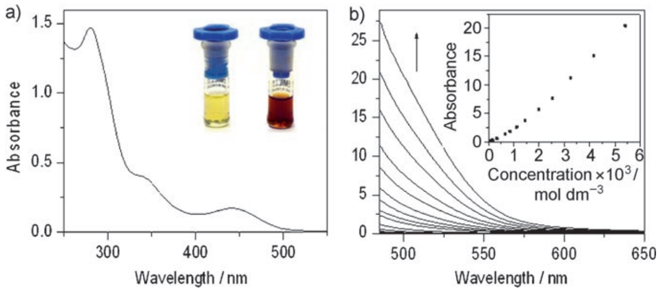

Figure 2. a) UV/Vis absorption spectrum of Au_{36} in dichloromethane under dilute conditions (approx. 10^{-5} M). Inset: Photograph showing Au_{36} in dilute (left) and concentrated (right, approx. 10^{-3} M) solution. b) UV/Vis absorption spectral changes of Au_{36} in dichloromethane as the concentration increases from 2.1×10^{-5} to 5.4×10^{-3} M. Inset: Plot of the absorbance at 500 nm as a function of concentration. The absorbance values have been corrected to a 1-cm path-length equivalence.

monomer **I** (see Figure S1 in the Supporting Information). The low-energy absorption band at 440 nm, which has a much larger extinction coefficient than that found in the HCl salt of the free amine ligand ($\lambda = 260$ s ($\varepsilon = 6020$), 324 s (165), 434 nm (210 $M^{-1}cm^{-1}$)), is tentatively assigned as arising predominantly from the ligand-to-metal-metal charge transfer LMMCT (thiocarbamate-to-gold-gold) transition of the Au_6 monomer, with some minor contribution from the ferrocenyl chromophore. The yellow solution turns dark red upon increasing the concentration (Figure 2a, inset), with a low-energy tail growing in at around 500 nm that does not follow Beer's Law (Figure 2b). The lack of a linear relationship between the absorbance at 500 nm and concentration and the upward curvature of the plot (Figure 2b inset) are suggestive of the self-assembly of the Au_6 monomer to give higher oligomers or aggregates. This low-energy tail becomes more obvious and appears as a shoulder in a less solubilizing solvent (dichloromethane/ethanol mixture; Figure 3), as revealed by the abrupt increase in the absorbance of the shoulder upon increasing the ethanol content of the mixture while keeping the concentration of the complex constant (Figure 3 inset). The low-energy absorptions at longer wavelengths are ascribed to LMMCT transitions of the higher oligomers as a result of the more extended $Au^I\cdots Au^I$ interactions involving more than one Au_6 unit in these oligomers. Attempts to prepare concentrations higher than the millimolar range were unsuccessful due to the limited solubility of the complex in solution. Excitation of both solid samples and solutions of the Au_6 monomer and the Au_{36} hexamer do not give rise to emission, probably as a result of the presence of the ferrocenyl moieties, which quench the LMMCT excited states.

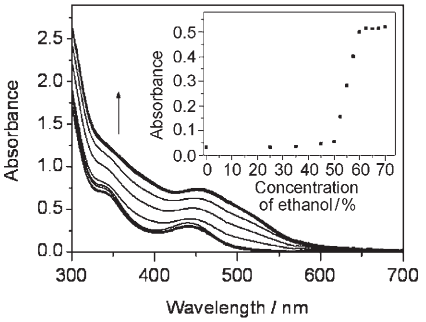

Figure 3. UV/Vis absorption spectral changes of Au_{36} in a dichloromethane/ethanol mixture (2.5×10^{-5} M) as the percentage of ethanol increases from 0% to 70%. Inset: Plot of the absorbance at 504 nm as a function of ethanol percentage.

In summary, an Au_{36} crown molecule, whose structure has been determined by NMR spectroscopic, MALDI-TOF mass spectrometric, and X-ray diffraction techniques, has been constructed by a metal–metal bonding interaction directed self-assembly. The solution self-assembly process has also been monitored by UV/Vis absorption spectroscopy. Chiral resolution of the enantiomeric monomers formed is currently in progress. This work provides a method for the construction of macrocyclic hosts from unique metal–metal bonding interactions and it is envisioned that the present work is not only promising for the development of supramolecular chemistry but also for nanostructured materials.

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