A Novel Au_{12} Supramolecule Composed of Two-, Three-, and Four-coordinated Au(I) Centers Constructed on the S_3 Scaffolding

Keiko Nunokawa, Tetsuya Sunahara, Satoru Onaka,* Kazuya Okazaki, Hiroyuki Imai,† Katsuya Inoue,† and Tomoji Ozeki††
Department of Environmental Technology, Graduate School of Engineering, Nagoya Institute of Technology,
Gokiso-cho, Showa-ku, Nagoya 466-8555
†*Institute for Molecular Science, Myodaiji, Okazaki 444-8585*
††*Department of Chemistry and Materials Science, Tokyo Institute of Technology,*
O-okayama, Meguro-ku, Tokyo 152-8551

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A novel Au_{12} supramolecule ($\mathbf{1}_2$) composed of two-, three-, and four-coordinated Au(I) centers was constructed on the S_3 scaffolding (trithiocyanurate, $S_3C_3N_3{}^{3-}$). $\mathbf{1}_2$ can be regarded as a tetramer of the Au_3 unit, $[AuP(3\text{-}CF_3\text{–}C_6H_4)_3]_3(S_3C_3N_3)$ by losing four $P(3\text{-}CF_3\text{–}C_6H_4)_3$ ligands upon tetramerization. A congener of the monomer unit $[AuP(2\text{-py})(C_6H_5)_2]_3(S_3C_3N_3)$ (**2**) was also synthesized; X-ray study on **2** revealed in turn a monomer structure.

Aurophilicity has been attracting proliferate interests for the past decade not only because of the phenomenological viewpoint, but also because of a new strategy for constructing higher dimensional molecules in terms of a self-assembling technique. In this vein, the $(S)_2R$- and/or $(S)_3R$-type ligand is a quite fascinating scaffolding for incorporating a number of Au units and connecting them by aurophilic interaction to produce novel supramolecular assemblies.[1–3] In the previous paper, we have obtained several intriguing supramolecules by incorporating the AuL (L = $P(3\text{-}CF_3\text{–}C_6H_4)_3$ and/or $P(2\text{-py})(C_6H_5)_2$) units into $(S)_2R$ and/or $(S)_3R$ scaffolds. Successful synthesis of a helical structure constructed by aurophilicity alone is the worthy of special mention among the outcomes in addition to the synthesis of quasi one-dimensional arrays.[4] Special role of the CF_3 substituent at a meta-position[5] was again highlighted in this paper. It is worthwhile to point out that the aurophilic interaction induces "polymerization" of the $(LAu)_xS_xR$ building block to yield infinite chains and/or infinite sheet structure or sometimes ceases at "dimerization" state in these complexes.[1–5] Therefore, it has been left as a challenging synthetic target to control the polymerization extent to an "oligomer" state in order to get a discrete supramolecule. The present paper reports on the new vistas of supramolecules constructed by aurophilic interaction in the course of introducing the AuL units into a $(S)_3R$ scaffold and our successful synthesis of an isolated Au_{12} supramolecule.

$Au_6(S_3C_3N_3)_2\{P(3\text{-}CF_3\text{–}C_6H_4)_3\}_4$ (**1**) was synthesized by reacting a CH_2Cl_2 solution of $Au(Cl)P(3\text{-}CF_3\text{–}C_6H_4)_3$ with a methanol solution of sodium trithiocyanurate, $Na_3(2,4,6\text{-}S_3\text{-}C_3N_3)$ (3:1 mole ratio) as colorless crystals in good yield.[6] Single crystal X-ray diffraction study has revealed the unique structure of **1** (Figure 1, top).[7] Two units of **1** are connected together by aurophilic interaction at five Au sites (Au2, Au3, Au4, Au5, and Au6) to afford the Au_{12} supramolecule (Figure 1, bottom). There is no aurophilic interaction between Au1 and other gold ions judged from the perusal of the molecular packing of **1**. Therefore, $\mathbf{1}_2$ is the first isolated Au_{12} supramolecule to the best of our knowledge. As a unit of $S_3C_3N_3$ ligand has −3 negative charge, the formal oxidation state for all gold ions is assigned to +1. The Au_{12} skeleton of $\mathbf{1}_2$ is composed from three types of coordination modes for Au(I), that is, linear two coordination (Au1), T-shaped three coordination (Au4, Au5), and severely distorted tetrahedral coordination (Au2, Au3, Au6). The shortest Au–Au distance is 2.9293(9) Å between Au2 and Au6 and the longest Au–Au distance is 3.2479(8) Å between Au3 and Au4. Another characteristic of **1** is that one of the N atoms in each $S_3C_3N_3$ scaffold is coordinated to one Au(I) ion, thus each $S_3C_3N_3$ scaffold functions as a tetradentate ligand (r(Au–N) = 2.090(1) and 2.118(1) Å). Such a tetradentate coordination mode for $S_3C_3N_3$ scaffold was previously reported by Che's group and Puddephatt's group;[9,10] a square-planar Au_4 unit constructed by

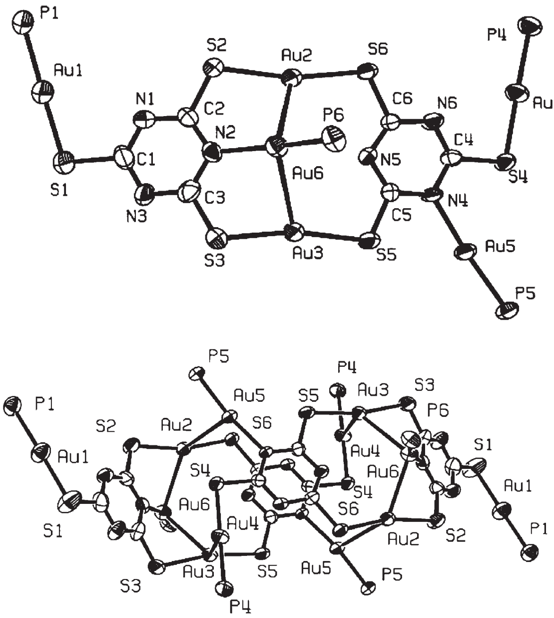

Figure 1. ORTEP drawing of the Au_6 molecular cluster (top) and the discrete Au_{12} supramolecule of $\mathbf{1}_2$ (bottom) ($CF_3\text{–}C_6H_4$ groups are omitted for clarity). Selected bond lengths (Å) and angles (°): Au2–Au5, 3.1199(7); Au2–Au6, 2.9293(9); Au3–Au4, 3.2479(8); Au3–Au6, 2.9465(8); Au1–P1, 2.246(6); Au4–P4, 2.250(5); Au5–P5, 2.216(5); Au6–P6, 2.228(4); Au1–S1, 2.296(7); Au2–S2, 2.298(4); Au3–S3, 2.305(4); Au3–S5, 2.285(4); Au4–S4, 2.321(5); Au2–S6, 2.273(3); Au5–N4, 2.09(1); Au6–N2, 2.12(1); S2–Au2–S6, 165.9(1); S3–Au3–S5, 168.1(1); S2–Au2–Au6, 80.5(1); S6–Au2–Au6, 112.8(1); S3–Au3–Au6, 77.30(9); S5–Au3–Au6, 113.0(1); N2–Au6–P6, 163.6(3); N4–Au5–P5, 165.5(3).

aurophilic interaction is a building block and then these blocks are connected by another aurophilic interaction to yield an extended sheet-like structure. The different feature of **1** from their $S_3C_3N_3$–Au complexes is that the inner nitrogen atom (N5) is free from coordination and instead one of the outer nitrogen atoms (N4) is coordinated to another Au atom. Au–S, Au–P, and Au–N bond lengths are in the normal range.[4,5,9,10]

The structural uniqueness of $\mathbf{1}_2$ is that a discrete isolated Au_{12} cluster is formed by intercluster aurophlicity and thus formed suprastructure is reinforced by strong π–π stacking between two $S_3C_3N_3$ scaffolds (the average distance between C and N atoms is about 3.2 Å). Che and Puddephatt have demonstrated that the Au_6 hexamer is yielded by losing two $PPhMe_2$ or *t*-BuNC, which are less bulky than $P(3\text{-}CF_3\text{–}C_6H_4)_3$, upon dimerization of the $(AuL)_3S_3C_3N_3$ fundamental units.[9,10] We surmise that the similar mechanism is operative for the construction of $\mathbf{1}_2$. However, there remains a query why the bulky $P(3\text{-}CF_3\text{–}C_6H_4)_3$ ligand can produce the hexamer **1** and the dodecamer $\mathbf{1}_2$. As was pointed out above, the inner nitrogen atom (N5) is prohibited from coordination to Au6 and thus distortion of this C_3N_3 ring is largely relaxed to lead to strong π–π stacking between two $S_3C_3N_3$ scaffolds; this π–π stacking should contribute to the stabilization of the dodecamer. The steric bulkiness of the $P(3\text{-}CF_3\text{–}C_6H_4)_3$ ligand has played the special role for constructing the discrete Au_{12} supramolecule of $\mathbf{1}_2$.

New entry to the combination of Au(I) with $S_3C_3N_3{}^{3-}$ ligand has been made by reacting $Au(Cl)P(2\text{-}py)(C_6H_5)_2$ with $Na_3(2,4,6\text{-}S_3\text{-}C_3N_3)$ to yield **2**.[11] Single crystal X-ray analysis (Figure 2) has demonstrated that **2** has a similar structure to that of the triphenyl phosphine analogue $\{AuP(C_6H_5)_3\}_3(2,4,6\text{-}S_3\text{-}C_3N_3)$.[10] It is worthy to point out that this triphenylphosphine analogue and **2** do not exhibit Au–Au interaction.[10] We have not yet obtained oligomeric products which should be related to **1** or $\mathbf{1}_2$ during recrystallization process of **2**. As described above, hexamers obtained by Che and Puddephatt have relatively small ligand.[10,11] In this vein, it is not surprising that neither hexamer nor dodecamer has not been obtained for $P(2\text{-}py)(C_6H_5)_2$ ligand, which demands the steric bulkiness than those of theirs. In addition, no aurophilic interaction is induced in solid state of **2**, although the molecular structure of **2** is quite similar to $\{AuP(2\text{-}py)(C_6H_5)_2\}_3(1,3,5\text{-}S_3\text{-}C_6H_3)$.[4]

As a concluding remark, it is worthy to point out that the unique Au_{12} discrete spramolecules has been synthesized for the first time by virtue of the specific contribution of the 3-CF_3 substituent. Perhaps intricate balance of the sterical demand of the phosphine ligand and/or coexisting ligand and the $S_3C_3N_3$ scaffolding is important for constructing nano molecules.

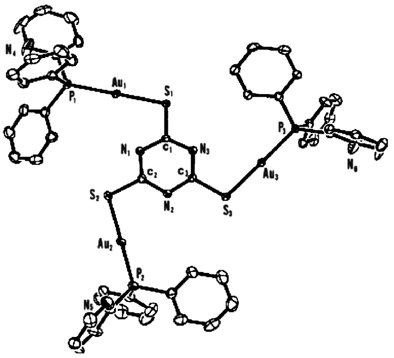

Figure 2. Molecular structure **2**. Selected bond lengths (Å) and angles (°): Au1–S1, 2.305(1); Au2–S2, 2.302(1); Au3–S3, 2.302(1), Au1–P1, 2.251(1); Au2–P2, 2.250(1); Au3–P3, 2.254(1); P1–Au1–S1, 177.72(4); P2–Au2–S2, 179.10(4); P3–Au3–S3, 178.16(4).

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6 To a methanol solution (3 mL) of $Na_3S_3C_3N_3$ (0.1 mmol) was added a CH_2Cl_2 solution (5 mL) of $Au(Cl)P(3\text{-}CF_3\text{–}C_6H_4)_3$ (0.3 mmol) at 25 °C. Solvents were distilled off after 2.5 h stirring and the residue was washed with small amount of water. Then the product was extracted with a mixed solvent of CH_2Cl_2–hexane to afford colorless needles of the trimer. Yield 92%. Satisfactory elementary analysis was obtained for this trimer. During the process of growing single crystals, the trimer is converted to the hexamer **1**; **1** is sensitive to air and turns to an opaque white product upon prolonged exposure to air. Anal. Calcd. for $C_{90}H_{48}Au_6F_{36}N_3P_4S_6$; C, 31.84; H 1.42; N, 2.48%. Found; C, 32.55; H, 1.64; N, 2.48%. $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 32.5(s, br) ppm. IR(KBr disk; below 2000 cm^{-1}): 1602 (w), 1559 (w), 1464 (w), 1447 (s), 1418 (w), 1405 (s), 1325 (vs), 1266 (m), 1250 (m), 1210 (m), 1166 (m), 1124 (s), 1111 (s), 1072 (s), 997 (m), 855 (m), 843 (m), 800 (m), 695 (m), 650 (m), 625 (w), 536 (m) cm^{-1}.

7 *Crystal data*: **1**: $C_{90}H_{48}Au_6F_{36}N_6P_4S_6$, $M_r = 3395$, monoclinic, $P2_1/n$, $a = 20.025(1)$, $b = 23.814(1)$, $c = 24.930(2)$ Å, $\beta = 112.91(1)°$, $Z = 4$, $V = 10951(1)$ Å^3, $\mu = 8.298$ mm^{-1}, $D_{calcd} = 2.136$ gcm^{-3}, $T = 293$ K. R (wR_2) = 0.056(0.15). Diffraction data were collected by use of a SAMRT-APEX diffractometer. ($\lambda = 0.71073$ Å). The structural solution and the refinement were made using Sir-97 and SHELXS-97 in a WinGX program package.[8] The refinements were made on F^2 data with anisotropic thermal parameters by full-matrix least-squares. F atoms were refined isotoropically, because several F atoms are disordered. CCDC 236950(**1**).

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11 To a methanol solution (5 mL) of $Na_3(2,4,6\text{-}S_3\text{-}C_3N_3)$ (0.1 mmol) was added a THF solution (30 mL) of $Au(Cl)P(2\text{-}py)(C_6H_5)_2$ (0.3 mmol) at 25 °C. Solvents were distilled off after 15 h stirring and filtration. The pale yellow residue was washed with each 5 mL of H_2O, MeOH, acetone, and ether successively. Then the product was recrystallized from CH_2Cl_2–hexane to afford pale yellow crystals of **2**. Yield 81%. Anal. Calcd. for $C_{54}H_{42}Au_3N_6P_3S_3\cdot 2CH_2Cl_2$; C, 38.99; H 2.69; N, 4.87%. Found; C, 38.90; H, 2.53; N, 4.83%. $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 37.2(s) ppm.

12 *Crystal data*: **2**: $C_{56}H_{46}Au_3N_6P_3S_3Cl_4$, $M_r = 1725.9$, triclinicc, $P\bar{1}$, $a = 11.729(1)$, $b = 12.266(1)$, $c = 20.417(1)$ Å, $\alpha = 84.308(1)$, $\beta = 89.216(3)$, $\gamma = 83.772(1)°$, $Z = 4$, $V = 7792.6(6)$ Å^3, $\mu = 1.08$ mm^{-1}, $D_{calcd} = 1.97$ gcm^{-3}, $T = 120$ K. R (wR_2) = 0.03 (0.07). Diffraction data were collected by use of a MAC DIP diffractometer. ($\lambda = 0.3282$ Å) in the BL04B2 beamline of the SPring-8 synchrotron rradiation facility. The structural solution and the refinement were made using Sir-97 and SHELXS-97 in a WinGX program package.[8] CCDC 227470 (**2**).

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