

# Extremely Facile Template Synthesis of Gold(III) Complexes of a Saturated Azamacrocyclic and Crystal Structure of a Six-Coordinate Gold(III) Complex

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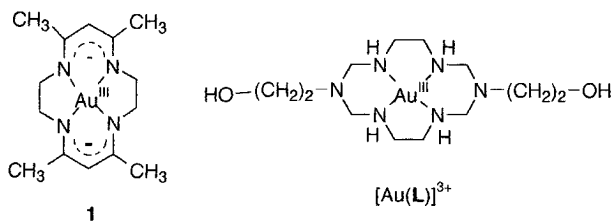
Two gold(III) complexes of the hexaazamacrocyclic ligand 1,8-bis(hydroxyethyl)-1,3,6,8,10,13-hexaazacyclotetradecane (**L**), four-coordinate  $[\text{Au}(\text{L})](\text{ClO}_4)_3 \cdot 1/2\text{H}_2\text{O}$  and six-coordinate  $[\text{Au}(\text{L})\text{Cl}_2]\text{AuCl}_4$ , were synthesized in high yield from the template condensation of ethylenediamine, formaldehyde, and ethanolamine in the presence of gold(III) ion. The gold(III) template cyclization is extremely fast compared with the corresponding nickel(II) template reaction. Both gold(III) complexes are diamagnetic.  $[\text{Au}(\text{L})\text{Cl}_2]\text{AuCl}_4$  ( $\text{Au}_2\text{C}_{12}\text{H}_{30}\text{N}_6\text{O}_2\text{Cl}_6$ ) crystallizes in the monoclinic space group  $P2_1/c$  with  $a = 6.987(2)$  Å,  $b = 14.945(1)$  Å,  $c = 11.151(3)$  Å,  $\beta = 98.83(1)^\circ$ , and  $Z = 2$ . The structure was solved by Patterson and the direct methods and refined to  $R$  values of  $R = 0.0868$  and  $R_w(F^2) = 0.1324$  for 2025 observed reflections measured with Mo  $K\alpha$  radiation on an Enraf Nonius CAD-4 diffractometer. The gold(III) ion of the macrocyclic cation displays a tetragonally distorted octahedral geometry, with four nitrogens in the plane and two chlorides on axial sites. The bond distances of Au–N and Au–Cl average 2.049(8) and 3.097(4) Å, respectively. The hydrogen atoms of secondary amines form hydrogen bonds with hydroxyl oxygen and the coordinated chloride of neighboring macrocyclic complexes.

## Introduction

Ni(II), Cu(II), and Co(III) complexes of various saturated polyazamacrocyclic ligands have been synthesized by the metal template condensation reactions with formaldehyde and amines.<sup>1–12</sup> In order to prepare the complexes of other metal ions, it would be useful to prepare free macrocycles. However, the macrocyclic ligands with N–CH<sub>2</sub>–N (methylenediamine) linkages are unstable when they are not coordinated to a metal ion. Therefore, we are interested in finding other metal ions that can be utilized in the metal template reactions. We are interested in the Au(III) ion because Au(III) macrocyclic complexes are rare and those already reported exhibit quite different chemical behavior from the corresponding Ni(II) complexes because of the higher Lewis acidity of the Au(III) ion.<sup>13,14</sup> The Au(III) ion has been seldom used as a metal

template for the synthesis of macrocyclic complexes except **1**,<sup>15,16</sup> probably because metallic gold and/or gold oxide are formed during the reaction.

In this paper, we show that Au(III) ion is a good metal template and remarkably facilitates the condensation of formaldehyde and amines. Macrocyclic Au(III) complexes are obtained in high yield in minutes. We also show that one of these products,  $[\text{Au}(\text{L})\text{Cl}_2]\text{AuCl}_4$ , is diamagnetic but it contains Au(III) ion in an uncommon six-coordinate geometry which has severe tetragonal distortion.



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- (1) Suh, M. P.; Shin, W.; Kim, H.; Koo, C. H. *Inorg. Chem.* **1987**, *26*, 1846.
- (2) Suh, M. P.; Kang, S. *Inorg. Chem.* **1988**, *27*, 2544.
- (3) Suh, M. P.; Shin, W.; Kang, S.-G.; Lah, M. S.; Chung, T. M. *Inorg. Chem.* **1989**, *28*, 1602.
- (4) Jung, S.; Kang, S.; Suh, M. P. *Bull. Kor. Chem. Soc.* **1989**, *10*, 362.
- (5) Suh, M. P.; Kang, S.; V. Goedken; Park, S. *Inorg. Chem.* **1991**, *30*, 365.
- (6) Suh, M. P.; Kim, I. S.; Cho, S.-J.; Shin, W. *J. Chem. Soc., Dalton Trans.* **1994**, 2765.
- (7) Suh, M. P.; Shim, B. Y.; Yoon, T.-S. *Inorg. Chem.* **1994**, *33*, 5509.
- (8) Bernhardt, P. V.; Curtis, L. S.; Curtis, N. F.; Lawrance, G. A.; Skelton, B. W.; White, A. H. *Aust. J. Chem.* **1989**, *42*, 797.
- (9) Fabbri, L.; Lanfredi, A. M. M.; Pallavicini, P.; Perotti, A.; Taglitti, A.; Ugozzoli, F. *J. Chem. Soc., Dalton Trans.* **1991**, 3263.
- (10) Blas, A. D.; Santis, G. D.; Fabbri, L.; Liccellini, M.; Lanfredi, A. M. M.; Pallavicini, P.; Poggi, A.; Ugozzoli, F. *Inorg. Chem.* **1993**, *32*, 106.
- (11) Geue, R. J.; Hambley, T. W.; Harrowfield, J. M.; Sargeson, A. M.; Snow, M. R. *J. Am. Chem. Soc.* **1984**, *106*, 5478.
- (12) Bottomley, G. A.; Clark, I. J.; Creaser, I. I.; Engelhardt, L. M.; Geue, R. J.; Hagen, K. S.; Harrowfield, J. M.; Lawrance, G. A.; Lay, P. A.; Sargeson, A. M.; See, A. J.; Skelton, B. W.; White, A. H.; Wilner, F. R. *Aust. J. Chem.* **1994**, *47*, 143.
- (13) Kimura, E.; Kurogi, Y.; Takahashi, T. *Inorg. Chem.* **1991**, *30*, 4118.

## Experimental Section

**Reagents.** All chemicals and solvents used in the synthesis were of reagent grade and were used without further purification. For the spectroscopic and physical measurements, organic solvents were dried and purified according to literature methods.<sup>17</sup>

**Measurements.** Infrared spectra were recorded with a JASCO IR-810 spectrophotometer. Electronic absorption spectra were obtained on a Shimadzu 260 UV/vis spectrophotometer. <sup>13</sup>C NMR spectra were recorded on a Varian 200 MHz FT NMR spectrometer. Conductance measurements were performed by using a TOA CM-30ET conductivity meter. Elemental analyses were performed by the Analytical Laboratory in Seo Kang University, Seoul. Magnetic susceptibility was measured with a Faraday type magnetometer.

- (14) Kimura, E.; Kurogi, Y.; Koike, T.; Shionoya, M.; Iitaka, Y. *J. Coord. Chem.* **1993**, *28*, 33.
- (15) Kim, J. H.; Everett, G. W., Jr. *Inorg. Chem.* **1979**, *18*, 3145.
- (16) Kim, J. H.; Everett, G. W., Jr. *Inorg. Chem.* **1981**, *20*, 853.
- (17) Perrin, D. D.; Armarego, W. L. F. *Purification of Laboratory Chemicals*, 3rd ed.; Pergamon Press: Oxford, England, 1988.

**Table 1.** Crystallographic Data for [Au(L)Cl<sub>2</sub>]<sub>2</sub>AuCl<sub>4</sub>

formula	Au <sub>2</sub> C <sub>12</sub> H <sub>30</sub> N <sub>6</sub> O <sub>2</sub> Cl <sub>6</sub>	cryst size, mm	0.50 × 0.20 × 0.10
fw	897.06	$\mu$ , mm <sup>-1</sup>	13.455
space group	<i>P</i> 2 <sub>1</sub> / <i>c</i>	2 $\theta$ range, deg	4.6–50.0
<i>a</i> , Å	6.987(2)	no. of data colled	2288
<i>b</i> , Å	14.945(1)	no. of unique data (all)	2025 [ <i>R</i> <sub>int</sub> = 3.0%]
<i>c</i> , Å	11.151(3)	no. of obsd data ( <i>F</i> > 4 $\sigma$ ( <i>F</i> ))	1161
$\beta$ , deg	98.83(1)	no. of variable params	130
<i>V</i> , Å <sup>3</sup>	1150.6(5)	<i>R</i> <sup>a</sup>	0.0443 (4 $\sigma$ data)
<i>Z</i>	2	<i>R</i> <sub>w</sub> ( <i>F</i> <sup>2</sup> ) <sup>b</sup>	0.0983 (4 $\sigma$ data)
$\rho_{\text{calc}}$ g/cm <sup>3</sup>	2.589	<i>R</i> <sup>a</sup> (all data)	0.0868
temp, °C	23	<i>R</i> <sub>w</sub> ( <i>F</i> <sup>2</sup> ) <sup>b</sup> (all data)	0.1324
$\lambda$ , Å	0.710 73		

$$^a R = \sum ||F_o| - |F_c|| / \sum |F_o|. \quad ^b R_w(F^2) = [\sum w(F_o^2 - F_c^2)^2 / \sum w(F_o^2)^2] \text{ where } w = 1/[\sigma^2(F_o^2) + (0.0421P)^2 + 28.83P] \text{ and } P = (F_o^2 + 2F_c^2)/3.$$

**Synthesis. Safety Note.** *Caution!* Perchlorate salts of metal complexes with organic ligands are potentially explosive. Only small amounts of material should be prepared, and these compounds should be handled with great care.

**[Au(L)](ClO<sub>4</sub>)<sub>3</sub>·1/2H<sub>2</sub>O.** Au(en)<sub>2</sub>Cl<sub>3</sub> was prepared as previously reported.<sup>18</sup> To a stirred methanol solution (65 mL) of Au(en)<sub>2</sub>Cl<sub>3</sub> (0.32 g), ethanolamine (0.13 mL) was added, and followed by 37% formaldehyde (0.4 mL). The mixture was heated at reflux for 10 min, filtered while hot to remove the dark precipitate of Au<sub>2</sub>O<sub>3</sub>, and then HClO<sub>4</sub> (1.0 mL) was added dropwise to the filtrate. The solution was allowed to stand at room temperature. A pale yellow precipitate [Au(L)](ClO<sub>4</sub>)<sub>3</sub>·1/2H<sub>2</sub>O formed and was filtered, washed with absolute MeOH, and dried *in vacuo*. Yield: 82%. Anal. Calcd for AuC<sub>12</sub>H<sub>30</sub>N<sub>6</sub>O<sub>14.5</sub>: C, 18.90; H, 4.07; N, 11.02. Found: C, 19.28; H, 4.16; N, 11.04.

**[Au(L)Cl<sub>2</sub>]<sub>2</sub>AuCl<sub>4</sub>.** The same template condensation procedure as above was performed, and HCl (200  $\mu$ L) was added instead of HClO<sub>4</sub> to the filtrate. The solution was allowed to stand in a refrigerator until yellow crystals formed, which were collected by filtration, washed with absolute EtOH, and dried *in vacuo*. Yield: 74%. Anal. Calcd for Au<sub>2</sub>C<sub>12</sub>H<sub>30</sub>N<sub>6</sub>O<sub>2</sub>Cl<sub>6</sub>: C, 16.66; H, 3.49; N, 9.7. Found: C, 16.99; H, 3.52; N, 9.25.

**X-ray Crystallography.** X-ray examination and data collection procedures were performed at room temperature on an Enraf-Nonius CAD-4 diffractometer. Data were collected with graphite-monochromated Mo K $\alpha$  radiation through the use of the  $\omega$  scan method. Lorentz and polarization corrections were applied to the data. An empirical absorption correction was applied to the data based on a  $\psi$ -scan method.<sup>19</sup> Of the 2025 independent reflections (0  $\leq h \leq 8$ , 0  $\leq k \leq 17$ , -13  $\leq l \leq 13$ ) measured within the 2 $\theta$  range of 4.6–50.0°, 1161 (57.3%) reflections were considered as observed with *F* > 4 $\sigma$ (*F*). The two Au atoms were located at the special positions. The positions of gold atoms were found by inspection of the Patterson synthesis, and the rest of the non-hydrogen atoms were determined by the direct method.<sup>20,21</sup> The refinement was performed on *F*<sup>2</sup> for all reflections including those generally believed to be unobserved [*F* < 4 $\sigma$ (*F*)]. The positions of all non-hydrogen atoms were refined with anisotropic displacement factors. Calculated positions of all hydrogen atoms except H(7) were allowed to ride on their bonded atoms with the isotropic displacement factors fixed with values of 1.2 times those of the bonded atoms. As the torsion angle involving H(7) could not be determined by the idealized geometry, the circular difference Fourier method using the SHELXL93 HFIX147 option was applied to locate H(7). H(7) thus found was only 1.4 Å from H(2) (*x*, 1/2 - *y*, 1/2 + *z*). The position of H(7) was refined by using the SHELXL93 HFIX83 option. All calculations were done by using the program SHELXL93.<sup>22</sup> The crystallographic data collection and refinement details are summarized

in Table 1. Complete details of the data collection and refinement process are given in Table S1 of the Supporting Information.

## Results and Discussion

**Synthesis.** Au(III) macrocyclic complexes are rare and seldom synthesized by the template condensation reaction. The Au(III) complex of **1** is the only one so far which has been prepared by the template reaction.<sup>15,16</sup> In most cases it is probable that Au(III) is reduced to metallic gold or Au<sub>2</sub>O<sub>3</sub>·*n*H<sub>2</sub>O, in a basic solution. The Au(III) complexes of macrocyclic ligand **L**, four-coordinate [Au(L)](ClO<sub>4</sub>)<sub>3</sub>·1/2H<sub>2</sub>O and six-coordinate [Au(L)Cl<sub>2</sub>]<sub>2</sub>AuCl<sub>4</sub>, were obtained in high yield in the present research from the reaction of eqs 1 and 2. Although the macrocyclic ligand **L** contains four secondary and two tertiary nitrogens as well as two pendant hydroxyl groups, only the four secondary nitrogens have coordinating ability.<sup>7</sup> The condensation reaction of eq 1 using the Au(III) template is remarkably faster than similar Ni(II) template reactions.<sup>7</sup> The former finishes macrocyclization in 10 min while the latter takes several hours to days. The crucial step of the cyclization may be the attack of the primary amine function on the -N=CH<sub>2</sub> imine bonds which are derived from the Schiff base condensation of terminal -NH<sub>2</sub> groups of coordinated ethylenediamine with formaldehyde. The electrophilicity of carbon atom in -N=CH<sub>2</sub> must be greatly enhanced by the acidic Au(III) ion coordinated at the nitrogen atom of the imine.



**Properties.** The complexes [Au(L)](ClO<sub>4</sub>)<sub>3</sub>·1/2H<sub>2</sub>O and [Au(L)Cl<sub>2</sub>]<sub>2</sub>AuCl<sub>4</sub> are soluble in water, Me<sub>2</sub>SO, and DMF and slightly soluble in MeCN. In the absence of added acid (HClO<sub>4</sub> or HCl), both complexes are unstable in water where they decompose slowly to Au<sub>2</sub>O<sub>3</sub> and/or metallic gold. The infrared, UV/vis, <sup>13</sup>C NMR, and conductance data are summarized in Table 2. The infrared spectra (Nujol mull) of [Au(L)](ClO<sub>4</sub>)<sub>3</sub>·1/2H<sub>2</sub>O and [Au(L)Cl<sub>2</sub>]<sub>2</sub>AuCl<sub>4</sub> showed  $\nu_{\text{OH}}$  of hydroxyl pendant groups at 3300 and 3325 cm<sup>-1</sup>, respectively, and  $\nu_{\text{NH}}$  of secondary amines at 3125 cm<sup>-1</sup> and at 2990 cm<sup>-1</sup>, respectively. The spectrum of [Ni(L)](ClO<sub>4</sub>)<sub>2</sub> showed  $\nu_{\text{OH}}$  at 3520 cm<sup>-1</sup> and  $\nu_{\text{NH}}$  at 3205 cm<sup>-1</sup>.<sup>7</sup> The low  $\nu_{\text{OH}}$  and  $\nu_{\text{NH}}$  values of the Au(III) complexes indicate that the pendant hydroxyl groups and secondary amines are extensively involved in hydrogen bonds, which is revealed by the crystal structure of [Au(L)Cl<sub>2</sub>]<sub>2</sub>AuCl<sub>4</sub>.

The value of molar conductance for [Au(L)Cl<sub>2</sub>]<sub>2</sub>AuCl<sub>4</sub> corresponds to a 1:3 electrolyte instead of 1:1,<sup>23</sup> indicating that the axial chlorides dissociate in Me<sub>2</sub>SO to give [Au(L)]<sup>3+</sup> species. Similar observation was made with the six-coordinate

(18) Block, B. P.; Bailar, J. C., Jr. *J. Am. Chem. Soc.* **1951**, *73*, 4722.

(19) North, A. C. T.; Philips, D. C.; Mathews, F. S. *Acta Crystallogr.* **1968**, *A24*, 321.

(20) Beurkens, P. T.; Noordick, J. H. *Acta Crystallogr.* **1971**, *A27*, 187.

(21) Beurkens, P. T.; Admiral, G.; Beurkens, G.; Bosman, W. P.; Garcia-Granda, S.; Gould, R. O.; Smits, J. M. M.; Smykalla, C. *The DIRDIF Program System. Technical Report of Crystallography Laboratory*; University of Nijmegen: Nijmegen, The Netherlands, 1992.

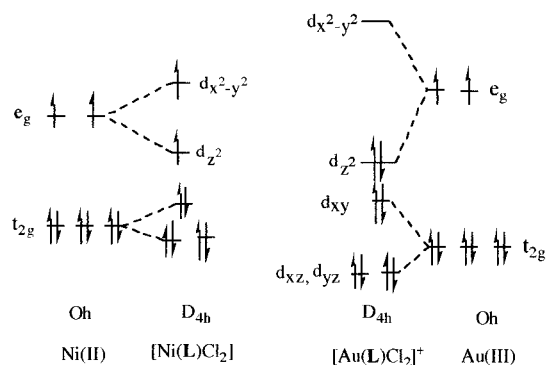
(22) Sheldrick, G. M. *SHELXL93. Program for the Refinement of Crystal Structures*; University of Gottingen: Gottingen, Germany, 1993.

(23) Geary, W. J. *Coord. Chem. Rev.* **1971**, *7*, 81.

**Table 2.** Properties of Au(III) Macrocyclic Complexes

compd	IR <sup>a</sup> cm <sup>-1</sup>		UV/vis $\lambda_{\text{Max}}$ , nm ( $\epsilon$ )	$\Lambda_{\text{M}}$ , $\Omega^{-1}$ cm <sup>-1</sup> M <sup>-1</sup>	<sup>13</sup> C NMR <sup>e</sup> $\delta$ , ppm			
	$\nu_{\text{NH}}$	$\nu_{\text{OH}}$			N—C—C—N	N—C—C—O	C—C—OH	N—C—N
[Au(L)](ClO <sub>4</sub> ) <sub>3</sub> ·1/2H <sub>2</sub> O	3125	3300	364 (660), <sup>b</sup> 389 (1800) <sup>c</sup>	213 <sup>d</sup>	52.0	52.3	59.1	68.7
[Au(L)Cl <sub>2</sub> ]AuCl <sub>4</sub>	2990	3325	324 (4500), 258 (6700) <sup>b</sup>	84 <sup>b</sup>	51.9	52.0	58.8	68.0

<sup>a</sup> Measured with Nujol mull. <sup>b</sup> Measured in Me<sub>2</sub>SO. <sup>c</sup> Measured in MeCN. <sup>d</sup> Measured in DMF. <sup>e</sup> Measured in Me<sub>2</sub>SO-*d*<sub>6</sub>.

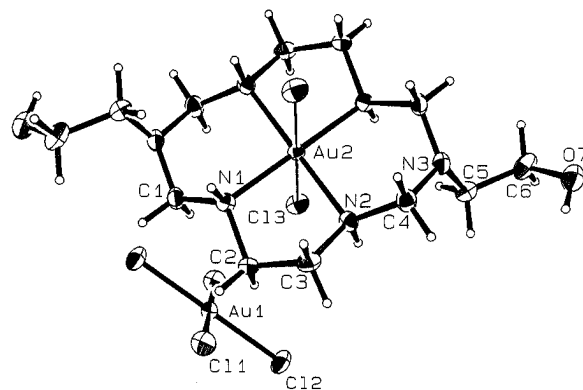
**Chart 1**

Ni(II) complex, [Ni(L)Cl<sub>2</sub>], in which axial Cl<sup>-</sup> ions were dissociated in H<sub>2</sub>O.<sup>7</sup> <sup>13</sup>C NMR spectrum of [Au(L)Cl<sub>2</sub>]AuCl<sub>4</sub> measured in Me<sub>2</sub>SO-*d*<sub>6</sub> is virtually same as that of [Au(L)]-(ClO<sub>4</sub>)<sub>3</sub>·1/2H<sub>2</sub>O due to the dissociation of axial chlorides.

The electronic absorption spectrum of [Au(L)](ClO<sub>4</sub>)<sub>3</sub>·1/2H<sub>2</sub>O is different from that of [Au(L)Cl<sub>2</sub>]AuCl<sub>4</sub> in Me<sub>2</sub>SO. For [Au(L)Cl<sub>2</sub>]AuCl<sub>4</sub>, the intense chromophore AuCl<sub>4</sub><sup>-</sup> dominates and the spectrum of the Au(III) macrocycle is obscure. The spectrum of [Au(L)](ClO<sub>4</sub>)<sub>3</sub>·1/2H<sub>2</sub>O measured in Me<sub>2</sub>SO is different from that measured in MeCN. This may be attributed to the fact that [Au(L)]<sup>3+</sup> interacts with the donating solvent molecules or to different degrees of deprotonation of the secondary amines in these solvents. The secondary amine in [Au(cyclam)]<sup>3+</sup> complex is deprotonated in aqueous solution, with a pK<sub>a</sub> value of 5.4.<sup>13</sup>

Magnetic susceptibilities measured for the solid samples of [Au(L)](ClO<sub>4</sub>)<sub>3</sub>·1/2H<sub>2</sub>O and [Au(L)Cl<sub>2</sub>]AuCl<sub>4</sub> indicate that they both are diamagnetic. The molar magnetic susceptibility ( $\chi_{\text{M}}$ ) value for [Au(L)Cl<sub>2</sub>]AuCl<sub>4</sub> is  $-67.11 \times 10^{-6}$  emu at 292 K. It is quite unusual that the six-coordinate Au(III) complex is diamagnetic. If the complex were in a perfect octahedral geometry, it should be paramagnetic with two unpaired electrons. However, the Au(III) ion causes strong ligand field splitting because of the high oxidation state and heavy metal character, and the perfect octahedral structure must be unstable since two electrons should occupy e<sub>g</sub> orbitals of high energy state. Therefore, the tetragonal distortion will occur to split the e<sub>g</sub> orbitals, which makes the Au(III) complex diamagnetic (Chart 1).

**Crystal Structure of [Au(L)Cl<sub>2</sub>]AuCl<sub>4</sub>.** An ORTEP<sup>24</sup> view of the complex is shown in Figure 1. Tables 3 and 4 show the selected fractional coordinates and bond distances and angles. The macrocyclic cation possesses an inversion center at the gold atom. The Au(III) ion is coordinated with four secondary nitrogens of the macrocycle and two chloride ions. The complex incorporates the hydroxyethyl pendants onto the bridgehead nitrogens, but neither the pendant hydroxyl groups nor the bridgehead nitrogens of the macrocycle are coordinated to the Au(III) ion. In the [Au(L)Cl<sub>2</sub>]<sup>+</sup> cation, the bond distances of Au—N and Au—Cl, averaging 2.049(8) and 3.097(4) Å, respectively, indicate severe tetragonal distortion of the complex.

**Figure 1.** ORTEP drawing of [Au(L)Cl<sub>2</sub>]AuCl<sub>4</sub> with the atomic numbering scheme. Thermal ellipsoids are drawn at the 30% probability level.**Table 3.** Fractional Atomic Coordinates ( $\times 10^4$ ) and Equivalent Isotropic Displacement Parameters ( $\text{\AA}^2 \times 10^3$ ) for [Au(L)Cl<sub>2</sub>]AuCl<sub>4</sub>

atom	x	y	z	U(eq) <sup>a</sup>
Au(1)	0	0	0	41(1)
Au(2)	5000	0	5000	26(1)
Cl(1)	2910(7)	721(3)	249(5)	62(1)
Cl(2)	-1599(7)	1321(3)	25(5)	63(1)
Cl(3)	978(5)	-12(3)	3385(4)	46(1)
N(1)	6494(16)	-33(8)	3563(10)	31(2)
N(2)	5123(17)	1367(8)	4828(11)	32(3)
N(3)	4032(19)	1643(9)	6772(12)	41(3)
C(1)	5832(23)	-776(10)	2689(14)	38(4)
C(2)	6358(24)	889(10)	3007(14)	37(4)
C(3)	6638(23)	1550(11)	4029(14)	42(4)
C(4)	5451(22)	1826(11)	6019(14)	40(4)
C(5)	2065(22)	1994(11)	6398(15)	42(4)
C(6)	1134(23)	2281(11)	7484(17)	50(5)
O(7)	2018(17)	3016(8)	8105(11)	57(3)

<sup>a</sup> Equivalent isotropic displacement parameter,  $U(\text{eq})$ , is defined as one-third of the trace of the orthogonalized  $U_{ij}$  tensor.

The average Au—N bond distance is comparable to 2.04 Å for the square-planar [Au(cyclam)](ClO<sub>4</sub>)<sub>1.5</sub>(NO<sub>3</sub>)<sub>1.5</sub>·H<sub>2</sub>O complex,<sup>14</sup> but it is significantly longer than that (1.98 Å) of a four-coordinate Au(III)  $\beta$ -diiminate, **1**.<sup>16</sup> Compared with that for the six-coordinate Ni(II) complex [Ni(cyclam)Cl<sub>2</sub>],<sup>25</sup> it is ca. 0.02 Å shorter although the covalent radius (1.50 Å) of Au(III) is larger than that (1.16 Å) of Ni(II). Apparently, the Au(III) ion in [Au(L)Cl<sub>2</sub>]<sup>+</sup> complex has no electron density in  $d_{x^2-y^2}$  orbital of the tetragonal field ( $D_{4h}$ ) because of the strong ligand field strength while the Ni(II) ion in [Ni(cyclam)Cl<sub>2</sub>] has a singly occupied  $d_{x^2-y^2}$  orbital (Chart 1). The Au—Cl bond distance of the macrocyclic cation is ca. 0.8 Å longer than that [average 2.275(3) Å] of AuCl<sub>4</sub><sup>-</sup> counteranion<sup>26–28</sup> and it is even longer than the normal bonding criterion of 2.90 Å. However, it is significantly shorter than the sum of van der Waals radii of Au and Cl (1.66 + 1.75 = 3.41 Å).<sup>29</sup> Moreover, the two Cl<sup>-</sup> ions locate exactly above and below the Au(III) ion and the

(24) Johnson, C. K. *ORTEPII*; Report ORNL-5138; Oak Ridge National Laboratory: Oak Ridge, TN, 1976.

(25) Ito, T.; Kato, M.; Ito, H. *Bull. Chem. Soc. Jpn.* **1984**, *57*, 2641.

(26) Drew, M. G. B.; Glaves, L. R.; Hudson, M. J. *J. Chem. Soc., Dalton Trans.* **1985**, 771.

(27) Hollis, L. H.; Lippard, S. J. *J. Am. Chem. Soc.* **1983**, *105*, 4293.

(28) Wang, S. N.; Fackler, J. P. *Organometallics* **1990**, *9*, 111.

(29) Bondi, A. J. *Phys. Chem.* **1964**, *68*, 441.

**Table 4.** Bond Distances (Å) and Angles (deg) for [Au(L)Cl<sub>2</sub>]<sup>+</sup>AuCl<sub>4</sub><sup>-</sup>

Au(1)–Cl(1)	2.280(5)	N(2)–C(3)	1.51(2)
Au(1)–Cl(2)	2.271(4)	N(3)–C(4)	1.42(2)
Au(2)–Cl(3)	3.097(4)	N(3)–C(1)′	1.42(2)
Au(2)–N(1)	2.043(11)	N(3)–C(5)	1.47(2)
Au(2)–N(2)	2.055(12)	C(2)–C(3)	1.50(2)
N(1)–C(1)	1.50(2)	C(5)–C(6)	1.52(2)
N(1)–C(2)	1.51(2)	C(6)–O(7)	1.39(2)
N(2)–C(4)	1.48(2)		
Cl(1)–Au(1)–Cl(2)	91.1(2)	C(4)–N(2)–Au(2)	112.3(9)
Cl(1)–Au(1)–Cl(2)′′	88.9(2)	C(4)–N(2)–C(3)	114.8(12)
Cl(3)–Au(2)–N(1)	94.1(3)	C(4)–N(3)–C(1)′	114.7(13)
Cl(3)–Au(2)–N(1)′	85.9(3)	C(4)–N(3)–C(5)	118.0(13)
Cl(3)–Au(2)–N(2)	89.9(4)	C(1)′–N(3)–C(5)	116.3(13)
Cl(3)–Au(2)–N(2)′	90.1(4)	N(3)–C(1)–N(1)	113.9(12)
N(1)–Au(2)–N(2)	85.2(5)	C(3)–C(2)–N(1)	107.3(12)
N(1)–Au(2)–N(2)′	94.8(5)	C(2)–C(3)–N(2)	107.9(12)
C(1)–N(1)–C(2)	114.6(11)	N(3)–C(4)–N(2)	114.5(12)
C(1)–N(1)–Au(2)	112.5(9)	N(3)–C(5)–C(6)	111.7(13)
C(2)–N(1)–Au(2)	107.0(9)	O(7)–C(6)–C(5)	114.1(14)
C(3)–N(2)–Au(2)	106.2(9)		

<sup>a</sup> Symmetry transformations used to generate equivalent atoms: prime,  $-x + 1$ ,  $-y$ ,  $-z + 1$ ; double prime,  $-x$ ,  $-y$ ,  $-z$ .

Cl–Au–Cl axis is almost perpendicular to the coordination plane with an average Cl–Au–N angle of 92.1°. Therefore, Au–Cl is regarded as the bonding interaction, and thus the Au(III) macrocyclic unit is described as a tetragonally distorted octahedral complex. The Au(III) ion generally forms square-planar complexes and no six-coordinate Au(III) macrocyclic complex has been reported so far. However, a few classical compounds such as *trans*-[Au(diars)<sub>2</sub>I<sub>2</sub>]<sup>+</sup>I<sup>-</sup> and [Au(dien)Cl<sub>3</sub>] are known to be six-coordinate.<sup>30–32</sup> In *trans*-[Au(diars)<sub>2</sub>I<sub>2</sub>]<sup>+</sup>I<sup>-</sup>,<sup>31</sup> the Au–I bond distance is 3.35 Å, which is 0.62 Å longer than the sum of the radii of Au and I atoms (1.40 + 1.33 = 2.73 Å). In [Au(dien)Cl<sub>3</sub>],<sup>32</sup> the Au–Cl(axial) bond distances are 3.121(4) and 3.183(3) Å, which are longer than 3.097(4) Å of the present complex, while the Au–Cl(equatorial) bond distance is 2.278(3) Å.

The macrocyclic ligand in [Au(L)Cl<sub>2</sub>]<sup>+</sup> adopts thermodynamically the most stable *R,R,S,S*-(*trans* III) configuration.<sup>33</sup> The five-membered chelate rings assume a guache conformation and the six-membered ones adopt a chair conformation. The bite distances of the five-membered and six-membered chelate rings are 2.775(17) and 3.017(16) Å, respectively. The bite angles of five-membered and six-membered chelate rings are 85.2(5) and 94.8(5)°, respectively. The average N–C bond distance and the average C–N–C angle involving uncoordinated bridgehead tertiary nitrogen N(3) are 1.44(1) Å and 116(8)°,

respectively, which indicates the partial contribution of sp<sup>2</sup> hybridization for the tertiary nitrogens. The shortening of the bonds and flattening of the bond angles involving the uncoordinated bridgehead tertiary amine have been commonly observed in other complexes.<sup>1–7,34</sup>

In accordance with the IR spectra, the secondary amine hydrogens of the macrocycle form hydrogen bonds with the hydroxyl oxygen and the axial Cl<sup>-</sup> of the neighboring complexes: N(2)–H(2)–O(7)<sup>i</sup>, 2.82(2) Å; ∠N(2)–H–O(7)<sup>i</sup>, 160°, and N(1)–H(1)–Cl(3)<sup>ii</sup>, 3.17(1) Å; ∠N(1)–H–Cl(3)<sup>ii</sup>, 143°. For the AuCl<sub>4</sub><sup>-</sup> anion, the average Au–Cl bond distance is 2.275(3) Å, which is comparable to the values reported previously.<sup>26–28</sup> The AuCl<sub>4</sub><sup>-</sup> anion does not interact with any atoms of the macrocyclic cation. The closest contact between anion and the cation is 3.731(4) Å, between Au(1) of AuCl<sub>4</sub><sup>-</sup> and Cl(3) of [Au(L)Cl<sub>2</sub>]<sup>+</sup>.

## Conclusions

We have shown that Au(III) macrocyclic complexes can be synthesized in high yield by a direct template condensation reaction of formaldehyde and amines, and the Au(III) template cyclization is extremely fast. The Au(III) macrocyclic complexes thus prepared are four-coordinate [Au(L)](ClO<sub>4</sub>)<sub>3</sub>·1/2H<sub>2</sub>O and six-coordinate [Au(L)Cl<sub>2</sub>]<sup>+</sup>AuCl<sub>4</sub><sup>-</sup>. The complexes incorporate the hydroxyethyl pendants onto the bridgehead nitrogens but hydroxyl groups are not involved in the intra- or intermolecular coordination. Although the complex [Au(L)Cl<sub>2</sub>]<sup>+</sup>AuCl<sub>4</sub><sup>-</sup> is diamagnetic, the structure around the Au(III) ion is a severely distorted octahedral geometry, composed of four secondary nitrogens and two chlorides. The secondary amine hydrogens form hydrogen bonds with the coordinated chloride and the hydroxyl oxygen of the neighboring complexes. It is likely that other Au(III) macrocyclic complexes may be synthesized by template condensation reactions, and some of them may be isolated as the six-coordinate form.

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**Supporting Information Available:** Tables S1–S4, listing complete crystallographic details, anisotropic displacement parameters, hydrogen atom positions, and bond distances and angles involving hydrogen atoms for [Au(L)Cl<sub>2</sub>]<sup>+</sup>AuCl<sub>4</sub><sup>-</sup>, and Figures S1–S5, showing a stereoview of the unit cell packing of [Au(L)Cl<sub>2</sub>]<sup>+</sup>AuCl<sub>4</sub><sup>-</sup> and <sup>13</sup>C and <sup>1</sup>H NMR spectra of [Au(L)](ClO<sub>4</sub>)<sub>3</sub>·1/2H<sub>2</sub>O and [Au(L)Cl<sub>2</sub>]<sup>+</sup>AuCl<sub>4</sub><sup>-</sup> (12 pages). Ordering information is given on any current masthead page.

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(30) King, R. B., Ed. *Encycl. Inorg. Chem.* **1994**, 3, 1324.

(31) Duckworth, V. F.; Stephenson, N. C. *Inorg. Chem.* **1969**, 8, 1661.

(32) Elder, R. C.; Watkins, J. W., II. *Inorg. Chem.* **1986**, 25, 223.

(33) Hancock, R. D. *Acc. Chem. Res.* **1990**, 23, 253.

(34) Kim, J.; Suh, M. P.; Shin, W. *Acta Crystallogr.* **1991**, C47, 745.

(35) The symmetry transformations are as follows: i,  $x$ ,  $1/2 - y$ ,  $-1/2 + z$ ; ii,  $1 + x$ ,  $y$ ,  $z$ .