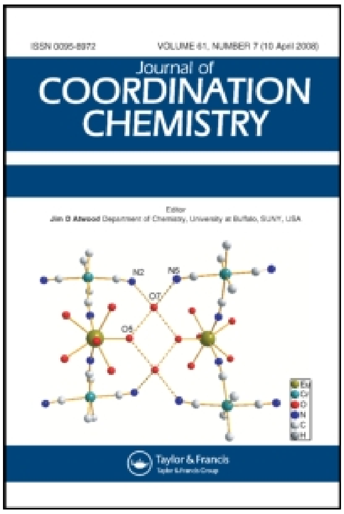

Journal of Coordination Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713455674

GOLD(III)-CYCLAM COMPLEXES. X-RAY CRYSTAL STRUCTURE AND A USEFUL MACROCYCLIC EFFECT ON THE REDUCTION OF GOLD(III)

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To cite this Article Kimura, Eiichi , Kurogi, Yasuhisa , Koike, Tohru , Shionoya, Mitsuhiko and Iitaka, Yoichi(1993) 'GOLD(III)-CYCLAM COMPLEXES. X-RAY CRYSTAL STRUCTURE AND A USEFUL MACROCYCLIC EFFECT ON THE REDUCTION OF GOLD(III)', Journal of Coordination Chemistry, 28: 1, 33 — 49
To link to this Article: DOI: 10.1080/00958979308035142
URL: http://dx.doi.org/10.1080/00958979308035142

J. Coord. Chem., 1993, Vol. 28, pp. 33–49
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GOLD(III)-CYCLAM COMPLEXES. X-RAY CRYSTAL STRUCTURE AND A USEFUL MACROCYCLIC EFFECT ON THE REDUCTION OF GOLD(III)

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(*Received March 23, 1992; in final form May 8, 1992*)

The X-ray crystal structure of the Au^{III}-cyclam complex **1** shows a four-coordinate square-planar N_4 geometry with the *trans* III conformation (or *RRSS* configuration) of cyclam and an average Au^{III}-N bond distance of 2.04 Å. A block-diagonal-matrix least-squares refinement yielded a final R value of 0.069 for 2463 independent reflections. Crystals of $\mathbf{1}\cdot(NO_3)_{1.5}(ClO_4)_{1.5}\cdot H_2O$ ($C_{10}H_{26}N_{5.5}O_{11.5}AuCl_{1.5}$) are triclinic, space group $P1$ with $a = 15.148(8)$, $b = 8.668(5)$, $c = 8.267(5)$ Å, $\alpha = 109.17(6)$, $\beta = 101.08(5)$, $\gamma = 82.08(4)$ Å, $V = 1003(1)$ Å^3, $d_{calcd} = 2.177$ g cm^{-3}, and $Z = 2$. The reduction potential for Au^{III} in **1** to Au^0 varies with pH: −0.16 V *vs* SCE (pH 1.0) to −0.55 V (pH 9.0) at $I = 0.50$ ($NaClO_4$) and 25°C, according to the degree of cyclam NH deprotonation. The macrocyclic gold(III) complex **1** has been found to possess very useful electrochemical properties for a novel gold-plating agent. The new properties of gold(III)-cyclam complexes have been characterized by the tetrafluorinated cyclam **7**, tetramethylcyclam **8**, and aminocyclam **9**. Dissociation of two protons from the macrocyclic NH amines in **7** readily occurs with extremely low pK_a values of 1.6 and 6.5 at 25°C and $I = 0.10$ ($NaClO_4$). Cyclic and dc polarograms of **8** in DMF (25°C, $I = 0.10$; Et_4NClO_4) show the $Au^{III/II}$ quasi-reversible reduction wave at $E_{1/2} = +0.18$ V *vs* SCE.

Keywords: Gold(III)-cyclam complexes, X-ray structure, gold-plating

INTRODUCTION

Recently, we synthesized the first saturated macrocyclic polyamine complexes of gold, the Au(III)-1,4,8,11-tetraazacyclotetradecane (cyclam) complex **1** and its homologues, by which the characteristic acidity of d^8 Au^{III} ion is well demonstrated (*e.g.*, $\mathbf{1} \rightleftharpoons \mathbf{2}$, see equation (*1*)).[1] It was found that the saturated macrocyclic tetraamines with their unique acid-base properties were the first useful chelating agents to be

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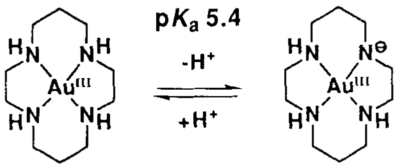
* Author for correspondence.

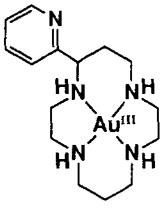
selective for Au^{III} over Cu^{II}, Fe^{III}, Co^{II} and Pd^{II} ions. A four-coordinate square-planar cyclam structure for **1** has been assigned mainly on the basis of ^1H and ^{13}C NMR data.



1 **2**

(1)

We now have succeeded in obtaining a good single crystal of **1** with mixed counteranions $(NO_3)_{1.5}(ClO_4)_{1.5}$, and have undertaken its X-ray structure analysis. We also have investigated the electrochemistry of **1** and its relevant Au^{III} complexes **3** and **4** at various pH values.[1] Coordination with macrocyclic polyamine ligands is known to dramatically affect the redox properties of transition-metal ions: *e.g.*, otherwise unstable Ni^I,[2] Ni^{III},[3] Ag^{II},[4] or Ag^{III}[5] are greatly stabilized. The novel electrochemical behaviour of Au^{III}-cyclam **1** has been disclosed in comparison to homologous linear polyamine complexes **5**[6] and **6**.[7] In **1** and its derivatives **3** and **4**, Au^{III} is more stabilized (with respect to Au^0) by the "macrocyclic effect" than in the linear homologue complexes **5** and **6**. The special Au(III) reduction properties would make **1** an excellent and pollution-free gold-plating agent.



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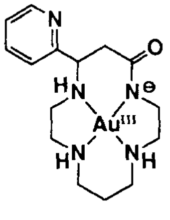

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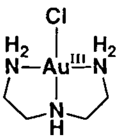

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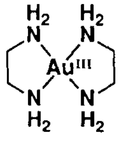

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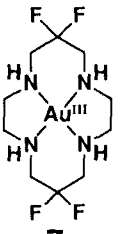
In addition, in order to further explore properties of Au(III), we have synthesized new Au(III) macrocyclic polyamine complexes **7**, **8** and **9** with tetrafluorinated cyclam (6,6,13,13-tetrafluoro-1,4,8,11-tetraazacyclotetradecane),[8] tetramethylcyclam (1,4,8,11-tetramethyl-1,4,8,11-tetraazacyclotetradecane),[9] and aminocyclam (6-amino-1,4,8,11-tetraazacyclotetradecane),[10] respectively. Significantly lowered pK_a values of NH for **7**, a new Au(III/II) redox couple with **8** in DMF, and a rare zwitterionic form for **9** at neutral pH have been disclosed.



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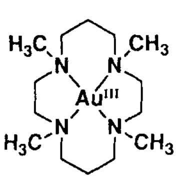

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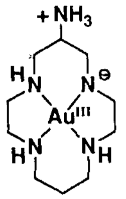

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EXPERIMENTAL

Materials

All materials were of analytical reagent grade and were used without further purification. HEPES (*N*-(2-hydroxyethyl)piperazine-*N*′-3-propanesulfonic acid) was purchased from DOJINDO Lab. and used without further purification. Tetrafluorinated cyclam (6,6,13,13-tetrafluoro-1,4,8,11-tetraazacyclotetradecane),[8] tetramethyl cyclam (1,4,8,11-tetramethyl-1,4,8,11-tetraazacyclotetradecane),[9] aminocyclam (6-amino-1,4,8,11-tetraazacyclotetradecane),[10] **3**$\cdot(ClO_4)_3\cdot HClO_4$,[1] **4**$\cdot(ClO_4)_2\cdot HClO_4$,[1] $Au^{III}(dien)Cl_3$ **5**$\cdot Cl_2$,[6] and $Au^{III}(en)_2Cl_3$ **6**$\cdot Cl_3$[7] ("dien" and "en" are 1,5-diamino-3-azapentane and 1,2-diaminoethane, respectively) were synthesized by the reported methods.

Preparation of Au^III Cyclam Complexes

Au^{III}-cyclam(1).

The procedure in the synthesis of Au^{III}-1,4,8,11-tetraazacyclotetradecane (Au^{III}-cyclam) as $Cl\cdot(ClO_4)_2$ salts reported earlier[1] was improved. Cyclam (200 mg, 1.0 mmol) and $NaAuCl_4\cdot 2H_2O$ (398 mg, 1.0 mmol) in 190 cm^3 of CH_3CN and 10 cm^3 of EtOH were heated at reflux for 1 h. After cooling the solution to room temperature, 10 cm^3 of aqueous 0.1 M HCl solution was added and then insoluble materials (Au^0 *etc.*) were filtered off. After concentrating the filtrate, the residue was purified by Dowex 50X4 cation exchange column chromatography (eluant: aqueous 3 M HCl). The obtained solid was recrystallized from 1 M aqueous $HClO_4$ solution as yellow needles of Au^{III}-cyclam$\cdot Cl\cdot(ClO_4)_2$ in 60% yield.

A single crystal suitable for X-ray analysis was obtained by recrystallization of Au^{III}-cyclam-$Cl\cdot(ClO_4)_2$ (100 mg) from aqueous 1 M HNO_3 solution. Colourless prisms of Au^{III}-cyclam as $(ClO_4)_{1.5}(NO_3)_{1.5}$ salts were obtained in 50% yield. Anal.

Calcd. for $C_{10}H_{24}N_4Au(ClO_4)_{1.5}(NO_3)_{1.5}\cdot H_2O$: C, 18.27; H, 3.99; N, 11.72%. Found: C, 18.58; H, 4.13; N, 12.05%. ^{1}H NMR (1 M DCl/D_2O): δ 1.9–2.0 (2H, m, CCH_2C), 2.41–2.57 (2H, m, CCH_2C), 3.1–3.2 (8H, m, NCH_2C), 3.2–3.4 (8H, m, NCH_2C). IR (KBr pellet): 3403 (s), 3170 (s), 1385 (vs), 1163 (m), 1121 (m), 1096 (s), 1059 (vs), 1032 (s), 889 (m), 826 (s), 627 (m) cm^{-1}.

Au^{III}-tetrafluorinated cyclam (*7*)

Tetrafluorinated cyclam (6,6,13,13-tetrafluoro-1,4,8,11-tetraazacyclotetradecane; 68 mg, 0.25 mmol) and $NaAuCl_4\cdot 2H_2O$ (100 mg, 0.25 mmol) in 50 cm^3 of CH_3CN were stirred for 1 h, and insoluble materials (Au^0 *etc.*) were filtered off. After concentration of the filtrate, recrystallization from 1 M aqueous $HClO_4$ solution afforded yellow needles of the Au^{III} complex as its $Cl\cdot(ClO_4)_2\cdot H_2O$ salt in 23% yield. Anal. Calcd. for $C_{10}H_{22}N_4F_4Au\cdot Cl\cdot(ClO_4)_2\cdot H_2O$: C, 16.67; H, 3.08; N, 7.77%. Found: C, 16.54; H, 3.22; N, 7.78%. ^{1}H NMR (1 M DCl/D_2O): δ 3.2–3.4 (8H, m, NCH_2C), 3.5–3.7 (8H, m, NCH_2C). IR (KBr pellet): 3461 (s), 3357 (s), 2986 (s), 2820 (s), 1447 (m), 1406 (m), 1343 (s), 1321 (m), 1144 (vs), 1123 (vs), 1090 (vs), 1055 (vs), 1011 (s), 947 (m), 891 (s), 818 (m), 627 (s) cm^{-1}.

Au^{III}-tetramethylcyclam(*8*)

Tetramethylcyclam (1,4,8,11-tetramethyl-1,4,8,11-tetraazacyclotetradecane; 256 mg, 1.0 mmol) and $NaAuCl_4\cdot 2H_2O$ (400 mg, 1.0 mmol) in 50 cm^3 of CH_3CN and 10 cm^3 of CH_3OH were stirred for 2 h at room temperature, and insoluble materials were filtered off. After concentration of the filtrate, recrystallization from 1 M aqueous $HClO_4$ solution afforded yellow needles of the Au^{III} complex as its $Cl\cdot(ClO_4)_2$ salt in 23% yield. Anal. Calcd. for $C_{14}H_{32}N_4Au\cdot Cl\cdot(ClO_4)_2$: C, 24.45; H, 4.69; N, 8.14%. Found: C, 24.39; H, 4.68; N, 7.96%. ^{1}H NMR (1 M DCl/D_2O): δ 2.5–2.9 (4H, m, CCH_2C), 3.25 (12H, s, CH_3), 3.6–3.9 (8H, m, NCH_2C), 4.1–4.4 (8H, m, NCH_2C). IR (KBr pellet): 3424 (m), 3005 (m), 2787 (m), 1471 (m), 1096 (vs), 1032 (m), 1005 (m), 951 (m), 845 (m), 790 (m), 750 (m), 625 (s), cm^{-1}.

Au^{III}-aminocyclam (*9*)

Aminocyclam (6-amino-1,4,8,11-tetraazacyclotetradecane; 224 mg, 1.0 mmol) and $NaAuCl_4\cdot 2H_2O$ (400 mg, 1.0 mmol) in 20 cm^3 of CH_3CN were heated at reflux for 1 h, after which 10 cm^3 of 0.1 M HCl aqueous solution was added, and insoluble materials (Au^0, *etc.*) were filtered off. After concentration of the filtrate, the residue was purified by Dowex 50X4 ion exchange column chromatography (eluant: 3 M HCl), and recrystallization from 1 M $HClO_4$ aqueous solution afforded colorless needles of the Au^{III} complex as its $4ClO_4$ salt in 20% yield. Anal. Calcd. for $C_{10}H_{26}N_5Au\cdot(ClO_4)_4$: C, 14.81; H, 3.23; N, 8.63. Found: C, 14.67; H, 3.48; N, 8.47. ^{1}H NMR (1 M DCl/D_2O): δ 1.8–2.0 (2H, m, CCH_2C), 3.0–3.3 (16H, m, NCH_2C), 3.39 (1H, br, H_2NCH). IR (KBr pellet): 3414 (s), 2832 (s), 1449 (m), 1144 (vs), 1117 (vs), 1008 (vs), 885 (m), 627 (s), cm^{-1}.

Potentiometric Titration

pH Titrations were carried out at 25.0 ± 0.1°C and $I = 0.10$ ($NaClO_4$). All solutions were deaerated in a stream of pure argon gas (>99.999%). The preparation of the test solutions and the calibration of the electrode system (Orior 811 pH meter) have been described earlier.[11] The calculation method for the deprotonation constants is the same as determined earlier.[11]

Spectrophotometry

^1H NMR (400 MHz) spectra were recorded on a JEOL GX-400 spectrometer, and 3-(trimethylsilyl)-propionic-2,2,3,3-d_4 acid (sodium salt) was used as internal reference. IR and electronic spectra were recorded on a Shimadzu FTIR-4200 and a Hitachi U-3200 spectrophotometer, respectively. Atomic absorption spectra were measured on a Shimadzu AA-646 spectrophotometer, where NaCl for the supporting electrolyte and HCl buffer were used instead of the potentially explosive $NaClO_4$ and $HClO_4$.

X-ray Structure Determination

An approximately equidimensional crystal of **1**$\cdot(ClO_4)_{1.5}(NO_3)_{1.5}\cdot H_2O$ with diameter 0.13 mm was used for data collection. The lattice parameters and intensity data were measured on a Philips PW1100 diffractometer with graphite monochromated Mo Kα radiation at room temperature. Crystal data and data collection parameters are given in Table I. The structure was solved by the heavy-atom method and refined anisotropically by block-diagonal-matrix least-squares methods to the final R value of 0.069. All the hydrogen atoms could not be located in a difference electron density map. The molecular structure is illustrated in Figure 1 by ORTEP drawings with 30% probability thermal ellipsoids. A perspective view of two molecules of Au^{III}-cyclam **1**, counter anions and two water molecules in the unit cell with the observed strong hydrogen bonds (<3 Å) is shown in Figure 2. Atomic positional parameters are given together with their equivalent isotropic temperature

TABLE I
Summary of crystallographic parameters for **1**$\cdot(ClO_4)_{1.5}(NO_3)_{1.5}\cdot H_2O$

formula	$C_{10}H_{26}N_{5.5}O_{11.5}Cl_{1.5}Au$
formula weight	657.5
crystal system	triclinic
space group	$P1$
cryst colour	colorless
cell dimens	
a, b, c, Å	15.148(8), 8.668(5), 8.267(5)
α, β, γ, deg	109.16(6), 101.08(5), 82.08(4)
V, Å^3	1003(1)
Z	2
d_{calcd}, g cm^{-3}	2.177
cryst diameter, mm	0.13
radiation	Mo Kα
μ, cm^{-1}	75.9
$2\theta_{max}$, deg	44
refinement	block-diagonal-matrix least-squares
no. of measd reflcns	4938
no. of used reflcns ($\|F_0\| > 3\sigma(F_0)$)	2463
R	0.069
R_W	0.079

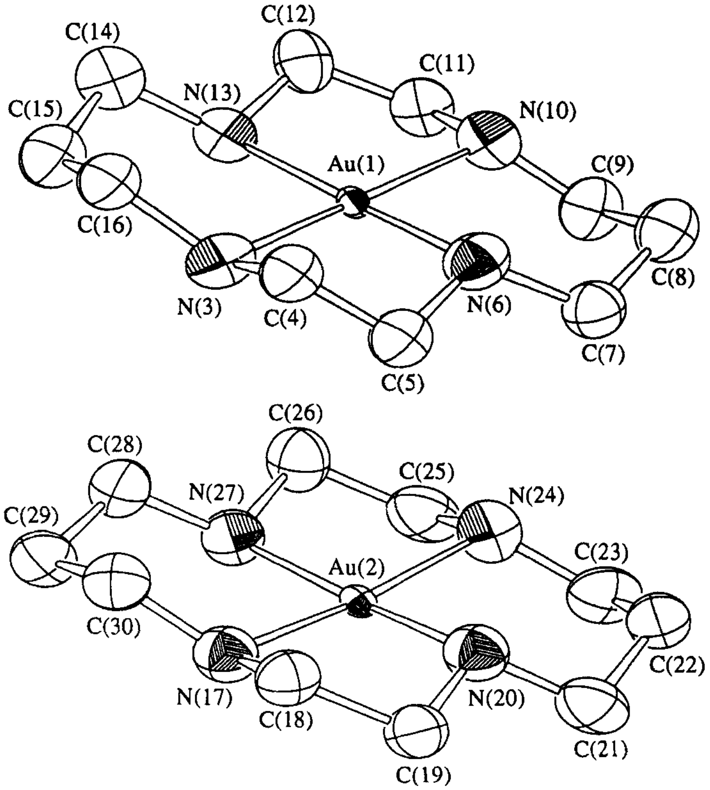


FIGURE 1 ORTEP drawings of two molecules of 1 in the unit cell; (a) Au(1)-cyclam, (b) Au(2)-cyclam. The counter anions and two water molecules are omitted for clarity. Atoms are drawn with 30% probability ellipsoids.

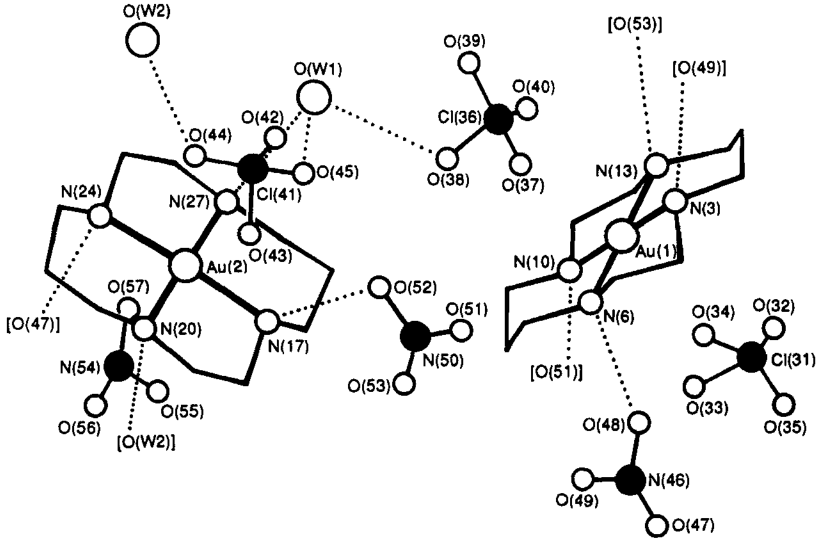


FIGURE 2 A perspective view of two molecules of 1, counter anions and two water molecules in the unit cell. The strong hydrogen bonds (<3 Å) are shown as dotted lines.

TABLE II

Fractional coordinates ($\times 10^4$) and equivalent isotropic temperature factors (Å^2) for $1\cdot(ClO_4)_{1.5}(NO_3)_{1.5}\cdot H_2O$

Atom	*x/a*	*y/b*	*z/c*	B_{eq}[a]
Au(1)	2572.1(0)	7477.1(0)	7073.9(0)	2.07(0.02)
Au(2)	7565.8(25)	2518.1(38)	2074.5(51)	2.11(0.02)
N(3)	1699.2(2)	8765.0(6)	5720.5(5)	5(1)
C(4)	1193.1(4)	7418.4(8)	4225.5(8)	6(1)
C(5)	1951.6(4)	6320.9(8)	3508.1(8)	6(1)
N(6)	2428.1(4)	5586.3(7)	4971.5(7)	7(1)
C(7)	3249.0(5)	4420.0(9)	4469.0(9)	7(1)
C(8)	3643.3(3)	3677.3(4)	5960.3(5)	3(1)
C(9)	4156.4(3)	5115.7(6)	7659.0(6)	4(1)
N(10)	3481.3(4)	6166.7(7)	8519.4(7)	7(1)
C(11)	3859.3(2)	7388.6(4)	10136.5(4)	2(1)
C(12)	3266.3(3)	8717.9(7)	10851.5(8)	5(1)
N(13)	2737.2(4)	9447.5(7)	9386.0(7)	7(1)
C(14)	1927.4(3)	10586.9(7)	9934.2(6)	4(1)
C(15)	1476.2(4)	11075.2(6)	8349.6(9)	6(1)
C(16)	1067.0(4)	9993.7(8)	6901.6(8)	6(1)
N(17)	6284.0(4)	1986.2(7)	2043.7(7)	7(1)
C(18)	6150.1(5)	310.3(9)	789.6(9)	7(1)
C(19)	6620.5(5)	130.5(9)	−804.0(9)	7(1)
N(20)	7574.0(4)	626.2(7)	35.4(7)	7(1)
C(21)	8016.4(4)	651.3(9)	−1408.2(10)	7(2)
C(22)	9021.4(4)	1057.7(8)	−593.3(8)	6(1)
C(23)	9224.2(4)	2762.2(6)	663.6(6)	5(1)
N(24)	8903.1(3)	2966.1(4)	2313.9(4)	4(1)
C(25)	8985.1(4)	4682.5(9)	3507.1(9)	6(1)
C(26)	8558.0(4)	4906.4(9)	5111.4(10)	7(2)
N(27)	7591.9(4)	4492.5(7)	5361.2(7)	7(1)
C(28)	7085.3(5)	4190.0(9)	5648.0(9)	7(1)
C(29)	6107.7(3)	3872.6(5)	5088.3(5)	3(1)
C(30)	6058.0(5)	2185.0(9)	3775.9(9)	7(1)
Cl(31)	724.2(1)	5884.3(2)	8561.0(2)	5(0)
O(32)	326.6(5)	6740.9(8)	7529.3(10)	16(2)
O(33)	1219.3(8)	4619.3(9)	7309.4(10)	17(3)
O(34)	1620.7(2)	5930.0(8)	9329.9(7)	9(1)
O(35)	312.7(3)	5084.6(5)	9327.3(7)	7(1)
Cl(36)	4379.0(1)	9024.3(1)	5744.4(1)	3(0)
O(37)	3711.2(4)	8166.1(7)	4543.9(7)	10(1)
O(38)	4936.9(4)	7591.0(7)	5519.1(17)	21(4)
O(39)	4903.7(4)	10003.1(13)	5569.0(15)	21(4)
O(40)	4310.0(5)	9513.8(11)	7361.3(8)	14(2)
Cl(41)	6538.1(1)	5406.8(3)	70.6(3)	8(0)
O(42)	6190.1(2)	6372.8(4)	−713.7(5)	4(1)
O(43)	6266.7(3)	3809.8(4)	−842.8(5)	5(1)
O(44)	7451.0(3)	5217.3(7)	437.4(8)	9(2)
O(45)	6125.7(4)	5825.4(9)	1643.9(6)	10(2)
N(46)	1194.8(4)	1820.4(7)	3724.0(12)	12(2)
O(47)	560.1(3)	997.0(5)	3037.1(5)	6(1)
O(48)	1154.3(2)	3193.0(3)	3366.1(4)	4(1)
O(49)	1933.3(2)	1380.2(6)	4292.1(6)	7(1)
N(50)	3947.6(2)	3073.7(3)	679.1(3)	2(0)
O(51)	3244.5(3)	3543.6(5)	−1.2(6)	7(1)
O(52)	4632.5(2)	3876.9(5)	930.1(6)	6(1)
O(53)	4062.0(3)	1857.9(5)	1071.5(6)	6(1)
N(54)	8600.6(4)	−434.9(7)	4218.1(7)	7(1)
O(55)	7848.7(3)	−654.6(7)	3469.9(7)	9(1)
O(56)	8962.3(4)	−1553.5(5)	5123.9(7)	8(1)
O(57)	8724.7(6)	975.1(7)	4841.3(8)	13(2)
O(W1)	6836.4(2)	7724.2(4)	5066.5(5)	4(1)
O(W2)	8392.8(3)	7397.6(6)	−77.9(9)	10(2)

[a] Anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter defined as $4/3\Sigma_i\Sigma_j\beta_{ij}a_ia_j$.

TABLE III

Selected bond distances (Å), intermolecular hydrogen bond distances (Å) and bond angles (deg) for **1**

Au(1)-N(3)	2.023(45)	Au(1)-N(6)	1.959(49)
Au(1)-N(10)	2.108(60)	Au(1)-N(13)	2.103(48)
Au(2)-N(17)	2.050(60)	Au(2)-N(20)	1.928(49)
Au(2)-N(24)	2.075(44)	Au(2)-N(27)	2.090(48)
O(38)···O(W1) [*x*, *y*, *z*]	2.99(8)	N(6···O(48) [*x*, *y*, *z*]	2.85(6)
N(17)···O(52) [*x*, *y*, *z*]	2.96(6)	N(27)···O(W1) [*x*, *y*, *z*]	2.79(6)
O(44)···O(W2)	2.70(9)	O(45)···O(W1) [*x*, *y*, *z*]	2.85(6)
N(24)···O(47) [*x* + 1, y, z]	2.91(6)	N(20)···O(W2) [*x*, *y* − 1, z]	2.88(8)
N(3)···O(49) [*x*, *y* + 1, z]	2.97(8)	N(13)···O(53) [*x*, *y* + 1, z + 1]	2.92(7)
N(10)···O(51) [*x*, *y*, *z* + 1]	2.92(9)		
N(3)-Au(1)-N(6)	86.9(21)	N(3)-Au(1)-N(13)	95.0(20)
N(6)-Au(1)-N(10)	94.0(24)	N(10)-Au(1)-N(13)	84.1(22)
N(17)-Au(2)-N(20)	85.4(24)	N(17)-Au(2)-N(27)	94.9(23)
N(20)-Au(2)-N(24)	96.1(20)	N(24)-Au(2)-N(27)	83.3(19)

factors in Table II. Selected bond distances, hydrogen bond distances, and bond angles are presented in Table III.

Electrochemical Measurements

Cyclic and dc voltammetries were performed with a Yanaco P-1100 polarigraphic analyzer system at 25.0 ± 0.1°C and $I = 0.50$ ($NaClO_4$ or NaCl). A three-electrode system was employed: a gold ($\phi = 1.6$ mm) or nickel ($\phi = 3.0$ mm) rotating-disk-electrode (RDE) as the working electrode, a glassy-carbon rod ($\phi = 3.0$ mm) as the counter electrode, and a saturated calomel electrode (SCE) as the reference electrode. All redox potentials in this article are given with reference to SCE. The cyclic and dc voltammograms were evaluated graphically at scan rates of 200 and 10 mV sec^{-1}, and electrode rotation rates of 0 and 2000 rpm, respectively. All working electrodes were polished between measurements with fine aluminium oxide powder (BAS Co.). All solutions were deaerated in a stream of pure argon gas ($>99.999\%$).

Controlled-potential coulometry was carried out with a Yanaco VE-9 potentiostat and a Yanaco V10-CM coulometer using a nickel plate (*ca* 10 cm^2, 99.9% purity) as the working electrode at −0.45 V *vs* SCE, pH 7.0 (20 mM HEPES buffer), 25°C, and $I = 0.50$ ($NaClO_4$). The aqueous solution used (50 cm^3) contained 1.0 mM of Au^{III}-cyclam **1**. The Au^{III}-reduction current was level within 25 min, where the UV absorption band for Au^{III}-cyclam (λ_{max} 360 nm, ε 2160 M^{-1} cm^{-1} at pH 7.0) almost disappeared ($<1\%$).[1] The coulometry of **1** was 3.02 ± 0.05 e/Au, which confirmed that three electron reduction ($Au^{III} \rightarrow Au^0$) occurred.

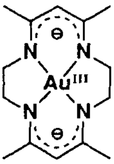
Dc polarograms (RDE) for 1.0 mM **8** in DMF were measured with a glassy carbon electrode at $I = 0.10$ (Et_4NClO_4) and 25°C. The total reduction current corresponds to 3e$^-$ (the same as $Au^{III} \rightarrow Au^0$ for **1** under the same conditions). However, for **8**, three step waves (each 1/3 of the total current) were observed.

RESULTS AND DISCUSSION

X-ray Crystal Structure of Au^{III}-cyclam (1)

A single crystal for X-ray analysis of **1**·$(ClO_4)_{1.5}(NO_3)_{1.5}\cdot H_2O$ was obtained by recrystallization of **1**·$Cl(ClO_4)_2$ from 1 M aqueous HNO_3 solution. The detailed molecular structure has been clarified by X-ray analysis of **1**·$(ClO_4)_{1.5}(NO_3)_{1.5}\cdot H_2O$. The crystal structure consists of two independent cations per unit cell with associated anions and two lattice water molecules. The cyclam ligands bound to Au(1) and Au(2) adopt the same overall stereochemistry with the most stable *trans* III (*RRSS*) conformation[12] (Figure 1). The Au^{III} atoms are located in the centres of the N_4 planes and the total equatorial angles for N–Au–N are 360.0° for Au(1)-cyclam and 359.7° for Au(2)-cyclam. Selected bond distances and angles around Au^{III} are summarized in Table III.

The cyclam in **1** takes the same configuration as other metal cyclam complexes. The average metal-N bond length of **1** (*ca* 2.04 Å) is close to those of the Pd^{II}- (2.05 Å),[13] Ni^{II}- (2.06 Å),[14] and Pt^{IV}-cyclam (2.04 Å) complexes.[15] In comparison with the unsaturated macrocyclic β-diminate complex **10**, in which the four Au^{III}-N bond lengths are almost equal (1.98 Å),[16] those in **1** are widely scattered, ranging from 1.93 Å to 2.11 Å. This is probably due to the more flexibility of the saturated macrocyclic N_4 ligand and the strong hydrogen bonds with counter anions. The amine hydrogens of **1**, whose acidity is reinforced by a strongly acidic Au^{III} ion,[1] closely associate with the anionic oxygens of ClO_4^- and NO_3^- ions, and the lattice water molecules (Figure 2). Interestingly, neither the anions nor the water molecules are sufficiently close to the Au^{III} for any significant interaction.



10

Electrochemistry of Au^{III}-cyclams (1), (3), and (4)

Cyclic voltammetry (CV) of **1** at pH 3.0 (20 mM citrate buffer), $I = 0.50$ ($NaClO_4$), and 25°C displayed irreversible reduction waves with peak potentials at −0.30 V (on nickel disk electrode) or −0.25 V (gold disk electrode), where no corresponding oxidation waves were observed. On repetition of the CV scans, the surface of the nickel-disk-electrode turned a golden colour due to gold deposition. Controlled-potential coulometry of 1.0 mM at −0.45 V (see Experimental) indicated an electron flow of 3.02 ± 0.05 e/Au. Into the final reduction solution was released 1.0 mM intact cyclam ligand, which was determined by the formation of an equimolar Cu^{II}-cyclam complex (λ_{max} 506 nm, ε 80).[17] We thus conclude that Au^{III} in **1** is completely converted to gold with quantitative recovery of metal-free cyclam (see reaction (*2*)).

$$[\mathrm{Au^{III}\text{-}cyclam}]^{3+} + 3e^- \rightarrow \mathrm{Au}^0 + \mathrm{cyclam} \qquad (2)$$

TABLE IV

Comparison of the reduction potentials ($E_{1/2}$, V vs SCE) of Au^{III}-polyamine complexes 1–6 at various pH values on a gold RDE at 25°C and $I = 0.50$ ($NaClO_4$)

	$E_{1/2}$[a]				
pH	**1**	**3**	**4**	**5**	**6**
1.0[b]	−0.16 (−0.16)[f]	−0.18	−0.17	+0.33	+0.13
3.0[c]	−0.24 (−0.25)[f]	−0.20	−0.28	+0.29	+0.10
7.0[d]	−0.44 (−0.47)[f]	−0.41	−0.46	−0.06	−0.12
9.0[e]	−0.55 (−0.55)[f]	−0.54	−0.77	−0.35	−0.24

[a] $E_{1/2}$ values are the half wave reduction potentials (Au^{III} → Au^0) in the first scan.
[b] $HClO_4$ buffer.
[c] 20 mM citrate buffer.
[d] 20 mM HEPES buffer.
[e] 20 mM phosphate buffer.
[f] The values in parentheses are measured with a nickel RDE under the same conditions.

In order to compare the irreversible reduction potentials of the Au^{III} complexes, **1**, **3**, **4**, **5** and **6**, we conducted a dc voltammetric study using nickel and gold rotating disk electrodes (RDE). Typical current-potential curves of **1** with a gold RDE at pH 3.0 are shown in Figure 3. Similar 3e$^-$ reduction RDE voltammograms with almost the same limiting current were observed for other Au^{III} complexes, **3**, **4**, **5** and **6** under the same conditions. The half wave reduction potentials ($E_{1/2}$) of these Au^{III} complexes in the first scan (from less negative side) are summarized in Table IV. Interestingly, in the second and the following repeated dc voltammetric scans (where the electrode is left unpolished) (Figure 3), the reduction waves of **1** gradually shifted

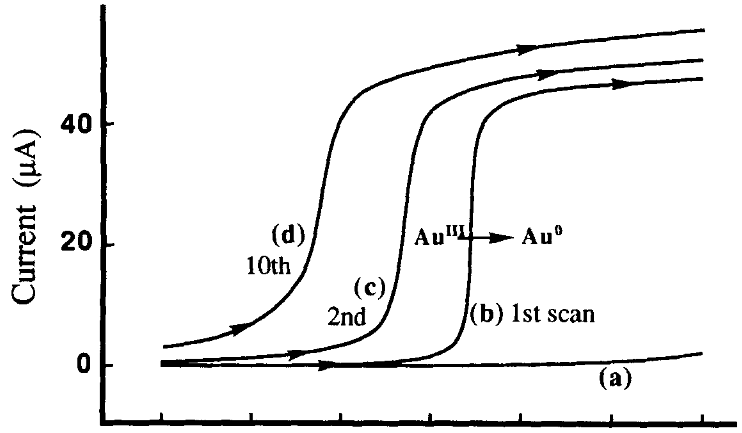


FIGURE 3 Dc voltammograms with a gold RDE at 2000 rpm, scan rate = 10 mV s^{-1}, $I = 0.50$ M ($NaClO_4$), pH 3.0 (20 mM citrate buffer), and 25°C; (a) in the absence of **1**; (b) 1.0 mM of **1** at the 1st scan ($E_{1/2} = -0.24$ V); (c) at the second scan ($E_{1/2} = -0.17$ V); (d) at the 10th scan ($E_{1/2} = -0.08$ V).

from $E_{1/2} = -0.24$ V to more positive potentials (-0.08 V at the 10th scan). Similar electrochemical behaviour and almost the same $E_{1/2}$ values (Table IV) were observed with a nickel RDE under the same conditions. This fact suggests that the electrode surface upon gold deposition enhances further electroreduction of **1**. The prospect of self-catalyzed gold deposition in the reduction of Au^{III}-cyclam **1** has prompted us to undertake Au^{III}-cyclam-mediated, gold-plating on a nickel substrate, as described below.

At a higher pH of 7.0 (20 mM HEPES buffer), Au^{III}-cyclam **1** is in a monodeprotonated form **2** (its pK_a is 5.4), and this shows a $3e^-$ reduction wave at -0.44 V during the first scan, far below the potential of -0.24 V of the undissociated form **1** (at pH 3). This is consistent with greater stabilization of Au^{III} by the coordination of an N^- anion. The $E_{1/2}$ values (first scan only) for a series of the Au^{III}-polyamine complexes **1**, **3**, **4**, **5** and **6** at different pH values (1, 3, 7, and 9) are compiled in Table IV. It is evident that in the macrocyclic complexes **1**, **3**, and **4**, Au^{III} ions are more difficult to reduce to A^0 relative to the linear homologues **5** and **6** at the given pH's. This result demonstrates that the Au^{III} state is stabilized by the macrocyclic ligands and this may be described as a "macrocyclic effect".

Gold Plating on Nickel Metal by a Non-electrolytic Method

Robust and smooth gold deposits, which cannot be scrubbed off, were produced by merely immersing a nickel plate into an acidic aqueous solution (pH 1.0 HCl buffer) of Au^{III}-cyclam complex **1** at $I = 0.50$ NaCl and room temperature. This is the first observation of direct chemical gold-plating on a pure nickel substrate, which is achieved only by the Au^{III}-macrocyclic tetraamine complex. This fact suggests the likelihood of gold-plating by the displacement reaction (*3*).

$$3Ni^0 + 2Au^{III}\text{-cyclam} \rightarrow 3Ni^{2+}_{aq} + 2Au^0 + 2\text{cyclam} \qquad (3)$$

The reduction potential of Au^{III}-cyclam **1** on the nickel RDE at pH 1.0 was -0.16 V in the first scan (Figure 4b), while the oxidation of the nickel RDE electrode as expressed in reaction (*4*) was observed at $\sim +0.1$ V (Figure 4a). Theoretically, therefore, the reduction of Au^{III} in **1** to Au^0 by nickel metal (reaction (*3*)) should not be feasible. It is thus considered that the observed "underpotential gold deposition" would involve some self-catalytic action.[18] As displayed by Figure 4c, the reduction potential of **1** becomes closer to the oxidation potential of Ni^0, as the gold-plating proceeds.

$$Ni^0 \rightarrow Ni^{2+}_{aq} + 2e^- \qquad (4)$$

For investigation of the reaction (*3*), the plating process on a nickel plate ($0.3 \times 10 \times 10$ mm, purity >99.9%) with 0.15 mM of Au^{III}-cyclam **1** with mechanical stirring (500 rpm) at $I = 0.50$ (NaCl), pH 1.0 (HCl buffer), and 25°C was followed by atomic absorption spectroscopy for Ni^{2+} ion, and by UV spectroscopy for disappearing Au^{III}-cyclam **1** (λ_{max} 220 nm, ε 12300 at pH 1.0). During the initial 60 min *ca* half of the Au^{III}-cyclam was rapidly reduced. The generated Ni^{2+} ion was 0.54 mM, far more than the *ca* 0.11 mM value theoretically predicted from reaction (*3*). Apparently unavoidable reaction (*5*) is simultaneously occurring. The reduction of **1** with copper metal did not occur, as rationalized by the lower ionization tendency (or higher ionization potential) of copper metal.

$$Ni^0 + 2H^+ \rightarrow Ni^{2+}_{aq} + H_2\uparrow \qquad (5)$$

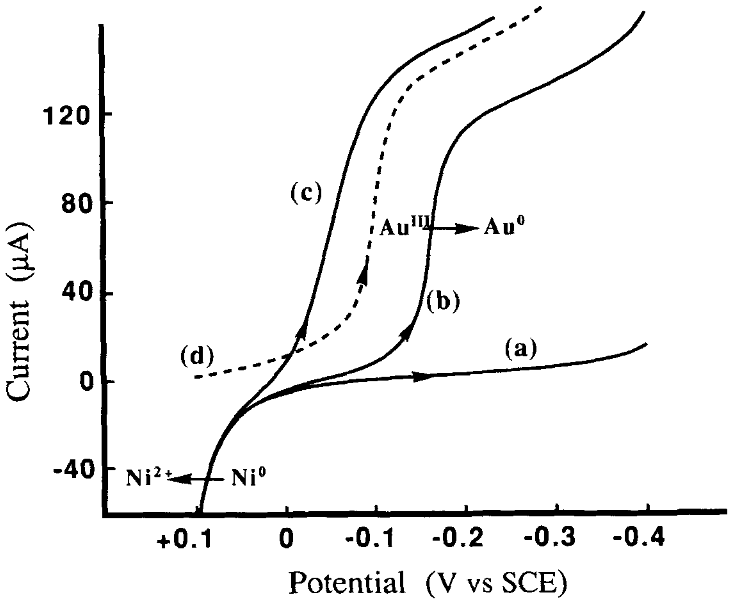


FIGURE 4 Dc voltammograms with a nickel RDE at 2000 rpm, scan rate = 10 mV s^{-1}, $I = 0.50$ M (NaCl), pH 1.0 (HCl buffer), and 25°C: (a) in the absence of **1**; (b) 1.0 mM of **1** at the 1st scan ($E_{1/2} = -0.16$ V); (c) at the 10th scan ($E_{1/2} = -0.07$ V); (d) after electrolytic gold-plating at an applied potential of -0.15 V *vs* SCE for 15 min ($E_{1/2} = -0.10$ V).

By contrast, reductions of Au^{III} in the linear amine complexes, $[Au^{III}(dien)Cl]^{2+}$ **5** ($E_{1/2} = +0.33$ V at pH 1), $[Au^{III}(en)_2]^{3+}$ **6** ($E_{1/2} = +0.13$ V at pH 1), and $[Au^{III}Cl_4]^-$ ($E(Au^{III/0}) = +0.76$ V)[19] with nickel metal (Ni^0) looked much easier in the light of their more positive potentials (Figure 5). However, the reduction of these Au^{III} species with nickel metal plate did not yield smooth gold plating. Instead, black Au^0 particles quickly precipitated.

Recently, non-electrolytic ("electroless") gold-plating attracted great attention, especially for selective plating on patterned substrates (*e.g.*, nickel, copper) for electronic devices.[18,20] Conventional methods employ $KAu^I(CN)_2$, $KAu^{III}(CN)_4$, or $KAu^{III}Cl_4$ (as gold source), in the presence of reducing agents (*e.g.*, KBH_4, HCHO, NH_2NH_2, or NaH_2PO_2).[18,20] Our non-electrolytic plating procedure (on nickel) is much simpler. However, attempts at non-electrolytic gold-plating on copper with **1** in the presence of reducing agents have thus far ended in failure.

Gold Plating on Nickel Metal by an Electrolytic Method

The electrochemical reduction of Au^{III}-cyclam **1** produced fine and smooth-looking gold deposition on a nickel RDE electrode at pH 1.0 ($HClO_4$ buffer), applied potential -0.16 V (or at pH 3.0 (20 mM citrate buffer) and -0.25 V), $I = 0.50$ ($NaClO_4$), rotating rate 2000 rpm, and 25°C. We found that electrolyte gold-plating under acidic conditions gave the best results. A dc voltammogram of the gold-plated nickel RDE from 1.0 mM **1** (at pH 1.0 (HCl buffer), $I = 0.50$ (NaCl), and applied potential of -0.15 V for 15 min) indicated no oxidation wave of nickel near $+0.1$ V

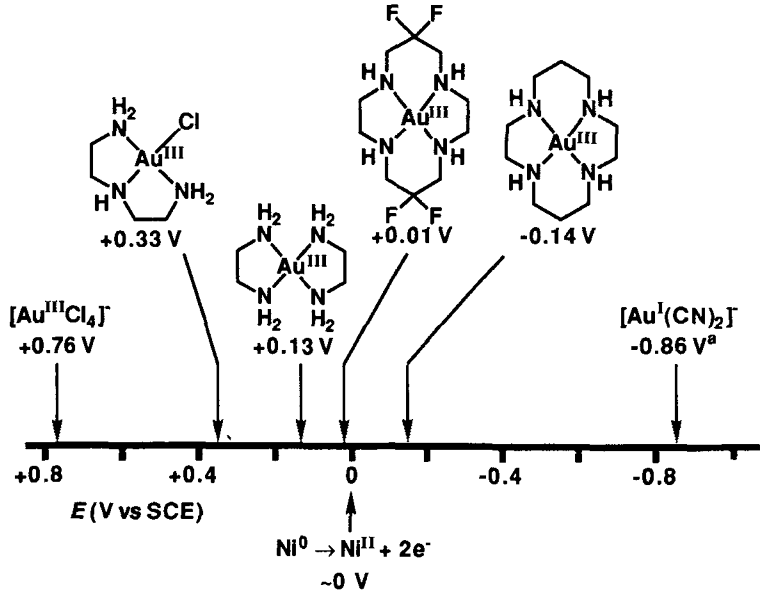


FIGURE 5 Comparison of reduction potentials of Au^{III} or Au^{I} to Au^0 on an Au-RDE at 2000 rpm, pH 1.0 ($HClO_4$ buffer), and 25°C. [a]pH 9.0.

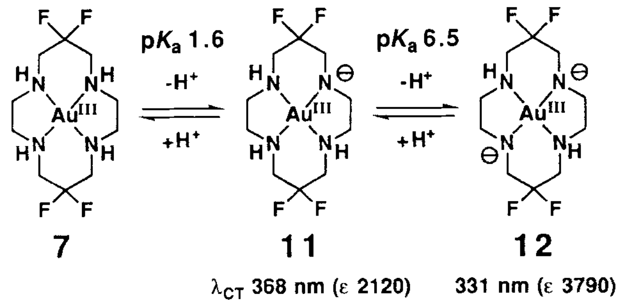
(Figure 4d), implying that the nickel electrode is completely covered and protected with gold. At pH 7 (20 mM HEPES buffer) the application of −0.47 V to **1** precipitated only black gold particles on the nickel RDE.

The electrochemical reduction of the linear amine complexes, $[Au^{III}(dien)Cl]^{2+}$ **5** at +0.33 V and $[Au^{III}(en)_2]^{3+}$ at +0.13 V **6**, failed to produce good gold-plating. The difference in the ease of Au^{III} reduction to Au^0 metal and/or Au^0 dissociation (from the chelates) rates for these complexes may be responsible for success or failure in gold plating (Figure 5): the more difficult (or slower) the dissociation from macrocyclic cyclam, the longer the gold depositing time (resulting in good plating), or the easier (or faster) the dissociation from ethylenediamine or diethylenetriamine, the faster the gold precipitation (resulting in no plating).

Our electrolytic gold-plating products look as good as currently most widely adopted ones from $[Au^{I}(CN)_2]^-$ (in the presence of excess CN^- at pH 4 ~ 9 and *ca* −0.9 V).[19,20] Note that the reduction potential of Au^{I} in the cyanide complex is much more negative (Figure 5). The significance of our Au^{III}-cyclam **1** is in the optimum acidic pH and the non-use of the pollutant CN^-. Moreover, in our simple gold-plating system, we can recycle the macrocyclic ligands and also start with a quantified Au^{III} source.

Au^{III}-Tetrafluorinated cyclam (6,6,13,13-tetrafluoro-1,4,8,11-tetraazacyclotetradecane) (7)

Treatment of $NaAuCl_4 \cdot 2H_2O$ with equimolar tetrafluorinated cyclam in CH_3CN for 1 h yielded **7**$\cdot Cl \cdot (ClO_4)_2 \cdot H_2O$ as yellow needles, which were recrystallized from aqueous 1 M $HClO_4$ solution.

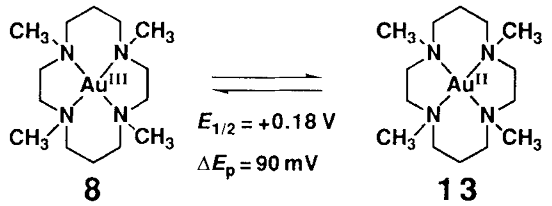


As was observed for Au^{III}-cyclam **1** (pK_a = 5.4), reversible deprotonation to **11** with pK_a value of 1.6 ± 0.1 (at 25°C, I = 0.10; $HClO_4$/$NaClO_4$ buffer) was measured by the emergence of the CT absorption band at 368 nm (ε 2120) with an increase in pH, which is a characteristic (N^-) → Au^{III} charge transfer (CT) absorption band.[1,6] The NH dissociation constant of **7** to **11** is ~ 10^4 times lower than that of **1** (pK_a = 5.4) caused by the strong electron-withdrawing effect of F groups. Aqueous solution of **7** showed pH ~3, which means a major species in aqueous solution of **7** is **11**.

The pH-titration of **11** with 0.1 M NaOH showed removal of a proton with pK_a value of 6.49 ± 0.03 (at 25°C and I = 0.10; $NaClO_4$), which is assigned to the second deprotonation, as depicted in **12**. The deprotonated **12** showed λ_{max} 331 nm (ε 3790), reversibly. *The dissociation of two NH protons from the cyclam complexes at neutral pH is the first case of its kind.*

Au^{III}-Tetramethylcyclam (1,4,8,11-tetramethyl-1,4,8,11-tetraazacyclotetradecane((**8**)

Treatment of $NaAuCl_4 \cdot 2H_2O$ with equimolar tetramethylcyclam in CH_3CN/CH_3OH (5:1) for 2 h yielded **8**·Cl·$(ClO_4)_2$ as yellow needles, which were recrystallized from aqueous 1 M $HClO_4$ solution.



The dc polarogram of **8** on a glassy carbon electrode in DMF (25°C, I = 0.10; Et_4NClO_4) shows three-step 3e-reduction waves at +0.17 (for Au^{III} → Au^{II}), −0.09 (for Au^{II} → Au^{I}), and −0.90 V (for Au^{I} → Au^{0}) *vs* SCE, each consisting of 1e$^-$ reduction process (Figure 6a). The cyclic voltammogram of **8** for the 1st reduction wave showed an Au^{II}/Au^{III} (*i.e.* **8** ⇌ **13**) *quasi*-reversible reduction wave ($E_{1/2}$ = +0.18 V *vs* SCE, ΔE = 90 mV, Figure 6b). On the other hand, the cyclic and dc polarograms of Au^{III}-cyclam **1** showed only one-step 3e-reduction wave at −0.64 V under the same conditions, which is interpreted as the reduction of Au^{III} directly to Au^{0}. Isolation of Au^{II}-complex **13** by electrochemical reduction of **8** at +0.10 V was unsuccessful due to the instability of **13**.

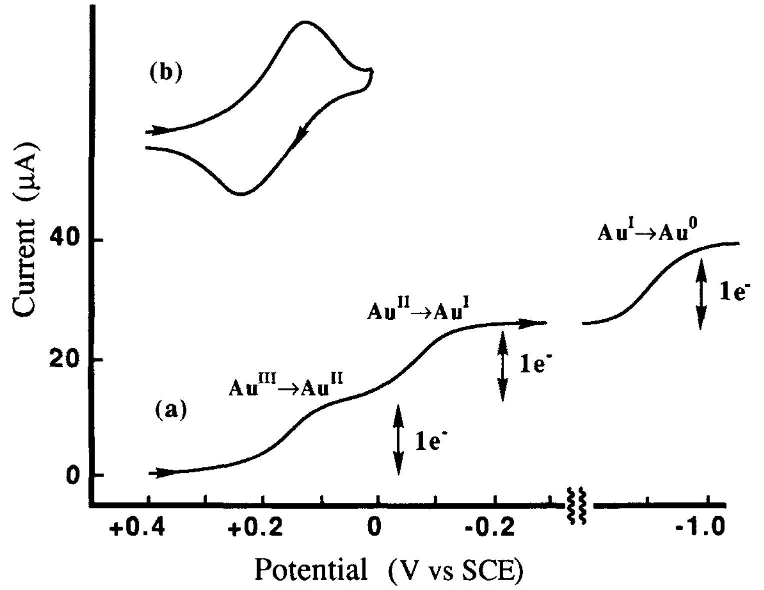
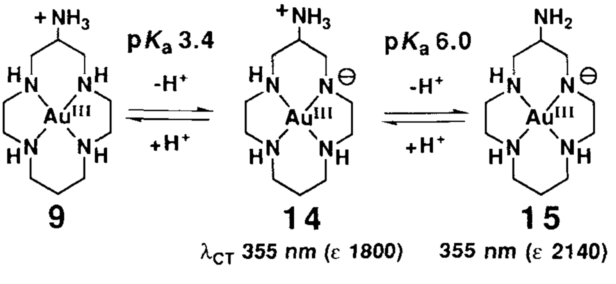


FIGURE 6 Dc and cyclic voltammograms of **8** with a glassy carbon electrode in DMF at $I = 0.10$ M (Et_4NClO_4) and 25°C; (a) RDE at 2000 rpm, scan rate = 10 mV s^{-1}; (b) CV of scan rate = 500 mV s^{-1}.

Tetramethylcyclam is well-known to stabilize metal ions with unusually low oxidation states: *e.g.*, Cu^I,[21] Ni^I,[22] or Pd^I.[23]

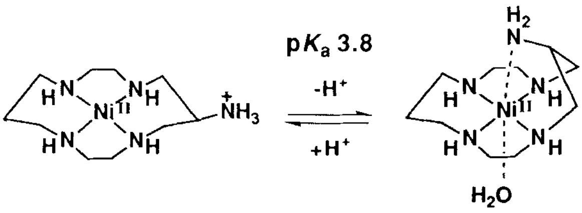
Au^{III}-Aminocyclam (6-Amino-1,4,8,11-tetraazacyclotetradecane) (***9***)

Treatment of $NaAuCl_4 \cdot 2H_2O$ with equimolar aminocyclam in refluxing CH_3CN for 1 h yielded **9**·$(ClO_4)_4$ as colourless needles, which were purified by Dowex 50X4 ion exchange column chromatography (eluant: 3 M HCl) and recrystallization from aqueous 1 M $HClO_4$ solution.



The pH-titration of **9** with 0.1 M NaOH showed removal of a proton with pK_a value of 3.4 ± 0.1 (at 25°C, $I = 0.10$; $NaClO_4$), which is assigned to the deprotonation from one of the secondary amines of aminocyclam to **14**. The deprotonated **14** has a characteristic $(N^-) \rightarrow Au^{III}$ CT absorption band at λ_{max} 355 nm (ε 1800), which reversibly diminished upon protonation to **9**. The dissociation constant of a proton from the aminocyclam NH is 100 times smaller than that of Au^{III}-cyclam **1** (pK_a = 5.4), caused by the electron-withdrawing effect of the protonated NH_3^+ group.

The second deprotonation occurs at the arm amino group with pK_a 6.03 ± 0.02 for **14** ⇌ **15**. It is significant that the NH_3^+ proton dissociates only after the cyclam-NH dissociates, despite the former normally being far more acidic than the latter. This is an unambiguous illustration of the strong Au^{III} (d^8) acidity extending only to the N_4 square-planar direction. The pK_a value of 6.0 for **14** ⇌ **15** should be compared with that for the free ligand (pK_a = 6.1). Apparently, axial bonding of the NH_2 arm to Au^{III} (d^8) does not occur. For comparison, in the Ni(II) complex of the aminocyclam, the arm NH_3^+, upon deprotonation (with pK_a 3.8), axially binds to Ni^{II} (*i.e.*, **16** ⇌ **17**).[10]



16 **17**

SUPPLEMENTARY MATERIAL

Full lists of anisotropic temperature factors, bond distances and angles, and calculated and observed structure factors are available on request from the authors.

REFERENCES

1. E. Kimura, Y. Kurogi and T. Takahashi, *Inorg. Chem.*, **22**, 4117 (1991).
2. F.V. Lovecchio, E.S. Gore and D.H. Busch, *J. Am. Chem. Soc.*, **96**, 3109 (1974).
3. E.K. Barefield and M.T. Modella, *J. Am. Chem. Soc.*, **97**, 4238 (1975); E. Zeigerson, G. Ginzburg, N. Schwartz, Z. Lus and D. Meyerstein, *J. Chem. Soc., Chem. Commun.*, 241 (1979).
4. M.O. Kestner and A.L. Allred, *J. Am. Chem. Soc.*, **94**, 7189 (1972).
5. E.K. Barefield and M.T. Mochella, *Inorg. Chem.*, **12**, 2829 (1973).
6. W.H. Baddley, F. Basolo, H.B. Gray, C. Nölting and A. Pöe, *Inorg. Chem.*, **2**, 921 (1963); G. Nardin, L. Randaccio, G. Annibale, G. Natile and B. Pitteri, *J. Chem. Soc., Dalton Trans.*, 220 (1970).
7. B.P. Block and J.C. Bailar Jr., *J. Am. Chem. Soc.*, **73**, 4722 (1951).
8. M. Shionoya, E. Kimura and Y. Iitaka, *J. Am. Chem. Soc.*, **112**, 9237 (1990).
9. R. Buxtorf and T.A. Kaden, *Helv. Chim. Acta*, **57**, 1035 (1974).
10. E. Kimura and T. Koike, paper in preparation.
11. E. Kimura, T. Koike, K. Uenishi, M. Hediger, M. Kuramoto, S. Joko, Y. Arai, M. Kodama and Y. Iitaka, *Inorg. Chem.*, **26**, 2975 (1987).
12. V.J. Thöm, C.C. Fox, J.C.A. Toeyens and R.D. Hancock, *J. Am. Chem. Soc.*, **106**, 5947 (1984); G. Bosnich, C.K. Poon and M.L. Tobe, *Inorg. Chem.*, **4**, 1102 (1965).
13. M. Yamashita, H. Ito, K. Toriumi and T. Ito, *Inorg. Chem.*, **22**, 1566 (1983).
14. B. Bosnich, R. Mason, P.J. Pauling, G.B. Robertson and M.L. Tobe, *J. Chem. Soc., Chem. Commun.*, 97 (1965).
15. D. Waknine, M.J. Heeg, J.F. Endicott and L.A. Ochrymowycz, *Inorg. Chem.*, **30**, 3691 (1991).

16. J.-H. Kim and G.W. Everett Jr., *Inorg. Chem.*, **20**, 853 (1981).
17. E. Kimura, T. Koike, R. Machida, R. Nagai and M. Kodama, *Inorg. Chem.*, **23**, 4181 (1984).
18. H.O. Ali and I.R.A. Christie, *Gold Bull.*, **17**, 118 (1984).
19. R.J. Puddephatt, In *Comprehensive Coordination Chemistry*, S.G. Wilkinson (ed.), Vol. 5, Pergamon Press, 1987, Ch. 55, p. 895.
20. Y. Okinaka, In *Gold Plating Technology*, Electrochemical Publications, Ayr, Scotland, 1973, Ch. 11, p. 82; Y. Okinaka, R. Sard, C. Wolowodiuk, W.H. Craft, T.F. Retajczyk, *J. Electrochem. Soc.*, **121**, 56 (1974); Y. Okinaka, *J. Electrochem. Soc.*, **120**, 739 (1973).
21. N. Jubran, H. Cohen, Y. Koresh and D. Meyerstein, *J. Chem. Soc., Chem. Commun.*, 1683 (1984).
22. N. Jubran, G. Ginzburg, H. Cohen, Y. Koresh and D. Meyerstein, *Inorg. Chem.*, **24**, 251 (1985).
23. A.J. Blake, R.O. Gould, T.I. Hyde and M. Schröder, *J. Chem. Soc., Chem. Commun.*, 1730 (1987).