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Highly Stable Gold(III) Complex with a Hydantoin Ligand in Alkaline Media

Kenichi Oyaizu,[†] Yutaka Ohtani,[‡,§] Asako Shiozawa,[‡] Kenji Sugawara,[‡] Takashi Saito,[‡] and Makoto Yuasa*,[†,‡]

Institute of Colloid and Interface Science, Tokyo University of Science, Tokyo 162-8601, Japan, Department of Pure and Applied Chemistry, Faculty of Science and Technology, Tokyo University of Science, Noda 278-8510, Japan, and Tanaka Kikinzoku Kogyo K.K., Hiratsuka 254-0076, Japan

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A novel gold(III) complex with a monodentate 5,5-dimethylhydantoin ligand, $[Au(dmh)_4]^-$, is square planar in geometry, inert and highly stable in alkaline solutions because of soft acid–base interactions, and electrochemically reduced near –0.3 V vs Ag/AgCl to give a gold(0) film with a high current efficiency.

Here we report the preparation and structural determination of a remarkable gold(III) complex with a 5,5-dimethylhydantoin (Hdmh) ligand. This investigation has particular significance in that gold complexes are especially important in a variety of applications including organic light-emitting device display technology as dopant emitters,[1] cancer therapy based on their cytotoxic effects on tumor cell lines,[2] and gold plating as gold sources.[3] In particular, water-soluble gold complexes are essential for gold-plating technologies that are exploited in microbump fabrication on silicon chips using organic photoresists for pattern formation.[4] Wirebonding applications frequently use an aqueous bath for electroless gold as a suitable finish for mounting chips to chip carriers.[5] Indeed, gold is the first choice for these purposes because it is soft enough for wirebond processing, capable of withstanding mechanical stress, and highly resistant to corrosion and oxide formation.

A commonly used gold bath employs $KAu(CN)_2$ as a gold source owing to its high stability in water.[5] However, a noncyanide bath is favorable for fabrication of fine circuit patterns because a cyanide bath is incompatible with the conventional photoresist. Moreover, the cyanoaurate ion is reduced at very negative potentials according to $[Au^I(CN)_2]^- + e^- = Au^0 + 2CN^-$ ($E° = -0.61$ V vs NHE), for which typical water-soluble reducing agents for electroless deposition are unavailable. A possible alternate to the cyanide is a sulfite,[6,7] which yields a gold deposit according to $[Au^I(SO_3)_2]^{3-} + e^- = Au^0 + 2SO_3^{2-}$, but the plating bath must be deaerated to avoid autoxidation of SO_3^{2-} to SO_4^{2-}. A mixture of the sulfite and a thiosulfate[8] is less susceptible to the degradation,[9−11] but sulfur contamination is inevitable, which significantly degrades the gold deposit in terms of softness.[12,13]

In search of sulfur-free gold complexes that are stable under aerobic conditions, we turned to water-soluble gold(III) complexes. Aurate ions having the general formula $[AuX_4]^-$ ($X = Cl^-, CN^-, NO_3^-$, and CH_3COO^-) would be the most commonplace gold(III) complex, but the dominant species in water should contain hydroxoaurate ions, $[AuX_x(OH)_{4-x}]^-$ ($x = 0-4$), because of the strong acidity of the gold(III) center. In alkaline solutions, gold(III) may exist as $[Au(OH)_4]^-$, which is reduced at $E° = 0.485$ V vs NHE according to $[Au(OH)_4]^- + 3e^- = Au^0 + 4OH^-$.[14] Because the hydroxide ion can be oxidized at even more

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* To whom correspondence should be addressed. E-mail: yuasa@rs.noda.tus.ac.jp.

[†] Institute of Colloid and Interface Science, Tokyo University of Science.

[‡] Department of Pure and Applied Chemistry, Faculty of Science and Technology, Tokyo University of Science.

[§] Tanaka Kikinzoku Kogyo K.K.

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negative potentials according to $4OH^- = O_2 + 2H_2O + 4e^-$ ($E° = 0.401$ V vs NHE), $[Au(OH)_4]^-$ is inherently unstable and gives rise to a gold precipitate according to $4[Au(OH)_4]^- = 3O_2 + 6H_2O + 4Au^0 + 4OH^-$. The essential low stability of conventional aurate ions prompted us to explore a novel complexing agent to give an inert complex.

Hydantoins, known as drugs and agrochemicals,[15] are weak acids ($pK_a \sim 9.1$) and complex a number of metal ions such as Cu^+ and Ag^+.[16] A 1:2 gold(I) complex with a *N*-methylhydantoinate ion has been isolated,[17] which slowly decomposes upon exposure to light. On the other hand, we have found that gold(III) forms a four-coordinate light-stable complex with dmh^-. The product, $[Au(dmh)_4]^-$, of the reaction of $[AuCl_x(OH)_{4-x}]^-$ with dmh^- was characterized by X-ray crystallography.[18] The entire crystal structure was represented by the formula $Na[Au(dmh)_4](Hdmh)_2(NaCl)(H_2O)_8$.[19] Figure 1 shows the structure of the $[Au(dmh)_4]^-$ ion, which is square planar in geometry. Although the molecule occupies a general equivalent position without crystallographic site symmetry, it appears to consist of 4-fold rotational symmetry. Its unique geometry may be characterized by the approximate 4-fold axis perpendicular to the equatorial plane, and a propellerlike shape is clearly apparent when the molecule is viewed along this axis. The bond distance and angles in $[Au(dmh)_4]^-$ adhere closely to the approximate C_4 symmetry.

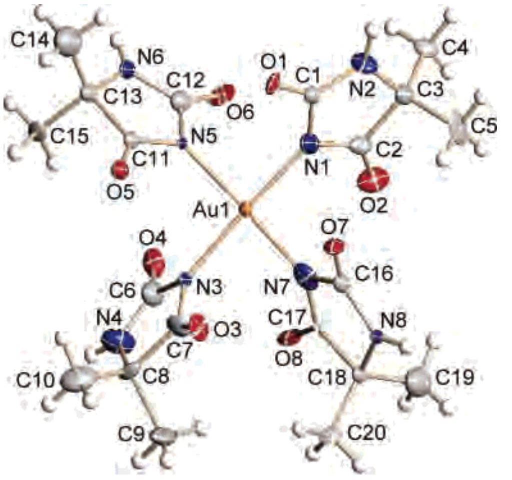

Figure 1. ORTEP view of the aurate ion in $Na[Au(dmh)_4](Hdmh)_2(NaCl)(H_2O)_8$ (30% probability ellipsoids). Selected atom distances (Å) and angles (deg): Au1−N1, 1.980(10); Au1−N3, 1.959(15); Au1−N5, 1.978(14); Au1−N7, 2.004(11); N1−Au1−N3, 177.5(6); N1−Au1−N5, 92.1(2); N1−Au1−N7, 91.5(5); N3−Au1−N5, 90.0(6); N3−Au1−N7, 86.4(2); N5−Au1−N7, 176.3(6).

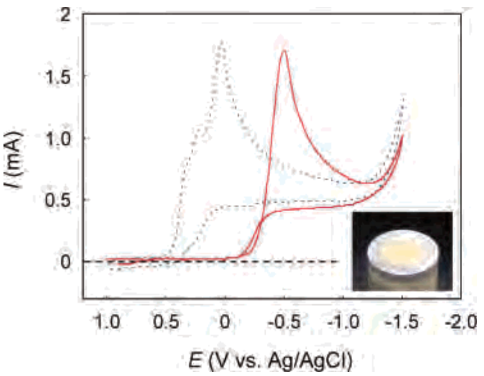

Figure 2. Cyclic voltammogram for electrodeposition of gold(0) at a glassy carbon disk electrode (0.071 cm^2) from a solution prepared by dissolving $HAuCl_4 \cdot 4H_2O$ (0.04 M) in a sodium phosphate buffer (pH 8) under argon (blue dotted curve). A small amount of thallium(I) formate (10 ppm) was used to refine the deposited grains. The red solid curve corresponds to the voltammogram obtained after the addition of Hdmh (0.24 M) to the solution. The potential was first scanned from 1.0 to −1.5 V and then back to 1.0 V at a rate of 100 mV/s. The inset shows the carbon electrode after gold deposition from $[Au(dmh)_4]^-$.

Gold deposition from $[Au(dmh)_4]^-$ was observed at potentials more negative than −0.2 V vs Ag/AgCl[20] in cyclic voltammetry, as shown by the solid curve in Figure 2. The deposited film was uniform and dense with high solderability. The current efficiency for the reduction of $[Au(dmh)_4]^-$ amounted to ca. 95%, according to $[Au(dmh)_4]^- + 3e^- = Au^0 + 4dmh^-$. The voltammogram reveals that an intermediate gold(I) complex, which may intervene during the reduction of $[Au(dmh)_4]^-$, should readily disproportionate,[17] giving rise to the single cathodic wave. A noteworthy feature of the complex is significant inertness to hydrolysis. The dotted curve in Figure 2 demonstrates that the aurate ion in the absence of the dmh^- ligand is reduced at more positive potentials, suggesting that the monodentate dmh^- does not undergo ligand exchange, at least during the course of the voltammetric experiment, and hence $[Au(dmh)_4]^-$ is sufficiently inert in alkaline solutions. The complex was indeed much more stable than other previously reported aurate salts in water and existed for days at pH 8.

The high stability of $[Au(dmh)_4]^-$ would be ascribed to the soft acid−base interaction. Unlike common aliphatic N-donor ligands, dmh^- is a soft base because the carbonyl π^* orbitals can participate in back-bonding interaction. The carbonyl stretching band for dmh^- at 1720 cm^{-1} shifted to 1689 cm^{-1} upon coordination to a "soft" gold(III) center, as a result of the π back-donation (Figure 3a).[21] Added support

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(18) A solution of Hdmh (1.92 g, 15 mmol) in 15 mL of H_2O was adjusted to pH 11−12 by the addition of an aqueous NaOH solution (2 M). The addition of $HAuCl_4 \cdot 4H_2O$ (1.03 g, 2.5 mmol) to the resultant solution followed by stirring at 60 °C for 1 h gave rise to a colorless solution containing the $[Au(dmh)_4]^-$ complex. After removal of H_2O by evaporation and drying under vacuum at 80 °C for 8 h, the product was extracted with dehydrated ethanol. Recrystallization from acetone/water produced colorless prismatic crystals. Yield: 1.9 g (64%). IR (KBr, cm^{-1}): 1689 ($\nu_{C=O}$). ^{1}H NMR (500 MHz, D_2O, ppm): δ 1.274 (s, CH_3). ^{13}C NMR (500 MHz, D_2O, sodium 3-(trimethylsilyl)-propionate-*2,2,3,3-d$_4$*, ppm): δ 26.26, 63.37, 160.8, 185.0. Spectroscopic and electrochemical measurements were performed at 60 °C.

(19) Crystal data for $Na[Au(dmh)_4](Hdmh)_2(NaCl)(H_2O)_8$: $C_{30}H_{60}AuClN_{12}Na_2O_{20}$, $M = 1187.30$, monoclinic space group *Cc* (No. 9), $a = 29.858(2)$ Å, $b = 11.1802(8)$ Å, $c = 17.2993(12)$ Å, $\beta = 125.1860(10)°$, $V = 4719.6(6)$ Å^3, $Z = 4$, $D_{calcd} = 1.671$ g/cm^3, μ(Mo Kα) = 3.278 mm^{-1}. The data were collected at 90(2) K. All measurements were made on a Bruker SMART APEX using a CCD area detector with graphite-monochromated Mo Kα radiation ($\lambda = 0.710\,73$ Å). Of the 16 957 reflections, 8768 were unique ($R_{int} = 0.0382$). The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were refined isotropically. The final cycle of the full-matrix least-squares refinement was based on reflections with $I > 2\sigma(I)$ and 607 variable parameters and converged with $R = \Sigma||F_o| - |F_c||/\Sigma|F_o| = 0.0378$ and $R_w = (\Sigma w(|F_o| - |F_c|)^2/\Sigma wF_o^2)^{1/2} = 0.0932$.

(20) The $[Fe(CN)_6]^{4-/3-}$ redox couple was observed at $(E_{pa} + E_{pc})/2 = 0.27 \pm 0.002$ V vs this Ag/AgCl electrode in cyclic voltammetry.

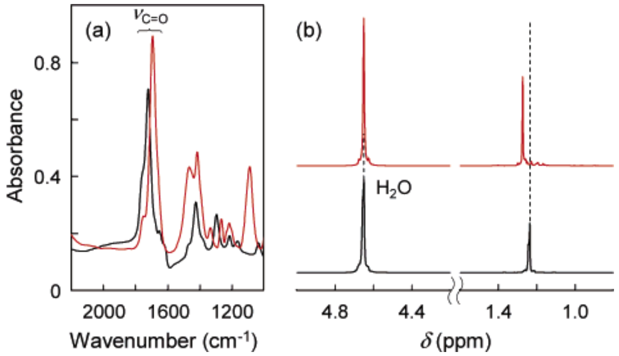

Figure 3. IR (a) and ^1H NMR (b) spectra for a solution prepared by dissolving Hdmh (0.16 M) in an aqueous buffer at pH 8 in the absence (black curve) and presence (red curve) of $HAuCl_4 \cdot 4H_2O$ (0.04 M). The optical path length of the IR cell (CaF_2) was 20 μm. In NMR, residual H_2O in D_2O was used as an internal standard.

for this interpretation was provided by the significant elongation of the C−O length in $[Au(dmh)_4]^-$ (1.22−1.28 Å) compared with those in neutral hydantoin derivatives (ca. 1.20 Å).[22,23] The relatively short coordinate bonds in $[Au(dmh)_4]^-$ (1.959−2.004 Å), compared with those containing other N-donor ligands (2.01−2.22 Å),[24−29] are also indicative of the strong Au−N interaction.

^1H NMR spectra were consistent with the strong binding of dmh^- to gold(III). In buffered D_2O at pH 8, the resonance of methyl protons in $[Au(dmh)_4]^-$ was observed downfield relative to the free ligand (Figure 3b) because of the σ electron donation of dmh^- to gold(III). The ^1H NMR spectra also revealed the absence of free dmh^- in a mixture of dmh^-/$[AuCl_x(OH)_{4-x}]^-$ up to a composition of 4:1, which indicated the quantitative complexation to produce $[Au(dmh)_4]^-$.

Determination of a stability constant for $[Au(dmh)_4]^-$ using UV−visible spectral changes upon coordination of dmh^- to gold(III) (Figure S1 in the Supporting Information) and further characterization of the deposited gold film are the topics of our continuous research. This research also inspires extensive studies of related reactions including the formation of gold(III) complexes with other hydantoin ligands.

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Supporting Information Available: UV−visible spectrum of the $[Au(dmh)_4]^-$ complex and a X-ray crystallographic file in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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[21] A small shoulder near 1750 cm^{-1} in the carbonyl stretching band may correspond to the presence of two inequivalent carbonyl groups in dmh^-.

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