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Properties of Gold(III) Hydroxide and Aquahydroxogold(III) Complexes in Aqueous Solution

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Abstract—Gold(III) hydroxide is found to not precipitate upon rapid mixing of aqueous solutions of $NaAu(OH)_4$ and perchloric acid provided that $c_{Au} < 1.5 \times 10^{-3}$ mol/l and $c_H > 1$ mol/l. For c_{HClO_4} ranging from 1 to 8 mol/l, $Au(OH)_2(H_2O)_2^+$ is virtually the only aqueous species. Its standard potential is $E^0_{3/0} = 1.50$ V. The following protonation constants are determined: for $Au(OH)_4^- + H^+ = Au(OH)_3(H_2O)^0$, $\log K_{H1} = 3.0 \pm 0.1$, and, for $Au(OH)_3(H_2O)^0 + H^+ = Au(OH)_2(H_2O)_2^+$, $\log K_{H2} = 1.8 \pm 0.2$ ($T = 25°C$, aqueous solution, $I \approx 0$). The solubility of the stable (red) gold(III) hydroxide is $S_0 = 2.5 \times 10^{-8}$ mol/l; the solubility of the least stable (white) gold(III) hydroxide is $S_0^* = 2.5 \times 10^{-5}$ mol/l.

Tetrahydroxo complex $Au(OH)_4^-$ and several chlorohydroxo complexes $Au(OH)_{4-i}^-$ are the best studied among the hydroxogold(III) complexes. For the equilibria

$$AuCl_4^- + iOH^- = Au(OH)_{4-i}^- + iCl^-, \beta_i \qquad (1)$$

$\log \beta_i$ ($T = 25°C$, $I = 1.0$ mol/l) is 7.87 (for $i = 1$), 14.79 ($i = 2$), 20.92 ($i = 3$), and 25.98 ($i = 4$) [1]. The standard potential of the tetrahydroxo complex ($Au(OH)_4^- + 3e = Au^0 + 4OH^-$, $E^0_{3/0} = 0.488 \pm 0.003$ V [1, 2]) is higher than the oxygen potential; therefore, metal gold is very slowly formed as a black precipitate in the solutions containing sufficient $Au(OH)_4^-$ concentrations. Acidification of the solutions containing $Au(OH)_4^-$ produces a gold(III) hydroxide precipitate:

$$Au(OH)_4^- = 1/2(Au_2O_3 \cdot xH_2O)_{solid} + OH^-, \quad \log K_{S1} = -3.4 \pm 0.2. \qquad (2)$$

The specified $\log K_{S1}$ value refers to the red hydroxide obtained from chloride solutions (1 mol/l NaCl, pH 7.3–8.5, $c_{Au} > 0.1$ mol/l) and aged under the solution for 2 months [1].

Gold(III) hydroxide is not precipitated when perchloric acid is rapidly added with stirring to a solution containing $Au(OH)_4^-$ and free of ligands other than OH^- to create an acid concentration no lower than 1 mol/l and an overall gold(III) concentration no higher than 1.5×10^{-3} mol/l. Such a solution is long-term stable. A black gold metal cloud appears in the solution only in several days, which is evidence of the redox decomposition of water. However, even in one week, the gold concentration of the solution does not change by more than 1–2%, which is the determination error. Complex $Au(OH)_2(H_2O)_2^+$ is the major and virtually the only gold species under the above conditions. This gold species can be used to synthesize new complexes that cannot be prepared from $AuCl_4^-$ because of its high stability.

EXPERIMENTAL

To prepare an $NaAu(OH)_4$ solution free of complex species other than OH^-, aqueous NaOH was added in an amount 1–2% above the stoichiometry ($n_{NaOH}/n_{Au} = 5 : 1$) to a ~0.1 M $HAuCl_4$ solution to neutralize H^+ and to fully substitute OH^- for Cl^-. The solution was allowed to stand for 24 h. The solution pH had to be 10–11, which was sufficient for OH^- to fully substitute for Cl^- without gold(III) hydroxide formation at $c_{Au} = 0.01–0.1$ mol/l [1]. Next, an $AgClO_4$ solution was added ($n_{Ag}/n_{Au} \approx 4 : 1$) until the white AgCl precipitate became brown due to the appearance of Ag_2O; the pH decreased in association. The precipitate was filtered off, and the solution pH was brought to 10–11 with NaOH. The hydroxosilver(I) complex has a low stability ($\log \beta_1 = 2.3$), and the solubility products of Ag_2O

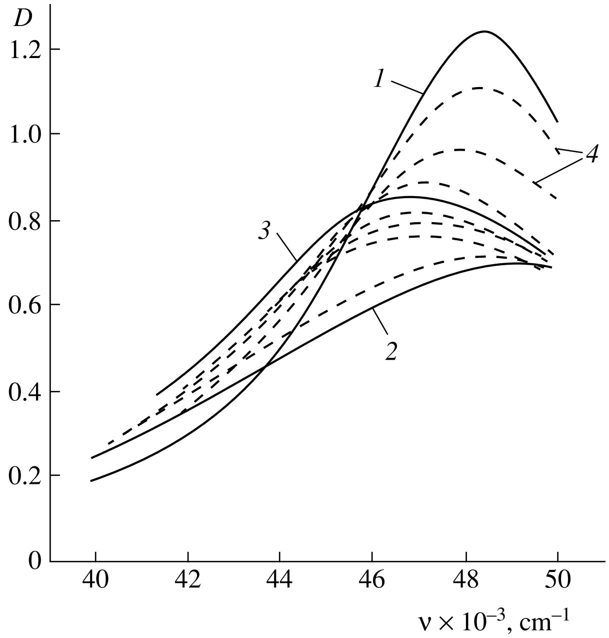

Fig. 1. Absorption spectra (*1–3*) for solutions with (*1*) pH > 4.5, (*2*) $[H^+] > 1$ mol/l, and (*3*) pH 2.47 and (*4*) for intermediate compositions (portions of the curves are shown with dashes). In all the solutions, $c_{Au} = 2.14 \times 10^{-4}$ mol/l. The cell length *l* is 0.5 cm. *D* stands for optical density.

and AgCl are equal to 10^{-8} and 10^{-10}, respectively. Therefore, the above procedure, on the one hand, provided the virtually full removal of Cl^- ions and, on the other, did not generate significant amounts of Ag^+ ions in the solution. Thus, the resulting solution contained Na^+ and ClO_4^- ions along with about 10^{-2} mol/l $Au(OH)_4^-$. The exact gold(III) concentration was determined from the $AuCl_4^-$ spectrum ($\varepsilon = 5600$ l/(mol cm) at 32000 cm^{-1}) after adding excess HCl to the solution sample.

The stock $HAuCl_4$ solution was prepared by dissolving high-purity gold in aqua regia and repeatedly concentrating the solution with HCl and water. An $AgClO_4$ solution with $c_{Ag} \approx 0.1$ mol/l was prepared by dissolving Ag_2O with perchloric acid being dropped. Reagent grade perchloric and nitric acids and carbonate-free NaOH were also used. The solution pH was measured using an Elwro 5170 instrument with a glass electrode calibrated against HCl solutions of known concentrations. For the $HClO_4$ solutions with concentrations higher than 0.1 mol/l, it was set that $[H^+] = c_H$. The spectra were recorded on a Specord UV-Vis spectrophotometer at $\nu = 28000$–50000 cm^{-1}. The equilibria were studied at $T = 25°C$.

RESULTS AND DISCUSSION

Recall that the rapid change from an alkaline to a high-acidity ($HClO_4$) medium in an $Au(OH)_4^-$ solution did not cause the precipitation of gold(III) hydroxide. Evidently, the almost instantaneous protonation of OH^- groups in $Au(OH)_4^-$ to form cationic species caused by an abrupt transfer to the acid medium allowed avoiding the intermediate pH range (8–3), which is most favorable for gold(III) hydroxide precipitation. We also noticed that the increasing acid concentrations strongly slow down this process. A stable solution was obtained when $c_H > 1$ mol/l and $c_{Au} < 1.5 \times 10^{-3}$ mol/l.

The spectrum of the solution differed from the $Au(OH)_4^-$ spectrum in both the intensity and the line shapes (Fig. 1). The increasing acidities from 1 to 8 mol/l $HClO_4$ did not appreciably change the spectrum. This fact proves that the same gold(III) species in constant concentrations existed over the entire range of $[H^+] = 1$–8 mol/l. The fulfillment of the Beer law was verified for $c_{Au} = 5 \times 10^{-5}$ to 1×10^{-3} mol/l.

For the gold concentration at a level of 1×10^{-3} mol/l, the solutions with $c_H < 1$ mol/l, especially, with $c_H < 0.4$ mol/l, were unstable: a white cloud of the hydroxide appeared in them in less than 1–2 min; the hydroxide amount systematically increased, and it yellowed and darkened. In 2 days, the gold(III) concentration in the solution over the orange precipitate was lower than 1×10^{-5} mol/l.

For the solutions with $[H^+] < 0.5$ mol/l ($c_{Au} = 5 \times 10^{-4}$ mol/l), the spectra were recorded immediately after preparation. Although the recording time was short (less than 1.5 min), a gold(III) hydroxide cloud was observed by the end. The spectral evolution with increasing pH is illustrated by Fig. 1. Initially (for pHs from 0 to 2.3), the intensity increased and the maxima shifted toward longer wavelengths. At pH > 2.3, the shift direction reversed; at pH > 4.5, the spectrum fully corresponded to the $Au(OH)_4^-$ spectrum. Spectrum *2* in Fig. 1 refers to solutions with $[H^+] > 1$ mol/l, spectrum *1* refers to solutions with pH > 4.5 (this spectrum remained unchanged over the entire range to pH 12), and spectrum *3* refers to a solution in which another species exists (this species does not exist in either the high-acidity or the alkaline solutions). Thus, our observations prove the existence of three aquahydroxogold(III) complex species. We know from gold(III) chemistry that $Au(OH)_4^-$ is the major species at pH > 4. In the range of pH 1.5–3, $Au(OH)_3(H_2O)^0$ exists in significant amounts; spectrum *3* in Fig. 1 is the spectrum of this species with a small contribution from other species. At pHs < 1, $Au(OH)_2(H_2O)_2^+$ is dominant. The holding of Beer's law proves the nonexistence of variously polymerized species.

The equilibrium constants for protonation

$$\begin{aligned} Au(OH)_4^- + H^+ &= Au(OH)_3(H_2O)^0,\ K_{H1} \\ Au(OH)_3(H_2O)^0 + H^+ &= Au(OH)_2(H_2O)_2^+,\ K_{H2} \end{aligned} \tag{3}$$

can be determined in an ordinary way [3] with the help of auxiliary function ε^*

$$\varepsilon^* = \frac{D}{c_{\mathrm{Au}} l} = \frac{\varepsilon_2 K_{\mathrm{H1}} K_{\mathrm{H2}} [\mathrm{H}^+]^2 + \varepsilon_3 K_{\mathrm{H1}} [\mathrm{H}^+] + \varepsilon_4}{K_{\mathrm{H1}} K_{\mathrm{H2}} [\mathrm{H}^+]^2 + K_{\mathrm{H1}} [\mathrm{H}^+] + 1}, \quad (4)$$

where D is the optical density; l is the cell length; and ε_2, ε_3, and ε_4 are the extinction coefficients for the $Au(OH)_2(H_2O)_2^+$, $Au(OH)_3(H_2O)^0$, and $Au(OH)_4^-$ species, respectively. The ε_2 and ε_4 values are known from spectroscopic data for solutions in the high-acidity and alkaline regions. The unknown ε_3, K_{H1}, and K_{H2} can be derived from an experimental $\varepsilon^*([H^+])$ plot by means of nonlinear least-squares fits. In this case, in D and c_{Au} determinations in the range of pH 1–4, one has to take into account the influence of the hydroxide cloud both on light absorption and on the binding of some gold(III) by the cloud. The optical density versus time function $D(\tau)$ with extrapolation to $\tau = 0$ can help, since the gold(III) hydroxide formation is not a rapid process. Nonetheless, additional systematic errors appear as a result. In view of this, for equilibria (3) and (4), it was found that $\log K_{H1} = 3.0 \pm 0.1$ and $\log K_{H2} = 1.8 \pm 0.2$ ($T = 25°C$, $I \approx 0$). Another piece of evidence is provided by Fig. 2. The increasing pH shifts the absorption maximum (Fig. 1) first toward longer wavelengths then to shorter ones. The maximal long-wavelength shift corresponds to the greatest contribution (the greatest mole fraction) of $Au(OH)_3(H_2O)^0$. On the other hand, it is well known that, for two-step equilibria, the greatest fraction of an intermediate species is achieved when $pH = 0.5\log(K_{H1}K_{H2})$. In the case at hand (Fig. 2), the maximal accumulation of the $Au(OH)_3(H_2O)^0$ intermediate species falls in the range of pH 2.2–2.5, which corresponds to $\log(K_{H1}K_{H2}) = 4.4$–5.0.

Using the $Au(OH)_4^-$ standard potential ($E^0_{3/0}$ = 0.488 V), the ion product of water ($\log K_w = -14.0$), and the $\log K_{H1}$ and $\log K_{H2}$ values obtained from (3), we can calculate the standard potentials for the $Au(OH)_2(H_2O)_2^+$ and $Au(OH)_3(H_2O)^0$ species: 1.50 V for $Au(OH)_2(H_2O)_2^+ + 3e + 2H^+ = Au^0 + 4H_2O$ and 1.53 V for $Au(OH)_3(H_2O)^0 + 3e + 3H^+ = Au^0 + 4H_2O$.

The absorption spectrum of the solution remained virtually unchanged over the entire range of the $HClO_4$ concentrations (1–8 mol/l). Therefore, $Au(OH)_2(H_2O)_2^+$ is the only species existing in this pH range. This goes in line with other data available. The aquagold(III) ion $Au(H_2O)_4^{3+}$ cannot be obtained because of its extremely high hydrolyzability. The standard potential of the aquagold(III) ion estimated by an indirect method is 1.58 V [2, 4]. Therefore, for the equilibrium $Au(OH)_2(H_2O)_2^+ + 2H^+ = Au(H_2O)_4^{3+}$, $K_{H3}K_{H4} = 10^{-4}$; i.e., at ordinary temperatures and pressures, this equilibrium strongly shifts to the reactants.

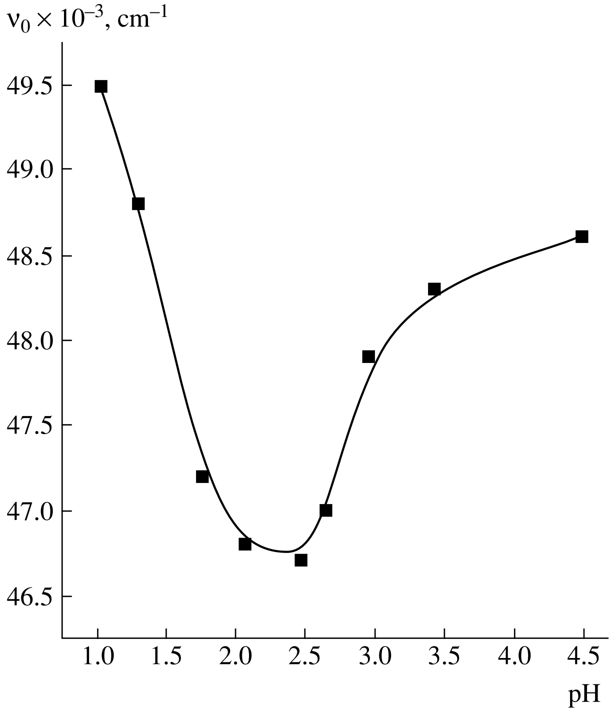

Fig. 2. Spectral band maximum position vs. solution pH.

Knowing the $\log\beta_4$ (1), $\log K_{H1}$, and $\log K_{H2}$, we can calculate the equilibrium constant for

$$AuCl_4^- + 4H_2O = Au(OH)_2(H_2O)_2^+ + 2H^+ + 4Cl^-, \quad (5)$$
$$\log K_{4,\,H_2O} = -25.2.$$

With $[Cl^-]$ buffered by the chloromercury(II) complex system [5], the constant was estimated for the equilibrium

$$AuCl_4^- + 2H_2O = AuCl_2(OH)(H_2O)^0 + H^+ + 2Cl^-, \quad (6)$$
$$\log K_{2,\,H_2O} = -10.7 \pm 0.2.$$

The number of the Cl^- ions substituted here is one half the number substituted in equilibrium (5). Taking into account possible stepwise effects [3] and the different ionic strengths, the $\log K_{4,\,H_2O}$ value is in agreement with $\log K_{2,\,H_2O}$.

The possibility of $Au(OH)_2(H_2O)_2^+$ formation was suggested in [4, 6]. A value of 5.5 was reported as a probable estimate of $\log(K_{H1}K_{H2})$. The extremely low gold(III) concentrations (10^{-6} to 10^{-8} mol/l [6]), the formation of nitrato complexes [3], and the instability of

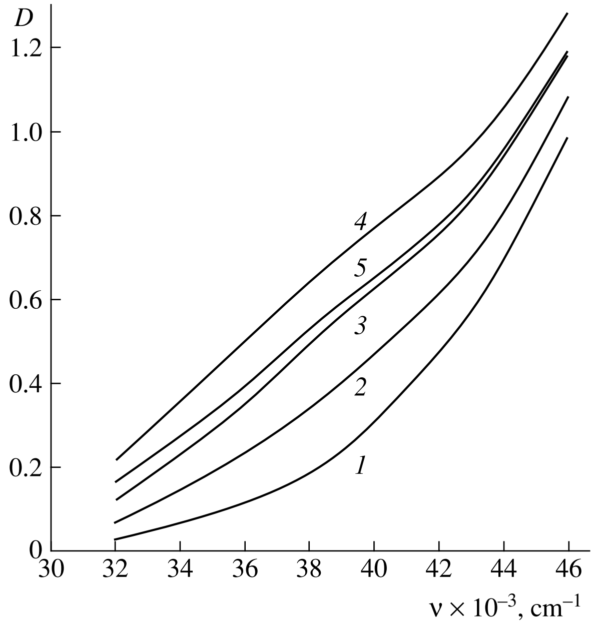

Fig. 3. Ethanol effect on the absorption spectra of solutions. $c_{Au} = 3.75 \times 10^{-4}$ mol/l, and $l = 0.5$ cm. Ethanol concentration: (*1*) 0, (*2*) 20, (*3*) 40, (*4*) 60, and (*5*) 40%. c_{HClO_4} = (*1–4*) 2.7 and (*5*) 4.5 mol/l.

the characteristics of gold(III) hydroxide did not allow us to draw more definite conclusions about the existence and properties of this complex species.

The feasibility of preparing the $Au(OH)_2(H_2O)_2^+$ species in concentrations of $(1–1.5) \times 10^{-3}$ mol/l is extremely important for the chemistry of gold. As a rule, new species are prepared from $AuCl_4^-$ by substituting other ligands for its Cl^-. The practicality of this route is affected by the substitution constant: if the substitution constant is low, the target complex cannot be obtained. However, the Cl^- ion is a sufficiently tenacious ligand for gold(III). Therefore, new complexes with weaker ligands cannot be obtained from $AuCl_4^-$. The $Au(OH)_2(H_2O)_2^+$ species ($E^0_{3/0} = 1.50$ V) increases the substitution constant for the same ligands by more than 20 log units against $AuCl_4^-$ ($E^0_{3/0} = 1.00$ V).

When ethanol was added to an $Au(OH)_2(H_2O)_2^+$ solution, a rise in the optical density was observed in the region 35000–45000 cm^{-1} (Fig. 3). The change in *D* was nearly proportional to the ethanol concentration. At a fixed ethanol concentration (40%), however, the change in c_{HClO_4} from 2.7 to 4.5 mol/l did not significantly affected the spectrum. Therefore, it is most likely that the observed rise in the optical density is not associated with the formation of new protonated species such as $Au(OH)(H_2O)_3^{2+}$. It is likewise doubtful whether ethanol can substitute for inner-sphere water molecules. The rise in *D* can be explained by $Au(OH)_2(H_2O)_2^+$ polymerization or a shift of the *cis*-$Au(OH)_2(H_2O)_2^+ \longleftrightarrow$ *trans*-$Au(OH)_2(H_2O)_2^+$ equilibrium caused by the changing medium. Water–ethanol solutions are unstable: a blue color, characteristic of colloidal gold(0), appears in 10 min; in 1 h, almost all of the gold(III) is reduced to the metal.

Using the equilibrium constants for (2) and (3), we can calculate the intrinsic solubility S_0 for aged gold(III) hydroxide:

$$1/2(Au_2O_3 \cdot xH_2O)_{solid} = Au(OH)_3(H_2O)^0_{aq}, K_{S0}. \quad (7)$$

The solubility is equal to $\log K_{S0} = \log S_0 = -\log K_{S1} + \log K_{H1} + \log K_w = -7.6$. A similar solubility value was derived experimentally [6]: $S = (2.6 \pm 1.5) \times 10^{-8}$ mol/l. From the standard potentials of the aqua ion $Au(H_2O)_4^{3+}$ ($E^0_{3/0} = 1.58$ V) and the tetrahydroxo complex $Au(OH)_4^-$ ($E^0_{3/0} = 0.488$ V) and from the constant of equilibrium (2), we can find the solubility product for aged gold(III) hydroxide: $\log SP_{Au(OH)_3} = -52.0$.

Gold(III) hydroxide aging is well understood [2, 4]. The aging involves polymerization, release of water, particle coarsening, reduction in solubility, and a change in the color. The white precipitate was shown to have particle sizes less than 80 nm; the yellow, orange, and red hydroxides have coarser particles [7]. Synthesis of red Au_2O_3 single crystals by heating a hydroxide precipitate with perchloric acid in a closed fused quartz tube and structural data are reported in [8, 9]. A gold atom has an ordinary square-planar oxygen coordination; some of the oxygen atoms are bridging and are, in addition, linked to one or two more gold atoms.

Precipitation of the red hydroxide was solely observed for rather high gold(III) concentrations ($c_{Au} >$ 0.1 mol/l) and chloride concentrations (c_{Cl} = 1 mol/l), i.e., under the dominance of the chlorohydroxogold(III) complexes [1]. In many cases, the precipitate appeared after some time (up to 30 min) elapsed since the solution was prepared. This is evidence of kinetic effects in the solution, namely, the slow formation of polymeric species preceding the precipitation. In the experiments described above (where the solution was free of ligands other than OH^- and ions other than H^+, Na^+, and ClO_4^-), we observed white gold(III) hydroxide solely. The precipitate yellowed with time converting into more stable species. A value of 1.5×10^{-3} mol/l was experimentally found for the boundary gold(III) concentration in 1 M $HClO_4$ below which the solution is stable. If we identify this boundary value with the solubility of the least aged (white) hydroxide species at the given acidity and if we take into account (3), the equilibrium constant for

$$1/2(Au_2O_3 \cdot xH_2O)^*_{solid} = Au(OH)_3(H_2O)^0_{aq},\ K^*_{S0} \quad (8)$$

is $\log K^*_{S0} = \log S^*_0 = -4.6$. The same value is found from the appearance pH of the first hydroxide traces if the $Au(OH)_4^-$ solution is titrated with perchloric acid: $S^*_0 \approx c_{Au}K_{H1}[H^+]_b$, where $[H^+]_b$ is the $[H^+]$ bound at which the precipitate appears. For $c_{Au} = 0.1$ mol/l, the hydroxide appears at pH 7–8 [8]; from this, $S^*_0 = 10^{-6}$ to 10^{-5} mol/l. We obtained a smaller value ($S^*_0 = 10^{-4.6}$ mol/l). However, firstly, the observations made in [7] were qualitative; secondly, local supersaturations are hardly avoidable with the use of high-concentration $NaAu(OH)_4$ and $HClO_4$ solutions. Once the hydroxide has appeared or it has been inserted into the solution, it never dissolves even though the solution is strongly acidified with perchloric acid. This proves the rapid aging and the very slow dissolution kinetics. Our data for the lower gold(III) and acid concentrations than used in [7] are listed in the table.

In the process of $HClO_4$ addition to the $Au(OH)_4^-$ solution, the glass-electrode potentials are first stable. Then, the potential starts rapidly decreasing (proving the release of OH^- ions) and a white hydroxide cloud appears in a short time. The pH' values listed in the table refer to the solution in which the potential is still stable and the pH'' values to the solution in which the potential already drifts. The $-\log c_{Au}$ + pH' values listed in the last column, which were calculated from the pH' values, are likely systematic overestimates. However, from comparison of the pH' and pH'', this error hardly exceeds 0.3. Note that we could not locate the onset pH of hydroxide precipitation better because of the low buffer capacity of the system. The average $-\log c_{Au}$ + pH' value is 7.6 ± 0.3 and is equal to the logarithmic equilibrium constant for $Au(OH)_4^- + H^+ = 1/2(Au_2O_3 \cdot xH_2O)^*_{solid}$. From these data, $\log S^*_0 \approx \log c_{Au} - pH' + \log K_{H1} = -4.6 \pm 0.3$. This value, although determined in a completely autonomous way, coincides with the value obtained above for equilibrium (8). The different conditions also count: in the first case, S^*_0 was derived from the solubility bound in the presence of a high acid ($HClO_4$) excess; in the second case, all the ions had concentrations at a level of 10^{-3} to 10^{-2} mol/l.

From the above data, the solubilities of the boundary (the best and the least aged) gold(III) hydroxide species differ by three orders of magnitude: $\log(S^*_0/S_0) = 3.0$. This difference cannot be due to the precipitate particle size solely; rather, it indicates chemical transformations during aging. Further investigations are needed to elucidate under which conditions the more stable hydroxide species will precipitate immediately instead of white gold(III) hydroxide.

Conditions for gold(III) hydroxide precipitation upon titration of $Au(OH)_4^-$-containing solutions with perchloric acid

Run no.	$c_{Au} \times 10^3$, mol/l*	pH'	pH''	$-\log c_{Au}$ + pH'
1	2.53	5.26	4.3	7.9
2	0.268	3.63	3.5	7.3**
3	1.91	4.63	4.0	7.4
4	2.45	5.07	4.7	7.7
5	1.85	4.86	4.1	7.6

* At point pH'.

** Taking that 25% gold(III) is in the $Au(OH)_3H_2O^0$ species.

The gold(III) hydroxide solubility in nitric acid was studied in [4, 10]. The solid hydroxide was dissolved in concentrated HNO_3, and the solution was diluted with water to set concentrations c_{HNO_3}. The hydroxide precipitate was filtered off, and gold was determined in the solution. Since the procedure included slow stages (precipitation and precipitate separation), we may state that the gold hydroxide samples dealt with in [4, 10] were partially aged. The solubilities quoted also argue for the partial aging: a value of 2.0×10^{-4} mol/l was found for S in 1 M HNO_3, which is almost one order of magnitude lower than S^* in 1 M $HClO_4$. Since $Au(OH)_2(H_2O)_2^+$ is the only aquahydroxo species in high-acidity ($[H^+] > 1$ mol/l) solutions (it should provide the change in the hydroxide solubility in proportion to the first order of $[H^+]$), the precipitation observed upon dilution is evidence of a significant contribution of nitrate complexes. It was mentioned in [4, 10] that, if the starting solutions were in 3 M HNO_3 rather than in concentrated HNO_3, their dilution would not cause gold(III) hydroxide precipitation. We attempted to estimate the stability constants for the nitrate complexes on the basis of solubility data [10] on the assumption that the degree of aging of the hydroxide at all points was roughly the same and that the major equilibrium was

$$\begin{aligned} &Au(OH)_2(H_2O)_2^+ + NO_3^- \\ &= Au(OH)_2(H_2O)(NO_3)^0,\ K_{NO_3}. \end{aligned} \quad (9)$$

Then, taking into account protonation (3), the solubility will be related to $[NO_3^-] \approx c_{NO_3}$ through

$$S/S'_0 = 1 + K_{2H}[H^+](1 + K_{NO_3}[NO_3^-]). \quad (10)$$

Here S_0' is the intrinsic solubility, which presumably remains constant but is not equal to either S_0^* or S_0. Thus, K_{NO_3} can be calculated from the change in solubility as a function of increasing c_{NO_3}. An estimate that ignores the medium effect (the changing ionic strength) leads to $K_{NO_3} = 0.25 \pm 0.05$ (the error is indicated as the doubled standard deviation). Model (10) satisfactory fits the data from [10] up to $c_{HNO_3} = 3$ mol/l. The more abrupt increase in the solubility caused by the further increasing HNO_3 concentration can be explained by both the formation of complex species with greater numbers of inner-sphere nitrate ions and the protonation of $Au(OH)_2(H_2O)(NO_3)^0$.

REFERENCES

1. I. V. Mironov and L. D. Tsvelodub, Zh. Neorg. Khim. **45** (4), 706 (2000) [Russ. J. Inorg. Chem. **45** (4), 633 (2000)].
2. B. I. Peshchevitskii, V. I. Belevantsev, and S. V. Zemskov, Izv. Sib. Otd. Akad. Nauk SSSR, Ser. Khim., No. 4 (2), 24 (1976).
3. V. I. Belevantsev and B. I. Peshchevitskii, *Investigation of Complex Equilibria in Solution* (Nauka, Novosibirsk, 1978) [in Russian].
4. B. I. Peshchevitskii, Doctoral Dissertation in Chemistry (Inst. of Inorg. Chem., Sib. Div., Acad. Sci. USSR, Novosibirsk, 1969).
5. V. I. Belevantsev, A. P. Ryzhikh, E. V. Makotchenko, and V. I. Malkova, Zh. Neorg. Khim. **44** (4), 608 (1999) [Russ. J. Inorg. Chem. **44** (4), 554 (1999)].
6. G. M. Varshal and T. K. Velyukhanova, in *Thermodynamics and Structure of Hydroxo Complexes in Solutions* (Leningr. Gos. Univ., Leningrad, 1986), p. 115 [in Russian].
7. G. Jander and G. Krien, Z. Anorg. Allg. Chem. **304**, 154 (1960).
8. E. Schwarzmann, J. Mohn, and H. Rumpel, Z. Naturforsch., A: Phys. Sci. **31** (1), 135 (1976).
9. P. G. Jones, H. Rumpel, E. Schwarzmann, *et al.*, Acta Crystallogr., Sect. B: Struct. Sci. **35** (6), 1435 (1979).
10. A. A. Bezzubenko and B. I. Peshchevitskii, Izv. Sib. Otd. Akad. Nauk SSSR, Ser. Khim., No. 8, 62 (1961).