

# Studies on Gold Complexes. I. Robustness, Stability and Acid Dissociation of the Tetramminegold(III) Ion

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This paper presents a study of the stability and robustness of the tetramminegold(III) ion. The acidic character of this complex ion has been demonstrated;  $pK_a$  has been determined to be  $7.48 \pm 0.04$  in 1 M (Na,  $NH_4$ )ClO<sub>4</sub> at 25 °C. The slow hydrolysis of the tetrammine complex in acid solution leads to a stationary equilibrium between this complex and hydroxotriamminegold(III) in the pH-range 2–5. The kinetics of this reaction was studied spectrophotometrically, and the hydrolysis equilibrium constant  $K_h$  estimated to be 0.7 mol/l at 25 °C. The aquatriamminegold(III) ion is a strong acid, the  $pK_a$  of which was found to be  $\approx -0.7$ . Combining this value with  $K_h$ , the 4th consecutive stability constant is determined to be  $2 \times 10^{10}$  l/mol, which by generalization from other square planar tetrammine complexes gives an estimate of the cumulative constant  $\beta_4 \approx 10^{46}$  l<sup>4</sup>/mol<sup>4</sup> for the tetramminegold(III) ion.

The first to prepare tetramminegold(III) salts was Weitz<sup>1</sup> in 1915. He prepared the nitrate by leading gaseous ammonia into a solution of  $AuCl_4^-$  in concentrated  $NH_4NO_3$ . However, the conditions are critical, and this is probably the reason why Addison *et al.*<sup>2</sup> had no success when they recently tried to prepare the salt by this method. According to our experience the preparation runs successfully when a supersaturated solution of  $NH_4NO_3$  is used and addition of ammonia is stopped at pH 7–8.

The tetramminegold(III) ion has a certain robustness, but is slowly irreversibly hydrolyzed even in 10 M  $NH_4NO_3$ . However, the first hydrolysis product  $Au(NH_3)_3OH^{2+}$  seems to be in a stationary equilibrium with the tetrammine

ion in the pH-range 2–5. The kinetics of this reaction was studied spectrophotometrically in the temperature range 50–80 °C, and the hydrolysis constant  $K_h$  was estimated. At higher pH there is an instantaneous equilibrium between the tetrammine ion and  $Au(NH_3)_3NH_2^{2+}$ . The acid dissociation constant  $K_a$  as well as the absorption spectrum of the amide complex was determined. At pH lower than  $\approx 1$ ,  $Au(NH_3)_3OH^{2+}$  begins to be protonated forming the corresponding aqua ion  $Au(NH_3)_3H_2O^{3+}$ . It was therefore possible also to obtain an estimate of  $K_4$ , the 4th consecutive stability constant of the tetramminegold(III) ion.

## EXPERIMENTAL

*Chemicals and solutions.* “Goldtrichloride” from H. Drijfhout & Zoon’s, Amsterdam, was used as the starting gold compound. The ammonia was taken from a cylinder and purified by passing through a sodium hydroxide solution. A stock solution of ammonia perchlorate was prepared from ammonia and perchloric acid and the neutralization was checked by pH measurements according to the procedure described by one of the authors.<sup>3</sup> All other chemicals used were of analytical grade.

*Preparation of  $Au(NH_3)_4(NO_3)_3$ .* The following procedure was found to give maximum yield of tetramminegold(III) nitrate: “Goldtrichloride” corresponding to 0.5 g of gold was dissolved in a supersaturated solution of 95 g  $NH_4NO_3$  and 70 ml water. To this solution gaseous  $NH_3$  is passed until pH  $\sim 7$  with simultaneous cooling with icewater. The reaction mixture is left overnight in a stoppered flask and a white precipitate of tetramminegold(III) nitrate is formed. The crude product is obtained in a yield of  $\sim 95\%$ . Recrystallization at 50 °C from 12 ml  $10^{-3}$  M  $HNO_3$  per g

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gold salt gives a residue which consists of hydrolyzed species having a too high gold content ( $\sim 50\%$ ). The filtered solution is acidified with 1 ml 4 M  $\text{HNO}_3$  for each 12 ml and cooled with icewater. A second fraction can be obtained on precipitation with an equal volume of ethanol. The two fractions show no systematical deviation on analysis. The product is washed with a little icewater and icecooled ethanol and dried at room temperature. The yield after recrystallization is  $\sim 65\%$ . The complex contains less than 0.5% water determined by drying at 105 °C. (Typical analyses were: Au 43.40; N 21.59; H 2.57;  $\text{NH}_3$  14.6, and Au 43.81; N 20.78; H 2.53;  $\text{NH}_3$  14.4. Calc. for  $\text{Au}(\text{NH}_3)_4(\text{NO}_3)_3$ : Au 43.68; N 21.73; H 2.69;  $\text{NH}_3$  15.10). Total N and H was determined in the microanalytical laboratory of this institute. Au was determined by weighing in a silica crucible after ignition, and  $\text{NH}_3$  by a micro Kjeldahl distillation. Thermogravimetric analysis showed no decomposition of the complex up till  $\approx 230$  °C, then decomposition to metallic gold occurs over a short temperature range and not stepwise.

*Preparation of  $\text{Au}(\text{NH}_3)_4(\text{ClO}_4)_3$ .* The tetramminegold(III) nitrate was converted into the perchlorate as already described by Weitz.<sup>1</sup> (Found: Au 35.5; N 10.7; H 2.25; Cl 18.2. Calc. for  $\text{Au}(\text{NH}_3)_4(\text{ClO}_4)_3$ : Au 35.0; N 10.0; H 2.15; Cl 18.9). (*Warning:* The perchlorate explodes easily on heating).

*pH-measurements* were performed with a digital pH-meter Radiometer PHM 52 with Radiometer's glass electrode type G 202 B selected to have almost theoretical slope in the actual medium. A commercial saturated potassium

chloride calomel electrode was modified to 1 M sodium chloride and used as reference electrode. This modification was necessary in order to avoid precipitation of  $\text{KClO}_4$  in the boundary between the medium and the electrode. The definition  $\text{pH} = -\log [\text{H}^+]$  was employed throughout, and *concentration* pH-standards were made in the actual salt medium.

*Spectrophotometric measurements* were all made on a Cary 14 spectrophotometer in 1 cm silica cells at 25 °C.

#### Acid dissociation constant of $\text{Au}(\text{NH}_3)_4^{3+}$ and spectrum of $\text{Au}(\text{NH}_3)_3\text{NH}_2^{2+}$

The tetramminegold(III) ion is a weak acid forming amidotriamminegold(III) in basic solution, the latter being rather sensitive to further decomposition. A direct titration with strong base gives the correct S-shaped titration curve, but at the end of the titration precipitation occurs. The acid-base equilibrium was therefore studied in 1 M  $(\text{Na}, \text{NH}_4)\text{ClO}_4$ -ammonia buffer solutions in order to determine the constant

$$K_{\text{amid}} = \frac{[\text{NH}_4^+][\text{Au}(\text{NH}_3)_3\text{NH}_2^{2+}]}{[\text{NH}_3][\text{Au}(\text{NH}_3)_4^{3+}]}$$

which is connected by the acid dissociation constant of  $\text{Au}(\text{NH}_3)_4^{3+}$  by the relationship

$$K_a(\text{Au}(\text{NH}_3)_4^{3+}) = K_{\text{amid}} \times K_a(\text{NH}_4^+)$$

Table 1. Determination of the acid-base constant of  $\text{Au}(\text{NH}_3)_4^{3+}$  in 1 M  $(\text{Na}, \text{NH}_4)\text{ClO}_4$ -ammonia buffer solutions at 25 °C.

$C^0_{\text{Au}(\text{NH}_3)_4^{3+}}$	$C^0_{\text{NH}_3}$	$C^0_{\text{NH}_4^+}$	$\text{pH} = -\log[\text{H}^+]$	$\text{p}K_a(\text{NH}_4^+)$	$\alpha$	$K_{\text{amid}}$
0.00937	0.01195	0.0999	8.094	9.463	0.787	87
0.00936	0.0378	1.000	7.903	9.420	0.769	109
0.0200	0.0378	1.000	7.783	9.420	0.721	112
0.00922	0.00574	0.1088	7.461	9.463	0.500	100
0.0192	0.00909	0.1007	7.349	9.463	0.430	98
0.00938	0.00384	0.1652	7.162	9.460	0.319	93
0.0117	0.00288	0.1000	6.963	9.463	0.219	89
0.0169	0.00384	0.1652	6.902	9.460	0.200	91
0.0185	0.00288	0.1000	6.713	9.463	0.146	96
						$K_{\text{amid}} = 97 \pm 4$

$C^0_x$  denotes the initial concentrations of  $\text{Au}(\text{NH}_3)_4^{3+}$ ,  $\text{NH}_3$  and  $\text{NH}_4^+$ . As  $[\text{H}^+]$  and  $[\text{OH}^-]$  are less than  $10^{-6}$  M, then the following relationships are valid:

$$[\text{NH}_3] = K_a(\text{NH}_4^+) \times [\text{NH}_4^+]/[\text{H}^+],$$

$$[\text{NH}_4^+] = C^0_{\text{NH}_4^+} + \alpha C^0_{\text{Au}(\text{NH}_3)_4^{3+}},$$

$$\alpha = (C^0_{\text{NH}_3} - [\text{NH}_3])/C^0_{\text{Au}(\text{NH}_3)_4^{3+}}, \text{ and finally } K_{\text{amid}} = \alpha[\text{NH}_4^+]/(1 - \alpha[\text{NH}_3]).$$

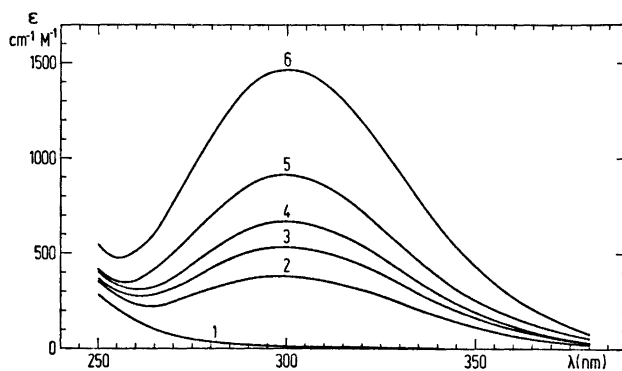


Fig. 1. Spectra of tetramminegold(III) nitrate in 1.0 M  $\text{NH}_4\text{ClO}_4$ - $\text{NH}_3$  buffer solutions. Curve 1 is the spectrum of  $\text{Au}(\text{NH}_3)_4^{3+}$  obtained from measurements of solutions of the nitrate in 1.0 M  $\text{NH}_4\text{ClO}_4$  at pH 2.0. The spectra recorded in  $\text{NH}_4^+$ ,  $\text{NH}_3$  buffer solutions have the following values for  $\alpha = [\text{Au}(\text{NH}_3)_3\text{NH}_2^{2+}]/C_{\text{Au(III)}}$ : Curve 2,  $\alpha = 0.25$ ; 3,  $\alpha = 0.36$ ; 4,  $\alpha = 0.45$ ; and 5,  $\alpha = 0.62$ . Curve 6 is the spectrum of  $\text{Au}(\text{NH}_3)_3\text{NH}_2^{2+}$  calculated from the mixed spectra. All spectra were recorded immediately after mixing the solutions, and the absorption curves given are corrected for the nitrate absorption. The maximum at 300 nm has a molar absorptivity of  $1467 \pm 15 \text{ cm}^{-1} \text{ M}^{-1}$ .

Glass electrode measurements were performed in solutions in which the  $\text{NH}_4^+$ -concentration was varied between 0.1 and 1 M. There was a small drift towards higher pH (especially in the solutions with lowest ammonium concentration) and therefore pH was in all cases extrapolated back to the time of mixing. The possibility of  $\text{Au}(\text{NH}_3)_3\text{OH}^{2+}$  formation was excluded because hydroxo complex formation will cause only infinitesimally small changes in pH in a medium containing excess ammonium ions. The acid dissociation constant for  $\text{NH}_4^+$  at ionic strength 1.0, necessary to calculate  $\text{p}K_a$  for  $\text{Au}(\text{NH}_3)_4^{3+}$ , was determined in 0.1 M as well as in 1 M  $\text{NH}_4^+$  solution, and the following interpolation formula was derived

$$\text{p}K_a(\text{NH}_4^+) = 9.468 - 0.048[\text{NH}_4^+]$$

The experimental data are given in Table 1.  $K_{\text{amid}}$  was found to be  $97 \pm 4$  at  $25^\circ\text{C}$  in 1 M  $(\text{Na},\text{NH}_4)\text{ClO}_4$ , and  $\text{p}K_a(\text{Au}(\text{NH}_3)_4^{3+})$  to be  $7.48 \pm 0.04$ . The value found for  $\text{p}K_a$  is compared in Table 4 with the few known values for other metal ammine complexes. The absorption spectrum for amidotriamminegold(III) shown in Fig. 1 was calculated from the mixed absorption spectra of tetramminegold(III) in 1 M  $(\text{Na},\text{NH}_4)\text{ClO}_4$ -ammonia buffer solutions.

#### Hydrolysis of $\text{Au}(\text{NH}_3)_4^{3+}$ in acid solution

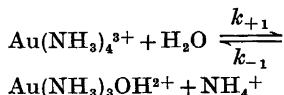
The tetramminegold(III) ion hydrolyzes rapidly in alkaline solution forming an orange-brown, amorphous, and highly explosive precipitate known as fulminating gold. In acid solution the tetramminegold(III) ion is stabilized and the hydrolysis is slow.

The change in the absorption spectrum as function of time in acid ammonium solutions corresponds to first order kinetics. The rate and the degree of hydrolysis depend on the ammonium concentration but not on the hydrogen ion concentration in the pH-range 2-4 as illustrated by an example in Table 2. The

Table 2. Hydrogen ion concentration influence on the rate and on the degree of hydrolysis of  $\text{Au}(\text{NH}_3)_4^{3+}$  in 1.0 M  $(\text{Na},\text{NH}_4)\text{ClO}_4$  at  $80.0^\circ\text{C}$  from calculations at  $\lambda = 320 \text{ nm}$ .  $C_{\text{Au}} \approx 0.003 \text{ M}$ .  $\epsilon_{\text{eq}}$  is the formal molar absorptivity at equilibrium obtained from the regression analysis; see text.

$[\text{NH}_4^+]$	pH	$10^3 k_{\text{obs}} \text{ s}^{-1}$	$\epsilon_{\text{eq}} \text{ cm}^{-1} \text{ M}^{-1}$
1.0	2.0	$1.74 \pm 0.05$	88
1.0	3.0	$1.80 \pm 0.08$	86
0.50	2.0	$1.38 \pm 0.06$	102
0.50	3.0	$1.32 \pm 0.12$	103

experimental observations fit with the following reaction scheme:



This reaction was investigated in the temperature range 50–80 °C by spectrophotometric measurements. Aliquots, removed at known times from thermostated acid solutions (~3 mM in  $\text{Au}(\text{NH}_3)_4(\text{NO}_3)_3$  in 1.0 M  $(\text{Na},\text{NH}_4)\text{ClO}_4$ ) were cooled in icewater, and the spectra recorded at room temperature. The absorption spectrum changes to an almost constant spectrum, which, however, continues to change especially at low ammonium concentration due to irreversible hydrolysis processes. As no final reading could be obtained, the reaction was studied kinetically. The over-all rate constant  $k_{\text{obs}}$  of the equilibrating process was determined at varying ammonium ion concentrations at pH=2.0 in 1.0 M  $(\text{Na},\text{NH}_4)\text{ClO}_4$ . From the absorbance as a function of time the pseudo first order rate constant  $k_{\text{obs}}$  was calculated at the wavelengths 310, 320, and 330 nm by means of nonlinear regression analysis as shown in Fig. 2. A final reading is not necessary in this method of calculation, and values corresponding to the slowly increasing absorbance were excluded in the calculations. At a fixed temperature the rate constant  $k_{\text{obs}}$  obeys the expression

$$k_{\text{obs}} = k_{+1} + k_{-1}[\text{NH}_4^+]$$

In Fig. 3  $k_{\text{obs}}$  determined at varying ammonium ion concentrations is shown. By means of weighted linear regression analysis values of  $k_{+1}$  and  $k_{-1}$  were calculated at 80.0, 70.0, 60.0, and 50.0 °C as given in Table 3 together with the calculated equilibrium constant,  $K_h$ . The values of  $k_{+1}$  and  $k_{-1}$  at the same temperature are strongly negative correlated, and in the final calculations of the equilibrium constant and the activation energies the non-diagonal elements in the experiment variance matrix must be included. Therefore the activation parameters cannot be obtained from a conventional Arrhenius plot as such a plot neglects the correlation between the rate constants. When the rate constants were fitted to the equation  $k = Z \exp(-E_a/RT)$ , activation energies of  $E_{a(+1)} = 24 \pm 6$  kcal/mol and  $E_{a(-1)} = 20 \pm 16$  kcal/mol, respectively, were calculated, whereas when the logarithm of the rate constant was fitted to  $\ln k = \ln Z - E_a/RT$ ,  $E_{a(+1)} = 27 \pm 3$  kcal/mol and  $E_{a(-1)} = 17 \pm 8$  kcal/mol were obtained. These two sets of parameters are, within the estimated standard deviations, identical. The conclusion is, however, that the experiments do not allow one to get usable values for the activation energies and for  $\Delta H^\circ$  for the reaction. By analogy with the corresponding reaction for  $\text{Hg}(\text{II})$ , it is, however, possible to estimate a value for  $\Delta H^\circ$ ; see discussion.

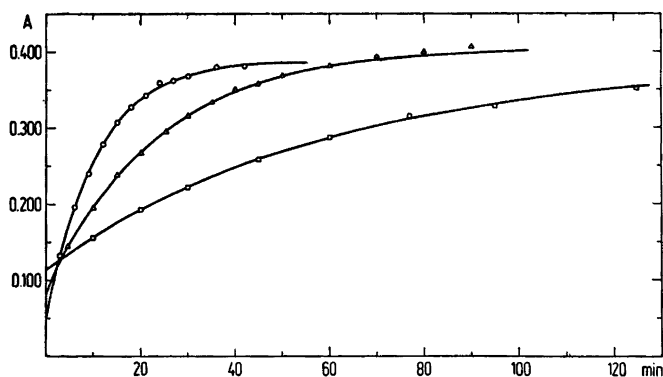


Fig. 2. Determinations of the rate of hydrolysis of  $\text{Au}(\text{NH}_3)_4^{3+}$  from plots of absorbance versus time. Solutions ~3 mM in  $\text{Au}(\text{NH}_3)_4^{3+}$  were hydrolyzed in 1.0 M  $(\text{Na},\text{NH}_4)\text{ClO}_4$  at pH=2.0. The absorbance at the wavelengths 310, 320, and 330 nm as function of time was fitted to the expression  $A = a_1 + a_2 \times \exp(-k_{\text{obs}}t)$  by means of nonlinear regression analysis. The examples given in the figure are experiments with  $[\text{NH}_4^+] = 0.80$  M at 80.0 °C, 70.0 °C and 60.0 °C monitored at  $\lambda = 310$  nm.

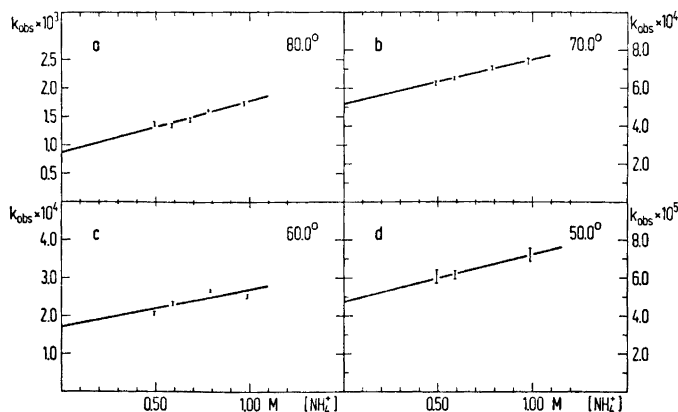
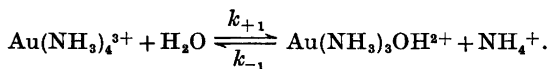


Fig. 3a–d. The influence of ammonium ion concentration on the rate of hydrolysis of  $\text{Au}(\text{NH}_3)_4^{3+}$  at four temperatures. The values of  $k_{\text{obs}}$  in  $\text{s}^{-1}$ , determined in 1.0 M  $(\text{Na}, \text{NH}_4)\text{ClO}_4$  at  $\text{pH} = 2.0$  as shown in Fig. 2, are split up into  $k_{+1}$  and  $k_{-1}$  by means of weighted linear regression analysis according to the expression:  $k_{\text{obs}} = k_{+1} + k_{-1}[\text{NH}_4^+]$ .

Table 3. Summary of the results of the kinetic experiments on the hydrolysis of  $\text{Au}(\text{NH}_3)_4^{3+}$  in 1.0 M  $(\text{Na}, \text{NH}_4)\text{ClO}_4$  at  $\text{pH} = 2.0$ .

The rate constants of the forward reaction  $k_{+1}$  and the reverse reaction  $k_{-1}$  of the hydrolytic equilibrating process:



The correlation coefficients,  $r$ , illustrate the strong negative correlations between the determined rate constants at the same temperature; see Fig. 3.

$t$ °C	$k_{+1}$ $\text{s}^{-1}$	$k_{-1}$ $\text{M}^{-1} \text{s}^{-1}$	$r(k_{+1}, k_{-1})$	$K_{\text{h}}$ mol/l
80.0	$(8.72 \pm 0.87) \times 10^{-4}$	$(9.2 \pm 1.1) \times 10^{-4}$	-0.984	$1.0 \pm 0.2$
70.0	$(5.10 \pm 0.30) \times 10^{-4}$	$(2.42 \pm 0.43) \times 10^{-4}$	-0.977	$2.1 \pm 0.5$
60.0	$(1.72 \pm 0.23) \times 10^{-4}$	$(9.8 \pm 2.9) \times 10^{-5}$	-0.970	$1.8 \pm 0.8$
50.0	$(4.73 \pm 0.58) \times 10^{-5}$	$(2.48 \pm 0.83) \times 10^{-5}$	-0.964	$1.9 \pm 0.9$

#### Acid dissociation constant of $\text{Au}(\text{NH}_3)_3\text{H}_2\text{O}^{3+}$

The spectrum of a partially hydrolyzed solution of  $\text{Au}(\text{NH}_3)_4^{3+}$  changes when acidified below  $\text{pH} \approx 1$ . The spectral data of such an experiment performed with  $\text{Au}(\text{NH}_3)_4(\text{ClO}_4)_3$  in perchloric acid solutions are shown in Fig. 4. The hydrogen ion activity in the concentrated  $\text{HClO}_4$  solution was expressed in the Hammett acidity function<sup>5</sup> redefined with standard state in 1 M  $\text{HClO}_4$ , which corresponds to the medium used in the hydrolysis experiments. Plotting the absorptivity against the Hammett acidity function, one gets an S-shaped "titration curve" with  $\text{p}K_{\text{a}} \approx -0.7$ .

In Table 4 this value found for the aquatriamminegold(III) ion is compared with known values for some ammine and aquaammine complexes, and it will be seen that the difference between the  $\text{p}K_{\text{a}}$  of  $\text{Au}(\text{NH}_3)_4^{3+}$  and  $\text{Au}(\text{NH}_3)_3\text{H}_2\text{O}^{3+}$  is of expected order of magnitude. The red shift in the absorption curve upon exchanging  $\text{NH}_3$  with  $\text{H}_2\text{O}$  and  $\text{OH}^-$  is in accordance with the spectrochemical series.

#### DISCUSSION

Combining thermochemical data from Yatsimirskii and Milyukov<sup>16</sup> and Anderegg *et al.*<sup>17</sup> one can calculate for the enthalpy change of the reaction

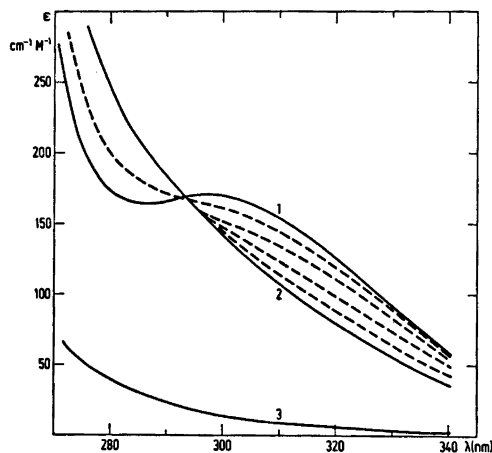
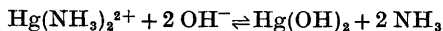


Fig. 4. Spectra and acid dissociation constant of the aquatrimminegold(III) system at 25 °C. A solution with  $C_{\text{Au}(\text{NH}_3)_3(\text{ClO}_4)_3} = 0.00293$  M and  $\text{pH} = 2.0$  was hydrolyzed at 80 °C for 15 min. From the spectrum the following concentrations after dilution to the double volume could be calculated:

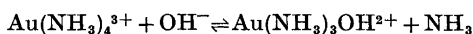
$$[\text{Au}(\text{NH}_3)_4^{3+}] = 0.00080 \text{ M}; [\text{Au}(\text{NH}_3)_3\text{OH}^{2+}] = 0.00070 \text{ M}.$$

Spectra of solutions of this composition with increasing acidity were measured. The absorption curves corrected for the  $\text{Au}(\text{NH}_3)_4^{3+}$  absorption (curve 3) are given in the figure.

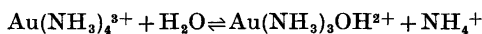
Absorption curve 1 with  $\epsilon_{\text{max}} \approx 170$  at 297 nm recorded at  $\text{pH} = 2.0$  represents the molar absorptivity of  $\text{Au}(\text{NH}_3)_3\text{OH}^{2+}$ . Curve 2 is the absorption spectrum in 5.89 M  $\text{HClO}_4$  ( $H_0' = -2.65$ ), which corresponds to a solution of  $\text{Au}(\text{NH}_3)_3\text{H}_2\text{O}^{3+}$ . The dotted curves are mixed spectra at the following concentration of  $\text{HClO}_4$ : 1.00 M ( $H_0' = 0.00$ ), 1.94 M ( $H_0' = -0.55$ ), 2.88 M ( $H_0' = -1.00$ ) and 4.41 M ( $H_0' = -1.73$ ).  $H_0'$  given in the brackets is the Hammett acidity function defined with standard state in 1 M  $\text{HClO}_4$ . From the spectral changes as a function of  $H_0'$  one calculates  $\text{p}K_a \approx -0.7$ .



in homogeneous solution,  $\Delta H^\circ = 8.7$  kcal/mol, or on an average 4.4 kcal/mol for the exchange of an ammonia molecule with a hydroxide ion. The endothermic character of this reaction is that expected from a consideration of  $\text{Hg}(\text{II})$  as a soft metal, and therefore according to the HSAB criterion as preferring ammonia to hydroxide ion. For the analogous hydrolysis reaction for  $\text{Au}(\text{III})$ , a metal with a softness greater than but comparable to that of  $\text{Hg}(\text{II})$ , an estimate of  $\Delta H^\circ \approx 5$  kcal/mol seems reasonable for the reaction:



Combination of this value with the protonation enthalpies for ammonia  $-12.4$  kcal/mol,<sup>14</sup> and for  $\text{OH}^-$   $-13.4$  kcal/mol,<sup>15</sup> gives  $\Delta H^\circ \approx 6$  kcal/mol for the reaction



On extrapolation of the hydrolysis constant  $K_h$  determined at elevated temperatures to 25 °C by means of  $\Delta H^\circ \approx 6$  kcal/mol, one gets  $K_h \approx 0.7$  mol/l. The corresponding constant for the hexamminechromium(III) ion  $K_h = 150$  mol/l (4.5 M  $\text{NH}_4\text{Cl}$ )<sup>4</sup> and for the hexamminecobalt(III) ion  $K_h = 0.032$  mol/l (1.0 M  $\text{NH}_4\text{Cl}$ )<sup>3</sup>

The fourth consecutive stability constant of  $\text{Au}(\text{NH}_3)_4^{3+}$  is given by the expression

$$K_4 = K_a(\text{Au}(\text{NH}_3)_3\text{H}_2\text{O}^{3+}) / (K_h \times K_a(\text{NH}_4^+))$$

Introducing the estimated values for  $K_h \approx 0.7$  mol/l in 1 M  $(\text{NH}_4, \text{Na})\text{ClO}_4$  at 25 °C, and the corresponding  $K_a$  values,  $K_4$  is calculated to be  $2 \times 10^{10}$  l/mol. An estimate of  $\beta_4$  ( $\text{Au}(\text{NH}_3)_4^{3+}$ ) can be obtained in the following way. The

Table 4. Comparison of acidities of ammine and aquaammine metal complexes at room temperature.

	$\text{p}K_a$	$I$	Ref.		$\text{p}K_a$	$I$	Ref.
$\text{Au}(\text{NH}_3)_4^{3+}$	7.48	1.0		$\text{Au}(\text{NH}_3)_3\text{H}_2\text{O}^{3+}$	-0.7	(1.0)	
$\text{Pt}(\text{NH}_3)_6^{4+}$	7.75	0.1	6	$\text{Pt}(\text{NH}_3)_5\text{H}_2\text{O}^{4+}$	?		
$\text{Ru}(\text{NH}_3)_6^{3+}$	12.4	var.	7	$\text{Ru}(\text{NH}_3)_5\text{H}_2\text{O}^{3+}$	4.2	var.	10
$\text{Rh}(\text{NH}_3)_6^{3+}$	> 14		8	$\text{Rh}(\text{NH}_3)_5\text{H}_2\text{O}^{3+}$	6.40	0.1	11
$\text{Co}(\text{NH}_3)_6^{3+}$	> 14		8	$\text{Co}(\text{NH}_3)_5\text{H}_2\text{O}^{3+}$	6.40	1.0	3
				$\text{Co}(\text{NH}_3)_4\text{H}_2\text{O}^{3+}$	6.03	0.1	3
				$\text{Cr}(\text{NH}_3)_5\text{H}_2\text{O}^{3+}$	5.10	0.1	12
$\text{Au en}_2^{3+}$	6.8	var.	9				
$\text{Au pn}_2^{3+}$	6.6	var.	9				

tetramminegold(III) complex has the same square planar configuration as the tetrammines of Cu(II) and Pd(II), and the properties of the three complexes may also in other respect be comparable. The spreading of the consecutive constants (especially  $K_2/K_3$ ), although larger in the Pd(II)- than in the Cu(II)-system, are of the same order of magnitude in the two systems. Thus the ratio  $\sqrt[4]{\beta_4}/K_4$  has in the Cu(II)-system<sup>3</sup> the value  $10^{1.03}$  and in the Pd(II)-system<sup>13</sup> the value  $10^{1.4}$ . Combining the average value  $10^{1.2}$  with the estimated value for  $K_4(\text{Au(III)})$  at 25 °C, the stability constant  $\beta_4(\text{Au(III)})$  is calculated to be about  $10^{46}$  l<sup>4</sup>/mol<sup>4</sup> as compared with  $\beta_4(\text{Cu(II)}) = 10^{12.61}$  l<sup>4</sup>/mol<sup>4</sup> (in 1 M  $\text{NH}_4\text{NO}_3$  at 25 °C) and  $\beta_4(\text{Pd(II)}) \approx 10^{22.8}$  l<sup>4</sup>/mol<sup>4</sup>.

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