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The Chloro Complexes of Gold(I) in Acetonitrile and Comparison with Those of Copper(I) and Silver(I)

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The chloro complexes of gold(I) in acetonitrile have been investigated by potentiometry. The stepwise formation constants for AuCl and $AuCl_2^-$ are $10^{12.63}$ and $10^{8.89}$. A striking difference in the solution equilibria of copper(I) chloride, silver(I) chloride, and gold(I) chloride is noted.

Introduction

Hydrated gold(I) ion, like hydrated copper(I) ion, is unstable in water, disproportionating to gold(III) and metallic gold.[1] In acetonitrile because copper(I) is more strongly solvated than copper(II), copper(I) ion is stable, in contrast to the situation in water.[2] Similarly, solvated gold(I) ion in acetonitrile should be stable. In successfully preparing bis(acetonitrile) gold(I) perchlorate from acetonitrile solution by oxidation of gold metal with nitrosyl perchlorate, Bergerhoff has shown this to be the case.[3] In voltammetric and chronopotentiometric studies of *ca.* 5×10^{-4} *M* solutions of gold(I) perchlorate in acetonitrile in this laboratory, a one-electron reduction step at *ca.* + 1 v *vs.* S.C.E. (aq) at a platinum electrode, in agreement with the recent report of Goolsby and Sawyer,[4] was observed. No oxidation step, however, was evident on anodic scans out to +2.8 v *vs.* S.C.E. with a rotating platinum electrode. From this observation, it appears that if the gold(I) to gold(III) electrochemical oxidation step at a platinum electrode is reversible, the potential of the gold(III)/gold(I) couple in acetonitrile is greater than +2.8 v *vs.* S.C.E. (aq).

Because of our previous studies of the chloro complexes of copper(I)[5] and of silver(I)[6] in acetonitrile, it was of special interest to us to examine the chloro complexes of gold(I) ion in acetonitrile.

Experimental Section

Fisher « Certified » reagent grade acetonitrile was purified by distillation from calcium hydride, followed by fractional distillation from phosphorus(V) oxide. Karl Fischer titration showed the water content of the distillate to be less than 0.002 *M*.

Tetraethylammonium perchlorate was prepared as described previously.[7] Tetraethylammonium chloride (Eastman) was recrystallized three times from water and dried *in vacuo* at 80°. Bis(acetonitrile)gold(I) perchlorate was prepared by the addition of excess gold powder to a suspension of dry nitrosyl perchlorate in acetonitrile. The mixture was stirred for several hours, then filtered to remove the excess gold. The filtrate was evaporated to a small volume and cooled at –78°. The crystals of bis(acetonitrile)-gold(I) perchlorate obtained were washed with small amounts of cold acetonitrile. Rather than storing the solid salt, the solvated gold(I) perchlorate was dissolved in acetonitrile and the solution was placed in a black bottle previously filled with nitrogen. Bis(acetonitrile)gold(I) perchlorate was observed to decompose as soon as some of the coordinated acetonitrile is lost. The concentration of gold(I) of the solution was determined by electrodeposition on a platinum electrode. Nitrosyl perchlorate was obtained by a procedure described previously.[8]

Potentiometric data were obtained with a Leeds and Northup K-2 potentiometer. The cell was a *ca.* 2 cm diameter test tube of 30 ml capacity to which a side arm of *ca.* 1 cm diameter was attached near the bottom of the cell at an angle of 30° A capillary tube, to pass nitrogen through the solution, was connected near the base of the cell. The flow of purified nitrogen, saturated with the solvent, into the cell stirred the solution and protected it from atmospheric moisture and oxygen. A gold-plated platinum wire served as the indicator electrode, and was placed in the side arm. One end of a salt bridge containing 0.10 *F* tetraethylammonium perchlorate solution in acetonitrile and connected to an acetonitrile calomel electrode was placed in the main compartment. The acetonitrile calomel electrode which served as the reference electrode consisted of a mercury pool; a paste of mercurous chloride, potassium chloride, and potassium perchlorate; and a 0.10 *F* solution of tetraethylammonium perchlorate.[9] The potential of this electrode *vs.* the saturated aqueous calomel electrode is –0.002 v. The titrant, a tetraethylammonium chloride solution in acetonitrile standardized against a standard aqueous

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(1) W. M. Latimer, « Oxidation Potentials », 2nd ed., Prentice-Hall, Inc., New York, N. Y., 1952, Chapter 11.

(2) I. M. Kolthoff and J. F. Coetzee, *J. Am. Chem. Soc.*, 79, 1852 (1957).

(3) G. Bergerhoff, *Z. Anorg. Allg. Chem.*, 327, 139 (1964).

(4) A. D. Goolsby and D. T. Sawyer, *Anal. Chem.*, 40, 1978 (1968).

(5) S. E. Manahan and R. T. Iwamoto, *Inorg. Chem.*, 4, 1409 (1965).

(6) D. C. Leuhrs, R. T. Iwamoto, and J. Kleinberg, *Inorg. Chem.*, 5, 201 (1966).

(7) F. Farha, Jr., and R. T. Iwamoto, *J. Electroanal. Chem.*, 13, 390 (1967).

(8) B. J. Hathaway and A. E. Underhill, *J. Chem. Soc.*, 3705 (1960).

(9) O. Bravo and R. T. Iwamoto, *J. Electroanal. Chem.*, 23, 419 (1969).

silver nitrate solution, was added from a 10 ml microburet. An ionic strength of 0.10 *F* was maintained throughout the titrations with tetraethylammonium perchlorate in 0.10 *F* concentration in the solution being titrated and in the titrant. The gold(I) perchlorate solutions varied in concentration from 2×10^{-3} to 6×10^{-3} *F*, and the tetraethylammonium chloride solutions from 4×10^{-2} to 10^{-1} *F*.

Calculation. In the calculation of the stability constants, it was initially assumed that only mononuclear complex species were formed. No systematic change in the stability constants calculated from data obtained over a five-fold variation of the concentration of gold(I) perchlorate in the solutions titrated strongly suggests that this assumption is valid. From the stoichiometric ratios of gold(I) and chloride at the two breaks in the titration curves, the formation of stable soluble complex species AuCl and $AuCl_2^-$ was established.

The potential of the gold electrode after the addition of chloride is given by the expression

$$E = E^{\circ\prime}_{Au^+,Au} + 0.059 \log \frac{C_M}{1+[Cl^-]K_{f1}+[Cl^-]^2K_{f1}K_{f2}} \qquad (1)$$

where $E^{\circ\prime}_{Au^+,Au}$ is the formal potential of the gold(I), gold couple in 0.10 *F* tetraethylammonium perchlorate ($E^{\circ\prime}_{Au^+,Au} = E^{\circ}_{Au^+,Au} + 0.059 \log f_{Au^+}$), C_M is the total concentration of gold(I) species, and $\frac{1}{1+[Cl^-]k_{f1}+[Cl^-]^2K_{f1}K_{f2}}$ is the fraction of uncomplexed gold(I) ion. The constants K_{f1} and K_{f2} are the stepwise formation constants for AuCl and $AuCl_2^-$. In a separate experiment, the expression $E = E^{\circ\prime}_{Au^+,Au} + 0.059 \log C_{Au^+}$ was shown to be obeyed in 0.10 *F* tetraethylammonium perchlorate over the range 6×10^{-3} to 6×10^{-5} *F* gold(I) perchlorate. A slope of -0.059 was obtained for the plot of E *vs.* $-\log C_{Au^+}$, and a value of +1.348 v for $E^{\circ\prime}_{Au^+,Au}$.

In the first half of the titration involving formation of AuCl, with $K_{f1} \gg K_{f2}$,

$$E = E^{\circ\prime}_{Au^+,Au} + 0.059 \log \frac{C_M}{1+\frac{V}{V_e-V}} \qquad (2)$$

The quantities V and V_e are the volume of titrant added and the volume required to obtain complete complexation to the monochloro species, respectively. They appear in the expression as the result of the substitution of $\frac{V}{(V_e-V)K_{f1}}$ for $[Cl^-]$. (Au^+ and AuCl are assumed to be the only gold species in solution in this part of the titration.)

In the second half of the titration involving formation of $AuCl_2^-$, with $K_{f1} \gg {}_{f2}$,

$$E = E^{\circ\prime}_{Au^+,Au} + 0.059 \log \frac{K_{f2}}{K_{f1}} + 0.059 \log \frac{C_M}{\frac{V-V_e}{2V_e-V}\left(1+\frac{V-V_e}{2V_e-V}\right)} \qquad (3)$$

(Here, AuCl and $AuCl_2^-$ are assumed to be the only gold species in solution.) Finally, beyond the equivalence point for the formation of $AuCl_2^-$,

$$E = E^{\circ\prime}_{Au^+,Au} - 0.059 \log K_{f1}K_{f2} + 0.059 \log \frac{V_e(V_o+V)}{C_a(V-2V_e)^2} \qquad (4)$$

In this expression ,V_o is the initial volume of the solution of gold(I), and C_a is the concentration of chloride in the titrant. ($AuCl_2^-$ is assumed to be the only gold species in this region.)

The quantities $E^{\circ\prime}_{Au^+,Au}$, $E^{\circ\prime}_{Au^+,Au} + 0.059 \log \frac{K_{f2}}{K_{f1}}$, and $E^{\circ\prime}_{Au^+,Au} - 0.059 \log K_{f1}K_{f2}$ were determined and used to obtain K_{f1} and K_{f2}.

In the analysis described above, the formal concentration of unbound chloride (to Au^I) was used. Correction for ion-pair formation between tetraethylammonium ion and chloride ion was made by calculating the fraction of free chloride ion ($\alpha = \frac{1}{1+K_{f(C_2H_5)_4N^+,Cl^-}[(C_2H_5)_4N^+]}$) and dividing the stepwise formation constants by this quantity, *e.g.*, K_{f1}/α. The value of α is essentially constant throughout the titration; the variation is negligible. For the experimental conditions described in Table I, α is 0.313. To calculate α, the equilibrium concentration of tetraethylammonium ion was obtained by the method of successive approximations using the expressions:

$$C_{(C_2H_5)_4N^+} = [(C_2H_5)_4N^+, ClO_4^-] + [(C_2H_5)_4N^+, Cl^-] + [(C_2H_5)_4N^+] \qquad (5)$$

$$C_{ClO_4^-} = [(C_2H_5)_4N^+, ClO_4^-] + [ClO_4^-] \qquad (6)$$

$$C_{Cl^-} = [(C_2H_5)_4N^+, Cl^-] + [Cl^-] \qquad (7)$$

For $K_{f(C_2H_5)_4N^+,Cl^-}$ and $K_{f(C_2H_5)_4N^+,ClO_4^-}$, ion-pair formation contants, the values 35 and 11.2[10] were used.

Results and Discussion

Table I, under column *E°, shows a typical set of values obtained for $E^{\circ\prime}_{Au^+,Au}$, $E^{\circ\prime}_{Au^+,Au} + 0.059 \log \frac{K_{f2}}{K_{f1}}$, and $E^{\circ\prime}_{Au^+,Au} - 0.059 \log K_{f1}K_{f2}$. The data show that eq 2 and 3 hold very well in the parts of the titration involving formation of AuCl and $AuCl_2^-$, as indicated by the reproducibility of $E^{\circ\prime}_{Au^+,Au}$ and $E^{\circ\prime}_{Au^+,Au} + 0.059 \log \frac{K_{f2}}{K_{f1}}$. From a number of titrations, $E^{\circ\prime}_{Au^+,Au}$ was found to be 1.348 ± 0.001 v and $E^{\circ}_{Au^+,Au} + 0.059 \log \frac{K_{f2}}{K_{f1}}$ to be 1.127 ± 0.002 v. The first of these values is identical with the value for $E^{\circ\prime}_{Au^+,Au}$ obtained in a separate potentiometric experiment (1.348 v) and given earlier. In the part of the titration involving excess chloride, the value of $E^{\circ\prime}_{Au^+,Au} - 0.059 \log K_{f1}K_{f2}$ was a constant only at large excess chloride concentrations. No satisfactory

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(10) C. W. Davies, « Ion Association », Butterworths, Washington, D.C., 1962. p. 96.

explanation can be given for this behavior. The value obtained from a number of titrations for $E^{o\prime}_{Au^+,Au} - 0.059 \log K_{f1} K_{f2}$ was 0.135 ± 0.005 v.

The stability constants of the gold(I)-chloride complexes obtained from the $^*E^o$ values are:

$$K_{f1} = 10^{12.13 \pm 0.11}$$

$$K_{f2} = 10^{8.39 \pm 0.06}$$

Correction for ion-pair formation between tetraethylammonium ion and chloride in 0.10 *F* tetraethylammonium chloride solution using α, the fraction of free chloride ion (see Experimental section), yielded:

$$K_{f1(c)} = 10^{12.63 \pm 0.11}$$

$$K_{f2(c)} = 10^{8.89 \pm 0.06}$$

Using an approximated value of 10 for the formation constant of the tetraethylammonium dichloroaurate(I) ion-pair, we considered the effect of this ion-pair formation on α. A negligibile change in α of only + 0.2% was found.

Table I. Typical Set of Potential Data for the Gold(I)-Chloride System in Acetonitrile Solution, 0.10 *F* Tetraethylammonium Perchlorate[a]

V, ml $(C_2H_5)_4NCl$	E_{Au} *vs.* A.C.E. volt	0.0591 log B,[b] v	$^*E^{o\prime}$,[c] v
Formation of AuCl			
0.00	1.1864	0.1617	1.3481
0.10	1.1833	0.1651	1.3484
0.20	1.1794	0.1690	1.3484
0.30	1.1750	0.1735	1.3485
0.40	1.1710	0.1788	1.3498
0.50	1.1647	0.1857	1.3504
Formation of $AuCl_2^-$			
1.00	0.9964	0.1320	1.1284
1.10	0.9760	0.1527	1.1282
1.20	0.9574	0.1703	1.1277
1.30	0.9375	0.1889	1.1264
1.40	0.9165	0.2097	1.1262
1.50	0.8897	0.2366	1.1263
Excess Chloride			
3.00	0.2986	0.1429	0.1557
3.50	0.2747	0.1270	0.1477
4.00	0.2596	0.1153	0.1443
4.50	0.2476	0.1058	0.1418
5.00	0.2377	0.0982	0.1395
5.50	0.2300	0.0915	0.1385
6.00	0.2236	0.0856	0.1380

[a] Solution titrated = 16.0 ml, 1.84×10^{-3} *F* $Au(AN)_2ClO_4$, 0.10 *F* $(C_2H_5)_4NClO_4$ Titrant: 3.50×10^{-2} *F* $(C_2H_5)_4NCl$, 0.10 *F* $(C_2H_5)_4NClO_4$. [b] The log term containing the volume quantities in eq. 2,3 and 4. [c] These values are $E^{o\prime}_{Au^+,Au}$ in eq. 2, $E^{o\prime}_{Au^+,Au} + 0.059 \frac{K_{f2}}{K_{f1}}$ in eq. 3, and $E^{o\prime}_{Au^+,Au} - 0.059 \log K_{f1}K_{f2}$ in eq. 4 for the first, second, and third sets of values, respectively.

The agreement between the value of K_{f1} (uncorrected for ion-pairing) obtained by us ($10^{12.13}$) and that found by Goolsby and Sawyer ($10^{12.15}$) is fortuitous. The value of K_{f2} (uncorrected for ion pairing) reported by the latter investigators ($10^{7.79}$) is smaller than that ($10^{8.39}$) found by us. The difference in K_f values arises from a combination of (1) use of potential data for the calculation of β_{AuCl_2} from different regions of excess chloride. (The point in the titration curve selected by Goolsby and Sawyer is in a region in which we found $E^{o\prime}_{Au^+,Au} - 0.059 \log K_{f1} K_{f2}$ values not to be constant) and (2) difference in the potential values obtained for the midpoint in the titration curves between the first and second breaks (the potential obtained by Goolsby and Sawyer results in a larger ratio of K_{f1}/K_{f2}. In eighteen titrations, we did not obtain potential values which would lead to their ratio of K_{f1}/K_{f2}).

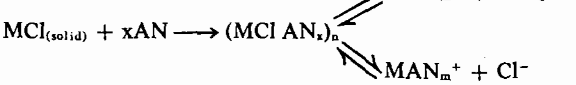
Previously, potentiometric titration of *ca.* millimolar solutions of copper(I) and of silver(I) perchlorate in acetonitrile with solutions of tetraethylammonium chloride in acetonitrile under essentially identical conditions showed that in the case of copper(I), only a single break is obtained in the titration curve at a ratio of 2:1 for added chloride to copper(I), while in the case of silver(I), two breaks, one at 1:1 ratio of added chloride to silver(I) and the other at 2:1, are obtained Precipitation of silver chloride occurred in the first step, and dissolution of the precipitate in the second. In the titration of copper(I) ion, no precipitation of copper(I) chloride occurred. The overall formation constants of the 2:1 chloro complexes of copper(I) and silver(I)[12] obtained are $10^{10.8}$ and $10^{12.6}$, respectively. ($\beta_{AgCl_2^-}$ of $10^{13.6}$ was obtained by voltammetry.)[6]

Interestingly, titration of gold(I) perchlorate solution in acetonitrile with tetraethylammonium chloride under similar conditions, yielded a titration curve with two breaks at added chloride to gold(I) ratios of 1:1 and 2:1, but no precipitation of gold(I) chloride occurred in the first step.

Table II. Stability Constants of Copper(I)-Chloride, Silver(I)- and Gold(I)-Chloride Complex Species and Solubility Product of Silver(I) Chloride in Acetonitrile.

Cu		Ag		Au	
	$K_{f1} = 10^{4.9}$		$K_{sp} = 10^{-12.4}$		$K_{f1} = 10^{12.63}$
	$K_{f2} = 10^{5.9}$		$\beta_2 = 10^{12.6}$		$K_{f2} = 10^{8.89}$

In the coordination model for nonaqueous solvent-solute interactions, the equilibria involved in solutions of the metal(I) chlorides in acetonitrile are represented as follows:[12,13]



$$MCl_{(solid)} + xAN \longrightarrow (MCl\,AN_x)_n \begin{array}{l} \rightleftharpoons MAN_m^+ + MCl_2^- \\ \rightleftharpoons MAN_m^+ + Cl^- \end{array}$$

With solutions of copper(I) chloride in acetonitrile,

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[11] A value of $10^{13.4}$ has been reported for $\beta_{AgCl_2^-}$. R. Alexander, E. C. F. Ko, Y. C. Mac, and A. J. Parker, *J. Am. Chem. Soc.*, 89, 3703 (1967).

(12) D. W. Meek in « The Chemistry of Non-Aqueous Solvents », Vol. I, J. J. Lagowski, Ed., Academic Press, New York, N. Y., 1966, Chapter 1.

(13) R. S. Drago and K. F. Purcell in « Progress in Inorganic Chemistry », Vol. 6, F. A. Cotton, Ed., Interscience Publishers, New York, N. Y., 1964, Chapter 4.

the equilibria are over to the top right, *i.e.*, formation of $CuCl_2^-$; for silver(I) chloride, they are over to the left; and in the case of gold(I) chloride, in between the previous cases, *i.e.*, $AuClAN_x$. The stability constants of the metal(I)-chloride species in acetonitrile are summarized in Table II.[5,6] Attention is directed to the values of K_{f2}/K_{f1} for copper(I)-chloride and gold(I)-chloride complexes.

The reason for this striking difference in the solution equilibria of the three metal chlorides in acetonitrile is currently under investigation.

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