Complex Formation of Silver(I) Ion with Some Aliphatic Diamines

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Complex formation of silver(I) ion with 1,3-propanediamine and 1,4-butanediamine has been studied potentiometrically at 25 °C in 3 mol dm^{-3} $LiClO_4$ aqueous solution. Some additional experiments have been carried out in the system of silver–1,2-ethanediamine of large diamine/Ag ratios, the system having been examined in a previous work at small diamine/Ag ratios. Over the pH range of 6—10.4, the emf data obtained in the silver–diamine solutions could be explained in terms of the formation of the following complexes (L denotes the free diamine molecule): In a solution of low pH (pH=6—8), the $AgHL^{2+}$ and $AgH_2L_2^{3+}$ complexes are formed. In an alkaline solution, the AgL^+, $Ag_2L_2^{2+}$, and AgL_2^+ complexes are formed, and the relative amounts of the complexes depend on the concentrations of the metal and ligand (L) and also the ratio of these concentrations. The Ag(OH)L complex becomes a main species at the highest pH examined. In some cases the formation of the $AgHL_2^{2+}$, $Ag_2HL_2^{3+}$, and Ag_2L^{2+} complexes is suggested from the graphical or computer analysis of the data, but the formation constants of the complexes are rather uncertain. Over the whole pH range examined, the $AgHL^{2+}$, $AgH_2L_2^{3+}$, AgL^+, and $Ag_2L_2^{2+}$ complexes are predominant in all the systems.

In a previous work we studied the complex formation of silver(I) ion with 1,2-ethanediamine and 1,2-propanediamine, and found various protonated and polynuclear complexes.[1] The equilibria between silver(I) and the diamines were more complicated than those described in the preceding papers.[2,3] In addition to the study on the effect of the methyl group attached to the methylene chain previously examined,[1] the effect of the length of the methylene chain on the reaction between silver(I) and diamines was explored in the present work.

Experimental

Reagents. 1,3-Propanediammonium perchlorate and 1,4-butanediammonium perchlorate were prepared from the corresponding diamines and perchloric acid. 1,3-Propanediamine and 1,4-butanediamine were purchased from Wako Pure Chemicals Co., Osaka and Aldrich Chemical Co., Inc., Milwaukee, USA, respectively. The method of preparation of the reagents was described in the previous paper.[1] Other chemicals were the same as those used previously.[1]

Apparatus. Beckman (Nos. 40495 and 40498) glass electrodes were used in combination with the Kawai-type of the half cell[4] for emf measurements. An Orion Digital pH Meter Model 801 was used.

Method of Measurements. During the potentiometic titrations the total concentration of perchlorate ions was kept constant at 3 M (M=mol dm^{-3}) by using lithium perchlorate. The concentrations of silver and diamines were changed over the range of 2—40 mM and 5—160 mM, respectively. The ratio of the concentration of the diamines to that of silver ion (C_L/C_{Ag}) was changed from 0.5—40.

Twelve titrations for silver–1,3-propanediamine and fifteen titrations for silver–1,4-butanediamine solutions were performed at 25.00±0.01 °C in a paraffin oil thermostat, which was placed in a room thermostated at 25±1 °C. Some additional titrations were carried out for silver–1,2-ethanediamine solutions under the same experimental conditions. The C_L/C_{Ag} ratio was 5 and 10 in this work, whereas the ratio had been 2—4 in the previous work.[1]

Details of the method of measurements were described elsewhere.[1]

Results

Titration curves of silver–1,3-propanediamine and –1,4-butanediamine solutions are shown in Figs. 1 and

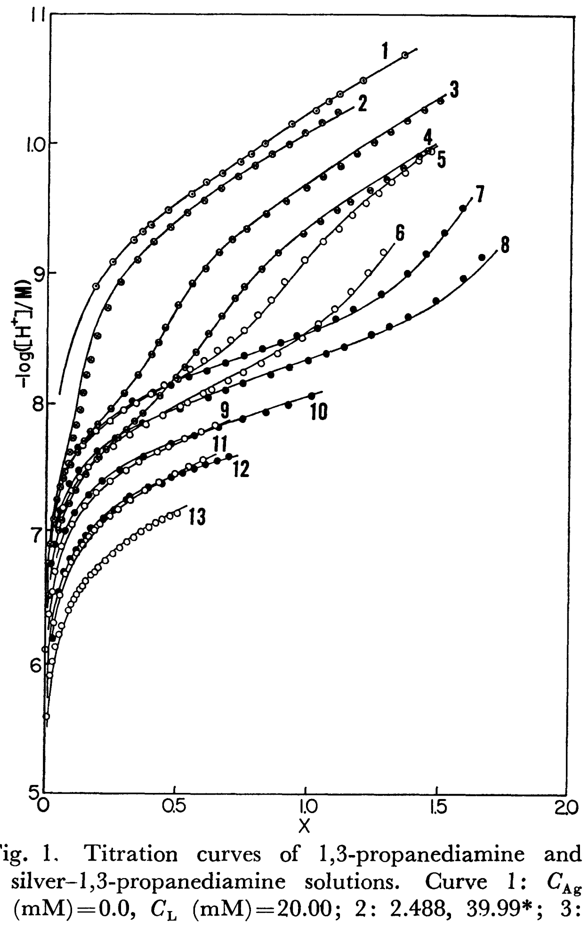

Fig. 1. Titration curves of 1,3-propanediamine and silver–1,3-propanediamine solutions. Curve 1: C_{Ag} (mM)=0.0, C_L (mM)=20.00; 2: 2.488, 39.99*; 3: 2.488, 20.02; 4: 5.169, 39.99; 5: 2.494, 10.01; 6: 5.170, 20.42; 7: 2.518, 5.035; 8: 5.017, 10.02; 9: 10.09, 39.99; 10: 9.993, 20.01; 11: 20.37, 80.08; 12: 20.10, 39.80; 13: 40.37, 160.1.

* The concentration of the ligand was changed by dilution during the titration. Curves are calculated ones by using constants in Table 2.

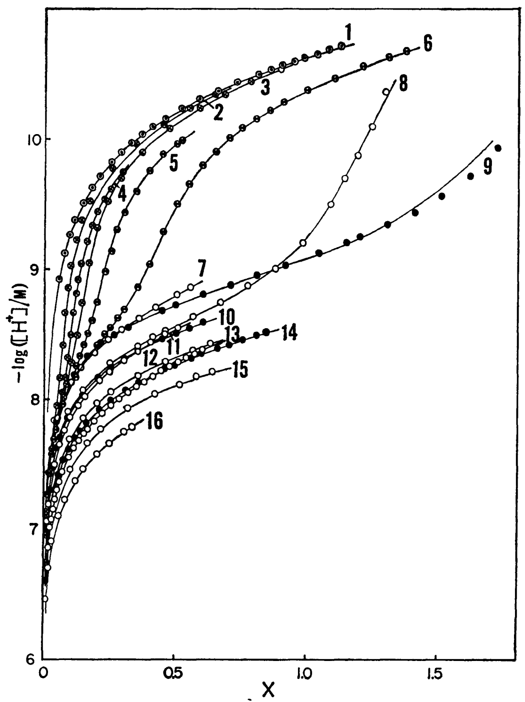

Fig. 2. Titration curves of 1,4-butanediamine and silver–1,4-butanediamine solutions. Curve 1: C_{Ag} (mM) = 0.0, C_L (mM) = 5.004; 2: 2.516, 80.06*; 3: 2.516, 39.97*; 4: 2.526, 80.03; 5: 2.519, 40.01; 6: 2.524, 20.00; 7: 2.513, 9.990; 8: 5.044, 9.973*; 9: 2.540, 5.012; 10: 5.012, 9.990; 11: 5.008, 20.01; 12: 10.06, 9.973*; 13: 9.993, 40.62; 14: 10.01, 20.32; 15: 19.86, 10.03*; 16: 20.01, 80.03.

* The concentration of the ligand was changed by dilution during the titration. Curves are calculated ones by using constants in Table 2.

2, respectively.

The pK Values of the Diammonium Perchlorates were obtained from the titration curves of the solutions without silver ion (curve 1 in Figs. 1 and 2). The pK values are tabulated in Table 1, together with the pK

Table 1. Acid dissociation constants of 1,2-ethanediamine, 1,3-propanediamine and 1,4-butanediamine (25 °C, 3 M $LiClO_4$).

	en	pn	bn
pK_1	7.93	9.71	10.39
pK_2	10.74	10.93	11.05
ΔpK=pK_2−pK_1	2.81	1.22	0.66

values of 1,2-ethanediammonium perchlorate which were recalculated in the present work. Compared with the values reported by Ohtaki and Tanaka in a 0.1 M NaCl medium,[5] the pK values found in the 3 M $LiClO_4$ medium were larger, but ΔpK=pK_2−pK_1 more rapidly converged to the statistical value of 0.6.

Estimation of the Composition and Formation Constants of Silver–Diamine Complexes. Along the line described in the previous paper,[1] we estimated the composition and the formation constants of the silver–diamine complexes first with the graphical method and then the mathematical treatment by using a high speed electronic computer in order to refine the constants.

In the course of the computer calculations, some complexes were assumed in addition to the complexes graphically estimated in order to obtain a better fit of calculated titration curves with experimental ones.

At lower pH where most diamine molecules are present as H_2L^{2+} (L denotes the free base of diamine), the equilibrium between silver ion and a diamine may be written by Eq. 1.

$$p\mathrm{Ag}^+ + r\mathrm{H_2L}^{2+} = \mathrm{Ag}_p\mathrm{H}_q\mathrm{L}_r{}^{(p+q)+} + (2r-q)\mathrm{H}^+. \quad (1)$$

The equilibrium constant is defined as follows:

$$\kappa_{pqr} = \frac{[\mathrm{Ag}_p\mathrm{H}_q\mathrm{L}_r{}^{(p+q)+}][\mathrm{H}^+]^{(2r-q)}}{[\mathrm{Ag}^+]^p[\mathrm{H_2L}^{2+}]^r} = \beta_{pqr}K_1{}^rK_2{}^r, \quad (2)$$

where β_{pqr} is the overall formation constant of the complex $\mathrm{Ag}_p\mathrm{H}_q\mathrm{L}_r{}^{(p+q)+}$;

$$\beta_{pqr} = \frac{[\mathrm{Ag}_p\mathrm{H}_q\mathrm{L}_r{}^{(p+q)+}]}{[\mathrm{Ag}^+]^p[\mathrm{H}^+]^q[\mathrm{L}]^r}. \quad (3)$$

Here [ ] represents the concentration (M=mol dm^{-3}) of the species. From the material balance of the metal ion, Eq. 4 can be readily derived.

$$\frac{C_M-[\mathrm{Ag}^+]}{[\mathrm{Ag}^+]} = \phi - 1 = \sum_p\sum_q\sum_r p\kappa_{pqr}[\mathrm{Ag}^+]^{p-1}[\mathrm{H}^+]^{-(2r-q)}[\mathrm{H_2L}^{2+}]^r. \quad (4)$$

If we assume as a first approximation that only one complex is formed in this pH range, the summations in Eq. 4 are dropped. If the assumption is acceptable, the plot of log (ϕ−1) against −log [H$^+$] should give straight lines with a slope of (2r−q), the lines depending on the concentrations of the silver ion and diamine. However, the plots were independent of the concentration of the silver ion as is seen in Fig. 3. Therefore, it is obvious that the main species formed in the pH range shown in Fig. 3 is mononuclear with respect to silver. Since the slope of the line was approximately unity, (2r−q) should be unity. Since it is readily found that the family of the straight lines is a function of log C_L (C_L is approximately equal to [H_2L^{2+}] under the

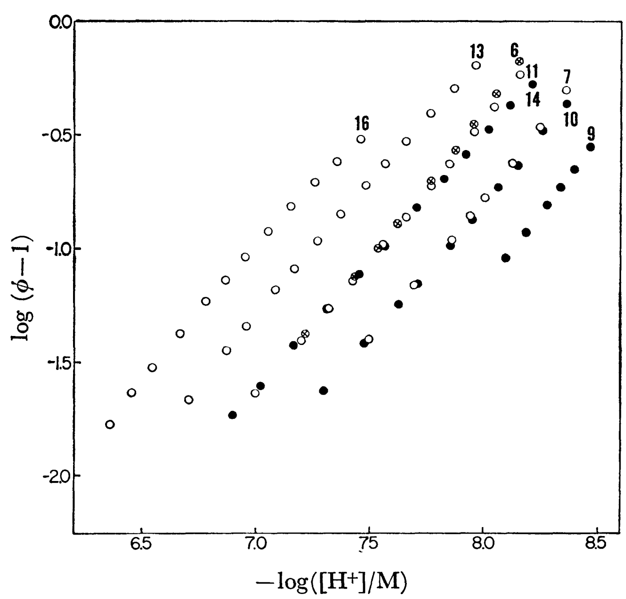

Fig. 3. Relationships between log (ϕ−1) and −log [H$^+$]. Numbers in the figures correspond to those of Fig. 2.

present conditions), r should be unity, and thus $q=1$. Thus the composition of the species was determined to be $AgHL^{2+}$. Another species was found from the analysis of the second approximation of Eq. 4 by assuming two complexes, $AgHL^{2+}$ and $Ag_{p'}H_{q'}L_{r'}{}^{(p'+q')+}$, because the slope of the lines in Fig. 3 was slightly larger than unity. In order to avoid duplication of description, the treatment of the data is not described here and should be referred to the previous paper, Eqs. 14—17 of Ref. 1.[6] The second species $Ag_{p'}H_{q'}L_{r'}$ was $AgH_2L_2{}^{3+}$.

At higher pH the AgL^+ complex was found. In solution containing a large excess of a diamine compared with the silver ion, the $Ag_2L_2{}^{2+}$ and $AgL_2{}^+$ complexes were found in the same pH range.[7]

At the highest pH a hydrolyzed species Ag(OH)L formed.

The formation constants of the complexes, together with some other complexes which were not detected by the graphical treatment, were refined by the least squares method in which the error square sum $U=\sum(X-X_{calcd})^2$ was minimized by searching the best values of β_{pqr} for a set of the complexes $Ag_pH_qL_r{}^{(p+q)+}$. Here X denotes the ratio of the concentration of hydroxide ions added to the total concentration of a diamine in the solution, and X_{calcd} represents the calculated value of X and is given by Eq. 5.

$$X_{calcd}=\frac{2C_L+K_w/[H^+]-[H^+]-\sum_p\sum_q\sum_r q\beta_{pqr}[Ag^+]^p[H^+]^q[L]^r}{C_L}, \tag{5}$$

where K_w denotes the autoprotolysis constant of water in the 3 M $LiClO_4$ and is $10^{-13.867\pm0.009}$ M^2.[8]

The results are summarized in Table 2 in terms of $\log\beta_{pqr}$. For the silver–1,2-ethanediamine complexes, the formation constants of the complexes reported in the previous paper were recalculated by using all the data given in Ref. 1 and obtained in the present work. Some other complexes such as $AgHL_2{}^{2+}$, $Ag_2HL_2{}^{3+}$, and $AgL_2{}^+$ were found in the present calculation; these complexes have not been obtained in solutions of relatively small C_L/C_{Ag} ratios in the previous work.[1] On the other hand, the formation constant of the Ag_2L^{2+} complex was not detected with reasonable accuracy in the present calculation.

The $Ag_2HL_2{}^{3+}$ complex was not detected with reasonable certainty in both the systems of silver–1,3-propanediamine and –1,4-butanediamine. The formation constant of the $AgL_2{}^+$ complex was also not obtained in the former system by the least squares calculations. The value estimated by the graphical method is given in parentheses as reference in Table 2. For the silver–1,4-butanediamine solutions, the formation constant of the AgL^+ complex was uncertain as is shown in parentheses in Table 2. Some minor complexes added in the least squares caculation may sometimes refine the results, but the existence of the complexes is less certain and the formation constants obtained are rather unreliable. The $Ag_2HL_2{}^{3+}$ complex detected as a minor species in the present calculation is uncertain with this reason.

TABLE 2. FORMATION CONSTANTS OF THE $Ag_pH_qL_r{}^{(p+q)+}$ COMPLEXES, $\log\beta_{pqr}$, IN 3 M $LiClO_4$ AT 25°C
$\beta_{pqr}=[Ag_pH_qL_r{}^{(p+q)+}]/[Ag^+]^p[H^+]^q[L]^r$ $M^{-(p+q+r-1)}$.

Complex	en	pn	bn	en[2]	pn[3]	bn[3]
HL	10.74	10.96	11.05	10.03	10.64	10.82
H_2L	18.67	20.65	21.44	17.25	19.52	20.42
AgHL	13.53	14.32	14.68	12.38	13.2	13.9
AgH_2L_2	27.48	28.90	29.83	—	—	—
$AgHL_2$	18.8_6	19.2_5	19.1_5	—	—	—
Ag_2HL_2	21.9_2	—	—	—	—	—
Ag(OH)L	-4.8_1	-3.5_7	-4.4_0	—	—	—
AgL	5.2_6	6.59	(6.4)[a]	4.7	5.8	5.9
Ag_2L_2	14.90	15.90	15.27	13.2	—	—
AgL_2	9.45	(9.8)[a]	8.6_2	7.7	—	—
Ag_2L	—	—	7.2_3	6.5	6.4	—

a) Values in parentheses are those estimated by curve-fitting in the concentration ranges where appreciable amounts of the relevant complexes are expected to be present, but these constants are not refined by the least-squares calculations with reasonable certainty.

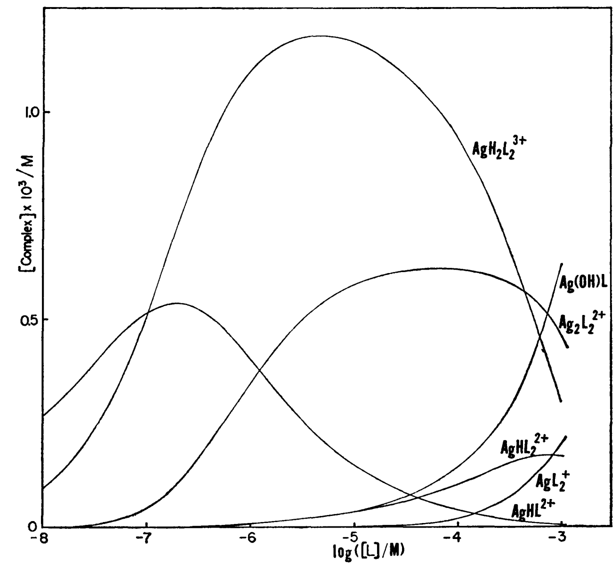

Fig. 4. Distribution of silver–1,4-butanediamine complexes.
$C_{Ag}=2.542$ mM, $C_L=20.00$ mM.

A typical set of the distribution curves of the complexes listed in Table 2 is shown for the 1,4-butanediamine system in Fig. 4. Similar sets of the distribution curves of the complexes were obtained for the 1,2-ethanediamine and 1,3-propanediamine systems. As is seen from the figure, $AgHL^{2+}$ is a major component of the complexes at the lowest pH's (pH=6—7). The $AgH_2L_2{}^{3+}$ complex is a main species over a wide range of pH examined. The $Ag_2L_2{}^{2+}$ complex and sometimes the AgL^+ complex become the main species. In the highest pH range the Ag(OH)L complex becomes one of the most important species in the solution.

Discussion

Stepwise formation constants of the $AgHL^{2+}$ and $AgH_2L_2{}^{3+}$ complexes are readily calculated from the values in Tables 1 and 2.

$$Ag^+ + HL^+ = AgHL^{2+}, \quad (6)$$

$\log K(\mathrm{AgHL/HL}) = 2.79(\mathrm{L=en}),\ 3.39(\mathrm{pn}),\ 3.63(\mathrm{bn}),$

and

$$AgHL^{2+} + HL^+ = AgH_2L_2^{3+}, \quad (7)$$

$\log K(\mathrm{AqH_2L_2/HL}) = 3.16(\mathrm{L=en}),\ 3.65(\mathrm{pn}),\ 4.10(\mathrm{bn}),$

where the constants $K(\mathrm{AgHL/HL})$ and $K(\mathrm{AgH_2L_2/HL})$ are defined as follows:

$$K(\mathrm{AgHL/HL}) = \frac{[\mathrm{AgHL^{2+}}]}{[\mathrm{Ag^+}][\mathrm{HL^+}]},$$

$$\text{and} \quad K(\mathrm{AgH_2L_2/HL}) = \frac{[\mathrm{AgH_2L_2^{3+}}]}{[\mathrm{AgHL^{2+}}][\mathrm{HL^+}]}, \quad (8)$$

and en, pn, and bn denote 1,2-ethanediamine, 1,3-propanediamine and 1,4-butanediamine, respectively.

The second formation constant $K(\mathrm{AgH_2L_2/HL})$ is larger than the first one $K(\mathrm{AgHL/HL})$ in all the cases, as has been pointed out in the previous paper.[1] The values of log $K(\mathrm{AgHL/HL})$ and log $K(\mathrm{AgH_2L_2/HL})$ approach the corresponding stepwise formation constants of the silver–ammine complexes, log $K_1=3.58$ and log $K_2=4.19$[9] with the length of the methylene chain. The values of the stepwise formation constants of the silver–1,4-butanediamine complexes are very close to those of the silver–ammine complexes. This fact suggests that the electrostatic repulsion between protons on the diamine molecules and the silver ion becomes negligible when they are separated by four methylene groups. The result that ΔpK of 1,4-butanediamine was close to the statistical value (0.6, see Table 1) supports this consideration. That the first stepwise formation constant is smaller than the second one is a known fact for a complex having a linear structure.

The stepwise formation constants of the AgL_n complex are given as follows:

$$Ag^+ + L = AgL^+, \quad (9)$$

$\log K(\mathrm{AgL/L}) = 5.2_6(\mathrm{L=en}),\ 6.59(\mathrm{pn}),\ (6.4)(\mathrm{bn}),$

and

$$AgL^+ + L = AgL_2^+, \quad (10)$$

$\log K(\mathrm{AgL_2/L}) = 4.1_9(\mathrm{L=en}),\ (3.2)(\mathrm{pn}),\ (2.2)(\mathrm{bn}).$

The values in parentheses are uncertain because the overall formation constants of these complexes were not determined with reasonable accuracy. However, we may still say that $K(\mathrm{AgL/L})$ is larger than $K(\mathrm{AgL_2/L})$, and the values of $K(\mathrm{AgL/L})$ for all the diamine complexes are smaller than β_2 of the diammine silver(I) complex. It is seen that $K(\mathrm{AgL/L})$ is much larger than K_1 of the monoammine silver complex and $K(\mathrm{AgHL/HL})$ of the $AgHL^{2+}$ complex. Therefore, we concluded that the diamine molecule combines with the silver ion as a bidentate ligand. The AgL_2^+ complex may have a tetrahedral configuration. The AgL^+ complex would have either a bent linear or a distorted tetrahedral structure with additional two water molecules attached to the vacant sites of the tetrahedron. As we will discuss later for the formation constant of the Ag(OH)L complex, the latter structure seems to be more possible than the former.

A large dimerization constant of the AgL^+ complex suggests a ring structure of the $Ag_2L_2^{2+}$ complex, as has been described by Schwarzenbach, *et al.*[2]

The formation constant of the $AgHL_2^{2+}$ complex from the AgL^+ and HL^+ complexes is given as follows:

$$AgL^+ + HL^+ = AgHL_2^{2+};$$

$$K(\mathrm{AgHL_2/HL}) = \frac{[\mathrm{AgHL_2^{2+}}]}{[\mathrm{AgL^+}][\mathrm{HL^+}]}, \quad (11)$$

$\log K(\mathrm{AgHL_2/HL}) = 2.8_6(\mathrm{L=en}),\ 1.7_0(\mathrm{pn}),\ (1.7)(\mathrm{bn}).$

Stabilization of the $AgHL_2^{2+}$ complex by combination of AgL^+ with HL^+ suggests that the $AgHL_2^{2+}$ complex has also a ring structure. The formation constant $K(\mathrm{AgHL_2/HL})$ smaller than $K(\mathrm{Ag_2L_2/AgL})$ may be attributed to the weaker H_2N–H^+–NH_2 bond than the H_2N–Ag^+–NH_2 bond in the ring structures.

The hydrolysis constant of the AgL^+ complex is given by Eq. 12.

$$AgL^+ + H_2O = Ag(OH)L + H^+;$$

$$K(\mathrm{Ag(OH)L/H_2O}) = \frac{[\mathrm{Ag(OH)L}][\mathrm{H^+}]}{[\mathrm{AgL^+}]}, \quad (12)$$

$\log K(\mathrm{Ag(OH)L/H_2O}) = -10.0_8(\mathrm{L=en}),\ -10.1_6(\mathrm{pn}),\ (-10.8)(\mathrm{bn}).$

These values are almost the same as the hydrolysis constant of the aqua silver(I) ion:

$$Ag^+ + H_2O = AgOH + H^+;$$

$$\log K(\mathrm{AgOH/H_2O}) = -11.1\ (1\ \mathrm{M\ AgNO_3}^{10)}). \quad (13)$$

The fact may show that no H_2N–Ag bond cleavage occurs by the hydrolysis of the AgL^+ complex. Therefore, the silver ion within the Ag(OH)L complex might be combined with at least three ligand atoms (two N and one O), and more probably the metal ion would be coordinated with two amino groups, one hydroxide ion and one water molecule.

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6) Equation 16 of Ref. 1 should read $[\mathrm{HL^+}]=[\{(1+K_1^{-1}[\mathrm{H^+}]+\beta_{111}K_2[\mathrm{Ag^+}])^2+8\beta_{122}K_2^2[\mathrm{Ag^+}]C_L\}^{1/2}-(1+K_1^{-1}[\mathrm{H^+}]+\beta_{111}K_2[\mathrm{Ag^+}])]/4\beta_{122}K_2^2[\mathrm{Ag^+}]$.
7) The third term of the right hand side of Eq. 19 of Ref. 1 should read $K_1^{-1}K_2^{-1}[\mathrm{H^+}]^2[\mathrm{L}]$. Equation 22 should read $[\mathrm{L}]=\{(B^2+8AC)^{1/2}-B\}/4A$.
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