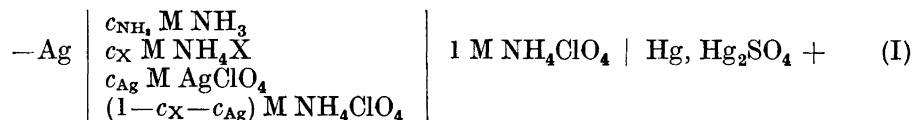# A Potentiometric Study of the Reaction of the Diammine Silver Ion with Chloride and with Bromide

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Measurements of the solubility of silver chloride and silver bromide in ammonia have indicated that the saturated solutions contain several complexes other than the diammine silver ion (*vide* Ref.[1]). Potentiometric measurements in unsaturated solutions reported below indicate mixed complexes of the type, $Ag(NH_3)_m X_n^{1-n}$, where $(m,n) = (1,1)$ and $(2,1)$, if $X = Cl$, and $(m,n) = (2,1)$ and $(2,2)$, if $X = Br$. The equilibrium constants computed from the measurements are given in Table 3. They are valid at 25°C and for the ionic strength 1 M (NH_4ClO_4).

The e.m.f. of the following cell (I) was measured at 25°C. X represents Cl or Br.

$$-Ag \left| \begin{array}{l} c_{NH_4}\ M\ NH_3 \\ c_X\ M\ NH_4X \\ c_{Ag}\ M\ AgClO_4 \\ (1-c_X-c_{Ag})\ M\ NH_4ClO_4 \end{array} \right| \quad 1\ M\ NH_4ClO_4\ |\ Hg,\ Hg_2SO_4\ + \qquad (I)$$

No change of the mercury, mercurous sulfate electrode could be detected during the time used for the measurements. Its drift was less than 1 mV a month. The main investigation consisted of a series of potentiometric titrations. In each titration the concentrations of ammonia and silver were kept constant, while the concentration of ammonium halide was increased from 0 to 0.5 M. The e.m.f. of the cell (I), E mV, is given by

$$E = E_0 - 59.16 \log [Ag^+] - E_j \qquad (1)$$

The sign [] denotes concentrations, in M, of species in the left hand solution of cell I.

The standard potential E_0 mV (standard state: 1 M NH_4ClO_4) was determined from solutions, in which $c_X = c_{NH_4} = 0$, and $0.002 < c_{Ag} = [Ag^+] < 0.01$. This gave
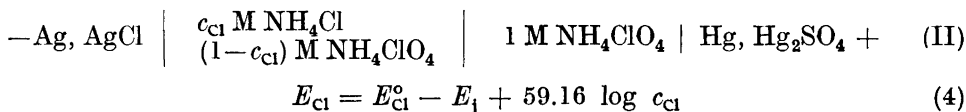
$$E_0 = 61.0 \pm 0.2 \qquad (2)$$

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In the bromide case no correction was made for the liquid junction potential, E_j. For the chloride measurements, E_j (mV) was calculated from the equation

$$E_j = 1.7 \; c_{Cl} \tag{3}$$

This equation, valid for $c_{Cl} < 0.5$ (M), results approximately (accuracy 0.05 mV) from Henderson's formula (Büchi [2]). The ionic mobilities used for NH_4^+, Cl^- and ClO_4^- were taken for zero ionic strength as tabulated by Landolt-Börnstein (Eg III c, p. 2059). This method of computing E_j was supported by measurements of the following cell (II), e.m.f. E_{Cl} mV.

$$-Ag, AgCl \; \left| \; \begin{array}{l} c_{Cl} \; M \; NH_4Cl \\ (1-c_{Cl}) \; M \; NH_4ClO_4 \end{array} \right| \; 1 \; M \; NH_4ClO_4 \; | \; Hg, Hg_2SO_4 + \quad (II)$$

$$E_{Cl} = E_{Cl}^{\circ} - E_j + 59.16 \; \log \; c_{Cl} \tag{4}$$

E_{Cl} was measured for $0 < c_{Cl} < 0.5$. If E_j from eqn. (3) is inserted, one value of E_{Cl}° can be computed from each E_{Cl} measured. All these values of E_{Cl}° (mV) lay within the limits

$$E_{Cl}^{\circ} = 489.9 \pm 0.05 \tag{5}$$

This perfect constancy also indicates that the activity factor of the chloride ions is not affected, even though as much as half of the perchlorate ions is exchanged for chloride ions. A cell corresponding to (II) but with bromide instead of chloride was also measured. This gave

$$E_{Br}^{\circ} = 644.4 \pm 0.3 \tag{6}$$

The concentration of the ammonia was kept sufficiently high in all the series of the main investigation to avoid any precipitation of silver halide. The silver in the solution is to be found in the species $Ag(NH_3)_m X_n^{1-n}$. That no polynuclear complexes are present follows from the fact that the function F_0, defined below, is independent of c_{Ag}. The equilibrium constant $\beta_{m,n}$ $M^{-(m+n)}$ for the formation of the complex from its $m + n + 1$ constituents is

$$\beta_{m,n} = [Ag(NH_3)_m X_n^{1-n}] \cdot [Ag^+]^{-1} a_{NH_3}^{-m} \; [X^-]^{-n} \tag{7}$$

Hence

$$c_{Ag} = \sum_{m=0}^{M} \sum_{n=0}^{N-m} Ag(NH_3)_m X_n^{1-n} = [Ag^+] \sum_{m=0}^{M} \sum_{n=m}^{N-m} \beta_{m,n} a_{NH_3}^{m} [X^-]^n \tag{8}$$

M is the maximum number of ammonia molecules bound in one complex, and N is the maximum coordination number of the silver ion. We define F_0 as

$$F_0 = \frac{c_{Ag}}{[Ag^+]} = \sum_{m=0}^{M} \sum_{n=0}^{N-m} \beta_{m,n} \; a_{NH_3}^{m} [X^-]^n \quad (\beta_{0,0} = 1) \tag{9}$$

In practice, the summations have to be carried out for all values of m and n corresponding to species which are present in high enough concentrations to

influence the measurements noticeably. For the calculation of F_0 eqn. (1) may be rewritten as

$$E = E_0 - E_j + 59.16(\log F_0 - \log c_{Ag}) \tag{10}$$

Every titration series begins with a measurement of the potential $E = E_1$ in a solution free from chloride. Practically all of the silver in this solution is present as diammine silver ions for the range of ammonia concentrations taken (*vide* Bjerrum [3]). Hence for these initial solutions, $c_{Ag} = [Ag(NH_3)_2^+]$ and $F_0 = \beta_{2;0} \times a_{NH_3}^2$, which changes eqn. (10) to

$$E_1 = E_0 + 59.16 \log (\beta_{2;0} \cdot a_{NH_3}^2) - 59.16 \log c_{Ag} \tag{11}$$

During a titration c_X increases from 0 and E from E_1. We write

$$E = E_1 + \Delta E \tag{12}$$

Combination of eqns. (10), (11) and (12) gives

$$\Delta E = 59.16 \log (F_0 \cdot \beta_{2,0}^{-1} \cdot a_{NH_3}^{-2}) - E_j \tag{13}$$

Finally we introduce a function φ_0, from which some equilibrium constants can be easily computed.

$$\varphi_0 = F_0 \, \beta_{2,0}^{-1} \, a_{NH_3}^{-2} = \beta_{2,0}^{-1} \sum_{m=0}^{M} \sum_{n=0}^{N-m} \beta_{m;n} \, a_{NH_3}^{m-2} \, [X^-]^n \tag{14}$$

For each titration series with constant a_{NH_3} a plot of φ_0 against $[X^-]$ shows all sufficiently large terms in the double sum. Each such term corresponds to a detectable complex species in the solution. φ_0 is calculated from

$$\log \varphi_0 = \frac{\Delta E + E_j}{59.16} \tag{15}$$

ΔE (mV) is determined directly in the experiments as a difference between two e.m.f.'s. E_j is calculated from eqn. (3) for the chloride measurements. For the bromide case $E_j = 0$.

EXPERIMENTAL DETAILS

The chemicals used were the same as previously described (Ref.[1]).

The solutions were kept free from air by bubbling nitrogen through them during the titration. The nitrogen was passed over hot copper wires to remove traces of oxygen, and then through two washing flasks containing 1 M ammonium perchlorate and ammonia of the same concentration as in the electrode vessel. In this way, changes in concentration due to the nitrogen stream could be avoided in the electrode vessel. The ammonia concentration was standardised against hydrochlorid acid after each potentiometric titration.

The silver electrodes were silver plated platinum wires sealed in glass tubes.

The potentiometer set up was from N. C. Jensen, Copenhagen, type 10 A, with a light spot galvanometer from Norma Fabrik, Wien. Its sensibility was 2×10^{-9} A/mm. The Weston cell, type D-402-B (saturated), was from Muirhead & Co Ltd.

All the measurements were carried out in a well controlled water thermostat at $25 \pm 0.01°C$.

The electrode vessel for the reference electrode was of the simple type with a side tube dipping into a test tube with 1 M NH_4ClO_4. The vessel for the main titrations was

Table 1. The e.m.f., $E_I + \varDelta E$ mV, of cell (I). X = Cl.

c_{NH_3} (M) →	0.5	1.00	1.94	2.92	3.90
f_{NH_3} →	1.00	1.02	1.07	1.14	1.21
E_I^*(mV) →		492.5	529.2	551.3	570.5
$10^{-7}\beta_{2,0}$ →	2.2	2.2	2.2	2.1	2.2
$10^3 \cdot c_{Cl}$	$\varDelta E$ (mV)				
32	1.1	0.9	0.7	0.8	0.7
167	3.1	3.1	2.7	2.6	2.4
286	4.8	4.3	4.2	3.9	3.7
444	6.9	6.0	6.2	5.5	5.1
500	7.6	6.5	6.9	6.0	5.7
Uncertainty →	± 0.4	± 0.3	± 0.1	± 0.1	± 0.2

* These values are for $c_{Ag} = 0.01$. With $c_{NH_3} = 0.5$ and 1.00, E_I was measured for $c_{Ag} = 5.10^{-3}$ which gave $E_I = 474.7$ and 509.2 respectively. With $c_{NH_3} = 0.5$ and $c_{Ag} = 2.5.10^{-3}$, E_I became 490.8. All these values give $\beta_{2,0} = 2.2 \times 10^7$. $\varDelta E$ was independent of c_{Ag} in all cases.

connected to this test tube by means of a bent stopcock tube containing 1 M NH_4ClO_4. The electrode vessel was closed with a stopper with holes for a connection tube, electrodes, tube for inlet of nitrogen and burette tip.

COMPUTATION OF THE COMPLEXITY CONSTANTS

The results of the measurements are shown in Table 1 for the chloride and in Table 2 for the bromide.

The ammonia activity a_{NH_3} M was calculated from

$$a_{NH_3} = f_{NH_3} \cdot (c_{NH_3} - 2 c_{Ag}) \tag{16}$$

where the activity factors, f_{NH_3}, are those used by Bjerrum [3].

In all cases, $\varDelta E$ was independent of c_{Ag}. φ_0, calculated from eqn. (15), is plotted against c_{Cl} in Fig. 1 for the chloride case. The total chloride concentration c_{Cl} and the concentration, [Cl⁻], of f r e e chloride ions agree as closely as the former can be used at the calculations instead of the latter. φ_0 is represented by a straight line, which is almost the same for all the titration series. Hence the predominating complexes are $Ag(NH_3)_2^+$ and $Ag(NH_3)_2Cl$ (*vide* eqn. (14)). The difference between the lines for the titration series with different a_{NH_3} is not much greater than the experimental uncertainty. If it is real, it may be caused by any or both of the following reasons: (i) Changes of activity

Table 2. The e.m.f., $E_I + \Delta E$ mV, for cell (I). X = Br.

$c_{NH_3}(M)$ →	10	8	6
f_{NH_3} →	1.9	1.6	1.4
$10^3 \cdot c_{Ag}$ →	10	8	6
E_I (mV) →	632	617	604
$10^{-7} \cdot \beta_{2,0}$ →	1.4	1.4	1.5
$10^3 \cdot c_{Br}$	ΔE (m)V		
48	3.5	3.4	3.5
91	5.9	5.6	5.8
167	9.9	9.6	9.4
231	13.2	12.9	12.6
310	17.1	17.0	16.6
375	20.2	20.1	19.7
444	23.3	23.3	22.9
500	25.3	25.6	25.5
Uncertainty	± 0.2	± 0.2	± 0.3

factors caused by different a_{NH_3}. (ii) The presence of the complexes $AgNH_3Cl_n^{1-n}$ in small amounts, though increasing with decreasing ammonia concentrations. Since φ_0 is represented by straight lines $n = 1$ is selected. Probably species with other values of n also exist [1], even though the accuracy of the measurements does not permit us to conclude anything about an eventual curvature of φ_0. Hence it can be expected that the calculated complexity constant, $\beta_{1,1}$, of $AgNH_3Cl$ becomes too high (*cf.* Table 4). If (ii) is assumed to be valid, φ_0 is simplified to

$$\varphi_0 = 1 + (\beta_{2,1} \cdot \beta_{2,0}^{-1} + \beta_{1,1} \cdot \beta_{2,0}^{-1} \cdot a_{NH_3}^{-1}) \cdot [Cl^-] \qquad (17)$$

The straight lines in Fig. 1 are drawn with $\beta_{2,1} \cdot \beta_{2,0}^{-1} = 0.52 \pm 0.05$ (M^{-1}) and $\beta_{1,1} \cdot \beta_{2,0}^{-1} = 0.1_1 \pm 0.05$, which gives the slope of each line. The intercept of the lines is 1.02 instead of 1 corresponding to an e.m.f. error of 0.5 mV. This difference cannot be caused by some effect of complex formation or change of activity factors. This means that the silver electrode does not function very well in the ammonia solutions. It seems to us that the electrode potentials are more stable in those solutions where a part of the ammonium perchlorate has been exchanged for ammonium chloride.
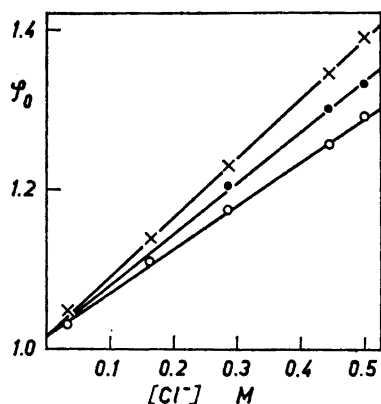
Fig. 1. The function $\varphi_0(\text{Cl}^-)$. Each line represents eqn. (17) at one ammonia concentration, 0.5 M ($\times$), 1 M ($\bullet$) and 3.9 M (O), respectively. The points are calculated from the $\varDelta E$ values of Table 1 by means of eqn. (15).
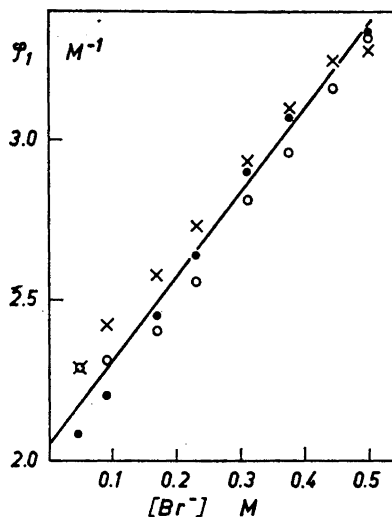

Fig. 2. The function $\varphi_1(\text{Br}^-)$ M^{-1}. The line represents the equation

$$\varphi_1 = (\beta_{2,1} + \beta_{2,2}\,[\text{Br}^-]) \cdot \beta_{2,0}^{-1}$$

The points are calculated from the $\varDelta E$ values of Table 2 by means of eqns. (15) and (18). Points from series with different ammonia concentrations, 10 M ($\times$), 8 M ($\bullet$) and 6 M (O), coincide approximately on the the same line.

For the bromide solutions, φ_0 could be determined only for rather high ammonia concentrations because of the low solubility of silver bromide. $\varDelta E$, and hence, φ_0, are independent of the ammonia concentration within the uncertainty of the experiments. Also in this case, φ_0, plotted against [X$^-$], gave a value for the intercept which was too high, *viz.* 1.04 instead of the theoretical value 1. To determine the complexity constants, φ_1 (M^{-1}) is plotted in Fig. 2 against [Br$^-$].

$$\varphi_1 = (\varphi_0 - 1.04) \times [\text{Br}^-]^{-1} \tag{18}$$

The difference between c_{Br} and [Br$^-$] is small and easily computed, *e.g.* with the aid of an $\bar{n}$-curve and the equation $c_{\text{Br}} - [\text{Br}^-] = \bar{n} \cdot c_{\text{Ag}}$. Since φ_1 is independent of a_{NH_3}, only species with two ammonia molecules are involved. In addition, since φ_1 is a straight line, the only mixed complexes in the solutions are Ag(NH$_3$)$_2$Br and Ag(NH$_3$)$_2$Br$_2^-$ (*cf.* eqns. (14) and (18)). φ_1 in Fig. 2 gives $\beta_{2,1}/\beta_{2,0} = 2.0_5$ (M^{-1}) as the intercept, and $\beta_{2,2}/\beta_{2,0} = 2.7$ (M^{-2}) as the slope of the line.

The solubility products, L_{AgX} M^2, of silver chloride and silver bromide may be obtained from

$$E_x^0 - E_0 = 59.16 \cdot \log L_{\text{AgX}} \tag{19}$$

Table 3. Complexes and equilibrium constants. 1 M NH_4ClO_4. 25°C.

$L_{AgCl} = 4.9 \times 10^{-10}$ (M^2)　　　　　　　　　$L_{AgBr} = 1.2 \times 10^{-12}$ (M^2)
$Ag(NH_3)_2Cl$: $\beta_{2,1} = 1.2 \times 10^7$ (M^{-3})　　　$Ag(NH_3)_2Br$: $\beta_{2,1} = 4.4 \times 10^7$ (M^{-3})
$AgNH_3Cl$　: $\beta_{1,1} = 2 \times 10^6$ (M^{-2})　　　$Ag(NH_3)_2Br_2^-$: $\beta_{2,2} = 5.8 \times 10^7$ (M^{-4})
　　　　　　　　$Ag(NH_3)_2^+$: $\beta_{2,0} = 2.2 \times 10^7$ (M^{-2})

where the values of E_x^0 and E_0 are from eqns. (2), (5) and (6). The values of $\beta_{2,0}$ M^{-2}, computed in Table 1 and 2, were obtained from eqn. (11), where E_1 mV is the first e.m.f. measured in each titration.

The complexes that were found and their equilibrium constants are given in Table 3.

DISCUSSION

Equilibrium constants, $K_{s,m,n}$ M^{2-n-m} for dissolving solid silver halide in ammonia have recently been determined (Ref.[1]). These constants are connected by the equilibrium constants reported in the present paper by the equation

$$K_{s,m,n} = L_{AgX} \cdot \beta_{m,n} \qquad (20)$$

The two sets of constants, which are computed from two quite independent methods, are compared in Table 4. They all agree within the experimental uncertainty.

The existence of mixed bromide complexes containing only one ammonia molecule could not be demonstrated by the potentiometric measurements. This was due to the high ammonia concentration, which is necessary to keep the silver concentrations as high as is essential for obtaining stable e.m.f.'s.

Table 4. Comparision of the equilibrium constants, $K_{s,m,n}$ M^{2-m-n}, from the potentiometric measurements with those from the solubility determinations (Ref.[1]).

(m,n)	$K_{s,m,n} \times 10^3$ (chloride)		$K_{s,m,n} \times 10^5$ (bromide)	
	Ref.[1]	This paper	Ref.[1]	This paper
(2,0)	11.1 ± 0.1	11 ± 0.5	$2.6_3 \pm 0.05$	2.6 ± 0.2
(2,1)	5 ± 1	5.7 ± 0.5	4.3 ± 0.5	5.3 ± 0.5
(2,2)			5 ± 2	7.0 ± 1
(1,1)	0.4 ± 0.4	$1^* \pm 0.5$	4.5 ± 0.5	
(1,2)	1.5 ± 0.5		8 ± 4	
(1,3)			20 ± 10	

* This value is probably too high, because the existence of other monammine species had to be disregarded in the calculations (*cf.* p. 1145).
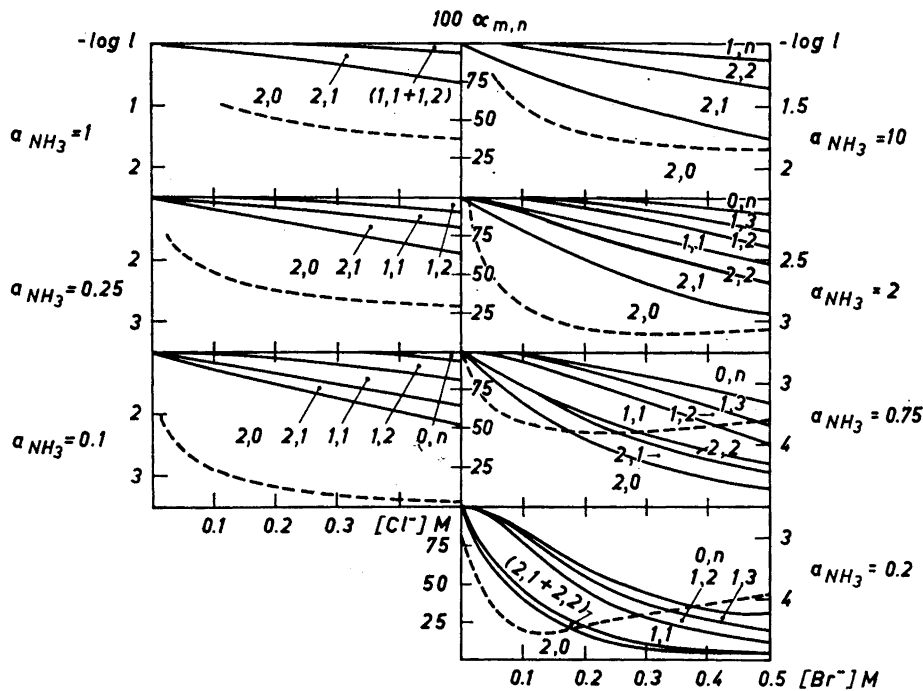
Fig. 3. The distribution, $a_{m,n}$ of silver on the species $Ag(NH_3)_m X_n^{1-n}$ for some ammonia activities, a_{NH_3} M. m and n are given in each field. The solubility, l M, of AgX. The dashed curve gives $-\log l$. X = Cl to the left, X = Br to the right.

At these high ammonia concentrations the monoammine species would be quite negligible, if their complexity constants, computed from the solubility measurements, are true (*cf.* Fig. 3).

The distribution of the silver on the different complexes is shown in Fig. 3, which also shows the solubility calculated from the constants in Table 4. Since no polynuclear species are formed, the distribution is independent of the total silver concentration of the solutions. The fraction, $a_{m,n}$, of silver present as $Ag(NH_3)_m X_n^{1-n}$ is

$$a_{m,n} = \frac{\beta_{m,n} \cdot a_{NH_3}^m \cdot [X^-]^n}{\sum\limits_{m=1}^{2} \sum\limits_{n=0}^{4-m} \beta_{m,n} \cdot a_{NH_3}^m \, [X^-]^n} \tag{21}$$

In practise, the summation is carried out for the values of (m,n) in Table 4. It is quite obvious from the figures that the mixed complexes are far from negligible in systems containing ammonia, silver ions and halide ions.

A survey of the results is shown in Table 5. For each species log $\beta_{m,n}$ is also given. Let $K_{m,n}$ M^{-1} be the equilibrium constant for the stepwise uptake of ammonia, described by the reaction

$$Ag(NH_3)_m X_n^{1-n} + NH_3 \rightleftharpoons Ag(NH_3)_{m+1} X_n^{1-n}$$
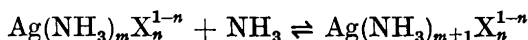
Then $\log K_{m,n} = \log (\beta_{m+1,n}/\beta_{m,n})$ can be read off directly as the difference between two consecutive numbers in a horizontal line in Table 5. Correspondingly, the logarithm of the equilibrium constant $k_{m,n} = \beta_{m,n+1}/\beta_{m,n}$ (M^{-1}) for the stepwise uptake of halide ions by the reaction

$$Ag(NH_3)_m X_n^{1-n} + X^- \rightleftharpoons Ag(NH_3)_m X_{n+1}^n$$
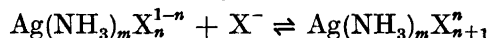
is obtained as differences between consecutive numbers in a vertical line of the table. The differences mentioned are a measure of the affinity of the complex for taking up a further ligand, since they are proportional to $-\Delta G_0$ for the reaction.

From these differences it is obvious that in all cases shown in the table a (linear) species already containing two ligands has a rather low affinity for a third ligand. Using Bjerrum's [3] terminology, this means that the silver ion has a characteristic coordination number of two.

Silver(I) species bind ammonia molecules stronger than chloride ions, since $\log (K_{m,n}/k_{m,n}) = \log (\beta_{m+1,n}/\beta_{m,n+1}) = 1 \pm 0.3$ for all but two species in the chloride system. This is seen from those diagonal rows of Table 5, in which $m + n$ is a constant. In these rows the value of $\log \beta$ increases with about one unit for each substitution of a chloride ion for an ammonia molecule. The one exception is $Ag(NH_3)_2^+$, which does not take up ammonia at all in aqueous solution, although it binds chloride ions to form $Ag(NH_3)_2Cl$. The other is the silver ion, for which $\log (K_{0,0}/k_{0,0})$ is as low as 0.3. This may mean that the negative residual effect (Bjerrum [3]) in the silver ammonia system, depends on an abnormal unstability of $AgNH_3^+$ rather than on an extra stability of $Ag(NH_3)_2^+$.

Bromide ions and ammonia molecules have about the same strength as complexing agents for silver ions, *i.e.* the values of $\beta_{m,n}$, for which $m + n$ is constant, are of the same order of magnitude. For example, when $m + n = 3$, $\log \beta_{m,n}$ is 7.9, 7.8 or 7.6 (*vide* the corresponding diagonal row in Table 5). From statistical reasons we cannot expect $\beta_{m,n}$-values, for which $m + n = $ constant $= i$, to be quite equal, even if $\beta_{i,0}$ were exactly equal to $\beta_{0,i}$. If statistical reasons alone determined the equilibrium constants, the following relations would be valid for $\beta_{1,1}$, if the "stop" of the complex formation after the uptake of two ligands is sufficiently pronounced (*cf.* Bjerrum [3], Fronæus [4], Marcus [5]).

$$\beta_{1,1} = \beta_{1,0} \cdot \beta_{01}/2 \quad \text{and} \quad \beta_{1,1}^2 = \beta_{2,0} \cdot \beta_{0,2}/4$$

ble 5. Silver(I) species in the ammonia-chloride-silver and ammonia-bromide-silver system together with $\log \beta_{m,n}$. $\beta_{m,n}$ in M$^{-(m+n)}$.

+	AgNH$_3^+$ (3.3)[3]	Ag(NH$_3$)$_2^+$ (7.3)	Ag$^+$	AgNH$_3^+$ (3.3)[3]	Ag(NH$_3$)$_2^+$ (7.3)
Cl (3.0)[4]	AgNH$_3$Cl (6.3)	Ag(NH$_3$)$_2$Cl (7.1)	AgBr (4.3)[5]	AgNH$_3$Br (7.6)[1]	Ag(NH$_3$)$_2$Br (7.6)
Cl$_2^-$ (5.0)[4]	AgNH$_3$Cl$_2^-$ (6.5)[1]		AgBr$_2^-$ (7.2)[5]	AgNH$_3$Br$_2^-$ (7.8)[1]	Ag(NH$_3$)$_2$Br$_2^-$ (7.7)
Cl$_3^{2-}$ (5.3)[4]			AgBr$_3^{2-}$ (7.9)[5]	AgNH$_3$Br$_3^{2-}$ (8.2)[1]	
Cl$_4^{3-}$ (5)[4]			AgBr$_4^{3-}$ (8.0)[5]		

Since the pure ammonia and halide systems are not themselves statistical, both the relations cannot be expected to hold true. The second, however, corresponds to the experimental values within their limits of uncertainty. This means that the reaction

$$Ag(NH_3)_2^+ + AgX_2^- \rightleftharpoons 2\ AgNH_3X$$
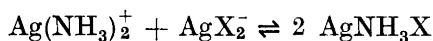
has an equilibrium constant, $\beta_{1,1}^2 \cdot \beta_{0,2}^{-1} \cdot \beta_{2,0}^{-1}$, close to the statistical value 4.

From the table it is also obvious that the affinity for X^- is the same for Ag^+ and $AgNH_3^+$. Then the affinity for NH_3 is also the same for Ag^+ and AgX. This follows from the nonstatistical relation $\beta_{1,1} = \beta_{1,0} \cdot \beta_{0,1}$ between the experimental values in Table 5.

Silver complexes with more than two ligands should probably not be regarded as species with some of the ligand atoms in an "outer sphere". This is known directly for the saturated pure iodide complex, in which the iodide ions are tetrahedrally arranged around the silver ion (Nilsson[6]). If $Ag(NH_3)_2X$ did contain its halide ion in an outer sphere, it should also be expected that the species would be more stable with $X = Cl$ than with $X = Br$, because of the minor radius and greater electronegativity of the chloride ion. As is seen from Table 5, the opposite is true. For $Co(NH_3)_6^{3+}$ Evans and Nancollas [9] have found that the strength of its outer halide complexes decreases in the order $Cl^- > Br^- > I^-$. From Table 5 we also learn that compared with other three-ligand-species $Ag(NH_3)_2X$ is only a little weaker than would be expected from statistical reasons. The strength of $Ag(NH_3)_2Br_2^-$ is also comparable with the other four-ligand-species. Hence, there does not seem to be much reason why $Ag(NH_3)_2X$ and $Ag(NH_3)_2X_2^-$ would be examples of outer complexes in contrast to other silver complexes with more than two ligands, even if the entrance of a halide ligand into $Ag(NH_3)_2^+$ is slightly less favoured than into other silver species already containing two ligands. In this connection it would be interesting to know the structure of solids like $Ag(NH_3)_2X$ and $MeAg(NH_3)_2X_2$.

REFERENCES

1. Leden, I. and Persson, G. *Acta Chem. Scand.* **15** (1961) 607.
2. Büchi, P. *Z. Elektrochem.* **30** (1924) 443.
3. Bjerrum, J. *Metal Ammine Formation in Aqueous Solution* (Diss.), Copenhagen, 1941, pp. 135, 141, 73, 57, 41.
4. Berne, E. and Leden, I. *Svensk Kem. Tidskr.* **65** (1953) 88.
5. Berne, E. and Leden, I. *Z. Naturforsch.* **8a** (1953) 720.
6. Fronæus, S. *Acta Chem. Scand.* **5** (1951) 148.
7. Marcus, Y. *Ibid.* **11** (1957) 811.
8. Nilsson, R. *Arkiv Kemi* **12** (1958) 513.
9. Evans, M. G. and Nancollas, G. H. *Trans. Faraday Soc.* **49** (1953) 363.