

# Metal Amine Formation in Solution. XXVI. Stability Constant and UV Absorption Spectrum of the Triammine Silver(I) Complex

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It was found by spectrophotometric measurements in the UV that the diammine silver(I) ion forms a triammine complex in aqueous ammonia. The stability constant:  $K_3 = ([Ag(NH_3)_3^+] a_{H_2O}) / ([Ag(NH_3)_2^+] a_{NH_3})$  was determined to be 0.0251 in 0.1 M  $NH_4ClO_4$  at 25 °C. The corresponding value of  $K_3$  for the copper(I)triammine complex is 0.0544. The absorption band of the triammine silver complex is situated at 228 nm with  $\epsilon_{max} = 1410$ . The diammine silver ion has its first band at 210 nm with  $\epsilon_{max} = 910$ .

It is generally accepted that the silver(I) ion in aqueous ammonia is present as a diammine complex.<sup>1</sup> The corresponding diammine copper(I) complex has recently been shown to form a triammine complex in aqueous ammonia,<sup>2,3</sup> and it would therefore be expected that the silver(I) ion also forms a triammine complex at sufficiently high ammonia concentrations. A spectrophotometric study of the UV absorption in aqueous ammonia confirmed that this is indeed the case.

## Experimental

The UV measurements were made with a Cary 118 spectrophotometer thermostatted at 25 °C. In order to correct for the ion absorption of ammonia, the solutions were made 0.1 M with ammonia-filled with the same medium as that for the silver solution. Silver sulphate was chosen as the silver salt. This salt is easy to prepare pure, is sufficiently soluble and is just as optically transparent in the UV as silver perchlorate. In order to suppress the dissociation of the aqueous ammonia, the solutions were made 0.1 M with ammonium perchlorate. The ammonia activity  $a_{NH_3} = f_{NH_3}[NH_3]$  and water activity  $a_{H_2O}$  in the solutions

were calculated at 25 °C from Perman's vapour pressure measurements.<sup>4</sup>

## Data and Calculations

The  $\epsilon, \lambda$  absorption curves of some silver/ammonia solutions in the UV are shown in Fig. 1. A close examination of these curves shows that they correspond to a mixture of only two species. This is demonstrated in Table 1 where the consecutive fractions  $\Delta\epsilon/(\epsilon_a - \epsilon_f)$  for the curves from a to f are calculated at four selected wavelengths. The calculated fractions from curve a to the next following curves are seen to be independent of the wavelength within experimental uncertainty, confirming that we are dealing with a system of only two species, viz. the diammine silver(I) ion and a new complex. Assuming that the new complex is the triammine silver(I) ion, the stability constant is given by the expression:

$$K_3(\text{uncorr}) = \frac{[Ag(NH_3)_3^+]}{[Ag(NH_3)_2^+] a_{NH_3}} \quad (1)$$

If corrected for the decrease in the water activity ( $a_{H_2O} = 1$  for  $C_{NH_3} = 0$ ) the expression is:

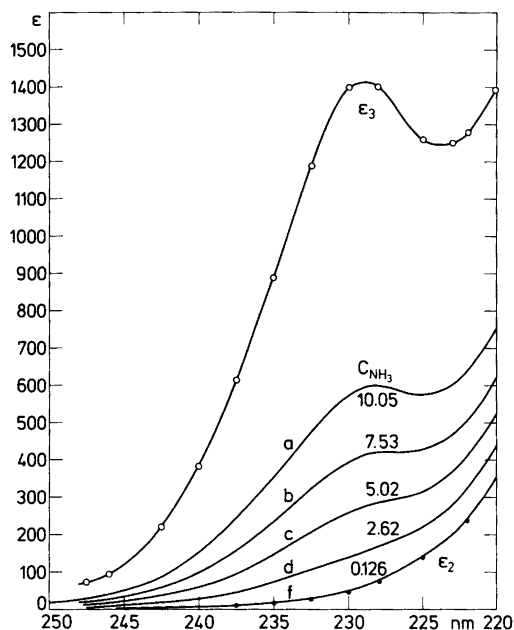


Fig. 1.  $\epsilon, \lambda$  absorption curves for silver/ammine solutions with ammonia concentrations varying from  $\sim 0.1$  M to 10 M. The absorption curve through the  $\circ$  points shows the calculated spectrum of the pure triammine complex ( $\epsilon_3$ ). The spectrum of the diammine complex ( $\epsilon_2$ ), which is nearly identical with curve f, is indicated by the  $\bullet$  points.

$$K_3(\text{corr}) = \frac{[\text{Ag}(\text{NH}_3)_3^+] a_{\text{H}_2\text{O}}}{[\text{Ag}(\text{NH}_3)_2^+] a_{\text{NH}_3}} \quad (2)$$

Since the aqua silver(I) ion has been shown to be a tetraaqua ion,<sup>5</sup> the uptake of the 3rd ammonia molecule must be accompanied by loss of a water molecule. Expression (2) can therefore be assumed to be a better approximation of the true activity constant than expression (1). In an isobestic system, three absorption curves are required to calculate the equilibrium constant. Using, e.g., the curves a, b and c with the molar absorbances  $\epsilon_a$ ,  $\epsilon_b$  and  $\epsilon_c$  (decreasing in that order) the constant (in our case  $K_3$ ) can be calculated directly from the previously derived expression<sup>6</sup>:

$$\frac{a_a - a_b + \{a_a a_c - a_b a_c\} K_3}{a_a - a_c + \{a_a a_b - a_b a_c\} K_3} = \frac{\epsilon_a - \epsilon_b}{\epsilon_a - \epsilon_c} \quad (3)$$

in which  $a_a$ ,  $a_b$  and  $a_c$  are the ammonia activities or the corrected ammonia activities ( $a_{\text{NH}_3}/a_{\text{H}_2\text{O}}$ ), respectively. Results of calculations of  $K_3$  from equation (3) with various qualified combinations of the data (ammonia activities and estimated mean molar absorbance fractions) for the six absorption curves in Table 1, are given in Table 2.

The molar absorbances of the pure complexes ( $\epsilon_3$  and  $\epsilon_2$ ) were calculated by use of the derived mean value for  $K_3(\text{corr})$  0.0251. The fraction of the triammine complex ( $\alpha_3 = [\text{Ag}(\text{NH}_3)_3^+]/C_{\text{Ag}}$ ) was thus calculated to be 0.387 in sol. a and 0.0027 in sol. f, and the following expressions were derived for the molar absorbances of the pure complexes:

$$\epsilon_3 = \epsilon_a + \frac{1 - 0.387}{0.387 - 0.003} (\epsilon_a - \epsilon_f) \text{ and}$$

Table 1. Molar absorbances at four selected wavelengths (in nm) for six silver(I)-ammonia solutions numbered a to f with  $C_{\text{NH}_4\text{ClO}_4} = 0.1066$  M at 25.0 °C. The calculated consecutive fractions  $\Delta\epsilon/(\epsilon_a - \epsilon_f)$  are indicated for each of the wavelengths used.  $[\text{NH}_3] = C_{\text{NH}_3} - 2C_{\text{Ag}}$ ,  $a_{\text{NH}_3} = f_{\text{NH}_3}[\text{NH}_3]$ .

$C_{\text{Ag}}$	$C_{\text{NH}_3}$	$a_{\text{NH}_3}$	$a_{\text{NH}_3}/a_{\text{H}_2\text{O}}$	235	230	228	225	$\Delta\epsilon/(\epsilon_a - \epsilon_f) \text{ Av}$
a	0.00120	10.05	19.00	353.3	570	586.7	573.3	
				0.357	0.340	0.334	0.342	0.343 ± 0.010
b	0.00120	7.536	11.75	233.3	393.3	416.7	426.7	
				0.253	0.263	0.266	0.261	0.261 ± 0.006
c	0.00120	5.024	6.58	148.3	256.7	281.7	315.0	
				0.221	0.224	0.227	0.215	0.222 ± 0.005
d	0.0100	2.620	2.92	74.0	140.0	166.0	223.0	
				0.094	0.095	0.095	0.091	0.094 ± 0.002
e	0.00400	1.310	1.361	42.5	90.25	117.5	183.8	
				0.074	0.077	0.077	0.091	0.080 ± 0.007
f	0.0100	0.1256	0.106	17.6	50.0	78.4	144.8	

Table 2. Calculated values of  $K_3$ .

Combinations	abf	acf	adf	ace	bcf	average
$K_3(\text{uncorr})$	0.0107	0.0137	0.0109	0.0162	0.0199	$0.0143 \pm 0.0039$
$K_3(\text{corr})$	0.0195	0.0240	0.0231	0.0283	0.0308	$0.0251 \pm 0.0046$

Table 3. Stability Constants for the copper(I), silver(I) and mercury(II) ammine complexes.

	$K_1$	$K_2$	$\beta_2$	$K_3$	$K_4$
$\text{Cu(I), NH}_3^8$	$10^{5.93}$	$10^{4.93}$	$10^{10.86}$	0.055	
$\text{Ag(I), NH}_3^1$	$10^{3.15}$	$10^{3.75}$	$10^{6.90}$	0.025	
$\text{Hg(II), NH}_3^1$	$10^{8.8}$	$10^{8.7}$	$10^{17.5}$	10	5.7

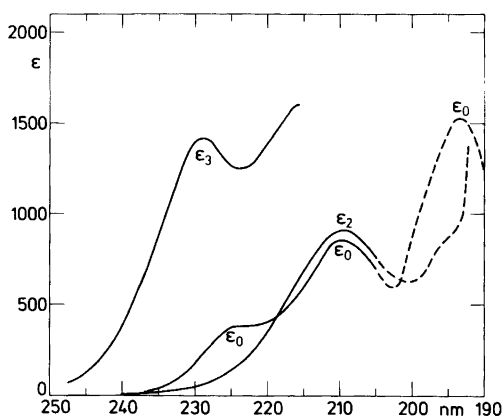


Fig. 2. Absorption spectra of the aqua silver ( $\epsilon_0$ ), the diammine silver ( $\epsilon_2$ ) and the triammine silver ( $\epsilon_3$ ) ions. The continuation of the curves of the aqua and diammine silver ions below 205 nm – the dotted part of the curves – are reproduced from Volbert.<sup>7</sup>

$$\epsilon_2 = \epsilon_t - \frac{0.0027}{0.387 - 0.003} (\epsilon_a - \epsilon_t)$$

## Discussion

The absorption curve for the triammine complex ( $\epsilon_3$ ) is plotted in Fig. 1. It can be seen that the maximum at  $\sim 228$  nm with  $\epsilon_{\text{max}} = 1410$  is more pronounced than for the family of absorption curves a–f from which it is derived. The absorbance of ammonia which has to be compensated for is, in the case of high ammonia concentra-

tions, several times greater than that of the silver complexes at wavelengths lower than 220 nm, and for this reason, the molar absorbances of the triammine complex can not be determined at wavelengths much lower than 220 nm. This is not the case for the aqua and diammine silver ions for which the absorbances can be followed further into the UV. The results of such measurements are shown in Fig. 2.

The present measurements in this range of wavelengths are in good agreement with those of Volbert<sup>7</sup> who used photographic techniques to extend the measurements further into the UV than is possible with the Cary 118 instrument (the dotted part of the curves in the figure below  $\sim 205$  nm). The absorption curve for the diammine complex ( $\epsilon_2$ ), which is nearly identical with curve f in Fig. 1, has a maximum at 210 nm with  $\epsilon_{\text{max}} = 910$ . At 224 nm, the aqua silver ion has a pronounced shoulder followed by two intense bands at 210 and 193 nm.

In the preliminary experiments,  $K_3$  was first determined by analysis of the absorption at the foot of the first band at 246 nm. For a series of ammonia solutions with silver sulphate concentrations higher than 0.01 M,  $K_3$  was determined in the same way as with copper(I). See Ref. 3.  $K_3(\text{corr})$  was found to be  $0.0232 \pm 0.0030$  in fine agreement with the mean value in Table 2, and  $\epsilon_3(246 \text{ nm}) = 97 \pm 2$ . In the copper(I) system<sup>3</sup>,  $K_3(\text{uncorr})$  at the shoulder at 290 nm was determined as 0.038 with  $\epsilon_3 = 303$ . Recalculated for the change in the water activity with increasing ammonia activity, the value  $0.0544 \pm 0.0053$  with

$\epsilon_3$  (290 nm) =  $209 \pm 8$  is obtained for  $K_3(\text{corr})$ .

The stability constants for the silver ammine complexes are compared in Table 3 with those for the copper(I) and mercury (II) ammine complexes. All three systems have a characteristic coordination number, two, with  $\beta_2$  increasing in the order  $\text{Ag(I)} < \text{Cu(I)} < \text{Hg(II)}$ . It can be seen that the small affinity for uptake of further ammonia molecules increases in the same order. The silver ion in liquid ammonia has, according to a Raman spectroscopic study,<sup>9</sup> tetrahedral symmetry. It must therefore be assumed that the silver ion, and probably also the copper(I) ion, exist under such extreme conditions as tetraammine complexes.

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