added water has any effect on the results, up to 1% water by volume was added without causing any significant spectral changes. This is in accord with results of alkali metal cryptate stability constant determinations,[24] although a marked kinetic effect of added water was noted[7] in the dissociation of Cu^{2+}-$\subset$222 in $(CH_3)_2SO$.

The use of $(CH_3)_2SO$ as a solvent removes complications due to lanthanide ion hydrolysis and the usual acid-base chemistry of the cryptands. The absence of a supporting electrolyte removes to some extent problems associated with the interaction of anions with lanthanide cryptate complexes.[8,9] To examine the effect of added electrolyte in these systems, the most stable alkaline earth cryptate ($Sr^{2+}\subset$221) and one of the most stable lanthanide cryptates ($Yb^{3+}\subset$222) were examined in the presence of added electrolyte (0.02 M $(CH_3)_4NCl$).[29] The Sr^{2+}-murexide and Yb^{3+}-murexide complexes have lower stability constants in the presence of added electrolyte. This result is not unexpected since the reaction is an ion association. However, while the formation of $Sr^{2+}\subset$221 is unaffected by added electrolyte within the limits of experimental error, $Yb^{3+}\subset$222 shows a marked decrease in stability. This is a striking result, and the reason for it is certainly not yet clear. It is possible that chloride ion interacts with lanthanide ions and/or lanthanide cryptates. Electrochemical results[8,9] first suggested the idea of the interaction of small anions in solution with lanthanide cryptates, but such effects were observed for F^- and OH^-, with only small or negligible effects being observed with Cl^-. However, further support for the association of anions with encapsulated lanthanide ions is found in the structures[10,12] of NO_3^- and ClO_4^- salts of lanthanide cryptates, which show direct anion coordination to the metal ion. This is not surprising in itself since the lanthanides display coordination numbers up to 9 with simple unidentate ligands.[25,26] Anion coordination to lanthanide cryptates in solution cannot be general, however, as conductance measurements in CH_3CN show $Eu(ClO_4)_3$ to behave as a 2:1 electrolyte[27] while $(Eu^{3+}\subset 222)(ClO_4)_3$ behaves as a 3:1 electrolyte.[12] X-ray diffraction studies on saturated aqueous lanthanide chloride solutions[26] show no significant inner-sphere chloride, although the authors do point out that experiments were never carried out with an excess of Cl^-. Crystal structures of hydrated lanthanide chloride salts frequently show inner-sphere chloride.[30] The above results from the recent literature show no clear general pattern of behavior concerning the interaction of small anions with lanthanides or lanthanide cryptates. They do support the contention that such interactions are possible, and we suggest that this is responsible for the observed dependence of the $Yb^{3+}\subset$222 stability constant on ionic strength.[31]

Acknowledgment. Support for this work by the National Institutes of Health (Grant GM24748) is gratefully acknowledged.

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(29) This is almost the limit of solubility of $(CH_3)_4NCl$ in $(CH_3)_2SO$.

(30) A discussion of solid-state structures is in ref 26.

(31) ^{35}Cl NMR studies concerning Cl^- interaction with K^+-18C6 have recently been reported (Sugawara, T.; Ydasaka, M.; Yokoyama, Y.; Fujiyama, T.; Iwamura, H. *J. Phys. Chem.* **1982**, *86*, 2705). An interaction of Cl^- with K^+ incorporated in the crown ether is reported in aqueous solution.

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Stability of Silver(I) Complexes of *N*-Methyl-Substituted 4-Methyldiethylenetriamines in Aqueous Solution

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With use of potentiometric pH and pAg measurements the stability constants and the stoichiometric composition of the Ag(I) complexes with some *N*-methyl-substituted 4-methyldiethylenetriamines in aqueous solution in a medium of ionic strength 1.3 and at a temperature of 25 °C have been determined. It is found that, besides mononuclear complexes, polynuclear and protonated complexes are formed. There is evidence for the formation of hydroxo complexes. The values of the stability constants are discussed in terms of possible structures. The mean amounts of complexed Ag^+, H^+ or OH^-, and L are calculated, by using pH and pAg data and without making any assumption about the stoichiometric composition of the formed complexes.

Introduction

Much work is done[1] on the complexation of Ag(I) with primary and secondary monoamines, in contrast to the quantity of work done on tertiary aliphatic monoamines and polyamines. The latter has something to do with the fact that the complex formation between Ag(I) and polyamines is rather intricate as has been demonstrated by studies performed on the complex formation between Ag(I) and some primary diamines.[2-8] Indeed it has been found that the presence of polynuclear, protonated, and even hydroxo complexes must be taken into account. On the other hand, there exist a great deal of papers where the experimental data of the formation of Ag(I) complexes with polyamines are treated as if the complex formation is purely mononuclear. Nowadays a lot of computer programs are available that can handle complicated systems, and besides, with use of automated or half-automated apparatus, a greater number of experimental data, covering an extended concentration range, can be obtained in an acceptable time. Moreover the calculation and the concentration of free ligand[9] and the complexity sum[10] *S* makes a more accurate analysis of the experimental data possible.

In this investigation the Ag(I) complexes of the following ligands are studied: 1,4-dimethyldiethylenetriamine (STP), 1,4,7-trimethyldiethylenetriamine (STS), 1,1,4-trimethyldiethylenetriamine (TTP), and 1,1,4,7,7-pentamethyldiethylenetriamine (TTT). The shorthand rotations given in

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(1) Smith, R. M.; Martell, A. E. "Critical Stability Constants"; Plenum Press: New York, 1975; p 2.

(2) Preu, J. E.; Schwarzenbach, G. *Helv. Chim. Acta* **1950**, *33*, 985.

(3) Schwarzenbach, G.; Ackerman, H.; Maissen, B.; Anderegg, S. *Helv. Chim. Acta* **1952**, *35*, 2337.

(4) Schwarzenbach, G. *Helv. Chim. Acta* **1953**, *36*, 23.

(5) Ohtaki, H.; Ito, Y. *J. Coord. Chem.* **1973**, *3*, 131.

(6) Van Poucke, L. C. *Talanta* **1976**, *23*, 161.

(7) Ohtaki, H.; Cho, K. *Bull. Chem. Soc. Jpn.* **1977**, *50*, 2674.

(8) Magyar, B.; Schwarzenbach, G. *Acta Chem. Scand., Ser. A* **1978**, *A32*, 943.

(9) Van Poucke, L. C.; Yperman, J.; François, J.-P. *Inorg. Chem.* **1980**, *19*, 3078.

(10) Sillén, L. G. *Acta Chem. Scand.* **1961**, *15*, 1981.

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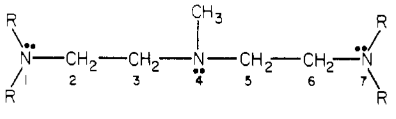
parentheses indicate whether the amino groups, in the sequence end, central, and end, are primary (P), secondary (S), or tertiary (T):



$R \equiv CH_3$ or H

In this study the influence of the number of methyl substituents on the stoichiometric composition, structure, and stability of the formed complexes is investigated.

Experimental Section

Apparatus. pH and pAg measurements are performed simultaneously with use of two Radiometer pHM-64 pH meters, one equipped with an Ingold HA-201 glass electrode and the other provided with an Orion 94-16A Ag_2S electrode. In both cells the same reference electrode is used, i.e. a double-junction saturated calomel electrode (Radiometer K 1301). The electrolyte bridge is filled with a 2 M KNO_3 solution. The reaction vessel is surrounded with a thermostated jacket (25.00 ± 0.05 °C) and placed in a thermostated cage (25.0 ± 0.5 °C). All measurements are done under nitrogen atmosphere. Before use the nitrogen is washed with soda lime, a 3 M H_2SO_4 solution, a saturated $Ca(OH)_2$ solution, distilled water, and a 1.3 M KNO_3 solution. The titrant is added to the solution with use of a very precise Ströhlein piston buret.

Reagents. The KOH solutions are prepared with use of Titrisol (Merck, p.A.). When a Gran plot[11,12] from the titration of a HNO_3 solution with this KOH solution was used, the presence of CO_2 could not be detected.

KNO_3 (Merck, p.A.) is used as indifferent electrolyte without further purification.

The *N*-methyl-substituted triamines were purchased from Ames Laboratories. These triamines are converted into the ammonium form by adding 3 equiv of HNO_3 to a dilute solution at 0 °C. The formed salt is concentrated by vacuum distillation. The salt is washed several times with ethanol and ether and dried in a vacuum desiccator (P_4O_{10}). All solutions are prepared with use of deionized and bidistilled water.

Measurements. All measurements are performed at an ionic strength of 1.3 M with KNO_3 as indifferent electrolyte.

pH values are obtained by means of a calibration procedure using Gran plots. These Gran plots represent titrations of 0.01 M HNO_3 solutions with KOH solutions, ranging from 0.1000 to 0.4000 M, in such conditions that the ionic strength is 1.3 M.

The Ag_2S electrode is tested for Nernstian behavior with the help of seven $AgNO_3$ solutions with concentrations ranging from 0.032 to 0.000370 M. A linear relationship is found between the measured potential and log $[Ag^+]$. The slope is exactly 59.16 mV, and the $E°$ calculated from these data is 538.95 ± 0.05 mV. These experiments are also performed at an ionic strength of 1.3 M.

As polynuclear complexes are expected, a large concentration range is needed. On the other hand, it is very likely that the concentration of free ligand should be calculated without any assumption about the stoichiometric composition of the formed complexes, i.e. with the Österberg method[13] or any analogous method.[9]

We have performed two sets of titration curves. In the first set C_{Ag} and in the second set C_{Ag}/C_L are held constant. The first set can be treated with the Österberg method[9,13] and the other set is treated with a method that we have called the "dilution method", which has been described earlier.[9] As the stability constants are finally calculated with the computer program MINIQUAD[14] and the knowledge of the concentration of free ligand is not needed then, the experimental data are augmented with a third set in which C_{Ag}/C_L and C_{Ag} are changed for each titration curve.

In the first set of experimental data C_{Ag} is equal to 0.0040 M. Five titration curves are obtained with starting values for C_L/C_{Ag} equal to 10, 8, 6, 4, and 2. For each titration, to a solution of 20 mL of 0.0040 M $AgNO_3$ and an appropriate amount of ligand, in the fully protonated form, are added a quantity of a 0.1000 M solution of KOH and the same quantity of a 0.0080 M $AgNO_3$ solution. The difference between two successive titration points may never exceed 5 mV, otherwise poor results are obtained with the Österberg method.

In the second set of titration curves C_L/C_{Ag} is equal to 3. The starting solution of each titration is composed of 20.00 mL of a solution containing $AgNO_3$ and ligand in the fully protonated form, *x* mL of 0.4000 M KOH, and 5 − *x* mL of 1.3 M KNO_3. The *x* values are different for each titration and vary from 0 to 5 mL. These *x* values are chosen in such a way that the *E* difference between two successive titration curves never exceeds 10.0 mV for the pH curves as well as for the pAg curves. These solutions are titrated with a 1.3 M KNO_3 solution until an end volume of 150 mL is reached. In this way C_{Ag} is varied between 0.008 and 0.001 33 M and C_L between 0.023 94 and 0.003 990 M for STP, between 0.022 79 and 0.003 798 M for TTP, between 0.023 86 and 0.003 977 M for STS, and between 0.023 74 and 0.003 957 M for TTT.

In the third set of experimental data the following C_L/C_{Ag} ratios are studied: 10, 5, 2, 1, 0.5, and 0.25.

Results and Discussion

The formation of the complexes can be represented by eq 1. The overall stability constant β_{pqr} of reaction 1 is defined

$$pAg^+ + qL + rH^+ \rightleftharpoons Ag_pL_qH_r^{(p+r)+} \qquad (1)$$

by eq 2. β_{pqr} is given in concentration units. The value of

$$\beta_{pqr} = \frac{[Ag_pL_qH_r^{(p+r)+}]}{[Ag^+]^p[L]^q[H^+]^r} \qquad (2)$$

r can be positive, zero, or negative. For $r > 0$ protonated and for $r < 0$ hydroxo complexes are formed. The complexity sum is given by eq 3. The mass-balance equations are given by

$$S = \sum_p\sum_q\sum_r [Ag_pL_qH_r^{(p+r)+}] = \sum_p\sum_q\sum_r \beta_{pqr}[Ag^+]^p[L]^q[H^+]^r \qquad (3)$$

eq 4–6. The values for β_{01r}, the formation constants of the

$$C_{Ag} = [Ag^+] + \sum_p\sum_q\sum_r p\beta_{pqr}[Ag^+]^p[L]^q[H^+]^r \qquad (4)$$

$$C_L = [L] + \sum_r \beta_{01r}[L][H]^r + \sum_p\sum_q\sum_r q\beta_{pqr}[Ag^+]^p[L]^q[H^+]^r \qquad (5)$$

$$C_H = [H] - [OH] + \sum_r r\beta_{01r}[L][H]^r + \sum_p\sum_q\sum_r r\beta_{pqr}[Ag^+]^p[L]^q[H^+]^r \qquad (6)$$

three protonated forms of L, have been given earlier.[15]

As pH and pAg are obtained in concentration units, the mass balances can be used in the computations. The Österberg method,[9] used for the calculation of [L], can be represented by eq 7 and 8. Primes indicate in eq 7 and 8 solutions in which

$$\log \frac{[L]}{[L]'} = \left\{ \frac{\partial}{\partial C_L}\left[\int_{pH'}^{pH} C_H \, dpH \right]_{C_{Ag},C_L} \right\}_{C_{Ag},pH} \qquad (7)$$

$$\log \frac{[L]}{[L]'} = \left\{ \int_{pH'}^{pH} \left(\frac{\partial C_H}{\partial C_L} \right)_{C_{Ag},pH} dpH \right\}_{C_{Ag},pH} \qquad (8)$$

the values of [L] are known. [L] can be calculated from mass-balance equations of solutions with low pH values, so that complex formation is completely suppressed.

This method is only applied to TTT. Hereby it is found that there exists a linear relationship between the integral of eq 7 and C_L at constant pH values and for any pH value. Moreover, all these lines go through the origin. An explanation for

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[15] Yperman, J.; Mullens, J.; François, J.-P.; Van Poucke, L. C. *J. Phys. Chem.* **1982**, *86*, 298.

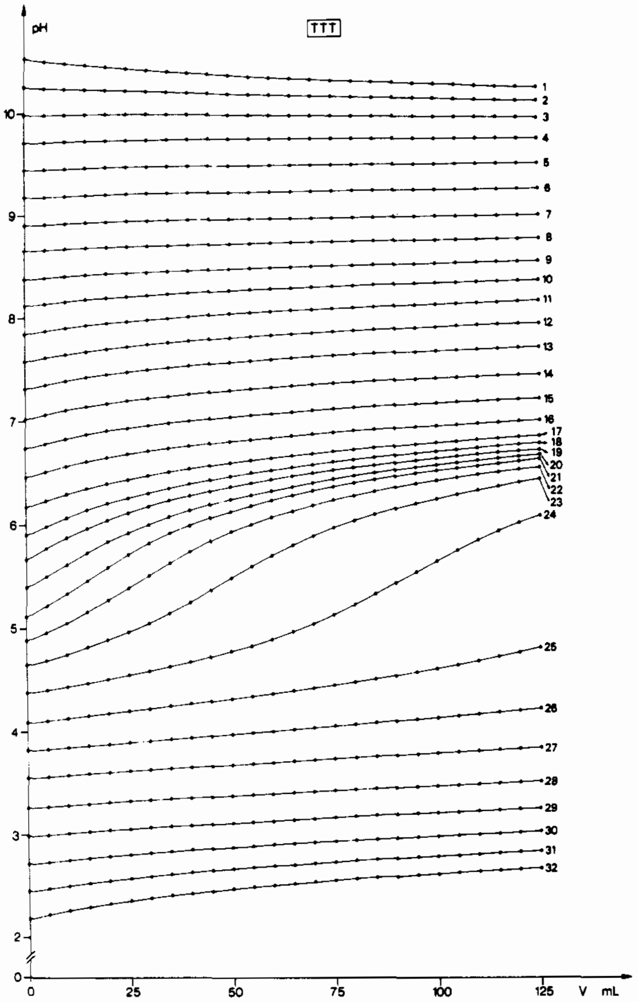

Figure 1. Measured pH vs. the added quantity V of 1.3 M KNO_3, according to the "dilution method", for TTT and Ag^+. h values (mmol) for the curves in the figure are as follows: (1) −0.0072; (2) 0.0280; (3) 0.0728; (4) 0.1408; (5) 0.2326; (6) 0.3528; (7) 0.4768; (8) 0.5848; (9) 0.6888; (10) 0.7808; (11) 0.8808; (12) 0.9808; (13) 1.0688; (14) 1.1264; (15) 1.1560; (16) 1.1728; (17) 1.1796; (18) 1.828; (19) 1.1840; (20) 1.1848; (21) 1.1872; (22) 1.1896; (23) 1.1928; (24) 1.1992; (25) 1.2104; (26) 1.2288; (27) 1.2608; (28) 1.3208; (29) 1.4048; (30) 1.5128; (31) 1.6408; (32) 1.7808.

this relationship cannot be given at the moment.

The dilution method can be represented[9] by eq 9–11. m,

$$C - C_0 = -2.303\left[\int_{h_0}^{h}\left(\frac{\partial \log [\mathrm{H}^+]}{\partial V}\right)_{m,l,h} \mathrm{d}h\right]_{m,l,V} \qquad (9)$$

$$C_{\mathrm{M}} \ln \frac{[\mathrm{M}]}{[\mathrm{M}]_0} + C_{\mathrm{L}} \ln \frac{[\mathrm{L}]}{\mathrm{L}]_0} + \int_{\ln [\mathrm{H}^+]_0}^{\ln [\mathrm{H}^+]} C_{\mathrm{H}}\, \mathrm{d} \ln [\mathrm{H}^+] - (C - C_0) = 0 \qquad (10)$$

$$C - C_0 = -2.303\left[\frac{\partial}{\partial V}\left(\int_{h_0}^{h} \log [\mathrm{H}^+]\, \mathrm{d}h\right)_{m,l,V}\right]_{m,l,h} \qquad (11)$$

l, and h are the total number of moles of Ag^+, L, and H^+, respectively. V is the volume of the solution; C and C_0 represent the total concentration of solutes for two different solutions, i.e., x values. C_0 can be calculated from mass-balance equations of solutions at low pH, where no complexation occurs.

The experimental data used in this method are represented in Figures 1 and 2 for the case of TTT, as an example. In Figure 1, pH vs. V curves are given for constant values of m, h, and l. In Figure 2 the corresponding pAg vs. V curves are given. For high values of h ($h > 1.1828$ mmol) all curves coincide. Moreover in this region, which corresponds with the first step in the neutralization of the protonated ligand, $[Ag^+]$ equals C_{Ag}. This means that in this region complexes are not formed in detectable amounts. For $h < 1.18$ mmol the dilution curves differ and pAg values increase with increasing values for V. However, at very low values for h, pAg values decrease with increasing V. A possible explanation for this rather unexpected phenomenon is that on dilution polynuclear species dissociate in less stable mononuclear species. Obviously, values for $\bar{p}$, $\bar{q}$, and $\bar{r}$ are extremely inaccurate in the region where the complex formation is negligibly small. Therefore, only experimental data above a pH value where complex formation becomes perceptible are used for the calculation of $\bar{p}$, $\bar{q}$, and $\bar{r}$.

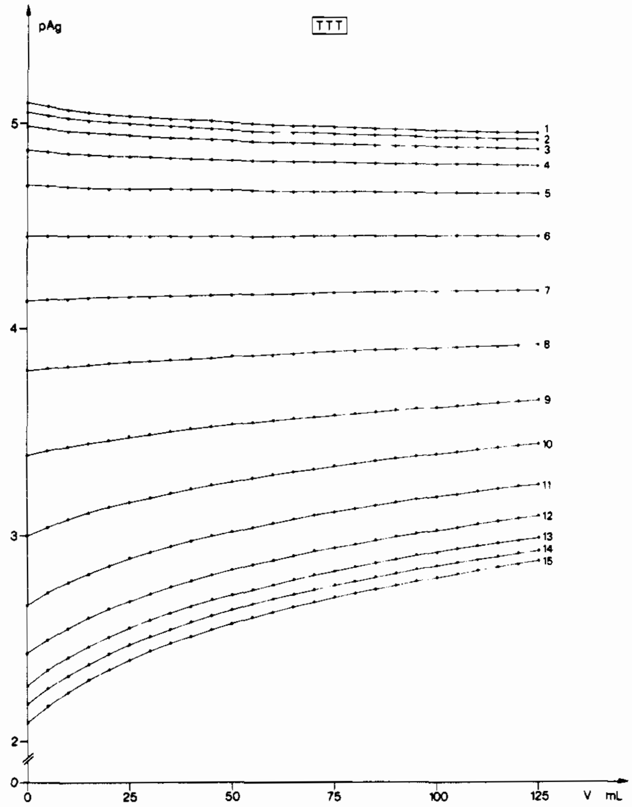

Figure 2. Measured pAg vs. the added quantity V of 1.3 M KNO_3, according to the "dilution method", for TTT and Ag^+. h values (mmol) for the curves in the figure are as follows: (1) −0.0072; (2) 0.0280; (3) 0.0728; (4) 0.1408; (5) 0.2328; (6) 0.3528; (7) 0.4768; (8) 0.5848; (9) 0.6888; (10) 0.7808; (11) 0.8808; (12) 0.9808; (13) 1.0688; (14) 1.1264; (15) 1.1828–1.7808.

The results for TTT obtained by means of the Österberg method are represented in Figure 3. The values of $\bar{p}$ and $\bar{q}$ are near 1 and $\bar{r}$ varies between 0.3 and −0.1.

The same values obtained by means of the dilution method are shown in Figures 4–7. For TTT (Figure 4) the values of $\bar{p}$ are slightly lower than 1, obviously due to experimental errors. From Figures 4 (ligand TTT) and 5 (ligand STS) it seems that the mononuclear species are the dominating ones. However, polynuclear complex formation is not negligible for TTP (Figure 6) and STP (Figure 7). No value of $\bar{p}$ exceeding 1.5 is found. The values of $\bar{q}$ are always higher than the corresponding $\bar{p}$ values. Values for $\bar{r}$ vary between 1.0 and −0.1.

From these results it can be concluded that mononuclear species are formed for each system. The most probable of these species are AgL and AgLH. If we accept that the complex formation is successive, the experimental condition $\bar{p}/\bar{q} < 1$ is fullfilled by accepting the presence of AgL_2 and AgL_2H. As polynuclear complexes are also formed, Ag_2L_2

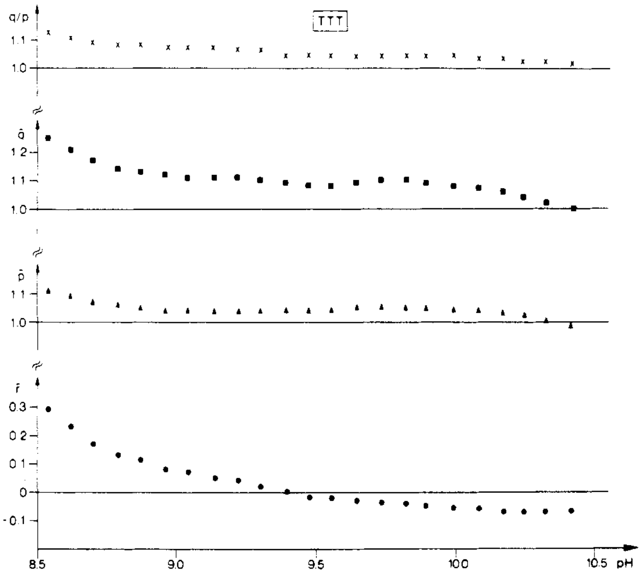

Figure 3. q/p ratio vs. the pH (top curve) and $\bar{q}$, $\bar{p}$, and $\bar{r}$, the mean amounts of complexed ligand, complexed silver ion, and complexed hydrogen or hydroxide, respectively, vs. pH (lower curves) for TTT and Ag^+, according to the Österberg method (C_L = 0.0105 M and C_{Ag} = 0.0040 M, both being constant for the whole pH range).

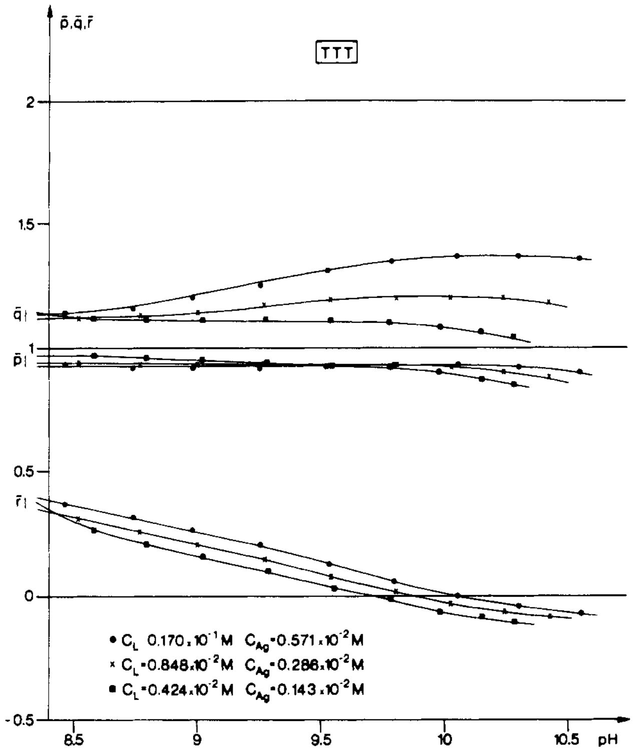

Figure 4. $\bar{p}$, $\bar{q}$, and $\bar{r}$ vs. pH for three different, but constant, C_L and C_{Ag} values, according to the "dilution method", for TTT and Ag^+.

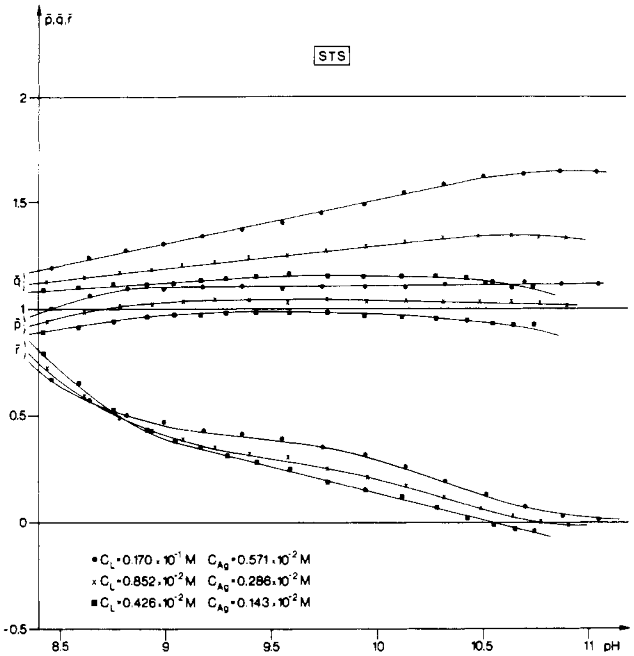

Figure 5. $\bar{p}$, $\bar{q}$, and $\bar{r}$ vs. pH for three different, but constant, C_L and C_{Ag} values, according to the "dilution method", for STS and Ag^+.

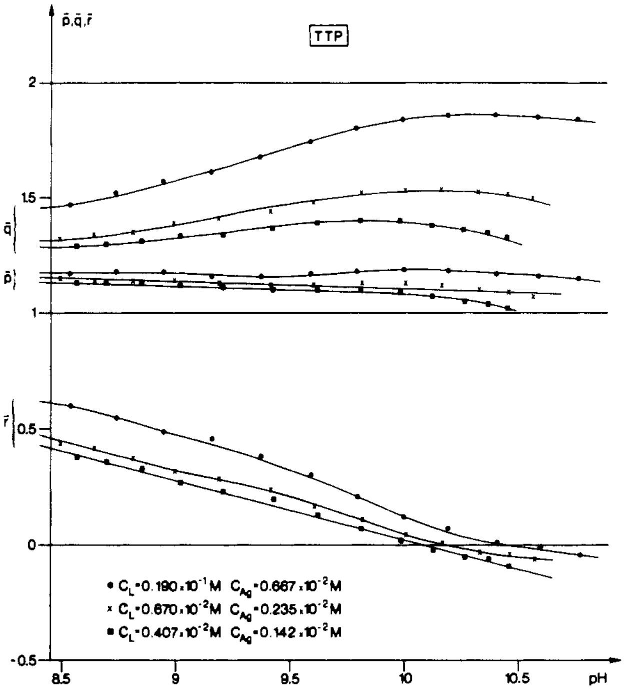

Figure 6. $\bar{p}$, $\bar{q}$, and $\bar{r}$ vs. pH for three different, but constant, C_L and C_{Ag} values, according to the "dilution method", for TTP and Ag^+.

and the corresponding protonated species must be taken into account. Also some hydroxo complexes are to be considered, like AgL(OH).

All expermental points are treated with the computer program MINIQUAD.[14] In this program one searches for the best model, i.e. the stoichiometric composition and stability constants, that gives the best fit with the experimental data. The goodness of fit is determined by the U function. Equation 12

$$U = \sum_i \sum_k (C_{i,k}^{\text{exptl}} - C_{i,k}^{\text{calcd}})^2 \qquad (12)$$

gives the definition of this function. $C_{i,k}^{\text{exptl}}$ is the total concentration of the metal ion (i = 1), the ligand (i = 2), and the hydrogen ion (i = 3) respectively. $C_{i,k}^{\text{calcd}}$ values are calculated from eq 4–6 with use of the proposed model. k indicates the number of the experimental point.

In the starting model the following complexes are considered: AgL, AgLH, AgL_2, and AgL(OH), i.e. the most probable mononuclear complexes. New complexes are added successively. When β_{pqr} becomes negative, the complex $Ag_pL_qH_r$ is eliminated from the model. Also when the standard deviation of β_{pqr}, expressed in log units, exceeds 0.05, the corresponding complex is rejected. Moreover, if the addition of a new complex does not result in a significant lowering (at least 10%) of the U value, the added complex is also rejected. According to the method used and preceding remarks taken into account, the best model is calculated with the computer program MINIQUAD. It is found that all three

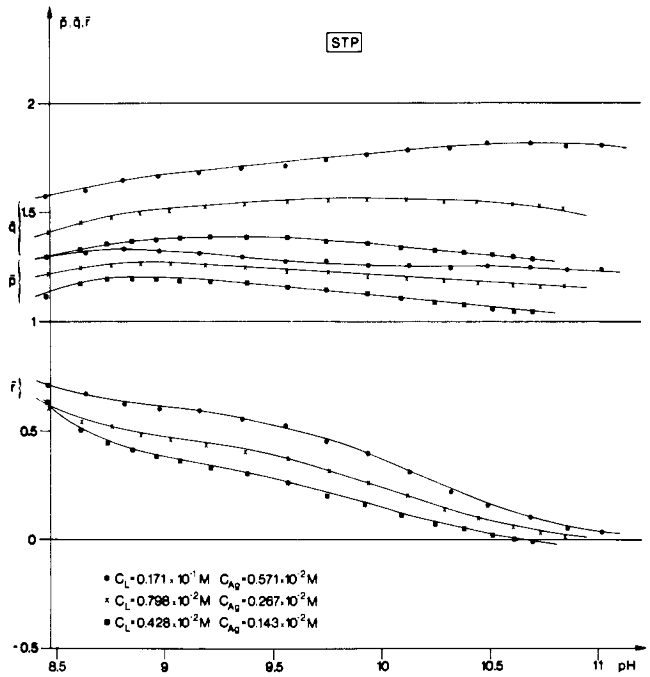

Figure 7. $\bar{p}$, $\bar{q}$, and $\bar{r}$ vs. pH for three different, but constant, C_L and C_{Ag} values, according to the "dilution method", for STP and Ag^+.

methods give the same solution with the same log β_{pqr} values. For each ligand the final model and final values of log β_{pqr}, which are summarized in Table I, are calculated by using all corresponding experimental data. The number in parentheses indicates the standard deviation. In this way, more than 1000 titration points, for each system, are fit over a quite wide concentration field. So it guarantees that the proposed complexes are the dominating ones and that each set reflects the best experimental data.

According to these calculations, for each ligand the following complexes are found: AgL^+, $AgLH^{2+}$, AgL_2^+, $Ag_2L_2^{2+}$, $Ag_3L_2^{3+}$, and AgL(OH). Also a number of protonated complexes derived from AgL_2^+ are detected. The complex $Ag_2L_2H_2^{4+}$ seems to be present in the STP system but has a high standard deviation. For the same reason the existence of $Ag_2L_2^{2+}$ for TTT and AgL_2H for STS is also very peculiar.

For further discussions the equilibria with corresponding equilibrium constants given by eq 13–22 are taken into account.

$$AgL^+ + L \rightleftharpoons AgL_2^+ \qquad K_2 = \beta_{120}/\beta_{110} \qquad (13)$$

$$Ag^+ + LH^+ \rightleftharpoons AgLH^{2+} \qquad K_{111} = \beta_{111}/\beta_{011} \qquad (14)$$

$$AgL^+ + H^+ \rightleftharpoons AgLH^{2+} \qquad K_{111}' = \beta_{111}/\beta_{110} \qquad (15)$$

$$Ag^+ + LH^+ + L \rightleftharpoons AgL_2H^{2+} \qquad K_{121} = \beta_{121}/\beta_{011} \qquad (16)$$

$$AgL_2^+ + H^+ \rightleftharpoons AgL_2H^{2+} \qquad K_{121}' = \beta_{121}/\beta_{120} \qquad (17)$$

$$Ag^+ + 2LH^+ \rightleftharpoons AgL_2H_2^{3+} \qquad K_{122} = \beta_{122}/\beta_{011}^2 \qquad (18)$$

$$AgL_2H^{2+} + H^+ \rightleftharpoons AgL_2H_2^{3+} \qquad K_{122}' = \beta_{122}/\beta_{121} \qquad (19)$$

$$AgL_2^+ + Ag^+ \rightleftharpoons Ag_2L_2^{2+} \qquad K_{22} = \beta_{220}/\beta_{120} \qquad (20)$$

$$2AgL^+ \rightleftharpoons Ag_2L_2^{2+} \qquad K_d = \beta_{220}/\beta_{110}^2 \qquad (21)$$

$$Ag_2L_2^{2+} + Ag^+ \rightleftharpoons Ag_3L_2^{3+} \qquad K_{32} = \beta_{320}/\beta_{220} \qquad (22)$$

The log K and log K' values can be calculated by using the log β_{pqr} values of Table I and log β_{01r}, the formation constants[15] of the three protonated forms of L. They are given in Table II.

Table I. log β_{pqr} Values of the Ag^+ Complexes Formed according to Reaction 1, Calculated by Using the Minimalization Program MINIQUAD[a]

complex	ligand STP	STS	TTP	TTT
AgLH	13.68 (1)	13.52 (0)	13.00 (0)	12.10 (1)
AgL	5.35 (1)	5.18 (0)	5.11 (0)	4.67 (0)
AgL_2H_2	27.13 (1)		25.63 (2)	24.09 (3)
AgL_2H	17.74 (1)	16.95 (5)	16.76 (3)	
AgL_2	7.83 (1)	7.38 (1)	7.64 (1)	6.50 (1)
$Ag_2L_2H_2$	28.97 (5)			
Ag_2L_2H				
Ag_2L_2	13.75 (0)	12.40 (1)	12.30 (1)	9.90 (5)
Ag_3L_2	15.33 (1)	14.29 (1)	14.29 (1)	12.10 (3)
AgL(OH)	−6.35 (3)	−6.67 (3)	−6.19 (2)	−6.59 (1)

[a] For AgL(OH) the following equilibrium must be considered: $Ag^+ + L + H_2O \rightleftharpoons AgL(OH) + H^+$.

Table II. Stability Constants Corresponding to Reactions 13–22

constant	ligand STP	STS	TTP	TTT	complex
log K_2	2.48	2.20	2.53	1.83	AgL_2 (13)
log K_{111}	3.44	3.16	3.13	2.55	AgLH (14)
log K_{111}'	8.33	8.34	7.89	7.43	AgLH (15)
log K_{121}	7.50	6.60	6.89		AgL_2H (16)
log K_{121}'	9.91	9.57	9.12		AgL_2H (17)
log K_{122}	6.65		5.89	4.99	AgL_2H_2 (18)
log K_{122}'	9.39		8.87		AgL_2H_2 (19)
log K_{22}	5.92	5.02	4.66	3.40	Ag_2L_2 (20)
log K_d	3.05	2.04	2.08	0.56	Ag_2L_2 (21)
log K_{32}	1.58	1.89	1.99	2.20	Ag_3L_2 (22)

Although completely comparable data are not available, it can safely be assumed that the log β_{120} values for AgL_2 do not differ very much from the log β_{12} values of the corresponding monodentate aliphatic amines. Values of 7 for log β_{12} are not unusual especially with ligands with a long aliphatic chain.[1] It seems that AgL_2 has a chain structure corresponding with the characteristic linear structure of AgL_2 in which the ligand is a monoamine. Another argument for this statement is the absence of complexes with more than two ligand molecules per Ag^+.

On the other hand, the log β_{110} values differ significantly from the log β_{11} values of the Ag(I) complexes with monoamines. The difference varies between 1.5 and 2 log K units. This is also demonstrated by the fact that $\beta_{110} >> K_2$. This is not in agreement with the property $K_1 < K_2$ shown by most of the Ag(I) complexes with monoamines.[1] The unusually high stability of AgL can be explained by chelate formation. Either five- or eight-membered rings can be considered. But the eight-membered ring is more probable if the tendency to form linear structures is taken into account. When a second ligand is bound, the chelate structure is broken, explaining the unusual low values for log K_2.

The log β_{111} values are rather high, but the difference in the stability with corresponding Ag(I) monoamine complexes is not so striking as in the case of AgL complexes. The stability of the AgLH complexes can equally well be explained by chelate structure or by a structure in which the Ag^+ ion is bound to one and the H^+ is bound to the other end group of the ligand. The log K_{111}' values, as is shown in Table II, indicate that the latter (chain structure) takes place but do not exclude the former (ring structure).

As can be seen from log K_{121} values and corresponding log β_{120} values, the presence of an H^+ ion lowers the stability of the formed complex. However, besides the presence of an additional positive charge the reorganization of the molecule must be considered. It is difficult to make conclusions here.

In all cases AgL(OH) is accepted. The formation of these hydroxo complexes has been reported by Ohtaki et al.[5,7] for Ag^+ complexes with diamines.