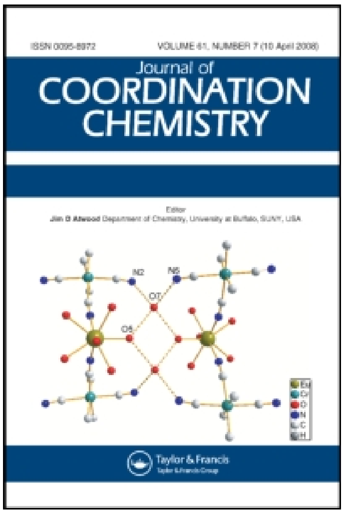

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SILVER(I) COMPLEX FORMATION WITH 1,4-DIAMINOBUTANE AND 1,5-DIAMINOPENTANE: A POTENTIOMETRIC STUDY IN 1.0 MKN0_3

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SILVER(I) COMPLEX FORMATION WITH 1,4-DIAMINOBUTANE AND 1,5-DIAMINOPENTANE: A POTENTIOMETRIC STUDY IN 1.0 M KNO_3

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By means of potentiometric pH measurements, the acidity constants of 1,4-diaminobutane and 1,5-diaminopentane have been determined in 1.0 M KNO_3 at 25.0°C. Combined pH/pAg data were used at the same temperature in aqueous 1.0 M KNO_3 to study the complexation of Ag(I) with the diamines. Protonated and non-protonated mononuclear and polynuclear complexes were detected. No evidence was found for the existence of hydroxo complexes. The resulting overall stability constants have been compared with previously determined stability constants for Ag(I)–ethylenediamine and Ag(I)–1,3-propylenediamine complexes. Some relationships concerning the length of the CH_2 backbone have been identified.

Keywords: Aliphatic diamines; silver; stability constants

INTRODUCTION

To the best of our knowledge, the complexation of Ag(I) with longer aliphatic chain diamines, $H_2N{-}(CH_2)_n{-}NH_2$, has hardly been investigated. Only a few indicative values of formation constants for these Ag(I) complexes in aqueous solution are available in the literature.[1–6] Recently, however, there has been growing interest in the complexation of biogenic amines such as 1,4-diaminobutane, which occurs in the cells of living organisms and participates in the genetic information transfer.[7]

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It has also been reported that, in chemotherapy, these longer chain diamines play a crucial role as ligands in dinuclear platinum anticancer complexes, showing a different spectrum of antitumor activity than cisplatin.[8] The complexation of Ag(I) with 1,4-diaminobutane (BN) and 1,5-diaminopentane (PN) has been studied in aqueous 1.0 M KNO_3. In addition, the acidity constants of both diamines were determined in same medium. In Table I the respective K_A values of BN and PN found in the literature are summarized. The following equilibria are considered:

$$LH_2^{2+} \rightleftharpoons LH^+ + H^+ \quad K_{A_1} = [H^+][LH^+]/[LH_2^{2+}] \tag{1}$$

$$LH^+ \rightleftharpoons L + H^+ \quad K_{A_2} = [H^+][L]/[LH^+] \tag{2}$$

L being the corresponding diamine, BN or PN.

EXPERIMENTAL

Reagents

$AgNO_3$ (Acros p.a.) and KNO_3 (Merck p.a.) were used without further purification. KOH and HNO_3 solutions were prepared from Titrisol (Merck p.a.) ampoules. In preparing stock solutions of KOH every effort was made to exclude CO_2. Therefore these solutions are prepared under N_2 with freshly boiled deionized, bidistilled water and kept in a polyethylene bottle fitted with a soda lime tube. Only KOH solutions with a carbonate content of less than 0.5% were used, within two weeks of titration. The ionic strength of all solutions was kept constant at 1M NO_3^- with KNO_3 (Merck p.a.).

The diamines 1,4-diaminobutane (Fluka > 99%) and 1,5-diaminopentane (Fluka > 97%) were received in the amine form. They were converted to their corresponding dinitrate salts by adding 2 equivalents of HNO_3 to a dilute solution at 0°C. The resulting dinitrate salts were purified by repeated crystallization from ethanol and dry diethylether. Drying over P_4O_{10} in a vacuum desiccator of the very hygroscopic products yielded colourless white crystals in the case of BN. By contrast, in the case of PN yellow-brown crystals were obtained after repeated crystallization, treatment with activated charcoal (Merck p.a.) and a long drying period.[10]

Automated Apparatus

The pH measurements were carried out using a Radiometer pHM 84 (resolution 0.1 mV) with a glass (Ingold pH0-14 HA265-S7/120) and a reference

TABLE 1 Literature values for the acidity constants (in log units) of 1,4-diaminobutane (BN) and 1,5-diaminopentane (PN) with respect to (1) and (2)

	Ref. [1]	*Ref.* [2]	*Ref.* [3]	*Ref.* [4]	*Ref.* [5]	*Ref.* [9]	*Ref.* [10]	*Ref.* [11]
BN								
Temperature (°C)	25	25	25	20	20	25	25	25
Ionic strength	1M NO_3^-	3 M $LiClO_4$	1 M	?	0.1M NO_3^-	?	0.1M NO_3^-	0.5 M NO_3^-
$\log K_{A_1}$	—	10.39	9.91 ± 0.03 9.44 ± 0.05^a 9.69 ± 0.06^b	9.35 ± 0.01	9.61 ± 0.01	9.20 ± 0.02	9.842	9.634 ± 0.003
$\log K_{A_2}$	11.08 ± 3	11.05	11.11 ± 0.04 10.72 ± 0.07^a 10.87 ± 0.07^b	10.80 ± 0.06	10.82 ± 0.02	10.65 ± 0.02	11.063	10.804 ± 0.002
PN								
Temperature (°C)	25				20		25	25
Ionic strength	0.1M NO_3^-				0.1M NO_3^-		0.1M NO_3^-	0.5M NO_3^-
$\log K_{A_1}$	9.85 10.15^b				10.02 ± 0.02		10.195	10.050 ± 0.008
$\log K_{A_2}$	10.78 10.92^b				10.96 ± 0.02		11.200	10.916 ± 0.004

[a] 0.1 M; [b] 0.5 M.

(Ingold Argental 363-S7) electrode couple. The latter was placed in a salt bridge, Schott-Geräte B512 with ceramic plug, filled with 1.5 M KNO_3.

Combined pH/pAg measurements were performed with a Radiometer pHM 84 (pH) and a Knick pH meter 764 multicalimatic (pAg) (resolution 0.1 mV). A glass (Ingold pH0-14 HA265-S7/120) in combination with a reference (Ingold Argental 363-S7) electrode and a reference electrode (Ingold Argental 363-S7) combined with an Ag/Ag_2S (Orion 94-16) electrode were used. The design of the fully automated experimental set-up for both pH and combined pH/pAg measurements has been described elsewhere.[12-15]

Titrations

Acid–Base Equilibria

By titrating $25\,cm^3$ of ($0.005\,M\ HNO_3 + 0.995\,M\ KNO_3$) with ($0.1\,M\ KOH + 1.0\,M\ KNO_3$) using the glass/Argental electrode couple the glass electrode parameters could be determined. The relationship between the measured potential and these parameters in acidic and basic medium is expressed by the Nernst equation,

$$E = E^0 + 59.159 \log[H^+] + E_j, \tag{3}$$

where $E_j = j_H[H^+] + j_{OH}[OH^-]$. It has been found[12] that j_{OH} is negligible until pH = 12, $j_H = -(40 \pm 10)\,mV\,dm^3\,mol^{-1}$ and $E_j = 0.2\,mV$ at pH = 2.30.[12,15]

(E, V) data couples were used in a Gran plot.[16] By means of the program EOTIT[15] the operational pKw, $\%CO_2$ contamination and E^0 were computed. The resulting pKw = 13.775 ± 0.004, $\%CO_2$ contamination = 0.2 and $E^0 = (420.1 \pm 0.2)\,mV$ values are in good agreement with literature values.[12,15]

In order to determine the acidity constants of BN and PN, starting solutions of ($0.01\,M\ LH_2(NO_3)_2 + 0.98\,M\ KNO_3$) were titrated against ($0.1\,M\ KOH + 1.0\,M\ KNO_3$) to pH = 11.500. Before and after each titration, E^0 of the glass electrode was checked in $0.005\,M\ HNO_3$. Each titration was performed at least in duplicate. The number of titration points varied between 70 and 100.

Complexation Equilibria

The characteristics of the glass electrode were checked again in preliminary titrations. The Ag/Ag_2S electrode was calibrated using the 'batch' method[15]

TABLE II Final composition of the starting solutions used in the standard ratio technique for complexometric Ag(I)–diamine titrations

Ratio (C_{Ag}/C_L)	*Composition of starting solution* (mL)
1/8	20 mL LS + 2.5 mL MS + 17.5 mL 1.0 M KNO_3
1/4	20 mL LS + 5 mL MS + 15 mL 1.0 M KNO_3
1/2	20 mL LS + 10 mL MS + 10 mL 1.0 M KNO_3
1/1	20 mL LS + 20 mL MS
2/1	20 mL LS + 40 mL MS

and showed Nernstian behaviour with $E^0_{Ag/Ag_2S} = (585.1 \pm 0.1)$mV. No corrections were made for diffusion effects as long as pH > 2.30.[17]

Using the standard ratio technique[15] several different C_{Ag}/C_L ratios varying from 2/1 to 1/8 were examined, C_{Ag} and C_L being the total concentrations of silver and ligand. Starting solutions to be titrated were prepared from the following stock solutions.

$$0.01\,\text{M}\ LH_2(NO_3)_2 + 0.98\,\text{M}\ KNO_3 = \text{Ligand Solution (LS)},$$
$$0.01\,\text{M}\ AgNO_3 + 0.99\,\text{M}\ KNO_3 = \text{Metal Solution (MS)}.$$

In Table II the final compositions of the starting solutions according to each ratio is illustrated.

Each starting solution was titrated at least twice against (0.1 M KOH + 1.0 M KNO_3) until both protons were liberated from the ligand or until precipitation of Ag_2O was determined either by erratic electrode response or visually. Calibration of the glass electrode and the Ag/Ag_2S electrode was performed externally before and after each titration.

RESULTS AND DISCUSSION

Acidity Constants for 1,4-Diaminobutane and 1,5-Diaminopentane

Resulting (E, V) data from the pK_A titrations were analysed using the weighted option of the program SUPERQUAD ($\sigma_{E\text{glass}} = 0.2$ mV and $\sigma_V = 0.002$ mL).[18–21] The pKw, mass balances and the electrode parameters were kept constant during refinement. All computations were performed on a DEC Alpha 3000/800X/AXP computer. SUPERQUAD minimizes the error square sum of a function $U = \sum_{i=1}^{n} W_i(E_i^{\text{exp}} - E_i^{\text{calc}})^2$ using the Nernst equation. W_i is the weighted matrix, which is the inverse of the variance covariance matrix of the observations.

TABLE III Summary of the acidity constants (in log units) of ethylenediamine, 1,3-propylenediamine, 1,4-diaminobutane and 1,5-diaminopentane using the weighted option in SUPERQUAD. Standard deviations and S values are indicated

	$\log K_{A_1}$	$\log K_{A_2}$	$\log K_{A_2}/K_{A_1}$ (ΔpK_A)	S
Ethylenediamine	7.490 ± 0.001	10.170 ± 0.001	2.680	1.40
1,3-Propylenediamine	9.091 ± 0.001	10.736 ± 0.001	1.645	0.20
1,4-Diaminobutane	9.787 ± 0.002	10.933 ± 0.002	1.146	1.42
1,5-Diaminopentane	10.262 ± 0.003	11.221 ± 0.004	0.959	1.65

Goodness-of-fit is judged by the overall fit statistic or sample deviation,

$$S = \left(\varepsilon^T W\varepsilon/(n-m)\right)^{1/2} = \left(U_{\min}/(n-m)\right)^{1/2}, \tag{4}$$

where ε is the vector of residuals in potential, n is the number of observations and m is the number of parameters to be refined. Ideally, the S value should be 1, but in general a value between 1 and 3 is acceptable.

The acidity constants obtained with SUPERQUAD, the standard deviations and the S values for BN and PN are given in Table III. K_{A_1} and K_{A_2} refer respectively to (1) and (2). For the sake of completeness, K_{A_1} and K_{A_2} values for ethylenediamine (EN) and 1,3-propylenediamine (TN) are also reported.[15]

It should be noted that the standard deviations of both K_{A_1} and K_{A_2} are somewhat higher in the case of PN, probably due to impurities in the dinitrate salt. Confirming the findings of other authors,[2,10,11] it is clear that values for pK_{A_1} increase as the number of methylene groups increases, but the increment becomes smaller. This tendency is even more pronounced for the pK_{A_2} values. With increasing n in $H_2N{-}(CH_2)_n{-}NH_2$ the distance between the two positive centres increases, resulting in a smaller repulsion and a smaller ΔpK_A value.

Ag(I)–Diamine Complexes with 1,4-Diaminobutane and 1,5-Diaminopentane

Generally, the reaction between a metal M, a ligand L and a proton H is expressed by the equation

$$pM + qL + rH \rightleftharpoons M_pL_qH_r \quad \beta_{pqr} = [M_pL_qH_r]/[M]^p[L]^q[H]^r, \tag{5}$$

β_{pqr} being the overall formation constant of the complex $M_pL_qH_r$, p and $q > 0$. For $r < 0$ hydroxo complexes and $r > 0$ protonated complexes are formed.

TABLE IV A list of the calculated formation for different Ag(I)–diamine systems

	EN	*TN*	*BN*	*PN*
K_{111}	2.46	3.01	3.28	3.33
K'_{122}	5.05	6.24	6.50	7.58
K_{120}	−17.62	−19.80		−21.69
K_{220}	8.36	8.61	7.95	7.47

For notational convenience, the following equilibria are defined.

$$Ag^+ + LH^+ \rightleftharpoons AgLH^{2+} \quad K_{111} = \beta_{111}/\beta_{011} \tag{6}$$

$$Ag^+ + 2LH^+ \rightleftharpoons AgL_2H_2^{3+} \quad K'_{122} = \beta_{122}/\beta_{011}^2 \tag{7}$$

$$AgL_2H_2^{3+} \rightleftharpoons AgL_2^+ + 2H^+ \quad K_{120} = \beta_{120}/\beta_{122} \tag{8}$$

$$AgL_2H_2^{3+} + Ag^+ + 2L \rightleftharpoons Ag_2L_2^{2+} + 2LH^+ \quad K_{220} = \beta_{220} \cdot \beta_{011}^2/\beta_{122} \tag{9}$$

$$2AgL^+ \rightleftharpoons Ag_2L_2^{2+} \quad K_D = \beta_{220}/\beta_{110}^2 \tag{10}$$

An overview of the calculated formation constants for Ag(I)–EN,[15] Ag(I)–TN,[15] Ag(I)–BN and Ag(I)–PN is presented in Table IV.

Combined pH/pAg data of 760 titration points were analysed (1500 data points in total) using the weighted option in SUPERQUAD ($\sigma_{E\text{glass}} = 0.2\,\text{mV}$; $\sigma_{E\text{Ag/Ag}_2\text{S}} = 0.1\,\text{mV}$ and $\sigma_V = 0.002\,\text{mL}$). The model selection criteria are defined as follows: A good overall fit (fit statistic S should not exceed 3), a low standard deviation, a significant % species presence (an arbitrary minimum value of 3%) and arbitrary (5%) of titration points were taken to be significant; pK_A values, pKw, mass balances and electrode characteristics were kept constant during refinement in SUPERQUAD.

A list of the computed overall formation constants of the best complexation models of Ag(I) with 1,4-diaminobutane and 1,5-diaminopentane is shown in Table V. Standard deviations, the maximum % species presence over the total complexation area of the individual species and the S value are indicated. To make further discussion clearer, overall formation constant values are also reported for Ag(I)–EN and Ag(I)–TN systems.[15]

A set of distribution curves of complexes of PN with Ag(I) ($C_{Ag}/C_L = 1/4$) is illustrated in Figures 1–3.

TABLE V A list of the overall formation constants (in log units), standard deviations and the maximum % species presence of EN, TN, BN and PN with Ag(I) using the weighted option in SUPERQUAD. Charges are omitted for simplicity

Species	*EN*	*Max. % presence*	*TN*	*Max. % presence*	*BN*	*Max. % presence*	*PN*	*Max. % presence*
AgL					5.45 ± 0.04	29	6.22 ± < 0.01	94
AgL_2	7.67 ± < 0.01	45	7.81 ± 1	16			8.33 ± 0.09	9
Ag_2L					7.24 ± 0.09	4		
Ag_2L_2	13.41 ± < 0.01	93	14.86 ± < 0.01	98	14.45 ± 0.02	35	15.05 ± 0.01	48
AgLH	12.63 ± < 0.01	24	13.75 ± < 0.01	20	14.20 ± 0.02	19	14.55 ± 0.04	14
AgL_2H	16.59 ± 5	4					20.08 ± 0.02	37
AgL_2H_2	25.39 ± < 0.01	16	27.72 ± < 0.01	20	28.36 ± 0.04	10	30.02 ± 0.02	22
Ag_2L_2H	20.20 ± 2	4					23.58 ± 0.05	4
S statistics	2.88		2.07		2.33		2.41	

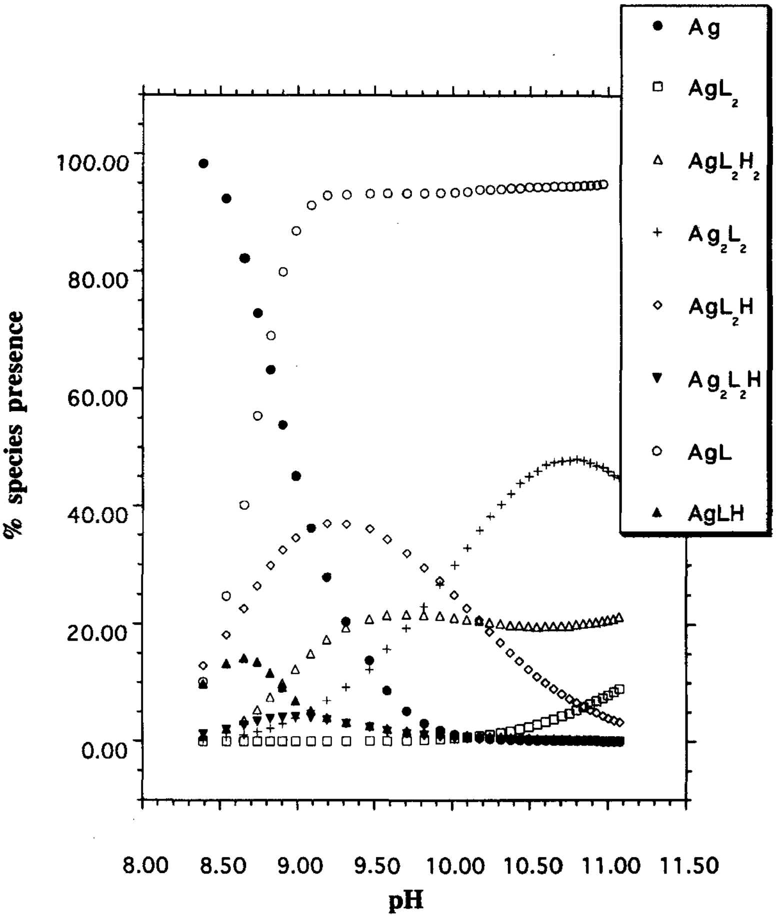

FIGURE 1 Species distribution of Ag(I)–1,5-diaminopentane complexes *vs* pH; C_{Ag} = 0.00125 M, C_{L} = 0.00500 M.

From the results shown in Table V and regarding the model selection criteria previously stated one can generally conclude that the most reliable formation constant values, comparing BN and PN silver–diamine systems, are those for the Ag_2L_2, the AgLH and the AgL_2H_2 complexes. To examine the effect of the length of the CH_2 backbone we compare in detail the formation constants from Table V (BN and PN) with previously reported values for silver–ethylenediamine and silver–1,3-propylenediamine systems.[13–15,22,23]

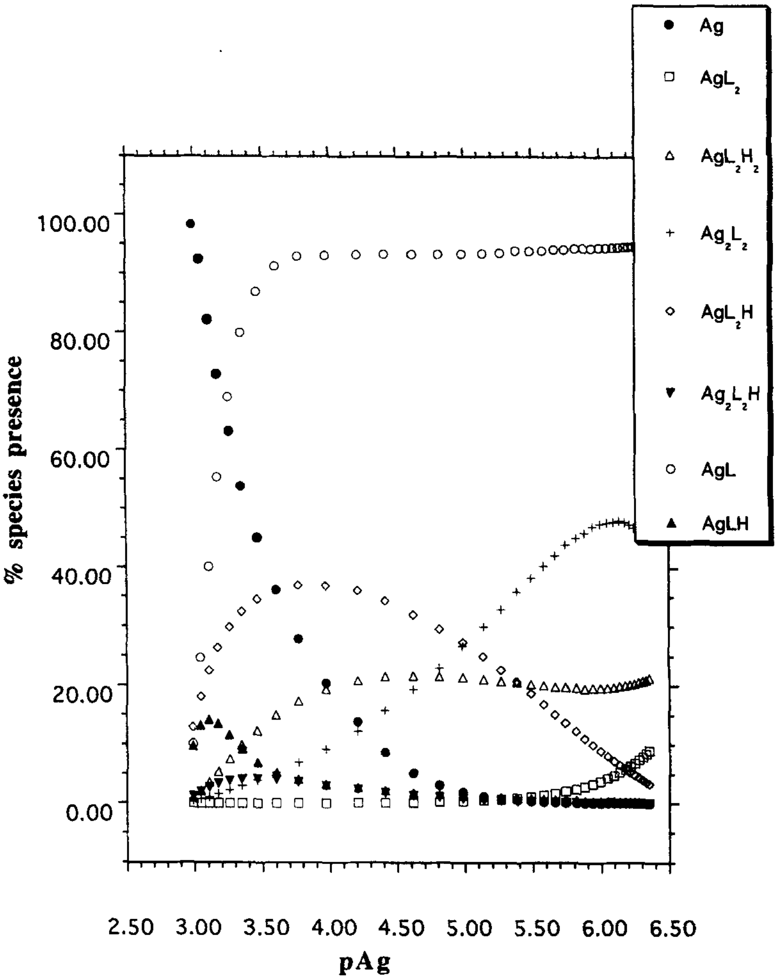

FIGURE 2 Species distribution of Ag(I)–1,5-diaminopentane complexes *vs* pAg; $C_{Ag} = 0.00125\,M$, $C_L = 0.00500\,M$.

The Non-Protonated Mononuclear and Polynuclear Complexes: AgL, AgL_2, Ag_2L_2

It is seen from Table VI that the Ag_2L_2 complex becomes more stable as the length of the CH_2 backbone increases. If one assumes that Ag_2L_2 has a cyclic structure, a 16-membered ring (in the case of PN) resembles more closely the linear N–Ag–N configuration than a 10 (EN)-, 12 (TN)- or 14(BN)-membered ring.[22] This explains the more stable Ag_2L_2 complex in the case of PN. In contrast to EN and TN, the AgL complex is detected in the case of BN

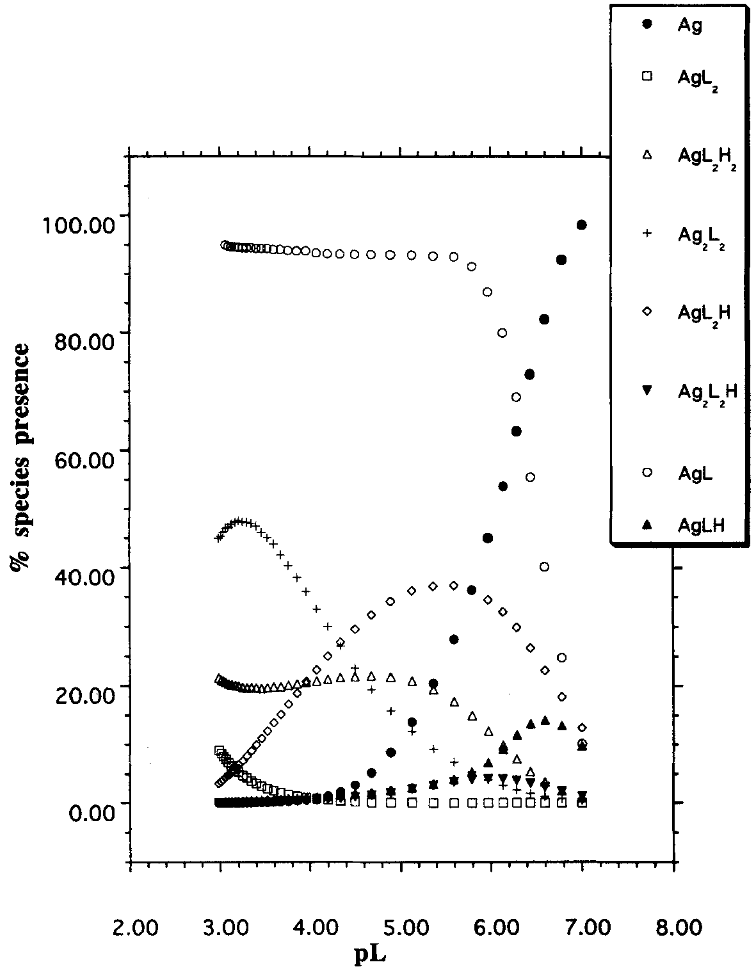

FIGURE 3 Species distribution of Ag(I)–1,5-diaminopentane complexes *vs* pL; $C_{Ag}=0.00125\,M$, $C_L=0.00500\,M$.

TABLE VI A comparison of the overall stability constant β_{220} (in log units) with increasing length of the CH_2 backbone of the ligand L

Species	*EN*	*TN*	*BN*	*PN*
Ag_2L_2	13.41 ± < 0.01	14.86 ± < 0.01	14.45 ± 0.02	15.05 ± 0.01

and PN. The respective stability constants 5.45 ± 0.04 and 6.22 ± < 0.01 (Table V) are relatively high compared with the formation constants of Ag(I) complexes with monoamines. On the other hand, the calculated values for the dimerization constant, K_D, respectively $\log K_{D_{(BN)}} = 3.54$,

$\log K_{D_{(PN)}} = 2.60$, provide some information about the simultaneous existence of AgL and Ag_2L_2, showing the predominance of the dimeric Ag_2L_2 species.

The AgL_2 complex which is detected with EN and TN is not formed in the case of BN and with PN the overall stability constant value is unreliable because of its high standard deviation. This can be understood in terms of two possible explanations. A first explanation refers to (9) with its formation constant $K_{220} = \beta_{220} \cdot \beta_{011}^2 / \beta_{122}$. It is possible that increasing stability of both the Ag_2L_2 complex and the acid LH prevents the formation of AgL_2 from AgL_2H_2. In that case however, K_{220} would increase as a function of chain length; this is not supported by the data (see Table IV). A second explanation refers to (8) and its constant $K_{120} = \beta_{120}/\beta_{122}$. From Table IV it is seen that with increasing *n* the acid AgL_2H_2 becomes very weak at the pH value of AgL_2 formation. This particular pH value is possibly situated in the precipitation domain and as a result AgL_2 cannot be detected. It is clear that the second explanation is the better.

The Mononuclear Protonated Complexes: AgLH and AgL_2H_2

It was stated in a previous article of this series[14] that these species can be considered as aliphatic monoamine complexes of the type AgL′ and AgL'_2, LH reacting as a monodentate ligand L′. The calculated values K_{111} and K'_{122} (Table IV) yield further evidence that the increasing chain length of the diamine results in an increased stabilization of the species AgLH and AgL_2H_2 through decreasing $Ag^+ \leftrightarrow LH^+$ repulsion.[24]

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