The Silver(I) Complexes of Ethylenediamine in Solution

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Dedicated to Jannik Bjerrum on the occasion of his 70th birthday

The silver(I) complexes of ethylenediamine “en” were investigated in solution. The stability constants of $\text{Ag}(\text{Hen})^{2+}$, $\text{Ag}(\text{en})^+$, $(\text{Ag}_2(\text{en}))^{2+}$ and $\text{Ag}_2(\text{en})_2^{2+}$ have been obtained from potentiometric titrations of H_2en^{2+} with solutions of KOH in the presence of Ag(I). At high concentrations of equimolar mixtures of Ag(I) and “en” the binuclear species $\text{Ag}_2(\text{en})_2^{2+}$ becomes the dominant complex. This is unambiguously demonstrated by salt cryoscopy, three-phase vapour tensiometry and solubility measurements. The heat of formation of the complexes $\text{Ag}(\text{en})^+$, $\text{Ag}(\text{en})_2^{2+}$ and $\text{Ag}_2(\text{en})_2^{2+}$ were also determined.

Ethylenediamine is the first chelating ligand ever applied and was often used after its introduction in Copenhagen in 1889¹ because of the greater stability of its complexes in comparison to the corresponding ammonia adducts. Half a century later – again in Copenhagen² – the impressive stability increase to be achieved with “en” was demonstrated by means of ionic equilibria studies, mainly for the $3d^9$ -transition metal(II) cations. These form the series of complexes $[\text{M}(\text{en})_n]^{2+}$, and only half as many “en” are bonded as there are ammonia molecules coordinated in the corresponding NH_3 -metal system. The stability constants K_1 , K_2 , K_3 are considerably larger than the quantities β_2 , β_4/β_2 and β_6/β_4 of the ammonia complexes.

The silver cation behaves differently, however. With electrodes of metallic silver it was found that although the maximum coordination number of Ag^+ is $N=2$, in the ammonia system this cation also adds two molecules of bidentate “en” and

furthermore that the stability constants β_2 of $[\text{Ag}(\text{NH}_3)_2]^+$ and $[\text{Ag}(\text{en})_2]^+$ are almost the same.³ By applying Bjerrum's pH-method² – whereby the cation H_2en^{2+} has to be deprotonated in the presence of Ag^+ – it is found that the neutralisation function $[\text{H}](\bar{p})$ (see eqn. (1)) cannot be interpreted with the formation of only $\text{Ag}(\text{en})^+$ and $\text{Ag}(\text{en})_2^+$. These results are not surprising in view of the preferred linear arrangement N–Ag–N in the diammine-silver cation and the impossibility of spanning the bridge between the opposite atoms with a link of two C-atoms only. A linear arrangement N–Ag–N could only be achieved by adding two “en” molecules as unidentate ligands which explains the stability found for $\text{Ag}(\text{en})_2^+$. However, when only one N of “en” coordinates, the other amino group must be able to add a proton as well as Ag^+ again which leads to the adducts $\text{Ag}(\text{en})^+$, $\text{Ag}(\text{Hen})^{2+}$ and $\text{Ag}_2(\text{en})^{2+}$ which were identified in the presence of comparatively high concentrations of free Ag^+ , implying a low concentration $[\text{en}]$ of uncomplexed ligand.⁴ For the formation of the 1:2-complex on the other hand, $[\text{en}]$ must be large, so that the 2:1- and the 1:2-complexes cannot be present simultaneously.

Contrary to expectation, however, it was found⁴ that the equilibrated mixtures also contain $\text{Ag}_2(\text{en})_2^{2+}$. A certain support for the formation of this 2:2-complex came recently from a new investigation of the system $\text{Ag}^+ - \text{en}$;⁵ Sillen's method was applied and it was found that the reproduction of the experimental data (pH, pAg) by back-computing was improved when the presence of $\text{Ag}_2(\text{en})_2^{2+}$ was postulated. We want to point out that the results obtained 26 years ago were much less vague; the

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dimer $(\text{Ag(en)})_2^{2+}$ is strikingly exhibited when H_2en^{2+} is deprotonated in the presence of silver and the concentration of uncomplexed Ag^+ is thereby kept constant.⁶ The formation of the dinuclear complex can be demonstrated unambiguously also by Salt Cryoscopy and Three Phase Vapour Tensiometry.⁷ Also the solubility of the solid salt $\{\text{Ag(en)ClO}_4\}$ in solutions of constant ionic strength containing NaNO_3 and NaClO_4 can be accounted for quantitatively when it is assumed that the salt dissolves in forming the dinuclear cations mainly, although the units "en" are connected to endless chains by Ag^+ within the solid.⁸ Finally we have determined also the heat production in the formation of Ag(en)^+ , $\text{Ag}_2(\text{en})_2^{2+}$ and Ag(en)_2^+ . These thermodynamic data suggest that the 1:1-complex is a hydrated chelate with some strain within the 5-membered chelate ring, whereas both metal cations are linearly bonded to two nitrogens each in the 2:2-species, very much as in $\text{Ag}(\text{NH}_3)_2^+$. The atoms of the 2:2-complex present in solution therefore must form a 10-membered ring system which makes it unlikely that higher polymers $\text{Ag}_n(\text{en})_n^{n+}$ with $n > 2$ will be present as well in the equilibrium mixtures.

RESULTS AND DISCUSSION

Equilibria. The protolytic equilibria have been studied by titrating the diprotonated ligand H_2en^{2+} with alkali hydroxide, keeping the ionic strength constant with alkali nitrate. The procedure was then repeated in the presence of silver and the concentration $[\text{Ag}]$ kept constant either by replacing an appreciable amount of the inert electrolyte by AgNO_3 ($[\text{Ag}] \gg [\text{en}]_{\text{tot}}$) or by adding an excess of

the sparingly soluble $\{\text{AgBrO}_3\}$, which remains mainly in suspension, and simultaneously replacing a part of the anion NO_3^- by BrO_3^- , which fixes $[\text{Ag}]$ at lower values. When $[\text{Ag}]$ remains constant, the protonation of the ligand can be described with function (1) (for the definition of $\bar{p}'$, κ'_n , see eqns. (7') and (9')) as long as only complexes containing a

$$\sum_{n=0}^{n=2} (\bar{p}' - n) \kappa'_n [\text{H}]^n = 0, (\kappa'_0 = 1) \quad (1)$$

single molecule of "en" are involved. Deviations from this function are caused by species containing more than a single "en" and the deviations observed can be accounted for quantitatively by postulating the formation of the dimer $\text{Ag}_2(\text{en})_2^{2+}$. The apparent protonation constants κ'_1 and κ'_2 furnish the stability constants of the species Ag(en)^+ , $\text{Ag}_2(\text{en})_2^{2+}$ and Ag(Hen)^{2+} . The stability of Ag(en)_2^+ is known⁹ whereas the stability of Ag(Hen)_2^{3+} can be estimated assuming that the ratio K_1/K_2 of the stability constants of Ag(Hen)^{2+} and Ag(Hen)_2^{3+} is the same under the conditions used in our laboratory ($I = 1.0 \text{ M}$, KNO_3 , 25°C) and the medium of Ref. 5 ($I = 3 \text{ M}$, LiClO_4 , 25°C). All of these data are collected in Table 1. The data of the first column are from Ref. 4 and those of the second are the results of a new study applying essentially the same procedure at $I = 1 \text{ M}$ and 25°C . In the last column the results of Ref. 5 are reported.

Fig. 1 illustrates the formation of the various complexes during the alkalimetric titration of H_2en^{2+} at the silver concentrations $[\text{Ag}] = 0.1$ and 0.0013 M . When $[\text{Ag}]$ is large, the removal of the first proton of H_2en^{2+} furnishes mainly AgHen^{2+} , which accumulates to a concentration of about

Table 1. Stability constants of proton and silver complexes of ethylenediamine "en". (Errors are given as confidence limits L_{95} for the 95% confidence level).

Reaction	Constant	20 °C $I = 0.1 \text{ M}$ (NaNO_3) ⁴	25 °C $I = 1 \text{ M}$ (KNO_3)	25 °C $I = 3 \text{ M}$ (LiClO_4) ⁵
$\text{H}^+ + \text{en} = \text{Hen}^+$	$\text{p}K_1$	10.03	10.24 ± 0.02	10.65
$\text{H}^+ + \text{Hen} = \text{H}_2\text{en}^{2+}$	$\text{p}K_2$	7.22	7.52 ± 0.02	8.04
$\text{Ag}^+ + \text{en} = \text{Ag(en)}^+$	$\log K_{\text{Ag(en)}}$	4.7	5.06 ± 0.06	6.13
$\text{Ag(en)}^+ + \text{en} = \text{Ag(en)}_2^+$	$\log K_{\text{Ag(en)}_2}$	3.0	(2.6)	—
$\text{Ag}^+ + \text{Hen}^+ = \text{Ag(Hen)}^{2+}$	$\log K_{\text{Ag(Hen)}}$	2.35	2.42 ± 0.17	2.91
$\text{Ag(Hen)}^{2+} + \text{Hen}^+ = \text{Ag(Hen)}_2^{3+}$	$\log K_{\text{Ag(Hen)}_2}$	—	(2.7)	3.16
$\text{Ag}^+ + \text{Ag(en)}^+ = \text{Ag}_2(\text{en})_2^{2+}$	$\log K_{\text{Ag}_2(\text{en})}$	1.76	1.20 ± 0.45	1.54
$2\text{Ag}^+ + 2\text{en} = \text{Ag}_2(\text{en})_2^{2+}$	$\log K_{\text{Ag}_2\text{en}_2}$	13.23	13.17 ± 0.25	14.53
$\text{Ag(en)}^+ + \text{Ag(en)}^+ = \text{Ag}_2(\text{en})_2^{2+}$	$\log K_d$	3.83	3.05 ± 0.29	2.27

Fig. 1. Fraction [%] of "en" present in a given species and the degree $\bar{p}'$ of protonation of "en" as a function of pH at two different and constant concentrations of the free silver ion Ag(I) .

80 % of the total amount of ethylenediamine present at $\bar{p}'=1$ (pH=6). This species is further deprotonated between pH 6 and 9 giving rise to the production of $\text{Ag}_2(\text{en})^{2+}$ (47 %), $\text{Ag}(\text{en})^+$ (30 %) and $\text{Ag}_2(\text{en})_2^{2+}$ (containing 22 % of $[\text{en}]_{\text{tot}}$). The situation is very different at the lower silver concentration. The main product after removal of one proton of H_2en^{2+} ($\bar{p}'=1$ at about pH 7.6) now is Hen^+ (36 %) accompanied by $\text{Ag}(\text{Hen})^{2+}$ (11 %). One quarter of the original H_2en^{2+} is still fully protonated and another quarter is fully deprotonated being present as $\text{Ag}(\text{en})^+$ (15 %), $\text{Ag}_2(\text{en})_2^{2+}$ (8 %). When the value $\bar{p}'=0$ is reached (pH=10), the solution contains practically only the dimer $\text{Ag}_2(\text{en})_2^{2+}$ (with 52 % of $[\text{en}]_{\text{tot}}$) and the monomer $\text{Ag}(\text{en})^+$ (46 %). The various mononuclear 1:2-species are of practically no importance; $\text{Ag}(\text{Hen})_2^{3+}$ being the most important of these complexes reaches 2.4 % at large concentrations of uncomplexed silver (pH=6) and reaches 3.3 %, its maximum concentration, in the presence of solid AgBrO_3 creating a constant and low $[\text{Ag}]$. The conditions therefore can be chosen such that the main products are $\text{Ag}(\text{Hen})^{2+}$ and $\text{Ag}_2(\text{en})^{2+}$, or $\text{Ag}(\text{en})^+$ and $\text{Ag}_2(\text{en})_2^{2+}$.

It is the special advantage of the method used that the concentration of $\text{Ag}_2(\text{en})_2^{2+}$ can be obtained as the ratio of two quantities read off directly. A rather

reliable value for the stability constant of the dimer is obtained. Although the formation of higher polymers $\text{Ag}_n(\text{en})_n^{n+}$ cannot be excluded completely, it can be stated that they are produced in very small quantities at the most.

From the high stability of $\text{Ag}(\text{en})^+$, in comparison with the stability of 1:1-complexes of unidentate monoamines ($\log K_1 \sim 3.4$), we conclude that $\text{Ag}(\text{en})^+$ must be a chelate with both basic nitrogens of "en" coordinated. However, $K_{\text{Ag}(\text{en})}$ is not as large by far as the stability constants of 1:2-complexes of monoamines ($\log \beta_2 \sim 7.3$) which probably is due to some strain within the chelate ring of $\text{Ag}(\text{en})^+$ and the release of that strain may be the driving force for the dimerisation. It is remarkable that $K_{\text{Ag}(\text{en})}$ increases considerably with increasing ionic strength whereas simultaneously K_d becomes smaller. It looks as if the strain within $\text{Ag}(\text{en})^+$ is lessened with increasing I reducing the tendency for dimerisation. The ratio $q = K_1/K_2$ in the sequence $\text{Ag}^+ \rightarrow \text{Ag}(\text{en})^+ \rightarrow \text{Ag}(\text{en})_2^+$ is very much larger ($q=300$) than for unidentate monoamine complexes ($q=0.3$) which is also explained with the assumption that $\text{Ag}(\text{en})^+$ is a chelate. The ratio q on the other hand is only slightly larger than usual in the sequence $\text{Ag}^+ \rightarrow \text{Ag}(\text{Hen})^{2+} \rightarrow \text{Ag}(\text{Hen})_2^{3+}$ ($q=0.5$), which is also reasonable.

Mean nuclearity. Although highly soluble, salts of

the 1:1-complex of silver and ethylenediamine can be obtained crystalline: $[\text{Ag}(\text{en})]_2\text{SO}_4 \cdot \text{H}_2\text{O}$; $[\text{Ag}(\text{en})]\text{ClO}_4$; $[\text{Ag}(\text{en})]\text{NO}_3 \cdot \text{H}_2\text{O}$. According to the data of Table 1, solutions of these salts should contain mainly the dinuclear cation $\text{Ag}_2(\text{en})_2^{2+}$ besides the appropriate anion, if they are not too dilute [the dissociation into mononuclear $\text{Ag}(\text{en})^+$ and the hydrolysis of the latter $\text{Ag}(\text{en})^+ + \text{H}_2\text{O} \rightarrow \text{Ag}^+ + \text{Hen}^+ + \text{OH}^-$] should amount to less than 3% at concentrations $[\text{Ag}]_{\text{tot}}$ above 0.1 M]. It must be possible therefore to demonstrate this cryoscopically.

The cryoscopic and the ebullioscopic methods applied to ionic compounds in a solvent consisting of uncharged molecules have two main disadvantages: 1. Not only the complex ion, the nuclearity of which is to be investigated, but also its counter ion (SO_4^{2-} , NO_3^- , ClO_4^- of the salts mentioned) contribute to ΔT (freezing point depression, elevation of boiling point). 2. The strong deviations from Raoult's law become negligible only at high dilution after ΔT has become so small that it can no longer be determined accurately. Unfortunately ΔT does not change linearly with the salt concentration m (mol salt per kg of solvent) which makes extrapolation difficult. In the case of complexes which are labile and of moderate stability only, such as $\text{Ag}_2(\text{en})_2^{2+}$, dilution furthermore would lead to dissociation, so that the measurements have to be carried out at concentrations which are not extremely small. In studying ionic equilibria, the difficulties arising from nonideality due to the interionic forces are overcome by adding an inert electrolyte which keeps the activity coefficients of the ionic equilibrium participants constant. Similarly it is advantageous to carry out cryoscopic and ebullioscopic measurements in the presence of an inert salt which already contains the counter ion of the complex salt to be investigated. The complex $[\text{Ag}(\text{en})]_2\text{SO}_4$ for instance may be dissolved in molten Glauber's salt (the decahydrate $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$), which actually is a suspension of the anhydrous sodium sulfate in its saturated solution. The transition:

is a fixed point according to the phase rule at constant pressure, taking place exactly at 32.384 °C under atmospheric conditions. In the presence of a foreign solute this transition point is lowered, but neither Na^+ nor SO_4^{2-} — being constituents of the

medium — are foreign solutes and are therefore cryoscopically active. The anion of the salt $[\text{Ag}(\text{en})]_2\text{SO}_4$ therefore does not contribute to the lowering of the transition point of Glauber's salt, which makes it easy to distinguish between mononuclear and polynuclear complex cations. The complex sulfate produces the same depression as K_2SO_4 if the complex cation in solution is mononuclear, but the depression is only half as great if dinuclear units $\text{Ag}_2(\text{en})_2^{2+}$ are present. This is exactly true only at infinite dilution, but the ratio $\Delta T/m$ changes only little with concentration m and the function is linear, so that extrapolation to $m=0$ does not create any difficulty.

The following values were found on extrapolation:¹⁰

$$\begin{aligned} (\Delta T/m)_{m \rightarrow 0} &= 6.1 \text{ }^\circ\text{C kg mol}^{-1} \text{ for } \text{K}_2\text{SO}_4 \\ &= 3.1 \text{ }^\circ\text{C kg mol}^{-1} \text{ for } [\text{Ag}(\text{en})]_2\text{SO}_4 \end{aligned}$$

These data prove that the solution of the silver complex in the melt of Glauber's salt contains the dinuclear species $[\text{Ag}_2(\text{en})_2]^{2+}$.

Whereas Glauber's salt has been used as a cryoscopic medium for 80 years,¹¹ although without recognizing its implications and usefulness, the Three-Phase Vapour Tensiometry (TPVT) analogue to salt-cryoscopy has been developed only recently.⁷ In this technique we have a two-phase medium of a crystalline inert salt and its saturated solution and a third phase, the gaseous phase. According to Gibbs phase rule, such a system has a definite vapour pressure just as pure water. Any addition of foreign solute molecules — charged or uncharged — to the two-phase medium causes a lowering of the vapour pressure, and again the ions of the inert salt are inactive. If the inert salt for instance is KNO_3 — the two-phase medium being now solid potassium nitrate and its saturated solution — and dissolved AgNO_3 , only the cation Ag^+ causes a lowering of the water pressure p above the medium, the anion NO_3^- does not. Nitrate is again inactive when we dissolve the complex $[\text{Ag}(\text{en})]\text{NO}_3$, but the depression of p amounts now only to half the value obtained with AgNO_3 for equimetallic concentrations, if the complex salt produces a dinuclear cation $\text{Ag}_2(\text{en})_2^{2+}$.

The isothermic pressure lowering $[\Delta p]_T$ is thermodynamically equivalent to the isobaric temperature enhancement $[\Delta T]_p$, which must be maintained between the two media with and without the foreign solute to get the same vapour pressure above both media.

In order to avoid cumbersome vapour pressure determinations, Hill's method¹² has been applied. In this method $[\Delta p]_T$ or $[\Delta T]_p$ are obtained by determination of the stationary temperature difference ΔT_s , ($\Delta T_s \leq [\Delta T]_p$), which sets in between the two media with and without the foreign solute if they are kept in the atmosphere of the pure two-phase medium. ΔT_s was measured using thermistors with a Wheatstone bridge. The signal S of this bridge is proportional to " i_f ", the number of foreign species created by the dissolution of AgNO_3 or Ag(en)NO_3 .

$$i_f = \frac{55.51[\Delta p]_T}{p_0 m_{\text{Ag}}} = \frac{[\Delta T]_p}{E m_{\text{Ag}}} = \frac{\Delta T_s}{k_T m_{\text{Ag}}} = \frac{S}{k_S m_{\text{Ag}}} \quad (2)$$

p_0 is the vapour pressure of the pure two-phase medium at the temperature T and E is the three-phase ebullioscopic constant.

The calibration constants k_T and k_S were determined by using KCl as solute with $i_f = 1$. The quantity i_f varies linearly with the concentration of the solute and the slope of the line can be predicted (see Ref. 7 and Fig. 2).

Fig. 3 illustrates the salt-ebullioscopic titration with ethylenediamine of a solution of AgNO_3 in the saturated solution of KNO_3 (molality $m_{\text{Ag}} = 0.5$ mol per kg of water in the two-phase medium).

Before the start of the titration, the number of foreign solute molecules is $i_f = 1$ (the cation Ag^+). The free base "en" which is now added is bonded quantitatively and i_f would not change if the product of the reaction would be mononuclear Ag(en)^+ (line 1). However, although a new substance is introduced, i_f is lowered at the beginning of the titration. The slope at the very start is -1 (line 2) because of the formation of $\text{Ag}_2(\text{en})^{2+}$. But the 2:1-complex is not very stable (Table 1) and adds "en" very efficiently:

The slope changes therefore soon with increasing $[\text{en}]_{\text{tot}}/[\text{Ag}]_{\text{tot}}$ to -0.5 (line 3), the dominant reaction becoming:

When one mol of "en" per silver has been added, almost all the metal and all of the diamine are present in the form of $\text{Ag}_2(\text{en})_2^{2+}$ and the number of solute species per metal is only slightly larger than $i_f = \frac{1}{2}$. With further amounts of base introduced, i_f increases again, (line 3'), demonstrating the change of the nuclearity from the value 2 back to 1 again:

Fig. 2. The dependence of i_f , the apparent number of foreign species per silver atom present after the dissolution of AgNO_3 or $[\text{Ag(en)}]\text{NO}_3$ in the saturated solution of the two-phase medium with the inert salt KNO_3 , on the molality m_{Ag} (= the total number of mol Ag per kg of water present in the two-phase medium). Lines 1, 2, 3, 4 and 5 represent the predicted values of i_f for the nuclearity $n = 1, 2, 3, 4$ and 5 of the complex $[\text{AgL} \times \text{aq}]_n(\text{NO}_3)_n$ ($\text{L} = \text{en}$ or H_2O).

Fig. 3. The TPVT-titration of AgNO_3 with "en", both dissolved in the solution of the two-phase medium with KNO_3 at constant $m_{\text{Ag}} (=0.5 \text{ mol/kg})$. Lines 1, (2,2') and (3,3') are predicted courses of the function $i_f ([\text{en}]_{\text{tot}}/[\text{Ag}]_{\text{tot}})$ for the formation of the mononuclear $\text{Ag}(\text{en})^+$ only, the dinuclear $\text{Ag}_2(\text{en})_2^{2+}$ only or the dinuclear $\text{Ag}_2(\text{en})_2^{2+}$ only.

This titration shows up the dimerisation of $\text{Ag}(\text{en})^+$ strikingly.

Solubility of $[\text{Ag}(\text{en})](\text{ClO}_4)$. During TPVT-measurements we found that the perchlorate $[\text{Ag}(\text{en})](\text{ClO}_4)$ was salted out by ethyltrimethylammonium perchlorate, which we first intended to use as an inert salt. This observation led us to the assumption that the interpretation of solubility curves $[\text{Ag}]_{\text{tot}}([\text{ClO}_4^-])$ could yield additional evidence about the nuclearity of the dominating complex in the saturated solution of $[\text{Ag}(\text{en})](\text{ClO}_4)$.

As a matter of fact, the solubility curve is described at concentrations $[\text{Ag}]_{\text{tot}}$ between 123 and 6 mM by eqn. 3 which is easily obtained by the assumption of the presence of only two complexes $\text{Ag}(\text{en})^+$ and $\text{Ag}_2(\text{en})_2^{2+}$ in the saturated solution of $[\text{Ag}(\text{en})](\text{ClO}_4)$:

$$-\log [\text{Ag}]_{\text{tot}} = -\log(K_{\text{sp}}/[\text{ClO}_4^-]) + 2K_{\text{sp}}K_{\text{d}}/[\text{ClO}_4^-]^2 \quad (3)$$

At low perchlorate ion concentrations the quadratic term of the sum becomes dominant and causes the quasi-linear form of the solubility curve $-\log[\text{Ag}]_{\text{tot}}$ ($-\log[\text{ClO}_4^-]$) (see Fig. 4). The slope calculated

from the 12 points at low $[\text{ClO}_4^-]$ -values differs only by 5 % from the theoretical value of -2 . Therefore, higher polymers $[\text{Ag}(\text{en})]_n^{n+}$ with $n > 2$ are either not present at all or only in small concentration. Nevertheless, a very elegant but risky hypothesis of a "continued polymerisation" of $\text{Ag}(\text{en})^+$ was presented¹³ recently. In our opinion the calculation of more than one constant from these solubility data is mathematically possible but has no real meaning chemically because the part of the solubility curve at high $[\text{ClO}_4^-]$ -values cannot be determined accurately for the following reasons: (a) besides the two main complexes $\text{Ag}(\text{en})^+$ and $\text{Ag}_2(\text{en})_2^{2+}$ there are 4 other complexes present. The distribution of silver (as % Ag in a given complex of the totally dissolved Ag) was calculated for the saturated solution of $[\text{Ag}(\text{en})](\text{ClO}_4)$ and experimental conditions given in the legend for Fig. 4 using the data of Table 1 for 1 M KNO_3 and the stability constant⁵ of $[\text{Ag}(\text{en})\text{OH}]$: $\text{Ag}(\text{Hen})^+$ (1.24 %), $[\text{Ag}(\text{en})\text{OH}]$ (4.02 %), $\text{Ag}(\text{en})_2^+$ (4.15 %), $\text{Ag}(\text{Hen})_3^+$ (9.07 %), $\text{Ag}(\text{en})^+$ (23.65 %) and $\text{Ag}_2(\text{en})_2^{2+}$ (53.71 %), (b) the solid $\{[\text{Ag}(\text{en})](\text{ClO}_4)\}$ is not stable if it is suspended in a solution of 0.01 M HenClO_4 and partially decomposes to Ag_2O involving the liberation of Hen^+ and the enhancement of $[\text{Ag}]_{\text{tot}}$. This enhancement is negligible at high $[\text{Ag}]_{\text{tot}}$ -values but causes

Fig. 4. The solubility of $[\text{Ag}(\text{en})]\text{ClO}_4$ in water containing 0.01 M HNO_3 , $([\text{ClO}_4^-] - [\text{Ag}]_{\text{tot}})$ M NaClO_4 and $(0.99 - [\text{ClO}_4^-])$ M KNO_3 at 25 °C ($K_{\text{sp}} = [\text{Ag}(\text{en})^+][\text{ClO}_4^-]$).

serious interference at low values of $[\text{Ag}]_{\text{tot}}$.

For these reasons the seven points at high $-\log[\text{Ag}]_{\text{tot}}$ -values (see Fig. 4) were omitted in the calculation of the solubility product K_{sp} . In this calculation the dimerisation constant K_d of $10^{3.05}$ (see Table 1) was taken and K_{sp} calculated from eqn. 3 using all other points of the solubility curve. The average value of $\log K_{\text{sp}}$ was -3.08 ± 0.01 and was used to calculate the solid line in Fig. 4 by means

of eqn. 3. If $[\text{Ag}]_{\text{tot}}^{\text{calc}}$ is corrected for the contribution of the first 4 complexes mentioned above, a better representation of the experimental points results (see dotted line "corr" in Fig. 4). For the calculation of a still better "corrected line" the amount of the Hen^+ liberated in the decomposition of $\{[\text{Ag}(\text{en})] \cdot (\text{ClO}_4)_2\}$ should be measured. The use of stability constants determined in the same medium would also improve the fit somewhat.

Table 2. Comparison of thermodynamic data of Ag(I) complexes of ammonia,¹⁴ ethylenediamine "en", 1,3-propanediamine "pn",¹⁵ 1,4-butanediamine "bn",¹⁵ and ethalnodamine "ea".¹⁶ ($\pm$ values are the 95 % confidence limits, L_{95}).

Reaction	ΔG kJ/mol	ΔH kJ/mol	ΔS J/mol K
$\text{Ag}^+ + \text{en} = \text{Ag}(\text{en})^+$	-28.9 ± 0.3	-48.5 ± 1.4	-66 ± 5
$\text{Ag}^+ + 2\text{en} = \text{Ag}(\text{en})_2^+$	-43.7 ± 0.6	-55.2 ± 1.3	-39 ± 5
$2\text{Ag}^+ + 2\text{en} = \text{Ag}_2(\text{en})_2^{2+}$	-75.2 ± 1.4	-107.8 ± 2.7	-109 ± 9
$\text{Ag}(\text{en})^+ + \text{Ag}(\text{en})^+ = \text{Ag}_2(\text{en})_2^{2+}$	-17.4 ± 1.7	-10.8 ± 0.1	$+22 \pm 6$
$\text{Ag}^+ + 2\text{NH}_3 = \text{Ag}(\text{NH}_3)_2^+$	-41.2	-56.1 ± 0.6	-50 ± 2
$\text{Ag}^+ + \text{pn} = \text{Ag}(\text{pn})^+$	-32.9	-61.2 ± 9.7	-95 ± 32
$\text{Ag}^+ + \text{bn} = \text{Ag}(\text{bn})^+$	-31.6	-47.7 ± 3.9	-54 ± 13
$\text{Ag}^+ + \text{ea} = \text{Ag}(\text{ea})^+$	-18.1	-23.0 ± 5.6	-16 ± 19
$\text{Ag}(\text{ea})^+ + \text{ea} = \text{Ag}(\text{ea})_2^+$	-20.7	-27.1 ± 7.7	-21 ± 26

^a All succeeding values were calculated from $\log K$ values^{15,16} measured at 10, 20, 30 and 40 °C using the constants A , B and the standard deviation σ_B of the corresponding linear regression $\log K = A + B/T$: $\log K_{25} = B/298.15 + A$, $-\Delta G = 5.708 \log K_{25}$, $-\Delta H = 0.019144B$, $L_{95}(\Delta H) = 0.0304\sigma_B$, $\Delta S = 3.354(\Delta H - \Delta G)$ and $L_{95}(\Delta S) = 3.35L_{95}(\Delta H)$.

Heats of formation. The heat production in the reaction of Ag(I) with "en" at various pH-values and the heat consumption in the dissociation of $\text{Ag}_2(\text{en})_2^{2+}$ to $2 \text{Ag}(\text{en})^+$ by dilution with solutions of KNO_3 were measured. Using these data and the stability constants of Table 1 for 1 M KNO_3 the heats and entropies of formation were calculated and compared in Table 2 with corresponding values of Ag(I) complexes of ammonia, and some amines.

The heat of formation of $\text{Ag}(\text{en})_2^+$, $\text{Ag}(\text{ea})_2^+$, $\text{Ag}(\text{pn})^+$ and $\text{Ag}(\text{bn})^+$ agree within the 95 % confidence limits. Additionally, the number of Ag—N bonds is certainly two in these complexes. Therefore, we calculated the most probable value $\Delta H_{\text{Ag-N}}$ for the enthalpy of formation of an Ag—N bond as the half of the weighted average of the ΔH values of the four complexes mentioned above and obtained the value of -27.9 ± 0.3 kJ/mol. Because $\Delta H_{\text{Ag(en)}}$ is 1.74 times larger than $\Delta H_{\text{Ag-N}}$, the complex $\text{Ag}(\text{en})^+$ must be a chelate. The deficit of 7.3 kJ/mol is presumably due to some strain within the chelate ring. We can also assume that a strained chelate ring is more hydrated than linear or large ring complexes. In the dimerisation reaction the ring relaxes and water molecules become free. This enhancement of the total number of particles involved in the dimerisation reaction is demonstrated by the positive entropy change of this reaction. Due to the poor precision of the entropy data no further discussion of entropy effects is possible. Nevertheless, it is very interesting to note that $3(\Delta H_{\text{Ag-N}})$ and $4(\Delta H_{\text{Ag-N}})$ are -83.7 ± 0.9 and -111.6 ± 1.2 kJ/mol, respectively. As the latter value is almost the same as the enthalpy of formation of $\text{Ag}_2(\text{en})_2^{2+}$, the number of the Ag—N bonds in the dimer must be four. Hence a linear arrangement of $\text{Ag}_2(\text{en})_2^{2+}$ would provide only three Ag—N bonds, the dissolved complex has most probably the 10-membered ring structure proposed⁴ 26 years ago. The relatively small ring stabilization energy of -14 kJ/mol Ag can of course easily be compensated by lattice packing energies. The difference of the crystal structure⁸ and the molecular structure of the dominant complex in the saturated solution of $[\text{Ag}(\text{en})](\text{ClO}_4)$ is therefore not a real contradiction at all.

METHODS AND EXPERIMENTAL

Potentiometric titrations. The calibration of the cell Hg° , $\text{Hg}_2\text{Cl}_2/3.5 \text{ M KCl}/1 \text{ M KNO}_3/\text{Glass}$ was carried out by titration of 100 m^3 of a solution con-

taining 0.01 M HNO_3 and 0.99 M KNO_3 with a solution of 0.5 M KOH and 0.5 M KNO_3 at $25 \pm 0.2^\circ \text{C}$ under nitrogen. From the combination ($E^\circ_{\text{H}} - E^\circ_{\text{OH}}/59.16$, a $-\log[\text{H}][\text{OH}]$ value of 13.76 was obtained. Using this cell, 100 cm^3 aliquots of the following 6 solutions were titrated in the same way:

- (1) $10^{-3} \text{ M } [\text{H}_2\text{en}](\text{ClO}_4)_2$,
- (2) $10^{-2} \text{ M } [\text{H}_2\text{en}](\text{ClO}_4)_2$,
- (3) $10^{-3} \text{ M } [\text{H}_2\text{en}](\text{ClO}_4)_2$, 0.2 M KBrO_4 and 1 g AgBrO_3 ,
- (4) $10^{-3} \text{ M } [\text{H}_2\text{en}](\text{ClO}_4)_2$, $5 \times 10^{-2} \text{ M KBrO}_3$ and 1 g AgBrO_3 ,
- (5) $10^{-3} \text{ M } [\text{H}_2\text{en}](\text{ClO}_4)_2$ and 0.1 M AgNO_3 and
- (6) $10^{-2} \text{ M } [\text{H}_2\text{en}](\text{ClO}_4)_2$ and 0.2 M AgNO_3 .

All solutions contained KNO_3 in such a concentration that the ionic strength was 1 M. The concentration of free silver ion in solutions 3 and 4 was obtained from eqn. (4):

$$[\text{Ag}] = K_{\text{sp}}^*/([\text{KBrO}_3] + [\text{Ag}]_{\text{tot}}) \quad (4)$$

where K_{sp}^* is the solubility product of AgBrO_3 . The value of $(2.60 \pm 0.03)10^{-4} \text{ M}^2$ was used, which was obtained by atomic absorptiometric determination of $[\text{Ag}]$ in filtrates ($0.45 \mu\text{m}$ membrane filter) of suspensions and precipitations of AgBrO_3 in 1 M solutions of KNO_3 containing 10^{-3} M HNO_3 .

Because of the presence of silver in excess, the concentration of uncomplexed Hen^+ and en will always remain so small in these solutions that mononuclear 1:2-complexes cannot form in significant amounts. The diprotonated H_2en^{2+} therefore was expected to be in equilibrium with protonated species Hen^+ , $\text{Ag}(\text{Hen})^{2+}$ and three completely deprotonated species en, $\text{Ag}(\text{en})^+$, $\text{Ag}_2(\text{en})_2^{2+}$. Because of the constancy of the concentration $[\text{Ag}]$, the following concentration ratios remain constant throughout the process:

$$\begin{aligned} \frac{[\text{Ag}(\text{Hen})]}{[\text{Hen}]} &= [\text{Ag}]K_{\text{AgHen}}, \quad \frac{[\text{Ag}(\text{en})]}{[\text{en}]} = [\text{Ag}]K_{\text{Agen}}; \\ \frac{[\text{Ag}_2(\text{en})]}{[\text{en}]} &= [\text{Ag}]^2K_{\text{Agen}}K_{\text{Ag}_2\text{en}} \end{aligned} \quad (5)$$

(the formation constants K_{Agen} , K_{AgHen} , $K_{\text{Ag}_2\text{en}}$ are defined in Table 1). Now the concentration of acidic hydrogen bonded to the free or complexed ligand, i.e. the degree of protonation ($\bar{p}$ when silver is absent or $\bar{p}'$ in the presence of silver) is obtained with eqn. (6); $[\text{H}]_{\text{tot}}$ being the total concentration of acidic hydrogen ($= 2[\text{en}]_{\text{tot}} - [\text{KOH}]$):

$$\bar{p} \text{ (or } \bar{p}') = \frac{[\text{H}]_{\text{tot}} - [\text{H}] + [\text{OH}]}{[\text{en}]_{\text{tot}}} \quad (6)$$

The quantities $\bar{p}$ and $\bar{p}'$ can also be expressed by (7) and (7')

$$\bar{p} = \frac{[\text{Hen}] + 2[\text{H}_2\text{en}]}{[\text{en}] + [\text{Hen}] + [\text{H}_2\text{en}]} \quad (7)$$

$$\bar{p}' = \frac{[\text{Hen}]' + 2[\text{H}_2\text{en}]}{[\text{en}]' + [\text{Hen}]' + [\text{H}_2\text{en}]} \quad (7')$$

with

$$\begin{aligned} [\text{Hen}]' &= [\text{Hen}] + [\text{AgHen}] \\ [\text{en}]' &= [\text{en}] + [\text{Agen}] + [\text{Ag}_2\text{en}] \end{aligned} \quad (8)$$

Eqn. (9) defines the usual basicity constants and

$$\begin{aligned} \frac{[\text{Hen}]}{[\text{H}][\text{en}]} &= 10^{\text{p}K_1} = \kappa_1; \\ \frac{[\text{H}_2\text{en}]}{[\text{H}][\text{Hen}]} &= 10^{\text{p}K_2} = \kappa_2/\kappa_1 \end{aligned} \quad (9)$$

analogous expressions are used for the apparent basicities of en' and Hen' in the presence of silver:

$$\begin{aligned} \frac{[\text{Hen}]'}{[\text{H}][\text{en}']} &= 10^{\text{p}K'_1} = \kappa'_1; \\ \frac{[\text{H}_2\text{en}]}{[\text{H}][\text{Hen}']} &= 10^{\text{p}K'_2} = \kappa'_2/\kappa'_1 \end{aligned} \quad (9')$$

Replacement of the concentrations of the metal-containing species in (8) and (9') with the help of (5) leads to the expressions (10) for the apparent basicity constants determined in the presence of silver [eqn. (10)].

$$10^{\text{p}K'_1} = \frac{[\text{Hen}](1 + [\text{Ag}]K_{\text{AgHen}})}{[\text{H}][\text{en}](1 + [\text{Ag}]K_{\text{Agen}} + [\text{Ag}]^2K_{\text{Agen}}K_{\text{Ag}_2\text{en}})} \quad (10)$$

$$10^{\text{p}K'_2} = \frac{[\text{H}_2\text{en}]}{[\text{H}][\text{Hen}](1 + [\text{Ag}]K_{\text{AgHen}})}$$

According to (10) the dashed $\text{p}K$'s ($\text{p}K'_1$ and $\text{p}K'_2$) differ from the ($\text{p}K$)'s determined when silver is absent (eqn. 9) by a term remaining constant because of the constancy $[\text{Ag}]$. The protonation in the presence of silver can therefore be described with a function $\text{pH}(\bar{p}')$ analogous to that when the metal is absent $\text{pH}(\bar{p})$. A combination of (7) and (9) furnishes (11) and a combination of (7') and (9') the eqn. (11')

$$\bar{p} + (\bar{p} - 1)10^{(\text{p}K_1 - \text{pH})} + (\bar{p} - 2)10^{(\text{p}K_1 + \text{p}K_2 - 2\text{pH})} = 0 \quad (11)$$

$$\bar{p} + (\bar{p}' - 1)10^{(\text{p}K'_1 - \text{pH})} + (\bar{p}' - 2)10^{(\text{p}K'_1 + \text{p}K'_2 - 2\text{pH})} = 0 \quad (11')$$

It is readily recognized that the stability constants of the three complexes assumed to form in the presence of an excess of silver can be calculated from the differences ($\text{p}K_1 - \text{p}K'_1$) and ($\text{p}K_2 - \text{p}K'_2$). From (10), (11) and (11') we obtain:

$$\begin{aligned} (\text{p}K_2 - \text{p}K'_2) &= \log(1 + [\text{Ag}]K_{\text{AgHen}}) \\ (\text{p}K_1 - \text{p}K'_1) + (\text{p}K_2 - \text{p}K'_2) &= \log(1 + [\text{Ag}]K_{\text{Agen}} + [\text{Ag}]^2K_{\text{Agen}}K_{\text{Ag}_2\text{en}}) \end{aligned} \quad (12)$$

At least three titrations are needed therefore if the three unknown constants K_{AgHen} , K_{Agen} and $K_{\text{Ag}_2\text{en}}$ are to be calculated: the deprotonation of H_2en without any silver present gives $\text{p}K_1$ and $\text{p}K_2$ [eqn. (11)] and titrations at two different concentrations $[\text{Ag}]$ furnish two pairs $\text{p}K'_1$, $\text{p}K'_2$

Fig. 5. Deprotonation of H_2en^{2+} : (A) without Ag(I) ($\text{p}K_1 = 10.21$, $\text{p}K_2 = 7.50$), (B) $[\text{Ag}] = 4.66 \cdot 10^{-3}$ M, constant (B' calculated with $\text{p}K'_1 = 7.74$ and $\text{p}K'_2 = 7.22$) and (C) $[\text{Ag}] = (0.195 \pm 0.005)$ M [C' calculated from the protonation function (11') using $\text{p}K'_1 = 7.09$ and $\text{p}K'_2 = 5.72$].

[eqn. (11')] allowing the calculation of the stability constants with (12).

A set of three protonation curves illustrating the procedure is shown in Fig. 5. When no silver is present (curve A) the buffer regions $\text{en} \rightarrow \text{Hen}^+$ ($\text{p}K_1 \sim 10.2$) and $\text{Hen}^+ \rightarrow \text{H}_2\text{en}^{2+}$ ($\text{p}K_2 \sim 7.5$) are well separated. In the presence of silver, however, an uninterrupted flat region of gradually falling pH between $\bar{p}' = 0.1$ and 1.9 is obtained (curves B and C). This phenomenon is caused by the higher stability of $\text{Ag}(\text{en})^+$ in comparison to $\text{Ag}(\text{Hen})^{2+}$ ($K_{\text{Ag(en)}} \gg K_{\text{Ag(Hen)}}$) making the difference ($\text{p}K_1 - \text{p}K'_1$) much larger than ($\text{p}K_2 - \text{p}K'_2$) and consequently ($\text{p}K_1 - \text{p}K_2$) larger than ($\text{p}K'_1 - \text{p}K'_2$). In the case of curve A $\text{p}K_1$ is obtained from the upper buffer region with the first two terms of eqn. (11), the third term being negligibly small in the range $0 < \bar{p} < 1$; whereas $\bar{p}$ in eqn. (11) may be neglected in the lower buffer region ($1 < \bar{p} < 2$) which is determined practically only by $\text{p}K_2$.

The apparent basicities $\text{p}K'_1$ and $\text{p}K'_2$ cannot be obtained so simply from the curves B and C, their difference being so small that all the terms of (11') make an appreciable contribution over the entire buffer region $0 < \bar{p}' < 2$, i.e. the species containing en' , Hen' and H_2en are present simultaneously. Both $\text{p}K'$ -values have to be taken into account over the whole region. On the other hand this situation makes it also possible to find both $\text{p}K'$ -values from only a part of the extended buffer region. A graphical method proved to be especially suitable, first to find out whether the experimental curves (B and C, Fig. 5) can be reproduced with eqn. (11') and second to obtain the values $\text{p}K'_1$ and $\text{p}K'_2$. When eqn. (11') is divided by the factor $10^{(\text{p}K'_1 - \text{pH})}$ a linear eqn. (13) is obtained of the variables x and y defined as: $x = 10^{-\text{p}K'_1}$ and $y = 10^{\text{p}K'_2}$. Every point of the experimental protonation curve $\bar{p}'(\text{pH})$ furnishes a straight line in a plot

$$x\bar{p}'/[\text{H}] + y(\bar{p}' - 2)[\text{H}] + (\bar{p}' - 1) = 0 \quad (13)$$

$y(x)$ according to (13) and when the eqn. (11') is valid, these straight lines have a common point of intersection at the values:

$$x_0 = 10^{-\text{p}K'_1}; y_0 = 10^{\text{p}K'_2}$$

The lines were drawn by connecting the axial intercepts:

$$\text{for } y = 0: x = \frac{(1 - \bar{p}')}{\bar{p}'} [\text{H}]$$

$$\text{for } x = 0: y = \frac{(1 - \bar{p}')}{(\bar{p}' - 2)[\text{H}]}$$

Applying this criterion it is found that only about half of the experimental curves taken in the presence of silver (B and C, Fig. 1) can be represented by (11'), only the part at lower pH-values, where $\bar{p}' > 1$. Starting the investigation at the acidic end of the curve, the lines [eqn. (13)] from consecutive points with $\bar{p}' = 1.9, 1.8, 1.7$ etc. first all cross at the same point, but deviate later more and more from that common point of intersection at higher pH values when $\bar{p}' < 1$. The experimental curves taken at constant $[\text{Ag}]$ are as expected only at the beginning of the deprotonation of H_2en^{2+} , but in the later stages of the process the pH-value does not rise as much as it should according to eqn. (11') with descending $\bar{p}'$. This result is illustrated in Fig. 5 with B' and C' which show the expected course of the curves calculated with $\text{p}K'_1$ and $\text{p}K'_2$ from the common point of intersection at the start of the deprotonation in the region $\bar{p}' \geq 1.4$.

The described deviation from eqn. (11') must be caused by the formation of species containing more than a single molecule of "en". Of the mononuclear 1:2-complexes $\text{Ag}(\text{en})_2^+$, $\text{Ag}(\text{en})(\text{Hen})^{2+}$ and $\text{Ag}(\text{Hen})_2^{3+}$ which might be considered only the last is of some importance,* but even $\text{Ag}(\text{Hen})_2^{3+}$ can only be formed, at the most, in amounts of a few percent of $[\text{en}]_{\text{tot}}$.

This causes hardly any changes in the protonation curve. Furthermore the small deviations from (11') caused by $\text{Ag}(\text{Hen})_2^{3+}$ are largest at $\bar{p}' = 1$. Clearly, however, the observed deviations begin only at this position and become more and more pronounced with falling $\bar{p}'$. This fact indicates that the complex causing the deviation contains completely deprotonated "en" and more than a single molecule of it. The mononuclear $\text{Ag}(\text{en})_2^+$ can be ruled out, it must be a species containing not only more than a single "en" but more than a single Ag^+ as well and indeed, the experimental curves can be reproduced qualitatively by assuming the formation of $\text{Ag}_2(\text{en})_2^{2+}$.

The concentration of this 2:2-complex is obtained immediately from the difference $(\bar{p}')^{\text{obs}} - (\bar{p}')^*$ given by the curves B and B' or C and C', respectively.

* The comparatively small constant $[\text{Ag}(\text{en})_2]/[\text{Ag}(\text{en})][\text{en}]$ (~ 500) is obtained from β_2 (Refs. 3 and 9) and $K_{\text{Ag(en)}}$. In the presence of an excess of silver the deprotonation of H_2en^{2+} takes place at comparatively low pH values so that $[\text{en}]$ becomes extremely small and also the concentration $[\text{Ag}(\text{en})_2]$ (order of magnitude 10^{-7} M). The concentration of Hen^+ of course is much larger than $[\text{en}]$ in these pH-ranges, but Hen^+ is not as good a ligand as "en" and the concentration of $\text{Ag}(\text{en})(\text{Hen})^{2+}$ is not expected to be important. The constant $[\text{Ag}(\text{Hen})_2]/[\text{Ag}(\text{Hen})][\text{Hen}]$ can be guessed from $K_{\text{Ag(Hen)}}$ and K_1/K_2 -ratios of other amine-complexes of silver. Its order of magnitude is also about 500.

Inspection of eqn. (6) used to find the experimental $(\bar{p}')^{\text{obs}}$ and comparison with (7') which is involved when $\bar{p}'$ is calculated with (11') from the constants pK'_1 , pK'_2 found in the high acidity range ($\bar{p}' > 1$), gives:

$$[\text{H}]_{\text{tot}} - [\text{H}] + [\text{OH}] = [\text{Hen}]' + 2[\text{H}_2\text{en}]$$

and therefore:

$$(\bar{p}')^* ([\text{en}]' + [\text{Hen}]' + [\text{H}_2\text{en}]) = (\bar{p}')^{\text{obs}} [\text{en}]_{\text{tot}} \quad (14)$$

The degree of protonation $(\bar{p}')^*$ calculated with (11') and the primed pK 's is larger than the observed $(\bar{p}')^{\text{obs}}$ (see Fig. 5), but the sum $[\text{en}]_{\text{tot}}$ is larger than the sum in brackets on the left hand side of the equation [see eqn. (8)] because of the presence of the 2:2-complex:

$$[\text{en}]_{\text{tot}} = [\text{en}]' + [\text{Hen}]' + [\text{H}_2\text{en}] + 2[\text{Ag}_2(\text{en})_2], \quad (15)$$

the concentration of which is obtained by combining (14) and (15):

$$[\text{Ag}_2(\text{en})_2] = \frac{1}{2} [\text{en}]_{\text{tot}} \left(1 - \frac{(\bar{p}')^{\text{obs}}}{(\bar{p}')^*} \right) \quad (16)$$

In order to obtain $K_{\text{Ag}_2\text{en}_2}$, according to its definition $[\text{Ag}_2(\text{en})_2]/[\text{Ag}]^2[\text{en}]^2$ we need first to calculate $[\text{en}]$ the concentration of the free "en". Introducing the constants already obtained at this stage, we get eqn. (17) from (14). In the calculation

$$[\text{en}]_{\text{tot}} \frac{(\bar{p}')^{\text{obs}}}{(\bar{p}')^*} = [\text{en}] [10^{(pK'_1 + pK'_2 - 2pH)} + 1 + 10^{(pK'_1 - pH)} + [\text{Ag}] K_{\text{Ag}(\text{Hen})} 10^{(pK'_1 - pH)} + [\text{Ag}] K_{\text{Ag}(\text{en})} + [\text{Ag}]^2 K_{\text{Ag}_2\text{en}} K_{\text{Ag}(\text{en})}] \quad (17)$$

of $[\text{en}]$ from (17) the weighted averages of the constants obtained from titrations 3–6 were used (see Table 1).

Finally, $\log K_d$ was obtained from the difference

$$(\log K_{\text{Ag}_2\text{en}_2} - 2 \log K_{\text{Ag}(\text{en})}).$$

Three-phase vapour tensiometry (TPVT). The TPVT-measurements were carried out as described earlier.⁷ Weighted samples of the solid $[\text{Ag}(\text{en})]\text{NO}_3 \cdot \text{H}_2\text{O}$ and ca. 400 mg KNO_3 were mixed with 1 g water and equilibrated at 30 °C for 20–40 h before introduction into the cell, which was thermostated at 30 °C. The solid was prepared by addition of a mixture of 22 cm³ 1 M "en" and 2 cm³ 1 M HNO_3 to the solution of 20 mmol AgNO_3 in a small amount of water. The crystals were washed twice with small quantities of cold water and dried in vacuo (ca. 1 Pa) at room temperature (ca. 25 °C).

In the PTVT-titration, quantities of 1 g of a 0.5 m

(mmol Ag/g H_2O) AgNO_3 solution were mixed with various amounts of a solution containing 5 m "en" and 0.25 m HNO_3 . After the addition of ca. 400 mg KNO_3 the apparent number of foreign species i_f was determined as described above. The addition of HNO_3 was necessary to avoid the precipitation of Ag_2O by mixing of the two solutions. As the contribution of Hen^+ produced by the HNO_3 addition to i_f is limited to 5–10 %, it is comparable with the relative standard deviation of i_f , hence no corrections were made.

Solubility measurements. Solubility data should be independent of crystalline form and method of measurement. Therefore crystals of different size were dissolved (s. empty circles in Fig. 4). Although the dissolution process seems to be rapid, suspensions (100 cm³ saturated solution and 1 g solid) were equilibrated at (25 ± 0.2) °C a relatively long time (15–70 h) in closed vessels under nitrogen. The solvent consisted of 0.01 M HenNO_3 , (0–0.99) M NaClO_4 and $(1 - [\text{NaClO}_4] - [\text{Ag}]_{\text{tot}})$ M NaNO_3 . At the start of the experiment $[\text{Ag}]_{\text{tot}}$ was estimated using eqn. 3 with an estimated value of $K_{\text{sp}} (10^{-3} \text{ M}^2)$. Aliquots of 2 or 5 cm³ were taken when the solution became clear (10 min after interruption of the magnetic stirrer). The aliquots were immediately filtered on membrane filter of porosity 0.45 μm . Both filtrates were acidified with HNO_3 to ca. 0.1 M and analysed using atomic absorption spectrometry (AAS) for the determination of $[\text{Ag}]_{\text{tot}}$. After sampling 20–50 cm³ of a solution containing 0.01 M HenNO_3 and 0.99 M NaClO_4 were added to the rest of the equilibrated suspension which was stirred and equilibrated again. The addition of this solution caused the precipitation of $[\text{Ag}(\text{en})]\text{ClO}_4$, or in other words, the equilibrium was approached from the opposite side (s. filled circles in Fig. 4. Sampling and analysis of the filtrates was carried out as described above).

The preparation of small crystals was carried out by mixing the precooled (~ 0 °C) solution of 110 mmol "en" in ca. 100 cm³ water and 10 cm³ 1 M HClO_4 with 100 cm³ precooled 1 M solution of AgClO_4 . After 1 h in ice water the colorless crystals were filtered off and washed with small quantities of cold water. A part was immediately used for the solubility experiments. Another part was dried as described for $[\text{Ag}(\text{en})]\text{NO}_3 \cdot \text{H}_2\text{O}$. A third part was recrystallized from a 0.1 M solution of HenClO_4 ; the crystals were dissolved at ca. 70 °C and the filtered solution was cooled very slowly. Large, slightly yellowish brown crystals were obtained which, like the small crystals, became darker on drying. Anal. $[\text{Ag}(\text{en})\text{ClO}_4]$: Ag, "en".

No systematic dependence of the solubility of $[\text{Ag}(\text{en})]\text{ClO}_4$ on the size of the crystals, performance of the experiment (dissolution or precipitation and time of equilibration), was found. Never-

theless, the deviations of the $-\log[\text{Ag}]_{\text{tot}}$ -values determined at a given, high perchlorate ion concentration, were about 20 times poorer than the 95 % confidence limit of the AAS determinations for the same filtrate [$L_{95}(-\log[\text{Ag}]_{\text{tot}}^{\text{AAS}}) = 0.0027$ on average].

Because of the high sensitivity and selectivity of the AAS-determinations this low confidence limit remains about the same over the whole concentration range of $[\text{Ag}]_{\text{tot}}$. The bad reproducibility of $-\log[\text{Ag}]_{\text{tot}}$ in ca. 1 M solutions of NaClO_4 (see Fig. 4) is caused by decomposition of $[\text{Ag(en)}]\text{ClO}_4$ which set in irregularly and enhances the solubility from suspension to suspension by somewhat different amounts.

As the dissolution of one mol Ag is accompanied by the liberation of one mol ClO_4^- , $-\log[\text{ClO}_4^-]$ was obtained as $-\log([\text{NaClO}_4] + [\text{Ag}]_{\text{tot}})$.

Calorimetry. The consumption of heat Q in the dissociation reaction $\text{Ag(en)}_2^+ \rightarrow 2\text{Ag(en)}^+$ was determined by measuring the temperature decrease of 80 cm³ of a solution containing

- (a) 10^{-3} M $\text{H}_2\text{en}(\text{ClO}_4)_2$, 10^{-3} M KOH and 0.998 M KNO_3
- (b) 10^{-3} M "en", 10^{-3} M HNO_3 and 0.999 M KNO_3 ,

after the addition of 0.2–2 cm³ aliquots ($= V_{\text{std}}$) of a solution ("std") containing 0.5 M $[\text{Ag(en)}]\text{NO}_3$ ($= [\text{Ag}]_{\text{std}}$), 0.1 M HenNO_3 and 0.4 M KNO_3 . The calorimeter was thereafter calibrated by heat generation of an electrical power of 200 mW during 2 min. Finally, the background heat conversion Q_b was also measured in the same way, whereby 0.2–2 cm³ aliquots of a blank solution containing 0.1 M HenNO_3 and 0.4 M KNO_3 are added to 80 cm³ of the solutions a and b. The enthalpy of dimerisation was then calculated from eqn. (18), where ΔH_{av} is

$$\frac{1}{2}\Delta H_d = -(Q - Q_b)/V_{\text{Ag}}[\text{Ag}]_{\text{std}}(1 - f_{\text{Ag}_2\text{en}_2}) - \Delta H_{\text{av}}f_{\text{Ag}} \quad (18)$$

an average value of reaction enthalpies of simultaneous formation of Ag(I)-en-complexes in the pH-range of 8.7–10.5. A value of -53.4 ± 0.9 was obtained in the experiments described below. f_x is the fraction of silver present in the complex X in question, e.g. $f_{\text{Ag}_2\text{en}_2} = 2[\text{Ag}_2(\text{en})_2]/[\text{Ag}]_{\text{tot}}$ and $f_{\text{Ag}} = [\text{Ag}]/[\text{Ag}]_{\text{tot}}$.

In the calculation of the f_x values $[\text{Ag}]_{\text{tot}}$, pH and $[\text{en}]_{\text{tot}}$, the total concentration of "en" not bonded to Ag(I) are needed. Because the dissolution of $[\text{Ag(en)}]\text{NO}_3$ was always accompanied by some decomposition; the solution was filtered off and the quantity of Ag precipitated as Ag_2O was measured by AAS after dissolution of the Ag_2O in a solvent

containing 0.1 M NH_3 and 0.01 M KCN. The $[\text{Ag}]_{\text{std}}$ and $[\text{en}]_{\text{std}}$ values computed from the weight in quantities of $[\text{Ag(en)}]\text{NO}_3$ and "en" were corrected for decrease and increase, respectively, effected by this decomposition (about 1 %) of $[\text{Ag(en)}]\text{NO}_3$. The pH value was measured with the cell described above, whereby exactly the same dilutions were made as in the calorimeter. $[\text{en}]$ was obtained from eqn. (19).

$$[\text{en}] = \frac{[\text{en}]_{\text{tot}}'' 10^{(\text{pH} - \text{p}K_1)}/[10^{(\text{p}K_2 - \text{pH})} + 1 + 10^{(\text{pH} - \text{p}K_1)}]}{\quad} \quad (19)$$

With the known values of pH and $[\text{en}]$ all mol ratios $[\text{X}]/[\text{Ag}]$ can be calculated. Using the constants of Table 1 for 1 M KNO_3 the following ratios were calculated and inserted in eqn. (20).

$$[\text{Ag}]_{\text{tot}} = [\text{Ag}] \left(1 + \frac{[\text{Ag(Hen)}]}{[\text{Ag}]} + \frac{[\text{Ag(Hen)}_2]}{[\text{Ag}]} + \frac{[\text{Ag(en)}]}{[\text{Ag}]} + \frac{[\text{Ag(en)}_2]}{[\text{Ag}]} \right) + [\text{Ag}]^2 \left(\frac{2[\text{Ag}_2(\text{en})]}{[\text{Ag}]^2} + \frac{2[\text{Ag}_2(\text{en})_2]}{[\text{Ag}]^2} \right) \quad (20)$$

Eqn. (20) was then solved for $[\text{Ag}]$ and the f_x values calculated by multiplication of the corresponding term with $[\text{Ag}]/[\text{Ag}]_{\text{tot}}$ or $[\text{Ag}]^2/[\text{Ag}]_{\text{tot}}$.

The heat production Q in the reaction of AgNO_3 with "en" at various pH values was determined by measurement of the increase in temperature of 80 cm³ of a solution containing $(5-20) \times 10^{-3}$ M $[\text{en}]_{\text{tot}}''$, $(0-10^{-2})$ M $\text{Ag(en)}\text{NO}_3$ and KNO_3 (to keep I at 1 M) by additions of 0.2–1 cm³ aliquots of a standard Ag solution containing 0.5 M AgNO_3 and 0.5 M KNO_3 . The pH value and the background Q_b were determined again by carrying out the separate measurements mentioned above. The reaction enthalpy ΔH_m of formation of a mixture of Ag(I)-en-complexes was obtained from eqn. (21).

$$\Delta H_m = (Q - Q_b)/0.5V_{\text{std}}(1 - f_{\text{Ag}}) \quad (21)$$

In order to obtain the enthalpies of the main complexes present in the mixtures, two ΔH_m were combined according to eqn. (22).

$$\Delta H_m - \frac{1}{2}\Delta H_d f_{\text{Ag}_2\text{en}_2} - \Delta H_{\text{av}}(1 - f_{\text{Ag(en)}} - f_{\text{Ag(en)}_2} - f_{\text{Ag}_2\text{en}_2}) = \Delta H_{\text{Ag(en)}}f_{\text{Ag(en)}} + f_{\text{Ag}_2\text{en}_2} + \Delta H_{\text{Ag(en)}_2}f_{\text{Ag(en)}_2} \quad (22)$$

First estimates of the f_x values were obtained from (20) as described above. Thereby it was assumed that one mol of Ag(I) would bind one mol "en". The true values ($[\text{en}]_{\text{tot}}''$) and f_x were obtained by an iteration, because $[\text{Ag}]$ and $[\text{Ag(Hen)}_2]$ were not

always diminishingly small and $[\text{Ag(en)}_2]$ was relatively large at high pH and $[\text{en}]_{\text{tot}}''$ values.

The iteration was carried out according to eqn. (23), where n is the number of iteration. No more

$$([\text{en}]_{\text{tot}}'')_n = [\text{en}]_{\text{tot}} - [\text{Ag}]_{\text{tot}}(1 + f_{\text{Ag(Hen)}_2} + f_{\text{Ag(en)}_2} - f_{\text{Ag}})_{n-1} \quad (23)$$

than 2 iterations were ever needed. Finally, the iterated f_x and the ΔH_m values from the pH range 9.7–10.5 were used to calculate the enthalpies of formation. The averages and their 95 % confidence limits obtained from 15 combinations according to eqn. 22 are given in Table 2.

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