Polynuclear Thiolate Complexes in Solution. Solution Equilibria Studies of Silver(I) Complexes of 4-Mercapto-1-methylpiperidine

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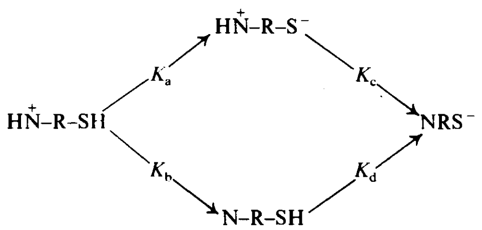
Polynuclear complex formation at 25 °C in 2 mol dm^{-3} $NaNO_3$ (10% v/v MeOH) between Ag^I and 4-mercapto-1-methylpiperidine has been studied by means of two different sets of titrations. The first set allows one to establish that $[Ag_p(AH)_q]^{p+}$ species with the p,q values 12,12; 10,9; 8,6; 7,6; 6,4; and 6,3 are present in strongly acidic solutions, AH being the monoprotonated ligand. The second set indicates that at increasing pH values, pH $\leqslant$ 8.5, the only species with $p = q$, $[Ag_{12}(AH)_{12}]^{12+}$, coexists and eventually transforms into complexes with $p < q$: 7,8; 6,8; 2,3; and 1,3. In both cases, graphical methods were applied prior to the mathematical treatment of data. An adaptation of the extended-variation method to metal electrode data has been carried out.

Despite the fact that neutral homoleptic silver thiolate complexes have been known for a long time, definite information about the structure of solid $[Ag(SR)]_n$ compounds is still restricted to very few examples. Thus, with alkanethiols as ligands a cyclic molecule, $[Ag(SC_6H_{11})]_{12}$,[1] and a one-dimensional solid, $[Ag(SCMeEt_2)]_\infty$,[2] are the only complexes fully characterized structurally. With sterically hindered (triorganosilyl)methanethiols, $(RR'R''Si)_nCH_{3-n}SH$, discrete molecular rings of different nuclearities, Ag_3S_3, and Ag_4S_4, have been reported recently.[3]

The great difficulties in obtaining adequate crystals for structure determination of $[Ag(SR)]_n$ complexes has led in the past to studies in the solution state. Thus, Åkerström[4] investigated the relation between the molecularity, n, of $[Ag(SR)]_n$ species in solution and the degree of branching at the thiol α-carbon atom. Later, Tunaboylu and Schwarzenbach[5] carried out potentiometric titrations in solutions containing Ag^I and 2-mercaptoethanol or 2-[tris(hydroxymethyl)]ethane-1-thiol. Their observation that solid [Ag(SR)] complexes form soluble species of formula $[Ag(AgSR)_n]^+$ or $[SR(AgSR)_n]^-$ in the presence of an excess of Ag^I or thiol, respectively, agrees nicely with recent reports on crystallization from non-aqueous solutions, together with structure determination, of several polynuclear anionic species $[Ag_x(SR)_y]^{x-y}$, where $1 < x < y$.[6] No example of a discrete cation with $x > y$ has been published yet.

Our solution equilibria studies with γ-mercaptoamines and d^{10} metal ions[7] has encouraged us to investigate the stoicheiometry and corresponding stability constants of silver(I) complexes of 4-mercapto-1-methylpiperidine in a 2 mol dm^{-3} (sodium) nitrate medium (+10% v/v MeOH). It seems very likely that, owing to the predominance of the zwitterionic form of the ligand over a wide pH range, the solubility of complex species in aqueous solutions is much greater than those of monofunctional thiol ligands. Moreover, co-ordination through the sulphur atom exclusively will be favoured until the second deprotonation of the ligand takes place, which will not occur until pH ≈ 8.5.[†] The structure of several solid complexes with the γ-mercaptoamine ligands in zwitterionic form justifies the previous assumptions.[8,9] Consequently, we hope that the results obtained in this work can be taken as a model for the behaviour of unidentate thiol ligands in solutions containing silver(I) ions. The use of the alcohol function as a solubilizing group in thiol ligands is not as convenient as it has been shown crystallographically that it also acts as a co-ordinating group.[10]



The strong affinity of silver(I) ions for mercaptide sulphur results in the formation of thiolate complexes even under very unfavourable conditions, such as very low pH values. Thus, the common methods used to study complex formation by means of potentiometric titrations[11] have to be modified or adapted to this particular case, which is seldom found in the literature. The experimental procedure and graphical treatment followed in this work will hopefully contribute to the solution of similar problems encountered in solutions containing soft acids, such as Cu^I or Hg^{II}, and thiol ligands.

Experimental

Reagents.—An acidified stock solution of silver nitrate, previously recrystallized once in ethanol and twice in water, was standardized gravimetrically as AgCl. From 4-mercapto-1-methylpiperidine, which had been synthesized, purified, and analyzed as previously,[7a] the corresponding acidified stock solution (pH ≈ 4.5) was prepared. A stock solution of nitric acid was made from concentrated HNO_3 (Merck p.a.) and analyzed with standard anhydrous sodium carbonate (Merck p.a.). The sodium nitrate stock solution was prepared according to the procedure reported for sodium perchlorate.[12] Sodium hydroxide solution was prepared from freshly filtered 50% NaOH solution and CO_2-free water. Methanol (p.a.) was used without further purification.

[†] Because of the proximity between the acid dissociation constants of the ligand, K_1 and K_2, the following relations have to be taken into account: $K_1K_2 = K_aK_c = K_bK_d$, $K_1 = K_a + K_b$, and $K_2 = K_cK_d/(K_c + K_d)$, where K_a, K_b, K_c, and K_d are referred to as microconstants. The species distribution of curves as a function of pH indicate that under our experimental conditions the zwitterionic form $H\overset{+}{N}$–R–S^- predominates over the uncharged one, N–R–SH, at all pH values and that the species N–R–S^- starts to appear at pH ≈ 8.5.

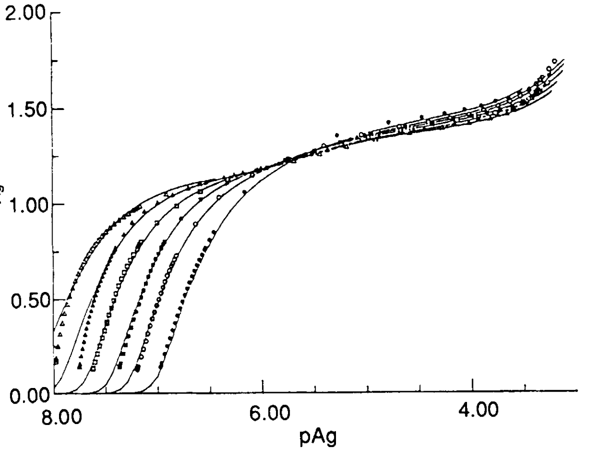


Figure 1. Formation curve for $Ag_p(AH)_q$ species at constant pH (pH = 1) and at different analytical ligand concentrations. The lines drawn were calculated from the constants in Table 2. c_L = 0.245 (●), 0.550 (○), 1.00 (■), 2.01 (□), 4.01 (▲), and 8.00 (△) mmol dm^{-3}

Apparatus.—The titrations were performed in an oil thermostat at 25.0 ± 0.1 °C and under a nitrogen atmosphere. The working electrodes used were either glass (Ingold HA 201) or silver coated with silver sulphide. The latter was prepared by anodic oxidation in a 1 mol dm^{-3} HNO_3 solution through which hydrogen sulphide was passed. Both electrodes were standardized in concentration units and *in situ* before each titration. A silver electrode coated with silver chloride[13] (prepared by anodic oxidation of a HCl solution) in conjunction with a Wilhelm glass apparatus was used as reference half-cell. Three microburettes (Hamilton, Microlab M) and one potentiometer (Crison, Digilab) were controlled automatically by means of an HP-85 microcomputer and the corresponding program.[14]

Titration Methods.—Acid dissociation constants of the cation 4-mercapto-1-methylpiperidinium in 2 mol dm^{-3} (sodium) nitrate medium (+10% v/v MeOH) were calculated from three potentiometric titrations of solutions of the ligand with an excess of nitric acid. These titrations were conducted at constant analytical ligand concentration, c_L, with use of a glass electrode (g.e.) and the cell r.e.|2 mol dm^{-3} $NaNO_3$, 10% v/v MeOH||s.p.|g.e., where s.p. denotes the test solution and r.e. the reference half-cell, Ag, AgCl|1.99 mol dm^{-3} $NaNO_3$, 0.01 mol dm^{-3} NaCl, 10% v/v MeOH. In each titration the concentration of free hydrogen ion, [H], was varied by adding variable-volume aliquots of sodium hydroxide in the nitrate medium. The value for K_w (pK_w = 13.81 ± 0.02) in the medium used was calculated with the program MINIQUAD[15] from primary data corresponding to three strong acid–strong base titrations.

Silver complex-formation constants in 2 mol dm^{-3} (sodium) nitrate medium (+10% v/v MeOH) were calculated from two sets of titrations in order to study first the complex species existing in a strong acidic medium and then those present in solutions with higher pH values, pH < 8. The first set, consisting of nine titrations, was divided into two series: one at constant free hydrogen-ion concentration, pH 1, and the other at constant analytical ligand concentration, c_L = 1 mmol dm^{-3}; c_L and [H] were varied in the range $0.24 < c_L < 8$ mmol dm^{-3} and $0.05 < [H] < 0.2$ mol dm^{-3}, respectively. The high concentration of hydrogen ions assures that the free metal-ion concentration, [Ag], is always superior to 10^{-10} mol dm^{-3} and thus it can be measured accurately. Also, [H] determines the upper limit of c_L as protons generated by the ligand have to be negligible compared to [H], otherwise the graphical treatment of the experimental data would be affected. In each titration of this first set Ag^I was added to an acidified solution of the ligand. After each addition pAg was calculated from the e.m.f. of the cell: r.e.|1.9 mol dm^{-3} $NaNO_3$, 0.1 mol dm^{-3} HNO_3, 10% v/v MeOH||s.p.|Ag_2S|Ag where r.e. ≡ Ag, AgCl|1.89 mol dm^{-3} $NaNO_3$, 0.1 mol dm^{-3} HNO_3, 0.01 mol dm^{-3} NaCl, 10% v/v MeOH.

In the second set seven potentiometric titrations of solutions of differing concentrations containing silver nitrate and 4-mercapto-1-methylpiperidinium nitrate in an excess of nitric acid were carried out. In each titration the total concentration of metal, c_{Ag}, and that of the ligand, c_L, were held constant while the pH was varied by adding a sodium hydroxide solution in the nitrate medium; c_{Ag} was varied in the range 0.8—4 mmol dm^{-3} and c_L according to the molar ratio $2.5 < c_L/c_{Ag} < 6.5$. The hydrogen-ion concentration in the test solution was calculated from the e.m.f. of the cell r.e.|2.0 mol dm^{-3} $NaNO_3$, 10% v/v MeOH||s.p.|g.e. where r.e. ≡ Ag, AgCl|1.99 mol dm^{-3} $NaNO_3$, 0.01 mol dm^{-3} NaCl, 10% v/v MeOH.

Calculations and Results

Acid Dissociation Constants of the Cation 4-*Mercapto*-1-*methylpiperidinium from E.m.f. Data*.—The pK values corresponding to the equilibria $H_2A \rightleftharpoons HA + H$ (pK_1) and $HA \rightleftharpoons A + H$ (pK_2) (charges are omitted throughout for clarity) were calculated from 87 pairs of values of the experimental function $\bar{n}_H$, which refers to the average number of dissociable protons bound to the ligand, and the corresponding pH; $\bar{n}_H$ was calculated from the primary data and from the value found for K_w in the medium used (pK_w = 13.81 ± 0.2) according to equation (1). A first estimate for pK_1 and pK_2 was

$$\bar{n}_H = \frac{c_H - [H] + K_w[H]^{-1}}{c_L} \tag{1}$$

obtained from the pH values at $\bar{n}_H$ = 1.5 and 0.5, respectively, in the Bjerrum plots.[16] The constants were subsequently refined by means of the computer program SUPERQUAD (the Florence version was employed).[17] Final values are $pK_1 = 8.75 \pm 0.01$ and $pK_2 = 10.55 \pm 0.01$. Calculated curves of $\bar{n}_H$ *vs*. log[H] [equation (1)] were in very good agreement with the experimental points.

Silver Complex Species in an Acidic Medium.—In order to get some information about the stoicheiometry of the soluble complex species existing in a strong acidic medium the extended variation method,[18] adapted to metal electrode data, was used. The method, which applies to mono- and poly-nuclear metal complexes, implies acquiring two data sets. Accordingly, a first series of titrations at constant pH (Figure 1) and a second one at constant c_L (Figure 2) were carried out. Data exclusively from the 'common point' titration, together with equations (2)—(5) allowed us to calculate the average stoicheiometric coefficients for $Ag_pA_qH_r$ complexes where S = Sillén's complexity

$$\bar{p} = (c_{Ag} - [Ag])/S' \tag{2}$$

$$\bar{q} = \{c_L - [A] - ([A][H]/K_2) - ([A][H]^2/K_1K_2)\}/S' \tag{3}$$

$$\bar{r} = \{c_H - ([A][H]/K_2) - (2[A][H]^2/K_1K_2) - [H] + (K_w/[H])\}/S' \tag{4}$$

$$S' = S - ([A]/K_2) - ([A][H]^2/K_1K_2) \tag{5}$$

sum[11c] = sum of concentrations of all complex species present in solution.

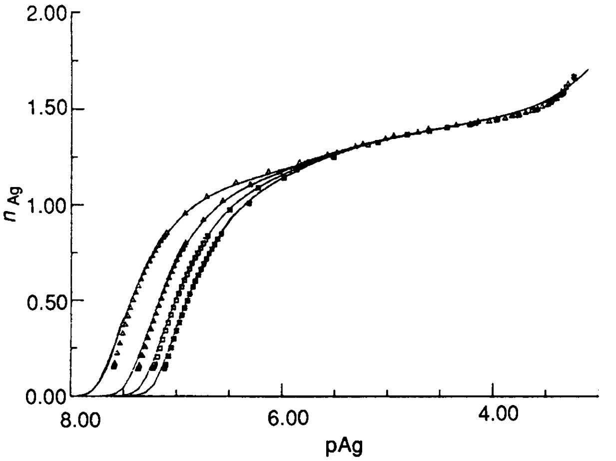


Figure 2. Formation curve for $Ag_p(AH)_q$ species at constant analytical ligand concentration (c_L = 1.00 mmol dm^{-3}) and at different pH values. The lines drawn were calculated from the constants in Table 2. 10^3[H] = 50.0 (△), 100.0 (▲), 150.0 (□), and 200.0 (■) mmol dm^3

Despite the complexity of the mathematical treatment involved[18] and the inevitable approximations made when calculating $\bar{p}$, $\bar{q}$, and $\bar{r}$, their variation with pAg suggests that the following assumptions can be made. On the one hand, it seems likely that the complexed ligand in species $Ag_pA_qH_r$ is in a monoprotonated form or that the complex species can be formulated as $Ag_p(AH)_q$.* Solution equilibria studies with the same ligand[7a,b] and with other γ-mercaptoamines[7c,d] reinforce this assumption. On the other hand, it is clear that the nuclearity of the soluble complexes decreases as the free silver-ion concentration increases, $\bar{p}$ and $\bar{q}$ being ≈ 5 and ≈ 3, respectively, at the maximum [Ag] studied. However, the information contained in these curves for pAg > 6 is too ambiguous, and thus it seemed convenient to apply other graphical methods.

Consequently, the experimental function $\bar{n}_{Ag} = (c_{Ag} - [Ag])/c_L$, representing the average number of bound silver ions per ligand which can be calculated from experimental data, was plotted *versus* pAg for titrations referred to as series at constant pH, Figure 1, and for those corresponding to series at constant c_L, Figure 2.

The shape of the curves $\bar{n}_{Ag}$ *vs.* pAg, Figure 1, indicates that up to $\bar{n}_{Ag} \approx 1.25$ the 'core + links' hypothesis[11a,b] may be used. Despite the fact that Sillén's graphical methods were developed for experimental data obtained at constant analytical metal and ligand concentrations and variable pH values, they can easily be adapted to our experimental conditions. Accordingly, complexes of formula $Ag_p(AH)_q$ can be written in the form $(AH)[(AH)Ag_t]_n$, where t is a constant and n a variable integer. The value for t in the region $\bar{n}_{Ag} < \bar{n}_{max.}$, where $\bar{n}_{max.}$ corresponds to the point where all the curves intersect, was determined from the slope of the lines log c_L *vs.* log [Ag] at constant $\bar{n}_{Ag}$.

After calculating the regression lines with a computer, the final value, with its standard deviation in parentheses, for the range $0.2 < \bar{n}_{Ag} < 0.9$ is $t = 1.42(5)$. Thus, the value for t should be in the range $1.26 < t < 1.58$.

Experimental data at constant c_L, Figure 2, were also treated, as they can furnish information about the range of variation of the ratio $\bar{p}/\bar{q}$ in $Ag_p(AH)_q$ complexes existing in an acidic medium. By expressing $\bar{n}_{Ag}$ as a function of the equilibrium constant $\psi^*_{p,q}$,† which corresponds to the reaction (6) and by considering two points, from different titrations of the mentioned series, with the same $\bar{n}_{Ag}$ value, one can derive expression (7). Assuming that only one complex species is present, $[H_2A] = c_L - q[Ag_p(AH)_q]$ and $\bar{n}_{Ag} = p[Ag_p(AH)_q]/c_L$, it is easily deduced that $[H_2A] = c_L[1 - (q/p)\bar{n}_{Ag}]$. Thus, for two points with the same $\bar{n}_{Ag}$ value it holds that $[H_2A]_1 = [H_2A]_2$ which when introduced into equation (7) gives $[Ag]^p_1[H]^{-q}_1 = [Ag]^p_2[H]^{-q}_2$ and may be rearranged to equation (8).

$$pAg + qH_2A \rightleftharpoons Ag_p(AH)_q + qH$$

$$\psi^*_{p,q} = \frac{[Ag_p(AH)_q][H]^q}{[Ag]^p[H_2A]^q} \qquad (6)$$

$$\bar{n}_{Ag} = \Sigma p\psi^*_{p,q}[Ag]^p_1[H_2A]^q_1[H]^{-q}_1/c_L$$

$$\Sigma p\psi^*_{p,q}[Ag]^p_2[H_2A]^q_2[H]^{-q}_2/c_L \qquad (7)$$

$$\left(\frac{\Delta pH}{\Delta pAg}\right)_{c_L,\,\bar{n}_{Ag}} = \frac{p}{q} \qquad (8)$$

When many species are simultaneously present relation (7) still holds and (8) will provide us with the average stoicheiometric coefficients of $Ag_p(AH)_q$ complexes. In the range from $\bar{n}_{Ag} = 0.2$ to 1.0 the curves $\bar{n}_{Ag}$ *vs.* log[Ag], Figure 2, are practically parallel which means that $\bar{p}/\bar{q}$ changes very little under these experimental conditions. Thus, the value for $\bar{p}/\bar{q}$ was determined from the slope of the lines pH *vs.* pAg. The calculated regression lines led us to the final value $\bar{p}/\bar{q} = 1.19(4)$ for $0.2 < \bar{n}_{Ag} < 1.0$. Consequently, the value for $\bar{p}/\bar{q}$ should be in the range $1.07 < \bar{p}/\bar{q} < 1.31$. Taking into account that $\bar{n}_{max.}$ in the curves $\bar{n}_{Ag}$ *vs* pAg is 1.25, Figure 2, the upper limit for the ratio $\bar{p}/\bar{q}$ was fixed at this value.

The first set of possible species existing in solution, Table 1, was deduced from a numerical method. The limiting conditions $1.26 < t < 1.58$, $1.07 < p/q < 1.25$, and $p_{max.} = 14$ were imposed on the relations $p = tn$ and $q = n + 1$ which are easily derived from the formulae $Ag_p(AH)_q$ and $(AH)[(AH)Ag_t]_n$. The p,q pairs were obtained by varying n in integer numbers for t values (which were increased by 0.005 units) within the given range. The maximum nuclearity allowed for the complex species, $p_{max.} = 14$, is based mainly upon the structure of a solid silver(I) complex of the same ligand,[20] and also on solid silver(I)-thiolate complexes of known structure.[1,21] To the set of possible species given in Table 1 were added: (*a*) those combinations of p = 6,7,8 and q = 5,6,7 and of p = 4,5,6 and q = 2,3,4 following the condition $p/q \geqslant \bar{n}_{max.}$, as their possible existence could be inferred from the curves $\bar{p}$, $\bar{q}$, and $\bar{r}$ *vs.* pAg and (*b*) complex species of formula $[Ag(AH)]_n$, $6 \leqslant n \leqslant 12$, as solid homoleptic silver(I) thiolate complexes with high nuclearities and a metal-to-thiol ratio of 1:1 have been reported.[1]

Approximate formation constants corresponding to the species in the model were calculated as follows. First, possible complexes were gathered in 'core + links' families. Then, within each family, the reaction constants $\psi^*_{p,q}$ [equation (6)] of the two members with lower nuclearity were estimated by assuming that at $\bar{n}_{Ag} = p/q$, Figure 2, $Ag_p(AH)_q$ was the only species present, therefore its concentration at equilibrium could be calculated as

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* The complexed monoprotonated ligand is denoted by AH as it is a particular case, $q = r$, of the general expression $Ag_pA_qH_r$. However, HA refers to the free monoprotonated ligand and according to the footnote on the title page it includes the zwitterionic, $H\overset{+}{N}$–R–S$^-$, and the uncharged form, N–R–SH.

† $\psi^*_{p,q}$ [equation (6)] and $\psi_{p,q}$ [equation (9)] are related: $\psi^*_{p,q} = \psi_{p,q}K_1{}^q$. The overall formation constant $\beta_{p,q,q}$ and $\psi_{p,q}$ are related by $\beta_{p,q,q} = \psi_{p,q}K_2^{-q}$, where K_1 and K_2 are defined in the text.

Table 1. Set of possible p,q values for $Ag_p(AH)_q$ species which meet the requirements $p_{max.} = 14$, $1.26 < t < 1.58$, and $1.07 < p/q < 1.25$

p	6	7	8	9	10	10	11	12	13	14
q	5	6	7	8	9	8	9	10	11	12

Table 2. Silver complex-formation constants for the species $Ag_p(AH)_q$ at 25 °C and $I = 2.0$ mol dm^{-3} ($NaNO_3$) (+10% v/v MeOH) from the silver electrode data and the program SUPERQUAD[17]

Species	p	q	$\log \psi_{p,q}$
(a)	6	3	63.67 ± 0.04
(b)	6	4	79.95 ± 0.03
(c)	8	6	117.37 ± 0.04
(d)	7	6	111.72 ± 0.05
(e)	10	9	166.01 ± 0.09
(f)	12	12	212.2 ± 0.4

Number of points 384, from nine separate titrations. Estimated variances of the electrode and volume readings are respectively σ_E = 0.2—0.3 mV and σ_V = 0.01 cm^3. Sample standard deviation: σ = 4.87; σ_E, σ_V, and σ are defined as in ref. 17.

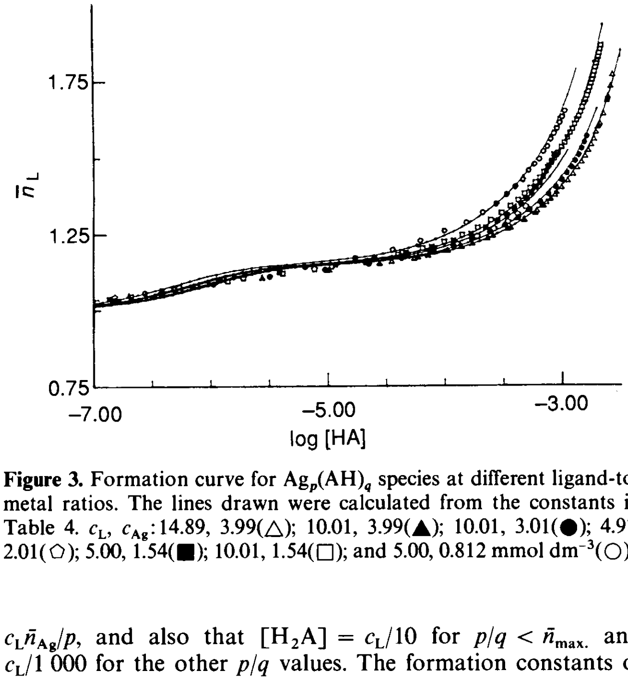

Figure 3. Formation curve for $Ag_p(AH)_q$ species at different ligand-to-metal ratios. The lines drawn were calculated from the constants in Table 4. c_L, c_{Ag}: 14.89, 3.99(△); 10.01, 3.99(▲); 10.01, 3.01(●); 4.97, 2.01(⬠); 5.00, 1.54(■); 10.01, 1.54(□); and 5.00, 0.812 mmol dm^{-3}(○)

$c_L\bar{n}_{Ag}/p$, and also that $[H_2A] = c_L/10$ for $p/q < \bar{n}_{max.}$ and $c_L/1\,000$ for the other p/q values. The formation constants of the other members of the family can now be calculated using Sillén's hypothesis.[7b,11b] From all these $\psi^*_{p,q}$ values the corresponding formation constants $\psi_{p,q}$ [equation (9)], are estimated very easily.

In order to determine the set of $[Ag_p(AH)_q]^{p+}$ species and equilibrium constants $\psi_{p,q}$, for the reaction (9) that best fit the experimental data we have referred to up to now, the program SUPERQUAD[17] was used in conjunction with a VAX/VMS computer. However, the following modification had to be carried out in order to avoid errors arising from variations in in the liquid junction potential, E_j. Owing to the fact that during each titration silver(I) ion is added to the initial solution, complex formation is accompanied by liberation of protons. This causes E_j to change according to $\Delta(E_j)_i = D_h([H]_i - [H]_0)$, where D_h is a constant and $[H]_i$ and $[H]_0$ denote the free hydrogen-ion concentration in the test solution when [Ag] corresponds to the point i or is zero, respectively. In a 2.0 mol dm^{-3} $NaNO_3$ medium D_h can be taken as 30 mV dm^3 mol^{-1}.[22] Accordingly, the program calculated the theoretical electrode potential, E_t, from a given set of constants by means of the equation $E_t = E_0 - 59.16 \log[Ag] - D_h([H]_i - [H]_0)$. Results are given in Table 2 together with the statistical data characteristic of the refinement.

$$p\,Ag^+ + q\,HA \rightleftharpoons [Ag_p(AH)_q]^{p+}$$

$$\psi_{p,q} = \frac{[Ag_p(AH)_q]^{p+}}{[Ag^+]^p[HA]^q} \qquad (9)$$

Silver Complex Species in Solutions at pH *Values in the range* $4 \leqslant pH \leqslant 8$.—Experimental data from the second set of titrations allowed us to construct the plots of $\bar{n}_H$ *vs.* pH and $\bar{n}_L$ *vs.* log[HA] (Figure 3). The experimental function $\bar{n}_L$ refers to the average number of ligands bound to one metal atom and [HA] denotes the concentration of free monoprotonated ligand; $\bar{n}_H$, $\bar{n}_L$, and [HA] were calculated, respectively, from equation (1) and from $\bar{n}_L = c_L(\bar{n}_H - X)/c_{Ag}(1 - X)$ where $X = (2/[H]^2 + K_1[H])/([H]^2 + K_1[H] + K_1K_2)$ and $[HA] = (c_L - \bar{n}c_{Ag})K_1[H]/([H]^2 + K_1[H] + K_1K_2)$.

Knowing that 4-mercapto-1-methylpiperidinium cation has two dissociable protons, $(\bar{n}_H)_{max.} = 2$, the curves $\bar{n}_H$ *vs.* pH clearly indicate that complexation starts at pH < 4. Complex species existing in a strong acidic medium have already been reported in this work. It also appears that in the range $4 \leqslant pH \leqslant 7$ the complexed ligand behaves as a 'monoprotonated ligand' as of all experimental points $\bar{n}_H > 1.15$. For this value of $\bar{n}_H$ the fraction of unprotonated ligand, $[A]/c_L$, where [A] denotes the concentration of free completely deprotonated ligand, is at most 5%.* This behaviour, which is in agreement with results found for γ-mercaptoamine systems with Zn^{II} and Cd^{II} within practically the same pH range,[7] allows us to assume that the complex species may be formulated as $Ag_p(AH)_q$.

If the system is reduced to a two-component one, the core + links' hypothesis can be used. The displacement of the curves $\bar{n}_L$ *vs.* log [HA] towards smaller values of −log[HA] at increasing c_{Ag} indicates that $[Ag] \ll c_{Ag}$ and thus, according to Sillén,[11a,b] 'core + links' complexes have to be formulated as $(HA)_r[Ag(HA)_t]_n$ where $r,t > 0$. The value of r was deduced from the slope of the lines $\log c_{Ag}$ *vs.* log[HA] at constant $\bar{n}_L$, calculated by linear regression. The value found, with its standard deviation in parentheses, for the range $1.45 < \bar{n}_L < 1.60$ is r = 1.88(16), and thus $1.40 < r < 2.36$. In order to know the value of t, the expression $(\bar{n}_L)_{min.} = t + r/n_{max.}$[11a] was used; where $(\bar{n}_L)_{min.} = 1$, according to Figure 3, r should be in the range given above, and the maximum nuclearity of the complex species, $n_{max.}$, was taken as 12 in agreement with results given in Table 2. All these conditions revealed that t should be in the range $0.80 < t < 0.88$.

Once again, a numerical method was used in order to know the first set of species existing in solutions under our experimental conditions. By comparing the formulae $Ag_p(HA)_q$ and $(HA)_r[Ag(HA)_t]_n$ the following relations hold: $p = n$, n being an integer, and $q = nt + r$. By applying the restrictions $0.80 < t < 0.88$, $1.40 < r < 2.36$, $p_{max.} = 12$, and $1 < p/q \leqslant 3$, the set of p,q pairs given in Table 3 was obtained. The lower limit for the ratio p/q was fixed by that found in the species of highest nuclearity, *i.e.* $Ag_{12}(HA)_{12}$ (Table 2), while the upper one was deduced from bibliographic data.[23]

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* In order to get a rough estimate of the value of $\bar{n}_H$ corresponding to $[A]/c_L = 0.05$, the mass-balance equation $c_L = [A]\{1 + ([H]/K_2) + ([H]^2/K_1K_2)\}$ is solved for [H]. The value for $\bar{n}_H$ can now be found either by means of equation (1) or from the plots of $\bar{n}_H$ *vs.* [H] in the absence of metal.

Table 3. Set of possible p,q values for $Ag_p(AH)_q$ species which meet the requirements $p_{max.} = 12$, $1.45 < \bar{n}_{Ag} < 1.6$, $0.8 < t < 0.88$, $1.40 < r < 2.36$, and $1 < q/p \leqslant 3$

p	1	2	2	3	3	4	4	5	6	7	8	9	10	11	12
q	3	3	4	4	5	5	6	6	7	8	9	10	11	12	13

Table 4. Silver complex-formation constants for the species $Ag_p(AH)_q$ at 25 °C and $I = 2.0$ mol dm^{-3} ($NaNO_3$) (+10% v/v MeOH) from the pH electrode data and the program SUPERQUAD[17]

Species	p	q	$\log \psi_{p,q}$
(g)	7	8	128.52 ± 0.06
(h)	6	8	113.4 ± 0.2
(i)	2	3	36.67 ± 0.09
(j)	1	3	20.71 ± 0.04

Number of points 238, from seven separate titrations. Estimated variances of the electrode and volume readings are respectively $\sigma_E = 0.1$ mV and $\sigma_V = 0.01$ cm^3. Sample standard deviation: $\sigma = 8.76$.

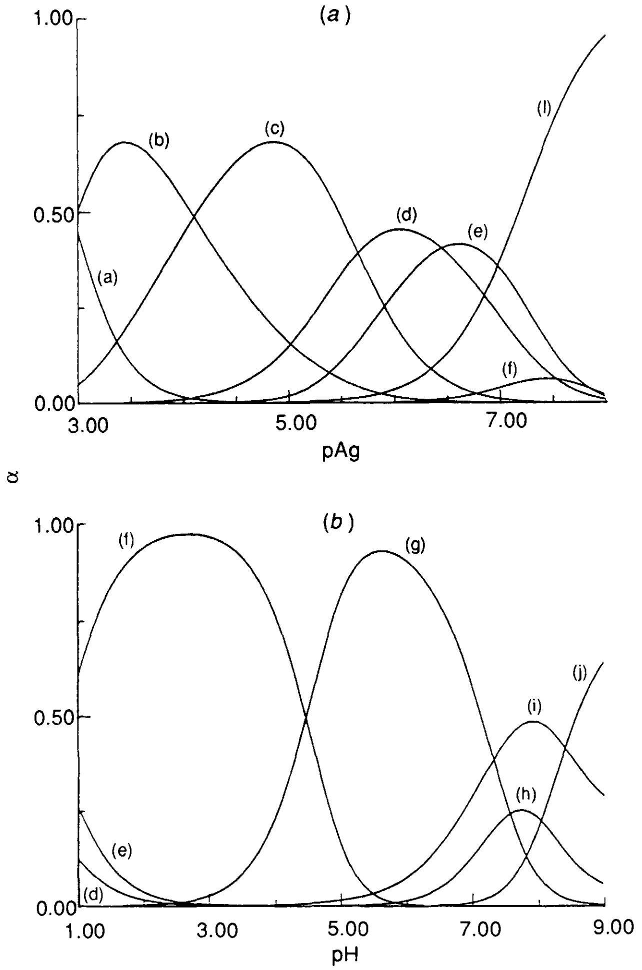

Figure 4. Species distribution curves: (a) as a function of pAg at c_L = 8.00, [H] = 100.0 mmol dm^{-3}; (b) as a function of pH at c_{Ag} = 3.00, c_L = 10.0 mmol dm^{-3}. For the key to the symbols see Tables 2 and 4; (l) denotes the free ligand, diprotonated H_2A

Reported solid metal(I) thiolate complexes (M^I = Cu or Ag) of known structure have the same ligand-to-metal ratio as that of the soluble $Ag_p(HA)_q$ species with p,q values 1,3;[23] 4,6;[23a,24] and 5,6[9b,25] given in Table 3. Considering that the set of possible species is formed by the families $(HA)[(HA)Ag]_n$ (n = 1—12 and $(HA)_2[(HA)Ag]_n$ where n = 1—6, not only the species of Table 3 but also those with the same stoicheiometric ratio as that of other metal(I) thiolate solid complexes (5,7;[26] 6,8;[6] 12,16;[6] and 1,2[23b,27]) should be included. Thus, both mentioned families together with the corresponding approximate formation constants, calculated as already indicated, were introduced in the program SUPERQUAD.[17]

While refining the model, the species $Ag_{12}(HA)_{12}$ and $Ag_{10}(AH)_9$ together with their formation constants were included as they are present in solutions corresponding to $\bar{n}_L \approx 1$. The set of species and constants that gave the lowest values for σ,[17] and thus constituting the best set, is given in Table 4.

Discussion

Results from the numerical treatment, Tables 2 and 4, allow us to conclude that under our experimental conditions all species present in solution can be represented by the general formula $[Ag_p(AH)_q]^{p+}$, AH denoting 4-mercapto-1-methylpiperidine in a monoprotonated form, and also that all soluble species are polynuclear, $p > 1$, except for $[Ag(AH)_3]^+$. Data given in these tables enable the species distribution curves to be calculated. Those corresponding to a particular constant value of c_L and pH at varying free silver(I)-ion concentration and to a fixed ratio c_L/c_{Ag} at varying pH are given in Figure 4(a) and (b), respectively.

Even though the complexed ligand, AH, can be either in its uncharged or in its zwitterionic form, arguments such that (a) the already well known strong affinity of Ag^I for mercaptide sulphur, (b) the predominance of the zwitterionic form of the ligand over the uncharged one even in the absence of metal ions, (c) the structure of several solid complexes with the γ-mercaptoamine ligands in zwitterionic form,[8,9] meanwhile a complex with this type of ligands in their uncharged form has not been found yet, strongly indicate that the complexed monoprotonated ligand corresponds exclusively to 1-methylpiperidinium-4-thiolate. The same assumption has been used previously in other solution equilibria studies.[7]

The stoicheiometry of the soluble species at acidic pH, Figure 4(a), agrees well with the variation of the calculated average stoicheiometric coefficients of species existing at the same pH value. Thus, the nuclearity, p, of $[Ag_p(HA)_q]^{p+}$ species is high at low free metal-ion concentration, $p = 12$ at pAg = 7.5, Figure 4(a), and it goes on decreasing as this concentration increases, $p = 6$ at pAg $\leqslant$ 3.5. At the same time the ratio $p/q = 1:1$ at pAg = 7.5 and from then on it increases steadily up to $p/q = 2:1$. The values $\bar{p} = 6$ and $\bar{q} = 3.5$ at pAg ≈ 3, deduced from Figure 4(a), are not far from those expected from the graphical treatment, despite its being only indicative because of the elaborate calculus involved and the approximations required. It is worth noting that a rigorous adaptation of the extended variation method[18] to this particular system would have needed a series of titrations at constant analytical hydrogen-ion concentration, c_H, instead of that at constant free hydrogen-ion concentration. The choice is not an easy one because the graphical treatment of $\bar{n}_{Ag}$(pAg) curves requires constant pH. Despite the fact that under our experimental conditions the above two concentrations do not differ much and that important deviations have not been detected, we have tried the alternative c_H = constant in the following paper.[22]

While in solutions with pH 1 the stoicheiometric coefficients of the complex species obey the relation $p \geqslant q$, at increasing pH which at the same time implies increasing concentration of monoprotonated ligand, species with $p \leqslant q$ are the only soluble complexes, as is shown in Figure 4(b). The only species found with $p = q$ corresponds to $[Ag_{12}(AH)_{12}]^{12+}$. This cationic complex has the highest nuclearity of all soluble species and is on the borderline between complexes $[Ag_p(AH)_q]^{p+}$ with $p > q$ and $p < q$. This nuclearity agrees very well with the molecularity of crystalline (cyclohexanethiolato)silver(I) and with that expected for Ag(SR) compounds dissolved in non-polar solvents when R is a secondary alkyl group.[1,4] The main difference between $[Ag_{12}(AH)_{12}]^{12+}$ and the complexes just mentioned lies in the overall electric charge of the former, which may account for its good solubility and high predominance over a quite large pH range in aqueous–methanolic solution, Figure 4(*b*). On the other hand, the set of species found in this work confirms Schwarzenbach's hypothesis that the well known slightly soluble Ag(SR) complexes give rise to polynuclear $[Ag(AgSR)_n]^+$ and $[SR(AgSR)_n]^-$ species in aqueous solutions in the presence of an excess of Ag^+ or SR^-, respectively.[5]

While no solid species of formula $[M_x(SR)_y]^{x-y}$ ($x > y$, M = Ag^I or Cu^I) has been reported to date, several polynuclear species with $x < y$ have been fully characterized. The idealized structures of $[Cu_4(SR)_6]^{2-}$,[23a,24] $[Cu_5(SR)_6]^-$,[25] $[Ag_5\{S(CH_2)_3NMe_2\}_3[S(CH_2)_3NHMe_2\}_3]^{2+}$,[9b] $[M_5(SR)_7]^{2-}$ (M = Cu^I or Ag^I),[26] and $[Ag_6(SR)_8]_n{}^{2n-}$ ($n = 1$ or 2)[6] have suggested the existence of a polyhedral expansion mechanism relating M_4S_6, M_5S_7, and M_6S_8 cages as well as a polyhedral contraction between M_5S_7 and M_5S_6, and also topological relationships between the cage and metal polyhedra.[28]

The structure of the mononuclear anion $[Cu(SPh)_3]^{2-}$[23b] has also been reported. This diversity of complex species, often isolated from solutions very similar in composition and with excess of thiolate ligand,[6] indicates that metal(I) thiolate systems are involved in very complex solution equilibria and thus small changes in the experimental conditions such as the solvent composition and temperature determine the nature of the solid phases. The importance of identifying the $[M_x(SR)_y]^{x-y}$ species in solution and their relative concentrations is then obvious. Under the present experimental conditions the $[Ag_p(AH)_q]^{p+}$ species with $q > p$ have the following *p*,*q* values: 7,8; 6,8; 2,3; and 1,3; the first predominates over a wide pH range, Figure 4(*b*). As indicated above, no thiolate of Ag^I or Cu^I with the same stoicheiometric coefficients as that of species 7,8 and 2,3 has been reported yet. However a silver(I) complex, $[Ag_{14}(\mu\text{-}SBu^t)_{14}(PPh_3)_4]$,[21a] with a nuclearity twice as great as that of species 7,8 and copper(I) thiolates, $[Cu_4(SR)_6]^{2-}$,[23a,24] with the same stoicheiometric ratio as that of species 2,3 are known. As no solid separated out from potentiometric solutions even after a few days in the dark, it is not possible to know whether the soluble species 7,8 and 2,3 are structurally related or can be considered as precursors of the silver and copper complexes just mentioned.

By means of the complex-formation constants given in Tables 2 and 4, theoretical curves corresponding to all the experimental functions have been drawn, (Figures 1—3). In general, the agreement is very good except for some points of the curves of ($\bar{n}_{Ag}$ *vs.* pAg), Figure 2, corresponding to $c_L = 8.00$ and 4.01 mmol dm^{-3}. In both cases, comparison of the experimental and theoretical slopes made us discard species with $q > p$. Consequently, several complexes with $q < p$, up to $p = 28$,[20] were introduced in the mathematical treatment of data, but this was unsuccessful. Thus, these points were not considered in the final refinement.

A comparison of the behaviour of Ag^I in solutions containing different aliphatic γ-mercaptoamine ligands[22] as well as several solid complexes obtained under varied experimental conditions[9b,20] have been reported.

Acknowledgements

Grants from the Comisión Asesora de Investigación Científica y Técnica (1058–84) and the Comisión Interministerial de Ciencia y Tecnología (PB87–0188) are gratefully acknowledged.

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Received 22nd *September* 1989; *Paper* 9/04051J