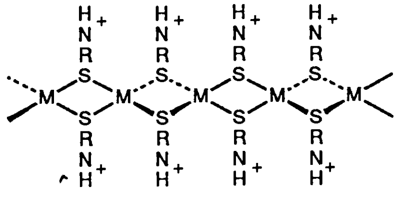
Polynuclear Thiolate Complexes in Solution. Solution Equilibria Studies of Silver(I) Complexes of 3-(Dimethylamino)propane-1-thiol and 3-Aminopropane-1-thiol and Comparative Study with 4-Mercapto-1-methylpiperidine

Pilar González-Duarte * **and Josep Vives**
Departament de Química, Universitat Autònoma de Barcelona, 08193 Bellaterra, Barcelona, Spain

The complexation of Ag^I by the ligands 3-(dimethylamino)propane-1-thiol and 3-aminopropane-1-thiol has been studied first in strong acidic solutions and then at increasing pH values, up to pH $\leqslant 8$, at 25 °C in 0.1 mol dm^{-3} NaNO$_3$ (10% v/v MeOH). The extended-variation method and other graphical methods based on the 'core + links' hypothesis have been used and give results in accord with the final equilibrium model obtained by means of the program SUPERQUAD. Species [Ag$_p$(AH)$_q$]$^{p+}$, AH denoting the monoprotonated ligand, in a strong acidic medium have the same stoicheiometric coefficients and comparable formation constants with both ligands; p,q values are 6,3; 6,4; 8,6; 7,6; 10,9; and 12,12. The species 5,6 is already present at low pH with H$_2$N(CH$_2$)$_3$SH. More basic solutions contain species with p,q values 5,6; 4,6; and 1,3 in the case of Me$_2$N(CH$_2$)$_3$SH and 5,6; 5,7; 4,6; 2,4; and 1,3 in that of H$_2$N(CH$_2$)$_3$SH. These results together with those obtained with 4-mercapto-1-methylpiperidine indicate that the species existing in a strong acidic medium are independent of the aliphatic chain of the ligand, whereas at higher pH values the nuclearity and the number of species present depend on the nature of the γ-mercaptoamine.

Previous papers from this laboratory have reported solution equilibria studies of metal aliphatic γ-mercaptoamine systems by potentiometric titrations in aqueous media (+10% v/v MeOH). A main feature of these ligands is that, while they behave as monofunctional thiols over a wide pH range, they also give rise to complex species with adequate solubility in water to be studied by known potentiometric methods. The corresponding zwitterionic form of the ligands, $^-$S–R–$\overset{+}{\text{N}}$H, accounts for this behaviour. However, the slight solubility of metal–simple thiol complexes, derived from their polymeric nature, renders the direct determination of the stoicheiometry of soluble species practically impossible.

Soluble zinc and cadmium complexes with 4-mercapto-1-methylpiperidine [MeNC$_5$H$_9$SH],[1] 3-(dimethylamino)-propane-1-thiol [Me$_2$N(CH$_2$)$_3$SH],[2] and 3-aminopropane-1-thiol [H$_2$N(CH$_2$)$_3$SH][3] up to pH ≈ 9 clearly indicate that polynuclear species of formula [M$_p$(AH)$_q$]$^{2p+}$ ($q < 2p + 2$, where AH denotes the ligand in zwitterionic form) are the precursors of complexes with the same formula but with $q = 2p + 2$, which correspond to short fragments ($p_{\text{max.}} = 5$) of the one-dimensional polymeric chain depicted below. This structure, expected for solid homoleptic thiolate complexes of divalent metals with tetrahedral co-ordination, has already been found in the cation bis(4-mercapto-1-methylpiperidine)cadmium[4a] and in thiolates and selenolates of Hg^{II}.[4b–d]



Soluble silver complexes of 4-mercapto-1-methylpiperidine cannot be compared with those of cadmium and zinc despite they all are d^{10} metal ions. Their different affinities for mercaptide sulphur and co-ordination preferences are well reflected in the structures found for solid silver(I) thiolate complexes and those of Zn^{II} and Cd^{II}.[5] Up to now, most homoleptic silver thiolates of known structure correspond to anionic aggregates of formula [M$_x$(SR)$_y$]$^{x-y}$, $1 < x < y$, which are structurally related. The topological relationships between the different cages found is particularly apparent if copper(I)–thiol complexes are also included.[6] Also, reinforcing our previous comparison between γ-mercaptoamines and simple thiols, it is worth noting that a 3-(dimethylamino)propane-1-thiol complex of Ag^I has afforded the first example of a trigonal bipyramido-M$_5$-trigonal prism-S$_6$ polyhedral stereochemistry,[7] that was lacking in the mentioned M^I_xS$_y$ (M = Cu or Ag) series of complexes.[6]

Reported results on solution equilibria studies of silver(I)–4-mercapto-1-methylpiperidine systems in aqueous medium (+10% v/v MeOH)[8] reveal that over a wide pH range the soluble species correspond to the formula [Ag$_p$(AH)$_q$]$^{p+}$, where AH represents the zwitterionic form, and that the only species with $p = q$, [Ag$_{12}$(AH)$_{12}$]$^{12+}$, transforms into complexes with $p > q$ or $p < q$ at increasing concentration of metal or ligand, respectively. We now report the stoicheiometry and corresponding formation constants when the ligands are Me$_2$N(CH$_2$)$_3$SH and H$_2$N(CH$_2$)$_3$SH and compare these results with those for 1-mercapto-4-methylpiperidine.

Experimental

Reagents.—The syntheses of Me$_2$N(CH$_2$)$_3$SH from 3-dimethylaminopropan-1-ol (Fluka) and that of H$_2$N(CH$_2$)$_3$SH from 3-aminopropan-1-ol (Fluka) were carried out according to known procedures.[9] The purification and analytical methods used for both compounds have been reported.[2,3] Solutions of the ligands in presence of nitric acid as well as stock solutions of silver nitrate, sodium nitrate, nitric acid, and sodium hydroxide in aqueous methanol (10% v/v MeOH) were prepared as indicated in the preceding paper.[8]

Apparatus and Procedures.—The titrations were performed in 10% (v/v) aqueous–methanolic solutions at constant temperature (25.0 ± 0.1 °C) and ionic strength (0.1 mol dm^{-3} NaNO$_3$),

Table 1. Experimental data for potentiometric titrations[a]

Titration no.	Ag^I–$Me_2N(CH_2)_3SH$			Ag^I–$H_2N(CH_2)_3SH$		
	c_L	c_H	c_{Ag}	c_L	c_H	c_{Ag}
	mmol dm^{-3}			mmol dm^{-3}		
1	0.385	50.0		0.375	50.0	
2[b]	0.735	50.0		0.750	50.0	
3	1.50	50.0		1.50	50.0	
4[c]	3.01	50.0		3.02	50.0	
5	6.00	50.0		5.98	50.0	
6	3.01	25.0		3.02	25.0	
4[c]	3.01	50.0		3.02	50.0	
7	3.01	100.0		3.02	100.0	
8	0.735	25.0		0.750	25.0	
2[b]	0.735	50.0		0.750	50.0	
9	0.735	100.0		0.750	100.0	
10	2.50		1.50	2.53		1.50
11	5.00		1.50	5.00		0.753
12	9.99		1.50	5.00		1.50
13	15.01		3.00	10.00		1.50
14	9.99		3.00	10.00		3.00
15	9.99		5.99	10.00		5.97
16				14.98		3.00

[a] At 25 °C; ionic strength adjusted to 0.1 mol dm^{-3} with $NaNO_3$. [b,c] 'Common point' titrations.

under a nitrogen atmosphere. The compositions of the titrated solutions are given in Table 1. The relatively low ionic strength is determined by the well known slight solubility of $[Ag(SR)]_n$ complexes, which decreases at increasing concentration of the medium salt. The standardization of the glass (Ingold HA 201) and silver sulphide working electrodes, as well as the remainder of the computer-controlled potentiometric system, has been described.[8] The titration procedures employed to determine the acidity constants of the open chain γ-mercaptoamine ligands are the same as that used for the cyclic one,[8,10] as were those corresponding to the formation constants of the soluble complexes.[8] The only differences, Table 1, are: (*a*) the set of titrations referred to as series at constant pH has been replaced in this case by one at constant analytical hydrogen-ion concentration, c_H; (*b*) two series of titrations, instead of one, referred to as series at constant analytical ligand concentration c_L, have been carried out; (*c*) the cells used to calculate the concentration of free silver and hydrogen ions are, respectively, r.e.|0.05 mol dm^{-3} $NaNO_3$, 0.05 mol dm^{-3} HNO_3, 10% v/v MeOH||s.p.|Ag_2S|Ag where s.p. denotes the test solution and r.e. the reference electrode is represented by Ag, AgCl|0.04 mol dm^{-3} $NaNO_3$, 0.05 mol dm^{-3} HNO_3, 0.01 mol dm^{-3} NaCl, 10% v/v MeOH, and r.e.|0.1 mol dm^{-3} $NaNO_3$, 10% v/v MeOH||s.p.|g.e. where g.e. denotes the glass electrode and r.e. corresponds to Ag, AgCl|0.09 mol dm^{-3} $NaNO_3$, 0.01 mol dm^{-3} NaCl, 10% v/v MeOH.

In all titrations belonging to the set referred to as that at constant c_L and c_{Ag} and varying pH, c_{Ag} being the analytical silver-ion concentration, c_L/c_{Ag} has to be greater than one otherwise silver(I) oxide separates out.

Calculations and Results

Acid Dissociation Constants of the Cations 3-(*Dimethylammonio*)*propane*-1-*thiol and* 3-*Ammoniopropane*-1-*thiol from E.m.f. Data.*—For both ligands three potentiometric titrations of the corresponding acidified solutions at constant c_L were carried out. From 135 (3-Me_2N) or 101 (3-H_2N) pairs of values of log[H] and $\bar{n}_H$, which refers to the average number of dissociable protons bound to ligand, the acid dissociation constants K_1 and K_2 ($H_2A \xrightarrow{K_1} HA \xrightarrow{K_2} A$) in 0.1 mol dm^{-3} (sodium) nitrate medium (+10% v/v MeOH) were calculated with the program SUPERQUAD,[11] as already described. The value found for K_w in this medium ($pK_w = 13.81 \pm 0.02$) did not differ from that calculated in a 2 mol dm^{-3} (sodium) nitrate aqueous–methanol solution.[8] Final pK_1 and pK_2 values are: $Me_2H\overset{+}{N}(CH_2)_3SH$, $pK_1 = 8.80 \pm 0.01$, $pK_2 = 10.63 \pm 0.01$; $H_3\overset{+}{N}(CH_2)_3SH$, $pK_1 = 8.87 \pm 0.02$, $pK_2 = 10.19 \pm 0.02$. The theoretical $\bar{n}_H$ *vs.* log[H] curves calculated with these values agree very well with the experimental points.

Silver-3-(*Dimethylamino*)*propane*-1-*thiol Soluble Species and Corresponding Complex-formation Constants.*—A detailed explanation concerning the choice and the conclusions drawn from the graphical methods used throughout this work can be found in the preceding paper.[8]

Acquisition of experimental data. Fifteen potentiometric titrations were divided into two sets, Table 1, as is required in those systems where complex species are already present in a strong acidic medium. The first set included nine titrations that were distributed in three series, one at constant c_H and the other two at constant c_L; c_H and c_L were varied, respectively, in the ranges $25 < c_H < 100$ and $0.38 < c_L < 6$ mmol dm^{-3}. These values assure that the free silver-ion concentration, [Ag], is always high enough to be measured accurately and also that the free hydrogen-ion concentration, [H], is always close to the value of c_H. Thus, if c_H is kept constant the pH can be considered as approximately constant. During each of these nine titrations variable-volume aliquots of $AgNO_3$ titrant were added to an acidified solution of the ligand. Following each addition, the pAg was calculated from the metal electrode reading. The second set included six titrations at constant c_L and c_{Ag}. The latter was varied in the range $1.5 < c_{Ag} < 6$ mmol dm^{-3} and c_L according to the molar ratio $1.6 < c_L/c_{Ag} < 6.7$. The highest c_{Ag} is limited by the ionic strength, which at the same time is determined by the solubility of the complex species, as already indicated. During these titrations variable-volume aliquots of NaOH titrant were successively added to the test solution and then the pH was calculated from the glass electrode reading.

Silver complex species with $Me_2N(CH_2)_3SH$ *in acidic medium.* Experimental data from the two 'common point' titrations, Table 1, together with known equations[8] allow one to calculate the variation of the average stoicheiometric coefficients of $Ag_pA_qH_r$ complexes (charges are omitted throughout for clarity) as a function of pAg for two different (c_L,c_H) pairs of values. The results obtained for the pair (3.01, 50 mmol dm^{-3}) indicate that all complex species have the same number of completely deprotonated ligands, A, as that of protons, $q = r$, and that the nuclearity, p, of the complexes, which is undetermined but very high for pAg > 6.5, tends to ≈7 at higher free silver-ion concentrations. The behaviour of this ligand is thus similar to that of 4-mercapto-1-methylpipridine.[8] The curves $\bar{p},\bar{q},\bar{r}$ *vs.* pAg for $c_L = 0.735$ mmol dm^{-3} and $c_H = 50$ mmol dm^{-3} completely confirmed but did not enlarge upon the previous information. Consequently, the assumption that the system can be reduced to a two-component one, $Ag_p(AH)_q$, was made.

Under the experimental conditions corresponding to titrations 1—9 of Table 1, in which pAg is determined at each titration point, Sillén's core + links hypothesis[12] requires that the complexes be written as $(AH)[(AH)Ag_t]_n$, where t is a constant and n an integer, and also that the pH is kept constant during each titration. Despite the fact that in our case c_H was constant, instead of constant pH, Sillén's methods could be successfully applied, as is shown by the parallelism of the curves

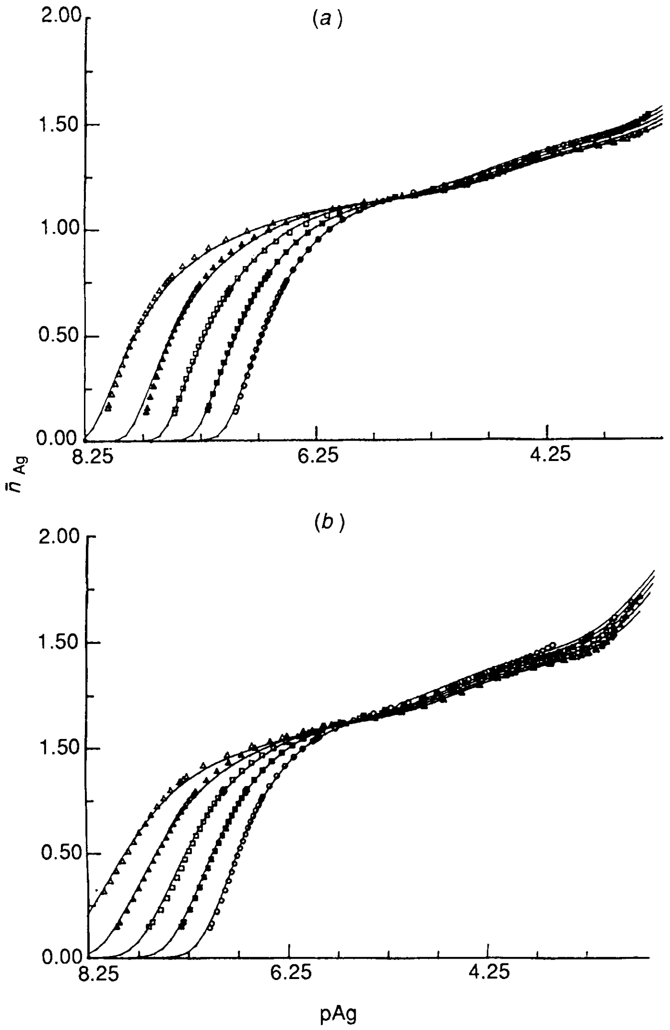


Figure 1. Variation of the experimental function $\bar{n}_{Ag}$, *i.e.* the average number of silver ions bound per ligand, as a function of pAg at different c_L values and constant c_H (50.0 mmol dm^{-3}): (*a*) $Me_2N(CH_2)_3SH$; (*b*) $H_2N(CH_2)_3SH$. The lines drawn were calculated from the constants in Table 3 (*a*), (*b*); c_L = 0.385, 0.375 (○), 0.735, 0.750 (■), 1.50, 1.50 (□), 3.01, 3.02 (▲), and 6.00, 5.98 (△) mmol dm^{-3}

Table 2. Set of possible *p,q* values for $Ag_p(AH)_q$ species with $Me_2N(CH_2)_3SH$ ligand which meet the requirements $p_{max.} = 14$, $p_{min.} = 6$, $0.2 < \bar{n}_{Ag} < 0.8$,[a] $1.0 < \bar{t} < 1.24$,[b] and $0.93 < p/q < 1.17$

p	6	7	8	9	10	10	11	12	12	13	13	14	14	14
q	6	7	8	9	9	10	11	11	12	12	13	13	14	15

[a] $\bar{n}_{Ag}$ is defined in the text. [b] The $Ag_p(AH)_q$ complexes can also be written as $(AH)[(AH)Ag_t]_n$, *n* being an integer.

$\bar{n}_{Ag}$ *vs.* pAg, Figure 1(*a*), and $\bar{n}_{Ag}$ *vs.* pAg, Figure 2(*a*) and (*b*), over a wide pAg range, $\bar{n}_{Ag}$ denoting the average number of bound silver ions per ligand.

By analogous procedures to those used in the preceding paper,[8] information about the stoicheiometry of species existing at pAg > 6.30 and thus of complexes of high nuclearities in an acidic medium was obtained. From the region $0.2 < \bar{n}_{Ag} < 0.8$ in the plots of $\bar{n}_{Ag}$ *vs.* pAg, Figure 1(*a*), it was deduced that the value of *t* in $(AH)[(AH)Ag_t]_n$ should be in the range $1.0 < t < 1.24$. Besides, the curves $\bar{n}_{Ag}$ *vs.* pAg for both c_L values [Figure 2(*a*) and (*b*)] gave practically identical results for the range of variation of the ratio $\bar{p}/\bar{q}$ in $Ag_p(AH)_q$ complexes: c_L = 3.01 mmol dm^{-3}, $0.25 < \bar{n}_{Ag} < 0.9$, $\bar{p}/\bar{q} = 1.17$, $\sigma = 0.08$, $0.93 < \bar{p}/\bar{q} < 1.41$; $c_L = 0.735$ mmol dm^{-3}, $0.2 < \bar{n}_{Ag} < 0.9$, $\bar{p}/\bar{q} = 1.16$, $\sigma = 0.07$, $0.95 < \bar{p}/\bar{q} < 1.37$. By considering that the value of $\bar{n}_{Ag}$ where all the curves intersect, $\bar{n}_{max.}$, in plots of $\bar{n}_{Ag}$ *vs.* pAg indicates more accurately the upper limit of the ratio $\bar{p}/\bar{q}$ for species existing at $\bar{n}_{Ag} < \bar{n}_{max.}$, this limit was fixed at 1.17. A numerical treatment of these results yielded the first set of possible species, Table 2.

According to curves $\bar{p}$, $\bar{q}$, $\bar{r}$ *vs.* pAg all possible complexes existing at pAg < 6.30, which correspond to species with $p/q \geqslant \bar{n}_{max.}$, were added to the previous set. Based on these curves complexes with stoicheiometry $p = q = 6$—8 (Table 2) were discarded. Approximate formation constants were calculated as indicated elsewhere, except for the species with the same stoicheiometry as those already found in the 4-mercapto-1-methylpiperidine system.[8] In this case, the corresponding constants were taken as the initial value. The least-squares fitting analysis was carried out by means of the program SUPERQUAD,[11] conveniently modified[8] in order to avoid errors arising from variations in the liquid junction potential. According to the literature[13] the value for the constant D_h in a 0.1 mol dm^{-3} $NaNO_3$ medium was taken as 250 mV dm^3 mol^{-1}. The set of constants and stoicheiometric coefficients that best fit the experimental data is given in Table 3.

Silver complex species with $Me_2N(CH_2)_3SH$ *in solutions at* $4 \leqslant pH \leqslant 8$. Experimental data from the set of titrations at constant c_L and c_{Ag}, Table 1, allowed us to construct curves of $\bar{n}_H$ *vs.* pH and $\bar{n}_L$ *vs.* log[HA], $\bar{n}_H$ denoting the average number of protons bound to one ligand and $\bar{n}_L$ that of ligands bound to one metal atom. Both experimental functions were calculated from known equations.[8] Data from the $\bar{n}_H$ *vs.* pH curves allowed us to conclude that complex species were already present at pH < 4 and that up to pH ≈ 8.5 the complexed ligands were monoprotonated. Thus, the system could be treated as a two-component one. The existence of polynuclear complexes was inferred from the dependence of $\bar{n}_L$ on c_{Ag}. Besides, the displacement of these curves towards higher concentrations of free monoprotonated ligand at increasing c_{Ag} indicates that the 'core + links' complexes should be written as $(HA)_r[Ag(HA)_t]_n$, where r, $t > 0$. The horizontal spacing between the mentioned curves, the minimum value of the $\bar{n}_L$ function, $(\bar{n}_L)_{min.} \approx 1$, the assumption that the maximum nuclearity of complex species, $n_{max.}$, is 12 together with the relation $(\bar{n}_L)_{min.} = t + r/n_{max.}$[12a] led to the following results: $1.83 < r < 2.19$, $0.82 < t < 0.85$. Despite the fact that in this case we only had two points for each log c_{Ag} *vs.* log[HA] line, the value found for *r*, 2.01(6), was considered good enough and thus the number of titrations was not enlarged. A numerical treatment already reported together with the limiting conditions, $p_{max.} = 12$ and $1 < q/p \leqslant 3$, gave us the first set of possible complexes under these experimental conditions, Table 4. To this set, $Ag_p(AH)_q$ complexes with *p,q* values corresponding to the same stoicheiometry as that found in metal(I)thiolate complexes (M = Ag or Cu) of known structure were added: 4,6;[6,14] 5,7;[6,15] 6,8;[6] 12,16.[6] Also, the mononuclear complex 1,2[16,17] and the species 3,5, which can be considered as belonging to the same 'core + links' family as 1,3, 2,4, 4,6, and 5,7, were included. Rough estimates of the formation constants were determined as indicated. This initial model was treated with the program SUPERQUAD.[11] During the refinement process complexes with *p,q* values 12,12 and 10,9 and corresponding constants, which were kept fixed, were introduced. The final equilibrium model is given in Table 5.

Silver–3-Aminopropane-1-thiol Soluble Species and Corresponding Complex-formation Constants.—The information given below has been restricted to numerical data relevant for this particular system. The reasonings and/or explanations that

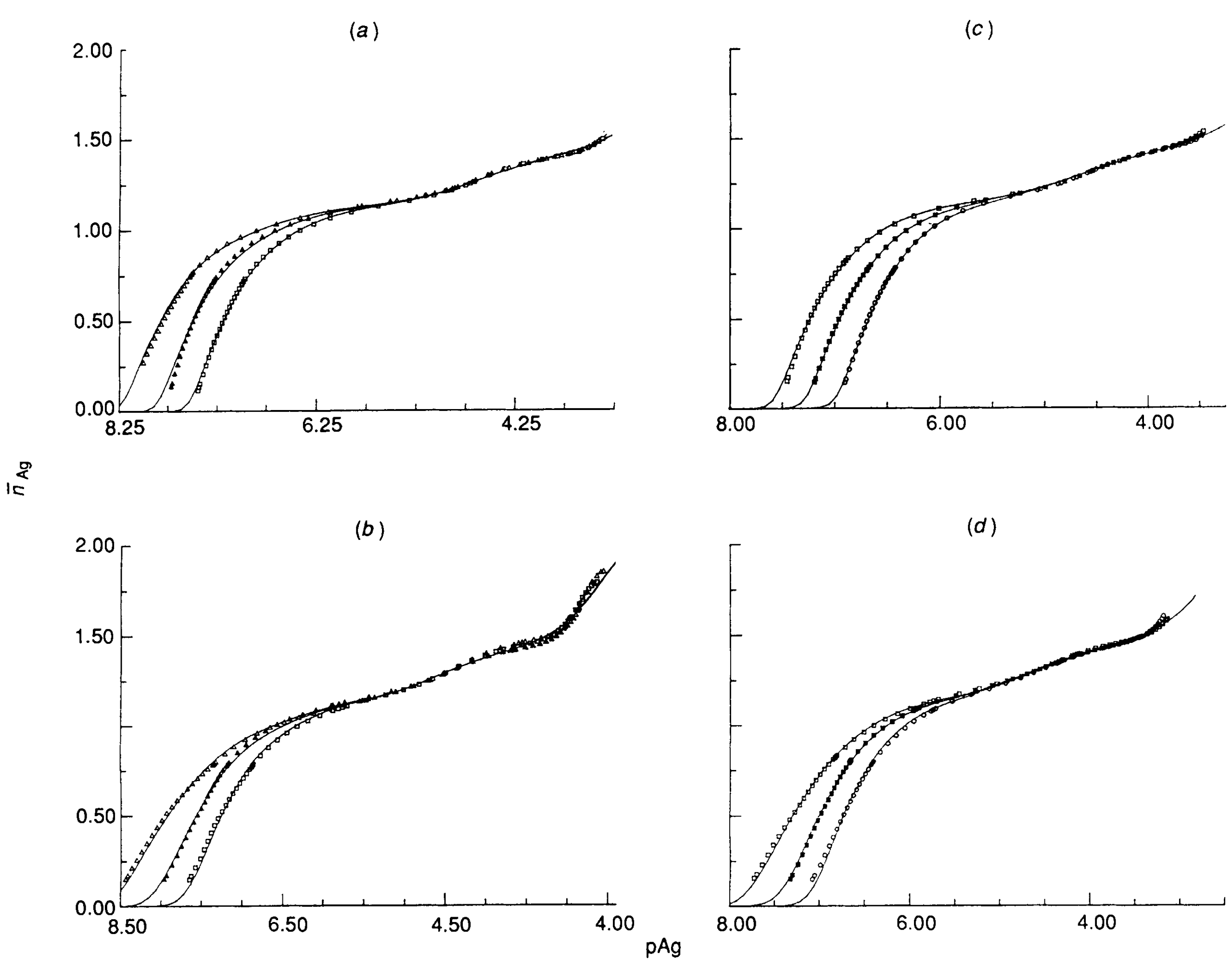


Figure 2. Average number of silver ions bound per ligand, $\bar{n}_{Ag}$, as a function of pAg for two sets at constant c_L and different c_H values: (*a*), (*b*) $Me_2N(CH_2)_3SH$; (*c*), (*d*) $H_2N(CH_2)_3SH$. The lines drawn were calculated from the constants in Table 3. c_L = 3.01 (*a*), 0.735 (*b*), 3.02 (*c*), and 0.750 mmol dm^{-3} (*d*); c_H = 25.0 (△), 50.0 (▲), 100.0 (□) (*a*), (*c*); 25.0 (□), 50.0 (■), and 100.0 (○) mmol dm^{-3} (*b*), (*d*)

Table 3. Silver complex-formation constants for the species $Ag_p(AH)_q$ at 25 °C and I = 0.1 mol dm^{-3} ($NaNO_3$) (+10% v/v MeOH) from silver electrode data using the program SUPERQUAD[11]

			log $\psi_{p,q}$	
p	q	Species	$Me_2N(CH_2)_3SH$[a]	$H_2N(CH_2)_3SH$[b]
6	3	(*a*)	61.4 ± 0.1	61.60 ± 0.06
6	4	(*b*)	77.35 ± 0.03	77.83 ± 0.04
8	6	(*c*)	113.85 ± 0.04	114.58 ± 0.06
7	6	(*d*)	109.10 ± 0.04	109.84 ± 0.06
10	9	(*e*)	162.64 ± 0.06	163.76 ± 0.09
12	12	(*f*)	209.22 ± 0.09	211.2 ± 0.1
5	6	(*g*)		96.58 ± 0.09

[a] Number of points 441, 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 = 5.53; σ_E, σ_V, and σ are defined as in ref. 11. [b] 545 Points from nine titrations; σ_E = 0.2—0.3 mV, σ_V = 0.01 cm^3, and σ = 7.35.

Table 4. Set of possible p,q values for $Ag_p(AH)_q$ species with $Me_2N(CH_2)_3SH$ ligand which meet the requirements $p_{max.}$ = 12, $1.80 < \bar{n}_L < 2.30$,[a] $0.82 < t < 0.85$,[b] $1.83 < r < 2.19$,[c] and $1 < q/p \leqslant 3$

p	1	2	4	5	6	7	8
q	3	4	5	6	7	8	9

[a] $\bar{n}_L$ is defined in the text. [b,c] Complexes written as $(AH)_r[Ag(AH)_t]_n$ where $r,t > 0$, according to the 'core + links' hypothesis.

would accompany them have already been given either in the study of the $Me_2N(CH_2)_3SH$, or in the preceding paper.[8]

Acquisition of experimental data. Sixteen potentiometric titrations divided into two sets, as indicated in Table 1, were carried out. In the first set, including nine titrations gathered in one series at constant c_H and two series at constant c_L, c_L and c_H were varied in the ranges $0.37 < c_L < 6$ mmol dm^{-3} and $25 < c_H < 100$ mmol dm^{-3}. The second set included seven titrations at constant c_L and c_{Ag}; c_{Ag} was varied in the range $0.75 < c_{Ag} < 6$ mmol dm^{-3} and c_L according to the molar ratio $1.6 < c_L/c_{Ag} < 6.7$.

Silver complex species with $H_2N(CH_2)_3SH$ *in an acidic medium.* The more general information about soluble complexes existing in a strong acidic medium was again obtained from experimental data corresponding to the 'common point' titrations, Table 1. The variation of the average stoicheiometric coefficients as a function of pAg for c_L = 3.02 and c_H = 50.0 mmol dm^{-3} was plotted. The main difference between these plots and those corresponding to the other ligands is that species with the highest nuclearity appear only at pAg values in the range 6.5—7. Also, it can be deduced that the

Table 5. Silver complex-formation constants for the species $Ag_p(AH)_q$ at 25 °C and $I = 0.1$ mol dm^{-3} ($NaNO_3$) (+10% v/v MeOH) from pH electrode data using the program SUPERQUAD[11]

$Me_2N(CH_2)_3SH$[a]				$H_2N(CH_2)_3SH$[b]			
p	q	Species	$\log \psi_{p,q}$	p	q	Species	$\log \psi_{p,q}$
5	6	(*g*)	91.31 ± 0.06	5	7	(*h*)	102.6 ± 0.1
4	6	(*h*)	77.41 ± 0.08	4	6	(*i*)	83.59 ± 0.09
				2	4	(*j*)	44.84 ± 0.03
1	3	(*i*)	21.35 ± 0.03	1	3	(*k*)	24.35 ± 0.03

[a] 135 Points from six titrations; $\sigma_E = 0.1$ mV, $\sigma_V = 0.01$ cm^3, and $\sigma = 10.9$. [b] 125 Points from seven titrations; $\sigma_E = 0.1$ mV, $\sigma_V = 0.01$ cm^3, and $\sigma = 9.73$.

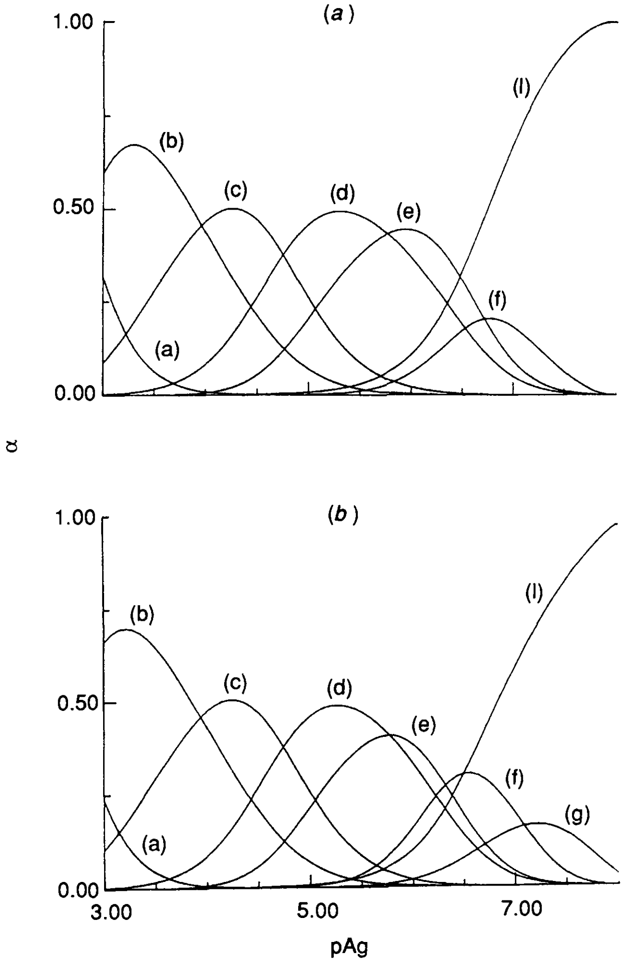


Figure 3. Species distribution curves as a function of pAg at constant c_L 3.00 mmol dm^{-3} and c_H 50 mmol dm^{-3}: (*a*) $Me_2N(CH_2)_3SH$; (*b*) $H_2N(CH_2)_3SH$. For key to symbols see Table 3; (l) denotes the free diprotonated ligand H_2A

maximum nuclearity of the complexes will not exceed that of the species with the other ligands. Even though it can be concluded that the complexed ligands are monoprotonated at least up to pAg 7, it seems that the nuclearity of complexes, p, goes down suddenly from this pAg value.

By considering a two-component system, the curves $\bar{n}_{Ag}$ *vs.* pAg, Figure 1(*b*), and $\bar{n}_{Ag}$ *vs.* pAg, Figure 2(*b*), were plotted and the 'core + links' hypothesis[12] applied in order to know the stoicheiometry of soluble species at high pAg values. From the first set of curves, Figure 1(*b*), the lines $\log c_L$ *vs.* log[Ag] were drawn and thus the value for t in the formula $(AH)[(AH)Ag_t]_n$ was calculated. The results obtained were $0.81 < t < 1.43$ for $0.2 < \bar{n}_{Ag} < 0.8$ but the dependence of t on $\bar{n}_{Ag}$ in this case is not negligible, and thus it had to be assumed that $Ag_p(AH)_q$ species with $p/q > \bar{n}_{max.}$ were also present in solution. This, together with the fact that $\bar{n}_{Ag}$ *vs.* pAg curves, Figure 2(*b*), are not parallel, which prevents calculation of the range of variation of the ratio $\bar{p}/\bar{q}$, made it difficult to limit the number of possible species. The set of species given in Table 6 is thus only limited by the range of t, by $p/q < 1.16$, deduced from Figure 1(*b*), and by the assumption $p_{max.} = 12$. All these species together with the corresponding approximate formation constants were introduced stepwise in the modified version of the program SUPERQUAD,[11] that is forming different groups by a trial-and-error method. The program eventually afforded the equilibrium model shown in Table 3.

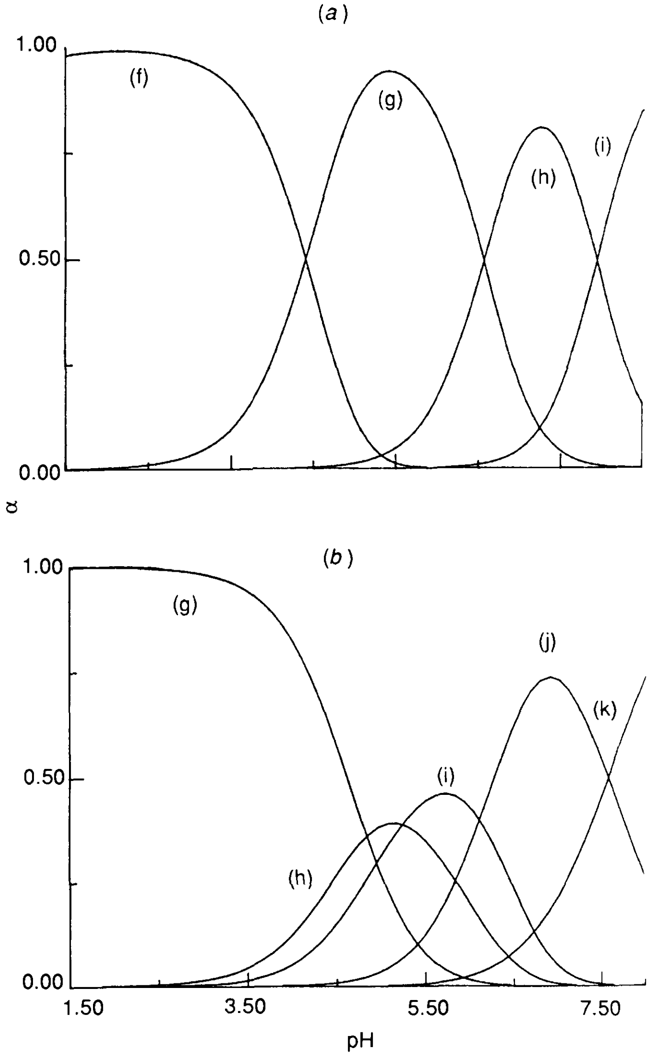


Figure 4. Species distribution curves as a function of pH at constant c_L 15.00 mmol dm^{-3} and c_{Ag} 3.00 mmol dm^{-3}: (*a*) $Me_2N(CH_2)_3SH$; (*b*) $H_2N(CH_2)_3SH$. For key to symbols see Table 5

Silver complex species with $H_2N(CH_2)_3SH$ *in solutions at* $4 \leqslant pH \leqslant 8$. The first information about equilibria in this pH range was obtained from the curves of $\bar{n}_H$ *vs.* pH. The fact that $\bar{n}_H < 2$ from pH < 4 indicates that the ligand is already complexed in strong acidic solutions. Evidently, the species present are those found in the first part of the study, at constant

Table 6. Set of possible *p*,*q* values for $Ag_p(AH)_q$ species with $H_2N(CH_2)_3SH$ ligand which meet the requirements $p_{max.} = 12$, $0.2 < \bar{n}_{Ag} < 0.8$, $0.81 < t < 1.43$, and $p/q < 1.16$*

p	1	2	3	3	4	4	5	4	5	6	5	6	7	8	6	7	8	9	7	8	9	10	8	9	10	11	8	9	10	11	12	9	10	11	12	10	11	12	11	12	12
q	2	3	3	4	4	5	5	6	6	6	7	7	7	7	8	8	8	8	9	9	9	9	10	10	10	10	11	11	11	11	11	12	12	12	12	13	13	13	14	14	15

* See footnotes to Table 2.

Table 7. Set of possible *p*,*q* values for $Ag_p(AH)_q$ species with $H_2N(CH_2)_3SH$ ligand which meet the requirements $p_{max.} = 5$, $1.80 < \bar{n}_L < 2.3$, $0.78 < t < 0.89$, $1.55 < r < 2.11$, and $1.2 < q/p \leqslant 3$*

p	1	2	2	3	4
q	3	3	4	4	5

* See footnotes to Table 4.

c_H, and thus they are already known. By comparing these curves with those for the $Me_2N(CH_2)_3SH$ ligand, one observes that in the case of $H_2N(CH_2)_3SH$ the solution is more buffered, which can be attributed to the species $[Ag_5(AH)_6]^{5+}$, already present in a strong acidic medium, Figure 3(*b*). As $\bar{n}_H > 1.17$ for all experimental points it was assumed that the complexed ligands are monoprotonated over the whole pH range studied and thus the system was considered as a two-component one. Consequently, the curves $\bar{n}_L$ *vs*. log[AH] were plotted, which, because of their dependence on c_{Ag} and not on c_L, confirmed the previous assumption. By formulating the complex species as $(AH)_r[Ag(AH)_t]_n$, where $r, t > 0$, and also, from the slope of the curves log[Ag] *vs*. log[HA], it was deduced that $1.55 < r < 2.11$ for $1.80 < \bar{n}_L < 2.30$. This range of variation of *r*, together with the conditions $(\bar{n}_L)_{min.} = 1.2$, $n_{max.} = 5$ {which is the nuclearity of the species $[Ag_5(AH)_6]^{5+}$ present at $\bar{n}_L = 1.2$}, yielded that *t* should be in the range $0.78 < t < 0.89$. The previous conditions and a numerical treatment gave the first set of possible species, as indicated in Table 7. By adding to this set species of the same stoicheiometry as those indicated in the $Me_2N(CH_2)_3SH$ system, by estimating all the corresponding formation constants and by means of the program SUPERQUAD[11] the set of species and constants given in Table 5 was obtained as the equilibrium model. During the refinement process species 12,12 and 5,6 were introduced and their formation constants kept fixed.

Discussion

Values given in Tables 3 and 5 for the ligands $Me_2N(CH_2)_3SH$ and $H_2N(CH_2)_3SH$ allow one to obtain the corresponding species distribution curves. Those at constant c_L and c_H and varying [Ag] and at constant c_L and c_{Ag} and varying pH are given, respectively, in Figures 3 and 4. The theoretical curves in Figures 1 and 2 agree well with the experimental points and thus confirm the validity of the graphical methods used to get information on the stoicheiometry of the soluble species. Small deviations, such as those observed in the curves $\bar{n}_L$ *vs*. log(HA] for $Me_2N(CH_2)_3SH$ in the range $5 < -\log[HA] < 7$, are not significant, because they are in a region corresponding to a pH jump. To these points, which always have a higher experimental error, the program used[11] assigns a smaller statistical weight than to the remainder and thus the influence of the deviation on the determination of the species is negligible.

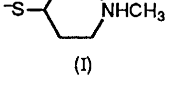
The behaviour of the propanethiol ligands towards Ag^I shows the same general trends as that of 4-mercapto-1-methylpiperidine,[8] which can be summarized as follows: (*a*) in all complex species the ligand is monoprotonated and thus the complexes can be formulated as $[Ag_p(AH)_q]^{p+}$; (*b*) the highest-nuclearity species, $[Ag_{12}(AH)_{12}]^{12+}$ in the three cases, is the only species with $p = q$ and it is present at high pAg values and under strong acid conditions; (*c*) at decreasing pAg values the dodecameric species transforms into complexes in which $1 < q < p$ while at increasing pH it changes to species with $q > p$, those with $p > 1$ predominating.

A remarkable feature of silver complexes existing in an acidic medium is that the stoicheiometry of all $[Ag_p(AH)_q]^{p+}$ with $q < p$ coincides for the three ligands (Table 3 and Table 2 of ref. 8). The only difference is that one additional species with $q > p$, $[Ag_5(AH)_6]^{5+}$, is present at very low pH values when the ligand is $H_2N(CH_2)_3SH$, Figure 3(*b*). The great stability of this species which predominates up to pH ≈ 4.5, Figure 4(*b*), has to be the reason for its presence under those conditions in which the complex $[Ag_{12}(AH)_{12}]^{12+}$ forms and predominates if ligands are the piperidinethiol, or $Me_2N(CH_2)_3SH$ as is shown in Figures 3 and 4 and Figure 4 of the preceding paper. Also, the $[Ag_5(AH)_6]^{5+}$ species accounts for the shape of the curves $\bar{n}_{Ag}$ *vs*. pAg, Figure 1(*b*), and $\bar{n}_{Ag}$ *vs*. pAg, Figure 2(*b*), which are not parallel over the whole range and thus do not yield as much information about the system as with the other ligands.

Not only the stoicheiometry of $[Ag_p(AH)_q]^{p+}$ species with $p > q$ but also the corresponding formation constants, $\psi_{p,q}$, corroborate that the aliphatic chain linked to the sulphur atom has very little influence on these thiolate complexes formed in a strong acidic medium. Meanwhile the direct comparison of $\psi_{p,q}$, $p > q$, for the complexes of $Me_2N(CH_2)_3SH$, with those of the piperidinethiol (Table 2 of preceding paper) would not be rigorous because of the different ionic strength; the successive formation constants, Table 8, indicate that in both cases the relative stability of the complex species is very similar. Besides, if instead of considering $\psi_{p,q}$, $p > q$, for the propanethiols, the influence of the first acid-dissociation constants of the ligands, K_1, is taken into account and thus the constants $\psi^*_{p,q} = \psi_{p,q}K_1{}^q$ are compared, Table 8, it can be concluded that the stability of $[Ag_p(AH)_q]^{p+}$ species, $p > q$, is practically of the same order.

Despite the fact that the $[Ag_{12}(AH)_{12}]^{12+}$ complex is present in the three silver–γ-mercaptoamine systems as the borderline separating those species with $p > q$ from those with $p < q$ and that the stoicheiometry of the soluble species formed in a strong acidic medium, $p > q$, does not depend on the particular ligand, this is not the case for solutions at higher pH values, see Figure 4 and Figure 4(*b*) of the preceding paper, even though the three ligands remain monoprotonated in the complexes formed over the whole pH range studied. That is, while *p*,*q* values, $p < q$, for the ligand $H_2N(CH_2)_3SH$ 5,6; 5,7; 4,6; 2,4; 1,3 include the three existing with $Me_2N(CH_2)_3SH$, 5,6; 4,6; 1,3, those with piperidinethiol, 7,8; 6,8; 2,3; and 1,3 do not coincide except for the only mononuclear species present in the three systems.

By comparing the ligands in their zwitterionic forms it is reasonable to propose that the different behaviour of the piperidinethiol (**I**) compared to that of the propanethiols (**II**) and (**III**) comes from the steric constraints imposed by the aliphatic ring and that ligand volume is unimportant for those


(I)

$^{-}SCH_2CH_2CH_2\overset{+}{N}HMe_2$

(II)

$^{-}SCH_2CH_2CH_2\overset{+}{N}H_3$

(III)

Table 8. Comparison between complex-formation constants of $Ag_p(AH)_q$ species in an acidic medium for the three ligands

(*a*) Successive stability constants

	pK^a	
	4-Mercapto-1-methylpiperidine	$Me_2N(CH_2)_2SH$
$[Ag_{12}(AH)_{12}] \rightleftharpoons [Ag_{10}(AH)_9] + 2Ag + 3HA$	46.19	46.58
$[Ag_{10}(AH)_9] \rightleftharpoons [Ag_7(AH)_6] + 3Ag + 3HA$	54.29	53.54
$[Ag_7(AH)_6] + Ag \rightleftharpoons [Ag_8(AH)_6]$	−5.65	−4.75
$[Ag_8(AH)_6] \rightleftharpoons [Ag_6(AH)_4] + 2Ag + 2HA$	37.42	36.50
$[Ag_6(AH)_4] \rightleftharpoons [Ag_6(AH)_3] + HA$	16.28	15.94

(*b*) Complex-formation constants according to the reaction $pAg + qH_2A \rightleftharpoons [Ag_p(AH)_q] + qH$

		$Me_2N(CH_2)_3SH^b$ pK_1 = 8.80		$H_2N(CH_2)_3SH^b$ pK_1 = 8.87	
p	q	log $\psi_{p,q}$	log $\psi^*_{p,q}$	log $\psi_{p,q}$	log $\psi^*_{p,q}$
6	3	61.41	35.01	61.60	34.98
6	4	77.35	42.15	77.83	42.34
8	6	113.85	61.05	114.58	61.35
7	6	109.10	56.30	109.84	56.60
10	9	192.64	83.44	163.76	83.90
12	12	209.2	103.6	211.2	104.8

[a] K is the ratio of the complex-formation constants, $\psi_{p,q}$, of the species involved in the equilibrium; $\psi_{p,q}$ values are given in Table 3 and in Table 4 of ref. 8. [b] $\psi^*_{p,q} = \psi_{p,q}K_1^q$; $\psi_{p,q}$ values are given in Table 3.

species with a silver/thiol ratio greater than 1:1. Unfortunately, the absence of structural data for $[Ag_x(SR)_y]^{x-y}$ species with $x > y$ does not allow us to go beyond this assumption. On the other hand, one would expect the same stoicheiometry for $[Ag_p(AH)_q]^{p+}$ species with ligands (**II**) and (**III**), because their steric demands and their electron density at the sulphur atom have to be very similar. Solution equilibria data obtained in this work lead us to conclude that, when $p < q$, (**III**) gives rise to more and more stable cationic species.

Homoleptic copper and silver thiolates with the same stoicheiometry as that of the soluble complexes 12,12; 5,7; 5,6; 4,6; and 1,3; mainly with benzenethiol as ligand, have been fully characterized structurally.[5a,6] No instance of a 2,4 metal(I) thiolate species has yet been reported, but there are precedents in $[ClCu(\mu\text{-}Cl)_2CuCl]^{2-}$ [18a] and $[Ag_2(S_6)_2]^{2-}$.[18b] Despite the fact that previous experimental data had led to the conclusion that only silver *sec*-alkanethiolates are dodecameric in solution,[19] our results indicate that also soluble n-alkanethiolates may be present in such a dodecameric form.

Acknowledgements

We thank the Comisión Asesora de Investigación Científica y Técnica (Grant 1058-84) and the Comisión Interministerial de Ciencia y Tecnología (Grant PB87-0188) for financial support.

References

1 J. C. Bayón and P. González-Duarte, *J. Chem. Soc., Dalton Trans.*, 1982, 487; J. C. Bayón, P. González-Duarte, and J. Vives, *ibid.*, 1984, 2671.
2 P. González-Duarte and J. Vives, *Inorg. Chem.*, 1989, **28**, 25.
3 P. González-Duarte and J. Vives, *J. Chem. Soc., Dalton Trans.*, 1989, 13.
4 (*a*) J. C. Bayón, M. C. Briansó, J. L. Briansó, and P. González-Duarte, *Inorg. Chem.*, 1979, **18**, 3478; (*b*) N. R. Kunchur, *Nature (London)*, 1964, **204**, 468; (*c*) A. P. Arnold and A. J. Canty, *Inorg. Chim. Acta*, 1981, **55**, 171; (*d*) A. P. Arnold, A. J. Canty, B. W. Skelton, and A. H. White, *J. Chem. Soc., Dalton Trans.*, 1982, 607.
5 (*a*) I. G. Dance, *Polyhedron*, 1986, **5**, 1037; (*b*) P. J. Blower and J. R. Dilworth, *Coord. Chem. Rev.*, 1987, **76**, 121; (*c*) I. G. Dance, *Polyhedron*, 1988, **7**, 2205.
6 I. G. Dance, *Inorg. Chem.*, 1981, **20**, 1487.
7 P. González-Duarte, J. Sola, J. Vives, and X. Solans, *J. Chem. Soc., Chem. Commun.*, 1987, 1641.
8 P. González-Duate and J. Vives, preceding paper.
9 B. C. Cossar, J. O. Fournier, D. L. Fields, and D. D. Reynolds, *J. Org. Chem.*, 1962, **27**, 93.
10 H. Barrera, J. C. Bayón, P. González-Duarte, J. Sola, and J. Vives, *Talanta*, 1983, **30**, 537.
11 P. Gans, A. Vacca, and A. Sabatini, *J. Chem. Soc., Dalton Trans.*, 1985, 1195.
12 L. G. Sillén, *Acta Chem. Scand.*, 1954, **8**, (*a*) 299; (*b*) 318.
13 C. F. Baes and R. E. Mesmer, 'The Hydrolysis of Cations,' Wiley, New York, 1976, pp. 14—17.
14 I. G. Dance, G. A. Bowmaker, G. R. Clark, and J. K. Seadon, *Polyhedron*, 1983, **2**, 1031.
15 I. G. Dance, *Aust. J. Chem.*, 1978, **31**, 2195.
16 S. A. Koch, R. Fikar, M. Millar, and T. O'Sullivan, *Inorg. Chem.*, 1984, **23**, 212.
17 D. Coucouvanis, C. N. Murphy, and S. K. Kanodia, *Inorg. Chem.*, 1980, **19**, 2993.
18 (*a*) L. Banci, A. Bencini, A. Dei, and D. Gatteschi, *Inorg. Chim. Acta*, 1984, **84**, L11; (*b*) A. Muller, E. Krickemeyer, M. Zimmermann, M. Romer, H. Bogge, M. Penk, and K. Schmitz, *ibid.*, **90**, L69.
19 S. Åkerström, *Ark. Kemi*, 1965, **24**, 505; K. Tang, M. Aslam, E. Block, T. Nicholson, and J. Zubieta, *Inorg. Chem.*, 1987, **26**, 1488; I. G. Dance, L. J. Fitzpatrick, A. D. Rae, and M. L. Scudder, *ibid.*, 1983, **22**, 3785.

Received 22*nd September* 1989; *Paper* 9/04052H