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THERMOCHEMICAL STUDY OF THE COMPLEX FORMATION OF Ag(I) WITH SOME SULPHUR-CONTAINING AMINOPYRIDINES

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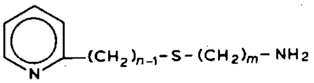
ABSTRACT

The enthalpies of formation of the complexes between the silver(I) ion and some sulphur-containing aminopyridines of general formula

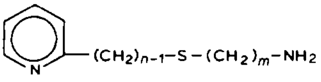


where $n = 1$, and $m = 1,2$; 1,3; 2,2; 2,3 have been determined by direct calorimetric titration at 25°C in 0.5 M (K)NO_3 solution. The corresponding entropy terms, ΔS, have been calculated using the obtained enthalpy values and the previously reported ΔG values.

In acid medium (pH < 3) coordination occurs through the thioether group and the protonated species $AgLH_2^{3+}$ and $AgL_2H_4^{5+}$ are enthalpy-stabilized and entropy-destabilized. At higher pH values (pH > 3) additional chelation through the pyridine nitrogen is obvious by a marked increase in the enthalpy of formation of the complexes $AgL_2H_3^{4+}$, $AgL_2H_2^{3+}$ and $AgLH^{2+}$. The last complex dimerizes into a cyclic dimer $Ag_2L_2H_2^{4+}$. At still higher pH values (pH > 6) the participation of the amino group in the dimeric chelates $Ag_2L_2H^{3+}$ and $Ag_2L_2^{2+}$ is revealed again by a marked increase in the heat of complexation.

INTRODUCTION

In a previous study [1] we reported the stability constants of the Ag(I) complexes with a number of sulphur-containing aminopyridines of general formula



where $n = 1$, and $m = 1,2$; 1,3; 2,2; 2,3.

From a comparison of the stabilities of the different species with the inductive effect parameters of the substituents on the thioether donor atom

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the following conclusions were drawn. In acid medium the complexes $AgLH_2^{3+}$ and $AgL_2H_4^{5+}$ are formed and coordination occurs through the thioether group. At higher pH values (> 3) additional chelation occurs through the pyridine-nitrogen donor in the species $AgLH^{2+}$, $AgL_2H_3^{4+}$ and $AgL_2H_2^{3+}$. The first species, however, is extensively dimerized into a cyclic $Ag_2L_2H_2^{4+}$ compound wherein the pyridine-nitrogen and sulphur donor-atoms of each ligand are bound to a different Ag(I) ion. At still higher pH values (> 6) the amino group also participates in chelation in the dimeric species $Ag_2L_2H^{3+}$ and $Ag_2L_2^{2+}$. The aim of this study is to check these conclusions concerning the enthalpy and entropy changes (accompanying the formation of these complexes) using calorimetric titration.

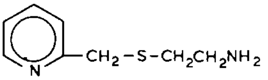
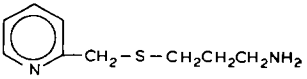
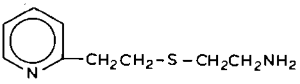
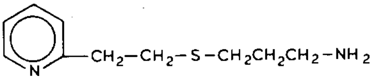
EXPERIMENTAL

Reagents

The IUPAC names, formulae and abbreviations of the studied ligands are listed in Table 1. The syntheses of the ligands and the standardization of their solutions are performed as described previously [2,3]. All other reagents were analytical grade. The different solutions were made up to an ionic strength of 0.5 M $(K)NO_3$.

TABLE 1

Formulae and abbreviations of the ligands studied

Ligand	Formula	Abbreviation [a]
1-(2-pyridyl)-4-amino-2-thia-butane		2,2-N_pSN
1-(2-pyridyl)-5-amino-2-thia-pentane		2,3-N_pSN
1-(2-pyridyl)-5-amino-3-thia-pentane		3,2-N_pSN
1-(2-pyridyl)-6-amino-3-thia-hexane		3,3-N_pSN

[a] The abbreviation contains consecutively the donor atoms, preceded by the number of methylene groups between them.

Calorimetric titrations

The calorimetric measurements were performed with an LKB-8700/2 titration calorimeter thermostatted at 25 ± 0.001°C. The heats of reaction were determined according to Wadsö [4].

The heats of formation of the fully protonated species $AgLH_2^{3+}$ and $AgL_2H_4^{5+}$ were determined by stepwise addition of an acidified $AgNO_3$ solution to a protonated ligand solution (pH < 3) and (or) vice versa. The heats of formation of the less protonated species were determined from a set of titrations of the ligand solution at higher pH values with $AgNO_3$ and from titrations of a mixture of $AgNO_3$ and protonated ligand at different ratios with KOH. However, at a $AgNO_3$/ligand ratio lower than 1 a white precipitate was formed in alkaline medium. As a consequence the enthalpy of formation of the AgL_2^+ species could not be determined.

The enthalpies of formation were calculated from the thus obtained calorimetric data with a computer method described previously [5]. The entropy changes were calculated by means of the equation

$$\Delta G = \Delta H - T\Delta S$$

RESULTS AND DISCUSSION

The thermodynamic functions for the stepwise complexation of the ligands n,m-N_pSN with Ag(I) are represented in Table 2. As stated previously [1], in strong acid medium (pH < 3) where the pyridine and amino group are protonated (n,m-$N_p^+SN^+$), complexation occurs via the "soft" thioether group. The thermodynamic data in Table 2 show that the Ag^+–S bond in the

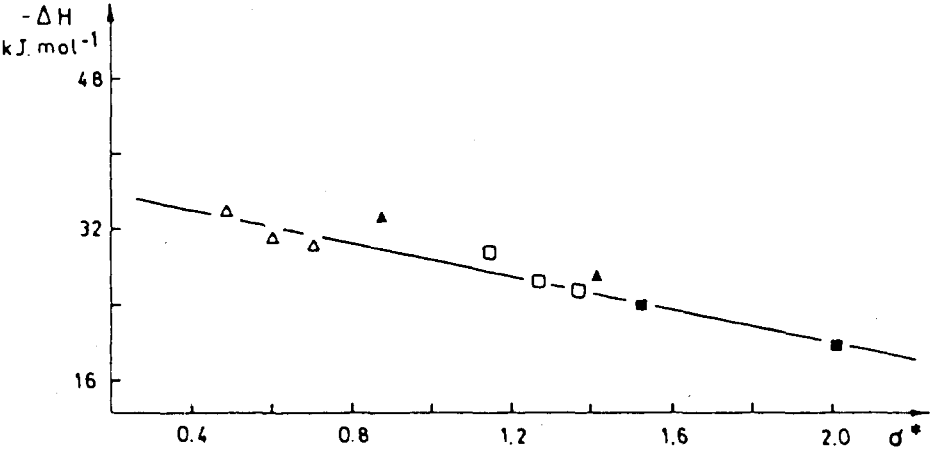


Fig. 1. The relationship between the enthalpies of the Ag^+ complexes (AgL′) and the Taft σ^* parameters. ■, 2,m-$N_p^+SN^+$; ▲, 3,m-$N_p^+SN^+$; □, 2-$N_p^+S(R)$; △, 3-$N_p^+S(R)$.

TABLE 2

The thermodynamic functions [a,b,c] for the Ag(I)-complex species of the ligands n,m-N_pSN

Reaction [d]	2,2-N_pSN	2,3-N_pSN	3,2-N_pSN	3,3-N_pSN
$Ag + LH_2 \rightleftarrows AgLH_2$				
$-\Delta G$	6.6 (2)	10.4 (2)	11.1 (1)	15.2 (1)
$-\Delta H$	20 (2)	24 (1)	27 (1)	34 (1)
ΔS	−45 (7)	−46 (4)	−53 (4)	−63 (4)
$Ag + 2\ LH_2 \rightleftarrows AgL_2H_4$				
$-\Delta G$	10.8 (4)	15.0 (3)	14.3 (2)	22.1 (2)
$-\Delta H$	[e]	46 (2)	49 (1)	63 (2)
ΔS		−104 (8)	−116 (4)	−137 (7)
$Ag + LH_2 + LH \rightleftarrows AgL_2H_3$				
$-\Delta G$	24 (1)	30.8 (5)	26.3 (6)	32.5 (5)
$-\Delta H$	41 (2)	66 (1)	59 (1)	69 (1)
ΔS	−57 (10)	−118 (5)	−110 (5)	−122 (5)
$Ag + 2\ LH \rightleftarrows AgL_2H_2$				
$-\Delta G$	37.2 (1)	42.4 (6)	32.5 (1)	37.4 (3)
$-\Delta H$	65.6 (8)	68.6 (6)	60.5 (6)	64.0 (6)
ΔS	−95 (3)	−88 (2)	−94 (2)	−89 (3)
$Ag + LH \rightleftarrows AgLH$				
$-\Delta G$	+ 18.9 (4)	21.8 (5)	18.0 (4)	21.5 (5)
$-\Delta H$	31.8 (6)	36.9 (4)	29.0 (4)	36 (1)
ΔS	−43 (3)	−51 (3)	−37 (3)	−49 (5)
$2\ Ag + 2\ LH \rightleftarrows Ag_2L_2H_2$				
$-\Delta G$	51 (1)	58.9 (6)	48.5 (5)	56.4 (5)
$-\Delta H$	87.7 (8)	100.5 (8)	93.7 (8)	107 (1)
ΔS	−123 (6)	−140 (5)	−152 (5)	−170 (5)
$2\ Ag + LH + L \rightleftarrows Ag_2L_2H$				
$-\Delta G$	72.9 (5)	75.2 (5)	70.6 (5)	73.2 (3)
$-\Delta H$	115 (1)	121 (1)	115.8 (6)	117 (1)
ΔS	−141 (5)	−154 (5)	−152 (4)	−147 (4)
$2\ Ag + 2\ L \rightleftarrows Ag_2L_2$				
$-\Delta G$	87.2 (1)	86.3 (1)	86.5 (1)	84.12 (6)
$-\Delta H$	133.6 (6)	127.4 (4)	133.6 (4)	122 (1)
ΔS	−156 (2)	−138 (2)	−158 (2)	−127 (4)

[a] Free energy data from ref. 1.

[b] 25°C; 0.5 mole dm^{-3} $(K)NO_3$; ΔG and ΔH in kJ $mole^{-1}$; ΔS in J K^{-1} $mole^{-1}$.

[c] Values in parentheses are the standard deviations on the last significant figure.

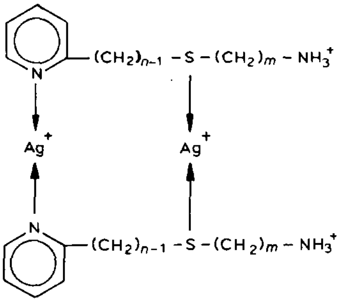
[d] Charges of ions are omitted for simplicity.

[e] Reaction heat could not be determined with sufficient accuracy.

$AgLH_2^{3+}$ and $AgL_2H_4^{5+}$ species is enthalpy-stabilized and that the entropy change strongly counteracts complex formation. This behaviour and the fact that the enthalpy change of the biligand species is about twice as large as that of the monoligand species are typical for soft–soft interactions [6].

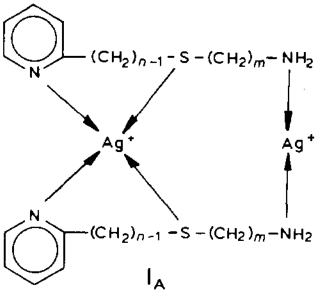
Moreover, the Ag^+–S bond strength depends upon the substituents on the thioether group. This may be seen from an increase in the heat of formation of both species with increasing distance of the ammonium and pyridinium groups (see Table 2). The influence of the substituents is also illustrated in Fig. 1 where the formation enthalpy of the monoligand complexes is plotted against the Taft [7] σ^* parameters of the substituents on the thioether group. Some previously investigated ligands [8] are also included in Fig. 1. The Taft parameters of the substituents were taken from the publications of Barlin and Perrin [9] and Charton [10] or derived in a previous paper [2].

At higher pH values (> 3) the pyridine nitrogen becomes deprotonated (n,m-N_pSN^+) and available for chelation in the species $AgLH^{2+}$, $AgL_2H_2^{3+}$ and $AgL_2H_3^{4+}$. This is suggested by the heats of formation which are much higher for these three species than for the corresponding ones formed with fully protonated ligands (see Table 2). The destabilizing effect of a nearby ammonium group is still reflected in the heats of formation of the $AgLH^{2+}$ and $AgL_2H_2^{3+}$ chelates. Indeed the following sequences are found for both series of complexes (see Table 2): 2,2-$N_pSN^+ <$ 2,3-N_pSN^+ and 3,2-$N_pSN^+ <$ 3,3-N_pSN^+. On the other hand, within the same series the enthalpy sequences 2,2-$N_pSN^+ >$ 3,2-N_pSN^+ and 2,3-$N_pSN^+ >$ 3,3-N_pSN^+ indicate that five-membered Ag^+ chelates are more stable than six-membered ones. As reported previously [1], the monomeric $AgLH^{2+}$ species is extensively dimerized into a cyclic $Ag_2L_2H_2^{4+}$ compound

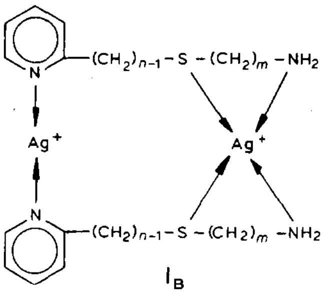


The Ag^+–N_p and Ag^+–S bond strengths in such a dimer are expected to increase with (i) increasing distance between both Ag^+ ion coordination centres, and (ii) increasing distance between the Ag^+ ion and the ammonium group. The first factor may explain the following enthalpy sequences for that dimer (see Table 2): 2,2-$N_pSN^+ <$ 3,2-N_pSN^+ and 2,3-$N_pSN^+ <$ 3,3-N_pSN^+, whereas the second factor explains the sequences 2,2-$N_pSN^+ <$ 2,3-N_pSN^+ and 3,2-$N_pSN^+ <$ 3,3-N_pSN^+. So it is not surprising that the heat of formation of the $Ag_2L_2H_2^{3+}$ dimer with the 3,3-N_pSN^+ ligand shows the highest value ($-\Delta H = 107$ kJ mole^{-1}). This value may best be compared with the sum of the enthalpy values for the biligand complexes of $S(CH_2CH_2OH)_2$ ($-\Delta H = 61.9$ kJ mole^{-1}) [11] and pyridine ($-\Delta H = 47.1$ kJ mole^{-1}) [12].

At still higher pH values (> 6) the ammonium group also deprotonates so that all three donor atoms of the investigated ligands (n,m-N_pSN) are competitive for coordination. In an excess of ligand, however, a white precipitate is formed, so that only the enthalpies of the deprotonated dimeric species $Ag_2L_2H^{3+}$ and $Ag_2L_2^{2+}$ could be obtained. From Table 2 it can be seen that the original trend in the stabilities ($-\Delta G$) of the $Ag_2L_2H_2^{4+}$ dimers, originating from the inductive effect of the nearby ammonium group, is levelled out in the $Ag_2L_2^{2+}$ dimers and that the latter stabilities are markedly higher. This lets us assume that all three donor atoms are coordinated. However, several structures are possible [1], two of which are given below



I_A



I_B

On the basis of a comparison of the stabilities ($-\Delta G$) of these dimers with the sum of the stabilities of the corresponding tetrahedral biligand chelates and linear biligand complexes from which the dimeric structure is made up, we argued in a previous publication [1] that structure I_A should be somewhat more plausible than I_B. The Gibbs free energy, however, is a complex function of the enthalpy and entropy terms so that not one of the possible structures may be excluded: 3,3-N_pSN forms a $Ag_2L_2^{2+}$ dimer with clearly the lowest heat of complexation (122 kJ mole^{-1}). This is not surprising because in every possible structure a six-membered chelate ring must be formed. 2,2-N_pSN and 3,2-N_pSN form a dimer. Both have the same and markedly higher heat of complexation (133.6 kJ mole^{-1}). This could be an indication of a structure similar to I_B where the sulphur and amino-nitrogen are coordinated in a five-membered chelate ring. For the 2,3-N_pSN ligand an intermediate $-\Delta H$ value is found (127.4 kJ mole^{-1}). This might be explained by a structure of the type I_A where the sulphur and pyridine-nitrogen are coordinated in a five-membered ring. Five-membered Ag^+ chelates with 2-$N_pS(R)$ [5] ligands show indeed a lower exothermicity than those with 2-NS(R) [5] ligands.

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