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CALORIMETRIC DETERMINATION OF THE THERMODYNAMIC PROPERTIES INVOLVED IN THE COMPLEX FORMATION OF SILVER(I) WITH SOME SULPHUR-CONTAINING PYRIDINES

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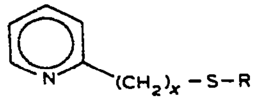
ABSTRACT

The enthalpy changes involved in the complex formation of Ag^+ with several sulphur-containing pyridines of general formula

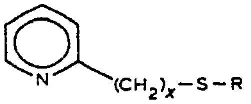


where $R = CH_3$, C_2H_5 and CH_2CH_2OH and $x = 1,2$ have been determined by direct calorimetric measurements at 25°C in 0.5 M KNO_3 solution.

From the ΔH values obtained and from the free energy changes reported in an earlier publication, the corresponding entropy changes ΔS have been calculated. Changes in ΔH and ΔS are discussed in terms of inductive and steric effects. It is shown that enthalpy values are linearly correlated with the Taft σ^* parameters of the substituents on the ligand.

INTRODUCTION

The protonation constants and the stability constants of the Ag^+ complexes of a number of ligands of general formula



where $R = CH_3$, C_2H_5, CH_2CH_2OH and $x = 1,2$ have been reported recently [1,2]. This study revealed that in acid medium the complexes $AgLH^{2+}$ and $AgL_2H_2^{3+}$ are formed whereas with increasing pH deprotonation of the complexes occurs with formation of the species AgL_2H^{2+}, AgL_2^+, AgL^+, $Ag_2L_2^{2+}$ and Ag_2L^{2+}.

To further the study of the complex formation, the enthalpy and entropy changes accompanying the formation of these complexes as obtained through calorimetric titrations are reported in this paper.

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EXPERIMENTAL

Reagents

The ligands (IUPAC names), formulae and abbreviations are listed in Table 1. The syntheses of the ligands and the standardization of their solutions are performed as described previously [1,2]. The other reagents used (KNO_3, HNO_3, KOH and $AgNO_3$) were analytical grade. In all solutions, the ionic strength has been maintained at 0.50 mole dm^{-3} KNO_3.

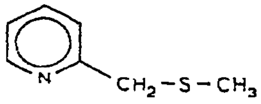
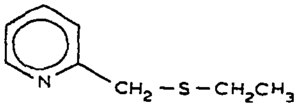
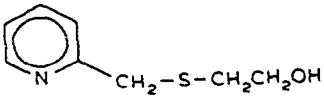
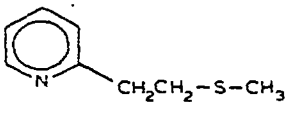
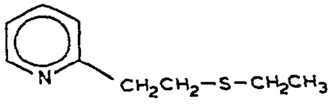
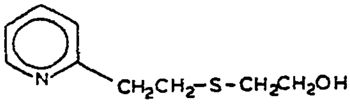
Calorimetric study

The calorimetric titrations were performed with a LKB-8700/2 Precision Calorimeter thermostatted at 25 ± 0.001°C. The procedure followed for the determination of the heats of reaction is described by Wadsö [3].

The heats of formation of the protonated species $AgLH^{2+}$ and $AgL_2H_2^{3+}$ were determined by stepwise addition of an acidified $AgNO_3$ solution to a protonated ligand solution and (or) vice versa.

TABLE 1

The ligands, formulae and abbreviations

Ligand	Formula	Abbreviation [a]
1-(2-pyridyl)-2-thia-propane		2-$N_pS(CH_3)$
1-(2-pyridyl)-2-thia-butane		2-$N_pS(C_2H_5)$
1-(2-pyridyl)-4-hydroxy-2-thia-butane		2-$N_pS(C_2H_4OH)$
1-(2-pyridyl)-3-thia-butane		3-$N_pS(CH_3)$
1-(2-pyridyl)-3-thia-pentane		3-$N_pS(C_2H_5)$
1-(2-pyridyl)-5-hydroxy-3-thia-pentane		3-$N_pS(C_2H_4OH)$

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[a] The abbreviation {n-$N_pS(R)$} contains the donor atom (the pyridine nitrogen N_p and the sulphur atom S) preceded by the number of carbon links between them.

For the more soluble ligands n-$N_pS(C_2H_4OH)$ the determination of the ΔH values of the species formed in alkaline medium was also possible by the titration with KOH of solutions with different ratios of Ag^+ and ligand.

The enthalpies of formation were calculated from the obtained data with a method described previously [4], whereas the entropies were calculated from the equation $\Delta G = \Delta H - T\Delta S$.

RESULTS AND DISCUSSION

The thermodynamic parameters for the complexation of Ag^+ with the investigated ligands are reported in Table 2.

As was stated previously [1], in acid medium when the pyridine group is protonated, complexation occurs via the soft thioether group. The thermodynamic values indicate that, despite an unfavourable entropy change, the enthalpy change is so large that it is the driving force for the formation of the $AgLH^{2+}$ complex. The same observations apply to the $AgL_2H_2^{3+}$ complexes and moreover the corresponding enthalpy changes for the 3-$N_pS(R)$ ligands are about twice as large as for the $AgLH^{2+}$ species. This behaviour is typical for soft–soft interactions [5].

The relatively smaller ΔH values for the $AgL_2H_2^{3+}$ complexes of the 2-$N_pS(R)$ ligands may be explained by the shorter distance between the Ag^+ ion and the positively charged pyridinium ion. The influence of the substituents on the stability of the Ag–S bond is illustrated in Fig. 1 where the complexation enthalpy of the $AgLH^{2+}$ and $AgL_2H_2^{3+}$ complexes is plotted against the σ^* Taft parameters of the investigated ligands. Some previously investigated ligands [4,6] are included in the same figure. Each ligand was considered as being built around the thioether group R_1–S–R_2. The Taft parameters of the substituents R_1 and R_2 were taken from the publications of Barlin [7] and Charton [8]. The parameters of the pyridyl groups were derived from the basicity of aminoalkylpyridines [1,9,10]. The enthalpy changes, ΔH, being related to the bond strengths, thus are seen to be correlated with the Taft σ^* functions of the substituents on the ligand.

At higher pH values, where the pyridine nitrogen becomes deprotonated and available for complex formation, the species AgL_2^+, $Ag_2L_2^{2+}$ and AgL^+ are formed. The ΔH value of the AgL^+ complex could not be determined because its distribution coefficient was too low (about 10%). In the calculations therefore its ΔH value was taken as one half that of the AgL_2^+ complex. From Table 2 it is seen that the enthalpy change for the AgL_2^+ complex of 2-$N_pS(C_2H_4OH)$ is much higher than that of the corresponding $AgL_2H_2^{3+}$ species and also much higher than that of the corresponding complex with pyridine ($-\Delta H = 47.11$ kJ mole^{-1}) [11]. This leads us to assume that chelation occurs via the sulphur and pyridine nitrogen donor atoms. For the 3-$N_pS(C_2H_4OH)$ ligand the increase in enthalpy in going

TABLE 2

The formation constants[a] and the thermodynamic functions[b] for the ligand species[c] and some Ag^+-complex species[d] of the ligands n-$N_pS(R)$

Ligand	Reaction[c]	log K[e]	$-\Delta G$	$-\Delta H$	ΔS
$2-N_pS(CH_3)$	$L+H \rightleftharpoons LH$	4.723(4)	26.95(2)	19.7(2)	24.3(7)
	$Ag+LH \rightleftharpoons AgLH$	2.12(2)	12.1(1)	27.0(4)	−50(2)
	$Ag+2\,LH \rightleftharpoons AgL_2H_2$	3.28(5)	18.7(3)	41.2(5)	−75(3)
$2-N_pS(C_2H_5)$	$L+H \rightleftharpoons LH$	4.720(4)	26.94(2)	19.3(1)	25.6(4)
	$Ag+LH \rightleftharpoons AgLH$	2.49(1)	14.22(4)	30.0(5)	−53(2)
	$Ag+2\,LH \rightleftharpoons AgL_2H_2$	4.01(3)	22.9(2)	46.5(6)	−79(3)
$2-N_pS(C_2H_4OH)$	$L+H \rightleftharpoons LH$	4.613(5)	26.33(3)	20.5(2)	19.6(8)
	$Ag+LH \rightleftharpoons AgLH$	2.03(5)	11.6(3)	25.8(5)	−48(3)
	$Ag+2\,LH \rightleftharpoons AgL_2H_2$	3.23(9)	18.4(5)	38.3(7)	−67(4)
	$Ag+2\,L \rightleftharpoons AgL_2$	7.87(1)	44.89(4)	67(1)	−74(3)
	$2\,Ag+2\,L \rightleftharpoons Ag_2L_2$	10.74(6)	61.3(3)	108[f]	−157[f]
$3-N_pS(CH_3)$	$L+H \rightleftharpoons LH$	5.331(3)	30.42(2)	22.7(2)	25.9(7)
	$Ag+LH \rightleftharpoons AgLH$	3.00(1)	17.11(4)	30.8(3)	−46(1)
	$Ag+2\,LH \rightleftharpoons AgL_2H_2$	4.84(1)	27.61(4)	58.7(5)	−104(2)
$3-N_pS(C_2H_5)$	$L+H \rightleftharpoons LH$	5.330(3)	30.42(2)	22.4(2)	26.9(7)
	$Ag+LH \rightleftharpoons AgLH$	3.34(1)	19.06(4)	34.1(3)	−50(1)
	$Ag+2\,LH \rightleftharpoons AgL_2H_2$	5.35(1)	30.53(4)	63.0(5)	−109(2)
$3-N_pS(C_2H_4OH)$	$L+H \rightleftharpoons LH$	5.277(3)	30.12(2)	23.5(3)	22(1)
	$Ag+LH \rightleftharpoons AgLH$	2.89(1)	16.48(4)	30.0(4)	−45(2)
	$Ag+2\,LH \rightleftharpoons AgL_2H_2$	4.67(1)	26.65(4)	56.0(6)	−98(2)
	$Ag+2\,L \rightleftharpoons AgL_2$	7.25(1)	41.38(4)	65.7(8)	−82(3)
	$2\,Ag+2\,L \rightleftharpoons Ag_2L_2$	10.84(5)	61.8(3)	98[f]	−121[f]

[a,b,c] Data from ref. 2.

[a,d] Data from ref. 1.

[b] 25°C; 0.5 mole dm^{-3} KNO_3; ΔG and ΔH in kJ $mole^{-1}$; ΔS in J K^{-1} $mole^{-1}$; Standard state of 1 mole. dm^{-3}.

[c] Charges of ions are omitted for simplicity.

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

[f] See remarks elsewhere in this section.

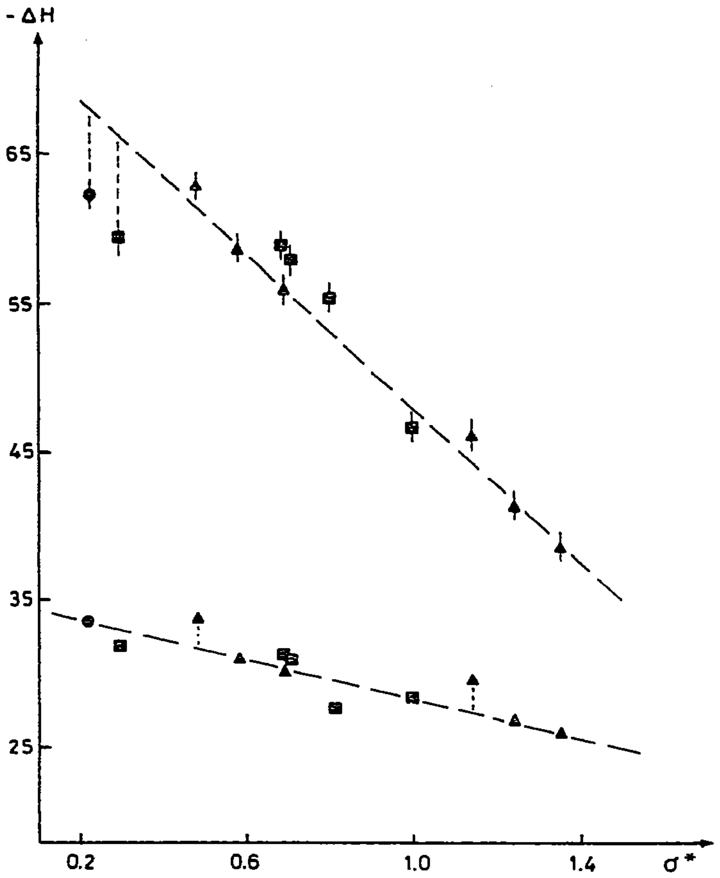

Fig. 1. The relationship between the enthalpies of the Ag^+-complexes (AgL' and AgL'_2) and the Taft σ* parameters. ●, $HO-(CH_2)_2-S-(CH_2)_2-OH$; AgL. ▲, n-$N_pS(R)$; AgLH. ■, n-NS(R); AgLH. ●, $HO-(CH_2)_2-S-(CH_2)_2-OH$; AgL_2. ▲, n-$N_pS(R)$; AgL_2H_2. ■, n-NS(R); AgL_2H_2.

from the $AgL_2H_2^{3+}$ to the AgL_2 species is less pronounced, indicating that the six membered Ag^+ chelates are less stable than the five membered ones. This behaviour may be compared with that of the sulphur-containing amines [4,12]. The dimeric $Ag_2L_2^{2+}$ complexes contain two Ag^+–S bonds and two Ag^+–pyridine nitrogen bonds, and ΔH values may best be compared with the sum of the enthalpy changes for the bi-ligand complexes of $S(CH_2OH)_2$ ($-\Delta H = 61.9$ kJ $mole^{-1}$) [6] and pyridine ($-\Delta H = 47.1$ kJ $mole^{-1}$) [11].

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