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THE THERMODYNAMICS OF COMPLEXATION BETWEEN Ag(I) AND SOME SULPHUR-CONTAINING α,ω-DIAMINES

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ABSTRACT

The enthalpies of the reactions between Ag(I) ions and a number of sulphur-containing α,ω-diamines of general formula $NH_2-(CH_2)_n-S-(CH_2)_m-NH_2$ ($n,m = 2,2$; 2,3; 2,4; 3,3; 3,4 and 4,4) in 0.5 M $(K)NO_3$ at 25 °C have been determined by means of direct calorimetric titrations. By use of the ΔG values reported elsewhere, the corresponding ΔS values have been calculated. It has been shown that in the dimeric Ag_2L^{2+} and $Ag_2L_2^{2+}$ species the ligands are coordinated through all three available donor atoms, whereas in the AgL_2^+ species each ligand is coordinated through only two donors.

INTRODUCTION

In a previous study [1] we reported on the complexation behaviour of the silver(I) ion towards some possibly tridentate sulphur-containing α,ω-diamines of general formula $NH_2-(CH_2)_n-S-(CH_2)_m-NH_2$ ($n,m = 2,2$; 2,3; 2,4; 3,3; 3,4 and 4,4).

In acid medium the protonated species $AgLH_2^{3+}$ and $AgL_2H_4^{5+}$ are formed and coordination occurs via the thioether donor group. At higher pH values the amino groups also become available for coordination and a series of deprotonated species are formed: $AgLH^{2+}$, $Ag_2L_2H_2^{4+}$, $Ag_2L_2H^{3+}$, $AgL_2H_3^{4+}$, $AgL_2H_2^{3+}$, AgL_2H^{2+}, Ag_2L^{2+}, $Ag_2L_2^{2+}$ and AgL_2^+, the last two being the main species in alkaline medium.

A comparison of the stability constants for the various species suggested that all three donor atoms of each ligand were coordinated in the $Ag_2L_2^{2+}$ dimer, whereas the ligands behaved as bidentates in the AgL_2^+ complex, leading to a tetrahedral surround of the Ag(I) ion.

The aim of this investigation is to determine the enthalpy changes of the complex formation by direct calorimetric titrations, and to check the above conclusions on the thermodynamic functions.

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EXPERIMENTAL

Reagents

The ligands investigated are listed in Table 1. Their synthesis has already been described [2,3]. The molecular weights of all synthesized amines were determined by titration with standardized HNO_3 following Gran [4]. All other reagents used were analytical grade. To all solutions an appropriate amount of solid potassium nitrate was added to maintain the total NO_3^- concentration at 0.5 mol dm^{-3}.

Apparatus

The calorimetric measurements were carried out with an LKB-8700/2 titration calorimeter thermostatted at $25 \pm 0.001°C$. The titrant was automatically added with a piston buret Tacussel Electro-burap. Details concerning the procedure for determination of the heats of formation are described by Wadso [5].

Calorimetric titrations

For practical reasons only the reaction heats for the complexes formed in extreme acid and alkaline medium were determined. Before each measurement the titration conditions were optimized by the program EQUIL [6]. The heats of formation of the $AgLH_2^{3+}$ and $AgL_2H_4^{5+}$ species were determined by stepwise addition of a 0.5 mol dm^{-3} acidified silver(I) nitrate solution to a protonated ligand solution of ~ 5 mmol. The calorimetric vessel contained an initial volume of about 0.070 dm^3. The reaction heat accompanying the formation of the deprotonated $Ag_2L_2^{2+}$ and AgL_2^+ species was determined by an analogous procedure.

TABLE 1

Formulae and abbreviations of the ligands studied

Ligand	Formula	Abbreviation [a]
1,5-diamino-3-thia-pentane	$NH_2-(CH_2)_2-S-(CH_2)_2-NH_2$	2,2-NSN
1,6-diamino-3-thia-hexane	$NH_2-(CH_2)_2-S-(CH_2)_3-NH_2$	2,3-NSN
1,7-diamino-3-thia-heptane	$NH_2-(CH_2)_2-S-(CH_2)_4-NH_2$	2,4-NSN
1,7-diamino-4-thia-heptane	$NH_2-(CH_2)_3-S-(CH_2)_3-NH_2$	3,3-NSN
1,8-diamino-4-thia-octane	$NH_2-(CH_2)_3-S-(CH_2)_4-NH_2$	3,4-NSN
1,9-diamino-5-thia-nonane	$NH_2-(CH_2)_4-S-(CH_2)_4-NH_2$	4,4-NSN

[a] The abbreviation contains consecutively the donor atoms present in the molecule chain, preceded by the number(s) of methylene groups between two donor atoms.

Calculations

The calculation of the enthalpy changes, ΔH, for the formation of the complex species was performed by the FORTRAN IV program KALO [7].

The entropy changes, ΔS, of the complexes were calculated from the obtained ΔH values and the corresponding free-energy changes ΔG [1], via the equation $\Delta G = \Delta H - T\Delta S$.

RESULTS AND DISCUSSION

The calorimetric results for the stepwise complexation of the fully protonated ligands (LH_2^{2+} or n,m-N^+SN^+) with silver(I) in acid medium are reported in Table 2. The enthalpy and entropy changes may best be compared to those of other silver(I)–thioether complexes [7–10]. They are typical for soft–soft interactions [11]: (i) complex formation is favoured by the enthalpy and counteracted by the entropy term; and (ii) the overall enthalpy for the biligand complexes is about twice as large as that for the monoligand complex. From Table 2 it may also be seen that within the series of investigated ligands the complexation entropy in the first as well as in the second step remains fairly constant, whereas the exothermic heat of complexation increases with increasing distance between the destabilizing ammonium group and the coordinating sulphur donor. The influence of these ammonium substituents is compared with that of other substituents in Fig. 1. The complexation enthalpies of the mono- and biligand species, plotted vs. the $\sigma^*_{(R_1+R_2)}$ Taft parameters [12–14] of the substituents on S of this series and of some previously investigated [9] thioether ligands (R_1–S–R_2) show the expected [15] fairly linear relationship between ΔH, or the bond strength, and the inductive effect of the substituent.

TABLE 2

The stability constants [a] and the thermodynamic functions [b] for the protonated Ag(I) complex species of the ligands n,m-NSN [c]

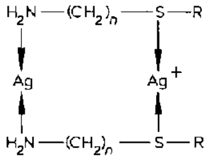
Ligands	$Ag^+ + LH_2^{2+} \rightleftarrows AgLH_2^{3+}$				$Ag^+ + 2\,LH_2^{2+} \rightleftarrows AgL_2H_4^{5+}$			
	log K	$-\Delta G$	$-\Delta H$	ΔS	log K	$-\Delta G$	$-\Delta H$	ΔS
2,2-NSN	1.52 (3)	8.7 (2)	22 (1)	−45 (4)	2.3 (1)	13.1 (6)	39 (2)	−87 (9)
2,3-NSN	2.30 (2)	13.1 (1)	28.0 (7)	−50 (3)	3.17 (5)	18.1 (3)	56 (2)	−127 (8)
2,4-NSN	2.62 (1)	14.95 (6)	30.1 (4)	−51 (2)	3.70 (1)	21.11 (6)	61 (1)	−134 (4)
3,3-NSN	3.04 (1)	17.35 (6)	31.8 (4)	−48 (2)	4.48 (1)	25.57 (6)	64.8 (7)	−132 (3)
3,4-NSN	3.23 (1)	18.43 (6)	33.1 (4)	−49 (2)	5.10 (1)	29.10 (6)	66.9 (7)	−127 (3)
4,4-NSN	3.53 (1)	20.15 (6)	34.3 (4)	−47 (2)	5.85 (1)	33.39 (6)	69.9 (6)	−123 (2)

[a] Data ref. 1.

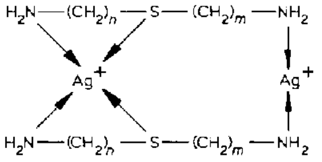
[b] 25 °C; 0.5 mol dm^{-3} (K)NO_3; ΔG and ΔH in kJ mol^{-1}; ΔS in J mol^{-1} K^{-1}.

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

The thermodynamic results for the $Ag_2L_2^{2+}$ and AgL_2^+ complexes formed with the fully deprotonated ligands (L or *n*,*m*-NSN) are compared to those of some previously investigated [7] bidentate ligands (*n*-NS(R)) in Table 3. For the $Ag_2L_2^{2+}$ dimeric compounds a gain in exothermic heat of complexation of some 10–20 kJ mol^{-1} is formed in going from the 2-NS(R) series (**I**) to the 2,*m*-NSN series (**II**). This effect must be ascribed to an additional chelate bond (**II**) and confirms our previously made assumptions [1].



(I)



(II)

The gain in exothermicity between the $Ag_2L_2^{2+}$ dimer of 3,4-NSN and that of 3-NS(CH_3) is somewhat less. This is not surprising because it has been

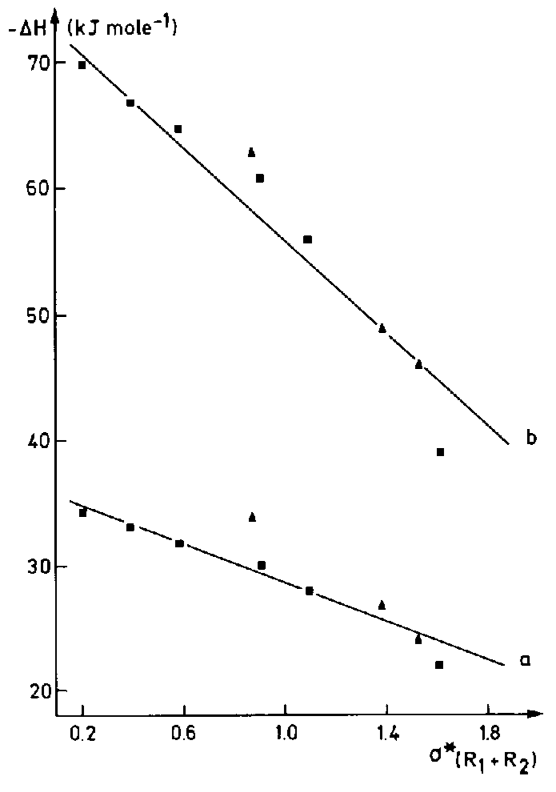


Fig. 1. Influence of the inductive effect of substituents on S on the complexation enthalpy of the monoligand (a) and biligand (b) complexes of some thioether ligands: (■) *n*,*m*-N^+SN^+, (▲) *n*,*m*-$N_p^+SN^+$.

TABLE 3

The thermodynamic functions[a] for the $Ag_2L_2^{2+}$ and AgL_2^+ complexes of some sulphur-containing amines

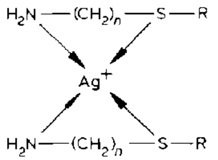
Reaction	$2\ Ag^+ + 2\ L \rightleftarrows Ag_2L_2^{2+}$			$Ag^+ + 2\ L \rightleftarrows AgL_2^+$		
	$-\Delta G$	$-\Delta H$	ΔS	$-\Delta G$	$-\Delta H$	ΔS
2,2-NSN	98.2 (1)	143.9 (4)	−153 (2)	55.93 (6)	78.3 (4)	−75 (2)
2,3-NSN	95.59 (6)	139.2 (4)	−146 (2)	56.10 (6)	79.6 (4)	−79 (2)
2,4-NSN	98.16 (6)	140 (1)	−140 (4)	56.27 (6)	79.8 (4)	−79 (2)
3,4-NSN	89.94 (4)	127.6 (4)	−126 (2)	49.76 (6)	68.0 (4)	−61 (2)
$2\text{-}NS(CH_3)$[b]	74.3 (2)	122.6 (8)	−162 (3)	53.02 (6)	82.0 (4)	−96.7 (2)
$2\text{-}NS(C_2H_5)$[b]	77.9 (2)	127.1 (4)	−165 (2)	55.13 (6)	84.9 (8)	−99.6 (3)
$2\text{-}NS(^nC_3H_7)$[b]	77.56 (6)	130.1 (4)	−177 (2)	55.36 (6)	84.5 (2)	−97.9 (3)
$3\text{-}NS(CH_3)$[b]	78.16 (4)	123.8 (4)	−154 (1)	44.63 (6)	72.8 (8)	−94.6 (3)

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

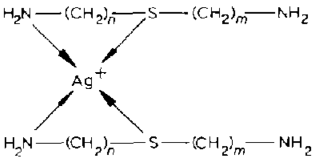
[b] Data from ref. 7 given for comparison.

shown [7,16,17] that six-membered Ag(I) chelate rings are less stable than five-membered rings.

Comparing the thermodynamic values for the AgL_2^+ species for the bidentate [7] *n*-NS(R) series (**III**) and the possibly tridentate *n*,*m*-NSN series of ligands it is seen that the latter series coordinates some 4 kJ mol^{-1} less exothermic. The entropy term, on the contrary, is some 11–20 J mol^{-1} more favourable. Both opposing effects confirm the earlier assumption [1] that in the biligand AgL_2^+ species these *n*,*m*-NSN ligands behave only as bidentates.



(III)



(IV)

The non-bonded amino group excerts an electron withdrawing effect on the coordinating sulphur donor leading to a less exothermic enthalpy effect. On the other hand, there are four possibilities to arrange one N and one S donor from each ligand in a tetrahedral configuration (**IV**) around the Ag(I) ion. This statistical reason corresponds to a more favourable entropy of $\delta(\Delta S) = R\ \ln(4/1) = 8.31$ J mol^{-1} K^{-1}. Ln $4 = 11.5$ J K^{-1} mol^{-1} and explains well the experimental results.

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