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THERMODYNAMICS OF COMPLEX FORMATION OF Ag(I). VI. Ag(I)–THIOCARBONYL LIGAND SYSTEMS IN AQUEOUS SOLUTION *

DOMENICO DE MARCO **, GABRIELLA MAUCERI, ANTONINO MARCHESE and ATHOS BELLOMO

Institute of Analytical Chemistry, University of Messina, Via dei Verdi, 98100 Messina (Italy)

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ABSTRACT

The formation of complexes between Ag(I) and substituted thioureas has been studied by potentiometric measurements in aqueous solution at $\mu = 0$ and various temperatures.

Under these experimental conditions, three-coordinated complexes are formed with all the ligands. The influence of the substituents is mainly an "external" effect and causes a more positive ΔH and ΔS value for the formation of complexes with substituted thioureas compared to those with thioureas.

INTRODUCTION

The coordinating properties of donor or acceptor atoms depend on their chemical environment [1]. Sometimes it can greatly modify the electronic structure of a metal ion or ligand and, consequently, metal–ligand interactions. The *trans*-effect and the *trans*-influence of various ligands have been widely studied in Pt(II) chemistry and it is well known that very soft ligands stabilize hard liganols in the *trans* position in the square planar geometry [2].

In aqueous solution, Ag(I) complexes of ligands with different donor atoms show the stability sequence N < S < P [3,4]. This sequence has been established using, for sulfur donors, stability constants for the formation of monocoordinated complexes with thioethers [5–7], which are in the range 10^3–10^4.

Ag(I)-thiocarbonyl complexes have higher thermodynamic stability ($\log \beta_1 = 7$–9) [8–13] and K_1/K_2 ratios > 100 so that their formation curves are

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** Author to whom correspondence should be addressed.

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similar to those of Ag(I) complexes with π-acceptor ligands. Ahrland ascribed the value $K_1/K_2 > 100$ to the presence of π-backbonding in complexes with suitable ligands.

The electronic structure of the thiocarbonyl group (which has one σ-bond, one π-bond and non-bonding electrons on the sulfur atom) is affected by the nature of the radicals bound to it [14–18]. Such changes modify the reactivity of thiocarbonyl and the total effect on a complexing reaction in solution depends on the quantitative balance of metal–ligand, metal–solvent, ligand–solvent, complex–solvent and solvent–solvent interactions.

In this paper, the results of a potentiometric investigation in aqueous solution (at $\mu = 0$ and different temperatures) on thermodynamics of complex formation between Ag(I) and a series of substituted thioureas (see notation) are reported. ΔH and ΔS are deduced from the linear dependence of ΔG on temperature.

EXPERIMENTAL

Measurements

Potentiometric measurements were made in a thermostatted room, using an Amel potentiometer (model 335) and the following cell

$$\mathrm{Ag/Ag(I)\ (test\ solution)/KNO_3(sat.\ salt\ bridge)/KCl(sat.)/Ag} \qquad (1)$$

Solutions containing constant concentrations of Ag(I) were titrated with 10^{-2} M ligand solution. At each temperature, five different $|\mathrm{Ag(I)}|_{\mathrm{tot}}$ (equally spaced over the concentration range reported in eqn. 2) were titrated. Initial volumes were kept constant (10 ml) and the same quantities of ligand were always added.

$$2 \times 10^{-6}\ \mathrm{M} \le |\mathrm{Ag(I)}|_{\mathrm{tot}} \le 1 \times 10^{-5}\ \mathrm{M}$$

$$1 \times 10^{-4}\ \mathrm{M} \le |\mathrm{L}|_{\mathrm{tot}} \le 2 \times 10^{-3}\ \mathrm{M} \qquad (2)$$

Reagents

$AgNO_3$ and ligand solutions were prepared by direct weighing of samples dried on P_2O_5 [19] (the ligands were recrystallized from ethanol).

Calculations

Starting from the experimental values of function (3) at different $|\mathrm{Ag(I)}|_{\mathrm{tot}}$ concentrations and constant $|\mathrm{L}|_{\mathrm{tot}}$, the values in eqn. (4) (extrapolated to $|\mathrm{Ag(I)}|_{\mathrm{tot}} = 0$ and referred only to mononuclear complexes [20] were calculated (this condition also implies $|Ag(I)|_{free} = 0$ and $|L|_{free} = |L|_{tot}$).

$$\log \eta = \log(|Ag(I)|_{tot}/|Ag(I)|_{free}) = f(|Ag(I)|_{tot})_{|L|_{tot}=const.} \quad (3)$$

$$\log \eta_0 = \lim_{Ag(I)\to 0} \log \eta \quad (4)$$

The experimental conditions referred to in eqn. (2) (which verify both relationships $|L|_{tot} > |Ag(I)|_{tot}$ and $10 \leq |L|_{tot}/|Ag(I)|_{tot} \leq 1000$) were selected for meaningful extrapolations. By rough estimation, for the lowest ligand concentration

$$0.9|L|_{tot} \leq |L|_{free} \leq 0.98|L|_{tot} \quad (5)$$

can be found; while for the highest

$$0.98|L|_{tot} \leq |L|_{free} \leq 0.997|L|_{tot} \quad (6)$$

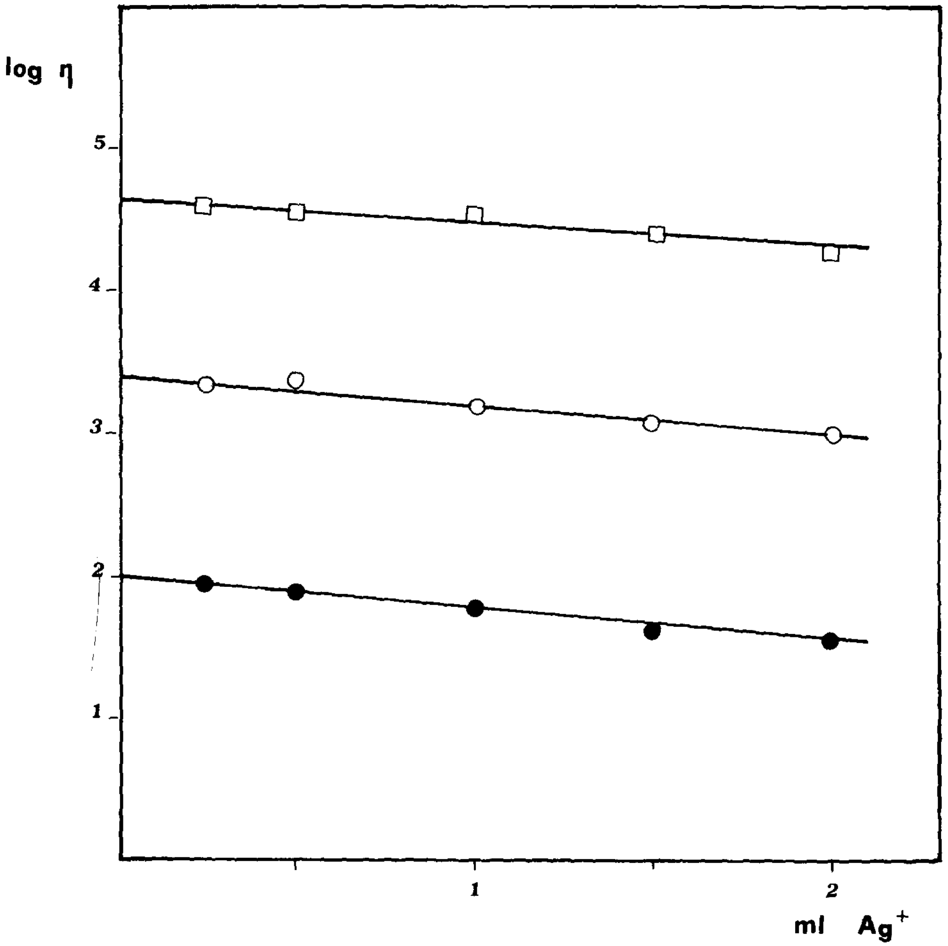

Fig. 1. Relationships between log η and volume of 10^{-4} M Ag(I) at $|Me_4Tu|_{tot}$ = const. Initial volume = 10 ml; volume of solution = 10 ml + vol. of ligand added; $t = 30$°C. Volume of 10^{-2} M Me_4Tu = (●) 0.1 ml, (○) 0.5 ml, (□) 1.5 ml.

so that the extrapolation for $|Ag(I)|_{tot} = 0$ must cover only a short concentration range.

The configuration of each system was identified by mathematical analysis [21,22] of the function $\eta_0 = f(|L|)$ and the best values of $\log \beta_n$ were obtained by non-linear least-squares fitting. More detailed information on experimental, calculations and programs can be obtained on request to the authors.

RESULTS AND DISCUSSION

Figures 1 and 2 show some of the results obtained in the system Ag(I)–Me_4Tu at $t = 30°C$. Figure 1 refers to the measured values of $\log \eta$ at different $|Ag(I)|_{tot}$ concentrations (these are reported in Fig. 1 as millilitres of 10^{-3} M $AgNO_3$ solution drawn for the titration). Curves a, b, and c refer to the addition of 0.1, 0.5 and 1.5 ml of 10^{-2} M ligand solution, respectively. For a $6 \leq |Me_4Tu|/|Ag(I)|_{tot} \leq 20$; while for c $60 \leq |Me_4Tu|/|Ag(I)|_{tot} \leq 800$. As can be seen, function (3) shows a small, almost constant, dependence on $|Ag(I)|_{tot}$, so that the intercepts ($\log \eta_0$) are clearly located. The behaviour drawn in Fig. 1 is also representative of the other systems, because it depends on appropriate selection of the experimental conditions.

Figure 2 shows the dependence of $\log \eta_0$ on $\log|Me_4Tu|$. In the studied concentration range (reported in Fig. 2), $\bar{n} = 1.7$–2.33 is found.

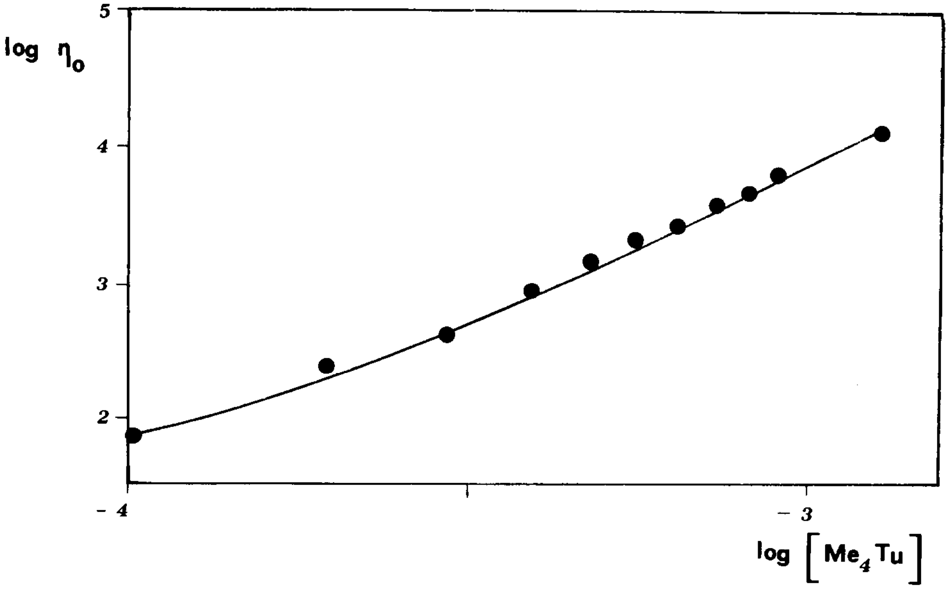

Fig. 2. Relationship between $\log \eta_0$ and $\log|Me_4Tu|$ at $t = 30°C$ and $\mu = 0$. The average coordination number ($\bar{n}$) in the range $-\log |Me_4Tu| = 3.8$–3.1 is 2.3.

TABLE 1

$\log \beta$ and ΔG for the formation of complexes of Ag(I) with substituted thioureas at different temperatures and $\mu = 0$ in aqueous solution

	n	$t = 0$		$t = 5$		$t = 10$		$t = 15$		$t = 20$		$t = 25$	
		$\log \beta$	$-\Delta G$	$\log \beta$	$-\Delta G$	$\log \beta$	$-\Delta G$	$\log \beta$	$-\Delta G$	$\log \beta$	$-\Delta G$	$\log \beta$	$-\Delta G$
MeTu	1	5.92 ± 0.3	30.94	6.89 ± 0.1	36.7	6.39 ± 0.1	34.62	6.9 ± 0.3	38.1	5.96 ± 0.1	33.9	–	–
	2	10.05 ± 0.1	52.50	11.01 ± 0.2	58.62	10.67 ± 0.1	57.86	10.15 ± 1	56.0	10.09 ± 0.1	56.65	–	–
	3	13.33 ± 0.1	69.71	14.90 ± 0.1	79.34	14.01 ± 0.1	75.99	14.29 ± 1	78.8	14.05 ± 0.1	78.84	–	–
Me_2Tu	1	7.04 ± 0.7	36.8	–	–	5.11 ± 1	27.65	–	–	6.44 ± 0.1	36.17	–	–
	2	13.11 ± 0.3	59.16	–	–	10.31 ± 0.1	55.85	–	–	10.27 ± 0.2	57.78	–	–
	3	14.75 ± 0.5	77.16	–	–	13.18 ± 0.1	71.47	–	–	14.12 ± 0.0	79.26	–	–
Me_4Tu	1	5.91 ± 0.1	30.30	6.25 ± 0.1	33.24	5.21 ± 0.8	28.26	5.95 ± 0.0	32.8	5.46 ± 0.0	30.65	5.75 ± 0.0	32.8
	2	9.33 ± 0.7	49.86	10.58 ± 0.1	56.35	8.95 ± 1.4	48.48	9.87 ± 0.0	54.4	9.70 ± 0.1	54.43	10.07 ± 0.0	57.48
	3	13.69 ± 0.0	71.59	13.64 ± 0.1	72.64	13.02 ± 0.2	70.63	–	–	13.1 ± 0.0	73.44	12.88 ± 0.1	66.11
EtTu	1	8.63 ± 0.8	45.1	–	–	5.81 ± 0.7	31.48	–	–	7.05 ± 0.2	39.57	–	–
	2	12.91 ± 0.3	67.53	–	–	11.27 ± 0.2	61.13	–	–	10.77 ± 0.0	60.42	–	–
	3	–	–	–	–	14.66 ± 0.1	79.47	–	–	14.48 ± 0.0	81.27	–	–
Et_2Tu	1	6.23 ± 0.1	32.57	–	–	5.46 ± 0.1	31.23	–	–	7.63 ± 0.4	42.83	–	–
	2	10.01 ± 0.3	52.38	–	–	9.38 ± 0.3	50.83	–	–	11.50 ± 0.3	64.56	–	–
	3	13.41 ± 0.9	70.13	–	–	13.11 ± 0.1	71.09	–	–	–	–	–	–
EnTu	1	5.64 ± 1.3	29.48	6.66 ± 0.1	35.46	5.54 ± 0.1	30.02	5.5 ± 0.0	30.35	6.06 ± 0.1	34.0	6.8 ± 0.1	38.81
	2	9.82 ± 0.3	51.33	11.27 ± 0.1	60.0	9.0 ± 0.2	57.63	9.15 ± 0.1	50.49	10.82 ± 0.2	60.7	9.43 ± 0.2	53.84
	3	14.11 ± 0.0	73.77	14.29 ± 0.1	76.12	13.76 ± 0.1	77.41	14.1 ± 0.0	77.75	13.71 ± 0.3	79.61	13.25 ± 0.2	75.66
ALTu	1	6.73 ± 1.1	35.21	–	–	5.88 ± 0.7	36.13	–	–	6.21 ± 0.2	34.21	–	–
	2	11.12 ± 0.4	58.15	–	–	10.84 ± 0.4	58.78	–	–	11.2 ± 0.2	62.68	–	–
	3	15.29 ± 0.0	79.97	–	–	14.43 ± 0.1	78.21	–	–	14.38 ± 0.3	80.68	–	–

TABLE 1 (*continued*)

	n	$t = 30$		$t = 35$		$t = 40$		$t = 45$		$t = 50$	
		$\log \beta$	$-\Delta G$	$\log \beta$	$-\Delta G$	$\log \beta$	$-\Delta G$	$\log \beta$	$-\Delta G$	$\log \beta$	$-\Delta G$
MeTu	1	7.16 ± 0.1	41.50	5.06 ± 0.0	29.77	6.66 ± 0.0	40.14	6.12 ± 0.1	37.3	6.68 ± 0.0	41.25
	2	10.64 ± 0.3	61.78	8.79 ± 0.0	51.81	10.02 ± 0.1	60.05	9.29 ± 0.3	57.1	9.93 ± 0.1	61.39
	3	–	–	11.17 ± 0.3	65.82	12.40 ± 0.0	74.27	12.63 ± 0.1	76.8	–	–
Me_2Tu	1	6.15 ± 0.1	35.7	–	–	6.35 ± 0.0	38.01	–	–	5.7 ± 0.1	35.21
	2	10.54 ± 0.0	61.17	–	–	10.25 ± 0.0	61.18	–	–	10.0 ± 0.0	62.26
	3	–	–	–	–	–	–	–	–	–	–
Me_4Tu	1	5.88 ± 0.0	34.12	5.73 ± 0.1	33.89	5.6 ± 0.0	33.54	5.95 ± 0.2	36.21	4.79 ± 0.1	29.61
	2	9.28 ± 0.1	53.84	9.60 ± 0.1	56.58	9.08 ± 0.2	54.36	9.68 ± 0.2	59.00	8.66 ± 0.1	53.52
	3	12.68 ± 0.0	73.56	12.88 ± 0.1	75.9	13.29 ± 0.1	79.58	12.12 ± 0.6	73.72	12.03 ± 0.0	74.31
EtTu	1	5.88 ± 0.4	34.12	–	–	6.47 ± 0.1	38.76	–	–	–	–
	2	10.64 ± 0.0	61.8	–	–	9.8 ± 0.3	58.25	–	–	–	–
	3	–	–	–	–	12.43 ± 0.7	74.47	–	–	–	–
Et_2Tu	1	4.99 ± 0.2	28.96	–	–	5.06 ± 0.1	30.32	–	–	4.72 ± 0.0	29.19
	2	8.87 ± 0.1	51.5	–	–	9.03 ± 0.0	54.11	–	–	7.15 ± 0.3	44.20
	3	12.10 ± 0.0	70.21	–	–	–	–	–	–	10.84 ± 0.0	66.95
EnTu	1	4.6 ± 0.1	27.71	5.29 ± 0.1	31.24	5.17 ± 0.2	30.94	5.78 ± 0.1	35.13	5.32 ± 0.2	32.87
	2	9.56 ± 0.2	55.48	10.27 ± 0.1	60.51	7.97 ± 0.7	47.71	9.90 ± 0.1	60.26	8.95 ± 0.1	55.28
	3	12.46 ± 0.2	77.35	12.82 ± 0.4	75.56	12.24 ± 0.1	74.14	12.25 ± 0.3	75.52	–	–
ALTu	1	6.91 ± 0.0	40.07	–	–	7.31 ± 0.1	43.78	–	–	6.23 ± 0.3	38.51
	2	9.5 ± 1.2	55.22	–	–	9.58 ± 0.3	57.37	–	–	10.56 ± 0.0	65.20
	3	13.77 ± 0.1	79.93	–	–	13.53 ± 0.3	81.08	–	–	–	–

TABLE 2

Most probable values of log β, ΔG, ΔH and ΔS for formation of complexes of Ag(I) with substituted thioureas at 25°C and $\mu = 0$ in aqueous solution

	n	log β	$-\Delta G$	ΔH	ΔS	$T\Delta S$	i
Tu	1	7.30	41.4	−154.4	−376.8	−112.1	
		9.35	47.7	−103.8	−175.8	−52.4	
	2	10.6	60.23	−108.4	−150.7	−44.9	
		10.79	61.54	−136.1	−274.0	−73.6	
	3	12.80	72.84	−109.3	−121.4	−36.1	
		13.6	77.45	−81.6	−13.4	−4.0	
MeTu	1	6.34	36.4	−18.1 ± 1.4	−62.8 ± 35	+18.8	3*
	2	10.08	57.3	−46.4 ± 0.9	+37.6 ± 25	+11.3	3*
	3	12.29	74.1	−124.3 ± 1.6	−167.0 ± 60	−49.8	0
Me_2Tu	1	6.12	34.7	0 ± 1.6	+117.2 ± 54	+34.7	3*
	2	10.38	59.4	−17.8 ± 0.4	+138.6 ± 16	+41.0	3*
	3	13.59	77.4	−46.0 ± 10	+104.6 ± 40	+31.4	0*
Me_4Tu	1	5.69	32.6	−6.3 ± 0.4	+87.9 ± 16	+26.3	3*
	2	9.55	54.4	−20.1 ± 0.9	+117.2 ± 25	+34.7	3*
	3	13.07	74.5	−36.8 ± 0.4	+125.6 ± 21	+37.3	3*
EtTu	1	6.38	36.4	−54.8 ± 3.5	−61.5 ± 125	−18.2	3
	2	10.64	60.7	−108.4 ± 3.0	−161.2 ± 108	−48.1	3
	3	13.68	78.3	−133.9 ± 4.0	−188.8 ± 125	−56.1	0
Et_2Tu	1	5.82	33.5	−88.3 ± 1.8	−206.3 ± 62	−61.5	3
	2	9.12	51.9	−83.7 ± 0.8	−101.3 ± 33	−30.1	3
	3	12.6	69.1	−88.7 ± 0.8	−65.3 ± 33	−19.7	0
EnTu	1	5.65	32.2	−30.9 ± 1.4	+4.2 ± 33	+1.3	3*
	2	9.68	55.3	−52.3 ± 0.8	−10.4 ± 25	−2.9	3
	3	13.16	72.0	−88.3 ± 0.8	−46.5 ± 25	−13.8	0
ALTu	1	6.67	38.1	+20.1 ± 0.4	+192.6 ± 12	+57.3	3*
	2	10.38	59.2	−66.1 ± 0.8	−20.9 ± 30	−62.8	3
	3	14.07	80.4	−61.9 ± 0.4	+60.7 ± 12	+18	2*

Table 1 refers to the complexes identified and to their log β_n and ΔG values as obtained directly at the various temperatures from the experimental data.

From Table 1, the log β_n, ΔG, ΔH, and ΔS values given in Table 2 are deduced by linear interpolation and can be considered as the most probable values at $t = 25°C$. In this procedure, the original data of Table 1 were locally smoothed by linear interpolation on two or three points (as indicated in the last column of Table 2). For comparison, the thermodynamic data for the complexing reaction of Ag(I) with thiourea, published in a previous paper [11,12] at $\mu = 0$ and 1 for KNO_3 are also reported.

The values of free energy changes for the formation of monocoordinated complexes (ΔG_1) with substituted thioureas are more positive than the value for the formation of $AgTu^+$ and lie in a narrow range. The range becomes narrower as the coordination number increases from 1 to 2. In fact the formation of monocoordinated Ag(I) with substituted thioureas involves a more positive free energy ($\simeq$ 5–10 kJ mol^{-1}) than that of $AgTu^+$. The differences in ΔG are less evident in reaction (7).

$$Ag^+ + 2L = AgL_2^+ \qquad (7)$$

where ΔG_2 values remain more positive compared to ΔG_2 for L = Tu.

TABLE 3

Log K, $\overline{\Delta G}$, $\overline{\Delta H}$, and $\overline{\Delta S}$ for the stepwise formation of complexes of Ag(I) with substituted thioureas at $t = 25°C$ and $\mu = 0$ in aqueous solution

	n	log K	$-\Delta G$	ΔH	ΔS	$-\lvert\Delta \ln K\rvert_{n-1}^{n}$	K_{n-1}/K_n
Tu	1	7.3	41.4	−154.4	−376.8		
		8.35	47.7	−103.8	−175.8		
	2	3.3	18.8	+48.5	+226	4.0	10^4
		2.44	13.8	−32.2	−71	5.9	8.1×10^5
	3	2.2	12.5	−3.3	+29	1.1	12.6
		2.93	15.9	+54.4	+233	−0.5	0.3
MeTu	1*	6.34	36.4	−18	+63		
	2	3.73	20.9	−28	−25.1	2.6	403
	3	2.9	16.7	−78	−205.6	0.8	6.7
Me_2Tu	1	6.1	34.7	0	+117		
	2*	4.26	24.7	−17.6	+21	1.9	74
	3	3.2	18	−28.5	−33.5	1.0	11
Me_4Tu	1*	5.69	32.6	−6.3	+88		
	2*	3.87	21.7	−13.8	+29	1.8	667
	3*	3.52	20.1	−16.7	+8	0.3	2
EtTu	1	6.38	36.4	−54.8	−61.5		
	2	4.04	24.3	−53.6	−99.6	2.4	221
	3	3.04	17.6	−25.5	−27.2	1	10
Et_2Tu	1	5.82	33.5	−88.3	−206		
	2	3.3	18.4	+4.2	+105	2.5	330
	3*	3.04	17.1	−5	+36	0.3	1.8
EnTu	1*	5.65	32.2	−31	+4.2		
	2	4.04	23.0	−21	−14.6	1.6	40
	3	3.47	19.7	−36	−35.5	0.6	4
ALTu	1*	6.69	38.1	+20.1	+192.5		
	2	3.69	20.9	−86.2	−226	3	992
	3*	3.69	20.9	+41.9	+79.5	0	1

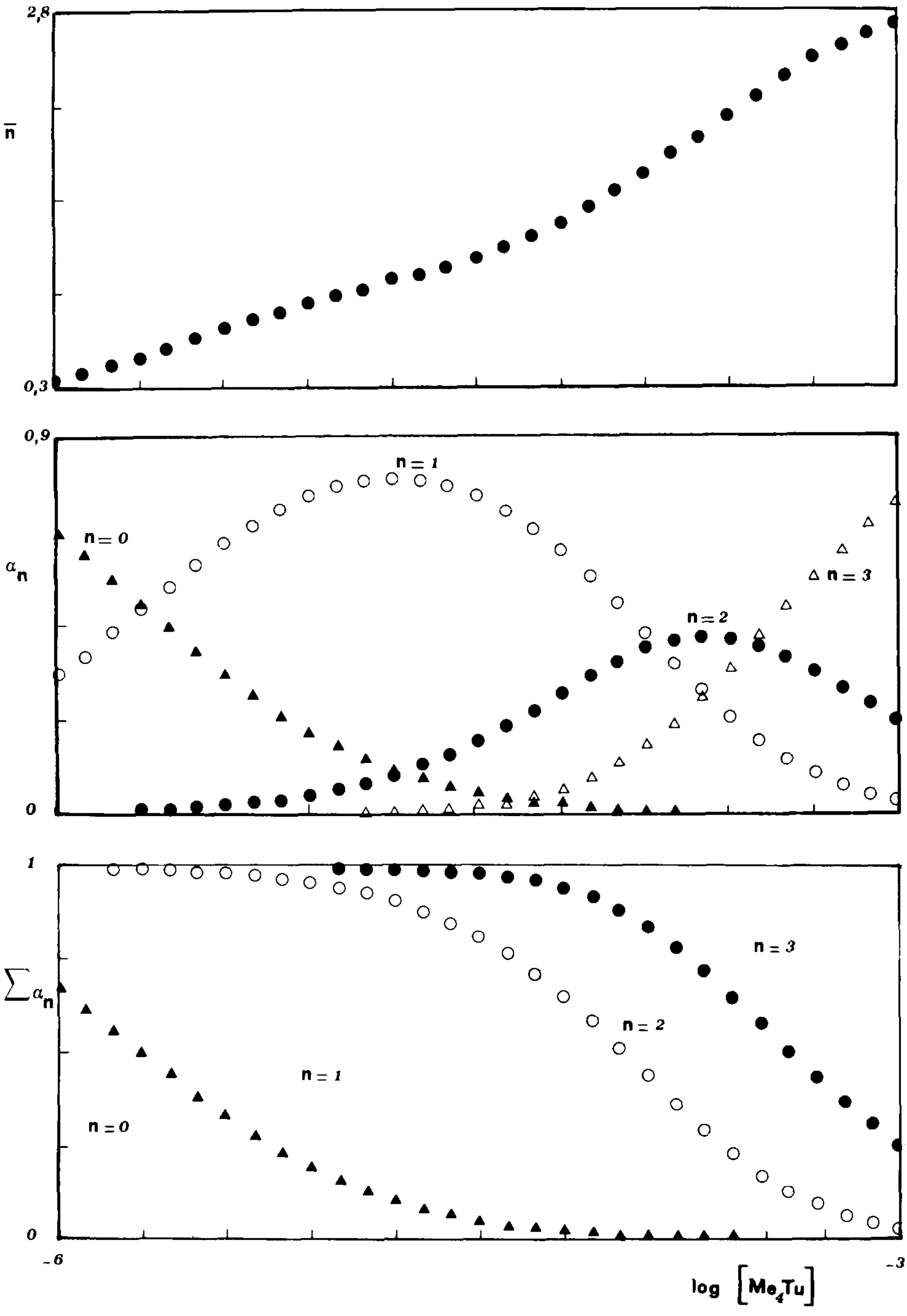

Fig. 3. Relationships between $\bar{n}$, α_n, $\Sigma\alpha_n$ and log $|Me_4Tu|$, for $Ag(Me_4Tu)_n^+$ complexes at $t = 25°C$ and $\mu = 0$ (as obtained with the data of Table 2).

For reaction (8)

$Ag^+ + 3L = AgL_3^+$

ΔG_3 for Tu complexes does not occupy the lower end of the set. As a consequence the presence of radicals on thiourea produces only little change in the relative position of the free energy levels of reagents and products, which depends more on the extent of complexation of Ag(I) than on the nature and number of substituents.

For the stepwise changes of free energy, $\overline{\Delta G}$, reported in Table 3, a similar trend can be seen to that already found for $AgTu_n^+$ ($n = 1$–3) ($\overline{\Delta G}_1 \ll \overline{\Delta G}_2 < \overline{\Delta G}_3$) with a sharp loss of stability in the stepwise coordination of the second molecules of the ligand. The difference between $\overline{\Delta G}_1$ and $\overline{\Delta G}_2$ is lower for the complexes with substituted thioureas than that for $AgTu_n^+$ complexes. Notwithstanding, the range of ligand concentration where the formation of monocoordinated complexes predominates is rather large (Fig. 3). The 2nd and 3rd stepwise coordinations of substituted thioureas exhibit more favourable free energy changes with respect to the corresponding $AgTu_2^+$ and $AgTu_3^+$. It is evident that the lower overall stability ($-\Delta G_n^2$) of the complexes with substituted thioureas arises from the first coordination which engages, to a lower extent than Tu, the coordinating abilities of the metal ion. In such a way Ag(I) is more available to successive coordination in inverse dependence on the stability of the reagent substrate ($\overline{\Delta G}_n$ for AgL_n^+ ($L \neq Tu$) $< \overline{\Delta G}_n$ for $AgTu_n^+$ ($n = 2$–3)).

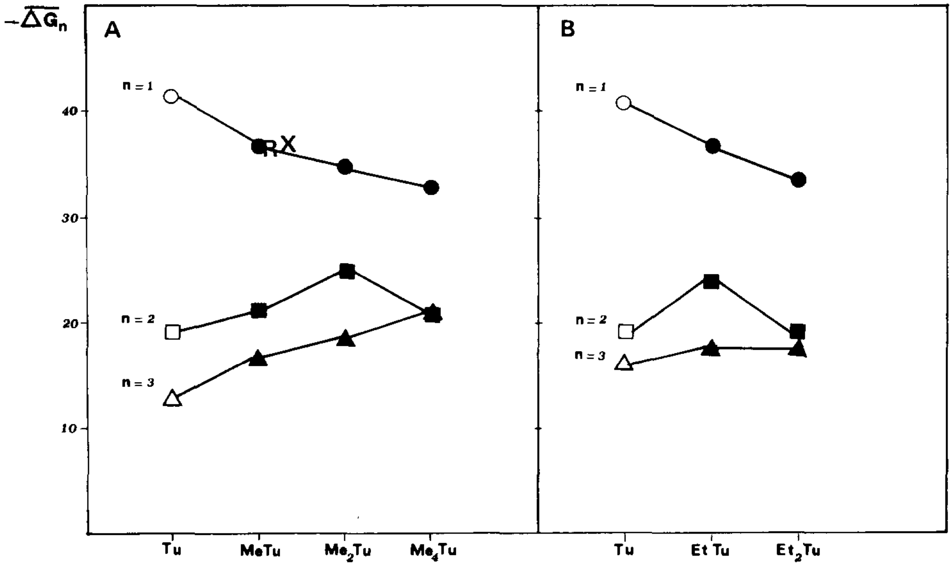

Fig. 4. Relationships between the stepwise free energy change and the number of substituents. (A) Methyl-substituted thioureas; (B) ethyl-substituted thioureas.

The effect of the nature of the substituent on the formation of the complexes varies with coordination number of the substrate. The successive substitution of hydrogen atoms with CH_3– lead to $-\overline{\Delta G}_1$ decreasing with the number of methyl groups, while for the 2nd and 3rd coordinations the pattern is inverted (Fig. 4). The same pattern can be observed for the ethyl-substituents.

$|\Delta \log K|_{n-1}^{n}$ decreases uniformly as n increases. The highest $|\Delta \log K|_1^2$ value is found for ALTu complexes, so that the formation of Ag(ALTu)$_3^+$ is unfavoured in comparison to the other systems (see Figs. 5 and 3).

The free energy changes for the Ag(I)–substituted thiourea complexes come from a different enthalpy–entropy balance compared to the AgTu$_n^+$ complexes. For AgTu$_n^+$ complexes the highly negative ΔH_n values are counteracted by unfavourable entropy changes which "neutralize" (for the overall 1st and 2nd coordinations) 50–70% of the overall ΔH_n. This behaviour is typical of soft–soft interaction in aqueous solution where large enthalpy losses coupled with negative entropy changes are observed [23]. This surely applies when a complexing reaction has a sufficiently negative ΔH. When $\Delta H \simeq 0$, however, exceptions can be found (even if metal–ligand interactions are still soft–soft in nature). In Tables 2 and 3, asterisks indicate cases in which $\Delta H < 0$ and $\Delta S > 0$ act in the same direction on resulting free energy changes. Figure 6, which includes all the enthalpy–entropy data [25] for the systems under investigation, shows a sharp compensative interplay of ΔH vs. ΔS so that the external [24] (or proportional [25]) contribution to these complexing reaction depends on temperature [25]. The behaviour described by Ahrland [23] (according to whom soft–soft interaction leads to $\Delta H < 0$ coupled with $\Delta S < 0$) is represented by points lying in the 3rd quadrant in a space (ΔH, ΔS). However, Fig. 6 clearly shows that there are reactions with $\Delta H < 0$ and $\Delta S > 0$ and also $\Delta H > 0$ and $\Delta S > 0$ for the same soft–soft interaction. In a homologous set of reactions, examples with $\Delta H < 0$ and $\Delta S > 0$ will be numerous as ΔH_{int} (or residual [25]) is more negative and the lower the angular coefficient of the trend on which the reactions lie. Figure 6 also shows that the reactions of Table 3 form two homologous sets of reactions and the influence of the substituents manifests itself mainly as an "external" effect [24,25] and produces more positive overall ΔH_n values than the formation of AgTu$_n^+$ complexes. This effect is less evident in the 2nd and 3rd overall coordinations. Moreover, a different pattern is found for AgTu$_n^+$ complexes compared to AgL$_n$ (L $\neq$ Tu) ($\overline{\Delta H}_n < \overline{\Delta H}_{n-1}$ for AgL$_n^+$ and vice versa for AgTu$_n^+$. In between seems to lie the complexes with Et$_2$Tu).

The overall entropy changes increase sharply with n ($\Delta S_n > \Delta S_{n-1}$) in the formation of AgTu$_n^+$ and Ag(Et$_2$Tu)$_n^+$ ($n = 1$–3) and decrease ($\Delta S_n < \Delta S_{n-1}$) for complexes with MeTu, EtTu, EnTu and probably also with ALTu (in this last case $\Delta S_2 < \Delta S_1$ but $\Delta S_1 < \Delta S_3 < \Delta S_2$). Therefore the entropy term shows a more favourable effect in the stepwise 2nd and 3rd complexations of

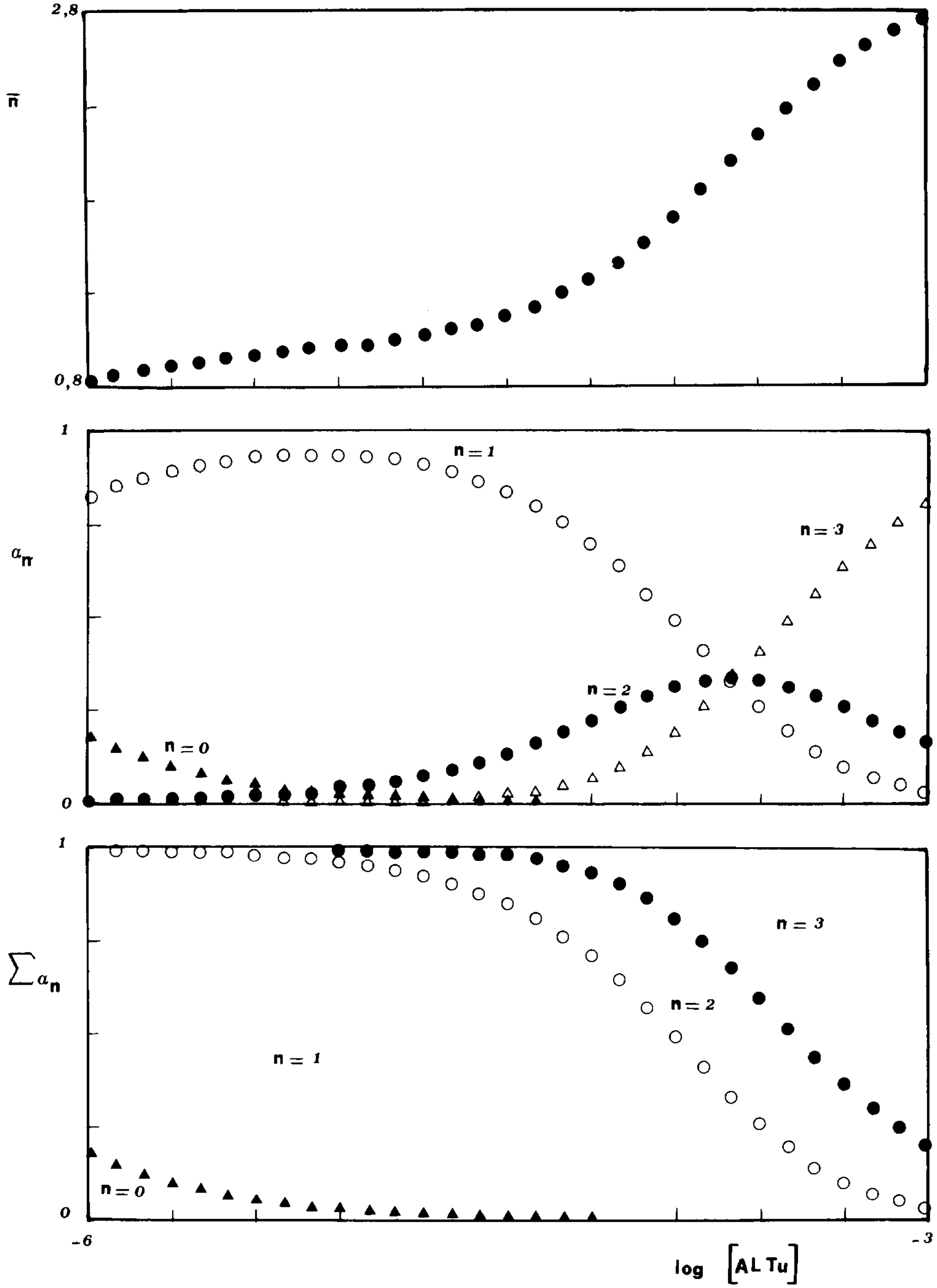

Fig. 5. Relationships between $\bar{n}$, α_n, $\Sigma\alpha_n$ and log |ALTu|, for $Ag(ALTu)_n^+$ complexes at $t = 25°C$ and $\mu = 0$ (as obtained with the data of Table 2).

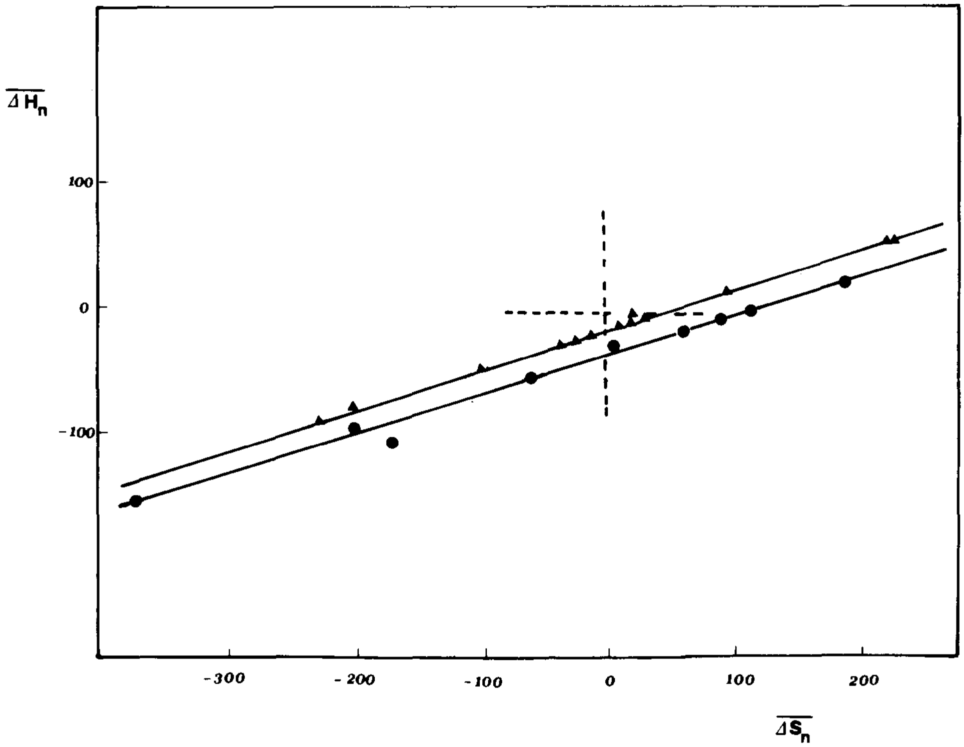

Fig. 6. Relationships between $\overline{\Delta H_n}$ and $\overline{\Delta S_n}$ in the complexing reactions of Ag(I) with thiocarbonyl ligands in aqueous solution. (●) $n = 1$; (▲) $n = 2$. (Lower line) $\overline{\Delta H_1} = -36.28(2.4)+0.309(0.01)\overline{\Delta S_n}$ ($R = 0.99$). (Upper line) $\overline{\Delta H_n} = -16.98(2.3)+0.309(0.02)\overline{\Delta S_n}$ ($R = 0.97$), $n = 2$–3.

Ag(I) with thiourea compared to substituted thioureas. It is evident that the formation of complexes with Ag(I)/L = 1 : 1 with substituted thioureas leads to the release of a greater number of solvent molecules. In contrast, in the 2nd and 3rd stepwise coordinations, the entropy changes are more favourable in the coordination of Tu.

Finally, homogeneous behaviour with respect to the number of substituent radicals (independent of its nature) can be found in the stepwise $\overline{\Delta S_2}$ value. In fact the monosubstituted thioureas lead to $\Delta S_2 < 0$ (with the sequence MeTu > EtTu > ALTu); while more substituted ligands exhibit $\Delta S_2 > 0$ increasing in the order $Me_2Tu < Me_4Tu < Et_2Tu$. EnTu seems to lie in between.

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NOTATION

Tu	thiourea
MeTu	*N*-methyl-thiourea
Me_2Tu	*N*,*N*′-dimethyl-thiourea
Me_4Tu	*N*,*N*,*N*′,N′-tetramethyl-thiourea
EtTu	*N*-ethyl-thiourea
Et_2Tu	*N*,*N*′-diethyl-thiourea
EnTu	ethylen-thiourea
ALTu	allyl-thiourea
L	ligand
$\|X\|_{\mathrm{tot}}$	overall concentration of X
$\|X\|_{\mathrm{free}}$	concentration of free X
η	$\|\mathrm{Ag(I)}\|_{\mathrm{tot}}/\|\mathrm{Ag(I)}\|_{\mathrm{free}}$
η_0	$\|\mathrm{Ag(I)}\|^{\mathrm{Lim}\,\eta}_{\mathrm{tot}} \rightarrow 0$
$\bar{n}$	average coordination number
α_n	$\|\mathrm{AgL}_n^+\|/\|\mathrm{Ag(I)}\|_{\mathrm{tot}}$
β_n	overall stability constant
K_n	stepwise stability constant
$\|\log K\|^n_{n-1}$	$\log K_n - \log K_{n-1}$
ΔG_n, ΔH_n, ΔS_n	overall free energy, enthalpy and entropy changes, respectively (in kJ mol^{-1} and kJ mol^{-1} K^{-1}) for the reaction $Ag^+ + nL = AgL_n^+$
$\overline{\Delta G_n}$, $\overline{\Delta H_n}$, $\overline{\Delta S_n}$	stepwise free energy, enthalpy and entropy changes, respectively, for the reaction $AgL_{n-1}^+ + L = AgL_n^+$

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