THERMODYNAMICS OF COMPLEX FORMATION OF Ag^I. VII. Ag^I–THIOCARBONYL LIGAND SYSTEMS IN METHANOL *

DOMENICO DE MARCO ** and ANTONINO MARCHESE

Institute of Analytical Chemistry, University of Messina, Salita Sperone 31,
CP 30, 98166 S. Agata, Messina (Italy)

WOLFGANG LINERT

Institute of Inorganic Chemistry, Technical University of Vienna,
Getreidemarkt 9, A-1060 Vienna (Austria)

(Received 24 October 1989)

ABSTRACT

Complex formation between Ag^I and some alkyl-substituted thioureas in methanol has been studied at ionic strength $\mu = 0$ and in the temperature range 0–40°C.

In all cases, step-wise formation of tris-coordinated complexes was found. The behaviour of the investigated systems does not suggest any notable differences between water and methanol. Very strict free energy or enthalpy relationships between the step-wise reaction series in the two solvents were not found.

The step-wise complex formation reactions in methanol form a series of "homologous" reactions for which there are very strict enthalpy–entropy linear relationships. The corresponding isoequilibrium temperatures in methanol are a little lower than in water.

Tetramethylthiourea behaves differently in comparison with the other ligands.

INTRODUCTION

In water solution at 25°C and ionic strength $\mu = 0$, *N*-alkyl-substituted thioureas exhibit chemical affinities towards Ag^I or Hg^{II} which are slightly dependent on the presence and the number and nature of the alkyl substituents [1,2]. In spite of that, the overall and the step-wise free energy changes arise from negative (with some exceptions) and remarkably different enthalpy and entropy contributions, according to the substituent. The changes are more favourable in the case of Hg^{II} complexes compared to Ag^I complexes.

** Author to whom correspondence should be addressed.

For Hg^{II}–substitued thiourea systems in H_2O, two distinct sets have been identified on the basis of the internal relationships in the enthalpy changes for the complex formation [2]. One set is formed by Hg^{II}–thiourea and Hg^{II}–symmetrically substituted thioureas, and the other by Hg^{II}–singly (and then unsymmetrically) substituted thioureas.

Free energy changes for Ag^I step-wise complex formation in aqueous solution with some hard or soft ligands are linearly related to the free energy changes for the corresponding Hg^{II} complexes. The relationships are fairly different for the hard or soft ligand series. This proves that the two metal ions have some hard–soft discriminating ability [3]. No strictly linear free energy relationship is found between Ag^I and Hg^{II} complexes with thiourea and substituted thioureas, although a roughly direct proportionality occurs in H_2O [2]. Notwithstanding, the two step-wise reaction series have the following meaningful points in common.

(i) In both cases, Hg^{II} and Ag^I, two very strict ΔH–ΔS linear, parallel relationships are found. One refers to formation of the $1:1$ M:L complex ($M + L = ML$) and the other simultaneously embraces the second ($ML + L = ML_2$) and third ($ML_2 + L = ML_3$) step-wise coordinations.

(ii) The stepwise enthalpy variabilities (ΔH_1, ΔH_2, ΔH_3) for both Hg^{II} and Ag^I complex formation with thiourea are higher in comparison with the variabilities of the same parameters for the complex formation of the same metal ions with substituted thioureas. Owing to the previously mentioned enthalpy–entropy interdependence, the same behaviour is found for the step-wise entropy variabilities (ΔS_1, ΔS_2, ΔS_3).

(iii) In both cases, the monocoordinated complex formation with thiourea yields the most favourable enthalpy (unfavourable entropy) changes along the series of monocoordinated complexes with the same metal ion.

The isoequilibrium relationships found in water strongly suggest that thiourea and substituted thioureas interact with the central ion (both Ag^I and Hg^{II}) by fundamentally the same mechanism [4–9]. The role of the alkyl substituent (or at least its principal part) is in modifying the solvation states of the reacting free ligand and the complex produced.

EXPERIMENTAL

Chemicals

Ag^I solutions were prepared by direct weighing of $AgNO_3$ samples stored over P_2O_5.

Commercial samples of the ligands were recrystallised from acetone and vacuum dried over P_2O_5. The solutions were prepared by direct weighing.

Methanol (Riedel de Haen) was used without further purification and contained less than 0.05% water, as determined by Karl Fischer titration.

Measurements and calculations

Potentiometric measurements were performed in a thermostatted cell using an AMEL model 335 potentiometer and the following electrode system:

Ag	AgNO$_3$	LiNO$_3$ sat.	KCl	Ag
	test sol.	salt bridge	sat. sol.	
	in CH$_3$OH	in CH$_3$OH	in H$_2$O	
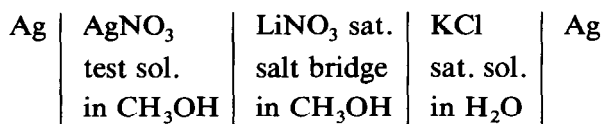
The reference electrode was prepared by immersing a silver wire into an aqueous saturated KCl solution. This reference cell became stable after 4–5 days.

A 20 cm LiNO$_3$ saturated methanol salt bridge was used in order to avoid H$_2$O diffusion from the reference to the test half-cell. This solution was periodically replaced.

The cell arrangement was tested for its potentiometric response within the temperature range 0–40°C and AgNO$_3$ concentration range 10^{-5}–10^{-4} M in the absence of ligands and background electrolyte. It displays the theoretically expected Nernst slopes, ±3%. The temperature dependence of the standard potential Ag/Ag^I with respect to the reference electrode used is described by the linear relation $E_{0,t} = 736.9 - 0.3554 \times t$ (t = Celsius temperature), obtained by the linear least-squares fitting of nine $E_{0,t}$ points equally spaced within the investigated temperature range.

The metal ion and ligand concentration ranges investigated were $[Ag^I]_{tot} = 1 \times 10^{-5}$ to 5×10^{-5} M and $[L]_{tot} = 1.33 \times 10^{-4}$ to 1.8×10^{-3} M. At each temperature, five different Ag^I solutions of total concentration, equally spaced in the above-mentioned range, were suitably titrated with ligand solution. Ag^I solution was slowly added with continuous stirring to an excess of ligand solution which was free from acid or bases and colourless. Very stable solutions are obtained which can be titrated by the ligand. In contrast when ligand is added to uncomplexed Ag^I solutions, unstable solutions are formed. In this case, the Ag/Ag^I electrode potential drifts downward and a black product, probably Ag$_2$S and/or Ag^0, is formed by solvolysis and/or oxidation of the ligand. The titration solutions were prepared by adding AgNO$_3$ to solutions containing $[L]_{tot} = 1.33 \times 10^{-4}$ M, always exceeding the investigated Ag^I total concentrations, and then titrating with further additions of ligand solution.

For each titration the ionic medium is specified by the total amount of AgNO$_3$. The experimental $\Delta E = E_{cal} - E_{exp}$ data were numerically extrapolated to $[Ag^I]_{tot} = 0$ while maintaining a constant $[L]_{tot}$. With these conditions, the function $E^{\ominus} = RT/F \ln \eta_0 = RT/F \ln(\Sigma \beta_n [L]^n)$, referring to mononuclear complexes AgL$_n$ ($n = 1-N$), was evaluated as a function of $[L]_{tot}$. (As can be inferred from the central ion and ligand concentration ranges, the ratios $[L]_{tot}/[Ag^I]_{tot}$ were varied within the range 2.66–180. Thus

TABLE 1

Overall stability constants (β_n, dm^{3n} mol^{-n}) and free energy changes (ΔG, kJ mol^{-1}) for the complex formation between Ag^I and thiourea or substituted thioureas, at various temperatures and $\mu = 0$, in methanol

Ligand	n	T=0°C log β	T=0°C −ΔG	T=5°C log β	T=5°C −ΔG	T=10°C log β	T=10°C −ΔG	T=15°C log β	T=15°C −ΔG	T=20°C log β	T=20°C −ΔG
Tu	1	10.66±0.1	56.74	10.29±0.03	54.79	10.13±0.09	54.91	9.37±0.03	51.69	–	–
	2	14.37±0.1	75.14	14.03±0.04	74.71	13.75±0.22	74.54	13.62±0.22	75.13	–	–
	3	18.07±0.1	94.49	17.26±0.04	91.91	17.28±0.09	93.67	16.50±0.05	91.02	–	–
MeTu	1	10.10±0.1	52.82	9.36±0.06	49.84	9.13±0.09	50.37	9.39±0.06	52.70	8.96±0.17	50.57
	2	12.60±0.13	65.89	12.33±1.97	65.66	11.77±0.00	63.80	13.37±0.13	73.75	13.46±0.08	75.54
	3	17.90±0.07	93.60	17.53±0.03	93.35	17.26±0.04	93.56	16.97±0.09	93.06	16.59±0.08	93.11
Me₂Tu	1	9.06±0.15	47.38	9.20±0.12	48.99	8.92±0.08	47.81	9.44±0.11	52.08	9.16±0.07	51.41
	2	13.85±0.4	72.43	13.25±0.06	70.56	12.64±0.25	68.03	13.56±0.02	74.80	12.57±0.11	70.54
	3	17.66±0.12	92.35	16.12±0.07	85.84	16.53±0.06	89.60	–	–	15.62±0.09	87.66
Me₄Tu	1	7.37±0.07	38.54	6.12±0.40	32.59	–	–	6.25±0.00	38.34	6.54±0.04	36.70
	2	10.89±0.18	55.38	10.05±0.25	53.52	–	–	9.68±0.01	53.40	10.01±0.06	56.18
	3	13.57±0.15	70.96	13.07±0.22	69.60	–	–	12.75±0.07	70.33	12.31±0.21	69.09
EtTu	1	10.51±0.04	54.96	10.69±0.13	56.92	10.12±0.13	54.86	10.38±0.00	57.26	9.92±0.13	55.67
	2	14.49±0.04	75.77	14.85±0.04	79.08	14.35±0.00	77.79	13.99±0.00	77.18	13.95±0.05	78.29
	3	18.01±0.09	96.18	18.20±0.05	96.92	17.58±0.13	95.30	16.82±0.00	92.79	16.59±0.22	93.11
Et₂Tu	1	8.73±1.60	45.65	8.98±0.22	47.82	9.34±0.17	50.63	8.75±0.20	48.25	9.17±0.13	51.46
	2	13.43±0.17	70.23	13.05±0.04	69.49	12.34±0.09	66.89	13.29±0.00	73.26	12.93±0.26	72.57
	3	16.11±0.35	84.24	16.36±0.30	87.12	16.51±0.26	89.50	–	–	16.65±0.04	93.44
EnTu	1	9.53±0.04	49.84	9.46±0.06	50.37	7.69±0.22	41.69	9.38±0.05	51.74	8.56±0.09	48.04
	2	13.32±0.04	69.65	13.53±0.08	72.05	12.69±0.13	68.79	13.01±0.09	71.77	12.77±0.13	71.67
	3	16.99±0.17	88.85	16.69±0.07	88.87	16.02±0.13	86.84	12.10±0.00	66.75	16.08±0.09	90.24
(IsPr)₂Tu	1	–	–	9.15±0.00	48.72	10.05±0.09	54.32	8.95±0.09	49.37	7.95±0.04	44.62
	2	–	–	12.95±0.37	68.96	13.33±0.26	72.26	12.25±0.26	67.58	14.74±0.09	65.89
	3	–	–	17.31±0.37	92.18	16.49±0.17	89.39	15.76±0.07	86.94	15.50±0.04	86.99
ALTu	1	11.12±0.17	58.15	11.25±0.04	59.91	10.56±0.09	56.70	9.30±0.30	51.30	10.12±0.05	56.80
	2	15.50±0.04	81.05	15.29±0.07	81.42	14.59±0.04	79.09	14.33±0.17	79.05	14.20±0.06	76.69
	3	18.37±0.04	96.06	18.11±0.09	96.44	17.09±0.13	92.64	17.37±0.13	95.82	17.02±0.10	95.52

Ligand	n	T = 25 °C log β	−ΔG	T = 30 °C log β	−ΔG	T = 35 °C log β	−ΔG	T = 40 °C log β	−ΔG
Tu	1	7.96±0.09	45.43	8.17±0.4	47.42	8.25±0.09	48.67	8.20±0.09	49.16
	2	12.38±1.09	70.66	13.29±0.12	77.13	12.86±0.00	75.87	12.43±0.09	74.52
	3	15.18±0.09	88.36	–	–	15.69±0.10	92.56	15.20±0.22	91.12
MeTu	1	8.86±0.17	50.57	8.00±0.19	46.43	8.97±2.90	52.92	–	–
	2	13.48±0.02	76.94	13.12±0.04	76.14	13.92±0.90	81.53	–	–
	3	15.82±0.09	90.30	15.44±0.16	89.61	–	–	–	–
Me₂Tu	1	8.58±0.10	48.97	8.68±0.10	50.38	8.16±0.07	48.14	–	–
	2	12.52±0.06	71.46	12.20±0.13	70.80	12.24±0.03	72.21	–	–
	3	15.21±0.10	86.82	15.11±0.13	87.69	14.54±0.11	87.55	–	–
Me₄Tu	1	6.28±0.05	35.85	6.38±0.07	37.03	6.15±0.13	36.28	–	–
	2	9.67±0.08	55.20	9.56±0.15	55.84	9.48±0.26	55.96	–	–
	3	12.59±0.08	71.86	12.68±0.10	73.59	12.66±0.15	74.92	–	–
EtTu	1	10.21±0.26	58.28	9.86±0.26	57.22	9.55±0.04	56.34	9.73±0.09	58.33
	2	13.82±0.39	78.88	13.19±0.00	76.55	13.41±0.00	79.11	12.18±0.43	73.02
	3	17.02±0.24	97.15	15.30±0.13	88.80	–	–	15.64±0.39	93.76
Et₂Tu	1	9.19±0.09	52.46	9.20±0.13	53.39	8.55±0.04	50.44	–	–
	2	13.97±0.17	79.74	13.04±0.09	75.68	12.18±0.04	71.85	–	–
	3	16.79±0.17	95.84	15.09±0.65	87.58	14.81±0.13	87.37	–	–
EnTu	1	9.08±0.05	51.83	8.16±0.09	47.36	–	–	–	–
	2	12.77±0.06	72.89	12.25±0.09	71.09	–	–	–	–
	3	15.20±0.09	86.86	15.16±0.13	87.98	–	–	–	–
(IsPr)₂Tu	1	8.08±0.26	46.12	8.49±0.01	49.27	7.99±0.09	47.14	7.90±0.43	47.36
	2	12.25±0.13	69.92	12.25±0.08	71.09	11.55±0.13	68.14	11.86±0.17	71.10
	3	15.42±0.09	88.02	15.03±0.26	87.23	14.59±0.09	86.07	14.33±0.69	85.91
ALTu	1	9.73±0.08	55.54	9.68±0.04	56.18	9.25±0.35	54.57	8.99±0.13	53.90
	2	13.98±0.02	79.80	13.77±0.00	79.92	13.50±0.09	79.64	13.38±0.03	80.21
	3	16.03±0.17	91.50	15.81±0.13	91.57	16.33±0.09	96.34	16.20±0.17	97.12

the ligand in solution is predominantly "free". In the case when $[L]_{tot} = 1.33 \times 10^{-4}$ M and $[Ag^I]_{tot} = 5 \times 10^{-5}$ M (corresponding to the lowest metal-to-ligand ratio), the calculated "free" ligand concentration, assuming quantitative formation of AgL complex, is larger then 60% of the total ligand concentration. For the other experiments, the differences between $[L]_{tot}$ and $[L]_{free}$ are smaller. With these conditions, the ΔE values measured show only small variabilities in dependence on $[Ag^I]_{tot}$ at constant total ligand concentration [10]. It was therefore straightforward to extrapolate the tabulated function E to $[Ag^I]_{tot} = 0$ at constant $[L]_{tot}$ (see ref. 1, Fig. 1). When $[Ag^I]_{tot} = 0$, $[L]_{free} = [L]_{tot}$.

The configuration of each system and the starting $\{\ln \beta_n\}$ set of values were obtained by mathematical analysis of the $\{n_0, [L]\}$ values by the so-called divided differences method [11]. The best set was calculated by optimising the $\{\ln \beta_n\}$ values on the $\{\ln \eta_0, [L]\}$ data by non-linear least-squares fitting of the function $\ln \eta_0 = \ln(\Sigma \exp(\ln \beta_n) [L]^n)$.

RESULTS AND DISCUSSION

Table 1, lists the configuration of the systems, the logarithms of the overall stability constant ($\log \beta_n$, β in dm^{3n} mol^{-n}) and the corresponding free energy changes (ΔG, kJ mol^{-1}) for the various temperatures and ionic strength $\mu = 0$.

Step-wise formation of the AgL_n complexes up to tris-coordinated species are found with increasing ligand concentration for methanol, as was previously observed in aqueous solution [1].

Assuming a linear dependence of ΔG on temperature (see the trend of the data in Table 1) in the investigated concentration range, the overall enthalpy (kJ mol^{-1}) and entropy (kJ mol^{-1} K^{-1}) changes are evaluated by least-squares fitting from the data in Table 1 smoothed on I points, see Table 2). The ΔG values in Table 2 are interpolated values, and ΔH and ΔS are given as the statistically most probable values within the investigated concentration range ($t = 0$–$40\,^{\circ}$C).

Owing to the assumption of linear dependence of ΔG on t, it follows that ΔH and ΔS are the constant parameters of a straight line. Therefore the values reported in this contribution can be interpreted: (i) as constant parameters within the temperature range; or (ii) as the values referred to the average temperature; or, more generally, (iii) as the most probable values within the investigated temperature range. Their probability decreases on moving from the average temperature towards the extremes.

Table 3 refers to the step-wise thermodynamic data inferable from Table 2.

TABLE 2

Most probable overall stability constant, ΔG, ΔH and ΔS values (dm^{3n} mol^{-n}, kJ mol^{-1}, kJ mol^{-1} and kJ mol^{-1} T^{-1} respectively) for the complex formation between Ag^I and thioureas or substituted thioureas, at $t = 25°C$ and $\mu = 0$, in methanol

Ligand	n	$\log \beta_n$	$-\Delta G$	ΔH		ΔS		I [a]
Tu	1	8.63	49.26	-127	± 15	$-261 \pm$	52	3
	2	13.09	74.74	-66	± 9	$+24 \pm$	31	3
	3	15.94	90.98	-118	± 8	$-92 \pm$	27	3
MeTu	1	8.81	50.28	-56	± 8	$+19 \pm$	30	3
	2	13.38	76.37	$+86$	± 14	$+544 \pm$	49	3
	3	16.03	91.50	-128	± 9	$-123 \pm$	31	3
Me_2Tu	1	8.77	50.06	-37	± 14	$+44 \pm$	49	3
	2	12.52	71.48	-60	± 8	$+36 \pm$	30	3
	3	15.24	87.02	-110	± 7	$-77 \pm$	23	3
Me_4Tu	1	6.39	36.48	-33.8	± 7	$+9 \pm$	23	3
	2	9.70	55.39	-32.4	± 4	$+77 \pm$	13	3
	3	12.58	71.82	-32.0	± 15	$+133 \pm$	51	3
EtTu	1	9.97	56.9	-39.6	± 3	$+58 \pm$	12	3
	2	13.58	77.5	-84.9	± 7	$-25 \pm$	25	3
	3	16.38	93.5	-119.9	± 7	$-88 \pm$	22	3
Et_2Tu	1	9.06	51.7	$+2.06$	± 6	$+180 \pm$	22	3
	2	13.17	75.2	-22.0	± 16	$+326 \pm$	60	3
	3	16.03	91.5	-47.3	± 30	$+148 \pm 104$		3
EnTu	1	8.71	49.7	-12.9	± 22	$+123 \pm$	75	3
	2	12.63	72.1	-44.2	± 7	$+94 \pm$	26	3
	3	15.45	88.2	-89	± 7	$-2 \pm$	25	3
$(IsPr)_2Tu$	1	8.39	47.9	-82	± 3	$-115 \pm$	66	3
	2	12.12	69.2	-57	± 12	$+41 \pm$	41	3
	3	15.31	87.4	-117	± 7	$-99 \pm$	25	3
ALTu	1	9.70	55.16	-76	± 12	$-71 \pm$	41	3
	2	13.89	79.3	-82.3	± 10	$-10 \pm$	35	3
	3	16.48	94.08	-105.2	± 10	$-37 \pm$	33	3

[a] This column refers to the number of points used for smoothing the original data.

Free energy changes

Figure 1 shows the overall ($Ag^I + nL = AgL_n$, Fig. 1A) and the step-wise ($AgL_{n-1} + L = AgL_n$, Fig. 1B) free energy changes for the formation of alkyl-substituted thiourea complexes of Ag^I. The overall free energy changes at 25°C (Fig. 1A) are spread over 20–25 kJ mol^{-1}. The step-wise $\overline{\Delta G}$ dispersion (Fig. 1B) halves for AgL as reacting substrate (the second coordination step) and pratically vanishes for the third coordination step

TABLE 3

Most probable step-wise stability constant, ΔG, ΔH and ΔS values (dm^{3n} mol^{-1}, kJ mol^{-1}, kJ mol^{-1} and kJ mol^{-1} T^{-1} respectively) for the complex formation of Ag^I with thiourea or substituted thioureas, at $t = 25°C$ and $\mu = 0$, in methanol

Ligand	n	$\log K$	$-\Delta G$	ΔH	ΔS	$-|\log K|_{n-1}^{n}$
Tu	1	8.63	49.26	−127	−261	−
	2	4.46	25.48	+61	+285	4.17
	3	2.85	16.24	−52	−116	1.61
MeTu	1	8.81	50.28	−56	+19	−
	2	4.57	26.09	+142	+535	4.24
	3	2.65	15.13	−214	−667	1.92
Me$_2$Tu	1	8.77	50.06	−37	+44	−
	2	3.75	21.42	−23	−8	5.02
	3	2.72	15.54	−50	−113	1.03
Me$_4$Tu	1	6.39	36.48	−33.8	+9	−
	2	3.31	18.91	+1.4	+68	3.08
	3	2.88	16.43	+0.4	+56	0.43
EtTu	1	9.97	56.9	−39.6	+58	−
	2	3.61	20.6	−45.3	−83	6.36
	3	2.80	16.0	−35.0	−63	0.81
Et$_2$Tu	1	9.06	51.7	+2.0	+180	−
	2	4.11	23.5	+20.0	+146	4.95
	3	2.86	16.3	−69.0	−178	1.25
EnTu	1	8.71	49.7	−12.9	+123	−
	2	3.92	22.4	−31.3	−29	4.79
	3	2.82	16.1	−44.8	−96	1.10
(IsPr)$_2$Tu	1	8.39	47.9	−82.0	−115	nbl
	2	3.73	21.3	+25.0	+156	4.66
	3	3.19	18.2	−60.0	−140	0.54
ALTu	1	9.70	55.36	−76.0	−71	−
	2	4.19	23.94	−6.3	+61	5.51
	3	2.59	14.78	−22.9	−27	1.60

($AgL_2 + L = AgL_3$). It is clear that the solvent mainly affects the reactants of the first coordination ($Ag^I + L = AgL$).

The point pattern of Fig. 1A shows that the complexing reaction can be divided into two sharply discriminated groups: the first includes thiourea and partially substituted thioureas; the other consists tetramethyl-thiourea alone whose overall complex formation with Ag^I in methanol at $25°C$ is unfavoured by some 10 kJ mol^{-1}, independent of the coordination level. The mutual metal ion-to-ligand chemical affinity sequence ($-\Delta G$), according to the overall complex formation reactions, is almost independent of the coordination level as demonstrated by the few points of intersection among
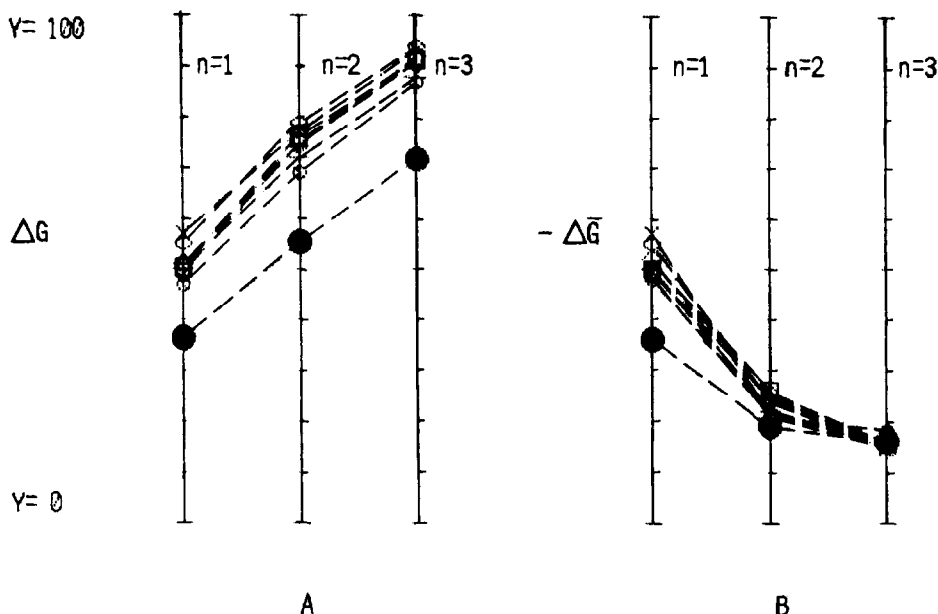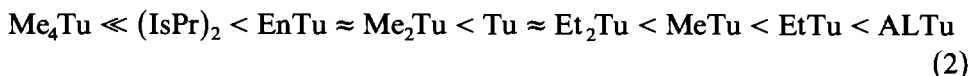
Fig. 1. Free energy change diagrams for complex formation of Ag^I with thiourea and substituted thioureas in methanol as a function of the coordination number n at $\mu = 0$ and $t = 25°C$. A, ΔG for the reaction $Ag^I + nL = AgL_n$; B: ΔG for the reaction $AgL_{n-1} + L = AgL_n$. $\circ$, Tu; $\square$, MeTu; 0, Me_2Tu; $\bullet$, Me_4Tu; $\times$, EtTu; $\diamond$, Et_2Tu; $+$, EnTu; $\otimes$, $(IsPr)_2Tu$; $\ominus$, ALTu.

the crossing lines in Fig. 2A. For the first complexation ($Ag^I + L = AgL$) it is found that

$$Me_4Tu \ll (IsPr)_2Tu < EnTu \leq Tu < Me_2Tu < MeTu < Et_2 < ALTu < EtTu \tag{1}$$
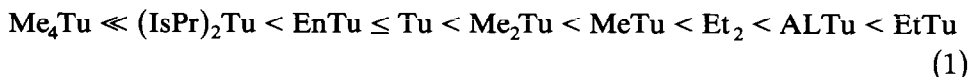
While for the second complexation ($Ag^I + 2L = AgL_2$), the sequence is

$$Me_4Tu \ll (IsPr)_2 < EnTu \approx Me_2Tu < Tu \approx Et_2Tu < MeTu < EtTu < ALTu \tag{2}$$

which includes three inversions relative to the previous one ($Tu–Me_2Tu$, $MeTu–Et_2Tu$, $EtTu–ALTu$).

For the third complexation, the stability sequence $(-\Delta G_3)$ is

$$Me_4Tu \ll Me_2Tu \leq (IsPr)_2Tu \leq EnTu < Tu < Et_2Tu < MeTu$$
$$< EtTu < ALTu \tag{3}$$
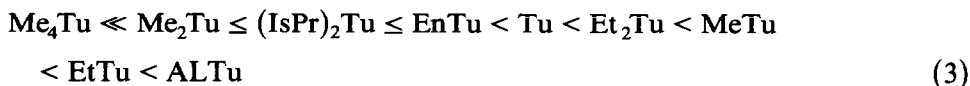
which shows a single inversion both with respect to sequence (1) for the first coordination ($Me_2Tu–/(IsPr)_2Tu < EnTu < Tu/$) and to sequence (2) for the second coordination ($Me_2Tu–/(IsPr)_2Tu < EnTu/$).

According to the step-wise complexing reactions (Fig. 1B), the AgL_n ($n = 0–2$) substrate-to-ligand mutual affinity decreases with increasing sta-
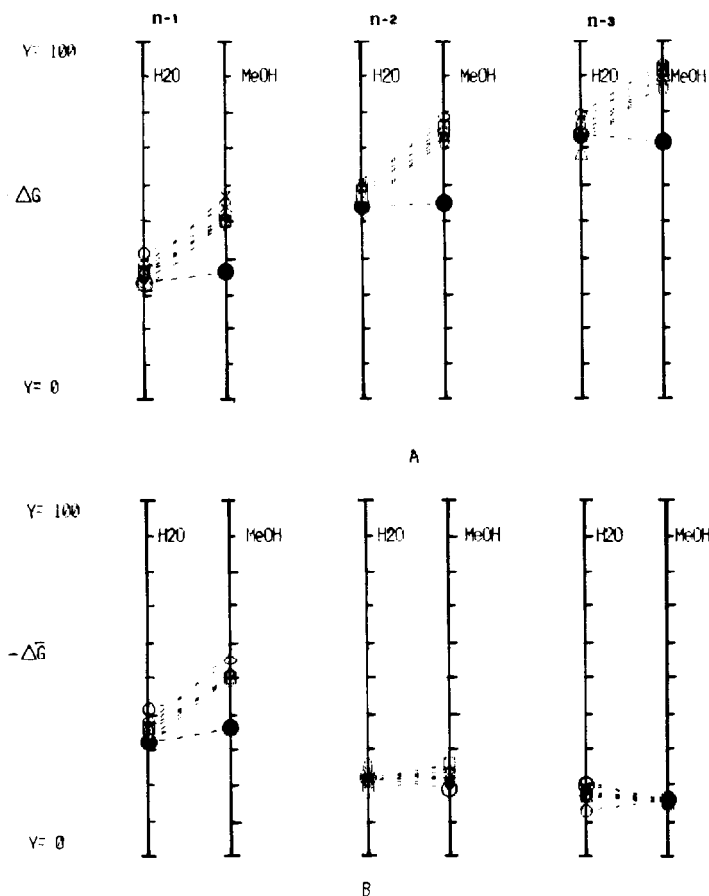
Fig. 2. Free energy change comparison between water and methanol for complex formation of Ag^I with thiourea and substituted thioureas as a function of coordination number n at $\mu = 0$ and $t = 25\,^\circ C$. A, B and symbols as in Fig. 1.

bility of the substrate with a sharp drop between $n = 0$ and $n = 1$ ($\Delta\overline{G}_1 \ll \Delta\overline{G}_2 \leq \Delta\overline{G}_3$). The relative position of the various systems on the different n coordinates of Fig. 1B, is changed and several inversions occur on the $n = 2$ coordinate with respect to $n = 1$, and on $n = 3$ with respect to $n = 2$.

At $25\,^\circ C$ the transfer from water to methanol of the overall complexing reactions ($Ag^I + nL = AgL_n$, Fig. 2A) favours the complex formation between Ag^I and Tu or partially alkyl-substituted thioureas. It involves transfer free energy changes (Table 4) from ≈ -8 kJ mol^{-1} (for L = Tu, $n = 2$) to ≈ -23 kJ mol^{-1} (for L = Et_2Tu, $n = 2$). In contrast with the other ligands, the complexing reaction with tetramethylthiourea does not involve much change in the Ag^I-to-ligand chemical affinity for $n = 1, 2$ when passing from water to methanol (ΔG(tr. $H_2O \rightarrow MeOH$) = -4 and -1 respectively for $n = 1$ or 2). The simultaneous coordination of three Me_4Tu

TABLE 4

Overall and step-wise transfer free energy, enthalpy and entropy ($kJ\ mol^{-1}$, $kJ\ mol^{-1}$ and $kJ\ mol^{-1}\ T^{-1}$) from water to methanol for the complex formation of Ag^I with thiourea or substituted thioureas at $t = 25\,^\circ C$ and $\mu = 0$

Ligand	Reaction						
	$Ag^I + nL = AgL_n$				$AgL_{n-1} + L = AgL_n$		
	n	ΔG	ΔH	ΔS	ΔG	ΔH	ΔS
Tu	1	−7.9	+27	+115	−7.9	+27	+115
	2	−14.5	+42	+175	−6.6	+15	+60
	3	−18.1	−9	+29	−3.6	−51	−146
MeTu	1	−13.9	−38	+82	−13.9	−38	+82
	2	−19.1	+132	+506	−5.2	+170	+424
	3	−17.4	−4	+39	+1.7	−136	−467
Me$_2$Tu	1	−15.4	−37	−73	−15.4	−37	−73
	2	−12.1	−42	−103	+3.3	−5	−30
	3	−9.6	−64	−182	+2.5	−22	−79
Me$_4$Tu	1	−3.9	−28	−40	−3.9	−28	−79
	2	−1	−12	−40	+2.9	+16	+39
	3	+2.7	+5	+7	+3.7	+7	+47
EtTu	1	−20.5	+15	+119	−20.5	+3.7	+8
	2	−16.8	+23	+136	+3.7	+8	+17
	3	−15.2	+14	+101	+1.6	−9	−35
Et$_2$Tu	1	−18.2	+90	+386	−18.2	+90	+386
	2	−23.3	+106	+427	−5.1	+16	+41
	3	−22.4	+41	+213	+1	−65	+214
EnTu	1	−17.5	+18	+119	−17.5	+18	+119
	2	−16.8	+8	+104	+0.7	−10	−15
	3	−16.2	−1	+44	+0.6	−9	−60
ALTu	1	−17.3	−96	−264	−17.3	−96	−264
	2	−20.1	−16	+11	−2.8	+80	+275
	3	−18.7	−43	−98	+1.4	−27	−109

groups is slightly disfavoured in methanol with respect to water (ΔG_3(tr. $H_2O \rightarrow MeOH$) $= +2.7\ kJ\ mol^{-1}$).

By examining the step-wise data (reaction $AgL_{n-1} + L = AgL_n$, Fig. 2B), it can be inferred with some exceptions (see Table 4) that the transfer process is mainly related to the thermodynamic characteristics of the reactants and products of the first coordination. These characteristics disappear when the reacting substrate is mono- or dicoordinated Ag^I. This behaviour is in accordance with the previously mentioned similar statement for the overall and step-wise free energy changes and their relation to the first coordination stage.

In spite of that, the variability of the transfer free energy data (see Table 4) indicates detectable contributions from the substituents. Although these contributions seem to be quite complicated at first sight, they can be rationalised.

Focusing on the reaction for the first complex formation, $Ag^I + L = AgL$, the successive substitution of the hydrogen atoms of thiourea with similar radicals (methyl-substituted or ethyl-substituted ligands) results in favourable contributions to the transfer process. These contributions pass through a maximum corresponding to the monosubstituted ligands and are more favourable when compared with thiourea ($\Delta G_{1,L=Tu}$(tr. $H_2O \rightarrow MeOH$) > $\Delta G_{1,L=MeTu}$(tr. $H_2O \rightarrow MeOH$) $\leq \Delta G_{1,L=Me_2Tu}$(tr. $H_2O \rightarrow MeOH$) < $\Delta G_{1,L=Me_4Tu}$(tr. $H_2O \rightarrow MeOH$); $\Delta G_{1,L=Tu}$(tr. $H_2O \rightarrow MeOH$) > $\Delta G_{1,L=EtTu}$(tr. $H_2O \rightarrow MeOH$) < $\Delta G_{1,L=Et_2Tu}$(tr. $H_2O \rightarrow MeOH$)).
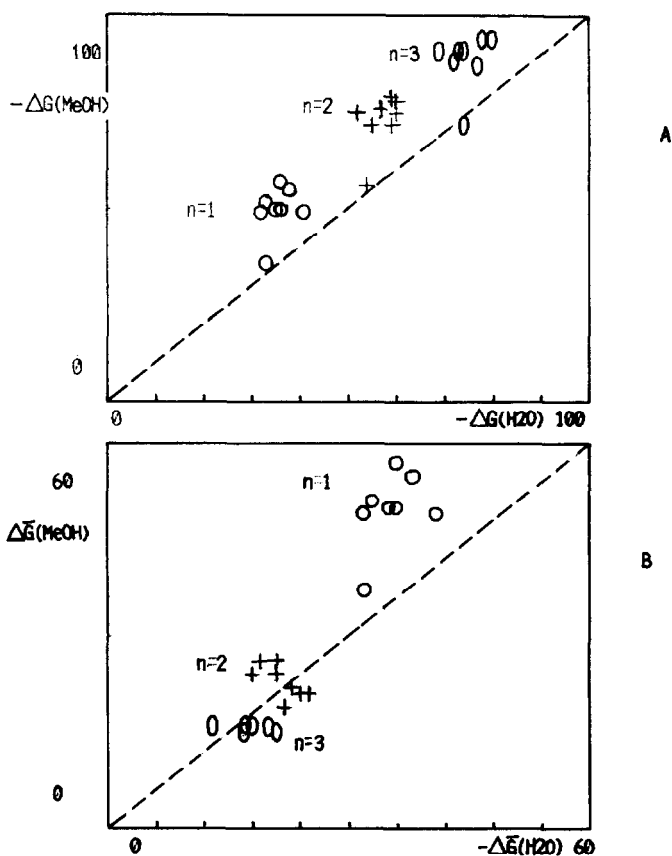
Fig. 3. Free energy change relationships between water and methanol for complex formation of Ag^I with thiourea and substituted thioureas at $\mu = 0$ and $t = 25°C$. A and B as in Fig. 1.

For the mono-substituted ligands, the transfer process also passes through a maximum which depends on the length of the alkyl chain of the substituent. The maximum corresponds to EtTu: $\Delta G_{1,L=Tu}(\text{tr. } H_2O \rightarrow MeOH) > \Delta G_{1,L=MeTu}(\text{tr. } H_2O \rightarrow MeOH) > \Delta G_{1,L=EtTu}(\text{tr. } H_2O \rightarrow MeOH) < \Delta G_{1,L=ALTu}(\text{tr. } H_2O \rightarrow MeOH)$. The same behaviour, with some exceptions for the ethyl-substituted ligands (see Table 4), is found for $n = 2$ and 3.

Figure 3 shows the interdependence of the complexing reaction series in water and methanol. Well discriminated point-clusters for the coordination levels are evident. The data for the reaction series are only roughly proportional to each other. Methanol and water have the same discriminating ability towards the overall complexing reactions (Fig. 3A) and the same susceptibility both inside a single cluster (which refers to a complexing reaction at the same coordination level) and among the clusters (the discriminating ability with respect to different coordination levels).

Data concerning the reaction $AgL + L = AgL_2$ and $AgL_2 + L = AgL_3$ (Fig. 2B, $n = 2$, 3) have a spread in their respective clusters which shows negative dependence but the same discriminating ability of the two solvents for $n = 2$ and a lack of susceptibility of methanol for $n = 3$.

Enthalpy and entropy changes

The following figures show some enthalpy relationships. Figure 4 reproduces overall (A) and step-wise (B) changes in enthalpy which are dependent
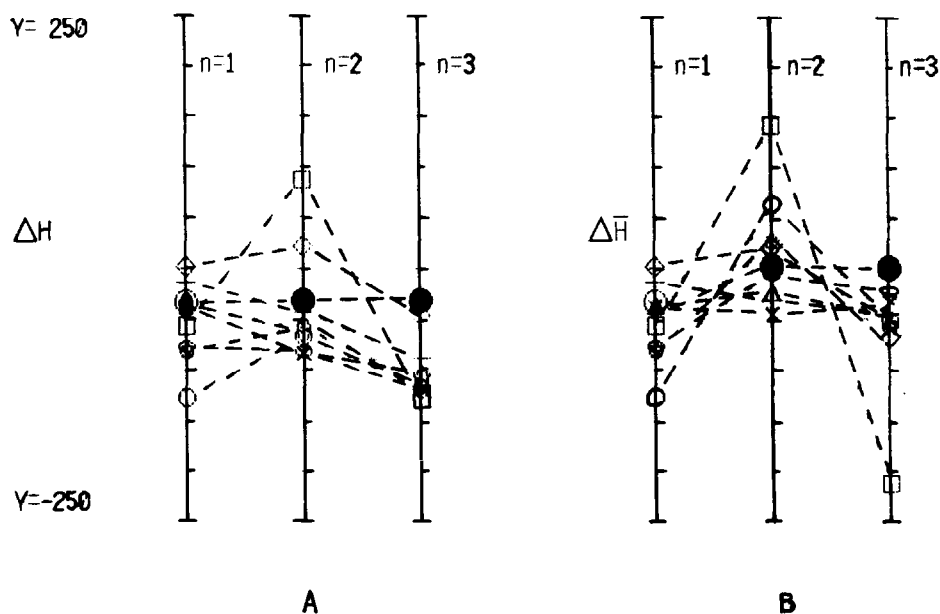
Fig. 4. Enthalpy change diagrams for complex formation of Ag^I with thiourea and substituted thioureas in methanol as a function of coordination number n at $\mu = 0$ and $t = 25°C$. A, B and symbols as in Fig. 1.

on coordination number, n. The data indicate overall exothermal reactions except for the formation of $Ag(MeTu)_2$ ($\Delta H = +86$ kJ mol^{-1}), $Ag(EtTu)_2$ ($\Delta H = +22.0$ kJ mol^{-1}) and AgEtTu whose value is close to zero in comparison with the corresponding reactions with the other ligands.

The ΔH pattern is less homogeneous than the one given in Fig. 1A which is related to ΔG changes. However, a pattern, more evident in the partial data diagram (Fig. 4B), can be discerned. The ligands can be classified into two groups which totally differ from those previously indentified on the basis of the free energy. For the group containing Tu, MeTu, $(IsPr)_2Tu$ and ALTu, and probably Et_2Tu, the relationships $\Delta H_1 < \Delta H_2 > \Delta H_3$, for the overall enthalpy changes, and $\Delta \bar{H}_1 < \Delta \bar{H}_2 > \Delta \bar{H}_3$ with $\Delta \bar{H}_1 < 0$ and $\Delta \bar{H}_3 < 0$, for the step-wise enthalpy changes, is clearly defined. In Figs. 4A and B, this group is identified by the cuspidate lines.
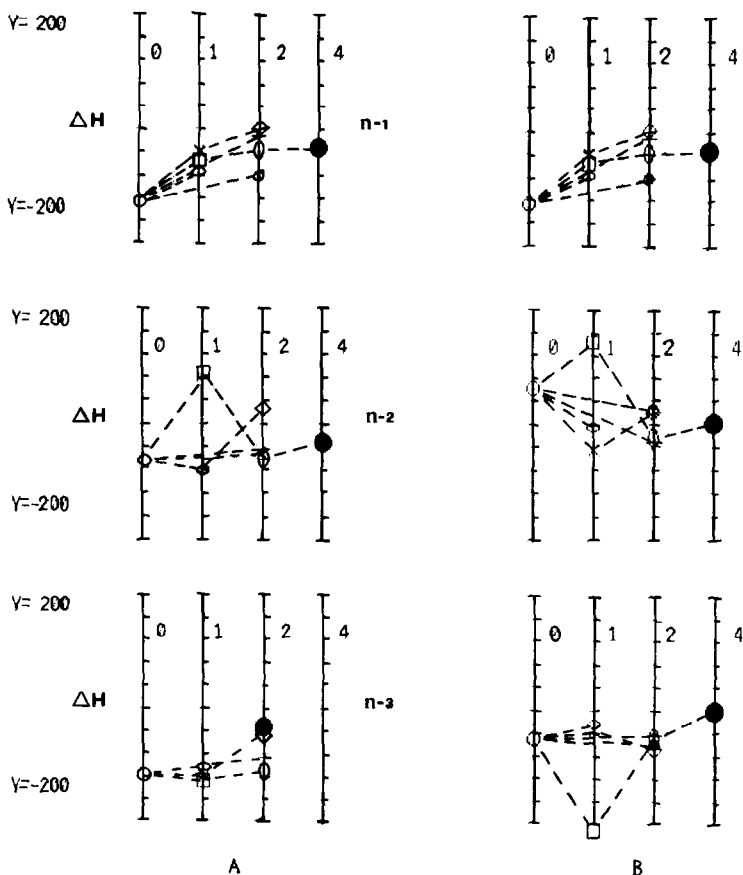
Fig. 5. Overall and stepwise enthalpy changes at $\mu = 0$ and $t = 25\,^\circ C$ for complex formation of Ag^I with thiourea and substituted thioureas as a function of the number and nature of the substituents. A, B and symbols as in Fig. 1.

A different overall ΔH sequence ($\Delta H_1 > \Delta H_2 > \Delta H_3$) and a more limited relationship among step-wise $\Delta \overline{H}$ values characterise the groups of the remaining ligands. In general, the overall enthalpy changes for Ag^I complex formation with substituted thioureas are found to be more positive (see Table 2) or else equal to the values found for the corresponding Ag^I–Tu complexes. For the reaction $Ag^I + L = AgL$ (L = thiourea or methyl-substituted thioureas), an asymptotic tendency with increasing number of substituted hydrogen atoms is observed for ΔH_1, with a quite regular, homogeneous trend ($\Delta H_1(L = Tu) < \Delta H_1(L = MeTu) < \Delta H_1(L = Me_2Tu) \leq \Delta H_1(L = Me_4Tu)$. The same trend is observed for ethyl-substituted thioureas (Fig. 5A, $n = 1$)).
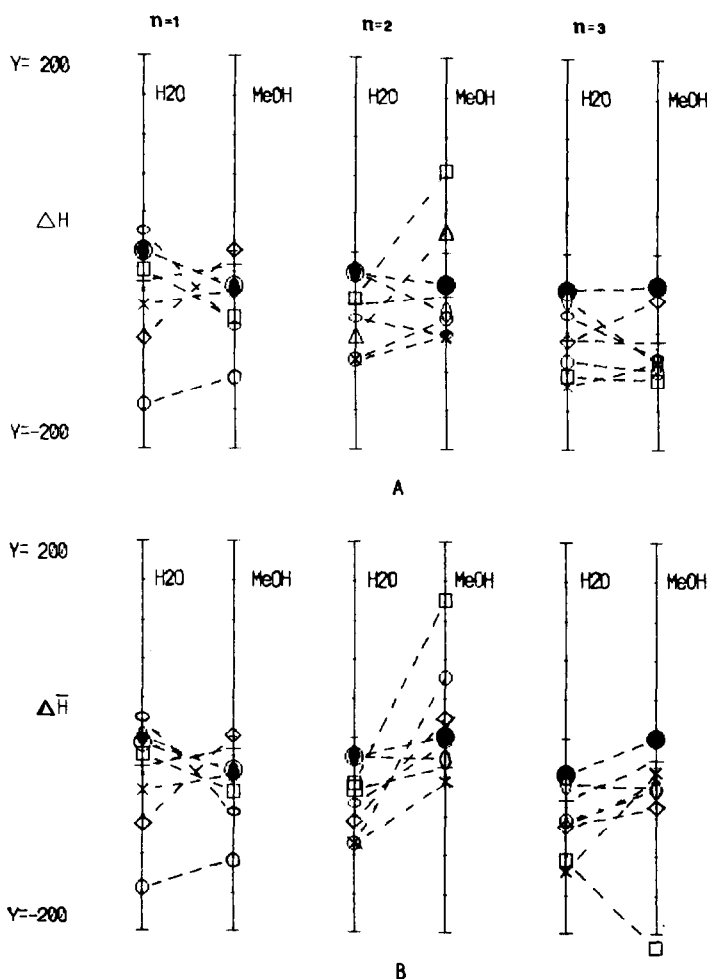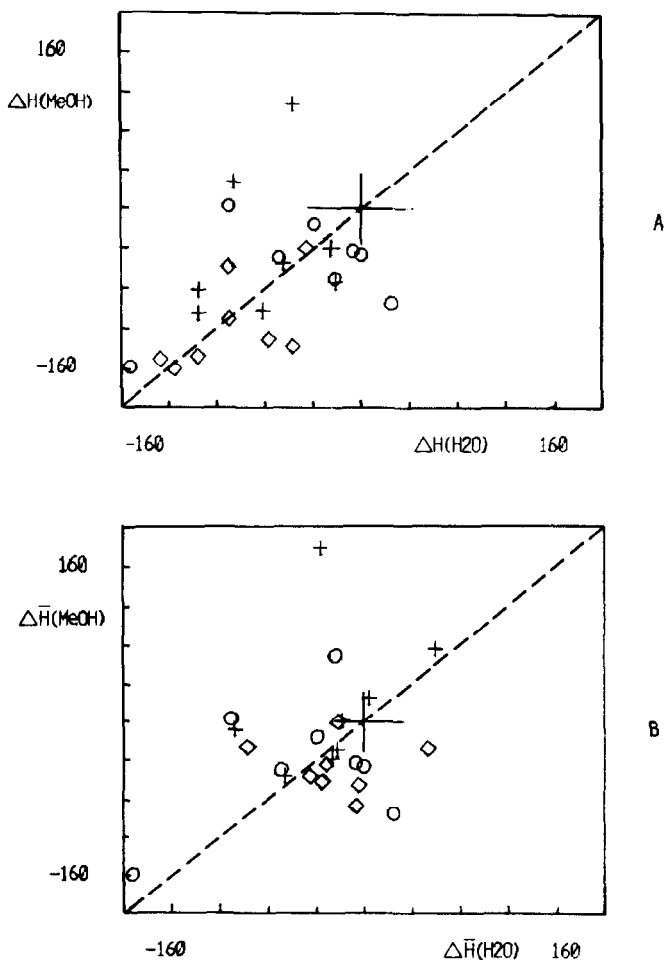

Fig. 6. Enthalpy change comparison between water and methanol for complex formation of Ag^I with thiourea and substituted thioureas as a function of coordination number n at $\mu = 0$ and $t = 25\,°C$. A, B and symbols as in Fig. 1.

The overall ΔH_3 pattern is also uniform and regular, although to a different extent and in a different way when compared with the one just discussed. It shows enthalpy increasing with both the number of the substituted hydrogen atoms and the complexity of the substituents. Variability is encountered in the second coordination ($Ag^I + 2L = AgL_2$; Fig. 5A). Because of this behaviour, two related patterns are observed for the step-wise $\Delta\overline{H}_2$ and $\Delta\overline{H}_3$): if an increasing (decreasing) tendency occurs for $\Delta\overline{H}_2$ on going from one ligand to another, then a decreasing (increasing) tendency is found in the respective step-wise $\Delta\overline{H}_3$ pattern, e.g. $\Delta\overline{H}_2(L = Tu) < \Delta H_2(L = MeTu)$ but $\Delta\overline{H}_3(L = Tu) > \Delta\overline{H}_3(L = EtTu)$.

Fig. 7. Enthalpy change relationships between water and methanol for complex formation of Ag^I with thiourea and substituted thioureas at $\mu = 0$ and $t = 25°C$. A and B as in Fig. 1. o, $n = 1$; +, $n = 2$; ◊, $n = 3$.
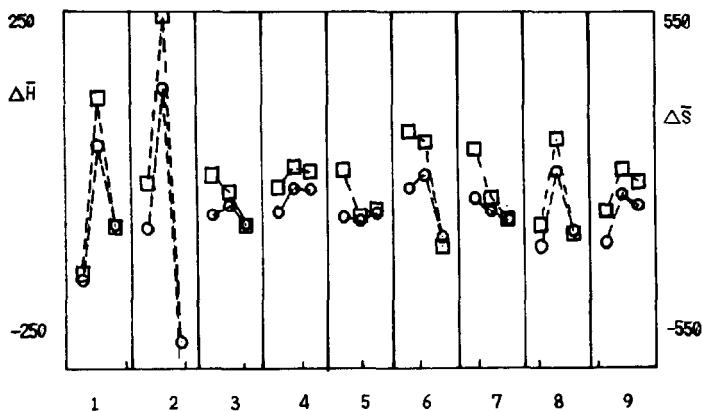
Fig. 8. Enthalpy–entropy coupling for step-wise complex formation of Ag[1] with thiourea and substituted thioureas in methanol at $\mu = 0$ and $t = 25\,^{\circ}$C. ○, Enthalpy change; □, entropy changes. The numbers refer to the ligands ordered as in the list of symbols.

The diagram of the transfer enthalpy from water to methanol (Fig. 6) is quite complicated owing to the almost complete lack of correlation between ΔH in MeOH and ΔH in H_2O for the overall as well as for the step-wise reactions (Fig. 7). Although the reaction enthalpy changes are comparable in their respective values and range, the transfer enthalpy changes are influenced by the nature of the substituents. The processes are both endo- or exothermic in strict dependence on the nature and number of substituents and on the coordination number.

The most striking feature of the enthalpy diagrams is the high variability of the enthalpy data compared with that of the corresponding free energy data. Obviously the enthalpy changes are compensated by the entropy changes (and vice versa), flattening the ΔG variability. In Fig. 8, the step-wise enthalpy and entropy changes are plotted on one diagram. They exhibit parallel lines so statistical analyses were performed on the logarithms of the step-wise stability constant deduced from Table 1, in order to search for the occurrence of isoequilibrium conditions [12]. The step-wise data are used because the reactions $AgL_{n-1} + L = AgL_n$ (L = a set of ligands which differ in the systematic introduction of groups more or less far from the donor or acceptor centres) can be regarded as a series of "homologous" reactions, in which the status of reagents and products is gradually modified in more or less remote positions from the reacting centres.

The results of the data analysis for the reaction $Ag^{1} + nL = AgL_n$ are shown in Fig. 9. The set of straight lines shows a single intersection point ($T_{iso} = 292.6$ K, ln $K = 8.91$ with $F = 0.446$). The lines for the system with Me_4Tu, EtTu and ALTu have been excluded from the constrained lines. Similar results are obtained for the reactions $AgL + L = AgL_2$ ($T_{iso} = 290.5$ K, ln $K = 3.94$, $F = 1.24$) and $AgL_2 + L = AgL_3$ ($Ti_{iso} = 295.0$ K, ln $K = 3.05$, $F = 0.53$), Therefore, the $\Delta \bar{H} - \Delta \bar{S}$ parameters for the step-wise com-
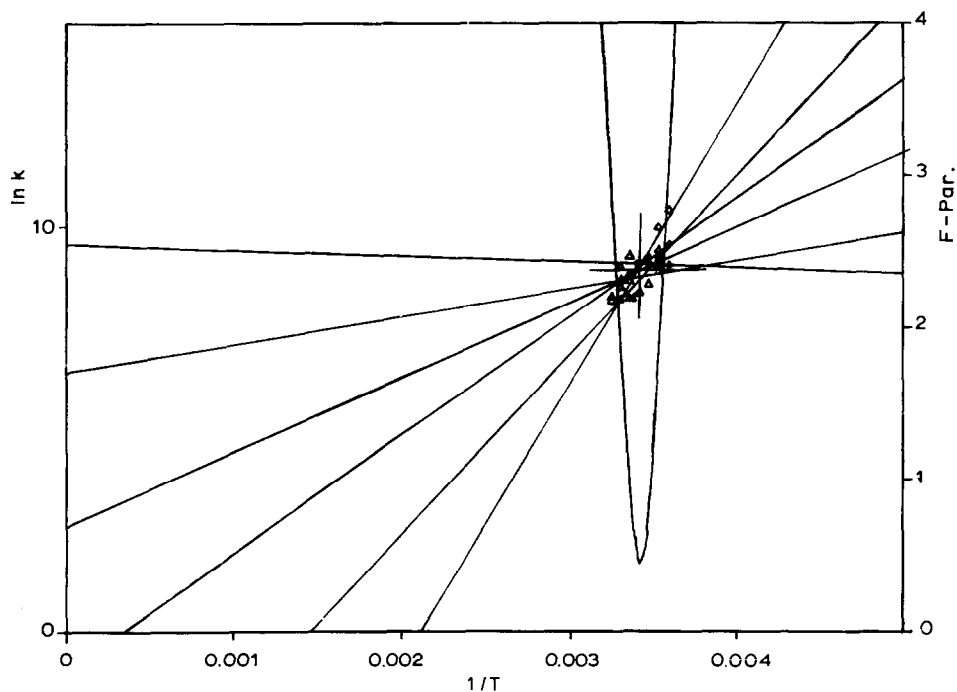
Fig. 9. Arrhenius diagrams $\ln K$ vs. $1/T$ for the reaction $Ag^I + L = AgL$ ($L \equiv Tu$ and substituted thioureas). The parabolic curve shows the behaviour of the test in the proximity of the minimum ($\ln K = 8.91$; $1/T = 3.412 \times 10^{-3}$; $F_{atm} = 0.446$).

plex formation are almost linearly related (Fig. 10). In contrast with the results of statistical analysis, only the system with tetramethylthiuorea in the first coordination reaction falls obviously off the line.
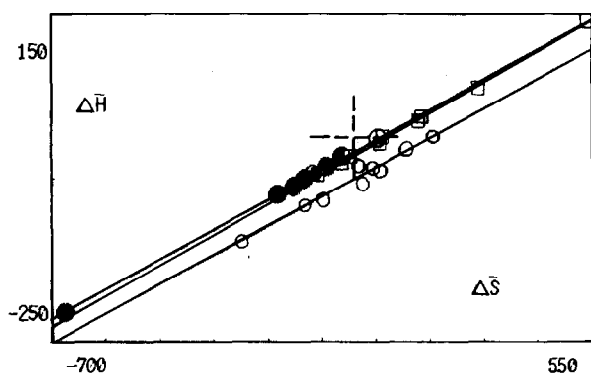

Fig. 10. Step-wise enthalpy–entropy change relationships for complex formation of Ag^I with thiourea and substituted thioureas in methanol at $\mu = 0$ and $t = 25\,^\circ C$. $\circ$, reaction $Ag^I + L = AgL$, $\Delta\bar{H} = -50.99(2.46) + 0.291(0.02)\Delta\bar{S}$; $\square$, reaction $AgL + L = AgL_2$, $\Delta\bar{H} = -21.89(0.99) + 0.302(0.004)\Delta\bar{S}$; $\bullet$, reaction $AgL_2 + L = AgL_3$, $\Delta\bar{H} = -16.62(0.44) + 0.296(0.002)\Delta\bar{S}$ (standard deviations are reported in parentheses).

CONCLUSIONS

The behaviour of the systems formed by Ag^I with thiourea or substituted thioureas in methanol solutions are not significantly different from their behaviour in water solutions. At 25°C, the use of methanol as solvent favours the formation of Ag^I complexes with thiourea or substituted thioureas. It modifies the ligand stability sequences, e.g. the relative position of thiourea is at one extremity in H_2O and in the middle of the sequence in CH_3OH, but some peculiarities remain unchanged. The sequence of the step-wise free energy changes in methanol, $\Delta \bar{G}_1 \ll \Delta \bar{G}_2 \leq \Delta \bar{G}_3$, valid for all the ligands inclusive of tetramethylthiourea (which has lower differences among the successive step-wise $\Delta \bar{G}_n$ ($n = 1$–3)) is identical to the sequence found in water. Also identical is the discriminating ability of Ag^I towards the incompletely substituted ligands in the two solvents, while in methanol the peculiar behaviour (peculiar in respect to the other ligands) of tetramethylthiourea is emphasised.

The discriminating ability in methanol is fundamentally manifested in the first coordination. Mono- and dicoordinated AgL_n ($n = 1$, 2) substrate have no discriminating ability with respect to tetramethylthiourea.

For the following common relationship between partial $\Delta \bar{G}_n$ and $\Delta \bar{G}_{n+1}$ for different ligands

$$\Delta \bar{G}_n < (>) \Delta G'_n \Rightarrow \Delta \bar{G}_{n+1} > (<) \Delta \bar{G}'_{n+1} \tag{4}$$

where $\Delta \bar{G}$ and $\Delta G'$ are the step-wise free energy changes for Ag^I complex formation with L and L', there are several inversions in the stability sequence of the ligand series with respect to successive AgL_n ($n = 1$, 2) substrates. This sequence must be considered as the directly negative influence of the nth step-wise coordination on the following one (negative because the greater stability of a complex leads to a corresponding lower stability of the following one). This should not be considered as a general case although it has also been previously found for the complex formation of Hg^{II} with the same ligands as investigated here. In fact, when there is a great difference between the stabilities of the complexes with L and L', the reversing of order in the relationship between successive step-wise $\Delta \bar{G}_n$ values does not necessarily occur. Generalisation (if it can be done) of the above findings probably requires a suitable normalisation procedure.

The interdependences of the $\Delta \bar{H}$ and ΔS changes, associated with iso-equilibrium conditions, demonstrate that the considered ligands (i.e. thio-carbonyl with S as donor atom) in methanol, as in water, form a "homologous" series of complexing reactions. In water only, there are two linear trends for both Ag^I and Hg^{II} complexes [1,2]: the first related to the first complexing reaction (M + L = ML, M $\equiv Ag^I$ or Hg^{II}) and the second simultaneously related in an indiscriminating way to the second (ML + L = ML_2) and third (ML_2 + L = ML_3) complexing reactions. In methanol, the

three reaction series for the step-wise Ag^I complexes are differentiated by different intercepts ($\Delta \overline{H}_{res}$) and probably by a slightly different $\Delta \overline{H} - \Delta \overline{S}$ susceptibility.

Moreover, lower isoequilibrium temperatures are found in methanol than in water. Therefore the complexing reactions are more entropy-controlled in methanol than in water.

Because of the different isoequilibrium temperatures of the corresponding trends in water and methanol, the step-wise transfer enthalpy changes are not linearly related to the step-wise transfer entropy changes. However, they can be represented by the following equation

$$\Delta H_{tr} = \Delta (\Delta H_{res}) + \tau_{CH_3OH} \times \Delta S_{CH_3OH} - \tau_{H_2O} \times \Delta S_{H_2O} \qquad (5)$$

where τ is the isoequilibrium Kelvin temperature. Similar equations can be written for the other transfer thermodynamic parameters.

In conclusion, the interactions between Ag^I and the thiocarbonyl group of the substituted thioureas do not turn out to be dependent on the presence of the alkyl substituents on the ligand molecule because, if they are present, the change in the σ-donor strength is counterbalanced by the change in the π-acceptor ability of the donor atom. Therefore the affinities ($-\Delta G$) of the substrate to the ligands derive from different solvent–solute interaction possibly mainly due to the number of solvent molecules involved. The solvent molecules bound to the acceptor and to the donor atoms are ejected from the solvation sphere as a consequence of the metal-ion-to-ligand association. The process is counterbalanced by coordination of the solvent molecules on the external sphere to the hydrogen atoms (atom) of the coordinated ligand whose positive charge is increased by the influence of the central ion. It is probable that at this stage, ligand-specific factors become important and these produce the differences in the transfer and complexing thermodynamic parameters related to the first complexation, where the solvent interaction is certainly greater. It is obvious that those ligands having no centres whose "solvophilicity" can be emphasised by coordination or that have centres to which access by solvent molecules is sterically hindered, are excluded from this mechanism.

In methanol, tetramethylthiourea, which has no solvophilic hydrogen atom, does not follow the trend for the first coordination: it has a higher enthalpy and lower entropy with respect to its position is the $\Delta H - \Delta S$ trend. It would be interesting to determine the behaviour of other totally substituted ligands, of both similar and different natures from the investigated ligands here.

REFERENCES

1 D. De Marco, G. Mauceri, A. Marchese and A. Bellomo, Thermochim. Acta, 99 (1986) 93.
2 D. De Marco, A. Marchese, P. Migliardo and A. Bellomo, Ann. Chim., 78 (1985) 25.
3 R.D. Hannock, N.P. Finkelstein and A. Evers, J. Inorg. Nucl. Chem., 36 (1974) 2539.
4 D. De Marco, G. Mauceri and A. Marchese, Thermochim. Acta, 95 (1985) 7.
5 W. Linert, Chem. Phys., 12C (1989) 381.
6 W. Linert and L. Sapunow, Chem. Phys., 119 (1988) 265 and references cited therein.
7 W. Linert, Atti Acc. Pel. dei Per., in press.
8 L.G. Hepler, Thermochim. Acta, 100 (1986) 171.
9 O. Exner, Enthalpy–Entropy Relationship, in R.W. Taft (Ed.), Progress in Physical Organic Chemistry, Wiley, New York, 1973.
10 R. Wells, Linear Free Energy Relationships, Academic Press, London, 1968.
11 F.B. Hildebrandt, Analisi Numerica, Ambrosiana (Ed.), Milano, Italy, 1967.
12 W. Linert, Inorg. Chim. Acta., 141 (1988) 233.

LIST OF SYMBOLS

Tu	thiourea
MeTu	N-methylthiourea
Me_2Tu	N, N'-dimethylthiourea
Me_4Tu	N, N, N', N'-tetramethylthiourea
EtTu	N-ethylthiourea
Et_2Tu	N, N'-diethylthiourea
EnTu	N, N'-ethylenethiourea
$(IsPr)_2Tu$	N, N'-diisopropylthiourea
ALTu	N-allylthiourea
L	ligand
η	$|Ag^I|_{tot}/|Ag^I|_{free}$
η^0	$\lim \eta_{(Ag^I \to 0)}$
β_n	overall stability constant (dm^{3n} mol^{-n}) for the reaction $Ag^I + nL = AgL_n$ *
K_n	step-wise stability constant (dm^3 mol^{-1}) for the reaction $AgL_{n-1} + L = AgL_n$
ΔG_n, ΔH_n, ΔS_n	overall free energy, enthalpy and entropy changes (kJ mol^{-1}, kJ mol^{-1} and kJ mol^{-1} T^{-1} respectively) for the reaction $Ag^I + nL = AgL_n$
$\Delta G_n'$, $\Delta H_n'$, $\Delta S_n'$	step-wise free energy, enthalpy and entropy changes (in the same units as above) for the reaction $AgL_{n-1} + L = AgL_n$
$-|\log K|_{n-1}^n =$	$\log K_{n-1} - \log K_n$

---

* For simplicity, charges are omitted.