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Thermodynamics of complex formation of Ag(I) XI. Systems Ag(I)–thiocarbonyl bidentate ligands in aqueous solution

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Abstract

Complex formation in aqueous solution between Ag(I) and dithioxamide, thiobiuret, dithiobiuret, 2-thiouracil, 4-propyl-2-thiouracil, acetyl-thiourea were investigated by potentiometry at $T = 278.2-318.2$ K and ionic strength $\mu = 0$. The formation of mono-coordinate AgL complexes in the systems Ag(I)–dithioxamide, Ag(I)–thiobiuret and Ag(I)–acetyl-thiourea, the stepwise formation of di-cordinate AgL_n ($n = 1, 2$) complexes in the system Ag(I)–4-propyl-2-thiouracil and the stepwise formation of three-coordinate AgL_n ($n = 1-3$) complexes in the systems Ag(I)–dithiobiuret and Ag(I)–thiobiuret have been found. The standard ΔH_n^0 and ΔS_n^0 values were deduced from the dependence of ΔG_n^0 on temperature. The values of ΔH_1^0 and ΔS_1^0 for the series of complex reactions $Ag(I) + L_{(i)} = AgL_{(i)}$ are linearly related to each-other. The evaluated isoequilibrium temperature is $T_{iso} = 294$ K. The influence of the coordinated ligand on the subsequent ligand coordination in the stepwise complex formation reactions is discussed. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Silver complexes; Thiocarbonyl complexes; Enthalpy–entropy relationships

1. Introduction

In comparison with the complex formation between metal ions and mono-dentate ligands, complex formation with multi-dentate ligands is a much more complicated process. Multi-dentate ligands may be coordinated to central metal ions by means of one or more of their donor sites in conformity with the mutual donor–acceptor affinities, the relative position of the donor sites, the flexibility of the molecular skeleton of the ligand and the coordination ability of the acceptor. Moreover, in stepwise coordination reactions the ligands coordinated to the reacting substrata influence both the structures of the complexes [1,2] and the affinities of the substrata towards subsequent coordination [3–5].

The present paper is concerned with the complex formation in aqueous solution between Ag(I) and several dithiocarbonyl or carbonyl–thiocarbonyl bidentate ligands. Some of the ligands investigated have rigid, some flexible molecular skeleton and the donor atoms, for their relative position, exert mutual influence on the respective electronic structures.

Abbreviations: DTO, dithioxamide; TB, thiobiuret; DTB, dithiobiuret; TUR, 2-thiouracil; 4PTUR, 4-propyl-2-thiouracil; AcTu, acetyl-thiourea

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Nomenclature

$[Ag(I)]_{tot}$	total concentration of Ag(I)
$[Ag(I)]_{free}$	concentration of solvated (free) Ag(I)
$[L]_{tot}$	total concentration of ligand
$[L]_{free}$	concentration of solvated (free) ligand
$\Delta G_n^0, \Delta H_n^0, \Delta S_n^0$	standard free energy (kJ mol^{-1}), enthalpy (kJ mol^{-1}) and entropy changes (J mol^{-1} K^{-1}) for the complex reaction $Ag(I) + nL = AgL_n$
β_n	overall stability constant for the complexing reaction Ag(I) $+nL = AgL_n$ as mol^{-n} dm^{3n}

2. Experimental

2.1. Chemicals

Silver nitrate were used as source of Ag(I). The solutions were prepared by diluting standardized $AgNO_3$ solutions. The ligands were commercial products (purity grade >98%). They were recrystallized in our laboratory from ethanol, dried and maintained over P_2O_5.

2.2. Measurements and calculations

The complex formation was investigated by potentiometry by an AMEL Model 335 potentiometric apparatus and the following measuring cell:

Ag	$[Ag(I)]_{tot}$= Const.	KNO_3	KCl	Ag
Test	$[L]_{tot}$=Var.	salt	Sat.	Ref.
electr.	solut. test	bridge	solut.	electr.

(1)

The measurements were carried out in thermostat cell at different temperatures. At each temperature, five different Ag(I) solutions (10 ml) with initial $[Ag(I)]_{tot} = 1.0,\ 2.5,\ 4.0,\ 5.5,\ 7.0 \times 10^{-6}$ M were titrated with ligand solution 10^{-3} M. The concentration range of the ligand investigated was $[L]_{tot} = 1.25 \times 10^{-5}$ to $3 \times 10^{-4}\,M$. For each titration the ionic medium is specified by the total amount $AgNO_3$.

The experimental $\Delta E = E_{cal} - E_{exp}$ data were numerically extrapolated to $[Ag(I)]_{tot} = 0$ while maintaining constant $[L]_{tot}$. Being $[L]_{tot} \gg [Ag(I)]_{tot}$ with $1.8 \leq [L]_{tot}/[Ag(I)]_{tot} = 300$, the sets of ΔE values at $[L]_{tot}$ = constant show only a slight linear dependence on $[Ag(I)]_{tot}$ and can be easily linearly extrapolated [6,7] to $[Ag(I)]_{tot} = 0$. In this way, the values of the function $\ln \eta = \ln([Ag(I)]_{tot}/[Ag(I)]_{free}) = \ln\left(\sum_0^N \beta_n [L]^n\right) = \Delta E/(RT/F)$, which refers to the mononuclear complexes AgL_n, was obtained [6].

The configuration of each system and the starting set of $\ln \beta_n$ values were obtained by mathematical analysis of the η versus [L] relationships by the divided differences method. The best set was calculated by optimizing the initial $\{\ln \beta_n\}$ values on the $\{\ln \eta, [L]\}$ data by non-linear least square fitting of the function $\ln \eta = \ln\left(\sum_0^N \exp(\ln \beta_n)[L]^n\right)$.

3. Results

The formation curves $\ln \eta$ versus $[L]_{tot}$ for the systems Ag(I)–dithioxamide (DTO), Ag(I)–dithiobiuret (DTB) and Ag(I)–acetyl-thiourea (AcTu) can be explained with the formation in solution of the sole mono-coordinated AgL complex, for the system Ag(I)–4-propyl-2-thiouracil (4PTUR) with the stepwise formation of two AgL_n ($n = 1, 2$) complexes and with the stepwise formation of three complexes AgL_n ($n = 1-3$) for the systems Ag(I)–thiobiuret (TB) and Ag(I)–2-thiouracil (TUR).

In Table 1, the calculated of $\ln \beta_n$ and the corresponding overall free energy changes ΔG_n^0 for the complex reaction $Ag(I) + nL = AgL_n$, at various temperatures are reported. On assuming linear dependence of ΔG_n^0 on T in the investigated temperature range, the values of ΔG_n^0 (interpolated), $\ln \beta_n$, ΔH_n^0 and ΔS_n^0 (Table 2) are calculated and must be considered as the most probable values at $T = 298.2$ K.

The enthalpy and the entropy changes for the formation of mono-coordinated complexes are linearly correlated with compensate mechanism (Fig. 1. $\Delta H = -35.26\ (\pm 7.1) + 0.294\ (\pm 0.02)\ \Delta S$; correlation coefficient = 0.989. Standard deviations are reported in parenthesis).

Table 1
Stability constants ln β_n (β_n as $dm^{3n}\ mol^{-n}$) and standard free energy changes ΔG_n^0 (kJ mol^{-1}) for the complex formation reactions[a]

Ligand	n	T (278.2 K)		T (288.2 K)		T (293.2 K)		$T = 298.2$ K		T (303.2 K)		T (308.2 K)		T (318.3 K)	
		ln β_n	$-\Delta G_n^0$	ln β_n	$-\Delta G_n^0$	ln β_n	$-\Delta G_n^0$	ln β_n	$-\Delta G_n^0$	ln β_n	$-\Delta G_n^0$	ln β_n	$-\Delta G_n^0$	ln β_n	$-\Delta G_n^0$
DTO	1	25.7 ± 0.2	59.50	22.3 ± 0.3	53.52	25.7 ± 0.6	62.55	23.3 ± 0.4	57.87	24.1 ± 0.3	60.75	23.0 ± 0.1	58.95	21.9 ± 0.2	57.99
TB	1	13.6 ± 0.1	31.51	11.3 ± 0.1	27.11	12.6 ± 0.1	30.65	13.3 ± 0.1	33.01	15.4 ± 0.1	38.83	–	–	15.4 ± 0.0	40.67
DTB	1	13.6 ± 0.4	31.38	11.4 ± 0.4	27.36	16.6 ± 0.5	41.34	18.1 ± 0.1	44.81	16.2 ± 0.2	38.20	15.6 ± 0.1	32.87	14.3 ± 0.1	37.70
	2	25.2 ± 0.4	58.29	23.2 ± 0.4	55.57	27.3 ± 0.6	66.57	29.8 ± 0.1	73.81	26.7 ± 0.1	67.32	24.9 ± 0.3	63.68	23.1 ± 0.2	61.17
	3	37.4 ± 0.7	87.24	35.2 ± 1	84.23	38.0 ± 0.5	92.51	39.1 ± 0.1	97.03	37.9 ± 0.5	95.52	34.8 ± 0.2	89.58	33.2 ± 0.1	87.78
TUR	1	7.2 ± 0.5	16.65	9.2 ± 0.4	22.05	–	–	13.1 ± 0.5	32.59	9.7 ± 0.3	21.52	7.1 ± 0.6	18.12	5.7 ± 0.9	14.98
	2	20.5 ± 0.8	47.36	20.6 ± 0.4	49.29	–	–	22.3 ± 0.1	55.19	20.5 ± 0.1	51.8	14.8 ± 0.7	44.77	17.3 ± 0.3	45.82
	3	29.0 ± 0.3	66.99	30.5 ± 0.3	72.22	–	–	31.5 ± 0.2	78.12	29.6 ± 2	74.69	29.5 ± 0.5	75.48	28.1 ± 0.1	74.39
4PTUR	1	9.4 ± 0.4	21.67	–	–	–	–	11.8 ± 0.4	29.25	11.3 ± 0.1	28.58	10.7 ± 0.2	27.45	9.9 ± 0.2	26.15
	2	21.3 ± 0.3	49.21	–	–	–	–	–	–	21.0 ± 0.2	52.89	22.4 ± 0.1	27.45	20.6 ± 0.1	54.48
AcTu	1	11.4 ± 0.3	26.36	11.7 ± 0.2	28.12	10.8 ± 0.1	26.28	–	–	16.3 ± 0.2	40.96	15.0 ± 0.2	38.41	14.8 ± 0.6	39.19

[a] $Ag + nL = AgL_n$ in aqueous solutions at different temperatures and ionic strength $\mu = 0$

Table 2
Most probable values of ln β_n (β_n as dm^{3n} mol^{-n}), ΔG_n^0 (kJ mol^{-1}), ΔH_n^0 (kJ mol^{-1}) and ΔS_n^0 (J K^{-1} mol^{-1}) for the overall complex formation reactions[a]

Ligand	n	ln β_n	$-\Delta G_n^0$	ΔH_n^0	ΔS_n^0	I
DTO	1	23.3 ± 0.4	59.1	−45.8 ± 3.7	44.3 ± 12	3
TB	1	13.3 ± 0.1	33.8	90 ± 5.9	415 ± 20	3
DTB	1	18.1 ± 0.1	38.5	32.6 ± 11	238 ± 37	3
	2	29.8 ± 0.1	66.5	9.5 ± 7.5	187 ± 45	3
	3	39.1 ± 1	91.6	−46.9 ± 11	151 ± 37	3
TUR	1	13.1 ± 0.5	23.7	−80.3 ± 13	−189 ± 45	3
	2	22.3 ± 2	50.4	−93.5 ± 7.7	−145 ± 2.5	3
	3	31.5 ± 0.2	74.5	−38.2 ± 5.7	122 ± 19	3
4PTUR	1	11.8 ± 0.4	27.2	−7.9 ± 6	64.4 ± 22	3
	2	20.9 ± 0.4	52.9	−4.2 ± 6	163 ± 20	–
AcTu	1	13.2 ± 0.3	33.5	127 ± 0.9	540 ± 3	3

[a] $\mathrm{Ag} + n\mathrm{L} = \mathrm{AgL}_n$ in aqueous solutions at $T = 298.2$ K and ionic strength $\mu = 0$, as deduced from $\{\Delta G, T\}$ data of Table 1 by fitting the Gibbs equation. The original data are locally smoothed on I points (last column).

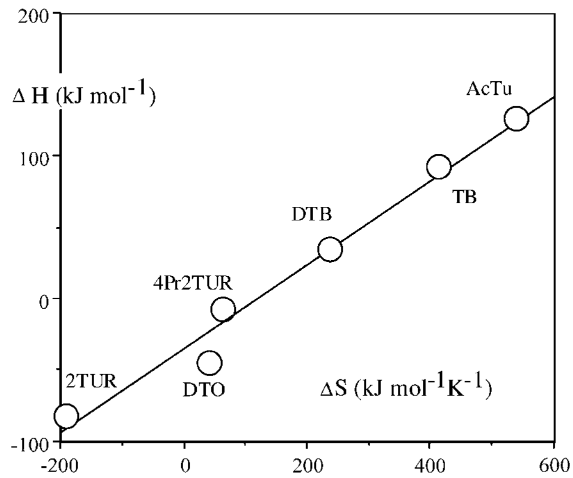

Fig. 1. ΔH–ΔS relationship in the series of complex formation reactions $\mathrm{Ag(I)} + n\mathrm{L} = \mathrm{AgL}_n$ at $T = 25$ °C and ionic strength $\mu = 0$; $\Delta H = -35.26\ (\pm 7.1) + 0.294\ (\pm 0.02)\ \Delta S$; correlation coefficient = 0.989; standards deviations are reported in parenthesis; $T_{\mathrm{iso}} = 294$ K.

4. Discussion

The ligands investigated coordinate to Ag(I) by means of their sulfur atom (atoms). This can be inferred from the closely comparable values of the affinities of Ag(I) towards the ligands investigated with the value of Ag(I)–thiourea affinity in Ag(I)–thiourea complexes [7] and from the similarities in the electronic structures of thiocarbonyl ligands [8–11]. Because the affinity Ag(I)–DTO is appreciably greater than the affinities of Ag(I) towards thiourea and towards the other ligands in Table 2, it can be supposed that DTO is coordinated to Ag(I) by both the sulfur donor atoms.

Towards TB, TUR and 4PTUR the affinity of Ag(I) is lower. The carbonyl group in TB, TUR and 4PTUR decreases the donor ability of the sulfur atom of the thiocarbonyl group by decreasing the electron density of the sulfur atom. Differently in DTB the presence of the second thiocarbonyl group results in a much smaller influence.

With respect to ligands with soft donor atoms, Ag(I) has maximum coordination number of 4, with the affinity sequence for the reactions $\mathrm{Ag(I)} + \mathrm{L} = \mathrm{AgL}$ ($n = 1-4$) [12]

$$\Delta G_1^0 < \Delta G_2^0 \approx \Delta G_3^0 < \Delta G_4^0$$

The same sequence has been found in the coordination of thiourea and *N*-alkyl-substituted thiourea in H_2O, CH_3OH and C_2H_5OH [7,13–15].

In the systems Ag(I)–DTO more concentrated solutions of free (solvated) ligand probably lead to the formation of Ag(I) complexes with coordination number >1 (AgL_n, $n > 1$) and the results of the present investigation must be interpreted as the inability of the ligands L to bind their monocoordinated complex substrata AgL in the actual condition of free ligand concentration. The absence of complexes with coordination number >1 demonstrates that the chemical affinity of the mono-coordinated substratum AgL towards a further incoming ligand L to form AgL_2 is quite low.

The origin of the small affinity AgL– L in the case of Ag(I)–DTO complex is different with respect to the cases of Ag(I)–TB and Ag(I)–AcTu complexes.

The chemical properties of donor and acceptor atoms are often sensitively dependent on their environments. In Ag(I) complexes in aqueous solution, it has been demonstrated that the coordinated ligands decrease the coordination ability of Ag(I) in complexes in greater extent greater are the affinities of the coordinated ligands towards Ag(I) [14]. Therefore, the Ag(I)–L affinity influences the stepwise coordination reaction $\mathrm{AgL} + \mathrm{L} = \mathrm{AgL}_2$ in two opposite directions.

On the one hand the coordination of the incoming ligand L is favored by the greater tendency of L to coordinate with AgL substratum and on the other hand it diminishes the tendency of the AgL to bind another incoming ligand L.

Among the ligands investigated, DTO has the greatest affinity towards solvated Ag(I) but reduces to the greatest extent the coordination ability of Ag(I) in Ag(DTO) towards the coordination of the second DTO according to the stepwise reaction $\mathrm{AgDTO} + \mathrm{DTO} = \mathrm{Ag(DTO)_2}$.

The lower affinities of TB and AcTu towards solvated Ag(I), compared with the affinity of DTO, produce less stable AgL (L = TB or AcTu) complexes but at the same time TB and AcTU reduce to a lesser extent than DTO the coordination ability of Ag(I) in AgTB and AgAcTu towards a further TB or AcTu ligand, respectively. It follows that, in the stepwise coordination reaction $\mathrm{AgL} + \mathrm{L} = \mathrm{AgL_2}$, AgTB or AgAcTu complexes are more prone than AgDTO to form their bis-coordinate complexes, but at the same time TB or AcTu are less prone than DTO to form the bis-coordinate complexes. The interplay of the two effects produces the formation of sole mono-coordinate also in the cases of the systems Ag(I)–TB and Ag(I)–AcTu.

Such interpretation stresses as corollary the formation of chelate complex in the case of AgDTO.

The functional interdependence ΔH–ΔS (Fig. 1) for the series of reactions $\mathrm{Ag(I)} + \mathrm{L} = \mathrm{AgL}$ indicates that a single mechanism [14,15] control the energetics of the reactions of the series. The constant sensitivity $\tau = \mathrm{d}H/\mathrm{d}S = \Delta(\Delta H)/\Delta(\Delta S)$ gives the isoequilibrium temperature $T_{\mathrm{iso}} = 294$ K which is the inversion point for the Ag(I)-to-ligand affinity sequences.

With the exclusion of the reaction $\mathrm{Ag(I)} + \mathrm{TUR} = \mathrm{Ag(TUR)}$, whose ΔS is <0, the entropy changes for the other reactions show that in the there is an increase in flexibility as results of the complex formation, especially, with the ligands coordinating to Ag(I) with one donor.

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