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The Complexation Reactions of N-methylated Polyamines with Silver(I) in Dimethylsulfoxide

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The thermodynamic parameters for the complex formation reactions in dimethylsulfoxide (dmso) between Ag(I) and the following polyamines: N,N′-dimethylethylenediamine (dmen), N,N,N′,N′-tetramethylethylenediamine (tmen), N,N″-dimethyldiethylenetriamine (dmdien) and N,N,N′,N″,N″-pentamethyldiethylenetriamine (pmdien) have been determined by potentiometric and calorimetric techniques at 298 K and 0.1 mol dm^{-3} ionic strength (NEt_4ClO_4). Only mononuclear complexes are formed (AgL_j^+ j = 1, 2) where the ligands act prevalently as chelate agents. All the complexes are enthalpy stabilized whereas the entropy changes counteract the complex formation. The results are discussed in terms of different basicities and steric requirements of both the ligands and the complexes formed.

Keywords: Silver(I); N-methylated polyamines; Complexes; Dimethylsulfoxide; Thermodynamics

INTRODUCTION

In the last years great efforts have been devoted to the study of the interactions of neutral N-donor ligands with metal ions in water [1–8] as well as in nonaqueous and mixed solvents [9–16]. The main purpose of these studies was to design ligands for selective complexation of metal ions. The ligands investigated ranged from the simplest monoamines and linear polyamines to the more complicated macrocycles, cryptands and coronands, whose syntheses has undergone spectacular growth in the last few years since the first works of Lehn [17], Cram [18] and Pedersen [19].

Many of these works have investigated the complexation reactions of these ligands with Group 11 metals which in general have shown great affinities toward the N-coordination [8–16]. In particular the stabilities of these complexes have been found to be mainly affected by: (*i*) the number of nitrogen atoms present in the ligands; (*ii*) their donating properties; (*iii*) the nature of the solvent; (*iv*) the different chelate ring sizes that these ligands can form, when polydentates are concerned; (*v*) the size match between the cavity of the ligand and the cation radius, when macrocyclic are concerned. The variety of macrocycles investigated, on the other hand, have now developed a renewed interest in defining the coordination properties of open chain polyamine ligands mainly focused to the

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*Corresponding author. Tel.: +39-0432-558882, Fax: +39-0432-558803, e-mail: tolazzi@dstc.uniud.it direct comparison with the corresponding macrocyclic ligands [20].

In this contest and as an extension of previous works [11], we report here the results of a thermodynamic study on the complexation reactions of the following secondary and tertiary linear polyamines: N,N′-dimethylethylenediamine (dmen), N,N,N′,N′-tetramethylethylenediamine (tmen), N,N″-dimethyldiethylenetriamine (dmdien) and N,N,N′,N″,N″-pentamethyldiethylenetriamine (pmdien) with silver(I) ion in the aprotic solvent dimethylsulfoxide (dmso). Aim of this work is to provide information on how the N-alkylation of the ligands may affect their coordination abilities toward metal ions. A comparison with thermodynamic data previously determined concerning silver(I) complexation with the analogous primary polyamines ethylenediamine (en) and diethylenetriamine (dien) [11b, c] may in fact well rationalize the influence of the different basicities and steric properties of the ligands both on the solvation of the species involved and/or on the structural properties of the complexes formed and may provide a set of useful data of comparison for a better comprehension of similar macrocyclic systems.

Potentiometric and calorimetric measurements have been used to obtain the free energy and the enthalpy of the reactions respectively. All measurements have been performed at 298 K and in an ionic medium 0.1 mol dm^{-3} with NEt_4ClO_4 as neutral salt.

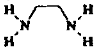
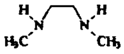
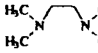
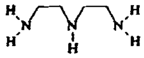
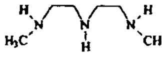
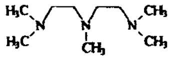
RESULTS

The best fit of the potentiometric data for each system studied was obtained when the species reported in Table I were taken into account. In the table, the overall stability constants and free energies of formation, with the limits of error indicated, are listed for the reactions: $Ag^+ + jL \rightleftharpoons AgL_j^+$ (j = 1, 2; L is the ligand concerned). The distribution of silver(I) between the different complexes as a function of the ligand-to-metal ratio, $R_c = C_L/C_M$, for all the systems studied is plotted in Figure 1.

The experimental data obtained from the calorimetric measurements are reported in Figure 2 as Δh_v, the total heats of reaction per mole of metal ion, *vs.* R_c.

From an examination of the shape of these curves some conclusions can be drawn about

TABLE I Overall stability constants and thermodynamic functions for the reaction $Ag^+ + jL \rightleftharpoons AgL_j^+$ in dmso at 298 K and I = 0.1 mol dm^{-3}. The errors quoted correspond to three standard deviations

Ligand	Complex	$\log\beta_j$	$-\Delta G^\circ_{\beta_j}$/kJmol^{-1}	$-\Delta H^\circ_{\beta_j}$/kJmol^{-1}	$-\Delta S^\circ_{\beta_j}$/Jmol^{-1}K^{-1}
en[a]	AgL	5.34	30.5	63	109
	AgL_2	9.50	54.2	85	103
dmen	AgL	4.31 ± 0.03	24.6 ± 0.1	43.7 ± 1.6	64
	AgL_2	8.31 ± 0.04	47.4 ± 0.2	79.3 ± 1.5	107
tmen	AgL	3.25 ± 0.02	18.6 ± 0.1	30.8 ± 0.8	41
	AgL_2	6.24 ± 0.01	35.6 ± 0.1	69.3 ± 0.7	113
dien[a]	AgL	7.46	42.6	78.2	119
	AgL_2	10.2	58.2	94	120
dmdien	AgL	6.42 ± 0.03	36.6 ± 0.1	64.5 ± 1.2	94
	AgL_2	9.31 ± 0.04	53.1 ± 0.3	98.0 ± 2.5	150
pmdien	AgL	5.44 ± 0.01	31.0 ± 0.1	54.5 ± 0.8	79
	AgL_2	6.97 ± 0.06	39.8 ± 0.4	81.5 ± 1.7	140

[a] Ref. [11c].

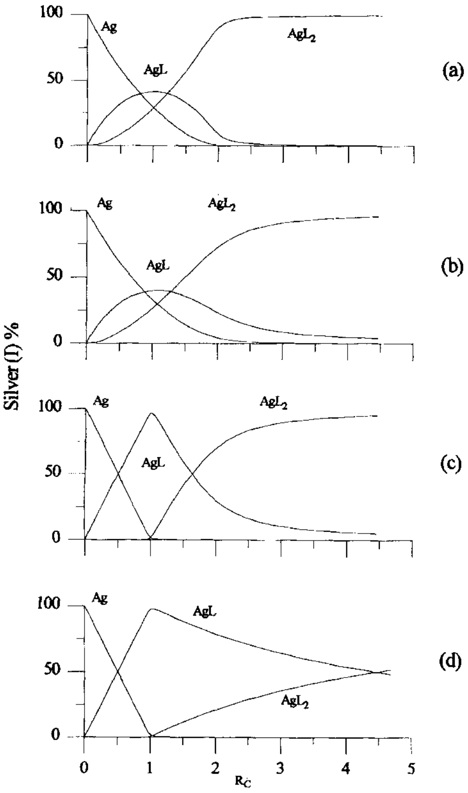


FIGURE 1 The percent distribution of the metal ion in the silver(I)-polyamine systems in dmso at C°_{Ag} = 10 mmol dm^{-3}. (a) dmen; (b) pmen; (c) dmdien; (d) pmdien.

the prevalent coordinated species formed, which are fully consistent with the information obtained from the analysis of the potentiometric data.

For silver(I)-tmen system, the splitting of the curves is only indicative of formation of weak complex(es), whereas for silver(I)-dmen system the enthalpy data which coincide up to $R_c = 1$, slightly diverge at the inflection point ($R_c = 2$) and superimpose at higher R_c values can be easily explained by the formation of only two successive, almost equally stable, mononuclear Ag(I)-dmen complexes.

The curves representing the complexation of silver(I) with dmdien and pmdien which superimpose up to $R_c = 1$ and diverge at higher R_c values, reflects the formation of 1:1 complexes of high stability and of one (or more) successive and much weaker complex(es).

The enthalpy values and the overall stability constants in Table I were used to calculate the full lines in Figure 2. The fit of the experimental data is quite good indicating that all the systems are satisfactorily described. In Table I are also reported, for comparison, the stability constants and the thermodynamic functions for the complexation reactions of Ag(I) by the ligands ethylenediamine (en) and diethylenetriamine (dien) previously determined in dmso [11b, c].

DISCUSSION

The silver(I) complexes with these polyamines are all mononuclear which is to be expected as the dielectric constants of dmso is sufficiently high ($\varepsilon = 46.4$) such that the formation of higher aggregates should be negligible and ion pair formation of either the solvated or coordinated d^{10} cations with the ClO_4^- anion is unimportant [21, 15].

A common feature of all the systems is that the formation of the silver(I) complexes is strongly exothermic whereas the entropy terms are negative and therefore oppose the complex formation. This trend is typical of complex formation of soft acceptors such as silver(I) as a result of both the formation of strong coordinate bonds of marked covalent character and the relatively weak solvation of the species involved in complex formation [21].

It is of interest to compare the stability constants of the complexation steps for similar ligands differently N-methylated, *i.e.*, the diamines en, dmen and tmen and the triamines dien, dmdien and pmdien.

Logβ_1 drops of about two orders of magnitude on going from primary to tertiary amino groups. The reason for this should be connected to the following effects: (*i*) different basicity of the amino group, which decreases in the order $—NH_2 > —NHR > —NR_2$ in dmso as pointed out by Mucci, Benoit *et al.* [22]; (*ii*) the large

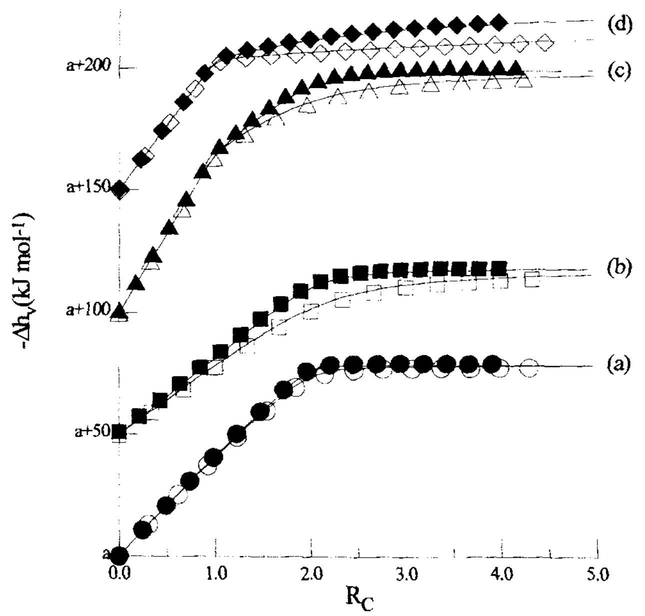


FIGURE 2 The total molar enthalpy changes, Δh_v, as a function of $R_c = C_L/C_M$ for silver(I) polyamine systems in dmso. (a) a = 0 for dmen: (○) 5.10, (●) 19.85 mmoldm^{-3} in Ag$^+$; (b) a = −50 for tmen: (□) 4.85, (■) 19.98 mmoldm^{-3} in Ag$^+$; (c) a = −100 for dmdien: (△) 5.05, (▲) 19.62 mmoldm^{-3} in Ag$^+$ (d) a = −150 for pmdien: (◇) 4.91, (◆) 19.55 mmoldm^{-3} in Ag$^+$. Only some of the experimental points, chosen at random, have been plotted. The solid lines have been calculated from the values of β_j and $\Delta H^\circ_{\beta_j}$ in Table I.

increase in steric hindrance as the ligands become more and more bulky [3] which causes an elongation of M—N bonds and (*iii*) the decreased solvation of the complexes, as a consequence of their increased radii [3,7,8].

A glance to the enthalpy and entropy values in Table I should give more information about the influence of these effects.

The thermodynamic functions relative to the first complexation step of silver(I) with dmen and tmen seem to indicate that the ligands behave as bidentate coordinating silver(I) in a tetrahedral configuration: monodentation, in fact, would result in lower β_1 values, as previously found for the silver(I) complex formation with secondary and tertiary monoamines in dmso [11a,16].

A rationale for the decrease in β_1 and for the less exothermic ΔH°_1 values on going from en, containing only primary amino groups, to tmen, with tertiary N donors only, might be a minor strength in the M—N bond, due both to the decreased basicity of the N-atoms [22] and to the steric crowding produced by N-alkyl groups when chelation occurs [3]. The less unfavorable entropy terms from en to dmen and tmen agree with the minor solvation, *via* hydrogen bonds, both of the N-methylated diamines and of the more and more sterically hindered complexes formed.

The low values of K_1/K_2 ratio for the silver(I)-diamine systems and the stepwise enthalpy and entropy changes for the second complexation step seems to indicate that in the second complex the ligands behave also as bidentate.

As far as the silver(I)-dmdien and -pmdien complexes are concerned, the thermodynamic data indicate that these ligands act as tridentate, forming two fused five-membered chelate rings, at least in the first coordination step, the trend of the thermodynamic functions being also highly influenced by the different basicities and steric requirements of the ligands as described above for the silver(I) diamine systems. The AgL_2 complex of the triamines is much less stable so that the ratios K_1/K_2 are quite large ($K_1/K_2 \approx 10^{3 \div 4}$): this indicates a rearrangement of the ligands around the metal ion [21] which probably requires the removal of one coordinated nitrogen atom and the formation of a new chelate ring by the entering ligand in the case of Ag(I)-dmdien system. As for silver(I)-pmdien system, the lower values in particular of the stepwise stability constant and enthalpy change associated with the reaction:

$$ML + L \rightleftharpoons ML_2\,(\log K_2 = 1.53; \Delta H^\circ_{K_2} = -27\,\mathrm{KJmol^{-1}};\ \Delta S^\circ_{K_2} = -61\,\mathrm{Jmol^{-1}K^{-1}})$$

might be better explained in term of monodentation of the second ligand. The low basicity of the tertiary amino groups and/or the bulky nature of pmdien is likely the reason why chelation is prevented in this complexation step.

To sum up, these data clearly show that little differences in the ligands' design strongly influence the efficiency toward the silver ion in dmso. This efficiency, in particular, is the net result of the influence both of the different basicities and, mainly, of the different steric requirements of the ligands which play an important role on the solvation of the species concerned.

MATERIALS AND METHODS

Chemicals

Anhydrous silver perchlorate was obtained from $AgClO_4 \cdot H_2O$ (Fluka puriss) as described previously [11a]. Dimethyl sulfoxide (Fluka > 99%) was purified by distillation according to the described procedures [11a] and stored over activated 4 Å molecular sieves. The background salt NEt_4ClO_4 was recrystallized twice from methanol and dried at 110°C. The ligands dmen, tmen and pmdien (Aldrich > 98%) were purified by fractional distillation [23]. The N,N″-dimethyldiethylenetriamine ligand was synthesized and purified as decribed earlier [2]. Its purity (> 99%) was checked by ^1H and ^{13}C NMR techniques.

The silver(I) solutions were prepared from anhydrous $AgClO_4$ and freshly distilled dmso. The metal concentration in these solutions was checked by potentiometric titrations with chloride. Solutions of the ligands were prepared by dissolving weighted amounts in the anhydrous solvent. NEt_4ClO_4 was used to obtain the required ionic strength. The water content in the solutions, typically $10 \div 20$ ppm, was determined by a Metrohm 684 KF Coulometer. All the solutions were prepared afresh before each experiment in a glove box under atmosphere of dry nitrogen to avoid moisture.

Potentiometric Measurements

All measurements were carried out under dry nitrogen in a thermostated cell maintained at 298.0 ± 0.1 K. The experimental data required for the determination of the stability constants of the complexes were the equilibrium concentrations of the silver ion, which were obtained from potentiometric measurements. The galvanic cell and other experimental details were previously described [11a]. The emf were measured by means of an Amel 338 pHmeter equipped with a Metrohm 6.0328.000 silver electrode as a working electrode and a Metrohm 6.0718.000 silver electrode as a reference. In general, a given experimental run consisted in collecting many equilibrium data points when solutions of silver perchlorate ($2.00 < C^\circ_M < 20.0\,\mathrm{mmol\ dm^{-3}}$) were titrated with solutions of the ligands ($50 < C^\circ_L < 200\,\mathrm{mmol\ dm^{-3}}$). Titrations were performed with at least three different initial silver(I) concentrations and some titrations were carried out in duplicate to verify the reproducibility of the system. The electrode couple was periodically checked in dmso solutions containing no coordinating ligands. In the concentration range $10^{-5} < [Ag^+] < 10^{-2}\,\mathrm{mol\ dm^{-3}}$, the emf values varied with the metal ion concentration according to Nernst's law.

The computer program Hyperquad [24] was used for the calculation of the stability constants.

Calorimetric Measurements

A Tronac model 87-558 precision calorimeter was employed to measure the heats of reaction. The calorimeter was checked by titration of tris(hydroxymethyl)aminomethane (tham) with a standard solution of HCl in water. The experimental value of the heat of neutralization of tham was found to be $\Delta H^\circ = -47.57\,\mathrm{kJ\,mol^{-1}}$, in good agreement with the accepted value of $-47.53 \pm 0.13\,\mathrm{kJ\,mol^{-1}}$ [1].

The calorimetric titrations were performed at $298.00 \pm 0.02\,\mathrm{K}$ by adding known volumes of ligand solutions ($50 < C_L^\circ < 200\,\mathrm{mmol\,dm^{-3}}$) to 20 ml of silver(I) solution ($2.00 < [\mathrm{Ag}^+] < 20.0\,\mathrm{mmol\,dm^{-3}}$). The heats of dilution of the reactants, determined in separate runs, were found negligible. The least squares computer program Letagrop Kalle [25] was used for the calculation of the enthalpy changes.

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