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Zinc(II) Complexes with Saturated and Unsaturated Tetraazamacrocyclic Ligands: Enthalpy Contribution to Their Solution Stability

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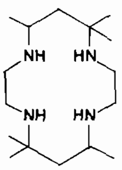
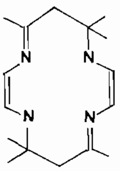
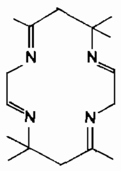
The thermodynamics of the formation of metal complexes with saturated macrocyclic ligands has received considerable attention in the recent years and the factors affecting the enhanced stability in solution of such compounds have been widely discussed [1–7]. However, although several studies of these systems have been published, no data are to date available for reactions involving unsaturated ligands. It therefore seemed desirable to obtain some information about the energetics of the formation of metal complexes with the latter class of ligands, particularly from the standpoint of metal–ligand and solute–solvent interactions. In the work under discussion this has been achieved by comparing, through an appropriate thermochemical study in different medium solvents, the donor properties of a saturated tetradentate macrocyclic ligand with those of the analogous unsaturated one.

This paper gives the enthalpies of complex formation of zinc(II) with the saturated ligand *meso*-5,5,7,12,12,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane ($Me_6[14]aneN_4$, I) and the analogous unsaturated 5,5,7,12,12,14-hexamethyl-1,4,8,11-tetraazacyclotetradeca-2,4,9,11-tetraene ($Me_6[14]tetraeneN_4$, IIa), which coordinates in the tautomeric 1,4,8,11-tetraene form IIb [8].





IIa



IIb

(I) $Me_6[14]aneN_4$ (II) $Me_6[14]tetraeneN_4$

These quantities were determined in two different solvent media: (i) acetonitrile–chloroform 74% (w/w) (74% chloroform) 0.15 *M* NEt_4Br, and (ii) methanol–acetone 50% (w/w) 0.15 *M* NEt_4Br. This procedure allowed us to get an idea of the effect of solute–solvent interactions on the thermochemical balance of the reactions of complex formation. The solvent mixtures with those compositions were necessary in order to maximize the solubility of reagents and products.

The zinc(II) ion was chosen from the 3d metal ions in order to compare complexes having the same spin multiplicity and to exclude crystal field stabilization energy effects.

The calorimetric experiments concern the reaction

$$ZnBr_4^{2-} + L \rightarrow ZnLBr_n^{(2-n)+} + (4-n)Br^- \qquad (1)$$

where the zinc(II) complexes, indicated by the symbolic formula $ZnLBr_n^{(2-n)+}$, should be assumed to have the same coordination number. Conductometric measurements (see Experimental) suggest that this is presumably true for the methanol–acetone 50% medium the complex $Zn(Me_6[14]aneN_4)Br_2$ has a lent electrolytes. In the acetonitrile–chloroform 74% medium the complex $Zn(Me_6[14]aneN_4)Br2$ has a molar conductivity intermediate between those of uni–univalent electrolytes and non-electrolytes; in contrast with this behaviour, in the same medium the $Zn(Me_6[14]tetraeneN_4)Br_2$ complex behaves as a typical uni–univalent electrolyte. However this discrepancy does not affect the sense of the main conclusions which can be drawn.

Reaction (1) is completely shifted to the right at room temperature in the two solvent media taken into consideration. In acetonitrile–chloroform 74% the rate of this reaction is sufficiently fast to allow the enthalpy changes to be determined by using an isoperibolic calorimeter. In methanol–acetone 50% the same reaction is too slow to be studied calorimetrically with sufficient accuracy. For this reason the solution heats of pure solid reagents and products in the two solvent mixtures have been measured and the enthalpy changes associated with reaction (1) in methanol–acetone have been calculated using the thermochemical cycle (2).

The enthalpy changes of the reactions in acetonitrile–chloroform 74% 0.15 *M* NEt_4Br between the tetrabromizincate(II) ion and the two macrocyclic ligands, as well as the solution heats of pure reagents and products in the same solvent and in methanol–acetone 50% 0.15 *M* NEt_4Br, are given in Table I. By the proper substitution of these values in the relationship

$$\Delta H_L^{o\prime} = \Delta H_L^o + (\Delta H_A^S - \Delta H_A^{S\prime}) + (\Delta H_B^S - \Delta H_B^{S\prime}) + (\Delta H_C^{S\prime} - \Delta H_C^S) + 2(\Delta H_D^{S\prime} - \Delta H_D^S) \qquad (3)$$

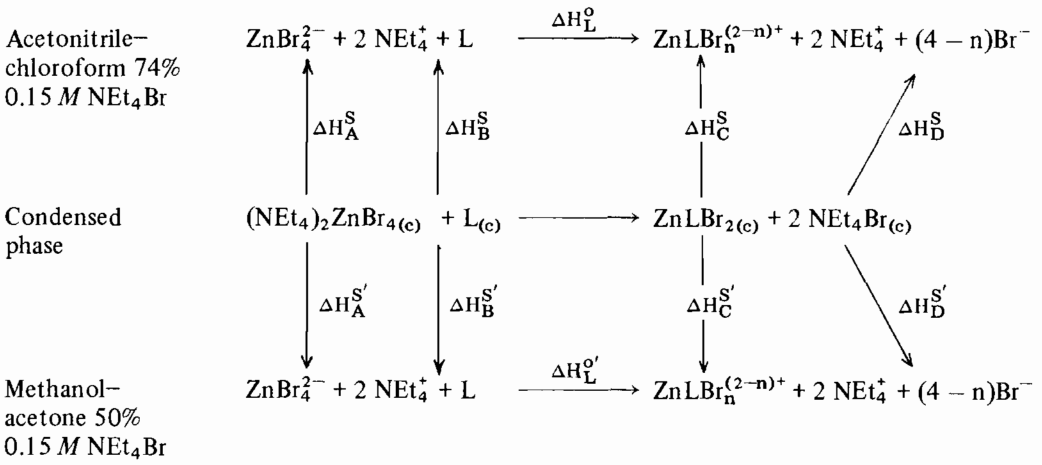
the enthalpy changes involved in the formation of the two zinc(II) macrocyclic complexes in methanol–acetone 50% 0.15 *M* NEt_4Br were obtained. These values are also given in Table I.

In order to discuss these results, the following metathetic reactions should be considered:

TABLE I.[a] Thermochemical Data.

	Solvent	
	Acetonitrile–Chloroform 74% (w/w) 0.15 *M* NEt_4Br	Methanol–Acetone 50% (w/w) 0.15 *M* NEt_4Br
i) Enthalpies of formation at 25 °C of zinc(II) complexes Reaction: $ZnBr_4^{2-} + L \rightleftharpoons ZnLBr_n^{(2-n)+} + (4 - n)Br^-$	ΔH_L^o	$\Delta H_L^{o\prime}$
L = $Me_6[14]aneN_4$	−27.6 (3)	−16.8 (1.2)[b]
L = $Me_6[14]tetraeneN_4$	−10.7 (1)	−6.2 (9)[b]
ii) Heats of solution at 25 °C		
$(NEt_4)_2ZnBr_4$	ΔH_A^S = 2.2 (1)	$\Delta H_A^{S\prime}$ = 7.9 (1)
$Me_6[14]aneN_4$	ΔH_B^S = 3.6 (1)	$\Delta H_B^{S\prime}$ = −1.6 (1)
$Me_6[14]tetraeneN_4$	ΔH_B^S = 5.1 (1)	$\Delta H_B^{S\prime}$ = 7.8 (1)
$Zn(Me_6[14]aneN_4)Br_2$	ΔH_C^S = 1.0 (1)	$\Delta H_C^{S\prime}$ = 4.1 (1)
$Zn(Me_6[14]tetraeneN_4)Br_2$	ΔH_C^S = −1.0 (1)	$\Delta H_C^{S\prime}$ = 3.9 (1)
NEt_4Br	ΔH_D^S = −0.8 (1)	$\Delta H_D^{S\prime}$ = 3.2 (1)

[a] All the values are expressed in kcal/mol. The reported values are the mean of at least two calorimetric measurements; the standard deviations are reported in parentheses. [b] Calculated values from the relationship (4) (see text).



$$Zn(Me_6[14]tetraeneN_4) + Me_6[14]aneN_4 \rightarrow Zn(Me_6[14]aneN_4) + Me_6[14]tetraeneN_4 \quad (4)$$

The enthalpy changes of this reaction can be obtained by determining the differences between the respective enthalpies of formation of the two complexes in the same solvent. This quantity is in each case negative, being −17 kcal/mol in acetonitrile–chloroform 74% 0.15 *M* NEt_4Br and −10 kcal/mol in methanol–acetone 50% 0.15 *M* NEt_4Br.

The strongly exothermal character of reaction (4) in both solvents may indicate the existence of stronger zinc(II)–nitrogen bond interactions in the $Zn(Me_6[14]aneN_4)$ complex than in the $Zn(Me_6[14]tetraeneN_4)$ complex, as a result of the different donor power of amine and imine nitrogens.

Contributions deriving from repulsive non-bonding interactions due to coordination of the ligand around the metal ion, although not to be overlooked, probably do not play a determining role and are furthermore difficult to evaluate. On the basis of qualitative considerations, a more favourable internal energy change could be expected for the saturated $Me_6[14]aneN_4$, considering the less rigid character of the free ligand. It should also be noted that the $Me_6[14]$-tetraeneN_4 ligand exists in solution in the IIa form but coordinates in the tautomeric IIb form: this interconversion is probably endothermal and could therefore reduce the exothermal effect due to complex formation.

The enthalpy changes involved in complex formation in reaction (1) decrease on passing from acetonitrile–chloroform to methanol–acetone, as a result of the balance of the solvation enthalpies $(\Delta H_i^S - \Delta H_i^{S'})$ of the reagents and products; but the main result of the change in solvent medium is the fact that the enthalpy of the metathetic reaction (4) also decreases by 7 kcal/mol. As shown by our data (see Table I), this result can largely be attributed to the differences in solvation enthalpies of the two ligands in the two solvents, these differences being –5.3 and +2.7 kcal/mol for the saturated $Me_6[14]aneN_4$ and unsaturated $Me_6[14]tetraeneN_4$ ligands respectively. These data are consistent with the idea that the saturated ligand $Me_6[14]aneN_4$ interacts much more with the solvent medium methanol–acetone 50% 0.15 *M* NEt_4Br than the unsaturated $Me_6[14]tetraeneN_4$ one. Owing to the neutral character of the two ligands, it seems reasonable to suggest that this stronger interaction occurs through the formation of more and stronger hydrogen bonds: as a consequence, in the complex formation process a larger ligand desolvation energy is required, thus reducing the exothermal effect of metathetic reaction (4) in methanol–acetone.

The contribution arising from the differences of the solution enthalpies of metal complexes (which are comprehensive of the differences of solvation enthalpies and of the different interactions with the counterion in the two solvent media) is small and is not the determining factor for the enthalpy changes difference of the reaction (4) in the two solvent media.

The above results and observations therefore suggest that, as the polarity of solvent medium increases, the contribution of the solvation terms becomes particularly favourable for complexes formed by unsaturated macrocyclic ligands. In this sense ligands possessing a relatively low coordinative power can form metal complexes, which have a comparatively high thermodynamic stability. This could serve as a model for explaining the thermodynamics involved in the formation of many naturally occurring macrocyclic metal complexes.

Experimental

Materials

Reagent grade acetonitrile and chloroform (Erba-RPE) were further purified by distillation over P_2O_5 and $CaCl_2$; reagent grade absolute methanol and acetone (Erba-RPE) were used without further purification. NEt_4Br (Fluka *purum*) was twice recrystallized from ethanol and dried over P_2O_5 under vacuum. $(NEt_4)_2ZnBr_4$ was prepared as described [9]. The ligand $Me_6[14]aneN_4$ was synthesized and dehydrated according to literature methods [10, 11]. The ligand $Me_6[14]tetraeneN_4$ was synthesized according to Goedken and Busch [8]. The complexes $Zn(Me_6[14]aneN_4)Br_2$ and $Zn(Me_6[14]tetraeneN_4)Br_2$ were synthesized by mixing a hot solution of $ZnBr_2$ in ethanol with a solution of the proper ligand in the same solvent. The complexes precipitate on cooling. *Anal.*: $Zn(Me_6[14]aneN_4)Br_2$: calcd. for $C_{16}H_{36}Br_2N_4Zn$, C, 37.71, H, 7.12, N, 10.99; found C, 37.7, H, 7.1, N, 11.0; $Zn(Me_6[14]tetraeneN_4)Br_2$, calcd. for $C_{16}H_{28}Br_2N_4Zn$, C, 38.31, H, 5.62, N, 11.17; found C, 38.3, H, 5.6, N, 11.2%.

Calorimetric Measurements

Calorimetric measurements were carried out on a LKB 8700/1 reaction calorimeter, following an already reported procedure [3]. All the measurements were carried out with the reaction system thermostatted at 25.000 ± 0.001 °C. The enthalpy changes for the reactions between the tetrabromozincate(II) ion and the two macrocyclic ligands in acetonitrile–chloroform were also studied with a LKB 10700-2 batch microcalorimeter. Results were in agreement with those obtained with the isoperibolic instrument.

Conductivity Measurements

The molar conductivity values were measured on a WTW Model LBR/B conductance bridge. Concentrations of the solutions were approximately 10^{-3} *M*. The following molar conductivity values (ohm^{-1} cm^2) were obtained: (i) acetonitrile–chloroform 74% (w/w): $Zn(Me_6[14]aneN_4)Br_2$, 29; $Zn(Me_6[14]tetraeneN_4)Br_2$, 69; NEt_4Br (reference), 68; (ii) methanol–acetone 50% (w/w): $Zn(Me_6[14]aneN_4)Br_2$, 98; $Zn(Me_6[14]tetraeneN_4)Br_2$, 116; NEt_4Br (reference), 119.

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