A Further Investigation on the Nature of Macrocyclic Effect [a]

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The enthalpy change at 25° C of the metathetic reaction[!]

Cu(2,3,2-tet) + cyclam ⇌ Cu(cyclam) + 2,3,2-tet (2, 3,2-tet = 1,4,8,11-tetrazaundecane; cyclam = 1,4,8,11-tetrazacyclotetradecane) has been determined as difference of the relative enthalpies of formation in acetonitrile-chloroform (74% chloroform) 0.15 M NEt₄Br. Using an appropriate thermochemical cycle, the enthalpy change of this reaction in ethanol-water 50% has also been calculated. On the basis of the obtained results, it is suggested that the macrocyclic effect is due both to stronger copper (II)–nitrogen bond interactions for the Cu(cyclam)²⁺ complex and to favourable solvation enthalpy contributions.

Introduction

The macrocyclic effect was introduced in the chemical literature by Cabbiness and Margerum[1] in order to indicate the larger stability in aqueous solution of metal complexes formed by tetramine macrocyclic ligands with respect to stability of the analogous open-chain complexes.

The favourable free energy change for the metathetic reaction

$$ML_{(oc)} + _{(mac)} \rightleftharpoons ML_{(mac)} + L_{(oc)} \qquad (1)$$
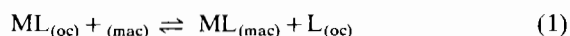
(where $L_{(oc)}$ and $L_{(mac)}$ indicate the open-chain and macrocyclic ligands respectively) has been tentatively attributed either to a favourable entropy contribution due to different loss of configurational entropy for the two kinds of ligand,[1,2] and to a favourable enthalpy effect.[3]

Owing to the inertness of the macrocyclic complexes in aqueous solution,[4,5] their reactions of formation cannot be investigated by direct calorimetric studies. Thus, enthalpy and entropy changes must be determined using an indirect method.


We have found that the equilibrium of the reaction

$$CuBr_4{}^{2-} + L \rightleftharpoons CuLBr_n{}^{(2-n)+} + (4-n)Br^- \qquad (2)$$
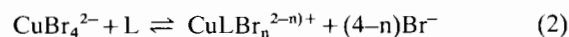
(L = tetramine macrocyclic ligand) can be quickly achieved at room temperature in acetonitrile–chloroform mixtures. The enthalpy changes for the reaction (2) can be therefore experimentally determined in this medium and, by using an appropriate thermochemical cycle, the enthalpy change in aqueous solution or in any other solvent can be calculated.

Here the enthalpies of complex formation at 25° C of copper(II) with the macrocyclic ligand 1,4,8,11-tetrazacyclotetradecane (I, cyclam) and with the open-chain ligand 1,4,8,11-tetrazaundecane (II, 2,3,2-tet) in acetonitrile–chloroform (74% chloroform) 0.15 M NEt₄Br are reported as well as the calculated enthalpies for the same reactions in ethanol–water 50%.
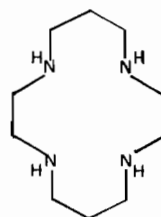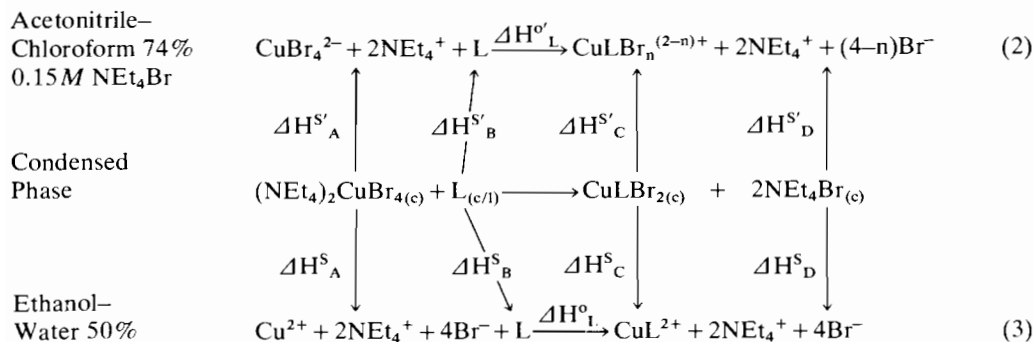

(I)
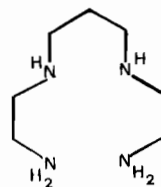
(II)

These results are compared among themselves and with those recently reported[6] for the formation of the Ni(cyclam)²⁺ complex in aqueous solution.

Procedure

The following thermochemical cycle was considered:

Acetonitrile–
Chloroform 74%
0.15M NEt$_4$Br

$$CuBr_4^{2-} + 2NEt_4^+ + L \xrightarrow{\Delta H^{o'}_L} CuLBr_n^{(2-n)+} + 2NEt_4^+ + (4-n)Br^- \qquad (2)$$

$$\Delta H^{S'}_A \qquad \Delta H^{S'}_B \qquad \Delta H^{S'}_C \qquad \Delta H^{S'}_D$$

Condensed
Phase

$$(NEt_4)_2CuBr_{4(c)} + L_{(c/l)} \longrightarrow CuLBr_{2(c)} \quad + \quad 2NEt_4Br_{(c)}$$

$$\Delta H^S_A \qquad \Delta H^S_B \qquad \Delta H^S_C \qquad \Delta H^S_D$$

Ethanol–
Water 50%

$$Cu^{2+} + 2NEt_4^+ + 4Br^- + L \xrightarrow{\Delta H^o_L} CuL^{2+} + 2NEt_4^+ + 4Br^- \qquad (3)$$

where $\Delta H^{o'}_L$ is the enthalpy change associated to the formation of copper(II) complexes of tetramine ligands in acetonitrile–chloroform 74% according to reaction (2), ΔH^o_L is the analogous quantity in ethanol–water 50% (reaction (3)), ΔH^S_i and $\Delta H^{S'}_i$ are the heats of dissolution of pure reactants and products in the two solvent mixtures. The solvent mixtures and those compositions were necessary in order to dissolve the cyclam ligand.

From the above thermochemical cycle, the following equation can be obtained

$$\Delta H^o_L = \Delta H^{o'}_L + (\Delta H^{S'}_A - \Delta H^S_A) + (\Delta H^{S'}_B - \Delta H^S_B) + (\Delta H^{S'}_C - \Delta H^S_C) + 2(\Delta H^S_D - \Delta H^{S'}_D) \qquad (4)$$

The thermodynamic quantities reported on the right of the above equation can be experimentally determined in such a way that ΔH^o_L values can be calculated.

Experimental

Materials

Reagent grade acetonitrile and chloroform (Erba RPE) were further purified by distillation over P_2O_5 and $CaCl_2$ respectively; reagent grade absolute ethanol (Erba RPE) was used without further purification. NEt$_4$Br (Fluka Purum) was recrystallized from ethanol and dried over P_2O_5 under vacuum. (NEt$_4$)$_2$ CuBr$_4$ was prepared as described.[7] Commercial 2,3,2-tet (Eastman Kodak) was dried over KOH and then twice distilled under vacuum. The macrocyclic ligand cyclam was prepared according to Barefield.[8] The complexes Cu(2,3,2-tet)Br$_2$ and Cu(cyclam)Br$_2$ were prepared by mixing a hot solution of CuBr$_2$ in ethanol with a solution of the proper tetramine in the same solvent. The complexes precipitate on cooling; they were collected on a sintered glass funnel, washed with cold ethanol and dried *in vacuo* at 70°C. (*Anal.* Cu (2,3,2-tet)Br$_2$: calcd. for C$_7$H$_{20}$CuBr$_2$N$_4$, C, 21.91; H, 5.25; N, 14.40; found C, 21.9; H, 5.4; N, 14.4.

Cu(cyclam)Br$_2$: calcd. for C$_{10}$H$_{24}$CuBr$_2$N$_4$, C, 28.32; H, 5.71; N, 13.22; found C, 28.3; N, 13.3; H, 5.9).

Spectrophotometric Measurements

Absorption spectra were carried out with a Beckman DK2A spectrophotometer, using 1 cm silica cells. The spectral features of cyclam solutions in acetonitrile–chloroform, containing different amounts of (NEt$_4$)$_2$ CuBr$_4$ were found to be time-independent.

Calorimetric Measurements

Calorimetric measurements were carried out on a LKB 8700/1 reaction calorimeter, whose standardization procedure has been already reported.[9] The ampoules containing weighted amounts of reactants (0.3–0.5 mmol) were broken into *ca.* 100 ml of solvent or solution containing the stoichiometric amounts of ligand. All the measurements were carried out with the reaction system thermostatted at 25.000 ± 0.001°C. Thermal effects were graphically calculated.

The heats of dissolution of ionic compounds in acetonitrile–chloroform were found to be concentration dependent. In order to avoid this effect, a solution 0.15M NEt$_4$Br was used. This dependence was not observed, at least in the range of concentration investigated, in water or in ethanol–water 50%.

The heats of dissolution of the tetramine ligands and of the (NEt$_4$)$_2$CuBr$_4$ complex in ethanol–water 50% have been measured using 0.2M KOH and 0.001M HBr solutions respectively, in order to avoid thermal effects due to hydrolysis.

Results

The enthalpy changes of the reactions in acetonitrile–chloroform 74% 0.15M NEt$_4$Br between the tetrabromocuprate ion and the two tetramine ligands as

TABLE I[a]. Enthalpies of Formation.

Enthalpies of Formation at 25° C of Copper(II) Complexes in Acetonitrile–Chloroform 74% 0.15 M NEt$_4$Br:

$CuBr_4^{2-}$ + cyclam $\rightleftharpoons$ Cu(cyclam)Br$_n^{(2-n)+}$ + (4–n)Br$^-$ $\Delta H°_L = -61.9(2)$

$CuBr_4^{2-}$ + 2,3,2-tet $\rightleftharpoons$ Cu(2,3,2-tet)Br$_n^{(2-n)+}$ + (4–n)Br$^-$ $\Delta H°_L = -55.0(3)$

Heats of Dissolution at 25° C:

Compound	Solvent	
	Acetonitrile–Chloroform 74% 0.15 M NEt$_4$Br	Ethanol–Water 50%
(NEt$_4$)$_2$CuBr$_4$	2.92(8)	3.08(3)[b]
cyclam	5.60(12)	2.65(1)[c]
2,3,2-tet	−1.25(5)	−11.13(2)[c]
Cu(cyclam)Br$_2$	0.42(5)	7.12(10)
Cu(2,3,2-tet)Br$_2$	3.26(12)	7.33(11)
NEt$_4$Br	−0.77(3)	3.99(1)

Enthalpies of Formation at 25° C of Copper(II) Complexes in Ethanol–Water 50%:[d]

Cu^{2+} + cyclam $\rightleftharpoons$ Cu(cyclam)$^{2+}$ $\Delta H°_L = -42.9(6)$

Cu^{2+} + 2,3,2-tet $\rightleftharpoons$ Cu(2,3,2-tet)$^{2+}$ $\Delta H°_L = -31.7(7)$

[a] All 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] 0.001 M HBr solution. [c] 0.2M KOH solution. [d] Calculated values from relationship (4) (see text).

well as those of the dissolution of the pure reagents and products in the same solvent and in ethanol–water 50% are reported in Table I. By substituting properly these values in the relationship (4), the enthalpy changes relative to formation of the two copper(II) tetramine complexes in ethanol–water 50% are obtained. These values are also reported in Table I.

In order to check this procedure, the enthalpy of formation in aqueous solution 0.5M KNO$_3$ of copper (II) with 2,3,2-tet has also been calculated through direct measurement of the dissolution heats of reactants and products. The obtained value of 28.2 kcal/mol satisfactorily agrees with that of 27.7 previously reported from direct calorimetric measurement.[10]

Discussion

Our interest resides on the following metathetic reaction:

Cu(2,3,2-tet) + cyclam $\rightleftharpoons$ Cu(cyclam) +
2,3,2-tet   (5)
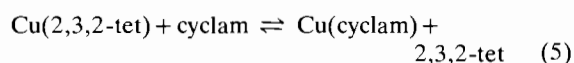
where copper(II) complexes, indicated by symbolic formulae, are assumed to have a similar co-ordinative environment, on account of the strict similarity of their absorption spectra.

The enthalpy changes of reaction (5) are obtained as the difference between the relative enthalpies of formation of the two complexes in the same solvent. This quantity is always negative, being −7 kcal/mol in

acetonitrile–chloroform 74% 0.15M NEt$_4$Br and −11 kcal/mol in ethanol–water 50%.

Enthalpy of formation of metal complexes in solution can be considered as the result of the balance of several energy contributions, which can be summarized as follows: (a) bond interactions between metal and donor atoms; (b) repulsive non bonding interactions arising from the co-ordination arrangement of the ligand around the metal ion; (c) difference between solvation enthalpies of reactants and products.

The enthalpy change of reaction (5) is more negative in ethanol–water than in acetonitrile–chloroform. This fact can be substantially attributed to the difference of the solvation enthalpies of the ligands and complexes in the two solvents. The problems remains whether this difference alone is able to account for the observed values.

Recently Hinz and Margerum[6] determined the thermodynamic functions for the following metathetic reaction in water

Ni(2,3,2-tet)$^{2+}$ + cyclam $\rightleftharpoons$ Ni(cyclam)$^{2+}$ +
2,3,2-tet   (6)
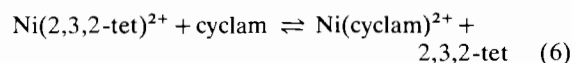
The reported $\Delta G°$, $\Delta H°$ and $\Delta S°$ values are −9.2 kcal/mol, −14 kcal/mol and −16 e.u. respectively. These authors suggested that the negative enthalpy value is completely due to the differences in the hydration enthalpies of the ligands only. From our data reported in Table I, it results that the differences of solvation enthalpies of the ligands in the two solvents ($\Delta H^{S'}_B - \Delta H^S_B$) are less unfavorable for cyclam than

for 2,3,2-tet. This supports the hypothesis that the open-chain ligand interacts much more with the pseudo-aqueous solvent than the macrocyclic one. However this effect is partially counterbalanced by solvation terms associated to the complexes.

The difference of 4 kcal/mol observed for reaction (5) in the two solvents could be consistent with the idea that the negative value associated to this kind of reactions is due to type (c) energy contributions. However, it is reasonable to believe that this contribution is small in 74% acetonitrile–chloroform in comparison with the observed value of -7 kcal/mol. The latter suggestion is quite realistic if one thinks that the overall difference relative to solvation terms for the two solvents is only 4 kcal/mol. Therefore, these results and considerations strongly suggest that the negative enthalpy values associated to reaction (5) must involve also a stronger copper(II)–nitrogen bond interaction for the Cu(cyclam) complex with respect to the Cu (2,3,2-tet) one. This is consistent with the suggested "mechanical restriction effect" of the macrocyclic ligand on the metal ion,[5,11] as spectroscopically evidenced for nickel(II) and copper(II) complexes.[3,12]

Acknowledgements

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