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Heats of Reaction between the Branched Hexaamine *N,N,N′,N′*-tetrakis(3-aminopropyl) Ethylenediamine (TAPEN) and Hydrogen, Ni(II), Cu(II), Zn(II) Ions

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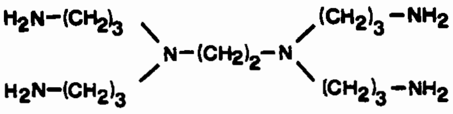
Abstract

The enthalpies of reaction between the branched hexaamine *N,N,N′,N′*-tetrakis(3-aminopropyl) ethylenediamine (TAPEN) and hydrogen, Ni(II), Cu(II) and Zn(II) ions have been determined at 25 °C, $I = 0.5$ mol dm^{-3} by continuous titration calorimetry and batch microcalorimetry. By combining these reaction enthalpies with the previously obtained equilibrium constants, the entropic contributions to the studied equilibria are determined and discussed. The results obtained for the enthalpy of the reaction which involves the addition of one hydrogen ion to the 1:1 complex show that TAPEN behaves as a pentadentate ligand. Comparisons with some related, branched hexaamines have been made.

Introduction

In a previous paper [1] we have reported the synthesis and equilibrium studies of the branched polyamine: *N,N,N′,N′*-tetrakis(3-aminopropyl)ethylenediamine (hereafter abbreviated as TAPEN) with many metal ions. In order to understand how many nitrogen donor atoms of TAPEN are involved in the formation of the metal complexes, the heats of protonation and of complex formation should be known. Furthermore, the presence of many propylenic chains in the ligand molecule allow the study of the influence on the complex formation enthalpy due to the presence of many six-membered chelate rings (Scheme 1).



Scheme 1.

Experimental

Ligand and Reagents

The preparation of TAPEN and its purification as TAPEN·6HCl have been described in ref. 1. Standardized CO_2-free solutions of sodium hydroxide were prepared as described elsewhere [2]. 0.5 mol dm^{-3} KNO_3 (C. Erba product, high purity grade) was used as the ionic medium for all calorimetric measurements.

Enthalpy of Protonation and Complex Formation

The enthalpies of protonation of TAPEN as well as the enthalpies of complex formation with Cu(II) and Zn(II) were determined with an LKB calorimeter (Model 8700), by employing the continuous titration technique. The apparatus and the experimental procedure have already been reported [3]. The calorimetric system was controlled by an Apple II Europlus microcomputer, equipped with a 9-inch video display, and one minifloppy disk drive. A computer program was written in BASIC*, with some routines in assembler, to monitor for each titration point, the voltage of the unbalanced wheatstone bridge, the time and the volume of the titrant added. The collected experimental data, stored on the floppy

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*A listing of the calorimetric data acquisition program (written in BASIC and ASSEMBLER) may be obtained on request from the authors.

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TABLE I. Thermodynamic Parameters of Stepwise Protonation of TAPEN and Related Ligands (Aqueous Solution, 25 °C, I = 0.5 mol dm^{-3} (KNO_3), Standard State = 1 mol dm^{-3})

	Step	TAPEN	PENTEN[a]	PTETRAEN[a]
$-\Delta G°$ (kcal mol^{-1})	1	14.55(3)[b]	13.75	13.97
	2	14.00(2)	13.07	13.04
	3	13.52(3)	12.26	12.52
	4	12.48(2)	11.48	11.51
	5	9.17(3)	1.81	3.41
	6	4.66(20		
$-\Delta H°$ (kcal mol^{-1})	1	11.36(10)	11.3	11.0
	2	13.27(9)	11.5	11.6
	3	12.26(9)	11.2	12.7
	4	11.92(7)	12.0	12.4
	5	8.53(7)	4.5	4.3
	6	7.81(6)		
$\Delta S°$ (cal K^{-1} mol^{-1})	1	10.7(3)	8	10
	2	2.4(2)	5	5
	3	4.2(2)	−3	−1
	4	1.9(1)	−2	−3
	5	2.1(1)	−9	−3
	6	−10.6(2)		

[a] Taken from ref. 8. [b] Values in parentheses are standard deviations in the least significant figure.

disk, were further processed to determine the stepwise enthalpy of reaction [3]. The enthalpy of ionization of water was determined by adding an NaOH solution to a solution of HCl contained in the calorimetric vessel. The measured value, 13.50(3) kcal mol^{-1}, was in agreement with the accepted literature value [4]. Because of the slowness of the formation reaction, the enthalpy of the Ni(II)–TAPEN complex was determined by using a model 10700–2 LKB batch microcalorimeter. A full description of the apparatus, its calibration and the calorimetric procedure have been previously reported [5]. In a typical experiment an aqueous solution of Ni^{2+} and a solution of the neutralized ligand were mixed. Under the reaction conditions and employing the determined stability constants [1], the species present and their percentages at equilibrium before and after mixing were calculated by means of the DISPOL [6] computer program. The only significant species present at equilibrium before and after mixing were the free non-protonated ligand and the complex $[NiL]^{2+}$, respectively. Blank experiments were carried out to correct for the enthalpy of dilution of the NaOH solution.

Results and Discussion

Protonation Thermodynamics

The observed thermodynamic parameters for TAPEN are given in Table I. The same parameters for the related ligands: *N,N,N′,N′*-tetrakis(2-aminoethyl)-ethylenediamine (PENTEN) [7] and *N,N,N′,N′*-tetrakis(2-aminoethyl)trimethylenediamine (PTETRAEN) [7] are also reported for the purpose of comparison. As already found, TAPEN behaves as a strong polybase. Its high basicity is also reflected by the high exothermicity of each protonation step: the enthalpy of the overall protonation reaction $L + 6H^+ = H_6L^{6+}$ is −65.15 kcal mol^{-1} (see Table I). The inductive effect is one of the most relevant contributions to such basicity behavior. Furthermore, the long propylenic chains strongly reduce the repulsions between positive charges in the polyprotonated species of TAPEN, providing stability to them and causing their formation reactions to be more exothermic. Due to the above mentioned reasons, TAPEN is more basic than PENTEN and PTETRAEN (see Table I). Indeed, in the case of TAPEN all the stepwise protonation enthalpies are considerably negative. The overall trend is: $|\Delta H°_1| < |\Delta H°_2| > |\Delta H°_3| > |\Delta H°_4|$. As previously observed for both open chain [8] and cyclic polyamines [9], $|\Delta H°_2|$ is higher than $|\Delta H°_1|$, the difference being particularly high for TAPEN because of the high exothermicity of the second protonation step (−13.27 kcal mol^{-1}). In the case of open chain polyamines the trend $|\Delta H°_2| > |\Delta H°_1|$ has been rationalized by a particularly favorable arrangement of water molecules around the diprotonated species [10]. The last two protonation steps are both very

TABLE II. Thermodynamic Parameters[a] of Formation of Cu(II), Ni(II) and Zn(II) Complexes with TAPEN (Aqueous Solution, 25 °C, I = 0.5 mol dm^{-3} (KNO$_3$), Standard State = 1 mol dm^{-3})

Reactions	M = Ni(II)			M = Cu(II)			M = Zn(II)		
	$-\Delta G°$	$-\Delta H°$	$\Delta S°$	$-\Delta G°$	$-\Delta H°$	$\Delta S°$	$-\Delta G°$	$-\Delta H°$	$\Delta S°$
$M^{2+} + L = ML^{2+}$	18.8(1)	17.0(2)	6.0(6)	26.71(1)	23.25(9)	11.6(3)	16.74(2)	11.01(9)	19.2(3)
$M^{2+} + L + H^+ = MLH^{3+}$				39.80	35.46	14.6	29.39	22.47	23.2
$M^{2+} + L + 2H^+ = MLH_2^{4+}$				49.68	44.11	18.7	39.11	31.65	25.0
$M^{2+} + L + 3H^+ = MLH_3^{5+}$				55.19	48.55	22.3			
$ML^{2+} + H^+ = MLH^{3+}$				13.09	12.21	3.0	12.65	11.46	4.0
$MLH^{3+} + H^+ = MLH_2^{4+}$				9.88	8.65	4.1	9.72	9.18	1.8
$MLH_2^{4+} + H^+ = MLH_3^{5+}$				5.51	4.44	3.6			
$M^{2+} + HL^+ = MLH^{3+}$				25.25	24.10	3.9	14.84	11.11	10.1
$M^{2+} + H_2L^{2+} = MLH_2^{4+}$				21.13	19.48	5.5	10.56	7.02	11.9
$M^{2+} + H_3L^{3+} = MLH_3^{5+}$				13.12	11.66	4.9			

[a]Units of $\Delta G°$ and $\Delta H°$ are kcal mol^{-1}, of $\Delta S°$ are cal K^{-1} mol^{-1}.

exothermic, −8.53 and −7.81 kcal mol^{-1}, respectively, compared with those of PENTEN and PTETRAEN (−4.5 and −4.3 kcal mol^{-1} respectively for the fifth protonation step, the last one being unmeasurable). In other words the $|\Delta H°_3|$ and $|\Delta H°_4|$ values in the case of TAPEN are much less affected by a neighboring charged nitrogen atom than those of PENTEN and PTETRAEN. Because the last two nitrogen atoms to be protonated are the tertiary ones, which are separated by an ethylenic bridge, it is reasonable to compare the enthalpies of the last two protonation steps of TAPEN with those of tetramethylated ethylenediamine. Even in this case the last two protonations of TAPEN, −8.53 and −7.81 kcal mol^{-1}, are more exothermic than the stepwise protonation enthalpies of the *N,N,N′,N′*-tetramethylethylenediamine, −7.40 and −6.64 Kcal mol^{-1}, respectively [11].

Metal Complexes

The thermodynamic parameters of metal complex formation between TAPEN and the metal ions Ni(II), Cu(II), Zn(II) are reported in Table II.

Nickel(II) Complex

As observed [1], the slowness of the formation reaction and the presence of species with different spin multiplicities make the Ni(II)/TAPEN system a rather complicated one. In order to overcome some experimental difficulties we determined the enthalpy of formation of the species [NiL]$^{2+}$ by a microcalorimetric procedure (see 'Experimental'). Unfortunately, only the enthalpy of formation of the species [NiL]$^{2+}$ has been determined. The [NiL]$^{2+}$ complex of TAPEN is less stable than the corresponding complexes of PENTEN and PTETRAEN. Such lower stability is due to both a smaller (less negative) enthalpy of formation and a less positive entropy of formation of the [NiL]$^{2+}$ complex, compared with those of the two related ligands [7].

Copper(II) Complexes

The branched TAPEN has a great tendency to form protonated metal complexes; in Table II the enthalpies of formation of all the species formed by the Cu(II) ion and the ligand TAPEN in our experimental conditions have been reported. In the case of TAPEN we have to make hypotheses on the number of donor atoms involved in the formation of the 1:1 complex. For the Cu(II) complex the protonation reaction of the [CuL]$^{2+}$ complex (CuL^{2+} + H$^+$ = CuLH^{3+}) is even more exothermic with respect to the first protonation step of the free ligand (see Tables I and II). This fact clearly indicates that the nitrogen atom, which undergoes protonation in the [CuL]$^{2+}$ complex is not bonded to the central Cu(II) ion, and TAPEN behaves as a pentadentate ligand. The protonation of the monoprotonated complex [CuLH]$^{3+}$ to form [CuLH$_2$]$^{4+}$ is, on the other hand, significantly less exothermic than the second protonation step of the free ligand (see Tables I and II), indicating that the nitrogen atom involved in that protonation is bonded to the central metal ion. In this situation some energy to break the M–N bond has to be spent, and the overall process M–N + H$^+$ = M + N–H$^+$ would be less exothermic than the simple protonation of the free ligand.

Zinc(II) Complexes

In the Zn(II)/TAPEN system there are three species: [ZnL]$^{2+}$, [ZnLH]$^{3+}$ and [ZnLH$_2$]$^{4+}$. The [ZnL]$^{2+}$ complex is the least stable one, and its formation is less exothermic than that of the corresponding complexes of PENTEN and PTETRAEN. As already found for the Cu(II) complex, the protonation of the $[ZnL]^{2+}$ complex to form $[ZnLH]^{3+}$ is more exothermic than the first step of protonation of the free ligand. This also means that in the case of Zn(II) complexes TAPEN employs at most five nitrogen atoms for coordination.

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