Magnesium and Lithium Complexation by 1,4,7,10-Tetraazacyclododecane

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(Received June 16, 1987)

Abstract

The stability constants of magnesium and lithium complexes of 1,4,7,10-tetraazacyclododecane (cyclen) have been determined in 0.5 M KNO_3 at 25 °C by means of potentiometric titration, as K_{MgL} = 1.77×10^2 and $K_{LiL} < 10^{-2}$, respectively. *Ab initio* calculations on the protonated species of the cyclen ligand have been performed in order to obtain a better understanding of experimental protonation constants, and to compare them to previous calculations on the investigated metal complexes.

Introduction

In previous works, theoretical calculations on the alkali and alkaline earth metal ion complexes with macrocyclic compounds, such as 1,4,7,10-tetraazacyclododecane (cyclen), were performed in order to study the factors determining the macrocyclic effect [1–3] and the stabilization energies of these complexes compared to the hydrated metal ions [4].

The results of these calculations had indicated that only the magnesium/cyclen and possibly also the lithium/cyclen complex should exist in aqueous solution within the studied series [4].

Complexation of magnesium and lithium ion with cyclen was, therefore, investigated experimentally. The potentiometric titration was chosen as the most appropriate method to determine the stability constants in this system of rather low solubility.

As the protonation constants of the ligand also play an important part in the complex equilibria during the process of the data evaluation [5], they have been evaluated simultaneously. For completion of these studies, quantum chemical calculations were carried out for the protonated ligand species, too.

Experimental

The potentiometric titrations were carried out at 25 ± 0.1 °C using an Ingold U-402-M3 combined electrode. The electrode was calibrated by standard buffer solution, so that pH errors did not exceed 0.02 units.

The ionic strength on the solutions was adjusted to 0.5 M by potassium nitrate. The titrator solution of sodium hydroxide (in 0.5 M KNO_3), kept in nitrogen atmosphere, was regularly controlled by titration with 0.1 M standard hydrochloric acid. The initial volume of each titration was 50.0 cm³.

All titrations were performed under vapour saturated nitrogen atmosphere. The pH range and the initial concentrations of each titration are shown in Table I.

TABLE I. Experimental Data Used in Refinements

Titration	Initial concentration (mM)			pH Range	Data points
	Metal ions	Cyclen	HCl		
1	–	0.372	1.368	3.3–11.7	66
2	–	0.697	2.929	2.9–11.3	50
3	–	0.984	3.618	2.8–11.2	71
4	–	1.493	5.490	2.7–11.1	83
5	Mg^{2+} 0.899	0.847	3.604	2.8–11.0	41
6	Mg^{2+} 1.069	0.997	4.240	2.8–11.0	40
7	Mg^{2+} 1.131	1.099	4.673	2.7–11.0	31
8	Mg^{2+} 1.457	0.687	2.920	2.9–11.0	38
9	Mg^{2+} 1.636	1.811	6.624	2.6–11.0	46
10	Li^+ 0.894	0.924	3.929	2.7–11.8	84
11	Li^+ 0.918	0.690	0.730	2.9–11.3	51
12	Li^+ 3.512	0.825	3.508	2.8–11.1	48

The stability constants of the metal ion/cyclen complexes and the protonation constants of cyclen were obtained together with the dissociation constant of water (K_w) by simultaneous optimization using the program MINIQUAD [6].

The stepwise protonation constants K_n [7] and the stability constants of the magnesium/cyclen complex (K_{MgL}), are shown in Table II, as obtained from the computer refinements using the data of titration curves 1–4 and 5–9 of Table I, respectively. A stability constant of the lithium/cyclen complex ($K_{LiL} < 0.01$, refined from the data of curves 10–12 of Table I) could not be determined accurately.

Ab initio Calculations

The total energies of the protonated species of cyclen were calculated with minimal GLO basis set

TABLE II. Protonation Constants of Cyclen Ligand and the Stability Constant of Mg^{2+}/cyclen Complex in 0.5 M KNO_3 at 25 °C

$\log K$	Refinements	
	Ligand	Complex
$\log K_1$	11.27 ± 0.03	11.23 ± 0.11
$\log K_2$	9.96 ± 0.03	9.82 ± 0.16
$\log K_3$	2.18 ± 0.20	1.52 ± 0.47
$\log K_4$	1.74 ± 0.64	2.61 ± 0.77
$\log K_w$	-13.93 ± 0.00	-13.89 ± 0.01
$\log K_{MgL}$		2.25 ± 0.55

TABLE III. Stabilization Energies and the Total Energies of Cyclen's Protonated Species Corresponding to their Optimized Distances of $H^+ \cdots N$ Bond

Species	$H^+ \cdots N$ bond (Å)	Total energy (a.u.)	Stabilization energy (Kcal/mol)
L		-452.15592	
LH^+	1.20	-452.56596	-257.3
LH_2^{2+}	1.16	-452.79640	-144.6
LH_3^{3+}	1.16	-452.81658	-12.7
LH_4^{4+}	1.16	destabilized	~ 90

[8] using the HONDO [9] program. The optimized structure of cyclen has been taken from refs. 2 and 10. The hydrogen bond length between protons and nitrogen atoms of cyclen was optimized assuming tetrahedral angles at the protonated nitrogens.

The results of the distance optimization, total energies and stabilization energies of protonated species are reported in Table III.

Discussion

The data for the protonation constants of the system with and without magnesium ion are in good agreement with results reported by Kodama [11] and Kaden [12]. The pK values of the first two protonation constants are obtained nearly identical for ligand and complex but the third and fourth constants differ. Determination of K_3 and K_4 in these systems seems to be somewhat problematic as indicated already in previous works [12], due to their low values compared to the first and second protonation constant.

The dissociation constant of water obtained from the refinements of the system with and without magnesium ion remains almost constant, being a criterion for the quality of data evaluation. The mag-

nitude of the stability constant of the magnesium/cyclen complex, K_{MgL}, $= 1.77 \times 10^2$, seems to be in good relation to the constants of the strong complexes with bivalent metal ions such as Cu^{2+}, Zn^{2+}, Co^{2+} and Ni^{2+} [11, 12].

The stabilization energies of the ligand's protonated species derived from total energies (Table III), have been investigated with respect to their relation to the corresponding protonation constants. The most noteworthy result is the destabilization resulting for the species LH_4^{4+} and the very small proton affinity for H_2^{2+}, indicating a low probability for LH_3^{3+} formation. These data help in understanding the difficulty in the determination of K_3 and K_4 and make the formation of these species within the normal pH scale appear questionable (K_3) if not impossible (K_4), when compared to the proton affinity of the water molecule (-172.9 kcal/mol with same basis set).

The stabilization energy ΔE is closely related to the reaction enthalpy ΔH ($\Delta E = \Delta H - P\,\Delta V$). As volume changes in the system can be expected to be very small, the stabilization energy of the system will nearly equal the reaction enthalpy. The logarithm of the equilibrium constant is partly dependent on the enthalpy ($\Delta H = \Delta G + T\,\Delta S$ and $\Delta G = -2.303RT \log K$). The relation between the stabilization energies and their $\log K$ values could be linear, therefore, if ΔS and solvation contribution to ΔH were constant for all protonation processes. A tendency towards such a linear correlation between calculated stabilization energies and corresponding $\log K$ values of this system cannot be recognized (see Fig. 1). Apparently differences in ΔS and probably also in solvation of the protonated species are important cofactors determining the equilibrium constants. These factors are not assumed, however, to be large enough to stabilize the species LH_4^{4+}.
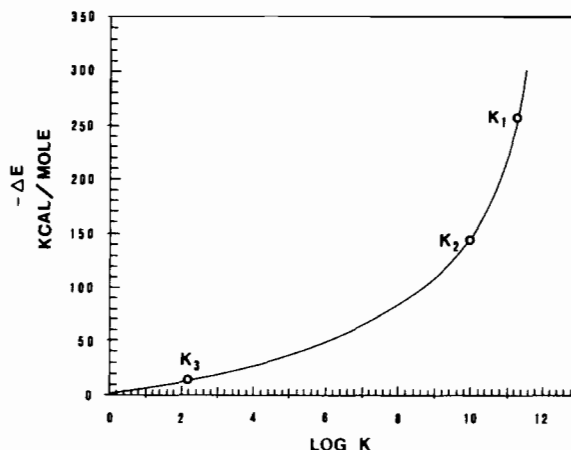

Fig. 1. Correlation between the stabilization energies of cyclen's protonated species and their $\log K$.

The investigations of this paper show that quantum chemical calculations of isolated species, although not directly comparable to data obtained experimentally in solution, are a valuable tool not only for the interpretation of the experimental data, but also for certain predictions about the formation and stability of species in the solution. The increasing ease of routine MO calculations combined with the experimental works performed in this work, appear, therefore, a useful method for the treatment of complex equilibria.

Acknowledgements

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