



# Interaction of Na<sup>+</sup> and K<sup>+</sup> ions with DTPA-amide dioxapentaazacyclophanes: effect of electrostatic field in macrocyclic cavity on UV absorption spectra and protonation

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## Abstract

The effects of electrolytes on protonation were studied by UV spectrometry on the geometrical isomers of dioxapentaazacyclophanes that were synthesized by 1+1-cyclization of diethylenetriaminepentaacetic (DTPA) dianhydride with aromatic diamine involving 1,3- or 1,4-phenylenebis(methyleneoxy) group. Absorption bands at 245 and 280 nm respond to pH in association with the protonation status confirmed by <sup>1</sup>H NMR. The logarithmic first-protonation constants, determined from the absorptivity versus pH curves, depend on coexisting alkali metal ions in a range of 7.7–8.2 in 0.01 M solutions of the chlorides. The more pronounced effect of alkali metals occurs in the dissociation of amide proton; the logarithmic deprotonation constant, log  $K_{p-1}$ , of the 1,3-oxymethyl isomer is –9.48 in 0.01 M NaCl and –10.35 in 0.01 M KCl; the constant of the 1,4-oxymethyl isomer, –9.79 in 0.01 M NaCl and –11.58 in 0.01 M KCl; no amide deprotonation is observable in 0.01 M LiCl. Alkali metal ions Na<sup>+</sup> and K<sup>+</sup> are accommodated in a macrocyclic cavity through interaction with the oxa-donor sites, and produce an intense electrostatic field within the cavity. The resulting field causes large changes in absorptivity, and also enforces amide deprotonation. Sodium ion is so effective that the deprotonation occurs at pH as low as 9.5–9.8. Potassium ion is less effective on the amide deprotonation, but the action is selective towards the isomers.

**Keywords** Oxaazamacrocycles · DTPA derivatives · UV spectra · Electrolyte effects · Protonation

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The DTPA moiety involves a central double-ionic NH<sup>+</sup>CH<sub>2</sub>CO<sub>2</sub><sup>–</sup> arm and two outer NCH<sub>2</sub>CO<sub>2</sub>H arms; this protonation mode is consistent with solution <sup>1</sup>H NMR.

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## Introduction

In the complexation of a macrocycle with metallic or organic ions, alkali metal ions are supposed to work cooperatively or competitively at a high concentration of a supporting electrolyte used in spectrometric and potentiometric experiments. Since electrolytes are concentrated in biological environments as well, the effect of alkali metal ions is a factor that should be taken into account in the design of receptors. To study such electrolyte effects, in the present work, we have designed DTPA-amide oxaaza-cyclophanes shown in Scheme 1, from the viewpoint described below.

The functions of macrocyclic compound are controlled by the combined factors of constituting donor atoms, cavity size, molecular rigidity, and others [1–6]. An example has been given by macrocycles of DTPA(diethylenetriaminepentaacetate) cyclized with diamines through