Spectroscopic Study of the Complexation of an Aza-15-Crown-5 Containing Chromofluoroionophore with Ba$^{2+}$ and Ca$^{2+}$ Cations

Dedicated to Prof. Dr. Karl-Heinz Drexhage on the occasion of his 60th birthday

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Abstract. The complexation of 1-[(4-benzothiazolyl)phenyl]-4,7,10,13-tetraoxa-1-aza-cyclopentadecane with Ba$^{2+}$ and Ca$^{2+}$ cations was investigated spectrophotometrically and spectrofluorometrically. The stability constants of the complexes formed are: for Ba$^{2+}$ log $K_{st} = 3.17 \pm 0.01$ (absorption) and log $K_{st} = 2.95 \pm 0.03$ (fluorescence); for Ca$^{2+}$ log $K_{st} = 3.71 \pm 0.02$ (absorption) and log $K_{st} = 3.58 \pm 0.05$ (fluorescence). Protonation of the ligand leads to fluorescence quenching. AM1 and PPP quantum chemical calculations were used to predict molecular geometry, proton affinities and the spectra of the compounds studied.

Key words: Aza-15-crown-5, chromoionophore, fluoroionophore, complex formation, alkali and alkaline earth metal ions.

1. Introduction

Chromophores and fluoroionophores containing macrocycles are often useful reagents for metal ion recognition, based on the changes in their photophysical properties upon complex formation [1, 2]. Such compounds, when able to complex with different substrates, could also serve as recognition sites in enzyme mimicking reactions [3, 4].

The changes in the absorption and emission properties depend on the reagent, the charge density of the ions and the cavity size as well as on the reaction medium [1, 5–8].

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The aza-15-crown-5 cavity is known mainly as a complex-forming agent for alkali and alkaline earth metal ions as well as for $\text{H}^+$, $\text{NH}_4^+$ and $\text{Ag}^+$ [9, 10]. Several interesting reagents were obtained combining this macrocycle with some chromophores and fluorophores, and these could be used for analytical purposes [4–12].

We recently reported the synthesis of a new chromofluoroionophore 1 (Figure 1) and related compounds and their interaction with some metal ions [13]. It was shown that, among the metal ions tested, the strongest influence on the photophysical properties of 1 and 5 (Figure 1) were caused by $\text{Ba}^{2+}$ and $\text{Ca}^{2+}$ cations.