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Preferential binding of the magnesium ion by anthraquinone based chromogenic receptors

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Abstract

Two new anthraquinone based receptors have been synthesized. A colour change for both these receptors could be detected when group IIA metal ions were added in DMF solution at room temperature. No such colour change was noticed for group IA metal ions. Association constants for these receptors towards Mg^{2+}, Ca^{2+}, Sr^{2+} and Ba^{2+} were evaluated by systematic spectrophotomeric titrations and they follow the order $K_{Mg(II)} \gg K_{Ca(II)} > K_{Sr(II)} \gg K_{Ba(II)}$. The association constants for $\mathbf{L}_1$ were found to be higher than those for $\mathbf{L}_2$ toward group IIA metal ions. Ab initio quantum chemical calculations have been performed to rationalize these observed results. X-ray structural analysis shows a helical structure for one of the receptor molecules.

Keywords: Chromogenic sensors; X-ray structure; Receptors; Metal ions; Ab initio calculations; Magnesium ion

1. Introduction

Alkaline earth metal ions are the most abundant divalent cations in living cells and play vital roles in many cellular processes, for example, as an enzyme cofactor, stabilization of DNA conformation, ion transport through membranes, maintenance of cell shape and signal transduction. In particular, the measurement of the concentration of the magnesium ion (Mg^{2+}) in biological samples has been of considerable interest and a great deal of effort has been devoted to the design and synthesis of sensitive and selective sensors for this ion [1–5]. Therefore, the search for easily synthesizable sensor molecules for the Mg^{2+} ion is still an active area of research. Herein, we report two new colorimetric sensor molecules, which can easily be synthesized and have shown specificity towards the Mg^{2+} ion. We have used anthraquinone derivatives which constitute a commercially important class of compounds used either as a dyeing agent or as a colorimetric signalling unit in sensor molecules [6–9]. The higher affinity of the Mg^{2+} ion towards these receptors has been examined by ab initio quantum chemical calculations.

2. Experimental

2.1. Materials and methods

1,2-Dihydroxy-9,10-anthraquinone, $Ca(ClO_4)_2$, $Mg(ClO_4)_2$, $Sr(ClO_4)_2$, $Ba(ClO_4)_2$ and dimethyl sulfate were obtained from Aldrich. All other reagents used for the study were of reagent grade and obtained locally (SD Fine chemicals, India). Solvents for reactions and various studies were used as received from Merck (India) – except THF and DMF were dried prior to use following standard methods.

2.2. General procedures

Microanalyses (C, H, N) were performed using a Perkin–Elmer 4100 elemental analyzer. FTIR spectra were recorded

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either as KBr pellets or as a solution in a cell provided with a KBr window, using a Perkin–Elmer Spectra GX 2000 spectrometer. ^{1}H NMR spectra were recorded on a Bruker 200 MHz FT NMR (model: Avance-DPX 200) using $CDCl_3$ as the solvent and tetramethylsilane (TMS) as an internal standard. Electronic spectra were recorded with a Shimadzu UV-3101 PC or a Cary 500 Scan UV–Vis-NIR spectrometer; while room temperature luminescence spectra were recorded with a Perkin–Elmer LS 50B luminescence spectrofluorimeter. Electrochemical experiments were performed on a CH-660A (USA) electrochemical instrument with a conventional three-electrode cell assembly. Saturated Ag/AgCl as a reference and platinum as a working electrode were used for all measurements. Ferrocene was added at the end of each experiment as an internal standard and all potentials are quoted versus the ferrocene/ferrocenium (Fc/Fc^+) couple. X-ray single crystal data for $\mathbf{L}_2$ was collected using Mo Kα ($\lambda = 0.7107$ Å) radiation on a SMART APEX diffractometer equipped with a CCD area detector. Data collection, data reduction [10] and structure solution/refinement [11,12] were carried out using the software package of SMART APEX. The structure was solved by direct methods and refined in a routine manner. All hydrogen atoms were geometrically fixed at their idealized position. Graphics were generated using Mercury 1.4.1 [13].

2.3. Synthesis

2.3.1. 1-Hydroxy-2-methoxy-anthraquinone ($\mathbf{L}_1$)

1.0 g (4.16 mM) of 1,2-dihydroxy-9,10-anthraquinone was dissolved in 30 ml of acetone. To this, 1.6 g of anhydrous K_2CO_3 was added and the mixture was stirred at room temperature for a few minutes. Then 1.049 g dimethyl sulfate (8.33 mM) dissolved in 5 ml of acetone was added from a dropping funnel over 30 min. The resulting solution was then refluxed for 4 h. Then acetone was partially removed under reduced pressure (~5 ml). To this about 25 ml of diethylether was added and the undesired compounds were discarded in the water layer by solvent extraction. The ether solution was then dried over anhydrous $MgSO_4$ and ether was removed to yield the crude product. Purification of the desired product was achieved by gravity chromatography using SiO_2 as the stationary phase and *n*-hexane–$CHCl_3$ (3:7; v/v) as the eluent. Yield: 0.25 g (23%). ^{1}H NMR (200 MHz, $CDCl_3$): 13.05 (s, 1H, –OH), 8.25–8.2 (m, 2H, H^5, H^8), 8.078 (d, 1H, $J = 8.4$ Hz, H^4), 7.89–7.83 (m, 2H, H^6, H^7), 7.24 (1H, d, $J = 8.4$ Hz, H^3), 3.94 (s, 3H, $-OCH_3$). FT-IR (KBr; cm^{-1}): 3329 (NH), 3272 (NH), 1651 (–C=O). ESI MS [*m/z* (positive ion mode)]: 278 ($M^+ + Na^+$, 20%), 255 (M^+, 38%). Elemental analysis for $C_{15}H_{10}O_4$: *Anal.* Calc.: C, 70.86; H, 3.96. Found: C, 70.7; H, 4.0%. UV–Vis spectra (DMF, λ_{max} nm (ε M^{-1} cm^{-1})): 278 (1.10×10^5), 369 (4.44×10^4).

2.3.2. 1,2-Dimethoxy-anthraquinone ($\mathbf{L}_2$)

2 g (34 mM) of 1,2-dihydroxy-9,10-anthraquinone and 12.4 g anhydrous K_2CO_3 were mixed in 40 ml of acetone and then stirred at room temperature for a few minutes. To this resulting mixture, 14 ml dimethyl sulfate (150 mM) dissolved in 20 ml of acetone was added from a dropping funnel over 30 min. The resulting solution was then refluxed for 4 h. Then acetone was partially removed under reduced pressure (~15 ml) and about 50 ml of diethyl ether was added. The starting compound and any $\mathbf{L}_1$ formed due to partial conversion were removed in the water layer, whose pH was maintained at 9.5. The ether was dried under reduced pressure to recover the crude product. This was further purified by chromatography using a SiO_2 column and *n*-hexane–$CHCl_3$ (1:1; v/v) as eluent. Yield: 0.7 g (39%). ^{1}H NMR (200 MHz, $CDCl_3$): 8.28–8.23 (m, 2H, H^5, H^8), 8.174 (d, 1H, $J = 8.6$ Hz, H^4), 8.78–8.74 (m, 2H, H^6, H^7), 7.28 (1H, d, $J = 8.6$ Hz, H^3), 4.0 (s, 3H, $-[OCH_3]^1$), 3.03 (s, 3H, $-[OCH_3]^2$) . FT-IR (KBr; cm^{-1}): 1336, 1270 ($O-CH_3$), 1670 (–C=O). ESI MS [*m/z* (positive ion mode)]: 291 ($M + Na^+$, 50%); 269 ($M + H^+$; 90%); Elemental analysis for $C_{15}H_{10}O_4$: *Anal.* Calc.: C, 71.64; H, 4.52. Found: C, 72.0; H, 4.5%. UV–Vis spectra (DMF, λ_{max} nm (ε M^{-1} cm^{-1})): 279 (1.59×10^4), 328 (7.6×10^3), 425 (9.20×10^3). The structure for $\mathbf{L}_2$ was further established by single crystal X-ray studies.

2.4. Spectrophotometer titrations

A 1.0×10^{-3} M solution of the receptor $\mathbf{L}_1$ and a 1.0×10^{-3} M solution of the receptor $\mathbf{L}_2$ in DMF were prepared and stored in the dark. These solutions were used for all spectroscopic studies after the appropriate dilution. 1.0×10^{-3} M solutions of $MClO_4$ (M is an alkali metal ion) or $M'(ClO_4)_2$ (M' is an alkaline earth metal ion) were prepared in dried and distilled DMF, and were stored under an inert atmosphere. All titration experiments were performed using 1.0×10^{-4} M solutions of receptor $\mathbf{L}_1$ and 1.35×10^{-5} M solutions of receptor $\mathbf{L}_2$ in DMF and various concentrations of the cations (5.0×10^{-6} to 5.0×10^{-4} M) in DMF. Affinity constants were evaluated after calculating the concentrations of the respective species, like free $\mathbf{L}_1$, $\mathbf{L}_2$, $\mathbf{M}^{2+}$ and the associated complexes, e.g. $\mathbf{L}_1 \cdot \mathbf{M}^{2+}/\mathbf{L}_2 \cdot \mathbf{M}^{2+}$. The effect of the ionic strength on the affinity constant value was also examined by repeating the studies at various 0–0.1 M $[(^t\text{Bu}_4\text{N})\text{ClO}_4]$ supporting electrolyte concentrations. The affinity constant values were evaluated from the absorbance data of the titration curve using 519 nm as the probe wavelength.

2.5. Luminescence titration

The standard solutions mentioned above were also used for luminescence titration studies. For all measurements, λ_{ext} used was 517 nm ($\mathbf{L}_1$)/514 nm ($\mathbf{L}_2$) with an excitation and emission slit width of 5 nm. All titration experiments were performed using 2.5×10^{-5} M solutions of receptors $\mathbf{L}_1$ and $\mathbf{L}_2$ in DMF (thoroughly degassed before measurement with IOLAR grade dinitrogen gas) and solutions of various cations (3.0×10^{-5} to 5.0×10^{-4} M) in DMF.