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Metal–heptaiodide interactions in cyclomaltoheptaose (β-cyclodextrin) polyiodide complexes as detected via Raman spectroscopy

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Abstract—The Raman spectra of the cyclomaltoheptaose (β-cyclodextrin, β-CD) polyiodide complexes $(\beta\text{-CD})_2{\cdot}NaI_7{\cdot}12H_2O$, $(\beta\text{-CD})_2{\cdot}RbI_7{\cdot}18H_2O$, $(\beta\text{-CD})_2{\cdot}SrI_7{\cdot}17H_2O$, $(\beta\text{-CD})_2{\cdot}BiI_7{\cdot}17H_2O$ and $(\beta\text{-CD})_2{\cdot}VI_7{\cdot}14H_2O$ (named β-M, M stands for the corresponding metal) are investigated in the temperature range of 30–140 °C. At room temperature all systems show an initial strong band at $178\ cm^{-1}$ that reveals similar intramolecular distances of the disordered I_2 units (~2.72 Å). During the heating process β-Na and β-Rb display a gradual shift of this band to the final single frequency of $166\ cm^{-1}$. In the case of β-Sr and β-Bi, the band at $178\ cm^{-1}$ is shifted to the final single frequencies of 170 and $172\ cm^{-1}$, respectively. These band shifts imply a disorder–order transition of the I_2 units whose I–I distance becomes elongated via a symmetric charge-transfer interaction $I_2{\leftarrow}I_3^-{\rightarrow}I_2$. The different final frequencies correspond to different bond lengthening of the disordered I_2 units during their transformation into well-ordered ones. In the Raman spectra of β-V, the initial band at $178\ cm^{-1}$ is not shifted to a single band but to a double one of frequencies 173 and $165\ cm^{-1}$, indicating a disorder–order transition of the I_2 molecules via a non-symmetric charge-transfer interaction $I_2{\leftarrow}I_3^-{\longrightarrow}I_2$. The above spectral data show that the ability of I_3^- to donate electron density to the attached I_2 units is determined by the relative position of the different metal ions and their ionic potential q/r. The combination of the present results with those obtained from our previous investigations reveals that cations with an ionic potential that is lower than ~1.50 (Cs^+, Rb^+, Na^+, K^+ and Ba^{2+}) do not affect the Lewis base character of I_3^-. However, when the ionic potential of the cation is greater than ~1.50 (Li^+, Sr^{2+}, Cd^{2+}, Bi^{3+} and V^{3+}), the $M^{n+}{\cdots}I_3^-$ interactions become significant. In the case of a face-on position of the metal (Sr^{2+}, Bi^{3+}) relative to I_3^-, the charge-transfer interaction is symmetric. On the contrary, when the metal (Li^+, Cd^{2+}, V^{3+}) presents a side-on position relative to I_3^-, the charge-transfer interaction is non-symmetric.

Keywords: Cyclomaltooligosaccharides; β-Cyclodextrins; Heptaiodide ions; Raman spectroscopy; Inclusion complexes; Disorder–order

1. Introduction

The polyiodide inclusion complexes of cyclomaltoheptaose (β-cyclodextrin, β-CD) with various metal ions display isomorphous crystal structures (monoclinic $P2_1$) that consist of non-interacting heptaiodide units of Z-shape.[1–4] In these channel-type systems, the β-CD molecules are arranged head to head, producing dimers that are stacked like coins in a roll and form slightly zigzagged cylinders.[1] The I_7^- ions can be formulated as $I_2{\cdot}I_3^-{\cdot}I_2$ with the I_2 and I_3^- nearly perpendicular to each

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other (Fig. 1). More explicitly, the central I_3^- unit is well-ordered and located in the space between two neighbouring β-CD dimers (near their O(6) rims). The two disordered I_2 units are attached to the I_3^- ion and included within the cavities of the dimers (near their O(2), O(3) rims). The counterions are located between the dimers but outside the β-CD cylinders interacting with the O(6)H hydroxyl groups and the water molecules of the interstices.

In our previous papers, we have investigated a variety of β-cyclodextrin polyiodide complexes with different metal ions (Ba^{2+}, Cd^{2+}, K^+, Li^+ and Cs^+)[2–4] by using several techniques to achieve a thorough characterization of their physicochemical properties. Raman spectroscopy has proven to be one of the most powerful methods for the detection of the heptaiodide structural changes with temperature. Our spectroscopic study has been focused on the frequency range of 140–210 cm^{-1}, where the perturbations of the iodine molecules can be observed. The β-CD molecules exhibit significantly intense bands in a range of higher frequencies (2800–3500 cm^{-1}) according to the detailed investigation of Moreira da Silva et al.[5] At room temperature, all of these systems showed a strong band at 178–179 cm^{-1} that was assigned to the v_1 mode of the disordered iodine molecules in the heptaiodides. This frequency

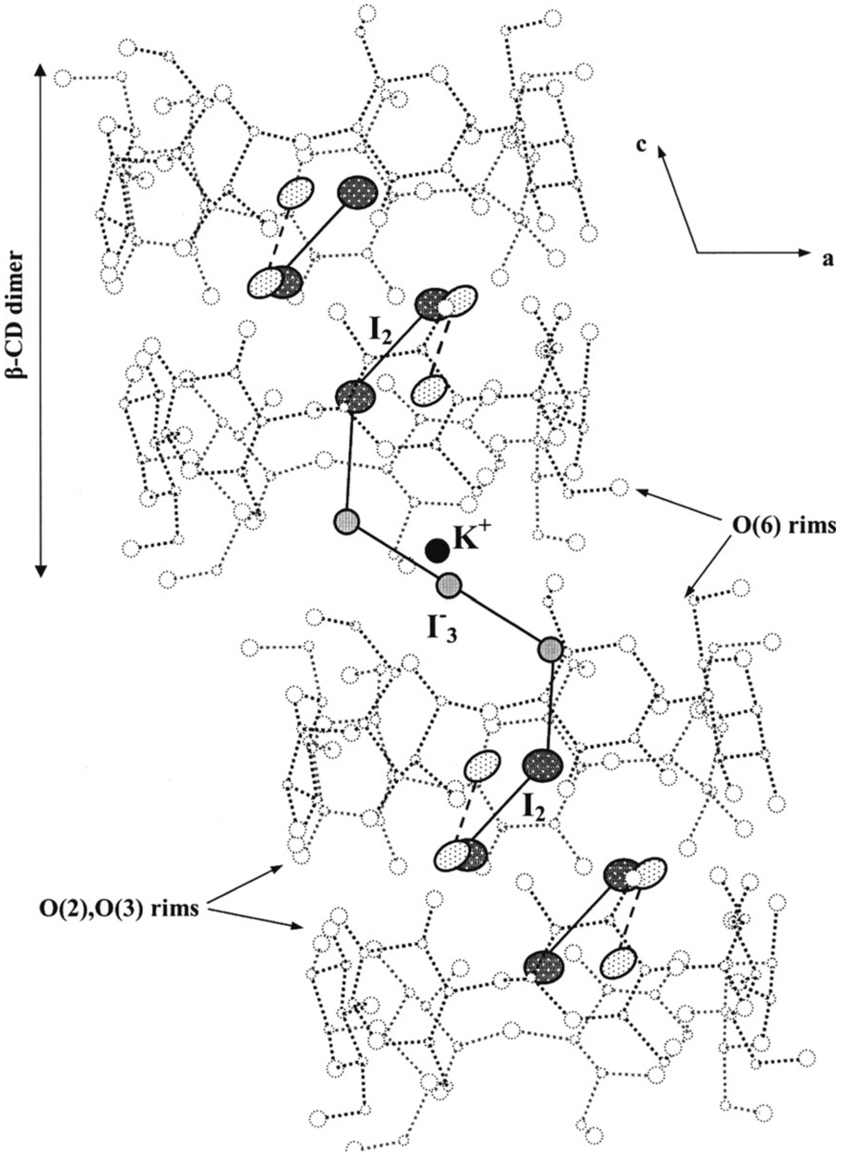

Figure 1. The geometry of the heptaiodide ions (along the *b*-axis) embedded in the β-CD dimers of the monoclinic $(\beta\text{-CD})_2\cdot KI_7\cdot 9H_2O$, according to the single- crystal X-ray analysis.[1] The white ellipsoids with the black spots correspond to the disordered iodine atoms of I_2 that are in positions of minor occupancies (d(I–I) < 2.77 Å). The grey ellipsoids with the white spots correspond to the disordered iodine atoms of I_2 that are in positions of main occupancies (d(I–I) = 2.77 Å). The well-ordered atoms of I_3^- are presented as grey spheres, whereas the potassium ion is presented as a black sphere.