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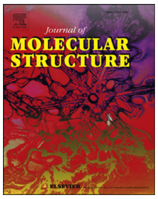

Sugar-metal ion interactions: The coordination behavior of cesium ion with lactose, D-arabinose and L-arabinose

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ABSTRACT

The novel cesium chloride–lactose complex ($CsCl\cdot C_{12}H_{22}O_{10}$ (Cs-Lac), cesium chloride-D-arabinose and L-arabinose complexes ($CsCl\cdot C_5H_{10}O_5$, Cs-D-Ara and Cs-L-Ara) have been synthesized and characterized using X-ray diffraction, FTIR, FIR, THz and Raman spectroscopies. Cs^+ is 9-coordinated to two chloride ions and seven hydroxyl groups from five lactose molecules in Cs-Lac. In the structures of CsCl-D-arabinose and CsCl-L-arabinose complexes, two kinds of Cs^+ ions coexist in the structures. Cs1 is 10-coordinated with two chloride ions and eight hydroxyl groups from five arabinose molecule; Cs2 is 9-coordinated to three chloride ions and six hydroxyl groups from five arabinose molecules. Two coordination modes of arabinose coexist in the structures. α-D-arabinopyranose and α-L-arabinopyranose appear in the structures of Cs-D-Ara and Cs-L-Ara complexes. FTIR and Raman results indicate variations of hydrogen bonds and the conformation of the ligands after complexation. FIR and THz spectra also confirm the formation of Cs-complexes. Crystal structure, FTIR, FIR, THz and Raman spectra provide detailed information on the structure and coordination of hydroxyl groups to metal ions in the cesium chloride–lactose, cesium chloride-D- and L-arabinose complexes.

1. Introduction

The interactions between metal ions and carbohydrates may be involved in many important biochemical processes, such as the transport and storage of metal ions, stabilization of membrane structures, binding of glycoproteins to cell surfaces, toxic metal metabolism, binding of protein to sugar, and so on [1–3]. It has also been exploited in metal-catalyzed enantioselective synthesis, therapeutic agents, catalysts and diagnostic tracers, etc. [4–9]. A series of crystal structures of metal-sugar complexes have been reported, most of them are related to calcium and lanthanide complexes [10–15]. The coordination structures of metal-saccharides complexes are complicated, even metal-promoted deprotonation of alcoholic OH groups in aqueous solutions of low pH can be observed [16–18]. Na and K ions are the most important metal ions *in vivo*. Sodium-potassium pump is an important process in life. Transport is related to the binding of Na, K with biological molecules. No crystal structure of K with carbohydrates is available at present. The crystal structures of Na-carbohydrate complexes are limited [19–21], which is not enough to serve as references of the structures of K with saccharides. In the periodic table of the elements, K is located between Na and Cs. K with saccharide may demonstrate properties between Na-saccharide and Cs-saccharide. Thus, the structures of Cs-saccharides complexes are helpful in understanding the physiological nature of K-saccharide interactions. Here CsCl-lactose, CsCl-D-arabinose and CsCl-L-arabinose complexes are investigated to simulate the interactions between K and carbohydrates.

Lactose ($C_{12}H_{22}O_{11}$) is a disaccharide consisting of D-glucose and D-galactose moieties joined by a β-1-4-glycosidic linkage. The crystal structures of $CaBr_2$-lactose ($C_{12}H_{22}O_{11}\cdot CaBr_2\cdot 7H_2O$) and

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$CaCl_2$-lactose ($C_{12}H_{22}O_{11}\cdot CaCl_2\cdot 7H_2O$) have been reported [11,22,23]. Rao group has reported the synthesis and characterization of Fe(III)-lactose [24], Ce-lactose [25], Pr and Nd-lactose and arabinose complexes under alkaline conditions by various spectral and analytical techniques, and appropriate structures are assigned [26]. The interactions of lactose with metal ions in water solution have been studied by employing conductance measurements, ultrasonic velocity, density and viscosity, volumetric parameters, etc. [27–31].

The single crystal structures of $CaCl_2$-β-L-arabinose ($C_5H_{10}O_5\cdot CaCl_2\cdot 4H_2O$), $CaCl_2$-α-L -arabinose ($C_5H_{10}O_5\cdot CaCl_2\cdot 4H_2O$) prepared in neutral condition, $[(en)_2Pd_2(\beta\text{-D-Ara}p_{1,2,3,4}\,H_{-4})]$ under alkaline conditions, and bis(4-dehydro-L-arabinose) calcium methanol bishydrate ($Ca(C_5H_9O_5)_2\cdot CH_3OH\cdot 2H_2O$) have been reported [18,32–34]. The reactions between L-arabinose and Mg^{2+}, Sr^{2+}, Ba^{2+}, Zn^{2+}, Cd^{2+}, Hg^{2+} and UO_2^{2+} have been studied in aqueous solution and adducts by means of FTIR, ^1H NMR spectroscopy, molar conductivity and X-ray powder diffraction measurements [35–39]. Experimental and theoretical studies of sodium cation interactions with D-arabinose, xylose, glucose, and galactose suggest the possible coordination structures [40]. Interactions of D- or L-arabinose with metal ions in aqueous solution have been investigated by volumetric parameters, ^1H NMR and circular dichroism spectra, etc. [41–43].

Crystal structures provide definite information about coordination structures, bond lengths and bond angles of metal-sugar complexes. Here novel structures of cesium chloride–lactose (denoted as Cs-Lac), cesium chloride-D-arabinose (denoted as Cs-D-Ara) and cesium chloride-L-arabinose (denoted as Cs-L-Ara) are observed. The single crystals of metal-sugar complexes are difficult to prepare. For the compounds that are surely coordination compounds but which cannot form a single crystal for the X-ray analysis, IR, Raman, FIR and THz spectra are effective methods to deduce the unknown structures, so here the relationship between these spectra and crystal structure results is also discussed. The complexity of Cs binding with carbohydrate may be a reference for understanding the mechanism of sodium-potassium pump.

2. Experimental section

2.1. Materials and methods

CsCl, lactose, D- and L-arabinose were purchased from J&K company in China, and were used without further purification.

2.2. Synthesis of Cs-Lac, Cs-D-Ara and Cs-L-Ara complex

The procedures of preparation of the cesium chloride–lactose complex (Cs-Lac) was as follows: 1.010 g CsCl and 1.027 g lactose were dissolved in 4 ml H_2O/6 ml ethanol and heated on a water bath at about 80 °C. Small aliquots of EtOH (Analytical Reagent) were periodically added to the solution during the heating process to prolong the reaction time, leading to the formation of the complexes. The total reaction time was about 120 h and about 38 ml H_2O/ethanol were used. Then the concentrated solutions were cooled down for crystallization. The Cs-Lac complex is stable, and the percentage yield of the product was about 50%.

The same method was applied for the preparation of cesium chloride-D-arabinose (Cs-D-Ara) and cesium chloride-L-arabinose (Cs-L-Ara). For Cs-D-Ara, 0.253 g CsCl and 0.168 g D-arabinose were dissolved in 4 ml H_2O/6 ml ethanol and heated on a water bath at about 80 °C. The total reaction time was about 120 h and about 60 ml H_2O/ethanol were used. The Cs-D-Ara complex is stable, and the percentage yield was about 40%.

For Cs-L-Ara, 0.758 g CsCl and 0.451 g L-arabinose were used. The total reaction time was about 200 h and about 60 ml H_2O/ethanol were used. The Cs-D-Ara complex is stable, and the percentage yield was about 40%.

Anal. Calcd for Cs-Lac ($CsCl\cdot C_{12}H_{21}O_{11}$): C, 28.28; H, 4.15. Found: C, 28.05; H, 4.21. Anal. Calcd for Cs-D-Ara ($CsCl\cdot C_5H_{10}O_5$): C, 18.86; H, 3.16. Found: C, 18.12; H, 3.01. Anal. Calcd for Cs-L-Ara ($CsCl\cdot C_5H_{10}O_5$): C, 18.86; H, 3.16. Found: C, 18.69; H, 3.07.

The characteristic IR bands are as follows: for Cs-Lac, 3422, 3357, 3286, 2979, 2936, 2890, 2866, 1462, 1440, 1420, 1369, 1321, 1283, 1264, 1198, 1166, 1150, 1119, 1094, 1063, 1033, 1018, 987, 916, 903, 876, 846, 786, 771, 722, 688 and 661 cm^{-1}. For Cs-D-Ara, 3346, 2940, 2903, 2874, 1460, 1438, 1408, 1389, 1375, 1343, 1300, 1257, 1210, 1139, 1122, 1104, 1079, 1058, 1000, 946, 932, 891, 871, 840, 782 and 696 cm^{-1}. For Cs-L-Ara, 3354, 2973, 2940, 2905, 2863, 2825, 1467, 1436, 1390, 1376, 1343, 1302, 1275, 1256, 1214, 1139, 1122, 1104, 1079, 1060, 1034, 1001, 945, 928, 891, 871, 840, 781 and 694 cm^{-1}.

2.3. Physical measurements

Data for the metal complexes were collected on a Xcalibur, Eos, Gemini diffractometer using fine-focus sealed tube ($\lambda = 0.71073$ Å) at 105(2) K. Using Olex2, the structures of three metal complexes were solved with the XS structure solution program using direct method and refined with the XL refinement package using least squares minimization. Anisotropic thermal parameters were used for the non-hydrogen atoms and isotropic parameters for the hydrogen atoms. Hydrogen atoms were added geometrically and refined using a riding model [44].

The mid-IR spectra in the 4000–600 cm^{-1} region were measured on a Nicolet Magna IN10 spectrometer using micro-IR method at 4 cm^{-1} resolution and 64 scans. The variable temperature FTIR spectra of the metal complexes were measured on a Bruker VERTEX 80v FTIR spectrometer with variable temperature attachment at 4 cm^{-1} resolution and 32 scans. The Elemental analyses were carried out on an Elementar Vario EL spectrometer. The THz absorption spectra in the 0.2–2.6 THz region were recorded on the THz time-domain device of Capital Normal University of China. The experimental apparatus for terahertz transmission measurements was discussed in detail elsewhere [45]. The far-IR spectra of the molecules in the 650–50 cm^{-1} region were measured using polyethylene pellet method and were taken on a Bruker VERTEX 80v FTIR spectrometer at room temperature and at 4 cm^{-1} resolution and 32 scans. The Raman spectra were recorded on a Nicolet 6700 FTIR NXR FT-Raman module at 4 cm^{-1} resolution and 256 scans.

3. Results and discussion

3.1. Crystal structures of cesium chloride–lactose complex and cesium chloride-D-, and L-arabinose complexes

The crystal structures of cesium chloride–lactose and cesium chloride-D-, and L-arabinose complexes are shown in Fig. 1. All H atoms are not shown here for clarity. The crystal data and structure refinements of Cs-Lac, Cs-D-Ara and Cs-L-Ara complexes are listed in Table 1. The selected bond lengths and bond angles for Cs-Lac, Cs-D-Ara and Cs-L-Ara complexes are listed in Table S1.

The symmetry space group of Cs-Lac is $P2_1$, which is the same with α-lactose itself. Cs^+ is 9-coordinated to two chloride ions, O5′, O6′ from one lactose molecule, two O2′ atoms from two lactose molecules, O3 and O4 from the fourth lactose molecule and O3 from the fifth lactose in Cs-Lac, so one Cs^+ is connecting with five lactose molecules. For one lactose molecule, its O5′ (the oxygen atom in the ring) and O6′ is coordinated to the first cesium ion, O2′