



Short communication

# Interactions of D-cellobiose with selected chloride salts: A $^{13}\text{C}$ NMR and FT-IR study



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## ABSTRACT

The interactions of cellulose model compound D-cellobiose with chloride salts of  $\text{Zn}^{2+}$ ,  $\text{Ca}^{2+}$ ,  $\text{Li}^+$ ,  $\text{Sn}^{2+}$ ,  $\text{La}^{3+}$ ,  $\text{Mg}^{2+}$ ,  $\text{K}^+$  and  $\text{NH}_4^+$  were evaluated by measuring the  $^{13}\text{C}$  NMR chemical shift changes ( $\Delta\delta$ ) of the disaccharide due to the addition of salts in  $\text{D}_2\text{O}$ . The KCl and  $\text{NH}_4\text{Cl}$  showed similar  $\Delta\delta$  changes due to interactions only with the  $\text{Cl}^-$  anion. Whereas other chloride salts showed interactions with both cation and anion. Among these salts the total interactions are in the order:  $\text{Zn}^{2+} > \text{Sn}^{2+} > \text{Li}^+ > \text{Ca}^{2+} \sim \text{La}^{3+} > \text{Mg}^{2+}$ . The FT-IR spectra of D-cellobiose–chloride salt 1:2 mixtures also indicate that KCl and  $\text{NH}_4\text{Cl}$  interacts similarly with D-cellobiose in the solid state.

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## 1. Introduction

The depolymerization or hydrolysis of cellulose to glucose is a formidable challenge due to its complex molecular architecture with stiff polymeric chains and close packing via strong, inter and intramolecular hydrogen bonds [1]. The currently used technology for this process is the high temperature–pressure dilute acid pretreatment followed by the use of a cellulase enzyme cocktail for the hydrolysis [1,2]. However certain deficiencies in the current technologies like enzyme costs and energy consuming pretreatment requirements have encouraged the research into more efficient catalytic methods for harvesting the full potential of the most abundant renewable carbohydrate polymer.

There are a number of ways to affect non-enzymatic cellulose depolymerization in relatively low yield, and a few researchers have taken interest in the mechanisms of these processes in an attempt to develop efficient catalytic systems for the important cellulose depolymerization step. The widely studied approaches include the use of dilute mineral acids [3], solid acids [4–6], mineral acid in neutral ionic liquids [7], acidic ionic liquids [8,9], metal salts in mineral acid solutions and ionic liquid solutions [10].

Even though metal salts or complexes are the traditional catalytic systems in most industrial catalytic processes the use of transition metal salts have not attracted attention in the cellulose hydrolysis until recently. The new developments in this direction have shown

that incorporation of transition metal ions like  $\text{Mn}^{2+}$ ,  $\text{Fe}^{3+}$ ,  $\text{Cu}^{2+}$ , and  $\text{Zn}^{2+}$  as Lewis acid co-catalysts to the Brønsted acid system can be used to improve the cellulose pretreatment and acid hydrolysis efficiencies [11–14]. In addition, we have recently found that addition of a catalytic amount of  $\text{Mn}^{2+}$ ,  $\text{Fe}^{3+}$  or  $\text{Co}^{2+}$  chloride salt can be used to improve the sugar yields during the acid catalyzed saccharification of corn stover in water at 140–170 °C [15].

These co-catalytic effects of the metal ions in cellulose depolymerization and pretreatments are most likely due to interaction or chelation of salts with carbohydrate. There are several reports on isolation of monosaccharide–metal complexes and structure determination using X-ray crystallography, this includes  $\text{Ca}^{2+}$  complexes of D-fructose [16], D-galactose [17], lactose [18], D-mannose [19], trehalose [20], D-xylose [21], D-arabinose [22], D-ribose [23] and  $\text{LaCl}_3$ -ribose [24]. However, the only structural study of a metal complex of the cellulose model compound D-cellobiose is the X-ray structure of  $\alpha$ -cellobiose  $\cdot 2\text{NaI} \cdot 2\text{H}_2\text{O}$  complex [25]. The theoretical calculations could also be used to elucidate the interactions between carbohydrates and metal ions. Nevertheless, only a few studies are reported in the literature, which include the molecular dynamics studies on  $\text{Na}^+$ -glucose interactions [26], computational evidence for the complex formation between  $\text{Cr}^{3+}$  [27], and  $\text{Cr}^{2+}$  [28] with glucose. Furthermore, only a handful of studies have attempted to address the mechanisms of metal promoted depolymerization and dissolutions of cellulose [29]. In a recent example, Zhang et al. have studied the role of  $\text{Li}^+$  and  $\text{Cl}^-$  ions in the dissolution of cellulose in dimethyl acetamide (DMAC)–LiCl system by NMR methods [30]. Where they found that the hydroxyl protons of cellulose form strong hydrogen bonds with the  $\text{Cl}^-$  during which the intermolecular

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hydrogen bonding networks of cellulose is broken with simultaneous splitting of the  $\text{Li}^+$  and  $\text{Cl}^-$  ion pairs. The  $\text{Li}^+$  cations are further solvated by free DMAc molecules, which accompany the hydrogen-bonding of  $\text{Cl}^-$  to meet the charge balance. Thereafter, the cellulose chains are dispersed in the solvent system to form homogeneous solution. This work clarifies the interactions in the cellulose/DMAc/LiCl solutions at molecular level and the dissolution mechanism of cellulose in DMAc/LiCl system [30]. In another example, solvation state of cellulose in aqueous onium hydroxide solutions are discussed with the aid of  $^{13}\text{C}$  NMR chemical shift of D-cellobiose signals in these solutions where Abe and coworkers related cellulose dissolution ability to chemical shifts of D-cellobiose carbons in aqueous onium hydroxide solutions [31].

Since a number of recent studies as well as our own experiments on using metal ions like  $\text{Mn}^{2+}$ ,  $\text{Fe}^{3+}$  and  $\text{Co}^{2+}$  have shown to improve the acid hydrolysis of cellulose, most likely *via* interaction of the metal salts with carbohydrate, we instigate a study on interactions of metal salts with cellulose and cellulose model compound D-cellobiose in water [32]. As a part of this study we have examined the  $^{13}\text{C}$  NMR chemical shift changes in D-cellobiose due to the addition of some common diamagnetic chloride salts in an attempt to evaluate the interactions of salts with the cellulose model compound.

## 2. Experimental

### 2.1. Instrumentation and materials

D-Cellobiose (99.9%), analytical grade chloride salts; LiCl,  $\text{CaCl}_2$ ,  $\text{LaCl}_3$ ,  $\text{ZnCl}_2$ ,  $\text{SnCl}_2$ ,  $\text{MgCl}_2$ ,  $\text{NH}_4\text{Cl}$  and KCl were purchased from Aldrich Chemical Co and were used without further purification.  $^{13}\text{C}$  NMR spectra in  $\text{D}_2\text{O}$  were recorded on a Varian Mercury plus spectrometer operating at 100 MHz,  $rd = 1$  s, spectral width of 17,094 Hz, and typically 4000 scans were collected for  $^{13}\text{C}$  spectra. All NMR spectra were collected at room temperature, 25 °C. FT-IR spectra were recorded on a Thermo Nicolet IR 200 using KBr pellets at  $1.0\text{ cm}^{-1}$  resolution.

### 2.2. Interaction of D-cellobiose with chloride salts – $^{13}\text{C}$ NMR study, general procedure

A solution of D-cellobiose (50.0 mg, 0.146 mmol) in 0.50 mL of  $\text{D}_2\text{O}$  was prepared in a 5-mm NMR tube. The sample was allowed to stabilize

at room temperature for 4 h, then  $^{13}\text{C}$  NMR ( $rd = 1$  s,  $SW = 17,094$  Hz,  $NS = 4000$ ) spectrum was recorded as the initial baseline data. Afterward, chloride salt (2.20 mmol) was added and thoroughly mixed using EW-04726-01 Cole-Parmer Vortex Mixer for 2.0 min, allowed to stabilize at room temperature for 4 h. Then  $^{13}\text{C}$  NMR spectrum was recorded as with pure cellobiose solution. The  $^{13}\text{C}$  NMR chemical shift change ( $\Delta\delta$ ) was calculated for each signal in the spectrum using the formula:

$$\Delta\delta = \text{chemical shift of pure D-cellobiose} - \text{chemical shift of D-cellobiose in chloride salt.}$$

The  $\Delta\delta$  values for 18 signals from the  $\alpha$  and  $\beta$  D-cellobiose epimers were used to draw the plot shown in Fig. 2.

### 2.3. Interaction of D-cellobiose with chloride salts – FT-IR study, general procedure

A mixture of D-cellobiose (45.0 mg, 0.5 mmol) and metal chloride (1.0 mmol) were prepared and ground together for 2.0 min in a pestle and mortar. Then a 5 mg portion of the mixture was thoroughly mixed with 100 mg of dry KBr and was used in making the KBr pellet for recording the spectrum. All spectra were collected with 32 scans and  $1.0\text{ cm}^{-1}$  resolution. A FT-IR spectrum of pure cellobiose recorded under identical conditions was used as the reference spectrum.

## 3. Results and discussion

### 3.1. $^{13}\text{C}$ NMR study

The interactions of eight chloride salts with D-cellobiose in  $\text{D}_2\text{O}$  were studied by  $^{13}\text{C}$  NMR spectroscopy in the first part of this work. In the set of chloride salts studied,  $\text{SnCl}_2$  has the lowest molar solubility in water at 25 °C [33]. In the preliminary experiments we have found that a maximum amount of 2.20 mmol of anhydrous  $\text{SnCl}_2$  can be dissolved in the NMR sample containing 50 mg of D-cellobiose in 0.5 mL of  $\text{D}_2\text{O}$  at 25 °C. Therefore, in all NMR experiments 2.20 mmol of anhydrous chloride salts were used to achieve uniform salt concentrations. A representative  $^{13}\text{C}$ -NMR spectrum of  $\alpha/\beta$  D-cellobiose- $\text{SnCl}_2$  mixture in  $\text{D}_2\text{O}$  at 25 °C is shown in Fig. 1. The  $^{13}\text{C}$  NMR spectra of D-cellobiose in different salt mediums were recorded under identical conditions and changes in

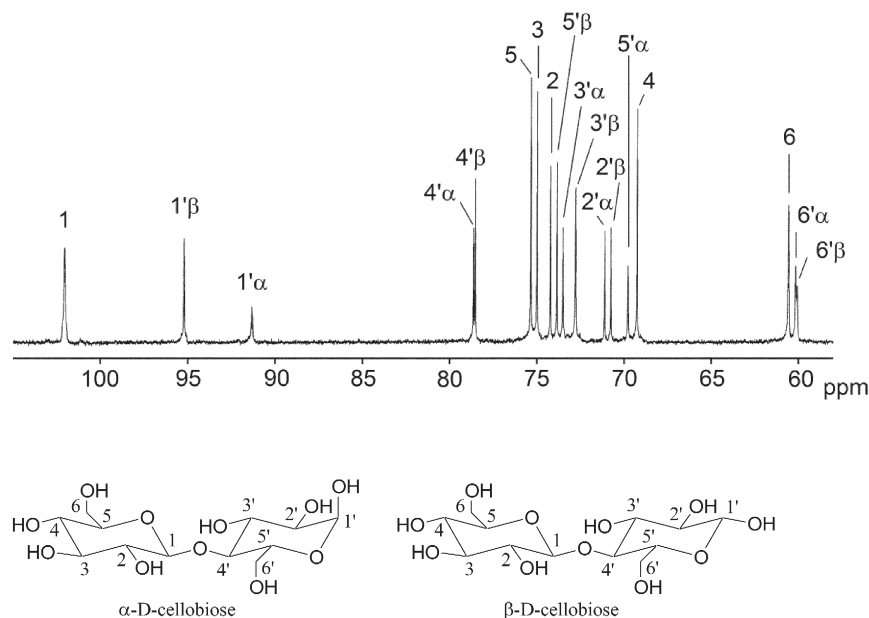


Fig. 1.  $^{13}\text{C}$ -NMR spectrum of  $\alpha/\beta$  D-cellobiose- $\text{SnCl}_2$  mixture in  $\text{D}_2\text{O}$  at 25 °C as a representative example (0.146 mmol of D-cellobiose and 2.20 mmol of  $\text{SnCl}_2$  in 0.5 mL of  $\text{D}_2\text{O}$ ).

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