

# Complex Formation of 1,6-Anhydro- $\beta$ -Maltose and Sodium Ions Using Single-Crystal X-Ray Crystallography and NMR Spectroscopy

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## ABSTRACT

Complex formation of 1,6-anhydro- $\beta$ -maltose and sodium ions was characterized using single-crystal X-ray crystallography and solution- and solid-state NMR spectroscopy. The 7-coordination structure, comprising two 1,6-anhydro- $\beta$ -maltoses, a thiocyanate ion and a sodium ion, was identified in the crystal of the complex, where a sodium ion was positioned in the center of the pentagon. In the NMR study, the line broadening of <sup>23</sup>Na signals and the decrease of the spin-lattice relaxation times ( $T_1$ ) of <sup>23</sup>Na were observed in CD<sub>3</sub>OD in the presence of 1,6-anhydro- $\beta$ -maltose, indicating complex formation.

**Keywords:** 1,6-Anhydro- $\beta$ -Maltose; Complex Formation; Single-Crystal X-Ray Crystallography; Solid-State NMR Spectroscopy

## 1. Introduction

The abilities of carbohydrates to form complex with cations have been used in the separation of sugar mixtures and the isolation of single tautomeric forms in solution. One of its application is separation of sugars using cation-exchange chromatography [1,2]. For instance, D-glucose and D-fructose were separated using a Ca<sup>2+</sup> column [3], and  $\alpha$  and  $\beta$  anomers of D-allose (both as pyranose and furanose forms) were isolated owing to the difference of ability to coordinate with cations [4]. The structural feature of carbohydrates is hydroxyl groups, which is feasible to form complexes in solution with monovalent cations [5,6]. Electrophoretic studies demonstrated that alkali metal ions were able to form complexes with polyhydroxy compounds. The migration rate of 1,6-anhydro- $\beta$ -D-glucopyranose in the presence of metal ion was extremely higher than that alone, indicating complex formation [6].

Our group has been studying the complex formation of alkali metal ions and 1,6-anhydro sugars [7,8], which were prepared from the corresponding free sugars through intramolecular dehydration. In past studies, the complexation of 1,6-anhydro- $\beta$ -maltose with rubidium,

which of 1,6-anhydro- $\beta$ -D-glucopyranose with rubidium [9] and which of 1,6-anhydro- $\beta$ -maltotriose with potassium [10], was characterized using NMR spectroscopy. Besides these studies, interactions between sucrose and various metal ions were investigated by Rondeau *et al.* using mid-infrared and <sup>13</sup>C NMR spectroscopies [11,12]. The crystal structure of the complex formed by two 1,6-anhydro- $\beta$ -maltoses with a peroxide and two sodium ions, [Na<sub>2</sub>(1,6-anhydro- $\beta$ -maltose)<sub>2</sub>(H<sub>2</sub>O)<sub>3</sub>]O<sub>2</sub>, was determined by single-crystal X-ray crystallography [13]. The O<sub>2</sub> moiety was identified as a discrete peroxide dianion, whereas two sodium and two carbohydrate molecules constituted a binuclear complex counter cation. The crystal structure of 1,6-anhydro- $\beta$ -maltose forming an inclusion complex with a potassium ion was also determined [14]. In the crystal structure, both 8- and 9-coordination forms were identified. The 8-coordination structure, which can be defined as the distorted capped pentagonal bipyramidal structure, comprised two 1,6-anhydro- $\beta$ -maltoses, a thiocyanate ion, a methanol and a potassium ion. A potassium ion was positioned in the center of the bipyramidal structure, where two 1,6-anhydro- $\beta$ -maltoses, possessing identical conformation, surrounded a potassium ion. The

9-coordination structure, which can be defined as the capped hexagonal bipyramidal structure, comprised three 1,6-anhydro- $\beta$ -maltooses, a thiocyanate ion and a potassium ion. Although a potassium ion was positioned in the center of the bipyramidal structure as observed in 8-coordination structure, three 1,6-anhydro- $\beta$ -maltooses, possessing identical conformation, surrounded a potassium ion. For the purpose of elucidating the mechanism of 1,6-anhydro sugar-forming complexes with alkali metal ions, we have investigated the complex formation of 1,6-anhydro- $\beta$ -maltose (**Figure 1**) with sodium ions using single-crystal X-ray crystallography and NMR spectroscopy. The crystals of the free form of 1,6-anhydro- $\beta$ -maltose and those of an inclusion complex with a sodium ion were also used in the analysis of the solid-state NMR spectroscopy.

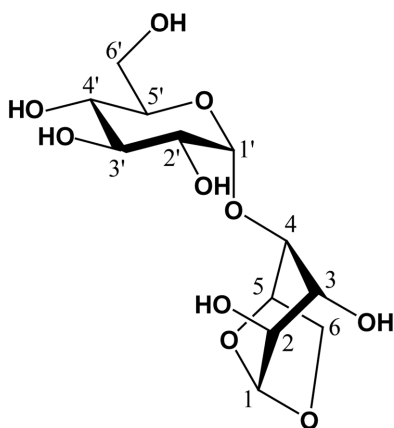
## 2. Experimental

### 2.1. Single-Crystal X-Ray Crystallography

Equal molar amounts of 1,6-anhydro- $\beta$ -maltose (324 mg) and NaSCN (78.6 mg) were dissolved in 3 ml methanol, and the solution was kept at room temperature for 48 hr. After filtration, a colorless prism, having approximate dimensions of  $0.20 \times 0.20 \times 0.20$  mm, was mounted in a loop. The 1,6-anhydro- $\beta$ -maltose (324 mg) was dissolved in 5 ml methanol, and the solution was kept at room temperature for 48 hr. After filtration, a colorless prism, having approximate dimensions of  $0.20 \times 0.20 \times 0.20$  mm, was mounted in a loop. All measurements were carried out using a Rigaku RAXIS RAPID imaging plate area detector with graphite monochromated Mo- $K\alpha$  radiation at 123 K. The crystal and experimental data of the 1,6-anhydro- $\beta$ -maltose forming an inclusion complex with a sodium ion and its free form are given in **Table 1**.

### 2.2. Solid-State NMR Spectroscopy

Crystals of an inclusion complex with a sodium ion and



**Figure 1.** Structure of 1,6-anhydro- $\beta$ -maltose.

**Table 1.** Crystal and experimental data of 1,6-anhydro- $\beta$ -maltose forming an inclusion complex with a sodium ion and the free form of 1,6-anhydro- $\beta$ -maltose.

|  | complex                            | free                           |
|--|------------------------------------|--------------------------------|
| Formula  | $C_{13}H_{20}Na_1N_1O_{10}S_1$     | $C_{24}H_{42}O_{21}$           |
| Formula weight   | 405.35                             | 666.58                         |
| Crystal system   | monoclinic                         | triclinic                      |
| Space group  | $P 2_1$ $Z=2$                      | $P 1$ $Z=1$                    |
| Crystal dimensions (mm)  | $0.20 \times 0.20 \times 0.20$     | $0.20 \times 0.20 \times 0.20$ |
| Temperature (K)  | 123                                | 123                            |
| $a$ (Å)  | 8.864(4)                           | 8.323(4)                       |
| $b$ (Å)  | 12.208(4)                          | 9.246(5)                       |
| $c$ (Å)  | 9.010(4)                           | 9.798(4)                       |
| $V$ (Å <sup>3</sup> )  | 821.8(6)                           | 685.8(6)                       |
| $D_{calc}$ (g/cm <sup>3</sup> )                                | 1.638                              | 1.638                          |
| No. of reflections   | 9924                               | 8255                           |
| $2\theta_{max}$ (with Mo- $K\alpha$ )                          | 60.1                               | 60.1                           |
| $R$  | 0.0249                             | 0.0351                         |
| Max. shift/error in final cycle                                | 0.000                              | 0.000                          |
| Max. peak in final diff. map (e <sup>-</sup> /Å <sup>3</sup> ) | 0.50                               | 1.11                           |
| Min. peak in final diff. map (e <sup>-</sup> /Å <sup>3</sup> ) | -0.31                              | -1.24                          |
| Measurements   | R-Axis RAPID (Rigaku, 2000)        |                                |
| Program system   | Crystal structure 4.0              |                                |
| Structure determination  | SIR2004 [15]                       |                                |
| Refinement   | Full-matrix least-squares on $F^2$ |                                |

of the free form of 1,6-anhydro- $\beta$ -maltose, and NaSCN alone were used for the measurements of the solid-state NMR spectroscopy. The <sup>23</sup>Na spectra were acquired on a JNM-ECA600 spectrometer equipped with a 1 mm CP-MAS probe at a spinning speed of 70 kHz. The experimental parameters of <sup>23</sup>Na for an inclusion complex were number of scans = 640, recycle time = 1.0 s, and those for NaSCN alone were number of scans = 256, recycle time = 3.0 s. The <sup>23</sup>Na  $T_{1\rho}$  were measured using a saturation recovery method on a JNM-ECA920 spectrometer equipped with a 4 mm MQ-MAS probe at a spinning speed of 15 kHz. The experimental parameters were number of scans = 8, recycle time = 1.0 s. The pulse intervals were 15 steps. The <sup>13</sup>C CP-MAS spectra were acquired on a JNM-ECA500 equipped with a 4 mm CP-MAS probe at a spinning speed of 15 kHz. The experimental parameters of <sup>13</sup>C CP-MAS were number of scans = 319, recycle time = 1.0 s.

### 2.3. Solution-State NMR Spectroscopy

Conventional <sup>1</sup>H, <sup>13</sup>C and <sup>23</sup>Na NMR spectra were acquired on a Varian 600 spectrometer using 250  $\mu$ L sam-

ple solutions of 30 mM 1,6-anhydro- $\beta$ -maltose in the presence and absence of 30 mM NaSCN and 30 mM NaSCN alone in 99.9% CD<sub>3</sub>OD in Shigemi tubes at 30°C. In preparation of the sample solution of 1,6-anhydro- $\beta$ -maltose in the presence of NaSCN, crystals of an inclusion complex with a sodium ion were dissolved in CD<sub>3</sub>OD. The <sup>1</sup>H and <sup>13</sup>C assignments were carried out using the conventional 1D and 2D NMR techniques. The <sup>13</sup>C and <sup>23</sup>Na-*T*<sub>1</sub> measurements were carried out using the inversion recovery method, and the measurements of <sup>1</sup>H diffusion coefficients were carried out as described previously [10].

### 3. Results and Discussion

#### 3.1. Single-Crystal X-Ray Crystallography

The crystal structures of 1,6-anhydro- $\beta$ -maltose forming an inclusion complex with a sodium ion and its free form were determined using single-crystal X-ray crystallography (Table 1). In the crystal structure of the complex, the 7-coordination structure, which can be defined as the distorted pentagonal bipyramidal structure, was identified as shown in Figure 2(a). It comprised two 1,6-anhydro- $\beta$ -maltoses (designated as anhydro sugars A and B), a thiocyanate ion and a sodium ion. A sodium ion was positioned in the center of the pentagon, where two 1,6-anhydro- $\beta$ -maltoses, possessing identical conformation, surrounded a sodium ion. The sodium ion made close contacts to all oxygen atoms involved in the 7-coordination structure. Its distances were in the range of 2.40 - 2.68 Å (Table 2). The pentagon comprised O5, O1' and O2' of anhydro sugar A and O3 and O6 of anhydro sugar B. The O2 of anhydro sugar A and a sulfur atom of a thiocyanate ion corresponded to the peak of each pyramid (Figures 2(a) and (b)). Four of these six oxygen atoms, O2, O3, O5 and O6 were involved in 1,6-anhydro moiety. The tendency forming bipyramidal structures was also identified in the crystal structure of 1,6-anhydro- $\beta$ -maltose forming an inclusion complex with a potassium ion [14]. These results indicate the importance of 1,6-anhydro moiety in forming complex with alkali metal ions, and provide an insight into the accommodation pattern of 1,6-anhydro- $\beta$ -maltose for an alkali metal ion.

In the crystal structure of the free form of 1,6-anhydro- $\beta$ -maltose, asymmetric structures, designated as anhydro sugars A and B, were identified as shown in Figure 2(c). A water molecule was surrounded by three molecules of 1,6-anhydro- $\beta$ -maltose, forming the 6-coordination structure (Figures 2(c) and (d)). The close contacts between an oxygen atom of water and 1,6-anhydro- $\beta$ -maltoses are summarized in Table 2. Only two oxygen atoms in 1,6-anhydro-moiety made close contacts to an oxygen atom of water. This structural feature was opposite to the 7-coordination structure identified in the

**Table 2. Distances (Å) around a sodium ion in the crystal structure of the complex and those around an oxygen atom of the water in the crystal structure of the free form of 1,6-anhydro- $\beta$ -maltose.**

| Complex                               |           | Free                      |           |
|---------------------------------------|-----------|---------------------------|-----------|
| Atoms                                 | Distances | Atoms                     | Distances |
| Na <sup>+</sup> ···O2(A) <sup>a</sup> | 2.44      | W <sup>b</sup> ···O2(A)   | 2.90      |
| Na <sup>+</sup> ···O3(B)              | 2.68      | W <sup>b</sup> ···O5(A)   | 3.14      |
| Na <sup>+</sup> ···O5(A)              | 2.49      | W <sup>b</sup> ···O1'(A)  | 3.09      |
| Na <sup>+</sup> ···O6(B)              | 2.40      | W <sup>b</sup> ···O2'(A)  | 2.73      |
| Na <sup>+</sup> ···O1'(A)             | 2.49      | W <sup>b</sup> ···O6'(B)  | 2.79      |
| Na <sup>+</sup> ···O2'(A)             | 2.49      | W <sup>b</sup> ···O6'(A') | 2.76      |
| Na <sup>+</sup> ···SCN <sup>-</sup>   | 3.04      |                           |           |

<sup>a</sup>“A” means anhydro sugar A defined in Figures 2(a) and (b). <sup>b</sup>“W” means an oxygen atom of the water defined in Figures 2(c) and (d).

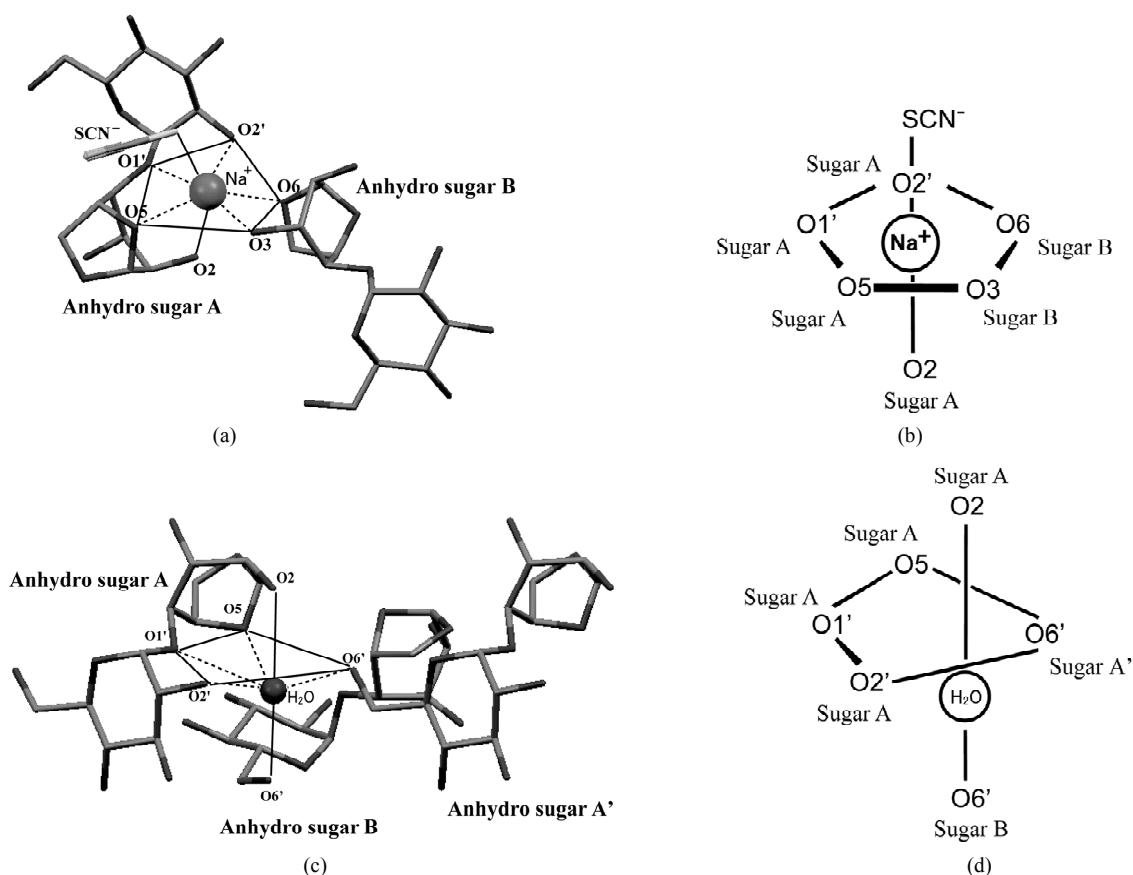
crystal structure of the complex.

#### 3.2. Solid-State NMR Spectroscopy

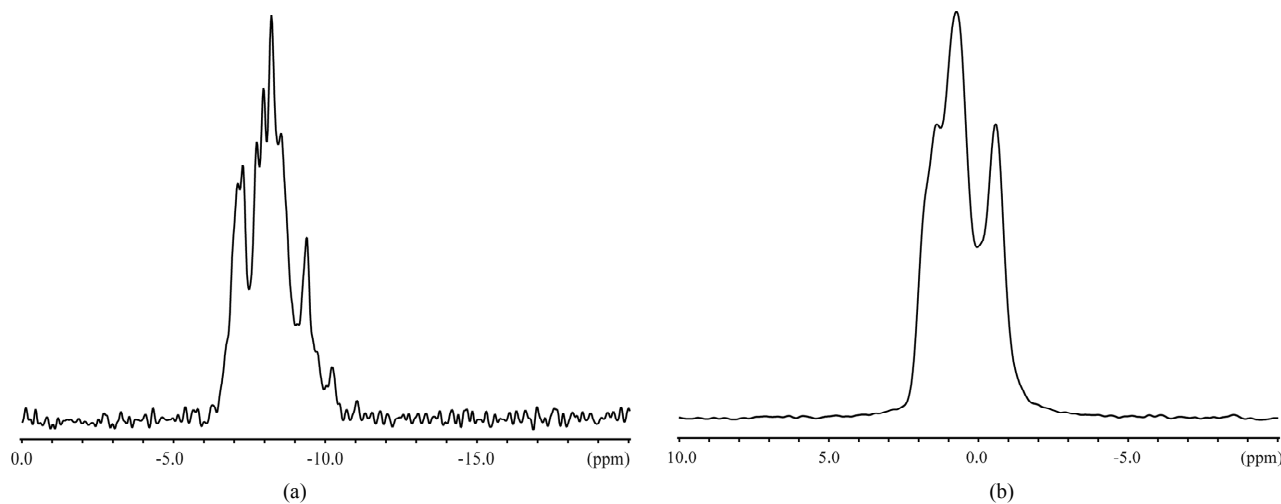
The <sup>23</sup>Na solid-state spectra were acquired for the crystals of an inclusion complex with a sodium ion and NaSCN alone as shown in Figure 3. The signal resonating at -0.06 ppm in the free form of NaSCN could be water (Figure 3(b)), considering the hygroscopic property of NaSCN. The <sup>23</sup>Na *T*<sub>1ρ</sub> were 0.649 s and 6.26 s for the complex and NaSCN alone, respectively. Comparisons of <sup>23</sup>Na spectra and *T*<sub>1ρ</sub> indicated the various close contacts between <sup>23</sup>Na and other nuclei in the inclusion complex. The <sup>13</sup>C CP-MAS spectra were acquired for crystals of an inclusion complex of 1,6-anhydro- $\beta$ -maltose with a sodium ion and those of its free form (Figure 4). As indicated in the single-crystal X-ray crystallography, the free form adopted asymmetric structures. This structural feature was reflected in the <sup>13</sup>C CP-MAS spectrum (Figure 4(b)). The signals resonating at 102.2 and 95.6 ppm were assigned as C1 and C1', respectively, referring the assignments in CD<sub>3</sub>OD (Table 4). Both signals split as doublet, and its chemical shift difference was 0.39 ppm. However, this doublet pattern could not clearly be identified in the other <sup>13</sup>C signals resonating in the upfield region of 64 - 75 ppm. For instance, the <sup>13</sup>C signals resonating in the region of 64 - 66 ppm, corresponding to C6 and C6', did not show the same splitting pattern. In the <sup>13</sup>C CP-MAS spectrum of the complex, the singlet pattern was observed for C1 and C1' (Figure 4(a)), which was expected in consideration of the identical conformation of 1,6-anhydro- $\beta$ -maltose.

#### 3.3. Solution-State NMR Spectroscopy

The <sup>23</sup>Na NMR spectra were acquired in CD<sub>3</sub>OD in the presence and absence of 1,6-anhydro- $\beta$ -maltose (Figure 5). The chemical shifts and half height widths of <sup>23</sup>Na



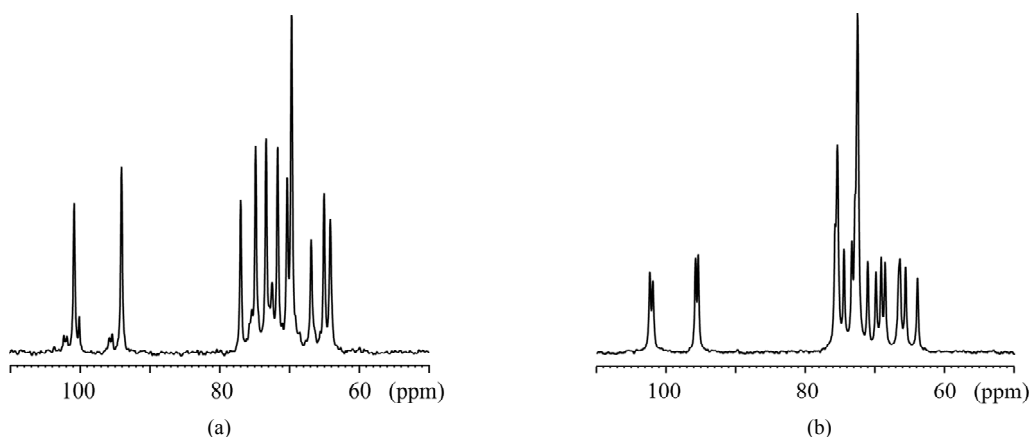
**Figure 2.** (a) The crystal structure of 1,6-anhydro- $\beta$ -maltose forming an inclusion complex with a sodium ion and (b) its schematic drawing. (c) The crystal structure of the free form of 1,6-anhydro- $\beta$ -maltose and (d) its schematic drawing. In (a), close contacts between 1,6-anhydro- $\beta$ -maltoses and a sodium ion are shown by dashed lines, and an outline of 7-coordination structure, corresponding to the schematic drawing of (b), is shown by solid lines. In (c), close contacts between 1,6-anhydro- $\beta$ -maltoses and an oxygen atom of water are shown by dashed lines, and an outline of 6-coordination structure, corresponding to the schematic drawing of (d), is shown by solid lines.



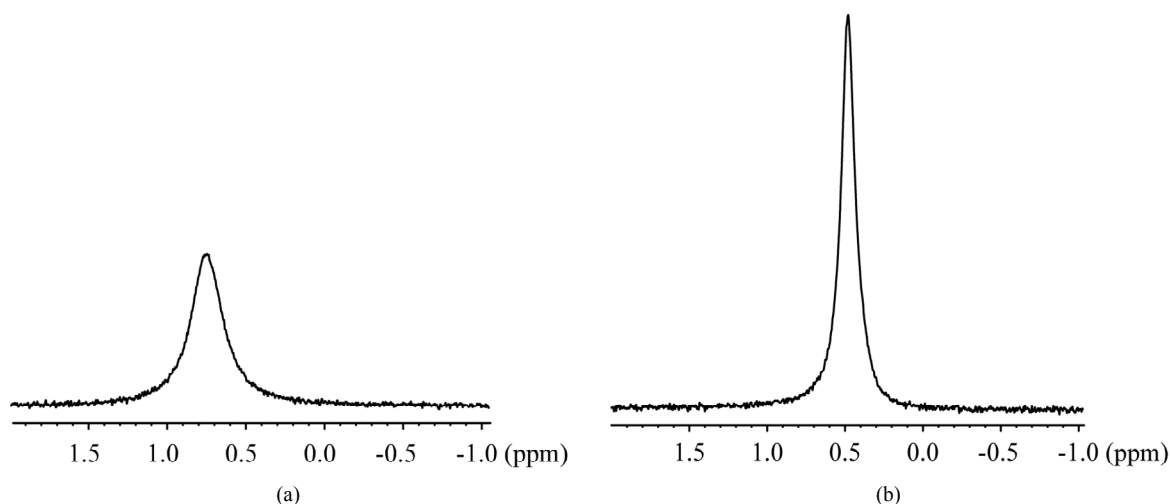
**Figure 3.** The  $^{23}\text{Na}$  solid-state NMR spectra of the (a) inclusion complex of 1,6-anhydro- $\beta$ -maltose with a sodium ion and (b) NaSCN.

signals in the presence and absence of 1,6-anhydro- $\beta$ -maltose were 0.748 ppm and 32.3 Hz, and 0.479 ppm

and 16.8 Hz, respectively. The significant line broadening was observed in the presence of 1,6-anhydro- $\beta$ -



**Figure 4.** The  $^{13}\text{C}$  CP-MAS NMR spectra of the crystals of the (a) inclusion complex of 1,6-anhydro- $\beta$ -maltose with a sodium ion and (b) free form of 1,6-anhydro- $\beta$ -maltose.



**Figure 5.** The  $^{23}\text{Na}$  NMR spectra of the (a) inclusion complex of 1,6-anhydro- $\beta$ -maltose with a sodium ion and (b) NaSCN in  $\text{CD}_3\text{OD}$ .

maltose. The  $^{23}\text{Na}$ - $T_1$  values were 9.49 and 21.8 ms in the aforesaid order. The changes of the half height widths and  $^{23}\text{Na}$ - $T_1$  unambiguously indicated complex formation of 1,6-anhydro- $\beta$ -maltose with sodium ions in  $\text{CD}_3\text{OD}$ .

The  $^1\text{H}$  NMR spectra of 1,6-anhydro- $\beta$ -maltose in the presence and absence of NaSCN are shown in **Figures 6(a)** and **(c)**. The distinct changes of the spectral pattern were observed in the chemical shift range of 3.24 - 3.75 ppm. The maximum difference of  $^1\text{H}$  chemical shift was 0.04 ppm in H4, and the overall  $^1\text{H}$  chemical shift changes were relatively small (**Table 3**). The  $^1\text{H}$  diffusion coefficients were calculated only for the isolated signals, and ca. 14% decrease was identified in the presence of NaSCN (**Table 3**). The diffusion coefficient of a molecule is inversely proportional to the molecular radius, and the lowered diffusion is attributable to the complex formation. The  $^{13}\text{C}$  NMR spectra of 1,6-anhydro- $\beta$ -maltose in the presence and absence of NaSCN are shown in **Figures 6(b)** and **(d)**, and comparisons of  $^{13}\text{C}$

chemical shifts and  $^{13}\text{C}$ - $T_1$  are listed in **Table 4**. The  $^{13}\text{C}$  chemical shifts of C3 and C1' were both upfield shifted for 0.7 ppm in the presence of NaSCN. In comparison of  $^{13}\text{C}$ - $T_1$ , a ca. 14% decrease was observed for C1, C2 and C3 in the presence of NaSCN (**Table 4**). The C1, C2 and C3 are positioned adjacent to the oxygen atoms forming the 7-coordination structure (**Figure 2(b)**), which could be the reason of affecting its  $^{13}\text{C}$ - $T_1$ . Because the distinct decrease of  $^{13}\text{C}$ - $T_1$  was identified in a portion of 1,6-anhydro moiety, the results of  $^{13}\text{C}$ - $T_1$  studies indicated the importance of the 1,6-anhydro moiety in the complex formation, which was also supported in the analysis of the X-ray crystal structure.

#### 4. Conclusion

Complex formation of 1,6-anhydro- $\beta$ -maltose and sodium ions has been elucidated using single-crystal X-ray crystallography and  $^1\text{H}$ ,  $^{13}\text{C}$  and  $^{23}\text{Na}$  NMR spectroscopy.

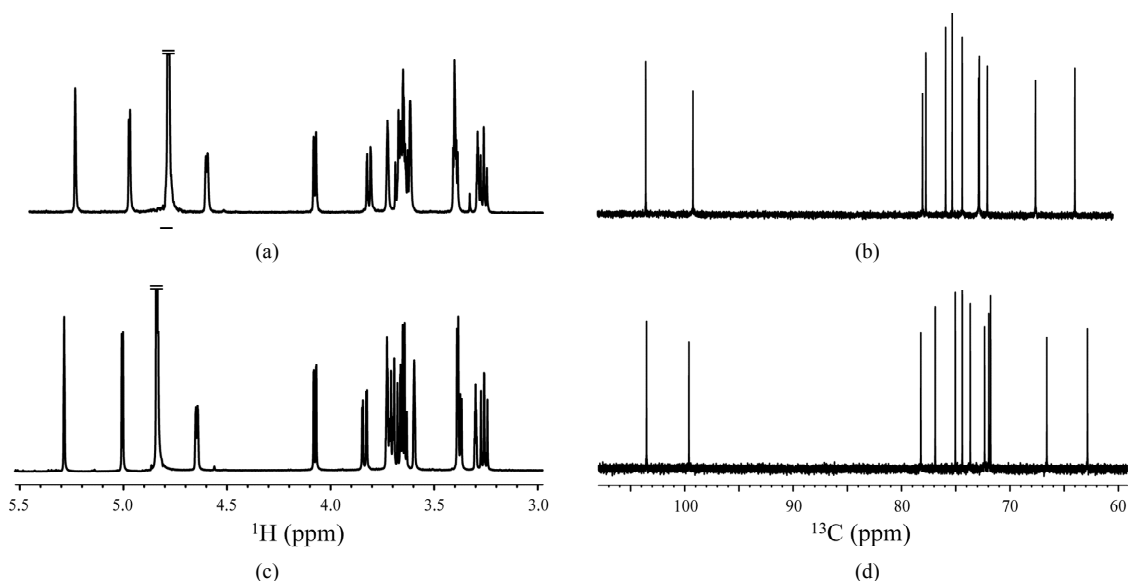


Figure 6. The  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra of 1,6-anhydro- $\beta$ -maltose in the (a,b) presence and (c,d) absence of NaSCN in  $\text{CD}_3\text{OD}$ .

Table 3. Comparison of the  $^1\text{H}$  chemical shifts and  $^1\text{H}$  diffusion coefficients ( $D$ ) of 1,6-anhydro- $\beta$ -maltose in the presence and absence of NaSCN.

|     | $\delta^1\text{H}$ (ppm) |           |           | $^1\text{H}\text{-}D$ ( $\times 10^{-10}$ m $^2$ /s) |                 |       |
|-----|--------------------------|-----------|-----------|--|-----------------|-------|
|     | free                     | +NaSCN    | $\Delta$  | free   | +NaSCN          | ratio |
| H1  | 5.28                     | 5.29      | 0.01      | $6.66 \pm 0.05$                                      | $5.88 \pm 0.03$ | 0.88  |
| H2  | 3.39                     | 3.41      | 0.02      |  |                 |       |
| H3  | 3.73                     | 3.75      | 0.02      | $5.61 \pm 0.02$                                      |                 |       |
| H4  | 3.60                     | 3.64      | 0.04      | $6.66 \pm 0.04$                                      | $5.80 \pm 0.01$ | 0.87  |
| H5  | 4.65                     | 4.64      | -0.01     | $6.59 \pm 0.03$                                      | $5.58 \pm 0.02$ | 0.85  |
| H6  | 4.08/3.65                | 4.10/3.66 | 0.02/0.01 | $6.74 \pm 0.06$                                      | $5.77 \pm 0.02$ | 0.86  |
| H1' | 5.00                     | 5.02      | 0.02      | $6.82 \pm 0.08$                                      | $5.81 \pm 0.04$ | 0.85  |
| H2' | 3.38                     | 3.41      | 0.03      |  |                 |       |
| H3' | 3.69                     | 3.69      | 0.00      |  |                 |       |
| H4' | 3.26                     | 3.26      | 0.00      | $6.79 \pm 0.06$                                      | $5.73 \pm 0.02$ | 0.84  |
| H5' | 3.71                     | 3.68      | -0.03     |  |                 |       |
| H6' | 3.84/3.65                | 3.84/3.65 | 0.00/0.00 | $6.75 \pm 0.06$                                      | $5.68 \pm 0.02$ | 0.84  |

Table 4. Comparison of the  $^{13}\text{C}$  chemical shifts and  $^{13}\text{C}\text{-}T_1$  of 1,6-anhydro- $\beta$ -maltose in the presence and absence of NaSCN.

|     | $\delta^{13}\text{C}$ (ppm) |        |          | $^{13}\text{C}\text{-}T_1$ (s) |                 |       |
|-----|-----------------------------|--------|----------|--------------------------------|-----------------|-------|
|     | free                        | +NaSCN | $\Delta$ | free                           | +NaSCN          | ratio |
| C1  | 103.5                       | 103.4  | -0.1     | $0.81 \pm 0.01$                | $0.70 \pm 0.04$ | 0.87  |
| C2  | 72.3                        | 71.9   | -0.4     | $0.80 \pm 0.01$                | $0.68 \pm 0.06$ | 0.85  |
| C3  | 71.8                        | 71.1   | -0.7     | $0.84 \pm 0.02$                | $0.73 \pm 0.04$ | 0.87  |
| C4  | 78.2                        | 77.2   | -1.0     | $0.77 \pm 0.02$                | $0.81 \pm 0.05$ | 1.06  |
| C5  | 76.9                        | 76.9   | 0.0      | $0.72 \pm 0.02$                | $0.77 \pm 0.05$ | 1.07  |
| C6  | 66.6                        | 66.5   | -0.1     | $0.46 \pm 0.01$                | $0.45 \pm 0.02$ | 0.99  |
| C1' | 99.6                        | 98.9   | -0.7     | $0.73 \pm 0.01$                | $0.68 \pm 0.03$ | 0.93  |
| C2' | 73.7                        | 73.5   | -0.2     | $0.71 \pm 0.01$                | $0.65 \pm 0.04$ | 0.92  |
| C3' | 75.0                        | 75.0   | 0.0      | $0.75 \pm 0.01$                | $0.78 \pm 0.07$ | 1.04  |
| C4' | 72.0                        | 71.8   | -0.2     | $0.74 \pm 0.01$                | $0.81 \pm 0.05$ | 1.10  |
| C5' | 74.5                        | 74.4   | -0.1     | $0.74 \pm 0.01$                | $0.74 \pm 0.04$ | 1.00  |
| C6' | 62.8                        | 62.8   | 0.0      | $0.42 \pm 0.01$                | $0.42 \pm 0.03$ | 0.99  |

In solution, the comparisons of  $^1\text{H}$  diffusion coefficients and  $^{23}\text{Na}$ - $T_1$  unambiguously indicated complex formation, and  $^{13}\text{C}$  NMR studies indicated importance of 1,6-anhydro moiety in the complex formation. A contribution of 1,6-anhydro moiety was also recognized in the 7-coordination structure identified in the single-crystal X-ray structure.

## 5. Supplementary Data

Crystallographic data, excluding structure factors, have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication with CCDC No. 927906 and 922475 for the free form of 1,6-anhydro- $\beta$ -maltose and its complex with NaSCN, respectively. Copies of the data can be obtained free of charge on application with the Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax +44-1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

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