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Crystallographic analysis of the thermal motion of the inclusion complex of cyclomaltoheptaose (β-cyclodextrin) with hexamethylenetetramine

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Abstract

The crystal structure of the inclusion complex of cyclomaltoheptaose (β-cyclodextrin) with hexamethylenetetramine was determined at temperatures of 123, 173, 223, and 293 K. The rigid-body motion of the host and guest molecules was evaluated by means of the TLS method that represents the molecular motion in terms of translation, libration, and screw motion. In increasing the temperature from 123 to 293 K, the amplitude of the rigid body vibration of the host molecule was increased from 1.0 to 1.3° in the rotational motion and from 0.16 to 0.17 Å in the translational motion. The cyclomaltoheptaose molecule has the flexibility in seven α-(1→4)-linkages, and each glucose unit was in the rotational vibration around an axis through two glycosidic oxygen atoms. As a result, the rigid-body parameters of cyclomaltoheptaose were considered to be overestimated because of including the contribution from the local motion of glucose units. In contrast, for the guest molecule having no structural flexibility, the TLS analysis demonstrated that the atomic thermal vibration was mostly derived from the rigid body motion. The rotational amplitude of hexamethylenetetramine was changed from 5.2 to 6.6° in increasing the temperature from 123 to 293 K, while the change of the translational amplitude was from 0.20 to 0.23 Å. The translational motion of the guest molecule was hindered by the inside wall of the host cavity. The molecular motion was characterized by the rotational vibration around the axis through two nitrogen atoms that were involved in the hydrogen-bond formation.

Keywords: Crystal structure; Rigid-body motion; Host–guest interaction; Inclusion complex; Cyclodextrin

1. Introduction

Cyclomaltooligosaccharides (cyclodextrins), cyclic oligosaccharides consisting of six or more α-(1→4)-linked glucose units, form inclusion complexes with a variety of guest molecules.[1] As has been demonstrated by a number of X-ray structures,[2] guest molecules included in cyclomaltoses are bound by such interactions as van der Waals interactions, hydrogen bonds, etc. Because of this reason, the guest molecules have relatively large mobility, and static disorder has been sometimes observed.[3–5] The mobility of the guest molecule in the host cavity reflects the physicochemical properties of the inclusion complex, such as chemical and physical stabilization, stereoselective binding, catalytic activity. However, we have little knowledge about the dynamic behavior of the guest molecule included in the cyclomaltose cavity. In the previous paper,[6] we tried to elucidate the characteristics of the molecular motion of *p*-nitrophenol included in methylated cyclomaltoheptaose (β-cyclodextrin) and demonstrated the important role of the rigid-body motion in the thermal motion of the guest molecule. This paper deals with the thermal motion of hexamethylenetetramine included in cyclomaltoheptaose. Hexamethylenetetramine is a rigid molecule with spherical shape that lends itself to the analysis of the rigid-body motion. For the analysis of the effect of the temperature on the mobility of the guest molecule, the crystal structure of the complex was determined at four temperatures, 123, 173, 223, and 293 K. The thermal motion of the guest and host molecules was evaluated by using the TLS model[7] that expresses

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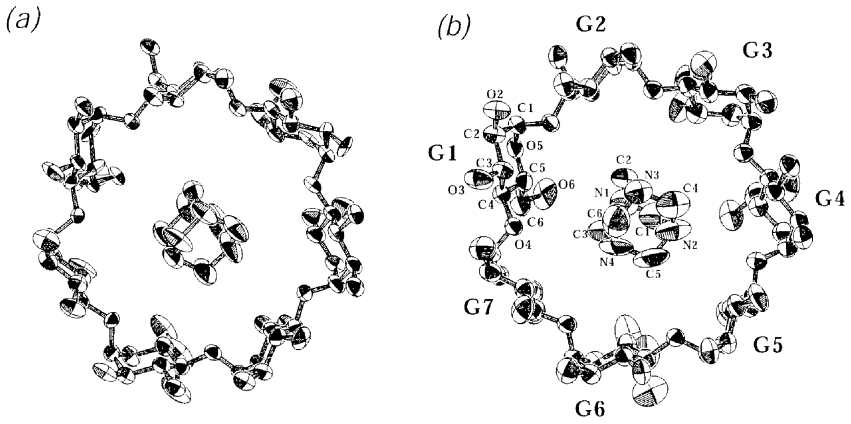

Fig. 1. Structure of the cyclomaltoheptaose complex with hexamethylenetetramine at (*a*) 123 K and (*b*) 293 K. The thermal ellipsoids are drawn with 75% probability.

the rigid-body motion in terms of translation, libration, and screw motion.

2. Results and discussion

2.1. Crystal structure at low temperature

The molecular structures of the cyclomaltoheptaose complex with hexamethylenetetramine at 123 and 293 K are shown in Fig. 1. The crystal of the complex shows a typical cage-type packing structure as shown in Fig. 2. The hexamethylenetetramine molecule is encapsulated in the isolated 'cage' created by the herring-bone-like arrangement of the host molecule. Six water molecules are distributed in intermolecular space and participate in forming the hydrogen-bond network that maintains the host lattice structure. The inside wall of the cyclomaltoheptaose cavity that accommodates the guest molecule is mostly made of hydrogen atoms of H-3, H-5 methine groups, and H-6, 6a methylene groups. Hexamethylenetetramine is a spherically shaped molecule with twelve hydrogen atoms on the molecular surface. Therefore, the van der Waals contact between hydrogen atoms dominates the intermolecular contacts with the inner surface of the cyclomaltoheptaose cavity. A nitrogen atom (N-3) located at the secondary hydroxyl side of the host cavity forms a hydrogen bond with a hydroxyl group (O-2(3)) of the adjacent cyclomaltoheptaose molecule. A water molecule (W1) located at the primary hydroxyl end of the cavity is hydrogen-bonded to another nitrogen atom (N-1).

X-ray diffraction data were measured at four temperatures, 123, 173, 223, and 293 K. The lattice constants slightly decreased by the cooling (Table 1). The crystal structure showed no significant change between temperatures of 123 and 293 K, although the temperature factor was ca. 30% decreased by the cooling to 123 K. The average temperature factor decreased from 0.052 to 0.036 Å^2 in cyclomaltoheptaose and from 0.087 to 0.068 Å^2 in the guest molecule. A rapid decrease of U_{eqv} was observed between 293 and 223 K. At 293 K, two of the six water molecules (W3 and W4) were disordered, while another water molecule (W1) was modeled as disorder in the lower temperature. The same $\langle U_{eqv} \rangle$ values at 173 and 123 K (Table 1) imply that the temperature factor will not decrease further, even at the lower temperature. In contrast, the average anisotropy

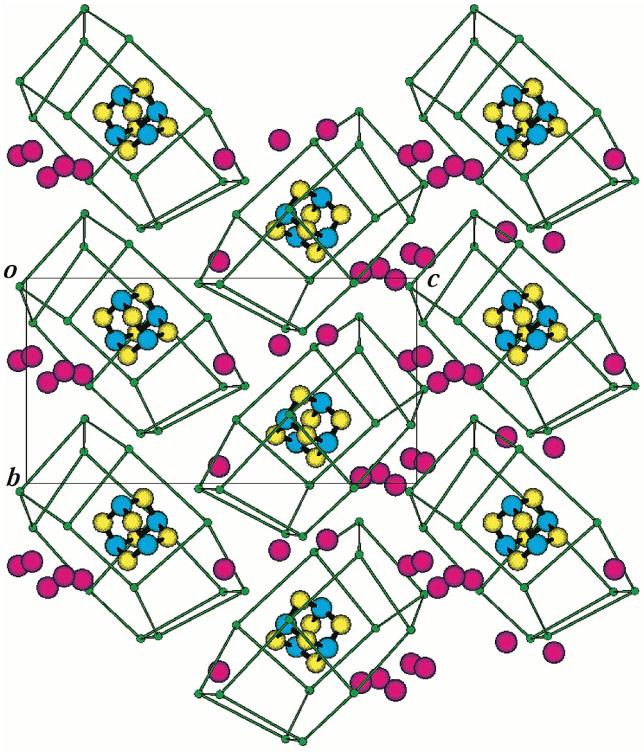

Fig. 2. Crystal packing viewed along the *a* axis. Cyclomaltoheptaose rings are shown by the truncated heptagonal cone with green color. Carbon and nitrogen atoms of hexamethylenetetramine are rendered with yellow and cyan, respectively. Water oxygen atoms are shown with pink-colored circles.

Table 1
Crystal data and summary of the structure refinement

Chemical formula	$C_{42}H_{70}O_{35}\cdot C_6H_{12}N_4\cdot 6H_2O$			
Formula weight (Da)	1383.3			
Temperature (K)	123	173	223	293
Cell dimensions				
a (Å)	15.228(1)	15.224(2)	15.253(1)	15.252(1)
b (Å)	10.309(1)	10.312(2)	10.337(1)	10.324(1)
c (Å)	20.018(1)	20.004(2)	20.041(2)	20.083(1)
β (°)	102.48(1)	102.69(1)	102.41(1)	102.13(1)
V (Å^3)	3068.2(5)	3067.7(6)	3086.0(4)	3091.8(3)
D_x (g cm^{-3})	1.497	1.497	1.488	1.486
μ(mm^{-1})	1.296	1.296	1.288	1.286
Number of reflections	6458	6451	6475	6589
R_{int}	0.035	0.032	0.030	0.022
Number of parameters	902	902	893	884
R (all data)	0.057	0.055	0.052	0.046
Shift/esd (mean/max.)	0.000/0.000	0.000/0.000	0.002/0.033	0.000/0.000
Residual density (e/Å^3) (min./max.)	−0.35/0.60	−0.31/0.59	−0.31/0.57	−0.24/0.38
$\langle U_{eqv}\rangle$ (Å^2) (host/guest)	0.036/0.068	0.036/0.068	0.040/0.072	0.052/0.087
Anisotropy factor (host/guest) [a]	0.36/0.54	0.48/0.52	0.36/0.50	0.36/0.46

[a] Anisotropy factor is defined as: $[\Sigma(\lambda_i-\lambda_{ave})]/\Sigma\lambda_i$, where λ_i is an eigenvalue of the tensor matrix of the anisotropic temperature factors and λ_{ave} is the average value of the three eigenvalues.

factor of the guest molecule increases with decreasing temperature. The guest molecule may exhibit a static disorder that is too small to be resolved in the electron-density map but can be detected by the temperature dependence of the anisotropy of the atomic thermal vibration.

2.2. Rigid-body motion of cyclomaltoheptaose

The rigid body motion of the host and guest molecules was evaluated by means of the TLS model.[7] The tensor elements of T, L, and S motions of cyclomaltoheptaose are given in Table 2. The translational motion of cyclomaltoheptaose is little affected by the temperature change. The amplitude of translational motion averaged for three principal axes was 0.16 Å (123 K), 0.16 Å (173 K), 0.17 Å (223 K), and 0.17 Å (293 K). In contrast, the average rotational amplitude was slightly increased as 1.1° (123 K), 1.0° (173 K), 1.2° (223 K), and 1.3° (293 K). These rotational amplitudes correspond to about 0.1 Å movement of atoms. Cyclomaltoheptaose molecules are linked by many intermolecular hydrogen bonds that impose restraints on the rigid-body motion. On the other hand, the cyclomaltoheptaose molecule has intramolecular flexibility related to the glycosidic linkages. The large discrepancy (35–41%) between U_{ij}^{obs} and U_{ij}^{cal} (Table 2) indicates that the thermal motion of cyclomaltoheptaose involves both the rigid-body motion and the local motion of each glucose unit. Therefore, the TLS parameters of cyclomaltoheptaose are considered to be overestimated.

The TLS parameters were determined for each glucose unit. As shown in Fig. 3, the rigid body motion of the glucose unit is represented with thermal ellipsoids that were calculated by using the TLS parameters, is nearly same as the observed atomic thermal motion. The discrepancy between the observed and calculated temperature factors at 293 K was in the range from 2.6% to 10.1% for U_{iso} and from 10.1% to 23.6% for U_{ij}. A large discrepancy was observed for the glucose units, G3, G4, and G6, which have the disordered primary hydroxyl groups. The structure of cyclomaltoheptaose has been considered to be rigid because the adjacent glucose units form hydrogen bonds between 2-OH and 3-OH hydroxyl groups. The intramolecular hydrogen bonds impose restriction on the rotational flexibility of glucose units around the glycosidic linkage. The structure of methylated cyclomaltoheptaose has shown that the conformational flexibility of the cyclomaltoheptaose ring increases by the lack of intramolecular hydrogen bonds.[8,9] The analysis of the rigid body motion of each glucose unit demonstrates that the cyclomaltoheptaose ring has a rigid structure, but a small flexibility of α-(1→4)-linkage still remains. The average translational amplitude of glucose units (0.16–0.19 Å) is comparable to that of the whole molecule (0.17 Å). In contrast, the rotational amplitude (2.0°–3.3°) is about twice larger than the rotational amplitude

Table 2
Rigid-body parameters of cyclomaltoheptose

	123 K	173 K	223 K	293 K
(1) TLS matrix				
$T/10^{-4}$ (Å^2)	$\begin{pmatrix} 294(5) & 13(2) & -23(2) \\ 13(2) & 263(7) & -29(3) \\ -23(2) & -29(3) & 206(7) \end{pmatrix}$	$\begin{pmatrix} 402(5) & 29(2) & -5(2) \\ 29(2) & 306(7) & -13(3) \\ -5(2) & -13(3) & 151(7) \end{pmatrix}$	$\begin{pmatrix} 334(5) & 13(2) & -31(2) \\ 13(2) & 282(7) & -40(3) \\ -31(2) & -40(3) & 215(7) \end{pmatrix}$	$\begin{pmatrix} 400(6) & 7(3) & -72(3) \\ 7(3) & 243(8) & -82(3) \\ -72(3) & -82(3) & 273(8) \end{pmatrix}$
$L/10^{-5}$ (rad^2)	$\begin{pmatrix} 79(3) & -7(1) & -8(1) \\ -7(1) & 22(2) & -2(1) \\ -8(1) & -2(1) & 21(2) \end{pmatrix}$	$\begin{pmatrix} 53(3) & -9(1) & -4(1) \\ -9(1) & 20(2) & -2(1) \\ -4(1) & -2(1) & 12(2) \end{pmatrix}$	$\begin{pmatrix} 85(3) & -10(1) & -9(1) \\ -10(1) & 30(2) & -6(1) \\ -9(1) & -6(1) & 29(2) \end{pmatrix}$	$\begin{pmatrix} 120(4) & -13(1) & -13(1) \\ -13(1) & 41(3) & -14(1) \\ -13(1) & -14(1) & 48(3) \end{pmatrix}$
$S/10^{-5}$ (rad Å)	$\begin{pmatrix} 1(6) & -5(6) & 7(6) \\ -5(6) & -4(5) & 7(5) \\ 7(6) & 7(5) & 3(8) \end{pmatrix}$	$\begin{pmatrix} 32(6) & -16(6) & -26(6) \\ -16(6) & -12(5) & 9(5) \\ -26(6) & 9(5) & -19(8) \end{pmatrix}$	$\begin{pmatrix} 9(6) & -10(6) & 2(6) \\ -10(6) & -12(5) & 8(5) \\ 2(6) & 8(5) & 3(8) \end{pmatrix}$	$\begin{pmatrix} -13(6) & 6(7) & 11(7) \\ 6(7) & -4(5) & 8(5) \\ 11(7) & 8(5) & 18(8) \end{pmatrix}$
(2) Amplitudes of rotational motion (°) for three principal axes:	(1.63 0.88 0.77)	(1.54 0.78 0.58)	(1.69 1.08 0.82)	(2.01 0.97 0.93)
(3) Amplitudes of translational motion (Å) for three principal axes:	(0.10 0.16 0.14)	(0.20 0.17 0.12)	(0.19 0.17 0.14)	(0.21 0.18 0.13)
(4) Discrepancy [a] between observed and calculated U's:				
$R(U_{eqv})$	0.256	0.215	0.253	0.185
$R(U_{ij})$	0.414	0.387	0.404	0.353

[a] $R(U)$ is defined as: $R(U) = \Sigma|U^{obs} - U^{cal}|/\Sigma|U|$, where U^{cal} was calculated by the TLS equation.

of the molecule (1.3°). Fig. 4 shows the principal axes of translation and rotation in the G1 unit. The translational motion is rather isotropic with amplitudes of 0.15, 0.17, and 0.19 Å for the three principal axes, while the rotational motion shows strong anisotropy. The rotational amplitude around the axis perpendicular to the pyranose ring is small (1.9°) because of the constraint imposed by glycosidic linkages. The largest amplitude (5.2°) is observed around the axis that is in the direction along the line through O-4(1) and O-4(2) atoms. Therefore, the rigid-body motion of glucose units is roughly expressed as a combination of the rigid-body motion of the cyclomaltoheptaose ring and the local motion of each glucose unit that is mostly rotational vibration around the glycosidic linkage.

2.3. Rigid-body motion of hexamethylenetetramine

The TLS parameters of hexamethylenetetramine are given in Table 3. As shown in Fig. 5, the calculated thermal motion according to the TLS method is in good agreement with the observed thermal motion. The atomic thermal motion of hexamethylenetetramine is mostly derived from the rigid-body motion. The discrepancy between U^{obs} and U^{cal} is about 5% for U_{iso} and 15% for U_{ij}. The translational motion is rather isotropic. The average translational amplitude is 0.20 Å (123 K), 0.20 Å (173 K), 0.21 Å (223 K), and 0.23 Å (293 K), which are ca. 25% larger than the translational motion of cyclomaltoheptaose. The thermal motion of hexamethylenetetramine is characterized by relatively large rotational motion. The average amplitude of rotational vibration is 5.2° (123 K), 5.4° (173 K), 5.9° (223 K), and 6.6° (293 K). The guest molecule is closely packed in the host cavity, and the hydrogen atoms of the methylene groups are in van der Waals contact with the hydrogen atoms of methine and methylene groups that are located on the inside wall of the cyclomaltoheptaose cavity. As the result, the translational motion of the guest molecule is suppressed by the cavity wall. The large contribution of the rotational motion to the atomic vibration is obvious in the structure represented with thermal ellipsoids that are disk-shaped rather than

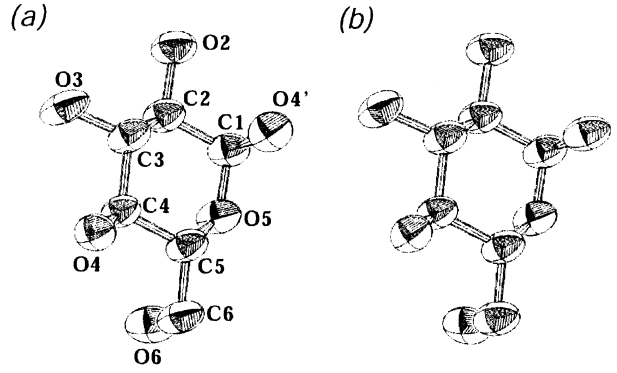

Fig. 3. (*a*) Observed thermal motion of the G1 unit at 293 K and (*b*) calculated rigid-body motion by using the TLS parameters. Thermal ellipsoids are drawn with 75% probability.

Table 3
Rigid-body parameters of hexamethylenetetraamine

	123 K	173 K	223 K	293 K
(1) TLS matrix				
$T/10^{-3}$ (Å)	$\begin{pmatrix} 35(2) & 0(1) & -7(1) \\ 0(1) & 36(2) & 0(1) \\ -7(1) & 0(1) & 53(2) \end{pmatrix}$	$\begin{pmatrix} 35(2) & 0(1) & -6(1) \\ 0(1) & 38(2) & 0(1) \\ -6(1) & 0(1) & 57(2) \end{pmatrix}$	$\begin{pmatrix} 37(2) & 0(1) & -7(1) \\ 0(1) & 42(2) & 2(1) \\ -7(1) & 2(1) & 58(2) \end{pmatrix}$	$\begin{pmatrix} 47(2) & 6(1) & -11(1) \\ 6(1) & 59(3) & 3(1) \\ -11(1) & 3(1) & 63(2) \end{pmatrix}$
$L/10^{-4}$ (rad^2)	$\begin{pmatrix} 71(11) & -13(4) & 15(5) \\ -13(4) & 66(11) & -44(4) \\ 15(5) & -44(4) & 130(12) \end{pmatrix}$	$\begin{pmatrix} 72(11) & -9(4) & 18(4) \\ -9(4) & 61(10) & -44(4) \\ 18(4) & -44(4) & 154(11) \end{pmatrix}$	$\begin{pmatrix} 97(11) & -9(4) & 15(5) \\ -9(4) & 78(10) & -44(4) \\ 15(5) & -44(4) & 155(11) \end{pmatrix}$	$\begin{pmatrix} 178(15) & 11(5) & 1(6) \\ 11(5) & 99(13) & -44(5) \\ 1(6) & -44(5) & 136(14) \end{pmatrix}$
$S/10^{-3}$ (rad Å)	$\begin{pmatrix} 2(1) & 0(1) & 1(1) \\ 0(1) & 2(1) & 1(1) \\ 1(1) & 1(2) & -4(2) \end{pmatrix}$	$\begin{pmatrix} 1(1) & 0(1) & 1(1) \\ 1(1) & 3(1) & 2(1) \\ 1(1) & 2(1) & -4(1) \end{pmatrix}$	$\begin{pmatrix} 2(1) & 0(1) & 1(1) \\ 0(1) & 3(1) & -1(1) \\ 1(1) & -1(1) & -5(1) \end{pmatrix}$	$\begin{pmatrix} 4(1) & 0(1) & -1(1) \\ 0(1) & -1(1) & -3(1) \\ -1(1) & -3(1) & -3(1) \end{pmatrix}$
(2) Amplitudes of rotational motion (°) for three principal axes:				
	(4.7 3.8 7.2)	(4.7 3.8 7.6)	(5.6 4.4 7.7)	(7.3 4.8 7.7)
(3) Amplitudes of translational motion (Å) for three principal axes:				
	(0.18 0.19 0.24)	(0.18 0.19 0.24)	(0.19 0.20 0.25)	(0.20 0.25 0.25)
(4) Discrepancy [a] between observed and calculated U's:				
$R(U_{iso})$	0.054	0.050	0.043	0.048
$R(U_{ij})$	0.151	0.150	0.154	0.158

[a] $R(U)$ is defined as: $R(U) = \Sigma|U^{obs} - U^{cal}|/\Sigma|U|$, where U^{cal} was calculated by the TLS equation.

spherical. The guest molecule is hydrogen-bonded to the O-2(3) hydroxyl group of an adjacent cyclomaltoheptaose and a water molecule (W1) located at the primary hydroxyl side of the cyclomaltoheptaose ring. These hydrogen bonds impose restriction, not only on the translational motion, but also on the rotational motion. The principal axes of translation and rotation are shown in Fig. 6. The center of rotation is shifted to the midpoint of two nitrogen atoms, N-1 and N-3, which are fixed by hydrogen bonds. One principal axis of the rotational motion is almost parallel to the line through these two nitrogen atoms. Therefore, the rigid-body motion of hexamethylenetetramine is characterized by the rotational vibration around the axis that is in the direction perpendicular to the cyclomaltoheptaose ring. These results suggest that the analysis of rigid body motion based on the crystallographic temperature factor is a powerful tool to elucidate the

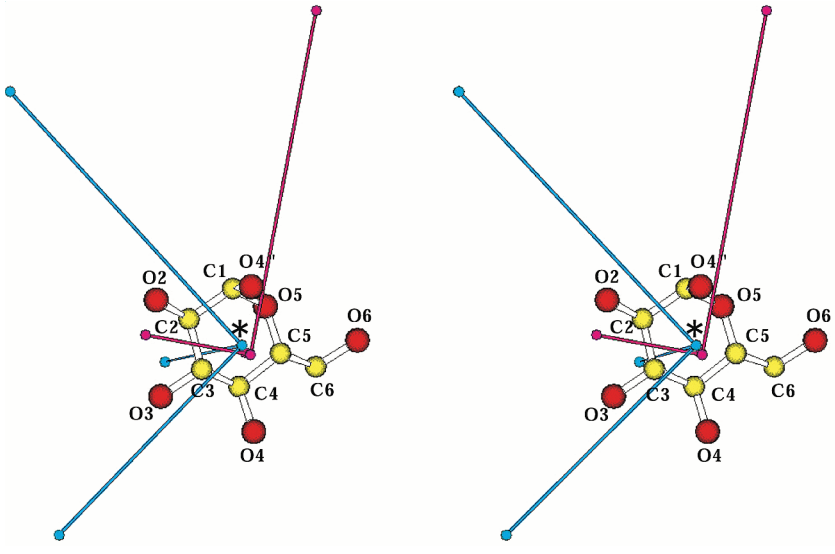

Fig. 4. A stereoview showing the principal axes of the translational motion (blue) and the rotational motion (red) of the G1 unit. The principal axes of the translational motion are drawn from the center of gravity. The center of rotation is 0.85 Å shifted from the center of gravity denoted by an asterisk.

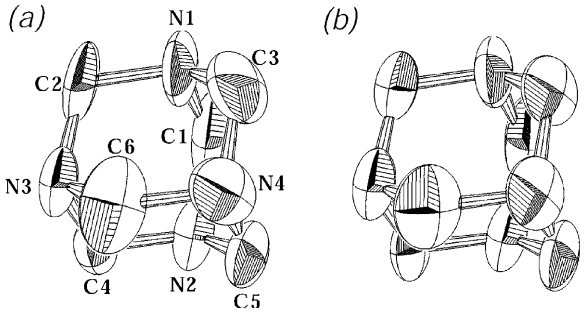

Fig. 5. (*a*) Observed thermal motion of hexamethylenetetramine at 293 K and (*b*) calculated rigid-body motion by using the TLS parameters. Thermal ellipsoids are drawn with 75% probability.

dynamic motion of the guest molecule within the inclusion complex.

3. Experimental

3.1. X-ray analysis

Crystals of the 1:1 complex of cyclomaltoheptaose with hexamethylenetetramine were obtained at room temperature by slow evaporation of an aqueous solution containing cyclomaltoheptaose and hexamethylenetetramine in a 1:1 molar ratio. The X-ray measurements were carried out on a Nonius CAD4 diffractometer with graphite-monochromated CuKα radiation. The crystal was sealed in a glass capillary and put in a temperature-regulated nitrogen gas stream. The intensity data were collected at temperatures of 123 K, 173 K, 223 K, and 293 K by using one crystal. The structure at each temperature was refined by the full-matrix least-squares method (SHELX-97),[10] starting from the reported structure that was determined at room temperature.[11] The atomic coordinates of hydrogen atoms in methylene and methine groups were calculated and included in the structure factor calculation with isotropic temperature factor that was 1.5 times of U_{eqv} of the bonded carbon atom. The summary of data collection and structure refinement is given in Table 1.

3.2. Analysis of thermal motion

The anisotropic temperature factors used in the least-squares refinement were of the form:

$$\exp[-2\pi^2(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2} + 2U_{12}hka^*b^* + 2U_{23}klb^*c^* + 2U_{13}hla^*c^*)].$$

Calculation of equivalent isotropic temperature factors (U_{eqv}) and transformation of U_{ij} to the Cartesian system were carried out as described by Willis & Pryor (1975).[12] When a molecule performs rigid-body motion in the crystalline state, each term of anisotropic temperature factors is expressed as a linear function of three tensors for translation (T), libration (L), and screw motion (S), as follows:[7]

$$U_{ij} = \sum G_{ijkl}L_{kl} + \sum H_{ijkl}S_{kl} + T_{ij}$$

where G_{ijkl} and H_{ijkl} are functions of atomic coordinates. Tensor elements of T, L, and S were determined by the least-squares fit to U_{ij}. The quantity minimized was $\Sigma w_{ij}(\Sigma G_{ijkl}L_{kl} + \Sigma H_{ijkl}S_{kl} + T_{ij} - U_{ij})^2$, where $1/\sigma(U_{ij})$ was used for the weighting function, w_{ij}. Diagonal terms of the S tensor were constrained as: $S_{11} + S_{22} + S_{33} = 0$. The center of libration was so chosen as if the S tensor was symmetrical.

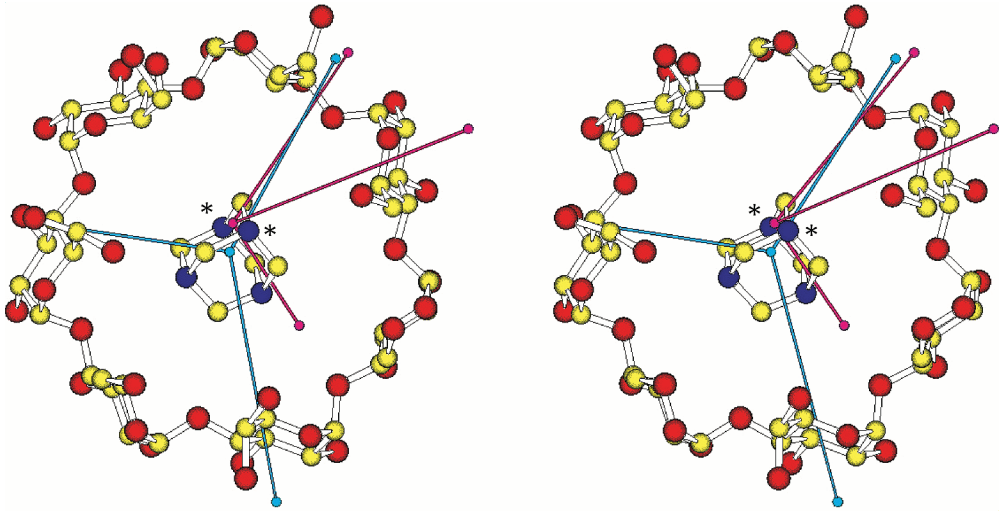

Fig. 6. A stereoview showing the principal axes of the translational motion (blue) and the rotational motion (red) of hexamethylenetetramine. The principal axes of the translational motion are drawn from the center of gravity. The center of rotation is 0.86 Å shifted from the center of gravity and located at the midpoint of the two nitrogen atoms denoted by asterisks.

References

1. Szejtli, J. *Cyclodextrins and Their Inclusion Complexes*; Akadémiai Kiadó: Budapest, 1982.
2. Harata, K. *Chem. Rev.* **1998**, *98*, 1803–1827.
3. Hingerty, B.; Saenger, W. *J. Am. Chem. Soc.* **1976**, *98*, 3357–3365.
4. Hamilton, J. A.; Sabesan, M. N. *Carbohydr. Res.* **1982**, *102*, 31–46.
5. Harata, K.; Kawano, K. *Carbohydr. Res.* **2002**, *337*, 537–547.
6. Harata, K. *Chem. Commun. (Cambridge)* **1999**, 191–192.
7. Schomaker, V.; Trueblood, K. N. *Acta Crystallogr., Sect. B* **1968**, *24*, 63–76.
8. Harata, K.; Uekama, K.; Otagiri, M.; Hirayama, F. *J. Incl. Phenom.* **1984**, *1*, 279–293.
9. Aree, T.; Hoier, H.; Schulz, B.; Reck, G.; Saenger, W. *Carbohydr. Res.* **2000**, *328*, 399–407.
10. G.M. Sheldrick, SHELX-97: Program for Crystal Structure Refinement, University of Göttingen, Germany, 1997.
11. Harata, K. *Bull. Chem. Soc. Jpn.* **1984**, *57*, 2596–2599.
12. Willis, B. T. M.; Pryor, A. W. *Thermal Vibrations in Crystallography*; Cambridge University Press: London, 1975.