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**Abstract**

A solid complex of  $C_{60}$  with  $\gamma$ -cyclodextrin ( $\gamma$ -CyD) was examined with NMR spectroscopic methods in order to understand the dynamics of  $C_{60}$ , and the interaction between  $C_{60}$  and  $\gamma$ -CyD. A  $^{13}\text{C}$  solid-state cross-polarization magic angle spinning (CP/MAS) NMR spectra shows  $C_{60}$  resonance at 142.6 ppm. This provides the evidence of interaction between  $^{13}\text{C}$  spins in  $C_{60}$  and  $^1\text{H}$  spins in the  $\gamma$ -CyD host. Ambient temperature experiments on the  $^{13}\text{C}$  CP/MAS NMR, with varying contact time, shows that the water associated with  $\gamma$ -CyDs plays an important role in the nuclear relaxation processes. The dynamics of  $C_{60}$  in  $\gamma$ -CyD was investigated using temperature and field-dependent  $^{13}\text{C}$  spin-lattice relaxation time measurements. The influence of water on the dynamics of  $C_{60}$  was less significant below 250 K. © 1997 Elsevier Science B.V.

**Keywords:**  $C_{60}$ ;  $\gamma$ -cyclodextrin ( $\gamma$ -CyD); Solid state NMR; Cross-polarization (CP); Spin-lattice relaxation

**1. Introduction**

The guest–host chemistry of the fullerenes has attracted exceptional attention recently, since these bulky molecules are considered as potential hosts for small metal ions and inert gas molecules [1,2]. In addition, fullerenes can themselves be guests accommodated in other large host matrices [3–9], and interesting physical, chemical and biological properties may be expected in such complexes. After the exciting report of the inhibition of HIV-1 protease by

$C_{60}$  derivatives [10], many investigators have devoted their efforts to increase the solubility of fullerenes in water, particularly through fullerene inclusion chemistry [11–18]. It has been suggested that cyclodextrins (CyDs) with a cavity size of the same order as  $C_{60}$  are among the most suitable molecules for such a purpose. This has renewed the interest in cyclodextrin inclusion compounds which have been studied thoroughly since the 1940s [19]. Stable, water-soluble complexes of  $C_{60}$ – $\gamma$ -CyD [11–16],  $C_{60}$ –DM $\beta$ -CyD [17] and  $C_{70}$ – $\gamma$ -CyD [18] have recently been reported. Molecular modeling [11] was used to predict the structure of  $C_{60}$ – $\gamma$ -CyD complex (for  $\gamma$ -CyD structure, see Fig. 1) as being  $C_{60}(\gamma\text{-CyD})_2$ . FAB/SIMS [15,16], elemental analysis [13],  $^{13}\text{C}$  and  $^1\text{H}$  NMR [14,15], and photophysical [11–13] studies all confirmed this prediction.

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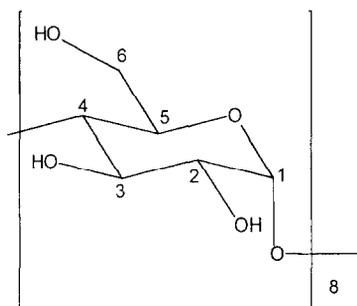


Fig. 1. Structure of the glucosidic unit of the  $\gamma$ -CyD molecule. Carbons are numbered.

Kim and Jeon [20] have reported the theoretical calculations of the inclusion–complexion kinetics for  $C_{60}$  and  $\gamma$ -CyD. They showed that in order to accommodate  $C_{60}$ , the internal strain energy is required to make the conformation of  $\gamma$ -CyD more symmetrical. This more symmetrical conformation of  $\gamma$ -CyD is not the most stable structure in itself. Along with this internal energy contribution, the hydrophobic van der Waals' interaction is believed to play the role of stabilizing the complex, while the electrostatic interaction between  $C_{60}$  and  $\gamma$ -CyD has been estimated to be much smaller in comparison with these former factors [20]. Water molecules associated with the complex were not included into the energy calculation, because they are considered to have a negligible effect on the lowering of the total energies calculated for the  $C_{60}(\gamma\text{-CyD})_2$  molecule. However, it has been reported that hydration water do indeed transform the conformation of  $\gamma$ -CyD in aqueous solution [21]. Circular dichroism spectra, which are sensitive to intramolecular interactions, also demonstrated an increase in band intensity with the extent of dehydration of the  $C_{60}(\gamma\text{-CyD})_2$  powders [14]. Therefore, water molecules may have a different effect on the complex with varying temperature.

In order to verify the role of water, a solid-state investigation of  $C_{60}(\gamma\text{-CyD})_2$  depending on the water content was carried out in the present study with the help of NMR spectroscopic techniques. A solid-state study may provide crucial information on the mechanisms of interaction between  $C_{60}$  and  $\gamma$ -CyD, which is not easily carried out for the 1:2 complex in aqueous solution. The complex's very low solubility about  $10^{-5}$  M in aqueous solution [11,13], and its

poor stability due to the equilibrium between the 1:1 and 1:2 complexes [13,16] make its study in solution problematic.

In this study, the cross-polarization time,  $T_{CH}$ , and relaxation times,  $T_{1\rho}^H$ ,  $T_{1\rho}^C$  and  $T_1^C$ , of the complex which employed the CP/MAS technique were used to show the effects of water molecules in the complex. Field and temperature dependent  $T_1^C$  of  $C_{60}$  in the complex. The experimental data obtained for the lyophilized samples were compared with those of the hydrated samples in order to reveal the differences in water effect.

## 2. Theoretical approach in NMR relaxation experiments

### 2.1. Dynamics of cross-polarization

In  $^{13}\text{C}$  CP/MAS experiments, magnetization,  $M(t)$ , is a function of a set of the following parameters: the  $^{13}\text{C}$ - $^1\text{H}$  CP time constant ( $T_{CH}$ ); the proton spin-lattice relaxation time in the rotating frame ( $T_{1\rho}^H$ ); the carbon spin-lattice relaxation time in the rotating frame ( $T_{1\rho}^C$ ); and the  $^{13}\text{C}$ - $^1\text{H}$  CP contact time ( $\tau$ ). The equation relating  $M(t)$  with  $T_{CH}$ ,  $T_{1\rho}^H$ ,  $T_{1\rho}^C$  and  $\tau$  is as follows [22]:

$$M(t) = \frac{M_0}{\lambda} \left[ 1 - \exp\left(-\frac{\lambda\tau}{T_{CH}}\right) \right] \exp\left(-\frac{\tau}{T_{1\rho}^H}\right) \quad (1)$$

where

$$\lambda = 1 + \frac{T_{CH}}{T_{1\rho}^C} - \frac{T_{CH}}{T_{1\rho}^H} \quad (2)$$

and  $M_0$  is a proportionality constant. In this case, to avoid ambiguous fitting,  $T_{1\rho}^H$  and  $T_{1\rho}^C$  for each sample were obtained in independent experiments and inserted into Eqs. (1) and (2) for further fittings to get  $T_{CH}$  values for each  $^{13}\text{C}$  signal of the complex.

The CP process occurs through the  $^{13}\text{C}$ - $^1\text{H}$  dipole–dipole interaction, and its effect is inversely proportional to the sixth power of the  $^{13}\text{C}$ - $^1\text{H}$  distance ( $r_{CH}$ ) in a rigid molecular system. Another factor that will affect the CP process is the internal motion of molecules. The faster the internal motion of the molecule, the less effective the CP process and the longer the  $T_{CH}$  value [23,24].

## 2.2. $^{13}\text{C}$ relaxation of $\gamma\text{-CyD}$

The major relaxation process for the carbons of  $\gamma\text{-CyD}$  is the  $^{13}\text{C}\text{-}^1\text{H}$  dipole–dipole interaction, since each of them is bonded to at least one proton. In order to elucidate the character of the motion of  $\gamma\text{-CyD}$  carbons in the  $\text{C}_{60}(\gamma\text{-CyD})_2$  complex, the effective reorientational correlation time ( $\tau_c$ ) from the dipolar relaxation was calculated using the carbon spin-lattice relaxation time in the laboratory frame ( $T_1^C$ ). The effective reorientational correlation time was evaluated on the assumption that molecules are subject to Brownian motion. Though one may suspect jump motion, there is no direct way to distinguish between Brownian and jump motion on the basis of NMR relaxation studies. The following equations for a pure dipole–dipole interaction can be used for the calculation of  $\tau_c$  [25].

$$\left(\frac{1}{T_1^C}\right)_{\gamma\text{-CyD}} = \frac{2}{15} \frac{\gamma_C^2 \gamma_H^2 \hbar^2 S(S+1)}{r_{\text{CH}}^6} \times [J(\omega_C - \omega_H) + 3J(\omega_C) + 6J(\omega_C + \omega_H)] \quad (3)$$

where the spectral density function,  $J(\omega)$ , is expressed by

$$J(\omega) = \frac{\tau_c}{1 + \omega^2 \tau_c^2} \quad (4)$$

$\gamma_C$  and  $\gamma_H$  are carbon and proton gyromagnetic ratios, respectively;  $\hbar$  is the reduced Planck's constant;  $\omega_C$  and  $\omega_H$  are the Larmor frequencies of carbon and proton, respectively, under static magnetic field,  $B_0$ ;  $S$  is the proton nuclear spin which is equal to 1/2. The required  $r_{\text{CH}} = 1.08 \text{ \AA}$  [26] was used in the present work for the evaluation of  $\tau_c$  for  $\gamma\text{-CyD}$ .

## 2.3. $^{13}\text{C}$ relaxation of $\text{C}_{60}$

The dynamics of  $\text{C}_{60}$  capped by two  $\gamma\text{-CyD}$  molecules was examined in this work by also measuring  $T_1^C$  for the  $\text{C}_{60}$   $^{13}\text{C}$  NMR signal at different static magnetic field strengths and various temperatures. In general, the carbon spin-lattice relaxation rate  $1/T_1^C$  may include two terms: the contribution from the chemical shift anisotropy (CSA) interaction,

$1/T_1^{\text{CSA}}$ , and the contribution from interactions other than chemical shift anisotropy (non-CSA, NCSA),  $1/T_1^{\text{NCSA}}$ , hence the total spin-lattice relaxation rate can be expressed as [25]:

$$\left(\frac{1}{T_1^C}\right)_{\text{C}_{60}} = \frac{1}{T_1^{\text{CSA}}} + \frac{1}{T_1^{\text{NCSA}}} \quad (5)$$

The  $1/T_1^{\text{CSA}}$  term is given by

$$\frac{1}{T_1^{\text{CSA}}} = \frac{2}{15} \gamma_C^2 B_0^2 (\sigma_{\parallel} - \sigma_{\perp})^2 J(\omega) \quad (6)$$

where  $\sigma_{\parallel}$  and  $\sigma_{\perp}$  are principal components of the CSA tensor and refer to the shielding along and transverse to the symmetry axis in the axial symmetry system respectively.  $J(\omega)$  is defined analogously in Eq. (4) with  $\tau_c$  given as the effective reorientational correlation time due to the relaxation of anisotropic chemical shift interaction on  $^{13}\text{C}$  of  $\text{C}_{60}$  in the complex. The effective reorientational correlation time was evaluated on the same assumption as for  $\gamma\text{-CyD}$  in Section 2.2. The temperature dependence of  $\tau_c$  is represented in a regular form

$$\tau_c = \tau_0 \exp\left(\frac{E_a}{RT}\right) \quad (7)$$

where  $E_a$  is the activation energy for the reorientation of the  $\text{C}_{60}$  molecule,  $R$  is the gas constant and  $T$  is the temperature in Kelvin. In Eq. (5), the main contribution to the second term  $1/T_1^{\text{NCSA}}$  for this system is associated mainly with dipolar interaction between carbons of  $\text{C}_{60}$  and protons of  $\gamma\text{-CyD}$  [13].

## 3. Experimental section

### 3.1. Synthesis of lyophilized $\text{C}_{60}(\gamma\text{-CyD})_2$

$\text{C}_{60}$  (of 99.9% purity; natural abundance of  $^{13}\text{C}$  isotopes) and  $\gamma\text{-cyclodextrin}$  were purchased from Material and Electrochemical Research Corp. (AZ, USA) and from Merck respectively. The violet solid complex was synthesized in accordance with the following procedures. The analogous procedures was also used and published elsewhere [14]. We mixed two liquid phases consisting of a solution of 335 mg  $\gamma\text{-CyD}$  in 50 ml water and a solution of 100 mg  $\text{C}_{60}$

in 50 ml toluene. After the mixture was refluxed at 110°C for 2 to 3 days with vigorous magnetic stirring, a violet suspension solution was observed. Then the mixture was centrifuged to remove the supernatant and the violet solid complex was obtained. After that we added about 30 ml water to the violet solid with supersonics and repeated the previous procedure four times in order to remove the excess  $C_{60}$  and  $\gamma$ -CyD as much as possible. Immediately after the final removal of the supernatant, the violet powder was frozen in liquid nitrogen to be ready for the next freeze-dry step. The violet precipitate was finally freeze-dried with a commercial setup Virtis 10-324 at  $-57^\circ\text{C}$  for 15 h under a vacuum about 50 mTorr. Elemental analysis was performed on a Perkin-Elmer 2400-CHN elemental analyzer. The typical C:H atomic ratio was revealed to be 51.66:5.96 for the lyophilized sample, which is best suited to a  $C_{60}(\gamma\text{-CyD})_2$  formula.

### 3.2. Preparation of hydrated $C_{60}(\gamma\text{-CyD})_2$

To prepare samples of enhanced residual water content, the lyophilized  $C_{60}(\gamma\text{-CyD})_2$  was soaked in water and then dried at  $60^\circ\text{C}$  for 2 h under a poor vacuum of about 10 Torr. The color of powder changed from violet to deep violet and showed no brown color of free  $C_{60}$ . The hydrated samples are denoted by  $C_{60}(\gamma\text{-CyD})_2/\text{H}_2\text{O}$ .

### 3.3. Preparation of physical mixtures of $C_{60}$ and $\gamma\text{-CyD}$

120 mg  $C_{60}$  and 432.4 mg  $\gamma\text{-CyD}$  (mole ratio 1:2) were physically mixed by grinding them together with a mortar and pestle till a homogenous brownish color appeared.

### 3.4. Characterization techniques

The powder X-ray diffraction (XRD) patterns of samples were recorded with a Scintag X1 diffractometer, using Ni-filtered  $\text{Cu K}\alpha$  radiation.

NMR measurements were performed on Bruker DMX-300 (7.05 T), AMX-400 (9.04 T) and MSL-500 (11.75 T) spectrometers at  $^{13}\text{C}$  frequencies of 75.5 MHz, 100.6 MHz and 125.8 MHz, respectively. Tetramethylsilane (TMS) was used as the reference

for the chemical shift of  $^{13}\text{C}$ . Room-temperature  $^{13}\text{C}$  CP/MAS experiments with varying  $\tau$  were performed in a magnetic field of 7.05 T with a typical  $\pi/2$  pulse of 5  $\mu\text{s}$  which corresponds to a 50 kHz  $B_1$  field for both  $^{13}\text{C}$  and  $^1\text{H}$  and with a spinning rate of 3 kHz.  $T_{1\rho}^{\text{C}}$  and  $T_{1\rho}^{\text{H}}$  were measured with the CP  $T_{1\rho}$  pulse sequence.  $T_1^{\text{C}}$  was measured with the CP  $T_1$  pulse sequence, while the temperature- and field-dependent  $T_1^{\text{C}}$  of  $C_{60}$  was measured with the inversion-recovery technique using pulse sequence  $\pi-\tau-\pi/2$ . Samples were sealed under a vacuum of  $10^{-2}$  to  $10^{-3}$  Torr for all NMR relaxation measurements except for CP/MAS. A commercial software package, Microcal Origin, was used to calculate the relaxation time constants ascribed in Section 2.

## 4. Results and discussion

### 4.1. Powder X-ray diffraction

Fig. 2a–d shows the XRD patterns of the pristine  $C_{60}$ ,  $\gamma\text{-CyD}$ , lyophilized  $C_{60}(\gamma\text{-CyD})_2$  and physical mixtures of  $C_{60}$  and  $\gamma\text{-CyD}$ , respectively. The XRD pattern of the physical mixtures shows mainly the diffraction peaks of  $C_{60}$ , because the X-ray diffraction intensity is much stronger for  $C_{60}$  than for that of  $\gamma\text{-CyD}$ . While the XRD pattern of  $C_{60}(\gamma\text{-CyD})_2$  is totally different from  $C_{60}$  and  $\gamma\text{-CyD}$  and shows no diffraction peaks from  $C_{60}$ , indicating that no evidence of crystalline  $C_{60}$  observed in the sample.

### 4.2. $^{13}\text{C}$ CP/MAS nuclear magnetic resonance spectra

In the  $^{13}\text{C}$  CP/MAS NMR (75.5 MHz, spinning at 3 kHz) spectra (Fig. 3a), the lyophilized sample produced a sharp line at 142.6 ppm, which was a slight upfield shift from the 143.0 ppm line of pristine  $C_{60}$  (Table 1). This minor difference 0.4 ppm reflected that  $\gamma\text{-CyD}$  host only slightly disturbed the local magnetic field seen by  $C_{60}$ . This is further evidence that the main interaction between  $C_{60}$  and the  $\gamma\text{-CyD}$  cages is the hydrophobic van der Waals' interaction ([13,20], rather than the charge transfer process proposed by Yoshida et al. [14]).

As with the NMR result for the aqueous solution [13], there were some minor differences between the

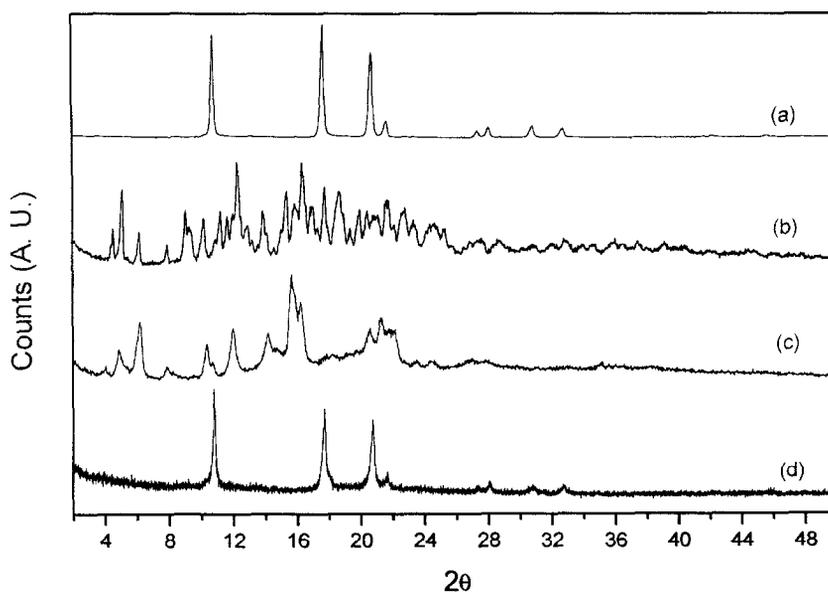


Fig. 2. Powder X-ray patterns of (a) the pristine  $C_{60}$ , (b) the pristine  $\gamma$ -CyD, (c) the lyophilized  $C_{60}(\gamma\text{-CyD})_2$  and (d) the physical mixtures of  $C_{60}$  and  $\gamma$ -CyD.

chemical shifts of  $C_{60}(\gamma\text{-CyD})_2$  and  $\gamma$ -CyD (Table 1). The line widths for the lyophilized  $\gamma$ -CyD were broader than for the lyophilized  $C_{60}(\gamma\text{-CyD})_2$  (Fig. 3a, b). This reveals that the conformation of the

former is more disordered than the latter. The effect of  $C_{60}$  molecule bicapped by the two  $\gamma$ -CyDs may account for the more ordered conformation of the  $\gamma$ -CyD of the complex. Splitting in a number of

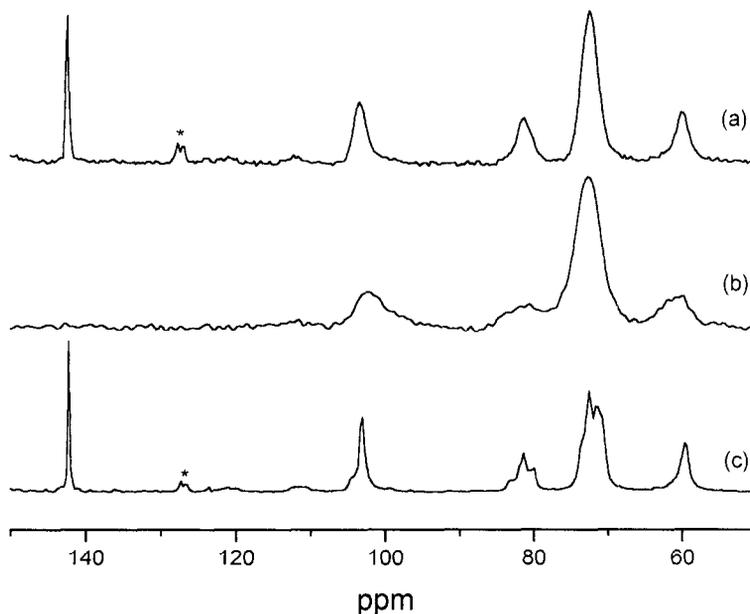


Fig. 3.  $^{13}\text{C}$  CP/MAS NMR spectra of (a) the lyophilized  $C_{60}(\gamma\text{-CyD})_2$ , (b) the lyophilized  $\gamma$ -CyD, (c) the hydrated  $C_{60}(\gamma\text{-CyD})_2/\text{H}_2\text{O}$  at 7.05 T field and MAS rate of 3 kHz. Asterisk marks a resonance from the residual toluene.

Table 1  
 $^{13}\text{C}$  CP/MAS NMR chemical shifts of the lyophilized  $\text{C}_{60}(\gamma\text{-CyD})_2$  and  $\gamma\text{-CyD}$  taken at a 7.05-T field and MAS rate 3 kHz

Carbon	Chemical shift (ppm)			Difference
	$\text{C}_{60}$	$\gamma\text{-CyD}$	$\text{C}_{60}(\gamma\text{-CyD})_2$	
$\text{C}_{60}$	143.0		142.6	-0.4
C-1		101.8	103.5	+1.7
C-2,3,5		72.3	72.0	-0.3
C-4		80.2	81.1	+0.9
C-6		59.6	59.9	+0.3

peaks was observed for the hydrated sample (Fig. 3c) which is likely to be associated with the conformational variations of  $\gamma\text{-CyD}$ . This is similar to the case of amylose, where it is due to alternation in the type of the intra- and intermolecular hydrogen bonding during the hydration process [27].

In general, the full line width at half maximum (fwhm) for  $\text{C}_{60}$  signal was reduced after the hydration process (Fig. 3a, c). For polycrystalline  $\text{C}_{60}$ , lyophilized  $\text{C}_{60}(\gamma\text{-CyD})_2$  and hydrated  $\text{C}_{60}(\gamma\text{-CyD})_2/\text{H}_2\text{O}$ , the fwhm's measured at 7.05 T are 3.7, 31.8 and 24.1 Hz, respectively. Two facts are worth noting here. First, the  $\text{C}_{60}$  signal in  $\text{C}_{60}(\gamma\text{-CyD})_2$  was essentially broader (31.8 Hz) compared to that for polycrystalline  $\text{C}_{60}$  (3.7 Hz). This could be caused by the  $^{13}\text{C}\text{-}^1\text{H}$  interaction [13,20], and/or by the slowing down of the reorientation of the guest fullerene molecule. Second, the fwhm of the  $\text{C}_{60}$  line in the hydrated sample was typically narrower than in lyophilized ones: 24.1 Hz vs. 31.8 Hz. This fact might indicate faster  $\text{C}_{60}$  motion and therefore a weaker dipole-dipole interaction for the hydrated sample. Because the secondary hydroxyl groups form the intramolecular hydrogen bonding with the adjacent glucose units, the variation of the fwhm shows that water near the complex may modify some features of the system through interacting with the primary hydroxyl groups of  $\gamma\text{-CyD}$ .

#### 4.3. $^{13}\text{C}$ CP/MAS nuclear magnetic resonance: relaxation and the role of water

In order to elucidate the influence of water in the solid complex, NMR relaxation time constants in the lyophilized and hydrated samples were examined in CP/MAS experiments with varying contact time,  $\tau$ .

Fig. 4 presents typical curves for  $M(\tau)$  versus  $\tau$  for the  $\text{C}_{60}$  resonance in lyophilized  $\text{C}_{60}(\gamma\text{-CyD})_2$  and hydrated  $\text{C}_{60}(\gamma\text{-CyD})_2$ . Analogous curves for the carbon resonances of  $\gamma\text{-CyD}$  in the same samples are presented in Fig. 5. The corresponding relaxation data are presented in Table 2 and will be discussed in Sections 4.3.1 and 4.3.2.

##### 4.3.1. The cross polarization time of the complex

Since, as discussed in the Section 2.1, the CP process occurs through the  $^{13}\text{C}\text{-}^1\text{H}$  dipolar interaction, the magnitudes of  $T_{\text{CH}}$  for the carbons of the same sample should be in the order of  $\text{CH}_2$  (C-6 of  $\gamma\text{-CyD}$ ) <  $\text{CH}$  (C-1 ~ C-5 of  $\gamma\text{-CyD}$ ) <  $\text{C}$  ( $\text{C}_{60}$ ). From Table 2, it can be seen that the  $T_{\text{CH}}$  values for the carbons of  $\gamma\text{-CyD}$  were indeed about two orders shorter than that for the carbons of  $\text{C}_{60}$ .  $\text{C}_{60}$  has a much larger proton to carbon distance than  $\gamma\text{-CyD}$ , and the molecular motion of the bicapped  $\text{C}_{60}$  is much faster than that for  $\gamma\text{-CyD}$ . These two factors may reduce the CP efficiency considerably.

Although the C-6 has two direct bonding hydrogens, for the same sample, the  $T_{\text{CH}}$  values of the  $\gamma\text{-CyD}$  carbons were almost in the same order. This is due to the internal motion of the primary hydroxyl groups which reduces the effectiveness of the dipolar interaction and therefore the CP rate. Thus, the  $T_{\text{CH}}$  value for C-6 was found to be close to those of all the other carbons of  $\gamma\text{-CyD}$  in the complex.

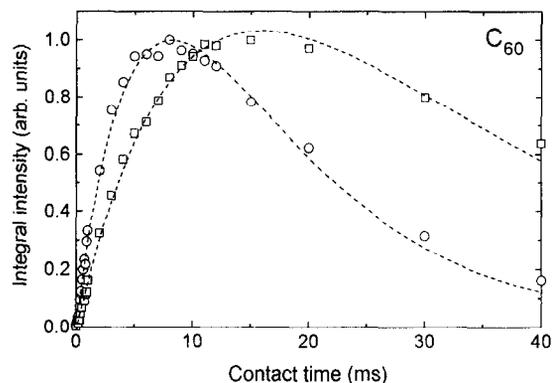


Fig. 4. Normalized integral intensity of the  $^{13}\text{C}$  CP/MAS NMR signal vs. contact time for  $\text{C}_{60}$  in the lyophilized  $\text{C}_{60}(\gamma\text{-CyD})_2$  (circle) and in the hydrated  $\text{C}_{60}(\gamma\text{-CyD})_2/\text{H}_2\text{O}$  (square) at 7.05 T, MAS rate of 3 kHz, 4.67 mT  $B_1^{\text{C}}$  field and 1.17 mT  $B_1^{\text{H}}$  field. Dashed line is a fitting result using Eqs. (1) and (2).

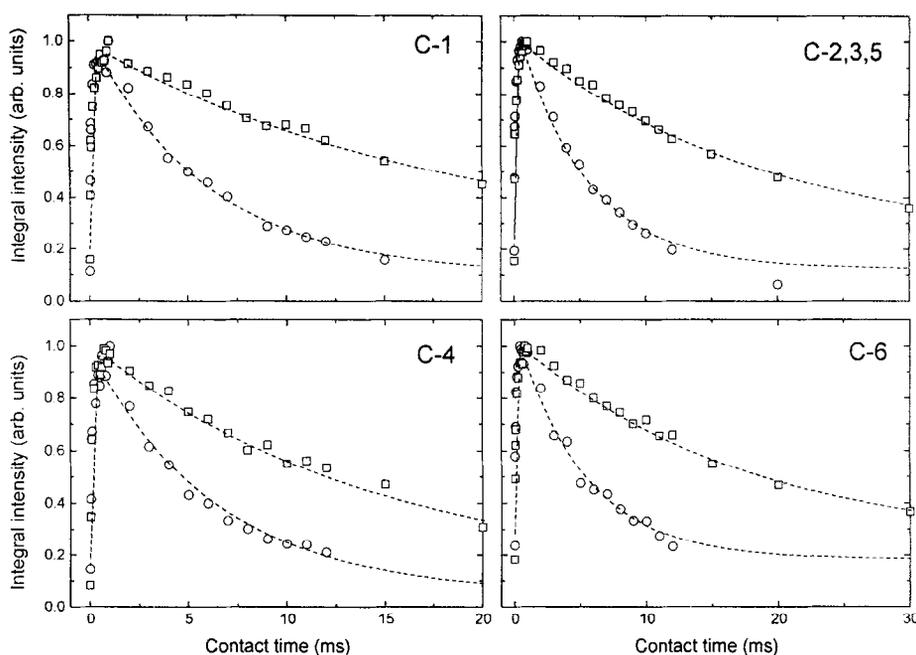


Fig. 5. Normalized integral intensity of  $^{13}\text{C}$  CP/MAS NMR signals vs. contact time for  $\gamma$ -CyD carbons in the lyophilized  $\text{C}_{60}(\gamma\text{-CyD})_2$  (circle) and in the hydrated  $\text{C}_{60}(\gamma\text{-CyD})_2/\text{H}_2\text{O}$  (square) at 7.05 T, MAS rate of 3 kHz, 4.67 mT  $B_1^{\text{C}}$  field and 1.17 mT  $B_1^{\text{H}}$  field. Corresponding carbons are indicated in the plots. Dashed line is a fitting result using Eqs. (1) and (2).

If we compare the  $T_{\text{CH}}$  values of the lyophilized and hydrated samples, the  $T_{\text{CH}}$  values were longer for the hydrated complex than for the lyophilized one. This may indicate that the flexibility of the complex increases after the hydration process, since the effective  $^{13}\text{C}$ - $^1\text{H}$  distance may not vary signifi-

cantly for  $\gamma$ -CyD in the hydrated sample. The effect can also be clearly seen in Fig. 4.

#### 4.3.2. $T_{1\rho}^{\text{H}}$ and $T_{1\rho}^{\text{C}}$ of the complex

For isotopically abundant nonisolated nuclei in solids, the relaxation times of different chemical types are often averaged by the spin diffusion [22,28]. Therefore, no big difference among the values of  $T_{1\rho}^{\text{H}}$  was found for any of the signals for each sample due to this effect for the  $^1\text{H}$  spins in  $\gamma$ -CyD (Table 2). Contrarily, because of the 1% natural abundance of  $^{13}\text{C}$ , the  $T_{1\rho}^{\text{C}}$  does not show the same effect as the  $T_{1\rho}^{\text{H}}$ . The magnitude of the  $T_{1\rho}^{\text{C}}$  on different carbons may reflect the differing mobility of the different functional groups in  $\gamma$ -CyD.

After the hydration process, significant elongations of  $T_{1\rho}^{\text{H}}$  and  $T_{1\rho}^{\text{C}}$  were observed (Table 2). We attribute these elongations to the rise of  $\gamma$ -CyD flexibility due to the increased free volume of the macro-ring segments in the presence of the water. A similar effect has been widely studied in polymers when plasticizers are applied to control polymer flexibility [29,30].

Table 2

Room temperature relaxation times evaluated from  $^{13}\text{C}$  CP/MAS NMR experiments performed at a 7.05-T field for the lyophilized  $\text{C}_{60}(\gamma\text{-CyD})_2$  and for the hydrated  $\text{C}_{60}(\gamma\text{-CyD})_2/\text{H}_2\text{O}$ . Accuracy of determination of  $T_{\text{CH}}$ ,  $T_{1\rho}^{\text{H}}$  and  $T_{1\rho}^{\text{C}}$  was 10%. The spin locking frequency,  $\omega_{\text{H}}$ , for measuring  $T_{1\rho}^{\text{H}}$  and  $T_{1\rho}^{\text{C}}$  was 50 kHz and the contact time was 2 ms. Labels of the  $\gamma$ -CyD carbons are shown in Fig. 1

Carbon	$\text{C}_{60}(\gamma\text{-CyD})_2$			$\text{C}_{60}(\gamma\text{-CyD})_2/\text{H}_2\text{O}$		
	$T_{\text{CH}}$ (ms)	$T_{1\rho}^{\text{H}}$ (ms)	$T_{1\rho}^{\text{C}}$ (ms)	$T_{\text{CH}}$ (ms)	$T_{1\rho}^{\text{H}}$ (ms)	$T_{1\rho}^{\text{C}}$ (ms)
$\text{C}_{60}$	10.2	5.5	—	12.7	20.5	—
C-1	0.07	5.1	34.9	0.15	20.1	122.0
C-2,3,5	0.10	5.7	18.2	0.13	19.3	53.8
C-4	0.08	5.4	39.3	0.11	18.6	83.1
C-6	0.08	5.1	2.5	0.13	17.3	12.0

#### 4.3.3. $T_1^C$ of the complex

In order to understand the motion characteristics of the complex, the  $T_1^C$  data and the effective reorientational correlation time,  $\tau_c$ , involved are listed in Table 3. In general, no significant change in  $T_1^C$  was observed for C-1, C-2,3,5 and C-4 with the hydration process. Since C-1 and C-4 are the carbons which form the glucosidic bonds between two adjacent glucose units, the reorientational motion should be the same. Thus, they could represent the overall motion of the complex. From Table 3, the  $\tau_c$  calculated for C-1 and C-4 were almost the same for both the lyophilized and hydrated samples. Because of the size of the complex, it is believed that this motion is on the slow motional side of the  $T_1^C$  minimum, the  $\tau_c$  being in the order of  $10^{-7}$  s. Otherwise, if one supposes that it is on the fast motional side of the  $T_1^C$  minimum, then the experimental data leads  $\tau_c$  to be in the order of  $10^{-12}$  s, which is too fast to be true for the reorientational process of  $C_{60}(\gamma\text{-CyD})_2$  in the solid state. Thus one may conclude that the excess water did not cause much change in the dynamics of the entire  $C_{60}(\gamma\text{-CyD})_2$  complex.

For the C-6, the  $T_1^C$  was measured in both samples and found to be much shorter than those for C-1 and C-4 (Table 3). One of the reasons for this was that there are two protons bonded to the C-6 methylene carbon. The  $T_1^C$  of C-6 was reduced from 2.7 s to 1.2 s (Table 3). It has been shown that the crystal structure of  $\gamma\text{-CyD}$  accommodates 19 molecules of  $H_2O$  per  $\gamma\text{-CyD}$  molecule and 12 of them are in the torus of the primary C(6)–OH hydroxyl groups [31].

Table 3

The room temperature  $T_1^C$  and the  $\tau_c$  evaluated from  $^{13}\text{C}$  CP/MAS NMR experiments performed at a 7.05-T field for the lyophilized  $C_{60}(\gamma\text{-CyD})_2$  and for the hydrated  $C_{60}(\gamma\text{-CyD})_2/H_2O$ . Accuracy of determination of  $T_1^C$  is 12%. Labels of the  $\gamma\text{-CyD}$  carbons are shown in Fig. 1

Carbon	$C_{60}(\gamma\text{-CyD})_2$		$C_{60}(\gamma\text{-CyD})_2/H_2O$	
	$T_1^C$ (s)	$\tau_c$ (s)	$T_1^C$ (s)	$\tau_c$ (s)
$C_{60}$	10.2	$1.1 \times 10^{-10a}$	16.3	$7.5 \times 10^{-11a}$
C-1	17.8	$6.1 \times 10^{-7}$	21.6	$7.3 \times 10^{-7}$
C-2,3,5	14.2	—	15.4	—
C-4	19.8	$6.7 \times 10^{-7}$	19.3	$6.5 \times 10^{-7}$
C-6	2.7	—	1.2	—

<sup>a</sup> The value was evaluated from the field-dependent  $T_1^C$  which is discussed in field-dependent  $T_1^C$  measurements in Section 4.4.

Therefore, the  $H_2O$  molecules introduced into the complex interact mainly with the primary hydroxyl groups and create a hydrogen bonding network with them. Therefore the water molecules in the hydrated sample hindered internal rotation (which was presumably in the motional narrowing region) [32] of the C-6, and further reduction of  $T_1^C$  was observed.

For  $C_{60}$  in the motional narrowing region of the  $T_1^C$  minimum after the hydration process, the  $T_1^C$  of  $C_{60}$  is increased from 10.2 s to 16.3 s. It is suggested that this increase is caused by the rise of the reorientational rate of  $C_{60}$ . First, in accordance with the molecular mechanics calculation for  $\gamma\text{-CyD}$  itself [33,34], the secondary C(2)–OH and C(3)–OH hydroxyl groups attached to the wider rim of  $\gamma\text{-CyD}$  are oriented inward, while the primary C(6)–OH hydroxyl groups attached to the narrower rim are directed outward. This has been revealed to be the most stable conformation and has been predicted to be the only one [35]. For  $C_{60}(\gamma\text{-CyD})_2$ , the conformation of  $\gamma\text{-CyD}$  is opposite to that for empty  $\gamma\text{-CyD}$ . To include  $C_{60}$  and avoid contact with the hydrophobic surface of  $C_{60}$ , the secondary hydroxyl groups are orientated outward while the primary hydroxyl groups are directed inward [20]. Second, water molecules have the tendency to interact with the primary hydroxyl groups, which directs the C(6)–OH bonds further inward. As a result, hydration increases the opening of the secondary hydroxyl rim and raise the flexibility of the macro-ring of  $\gamma\text{-CyD}$ . Consequently, the reorientational rate of  $C_{60}$  increased. The same effect was also observed by circular dichroism which showed an increase in band intensity with increasing dehydration of the initial  $C_{60}(\gamma\text{-CyD})_2$  powders dissolved in water [14].

#### 4.4. Dependence of $C_{60}$ carbon $T_1^C$ upon the NMR field strength

Fig. 6 presents plots of the spin-lattice relaxation rate  $1/T_1^C$  vs.  $B_0^2$  taken at 250 K and 300 K for the lyophilized  $C_{60}(\gamma\text{-CyD})_2$ . For both temperatures, because of the linear dependency of relaxation rate on  $B_0^2$ , the reorientational rate of the  $C_{60}$  falls in the  $\omega_c\tau_c \ll 1$  region and the data can be analyzed by using Eq. (5) on the assumption that the CSA term for this case is given by Eq. (6). The slopes gave

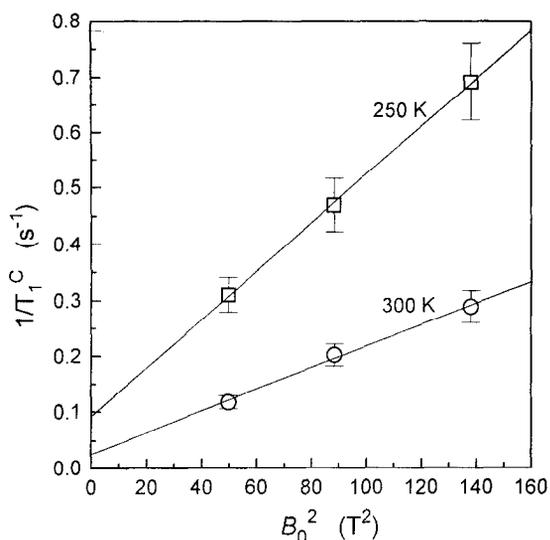


Fig. 6. A reciprocal  $^{13}\text{C}$  spin-lattice relaxation time vs. the square of the magnetic-field strength measured at 250 K and 300 K for  $\text{C}_{60}$  in the lyophilized  $\text{C}_{60}(\gamma\text{-CyD})_2$ . Experimental points are fitted by a linear regression. Error bar represents 10% error.

products of  $\tau_c(\sigma_{\parallel} - \sigma_{\perp})^2$  as  $7.2 \times 10^{-18}$  s and  $3.2 \times 10^{-18}$  s at 250 K and 300 K, respectively. We used the principal components of the CSA tensor of the pristine polycrystalline  $\text{C}_{60}$  [36], 30 ppm for  $\sigma_{\parallel}$  and 200 ppm for  $\sigma_{\perp}$ , to elucidate the  $\tau_c$  for  $\text{C}_{60}$  in the complex. The effective reorientational correlation time was elucidated with these tensor components and found to be  $2.5 \times 10^{-10}$  s and  $1.1 \times 10^{-10}$  s at 250 K and 300 K, respectively. This gave two conclusions. First, because the  $\tau_c$  of  $\text{C}_{60}$  at room temperature has been revealed to be within the time scale of  $10^{-11} \sim 10^{-12}$  s [37,38,33,34], the elongation of  $\tau_c$  by about one to two orders for  $\text{C}_{60}$  bicapped by  $\gamma\text{-CyDs}$  indicates that, when compared to pristine  $\text{C}_{60}$ , its reorientational motion essentially slows down. Second, in accordance with the intercept obtained from Fig. 6, the  $1/T_1^{\text{NCSA}}$  term was one order smaller than the  $1/T_1^{\text{CSA}}$ , hence the main relaxation mechanism is due to the CSA interaction.

The present data showed that the main interaction between the guest  $\text{C}_{60}$  and the host  $\gamma\text{-CyD}$  is the van der Waals' interaction, which, when compared with pristine  $\text{C}_{60}$ , should not alter the magnitude of CSA components significantly. However, even if that weak interaction is taken into account, it should mostly affect  $\sigma_{\parallel}$  rather than  $\sigma_{\perp}$ . Therefore, a minor chemi-

cal shift of 0.4 ppm observed for  $\text{C}_{60}$  in the complex as compared to that of pristine  $\text{C}_{60}$  gives an estimate for the variation of  $\sigma_{\parallel}$  to be only 1.2 ppm. Such a small value does not change  $(\sigma_{\parallel} - \sigma_{\perp})$  significantly and enables the use of the principal components of pristine  $\text{C}_{60}$  in our calculation.

#### 4.5. Dependence of $\text{C}_{60}$ carbon $T_1^C$ upon the temperature

Fig. 7 shows a plot of temperature vs.  $T_1^C$  for  $\text{C}_{60}$  carbons taken in the range 180–320 K in an 11.75-T field for the lyophilized and hydrated samples. Above 250 K,  $T_1^C$  was systematically shorter for the lyophilized sample than for the hydrated one. The shorter  $T_1^C$  reflected the longer reorientational correlation time which is consistent with the previous result from fwhm measurements. Therefore, a difference in  $T_1^C$  showed that the reorientational motion of  $\text{C}_{60}$  in the lyophilized complex was somewhat slower than that in the hydrated counterpart.

For both samples, in the given temperature range higher than 250 K, the  $\tau_c$  is fairly approximated by the activation law given by Eq. (7) for the reorienta-

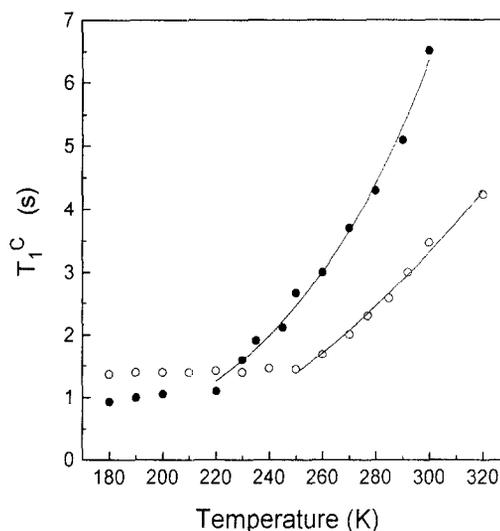


Fig. 7. The  $^{13}\text{C}$  nuclear spin-lattice relaxation time  $T_1^C$  vs. the temperature taken at 11.75 T for the carbons of  $\text{C}_{60}$ . Open circles are for the lyophilized  $\text{C}_{60}(\gamma\text{-CyD})_2$ , solid circles are for the hydrated  $\text{C}_{60}(\gamma\text{-CyD})_2/\text{H}_2\text{O}$ . The solid line in the high-temperature region is a fitting result using the activation law for the reorientational motion.

tional motion. The activation energy was elucidated to be  $10.7 \pm 0.4$  and  $10.9 \pm 0.4$  kJ/mol for the lyophilized and the hydrated samples, respectively. For the former sample,  $T_1^C$  was also measured in a 9.04 T field in the same temperature range (data are not shown). The activation energy was  $10.0 \pm 0.4$  kJ/mol. All values of  $E_a$  were in good agreement with each other. It is noted that current values of  $E_a$  are larger than the 4.04 kJ/mol (42 MeV) in pristine  $C_{60}$  reported by Tycko et al. [37]. The higher activation energy in our case supports the assumption that hindered motion of  $C_{60}$  in the complex compared to the motion in pristine  $C_{60}$ .

When comparing the reorientational motion of both samples, it seems that to reach the same reorientational rate, much lower temperatures were required for  $C_{60}$  in the hydrated complex than for the lyophilized one. Indeed, the temperature independent  $T_1^C$  process occurred below 220 K for the hydrated sample and below 250 K for its counterpart (Fig. 7). These turning points represented neither a usual minimum for the temperature-dependent spin-lattice relaxation time nor the minimum in the orientation ordering associated with the phase transition in pristine  $C_{60}$  [37]. For the lyophilized sample, we estimate the magnitude of  $\omega\tau_c$  at 250 K to be only 0.03. This gave the condition  $\omega^2\tau_c^2 \ll 1$  and a  $T_1^C$  minimum at this temperature was unexpected. Furthermore the respective temperature-dependent  $T_1^C$  for the complex and the solid  $C_{60}$  are absolutely different. For pure  $C_{60}$ , the  $T_1^C$  value decreases linearly down to 260 K and drops down abruptly due to the phase transition. With further decrease in temperature, it reaches the minimum center at 240 K and monotonously grows below 240 K. For  $C_{60}(\gamma\text{-CyD})_2$ , the  $T_1^C$  value decreases monotonously between 320 K and 220 K for the hydrated sample or 250 K for the lyophilized sample. Below the temperature specified by the turning point,  $T_1^C$  becomes almost temperature-independent. Moreover, if the turning point observed for  $C_{60}(\gamma\text{-CyD})_2$  complex should represent the phase transition of solid  $C_{60}$ , it will occur at the same temperature for both the lyophilized and the hydrated samples. Actually this was not the case observed in the experiment. Position of the turning point systematically shifted with the decrease or increase of water content. For the hydrated sample, it was observed at about 220 K, which is much lower

than the temperature of the phase transition in solid  $C_{60}$ . Probably, at low temperature the change in the conformation of  $\gamma\text{-CyDs}$  created a new environment for  $C_{60}$ , which led to a situation distinct from a regular shortening of the relaxation time with lowering temperature. This factor compensated the thermal activation of the reorientational motion of  $C_{60}$  and gave rise to the flat region in the temperature dependency graph (Fig. 7).

It is worth noting that once it fell to the flat region,  $T_1^C$  was almost the same for both the lyophilized and the hydrated samples (Fig. 7). The similarity in the relaxation behavior for both samples meant that the proposed low-temperature conformation of  $\gamma\text{-CyDs}$  was no longer significantly affected by the excess water associated with the complex. This fact agrees with the results of the molecular mechanics calculation done by Kim and Jeon [20], who showed that the participation of water molecules did not alter the total energies of the system minimized for the  $C_{60}(\gamma\text{-CyD})_2$  system. It should be noted that the most stable structure of the complex was only observable in low-temperature experiments. Our results may arise from the same situation. We conclude that in the low-temperature region, the reorientational rates for  $C_{60}$  in the lyophilized and hydrated samples were almost the same.

## 5. Conclusions

Solid  $C_{60}(\gamma\text{-CyD})_2$  complex has been systematically studied in this work by NMR spectroscopic techniques. The data obtained conclusively demonstrates that the van der Waals' interaction between the host  $C_{60}$  and the guest  $\gamma\text{-CyD}$  is the main interaction. From the field-dependent  $T_1^C$  measurements, the effective reorientational correlation time for  $C_{60}$  capped between two  $\gamma\text{-CyDs}$  was found to be about  $10^{-10}$  s at room temperature which is one to two orders longer than that published for pristine  $C_{60}$ . For the entire  $C_{60}(\gamma\text{-CyD})_2$  complex itself, the reorientational correlation time was evaluated to be in the order of  $10^{-7}$  s.

Water molecules introduced into the system brought about essential elongation of the NMR relaxation times for both the carbons of  $C_{60}$  and  $\gamma\text{-CyD}$ . Hence, the reorientational motion of  $C_{60}$  in

the deliberately hydrated samples was much faster than in the lyophilized ones and the flexibility of  $\gamma$ -CyD is raised by the water due to the increase of free volume in the  $\gamma$ -CyD macro-ring. Experiments on the temperature-dependent  $^{13}\text{C}$  relaxation showed that the influence of water associated with  $\gamma$ -CyD on the dynamics of  $\text{C}_{60}$  was less significant below 250 K. This may suggest that the conformation of the complex occurring at low temperature is close to the most stable conformation.

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