Mössbauer Spectroscopic Studies on Molecular Rotation and Lattice Dynamics of Cyclodextrin Clathrates of Bis(η-cyclopentadienyl)iron(II) and some of Its Ring-substituted Derivatives†

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Bis(η-cyclopentadienyl)iron(II) and some its ring-substituted derivatives (guest molecules) are included in the cavities of α-, β-, and γ-cyclodextrins (host molecules). The ^{57}Fe Mössbauer spectra for the clathrates have been examined at various temperatures from 78 to 320 K. The temperature-dependent relaxation of the electric field gradient (e.f.g.) tensor, *i.e.* the reorientation of the guest molecules, was observed in the Mössbauer spectra of the clathrates of bis(η-cyclopentadienyl)iron(II) derivatives with α-cyclodextrin. Activation energies for the reorientation increase with increase in size of the substituents on the cyclopentadienyl rings of the guest molecules. Limiting reorientation times decrease with the increase in dipole moment of the guest molecules. Lattice temperatures (θ_1) and effective vibrating masses (M_{eff}) for 12 clathrates and four guest molecules were determined from the temperature dependences of the Mössbauer parameters. The lattice temperatures and the effective vibrating masses decrease in the order of the clathrates of α-, β-, and γ-cyclodextrins. Slight decreases of both isomer shifts and quadrupole splittings were observed for the clathrates of α-cyclodextrin, suggesting that there is a difference in the interaction between the guest and host molecules.

Cyclodextrins (cyd) are some of the most interesting host molecules because of their structure and usefulness for drugs. They are cyclic oligosaccharides consisting of six or more α-1,4-linked glucopyranose rings and they all possess a cavity in the molecule. The cavity forms are toroidal with an inner aperture of *ca.* 0.45—0.55 (α-cyd), 0.70 (β-cyd), and 0.85 nm (γ-cyd) in diameter, and 0.67 (α-cyd) and 0.70 nm (β- and γ-cyd) in length. The internal diameters of cyclodextrins depend on the number of glucose residues in a molecule. The cavity of cyclodextrin is capable of including a variety of guest molecules, for example, paraffins, alkyl halides, halogens, and aromatic compounds.[1] The guest:host ratios of the clathrates in solution are almost 1:1, but in the crystal state their ratios are not stoicheiometric in most cases because of their three-dimensional structure.[2] The several types of crystal structures of such clathrates have been investigated by *X*-ray methods.[2,3] A cage-type structure is formed when a guest molecule is sufficiently small to be enclosed in a cavity.[4] In a channel-type structure, cyclodextrin molecules are stacked along two-fold axes to form endless channels and guest molecules are enclosed in the channels.[5]

Mössbauer spectroscopy is based on the measurement of an energy gap between a ground state and an excited state of a Mössbauer resonance nucleus. In the case where an internal magnetic field or electric field gradient (e.f.g.) at the position of a Mössbauer resonance nucleus fluctuates at a critical ratio with the inverse of the lifetime of a nuclear excited state, the spectrum is perturbed relative to the limits of fast or slow fluctuation. In the limit of fast relaxation at which e.f.g. tensors are fluctuating at a rate comparable with the inverse of the lifetime of an excited nuclear state, all molecular motions are time-averaged. The slow relaxation of the e.f.g. tensor has been treated theoretically and observed by Gibb[6] for the 1:3 clathrates of bis(η-cyclopentadienyl)iron(II), ferrocene (**1**), and thiourea by Fitzsimmons and Hume[7] for some ionic salts, and by Maeda *et al.*[8] for formylferrocene–α-cyd.

Mössbauer spectroscopy is also available for studying the lattice dynamics of covalent compounds, and has been applied for examining the lattice dynamics of some layered materials.[9] Lattice temperatures and effective vibrating masses, derived from Mössbauer spectra, possess important information for the structure or the packing of clathrates. In this paper the motion of the guest molecules in the cavity and the lattice dynamics of the clathrates were examined for ferrocene–cyclodextrin and some of its ring-substituted derivative–cyd clathrates using the guest molecules as a probe. The guest molecules (η-cyclopentadienyl)(η-methylcyclopentadienyl)iron(II) (**2**), (η-cyclopentadienyl)(η-ethylcyclopentadienyl)iron(II) (**3**), and (η-cyclopentadienyl)(η-formylcyclopentadienyl)iron(II) (**4**) were selected in this study.

Experimental

(*a*) *Preparation of Ring-substituted Derivatives of Ferrocene.*—Ferrocene was recrystallized from methanol; formylferrocene (**4**) (Aldrich Chemical Company, Inc.) was sublimed *in vacuo* at 130 °C and then recrystallized from methanol; (**2**) and (**3**) were prepared according to the method of Benkeser and Bach;[10] acetylferrocene and 1,1′-diacetylferrocene were synthesized using a method described by Rosenblum and Woodward.[11]

(*b*) *Preparation of Clathrates.*—An ethanol solution of the ferrocene derivatives was slowly added to an aqueous solution of cyclodextrin with heating and stirring for 1 h. The solution was filtered and cooled to room temperature. Yellow products precipitated which were filtered off and washed with ethanol. Ethanol–water ratios used in the preparation were changed according to the individual clathrates.

(*c*) *Determination of Guest:Host Ratio.*—Molar ratios of guest:host were determined on the basis of iron contents. Concentrated sulphuric acid (*ca.* 5 cm^3) was added to the clathrates (*ca.* 20 mg). The solution was heated for 6 h, and dilute nitric acid (20 cm^3) was added. The solution was diluted and the iron concentration determined by atomic absorption analysis.

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† *Non-S.I. units employed:* a.m.u. ≈ 1.66×10^{-27} kg, Ci = 3.7×10^{10} Bq, D ≈ 3.34×10^{-30} C m.

Table 1. Guest:host ratios* of the clathrates

Guest molecule	α-cyd	β-cyd	γ-cyd
(**1**)	0.48	1.00	0.36
(**2**)	0.50	0.97	1.00
(**3**)	0.47	1.04	0.97
(**4**)	0.53	0.95	0.49

* Expressed as decimal fractions (guest/host).

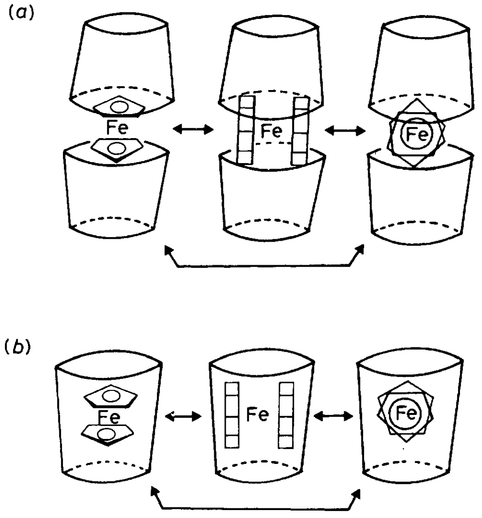

Figure 1. Schematic representations assumed for a ferrocene molecule in (*a*) a α-cyd cavity and (*b*) a β-cyd cavity

(*d*) *Mössbauer Spectroscopy.*—Mössbauer spectra were measured with a constant-acceleration spectrometer described elsewhere.[12] A cobalt-57 source (10 mCi) diffused into palladium foil was used for the absorption measurement. The temperature was monitored with a calibrated copper–constantan thermocouple within a variable-temperature cryostat. The spectra were corrected for the absorption of iron impurity contained in the sample holder and the window of the counter because absorption intensities for the clathrates are very weak at high temperature; the spectra were then fitted by Lorentzian lineshapes using a least-squares method at the Computer Centre, Kyushu University. Isomer shift (δ) values were normalized with respect to the centre of the spectrum of metallic iron at 297 K.

Results and Discussion

Stoicheiometry of the Clathrates.—Guest:host ratios for the clathrates examined in this study are listed in Table 1. The inclusion compounds of *ca.* 1:2 (guest:host) stoicheiometry are prepared for α-cyd clathrates except large guest molecules. The guest molecules may be included in a intermolecular cavity comprising two α-cyd molecules as shown in Figure 1. The molecular diameter of ferrocene (**1**) is *ca.* 0.7 nm and the inner cavity size of α-cyd is *ca.* 0.45 nm, but the size of intermolecular cavity comprising two α-cyd molecules may be larger than 0.45 nm and the softness of molecular vibrations may enable slightly larger guest molecules than the cavity sizes of host molecules to be included. On the other hand, (η-cyclopentadienyl)-(η-hydroxymethylcyclopentadienyl)iron(II), (η-acetylcyclopentadienyl)(η-cyclopentadienyl)iron(II), bis(η-ethylcyclopentadienyl)iron(II), and bis(η-acetylcyclopentadienyl)iron(II) are not included in the cavity of α-cyd although these are included in the cavities of β-cyd and γ-cyd. The cavity sizes of β- and γ-cyd are large enough to include these guest molecules in an intramolecular cavity and 1:1 (guest:host) stoicheiometric inclusion complexes of β-cyd can be prepared. The stoicheiometry for the γ-cyd clathrates is less than 1:1 under the preparation examined in this study because guest molecules are eluted out in a washing process. The cavity size of γ-cyd is so large (0.85 nm) that bonding between guests and hosts may be weak.

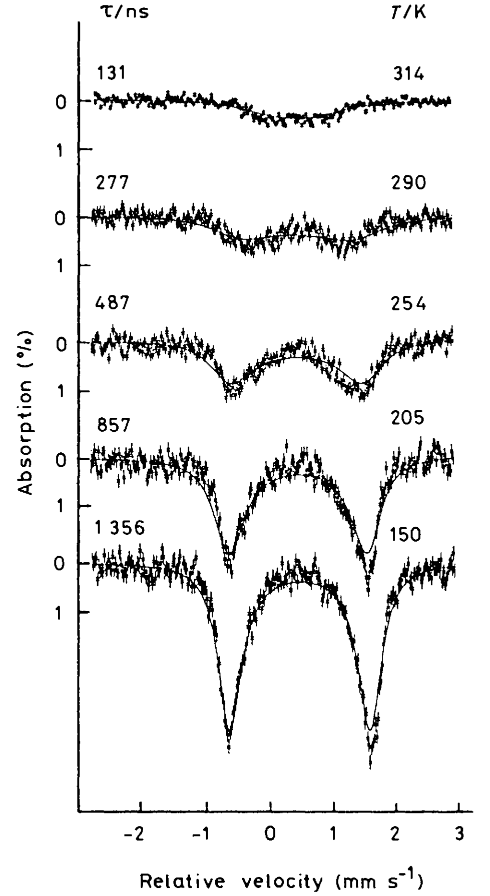

Figure 2. Mössbauer spectra and relaxation times of ferrocene–α-cyd, observed and simulated under the assumption of isotropic relaxation

Reorientation of the Guest Molecules.—It is well known that ferrocene and its ring-substituted derivatives show a quadrupole splitting (Δ) of *ca.* 2.2—2.6 mm s^{-1} which is slightly sensitive to substituents and insensitive to changes in temperature.[13] The main part of the quadrupole splitting in ferrocene arises *via* the removal of electrons from an iron atom into π-bonding orbitals on a cyclopentadienyl ring.[13] The Mössbauer spectra for the clathrates of β- and γ-cyd, except for those with (**4**), show a normal shape with a large quadrupole splitting over the temperature range observed.

The Mössbauer spectra for α-cyd clathrates examined here are anomalous and a representative example is shown in Figure 2. The temperature dependences of the quadrupole splitting are plotted in Figure 3, in which Δ values are calculated by analyzing the spectra as a doublet with two Lorentzian lines. Although the spectra at low temperature (Δ = 2.2—2.3 mm s^{-1}) are characteristic of those of derivatives of ferrocene itself, the splittings become small with rising temperature and finally

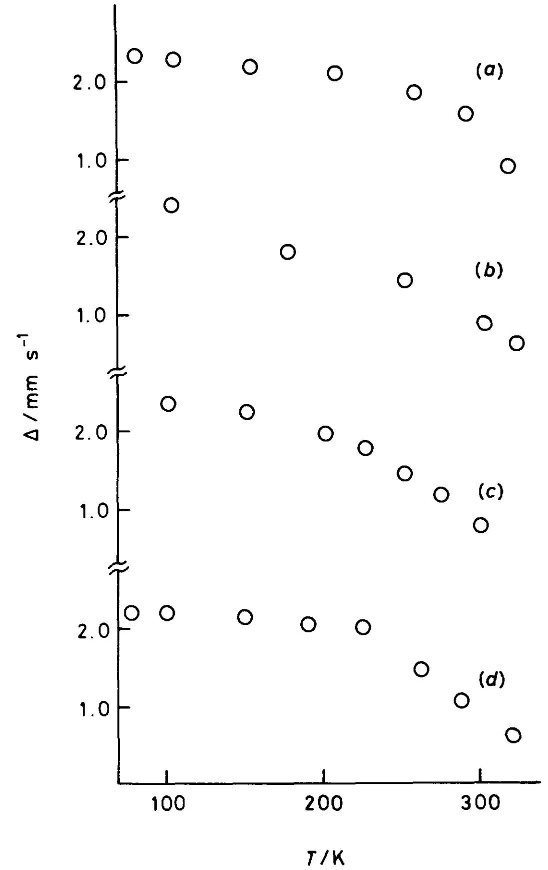

Figure 3. Temperature dependences of quadrupole splitting (Δ) for α-cyd clathrates of (*a*) (**1**), (*b*) (**2**), (*c*) (**3**), and (*d*) (**4**)

all splittings vanish to give a single peak. The temperature dependence of the spectra results in the type of spectra which would arise if the e.f.g. is fluctuating as rapidly as the Mössbauer lifetime (1×10^{-7} s) owing to the reorientation of the molecule. Only a few examples of this effect are known.[6–8] A complete description for such an effect has been given by Gibb[6] for the 1:3 clathrates of ferrocene and thiourea.

Nuclei embedded in a rotating molecule experience a rapidly fluctuating e.f.g. For pure isotropic relaxation in this model Mössbauer lineshape is represented as in equation (1) and

$$G_p = \frac{p + 3W}{p^2 + 3pW + 4a^2} \qquad (1)$$

$\tau = (0.97 \times 10^{-7})\ W^{-1}$, where the transition probability per unit time, W, is identifiable with the transition probabilities for the principal components of the electric field flipping from one to another, p is the population of each molecular orientation, τ the relaxation time, and $a = \Delta/4$. If the relaxation is anisotropic, the reorientation of the principal component of e.f.g. from Z to X, Y has a different relaxation time from a reorientation between X and Y.

Full curves in Figure 2 are the best fit as determined by a least-squares program under the isotropic relaxation for (**2**)–α-cyd. The fit is not very good because of the heterogeneous properties of the guest sites and/or anisotropic relaxation. On the other hand a ferrocenium ion shows a small quadrupole splitting. Ferrocene turns blue when it is oxidized to ferrocenium ion. The colour of the clathrates is unchanged over the range of temperature observed. These results lead to the conclusion that the relaxation of the e.f.g. tensor is caused by the reorientation of guest molecules in the cavity of α-cyd. The small activation energy for reorientation in the cavity is predicted because of the spherical structure of a ferrocene molecule. The Mössbauer spectra of clathrates of ring-substituted ferrocene derivatives of α-cyd give a single peak at room temperature except that (**1**)–α-cyd shows a small quadrupole splitting even at 314 K. The rotational process is sensitive to substituents on an α-cyclopentadienyl ring. There is a report that the introduction of methyl groups sterically hinders the rotational process for (η-cyclohexatriene)(η-cyclopentadienyl)iron(II) hexafluorophosphate derivatives.[7] However, this case is not consistent with expectation. The fact that monosubstituted ferrocene derivative clathrates are more easy to reorientate than a ferrocene clathrate suggests that besides thermal energy, electric dipole interaction between a guest and a host plays some role in the reorientation of a molecule.

Table 2. Activation energies for the molecular reorientation and limiting reorientation lifetime of guest molecules in a α-cyclodextrin cavity and the dipole moment (μ) of the guests

Guest molecule	μ/D	E^a/kJ mol⁻¹	$\tau_0{}^b$/ns
(**1**)	0.00	5.1 ± 1.4	33 ± 17
(**2**)	0.37	4.1 ± 1.4	25 ± 12
(**3**)	0.58	8.8 ± 0.9	5.0 ± 1.7
(**4**)	3.10	11 ± 1	1.8 ± 0.4

[a] Activation energy. [b] Limiting reorientation lifetime.

The system can be specified in terms of activation energy E and relaxation time τ using the Arrhenius plot of $\tau = \tau_0 \exp(-E/RT)$. The activation energies and limiting relaxation times evaluated for the reorientation of the guest molecules are listed in Table 2 together with dipole moments of the guests. These values must be considered to be very approximate because the model is based on so many assumptions; they are given here only to lend some support to the proposed explanation for the observations. The activation energy increases with increase of size of the guest molecules (the size of substitution). A similar result was found for the fluxional molecules $[Fe(CO)_2(\eta^5\text{-}C_5H_5)(R^1R^2C{=}C{=}CR^3R^4)]$.[14] The Gibbs free energy $\Delta G^\ddagger$ for fluxional rotation increases with increasing size of $R^1R^2C{=}C{=}CR^3R^4$. The limiting relaxation time τ_0 is evaluated by extrapolating plots of τ *vs.* $1/T$ to the intercept. It decreases with increase of dipole moment of the guest molecules. On the basis of transition-state theory for chemical reaction, $\tau = (kT/\boldsymbol{h})\exp(-\Delta H^\ddagger/RT)\exp(\Delta S^\ddagger/R)$ is reduced to $\tau = (kT/\boldsymbol{h})\exp(-\Delta H^\ddagger/RT)$, where $\boldsymbol{h}$ is Planck's constant, k is Boltzmann's constant, and R the gas constant, because molecular rotation is a one-molecule process. Therefore, $\tau \approx kT/\boldsymbol{h} \approx 10^{-13}$ s is estimated. However, the values observed are larger than this. Ferrocene molecules which have no dipole moment reorientate in the cavity of α-cyd; this fact supports the following explanation. The reorientation is modulated by thermal excitation but its rate may be affected by the interaction of the dipole moment of the guest molecules with the intermolecular or intramolecular vibrations of the host molecules at limiting temperature, and thus there is no effect from the activation energy barrier, and dipole moment has a significant effect for molecular reorientation.

In practice, it proved difficult to achieve a good fit and the rotational processes are mixed in nature: isotropic rotation and the broad distributions of reorientation rates. The electrostatic atmosphere of the cavity comprising two α-cyd molecules is more spherical (or symmetric) than that of intramolecular cavities of both β- and γ-cyd, which may bring about a low

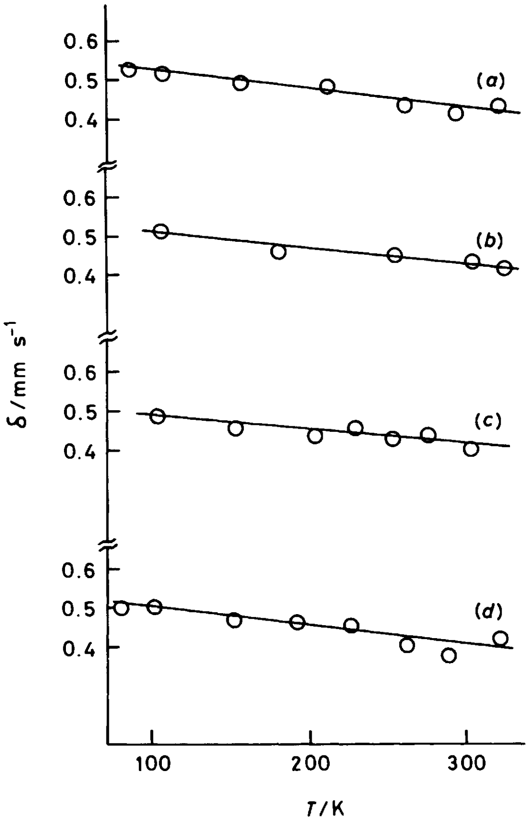

Figure 4. Temperature dependences of isomer shift (δ) for α-cyd clathrates of (*a*) (**1**), (*b*) (**2**), (*c*) (**3**), and (*d*) (**4**)

activation energy for the reorientation of guest molecules in an α-cyd cavity.

The values of activation energy compare with those previously found for other clathrates. For example, values of 18, 1.7—15, and 32 kJ mol^{-1} have been reported for (η-cyclohexatriene)(η-cyclopentadienyl)iron(II) hexafluorophosphate,[7] ferrocene–thiourea,[6] and acetophenone–deoxycholic acid clathrates,[15] respectively.

The spectroscopic behaviour of (**4**) in the cavities of both β- and γ-cyd is abnormal and work on this problem is in progress.

Lattice Dynamics.—In most cases a distribution between intermolecular and intramolecular vibrations is not clear and it is therefore not obvious what is the effective mass. However, the appropriate effective mass is necessary for describing the dynamic behaviour of a Mössbauer atom. A dominant contribution to second-order Doppler shift comes from the intermolecular vibration. Using a Debye model for a solid in the high-temperature limit ($T = \theta_D/2$), the temperature dependence of isomer shift is primarily due to the second-order Doppler shift, and can be evaluated from the Thirring expansion (2). Ignoring all but the term linear in T gives equation (3), where E_γ

$$\delta = \frac{-3E_\gamma kT}{2M_{eff}c^2}\left[1 + \frac{1}{12}\left(\frac{\theta_M}{T}\right)^2 - \frac{1}{720}\left(\frac{\theta_M}{T}\right)^4 + \dots\right] \quad (2)$$

$$M_{eff} = -\frac{3E_\gamma k}{2c^2}\cdot\frac{dT}{d(\delta)} = (-4.168 \times 10^{-2})[d(\delta)/dT]^{-1} \quad (3)$$

is the energy of γ-rays and c the velocity of light.

Table 3. Effective vibrating masses of the clathrates and the guests

Clathrates or guests	$M_{eff}{}^a$/a.m.u.	Range^b T/K	C.c.^{c}
(**1**)	139 ± 19	78—155 (4)	0.977
(**1**) in α-cyd	91 ± 11	78—314 (7)	0.986
(**1**) in β-cyd	113 ± 10	78—275 (8)	0.977
(**1**) in γ-cyd	85 ± 9	78—229 (6)	0.989
(**2**)	116 ± 2	78—224 (7)	0.999
(**2**) in α-cyd	126 ± 14	100—320 (5)	0.977
(**2**) in β-cyd	121 ± 6	78—295 (10)	0.988
(**2**) in γ-cyd	88 ± 9	100—225 (6)	0.974
(**3**)	159 ± 10	78—225 (7)	0.985
(**3**) in α-cyd	122 ± 15	100—300 (8)	0.943
(**3**) in β-cyd	113 ± 9	100—290 (9)	0.982
(**3**) in γ-cyd	104 ± 10	78—180 (7)	0.984
(**4**)	111 ± 9	78—295 (10)	0.990
(**4**) in α-cyd	97 ± 18	78—288 (7)	0.877
(**4**) in β-cyd	90 ± 3	109—325 (9)	0.997
(**4**) in γ-cyd	88 ± 3	78—275 (8)	0.997

[a] Effective vibrating masses calculated from equation (3). [b] The determination of M_{eff} was carried out in the temperature range in which the plot of the data is linear. The number of data observed is given in parentheses. [c] Correlation coefficient of a least-squares calculation for M_{eff}.

Table 4. Lattice temperatures of the clathrates and the guests

Clathrates or guests	θ^a/K	θ′^{b}/K	Range^c T/K	C.c.^{d}
(**1**)	144 ± 10	93 ± 10	78—155 (5)	0.968
(**1**) in α-cyd	139 ± 3	110 ± 8	78—288 (5)	0.998
(**1**) in β-cyd	121 ± 1	86 ± 4	78—225 (5)	0.999
(**1**) in γ-cyd	104 ± 3	85 ± 5	78—229 (6)	0.995
(**2**)	130 ± 3	91 ± 2	78—224 (7)	0.998
(**2**) in α-cyd	121 ± 8	82 ± 7	100—320 (5)	0.970
(**2**) in β-cyd	121 ± 3	77 ± 3	78—295 (10)	0.989
(**2**) in γ-cyd	84 ± 1	67 ± 4	100—250 (7)	0.999
(**3**)	129 ± 2	78 ± 4	78—225 (7)	0.998
(**3**) in α-cyd	132 ± 3	91 ± 7	100—272 (7)	0.994
(**3**) in β-cyd	102 ± 5	73 ± 4	100—290 (7)	0.976
(**3**) in γ-cyd	82 ± 2	61 ± 3	78—180 (7)	0.996
(**4**)	140 ± 4	101 ± 5	78—295 (10)	0.980
(**4**) in α-cyd	146 ± 6	113 ± 13	78—228 (7)	0.980
(**5**) in β-cyd	128 ± 2	102 ± 3	109—176 (5)	0.998
(**5**) in γ-cyd	124 ± 3	100 ± 3	78—225 (7)	0.996

[a] Lattice temperature calculated from equation (6). [b] Lattice temperature calculated from equation (7). [c] The determination of lattice temperatures was carried out in the temperature range in which the plot of the data is linear. The number of data observed is given in parentheses. [d] Correlation coefficient of a least-squares calculation for lattice temperature.

For the purpose of the present discussion, the values of d(δ)/dT observed experimentally are used to calculate the effective vibrating mass (M_{eff}) of the molecular moiety containing an iron atom. Mössbauer spectra were measured in the temperature range 78—320 K to obtain the effective vibrating masses and lattice temperatures for the clathrates. A typical data set is shown in Figure 4 for α-cyd clathrates, for example, in which the data points for (**1**)–α-cyd clathrate yield a slope of -4.58×10^{-4} mm s^{-1} K^{-1}, corresponding to a value of M_{eff} = 91 a.m.u., with a correlation coefficient of 0.986. Effective vibrating masses for other clathrates and guests examined in this study are summarized in Table 3, from which it is seen that the effective vibrating masses of the clathrates are 85—126 a.m.u. These values are in accordance with 111 ± 9 a.m.u. for (**4**), 159 ± 10 a.m.u. for (**3**), 116 ± 2 a.m.u. for (**2**), and 139 ± 19 a.m.u. for (**1**), in contrast to the free-atom value of 57 a.m.u. with d(δ)/dT = -7.305×10^{-4} mm s^{-1} K^{-1}. These excess

Table 5. Lattice temperatures for the host molecules

Clathrates	θ_{host}/K	θ'_{host}/K
α-cyd in (1)–cyd	61 ± 1	48 ± 1
α-cyd in (2)–cyd	55 ± 4	37 ± 3
α-cyd in (3)–cyd	62 ± 2	43 ± 3
α-cyd in (4)–cyd	69 ± 3	53 ± 6
Average for α-cyd	62 ± 5	45 ± 8
β-cyd in (1)–cyd	49 ± 1	35 ± 2
β-cyd in (2)–cyd	45 ± 1	31 ± 1
β-cyd in (3)–cyd	44 ± 2	32 ± 2
β-cyd in (4)–cyd	55 ± 1	44 ± 1
Average for β-cyd	48 ± 3	36 ± 3
γ-cyd in (1)–cyd	41 ± 1	33 ± 2
γ-cyd in (2)–cyd	33 ± 1	26 ± 2
γ-cyd in (3)–cyd	33 ± 1	24 ± 1
γ-cyd in (4)–cyd	50 ± 1	41 ± 1
Average for γ-cyd	40 ± 2	31 ± 3

Table 6. Summary of ^{57}Fe Mössbauer data

Clathrates or guests	δ(78 K)^a/ mm s^{-1}	δ(0 K)^b/mm s^{-1}	Δ(78 K)^c/ mm s^{-1}
(1)	0.557	0.588 ± 0.006	2.45
(1) in α-cyd	0.528	0.571 ± 0.006	2.38
(1) in β-cyd	0.616	0.652 ± 0.006	2.46
(1) in γ-cyd	0.628	0.655 ± 0.007	2.47
(2)	0.521	0.549 ± 0.003	2.40
(2) in α-cyd	0.508	0.532 ± 0.102	2.38
(2) in β-cyd	0.520	0.546 ± 0.004	2.38
(2) in γ-cyd	0.589	0.639 ± 0.009	2.38
(3)	0.497	0.520 ± 0.003	2.34
(3) in α-cyd	0.495	0.522 ± 0.010	2.09
(3) in β-cyd	0.529	0.545 ± 0.007	2.25
(3) in γ-cyd	0.569	0.599 ± 0.006	2.42
(4)	0.513	0.542 ± 0.004	2.22
(4) in α-cyd	0.498	0.541 ± 0.021	2.21
(4) in β-cyd	0.522	0.522 ± 0.002	2.24
(4) in γ-cyd	0.617	0.656 ± 0.003	2.29

[a] Error less than ±0.010 mm s^{-1}. [b] Data obtained from extrapolation of the linear δ *vs.* T plot to the intercept. [c] Error less than ±0.020 mm s^{-1}.

masses for the clathrates reflect the significant covalency in the bonding interaction between an iron atom and its nearest-neighbour atoms. These results indicate that the value of M_{eff} for an appropriate guest molecule is significantly dominated by the chemical bonding in the first co-ordination sphere of an iron atom, and can be used to elucidate the role played by intramolecular bonding forces in the solids. The strong dependence of M_{eff} on the nature of the cavity is a reflection of co-ordination abilities of ferrocene derivatives in the solid state and demonstrates that an iron atom in ferrocene derivatives has active bond orbitals, $d_{x^2-y^2}$ and d_{xy}.

The temperature dependence of a recoil-free fraction has been used to elucidate the role of the intermolecular bonding forces. Using a Debye model for the solid in the high-temperature limit and assuming that the appropriate mass of a probe atom corresponds to the free-atom value, the temperature dependence of the recoil-free fraction, f, is given by equation (4), in which E_R is

$$d(\ln f)/dT = -6E_R/(k\theta_D^2) \qquad (4)$$

the recoil energy after a γ-ray emission, and θ_D is the Debye temperature for the solid lattice. The temperature dependence of the area under a resonance curve can be used to estimate a 'lattice temperature' θ_l based on the thermal motion of a Mössbauer atom. In equation (4), $d(\ln f)/dT$ can be replaced for a thin absorber by $d(\ln A)/dT$, where A is the area under the resonance curve, to yield the relationships (5) and (6), where M is the atomic mass of ^{57}Fe.

$$\theta_l = \frac{E_\gamma}{c}\left\{\frac{-3}{(Mk)\,d\ln[A(T)/A(100)]/dT}\right\}^{\frac{1}{2}} \qquad (5)$$

$$= 11.659\left\{\frac{-d\ln[A(T)/A(100)]}{dT}\right\}^{-\frac{1}{2}} \qquad (6)$$

A limitation of this approach is that when the Mössbauer atom is incorporated in the solids by largely covalent bonding forces the appropriate mass needed to describe its motion may be significantly larger than the atomic mass. Using the M_{eff} values obtained from equation (3) for M in equation (5), a modified lattice temperature θ'_l is calculated as in equation (7).

$$\theta'_l = (4.3202 \times 10^2)\left\{\frac{d(\delta)/dT}{d\ln[A(T)/A(100)]/dT}\right\}^{\frac{1}{2}} \qquad (7)$$

Lattice temperatures for the clathrates were determined over the temperature range of linear δ and $A(T)/A(100)$ *vs.* T plots and are summarized in Table 4. The strength of the intermolecular interaction affects both θ_l and θ'_l. The values for an appropriate guest molecule decrease in the order of α-, β-, and γ-cyd clathrates. Therefore, it is concluded that a guest molecule in a small cavity is bonded more strongly with host molecules than that in a large cavity.

In cases where the guest molecule is an impurity in a host lattice, the relation $(M_{guest}/M_{host})^{\frac{1}{2}} = \theta_{host}/\theta_{guest}$ may be used approximately.[16] Applying this relation to equation (4), the values of θ_{host} are determined to be 62 ± 5, 48 ± 3, and 40 ± 2 K for α-, β-, and γ-cyd, respectively. The values for the individual cases are listed in Table 5. For this calculation the molecular weight used was M_{guest}; if the M_{eff} value is used for M_{guest}, the value of θ_{host} becomes smaller. That the relative values of θ_{host} are in the order α- > β- > γ-cyd is more important than the absolute value of θ_{host}.

Isomer Shift.—The values of δ at 78 K, those evaluated by extrapolation of the linear δ *vs.* T plots to 0 K for the clathrates, and those for guests are collected in Table 6. The δ values for the clathrate increase in the order of α-, β-, and γ-cyd clathrates for an appropriate guest molecule. The effect of secondary Doppler shift is excluded in the values at 0 K. The δ value for the guest molecule is between or near those for the α-cyd and β-cyd clathrates. These systematic variations are also observed in the variation of the value of Δ except for the series of clathrates of (2) (Table 6). This supports the observation that the electronic configuration of a guest molecule is effected by an electrostatic field in the cavity of cyclodextrin, suggesting that guest molecules in the cavity of α-cyd experience positive pressure and guest molecules in the cavities of β- and γ-cyd negative pressure, because positive pressure increases the overlap between the inner *s* shells of an iron atom and the valence orbitals of the ligands, and a decrease of δ with pressure is observed for ferrocene.[17]

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