Elastic and Thermodynamic Properties of Dianin's Inclusion Compounds and Their Guest−Host Interactions

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Single crystals of the 1,6-hexanediol Dianin's clathrate have been studied by Brillouin spectroscopy to obtain its complete elastic tensor. A reevaluation of the elastic constants of the structurally related heptanol Dianin's clathrate is also presented. These results are used to elucidate the microscopic origins of elastic trends within Dianin's system on the basis of guest size, shape, and functionality. The guests cause a reduction in stiffness compared to the clathrand. Decreased stiffness of the c_{33} elastic constant with expansion of cage hydrogen-bonded hexamer rings at the top and bottom of the cages is associated with competitive guest hydrogen bonding. The bulk moduli and linear compressibilities calculated from the elastic tensors are presented and acoustic absorption results are shown to be consistent with thermal conductivity measurements.

1. Introduction

Though the focus of chemistry has classically been the single molecular unit, advances have forced an appreciation of cooperative interactions associated with collections of molecules. Some areas strongly influenced by collective phenomena are solid state reactions, conformational polymorphism, and bulk properties of materials such as the elasticity. The interplay between individual molecular interactions and collective ones is particularly important in mesoscale systems. For example, conformational polymorphism arises from interactions that simultaneously provide optimal molecular and lattice geometries. Control of this phenomenon, one of extreme importance to the pharmaceutical industry, is unlikely to be mastered until the collective interactions of the structurally labile molecules producing the global lattice potential can be understood.

Inclusion compounds, which may be regarded as supramolecular systems, can be used to study collective interactions by systematic perturbation of a known lattice by various guests. Of particular interest are systems where guests are incorporated into cavities created by the assembly of host molecules into a stable, guest-free, framework. Clathrates are inclusion compounds in which a guest is trapped within steric barriers created by a host lattice. Guests and hosts are associated by weak intermolecular forces such as van der Waals, hydrogen bonding, and charge-transfer interactions.[1−3] Dynamic interactions between the guest and host often have been neglected in favor of a more simplified physical picture of noninteracting, interpenetrating lattices.[4,5] However, such guest−host interactions have been shown to significantly affect the physical characteristics of clathrates.[6−8]

The interactions of guests with their host, and the resulting changes in macroscopic physical and chemical behaviors arising from such interactions, are not thoroughly understood. Therefore, the study of collective properties of inclusion compounds with similar structural characteristics allows determination of the contributions that a guest's conformation, size, and functionality make to the bulk properties. Specific interactions can then be quantified and new materials engineered with desired mesoscopic and macroscopic properties. Clathrate systems provide useful vehicles for isolation and study of specific guest−host interactions.[9]

This contribution, part of an ongoing program investigating how microscopic interactions of molecules give rise to bulk (collective) properties, deals with guest−host interactions in Dianin's inclusion compounds. In particular, it examines effects caused by guests with modified functionalities that are selected for their relationships to a previous study of guests in Dianin's clathrates.[10] The modifications are intended to elucidate guest−host interactions that are associated with changes in the clathrates' elastic properties. Elastic properties are of particular interest in molecular crystals because elastic constants may be viewed as representations of "bonding" in these crystals.

Dianin's clathrates are well suited for studying guest−host interactions. The isostructural guest-free clathrand and the large variety of guests that can be enclathrated enable comparative studies where similar guests with small changes in size and functional groups are used.[11,12] Unlike clathrates that do not exist in the guest-free state and whose pure host properties must be inferred, Dianin's clathrand allows for direct observation of the guest's effect on the host.

These systems may be regarded as being midway along a continuum of inclusion compound behavior. At one extreme there are those inclusion compounds, such as the cyclodextrins, where the host, usually a covalently bound moiety, is essentially uninfluenced by guests where the latter do almost all the adaptation to form the complex.[13,14] At the other extreme are inclusion compounds, such as those with urea hosts, where the cage structure cannot form without a guest because specific interaction between host and guest molecules is required, a situation that can lead to "templating" phenomena exhibited by commensurate/incommensurate behavior.[15,16] Between the fixed-cage and template-cage compounds are the labile-cage systems, such as Dianin's inclusion compounds, where the host is able

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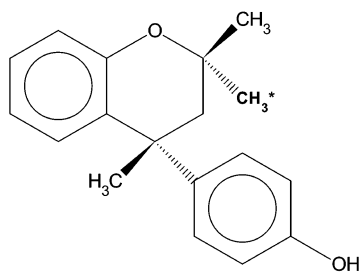† Current address: Pfizer, Kalamazoo, MI.

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Figure 1. 4-(*p*-Hydroxphenyl)-2,2,4-trimethylchroman (Dianin's compound).
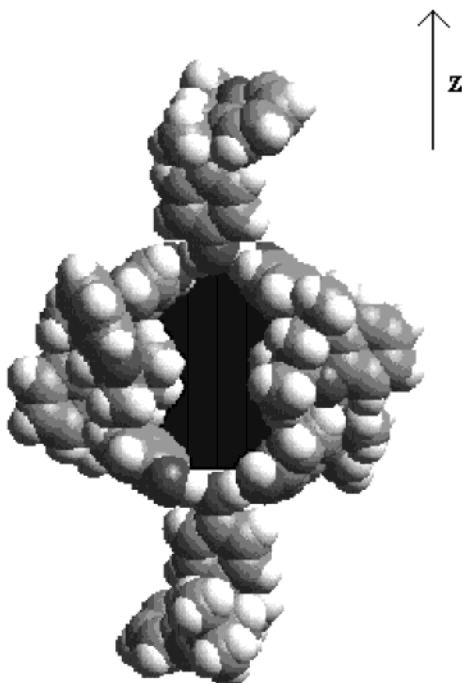

Figure 2. *ac*-plane projection of the supramolecular structure formed by six Dianin molecules. The front and back molecules of a single cage have been removed to show the hourglass shape.

to form a cage independently of a guest that, when present, may be capable of affecting the cage.

Dianin's chroman molecule (Figure 1) forms the Dianin compound's host lattice. Baker et al. established the hydrogen-bonded structure of the host cage and prepared over 50 adducts.[11] Dianin's compound clathrand and all related clathrates for which structures are available crystallize in the trigonal $R\bar{3}$ space group.[12,17−22] The host lattice retains its basic structure except for slight variations in cage size.

In the solid state, six molecules of Dianin's compound form an hourglass-shaped cage (Figure 2). It is held together at the top and bottom by a nearly planar, hydrogen-bonded hexamer ring consisting of six phenolic hydroxyl groups. The latter alternate above and below a given hexamer ring with a cage formed by three Dianin's chroman moieties from the cage's top hexamer ring and three from the cage's bottom hexamer ring. These two different Dianin's chroman groups are of opposite chirality. The methyl group marked by an asterisk in Figure 1 forms the equatorial waist of the cage. Unlike open-channel inclusion compounds, Dianin's compound forms discrete columns of independent cages. The interior of the cage extends ∼11 Å in the crystallographic *c* direction and is ∼6.2 Å across at its widest points ($z \sim 0.3$ and ∼0.7). The waist of the cage ($z \sim 0.5$) is ∼4 Å in diameter.

The stability of the cage, hence the existence of the clathrand, has been attributed to the hydrogen-bonded hexamer ring.[11,12] However, a ^{13}C nuclear magnetic resonance (NMR) study performed on Dianin's clathrand and its xenon clathrate suggests there is disorder in the empty cages resulting from the torsional motion of the flexible parts of the host lattice molecules.[23] Dynamic motion of the cage was also posited to occur in a similar study on Dianin's ethanol clathrate in which two ethanol guests in a single cage interchanged positions between the two cage lobes.[24] Due to ethanol's size, this interchange requires structural lability of the cage and a motion that enlarges its waist.

Recent studies of Dianin's clathrates have attempted to correlate observed physical behavior with the number and type of guests.[10,15,16,20,25−27] Unfortunately, except for the cited urea studies, large structural differences in the guests have made absolute correlation between the type and functionality of the guest and the resulting physical behavior difficult. A recent study of the clathrand and the ethanol and heptanol Dianin's clathrates examined the influence of the guests on the elastic properties of the respective crystals.[10] Because elastic constants may be regarded as descriptors of the "bonding" of a molecular crystal, these quantities were used to describe guest−host interactions. In particular, the role of competitive hydrogen bonding between guest and host molecules was deemed to have an important effect on elastic behavior.

Compared to the clathrand, there is a decrease in stiffness along the crystallographic *c*-axis direction (c_{33}) for the ethanol and heptanol clathrates with the latter exhibiting lower elasticity for this direction. This was attributed to the interaction of the guest's hydroxyl group with the cage's hydrogen-bonded hexamer ring. However, the number of guests and structural differences between the ethanol and heptanol molecules allowed only approximate comparison of the guest−host hydrogen-bond's dependence on the c_{33} elastic constant. Guests with more pronounced hydrophilic or hydrophobic character are required.

A guest closely resembling heptanol, 1,6-hexanediol, has been selected for the study reported here. The hexanediol and heptanol molecules have the same number of heavy atoms in their backbones. With hydroxyl groups at both ends of the molecule, the hexanediol may be expected to afford significantly more hydrogen-bond interaction than the heptanol. Given similar structures within the host, comparison of the heptanol and 1,6-hexanediol inclusion compound elastic constants may be expected to not only test the role of competitive hydrogen-bonding but also provide insight into other properties that may be influenced by the diol functionality.

Prior results found that the c_{11} and c_{12} elastic constants for the ethanol clathrate were larger than those of the clathrand and the heptanol clathrate.[10] This was attributed to the two ethanol molecules occupying most of the cage's volume thereby providing a "buttressing" effect against cage deformation in the *xy*-plane. Transverse *ac* and *bc* plane-polarized acoustic phonon modes were not observed for either the ethanol or heptanol clathrates.[10] A similar effect has been reported for the clathrate hydrates.[28,29] This intensity loss was attributed to attenuation of the transverse modes by optic-acoustic coupling of the guest and host. This conclusion is supported by observation of these modes in Dianin's clathrand Brillouin spectra.[10] Also, thermal conductivity measurements report that the carbon tetrachloride guest does not affect acoustic mode lifetimes.[26] This study also addresses these findings.

The subsequent section delineates specifics of the experiment. The elastic constants, bulk moduli, and linear compressibilities

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TABLE 1: Selected Crystallographic Data for the 1,6-Hexanediol, 1-Heptanol, and Ethanol Dianin's Clathrates and the Clathrand

crystal data	1,6-hexanediol[22]	1-heptanol[19]	ethanol[18]	clathrand[12]
no. of guests	1	1	2	0
crystal system	trigonal	trigonal	trigonal	trigonal
symmetry	$R\bar{3}$	$R\bar{3}$	$R\bar{3}$	$R\bar{3}$
a (Å)	27.185	27.12	26.969	26.965
c (Å)	11.050	11.02	10.990	10.933
α (deg)	90.00	90.00	90.00	90.00
β (deg)	90.00	90.00	90.00	90.00
γ (deg)	120.00	120.00	120.00	120.00
Z (hexagonal)	21	21	24	18
ρ_{calc} (kg/m³)	1217	1210	1223	1165

for the systems studied are then reported and discussed. Finally, acoustic attenuation results are discussed.

2. Experimental Section

Dianin's compound that was synthesized and purified for a prior study was used.[10] No further processing was required. All other chemicals, except water, were obtained from Aldrich Chemical Co.

2.1. Crystal Growth. Saturated solutions at 60 °C of the pure Dianin's compound in 1,6-hexanediol were sealed into the growth chamber and the temperature was raised to 65 °C. The solutions were then cooled to 45 °C at a rate of 1 C° per day. Seed crystals were introduced but the resulting rhomboidal crystals were not defect free. Because defects were mainly located at the crystals' centers, light scattering experiments from selected defect-free volumes were possible. Scattering volumes were optically clear with no grain boundaries, twinning, or intergrowths observed with a polarizing microscope.

Because 1,6-hexanediol (mp = 43 °C) is a solid at room temperature, harvested crystals could be destroyed or the faces rendered unusable by the mechanical stress of the rapidly freezing solvent at room temperature. To prevent this, freshly harvested crystals were held at 70 °C with residual solvent removed by wicking.

Faces were indexed by X-ray diffraction and optical goniometry. The angle between normals to the major faces matched theoretical values within ±0.5°. The major faces of the hexanediol clathrate crystal's morphology were $(3\bar{1}1)$, $(\bar{1}\bar{2}1)$, and $(\bar{2}31)$. The preparation and characteristics of the heptanol Dianin's clathrate crystal have been reported in a prior study.[10]

2.2. Structure. Crystal data (Table 1) show that changes in the host lattice correspond to a guest-dependent variation in the unit cell dimensions and an associated expansion of the cage's hydrogen-bonded, hexamer ring.[12,19,22] Guests are triply disordered around the triad c-axis.

The statistics of the X-ray diffraction for these clathrates, the X-ray density, and the density measured by buoyancy agree on one guest per cage. For the hexanediol guest system our buoyancy measurements yield 1.216 ± 0.005 g/mL, which is within error of the density of 1.217 ± 0.003 g/mL calculated from the X-ray data.[22] Buoyancy measurements for the heptanol guest system yield 1.208 ± 0.005 g/mL, which is within error of the density of 1.210 ± 0.005 g/mL calculated from the X-ray data.[19] This density is also consistent with one guest in each cage.

3. Brillouin Scattering

Brillouin scattering is the coherent Bragg reflection of monochromatic light from propagating fluctuations of the dielectric constant induced by the passage of thermally activated acoustic waves.[30-32] The Brillouin shift equation for an anisotropic medium is given by

$$\Delta\omega_e = \pm\frac{v_e\omega_i}{c}(n_i^2 + n_s^2 - 2n_in_s\cos\theta)^{1/2} \qquad (1)$$

where $\Delta\omega_e$ is the frequency shift of the inelastically scattered light, v_e is the velocity of the observed acoustic phonon, ω_i is the angular frequency of the incident light, c is the speed of light, n_i and n_s are the refractive indices encountered by the incident and scattered light respectively, and θ is the scattering angle.

In the absence of body forces, the spatial variation of stress for an acoustically vibrating medium in a Cartesian coordinate system, r_i, is

$$\rho\left(\frac{\partial^2 u_i}{\partial t^2}\right) = c_{ijkl}\left(\frac{\partial^2 u_l}{\partial r_j\partial r_k}\right) \qquad (2)$$

This relates the dependence of the local (ith) particle's dynamic displacement, u_i, to the elastic constant, c_{ijkl}. In the long wavelength limit, close to the center of the Brillouin zone, the velocity of sound is independent of frequency.[33-35] The plane wave solution of eq 2 yields

$$|c_{ijkl}\hat{q}_j\hat{q}_k - \rho v_e^2\delta_{il}| = 0 \qquad (3)$$

where $\hat{q}_j$ and $\hat{q}_k$ are the direction cosines of the wavevector and ρ is the crystal density. Equation 3 is the Christoffel determinant that relates acoustic mode velocities and directions to the stiffness tensor. Thus, measurement of the velocity of acoustic waves propagating in selected directions in a crystal can be used to determine the elastic constants of the system.

Although Brillouin scattering is based on dynamical waves propagating through a lattice, it does not directly detect the actual dynamics of group or atomic motion. Magnetic resonance techniques must be employed for such determinations.

The elastic constants for Dianin's clathrates obtained in this work were determined by an iterative, least-squares minimization[36] that solves for the elastic constants by reduction of an error vector produced by the difference between the observed and calculated phonon velocities for the specified phonon wavevectors. Because this approach does not rely on propagation of phonons along special directions, experimental errors do not accumulate and ambiguities arising from solving coupled quadratic or cubic equations are eliminated.

3.1. Instrumentation and Measurements. Scattering experiments were performed with a four-circle light scattering apparatus described elsewhere.[37] Free spectral ranges (FSR) of 1.06 cm⁻¹ (31.8 GHz), 1.16 cm⁻¹ (34.8 GHz), and 1.58 cm⁻¹ (47.4 GHz) were employed to eliminate peak-order overlap. Benzene was used as the calibration standard.[38] At least two crystals of each clathrate were used for scattering measurements. All Brillouin spectra were the sum of at least 400, ten-second, Fabry–Perot interferometer scans. A total of at least 50 nonequivalent Brillouin shifts were used. Figure 3 shows a typical Brillouin spectrum for the hexanediol clathrate.

3.2. Refractive Indices. The symmetry of Dianin's clathrates requires a uniaxial optical indicatrix where the crystallographic ab plane is isotropic and the optic axes are parallel to both the crystallographic c-axis and its zonal faces. The principal indices of refraction were determined by sampling the reflectivity of the crystal faces with 514.5 nm light polarized along the crystal faces' principal directions. The refractive index obtained for the

TABLE 2: Elastic, c_{ij}, and Compliance (s_{ij}) Constants for the 1,6-Hexanediol, the 1-Heptanol, and the Ethanol Dianin Clathrates, and the Guest-Free Clathrand[a]

elastic constants [N/m^2] $\times$ 10^{10} ([m^2/N] $\times$ 10^{-10})	1,6-hexanediol	1-heptanol	ethanol[10]	clathrand[10]
c_{11} (s_{11})	0.694 (2.083)	0.684 (2.069)	0.861(1.772)	0.821(1.966)
c_{12} (s_{12})	0.119 (0.120)	0.237 (−0.637)	0.351(−0.0486)	0.298(−0.322)
c_{13} (s_{13})	0.361 (−1.095)	0.283 (−0.564)	0.429(0.651)	0.526(−0.830)
c_{14} (s_{14})	0.074 (−0.466)	0.103 (−0.978)	0.103(−0.729)	0.108(−0.752)
c_{33} (s_{33})	0.726 (2.467)	0.719 (1.835)	0.846(1.840)	1.061(1.765)
c_{44} (s_{44})	0.312 (3.618)	0.285 (4.245)	0.318(3.123)	0.333(3.641)
c_{25} (s_{25})	0.069 (0.434)	0.021 (−0.199)	−0.009(0.068)	0.060(−0.418)
L	1.4%	0.4%	0.2%	0.5%
T_f	10%	4.3%	1.9%	2.6%
T_s	2.6%	2.7%	2.2%	1.2%

[a] Constants are in Voigt notation and reflect an RII trigonal topology. Uncertainty in the elastic constants is 0.009 (N/m^2) $\times$ 10^{10}. The average percent values of the differences between the observed and calculated velocities for the longitudinal (L) and two transverse acoustic modes (T_f, T_s) are presented in the last three rows.
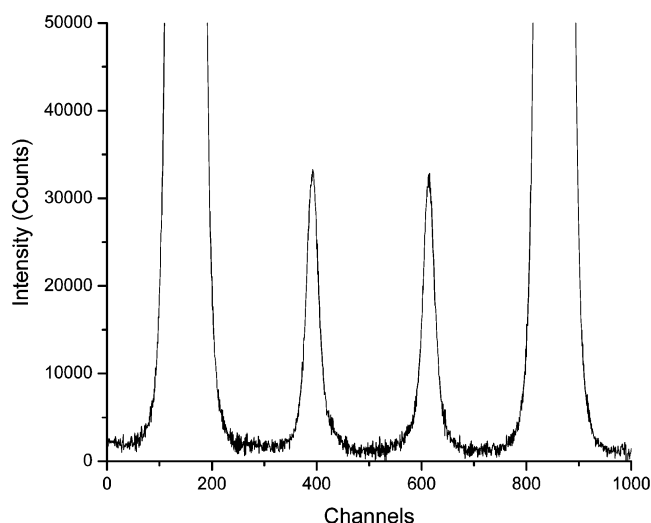

Figure 3. Typical VV polarization Brillouin spectrum of the hexanediol clathrate. The FSR = 1.06 cm^{-1} (31.8 GHz) and the scattering is from the (0.9855, 0.1461, 0.0861) phonon.

hexanediol Dianin's clathrate is, within experimental error, the same for the ordinary and extraordinary ray directions: 1.69.

When incident and scattering polarizations are along the crystal's ordinary direction, the extraordinary beam's cross section is circular[35,39] and Snell's law gives the incident and scattering wave directions propagating within the crystal. Because the refractive indices along the major axis (optic axis) and the minor axes (xy plane) are, within error, the same, the divergence of the ordinary and extraordinary ray is minimal and Snell's law was assumed valid for all scattering angles. Usable (001) faces for c-axis incident scattering were obtained by polishing capping faces with solvent-wetted filter paper.

4. Results and Discussion

4.1. Elasticities. The stiffness constants for the hexanediol and heptanol Dianin's clathrates, along with the average errors of the minimized sound velocities relative to the experimentally determined velocities are presented in Table 2. The elastic constants for Dianin's heptanol clathrate were previously obtained using an expanded set of experimentally determined phonon velocities that had been used formerly.[10] However, to more closely correlate to the methodology used in this work, backscattering measurements from a polished (001) face were obtained and a revised set of elastic constants was calculated. The differences for the two fittings for the c_{11}, c_{12}, c_{14}, c_{15}, c_{44}

and their symmetry related elements are within 9 $\times$ 10^{-3} N/m^2. The differences in c_{11}, c_{12}, and c_{15} fall within the estimated error of the original fitting ($\pm$3 $\times$ 10^{-3} N/m^2), but there is a 35% increase in c_{13} and a 9.8% decrease in c_{33}. The changes in these values do not materially affect previous conclusions but correlate better with results reported here.

Relative velocity errors are similar to those for other organic materials. The errors for the hexanediol clathrate are larger than found for other reported Dianin's clathrates due to the small number of observable transverse modes and the larger error in determining their frequency shifts. As a result, elastic constants that couple to shear strains are likely to be underdetermined.

The Christoffel determinant must be positive definite for every direction of propagation for the two systems studied and it was. This places certain restrictions on the elastic constants: (c_{11} + c_{12})c_{33} > 2c_{13}^2, (c_{11} − c_{12})c_{44} > 2(c_{14}^2 + c_{15}^2), c_{33} > 0, and c_{44} > 0, which were obtained for each elastic constant matrix.[40−42]

Although elasticity is a macroscopic property, it arises from the microscopic collective interactions of the molecular units within the crystal. Thus, in Dianin's system, the elasticity depends on van der Waals interactions, hydrogen bonding, guest−host mechanostructural interactions, and the crystal density. The dependence of the elasticity on any one of these properties may change with the type and direction of the strain response in the clathrate.

A set of stress components applied to the crystal is chosen in such a way that all components of the induced strain, except for one normal component or a pair of shear components, vanish.[42] In this way, the experimentally determined elastic constants can be related to the dynamical picture of the guest−host interaction.

The c_{33} elastic constant, uniquely determined by the [001] phonon, couples the resulting uniaxial strain in the z-direction to a stress applied in that direction. It is sensitive to perturbations that affect cage expansion along the crystallographic c-axis such as inclusion of a guest in Dianin's host lattice especially if the guest is largely oriented along the 3-fold axis of the cage. The c_{33} elastic constants for the two clathrates listed in Table 2 show a decrease in stiffness upon guest inclusion. Previous work[10] on Dianin's heptanol clathrate concluded that the reduction in the c_{33} elastic constant was a direct result of the hydrogen bonding between the heptanol and the hydrogen-bonded, hexamer ring. To test this, a comparison to the hexanediol clathrate, in which the guest can hydrogen bond to both the top and bottom of the cage, and the heptanol clathrate is appropriate.

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TABLE 3: Density and c_{33} and c_{44} Elastic Constant Changes for Selected Dianin's Clathrates[a]

guest	density (kg/m^3)	ΔC %	$10^{10}c_{33}$ (N/m^2)	ΔC %	$10^{10}c_{44}$ (N/m^2)	ΔC %
none	1162	0	1.061	0	0.333	0
ethanol	1223	5.25	0.846	−20.3	0.318	−4.50
heptanol	1210	4.13	0.719	−32.2	0.285	−14.4
hexanediol	1217	4.73	0.726	−31.6	0.312	−6.31

[a] ΔC % represents the percent increase or decrease from the clathrand values.

There is a 1% increase in stiffness in c_{33} for the hexanediol clathrate compared to the heptanol clathrate. The c-axis unit cell length for the heptanol clathrate is 0.4% greater than that of the hexanediol clathrate. Though there is little difference in the overall length of the cages, there is a 2.6% increase in the oxygen−oxygen atom separation in the hydrogen-bonded, hexamer ring for the heptanol clathrate over the hexanediol clathrate, and the distances of the two hydrogen-bonds between the hydroxyl groups on the hexanediol and the hexamer ring are shorter than the hydrogen-bond distance between heptanol's hydroxyl group and the hexamer ring. Also, the heptanol guest occupies a volume of 139.7 Å^3, whereas that of the hexanediol is 132.0 Å^3.[43] The increase in the oxygen atom separation in the hexamer ring for the heptanol clathrate is attributed to the influence of the bulkier terminal methyl group on the heptanol guest. The decrease in this distance in the hexanediol clathrate can also be viewed as an induced contraction of the hexamer ring by the hexanediol hydroxyl groups, which are slightly below (above) the ring and thus may attract the protons that comprise it. Thus, in comparing these two clathrates, the larger c_{33} elastic constant for the heptanol clathrate can be attributed to interactions involving guest influence of the hydrogen bonding of the hexamer ring.

If the c_{33} elastic constant for Dianin's clathrates solely depended on the expansion of the waist of the cage, the values for the heptanol and hexanediol clathrate would be expected to be the same.[22] Therefore, the stiffness along the z-axis in Dianin's cage apparently depends on the disruption of the hydrogen-bonded hexamer ring, the expansion of the cage waist, and motion of the guest(s) in the cavity.

Because the c_{33} and c_{44} elastic constants can be calculated independently, they do not depend on other elastic constants. Thus, the effect of the crystal density (see eq 3) can be directly considered. Table 3 shows the density and values of c_{33} and c_{44} for Dianin's two clathrates. The percentage changes from the clathrand values are also given. It is immediately apparent that the change in density cannot account for the lowering of either elastic constant with respect to the clathrand. The densities automatically account for the guest occupancies.

The c_{44} elastic constant (c_{yzyz}) measures resistance to shear deformation in the yz plane induced by passage of y-polarized transverse sound waves propagating in the z-direction.[30,42] Thus, it is sensitive to interactions both parallel and perpendicular to the z-axis. Compared to that for the clathrand, the c_{44} elastic constants for the hexanediol (6.3% lower), and heptanol (14% lower) clathrates mirror the trend of the c_{33} elastic constants. The shape of the guests is expected to play an important role here. A yz-shear would induce strain in a rodlike guest and create resistance to the cage's motion along the entire length of the cage.

Except for c_{33} and c_{44}, the elastic constants are coupled, making independent analysis difficult. For these, disruption of the hydrogen-bonded hexamer ring by guests causes a reduction in the systems' stiffness. The included volumes in the cavity

TABLE 4: Bulk Modulus and Linear Compressibilities of Dianin's Clathrates and Clathrand

guest	$10^9 B_s$ (N/m^2)	$10^{10}\beta_{xx}$	$10^{10}\beta_{yy}$	$10^{10}\beta_{zz}$
none[51]	5.58	0.844	0.844	0.106
ethanol[51]	5.53	0.634	0.634	0.539
heptanol	4.09	0.868	0.868	0.707
hexanediol	4.01	1.11	1.11	0.276

and at the waist of the cage also reduce the stiffness but have less effect on the elasticity for nonshear strains. Thus, the elastic response to shear strain is mostly dependent on the shape and size of the guest.

4.2. Bulk Modulus and Linear Compressibility. In the previous discussion, the elastic constants were treated as independent parameters that couple the strain of the clathrate crystal to a stress in a given direction. Alternative analysis involves the comparison of thermodynamic parameters, the adiabatic bulk modulus and linear compressibilities calculated from the experimentally determined elastic constants. The bulk modulus is

$$B_s = [\sum_{ij}^{3} s_{ijkl}]^{-1} \qquad (4)$$

where s_{ijkl} is an element of the compliance tensor.[42] It is the ratio of the applied hydrostatic pressure to the resultant fractional change in volume. The bulk moduli for the clathrand and the two clathrates (Table 4) follow the trend in the reduction in the c_{33} stiffness constants.

The linear compressibility, β, is defined as the relative decrease in the length of a line under unit hydrostatic pressure.[42] It is related to the compliance tensor by

$$\beta = s_{ijkl}\hat{q}_i\hat{q}_j \qquad (5)$$

The clathrand shows the smallest linear compressibility along the z-axis and has the highest bulk modulus. This reinforces the observation that inclusion of axial guests in a Dianin's cage weakens the lattice in the z-direction.

The heptanol and hexanediol guests increase the linear compressibility in the xy-plane. The inclusion of a CH$_2$ group at the center of Dianin's cage should increase the stiffness, i.e., lower compressibility in the x- and y-directions. Thus, the increased linear compressibility due to the inclusion of rod-shaped guests may result from a weakening of the hydrogen-bonded hexamer ring and the elongation of the cage in the crystallographic c-direction in these clathrates.

4.3. Acoustic Absorption. In an ideal crystal, acoustic waves propagate without attenuation of their amplitude such that standing waves in the lattice are formed. In molecular crystals, structural defects such as lattice vacancies, dislocations, and solvent inclusions act as traps for the propagation of acoustic energy through the lattice.[44] In inclusion compounds and other orientationally disordered systems, translational−rotational coupling between the guest and host can also transfer acoustic energy to optical modes.[45]

Experimentally, the absorption coefficient, α, is determined from acoustic phonon line widths by

$$\alpha = \frac{\Gamma(\text{FWHM})}{v_e} \qquad (6)$$

where v_e is the velocity of the acoustic phonon and Γ(FWHM)

is the full width at half-maximum of the phonon line normalized to the width of the Rayleigh line.[46−49]

The clathrand has the least anisotropy for the acoustic absorption in the *xz*-plane,[50] whereas the ethanol and heptanol clathrates display increasing FWHM with increasing scattering angles in the *ac(xz)*-plane. Because the acoustic absorption coefficients, α_{11}, for the *x(a)*- and *y(b)*-axes of the ethanol and heptanol clathrates and the clathrand are, within error, the same, any change in thermodynamic phenomena that correlates to acoustic-phonon propagation lifetimes in these systems should be primarily dependent on changes in the acoustic absorption, α_{33}, along the *z(c)*-axis. The ethanol clathrate's acoustic absorption along the *z(c)*-axis increases by 47% over the clathrand. This agrees with thermal conductivity measurements that report a 50% decrease in thermal conductivity for the ethanol clathrate from that of the clathrand.[27] Due to the crystal morphology of the hexanediol clathrate, pure *ac(xz)* and *bc(yz)* phonons could not be measured and no comparison can be made.

The Brillouin spectra of Dianin's ethanol and heptanol clathrates in the *xz*- and *yz*-planes lack transverse mode intensity[50] However, the corresponding clathrand spectra exhibit such intensity. Thus, transverse mode attenuation has been attributed to guest inclusion.[10] The complete attenuation of transverse mode intensity has also been observed in Brillouin studies of clathrate hydrates.[28] In both these studies, it was posited that the transverse (shear) modes were attenuated by translational-rotational coupling to the disordered guests.

5. Conclusions

Dianin's clathrates and its clathrand provide a unique system of study in which guests of varying size, shape, and functionality can be incorporated into nearly isostructural host lattices. With asymmetric guest substitution, microscopic differences between guests can be associated with macroscopic physical properties. Recent studies on Dianin's inclusion compounds have correlated both lattice structure and guest properties to physical phenomena.

In Dianin's clathrates, the guest affects the elasticity on the basis of its size, shape, and ability to hydrogen bond to the hexameric ring at the top and bottom of the cage. The elastic properties of the systems that have been studied show a general decrease in stiffness upon guest inclusion. For uniaxial strain in the *z*-direction induced by a stress in that direction, these systems show that the rod-shaped guests, heptanol and hexanediol, create the large decreases in stiffness.

Because the elasticity of the lattice is closely related to the lattice potential, the variance of the elastic constants with different guests shows that the contents of Dianin's cage measurably influences the intermolecular interactions of the molecules forming the supramolecular structure. This effect is less clear from the structural data and shows that measurement of quantities that relate to the energetics of the supramolecular interactions is an effective approach to understanding these systems.

Because the hexameric ring expansion is also related to the competitive hydrogen bonding from the heptanol and hexanediol guests, comparison between these two guests showed that functionality is important. Further studies involving such guests as 1,5-pentenediol and octane should be done to compare the guest length and functionality.

This study has demonstrated that the elasticities and hence various thermodynamic properties of inclusion compounds can be directly related to the microscopic behavior of guests within the host lattice. Therefore, structural variances within the host lattice influence the collective properties of the supramolecular system.

The size and nature of the included guests render lattice dynamical calculations difficult and, to date, it has not been possible to develop potentials adequate for description of these systems. However, acoustic phonons can only be the result of intermolecular interactions and the results of this investigation should prove useful in testing any potentials that may be developed for these inclusion compounds.

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