Investigations of the Phase Transitions in Thiourea Inclusion Compounds with Cycloheptane, Cyclooctane, and Cyclooctanone

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Variable temperature single-crystal X-ray diffraction and solid-state NMR experiments have been performed on the thiourea cycloheptane (TC7), cyclooctane (TC8), and cyclooctanone (TCO8) inclusion compounds. Three different phases have been evidenced for TC7 and four for TC8, while only one phase change at high temperature has been found for TCO8. At room temperature, the cyclooctane and cycloheptane adducts exhibit the classical rhombohedral lattice (space group $R\bar{3}c$). In these structures, the well-resolved host thiourea structure is composed of one-dimensional nonintersecting channels running along the *c* axis. The guest molecules, located in the center of the channels, are highly disordered as confirmed by the solid-state ^{13}C NMR spectra. Lowering temperature leads to a monoclinic phase resulting from the distortion of the room-temperature lattice where the guest molecules still have some degrees of disorder. Refinement has been performed with a model involving two cycloalkane rings. For TC8, a supplementary phase with a doubling of the *b* axis is observed below 200 K, having two apparently ordered cyclooctane rings with the same conformation. The cyclooctanone adduct, TCO8, is already monoclinic at room temperature with an ordered guest molecule stabilized within the thiourea channels by a hydrogen bond. Upon heating, a phase change can be detected by solid-sate NMR and X-ray powder diffraction just before decomposition.

Introduction

Thiourea is known from 1947 to form inclusion compounds with a variety of organic guest molecules.[1,2] The host lattice of these adducts was first described by Hermann[3] and Lenné[4] who found a structure made of hexagonal channels with an approximate diameter of 6.1 Å. These channels can accommodate small molecules such as CCl_4,[5] chloroform, larger molecules such as the long-branched hydrocarbons,[6,7] cycloalkanes,[8−10] some substituted aromatic ring systems,[11,12] and even some organometallic compounds.[13−15]

Thiourea inclusion compounds have attracted a great deal of interest for their structural similarities to the zeolite. For example, the aluminophosphate $AlPO_4$-5 has the same one-dimensional pore system[16] running in parallel ("AFI" network) as found in urea and thiourea inclusion compounds. Within these channels, it is possible to adsorb small molecules such as linear alkanes in specific locations, in a similar way to that observed in thiourea inclusion compounds. From the variable dimensions along the direction of the channels, the thiourea lattice might be best regarded as a cage-type rather than as a channel-type host lattice.[17]

The inclusion compounds of thiourea have been widely studied for the properties displayed by the guest molecules in their inclusion environment. The behavior of the guest molecules trapped in the thiourea host matrix can be rather different from that found in the liquid or in the solid state. For example, the halogenocyclohexane molecules, which are known to preferably

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(1) Angla, B. *C. R. Acad Sci., Paris* **1947**, *224*, 402.

(2) Angla, B. *C. R. Acad Sci., Paris* **1947**, *224*, 1166.

(3) Hermann, C.; Lenné, H. U. *Die Naturwissenschaften* **1952**, *10*, 234.

(4) Lenné, H. U. *Acta Crystallogr.* **1954**, *7*, 1.

(5) Fait, J. J.; Fitzgerald, A.; Caughlan, C. N.; McCandless, F. P. *Acta Crystallogr.* **1991**, *C47*, 332.

(6) Takemoto, K.; Sonoda, N. In *Inclusion Compounds*; Atwood, J. L., Davies, J. E. D., MacNicol, D. D., Eds; Academic Press: London, 1984; Vol. 2, Chapter 2, pp 47−67.

(7) Harris, K. D. M. *J. Mol. Struct.* **1996**, *374*, 241.

(8) Clément, R.; Jedougez, J.; Mazières, C. *J. Solid State Chem.* **1974**, *10*, 46.

(9) Poupko, R.; Furman, E.; Müller, K.; Luz, Z. *J. Phys. Chem.* **1991**, *95*, 407. Clément, R.; Mazières, C.; Gourdji, M.; Guibé, L. *J. Chem. Phys.* **1977**, *67*, 5381.

(10) MacIntosh, M. R.; Fraser, B.; Gruwel, M. L. H.; Wasylishen, R. E.; Cameron, T. S. *J. Phys. Chem.* **1992**, *96*, 8572.

(11) Penner, G. H.; Polson, J. M.; Stuart, C.; Ferguson, G.; Kaitner, B. *J. Phys. Chem.* **1992**, *96*, 5121.

(12) Shindo, T.; Shindo, M.; Ohnuma, H.; Kabuto, C. *Bull. Chem. Soc. Jpn.* **1993**, *66*, 1914.

(13) Tam, W.; Eaton, D. F.; Calabrese, J. C.; Williams, I. D.; Wang, Y.; Anderson, A. G. *Chem. Mater.* **1989**, *1*, 128.

(14) Lowery, M. D.; Wittebort, R. J.; Sorai, M.; Hendrickson, D. N. *J. Am. Chem. Soc.* **1990**, *112*, 4214.

(15) Heyes, S. J.; Clayden, N. J.; Dobson, C. M. *J. Phys. Chem.* **1991**, *95*, 1547.

(16) Bennet, J. M.; Cohen, J. P.; Flanigen, E. M.; Pluth, J. J.; Smith, J. V. *Am. Chem. Soc. Symp. Ser.* **1983**, *218*, 109.

(17) Hollingsworth, M. D.; Harris, K. D. M. *Comprehensive Supramolecular Chemistry*; MacNicol, D. D., Toda, F., Bishop, R., Eds.; Pergamon: New York, 1996; Vol. 6, pp 177−237.

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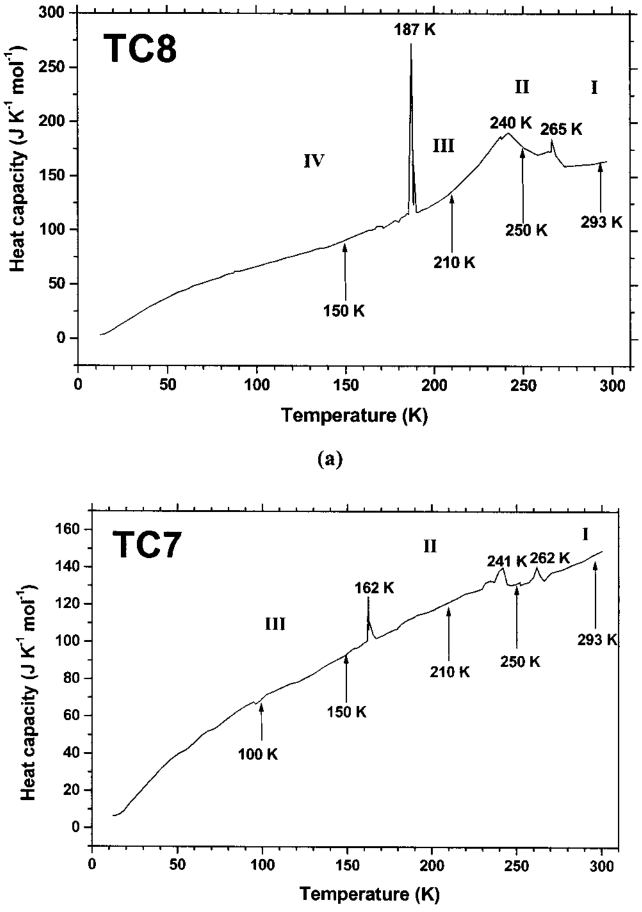
adopt the equatorial conformation in the liquid and vapor phase, are in the axial conformation at low temperature in their inclusion compounds with thiourea.[18−20] The ring inversion of substituted cyclohexanes and similar cycloalkanes systems included in thiourea[19,21−23] have been investigated using solid-state NMR techniques. Second harmonic generation has been observed for organometallic guests with a high molecular second-order hyperpolarizability.[13] Many of these guest molecules are not able to display this property in their crystal structure.

At room temperature, most of the thiourea clathrate structures reported to date have a rhombohedral lattice corresponding to a host:guest ratio of 3:1. In these adducts, the guest molecules are located on sites of high symmetry, where the channel diameter is larger, and they generally exhibit considerable orientational disorder. X-ray single-crystal experiments on thiourea inclusion compounds are generally difficult to perform; a few crystal structures of thiourea adducts are reported in the Cambridge Structural Database. The high disorder of the guest molecule makes structural analysis at room temperature complicated, and if a phase change occurs when lowering the temperature, attempts to cool a single crystal of the rhombohedral form through the phase change often lead to transformation twinning.

In this paper we have investigated the thermal behavior of the thiourea cyclooctane (TC8), cycloheptane (TC7), and cyclooctanone (TCO8) inclusion compounds by variable temperature single-crystal X-ray diffraction over a wide temperature range, complemented by solid-sate ^{13}C NMR experiments. Phase changes on the thiourea cyclooctane and thiourea cycloheptane inclusion compounds were first reported by Cope, Gannon, and Parsonage[24] from heat capacity measurements (Figure 1). They found for TC8 a weak peak at 265 K (attributed possibly to a ferroelectric transition), a sharp phase change at 187 K, and more surprisingly, a large signal maximum at 240 K. From the high molar enthalpy associated with this last phenomenon, the possibility of an order−disorder phase transition was excluded and it was suggested that the cyclooctane ring was involved in conformational changes. No such signal was observed for TC7 but small peaks were detected at 162, 241, and 262 K.

Clément et al.[8] have also investigated the thermal behavior of these inclusion compounds by differential thermal analysis (DTA) measurements and X-ray photography. For the cyclooctane adduct, these authors reported a sharp phase change detected with DTA at 186 K. A symmetry change has also been observed from the X-ray exposures at 268 K where the rhombohedral room-temperature phase is transformed into a monoclinic structure. Decreasing the temperature resulted in a distortion of the crystal lattice, until 213 K where new reflections appeared. Below this temperature, the film was indexed with the same basic monoclinic cell but with a doubled *b* axis. Only one phase change, similar to the first one observed for TC8, was reported for the cycloheptane adduct at 238 K.



(a)

(b)

Figure 1. Heat capacity curves for (a) TC8 and (b) TC7 from Cope, Gannon, and Parsonage.[24] The indicated temperatures refer to the cell lattice or the crystal structure determinations as reported in Tables 2 and 3.

Experimental Section

Sample Preparation. The clathrates were prepared by adding the guest molecule to a solution of thiourea in methanol or ethanol. Starting materials were purchased from Lancaster Synthesis Ltd. and used without further purification. Heating followed by a slow evaporation of the solution gives needlelike or prismatic hexagonal crystals. The crystals were filtered from the mother liquor and washed with methanol. Elemental analysis results are consistent with a host:guest ratio of 3:1, as is usually found in many of these clathrates (calc/exp: thiourea cyclooctane $C_{11}H_{28}N_6S_3$: C, 38.80/38.21; H, 8.29/8.35; N, 24.70/24.71; S, 28.24/30.01. thiourea cycloheptane $C_{10}H_{26}N_6S_3$: C, 36.78/36.38; H, 8.04/8.03; N, 25.74/25.83; S, 29.46/31.20. thiourea cyclooctanone $C_{11}H_{26}N_6S_3O$: C, 37.26/37.45; H, 7.36/7.40; N, 23.70/24.21; S, 27.13/26.98). Purity of the samples was checked by indexation of the powder X-ray diffraction patterns recorded over the 2θ angular range 3°−70° on a Philips PW1729 diffractometer using Cu Kα radiation.

Single-Crystal X-ray Diffraction. The cell dimensions were measured in the range 290−120 K from a single plate exposure on an Enraf-Nonius DIP2020 imaging plate diffractometer equipped with an Oxford Cryosystems CRYOSTREAM cooler and using Mo Kα radiation. Details for the data collection for the different crystal structure determinations are

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(18) Harris, K. D. M.; Thomas, J. M. *J. Chem. Soc., Faraday Trans.* **1990**, *86*, 1095.

(19) Müller, K. *Magn. Reson. Chem.* **1995**, *33*, 113.

(20) Jones, M. J.; Shannon, I. J.; Harris, K. D. M. *J. Chem. Soc., Faraday Trans.* **1996**, *92*, 273.

(21) Müller, K. *Magn. Reson. Chem.* **1992**, *30*, 228.

(22) Müller, K. *J. Phys. Chem.* **1992**, *96*, 5733.

(23) Harris, R. K.; Nordon, A.; Harris, K. D. M. *Magn. Reson. Chem.* **1999**, *37*, 15.

(24) Cope, A. F. G.; Gannon, D. J.; Parsonage, N. G. *J. Chem. Thermodyn.* **1972**, *4*, 829.

Table 1. Data Collection Parameters for TC7, TC8, and TCO8

	TC7 at 293 K	TC7 at 150 K	TC8 at 293 K	TC8 at 210 K
space group	$R\bar{3}c$	$P2_1/c$	$R\bar{3}c$	$P2_1/c$
wavelength (Å)	1.5418	1.5418	1.5418	1.5418
crystal dimension (mm^3)	0.2 × 0.2 × 0.8	0.2 × 0.2 × 0.8	0.13 × 0.13 × 0.5	0.1 × 0.3 × 0.6
a (Å)	16.012(2)	12.406(8)	16.225(2)	12.465(5)
b (Å)	16.012(2)	15.535(8)	16.225(2)	15.555(7)
c (Å)	12.447(2)	10.140(9)	12.488(4)	10.392(4)
β (deg)	90	114.27(3)	90	113.99(3)
V (Å^3)	2763.7(7)	1782(2)	2847(1)	1841(1)
Z	6	4	6	4
calc density (g cm^{-3})	1.280	1.217	1.192	1.229
μ (mm^{-1})	3.8	3.8	3.54	3.7
range	$-20 \leq h \leq 1$	$-2 \leq h \leq 15$	$-1 \leq h \leq 20$	$-15 \leq h \leq 15$
	$0 \leq k \leq 17$	$-19 \leq k \leq 19$	$-1 \leq k \leq 20$	$-1 \leq k \leq 19$
	$-5 \leq l \leq 15$	$-11 \leq l \leq 1$	$-15 \leq l \leq 15$	$-1 \leq l \leq 12\leq$
	$2.2 \leq \theta \leq 74.3$	$2.2 \leq \theta \leq 74.3$	$2.2 \leq \theta \leq 74.3$	$2.2 \leq \theta \leq 74.3$
measured reflections	744	3982	2466	4663
unique reflections	667	3732	1309	3651
merging R factor	0.03	0.010	0.0344	0.0335
observed reflections	524	2927	923	2947
no. of parameters	22	236	23	227
residual density (e Å^{-3})	$-0.59 \leq \rho \leq 0.51$	$-1.10 \leq \rho \leq 1.01$	$-0.91 \leq \rho \leq 1.07$	$-0.54 \leq \rho \leq 0.64$
R	0.0827	0.0765	0.0922	0.0573
R_w	0.1080	0.0944	0.1090	0.0673

	TC8 at 150 K	TCO8 at 293 K	TCO8 at 280 K	TCO8 at 120 K
space group	$P2_1/c$	$P2_1/c$	$P2_1/c$	$P2_1/c$
wavelength (Å)	0.71069	1.5418	1.5418	1.5418
crystal dimension (mm^3)	0.1 × 0.3 × 0.6	0.2 × 0.3 × 0.6	0.16 × 0.19 × 0.8	0.16 × 0.19× 0.8
a (Å)	12.4160(6)	12.2365(15)	12.219(7)	12.0830(14)
b (Å)	30.9180(13)	15.631(2)	15.6205(7)	15.518(2)
c (Å)	10.3710(5)	10.3603(13)	10.3555(14)	10.2930(14)
β (deg)	113.848(3)	111.82(2)	111.82(1)	111.77(1)
V (Å^3)	3641.3(3)	1839.7(4)	1834.9(1)	1792.3(4)
Z	8	4	4	4
calc density (g cm^{-3})	1.243	1.280	1.284	1.314
μ (mm^{-1})	0.39	3.8	3.8	3.9
range	$-14 \leq h \leq 14$	$-15 \leq h \leq 0$	$-15 \leq h \leq 14$	$-15 \leq h \leq 14$
	$0 \leq k \leq 35$	$-19 \leq k \leq 0$	$-19 \leq k \leq 1$	$-19 \leq k \leq 1$
	$0 \leq l \leq 11$	$-11 \leq l \leq 12$	$-1 \leq l \leq 12$	$-1 \leq l \leq 12$
	$0 \leq \theta \leq 26.6$	$2.2 \leq \theta \leq 74.3$	$2.2 \leq \theta \leq 74.3$	$2.2 \leq \theta \leq 74.3$
measured reflections	12055	4068	4835	4718
unique reflections	5499	3741	4005	3901
merging R factor	0.0490	0.040	0.040	0.050
obs reflections	3703	3428	3636	3798
no. of parameters	361	191	191	191
residual density (e Å^{-3})	$-0.33 \leq \rho \leq 0.45$	$-0.65 \leq \rho \leq 0.67$	$-0.80 \leq \rho \leq 0.38$	$-0.42 \leq \rho \leq 0.42$
R	0.0432	0.0680	0.0354	0.0380
R_w	0.0545	0.0750	0.0436	0.0434

given in Table 1. Room-temperature data sets for all the clathrates were measured using an Enraf-Nonius CAD-4 diffractometer with Cu Kα radiation. Data collection for the lower temperature phase of TC8 was performed on the DIP2020 diffractometer at 150 K. After a slow decrease of the temperature, a full data set was collected by the rotation method; 90 frames were recorded with 2° of rotation per frame. Indexing and scaling of the reflections were performed using the HKL suite programs.[25] Low-temperature data sets for TC7 and TCO8 were collected on an Enraf-Nonius MACH-3 diffractometer equipped with Cu Kα radiation and using the same cooling device.

Structures were solved by direct methods with SIR92[26] or SIR97.[27] Hydrogen atoms were placed geometrically and allowed to ride on the atom to which they were bonded. Crystal structure refinements were carried out with CRYSTALS.[28] Atomic scattering factors were taken from *International Tables for Crystallography*".[29] A three coefficients Chebychev polynomial weighting scheme[30] was applied. Molecular and packing diagrams were performed using the drawing package CAMERON.[31] Atomic coordinates, anisotropic displacement parameters, bond distances and angles, and intermolecular contacts and hydrogen bonds are available in the Supporting Information.

Solid-State NMR. Solid-state ^{13}C NMR spectra were recorded on a CMX200 infinity spectrometer operating at a frequency of 50.305761 MHz for ^{13}C. Samples were packed in 7.5-mm zirconia rotor and spun at a frequency between 3 and 5 kHz using a double-resonance MAS probe. Variable temperature experiments were performed by passing cooled or heated nitrogen gas over the sample. Typically, between 100 and 150

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(25) Otwinoswki, Z.; Minor, W. Processing of X-ray Diffraction Data Collected in Oscillation Mode. In *Methods Enzymol*; C. W. Carter, R. M. Sweet, Eds.; Academic Press: London, 1997; Vol. 276.

(26) Altomare, A.; Cascarano, G.; Giacovazzo, C.; Guagliardi, A.; Burla, M. C.; Camalli, M. *J. Appl. Crystallogr.* **1994**, *27*, 435.

(27) Altomare, A.; Cascarano, G.; Giacovazzo, C.; Guagliardi, A.; Moliterni, A. G. G. *SIR97, A package for crystal structure solution by direct methods and refinement*; Istituto di Ricerca per lo Sviluppo di Metodologie Cristallografiche, CNR, c/o Dipartimento Geomineralogico, Campus Universitario: Bari, Italy, 1997.

(28) Watkin, D. J.; Prout, C. K.; Carruthers, J. R.; Betteridge, P. W. *CRYSTALS Issue 10*; Chemical Crystallography Laboratory: Oxford, U.K., 1996.

(29) Wilson, A. J. C. *International Tables for Crystallography*; Kluwer Academic Publishers: Dordrecht, 1995.

(30) Carruthers, J. R.; Watkin, D. J. *Acta Crystallogr.* **1979**, *A35*, 698.

(31) Watkin, D. J.; Prout, C. K.; Pearce, L. J. *CAMERON*; Chemical Crystallography Laboratory: Oxford, U.K., 1996.

Table 2. Unit Cell Lattice Parameters for TC8

T (K)	*a* (Å)	*b* (Å)	*c* (Å)	α (deg)	*β* (deg)	*γ* (deg)
293	16.225(2)	16.225(2)	12.488(4)	90	90	120
250	32.25(3)	32.25(3)	12.49(1)	90	90	120
220	12.48(1)	15.69(2)	10.30(1)	90	114.12(5)	90
210	12.52(1)	15.71(2)	10.45(1)	90	114.07(5)	90
200	12.57(1)	31.51(3)	10.51(2)	90	114.03(9)	90
175	12.52(1)	30.64(3)	10.37(1)	90	114.16(1)	90
150	12.416(1)	30.918(1)	10.371(1)	90	113.85(1)	90

transients were accumulated. FID were Fourier transformed to the frequency domain without any extra line broadening or exponential multiplication.

Results and Discussion

(1) TC8. (a) X-ray Diffraction. The cell lattice parameters measured for TC8 at various temperatures are reported in Table 2. The heat capacity curves extracted from the article of Cope, Gannon, and Parsonage[24] are also given in Figure 1 with indication of some temperatures where the crystal cell has been determined. At room temperature TC8 has a rhombohedral lattice with cell lengths $a = 16.225(2)$ Å and $c = 12.488(4)$ Å. At 250 K, a second rhombohedral cell with doubled *a* and *b* axes is found. This cell (with a huge volume of 12 800 Å^3) may be thought to be unrealistic, but we have observed the same phenomenon of axis doubling upon cooling for many of the thiourea inclusion compounds we have tested (e.g., with camphor, camphorquinone, and cycloheptanone). Measurements made on the DIP2020 show that these unit cells are different from the classic ones (with the cell lattice edges *a* and *b* around 15 Å) by the appearance of some weak reflections. These large cells are the subject of a continuing investigation. Cooling to 175 K gave another monoclinic lattice with a long *b* axis of 30.64 Å as observed by Clément et al.[8] Upon heating back from this temperature, a new monoclinic phase appeared between 200 and 210 K with a *b* parameter of 15.71 Å, half the former value. All these results are consistent with the heat capacity measurements of Cope et al.[24] with a different phase found between each thermal event detected by these authors (Figure 1). The only difference with their measurements is the delay for the thermal event we detected between 200 and 210 K and that is found at 187 K in the heat capacity curve. Such a difference may be explained by the difference in the heating rate, which was faster in our experiment. According to these results, the phase sequence can be summarized as

$$\mathrm{IV}(P2_1/c) \xrightarrow{187/200\ \mathrm{K}} \mathrm{III}(P2_1/c) \xrightarrow{\approx 245\ \mathrm{K}} \mathrm{II} \xrightarrow{265\ \mathrm{K}} \mathrm{I}(R\bar{3}c)$$

Room-Temperature Phase (I). The host substructure (sulfur, carbon, and one nitrogen atom from the thiourea molecule) is easily found with direct methods and can be refined without difficulties. However, within the channel at the position where the guest molecules are expected, no recognizable molecular fragment can be located from the difference Fourier map, but some significant discrete maxima in the electronic density were clearly visible. Usually, the guest molecules are situated within the thiourea channels at the same locations of symmetry 3_2 where the sulfur atoms point toward the center of the channel. The cyclooctane molecule, which does not have this point symmetry, has to exhibit a high degree of disorder to match the symmetry site.

The program CRYSTALS allows the refinement of a continuous electron density distribution for disordered models using simple geometrical shapes such as lines, rings, or spherical surfaces.[32] These special shapes have been introduced by an extension of the structure factor and a modification of the conventional atomic displacement parameter expression. This facility was used for the refinement of the guest electronic density as a spherical surface. This surface was constrained in special positions and only the radius and an overall isotropic atomic displacement parameter were refined. The spherical surface was found to be a better representation of the electron density than a line or a ring. This surface with a radius of 1.859(8) Å describes the region where the atoms from the disordered rings are expected. The host lattice is similar to the hexagonal network of thiourea molecule described by Lenné[4] for the cyclohexane adduct (Figure 2). The cohesion of this framework is via the network of N−H···S hydrogen bonds with two different N···S distances of 3.487(3) and 3.464(4) Å.

Intermediate Phase at 210 K (III). The intermediate phase of TC8 was investigated by a data collection performed at 210 K. The initial model obtained by direct methods showed three thiourea molecules, a complete cyclooctane ring, and a portion of what seemed to be the part of a second cyclooctane ring. A Fourier difference map revealed two supplementary peaks giving, with the initial fragment, a ring portion of six carbon atoms. Refinement was first carried out using this starting model where only one part of the cyclooctane ring was disordered. The refinement converged with a residual factor of 6.8%, but some atomic displacement parameters for the complete cyclooctane ring were abnormally large. The splitting of these atoms in two positions led to a model involving disorder between two cyclooctane rings. Refinement of the occupancy factors gave nearly equal population for the two rings (0.514(6) and 0.486(6)). At the end of the refinement, the residual factor was slightly lower (5.73%) compared to the one obtained with the previous model.

The host structure is still made of a hexagonal channel but distorted with one diagonal 1 Å longer than the two others. Compared to the room-temperature phase, the distortion is made via the modification of the length of the hydrogen bonds and the cohesion of the host lattice is here achieved by 12, instead of 2, crystallographically independent N−H···S hydrogen bonds with N···S distances ranging from 3.416(2) to 3.471(3) Å. The stacking along the *b* axis shows a repetitive pattern of two different channels related by a rotation of nearly 120° (Figure 3a). The conformation of each cyclooctane ring is very close to the most stable conformation, the boat-chair conformation, as expected from molecular mechanics[33,34] or ab initio[35] calculations.

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[32] Schröder, L.; Watkin, D. J.; Paulus, W.; Coulson, A., submitted to *J. Appl. Crystallogr.*

[33] Hendrickson, J. B. *J. Am. Chem. Soc.* **1967**, *89*, 7036.

[34] Bixon, M.; Lifson, S. *Tetrahedron* **1967**, *23*, 769.

[35] Rocha, W. R.; Plegio, J. R., Jr.; Resende, S. M.; Dos Santos, H. F.; De Oliveira, M. A.; De Almeida, W. B. *J. Comput. Chem.* **1998**, *98*, 524.

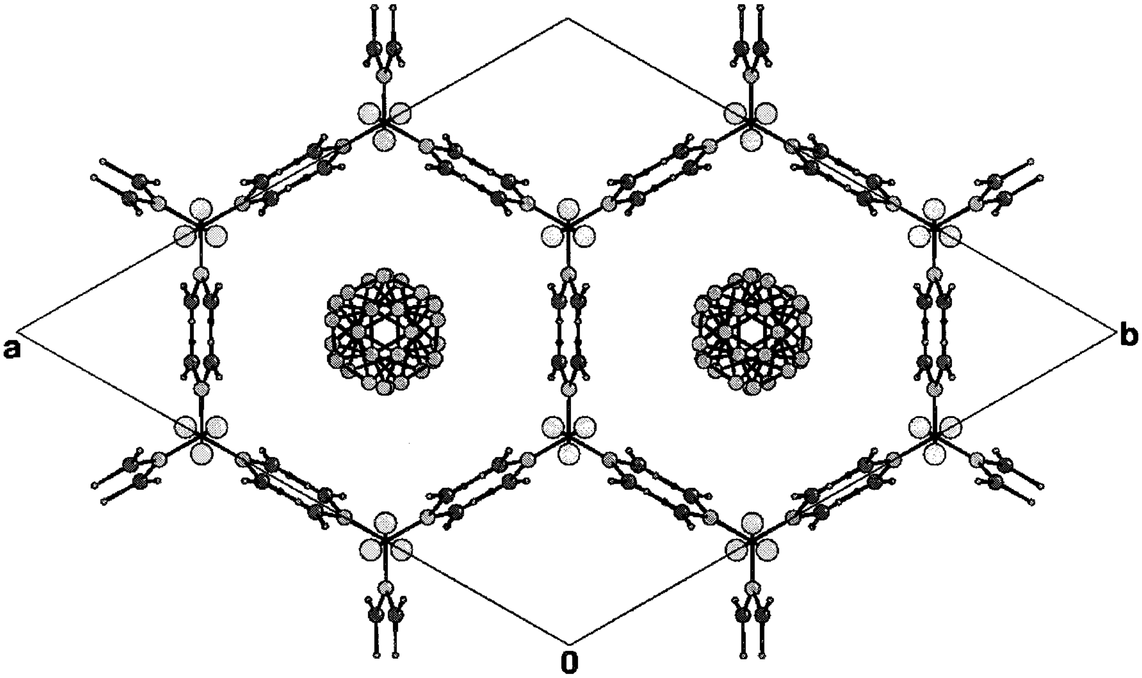


Figure 2. Host lattice of the room-temperature phase of TC7 and TC8. The discrete points within the thiourea channel show the area where the guest molecules lie.

Low-Temperature Phase at 150 K (IV). In this phase, with a doubled *b* axis, the asymmetric unit is composed of six thiourea ribbons and two well-defined cyclooctane rings. Refinement carried out on positional and anisotropic displacement parameters for all the non-hydrogen atoms led to a residual factor of 4.3% (see Table 1). The channels of the thiourea lattice are similar in dimension and shape to those found in the intermediate phase at 210 K. Each channel still has one length longer than the two other ones. In the projection along the *a* axis, the channels are organized by pairs, alternating their orientation by 120° (Figure 3b).

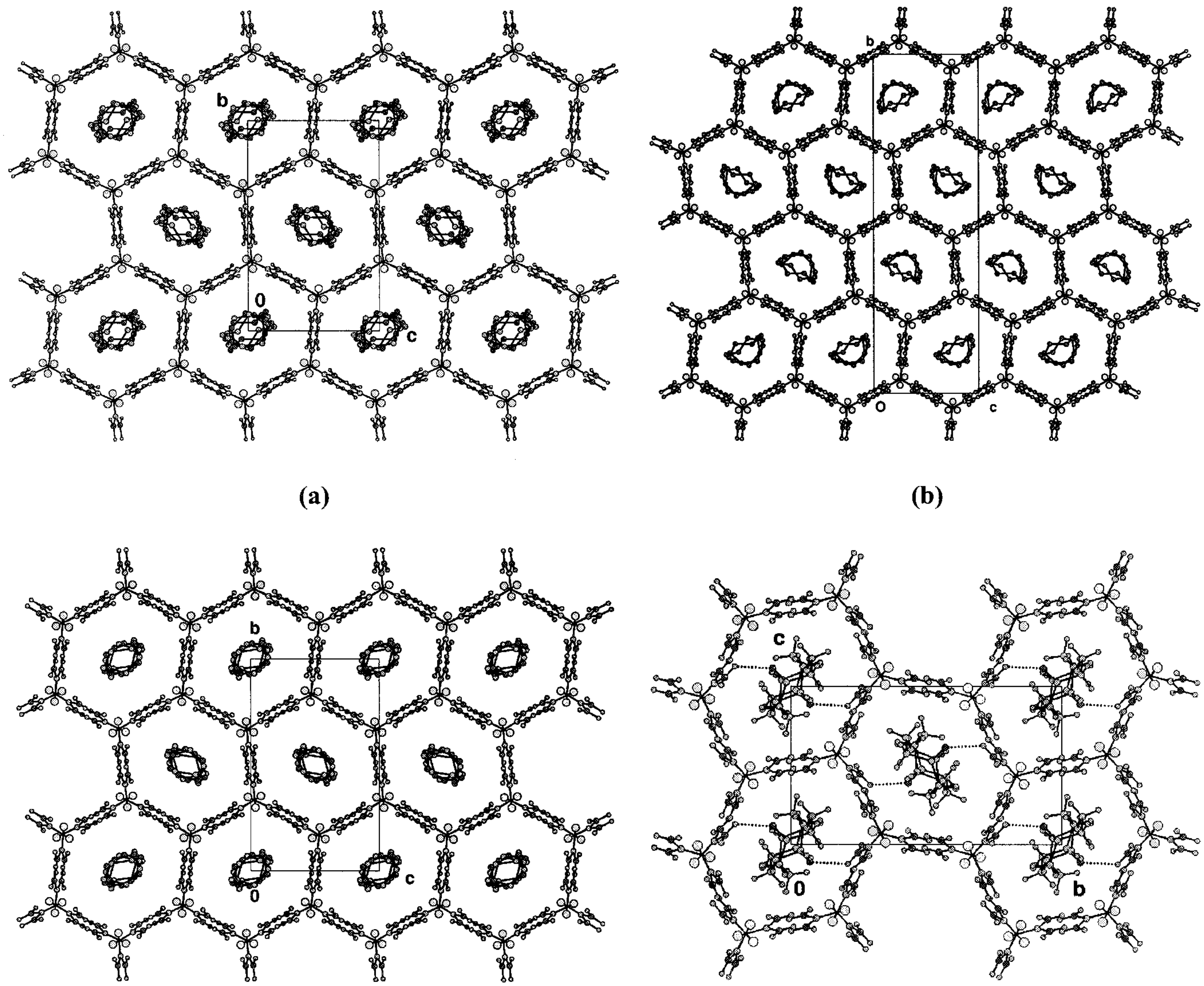
The host lattice is built with 24 independent hydrogen bonds (N···S distance between 3.394(3) and 3.472(3) Å). The two cyclooctane rings have standard geometrical values for distances and angles and do not appear to be disordered. They are both characterized by a nearly symmetric boat-chair conformation. They only differ by the orientation they adopt within the channels.

(b) Solid-State NMR Experiment. The ^{13}C MAS NMR spectrum at room temperature (Figure 4a) contains only one resonance for the cyclooctane molecule at $\delta = 27.7$ ppm and one resonance for the thiocarbonyl carbon of the thiourea molecule at 182 ppm. The line shape for the cyclooctane molecule is extremely sharp, similar to what is observed in the liquid state. This observation can be attributed to the presence of fast overall molecular motions of the guest molecule, leading to reduction of all anisotropic magnetic interactions such as the dipolar coupling and the chemical shift anisotropy. The extent and the rate of the motion are so high that a spectrum recorded with no magic angle spinning still displayed a sharp line for the cyclooctane resonance. As a result, using the usual cross-polarization sequence was ineffective and spectra were acquired using a one-pulse sequence followed by high-power proton decoupling ("PDA" pulse sequence). The high motion evidenced by NMR is consistent with the high disorder of the guest molecule observed by XRD in the room-temperature phase.

After the first phase change (T < 245 K), it became possible to acquire spectra with the cross-polarization sequence, meaning that the rate and the extent of the motion were both decreasing. However, the spectra were still characteristic of cyclooctane molecules subject to a high degree of motion. Below the second phase change (T < 187 K), it became again difficult to acquire spectra with cross-polarization, and we had to use again the PDA pulse sequence. Even if the crystal structure showed an apparently fully ordered structure, these difficulties may indicate that slow motions, compared to the NMR time scale, are still present at very low temperatures.

(2) TC7. (a) X-ray Diffraction. The cell lattice measurements shown in Table 3 are compatible with the occurrence of two phase changes. At 293 K, TC7 is also rhombohedral with smaller parameters compared to TC8: $a = 16.012(2)$ Å and $c = 12.447(2)$ Å. A first phase change occurs below 250 K; it can be related to the anomaly found on the heat-capacity curve at 241 K. A unit cell similar to that for TC8 is found at 210 K with the doubled *a* and *b* axes. A second phase change is observed below 210 K and corresponds to the peaks found on the heat-capacity curve at 162 K. The cell lattice parameters at 150 K are those of a monoclinic phase equivalent to the 210 K intermediate phase of TC8 described above. At 100 K, the same cell lattice is found and no doubling of the *b* axis occurred. Heating back to 250 K gives the initial rhombohedral phase, showing that the phase changes are reversible. Only for the thermal event detected by Cope et al.[24] at 262 K no change in the cell lattice parameters can be seen. The phase sequence for TC7 as seen by these investigations can be summarized as

$$\mathrm{III}(P2_1/c) \xrightarrow{162\ \mathrm{K}} \mathrm{II} \xrightarrow{241\ \mathrm{K}} \mathrm{I}\ (R\bar{3}c)$$



(a) (b) (c) (d)

Figure 3. Projection along the *a* axis of the structure for (a) TC8 at 210 K, (b) TC8 at 150 K, (c) TC7 at 150 K, and (d) TCO8 at 120 K. For TC8 and TC7 hydrogen atoms of the guest molecules are omitted for clarity. For TCO8 the hydrogen bonds between the host thiourea and the guest cyclooctanone molecules are shown. For this representation the cell has been transformed to have the channel axis running along the crystallographic *a* axis (see text).

Room-Temperature Phase (I). The structure at 293 K has many similarities to the structure of TC8 particularly regarding the disorder of the guest molecules. The host lattice has the same hexagonal organization with a smaller diameter. The channels are built from thiourea ribbons linked by hydrogen bonds, hydrogen with one N···S length similar to (3.461(3) Å) and the other one smaller than (3.419(4) Å) those in TC8. The guest molecule has been refined in a similar way as in the cyclooctane clathrate. At the end of the refinement, the radius of the sphere was 1.667(11) Å, a smaller value compared to the cyclooctane one as expected.

Low-Temperature Phase (III). At 150 K the structure can be solved by direct methods giving three thiourea molecules and four atoms of the cycloheptane ring. This initial model was completed by subsequent Fourier difference maps giving a complete cycloheptane ring. Further refinement cycles and difference Fourier map calculations showed large residual electronic density peaks in the vicinity of the cycloheptane ring. Moreover, some of the anisotropic displacement parameters were large, suggesting the presence of disorder for the guest molecules. A second cycloheptane ring was built from the positions of the residual peaks and the splitting of the atoms having the larger atomic displacement parameters. Refinement of this model involving two cycloheptane rings with restraints led to a residual factor of 7.6%. The refined populations of the two rings were close to 0.5 (0.447(19) versus 0.553(19)).

In this phase the 12 different N−H···S hydrogen bonds have their N···S distances ranging from 3.356(6) to 3.422(5) Å. Along the *a* axis, the host lattice is the same repetitive pattern found in the TC8 intermediate monoclinic phase, that is, a superposition of layers made of the tilted hexagonal channels running in parallel to the *b* axis (Figure 3c). The two cycloheptane rings have a conformation close to the twisted chair conformation, the more stable conformation obtained in the calcula-

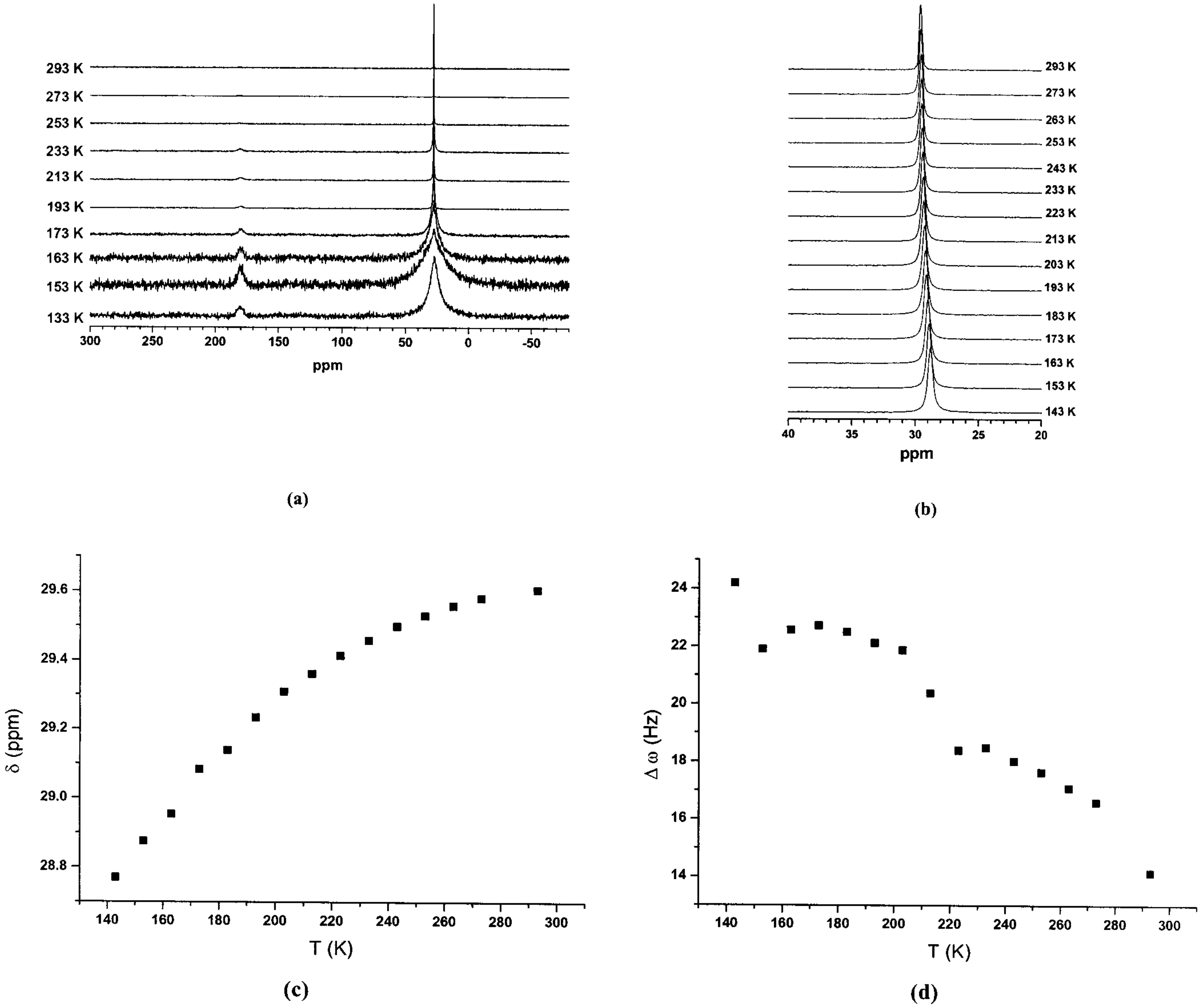


Figure 4. Variable temperature solid-state ^{13}C NMR spectra for (a) TC8 and (b) TC7. (c) Chemical shift and (d) line-width variation with temperature for TC7.

Table 3. Unit Cell Lattice Parameters for TC7

T (K)	a (Å)	b (Å)	c (Å)	α (deg)	β (deg)	γ (deg)
293	16.01(2)	16.01(2)	12.44(1)	90	90	120
250	15.941(4)	15.944(4)	12.408(3)	90	90	120
210	32.26(1)	32.26(1)	12.61(1)	90	90	120
150	12.66(1)	16.05(3)	10.33(1)	90	114.49(6)	90
100	12.34(1)	15.92(1)	10.05(1)	90	114.25(9)	90

tions from Hendrickson;[33] however, some deviations in the values of some torsional angles are observed for one of the rings.

(b) Solid-State NMR Experiment. ^{13}C MAS NMR spectra recorded in the temperature range 143−293 K are shown in Figure 4b. Figures 4c and 4d show the evolution of the chemical shift and the line width, respectively. All these spectra have been acquired using the PDA sequence. At room temperature, the spectrum is consistent with the crystallographic observation of a high disorder for the cycloheptane molecule. Only a sharp line is observed for the cycloheptane ring at 29.6 ppm. When the temperature is decreased, this signal is more and more broadened but no sharp change seems to affect the line shape at the temperature where the transitions are expected. Only the line-width variation shows some discontinuities near the temperatures transition.

(3) TCO8. (a) X-ray Diffraction. Structural investigations of the inclusion compound of thiourea with cyclooctanone show that a little modification in the guest molecule can result in a different behavior for the whole adduct. In effect, no evidence of disorder has been found from three crystal structure determinations performed at 293, 280, and 120 K (see Table 1). In this compound, the channel axis is running along the bisector of the (a, c) plane, but the cell can be transformed for comparison purposes to have the channel axis along the crystallographic *a* axis (Figure 3d). The crystal structure of TCO8 is already monoclinic at room temperature and no phase change has been detected upon cooling. In the temperature range 120−300 K, at each temperature investigated, the cyclooctanone stays in an ordered state and keeps the same orientation and conformation. This stability is attributed to the presence of a hydrogen bond between the carbonyl oxygen and one of the nitrogens of the thiourea lattice (shown in Figure 3d). This results in a marked distortion of the channel by shifting the thiourea ribbon involved in the hydrogen bond. As a

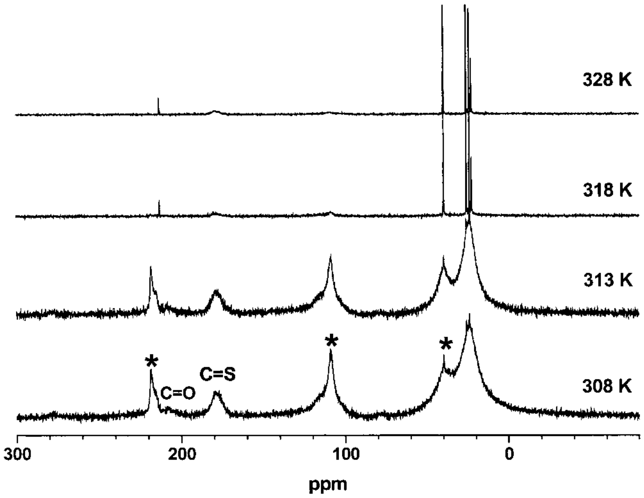


Figure 5. Variable temperature solid-state NMR spectra of TCO8. Spectra were acquired using the PDA sequence (see text) with a MAS rate of 5 kHz, pulse delay of 5 s. The signal near 100 ppm is due to the Teflon (overlapped with a sideband) of the sample holder and sidebands are indicated by the asterisk*.

result, the hydrogen of this thiourea molecule is involved in a three-centered hydrogen bond with two acceptor atoms, the oxygen from the cyclooctanone ring and one sulfur atom of a neighboring thiourea molecule. As expected in this case, the sum of the three angles N−H−S, N−H−O, and S−H−O is close to 360° (359.8°).[36] This hydrogen bond pattern between host and guest molecules is similar to that observed in some ketone−urea inclusion compounds.[37,38]

(b) Solid-State NMR Experiment. Figure 5 shows the ^{13}C NMR spectra at four different temperatures between 238 and 328 K. At low temperature, the line shapes are broadened with the same characteristics as those observed for the low-temperature phase of TC8. Between 313 and 318 K, a sharp change occurs, leading to a spectrum with extremely narrow lines. The spectrum at 318 K displays four narrow lines at 25.3, 26.6, 28.5, and 42.4 ppm (signal of the carbonyl atom), values similar to the one found in the spectrum of pure liquid cyclooctanone. When cooling back, the spectrum came back to its original appearance and the modification is fully reversible. As the temperature where the sharp change in the spectrum is close to the melting point of the pure cyclooctanone, we also performed a variable temperature ^{13}C NMR study on pure solid cyclooctanone and checked that the spectrum when coming back below 315 K did not contain contribution from released and re-crystallized pure cyclooctanone.

To check if this variation in the NMR spectrum was due to a phase change similar to the one found for cyclooctane, several attempts were made to collect data on a single crystal at 320 K. However, all the tested crystals lost their diffraction power when heated and became opaque, but still kept their hexagonal shape. Alternatively, powder patterns were recorded at room temperature, at 320 and 340 K. The patterns above 320 K were found to be those of a mixture of pure thiourea with another phase. As the phase change occurs just before decomposition, no attempt was made to perform a full structural characterization. The powder pattern for the phase at 340 K can be successfully indexed with a rhombohedral phase similar to the usual room-temperature phase of the thiourea adducts with cell lattice parameters $a = 16.418(5)$ Å and $c = 12.547(4)$ Å. However, this new phase seems not to be very stable because the phase change occurs in the same time as decomposition, mainly by the removal of the cyclooctanone from the channels, leading to pure thiourea.

(4) Discussion on the Phase Changes. At room temperature, both NMR and crystallographic studies indicate that hydrocarbon guest molecules are in a liquid-like state within the channels. In this state one expects both orientation and translation disorder, meaning that the guest molecules are free to move along the channel axis. This is consistent with the poor stability of the thiourea inclusion compounds at room temperature; these compounds have a strong tendency to decompose by losing their guest molecules. Decreasing the temperature leads to a gradual freezing of the guest substructure, the whole process being stepwise with two or three phase changes. Apparently, only for TC8 are the guest molecules able to freeze within the thiourea channels to give a commensurate and ordered phase.

The first phase change, both affecting TC7 and TC8, gives an apparent large rhombohedral unit cell. As we have not been able to collect and solve successfully a data set for these phases, we cannot give a full description of them. However, the fact that the hexagonal lattice is kept means that the guest molecules should still be highly disordered because they are in the room-temperature phase. This is confirmed by the solid-state NMR spectra recorded in the temperature range where these large unit cells are expected; they do not display any major change compared to those recorded at room temperature and are still compatible with a high degree of motion for the guest molecule.

The doubling of both the *a* and *b* axes may result from small distortions of the thiourea host lattice. These distortions should differentiate some atoms of the thiourea molecule that are equivalent in the room-temperature phase. A possible explanation is to consider that the observed supercell results from a twinning of the monoclinic low-temperature cell. A similar behavior has been found in the *p*-*tert*-butyl[4]arene-toluene inclusion compounds.[39] In this tetragonal structure, when cooling, a phase transition occurs from the high-symmetry phase to a lower distorted form through a superlattice characterized by the apparition of half-integral reflections of *h* and *k*. This apparition has been explained by a short-lived correlation in the orientation of adjacent guest−host units.

It is also interesting to note that, in the temperature range where these phases are expected for TC7 and TC8, small peaks in the heat capacity curve have been

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(36) Jeffrey, G. A. *An Introduction to Hydrogen Bonding*; Oxford University Press: Oxford, 1997.

(37) Hollingsworth, M. D.; Brown, M. E.; Hillier, A. C.; Santarsiero, B. D.; Chaney, J. D. *Science* **1996**, *273*, 1355.

(38) Brown, M. E.; Chaney, J. D.; Santarsiero, B. D.; Hollingsworth, M. D. *Chem. Mater.* **1996**, *8*, 1588.

(39) Brouwer, E. B.; Enright, G. D.; Ratcliffe, C. I.; Ripmeester, J. A. *Supramol. Chem.* **1996**, *7*, 79.

(40) Dénoyer, F.; Currat, R. In *Incommensurate Phases in Dielectrics, Vol. 2*; North-Holland: Amsterdam, 1986.

(41) Tanisaki, S.; Mashiyama, H. *Acta Crystallogr.* **1988**, *B44*, 441.

Table 4. Unit Cell Lattice Parameters of Some Other Thiourea Inclusion Compounds

guest molecule	T (K)	a (Å)	b (Å)	c (Å)	β (deg)	SG
cycloheptanone	293	15.998(4)	15.998(4)	12.494(3)		$R\bar{3}c$
cyclodecane	293	12.375(2)	16.431(2)	9.925(3)	113.18(2)	$P2_1/c$
	140	12.243(1)	16.310(1)	9.827(2)	113.09(1)	$P2_1/c$
1,5-cyclooctadiene	293	16.067(5)	16.06795)	12.473(2)		$R\bar{3}c$
	140	12.459(8)	15.466(25)	10.288(16)	114.63(1)	$P2_1/c$

reported by Cope, Gannon, and Parsonage.[24] From the small enthalpy and entropy changes of these signals, these authors concluded that they were associated with some possible ferroelectric phase changes, as observed in thiourea, which is known to have ferroelectric transition,[40,41] though this is unlikely because all the phases found thus far have centrosymmetric structures.

When the temperature is decreased further, the guest molecule motion starts to be reduced until the occurrence of a second phase change. Below the temperature of this new phase transformation, it is possible to locate by X-ray diffraction the cycloalkane rings in a less disordered state. As the guest structure is less isotropic in shape compared to the room-temperature phase, the host lattice has to deform and lose the perfect hexagonal shape of the channels to accommodate the space now filled by the rings in their reduced configurations, and this leads to the reduction of the symmetry of the whole structure. The temperature of this transition where the symmetry is moved from a rhombohedral system to a monoclinic one seems to increase with the size of the cycloalkane ring. It has been detected with the thiourea/cyclohexane clathrate at 126 K;[8] it occurs at 162 K for TC7 and at higher temperature (187 K) for TC8.

The crystal structure determinations performed on the monoclinic phases resulting from this transition shows two different molecules differing by their orientation, as if, at first appearance, the disorder was mostly orientational. However, none of the ^{13}C NMR spectra recorded in the whole temperature range display a doubling of the cycloalkane signals, as should be expected if the two rings were crystallographically independent. Instead, only one single line was found, meaning that the two rings cannot be discriminated on the NMR time scale. A possible explanation for these two different observations could be a process of interconversion or exchange between the two different rings occurring in the “fast limit” compared to on the NMR time scale. In this case, when lowering the temperature, the decreasing motion rate should give a coalescence eventually followed by a splitting of the resonances. Such a phenomenon has not been observed in the low-temperature spectra of TC7 and TC8, meaning that if this interconversion process occurs, the coalescence temperature is below the minimal temperature of the experiment and the splitting of resonance cannot be observed.

More cooling gives a new phase transformation for TC8 while no phase change has been observed for TC7 and other smaller cycloalkanes we have investigated (Table 4). This new phase change may be looked at as the end of a gradual freezing of the cycloalkane molecule within the channels when decreasing the temperature.

Solid-sate NMR and X-ray crystallography give complementary information related to different dimensions and time scale. While the X-ray crystallography studies, sensitive to the whole averaged structure, indicate a stepwise ordering of the guest molecule within the channels, the NMR data, probing a local order, indicate that the disorder is principally dynamic with both the rate and the extent of the motion evolving continually over the whole temperature range. Thus, in the low-temperature phases, mainly for TC8 and TCO8, even if the structural data show an apparently ordered structure of the host and guest components, the difficulties in acquiring CP/MAS ^{13}C NMR spectra indicate that there is still some motion at these temperatures. These motions are not detectable on the time-averaged picture given by the single-crystal X-ray analysis.

When considering this phase change for TC8, Cope et al.[24] excluded an order−disorder mechanism involving rigid molecules on the basis of their estimation of the entropy and have proposed instead a mechanism involving a continuous process of conformational interconversion. This assumption was based on the low difference in energy between the different stable conformations calculated for the cyclooctane rings. In the thiourea inclusion compounds, the shape of the cavity of the host lattice has an influence on these energy barriers and a consequence can be the limitation in the number of possible conformations or orientations experienced by the guest molecule.

A conformational disorder of the cyclooctane ring cannot be excluded as NMR experiments on substituted cyclooctanes with deuterium or fluorine[42] have shown that the cyclooctane ring is able to perform inversion and pseudorotations with a rate in the time scale not compatible with the X-ray analysis.

On the whole, for TC8, the occurrence of the different phases is consistent with the thermal events detected in the heat capacity curve measured by Cope, Gannon, and Parsonage.[24] The agreement for TC7 is poorer because no clear and significant phase change has been found by X-ray crystallography near 241 K.

Conclusions

The ordering through a hydrogen bond found in TCO8 at room temperature is not observed in the other thiourea inclusion compounds with the smaller cycloketones (such as cyclohexanone and cycloheptanone). These clathrates do not display the same stabilization by a hydrogen bond. They crystallize in the usual rhombohedral unit cell at room temperature, have their guest molecule disordered, and display a behavior similar to the cycloheptane inclusion compound with a phase change upon cooling. The stabilization for TCO8 and TC8 seems to be helped by an apparent perfect fit of the shape and the dimensions of the cyclooctanone ring within the thiourea channel compared to the smaller ring. More generally, the cyclooctane and other

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(42) Anderson, J. E.; Glazer, E. S.; Griffith, D. L.; Knorr, R.; Robert, J. D. *J. Am. Chem. Soc.* **1968**, *91*, 1386.

eight-membered ring molecules can be considered as unique compared to other cycloalkane molecules. The flexibility of the ring allows the molecule to be accommodated in the hexagonal lattice at room temperature, and their shape and dimensions, fitting well the cavity of the thiourea channels, result in a low-temperature arrangement with a commensurate ordering between the guest and the thiourea lattice. Smaller cycloalkane cannot reach such a degree of ordering because of their reduced dimension compared to the channel. Larger cycloalkanes can also be included in thiourea but the channel has to be distorted to accommodate them, generally leading directly to the monoclinic lattice as observed for the cyclodecane ring (see Table 4).

Other eight-membered ring cycloalkanes have, generally, rich thermal behavior with the occurrence of at least one phase transition. For example, the inclusion compound of 1,5-cyclooctadiene is also rhombohedral at room temperature with $a = 16.05(1)$ Å and $c = 12.471(2)$ Å but is subject to a phase change, giving the monoclinic adduct described by Garneau et al.[43] where the cyclooctadiene ring seems only slightly disordered.

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Supporting Information Available: Tables of X-ray data collection and refinement parameters, atomic position parameters, anisotropic displacement parameters as well as bond lengths and angles, torsional angles and hydrogen bonds for TC8 at 293, 210, and 150 K, TC7 at 293 and 150 K, and TCO8 at 293, 280, and 120 K, and powder pattern refinement for the high-temperature phase of TCO8 (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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(43) Garneau, I.; Raymond, S.; Brisse, F. *Acta Crystallogr.* **1995**, *C51*, 538.