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Dicyclohexylamine-Thiourea Clathrate

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The reaction of dicyclohexylamine (DCHA) with thiourea leads to the formation of the inclusion compound DCHA(6 Thiourea). Room temperature, single crystal X-ray diffraction analysis shows the product has a trigonal structure, $\alpha=\beta=90°$, $\gamma=120°$, a=b=15.801(2)A, c=12.451(3)A, which may be described as a thiourea matrix defining hexagonal cavities where the di-cyclohexylamine molecules are accommodated. ^{13}C-cross polarization magic angle spinning (CP-MAS) NMR study indicates the guest inside the cavities has a relatively free rotation and that the channels are, concerning this amine, perfect van der Waals cavities. Thermal studies indicates that the structural identity of the thiourea matrix endures after a partial loss of amine.

Keywords: Inclusion compounds, thiourea, dicyclohexylamine, clathrates

INTRODUCTION

Thiourea forms crystalline adducts with a variety of organic species[1–4]. Many of these compounds may be described as inclusion compounds in which thiourea molecules define a structure containing linear, hexagonal channels where individual guest molecules are accommodated. Most available information deals with hydrocarbon-thiourea systems, among others with cyclohexane. They have been extensively studied by various physical methods including solid-state NMR techniques, X-ray-diffraction analysis and thermochemistry[5]. The information about systems containing guest species with functional groups like amines is however rather limited. In a previous communication we have reported about the synthesis of thiourea-amine inclusion compounds indicating that the more appropriate amines to form inclusion compounds are the secondary amines with saturated bicyclic substituents [6]. Indeed on the basis of powder X-ray diffraction analysis and composition data it was shown that these amines, contrasting with other bifunctional amines which lead to laminar products[7,8], form conventional thiourea inclusion compounds. In this paper we describe the complete characterization using single-crystal X-ray diffraction analysis. ^{13}C CP-MAS NMR spectroscopy, and thermal analysis, DTA and TG, of the tittle compound.

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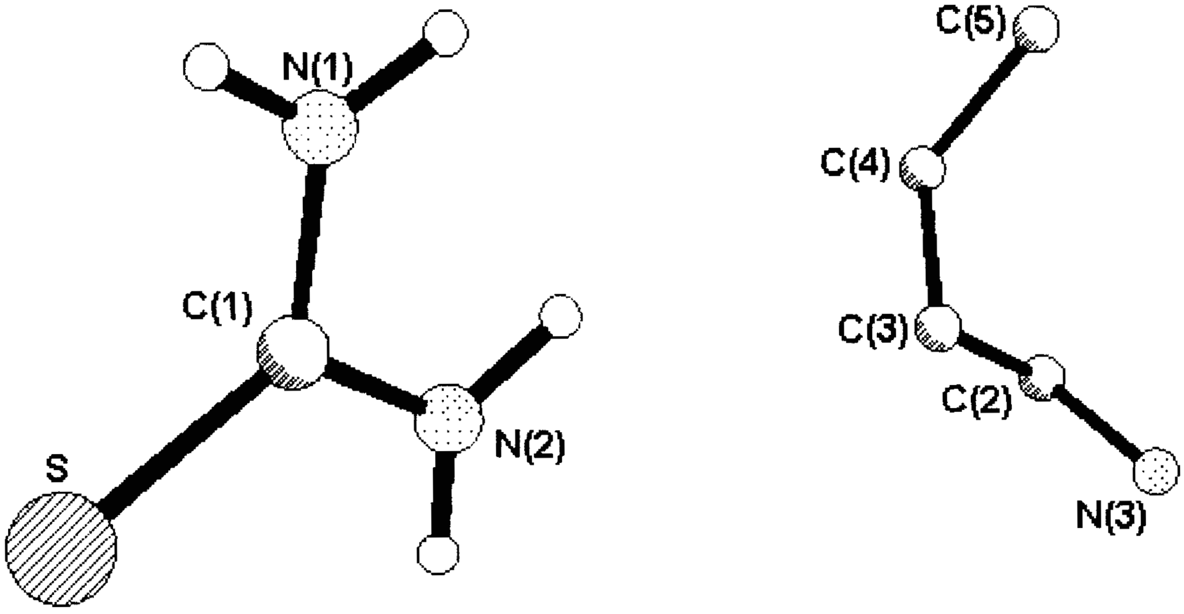

FIGURE 1 Representation of the molecular components in the structure of DCHA-(6 Thiourea)

EXPERIMENTAL

Reagents being commercially available were used as received. Crystals of the dicyclohexyl / thiourea inclusion compound were obtained by slow evaporation of solvent at room temperature from solutions of both the amine and the thiourea in methanol. Used amine to thiourea molar ratios were always greater than the ratios expected for the product. After about 24 h, crystals with well formed faces may be separated. Hexagonal prisms showing a characteristic behavior under the polarized light microscope, may be rapidly distinguished from pure thiourea which crystallize as tetragonal prisms. Products were washed with cold methanol and dried under vacuum. Crystals decompose in water producing a characteristic visually observable dynamic effect [9]. The ^{13}C CP-MAS NMR spectra were recorded on a Bruker MSL-100 spectrometer at a frequency of 100.63 MHz for ^{13}C. The number of scans was 400 with 5.5 μs 90° pulses, 1 ms cross-polarization contract time; 41 ms acquisition time during proton decoupling and 5 s recycle delay. The polycrystalline powder sample was spun at a frequency of 4 kHz using a Bruker CP-MAS probe. The chemical shifts are given relative to tetramethylsilane (TMS) used as internal standard. A single crystal was selected for the X-ray diffraction analysis. Data was collected on a Siemens R3m / V diffractometer with graphite monochromated Mo $K_\alpha$radiation ($\lambda = 0.71073$ Å) at 293 K. Intensity data for 541 reflections (h=0 to 16, k=0 to 16, l=-0 to 14) was collected in the 2θ scan mode in the range $5° < 2\theta < 50°$. From 536 independent reflections ($R_{int}=0.046$), 383 were observed with $I > 2\sigma(I)$. Intensity data was corrected for Lorentz polarization but not for absorption. The crystal corresponds to the space group R3. The structure was solved by direct methods using Siemens SHELXTL PLUS (PC version 4.2) programs[10].

Positions for the hydrogen atoms were calculated geometrically using the riding model with fixed isotropic temperature factors. Refinement of F^2 was done against all reflections. The weighted R factor wR and goodness of fit S are based on F^2. Values of the obtained final indices were R=8.8% and wR=0.33 with S=1.14 A final difference Fourier electron-density map showed a maximum and minimum peaks of 0.29 and –0.212 $e\text{Å}^{-3}$ respectively. Atomic scattering factors, dispersion corrections, and absorption coefficients were taken from the *International Tables for Crystallography* (1992, Vol C).

TABLE I Structural parameters and selected bond distances and angles in the product of the inclusion of DCHA in Thiourea

Unit cell dimensions	
Crystal system, Space group: R-3, Trigonal	
a = 15.801(2) Å	alpha = 90°
b = 15.801(2) Å	beta = 90°
c = 12.451(3) Å	gamma = 120°
Volume: 2692.2(8) Å^3	
Bond lengths	
S-C(1)	1.696(7)
C(1)-N(1)	1.321(6)
C(1)-N(2)	1.338(7)
C(4)-C(3)	1.5116
C(4)-C(5)	1.6234
C(3)-C(2)	1.5046
N(3)-C(2)	1.4715
Bond angles	
N(1)-C(1)-N(2)	118.0(6)
N(1)-C(1)-S	122.1(5)
N(2)-C(1)-S	119.9(5)
C(3)-C(4)-C(5)	121.0
C(2)-C(3)-C(4)	90.9
N(3)-C(2)-C(3)	101.9

RESULTS AND DISCUSSION

The structural determination of the studied compound was performed. A representation of the molecular elements of the structure is reproduced in Fig. 1. As shown in Fig. 2, the product may be described as a series of linear, infinite, non interacting channels with hexagonal cross-sections of 9.2 Å diameter in which the dicyclohexylamine guest molecules are located. However, due to substantial disorder of the dicyclohexylamine molecule neither its geometry or orientation could be exactly determined. Nonetheless, the basic structure appears to be commensurate.

Structural parameters, as well as most relevant bond distances and angles are given in Table I.

In comparison with other inclusion compounds, the topotactic nature of the corresponding formation reactions

$$\text{host} + \text{guest} = \text{inclusion compound}$$

is in the case of most clathrates rather limited. There, the existence of the matrix structure usually needs the presence of the guest, so the escape of the guest bears to the destruction of the host structure. However in the dicyclohexylamine/thiourea clathrate discussed here, as shown by its thermal behavior, the topotactic properties of the system appear to be present in some extent. Indeed the differential thermal analysis of the product illustrated in Fig. 3 shows an unique relatively wide, slightly asymmetric strong peak centered at 174 °C, the melting temperature of the thiourea[11]. This behavior is rather different from that observed for the thiourea cyclohexane compound in which, in addition to the melting of the thiourea, an asymmetric peak at 140–160 °C due to the disintegration of the complex is observed[12]. Asymmetry of the peak observed in the DTA in Fig. 3 may be attributed to an additional process, also endothermic but with a relatively lower heat tone, occurring between 160 and 170 °C which could be assigned to the decomposition of the clathrate

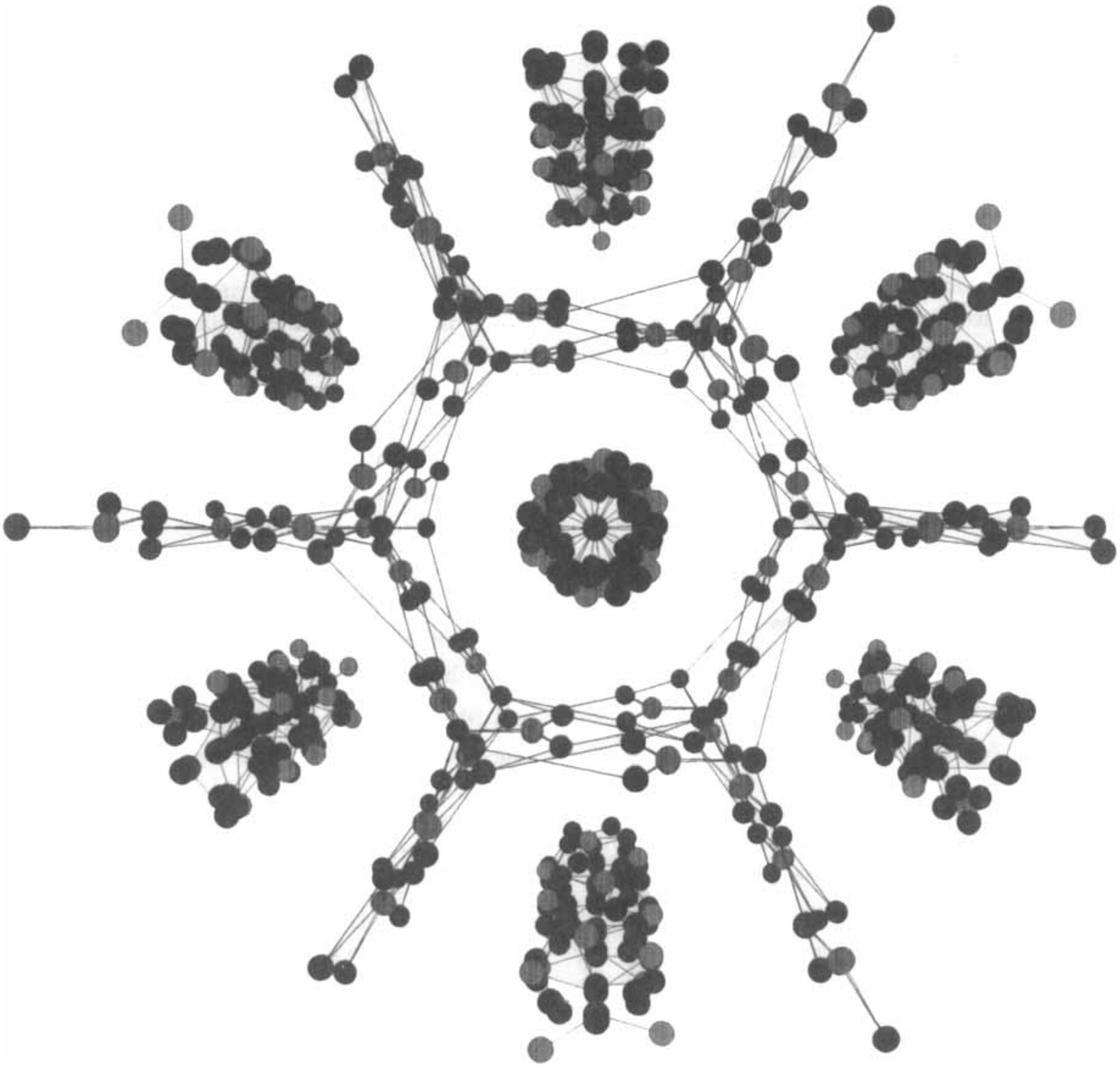

FIGURE 2 Structure of the compound DCHA-(6 Thiourea). View along the host hexagonal channels

to orthorhombic thiourea. The interpretation of this feature as a thermal process in which the compound is stable enough for enduring with the same structure until near the melting point of the thiourea is corroborated by the TG in which the partial loss of the guest begins at 115–130 °C. At 160 °C when a 50% of the amine inserted originally is lost, a clear change of the mass loss rate is observed. About 37 % of the amine remains retained by the thiourea melt after the decomposition of the solid. The topotactic process evidenced by the thermal analysis in this case may also be visualized in an interesting experiment. If the crystals of the product are left in contact with a high polarity solvent as DMSO or water[9], the amine appears to be rashly extracted from the solid propelling the crystal through the liquid surface. The evolving of the amine may visually

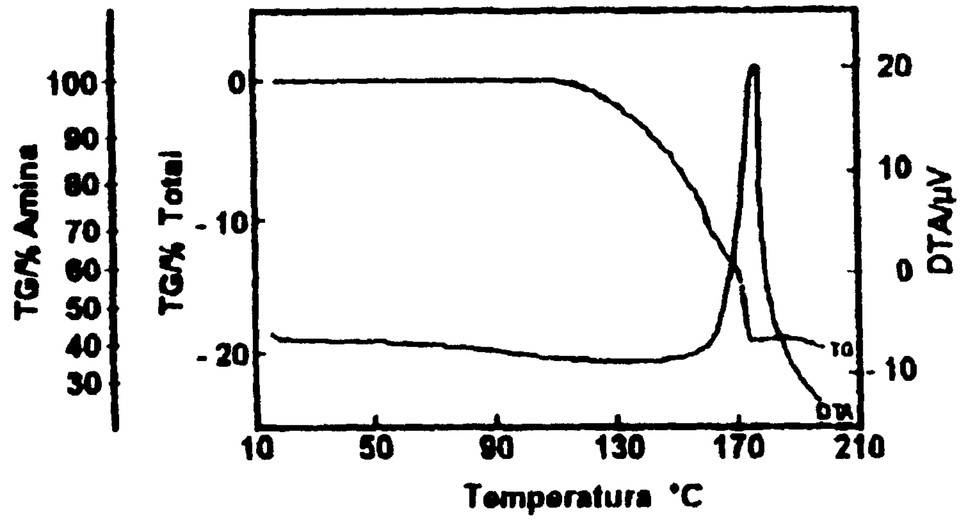

FIGURE 3 Thermal analysis, DTA and TG of DCHA-(6 Thiourea)

observed by adding phenophtaleine to the solution. The motive effect is thus accompanied by the formation of a beautiful red "wake" in the liquid. These experiments suggest that the thiourea host structure does not experiences decomposition before melting.

For ^{13}C nuclei bonded directly to nitrogen (^{14}N, I=1), MAS frequently gives NMR patterns consisting in approximately 1:2 (or 2:1) doublets because of ^{13}C-^{14}N residual dipolar interactions are averaged to zero by ^{13}C MAS NMR. In the nitrogen compounds the axis of quantization of the ^{14}N nucleus is tilted from the direction of the magnetic field as a consequence of the interaction between the ^{14}N nuclear quadrupole moment and the electric field gradient at the same nucleus[7, 13–16].

As shown in Fig. 4 which reproduces the ^{13}C CP-MAS NMR spectrum of the studied inclusion compounds at room temperature, high amplitude motions of the amine guest molecules in the channel average the residual dipolar interactions between ^{13}C and ^{14}N to less than 25 Hz, showing the spectrum only a single sharp line for C, so the typical asymmetric doublet is not observed.

TABLE II Medium effects on ^{13}C-NMR chemical shifts in dicyclohexylamine

C-atom in dicyclohexyl-amine.	*^{13}C-NMR chemical shifts (ppm) in*			
	CCl_4 (50%)	*CCl_4 (1%)*	*$CDCl_3$ (10%)*	*Thiourea*
C-1	52.80	52.84	53.21	54.20
C-2	34.40	34.41	34.52	36.17
C-3	26.32	26.34	26.29	26.50
C-4	25.00	25.04	25.36	26.50

The classic clathrate structure as well as the topotactic nature of the compound discussed above imply a relative weak amine-thiourea host interaction which does not compete with the H-bond interactions involved in the existence of the thiourea matrix. The relatively high movement of the guest observed in the X-ray diffraction pattern still commented above may be also visualized in the ^{13}C NMR spectrum of the solid.

In Table II are reported the chemical shifts of dicyclohexylamine inserted in the thiourea matrix with those of the amine in other media. The behavior of organic molecules placed in

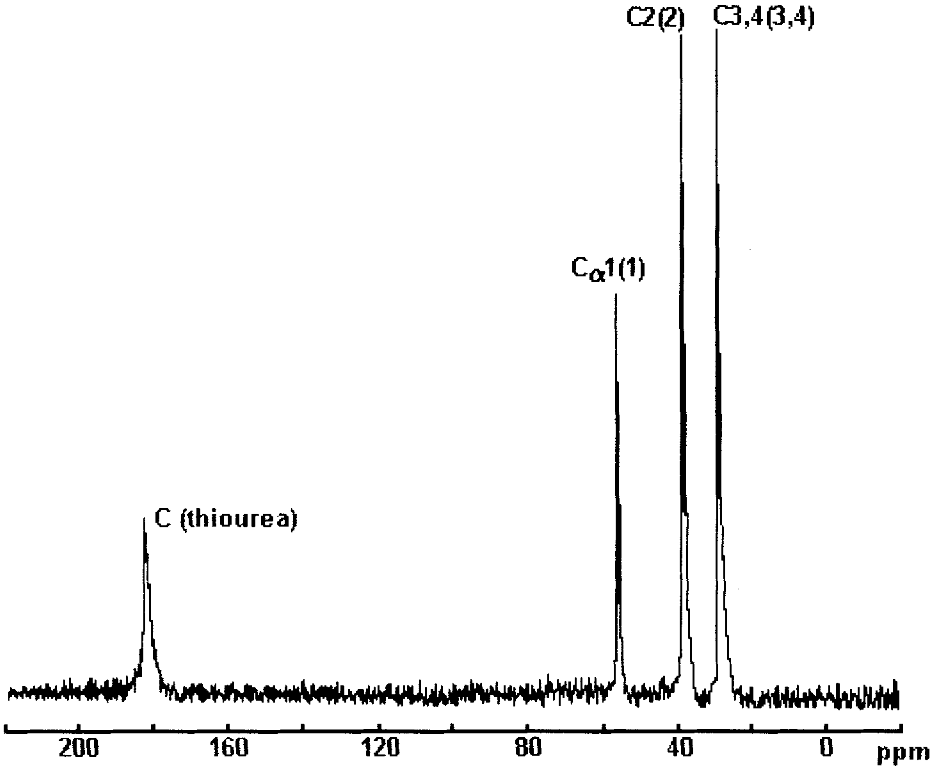

FIGURE 4 ^{13}C CP-MAS NMR spectrum of DCHA-(6 Thiourea) at room temperature

environments such as those occurring within clathrates cavities is expected, in general, to differ from those of the same molecule in other phases[17–19]. In this work, the ^{13}C CP-MAS NMR behavior of the dicyclohexylamine was analyzed in detail. Indeed, the effect of the amine self-association on the chemical shifts can be appreciated by observing the shift on going from the pure liquid to the dilute solution in $CDCl_3$. Interestingly, the ^{13}C-chemical shifts of the cyclohexylamine inserted in the thiourea correspond to the free amine or at least to an amine undergoing weaker interactions with the medium than the amine dissolved in an inert solvent. Thiourea channels appear to be concerning this secondary amine, a perfect van der Waals cavity.

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