

**IR AND ¹³C-NMR SPECTRAL PROPERTIES OF THE LAYERED
INCLUSION COMPOUND BIS(THIOUREA)HEXAMETHYLENETETRAMINE.**

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ABSTRACT

The structure of the 1: 2 adduct of hexamethylenetetramine and thiourea was reanalyzed reinterpreting X-ray diffraction data and providing additional IR and NMR spectroscopic features. The product is thus described as supramolecular commensurate host-guest complex corresponding to the intercalation of hexamethylenetetramine in a layered thiourea matrix. FT-IR spectra evidence a simultaneous strengthening of both C-N and C-S bonds, that appearing as a pattern characteristic for described layered thiourea matrix. ¹³CP MAS-NMR spectra of the intercalated hexamethylenetetramine is essentially determined by nuclear dipolar magnetic interactions and host-guest chemical interactions arising from ¹³C-14N residual dipolar interaction not averaged to zero by MAS-NMR and from the magnetic non-equivalence of the guest carbon atoms caused by the hydrogen bonding interaction with the thiourea matrix .

Key Words: Thiourea, hexamethylenetetramine, inclusion compound.

INTRODUCTION

Host-guest supramolecular complexes are of special interest for understanding the chemistry in low dimensional spaces. The molecular recognition involved in the formation of such structures sometimes may be a relevant model for the kind of organized system usually found in living organisms. Matrix effects and anisotropic features which are habitual of the chemistry in restricted spaces also appear as useful for the development of new material of scientific and technological importance¹).

Urea and thiourea clathrates constitute interesting systems in which the matrix being structured by hydrogen bond interactions has a relatively high liability to structural changes caused by the interaction with the host²). In the frame of studies directed to investigate the influence of the basicity of the guest on the structure of the clathrate in thiourea-amine supramolecular complexes³⁻⁷) we have focused our attention in the adduct hexamethylenetetramine-thiourea discovered by Mak et al⁸). This phase presents a structure which differs from that observed in the conventional thiourea clathrates, that possibly due to the relative strong interaction of the amine with the thiourea. We have therefore reanalyzed such structure providing further additional IR and NMR spectroscopic features in order to get a better understanding of the interactions which govern the formation of this kind of compounds.

EXPERIMENTAL

The product was prepared by mixing in a stoichiometric ratio 2:1 the thiourea (Aldrich) and the amine (Merck), both dissolved in methanol (Merck), at room temperature. Slow solvent evaporation leads to large plate-shaped crystals which were collected, washed with cold methanol, and dried under vacuum. The colorless crystalline product melts at 429 K has the composition $C_8N_8H_{20}S_2$ (Analytical data, found (calculated): C 33.03 (32.86); N 37.97 (38.32); H 7.18 (6.89).

X-Ray diffraction analysis was performed using a single crystal with dimensions 0.14, 0.20, 0.24 mm. The structure was solved by direct methods (Siemens R3m/V diffractometer with graphite monochromated Mo K α radiation ($\lambda = 0.71073$ Å)) at 298 K. Positions for the hydrogen atoms were calculated geometrically using the riding model with fixed isotropic temperature factors. Values of the obtained final indices were $R = 4.04\%$ and $R_w = 4.78\%$. A final difference Fourier electron-density map showed a maximum peak of $0.22 \text{ e}\text{\AA}^{-3}$. IR determinations were performed in a FT-IR Perkin Elmer 2000 spectrophotometer using spectroscopic potassium bromide disk (Merck) in the range 4000 a 450 cm^{-1} .

RESULTS AND DISCUSSION

Structural Aspects

The ORTEP representation ([Figure 1](#)) and obtained structural data, some of which are reproduced in [Table 1](#), are fully consistent with those mentioned in the paper of Mak et al⁸). In that work the macromolecular structure of the compound is described as formed by corrugated layers consisting each of infinite zigzag chains, constituted by 1:2 amine-thiourea molecular aggregates, cross-linked by relatively weaker hydrogen bonds. However, analyzing obtained structural data we have arrived to an alternative description of the same structure: A layered thiourea matrix with HMTU molecules located in the interlaminar spaces. This view, which emphasizes the host-guest complex nature of the product, permits the comparison of this entity with other thiourea supramolecular species, thus contributing to the understanding of the influence of the guest on the structural characteristic of the inclusion compound.

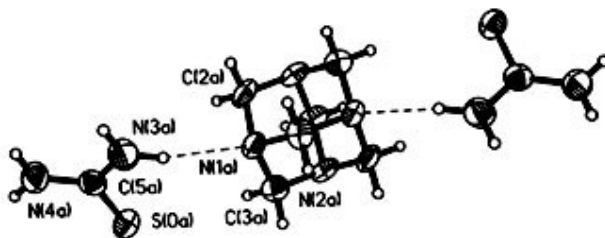


Fig. 1: ORTEP diagram of (2Thiourea)(HMTA). Thiourea and Hexamethylenetetramine are regularly associated. Each hexamethylenetetramine is tethered to two different thiourea molecule through H-bonds ($N_{\text{host}}(3a)-N_{\text{guest}}(1a)=3.73$ Å)

Table 1. Structural parameters and other information relating to the crystal structure refinement of (2 Thiourea) (HMTA).

Space group

C2/c

Lattice parameters a = 18.424(4) Å, b = 8.39(2) Å,
 C = 9.485(11) Å; $\alpha = \beta = 90^\circ$,
 $\gamma = 109.85(3)^\circ$
 No of unique reflexions with I >
 4 σ (\bar{I}) 548
 R 0.0514

Atom	x	y	Z	U ₁₁ / Å ² U ₂₃ / Å ²	U ₂₂ / Å ² U ₁₃ / Å ²	U ₃₃ / Å ² U ₁₂ / Å ²
S	0.345(1)	0.2528(1)	0.2028(1)	0.035(1) 0.007(1)	0.043(1) 0.012(1)	0.049(1) - 0.002(1)
N(1)	0.4513(1)	0.1592(1)	0.6238(1)	0.023(1) 0.002(1)	0.045(1) 0.008(1)	0.040(1) 0.001(1)
N(2)	0.5517(1)	0.3662(1)	0.6954(1)	0.027(1) 0.000(1)	0.041(1) 0.022(1)	0.057(1) - 0.002(1)
N(3)	0.3097(1)	0.0390(1)	0.3731(1)	0.054(1) 0.004(1)	0.051(1) 0.017(1)	0.044(1) - 0.013(1)
N(4)	0.2169(1)	0.0838(1)	0.1453(1)	0.048(1) - 0.001(1)	0.066(1) 0.014(1)	0.045(1) - 0.020(1)
C(1)	0.5000	0.0601(1)	0.7500	0.043(1) 0.000(1)	0.034(1) 0.008(1)	0.043(1) 0.000(1)
C(2)	0.4030(1)	0.2623(1)	0.6811(1)	0.020(1) 0.011(1)	0.049(1) 0.011(1)	0.053(1) 0.004(1)
C(3)	0.5034(1)	0.2622(1)	0.5747(1)	0.041(1) 0.003(1)	0.052(1) 0.018(1)	0.043(1) - 0.002(1)
C(4)	0.5000	0.4630(1)	0.7500	0.043(1) 0.000(1)	0.037(1) 0.035(1)	0.077(1) 0.000(1)
C(5)	0.2859(1)	0.1168(1)	0.2428(1)	0.044(1) - 0.007(1)	0.036(1) 0.018(1)	0.039(1) - 0.001(1)

Bond lengths (Å)

S $\frac{3}{4}$ C(5)	1.708(1)	N(3) $\frac{3}{4}$ C(5)	1.334(1)
N(4) $\frac{3}{4}$ C(5)	1.323(1)	N(1) $\frac{3}{4}$ C(2)	1.471(1)
N(1) $\frac{3}{4}$ C(3)	1.479(1)	N(1) $\frac{3}{4}$ C(1)	1.483(1)
N(2) $\frac{3}{4}$ C(3)	1.474(1)	N(2) $\frac{3}{4}$ C(4)	1.474(1)
N(2) $\frac{3}{4}$ C(2A)	1.471(1)	C(2) $\frac{3}{4}$ N(2a)	1.471(1)
C(4) $\frac{3}{4}$ N(2A)	1.474(1)	C(1) $\frac{3}{4}$ N(1A)	1.483(1)

Bond angles (°)

C(2) ^{3/4} N(1) ^{3/4} C(3)	108.1(1)	C(2) ^{3/4} N(1) ^{3/4} C(1)	107.9(1)
C(3) ^{3/4} N(1) ^{3/4} C(1)	107.6(1)	C(3) ^{3/4} N(2) ^{3/4} C(4)	107.9(1)
C(3) ^{3/4} N(1) ^{3/4} C(1)	107.3(1)	C(4) ^{3/4} N(2) ^{3/4} C(2A)	107.8(1)
S ^{3/4} C(5) ^{3/4} C(3)	119.9(1)	S ^{3/4} C(5) ^{3/4} N(2A)	121.3(1)
N(3) ^{3/4} C(5) ^{3/4} N(4)	118.8(1)	N(1) ^{3/4} C(2) ^{3/4} C(2A)	113.1(1)
N(1) ^{3/4} C(3) ^{3/4} N(2)	112.8(1)	N(2) ^{3/4} C(4) ^{3/4} N(2A)	113.1(1)
N(1) ^{3/4} C(1) ^{3/4} N(1A)	111.8(1)		

The basic unit of this kind of thiourea matrix is a dimer formed by two thiourea molecules hydrogen bonded each other via their N-H protons cis to sulfur as illustrated in scheme of [Figure 2](#). Both the thiourea molecules and the dimers are practically planar species (mean deviation to planarity is about 0,002 Å). Each dimeric unit is in turn hydrogen bonded to other four ones oriented perpendicularly to the former via the same nitrogen and sulfur atoms involved in the formation of the dimer, *a* and *b* in the scheme above, thus bearing to the zigzag surfaces illustrated in [Figure 3](#). One of the protons of the NH₂ groups, labeled with *c* in [Figure 2](#), does not participate in the formation of the thiourea network being directed towards the spaces between the thiourea layers where the guest species HMTA are located. Each amine molecule is indeed hydrogen bonded to two thiourea molecules in adjacent sheets, in the way described schematically in [Figure 4](#), thus bearing to a pillared structured solid. [Figure 5](#) shows two views of the supramolecular structure of (2 Thiourea)(HMTA) illustrating the layered arrangement of thiourea molecules are intercalated.

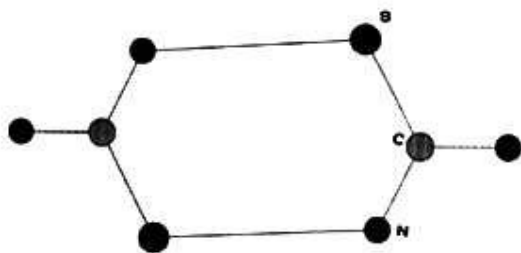


Fig. 2: Schematic representation of the dimeric basic unit in the matrix structure for the inclusion compound (2 Thiourea)(HMTA). Hydrogen bond (N...S) distances: 3.45 Å.

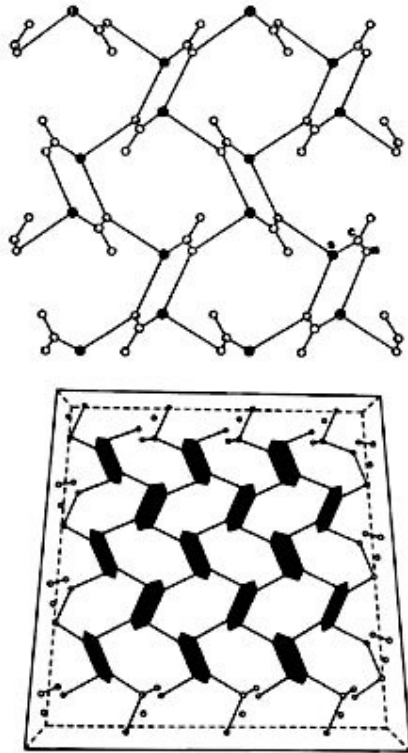


Fig. 3: Two structural representation of the layers in the thiourea matrix for the compound (2 Thiourea)(HMTA). In (b) the dimeric basic units are represented by filled hexagons

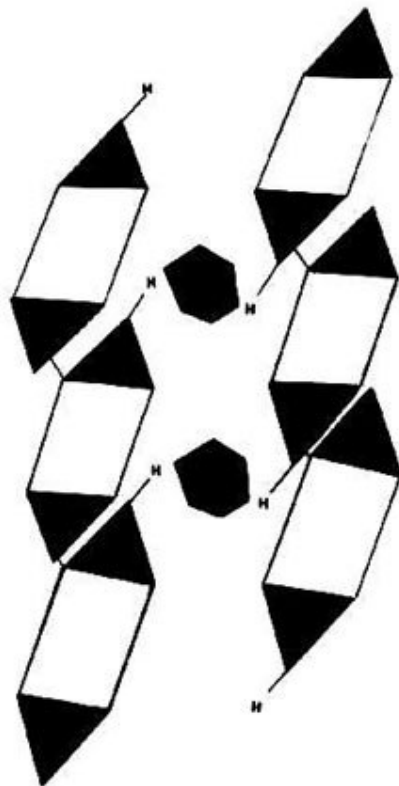


Fig. 4: Scheme of the location and bonding of the hexamethylenetetramine molecules to two adjacent thiourea layers.

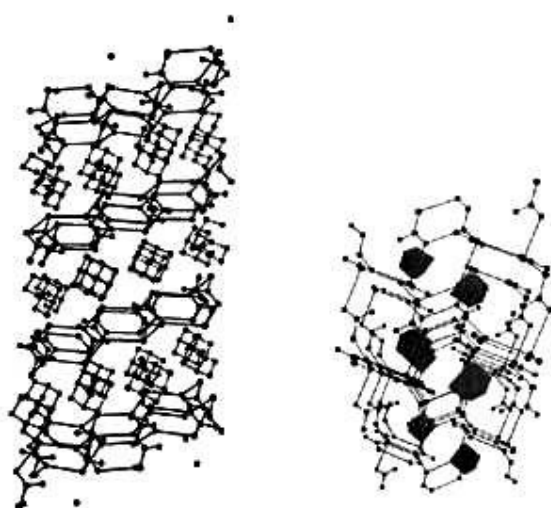


Fig. 5: The supramolecular structure of (2 Thiourea)(HMTA) illustrating the layered arrangement of thiourea molecule in which the hexamethylenetetramine molecules are intercalated. (a) View of the layers directional plane. (b) A view perpendicular to the layer, where hexamethylenetetramine are represented by filled polyhedra.

Infrared Spectra

The host structure described above is evidenced too by the IR spectrum of the product. As observed in Table 2 characteristic bands of the thiourea as well as some absorption arising from the guest may be identified. The effect of the inclusion on the thioamide bond can be there clearly observed. As shown in Table 2, shifts of both C-S and C-N stretching modes to higher frequencies respect to those in the orthorhombic thiourea are observed. Such a reinforcement of the C-N bond is also observed in the formation of typical clathrates (rhombohedral); however, the simultaneous strengthening of the C-S bond appears to be a feature characteristic for the layered thiourea matrix described here. The dimeric nature of the structural ground units (scheme of Figure 2) and the way by which these dimers are arranged in the thiourea network, in which both S-lone pairs are involved, lead to an amide bond description in which the typically sp^2 sulfur hybrid atomic orbital display a relatively higher s character. The strengthening of the S-C bond caused by such an electronic configuration, in addition to the π delocalization proper for the thioamide bond, explains the observed spectroscopic features.

Table 2. Stretching frequencies (cm^{-1}) of thiourea pure and in some inclusion compounds.

Thiourea Compound	ν (C-N)	ν (N-H)	ν (C-S)
Orthorhombic Thiourea	1465	3165	725
(6 Thiourea)(Dicyclohexylamine)	1490	3165	720
(3 Thiourea)(Quinuclidine)	1470	3165	720
(2 Thiourea)(Hexamethylenetetramine)	1480	3165	730

The strong bands associated to the N-H amide bonds, remains practically unaltered and no information about the host-guest interactions may be obtained by this method.

Table 3. Medium effects on ^{13}C -NMR chemical shifts in hexamethylenetetramine.

Medium	^{13}C -NMR Chemical Shifts (ppm)
Thiourea	73.96 75.78*
CDCl_3^{a}	74.89
CDCl_3^{b}	74.91
CCl_4	75.78

^a 1% p/v

^b Saturated solution

*Doublet with intensity 2:1

^{13}C -NMR Spectra

In table 3 are reported the ^{13}C -NMR spectra of HMTA in the solvents CCl_4 and CDCl_3 as well as in the intercalation described above. As observed in [Figure 6](#), the HMTA ^{13}C -NMR spectrum in the intercalation product corresponds to two complexes, broad signals with maxima at 73.96 and 75.78 ppm, respectively. That contrast with the spectrum of free HMTA with six magnetically equivalent carbon atoms, for which only one ^{13}C -NMR only one signal is expected. Thus in a CCl_4 solution the observed chemical shift is indeed 75.78 ppm. The complexity of the spectrum in the solid phase essentially arises from two different factors, one due to nuclear dipolar magnetic interactions and the other to host-guest chemical interactions. A more detailed analysis of the spectrum can be obtained of the spectrum deconvolution considering both, the host-guest chemical interactions and dipolar nuclear magnetic interactions; results are illustrated by the segmented lines in [Figure 6](#). The magnetic non-equivalence of the HMTA carbons is produced by the interaction with the TU-matrix. As shown in the structural description above, the amine is anchored to the matrix only by two of its four nitrogen atoms. As deduced from the interaction scheme illustrated in [Figure 5](#), two of the six methylen groups should be more affected by the host-guest hydrogen-bond interactions, Thus, three signals with intensities 1:4:1 centered at 76.8, 74.0 and 73.0 ppm are expected. The chemical shifts indicate that the matrix effects on the methylene groups are similar to those occurring in the carbon tetrachloride and chloroform solutions, respectively. The relative magnitude of the effect on the two methylene groups are also in accordance with the acceptor capacities observed for these solvents which have acceptor numbers of 8.6 and 23.1 relative to n-hexane⁹). Moreover, each line is in turn splitted into two lines of the same intensity separated approximately 1.8 ppm, that agreeing with the observed signal intensities. That because for ^{13}C nuclei directly bonded to nitrogen (^{14}N , $I=1$), MAS of microcrystalline samples frequently give patterns consisting in doublets caused by ^{13}C - ^{14}N residual dipolar interaction, not averaged to zero by MAS-NMR¹⁰). The axis of quantization of the ^{14}N nucleus is tilted from the direction of the static magnetic field as a

consequence of the interaction between ^{14}N nuclear moment and the electric field gradient at the ^{14}N nucleus^{4, 10}). That bearing the splitting into doublets of the two signals already commented. The residual dipolar interaction between ^{13}C and ^{14}N which results to be about 250 Hz, is about ten fold higher than in C_α of amine in typical clathrates³⁻⁷).

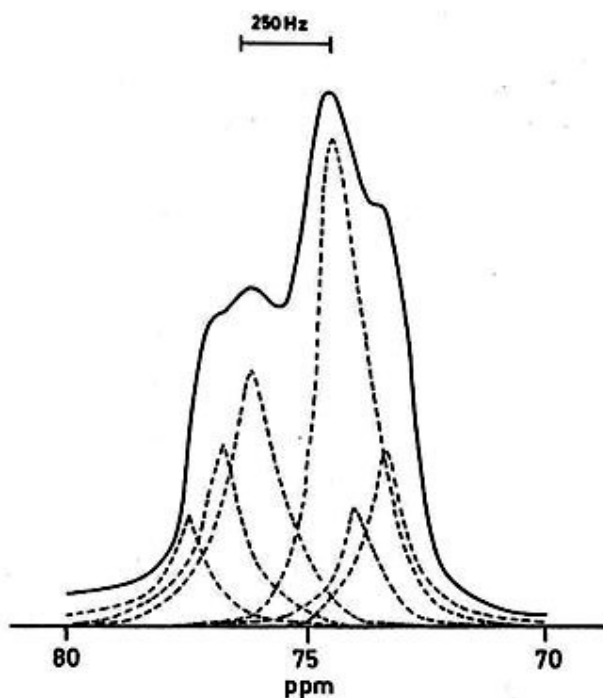


Fig. 6: HMTA ^{13}C -NMR spectrum zone of (2 Thiourea)(HMTA) and its deconvolution, considering the host-guest and dipolar nuclear magnetic interactions.

Furthermore, the MAS ^{13}C -NMR spectrum of the compound shows a resonance line at 182.0 ppm corresponds to the carbon of the thiourea molecule, different chemical values have been reported previously³⁻⁷) or amine-thiourea systems (about 180-182 ppm). ^{13}C -NMR measurements of crystalline thiourea and of thiourea in CDCl_3 solution show single resonance lines at 180.8 and 184.5 ppm, respectively.

CONCLUSIONS

The thiourea-hexamethylenetetramine supramolecular complex described here is a commensurate host-guest complex which can be described as an intercalation of hexamethylenetetramine in a layered thiourea matrix. The IR and ^{13}C -NMR analysis of the compound indicate features that totally agree with the observed structure and show that both matrix and host are altered by the interaction. Indeed, the guest induces in this case a host structure different to classical thiourea clathrates and, simultaneously matrix effects are altering the electronic structure of the intercalated HMTA. The different nature of the hydrogen bonds and the structural versatility of the amide and thioamide matrices²) involved in such complexes make them suitable, at least in a first approximation, as alternative models for molecular

biological systems. Dynamic NMR studies which could improve this perspective are in progress.

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