Bis(thiourea)-1,2-diazabicyclo[2.2.2]octane. A new layered thiourea inclusion compound

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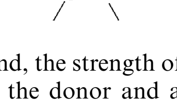
Thiourea reacts with 1,4-diazabicyclo[2.2.2]octane (DABCO) in methanol, leading to the layered inclusion compound (thiourea)$_2$·(DABCO). Single crystal X-ray diffraction analysis was carried out. The structure may be described as a supramolecular arrangement in which the DABCO molecules are intercalated in a layered network formed by two-dimensional nesting of thiourea molecules. The solid state ^{13}C CP-MAS NMR study of the compound shows only a single line for C_α with a residual dipolar interaction between ^{13}C and ^{14}N of less than 80 Hz, attributed to weak guest–host interaction.

Introduction

Urea and thiourea are known to form numerous crystalline "host–guest" inclusion compounds. In these products, the urea or thiourea molecules form extensive hydrogen bonded host structures in which a variety of guest molecules of appropriate size and shape are included.[1–3] The nature of both the vacancies in the amidic host and the host–guest interactions, as well as the "self assembling" capability of the system may be considered as a model for biological systems, especially for features occurring in cavities inside protein structures. From this point of view, it is interesting to investigate the conditions determining this type of molecular self-organisation.

Thiourea frequently forms macromolecular complexes displaying stoichiometries with guest–host ratios of 1 : 3*n* where *n*, which is approximately an integer, depends on the size of the guest. In these conventional inclusion compounds, thiourea molecules are arranged in hydrogen bonding networks which define one-dimensional, non-interacting tunnels.[4–7] This is indeed the most stable configuration for products arising from the inclusion of inert host molecules as hydrocarbons[1–7] or some mono-functional amines[8] in the thiourea matrix. Thioamide compounds interact with Lewis bases (**D**) and acids (**A**) *via* the formation of hydrogen bonds and by classical coordinative interactions respectively:



For a given compound, the strength of the interaction will be mainly determined by the donor and acceptor capacity of **A** and **D**.[9] Considering the Donor Numbers[10] or other similar scales[11] as a measure of the donor strength of Lewis bases, the basicity of amines is generally considerably higher than that of oxygen donors like alcohols, ethers, amides or sulfoxides. Amines could therefore compete for hydrogen bonding with the thiourea affecting the formation of the host structure. An example of this feature is the 1 : 2 molecular inclusion compound produced by the reaction of hexamethylenetetramine (1,3,5,7-tetrazadamantane) and thiourea.[12] In the crystal lattice of this compound dimeric thiourea molecular components are connected by N···H–N and S···H–N hydrogen bonds to form corrugated layers normal to the *b*-axis giving a structure which may be described as a layered network formed by two-dimensional nesting of thiourea molecules in which the hexamethylenetetramine (HMTA) molecules are intercalated.[13] The formation of a laminar structure is possibly related not only to the basicity of the guest but also to the presence of two functional groups located symmetrically in the molecule. In order to corroborate such a hypothesis, the reaction of thiourea with 1,4-diazabicyclo[2.2.2]octane, DABCO, reported in this paper, was studied. The product corresponds to a new pillared supramolecular structure in which two-dimensional thiourea networks are stacked by guest bridges.

Experimental

Commercially available thiourea (Aldrich) and DABCO (Aldrich) were used as received. The product was prepared by mixing at room temperature the thiourea and the amine, both dissolved in methanol (Merck), in the stoichiometric ratio 2 : 1. Slow solvent evaporation leads to large plate-shaped crystals which were collected, washed with cold methanol, and dried under vacuum. The colourless crystalline product melting at 429 K has the composition $C_8H_{20}N_6S_2$ (Found (calc.): C, 37.11 (36.82); N, 25.18 (25.03); H, 7.57 (7.66)%).

A single crystal with dimensions 0.40 × 0.40 × 0.60 mm was selected for the X-ray diffraction analysis. Data were collected on a Siemens R3m/V diffractometer with graphite monochromated Mo-Kα radiation ($\lambda = 0.71073$ Å) at 293 K. Intensity data for 1347 reflections ($h = -4$ to 11, $k = 0$ to 9, $l = -21$ to 21) were collected in the $2\Theta/\Theta$ scan mode in the range $5° < 2\Theta < 50°$. From 1328 independent reflections ($R_{\text{int}} = 0.7\%$), 999 were observed with $I > 2\sigma(I)$. Intensity data were corrected for Lorentz polarisation but not for absorption. The crystal corresponds to the space group *Cl*c. Data collection and crystal parameters are reported in Table 1.†

The structure was solved by direct methods and refined on F^2 against all reflections by full-matrix least-square adjustment methods using the Siemens SHELXS-97.[14] Positions for the hydrogen atoms were calculated geometrically using the riding

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† CCDC reference number 188/252. See http://www.rsc.org/suppdata/p2/a9/a908919e/ for crystallographic files in .cif format.

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model with fixed isotropic temperature factors. Values of the obtained final indices were $R = 9.4\%$ for all reflections. A final difference Fourier electron-density map showed a maximum peak of 0.93 e A^{-3}. Atomic scattering factors were taken from the *International Tables for Crystallography* (1992, Vol. C).

Solution, high resolution ^{1}H and ^{13}C NMR data were obtained with a Bruker AMX-300 spectrometer. The cross-polarisation magic angle spinning ^{13}C CP-MAS solid state NMR study was performed on Bruker MSL-100 equipment at a frequency of 25.14 MHz. The polycrystalline powder samples were spun at a frequency of 4 MHz. The number of scans varied between 200 and 1200 with 5.5 μs, 90° pulses; 1 ms cross-polarisation contact time; 41 ms acquisition time during proton decoupling; and 5 s recycle delay. The chemical shifts are given relative to tetramethylsilane (TMS).

Results and discussion

A complete structural determination of the studied compound was performed. The ORTEP representation is illustrated in Fig. 1. Selected bond distances and angles for the studied structure are given in Table 2. The structure corresponds to a supramolecular laminar arrangement in which the thiourea molecules are forming solid layers among which the DABCO molecules are intercalated as illustrated in Fig. 2. The DABCO molecules are linked to the layers *via* N(DABCO)··· H–N(thiourea) hydrogen bonds. So the guest molecule rotates about its N–N axis. Such a feature can be observed in the thermal displacements (*vide infra*).

The thiourea–DABCO host–guest complex may be thus described as a pillared structure in which laminar thiourea networks are held together by DABCO bridges. In Fig. 3a and 3b are illustrated the structure of a thiourea layer and a transversal view along the spaces between two layers respectively. The host solid layers appear thus as an orthogonal arrangement of thiourea molecules defining parallelepipedal spaces of about 159.6 Å^{3} (see Fig. 3a). Facing these spaces in the middle point between two parallel layers, the bifunctional guest DABCO molecules are working as pillars thus resulting in interlaminar distances of 7.8 Å (see Fig. 3b).

Table 1 Crystallographic data for TU_2·DABCO

Chemical formula	$C_8H_{20}N_6S_2$
Formula weight	264.42
Crystal system	monoclinic
Space group	*C*/*c*
μ/cm^{-1}	3.715
R Values	0.0939; 0.2290
Unit cell dimensions/Å	$a = 9.680(3)$
	$b = 7.870(3)$
	$c = 18.254(6)$
	$\beta = 95.27(3)°$
Unit cell volume/Å^{3}	1384.7(8)
Temperature of data collection/K	393
Z	4
Measured/Independent reflections; *R*(int)	1347/1328; 0.007

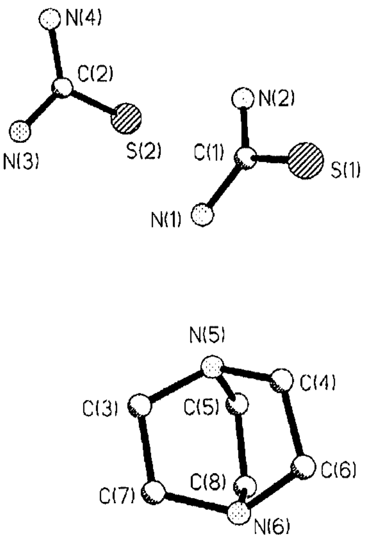

Fig. 1 ORTEP representation of the molecular structure of the compound (thiourea)$_2$·DABCO.

The MAS ^{13}C NMR spectrum of the compound shows a relatively broad resonance at 182 ppm corresponding to the thiourea carbon nuclei. The chemical shift value for DABCO inserted in thiourea is 47.42 ppm and is similar to those in $CDCl_3$ 1% (47.37 ppm) and $CDCl_3$ saturated solution (47.39 ppm) and somewhat lower than in CCl_4 (47.92 ppm). This last feature indicates that relatively strong host–guest interactions are actually occurring.

For ^{13}C nuclei directly bonded to nitrogen (^{14}N, $I = 1$), MAS frequently gave powder patterns consisting of approximately 1:2 (or 2:1) doublets because of the ^{13}C–^{14}N residual dipolar interaction which is not averaged to zero by MAS-NMR.[15] 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 the ^{14}N nuclear quadrupole moment and the electric field gradient at the ^{14}N nucleus.[16,17] As shown in Fig. 4, which reproduces the ^{13}C CP-MAS NMR spectrum of the (thiourea)$_2$·DABCO inclusion compound, residual dipolar interaction between ^{13}C and ^{14}N is less than 80 Hz. This entry is however higher than for the C_α of amines in typical clathrates.[18] The spectrum thus shows only a single line for C_α, with the typical asymmetric doublet not being detected. Similar behaviour has been observed for solid free DABCO at 355 K; however it is known that at lower temperature the doublet is observed.[19]

It is then expected that the splitting of the C_α resonance line caused by the ^{13}C–^{14}N interactions already commented on be

Table 2 Selected bond lengths (Å) and bond angles (°) of Tu_2·DABCO

Bonds				Hydrogen bonds	
C(1)N(2)	1.337(8)	N(6)C(6)	1.47(1)	N(1)H(1)N(5)	2.070
S(2)C(2)	1.694(7)	N(6)C(7)	1.49(1)	N(2)H(2)S(2)	2.463
C(2)N(3)	1.336(8)	N(6)C(8)	1.50(1)	N(2)H(1)S(2)	2.579
(C2)N(4)	1.331(8)	C(3)C(7)	1.50(1)	N(3)H(1)S(1)	2.554
N(5)C(3)	1.48(1)	C(4)C(6)	1.49(1)	N(3)H(2)S(1)	2.493
N(5)C(4)	1.47(1)	C(5)C(8)	1.50(1)		
N(5)C(5)	1.49(1)				
Angles					
N(1)C(1)N(2)	117.9(8)	N(4)C(2)S(2)	121.8(7)	C(3)N(5)C(5)	107.2(6)
N(1)C(1)S(1)	120.8(7)	N(3)C(2)S(2)	120.4(7)	C(6)N(6)C(7)	122.7(6)
N(2)C(1)S(1)	121.3(7)	C(4)N(5)C(3)	113.7(6)		
N(4)C(2)N(3)	117.7(8)	C(4)N(5)C(5)	101.8(6)		

Table 3 Comparison of the anisotropic displacement parameters ($U/10^{-3}$ Å^2) of hexamethylenetetramine (HMTA) and 1,4-diazabicyclo[2.2.2]-octane (DABCO) in their inclusion compounds with thiourea

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
HMTA						
N(1)	23(1)	45(1)	40(1)	02(1)	08(1)	01(1)
N(2)	27(1)	41(1)	57(1)	00(1)	22(1)	−02(1)
C(1)	43(1)	34(1)	43(1)	00(1)	08(1)	00(1)
C(2)	20(1)	49(1)	53(1)	11(1)	11(1)	04(1)
C(3)	41(1)	52(1)	43(1)	03(1)	18(1)	−02(1)
C(4)	43(1)	37(1)	77(1)	00(1)	35(1)	00(1)
DABCO						
N(5)	45(6)	65(8)	40(5)	02(5)	23(5)	06(6)
N(6)	53(6)	37(5)	47(6)	03(5)	15(5)	−09(5)
C(3)	102(12)	92(10)	92(11)	−28(9)	29(9)	−46(9)
C(4)	253(35)	407(50)	282(39)	271(40)	233(34)	222(36)
C(5)	118(13)	130(14)	43(6)	0.5(6)	−04(7)	−78(10)
C(6)	159(18)	103(12)	160(16)	100(12)	117(15)	72(12)
C(7)	252(25)	73(9)	147(16)	57(10)	166(18)	65(13)
C(8)	76(1)	142(14)	48(7)	23(8)	06(6)	−41(10)

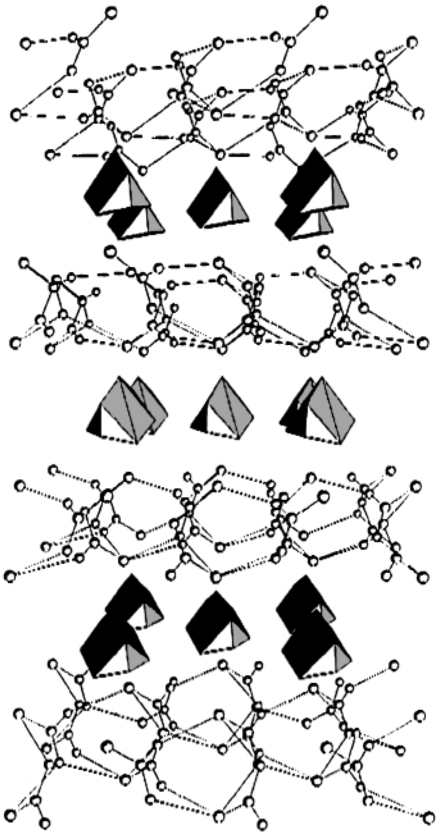

Fig. 2 Laminar nature of the supramolecular structure of the compound (thiourea)$_2$·DABCO.

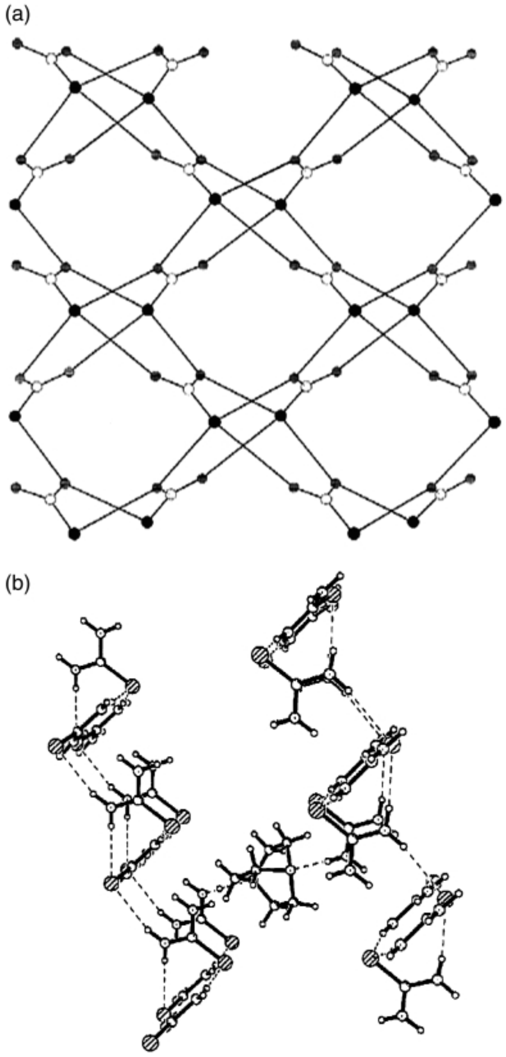

Fig. 3 Structure of a layer of the thiourea matrix (a) and transversal view of the supramolecular structure (b) of the compound (thiourea)$_2$·DABCO.

related to the thermal movement of the guest in the interlayer host spaces. That can be analysed by comparing the thermal disorder observed in their diffraction pattern obtained for both DABCO and HMTA intercalated in thiourea[13] under similar conditions. As observed in Table 3, the anisotropic displacement parameters are considerably larger for the DABCO than for the HMTA derivative. The comparatively lower broadening of the C_α resonance observed for the compound with DABCO may thus be attributed to a higher flexibility of the guest than for that with HMTA. Since the hydrogen bond distances N_{host}–H···N_{guest} for DABCO and HMTA, 3.055 and 3.073 Å respectively, may suggest a weaker host–guest interaction in the case of the HMTA, so the higher rigidity of the latter should be attributed at least partially to intermolecular interactions induced by the presence of its two nitrogen atoms not involved in the interaction with the thiourea.

Evidence for the host structure described above is also given by the IR spectrum of the product. As shown in Table 4, the stretching frequency ν(N–H) is considerably lower than those observed for other thiourea–amine supramolecular com-

Table 4 Stretching frequencies, ν/cm^{-1}, of pure thiourea and some thiourea inclusion compounds

Thiourea compound	ν(C–N)	ν(N–H)	ν(C–S)
Orthorhombic thiourea	1465	3165	725
(Thiourea)$_6$·dicyclohexylamine	1490	3165	720
(Thiourea)$_3$·quinuclidine	1470	3165	720
(Thiourea)$_2$·hexamethylenetetramine	1480	3165	730
(Thiourea)$_2$·DABCO	1490	3145	720

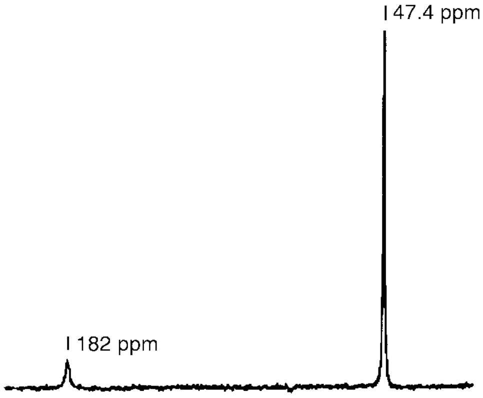

Fig. 4 ^{13}C CP-MAS NMR spectrum of the compound (thiourea)$_2$·DABCO at room temperature.

pounds, revealing strong thiourea–DABCO hydrogen bonding and thus totally agreeing with the relatively short N_{host}–$H \cdots N_{guest}$ distance commented on above. Moreover, as shown in data reported in Table 3, the shifting of both C–S and N–H stretching modes to lower frequencies and the simultaneous strengthening of the C–N linkage with respect to those in the orthorhombic thiourea is observed. Such behaviour is qualitatively similar to, although not so strong as, that observed in the formation of traditional clathrates. The comparison of data in Table 4 under similar conditions with the IR pattern of the also-layered HMTA derivative shows however that the hybridisation changes of sulfur orbitals, deduced from the relative strengthening of ν(C–S) in the latter,[13] do not occur in the case of DABCO.

Acknowledgements

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