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Crown Ether Molecular Complexes with Urea and Thiourea

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Abstract. Crystalline complexes of urea and thiourea with crown ethers, have been prepared, viz., 18-crown-6 (18C6), benzo-18-crown-6 (B18C6), dibenzo-18-crown-6 (DB18C6), dicyclohexano-18-crown-6 (DC18C6) and dibenzo-24-crown-8 (DB24C8). While the complexes of the large ring size crown ether, DB24C8, have high ether to (thio)urea ratios, the stoichiometry of the others lies between one molecule of crown ether and from one to six molecules of (thio)urea. An IR spectral study of the urea and thiourea complexes showed that the behavior of thiourea in these complexes is clearly different from that of urea, indicating the role of sulphur in the interaction of thiourea with crown ethers. The urea and thiourea complexes were classified according to their stoichiometries and their IR spectral behavior into three classes for which credible structures were proposed.

Key words: Solid molecular complexes, crown ethers, urea, thiourea, stoichiometry, IR spectra.

1. Introduction

The property of crown ethers that initially attracted wide attention is their tendency to form complexes with alkali and alkaline earth metal cations. These complexes had been extensively investigated. However the study of well-defined complexes formed between uncharged molecules and crown ethers has recently been receiving increasing interest [1].

Pedersen, in his second paper on macrocyclic polyethers [2], reported a number of crystalline complexes with thiourea. Vögtle and Muller [3] synthesized the 18C6/thiourea complex. The nature of the bonding between the host and the guest in these complexes was not further investigated.

Urea, on the other hand, was reported to increase the solubility of DB18C6 in methanol [2], but crystalline complexes of urea with polyethers could not be obtained with the exception of the 18C6/urea (1 : 5) complex which was synthesized by Uiterwijk *et al.* [4] and the crystal structure obtained using X-ray diffraction. The structure could be described as alternating layers of urea/crown ether complexes and urea molecules. Two molecules of urea were found within the ether cavity (cavitant ureas), each of them forming two hydrogen bonds to 18C6 oxygens and two hydrogen bonds to the outer urea layer which consist of three molecules of

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urea (outer-layer ureas). Attempts to prepare crystalline complexes of urea with B18C6, DB18C6 and DC18C6 and DB24C8 were not successful [4].

The present work was therefore planned in order to try to prepare these complexes as well as those previously reported. This combined study of the stoichiometry of these complexes and their infrared spectroscopic properties should give some insight as to their possible structures.

2. Experimental

IR spectra were recorded in the region 4000–400 cm^{-1} using a Nicolet Impact 400 FTIR spectrometer. A polystyrene film was used to calibrate the spectrometer. KBr discs were used for all samples. Elemental analyses were carried out by Guelph Chemical Laboratories Ltd., Ontario, Canada and M.H.W. Laboratories, Phoenix, Arizona, U.S.A. Melting points were determined using a Harris melting point apparatus with a Gold Brand thermometer (Brand, Germany). All melting points were reported as measured without correction.

2.1. Chemicals

Urea (für Analyse, Riedel-deHaen), thiourea (puriss. A.R., Koch-Light Lab.), 18-crown-6, benzo-18-crown-6, dibenzo-18-crown-6, dicyclohexano-18-crown-6 (for synthesis, Merck), dibenzo-24-crown-8 (purum, Fluka), methanol, chloroform, and diethylether (AR, C.B.H.), were all used without further purification.

2.2. Preparation of complexes

Thiourea complexes of B18C6, DB18C6, and DC18C6 were prepared according to the procedure described by Pedersen [2]. Attempts to prepare the other complexes by the same method failed. They were therefore prepared according to the procedure described for the preparation of the 18C6/urea complex by Uiterwijk *et al.* [4] with some modifications: 1.0 mmol of the crown ether and 1.0 mmol of urea or thiourea were dissolved in a mixture of 4 mL methanol and 4 mL chloroform. The mixture was heated just enough to ensure complete dissolution, and after cooling to room temperature diethyl ether was added dropwise until the mixture became slightly turbid. Upon further cooling colorless crystals were formed. However, attempts to prepare the B18C6/urea complex by either of these two methods were without success.

The melting points and the elemental analysis results for these complexes are given in Table I.

Table I. Some experimental and physical properties of crown ether complexes with urea (u) and thiourea (tu)

No.	Complex (ratio)	m.p. °C	Molecular formula	Elemental analysis*			Other works and remarks
				%C	%H	%N	
1	18C6/u (1 : 5)	142–144	$C_{17}H_{44}O_{11}N_{10}$	35.96 (36.17)	7.68 (7.85)	24.29 (24.81)	Ref. [4]: m.p. = 145–147 ratio (1 : 5)
2	DB18C6/u (1 : 2)	155–157	$C_{22}H_{32}O_8N_4$	55.33 (54.99)	6.64 (6.71)	10.83 (11.66)	
3	DC18C6/u (1 : 6)	130–132	$C_{26}H_{60}O_{12}N_{12}$	42.53 (42.61)	8.41 (8.25)	23.29 (22.94)	
4	DB24C8/u (5 : 2)	94–97	$C_{122}H_{168}O_{42}N_4$	61.73 (62.02)	7.31 (7.17)	2.57 (2.37)	
5	18C6/tu (1 : 4)	163–166	$C_{16}H_{40}O_6N_8S_4$	33.60 (33.79)	7.09 (7.09)	19.23 (19.70)	Ref. [3]: m.p. = 168–174 ratio (1 : 4)
6	B18C6/tu (1 : 1)	121–122	$C_{17}H_{28}O_6N_2S$	53.46 (52.56)	7.43 (7.26)	7.04 (7.21)	Ref. [2]: m.p. = 127 ratio (1 : 1)
7	DB18C6/tu (1 : 3)	165–166	$C_{23}H_{36}O_6N_6S_3$	47.41 (46.92)	5.73 (6.16)	14.16 (14.27)	Ref. [2]: m.p. = 165–166 ratio (1 : 1)
8	DC18C6/tu (2 : 5)	168–173	$C_{45}H_{92}O_{12}N_{10}S_5$	48.45 (48.02)	8.49 (8.24)	11.99 (12.44)	Ref. [2]: m.p. = 168–173 ratio (1 : 6)
9	DB24C8/tu (3 : 2)	91–93	$C_{74}H_{104}O_{24}N_4S_2$	59.23 (59.34)	7.07 (7.00)	3.75 (3.74)	Ref. [2]: m.p. = 105–106 ratio (2 : 7)

* Calculated values are given in parentheses.

3. Results and Discussion

3.1. The stoichiometry of crown ether complexes with urea and thiourea

The 18C6/urea (1 : 5) complex was found to have the same melting point and molar ratio as obtained by Uiterwijk *et al.* [4] using the same method of preparation. Vögtle and Muller prepared the 18C6/thiourea (1 : 4) complex by refluxing 1 mmole of crown ether and 4 mmole of thiourea in methanol. Interestingly, the same ratio and melting point were obtained in the present work using the method described in the experimental part in which 1 mmol of crown ether and 1 mmol of thiourea were used. This may imply that, for this complex, this ratio is favored under different conditions. The B18C6/thiourea prepared in the present work has the same stoichiometry (i.e. 1 : 1) as reported in Pedersen's work [2], while DB18C6/thiourea (1 : 3), DC18C6/thiourea (2 : 5) and DB24C8/thiourea (3 : 2) are found to have dif-

Table II. IR absorption bands of urea complexes in the region 4000–400 cm^{-1}.[a]

Assignment[b]	Urea (u)	18C6/u (1 : 5)	DB18C6/u (1 : 2)	DC18C6/u (1 : 6)	DB24C8/u (5 : 2)
$\nu_{as}NH_2$	3446 (s)	3446 (sh)		3447 (s)	
		3408 (s)	3500–3300		3500–3300
ν_sNH_2	3348 (s)	3348 (s)	(br)	3345 (s)	(br)
Associated νNH_2:					
• (u—u)[c]	3259 (m)		3252 (sh)	3259 (m)	
• (u—CE)[d]		3197 (s)	3190 (s)	3203 (m-s)	3200 (m-s)
$\nu C{=}O$, βNH_2	1683 (s)	1683 (s)	1668 (s)	1683 (s)	1674 (s)
		1657 (s)	1660 (s)		1657 (s)
		1651 (sh)	1652 (sh)		
βNH_2	1629 (s)	1627 (s)	1618 (s)	1629 (s)	1629 (s)
βNH_2, $\nu C{=}O$	1600 (s)	1600 (s)	*	1600 (s)	*
$\nu_{as}N—C—N$	1465 (s)	*	*	1465 (s)	*
		1456 (s)			
ρNH_2	1155 (m)	1166 (m)	1162 (w)	1163 (sh)	*
ρNH_2	1055	*	*	*	*
$\nu_sN—C—N$	1005	*	*	*	*
$\omega C{=}O$	788 (w)	788 (w)	*	788 (w)	*
				776 (w)	
Torsional NH_2	720 (w)	740 (sh)	*	*	*
		669 (m, br)	633 (w)	660 (w)	
$\delta N—C—O$		601 (s)	601 (s)	600 (m)	
	574 (s)	591 (sh, m)	581 (sh, m)	574 (s)	*
$\delta N—C—N$	561 (s)	547 (m)	540 (m)	547 (s)	*
ωNH_2	534 (br, s)	532 (m)	530 (m)	527 (m)	*

* These positions were overshadowed by strong crown ether absorption.
[a] Key: ν_{as}; asymmetric stretching, ν_s; symmetric stretching, δ; in plane bending, ρ; rocking, ω; wagging, (s); strong, (m); medium, (w); week, (sh); shoulder, (br); broad.
[b] References for assignment are [5], [11], [12] and [13].
[c] Hydrogen bonded NH_2 of urea to urea.
[d] Hydrogen bonded NH_2 of urea to crown ether.

ferent stoichiometries; see Table I for comparison. A literature search has shown that the DB18C6/urea (1 : 2), DC18C6/urea (1 : 6) and DB24C8/urea (5 : 2) complexes have not been prepared previously.

3.2. Effect of complexation on the urea and thiourea absorption bands

The absorption bands for the urea and thiourea complexes in the range 4000–400 cm^{-1} are given in Tables II and III, respectively.

Table III. IR absorption bands of thiourea complexes in the region 4000–400 cm^{-1}.[a]

Assignment[b]	Thiourea (tu)	18C6/tu (1 : 4)	B18C6/tu (1 : 1)	DB18C6/tu (1 : 3)	DC18C6/tu (2 : 5)	DB24C8/tu (3 : 2)
				3522 (w)		
			3492 (sh)	3497 (w)		
			3461 (w)	3477 (w)		
			3425 (s)	3452 (m)	3440 (s)	
$\nu_{as}NH_2$	3384 (s)			3385 (sh)		3381 (s)
			3360 (sh)	3365 (vs)		
		3348 (s)	3348 (s)	3350 (s)		
					3303 (s)	
ν_sNH_2	3276 (s)	3276 (s)	3290 (s)	3278 (m)	3298 (s)	3275 (s)
	3253 (sh)	3246 (sh)	3240 (m)	3250 (sh)	3245 (sh)	
Associated						
νNH_2:					3190 (sh)	
• (tu—tu)[c]	3178 (s)		3184 (m)	3178 (s, br)	3165 (s)	3174 (s)
• (tu—CE)[d]		3151 (s, br)	3136 (s)		3145 (sh)	
δNH_2	1618 (s)	1622 (s)		1619 (s)		1620 (sh)
	1610 (sh, s)	1610 (s)	1612 (s)	1611 (s)	1608 (s)	1608 (s)
νC—N	1473 (s)	1470 (m)	1477 (sh)	1473 (s)	1476 (m)	*
		1458 (m)				
νC=S			1438 (s)			
	1413 (vs)	1419 (s)	1423 (s)	1415 (s)		1412 (m)
		1410 (m)				
		1402 (m)				1404 (sh)
		1394 (m)	1391 (w)	1399 (s)	1398 (s)	1400 (m)
		1386 (w)	1382 (w)	1387 (sh)	1390 (s)	
		1374 (w)			1374 (m)	
ρNH_2	1083 (m-s)	*	*	*	1094 (sh)	*
ωC=S		745 (sh)			736 (s)	
	729 (s)	725 (s)	*	*	726 (s)	*
Torsional NH_2		655 (m)			658 (sh)	
	632 (m)		633 (m)	632 (w)	644 (s)	*
		629 (s)			622 (s)	
		613 (s)				
		595 (s)	603 (s)		607 (s)	
			588 (s)			
		577 (sh, m)	572 (m-s)			
			560 (m-s)	561 (m, br)	560 (sh)	
			542 (m)		544 (sh)	
δN—C—S	500 (sh, s)	533 (w)	513 (m-s)	522 (m)	520 (w)	*
				507 (m)		
δN—C—N	486 (s)	486 (s)	486 (s)	486 (m)	483 (s)	*
		478 (s)	476 (w)	472 (m)		
ωNH_2	463 (br, s)		450 (w)	464 (m)		
		450 (w)				
					432 (w)	

* These positions were overshadowed by strong crown ether absorption.
[a] Key: as in Table II.
[b] References for assignments are [14] and [15].
[c] Hydrogen bonded NH_2 of thiourea to thiourea.
[d] Hydrogen bonded NH_2 of thiourea to crown ether.

Table IV. The difference between the band centres ν_m (of ν_{as} and ν_s) in urea or thiourea and the characteristic new band frequencies ν_c in the complexes.

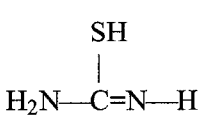
	18C6	B18C6	DB18C6	DC18C6	DB24C8
$\nu_{m(u)}$—ν_c	200		207	194	197
$\nu_{m(tu)}$—ν_c	179	194	*	165	*

* No characteristic new band was observed for these complexes.

The spectra of urea, thiourea and their complexes in the 3600–3000 cm^{-1} region are shown in Figures 1 and 2. Among the general features of the urea spectrum in this region are those usually due to a hydrogen bonding interaction, as shown by the broadening and overlapping of the νNH_2 stretching bands. However, the appearance in the spectra of the complexes of new bands at about 3200 cm^{-1} may be attributed to complex formation since they are absent in the spectra of uncomplexed urea and crown ethers. The difference between the band centre ν_m (of uncomplexed urea) and those new bands of the complexes are given in Table IV. The values fall in the range 194–207 cm^{-1} and show the extent of the strength of the hydrogen bonding interaction in these complexes, which follows the order:

DB18C6/u > 18C6/u > DB24C8/u > DC18C6/u.

On the other hand, some of the thiourea complexes showed a different behavior, viz., splitting and appearance of some bands at frequencies higher than the $\nu_{as}NH_2$ band of uncomplexed thiourea (see Table III and Figure 2). These bands cannot all be attributed merely to Fermi resonance (with the first overtone of the $\beta NH_2(B_1)$ or combination bands of other modes of vibration). The appearance of strong bands at frequencies higher than the $\nu_{as}NH_2$ band of uncomplexed thiourea was noted in the complexes of B18C6, DB18C6 and DC18C6. These bands, which have no counterparts in urea complexes, may be due to the presence of the sulphur atom and could be related to either: (i) charge-transfer from oxygens or the π-system of benzo-crown ethers to the empty *d*-orbital of the sulphur atom in thiourea: this will decrease the contribution of resonance forms **IIa** and **b**, thus effectively leading to a higher frequency for νNH_2; or: (ii) from a tautomeric form (thioimido)



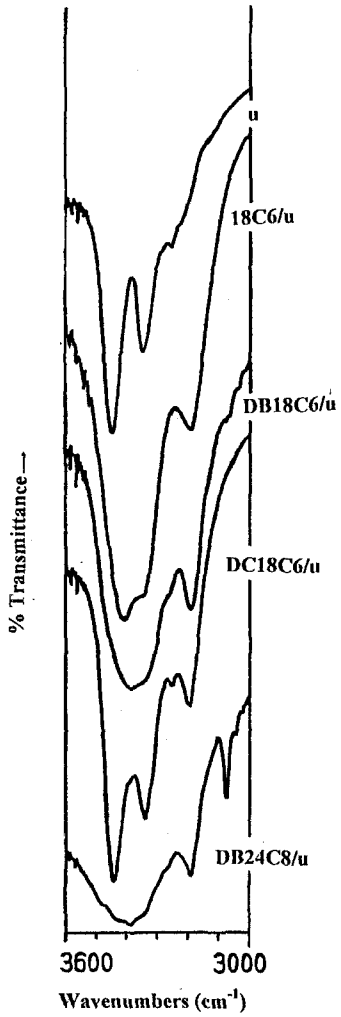
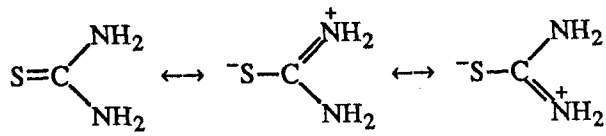


Figure 1. νNH_2 absorption bands of urea (u) and urea complexes with crown ethers.

in which the =N—H stretching vibration lies at higher frequency than that of the NH_2 stretching vibration. The latter, if present, should give rise to an S—H vibration which was not observed in the present work.



I **IIa** **IIb**

Similar to urea complexes, some thiourea complexes (viz., 18C6, B18C6, DC18C6) also show new bands in the range 3136–3151 cm^{-1} which may also

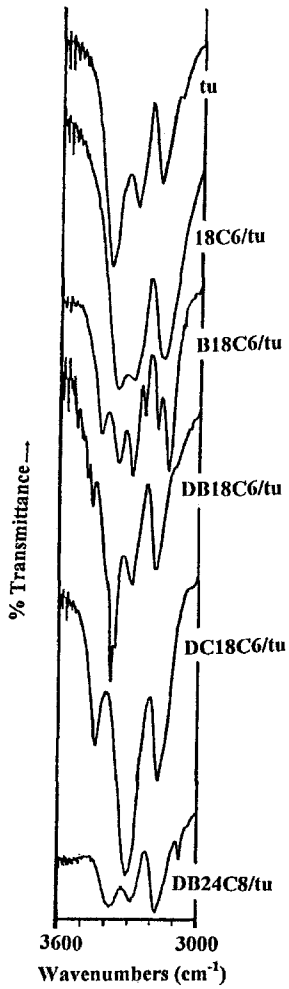


Figure 2. νNH_2 absorption bands of thiourea (tu) and thiourea complexes with crown ethers.

be attributed to complex formation since they are absent in the spectra of the uncomplexed thiourea and crown ethers. The difference between the band centre ν_m (of uncomplexed thiourea) and those new bands of the complexes are given in Table IV, from which the following trend can be inferred about the strength of hydrogen bonding interaction:

B18C6/tu > 18C6/tu > DC18C6/tu

In both this sequence and the one for urea complexes, the presence of the aromatic ring seems to enhance the interaction of the small ring-size crown ethers.

The NH_2 deformation and C=O stretching vibrations are coupled with each other in the spectrum of urea [5], so it is not easy to explain the behavior of these bands

Table V. The 18C6 absorption bands of the urea and thiourea complexes.*

Assignment	18C6	18C6/u (1 : 5)	18C6/tu (1 : 4)
			2912 (s)
$\nu_{as}CH_2$	2894 (s)	2908 (s)	2896 (s)
			2887 (s)
ωCH_2	1350 (s)	1353 (s)	1350 (s)
			1296 (m-w)
Aliphatic ν_{as}C—O—C	1107 (vs)	1107 (vs)	1105 (vs)
	1075 (w)	1075 (w)	1075 (m)
			1061 (m-w)
			1037 (w)
	1019 (m, sh)		
Aliphatic ν_sC—O—C	965 (vs)	962 (vs)	959 (m)
			950 (m)
			925 (w-m)
			912 (w-m)
νC—C	843 (sh)		844 (s)
	837 (s)	838 (s)	836 (sh)
			815 (w)
			759 (w)

* Key: as in Table II.

in the complexes. However, the NH_2 rocking band at 1155 cm^{-1} in uncomplexed urea was found shifted to higher frequency in all complexes (see Table II) which could be due to hydrogen bond interaction. The νC—N stretching band at 1465 cm^{-1} in uncomplexed urea was found to be overshadowed by strong crown ether absorption in the complexes.

The NH_2 deformation and C—N stretching bands of thiourea were hardly affected upon complexation with crown ethers, while the νC=S band was split into several bands in thiourea complexes which indicate that the interaction site may be the sulphur atom rather than/or in addition to the NH_2 of thiourea. In the B18C6/thiourea complex the νC=S band was clearly shifted to higher frequency (see Table III) which can also be explained by the decrease of the contribution of the resonance forms **IIa** and **IIb** as a result of the interaction possibly between the sulphur atom of thiourea and the ether oxygens. Sulphur–oxygen interaction in the solid state was reported to be of a strength comparable with that of a hydrogen bonding interaction [6, 7].

The torsional NH_2 vibration at 720 cm^{-1} in uncomplexed urea was observed as a broad shoulder at 740 cm^{-1} in the 18C6/urea complex while it was not observed for other complexes. The in-plane N–C–O bending (δNCO) of urea was shifted to higher frequency in the complexes, while that of the in-plane N—C—N bending (δNCN) was shifted to lower frequency. This can be explained in the following

way: as the N—C—N angle decreases by the effect of hydrogen bonding to the crown ether, the bending frequency decreases, but at the same time the N—C—O angle increases, leading to an increased N—C—O bending frequency [8].

The torsional NH_2 vibration of thiourea was shifted to higher frequency in the 18C6 and DC18C6 complexes as a result of hydrogen bond interaction, while, strangely, it remained constant in the B18C6 and DB18C6 complexes. In this region (630–530 cm^{-1}), rather strong bands appeared in thiourea complexes of the 18C6 ethers (see Table III) which cannot be considered as a simple shift of uncomplexed thiourea bands. It seems that they may belong to some structures in which the sulphur of thiourea is strongly involved.

3.3. Effect of complexation on crown ether absorption bands

While both the B18C6 and DC18C6/thiourea complexes did not show marked changes in the crown ether spectral bands, the others, which are discussed below, presented some interesting spectral features.

3.3.1. *18C6/Urea and Thiourea Complexes*

Some IR absorption bands of 18C6 compared to those in the urea and thiourea complexes are given in Table V. The observed splitting in the bands of the thiourea complex of 18C6 ($\nu_{as}CH_2$, ωCH_2, ν_{as}C—O—C, ν_sC—O—C and νC—C), which was not observed in those of the urea complex, can be explained by the fact that the urea complex is highly symmetric with 18C6 adopting a D_3d symmetry [4], while the thiourea complex is expected to be less symmetric due to the effect of the sulphur atom of thiourea, which may distort the ether ring upon complexation.

3.3.2. *DB18C6/Urea and Thiourea Complexes*

One of the interesting features of the spectra of the DB18C6/urea and thiourea complexes is, respectively, the pronounced weakening and the disappearance of the aliphatic ν_sC—O—C band which appears at 996 cm^{-1} in uncomplexed DB18C6. This is probably due to the guest molecules causing the two aliphatic C—O—C moieties of the ether to be arranged more symmetrically about the centre of symmetry of the DB18C6 molecule so that the net change in dipole moment, resulting from the two symmetrical stretching vibrations, becomes close to zero. Interestingly, the same band was found to disappear in the DB18C6 complexes with alkali-metal salts [9], which may also be expected to behave in the same way.

3.3.3. *DC18C6/Urea Complex*

The broad band at 1099 cm^{-1} in uncomplexed DC18C6, which contains the asymmetrical stretching of the two types of C—O—C bonds, (a) and (b) in **III**, is split into two strong bands at 1091 and 1074 cm^{-1} in the urea complex; see Figure

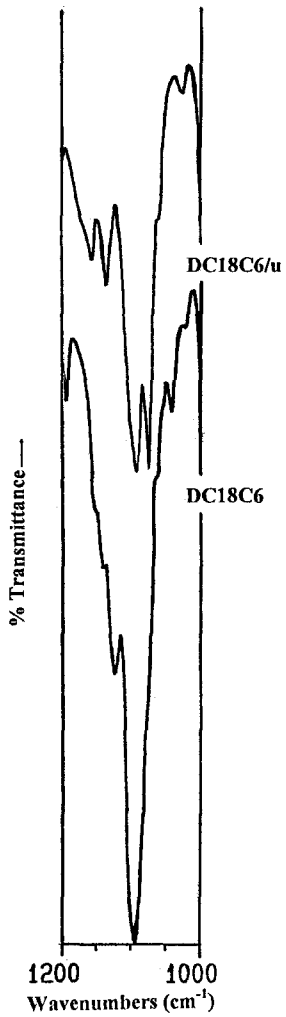
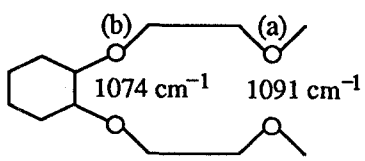


Figure 3. ν_{as}C—O—C of DC18C6 and of the DC18C6/urea complex.

3. The band at 1091 cm^{-1} in the complex can be assigned to the asymmetrical C—O—C stretching of type (a), and the band at 1074 cm^{-1} to that of type (b) which are separated from each other by the stronger hydrogen bonding interaction between urea and the more basic oxygens attached to the cyclohexane ring.



III

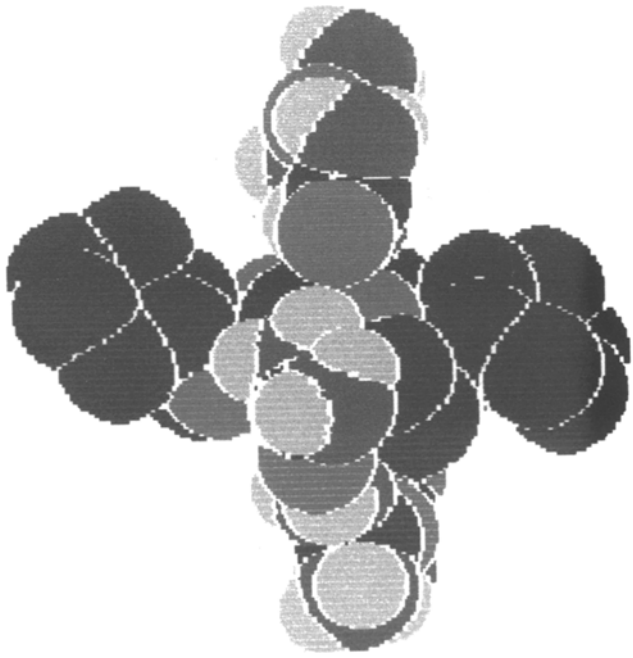


Figure 4. Space-filling model proposed for the structure of the DC18C6/urea (1 : 6) complex. Carbon, hydrogen, nitrogen, and oxygen atoms are shown.

3.3.4. *DB24C8/Urea and Thiourea Complexes*

With five and three DB24C8 molecules, respectively, involved in the urea and thiourea complexes, hardly any changes were observed in the absorption bands of the ether. In contrast, greater changes were observed in the vibrational bands of the urea and thiourea molecules of these complexes (see Tables II and III). Such behaviour may indicate that while the urea and thiourea molecules are strongly interacting among themselves, the ether molecules are weakly affected.

3.4. CLASSIFICATION OF COMPLEXES

Depending on the ether : (thio)urea stoichiometries and the infrared spectral behavior, urea and thiourea complexes with crown ethers can be classified into three classes:

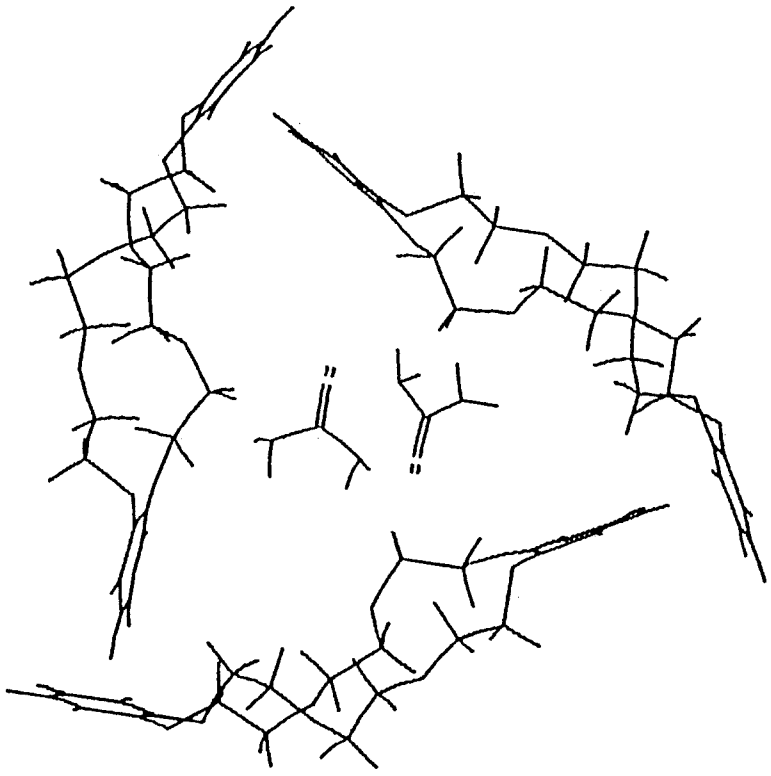


Figure 5. Representation of a model structure of the DB24C8/thiourea (3 : 2) complex.

3.4.1. *Class I: Complexes with Low Ratio of Crown Ether to Urea or Thiourea: 18C6/Urea (1 : 5), 18C6/Thiourea (1 : 4), DB18C6/Thiourea (1 : 3), DC18C6/Urea (1 : 6) and DC18C6/Thiourea (2 : 5)*

By comparison with the reported X-ray structure of the 18C6/urea (1 : 5) complex [4], these complexes can be considered to consist of alternating layers of (thio)urea–crown ether complexes and (thio)urea molecules. Some urea or thiourea molecules lie within the ether cavity (cavitant ureas or thioureas), each of which forms hydrogen bonds with the ether oxygens and hydrogen bonds with the outer layer urea or thiourea. These complexes are characterized by having both shifted and unshifted IR absorption bands with reference to the bands in solid urea or thiourea, particularly ν_{as} and ν_s NH_2, βNH_2, $\nu C{=}O$ and $\nu C{=}S$ absorption bands (Tables II and III). The shifted bands are those of the cavitant urea or thiourea molecules and the unshifted bands are those of the outer-layer molecules.

Since the DC18C6/urea (1 : 6) complex showed mainly the outer-layer urea absorption bands, i.e. unshifted with respect to solid urea (see Table II), an annular structure was assumed in which the six urea molecules are arranged through hydrogen bonding involving —NH· · ·O=C of the ureas around the DC18C6 mole-

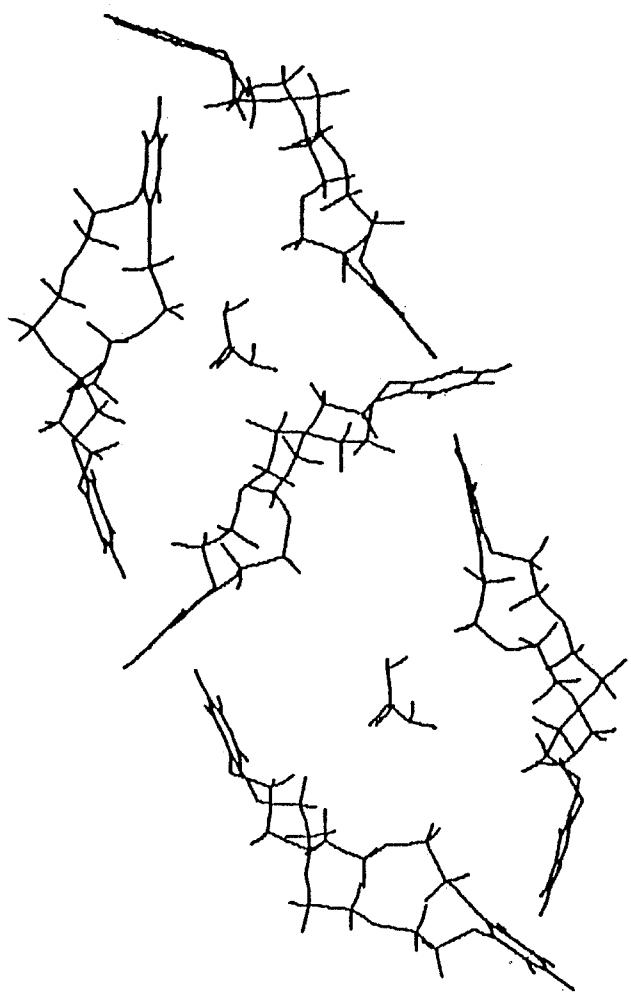


Figure 6. Representation of a model structure of the DB24C8/urea (5 : 2) complex.

cule occupying an axial position as illustrated in the proposed space-filling model shown in Figure 4.

3.4.2. *Class II: Complexes with 1 : 1 and 1 : 2 Stoichiometry: B18C6/Thiourea (1 : 1) and DB18C6/Urea (1 : 2)*

Because of the (1 : 1) and (1 : 2) stoichiometries of these complexes, it is most unlikely that the crown ethers are incorporated in urea or thiourea channels or layers. Depending on this, and on the fact that these complexes show mainly shifted urea or thiourea absorption bands, the structure of these complexes may be considered as an inclusion of urea or thiourea molecule(s) in the ether cavity.

3.4.3. *Class III: Complexes with a High Ratio of Crown Ether to Urea or Thiourea; DB24C8/Urea (5 : 2) and DB24C8/Thiourea (3 : 2) Complexes*

These ratios are characteristic of the complexes of the larger ring size crown ether, namely DB24C8. The possible structures of these unique complexes can be considered as channels of DB24C8 in which the urea or thiourea molecules are incorporated, as shown in Figures 5 and 6. These channels are constructed so that they permit the aromatic C—H bond of one DB24C8 to be perpendicular to the plane of the benzene ring of the other DB24C8 which is expected to give a strong interaction [10], as shown in the model drawn in Figure 5. Attempts to incorporate two urea molecules in the five-membered DB24C8 channel is too loose to account for the appearance of a distinct hydrogen-bonded νNH_2 band (see Figure 1). So the structure shown in Figure 6, in which two channels were assumed, is more reasonable because it better accounts for such an interaction.

4. Concluding Remarks

Urea complexes show the usual features of hydrogen bonding interaction in their IR spectra, viz., broadening and shifts of the NH_2 stretching bands to lower frequencies, while thiourea complexes show a different behavior, viz., splitting and shifting of some νNH_2 bands to higher frequencies. These facts, together with the large distortion of the $\nu C{=}S$ band in thiourea complexes, and the marked effect that the sulphur atom has on the crown ether IR absorption bands could lead to the conclusion that, while the hydrogen bonding interaction is the predominant type of interaction in the urea complexes, other types of interactions involving the sulphur atom may be significant in the thiourea complexes, possibly through the sulphur *d*-orbital. Furthermore, the observed trends concerning the strength of interaction in urea and thiourea complexes reveal the importance of the donacity of crown ethers (rendered by the benzo substituents, as in B18C6 and DB18C6) over the basicity of the crown ether oxygen.

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