cyclopropyldicarbinyl biradical), in the same way as a substituent affects the equilibrium between norcaradiene and cycloheptatriene. In the latter case, it was known that electron-accepting groups (such as Ph, CN, *etc.*) strengthen the opposite bond in the cyclopropyl ring and hence favor the equilibrium towards norcaradiene, whereas electron-donating groups weaken the same bond and hence favor cycloheptatriene (Hoffman & Stohrer, 1971; Wehner & Günther, 1975). Iwamura *et al.* (1980) have rationalized the exclusive formation of (2) from (1) by arguing that vinyl–benzo bridging is favored close to the bridgehead phenyl group. In addition, the 1,3-biradical formed is more stable than that formed *via* the alternative pathway because of the stabilization offered by the phenyl substituent in the former case. Traces of COT (3) formed in acetone (Fig. 1) may be attributed to partial direct excitation of the starting material.

Structure of COT (3)

On direct irradiation, a product (3), spectroscopically consistent with a COT structure, is formed *via* the singlet excited state of (1) (since it is not formed in the presence of a triplet energy sensitizer). The actual structure of the COT may be either that derived by a $(2\pi + 2\pi)$ mechanism or that from the fragmentation of biradical (5) (Fig. 4), which is difficult to distinguish based on spectral data (Pokkuluri *et al.*, 1993). Hence, a single-crystal X-ray structure determination was carried out which proved the structure of (3) to be that derived from the fragmentation of biradical (5) (Fig. 4). Based on GC retention times, the COTs formed in solution and in the solid-state photolysis of (1) are the same.

This study provides another example of the unexpected behavior of the singlet excited state of a bridgehead-substituted dibenzobarrelene in producing an abnormal COT, while reacting as expected *via* the triplet excited state. It can also be taken as additional support for the assignment of the di-π-methane rearranged structure for the semibullvalene formed in the triplet sensitized photolysis of the 9,10-dimethyl compound (Pokkuluri *et al.*, 1993). The reasons for not obtaining any ester migration product from (1), similar to that observed in the solid-state photolysis of the 9,10-dimethyl compound, are not clear.

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References

ALLEN, F. H. (1981). *Acta Cryst.* B**37**, 890–900.
DUNITZ, J. D. (1968). *Perspectives in Structural Chemistry*, Vol. 2, edited by J. D. DUNITZ & J. A. IBERS p. 47. New York: Wiley.
GARCIA-GARIBAY, M., SCHEFFER, J. R., TROTTER, J. & WIREKO, F. C. (1990). *Acta Cryst.* B**46**, 79–87, 431–440.
HOFFMANN, R. & STOHRER, W.-D. (1971). *J. Am. Chem. Soc.* **93**, 6941–6948.
IWAMURA, M., TUKADA, H. & IWAMURA, H. (1980). *Tetrahedron Lett.* **21**, 4865–4868.
Molecular Structure Corporation (1990). *TEXSAN Structure Analysis Software*. MSC, 3200A Research Forest Drive, The Woodlands, TX 77381, USA.
PADDICK, R. G., RICHARDS, K. E. & WRIGHT, G. J. (1976). *Aust. J. Chem.* **29**, 1005–1015.
POKKULURI, P. R., SCHEFFER, J. R. & TROTTER, J. (1993). *Acta Cryst.* B**49**, 107–116.
RICHARDS, K. E., TILLMAN, R. W. & WRIGHT, G. J. (1975). *Aust. J. Chem.* **28**, 1289–1300.
TROTTER, J. & WIREKO, F. C. (1990). *Acta Cryst.* C**46**, 103–106.
WEHNER, R. & GÜNTHER, H. (1975). *J. Am. Chem. Soc.* **97**, 923–924.

Acta Cryst. (1993). B**49**, 760–768

Stabilizing Role of Included Solvent in Ternary Complexation: Synthesis, Structures and Thermal Analyses of Three 18-Crown-6/Sulfonamide/Acetonitrile Inclusion Compounds

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Abstract

The synthesis, thermal analyses and X-ray crystal structures of three ternary inclusion compounds, each containing 1,4,7,10,13,16-hexaoxacyclooctadecane (18-crown-6), ethanenitrile (acetonitrile) and a sulfonamide, in different molar ratios, are reported. The compounds are: (I) 1,4,7,10,13,16-hexaoxacyclooctadecane–4-amino-*N*-(5-methoxy-2-pyrimidinyl)benzenesulfonamide–ethanenitrile (1/2/4),

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$C_{42}H_{60}N_{12}O_{12}S_2$, $M_r = 989.13$, $I2/c$, $a = 16.304$ (6), $b = 20.321$ (8), $c = 15.939$ (6) Å, $\beta = 102.25$ (2)°, $V = 5161$ (3) Å^3, $Z = 4$, $D_x = 1.273$ g cm^{-3}, λ(Mo $K\alpha$) = 0.7107 Å, $\mu = 1.63$ cm^{-1}, $F(000) = 2096$, $R = 0.051$ for 3446 unique reflections. (II) 1,4,7,10,13,16-hexaoxacyclooctadecane–4-amino-*N*-2-thiazolylbenzenesulfonamide–ethanenitrile (1/1/1), $C_{23}H_{36}N_4O_8S_2$, $M_r = 560.68$, $P2_1/n$, $a = 8.355$ (4), $b = 40.104$ (4), $c = 9.339$ (2) Å, $\beta = 111.13$ (3)°, $V = 2919$ (2) Å^3, $Z = 4$, $D_x = 1.276$ g cm^{-3}, λ(Mo $K\alpha$) = 0.7107 Å, $\mu = 2.21$ cm^{-1}, $F(000) = 1192$, $R = 0.041$ for 4236 unique reflections. (III) 1,4,7,10,13,16-hexaoxacyclooctadecane–4-amino-*N*-(4-methyl-2-pyrimidinyl)benzenesulfonamide–ethanenitrile (1/2/2), $C_{38}H_{54}N_{10}O_{10}S_2$, $M_r = 875.03$, $P2_1/c$, $a = 13.558$ (3), $b = 14.570$ (3), $c = 11.404$ (1) Å, $\beta = 95.38$ (1)°, $V = 2243$ (1) Å^3, $Z = 2$, $D_x = 1.296$ g cm^{-3}, λ(Mo $K\alpha$) = 0.7107 Å, $\mu = 1.74$ cm^{-1}, $F(000) = 928$, $R = 0.047$ for 3234 unique reflections. These compounds show analogous behaviour on heating. Differential scanning calorimetric traces recorded in the range 300–500 K indicate loss of CH_3CN as the first step, followed by recrystallization of the resulting binary crown ether–sulfonamide complex and finally, melting of the latter with decomposition. X-ray analysis reveals distinctly different modes of CH_3CN inclusion. In (I), CH_3CN molecules engage in cavitate binding (C—H···O) to the host crown ether as well as clathrate binding, occupying channels in the crystal. The sulfonamide is not directly associated with the host. In (II), the host displays face differentiation, with CH_3CN ligated (C—H···O) to one face and the sulfonamide ligated (N—H···O, C—H···O) to the other face. The CH_3CN molecules in (III) occupy channels only, while the amino groups of two inversion-related sulfonamide molecules are hydrogen bonded (N—H···O) to opposite faces of the crown ether.

Introduction

Numerous structural studies of binary complexes formed between crown ethers and sulfonamides on the one hand, and between crown ethers and the solvent acetonitrile on the other, have appeared in the crystallographic literature. Recently reported examples of complexes in the former class include 1:1 benzenesulfonamide–(18-crown-6) (Buchanan, Morat, Charland, Ratcliffe & Ripmeester, 1989) and complexes of sulfaguanidine with dicyclohexano-18-crown-6 isomers (Simonov, Battaglia, Corradi, Ianelli, Pelosi, Ganin & Lukjanenko, 1990). Host–guest interactions in these species usually comprise multiple moderately strong N—H···O hydrogen bonds. Complexes in the second class owe their existence to very weak (solvent)C—H···O(crown ether) hydrogen bonds. The importance of this type of interaction in molecular recognition has been highlighted in recent studies of 18-crown-6.2CH_3CN (Rogers, Richards & Voss, 1988; Garrell, Smyth, Fronczek & Gandour, 1988; Weller, Borgholte, Stenger, Vogler & Dehnicke, 1989), dibenzo-18-crown-6.2CH_3CN (Rogers, 1988) and dinaphthopyridino-18-crown-6.2CH_3CN (Panneerselvam, Chacko, Weber & Köhler, 1990).

We have begun a study of complexation between crown ethers and various sulfonamides using acetonitrile as the common solvent for these species. Under these conditions, ternary crystalline inclusion compounds result. The acetonitrile molecules included in these compounds may stabilize the resulting crystal structures either by clathrate binding (occupying voids or channels in the crystal and engaging in van der Waals interactions only), by cavitate binding (complexing with the crown ether host by C—H···O hydrogen bonding), or by a combination of the two. The sulfonamides referred to in the present study are 4-amino-*N*-(5-methoxy-2-pyrimidinyl)benzenesulfonamide, 4-amino-*N*-2-thiazolylbenzenesulfonamide and 4-amino-*N*-(4-methyl-2-pyrimidinyl)benzenesulfonamide, commonly known as 5-methoxysulfadiazine, sulfathiazole and sulfamerazine respectively. We report the preparation, thermal analysis and X-ray crystal structures of three ternary inclusion compounds with the formulations: (I) [(18-crown-6)(CH_3CN)$_2$](5-methoxysulfadiazine)$_2$.2CH_3CN, (II) [(18-crown-6)(sulfathiazole)(CH_3CN)] and (III) [(18-crown-6)(sulfamerazine)$_2$].2CH_3CN and we discuss the nature of their host–guest interactions in relation to those existing in relevant model binary complexes.

Experimental

Crystal preparation and initial characterization

Compounds (I)–(III) were prepared by mixing a solution of 18-crown-6 in CH_3CN with a solution of the appropriate sulfonamide in CH_3CN, followed by heating of the resultant solution between 328 and 333 K for 15 min. For (I), 0.356 mmol of the crown ether in 4 cm^3 CH_3CN and 0.712 mmol of the sulfonamide in 15 cm^3 CH_3CN were mixed. For each of (II) and (III), 0.378 mmol of the crown ether in 2 cm^3 CH_3CN and 0.756 mmol of the sulfonamide in 15 cm^3 CH_3CN were mixed. In each case the solution was cooled to 293 K and colourless prismatic crystals grew by slow evaporation over a period of 2–3 weeks. Elemental analyses were performed with a Heraeus universal combustion analyzer, model CHN-Rapid. Thermogravimetry (TG) and differential scanning calorimetry (DSC) were performed using a Perkin–Elmer PC7-Series Thermal Analysis System calibrated with indium and zinc standards.

Sample masses for TG were 4–10 mg and for DSC 3–13 mg. Scan rates of 10 K min^{-1} were generally used for both methods. Samples were placed in vented pans and an N_2-purge at 40 cm^3 min^{-1} was used. Melting or other temperatures reported are from the extrapolated onset to peak temperature.

X-ray analyses

Crystals of (I) and (III) suffered rapid initial loss of CH_3CN on exposure to air. During their mounting in Lindemann capillaries filled with mother liquor, the crystals were prevented from contact with air. Crystals of (II) appeared to be relatively stable and a single crystal was mounted in a sealed capillary containing a trace of mother liquor. Preliminary unit-cell and space-group data were obtained from precession photographs. Intensity data were collected to $2\theta_{max} = 50°$ on an Enraf–Nonius CAD-4 diffractometer using graphite-monochromated Mo $K\alpha$ radiation ($\lambda = 0.7107$ Å). All reflection intensities were prescanned and those with $I < \sigma(I)$ were flagged as weak. The prescan intensity was accepted for reflections with $I \geq 20\sigma(I)$. For all other reflections, final scans were performed at a calculated maximum allowable speed, subject to a maximum measuring time of 40 s per reflection. The intensities of three standard reflections were checked every hour and orientation control was performed every 200 measured reflections. Data were corrected for Lorentz and polarization effects. Empirical absorption corrections from program *EAC* (Enraf–Nonius, 1979) were applied to the data for (II) (with largest crystal size and largest μ value). Since the variation in the transmission factors was negligible (0.9792–0.9992), absorption corrections for (I) and (III) were deemed unnecessary. The structure of (I) was solved by direct methods using program *SHELXS*86 (Sheldrick, 1985). The coordinates of the two independent S atoms in (II) and those of the S atom in (III) were determined by inspection of sharpened Patterson syntheses calculated with *SHELX*76 (Sheldrick, 1976) and were used for initial phasing. The remaining non-H atoms were revealed in subsequent $\Delta\rho$ syntheses. All H atoms were located in $\Delta\rho$ maps. In particular, no substantial evidence for rotational disorder of the H atoms of the ligating CH_3CN molecules was detected in the analyses of (I) and (II). These H atoms were found in the $\Delta\rho$ range 0.22–0.37 e $Å^{-3}$ and were successfully modelled as rigid bodies with C—H fixed at 1.00 Å and with a common variable U_{iso} in each structure. Refined U_{iso} values were 0.19 (2) and 0.17 (1) $Å^2$ for (I) and (II), respectively. [The validity of using a single U_{iso} parameter for the H atoms of both cavitate- and clathrate-bound CH_3CN in (I) was subsequently confirmed in a separate refinement which yielded individual values of 0.20 (3) and 0.22 (3) $Å^2$, respectively.] This modelling yielded final $\Delta\rho$ maps which were practically featureless ($\Delta\rho < 0.14$ e $Å^{-3}$) in the region of the CH_3CN methyl groups. The remaining H atoms were added in idealized positions with the exception of those attached to the sulfonamide N atoms, where free refinement was allowed. All non-H atoms were treated anisotropically and H atoms were assigned common variable U_{iso} values for chemically related groups. Refinement by full-matrix least squares using program *SHELX*76 (Sheldrick, 1976) was based on minimizing $\sum w(|F_o| - |kF_c|)^2$ using the criterion $I_o > 2\sigma(I_o)$ for observed reflections in all cases. Weighting schemes were chosen to yield uniform distributions of $\langle w(\Delta F)^2 \rangle$ with $\sin\theta$ and $(F/F_{max})^{1/2}$. Data for (I) were collected for the setting $C2/c$ with $a = 20.238$ (8), $b = 20.321$ (8), $c = 15.939$ (6) Å, $\beta = 128.07$ (2)°. Least-squares refinement in this setting yielded correlation coefficients in the range 0.60–0.64 between the x and z coordinates of all atoms. This was attributed to the large β angle (Stout & Jensen, 1968). These correlations were eliminated after transformation of all data to the non-standard setting $I2/c$, with β closer to 90° as reported here. The general equivalent positions in $I2/c$ are $[(0,0,0; \frac{1}{2},\frac{1}{2},\frac{1}{2}) + x, y, z; -x, -y, -z; -x, y, \frac{1}{2} - z; x, -y, \frac{1}{2} + z]$. Complex neutral atomic scattering factors for non-H atoms were employed (Cromer & Mann, 1968) and for H atoms, those of Stewart, Davidson & Simpson (1965). Dispersion corrections were from Cromer & Liberman (1970). Other programs used included *PARST* (Nardelli, 1983) and *PLUTO*89 (Motherwell, 1989).

Results and discussion

Thermal analyses

The TG and DSC curves shown in Fig. 1 for compound (I) are representative of the behaviour of all three title compounds on heating. Endotherm *A* in the DSC curve is associated with a significant mass loss recorded by TG and reflects the release of CH_3CN as the first step in the thermal decomposition of these compounds. The binary sulfonamide/18-crown-6 species resulting from the desolvation undergoes a phase change (endotherm *B*) to form a species which finally melts with decomposition (endotherm *C*). The absence of an initial plateau in the TG curve is due to rapid initial loss of CH_3CN from the crystals. Within 1 min, clear crystals of (I) and (III) become opaque on exposure to air. This rendered accurate mass-loss measurement and quantitative DSC difficult. Desolvation onset temperatures from duplicate DSC measurements were 353, 352 and 373 K for (I), (II) and (III), respectively, and were reproducible within 5 K. Enthalpies of desol-

Table 1. *Elemental analyses and TG percentage mass losses*

		% C	% H	% N	% Mass loss
(I)	Calculated	51.0	6.1	17.0	16.6
	Experimental	50.6	6.0	16.6	14.2
(II)	Calculated	49.3	6.5	10.0	7.3
	Experimental	48.9	5.8	10.1	6.8
(III)	Calculated	52.2	6.2	16.0	9.4
	Experimental	52.3	5.6	16.2	8.5

vation are not quoted as these were not reproducible due to CH_3CN loss during weighing and transfer to the DSC apparatus. The data listed in Table 1 were used to establish the following molar ratios of 18-crown-6:sulfonamide:CH_3CN for the compounds studied: (I) 1:2:4, (II) 1:1:1, (III) 1:2:2. These widely differing stoichiometries for compounds displaying essentially the same behaviour on heating prompted further investigation by X-ray crystallographic analysis.

X-ray crystal structures: overall description

Crystal data and details of data collection and refinements are given in Table 2. Fractional atomic coordinates for compounds (I)–(III) are listed in Table 3.*

Structural elucidation of compounds (I)–(III) revealed three distinct modes of inclusion of CH_3CN. In (I) (Fig. 2) the host 18-crown-6 coronates two CH_3CN molecules whose N atoms are acceptors in hydrogen bonding to the amino group of 5-methoxysulfadiazine. Two additional CH_3CN molecules in the formula unit of (I) fill channels in the crystal. (I) is a rare example of an inclusion compound displaying both cavitate and clathrate binding of the same guest within the same crystal (Weber, Franken, Ahrendt & Puff, 1987; Panneerselvam *et al.*, 1990). Compound (II) (Fig. 3), has a CH_3CN molecule ligated to one face of the macrocycle and a sulfathiazole molecule ligated to the other. Thus, only cavitate binding of CH_3CN occurs in this case. Since 18-crown-6 cannot generally act as a face-differing receptor (Weber, 1987), the structure of (II) is both unusual and unexpected. One example of a well documented species with this feature and containing neutral ligands is the 18-crown-6/cyanoacetic acid/water complex (Elbasyouny *et al.*, 1983). In compound (III) (Fig. 4), two inversion-related sulfamerazine molecules are hydrogen bonded (N—H···O) to the host and the CH_3CN molecules are present in clathrated form only, occupying channels in the crystal. Detailed discussion of host–guest binding in (I)–(III) follows, with concluding remarks on the interpretation of thermal analysis results in terms of the known structures. An attempt to explain the widely differing stoichiometries of these compounds is also presented.

Table 2. *Crystal data, data-collection parameters and details of refinements*

	(I)	(II)	(III)
Formula	$C_{42}H_{60}N_{12}O_{12}S_2$	$C_{23}H_{36}N_4O_8S_2$	$C_{38}H_{54}N_{10}O_{10}S_2$
M_r	989.13	560.68	875.03
Space group	*I*2/*c*	$P2_1/n$	$P2_1/c$
a (Å)	16.304 (6)	8.355 (4)	13.558 (3)
b (Å)	20.321 (8)	40.104 (4)	14.570 (3)
c (Å)	15.939 (6)	9.339 (2)	11.404 (1)
β (°)	102.25 (2)	111.13 (3)	95.38 (1)
V (Å^3)	5161 (3)	2919 (2)	2243 (1)
Z	4	4	2
D_x (g cm^{-3})	1.273	1.276	1.296
Crystal size (mm)	0.34 × 0.38 × 0.34	0.35 × 0.50 × 0.60	0.36 × 0.50 × 0.40
Crystal shape	Prismatic	Prismatic	Prismatic
μ(Mo $K\alpha$) (cm^{-1})	1.63	2.21	1.74
F(000)	2096	1192	928
Scan mode	ω–2θ	ω	ω–2θ
Scan width (°)	0.80 + 0.35 tanθ	0.70 + 0.35 tanθ	0.80 + 0.35 tanθ
Aperture width (mm)	1.12 + 1.05 tanθ	1.12 + 1.05 tanθ	1.12 + 1.05 tanθ
θ range (°)	1–25	1–25	1–25
h range	−18,18	−9,9	−16,16
k range	0,24	0,47	0,17
l range	0,18	0,11	0,13
No. of reflections measured	4840	5534	4330
No. of unique reflections	3446	4236	3234
R_{int}	0.096	0.015	0.017
Decay of standards (%)	+0.5	+3.1	−1.0
No. of observed reflections [$I > 2\sigma(I)$]	2159	3055	2356
No. of refined parameters	331	352	292
Max. Δ/σ	0.95	0.10	0.10
$R = \Sigma\|\|F_o\| - \|F_c\|\|/\Sigma\|F_o\|$	0.051	0.041	0.047
$wR = [\Sigma w(\Delta F)^2/\Sigma wF_o^2]^{1/2}$	0.054	0.037	0.042
S	1.519	2.537	2.083
g in weighting scheme $w \propto [\sigma^2(F_o) + gF_o^2]^{-1}$	1.418 × 10^{-3}	0	0
Final $(\Delta\rho)_{max}$ (e Å^{-3})	0.21	0.17	0.18
Final $(\Delta\rho)_{min}$ (e Å^{-3})	−0.25	−0.29	−0.25

* Lists of structure factors, anisotropic temperature factors, bond lengths, bond angles, H-atom parameters and torsion angles have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 55964 (62 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: AB0298]

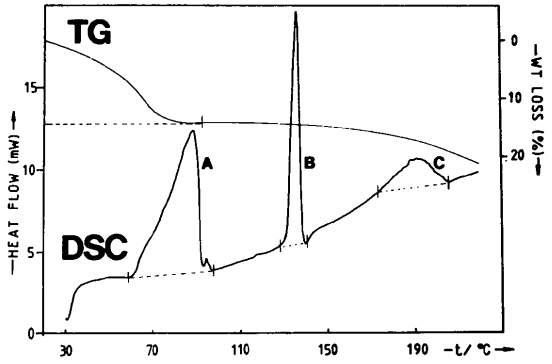

Fig. 1. TG and DSC curves for compound (I).

Geometry of host–guest binding and host conformations

Table 4 lists the parameters describing the C—H···O, N—H···O and other intermolecular

Table 3. *Fractional atomic coordinates* ($\times 10^4$) *and equivalent isotropic thermal parameters* ($Å^2 \times 10^3$) *with e.s.d.'s in parentheses for compounds* (I)–(III)

$U_{eq} = (1/3)\Sigma_i \Sigma_j U_{ij} a_i^* a_j^* \mathbf{a}_i . \mathbf{a}_j .$

	x	y	z	U_{eq}
(I)				
C(1)	7146 (2)	−491 (2)	8043 (3)	47 (1)
C(2)	6402 (3)	−145 (2)	7797 (3)	58 (2)
C(3)	6011 (3)	105 (2)	8399 (3)	61 (2)
C(4)	6340 (3)	27 (2)	9278 (3)	56 (2)
C(5)	7088 (3)	−328 (2)	9523 (3)	58 (2)
C(6)	7482 (3)	−586 (2)	8912 (3)	54 (2)
N(7)	5958 (3)	292 (2)	9878 (3)	75 (2)
S(8)	7665 (1)	−812 (1)	7289 (1)	54 (0)
O(9)	8541 (2)	−871 (1)	7671 (2)	63 (1)
O(10)	7416 (2)	−458 (1)	6505 (2)	69 (1)
N(11)	7370 (3)	−1581 (2)	7113 (3)	59 (2)
C(12)	6547 (3)	−1800 (2)	6827 (3)	53 (2)
N(13)	5968 (2)	−1360 (2)	6524 (2)	61 (1)
C(14)	5181 (3)	−1588 (2)	6269 (3)	63 (2)
C(15)	4995 (3)	−2240 (2)	6329 (3)	62 (2)
C(16)	5656 (3)	−2653 (2)	6651 (3)	70 (2)
N(17)	6445 (2)	−2441 (2)	6912 (2)	61 (2)
O(18)	4218 (2)	−2518 (2)	6108 (3)	89 (2)
C(19)	3532 (3)	−2084 (3)	5899 (4)	79 (2)
C(20)	3573 (4)	4039 (3)	7647 (5)	110 (3)
O(21)	3731 (2)	3421 (2)	7289 (3)	100 (2)
C(22)	3827 (5)	3481 (3)	6439 (5)	128 (4)
C(23)	3935 (5)	2814 (4)	6095 (5)	132 (4)
O(24)	3155 (3)	2469 (2)	5952 (3)	104 (2)
C(25)	3209 (5)	1828 (3)	5651 (4)	110 (3)
C(26)	2384 (5)	1489 (3)	5597 (4)	105 (3)
O(27)	2266 (2)	1377 (2)	6436 (3)	90 (2)
C(28)	1503 (4)	1059 (3)	6448 (5)	104 (3)
C(29)	9475 (4)	−519 (5)	6132 (5)	130 (4)
C(30)	9993 (4)	−729 (3)	5571 (4)	88 (2)
N(31)	10412 (3)	−895 (3)	5144 (4)	126 (3)
C(32)	3416 (4)	2015 (3)	8172 (4)	110 (3)
C(33)	3987 (3)	1560 (3)	8632 (4)	79 (2)
N(34)	4448 (4)	1196 (3)	9004 (4)	153 (3)
(II)				
C(1)	9816 (3)	2029 (1)	6606 (3)	48 (1)
C(2)	11483 (3)	1920 (1)	7373 (3)	53 (1)
C(3)	12779 (4)	2030 (1)	6921 (3)	56 (1)
C(4)	12457 (4)	2251 (1)	5705 (3)	54 (1)
C(5)	10765 (4)	2350 (1)	4913 (3)	59 (1)
C(6)	9474 (4)	2243 (1)	5358 (3)	55 (1)
N(7)	13745 (4)	2370 (1)	5294 (4)	81 (2)
S(8)	8179 (1)	1920 (0)	7261 (1)	60 (0)
O(9)	7353 (3)	2226 (1)	7439 (3)	82 (1)
O(10)	8920 (2)	1714 (1)	8600 (2)	77 (1)
N(11)	6743 (3)	1728 (1)	5894 (3)	58 (1)
C(12)	6899 (3)	1408 (1)	5722 (3)	49 (1)
S(13)	8405 (1)	1126 (0)	6840 (1)	67 (0)
C(14)	7436 (4)	805 (1)	5612 (4)	70 (2)
C(15)	6078 (4)	906 (1)	4468 (4)	69 (2)
N(16)	5788 (3)	1241 (1)	4538 (3)	66 (1)
O(17)	2422 (3)	1512 (1)	3160 (3)	76 (1)
C(18)	2068 (5)	1782 (1)	2109 (4)	99 (2)
C(19)	3702 (6)	1884 (1)	1927 (4)	103 (2)
O(20)	4237 (3)	1615 (1)	1235 (3)	83 (1)
C(21)	5865 (5)	1671 (1)	1113 (5)	103 (2)
C(22)	6236 (5)	1391 (1)	229 (5)	107 (2)
O(23)	6506 (3)	1097 (1)	1095 (3)	85 (1)
C(24)	6975 (5)	822 (1)	362 (5)	113 (3)
C(25)	7210 (5)	521 (1)	1335 (5)	109 (2)
O(26)	5617 (3)	412 (1)	1310 (3)	89 (1)
C(27)	5737 (5)	115 (1)	2173 (5)	107 (2)
C(28)	4055 (6)	46 (1)	2308 (5)	107 (2)
O(29)	3774 (3)	288 (1)	3279 (3)	91 (1)
C(30)	2173 (5)	253 (1)	3472 (5)	109 (2)
C(31)	1980 (5)	532 (1)	4439 (5)	113 (3)
O(32)	1682 (3)	829 (1)	3617 (3)	87 (1)
C(33)	1421 (5)	1104 (1)	4457 (5)	113 (3)
C(34)	987 (5)	1402 (1)	3467 (5)	108 (2)
C(35)	2202 (4)	912 (1)	216 (4)	86 (2)
C(36)	1423 (5)	641 (1)	−788 (5)	90 (2)
N(37)	776 (5)	431 (1)	−1575 (5)	164 (2)
(III)				
C(1)	7805 (2)	6165 (2)	2028 (3)	37 (1)
C(2)	7255 (2)	5385 (2)	1718 (3)	51 (1)
C(3)	6733 (3)	4970 (2)	2526 (3)	55 (1)
C(4)	6722 (2)	5317 (2)	3676 (3)	44 (1)
C(5)	7271 (2)	6111 (2)	3955 (3)	42 (1)

Table 3 (*cont.*)

	x	y	z	U_{eq}
C(6)	7816 (2)	6522 (2)	3153 (3)	39 (1)
N(7)	6222 (3)	4876 (2)	4488 (3)	64 (1)
S(8)	8497 (1)	6682 (1)	996 (1)	45 (0)
O(9)	8850 (2)	7550 (2)	1441 (2)	60 (1)
O(10)	7947 (2)	6650 (2)	−141 (2)	55 (1)
N(11)	9433 (2)	5990 (2)	831 (2)	47 (1)
C(12)	10082 (2)	5651 (2)	1724 (3)	40 (1)
N(13)	10089 (2)	6034 (2)	2781 (2)	47 (1)
C(14)	10714 (3)	5664 (3)	3634 (3)	52 (1)
C(15)	11314 (3)	4936 (3)	3406 (3)	66 (2)
C(16)	11249 (3)	4591 (3)	2273 (3)	61 (2)
N(17)	10627 (2)	4942 (2)	1415 (2)	46 (1)
C(18)	10731 (3)	6079 (3)	4840 (3)	75 (2)
O(19)	3820 (2)	4749 (2)	2850 (2)	75 (1)
C(20)	4007 (3)	3923 (4)	2225 (4)	90 (2)
C(21)	4032 (3)	3134 (3)	3046 (4)	92 (2)
O(22)	4837 (2)	3238 (2)	3890 (3)	76 (1)
C(23)	4891 (4)	2522 (3)	4743 (5)	95 (2)
C(24)	5762 (3)	2692 (3)	5625 (5)	96 (2)
O(25)	5567 (2)	3437 (2)	6335 (3)	78 (1)
C(26)	6398 (3)	3642 (4)	7163 (4)	99 (2)
C(27)	6166 (3)	4469 (4)	7856 (4)	105 (3)
C(28)	8870 (4)	3231 (4)	2097 (4)	111 (3)
C(29)	8408 (3)	3325 (3)	902 (5)	82 (2)
N(30)	8041 (3)	3388 (3)	−17 (4)	111 (2)

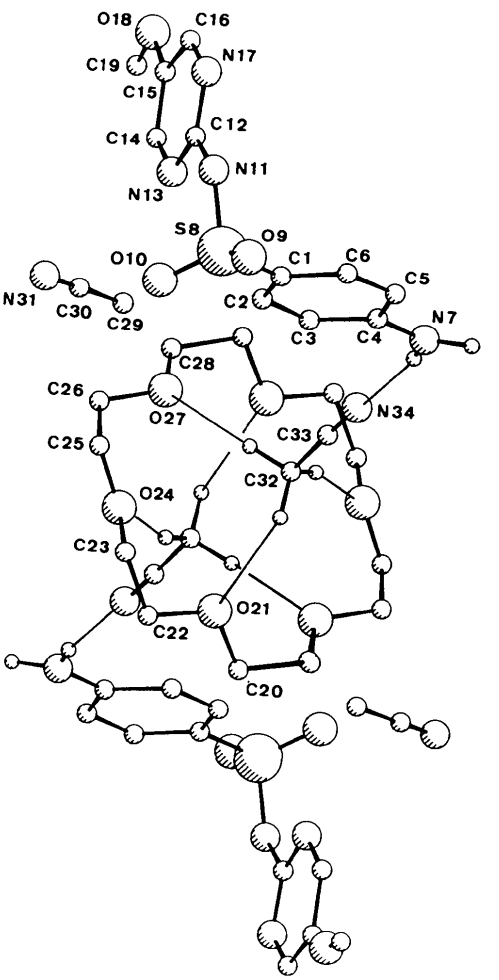

Fig. 2. Structure of compound (I). Thin lines represent hydrogen bonds. Only the solvent methyl H and sulfonamide amino H atoms are included.

associations occurring in crystals of (I)–(III). Torsion angles defining the conformations of 18-crown-6 observed are listed in Table 5. For compounds (I)–(III), the ranges of distances and angles in the macrocycle are: C—C 1.420 (11)–1.498 (7), C—O 1.393 (5)–1.433 (6) Å, C—O—C 111.4 (3)–113.7 (3), C—C—O 107.4 (4)–110.4 (4)°. These are similar to those found in other 18-crown-6 complexes (Garrell *et al.*, 1988). In compound (I) (Fig. 2), the host resides around a centre of symmetry and adopts the well known D_{3d} conformation (Goldberg, 1984). Each of the inversion-related CH_3CN molecules presents its CH_3 group to a host face, forming three-point C—H···O contacts to alternate host O atoms [C···O range 3.264 (7)–3.336 (9) Å, C—H···O angle range 145 (1)–177 (1)°]. The 'tilt' angle (Garrell *et al.*, 1988), defined as that between the C—C≡N axis and the normal to the mean plane of the six host O atoms, is only 10.6 (2)°. To assess the role of C—H···O interactions in (I), we compare the geometrical parameters quoted above with those recently reported for the binary complex 18-crown-6.-$2CH_3CN$ (Rogers *et al.*, 1988; Garrell *et al.*, 1988; Weller *et al.*, 1989), a compound having special significance in the crown ether field because of its instability and practical utility in the purification of 18-crown-6. Compound (I) may be regarded as an extension of this binary complex to a ternary one by inclusion of a second guest, namely 5-methoxysulfadiazine, which is involved in 'second-sphere coordination' to the N-terminus of the ligating acetonitrile molecule. Conflicting results have been reported for independent determinations of the X-ray crystal structure of the monoclinic modification of 18-crown-6.2CH_3CN at 295 K (Garrell *et al.*, 1988) and at 292 K (Weller *et al.*, 1989). In the former study, definite evidence for disorder of the acetonitrile methyl H atoms was found in difference electron-density maps. These atoms were modelled with six half-populated sites distributed at *ca* 60° torsion angle intervals about the CH_3CN principal axis and the disorder was cited as evidence for the lack of any strong orientational influence on the C—H···O interactions. The tilt angle in this species is 31.7°. Weller *et al.* (1989) gave no details for the location of the solvent methyl H atoms in their analysis, but their model clearly implies an ordered arrangement, with alternate host O atoms engaging in three C—H···O contacts, similar to the situation in compound (I). However, the relatively large tilt angle of 31.7° results in a wider range for the H···O contacts (2.43–2.67 Å quoted) than we observe in (I) [2.296 (7)–

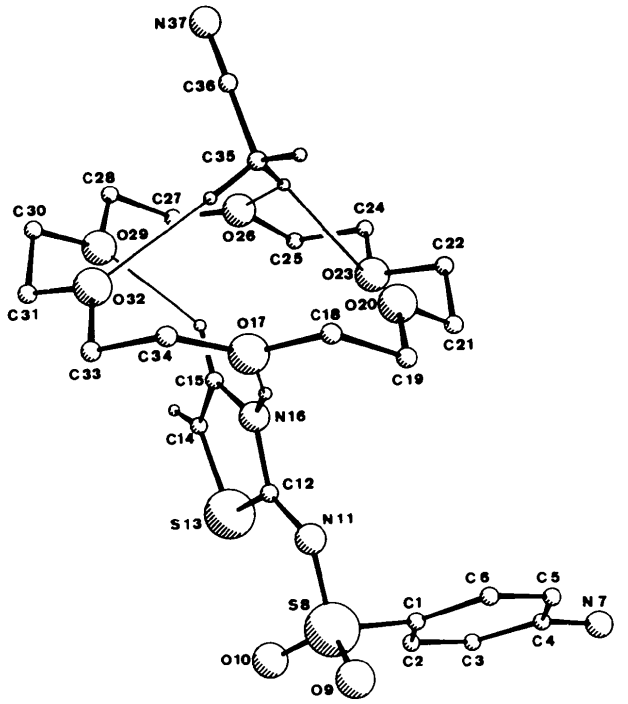

Fig. 3. Structure of compound (II). Thin lines represent hydrogen bonds. Only the solvent methyl H atoms and the H atoms of the thiazole ring are included.

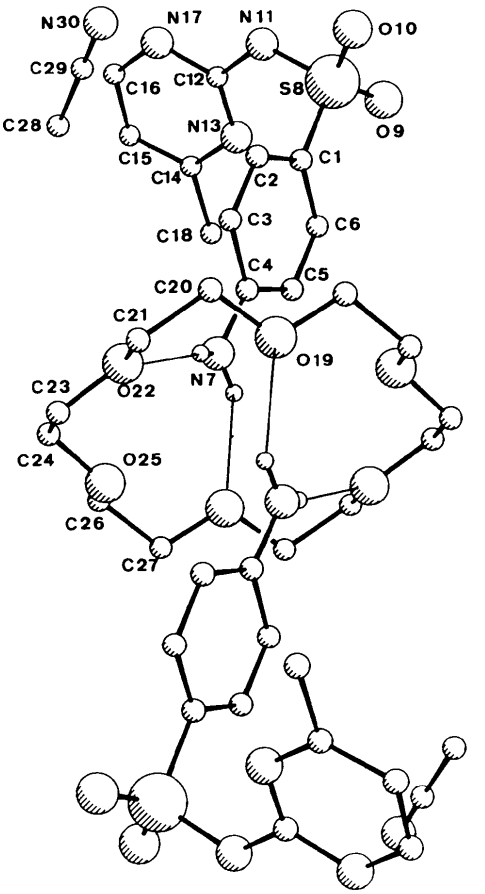

Fig. 4. Structure of compound (III). Thin lines represent hydrogen bonds. Only the sulfonamide amino H atoms are included.

Table 4. *Hydrogen-bond data* (Å, °) *for compounds* (I)–(III) *with e.s.d.'s in parentheses*

Donor—H		Donor···Acceptor		H···Acceptor		Donor—H···Acceptor	
(I)							
C(32)—H(321)	1.00	C(32)···O(27)	3.264 (7)	H(321)···O(27)	2.296 (7)	C(32)—H(321)···O(27)	165.2 (7)
C(32)—H(322)	1.00	C(32)···O(21)	3.273 (8)	H(322)···O(21)	2.407 (8)	C(32)—H(322)···O(21)	144.8 (7)
C(32)—H(323)	1.00	C(32)···O(24')	3.336 (9)	H(323)···O(24')	2.339 (9)	C(32)—H(323)···O(24')	177.2 (6)
N(7)—H(72)	0.91 (5)	N(7)···N(34)	3.150 (7)	H(72)···N(34)	2.25 (5)	N(7)—H(72)···N(34)	170 (4)
N(7)—H(71)	0.97 (5)	N(7)···O(10^{ii})	3.142 (5)	H(71)···O(10^{ii})	2.28 (5)	N(7)—H(71)···O(10^{ii})	148 (4)
N(11)—H(11)	0.80 (4)	N(11)···N(17^{iii})	2.970 (6)	H(11)···N(17^{iii})	2.18 (4)	N(11)—H(11)···N(17^{iii})	176 (4)
(II)							
C(35)—H(352)	1.00	C(35)···O(32)	3.375 (5)	H(352)···O(32)	2.375 (5)	C(35)—H(352)···O(32)	178.6 (4)
C(35)—H(351)	1.00	C(35)···O(23)	3.468 (5)	H(351)···O(23)	2.544 (4)	C(35)—H(351)···O(23)	154.1 (4)
C(35)—H(351)	1.00	C(35)···O(26)	3.332 (5)	H(351)···O(26)	2.564 (5)	C(35)—H(351)···O(26)	133.7 (4)
N(16)—H(16)	0.82 (3)	N(16)···O(17)	2.853 (4)	H(16)···O(17)	2.09 (3)	N(16)—H(16)···O(17)	157 (3)
C(15)—H(15)	1.00 (5)	C(15)···O(29)	3.089 (5)	H(15)···O(29)	2.239 (5)	C(15)—H(15)···O(29)	141.9 (4)
N(7)—H(71)	0.92 (3)	N(7)···O(9^{v})	3.013 (4)	H(71)···O(9^{v})	2.13 (3)	N(7)—H(71)···O(9^{v})	161 (3)
N(7)—H(72)	0.91 (3)	N(7)···O(9^{v})	2.975 (5)	H(72)···O(9^{v})	2.10 (3)	N(7)—H(72)···O(9^{v})	163 (3)
(III)							
N(7)—H(71)	0.85 (4)	N(7)···O(19^{vi})	3.090 (4)	H(71)···O(19^{vi})	2.30 (3)	N(7)—H(71)···O(19^{vi})	155 (3)
N(7)—H(72)	0.79 (4)	N(7)···O(22)	3.074 (4)	H(72)···O(22)	2.31 (4)	N(7)—H(72)···O(22)	166 (4)
N(11)—H(11)	0.85 (3)	N(11)···N(17^{vii})	2.893 (3)	H(11)···N(17^{vii})	2.05 (3)	N(11)—H(11)···N(17^{vii})	176 (3)

Symmetry code: (i) $\frac{1}{2}-x, \frac{1}{2}-y, 1\frac{1}{2}-z$; (ii) $x, -y, \frac{1}{2}+z$; (iii) $1\frac{1}{2}-x, -\frac{1}{2}-y, 1\frac{1}{2}-z$; (iv) $1+x, y, z$; (v) $\frac{1}{2}+x, \frac{1}{2}-y, -\frac{1}{2}+z$; (vi) $1-x, 1-y, 1-z$; (vii) $2-x, 1-y, -z$.

Table 5. *Torsion angles* (°) *with e.s.d.'s in parentheses for* 18-*crown*-6 *in compounds* (I)–(III)

(I)	
C(20)—O(21)—C(22)—C(23)	−176.5 (6)
O(21)—C(22)—C(23)—O(24)	72.0 (7)
C(22)—C(23)—O(24)—C(25)	−178.2 (6)
C(23)—O(24)—C(25)—C(26)	175.0 (6)
O(24)—C(25)—C(26)—O(27)	−69.7 (7)
C(25)—C(26)—O(27)—C(28)	180.0 (5)
C(26)—O(27)—C(28)—C(20')	−179.9 (5)
O(27)—C(28)—C(20')—O(21')	72.2 (7)
C(28)—C(20')—O(21')—C(22')	178.8 (6)
(II)	
C(18)—O(17)—C(34)—C(33)	175.2 (3)
C(34)—O(17)—C(18)—C(19)	177.9 (3)
O(17)—C(18)—C(19)—O(20)	64.9 (4)
C(18)—C(19)—O(20)—C(21)	−175.2 (3)
C(19)—O(20)—C(21)—C(22)	−174.2 (4)
O(20)—C(21)—C(22)—O(23)	−68.5 (4)
C(21)—C(22)—O(23)—C(24)	−176.3 (4)
C(22)—O(23)—C(24)—C(25)	−179.1 (4)
O(23)—C(24)—C(25)—O(26)	71.2 (4)
C(24)—C(25)—O(26)—C(27)	177.6 (4)
C(25)—O(26)—C(27)—C(28)	170.7 (4)
O(26)—C(27)—C(28)—O(29)	−69.8 (4)
C(27)—C(28)—O(29)—C(30)	178.6 (4)
C(28)—O(29)—C(30)—C(31)	−176.8 (4)
O(29)—C(30)—C(31)—O(32)	72.0 (4)
C(30)—C(31)—O(32)—C(33)	177.8 (4)
C(31)—O(32)—C(33)—C(34)	−175.8 (4)
O(32)—C(33)—C(34)—O(17)	−70.2 (5)
(III)	
O(19)—C(20)—C(21)—O(22)	−65.0 (5)
C(20)—C(21)—O(22)—C(23)	177.8 (4)
C(21)—O(22)—C(23)—C(24)	−179.0 (4)
O(22)—C(23)—C(24)—O(25)	71.4 (5)
C(23)—C(24)—O(25)—C(26)	−177.9 (4)
C(24)—O(25)—C(26)—C(27)	177.3 (4)
O(25)—C(26)—C(27)—O(19")	−72.4 (5)
C(26)—C(27)—O(19")—C(20")	−178.1 (4)
C(27)—O(19")—C(20")—C(21")	−177.1 (4)

Symmetry code: (i) $\frac{1}{2}-x, \frac{1}{2}-y, 1\frac{1}{2}-z$; (ii) $1-x, 1-y, 1-z$.

2.407 (8) Å]. A low-temperature (123 K) analysis of the triclinic form of 18-crown-6.2CH_3CN (Rogers *et al.*, 1988) revealed two crystallographically distinct complex units, each residing at a centre of symmetry with similar geometries of acetonitrile ligation. Coordinates for the methyl H atoms were obtained by Rogers *et al.* from a $\Delta\rho$ map but their successful refinement was not possible even at the low temperature of the analysis. The results of rigid-body CH_3 group refinement indicated that only two of the H atoms engage in C—H···O interactions with the host. One of these H atoms probably forms a bifurcated hydrogen bond to two O atoms of a single O—C—C—O host unit. The tilt angles [calculated from the data of Rogers *et al.* (1988)] are 30.6 and 36.9°, and the C···O distances span a wide range [3.189 (8)–3.598 (8) Å]. We attribute the ordered pattern of methyl H atoms and the more specifically directed nature of the C—H···O hydrogen bonds observed in (I) at room temperature to enhanced acidity of the C—H groups, acquired through the formation of a linear CH_3CN···H—N(amino) hydrogen bond linking the acetonitrile and sulfonamide moieties. The tilt angle of 10.6 (2)° is the smallest hitherto reported for 18-crown-6 complexes with guest methyl groups, the latter including CH_3CN, CH_3NO_2, $(CH_3)_2SO_2$, $(CH_3O)_2SO_2$ and $CH_3OOCC{\equiv}CCOOCH_3$ (Garrell *et al.*, 1988).

The complex unit linked by C—H···O and N—H···N hydrogen bonds shown in Fig. 2 is in fact part of a polymeric array. Each 5-methoxysulfadiazine molecule in (I) forms a 'dimer' through a pair of inversion-related N(11)—H(11)···N(17^{iii}) hydrogen bonds (Table 4). The same association between 5-methoxysulfadiazine molecules occurs in polymorphic form II of this drug (Caira, 1993). The crystal structure of compound (I) is shown in Fig. 5. Channel occupation by the clathrate-bound acetonitrile molecules is evident.

In compound (II) (Fig. 3), the host molecule has symmetry approximating D_{3d} with deviations of the O atoms from their mean plane in the range 0.153 (3)–0.288 (3) Å. The presence of different ligands on opposite faces of the host molecule accounts

for the small departures from the ideal crown conformation. In contrast to (I), coronation of the CH_3CN methyl group in (II) is unsymmetrical. One H atom forms a linear C—H···O hydrogen bond to atom O(32) while a second engages in bifurcated hydrogen bonding to atoms O(23) and O(26). The tilt angle defined above is 42.7 (1)° and the third C—H bond vector is directed away from the host cavity. This arrangement is very similar to that found in the triclinic modification of 18-crown-6.2CH_3CN (Rogers *et al.*, 1988). Atom N(37) of the ligating acetonitrile molecule in (II) does not engage in hydrogen bonding, so the directional influences mentioned in connection with compound (I) are absent here. The sulfathiazole molecule occurs in the imido tautomeric form [with the H atom bonded to N(16) as opposed to N(11)], as observed in various polymorphs of this drug (Anwar, Tarling & Barnes, 1989; Kruger & Gafner, 1971, 1972) and it is noteworthy that it does not utilize the amino group for ligation to the host. This is atypical of sulfonamide ligands (Goldberg, 1984). Instead, the thiazole ring is directed into the host cavity and binding results from two hydrogen bonds, N(16)—H(16)···O(17) and C(15)—H(15)···O(29). Thus, C—H···O interactions play a major role in stabilizing compound (II). Fig. 6 shows the packing in the crystal of (II). Complex units are linked *via* intermolecular N(7)—H···O(sulfonyl) hydrogen bonds only.

The host in compound (III) (Fig. 4) resides around a crystallographic centre of symmetry and adopts the D_{3d} conformation. Each of the two inversion-related sulfamerazine molecules binds to the macrocycle *via* two N(7)—H···O hydrogen bonds. This binding mode prevails in binary complexes of stoichiometry 1:2 between 18-crown-6 and uncharged NH_2—donor moieties (Goldberg, 1984). Further stabilization of the crystal of (III) is achieved through 'dimerization' of the sulfamerazine molecules by complementary N(11)—H(11)···N(17^{ii}) hydrogen-bond pairs (Table 4) analogous to those described for the sulfonamide in (I). Identical hydrogen-bond pairs give rise to dimeric motifs in two polymorphic forms of sulfamerazine (Acharya, Kuchela & Kartha, 1982; Caira & Mohamed, 1992). As shown in Fig. 7, the solvent CH_3CN molecules do not participate in hydrogen bonding and merely occupy channels in the crystal of (III).

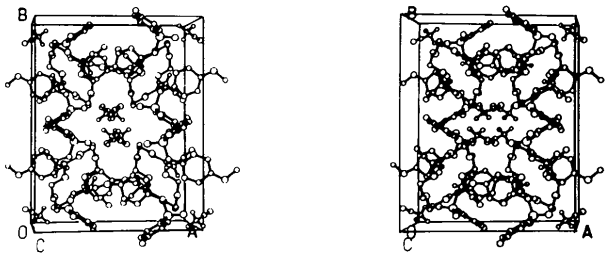

Fig. 5. Stereoscopic view of the crystal packing in (I). Clathrated solvent molecules reside in channels parallel to (001).

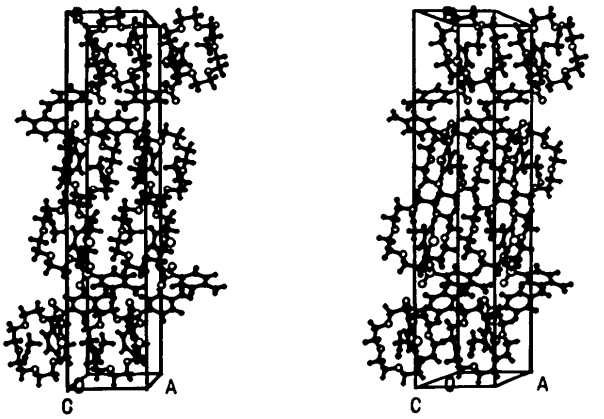

Fig. 6. Stereoscopic view of the crystal packing in (II).

Concluding remarks

It is of interest to assess the value of thermal analysis in the preliminary study of compounds (I)–(III). Apart from providing quantitative thermodynamic data for phase changes accompanying the thermal decomposition of inclusion compounds, TG and DSC techniques can, in favourable cases, yield features from which structural information can be inferred. An example is the stepwise loss of mass, with corresponding DSC endotherms, observed on heating hydrates containing water molecules in crystallographically different sites (Wunderlich, 1990). In retrospect, thermal analysis of compound (I), which contains both cavitate- and clathrate-bound acetonitrile, might have been expected to distinguish these by resolving the desolvation process into two steps. The fact that this did not occur, even at heating rates less than 10 K min^{-1}, is interpreted as indicating that CH_3CN molecules from the two crystal sites are probably lost simultaneously. This is consistent with

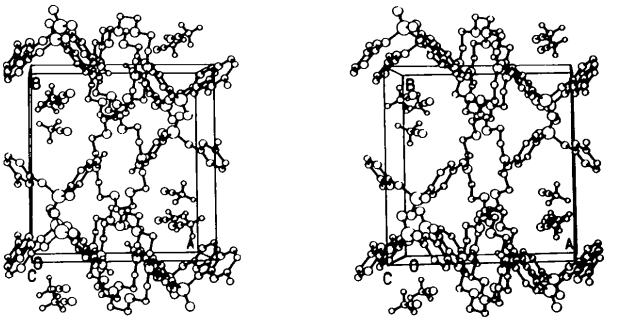

Fig. 7. Stereoscopic view of the crystal packing in (III) showing channel occupation by solvent molecules.

the observation that crystals of this type are extremely labile and also with the crystallographic data which confirm the tenuous nature of the C—H···O hydrogen bonds for ligated CH_3CN. X-ray results for compounds (II) and (III), which reveal only cavitate- and only clathrate-bound CH_3CN respectively, are consistent with single-step desolvation processes, as indicated by DSC.

Although compounds (I)–(III) were prepared under essentially the same conditions, they display a variety of stoichiometries and structures and it is necessary to attempt to rationalize this finding. To do so, we note that their preparation involved prior dissolution in CH_3CN of the separate species 18-crown-6 and sulfonamide. Since 18-crown-6 and acetonitrile form a complex in solution (Gold & Rice, 1982), the formation of (I)–(III) can be viewed as the outcome of competition between the sulfonamide and acetonitrile for complexation to 18-crown-6. The observed values of zero, one and two for the respective numbers of sulfonamide molecules directly bound to 18-crown-6 in (I)–(III) establishes the 'donor ability' of the sulfonamides towards the crown ether (*vis-à-vis* CH_3CN) as 5-methoxysulfadiazine < sulfathiazole < sulfamerazine. Ternary compounds with different crown ethers and a range of sulfonamides are being studied to reconcile the notion of donor ability with sulfonamide structure. The effect of varying the molar ratios of crown ether and sulfonamide on resultant complex stoichiometries also requires further investigation.

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References

ACHARYA, K. R., KUCHELA, K. N. & KARTHA, G. (1982). *J. Crystallogr. Spectrosc. Res.* **12**, 369–376.

ANWAR, J., TARLING, S. E. & BARNES, P. (1989). *J. Pharm. Sci.* **78**, 337–342.

BUCHANAN, G. W., MORAT, C., CHARLAND, J. P., RATCLIFFE, C. I. & RIPMEESTER, J. A. (1989). *Can. J. Chem.* **67**, 1212–1218.

CAIRA, M. R. (1993). In preparation.

CAIRA, M. R. & MOHAMED, R. (1992). *Acta Cryst.* B**48**, 492–498.

CROMER, D. T. & LIBERMAN, D. (1970). *J. Chem. Phys.* **53**, 1891–1898.

CROMER, D. T. & MANN, J. B. (1968). *Acta Cryst.* A**24**, 321–325.

ELBASYOUNY, A., BRÜGGE, H. J., VON DEUTEN, K., DICKEL, M., KNÖCHEL, K., KOCH, K. U., KOPF, J., MELZER, D. & RUDOLPH, G. (1983). *J. Am. Chem. Soc.* **105**, 6568–6577.

Enraf–Nonius (1979). *Structure Determination Package*. Enraf–Nonius, Delft, The Netherlands.

GARRELL, R. L., SMYTH, J. C., FRONCZEK, F. R. & GANDOUR, R. D. (1988). *J. Incl. Phenom.* **6**, 73–78.

GOLD, H. S. & RICE, M. R. (1982). *Talanta*, **29**, 637–640.

GOLDBERG, I. (1984). *Inclusion Compounds*, Vol. 2, edited by J. L. ATWOOD, J. E. D. DAVIES & D. D. MACNICOL, pp. 261–335. London: Academic Press.

KRUGER, G. J. & GAFNER, G. (1971). *Acta Cryst.* B**27**, 326–333.

KRUGER, G. J. & GAFNER, G. (1972). *Acta Cryst.* B**28**, 272–283.

MOTHERWELL, W. D. S. (1989). *PLUTO*89. Program for plotting molecular and crystal structures. Univ. of Cambridge, England.

NARDELLI, M. (1983). *Comput. Chem.* **7**, 95–98.

PANNEERSELVAM, K., CHACKO, K. K., WEBER, E. & KÖHLER, H.-J. (1990). *J. Incl. Phenom.* **9**, 337–347.

ROGERS, R. D. (1988). *J. Incl. Phenom.* **6**, 629–645.

ROGERS, R. D., RICHARDS, P. D. & VOSS, E. J. (1988). *J. Incl. Phenom.* **6**, 65–71.

SHELDRICK, G. M. (1976). *SHELX*76. Program for crystal structure determination. Univ. of Cambridge, England.

SHELDRICK, G. M. (1985). *SHELXS*86. In *Crystallographic Computing* 3, edited by G. M. SHELDRICK, C. KRÜGER & R. GODDARD, pp. 175–189. Oxford Univ. Press.

SIMONOV, Y., BATTAGLIA, L. P., CORRADI, A. B., IANELLI, S., PELOSI, G., GANIN, E. & LUKJANENKO, N. (1990). *J. Incl. Phenom.* **9**, 181–194.

STEWART, R. F., DAVIDSON, E. R. & SIMPSON, W. T. (1965). *J. Chem. Phys.* **42**, 3175–3187.

STOUT, G. H. & JENSEN, L. H. (1968). *X-ray Structure Determination, a Practical Guide*, p. 393. New York: Macmillan.

WEBER, E. (1987). *Synthesis of Macrocycles: the Design of Selective Complexing Agents*, edited by R. M. IZATT & J. J. CHRISTENSEN, pp. 337–419. New York: Wiley.

WEBER, E., FRANKEN, S., AHRENDT, J. & PUFF, H. (1987). *J. Org. Chem.* **52**, 5291–5292.

WELLER, F., BORGHOLTE, H., STENGER, H., VOGLER, S. & DEHNICKE, K. (1989). *Z. Naturforsch. Teil B*, **44**, 1524–1530.

WUNDERLICH, B. (1990). *Thermal Analysis*, pp. 167–169. San Diego: Academic Press.