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Crystal Structure of Inclusion Compounds: The Complexes of the *cis-syn-cis* and the *cis-anti-cis* Isomers of Dicyclohexano-18-crown-6 with 4-Methylbenzenesulfamide

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Abstract. The crystal structure of two complexes of the isomers *cis-syn-cis* (isomer A) and *cis-anti-cis* (isomer B) of dicyclohexano-18-crown-6 with 4-methylbenzenesulfamide have been determined by X-ray single crystal diffraction methods. The two structures have been solved by direct methods and refined to agreement values of 0.067 and 0.038 for isomers A and B respectively. The first isomer forms an inclusion compound with a host/guest ratio of 1:1; the second one of 1:2. The amino groups of the guest molecules are connected by N—H···O hydrogen bonds with oxygen atoms of the polyether molecules. The methyl groups of 4-methylbenzenesulfamide do not form hydrogen bonds.

The host–guest interactions in the molecular complexes, the reciprocal influence of the two molecules on their conformation and the intermolecular contacts between the molecules in the crystal are discussed.

Key words. crown ether, crystal structure, inclusion compound, isomers of dicyclohexano-18-crown-6.

Supplementary data relating to this paper are deposited with the British Library as Supplementary Publication No. SUP 82086 (58 pages)

1. Introduction

The isomers of dicyclohexano-18-crown-6 (hereinafter DC-18-C-6^{A} for the *cis-syn-cis* isomer and DC-18-C-6^{B} for the *cis-anti-cis* isomer) form stable complexes with the elements of Groups IA and IIA and with those of the lanthanide series. Different kinds of complexes can be obtained depending on the topological relationship between the cation and the macrocyclic cavity and on the basicity of the solution used. These complexes contain the metal in the cavity of the macrocycle as found in the complex of DC-18-C-6 with lanthanum nitrate [1] or the two potassium complexes [K(DC-18-C-6^{A})] [AuCN] [2] and [K(DC-18-C-6^{A})·K·2-nitrophenoxide] [3].

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The ionic interaction between the macrocycle and the cations NH_4^+ and H_3O^+ contributes significantly to the formation of a second group of complexes. These cations may substitute in part the metals and interact with ether oxygens of the macrocycle as observed in the complex $[Ce(NO_3)_6][DC\text{-}18\text{-}C\text{-}6^B \cdot H_3O]_2$ $[DC\text{-}18\text{-}C\text{-}6^B \cdot H_2O]_2 \cdot H_2O$ [4].

A further group is formed by host–guest complexes [5] in which neutral molecules possessing the structural element XH_2 (X = O, N, C) interact through hydrogen bonds with the macrocycle as found in $[UO_2(NO_3)_2] \cdot 2\,H_2O$[18-crown-6] [6], $[(CH_3)_2SnCl_2 \cdot H_2O]$ [18-crown-6] [7] and in $[Tm(H_2O)_3(NO_3)_3][DC\text{-}18\text{-}C\text{-}6^A] \cdot 0.5\,CH_3CN$ [8] for which the kind of activation of the CN structural element may be appreciated by reference to the CH_2 analogy [5]. A particular place in this kind of derivative is occupied by crown–ether complexes with neutral organic host molecules for which the N—H···O and O—H···O hydrogen bonds and the weaker C—H···O interactions play a fundamental role. The interest in these compounds range from the fields of analytical chemistry, biology, molecular biology, chemistry of supermolecules (following the definition of Lehn [9]) and in the field of models of receptor systems [10]. The general rules of their synthesis have already been analyzed in detail [5, 11]. In particular the five isomers of DC-18-C-6 may form different types of complexes depending on the diameter of the cavity and on the radius of the cation [1]. The isomeric dependence was shown in the complexation of DC-18-C-6 with malononitrile [12], while in the complexation with aminosulfamide and its derivatives, practically identical complexes, with both isomers of DC-18-C-6, were obtained [13]. It was also shown [12, 14] that interactions of the type C—H···O may be important in the formation of some inclusion compounds. Moreover dipole–dipole interactions may play an important role in this kind of complex [5].

The complexes formed between the two isomers of $[DC\text{-}18\text{-}C\text{-}6] \cdot 2\,CH_3CN$ and 4-aminobenzosulfamide [15] both have a 1:2 host:guest ratio. In contrast, the present study reveals that in the complexation of the two isomers of DC-18-C-6 with 4-methylbenzenesulfamide, two different products with host:guest ratios of 1:1 (isomer A) and 1:2 (isomer B) are obtained.

2. Experimental

Single crystals of the complexes formed between isomer A ($DC\text{-}18\text{-}C\text{-}6^A \cdot CH_3PhSO_2 \cdot NH_2$) and B ($DC\text{-}18\text{-}C\text{-}6^B \cdot 2\,CH_3PhSO_2 \cdot NH_2$) were recrystallized from a saturated solution in methanol. Colorless single crystals were used for X-ray analysis. Preliminary cell parameters were obtained as part of the alignment process of the crystals on the diffractometer using, for both compounds, the angular values of 30 reflections automatically well centered with a routine which repeatedly improves the angular values to reach the maximum of the peaks until the angles change by not more than 0.001°. The intensity data were collected at room temperature in the range $3 \leqslant \theta \leqslant 28°$ on a Siemens AED single crystal diffractometer equipped with a IBM PS2/30 personal computer through a modified version [16] of the Lehmann and Larsen procedure [17]. For both compounds MoK_α radiation ($\lambda = 0.71069$ Å) was employed. One standard reflection was monitored for both compounds at regular intervals without significant variations in intensity. Crystal

Table I. Crystal and experimental data

	Isomer A	Isomer B
Chemical Formula	$C_{27}H_{45}NO_8S$	$C_{34}H_{54}N_2O_{10}S_2$
M.W.	543.7	714.9
Space group	$P2_1/c$	$P\bar{1}$
a(Å)	9.193(3)	14.322(2)
b(Å)	24.898(2)	17.018(2)
c(Å)	12.839(2)	8.416(1)
α (deg)	90	104.30(5)
β (deg)	98.47(3)	107.02(5)
γ (deg)	90	98.51(5)
V(Å^3)	2907(1)	1846(1)
Z	4	2
D_c (g cm^{-3})	1.24	1.29
Specimen dimensions (mm)	0.7 × 0.8 × 1.1	0.6 × 1.1 × 1.2
μ (cm^{-1})	1.50	1.91
Scan speed range (°/min)	0.3–1.2	0.3–1.2
Scan width (°)	$1.40 + 0.35 \cdot \tan\theta$	$1.40 + 0.35 \cdot \tan\theta$
Radiation	MoK_α	MoK_α
h range	−10/12	−15/16
k range	0/32	−22/22
l range	0/16	0/11
Scan mode	$\Omega - 2\theta$	$\Omega - 2\theta$
No. measured refl.	7201	8951
Condition for obs.	$I \geqslant 2\sigma(I)$	$I \geqslant 2\sigma(I)$
No. refining refl.	3196	6114
No. refined parameters	372	326

and experimental data are summarized in Table I. The intensities were corrected for Lorentz and polarization effects but not for absorption. All the calculations were performed with the SHELX76 [18] system of programs through the CRYSRULER package [19] using an IBM PS2/80 personal computer. Scattering factors were those of SHELX.

The structures, solved by direct methods, are refined using the block-matrix least-squares technique. The hydrogen atoms of isomer A were only partly located in a difference Fourier map, because of the probable partial disorder in the polyoxyethylene fragment of the crown–ether. Refinements of the non-H atoms were performed with anisotropic temperature factors while the hydrogens were refined isotropically.

The final agreement factors were $R = 0.067$ and $R_w = 0.074$ with $w = 1.317/(\sigma^2 F + 0.001591\ F^2)$ for isomer A and $R = 0.038$ with unitary weights for isomer B.

3. Results and Discussion

Anisotropic temperature factors, hydrogen coordinates and structure factors list have been deposited as Supplementary Data.

The final positional parameters are given in Tables II and III for the complexes formed with isomers A and B respectively. Figures 1 and 2 report projections of the two complexes.

Table II. Atomic fractional coordinates ($\times 10^4$) for the complex with isomer A

	x/a	*y/b*	*z/c*
S(1A)	3923(1)	3599(1)	3879(1)
O(1A)	4860(3)	3172(1)	3656(2)
O(2A)	3664(4)	4036(1)	3162(2)
N(1)	2360(4)	3336(2)	3988(3)
C(1A)	4688(4)	3869(2)	5108(3)
C(2A)	5664(6)	3582(2)	5794(4)
C(3A)	6265(6)	3804(2)	6747(4)
C(4A)	5928(5)	4315(2)	7016(4)
C(5A)	4923(6)	4598(2)	6333(4)
C(6A)	4314(6)	4380(2)	5374(4)
C(7A)	6608(11)	4565(3)	8047(5)
O(1)	−23(3)	4159(1)	4265(2)
O(4)	−1496(12)	3590(3)	2428(5)
O(7)	−1418(5)	2202(2)	3113(5)
O(10)	898(5)	1763(2)	4631(3)
O(13)	2696(4)	2544(1)	5764(2)
O(16)	725(4)	3409(1)	5966(2)
C(2)	−888(5)	4398(2)	3374(4)
C(3)	−2132(7)	4050(3)	2839(5)
C(5)	−1534(6)	3168(8)	2959(2)
C(6)	−2103(12)	2744(4)	2503(9)
C(8)	−1609(11)	2069(6)	4095(10)
C(9)	−516(14)	1721(9)	4611(14)
C(11)	1927(7)	1600(2)	5525(4)
C(12)	3164(6)	2000(2)	5657(4)
C(14)	2104(16)	2653(3)	6689(6)
C(15)	1817(10)	3232(3)	6797(4)
C(17)	359(8)	3952(3)	6088(4)
C(18)	−703(6)	4136(3)	5176(4)
C(19)	115(6)	4570(2)	2617(4)
C(20)	−3014(7)	4356(3)	1930(5)
C(21)	−2003(8)	4531(3)	1151(6)
C(22)	−702(8)	4859(2)	1651(5)
C(23)	2517(8)	1042(2)	5379(4)
C(24)	3337(7)	1022(2)	4450(5)
C(25)	4565(7)	1436(2)	4529(6)
C(26)	4002(6)	1990(2)	4732(4)

3.1. THE COMPLEX WITH ISOMER A: DC-18-C-6^A·$NH_2SO_2PhCH_3$

Bond distances, bond angles and selected torsion angles are reported in Table IV.

The molecules complex in a host–guest ratio of 1 : 1 linked by strong N—H···O hydrogen bonds (see Table V). The values of these bond lengths are in agreement with those found in other crown ether complexes in which the guest molecule contains an amino group [13, 20, 21]. The hydrogen bonds involve only one part of the polyoxyethylenic chain [O(1)—C(18)—···—O(13)] and this behaviour significantly deforms the remaining part of the chain [O(4)—C(5)—···—O(10)] with a

Table III. Atomic fractional coordinates ($X10^4$) for the complex with isomer B

	guest A			guest B		
	x/a	*y/b*	*z/c*	*x/a*	*y/b*	*z/c*
S(1)	545(1)	3280(1)	8020(1)	4455(1)	1720(1)	14195(1)
O(1)	140(2)	2680(1)	8722(3)	4861(2)	2322(1)	15903(2)
O(2)	160(2)	3148(1)	6178(2)	4840(1)	1852(1)	12867(2)
N(1)	377(2)	4160(2)	8940(4)	4623(2)	838(1)	14400(3)
C(1)	1850(2)	3345(2)	8616(3)	3148(2)	1658(1)	13419(3)
C(2)	2311(3)	2933(2)	9737(4)	2689(3)	2072(2)	14496(4)
C(3)	3336(3)	2991(2)	10179(5)	1663(3)	2011(2)	13851(4)
C(4)	3915(2)	3455(2)	9532(4)	1085(2)	1548(2)	12163(4)
C(5)	3441(2)	3865(2)	8417(4)	1557(2)	1131(2)	11101(4)
C(6)	2421(2)	3814(2)	7946(4)	2578(2)	1182(2)	11705(4)
C(7)	5024(3)	3505(3)	9963(6)	−31(2)	1479(3)	11416(6)
	host A			host B		
O(1)	2139(1)	5655(1)	11822(2)	2862(1)	−655(1)	4029(2)
C(2)	2120(2)	5873(2)	13566(3)	2878(2)	−871(1)	5570(3)
C(3)	1833(2)	5058(2)	13937(3)	3166(2)	−59(1)	7043(3)
O(4)	850(1)	4614(1)	12737(2)	4153(1)	388(1)	7275(2)
C(5)	324(2)	4074(2)	13414(4)	4676(2)	929(2)	9012(3)
C(6)	−702(2)	3659(2)	12099(4)	5702(2)	1337(2)	9144(3)
O(7)	−1252(1)	4281(1)	11831(2)	6250(1)	719(1)	8797(2)
C(8)	−2251(2)	3932(2)	10624(4)	7252(2)	1067(2)	8941(3)
C(9)	2335(1)	6360(2)	11259(4)	2663(2)	−1359(2)	2563(3)
C(10)	3146(2)	6369(2)	14910(4)	1853(2)	−1369(2)	5393(4)
C(11)	3942(2)	5887(2)	14882(5)	1056(2)	−886(2)	5051(5)
C(12)	3638(2)	5050(2)	15171(5)	1355(2)	−49(2)	6474(5)
C(13)	2611(2)	4548(2)	13856(4)	2390(2)	453(2)	6711(4)

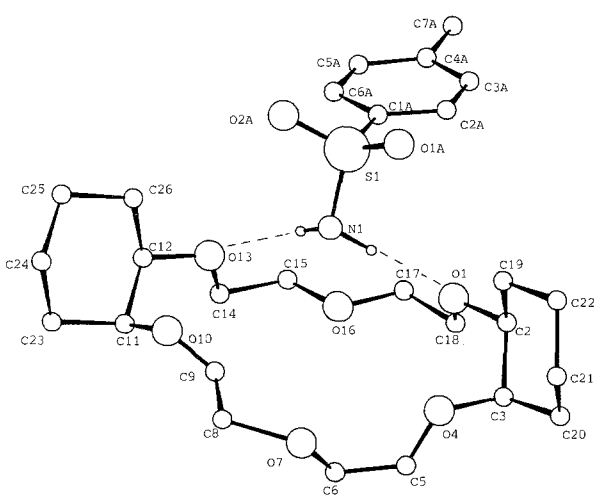


Fig. 1. Projection of the complex formed with isomer A. Hydrogen atoms have been omitted for clarity.

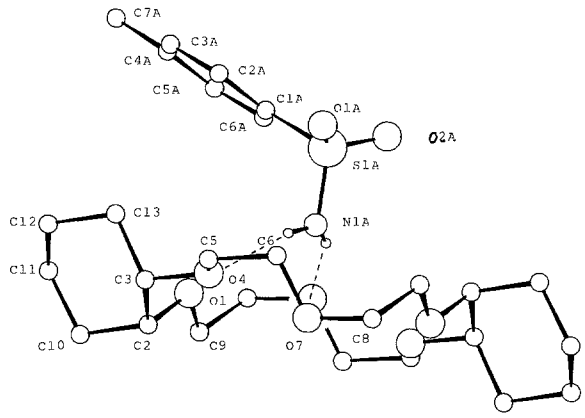


Fig. 2. Projection of the complex formed with isomer B. Only one part of the two independent molecules in the unit cell is illustrated.

remarkable increase of the thermal parameters of atoms and with a significant deviation of the geometrical parameters from standard values. Attempts to define a localized disorder failed so that the chain behaviour may be described as due to high thermal motion justified by the absence of strong contacts involving this chain fragment. The hydrogen atoms of this fragment were, of course, not localized.

The guest phenyl ring is planar within 0.01 Å with mean C—C bond lengths and C—C—C internal angles of 1.373(4) Å and 119.9(4)°. The *syn*-cyclohexyl rings show chair conformations with mean C—C values of 1.517(5) and 1.510(3) Å for rings C(2)—C(22) and C(11)—C(23), respectively, which agree well with those found in similar derivatives [2, 4, 12, 13]. The mean bond distances in the macrocycle (without the disordered fragment) are C—C = 1.496(9) and C—O = 1.419(5) Å.

The conformation of the macrocyclic ring may be studied by analyzing the two fragments separated by *gauche* bonds, together with the signs of their torsion angles. As explained in [22] looking along the axis of a bond, a + sign means clockwise rotation of the rear ring bond away from the front-ring bond, a − sign signifies a counterclockwise rotation. In our compound the atom C(12) represents the central atom of two consecutive +*gauche* bonds and this fact constitutes the greater difference with respect to the free molecules of DC-18-C-6 as reported in [23, 24]. This conformational arrangement causes a rotation of some hydrogens of the groups involved leading to significant C—H···O interactions [O(13)···H(12) = 1.88(4), O(13)···H(13) = 1.95(7), O(13)···H(14) = 1.80(8), O(10)···H(11) = 1.87(5), O(10)···H(9) = 1.80(6) Å].

In the previously quoted papers [2, 3] and in the complexes [DC-18-C-6^{A}·H_3O]$^{+}$$ClO_4^{-}$ [25], [DC-18-C-6^{A}·H_3NSO_2] and [DC-18-C-6^{B}·H_3NSO_2] [26] the symmetry of the macrocycle was close to D_{3d} showing *trans* and *gauche* conformations for all the C—O and C—C bonds, respectively. In the present case only ten of the twelve C—O bonds are in *trans* conformations while all the C—C bonds are in *gauche* conformations.

Table IV. Bond distances (Å), bond angles (°) and selected torsion angles (°) for the complex with isomer A

S(1)—O(1A)	1.424(3)	O(13)—C(14)	1.404(11)
S(1)—O(2A)	1.423(3)	O(16)—C(15)	1.423(7)
S(1)—N(1)	1.604(4)	O(16)—C(17)	1.408(8)
S(1)—C(1A)	1.763(4)	C(2)—C(3)	1.516(8)
C(1A)—C(2A)	1.363(6)	C2—C(19)	1.497(8)
C(1A)—C(6A)	1.374(7)	C(3)—C(20)	1.523(9)
C(2A)—C(3A)	1.382(7)	C(5)—C(6)	1.281(22)
C(3A)—C(4A)	1.366(7)	C(8)—C(9)	1.415(21)
C(4A)—C(5A)	1.371(7)	C(11)—C(12)	1.502(8)
C(4A)—C(7A)	1.512(8)	C(11)—C(23)	1.513(8)
C(5A)—C(6A)	1.386(7)	C(12)—C(26)	1.508(8)
O(1)—C(2)	1.424(5)	C(14)—C(15)	1.476(11)
O(1)—C(18)	1.406(6)	C(17)—C(18)	1.482(8)
O(4)—C(3)	1.422(11)	C(19)—C(22)	1.532(8)
O(4)—C(5)	1.256(20)	C(20)—C(21)	1.526(11)
O(7)—C(6)	1.639(13)	C(21)—C(22)	1.511(10)
O(7)—C(8)	1.340(15)	C(23)—C(24)	1.503(9)
O(10)—C(9)	1.301(14)	C(24)—C(25)	1.521(8)
O(10)—C(11)	1.434(7)	C(25)—C(26)	1.509(7)
O(13)—C(12)	1.434(6)		
N(1)—S(1)—C(1A)	108.8(1)	O(4)—C(3)—C(2)	107.7(6)
O(2A)—S(1)—C(1A)	107.1(1)	C(2)—C(3)—C(20)	110.0(5)
O(2A)—S(1)—N(1)	107.6(2)	O(4)—C(3)—C(20)	108.7(5)
O(1A)—S(1)—C(1A)	106.9(1)	O(4)—C(5)—C(6)	118.9(13)
O(1A)—S(1)—N(1)	106.8(2)	O(7)—C(6)—C(5)	111.0(10)
O1(A)—S(1)—O(2A)	119.3(1)	O(7)—C(8)—C(9)	114.2(10)
S(1)—C(1A)—C(6A)	119.6(3)	O(10)—C(9)—C(8)	126.8(12)
S(1)—C(1A)—C(2A)	121.1(3)	O(10)—C(11)—C(23)	111.5(4)
C(2A)—C(1A)—C(6A)	119.3(4)	O(10)—C(11)—C(12)	107.6(4)
C(1A)—C(2A)—C(3A)	120.1(4)	C(12)—C(11)—C(23)	110.1(5)
C(2A)—C(3A)—C(4A)	121.4(4)	O(13)—C(12)—C(11)	113.8(4)
C(3A)—C(4A)—C(7A)	121.7(5)	C(11)—C(12)—C(26)	111.5(4)
C(3A)—C(4A)—C(5A)	118.3(4)	O(13)—C(12)—C(26)	106.6(3)
C(5A)—C(4A)—C(7A)	120.1(4)	O(13)—C(14)—C(15)	111.4(6)
C(4A)—C(5A)—C(6A)	120.8(4)	O(16)—C(15)—C(14)	110.4(5)
C(1A)—C(6A)—C(5A)	120.0(4)	O(16)—C(17)—C(18)	110.4(5)
C(2)—O(1)—C(18)	114.9(3)	O(1)—C(18)—C(17)	110.4(4)
C(3)—O(4)—C(5)	115.3(9)	C(2)—C(19)—C(22)	112.6(4)
C(6)—O(7)—C(8)	124.0(7)	C(3)—C(20)—C(21)	109.8(5)
C(9)—O(10)—C(11)	122.2(8)	C(20)—C(21)—C(22)	113.3(5)
C(12)—O(13)—C(14)	115.0(4)	C(19)—C(22)—C(21)	110.7(4)
C(15)—O(16)—C(17)	111.6(4)	C(11)—C(23)—C(24)	111.1(4)
O(1)—C(2)—C(19)	108.5(4)	C(23)—C(24)—C(25)	112.3(5)
O(1)—C(2)—C(3)	114.8(4)	C(24)—C(25)—C(26)	111.2(5)
C(3)—C(2)—C(19)	111.4(4)	C(12)—C(26)—C(25)	112.3(4)
C(2)—O(1)—C(18)—C(17)	−172.1(4)	C(14)—O(13)—C(12)—C(11)	66.6(7)
C(18)—O(1)—C(2)—C(3)	−74.4(6)	C(15)—O(16)—C(17)—C(18)	176.1(5)
C(3)—O(4)—C(5)—C(6)	125.9(14)	C(12)—O(13)—C(14)—C(15)	173.2(6)
C(5)—O(4)—C(3)—C(2)	102.2(11)	C(17)—O(16)—C(15)—C(14)	176.1(6)
C(6)—O(7)—C(8)—C(9)	−156.8(11)	O(1)—C(2)—C(3)—O(4)	−64.1(7)
C(8)—O(7)—C(6)—C(5)	65.2(14)	O(4)—C(5)—C(6)—O(7)	154.2(12)
C(9)—O(10)—C(11)—C(12)	−141.6(10)	O(7)—C(8)—C(9)—O(10)	45.2(22)
C(11)—O(10)—C(9)—C(8)	146.9(14)	O(13)—C(14)—C(15)—O(16)	64.0(9)
O(10)—C(11)—C(12)—O(13)	56.3(6)	O(16)—C(17)—C(18)—O(1)	−68.8(6)

Table V. Hydrogen bonds (Å) with angles between the atoms involved (°)

Isomer A complex		
N(1)···O(1) = 3.058(5)	H(1NA)···O(1) = 2.31(4)	N(1)—H(1NA)···O(1) = 174(4)
N(1)···O(13) = 2.996(5)	H(2NA)···O(13) = 2.02(3)	N(1)—H(2NA)···O(13) = 178(4)
Isomer B complex		
Molecule A		
N(1A)···O(4) = 2.937(4)	H(1NA)···O(4) = 2.26(4)	N(1A)—H(1NA)···O(4) = 167(4)
N(1A)···O(7) = 3.062(4)	H(2NA)···O(7) = 2.25(4)	N(1A)—H(2NA)···O(7) = 160(3)
Molecule B		
N(1B)···O(4) = 2.934(3)	H(3NB)···O(4) = 2.25(4)	N(1B)—H(3NB)···O(4) = 169(3)
N(1B)···O(7) = 3.058(3)	H(4NB)···O(7) = 2.25(3)	N(1B)—H(4NB)···O(7) = 154(3)

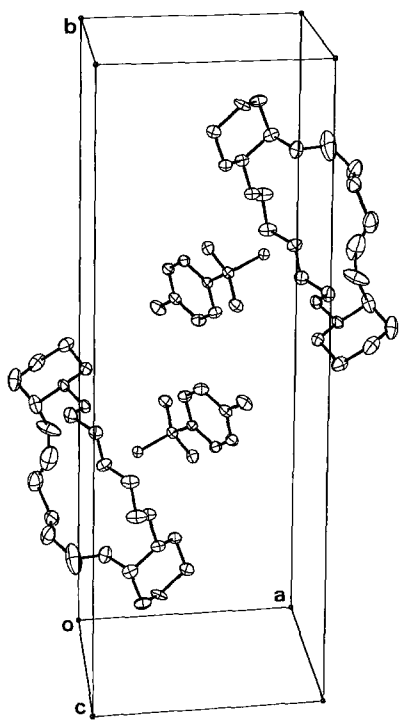


Fig. 3. Perspective view of the molecular packing of the complex formed with isomer A.

The packing of the molecules in the crystal is mainly determined by Van der Waals interactions as shown in Figure 3. The guest methyl group does not participate in the interactions with DC-18-C-6^{A}.

3.2. THE COMPLEX WITH ISOMER B: DC-18-C-6^{B}·2 $NH_2SO_2PhCH_3$

Bond distances, bond angles and selected torsion angles of the complex depicted in Figure 2, are reported in Table VI.

In the unit cell there are two crystallographic independent molecules of the complex which has a host : guest ratio of 1 : 2. The geometrical parameters of the two independent molecules are comparable. A projection of the molecular packing in the (001) plane shows a *C*-type lattice pseudosymmetry in agreement with the systematic absences observed for the *hk*0 reflections ($h + k \neq 2n$). This pseudosymmetry disappears in a three dimensional view (Figure 4) in agreement with the absence of systematic extinctions in the *hkl* reflections. In this compound too the molecules of the complexes are linked by strong N—H···O hydrogen bonds (see Table V). These four bonds cause a conformational variation of the macrocycle and the C(8) atom separates two molecular fragments united by two *gauche* bonds with the same negative sign. The correlation between NH···O distance and angle, postulated by Weber and Sheldrick [27], is not confirmed in this analysis. The mean C—O and C—C aliphatic distances are 1.428(3), 1.427(3) and 1.504(7), 1.502(8) Å for the two independent molecules, respectively. The cyclohexyl rings are in *chair* conformations and their mean bond distances are 1.523(4) and 1.519(4) Å for the two independent molecules, respectively. The aromatic rings of the guest A and B molecules are both planar within 0.003 Å. Their mean C—C bond lengths and C—C—C internal angles are 1.383(2), 1.386(3) Å and 120.0(6), 119.9(6)° respectively. The methyl group of the guest molecule does not participate in the interactions with the crown–ether, so that the single molecules of complex are connected in the crystal by Van der Waals contacts only (Figure 4).

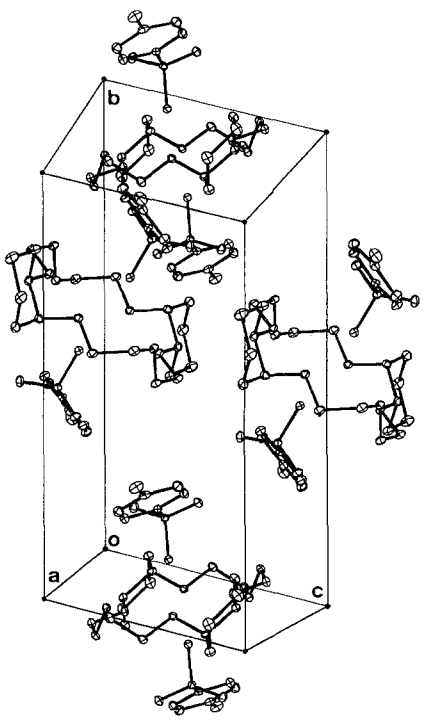


Fig. 4. Perspective view of the molecular packing of the complex formed with isomer B.

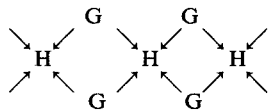
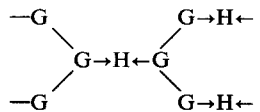
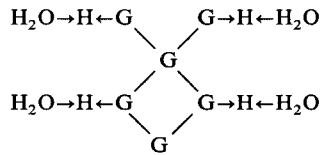
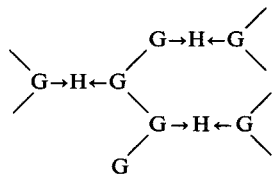
Table VI. Bond distances (Å), bond angles (°) and selected torsion angles (°) for the complex with isomer B

	guest A	guest B		host A	host B
S(1)—O(1)	1.432(3)	1.436(2)	O(1)—C(2)	1.432(3)	1.428(3)
S(1)—O(2)	1.431(2)	1.432(2)	O(1)—C(9)	1.515(4)	1.415(3)
S(1)—N(1)	1,595(3)	1.597(2)	C(2)—C(3)	1.520(5)	1.517(3)
S(1)—C(1)	1.766(3)	1.770(3)	C(2)—C(10)	1.530(3)	1.529(4)
C(1)—C(2)	1.385(5)	1.386(5)	C(3)—O(4)	1.431(3)	1.436(3)
C(1)—C(6)	1.387(5)	1.393(3)	C(3)—C(13)	1.517(5)	1.516(4)
C(2)—C(3)	1.387(6)	1.387(6)	O(4)—C(5)	1.429(4)	1.427(3)
C(3)—C(4)	1.374(6)	1.375(4)	C(5)—C(6)	1.496(4)	1.489(4)
C(4)—C(5)	1.385(5)	1.393(5)	C(6)—O(7)	1.433(4)	1.426(4)
C(5)—C(6)	1.380(4)	1.382(4)	O(7)—C(8)	1.425(3)	1.427(3)
C(4)—C(7)	1.506(5)	1.511(4)	C(8)—C(9′)	1.502(5)	1.499(4)
			C(10)—C(11)	1.502(5)	1.505(5)
			C(11)—C(12)	1.526(5)	1.524(5)
			C(12)—C(13)	1.525(4)	1.528(4)

	guest A	guest B		host A	host B
N(1)—S(1)—C(1)	108.7(2)	108.9(2)	O(1)—C(2)—C(10)	112.1(2)	112.2(2)
O(2)—S(1)—C(1)	107.6(2)	107.3(1)	O(1)—C(2)—C(3)	106.7(2)	107.0(2)
O(2)—S(1)—N(1)	106.8(2)	106.7(1)	C(3)—C(2)—C(10)	108.7(2)	108.8(2)
O(1)—S(1)—C(1)	106.9(2)	106.9(2)	C(2)—C(3)—C(13)	111.2(3)	111.4(2)
O(1)—S(1)—N(1)	107.6(2)	107.7(1)	C(2)—C(3)—O(4)	108.7(2)	108.9(2)
O(1)—S(1)—O(2)	119.1(2)	119.0(2)	O(4)—C(3)—C(13)	112.4(2)	112.4(2)
S(1)—C(1)—C(6)	119.5(2)	119.2(3)	C(3)—O(4)—C(5)	112.8(2)	113.0(2)
S(1)—C(1)—C(2)	121.0(3)	120.8(2)	O(4)—C(5)—C(6)	109.0(2)	109.1(2)
C(2)—C(1)—C(6)	119.5(3)	119.9(3)	C(5)—C(6)—O(7)	109.2(3)	109.8(3)
C(1)—C(2)—C(3)	119.9(3)	119.5(3)	C(6)—O(7)—C(8)	112.6(2)	112.9(3)
C(2)—C(3)—C(4)	121.4(4)	121.7(4)	O(7)—C(8)—C(9′)	115.0(3)	114.8(3)
C(3)—C(4)—C(7)	122.0(3)	122.9(3)	C(2)—C(10)—C(11)	111.9(3)	111.8(3)
C(3)—C(4)—C(5)	117.8(4)	118.1(3)	C(10)—C(11)—C(12)	110.7(3)	111.0(3)
C(5)—C(4)—C(7)	120.2(3)	119.0(3)	C(11)—C(12)—C(13)	111.4(3)	111.6(3)
C(4)—C(5)—C(6)	122.0(3)	121.6(3)	C(3)—C(13)—C(12)	110.0(3)	110.4(3)
C(1)—C(6)—C(5)	119.3(3)	119.2(3)	C(8)—C(9′)—O(1′)	108.9(2)	113.3(2)
			C(2)—O(1)—C(9)	112.8(2)	113.0(2)

	host A	host B		host A	host B
C(9)—O(1)—C(2)—C(3)	176.2(3)	176.6(3)	O(4)—C(5)—C(6)—O(7)	−62.8(4)	−61.0(4)
O(1)—C(2)—C(3)—O(4)	−61.9(3)	−61.8(3)	C(5)—C(6)—O(7)—C(8)	−178.4(3)	−178.6(3)
C(2)—C(3)—O(4)—C(5)	−152.7(3)	−153.1(3)	C(6)—O(7)—C(8)—C(9′)	−75.5(4)	−75.9(4)
C(3)—O(4)—C(5)—C(6)	178.3(3)	177.7(3)	O(7)—C(8)—C(9′)—O(1′)	−72.7(4)	72.8(3)

Table VII. Principal structural kinds of complexes of RSO_2NH_2 with DC-18-C-6. The complexes **1**, **2**, **7** and **8** are molecular compounds, **3** and **4** are polymers, while **5** and **6** are bi- and tri-dimensional compounds respectively

Guest	Host	Ratio	Structural type	Ref.
1 SO_3NH_3	DC-18-C-6[A]	1:1	H ← G	[25]
2 SO_3NH_3	DC-18-C-6[B]	1:1	H ← G	[25]
3 $NH_2PhSO_2NH_2$	DC-18-C-6[B]	2:1		[13]
4 $CH_3CONHPhSO_2NH_2$	DC-18-C-6[B]	2:1		[13]
5 $NH_2PhSO_2N{=}C(NH_2)_2$	DC-18-C-6[A]	2:1		[15]
6 $NH_2PhSO_2N{=}C(NH_2)_2$	DC-18-C-6[B]	2:1		[15]
7 $CH_3PhSO_2NH_2$	DC-18-C-6[A]	1:1	H←G	[this work]
8 $CH_3PhSO_2NH_2$	DC-18-C-6[B]	2:1	G→H←G	[this work]

4. Conclusions

In Table VII the principal structural kinds of complexes formed between $R—SO_2—NH_2$ molecules as guest with the two isomers of DC-18-C-6 as host are reported. These data indicate that different types of molecular structure (chains, bi- or tridimensional networks) may be synthesized depending on the geometrical properties of the guest molecule or on the isomeric composition of DC-18-C-6.

Finally it is interesting to note that the 1 : 2 complexes formed between the two isomers of DC-18-C-6 and 4-aminobenzosulfamide [15], have two different types of guest molecule. In the centrosymmetric complex of the B isomer both guest molecules interact with the crown ether, while in the complex of the A isomer only one guest molecule forms N—H···O interactions with the host molecule and the second one remains in the crystal as solvent. In our case, in contrast, in the complexation of the two isomers of DC-18-C-6 with 4-methylbenzenesulfamide, two different products were obtained: whilst a host/guest ratio of 1 : 1 was found with isomer A, a ratio of 1 : 2 was obtained by complexing the B isomer.

References

1. M. Mercer and M. R. Truter: *J. Chem. Soc. Dalton Trans.* 2215, (1973).
2. N. F. Krasnova, Yu. A. Simonov, V. K. Bel'skii, B. M. Abaskin, V. V. Yakshin, T. I. Malinowskii and B. N. Laskorin: *Dokl. Akad. Nauk. SSSR* **276**, 607 (1984).
3. F. R. Fronczek, R. D. Gandour, L. M. B. Gehrig, L. R. Caswell, K. A. McDowell and I. Alam: *J. Incl. Phenom.* **5**, 379 (1987).
4. A. A. Dvorkin, N. F. Krasnova, Yu. A. Simonov, V. M. Abaskin, V. V. Yakshin and T. I. Malinowskii: *Kristallografiya* **29**, 282 (1984).
5. A. Elbasyouny, H. J. Brugge, K. von Deuten, M. Dickel, A. Knochel, K. U. Koch, J. Kopf, D. Melzer and G. Rudolph: *J. Am. Chem. Soc.* **105**, 6568 (1983).
6. G. Bombieri, G. De Paoli and A. Immirzi: *J. Inorg. Nucl. Chem.* **40**, 799 (1978).
7. M. M. Amini, A. L. Rheingold, R. W. Taylor and J. J. Zuckerman: *J. Am. Chem. Soc.* **106**, 7289 (1984).
8. N. F. Krasnova, Yu. A. Simonov, V. K. Bel'skii, A. T. Fedorova and V. V. Yakshin: *Kristallografiya* **31**, 650 (1986).
9. J. M. Lehn: *Chemica Scripta* **28**, 237 (1988).
10. D. F. Cram: *Chemica Scripta* **28**, 263 (1988).
11. E. Weber: in *Synthesis of Macrocycles. The Design of Selective Complexing Agents: Progress in Macrocyclic Chemistry* (Ed. R. M. Izatt and F. F. Christensen) Vol. 3. Wiley, New York (1987).
12. F. R. Damewood, F. F. Urban, T. C. Williamson and A. L. Rheingold: *J. Org. Chem.* **53**, 167 (1988).
13. Yu. A. Simonov, T. I. Malinowskii, A. A. Dvorkin, M. S. Fonar, Ed. V. Ganin and S. A. Kotlar: *Z. Kristallogr.* **185**, 249 (1988).
14. D. R. Rogers, P. D. Richards and E. J. Voss: *J. Incl. Phenom.* **6**, 65 (1988).
15. Yu. A. Simonov, L. P. Battaglia, A. Bonamartini Corradi, S. Ianelli, G. Pelosi, Ed. V. Ganin, N. G. Lukjanenenko: *J. Incl. Phenom.* (submitted).
16. D. Belletti, A. Cantoni and G. Pasquinelli: in *Gestione on Line di Diffrattometro a Cristallo Singolo Siemens AED con Sistema IBM PS2/30.* Centro di Studio per la Strutturistica Diffrattometrica del C.N.R., Parma, Italy. Internal Report 1/88 (1988).
17. M. S. Lehmann and F. K. Larsen: *Acta Crystallogr.* **A30**, 580 (1974).
18. G. M. Sheldrick: in *SHELX76,* Program for Crystal Structure Determination, University of Cambridge, England (1976).
19. C. Rizzoli, V. Sangermano, G. Calestani and G. D. Andreetti: in 'CRYSRULER, An Integrated System of Computer Programs for Crystal Structure Analysis on a Personal Computer, *J. Appl. Crystallogr.* **20**, 436 (1987).

20. A. Knochel, J. Kopf, J. Oehler and G. Rudolph: *J. Chem. Soc. Chem. Commun.* 595 (1978).
21. F. Seel, N. Klein, B. Krebs, M. Dartmann and G. Henkel: *Z. Anorg. Allg. Chem.* **524**, 95 (1985).
22. J. Dale: *Acta. Chem. Scand.* **27**, 1115 (1973).
23. N. K. Dalley, J. S. Smith, S. B. Larson, J. J. Christensen and R. M. Izatt: *J. Chem. Soc. Chem. Commun.* **43** (1975).
24. Yu. A. Simonov, N. F. Krasnova, N. A. Charenko, V. K. Bel'skii, V. V. Yakshin and B. N. Laskorin: *Dokl. Akad. Nauk SSSR* **285**, 893 (1985).
25. Yu. A. Simonov, N. G. Krasnova, A. A. Dvorkin, V. V. Yakshin, V. B. Abashkin and B. V. Laskorin: *Dokl. Akad. Nauk SSSR* **272**, 1129 (1985).
26. M. S. Fonar, Yu. A. Simonov, A. A. Dvorkin, T. I. Malinowsky, Ed. V. Ganin, S. A. Kotlyar and V. F. Makarov: *J. Incl. Phenom.* **7**, 613 (1989).
27. G. Weber and G. M. Sheldrick: *Acta Crystallog.* **B37**, 2108 (1981).