Synthesis of R-(−)-2-Ethyl-*N*-benzyl (monoaza-15-crown-5) and the Crystal Structure of Its Sodium Perchlorate Complex

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Abstract

A new complex of a chiral monoaza-crown ether, [R-(−)-2-ethyl-*N*-benzyl-4,7,10,13-tetraoxa-1-azacyclopentadeceane) $NaClO_4$], has been prepared and studied by x-ray diffraction. The compound crystallizes in space group $P2_1$ with cell dimensions $a = 9.480(1)$, $b = 15.978(2)$, $c = 15.816(2)$ Å, $\beta = 105.51(1)°$, $Z = 4$. The final R value is 0.055 for 2711 observed reflections and 540 parameters. There are two molecules in the asymmetric unit labelled A and B. The sodium ion is hexacoordinated. The average values for the Na—O_{eth} (etheric) distances are 2.364(6), 2.317(7) Å and the Na–N distances are 2.679(6), 2.611(7) Å; the Na—$O(ClO_4)$ contacts are 2.497(7) and 2.257(10) Å, for A and B, respectively.

Introduction

There has been a great interest in the chemistry of crown ethers for two decades. One of the most interesting aspects of these compounds is their similar catalytic and recognition properties to those of natural compounds such as enzymes [1]. Cram and co-workers [2–4] as well as others [5] have shown that chiral crown ethers have the ability to discriminate between chiral alkylammonium salts using NMR spectroscopy [5], solvent extraction [3], chromatographic techniques [4] and liquid membrane transport processes. They have also successfully been used as chiral catalysts or chiral templates in many asymmetric reactions, e.g., Michael addition [6], reduction [7], and hydrogen cyanide addition [8].

Despite the well-established knowledge of crown ether chemistry, there is still a lack in the understanding of factors affecting intermolecular interactions in complexes of crown ethers with guest molecules [9]. To enhance the structural selectivity of crown ethers many chiral macrocyclic compounds have been designed. Derivatives of binaphthol [10] and *vic*-cyclohexanediol [11], carbohydrates [12], tartaric acid [13], and amino acids [14] have been used as building-blocks [1].

We aimed to synthesise chiral crown ethers with enhanced structural selectivity starting with R-(−)-2-amino butanol as a chiral building-block, produced largely in industry for the synthesis of ethambutol, a drug for treatment of tuberculosis [15]. In this work, we report the synthesis and the structural characterization of a new complex of a chiral mono aza-15-crown-5 derivative. The solid state structure of the complex is determined by x-ray diffraction in order to verify its formula and also to determine the conformation of the macrocycle.

Experimental

Apparatus and chemicals

All chemicals were reagent grade unless otherwise specified. Melting points were determined with a Gallenkamp Model apparatus with open capillaries. Infrared spectra were recorded on a Midac-FTIR Model 1700 Spectrometer. The elemental analyses were obtained with a Carlo-Erba Model 1108 apparatus. Optical rotations were recorded using a Atago DR Model 21949 polarimeter. ^{1}H (400 MHz) and ^{13}C (100 MHz) NMR spectra were recorded on a Bruker DPX-400 High Performance Digital FT-NMR spectrometer. Refraction indexes were measured using a Atago Abbe refractometer.

Synthesis

R-(−)-N-benzyl-2-amino-1-butanol (**I**)

R-(−)-2-amino-1-butanol (71.2 g, 0.8 mol), benzyl chloride (25.3 g, 0.2 mol) and Na_2CO_3 (20 g, 0.18 mol) were placed in a 250 mL two-necked round bottomed flask equipped with an addition Dean Stark apparatus. The mixture was stirred at 100 °C for 8 h in an oil bath under dry N_2. Then the mixture was cooled and $CHCl_3$ (100 mL) was added to the mixture and refluxed for 1 h. The $CHCl_3$ layer was separated
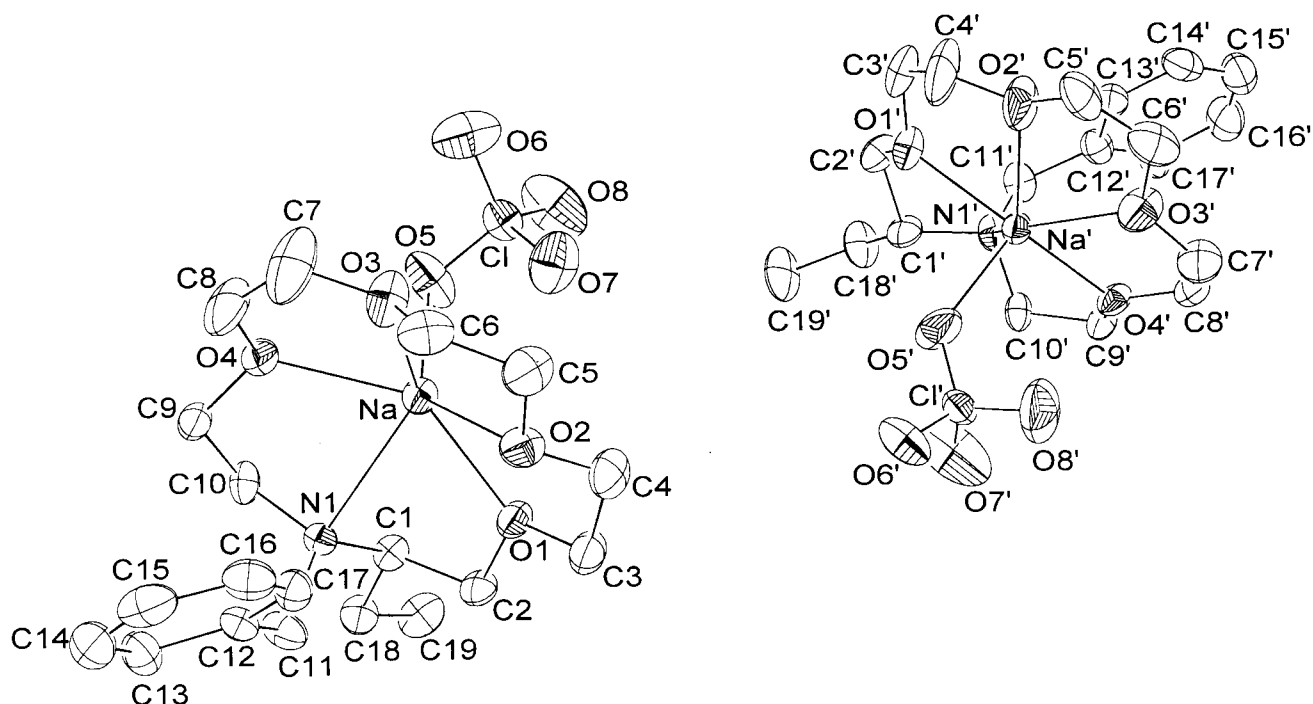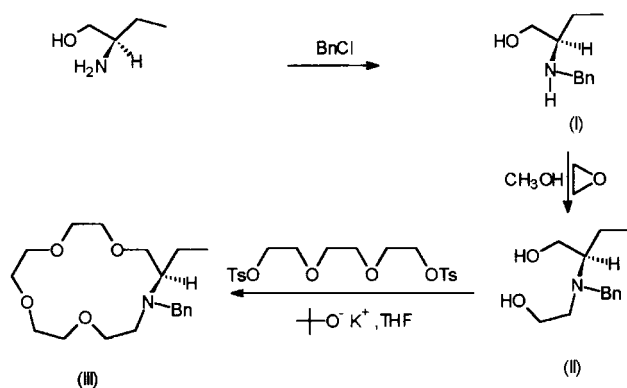
Figure 1. ORTEP drawing of the title compound showing two molecules in the asymmetric unit with the numbering scheme. Displacement ellipsoids are drawn with 35% probability and H atoms are omitted for clarity.

Scheme 1.

from the solid phase. The remaining solid was reextracted with CHCl$_3$ (3 × 25 mL). The combined CHCl$_3$ layers were dried over Na$_2$SO$_4$ and evaporated. The product was distilled at reduced pressure after distilling excess amine. The product (**I**) was distilled at 98-100 °C/0.1 mmHg to give 33 g (94%) m.p. 71–72 °C [16]. M.w. 179 g/mol (Found: C, 73.67; H, 9.63; N, 7.74; C$_{11}$H$_{17}$NO requires C, 73.70; H, 9.56; N, 7.80%). IR (KBr): 3287, 3076, 2931, 2836, 1467, 1361, 1068 cm^{-1}. ^{1}H NMR (CDCl$_3$) δ 0.98 (3H, t, J = 7.48 Hz), 1.48–1.63 (2H, m), 2.64–2.68 (1H, m), 3.38–3.85 (2H, ddd), 3.75–3.85 (2H, dd), 7.29–7.39 (5H, m) ppm. ^{13}C NMR (CDCl$_3$) δ 10.73, 24.64, 51.48, 60.21, 63.05, 127.45, 128.86, 140.83 ppm.

R-(−)-N-benzyl-4-hydroxymethyl-3-azahexane-1-ol (**II**)

A solution of 47 g (260 mmol) of (**I**) in 100 mL of methanol was cooled to −20 °C in a 250 mL flask. 11.52 g (260 mmol) of ethylene oxide in 50 mL of methanol at −20 °C was added

to the solution dropwise at −20 °C. The mixture was kept at −20 °C during addition in a deepfreeze. After addition the mixture was stirred for 12 h at −20°C and then 24 h at +4 °C. The mixture was kept for one day at room temperature in a closed flask.

Methanol was evaporated in vacuo. The product was purified by distillation under reduced pressure at 155 °C/0.1 mmHg to give 56 g (94%) of (**II**). η_I^{20} = 1.524 [α]$_D^{20}$ = - 14.89 (c = 0.08, EtOH). M.w. = 223 g/mol (Found: C, 66.76; H, 9.04; N, 6.08, C$_{13}$H$_{21}$NO$_2$ requires C, 66.90; H, 9.07; N, 6.00%) IR (neat film): 3368, 3085, 3061, 3026, 2957, 2876, 1602, 1494, 1453, 1372, 1155, 1054, 729, 698 cm^{-1}. ^{1}H NMR (CDCl$_3$) δ 0.98 (3H, t, J = 7.47 Hz), 1.22–1.29 (1H, m), 1.60–1.67 (1H, m), 2.59–2.85 (2H, ddt), 2.71–2.76 (1H, m), 3.41 (2H, t, J = 10.28 Hz), 3.45–3.56 (2H, ddd), 3.62–3.84 (2H, dd), 7.27–7.37 (5H, m) ppm. ^{13}C NMR (CDCl$_3$) δ 12.23, 19.72, 51.87, 55.32, 60.52, 61.90, 63.41, 127.41, 128.76, 129.16, 140.52.

R-(−)-2-ethyl-N-benzyl-4,7,10,13-tetraoxa-1-azacyclopentadeceane (**III**)

Tertiary butanol (74.2 g, 1 mol) and metallic potassium (6.825 g, 175 mmol) were added simultaneously to a solution of dry THF (500 mL) in a four necked flask. The mixture was stirred at 80 °C under dry N$_2$ until all the metallic potassium was dissolved. R-(−)-N-benzyl-4-hydroxymethyl-3-azahexane-1-ol (7.8 g, 35 mmol) was added dropwise to the solution for 2.5 h under dry N$_2$. The mixture was stirred for 1 h at 80 °C. Then triethylene glycol bistoluene-*p*-sulphonate (TEGD) (16.03 g , 35 mmol) in THF (100 mL) was added dropwise to the stirring mixture for 2 h. The mixture was then stirred and refluxed at 80 °C for 24 h under dry N$_2$, cooled to the room temperature, filtered and the solvent
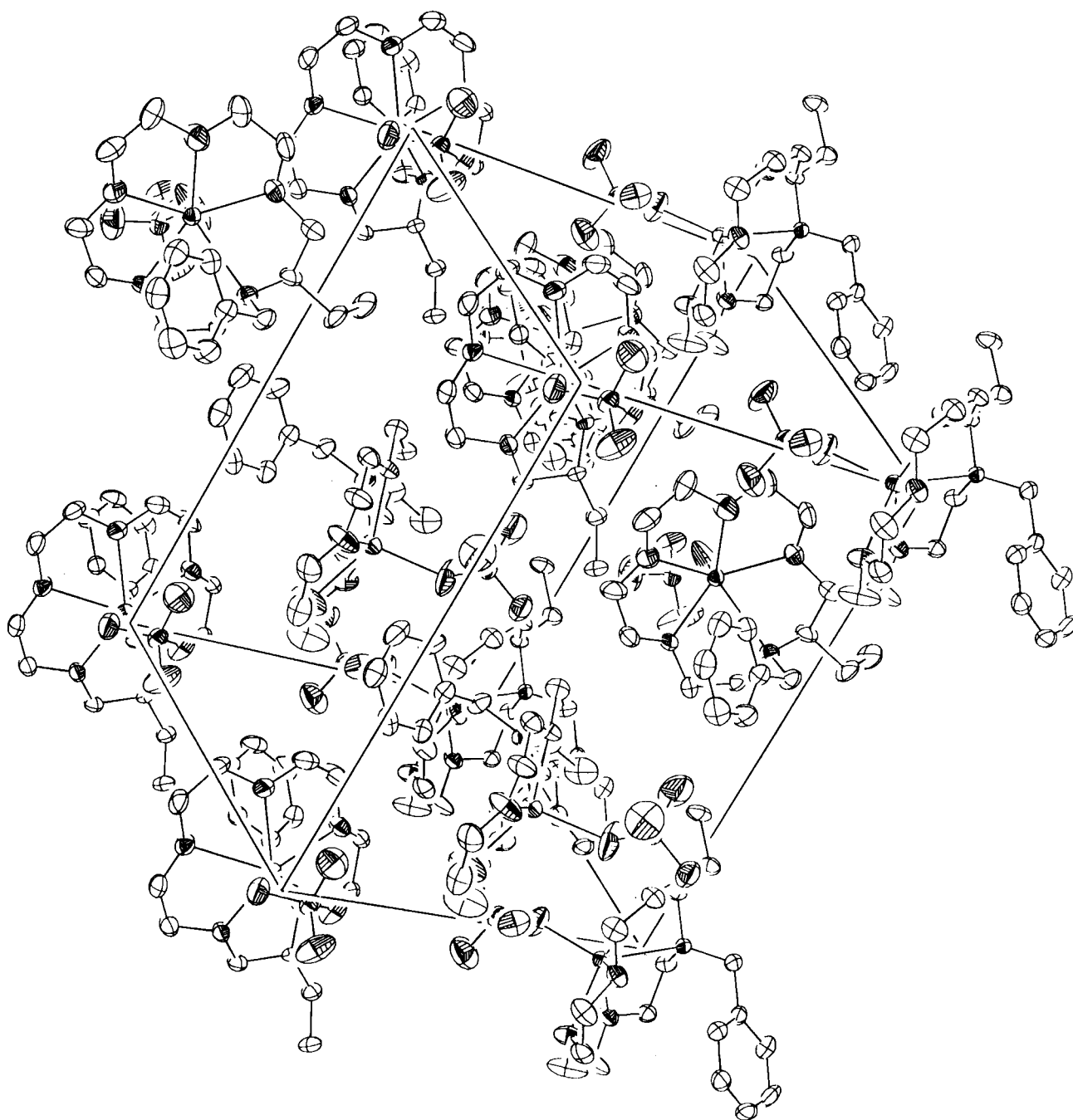
Figure 2. The packing of R-(−)-2-ethyl-*N*-benzyl(monoaza-15-crown-5) NaClO₄ molecules in the unit cell.

was evaporated. The residue was dissolved in chloroform and washed with water, dried (Na₂SO₄) and evaporated. The residual oil was purified by flash column chromatography on silica (triethylamine-ethylacetate-petroleum ether (40–60); 3 : 30 : 67 and 3 : 17 : 80, respectively). The product was obtained as a colourless oil, 8.2 g 69% of (**III**).

*NaClO₄ complex of (***III***)*

A solution of 3.8 g (11 mmol) of host (III) in 20 mL of ethylacetate was added to 1.58 g (11 mmol) NaClO₄·H₂O dissolved in 10 mL of ethylacetate. The mixture was stirred for 1 h and kept for 24 h at room temperature. The product was filtered and recrystallized from ethylacetate. M.p. 132-

133 °C; $[\alpha]_D^{20}$ = - 28.8 (*c* = 0.04 EtOH). M.w. 459.5 g/mol (Found: C, 49.57; H, 6.74; N, 2.98; C₁₉H₃₁NO₄. NaClO₄ requires C, 49.62; H, 6.75; N, 3.04%) IR (KBr) : 3062, 3027, 2925, 2873, 1601, 1479, 1454, 1353, 1246, 1121, 973, 954, 832, 799, 741, 704, 624 cm⁻¹. ¹H NMR (CDCl₃) δ 0.86 (3H, t, J= 7.21 Hz), 1.16 (1H, bs), 1.56 (1H, bs), 2.80–4.10 (21H, m), 7.25–7.35 (5H, m) ppm. ¹³C NMR (CDCl₃) δ 12.05, 17.92, 68.50, 68.75, 68.95, 69.90, 127.31, 128.78, 128.94 ppm.

Table 1. Crystal data and details of the structure determination for R-(−)-2-ethyl-*N*-benzyl (monoaza-15-crown-5) NaClO₄

Crystal data:	
Formula	$C_{19}H_{31}ClNNaO_8$
Formula weight	459.89
Crystal system	Monoclinic
Space group	$P2_1$ (No. 4)
a, Å	9.480(1)
b, Å	15.978(2)
c, Å	15.816(2)
β, deg	105.51(1)
V, Å³	2308.5(4)
Z	4
D_c, g cm⁻³	1.323
$F(000)$	976
μ, cm⁻¹	2.2
Crystal size, mm	$0.48 \times 0.20 \times 0.60$
Data Collection:	
Temperature (K)	295
Radiation, λ	MoK$_\alpha$, $\lambda = 0.71069$ Å
Range of relative transm. factors, %	92.9-99.9
Range of θ, deg	2.1, 25.4
Range of hkl	1: 11; 0: 19; −19: 18
Scan type	$\omega - 2\theta$
Number of collected reflections	4649 total, 4363 unique
Standard reflections	3 measured every 120 min.
R_{int}	1.4%
Structure refinement:	
No. of reflections included	2711 with $I > 2.0\sigma(I)$
No. of refined parameters	540
$R = \Sigma |\Delta F| / \Sigma |F_0|$	0.0550
$wR = [\Sigma w |\Delta F|^2 / \Sigma w |F_0|^2]^{1/2}$	0.0590
Goodness of fit	0.89
Max. and Av. Shift/Error	0.00, 0.00
Final $\Delta\rho_{max}$, $\Delta\rho_{min}$, e Å⁻³	0.32, −0.07

X-Ray data collection, structure determination and refinement

Data collection was carried out on an Enraf-Nonius CAD4 diffractometer in the $\omega/2\theta$ scan mode using graphite mono-chromated Mo radiation. The crystal used for data collection was colourless, transparent and prismatic shaped. Accurate cell dimensions were obtained by the least-squares analysis of the setting angles of 25 reflections in the range $11 \leq \theta \leq 18°$. During data collection, three reflections were monitored every two hours and showed no significant intensity variations. All data were treated for Lp effects and for absorption using empirical psi-scan corrections. Crystal data and a summary of intensity data collection and structure refinement are presented in Table 1.

The structure was solved by direct methods using the program SIR in the MolEN program package [17]. Two chemically similar but crystallographically distinct molecules in the asymmetric unit were found. Least-squares refinement with isotropic thermal parameters led to $R = 0.118$. High thermal motion, which is a common feature

Table 2. Selected interatomic distances (Å) and bond angles (°) for both molecules in the asymmetric unit of R-(−)-2-ethyl-*N*-benzyl (monoaza-15-crown-5) NaClO₄

	A	B
Cl—O(5)	1.407(7)	1.352(8)
Cl—O(6)	1.409(8)	1.422(7)
Cl—O(7)	1.413(8)	1.373(10)
Cl—O(8)	1.369(8)	1.373(10)
Na—O(1)	2.297(6)	2.308(6)
Na—N(1)	2.679(7)	2.611(7)
Na—O(5)	2.497(8)	2.257(10)
Na—O(2)	2.445(6)	2.372(7)
Na—O(3)	2.377(7)	2.302(7)
Na—O(4)	2.339(6)	2.285(6)
O(1)—C(2)	1.424(9)	1.425(10)
O(1)—C(3)	1.425(10)	1.398(9)
O(2)—C(4)	1.392(10)	1.378(12)
O(2)—C(5)	1.418(11)	1.333(13)
O(3)—C(6)	1.356(11)	1.285(13)
O(3)—C(7)	1.393(13)	1.344(14)
O(4)—C(9)	1.391(9)	1.397(11)
O(4)—C(8)	1.407(16)	1.380(13)
N(1)—C(1)	1.482(8)	1.516(10)
N(1)—C(11)	1.474(10)	1.498(10)
N(1)—C(10)	1.457(9)	1.455(10)
C(1)—C(2)	1.494(10)	1.523(11)
C(1)—C(18)	1.551(11)	1.601(13)
C(3)—C(4)	1.498(12)	1.496(14)
C(5)—C(6)	1.468(13)	1.437(16)
C(7)—C(8)	1.280(18)	1.37(2)
C(9)—C(10)	1.514(10)	1.49(14)
O(5)—Cl—O(6)	109.2(6)	110.4(5)
O(5)—Cl—O(8)	109.1(5)	110.6(6)
O(6)—Cl—O(7)	107.9(5)	108.7(5)
O(7)—Cl—O(8)	112.5(5)	108.0(6)
O(1)—Na—N(1)	69.0(2)	71.4(2)
O(2)—Na—O(4)	126.9(2)	131.8(3)
O(2)—Na—N(1)	111.9(2)	123.2(3)
O(3)—Na—O(4)	70.5(2)	69.9(3)
O(1)—Na—O(2)	68.5(2)	68.8(2)
O(1)—Na—O(4)	139.6(2)	141.0(2)
O(5)—Na—N(1)	105.8(2)	105.6(3)
O(3)—Na—N(1)	128.3(2)	127.9(3)
O(4)—Na—N(1)	70.7(2)	69.9(2)
Na—O(1)—C(2)	119.4(4)	118.0(4)
C(2)—O(1)—C(3)	115.1(5)	114.4(6)
Na—O(2)—C(5)	110.0(5)	115.6(6)
C(4)—O(2)—C(5)	116.7(6)	122.7(8)
Na—O(3)—C(6)	115.3(5)	120.0(6)
C(6)—O(3)—C(7)	117.6(7)	124.0(9)
C(8)—O(8)—C(9)	115.4(7)	118.6(7)
Na—O(4)—C(9)	119.2(4)	119.8(5)
Cl—O(5)—Na	104.7(4)	129.0(6)
Na—N(1)—C(10)	96.9(4)	94.6(5)
Na—N(1)—C1	91.2(4)	93.2(4)
C(1)—N(1)—C(10)	112.2(5)	110.5(6)
N(1)—C(1)—C(2)	111.1(6)	109.6(6)
O(1)—C(2)—C(1)	108.1(5)	107.3(6)
O(1)—C(3)—C(4)	107.9(6)	108.2(7)
O(2)—C(4)—C(3)	108.5(6)	108.7(8)

Table 2. Continued

	A	B
O(2)—C(5)—C(6)	109.2(7)	112.8(9)
O(3)—C(6)—C(5)	110.3(7)	116.4(9)
O(3)—C(7)—C(8)	121.5(11)	116.6(12)
O(4)—C(8)—C(7)	118.2(9)	114.0(9)
O(4)—C(9)—C(10)	110.2(6)	108.6(7)
N(1)—C(10)—C(9)	114.8(6)	113.0(7)
N(1)—C(11)—C(12)	113.9(6)	113.3(7)

Table 3. Torsion angles about the monoaza-15-crown-5 ligand (°)

	A	B
C(2)—C(1)—C(3)—C(4)	−171.5(7)	−175.4(7)
O(1)—C(3)—C(4)—O(2)	54.1(9)	52.6(10)
C(5)—O(2)—C(4)—C(3)	178.1(7)	165.7(8)
C(4)—O(2)—C(5)—C(6)	165.5(7)	171.5(9)
O(2)—C(5)—C(6)—O(3)	−58.8(9)	−29.9(13)
C(7)—O(3)—C(6)—O(3)	176.5(8)	−177.2(13)
C(6)—O(3)—C(7)—C(8)	−119.2(13)	−140.4(12)
O(6)—O(3)—C(7)—C(8)	−23.8(19)	−33.2(16)
C(9)—O(4)—C(8)—C(7)	160.6(10)	176.4(9)
C(8)—O(4)—C(9)—C(10)	−166.6(8)	−167.5(7)
O(4)—C(9)—C(9)—C(10)	59.7(8)	57.9(9)
C(1)—N1—C(10)—C(9)	−149.0(6)	−157.1(7)
C(10)—N(1)—C(1)—C(2)	165.0(6)	161.5(7)
N(1)—C(1)—C(2)—O(1)	−61.4(7)	−65.5(8)
C(3)—O(1)—C(2)—C(1)	163.7(6)	168.9(7)
C(1)—N(1)—C(11)—C(12)	156.3(7)	146.9(7)
N(1)—C(1)—C(18)—C(19)	170.5(6)	156.6(8)

of similar structures, was noted for most atoms, especially perchlorate oxygen atoms and some of the atoms of the ligand. The geometrically constrained hydrogen atoms were placed in calculated positions 0.95 Å from the bonded carbon. For all H atoms, a riding model was used with B fixed at $1.3U_{eq}$ of the bonded carbon atom. Refinement of non-hydrogen atoms with anisotropic temperature factors led to the final R value of 0.055 and $R_w = 0.059$. Selected bond lengths and angles are given in Table 2, while important torsion angles are listed in Table 3. Fractional atomic coordinates with equivalent isotropic displacement parameters of the non-hydrogen atoms, positions of hydrogen atoms, anisotropic displacement parameters for non-hydrogen atoms are included in the supplementary material (Tables 4–6).

Results and discussion

The perspective view of the asymmetric unit of the title compound with the crystallographic numbering scheme is shown in Figure 1. Two independent molecules in the asymmetric unit exhibit slightly different conformations. In the molecules, the 15-membered ring is severely strained and deviates from the expected conformation of 15-crown-5 type molecules. This is established by the torsion angles listed in Table 3. This strain is expected because of the presence of the phenyl and ethyl groups bonded to the N(1) and asymmetric C(1) atoms, respectively, of the ether ring and also the perchlorate anion. The macrocycle oxygen atoms are on average 0.229(6) Å for the unprimed molecule, hereafter A, and 0.088(7) Å for the primed molecule, hereafter B, alternately above and below the oxygen's mean plane. In both molecules, the sodium ion resides significantly out of the plane by −0.523(3) and 0.477(3) Å for A and B, respectively. The deviations of the nitrogen atoms from the plane are 1.107(5) Å in A and −0.885(6) Å in B.

The sodium ion is bound to all heteroatoms of the macrocycle. The coordination shell of the sodium is completed by an oxygen atom of the perchlorate anion. Thus the sodium is hexacoordinated. The average values for the Na—O_{eth} (etheric) distances are 2.364(6), 2.317(7) Å and the Na—N distances are 2.679(6), 2.611(7) Å for A and B. The perchlorate anions are asymmetrically bound with Na—O(5), O(5)′ contacts of 2.497(7) and 2.257(10) Å, respectively. The effective ionic radius for hexacoordinated Na^+ is 1.02 Å [18]. A complex's mean cavity radius can be determined from the structural data as defined by Mathieu et al. [19]. For molecule A, the macrocycle's mean cavity radius of 1.06 Å is larger than the 0.94 Å found for molecule B in the title compound. The mean cavity radius is reported as 1.08 Å in 10-methyl-9-[2-methyl-4-(1,4,7,10-tetraoxa-13-aza-13-cyclopentadecyl)phenyl]- acridinium perchlorate sodium thiocyanate in which the Na atom is five coordinated [20].

The perchlorate anion is located over the best plane of the macrocycle in an apical position. The phenyl ring is located underneath the plane of the macrocycle; the dihedral angle between the planes of the four ring oxygen atoms and the phenyl ring is 48.4(3) and 45.0(3)° for the A and B molecules, respectively.

The packing of R-(−)-2-ethyl-*N*-benzyl (monoaza-15-crown-5) $NaClO_4$ molecules in a unit cell is shown in Figure 2. The shortest contacts between molecules indicated van der Waals interaction that might be beneficial to stabilization of the crystal.

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