In (I) the Na⁺ cations are small enough to insert in the hollows of the crossed polymeric chains. These cations are surrounded by six O atoms, five from pht anions and one from a water molecule (Fig. 3), with Na—O distances in the range 2·286–2·781 Å.

In (II) the K⁺ cations interpose between adjacent chains (Fig. 6) and are surrounded by seven O atoms (at distances in the range 2·616–3·190 Å) belonging to pht anions and to water molecules. K–O interactions together with hydrogen bonds between water molecules and pht anions join the chains in layers parallel to (101).

Packing of the layers in both compounds is determined by normal van der Waals contacts.

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The Crystal and Molecular Structure of 4-Nitrobenzo-1,4,7,10,13,16-hexaoxacyclooctadecane.RbSCN, C₁₇H₂₃O₈N₂SRb

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The crystal and molecular structure of the title compound (4-nitrobenzo-18-crown-6.RbSCN) has been determined from 1935 observed three-dimensional data measured on a Syntex $P2_1$ single-crystal automated diffractometer. The unit cell is monoclinic with $a = 13·222$ (3), $b = 8·179$ (2), $c = 21·150$ (4) Å, $\beta = 110·54$ (1)°, $V = 2142$ (1) Å³ and contains four formula units. The space group is $P2_1/c$. The crystal structure was solved by the heavy-atom method and refined by the block-diagonal least-squares method. The final R value is 0·056.

Introduction

One of the important properties of macrocyclic polyethers is their ability to form complexes with various inorganic cations by means of ion–dipole interactions between the cation and electronegative O atoms arranged symmetrically in the macro-ring.

In recent years, a number of papers have been published reporting structures of the above type containing 1,4,7,10,13,16-hexaoxacyclooctadecane (Bright & Truter, 1970; Bush & Truter, 1971; Dunitz, Dobler, Seiler & Phizackerley, 1974; Goldberg, 1975; Hašek, Hlavatá & Huml, 1977; Mallinson, 1975).

Dunitz et al. (1974) showed that the six O atoms in 1,4,7,10,13,16-hexaoxacyclooctadecane formed, for the K⁺ cation, an almost regular planar hexagon having a side length of approximately 2·81 Å. For cations with a higher van der Waals radius the O hexagon remains almost without change, and the cation moves away from the mean O plane.

In the case of the Na⁺ cation the hexagon of O atoms is greatly deformed. One of the O atoms deviates from the mean plane of the other five by some 1·95 Å.

In an attempt to elucidate the pronounced effect of substituents in an 18-membered ring on selectivity towards various cations (Petránek & Ryba, 1974), work was started in order to solve a number of structures containing 1,4,7,10,13,16-hexaoxacyclooctadecane with various substituents (Hašek & Huml, 1975; Hašek, Hlavatá & Huml, 1977). In this paper we present the crystal and molecular structure of the complex 4-nitrobenzo-1,4,7,10,13,16-hexaoxacyclooctadecane.RbSCN.

Experimental

The crystals used in the measurements were prepared by Petránek & Ryba (1974). They were yellow, in the

Table 1. Crystal data

Monoclinic, $P2_1/c$
$a = 13 \cdot 222$ (3) Å
$b = 8 \cdot 179$ (2)
$c = 21 \cdot 150$ (4)
$\beta = 110 \cdot 54$ (1)°
$V = 2142$ (1) Å³
FW 500·8

$C_{17}H_{23}O_8N_2SRb$
$\mu_{Mo K\alpha} = 25 \cdot 8$ cm⁻¹
$D_m = 1 \cdot 55$ g cm⁻³
$D_x = 1 \cdot 55$
$Z = 4$
$F(000) = 1024$
m.p. 178–179 °C

form of thin sticks. The molecular formula was confirmed by elemental analysis. Crystal data are given in Table 1.

The space group was determined from Weissenberg photographs. Systematically absent reflexions ($0k0$ when k odd and $h0l$ when l odd) were checked by the ψ scan on a Syntex $P2_1$ diffractometer.

The unit-cell parameters were obtained by refining on 15 reflexions measured with an automatic Syntex $P2_1$ diffractometer [λ(Mo $K\alpha$) = 0·71069 Å, graphite monochromator, room temperature, crystal ground to a sphere $r = 0 \cdot 2$ mm]. Density was measured by the flotation method in a heptane and CCl_4 solution.

Intensity measurement

Diffracted intensities were measured by the ω–2θ scan method with a graphite monochromator in an equatorial arrangement. If the scintillation counter recorded more than 5×10^3 counts s⁻¹, the intensity was corrected for pulse coincidence (dead time = 3×10^{-6} s). If the rate exceeded 50×10^3 counts s⁻¹, the reflexions were remeasured with a lower anode current and scaled with respect to the three reference reflexions. The scan interval was 1° below $K\alpha_1$ to 1° above $K\alpha_2$ of the Mo $K\alpha$ doublet. The right and left backgrounds were measured for half the time needed for measuring the maximum. The minimum scan rate was 1·2° min⁻¹. The intensities measured were corrected with three reference reflexions measured after each set of 30 reflexions. The intensities of all three reference reflexions decreased by some 5% during the measurement (200 h, 46 kV 20 mA).

2683 independent reflexions were measured, of which 1935 were observed up to sin $\theta_{max}/\lambda = 0 \cdot 53$ Å⁻¹. A reflexion was taken as unobserved if $I_{obs} < 1 \cdot 96\sigma(I)$, where $\sigma(I)$ was calculated from counting statistics.*

The intensities were corrected for Lorentz–polarization effects by means of the relation:

$$Lp = [(1 + \cos^2 2\theta_M \cos^2 2\theta)/(1 + \cos^2 2\theta_M) + (1 + \cos 2\theta_M \cos^2 2\theta)/(1 + \cos 2\theta_M)]/2 \sin 2\theta$$

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* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 32989 (54 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

Table 2. Final positional parameters of non-hydrogen atoms, and their e.s.d.'s

The fractional coordinates have been multiplied by 10^4, except those for Rb⁺ which have been multiplied by 10^5.

	x	y	z
O(2)	2807 (4)	3183 (7)	4176 (2)
O(5)	634 (4)	2317 (6)	3376 (3)
O(8)	−58 (4)	1977 (8)	1957 (2)
O(11)	1238 (4)	4029 (6)	1469 (2)
O(14)	3452 (4)	4610 (6)	2227 (2)
O(17)	4106 (4)	4299 (7)	3629 (2)
C(1)	3902 (5)	2915 (10)	4518 (3)
C(3)	2075 (6)	2574 (10)	4458 (4)
C(4)	986 (7)	3075 (12)	4041 (4)
C(6)	−431 (6)	2693 (11)	2973 (5)
C(7)	−762 (5)	1683 (12)	2352 (5)
C(9)	−491 (6)	2961 (12)	1381 (4)
C(10)	321 (7)	3136 (12)	1046 (4)
C(12)	2039 (7)	4212 (11)	1174 (4)
C(13)	2875 (7)	5338 (11)	1588 (4)
C(15)	4156 (7)	5745 (11)	2656 (4)
C(16)	4800 (7)	4910 (11)	3266 (4)
C(18)	4566 (6)	3579 (10)	4210 (4)
C(19)	5716 (6)	3355 (10)	4529 (4)
C(20)	6116 (7)	2540 (10)	5125 (4)
C(21)	5407 (6)	1919 (10)	5416 (3)
C(22)	4299 (6)	2083 (11)	5135 (4)
N(23)	5906 (6)	995 (9)	6042 (3)
O(24)	6834 (4)	756 (8)	6284 (3)
O(25)	5257 (6)	480 (10)	6302 (3)
S(26)	−1559 (2)	3806 (4)	4569 (1)
C(27)	−2223 (6)	4482 (9)	3810 (4)
N(28)	−2671 (6)	4927 (9)	3270 (4)
Rb⁺	22965 (6)	20914 (9)	27103 (3)

Table 3. Final parameters of hydrogen atoms, and their e.s.d.'s

Fractional coordinates are $\times 10^3$. Atom H(201) was fixed in an ideal planar position so that the C–H length was 1·0 Å.

	x	y	z	B (Å²)
H(31)	215 (7)	310 (10)	495 (4)	8 (2)
H(32)	201 (7)	122 (10)	442 (4)	8 (2)
H(41)	99 (5)	433 (8)	400 (3)	4 (1)
H(42)	52 (6)	274 (10)	419 (4)	7 (2)
H(61)	−56 (7)	405 (10)	287 (4)	8 (2)
H(62)	−94 (5)	236 (7)	324 (2)	4 (1)
H(71)	−137 (7)	182 (10)	202 (4)	8 (2)
H(72)	−70 (5)	21 (8)	246 (3)	4 (2)
H(91)	−67 (5)	409 (8)	155 (3)	4 (2)
H(92)	−111 (6)	225 (10)	105 (4)	6 (2)
H(101)	7 (6)	356 (10)	72 (4)	7 (2)
H(102)	59 (5)	200 (9)	99 (3)	5 (1)
H(121)	170 (5)	483 (8)	81 (3)	5 (2)
H(122)	247 (5)	310 (8)	122 (3)	5 (1)
H(131)	253 (5)	640 (9)	162 (3)	5 (2)
H(132)	334 (5)	568 (9)	135 (3)	5 (2)
H(151)	379 (7)	662 (10)	282 (4)	9 (3)
H(152)	487 (8)	593 (10)	245 (5)	10 (3)
H(161)	527 (4)	556 (7)	355 (3)	3 (1)
H(162)	502 (7)	389 (10)	311 (4)	9 (2)
H(191)	633 (10)	405 (10)	436 (6)	14 (4)
H(201)	691 (0)	239 (0)	535 (0)	10 (0)
H(221)	352 (4)	183 (6)	524 (2)	2 (1)

where $2\theta_M$ is the diffraction angle of the mono-chromator and 2θ is the diffraction angle of the reflexion. No correction for absorption was made.

Structure determination and refinement

The phase problem was solved by the heavy-atom method. The structure was refined by the least-squares method in a block-diagonal approximation (matrix 9 × 9 for the anisotropic and 4 × 4 for the isotropic temperature factor) by means of the *XTL-SYNTEX* system. The function minimized was $\Sigma\,w(|F_o| - |F_c|)^2$. The weighting scheme at the end of refinement was $w = w_1w_2$. It should be noted that $w_1 = 4I_o/\sigma_I^2$, where $\sigma_I^2 = \sigma_I^2(\text{counting}) + (kI_o)^2$ and the correction coefficient $k = 0.018$, $w_2 = \sin\theta/\lambda$ for $\sin\theta/\lambda \le 0.3$, and $w_2 = 1$ for $\sin\theta/\lambda > 0.3$. The reflexions with $I_o < 1.96\sigma_I$ were excluded from refinement.

The atomic scattering factors of all non-hydrogen atoms were taken from *International Tables for X-ray*

Crystallography (1974). The Rb atom was regarded as singly ionized. The scattering factors of the H atoms were taken as a spherical approximation of the bonded atom in the hydrogen molecule (Stewart, Davidson & Simpson, 1965).

At the beginning the H atoms were fixed in calculated positions and only their isotropic temperature factors were refined. Before each subsequent cycle their positions were recalculated and corrected. After four cycles of refinement, the shifts of all atoms were smaller than 0.002 Å. At this point all fixed parameters were released and the weighting scheme was adjusted for the last time. After another two cycles of refinement, the parameters of H(201) assumed unreal values, and the atom was therefore fixed again in the plane of the benzene ring at a distance of 1 Å from the C(20) atom. The refinement was ended when shifts of all parameters had dropped below 0.2 e.s.d.

In the last refinement cycle, $n = 351$ parameters were refined and all the $m = 1935$ reflexions observed were used. The final factors were:

$$R_1 = \Sigma\,(|F_o| - |F_c|)/\Sigma\,|F_o| = 0.056,$$

$$R_2 = [\Sigma(|F_o| - |F_c|)^2/\Sigma\,|F_o|^2]^{1/2} = 0.053,$$

$$S = [\Sigma\,w(|F_o| - |F_c|)^2/(m - n)]^{1/2} = 1.65.$$

On the resulting difference map the 0.8 e Å^{-3} maximum of the residual electron density was situated at a distance of 1.0 Å from S(26) perpendicular to the S(26)—C(27) bond; the 0.6 e Å^{-3} peak was at a distance of 1.1 Å from C(20) in a direction towards the benzene ring, the 0.5 e Å^{-3} peak lay at a distance of 1.2 Å from the Rb atom, and the 0.4 e Å^{-3} peaks were 1 Å from the O(2) and O(5) atoms such that the
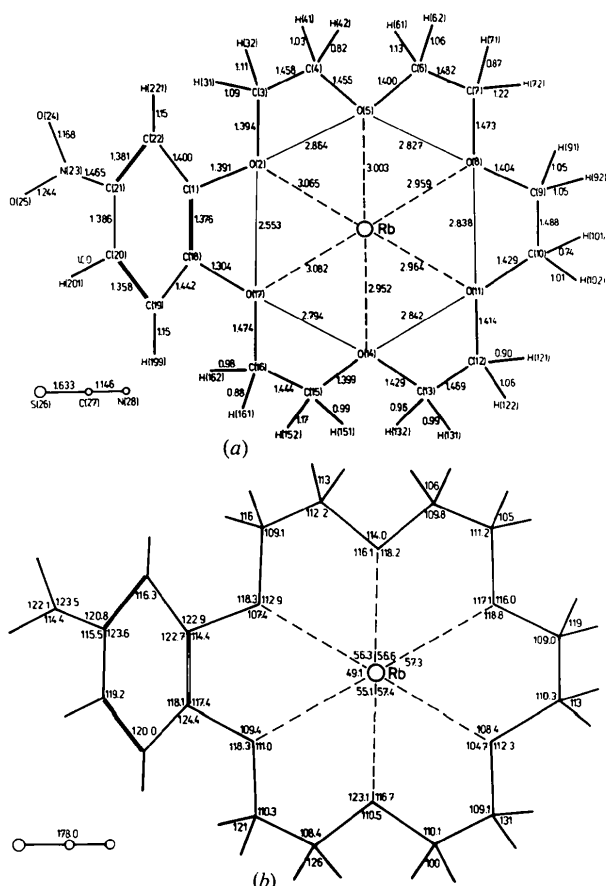

Fig. 1. Numbering scheme of the complex 4-nitrobenzo-18-crown-6.RbSCN showing (*a*) the bond lengths (Å) and (*b*) some valence angles (°) of non-hydrogen atoms. E.s.d.'s are in the range from 0.005 to 0.013 Å for bond lengths and from 0.4 to 0.7° for valence angles.
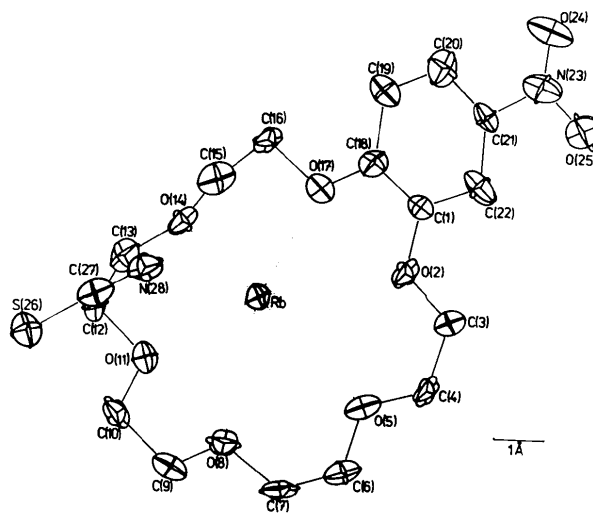

Fig. 2. Thermal motion ellipsoids of 30% probability of the complex 4-nitrobenzo-18-crown-6.RbSCN. Projection along the [0̄10] direction.

connecting line between each O atom and its corresponding maximum bisected the C—O—C angle.

The final positional parameters of all the atoms and H isotropic thermal parameters, with their estimated standard deviations, are given in Tables 2 and 3.*
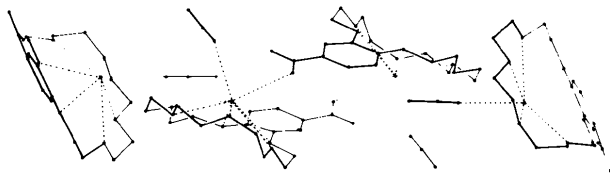
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* See deposition footnote on p. 417.

Fig. 3. Projection of 4-nitrobenzo-18-crown-6.RbSCN along the |522| direction. The molecules are in equivalent positions $1 - x, \frac{1}{2} + y, \frac{1}{2} - z$; x,y,z; $1 - x, -y, 1 - z$; $x, -\frac{1}{2} - y, \frac{1}{2} + z$, respectively.
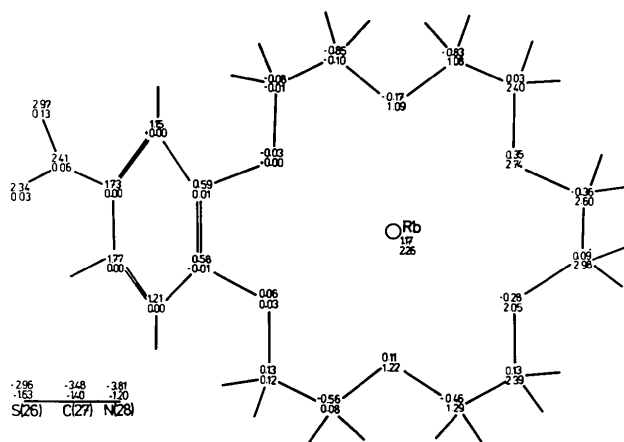

Fig. 4. Diagram of the complex 4-nitrobenzo-18-crown-6.RbSCN showing deviations of the atoms (Å) from: (i) weighted mean plane through the benzene ring (first row), (ii) weighted mean plane through the oxygen atoms of the 18-membered ring (second row).

Structure description and discussion

The numbering scheme with the bond distances, the $O \cdots O$ and $Rb \cdots O$ distances and selected valency angles is shown in Fig. 1. The e.s.d. of the $Rb \cdots O$ distances is 0·005 Å, that of the distances between adjacent O atoms in the macrocycle is 0·008 Å, and the e.s.d.'s of the bond distances proper lie within the range 0·010–0·013 Å. The e.s.d.'s of the interbond angles vary between 0·4 and 0·7°.

Fig. 2 shows the thermal ellipsoids of 30% probability of the non-hydrogen atoms. The projection of the crystal structure along the |522| direction is seen in Fig. 3.

Coordination of the Rb^+ cation and the position of the anion

The Rb^+ cation is bonded in the molecule by ionic interaction with the SCN group and further by the ion–dipole interaction with six O atoms of the 18-membered ring. With respect to the Rb^+ cation the nitro group of the molecule related by a centre of symmetry is situated so that the distance, 3·81 Å, between $Rb^+ \cdots O(25^i)$ is much larger than the distance $Rb^+ \cdots O(24^i)$, 3·09 Å (Fig. 3). The short distance between $Rb^+ \cdots O(24^i)$ indicates that the dipole moment induced on the nitro group interacts with the cation. Other intermolecular contacts shorter than the sum of the van der Waals radii were not observed.

The O atoms in the 18-membered ring exhibit deviations of up to 0·35 Å from their mean plane (Fig. 4). If only the atoms O(2), O(5), O(11), O(14), O(17) are tested for planarity, the maximum deviation from the mean plane is 0·1 Å.

The atoms S(26), C(27), N(28) lie approximately on a straight line (Fig. 1). The angle $Rb^+ \cdots N(28)—C(27)$ is 138·5 (7)°.

Table 4. *Some weighted mean planes through* 1,4-*nitrobenzo*-18-*crown*-6.RbSCN

Equations of the planes are related to an orthonormal system of coordinates, where x is along **a**, y is along **b**, z is along **c***.

Plane	Atoms defining the plane and some deviations in Å	χ^2	Equation of the plane
a	NO$_2$	0·0	$0·0823x - 0·8468y - 0·5256z + 6·7050 = 0$
b	Benzene group (deviations are in Fig. 4)	2·7	$0·1322x - 0·8582y - 0·4961z + 6·2538 = 0$
c	C(1) O(2) C(3) C(18) O(17) C(16) 0·02 −0·01 0·01 −0·02 −0·01 0·04	44·9	$0·1290x - 0·8715y - 0·4731z + 6·0976 = 0$
d	O(2) O(5) O(8) O(11) O(14) O(17) (deviations are in Fig. 4)	7493·0	$0·3974x - 0·9145y - 0·0753z + 2·7310 = 0$
e	O(2) O(5) O(11) O(14) O(17) −0·03 0·06 −0·07 0·10 −0·05	746·8	$0·3342x - 0·9353y - 0·1166z + 3·1655 = 0$
f	Rb$^+$ S(26) C(27) N(28) 0·000 0·000 −0·007 0·003	0·87	$−0·3415x - 0·9043y - 0·2562z + 3·2720 = 0$

Acute angles between selected planes: a–b 3·4, b–c 1·5, c–d 27·9, b–d 29·0, b–f 30·9, e–f 44·7°.

Conformation of the macro-ring

Similarity to 4-nitrobenzo-18-crown-6.CsSCN (Hašek, Hlavatá & Huml, 1977), the Rb^+ atom lies at the top of an irregular hexagonal pyramid, the base of which consists of O atoms. The mean distance of Rb from the O atoms of the macro-ring is 3·00 Å [compare with 3·02 Å for 18-crown-6.RbSCN (Dobler & Phizackerley, 1974)]. The Rb atom is situated at 1·17 Å from the weighted mean plane through six O atoms of the macro-ring [compare with 1·19 Å (Dunitz et al., 1974)]. The distances between adjacent O atoms in the macro-ring vary between 2·79–2·86 Å (mean 2·833 Å), with the exception of 2·55 Å for O(2)—O(17). This short distance and the diminished angles C(18)—C(1)—O(2), 114·4°, and O(17)—C(18)—C(1), 117·4° (Fig. 1), can also be observed in the complex dibenzo-18-crown-6.RbSCN (Bright & Truter, 1970) and in the complex 4-nitrobenzo-18-crown-6.CsSCN (Hašek, Hlavatá & Huml, 1977).

Atoms in groups of C—C—O—C—C type in the macro-ring lie approximately in a plane. Similarly to the complex nitrobenzo-18-crown.CsSCN, one group has considerably larger deviations from the mean plane than the others. In the case of the Rb^+ cation this group is formed by atoms C(6), C(7), O(8), C(9), C(10); deviations of the atoms from their mean planes are 0·43 Å for C(7) and 0·52 Å for C(9).

Nitrobenzene substituent

The whole nitrobenzene group and the atoms O(2), C(3), O(17), C(16) lie, with a maximum deviation of 0·1 Å, in one plane. Deviations from the weighted mean plane through the benzene ring are given in Fig. 4.

Angles between the planes through the nitro group, benzene ring, C(1), O(2), C(3), C(18), O(17), C(16) group and six O atoms of the macro-ring are given in Table 4. Similarly to the case when Cs is the cation, the plane of the nitro group is rotated from the plane of the benzene ring by 3·4° towards the cation.

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The Crystal Structure of (+)589-fac-Tris(meso-2,4-pentanediamine)cobalt(III) Hexacyanocobaltate(III) Pentahydrate

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Crystals of the title compound are orthorhombic, space group $P2_12_12_1$, with $a = 17·953$ (2), $b = 18·382$ (2), $c = 10·161$ (2) Å and $Z = 4$. The structure has been refined to a residual of 0·042 with 4282 independent significant reflexions collected by diffractometry. The complex ion has approximate threefold symmetry. The six-membered chelate rings adopt the chair conformation with both C—CH_3 bonds in equatorial positions. The absolute configuration of the complex ion can be designated as Λ.

Introduction

The mer and fac isomers of $[Co(meso\text{-}ptn)_3]^{3+}$ have recently been separated and resolved by column chromatography on SP-Sephadex (Kojima & Fujita, 1976). Crystals of $(+)_{589}\text{-}[Co(meso\text{-}ptn)_3][Co(CN)_6].5H_2O$ were subjected to X-ray structure analysis in order to reveal the conformational details of