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The Crystal and Molecular Structure of the Complex Formed by Rubidium Thiocyanate and Benzo-1,4,7,10,13,16-hexaoxacyclooctadecane (Benzo-18-crown-6)

BY J. HAŠEK AND K. HUML

Institute of Macromolecular Chemistry, Czechoslovak Academy of Sciences, 162 06 Praha 6, Czechoslovakia

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The crystal and molecular structure of the title compound (benzo-18-crown-6.RbSCN) has been determined from 1844 observed three-dimensional data measured by a single-crystal automated Syntex $P2_1$ diffractometer. The unit cell is monoclinic with $a = 11{\cdot}351\ (4)$, $b = 9{\cdot}050\ (3)$, $c = 22{\cdot}950\ (7)$ Å, $\beta = 119{\cdot}03\ (2)°$, $V = 2061\ (1)$ Å^3 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 0·049.

Introduction

In earlier papers (Hašek, Hlavatá & Huml, 1977; Hlavatá, Hašek & Huml, 1978) we discussed the crystal and molecular structures of complexes of 4-nitrobenzo-1,4,7,10,13,16-hexaoxacyclooctadecane with CsSCN and RbSCN. It was found that the nitrobenzene group participated in the interaction with the cation, thus importantly affecting the selectivity of these compounds towards various cations.

In order to find out how the geometrical order of the complex changes in space without the interaction between the nitro group and the cation, an attempt was made to determine the crystal and molecular structure of the title compound, also referred to in the literature as benzo-18-crown-6.RbSCN.

Experimental

The title compound was prepared by Petránek & Ryba (1974). The molecular formula was confirmed by elemental analysis. The crystals were small, irregular and white. The crystal used for the investigation was ground to a sphere with a diameter $d = 0{\cdot}25$ mm.

Crystal data

Monoclinic, $P2_1/c$, $a = 11{\cdot}351\ (4)$, $b = 9{\cdot}050\ (3)$, $c = 22{\cdot}950\ (7)$ Å, $\beta = 119{\cdot}03\ (2)°$, $V = 2061\ (1)$ Å^3, $C_{17}H_{24}O_6NSRb$, FW 455·8, μ(Mo $K\alpha$) = 26·3 cm^{-1}, $D_m = 1{\cdot}45$, $D_x = 1{\cdot}47$ g cm^{-3}, $Z = 4$, $F(000) = 936$, m.p. 144–145 °C.

The preliminary dimensions of the elementary cell and systematic absences ($h0l$: $l = 2n + 1$; $0k0$: $k = 2n + 1$) were determined from oscillation and Weissenberg photographs. The final parameters were obtained by refining 15 reflexions measured with an automatic Syntex $P2_1$ diffractometer [λ(Mo $K\alpha$) = 0·71069 Å], and a graphite monochromator at room temperature. The density was measured by the flotation method in a heptane–CCl_4 solution.

Intensity measurements

The intensities were measured with the same diffractometer by the ω–2θ method. The minimum scan rate was 1° min^{-1}. The other measurement data are the same as in Hašek, Hlavatá & Huml (1977). During the measurement (45 kV, 20 mA, 240 h) there was no significant reduction of the diffracted intensities. The measurements were performed up to $\sin\theta_{max}/\lambda = 0{\cdot}5499$ Å^{-1}; 2911 independent reflexions were determined, 1844 of which were taken as observed.*

A reflexion was taken as unobserved if $I_o < 1{\cdot}96\sigma_I$, where σ_I was calculated from the counting statistics. The reflexions were corrected for the Lorentz–polarization factor, as in Hašek, Hlavatá & Huml (1977). No corrections for extinction or absorption were made ($\mu r = 0{\cdot}33$).

Structure determination and refinement

The phase problem was solved by the heavy-atom method. The positions of Rb and S were determined from the Patterson map sharpened with the Lp factor. The positions of all nonhydrogen atoms were determined only after two subsequent successive Fourier maps.

* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 33088 (31 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

The structure was refined by the least-squares method in the block-diagonal approximation by means of the program *BLOCK* from the *XTL* system of the Syntex Co. (release II); the function minimized was $\Sigma w(|F_o| - |F_c|)^2$. The atom form factors were taken from *International Tables for X-ray Crystallography* (1974). The Rb atom was considered as singly ionized. Correction for anomalous scattering was included for nonhydrogen atoms. The atomic scattering factors of H atoms were taken as a spherical approximation of the atom in the H molecule (Stewart, Davidson & Simpson, 1965). Unobserved reflexions were excluded from refinement. All nonhydrogen atoms were refined anisotropically, H atoms isotropically.

The weighting scheme at the end of the refinement was $w = 1/[\sigma_F^2 + (0{\cdot}022F_o)^2]$. The coefficient in this weighting scheme during the refinement was chosen to ensure reasonable constancy of $w(\Delta F)^2$ with respect to $|F_o|$ and sin θ.

The refinement was finished when shifts of all atomic parameters had dropped below 0·35 e.s.d.'s. The coefficients describing the agreement of the refined model with the experimental are: $R_1 = \Sigma(|F_o| - |F_c|)/\Sigma|F_o| = 0{\cdot}049$, $R_2 = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{1/2} = 0{\cdot}047$, and $S = [\Sigma w(|F_o| - |F_c|)^2/(m-n)]^{1/2} = 1{\cdot}30$, where $n = 331$ parameters were refined, and all $m = 1844$ observed reflexions were used. The final difference map did not contain maxima higher than 0·4 e Å^{-3}.

Table 1. *Final positional parameters* (×10⁴) *and e.s.d.'s of the nonhydrogen atoms*

	x	*y*	*z*
C(1)	5486 (6)	1067 (6)	848 (3)
O(2)	4521 (4)	129 (4)	825 (2)
C(3)	4806 (7)	−1418 (7)	918 (4)
C(4)	5175 (8)	−1880 (8)	1598 (4)
O(5)	4038 (5)	−1806 (5)	1686 (2)
C(6)	4246 (10)	−2310 (9)	2341 (4)
C(7)	2964 (11)	−2049 (12)	2348 (4)
O(8)	2728 (5)	−561 (7)	2360 (2)
C(9)	1433 (9)	−219 (12)	2359 (3)
C(10)	1295 (8)	1319 (13)	2379 (4)
O(11)	1194 (4)	2010 (7)	1814 (2)
C(12)	1025 (7)	3581 (11)	1213 (4)
C(13)	984 (7)	4177 (9)	1214 (4)
O(14)	2259 (4)	3973 (5)	1255 (2)
C(15)	2303 (7)	4580 (7)	688 (3)
C(16)	3665 (6)	4436 (7)	774 (3)
O(17)	3965 (4)	2891 (4)	788 (2)
C(18)	5164 (5)	2552 (6)	805 (3)
C(19)	6049 (6)	3564 (7)	793 (3)
C(20)	7234 (6)	3153 (9)	833 (3)
C(21)	7561 (6)	1729 (9)	879 (4)
C(22)	6691 (7)	672 (8)	885 (4)
S(23)	1572 (2)	2052 (2)	3950 (1)
C(24)	797 (7)	2908 (7)	4286 (3)
N(25)	221 (6)	3466 (7)	4521 (3)
Rb$^+$	2113 (1)	632 (1)	959 (0)

The resulting positional parameters of all nonhydrogen atoms are given in Table 1. The parameters of the H atoms are given in Table 2.

Description and discussion of structure

The numbering scheme, bond distances, and O···O and O···Rb distances are given in Fig. 1. E.s.d.'s of the bond distances involving nonhydrogen atoms vary between 0·004 and 0·010 Å, and those involving H between 0·04 and 0·08 Å. E.s.d.'s of the O···O and Rb···O distances are 0·005 Å in all cases.

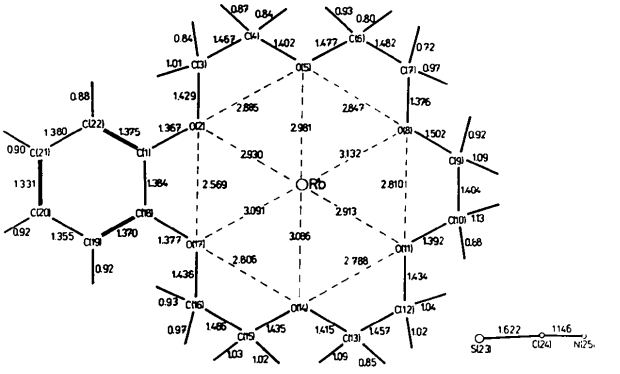

Fig. 1. The numbering scheme of the complex of benzo-1,4,7,10,13,16-hexaoxacyclooctadecane with RbSCN with interatomic distances (Å). E.s.d.'s of the distances between the nonhydrogen atoms are 0·004 to 0·010 Å; e.s.d.'s of bonds involving H atoms are 0·04 to 0·08 Å.

Table 2. *Final positional* (×10³) *and isotropic thermal parameters and e.s.d.'s of the hydrogen atoms*

	x	*y*	*z*	*B* (Å²)
H(31)	538 (5)	−171 (6)	71 (2)	6 (1)
H(32)	409 (5)	−186 (6)	66 (2)	6 (1)
H(41)	585 (6)	−132 (7)	186 (3)	10 (2)
H(42)	550 (5)	−272 (6)	173 (2)	7 (2)
H(61)	494 (5)	−167 (6)	261 (3)	7 (1)
H(62)	445 (8)	−315 (10)	245 (4)	17 (3)
H(71)	301 (7)	−236 (8)	265 (3)	13 (2)
H(72)	214 (5)	−238 (6)	197 (3)	8 (2)
H(91)	152 (7)	−79 (8)	271 (3)	12 (2)
H(92)	79 (5)	−96 (6)	195 (3)	7 (1)
H(101)	207 (7)	208 (8)	277 (3)	12 (2)
H(102)	58 (5)	162 (5)	240 (2)	6 (1)
H(121)	186 (7)	410 (8)	219 (3)	12 (2)
H(122)	13 (6)	382 (7)	180 (3)	10 (2)
H(131)	88 (9)	511 (10)	121 (4)	17 (3)
H(132)	22 (4)	367 (5)	75 (2)	5 (1)
H(151)	208 (4)	567 (5)	68 (2)	4 (1)
H(152)	162 (5)	395 (6)	30 (3)	7 (2)
H(161)	429 (5)	486 (5)	120 (2)	5 (1)
H(162)	369 (5)	487 (6)	41 (3)	7 (1)
H(191)	580 (4)	454 (4)	75 (2)	3 (1)
H(201)	777 (5)	383 (6)	77 (2)	6 (1)
H(211)	823 (6)	132 (7)	83 (3)	11 (2)
H(221)	678 (4)	−29 (5)	87 (2)	4 (1)

Selected interatomic angles and angles of the type Rb···O–C and O···Rb···O are given in Fig. 2. E.s.d.'s of the interatomic angles involving non-hydrogen atoms are 0·5 to 0·9°, for angles of the type H–C–H they are 3 to 8°, and for angles of the type C–C–H 3° in all cases. The angles of the type O···Rb···O have e.s.d.'s of 0·1°, while those of the type C–O···Rb have e.s.d.'s of 0·3–0·5°.

The geometrical ordering of the complex of benzo-1,4,7,10,13,16-hexaoxacyclooctadecane with RbSCN is shown in Fig. 3. The formation is centrosymmetric. Each cation in this dimer is bound by the ion–dipole interaction with six O atoms in the macro-ring [Rb···O (mean) is 3·02 Å] and by two interactions with anions (Rb···N, Rb···N^{i} being 3·04 and 3·05 Å). The distance between the weighted mean planes drawn through the O atoms of the macro-rings of the centrosymmetric dimer is 7·27 Å. The distance of the cation from the weighted mean plane drawn through the O atoms of the nearer macro-ring is 1·24 Å. The O···O distances roughly correspond to the sum of the van der Waals O radii, with the exception of the shorter distance O(2)···O(17), 2·569 (5) Å. The departures of the O atoms from their weighted mean plane are highly significant (Table 3). The dihedral angle between the mean planes drawn through O(2), O(5), O(8), O(11) and O(11), O(14), O(17), O(2) is 20°.

Table 3. *Some weighted mean planes in the complex of benzo*-1,4,7,10,13,16-*hexaoxacyclooctadecane with* RbSCN

Plane	Atoms defining mean plane	χ^2	Maximum deviation
a	O(2),O(5),O(8),O(11),O(14),O(17)	16475	0·387 Å
b	Benzene ring	2	0·005
c	C(1),O(2),C(3),C(16),O(17),C(18)	208	0·086
d	C(18),C(1),O(2),C(3),C(4)	9440	0·490
e	C(3),C(4),O(5),C(6),C(7)	42	0·033
f	C(6),C(7),O(8),C(9),C(10)	2	0·006
g	C(9),C(10),C(11),C(12),C(13)	10	0·020
h	C(12),C(13),O(14),C15),C(16)	97	0·043
i	C(15),C(16),O(17),C(18),C(1)	156	0·047

Selected angles (°) between planes

$a \wedge b$ 33·9, $a \wedge c$ 33·5, $b \wedge c$ 1·6, $d \wedge e$ 73·8, $e \wedge f$ 71·3, $f \wedge g$ 61·6, $g \wedge h$ 68·6, $h \wedge i$ 62·4, $i \wedge d$ 70·0

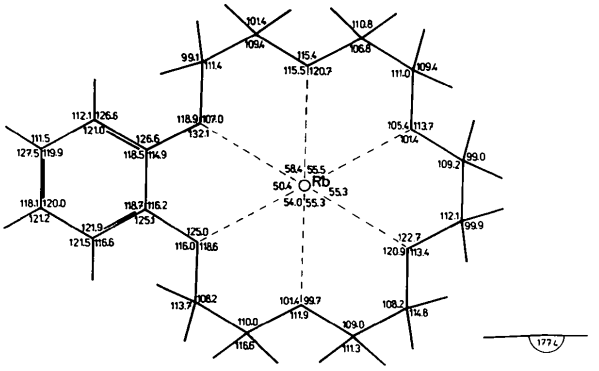

Fig. 2. The complex benzo-1,4,7,10,13,16-hexaoxacyclooctadecane.RbSCN showing some valence angles (°). E.s.d.'s of angles not involving H atoms are 0·1 to 0·9°. E.s.d.'s of angles of the type H–C–H and C–C–H are 3 to 8°.

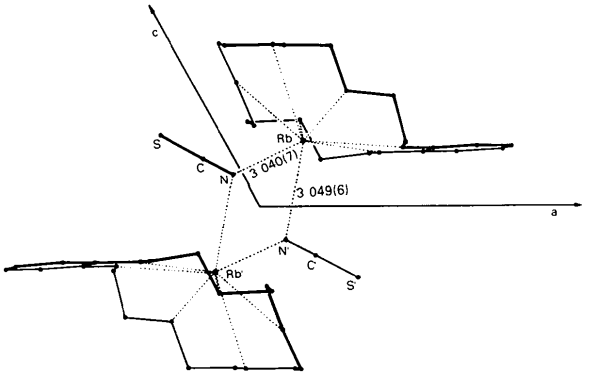

Fig. 3. Centrosymmetric dimer of the complex benzo-1,4,7,10,13,16-hexaoxacyclooctadecane.RbSCN (projection along the [010] direction). Interactions between the cation and O atoms of the macro-ring, and between the cation and anion are denoted with dotted lines.

Atoms in the groups of the type C–C–O–C–C lie approximately in the plane (Table 3), but, similarly to the complexes of 4-nitrobenzo-18-crown-6 with CsSCN (Hašek, Hlavatá & Huml, 1977) and RbSCN (Hlavatá, Hašek & Huml, 1978), one group exhibits much larger deviations from the mean plane than the others.

Except for interactions inside the dimer described above, no further intermolecular contacts shorter than the sum of the van der Waals radii were found.

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