

Complex of Potassium Thiocyanate and Dibenzo[*b,q*][1,4,7,10,13,16,19,22,25,28]decaoxacyclotriacontane (Dibenzo-30-crown-10)

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Abstract

$C_{28}H_{40}KO_{10}^+SCN^-$ is monoclinic, *Cc*, with $a = 18.749$ (3), $b = 9.808$ (2), $c = 17.681$ (4) Å, $\beta = 98.64$ (2)°, $V = 3214$ (1) Å³, $Z = 4$, $D_c = 1.31$, $D_m = 1.29$ (2) Mg m⁻³ (floatation in heptane-CCl₄ solution), $M_r = 633.8$, m.p. = 411–412 K, $F(000) = 1344$, $\mu(\text{Mo } K\alpha) = 0.294$ mm⁻¹. The structure has been determined by direct methods and refined to $R = 0.030$ for 1625 observed reflexions. Conformations of three complexes of this thirty-membered polyether and the uncomplexed molecule are compared.

Introduction

Complexes of macrocyclic polyethers have become of interest because of their high selectivity towards alkali-metal cations, especially K⁺. The structure determination of the title compound supplements a study of the series of complexes containing dibenzo[*b,q*][1,4,7,10,13,16,19,22,25,28]decaoxacyclotriacontane (dibenzo-30-crown-10) (Bush & Truter, 1972; Hašek, Huml & Hlavatá 1979).

Colourless, transparent, rod-like crystals were prepared by Petránek & Ryba (1974). The molecular formula was confirmed by elemental analysis. All measurements were performed at room temperature.

Systematic absences (for hkl : $h + k = 2n + 1$ and for $h0l$: $l = 2n + 1$) were determined from Weissenberg photographs and confirmed by the ψ scan on a Syntex P2₁ diffractometer. The unit-cell parameters (15 reflexions refined) and intensities were measured with the same four-circle diffractometer [$\lambda(\text{Mo } K\alpha) = 0.71069$ Å, graphite monochromator in the equatorial arrangement, $\theta-2\theta$ scan]. A crystal was ground to a sphere of diameter 0.4 mm and placed on the goniometric head in a general position. 2889 independent reflexions were measured up to $\sin \theta/\lambda = 0.60$ Å⁻¹, of which 1625 with $I > 4\sigma(I)$ were regarded as observed [$\sigma(I)$ was calculated from counting statistics]. No pronounced decrease in the intensities of the reference reflexions was observed. For the Lp

correction formula and other measurement details see Hašek, Hlavatá & Huml (1977).

The phase problem was solved by *MULTAN* 74 (Main, Woolfson, Lessinger, Germain & Declercq, 1974). Without introducing preliminary information about the structure this method failed. Introducing the benzene rings and three atomic groups at unknown positions and random orientation was not successful either. The correct solution, giving the positions of almost all the non-H atoms, was obtained when the geometry of the macrocycle, approximately known from the complex of dibenzo-30-crown-10 and KI (Bush & Truter, 1972), was used as a structure fragment in a random orientation and position.

The structure was refined by the block-diagonal least-squares method with a modified version of the *NRC-10* program (Ahmed, Hall, Pippy & Huber, 1966), where 9×9 blocks were used for non-H and 4×4 blocks for H atoms. The function minimized was $\sum w\Delta^2$, where $\Delta = |F_o| - |F_c|$, $1/w = \sigma_F^2 + (0.02F_o)^2$ and σ_F^2 was determined from counting statistics. Scattering factors for the non-H atoms were taken from *International Tables for X-ray Crystallography* (1962) and for the H atoms they were taken as a spherical approximation of the bonded atom in the hydrogen molecule (Stewart, Davidson & Simpson, 1965).

The refinement was performed until all shifts dropped below 0.3 of their e.s.d.'s. This led to $R_1 = \sum |\Delta|/\sum |F_o| = 0.029$, $R_2 = [\sum \Delta^2/\sum |F_o|^2]^{1/2} = 0.028$, $RW_2 = [\sum w\Delta^2/\sum w|F_o|^2]^{1/2} = 0.035$ and $S = [\sum w\Delta^2/(m - n)]^{1/2} = 1.36$, where $n = 539$ refined parameters and $m = 1625$ reflexions. On the last difference map no maximum higher than $0.2 \text{ e } \text{Å}^{-3}$ was observed.

Final positional and B_{eq} thermal parameters (Hamilton, 1959) of the non-H atoms are given in Table 1; coordinates and B_{iso} thermal parameters of the H atoms are in Table 2.*

* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 35221 (32 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. *Final coordinates of the non-hydrogen atoms ($\times 10^4$) and their e.s.d.'s and B_{eq} (\AA^2)*

	<i>x</i>	<i>y</i>	<i>z</i>	B_{eq}		<i>x</i>	<i>y</i>	<i>z</i>	B_{eq}
O(1)	7923 (1)	3430 (3)	1971 (2)	4.3	C(22)	6486 (3)	3110 (5)	520 (3)	6.0
C(2)	8161 (3)	2882 (5)	2730 (3)	5.6	O(23)	6610 (2)	4470 (3)	432 (2)	5.9
C(3)	7599 (3)	3131 (6)	3189 (3)	6.5	C(24)	6078 (4)	5274 (8)	-114 (3)	8.9
O(4)	7411 (2)	4553 (3)	3300 (2)	5.1	C(25)	6331 (4)	6578 (8)	-226 (4)	8.9
C(5)	7935 (3)	5173 (6)	3792 (3)	6.6	O(26)	6356 (2)	7380 (4)	520 (2)	6.1
C(6)	7675 (3)	6640 (6)	3892 (3)	6.3	C(27)	6634 (3)	8720 (5)	536 (3)	6.9
O(7)	7695 (2)	7306 (3)	3236 (2)	5.9	C(28)	7443 (3)	8740 (6)	574 (4)	7.1
C(8)	7450 (4)	8654 (7)	3296 (4)	8.1	O(29)	7687 (2)	8201 (4)	1295 (2)	5.8
C(9)	6673 (4)	8778 (7)	3151 (4)	9.1	C(30)	8475 (3)	8042 (7)	1433 (4)	7.8
O(10)	6356 (2)	8164 (4)	2432 (2)	6.8	C(31)	8701 (3)	6931 (6)	1136 (4)	7.8
C(11)	5599 (3)	8025 (5)	2287 (3)	7.2	O(32)	8455 (2)	5638 (3)	1373 (2)	5.2
C(12)	5307 (3)	6759 (5)	2701 (3)	5.3	C(33)	8689 (2)	4392 (5)	1162 (3)	4.9
O(13)	5586 (2)	5623 (3)	2292 (2)	5.1	C(34)	9141 (3)	4215 (6)	629 (3)	5.8
C(14)	5357 (2)	4414 (5)	2570 (2)	4.5	C(35)	9339 (4)	3032 (9)	447 (3)	9.4
C(15)	4864 (2)	4255 (7)	3096 (3)	7.0	C(36)	9086 (3)	1716 (6)	745 (3)	7.0
C(16)	4682 (3)	2864 (6)	3301 (3)	6.0	C(37)	8624 (3)	2038 (6)	1254 (4)	7.7
C(17)	4971 (4)	1936 (8)	2999 (4)	10.1	C(38)	8409 (3)	3276 (5)	1440 (3)	5.1
C(18)	5450 (3)	1940 (5)	2466 (3)	6.2	K(39)	7014 (2)	5859 (1)	1858 (2)	4.3
C(19)	5616 (2)	3228 (5)	2220 (3)	4.4	S(40)	4100 (1)	6356 (3)	4454 (1)	11.3
O(20)	6094 (2)	3436 (4)	1738 (2)	5.8	C(41)	4602 (6)	7687 (16)	4327 (7)	6.6
C(21)	5883 (4)	2867 (6)	1011 (3)	7.2	N(42)	4934 (2)	8758 (3)	4254 (2)	3.8

Table 2. *Fractional coordinates of the hydrogen atoms ($\times 10^3$), and their e.s.d.'s and B_{iso} (\AA^2)*

	<i>x</i>	<i>y</i>	<i>z</i>	B_{iso}		<i>x</i>	<i>y</i>	<i>z</i>	B_{iso}
H(21)	858 (3)	345 (5)	291 (3)	7.5 (1.2)	H(241)	560 (3)	540 (6)	18 (3)	9.9 (1.6)
H(22)	818 (3)	182 (5)	267 (3)	7.7 (1.3)	H(242)	601 (3)	485 (7)	-56 (3)	11.4 (1.7)
H(31)	776 (2)	278 (5)	373 (2)	6.6 (1.1)	H(251)	694 (3)	651 (6)	-36 (4)	11.2 (1.7)
H(32)	716 (2)	264 (5)	301 (3)	7.7 (1.2)	H(252)	611 (3)	704 (6)	-59 (3)	10.4 (1.6)
H(51)	796 (3)	472 (5)	423 (3)	8.2 (1.3)	H(271)	654 (3)	928 (5)	101 (3)	8.9 (1.4)
H(52)	838 (3)	508 (5)	360 (3)	7.9 (1.2)	H(272)	640 (3)	912 (5)	6 (3)	8.3 (1.4)
H(61)	805 (3)	711 (5)	422 (3)	7.8 (1.3)	H(281)	765 (3)	959 (5)	49 (3)	7.4 (1.3)
H(62)	727 (3)	670 (5)	399 (3)	9.5 (1.5)	H(282)	765 (3)	822 (5)	17 (3)	9.0 (1.4)
H(81)	765 (3)	907 (6)	376 (3)	9.4 (1.5)	H(301)	860 (3)	807 (6)	195 (3)	9.4 (1.5)
H(82)	757 (3)	913 (5)	287 (3)	8.4 (1.4)	H(302)	872 (3)	879 (5)	117 (3)	8.0 (1.3)
H(91)	644 (3)	826 (7)	346 (4)	11.6 (1.8)	H(311)	921 (3)	699 (5)	126 (3)	9.3 (1.5)
H(92)	658 (3)	981 (6)	303 (3)	9.3 (1.5)	H(312)	860 (3)	687 (6)	51 (3)	9.6 (1.5)
H(111)	536 (3)	888 (5)	239 (3)	9.0 (1.5)	H(151)	473 (2)	495 (5)	332 (3)	7.5 (1.2)
H(112)	548 (2)	791 (5)	170 (3)	7.6 (1.3)	H(161)	437 (3)	269 (5)	359 (3)	7.5 (1.2)
H(121)	551 (2)	667 (5)	325 (2)	6.5 (1.2)	H(171)	492 (4)	110 (7)	321 (4)	11.4 (1.8)
H(122)	479 (2)	671 (4)	262 (3)	6.7 (1.1)	H(181)	568 (3)	116 (5)	233 (3)	8.4 (1.4)
H(211)	575 (3)	189 (5)	109 (3)	8.9 (1.4)	H(341)	933 (2)	518 (4)	50 (2)	5.2 (1.0)
H(212)	539 (3)	322 (6)	79 (3)	10.0 (1.6)	H(351)	965 (3)	301 (6)	4 (3)	9.4 (1.6)
H(221)	701 (2)	268 (5)	82 (2)	6.9 (1.2)	H(361)	924 (3)	76 (6)	67 (3)	9.4 (1.5)
H(222)	633 (2)	270 (5)	6 (2)	6.1 (1.1)	H(371)	851 (3)	123 (5)	155 (3)	8.7 (1.4)

The numbering scheme and important interatomic distances and angles are shown in Fig. 1. The polyether ring is wrapped round the cation in a similar fashion to that in dibenzo-30-crown-10.RbSCN.H₂O (Hašek, Huml & Hlavatá, 1979) and dibenzo-30-crown-10.KI (Bush & Truter, 1972). The SCN⁻ anion is, as in other alkali-metal complexes of dibenzo-30-crown-10, completely separated from the cation.

The K...O distances range from 2.83 to 2.96 Å, mean 2.90 Å, which corresponds to the sum of the ionic radius of K⁺ for coordination number 10 (1.55 Å, Shannon & Prewitt, 1969) and the van der Waals

radius of O (1.40 Å). A similar value, 2.88 (5) Å, was found in dibenzo-30-crown-10.KI (Bush & Truter, 1972). Mean O—O distances, except O(1)...O(32) and O(13)...O(20) [2.84 (5)], and C(sp³)—O [1.42 (6)] and C(sp³)—C(sp³)[1.47 (9) Å], are very close to those in dibenzo-30-crown-10.RbSCN.H₂O (Hašek, Huml & Hlavatá, 1979). Average C—C distances of 1.39 (9) and 1.37 (8) Å for the two benzene rings are close to the normal value of 1.395 Å, but two unrealistic bonds were found in each of the benzene rings: C(15)—C(16), C(16)—C(17), C(34)—C(35) and C(35)—C(36).

Table 3. Some weighted least-squares planes, with deviations of atoms (Å) from them, and dihedral angles (°)

E.s.d.'s of angles are less than 0.5°.

Plane	Deviations of the atoms defining the plane						χ^2	Deviations of other atoms			
<i>a</i>	C(14)	C(15)	C(16)	C(17)	C(18)	C(19)	159	C(12)	O(13)	O(20)	C(21)
	-0.03 (0)	0.01 (0)	0.01 (0)	-0.02 (1)	-0.03 (1)	0.03 (0)		-0.11 (0)	-0.01 (0)	-0.04 (0)	1.04 (1)
<i>b</i>	C(33)	C(34)	C(35)	C(36)	C(37)	C(38)	77	C(31)	O(32)	O(1)	C(2)
	-0.02 (0)	0.02 (1)	0.00 (1)	-0.01 (1)	-0.01 (1)	0.02 (0)		-0.05 (1)	0.01 (0)	0.02 (0)	-1.12 (0)
<i>c</i>	O(1)	O(4)	O(7)	O(32)			125				
	0.02 (0)	-0.02 (0)	0.02 (0)	-0.01 (0)							
<i>d</i>	O(13)	O(20)	O(23)	O(26)			370				
	0.02 (0)	-0.04 (0)	0.03 (0)	-0.03 (0)							

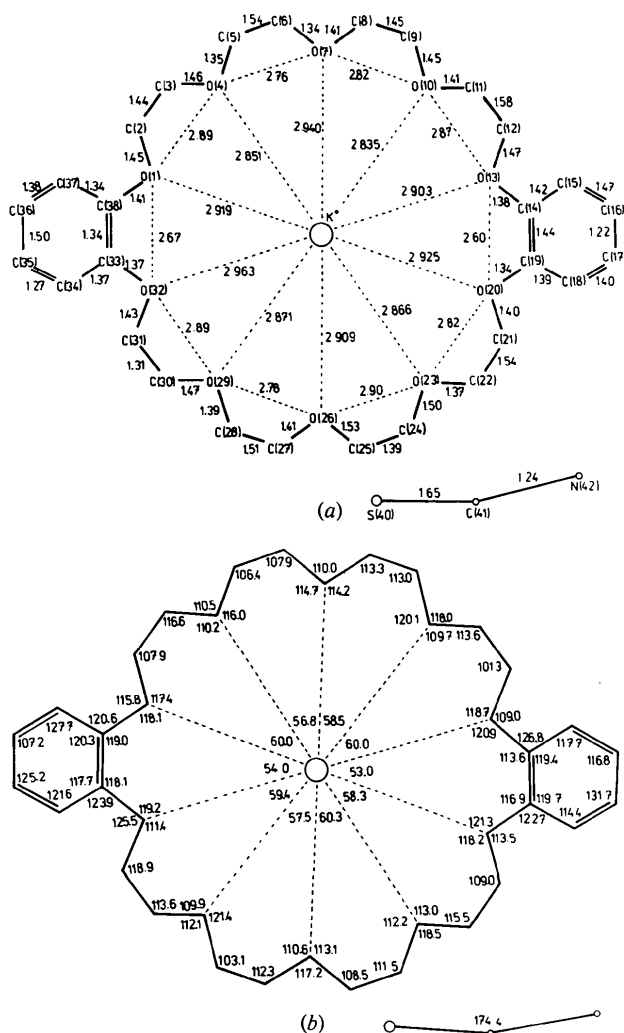
Angles between planes: *a*-*b* 1.3, *a*-*d* 15.0, *b*-*c* 17.5, *c*-*d* 16.8°.

Fig. 1. The numbering scheme of dibenzo-30-crown-10.KSCN showing (a) bond lengths (Å) and (b) angles (°) involving the non-H atoms. E.s.d.'s: K...O distances, 0.004 Å; distances between the adjacent O atoms in the polyether, 0.004 Å; bond distances in the macroring, 0.005-0.011 Å; K...O-C angles, 0.3°; interbond angles in the macroring, 0.3-0.7°; distances in the SCN group, 0.014 Å; the SCN angle, 1.1°.

Two attempts were made to improve these distances: (1) by including 400 additional reflexions with $2\sigma(I) < I < 4\sigma(I)$ in the refinement, and (2) by performing several cycles of least squares, starting with benzene atoms in ideal positions. In both cases we obtained the original unrealistic distances. Because comparison of F_o and F_c^* does not reveal significant systematic errors, we cannot give any explanation for these discrepancies.

Some weighted mean planes, their dihedral angles and deviations of atoms from them are given in Table 3. High χ^2 values for the benzene rings correspond to the inaccurately determined C(16) and C(35) atoms. Unlike the Rb complex (Hašek, Huml & Hlavatá, 1979), C(12) and C(31) lie approximately in the plane of the neighbouring benzene ring, while C(21) and C(2) deviate by more than 1 Å from it.

The benzene rings in the same molecule are nearly parallel (1.3°) (*cf.* 29.9° in the RbSCN.H₂O complex).

A general view of the structure is given in Fig. 2. No significant intermolecular contacts were observed.

* See deposition footnote.

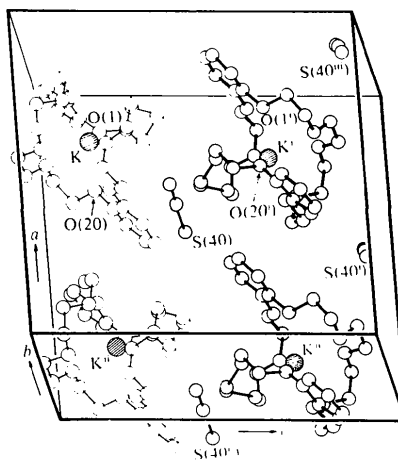


Fig. 2. Projection of the structure perpendicular to the plane defined by the atoms $K(x, y, z)$, $K^I(x - \frac{1}{2}, y - \frac{1}{2}, z)$, $K^{II}(x, 1 - y, z + \frac{1}{2})$ and $K^{III}(x - \frac{1}{2}, \frac{1}{2} - y, z + \frac{1}{2})$.

Table 4. Torsion angles ($^{\circ}$) in the macrorings of complexed and uncomplexed molecules of dibenzo-30-crown-10All e.s.d.'s are about 1° .

	(a)	(b)	(c)	(d)		(a)*	(b)†	(c)	(d)
C(33)–C(38)	–2	–4	–4	1	C(14)–C(19)	2	4	7	2
C(38)–O(1)	–154	–147	–116	–176	C(19)–O(20)	154	–147	–125	–107
O(1)–C(2)	148	–178	–180	167	O(20)–C(21)	–148	–178	–177	178
C(2)–C(3)	–67	–44	–61	64	C(21)–C(22)	67	–44	–61	–60
C(3)–O(4)	95	–62	–73	–174	C(22)–O(23)	–95	–62	–76	–85
O(4)–C(5)	–169	–172	–178	174	O(23)–C(24)	169	–172	–171	–161
C(5)–C(6)	–70	–69	–70	–71	C(24)–C(25)	70	–69	–68	–69
C(6)–C(7)	–180	169	–179	–167	C(25)–O(26)	180	169	177	–177
O(7)–C(8)	177	–84	–83	–69	O(26)–C(27)	–177	–84	–74	–83
C(8)–C(9)	–72	–62	–52	–58	C(27)–C(28)	72	–62	–67	–63
C(9)–O(10)	–175	176	170	170	C(28)–O(29)	175	176	176	158
O(10)–C(11)	177	–79	–80	–78	O(29)–C(30)	–177	–79	–82	–82
C(11)–C(12)	–63	–62	–68	–65	C(30)–C(31)	63	–62	–59	–68
C(12)–O(13)	–165	–175	–178	180	C(31)–O(32)	165	–175	–174	–177
O(13)–C(14)	174	174	–179	172	O(32)–C(33)	–174	174	179	177

References: (a) Dibenzo-30-crown-10 (Bush & Truter, 1972); (b) dibenzo-30-crown-10. KI (Bush & Truter, 1972); (c) dibenzo-30-crown-10. KSCN (this work); (d) dibenzo-30-crown-10. RbSCN. H_2O (Hašek *et al.*, 1979).

* Part of the molecule symmetrically related by $\bar{1}$.

† Part of the molecule symmetrically related by a twofold axis.

Discussion

A comparison of the conformations of structures containing dibenzo-30-crown-10 so far published is given in Table 4.

In the uncomplexed molecule, the torsion angles around all simple C–C bonds are approximately -60° (*gauche-*) in the independent and $+60^{\circ}$ (*gauche+*) in the centrosymmetrically related part of the molecule. 14 of the torsion angles around the C–O bonds are close to 180° (*trans*). Some deviations were found only on one side of the molecule in the vicinity of the benzene ring.

Wrapping of the polyether chain around the cation in the KI and KSCN complexes is accomplished by changing the conformations around the O(7)–C(8), O(10)–C(11), O(26)–C(27) and O(29)–C(30) bonds from *trans* to *gauche*. These changes are accompanied by a change in the sign of all positive *gauche* C–C torsion angles. There are only small differences between the conformations of these two complexes. In the complex with KI, torsion angles around the C(38)–O(1) and C(19)–O(20) bonds remain at $\sim 150^{\circ}$; in the complex with KSCN they drop to $\sim 120^{\circ}$. Torsion angles around the O(1)–C(2) and O(20)–C(21) bonds in both cases increase to 180° and those around the C(3)–O(4) and C(22)–O(23) bonds are close to 60° , unlike the uncomplexed polyether.

In the complex with RbSCN. H_2O , wrapping of the polyether chain is accompanied by additional changes. The sign of the *gauche* torsion angle around the C(2)–C(3) bond is reversed and the conformation around the C(3)–O(4) bond is changed from *gauche* to *trans*. Small shifts towards the ideal values of 180° and

60° were observed for the torsion angles around the C(38)–O(1) and O(7)–C(8) bonds, respectively. On the other hand, for the torsion angles around the O(1)–C(2), C(28)–O(29) and C(22)–O(23) bonds, greater deviations from their respective ideal values of 180° and 60° were found. The torsion angle around the C(19)–O(20) bond is lowered to -107° .

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References

- AHMED, F. R., HALL, S. R., PIPPY, M. E. & HUBER, C. P. (1966). NRC Crystallographic Programs for the IBM/360 System. National Research Council, Ottawa, Canada.
- BUSH, M. A. & TRUTER, M. R. (1972). *J. Chem. Soc. Perkin Trans. 2*, pp. 345–349.
- HAMILTON, W. C. (1959). *Acta Cryst.* **12**, 609–610.
- HAŠEK, J., HLAVATÁ, D. & HUML, K. (1977). *Acta Cryst.* **B33**, 3372–3376.
- HAŠEK, J., HUML, K. & HLAVATÁ, D. (1979). *Acta Cryst.* **B35**, 330–334.
- International Tables for X-ray Crystallography* (1962). Vol. III. Birmingham: Kynoch Press.
- MAIN, P., WOOLFSON, M. M., LESSINGER, L., GERMAIN, G. & DECLERCQ, J. P. (1974). *MULTAN 74. A System of Computer Programs for the Automatic Solution of Crystal Structures from X-ray Diffraction Data*. Univs. of York, England, and Louvain-la-Neuve, Belgium.
- PETRÁNEK, J. & RYBA, O. (1974). *Collect. Czech. Chem. Commun.* **39**, 2033–2036.
- SHANNON, R. D. & PREWITT, C. T. (1969). *Acta Cryst.* **B25**, 925–946.
- STEWART, R. F., DAVIDSON, E. R. & SIMPSON, W. T. (1965). *J. Chem. Phys.* **42**, 3175–3187.