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2,5,8,11,14,17,20-Heptaoxahenicosane–Barium Isothiocyanate, $C_{14}H_{30}O_7.Ba(NCS)_2^*$

BY GABRIELA WEBER, FUMITOSHI HIRAYAMA AND WOLFRAM SAENGER

Institut für Kristallographie der Freien Universität, Takustrasse 6, *D*-1000 *Berlin* 33, *Federal Republic of Germany*

AND GEORGE M. SHELDRICK

Institut für Anorganische Chemie der Universität, Tammannstrasse 4, *D*-3400 *Göttingen, Federal Republic of Germany*

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Abstract. M_r = 563·89, triclinic, $P\bar{1}$, a = 7·859 (3), b = 11·010 (4), c = 14·299 (4) Å, α = 89·65 (2), β = 78·39 (3), γ = 78·50 (3)°, V = 1186·9 (7) Å^3, Z = 2, D_x = 1·578 (1) Mg m^{-3}, λ(Mo $K\alpha$) = 0·71069 Å, μ = 1·87 mm^{-1}, F(000) = 568, T = 291 K, final R = 0·025 for 3979 observed reflections. The open-chain oligoether approximates to one turn of a helix, thus facilitating a sevenfold coordination of the cation to all the ether O atoms (mean 2·91 Å) and additional interactions with the two anions (mean $Ba^{2+}\cdots N^-$ distance = 2·83 Å). No linkages between the complex units were observed.

Introduction. Linear oligoethers containing $(-CH_2-CH_2-O-)_n$ units are well established ligands for alkali and alkaline-earth metal ions (Vögtle & Weber, 1979; Hilgenfeld & Saenger, 1982). Terminal donor groups such as aromatic bases (*e.g.* Vögtle & Sieger, 1977; Saenger, Suh & Weber, 1979), $-OH$ or $-CO_2H$ (capable of additional hydrogen bonding) (*e.g.* Hughes & Wingfield, 1978; Hughes, Mortimer & Truter, 1978; Yamaguchi, Miki, Yasuoka & Kasai, 1982) or, at least, terminal aromatic nuclei (*e.g.* Sieger & Vögtle, 1978; Hilgenfeld *et al.*, 1984) seemed essential for the stability of the complexes formed (*e.g.* Tümmler, Maass, Vögtle, Sieger, Heimann & Weber, 1979; Parsons, Truter & Wingfield, 1981). Complexes with unsubstituted oligoglymes could be obtained (Sieger & Vögtle, 1978) but X-ray investigations have been reported only for complexes with mercuric salts (Iwamoto, 1973), $CdCl_2$ (Iwamoto & Wakano, 1976) and for a compound in which potassium accepts additional π-interactions (Hodgson & Raymond, 1972). We report here the first structure determination of a complex between an alkaline-earth metal cation and an unsubstituted oligoglyme.

Experimental. Sample kindly provided by Professor F. Vögtle, University of D-5300 Bonn (FRG), crystal *ca* 0·7 × 0·3 × 0·1 mm, grown from ethyl acetate/petroleum ether; Stoe–Siemens four-circle diffractometer, cell dimensions from 2θ angles for 24 reflections ($20 \le 2\theta \le 25°$); 5261 profile-fitted (Clegg, 1981) data up to $2\theta = 50°$, $-9 \le h \le 1$, $-13 \le k \le -13$, $-17 \le l \le 17$; no significant decline in intensities of three standard reflections; empirical absorption correction based on ψ scans, max./min. transmission 0·63/0·53; 4169 reflections unique ($R_{\rm int}$ = 0·012), 3982 with $F > 3\sigma(F)$, three suppressed (machine fault); Ba^{2+} position from an $E \times F$ Patterson map, positions of remaining non-H atoms from a subsequent difference Fourier synthesis; structure refined anisotropically by blocked-cascade least squares on F, C(3)—C(4) restrained to 1·4800 ±0·0003 Å because of slight conformational (irresolvable) disorder; H atoms included in idealized positions [C—H = 0·96 Å; $U(H_i) = 1·2U_{\rm eq}(C_i)$], methylene H atoms treated as 'riding atoms', methyl groups as 'rigid groups'; 259 LS parameters, R = 0·025, wR = 0·027, $w^{-1} = \sigma^2(F) + 0·0004F^2$, S = 1·25, slope of normal probability plot 1·15, max. Δ/σ = 0·06 [rotation of methyl group C(1)], mean 0·004, largest peak 0·66 e Å^{-3} (close to Ba^{2+}), largest hole 0·35 e Å^{-3} in

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* Structures of Polyether Complexes. XXI. Part XX: Suh, Namgung, Ku Yoon, Saenger & Vögtle (1984).

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final map; scattering factors from *International Tables for X-ray Crystallography* (1974), program for structure solution, refinement *etc.* (*SHELXTL*) written by GMS, for diffractometer control by Dr W. Clegg, Göttingen (FRG).

Discussion. Final atomic parameters are given in Table 1;* the numbering scheme may be taken from Fig. 1. Widened C—O—C bond angles and shortened C—C bond lengths (Table 2) are common features in polyethers (*cf.* Maverick, Seiler, Schweizer & Dunitz, 1980).

It has been shown by X-ray studies on alkali-metal complexes of open-chain polyethers (Saenger *et al.*, 1979) that an equatorial coordination to the cation is strongly preferred by ligands of small or 'fitting' lengths; with longer polyethers a (pseudo) helical arrangement is observed, with some donor atoms remaining coplanar. From steric considerations and by analogy with annular crown ethers, the title ligand containing seven $-CH_2-O-CH_2-$ units is too long to retain a circular form while still coordinating the cation Ba^{2+}. Nevertheless, oxygens O(2), O(5), O(8) and O(11) are coplanar to within ±0·07 Å. These atoms, O(14) [deviating by −0·37 (1) Å from that plane] and, perhaps, O(17) [deviating by 0·66 (1) Å] may be considered the 'equatorial' donors: They form a fairly regular hexagon, with O···O distances between adjacent O atoms ranging from 2·748 (5) to 2·822 (5) Å, and with O(2)···O(17) = 3·130 (5) Å; the sequence of torsion angles g^-a ag^+a ag^-a ag^+a ag^- along O(2) to O(17) (Table 2) is typical of the 'round' conformation (*i.e.* exclusively $ag^{\pm}a$ with alternating signs) of annular polyethers when equatorially coordinating to a fitting cation (Dale, 1980).

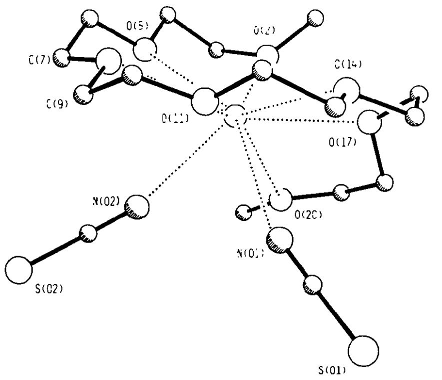

Fig. 1. A perspective view of the title complex. Radii are arbitrary, H atoms omitted for clarity. Interactions with the cation are indicated by dotted lines.

Table 1. *Atomic coordinates* (×10⁴) *and equivalent isotropic temperature factors* (Å² ×10³), *defined as one third of the trace of the orthogonalized* U_{ij} *matrix*

	x	y	z	U_{eq}
Ba	3342 (1)	1840 (1)	2697 (1)	32 (1)
S(01)	9167 (1)	3082 (1)	3842 (1)	57 (1)
C(01)	7668 (4)	2511 (3)	3439 (2)	41 (1)
N(01)	6585 (4)	2128 (3)	3172 (2)	57 (1)
S(02)	7491 (2)	−2845 (1)	1933 (1)	81 (1)
C(02)	6504 (4)	−1395 (3)	1971 (2)	48 (1)
N(02)	5781 (4)	−374 (3)	2013 (2)	68 (1)
C(1)	349 (8)	3940 (5)	1209 (4)	123 (3)
O(2)	1470 (4)	2793 (3)	1176 (2)	80 (1)
C(3)	1171 (6)	1806 (4)	586 (3)	92 (2)
C(4)	207 (5)	959 (4)	1185 (2)	75 (2)
O(5)	1345 (3)	377 (2)	1778 (2)	60 (1)
C(6)	551 (5)	−532 (3)	2316 (3)	66 (1)
C(7)	1754 (5)	−1132 (3)	2924 (3)	62 (1)
O(8)	1944 (3)	−223 (2)	3569 (2)	52 (1)
C(9)	2897 (5)	−705 (3)	4285 (3)	68 (1)
C(10)	2515 (5)	240 (4)	5057 (3)	68 (1)
O(11)	3126 (3)	1329 (2)	4704 (1)	54 (1)
C(12)	2473 (5)	2342 (4)	5377 (2)	72 (2)
C(13)	3309 (5)	3409 (4)	5040 (3)	71 (1)
O(14)	2837 (3)	3785 (2)	4161 (2)	61 (1)
C(15)	3469 (7)	4903 (4)	3843 (4)	90 (2)
C(16)	2818 (8)	5258 (4)	2981 (4)	99 (2)
O(17)	3497 (4)	4363 (2)	2212 (2)	69 (1)
C(18)	5172 (6)	4466 (3)	1627 (3)	75 (2)
C(19)	5474 (5)	3694 (3)	736 (3)	66 (1)
O(20)	5646 (3)	2433 (2)	959 (2)	56 (1)
C(21)	6081 (6)	1649 (4)	138 (3)	78 (2)

Table 2. *Bond lengths* (Å), *bond angles* (°), *torsion angles* (°) *and coordination distances* (Å)

S(01)–C(01)	1·640 (3)	C(01)–N(01)	1·151 (5)
S(02)–C(02)	1·626 (3)	C(02)–N(02)	1·151 (4)
O(2)–C(1)	1·383 (6)	O(2)–C(3)	1·464 (6)
C(3)–C(4)	1·480 (6)	C(4)–O(5)	1·414 (5)
O(5)–C(6)	1·424 (4)	C(6)–C(7)	1·469 (5)
C(7)–O(8)	1·414 (4)	O(8)–C(9)	1·427 (5)
C(9)–C(10)	1·465 (5)	C(10)–O(11)	1·431 (5)
O(11)–C(12)	1·421 (4)	C(12)–C(13)	1·489 (6)
C(13)–O(14)	1·418 (5)	O(14)–C(15)	1·453 (5)
C(15)–C(16)	1·450 (8)	C(16)–O(17)	1·425 (5)
O(17)–C(18)	1·436 (5)	C(18)–C(19)	1·488 (6)
C(19)–O(20)	1·409 (4)	O(20)–C(21)	1·405 (4)

S(01)–C(01)–N(01)	178·3 (2)	S(02)–C(02)–N(02)	178·7 (3)
C(1)–O(2)–C(3)	117·4 (4)	O(2)–C(3)–C(4)	110·7 (3)
C(3)–C(4)–O(5)	106·5 (4)	C(4)–O(5)–C(6)	109·1 (3)
O(5)–C(6)–C(7)	108·4 (3)	C(6)–C(7)–O(8)	108·3 (3)
C(7)–O(8)–C(9)	114·4 (2)	O(8)–C(9)–C(10)	108·1 (3)
C(9)–C(10)–O(11)	110·0 (3)	C(10)–O(11)–C(12)	111·3 (2)
O(11)–C(12)–C(13)	109·8 (3)	C(12)–C(13)–O(14)	108·6 (3)
C(13)–O(14)–C(15)	111·2 (3)	O(14)–C(15)–C(16)	107·0 (4)
C(15)–C(16)–O(17)	113·5 (3)	C(16)–O(17)–C(18)	115·7 (3)
O(17)–C(18)–C(19)	108·9 (4)	C(18)–C(19)–O(20)	109·7 (3)
C(19)–O(20)–C(21)	112·3 (3)		

C(1)–O(2)–C(3)–C(4)	−100·8 (4)	O(2)–C(3)–C(4)–O(5)	−64·6 (4)
C(3)–C(4)–O(5)–C(6)	−175·1 (3)	C(4)–O(5)–C(6)–C(7)	179·7 (3)
O(5)–C(6)–C(7)–O(8)	62·7 (3)	C(6)–C(7)–O(8)–C(9)	172·3 (3)
C(7)–O(8)–C(9)–C(10)	−162·4 (3)	O(8)–C(9)–C(10)–O(11)	−62·3 (4)
C(9)–C(10)–O(11)–C(12)	168·5 (3)	C(10)–O(11)–C(12)–C(13)	173·0 (3)
O(11)–C(12)–C(13)–O(14)	61·8 (4)	C(12)–C(13)–O(14)–C(15)	174·3 (3)
C(13)–O(14)–C(15)–C(16)	−176·1 (3)	O(14)–C(15)–C(16)–O(17)	−63·2 (5)
C(15)–C(16)–O(17)–C(18)	−86·4 (5)	C(16)–O(17)–C(18)–C(19)	−166·0 (3)
O(17)–C(18)–C(19)–O(20)	−65·1 (4)	C(18)–C(19)–O(20)–C(21)	−175·0 (4)

Ba···O(2)	2·939 (3)	Ba···O(5)	2·941 (2)
Ba···O(8)	2·887 (2)	Ba···O(11)	2·899 (2)
Ba···O(14)	2·917 (2)	Ba···O(17)	2·879 (3)
Ba···O(20)	2·919 (2)	Ba···N(01)	2·842 (3)
Ba···N(02)	2·825 (3)		

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* Anisotropic temperature factors, H-atom parameters and lists of structure factors have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 39523 (27 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

The seventh oxygen O(20) is 2·85 (1) Å above the basal hexagon, *i.e.* in an 'apical' position; this results from a change of C(15)—C(16)—O(17)—C(18) from the usual *anti* conformation to −86·4 (5)° and from the O(17)—C(18)—C(19)—O(20) unit displaying an $ag^{-}a$ conformation.

The same sign of the *gauche* angles about C(15)—C(16) and C(18)—C(19) is indicative of a helical structure, as found in crystalline poly(ethylene oxide) (Dale, 1980). C(1)—O(2)—C(3)—C(4) = −100·8 (4)° is probably a consequence of steric hindrance.

The observed conformation of the polyether is such as to allow (i) for all its O atoms Ba···O contacts only 0·1–0·2 Å longer than the sum of the respective radii and (ii) additional interactions between Ba^{2+} and the anions (Table 2).

There are no obvious linkages between the complex units.

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Order and Disorder in the Structure of Dibenzofuran, $C_{12}H_8O$

By William J. Reppart, Judith C. Gallucci, Alan P. Lundstedt and Roger E. Gerkin*

Department of Chemistry, The Ohio State University, Columbus, Ohio 43210, *USA*

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Abstract. $M_r = 168{\cdot}20$, orthorhombic, $Pnma$, $a = 7{\cdot}5154\ (8)$, $b = 19{\cdot}098\ (2)$, $c = 5{\cdot}7739\ (6)$ Å, $V = 828{\cdot}7\ (2)$ Å^3, $Z = 4$, $F(000) = 352$, $D_x = 1{\cdot}348$ g cm^{-3}, $T = 169$ K, $\lambda(\text{Mo } K\bar{\alpha}) = 0{\cdot}71069$ Å, $\mu = 0{\cdot}789$ cm^{-1}, $R = 0{\cdot}039$, $wR = 0{\cdot}040$ for 1254 reflections with $I > 3\sigma_I$. The dibenzofuran molecule has mirror symmetry, with the reflection plane passing through the O atom and bisecting the furan ring. The five- and six-membered rings are planar, and have a dihedral angle of 1·5°. The average C—C bond length in the six-membered ring is 1·392 Å. The structure is disordered, with 9% of the molecules adopting an alternative orientation. The disordered molecules are related to the ordered ones by a 180° rotation about an axis which passes through the center of mass and is perpendicular to the furan ring. Reanalysis of the data provided by previous studies of dibenzofuran at room temperature shows that disorder similar in both kind and degree was present, but was not reported. Accounting for the disorder brings the C—O bond length into agreement with values from similar compounds, thus removing an earlier discrepancy.

Introduction. The structure of dibenzofuran at room temperature has been reported by Dideberg, Dupont & André (1972) and by Banerjee (1973). The present determination of the structure at 169 K was undertaken in conjunction with low-temperature EPR experiments on the lowest triplet state of biphenyl dilutely oriented in dibenzofuran host crystals. Since certain aspects of the observed low-temperature magnetic resonance spectra could be reasonably ascribed to the

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* To whom correspondence should be addressed.

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