

## Structures of Polyether Complexes. X.\* A Binuclear Complex of a Linear Oligoether: 1,5-Bis{2-[5-(2-nitrophenoxy)-3-oxapentyloxy]phenoxy}-3-oxapentane–Potassium Isothiocyanate

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### Abstract

[ $o\text{NO}_2\text{C}_6\text{H}_4\text{OCH}_2\text{CH}_2\text{OCH}_2\text{CH}_2\text{O}o\text{C}_6\text{H}_4\text{OCH}_2\text{CH}_2\text{O}$ ] $_2\text{KSCN}$ ,  $\text{C}_{36}\text{H}_{40}\text{N}_2\text{O}_{13}\cdot 2\text{KSCN}$ ,  $C2/c$ ,  $a = 23.184$  (9),  $b = 9.051$  (3),  $c = 22.235$  (8) Å,  $\beta = 114.43$  (5)°,  $M_r = 903.1$ ,  $Z = 4$ ,  $d_c = 1.41$ ,  $d_o = 1.46$  Mg m<sup>-3</sup> (flotation in bromobenzene/ethyl acetate), m.p. 381–382 K,  $\mu = 3.412$  mm<sup>-1</sup>. In contrast to mononuclear helical complexes, the polyether chain in the title compound displays an *S*-like configuration with 2 ( $C_2$ ) symmetry. In the centre of each *S* loop one cation is coordinated to all the O atoms except to the O *ortho* to the nitro group. Twofold coordination of two O atoms and additional weak interactions to the 2-related K<sup>+</sup> stabilize this arrangement and provide each K<sup>+</sup> ion with sevenfold coordination. The disordered anions interact only weakly with the cations.

### Experimental

The colourless title complex was recrystallized from a mixture of methanol and ethyl acetate (Vögtle & Heimann, 1978). Intensities for 3335 unique reflexions were collected from a crystal of dimensions 0.4 × 0.15 × 0.15 mm with a four-circle diffractometer using Ni-filtered Cu  $K\alpha$  radiation in the  $\theta$ - $2\theta$  step-scan mode up to  $\sin \theta/\lambda = 0.57$  Å<sup>-1</sup>. Data were corrected for polarization but not for absorption.

An *E* map calculated with the 300 strongest *E* values based on the most probable phase set (Main, Lessinger, Woolfson, Germain & Declercq, 1977) revealed all the non-hydrogen atoms. Since the anion was found to be disordered, artificial scattering factors were used for both the terminal atoms (statistically N or S) of the SCN<sup>-</sup> group: they were assumed to have the mean scattering power of N and S (*International Tables for X-ray Crystallography*, 1974). After several cycles of

refinement by full-matrix least squares (Sheldrick, 1976) the positions of all the H atoms could be located from a difference Fourier synthesis. They were recalculated according to stereochemical criteria and refined only in the last cycle. After application of a weighting scheme based on counting statistics (Stout & Jensen, 1968) and a correction for extinction effects [ $X = 0.0030$  (1)] (Sheldrick, 1976) the final  $R_w = 0.055$  with all data included.

Table 1. Fractional atomic coordinates ( $\times 10^4$ ) of the non-hydrogen atoms and isotropic *B* values (e.s.d.'s about 0.2 Å<sup>2</sup>) calculated from the anisotropic *U* values

	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i> (Å <sup>2</sup> )
N, S	4100 (1)	4685 (3)	368 (1)	6.1
S, N	3327 (1)	5778 (3)	829 (1)	5.7
C	3595 (7)	5352 (17)	622 (9)	5.8
C'	3826 (7)	5037 (19)	585 (10)	4.7
K	4087 (0)	2952 (1)	1709 (0)	4.0
O(1)	5188 (1)	1630 (3)	1885 (1)	5.8
N(2)	5505 (1)	525 (4)	1929 (1)	4.5
C(3)	5385 (2)	-332 (4)	1339 (2)	3.7
C(4)	4774 (2)	-617 (4)	879 (2)	3.9
O(5)	4279 (1)	-93 (3)	999 (1)	4.6
C(6)	3649 (2)	-532 (5)	535 (2)	5.1
C(7)	3189 (2)	-156 (5)	816 (2)	5.3
O(8)	3126 (1)	1389 (3)	823 (1)	5.2
C(9)	2546 (2)	1898 (6)	841 (2)	6.3
C(10)	2538 (2)	1681 (6)	1504 (2)	5.9
O(11)	3009 (1)	2637 (3)	1955 (1)	4.8
C(12)	3060 (2)	2696 (4)	2589 (2)	4.4
C(13)	3540 (2)	3586 (4)	3025 (2)	4.2
O(14)	3897 (1)	4309 (3)	2750 (1)	4.3
C(15)	4413 (2)	5187 (5)	3184 (2)	5.0
C(16)	4680 (2)	6057 (4)	2792 (3)	5.2
O(17)	5000 (0)	5146 (3)	2500 (0)	4.0
O(18)	5925 (1)	139 (3)	2443 (1)	6.9
C(19)	5908 (2)	-872 (4)	1257 (2)	4.8
C(20)	5814 (2)	-1695 (4)	705 (2)	5.5
C(21)	5217 (2)	-2002 (4)	255 (2)	5.4
C(22)	4702 (2)	-1476 (4)	337 (2)	4.8
C(23)	2663 (2)	1948 (5)	2817 (2)	5.8
C(24)	2763 (3)	2105 (6)	3473 (3)	7.1
C(25)	3228 (3)	2947 (6)	3890 (2)	6.6
C(26)	3628 (2)	3704 (5)	3676 (2)	5.3

\* Part IX: Weber & Saenger (1979a).

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### Results and discussion

Atomic coordinates of non-hydrogen atoms are given in Table 1.\* Bond distances and angles are listed in Tables 2 and 3. Coordination distances, the numbering scheme and torsion angles are entered in Fig. 1. A stereoscopic view of the complex is shown in Fig. 2. A brief description of this structure has already been published (Weber & Saenger, 1979b).

#### Configuration of the ligand

A decadentate oligoether has recently been shown to wrap around one Rb<sup>+</sup> cation in a distorted helical manner in one and a half turns (Weber & Saenger, 1979a). In the present binuclear complex the polyether chain forms two *S* loops, each around one K<sup>+</sup>SCN<sup>-</sup> ion pair. The central O(17) atom of the ligand lies on a

\* Lists of structure factors, anisotropic thermal parameters and H atom positional parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 34808 (23 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 2. Bond distances (Å) of the non-hydrogen atoms

O(1)–N(2)	1.221 (4)	C(13)–O(14)	1.379 (5)
N(2)–C(3)	1.449 (5)	C(13)–C(26)	1.379 (6)
N(2)–O(18)	1.207 (3)	O(14)–C(15)	1.427 (4)
C(3)–C(4)	1.386 (4)	C(15)–C(16)	1.486 (8)
C(3)–C(19)	1.389 (6)	C(16)–O(17)	1.432 (6)
C(4)–O(5)	1.367 (5)	C(19)–C(20)	1.375 (6)
C(4)–C(22)	1.386 (6)	C(20)–C(21)	1.361 (6)
O(5)–C(6)	1.453 (4)	C(21)–C(22)	1.365 (7)
C(6)–C(7)	1.483 (8)	C(23)–C(24)	1.386 (8)
C(7)–O(8)	1.406 (6)	C(24)–C(25)	1.332 (7)
O(8)–C(9)	1.436 (6)	C(25)–C(26)	1.388 (8)
C(9)–C(10)	1.495 (8)	N,S–C'	0.997 (22)
C(10)–O(11)	1.428 (5)	N,S–C	1.613 (20)
O(11)–C(12)	1.366 (5)	S,N–C	0.992 (21)
C(12)–C(13)	1.391 (4)	S,N–C'	1.613 (21)
C(12)–C(23)	1.396 (7)		

Table 3. Bond angles (°) of the non-hydrogen atoms

O(1)–N(2)–C(3)	118.8 (3)	C(13)–C(12)–C(23)	119.1 (4)
O(1)–N(2)–O(18)	122.5 (3)	C(12)–C(13)–O(14)	114.8 (3)
C(3)–N(2)–O(18)	118.7 (3)	C(12)–C(13)–C(26)	120.3 (4)
N(2)–C(3)–C(4)	121.6 (4)	O(14)–C(13)–C(26)	124.9 (3)
N(2)–C(3)–C(19)	117.1 (3)	C(13)–O(14)–C(15)	117.0 (3)
C(4)–C(3)–C(19)	121.3 (3)	O(14)–C(15)–C(16)	109.6 (3)
C(3)–C(4)–O(5)	118.4 (3)	C(15)–C(16)–O(17)	112.4 (3)
C(3)–C(4)–C(22)	117.7 (4)	C(16)–O(17)–C(16)'	109.7 (4)
O(5)–C(4)–C(22)	123.8 (3)	C(3)–C(19)–C(20)	118.9 (3)
C(4)–O(5)–C(6)	116.4 (3)	C(19)–C(20)–C(21)	120.3 (5)
O(5)–C(6)–C(7)	108.9 (4)	C(20)–C(21)–C(22)	120.7 (4)
C(6)–C(7)–O(8)	109.2 (4)	C(4)–C(22)–C(21)	121.0 (3)
C(7)–O(8)–C(9)	115.0 (4)	C(12)–C(23)–C(24)	118.9 (4)
O(8)–C(9)–C(10)	112.3 (3)	C(23)–C(24)–C(25)	121.7 (6)
C(9)–C(10)–O(11)	107.2 (4)	C(24)–C(25)–C(26)	120.5 (5)
C(10)–O(11)–C(12)	117.7 (3)	C(13)–C(26)–C(25)	119.5 (4)
O(11)–C(12)–C(13)	116.4 (4)	S,N–C–N,S	173 (1)
O(11)–C(12)–C(23)	124.5 (3)	S,N–C'–N,S	171 (2)

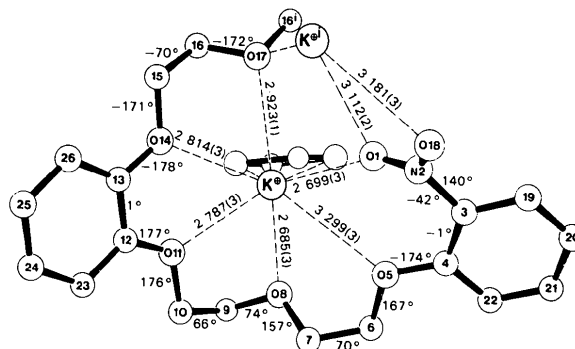


Fig. 1. Chemical structure, numbering scheme, torsion angles ( $\pm 3^\circ$ ) and coordination distances (Å) to K<sup>+</sup> within one *S* loop including two symmetry-related atoms K<sup>+</sup> and C(16)<sup>i</sup> ( $i = 1 - x, y, 0.5 - z$ ). Distances from the terminal atoms of the disordered (SCN<sup>-</sup>, <sup>-</sup>NCS) to K<sup>+</sup>: N,S(right)···K<sup>+</sup> = 3.380 (3); S,N(left)···K<sup>+</sup> = 3.259 (2) Å.

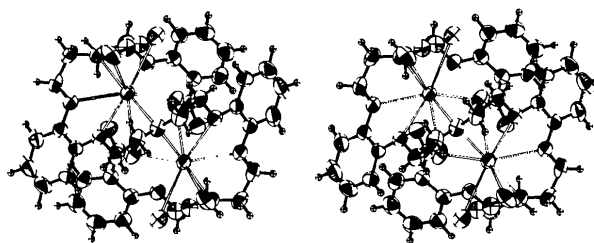


Fig. 2. A thermal-ellipsoid stereoplot of the complex indicating 50% probability boundaries (Johnson, 1965).

twofold crystallographic axis, *i.e.* the complex is rotationally symmetric and the asymmetric unit contains only one half of the complex.

The *S*-like configuration is stabilized by twofold and cross-linking coordination of O(17) and the nitro group. A configuration comparable to this has been found in a potassium complex of a linear oligoether with two terminal carboxy groups (Hughes, Mortimer & Truter, 1978): by sharing one O atom between two symmetry-related K<sup>+</sup> ions two mononuclear entities are linked such that a dimer is formed with two shallow helices lying side by side.

It might be that in complexes of oligoethers with bidentate terminal groups such as  $-\text{NO}_2$  or  $-\text{CO}_2\text{H}$ , dimeric structures or structures rolled up like a figure eight are preferred because of the possibility of twofold or cross-linking coordination.

In both linear (Suh, Weber & Saenger, 1978; Weber & Saenger, 1979c; Hughes, Mortimer & Truter, 1978) and cyclic complexes (Truter, 1973), C–O torsion angles are usually *trans* and ethyleneglycol C–C torsion angles are *gauche*. In general, this rule also holds for the present complex. Only the C(7)–O(8)–C(9)–C(10) torsion angle is *gauche* ( $74^\circ$ ) instead of *trans*. This kink enables atoms O(11), O(14) and O(17) to coordinate to the cation and is analogous to that

observed in the dimeric complex of a linear oligoether with  $K^+$  (Hughes, Mortimer & Truter, 1978).

The second 'irregularity' is observed in the  $C(4)-C(3)-N(2)-O(1)$  ( $-42^\circ$ ) and  $C(4)-C(3)-N(2)-O(18)$  ( $140^\circ$ ) torsion angles. The dihedral angle between the plane of the nitro group and that of the attached phenoxy group is  $41(5)^\circ$ . A comparable twist has also been found for another *ortho*-nitrophenoxy compound of this series (Suh, Weber & Saenger, 1980) and could be explained by (1) steric repulsion between O atoms, by (2) improved coordination to the cation or by (3) molecular packing in the cell. The last may be omitted from considerations since in the present structure there are no short intermolecular contacts evident (see below).

A rather small twist angle would probably result in a poorer coordination of  $O(1)$  to  $K^+$  and to  $K^{+1}$  and in an improved coordination of  $O(18)$  to  $K^{+1}$ . Thus the present rotation may be an energetically favoured compromise. On the other hand, the distance  $O(1)\cdots O(5) = 2.7 \text{ \AA}$  points to steric repulsion. Moreover, when a van der Waals radius of  $1.40 \text{ \AA}$  for O is assumed (*Handbook of Chemistry and Physics*, 1974), hard-sphere-model calculations lead to a dihedral angle of about  $50^\circ$  between the relevant planes which is in good agreement with the experimental findings.

The structures of many *o*-substituted nitrobenzene compounds, including *o*-nitrophenols and *o*-nitrophenolates, have been reported. Because of intramolecular H bridges and mesomeric effects in *o*-nitrophenols, the dihedral angles between the nitro group and the benzene ring are normally in the range from  $0$  to  $5^\circ$  (Kawai, Kashino & Haisa, 1976; Iwasaki & Kawano, 1977, 1978; Krogh Andersen & Krogh Andersen, 1975a). The shortenings of the phenolic C—O bond and two aromatic C—C bonds in these compounds indicate a contribution of an *o*-quinonoid resonance structure that strongly affects the dihedral angle. These contributions are even more evident in *o*-nitrophenolate anions (Krogh Andersen & Krogh Andersen, 1975b; Hughes, 1975). A rotation of *ca*  $15-20^\circ$  of the nitro group about the C—N bond might be explained by bridging coordination of the nitro group (Hughes, 1973) or by steric overcrowding of the nitro and phenol groups (Bush & Truter, 1971).

In the present ether, however, H bridges are impossible and resonance structures seem to be strongly reduced: the  $C(4)-O(5)$  bond is about  $0.08 \text{ \AA}$  longer than the average for *o*-nitrophenolates and about the same length as  $O(11)-C(12)$  and  $C(13)-O(14)$ . Moreover, N—O bond lengths are slightly shorter than in *o*-nitrophenolates, and systematic shortening of C—C bond lengths in the aromatic nucleus is not obvious. Without H bridges and resonance effects the twist angle seems to be significantly larger: in 1-chloro- and 1-bromo-2,4-dinitrobenzene the nitro group is rotated by *ca*  $40^\circ$  (Watson, 1960), in a picrate by  $56^\circ$

(Hughes, Mortimer & Truter, 1978), and in an O-bridged diphenyl by  $47^\circ$  (Gurtu, Chandler & Robertson, 1975). The twist angle of the non-hydrogen-bonded  $NO_2$  group of about  $13^\circ$  in 2,6-dinitrophenol (Iwasaki, Sato & Aihara, 1976) is probably due to molecular packing and to resulting intermolecular interactions. The angle of about  $40^\circ$  in the present structure would therefore appear to be mostly due to steric repulsion between one O of the nitro group and the ether O in the *ortho* position.

#### Coordination to the cation

As in other linear oligoether complexes (Saenger & Brand, 1979; Suh, Weber & Saenger, 1978; Weber & Saenger, 1979c; Hughes, Mortimer & Truter, 1978) a number of the hetero atoms are found to be coplanar. In this structure  $O(8)$ ,  $O(11)$ ,  $O(14)$  and  $O(17)$  are coplanar within  $\pm 0.03 \text{ \AA}$ .  $K^+$  is located  $0.3 \text{ \AA}$  above this plane which forms the normally stronger binding 'equatorial' region of the coordination sphere (Weber & Saenger, 1979b).

From van der Waals and ionic radii the  $K^+\cdots O$  distance should be about  $2.73 \text{ \AA}$  (*Handbook of Chemistry and Physics*, 1974). Atoms  $O(1)$  and  $O(8)$  with coordination distances less than  $2.73 \text{ \AA}$  show strong coordination to  $K^+$ . The distances  $K^+\cdots O(11)$  and  $K^+\cdots O(14)$  exceed the theoretical value marginally (see Fig. 1). The relatively long distance  $K^+\cdots O(17)$  can be attributed to the twofold coordination of this O atom to each  $K^+$  in both *S* loops. Even though, in general, cation $\cdots O$ (aliphatic) distances are shorter than cation $\cdots O$ (aromatic) (Saenger & Brand, 1979; Suh, Weber & Saenger, 1978), the poor coordination of  $O(5)$  is best explained by the low electronegativity of  $O(5)$  due to the nitro group in the *ortho* position and, probably, by steric constraints.

Additionally  $K^+$  interacts weakly with the two O atoms of the nitro group of the rotationally related *S* loop which occupy one apical region. This cross-linking coordination of  $O(1)$  and  $O(18)$  and the twofold coordination of  $O(17)$  seem to stabilize the *S* shape of the ligand. There is also an interaction of  $K^+$  with the anion which is located in the second apical region of the cation. The distances from the terminal atoms of the anion to  $K^+$  are  $3.380$  and  $3.259 \text{ \AA}$ , respectively. Since each position is occupied statistically by *S*, and since the  $K^+\cdots S$  coordination distance is  $3.18 \text{ \AA}$  (*Handbook of Chemistry and Physics*, 1974), a cation-dipole interaction ( $K^+\cdots S$ ) is probable but a cation-anion ( $K^+\cdots NCS$ ) is not.

To summarize: the  $K^+$  ion is provided with a strong fivefold coordination to O atoms of the ligand. Since the number of coordination atoms is an important criterion for the stability of a complex, weaker interactions such as  $K^+\cdots O(1)^{\dagger}$ ,  $K^+\cdots O(18)^{\dagger}$  and  $K^+\cdots S$  should also be taken into account, yielding in

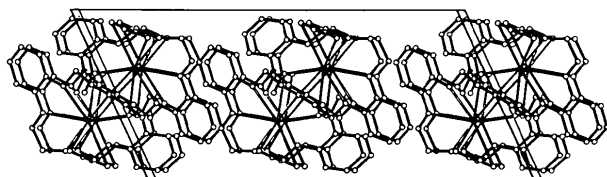


Fig. 3. A projection of half the unit cell ( $c$  from 0 to 0.5) looking down  $b$  (Johnson, 1965).

total an eight-coordinated  $K^+$  with irregular coordination geometry.

#### Molecular packing and the disordered anion

Molecules are stacked along  $b$  (Fig. 3). The stacking repeat of about 9 Å is, however, too large to allow  $\pi \cdots \pi$  interactions between the aromatic systems. The  $SCN^-$  anions, which display a statistical 'head-to-tail' disorder, are located between two benzene moieties related by a translation along  $b$ . Probably because of the ambidentate bonding capabilities of isothiocyanate, disorder of this anion is common. It is, however, mostly due to formal (Seiler, Dobler & Dunitz, 1974) or actual crystallographic symmetry (Moras, Metz, Herceg & Weiss, 1972), which is reflected by identical distances between the cation and each of the terminal atoms of the anion. In the present study these distances are significantly different, *i.e.* the disorder is not combined with crystallographic symmetry.

In a complex of a linear oligoether and  $NaSCN$  (Suh, Weber & Saenger, 1978) the anion was bound through N to a sevenfold-coordinated  $Na^+$  in a linear manner ( $Na^+ \cdots NCS \approx 180^\circ$ ). In the present structure the  $SCN^-$  is arranged nearly perpendicular to the cation [ $\angle K^+ \cdots C-N, S = 85.6$  (6),  $\angle K^+ \cdots C'-S, N = 84.6$  (9) $^\circ$ ] the shortest contact between cation and anion being  $K^+ \cdots C' = 2.99$  (2) Å. This perpendicular orientation is even more extreme than that observed in a complex of a macrocyclic ligand and  $KSCN$  (Moras, Metz, Herceg & Weiss, 1972). The disordered and perpendicular arrangement of the  $SCN^-$  anion may therefore indicate that the packing of the anion is relatively unimportant compared to the  $K^+ \cdots$  ligand interactions. On the other hand, the coordination sphere is more completely occupied in a perpendicular rather than in a linear orientation of  $SCN^-$ .

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