are statistically distributed among three equivalent positions and are therefore indistinguishable. As the C—O and C—C distances in ethanol are different (1·426 and 1·544 Å), this distribution causes an apparent vibrational effect. (b) As the CH_3—CH_2—OH angle is 109°, while those at the equivalent positions must be 120°, there is an apparent libration effect for the CH_3 and OH groups (atom labelled OC). Because of this effect, the bond between C(4) and the average position OC is greatly shortened: 1·12 (5) Å vs the expected mean value of 1·48 Å [see point (a)]. These apparent vibration and libration effects lead to values of b_{ij} for the ethanol atoms which are much larger than those of the other light atoms in the structure. (c) As the 32(a) point symmetry $(00\frac{1}{4})$ is present at 0·72 Å from the molecular plane, the atoms of the alcohol are distributed between two close symmetry-related positions.

Cl(1), as mentioned above, is surrounded octahedrally by six equivalent water molecules at distances of 3·165 (5) Å, very close to those in $HCl.6H_2O$ (Taesler & Lundgren, 1978); Cl(2) is involved in a close net of interactions with H atoms belonging to Ow, N(1) and C(2), Cl—H distances falling in the range 2·46–3·08 Å.

The coordination behaviour of dithiocarbazic acid derivatives can be correlated with their conformational properties (Manotti Lanfredi, Tiripicchio, Tiripicchio Camellini, Monaci & Tarli, 1977). These studies show that the most stable conformations for the free ligands L and L' are:

L: trans–cis
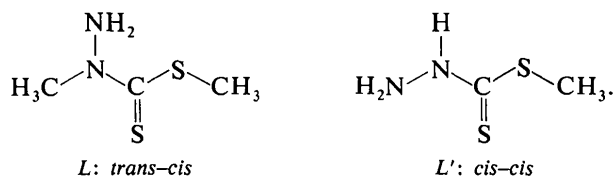
L': cis–cis

When it is coordinated, the ligand L must have the cis–cis conformation

L: cis–cis
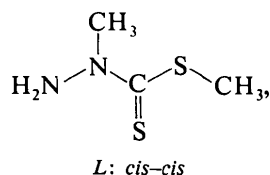
the only one allowing it to chelate to the Ni atom. The energy required for this conformational change probably decreases the coordinating ability of the ligand L compared to that of L'. Hence, under the same crystallization conditions, both $[NiL_2Cl_2]$ and $[NiL_3']Cl_2$ are formed.

In the presence of H_2O molecules, as we have observed from the structure determination, the $[NiL_3]^{2+}$ and $[(H_2O)_6Cl]^-$ complex ions are energetically preferred to the coordination of the Cl to the metal. The energy gain so obtained can lead to the conformational change (and therefore to the coordination to the metal atom) of a third ligand molecule.

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1,11-Bis(2-nitrophenoxy)-3,6,9-trioxaundecane–Potassium Isothiocyanate*

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Abstract. $C_{20}H_{24}N_2O_9.KSCN$, $M_r = 533·6$, $P2_1/c$, $a = 8·156$ (3), $b = 13·380$ (4), $c = 23·425$ (5) Å, $\beta = 97·84$ (5)°, $Z = 4$, $d_c = 1·399$ Mg m^{-3}, m.p. 368 K. The structure was solved from 2227 X-ray diffractometer data (graphite-monochromated Mo $K\alpha$ radiation), and refined to $R = 7·1\%$. The ligand wraps around the cation which is eightfold coordinated to all the ether O atoms, to one O atom of each nitro group and to the N

of SCN⁻. Benzene and nitro groups are stacked ~3·4 Å apart, giving rise to the deviation of one CCOC torsion angle from the expected *trans* to *gauche* (95·9°). In the crystal lattice, adjacent molecules are stacked with nitro–benzene interactions.

Introduction. A sample of the title compound (I) was kindly donated by Professor F. Vögtle and Dr H. Sieger, Bonn. Recrystallization by the slow cooling of a hot saturated solution of (I) in methanol/ethyl acetate produced needle-shaped yellowish crystals. A specimen 0·1 × 0·2 × 0·5 mm was used for all X-ray experiments. Integrated intensities up to $2\theta = 50°$ were measured in the $2\theta/\theta$ scan mode; the counting time was 56 s for the scan and 14 s for stationary backgrounds on both sides of each scan, using graphite-mono-chromated Mo $K\alpha$ radiation. Standard reflections monitored every 100 reflections were constant with time. Data were corrected for geometrical factors but not for absorption [μ(Mo $K\alpha$) = 0·1709 mm⁻¹]. The structure was solved by direct methods (*MULTAN*;

Main, Lessinger, Woolfson, Germain & Declercq, 1977) and refined by full-matrix least-squares techniques. H atoms were located from difference Fourier syntheses. The final $R = 7·1\%$ for all data, and a weighted $R = 3·9\%$ omitting 275 unobserved data with $F_{obs} > 3\sigma_{F_{obs}}$. $\sigma_{F_{obs}}$ was obtained from counting statistics.
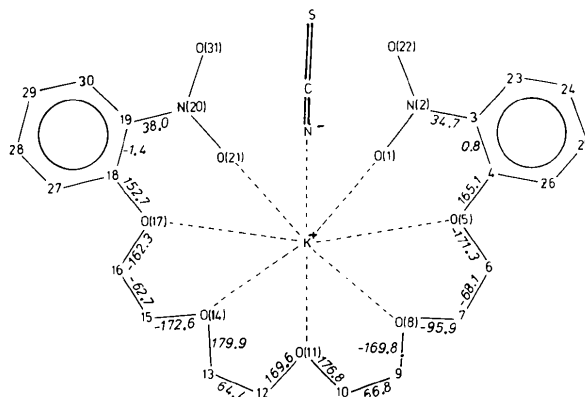

Fig. 1. Chemical structure and numbering scheme for (I). Torsion angles (°) along the oligoether chain are indicated; average e.s.d.'s are 0·5°.

Table 1. *Fractional atomic coordinates* (×10⁴) *and isotropic temperature factors* (Å²)

Average e.s.d.'s for B's are 0·08 Å².

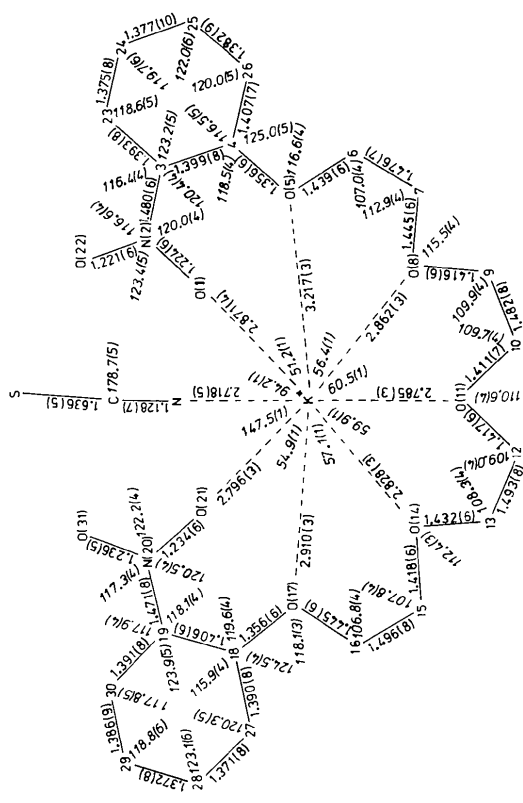|	x	y	z	B
K⁺	4902 (1)	1684 (1)	6778 (0)	4·53
S	9107 (2)	2093 (1)	8775 (1)	8·22
C	7755 (7)	1834 (4)	8213 (2)	4·74
N	6844 (6)	1662 (4)	7818 (2)	7·41
O(1)	6882 (4)	3146 (3)	6291 (1)	5·77
N(2)	7051 (3)	3624 (2)	5857 (1)	5·72
C(3)	5697 (4)	3652 (2)	5368 (1)	4·93
C(4)	4043 (4)	3643 (2)	5466 (1)	4·21
O(5)	3717 (4)	3620 (2)	6019 (1)	5·40
C(6)	2052 (4)	3860 (2)	6109 (1)	5·54
C(7)	2052 (4)	3944 (3)	6738 (1)	6·79
O(8)	2332 (5)	2999 (3)	7033 (2)	6·11
C(9)	889 (5)	2483 (3)	7140 (1)	9·46
C(10)	1347 (6)	1630 (3)	7534 (2)	7·34
O(11)	2220 (7)	911 (3)	7253 (2)	5·69
C(12)	2749 (7)	113 (3)	7633 (2)	6·41
C(13)	3382 (7)	−716 (3)	7296 (2)	6·37
O(14)	4819 (6)	−366 (4)	7068 (2)	5·50
C(15)	5513 (6)	−1108 (4)	6740 (2)	5·34
C(16)	7117 (6)	−713 (4)	6591 (3)	6·06
O(17)	6724 (7)	163 (4)	6238 (2)	4·92
C(18)	7877 (7)	501 (4)	5918 (2)	4·91
C(19)	7371 (7)	1032 (4)	5406 (2)	5·04
N(20)	5587 (7)	1178 (4)	5229 (2)	4·77
O(21)	4656 (7)	1345 (4)	5592 (2)	5·62
O(22)	8324 (6)	4063 (3)	5791 (2)	8·84
C(23)	6170 (7)	3695 (3)	4819 (2)	3·71
C(24)	4956 (7)	3701 (3)	4350 (3)	5·99
C(25)	3316 (9)	3678 (4)	4432 (2)	5·96
C(26)	2838 (8)	3659 (4)	4976 (2)	4·51
C(27)	9572 (6)	356 (4)	6057 (3)	6·28
C(28)	10647 (7)	745 (4)	5713 (2)	7·43
C(29)	10137 (7)	1277 (4)	5220 (3)	6·40
C(30)	8456 (8)	1409 (4)	5050 (3)	3·16
O(31)	5079 (8)	1137 (4)	4708 (2)	6·95

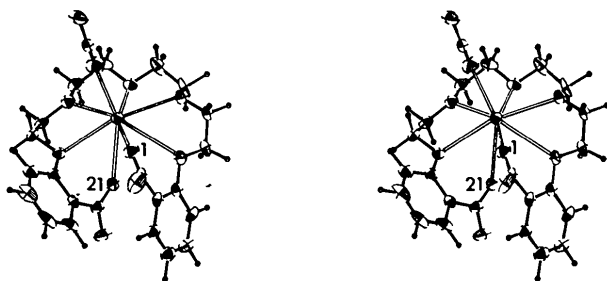Fig. 2. Bond distances (Å) and angles (°) and coordination distances (Å) for (I).

Fig. 3. A stereoplot of (I) (Johnson, 1965). Note mutual stacking of benzene rings and nitro groups.

Atomic coordinates are given in Table 1.* The chemical structure and numbering scheme are presented in Fig. 1 together with torsion angles defining the conformation of the oligoether chain. Bond angles and distances with e.s.d.'s obtained from the correlation matrix are entered in Fig. 2 and Fig. 3 is a stereodiagram showing the molecular structure.

Discussion. As shown in Fig. 3, K^+ is eightfold coordinated to N of SCN^-, to all the O atoms of the oligoether chain and to one O of each nitro group. The ligand is wound into a helical form, as is similarly observed for other complexes of cations with linear oligoethers (Suh, Weber & Saenger, 1978; Weber & Saenger, 1979; Saenger, Brand, Vögtle & Weber, 1977). The two 2-nitrophenoxy residues are stacked intramolecularly in an antiparallel mode such that the nitro and benzene groups overlap, Fig. 3. The two nitro–benzene interactions are not equivalent because distances from the planes of the two benzene rings attached at O(5), O(17) to the opposite nitro group are different. For the O(5) plane, distances are O(21) 3·070 (6), N(20) 3·326 (5), O(31) 3·408 (6) Å, while for the O(17) plane these are O(1) 3·499 (6), N(2) 3·516 (6), O(22) 3·917 (7) Å. The two benzene rings are not parallel but make an angle of 30·0 (2)°. In the unit cell, molecules are packed such that nitrophenoxy groups can stack intermolecularly.

Owing to steric repulsion by the *ortho* substituents O(5) and O(17), the nitro groups are rotated from the benzene planes by 34·7 (5) and 38·0 (7)°. Along the oligoether chain the conformation is as observed previously, with O–C–C–O torsion angles (±)-*gauche* while angles C–C–O–C and C–O–C–C are *trans*, Fig. 1. The angle C(6)–C(7)–O(8)–C(9), −95·9 (5)°, clearly deviates from the *trans* form, probably resulting from the structural constraints of the nitrobenzene stacking. A similar situation was found in an oligo-

ether–cation complex with stacked quinaldine heterocycles (Weber & Saenger, 1980a).

The bond distances and angles in the ligand display some peculiarities in the benzene groups. The geometry of the oligoether chain is normal, although the angle C(7)–O(8)–C(9), 115·5 (4)°, is more obtuse than usual and indicates some steric strain, as does the torsion angle C(6)–C(7)–O(8)–C(9) described above. In the nitrophenyl groups the relatively obtuse angles C(26)–C(4)–O(5), 125·0 (5)°, and C(27)–C(18)–O(17), 124·5 (4)°, may demonstrate a repulsion between C(26)–H, C(27)–H of the aromatic rings and methylene groups C(6)H₂, C(16)H₂. Of interest are the endocyclic angles in both benzene rings: ~123° at the nitro-substituted C(3) and C(19) as well as at the *para* positions C(25) and C(28); this is in contrast to the relatively small angles at the O-substituted C(4), 116·5 (5)°, and C(18), 115·9 (4)°.

From the sums of the ionic and van der Waals radii, the $K^+ \cdots O$ and $K^+ \cdots N$ distances should be 2·73 and 2·83 Å. The corresponding data entered in Fig. 3 show that $K^+ \cdots NCS^-$ is considerably shorter than 2·83 Å, probably as a result of the negative charge associated with SCN^- which renders this interaction more of the ionic–ionic type, rather than ionic–dipole. The $K^+ \cdots O$ distances are all greater than 2·73 Å. As discussed previously (Saenger, Brand, Vögtle & Weber, 1977), the cation $\cdots O$ distances to oxygens attached to aromatic systems are, in general, longer than those to aliphatic O atoms. This can be explained by the higher electronegativity of the latter compared with that of the former. In this complex, the electronegativities of O(5) and O(17) should be especially low due to the nitro groups substituted in *ortho* positions and, indeed, the $K^+ \cdots O(5)$ and O(17) distances, 3·217 (3) and 2·910 (3) Å, are the longest observed for the K^+ coordination in this structure.

As in other complexes between cations and linear oligoethers, some of the coordinated O atoms are located within a plane. The best plane in the complex is defined by atoms O(1), O(8), O(11), O(14) and K^+, with deviations of −0·019 (1), 0·047 (2), −0·062 (3), 0·040 (2) and −0·007 (2) Å respectively. The SCN^- anion is oriented nearly perpendicular to this plane and the other O atoms O(5), O(17) and O(21) deviate by −1·403 (4), 0·908 (7) and −2·530 (5) Å respectively.

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* Lists of structure factors, anisotropic thermal parameters and H-atom coordinates have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 35038 (16 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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