tural data of saturated aliphatic compounds with extensive Cl substitution have suggested paraffinic C-Cl bond lengths for mono- and di-substituted carbon of 1.788 and 1.772 Å, respectively (Bart, Bassi & Calcaterra, 1979). The C-Cl bond distances in (I) differ significantly, namely 1.802 (4) and 1.772 (7) Å on average (range 1.765-1.779 Å) for mono- and disubstituted C atoms, respectively, and confirm the trend for the aforementioned variety of small molecules determined by various techniques, mainly in the gas phase.

The shortest intermolecular distances for $C \cdots Cl$, $C \cdots C$, $C \cdots H$, $Cl \cdots Cl$, $Cl \cdots H$ and $H \cdots H$ are 3.61, >4.0, 3.87, 3.40, 2.94 and 3.01 Å as compared with the expected van der Waals distances of 3.55, 3.60, 3.00, 3.50, 2.95 and 2.40 Å, respectively. Noteworthy is the absence of $C \cdots C$, $C \cdots H$ and $H \cdots H$ contacts, indicating that the crystal packing is mainly governed by Cl atoms, as is also clearly visible in the arrangement of the chlorocarbon (I) in the unit cell (Fig. 2).

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Structures of Polyether Complexes.

XI.* A Pseudo-Binuclear Complex Formed by a Linear Oligoether and a Neutral Guest Molecule: Bis[(8-quinolyloxy)ethoxyethyl] Ether-Thiourea

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Abstract

 $C_{26}H_{28}N_2O_5$. CH_4N_2S is monoclinic, $P2_1/c$, with $a = 13 \cdot 291$ (3), $b = 13 \cdot 080$ (4), $c = 16 \cdot 075$ (5) Å, $\beta = 103 \cdot 20$ (9)°, $M_r = 524 \cdot 64$, Z = 4, $d_c = 1 \cdot 281$, m.p. = 415 K, $\mu = 1 \cdot 389$ mm⁻¹. The thiourea molecule is hydrogen bonded through two N-H-N and one N-H-O(ether) interaction with three of the seven hetero-atoms of the ligand. The remaining four O atoms interact only weakly with the thiourea. The ligand displays an S-like configuration with each S loop wrapping around one N atom of the thiourea. This is similar to a binuclear linear oligoether complex.

Introduction

The ability of linear polyethers to form stable complexes with alkali- and alkaline-earth-metal cations is well known (Tümmler, Maass, Weber, Wehner & Vögtle, 1977; Vögtle & Sieger, 1977). With polar neutral guest molecules, however, complexes are mostly observed with cyclic crown ethers (Knoechel, Kopf, Oehler & Rudolph, 1978; Goldberg, 1975).

In a stoichiometric complex of quinol and urea (Mahmoud & Wallwork, 1975), the rather acidic OH groups are involved in hydrogen bridges, but hydrogen bonds to O atoms of linear polyethers have only seldom been reported (Suh & Saenger, 1978).

Since the structure of a complex of the title ligand with RbI has been published previously (Saenger & Brand, 1979) and since the distances $Rb^+ \cdots O$ (2.87

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^{*} Part X: Weber & Saenger (1980).

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Å) (Handbook of Chemistry and Physics, 1974) and N...O in hydrogen bridges (2.88 Å) (International Tables for X-ray Crystallography, 1968) are nearly identical, it seemed worthwhile to study the structure of the hydrogen-bonded complex of bis[(8-quinolyloxy)-ethoxyethyl] ether and thiourea.

Experimental

Colourless platelets were obtained upon slow cooling of a hot saturated solution of the title compound in a mixture of methanol and acetone (Rasshofer & Vögtle, 1978). Intensities for 3933 unique reflexions with $2\theta \le$ 123° were collected from a crystal 0.5 × 0.5 × 0.1 mm mounted on a four-circle diffractometer set in the θ -2 θ step-scan mode using Ni-filtered Cu K α radiation. Data were corrected for Lp but not for absorption effects.

The structure was solved by a straightforward application of MULTAN (Main, Lessinger, Woolfson, Germain & Declercq, 1977); all the non-hydrogen atoms were located in the E map based on the most self-consistent set of phases (374 E values ≥ 1.7). After several cycles of full-matrix least-squares refinement (Sheldrick, 1976) with a weighting scheme based on counter statistics (Stout & Jensen, 1968) H-atom positions could be located from a three-dimensional Fourier difference map. H-atom positions of the ligand were recalculated according to stereochemical considerations and along with the H atoms of the thiourea they were treated as 'riding atoms' (Sheldrick, 1976). Application of an extinction correction [x =0.0103 (2)] (Sheldrick, 1976) led to a final $R_{w} = 0.054$ with all data included.

Results and discussion

The chemical structure, the numbering scheme, torsion angles along the oligoether chain and distances and angles of the hydrogen bridges are given in Fig. 1.



Fig. 1. Chemical structure, numbering scheme, torsion angles $(\pm 3^{\circ})$, distances (Å) $(\pm 0.03$ Å) and angles (in italics) $(\pm 0.3^{\circ})$ in hydrogen bridges. H atoms of thiourea indicated by 1 or 2 are referred to as H' or H", respectively, in the tables and in the text.

Table 1. Fractional atomic coordinates $(\times 10^4)$ of non-hydrogen atoms and H atoms and their isotropic B values (e.s.d.'s ca 0.1-0.2 Å²) calculated from anisotropic U values

	х	у	Ζ	B (Å ²)
N(1)	8899 (2)	8468 (2)	1830 (2)	5.0
C(2)	9286 (3)	9234 (3)	1461 (3)	6.3
C(3)	10005 (3)	9919 (3)	1904 (3)	8.2
C(4)	10343 (3)	9829 (3)	2747 (3)	7.9
C(5)	10187 (4)	8902 (4)	4078 (4)	10.4
C(6)	9788 (4)	8149 (4)	4468 (3)	9.9
C(7)	9045 (3)	7471 (3)	3964 (2)	6.9
C(8)	8778 (2)	7569 (2)	3099 (2)	4.8
C(9)	9222 (2)	8370 (2)	2686 (2)	4.9
C(10)	9949 (3)	9043 (3)	3196 (3)	7.0
O(11)	8081 (1)	6973 (1)	2558 (1)	4.5
C(12)	7418 (3)	6316 (2)	2918 (2)	5.2
C(13)	6534 (2)	5992 (2)	2226 (2)	5.1
O(14)	6896 (1)	5338 (1)	1650 (1)	4.6
C(15)	6055 (2)	4850 (2)	1079 (2)	5.2
C(16)	6481 (3)	4210 (2)	469 (2)	5.4
O(17)	6791 (2)	4862 (1)	-142 (1)	5.0
C(18)	7176 (3)	4296 (2)	-766 (2)	5.8
C(19)	7331 (2)	5002 (3)	-1455 (2)	5.2
O(20)	6346 (1)	5253 (1)	-1962 (1)	4.7
C(21)	6407 (2)	5874 (2)	-2678 (2)	4.6
C(22)	5340 (2)	6051 (2)	-3185 (2)	4.6
O(23)	4849 (1)	6718 (1)	-2687 (1)	4.5
C(24)	3813 (2)	6844 (2)	-2930 (2)	3.7
C(25)	3185 (3)	6428 (2)	-3645 (3)	4.6
C(26)	2114 (3)	6590 (3)	-3807 (2)	5.5
C(27)	1673 (3)	7148 (2)	-3268 (2)	5.4
C(28)	1910 (3)	8153 (2)	-1927 (2)	5.4
C(29)	2569 (3)	8586 (3)	-1250 (2)	5.6
C(30)	3623 (3)	8437 (2)	-1145 (2)	4.9
N(31)	4040 (2)	7879 (2)	-1670 (1)	4.2
C(32)	3383 (2)	7454 (2)	-2359 (2)	3.7
C(33)	2304 (2)	7576 (2)	-2526 (2)	4.4
S(34)	6580 (1)	8992 (1)	-90 (1)	5.0
C(35)	6674 (2)	7697 (2)	-60 (2)	4.1
N(36)	6085 (2)	7128 (2)	-661 (1)	4∙8
N(37)	7348 (2)	7228 (2)	557 (2)	5.2
H′(N36)	5464 (2)	7363 (2)	-1056 (1)	4.7
H"(N36)	6163 (2)	6431 (2)	-645 (1)	4.7
H′(N37)	7398 (2)	6560 (2)	596 (2)	5.2
H"(N37)	7775 (2)	7593 (2)	989 (2)	5.2

Fractional atomic coordinates are listed in Table 1,* bond distances and angles in Tables 2 and 3, respectively. A stereoscopic view of the complex is shown in Fig. 2.

Wrapping of the ligand

In the present conformation of the ligand no stereochemical restrictions are violated. All C-C-O-C and C-O-C-C torsion angles along the ether chain are

^{*} Lists of structure factors, anisotropic thermal parameters and H-atom positions have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 34835 (27 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 non-hydrogen atoms of
	the ligand and the thiourea molecule

N(1)-C(2)	1.327 (5)	C(21)–C(22)	1.483 (4)
N(1) - C(9)	1.350 (5)	C(22)-O(23)	1.438 (4)
C(2) - C(3)	1.382 (5)	O(23) - C(24)	1.353 (3)
C(3) - C(4)	1.331 (8)	C(24) - C(25)	1.370 (4)
C(4) - C(10)	1.423 (7)	C(24) - C(32)	1.430 (4)
C(5) - C(6)	1.341 (8)	C(25) - C(26)	1.403 (5)
C(5) - C(10)	1.394 (8)	C(26) - C(27)	1.363 (5)
C(6) - C(7)	1.433 (6)	C(27) - C(33)	1.409 (4)
C(7) - C(8)	1.360 (5)	C(28) - C(29)	1.357 (4)
C(8) - C(9)	1.437(5)	C(28) - C(33)	1.413 (5)
C(8) = O(11)	1.363 (3)	C(29) - C(30)	1.386 (5)
C(9) - C(10)	1.420(5)	C(30) - N(31)	1.329 (4)
O(11) - C(12)	1.443(4)	N(31) - C(32)	1.363 (3)
C(12) - C(13)	1.483 (4)	C(32) - C(33)	1.406 (4)
C(13) = O(14)	1.423(4)	S(34) - C(35)	1.699 (3)
O(14) - C(15)	1.425 (3)	C(35) - N(36)	1.325 (3)
C(15) - C(16)	1.495 (5)	C(35) - N(37)	1.326(3)
C(16) - O(17)	1.431 (4)	N(36) - H'(N36)	0.969(3)
O(17) - C(18)	1.433 (4)	N(36) - H''(N36)	0.917(3)
C(18) - C(19)	1.493 (5)	N(37) - H'(N37)	0.877(3)
C(10) = O(20)	1.414(3)	N(37) - H''(N37)	0.024(3)
O(20) - O(21)	1.426(4)	$(37)^{-11}(137)$	0.724 (3)
U(20) = U(21)	1-420 (4)		



Fig. 2. Stereoscopic view (Johnson, 1965) of the complex.

 Table 3. Bond angles (°) of non-hydrogen atoms of the ligand and the thiourea molecule

C(2)-N(1)-C(9)	117.5 (3)	C(21)-C(22)-O(23)	106.7 (2)
N(1)-C(2)-C(3)	123-5 (4)	C(22)-O(23)-C(24)	118.4 (2)
C(2)-C(3)-C(4)	120.0 (4)	O(23)-C(24)-C(25)	125-3 (3)
C(3)-C(4)-C(10)	120-1 (4)	O(23)-C(24)-C(32)	114-4 (2)
C(6)-C(5)-C(10)	123-5 (5)	C(25)-C(24)-C(32)	120-2 (3)
C(5)-C(6)-C(7)	119-1 (4)	C(24)-C(25)-C(26)	119.6 (3)
C(6) - C(7) - C(8)	120.3 (4)	C(25)-C(26)-C(27)	121.8 (3)
C(7)-C(8)-C(9)	120-2 (3)	C(26)-C(27)-C(33)	119.5 (3)
C(7)-C(8)-O(11)	125-4 (3)	C(29)-C(28)-C(33)	119.8 (3)
C(9)-C(8)-O(11)	114-4 (3)	C(28)-C(29)-C(30)	119-2 (3)
N(1)-C(9)-C(8)	118.1 (3)	C(29)-C(30)-N(31)	123.8 (3)
N(1)-C(9)-C(10)	123.0 (3)	C(30)-N(31)-C(32)	117-2 (3)
C(8)-C(9)-C(10)	118-8 (3)	C(24)-C(32)-N(31)	118-2 (3)
C(4)-C(10)-C(5)	126.0 (4)	C(24)-C(32)-C(33)	118.8(2)
C(4)-C(10)-C(9)	115-8 (4)	N(31)-C(32)-C(33)	123.0(3)
C(5)-C(10)-C(9)	118-1 (4)	C(27)-C(33)-C(28)	123-2 (3)
C(8)-O(11)-C(12)	118-3 (2)	C(27)-C(33)-C(32)	120-0 (3)
O(11)-C(12)-C)13)	108-7 (2)	C(28)-C(33)-C(32)	116-8 (2)
C(12)-C(13)-O(14)	109-4 (3)	S(34)-C(35)-N(36)	120.8 (2)
C(13)-O(14)-C(15)	110.9 (2)	S(34)-C(35)-N(37)	121.0 (2)
O(14)-C(15)-C(16)	108-3 (3)	N(36)-C(35)-N(37)	118-1 (2)
C(15)-C(16)-O(17)	109-1 (2)	C(35)–N(36)–H'(N36)	124.9 (3)
C(16)-O(17)-C(18)	112-2 (2)	C(35)-N(36)-H"(N36)	119-6 (3)
O(17)-C(18)-C(19)	109-4 (3)	H'(N36)-N(36)-H''(N36)	114-1 (3)
C(18)-C(19)-O(20)	107.7 (3)	C(35)—N(37)—H'(N37)	122.8 (3)
C(19)-O(20)-C(21)	112-4 (2)	C(35)-N(37)-H''(N37)	121-2 (3)
O(20)-C(21)-C(22)	108.0 (2)	H'(N37)-N(37)-H''(N37)	115-9 (3)

trans and O-C-C-O torsion angles are gauche. Widened O(23)-C(24)-C(25) and C(22)-O(23)-C(24) bond angles as well as C(7)-C(8)-O(11) and C(8)-O(11)-C(12) may reflect steric repulsion between C(22) and C(25) and between C(7) and C(12).

In the complex of the title ligand with RbI, the host molecule wraps around the cation in a helical manner such that Rb^+ is coordinated by all the hetero-atoms (Saenger & Brand, 1979). In the present complex the ligand also fits its conformation to the geometry of the guest molecule. Major differences between the Rb^+ complex and the title compound are: the ligand of the latter (1) is wrapped in a more elongated configuration because of the larger 'diameter' of the thiourea molecule ($r_{\rm Rb^+} = 1.47$ Å; 'radius' of thiourea $\simeq 1.9$ Å) and (2) adopts an S-like configuration as in a binuclear oligoether complex (Weber & Saenger, 1979) because there are *two* NH₂ groups, each of which can accept electrons from the donor atoms.

In the RbI complex of the title ligand (Saenger & Brand, 1979) the five hetero atoms are coplanar and form part of a circle with r = 2.85 Å. Rb⁺ deviates by 0.75 Å from this plane, and thus the mean Rb⁺... hetero-atom distance is 2.95 Å, *i.e.* slightly longer than the ideal value.

In the present complex each S loop can be considered as a semicircle on which hetero-atoms are arranged; the approximate centres of the circles are each occupied by one NH₂ group of thiourea (in order to clarify the pseudo-binuclear character of the present complex both the RbI and thiourea complexes are superimposed in Fig. 3). N(1), O(11), O(14) and O(17)are coplanar within ± 0.11 Å and lie on a circle with r = 3.03 Å. N(37) deviates by 0.9, H'(N37) by 0.4 and H"(N37) by 0.7 Å from this plane. The mean N(37)...hetero-atom distance is 3.17 Å, *i.e.* about 0.2 A longer than the respective Rb⁺...hetero-atom distance observed (Saenger & Brand, 1979). The second circle with a mean r = 2.78 Å is formed by hetero-atoms O(17), O(20), O(23) and N(31) which are coplanar within 0.12 Å. However, N(36) deviates by 1.3, H'(N36) by 0.9 and H''(N36) by 0.8 Å from this second plane, and therefore the mean N(36)...heteroatom distance increases to 3.06 Å (Rb⁺...heteroatoms = 2.95 Å). The dihedral angle between the planes of the circles of the S loops is $73 (3)^{\circ}$.



Fig. 3. A comparison of bis[(8-quinolyloxy)ethoxyethyl] etherthiourea (shaded) and the RbI analogue. Molecules are superimposed such that one of the quinoline groups in one molecule overlaps as much as possible with that in the other molecule; Rb⁺ is drawn as a solid sphere. In the upper figure, the quinoline at the right and the attached chains of the two molecules are superimposed. The main deviation occurs at the C-C torsion angle indicated by an arrow which changes from (+) gauche in the RbI complex to (-) gauche in the thiourea complex. In the lower figure, the other quinolines are superimposed and the deviation occurs at a C-O torsion angle which in the thiourea complex is trans but adopts an unusual (+) gauche conformation in the RbI complex.

In contrast to a true binuclear oligoether complex (Weber & Saenger, 1979) where the two loops of the S are related by twofold crystallographic symmetry, the different radii of both circles of the present complex express the lack of symmetry. This is also indicated by the dihedral angles between the thiourea and the first circle N(1)–O(17), 110 (3)°, and the thiourea and the second circle O(17)–N(31), 118 (3)°.

Hydrogen bonds

According to the sums of the van der Waals radii, distances $O \cdots O$ should be about 2.8, $N \cdots O$ about 2.9, $H \cdots N$ less than 2.7 and $H \cdots O$ less than 2.6 Å in the hydrogen bridges. From the distances of N(36) to O(17) $[3 \cdot 162 (3) \text{ Å}]$, to O(20) $[3 \cdot 292 (3) \text{ Å}]$, to O(23) $[3 \cdot 339 (3) \text{ Å}]$ and to N(31) $[2 \cdot 995 (3) \text{ Å}]$, and of N(37) to N(1) $[3 \cdot 024 (3) \text{ Å}]$, to O(11) $[3 \cdot 159 (3) \text{ Å}]$, to O(14) $[3 \cdot 168 (3) \text{ Å}]$ and to O(17) $[3 \cdot 317 (3) \text{ Å}]$ it can be seen that there are few really strong hydrogen-bond bridges. These weak interactions are also indicated by the respective H…N and H…O distances (see Fig. 1).

H-atom parameters determined by X-ray methods are normally of low accuracy. Therefore, the H-atom positions of thiourea were calculated according to the geometry of thiourea obtained from neutron scattering data (Elcombe & Taylor, 1968). However, distances and angles in hydrogen bridges calculated with these 'theoretical' H positions did not differ substantially from those located by Fourier syntheses. Hydrogen bonds exist between H'(N36) and N(31), between H''(N37) and N(1) and probably between H''(N36)and O(17). No interactions are evident for $H'(N36)\cdots$ O(23) and $H''(N36) \cdots O(20)$ (distances >2.6 Å). Very weak interactions might be assumed between H'(N37) and O(17), O(14) and between H''(N37) and O(11), since the distances are approximately equal to the sum of the van der Waals radii. From these distances one might regard $H''(N37)\cdots N(1)$ and $H''(N37)\cdots O(11)$ as well as $H'(N37)\cdots O(14)$ and $H'(N37)\cdots O(17)$, in one S loop, as bifurcated hydrogen bonds, whereas in the second S loop there are only two 'normal' hydrogen bonds. This also reflects the asymmetry of the complex.

It is noteworthy that there are no interligand hydrogen bonds and that each thiourea molecule complexes with only one ligand molecule. Further, the molecular packing precludes stacking interactions between the quinoline groups.

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The Structures of Two 2-Acyl-1,3-indandiones

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Abstract

Crystals of 2-pivaloyl-1,3-indandione are monoclinic, space group $P2_1/m$, with two molecules positioned on mirror planes in a cell with dimensions a = 8.411 (3), b = 6.897 (6), c = 10.522 (4) Å, $\beta = 105.22$ (3)°; while crystals of 2-acetyl-1,3-indandione are monoclinic, space group $P2_1/n$, with four molecules in a cell of dimensions a = 5.305(3), b = 7.314(2), c = 23.214(10) Å, $\beta = 94.94$ (4)°. Both structures were solved via MULTAN, and each refined to a conventional R value of 0.038. Both compounds are in the enol form in the solid state, with the enolic H external to the indan system. Considerable steric strain is noted in the pivaloyl derivative due to the bulk of the tert-butyl group, and yet this compound is found to have a higher degree of delocalization (stronger internal hydrogen bonding) than the acetyl derivative. NMR and IR spectral analyses, as well as chemical-reactivity studies, support this conclusion derived from the single-crystal X-ray results. The indan portions of both molecules are essentially planar.

Introduction

The reaction of 2-acyl-1,3-indandiones with hydrazine leading to substituted indeno[1,2-c]pyrazol-4(1H)-ones

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has been extensively studied by Mosher & Meier (1970), Mosher, El-Zimaity & Lipp (1971), Mosher & Banks (1971), Mosher, Serridge & Lipp (1972) and Braun & Mosher (1958, 1959). Since the cyclization of β -ketoesters with thiosemicarbazides leads to triazepinones (Losse, Hessler & Barth, 1958) an attempt was made to prepare new and unique tricyclic heterocycles starting from 2-acyl-1,3-indandiones (1). When 2pivaloyl-1,3-indandione (1a) was treated with thiosemicarbazide in aqueous sodium carbonate, the expected product (2) did not form; instead, 1-hydroxy-4-methylphthalazine (3) was recovered (Lemke & Parker, 1976). However, when the same reaction was attempted with 2-benzoyl-1,3-indandione (1b) or with 2acetyl-1,3-indandione (1c), none of the retro-Claisen condensation product (3) formed. These results suggest important differences in molecular structure for compounds (1a) and (1b,c).



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