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Structures of Polyether Complexes. XXII.* 1-Phenoxy-11-(8-quinolyloxy)-3,6,9-trioxaundecane–Potassium Thiocyanate Monohydrate, $C_{23}H_{27}NO_5.KSCN.H_2O$ (I), and 1-(1-Naphthyloxy)-11-(8-quinolyloxy)-3,6,9-trioxaundecane–Potassium Thiocyanate, $C_{27}H_{29}NO_5.KSCN$ (II)

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Abstract. (I): $M_r = 512\cdot7$, triclinic, $P\bar{1}$, $a = 11\cdot637$ (3), $b = 12\cdot284$ (3), $c = 9\cdot349$ (2) Å, $\alpha = 93\cdot10$ (3), $\beta = 89\cdot40$ (3), $\gamma = 108\cdot70$ (3)°, $V = 1264\cdot0$ Å^3, $Z = 2$, $D_x = 1\cdot347$ Mg m^{-3}, Cu $K\alpha$, $\lambda = 1\cdot5418$ Å, $\mu = 2\cdot918$ mm^{-1}, $T = 295$ K, $F(000) = 540$, $R = 4\cdot6\%$, 3813 observed reflections. (II): $M_r = 544\cdot7$, orthorhombic, $Pna2_1$, $a = 8\cdot389$ (2), $b = 14\cdot344$ (3), $c = 22\cdot159$ (5) Å, $V = 2666\cdot4$ Å^3, $Z = 4$, $D_x = 1\cdot357$ Mg m^{-3}, λ(Cu $K\alpha$) = $1\cdot5418$ Å, $\mu = 2\cdot774$ mm^{-1}, $T = 295$ K, $F(000) = 1144$, $R = 3\cdot4\%$, 2057 observed reflections. In complex (I) the ligand wraps around the K^+ cation in a nearly circular manner such that five of the six heteroatoms (in addition to the thiocyanate N and the water molecule) are coordinated to the cation. The terminal phenoxy group points away from this circle so that the benzene and quinoline rings form a dihedral angle of 83°. In complex (II) all six heteroatoms of the ligand (in addition to the N of the anion) are coordinated around the cation. The ligand forms a helical structure with the quinoline and naphthalene rings stacked parallel to each other (dihedral angle 1·1°). The incomplete coordination of polyether O atoms in (I) is explained with the failure, due to sterical reasons, of benzene stacking with quinoline.

Introduction. The stability of linear polyether complexes with alkali and alkaline-earth metal ions is known to be significantly influenced by the terminal groups attached to the chain (*e.g.* Vögtle & Weber, 1979; Saenger, Suh & Weber, 1979; Hilgenfeld & Saenger, 1982). The polyethers can be divided into three classes (Hilgenfeld & Saenger, 1982; Hilgenfeld *et al.*, 1984) according to the type of terminal groups, as follows:

(*a*) ligands with terminal aromatic donor groups;

(*b*) ligands with terminal groups capable of hydrogen bonding;

(*c*) ligands without terminal donor groups.

Type (*a*) ligands form alkali metal ion complexes of much higher stability than do, for example, type (*c*) polyethers (Tümmler, Maass, Vögtle, Sieger, Heimann & Weber, 1979). This has been ascribed to the possible function of rigid aromatic donor groups as centres of nucleation of the binding process. To test this hypothesis, ligands having a strong aromatic donor group only at one end are of interest. The closely related phenyl and naphthyl analogues (Heimann & Vögtle, 1978) were chosen in this work to assess their influences on the complexation.

Experimental. The colourless title complexes were recrystallized from a mixture of ethyl acetate and petroleum ether. D_m not determined. Lattice parameters from 15 intermediate $\sin\theta$ axial reflections. 4256 [443 < $2\sigma(I)$] and 2298 [241 < $2\sigma(I)$] unique reflections for complexes (I) and (II), respectively, collected on an automated Stoe four-circle diffractometer. Ni-filtered Cu $K\alpha$ radiation, θ–2θ step-scan mode, $2\theta \leq 130°$. For (I) *hkl* −13,−14,0 to 13,14,0; for (II) *hkl* 0,0,0 to 9,16,25. Two standard reflections for (I), intensity decrease <5%; one standard for (II), decrease <3%. Data corrected for Lorentz–polarization factors but not for absorption. Structures solved by application of *MULTAN*80 (Main *et al.*, 1980) and refined by full-matrix least squares. All H-atom positions except those of the water molecule in complex (I) could be located from difference syntheses. $\sum w\big||F_o| - |F_c|\big|^2$ minimized with the weighting scheme: $w = 0$ if $|F_c| < 0\cdot5|F_o|$, else $w = XY$, where $X = 1$ if $\sin\theta > 0\cdot58$, else $w = \sin\theta/0\cdot58$ and $y = 1$ if $|F_o| < 4\cdot0$, else $Y = 4\cdot0/|F_o|$ for complex (I); the same weighting scheme was

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* For part XXI see Weber, Hirayama, Saenger & Sheldrick (1984).

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applied to complex (II) except that the $|F_o|$ limit of 4·0 was replaced by 8·0; a final inspection of the average $w||F_o| - |F_c||^2$ as a function of $\sin\theta$ and $|F_o|$ gave no indication of any bias. The final R values are 4·6% (R_w 6·1%) and 3·4% (R_w 4·5%) for complexes (I) and (II). For (I) $(\Delta/\sigma)_{\max} = 0{\cdot}4$, for (II) 0·9. For (I) $\Delta\rho$ peaks $-0{\cdot}2$ to $0{\cdot}204\ \text{e Å}^{-3}$, for (II) $-0{\cdot}2$ to $0{\cdot}15\ \text{e Å}^{-3}$. Secondary-extinction value $g = 0{\cdot}71 \times 10^{-3}$ for (I) and $1{\cdot}44 \times 10^{-3}$ for (II). Scattering factors from *International Tables for X-ray Crystallography* (1974) and corrections for anomalous dispersion from Cromer & Liberman (1970). The *XRAY*76 system (Stewart, Machin, Dickinson, Ammon, Heck & Flack, 1976) was used for all refinement procedures.*

Discussion. Final atomic parameters, bond distances and angles are presented in Tables 1, 2 and 3. Torsion angles are given in Table 4. Plots depicting the numbering scheme, coordination distances and stereoviews of the two complexes are shown in Figs. 1 and 2. A structural comparison between the ligands (I) and (II) is illustrated in Fig. 3, and Fig. 4 shows the crystal packing.

The wrapping mode of linear polyether ligands around cations is dependent on their lengths. Short ligands with five heteroatoms form circular structures while extension by one to five heteroatoms leads to helical structures. Very long ligands can wrap around two cations in an S-like configuration (Saenger, Suh & Weber, 1979).

The structures of the present complexes are significantly different from each other in spite of the same number of heteroatoms of the ligands. In complex (I) five heteroatoms of the ligand (in addition to the anion and the water molecule) coordinate to the cation in a circular manner: N(1), O(4), O(7) and O(10) are coplanar within ±0·2 Å; O(13) and the K^+ cation deviate by −0·67 and 0·43 Å from this plane, respectively. The atom O(16) does not participate in any interactions with the cation because the terminal phenoxy group points away from this circle and the ligand is not able to adopt a helical configuration. This arrangement is achieved by a change of the O(13)—C(14)—C(15)—O(16) torsion angle from the (−)*gauche* to the (+)*gauche* conformation. Thus, the sequence of torsion angles of the ligand is $(a\ ag^{+}a\ ag{-}a\ ag{+}a\ ag{+}a\ a)$ counted from O(4) to O(16), a conformation which forces the quinoline and benzene rings to be perpendicular to each other with a dihedral angle of 83°.

On the other hand, all six heteroatoms of the ligand in complex (II) (in addition to the N of the anion) coordinate to the cation and the ligand adopts a helical structure: O(4), O(7), O(19) and O(13) are coplanar

Table 1. *Fractional atomic coordinates* (×10⁴) *and equivalent isotropic thermal parameters* (Å² ×10²)

$$U_{\rm eq} = \tfrac{1}{3}\textstyle\sum_i\sum_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	$U_{\rm eq}$
Complex (I)				
K	8000 (1)	4832 (1)	7814 (1)	6·2 (1)
S	8775 (1)	736 (1)	7921 (1)	11·4 (1)
C	8931 (2)	2079 (3)	8116 (3)	7·6 (1)
N	9050 (3)	3059 (3)	8234 (4)	11·2 (1)
O(*W*)	10318 (4)	5650 (5)	8971 (6)	20·3 (3)
N(1)	6646 (2)	3904 (1)	10276 (2)	5·4 (1)
C(2)	6101 (2)	4528 (2)	11137 (2)	4·9 (1)
C(3)	6503 (2)	5749 (2)	11069 (2)	5·0 (1)
O(4)	7406 (1)	6186 (1)	10116 (2)	5·5 (1)
C(5)	7858 (3)	7417 (2)	10075 (3)	6·2 (1)
C(6)	8847 (2)	7732 (2)	8998 (3)	6·2 (1)
O(7)	8373 (1)	7248 (1)	7628 (2)	5·7 (1)
C(8)	9203 (2)	7676 (2)	6512 (3)	6·2 (1)
C(9)	8698 (2)	7034 (2)	5136 (3)	6·1 (1)
O(10)	8628 (1)	5867 (1)	5235 (1)	5·3 (1)
C(11)	8130 (2)	5205 (2)	3959 (2)	5·8 (1)
C(12)	8165 (2)	4010 (2)	4040 (3)	5·7 (1)
O(13)	7321 (1)	3415 (1)	5072 (2)	5·3 (1)
C(14)	7231 (2)	2230 (2)	5032 (3)	5·7 (1)
C(15)	6306 (2)	1624 (2)	6077 (3)	5·7 (1)
O(16)	5130 (1)	1454 (1)	5491 (2)	6·0 (1)
C(17)	4150 (2)	960 (2)	6328 (3)	5·5 (1)
C(18)	3021 (2)	815 (2)	5725 (3)	6·7 (1)
C(19)	1984 (2)	357 (2)	6497 (4)	7·8 (1)
C(20)	2051 (3)	30 (2)	7870 (4)	8·0 (1)
C(21)	3160 (3)	160 (2)	8465 (3)	7·4 (1)
C(22)	4222 (2)	619 (2)	7704 (3)	6·4 (1)
C(23)	6298 (3)	2787 (2)	10405 (3)	6·5 (1)
C(24)	5404 (3)	2207 (2)	11356 (3)	7·7 (1)
C(25)	4848 (3)	2818 (2)	12209 (3)	7·2 (1)
C(26)	5187 (2)	4018 (2)	12136 (2)	5·7 (1)
C(27)	4694 (2)	4731 (3)	13025 (3)	6·9 (1)
C(28)	5100 (2)	5880 (2)	12936 (3)	7·0 (1)
C(29)	6002 (2)	6405 (2)	11953 (2)	6·1 (1)
Complex (II)				
K	2709 (1)	4948 (5)	5062	5·0 (1)
S	6479 (2)	4946 (1)	5863 (1)	8·2 (1)
C	8122 (6)	4982 (3)	5460 (2)	5·4 (1)
N	9282 (6)	5012 (3)	5181 (3)	7·4 (2)
N(1)	1859 (4)	4595 (2)	3864 (1)	4·8 (1)
C(2)	2677 (4)	3973 (2)	3510 (2)	4·4 (1)
C(3)	3537 (5)	3244 (2)	3801 (2)	4·9 (1)
O(4)	3544 (4)	3272 (2)	4415 (1)	6·0 (1)
C(5)	3672 (8)	2417 (3)	4739 (2)	7·0 (2)
C(6)	3850 (7)	2623 (4)	5388 (2)	6·8 (2)
O(7)	2593 (3)	3183 (2)	5600 (1)	5·3 (1)
C(8)	2533 (8)	3214 (4)	6239 (2)	6·6 (2)
C(9)	1533 (7)	4017 (3)	6438 (2)	6·0 (1)
O(10)	2342 (4)	4852 (2)	6301 (1)	5·4 (1)
C(11)	1513 (6)	5662 (3)	6492 (2)	5·8 (1)
C(12)	2528 (7)	6496 (3)	6344 (2)	6·4 (2)
O(13)	2543 (3)	6631 (2)	5711 (1)	5·2 (1)
C(14)	3498 (7)	7405 (3)	5540 (2)	6·6 (2)
C(15)	3334 (7)	7566 (3)	4878 (2)	6·0 (2)
O(16)	4092 (3)	6793 (2)	4580 (1)	5·3 (1)
C(17)	4157 (4)	6809 (2)	3960 (2)	4·3 (1)
C(18)	3417 (5)	7456 (3)	3608 (2)	5·7 (1)
C(19)	3511 (6)	7372 (3)	2973 (2)	6·0 (1)
C(20)	4335 (5)	6677 (3)	2706 (2)	5·7 (1)
C(21)	6038 (5)	5280 (3)	2805 (2)	5·3 (1)
C(22)	6867 (5)	4666 (3)	3167 (2)	5·5 (1)
C(23)	6820 (5)	4756 (3)	3785 (2)	5·4 (1)
C(24)	5948 (5)	5436 (3)	4059 (2)	4·5 (1)
C(25)	5076 (4)	6078 (2)	3704 (2)	3·9 (1)
C(26)	5144 (4)	6010 (3)	3062 (2)	4·5 (1)
C(27)	1060 (5)	5253 (3)	3585 (2)	5·4 (1)
C(28)	1003 (6)	5378 (4)	2970 (2)	6·4 (2)
C(29)	1840 (6)	4776 (3)	2607 (2)	5·9 (2)
C(30)	2682 (5)	4033 (3)	2874 (2)	5·2 (1)
C(31)	3522 (6)	3369 (4)	2535 (2)	6·4 (2)
C(32)	4295 (6)	2656 (4)	2822 (2)	7·0 (2)
C(33)	4304 (6)	2587 (3)	3454 (2)	6·2 (1)

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* Lists of structure factors, anisotropic temperature factors and H-atom coordinates have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 39737 (41 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 2. *Bond lengths* (Å) *with e.s.d.'s in parentheses*

Complex (I)			
S–C	1·602 (4)	N–C	1·166 (5)
N(1)–C(2)	1·368 (3)	N(1)–C(23)	1·313 (3)
C(2)–C(3)	1·426 (3)	C(2)–C(26)	1·418 (3)
C(3)–O(4)	1·362 (3)	C(3)–C(29)	1·376 (4)
O(4)–C(5)	1·436 (3)	C(5)–C(6)	1·490 (4)
C(6)–O(7)	1·421 (3)	O(7)–C(8)	1·419 (3)
C(8)–C(9)	1·494 (3)	C(9)–O(10)	1·418 (3)
O(10)–C(11)	1·424 (3)	C(11)–C(12)	1·487 (4)
C(12)–O(13)	1·424 (3)	O(13)–C(14)	1·423 (3)
C(14)–C(15)	1·487 (3)	C(15)–O(16)	1·428 (3)
O(16)–C(17)	1·367 (3)	C(17)–C(18)	1·390 (4)
C(17)–C(22)	1·386 (4)	C(18)–C(19)	1·373 (4)
C(19)–C(20)	1·375 (5)	C(20)–C(21)	1·370 (5)
C(21)–C(22)	1·389 (4)	C(23)–C(24)	1·398 (4)
C(24)–C(25)	1·363 (5)	C(25)–C(26)	1·404 (4)
C(26)–C(27)	1·422 (4)	C(27)–C(28)	1·344 (4)
C(28)–C(29)	1·405 (3)		
Complex (II)			
S–C	1·642 (6)	C–N	1·154 (7)
N(1)–C(2)	1·372 (5)	N(1)–C(27)	1·312 (6)
C(2)–C(3)	1·424 (5)	C(2)–C(30)	1·413 (6)
C(3)–O(4)	1·361 (5)	C(3)–C(33)	1·376 (6)
O(4)–C(5)	1·425 (5)	C(5)–C(6)	1·476 (7)
C(6)–O(7)	1·406 (6)	O(7)–C(8)	1·416 (6)
C(8)–C(9)	1·492 (7)	C(9)–O(10)	1·410 (6)
O(10)–C(11)	1·418 (6)	C(11)–C(12)	1·504 (7)
C(12)–O(13)	1·416 (6)	O(13)–C(14)	1·421 (6)
C(14)–C(15)	1·490 (7)	C(15)–O(16)	1·438 (5)
O(16)–C(17)	1·376 (5)	C(17)–C(18)	1·362 (6)
C(17)–C(25)	1·419 (5)	C(18)–C(19)	1·413 (7)
C(19)–C(20)	1·350 (7)	C(20)–C(26)	1·414 (6)
C(21)–C(22)	1·379 (6)	C(21)–C(26)	1·408 (6)
C(22)–C(23)	1·377 (7)	C(23)–C(24)	1·363 (6)
C(24)–C(25)	1·415 (5)	C(25)–C(26)	1·427 (5)
C(27)–C(28)	1·377 (7)	C(28)–C(29)	1·373 (7)
C(29)–C(30)	1·409 (7)	C(30)–C(31)	1·403 (7)
C(31)–C(32)	1·368 (7)	C(32)–C(33)	1·405 (7)

within ±0·1 Å; N(1), O(16) and the cation lie 1·61, 0·61 and −0·27 Å, respectively, out of this plane. The sequence of torsion angles along the oligoether chain is (*a ag+a ag−a ag+a ag−a a*), *i.e.* the signs of the *gauche* angles are strictly alternating. In order to avoid interference of the quinoline and naphthalene rings and to allow their parallel stacking, the torsion angle C(2)–C(3)–O(4)–C(5) of 150° deviates considerably from an ideal antiperiplanar conformation of 180° and gives rise to a helical configuration of the ligand.

The K^+ cation is sevenfold coordinated in both complexes. The distances between the K^+ ion and O atoms in the ligands are in the range 2·77 to 3·08 Å. The average of 2·87 Å is somewhat longer than the sum of the van der Waals radii [1·33 Å for K and 1·4 Å for O (*Handbook of Chemistry and Physics,* 1974)]. Similar results were also obtained in other complexes (Weber & Saenger, 1979; Weber, Hirayama, Saenger & Sheldrick, 1984). The longest coordination distances are to the atoms O(13) and O(16) [2·98 and 3·08 Å in complexes (I) and (II), respectively] and seem to result from the large deviation from the plane of coordination because the adjacent terminal groups of the ligands [phenoxy in (I) and naphthyloxy in (II)] have no anchoring function to cations (type *c*). The anion is coordinated to the K^+ cation through the N atom ($K^+\cdots{}^-N$—C—S) from the opposite site of the phenyl or naphthyl groups, which avoids a steric crowding at one side and facilitates access between anion and cation. In

Table 3. *Bond angles* (°) *with e.s.d.'s in parentheses*

Complex (I)			
S–C–N	178·9 (3)	C(14)–C(15)–O(16)	108·5 (2)
C(2)–N(1)–C(23)	117·4 (2)	C(15)–O(16)–C(17)	117·5 (2)
N(1)–C(2)–C(3)	118·6 (2)	O(16)–C(17)–C(18)	115·8 (2)
N(1)–C(2)–C(26)	122·9 (2)	O(16)–C(17)–C(22)	124·6 (2)
C(3)–C(2)–C(26)	118·5 (2)	C(18)–C(17)–C(22)	119·6 (2)
C(2)–C(3)–O(4)	115·5 (2)	C(17)–C(18)–C(19)	120·2 (3)
C(2)–C(3)–C(29)	120·1 (2)	C(18)–C(19)–C(20)	120·4 (3)
O(4)–C(3)–C(29)	124·4 (2)	C(19)–C(20)–C(21)	119·7 (3)
C(3)–O(4)–C(5)	116·3 (2)	C(20)–C(21)–C(22)	121·0 (3)
O(4)–C(5)–C(6)	108·6 (2)	C(17)–C(22)–C(21)	119·1 (3)
C(5)–C(6)–O(7)	109·3 (2)	N(1)–C(23)–C(24)	123·8 (3)
C(6)–O(7)–C(8)	112·3 (2)	C(23)–C(24)–C(25)	119·2 (3)
O(7)–C(8)–C(9)	108·9 (2)	C(24)–C(25)–C(26)	119·8 (2)
C(8)–C(9)–O(10)	108·6 (2)	C(2)–C(26)–C(25)	116·8 (2)
C(9)–O(10)–C(11)	111·1 (2)	C(2)–C(26)–C(27)	119·4 (2)
O(10)–C(11)–C(12)	110·0 (2)	C(25)–C(26)–C(27)	123·8 (2)
C(11)–C(12)–O(13)	110·3 (2)	C(26)–C(27)–C(28)	120·5 (2)
C(12)–O(13)–C(14)	110·9 (2)	C(27)–C(28)–C(29)	121·2 (3)
O(13)–C(14)–C(15)	109·5 (2)	C(3)–C(29)–C(28)	120·4 (2)
Complex (II)			
S–C–N	179·4 (5)	C(18)–C(17)–C(25)	121·5 (4)
C(2)–N(1)–C(27)	117·1 (4)	C(17)–C(18)–C(19)	119·1 (4)
N(1)–C(2)–C(3)	118·2 (3)	C(18)–C(19)–C(20)	121·8 (4)
N(1)–C(2)–C(30)	122·2 (3)	C(19)–C(20)–C(26)	120·1 (4)
C(3)–C(2)–C(30)	119·7 (3)	C(22)–C(21)–C(26)	120·4 (4)
C(2)–C(3)–O(4)	115·7 (3)	C(21)–C(22)–C(23)	120·4 (4)
C(2)–C(3)–C(33)	119·2 (4)	C(22)–C(23)–C(24)	121·7 (4)
O(4)–C(3)–C(33)	125·2 (4)	C(23)–C(24)–C(25)	119·7 (4)
C(3)–O(4)–C(5)	118·6 (3)	C(17)–C(25)–C(24)	122·6 (4)
O(4)–C(5)–C(6)	109·1 (4)	C(17)–C(25)–C(26)	118·1 (3)
C(5)–C(6)–O(7)	111·4 (5)	C(24)–C(25)–C(26)	119·3 (3)
C(6)–O(7)–C(8)	112·3 (4)	C(20)–C(26)–C(21)	122·2 (4)
O(7)–C(8)–C(9)	109·9 (4)	C(20)–C(26)–C(25)	119·4 (3)
C(8)–C(9)–O(10)	108·8 (4)	C(21)–C(26)–C(25)	118·5 (3)
C(9)–O(10)–C(11)	113·3 (3)	N(1)–C(27)–C(28)	125·3 (4)
O(10)–C(11)–C(12)	108·0 (4)	C(27)–C(28)–C(29)	118·8 (5)
C(11)–C(12)–O(13)	109·2 (4)	C(28)–C(29)–C(30)	119·0 (4)
C(12)–O(13)–C(14)	112·1 (4)	C(2)–C(30)–C(29)	117·6 (4)
O(13)–C(14)–C(15)	109·3 (4)	C(2)–C(30)–C(31)	119·6 (4)
C(14)–C(15)–O(16)	107·0 (4)	C(29)–C(30)–C(31)	122·7 (4)
C(15)–O(16)–C(17)	117·7 (3)	C(30)–C(31)–C(32)	119·8 (5)
O(16)–C(17)–C(18)	124·4 (3)	C(31)–C(32)–C(33)	121·3 (5)
O(16)–C(17)–C(25)	114·2 (3)	C(3)–C(33)–C(32)	120·4 (4)

Table 4. *Dihedral angles* (°) *with e.s.d.'s in parentheses*

Complex (I)	
N(1)–C(2)–C(3)–O(4)	0·6 (3)
C(2)–C(3)–O(4)–C(5)	−177·4 (2)
C(29)–C(3)–O(4)–C(5)	1·1 (3)
C(3)–O(4)–C(5)–C(6)	179·0 (2)
O(4)–C(5)–C(6)–O(7)	60·8 (3)
C(5)–C(6)–O(7)–C(8)	169·6 (2)
C(6)–O(7)–C(8)–C(9)	173·8 (2)
O(7)–C(8)–C(9)–O(10)	−65·1 (3)
C(8)–C(9)–O(10)–C(11)	178·9 (2)
C(9)–O(10)–C(11)–C(12)	175·2 (2)
O(10)–C(11)–C(12)–O(13)	69·8 (2)
C(11)–C(12)–O(13)–C(14)	172·6 (2)
C(12)–O(13)–C(14)–C(15)	−177·6 (2)
O(13)–C(14)–C(15)–O(16)	76·1 (2)
C(14)–C(15)–O(16)–C(17)	−176·6 (2)
C(15)–O(16)–C(17)–C(18)	179·6 (2)
C(15)–O(16)–C(17)–C(22)	0·3 (3)
Complex (II)	
N(1)–C(2)–C(3)–O(4)	−4·1 (5)
C(2)–C(3)–O(4)–C(5)	150·8 (4)
C(33)–C(3)–O(4)–C(5)	30·3 (6)
C(3)–O(4)–C(5)–C(6)	173·3 (4)
O(4)–C(5)–C(6)–O(7)	55·5 (6)
C(5)–C(6)–O(7)–C(8)	166·5 (4)
C(6)–O(7)–C(8)–C(9)	163·1 (4)
O(7)–C(8)–C(9)–O(10)	−69·2 (5)
C(8)–C(9)–O(10)–C(11)	−178·0 (4)
C(9)–O(10)–C(11)–C(12)	177·6 (4)
O(10)–C(11)–C(12)–O(13)	71·2 (5)
C(11)–C(12)–O(13)–C(14)	−179·4 (4)
C(12)–O(13)–C(14)–C(15)	−174·4 (4)
O(13)–C(14)–C(15)–O(16)	−68·8 (5)
C(14)–C(15)–O(16)–C(17)	−177·1 (4)
C(15)–O(16)–C(17)–C(18)	−6·9 (6)
C(15)–O(16)–C(17)–C(25)	173·3 (3)
O(16)–C(17)–C(25)–C(24)	−4·8 (5)

complex (I) the water molecule displays a double action as is seen in other complexes (Hilgenfeld & Saenger, 1982), *i.e.* it binds to the cation and associates weakly with the anion, probably through an O—H···N hydrogen bond. Furthermore, this water molecule is integrated into the crystal lattice in such a way that it is coordinated simultaneously to two SCN^- groups, the cation and another water molecule. The water–water contact of only 2·52 Å is relatively short compared with O—H···O hydrogen bonds which are in general about 2·80 Å.

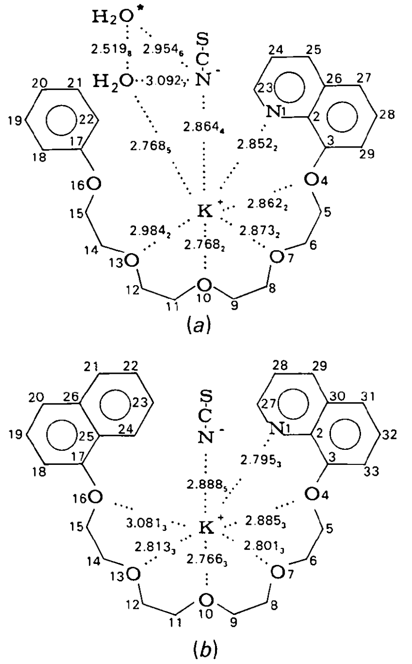

Fig. 1. (*a*) Complex (I) and (*b*) complex (II) with numbering scheme and coordination distances (Å). The last, subjacent digits indicate the standard deviations.

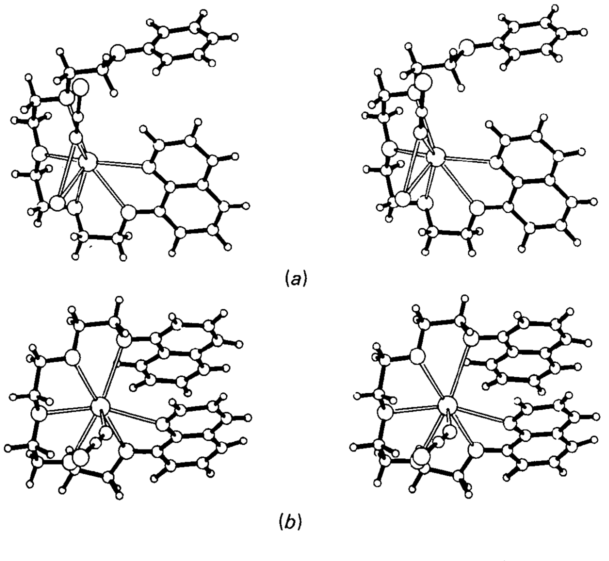

Fig. 2. Stereoscopic *ORTEP* plots (Johnson, 1965) of (*a*) complex (I) and (*b*) complex (II).

Why are the two complexes different? As discussed previously (Saenger, Brand, Vögtle & Weber, 1977), aromatic O atoms do not coordinate as strongly as aliphatic O atoms because their lone-pair electrons are delocalized in the aromatic ring systems. *A priori*, therefore, aromatic O atoms do not coordinate readily if there is not an extra factor contributing significantly.

From inspection of Fig. 3, it becomes clear that in complex (II) the aromatic systems overlap considerably and parallel arrangement of these groups gives rise to stacking which stabilizes the helical structure of this complex and leads to coordination of all ligand O atoms to the cation. In complex (I) such stacking is not

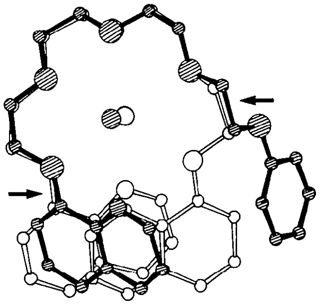

Fig. 3. A comparison of complexes (I) (shaded) and (II). The molecules are superimposed so that the O atoms of the ligands are in similar positions. The SCN^- ions and the water molecule are omitted for clarity. Arrows indicate the main differences occurring among the torsional angles.

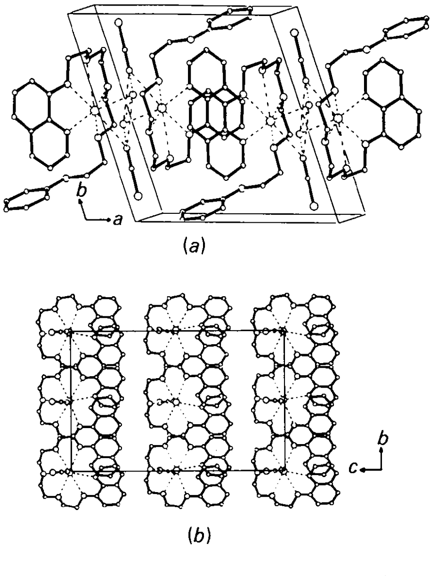

Fig. 4. Views of the crystal packing in (*a*) complex (I), approximate [001] projection, and (*b*) complex (II), [100] projection.

possible because the phenyl ring could, for sterical reasons, overlap only poorly (with C—H groups on one edge) with the 8-quinolyloxy system. This, it appears, is not sufficient to stabilize a helical form, and the phenolic O is displaced by the water molecule, which is a stronger coordinator.

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Interactions Squelette-Chaîne Latérale dans les Peptides. III. Structure de Pivaloyl-L-prolyl-*N*-méthyl-L-thréoninamide, $C_{15}H_{27}N_3O_4$

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Abstract. $M_r = 313$, hexagonal, $P6_5$, $a = 10{\cdot}308\,(1)$, $c = 28{\cdot}117\,(4)$ Å, $V = 2587$ Å^3, $Z = 6$, $D_x = 1{\cdot}205$ Mg m^{-3}, Cu $K\alpha$, $\lambda = 1{\cdot}54051$ Å, $\mu = 1{\cdot}06$ mm^{-1}, room temperature, $F(000) = 170$, final $R = 0{\cdot}052$ for 1240 unique reflexions $[I > 2\sigma(I)]$ among 1675 reflexions scanned, final $R_w = 0{\cdot}058$ $(w = 1/\sigma^2)$. The molecule accommodates a folded conformation of the βI type with, besides the classical 4→1 hydrogen bond, an intramolecular interaction between the NH and O$^{\gamma}$ sites of the threonine residue. The threonine hydroxyl group is intermolecularly hydrogen bonded to the proline carbonyl group.

Introduction. Le caractère globulaire des protéines est principalement assuré par un repliement de type 'β turn' de la chaîne peptidique, intéressant une courte séquence de quatre résidus (Smith & Pease, 1980). Certains résidus à chaîne latérale polaire (Ser, Thr, Asn, Asp...) s'y trouvent incorporés de façon préférentielle (Chou & Fasman, 1977) et il est probable que cette préférence est la conséquence d'interactions stabilisatrices du repliement β faisant intervenir ces chaînes latérales polaires qui comportent le plus souvent un site accepteur et un site donneur de proton. Afin de préciser la nature de ces interactions, nous avons entrepris l'étude de dipeptides modèles de formule *R*CO-L-Pro-*X*-NH*R'* où *X* est un résidu polaire. Nous décrivons ici la structure cristalline du dérivé ^{t}BuCO-L-Pro-L-Thr-NHMe.

Partie expérimentale. Composé obtenu par les méthodes classiques de la synthèse peptidique de façon analogue au dérivé homologue de séquence L-Pro-L-Ser

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