X-Ray Crystal Structures of Anhydrous Sodium and Potassium Complexes of an Open Chain Polyether Diol

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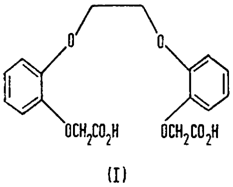
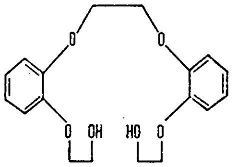
Summary The crystal structures of two anhydrous complexes of an open chain polyether diol show seven-co-ordination for the 1:1 sodium complex and ten-co-ordination for the 2:1 potassium complex.

Although open chain polyethers have lower formation constants with alkali metals than their corresponding cyclic polyethers, their increased flexibility still allows a variety of metal complexes to be isolated. A recent study of ion transport by α-carboxy ω-hydroxy polyethers postulates wrap-around complexation with internal hydrogen bonding.[1] This type of hydrogen bonding is not found in a di-acid complex of potassium,[2] nor in the sodium and potassium complexes of the diol (III) for which we now report the preparation and preliminary crystal structures.



(I)



(III)

Compound (III) is obtained by esterifying the di-acid (I) with concentrated sulphuric acid in ethanol, and reducing the resulting di-ester, (II), m.p. 106 °C, with lithium aluminium hydride in diethyl ether. The anhydrous product, m.p. 99 °C, is obtained by drying *in vacuo* at 65 °C. 1 : 1 molar portions of (III) and sodium thiocyanate in ethyl acetate yield NaSCN·(III), (IV), m.p. 125 °C. 1 : 1 molar portions of (III) and potassium thiocyanate in ethyl acetate gave a solid which on recrystallisation from $CHCl_3$–CCl_4 gave KSCN·$(III)_2$·$\frac{1}{2}CHCl_3$, (V), m.p. 109—110 °C. Satisfactory microanalyses were obtained for all new compounds.

Crystal data: (IV), $C_{18}H_{22}O_6$·NaSCN, $M = 415{\cdot}4$, monoclinic, space group $P2_1/c$. $a = 22{\cdot}103(5)$, $b = 20{\cdot}841(2)$, $c = 9{\cdot}049(1)$ Å, $\beta = 97{\cdot}89(1)°$, $U = 4129{\cdot}0$ Å^3, $Z = 8$, $F(000) = 1744$, $\mu(\text{Mo-}K_\alpha) = 2{\cdot}02$ cm^{-1}. (V), $[(C_{18}H_{22}O_6)_2{\cdot}KSCN]_2CHCl_3$, $M = 1651{\cdot}2$, triclinic, space group $P\bar{1}$, $a = 12{\cdot}184(2)$, $b = 17{\cdot}615(5)$, $c = 19{\cdot}497(3)$ Å, $\alpha = 94{\cdot}08(3)$, $\beta = 94{\cdot}48(2)$, $\gamma = 77{\cdot}14(2)°$, $U = 4060{\cdot}8$ Å^3, $Z = 2$, $F(000) = 1732$, $\mu(\text{Mo-}K_\alpha) = 3{\cdot}35$ cm^{-1}.

Crystals of both samples are clear and colourless, and are plate-shaped; those of (V) are euhedral whereas those of (IV) have no well-defined faces. Cell dimensions and *X*-ray intensity data for both samples were measured on an Enraf-Nonius CAD-4 diffractometer with monochromated Mo-K_α radiation. Structure analyses of the two crystals were by direct methods, using the program SHELX.[3] Refinement of (IV) was by full-matrix least-squares methods and converged at $R = 0{\cdot}072$ for 3374 reflections. For (V), refinement of the atomic parameters in five blocks is at present at $R = 0{\cdot}081$ for 3936 reflections.†

The open chain polyether and anions provide the co-ordination for the cations in these anhydrous complexes, and both structures have two independent cations. In structure (IV), the two cations, Na and Na′, are almost identically bound, and all the oxygens of the open chain polyether bond to sodium ions. Five of the oxygen atoms of one ligand form the equatorial plane of a pentagonal bipyramid, and the sixth (diol) oxygen atom is co-ordinated to a symmetry-related sodium ion (Figure 1). Seven-co-ordination of each sodium ion is completed in one apical position by the nitrogen atom of the thiocyanate ion, and in the other by the diol oxygen atom of another symmetry-related ligand, thus forming two independent chains of molecules [O(17) · · · Na^{I} and O′(17) · · · Na′^{IV}, *etc.*] along the glide planes parallel to the *c*-axis. Both chains are strengthened by hydrogen-bonding schemes; the two hydroxy groups of each ligand are bonded to a common sulphur atom in the same chain. The orientations and conformations of the open chain ligands are very similar. However, one of the ligands is disordered where there are two sites for each of the carbon atoms of a CH_2CH_2-OH group, but the corresponding atoms in the other ligand appear well ordered; this appears to arise from slight differences in the alignments of the chains in the *c*-directions.

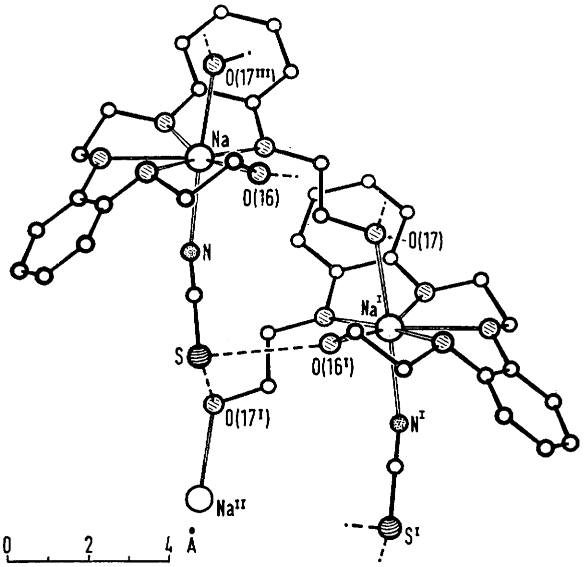


Figure 1. A fragment of one of the chains (non-primed atoms) of NaSCN·(III), compound (IV). Oxygen atoms are shown as hatched circles, and hydrogen bonds by broken lines.

In (V), two open chain ligands surround each of the two independent potassium ions. Five oxygen atoms from each ligand complete the 10-co-ordination of the potassium ions, which are not co-ordinated by the anions or further oxygen atoms from other ligands. A pseudo 2-fold axis of symmetry through the ligands and potassium ion is shown in the plane of Figure 2. The conformations of the catechol groups and the bridging OCH_2CH_2O linkage in each ligand are quite similar, but there are variations in the arrangement of the end groups. The orientations of the two complex cations in the crystal are quite different; the angle between the two pseudo axes of symmetry is 55°. There are also several areas of site disorder, mainly in one of the cation complexes where three of the four hydroxy groups have alternative sites; this allows variations in the co-ordination pattern and hydrogen-bonding schemes. In each complex cation, one hydroxy group of each ligand

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† The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.

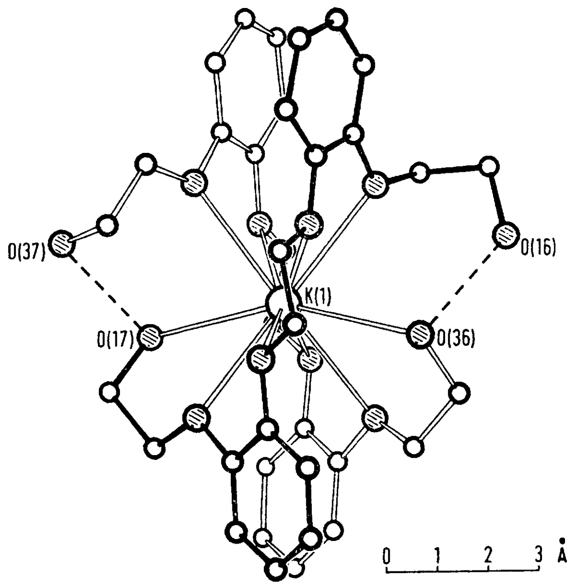

FIGURE 2. A cation complex group of KSCN·(III)$_2$·$\frac{1}{2}$CHCl$_3$, compound (V). Atoms of one ligand (solid bonds) are numbered 1—20; those of the other ligand (open bonds), 21—40. Hydrogen bonds within the group are shown (broken lines); those to thiocyanate ions are not shown.

is co-ordinated to the cation and also donates its hydrogen atom for a bond to the non-co-ordinated hydroxy group of the second ligand of the same cation group. This acceptor group in turn donates its hydrogen atom for a bond to a nitrogen or sulphur atom of a thiocyanate group.

Thus in both (IV) and (V), the ligands are not held in place by internal hydrogen bonds from one hydroxy group to the other of the same ligand; this may explain the poor transporting properties of (III).[1]

Compound (IV) shows a sharp C≡N stretching peak in the i.r. spectrum at 2095 cm^{-1} for the bonded thiocyanate ligand. Compound (V), however, has a broad peak centred at 2035 cm^{-1}; here, one thiocyanate group is tightly bound by hydrogen bonds, at one end from the chloroform molecule (S · · · H, 2·55 Å), and at the other from hydroxy groups of two cation complexes. The second anion is disordered over two sites, roughly head-to-tail, and is involved in hydrogen bonds of varying strengths in either orientation, linking other pairs of complex groups. Hydrogen-bonding through the thiocyanate anions thus links the cation complexes in chains (parallel to the *c*-axis) and also cross-links these chains in pairs.

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[3] G. M. Sheldrick, 'SHELX-76 Program for Crystal Structure Determination,' University of Cambridge, 1976.