Synthesis and Crystal Structures of Complexes between Caesium Thiocyanate and Two Isomeric Macrocyclic Crown Polyethers, 6,7,9,10,17,18,20,21-Octahydro-7*R*,9*R*,18*S*,20*S*-tetramethyldibenzo[*b*,*k*][1,4,7,10,13,16]hexaoxacyclo-octadecin (Isomer F) and 6,7,9,10,17,18,20,21-Octahydro-7*R*,9*R*,18*R*,20*R*-tetramethyldibenzo[*b*,*k*][1,4,7,10,13,16]-hexaoxacyclo-octadecin (Isomer G)

By Alfred J. Layton, Paul R. Mallinson, David G. Parsons, and Mary R. Truter*

(*Chemistry Department and A.R.C. Unit of Structural Chemistry, University College London,* 20 *Gordon Street, London* WC1H 0AJ)

Summary Two isomers, F and G, of tetramethyldibenzo-18-crown-6 each with 4 chiral carbon atoms give complexes with caesium thiocyanate; CsNCS(F) consists of centrosymmetrical dimeric molecules with Cs–N–Cs bridges, the other co-ordinating atoms being the six oxygens of F at 3·07—3·34 Å and the aryl carbon atoms at 3·79 Å, while CsNCS(G)$_2$ consists of Cs(G)$_2^+$ cations having $\bar{4}$ symmetry with 12 Cs–O contacts at 3·17—3·43 Å and disordered thiocyanate ions.

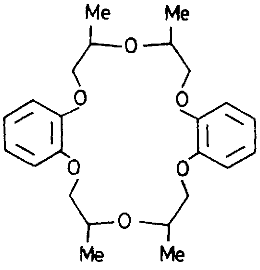
Chiral derivatives of Pedersen's[1] macrocyclic ethers have been produced with a change of donor atom, from oxygen to nitrogen[2] or by ingenious syntheses[3] from *ββ*′-dihydroxy-*αα*′-binaphthyl to make use of restricted rotation in this molecule. We have synthesised and isolated derivatives with chirality introduced solely by replacement of hydrogen atoms by methyl groups: these are the five isomers of (I). We have investigated their complex formation with alkali-metal salts and report the results for two isomers.

These isomers, designated F and G, were made from the same starting material, 2,4-dimethyl-3-oxapentane-1,5-diol. The mixture of isomers obtained on tosylation of the *meso* and racemic diols was separated by fractional crystallisation;[4] the racemic 2,2′-ditosyloxydi-isopropyl ether, m.p. 90—91°, was then treated with the sodium salt of catechol in Bu^{n}OH at reflux temperature under nitrogen, to give an 11% yield

---

* Present address: Molecular Structures Department, Rothamsted Experimental Station, Harpenden, Herts AL5 2JQ.

of the cyclic polyethers F and G. Fractional crystallisation gave first the *meso*-isomer F, m.p. 200°, then the racemic isomer G, m.p. 134°. Recrystallisation of the F isomer from methanol or ethyl acetate gave a monoclinic form, but from acetic acid or by sublimation a triclinic form was obtained. Reaction with caesium thiocyanate in 1 : 1 ratio by warming in ethanol and cooling, yielded products with different stoicheiometry, 1 : 1 for isomer F and 1 : 2 for isomer G. Crystal structures of both complexes were determined and established the configurations of the isomers.



(I)

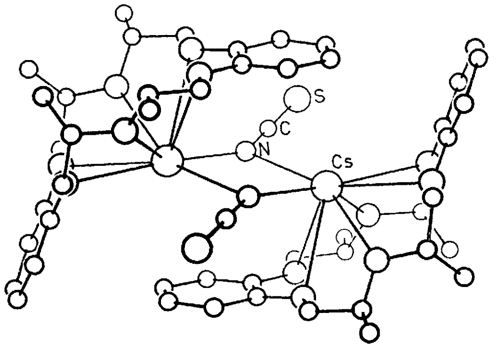


Figure 1. CsNCS(I isomer F) showing the centrosymmetrical dimeric unit found in the crystal. Cs–N distances are 3·20 and 3·26 Å, Cs–O distances range from 3·07—3·34 Å, and the nearest contact to the benzene ring in the other half of the dimer is 3·79 Å.

Crystal data: $C_{24}H_{32}O_6$ (isomer F) CsNCS, $M = 607$, triclinic, $a = 11·12(1)$, $b = 11·87(1)$, $c = 13·46(1)$ Å, $\alpha = 107·75(2)$, $\beta = 95·25(6)$, $\gamma = 121·90(4)$°, $Z = 2$, space group $P\bar{1}$; 2086 observations with Mo-K_α radiation on a diffractometer; current R 0·068.

Crystal data: $C_{48}H_{64}O_{12}$ (2 × isomer G) CsNCS, $M = 1023$, tetragonal, $a = 15·22(1)$, $c = 11·14(1)$ Å, $Z = 2$, space group $P4_2/n$; 2290 observations with Mo-K_α radiation on a diffractometer; current R 0·11. Molecular symmetry required, $\bar{4}$, NCS ions are disordered and not located.

Both structures were solved by the heavy-atom method and refined by full-matrix least-squares. Figure 1 shows the dimeric molecule of CsNCS(F) and Figure 2 the complex cation in CsNCS(G)$_2$. The *meso*-isomer (F) has an approximate plane of symmetry in the complex while the uncomplexed molecule is centrosymmetrical.[5]

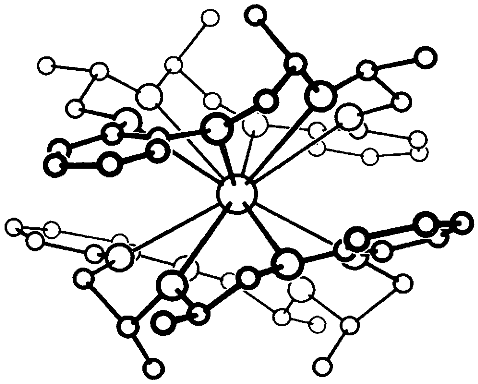


Figure 2. The complex cation Cs(I isomer G)$_2{}^+$; the caesium atom is surrounded by ligand molecules giving $\bar{4}$ symmetry, each ligand has a two-fold axis of symmetry and the two ligands are enantiomerically related. Cs–O distances range from 3·17—3·43 Å. Two Cs–O bonds are eclipsed by two others in one ligand.

The main difference in geometry between the co-ordinated ethers is that isomer G is 'flatter', *i.e.* the angle between the normal to the benzene ring and the plane through the oxygen atoms is 15° compared with angles of 27 and 39° for the two benzene rings in the isomer F complex. These values for isomer F, and the torsion angles in its macrocyclic ring are similar to the corresponding ones in dibenzo-18-crown-6 complexes[6] while the torsion angles for isomer G differ by 2—30° from the 'usual' values. These small changes allow the caesium to be twelve-co-ordinated; the Cs–O distance is 0·1 Å larger in the isomer G than in the isomer F complex, as expected for the higher co-ordination number.

(*Received*, 9*th July* 1973; *Com.* 969.)

[1] C. J. Pedersen, *J. Amer. Chem. Soc.*, 1967, **89**, 7017.

[2] F. Wudl and F. Gaeta, *J.C.S. Chem. Comm.*, 1972, 107.

[3] E. P. Kyba, M. G. Siegel, L. R. Lousa, G. D. Y. Sogah, and D. J. Cram, *J. Amer. Chem. Soc.*, 1973, **95**, 2691.

[4] 2,4-Dimethyl-3-oxapentane-1,5-diol was prepared by the methods of P. Vieles, *Ann. Chim.* (*Italy*), 1935, **3**, [11], 143, and C. C. Price, 1972, personal communication, who found the *meso* and racemic products occur in the ratio 1 : 3.

[5] P. R. Mallinson, to be published.

[6] M. A. Bush and M. R. Truter, *J. Chem. Soc.* (*B*), 1971, 1440.