A New Conformation of the Cyclic Polyether Benzo-15-crown-5 in its Solvated Complexes with Calcium Isothiocyanate: X-Ray Crystal Structure Analysis

By J. D. Owen* and J. N. Wingfield

(*Molecular Structures Department, Rothamsted Experimental Station, Harpenden, Herts* AL5 2JQ)

Summary The molecular structures of benzo-15-crown-5–Ca(NCS)$_2$.MeOH and the corresponding water-solvated complex show a new irregular conformation of the crown ether (consistent with the i.r. spectra), and eight-co-ordination of calcium, comprising five ether oxygen atoms, two isothiocyanate nitrogen atoms, and one oxygen atom from the solvent.

Previous studies[1] have shown that the i.r. spectrum ('fingerprint region') of benzo-15-crown-5 is sensitive to conformational change. As part of an investigation of alkaline earth metal co-ordination with the cyclic polyethers,[2] the two complexes, benzo-15-crown-5–Ca(NCS)$_2$–MeOH (I) and the corresponding water solvate (II), were isolated and found to have similar i.r. spectra, which differed from either of those of the sodium[3] and potassium[4] complexes of known structure. The new conformation was therefore determined by X-ray analysis of (I) and (II).

Crystals were prepared by the methods described in ref. 2. Crystals of (I), $C_{14}H_{20}O_5$–Ca(NCS)$_2$–CH$_3$OH, are triclinic, space group $P\bar{1}$, $a = 8{\cdot}665(1)$, $b = 11{\cdot}155(1)$, $c = 11{\cdot}942(1)$ Å, $\alpha = 95{\cdot}49(1)$, $\beta = 102{\cdot}21(1)$, $\gamma = 102{\cdot}47(1)^\circ$, $Z = 2$; intensity data were collected using monochromated Mo–K_α radiation on a 4-circle diffractometer. A total of 4245 reflections were classed as observed, of which 1990 with $\sin\theta/\lambda \leqslant 0{\cdot}5$ were used to solve the structure. The structure was solved by direct methods and refined to a conventional R-factor of 0·065 for the 1990 reflections. The resulting structure is shown in the Figure.

Crystals of (II), $C_{14}H_{20}O_5$–Ca(NCS)$_2$–H$_2$O, are monoclinic, space group, $P2_1/c$, $a = 11{\cdot}248(5)$, $b = 12{\cdot}929(7)$, $c = 17{\cdot}100(7)$ Å, $\beta = 123{\cdot}15(2)^\circ$, $Z = 4$; intensity data were collected using Zr-filtered Mo-K_α radiation on a 4-circle diffractometer. A total of 704 reflections were classed as observed. The structure was solved by direct methods and refined to a conventional R-factor of 0·049.

The crystal structures of (I) and (II) show different packing of very similar molecules. The conformation of the crown ether and the arrangement of the atoms co-ordinated to the metal ion are essentially identical in the two structures.

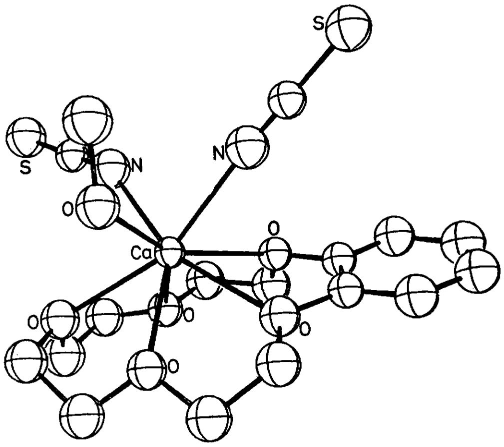

FIGURE. *X*-Ray structure of benzo-15-crown-5–Ca(NCS)$_2$–MeOH (I).

The eight-co-ordination of the calcium ion does not form any regular polyhedron; calcium is above the mean plane of the five ether oxygen atoms, and co-ordinated on the other side by two isothiocyanate nitrogen atoms (mean distance 2·44 Å) and an oxygen atom from the solvent. The mean Ca–O (solvent) distance of 2·39 Å shows the solvent molecule to be strongly bonded to calcium. The mean Ca–O (ether) distance (2·53 Å) and Ca–O (ether plane) distance (1·23 Å) are, as expected from their respective ionic radii, intermediate between those determined previously for sodium[3] and potassium[4] complexes. The conformation of the crown ether found here is different from that of both the sodium and potassium complexes. The deviation of the oxygen atoms from their mean plane is much larger and the ether ring does not exhibit even an approximate plane of symmetry. Several of the torsion angles again differ significantly from 60 and 180°.

The molecular structures of (I) and (II) differ in one important respect. Each has one Ca–N–CS angle of 153° but the other is different, 172° for (I) and 160° for (II). Both complexes therefore contain non-equivalent isothiocyanate groups which explain the splitting of the C–N stretching frequencies in their i.r. spectra.[2]

In each structure the sulphur atom of one of the isothiocyanate groups is hydrogen-bonded to the solvent co-ordinated on a neighbouring molecule (O—H···S distance 3·17 Å); the difference in packing arises because these bonds form dimers in (I), and polymeric chains along the crystallographic *b* axis in (II).

We are grateful to Dr. P. G. Owston for the use of the diffractometer at the Polytechnic of North London, and Dr. M. R. Truter and Dr. M. McPartlin for helpful discussions.

(*Received*, 18*th February* 1976; *Com.* 171.)

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