X-Ray Crystal Structure of the Barium Thiocyanate Complex of the Cyclic Poly-ether Dicyclohexyl-18-Crown-6 (Isomer A)

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Summary The crystal structure of the barium complex of isomer A of the cyclic poly-ether dicyclohexyl-18-crown-6 has been determined by *X*-ray diffraction; it has been found that isomer A is in the *cis-syn-cis*-conformation.

THE compound 2,5,8,15,18,21-hexaoxatricyclo[20,4,0,$0^{9,14}$]-hexacosane ($C_{20}H_{36}O_6$), commonly called dicyclohexyl-18-crown-6, is one of the cyclic poly-ethers synthesized by Pedersen.[1] These poly-ethers are of considerable interest because of their ability to form unusually strong complexes with alkali and alkaline earth metal cations[2,3] and because they enhance the transport of such metal ions through cellular membranes.[4] Dicyclohexyl-18-crown-6 is prepared by hydrogenation of 2,3;11,12-dibenzo-1,4,7,10,13,16-hexaoxacyclo-octadeca-2,11-diene,[1] commonly called dibenzo-18-crown-6.

Five isomers are possible[5] as a result of this hydrogenation but only two have been isolated:[2,3,5,6] isomer A (m.p. 61—62 °C[3,6]) and isomer B (m.p. 69—70 °C[3,6]). Both *cis* and *trans* hydrogenation have been proposed.[2,5,6,7] N.m.r. data have been recorded, but are contradictory: ^1H and ^{13}C n.m.r. results lead to *trans*[6] and *cis*[7] assignments, respectively. This study was initiated to clear up the disagreement regarding the conformational differences between the isomers.

Crystal data, $[Ba(C_{20}H_{36}O_6)](SCN)_2$: the clear crystals are orthorhombic, space group *Aba*2, $a = 21{\cdot}19$, $b = 13{\cdot}56$, $c = 9{\cdot}63$ Å; $Z = 4$; $D_m = 1{\cdot}53$ g cm^{-3}; $D_c = 1{\cdot}50$ g cm^{-3}. The systematic extinctions did not uniquely determine the space group since *Cmca* was also a possibility. However, as the structure analysis progressed, that space group possibility was ruled out. A small crystal was shaped to a sphere with a mean radius of 0·15 mm and mounted on a General Electric XRD-5 diffractometer fitted with a quarter circle orientater. Zr-filtered Mo radiation was used throughout the study. A total of 696 independent reflections were observed to a sin θ/λ limit of 0·49. Few reflections beyond that limit were observable so apparently the crystal was not of high quality. Intensities for two standard reflections were measured periodically as the data were collected and no significant changes were observed indicating that no decomposition of the crystal took place. No absorption correction was necessary. Of the 696 reflections 200 were considered unobserved and were not used in the structure determination.

The positional parameters for the barium atom, the thiocyanate ion and several of the light atoms of the ligand were obtained from the Patterson map. The atoms of each thiocyanate ion were in general positions, and therefore the correct space group must be *Aba*2. The trial model was completed using Fourier techniques and was refined by full-matrix least-squares. When isotropic thermal parameters were used the observation to parameter ratio was only 7·5 to 1. Therefore, no attempt was made to use anisotropic thermal parameters. When the weighted *R* value reached 9·5% a difference Fourier map was calculated. This map was featureless with the exception of a peak of appropriate magnitude for an oxygen atom which was located about 2·8 Å above the barium atom on the two-fold axis. This peak could be explained by the presence of a water of hydration co-ordinated to the barium atom. When this atom was added to the trial structure the weighted *R* value dropped to 8·5%. Chemical tests are now being made to verify the presence of the water molecule. Throughout the structure determination, computer programs from the *X*-ray 67 package[8] were used.

The symmetry of the space group requires the poly-ether molecule to possess C_2 symmetry and the barium atom to lie on the two-fold axis. The two-fold axis is perpendicular to the nearly planar central poly-ether ring. The barium atom is co-ordinated to the six oxygen atoms of the poly-ether molecule and the nitrogen atoms of two thiocyanate ions and probably to the oxygen atom of a water molecule. The Ba–O distances range from 2·77 to 2·89 Å and the BaN distance is 2·89 Å. The barium compound exists as an ion pair involving $[Ba(C_{20}H_{36}O_6)]^{2+}$ and $2SCN^-$ which is similar to the result found earlier for the rubidium thiocyanate complex of dibenzo-18-crown-6.[9] The average C–C and C–O distances in the Ba^{2+}-isomer A complex are 1·56 and 1·47 Å, respectively with the central poly-ether ring being nearly planar. These distances are very similar to those found in previous *X*-ray studies of cyclic poly-ether complexes.[9,10]

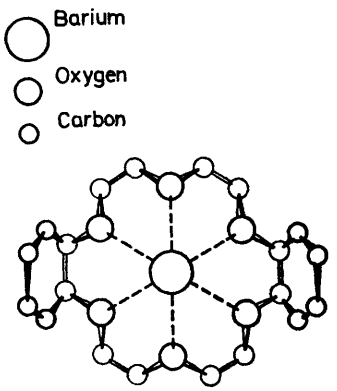

FIGURE. *Dicyclohexyl*-18-*crown*-6 *(isomer A) complex*

The hydrogen atoms could not be located but it is apparent from the location of the oxygen atoms and the existence of the two-fold axis that isomer A is the *cis-syn-cis*-isomer. The structure is shown in the Figure. The SCN^- ions which are omitted from the Figure are located below the atoms shown. The proposed oxygen atom of the water of hydration is directly above the barium atom. The cyclohexyl rings extend in a nearly perpendicular fashion above the plane of the cyclic polyether group as would be expected in the *cis-syn-cis* isomer. The dihedral angle between the least square planes of the cyclohexyl ring and the poly-ether ring is 114°.

Work is continuing to determine the structure of the uncomplexed isomer A and isomer B and the structure of metal complexes of isomer B.

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