

THE CRYSTAL STRUCTURE OF A 'MODEL CARRIER'
COMPLEX FORMED BETWEEN SODIUM BROMIDE AND
2,3,11,12-DICYCLOHEXYL-1,4,7,10,13,16-
HEXAOXOCYCLO-OCTADEC-2,11-DIENE ('DICYCLO-
HEXYL-18-CROWN-6')

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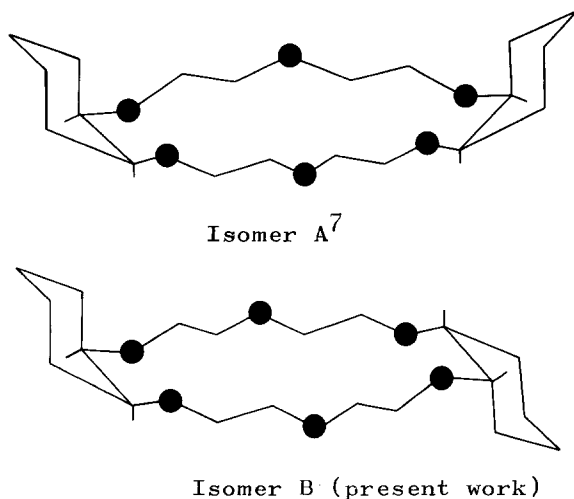
Summary: The determination of the crystal structure of a complex formed between sodium bromide and dicyclohexyl-18-crown-6 (IsomerB), has shown that the six oxygen atoms of the ligand form a planar ring round the sodium ion. The co-ordination sphere of the sodium ion is completed by two water molecules, one above and one below the plane of this ring. In the crystalline state the molecules are bonded into a chain system by H-bonds, which form between the water molecules and the bromide ions.

Introduction

The biological interest attached to the 'crown' compounds lies in their use as model systems, whose properties parallel the behaviour of naturally-occurring cyclic antibiotics.^{1,2,3} They were first synthesised by Pedersen,⁴ and have the ability to extract selectively alkali metals into non-polar solvents. For this reason, a systematic study of the structures of alkali metal complexes with crown compounds⁵ has been undertaken to obtain some insight into the environmental bonding factors which relate to selectivity.

Results

Dicyclohexyl-18-crown-6 is prepared by the hydrogenation of dibenzo-18-crown-6 and can, theoretically, be obtained in



Black circles represent O atoms

Figure 1.

five different isomeric forms, of which only two have so far been isolated.⁶ Figure 1 illustrates the difference between these two isomers, which is now clearly established. It had been suggested on the basis of n.m.r. evidence⁶ that both isomers would have the hydrogen atoms in the trans-configuration. X-ray crystal structure analysis has now shown conclusively that both isomers have the hydrogen atoms in the cis-configuration at the cyclohexyl bridging position.⁷

Crystals suitable for X-ray work were obtained when equimolar quantities of dicyclohexyl-18-crown-6 and sodium bromide were solubilised in an ethanol-acetone mixture and air-evaporation was allowed. The plate-shaped crystals were triclinic, space group $P\bar{1}$, one molecule of $\text{NaBr} \cdot \text{C}_{20}\text{H}_{36}\text{O}_6 \cdot 2\text{H}_2\text{O}$ per unit cell. Cell dimensions are $a = 10.32$, $b = 11.34$, $c = 6.67\text{\AA}$, $\alpha = 116^\circ 42'$, $\beta = 109^\circ 48'$, $\gamma = 100^\circ 10'$. 1510 independent reflections were measured on a Picker automatic 4-circle diffractometer.

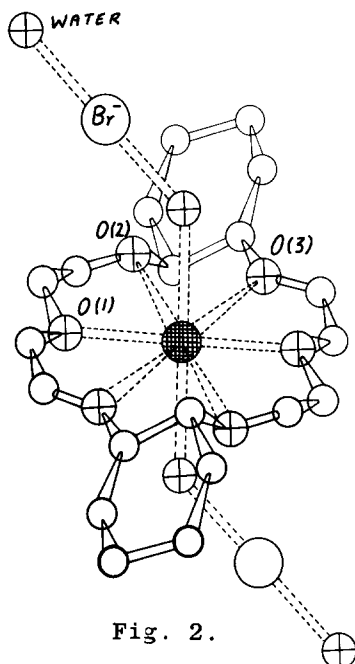


Fig. 2.

The structure was solved by Patterson and Fourier methods, and refined by full matrix least squares with anisotropic vibration parameters for Na, Br, and O atoms. All hydrogen atoms, with the sole exception of that forming the hydrogen bond between water and bromine, have been located. The present R value is 4.7%, with refinement continuing. Figure 2 shows one complete molecule of the structure, and an indication of the hydrogen bonded chain. Both the Na and the bromide ion are on crystallographic centres of symmetry. The sodium ion is surrounded by a planar ring of six oxygen atoms, from one ligand with Na-O bond distances at the long range of 2.6 - 3.0 Å. A more favourable bond length would be in the range 2.25 - 3.0 Å. Na-H₂O distances are 2.35 Å.

Discussion

An alkali metal ion (M) can be described as a charged

sphere, capable of bonding by electrostatic interaction with a source of negative charge, and with no directional restrictions imposed on the bonds from M. The oxygen atom (O) lone pairs in the 'crown' are in a tetrahedral environment with respect to the two O-C bonds and for maximum stability this places a directional requirement on the O-M bond. Theoretical considerations⁸ show that two orientations of the O lone pairs, with respect to M, would form a stable bond; (a) M is in a direct line with the tetrahedral direction of the lone pairs, (b) M is trigonally oriented with respect to both tetrahedral directions of the lone pairs. Hybridisation of the O lone pair orbitals make this a strong bonding situation. The order of bonding stability may be predicted as (b) \searrow (a) $\searrow\searrow$ the intermediate case where neither condition (a) or (b) holds precisely. In Figure 2, O(2) is the intermediate case and O(1) and O(3) are close to (a).

The presence of water molecules in complexes which are not electrostatically saturated by the ligand alone (e.g. this one) illustrates the point that the ligand replaces the solvation shell of the metal, there being a balance between ΔH_{solv} and $\Delta H_{\text{complex}}$. An excess of water destroys the complex liberating the ligand and M. The selectivity factors:

1. Size of cation in relation to the size of the ligand hole.
2. Size of cation in relation to number and location of donor sites.
3. Spatial arrangement of donor sites in relation to steric strain placed on ligand, i.e. the requirement of a flexible ligand, are followed by the model.

In addition, both the nature of the anion and the nature of the solvent affect the formation of complexes. Polar solvents favour

1:1 complexes with the alkali metal in the centre, and solvent attached above and below the ligand. In less polar solvents, contact ion pairs and higher ratios of crown to metal are favoured. Eisenman et al have postulated ratios of 3:1, 2:1, and 1:1 in the membrane to explain their results on permeability and conductance.⁹ So far we have not been able to isolate 3:1 species but the smaller ligands form 'sandwich' complexes with larger M, e.g. 2(benzo-15-crown-5)KI.¹⁰ In certain cases an excess of M can yield a complex containing two metal ions per cyclic polyether.¹¹ This we feel might be of interest with relation to multi-site carrier problems.

As the 'crowns' have not yet been found indigenous to natural systems it is of interest to assess our model. It has been shown,^{5,12} that 1:1 complex formation by a 'crown' ligand is accompanied by conformation changes which result in the O atoms turning towards M. In general, the smaller ligands form planar ring systems (cf. enniatins¹³), while a larger ligand⁵ will encapsulate the central metal atom, (cf. nonactin¹⁴).

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