Unusual Co-ordination in the Crystal Structure of the 1:2 Complex of 18,18′-Spirobi-(19-Crown-6) with Lithium Iodide Dihydrate

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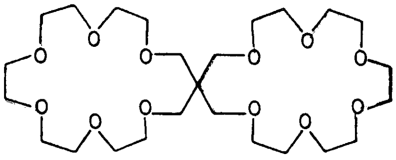
Summary Both the macro-rings in the double-loop title ligand, which has C_2 symmetry, bind one of the water molecules of solvation and an Li^+ ion in the same cavity; the metal ion interacts simultaneously with both captured and the free molecules of water of solvation.



(1)

MULTI-LOOP crown ethers synthesized recently[1] represent a new type of compound with multiple active sites and can be tailored to fit different ions.[1] Each hexaether ring in (**1**)† should ideally accommodate either a potassium or a barium ion,[2] complexes of which could be obtained in unhydrated form.[1] However, the binding of the considerably smaller metal ions and the accompanying water molecules in 2LiI.(**1**).$4H_2O$ could not be elucidated unambiguously by spectroscopic means. Thus an *X*-ray crystal structure was determined. Treatment of (**1**) (0·25 mmol) with 2 equiv. of LiI in 2 ml of boiling acetone, followed by the addition of ethyl acetate until the solution turns cloudy, yields (71%) the colourless crystalline complex of (**1**), 2LiI, and $4H_2O$; m.p. 72—74 °C; ν_{max} (KBr) 3410 br.vs, 2900, and 1085 cm^{-1}. Since very hygroscopic crystals were obtained, the selected specimen of 0·03 × 0·03 × 0·04 mm size was sealed in a cyanoacrylate glue.

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† For a new nomenclature of crown compounds see E. Weber and F. Vögtle, *Inorg. Chim. Acta*, 1980, **45**, L65; (**1**) = 18,18′-Spiro-{2}19·19 $< [O_6 - 1{\cdot}2_5{\cdot}1]_2$coronand-12 $>$.

Crystal data: $C_{25}H_{56}I_2Li_2O_{16}$, monoclinic, space group $C2/c$, $M = 912{\cdot}4$, $a = 1776{\cdot}8(5)$, $b = 1060{\cdot}3(2)$, $c = 2265{\cdot}8(8)$ pm, $\beta = 118{\cdot}00(2)°$, $Z = 4$, $R = 0{\cdot}038$ for 1212 observations with $I - 1\sigma(I) \geqslant 0$ collected on a Nonius CAD-4 diffractometer. The phase problem was initially solved in the space group Cc by use of the heavy-atom method and Fourier syntheses. In the course of refinement a twofold crystallographic symmetry was revealed which coincided with the molecular symmetry (C_2) and hence the space group was changed to $C2/c$. The positions of the methyl hydrogen atoms were generated from assumed geometries while those of the water hydrogen atoms, together with the co-ordinates of the Li^+ ion, were deduced from difference maps computed near the end of the least-squares refinement.‡ The shape of the molecule is depicted in the Figure. One of the water molecules of solvation is linked to the O(9) and O(15) atoms *via* two equally strong hydrogen bonds: O(15) · · · H(1O2w) 186(1) pm, ∠O(15)–H(1O2w)–O(2w) 149(1)°; O(9) · · · H(2O2w) 186(1) pm, ∠O(9)–H(2O2w)–O(2w) 139(1)°. Atom O(2w) is also an electron donor towards Li^+ thus establishing a connection between the two domains of co-ordination in each polyether ring. The metal ion occupies the opposite part of the ring and is at the centre of a distorted trigonal-bipyramid formed by O(1w), O(2w), O(3), O(6), and O(18). In accord with the VSEPR theorem[3] three shorter Li^+ · · · O contacts lie in the 'equatorial' plane of the polyhedron [Li · · · O(3) 198(2), Li · · · O(1w) 196(1), and Li · · · O(2w) 193(1) pm] while the two 'apical' distances are somewhat longer [Li · · · O(6) 221(2) and Li · · · O(18) 212(1) pm]. The intermolecular network in the lattice is completed by the I^- ion which is practically shielded from Li^+. It is hydrogen-bonded to O(1w): H(1O1w) · · · I(x, $-y$, $+\frac{1}{2}z$) 297(1) pm, ∠I–H(1O1w)–O(1w) 148(1)°, H(2O1w) · · · I($-x$, $-y$, $-z$) 249 pm, ∠I–H(2O1w)–O(1w) 140(1)°.

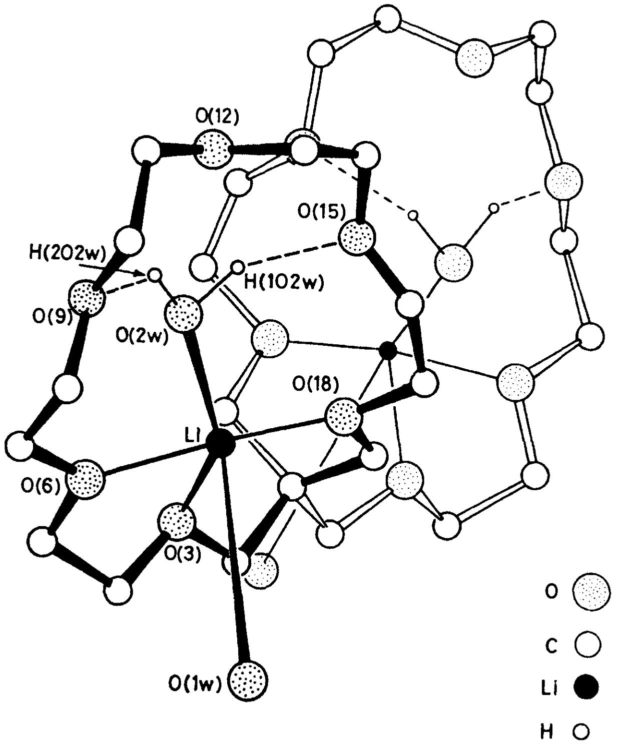

FIGURE. Perspective drawing of the molecule showing the crystallographic numbering. The I^- ions and the hydrogen atoms bonded to O(1w) are deliberately omitted from the drawing.

Owing to the similar host–guest dimensions, the hydrated Li^+ ion is bound to the hexaether in a similar manner to Ba^{2+} in hydrated $Ba(picrate)_2$ (dibenzo-24-crown-8).[4] However, in the latter complex, the anion is co-ordinated directly to Ba^{2+}. Our results may be relevant to the conclusions on the geometry of the $Li^+(H_2O)_2$ cluster drawn by Kollman on the basis of *ab initio* calculations.[5]

The torsion angles in the ring vary between 95(1) and 180(1)° for COCC and between 31(1) and 81(1)° for OCCO, respectively. Similarly low values for the OCCO torsion angles (*ca.* 30°) have been claimed for the symmetric form of 12-crown-4 complexed with Li^+, together with a 50 pm displacement of the cation from the mean plane of the oxygen atoms.[6] In our complex the Li^+ ion is placed 58(1) pm from the mean plane of O(3), O(6), O(18), and O(2w). Bond lengths agree with the corresponding ones for other polyether structures.[7]

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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. The structure factor table is available from the British Library as supplementary publication no. SUP 23069 (9 pp.). For details of obtaining this material, see Notice to Authors No. 7, *J. Chem. Soc., Dalton* or *Perkin Trans.*, Index Issues.

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