Crystal Structure of a Complex Showing Simultaneous Water–Barium Ion Co-ordination to 6,7,9,10,12,13,20,21,23,24,26,27-Dodecahydrodibenzo[*b*,*n*][1,4,7,10,13,16,19,22]octaoxacyclotetracosin (Dibenzo-24-crown-8)

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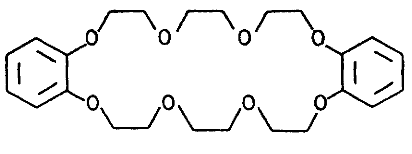
Summary The crystal structure of Ba(picrate)$_2$·(dibenzo-24-crown-8)·2H$_2$O shows that only five of the ether oxygens are co-ordinated to the barium ion and two of the three other ether oxygens are hydrogen-bonded to a water molecule, which is itself in the plane of the ether ring, co-ordinated to the barium, and related to it by a pseudo-centre of symmetry within the crown ligand.

Recent crystallographic studies of dibenzo-24-crown-8[1] (dbc) and its complexes[2,3] have shown it to be a versatile and flexible molecule for complexing alkali metals. Two metal ions are co-ordinated by the ether molecule in its potassium thiocyanate[2] and sodium *o*-nitrophenolate[3] complexes and in the latter structure two of the ether oxygen atoms are not involved in the co-ordination. In this study we report the structure of Ba(picrate)$_2$(dbc)·2H$_2$O (I) where only five of the ether oxygens co-ordinate the barium. Crystals of (I) were obtained as yellow needles, m.p. 104 °C, from a 1 : 1 mixture of barium picrate and dbc in ethyl acetate.†



dbc

Crystal data: $C_{36}H_{40}BaN_6O_{24}$, $M = 1078{\cdot}1$, triclinic, space group $P\bar{1}$, $a = 7{\cdot}369(1)$, $b = 11{\cdot}827(2)$, $c = 24{\cdot}859(3)$ Å, $\alpha = 96{\cdot}98$, $\beta = 92{\cdot}47$, $\gamma = 96{\cdot}51°$, $U = 2133{\cdot}0$ Å^3, $Z = 2$, $F(000) = 1092$, $\mu(\text{Mo-}K_\alpha) = 10{\cdot}2$ cm^{-1}.‡

Cell dimensions and intensity data (3321 unique reflections with above-zero intensities, θ in the range 1—20°) were measured on a CAD4 diffractometer with monochromated Mo-K_α radiation. The molecular structure of the complex, determined by the heavy atom method and at the present stage of refinement ($R = 0{\cdot}063$), is shown in the Figure.

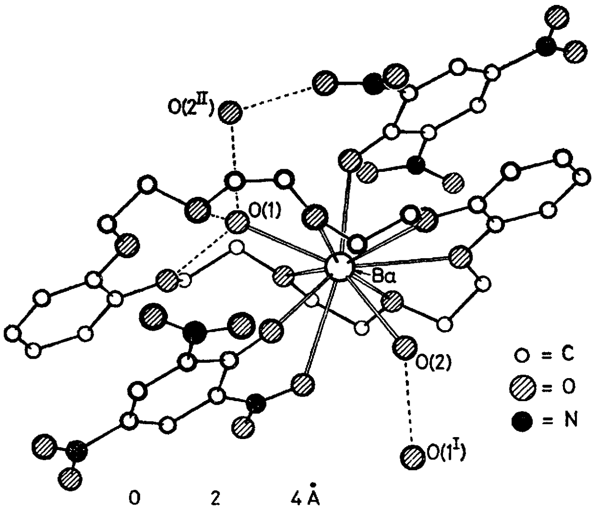


Figure. View of the molecule (I). Ba–O co-ordination bonds are represented by hollow lines, and the postulated hydrogen bonds as broken lines. Roman superscripts represent translations parallel to the *a*-axis: *viz.* (I) is ($x + 1$); (II) is ($x - 1$).

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† Compound (I) gave satisfactory microanalytical data.

‡ The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Rd., Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.

The barium ion and the oxygen atom O(1) of one of the water molecules are nearly equally displaced from a pseudocentre of symmetry of the ether ring, and thus the barium ion is co-ordinated by only five ether oxygens (Ba–O, 2·86—3·00 Å). The barium ion is further co-ordinated by oxygen O(1) (Ba–O, 2·73 Å), oxygen O(2) of the other water molecule (Ba–O, 2·77 Å), the phenolate oxygens of the two picrates, one chelating (Ba–O, 2·67 Å), and one monodentate (Ba–O, 2·71 Å), and an oxygen of the *ortho* nitro-group of the chelating picrate (Ba–O, 3·09 Å) to give a reasonably regular 10-co-ordination. The water molecule of O(1) occupies the space at the other end of the ether ring, and its hydrogen-bonding to two of the three remaining ether oxygens is enhanced by the oxygen co-ordination to barium. Whilst co-ordination of H_3O^+[4] and water molecules[5] to cyclic polyethers has been observed, this is the first example of both cation and water co-ordinated to the same molecule, *i.e.* co-ordination of a 'hydrated cation'. This barium–oxygen distance (2·73 Å), as expected from the lack of electrostatic repulsion, is shorter than the K–K (3·41 Å) or Na–Na (3·38 Å) distances in the 2 : 1 complexes, and suggests that a 2 : 1 alkaline earth complex with 2+ cations and dbc is unlikely, even though their ionic radii (Ca^{2+} to Ba^{2+}) approximate to those of sodium and potassium.

The structure is influenced by the presence of the potentially chelating picrate ion, since a recent structure of $Ba(ClO_4)_2\cdot$(dbc)[6] shows all ether oxygens to be co-ordinating to the barium. Further stability is also conferred on the present structure by the stacking of the picrate rings above and below the catechol rings of the crown ligand, and hydrogen-bonding between neighbouring molecules. Both these interactions connect molecules parallel to the *a*-axis.

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