

# Structural Aspects of Crown Complexes with Alkali and Alkaline Earth Cations. Benzo-15-crown-5 as a Discriminating Macrocycle

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**Abstract.** X-ray structural results have been reviewed for the related  $M^{z+} L^-$ -B15C5 complexes where  $M^{z+} = Li^+$  to  $Cs^+$  and  $Mg^{2+}$  to  $Ba^{2+}$ ,  $L^- = 2,4,6$ -trinitrophenolate (Picrate or Pic) and 3,5-dinitrobenzoate (Dnb), and B15C5 = benzo-15-crown-5. These results combined with those for some  $MX_z$ -B15C5 ( $X = NCS^-$ ,  $I^-$ ,  $NO_3^-$ ,  $ClO_4^-$ ,  $BPh_4^-$ ) complexes have revealed that B15C5 is a useful macrocycle with regard to the 'within-the-group' and 'between-the-groups' discriminations of  $M^{z+}$  in the solid state.

**Key words.** Benzo-15-crown-5, alkali cation, alkaline earth cation, X-ray diffraction, cation discrimination.

## 1. Introduction

Soon after the cyclic polyethers (crown ethers, Figure 1) were discovered [1] as potential ligands for alkali and alkaline earth cations ( $M^{z+}$ ) in 1967, the late Professor Ronald Nyholm

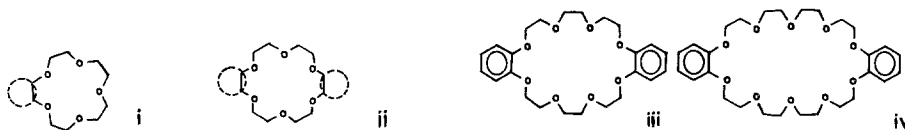
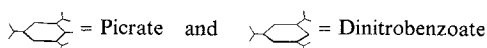
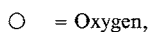
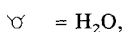
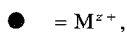
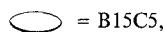


Fig. 1.★ Crowns: (i) benzo-15-crown-5 (B15C5, when broken circle represents benzo nucleus); 15-crown-5 (15C5, when broken circle represents no attached moiety), (ii) 18-crown-6 (18C6, when broken circle represents no attached moiety); dibenzo-18-crown-6 (DB18C6, when broken circle represents benzo nucleus); dicyclohexano-18-crown-6 (DC18C6, when broken circle represents cyclohexano nucleus), (iii) dibenzo-24-crown-8 (DB24C8), and (iv) dibenzo-30-crown-10 (DB30C10).

★ Notation used in the Figures:



initiated a program to develop the coordination chemistry of  $M^{z+}$  using such molecules as ligands. He invited the discoverer of the crown ethers, Charles Pedersen, to University College, London, for some initial work and successfully persuaded the Agriculture Research Council of the U.K. to establish a self-sufficient X-ray diffraction assembly to make possible prompt structural analysis of the  $M^{z+}$ -crown systems on a rather extended scale.

Mary Truter, the supervisor of the Structural Unit, undertook structural analysis of the products  $RbNCS(DB18C6)_2$  [2],  $NaBr(DB18C6) \cdot 2H_2O$  [3],  $NaI(B15C5) \cdot H_2O$  [4],  $KI(B15C5)_2$  [5], and  $KI(DB30C10)$  [6] in this order. She and her coworkers found that the complex  $RbNCS(DB18C6)_2$  was in fact  $(Rb_{0.55}Na_{0.45}NCS)_2(DB18C6)_3$ , including a molecule of uncomplexed crown. Rubidium is genuinely chelated through the six crown oxygens ( $Rb \cdots O$ , 2.86 to 2.94 Å) while the counteranion  $NCS^-$  is also paired ( $Rb \cdots NCS$ , 2.94 Å) with the complexed cation; sodium which was incorporated into the system as a 'contaminant' was also chelated by the crown through six oxygens ( $Na \cdots O$ , 2.74 to 2.89 Å) but did not interact with  $NCS^-$  ( $Na \cdots NCS > 3.3$  Å). For  $NaBr(DB18C6) \cdot 2H_2O$ , two types of molecules were noted wherein the cation chelation by all the crown oxygens was recorded ( $Na \cdots O$ , 2.54 to 2.89 Å) with axial positions filled by  $Br^-$  and/or  $H_2O$ . Sodium in  $Na^+(B15C5)(H_2O)I^-$  (Figure 2) was also found chelated by the crown ( $Na \cdots O$ , 2.35 to 2.43 Å) while the coligating water molecule from one of the axial directions ( $Na \cdots OH_2$ , 2.29 Å) displayed a 'double action' [7] and also held the iodide through a hydrogen bond. Potassium, in  $K^+(B15C5)_2I^-$  (Figure 3) [5], interestingly, was noted to constitute a charge-separated sandwich bonded to all the 10 oxygens of the crown molecules while the iodide was isolated from the cation. For the system  $K^+(DB30C10)I^-$  [6],  $K^+$  and  $I^-$  were also charge-separated, the potassium ion being concealed through a 'wrap-around' action of the crown.

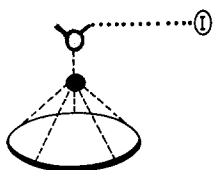


Fig. 2. Structural features of  $[Na(B15C5)(H_2O)]I$  [4].

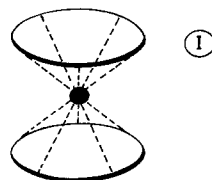


Fig. 3. Structural features of charge separated  $[K(B15C5)_2]I$  [5].

At this juncture of the development, one of us (N.S.P.) initiated a wide-range screening of the chemical interactivity patterns for  $M^{z+}$ -crown systems [8–10] where crown is any one of those shown in Figure 1. In the meantime, the Truter group also published structural results on  $Na(DC18C6)(H_2O)_2Br$  [11], the features of which, unfortunately, did not provide any novelty when compared to  $NaBr(DB18C6) \cdot 2H_2O$  or  $(Rb_{0.55}Na_{0.45}NCS)_2(DB18C6)_3$ . The bimetallic complex  $(KNCS)_2(DB24C8)$ , synthesized by Poonia in contrast to the reported formation of a monometallic complex [1], presented a novelty in showing not only the incorporation of two cations in the cavity of a crown but also in pairing of the anion ( $NCS^-$ ) with  $K^+$  [12] which is not possible in complexes of  $KX$  with B15C5 or DB30C10.

## 2. B15C5 as a Ligand

Increasing consciousness concerning the biological roles [13] of  $Na^+$ ,  $K^+$ ,  $Mg^{2+}$ , and  $Ca^{2+}$  and the lack of knowledge regarding the chemical principles linked with these roles made

chemical and structural investigations of  $M^{z+}$ -crown systems important. The main point of interest to an inorganic chemist had been the rather intriguing discriminatory transport of the otherwise chemically similar cations, viz.,  $Na^+$  and  $K^+$ , and  $Mg^{2+}$  and  $Ca^{2+}$ , across the cell membrane [14]. Our subsequent and sustained work in the Indian laboratories, which was directed to single out the chemical principles related to the discriminations of these cations in nature, led to the realization that:

- Interactivity differences between seemingly similar pairs of cations such as  $Na^+$  and  $K^+$  can indeed be noted through complexation studies on inorganic ( $MX_z$ ) as well as organic ( $ML_z$ ) salts of  $M^{z+}$  using crowns as ligands, especially B15C5.
- B15C5 is the most useful crown in view of its solubility characteristics in a wide range of solvent media and in view of the interactivity variety it displays towards  $MX_z$  and  $ML_z$ , including sandwich formation.
- The all-important *in vivo* membrane transport process of an  $M^{z+}$  is best modelled by sandwich encapsulation of the cation with a neutral macrocycle because the concerned cation is completely charge separated from the counteranion and is concealed within a neutral chelating environment through either process.
- The neutral ligand versus anion preference of  $M^{z+}$ , which is one of the main *in vitro* features of  $M^{z+}$  that needs to be explored to understand the intriguing discriminatory roles of these cations in biology, is also best studied using B15C5; the ring size, chelating order, and nucleophilicity of the crown being suited especially for complexation of the biologically important  $Na^+$ ,  $K^+$ ,  $Mg^{2+}$ , and  $Ca^{2+}$ .
- Finer interactivity differences between different  $M^{z+}$ , in particular their anion versus ligand preferences, can be studied and generalized best if the range of cations is examined under common conditions, preferably in the absence of a solvent, employing solid state studies.

Conclusions (a) to (e) led us to undertake synthesis and X-ray diffraction of a long list of related  $M^{z+}L_z^-(B15C5)_n$  complexes wherein  $M^{z+}$  is  $Li^+$  to  $Cs^+$  and  $Ca^{2+}$  to  $Ba^{2+}$ , and  $L^-$  is 2,4,6-trinitrophenolate (Picrate or Pic) or 3,5-dinitrobenzoate (Dnb). Other workers have also been reporting some structural information about  $MX_z$ -15C5 and  $MX_z$ -B15C5 systems. These results have been used in conjunction with our studies to reach the inferences being provided in this review.

### 3. B15C5 as a Discriminating Ligand

The structural information obtained from the very first two complexes,  $Na^+(H_2O)(B15C5)I^-$  [4] and  $K^+(B15C5)_2I^-$  [5], was important with regard to chemical inferences which were, unfortunately, not made. This was probably because at that time it was not realized that the structure of a system could reflect closely the chemistry of the involved cation. If, in the former complex, the water displaying double action, i.e., coordinated with the rather small sodium and hydrogen bonded to the iodide, is treated as 'anionic' then sodium in its complex (Figure 2) is crown-chelated in the state 'paired with the anion'. Potassium, on the contrary, is completely charge separated (Figure 3) by the sandwich encapsulation with the two neutral molecules of the crown. Ironically, the same chemical situation was also noted with the larger crown, DB30C10, where  $NaX$  ( $X = I^-$  or  $NCS^-$ ) salts yielded bimetallic and understandably *anion-paired* complexes [8] of the type  $(NaX)_2(DB30C10)$  while KI yielded a *charge-separated* 'wrap-around' complex wherein one molecule of the crown, for the purpose of charge separation and cation concealment, functioned as the two B15C5 molecules. However, the chemical significance of the results with DB30C10 was not realized in light of

the B15C5 results until one of us [9,15] highlighted this comparison and brought forth the conclusion that this constituted evidence for interactive differences between  $K^+$  and  $Na^+$ . Sodium behaves 'anionophilic', i.e., undergoes complexation with an electrically neutral crown in a state maintaining its contact with anionic species, while  $K^+$  displays a preference for the

Table I. Donor atom contacts around the cation in  $M^{z+}$ -B15C5 complexes

Compound	Bond distance (Å)	Reference
[Na(B15C5)(H <sub>2</sub> O)]I	Na...O, 2.35–2.43 Na...OH <sub>2</sub> , 2.29	[4]
[K(B15C5) <sub>2</sub> ]I	K...O, 2.78–2.96	[5]
[Li(Pic)·2H <sub>2</sub> O](B15C5)	Li...O, 1.85–2.03	[16]
Na(Pic)(B15C5)	Na...O, 2.40–2.50 Na...O <sup>-</sup> , 2.35; Na...ONO, 2.51	[17]
[K(B15C5) <sub>2</sub> ](Pic)	K...O, 2.81–3.00	[18]
Cs(Pic)(B15C5) <sup>a</sup>	Cs...O, 3.00–3.24 Cs...O <sup>-</sup> , 3.03; Cs...ONO, 3.01–3.42	[20]
[Ca(Pic) <sub>2</sub> ·3H <sub>2</sub> O](B15C5)	Ca...O <sup>-</sup> , 2.28, 2.32; Ca...ONO, 2.46–2.61 Ca...OH <sub>2</sub> , 2.42	[29]
Ba(Pic) <sub>2</sub> (B15C5)·H <sub>2</sub> O	Ba...O, 2.80–3.00 Ba...O, 2.64, 2.67; Ba...ONO, 2.83, 2.99 Ba...OH <sub>2</sub> , 2.71	[30]
NaClO <sub>4</sub> (B15C5)	Na...O, 2.37–2.46 Na...O <sup>-</sup> , 2.43, 2.63	[34]
[Na(B15C5) <sub>2</sub> ]ClO <sub>4</sub>	Na...O, 2.63–2.94	[34]
[Na(B15C5) <sub>2</sub> ]BPh <sub>4</sub>	Na...O, 2.48–3.30	[34]
Na(UO <sub>2</sub> Cl <sub>4</sub> )(B15C5) <sub>2</sub>	Na...O, 2.40–2.57 Na...Cl, 2.82, 2.95	[35]
[K(B15C5) <sub>2</sub> ]NO <sub>3</sub> ·H <sub>2</sub> O <sup>b</sup>	K...O, 2.78–3.00	
Mg(NCS) <sub>2</sub> (B15C5)	Mg...O, 2.17–2.20 Mg...N, av 2.06	[38]
Ca(NCS) <sub>2</sub> (B15C5)·H <sub>2</sub> O	Ca...O, 2.46–2.61 Ca...N, 2.42, 2.43 Ca...OH <sub>2</sub> , 2.40	[38]
Ca(NCS) <sub>2</sub> (B15C5)·MeOH	Ca...O, 2.51–2.55 Ca...N, 2.40, 2.49 Ca...O(MeOH), 2.38	[38]
[K(B15C5) <sub>2</sub> ](Dnb·2HDnb)	K...O, 2.76–3.10 K...O <sup>-</sup> , > 7	[42]
[Ca(Dnb) <sub>2</sub> (B15C5)](B15C5·3H <sub>2</sub> O)	Ca...O, 2.52–2.78 Ca...O <sup>-</sup> , 2.46, 2.47	[43]
[Ba(Dnb) <sub>2</sub> (B15C5)] <sub>2</sub>	Ba...O, 2.89–3.09 Ba...O <sup>-</sup> , 2.64–2.69	[44]

<sup>a</sup> The complex Rb(Pic)(B15C5) is isomorphous.<sup>b</sup> The complex Rb(B15C5)<sub>2</sub>NO<sub>3</sub>·H<sub>2</sub>O is isomorphous.

neutral ligand over anionic species, even its own charge neutralizer. This vital conclusion made the structural studies on  $M^{z+}$ -B15C5 complexes more exciting. We highlight below further generalizations concerning cation discrimination. Henceforth, we shall limit discussion to the anion/crown preferences of a cation in the complex. The precise donor atom environment of the cation is provided in Table I.

#### 4. The $M(\text{Pic})_2$ -Complexes

Systematic structural studies on  $M^{z+}(\text{Pic})(\text{B15C5})_n$  systems established that the affinity gradation of a cation for the crown from  $\text{Li}^+$  to  $\text{Cs}^+$  is perfectly understandable. The  $M^+$ -crown stoichiometry and/or 'crown-over-anion' preference of a cation is a direct function of its own Lewis acidity which can, of course, be modified by the charge neutralizing counteranion.

Thus, lithium in the complex  $\text{Li}(\text{Pic})(\text{H}_2\text{O})_2(\text{B15C5})$  (Figure 4(a)) escapes chelation with the crown and remains contained within the environment of the chelating  $\text{Pic}^-$  and the two

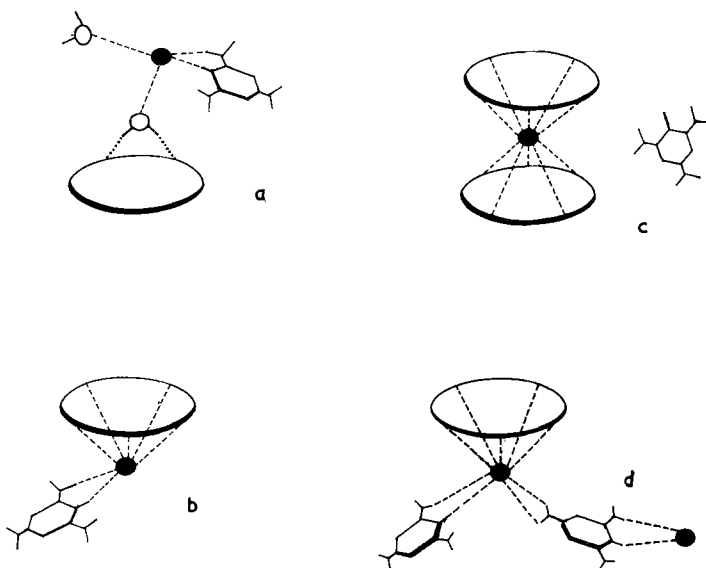


Fig. 4. Structural features of  $M(\text{Pic})(\text{B15C5})$  systems: (a)  $[\text{Li}(\text{Pic})(\text{H}_2\text{O})_2](\text{B15C5})$  [16], (b)  $[\text{Na}(\text{Pic})(\text{B15C5})]$  [17], (c) charge separated  $[\text{K}(\text{B15C5})_2](\text{Pic})$  [18], and (d)  $[\text{Cs}(\text{Pic})(\text{B15C5})]$  [20].

water molecules [16]. The higher charge density  $\text{Ca}^{2+}$  behaves similarly in the complex  $\text{Ca}(\text{Pic})_2(\text{H}_2\text{O})_3(\text{B15C5})$  (see below and Table I). This behaviour of  $\text{Li}^+$  is comparable to that of a formal proton in that the complex of  $\text{HPic}$ , viz.,  $\text{H}(\text{Pic})(\text{H}_2\text{O})_2(\text{B15C5})$  is isomorphous with the complex of  $\text{LiPic}$  (work in progress).

Sodium in the complex  $[\text{Na}(\text{Pic})(\text{B15C5})]$  (Figure 4(b)) is chelated by B15C5 [17] and paired with the chelating  $\text{Pic}^-$ ; the main difference from lithium is that sodium, although hydrated in the parent salt,  $\text{NaPic} \cdot n\text{H}_2\text{O}$ , because of interaction with the crown becomes anhydrous.

Potassium in  $[\text{K}(\text{B15C5})_2](\text{Pic})$  (Figure 4(c)) constitutes [18] a genuinely charge separated sandwich with the two crown molecules as it does [5] in  $[\text{K}^+(\text{B15C5})_2\text{I}^-]$  (Figure 3). It is

significant to note that a 1:2 complex is obtained, as for any other KX or KL species [8, 9] even when the B15C5 proportion is not more than 1:1 with respect to KPic.

RbPic [19] and CsPic [20] yield isomorphous 1:1 complexes of the type  $M(\text{Pic})(\text{B15C5})$  and not 1:2 charge separated sandwiches despite a larger size of  $\text{Rb}^+$  and  $\text{Cs}^+$  compared to the cavity size of the crown. The 1:2 complexes cannot be synthesized using excess B15C5 under any conditions. Structural analysis [20] of  $\text{Cs}(\text{Pic})(\text{B15C5})$  (Figure 4(d)) reveals  $\text{Cs}^+$  to be crown-chelated and paired with  $\text{Pic}^-$ . The cation, despite its state of coordinative unsaturation (normal coordination number 8 to 10 [7]), does not form the 1:2 sandwich as expected in view of the well-known ion cavity radius concept [1, 21]. Instead, it forces chelation on the *p*-nitro substituent of the  $\text{Pic}^-$  belonging to an adjacent complex molecule, a type of chelation unknown for any nitrophenolate towards  $M^{z+}$ , and not found even for the CsPic salt [22].  $\text{CsBPh}_4$  [23] and  $\text{CsClO}_4$  [24] have been found to yield 1:2 ( $\text{Cs}^+ : \text{B15C5}$ ) products which are apparently sandwiches, and CsI yields [25] also a genuine charge separated 1:2 sandwich with 15C5. Also, CsNCS yields a genuine sandwich with the much larger TMDB18C6G [26] where TMDB18C6G is isomer *G* of DB18C6 which has its ring symmetrically substituted with four methyl groups. Therefore, the 1:1 complexation for CsPic with B15C5 is unambiguously a chemical consequence of the Lewis acidity of  $\text{Cs}^+$  as modified by  $\text{Pic}^-$ . The controlling effect of  $\text{Pic}^-$  is so strong that  $\text{Rb}^+$  is also made to mimic  $\text{Cs}^+$  in yielding the isomorphous complex  $\text{Rb}(\text{Pic})(\text{B15C5})$  although, under most conditions [27]  $\text{Rb}^+$  displays the chemistry of  $\text{K}^+$ .

Information on the  $M(\text{Pic})_2$  systems is still incomplete. This is firstly because single crystals of the  $\text{Mg}(\text{Pic})_2\text{-B15C5}$  complex cannot be grown and, secondly,  $\text{Ca}(\text{Pic})_2$  yields more than one complex depending upon the proportion of  $\text{Ca}(\text{Pic})_2$  with B15C5 in the reaction and the presence of foreign PicH and/or water in the reaction medium (ethanol) [28]. Structural information is available for  $\text{Ca}(\text{Pic})_2(\text{H}_2\text{O})_3(\text{B15C5})$  [29] (Figure 5). This system is unique

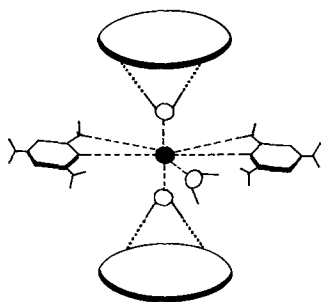


Fig. 5. Structural features of  $[\text{Ca}(\text{Pic})_2 \cdot 3\text{H}_2\text{O}](\text{B15C5})$  [29].

in that calcium is contained only within the anionic environment of the two  $\text{Pic}^-$  anions ( $\text{Ca} \cdots \text{ONO}$ , 2.69, 2.92 Å;  $\text{Ca} \cdots \text{O}$ , 2.28, 2.32 Å) and the three water molecules ( $\text{Ca} \cdots \text{OH}_2$ , 2.27 to 2.42 Å). The axially coordinated water molecules display double action in that they are also involved in bonding intra- and intermolecularly with the crown oxygens. This was the first example in the literature which displayed nonchelation of a crown with the central cation of a complex in the lattice; that of LiPic described above was the second. It confirmed the belief that a proton of a water molecule which is coordinated to a high charge density cation is so highly polarized that an anion (as noted for  $\text{Na}(\text{B15C5})(\text{H}_2\text{O})\text{I}$  [4]) or even a neutral ligand (as noted for the LiPic and  $\text{Ca}(\text{Pic})_2$  complexes) can 'coordinate' with it.

$\text{Sr}(\text{Pic})_2$  and  $\text{Ba}(\text{Pic})_2$  yield isomorphous 1:1 complexes of the formula  $\text{M}(\text{Pic})_2(\text{B15C5}) \cdot \text{H}_2\text{O}$ . Significantly, the composition of these complexes cannot be changed to 1:2 even if B15C5 is used in the reaction mixture in five-fold excess to the salt and 50 percent water is added to the reaction medium (ethanol) to weaken the  $\text{M}^{2+} \text{Pic}^-$  pair. X-ray structural analysis of  $\text{Ba}(\text{Pic})_2(\text{B15C5}) \cdot \text{H}_2\text{O}$  [30] (Figure 6) reveals that the crown-chelated barium is effectively paired with the chelating  $\text{Pic}^-$  ( $\text{Ba} \cdots \text{O}$ , 2.64, 2.65 Å;  $\text{Ba} \cdots \text{ONO}$ , 2.83, 3.05 Å) and is also hydrated ( $\text{Ba} \cdots \text{OH}_2$ , 2.74 Å).

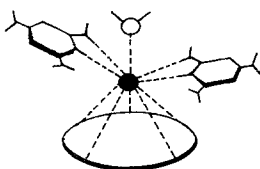


Fig. 6. Structural features of  $\text{Ba}(\text{Pic})_2(\text{B15C5}) \cdot \text{H}_2\text{O}$  [30].

When the collective results for the four complexes  $\text{Rb}(\text{Pic})(\text{B15C5})$ ,  $\text{Cs}(\text{Pic})(\text{B15C5})$ ,  $\text{Sr}(\text{Pic})_2(\text{B15C5}) \cdot \text{H}_2\text{O}$ , and  $\text{Ba}(\text{Pic})_2(\text{B15C5}) \cdot \text{H}_2\text{O}$  are examined in light of the  $\text{K}(\text{Pic})$  structure, it is apparent that the interaction stoichiometry of  $\text{M}^{z+}$  and B15C5 is not just a function of the cation size with respect to the cavity size of the macrocycle as usually believed [1, 21]. Interestingly, all four cations mimic  $\text{Na}^+$  rather than  $\text{K}^+$ . As elaborated previously [15], therefore, the interaction stoichiometry is indeed a chemical consequence of the Lewis acidity (charge density or charge/radius ratio parameter) of the cation which is modified by the charge neutralizing anion. The chemical reason responsible for the generation of an anion-paired complex for a higher charge density cation (smaller  $\text{Na}^+$  or the larger  $\text{Sr}^{2+}$  or  $\text{Ba}^{2+}$ ), however, has to be different from that for a lower charge density one ( $\text{Rb}^+$  or  $\text{Cs}^+$ ); for the former it being because of anionphilicity while for the latter because of poorer polarization of the neutral ligand.

For B15C5, 'ligand encapsulation' [15] of  $\text{K}^+$  is adequately supported by its 'self-encapsulation' so that  $\text{K}^+$  constitutes a 1:2 sandwich irrespective of the nature of the counteranion and the  $\text{K}^+ : \text{B15C5}$  in the reaction medium. The lower charge densities of  $\text{Rb}^+$  and  $\text{Cs}^+$  do not contribute enough self-encapsulation (at least under the chelating effect of  $\text{Pic}^-$ ) while the comparatively higher charge densities of  $\text{Sr}^{2+}$  and  $\text{Ba}^{2+}$  tend more towards anion-pairing than to self-encapsulation with respect to B15C5. The result is that none constitutes the charge separated sandwich (for  $\text{Pic}^-$ ) under any condition. The  $\text{Ba}^{2+} - \text{B15C5}$  interaction does result in the formation of a charge separated 1:2 sandwich,  $[\text{Ba}(\text{B15C5})_2](\text{Br}_2 \cdot 2\text{H}_2\text{O})$  [31]. However, significance needs to be attached to the stabilization of  $\text{Br}^-$  with the bonding water molecules as well as a stronger nucleophilicity (ligand encapsulation) of B15C5 which exploits self-encapsulation of the divalent barium.

## 5. The $\text{MX}_z$ -Complexes

For the strongly cation pairing anions such as  $\text{NCS}^-$  and  $\text{Eaa}^-$  (ethylacetoacetate), sodium yields *anion-paired* products  $\text{Na}(\text{NCS})(\text{B15C5})$  plus  $\text{Na}(\text{NCS})(\text{B15C5}) \cdot \text{H}_2\text{O}$  [32] and  $\text{Na}(\text{Eaa})(\text{B15C5})$  [33], respectively, even with the highly nucleophilic B15C5. However, the less nucleophilic B15C5 also forms 1:2 genuine charge separated sandwiches  $[\text{Na}(\text{B15C5})_2]\text{X}$  for the weakly competing  $\text{ClO}_4^-$  and  $\text{BPh}_4^-$  [34] in addition to the anion-paired complexes

$\text{NaX}(\text{B15C5})$  (for example, Figure 7). This establishes that the *original* Lewis acid status of an alkali cation towards a neutral ligand can be desirably modified through the change of its charge neutralizing anion. Obviously, the cationic behaviour of an alkali cation can be modified from system to system, a feature which nature appears to have exploited for the diverse roles of  $\text{M}^{z+}$  ions in biology. An intriguing point about these 1:2 species is that effective  $\text{Na}\cdots\text{O}$  coordination ( $\text{Na}\cdots\text{O}$ ,  $< 2.7 \text{ \AA}$ ) is found with fewer oxygens of the crown (Figure 8) for  $\text{ClO}_4^-$  compared to  $\text{BPh}_4^-$ . This could be because the charge separated anion maintains its influence on the stereochemical aspects of the 'lipid cation',  $\text{Na}(\text{B15C5})_2^+$ .

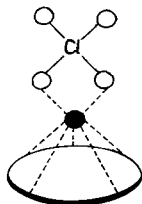


Fig. 7. Structural features of  $\text{NaClO}_4(\text{B15C5})$  [34].

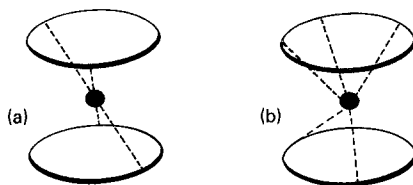


Fig. 8. Structural features of charge separated  $\text{Na}^+ - \text{B15C5}$  complexes: (a)  $[\text{Na}(\text{B15C5})_2]\text{ClO}_4$  and (b)  $[\text{Na}(\text{B15C5})_2]\text{BPh}_4$  [34]. Bond distances  $< 2.7 \text{ \AA}$  are shown.

In the complex  $\text{Na}_2(\text{tetrachlorodioxouranate})(\text{B15C5})_2$  [35], Figure 9, the  $\text{Na}(\text{B15C5})^+$  moieties act as 'lipid cations' with each crown-chelated sodium paired with two 'anionic' chlorides ( $\text{Na}\cdots\text{Cl}$ , 2.82, 2.95  $\text{ \AA}$ ); the complex is, in fact, a slow aerial oxidation product of the complex  $\text{UCl}_3(\text{B15C5})$  in THF wherein Na is incorporated, perhaps from the glass container.

We have recently synthesized some metal nitrate complexes of B15C5 [36] and have obtained structural information about  $\text{KNO}_3$  and  $\text{RbNO}_3$  complexes. These are genuine 1:2 sandwiches of formula  $\text{M}(\text{B15C5})_2\text{NO}_3 \cdot \text{H}_2\text{O}$  and are isomorphous. Herein the water proton stabilizes the anion through hydrogen bonding (Figure 10). From the collective examination

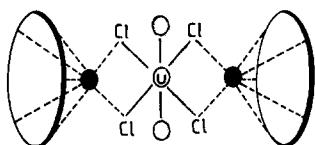


Fig. 9. Structural features of  $\text{Na}_2(\text{UO}_2\text{Cl}_4)(\text{B15C5})_2$  [35].

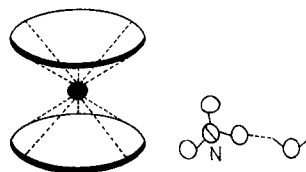


Fig. 10. Structural features of charge separated  $[\text{K}(\text{B15C5})_2]\text{NO}_3 \cdot \text{H}_2\text{O}$ .

of complexes of these cations for  $\text{Pic}^-$ ,  $\text{I}^-$  and  $\text{NO}_3^-$  it is possible to understand more subtle differences between  $\text{K}^+$  and  $\text{Rb}^+$ . Thus, complexes of  $\text{K}^+$  are consistently 1:2 charge separated products suggesting that (i)  $\text{K}^+$  is strongly ligandophilic but poorly anionophilic, and (ii)  $\text{K}\cdots\text{O}$  (crown) bonds are strong enough to resist the nucleophilic effect of the charge separated (electrostatically destabilized) counteranion. For  $\text{Rb}^+$ , however, the crown/anion preference is dictated rather distinctly by the anion. In the presence of the charge delocalized  $\text{NO}_3^-$ , which is stabilized also by a molecule of water, the  $\text{Rb}(\text{B15C5})_2^+$  sandwich is stable. For iodide a 1:2 sandwich is formed but the complex slowly decomposes precluding an X-ray



structural analysis. The chelating  $\text{Pic}^-$  quenches the Lewis acidity of  $\text{Rb}^+$  to the extent that the 1:2 complex is not even formed and the product is merely 1:1 anion-paired (see above).

The  $\text{M}^z+(\text{NCS})_z^-$  salts can be easily solubilized and studied in moderately polar organic media such as ethanol. This feature of  $\text{NCS}^-$ , which may be due to its partial covalent state of pairing with the cation, has its own consequence in that the crown-complexes of especially the higher charge density  $\text{M}^z+$  are cation-paired. Structures of  $\text{RbNCS}$  complexes with B15C5 have not been examined as yet. KNCS does yield a 1:2 complex [8] which should be a charge separated sandwich because  $\text{Rb}(\text{DB30C10})\text{NCS} \cdot \text{H}_2\text{O}$  [37] is a charge separated wrap-around system despite a weaker Lewis acidity of  $\text{Rb}^+$  and a higher conformation energy requirement of DB30C10 for complexation. The stoichiometry of the  $\text{LiNCS}$  and  $\text{NaNCS}$  complexes with B15C5 is invariably 1:1 [8], suggesting that  $\text{M}^+-\text{NCS}$  pairing for the crown-chelated cation is present. Sodium is also paired with  $\text{NCS}^-$  even in the 15C5 complex moieties  $\text{NaNCS}(15\text{C5}) \cdot \text{H}_2\text{O}$  and  $\text{NaNCS}(15\text{C5})$  [32], despite the fact that in the former, water is also a cation-stabilizing coligand.

In view of the above, it is not surprising that complexes of the divalent  $\text{Mg}^{2+}$  and  $\text{Ca}^{2+}$  are consistently anion-paired irrespective of their state of solvation in the lattice. Thus,  $\text{Mg}^{2+}$  in  $\text{Mg}(\text{NCS})_2(\text{B15C5})$  [38] is crown-chelated through the five oxygens as well as in contact with both the  $\text{NCS}^-$  anions ( $\text{Mg} \cdots \text{N}$ , ave 2.06 Å) (Figure 11), one from each axial side of the crown. The analogous anhydrous complex of  $\text{Ca}^{2+}$  is formed [39], but the structure is not known. The difference is that  $\text{Ca}(\text{NCS})_2$  yields  $\text{Ca}(\text{NCS})_2(\text{B15C5})$  which can be solvated with  $\text{H}_2\text{O}$  or  $\text{MeOH}$ . As seen in Figure 12, the crown-chelated cation is solvated as well as paired with the two anions [38]. During complexation,  $\text{Mg}(\text{NCS})_2$  obviously undergoes a transitory ionization (because S of  $\text{NCS}^-$  cannot pass through the cavity of the crown) for the purpose of juxtaposing one  $\text{NCS}^-$  on each axial side. On the contrary,  $\text{Ca}(\text{NCS})_2$  is complexed as an angular ion-pair. This supports the greater anionphilicity of  $\text{Ca}^{2+}$  noted from the study of the  $\text{Ca}(\text{Pic})_2$  complex. A 1:2  $\text{Ba}(\text{NCS})_2(\text{B15C5})_2$  has been reported [40] but structural information on  $\text{Sr}(\text{NCS})_2$  and  $\text{Ba}(\text{NCS})_2$  complexes is not known.

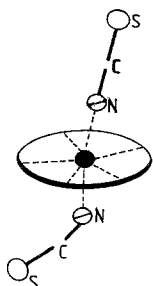


Fig. 11. Structural features of  $\text{Mg}(\text{NCS})_2(\text{B15C5})$  [38].

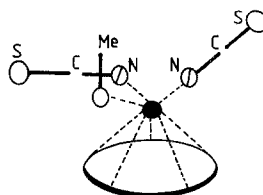


Fig. 12. Structural features of  $\text{Ca}(\text{NCS})_2(\text{B15C5}) \cdot \text{MeOH}$  [38].

## 6. $\text{M}(\text{Dnb})_z$ -Complexes

Information is not available for the  $\text{LiDnb}$  complex.  $\text{H}(\text{Dnb})(\text{B15C5}) \cdot \text{H}_2\text{O}$  has been synthesized and our X-ray analysis has revealed that the carboxy proton is *not* chelated with the crown. Instead, the carboxy proton is strongly bonded (2.55 Å) to the molecule of water and the latter is hydrogen bonded to two crown oxygens. This behaviour of the carboxy proton is comparable to that of  $\text{Li}^+$  and  $\text{Ca}^{2+}$  in the complexes  $\text{Li}(\text{Pic})(\text{H}_2\text{O})_2(\text{B15C5})$  (Figure 4(a))

and  $\text{Ca}(\text{Pic})_2(\text{H}_2\text{O})_3(\text{B15C5})$  (Figure 5), respectively, and suggests that high charge density cations including an acidic proton tend to be coordinated with water oxygen(s) and the polarized water protons then bond with the crown ring oxygens. That  $\text{Li}^+$  mimics this proton in the  $\text{LiDnb B15C5}$  complex is yet to be established. Sodium in  $\text{Na}(\text{Dnb})(\text{B15C5}) \cdot \text{H}_2\text{O}$  [41] is as expected crown-chelated in the anion-paired state (as in the  $\text{NaPic}$  system) while the water molecule is disordered.

The potassium preference [42] with  $\text{Dnb}^-$  and  $\text{B15C5}$ , irrespective of the reactant proportion and the solvating medium, is to form a 1:2 sandwich of the type noted for the system  $\text{KI-B15C5}$ ,  $\text{KNO}_3\text{-B15C5}$ ,  $\text{K(Pic)-B15C5}$ ,  $\text{K(Onp)-B15C5}$  and  $\text{K(Anth)-B15C5}$  [8,9] ( $\text{Onp}^- = o\text{-nitrophenolate}$  and  $\text{Anth}^- = \text{anthranilate (2-aminobenzoate)}$ ). The rather strongly proton-accepting  $\text{Dnb}^-$  in a state separated from the cation [42] undergoes disproportionation with the protic medium (ethanol) to generate  $\text{DnbH}$  and constitutes a hydrogen-bonded homoconjugate  $[\text{Dnb}(\text{HDnb})_2]$  shown in Figure 13. This is also observed for  $\text{Onp}^-$  [8] and  $\text{Anth}^-$  [9] in their respective systems.

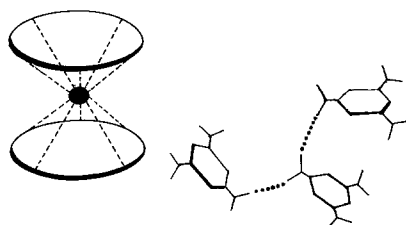


Fig. 13. Structural features of charge separated  $[\text{K}(\text{B15C5})_2](\text{Dnb} \cdot 2\text{HDnb})$  [42].

Although chelating style and Lewis acid behaviour of  $\text{Pic}^-$ ,  $\text{Onp}^-$ ,  $\text{Anth}^-$ , and  $\text{Dnb}^-$  differ widely, the  $\text{B15C5}$ -affinity of  $\text{Na}^+$  and  $\text{K}^+$  is consistent for all four counteranions in that complexed  $\text{Na}^+$  displays anionophilicity (1:1 complexation with the crown in a state paired with the anion) while  $\text{K}^+$  displays ligandophilicity towards the neutral crown. Structural information on the  $\text{Rb}(\text{Dnb})$  and  $\text{Cs}(\text{Dnb})$  complexes is not yet available but keeping in view the results of  $\text{Rb}(\text{Pic})$  and  $\text{Cs}(\text{Pic})$  complexes there should be no surprise if the  $\text{Cs}(\text{Dnb})$  and/or even  $\text{Rb}(\text{Dnb})$  complex is found to be a 1:1 anion-paired system.

The  $\text{Mg}(\text{Dnb})_2$  complex could not be grown as single crystals. Calcium in  $\text{Ca}(\text{Dnb})_2(\text{B15C5})_2 \cdot 3\text{H}_2\text{O}$  [43], which gave the impression of being a 1:2 charge separated sandwich, was found through X-ray analysis to be an anion-paired complex of the type  $[\text{Ca}(\text{Dnb})_2(\text{B15C5})](\text{B15C5} \cdot 3\text{H}_2\text{O})$  wherein the cation is 9-coordinate and the anions chelate  $\text{Ca}^{2+}$  through carboxylate oxygens (Figure 14). The second molecule of the crown is present just as solvate or to hydrogen bond with the hydrogen atoms of the water molecules. Barium in  $[\text{Ba}(\text{Dnb})_2(\text{B15C5})]_2$ , too, is anion-paired [44]. It is 9-coordinate in a different fashion (Figure 15). The system is dimerized in the lattice and each of the four  $\text{Dnb}^-$  anions bridge the two  $\text{Ba}^{2+}$  ions each in turn being chelated with one of the crown molecules. If anything, it reflects the loosening of the original  $\text{Ba} \cdots \text{O}^-(\text{Dnb})$  contacts by the crown in opposition to the behavior for  $\text{Ca}^{2+}$  in the analogous system and hence displaying a diminished anionophilicity of  $\text{Ba}^{2+}$  compared to  $\text{Ca}^{2+}$ . The interactive modes of  $\text{Sr}^{2+}$  can be comparable to those of  $\text{Ca}^{2+}$  or  $\text{Ba}^{2+}$  depending on the environment and the differences are minor. It would have been helpful to examine the relative behaviour of  $\text{Sr}^{2+}$  but unfortunately single crystals of the  $\text{Sr}(\text{Dnb})_2$  product could not be grown. Work on the remaining  $\text{M}(\text{Dnb})_2$

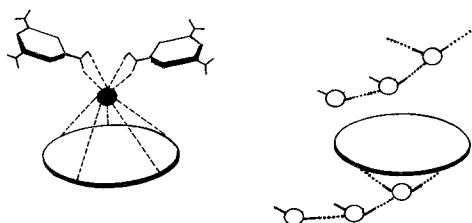


Fig. 14. Structural features of 1:2 anion paired  $[\text{Ca}(\text{Dnb})_2(\text{B15C5})](\text{B15C5} \cdot 3\text{H}_2\text{O})$  [43].

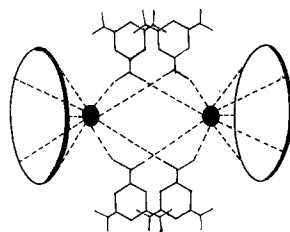


Fig. 15. Structural features of the dimerized  $[\text{Ba}(\text{Dnb})_2(\text{B15C5})]_2$  [44].

complexes can show whether  $\text{Dnb}^-$  is useful in aiding discrimination through B15C5 other than the  $\text{Na}^+ - \text{K}^+$  discrimination mentioned above.

Two types of observations may be cited to highlight the anion effect towards anionophilic ( $\text{Na}^+$  and  $\text{Ca}^{2+}$ , in particular) which could create interesting chemical consequences even when potentially complexing crowns are involved. Firstly, some  $\text{MX}_z$ -crown systems tend to drag  $\text{Na}^+$  ions from the glass of the containers. The system  $\text{RbNCS-DB18C6}$  picks up sodium to yield  $[\text{Rb}_{0.55}\text{Na}_{0.45}\text{NCS}(\text{DB18C6})]_2(\text{DB18C6})$  [2]. This mixed-cation complex carries also an uncomplexed molecule of the crown in the solid lattice. This suggests that the species which picked up  $\text{Na}^+$  from the glass could well be the cation-loosened  $\text{NCS}^-$  rather than the crown. The system  $\text{UCl}_3\text{-B15C5}$  in THF [35] also picks up  $\text{Na}^+$  and ultimately changes to  $\text{Na}_2(\text{UO}_2\text{Cl}_4)(\text{B15C5})_2$ . Here, too, the role played by the electrostatically destabilized  $\text{Cl}^-$  ions should be considered. The second observation is that the  $\text{M}^{z+}$ -crown interaction ratio may be effectively controlled by the anion. Thus, for  $\text{BPh}_4^-$  [39],  $\text{Dnb}^-$  (or  $\text{NCS}^-$ ) [38, 43] and  $\text{Pic}^-$  [29], the  $\text{Ca}^{2+} : \text{B15C5}$  ratio in the crystal lattice is 1:2, 1:1, and 1:0, respectively, suggesting that the anion greatly influences the environment around the cation.

## 7. Conclusions

Known X-ray diffraction results of a rather extensive group of complexes have revealed that B15C5 is a versatile, discriminating macrocycle which is capable of making discriminations between and within the group for different alkali and alkaline earth cations ( $\text{M}^{z+}$ ). Under the counteracting effect of picrate, B15C5 influences the hydration and  $\text{Pic}^-$  pairing of the  $\text{M}^{z+}$  ions in the order of their charge density gradation. The smallest  $\text{M}^+$  ( $\text{Li}^+$ ) and the rather small  $\text{M}^{2+}$  ( $\text{Ca}^{2+}$ ) exhibit a total preference for the anionic species over the crown, while the larger cations favor the  $\text{M}^{z+}$ -crown interaction. This trend also persists qualitatively under the counteracting effect of 3,5-dinitrobenzoate. Enough work has not been carried out using inorganic anions, but that reported so far using  $\text{NCS}^-$ ,  $\text{I}^-$ ,  $\text{NO}_3^-$ , and  $\text{ClO}_4^-$  indicates that cations constituting vitally important pairs such as  $\text{Na}^+$  and  $\text{K}^+$ , and  $\text{K}^+$  and  $\text{Rb}^+$  can be discriminated. The anion effect of the charge neutralizer on  $\text{M}^{z+}$ -crown complexation is important since it strongly modifies the  $\text{M}^{z+}$ -crown interaction stoichiometry as well as the Lewis acid status of a cation with respect to its congeners.

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