



Solid-state structures of some fluorescent macrocyclic complexes of alkali metal ions studied by single-crystal X-ray diffraction studies, vibrational spectroscopy and NMR spectroscopy: a review

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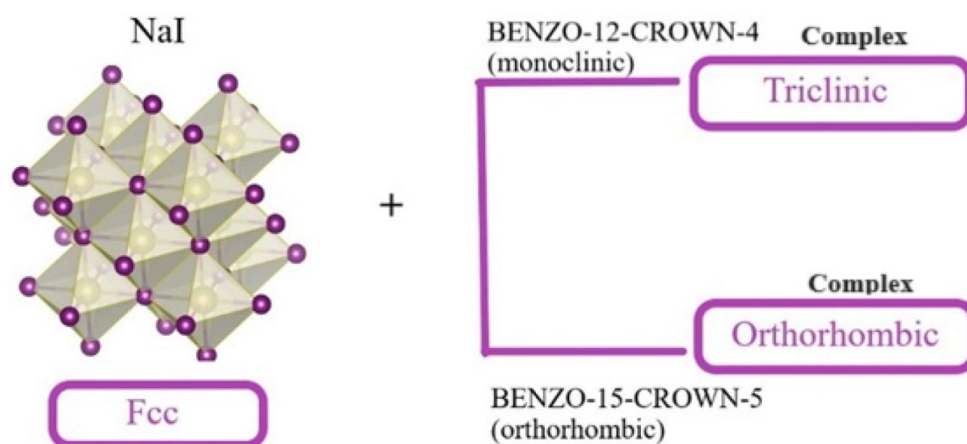
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Abstract

The aim of this review is to compile important results of single-crystal X-ray diffraction method, vibrational and NMR studies conducted on alkali metal ion complexes of some small ring benzo-crown ethers namely benzo-15-crown-5, dibenzo-15-crown-5 and benzo-12-crown-4 to determine their structure, stoichiometry and conformation in the solid-state. This review focuses on solid-state architectural diversity of alkali metal ion complexes studied by single-crystal X-ray diffraction method. Investigations of these complexes are significant as the interactions of alkali metal ions with these crown ethers mimic those present in nature between univalent ions and several bioligands. The benzo group in the macrocycle allows to monitor the complexation event by fluorescence studies and extends the applications of these crown ethers to fluorescent ion sensors. The selected small ring benzo oxa-crown ethers have cavities that match the size of the alkali metal ions and give stable complexes with them. The review presents results related to variation in infrared and Raman spectra of the ligands with changes in their crystal structure and conformation on complexation with alkali salts. Single-crystal X-ray diffraction studies of these complexes help to confirm the chemical structure, stoichiometry, stable conformation and presence of associated solvent molecules in the solid state. As noncovalent interactions are involved in the formation of these complexes, they are capable of forming supramolecular assemblies for building smart functional materials.

Graphical Abstract



Keywords Solid-state · Single-crystal · Spectroscopy · Alkali · Crown ethers

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Introduction

Solid-state studies form an interesting area of investigation in host-guest chemistry that involves noncovalent interactions. Alkali metal salts form complexes with crown ethers through ion-dipole interactions of the alkali metal ion with the donor atom of the macrocyclic ring. The equilibrium so generated mimics that found in nature that is developed through the interaction of alkali metal ions with many bioligands. Efforts by C. J. Pedersen to characterize these products led to a series of papers [1–3] which opened a versatile field in the area of macrocyclic complexes and supramolecular assemblies for future researchers. The synthesis of a cyclic polyether, capable of forming stable complexes with many salts of the alkali and alkaline earth metals, by C. J. Pedersen fetched him the Nobel prize in 1987 which he shared with his contemporaries D. J. Cram and J. M. Lehn [4]. With this unique property, crown ethers have found applications as sensitive sensors for metal ions [5–7], separating agents in nuclear waste treatment [8, 9], ion transport through membranes embedded with the crown ethers [10], sensors immobilized on polymeric membranes [11], as phase transfer catalysts [12, 13] and as model systems to study natural ionophores and antimicrobial activity [14–16]. Natural ionophores like monensin A and valinomycin show selectivity for sodium and potassium ions, respectively. Monensin A forms sodium-monensin hydrate with sodium ions [17], Fig. 1. and also an anhydrous complex that crystallizes in a monoclinic space group $P2_1$, $a = 9.218(5) \text{ \AA}$, $b = 12.702(1) \text{ \AA}$, $c = 16.274(7) \text{ \AA}$, $\beta = 101.029(1)^\circ$, $Z = 2$, while valinomycin gives a (valinomycin-potassium) picrate *m*-xylene solvate [18], Fig. 2, with two molecules of valinomycin potassium picrate per unit cell. Crown ether complexes with alkali metal ions also serve as good models

to study selective ion ligating systems and molecular assemblies formed between monovalent cations e.g. K^+ and Na^+ with DNA [19].

A survey of past literature shows a lack of reviews on the solid-state characterization and structure-spectroscopy correlation of complexes of small ring benzo-crown ethers with alkali metal ions involving noncovalent interactions. The aim of this paper is to present the structural diversity of these complexes as revealed by single-crystal X-ray diffraction method and correlation of structural features with spectra derived from vibrational and NMR studies conducted in solid state. The structures in the solid-state are studied without the interfering effects of the solvents. The dynamics in solution state is also avoided. The solid-state applications of these complexes include their use as phase transfer agents in organic synthesis [20–23], sequestering agents for immobilization of radioisotopes [24], halide ion conductor [25], unit in novel ion-imprinted polymers [26], materials for optical birefringence [27], as models to study photoinduced reversible structural rearrangements affecting the release of the cation and recoordination to determine selectivity and efficiency [28], building blocks for photonic logic gate [29] and as dopant in salt induced n-type doping of SWNT films [30]. Complexes in solid state show better stability and find application in separation science and devices of the complexes [31].

Crown ethers contain strong electronegative donor oxygen atoms in their ring that are suitable to form ion-dipole interactions with alkali metal ions that belong to the class of hard acids. The strength of such interactions depends on the charge density of the metal ion (electrical charge/ volume). Monovalent cations have low charge density (e.g. Na^+ ; 24 C mm^{-3}). In alkali metal ions, only Li^+ has a charge density of 52 C mm^{-3} [32]. Hence, complexes of alkali metal ions

Fig. 1 Sodium-monensin hydrate, orthorhombic space Group: $P2_12_12_1$, Cell: $a = 16.387(4) \text{ \AA}$, $b = 18.684(4) \text{ \AA}$, $c = 12.792(3) \text{ \AA}$, $\alpha = 90^\circ$, $\beta = 90^\circ$, $\gamma = 90^\circ$, CCDC deposition number: 1244444

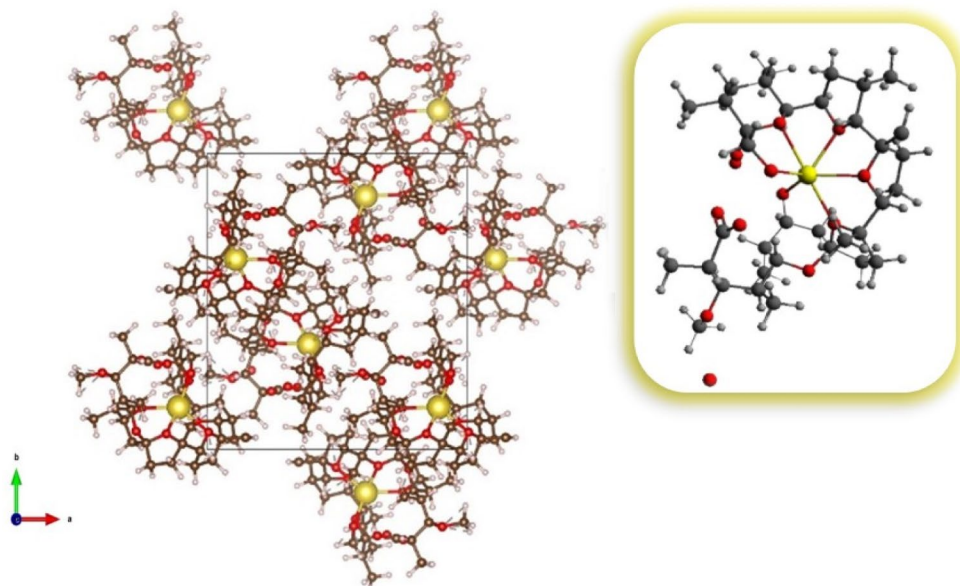


Fig. 2 (Valinomycin-potassium) picrate m-xylene solvate, monoclinic, space group: $P2_1$, Cell: $a = 13.240(10)\text{Å}$ $b = 22.343(16)\text{Å}$ $c = 13.685(10)\text{Å}$, $\alpha = 90^\circ$ $\beta = 108.82(3)^\circ$ $\gamma = 90^\circ$, CCDC deposition number: 1279590

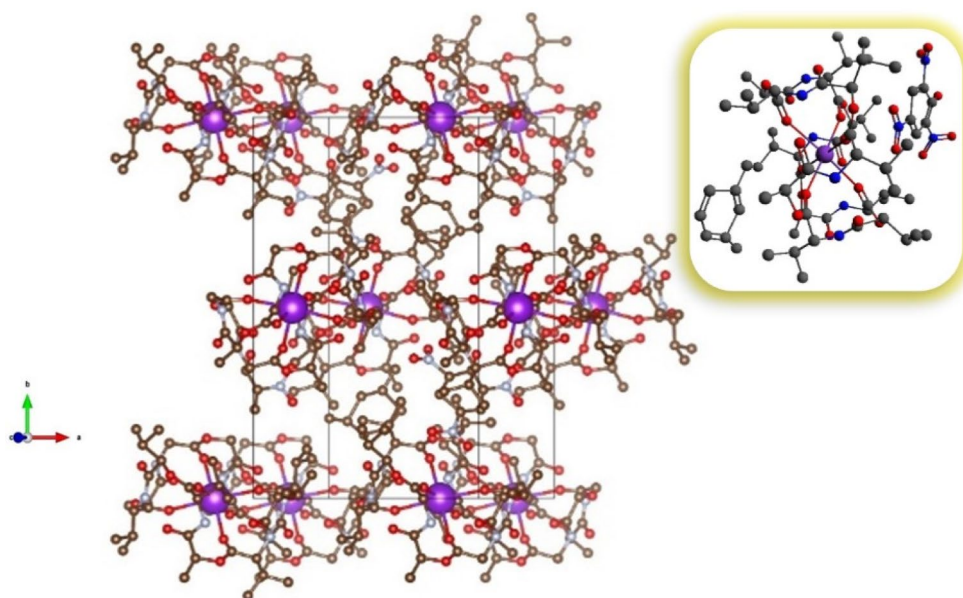


Table 1 Effective radii of alkali metal ions as per some of their coordination numbers*

Metal ion	Coordination number	Effective ionic radius/Å
Li ⁺	4	0.59
	6	0.74
Na ⁺	4	0.99
	5	1.00
	8	1.16
K ⁺	6	1.38
	8	1.51
	10	1.59
Rb ⁺	6	1.49
	8	1.60
Cs ⁺	12	1.73
	6	1.70
	10	1.81
	12	1.88

* [34]

in general lack stability and the driving force to form complexes arises from ligands that contain oxygen as a donor atom, that are multidentate for chelate effect to be operational and that are cyclic to benefit from the macrocyclic effect.

The cavity sizes of 12-crown-4 and 15-crown-5 are ~ 1.36 and ~ 1.8 Å, respectively [33–36]. The dimensions of cavities in some larger crown ethers like 16-crown-5 and 18-crown-6 are ~ 1.9 and ~ 2.7 Å, respectively [36]. The ionic diameters of alkali metal ions, Li⁺, Na⁺, K⁺, Rb⁺ and Cs⁺ are 1.48, 2.02, 2.76, 2.98 and 3.70 Å, respectively [36]. Table 1 highlights the variation in coordination numbers for alkali metal ions. The effective ionic radii of the alkali metal ion in their oxides based on $r(\text{VO}_2^-) = 1.40$ Å for the respective coordination numbers are also listed in Table 1 [34].

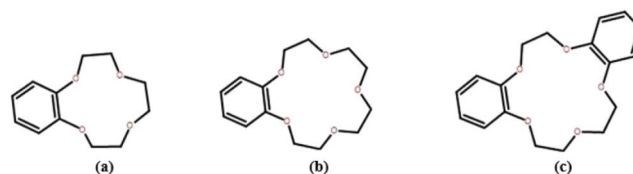


Fig. 3 Structures of selected benzo-oxa-crown ethers (a) benzo-12-crown-4 (b) benzo-15-crown-5 and (c) dibenzo-15-crown-5

The structures of the three crown ethers selected for the review were generated with the help of WebMO.21.0.010p and are shown in Fig. 3. The presence of benzene ring in benzo-crown ethers renders the carbons and protons non-equivalent and hence easily distinguishable by ¹H and ¹³C NMR spectroscopy as compared to 15-crown-5 and 12-crown-4. The fluorescence response of the benzo moiety in these macrocycles and their modified forms was used to probe their cation sensing ability and counterion association in solution state.

In case of crown ether complexes involving non-covalent interactions, stability and structural parameter like conformation may differ in solid, solution and gaseous state. The cation-ligand interactions in supramolecular assemblies in the solid state are commonly established by XRD method, solid state NMR spectroscopy and vibrational spectroscopic techniques. Single-crystal X-ray diffraction studies confirm the chemical structure, stoichiometry and conformation of the complexes in the solid state. Vibrational analysis data complements the results obtained from single-crystal X-ray diffraction studies. Infrared spectrum of a macrocyclic encaged metal ion complex affords valuable information on the nature and strength of the metal-ligand bond and thus the stability of the complex. Coordination event usually causes shifts in fundamental vibrations of the free ligand,

appearance of new bands and splitting of the degenerate modes due to lowering of symmetry and intensification of the spectra. The stronger the metal-ligand bond, the larger the splitting of the degenerate mode [37].

Vibrational spectroscopy has been employed to study the molecular structures of crown-metal ion complexes in solutions as well as in the solid state. Spectral changes in Raman spectra due to complex formation have been studied by Sato and Kusumoto [38] and by Hilliard et al. [39] and provide useful insight into the conformational changes accompanying complexation.

Single-crystal X-ray diffraction studies of small ring benzo oxa-crown ethers (benzo-15-crown-5, dibenzo-15-crown-5 and benzo-12-crown-4) and their alkali-complexes

Single-crystal X-ray diffraction studies play an important role in confirming the formation and chemical structure of complexes that are crystalline in solid-state specially when their formation involves noncovalent bonding. The important information obtained from single crystal of alkali-complex of benzo crown ether includes the nature of bonding between the anion and the cation, the conformation adopted by the ring, the geometry of coordination of the central metal ion, the plane of substituent aromatic ring(s) in the macrocycle, orientation of lone pair of electrons on donor oxygen atoms, metal ion sites in macrocyclic complex, presence of associated water/solvent molecule(s) with the complex and the stoichiometry of the complex. The structural information derived from single-crystals assists in describing mechanisms for the observed photophysical properties of these host-guest complexes. Solid-state X-ray studies are helpful in the field of molecular ionics and understanding linear and nonlinear optical properties of crown ethers and their

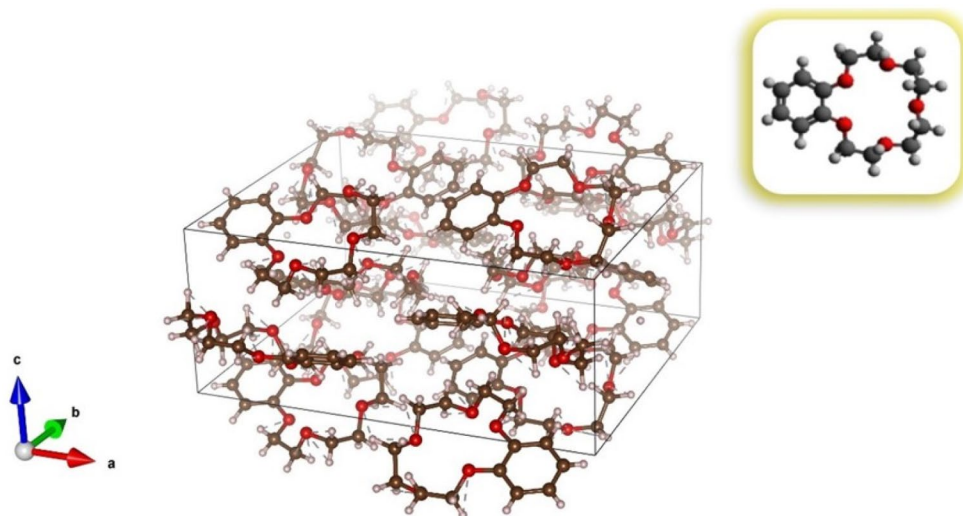
derivatives [27, 40]. They help to develop cation-induced properties like enhancement of H₂ gas storage capacity of metal-organic frameworks [41] and assist in studying phase transition behaviour for the purpose of designing switchable dielectric materials [42].

Crown ether complexes have been amply utilized in supramolecular chemistry and crystal engineering as modules for the construction of complex superstructures. It is necessary to have a knowledge of zero-negative thermal expansion along crystallographic axes in required temperature range to build organic crystalline supramolecular rotor [43, 44]. Tuning supramolecular interactions can change thermal expansion properties.

The crystallographic details of benzo-15-crown-5, dibenzo-15-crown-5, benzo-12-crown-4 and their complexes with some of the alkali salts have been studied in the past. The impact of size compatibility between the cation and the crown ether ring on the structural diversity of single-crystals of the complexes is evident from these studies. All single-crystal packing diagrams in this review were regenerated from VESTA software. The depth perspective has been included in the structures to simplify viewing and avoid crowding. The inset in the packing diagrams are the chemical structures of the single crystals of the complexes generated by Avogadro: an open-source molecular builder and visualization tool, Version 1.XX.

Benzo-15-crown-5 (6,7,9,10,12,13,15,16-Octahydrobenzo-1,4,7,10,13-pentaoxacyclopentadecin) crystallizes in an orthorhombic system, Space Group: *Pbca* (61), Cell: $a=20.111(4)\text{\AA}$ $b=16.515(3)\text{\AA}$ $c=8.354(2)\text{\AA}$, $\alpha=90^\circ$, $\beta=90^\circ$, $\gamma=90^\circ$ [45], Fig. 4. The complex between benzo-15-crown-5 and potassium iodide was synthesized and studied for its crystalline structural features by Mallinson and Truter [46], Fig. 5. Potassium iodide formed 2:1 (ligand: metal ion) complex with potassium ion sandwiched between two crown rings. The cation was coordinated to

Fig. 4 Benzo-15-crown-5 (6,7,9,10,12,13,15,16-Octahydrobenzo-1,4,7,10,13-pentaoxacyclopentadecin), CCDC Deposition Number: 1225909



the ten oxygen atoms of the two crown rings. The ten oxygen atoms formed an irregular pentagonal antiprism configuration with the cation. The iodide ions were found to occupy two sets of positions with 4 or $\bar{4}$ symmetry. The cation occupied a position with crystallographic symmetry $\bar{1}$. The single crystals belonged to a tetragonal crystal system in $P4/n$ space group with $a=b=17.84(1)$, $c=9.750(6)$ Å $\alpha=90^\circ$, $\beta=90^\circ$, $\gamma=90^\circ$ and $Z=4$.

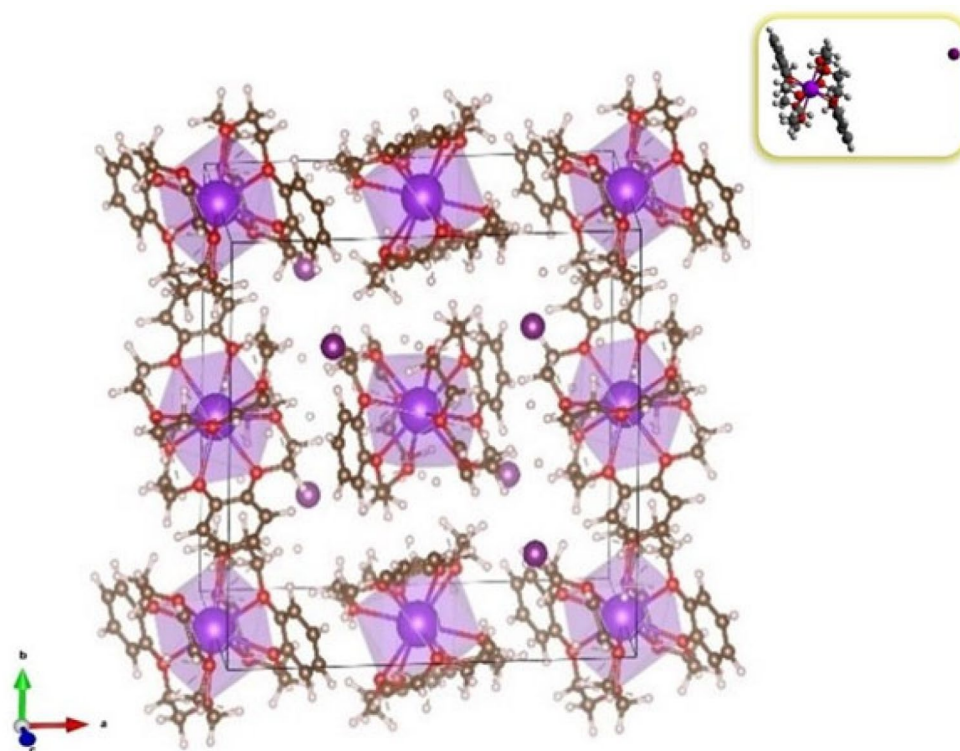
Isolation and paper chromatographic solution studies of MX (where $M^+ = Na^+$ and K^+ ; $X = Cl^-$, Br^- , I^- and NCS^-) complexes with macrocyclic polyether benzo-15-crown-5 (B15C5) were carried out by Poonia [47]. The sodium complexes of B15C5 displayed 1:1 stoichiometry and a water of crystallization associated with the complex having I^- and Br^- as counterions. Complexes with potassium ion displayed 2:1 (ligand: metal ion) stoichiometry and a water molecule was associated with complexes having bromide and thiocyanate counterions. In the complex (B15C5)-NaI, single-crystal X-ray structural analysis showed that the sodium ion was 0.75 Å outside the plane of polyether oxygens with a direct linkage to a water molecule. The iodide counterion was hydrogen bonded to this water molecule.

Venkatasubramanian et al. [48] have reported synthesis and single crystal structure of 1:1 complex of cesium picrate with benzo-15-crown-5, $[Cs(\text{benzo-15-crown-5})](\text{picrate})$. These were yellow prisms belonging to the triclinic crystal system, space group $P\bar{1}$ with $a=7.377(4)$, $b=11.372(2)$, $c=14.806(2)$ Å, $\alpha=90.31(1)$, $\beta=91.06(2)$, $\gamma=108.32(2)^\circ$. Unlike potassium, cesium formed a 1:1 complex. The

coordination number of Cs^+ was nine. It was coordinated to five oxygens of the crown ether, one oxygen atom of the phenoxide, one oxygen atom from the ortho nitro group of the picrate anion and two oxygens from a para nitro group of the picrate anion of adjacent molecule. The Cs^+ ion lay 2.07 Å out of the plane formed by the crown oxygen atoms. These studies revealed that apart from the cation and cavity size of the crown ether, the stoichiometry between a metal ion and a cyclic polyether also depended on the Lewis acid strength of the cation which can be regulated by the counterion.

The crystal structure of B15C5 with lithium picrate, diaqua-(benzo-15-crown-5)-(picrate-O, O')-lithium ($[Li(\text{benzo-15-crown-5})(H_2O)_2]picrate$), was determined by Bhagwat and co-workers [49]. It was monoclinic, space group $P2_1/n$, $a=7.335(5)$, $b=23.522(3)$, $c=14.770(3)$ Å and $\beta=93.4(1)^\circ$. The lithium ion was hydrogen bonded to two picrate oxygens and two water molecules was connected to the crown through four weak hydrogen bonds formed by the two coordinated water molecules. Sodium picrate gave 1:1 complex with benzo-15-crown-5 [50], Fig. 6. The sodium ion was linked to the oxygen atoms of the nitro and phenolic hydroxyl groups. Infrared studies showed that the complex existed in dehydrated form. However, in solution, a 2:1 sandwich complex, $Na^+(B15C5)_2pic^-$, was obtained with increasing amount of B15C5. The crystal structure of the complex of benzo-15-crown-5 with potassium picrate was studied by Bhagwat and coworkers [51]. A charge separated 2:1 (ligand: metal ion) solid

Fig. 5 Bis(2,3,5,6,8,9,11,12-Octahydro-1,4,7,10,13-benzo-pentaoxacyclopentadecine)-potassium iodide Synonym: bis(Benzo-15-crown-5)-potassium iodide, CCDC deposition number: 1115057



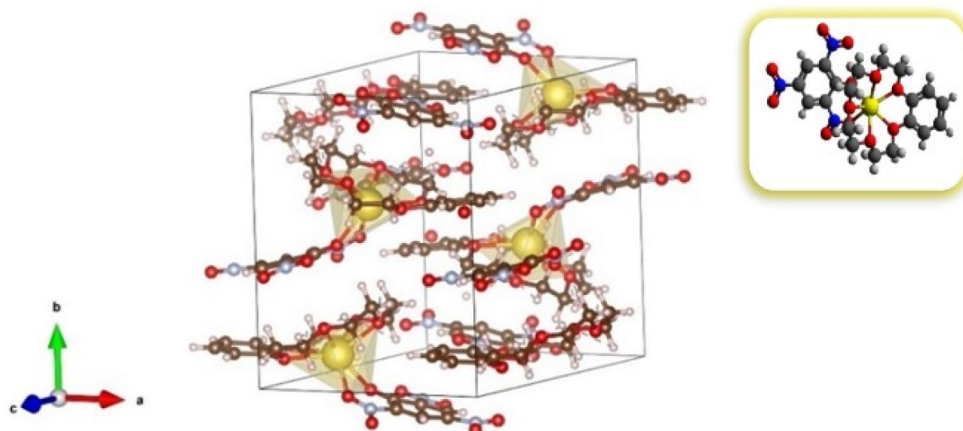
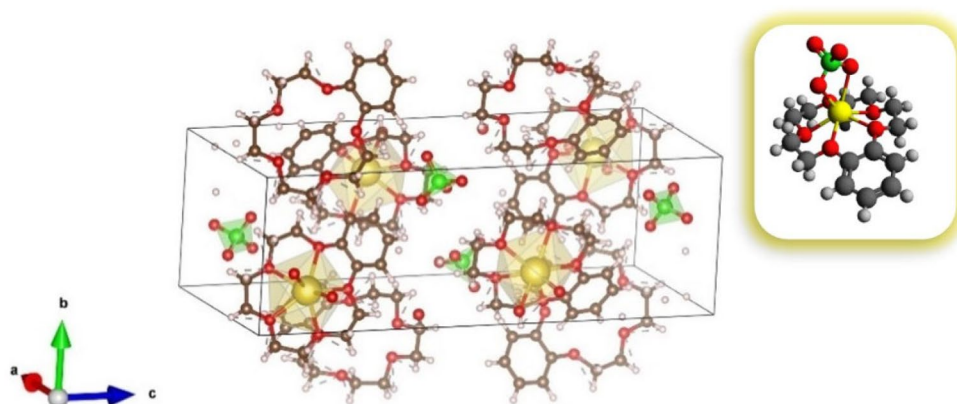


Fig. 6 (6,7,9,10,12,13,15,16-Octahydro-5,8,11,14,17-pentaoxabenzocyclopentadecene)-2,4,6-trinitrophenolato-sodium, CCDC deposition number: 1102758

Fig. 7 (2,3,5,6,8,9,11,12-Octahydro-1,4,7,10,13-benzopentaoxa-cyclopentadecin)-perchlorato-O, O'-sodium, CCDC deposition number: 1225916



state complex was obtained with space group: $P1(2)$, cell parameters: $a = 11.619(2)\text{\AA}$, $b = 12.038(2)\text{\AA}$, $c = 15.521(3)\text{\AA}$, $\alpha = 109.15(1)^\circ$, $\beta = 110.62(1)^\circ$, $\gamma = 83.37(1)^\circ$. The metal ion sandwiched between two crowns had no interaction with the picrate counterion.

Complexation of benzo-15-crown-5 with KNO_3 [52] produced monoclinic crystals of bis (benzo-15-crown-5) potassium nitrate monohydrate, $\text{K}(\text{B15C5})_2\text{NO}_3 \cdot \text{H}_2\text{O}$, $P2_1/c$, $a = 12.717(2)$, $b = 19.569(2)$, $c = 13.025(3)\text{\AA}$, $\beta = 100.79(1)^\circ$, $Z = 4$ with potassium ion coordinated to two benzo-crown rings through five oxygen atoms of each crown ring. The water and nitrate ion did not form part of the cation coordination sphere.

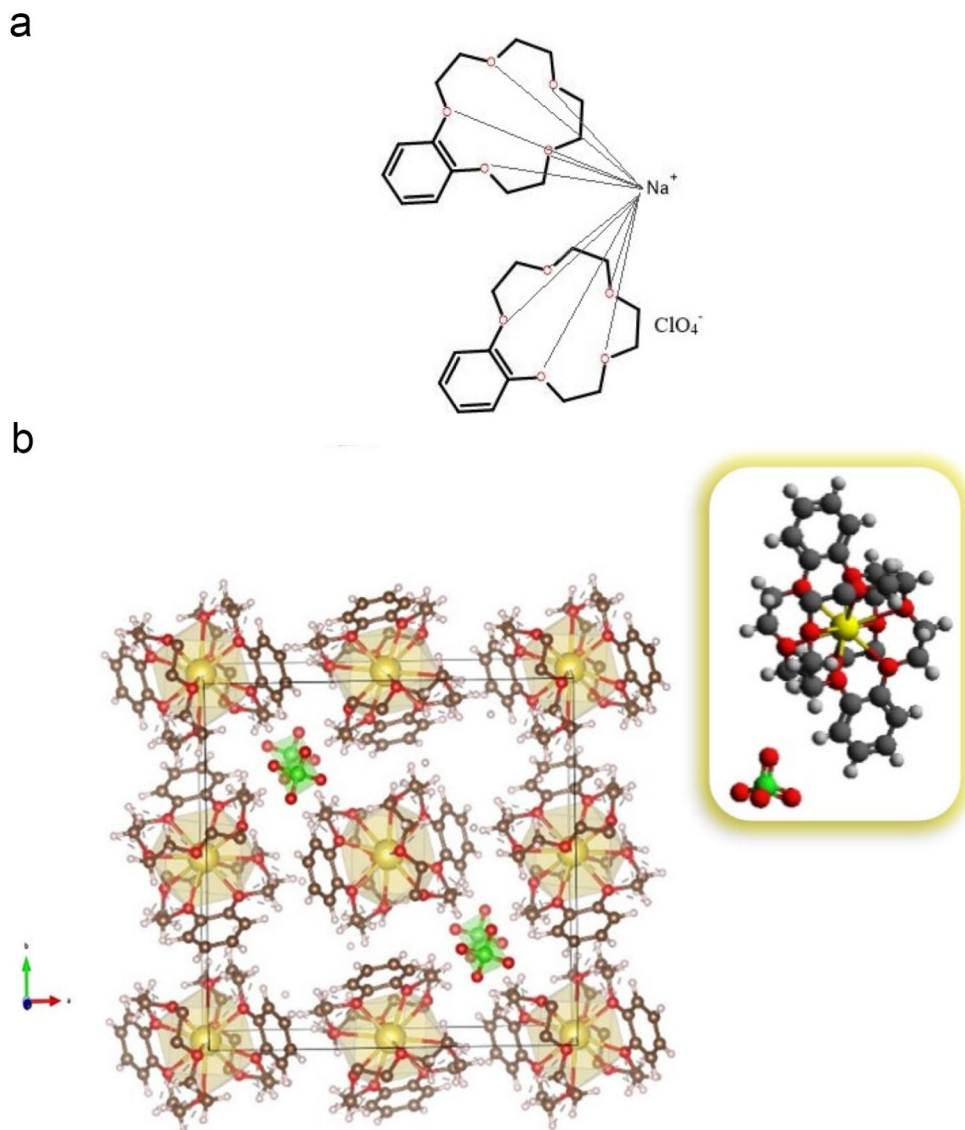
Momany et al. [53] have prepared complex of rubidium nitrate with B15C5 with 2:1 stoichiometry. The complex $\text{Rb}(\text{B15C5})_2\text{NO}_3 \cdot \text{H}_2\text{O}$ was monoclinic, space group $P2_1/c$, $a = 12.695(3)$, $b = 19.471(3)$, $c = 12.991(2)\text{\AA}$, $\beta = 99.60(2)^\circ$, $V = 3166\text{\AA}^3$. The rubidium ion was coordinated to the ten oxygen atoms of the two benzo-crowns.

Poonia et al. [54] have reviewed the structural aspects of benzo-15-crown-5 complexes with some organic salts of alkali and alkaline earth metals, M^zL^- , $\text{M}^z = \text{Li}^+$ to Cs^+

and Mg^{2+} to Ba^{2+} , $\text{L}^- = 2,4,6$ -trinitrophenolate (picrate) and 3,5-dinitrobenzoate (Dnb). These results were compared with those of $\text{MX}_z \cdot \text{B15C5}$ ($\text{X} = \text{NCS}$, I , NO_3 , ClO_4 , BPh_4) complexes. The combined study showed that B15C5 could distinguish 'within-the-group' and 'between-the-groups' discriminations of M^{z+} in the solid state.

The crystal structures of the two compounds of benzo-15-crown-5 with NaClO_4 in 1:1 and 2:1 ratio and one complex with NaBPh_4 in 2:1 ratio have been determined from diffractometer data collected with molybdenum radiation [55]. The 1:1 complex with NaClO_4 crystallized in the monoclinic space group $P2_1/c(14)$ with cell dimensions $a = 8.806(3)$, $b = 8.310(10)$, $c = 24.148(7)\text{\AA}$, $\beta = 99.16(1)^\circ$ and $Z = 4$, Fig. 7. The cation was irregularly co-ordinated to five oxygen atoms from the crown ligand and two from the anion. The structure of the 2:1 complex with NaClO_4 is presented in Fig. 8(a). It formed tetragonal crystals, space group $P4/n$ with unit cell, $a = 17.786(7)$, $c = 9.869(5)\text{\AA}$ and $Z = 4$, Fig. 8(b). The complex had a centrosymmetric sandwich structure and two conformers were present in the proportion 0.523:0.477. The 2:1 complex with NaBPh_4 was monoclinic, space group $P2_1/c$ with unit cell parameters,

Fig. 8 (a) Chemical structure of (2,3,5,6,8,9,11,12-Octahydro-1,4,7,10,13-benzopentaoxa-cyclopentadecin)-perchlorato-O, O'-sodium. (b) Bis(2,3,5,6,8,9,11,12-Octahydro-1,4,7,10,13-benzopentaoxacyclopentadecin)-sodium perchlorate, CCDC deposition number: 1225917



$a = 12.497(3)$, $b = 19.450(3)$, $c = 19.896(4)$ Å, $\beta = 94.76(2)^\circ$ and $Z = 4$. The conformations of the two independent ether molecules were similar to each other and to that found in the free-ligand crystals. The studies show that anions can affect the stoichiometry of a complex and more than one conformer could exist for a certain stoichiometry.

Bush and Truter [56] obtained crystal structures of complexes formed by alkali-metal salts with B15C5. The complex aquo-(2,3-benzo-1,4,7,10,13-pentaoxacyclopentadec-2-ene) sodium iodide crystallized in an orthorhombic unit cell having $a = 12.271(4)$, $b = 9.550(4)$, $c = 15.719$ Å(5), $\alpha = 90.00^\circ$, $\beta = 90.00^\circ$, $\gamma = 90.00^\circ$, $Z = 4$ and space group $P2_12_12_1$. The sodium ion was surrounded by a pentagonal pyramid of oxygen atoms. The base was formed by oxygen atoms of the cyclic ether with Na–O bond length being 2.35–2.43 Å and the sodium ion was 0.75 Å from this plane towards the apical water molecule (Na–O 2.29

Å). The iodide ion did not interact with the sodium ion but formed hydrogen bonds to water molecules.

Orthorhombic single crystals of complex formed from benzo-15-crown-5 with sodium bromide, aqua-(2,3,5,6,8,9,11,12-octahydro-1,4,7,10,13-benzopentaoxacyclopentadecine)-sodium bromide, space group: $P2_12_12_1(19)$, cell: $a = 9.4014(7)$, $b = 11.7964(8)$, $c = 15.4865(14)$ Å, $\alpha = 90.00^\circ$, $\beta = 90.00^\circ$, $\gamma = 90.00^\circ$ showed 1:1 stoichiometry [57], Fig. 9.

Single crystals containing one water molecule were obtained by Demina et al. [58] by reacting B15C5 with the lithium salts, LiX, in ethanol where $X = \text{Cl}^-$, I^- , ClO_4^- and NO_3^- . An anhydrous complex was obtained in case of LiBF_4 . These complexes were studied by XRD method and IR spectroscopy. In all structures, the lithium cation was coordinated to five crown ether oxygen atoms and to an additional ligand in the axial position of the lithium coordination

Fig. 9 Aqua-(2,3,5,6,8,9,11,12-octahydro-1,4,7,10,13-benzopentaoxacyclopentadecine)-sodium bromide, CCDC deposition number: 1033468

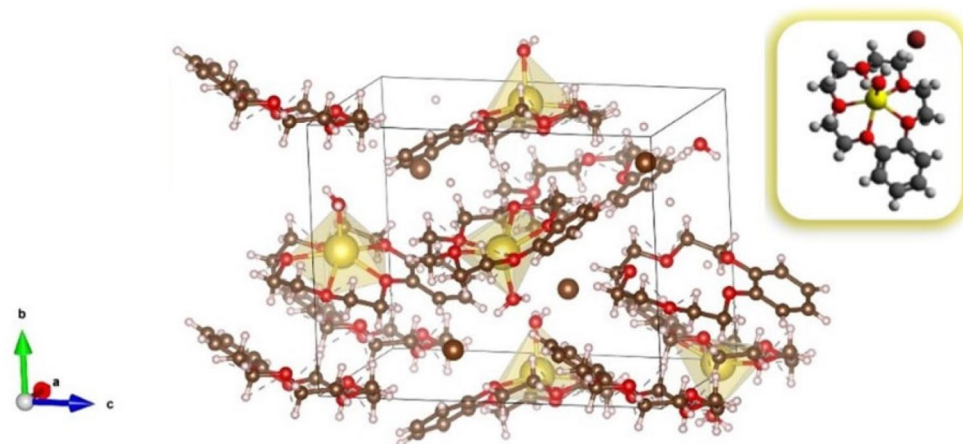


Fig. 10 Aqua-(2,3,5,6,8,9,11,12-octahydro-1,4,7,10,13-benzopentaoxacyclopentadecine)-lithium chloride, CCDC deposition number: 1588044

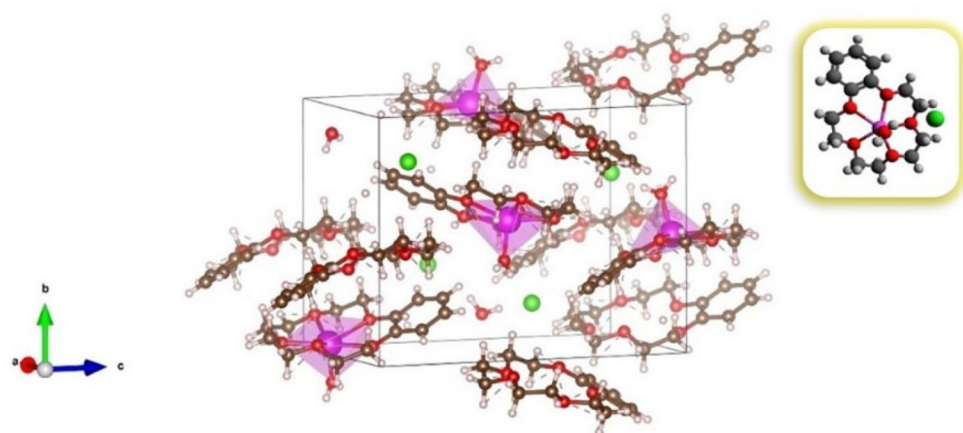
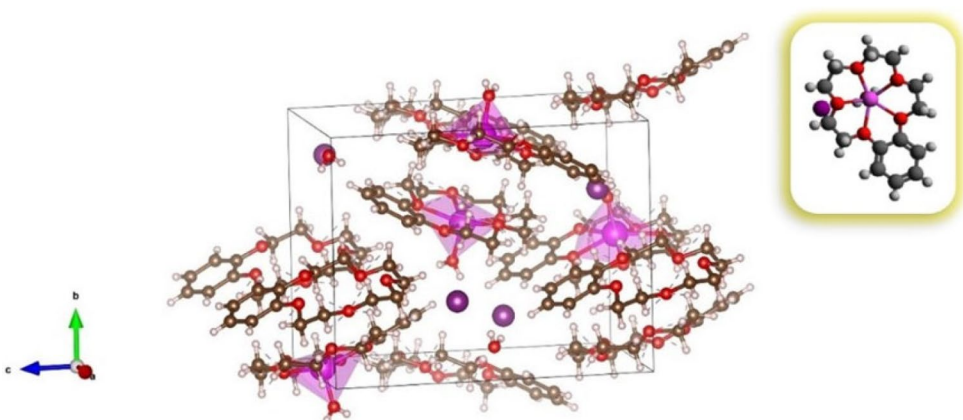


Fig. 11 Aqua-(2,3,5,6,8,9,11,12-octahydro-1,4,7,10,13-benzopentaoxacyclopentadecine)-lithium iodide, CCDC deposition number: 1588043



polyhedron, which was a pentagonal bipyramid. In case of counterions Cl^- , I^- and ClO_4^- , the axial position was occupied by oxygen of the coordinated water molecule, while in the case of BF_4^- , it was occupied by a fluorine of the tetrafluoroborate anion. The complex, $\text{Li} \cdot \text{B15C5} \cdot \text{H}_2\text{O} \cdot \text{Cl}$ crystallized in an orthorhombic system with space group $P2_12_12_1$, unit cell parameters: $a = 9.3114(4) \text{ \AA}$, $b = 11.5396(6) \text{ \AA}$, $c = 15.2753(7) \text{ \AA}$ and $V = 1641.33(13) \text{ \AA}^3$, Fig. 10 and $\text{Li} \cdot \text{B15C5} \cdot \text{H}_2\text{O} \cdot \text{I}$ crystallized in an orthorhombic system

with Space group $P2_12_12_1$, $a = 9.4309(3) \text{ \AA}$, $b = 11.9505(3) \text{ \AA}$, $c = 15.2973(5) \text{ \AA}$ and $V = 1724.07(9) \text{ \AA}^3$, Fig. 11. The perchlorate complex, $\text{Li} \cdot \text{B15C5} \cdot \text{H}_2\text{O} \cdot \text{ClO}_4$, crystallized in a monoclinic system with space group $P2_1/c$, unit cell parameters: $a = 14.4843(9) \text{ \AA}$, $b = 10.9246(7) \text{ \AA}$, $c = 11.6015(7) \text{ \AA}$ and $V = 1819.2(2) \text{ \AA}^3$, Fig. 12. The anhydrous complex $\text{LiBF}_4 \cdot \text{B15C5}$ crystallized in a monoclinic system with Space group $P2_1/c$, $a = 8.3554(7) \text{ \AA}$, $b = 24.102(2) \text{ \AA}$, $c = 8.7819(7) \text{ \AA}$ and $V = 1644.6(2) \text{ \AA}^3$.

Fig. 12 Aqua-(2,3,5,6,8,9,11,12-octahydro-1,4,7,10,13-benzopentaoxacyclopentadecine)-lithium perchlorate, CCDC deposition number: 1812520

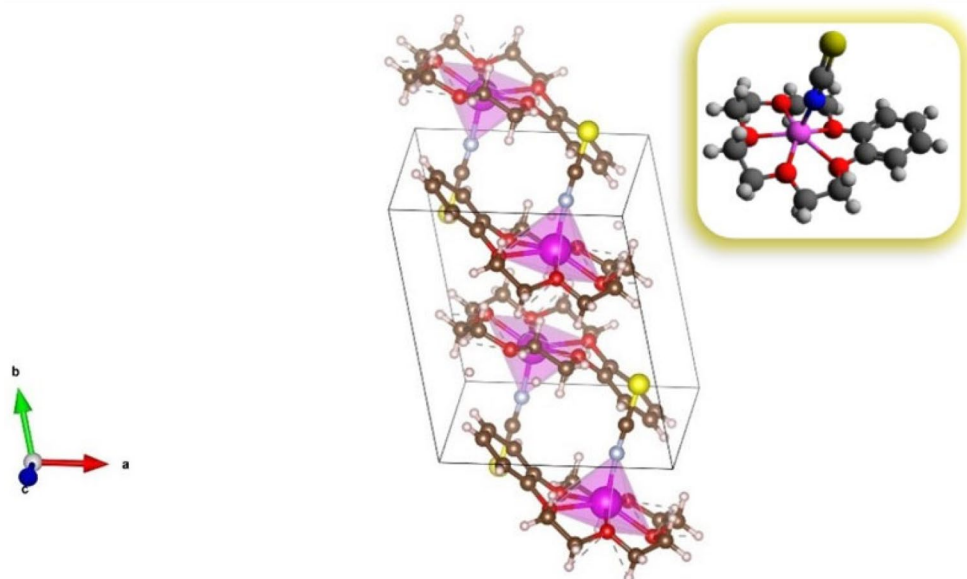
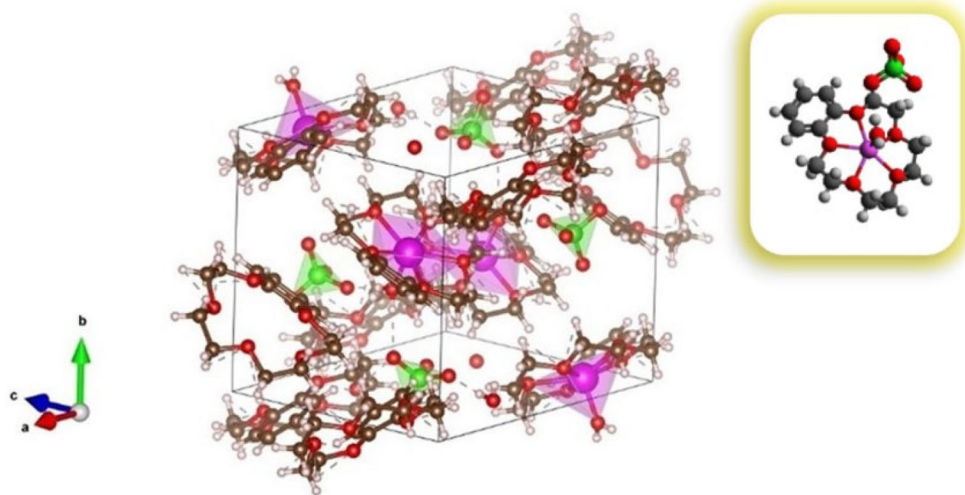


Fig. 13 (2,3,5,6,8,9,11,12-octahydro-1,4,7,10,13-benzopentaoxacyclopentadecine)-(isothiocyanato)-lithium Synonym: (benzo-15-crown-5)-(isothiocyanato)-lithium, CCDC deposition number: 1854309

Complexes Li.B15C5.NCS (I) and Li.B15C5.H₂O.NCS (II) were isolated by Kuz'mina et al. [59] during lithium extraction into a B15C5 solution in CHCl₃ from an aqueous solution of lithium thiocyanate. Complex (I) was characterized by X-ray diffraction and IR spectroscopy. Complex II was present in the organic phase. The IR spectra of II had bands attributed to coordinated state of water, crown ether and the anion. The complex Li.B15C5.NCS crystallized in a triclinic system, space group $P\bar{1}$, unit cell parameters $a=8.8968(8)$ Å, $b=9.8156(9)$ Å, $c=10.4517(10)$ Å, $\alpha=107.626(1)$ °, $\beta=92.243(1)$ °, $\gamma=102.975(1)$ ° and $V=842.00(14)$ Å³, Fig. 13. The lithium cation was coordinated to five crown ether oxygen atoms in the equatorial positions and to the thiocyanate nitrogen atom in the axial position. The lithium cation was coordinated to five crown

ether oxygen atoms in the equatorial positions and to the thiocyanate nitrogen atom in the axial position. From these studies it was deduced that the lone pair of each of the two oxygen atoms in this complex pointed towards the lithium cation to a lesser extent than in their studies with similar lithium benzo-15-crown-5 complexes with a coordinated water molecule in the axial position and I⁻, Cl⁻, ClO₄⁻ or BF₄⁻ as counter-ions.

The infrared spectra of the complexes showed that the $\nu_s(\text{COC})$, $\nu_{\text{as}}(\text{PhO})$ modes and C–O stretching modes of B15C5 were shifted to lower frequencies on complexation while the $\nu_s(\text{PhO})$ was split into two components. The presence of water molecule was also detected in the spectra of the complexes by infrared spectroscopy. Recently, Bezdomnikov and coworkers [60] during

extraction studies of perchlorates salts of Li, Na and K by the extraction system B15C5-CHCl₃-H₂O have identified another complex namely (benzo-15-crown-5)-aqua-lithium (benzo-15-crown-5) perchlorate when the ratio of Li: crown ether was 1:2. Its space group was $P2_1/c$ (14) and cell parameters were: $a=14.7880(11)\text{Å}$ $b=14.8510(12)\text{Å}$ $c=15.1405(13)\text{Å}$, $\alpha=90^\circ$ $\beta=104.474(3)^\circ$ $\gamma=90^\circ$. The anhydrous complex [Li(B15C5)(ClO₄)] was also isolated in its crystalline form. The evidence of the presence such complexes and their solubility data helps to improve the yield of lithium ion during extraction process. A comparative analysis of the infrared spectra of these isolated complexes further confirmed their structure. Bezdomnikov et al. [61] have also identified various complexes of B15C5 with lithium chloride salt in extraction systems based on alkylimidazolium-based ionic liquid for e.g. a three decked aqua-(2,3,5,6,8,9,11,12-octahydro-1,4,7,10,13-benzopentaoxacyclopentadecine)-lithium bis(trifluoromethane sulfonyl) amide hemikis-(2,3,5,6,8,9,11,12-octahydro-1,4,7,10,13-benzopentaoxacyclopentadecine), Space group: $Pc(7)$, Cell: $a=13.6943(14)\text{Å}$, $b=14.3352(15)\text{Å}$, $c=16.8203(18)\text{Å}$, $\alpha=90^\circ$ $\beta=111.917(4)^\circ$ $\gamma=90^\circ$, Fig. 14.

A green method for separation of lithium isotopes was developed by Xiao et al. [62] by using hydrophobic *ionic liquids* (ILs = [C_{4,6,8,10} mim]⁺[NTf₂]⁻) as extracting organic phase and benzo-15-crown-5 (B15C5) as complexing agent. The separation factor $\alpha(^6\text{Li}/^7\text{Li})=1.029\pm 0.001$, indicated that ⁶Li enriched the ionic liquid phase as its 1:2 complex, [Li⁺(B15C5)₂].

Buchanan et al. [63] have conducted NMR and X-ray crystallographic studies on dibenzo-15-crown-5 and its complex with NaNCS in solution and solid state. Dibenzo-15-crown-5-ether crystallized in orthorhombic space group $Pbca$, $a=8.4179(8)\text{Å}$, $b=8.5374(13)\text{Å}$, $c=45.328(6)\text{Å}$,

$\alpha=90^\circ$ $\beta=90^\circ$ $\gamma=90^\circ$, $V=3257.6\text{Å}^3$ and $Z=8$, Fig. 15. Its NaNCS complex crystals belonged to monoclinic system, space group $P2_1/n$, $a=12.1306(13)\text{Å}$, $b=8.8565(10)\text{Å}$, $c=18.269(3)\text{Å}$, $\alpha=90^\circ$ $\beta=90^\circ$ $\gamma=99.990(10)^\circ$, $V=1932.9(4)\text{Å}^3$ and $Z=4$. The complex displayed 1:1 stoichiometry. The alkali metal ion, Na⁺, was coordinated to the five oxygen atoms of the ether. The geometry of its NaNCS complex was described as pentagonal pyramidal. Coordination number of six of sodium ion was completed by coordination of Na⁺ to the nitrogen atom of the thiocyanate anion. Comparison of X-ray data for dibenzo-15-crown-5 and its complex with sodium thiocyanate revealed a major change in the dihedral angles in two C-O-C-C fragments (66.5° to 171.0° and 179.3° to 147.6°). All other dihedral angle changes were less than 15° .

Simonov [64] employed X-ray analysis to determine the structure of single crystals of two 12-membered crown ethers, benzo-12-crown-4 (B12C4) and naphtho-12-crown-4. Benzo-12-crown-4 was monoclinic, $P112_1/b$, $a=8.466(3)$, $b=8.019(3)$, $c=33.590(10)\text{Å}$, $\alpha=90^\circ$, $\beta=90^\circ$, $\gamma=90.99(3)^\circ$, $V=2279.8\text{Å}^3$ and $Z=8$. The unit cell had two crystallographically independent molecules of B12C4 with similar conformations. The crown ether adopted a rigid framework due to the small ring size and planarity of the benzene ring. The pyrocatechol fragment adopted a trans-cis-trans conformation (seen in 12–15 membered rings). Naphtho-12-crown-4 was monoclinic, $P2_1/a$, $a=24.148(8)$, $b=14.535(4)$, $c=7.987(5)\text{Å}$, $\alpha=90^\circ$, $\beta=90^\circ$, $\gamma=102.87(2)^\circ$, $V=2732.9\text{Å}^3$ and $Z=8$. The two independent molecules in the unit cell had significantly different conformations.

Luboch et al. [65] prepared single crystals of complexes of benzo-12-crown-4 with NaI and KI, Figs. 16 and 17.

Fig. 14 Aqua-(2,3,5,6,8,9,11,12-octahydro-1,4,7,10,13-benzopentaoxacyclopentadecine)-lithium bis(trifluoromethanesulfonyl) amide hemikis(2,3,5,6,8,9,11,12-octahydro-1,4,7,10,13-benzopentaoxacyclopentadecine), CCDC deposition number: 2220403

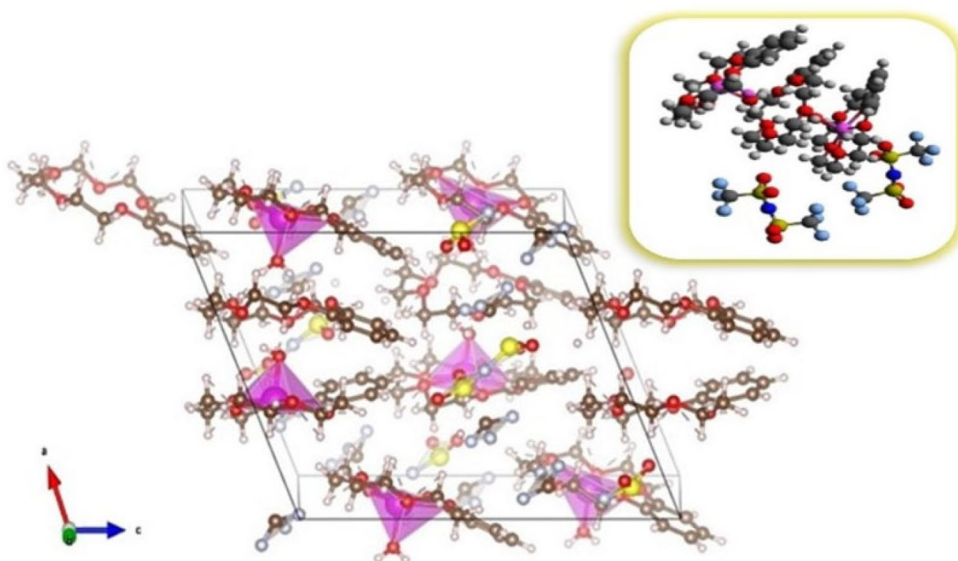


Fig. 15 Dibenzo-15-crown-5, CCDC deposition number: 1261452

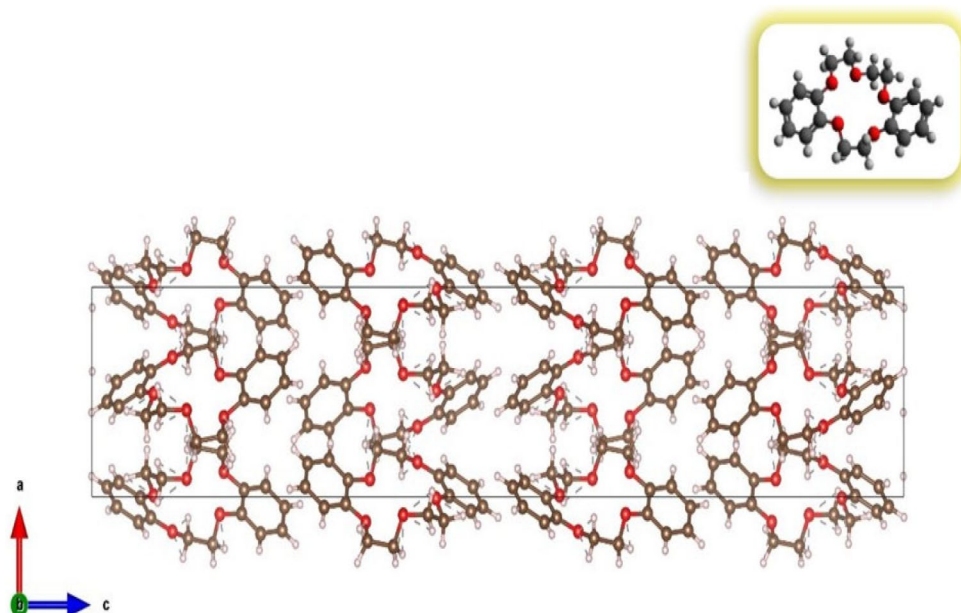
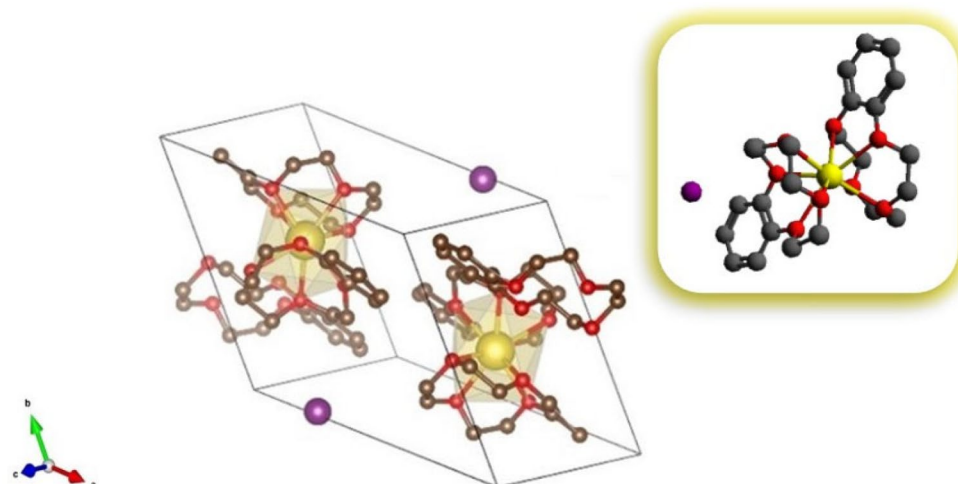


Fig. 16 Bis(2,3-Benzo-1,4,7,10-tetraoxacyclododec-2-ene)-sodium iodide, CCDC deposition number: 1312386



The NaI complex had a 2:1 (ligand: metal ion) stoichiometry and crystallized in a triclinic crystal system, space group $P\bar{1}$ and unit cell dimensions $a=13.368(8)$, $b=10.724(7)$, $c=0.325(4)$ Å, $\alpha=73.56(4)^\circ$, $\beta=77.73(4)^\circ$ and $\gamma=108.70(5)^\circ$, $V=1267.6$ Å³ and $Z=2$. The coordination number of sodium ion was 8 in the complex. Hydrated complexes, $\text{Na}(12\text{-crown-4})_2(\text{OH})\cdot 8\text{H}_2\text{O}$ and $\text{Na}(12\text{-crown-4})_2\cdot 1.5\text{H}_2\text{O}$ are also known where there is no direct linkage of the cation to the counterion. The KI complex with benzo-12-crown-4 also exhibited a 2:1 (ligand: metal ion) stoichiometry and had a monoclinic crystal system with space group $C2/c$ and unit cell dimensions, $a=15.807(8)$, $b=2.043(4)$, $c=15.601(6)$ Å, $\alpha=90^\circ$, $\beta=117.74(3)^\circ$, $\gamma=90^\circ$, $V=2629$ Å³ and $Z=4$. In solution, benzo-12-crown-4 formed complexes with sodium and potassium cations displaying both 1:1 and 2:1 stoichiometry, respectively.

Calorimetric analysis showed that the stability constants for the 1:1 ($\log K_1$) and 2:1 ($\log K_\beta$) sodium complexes in acetonitrile were 1.88 and 2.62, respectively while those for 1:1 and 2:1 potassium complexes were 1.76 and 1.08, respectively [66, 67]. The substitution of benzo moiety in 12-crown-4 reduces the conformational flexibility of the ring and affects selectivity which is a critical parameter for ion-selective membrane electrodes. A 2:1 complex of bis(Benzo-15-crown-5)-rubidium nitrate monohydrate, space group: $P2_1/c(14)$, Cell: $a=12.695(3)$, $b=19.471(3)$, $c=12.991(2)$ Å, $\alpha=90^\circ$, $\beta=99.60(2)^\circ$, $\gamma=90^\circ$, $V=3166$ Å³ and $Z=4$ [53] is shown in Fig. 18. The rubidium ion formed a charge separated complex and the nitrate ion was hydrogen bonded to a water molecule.

Crystal structure of dibenzo-12-crown-4 studied by Charland and coworkers [68] is shown in Fig. 19. The relatively

Fig. 17 Bis(2,3-Benzo-1,4,7,10-tetraoxacyclododec-2-ene)-potassium iodide, CCDC deposition number: 1312286

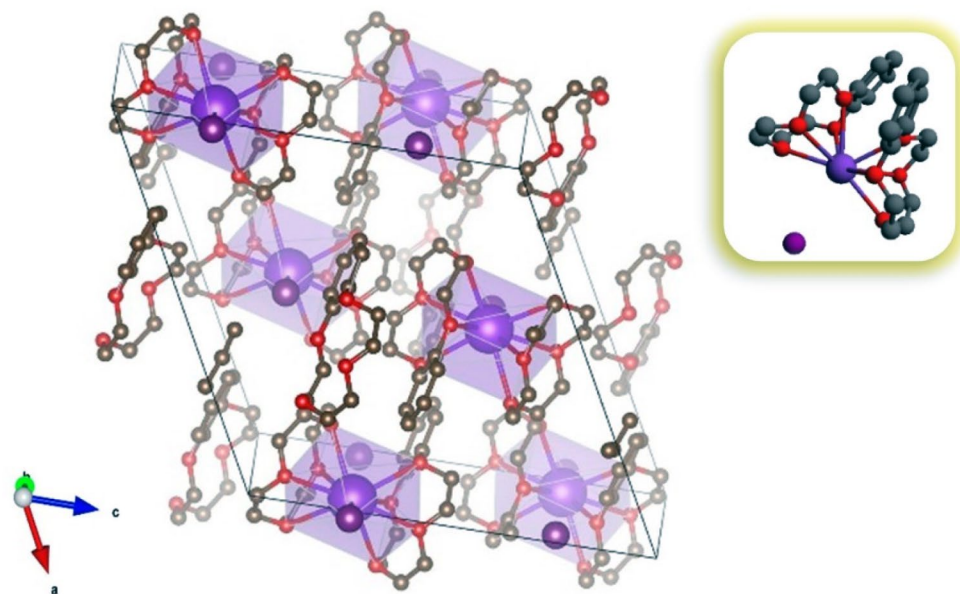
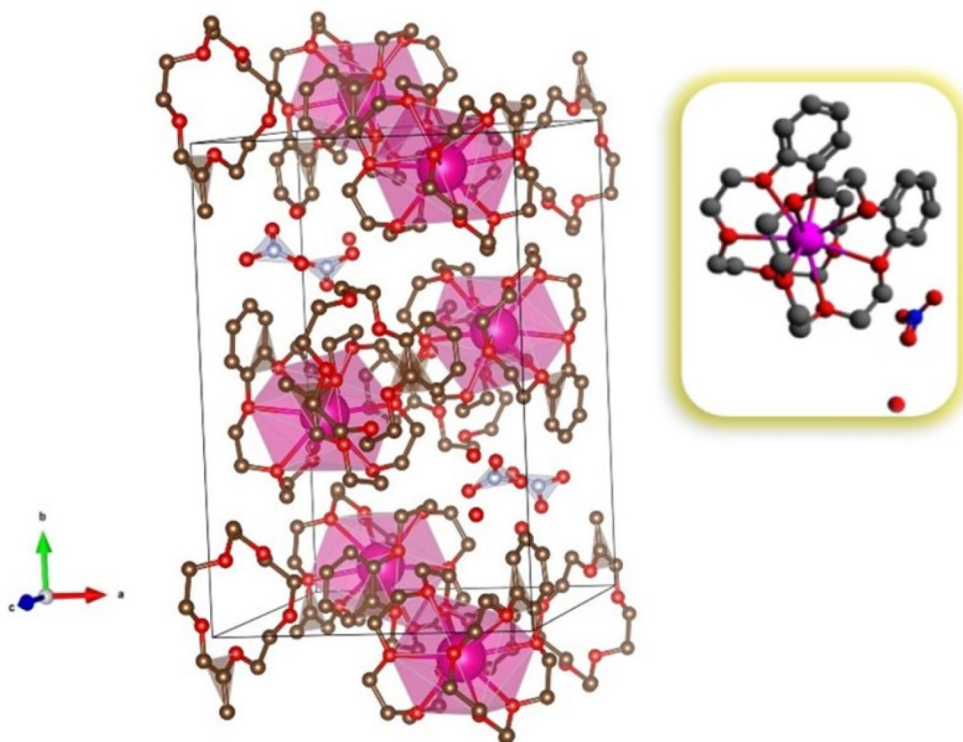


Fig. 18 Bis(benzo-15-crown-5)-rubidium nitrate monohydrate, CCDC deposition number: 1158666

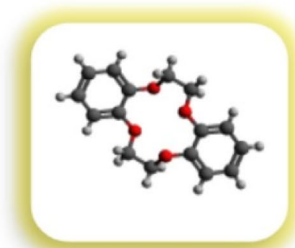
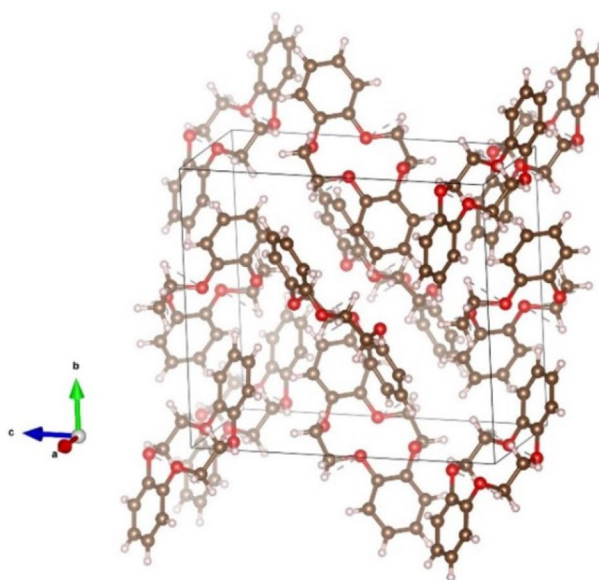


rigid complex crystallized in an orthorhombic system, *Pbca*, $a = 6.9774(2) \text{ \AA}$, $b = 13.0730(3) \text{ \AA}$, $c = 14.6363(3) \text{ \AA}$, $\alpha = 90^\circ$, $\beta = 90^\circ$, $\gamma = 90^\circ$, $V = 1335.06 \text{ \AA}^3$ and $Z = 4$. Rapid stereochemical averaging between conformers of dibenzo-12-crown-4 in solution gave rise to only four resonances in the ^{13}C NMR spectrum while the solid-phase ^{13}C spectrum showed eight resonances for dibenzo-12-crown-4 [69]. One of the lone pairs of electrons in the donor oxygen atom in one of the C-C-O-C moiety in the solid lay in the plane of the aromatic ring while the other was 60° out of plane.

Similarly in another C-C-O-C unit one of the lone pairs of electrons in the oxygen atom lay perpendicular to the plane of the ring while the other was ca. 15° out of plane. The optimal geometry for conjugative electron release is that where the orbitals on oxygen atoms are perpendicular to the plane of the aromatic ring.

Complexes of dibenzo-12-crown-4 with lithium ion have been studied for their H_2 storage capacity at the DFT level [70] and the negative binding energies of H_2 in complexes of dibenzo-12-crown-4 with lithium and potassium ions

Fig. 19 Dibenzo-12-crown-4 ether, CCDC deposition number: 1173272



compared to the positive binding energy of the free ligand points to their possible application in metal–organic frameworks (MOFs) for hydrogen storage. Benzo-13-crown-4 [71] crystallized in an orthorhombic system with space group $P2_12_12_1$, cell parameters $a=8.014(1)$, $b=8.309(1)$, $c=18.964(3)$, $V=1262.9(3)$ Å³ and $Z=4$. Crystals of its complex with LiSCN in the space group $Pbca$ have 8 molecules in unit cell of dimensions $a=11.870(2)$ Å, $b=13.453(2)$ Å, $c=19.105(3)$ Å, $V=3050.8(7)$ Å³ and $Z=8$. Lithium ion was pentacoordinated to four crown ether oxygens and the nitrogen atom of the SCN anion. Complex of benzo-14-crown-4 with lithium nitrate, (benzo-14-crown-4).LiNO₃ was obtained as monoclinic crystal, $P2_1/n$, $a=14.584(3)$, $b=9.074(3)$, $c=12.238(3)$ Å, $\beta=91.08(2)^\circ$, $V=1619.2$ Å³ and $Z=4$ [72]. Lithium ion was hexacoordinated to the four oxygen atoms of the crown-ether ring and to two oxygen atoms of the bidentate nitrate anion. Single crystal of 2:1 complex of benzo-10-crown-3 ether with LiClO₄, (benzo-10-crown-3)₂.LiClO₄, was studied by X-ray crystallography and solid state ¹³C NMR spectroscopy [73]. A pseudo-octahedral coordination involving the lithium ion was present in the complex. The space group of the crystal was $P2_1/c$, with $a=11.7842(3)$, $b=14.1405(4)$, $c=14.2311(3)$ Å, $\beta=89.90^\circ$, $V=2371.39(10)$ Å³ and $Z=4$. The ¹³C CPMAS spectrum supported the non-equivalent nature of the two benzo-10-crown-3 units in the complex arising from the spatial positioning of the anion in the complex.

Dibenzo-15-crown-4 [74] crystallized in a triclinic system, space group $P\bar{1}$, $a=9.4072(18)$ Å, $b=11.677(4)$ Å, $c=8.3147(24)$ Å, $\alpha=106.58(3)^\circ$, $\beta=105.800(19)^\circ$, $\gamma=100.516(21)^\circ$, $V=808.0(4)$ Å³ and $Z=2$. The sodium iodide complex of dibenzo-15-crown-4 displayed 2:2

stoichiometry and C_i symmetry. It had a monoclinic crystal system with $a=10.003(4)$, $b=16.639(4)$, $c=12.059(4)$, $\alpha=90.0^\circ$, $\beta=108.02(3)^\circ$, $\gamma=90.0^\circ$, $V=1908.7(10)$ Å³ and $Z=4$. Each sodium ion complexed to four oxygens of one crown unit and one oxygen of the neighbouring macrocyclic system. Coordination with an iodide ion completed the sixth site for each cation. Benzo-15-crown-5 complexes with one sodium ion like [Na(B15C5)ClO₄], [Na(B15C5)₂]ClO₄, [Na(B15C5)₂][BPh₄] and [Na(B15C5)H₂O]I have been structurally characterized by X-ray diffraction technique. He et al. [75] have reported B15C5 complex bis(benzo-1,4,7,10,13-pentaoxacyclopenta-dec-2-ene)-bis(thiocyanato)disodium(I), Na₂(SCN)₂(C₁₄H₂₀O₅)₂, consisting of two [Na(B15C5)]⁺ complex cations and two SCN⁻ anions. The sodium ion was coordinated to five oxygen atoms of B15C5. Its crystals adopted a monoclinic system, $C12/c1$, $a=17.708(5)$ Å, $b=11.236(3)$ Å, $c=17.821(5)$ Å, $\beta=106.816(4)^\circ$, $V=3394.2$ Å³ and $Z=4$ at 293 K.

Complexes of alkali-metal salts with chelating anions like 1-nitroso-2-naphtholate, 2-nitrophenolate, 2,4-dinitrophenolate and 2-hydroxybenzoate with benzo-15-crown-5 (B15C5), dibenzo-18-crown-6, dibenzo-24-crown-8 and dibenzo-30-crown-10 have also been reported by Poonia and Truter [76]. These include [potassium hydrogen(2-nitrophenolate)₂.(B15C5)₂]. The effect of solvent, presence of water and ratio of reactants on the isolation of complexes of LiX (X=Br, I, NCS) with B15C5 and of NaX and KX with B15C5 was also studied.

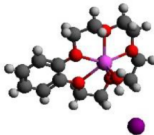
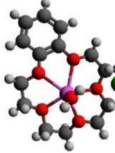

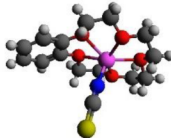
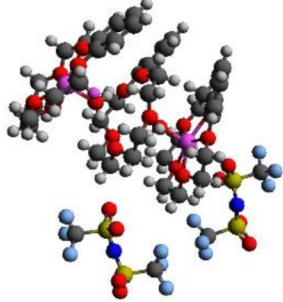
The 2:1 sandwiched complexes of alkali cations and benzo-crown ethers like benzo-15-crown-5 are charge separated. The anion plays an important role in charge separation. Anions like NCS⁻, I⁻, Br⁻, Cl⁻ and PO₄⁻³ failed to

stabilize the 2:1 ligand: metal ion complexes of benzo-15-crown-5 with potassium ion in ethanolic (methanolic) and aq-ethanolic (aq-methanolic) media [77]. The sodium ion formed a 1:1 complex with benzo-15-crown-5. The charged moiety $[\text{Na}(\text{benzo-15-crown-5})]^+$ carried nearly double the charge density compared to $[\text{K}(\text{benzo-15-crown-5})_2]^+$ and activation of only Cl^- and PO_4^{3-} was reported in this case. The complexation of K (3,5-dinitrobenzoate) with benzo-15-crown-5 (B15C5) in ethanol delivered a sandwich

complex of potassium (benzo-15-crown-5)₂ [3,5-dinitrobenzoate (3,5-dinitrobenzoic acid)₂]. It was found to be monoclinic, $P2_1/c$, $a = 11.063(2)$, $b = 10.680(1)$, $c = 46.548(8)$ Å, $\beta = 91.629(2)^\circ$ at 298 K [78].

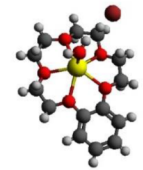
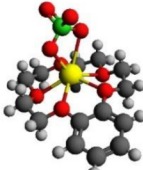


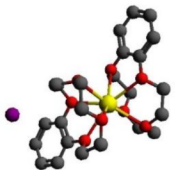
Tables 2, 3 and 4 show the stoichiometry, number of associated water molecule and the 3D view of chemical structures of complexes obtained from complexation of benzo crown ethers with some alkali salts.

Table 2 3D view of chemical structures of complexes obtained from complexation of benzo crown ethers with some lithium salts

S.No.	Crown ether/ Alkali metal ion/ Counter ion	Stoichiometry	Associated Water molecule(s)	3D view of the chemical structure of the complex	CCDC number for .mol file*
1.	B15C5/Li ⁺ /I ⁻	1:1	One		1588043
2.	B15C5/Li ⁺ /Cl ⁻	1:1	One		1588044
3.	B15C5/Li ⁺ /ClO ₄ ⁻	1:1	One		1812520
4.	B15C5/Li ⁺ / NCS ⁻	1:1	None		1854309
5.	B15C5/Li ⁺ / NTf ₂ -	3:2	None		2220403

*The .mol files were regenerated using Avogadro: an open-source molecular builder and visualization tool. Version 1.XX

Table 3 3D view of chemical structures of complexes obtained from complexation of benzo crown ethers with some sodium salts

S.No.	Crown ether/ Alkali metal ion/ Counter ion	Stoichiometry	Associated Water molecule(s)	3D view of the chemical structure of the complex	CCDC number for .mol file*
1.	B15C5/Na ⁺ /Br ⁻	1:1	One		1033468
2.	B15C5/Na ⁺ /ClO ₄ ⁻	1:1	None		1225916
3.	B15C5/Na ⁺ /ClO ₄ ⁻	2:1	None		1225917
4.	B15C5/Na ⁺ /picrate	1:1	None		1102758
5.	B12C4/Na ⁺ /I ⁻	2:1	None		1312386


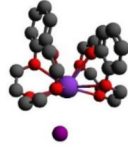
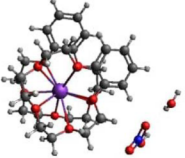
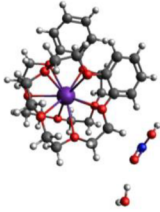
*The .mol files were regenerated using Avogadro: an open-source molecular builder and visualization tool. Version 1.XX

Infrared and Raman spectroscopy of small ring benzo-crown ethers (benzo-15-crown-5, dibenzo-15-crown-5 and benzo-12-crown-4) and their alkali-complexes

Vibrational spectroscopy is a common and information rich technique used to study functional molecules. Its sensitivity to changes in vibrational modes induced by local interactions helps in assigning most stable conformer on

complexation. The molecule may adopt various structures at different conditions of its physical state, local environment and temperature. Spectroscopic techniques like IR photodissociation spectroscopy (IRPD spectroscopy) and IR-UV double resonance spectroscopy (IR-UV DR spectroscopy), resonant two photon ionization (R2PI) etc. are also employed for studying molecules at low concentration. A comparison of IR-UV double resonance (IR-UV DR) spectroscopy and infrared photodissociation (IRPD)

Table 4 3D view of chemical structures of complexes obtained from complexation of benzo crown ethers with some potassium and rubidium salts

S.No.	Crown ether/ Alkali metal ion/ Counter ion	Stoichiometry	Associated Water molecule(s)	3D view of the chemical structure of the complex	CCDC number for .mol file*
1.	B15C5/K ⁺ /I ⁻	2:1	None		1115057
2.	B12C4/K ⁺ /I ⁻	2:1	None		1312286
3	B15C5/K ⁺ /NO ₃ ⁻	2:1	One		1146438
4	B15C5/Rb ⁺ /NO ₃ ⁻	2:1	One		1158666

*The .mol files were regenerated using Avogadro: an open-source molecular builder and visualization tool. Version 1.XX

spectroscopy spectra helps to obtain the energy for dissociation of the complex. Laser induced fluorescence (LIF) and ultraviolet-ultraviolet hole-burning (UV-UV HB) spectroscopy have been employed to study S₁-S₀ electronic transitions and to differentiate conformers and isomers of a functional molecular assembly.

Infrared spectroscopy, Raman spectroscopy and local conformation of polyethylene oxide

Papke and co-workers have studied the local conformation of solid complexes of PEO [79]. Infrared and Raman spectroscopic studies of crystalline sodium salt complexes

with PEO and amorphous rubidium and cesium thiocyanate complexes have also been conducted by them. A few key mid-IR active modes of PEO and PEO.alkali salt complexes are listed in Table 5 and assignment of selected Raman peaks of PEO and PEO.alkali salt complexes are presented in Table 6.

The mid-infrared data of these complexes indicated a gauche (G) or gauche minus (G⁻) conformation that exist about the O-(CH₂)₂-O linkage. Two strong infrared bands at about 880 and 944 cm⁻¹ for CH₂ rocking modes in a gauche conformation were observed, Table 1. The CH₂ rocking absorption bands for a trans conformation are expected around 773 and 992 cm⁻¹. As seen from Table 2, the ν(COC)_a peaks are cation sensitive.

Table 5 Mid-IR peaks of PEO and PEO.alkali salt complexes and their mode assignments *

Mode Assignment ***	Peak (cm ⁻¹)**						
	Pure PEO 600.000 (I)	I.NaBr	I.NaI	I.NaSCN	I.KSCN	I.RbSCN	I.CsSCN
$\delta(\text{CH}_2)_a$	1461 m	1459 s	1463 s	1458 sh	1463 sh	1464 m	1465 sh
$\delta(\text{CH}_2)_a$	1453 m	-	1455 sh	1450 m	1450 m	1447 m	1447 sh
$w(\text{CH}_2)_s$	1358 m	1350 s	1350 s	1350 s	1355 m	1347 s	1348 s
$w(\text{CH}_2)_a$	1342 s	-	1340 s	1340 s	1341 s	-	1340 sh
		1339 w	1335 sh	1335 sh	-		
$t(\text{CH}_2)_a$	1283 sh	1285 sh	1283 m	1287 m	1284 m	1285 m	1285 m
$t(\text{CH}_2)_s$	-	1279 ms	1277 m	1275 w	-	-	1277 m
$t(\text{CH}_2)_a$	1244 m	1241 s	1236 s	1238 s	1240 s	1246 s	1248 s
$v(\text{CC}), v(\text{COC})_a$	1147 s	1140 s	1147 s	1130 s	-	-	-
$v(\text{COC})_a$	1103 vs.	1095 vs.	1095 vs.	1085 vs.	1093 vs.	1100 vs.	1110 vs.
$r(\text{CH}_2)_a$	958 s	958 s	959 s	955 s	962 s	-	958 s
$r(\text{CH}_2)_s, v(\text{COC})_s$	948 m	948 sh	950 s	945 s	943 m	953 s	-
		923 w	920 mw	920 mw	-	-	-
		855 m	852 m	850 m			

*Table is adapted from [79]. ** vs.: very strong; s: strong, m: medium; w: weak; sh: shoulder; mw: medium-weak; ms: medium-strong. *** δ : bending; w: wagging; t: twisting; v: stretching and r: rocking

Table 6 Raman peaks of PEO and PEO.alkali salt complexes and their mode assignment*

Mode Assignment***	Peak (cm ⁻¹)**					
	Pure PEO 600.000 (I)	I.NaBr	I.NaI	I.NaSCN	I.NaBF ₄	I.KSCN
$\delta(\text{CH}_2)_s$	1487s	-	-	-	-	-
$\delta(\text{CH}_2)_a$	1480 s	1475 s	1475 m	1473 s	1477 s	1468
$t(\text{CH}_2)_a, t(\text{CH}_2)_s$	1281 s	1279 s	1279 m	1280 m	1283 m	1283 m
		1266 m	1265 mw	1262 m	1270 m	1270 m
$t(\text{CH}_2)_s$	1233 m	1234 m	1235 m	1235 m	1244 m	1236 mw
$v(\text{CC}), v(\text{COC})_a$	1144 m	1149 ms	1140 m	-	-	-
		1141 ms	1133 m	1135 m	1139 m	1134 m
$v(\text{CC}), w(\text{CH}_2)_s$	1125 mw	-	-	-	-	-
$v(\text{COC})_s, \tau(\text{CH}_2)_s$	1065 m	1061 mw	1055 mw	-	-	1063 mw
$r(\text{CH}_2)_s, v(\text{COC})_s$	861 mw	859 m	858 m	-	858 mw	-
$r(\text{CH}_2)_a$	846 s	844 w	838 m	-	832 mw	836 mw

A strong Raman active band at 870 cm⁻¹ for the PEO. LiCF₃SO₃ and PEO.LiBF₄ was also observed. The studies on poly(ethylene oxide) complexes of alkali metal salts by Shriver et al. [80] showed that the IR band of C-O and C-C stretching plus CH₂ rocking vibration of the trans O-CH₂-O moiety that appeared at 992 cm⁻¹ in the spectrum of molten PEO was not found in the solid state. Also, a new band at 810 cm⁻¹ was detected in the Raman spectrum of the molten polymer and was assigned to the CH₂ rocking mode of a trans O-CH₂-O unit.

*Table is adapted from [79]. ** s: strong; m: medium; w: weak; mw: medium-weak; ms: medium-strong.

*** δ : bending; τ : torsion; w: wagging; t: twisting; v: stretching and r: rocking.

As in the IR studies, the Raman spectra of the complexes were similar to those of pure PEO. However, one strong and new vibrational band at about 865 cm⁻¹ was common for all the complexes. Papke et al. [81] have studied the crystalline complexes of poly(ethylene oxide), PEO with various lithium salts by vibrational spectroscopic method.

Cation-dependent vibrational bands were identified in their Raman spectra. The Raman spectrum of PEO.LiNO₃ complex showed a band at 857 cm⁻¹. Cation-dependent far infrared bands were observed for the PEO complexes with Na⁺, K⁺, Rb⁺ and Cs⁺ salts and similar bands at about 400 cm⁻¹ were recorded for the PEO.LiX complexes. These bands are not Raman active and are similar to solvent-cage type vibrations observed for alkali metal salt solutions and crown ether complexes. Dupon et al. [82] have reported strong ion pairing in PEO.NaBH₄ complex and weak ion pairing in PEO.NaBF₄ complex. A maximum stoichiometry of 4:1 for the PEO-NaBF₄ complex was obtained at room temperature and recorded by x-ray diffraction. The internal modes of vibration of the anions and conductivity data indicated the presence of contact ion pair in PEO. NaBH₄. However, the PEO.NaBF₄ complex showed no anion dependence in its far-infrared spectra. As a result, the ionic conductivity is comparatively lower in the PEO. NaBH₄. The ionic conductivity of 4.5:1 PEO: NaBF₄ complex was 1.2 × 10⁻⁷ ohm⁻¹ cm⁻¹ at 303.15 K. In contrast,

the 4.5:1 PEO.NaBH₄ complex had conductivity which was almost 10² lower in value. Cation-dependent vibrational bands have been observed at 853 (mw), 830(m), 842(vw) and 843(vw) in the infrared region for the PEO-alkali metal salt complexes. These correspond to the motion of the alkali metal cations relative to their counter anions and surrounding ether oxygens [83].

Solvent-free systems like poly (ethylene oxide), poly (propylene oxide) and complexes of these polyethers with alkali metal salts have been considered as potential electrolytes in batteries and other electrochemical devices. These materials e.g., KSCN₄.(O-CH₂-CH₂-), exhibit ionic conductivities of the order of 10⁻⁴ ohm⁻¹ cm⁻¹ at 393.15 K. Pure PEO has been studied using Raman spectroscopy by Maxfield and Shepherd [84]. Sato and Kusumoto [38] have obtained Raman spectra for several crown ether alkali metal salt complexes. In all cases they observed an intense polarized band near 865–870 cm⁻¹. This band was tentatively assigned to A₁ mode involving a metal-oxygen breathing motion probably mixed with CH₂ rock mode. The strong intensity of this feature in the Raman spectra and absence in IR spectra indicated a somewhat symmetric ordering of oxygens around the metal cation. The conformation–spectrum correlations of poly (oxyethylene) have also been studied by Matsuura and Fukuhara [85].

Cyclic polyethers like 12-crown-4 and 15-crown-5 and their complexation with MnX₂ (X=Cl and Br) have been studied by IR and Raman spectroscopy by Li et al. [86]. The antisymmetric C-O-C stretching mode was either weak or absent in the Raman spectra. The weakening of CO bonds on complexation decreased the peak position by 10–60 cm⁻¹. The anion however did not affect the position of this band. Raman frequencies of 12C4 for ring bend, $\nu(\text{C-O-C})_{\text{sym}}$, $\nu(\text{CH}_2)_{\text{rock}}$, $\nu(\text{C-O-C})_{\text{asym}}$, $\nu(\text{CH}_2)_{\text{wag}}$, $\nu(\text{CH}_2)_{\text{twist}}$, $\nu(\text{CH}_2)_{\text{def}}$ and $\nu(\text{CH}_2)_{\text{str}}$ were observed at 483–602, 812–843, 899–1033, 1152, 1250–1292, 1450 and 2946–2990 cm⁻¹, respectively. The mid-IR frequencies of 12C4 for ring bend, $\nu(\text{C-O-C})_{\text{sym}}$, $\nu(\text{CH}_2)_{\text{rock}}$, $\nu(\text{C-O-C})_{\text{asym}}$, $\nu(\text{CH}_2)_{\text{wag}}$, $\nu(\text{CH}_2)_{\text{twist}}$, $\nu(\text{CH}_2)_{\text{def}}$ and $\nu(\text{CH}_2)_{\text{str}}$ were observed at 520, 845, 915–1020, 1073–1133, 1250–1292, 1306–1462 and 2905–2941 cm⁻¹, respectively.

Raman frequencies of 15C5 for ring bend, $\nu(\text{C-O-C})_{\text{sym}}$, $\nu(\text{CH}_2)_{\text{rock}}$, $\nu(\text{C-O-C})_{\text{asym}}$, $\nu(\text{CH}_2)_{\text{wag}}$, $\nu(\text{CH}_2)_{\text{twist}}$, $\nu(\text{CH}_2)_{\text{def}}$ and $\nu(\text{CH}_2)_{\text{str}}$ were observed at 481–600, 812, 912–993, 1045, 1155–1239, 1449 and 2905–2941 cm⁻¹, respectively. The mid-IR frequencies of 15C5 for ring bend, $\nu(\text{C-O-C})_{\text{sym}}$, $\nu(\text{CH}_2)_{\text{rock}}$, $\nu(\text{C-O-C})_{\text{asym}}$, $\nu(\text{CH}_2)_{\text{wag}}$, $\nu(\text{CH}_2)_{\text{twist}}$, $\nu(\text{CH}_2)_{\text{def}}$ and $\nu(\text{CH}_2)_{\text{str}}$ were observed at 520, 856, 939–982, 1042–1115, 1252–1293, 1356–1470 and 2859–2939 cm⁻¹, respectively.

Far-infrared spectra of complexes of 15-crown-5, benzo15-crown-5 and benzo12-crown-4 with acetonitrile and nitromethane in carbon tetrachloride solutions have

been reported by Belkin and coworkers [87]. The methyl group protons of acetonitrile and nitromethane form hydrogen bonds with the oxygen atoms of the crown ether. Bands due to intermolecular stretching vibration in the complexes of benzo15-crown-5 with acetonitrile and nitromethane were reported near 160 and 120 cm⁻¹ due to these symmetrical and antisymmetrical vibrations of hydrogen bonds, respectively. Ivanova et al. [88] have compared the IR spectrum of B15C5 with 4'-nitrobenzo-15-crown-5 (NB15C5). They have reported $\nu_{\text{s}}(\text{Ph-O})$ stretching mode of NB15C5 at 1280 cm⁻¹ and $\nu_{\text{as}}(\text{Ph-O})$ stretching mode at 1245 cm⁻¹. When compared with the IR spectrum of B15C5, the vibrational modes $\nu_{\text{s}}(\text{PhO})$ and $\nu_{\text{as}}(\text{PhO})$ appear as an intense doublet with maxima at 1264 and 1240 cm⁻¹ respectively.

The coordination of B15C5 through the anisole oxygen atoms was indicated by the decrease in the $\nu_{\text{as}}(\text{PhO})$ frequency. The pulsed vibration (ν_{pul}) of the free crown ether was visible as a low-intensity band at 800 cm⁻¹. The mixed stretching-deformation vibrations $\nu(\text{CH}_2) + \nu(\text{CO}) + \nu(\text{CC})$ of separate ethylene glycol units appeared along with the pulsed vibration of a macrocycle. The conformation-sensitive region was found to be in the range 700–1000 cm⁻¹. This region is more crowded in the spectrum of NB15C5 than in that of B15C5 as NB15C5 macrocycle has different conformations unlike B15C5. In the hydrated complex, Cu(NO₃).NB15C5.2H₂O, the water in the inner sphere was distinguishable from water molecule in the outer sphere by position of $\nu(\text{H}_2\text{O})$ at 3220 and 3475 cm⁻¹, respectively.

Conformation-sensitive vibrational modes of benzo oxa-crown ethers

The local conformation of the crown ether ring affects the band positions in their infrared and Raman spectra. Modes like CH₂ wagging, CH₂ twisting, CH₂ rocking and CO stretch were found to be conformation sensitive modes. The selective interactions between DB14C4 and LiCl were also examined by FT-IR measurements in the solid state [89]. After mixing DB14C4 with excess LiCl, NaCl, KCl, RbCl and CsCl salts in CH₃Cl/CH₃OH (9:1, v/v) solution, the solvent was removed completely under reduced pressure and the resulting mixtures were dried and analysed by FT-IR spectroscopy. Only the mixture with LiCl showed shifts in the ester and ethereal C–O stretching vibration bands which were from 1355, 1258, 1211 and 1062 cm⁻¹ to 1328, 1246, 1201 and 1047 cm⁻¹, respectively. These shifts to lower wavenumbers were attributable to the formation of a complex between DB14C4 and Li⁺ that causes more restriction in the C–O vibrations of the DB14C4 cavity. Egyed, O. and Izvekov [90] arrived at local conformers in B15C5 and its derivatives from their IR and Raman spectra. Conformation

Table 7 Conformation sensitive band frequencies for B15C5*

Frequency Assignment	B15C5	
	IR /cm ⁻¹	Raman /cm ⁻¹
CH ₂ wag, symmetric (coupled)	1412	-
CH ₂ wag, asymmetric (coupled)	1360	-
CH ₂ wag, symmetric (coupled)	1335	1338
CH ₂ twist ^a (coupled)	1295	1305
CH ₂ twist,	1260	1265
CH ₂ twist,	1232	1240
vCO	1040	1050
vCO	980	-
CH ₂ rock, asymmetric (coupled)	938	-
vCO + CH ₂ rock, asymmetric (coupled)	850	850
CH ₂ rock	815	820

*Table adapted from [90]

Table 8 Conformation sensitive vibrational modes for derivatives of B15C5*

Frequency Assignment	Local conformation
CH ₂ wag, symm. Coupled	t-t
CH ₂ wag, asymm.coupled	Gt-tG
CH ₂ wag symm.coupled	Tt-tG
CH ₂ twist symm. coupled	g-t
CH ₂ twist	tGg
CH ₂ twist	tGt
vCO	Tt-tG
vCO	Tt-g
CH ₂ rock asymm. (coupled)	Gt-tG
vCO + CH ₂ rock. Asymm. (coupled)	tGt
vCO + CH ₂ rock asymm (coupled)	Gt-tG
CH ₂ rocking	T

*Table adapted from [91]

sensitive vibrational modes for B15C5 are given in Table 7. They appear below 1500 cm⁻¹.

The local conformation of CH₂-CH₂-O-CH₂-CH₂ segments of the five-membered crowns were found to have partly GttG and partly TttG units. The O-CH₂-CH₂-O units in the oxyethylene ring are composed of parts with tGt and tGg local conformations. The band at 1235–1240 cm⁻¹ was characteristic of the oxyethylene unit in its stable tGt conformation. A band at 860–870 cm⁻¹ in the infrared was assigned to an in-phase mode of the five C-O stretching coupled to the CH₂ rocking librations. This band also confirmed a tGt sequence. The corresponding Raman band appeared at 855 cm⁻¹. The presence of tGg units were also deduced by the presence of bands of varying intensity at 1260–1270 cm⁻¹ assigned to the CH₂ twisting mode of the CH₂-CH₂-O unit. These bands appeared as shoulders of the Ar-O-C antisymmetric stretching vibration (very strong in IR but weak in Raman spectra). The CH₂-CH₂ wagging vibrations lay between 1380 and 1320 cm⁻¹ and depended upon the conformation about the C-C bond. For the GttG local conformation the antisymmetrically coupled CH₂ wagging vibrations were observed at 1360 cm⁻¹ and the CH₂ rocking vibrations were observed at 940–950 cm⁻¹. The bands at 1330–1340 cm⁻¹ (symmetrically coupled CH₂

wagging) and at 1050 cm⁻¹ (C-O stretching) were assigned to the TttG conformation. The band at 980–990 cm⁻¹ was assigned to C-O vibration belonging to the Ttg conformation. The derivatives were obtained by substituting the benzene ring by nitro, nitro and amino, nitro and N-methylamine and nitro and methylamide groups. Conformation sensitive vibrational modes for derivatives of B15C5 are given in Table 8.

Matsuura and Fukuhara [85] have correlated C-O, C-C stretching and CH₂ rocking modes with the conformation of the O-CH₂-CH₂-O fragment of the polymer chain CH₃-(OCH₂CH₂)_nOCH₃; *n* = 2, 3 and 6, in a solid, molten and aqueous state. The fragments were present in GT-TG, TT-TG, GT-GG, TT-TT and TT-GG (G: gauche and T: trans) conformations. The molten and aqueous solution of poly(oxyethylene) showed a Raman band at 832 cm⁻¹ originating from the trans conformation of the OCH₂-CH₂O group in the chain.

Synthetic ion channels are reported that are based on benzo(crown-ether) compounds [91]. Studies on benzo-12-crown-4 (B12C4) and its derivatives [92] showed correlations between structure and pharmacological activity in these compounds. The anticonvulsant activity in the maximum electroshock test at a dose of -100 mg/kg of benzo-12-crown-4 (B12C4) was twice that of acetylbenzo-12-crown-4 (ACBI2C4). The conformational states of these ligands in solution affected their complexing properties and their physiological activity. The spectra of B12C4 was compared with that of acetylbenzo-12-crown-4 (ACBI2C4) in the crystalline as well as in the solution state in acetonitrile. The IR spectra in the 1000–1300 cm⁻¹ region showed that the symmetrical and antisymmetric vibrations of C_{sp³}-O-C_{sp²} and C_{sp³}-O-C_{sp³} were highly sensitive to the conformational state of the COCCOC unit. Three bands with maxima at 1105 ± 3, 1127 ± 2, and 1148 ± 3 cm⁻¹ in the IR spectra of B12C4 and ACBI2C4 were assigned to ν_{as}COC vibrations. The ratios of the intensities of these bands correspond to different conformations (trans-gauche-trans and trans-gauche-gauche). The phase state and the polarity of the medium were seen to affect these ratios to different extents in B12C4 and ACBI2C4. The solid state spectrum of crystalline diphenylacetylbenzo-12-crown-4, DPAB12C4, showed splitting of ν_{as}COC which was absent in its solution state spectrum. The probable cause for the splitting was attributed to the interaction of these vibrations in the crystal lattice. The calculated structure of ACBI2C4 with minimum UMS value was found to be similar to that found by X-ray analysis. Based on the calculations, it was suggested that the diphenylacetyl group exerted electronic influence on the electron-donor, the veratrole oxygen atoms, in the macrocycle and hence affected the binding ability of the crown ether. The relative orientations of the lone pairs

Table 9 Selected characteristic vibrational frequencies (cm^{-1}) of 4'-(4'''-benzo-15-crown-5)methoxy-2,2':6',2''-terpyridine (L_1) and complexes of L_1 and 4'-(4'-benzo-15-crown-5)oxy-2,2':6',2''-terpyridine (L_2)^a

Assignment	Peak (cm^{-1})					
	L_1	L_2	[Na L_1 NCS]	[K(L_1) $_2$]NCS	[K(L_1) $_2$]I	[Na L_2 NCS]·2H $_2$ O
$\nu(\text{H}_2\text{O})$	-	-	-	-	-	3377
$\tau(\text{CH}_2)$, $\nu_{\text{as}}(\text{PhO})$	1250	1248	1242	1252	-	1246
	-	1246	1226	1243	1249	1213
$\nu_{\text{as}}(\text{COC})$	-	1127	1101	1107	1092	1119
	1119	1090	-	-	-	1090
$\nu_{\text{s}}(\text{COC})$,	1087	-	1089	-	1092	1080
$\nu(\text{CC})$	1055	1054	-	1045	-	1063
$\rho(\text{CH}_2) + \nu(\text{CO})$	870	867	878	-	-	854
	855	855	865	861	855	-
	845	846	849	-	-	-
	828	840	836	830	-	-
	808	829	819	-	-	830
ν_{resp}	791	-	865	861	855	854
$\delta(\text{CCO}) + \delta(\text{COC})$	697	665	696	699	700	-

^aTable adapted from [93]

of the oxygen atoms in the macrocycle have a considerable influence on the complexing ability and physiological activity of the macrocyclic ligands.

Infrared spectra of complexes of 4'-(4'''-benzo-15-crown-5)methoxy-2,2':6',2''-terpyridine (L_1) and 4'-(4'-benzo-15-crown-5)oxy-2,2':6',2''-terpyridine (L_2) with Na and K salts viz. [Na L_2 NCS]·2H $_2$ O, [K(L_1) $_2$]X (X=NCS, I, ClO $_4$), [K(L_2) $_2$]X (X=NCS, I, ClO $_4$ and [[K $_2$ {Zn(L_1) $_2$ }(I) $_2$](PF $_6$) $_2$] [93] show a large number of bands in conformation-sensitive regions arising from the $\nu_{\text{as}}(\text{COC})$ mode of vibration as shown in Table 9.

The shift in $\nu_{\text{as}}(\text{PhO})$ frequency of L_1 (1250 cm^{-1}) by 24 cm^{-1} in [Na L_1 NCS] (1226 cm^{-1}) pointed to the coordination of B15C5 through the anisole oxygen atoms. The conformation-sensitive regions were 1130–1100 and 860–800 cm^{-1} . The number of vibrations for $\rho(\text{CH}_2) + \nu(\text{CO})$ in L_1 (870, 855, 845, 828 and 808 cm^{-1}) and L_2 (867, 855, 846, 840 and 829 cm^{-1}) decreased in the spectra of complexes. The bands corresponding to $\nu_{\text{as}}(\text{COC})$ mode arising from conformations close to TGG and TGT appeared at about 1120 and 1100 cm^{-1} , respectively. A band at around 938 cm^{-1} in the region of $\nu(\text{CO}) + \nu(\text{CC}) + \rho(\text{CH}_2)$ mode of vibration originating from the TGT TGG ring fragment was observed in the spectra of alkali metal complexes.

Vibrational analysis of solid hydrates of benzo oxa-crown ether complexes

Poonia et al. [47] have reported the isolation and paper chromatographic solution studies of MX (where M=Na or K; X=Cl, Br, I, or NCS) complexes with macrocyclic polyethers, benzo-15-crown-5 (I). The $\nu(\text{OH})$ peaks were sufficiently sharp and intense (3410, 3500, and 3590 cm^{-1}) and

a water molecule appeared to be bonded to a metal ion. Single-crystal X-ray analysis of the complex (I).NaI, showed the sodium ion to be 0.75 Å outside the plane of polyether oxygens and confirmed a direct linkage of a water molecule with the sodium ion and the iodide counterion. Also, the complexes (I).LiBr and (I).LiI were hydrated whereas (I).LiNCS complex was not. The anion associated with the cation therefore is important in deciding the structure of the complex. The role of water in holding the supramolecular assemblies together was also brought forward by these studies.

On complexation, the cation binds to the ethereal oxygen atoms and one water molecule to complete its first coordination sphere. The anion binds through this water molecule to the cation, resulting in an increase in the dipole moment which is mirrored in the intensity of the band centered close to 3440 cm^{-1} [94]. An important feature of such hydrated complexes is the position of O-H stretching frequency which gives a clue to the type of hydrogen bonding involved. The hydroxyl symmetric stretching and asymmetric stretching modes (ν_1) and (ν_3) in case of water molecules are observed from 3700–3000 cm^{-1} [95–98]. The intensity, position and width of these confirms the type of intermolecular hydrogen bonding [99–104]. Investigations carried out by Collins and Washabaugh [102] showed that large monovalent ions like K $^+$, Cl $^-$, Br $^-$ and I $^-$ ions bind weakly to their adjacent water molecules while small monovalent ions like Li $^+$, Na $^+$ and F $^-$ attach more strongly to neighbouring water molecules. The transition from strong to weak hydration occurs at a radius (using ionic radii) of about 1.06 Å for monovalent cations. For strong hydrogen bonding, overtone 2 ν_2 of the deformation vibration, ν_2 , also overlaps with the stretching mode [105]. Hydrogen bonding is cooperative in nature and hence a single bridge hydrogen bond stretch is weaker than

a dimer. The broad peak observed close to 3440 cm^{-1} is an envelope of different types of bound water states. Anions are more strongly hydrated than cations for a given charge density. The resulting complexes are solvent-separated ion pairs, (SSIP). Ion pairing thus forms an important area of study [106]. The O–H stretching vibration frequencies of associated water show redshifts compared to a free water molecule, which were attributed to the non-covalent interactions including ion–water interaction and hydrogen bonds [107]. Kamarchik et al. [108] have performed quantum vibrational analysis of infrared spectra of micro hydrated sodium ions using an ab initio potential. Riera et al. [109] have studied $\text{Cs}^+(\text{H}_2\text{O})_3$ complex using many-body potential energy functions. Water anion interactions have been investigated by Bajaj and coworkers [110], Joel and coworkers [111] and Curnow et al. [112]. Lü et al. [113] have found unique patterns of vibronic (fine-structure) progressions that distinguish the “separated” from the “contact” ion pair in the crystalline solid state. They were identical to those dissolved in THF solvent and showed that the same X-ray structures persisted in solution.

Inorganic ions have an effect on the stretching band of associated water in the Raman spectra [114]. Zhelyazkov et al. [115] have studied the complexes of 12C4, 15C5 and 18C6 with sodium and potassium ions in aqueous solutions by Raman Spectroscopy. The ligand: metal ion stoichiometry observed for sodium and potassium complexes of 15C5 was 1:1 and 2:1, respectively. A 2:1 ligand: metal ion stoichiometry was obtained in complexes of 12C4. These results were consistent with the size compatibility between the cation and the macrocyclic cavity.

The UV-visible spectra also showed shifts in absorption values after complexation. Kudo and coworkers [116] observed a bathochromic shift of absorption maxima in B15C5 and B18C6 with alkali picrates. The complexes of a series of 4⁺-substituted benzo-15-crown-5 ligands with sodium picrate and their spectral properties have been reported by Wu and co-workers [117].

Sato and Kusumoto [38] have assigned the band at $865\text{--}870\text{ cm}^{-1}$ to a symmetric metal-oxygen breathing motion (A_{1g} mode) in the Raman spectra of several complexes of crown ether with alkali metal salts. By analogy, Papke et al. [81] have assigned the 870 cm^{-1} band in the PEO.LiX complexes to a M–O breathing mode. The highly symmetric structure of alkali metal complexes of 18-crown-6 and 15-crown-5 in liquid and crystalline states was revealed by Raman spectra.

Sato and Kusumoto [38] have also studied a number of crown ether-alkali complexes by Raman spectroscopy. An intense polarized band near $870\text{--}860\text{ cm}^{-1}$ was assigned to a symmetric A_{1g} mode involved in the oxygen ring breathing motion and was used as a useful monitor of t complex

formation by these crown ethers. Sato and Kusumoto [38] investigated the Raman spectra of 15C5, 18C6, and their complexes with Na and K salts viz. NaCl, NaBr, NaI, NaSCN, KCl, KBr, KI and KSCN in liquid and crystalline states to find that the crown rings in these complexes have highly symmetric conformations in viscous liquids. The widths of the bands of the sodium complexes (viscous liquids) were broader than those of the potassium complexes (viscous liquids) indicating many conformers for the former. Complexes of PEO with alkali metal salts, studied by Papke et al. [79], also showed similar bands in their Raman spectra indicative of complex formation. An intense polarized band near 860 cm^{-1} in the Raman spectra of liquid complexes of polyethylene glycol (PEG) with alkali metal salts confirmed complex formation. This band indicated a nearly symmetric ordering of the PEG chain around the metal cation. Raman spectra of liquid complexes of PEG with NaClO_4 , KClO_4 and RbClO_4 showed the appearance of an intense and sharp band near 860 cm^{-1} . The variation of metal cation in these PEG complexes did not affect the shift of this band. However, in the case of the complexes of crown ethers, the band was shifted to lower wave number with larger alkali cation.

Demina et al. [68] studied benzo-15-crown-5 ether complexes with lithium salts (LiCl , LiI , LiClO_4 and LiBF_4) by X-ray Diffraction and IR Spectroscopy. They obtained 1:1 isostructural hydrated complexes with all the salts except LiBF_4 . The complex formed with LiNO_3 was investigated by IR spectroscopy and the lithium ion was found to be coordinated to the oxygen atom of a water molecule as in the complexes formed by LiCl , LiI and LiClO_4 . In case of the anhydrous complex formed with LiBF_4 , one of the six coordination sites of lithium ion was occupied by the F atom of the tetrafluoroborate anion. The $\nu_s(\text{COC})$ band for B15C5 appeared at 980 cm^{-1} . This band was shifted by 24 cm^{-1} to lower frequencies indicating a weakening of the bond due to interaction of oxygen atom with the lithium ion. The band at 850 cm^{-1} , assigned to the C–O stretching vibration in the infrared spectra of B15C5, also registered a shift to low-frequency region by $10\text{--}20\text{ cm}^{-1}$ in the complexes. The region of $\nu_{\text{as}}(\text{COC})$ mode overlapped with that of the $\nu(\text{CC})$ and $\delta(\text{CH})$ modes and therefore both the number and the mutual positions of vibrational bands changed upon complex formation. The band due to $\nu_s(\text{PhO})$ mode was split into two on complexation and bands due to $\nu_{\text{as}}(\text{PhO})$ modes were shifted by $10\text{--}15\text{ cm}^{-1}$ to lower frequencies.

Comparative analysis of the IR spectra of the synthesized complexes of B15C5 with Li.B15C5.NCS (I) and $\text{Li.B15C5.H}_2\text{O.NCS}$ (II) was conducted by Kuz'mina et al. [59]. The band at 850 cm^{-1} in the infrared spectra of B15C5 and assigned to the C–O stretching vibrations also registered a shift to low-frequency region by 15 and 12 cm^{-1} for complexes I and II, respectively. The O–H stretching band

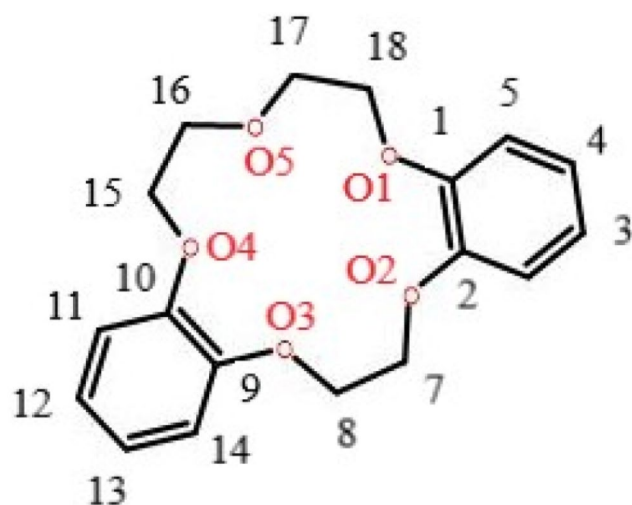


Fig. 20 Numbered atoms of dibenzo-15-crown-5 (2,3,8,9-dibenzo-1,4,7,10,13-pentaoxacyclopentadec-2-ene)

Table 10 Solid phase ^{13}C NMR chemical shifts (ppm) of DB15C5 and DB15C5.NaCNS

Carbon	DB15C5	DB15C5.NaCNS
C-2	150.17	146.94
C-2	149.38	145.70
C-3	116.42	115.15
C-4	118.85	124.36
C-5	121.03	125.54
C-6	111.11	113.08
C-7	66.90	67.14
C-8	67.36	67.14
C-9	149.38	144.99
C-10	147.93	146.94
C-11	112.10	111.87
C-12	121.03	121.10
C-13	121.03	122.80
C-14	112.10	111.52
C-15	70.59	69.26
C-16	68.75	67.14
C-17	65.25	66.01
C-18	61.88	65.00

of water in the spectrum of $\text{Li} \cdot \text{B15C5} \cdot \text{H}_2\text{O} \cdot \text{NCS}$ split into two components, $\nu_1 (3476 \text{ cm}^{-1})$ and $\nu_2 (3417 \text{ cm}^{-1})$. Therefore, the infrared studies showed that the water molecule participated in the coordination sphere of the cation and the anion was bonded to one hydrogen atom of the water molecule as in the case of $\text{Li} \cdot \text{B15C5} \cdot \text{H}_2\text{O} \cdot \text{X}$, where $\text{X} = \text{Cl}^-$ and I^- . This was also corroborated by X-ray diffraction studies. The knowledge of structure of complexes of lithium is particularly important in the extraction of lithium from aqueous solutions by a solution of B15C5 in chloroform.

Solid-state NMR studies

The solid-state spectra of nuclei are generally characterized by broad bands due to the superposition of signals from the randomly oriented single crystals. These broad bands are not observed in solution studies due to the rapid tumbling motion of molecules and as a result get averaged out. However, with the advent of advanced techniques like multiple-pulse ^1H cross-polarization, dipolar decoupling and magic angle spinning techniques (MAS) for polycrystalline materials, it is now possible to obtain well-resolved ^{13}C NMR line shapes, comparable to those in the liquid state. Solid state ^{13}C NMR can be a powerful method for the study of large amplitude molecular motions and is of particular utility in the study of guest–host interactions in crown ether chemistry [118].

Buchanan et al. [63] have conducted NMR studies on dibenzo-15-crown-5 and its complex with sodium thiocyanate in solution and solid state. The atoms were numbered as shown in Fig. 20. The ^1H and ^{13}C NMR chemical shifts for the NaCNS complex in the solution state were similar to those of free ligand in the solution state. However, substantial changes in chemical shifts were observed on examination of ^{13}C NMR spectra of free and complexed DB15C5 in the solid state. The resolution of methylene protons were better in the solid state. The solid phase ^{13}C NMR chemical shifts for DB15C5 and its complex DB15C5.NaCNS are listed in Table 10.

Belton and coworkers [119] have studied the high-resolution ^{13}C NMR of crystalline benzo-15-crown-5 using sideband suppression techniques. The conformational changes in the skeleton of the crown ether that accompanied complexation also gave rise to a change in dihedral angle H-C-C-H in the $\text{O-CH}_2\text{-CH}_2\text{-O}$ segment. ^{13}C NMR relaxation time measurements of macrocyclic ether complexes were employed by Erk and Zeidler [120] to arrive at the association constants of complexes of benzo-15-crown-5 and benzo-12-crown-4 with $\text{NaClO}_4 \cdot \text{H}_2\text{O}$ in solution state. Benzo-12-crown-4 displayed higher association constants as compared to benzo-15-crown-5 due to binding enthalpy-entropy compensations.

Solid-state ^1H NMR analyses have been employed to study the structures of 15-crown-5 and 18-crown-6 ether coordinated to Na^+ or K^+ in graphite intercalation compounds (GICs) [121]. Sodium and potassium complexes of benzo-15-crown-5 derivatives containing formyl and imine groups 1:1 ($\text{Na}^+:\text{ligand}$) and 1:2 ($\text{K}^+:\text{ligand}$) stoichiometries have been characterized by ^1H NMR and ^{13}C NMR technique [122].

The quadrupolar nature of alkali metal nuclei (nuclear spin quantum number, $I > 1/2$) requires solid-state NMR techniques for analysis [123]. Quadrupole effects in

complexes of lithium chloride, lithium bromide, lithium perchlorate and lithium nitrate with 12-crown-4 and of sodium nitrate with 15-crown-5 have been studied by ^7Li , ^{23}Na and ^{13}C solid-state NMR spectroscopy under static and magic angle spinning conditions [124].

Wong et al. [125] have employed solid-state ^{23}Na nuclear magnetic resonance to study sodium complexes with benzo-15-crown-5 (B15C5), 18-crown-6 (18C6), 12-crown-4 (12C4), dibenzo-24-crown-8 (DB24C8) and dibenzo-18-crown-6 (DB18C6). The ^{23}Na quadrupole coupling constants, QCC and chemical shifts were obtained from the analysis of ^{23}Na magic-angle spinning (MAS) NMR spectra of the complexes. It was found that the atomic valence of the donor ligand, the Na^+ -ligand distance and the coordination number (CN) around the sodium ion affected the ^{23}Na chemical shifts. The sodium ion in $\text{Na}(\text{B15C5})\cdot\text{I}\cdot\text{H}_2\text{O}$ adopted a pentagonal pyramid geometry, coordinated to five oxygen atoms from the benzo-15-crown-5 molecule and one oxygen atom from the water molecule.

The ^{23}Na chemical shift for $\text{Na}(\text{12C4})_2\text{ClO}_4$ at -6 ppm arose from a significantly shielded Na^+ environment. The complex, $\text{Na}(\text{12C4})_2\text{ClO}_4$, had a sandwich-like structure with the sodium ion being coordinated to eight donor oxygen atoms from the two 12-crown-4 molecules. The complex, $(\text{Na-o-nitrophenolate})_2(\text{DB24C8})$ had two crystallographically equivalent sodium sites in the relatively larger macrocyclic ring. Each of the sodium ions was found to be coordinated to six oxygen atoms by crystallographic studies. Two o-nitrophenolate ions bridged the two Na^+ ions from either side of the crown ring through nitro and phenolate groups. A relatively large ^{23}Na QCC, 2.65 MHz for $(\text{Na-o-nitrophenolate})_2(\text{DB24C8})$, was obtained from a very distorted Na^+ coordination environment. The ^{23}Na MAS spectrum of $\text{Na}(\text{DB18C6})\text{Br}\cdot 2\text{H}_2\text{O}$ also revealed the presence of two kinds of Na^+ sites. Each of the two Na^+ sites were at the center of a hexagonal bipyramid. However, one sodium site (Na_A) was coordinated by two water molecules as axial ligands, whereas the other sodium site (Na_B) had one water molecule and one bromide ion as axial ligands. The two independent complex molecules were linked by a bromide ion. A two-dimensional (2D) MQMAS spectrum for $\text{Na}(\text{DB18C6})\text{Br}\cdot 2\text{H}_2\text{O}$ confirmed the parameters for the two

sites. The Na_A site was more symmetrical than the Na_B site. Some important parameters from solid-state ^{23}Na nuclear magnetic resonance study of above mentioned sodium complexes with crown ethers are presented in Table 11.

Solid-state ^{87}Rb NMR has been used to study cation- π interactions [126]. Kim et al. [127] obtained quadrupole coupling constant $\text{CQ}(^{87}\text{Rb})$ by static ^{87}Rb NMR spectra for $\text{Rb}(\text{15C5})_2\text{Cl}$ but they observed much smaller values, approximately 5–7 MHz. In addition, they reported that the $\text{CQ}(^{87}\text{Rb})$ values in the $\text{Rb}(\text{18C6})\text{X}$ series ($\text{X}=\text{Cl}$, Br , I) were also of the order of 7–11 MHz. Solid-state ^{87}Rb NMR spectrum has been obtained for the complex $\text{Rb}(\text{B15C5})_2\text{BrH}_2\text{O}$ [128]. The NMR receptivity of ^{87}Rb is nearly 100 times more than that of ^{39}K . The study explored the possibility to use ^{87}Rb MAS NMR as an effective surrogate probe for studying K^+ ion binding in biological system. The ^{87}Rb NMR parameters for $\text{Rb}(\text{B15C5})_2\text{BrH}_2\text{O}$ like δ_{iso} was -5 ± 2 ppm, ^{87}Rb quadrupole coupling (QC) constant was 13.2 ± 0.5 MHz, and ηQ was 0.78 ± 0.05 . The relatively large $\text{CQ}(^{87}\text{Rb})$ value observed in $\text{Rb}(\text{B15C5})_2\text{BrH}_2\text{O}$ suggested a much distorted geometry around the rubidium ion.

Conclusion

Most crystalline alkali halides have a rock salt structure. On complexation with benzo crown ethers, these ions occupy a different lattice space and it affects their lattice dynamics. Any change in the lattice dynamics of alkali ions is reflected in the low-frequency region of infrared spectroscopy. The study involving noncovalent interactions in these complexes is made easier by the use of single-crystal X-ray method. Single-crystal X-ray studies help in unambiguous assignment of the 3D structure, stoichiometry, stable conformation and presence of associated solvent molecules in the complex in the solid state. The lattice energy is an important deciding factor for obtaining single crystals of these complexes.

As these complexes are formed by ion-dipole interactions between the metal ion and the donor atoms present in the macrocyclic ring, the dielectrics of the medium and the physical state in which the studies are performed become

Table 11 Key parameters from solid-state ^{23}Na nuclear magnetic resonance study of sodium complexes with crown ethers*

Sodium complexes with crown ethers	Stoichiometry (ligand: metal ion)	Coordination number of sodium ion	^{23}Na Chemical shift, δ /ppm	^{23}Na quadrupole coupling constants QCC/MHz	Asymmetry parameter, η
$\text{Na}(\text{B15C5})\cdot\text{I}\cdot\text{H}_2\text{O}$	1:1	6	13	1.45	0.50
$\text{Na}(\text{12C4})_2\text{ClO}_4$	2:1	8	-6	1.10	0
$(\text{Na-o-nitrophenolate})_2(\text{DB24C8})$	1:2	6	-4	2.65	0
$\text{Na}(\text{DB18C6})\text{Br}\cdot 2\text{H}_2\text{O}$	1:1	8 (Na_A) 8 (Na_B)	-13 (Na_A) -3 (Na_B)	1.70 (Na_A) 3.35 (Na_B)	0.32 (Na_A) 0.15 (Na_B)

* [125]

important parameters in deciding the stability and stoichiometry of these complexes. The hard oxygen donor atoms present in these fluorescent crown ethers give stable complexes of varying stoichiometry with the hard group I ions. The difference between the cation size and the ring size lends architectural diversity to single-crystals of the complexes. The formation and stoichiometry of these complexes highlights the role of charge density on the cation.

Single-crystal X-ray diffraction studies are particularly useful in establishing the presence of associated water or solvent molecules with the complex. The counterion plays a deciding role in accommodation of a solvent molecule to yield either a solvent separated ion pair (SSIP) or a direct contact ion pair (CIP). Hence, lithium in (I)-LiX (where $X^- = Br^-$ and I^-) complexes was found to be hydrated whereas the corresponding LiNCS complex was dehydrated. Complex of B15C5 with NaI with 1:1 stoichiometry also had an associated water molecule. The size of the cation and its charge density affects the association of water molecules with the complex as was seen while preparing complexes of benzo-15-crown-5 with sodium picrate and lithium picrate namely (6,7,9,10,12,13,15,16-Octahydro-5,8,11,14,17-pentaoxabenzocyclopentadecene)-2,4,6-trinitrophenolato-sodium and diaqua-(benzo-15-crown-5)-(picrate-O, O')-lithium, respectively. Complexes with potassium ion show 2:1 (ligand: metal ion) stoichiometry and a water molecule was associated with complexes formed with potassium bromide and potassium thiocyanate. Complexes of benzo-15-crown-5(1) with LiX ($X = Br, I, NCS$), NaX and KX ($X = 1$ -nitroso-2-naphtholate, 2-nitrophenolate, 2,4-dinitrophenolate and 2-hydroxybenzoate) led to several new complexes.

The structural properties of crown ethers depend on various factors like relationship between the cavity size of the crown ether and the cation diameter, number of donor atoms including additional binding sites, character of donor atoms, spatial arrangement of binding sites, conformational flexibility or rigidity of a crown ether, lipophilicity of the crown ether and the solvent employed in the reaction bath.

Limited data is available on the structural characterization of solid alkali-complexes of small ring benzo-oxa-crown ethers by infrared and Raman spectroscopy. The characteristic sharp and intense polarized band near the $870\text{--}860\text{ cm}^{-1}$ peak in the Raman spectra of complexes of alkali metal ion with crown ethers, polyethylene glycols (PEG) and polyethylene oxide (PEO) was indicative of complex formation. Several bands were obtained in conformation-sensitive regions, $\nu_{as}(COC)$ and $\nu(CO) + \rho(CH_2)$. As is evident from the data presented in the review, the presence of water of crystallization introduces new peaks in the spectra of the complexes. Vibrational spectroscopy captured the presence of ion-associated water molecules through the

stretching and bending modes of hydrogen-bonded water in mid-infrared region. Mid- and far-infrared spectroscopy were commonly employed to identify the presence of bridging water molecule in these complexes. Infrared and Raman spectroscopy provide useful information regarding the formation, conformation and local environment of associated water molecule in these complexes.

Transformations in crystal lattice on translation from free ligands to complexed form can be monitored by a comparative study of infrared and Raman spectroscopy. The low-frequency modes of the free and complexed ligands were also captured by infrared and Raman spectroscopy. The change in the point group of the ligand and water molecule on complexation led to the appearance or disappearance of bands in the infrared and Raman spectra.

Spectroscopy-structure correlation of crystal lattice transformations of alkali halides on complex formation with synthetic and bioligands is a challenging study. The review shows that complexation-induced crystal lattice transformations require further investigations by correlating structural changes to spectral variations. The studies can advance the understanding of noncovalent interactions such as hydrogen bonding and cation- π interactions in a supramolecular assembly. The structural information derived from single-crystals assists in describing mechanisms for the observed photophysical properties of these host-guest complexes including possibility of parallel energy transfer mechanisms. The studies could be particularly helpful in developing ion selective electrodes and in designing logic gates. Cation-ligand interactions in host-guest chemistry find application in drug designing. Solid-state X-ray diffraction studies can further the understanding of cation-induced properties in metal-organic frameworks. Thus, the data collected from solid-state studies of these complexes could help in building smart functional materials that find applications in the field of biophysical chemistry, analytical chemistry and crystal engineering.

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Declarations

Competing interests The authors declare no competing interests.

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