

Crowns and Crypts

A Fascinating Group of Multidentate Macrocyclic Ligands

Debasis Bandyopadhyay



Debasis Bandyopadhyay obtained his MSc in Chemistry from Burdwan University and received PhD from IIT,

Kharagpur. Presently, he teaches chemistry at Bankura Christian College, Bankura, West Bengal as a senior lecturer. He enjoys presenting new and more convincing approaches for chemistry problems to his students.

Crowns and crypts constitute a very interesting and important class of complexing ligands. Besides many metal complexes, these ligands made possible the formation of a variety of unusual species among which 'alkalides' and 'electrides' require special mention. The crowns and crypts are widely studied due to their increasing use in various improbable chemical and physical processes. Further interest in these ligands lies in their use as biochemical models. A brief discussion on the crowns and crypts is presented here.

Introduction

Three chemists¹ shared the 1987 Nobel Prize in chemistry for their work on the discovery and application of some very special multidentate macrocyclic reagents called crowns and crypts. Study of these reagents emerged as an area of particular research interest soon after the pioneering work of Pederson in this area was announced in 1967. Dramatic advancement was achieved within the next few years by new and modern syntheses followed by broader applications of these compounds. Crowns and crypts have the ability to form complexes even with the most reluctant alkali metal ions. This made the alkalies richer in coordination chemistry, which was otherwise impossible. The selectivity of the crown ligands towards alkali metals made possible the synthesis of stable complexes of all Group-I elements. Crypts form similar but much more stable complexes, also with the alkaline earths. The stabilization of less familiar oxidation states of a large number of elements using crowns and crypts became an easy task.

The basic and the oxidising properties of KOH and KMnO_4

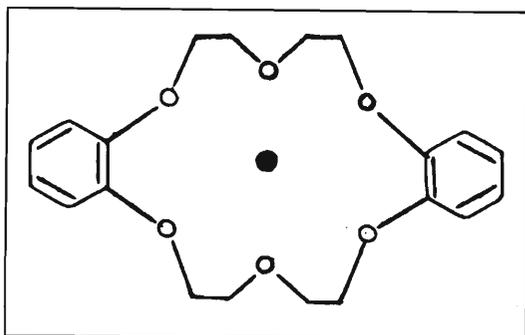
C J Pederson, J M Lehn and
D J Cram.

respectively could not be utilised in organic solvents due to their limited solubilities. However, the use of these agents with crowns or crypts enhances their solubilities in organic media. The formation of auride ion (Au^-), characterisation of the so-called zintl salts (composed of alkali metal cations and clusters of metals as anions) became possible. In addition, the improbable compounds like the alkalides and electrides that exist as complexed alkali metal cations and alkalide anions or electrons could be stabilized and studied. Even the existence of the ceside ion (Cs^-), the largest known monoatomic ion has been confirmed. The crowns and crypts have been widely studied as models for biological systems, especially to understand the perplexing and remarkably efficient selectivity between Na^+ and K^+ ions.

Crowns and Crypts

Crown ethers (or crowns) are a group of macrocyclic polyethers in which the ethereal O atoms are separated by two methylene ($-\text{CH}_2-$) groups. A typical example of a crown ether is 2, 3, 11, 12-dibenzo 1, 4, 7, 10, 13, 16-hexaoxacyclooctadeca-2, single 11-diene designated as dibenzo-18-Crown-6 (or simply 18-C-6 or Crown-6 as handy notations) having the structure given in Figure 1. The name dibenzo-18-Crown-6 indicates that there are two benzene rings and 18 atoms constitute the crown-shaped ring of which 6 are oxygen atoms. Thus when n is the ring size, m is the number of ethereal O atoms, the crown ether is abbreviated as n -C- m . Crown ethers with 3-20 ethereal oxygen atoms are now known. Examples include 14-C-4, 15-C-5, 30-C-10, etc. The

Figure 1. Graphic structure of 18-Crown-6, a macrocyclic polyether; the cavity [●] size depends on the size of the ring. Metal cation of appropriate size is trapped in this cavity to form a stable complex.



aromatic rings can be substituted, or replaced by naphthalene residues or reduced to cyclohexyl derivatives in order to get other similar crowns. These ligands, due to their very shape, have holes at the centre which accommodate metal ions of appropriate sizes. Generally stable complexes are obtained with alkali metals in which metal-oxygen bonds are formed. The remaining organic part of the molecule is

puckered to give a crown-like arrangement and hence the name 'crown ethers'.

Other related macropolycyclic ligands called 'cryptates' (or cryptands or simply, crypts) are more potent, selective and even stronger complexing agents for alkali metals. Besides, they show high complexing ability with alkaline earth cations, few transition and lanthanide ions also. The crypts are considered

to be the three-dimensional equivalents of crown ethers but incorporate N as well as O atoms (sometimes S or P atoms also) to show higher denticity than the crowns. The molecules are appropriately cross-linked with donor atoms correctly positioned in the bridging group to encapsulate metal ions in cage-like structures. A typical crypt is the molecule $\text{N}(\text{CH}_2\text{CH}_2\text{OCH}_2\text{CH}_2\text{OCH}_2\text{CH}_2)_3\text{N}$, called Crypt-222 (222 denotes the no. of ethereal O atoms in each N–N bridge) having the basic structure given in Figure 2. Cryptates (meaning hidden) are so called because they wrap around and hide the cation. Since the polyether bridges between the two N atoms resemble the seams of a football – this class of crypts is really called 'football ligands'. All these ligands form complexes with very high formation constants.

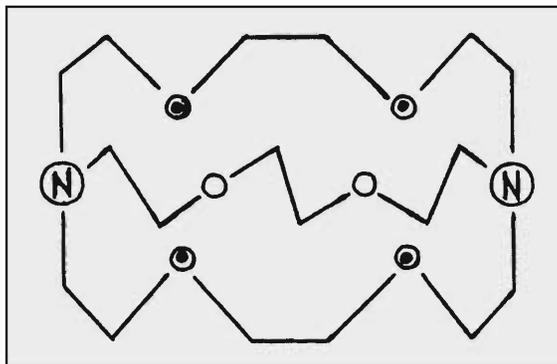


Figure 2. Graphic structure of a cryptand; when O atoms occupy © positions it is Crypt-222; Mixed donor cryptates result when S atoms or others occupy these. The ligands encapsulate metal ions in cage-like structures and form highly stable complexes.

The first synthesis of crowns was achieved in an attempt to prepare an alkyl phenolic ether. An unexpected product was obtained instead, due to the presence of contaminating catechol in the reaction mixture. The product was isolated to be dibenzo-18-Crown-6. Many other crowns were subsequently prepared in Pederson's laboratory. Later followed the synthesis and characterisation of a variety of crowns and crypts and their metal complexes, e.g. sepuhrates, anionic crypts and inorganic crypts (Box 1).

Complexes with Alkali Metals

A very important development in the chemistry of the alkali metals took place after the discovery of crowns and crypts. The

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Box 1. Sepulchrates, Anionic Crypts and Inorganic Crypts

Sepulchrates: A group of multicyclic encapsulating ligands called 'sepulchrates' are closely related to the football ligands. These are synthesised around a metal ion which cannot be released. Condensation of formaldehyde and ammonia on to the N atoms of Co(en)_3^{3+} (en = ethylene diamine) gives rise to a sepulchrates containing tris(methylene) amino caps on opposite faces of the coordination octahedron. Sepulchrates are stable over large pH ranges which makes easier the investigation of solution chemistry of elements like Mo, W which are prone to hydrolysis and polymerisation by changes in pH.

Anionic Crypts: Although cationic crypts has dominated in its complexes with alkali and few other metal cations for a long time – recently, anionic crypts viz., $[\text{CIN}(\text{CH}_2\text{CH}_2\text{NHCH}_2\text{CH}_2\text{NHCH}_2\text{CH}_2)_3\text{N}]^-$ have also come into existence.

Inorganic Crypts: Inorganic crypt may also completely surround a metal cation just like the crowns and crypts of organic origin; one such compound reported by Vogtle and Weber is $(\text{NH}_4)_{17}\text{Na}[\text{NaW}_{21}\text{Sb}_9\text{O}_{86}]\cdot 14\text{H}_2\text{O}$ where the heteropolytungstate, an inorganic crypt, completely surrounds the Na^+ ion. This compound is reported to have antiviral activity.

Box 2. Template Effect

The formation of macrocyclic rings is favoured by the presence of a cation of appropriate size that can serve to hold the partially formed ligand in position as the remainder of the ring is synthesised. This process is called template effect. A particular complex of choice can therefore be prepared in higher yields in the presence of an alkali metal, which is selective for that particular macrocycle.

alkali metals, due to their large size and low charge density, were known to be the most unwilling to form complexes. The stabilities of complexes with common ligands were low and generally found to decrease in the sequence $\text{Li} > \text{Na} > \text{K} > \text{Rb} > \text{Cs}$. Crowns and crypts have the unusual property to form stable complexes with all alkali metals. This exceptional stability has been attributed to the close fitting of the alkali metal ion in the hole at the centre of the ligand. In crown complexes like $\text{M}(18\text{-C-6})^+$ the polyetheral O atoms are arranged almost in a planar fashion with their lone pairs pointing inward towards the metal atom. The bonding M–O is largely electrostatic and the organic linkages joining the oxygen atoms look like the crown. A large number of stable alkali metal-crown complexes have been synthesised, also with some unusual coordination number of 10 as in $\text{K}(30\text{-C-10})^+$. Besides normal procedures, an interesting method of synthesis of these complexes is the use of so-called 'template effect' (Box 2).

The crown ethers show selectivity among the alkalis in forming complexes. The metal-crown binding is enhanced in the absence of non-coplanar donor O atoms and electron withdrawing substituents within the crown. The affinity of crown for an alkali

metal ion is strongly dependent on the size of the ring opening in the crown. A cation radius – crown cavity size ratio greater than or less than 1 results in less stable complexes since the crown ring will either be too small to surround or too big to interact with the cation effectively. Thus the overall stability of crown complexes depends on the (i) number of ethereal O atoms (ii) geometric disposition of ethereal O atoms (iii) size and shape of the macrocycle and (iv) size of the metal ion. By comparing the ionic diameters of the alkalis with the hole size, it is expected that Crown-4, Crown-5, Crown-6 should selectively complex with Li^+ , Na^+ , and K^+ , respectively. But, in practice, all these crowns prefer K^+ , due to the involvement of solvent effects.

Generally the complexes of alkali-crowns can survive indefinitely in non-aqueous solutions whereas those of alkali-crypts in aqueous solutions as well.

The crypts form stable complexes with alkali and other metal ions. The synthetic routes are similar to those of the crowns. Generally the complexes of alkali-crowns can survive indefinitely in non-aqueous solutions whereas those of alkali-crypts in aqueous solutions as well. The crypts show similar high selectivity towards the alkalis as that of crowns. For Crypt-222, for example, K^+ is appropriate to fit in the cavity but Li^+ , Na^+ are too small and Rb^+ , Cs^+ are too big to form stable complexes. Crypt 211, 221, and another type of ligands known as octopus ligands can however, form their most stable complexes with Li^+ and Na^+ , respectively (Box 3).

The X-ray crystal structure of many of these complexes have been determined. Two such structures, one of a crown complex, $[\text{Na}(15\text{-C-5})]^+$ and another of a crypt $[\text{Rb}(\text{Crypt-222})]^+$ are shown in Figure 3. In the former, five O atoms of the crown and one from a H_2O molecule bind to the Na^+ giving a coordination

Box 3. Octopus Ligands

Macrocycles, though extremely effective as polydentate ligands, are not essential for the production of stable alkali complexes; additional conformational flexibility without loss of coordinating power can be achieved by synthesising benzene derivatives with 2–6 pendant mercapto-polyether groups $\text{C}_6\text{H}_{6-n}\text{R}_n$ where R is $-\text{SC}_2\text{H}_4\text{OC}_2\text{H}_4\text{OMe}$, $-\text{S}(\text{C}_2\text{H}_4\text{O})_3\text{Bu}$, etc. These are called 'octopus ligands' and are more effective ligands than crowns and often equally as effective as crypts in sequestering alkali metal cations.



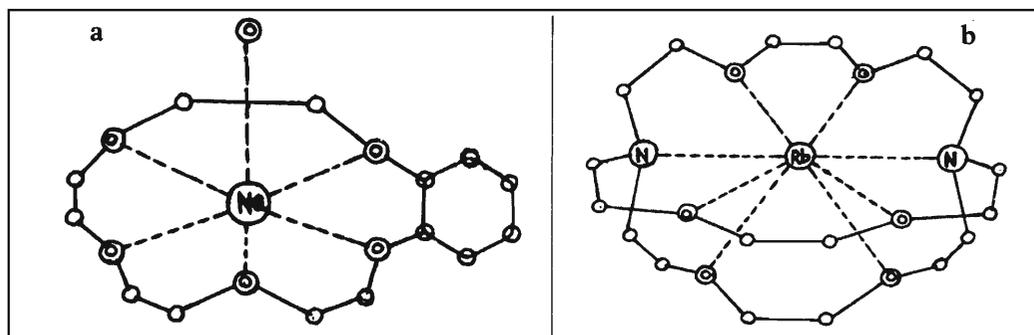


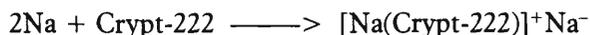
Figure 3. a) Structure of sodium-water-benzo-15-Crown-5 cation, a complex showing pentagonal pyramid coordination of Na^+ by 6 O atoms [⊙], five from the crown, one (top) from a H_2O molecule.

b) Structure of $[\text{Rb}(\text{C-222})^+]$ $\text{SCN}^- \cdot \text{H}_2\text{O}$, a typical crypt (or football ligand) complex (cage with bicapped trigonal prismatic polyhedra) having 8 coordination of Rb^+ by 6 O atoms and 2 N atoms.

number of six in a pentagonal pyramid geometry. In the crypt, six O atoms and two N atoms of the ligand gives a coordination number of eight. The ligand completely encloses the Rb^+ ion in a cage with a bicapped trigonal prismatic coordination polyhedra. From these observations, it has been established that a variety of coordination numbers or stereochemistry is possible for these types of complexes.

The Alkalides

Elemental Na or K dissolves very slightly in ethyl amine to form extremely dilute solutions. But when a macrocyclic ligand like Crypt-222 is added, the solubility increases dramatically by a factor of about 10^3 to 10^4 . By cooling such a concentrated solution containing Na below -15°C , an unusual golden compound $2\text{Na}(\text{Crypt-222})$ with interesting properties, was isolated. The compound was found to be actually $[\text{Na}(\text{Crypt-222})]^+\text{Na}^-$, a cryptated sodium sodide – one of the few known compounds containing an ‘alkalide’ ion.



The compound is supposed to be formed by shifting the disproportionation equilibrium $2\text{Na} \rightleftharpoons \text{Na}^+ + \text{Na}^-$ to the right although it is endothermic by about 438 kJ/mol. The high lattice energy of the Na crypt complex overcomes the endothermicity for this reaction. The stability of Na^- is due to the shielding effect of the cryptate on the cation where the large ligand completely isolates the former. Thus the electron transfer from Na^- to Na^+ is pre-



vented, which would otherwise take place to form metallic sodium.

A detailed crystal structure determination corroborated with the assignment $[\text{Na}(\text{Crypt})]^+\text{Na}^-$ with alternate layers of large complex cation and sodide anion in octahedral holes in a hcp arrangement. The Na^- is 555 pm from the nearest N and 516 pm from the nearest O atom of the crypt indicating that it is a separate entity in the crystal. Two distinct signals in the ^{23}Na NMR spectra of many complexes of this type also confirm the presence of M^- anion. Presence of a distinctive optical spectrum, diamagnetism and all other experimental evidences finally led to the firm establishment of the structure of alkalides.

Brown to gold-brown solids containing other M^- ions ($\text{M} = \text{K}, \text{Rb}, \text{Cs}$) also have been prepared with different crowns and crypts. The stability of Na^- is the most and Cs^- the least. The M^- ions are obviously much larger than the respective M atoms, sometimes even larger than I^- . The ceside ion, Cs^- having a radius of about 310-350 pm has been suggested as the largest known monoatomic anion on the basis of structures of $[\text{Cs}(\text{Crypt-222})]^+\text{Cs}^-$ and $[\text{Cs}(16\text{-C-6})_2]^+\text{Cs}^-$.

The Electrides

Alkali metals dissolve in ether readily in the presence of a suitable crown or crypt (C). The result is the formation of some very unusual complexes called 'electrides'. Electrides are usually black paramagnetic solids having the general formula $[\text{M}(\text{C})]^+e^-$. A common electride containing Cs is obtained by the reaction:



In these compounds an electron acts as a stable anion. Electrides adopt similar structures to those of alkalides. Since the electride anions cannot scatter X-rays, the structure of $[\text{Cs}(18\text{-C-6})]^+e^-$ shows only the complexed metal cation and no anions. The presence of cavities of radius ~ 240 pm formed by the complexed metal ion indicates the possible location of the electrons.

Box 4. Existence of Au^- , the auride ion

R Nyholm predicted earlier that two metals Cs and Au might combine to form ionic Cs^+Au^- rather than an alloy. But this could not be verified due to lack of sufficient evidence. Crowns and crypts helped stabilise the Cs^+ cation by complexation, further studies on which certainly proved the existence of Au^- , the auride as the counter anion. Unfortunately, due to premature death by accident, Nyholm could not see that his prediction was true.



Box 5. Triple-decker Crown Complex

The largest discrete cluster yet not fully characterised for any metal occurs in the black crown ether-alkali cation compound of formula $[\text{Cs}_9(18\text{-C-6})_{14}]^{9+} [\text{Rh}_{22}(\text{CO})_{35}\text{H}_x]^{5-} [\text{Rh}_{22}(\text{CO})_{35}\text{H}_{x+1}]^{4-}$ reported by Vidal and others. In addition to the two Rh_{22} clusters of average charge 4.5, the compound also features the unprecedented 'triple-decker' crown complex $[\text{Cs}_2(\text{Crown})_3]^{2+}$ which forms part of the array of counter cations $[\text{Cs}(\text{Crown})]_2^+$, $[\text{Cs}(\text{Crown})_2]_3^+$, $[\text{Cs}_2(\text{Crown})_3]_2^{2+}$.

Excess ligand normally favours the formation of electride while a mole ratio $M : C = 2 : 1$ tends to favour the alkalides. Both are, however, strongly reducing, thermally unstable and extremely air and moisture sensitive compounds.

Application and Uses

Crowns and crypts find many important applications and uses. These include preparative organic chemistry, solvent extraction, phase transfer catalysis, stabilisation of uncommon or reactive oxidation states and the promotion of other improbable reactions. A few examples are cited below :

- i] The solubility of alkali metal salts in organic media can be promoted using crowns and crypts due to the presence of large hydrophobic organic ring in the ligand; e.g. KOH and KMnO_4 can be used as an alkali and an oxidising agent, respectively in organic media also.
- ii] A number of zintl salts (*Box 6*) containing alkali metal cation and zintl anions viz. Te_3^{2-} , Sb_7^{3-} , Bi_4^{2-} , Sn_5^{2-} , Pb_5^{2-} and Sn_9^{4-} have been prepared with the help of crowns and crypts in anhydrous solvent.
- iii] Mixed metal complexes of the alkalies can be prepared by the exploitation of selectivity and differential stabilities of alkalides and metal complexes. For example, a K-Na alloy reacts with the crown 18-C-6 to give $[\text{K}(18\text{-C-6})]^+\text{Na}^-$ as the product which contains both the alkali metals, one as cation and other as anion.
- iv] Crown ethers can sometimes act as second coordination sphere ligands e.g. $[\text{Pt}(\text{bipy})(\text{NH}_3)_2]^{2+}$ gives a crystalline compound $[\text{Pt}(\text{bipy})(\text{NH}_3)_2(18\text{-C-6})]^{2+}$ with 18-C-6.

Box 6. Zintl Salts

Usually Zintl salts are composed of a characteristic homopolyatomic anion (zintl anion) and an alkali metal cation. The zintl anion generally is a cluster of *p*-block post-transition metals. Examples include Te_3^{2-} , Bi_3^{3-} , Sb_7^{3-} , Pb_7^{4-} , Sn_9^{4-} , etc. Compounds of this type had long been known to be formed in alkali metal-liquid NH_3 solution. But structural characterisation was not possible because all attempts to isolate the crystals failed due to decomposition of these compounds. Tendency to be converted to metal alloys further aggravated the problem. In 1975, the problem could be overcome for the first time by stabilising the cation as a crypt and zintl salts like $[\text{Na}(\text{Crypt})]_2\text{Pb}_3$, $[\text{Na}(\text{Crypt})]_4\text{Sn}_9$ could be prepared. Later, salts containing zintl cations viz. Bi_5^{5+} , Te_6^{4+} could also be synthesised.

v) **Biochemical modelling** : Since these ligands can imitate some biologically occurring natural compounds they are expected to provide insight into the biological phenomena occurring in living systems. For example, the mechanism of the sodium pump occurring across a cell membrane could be understood using the formation of the alkali metal-crown complex mechanism as a model.

Conclusion

Although much attention has been paid to the crowns and crypts, the study is not yet complete. The area is vast and a comprehensive knowledge is lacking. Mechanisms of many biochemical processes involving metal ions are still uncertain for which perfect models are necessary. These demand development of new ligands with newer applications. Therefore, further research in this area is still being continued.

Suggested Reading

- [1] C J Pederson, *J. Am. Chem. Soc.*, Vol. 89, p.2495, pp.7017-36, 1967.
- [2] N N Greenwood and A Earnshaw, *Chemistry of the elements*, Pergamon Press, 1989.
- [3] J E Huheey, E A Keiter and R L Keiter, *Inorganic Chemistry*, 4th Ed., Addison-Wesley Publishing Co., 1993.
- [4] K M Mackay and R A Mackay, *Introduction to Modern Inorganic Chemistry*, 4th Ed., Prentice Hall, 1989.
- [5] F A Cotton and G Wilkinson, *Advanced Inorganic Chemistry*, 5th Ed., Interscience, New York, 1988.
- [6] T Moeller, *Inorganic chemistry*, John Wiley and Sons, 1982.
- [7] J L Dye, *J. Chem. Education*, Vol.54, p.333, 1977.
- [8] D Parker, *Adv. Inorg. Chem. Radiochem.*, Vol.28, p.1, 1983.

Address for Correspondence
Debasis Bandyopadhyay
Department of Chemistry
Bankura Christian College
Bankura, West Bengal 722101,
India.