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Crown Ethers: Their Complexes and Analytical Applications

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ABSTRACT

The complexes and complexation mechanisms of crown ethers has been discussed. Examples of some crown ethers complexes have been reviewed. Applications of crown ethers in quantitative analysis and sample preparation for chemical analysis have been reviewed. The uses of crown ethers as an analytical chemical reagents and/or separation reagents have been also listed and discussed.

Keywords: Crown ethers, Complexes, Analytical applications.

INTRODUCTION

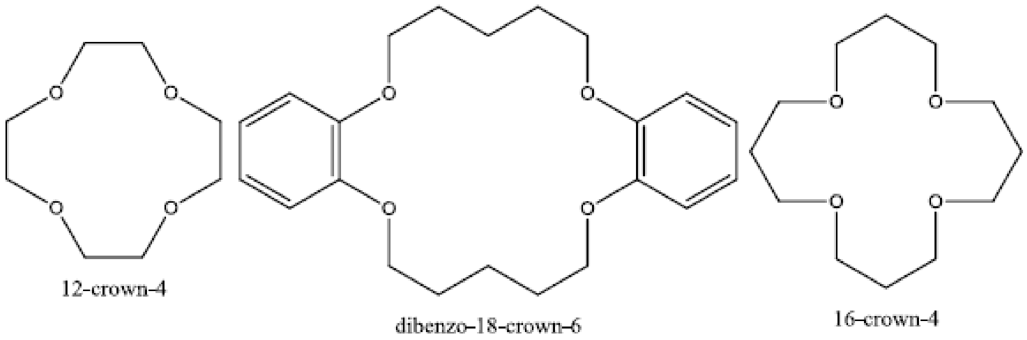
Crown ethers are cyclic chemical compounds that consist of a ring containing several ether groups. The most common crown ethers are oligomers of ethylene oxide, the repeating unit being ethyleneoxy, i.e., -CH_2CH_2O-. Important members of this series are the tetramer (n = 4), the pentamer (n = 5), and the hexamer (n = 6). The term "crown" refers to the resemblance between the structure of a crown ether bound to a cation, and a crown sitting on a person's head. The first number in a crown ether's name refers to the number of atoms in the cycle, and the second number refers to the number of those atoms that are oxygen [1]. Oxygen atoms are capable of acting as Lewis bases due to the presence of the lone pairs. The first crown ether, a cyclic hexaether, was accidentally discovered during the synthesis of bisphenols. Since Pedersen's discovery of crown ethers and their abilities to bind strongly with metal ions in 1967 [2,3], the study of crown ethers has grown at an incredible rate. The syntheses of many different types of crown ethers, *e.g.*, crown ether diesters, azacrown ethers, thiacrown ethers, and chiral crown ethers, have been documented in the literature and their binding properties such as binding selectivity and strength toward a wide range of metal ions, non metal ions, and neutral molecules have been investigated[4].

Crown ethers complexes

Because of their remarkable binding properties, the study of crown ethers has largely contributed to the development of host-guest chemistry and the emergence of supramolecular chemistry. Important advances in host-guest and supramolecular chemistry have been made later on [5,6,7]. Crown ethers selectively complex metal or ammonium salts, depending on their size, number and type of heteroatom. 12-Crown-4, for example, tends to complex with Li^+, while 18-crown-6 prefers K^+. The resulting metal complexes, in which crown ether acts as the host and the metal cation is the guest, fall into the class of host-guest chemistry. According to Pedersen proposal, the complex formation occurs through electrostatic interactions between the positively charged metal ion and the oxygen atoms of the crown ether ring (host-guest complexes). For the estimation of the stability of metal complexes with cyclic polyethers he stated that: the stability of the complexes directly depends on the match between the cavity size of the crown ether and the metal ion radius. As more experimental data became available, it appeared that the observed selectivity of crown ethers is not always explained by this rule. For example, 15-crown-5 forms stable complexes with Na^+ only in acetonitrile, whereas Na^+ complexes with 18-crown-6 are predominantly formed in methanol, water, and propylene carbonate. There are some factors influencing the stability of the complexes (the nature of the solvent and the anion, the type of the substituent in crown ether, *etc.*) [8]. The selectivity of the complexes of crown ethers is based on the size of the substrate and the ring size and distribution of the donor atoms in the crown. It is obvious that crown ethers of larger inner cores tend to bind larger ions. It should be noted that the relative flexibility of the crown rings leads to some degree of structural freedom during complexation. This is undesired with respect to selective binding and hence there have been efforts to improve the crown ether structures[9,10].

Crown ether ligands evidently have a much weaker affinity for transition-metal cations than for alkali and alkaline earth metal cations. The data show that crown ethers have a stronger tendency to hydrogen bond to the coordinated aqua ligands of the metal ion than to bond to metal ion itself [11].

The structures and functions of classical crown ethers have been continually evolved to meet the specific requirements for the recognition of more demanding target systems[12,13]. Since their initial discovery, that name has evolved to refer to a number of similar structures that make use of different heteroatoms joining carbon bridges of differing sizes and properties. Typically constructed using a modified Williamson Ether Synthesis to join individual monomers, these reactions can be adapted to create unique structures with similar basic pieces. In addition, substituted crown ethers can be used to enhance the properties to these compounds[14,15]. Examples of several commonly used crown ethers are shown in Figure 1.



12-crown-4

dibenzo-18-crown-6

16-crown-4

Figure 1. Examples of common crown ethers.

The complexation of alkali cations by neutral molecules was quite uncommon till the discovery of crown ethers by Pedersen, who prepared and studied several crown ether complexes of alkali and alkaline earth metal ions. Until now the complexation behaviour of alkali and alkaline earth metal ions with crown ethers has been extensively studied in various types of solvents [16-19].

There are two proposed mechanisms for the complexation of crown ethers with the metal ions. The first one is called Chock mechanism in which rapid conformational change of the crown ethers is followed by the rate determining formation of the complex. The second one is called Eigen-Winkler mechanism, which widely accepted for fast metal-ligand complex formation reactions. In this mechanism the outer sphere complex formation between the metal ion and the crown ether by the diffusion controlled approach of the counter species, precedes the rate determining inner sphere complex formation by the ligand rearrangement desolvation of the cation [20]. Bohman et. al. have studied the complexation of the alkali cations Na^+, K^+ and Rb^+ by the crown-ether, dibenzo-18-crown-6. The binding energies of cations as well as the counter ions (Cl^-, Br^- and I^-), oxygens and carbons have been measured. The results reveal strong back bonding effects. A comparison of the electron binding energies for the complexed and uncomplexed alkali halides was also studied [21].

A large number of lanthanide-crown ether complexes have been investigated and some have been studied by single-crystal X-ray diffraction methods [22,23].

Gan and Tan have studied the heavier lanthanide (Ln = Gd-Lu) nitrate complexes with dibenzo-24-crown-8 (DB24C8) have been prepared in acetonitrile. The complexes have been characterized by means of elemental analysis, IR spectra, ‘H NMR spectra and conductivity measurements. The crystal and-molecular structure of $[Gd(NO_3)_3(OH_2)_3]_*(DB24C8)$ has been determined by single-crystal X-ray diffraction. The gadolinium(III) ion is coordinated to the six oxygen atoms of three bidentate nitrate groups and three water molecules. The crown ether molecule is hydrogen bonded to these three water molecules. The Ln^{3+} ions can react with large cavity crown ethers to form two kinds of complexes with two different modes of coordination [24]. Many studied have been published on the complexation behavior of crown ethers and lanthanides and actinide ions [25-27].

The stability constants in of some transition elements complexes with the macrocyclic polyethers 15-crown-5, benzo-15-crown-5, 18-crown-6 and dicyclohexano-18-crown-6 were evaluated by conductometric titrations in mixed solvents system. The complexation studies indicate 1:1 complex formation between the metal ion and crown ether and the log K_{MLn+} values are in the range 1.0-3.0 [28].

Complexes have been prepared of 18-crown-6 with halides of manganese(II), cobalt(II) and nickel(II) from acetone solutions. With both manganese and nickel hydrated complexes are obtained which appear to undergo changes from square planar or octahedral to tetrahedral on heating. With cobalt a variety of complexes with varying amounts of water and acetone of crystallization, are obtained. With the fifteen membered rings, benzo-15-crown-5 and dibromobenzo-l5-crown-5, complexes with $CoCl_2$ and $MnBr_2$ appear to contain tetrahedrally coordinated metal [29].

Analytical applications

The complexes which the polyethers form with salts are held together by interactions between the cations and the C-O dipoles of the polyethers, that means, the polyethers are neutral ligands. Variable ring sizes as well as the type, the number and the positions of the donor atoms in the ether ring permit the selective adaption to a certain cation. Together with the cation an anion is taken up because of the electroneutrality. Complexation of organic molecules is also known. Cyclic polyethers find a wide range of application in analytical and preparative chemistry because of the variability of the ring systems by which a gradual complexation of inorganic salts and organic compounds is possible. Particularly the use of the polymers in ion chromatography, phase transfer catalysis and synthesis of living polymers must be mentioned [30].

Electroanalytical chemistry

Crown ethers, which feature prominently in supramolecular chemistry, can be used as sensing materials in the construction of potentiometric ion selective electrodes. Up to now, more than 200 potentiometric membrane sensors for cations and anions based on Schiff's bases and crown ethers have been reported [31,32]. One of the most important electrodes in electroanalytical chemistry are polymer membrane electrodes. The main part is the polymeric membrane, which is composed of a polymer such as polyvinylchloride (PVC), a plasticizer, and the ion carrier or exchanger. The response of these electrodes is highly selective and they have replaced many liquid membrane electrodes. Polymer electrodes have been used to determine ions such as K^+, Ca^{2+}, Cl^- and NO_3^-. Among organic receptors crown ethers are extensively exploited as sensing agent. These materials can be incorporated into the membranes as ionophores. Ionophores, or chelating agents, that selectively complex ions include crown ethers and the antibiotic valinomycin. The important feature of the neutral carrier molecule is its cavity which has dimensions approximately that of a molecule or ion [33,34].

Ion-Selective Electrodes with Chiral Ionophores. In this type of electrodes the ion-selective membrane contained chiral ionophore – a derivative of crown ether. As the model chiral analyte the phenylethylamine cation was used. The obtained results of small chiral resolution did not allow any application of the sensor but it initiated the new field of research in area of electrochemical sensors. The derivatives of crown ethers were also applied with the best results obtained for phenylethylamine hydrochloride, and phenylglycine methyl ester [35,36].

Chromatography

Among the numerous separation techniques, liquid chromatography by chiral stationary phases is proved to be the most precise and most effective one for enantioseparation and for the determination of enantiomeric composition [37-39]. Chiral crown ethers have been widely used in the resolution of various chiral compounds containing a primary amino group. Covalently bonded chiral stationary phases derived from (18-crown-6)-2,3,11,12-tetracarboxylic acid (18-C-6-TA) were developed and utilized for the resolution for several types of analytes [40]. Crown ether-based HPLC chiral stationary phases (CSPs) have been successfully utilized in the resolution of various racemic compounds containing a primary amino group. Especially, CSPs based on chiral crown ethers incorporating chiral binaphthyl unit or tartaric acid unit and based on phenolic pseudo chiral crown ethers have shown high chiral recognition efficiency.

M. Hyun reviewed the development of crown ether based HPLC CSPs, their structural characteristics and applications to the resolution of racemic compounds including chiral drugs containing a primary or secondary amino group with the variation of the type and the content of mobile phase components and with the variation of the column temperature [41]. Immobilization of enantiopure crown ethers on solid supports (e.g. silica gel, *Merrifield* type polymer resin, etc.) by covalent bonds results in chiral stationary phases. This technique combines the recyclability of the stationary phase and the selectivity of the macrocycle [39].

Crown ethers containing a pyridine subunit show outstanding complexation properties toward heavy metal ions and protonated primary amines thanks to their aromatic ring and the nitrogen atom [42]. A new pyridino-crown ether–based chiral stationary phases were made and studied by Kupai. The prepared columns were applied for chromatographic resolution of four chiral primary amines[39].

Even in gas chromatography, Crown ether-based chiral stationary phases have been used. **Xichun** et.al. have synthesized two chiral crown ethers containing end-alkenyl groups. They were anchored onto polyhydromethyl-siloxanes by hydrosilylation reaction, rendering two novel chiral polysiloxane stationary phases chirasil-man-18C6-25and chirasil-aza-15C5-25. The chromatographic properties and separation ability of these two phases for enantiomers have been studied. The chirasil-man-18C6-25 phase has efficient thermostability and considerable enantiomer-resolving power for racemics which have hydrogen-bonding force such as a-phenylacetol and phenylalanine isopropylester [43].

Liquid-Liquid Extraction

Macrocycles oxygen-containing compounds have been used extensively in extraction, because of the excellent compatibility between the crown-ring sizes and the ionic radii of metals. Solvent extraction with crown ethers is a convenient method for metal analysis because of their high selectivity and affinity towards specific metals. The benzene ring introduces much higher lipophilicity of a crown ether than the cyclohexyl ring does according to their distribution ratios. Besides, other pendent substituents on the crown ring also enhance the lipophilicity [44-46]. Crown ethers have been found to be powerful extracting agents for alkali metal salts [47].

Application of masking agents is one of the known methods for improving the selective separation of metal ions in the extraction processes [48]. Water-soluble crown ethers exhibit to be effective masking agents for enhancing separation factor in the extraction of rare earth metal ions [49,50].

Solid phase extraction

Asadoulahi *et al.* have developed a simple and sensitive flow injection system for separation, pre-concentration and determination of thallium, based on the analyte sorption on a microcolumn of dibenzo-18-crown-6 (DB18C6) immobilized on surfactant coated alumina with subsequent elution using a nitric acid solution (500 µL, 2 mol L-1). The concentration of thallium in the eluent was determined using electrothermal atomic absorption spectrometry. The method was applied for determination of thallium in water, hair, nail, and standard reference samples. The main benefits of this system were the easy preparation of the sorbent, high stability and repeatability of the microcolumns, high tolerance to interference from the matrix ions in different samples, enhanced sensitivity of ETAAS [51].
A method is described for the determination of Sr-90 in environmental samples using solid phase extraction Disk (Empore^{TM} Strontium Rad Disk) and GM Counter. The 47 mm diameter membrane disks are impregnated with crown ether that selectively retains Strontium. The method can potentially replace conventional sample preparation methods that utilize classical separation chemistry techniques [52].
A pre-concentration method for the determination of traces of copper in aqueous samples by FAAS based on sorption of Cu^{2+} ion on octadecyl silica membranes modified 3,6,9,14-tetrathiabicyclo[9.2.1]tetradeca-11,13-diene as a suitable ionophore. The unique feature of this method is the quantitative recovery of anlyte from membrane disk using thiourea solution. The proposed method has been successfully applied for the determination of trace amount of Cu^{2+} ion in water samples, ore and metallurgy products [53].
Ponlayuth Sooksamit et a have used an immobilized crown ether as an extractant in flow injection system for preconcentration and separation of Pb^{2+} prior to FAAS determination in digested soil samples is described and the method was validated by using certified reference materials [54]. The adsorption of barium complexes of dibenzo-18-crown-6 (DB18C6) and dicyclohexano-18-crown-6 (DCH18C6) ethers on alkylated silica gel in the presence of sodium dodecylsulfonate was studied by Petrukhin et al. The adsorbent capacity for the barium complex of DCH18C6 was higher than that for the complex of DB18C6 by a factor of about 4 [55]. Cs and Na have also been separated, using 12-crown-4, 15-crown-5, 18-crown-6, dibenzo-18-crown-6, diamino-dibenzo-18-crown-6 and dinitro-dibenzo-18-crown-6 on Chromosorb, as neutral macrocyclic ligands [56]. The application of such cross-linked polymers as selective sorbents in analytical and preparative chemistry is reported [57,58].A novel solid-phase microextraction (SPME) fiber containing hydroxydibenzo-14-crown-4 (OH-DB14C4)/hydroxy-terminated silicone oil (OH-TSO) was first prepared by a sol-gel method and investigated for the determination of phenols. The coating has stable performance in high temperature (to 350 °C) and solvents (organic and inorganic) due to the chemical binding between the coating and the fiber surface. The addition of crown ether enhances the polarity of the coating compared with that of the sol-gel OH-terminated silicone oil fiber and, accordingly, provides higher extraction efficiency for polar phenolic compounds [59].

Three solid-phase microextraction (SPME) fibers prepared by the sol-gel method, containing hydroxydibenzo-14-crown-4 (OH-DB14C4), dihydroxy-substituted saturated urushiol crown ether (DHSU14C4) and 3,5-dibutyl-unsymmetry-dibenzo-14-crown-4-dihydroxy crown ether (DBUD14C4), respectively, were evaluated for the determination of aromatic amine (aniline, m-toluidine, N,N-diethylaniline, N-ethyl-m-toluidine, 3,4-dimethylaniline). The method was applied to the determination of aromatic amines in wastewater samples from a pharmaceutical factory [60].

Spectrophotometry

A spectrophotometric methods of determining alkali metal ions with a chromogenic crown ether reagent was found to be more selective and sensitive than an ion-pairing method based on the same size of crown ether cavity. The chromogenic crown ether, 2″,4″-dinitro-6″-trifluoromeethylphenyl-4′-aminobenzo-14-crown-4was used by Wu and Pacey to determine lithium ion in treated blood serum samples in both a batch and flow injection method and results were compared with data obtained with atomic absorption; excellent agreement was obtained in all cases [61]. In addition to normal colorimetric spectroscopic methods, crown ethers have been used to create ions sensors which respond to the presence of target ions by fluorescence. Typically, these sensors contain a receptor unit (crown ether) and a fluorphore which is quenched by the free lone pair of one of the heteroatom within the crown ether. Binding a cation to these lone pairs removes the quenching effect and allows the fluorphore to fluoresce freely[13]. By utilizing modified 18-crown-6 and 15-crown-5 ethers, one group has successfully synthesized dyes which have been used in extraction spectroscopy to detect the presence of sodium and lithium in blood serum [62]. Sodium in human blood serum was successfully determined by using the (2-hydroxy-3,5-dinitrophenyl)oxymethyl-15-crown-5 reagent. The molar absorptivity of the sodium complex is 14 000 l mol^{-1} cm^{-1} at 423 nm [63]. Kim et al. have prepared a diazatetrathia crown ether derivative that has two appended nitrobenzoxadiazolyl moieties. The compound exhibited a pronounced chromogenic behavior toward Hg^{2+} ions by changing the solution color from light orange to yellow, which can easily be detected with naked-eye. The detection limit for the analysis of Hg^{2+} ions in 90% aqueous acetonitrile was found to be 4.8×10^{-6} M, which suggests that the compound may be used as a chemosensor for analyzing sub-millimolar Hg^{2+} ions in aqueous environments [64].

CONCLUSIONS

As has been illustrated in many occasions, both in the literature and in this review, crown ethers have clear advantages in term of complex formation, and versatility. Nowadays the promised uses of crown ethers in analytical chemistry field are sensors or solid phase extraction sorbents. The development of Schiff's bases based sensors and solid phase extraction sorbents is still in progress. Many papers emphasizing instrumental aspects and/or applications are published every year.

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