

Structure and Host-Guest Chemistry of Crown Ether Analogs

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In 1967 Charles Pedersen discovered a series of macrocyclic polyethers, which he called crown ethers (Figure 1).¹ These polyethers were capable of selectively complexing cations by noncovalent interactions.¹ Crown ethers show a remarkable resemblance to naturally occurring macrocyclic antibiotics, such as valinomycin and nonactin, that influence the transport of alkali metal cations across cell membranes.² Along with the ability to solubilize metal salts in non-polar solvents,³ crown ethers have applications in phase transfer catalysis, cation transport in biological systems, molecular recognition, and analytical sensors.²

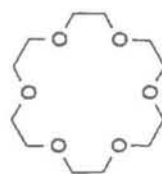


Figure 1. Structure of 18-crown-6

The IUPAC names for crown ethers tend to be rather unwieldy, and therefore an informal naming system has been devised, which describes the total number of atoms and oxygens in the ring: *m*-crown-*n*, where *m* is the total number of atoms in the ring and *n* is the number of oxygens. The properties of the crown ether can be varied by changing the size and shape of the cavity, by substituting the oxygen atoms with other coordinating groups, by changing the number of donor atoms in the ring, and by the addition of substituents onto the ring.⁴

A relatively new class of inorganic molecular recognition agents has been discovered: the metallacrowns, which are related to the crown ethers both structurally and functionally.⁴ In the metallacrowns, the ethylene units of the crown ether are replaced by a transition metal ion and a nitrogen atom (Figure 2).⁴ Hydroxamic acids are often used as the templating ligands in the metallacrown structure.⁵

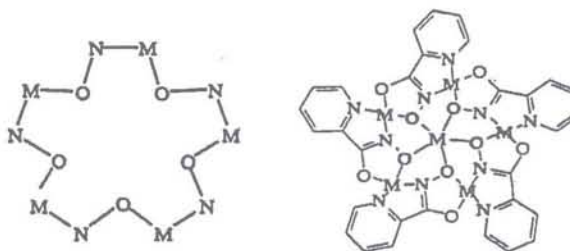


Figure 2. Structure of 15-Metallacrown-5

Metallacrowns 9-MC-3, 12-MC-4, and 15-MC-5 have been synthesized and have cavity sizes that are similar to those of their corresponding crown ethers. The metallacrowns are better ligands for highly charged cations, owing to the partial negative charge on the oxygen atoms in the crown.⁶ Metallacrowns can bind not only alkali and alkaline earth cations⁷ but also transition metal cations, f-metal cations,⁵ and anions.⁸

Possible applications include removal of radioactive isotopes from nuclear waste,⁹ molecular recognition of chiral anions,⁸ magnetic resonance imaging agents,⁵ and the preparation of chiral, porous materials.¹⁰

Other work in this area involves using diethyl keptinate as the templating ligand to prepare cyclic rings with a M-O-C-C-O-M connectivity,¹¹ and synthesizing fused dimers in which the rings are directly bound to each other with no bridging groups.¹²

Mercuracarborands are charge-reversed analogs of crown ethers in which the oxygen atoms in the crown are replaced by Hg, a Lewis acidic metal, and carborane cages serve as linking groups (Figure 3).¹³ The electrophilic mercuracarborand host molecule can efficiently coordinate halide ions and weak nucleophiles.¹⁴ The solubility of the mercuracarborand increases upon addition of alkyl substituents to the carborane ligand.¹⁵

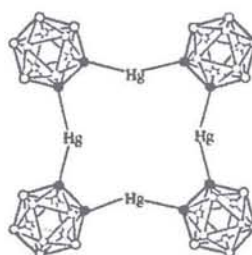


Figure 3. Structure of [12]-mercuracarborand-4

The mercuracarborand host is capable of binding halide ions reversibly.¹⁵ Mercuracarborands have potential applications in anion transport,¹⁶ as selective optical sensors,¹⁷ and as Diels-Alder catalysts.¹⁸ Another example of an anti-crown complex is trimeric perfluoro-*o*-phenylenemercury, which contains three mercury atoms arranged in a planar nine-membered cycle. This macrocycle is capable of binding borohydride, thiocyanate, and halide ions.¹⁹ Heterobimetallic macrocycles containing alkali, alkaline earth, or transition metals in the ring have also been prepared, and these species have been shown to bind O_2^{2-} in the cavity.²⁰

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