Inorganic Ion Pair Receptors

James C. Goloboy Literature Seminar October 25, 2001

Synthetic receptors for the coordination and recognition of either anions or cations have been studied for several decades. Organic[1] and inorganic[2] receptors have proven successful in binding ions for a variety of tasks, including electrochemical ion sensing[3] and transport through membranes.[4] Ion pair receptors, which bind a cation and anion simultaneously, build upon this base by allowing for the extraction, transport, and sensing of salts.

Inorganic-based receptors potentially have several unique advantages not found in organic receptors. Electrostatic interaction between a positively charged metal center and an anion can increase the stability of the bound complex. Well-defined geometries around metal centers can be controlled to create enhanced binding selectivity as well as strength. Other uses for metal centers that can be envisioned include electrochemical sensing, recognition through color changes or fluorescence, and catalysis.

Beer and coworkers[5, 6, 7] have prepared a number of ion pair receptors utilizing a bipyridyl anion binding site and a crown ether[7] or calix[4]arene[5, 6, 8] cation binding site. ^{1}H NMR titration experiments show these receptors to bind ion pairs in solution. X-ray crystal structure analysis (Figure 1) gives the structure of a bound complex in the solid state.

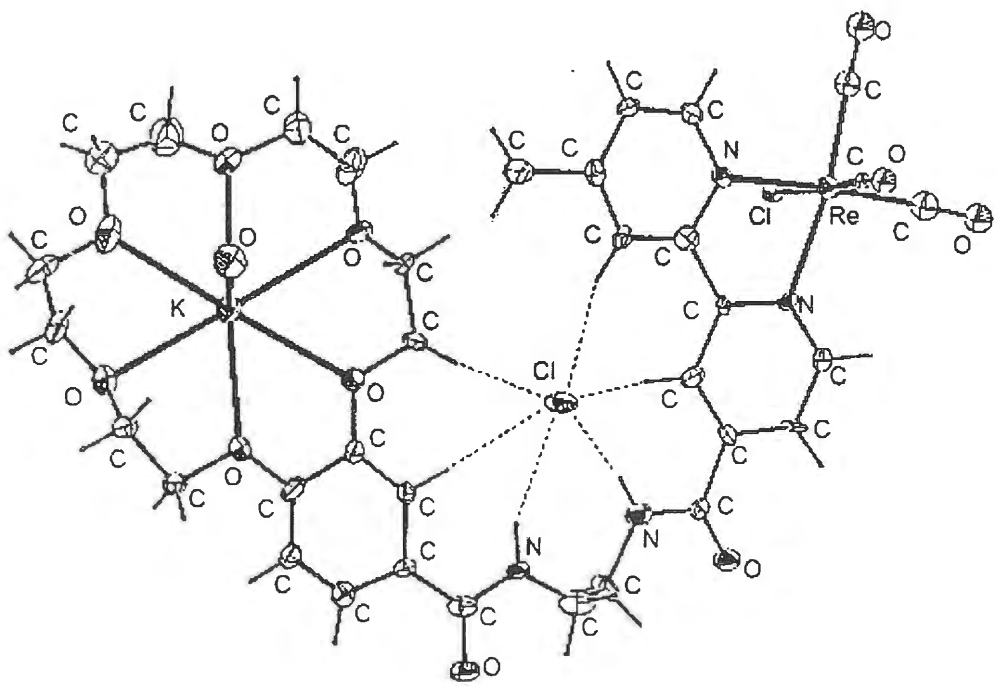

Figure 1. Crystal structure of the monomer unit of a rhenium(I) bipyridyl crown ether receptor with bound KCl.[7]

Reetz and coworkers synthesized ion pair receptors in which the metal center, either boron[9] or an aluminum[10], directly binds the anion whereas a crown ether moiety binds the cation. Reinhoudt and coworkers prepared receptors in which a uranyl (UO_2^+) center binds the anion with the help of hydrogen bonding from amido protons, and a crown ether or calix[4]arene moiety binds the cation.[11, 16]

One of the striking features of ion pair reception is that the anion and cation bind with positive cooperativity, that is, binding of the cation enhances the strength with which the anion is bound. This effect may be due to electrostatic interactions—the anion is more tightly bound to a receptor with a higher positive charge—or to allosteric effects, where the binding of the cation causes the anion binding site to be preorganized in a favorable way. For example, a receptor with a 15-crown-5 cation binding site forms a pseudomacrocyclic sandwich complex with potassium[12], arranging the bipyridyl site in a favorable conformation for anion binding.[7] The magnitude of the cooperative effect varies with the identity of the bound ions and the distance between the ions. Anion binding enhancement up to sixtyfold[6] due to selective cation binding has been observed.

Ion pair receptors mimic biological systems in their ability to transport amino acids and salts across liquid membranes. Reetz and coworkers[13] showed that a boron-based receptor transported L-phenylalanine across water/chloroform phase boundaries with a transport rate of up to 352 relative to a system with no carrier. Reinhoudt and coworkers[14] used their uranyl-based receptors to transport CsCl and $CsNO_3$ salts through a water/ether phase boundary, demonstrating the crucial role of ion pair binding in the transport of hydrophilic salts.

Receptors containing redox-active ferrocene centers can be used to sense ion pair binding by electrochemical techniques.[5, 15] Beer and coworkers discovered that cyclic and square-wave voltammograms of receptors with bound ion pairs contained unique features relative to those found in the voltammograms of simple ferrocene, the plain receptor, or the receptor with just a cation or anion bound. In one specific case[5] cathodic shift in oxidation potential induced by bromide coordination to a ferrocene-containing moiety was greatly amplified by the presence of lithium.

In future work on inorganic ion pair receptors, one can anticipate an increased focus on their transport and electrochemical properties. In a recent study, Coucouvanis and coworkers[17] demonstrated the ability of manganese and nickel-based receptors to transport tryptophan and serotonin across a water/chloroform phase boundary. Anion receptors have been shown to sense ions through their electrochemical response to binding,[3b,18] and initial studies on ion pair receptors indicate a high potential for similar success.

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