

**GAS-PHASE METAL ION CHEMISTRY IN A QUADRUPOLE
ION TRAP: CHELATION, COORDINATION AND HOST-
GUEST COMPLEXATION**

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Hui-Fen Wu, Ph.D.

The University of Texas at Austin, 1994

Supervisor: Jennifer S. Brodbelt

The study of molecular recognition has become an increasingly active area of research over the past two decades due to its fundamental importance in many biological and chemical phenomena. The process of complexation, in which a host and guest selectively bind through various types of interactions, is one particularly intriguing aspect of molecular recognition because many different types of binding interactions, including electrostatic, hydrogen-bonding, and covalent, may be involved.

In this thesis, an examination of the types of complexes formed from reactions of metal ions with a variety of polyethers, heteroaromatic compounds and quinone antibiotics has been undertaken in a quadrupole ion trap mass spectrometer. The metal ions are generated by laser desorption and the complexes are formed by subsequent ion-molecule reactions with neutral organic ligands. Various collision-activated dissociation (CAD) techniques are used to evaluate the structures of the metal/ligand complexes.

A study of the reactions of alkaline earth metal ions revealed their unusual gas-phase reactivity with polyether ligands in comparison to alkali metal ions and transition metal ions. Partial covalent-type binding or strong ionic bonds may exist between Mg^{2+} or Ca^{2+} ions and polyethers, caused by the delocalization of electrons from the oxygen atoms of the polyethers to the *s* orbitals of the metal ions. The net conceptual view of the formation of these alkaline earth metal/polyether complexes involves solvation of a ($\text{Mg}^{2+}\text{OH}^-$) or ($\text{Ca}^{2+}\text{OH}^-$) unit by a polyether in the gas phase, in some cases followed by spontaneous dehydration. The reactions of the transition metal ions with the polyethers can be size-selective with respect to dimerization reactions. Iron ions may insert into the skeletal bonds of the polyethers, thus promoting more energetic reactions.

The nature of the heteroatom donor has a strong influence on the complexation of different types of metal ions by the macrocyclic polyethers: 12-crown-4, cyclen and 1,4,7,10-tetrathiadodecane. The crown ethers that contain nitrogen or sulfur donors favor binding to transition metal ions, whereas the oxygenated macrocycles prefer complexation to the alkali metal ions.

The investigation of gas phase ion-molecule reactions between an array of heteroaromatic ligands and the metal ions were examined, and the relative order of cation binding affinities were determined by the ligand exchange technique. Typically terpyridine possesses the greatest binding strengths, followed by phenanthroline, dipyridine, then pyridine.