



INSTITUTIONEN FÖR KEMI OCH MOLEKYLÄRBIOLOGI

# Investigation of $[\text{N-X-N}]^+$ and $[\text{N-C-N}]^+$ Complexes in Solution

Exploring Geometry, Stability and Symmetry

Alavi Karim

Institutionen för kemi och molekylärbiologi  
Naturvetenskapliga fakulteten

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## Abstract

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Halogen bonding is a weak interaction. In this thesis the three center four electron halogen bond,  $[\text{N}-\text{X}-\text{N}]^+$ , has been studied. The lighter halogens form highly unstable halonium ions that are reactive towards nucleophiles and their complexes were therefore investigated at low temperatures. Whereas the chlorine-centered halogen bond was found to be symmetric, the fluorine-centered one is shown to be asymmetric in solution. These geometries have been determined by NMR spectroscopic evidences and computations at the DFT level. For determining the influence of the counterion on the iodine-centered halogen bond, the isotopic perturbation of equilibrium (IPE) technique was applied with  $^{13}\text{C}$   $\{^1\text{H}, ^2\text{H}\}$  NMR detection in solution, and X-ray diffraction in the solid state. The symmetric arrangement of  $[\text{N}-\text{I}-\text{N}]^+$  complexes possessing two equal N-I halogen bonds remains undisturbed, independent of the choice of counterion and also when it has been scavenged. In comparison, silver centered  $[\text{N}-\text{Ag}-\text{N}]^+$  complexes although similar in size to the iodonium center, show direct counterion coordination to the metal center.

The three center four electron complex of a positively charged carbenium ion trapped between two nitrogenous donors forming a thermodynamically stable pentavalent  $[\text{N}-\text{C}-\text{N}]^+$  complex has also been studied. The structure and properties of this complex is discussed based on NMR spectroscopic and reaction kinetic evidences in comparison to the analogous three-centered  $[\text{N}-\text{X}-\text{N}]^+$  halogen bond. A geometrically restrained bidentate Lewis base is shown to be necessary for the formation of this pentavalent complex. NMR spectroscopic and X-ray crystallographic evidences indicate that a monodentate Lewis base induces a reaction instead of stabilizing the reactive species as a thermodynamically stable complex. As the geometry of the pentavalent complex greatly resembles the  $\text{S}_{\text{N}}2$  transition state, it affords a smoothly modifiable model system for the investigation of fundamental reaction mechanisms and chemical bonding theories

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Keywords: three center four electron, halonium, carbenium, carbonium, pentavalent, symmetry, isotopic perturbation of equilibrium, NMR, variable temperature, counterion