Structural and Energetic Properties of H_3N–MX_3R Complexes

James Phillips[1], Anna Ley[1], Patrick Treacy[1], Benjamin Wahl[1], Brittany Zehner[1], Kelling Donald[2], and Samuel Gillespie[2]

[1]University of Wisconsin Eau Claire
[2]University of Richmond

May 15, 2020

Abstract

We have explored the structural and energetic properties of a series of RMX_3–NH_3 (M=Si, Ge; X=F, Cl; R=CH_3, C_6H_5) complexes using density functional theory and low-temperature infrared spectroscopy. In the minimum-energy structures, the NH_3 binds axially to a halogen, while the organic group resides in equatorial site about the metal. Remarkably, the primary mode of interaction in several of these systems seems to be hydrogen bonding (C-H–N), rather than a tetrel N-M interaction. This is particularly clear for the $RMCl_3$–NH_3 complexes, and analyses of the charge distributions of the acid fragment corroborate this assessment. We also identified a set of metastable geometries in which the ammonia binds axial to the organic substituent. Acid fragment charge analysis also provide a clear rationale as to why these configurations are less stable than their R-equatorial counterparts. In matrix-IR experiments, we see clear evidence of the minimum-energy form of CH_3SiCl_3–NH_3, but analogous results for CH_3GeCl_3–NH3 are less conclusive. Computational scans of the M-N distance potentials for CH_3SiCl_3–NH_3 and CH_3GeCl_3–NH_3, both in the gas phase and bulk dielectric media reveal a great deal of anharmonicity, and a propensity for condensed-phase structural change.

Hosted file

`H3N_MX3R_paper_sub.pdf` available at https://authorea.com/users/322265/articles/451313-structural-and-energetic-properties-of-h3n-mx3r-complexes