TWO-CENTER THREE-ELECTRON BONDING IN $ClNH_3$ REVEALED VIA HELIUM DROPLET INFRARED SPECTROSCOPY: ENTRANCE CHANNEL COMPLEX ALONG THE Cl + NH_3 → $ClNH_2$ + H REACTION

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Pyrolytic dissociation of Cl_2 is employed to dope helium droplets with single Cl atoms. Sequential addition of NH_3 to Cl-doped droplets leads to the formation of a complex residing in the entry valley to the substitution reaction, Cl + NH_3 → $ClNH_2$ + H. Infrared Stark spectroscopy in the NH stretching region reveals symmetric and antisymmetric vibrations of a C_{3v} symmetric top. Frequency shifts from NH_3 and dipole moment measurements are consistent with a $ClNH_3$ complex containing a relatively strong two-center three-electron (2c-3e) bond. The nature of the 2c-3e bonding in $ClNH_3$ is explored computationally and found to be consistent with the complexation-induced blue shifts observed experimentally. Computations of interconversion pathways reveal nearly barrierless routes to the formation of this complex, consistent with the absence of two other complexes, NH_3Cl and Cl-HNH_2, which are predicted in the entry valley to the hydrogen abstraction reaction, Cl + NH_3 → HCl + NH_2