

TWO-CENTER THREE-ELECTRON BONDING IN  $\text{ClNH}_3$  REVEALED VIA HELIUM DROPLET INFRARED SPECTROSCOPY: ENTRANCE CHANNEL COMPLEX ALONG THE  $\text{Cl} + \text{NH}_3 \rightarrow \text{ClNH}_2 + \text{H}$  REACTION

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Pyrolytic dissociation of  $\text{Cl}_2$  is employed to dope helium droplets with single Cl atoms. Sequential addition of  $\text{NH}_3$  to Cl-doped droplets leads to the formation of a complex residing in the entry valley to the substitution reaction,  $\text{Cl} + \text{NH}_3 \rightarrow \text{ClNH}_2 + \text{H}$ . Infrared Stark spectroscopy in the NH stretching region reveals symmetric and antisymmetric vibrations of a  $\text{C}_{3v}$  symmetric top. Frequency shifts from  $\text{NH}_3$  and dipole moment measurements are consistent with a  $\text{ClNH}_3$  complex containing a relatively strong two-center three-electron (2c-3e) bond. The nature of the 2c-3e bonding in  $\text{ClNH}_3$  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,  $\text{NH}_3\text{Cl}$  and  $\text{Cl-HNH}_2$ , which are predicted in the entry valley to the hydrogen abstraction reaction,  $\text{Cl} + \text{NH}_3 \rightarrow \text{HCl} + \text{NH}_2$ .