

CRYOGENIC ION SPECTROSCOPY OF ION-RECEPTOR INTERACTIONS IN OCTAMETHYL CALIX[4]PYRROLE COMPLEXES WITH HALIDE IONS^a

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Molecular recognition of ions is important in both the natural world within proteins and the synthetic world of supramolecular chemistry. Therefore, a deeper understanding of ion receptors and binding competitiveness in solution is desirable for the advancement of synthetic hosts for ionic guests. Octamethyl calix[4]pyrrole (omC4P), is a prototypical receptor for halide anions in aqueous solution chemistry.

We present cryogenic gas-phase infrared spectra of a series of anion-omC4P complexes of the form $[X^- \cdot \text{omC4P}]$ (X^- = fluoride, chloride, bromide), and assign spectral features using density functional theory calculations. The vibrational spectra encode the structures of and intermolecular forces in each complex, revealing the geometry of each complex and the binding motif of halide anions within the omC4P binding pocket. The position of the NH stretching modes depend on the identity of the anion, portraying a clear spectral response to changes in binding properties.

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