ISOLATION AND CHARACTERIZATION OF FORMATE/NI(CYCLAM)$^{2+}$ COMPLEXES WITH CRYOGENIC ION VIBRATIONAL PREDISSOCIATION

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Transition metal-based organometallic catalysts are a promising means of converting CO_2 to transportable fuels. Ni(cyclam)$^{2+}$(cyclam = 1,4,8,11-tetraazacyclotetradecane), a Ni^{II} complex ligated by four nitrogen centers, has shown promise as a catalyst selective for CO_2 reduction in aqueous solutions. The cyclam ligand has four NH hydrogen bond donors that can adopt five conformations, each offering distinct binding motifs for coordination of CO_2 close to the metal center. To probe the ligand conformation and the role of hydrogen bonding in adduct binding, we extract Ni(cyclam)$^{2+}$ complexes with the formate anion and some of its analogs from solution using electrospray ionization, and characterize their structures using cryogenic ion vibrational predissociation spectroscopy. Using the signature vibrational features of the embedded carboxylate anion and the NH groups as reporters, we compare the binding motifs of oxalate, benzoate, and formate anions to the Ni(cyclam)$^{2+}$ framework. Finally, we comment on possible routes to generate the singly charged Ni(cyclam)$^{+}$ complex, a key intermediate that has been invoked in the catalytic CO_2 reduction cycle, but has never been isolated through ion processing techniques.