Metal-containing ion-molecule complexes of the form $\text{M}^+\text{L}_n$, where $\text{L}=$CO$_2$, C$_2$H$_2$, H$_2$O, benzene, etc., are produced by laser vaporization in a pulsed nozzle cluster source, size-selected in a time-of-flight mass spectrometer and interrogated with infrared laser photodissociation spectroscopy. In strongly bound complexes, multiphoton processes are required to induce photodissociation. The process is enhanced on vibrational resonances, but spectra are broad and ill-defined. Mixed complexes that are tagged with rare gas atoms, e.g. $\text{M}^+\text{L}_n(\text{RG})_p$, photodissociate by the elimination of the more weakly bound rare gas atoms, and the spectra of these complexes are sharp. The ligand vibrations in these complexes are shifted in predictable ways from the vibrations of the free ligand molecule, and forbidden IR modes in these ligands become allowed in the reduced symmetry of the metal complex. In larger complexes with additional ligand layers, single photon photodissociation is efficient and sharp spectra can be measured without tagging. Size-dependent shifts in the ligand vibrations reveal the progressive solvation processes in the cluster. In several systems, new vibrational bands shifted far away from those of the ligand species suggest the presence of new chromophores, indicating that intracluster reactions have taken place. The measurements of structures, solvation behavior and intracluster chemistry in these systems are supplemented with density functional calculations, revealing a wealth of new insights into the dynamics of clustering at metal cation centers.