Lignins are the second most abundant naturally occurring polymer class, contributing to about 30% of the organic carbon in the biosphere. Their primary function is to provide the structural integrity of plant cell walls and have recently come under consideration as a potential source of biofuels because they have an energy content similar to coal. Herein, we employ cold ion spectroscopy (UV action and IR-UV double resonance) to unravel the spectroscopic signatures of G-type alkali metal cationized (X = Li\(^+\), Na\(^+\), K\(^+\)) lignin tetramers connected by \(\beta\)-O-4 linkages. The conformation-specific spectroscopy reveals a variety of conformers, each containing distinct infrared spectra in the OH stretching region building on recent studies on the neutral and alkali metal cationized \(\beta\)-O-4 dimers. Based on comparisons of our infrared spectra to density functional theory [M05-2X/6-31+G*] harmonic level calculations for structures derived from a Monte Carlo conformational search, the alkali metal ion is discovered to engage in M\(^+\)-OH-O interactions as important motifs that determine the secondary structures of these complexes. This interaction disappears in the major conformer of the K\(^+\) adduct, suggesting a reemergence of a neutral dimer segment as the metal binding energy decreases. Chelation of the metal cation by oxygen lone pair(s) of nearby oxygens in the \(\beta\)-O-4 linkage is observed to be the predominant driving force for 3D structure around the charge site, relegating OH-O H-bonds as secondary stabilizing elements.