METAL ION BINDING TO POLYPEPTIDES CHARACTERIZED BY IRMPD SPECTROSCOPY. METAL-AMIDE NITROGEN BINDING AND THE IMINOL TAUTOMERIZATION.

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We have recently uncovered a new binding mode for the complexation of metal ions with gas-phase peptides. Termed the iminol mode, this binding mode is adopted by strongly binding divalent metal ions including Mg2+ and Ni2+. The metal ion displaces the amide hydrogen, which moves to protonate the amide carbonyl oxygen. A spectroscopic signature of the tautomerization is the disappearance of the characteristic Amide II band normally seen in peptide ion infrared spectra. We find that in peptides up to pentapeptides, multiple iminol binding can take place, such that all amide linkages are tautomerized to the iminol form, and chelate the metal ion. However, the iminol tautomerization depends on the nature of the metal ion, as will be discussed. Spectra of the ions were acquired by irradiating the cell of the Fourier-transform ion cyclotron resonance mass spectrometer with infrared light from the FELIX laser at wavelengths in the approximate range 500 to 1900 cm^{-1}.