AN UNEXPECTED GAS-PHASE BINDING MOTIF FOR METAL DICATION COMPLEXATION WITH PEPTIDES: IRMPD SPECTROSCOPIC STRUCTURE DETERMINATION

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The favorable orientation of the amide linkage and the aromatic side chain of N-terminal Phe or Trp leads to several favorable motifs for metal ion binding to dipeptides, having distinct characteristics in the IR spectrum. Infrared multiple photon photodissociation spectroscopy using the FELIX free electron laser has enabled clear resolution of these isomeric forms. The spectral patterns of complexes of small dications (Mg^{2+}, Ni^{2+} and Co^{2+}) reveal an unexpected new isomeric form, in which the metal ion displaces the amide hydrogen, forming a metal-nitrogen bond with covalent character which is unprecedented in such gas-phase complexes. 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}.