

Investigation of the local structure of Fe(II) bleomycin and peplomycins using theoretical analysis of XANES

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Active site geometry of Fe(II)-bleomycin, peplomycin and its derivatives have been studied on the basis of theoretical full multiple scattering simulations of the Fe K-edge X-ray absorption near edge structure. Analysis of the theoretical spectra calculated for the different models of Fe(II)-bleomycin revealed serious distortion of the nearest to Fe octahedron. It includes the presence of one ligand with very short bond length and angular distortions. Reconstruction of the nearest environment of the Fe during perturbation or removal of axial ligands was investigated for peplomycin. It was found that the replacement of carbomoyl group of the mannose with solvent molecule led to a small increase of average radius (0.03 Angstrom) of the first atomic shell around Fe ion and elongation of the shortest bond length (0.1 Angstrom). Removal of axial amine of beta aminoalanine is accompanied by more complex reconstruction of geometry, including small nearest shell expansion (0.02 Angstrom).