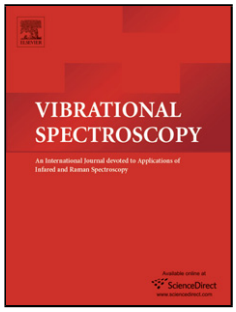

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Through-bond communication between polymer-bound phosphinic acid ligands and trivalent metal ions probed with FTIR Spectroscopy

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Abstract

The binding of trivalent metal ions to immobilized ligands is analyzed to determine the principal type of interaction, the extent of ion exchange, and changes due to through-bond communication. FTIR spectroscopy is found to be a readily accessible means of determining through-bond communication and spectra provide support for a molecular level interpretation of the interaction. The affinity of the phosphinic acid ligand for Al(III), La(III), Lu(III), Fe(III), and In(III) is quantified with distribution coefficients from 0.01 – 6 M nitric acid solutions. High affinities are evident with In(III) > Fe(III) > Lu(III) > La(III) > Al(III). The affinities correlate with the softness parameter and thus the polarizability of the metal ion. The FTIR spectrum of the phosphinic acid has two incompletely separated bands at 1168 / 1126 cm^{-1} associated with the P=O bond and two similar bands at 967 / 951 cm^{-1} due to the P-O(H) bond. The bands at 1168 / 951 and 1126 / 967 cm^{-1} are assigned to different hydrogen bonded conformers within the metal-free polymer. Through-bond communication is evident as the extent of metal ion binding increases: the P=O and P-O bands at 1168 and 951 cm^{-1}, respectively, collapse into a single band between 1040 – 1080 cm^{-1} representative of PO_2(M) while hydrogen bonding among unexchanged -P(O)OH ligands gives the bands at 1133 and 981 cm^{-1}.

1. Introduction

Ion-selective polymers are important to numerous applications, including chromatographic separations,[1] environmental remediation,[2] heterogeneous catalysis,[3] and hydrometallurgy.[4] Selectivity is dependent upon *through-space* communication as the ion approaches the ligand and *through-bond* communication as the ion passes a given distance threshold.[5] This report