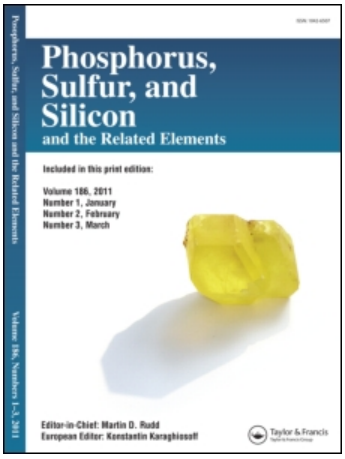

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Hexamethylphosphoramide Compounds: I. Preparation and Characterisation of Lanthanide Perrhenate Complexes

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Hexamethylphosphoramide Compounds: I. Preparation and Characterisation of Lanthanide Perrhenate Complexes

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Compounds with composition $[Ln(ReO_4)_2(HMPA)_2]ReO_4$ (Ln = La-Nd) and $[Ln(ReO_4)_2(HMPA)_4]ReO_4$ (Ln = Sm-Lu, Y) were synthesized by reaction of HMPA with the hydrated lanthanide perrhenate in ethanol followed by triethyl-orthoformate precipitation. The compounds from lanthanum to gadolinium are soluble enough and behave as 1:1 electrolytes in methanol. The remaining behave as 1:1 electrolytes in nitromethane and acetonitrile. Two types of IR spectra were observed, corresponding to the two different compositions. In all cases bands attributed to ionic and splittings due to coordinated bidentate perrhenate for the lighter and monodentate for the heavier ones were observed. Splittings and shifts of νPO could arise from at least two non-equivalent PO groups. The band at ~1190 or 1180 cm^{-1} (m) is attributed to a weakly bonded and that at 1125 cm^{-1} (m) to a strongly bonded, through the phosphoryl oxygen. The ν_{as} P-N-C and ν_s P-N-C bands are shifted to higher frequencies as compared to the free ligand. The absorption spectra of the neodymium compound in the hypersensitive $^4G_{5/2}$, $^2G_{7/2} \leftarrow {}^4I_{9/2}$ transition region were determined. The experimental data permit us to conclude that Nd^{3+} ions are not located in a cubic site. The nephelauxetic parameter, covalent factor and Sinha's parameter indicate an appreciable covalent character of the ligands: Nd^{3+} interaction. (CNPq, FAPESP, FINEP).