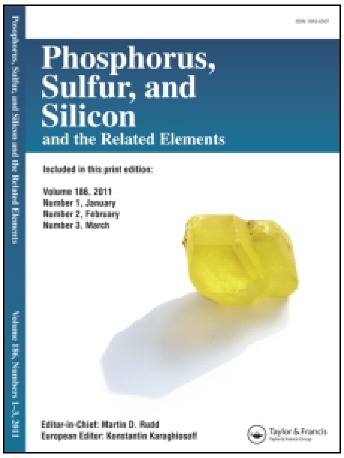

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LANTHANIDE AND TRANSITION METAL COMPLEXES OF DIALKYL α-HYDROXYIMINOPHOSPHONATES

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α-Hydroxyiminophosphonic acid derivatives are widely known not only as intermediates in the synthesis of the important aminophosphonic acids,[1,2] but also as phosphorylating agents,[3] potential metalloenzyme inhibitors,[4] and as compounds having fungicidal activity.[5] In this work the scope of these compounds has been extended considerably by the synthesis of a number of novel dialkyl derivatives. Novel lanthanide (La^{III}, Pr^{III}, Nd^{III}, Gd^{III} and Dy^{III}) and transition metal (Co^{II} and Ni^{II}) complexes of dialkyl α-hydroxyiminophosphonates $(RO)_2P(O)C(R')N(OH)$ where R = Et, Pr^i and R' = Me, Et have been prepared and the NMR shift properties of the Pr^{III} complex (R = Et; R' = Et) indicate the potential of these compounds as NMR shift reagents for the analysis of geometric isomers.[6,7] *X*-ray crystal structure analysis of $[Ni(L^1)_2Cl_2]$ (L^1: R = Et; R' = Et) shows a distorted *cis*-octahedral coordination at the nickel atom giving two symmetry related diethyl-(*E*)-α-hydroxyiminopropanephosphonate ligands and two chlorine donors, and those of $[Pr(L^2)_3Cl_3]$ and $[Nd(L^2)_2(NO_3)_3(H_2O)]$ (L^2: R = Pr^i; R' = Et) show nine-coordination geometries with asymmetric bidentate and monodentate L^2 bonding respectively. Thus the metal complexes show unusual coordination ambivalence, changing from symmetrically bidentate to asymmetrically bidentate and then to monodentate bonding modes, to accommodate the different steric requirements of the coordinating anions in facilitating neutral complex formation.

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