

Nickel(II) Complexing with p-Chlorobenzoic and Nicotinic Hydrazides in Water-Dimethyl Sulfoxide

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Abstract

Solvation and complex formation of nickel(II) with p-chlorobenzoic (L') and isonicotinic (L) hydrazides in water and water-dimethyl sulfoxide (DMSO) mixtures were studied by spectrophotometry and ^1H NMR spectroscopy. The spin-spin relaxation rate of H₂O or DMSO protons was analyzed as a function of composition of the solvent. On the basis of this analysis, a new procedure was developed for determining the mean coordination number of water molecules and DMSO in solvato complexes of nickel(II). Deviation of the fraction of coordinated DMSO molecules from the molar DMSO concentration in the solution is understood as a decrease in the bulk donor ability of water starting at a certain DMSO concentration. The formation constants were determined for the species $\text{Ni}(\text{L}')_2^{2+}$, $\text{Ni}(\text{L}')_2 + 2$, $\text{Ni}(\text{HL})_3^+$, NiL_2^+ , $\text{NiL}(\text{HL})_3^+$, and $\text{NiL}_2 + 2$ over the range of DMSO mole fractions of 0-0.68. The following factors in the stability of complexes were found: dehydration and steric repulsion of the ligands, a decrease in the donor ability of the coordinated hydrazine moiety upon protonation of the pyridine substituent L, the formation of an intracomplex hydrogen bond between the protonated and nonprotonated pyridine nitrogen atoms in $\text{NiL}(\text{HL})_3^+$, and stacking interaction between the heterocycles in $\text{NiL}_2 + 2$.
