

Complexation of Cobalt(II), Nickel(II), and Copper(II) Ions with Pyridine, 2-Methylpyridine, 3-Methylpyridine, and 4-Methylpyridine in Acetonitrile

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Thermodynamic data of the complexation of cobalt(II), nickel(II), and copper(II) ions with pyridine (py), 2-methylpyridine (2Me-py), 3-methylpyridine (3Me-py), and 4-methylpyridine (4Me-py) have been determined by calorimetry and spectrophotometry in acetonitrile (MeCN) containing 0.1 mol dm^{-3} $(\text{C}_2\text{H}_5)_4\text{NClO}_4$ as a constant ionic medium at 25°C . The calorimetric and spectrophotometric data for py, 3Me-py, and 4Me-py revealed the formation of $[\text{ML}]^{2+}$, $[\text{ML}_2]^{2+}$, $[\text{ML}_3]^{2+}$, and $[\text{ML}_4]^{2+}$ ($\text{M} = \text{Co}^{2+}$, Ni^{2+} , Cu^{2+} ; $\text{L} = \text{py}$, 3Me-py, 4Me-py). For 2Me-py, on the other hand, the formation of only one complex, $[\text{M}(2\text{Me-py})]^{2+}$ ($\text{M} = \text{Co}^{2+}$, Ni^{2+}), was detected. The stepwise thermodynamic quantities and the individual electronic spectra of the complexes suggest that all of these have a six-coordinate octahedral structure. The stability of the $[\text{M}(2\text{Me-py})]^{2+}$ ($\text{M} = \text{Co}^{2+}$, Ni^{2+}) complexes is much lower than that of the corresponding py, 3Me-py, and 4Me-py complexes. The difference in the stability of the 2Me-py complexes is mainly due to their unfavorable entropy changes because the differences of enthalpies for all the complexes are not so significant. The free energies for the formation of the mono complexes follow the order $\text{Mn(II)} > \text{Co(II)} > \text{Ni(II)} > \text{Cu(II)} < \text{Zn(II)}$ for the py, 3Me-py, and 4Me-py systems. The ΔH_1° values vary in the same order and the ΔS_1° values are similar. Hence, the stability difference of the mono complexes originates from the enthalpic term.