

# $^1\text{H}$ NMR Study of 4-Aminopyrimidine Coordinated to the Paramagnetic Undecatungstocobalto(II)silicate Anion: Rates of Internal Rotation of the Amine Group

Byung Ahn Kim and Hyunsoo So

Department of Chemistry, Sogang University, Seoul 121-742, Korea

$^1\text{H}$  NMR spectrum of a DMF- $d_7$  solution containing 4-aminopyrimidine and  $[\text{SiW}_{11}\text{Co}^{\text{II}}\text{O}_{39}]^{6-}$  ( $\text{SiW}_{11}\text{Co}$ ) shows separate peaks from two linkage isomers, **a** and **b**, in which N(1) and N(3) of the pyrimidine ring are coordinated to  $\text{SiW}_{11}\text{Co}$ , respectively. The amine group in the isomer **a** exhibits temperature-dependent line-shapes characteristic of a two-site exchange problem. Rates of internal rotation of the amine group were determined by simulating the NMR spectra at 5~35°C. The amine group of free 4-aminopyrimidine also shows temperature-dependent spectra at lower temperatures; rates of internal rotation at -25~25°C were determined. The internal rotation of the amine group in the complex is much slower than that for free 4-aminopyrimidine, indicating that  $\rho$ -character of the C-N bond increases on coordination to  $\text{SiW}_{11}\text{Co}$ . The amine group in the isomer **b** does not show such behavior. It is probable that hydrogen bonding between N-H and a bridging oxygen atom of  $\text{SiW}_{11}\text{Co}$  prevents it from rotating at low temperatures..