

¹H NMR Study of 4-Aminopyrimidine Coordinated to the Paramagnetic Undecatungstocobalto(II)silicate Anion: Rates of Internal Rotation of the Amine Group

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¹H NMR spectrum of a DMF-d₇ solution containing 4-aminopyrimidine and [SiW₁₁Co^{II}O₃₉]⁶⁻ (SiW₁₁Co) shows separate peaks from two linkage isomers, **a** and **b**, in which N(1) and N(3) of the pyrimidine ring are coordinated to SiW₁₁Co, respectively. The signal from the amine group in the isomer **a** exhibits temperature dependence that is 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 π -character of the C–N bond increases on coordination to SiW₁₁Co. 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 SiW₁₁Co prevents it from rotating at low temperatures.

Introduction

Structure and internal motions of the amine groups in aromatic compounds have been subjects of extensive studies, both experimental and theoretical.^{1,2} The amine group hydrogens are out of the aromatic plane by an amount which depends on a balance between π -electron delocalization across the C–N bond and the tendency of the amine group to form sp³ hybrid orbitals. Because of the pyramidalization the amine groups in aminobenzenes and aminopyrimidines can undergo inversion and internal rotation at relatively low temperatures. Calculated values of vibrational levels and barriers to amine group internal rotation and inversion for some aminobenzenes and aminopyrimidines were reported in two recent papers.^{1,2} Experimental values for the barriers in aniline were given, but no experimental data were presented for aminopyrimidines.

While studying ¹H NMR spectra of 4-aminopyrimidine coordinated to the paramagnetic polyoxometalate, [SiW₁₁Co^{II}O₃₉]⁶⁻ (SiW₁₁Co), in dimethylformamide-d₇ (DMF-d₇), we have observed that the amine group shows a temperature-dependent NMR signal that is characteristic of a two-site exchange problem. Rates of internal rotation of the amine group were determined by simulating the NMR spectra. Subsequent study has shown that the NMR signal from the amine group in free 4-aminopyrimidine is also split into two peaks at low temperatures. Rates of internal rotation at low temperatures were determined from this signal and compared with those from the complex.

Experimental Section

K₆[SiW₁₁Co(H₂O)O₃₉] · nH₂O was prepared according to the literature method³ and identified by its IR spectrum. 4-Aminopyrimidine was purchased from Aldrich. NMR samples were prepared by dissolving the polyoxometalate and a

ligand in a 1 : 1 molar ratio in DMF-d₇. The concentration was 10 mM for each of the polyoxometalate and the ligand.

¹H NMR spectra were obtained with a Varian Unity-INOVA (500 MHz) NMR spectrometer. NMR measurements were made at –55 °C to 40 °C. Tetramethylsilane (TMS) was used as an internal reference.

Results and Discussion

Free 4-Aminopyrimidine. The ¹H NMR spectrum of 4-aminopyrimidine in DMF-d₇ at room temperature consists of the following resonances:¹ 2-H 8.32 (s), 6-H 8.02 (d), NH₂ 6.80 (s), and 5-H 6.40 ppm (dd).⁴ The temperature dependence of the signal from the amine group is shown in Figure 1. The signal splits into two peaks below 0 °C, and each peak exhibits spin-spin splitting ($J = 2.1$ Hz) due to the other

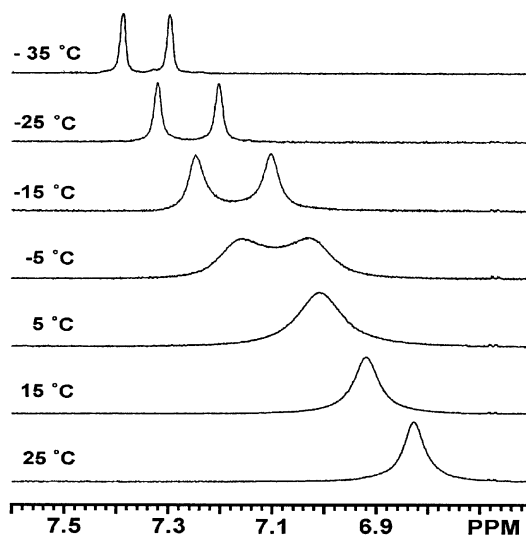


Figure 1. Temperature dependence of the ¹H NMR signal from the amine group of free 4-aminopyrimidine in DMF-d₇.

Table 1. Transition Probabilities (in Hz) for Internal Rotation of the Amine Group in 4-Aminopyrimidine

| Temp. (°C) | Free | SiW ₁₁ Co Complex | |
|---|------|------------------------------|------------------|
| | | Lower line-width | Upper line-width |
| -25 | 7 | | |
| -20 | 13 | | |
| -15 | 35 | | |
| -10 | 65 | | |
| -5 | 133 | | |
| 0 | 250 | | |
| 5 | 440 | 60 | - |
| 10 | - | 120 | 60 |
| 15 | 1050 | 200 | 160 |
| 20 | - | 400 | 350 |
| 25 | 1650 | 770 | 700 |
| 30 | | 1360 | 1300 |
| 35 | | 2360 | 2300 |
| ΔH^* (kJ mol ⁻¹) | | | |
| | | 79.9 | 95.8 |
| ΔS^* (J K ⁻¹ mol ⁻¹) | | | |
| | | 94.4 | 130.5 |

amine proton below -35 °C. It is noted that both chemical shifts and line shapes vary with temperature. The chemical shifts of the amino group are shifted upfield by 0.7 ppm as temperature increases from -55 °C to 25 °C, whereas the chemical shifts of the ring protons are temperature-independent.

Temperature-dependent line shapes were simulated using the modified Bloch equations.^{5,6} The half line-width in the absence of exchange was taken as 3.0 Hz from the spectrum at -45 °C.⁷ Accurate transition probabilities could be determined for the temperature range where the signal is split into two peaks. For the merged spectra at higher temperatures, separations of the two peaks in the absence of exchange must be estimated. Since the separation between the two peaks increases linearly with increasing temperature at -25 °C to -5 °C, the separations at higher temperatures estimated by extrapolation should be accurate. The resulting transition probabilities, *P*, between the two sites are listed in Table 1.

According to the transition state theory the Arrhenius equation can be expressed as⁸

$$P = \frac{kT}{h} \exp(\Delta S^*/R) \exp(-\Delta H^*/RT)$$

When values of $\ln(P/hkT)$ are plotted as a function of $1/T$, they fall on a straight line at -25 °C to 0 °C (Figure 2). The activation parameters determined from this temperature range are $\Delta H^* = 79.9$ kJ mol⁻¹ and $\Delta S^* = 94.4$ J K⁻¹ mol⁻¹.

SiW₁₁Co Complexes. The ¹H NMR spectrum of a DMF-d₇ solution containing 4-aminopyrimidine and SiW₁₁Co at room temperature is shown in Figure 3. The four resonances at 8.28, 7.97, 6.80, and 6.41 ppm originate from the free ligand (see above). The remaining spectrum consists of two sets of resonances, indicating that two linkage isomers, **a** and **b**, are formed.

All resonances were assigned by saturation transfer tech-

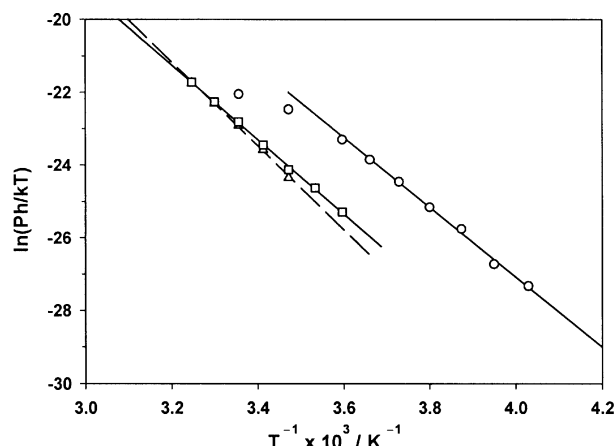


Figure 2. Least squares fits of $\ln(P/hkT)$ as a function of $1/T$ for free 4-aminopyrimidine and its SiW₁₁Co complex. Two straight lines were obtained for two sets of transition probabilities for the latter (see text). Symbols represent values determined by simulating the spectra: ○, free 4-aminopyrimidine; □, the complex with the lower limit of the line-width; Δ, the complex with the upper limit of the line-width.

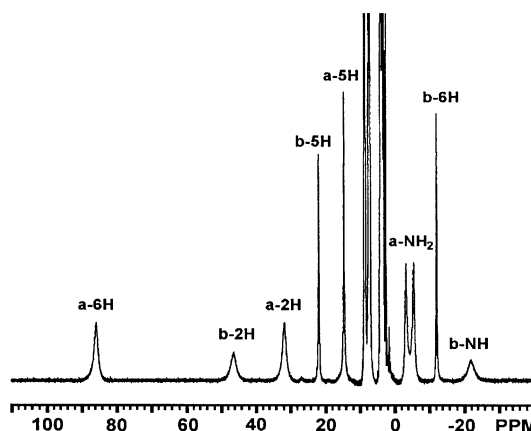
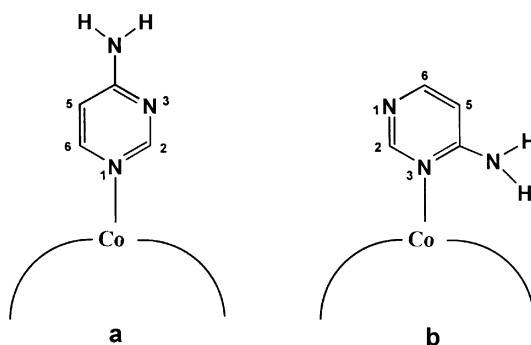


Figure 3. ¹H NMR spectrum of a DMF-d₇ solution containing 4-aminopyrimidine and [SiW₁₁Co(H₂O)O₃₉]⁶⁻ in a 1 : 1 molar ratio at 25 °C.



nique. The stronger set of resonances is attributed to the isomer **a**. The resonances at 85.7, 31.6, and 14.2 ppm originate from 6-H, 2-H, and 5-H, respectively. The two resonances at -3.70 and -5.87 come from the amine group. The weaker resonances at 46.2, 21.5, -12.5, and -22.3 ppm are assigned to 2-H, 5-H, 6-H, and one of the amine protons of the isomer **b**, respectively. Another signal originating from the other amine

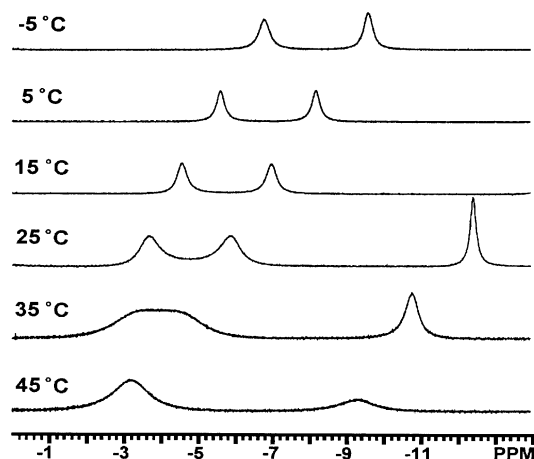


Figure 4. Temperature dependence of the ¹H NMR signal from the amine group of 4-aminopyrimidine coordinated to SiW₁₁Co in DMF-d₇. The signal at the high field is due to 6-H of the isomer **b**.

proton is probably hidden under the residual peak of DMF or HDO.⁹

The amine group in the isomer **a** exhibits two separate resonances at room temperature, which merge at 40 °C (Figure 4). Temperature-dependent line shapes of the signal from the amine group were simulated using the modified Bloch equations.^{5,6} The resulting transition probability between the two sites depends on the line-width in the absence of exchange, the upper and lower limits of which were estimated as follows. The minimum line-width of the amine group observed at 5 °C was taken as the upper limit. This choice of line-width assumes that no internal rotation occurs below this temperature. The line-widths at other temperatures were estimated by assuming that the temperature-dependent increment or decrement of the line-width is the same as that of 5-H (not shown in Figure 4). The lower limit was determined by decreasing the line-width gradually until the simulated spectrum deviates significantly from the measured spectrum at 5 °C. The line-widths at other temperatures were estimated as above. The lower limit was about 10 Hz smaller than the upper limit.

The resulting transition probabilities are listed in Table 1. It is noted that the transition probabilities for the lower limit of line-width are larger than the corresponding values for the upper limit by *ca.* 60 Hz. This agrees with the relation that the line-width increases by $P/2\pi$ for a slow exchange. Rates of internal rotation of the amine group in the complex decrease remarkably in the complex: for example, the transition probability at 5 °C is reduced from 440 to 60 Hz. This result suggests that the π -character of the C-N bond is increased on coordination of 4-aminopyrimidine to SiW₁₁Co. It seems that the π -d π interaction between the pyrimidine ring and the cobalt atom strengthens the C-N π -bond.

Activation parameters obtained by least squares fit of $\ln(\text{Ph}/kT)$ as a function of $1/T$ (Figure 2) are also listed in Table 1. It is noted that activation enthalpies for free 4-aminopyrimidine and the complex, especially the value for the lower limit of line-width, are very close, although their tran-

sition probabilities are quite different. However, the physical meaning of the activation enthalpies for this system is not clear; see below.

Barfield and Fagerness calculated inversion and internal rotation barriers (0.793 and 47.9 kJ mol⁻¹, respectively) for the amine group in 4-aminopyrimidine.¹ Since the inversion barrier is very small, our transition probabilities should be related with the internal rotation. The question arises how the activation enthalpy is related with the calculated energy barrier. A similar problem was encountered in interpreting the experimental rates of intramolecular electron transfer in a mixed-valence Cu(I)-Cu(II) system.¹⁰ It was shown that the activation energy (10.9 kJ mol⁻¹) from the Arrhenius equation is much smaller than the energy barrier (32.7 kJ mol⁻¹) obtained using the PKS model. When there are several vibrational levels below the energy barrier, the experimental transition probability is an average for these levels. As the vibrational quantum number increases, the transition probability increases rapidly although the population decreases. Therefore, contribution of excited vibrational levels to the average transition probability may be important. Since the Arrhenius equation can be derived from a model having a single energy level below the energy barrier, the barrier for a system having several vibrational levels must be much higher than the activation energy to produce the experimental transition probabilities.

The same argument may be applied to the internal rotation of the amine group. Since there are several vibrational levels below the energy barrier,¹ the barrier should be much larger than the activation energy.¹¹ The activation energies determined here are already much larger than the calculated energy barrier (83 *vs.* 47.9 kJ mol⁻¹). Therefore, the real energy barrier should be much higher than the calculated value. Theoretical work is needed to determine the energy barrier that agrees with the experimental transition probabilities.

Temperature dependence that is characteristic of a two-site exchange problem is not observed for the amine group in the isomer **b**. As was noted before,¹² 2-methylpyridine does not bind to SiW₁₁Co. If such complex were formed, one of the methyl protons should be within 2.3 Å from a bridging oxygen atom on SiW₁₁Co. This distance is much shorter than 2.6 Å suggested by Pauling for O...H van der Waals contact distance.¹³ On the other hand, 2-aminopyridine, 2-aminopyrimidine, and 4-aminopyrimidine {*via* N(3)} bind readily to SiW₁₁Co. When these ligands coordinate to SiW₁₁Co, the amine group may form a hydrogen bond with a bridging oxygen atom on SiW₁₁Co or it may be rotated to form a high-energy conformation in order to avoid the O...H contact. We have calculated the distances between the amine group and a bridging oxygen atom in the SiW₁₁Co complex, using the structural data for 2-aminopyridine¹ and a Co...N distance of 2.201 Å.¹⁴ The shortest distance between the amine nitrogen atom and a bridging oxygen atom on SiW₁₁Co is 2.8 Å and one of the protons is displaced 9° from the N...O vector. The structure being favorable for hydrogen bonding, it is quite likely that hydrogen bonding plays an

important role in complex formation between SiW_{11}Co and these ligands.

In summary, we have determined the transition probabilities for internal rotation of the amine group in both free 4-aminopyrimidine and its SiW_{11}Co complex. More work is needed to interpret the experimental transition probabilities in terms of a theoretical model.

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