¹H NMR Spectra of Some Amines Coordinated to the Paramagnetic Polyoxometalate, [SiW₁₁CoᴵᴵO₃₉]⁶⁻

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¹H NMR spectra of methyl-, ethyl-, propyl-, isopropyl-, butyl-, N-methylethyl-, N-methylpropyl-, and N-methylisopropylamine coordinated to the paramagnetic 11-tungstocobalto(II)silicate anion (SiW₁₁Co) in dimethylsulfoxide-d₆ or dimethylformamide-d- are reported. For these complexes the ligand exchange is slow on the NMR time scale and pure ¹H NMR signals have been observed at room temperature. No complex is detected in D₂O. From the pseudocontact shifts of the CH₂ and CH₃ groups in ethylamine the energy of the *gauche* conformers with respect to the *anti* conformer is estimated. Two diastereotopic protons in the CH₂ group of N-methylethylamine have quite different chemical shifts especially at low temperatures (e.g. -48.5 *vs.* 19.4 ppm at -10 °C). This may be attributed mainly to the different positions of the two protons in the most stable (gauche) conformer.

Introduction

The chemistry of heteropolyanions of tungsten and molybdenum continues to attract much attention, particularly with respect to potential catalytic activity, but also with respect to biological and medical applications.[1] We have studied NMR spectra of various ligands which coordinate to the paramagnetic polyoxometalates containing Co²⁺, Ni²⁺, Cu²⁺, etc.[2-6] Pyridine,[2] imidazole,[3] piperidine,[5] and aziridine[6] coordinate readily to SiW₁₁Co in D₂O, whereas acyclic amines do not. But we have found that acyclic amines bind to SiW₁₁Co in dimethylsulfoxide (DMSO) or dimethylformamide (DMF).

Only a few studies on acyclic amines coordinated to paramagnetic transition metal ions have been reported so far. ¹H NMR spectra of [Ni(bz)₆]²⁺ (bz = benzylamine) and ethylamine coordinated to bis(acetylacetonato)nickel(II) were reported.[7,8] Since these complexes exchange rapidly with free ligands, only a single averaged peak for each proton was observed. We have observed separate complexed and free ligand resonances for amines coordinated to SiW₁₁Co. We have also measured ¹H NMR spectra of some amines coordinated to 11-tungstonickelo(II)silicate anion (SiW₁₁Ni) in order to separate the isotropic shifts of the SiW₁₁Co complexes into contact and pseudocontact contributions. The pseudocontact shifts provide geometrical information about the conformations of the ligands. In addition, the NMR data on amines are useful in interpreting the NMR data of amino acids coordinated to [SiW₉Cu₃O₃₇]¹⁰⁻. This work will be published elsewhere.[9]

Experimental Section

Materials. All amines were used as supplied from Aldrich. Methylamine and ethylamine were supplied as concentrated aqueous solutions. The syntheses of K₆[SiW₁₁Co(H₂O)O₃₉]·nH₂O and K₆[SiW₁₁Ni(H₂O)O₃₉]·nH₂O were described before.[10,11] DMSO-d₆ or DMF-d₇ solutions were

prepared ~0.01 M in each of a ligand and a polyoxometalate.

Physical Measurements. ¹H NMR spectra were obtained with a Varian Unity-INOVA 500 spectrometer at ambient temperatures (22-25 °C). Tetramethylsilane (TMS) was used as an internal reference.

Results and Discussion

SiW₁₁Co Complexes. ¹H NMR spectra of several amines coordinated to SiW₁₁Co in DMSO-d₆ are shown in Figure 1. For these complexes the ligand exchange is slow on the NMR time scale and the pure signals of the free ligand and the complex appear separately at room temperature. The NMR spectrum of a DMSO-d₆ solution containing SiW₁₁Co and methylamine exhibits two peaks at 288.2 and 90.4 ppm from the complex along with the free ligand peaks (Figure 1a). The peak at 288.2 ppm disappears when a small amount of D₂O is added to the solution, indicating that the proton responsible for this peak is readily exchanged by deuteron. Therefore, this peak is attributed to the NH₂ group and the other peak to the CH₃ group.

The ¹H NMR spectrum of ethylamine coordinated to SiW₁₁Co consists of three peaks (Figure 1b). The broad peak at 291.9 ppm is assigned to the NH₂ group. The peaks at 47.3 and -7.1 ppm are assigned to the CH₂ and CH₃ groups, respectively, based on their relative intensities.

NMR signals of coordinated propylamine, N-methylethylamine, N-methylpropylamine, and N-methylisopropylamine were assigned similarly: Propylamine, NH₂ 289.4, α-CH₂ 25.0, β-CH₂ -20.0, CH₃ -12.5 ppm; N-methylethylamine, NH 251.3, N-CH₃ 69.1, N-CH₂ 39.3 and 30.8; N-C-CH₃ -24.0 ppm; N-methylpropylamine, N-CH₃ 74.7, N-CH₂ 24.6 and 14.1; N-C-CH₂ -32.4 and -34.3; N-C-C-CH₃ -12.1 ppm; N-methylisopropylamine, NH 250.1, N-CH₃ 71.1, N-CH 67.1; N-C-CH₃ -33.9 and -38.3 ppm. Chemical shifts for some other amines coordinated to SiW₁₁Co (not shown in Figure 1) are as follows: Isopropylamine, NH₂ 299.2, CH
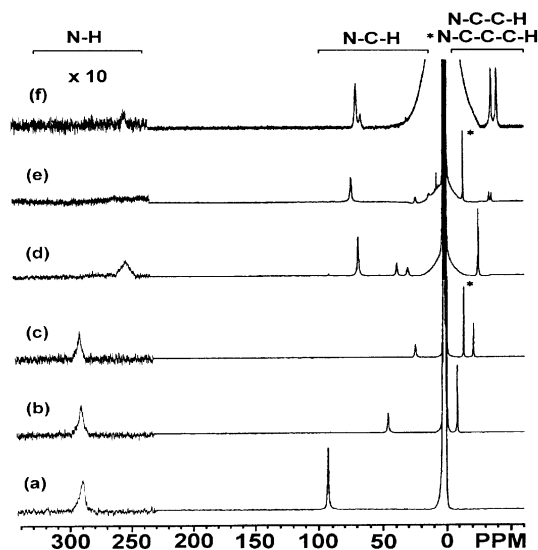
Figure 1. ^{1}H NMR spectra of DMSO-d$_6$ solutions containing [SiW$_{11}$CoO$_{39}$]$^{6-}$ and (a) methylamine, (b) ethylamine, (c) propylamine, (d) N-methylethylamine, (e) N-methylpropylamine, and (f) N-methylisopropylamine.

Figure 2. ^{1}H NMR spectra of DMSO-d$_6$ solutions containing [SiW$_{11}$NiO$_{39}$]$^{6-}$ and (a) methylamine and (b) ethylamine.

30.7, CH$_3$ -19.3 ppm; butylamine, NH$_2$ 292.8, α-CH$_2$ 20.9, β-CH$_2$ -19.3, γ-CH$_2$ -13.5, CH$_3$ -5.2 ppm. The peaks are shifted upfield until the number of chemical bonds between N and H increases to three, the ranges of chemical shifts being N-H 300-250, N-C-H 90-14, N-C-C-H (-7)–(-39) ppm. As the number of bonds increases further, the peaks are shifted downfield in propylamine and butylamine .

SiW$_{11}$Ni Complexes. The ^{1}H NMR spectra of the SiW$_{11}$Ni complexes also exhibit separate peaks for the coordinated and free ligands. However, their NMR peaks are broader than those of the SiW$_{11}$Co complexes, and the signals from the NH$_2$ groups are too broad to be observed. The ^{1}H NMR spectrum of a DMSO-d$_6$ solution containing SiW$_{11}$Ni and methylamine or ethylamine is shown in Figure 2. The CH$_3$ peak for methylamine appears at 129.1 ppm, and the peaks for the CH$_2$ and CH$_3$ groups in the ethylamine at 89.3 and 16.9 ppm, respectively. All peaks are shifted downfield from the corresponding peaks of the SiW$_{11}$Co complexes.
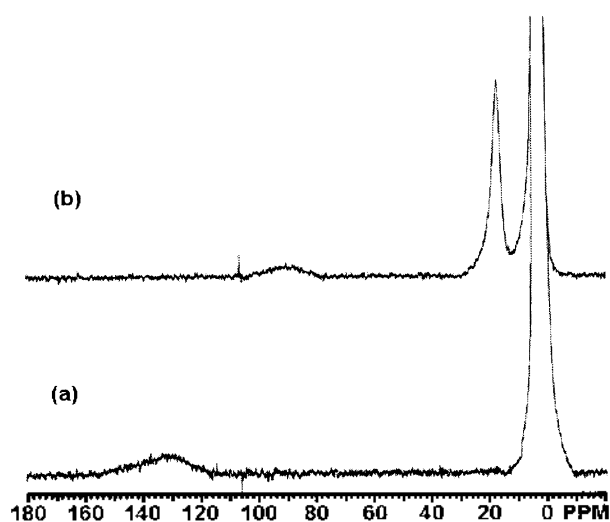
Contact and Pseudocontact Shifts. The isotropic NMR shift in paramagnetic systems, δ_{iso}, may be defined as the difference in the chemical shifts of the complex and the free ligand.

$$\delta_{iso} = \delta \text{(complex)} - \delta \text{(free ligand)}$$

The isotropic shifts contain contact and pseudocontact contributions.

$$\delta_{iso} = \delta_{con} + \delta_{dip}$$

Contact shifts, δ_{con}, occur when unpaired electron density is transferred from the metal to the ligand nucleus in question, whereas pseudocontact shifts, δ_{dip}, arise from a through-space dipolar interaction between the electronic and nuclear magnetic moments.

First we consider the nickel complexes. It has been shown that the pseudocontact contribution to isotropic shifts is small for octahedral nickel complexes.[12-14] The contact shifts occur from the transmission of π- and σ-type electrons. The Ni^{2+} ion in octahedral symmetry has two unpaired electrons in e_g orbitals that have σ symmetry. The contact interaction resulting from σ-electron delocalization is expected to cause a downfield shift of the NMR peak, and the shift will decrease as the number of chemical bonds between N and H increases. Shifts of all peaks are consistent with σ-electron delocalization. Although our complexes deviate considerably from octahedral symmetry, we may assume any pseudocontact shifts to be very small and neglect them.

The isotropic shifts for the cobalt complexes contain large pseudocontact shifts in addition to the contact shifts. The cobalt(II) ion in an octahedral complex has two unpaired electrons in e_g orbitals and one in a t_{2g} orbital. Since there is no π bonding between the ligand and the metal in the SiW$_{11}$Co complexes, the unpaired electron in the t_{2g} orbital may not be transmitted directly to the ligand. Horrocks has developed a semiquantitative method to separate the contact and pseudocontact shifts based on the assumption that the contact shifts of protons in a cobalt(II) complex are proportional to the corresponding isotropic shifts for a similar nickel complex, i.e., δ_{con}(Co) $= k \ \delta_{iso}$(Ni).[15] The proportionality constants, k, are 0.85 and 1.07 for quinuclidine and pyridine coordinated to SiW$_{11}$Co and SiW$_{11}$Ni in DMSO-d$_6$, respectively.[16]

Horrocks' method has been used mainly for rigid ligands. But it may also be applied to conformationally flexible amines coordinated to SiW$_{11}$Co and SiW$_{11}$Ni, for the conformers of the two complexes should have similar energies. The isotropic shifts for CH$_2$ and CH$_3$ groups in ethylamine coordinated to SiW$_{11}$Ni are 86.7 and 15.8 ppm at room temperature, respectively. Let us assume that the contact shifts in the SiW$_{11}$Co complex are the same as the corresponding isotropic shifts in the SiW$_{11}$Ni complex. Then the pseudo-

contact shifts of the CH_2 and CH_3 groups are -42.0 and -24.1 ppm, respectively. The relative pseudocontact shifts of the CH_2 and CH_3 groups can be calculated from the following staggered conformers.
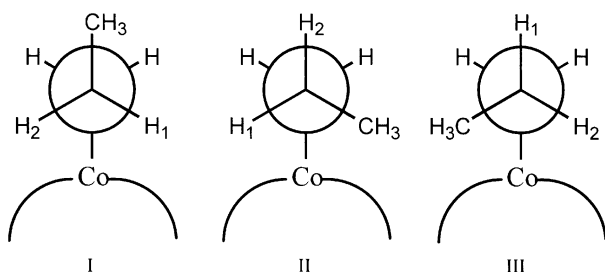
The *anti* conformer I is more stable than the *gauche* conformers II and III by $\Delta\varepsilon$. The pseudocontact shifts for the protons in the trans and gauche positions of the cobalt atom are designated by δ_t and δ_g, respectively. Then the population-weighted average pseudocontact shift for a proton in the CH_2 group is given by

$$\delta_{dip}\,(CH_2) = P_1\delta_g - P_2\delta_g + P_2\delta_t$$
$$= 0.5(\delta_g + \delta_t) - 0.5(\delta_g - \delta_t)/q$$

Here P_1 and P_2 are relative populations with $P_1 + 2P_2 = 1$, and $q = 1 + 2\exp(-\Delta\varepsilon/kT)$. If the ligand is rotating rapidly around the Co-N bond, the pseudocontact shift is proportional to the geometric factor, $(3\cos^2\theta-1)/r^3$. We calculated the geometric factors using the following bond lengths and angles: C-C 1.54, C-H 1.08, C-N 1.47, Co-N 2.187 Å[17] and all angles 109.5°. The calculated geometric factors for the trans and gauche protons are 0.02554 and 0.02151 Å^{-3}, respectively.

When the average pseudocontact shifts for the trans and gauche CH_3 groups are represented by δ_t' and δ_g', respectively, the average pseudocontact shift for a proton in CH_3 is given by

$$\delta_{dip}\,(CH_3) = P_1\delta_t' + 2P_2\delta_g'$$
$$= \delta_g' + (\delta_t' - \delta_g')/q$$

The average geometric factors for the protons in the trans and gauche CH_3 groups are 0.01446 and -0.005322 Å^{-3}, respectively. Now the ratio $\delta_{dip}(CH_2)/\delta_{dip}(CH_3)$ is a function of $\Delta\varepsilon$. The measured ratio $\delta_{dip}(CH_2)/\delta_{dip}(CH_3) = 1.75$ is obtained when $\Delta\varepsilon$ is 590 cm^{-1}.[18] This value is of the same order as the energy of the gauche form of butane, 280 cm^{-1} or 3.4 kJ mol^{-1}.[19]

Diastereotopic Groups. The signal originating from the CH_2 group in N-methylethylamine coordinated to $SiW_{11}Co$ is separated into two peaks (Figure 1d). The temperature dependence of these peaks is shown in Figure 3. Although the two diastereotopic protons may have different chemical shifts, the separation is much larger than those observed for diamagnetic molecules. As the temperature is raised, the two peaks approach each other, merging at 40 °C.

Again the observed isotropic shifts may be interpreted in terms of the following staggered conformers. Conformer I is assumed to be the most stable conformer, for the Co-N bond
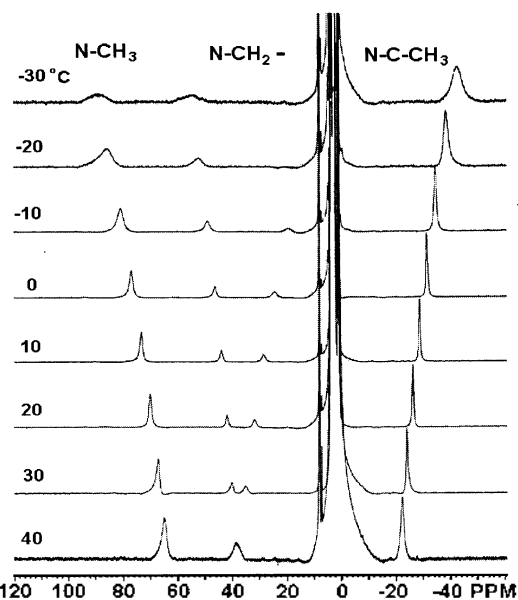
Figure 3. Temperature dependence of the ¹H NMR spectrum of N-methylethylamine coordinated to [SiW₁₁CoO₃₉]° in DMF-d₇. The peak for the NH₂ group is not shown.

is much longer than the N-C bond (2.187 vs. 1.47 Å).[17] In addition, choice of Conformer II as the most stable conformer produces unreasonable results. Energies of Conformers II and III are represented by $\Delta\varepsilon_2$ and $\Delta\varepsilon_3$, respectively. The isotropic shifts of the protons in the trans and gauche positions with respect to the cobalt atom are represented by $\delta_{iso}(t)$ and $\delta_{iso}(g)$, respectively.
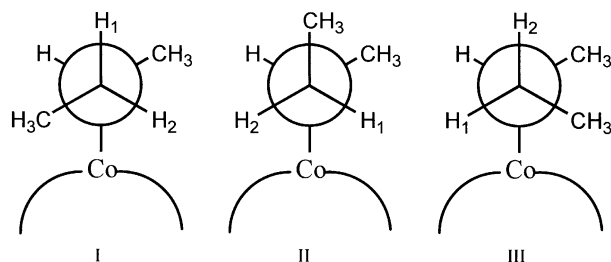
Now the observed isotropic shifts δ_1 and δ_2 may be expressed in terms of $\delta_{iso}(t)$ and $\delta_{iso}(g)$.

$$\delta_1 = P_1\,\delta_{iso}(t) + P_2\,\delta_{iso}(g) + P_3\,\delta_{iso}(g)$$
$$= \delta_{iso}(g) + P_1\,\{\delta_{iso}(t) - \delta_{iso}(g)\}$$
$$\delta_2 = P_1\,\delta_{iso}(g) - P_2\,\delta_{iso}(g) + P_3\,\delta_{iso}(t)$$
$$= \delta_{iso}(g) + P_3\,\{\delta_{iso}(t) - \delta_{iso}(g)\}$$

At low temperatures where $P_1 \approx 1$, δ_1 and δ_2 will be close to $\delta_{iso}(t)$ and $\delta_{iso}(g)$, respectively. It was shown that the contact shift for the trans proton is much larger than that of the gauche proton.[20] Since the pseudocontact shifts for these protons are comparable (see above), the low-field peak must be designated as δ_1. Since temperature dependence for the cobalt complex is difficult to determine,[21] we have not attempted to calculate δ_1 and δ_2. Instead, we may estimate $\delta_{iso}(g)$ and $\delta_{iso}(t)$ from the measured values of δ_1 and δ_2 using the following expressions.
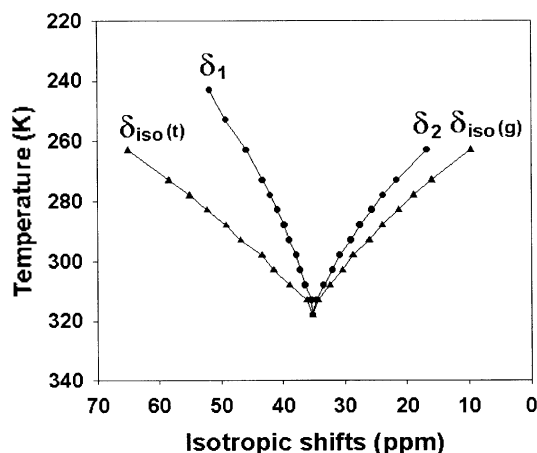
Figure 4. Estimated temperature dependence of $\delta_{iso}(g)$ and $\delta_{iso}(t)$ for the CH_2 group in N-methylethylamine coordinated to $[SiW_{11}CoO_{39}]^{6-}$ in DMF-d7.

$$\delta_{iso}(g) = \frac{P_1\delta_2 - P_3\delta_1}{P_1 - P_3}$$

$$\delta_{iso}(t) - \frac{\delta_1 - \delta_2}{P_1 - P_3} + \delta_{iso}(g)$$

The gauche conformer of butane is more stable than the anti conformer by 280 cm^{-1}. Assuming that there is some repulsive interaction between the CH_3 group and the polyoxometalate in Conformer I, we estimate that $\Delta\varepsilon_2$ is about 200 cm^{-1}. Energy of Conformer III should be similar to that of the gauche conformer of butane. Thus, using $\Delta\varepsilon_2 - 200$ and $\Delta\varepsilon_3 - 300$ cm^{-1}, we have calculated $\delta_{iso}(g)$ and $\delta_{iso}(t)$ as a function of temperature. The result is shown in Figure 4.

The isotropic shifts contain contact and pseudocontact contributions. Contact shifts are positive and are proportional to $1/T$.[22] Therefore, the contact contribution decreases with increasing temperature. The isotropic shift for the N-C-CH_3 is negative, indicating that the pseudocontact contribution is negative. Since the geometric factors for N-CH_3 and the trans and gauche protons in the N-CH_2 group have the same sign as that of N-C-CH_3, the pseudocontact shifts for all protons must be negative. Although it is not possible to express the temperature dependence of the pseudocontact shifts in a simple analytic form for the cobalt complexes,[21] they should increase with increasing temperature as for the N-C-CH_3 group. Therefore, the isotropic shifts can either increase or decrease with increasing temperature depending upon which component dominates. $\delta_{iso}(t)$ decreases with increasing temperature, indicating that the contact shift is dominant. On the other hand, $\delta_{iso}(g)$ increases with increasing temperature, indicating that the pseudocontact shift is dominant.

Two diastereotopic protons in the N-CH_2 group in N-methylpropylamine and two diastereotopic CH_3 groups in N-methylisopropylamine also have different chemical shifts (Figures 1e-f). One interesting observation is that two pro-

tons of the β-CH_2 group in N-methylpropylamine, which are not diastereotopic, have slightly different chemical shifts. The reason for this separation is not clearly understood.

To summarize, we have observed ^1H NMR spectra of various acyclic amines coordinated to $SiW_{11}Co$ in DMSO-d6 or DMF-d7. The isotropic shifts for some protons can be interpreted as population-weighted averages for the staggered conformers. The diasteretopic groups in amines coordinated to $SiW_{11}Co$ have very different chemical shifts because they occupy trans and gauche positions in the most stable conformers. More work is needed to extract quantitative information about the conformers from the NMR data.

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