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^{1}H NMR Study of Pyridine-Type Ligands Coordinated to the Paramagnetic $[Ni_3(PW_9O_{34})_2]^{12-}$ Anion

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^{1}H NMR spectra of pyridine, α-, β-, and γ-picoline coordinated to the paramagnetic heteropolyanion $[Ni_3(PW_9O_{34})_2]^{12-}$ (P_2Ni_3) are reported. NMR lines are assigned to $[Ni_3(ptl)_n(PW_9O_{34})_2]^{12-}$ ($n=1$, 2 or 3; ptl=pyridine-type ligand) on the basis of their $[P_2Ni_3]/[ptl]$ dependence. The formation constants for γ-picoline complexes at 25 ℃ are $K_1=80$, $K_2=610$, and $K_3=190$ L mol^{-1}. The monopicoline complex has greater affinity for γ-picoline than P_2Ni_3. A degradation product, $[Ni_2(WO_2)(PW_9O_{34})_2]^{12-}$, was also identified at low pH by measuring the NMR spectrum of pyridine coordinated to it. The isotropic NMR shifts come mainly from the contact interaction due to σ-electron delocalization.

Introduction

The chemistry of heteropolyanions of tungsten and molybdenum continues to attract much attention, particularly with respect to potential catalytic activity.[1] It is desirable to find methods which can be used to monitor interactions between substrates and heteropolyanions. Recently we have shown that interactions of pyridine- and imidazole-type ligands with paramagnetic heteropolyanions such as $[SiW_{11}O_{39}M]^{6-}$ (M $=Co^{2+}$ or Ni^{2+}; hereafter denoted as $SiW_{11}M$) can be studied by NMR spectroscopy.[2,3] These ligands coordinated to SiW_{11}-M undergo slow exchange on the NMR time scale, exhibiting NMR lines separated from those of free ligands. The slow exchange allowed us to measure the absolute isotropic NMR shifts directly.

More recently we have found that NMR spectroscopy can be used to study interactions of pyridine-type ligands with $[SiW_9O_{37}\{Cu(H_2O)\}_3]^{10-}$, which has $[\{Cu(OH_2)\}_3O_3]$ as a portion of the molecular surface.[4] NMR spectra cannot be observed for ordinary copper(II) complexes in which the electronic relaxation is slow. The electronic relaxation time in $[SiW_9O_{37}Cu_3(ptl)_n]^{10-}$ is reduced by two orders of magnitude because of spin frustration, and good NMR spectra with large isotropic shifts were observed. NMR lines were assigned to $[H_mSiW_9O_{37}Cu_3(ptl)_n]^{(10-m)-}$ ($n=1$, 2 or 3; $m=0$, 1 or 2). Identification of various species having different numbers of ligands and different degrees of protonation suggests that NMR spectroscopy may be useful in studying multisite or cooperative binding of substrates at some heteropolyanions.

We have extended our NMR studies to ligands coordinated to $[Ni_3(PW_9O_{34})_2]^{12-}$ (hereafter denoted as P_2Ni_3), which has the same structure as the copper(II) analogue.[5] Three Ni^{2+} ions are sandwiched between two $[PW_9O_{34}]^{9-}$ groups, and each Ni^{2+} ion is in a square pyramidal environment with an aqua ligand at an axial position (Figure 1). Good NMR spectra with large isotropic shifts have been observed. This paper reports the ^{1}H NMR spectra of pyridine, α-, β-, and γ-picoline coordinated to P_2Ni_3.

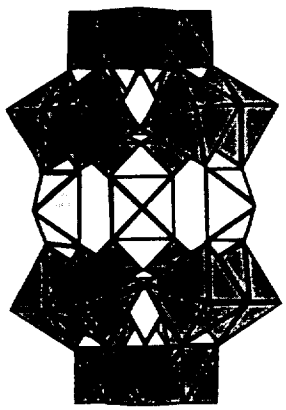


Figure 1. Polyhedral representation of $[Ni_3(PW_9O_{34})_2]^{12-}$. Octahedra represent WO_6 groups, and three square pyramids at the belt represent $Ni(H_2O)O_4$ groups.

Experimental

$K_{12}[Ni_3(PW_9O_{34})_2]\cdot nH_2O$ (**1**) and $K_{12}[Ni_2(WO_2)(PW_9O_{34})_2]\cdot nH_2O$ (**2**) were synthesized according to the methods in the literature.[5] The IR spectrum of **1** was similar to that of the cobalt analogue,[6] as was pointed out by Knoth *et al.*[5] The IR spectrum of **2** was more complex than that of **1** in agreement with the IR spectral data of the cobalt analogue.[5]

^{1}H NMR spectra were obtained with Varian Gemini-300 and -200 spectrometers at ambient temperatures (22-25 ℃). The residual water resonance in each spectrum was saturated by irradiating with a single frequency pulse which was

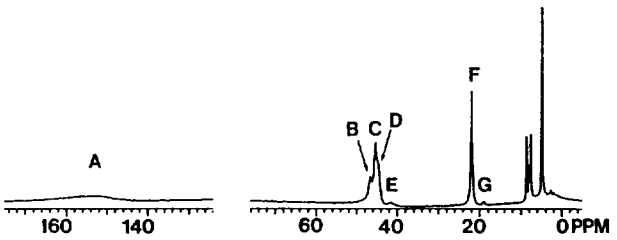


Figure 2. The ^{1}H NMR spectrum of a D_2O solution containing $[Ni_3(PW_9O_{34})_2]^{12-}$ and pyridine in the mole ratio of 1 at pH 7.5.

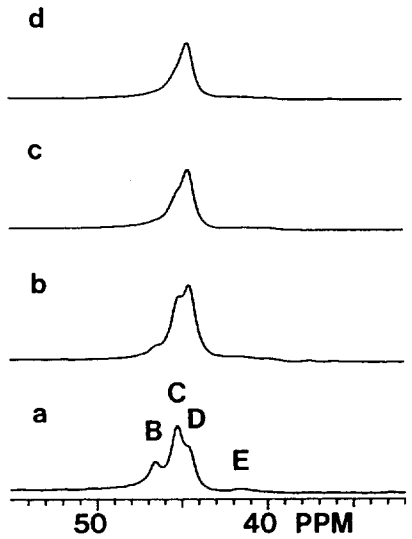


Figure 3. β-H lines in ^{1}H NMR spectra of D_2O solutions containing $[Ni_3(PW_9O_{34})_2]^{12-}$ and pyridine in the mole ratio of (a) 1, (b) 1/2, (c) 1/3, and (d) 1/4.

gated off during acquisition. Sodium salt of 3-(trimethylsilyl) propionic-2,2,3,3-d_4 acid (TSP) was used as an internal reference. The pH of solutions was adjusted by adding small amounts of D_2O solutions of H_2SO_4 or NaOD. The pH values of D_2O solutions are given as uncorrected pH meter readings. Infrared spectra were recorded on a Mattson FT IR spectrometer (Galaxy 2000).

Results and Discussion

Pyridine Complexes. The ^{1}H NMR spectrum of a D_2O solution containing P_2Ni_3 and pyridine (py) consists of three groups of lines ascribable to the pyridine complexes (Figure 2). By comparing with the spectrum of α-, β- or γ-picoline coordinated to P_2Ni_3, the three groups at ~154, 47-41, and 22-18 ppm are assigned to α-H, β-H, and γ-H in the coordinated pyridine, respectively. The lines at 7-9 ppm originate from the free ligand, and the line at 4.7 ppm from HDO.

The lines are designated by A-G, and their chemical shifts are listed in Table 1. The lines originating from β-H are best-resolved, consisting of B, C, D, and E. When the ratio $[P_2Ni_3]/[py]$ was reduced, the relative intensity of B decreased and that of D increased (Figure 3). Thus B, C, and D may be ascribed to mono-, di-, and tripyridine complexes, respectively. (Formation constants have been determined for

Table 1. Assignment of NMR Lines

Signal	Chemical shift (ppm) Pyridine	γ-Picoline	Intensity[a]	Assignment[b]
				[α-H]
A	~154	~150		1p, 2p, 3p
				[β-H]
B	46.7	45.0		1p
C	45.4	43.6		2p
D	44.6	42.7		3p
E	41.6	40.0		1Hp, 2Hp, 3Hp
				[γ-H]
F	21.8			1p, 2p, 3p
G	18.8			1Hp, 2Hp, 3Hp
				[γ-CH_3]
H		−6.5	2.0	1Hp
I		−6.9	2.4	2Hp
J		−7.7	5.0	3Hp
K		−9.0	28.5	3p
L		−9.7	37.4	2p
M		−10.9	11.6	1p

[a] Percentage of the intensity in the γ-CH_3 group for $[P_2Ni_3]=[\gamma\text{-picoline}]=2.0\times10^{-2}$ mol L^{-1}. The intensity of the free γ-picoline is 13.1. [b] 1p, 2p, and 3p represent mono-, di-, and triligand complexes, respectively, and 1Hp, 2Hp, and 3Hp mono-, di-, and tri-ligand, monoprotonated complexes, respectively.

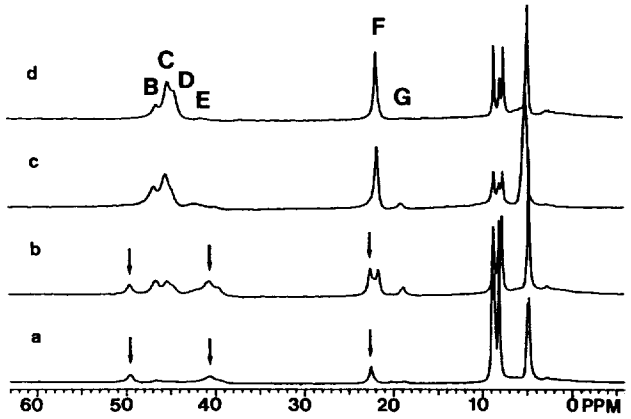


Figure 4. ^{1}H NMR spectra of D_2O solutions containing $[Ni_3(PW_9O_{34})_2]^{12-}$ and pyridine in the mole ratio of 1 at pH (a) 4.1, (b) 5.0, (c) 6.2, and (d) 8.7. A broad line at ~150 ppm originating from α-H is not shown; see Figure 1. The lines designated by arrows come from $[Ni_2(WO_2)(PW_9O_{34})_2]^{12-}$ (Figure 5).

corresponding γ-picoline complexes; see below.)

Shown in Figure 4 are NMR spectra for $[P_2Ni_3]/[py]=1$ at different pH's. The spectra show that the heteropolyanion is stable at pH 6.0-8.7. The spectra below pH 6.0 contain additional lines, which may be ascribed to a degradation product (see below). When pH was decreased, the relative intensity of E and G increased, indicating that more than one species with different degrees of protonation were involved in complex formation at pH 6-8.7.

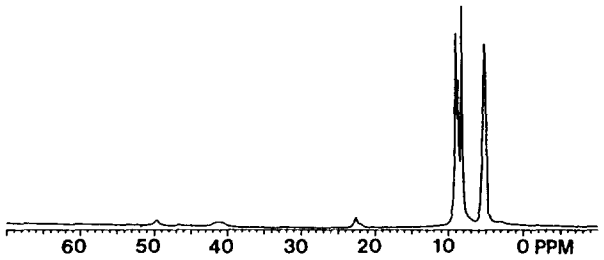


Figure 5. ^{1}H NMR spectra of D_2O solutions containing $[Ni_2(WO_2)(PW_9O_{34})_2]^{12-}$ and pyridine in the mole ratio of 1 at pH 4.2. A broad line at ~150 ppm originating from α-H is not shown.

The question arises as to which oxygen atoms are protonated. Terminal and bridging oxygen atoms are potential sites for protonation. The protonation behavior of polyvanadates and vanadotungstates suggested that the bridging oxygen atoms are more basic than the terminal oxygen atoms.[7-9] There are two types of bridging oxygen atoms in P_2Ni_3: those between two tungsten atoms, and those between one tungsten atom and one nickel atom. Since the bridging oxygen atoms between a WO^{4+} group and a Ni^{2+} ion have more negative charges than those between two WO^{4+} groups,[11] they must be protonated preferentially.

The potassium salt recrystallized from an aqueous solution contains the unprotonated anion, indicating that it is the major species at pH 6-8.7. The minor species then must be the monoprotonated species. So the two weak lines E and G may be assigned to the monoprotonated species and the others to the unprotonated species.

The NMR spectrum at pH 5 exhibits additional lines indicating that the heteropolyanion has degraded. It was shown that $[Ni_2(WO_2)(PW_9O_{34})_2]^{12-}$ (P_2Ni_2) was formed at pH 4-5.[5] The additional lines at 50, 40-41 and 22.5 ppm agree with those of pyridine coordinated to P_2Ni_2 (Figure 5). However, P_2Ni_2 is unstable in an aqueous solution and converts to a Keggin anion, $[PW_{11}O_{39}Ni]^{5-}$, within two hours at room temperature. The final product was identified by the NMR spectrum of pyridine coordinated to it and by the IR spectrum of its potassium salt.[10] A similar transformation was reported for the zinc analogue.[5]

Picoline Complexes. The ^{1}H NMR spectrum of a D_2O solution containing P_2Ni_3 and γ-picoline (pic) is quite similar to that of the pyridine complex except that the γ-H lines are replaced by the γ-CH_3 lines (designated by H-M) appearing at (−6)-(−12) ppm; see Figure 6c. Three weak lines H, I, and J may be assigned to γ-CH_3 of the monoprotonated species. γ-CH_3 lines have been assigned to mono-, di-, and tripicoline complexes on the basis of $[P_2Ni_3]/[pic]$ dependence (Table 1).

As the γ-CH_3 lines for various species were well-resolved, the following formation constants at 25 ℃ were determined from their intensities.

$$K_i=\frac{[P_2Ni_3(py)_i]}{[P_2Ni_3(py)_{i-1}][py]}\ (i=1,\ 2,\ \text{or}\ 3) \qquad (1)$$

$K_1=80,\ K_2=610,\ K_3=190$ L mol^{-1}

The value of K_2 is eight times as large as that of K_1, indicating that the monopicoline complex has much greater affinity for γ-picoline than P_2Ni_3. It is often found with biological oligomeric macromolecules that the binding of one substrate molecule at one site enhances the binding of subsequent molecules at the other sites. This so-called allosteric effect is ascribed to conformational change, and an inorganic example has also been reported.[12] But the behavior of P_2Ni_3 toward pyridine-type ligands is difficult to explain in terms of conformational change. More work is needed to understand this effect for P_2Ni_3.

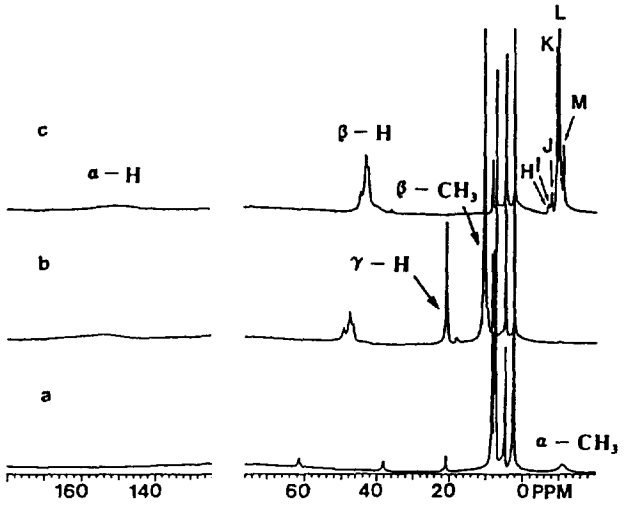


Figure 6. ^{1}H NMR spectra of D_2O solutions containing $[Ni_3(PW_9O_{34})_2]^{12-}$ and (a) α-picoline, (b) β-picoline, and (c) γ-picoline in the mole ratio of 1.

The ^{1}H NMR spectrum of a D_2O solution containing P_2Ni_3 and β-picoline is shown in Figure 6b. The ^{1}H NMR spectrum of a D_2O solution containing P_2Ni_3 and α-picoline shows only one set of lines, which may be attributed to the species with one coordinated α-picoline (Figure 6a). Species with more than one coordinated α-picoline is not formed. The two lines at 62 and 38 ppm are assigned to the two inequivalent β-H's. The formation constant at 25 ℃ for the α-picoline complex, $K=7.7$ L mol^{-1}, is much smaller than K_1 of the γ-picoline complex. The small K value may be ascribed to the steric hindrance due to the α-CH_3 group.

Contact Interaction. The isotropic NMR shifts (δ_{iso}) in paramagnetic systems contain contact and pseudocontact contributions. 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.

The pseudocontact shift for a given nucleus i in an axial system can be expressed as[13]

$$\delta_{dip}=\frac{\mu_0}{4\pi}\times\frac{\mu_B^2S(S+1)}{9kT}\times\frac{(3\cos^2\theta_i-1)}{r_i^3}\times(g_{\parallel}^2-g_{\perp}^2) \qquad (2)$$

where θ_i is the angle between the principal axis of the complex and the radius vector from the metal ion to the nucleus, i; r_i is the distance between the metal ion and the nucleus, i.

It was shown that the pseudocontact contribution to isotro-

Table 2. Comparison of Isotropic NMR Shifts in $[Ni_3(ptl)(PW_9O_{34})_2]^{12-}$ and Hyperfine Coupling Constants in Phenyl, and *o*-, *m*-, and *p*-Tolyl Radicals

Proton	δ_{iso} (ppm)	A_i (Gauss)	δ_{iso}/A_i
α-H[a]	145	17.4[b]	8.3
β-H[a]	39.1	6.3[b]	6.2
γ-H[a]	13.7	2.0[b]	6.9
α-CH_3[c]	−13.0	−1.9[d]	6.8
β-CH_3[c]	8.0	1.6[d]	5.0
γ-CH_3[c]	−13.6	−1.2[d]	11.3

[a]The data for the pyridine complex. [b]Experimental data from ref 17. [c]The data for the picoline complexes. [d]INDO/2 calculation data from ref 16.

pic shifts is small for $Ni(acac)_2(ptl)_2$.[13~15] For an octahedral Ni(II) complex, which has an orbitally non-degenerate $^3A_{2g}$ ground state with excited states far removed in energy, the orbital contribution is small and so is the magnetic anisotropy. Although the Ni^{2+} ion in P_2Ni_3 is in a square pyramidal environment, the magnetic anisotropy and thus the δ_{dip} values are expected to be small.

The Ni^{2+} ion in a square pyramidal environment has one unpaired electron each in $3d_{x^2-y^2}$ and $3d_{z^2}$ orbitals. It is most likely that the unpaired electron density is transferred from the $3d_{z^2}$ orbital to a σ molecular orbital of the ligand. Horrocks and Johnston have shown that σ-electron delocalization in pyridine derivatives coordinated to $Ni(acac)_2$ closely parallel the hyperfine coupling constants in σ species such as phenyl, and *o*-, *m*-, and *p*-tolyl radicals.[16] Experimental hyperfine coupling constants for phenyl radical observed in an EPR experiment[17] and INDO/2 calculation data for other radicals are listed in Table 2 along with the isotropic shifts in the monoligand complexes $[Ni_3(ptl)(PW_9O_{34})_2]^{12-}$. The sign of the isotropic shift is predicted correctly for all six protons. The ratios δ_{iso}/A_i for α-, β-, and γ-H are quite close, falling in the range 6.2-8.3. (If the isotropic shifts are determined by σ-electron delocalization alone, ideally a single ratio should be obtained.) The ratios for, α-, β-, and γ-CH_3 fall in a wider range, 5.0-11.3. However, it should be pointed out that the calculated hyperfine coupling constants deviate considerably from the experimental values. For example, the calculated value for γ-H is much larger than the measured value (3.9 *vs.* 2.0 G). Especially when A_i values are as small as those for the CH_3 groups, a small error in A_i can alter the ratio considerably.[18]

In summary, pyridine-type ligands coordinated to paramagnetic $[Ni_3H_m(PW_9O_{34})_2]^{(12-m)-}$ have been found to exhibit good ^1H NMR spectra, and several species with different numbers of coordinated ligands and different degrees of protonation have been identified. NMR techniques may be useful in studying interactions of other (more interesting) substrates with the same heteropolyanion.

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18. Another explanation for deviation of δ_{iso}/A_i from a single value may be that a small amount of π-electron delocalization also contributes to the isotropic shifts. Although there is no unpaired electron in $3d_{xz}$ or $3d_{yz}$ orbital of the Ni^{2+} ion, unpaired electron density can delocalize into the π molecular orbital of the ligand by spin polarization due to the unpaired electrons in $3d_{x^2-y^2}$ and $3d_{z^2}$ orbitals. However, a set of parameters that can explain the isotropic shifts of all six protons has not been found.