Trimetallo Derivatives of Lacunary 9-Tungstosilicate Heteropolyanions. 2. Isotropic NMR Shifts in Pyridine-Type Ligands Coordinated to the Paramagnetic 9-Tungsto-3-cuprio(II)silicate Anion

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Abstract: ^{1}H NMR spectra of pyridine and α-, β-, and γ-picoline coordinated to the paramagnetic heteropolyanion $[H_mSiW_9O_{37}Cu_3]^{(10-m)-}$ (SiW_9Cu_3) are reported. NMR lines are assigned to $[H_mSiW_9O_{37}Cu_3(ptl)_n]^{(10-m)-}$ ($n = 1$, 2 or 3; $m = 0$, 1 or 2; ptl = pyridine-type ligands) on the basis of their pH and $[SiW_9Cu_3]/[ptl]$ dependence. The isotropic NMR shifts come mainly from the contact shifts, which for some protons exceed 70% of those in analogous nickel complexes. The nuclear longitudinal relaxation times are 0.006, 0.06, and 0.1 s for α-, β-, and γ-H in pyridine coordinated to SiW_9Cu_3. The electronic correlation time calculated from the T_1 values is in the order of 10^{-11} or 10^{-12} s, which is two or three orders of magnitude smaller than those of ordinary copper complexes. It is suggested that spin frustration causes rapid electronic relaxation in these complexes in which the three Cu^{2+} ions form an equilateral triangle.

The chemistry of heteropolyanions of tungsten and molybdenum continues to attract much attention, particularly with respect to potential catalytic activity.[1] Recently we have reported trimetallo derivatives of 9-tungstosilicate heteropolyanions, $[SiW_9O_{37}M_3(H_2O)_3]^{n-}$ (M = Al, Ga, Cr^{III}, Fe^{III}, Mn^{II}, Co^{II}, Ni^{II}, or Cu^{II}).[2] These complexes, having $[\{M(OH_2)\}_3O_3]$ as a portion of the molecular surface (Figure 1), can be expected to model features of metal oxide surfaces such as multisite or cooperative binding and activation of ligand substrates.

While studying these complexes, we have noticed that α- and β-$[SiW_9O_{37}Cu_3(H_2O)_3]^{10-}$ (hereafter denoted as SiW_9Cu_3) exhibit no EPR signal at room temperature, indicating that the unpaired electron spins relax rapidly. This unexpected phenomenon prompted us to measure ^{1}H NMR spectra of pyridine-type ligands (ptl) coordinated to $[H_mSiW_9O_{37}Cu_3]^{(10-m)-}$. Good NMR spectra with large isotropic shifts have been observed.

The NMR spectra of paramagnetic transition metal complexes have been extensively studied.[3] Most NMR studies have been carried out on complexes of lanthanides, low spin Fe(III), high spin Co(II), and Ni(II) which have short electronic relaxation times. We have studied NMR spectra of pyridine- and imidazole-type ligands coordinated to $[SiW_{11}O_{39}M]^{6-}$ (M = Co^{2+} or Ni^{2+}).[4,5] So far NMR spectra have been observed for Cu(II) complexes only when the Cu^{2+} ion is coupled with a fast relaxing metal ion.[6,7] SiW_9Cu_3 is a different type of complex in which the electron spins relax fast because of geometrical arrangement of the three Cu^{2+} ions. The rapid electronic relaxation in this complex opens up the possibility of using NMR as a very sensitive probe to study interactions of various ligands with $[\{Cu(OH_2)\}_3O_3]$. This paper reports the ^{1}H NMR spectra of pyridine and α-, β-, and γ-picoline coordinated to $[H_mSiW_9O_{37}Cu_3]^{(10-m)-}$.

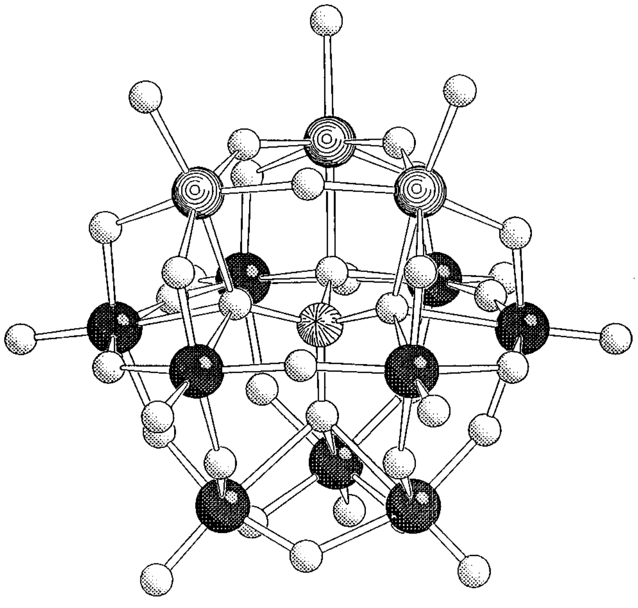

Figure 1. Presumed structure of β-$[SiW_9O_{37}\{Cu(H_2O)\}_3]^{10-}$. Large filled circles, W; large shaded circles, Cu; small shaded circles, O.

Experimental Section

The syntheses of potassium salts of α- and β-$[SiW_9O_{37}Cu_3(H_2O)_3]^{10-}$ were described before.[2] Pyridine-type ligands coordinated to α- and β-$[SiW_9O_{37}Cu_3(H_2O)_3]^{10-}$ exhibited essentially the same ^{1}H NMR spectra. So most NMR studies were performed using the more soluble

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[1] Pope, M. T.; Müller, A. *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 34−48.

[2] Liu, J.; Ortega, F.; Sethuraman P.; Katsoulis, D. E.; Costello, C. E.; Pope, M. T. *J. Chem. Soc., Dalton Trans.* **1992**, 1901−1906.

[3] Bertini, I.; Luchinat, C. *NMR of Paramagnetic Molecules in Biological Systems*; Benjamin/Cummings: Menlo Park, CA, 1986.

[4] Ko, M.; Rhyu, G. I.; So, H. *Bull. Korean Chem. Soc.* **1993**, *14*, 500−506.

[5] Ko, M.; Rhyu, G. I.; So, H. *Bull. Korean Chem. Soc.* **1994**, *15*, 673−679.

[6] Benelli, C.; Dei, A.; Gatteschi, D. *Inorg. Chem.* **1982**, *21*, 1284−1286.

[7] Bertini, I.; Lanini, G.; Luchinat, C.; Messori, L.; Monnanni, R.; Scozzafa, A. *J. Am. Chem. Soc.* **1985**, *107*, 4391−4396.

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Table 1. Assignment of NMR Lines

signal	chemical shift (ppm)	intensity[a]	assignment[b]
		[α-H]	
A	124.2	28	3py
B	122.4	4	
C	121.4	15	2py
D	115.4		1py (II2)
E	113.8	8	1py (II1)
F, G	112.2, 111.8	30	1py (00 + I0)
H	110.6	15	1py (I1)
		[β-H]	
I, J	47.7, 47.3	25	3py
K	44.5	10	
L (3 lines)	39.5	16	2py
M	37.6	5	1py (II1)
N (2 lines)	36.7	44	1py (00 + I0 + I1)
		[γ-H]	
O	18.0	6	
P	17.3	26	3py
Q	16.3	28	2py + 1py (I1)
R	16.0	14	1py (I0)
S	15.5	10	2py + 1py (II1)
T	14.8	16	1py (00)

[a] Percentage of the intensity in each group of α-, β-, and γ-H. [b] 1py, 2py, and 3py represent mono-, di-, and tripyridine complexes, respectively. The symbols such as II1 are described in the text.

β form. 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.

Most ^1H NMR spectra were obtained with a Varian Gemini-300 spectrometer at ambient temperatures (22−25 °C). The residual water resonance in each spectrum was saturated by irradiating with a single frequency pulse which was 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 spin−lattice relaxation times were measured for pyridine coordinated to SiW_9Cu_3 by using the inversion recovery method.[8,9] Values of T_1 were obtained by a three-parameter least-squares analysis of the signal intensity versus recovery time measurements.[9]

The magnetic susceptibility measurements at 5−300 K were performed using a SQUID magnetometer.

Results and Discussion

NMR Spectra. ^1H NMR spectra of D_2O solutions containing SiW_9Cu_3 and pyridine (py), α-, β-, or γ-picoline have been measured. The spectra for the pyridine complexes will be described in detail. Each spectrum 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 SiW_9Cu_3, the three groups at 126−110, 50−36, and 20−14 ppm are assigned to α-H, β-H, and γ-H in the coordinated pyridine, respectively. The broad line at 6−10 ppm originates from the free ligand, and the sharp line at 4.7 ppm from HDO.

The best resolved spectrum was observed for $[SiW_9Cu_3]/[py] = 1/2$ at pH 8.1. The lines are designated by A − T, and their chemical shifts and relative intensities are listed in Table 1. When the ratio $[SiW_9Cu_3]/[py]$ was reduced, the relative intensities of D − H, M, N, R, and T decreased (Figure 2). These lines may be assigned to monopyridine complexes and others to species having more than one coordinated pyridine.

Shown in Figure 3 are NMR spectra for $[SiW_9Cu_3]/[py] = 1$ at different pH's. The spectrum at pH 6 shows no free ligand peak, indicating that all pyridine molecules are coordinated. When pH was increased, the relative intensity of one set of lines (F, N, and T) increased, and finally at pH = 9.1 only these lines were observed (Figure 3c). The pH dependence of the spectrum suggests that more than one species with different degrees of protonation are involved in complex formation at pH 6−10. The lines get broader as the pH is lowered, and the lines originating from species with different degrees of protonation are not resolved below pH 5.[10]

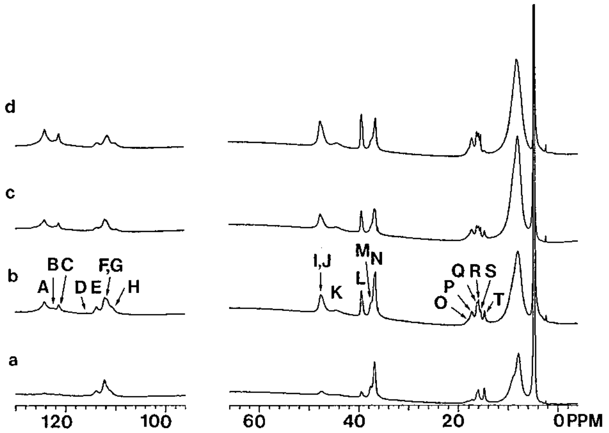

Figure 2. ^1H NMR spectra of D_2O solutions containing $[SiW_9Cu_3O_{37}]^{10-}$ and pyridine in the mole ratio of (a) 1, (b) 1/2, (c) 1/3, and (d) 1/4 at pH 8.1.

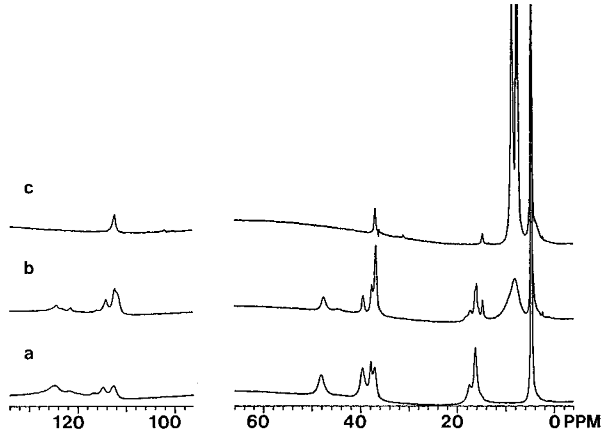

Figure 3. ^1H NMR spectra of D_2O solutions containing $[SiW_9Cu_3O_{37}]^{10-}$ and pyridine in the mole ratio of 1 at pH (a) 6.0, (b) 7.4, and (c) 9.1.

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.[11−13] There are several types of bridging oxygen atoms in SiW_9Cu_3: those between two tungsten atoms, those between one tungsten atom and one copper atom, and those between two copper atoms. When a WO^{4+} group in a heteropolyanion is replaced by a Cu^{2+} ion, the bridging oxygen atoms bonded to the copper atom get extra negative charges.[14] So the oxygen atoms between two copper atoms are most basic, and they must be protonated preferentially.

The number of expected NMR lines depends on the rates of inter- and intramolecular proton transfers. Observation of five

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(8) Martin, M. L.; Delpuech, J. J.; Martin, G. J. *Practical NMR Spectroscopy*; Heyden: London, 1980.

(9) Levy, G. C.; Peat, I. R. *J. Magn. Reson.* **1975**, *18*, 500−521.

(10) SiW_9Cu_3 is slowly converted to $[SiW_{11}Cu(H_2O)O_{39}]^{6-}$ at pH < 5, and the pK of pyridine is 5.17. Still we could observe ^1H NMR spectrum of pyridine coordinated to SiW_9Cu_3 at pH = 4.2.

(11) Day, V. W.; Klemperer, W. G.; Maltbie, D. J. *J. Am. Chem. Soc.* **1987**, *109*, 2991−3002.

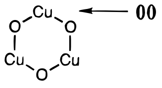
(12) Flynn, C. M., Jr.; Pope, M. T. *Inorg. Chem.* **1971**, *10*, 2524−2529.

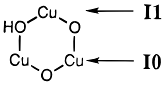
(13) Finke, R. G.; Rapko, B.; Saxton, R. J.; Domaille, P. J. *J. Am. Chem. Soc.* **1986**, *108*, 2947−2960.

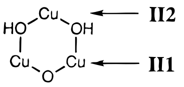
(14) Day, V. W.; Klemperer, W. G. *Science* **1985**, *228*, 533−541.

lines D − H for α-H's of the monopyridine species indicates that intermolecular proton transfer is slow on the NMR time scale. Otherwise, only one exchange-narrowed line would be observed for the monopyridine species. If the intramolecular proton transfer is fast on the NMR time scale, the three Cu^{2+} ions become equivalent, and only one NMR line will be observed for each of un-, mono-, di-, and triprotonated monopyridine species. Expected in this case are four sets of lines (or three sets if the triprotonated species is assumed not to contribute to the spectrum at pH 6−10). The spectra for $[SiW_9Cu_3]/[py] = 1/2$ exhibit five sets of lines, indicating that intramolecular proton transfer is slow on the NMR time scale. Norton *et al.* have shown that proton transfers involving oxo bridges between transition metal ions are quite slow.[15] The slow rate was attributed to extensive geometric and electronic rearrangement accompanying protonation and deprotonation.

In order to account for five sets of lines originating from the monopyridine species, we assume that $[H_mSiW_9Cu_3O_{37}(py)]^{(10-m)-}$ (m = 0, 1, and 2) contribute to the spectrum at pH 6−10. Triprotonated species are assumed not to exist at pH > 6. There are five different copper sites in these species, which are designated by the number of protons on the anion (0, I, or II) and the number of protonated oxygen atoms adjacent to the pyridine-coordinated copper atom (0, 1, or 2).







The NMR lines have been assigned on the basis of their pH and $[SiW_9Cu_3]/[py]$ dependence and relative intensities; see Table 1. The lines originating from monopyridine species, especially α-H lines, are well resolved, and all lines have been identified. The lines originating from the multipyridine species are not so well resolved. The broad lines (A, I + J, and P) appearing at lower fields are tentatively assigned to tripyridine species, and the higher-field lines (C, L, Q and S; Q and S are overlapped by monopyridine lines) to dipyridine species.

The intensity of the free ligand peak increases as the pH of the solution increases, indicating that protonated species have higher affinity for pyridine than the unprotonated species. This may be attributed to enhanced acidity of the copper ions on protonation of the bridging oxygen atom(s).

As the temperature is raised, the free ligand lines move downfield while the complex lines move upfield (Figure 4). And the lines from various species merge gradually. The temperature dependence of the spectrum can be explained in terms of the exchange rate of pyridine, which must increase with increasing temperature. We have also measured ^1H NMR spectra of pyridine coordinated to SiW_9Ni_3 and SiW_9Co_3. Each spectrum exhibits only one set of broad lines ascribable to the complex, indicating that the exchange rate of pyridine at each of these complexes is faster than at SiW_9Cu_3.

The ^1H NMR spectrum of a D_2O solution containing SiW_9Cu_3 and γ-picoline is quite similar to that of the pyridine complex except that the γ-H lines are replaced by the γ-CH_3 lines appearing at (−5) − (−9) ppm (Figure 5c). The ^1H NMR spectrum of a D_2O solution containing SiW_9Cu_3 and β-picoline is shown in Figure 5b. The complexity of the spectrum at 130−110 ppm comes from inequivalence of two α-H's.

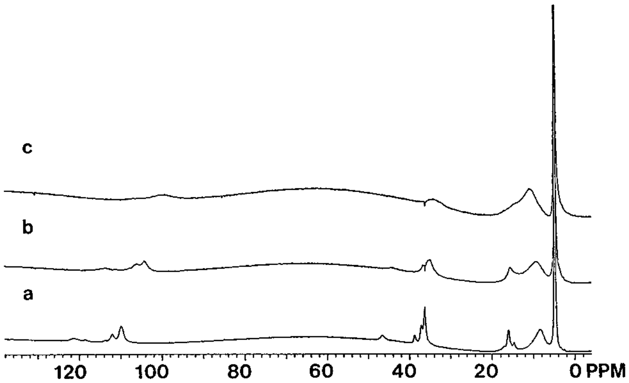


Figure 4. ^1H NMR spectra of D_2O solutions containing $[SiW_9Cu_3O_{37}]^{10-}$ and pyridine in the mole ratio of 1 at (a) 30, (b) 50, and (c) 70 °C.

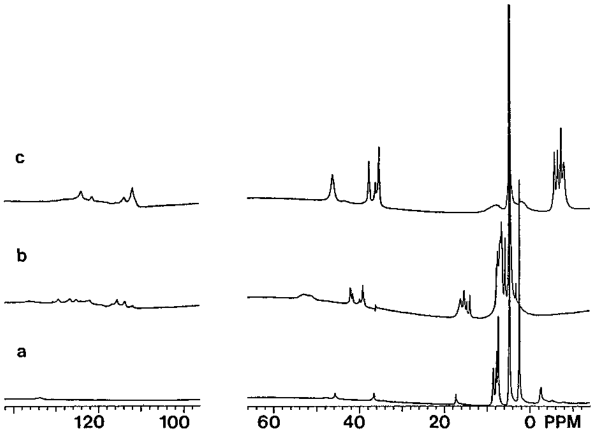


Figure 5. ^1H NMR spectra of D_2O solutions containing $[SiW_9Cu_3O_{37}]^{10-}$ and (a) α-picoline, (b) β-picoline, and (c) γ-picoline in the mole ratio of 1.

The ^1H NMR spectrum of a D_2O solution containing SiW_9Cu_3 and α-picoline shows only one set of lines, which may be attributed to a species with one coordinated α-picoline (Figure 5a). α-Picoline, which is not coordinated to $[SiW_{11}O_{39}Co]^{6-}$ because of steric hindrance,[4] forms a complex with SiW_9Cu_3, revealing subtle difference in their surfaces. However, species with more than one coordinated α-picoline is not formed.

Magnetic Susceptibilities. In order to analyze the isotropic NMR shifts and the relaxation times, we have to know the energy levels of SiW_9Cu_3. If the exchange interactions between two Cu^{2+} ions are assumed to be equal for all three pairs, the system can be described by the following spin Hamiltonian

$$\hat{H} = -J(S_1 \cdot S_2 + S_1 \cdot S_3 + S_2 \cdot S_3) \qquad (1)$$

When the spin states are represented by $S = S_1 + S_2 + S_3$, the resulting states are two doublets ($S = {}^1/_2$) and one quartet ($S = {}^3/_2$). The experimental molar magnetic susceptibility for this system can be expressed as[16,17]

$$\chi_M = \frac{N_A g^2 \mu_B^2}{4k(T-\theta)} \frac{1 + 5\exp(3J/2kT)}{1 + \exp(3J/2kT)} + \chi_{dia} M_W \qquad (2)$$

where M_w is the molecular weight and χ_{dia} is the diamagnetic susceptibility.

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(15) (a) Kramarz, K. W.; Norton, J. R. *Prog. Inorg. Chem.* **1994**, *42*, 1−65. (b) We can roughly estimate the proton transfer rate for SiW_9Cu_3 using a well-known equation for the two-site (A and B) equal-time process. The lifetime τ_A (= τ_B) for detecting two exchanging nuclei as separate resonances is given by

$$\tau_A > \frac{\sqrt{2}}{\pi(\nu_A^\circ - \nu_B^\circ)}$$

The separation between the lines designated by M and N in Figure 2 is 27 Hz, indicating that the τ_A is greater than 0.017 s at pH 8.1. These lines merge below pH 5. Norton *et al.* have presented examples of protonation at oxygen bridges several orders of magnitude slower than this.

(16) Chaudhuri, P.; Winter, M.; Vedova, B. P. C. D.; Bill, E.; Trautwein, A.; Gehring, S.; Fleischhauer, P.; Nuber, B.; Weiss, J. *Inorg. Chem.* **1991**, *30*, 2148−2157.

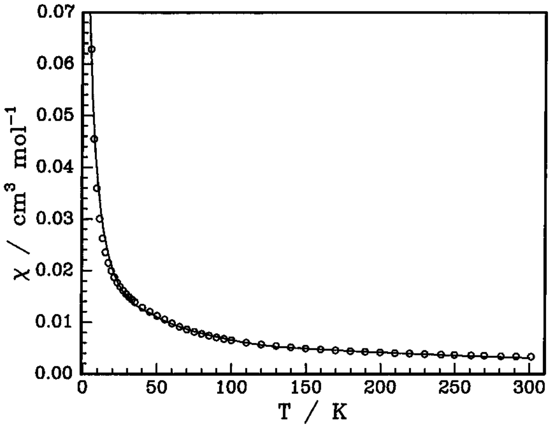

Figure 6. Temperature dependence of molar magnetic susceptibility of $K_6H_4[SiW_9O_{37}Cu_3(H_2O)_3]\cdot nH_2O$: o, measured; — calculated.

The g value was assumed to be equal to that of $[SiW_{11}O_{39}Cu(H_2O)]^{6-}$, i.e., $g = 2.209$. The magnetic susceptibility data of α-SiW_9Cu_3 at 5−300 K were fit to eq 2 by treating J, θ, and χ_{dia} as adjustable parameters. Satisfactory fit could not be obtained for any combination of the parameters. Considering the possibility that the exchange interactions among the three Cu^{2+} ions are not equal, we have tried to fit the measured data using two or three different J values without success. We have also tried without success a more rigorous expression obtained by replacing θ in eq 2 by $zJ'\{1 + 5\exp(3J/2kT)\}/4k\{1 + \exp(3J/2kT)\}$.[18] However, a reasonable fit was obtained (Figure 6), when the magnetic susceptibility data were divided into three temperature regions and the following J values were used: $J = -55$ cm^{-1} at $T \leq 45$ K, $J = -31.2 - 0.529T$ at $T = 45$−130 K, and $J = -100$ cm^{-1} at $T \geq 130$ K. Other parameters used are $\theta = -2.5$ K and $\chi_{dia} = -1.2 \times 10^{-7}$ emu/g. The value of χ_{dia} agrees with that of a diamagnetic heteropolyanion.[19]

Since J is negative, the ground state consists of two degenerate doublets ($S = 1/2$), and an excited quartet ($S = 3/2$) lies $-1.5J$ cm^{-1} above them. It is noted that the magnitude of J is constant down to 130 K, decreases linearly at 130−45 K, and then becomes constant again below 45 K. A possible explanation for the magnetic behavior is a geometric rearrangement of the heteropolyanion which increases the average Cu···Cu distance at low temperatures. We have found a similar temperature-dependence of J for $(NH_4)_{23}[KAs_4W_{40}Cu_2(H_2O)_2O_{140}]\cdot nH_2O$ ($J = 0.0060$ cm^{-1} at 298 K and $J = 0.0043$ cm^{-1} at 95 K) by single crystal EPR spectroscopy.[20]

Contact and Pseudocontact Contributions. 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, mononuclear complex can be expressed as[21]

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

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.

However, since the J value at room temperature is of the order of kT (207 cm^{-1}) for SiW_9Cu_3, the magnetic coupling and the magnetic anisotropy of the whole exchange-coupled system should be considered in calculating δ_{dip}. The system is axial with a C_3 axis. The molecular g values, $g_\parallel$(m) and $g_\perp$(m), can be estimated from the local g values of a CuO_4L (L = ligand) group in SiW_9Cu_3 and the structure of the Keggin anion.[22] For the $S = 3/2$ state $g_\parallel$(m) equals the g value in the direction of the C_3 axis, and $g_\perp$(m) equals the average g value of three CuO_4L groups in a direction perpendicular to the C_3 axis.[23] When the $S = 1/2$ states are not degenerate, their g values are different.[24] However, for our spin-frustrated system we may use the average values for the two doublet states, which are the same as those of the $S = 3/2$ state. When the population distribution is taken into account, the pseudocontact shift for a given nucleus i in this system can be expressed as

$$\delta_{dip} = \frac{\mu_o}{4\pi}\frac{\mu_B^2(3\cos^2\gamma_i - 1)}{9kTR_i^3}(g_\parallel(m)^2 - g_\perp(m)^2)\langle S(S+1)\rangle \qquad (4)$$

$$\langle S(S+1)\rangle = \frac{\sum_i S_i(S_i+1)(2S_i+1)\exp(-E_i/kT)}{\sum_i (2S_i+1)\exp(-E_i/kT)} \qquad (5)$$

where γ_i is the angle between the C_3 axis and the radius vector from the nucleus, i, to the center O of the equilateral triangle formed by the three Cu^{2+} ions; R_i is the distance between O and the nucleus, i. Equation 4 is valid if R_i is much larger than the distance between O and the metal ion.[25] The geometrical factors, $(3\cos^2\gamma_i - 1)/R_i^3$, have been calculated from X-ray data of a Keggin anion[22] and monopyridinecopper(II) acetate[26] and the following bond lengths: ring C−H 1.03, methyl-ring C−C 1.53, methyl C−H 1.09 Å. The g values are assumed to be the same as those of $[SiW_{11}O_{39}Cu(H_2O)]^{6-}$, $g_\parallel = 2.412$ and $g_\perp = 2.108$. Calculated molecular g values are $g_\parallel(m) = 2.371$ and $g_\perp(m) = 2.131$. Listed in Table 2 are calculated values of δ_{dip} and values of δ_{con} for monoligand complexes obtained by subtracting δ_{dip} from δ_{iso}.

It is of interest to compare the resulting δ_{con} values with δ_{iso} values of nickel(II) complexes. Since octahedral Ni(II) complexes have very small g anisotropy, δ_{dip} is negligible and δ_{iso} is close to δ_{con}. The Ni^{2+} ion in octahedral symmetry has two unpaired electrons in e_g orbitals which have σ symmetry. It is most likely that the unpaired electron density is transferred from the $3d_{z^2}$ orbital to the σ orbital system of the ligand. Horrocks and Johnston have shown that σ-electron delocalization in pyridine derivatives coordinated to bis(2,4-pentanedionato)-nickel(II) are roughly proportional to the hyperfine coupling constants in phenyl and *o*-, *m*-, and *p*-tolyl radicals.[27]

The Cu^{2+} ion in octahedral symmetry has one unpaired electron in the $3d_{x^2-y^2}$ orbital. Since the local symmetry of a Cu^{2+} ion in SiW_9Cu_3 is C_s, $3d_{x^2-y^2}$ and $3d_{z^2}$ orbitals can be

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[17] Brown, D. B.; Wasson, J. R.; Hall, J. W.; Hatfield, W. E. *Inorg. Chem.* **1977**, *16*, 2526−2529.

[18] O'Connor, C. J. *Prog. Inorg. Chem.* **1982**, *29*, 203−283. J' is the interaction parameter between two nearest SiW_9Cu_3 anions, and z is the number of nearest neighbors around a given anion.

[19] Flynn, C. M., Jr.; Pope, M. T. *Inorg. Chem.* **1973**, *12*, 1626−1634.

[20] Cho, Y. H.; So, H.; Pope, M. T. (to be published).

[21] Happe, J. A.; Ward, R. L. *J. Chem. Phys.* **1963**, *39*, 1211−1218.

[22] Robert, F.; Tézé, A.; Hervé, G.; Jeannin, Y. *Acta Crystallogr.* **1980**, *B36*, 11−15.

[23] Cho, Y. H.; So, H. *Bull. Korean Chem. Soc.* **1995**, *16*, 243−247.

[24] Bencini, A.; Getteschi, D. *Electron Paramagnetic Resonance of Exchange Coupled System*; Springer-Verlag: Berlin, 1990; p 107.

[25] (a) McConnell, H. M. *J. Chem. Phys.* **1957**, *27*, 226−229. (b) When R_i is not large, it is necessary to consider the appropriate molecular orbitals. See: Golding, R. M.; Pascual, R. O.; Stubbs, L. C. *Mol. Phys.* **1976**, *31*, 1933−1939.

[26] Barclay, G. A.; Kennard, C. H. L. *J. Chem. Soc.* **1961**, 5244−5251.

[27] Horrocks, W. D.; Johnston, D. L. *Inorg. Chem.* **1971**, *10*, 1835−1838.

Table 2. Comparison of Contact Shifts in $[H_mSiW_9O_{37}Cu_3(ptl)]^{(10-m)-}$ and $[P_2W_{18}O_{68}Ni_3(ptl)]^{12-}$

proton	δ_{iso}	δ_{dip}	δ_{con}	δ_{iso}(Ni)	$\delta_{con}/\delta_{iso}$(Ni)
α-H[a]	101.9	−1.7	103.6	140	0.74
β-H[a]	29.1	0.8	28.3	39.2	0.72
γ-H[a]	6.7	1.0	5.7	13.8	0.41
α-CH_3[b]	−5.0	−4.0	−1.0	−13.0	0.08
β-CH_3[b]	3.4	−0.7	4.1	8.0	0.51
γ-CH_3[b]	−9.1	0.8	−9.9	−13.6	0.73

[a] The data for the pyridine complex. [b] The data for the picoline complexes.

admixed and some unpaired electron density can delocalize onto the σ orbital system of the ligand. If the contact shifts are due to σ electron delocalization alone for both nickel(II) and copper(II) complexes, their δ_{con} ratios of various protons should closely parallel each other.

We have measured ^{1}H NMR spectra of pyridine-type ligands coordinated to Ni^{2+} in three heteropolyanions,[28] $[SiW_{11}O_{39}Ni]^{6-}$, $[SiW_9O_{37}Ni_3]^{10-}$, and $[P_2W_{18}O_{68}Ni_3]^{12-}$. As the δ_{iso} values are similar for all three compounds, those for $[P_2W_{18}O_{68}Ni_3(ptl)]^{12-}$ showing the best-resolved spectra are compared with δ_{con} in the copper(II) complexes (Table 2). The ratios of δ_{con} values in the copper(II) complexes to the δ_{iso} values in the nickel(II) complexes are also given.

Values of $\delta_{con}(Cu)/\delta_{iso}(Ni)$ for α-H, β-H, and γ-CH_3 are in good agreement with one another, the average being 0.73. It is noted that the δ_{iso} values for these protons are much larger than the δ_{dip} values. Values of $\delta_{con}(Cu)/\delta_{iso}(Ni)$ for the other protons, especially that of α-CH_3, are much smaller than 0.73. Since these protons have small δ_{iso} values, a small error in the calculation of δ_{dip} would change the $\delta_{con}(Cu)/\delta_{iso}(Ni)$ ratios considerably. Especially eq 4 may not be adequate for α-CH_3, for $R_i = 4.04$ Å is not much larger than the distance between O and the copper nucleus, 2.14 Å.

So more reliable δ_{con} values of the copper(II) complexes exceed 70% of those of nickel(II) complexes. These values are surprisingly large. Even if the unpaired electron in the $3d_{x^2-y^2}$ orbital is delocalized onto the ligand as extensively as that in the $3d_{z^2}$ orbital, the δ_{con} values of the copper(II) complex should be about 50% of those of the nickel(II) complexes.

Electronic Relaxation in SiW_9Cu_3. The electronic relaxation time in ordinary copper(II) complexes is $1-3 \times 10^{-9}$ s.[29] The ^{1}H NMR spectrum of a copper(II) complex can be observed if the electronic relaxation time is decreased at least two orders of magnitude. One way to achieve this is to couple a Cu^{2+} ion with a fast relaxing ion such as Co^{2+}. ^{1}H NMR spectra of some copper complexes were measured by this method.[6,7]

The electronic relaxation time in SiW_9Cu_3 was estimated from the longitudinal relaxation times of the protons in the coordinated pyridine. Values of T_1 measured by the inversion recovery method are 0.0063, 0.062, and 0.13 s for α-, β-, and γ-H, respectively. Nuclear relaxation arises from dipolar and contact interactions of the nuclear magnetic moments with the unpaired electron spin. The enhancement of the nuclear longitudinal relaxation rate, T_{1M}^{-1}, due to coupling with unpaired electrons for a mononuclear system having g anisotropy can be expressed as[30]

$$
\begin{aligned}
T_{1M}^{-1} = {} & \frac{2}{5}\left(\frac{\mu_o}{4\pi}\right)\frac{\gamma_N^2\mu_B^2 S(S+1)}{r^6} \times \\
& \left\{\left(\frac{1}{9}(16g_{\parallel}^2 + 9g_{\perp}^2 - 4g_{\parallel}g_{\perp}) + (g_{\parallel} - g_{\perp})^2\sin^4\theta + \right.\right. \\
& \left. \frac{7}{3}g_{\parallel}(g_{\perp} - g_{\parallel})\sin^2\theta\right)\frac{\tau_c}{1+\omega_z^2\tau_c^2} + \\
& \left(\frac{1}{9}(4g_{\parallel}^2 + g_{\perp}^2 + 4g_{\parallel}g_{\perp}) - (g_{\parallel} - g_{\perp})^2\sin^4\theta - \right. \\
& \left.\left. \frac{1}{3}(2g_{\parallel} - 5g_{\perp})(g_{\perp} - g_{\parallel})\sin^2\theta\right)\frac{\tau_c}{1+\omega_I^2\tau_c^2}\right\} + \\
& \frac{4}{9}\left(\frac{\mu_o}{4\pi}\right)\frac{\gamma_N\mu_B S(S+1)}{r^3}\frac{A_c}{\hbar}(g_{\parallel} - g_{\perp})(3\cos^2\theta - 1) \times \\
& \delta(\tau_c, \tau_e)\frac{\tau_c}{1+\omega_z^2\tau_c^2} + \frac{2}{3}\left(\frac{A_c}{\hbar}\right)^2 S(S+1)\frac{\tau_e}{1+\omega_z^2\tau_e^2} \qquad (6)
\end{aligned}
$$

where

$$\omega_z = g_{\parallel}\mu_B B_o/\hbar \qquad (7)$$

$$\frac{A_c}{\hbar} = \delta_{con}\frac{3\gamma_N kT}{g\mu_B S(S+1)} \qquad (8)$$

Again contributions of both $S = 3/2$ and $S = 1/2$ manifolds to the nuclear relaxation should be considered for our system. The electronic correlation time, τ_c, may be assumed to be equal to the electronic relaxation time, τ_e. The τ_c value is in principle different for each level. However, as the τ_c value for each level cannot be determined separately, it will be assumed to be the same for all levels. Then only $S(S + 1)$ in eqs 6 and 8 needs be replaced by an average value.

Two different approaches are possible. One method is to consider only the effect of the unpaired electron on the copper ion to which the ligand is coordinated. In this case r and θ are kept, g anisotropy is neglected, and the average value of $S(S + 1)$ is calculated taking the C_{i1} coefficients into account.[31] The resulting τ_c values are 5×10^{-12} s for α-H and 1×10^{-11} s for β-H and γ-H. (Ideally the τ_c values should be the same.)

The other method is to assume that all three electrons are located at the center of the equilateral triangle formed by the three Cu^{2+} ions. The r and θ in eq 6 are replaced by R and γ, and $S(S + 1)$ by $\langle S(S + 1)\rangle$ of eq 5. The resulting τ_c values are 3×10^{-12} s for α-H and 4×10^{-12} s for β-H and γ-H. Although the τ_c values from the second method are in better agreement with one another, the agreement may be fortuitous considering many approximations involved. Still we may conclude that the τ_c value in SiW_9Cu_3 is in the order of 10^{-11} or 10^{-12} s, which is two or three orders of magnitude smaller than those of ordinary copper(II) complexes. The calculations also show that the dipolar relaxation is the dominant mechanism.

The question arises as to what causes the decrease in the electronic relaxation time in SiW_9Cu_3. The ground state consists of two degenerate doublets, which can have different spin states for a given Cu^{2+} ion as shown schematically below[32]

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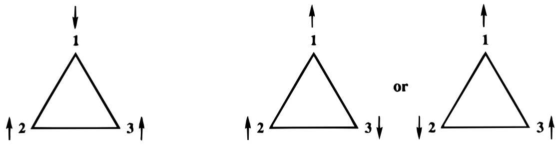
(28) ^{1}H NMR spectra of $[SiW_{11}O_{39}Ni(ptl)]^{6-}$ were reported in ref 4. ^{1}H NMR spectra of $[P_2W_{18}O_{68}Ni_3(ptl)_n]^{12-}$ also exhibit lines of mono-, di-, and triligand complexes. The spectra will be reported elsewhere. The structure of $[P_2W_{18}O_{68}Ni_3(H_2O)_3]^{12-}$ was described: Knoth, W. H.; Domaille, P. J.; Harlow, R. L. *Inorg. Chem.* **1986**, *25*, 1577−1584.

(29) Reference 3, p 77.

(30) Sternlicht, H. J. *J. Chem. Phys.* **1965**, *42*, 2250−2251. The equation is quoted in ref 3, pp 64−65.

(31) (a) Banci, L.; Bertini, I.; Luchinat, C. *Struct. Bonding* **1990**, *72*, 113−136. (b) Banci, L.; Bertini, I.; Luchinat, C. *Nuclear and Electron Relaxation*; VCH: New York, 1991; p 152. C_{i1} is defined in this reference.



As the system hesitates as for the nature of the ground state (this phenomenon is known as spin frustration[32]), the electron spins can relax rapidly. In the EPR spectrum of another copper trimer, $[As_2W_{18}O_{66}Cu_3(H_2O)_2]^{12-}$, the absence of EPR lines from the $S = 1/2$ manifolds was attributed to spin frustration.[23,33]

It is more difficult to explain the electronic relaxation at the excited $S = 3/2$ state in SiW_9Cu_3. The $S = 3/2$ state, which is only 150 cm^{-1} above the ground state, will be populated considerably at room temperature. Yet no EPR signal appears, whereas good NMR spectra are observed for the pyridine-type ligands coordinated to it, indicating that the electronic relaxation at the $S = 3/2$ state is also fast. On the other hand, $[As_2W_{18}O_{66}Cu_3(H_2O)_2]^{12-}$ exhibits a good EPR signal from the $S = 3/2$ state and no NMR spectrum for pyridine coordinated to it. The mechanism responsible for the fast electronic relaxation at the $S = 3/2$ level in SiW_9Cu_3 is not clearly understood.

In summary, pyridine-type ligands coordinated to paramagnetic $[H_mSiW_9O_{37}Cu_3]^{(10-m)-}$ have been found to exhibit good ^{1}H NMR spectra, and many 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 SiW_9-Cu_3 and its analogues.

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(32) Kahn, O. *Molecular Magnetism*; VCH: New York, 1993; p 241.

(33) Siedle, A. R.; Padula, F.; Baranowski, J.; Goldstein, C.; Deangelo, M.; Kokoszka, G. F.; Azevedo, L.; Venturini, E. L. *J. Am. Chem. Soc.* **1983**, *105*, 7447−7448.