

On the Degrees of Circularity for Various Kinds of Polarized Light in the Nonpolar Fluid Composed of Chiral Molecules

Dong J. Lee and Kyoung-Ran Kim

Department of Chemistry, National Fisheries University of Pusan, Nam-Gu, Pusan 608-787, Korea

Received July 27, 1995

The explicit results of the degrees of circularity for various kinds of completely polarized light in a nonpolar fluid composed of chiral molecules are obtained with the aid of the Ornstein-Zernike form for the correlation function of density fluctuations. Then, the results are in detail discussed in two limiting cases of critical region and compared with circular intensity differences.

Introduction

In 1987 one of the authors and his coworker¹ have proposed a general theory of multiple scattering for a nonpolar fluid composed of chiral molecules. It is based on a general theory² of the dielectric tensor well suited to study the dielectric behavior in the critical region. The theory of multiple scattering has been treated as the same way as that of single scattering in the phenomenological theory given by Einstein.³⁻⁴ The scattering intensity¹ has been expressed in terms of the correlation function, which gives the information about the effect of fluctuations of the dielectric tensor in the sample fluid and nature of the incident light. The dielectric tensor fluctuates due to the fluctuations in density and other thermodynamic variables. We have considered the scattering only due to the density fluctuations, which plays the most dominant role in the critical region. In the subsequent paper⁵ we have, for the first time, discussed the effect of the double scattering on the circular intensity differences in the critical region, where the Ornstein-Zernike theory holds. There are six basic polarizations in terms of which any arbitrary polarization may be expressed. They are judged by an observer into whose eye the light is travelling: horizontally linearly polarized light, vertically linearly polarized light, linearly polarized lights above the horizontal 45° and below the horizontal at 45°, right and left circularly polarized lights.⁶

The purpose of this paper is to obtain the degrees of circularity (DCs) for various kinds of basic complete polarized light in a nonpolar fluid composed of chiral molecules with the aid of the Ornstein-Zernike theory for the correlation function of density fluctuations and to compare the results with circular intensity difference (CID)s in the critical region. Up to our knowledge DCs has never been discussed in the critical region.

In the next section the general formula for the single scattering intensity and the most dominant part of the double scattering intensity are given in a nonpolar fluid composed of chiral molecules.⁵ Then, we express the kinds of basic polarized light with the aid of the polarization ellipse in a complex plane.⁶ The explicit result for DC is obtained by using the general formula for the single and double scattering intensities. The DC for each polarized light is in detail discussed in two limiting cases of the critical region, where the Ornstein-Zernike theory holds. Finally, the results for

DC are compared with CIDs.⁵ In a subsequent paper we shall discuss the critical scattering for a nonpolar binary liquid mixture, which is more suitable to verify the results by experiments than the pure fluid.

Theory

Let us consider a nonpolar fluid composed of chiral molecules. The single and most dominant part of double scattering intensities with the polarization \mathbf{u} and \mathbf{v} in the fluid are expressed as⁵

$$\mathbf{I}_{uv}^s(\mathbf{r}, \omega_0) = (4\pi)^{-2} [(\epsilon_0 + 2)/3]^2 \rho_0^2 \omega_0^2 S_2(\mathbf{k}_0 - \mathbf{k}_s) V_s [\mathbf{u} \cdot \gamma_c'(\mathbf{k}_0, k_s) \cdot \mathbf{E}_0] [\mathbf{v} \cdot \gamma_c(\mathbf{k}_s, k_s) \cdot \mathbf{E}_0]^*, \quad (1)$$

$$\mathbf{I}_{uv}^d(\mathbf{r}, \omega_0) = -i(8\pi^2)^{-1} [(\epsilon_0 + 2)/3]^4 \rho_0^4 \omega_0^4 \int_{V_0} d\mathbf{r}_1 \int_{V_L} d\mathbf{r}_2 \int_{-\infty}^{\infty} k dk S_2(\mathbf{k}_0 - k\Omega) S_2(\mathbf{k}_s - k\Omega) [\mathbf{u} \cdot \gamma_c(\mathbf{k}_0, k\Omega) \cdot K_c(k\Omega, \omega_0) \cdot \gamma_c'(k\Omega, k_0) \cdot \mathbf{E}_0]^* [\mathbf{v} \cdot \gamma_c(\mathbf{k}_s, k\Omega) \cdot K_c(r_{12}, \omega_0) \cdot \gamma_c(k\Omega, k_0) \cdot \mathbf{E}_0]^*, \quad (2)$$

where

$$\begin{aligned} \epsilon_0 &= [1 + (2/3)\alpha_0^0 \rho_0] / [1 - (1/3)\alpha_0^0 \rho_0], \\ \gamma_c(\mathbf{k}_0, k_s) &= \alpha_c^0 + i\beta_c^0 U \cdot (\hat{\mathbf{k}}_0 + \hat{\mathbf{k}}_s), \\ \hat{\mathbf{k}} &= [1 - (2/3)\alpha_0^0 \rho_0 x_1^0] \mathbf{k}, \quad k_s \simeq k_0 = n_0 \omega_0, \\ n_0 &= \epsilon_0^{1/2}, \quad \mathbf{r}_{12} = \mathbf{r}_1 - \mathbf{r}_2 = r_{12} \Omega. \end{aligned} \quad (3)$$

In the above equations ϵ_0 and ρ_0 are the dielectric constant and density of the fluid at equilibrium, respectively; ω_0 is the frequency of the incident field, \mathbf{E}_0 ; \mathbf{k}_0 and \mathbf{k}_s are the propagation vectors of the incident and scattered fields, respectively; α_0 and $\beta_0 U$ are the second and third order molecular polarizability tensors of the i th species averaged over the molecular orientations,² U being the Levi-Civita tensor; V_s is the scattering volumes, which is the cross section of the illuminated volume, V_L and observed volume, V_0 ; the explicit form of the renormalized propagator K_c has been given in ref. 5 and $S_2(\mathbf{k})$ is the static correlation function of concentration fluctuations. In this paper we use the Ornstein-Zernike theory for the correlation function of concentration fluctuations, which is given as follows:

$$S_2(\mathbf{k}) = k_B T \kappa / [1 + (\xi \mathbf{k})^2], \quad (4)$$

where $k_B T$ is the Boltzmann factor; κ and ξ are the isothermal compressibility coefficient and correlation length of the

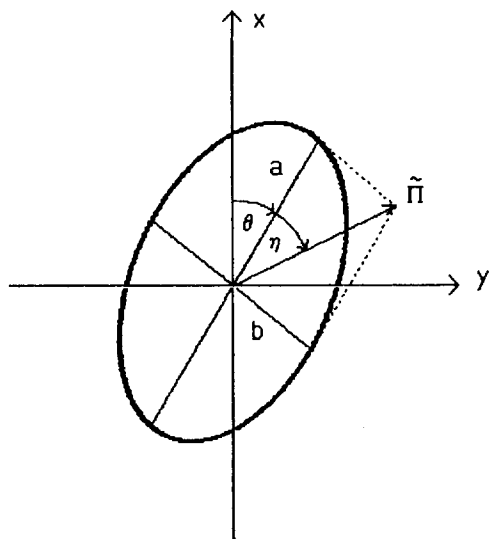


Figure 1. The polarization ellipse of the incident field propagating along the z -direction. θ and η are the ellipticity and azimuth, respectively and Π is the complex unit polarization vector. a and b are the major and minor axes of the ellipse, respectively.

density fluctuations, respectively.

In order to discuss various kinds of scattering phenomena in the nonpolar fluid, we have to know the polarization state of the incident field, E_0 . Let the direction of propagation of the incident monochromatic plane light be the z direction. The term E_0 can be written as a sum of two coherent fields linearly polarized in the x and y directions

$$E_0 = E_{0x}\hat{x} + E_{0y}\hat{y}, \quad (5)$$

where \hat{x} and \hat{y} are the unit vectors of x and y direction, respectively. The general pure polarization state can be described in terms of the ellipticity, η and azimuth, θ , as shown in the Figure. Then, the complex amplitude may be written as

$$E_0 = E_0[(\cos\theta \cos\eta + i\sin\theta \sin\eta)\hat{x} + (\sin\theta \cos\eta + i\cos\theta \sin\eta)\hat{y}], \quad (6)$$

where

$$-\frac{\pi}{2} \leq \theta \leq \frac{\pi}{2}, \quad -\frac{\pi}{4} \leq \eta \leq \frac{\pi}{4} \quad (7)$$

Then, the six basic polarization states of the incident field are given in the Table.

Let the directions of the incident and scattered lights be z and y directions, respectively. The detector, on the y axis at some point $\mathbf{r} = r\hat{y}$ far removed from the sample, measures the scattering intensity. In scattering at 90° the degree of circularity (DC) of the scattered light, which is the ratio of the intensity of the circularly polarized component to the total intensity can be expressed as, by using the definition of the Stokes parameters⁶

$$\gamma = -\frac{2\text{Im}(I_{xz})}{I}; \quad I = I_{xx} + I_{yy}, \quad (8)$$

where Im denotes the imaginary part of the xz component of scattering intensity and I_{xx} and I_{yy} are the scattering inten-

Table 1. The definition of the six basic polarized lights

kind of polarized light	θ	η	notation
horizontally linear polarized light	$\pi/2$	0	h
vertically linearly polarized light	0	0	v
linearly polarized light above the horizontal at 45°	$\pi/4$	0	$+$
linearly polarized light below the horizontal at 45°	$-\pi/4$	0	$-$
right circularly polarized light	0	$\pi/4$	R
left circularly polarized light	0	$-\pi/4$	L

sities perpendicular and parallel to the scattering plane, respectively.

Let us assume that the observed volume V_0 and illuminated volume V_L are concentric spheres and $V_0 \geq V_L$. Using the explicit forms of the renormalized propagator, following the similar procedures as that given in ref. 5 and taking the results up to the first order of $\beta_0 k_0$, we may obtain the following results for the sum of the single and double scattering intensities as

$$I = A(|E_{0x}|^2 + D[G_1(b)|E_{0x}|^2 + G_2(b)|E_{0y}|^2] + \frac{2\beta_0 k_0}{\alpha_0 \epsilon_0 (\epsilon_0 + 2)} \{ \epsilon_0 (4 - \epsilon_0) + D[\epsilon_0 (4 - \epsilon_0) G_3(b) + (\epsilon_0 - 1)(5\epsilon_0 + 2) G_4(b)] \} \text{Im}(E_{0x} E_{0y}^*)), \quad (9)$$

$$\begin{aligned} \text{Im}(I_{xz}) = & -A \left(\frac{\beta_0 k_0 (4 - \epsilon_0)}{\alpha_0 \epsilon_0 (\epsilon_0 + 2)} |E_{0x}|^2 + D G_5(b) \text{Im}(E_{0x} E_{0y}^*) \right. \\ & + D \frac{\beta_0 k_0}{\alpha_0 \epsilon_0 (\epsilon_0 + 2)} [\{ \epsilon_0 (4 - \epsilon_0) G_6(b) + (\epsilon_0 - 1)(5\epsilon_0 + 2) G_7(b) \} |E_{0x}|^2 \\ & + \{ \epsilon_0 (4 - \epsilon_0) G_8(b) + (\epsilon_0 - 1)(5\epsilon_0 + 2) G_9(b) \} |E_{0y}|^2], \end{aligned}$$

where the terms containing D are due to the double scattering and

$$A = (4\pi)^{-2} \left[\frac{(\epsilon_0 - 1)(\epsilon_0 + 2)}{3} \right]^2 \omega_0^4 S_2(\sqrt{2}k_0) V_s,$$

$$D = \frac{1}{2} \left[\frac{(\epsilon_0 - 1)(\epsilon_0 + 2)}{3} \right]^2 \omega_0^4 S_2(\sqrt{2}k_0) d_0,$$

$$b = \frac{2p^2}{1 + 2p^2}, \quad p = \xi k_0,$$

$$G_1(b) = \frac{1}{b^5} \left[2b - (5 + 3b^2) \ln \left(\frac{1+b}{1-b} \right) + \frac{4(2+b^2)}{\sqrt{2-b^2}} \ln \left(\frac{1+b\sqrt{2-b^2}}{1-b^2} \right) \right],$$

$$G_2(b) = \frac{1}{b^5} \left[2b + (1-b^2) \ln \left(\frac{1+b}{1-b} \right) - \frac{4(1-b^2)}{\sqrt{2-b^2}} \ln \left(\frac{1+b\sqrt{2-b^2}}{1-b^2} \right) \right], \quad (10)$$

$$\begin{aligned} G_3(b) = & \frac{1}{3b^6} \left[-6b(3 - 11b^2) + 3(9 - 26b^2 - 5b^4) \ln \left(\frac{1+b}{1-b} \right) \right. \\ & \left. + \frac{4(-7 + 20b^2 + 4b^4)}{\sqrt{2-b^2}} \ln \left(\frac{1+b\sqrt{2-b^2}}{1-b^2} \right) \right] \end{aligned}$$

$$G_4(b) = \frac{2}{4b^6} \left[2b - (2 + b^2) \ln \left(\frac{1+b}{1-b} \right) - \frac{1}{\sqrt{2-b^2}} \ln \left(\frac{1+b\sqrt{2-b^2}}{1-b^2} \right) \right],$$

$$G_5(b) = \frac{4}{b^3} \left[b - \ln \left(\frac{1+b}{1-b} \right) - \frac{1}{\sqrt{2-b^2}} \ln \left(\frac{1+b\sqrt{2-b^2}}{1-b^2} \right) \right],$$

$$G_6(b) = \frac{1}{12b^6} \left[10b(10+13b^2) - 3(55+70b^2+11b^4) \ln\left(\frac{1+b}{1-b}\right) + \frac{240(1+b^2)}{\sqrt{2-b^2}} \ln\left(\frac{1+b\sqrt{2-b^2}}{1-b^2}\right) \right],$$

$$G_7(b) = \frac{1}{b^4} \left[2b - (5+b^2) \ln\left(\frac{1+b}{1-b}\right) + \frac{8}{\sqrt{2-b^2}} \ln\left(\frac{1+b\sqrt{2-b^2}}{1-b^2}\right) \right],$$

$$G_8(b) = \frac{1}{4b^6} \left[-2b(11-17b^2) + (43-18b^2-96b^4) \ln\left(\frac{1+b}{1-b}\right) - \frac{16(4-b^2-2b^4)}{\sqrt{2-b^2}} \ln\left(\frac{1+b\sqrt{2-b^2}}{1-b^2}\right) \right],$$

$$G_9(b) = \frac{1}{b^4} \left[2b + (9-b^2) \ln\left(\frac{1+b}{1-b}\right) - \frac{4(1-b^2)}{\sqrt{2-b^2}} \ln\left(\frac{1+b\sqrt{2-b^2}}{1-b^2}\right) \right],$$

We may obtain the degree of circularity for each polarized light. For simplicity, however, let us consider the two limiting cases:

(A) When $p = \xi k_o \ll 1$, we obtain

$$I \simeq A_1 \left\{ \left(1 + \frac{16}{15} D_1\right) |E_{\alpha}|^2 + \frac{8}{15} D_1 |E_{\gamma}|^2 + \frac{2\beta_o k_o (4 - \epsilon_o)}{\alpha_o (\epsilon_o + 2)} \text{Im}(E_{\alpha} E_{\gamma}^*) \right\},$$

$$\text{Im}(I_{xx}) \simeq -A_1 \frac{\beta_o k_o (4 - \epsilon_o)}{\alpha_o (\epsilon_o + 2)} |E_{\alpha}|^2, \quad (11)$$

where

$$A_1 = (4\pi)^{-2} \left[(\epsilon_o - 1) \left(\frac{\epsilon_o + 2}{3} \right) \right]^2 \omega_o^4 k_B T \kappa V_s, \quad (12)$$

$$D_1 = \frac{1}{2} \left[(\epsilon_o - 1) \left(\frac{\epsilon_o + 2}{3} \right) \right]^2 \omega_o^4 k_B T \kappa d_o,$$

In Eq. (12) d_o is the radius of the observed volume. This case is where the system is far from the critical point. The terms containing $\beta_o k_o / \alpha_o$ and D_1 can be neglected, since the magnitudes of $\beta_o k_o / \alpha_o$ and D_1 are about 10^{-3} and 10^{-6} - 10^{-7} for most gases at the standard state in the optical frequency region.

(B) If $p \gg 1$, the results are

$$I \simeq A_2 \left\{ |E_{\alpha}|^2 + D_2 [(8 \ln(\xi k_o) - 0.70) |E_{\alpha}|^2] + \frac{2\beta_o k_o}{\alpha_o \epsilon_o (\epsilon_o + 2)} \{ \epsilon_o (4 - \epsilon_o) + D_2 [4(2\epsilon_o^2 + 9\epsilon_o - 2) \ln(\xi k_o) - 1.6\epsilon_o^2 + 26.8\epsilon_o - 2.4] \} \text{Im}(E_{\alpha} E_{\gamma}^*) \right\},$$

$$\text{Im}(I_{xx}) \simeq A_2 \left(\frac{\beta_o k_o (4 - \epsilon_o)}{\alpha_o \epsilon_o (\epsilon_o + 2)} |E_{\alpha}|^2 + 1.2 D_2 \text{Im}(E_{\alpha} E_{\gamma}^*) + \frac{\beta_o k_o}{\alpha_o \epsilon_o (\epsilon_o + 2)} D_2 [- (7\epsilon_o^2 + 45\epsilon_o + 2) \ln(\xi k_o) - 1.8\epsilon_o^2 - 5.9\epsilon_o + 1.6] |E_{\alpha}|^2 + (4.3\epsilon_o^2 + 17\epsilon_o - 4.0) |E_{\gamma}|^2 \right), \quad (13)$$

where

$$A_2 = (32\epsilon_o^2)^{-1} \left[(\epsilon_o - 1) \left(\frac{\epsilon_o + 2}{3} \right) \right]^2 k_B T \kappa \xi^{-2} \omega_o^2 V_s, \quad (14)$$

$$D_2 = \frac{1}{4\epsilon_o} \left[(\epsilon_o - 1) \left(\frac{\epsilon_o + 2}{3} \right) \right]^2 k_B T \kappa \xi^{-2} \omega_o d_o.$$

As the system approaches to the critical point, the effect of double scattering becomes important and thus the magnitude of D_2 is larger than D_1 by 10^3 - 10^4 in the optical region.

Now, let us discuss DC for each polarized light in the two limiting cases:

(A) When the system is far from the critical point, DCs are given as

$$\gamma_v = \gamma_+ = \gamma_- = \gamma_R = \gamma_L \simeq \frac{2\beta_o k_o (4 - \epsilon_o)}{\alpha_o (\epsilon_o + 2)}, \quad \gamma_h \simeq 0, \quad (15)$$

where the subscript indicates the kind of polarized light defined at the Table. The CIDs perpendicular and parallel to the scattering plane are given as⁵

$$\Delta_x \simeq \frac{2\beta_o k_o (4 - \epsilon_o)}{\alpha_o (\epsilon_o + 2)}, \quad \Delta_z \simeq 0. \quad (16)$$

The term γ_h corresponds to CID in the z direction, while the other terms have the same magnitude of CID in the x direction. However, it should be noted that the mechanism of DC is quite different from that of CID.^{5,7}

(B) If the system approaches very close to the critical point, we obtain

$$\gamma_v = \gamma_+ = \gamma_- \simeq \frac{2\beta_o k_o (4 - \epsilon_o)}{\alpha_o (\epsilon_o + 2)}, \quad \gamma_h \simeq \frac{\beta_o k_o (4.3\epsilon_o^2 + 17\epsilon_o - 4.0)}{\alpha_o (\epsilon_o + 2)},$$

$$\gamma_R \simeq \frac{2\beta_o k_o (4 - \epsilon_o)}{\alpha_o (\epsilon_o + 2)} + 2.5 D_2, \quad \gamma_L \simeq -\frac{2\beta_o k_o (4 - \epsilon_o)}{\alpha_o (\epsilon_o + 2)} + 2.5 D_2, \quad (17)$$

The effect of the double scattering on $\gamma_v = \gamma_+ = \gamma_-$ has been neglected, since the magnitude of the double scattering intensity due to the correlation between one fluctuating quadrupole density and three fluctuating dipole densities is less than the magnitude of the single scattering intensity caused by the correlation of fluctuating quadrupole and dipole densities by about 10^{-3} , unless the system is extremely close to the critical point. Thus, the single scattering plays the most dominant role on $\gamma_v = \gamma_+ = \gamma_-$. For the horizontally linearly polarized light DC due to the double scattering is comparable to $\gamma_v = \gamma_+ = \gamma_-$. There exist two most important terms in the DCs for the circularly polarized lights. One is due to the single scattering and the other is due to the double scattering. The magnitude of D_2 in γ_R and γ_L , which is caused by the correlation of four fluctuating dipole densities, is larger than or at least comparable with the term due to the single scattering. CIDs are⁸

$$\Delta_x \simeq \frac{2\beta_o k_o (4 - \epsilon_o)}{\alpha_o (\epsilon_o + 2)}, \quad \Delta_z \simeq \frac{2\beta_o k_o (4 - \epsilon_o) (-4.9\epsilon_o^2 + 45\epsilon_o - 0.75)}{\alpha_o \epsilon_o (\epsilon_o + 2)}. \quad (18)$$

CID perpendicular to the scattering plane is the same as $\gamma_v = \gamma_+ = \gamma_-$, while the magnitude of γ_h due to the double scattering is comparable with Δ_z . DCs for the circularly polarized lights show quite different phenomena from CIDs.

Acknowledgment. The authors would like to thank the Korean Science and Engineering Foundation for financial support (Grant No. 93-05-00-15).

References

1. Lee, D. J.; Kim, S. K. *J. Chem. Phys.* **1987**, *87*, 1540.
2. Kim, S. K.; Lee, D. J. *J. Chem. Phys.* **1981**, *74*, 359.
3. Einstein, A. *Ann. Phys.(Paris)* **1910**, *33*, 1275.
4. Boots, H. M.; Bedeaux, D.; Mazur, P. *Physica(Utrecht)* **1974**, *A79*, 397.
5. Lee, D. J.; Kim, S. K. *J. Chem. Phys.* **1988**, *88*, 1953.
6. de Figueiredo, I. M. B.; Raab, R. E. *Proc. R. Soc. Lond.*

1981, A375, 425.

7. Shurcliff, W. A. *Polarized light*; Harvard University Press: Cambridge, Massachusetts, U. S. A., 1962.8. There is an error in Δz of ref. 5. The present result is correct.

^1H NMR Study of Pyridine-Type Ligands Coordinated to the Paramagnetic $[\text{Ni}_3(\text{PW}_9\text{O}_{34})_2]^{12-}$ Anion

Han Young Woo, Ji Young Kim, and Hyunsoo So*

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

Received July 31, 1995

^1H NMR spectra of pyridine, α -, β -, and γ -picoline coordinated to the paramagnetic heteropolyanion $[\text{Ni}_3(\text{PW}_9\text{O}_{34})_2]^{12-}$ (P_2Ni_3) are reported. NMR lines are assigned to $[\text{Ni}_3(\text{ptl})_n(\text{PW}_9\text{O}_{34})_2]^{12-}$ ($n=1, 2$ or 3 ; ptl =pyridine-type ligand) on the basis of their $[\text{P}_2\text{Ni}_3]/[\text{ptl}]$ dependence. The formation constants for γ -picoline complexes at 25°C are $K_1=80$, $K_2=610$, and $K_3=190\text{ L mol}^{-1}$. The monopicoline complex has greater affinity for γ -picoline than P_2Ni_3 . A degradation product, $[\text{Ni}_2(\text{WO}_2)(\text{PW}_9\text{O}_{34})_2]^{12-}$, 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 $[\text{SiW}_{11}\text{O}_{39}\text{M}]^{6-}$ ($\text{M}=\text{Co}^{2+}$ 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 $[\text{SiW}_9\text{O}_{37}[\text{Cu}(\text{H}_2\text{O})_3]_3]^{10-}$, which has $[\{\text{Cu}(\text{OH}_2)_3\text{O}_3\}]$ 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 $[\text{SiW}_9\text{O}_{37}\text{Cu}_3(\text{ptl})_n]^{10-}$ 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 $[\text{H}_m\text{SiW}_9\text{O}_{37}\text{Cu}_3(\text{ptl})_n]^{(10-m)-}$ ($n=1, 2$ 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 $[\text{Ni}_3(\text{PW}_9\text{O}_{34})_2]^{12-}$ (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 $[\text{PW}_9\text{O}_{34}]^{9-}$ groups, and each Ni^{2+} ion is in a square pyramidal environment with an aqua ligand at an axial position (Figure 1). Good NMR

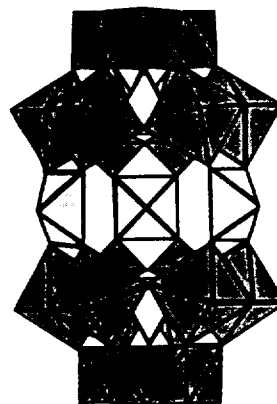


Figure 1. Polyhedral representation of $[\text{Ni}_3(\text{PW}_9\text{O}_{34})_2]^{12-}$. Octahedra represent WO_6 groups, and three square pyramids at the belt represent $\text{Ni}(\text{H}_2\text{O})\text{O}_4$ groups.

spectra with large isotropic shifts have been observed. This paper reports the ^1H NMR spectra of pyridine, α -, β -, and γ -picoline coordinated to P_2Ni_3 .

Experimental

$\text{K}_{12}[\text{Ni}_3(\text{PW}_9\text{O}_{34})_2] \cdot n\text{H}_2\text{O}$ (**1**) and $\text{K}_{12}[\text{Ni}_2(\text{WO}_2)(\text{PW}_9\text{O}_{34})_2] \cdot n\text{H}_2\text{O}$ (**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

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