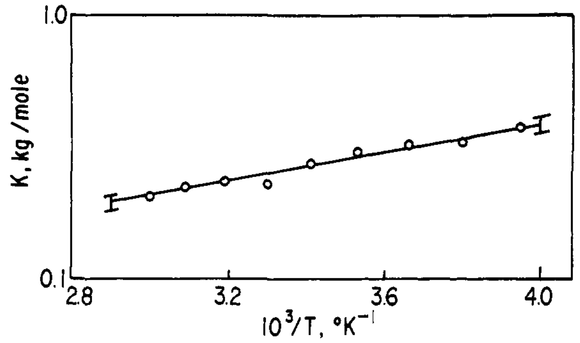

Figure 6. Dependence of the equilibrium constant on the reciprocal of the absolute temperature for DDT–ethyl acetate complex formation. The straight line drawn is the least-squares fit. Brackets show the standard error.

acetate complex, obtained from the plot in Figure 6, are listed in Table II. The enthalpy and entropy changes are both considerably less than those for formation of DDT complexes with the aromatic donors. Weaker binding and a much less specific spatial orientation of the complexing agent are indicated. This type of complex formation appears to depend on both the presence of the polar H—C—C(Cl$_3$) grouping in the DDT molecule and a highly polar complexing agent, such as one for which structures such as R—C(O$^-$)=O$^+$—R can be written. Preliminary measurements on DDT complexes with amides and ureas support these requirements.

A comparison of nmr parameters in the various systems studied is given in Table III. Additional nmr experiments are underway in this laboratory on complexes of DDT with model compounds of biological interest.

Acknowledgments. Dr. William E. Wilson and Dr. James D. McKinney have made many helpful suggestions regarding this work. Dr. David G. Hoel and Mrs. Rose Ferguson have provided valuable assistance.

Electron Paramagnetic Resonance Spectra of Copper(II) and Oxovanadium(IV) Complexes Oriented in Nematic Glasses from Liquid Crystal Solvents

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Abstract: The electron paramagnetic resonance (epr) spectra of a series of copper(II) and oxovanadium(IV) complexes oriented in nematic glasses formed from liquid crystals have been measured. Data are presented which show that anisotropic epr parameters obtained by this convenient, easily interpreted technique compare favorably with published values obtained by dilute single crystal procedures. The results are substantially better than data obtained from randomly oriented frozen solutions or powders. The applicability of available theories concerned with the order present in liquid crystal solutions is discussed as it relates to the precision of the epr parameters. As an illustration of the usefulness of the technique, epr parameters are obtained for ten copper(II) and seven oxovanadium(IV) metal–organic complexes. Molecular orbital coefficients are calculated for the copper(II) species.

Single-crystal electron paramagnetic resonance (epr) spectra have been exceedingly valuable in helping to interpret bonding and structural parameters in paramagnetic transition metal compounds.[2] However, this technique suffers especially from two inherent experimental difficulties, the need to grow suitable single crystals and the requirement that the paramagnetic material be magnetically dilute. This latter problem usually is alleviated by doping an ion or molecule into a diamagnetic host, a procedure that requires the availability of suitable host materials.

We show here that liquid crystals can be used to orient metal–organic complexes in magnetic fields in order to produce epr results that compare well with data obtained from oriented, magnetically dilute single-crystal measurements. Furthermore, the information is achieved without the inherent drawbacks of the single-crystal technique and without precise knowledge of the crystal structure of the complex provided the paramagnetic material of interest is soluble in the nematic liquid crystal and substantial orientational ordering of the solute occurs. A preliminary report of this work has been published.[3]

Experimental Section

Liquid Crystals. Butyl *p*(*p*-ethoxyphenoxycarbonyl)phenyl carbonate was obtained from Eastman Organic Chemicals; this compound has a nematic range from approximately 56 to 87°. VL-1047-N is a room temperature nematic of undisclosed structure obtained from Vari-Light Corp., Cincinnati, Ohio; this material has a nematic range from approximately 10 to 47°. *N*-(*p*-Methoxybenzylidene)-*p*-butylaniline, another room temperature

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(1) Abstracted in part from the thesis of J. D. L. submitted in partial fulfillment for the Ph.D. degree in 1970 at Case Western Reserve University.

(2) (a) B. R. McGarvey, *Transition Metal Chem.*, 3, 89 (1966), and references cited therein; (b) M. J. Weeks and J. P. Fackler, *Inorg. Chem.*, 7, 2548 (1968).

(3) J. P. Fackler and J. A. Smith, *J. Amer. Chem. Soc.*, **92**, 5787 (1970). G. Heppke and F. Schneider, *Ber. Bunsenges. Phys. Chem.*, 75, 61 (1971), obtained similar results with the nematic *N*-(*p*-methoxybenzylidene)-*p*-*n*-butylaniline.

nematic (18–41°) produced by Eastman organic chemicals, has similar physical properties to VL-1047-N (see ref 3).

Nematic Glass Preparation and Spectral Measurements. Spectra were recorded on a Varian (E-3) epr spectrometer operating at 9.1 GHz (X band). Temperature was controlled with a Varian (E-4540) variable temperature unit. The spectrometer frequency and magnetic field were calibrated by employing a series of standards with precisely known g and A values.

In general, the paramagnetic complexes were dissolved in the liquid crystal solvents to about $1\text{-}5 \times 10^{-3}$ M concentration at temperatures above the nematic mesophase. Degassing did not improve the spectra. (The inherent width of the epr lines of the metal complexes generally does not warrant degassing.) The sample contained in a 4-mm o.d. quartz tube is cooled to the nematic temperature range and the liquid crystal solvent is oriented by applying a magnetic field near 6000 G. While maintaining this field the temperature is lowered quickly to −140° to produce a glass. (Slow cooling allows crystallization of the liquid crystal solvent. This leads to disordering and spectra similar to those of isotropic frozen solutions (normal glasses) or powders from which anisotropic epr parameters also may be obtained but with considerably greater difficulty and decreased accuracy.) More efficient orientation can be obtained if the sample is kept in the field at the nematic temperature for at least 10–15 min before cooling to a glass. It also appears desirable to allow the sample to cool from the isotropic phase of the solvent while in the magnetic field.

In favorable cases epr spectra of tetragonal complexes taken at −140° before rotation of the sample tube show contributions due only to in-plane (perpendicular) components of the g and hyperfine tensors. The out-of-plane (parallel) components are obtained by rotation of the nematic glass sample about the epr tube axis 90° with respect to the magnetic field. Realignment of these nematic glasses with field direction was not observed at −140°.

Molecular Orbital Coefficients. Calculations of molecular orbital coefficients were accomplished on a Univac 1108 computer, using a program called MOPAR based on standard procedures.[2]

Metal Complexes. Copper(II) complexes reported in this study were prepared by published procedures[4] and characterized. The oxovanadium(IV) complexes were obtained from F. L. Urbach and R. Farmer of this department. Structural formulas are presented in Figure 1.

Results and Discussion

Ordering Solutes in Liquid Crystals. It has been well established[3,5–18] that liquid crystals can be used as orienting solvents for magnetic resonance studies. Nematic phases are not rigidly fixed but have mobility intermediate between that of a liquid and solid. Thus molecular properties of solute molecules measured in nematic phase solvents which have only short range nematic ordering are orientationally averaged. However, nematic mesophases of liquid crystal solvents are known to assume bulk-phase long-range ordering in strong magnetic fields, with the long molecular axes tending to align parallel to the field.[5,6] Epr spectroscopy has been used extensively as a probe to establish the degree of ordering of the mesophase[6–11] since anisotropic terms in the spin Hamiltonian of the solute are not averaged to zero. For paramagnetic solute molecules having approximately axial g and hyperfine tensors, the Zeeman term of the effective spin Hamiltonian may be written as eq 1, where the various symbols have their usual significance.[19]

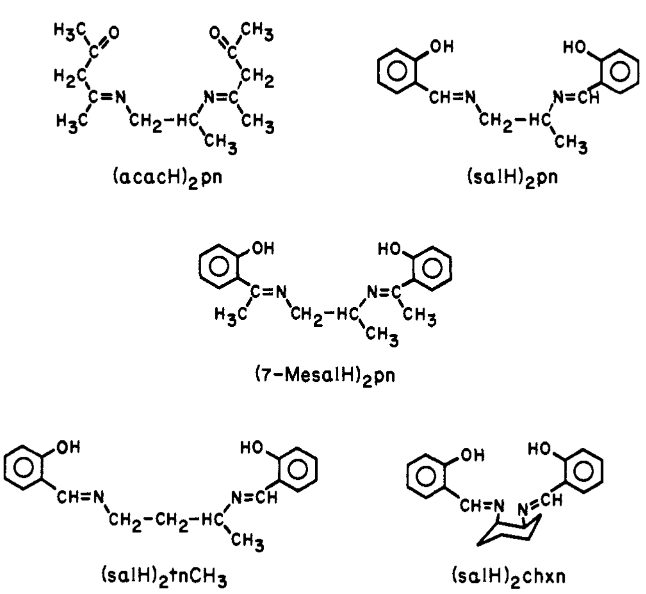

Figure 1. Structural formulas for the protonated ligands of the oxovanadium(IV) complexes studied.

$$\mathcal{H} = g_{\|}\beta H_zS_z + g_{\perp}\beta(H_xS_x + H_yS_y) + A_{\|}S_zI_z + A_{\perp}(S_xI_x + S_yI_y) \quad (1)$$

Glarum and Marshall demonstrated[7] that the *ordering and alignment in magnetic fields of certain solutes dissolved in nematic liquid crystals are often as good as the alignment of the nematic solvent itself.* This of course is dependent upon solute molecular geometry and symmetry. With respect to a magnetic field, a determination of the molecular orientation of the solute requires knowledge of the degree of order of the nematic. Deviations from complete alignment in strong magnetic fields reflect the microordering designated by an ordering parameter $\phi = {}^1/_2(3 \cos^2 \theta - 1)$, where θ is the angle of molecular misalignment. Thus the value of $3 \cos^2 \theta - 1$ is 2.0 and $\phi = 1.0$ when alignment is complete. Fryburg and Gelerinter[12] have noted that "nearly complete alignment" can be obtained at temperatures near the lower end of the nematic mesophase with small amounts (mole fraction $<10^{-3}$) of paramagnetic material dissolved into their liquid crystal.

It has been shown that certain room temperature[11] or viscous[12] nematic solvents containing paramagnetic probes exhibit epr spectra typical of glasses. Schwerdtfeger and Diehl[11] suggest that the epr spectrum of vanadyl acetylacetonate dissolved in a room temperature nematic can be accounted for by a long molecular tumbling time (as in a glass) and a high degree of alignment. Under these conditions perpendicular com-

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Table I. Epr and MO Coefficients for Some Copper(II) Complexes

	Epr parameters[a]				Optical transitions[a]		MO coefficients[a,b]			
Compd[c]	$g_{\parallel}$	$g_{\perp}$	$A_{\parallel}$	$A_{\perp}$	ΔE_1	ΔE_2	α	α'	β	β'
Cu(acac)$_2$	2.256	2.058	0.0192	0.0031	16.3[e]	18.5	0.91 (0.91)	0.48 (0.49)	0.90 (0.91)	0.90 (0.92)
d	2.291	2.058	0.0174	0.0031	16.3	18.5	0.90 (0.90)	0.51 (0.51)	0.96 (0.97)	0.91 (0.92)
Cu(DPM)$_2$	2.263	2.055	0.0186	0.0025	16.4[f]	18.2[f]	0.92 (0.92)	0.48 (0.48)	0.91 (0.92)	0.88 (0.90)
Cu(3-Ph(acac))$_2$	2.253	2.057	0.0193	0.0030	16.9[g]	19.0[g]	0.91 (0.91)	0.48 (0.48)	0.91 (0.92)	0.91 (0.92)
d	2.287	2.057	0.0176	0.0030	16.9	19.0	0.90 (0.90)	0.50 (0.50)	0.97 (0.98)	0.91 (0.93)
Cu(Bzac)$_2$	2.258	2.058	0.0191	0.0030	16.1[g]	18.1[g]	0.91 (0.91)	0.48 (0.48)	0.89 (0.91)	0.89 (0.90)
d	2.295	2.058	0.0170	0.0030	16.1	18.1	0.90 (0.90)	0.51 (0.51)	0.97 (0.98)	0.90 (0.92)
Cu(tropolonate)$_2$	2.259	2.060	0.0193	0.0028	15.0	18.1	0.92 (0.92)	0.46 (0.47)	0.86 (0.87)	0.89 (0.91)
					16.1	18.1	0.92 (0.92)	0.47 (0.47)	0.89 (0.90)	0.90 (0.91)
					15.0	23.1	0.92	0.47	0.96	1.00
d	2.298	2.060	0.0170	0.0028	15.0	18.1	0.90 (0.90)	0.50 (0.50)	0.93 (0.94)	0.91 (0.93)
					16.1	18.1	0.90 (0.90)	0.50 (0.50)	0.96 (0.98)	0.92 (0.93)
					15.0	23.1	0.90 (0.90)	0.50 (0.50)	0.92 (0.95)	1.01 (1.02)
Cu(3-Et(acac))$_2$	2.250	2.056	0.0194	0.0032	15.0	23.1	0.91 (0.91)	0.49 (0.49)	0.86 (0.87)	0.98 (0.98)
					15.0	18.1	0.91 (0.91)	0.49 (0.49)	0.85 (0.87)	0.88 (0.89)
					16.1	18.1	0.91 (0.91)	0.49 (0.49)	0.88 (0.90)	0.88 (0.89)
Cu(S$_2$CN(C$_2$H$_5$)$_2$)$_2$	2.088	2.024	0.0159	0.0042	16.0[h]	20.0	0.74 (0.73)[i]	0.78 (0.78)	0.74 (0.87)	0.84 (0.94)
Cu(MeSal)$_2$	2.219	2.036	0.0206	0.0023	17.1[g]	20.5[g]	0.93 (0.93)[j]	0.44 (0.45)	0.84 (0.85)	0.69 (0.71)
Cu(thiopic)$_2$	2.146	2.033	0.0167	0.0014	16.0	18.5	0.84 (0.84)[k]	0.63 (0.64)	0.77 (0.82)	0.79 (0.84)
				0.0010	16.0	18.5	0.85 (0.85)	0.62 (0.62)	0.76 (0.81)	0.78 (0.83)
				0.0025	16.0	18.5	0.82 (0.82)	0.66 (0.66)	0.79 (0.84)	0.81 (0.86)
				0.0025	16.0	20.0	0.82 (0.82)	0.66 (0.66)	0.79 (0.85)	0.83 (0.88)
Cu(HFacac)$_2$·bipy[l]	2.296	2.052	0.0165	0.0025	16.0	20.0	0.90 (0.90)	0.52 (0.52)	0.97 (0.98)	1.05 (1.06)
				0.0025	16.0	18.5	0.90 (0.90)	0.52 (0.52)	0.97 (0.98)	1.01 (1.02)
				0.0010	16.0	18.5	0.92 (0.92)	0.46 (0.46)	0.94 (0.95)	0.98 (0.99)
				0.0018	16.0	18.5	0.91 (0.91)	0.49 (0.49)	0.96 (0.96)	1.00 (1.00)

[a] See ref 2 for symbols; A in cm^{-1}, ΔE in 10^3 cm^{-1}, $\lambda = -828$ cm^{-1}, $P = 0.036$ cm^{-1}. [b] $V_L = 0.00$ and $V_L = 0.180$ in parentheses, $S = 0.076$, $T_{(n)} = 0.220$. Values in parentheses are for $V_L = 0.180$. [c] acac = pentane-2,4-dione, DPM = dipivaloylmethane, 3-Ph(acac) = 3-phenylpentane-2,4-dione, Bzac = benzoylacetone, 3-Et(acac) = 3-ethylpentane-2,4-dione, MeSal = methylsalicylaldiminate, HFacac = 1,1,1,5,5,5-hexafluoropentane-2,4-dione, thiopic = *N*-phenylthiopicolinamide [H. D. Porter, *J. Amer. Chem. Soc.*, **76**, 127 (1954)], bipy = α,α'-bipyridine. [d] Two epr signals observed suggesting solvent interaction. [e] J. Ferguson, R. L. Belford, and T. S. Piper, *J. Chem. Phys.*, **37**, 1369 (1962); T. S. Piper and R. L. Belford, *Mol. Phys.*, **5**, 169 (1962). [f] F. A. Cotton and J. J. Wise, *J. Amer. Chem. Soc.*, **88**, 3451 (1966). [g] R. L. Belford and J. W. Carmichael, *J. Chem. Phys.*, **46**, 4515 (1967); new optical assignments made recently by M. A. Hutchinson and R. L. Belford, *Inorg. Chem.*, **10**, 984 (1971), modify α and β slightly and suggest that γ may be as low as 0.72. [h] Reference 2. [i] $V_L = 0.450$ in parentheses, $S = 0.125$, $T_{(n)} = 0.350$. [j] $V_L = 0.135$ in parentheses, $S = 0.084$, $T_{(n)} = 0.276$. [k] $V_L = 0.270$ in parentheses, $S = 0.109$, $T_{(n)} = 0.342$. [l] The $g_{\parallel}$ and $A_{\parallel}$ values compare favorably with the single crystal data reported by M. V. Veides, G. H. Schreiber, T. E. Gough, and G. J. Palenik, *J. Amer. Chem. Soc.*, **91**, 1859 (1969).

ponents of the g tensors and hyperfine splitting constants can be obtained directly. Parallel parameters could be obtained by reorientation of the nematic alignment by 90° with respect to the magnetic field by application of a strong transverse electric field. Sackmann and Krebs[15] obtained similar results with an organic free radical from frozen anisotropic glasses produced by alignment of a liquid crystal employing an electric field. The striking feature of the nematic glass technique described here is that complete orientational ordering of the solute is not required in order to get enhancement of the relative intensities of the anisotropic epr components and consequently their increased precision.

Copper Complexes. The magnetic parameters extracted from the epr spectra of a number of copper(II) complexes are listed in Table I. Spectra taken with alignment of the long molecular axis parallel to the magnetic field show contributions to the intensity function from perpendicular (in-plane) components, $g_{\perp}$ and $A_{\perp}$, of the magnetic tensors, Figures 2B, 3A, 4A, and 5A. The "parallel" (out-of-plane) anisotropic components, $g_{\parallel}$ and $A_{\parallel}$, are nearly completely absent (perpendicular to the field so that $\cos\theta$ approaches zero). This absence of $g_{\parallel}$ and $A_{\parallel}$ components allows a very precise determination of $g_{\perp}$ and $A_{\perp}$ to be made. Out-of-plane components of the magnetic tensors are obtained by rotation of the sample tube about its axis by 90° with respect to the magnetic field. As seen in Figures 2C, 3B, 4B, and 5B the rotation causes an enhancement of the intensity of the out-of-plane, $g_{\parallel}$, components and diminishes the intensity of the in-plane, $g_{\perp}$, components. The extent of this orientation effect is illustrated by examination of parallel components at several orientations (Figure 6 and 7).

The anisotropic epr parameters obtained by this technique compare favorably with those values obtained by dilute single-crystal methods (Table II, ref 3) and are much better than values obtained from randomly oriented frozen solutions or powders.

Solute Alignment. Theories used to describe epr results in liquid crystals[7-10] are not applicable to nematic glasses or low temperature[11] or viscous[12] nematic mesophase solutions. Consequently we present here in some detail the theory as it pertains to a tetragonal copper(II) complex studied in a glass phase nematic.

The spin Hamiltonian for copper(II) complexes can be expressed as the sum of two parts $\mathcal{H} = H^{(0)} + H^{(2)}$ where $H^{(0)}$ is invariant under rotation and corresponds to the isotropic spin Hamiltonian

$$H^{(0)} = g\beta H_z S_z + aI\cdot S$$

The second term contains all second rank tensor interactions and vanishes under isotropic treatment, with loss of considerable information concerning the species under investigation. In the nematic phase only

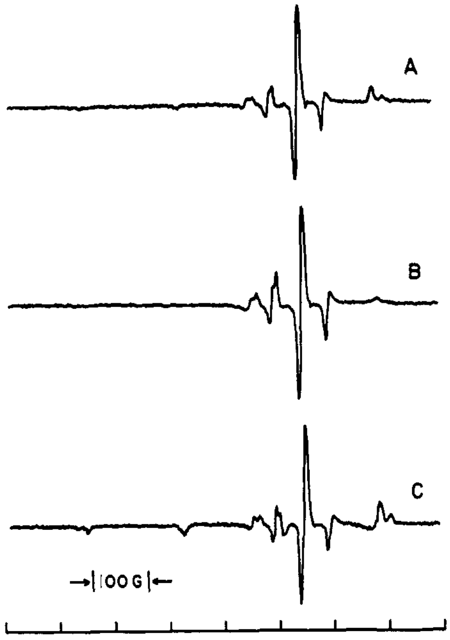

Figure 2. Epr spectra of copper(II) diethyldithiocarbamate at −140°: A, normal frozen solution using 50% chloroform–50% toluene; B, oriented nematic glass using VL-1047-N, 0° rotation; C, oriented nematic glass using VL-1047 N, 90° rotation.

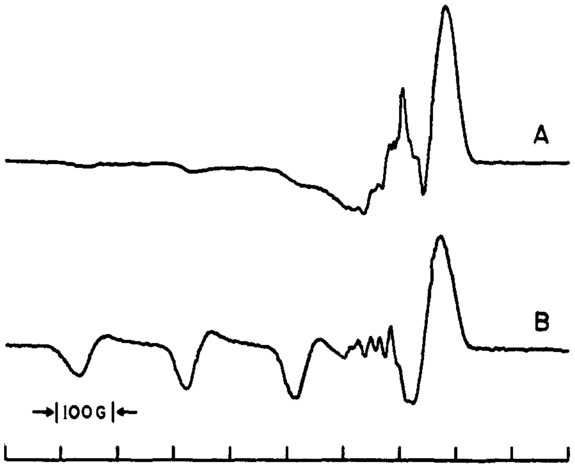

Figure 3. Epr spectra of bis(*N*-methylsalicylaldiminato)copper(II) oriented in a nematic glass (VL-1047-N) at −140°: A, 0° rotation; B, 90° rotation.

certain terms in $H^{(2)}$ still average to zero, and $H^{(2)}$ reduces to an expression containing anisotropic information, but complicated by an orientation dependence[12]

$$H^{(2)}_{\text{nematic}} = {}^1/_3[(g_{\parallel} - g_{\perp})\beta H_z + (A_{\parallel} - A_{\perp})]\langle 3\cos^2\theta - 1\rangle S_z$$

If $g_{\parallel} - g_{\perp}$ is small, absorption lines can be approximated by

$$\mathcal{H} = 2H_0/g - am_I - [(A_{\parallel} - A_{\perp})/3]\langle 3\cos^2\theta - 1\rangle m_I$$

In order to describe the orientational dependence, an ordering parameter ϕ_z can be defined as

$$\phi_z = {}^1/_2(3\cos^2\theta - 1)$$

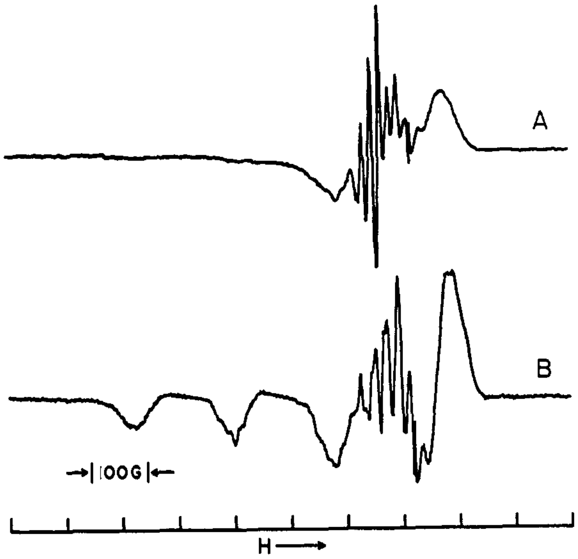

Figure 4. Epr spectra of bis(*N*-phenylthiopicolamido)copper(II) oriented in a nematic glass (VL-1047-N) at −140°: A, 0° rotation; B, 90° rotation.

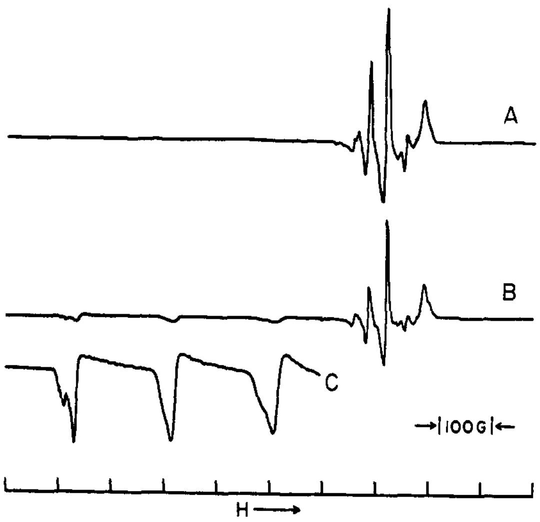

Figure 5. Epr spectra of bis(3-phenyl-2,4-pentanediono)copper(II) oriented in a nematic glass (butyl *p*-[*p*-ethoxyphenoxycarbonyl]phenyl carbonate) at −140°: A, 0° rotation; B, 90° rotation; C, same as B, at ten times the amplitude.

This can be related to the experimental epr parameters

$$\phi_z = {}^1/_2(\langle a\rangle - a)/(a - A_{\perp})$$

where $\langle a\rangle$ is the effective hyperfine splitting constant, a is the isotropic splitting constant, and $A_{\perp}$ is the in-plane component of the hyperfine tensor.

The ordering parameter, ϕ_z, is a direct measure of the alignment of the paramagnetic solute. When there is completely random orientation (isotropic solution or isotropic glass), ϕ_z is zero, whereas if the molecular z axis of the solute is aligned, the maximum value of ϕ_z is unity at $\theta = 0$ (the out-of-plane axis of the molecule parallel to the magnetic field) and the minimum value is $-{}^1/_2$ at $\theta = \pi/2$ (the out-of-plane molecular axis perpendicular to the field).

Employing the oriented nematic model, *complete* alignment is suggested, at least for copper(II) diethyldithiocarbamate, in nematic glasses[3] by comparison

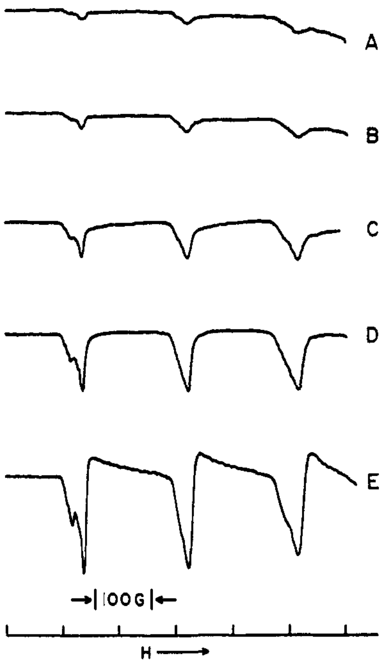

Figure 6. Low-field portion of epr spectra of bis(3-phenyl-2,4-pentanediono)copper(II) oriented in a nematic glass at −140°: A, 0° rotation; B, 30° rotation; C, 45° rotation; D, 60° rotation; E, 90° rotation.

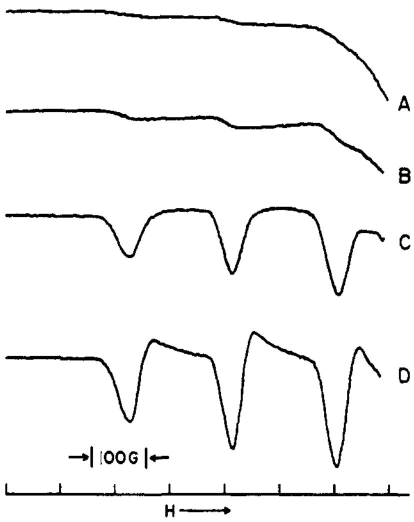

Figure 7. Low-field portion of epr spectra of bis(*N*-methylsalicylaldiminato)copper(II) oriented in a nematic glass at −140°: A, 0° rotation; B, 30° rotation; C, 60° rotation; D, 90° rotation.

of single crystal epr anisotropic parameters and the nematic glass values. Thus at 0° sample tube rotation $\langle a \rangle = A_\perp$ and therefore $\phi_z = -0.5$. This means the *average orientation* of the out-of-plane axis of the copper complex must be 90° with respect to the magnetic field. For $\phi_z = -0.5$ all rotation orientations about one in-plane axis (long axis) parallel to the field can be possible. This leaves the *z* axis always perpendicular to the direction of the magnetic field.

The above model deals with an *average* orientation of more or less freely tumbling molecules and does not adequately apply to rigidly oriented molecules. A better model is that developed for glassy epr spectra. The randomly oriented frozen model has been discussed extensively by Malley,[20] Sands,[21] and Kivelson and Neiman.[22] The nematic glass problem is but a special case of the randomly oriented model where θ is near $\pi/2$ at 0° rotation of the sample tube. For the random case the number of molecules $\mathrm{d}N$ between θ and $\theta + \mathrm{d}\theta$ is proportional to $\sin\theta\,\mathrm{d}\theta$, where θ for an axial system is the angle between the symmetry axis and the direction of the magnetic field. In order to describe a proper ordering parameter in terms of small deviations from alignment parallel to the field, a distribution function may be introduced into the expression for the "glass type" spectrum. Schwerdtfeger and Diehl[11] use a distribution function $\mathrm{f}(\theta)$ similar to one employed by Meier and Saupe[23] in studies of dielectric relaxation times in nematic mesophases, to obtain an expression

$$\mathrm{d}N = N_0\mathrm{f}(\theta)\sin\theta\,\mathrm{d}\theta \qquad (2)$$

Since the transition probability is independent of orientation, the absorption intensity in the magnetic field between H and $H + \mathrm{d}H$ is expressed by

$$\mathrm{d}N/\mathrm{d}H = (\mathrm{d}N/\mathrm{d}\theta)(\mathrm{d}\theta/\mathrm{d}H)$$

where $\mathrm{d}\theta/\mathrm{d}H$ is calculated from the spin Hamiltonian for the glassy state[22] and $\mathrm{d}N/\mathrm{d}\theta$ is given by eq 2.

Absorptions occur at various values of the magnetic field expressed approximately by [22,24]

$$H = h\nu/g\beta - Am_I/g\beta$$

where

$$g = (g_{\parallel}^2\cos^2\theta + g_\perp^2\sin^2\theta)^{1/2}$$

$$A = (A_{\parallel}^2g_{\parallel}^2\cos^2\theta + A_\perp^2g_\perp^2\sin^2\theta)^{1/2}/g$$

The absorption intensity is then roughly given by[22,24]

$$\mathrm{d}N/\mathrm{d}H = \frac{N_0g^2}{2\cos\theta}\left\{(g_{\parallel}^2 - g_\perp^2)H^0 + \frac{m_I}{\beta}\left[\frac{A_{\parallel}^2g_{\parallel}^2 - A_\perp^2g_\perp^2}{Ag} - \frac{2A(g_{\parallel}^2 - g_\perp^2)}{g}\right]\right\}^{-1}$$

where $H^0 = h\nu/g\beta$. It is seen that $\mathrm{d}N/\mathrm{d}H$ becomes infinite at $\theta = 90°$, $H = (h\nu/g_\perp\beta) - (A_\perp m_I/g_\perp\beta)$; and there is an abrupt absorption at $\theta = 0°$

$$H = h\nu/g_{\parallel}\beta - A_{\parallel}m_I/g_{\parallel}\beta$$

Schwerdtfeger and Diehl modify this randomly oriented model by inclusion of a distribution function

$$(\mathrm{d}N/\mathrm{d}H)_{\text{oriented}} = (\mathrm{d}N/\mathrm{d}H)_{\text{random}}\mathrm{f}(\theta)$$

where[5,23]

$$\mathrm{f}(\theta) = C\exp[-(q/kT)\sin^2\theta]$$

but the results obtained are disappointing. The distribution function may be inadequate for a completely frozen model.

It is expected that spectra can be fitted by an expression such as that used by Malley[20]

$$I(H) = \frac{1}{2}\int_0^\pi \frac{1}{\Delta H(\theta)}\mathrm{f}\left(\frac{H - H_0(\theta)}{\Delta H(\theta)}\right)\sin\theta\,\mathrm{d}\theta$$

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(20) M. M. Malley, *J. Mol. Spectrosc.*, **17**, 210 (1965).

(21) R. H. Sands, *Phys. Rev.*, **99**, 1222 (1955).

(22) R. Neiman and D. Kivelson, *J. Chem. Phys.*, **35**, 149, 156 (1961).

(23) G. Meier and A. Saupe, *Mol. Cryst.*, **1**, 515 (1966).

(24) L. D. Rollmann and S. I. Chan in "Electron Spin Resonance of Metal Complexes," T. F. Yen, Ed., Plenum Press, New York, N. Y., 1969, p 175.

using small values of dθ close to 0 and 90°, depending on sample tube rotation. In any event, inspection of the absorption expressions for glassy spectra clearly shows that the results obtained by the nematic glass technique are explained by an angle θ very close to 90°. Analysis of the out-of-plane components of the g and hyperfine tensors close to $\theta = 0$ or 90° generally shows the misalignment to be minor.

Since absorption occurs[22,24] for tetragonal complexes in glassy samples at fields corresponding to $g_\perp$ ($\theta = 0°$) and $g_{||}$ ($\theta = 90°$), a small degree of solute randomness in the nematic glass merely causes the appearance of weak $g_{||}$ and $A_{||}$ lines (usually well removed from $g_\perp$) in the 0° sample tube rotation. These lines seldom interfere with an accurate estimation of $g_\perp$ (and $A_\perp$). Rotation of the sample tube toward 90° generally gives an obvious increase in the intensity of $g_{||}$ even for compounds having molecular dimensions which are less tetragonal than those of the compounds reported here. The degree of alignment (as long as some alignment occurs) is not a critical factor required for the determination of anisotropic epr tensors by this technique.

Molecular Orbital Coefficients. If a simple molecular orbital model for metal–ligand bonding is assumed, it is possible to obtain orbital mixing coefficients from epr parameters and therefore a measure of metal–ligand bond covalency. These coefficients are calculated from epr and optical data according to the procedure of Maki and McGarvey,[2a,19,25] if the relative orientation of molecular and magnetic axes is known. For single-crystal studies the orientational relationship is determined from detailed X-ray crystal structures. The nematic glass technique cannot always be used to accurately evaluate the directional correspondence of the $g_{||}$ tensor with the principal (tetragonal) axial direction of the molecule and clearly cannot define the directions of the in-plane tensors in a slightly rhombic molecule. However, recognizing these limitations, molecular orbital coefficients for tetragonal complexes generally can be obtained which are comparable with those achieved from single crystal work where mosaic spread contributes to inaccuracies. The degree of molecular alignment can be estimated from the appearance (or lack of it) of the $g_{||}$ component in the 0° spectrum. With absent or very weak $g_{||}$ lines it can be assumed that the direction of the principal molecular axis corresponds to that of the $g_{||}$ tensor within a few per cent. Since $g_{||}$ and $g_\perp$ components should have comparable intensities if no molecular ordering occurs, the appearance of weak $g_{||}$ lines in the 0° spectrum probably indicates some molecular disordering rather than a misalignment between the magnetic tensor and the molecular axis.

Molecular orbitals for copper(II) complexes in D_{4h} symmetry are[26,27]

$$\mathrm{B_{1g}} = \alpha \mathrm{d}_{x^2-y^2} - \alpha^1(-\sigma_x{}^{(1)} + \sigma_y{}^{(2)} + \sigma_x{}^{(3)} - \sigma_y{}^{(4)})/2$$

$$\mathrm{B_{2g}} = \beta \mathrm{d}_{xy} - (1-\beta^2)^{1/2}(\mathrm{p}_y{}^{(1)} + \mathrm{p}_x{}^{(2)} - \mathrm{p}_y{}^{(3)} - \mathrm{p}_x{}^{(4)})/2$$

$$\mathrm{E_g} = \begin{cases} \gamma \mathrm{d}_{xz} - (1-\gamma^2)^{1/2}(\mathrm{p}_z{}^{(1)} - \mathrm{p}_z{}^{(3)})/\sqrt{2} \\ \gamma \mathrm{d}_{yz} - (1-\gamma^2)^{1/2}(\mathrm{p}_z{}^{(2)} - \mathrm{p}_z{}^{(4)})/\sqrt{2} \end{cases}$$

The square of the orbital coefficients can be related to the degree of covalent character of the metal–ligand bonds (0.5 for completely covalent to 1.0 for completely ionic bonding). Assuming a $^2\mathrm{B_{1g}}$ ground state, the spin Hamiltonian can have the following parameters in D_{4h} symmetry, after making some assumptions[2,28] such as neglect of π overlap.

$$g_{||} = 2.0023 - \left(\frac{8\lambda}{\Delta E_1}\right)\left(\alpha\beta - \frac{V_\mathrm{L}\alpha'\sqrt{1-\beta^2}}{2}\right)\left(\alpha\beta - \alpha'\beta S - \alpha'\frac{\sqrt{1-\beta^2}}{2}T_{(n)}\right) \quad (3)$$

$$g_\perp = 2.0023 - \left(\frac{2\lambda}{\Delta E_2}\right)\left(\alpha\gamma - \frac{V_\mathrm{L}\alpha^1\sqrt{1-\gamma^2}}{\sqrt{2}}\right)\left(\alpha\gamma - \alpha'\gamma S - \alpha\frac{\sqrt{1-\gamma^2}}{\sqrt{2}}T_{(n)}\right) \quad (4)$$

$$A_{||} = P\left(-\kappa - \frac{4}{7}\alpha^2 - \left[\frac{8\lambda\alpha\beta}{\Delta E_1}\right]\left[\alpha\beta - \frac{V_\mathrm{L}\alpha'\beta'}{2}\right] - \left[\frac{6}{7}\frac{\lambda\alpha\gamma}{\Delta E_2}\right]\left[\beta\gamma + \frac{V_\mathrm{L}\beta'\gamma'}{\sqrt{2}}\right]\right) \quad (5)$$

$$A_\perp = P\left(-\kappa + \frac{2}{7}\alpha^2 - \left[\frac{11}{7}\frac{\lambda\alpha\gamma}{\Delta E_2}\right]\left[\alpha\gamma + \frac{V_\mathrm{L}\beta'\gamma'}{\sqrt{2}}\right]\right) \quad (6)$$

In these expressions for anisotropic epr parameters, λ is the spin–orbit coupling constant for the free ion, ΔE_1 is the $x^2 - y^2 \rightarrow xy$ transition energy and ΔE_2 the $x^2 - y^2 \rightarrow xz$ transition energy, $T_{(n)}$ is an integral over ligand functions, S is the group overlap integral between metal d orbitals and ligand hybrid σ orbitals, and V_L is the ratio of one-electron spin–orbit coupling constant on the ligand atom to that on the metal ion. The expressions are similar to those used by Gersmann and Swalen[19] except that terms involving V_L have been included to account for ligand spin–orbit interaction.[2]

An expression involving the hyperfine interaction is obtained by substitution of eq 3 and 4 into eq 5

$$A_{||} = P\left[-\frac{4}{7}\alpha^2 - \kappa + (g_{||} - 2.0023) + \frac{3}{7}(g_\perp - 2.0023) - \frac{8\lambda}{\Delta E_1}\mathrm{f}(\beta) - \frac{6\lambda}{7\Delta E_2}\mathrm{f}(\gamma)\right] \quad (7)$$

where

$$\mathrm{f}(\beta) = \left[\alpha\beta - \frac{V_\mathrm{L}\alpha'\sqrt{1-\beta^2}}{2}\right]\left[\alpha'\beta S + \frac{\alpha'\sqrt{1-\beta^2}T_{(n)}}{2}\right]$$

$$\mathrm{f}(\gamma) = \left[\alpha\gamma - \frac{V_\mathrm{L}\alpha'\sqrt{1-\gamma^2}}{2}\right]\left[\alpha'\gamma S + \frac{\alpha'\sqrt{1-\gamma^2}T_{(n)}}{2}\right]$$

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(25) A. H. Maki and B. R. McGarvey, *J. Chem. Phys.*, 29, 31 (1958).

(26) The expressions used by McGarvey[2a] differ somewhat from those used here due to a rotation of the axis system by $\pi/4$. Reduction to D_{2h} symmetry would give equations that differ only in molecular orbital coefficient labels and values of excitation energies, although the full expression would require a difference in overlap for x and y out-of-plane π bonding.

(27) The molecular orbital coefficient labeling convention used here[2b] should not be confused with those of other workers.[2a] Correlation of the various sets of coefficients can be easily seen by referring back to the proper molecular orbital expression.

(28) R. Pettersson and T. Vanngard, *Ark. Kemi*, 17, 249 (1961).

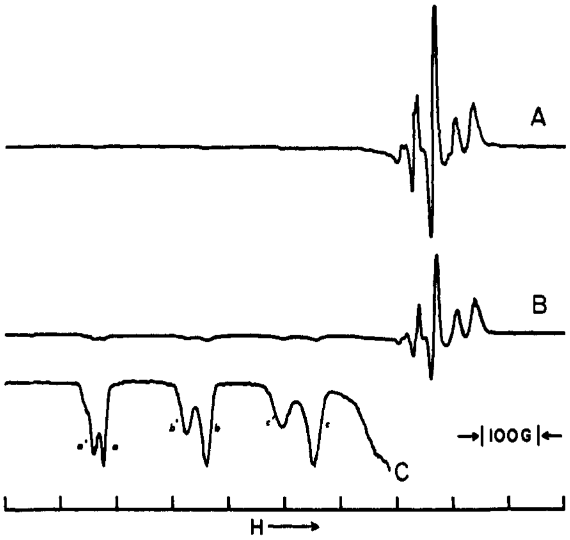

Figure 8. Epr spectra of bis(3-phenyl-2,4-pentanediono)copper(II) oriented in a nematic glass (VL-1047-N) at −140°: A, 0° rotation; B, 90° rotation; C, same as B, at ten times the amplitude.

where P is the free ion dipole term (proportional to $1/r^3$). Equation 7 is advantageous in that the terms in $f(\beta)$ and $f(\gamma)$ are small, allowing approximate values of the expression without knowledge of electronic transitions.[29a] Setting $V_L = 0.0$, these equations are the corrected equations of Kuska and Rogers,[29b] with γ equal to their δ.

The orbital coefficients for σ bonding can be readily determined from nematic glass epr data. However, for π bonding the results are often complicated by uncertainties in energies and assignments of electronic transitions. While it is beyond the scope of this paper to discuss in detail the electronic assignments of the various complexes studied, reasonable literature values have been used in the calculations of molecular orbital coefficients presented.

The coefficients in Table I were calculated using nematic glass epr spectra recorded in this work and published data for electronic transitions, using a computer program, MOPAR, which first calculates an initial α from the approximate expression

$$A_{\parallel} = P\left[-\frac{4}{7}\alpha^2 - \kappa + (g_{\parallel} - 2.0023) + \frac{3}{7}(g_{\perp} - 2.0023) + 0.04\right]$$

This initial α is used in eq 3 and 4 to obtain β and γ, which are in turn used to calculate α employing eq 7. This cyclic process is continued until all the values of α, α', β, and γ converge. The values of S, $T_{(n)}$, V_L, P, and λ used are those generally accepted.[2b,22] The calculated coefficients show the expected trends and are consistent with previous values for these and similar complexes.[2b,19,30] The coefficients for the various oxygen chelates are very similar; those which differ probably do so because of incorrect assignment of electronic transitions. It is to be noted that values of α depend strongly on the epr parameters and almost not at all upon optical transitions.

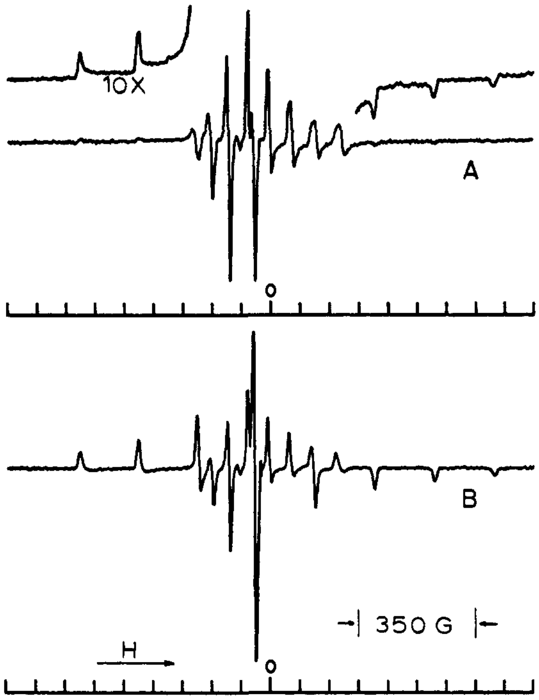

Figure 9. Epr spectra of VO(sal)₂pn oriented in a nematic glass at −150°: A, 0° rotation; B, 90° rotation.

Solvent Perturbation of Spectra. Several copper β-keto enolates gave two sets of epr values (Table I, Figure 8), presumably due to the presence of two differently solvated species. The solvent dependence is demonstrated by comparison of Figures 5 and 8. Porte and coworkers[31] have also observed this phenomenon in chloroform–toluene glasses and have attributed it to axial interaction between chloroform and the open coordination site on the 4-coordinate copper complexes. In the present study two sets of parallel anisotropic components are observed for certain complexes, but the perpendicular components for the differently solvated species are not resolved. (However, very little difference is observed between the calculated α coefficients for the two species. Differences between β and γ coefficients should be accepted only with caution due to lack of knowledge about the proper optical transitions of the solvated species.) The high-field parallel bands observed for $Cu(3\text{-}Ph(acac))_2$, Figure 8 (denoted a, b, c), can be assigned to the unperturbed complex by comparison of epr parameters and molecular orbital coefficients with other systems. The species which gives rise to peaks a′, b′, and c′ is probably a solvent-perturbed species, although we have no direct evidence for this point. Both species, however, must be similarly aligned with respect to the magnetic field, as the relative intensities of parallel components of the two are independent of sample rotation angle.

For bis(hexafluoro-2,4-pentanediono)bipyridinecopper(II), $Cu(HFacac)_2$, bipy, and bis(*N*-phenylthiopicolinamidato)copper(II), $Cu(thiopic)_2$ (Figure 4), $A_{\perp}$ cannot be readily determined because of superposition

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(29) (a) H. A. Kuska and M. T. Rogers in "Radical Ions," E. T. Kaiser and L. Kevan, Ed., Interscience, New York, N. Y., 1968, Chapter 13; (b) H. A. Kuska and M. Rogers, "Spectroscopy in Inorganic Chemistry," Vol. 2, Academic Press, New York, N. Y., 1971, p 175.

(30) M. A. Hitchman and R. L. Belford in "Electron Spin Resonance of Metal Complexes," T. F. Yen, Ed., Plenum Press, New York, N. Y., 1969, p 97.

(31) S. Antosik, N. M. D. Brown, A. A. McConnell, and A. L. Porte, *J. Chem. Soc. A*, 545 (1968).

of nitrogen superhyperfine lines. As is shown in Table I, however, uncertainties in $A_\perp$ cause only very small changes in the molecular orbital coefficients.

Some copper(II) complexes of interest are not sufficiently structurally anisotropic to be oriented by the nematic solvent. Also, we have found that in certain cases ordering may occur with nonprincipal molecular or magnetic axes parallel to the long axes of the liquid crystal molecules. These situations appear to be fairly uncommon, however, and usually can be anticipated by a consideration of the structural anisotropy of the molecule of interest.

Oxovanadium(IV) Complexes. Figure 9 shows a representative epr spectrum of a vanadyl complex in an oriented glass nematic. Figure 9A is taken at −150° with no sample rotation. The bands associated with $A_\parallel$ and $g_\parallel$ are almost completely absent and the bands arising from $A_\perp$ and $g_\perp$ absorptions are sharp and well defined. Near the center of the spectrum is a strong line with a lower intensity band slightly upfield from it. Upon rotating the epr tube 90° about its long axis and observing the spectrum under identical instrument conditions, the parallel bands appear with a much higher intensity, Figure 9B. In addition, the two bands in the central region of the spectrum have interchanged intensities enabling ready assignment.

The $g_\parallel$ and $g_\perp$ values (Table II) were calculated from the equations given by Kuska and Rogers.[29]

for $\mathbf{g}_\parallel$

$$H_\parallel = \mathbf{H}_{(m)} + A_\parallel \cdot m + \frac{A_\perp^2[\mathrm{I}(\mathrm{I}+1) - m^2]}{2\mathbf{H}_{(m)}} \tag{8}$$

and for $\mathbf{g}_\perp$

$$H_\perp = \mathbf{H}_{(m)} + A_\perp m + \frac{(A_\parallel^2 + A_\perp^2)[\mathrm{I}(\mathrm{I}+1) - m^2]}{4\mathbf{H}_{(m)}} \tag{9}$$

where $\mathbf{H}_{(m)}$ is the value of the magnetic field at the line being measured, m is the value of the magnetic quantum number of this line, and $\mathbf{I}$ is the spin of the nucleus ($\mathbf{I} = {}^7/_2$ for vanadium). The calculated magnetic field value is used to determine $\mathbf{g}$. It was found that the $\mathbf{g}_\parallel$ value calculated for the $m = -{}^1/_2$ line is statistically outside the standard deviation of the other values. This is probably due to the extra absorption calculated to be present.[22]

The epr parameters obtained for the oxovanadium(IV) complexes studied are presented in Table II. Compared with single-crystal work and studies in various organic solvents, the data suggest that the liquid crystal solvent interacts weakly with the complexes. The ability of oxovanadium(IV) complexes to interact axially with basic solvents is well known.[32]

The epr and optical absorption spectra of vanadyl acetylacetonate have been extensively investigated.[32] This complex is one of the first inorganic compounds to be used as a paramagnetic probe for liquid crystal epr. The $\mathbf{g}$ and $\mathbf{A}$ values associated with this complex are well established with an anisotropy of the in-plane parameters being reported.[33]

The nematic glass spectrum of VO(acac)$_2$ at −150° shows one $\mathbf{g}$ and $\mathbf{A}$ value (Figure 10A) without sample

Table II. Epr Parameters for Oxovanadium(IV) Complexes Studied[a]

Compd	$A_\parallel$[b]	A_x	$A_\perp$	A_y	A_0	$g_\parallel$[c]	g_x	$g_\perp$	g_y	g_0	Medium[d]
VO(acac)$_2$	168.4	63.1		58.4	(97.0)	1.9461 ± 0.0018	1.9752 ± 0.0018		1.9823 ± 0.0061	1.9678)	LC[e]
	170.5		67.0		97.8	1.9439 ± 0.0082		1.9827 ± 0.0009		1.9672	CT[e]
	170.5	63.5		59.6	98.4	1.943	1.979		1.985	(1.969)	T[f]
VO(acac)$_2$pn	166.4		57.4		94.0	1.9558 ± 0.0044		1.9811 ± 0.0016		(1.9726)	LC[e]
	164.8		56.1		91.0	1.9573 ± 0.0055		1.9815 ± 0.0028		1.9759	CT[e]
	162.2–166.2		56.5–59.3		92.2–95.2	1.952–1.956		(1.984–1.986)		1.974–1.975	V[g]
VO(sal)$_2$pn	162.3		58.3		(93.5)	1.9517 ± 0.0007		1.9838 ± 0.0012		(1.9731)	LC[e]
	161.8		55.7		90.0	1.9536 ± 0.0032		1.9843 ± 0.0021		1.9728	CT[e]
	164.7		(57.5)		92.7–93.8	1.949		(1.985)		1.973	V[h]
VO(sal)$_2$(+)pn	162.7		57.8		(93.2)	1.9516 ± 0.0004		1.9818 ± 0.0012		(1.9717)	LC
	160.7		55.7		92.4	1.953 ± 0.0032		1.9843 ± 0.0021		1.9728	CT[e]
VO(7-Mesal)$_2$(+)pn	161.4		55.8		(92.8)	1.9535 ± 0.0033		1.9848 ± 0.0048		(1.9741)	LC[e]
	160.8		55.1		89.2	1.9541 ± 0.0017		1.9831 ± 0.0015		1.9733	CT[e]
	164.7		57.5		92.0–92.2	1.949		(1.985)		(1.974)	V[h]
VO(sal)$_2$(+)chxen	163.1		57.1		(92.8)	1.9535 ± 0.0033		1.9844 ± 0.0048		(1.9741)	LC[e]
	160.7		55.7		89.2	1.9546 ± 0.0038		1.9844 ± 0.0021		(1.9746)	CT[e]
VO(sal)$_2$(+)tnCH$_3$	162.7	58.8		55.1	(92.5)	1.9507 ± 0.0012	1.9827 ± 0.0020		1.9842 ± 0.0025	(1.9725)	LC[e]
	162.7		55.1		90.8	1.9522 ± 0.0041		1.9842 ± 0.0021		1.9728	CT[e]
	157.6		54.3		88.3	1.9510 ± 0.0033		1.979 ± 0.0022		1.9722	PT[e]

[a] Values in parentheses are calculated rather than measured. [b] All hyperfine values are in cm^{-1} × 10^3; estimated error between measurements is ±1 × 10^{-4} cm^{-1}. [c] Estimated error between g value measurements is ±0.001; error estimates given are standard deviations from values calculated by use of eq 8 or 9. [d] LC = liquid crystal, CT = 40% chloroform–60% toluene, T = toluene, V = various solvents, PT = 40% pyridine–60% toluene. [e] This work. [f] Reference 32. [g] L. J. Boucher and T. F. Yen, *Inorg. Chem.*, **7**, 731 (1968). [h] L. J. Boucher and T. F. Yen, *ibid.*, **8**, 689 (1969).

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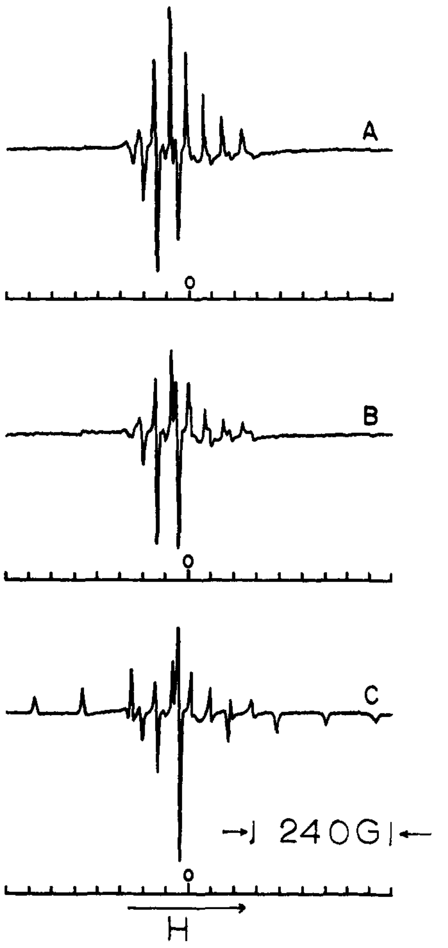
(32) J. Selvin, *Coord. Chem. Rev.*, **1**, 293 (1966).

(33) R. Wilson and D. Kivelson, *J. Chem. Phys.*, **44**, 154 (1966).



Figurd 10. Epr spectra of VO(acac)$_2$ oriented in a nematic glass at −150°: A, 0° rotation; B, 45° rotation; C, 90° rotation.

tube rotation. The 90° spectrum (Figure 10C) shows enhanced parallel bands and somewhat different **g** and **A** values. These values compare favorably with the parameters of Wilson and Kivelson[33] and demonstrate that it is possible to resolve anisotropic in-plane parameters by these liquid crystal methods. The spectra, taken at a 45° rotation of the nematic glass, in the crystallized nematic and in a chloroform–toluene glass are identical. Superposition of the 0 and 90° nematic glass spectra shows a band for band correlation in the parallel and perpendicular regions with the 45° spectrum and in addition strikingly shows the resolved anisotropic perpendicular values.

Another oxovanadium(IV) complex investigated was VO(sal)$_2$(+)tnCH$_3$, Figure 11. The crystal structure[34] of *N,N'*-propylenebis(salicylaldiminato)oxovanadium(IV), VO(sal)$_2$tn, shows the vanadium(IV) atom to be very close to the plane of the ligand oxygen and nitrogen atoms (0.31 Å). The structure also shows the compound to be polymeric with the oxygen from one V–O bond occupying the sixth position of another oxovanadium(IV) complex. This polymeric compound is sparingly soluble in most solvents. The (sal)$_2$(+)tnCH$_3$ derivative is more soluble, however, although its solubility was not sufficient to obtain meaningful molecular weight measurements in solution. The compound is probably polymeric in the solid state (having similar

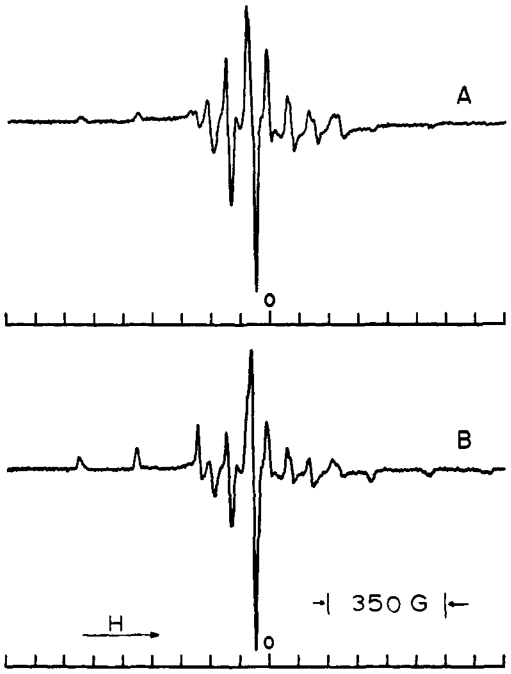


Figure 11. Epr spectra of VO(sal)$_2$(+)tnCH$_3$ oriented in a nematic glass at −150°: A, 0° rotation; B, 90° rotation.

spectra and other physical properties as the (sal$_2$tn) complex[35] and monomeric in solution. When it is dissolved in a coordinating solvent such as pyridine the absorption spectrum appears similar to monomeric vanadyl complexes that interact with basic solvents. The electronic spectrum in chloroform appears to be typical of square pyramidal VO^{2+} complexes. A tendency for axial interaction is apparent in the electron spin resonance measurements of the complex.[35]

While the β-keto enolate complexes of square-pyramidal oxovanadium(IV) complexes show a large solvent dependence,[36] the β-ketimines[37] and salicylaldimine complexes do not. The possible factors influencing this behavior are electronic and/or geometric. The former appears to be that favored by Bruins and Weaver[37] after their X-ray crystallographic determination of the structure of *N,N'*-ethylenebis(acetylacetoneiminato)oxovanadium(IV) which suggested an absence of any blocking of the sixth coordinations position on this complex.

Farmer[35] has found that VO(sal)$_2$(+)tnCH$_3$ shows solution properties different from the other salicylaldimines and reminiscent of the β-keto enolates. The epr spectra of 40% chloroform–60% toluene solutions show some in-plane anisotropy; however, it is not resolved. The epr parameters are close to that for the other salicylaldimine complexes. The spectrum in 40% pyridine–60% toluene shows some decrease in the isotropic **A** value and $g_\perp$ and consequently the isotropic **g** value.

The isotropic hyperfine coupling constant appears to indicate that there is a larger contribution of 4s character in the σ bonding in this VO^{2+} complex[38] compared with many other species. The pyridine–toluene spectrum, however, seems to show more evidence for an-

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[34] M. Mathew, A. J. Carty, and G. J. Palenik, *J. Amer. Chem. Soc.*, **92**, 3197 (1970).

[35] R. Farmer and F. L. Urbach, *Chem. Commun.*, 1515 (1970).

[36] F. A. Walker, R. L. Carlin, and P. M. Rieger, *J. Chem. Phys.*, **45**, 4181 (1966).

[37] D. Bruins and D. L. Weaver, *Inorg. Chem.*, **9**, 130 (1970).

[38] D. Kivelson and S. K. Lee, *J. Chem. Phys.*, **41**, 1896 (1964).

isotropic g behavior as would be expected if there is some distortion away from the square-pyramidal symmetry and/or relaxation of the dominance of the ligand field by the V–O multiple bond. While this anisotropy is not resolvable, the oriented liquid crystal spectra show much more clearly the anisotropic character of the perpendicular bands (Figure 9). There is enhancement of individual bands upon rotating the sample tube as seen for $VO(acac)_2$. The calculation of g_x and g_y shows them to be very close, whereas A_x and A_y are quite different (Table II). By analogy with the $VO(acac)_2$ spectrum the assignment given was made.

Optically Active Complexes. Buckingham and coworkers[39] and Stegemeyer and Mainusch[40] have shown that nematic liquid crystals containing optically active solutes can become cholesteric in their behavior (*i.e.*, rotate circularly polarized light). As the amount of optically active solute is increased the properties of the liquid crystals gradually shift from nematic to cholesteric, removing the possibility for their use in optical measurements. A further result was that even at the highest field used (5.9 kG) there was incomplete ordering even after a period of 10 min.[40] In the presence of mesotartaric acid, however, the orientation was complete. Solutions of racemic tartaric acid or racemic menthol produced no cholesteric properties.

The epr studies presented here show clearly that reasonable magnetic parameters are obtained even from optically active solutes. The epr spectra of $VO(sal)_2(+)pn$ and its racemic mixture are identical with no difference in their orientation properties. While there appears to be incomplete ordering with $VO(sal)_2(+)tnCH_3$ the magnetic tensors are readily obtained.

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(39) A. D. Buckingham, G. P. Ceasar, and M. B. Dunn, *Chem. Phys. Lett.*, 3, 540 (1969).

(40) H. Stegemeyer and K.-J. Mainusch, *ibid.*, 6, 5 (1970); H. Stegemeyer, K.-J. Mainusch, and E. Steigner, *ibid.*, 8, 425 (1971).

Partially Relaxed Fourier Transform Boron-11 Nuclear Magnetic Resonance Spectra. Resolution Enhancement in the Spectrum of *n*-Nonaborane(15)[1]

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Abstract: Partially relaxed Fourier transform (PRFT) ^{11}B nmr spectra, obtained by means of the 180–90° rf pulse sequence, are used for studying boron compounds in solution. Variations in ^{11}B spin–lattice relaxation times within a molecule cause intensity differences in a PRFT spectrum. In favorable cases, these intensity differences can be used to extract heretofore unresolved lines. For example, the downfield triplet of decaborane(14) is resolved into its two component doublets. The previously hidden $B(3)H_2$ triplet in *n*-nonaborane(15) is resolved by the PRFT method. PRFT spectra also provide evidence for deuteration at B(3) of n-B_9H_{15} in the exchange reaction of this compound with B_2D_6.

Fourier transform (FT) nmr[2] is being used increasingly[3] as a preferable alternative to continuous-wave nmr, not only because of the increased sensitivity of the FT method[2] but also because of the additional information that is often available from partially relaxed Fourier transform[4] (PRFT) spectra.[5,6] The PRFT technique is an extension of the old 180°–90° rf pulse method of Hahn[7a] and Carr and Purcell[7b] for measuring spin–lattice relaxation times (T_1). Until recently, measurements by means of the 180°–90° pulse sequence yielded only average T_1 values for various nonequivalent nuclei of the same spin species. In 1968, Vold and coworkers[4] showed that the 180°–90° pulse sequence could be used to measure individual T_1 values of resolved resonances by applying a Fourier transformation to the signal following the 90° pulse. Recently, Allerhand and coworkers have used carbon-13 PRFT spectra for studying the details of molecular motion of large organic molecules[5a,b] and biopolymers.[5c] We show below that ^{11}B PRFT spectra provide, in favorable cases, structural information that may not be available from normal spectra.

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