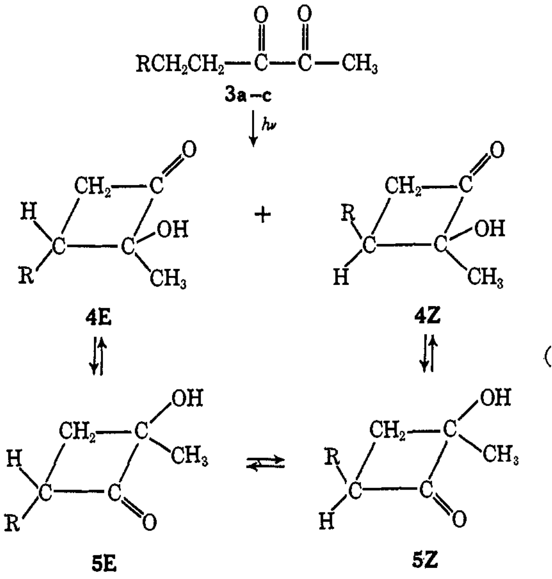
more basic solvents (water, dimethyl sulfoxide, or pyridine).

In such polar solvents at low dione concentrations and temperatures and with short irradiation times, this rearrangement can be so limited that only photocyclization occurs. Then only **1** is obtained, and **3a–c** give only **4a–cE** and **4a–cZ** with little stereoselectivity (**4aE**/**4aZ** = 1.0, **4bE**/**4bZ** = 1.2, and **4cE**/**4cZ** = 0.6). Under other conditions, these ratios **4E**/**4Z** are different, and **5E** and **5Z** appear in the photolysis products.

Ketol rearrangement (**4E** $\rightleftarrows$ **5E** and **4Z** $\rightleftarrows$ **5Z**) and epimerization *via* enolization[6] (**5E** $\rightleftarrows$ **5Z**) give equilibrium between the four isomers. Their ratios permit the first direct comparison of vicinal and transannular interactions in four-membered rings. Equilibrations occurred rapidly in sodium hydroxide solutions (0.02 *M*) in 20% aqueous pyridine. The compositions of these equilibrium mixtures (nmr integration of appropriate methyl absorptions) are given in Table II. They were obtained from pure substances (**5bE**, **5bZ**, **5cE**, **5cZ**, and the bishemiketal dimers[7] from **4aE**, **4bE**, and **4cE**) and various mixtures.



(2)

a, R = $CH_3$-
b, R = $(CH_3)_2CH$-
c, R = $C_6H_5(CH_3)_2C$-

Inversion of configurational preference is seen (Table II) between sets of epimeric pairs (**4** or **5**). The differences ($\Delta G$, **4E** – **4Z**, **5Z** – **5E**) observed are insensitive to the size of R. The relative importance of vicinal compared to transannular interactions is enhanced by groups larger than methyl, and is greater for **Z** than for **E** configurations. For a single methyl substituent $\Delta G$ (**5Z** – **4Z**) is positive and $\Delta G$ (**5E** – **4E**) negative, whereas, for the *gem*-dimethyl groups in **1** and **2**, 1,2 and 1,3 interactions are nearly equal. These results suggest that pseudoequatorial arrangement of both the 2-hydroxyl (here probably hydrogen bonded to solvent) and the 3 or 4 substituent is preferred. Both of these groups cannot be so placed in **4Z** and **5E**, and hence they are less stable than their epimers.

Different interactions obviously are involved in determining these equilibrium compositions and photochemical selectivities. The photocyclization of 4-methyl-2,3-pentanedione yields predominantly **5aE** (**5aE**/**5aZ** = 3.0), although **5aZ** is the most stable isomer (Table II, **5aE**/**5aZ** = 0.23). That of 6-methyl-2,3-heptanedione (**3b**) shows little selectivity (**4cE**/**4cZ** = 1.2), while **4cE** is thermodynamically preferred (Table II, **4cE**/**4cZ** = 2.2).

The degenerate rearrangement of 2-hydroxy-2-methylcyclobutanone was observed *via* its hydrogen exchange with deuterium oxide containing pyridine (0.8 *M*). The nmr absorptions of its 3- and 4-methylenes disappeared at approximately equal rates, but its methyl singlet was unchanged. Hence, its rearrangement is faster than its enolization and it does not occur by homoenolization[1c] at methyl.

A simple methyl migration is suggested by the stereospecificity of this rearrangement,[7b] and by the above lack of methyl deuteration. This evidence also makes it less likely that a ring reorganization sequence, as proposed for other cyclobutanone rearrangements,[3a] occurs. The latter mechanism deserved serious consideration since its two steps, ring contraction[8] and expansion,[9] have been observed separately.

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[6] N. J. Turro and R. B. Gagosian, *J. Amer. Chem. Soc.*, **92**, 2036 (1970).

[7] (a) W. H. Urry, D. J. Trecker, and D. A. Winey, *Tetrahedron Lett.*, 609 (1962); (b) W. H. Urry, J. C. Duggan, and M. H. Pai, unpublished.

[8] W. Ried and W. Kunkel, *Justus Liebigs Ann. Chem.*, **717**, 54 (1968).

[9] H. Bartsch and E. Hecker, *ibid.*, **725**, 142 (1969).

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## Electron Paramagnetic Resonance Spectra of Metal Complexes Oriented in Nematic Glasses

*Sir:*

Single-crystal electron paramagnetic resonance (epr) spectra have been exceedingly valuable in helping to interpret bonding and structural parameters in paramagnetic transition-metal compounds.[1,2] However, this technique suffers especially from two inherent experimental difficulties, the need to grow suitable single crystals and the requirement that the paramagnetic material must 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.

In principle, the use of liquid crystals to orient materials in magnetic fields can produce the same result that is obtained from oriented, magnetically dilute single-crystal epr measurements. Furthermore, data may be obtained without the drawbacks of the single-

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[1] B. R. McGarvey, *Transition Metal Chem.*, **3**, 89 (1966); A. H. Maki and B. R. McGarvey, *J. Chem. Phys.*, **43**, 404 (1965); A. H. Maki, N. Edelstein, A. Davison, and R. H. Holm, *J. Amer. Chem. Soc.*, **86**, 4580 (1964).

[2] M. J. Weeks and J. P. Fackler, *Inorg. Chem.*, **7**, 2548 (1968).

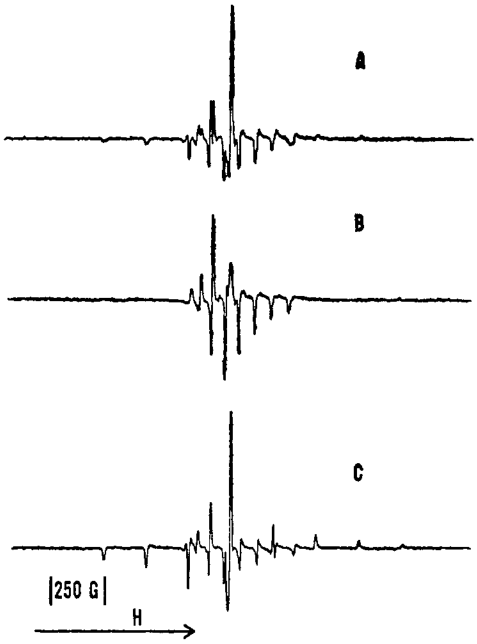

Figure 1. Epr spectra of oxovanadium(IV) acetylacetonate at −140°: (A) normal frozen solution using 50% chloroform–50% toluene, (B) oriented nematic glass using VL-1047-N,[12] (C) oriented nematic glass using VL-1047-N.[12] Rotation about the sample tube axes 90° with respect to the field.

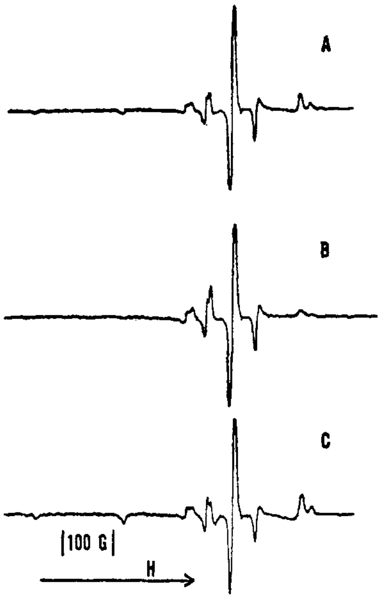

Figure 2. Epr spectra of copper(II) diethyldithiocarbamate at −140°: (A) normal frozen solution using 50% chloroform–50% toluene; (B) oriented nematic glass using VL-1047-N,[12] 0° rotation; (C) oriented nematic glass using VL-1047-N,[12] 90° rotation.

crystal technique, providing the paramagnetic material of interest is soluble in the nematic liquid crystal and orientational ordering of the solute occurs in the nematic. It is apparent from the results reported here that oriented liquid-crystal measurements of paramagnetic materials in nematic glasses can satisfy these requirements.

It is well known from magnetic resonance studies[3] that liquid crystals can be employed as orienting solvents. Owing to the orientational ordering in the mesophase of liquid crystal solvents, some 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 (I), where the various symbols have their

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

usual significance.[4]

Nematic mesophases of liquid-crystal solvents are known to assume bulk-phase ordering in strong magnetic fields with the long molecular axes tending to align parallel to the field.[5] Epr spectroscopy has been used extensively as a probe to establish the degree of ordering of the mesophase.[6–10] In particular, Fryburg and Gelerinter[10] have noted that "nearly complete alignment" can be obtained at temperatures near the lower end of the mesophase with small amounts (mole fraction $<10^{-3}$) of paramagnetic material dissolved into the liquid crystal.

It has been shown that certain room-temperature,[9] viscous[10] nematic solvents containing paramagnetic probes exhibit epr spectra typical of glasses. Schwerdtfeger and Diehl[9] suggest that the epr spectrum of vanadyl acetylacetonate dissolved in a room-temperature nematic can be accounted for by a slow molecular tumbling time (as in a glass) and a high degree of alignment. Under these conditions, perpendicular components 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[11] obtained similar results with an organic free radical from frozen anisotropic glasses produced by alignment of a liquid crystal employing an electric field.

By maintaining a very high degree of alignment through the formation of a "nematic glass" of known orientation, we have been able to obtain precise anisotropic epr parameters from a number of axial vanadium(IV) and copper(II) complexes dissolved in liquid crystals. In many cases the accuracy obtainable for the anistropic $g$ tensors and hyperfine coupling constants approaches that of dilute single-crystal methods. Typical liquid-crystal solvents used to obtain the results reported here are butyl $p$-($p$-ethoxyphenoxycarbonyl)phenyl carbonate and VL-1047-N.[12] In general, the paramagnetic complexes are dissolved in the liquid-crystal solvents to about 1–5 × $10^{-3}$ $M$ concentrations at temperatures above the nematic

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(3) A. Saupe, *Angew. Chem., Int. Ed. Engl.*, 7, 97 (1968).

(4) H. R. Gersmann and J. D. Swalen, *J. Chem. Phys.*, **36**, 3221 (1962).

(5) J. C. Rowell, W. D. Phillips, L. R. Melby, and M. Panar, *ibid.*, 43, 3442 (1965).

(6) S. H. Glarum and J. H. Marshall, *ibid.*, 44, 2884 (1966).

(7) P. Ferruti, D. Gill, M. A. Harpold, and M. P. Klein, *ibid.*, **50**, 4545 (1969).

(8) D. H. Chen and G. R. Luckhurst, *Mol. Phys.*, **16**, 91 (1969); *Trans. Faraday Soc.*, **65**, 656 (1969).

(9) C. F. Schwerdtfeger and P. Diehl, *Mol. Phys.*, 17, 417, 423 (1969).

(10) G. C. Fryburg and E. Gelerinter, *J. Chem. Phys.*, **52**, 3378 (1970).

(11) E. Sackmann and P. Krebs, *Chem. Phys. Lett.*, **4**, 65 (1969).

(12) A room-temperature nematic of undisclosed structure supplied by Varilight Corp., Cincinnati, Ohio.

Table I. Epr Parameters for Oxovanadium(IV) Acetylacetonate

| | $g_{\|\|}$ | $g_{\perp}$ | $A_{\|\|}$[a] | $A_{\perp}$[a] | Av $g$ | Av $A$[a] |
|---|---|---|---|---|---|---|
| Nematic glass | 1.944 | 1.988 | 17.2 | 6.2 | 1.974 | 9.9 |
| Normal glass[b] | 1.944 | 1.996 | 17.4 | 6.4 | 1.979 | 10.1 |
| Crystallized nematic | 1.946 | 2.003 | 16.9 | 7.4 | 1.984 | 10.1 |
| Isotropic solution | | | | | 1.974 | 9.9 |

[a] $A \times 10^3$ cm$^{-1}$. [b] Reference 4. D. Kivelson and S.K. Lee, *J. Chem. Phys.*, **41**, 1896 (1964), indicate that $g_{\perp}$ is incorrect.

Table II. Epr Parameters for Copper(II) Diethyldithiocarbamate

| | $g_{\|\|}$ | $g_{\perp}$ | $A_{\|\|}$[a] | $A_{\perp}$[a] | Av $g$ | Av $A$[a] |
|---|---|---|---|---|---|---|
| Nematic glass | 2.087 | 2.024 | 15.9 ($^{63}$Cu) | 4.2 | 2.045 | 8.1 ($^{63}$Cu) |
| | | | 16.7 ($^{65}$Cu) | | | 8.4 ($^{65}$Cu) |
| Normal glass[b] | 2.098 | 2.035 | 15.4 ($^{63}$Cu) | 4.0 ($^{63}$Cu) | 2.056 | 7.8 ($^{63}$Cu) |
| | | | 16.5 ($^{65}$Cu) | 4.3 ($^{65}$Cu) | | 8.4 ($^{65}$Cu) |
| Crystallized nematic | 2.099 | 2.031 | 17.7 | 4.6 | 2.054 | 9.0 |
| Single crystal[c] | 2.084 | 2.023 | 15.9 | 3.9 | 2.043 | 7.9 |
| Isotropic solution | | | | | 2.045 | 7.4 |

[a] $A \times 10^3$ cm$^{-1}$. [b] Reference 4. [c] Reference 2.

mesophase. The sample is cooled to the nematic temperature range and oriented by applying a magnetic field near 7000 *G*. While maintaining this field, the temperature is lowered quickly to −140° to produce the glass.[13]

In favorable cases spectra taken without perturbing the nematic glass[14] sample at −140° show contributions due only to perpendicular components (I) of the $g$ tensor and hyperfine splitting constant (Figures 1B and 2B), since the parallel (out-of-plane) anisotropic component is almost completely 90° with respect to the magnetic field. In a highly ordered axial system $g_{||}$ (and $A_{||}$) contributes almost nothing to the intensity function (cos $\theta$ approaches zero near 90°). Because of the absence of $g_{||}$ peaks and the presence of relatively sharp $g_{\perp}$ lines, very accurate measurements of $g_{\perp}$ and $A_{\perp}$ can be made. Even the position of the extra band predicted by Gersmann and Swalen[4] from a theoretical consideration of the intensity function may be determined as indicated in Figure 1B for oxovanadium(IV) acetylacetonate. The out-of-plane components of the $g$ and hyperfine tensors are obtained by rotation of the nematic glass sample about the epr tube axis 90° with respect to the magnetic field. As seen in Figures 1C and 2C, the rotation causes an enhancement of the intensity of the out-of-plane, $g_{||}$, components and diminishes the intensity of the in-plane, $g_{\perp}$, components.[15] Molecular realignment of these nematic glasses with the field direction has not been observed at −140°.

The anisotropic epr parameters obtained by this technique compare favorably with those values obtained by dilute single-crystal methods (Table II) and are much better than values obtained from randomly oriented frozen solutions or powders[16] (Tables I and II). The nematic glass technique also has been applied to a number of copper(II) complexes for which single-crystal data are not available in order to obtain molecular orbital coefficients and bonding parameters. One example, bis(3-ethyl-2,4-pentanediono)copper(II), is presented in Table III. The molecular orbital coefficients were evaluated by methods discussed previously[2] from the anisotropic epr parameters obtained using the nematic-glass technique. The molecular orbital coefficients are very similar to those for other copper(II) acetylacetonates.[17]

Table III. Molecular Orbital Coefficients for Bis(3-ethyl-2,4-pentanediono)copper(II)[a–c]

| | $V_{\text{L}} = 0.00$ | $V_{\text{L}} = 0.18$ |
|---|---|---|
| $\alpha$ | 0.91 | 0.91 |
| $\beta$ | 0.86 | 0.87 |
| $\gamma$ | 0.88 | 0.89 |

[a] $g_{||} = 2.250$; $g_{\perp} = 2.056$; $A_{||} = 0.0194$ cm$^{-1}$; $A_{\perp} = 0.0032$ cm$^{-1}$; $\Delta E_1 = 16{,}300$; $\Delta E_2 = 18{,}500$; $T_{\text{n}} = 0.220$; $P = 0.036$ cm$^{-1}$; $\lambda$ 828 cm$^{-1}$; $S = 0.076$. [b] See ref 2 for significance of symbols. A computer program, MOPAR, has been written to perform these calculations. [c] Values for electronic spectral transitions taken to be similar to those for bis(2,4-pentanediono)copper(II): J. Ferguson, R. L. Belford, and T. S. Piper, *J. Chem. Phys.*, **38**, 1509 (1962).

Some 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.[18]

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(13) 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.[4]

(14) Spectra were recorded on a Varian (E-3) epr spectrometer operating at 9.1 GHz (X-band). Temperature was controlled with a Varian (E4540) variable-temperature unit. The spectrometer frequency and magnetic field were calibrated by employing a series of standards with precisely known $g$ and $A$ values

(15) In this analysis it has been assumed that the solute molecules are reasonably flat and line up with their axial component perpendicular to the long axis of the liquid crystal. Conceivably there are cases where the opposite result may occur, and obviously all intermediate situations exist. The degree to which misalignment occurs, however, is readily determined by the observation of the relative intensities of the perpendicular and parallel components[4] of the spin tensors.

(16) The average $g$ and $A$ (hyperfine) tensors obtained from isotropic solution spectra and the average values obtained from the nematic glass may be compared. They indicate that the liquid-crystal solvents used affect the paramagnetic complexes to a similar degree to that of "noninteracting" solvents.

(17) M. A. Hitchman and R. L. Belford in "Electron Spin Resonance of Metal Chelates," T. F. Yen, Ed., Plenum Press, New York, N. Y., 1969, Chapter 7.

(18) We acknowledge the support of the National Science Foundation, Grant No. GP-7889, for this work.

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