

rate constants, this means that a range of  $10^5$  to  $10^6$  for the trans effect would correspond to a range of about  $10^{2.5}$  to  $10^3$  for the cis effect.

The inverse order of the cis and trans effect is less well confirmed by experiment. Although one of the earliest generalizations<sup>16,17</sup> derived from the experimental data was indeed such an inverse order, there are by now definite counterexamples.

### Conclusions

Although it is obvious that the present considerations do not explain the whole set of detailed experimental data on the trans and cis effects, the general trend seems rather well reproduced. Invoking the role of the ligand field activation energy apparently provides a way, by itself, to explain the main features of the experimental

(16) A. A. Grinberg, *J. Inorg. Chem. (USSR)*, **4**, 683 (1959).

(17) J. D. Bersuker, *J. Struct. Chem. (USSR)*, **4**, 419 (1963).

data. It seems certain that the LFAE plays an important role in the kinetic study of the square planar Pt(II) reactions.

This is not to imply that the trans influence and the role of 6s and 6p orbitals can be neglected. Indeed, these factors are known to be important in the phenomena under consideration.<sup>3,4</sup> From the present approach, however, it is impossible to estimate the relative importance of the ligand field activation energies and the other effects.

Finally, it is well to stress that eq 12 and 13 should not be used to study the influence of the leaving or incoming ligands. Indeed in these reactions, the bond energy will contribute an additional, very important variable to the total activation energy.

**Acknowledgment.** One of us (J. V.) is indebted to the I.W.O.N.L. (Belgium) for a predoctoral fellowship.

## Calculation of Lanthanide Induced Shifts from Molecular Structure<sup>1</sup>

Roger E. Cramer,\* Ronald Dubois, and Karl Seff

*Contribution from the Department of Chemistry, University of Hawaii, Honolulu, Hawaii 96822. Received May 17, 1973*

**Abstract:** The nmr spectra of  $\text{Eu}(\text{dpm})_3(\text{py})_2$  in  $\text{CS}_2$  at ambient temperature and  $\text{Eu}(\text{dpm})_3(3\text{-pic})_2$  in  $\text{CS}_2$  at low temperature ( $-105^\circ$ ) were studied and the lanthanide induced shifts for all protons, including those of the chelate, were calculated using the complete pseudocontact shift equation. The low temperature spectrum of  $\text{Eu}(\text{dpm})_3(3\text{-pic})_2$  shows peaks from both free and complexed ligands. Comparison of the integrated areas of the chelate peaks and the coordinated 3-pic peaks show that the species present is the 1:2 adduct. The magnetic anisotropies from a least-square fit of the data agree with single crystal anisotropy data, and their temperature dependence is in fair agreement with Bleaney's theoretical predictions. The results show that lanthanide induced shifts, at least for this type of complex, cannot be explained on the basis of a single term equation which assumes that the principal magnetic axis passes through the donor atom. They can be understood in terms of the more complete two-term equation.

In the original paper reporting the ability of  $\text{Eu}(\text{dpm})_3(\text{py})_2$  to induce large dipolar shifts in the nmr spectrum of Lewis base substrates, Hinckley<sup>3</sup> quoted the general equation derived for dipolar shifts by La Mar, Horrocks, and Allen.<sup>4</sup> Recent theoretical work<sup>5,6</sup> has shown that the dipolar shift<sup>†</sup> equation can be written in terms of molecular susceptibility anisotropies instead of  $g$  tensor anisotropies, so that the most general equation for dipolar shifts would be<sup>7</sup>

$$\frac{\Delta\nu}{\nu_0} = D_1 \left( \frac{3 \cos^2 \theta - 1}{r^3} \right) + D_2 \left( \frac{\sin^2 \theta \cos 2\Omega}{r^3} \right) \quad (1)$$

(1) This paper is abstracted from a dissertation submitted to the Graduate Division of the University of Hawaii by R. D. in partial fulfillment of the requirements for the Doctor of Philosophy Degree in Chemistry.

(2) Key: dpm = dipivalomethanato or 2,2,6,6-tetramethylheptane-3,5-dionato ion; py = pyridine.

(3) C. C. Hinckley, *J. Amer. Chem. Soc.*, **91**, 5160 (1969).

(4) G. N. La Mar, W. DeW. Horrocks, Jr., and L. C. Allen, *J. Chem. Phys.*, **41**, 2126 (1964).

(5) (a) W. DeW. Horrocks, Jr., *Inorg. Chem.*, **9**, 6901 (1970); (b) R. J. Kurland and B. R. McGarvey, *J. Magn. Resonance*, **2**, 286 (1970).

(6) B. R. McGarvey, *J. Chem. Phys.*, **53**, 86 (1970).

(7) R. von Ammon and R. D. Fischer, *Angew. Chem., Int. Ed. Engl.*, **11**, 675 (1972).

In this equation  $\Delta\nu$  is the dipolar shift,  $\nu_0$  is the probe frequency,  $r$  is the length of a vector which joins the metal atom and the nucleus being examined,  $\theta$  is the angle this vector makes with the  $z$  magnetic axis,  $\Omega$  is the angle which the projection of  $r$  into the  $xy$  plane makes with the  $x$  magnetic axis, and  $D_1$  and  $D_2$  are functions of the magnetic anisotropy of the complex. For the case where  $1/\tau_m \ll (\text{ZAE})$ ,  $D_1$  and  $D_2$  can be expressed as

$$D_1 = \frac{1}{3N}(\chi_x - \chi_x/2 - \chi_y/2) \quad (2)$$

$$D_2 = \frac{1}{2N}(\chi_x - \chi_y) \quad (3)$$

where  $\tau_m$  is the solution tumbling correlation time, (ZAE) is the Zeeman anisotropy energy,  $N$  is the Avogadro number and  $\chi_x$ ,  $\chi_y$ , and  $\chi_z$  are the principal molecular magnetic susceptibilities.<sup>8</sup> For molecules with threefold or higher symmetry  $\chi_x - \chi_y = 0$  so that

(8) W. DeW. Horrocks, Jr., and E. S. Greenberg, *Inorg. Chem.*, **10**, 2190 (1971).

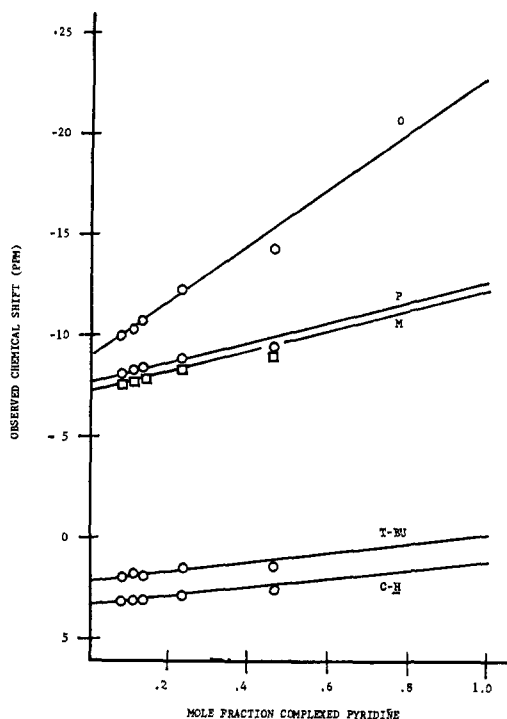


Figure 1. Plot of observed chemical shift vs. mole fraction complexed pyridine (X complex).

$D_2$  becomes zero and eq 1 reduces to

$$\frac{\Delta\nu}{\nu_0} = D_1 \frac{3 \cos^2 \theta - 1}{r^3} \quad (4)$$

Most workers have assumed that complexes formed between a shift reagent and a substrate have axial symmetry and have used eq 4 rather than eq 1.<sup>7-45</sup>

- (9) W. DeW. Horrocks, Jr., and J. P. Sipe III, *J. Amer. Chem. Soc.*, **93**, 6800 (1971).  
 (10) O. A. Gansow, M. R. Willcott, and R. E. Lenkinski, *J. Amer. Chem. Soc.*, **93**, 4296 (1971).  
 (11) P. V. Demarco, T. K. Elzey, R. B. Lewis, and E. Wenkert, *J. Amer. Chem. Soc.*, **92**, 5734 (1970).  
 (12) S. Farid, A. Ateya, and M. Maggio, *Chem. Commun.*, 1285 (1971).  
 (13) J. Briggs, F. A. Hart, and G. P. Moss, *Chem. Commun.*, 1506 (1970).  
 (14) J. Briggs, F. A. Hart, G. P. Moss, and E. W. Randall, *Chem. Commun.*, 364 (1971).  
 (15) B. L. Shapiro, J. R. Hlubucek, G. R. Sullivan, and L. F. Johnson, *J. Amer. Chem. Soc.*, **93**, 3282 (1971).  
 (16) C. C. Hinckley, M. R. Klotz, and F. Patil, *J. Amer. Chem. Soc.*, **93**, 2417 (1971).  
 (17) C. Beauté, Z. W. Wolkowski, and N. T. Thoai, *Tetrahedron Lett.*, 817 (1971).  
 (18) Z. W. Wolkowski, *Tetrahedron Lett.*, 821 (1971).  
 (19) Z. W. Wolkowski, *Tetrahedron Lett.*, 825 (1971).  
 (20) J. Goodisman and R. S. Matthews, *J. Chem. Soc., Chem. Commun.*, 127 (1972).  
 (21) E. Wenkert, D. W. Cochran, E. W. Hagaman, R. B. Lewis, and F. M. Schell, *J. Amer. Chem. Soc.*, **93**, 6271 (1971).  
 (22) J. Reuben and J. S. Leigh, Jr., *J. Amer. Chem. Soc.*, **94**, 2788 (1972).  
 (23) L. W. Morgan and M. C. Bourlas, *Tetrahedron Lett.*, 2631 (1972).  
 (24) H. Huber, *Tetrahedron Lett.*, 3559 (1972).  
 (25) P. V. Demarco, B. J. Cerimele, R. W. Crane, and A. L. Thahlear, *Tetrahedron Lett.*, 3539 (1972).  
 (26) M. Ochiai, E. Mizuta, O. Aki, A. Morimoto, and T. Okada, *Tetrahedron Lett.*, 3245 (1972).  
 (27) B. L. Shapiro, M. D. Johnston, Jr., A. D. Godwin, T. W. Proulx, and M. J. Shapiro, *Tetrahedron Lett.*, 3233 (1972).  
 (28) M. Hajek, L. Vodicka, Z. K. Sandr, and S. Landa, *Tetrahedron Lett.*, 4103 (1972).  
 (29) A. A. Chalmers and K. G. R. Pachler, *Tetrahedron Lett.*, 4033 (1972).  
 (30) R. Seux, G. Masel, and A. Fowcaud, *Tetrahedron Lett.*, 1003 (1972).

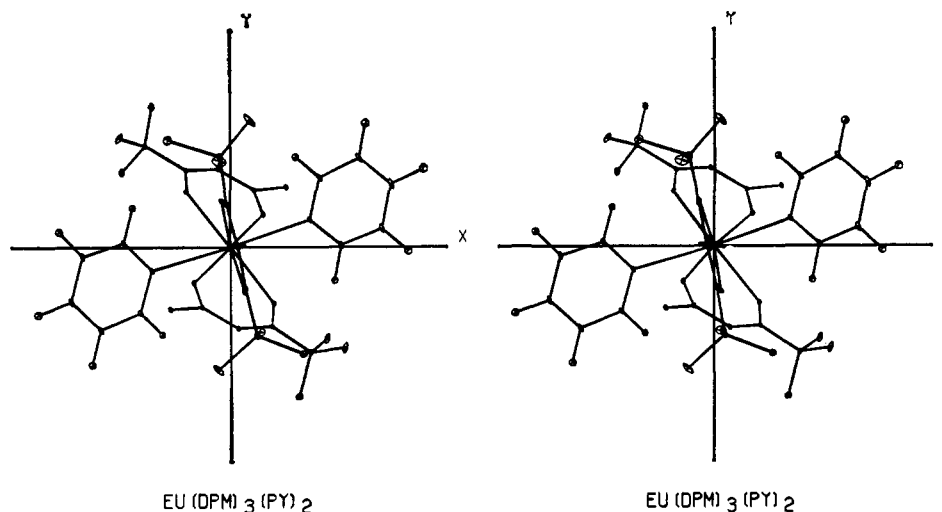
The validity of this assumption is seriously challenged by recent X-ray crystallographic structural determinations of shift reagent adducts,<sup>46-50</sup> which have shown, at most, twofold symmetry. In addition measurements of the anisotropy in the magnetic susceptibility for the series of complexes of the type  $\text{Ln}(\text{dpm})_3(4\text{-picoline})_2$  are in accord with low symmetry and yield large values of  $D_2$ .<sup>51</sup> In this paper we show that we can account for the lanthanide induced shifts of pyridine substrates through the use of eq 1 by using the structure found for  $\text{Eu}(\text{dpm})_3(\text{py})_2$  in the solid state<sup>47, 48</sup> and that we can also determine the location of the magnetic axes and the values of  $D_1$  and  $D_2$ .

## Experimental Section

Chemical shifts with respect to internal TMS in  $\text{CS}_2$  solution were measured from spectra obtained on a Varian HA-100 NMR spectrophotometer equipped with a V6040 temperature controller, operating in the HA mode for the room temperature experiments but in the HR mode at low temperature. Temperature was measured by means of a Digitec Series 590 thermocouple mounted in the probe.

Since the exchange between free and complexed pyridine is fast on the nmr time scale at ambient probe temperature, the chemical shifts for bound pyridine were obtained by an extrapolation procedure. A series of solutions which were  $4.00 \times 10^{-2} M$  in  $\text{Eu}(\text{dpm})_3$  and which contained various known amounts of pyridine was prepared. The mole fraction of coordinated pyridine was calculated from the total moles of pyridine and  $\text{Eu}(\text{dpm})_3$  present, assuming each  $\text{Eu}(\text{dpm})_3$  was complexed by two pyridines. A plot of observed chemical shift vs. mole fraction complexed pyridine (X complex) was prepared and is illustrated in Figure 1. The plot is linear at high py/ $\text{Eu}(\text{dpm})_3$  ratios but shows some curvature at low py/ $\text{Eu}(\text{dpm})_3$  ratios (4.39/1), presumably due to a rather low formation constant for the complex.<sup>32</sup> The straight portions of these lines were fit by least squares and extrapolated to X complex = 1.0 to obtain the chemical shifts for the complex  $\text{Eu}(\text{dpm})_3(\text{py})_2$ . Extrapolation to X complex = 0.0 yields values which are quite close to those accepted for the chemical shifts of the various pyridine protons. Both the methyl and methine peaks of the  $\text{dpm}^-$  chelate

- (31) C. Beaute, S. Cornuel, D. Lelandais, N. Thoai, and Z. W. Wolkowski, *Tetrahedron Lett.*, 1099 (1972).  
 (32) A. J. Rafalski, J. Barczewski, and M. Wieworowski, *Tetrahedron Lett.*, 2829 (1971).  
 (33) J. Passivorta, *Suom. Kemistilehti B*, **44**, 131 (1971).  
 (34) A. F. Cockerill and D. M. Rackham, *Tetrahedron Lett.*, 5149 (1970).  
 (35) A. Iys, G. Vecchio, and G. Garrea, *Tetrahedron Lett.*, 1543 (1972).  
 (36) P. Kristiansen and T. Ledaal, *Tetrahedron Lett.*, 4457 (1971).  
 (37) B. D. Cuddy, K. Trean, and B. J. Walker, *Tetrahedron Lett.*, 4433 (1971).  
 (38) R. Caple and S. C. Kuo, *Tetrahedron Lett.*, 4413 (1971).  
 (39) P. H. Maxxocchi, H. J. Tamburin, and G. R. Miller, *Tetrahedron Lett.*, 1819 (1971).  
 (40) K. E. Stensjö and U. Åhlin, *Tetrahedron Lett.*, 4729 (1971).  
 (41) H. G. Richey, Jr., and F. W. Von Rein, *Tetrahedron Lett.*, 3781 (1971).  
 (42) P. Granger, M. M. Clandon, and J. F. Giunet, *Tetrahedron Lett.*, 4167 (1971).  
 (43) J. M. Briggs, G. P. Moss, E. W. Randall, and K. D. Sales, *J. Chem. Soc., Chem. Commun.*, 1180 (1972).  
 (44) J. K. M. Sanders, S. W. Hanson, and D. H. Williams, *J. Amer. Chem. Soc.*, **94**, 5325 (1972).  
 (45) D. Schweudiman and J. I. Zink, *Inorg. Chem.*, **11**, 3051 (1972).  
 (46) W. DeW. Horrocks, Jr., J. P. Sipe III, and J. R. Luber, *J. Amer. Chem. Soc.*, **93**, 5258 (1971).  
 (47) R. E. Cramer and K. Seff, *J. Chem. Soc., Chem. Commun.*, 400 (1972).  
 (48) R. E. Cramer and K. Seff, *Acta Crystallogr., Sect. B*, **28**, 3281 (1972).  
 (49) S. J. S. Wasson, D. E. Sands, and W. F. Wagner, *Inorg. Chem.*, **12**, 187 (1973).  
 (50) J. J. Uebel and R. M. Wing, *J. Amer. Chem. Soc.*, **94**, 8910 (1972).  
 (51) W. DeW. Horrocks, Jr., and J. P. Sipe, III, *Science*, **177**, 994 (1972).  
 (52) L. Armitage, G. Dunsmore, L. D. Hall, and A. G. Marshall, *Can. J. Chem.*, **50**, 2119 (1972).



**Figure 2.** Stereoview of  $\text{Eu}(\text{dpm})_3(\text{py})_2$  down the molecular twofold axis showing the  $x$  and  $y$  magnetic axes. Some of the methyl carbons of the *tert*-butyl groups have been removed for clarity.

**Table I.** Chemical Shifts, Isotropic Shifts, Geometric Factors, and Calculated Isotropic Shifts for  $\text{Eu}(\text{dpm})_3(\text{py})_2$  at  $30^\circ$

	$(3 \cos^2 \theta - 1)/r^3$	$(\sin^2 \theta / \cos 2\Omega)/r^3$	Chemical shift, ppm	$(\Delta\nu/\nu_0)_{\text{obsd}}$	$(\Delta\nu/\nu_0)_{\text{calcd}}^a$	$(\Delta\nu/\nu_0)_{\text{calcd}}^b$	$(\Delta\nu/\nu_0)_{\text{calcd}}^c$
Methine	0.0090	-0.0028	3.24	8.77	8.69	9.15	7.27
<i>tert</i> -Butyl	0.0030	-0.0005	2.08	3.08	2.29	3.03	3.16
Para	-0.0019	+0.0028	-12.65	-5.07	-4.72	-1.91	-5.43
Meta	-0.0032	+0.0030	-12.71	-5.47	-5.72	-3.28	-6.35
Ortho	-0.0167	+0.0048	-24.05	-15.48	-15.65	-17.08	-15.89
					$R = 0.047$	$R = 0.214$	$R = 0.094$

<sup>a</sup> Calculated using eq 1. <sup>b</sup> Calculated using eq 4,  $D_1 = 1022 \pm 98$  VVk/mol magnetic axis along  $C_2$  axis. <sup>c</sup> Calculated using eq 4,  $D_1 = -1141 \pm 48$  VVk/mol magnetic axis along Eu-N line.

are found upfield and can be assigned according to their relative observed areas, 18/1 respectively. Due to the low equilibrium constant these peaks also experience a varying chemical shift as the  $\text{py}/\text{Eu}(\text{dpm})_3$  ratio is altered. The chemical shifts for these protons in the complex were obtained by extrapolation to X complex = 0.0 since under these conditions all  $\text{Eu}(\text{dpm})_3$  would be in the form  $\text{Eu}(\text{dpm})_3(\text{py})_2$ . At  $-105^\circ$ , exchange between free and complexed ligand is so slow that separate signals are observed for both free and complexed substrate, and the chemical shifts for the complexed species can be read directly from the spectra. The diamagnetic reference for the pyridine was taken as free pyridine and for the  $\text{dpm}^-$  protons was taken as  $\text{CH}_3 = -1.16$  ppm and  $\text{CH} = -5.75$  ppm as found for  $\text{Lu}(\text{dpm})_3$ .<sup>53</sup>

The  $z$  magnetic axis was assumed to be coincident with the twofold axis of the complex while the  $x$  axis was originally assumed to be parallel to the inter-nitrogen vector. Subsequent attempts to refine the orientation of the axis system were carried out by fixing one axis and rotating about it. For each orientation of the magnetic axes those values of the unknowns  $D_1$  and  $D_2$  which gave the best least-squares fits to the observed shifts were obtained. The criteria for the best magnetic axes was taken to be the minimum value of the  $R$  function as defined by Willcott, *et al.*<sup>54</sup>

The coefficients of  $D_1$  and  $D_2$  in eq 1, which are often referred to as geometric factors, were obtained from X-ray crystallographic results for  $\text{Eu}(\text{dpm})_3(\text{py})_2$ .<sup>47,48</sup> The positions of the methyl protons of 3-methylpyridine, 3-pic, were calculated using a C-C bond distance of 1.52 Å and tetrahedral angles about the carbon. The ring carbon-methyl carbon line was assumed to bisect the C-C-C ring angle centered on the meta carbon.

A view of  $\text{Eu}(\text{dpm})_3(\text{py})_2$  down the near twofold axis is shown in Figure 2. It can be seen from this figure or from the geometric factors in Table II that the two ortho and the two meta protons are in quite different environments in the complex. Since it is possible

that the pyridine rings have a sizable barrier to rotation,<sup>48,55</sup> the pyridine rings were assumed to be locked into the conformation found in the solid state.

Since for each position on the ring only a single signal is observed at  $30^\circ$ , fast exchange between the free and complexed ligand must be averaging the signals due to the two coordinated ortho environments and the single free ortho environment, producing the single observed peak and similarly for the meta position. To account for this the geometric factors for the two nonequivalent ortho positions were averaged, as were those of the two meta positions. In addition the values for those protons related by the twofold operation<sup>48</sup> were averaged. Fast exchange of the substrate also provides a mechanism by which the chelate rings may interchange so that the geometric factors for the chemically equivalent chelate protons were averaged. Two models were considered for the *tert*-butyl protons; in one the methyl protons were assumed to be fixed in space as found in the solid state, while in the other the methyl groups were considered to be freely rotating. For  $\text{Eu}(\text{dpm})_3(3\text{-pic})_2$  at low temperature, two ortho signals are observed so that the geometric factors for the two types of ortho position are no longer averaged. However, since only single peaks were observed for the meta protons, methyl protons, *tert*-butyl protons, and the methine protons even at low temperature, their geometric factors were averaged.

## Results

Table I lists the geometric factors, chemical shifts, and the calculated and observed dipolar shifts for the  $\text{Eu}(\text{dpm})_3(\text{py})_2$  system at ambient temperature, while Table II presents the same data in the nonexchanging region for  $\text{Eu}(\text{dpm})_3(3\text{-pic})_2$ . For  $\text{Eu}(\text{dpm})_3(\text{py})_2$  the best fit of the data was obtained for an  $x$  axis rotated  $10^\circ$  from the N-N vector toward the  $c$  crystallographic

(53) K. J. Eisentrant and R. E. Sievers, *J. Amer. Chem. Soc.*, **87**, 5254 (1965).

(54) M. R. Willcott, R. E. Lenkinski, and R. E. Davis, *J. Amer. Chem. Soc.*, **94**, 1744 (1972).

(55) R. E. Cramer and R. Dubois, *J. Amer. Chem. Soc.*, **95**, 3801 (1973).

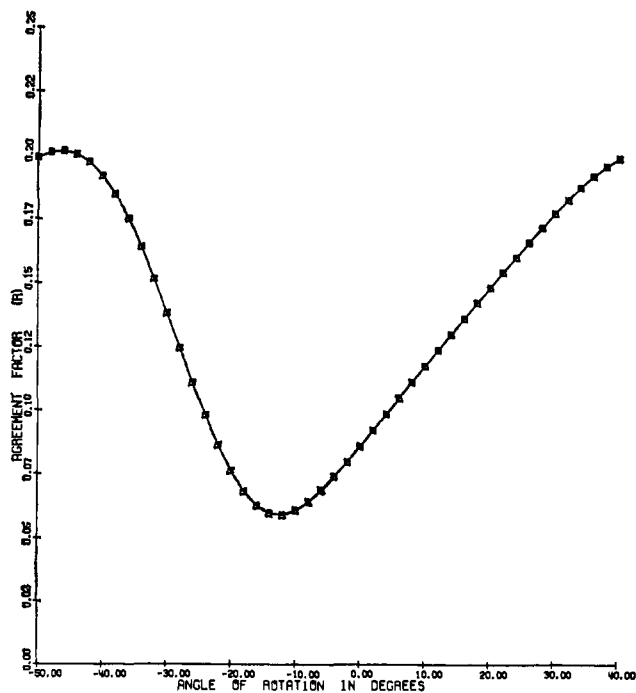


Figure 3. Plot of agreement index,  $R$ , vs. angle of rotation of the  $x$  axis from the N-N vector ( $0^\circ$ ) for  $\text{Eu}(\text{dpm})_3(\text{py})_2$  at ambient temperature. The  $c$  crystallographic axis is at  $-34^\circ$ .

Table II. Chemical Shifts, Isotropic Shifts, Geometric Factors, and Calculated Isotropic Shifts for  $\text{Eu}(\text{dpm})_3(3\text{-pic})_2$  at  $-105 \pm 3^\circ$

Assignment	$(3 \cos^2 \theta - 1)/r^3$	$(\sin^2 \theta \cos 2\Omega)/r^3$	Chemical shift, ppm	$(\Delta\nu/\nu_0)_{\text{obsd}}$	$(\Delta\nu/\nu_0)_{\text{calcd}}^a$
Methine	+0.0090	-0.0028	+29.0	34.8	36.5
<i>tert</i> -Butyl	+0.0030	-0.0006	9.7	10.9	10.4
Methyl	-0.0022	+0.0016	-18.5	-16.2	-14.2
Meta	-0.0032	+0.0032	-31.5	-24.5	-25.9
Ortho (1)	-0.0089	+0.0072	-70.35	-62.0	-62.0
Ortho (2)	-0.0246	+0.0040	-88.3	-80.0	-79.5
Para	-0.0019	+0.0030	-30.0	-22.7	-21.4

$R = 0.030$

<sup>a</sup> Calculated using eq 1.

axis, while for  $\text{Eu}(\text{dpm})_3(3\text{-pic})_2$  the best fit was found  $5^\circ$  from the N-N vector. Plots of the agreement index,  $R$ , vs. angle of rotation of the  $x$  axis are presented in Figure 3 for the  $\text{Eu}(\text{dpm})_3(\text{py})_2$  system and in Figure 4 for  $\text{Eu}(\text{dpm})_3(3\text{-pic})_2$ . The N-N vector is  $34^\circ$  from the  $c$  crystallographic axis. Attempts to find a better orientation of the  $z$  axis showed that the assumption of its coincidence with the twofold axis was correct. The non-rotating mode for the *tert*-butyl groups produced a better fit. The values of  $D_1$  and  $D_2$  at  $+30^\circ$  are calculated to be  $555 \pm 49$  and  $-1327 \pm 188$  VVk/mol, respectively, for  $\text{Eu}(\text{dpm})_3(\text{py})_2$  while at  $-105^\circ$  the corresponding numbers for  $\text{Eu}(\text{dpm})_3(3\text{-pic})_2$  are  $2305 \pm 16$  and  $-5757 \pm 239$  VVk/mol ( $1 \text{ VVk} = 10^{-6} \text{ cgsu}$ ).

In the nonexchange region for the system  $\text{Eu}(\text{dpm})_3(3\text{-pic})_2$ , independent comparison of the integrated intensities of the two ortho peaks, the combined meta and para peaks, as well as the combined methyl peaks with the methine peak of the chelate rings yields an average 3-picoline coordination number of  $2.2 \pm 0.2$ . Therefore, at least for the 3-pic substrate at low temperature, the species in solution is  $\text{Eu}(\text{dpm})_3(3\text{-pic})_2$ .

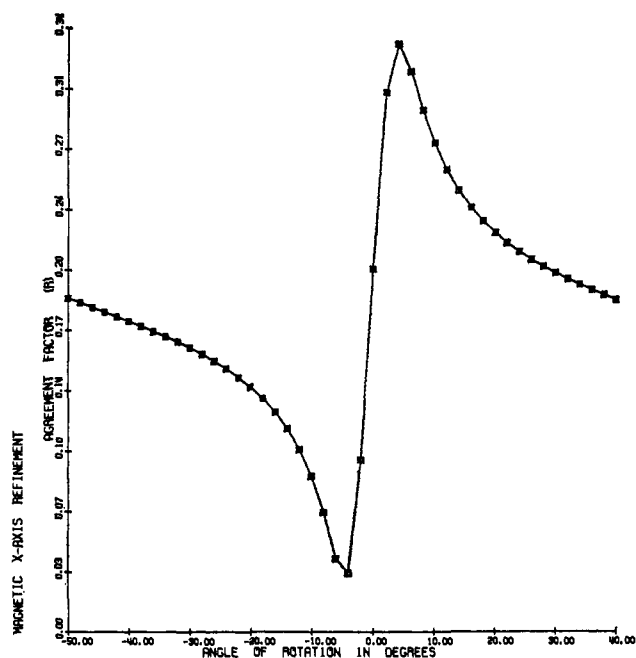


Figure 4. Plot of agreement index,  $R$ , vs. angle of rotation of the  $x$  axis from the N-N vector ( $0^\circ$ ) for  $\text{Eu}(\text{dpm})_3(3\text{-pic})_2$  at  $-105^\circ$ . The  $c$  crystallographic axis is at  $-34^\circ$ .

## Discussion

In addition to calculations using eq 1, two models using eq 4 were attempted and the results are presented in Table I. In the first model the magnetic axis was assumed to be colinear with the  $C_2$  axis, while in the second the axis was fixed along the Eu-N bond. The values of  $D_1$  which result are not in agreement with the solid-state susceptibility data.<sup>51</sup> Comparison of the  $R$  indices with those obtained using eq 1 *via* Hamilton's<sup>56</sup> test shows that the former model can be rejected at better than the 1% level and the latter at the 5% level. Similar tests with the low temperature data for 3-pic produce similar results. While this is the result theoretically expected<sup>7,46-50</sup> these results show that *the full two-term equation is necessary in order to account for lanthanide induced shifts*, at least for this type of complex.

Superior spectra obtained on a recently purchased Varian XL-100 NMR spectrometer as well as comparison with the low temperature spectrum of 3,5-lutidine have led us to change one of our previous assignments<sup>55</sup> in the low temperature spectrum of  $\text{Eu}(\text{dpm})_3(3\text{-pic})_2$ . The peak at  $-28.1$  ppm at  $-115^\circ$  also occurs in 3,5-lutidine and is thus not one of the meta peaks, but rather the para. The meta peak occurs at  $-29.4$  ppm.

Horrocks<sup>51</sup> working with only the substrate methyl protons for a series of  $\text{Ln}(\text{dpm})_3(4\text{-pic})_2$  complexes pointed out that the second term of eq 3 contributed less than 15% of the total shift but warned that this may not be a general result. The validity of that warning is borne out by our results (Table III) which show that the second term comprises from 29 to 80% of the total shift. The importance of the second term is quite apparent and it is obvious that work which attempts to correlate shifts with molecular structure using eq 4 will lead to incorrect geometries in those cases where

(56) W. C. Hamilton, *Acta Crystallogr.*, **18**, 502 (1965).

**Table III.** Isotropic Shift Contribution of Each Geometric Factor

Proton	$(3 \cos^2 \theta - 1)/r^3$	$(\sin^2 \theta \cos 2\Omega)/r^3$	Total shift
Pyridine			
Methine	4.99	3.70	8.69
<i>tert</i> -Butyl	1.66	0.63	2.29
Para	-1.05	-3.67	-4.72
Meta	-1.83	-3.89	-5.72
Ortho	-9.26	-6.39	-15.65
3-Methylpyridine			
Methine	20.75	15.75	36.50
<i>tert</i> -Butyl	6.92	3.48	10.40
Methyl	-5.07	-9.13	-14.20
Meta	-7.38	-18.52	-25.90
Ortho (1)	-20.51	-41.49	-62.00
Ortho (2)	-56.70	-22.80	-79.50
Para	-4.38	-17.02	-21.40

the second term from eq 1 is sizable. For example, an earlier analysis of the shifts of  $\text{Eu}(\text{dpm})_3(\text{py})_2$  via eq 4 has led to a Eu-N bond length of  $4 \text{ \AA}^{22}$  in sharp disagreement with the value of  $2.649 \pm 0.004 \text{ \AA}$  obtained from an X-ray diffraction study.<sup>47,48</sup> In light of the reported anisotropies and our results, it would seem that the second term must be considered, at least for those complexes which form 1:2 adducts.

In the course of this study we attempted a variety of models for the orientation of the magnetic axes, and we used several preliminary estimates of the dipolar shifts obtained from measurements at a single substrate concentration. A general result of these studies was the ability to obtain a reasonable fit for the pyridine protons over a wide variety of axis orientations and dipolar shifts. However, none of these models gave a satisfactory fit for the chelate protons, often producing errors greater than 100%. From this observation we conclude that the shifts of the substrate protons are not very sensitive to the model chosen, nor are those of the chelate protons when considered alone. However, the only model found which produced good results for both the chelate and substrate protons is the one presented here. This illustrates the importance of considering all the protons of the complex and suggests that such an approach may avoid some of the pitfalls inherent in the study of lanthanide induced shifts.

Upon comparing eq 1 and 4 it is apparent that eq 1 demands accurate values for the dipolar shifts, especially if the chelate protons are considered, while eq 4 will tolerate ratios of shifts. Unfortunately due to fast exchange and low formation constants, one cannot obtain accurate isotropic shifts from a single simple measurement.<sup>52</sup> The procedures described in the experimental section yield values good enough to produce an  $R$  value of 0.047 although a large standard deviation in  $D_2$  results. The more sophisticated procedures of Armitage, Dunsmore, Hall, and Marshall<sup>52</sup> should yield somewhat better numbers, but both procedures suffer from the requirement that careful measurements be made. A more accurate and simple procedure would involve the direct measurement of shifts of the complex in the absence of exchange.

Evans and Wyatt<sup>57</sup> have demonstrated that exchange can be stopped and that the signals for the complex can be directly observed in  $\text{CDCl}_3$  for  $\text{Eu}(\text{fod})_3(\text{DMSO})_2$

(57) D. W. Evans and M. Wyatt, *J. Chem. Soc., Chem. Commun.*, 312 (1972).

at  $-80^\circ$ . Although the exchange rates for diadducts of the less acidic  $\text{Eu}(\text{dpm})_3$  reagent are faster, we can reach low enough temperatures in  $\text{CS}_2$  solution so that exchange can be stopped and the shifts of the complex observed directly. Examination of the low temperature results in Table II reveals that agreement between calculated and observed shifts has significantly improved in spite of the much larger shifts observed at low temperatures. Thus while there are some difficulties with these low temperature measurements, such as insolubility of the complex at low temperature, they allow direct determination of accurate values for the shifts, leading to closer agreement between the calculated and observed numbers.

It is of course of interest to compare the values of  $D_1$  and  $D_2$  which we obtained from our least-squares fits in solution with those measured by Horrocks<sup>46</sup> for  $\text{Eu}(\text{dpm})_3(4\text{-pic})_2$  in the solid state. First of all we must recognize that  $\text{Eu}(\text{dpm})_3(\text{py})_2$  and  $\text{Ho}(\text{dpm})_3(4\text{-pic})_2$  crystallize in different space groups<sup>46</sup> so that the orientation of the molecular magnetic axes with respect to the crystal axes is different. In this regard it is useful to note that the  $a$  crystallographic axis of  $\text{Ho}(\text{dpm})_3(4\text{-pic})_2$  is equivalent to the  $c$  axis of  $\text{Eu}(\text{dpm})_3(\text{py})_2$ , but that no such correspondence exists for the other axes. Pyridine and 4-methylpyridine are very similar ligands so that we would expect similar, though perhaps not identical, values of  $D_1$  and  $D_2$  for the two complexes. The labeling of magnetic axes in the two studies is different, with Horrocks identifying the  $C_2$  molecular axis as  $y$  while we refer to it as  $z$ , and the other two axes are similarly permuted. This makes no difference in the calculated dipolar shifts, but it does change the identifying labels in eq 2 and 3 and changes the values of both geometric factors. When the  $x$  magnetic axis makes an angle of  $18^\circ$  with the  $a$  crystallographic axis, Horrocks' values for the magnetic susceptibilities in our axis system yields  $D_1 = 541 \text{ VV/k/mol}$ , which compares very favorably with our value of  $555 \pm 49 \text{ VV/k/mol}$ . Horrocks was unable to obtain an exact value for  $D_2$  since he was unable to obtain the direction cosine of the magnetic  $x$  axis with respect to the  $a$  crystal axis. Our best  $x$  magnetic axis makes an angle of  $24^\circ$  with the  $c$  crystal axis of  $\text{Eu}(\text{dpm})_3(\text{py})_2$ . While the large standard deviation on our  $D_2$  value makes comparisons between the calculated and measured values of  $D_2$  of little worth, our value falls within  $4\sigma$  of that of Horrocks. We conclude that the values of  $D_1$  and  $D_2$  calculated by our least-squares technique are in agreement with those measured experimentally and that therefore the procedure of guessing and then refining the location of the magnetic axes and seeking the best least-squares fits of measured dipolar shifts in order to find values for  $D_1$  and  $D_2$  appears to be a valid one.

Our values for  $D_1$  and  $D_2$  at both high and low temperature are roughly similar to those reported for  $\text{Eu}_2(\text{SO}_4)_3 \cdot 8\text{H}_2\text{O}$ .<sup>58</sup> As a consequence of the temperature-independent paramagnetism<sup>59</sup> of  $\text{Eu}^{3+}$ , the dependence of the shifts with temperature does not follow the Curie law. Bleaney has developed a theoretical equation for the temperature dependence of the magnetic susceptibility and hence the lanthanide induced shift of  $\text{Eu}^{3+}$ .<sup>60</sup> Comparison of our observed low

(58) D. Neogy and A. Mookherjee, *Indian J. Phys.*, **39**, 342 (1965).

(59) S. I. Weissman, *J. Amer. Chem. Soc.*, **93**, 4929 (1971).

(60) B. Bleaney, *J. Magn. Resonance*, **8**, 91 (1972).

temperature shifts with those at room temperature and of  $D_1$  and  $D_2$  at high and low temperature shows that they have increased by a factor of 4, while Bleaney's theory predicts a somewhat smaller increase over this temperature range. Our success in obtaining values of  $D_1$  and  $D_2$  from nmr data suggests that it may be possible to pursue studies of magnetic anisotropies in solution by an nmr method, without directly measuring magnetic susceptibilities.

The observation of two ortho peaks for  $\text{Eu}(\text{dpm})_3(3\text{-pic})_2$  can be explained by several models. The doubling of peaks could result from the presence of two isomers, whose signals appear after exchange has been stopped, or it could be due to restricted rotation about the Eu-N bond. We favor the latter explanation for several reasons. First of all, a sizable barrier to rotation for pyridine has been predicted from the structure of  $\text{Eu}(\text{dpm})_3(\text{py})_2$ .<sup>48</sup> In addition Armitage, *et al.*,<sup>61</sup> have reported that suitable agreement between calculated and observed shifts for aniline coordinated to  $\text{Eu}(\text{dpm})_3$  can only be obtained if the aniline does not freely rotate. Further the two peaks are of equal intensity, within experimental error, which is to be expected for a rotamer model while it is less likely that different isomers would occur in the same amount. The shifts are accounted for quite well on the basis of a rotamer model using the solid-state structure of  $\text{Eu}(\text{dpm})_3(\text{py})_2$ , while one would not expect this agreement to hold for two isomers.

The twofold symmetry of the structures of  $\text{Eu}(\text{dpm})_3(\text{py})_2$  and  $\text{Ho}(\text{dpm})_3(4\text{-pic})_2$  produce two types of ortho py protons, two types of meta py protons, and a single type of para proton. The molecular structures also show two types of chelate rings which produce a total of three types of *tert*-butyl groups and two types of methine protons. However, even in the lowest temperature spectra, only a single type of *tert*-butyl and a single type of methine proton is observed. Therefore there is an exchange process which is averaging the chelate protons even at the lowest temperature we can achieve. The exchange of the substrate molecules provides a mechanism by which the chelate rings can be interchanged without dissociation. If the ligand exchange mechanism is dissociative, as has been suggested,<sup>57</sup> then the dissociation will produce a seven-coordinate complex which will be attacked by an entering substrate. If this substrate enters the position from which the former occupant has departed, chelate ring exchange will not have been accomplished. However, if the attacking substrate enters between the two rings which were equivalent before dissociation, one of them will then be located between the substrates making it the unique ring and an intramolecular chelate exchange will have taken place. If the mechanism is associative, the attacking substrate will form a nine-coordinate complex, and if it approaches between the equivalent chelates, then chelate ring exchange will have again occurred. Therefore exchange of the substrate molecules could also produce chelate ring exchange.

The condition for observation of separate peaks for exchanging nuclei is

$$\frac{1}{\tau} \ll \Delta\nu$$

(61) I. M. Armitage, L. D. Hall, A. G. Marshall, and L. G. Werbelow, paper presented at 164th National Meeting of the American Chemical Society, Aug 1972, New York, N. Y.

where  $1/\tau$  is the exchange rate and  $\Delta\nu$  is the frequency separation between the protons in the exchangeable sites in the absence of exchange. In the case of  $\text{Eu}(\text{dpm})_3(3\text{-pic})_2$  at  $-105^\circ$ , we have reached a temperature at which the ligand exchange rate is slow enough to allow us to resolve peaks due to free and complexed 3-picoline. These are the most favorable situations for observing separate peaks since the peaks are far apart, the free pyridine is in excess, and the free pyridine lines are sharp. However, all of the chelate protons have larger natural line widths, due to their proximity to the paramagnetic  $\text{Eu}^{3+}$  ion, and their exchange is between two sites both of which are characterized by large line widths. Thus for the same exchange rate the chemical shift difference for the chelate protons must be greater in order for separate signals to be resolved.

The fact that the two meta signals are not resolved, and that even at lower temperatures the ability to resolve the methyl peaks depends on concentrations and ratios of substrate to shift reagent, suggests that the lowest temperature we can attain is not yet sufficient to eliminate the effects of exchange for all protons of the complex. Further the line width for the *tert*-butyl protons at  $-115^\circ$  is about 1500 Hz, a large value, suggesting that their coalescence temperature may be near. Further lowering of temperature may allow observation of the various separate chelate protons.

There has been considerable concern as to whether the dipolar shift dominates the Fermi contact term for lanthanide complexes. It has been concluded that the contact term dominates for  $^{17}\text{O}$  in aquo complexes of lanthanides and that it is also considerable for the protons.<sup>62</sup> Further for  $\text{Eu}(\text{dpm})_3(\text{py})_2$  it has been shown that the  $^{14}\text{N}$  shifts are upfield,<sup>63</sup> while a dipolar mechanism would require a downfield shift, so that the  $^{14}\text{N}$  shifts are dominated by the contact mechanism. Horrocks and Sipe,<sup>61</sup> on the other hand, have claimed that their ability to calculate the 4- $\text{CH}_3$  shifts of  $\text{Ln}(\text{dpm})_3(4\text{-pic})_2$  from magnetic susceptibility anisotropy data demonstrates the dipolar origin of the proton shifts. Our success in calculating the shifts of all of the protons in the complex with anisotropy values consistent with those of Horrocks and Sipe<sup>61</sup> strengthens and supports this conclusion.

Why then do dipolar shifts dominate for protons but not necessarily for  $^{13}\text{C}$ ,  $^{14}\text{N}$ , or  $^{17}\text{O}$ ? First of all such a situation could only result if Fermi contact shifts on a parts per million basis were in general larger for  $^{13}\text{C}$ ,  $^{14}\text{N}$ , and  $^{17}\text{O}$  than they are for protons. Doddrell and Roberts<sup>64</sup> have shown that  $^{13}\text{C}$  shifts are generally larger than proton shifts in  $\text{Ni}(\text{acac})_2(\text{py})_2$  in which the shifts are believed to be pure Fermi contact in nature. Further there is a fundamental reason why Fermi contact shifts should be smaller for hydrogen than for carbon. Examination of the equation for the Fermi contact shift and for the electron-nucleus hyperfine coupling constant reveals that the contact shift on a ppm basis is proportional to magnetic susceptibility,  $\chi$ , and the value of the square of the unpaired electron wave function at the nucleus,  $|\psi_{(0)}|^2$ . Since  $\chi$  is constant at constant temperature for a given molecule, the

(62) J. Reuben and D. Fiat, *J. Chem. Phys.*, **51**, 4909 (1969).

(63) M. Witanowski, L. Stefaniak, and H. Januszewski, *Chem. Commun.*, 1573 (1971).

(64) D. Doddrell and J. D. Roberts, *J. Amer. Chem. Soc.*, **92**, 6839 (1970).

smaller contact shifts for hydrogen must result from smaller values for  $|\psi_{(O)}|^2$ . There are two effects which could produce smaller values for  $|\psi_{(O)}|^2$  for hydrogen: (1) a larger coefficient in the unpaired electron wave function for the 2s orbital of the heavy element than for the 1s orbital of hydrogen, (2) the larger value of  $|\psi_{(O)}|^2$  for the 2s atomic orbital of  $^{13}\text{C}$ ,  $^{14}\text{N}$ , and  $^{17}\text{O}$  than for the 1s atomic orbital of  $^1\text{H}$ . The first effect will certainly dominate whenever the nucleus being examined is the donor atom, since the wave function of the unpaired electron on the metal will mix predominantly with the ligand lone pair orbital which will have a large contribution from the donor atom. This probably accounts for the apparent contact shift observed for  $^{14}\text{N}$  in  $\text{Eu}(\text{dpm})_3(\text{py})_2$ .<sup>63</sup> The second effect is probably responsible for the generally larger  $^{13}\text{C}$  contact shifts because even if the  $^1\text{H}$  and  $^{13}\text{C}$  s orbital coefficients are comparable, as they often are, the larger values of  $|\psi_{(O)}|^2$  for the  $^{13}\text{C}$  2s atomic orbital will tend to make the contact shift larger for  $^{13}\text{C}$ . It has been pointed out<sup>65,66</sup> that values of  $|\psi_{(O)}|^2$  for valence s

orbitals increase as the atomic number increases. Therefore there is good reason to believe that proton shifts will be largely free from contamination by a Fermi contact contribution but that this may not be true for heavier nuclei.<sup>67</sup>

**Acknowledgment** is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this research.

(65) R. E. Cramer and R. S. Drago, *J. Amer. Chem. Soc.*, **90**, 4790 (1968).

(66) C. J. Jameson and H. S. Gutowsky, *J. Chem. Phys.*, **51**, 2790 (1969).

(67) NOTE ADDED IN PROOF. Recent experiments with the substrates pyridine, 4-methylpyridine, and 3,5-dimethylpyridine in Freon 12 at temperatures as low as  $-150^\circ$  fail to reveal doubling of the ortho peaks or any splitting of the chelate protons. These results suggest that the barrier to rotation model we had advocated earlier [R. E. Cramer and R. Dubois, *J. Chem. Soc., Chem. Commun.*, 936 (1973)] may not be correct. The doubling observed for the ortho peaks of 3-pic may instead be due to a Fermi contact interaction. However the fact that the separation of the ortho peaks of  $\text{Eu}(\text{dpm})_3(3\text{-pic})_2$  is solvent dependent, being 18 ppm in  $\text{CS}_2$  but only 8 ppm in  $\text{CCl}_2\text{F}_2$  at  $-120^\circ$ , suggests that the splitting may be due to unequally populated conformers. Further experiments are in progress to resolve this matter.

## Magnetic Circular Dichroism of Some Complexes of Nickel(II) with Schiff Bases

Hajime Katô\* and Takashi Sakamoto

*Contribution from the Department of Chemistry, Faculty of Science, Kobe University, Nada-ku, Kobe 657, Japan. Received August 16, 1973*

**Abstract:** Magnetic circular dichroism (MCD) data of bis(*R-N*-salicylaldehyde)nickel(II) complexes ( $\text{R} = \text{H}, \text{OH}, \text{Me}, \text{Ph}, o\text{-tolyl}, m\text{-tolyl}, p\text{-tolyl}$ ) and bis(salicylaldehyde)ethylenediaminenickel(II) in chloroform and pyridine solutions are presented and analyzed. The MCD of an allowed transition  ${}^3\text{A}_{2g} \rightarrow {}^8\text{T}_{1u}$  of the paramagnetic and octahedral bispyridine adduct shows the negative sign of  $[\theta]_M$  at *ca.*  $26,000\text{ cm}^{-1}$ . The MCD of the high-intensity bands of  $\text{Ni}(\text{Sal-}N\text{-}o\text{Tol})_2$  in chloroform, which is diamagnetic planar, shows a negative *A* term pattern at *ca.*  $29,500\text{ cm}^{-1}$  and a positive *B* term pattern at *ca.*  $23,000\text{ cm}^{-1}$ . On the basis of the analysis on the sign and magnitude of the MCD, the band at *ca.*  $29,500\text{ cm}^{-1}$  is assigned to the transition  ${}^1\text{A}_g \rightarrow {}^1\text{B}_u(\sigma, x), {}^1\text{B}_u(\sigma, y); e_u(\sigma) \rightarrow b_{1g}-(d_{x^2-y^2})$  and the band at *ca.*  $23,000\text{ cm}^{-1}$  is assigned to the transition  ${}^1\text{A}_g \rightarrow {}^1\text{A}_u(\pi^*, z); a_{1g}(d_{z^2}) \rightarrow a_{2u}(\pi^*, z)$ .

Schiff base complexes of nickel(II) are of particular interest because of the variety of spatial configurations and multiplicities of the ground state, and a number of studies on these complexes have been reported.<sup>1-6</sup> However, the interpretation of spectra, especially of the strong absorption bands, is insufficient and left unsettled. The usefulness of MCD in assigning the nature of electronic transitions has been extensively demonstrated.<sup>7-10</sup> In this paper, we report

the MCD spectra of some complexes of nickel(II) with Schiff bases in "noncoordinating" solvent, chloroform, and in "coordinating" solvent, pyridine. The sign and magnitude of MCD will help considerably in assigning the transitions and in interpreting the electronic structure.

### Experimental Section

The following compounds used in this study were prepared and recrystallized according to previously reported procedures: bis(salicylaldehyde)nickel(II),<sup>11</sup> bis(salicylaldehyde)nickel(II),<sup>12</sup> bis(*N*-methylsalicylaldehyde)nickel(II),<sup>13</sup> bis(*N*-phenylsalicylaldehyde)nickel(II),<sup>14</sup> bis(*N*-*o*-tolylsalicylaldehyde)nickel(II),<sup>14</sup> bis(*N*-*m*-tolylsalicylaldehyde)nickel(II),<sup>14</sup> bis(*N*-*p*-tolylsalicylaldehyde)nickel-

\* Ramsay Fellow.

(1) L. Sacconi, "Transition Metal Chemistry," Vol. 4, R. L. Carlin, Ed., Marcel Dekker, New York, N. Y., 1968, pp 199-298.

(2) F. Basolo and W. R. Matoush, *J. Amer. Chem. Soc.*, **75**, 5663 (1953).

(3) R. H. Holm, *J. Amer. Chem. Soc.*, **82**, 5632 (1960).

(4) A. Chakravorty and R. H. Holm, *J. Amer. Chem. Soc.*, **86**, 3999 (1964).

(5) L. Sacconi, P. Paoletti, and G. D. Re, *J. Amer. Chem. Soc.*, **79**, 4062 (1957).

(6) R. H. Holm, G. W. Everett, and A. Chakravorty, *Progr. Inorg. Chem.*, **7**, 83 (1966).

(7) A. D. Buckingham and P. J. Stephens, *Annu. Rev. Phys. Chem.*, **17**, 399 (1966).

(8) P. N. Schatz and A. J. McCaffery, *Quart. Rev., Chem. Soc.*, **23**, 552 (1969).

(9) "Magneto Optical Effects," *Symp. Faraday Soc.*, No. 3 (1969), and reference cited therein.

(10) H. Katô, *J. Chem. Phys.*, **58**, 1964 (1973).

(11) G. N. Tyson, Jr., and S. C. Adams, *J. Amer. Chem. Soc.*, **62**, 1228 (1940).

(12) E. G. Cox, F. W. Pinkard, W. Wardlaw, and K. C. Webster, *J. Chem. Soc.*, 459 (1935).

(13) W. Klemm and K. H. Raddatz, *Z. Anorg. Allg. Chem.*, **250**, 207 (1942).

(14) R. H. Holm and K. Swaminathan, *Inorg. Chem.*, **1**, 599 (1962).