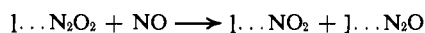


tunity for the reaction



is limited. Here, it is inferred that adsorbed N_2O_2 is the key intermediate for the disproportionation reaction; however, the adsorbed N_2O_2 on HY did not contribute at all to the disproportionation reaction. This indicates that the function of the zeolite in the catalyzed reaction may be more than just to bring three NO

molecules together at one site. The unique ability of certain zeolites to catalyze the reaction may be partly due to the stabilization of N_2O_2 in a particular configuration. At the present time there is still not enough evidence to decide which particular adsorbed N_2O_2 species contributes most to the disproportionation reaction.

Acknowledgment. This work was supported by The Robert A. Welch Foundation under Grant No. A-257.

Lanthanide Shift Reagents. A Survey

William DeW. Horrocks, Jr., and James P. Sipe, III

Contribution from Whitmore and Chandlee Laboratories,
Department of Chemistry, The Pennsylvania State University,
University Park, Pennsylvania 16802. Received January 27, 1971

Abstract: A quantitative study of the action of trivalent lanthanide chelate complexes of 2,2,6,6-tetramethylheptane-3,5-dione, $\text{Ln}(\text{dpm})_3$, $\text{Ln} = \text{Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, and Yb}$, on the pmr spectra of 4-vinylpyridine, 4-picoline *N*-oxide, and *n*-hexyl alcohol is reported. Upfield substrate ligand resonance shifts are obtained for the systems involving Pr, Nd, Sm, Tb, Dy, and Ho, while downfield shifts are observed for Eu, Er, Tm, and Yb. A linear dependence of the observed shifts on the $[\text{Ln}(\text{dpm})_3]/[\text{substrate}]$ ratio for values of this quantity less than 0.2 is observed. The shift ratios are found to correlate with calculated geometric factor ratios for 4-vinylpyridine, and the signs of the shifts correlate qualitatively with magnetic anisotropy data in the literature, indicating a dipolar origin of the resonance displacements. A survey of the relative proton resonance broadening abilities of the various lanthanide chelates is also presented.

Following the discovery by Hinckley¹ that large isotropic shifts $\Delta\nu_{\text{iso}}$ are produced for the proton resonances of cholesterol when this molecule is placed in solutions of the dipyrindinate of tris(dipivaloylmethanato)europium(III), $\text{Eu}(\text{dpm})_3(\text{py})_2$,² considerable interest has been shown³⁻¹⁹ in lanthanide "shift reagents."²⁰ Major discoveries include: (1) the finding that shift reagents cause isotropic shifts in a va-

riety of functional organic molecules including alcohols,^{1,3-5,7-9,15,16,18} amines,^{3,10,13,15,18} ketones,^{3,11,14,18} aldehydes,^{3,18} sulfoxides,^{6,17} and esters;^{12,13,15,18,19} (2) the observation³ that $\text{Eu}(\text{dpm})_3$ is more efficient in effecting such shifts than is $\text{Eu}(\text{dpm})_3(\text{py})_2$, presumably owing to the lack of competition with pyridine for coordination sites; (3) the discovery⁴ that $\text{Pr}(\text{dpm})_3$ causes upfield shifts of larger magnitude than the downfield displacements induced by $\text{Eu}(\text{dpm})_3$ and the observation¹³ of shifts for substrates in the presence of dpm complexes of Sm, Tb, Ho, and Yb as well; (4) the introduction¹⁰ of the chiral chelate, tris[(+)-3-pivaloylcamphorato]europium(III), a shift reagent for the determination of enantiomeric purity; (5) the observation that certain other lanthanide complexes⁴ as well as β -diketonate chelates with less bulky substituents^{18,21} than $\text{Ln}(\text{dpm})_3$ are inefficient as shift reagents, very likely owing to the lack of a preferred orientation of the substrate molecule when the stereochemical rigidity and the bulky substituents of the chelate rings are absent; (6) the finding¹⁹ that partially fluorinated chelates of a similar variety are superior shift reagents because of propitious solubility and Lewis acidity characteristics.

While the action of shift reagents is generally attributed to a through-space dipolar^{22,23} interaction, a through-bond Fermi contact interaction has been considered to contribute in some cases.^{5,8} Dipolar shifts are proportional to magnetic susceptibility anisotropy,²³⁻²⁵

- (1) C. C. Hinckley, *J. Amer. Chem. Soc.*, **91**, 5160 (1969).
- (2) Hdpm = 2,2,6,6-tetramethylheptane-3,5-dione.
- (3) J. K. M. Sanders and D. H. Williams, *Chem. Commun.*, 422 (1970).
- (4) J. Briggs, G. H. Frost, F. A. Hart, G. P. Moss, and M. L. Stanforth, *ibid.*, 749 (1970).
- (5) G. H. Wahl, Jr., and M. R. Peterson, Jr., *ibid.*, 1167 (1970).
- (6) R. R. Fraser and Y. Y. Wigfield, *ibid.*, 1471 (1970).
- (7) J. Briggs, F. A. Hart, and G. P. Moss, *ibid.*, 1506 (1970).
- (8) P. V. Demarco, T. K. Elzey, R. B. Lewis, and E. Wenkert, *J. Amer. Chem. Soc.*, **92**, 5734 (1970).
- (9) P. V. Demarco, T. K. Elzey, R. B. Lewis, and E. Wenkert, *ibid.*, **92**, 5737 (1970).
- (10) G. M. Whitesides and D. W. Lewis, *ibid.*, **92**, 6979 (1970).
- (11) C. C. Hinckley, *J. Org. Chem.*, **35**, 2834 (1970).
- (12) F. I. Carroll and J. T. Blackwell, *Tetrahedron Lett.*, 4173 (1970).
- (13) D. R. Crump, J. K. M. Sanders, and D. H. Williams, *ibid.*, 4419 (1970).
- (14) K. L. Liska, A. F. Fentiman, Jr., and R. L. Foltz, *ibid.*, 4657 (1970).
- (15) D. R. Crump, J. K. M. Sanders, and D. H. Williams, *ibid.*, 4949 (1970).
- (16) A. F. Cockerill and D. M. Rackham, *ibid.*, 5149 (1970).
- (17) K. K. Andersen and J. J. Uebel, *ibid.*, 5253 (1970).
- (18) J. K. M. Sanders and D. H. Williams, *J. Amer. Chem. Soc.*, **93**, 641 (1971).
- (19) R. E. Rondeau and R. E. Sievers, *ibid.*, **93**, 1525 (1971).
- (20) The use of paramagnetic transition metal β -diketonate complexes of cobalt(II) and nickel(II) to simplify the complex spectra of organic ligands and to obtain diamagnetic chemical shifts by extrapolation was first demonstrated several years ago: R. W. Kluiber and W. DeW. Horrocks, Jr., *ibid.*, **88**, 1399 (1966).

(21) (a) J. Jacobus, private communication; (b) J. P. Sipe, III, unpublished results.

(22) Sometimes referred to as pseudocontact.

(23) For a discussion and leading references, see W. DeW. Horrocks, Jr., *Inorg. Chem.*, **9**, 690 (1970).

and, for axially symmetric systems, to the geometric factor $\langle(3 \cos^2 \theta - 1)r^{-3}\rangle_{av}$, where r is the length of a radius vector from the metal atom to the resonating nucleus, θ is the angle made by this vector with the principal axis, and the average is taken over motions rapid on the nmr time scale. A number of workers^{1,6,8,9,11} have chosen to neglect the angular (θ) dependence and have attempted to correlate the shifts with r^{-3} on the basis of assumed models. The radial parameter r has occasionally been measured from the hydroxyl oxygen.^{8,9} In one instance¹⁶ this quantity was measured from the oxygen lone-pair perimeter, and correlation with the function r^{-2} was obtained. Others⁷ have achieved a reasonable correlation between the ratios of the observed shifts and geometric factors using the correct formulation of the latter quantities and an iterative method of model generation. All of the reported geometrical inferences have involved alcohols, where there are unknown geometrical parameters for the coordination to, or association with, the metal chelate complex. Thus the mechanism of action of lanthanide shift reagents has not been definitely established, nor have the capabilities of $\text{Ln}(\text{dpm})_3$ chelates other than those of Pr and Eu been extensively investigated.

We report here a survey of the action as shift reagents of all the paramagnetic $\text{Ln}(\text{dpm})_3$ complexes (with the exception of those of Ce and Pm) on three representative substrate ligands: 4-vinylpyridine, 4-picoline *N*-oxide, and *n*-hexyl alcohol. The first of these, 4-vinylpyridine, was chosen since it is a rigid ligand with five sets of protons, thus allowing an accurate determination of several geometric factors. The second, 4-picoline *N*-oxide, is a member of a class of ligands for which the action of lanthanide shift reagents has not been reported. The last, *n*-hexyl alcohol, is an alcohol, the class of molecule most studied *via* shift reagents.

Experimental Section

The $\text{Ln}(\text{dpm})_3$ complexes were prepared according to the method of Eisentraut and Sievers,²⁶ and purified by vacuum sublimation and/or recrystallization from methylcyclohexane. The elemental analyses and melting point data are set out in Table I.

Table I. Analytical^a and Melting Point^b Data

Complex	Calculated		Found		Mp, °C
	% C	% H	% C	% H	
Pr(dpm) ₃	57.38	8.32	57.14	8.26	214–219
Nd(dpm) ₃	57.11	8.28	57.44	8.33	211–214
Sm(dpm) ₃	56.61	8.21	56.39	8.11	195–197
Eu(dpm) ₃	56.48	8.19	56.21	8.17	186–188
Gd(dpm) ₃	56.06	8.13	55.98	8.13	183–185
Tb(dpm) ₃	55.93	8.11	56.10	8.09	177–179
Dy(dpm) ₃	55.64	8.07	55.72	8.13	181–183
Ho(dpm) ₃	55.46	8.04	55.61	8.15	181–183
Er(dpm) ₃	55.28	8.01	54.98	8.12	179–182
Tm(dpm) ₃	55.15	7.99	54.81	8.07	170–173
Yb(dpm) ₃	54.83	7.95	55.16	8.23	166–168

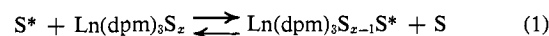
^a Galbraith Laboratories, Inc., Knoxville, Tenn. ^b Uncorrected.

Pmr spectra were obtained on deuteriochloroform solutions using Varian A-60 and A-60A spectrometers operating near 30° and em-

ploying tetramethylsilane, TMS, as an internal standard. All data were corrected to this temperature assuming a $1/T$ isotropic shift temperature dependence.

Results and Discussion

Concentration Dependence of the Shifts. Before describing our results on the relative shifting and broadening abilities of the various lanthanide complexes of dpm, it is appropriate to consider the concentration dependencies of resonance shifts in such systems. It has been observed^{16–19} that under certain conditions the isotropic shift of a given substrate ligand resonance in the presence of a shift reagent is linearly related to the mole ratio of shift reagent to substrate, $R_p = [\text{Ln}(\text{dpm})_3]/[\text{substrate}]$. This is the behavior to be expected for a labile equilibrium (rapid on the nmr time scale) of the type



where S represents the substrate molecule, present in excess, and the asterisk label is used to denote the exchange of identical ligand molecules. The number of coordinated substrate molecules x has not been definitely established in these systems. For heterocyclic amines, x is very likely two, since complexes of this stoichiometry have been isolated in the solid state.^{1,27} Analysis of the data in terms of equilibrium 1 will be valid only if the sole complex species in solution is $\text{Ln}(\text{dpm})_3\text{S}_x$. This condition will obtain if the formation constant of this complex is large and/or the substrate molecule S is present in large excess. Only for small values of R_p will the latter condition be met. Other workers^{16,19} have noted a deviation from linearity of a plot of $\Delta\nu^{\text{iso}}$ vs. R_p for R_p values greater than ca. 0.2 and also, even when such plots are linear, a dependence of the slope on the substrate concentration for R_p values greater than this.^{17,18} The present experiments were done on solutions with R_p in the range 0.030–0.252. Typical linear plots of chemical shift vs. R_p for two systems involving 4-vinylpyridine as a substrate are shown in Figure 1. Diamagnetic chemical shifts were estimated by extrapolation to $R_p = 0$, and in most cases the values are in good agreement with those found from the spectrum of the diamagnetic substance itself. The shifts, quoted for a given R_p value, were obtained from the slopes of these linear plots. In order to determine whether, in this range of R_p values, the slopes are dependent on substrate concentration, a study was made of the $\text{Eu}(\text{dpm})_3$ –4-picoline system at various total 4-picoline concentrations in the range 0.6–1.0 *M*. The results, shown in Figure 2, indicate that for this system the slopes are independent of the total substrate concentration. For such systems the shift of a given substrate resonance in the complex $\text{Ln}(\text{dpm})_3\text{S}_x$ is given by $\Delta\nu^{\text{obsd}}/xR_p$, provided, of course, that x is known. This simple interpretation is valid only under conditions where $\text{Ln}(\text{dpm})_3\text{S}_x$ is the sole complex species and complexes of the type $\text{Ln}(\text{dpm})_3\text{S}_{x-1}$, etc., and polymeric species are absent or present in only insignificant quantities. Under the conditions employed by us, this is likely the case, and the assumption will be made that the observed shifts are dependent on the geometrical and electronic structures

(27) Crystalline bis adducts of 2- and 4-picoline have been isolated in this laboratory.

(24) R. J. Kurland and B. R. McGarvey, *J. Magn. Resonance*, **2**, 286 (1970).

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

(26) K. J. Eisentraut and R. E. Sievers, *Inorg. Syn.*, **11**, 94 (1968).

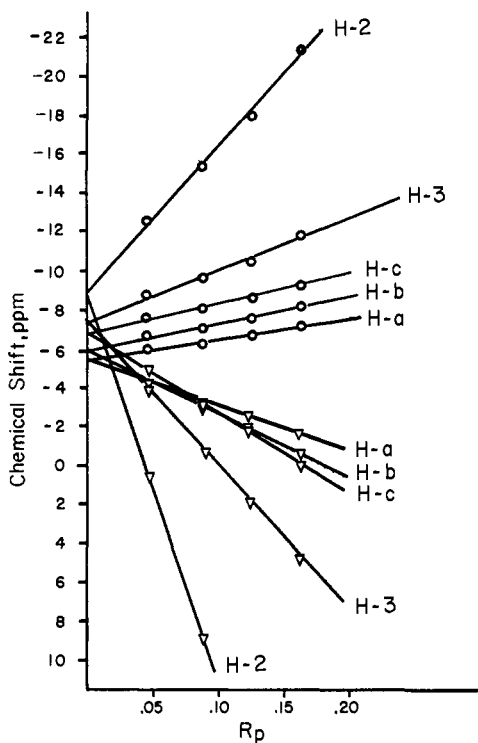


Figure 1. Chemical shift (parts per million from TMS) vs. R_p for 0.8 M 4-vinylpyridine solutions containing Er(dpm)₃ (○) or Ho(dpm)₃ (▽) in deuteriochloroform at 30°.

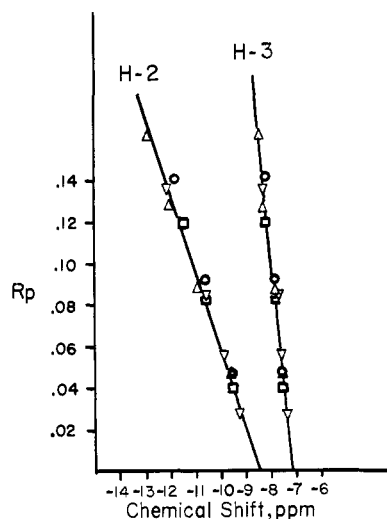


Figure 2. Chemical shift (parts per million from TMS) vs. R_p of the H-2 and H-3 proton resonances of 4-picoline for deuteriochloroform solutions of 0.61 M (○), 0.70 M (□), 0.80 M (Δ), and 1.00 M (▽) in 4-picoline in the presence of Eu(dpm)₃.

of the complexes and not upon differences in their formation constants.

Relative Shifting Abilities of the Various Lanthanide Complexes. Figure 3 shows a plot of the observed isotropic shifts, under specified conditions where a plot of shift vs. R_p is linear, for the most shifted resonance of each of the ligands (the H-2 resonance of 4-vinylpyridine and 4-picoline *N*-oxide, and the α -methylene proton resonance of *n*-hexyl alcohol²⁸). Of the early lanthanides, Pr complexes produce the largest upfield shifts and Eu the largest downfield resonance

(28) The hydroxyl proton resonance was not observed.

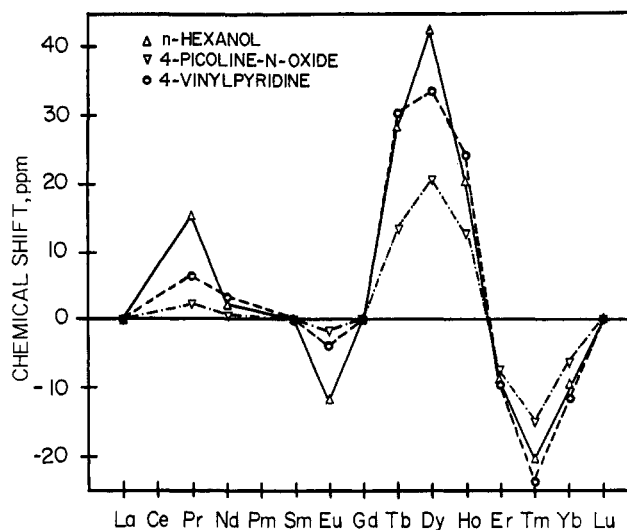


Figure 3. Observed isotropic shifts for the most shifted resonances of 0.8 M solutions of *n*-hexyl alcohol (H-1), 4-picoline *N*-oxide (H-2), and 4-vinylpyridine (H-2), in the presence of Ln(dpm)₃ with $R_p = 0.125$ (see text) measured at 30° on deuteriochloroform solutions.

displacements. Even larger shifts are produced by chelates of the later lanthanides, with Dy causing the largest upfield and Tm the largest downfield resonance displacements. In most cases, the spectra of the Gd(dpm)₃ systems were so severely broadened as to be unobservable. The methyl resonance of 4-picoline in the presence of this reagent was observed, however, and found to be unshifted. While contact shifts have been reported for some other Gd(III) complexes including tropolone chelates²⁹ and aquo species,³⁰ we feel that the lack of shift in the present Gd systems is consistent with, and indicative of, a dipolar origin for the shifts in the other lanthanide systems. Since each *f* orbital is singly occupied in Gd(III), there can be no orbital symmetry restriction on electron spin delocalization, and a contact shift, if present in any of the lanthanide complexes, would be expected to show up here.

Additional evidence for the dipolar origin of the isotropic shifts is the correlation to be found with magnetic susceptibility anisotropy and/or *g*-tensor anisotropy in several series of isostructural lanthanide salts. It has been shown²³⁻²⁵ that for a given structure dipolar shifts will be proportional to susceptibility tensor anisotropy.³¹ Since, to a good approximation, for a given structure (ligand field potential), the magnetic properties will depend only on the electronic configuration, it is reasonable to expect dipolar shifts to correlate qualitatively with magnetic anisotropy data. Thus, for the isostructural salts Ln(C₂H₅SO₄)₃·9H₂O, $\chi_{||} > \chi_{\perp}$ for Ln = Pr, Nd, Sm, Dy, and Ho, while $\chi_{||} < \chi_{\perp}$ for Ln = Er and Yb,³² in perfect correlation with the ob-

(29) E. L. Muetterties and C. M. Wright, *J. Amer. Chem. Soc.*, **87**, 4706 (1965).

(30) J. Reuben and D. Fiat, *J. Chem. Phys.*, **51**, 4909 (1969); no proper correction appears to have been made for bulk susceptibility shifts in this work.

(31) For a review, see W. DeW. Horrocks, Jr., and D. DeW. Hall, *Coord. Chem. Rev.*, **6**, 147 (1971).

(32) (a) K. S. Krishnan and A. Mookherjee, *Phil. Trans. Roy. Soc. London, Ser. A*, **237**, 135 (1938); (b) A. H. Cooke, R. Lazenby, and M. J. M. Leask, *Proc. Phys. Soc., London*, **85**, 767 (1965); (c) S. P. Chachra and A. Mookherjee, *Indian J. Pure Appl. Phys.*, **7**, 559 (1969); (d) A. Mookherjee and S. P. Chachra, *J. Phys. Chem. Solids*, **30**, 2399 (1969).

Table II. Isotropic Shift Data for 4-Vinylpyridine^a and Line-Width Data for 2-Picoline Adducts of Ln(dpm)₃

Ln	Observed H-2 isotropic shift, ppm ^b	Relative shifts					$\Delta\nu_{1/2}$, ^{b,d} Hz
		H-2 ^c	H-3	H _a	H _b	H _c	
Pr	+6.6	1.00	0.40	0.15	0.18		5.6
Nd	+3.2	1.00	0.34	0.11	0.14	0.23	4.0
Sm	+0.8	1.00	0.44	0.20	0.32	0.32	4.4
Eu	-3.5	1.00	0.38	0.13	0.19	0.23	5.0
Tb	+30.7	1.00	0.37	0.13	0.18	0.18	96
Dy	+33.8	1.00	0.39	0.09	0.15	0.22	200
Ho	+24.0	1.00	0.38	0.11	0.15	0.22	50
Er	-9.1	1.00	0.33	0.11	0.18	0.23	50
Tm	-23.6	1.00	0.34	0.12	0.17	0.19	65
Yb	-11.0	1.00	0.36	0.12	0.17	0.20	12
	$((3 \cos^2 \theta - 1)r^{-3})$	1.00	0.38	0.10	0.19	0.20	

^a Vinyl protons: H_a and H_b are gem, with H_b trans to H_c. The 4-vinylpyridine structural parameters used were those given by R. E. Cramer and R. S. Drago, *J. Amer. Chem. Soc.*, **92**, 66 (1970). ^b Measured at 30° for R_p = 0.125 (see text). ^c Shift of H-2 normalized to 1.00. ^d Width at half maximum for methyl of 2-picoline.

served signs of the shifts in the present systems. Furthermore, for scheelites of the structure LnNa(MoO₄)₂, it is observed³³ that $\chi_{||} > \chi_{\perp}$ for Tb, Dy, and Ho, while $\chi_{||} < \chi_{\perp}$ for Er, Tm, and Yb, again in perfect agreement. Likewise, electron paramagnetic resonance experiments on substituted impurities in LaCl₃ show³⁴ that $g_{||} > g_{\perp}$ for Pr, Nd, Tb, and Ho, while $g_{||} < g_{\perp}$ for Er, and $g_{||}$ is virtually identical with g_{\perp} for Gd and Sm, again correlating excellently with the present observed shifts.

Our data do not correlate with the function $L - 2S^{35}$ or $g_L - 1^{30,36}$ proposed elsewhere. No such correlation is to be expected for shifts arising from magnetic anisotropy.

Comparison of Relative Shifts. In Table II are presented the relative shifts for the 4-vinylpyridine adducts of the entire series of Ln(dpm)₃ chelates. The reasonable agreement between shift ratios from system to system, regardless of the sign of the shifts, is to be expected for shifts of a dipolar nature in isostructural series. For axially symmetric systems, dipolar shifts are proportional to the product of a magnetic anisotropy factor and a geometric factor, while for nonaxial systems two anisotropy and two geometric factors are involved. The actual stoichiometry and geometry of the 4-vinylpyridine complexes in solution have not been established, however the crystal structure of the bis(4-picoline) adduct of Ho(dpm)₃ has recently been determined in these laboratories³⁷ and may be of some pertinence. In the *solid state* the holmium atom is eight-coordinate, with a nearly square-antiprismatic coordination polyhedron. The 4-picoline nitrogen atoms occupy sites on *different* square faces, roughly trans to one another. The only molecular symmetry is a C₂ axis bisecting one of the chelate rings which carries one of the picoline ligands into the other. The complex is not axially symmetric with respect to the adduct ligands in the crystal. The N-Ho bond axes deviate ~20° from a likely principal magnetic axis. In the absence of magnetic anisotropy data, it is not possible to determine whether these systems approximate axial symmetry in a magnetic

Table III. Isotropic Shift^a and Ratio Data for 4-Picoline N-Oxide Adducts of Ln(dpm)₃

Ln	Shift, ppm H-2	Shift ratios		
		H-2/H-2	H-3/H-2	4-CH ₃ /H-2
Pr	+2.23	1.0	0.21	0.20
Nd	+0.58	1.0	0.29	0.20
Sm	^b			
Eu	-1.62	1.0	0.23	0.15
Gd	^c			
Tb	+14.0	1.0	0.36	0.24
Dy	+20.0	1.0	0.28	0.16
Ho	+12.7	1.0	0.33	0.25
Er	-7.4	1.0	0.27	0.16
Tm	-15.1	1.0	0.28	0.17
Yb	-6.47	1.0	0.26	0.14
	$((3 \cos^2 \theta - 1)r^{-3})_{av,d}$	1.00	0.33	0.17

^a At 30° with R_p = 0.125 and a total 4-picoline N-oxide concentration of 0.8 M. ^b Very small positive shifts. ^c No spectrum observed. ^d Calculated using structural parameters from ref 44, an Ln-O distance of 2.40 Å, an Ln-O-N angle of 120°, and free rotation about the O-N bond axis.

sense, nor is it known whether the solid-state structure persists in solution. Considering the stereochemical nonrigidity of eight-coordinate structures,³⁸ it cannot be surmised with any certainty what structure or structures exist in solution. It may be that the magnetic axes are determined by the disposition of the adduct ligands, and the *average* structure in solution approximates axiality. In the absence of knowledge of these unknown factors, we, as others, have attempted a correlation with geometric factors based on an axially symmetric model. Any geometrical inferences obtained in these or other shift reagent systems must be accepted with the above qualifications in mind. The geometric factors were calculated using the molecular parameters for 4-vinylpyridine indicated in Table II and the Ho-N distance of 2.53 Å found³⁷ for the 4-picoline adduct. This Ln-N distance is consistent with the 2.65-Å value found in the crystal structure³⁹ of La(NO₃)₃bipy. The correlation of the four independent observed shift ratios with the calculated geometric factor ratios is reasonable for both upfield and downfield shifting systems. The correlation with r^{-3} is considerably inferior,⁴⁰ nor is there any correspondence with the contact-shift pattern

(38) E. L. Muetterties and C. M. Wright, *Quart. Rev., Chem. Soc.*, **21**, 109 (1967).

(39) A. R. Al-Karaghoulis and J. S. Wood, *J. Amer. Chem. Soc.*, **90**, 6548 (1968).

(40) r^{-3} ratios, H-2:H-3:H_a:H_b:H_c = 1.00:0.23:0.06:0.10:0.09.

(33) L. Holmes and M. Schieber, *J. Phys. Chem. Solids*, **29**, 1663 (1968).

(34) C. A. Hutchinson and E. Wong, *J. Chem. Phys.*, **29**, 754 (1958).

(35) F. A. Hart, J. E. Newbery, and D. Shaw, *J. Inorg. Nucl. Chem.*, **32**, 3585 (1970).

(36) W. B. Lewis, J. A. Jackson, J. F. Lemons, and H. Taube, *J. Chem. Phys.*, **36**, 694 (1962).

(37) W. DeW. Horrocks, Jr., J. P. Sipe, III, and J. R. Lubner, *J. Amer. Chem. Soc.*, **93**, 5258 (1971).

Table IV. Isotropic Shift^a and Ratio Data of Alkyl^b Protons of *n*-Hexyl Alcohol

Ln	Shift, ppm H-2	Shift ratios					
		H-1/H-2	H-2/H-2	H-3/H-2	H-4/H-2	H-5/H-2	H-6/H-2
Pr	+4.73	3.30	1.00	0.53	0.26	0.21	0.11
Nd	+1.33	1.91	1.00	0.62	0.19	0.19	0.13
Sm	^c						
Eu	-3.11	-3.82	1.00	0.51	0.35	0.22	0.08
Gd	^d						
Tb	+16.58	1.70	1.00	0.65	0.36	0.21	0.12
Dy	+24.30	1.73	1.00	0.65	0.32	0.14	0.12
Ho	+10.48	1.92	1.00	0.70	0.49	0.21	0.13
Er	-4.6	1.75	1.00	0.63	0.34	0.24	0.12
Tm	-11.37	1.80	1.00	0.64	0.39	0.20	0.12
Yb	-5.68	1.73	1.00	0.65	0.32	0.19	0.11

^a At 30°, with $R_p = 0.125$ and a total *n*-hexyl alcohol concentration of 0.8 M. ^b Numbered as follows: HO-CH₂¹CH₂²CH₂³CH₂⁴-CH₂⁵CH₃. ^c Very small positive shifts. ^d No spectrum observed.

of 4-vinylpyridine coordinated to nickel(II).⁴¹ Additional support for the lack of a dominant contact interaction is the absence of a correlation with the mean values $\langle S_z \rangle$.⁴² This quantity is positive for Ln(III) complexes for the elements Ce through Eu and negative thereafter.

Isotropic shift and ratio data for 4-picoline *N*-oxide and *n*-hexyl alcohol are given in Tables III and IV, respectively. In every case the shifts are either all to high or all to low fields. Again this behavior is contrary to the known *contact*-shift characteristics of 4-picoline *N*-oxide. When this molecule is coordinated to octahedral nickel, the resonance is shifted upfield and the H-4 and 4-methyl signals suffer downfield displacements, with the methyl resonance experiencing the *largest* shift.⁴³ A reasonable semiquantitative correlation is obtained with geometric factor ratios, calculated from an assumed model with an angular coordination⁴⁴ of the *N*-oxide ligand (see Table III).

The shift ratios for the *n*-hexyl alcohol adducts (see Table IV), based on the β -methylene resonance, are in reasonable mutual agreement throughout the series, with the exception of the α -methylene resonances in the Pr and Eu systems. In these two cases the slopes of the plots of chemical shift *vs.* R_p appear to be too great by a factor of 2, and they do not extrapolate to the expected diamagnetic resonance positions.

While the trends in the shifts illustrated in Figure 3 are similar for the three ligands studied, there are some differences to be noted. For instance, in the Pr, Eu

and Dy systems, the α -methylene resonance of *n*-hexyl alcohol is the most shifted peak, while under identical conditions the H-2 resonance of 4-vinylpyridine is the most shifted in the Ho, Tm, and Yb systems. Such differences are reasonable and may be due to changes in magnetic anisotropy which will be a function of the effective ligand field around the central ion.

Relative Broadening Abilities of the Various Lanthanides. In order to assess the relative magnitudes of the dipolar broadening of the nuclear resonances, a line-width study was carried out for the methyl resonances of the 2-picoline adducts. This resonance was chosen because the proximity of the methyl group to the metal amplifies this effect and there is no complication from spin-spin splitting. The results, given in Table II, show that the later lanthanides, though better shifters, are also more efficient dipolar broadeners. Nevertheless, well-resolved spectra were obtained for all the adducts studied, save for the Gd systems. For instance, under the conditions of the data in Figure 1, H-3 of 4-vinylpyridine has an observed $\Delta\nu_{1/2}$ of 17 Hz for the Dy system. Only for the Pr, Sm, and Eu complexes was the 5-Hz spin-spin splitting of the H-2 resonance observable in the range of R_p values studied. Our results for the relative shifting and broadening abilities of the Sm, Tb, Ho, and Yb chelates agree qualitatively with those of Crump, *et al.*¹³

Conclusions

We conclude that the isotropic shifts caused by lanthanide shift reagents are exclusively or nearly exclusively dipolar in origin. In addition, we have demonstrated the ability of dpm chelates of the later lanthanides, particularly Tb, Dy, and Ho (upfield) and Tm (downfield), to cause shifts greater in magnitude than those of Pr and Eu which are in general use.

(41) Ratios of isotropic shifts for coordination to nickel(II), 1.00:0.47:0.03:0.09:-0.08: W. DeW. Horrocks, Jr., and D. L. Johnston, *Inorg. Chem.*, **10**, 1835 (1971).

(42) H. M. McConnell and R. E. Robertson, *J. Chem. Phys.*, **29**, 1361 (1958).

(43) R. W. Kluiber and W. DeW. Horrocks, Jr., *J. Amer. Chem. Soc.*, **87**, 5350 (1965).

(44) W. DeW. Horrocks, Jr., D. H. Templeton, and A. Zalkin, *Inorg. Chem.*, **7**, 1552 (1968).