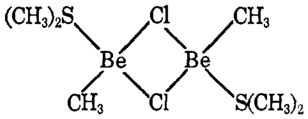
methyl sulfide solutions of dimethylberyllium (Figure 1). The methylberyllium chloride species resonates at slightly lower field (13 Hz) than $(CH_3)_2Be:(S(CH_3)_2)_2$ and is therefore assigned to $CH_3BeCl:(S(CH_3)_2)_2$. The greater electronegativity of chlorine relative to a methyl group is expected to reduce diamagnetic shielding and thus shift the resonance of the methyl group bonded to beryllium to lower field.[9] This argument predicts that proton resonance of the methyl groups bonded to beryllium in the monomeric 1:1 adduct, $CH_3BeCl:S(CH_3)_2$, or dimeric 1:1 adduct



would resonate at lower field than $(CH_3)_2Be:S(CH_3)_2$ at τ 10.77. The methylberyllium chloride species present in ethereal solution is monomeric.[10] The relatively high Be^9 resonance signal (4.24 ppm below aqueous beryllium nitrate) is further indication of a four-coordinate adduct species.[23]

In summary, this investigation has characterized the reaction between dimethylberyllium and dimethyl sulfide. Preliminary observations have indicated that dimethyl sulfide coordinates rather strongly to dimethylberyllium, contrary to earlier results.[1] Variable-temperature proton magnetic resonance analysis of dimethyl sulfide solutions of dimethylberyllium has provided *direct*, spectroscopic evidence of species present in solution. The species observed are analogous to those suggested for the reaction of dimethylberyllium with trimethylphosphine and diethyl and dimethyl ethers.[1] Thermodynamic data for equilibria between these species have been extracted from the nmr spectral data and interpreted successfully in terms of thermodynamic parameters for similar reactions.

Acknowledgment. We are indebted to the National Science Foundation for support of this work under Grant GP-8595.

(23) R. A. Kovar and G. L. Morgan, submitted for publication.

Observations on the Rare Earths. LXXXII.[1] Nuclear Magnetic Resonance and Calorimetric Studies of Complexes of the Tripositive Ions with Substituted Pyridine Molecules

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Contribution from the Noyes Chemical Laboratory, University of Illinois, Urbana, Illinois 61801. *Received February 6, 1969*

Abstract: Direct calorimetric measurements indicate that the ions Pr^{3+} and Nd^{3+} react exothermally with substituted pyridine molecules in anhydrous acetonitrile with enthalpy changes <-3 kcal mol^{-1} for the formation of 1:1 complexes and still less for the formation of higher order species. At ligand to metal ion mole ratios above six, the 3:1 complexes appear to be the most stable ones. Substitution of nitrate for perchlorate ion or of Nd^{3+} for Pr^{3+} ion does not affect the measured enthalpy change. Large isotropic shifts of resonances of the ligand protons are observed upon coordination to these paramagnetic cations. These shifts can be resolved qualitatively into contact and pseudocontact shifts of nearly equal magnitude but opposite sign. The contact shift at the *ortho* position of the pyridine ring is *ca.* -1000 cps from the diamagnetic value. In spite of the weakness of the covalent interaction, large contact shifts result, in part as a consequence of the large J values of the cations.

The use of nuclear magnetic resonance spectroscopy (nmr) to indicate the nature of bonding in paramagnetic complexes of metal ions is complicated by the difficulty in distinguishing between contact and pseudocontact shifts. The contact shift can yield information relating to the extent of covalent bonding and to the mechanisms of σ- and π-electron density delocalization in the paramagnetic species.[3] The pseudocontact shift can provide information relating to the geometrical configuration of ligands about a metal ion in solution[4] and to metal ion–solvent molecule interactions.[5] The contact and pseudocontact shifts often appear simultaneously in the spectrum of a complex, thus making the absolute interpretation of the isotropic nuclear shift difficult. With a d-transition metal complex, a reasonable assumption as to geometry in solution can lead to at least a qualitative estimate of the magnitude of the pseudocontact shift. Subtraction of the pseudocontact contribution from the total isotropic nuclear shift then usually leaves a large contact contribution which is useful in estimating the relative amounts of σ and π bonding in the species.

Estimating the size of the pseudocontact shift in the spectrum of a paramagnetic lanthanide complex in-

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(1) For the preceding communication in this series, see D. L. Campbell and T. Moeller, *J. Inorg. Nucl. Chem.*, **31**, 1077 (1969).

(2) Address correspondence to: Arizona State University, Tempe, Ariz. 85281.

(3) B. B. Wayland and R. S. Drago, *J. Amer. Chem. Soc.*, 88, 4597 (1966).

(4) G. N. La Mar, *J. Chem. Phys.*, **43**, 235 (1965).

(5) M. F. Rettig and R. S. Drago, *J. Amer. Chem. Soc.*, 88, 2966 (1966).

volves some additional problems. The steric-directing effect of the f orbitals is negligible when compared to that of the d orbitals. As a consequence, neither the coordination sphere of the cation nor the geometry of the complex can be readily predicted in solution. Since the bonding forces involving these cations are primarily electrostatic, solvent forces play an important role in determining coordination geometry. Thus, only rarely can it be assumed that the molecular structure found in a crystal will be the same in a solution of the substance in question. The electrostatic nature of the bonding also precludes the existence of contact shifts of the same order of magnitude as those noted for the d-transition metal complexes. However, although most reports of isotropic shifts observed in the spectra of lanthanide complexes consider them to be pseudocontact,[6-8] there is little evidence that true contact shifts must be absent. Even if the shift for a given species is largely pseudocontact, easily observable contact shifts should be present with as little as 1% covalency in the cation–ligand bond.

The present work is concerned with a series of complexes of the ions Pr^{3+} and Nd^{3+} with some substituted pyridine molecules as ligands.[8b] These molecules bond axially and are of such rigid geometry that geometrical relationships between the protons present are constant. The absolute magnitude of the pseudocontact shift in one of these systems is difficult, if not impossible, to measure, but the *ratios* of the pseudocontact shifts of the various protons on the ligand molecule can be obtained. A comparison of the calculated pseudocontact shift ratios with the observed ratios of the observed isotropic shifts should then reveal whether or not the observed shift is purely pseudocontact.[9]

Complexes of the lanthanide ions with these substituted pyridine molecules as ligands have not been isolated in the solid state. However, ethylenediamine complexes have been isolated from solutions in acetonitrile,[10] thus indicating that nitrogen-donor ligands can bond effectively in a nonaqueous polar medium of reduced donor strength.

Experimental Section

Materials. Purified lanthanide oxides (99.9%, from American Potash and Chemical Corp.) were converted to anhydrous nitrates by reaction with nitrogen(IV) oxide[11] or to anhydrous perchlorates through the hydrated salts as previously described.[10,12] The water content of the perchlorates, as determined by elemental analysis and infrared measurements, was below 0.2%.

Acetonitrile (Baker "Reagent") was obtained anhydrous by distillation from phosphorus(V) oxide. All aromatic amines (Reilly Tar and Chemical Co.) were distilled from barium oxide under vacuum (*ca.* 0.1 mm) and stored in a dry gloved box, maintained under positive pressure with dry nitrogen. All solutions were prepared in this box. Hamilton microsyringes and volumetric flasks were used to prepare solutions for spectroscopic examination.

Nuclear Magnetic Resonance Spectra. These spectra were obtained with Varian Model A-60A and A-56-60A spectrometers equipped with variable-temperature probes. Spectra were taken only after equilibration at probe temperature. Acetonitrile was used as an internal standard since only a small shift (<6 cps) from the diamagnetic resonance position, with respect to TMS, was observed upon addition of the paramagnetic lanthanide ions. Probe temperature was measured by means of the peak separation for a Varian sample of methanol.

Calorimetry. Calorimetric measurements were made in a nitrogen-flushed dry gloved bag maintained under positive pressure. The anhydrous lanthanide salt was dissolved in 225 ± 1 ml of acetonitrile contained in a 300-ml dewar flask. The heat evolved upon injection of a given volume of the ligand with a syringe was measured using a 100,000-ohm thermistor in a Wheatstone bridge in conjunction with a 1-mV Sargent SR recorder. The construction and operation of the calorimeter have been described previously.[10]

Calculations. Geometric factors were calculated with an IBM 1800 computer.

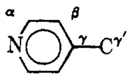
Results

Nuclear Magnetic Resonance Measurements. The substituted pyridines used as ligands are listed in Table I, together with their respective proton chemical shifts.

Table I. Observed Chemical Shifts in Proton Spectra of Uncomplexed Substituted Pyridines[a]

Ligand	Chemical shift, ~ cps from TMS α^b	β^b	γ^b	γ'^b
γ-Picoline (4-methylpyridine)	−507	−431	−142	
3,5-Lutidine (3,5-dimethylpyridine)	−494	−139	−442	
4-Ethylpyridine	−509	−432	−162	−76
4-*t*-Butylpyridine	−511	−442	−81	

[a] As 0.4 *M* solutions in acetonitrile. [b] Position of substituent (H–, CH_3–) in terms of



The shift reported for each free ligand is for a 0.4 *M* solution of the amine in acetonitrile and is concentration independent over the range studied. The addition of a diamagnetic lanthanum salt to a ligand solution effected only a very small perturbation of the ligand spectrum. Even at a 4:1 ligand to lanthanum ion mole ratio, the largest displacement of any ligand resonance was less than 10 cps. The chemical shifts of the ligand protons with the La^{3+} ion present were concentration dependent; but since the over-all shift was small, the resonance position for the 4:1 mole ratio solution was used as the diamagnetic standard for calculating the isotropic nuclear shift due to the presence of a paramagnetic ion.

The addition of a paramagnetic praseodymium(III) or neodymium(III) salt to the solution caused significantly larger shifts from the free ligand resonance position. These isotropic shifts were concentration dependent and, for a given lanthanide salt, all were in the same direction, irrespective of the ligands used. The dependence of the chemical shift on the metal ion concentration was linear at high ligand to metal ion mole ratios but not at low mole ratios. Figure 1 presents typical chemical-shift data as a function of metal ion concentrations.

The direction of the isotropic shift was the same for both Pr^{3+} and Nd^{3+} ions, but larger when the Pr^{3+} ion was used. The anionic dependence of the isotropic shift was more significant. With either Pr^{3+} or Nd^{3+} ion, the shifts were always positive in the presence of the nitrate ion and negative in the presence of the perchlorate ion. Since the lanthanide ion–ligand bonding

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(6) D. R. Eaton, *J. Amer. Chem. Soc.*, 87, 3097 (1965).

(7) F. A. Hart, J. E. Newberry, and D. Shaw, *Nature*, **216**, 261 (1967).

(8) (a) J. Reuben and D. Fiat, *Chem. Commun.*, 729 (1967); (b) pyridine itself was not used because of its complex proton spectrum.

(9) J. A. Happe and R. L. Ward, *J. Chem. Phys.*, **39**, 1211 (1963).

(10) J. H. Forsberg and T. Moeller, *J. Amer. Chem. Soc.*, **90**, 1932 (1968); *Inorg. Chem.*, 8, 883, 889 (1969).

(11) T. Moeller, V. D. Aftandilian, and G. W. Cullen, *Inorg. Syn.*, **5**, 37 (1957).

(12) L. C. Thompson, private communication.

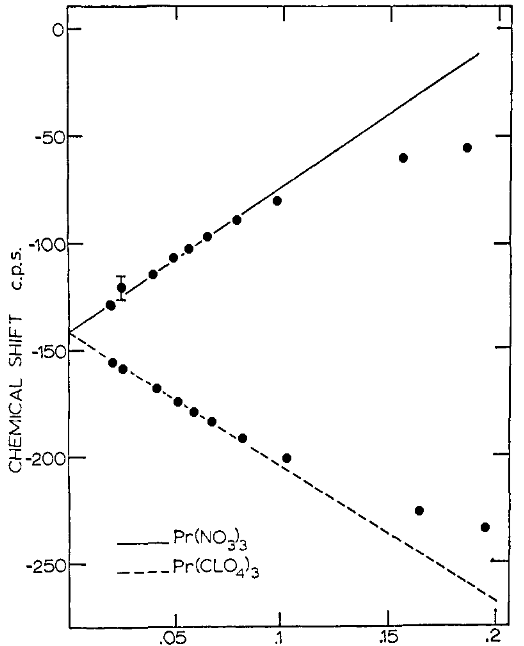

Figure 1. Variation of chemical shift of γ-CH_3 protons of γ-picoline with increasing concentration of $Pr(NO_3)_3$ and $Pr(ClO_4)_3$. (Concentration of γ-picoline = 0.4 *M*.)

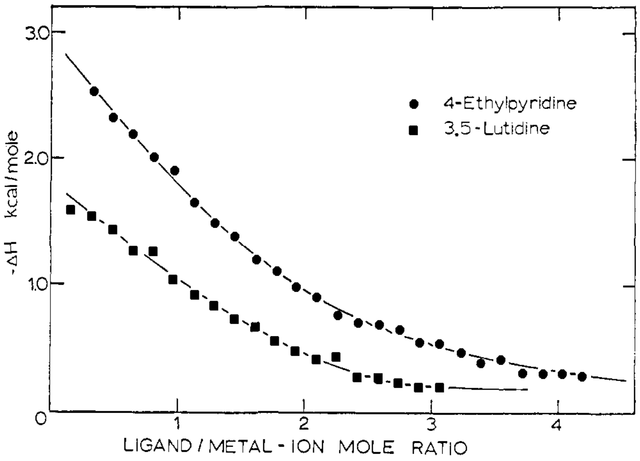

Figure 2. Enthalpy curves for formation of complexes in solutions 0.0356 *M* in $Nd(ClO_4)_3$.

should be similar in the presence of the two anions, the contact shifts should be essentially identical. However, the greater coordinating ability of the nitrate ion compared to the perchlorate ion could easily cause a change in the geometry of the complex in solution. This change could make a very large difference in the pseudocontact shifts of the two complexes. These observations indicate a substantial pseudocontact contribution to the isotropic shift. Shifts measured for complexes of the Sm^{3+} ion were experimentally significant only for the α protons.

The peaks in the nmr spectra were assigned by considering their relative intensities, the spin–spin splitting pattern, and the dependence of the spectra of the ligands on the concentration of the lanthanide ion. Spin–spin splittings in the ligand spectra were easily observed until the ligand to metal ion mole ratio decreased to below 9:1 for the paramagnetic systems. For example, the spectrum of the methyl group in the 4-ethylpyridine molecule was split into a triplet by the methylene group, whereas that of the methylene group was split into a quartet by the methyl group. The ratio of area of the triplet to that of the quartet was 3:2. Similarly the spectra of the α protons on the ring were split by the β protons and *vice versa*. The spectra of the α protons were always the most severely broadened by the paramagnetic cations, and the α–β proton splitting disappeared as the peaks broadened.

With the exception of those of 2,6-lutidine (dimethylpyridine) and 2,4,6-collidine (trimethylpyridine), the spectra of the ligands all showed isotropic nmr shifts. This observation reflects the steric forces of repulsion between methyl groups in the α position(s) and the lanthanide ion. The resonances of these two ligands in the paramagnetic systems were the same as those of the free ligand and were concentration independent.

Plots of $1/T$ *vs.* the chemical shift of the ligand protons for both Pr^{3+} and Nd^{3+} ions were linear in the presence of excess ligand, indicating adherence of these systems to the Curie law over the temperature range +40 to −40°.

Calorimetry. The enthalpy changes reported for complexation reactions of the lanthanide ions in aqueous solutions are commonly positive, indicating the processes to be endothermic.[13] However, the direct addition of increments of a solution of a substituted pyridine to a solution of a praseodymium or neodymium salt in acetonitrile resulted in the release of a measurable quantity of heat. A typical plot of calorimetric data is included in Figure 2. The absence of an easily distinguishable plateau in the curve is indicative of the fact that no single, relatively stable complex is formed at low ligand to metal ion ratios. For a given ligand, the calorimetric curves were nearly identical for either cation (Pr^{3+} or Nd^{3+}) or anion (NO_3^- or ClO_4^-).

The heat changes measured for the addition of incremental quantities of any of the *para*-substituted ligands to a solution containing Pr^{3+} or Nd^{3+} ion were the same, but that measured for the addition of 3,5-lutidine was about half that found for any of the other ligands at any given ligand to metal ion mole ratio. Steric repulsion effects are indicated for this reaction.

Discussion

Contact Shifts. The large shift in the diamagnetic resonances of protons on the ligand molecule resulting from the placing of unpaired electron spin density on the ligand through covalent bond formation with a paramagnetic cation is called a contact shift.[14] This effect can be described explicitly for a proton as

$$\Delta\nu = -A_i\frac{\gamma_e g\beta\nu_0}{\gamma_p}\frac{J(J+1)}{3kT} \qquad (1)$$

where A_i is the electron–proton hyperfine interaction constant of the *i*th proton; γ_e and γ_p are the electronic and nuclear gyromagnetic ratios, respectively; $\Delta\nu$ is the isotropic contact shift for the paramagnetic species; and ν_0 is the frequency of the resonance.[15]

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(13) T. Moeller, E. R. Birnbaum, J. H. Forsberg, and R. B. Gayhart, "Progress in the Science and Technology of the Rare Earths," L. Eyring, Ed., Vol. 3, Pergamon Press, Oxford, 1968, p 61.

(14) D. R. Eaton and W. D. Phillips, *Advan. Magnetic Resonance*, 1, 103 (1965).

(15) H. M. McConnell and D. B. Chestnut, *J. Chem. Phys.*, 28, 107 (1958).

The observed chemical shift (from TMS), δ_0, of the protons when a complex is undergoing rapid exchange with excess ligand in solution is the weighted average of the chemical shifts of the protons of the complexed ligand and those of the free ligand. This situation can be expressed as

$$\delta_0 = \frac{a}{n}(\delta_c - \delta_f) + \delta_f \tag{2}$$

where δ_c and δ_f are the chemical shifts of the protons of the complexed and free ligand, respectively; a is the number of moles of ligand complexed; and n is the total number of moles of ligand.[16] If only a single complex, with fixed coordination number of the metal ion, exists in solution, then a plot of δ_0 *vs.* metal ion concentration will be linear over a wide range of ligand to metal ion mole ratios. This behavior was observed above a 6:1 mole ratio, as shown in Figure 1. However, the number of ligand molecules bonded to a single lanthanide ion at these higher mole ratios is not known with certainty.

Ethylenediamine has been shown to form tetrakis chelates with the lanthanide perchlorates in anhydrous acetonitrile solution.[10] However, when the nitrate salts were used, calorimetric data indicated that the nitrate ion can compete successfully with the ethylenediamine molecule for coordination sites on the lanthanide ion after the bis complex has formed in solution. The large difference in base strength between ethylenediamine and the substituted pyridines suggests that it is unlikely that the latter molecules are capable of displacing nitrate ions from the coordination sphere of the lanthanide ion. Inasmuch as ethylenediamine can occupy readily only four coordination sites in a nitrate-containing solution in acetonitrile, one can assume that *four* is the maximum number of coordinated pyridine-type molecules in these nitrate systems.

The free energy change (ΔG) upon complexation by substituted pyridines in acetonitrile solutions should be determined primarily by the *enthalpy* change (ΔH) rather than by the *entropy* change (ΔS), as is true in aqueous medium,[10] since replacement of a unidentate rigid solvent molecule by a unidentate rigid ligand molecule should make the entropy change small. Furthermore, since acetonitrile is not a good hydrogen-bonding solvent, any entropy changes due to ordering effects in the bulk solvent should be smaller than those observed in aqueous solutions. If the enthalpy change then predominates in determining the free energy change, the value of ΔG for a given complexation reaction must be equal to or less than that for ΔH since the value of ΔS will probably be zero or slightly negative.

The absence of plateaus in the enthalpy curves (Figure 2) can thus be attributed to the small formation constants for the γ-substituted pyridine molecules with the lanthanide ions. The free energy change cannot be significantly larger than -3 kcal mol^{-1} for the formation of a 1:1 complex and must be still smaller for the formation of any higher complex. For a 1:1 complex, then, the value of the formation constant is *ca.* 10^2–10^3 mol l^{-1}.

The enthalpy changes measured near the 4:1 ligand to metal ion mole ratio are less than -1.0 kcal mol^{-1}, suggesting formation constants smaller than 10 mol l^{-1}. The linearity of a plot of chemical shift data *vs.* metal ion concentration above a 6:1 mole ratio imposes the restriction that if a fourth ligand molecule does coordinate to the metal ion it must do so before this 6:1 ratio is reached. This situation would appear to be unlikely in view of the small stability constant expected for the formation of a 4:1 complex. On the other hand, the slow decrease in measured enthalpy change out to 4:1 and 5:1 mole ratios renders untenable the suggestion that a maximum of only two ligand molecules is coordinating at higher mole ratios. Hence, we have used as an estimate three substituted pyridine ligands bonding to a lanthanide ion in the presence of the nitrate ion.

The number of bonded ligands in the presence of perchlorate ion may well be larger than three since that anion is a much weaker coordinating agent. However, similarities in the calorimetric data between the nitrate and perchlorate systems imply that the number of bonded ligands is the same in both. This argument is supported also by the fact that deviations from linearity in plots of chemical shift *vs.* metal ion concentration occur at essentially the same point in both anion systems (Figure 1). Thus it appears that the formation constant is too small to permit the presence of a significant quantity of the 4:1 complex in either system.

The enthalpy of interaction of 3,5-lutidine with either of the lanthanide ions is approximately half that found for any *para*-substituted ligand. However, the similarity among the isotropic shifts of all the ligands suggests that it is unlikely that the 3,5-lutidine complexes differ in geometry from the other complexes.

By application of eq 2 and use of a value of *three* for the coordination number (a), the chemical shifts of the complexes in solution (δ_c) can be calculated from the observed shifts at a 9:1 mole ratio. Subtraction of the value for the chemical shift of the protons for a given ligand when coordinated to the diamagnetic La^{3+} ion from the value for the Pr^{3+} or Nd^{3+} complex then gives the isotropic nuclear shift, $\Delta\nu$. Table II lists the values

Table II. Isotropic Proton Shifts ($\Delta\nu$) of Paramagnetic Complexes[a]

Ligand	Chemical shift, cps from TMS			
	α	β	γ	γ'
Pr(ClO$_4$)$_3$				
γ-Picoline	−317	−224	−84	
3,5-Lutidine	−225	−77	−152	
4-Ethylpyridine	−301	−208	−85	−66 ± 8
4-*t*-Butylpyridine	−290	−203	−78	
Pr(NO$_3$)$_3$				
γ-Picoline	+403	+117	+105	
3,5-Lutidine	+466	+101	+115	
4-Ethylpyridine	+448	+126	+125 ± 8	+78
Nd(ClO$_4$)$_3$				
γ-Picoline	−153	−116	−11	
3,5-Lutidine	−148	−33	−79	
4-Ethylpyridine	−150	−111	−18	−22
4-*t*-Butylpyridine	−159	−118	−25	
Nd(NO$_3$)$_3$				
γ-Picoline[b]	+106	+4	+72	
3,5-Lutidine	+118	+32	+24	
4-Ethylpyridine	+101	0	+60	+34
4-*t*-Butylpyridine	+101	0	+32	

[a] Three ligands assumed coordinated to one metal ion. Calculated from 9:1 ligand to metal ion mole ratio. [b] $\Delta\nu$ less accurate because concentration parameters less accurately known.

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[16] H. S. Gutowsky and A. Saika, *J. Chem. Phys.*, **21**, 1688 (1953).

so obtained for both nitrate and perchlorate systems. It is important to realize that the assumption of coordination number three affects only the magnitude of the isotropic shift. For a given ligand, the ratio of isotropic proton shifts is affected negligibly as coordination number changes from two to four. It is this ratio with which we are primarily concerned.

Pseudocontact Shifts. Electron-nuclear interactions can generate a paramagnetic shift that is similar to the contact shift but arises from the combined effects of electron spin-orbit, electron orbit-nuclear spin, and electron spin-nuclear spin coupling, rather than from a transfer of unpaired electron spin density to the resonating nucleus. These forces can generate a pseudocontact shift[17] that is related to the geometry of a complex species

$$\frac{\Delta\nu_i}{\nu_0} = -\left[\frac{f(g)\beta^2 J(J+1)}{3kT}\right]\left[\frac{(3\cos^2\theta_i - 1)}{r_i^3}\right] \quad (3)$$

where β, J, k, and T have the same meaning as before. The geometric factor, $(3\cos^2\theta_i - 1)/r_i^3$, is dependent upon both the distance r_i that the ith ligand proton is from Ln^{3+} ion and the angle θ_i between the distance vector and the principal molecular axis of the complex species. The term f(g) is usually given in terms of the anisotropy in the g value

$$f(g) = (g_{\parallel} + 2g_{\perp})(g_{\parallel} - g_{\perp})/9 \quad (4)$$

which is difficult to determine for a lanthanide ion and will not be discussed here. However, its value is the same for all of the protons in a given complex species. The pseudocontact shifts of these protons differ only by the magnitude of the geometric factor, which in turn varies as the positions of the protons vary. The ratios of this factor for the different protons present will then be the ratios of the pseudocontact shifts at these protons. Calculation of this factor depends solely upon the geometry of the species.

The orientation of given amine groups about the lanthanide ion in solution is unknown, and a condition of rapid ligand exchange is indicated by the presence in the spectrum of but a single resonance peak for each ligand proton at any temperature above the freezing point of the solution. The question then arises as to how large an effect the uncertainties in the metal ion-ligand bond distance and the position of the ligand with respect to the molecular axis of the complex have on this ratio of geometric factors.

The substituted pyridine molecules used in this study are neutral ligands which coordinate to the lanthanide ion through the dipole involving the nitrogen atom in the aromatic ring. This dipole lies along the axis of the ligand and is in a position to interact strongly with the lanthanide ion only when the negative end of the dipole is pointing directly at the metal ion. Tumbling or libration of the ligand with respect to the metal ion seriously reduces the forces of attraction between metal ion and ligand and results in a large increase in metal ion-ligand distance, r. Since the pseudocontact shift is proportional to r^{-3}, only geometries where the dipole is pointed directly at the lanthanide ion have been considered.

The calculation of geometric factors for the systems in question was carried out by selecting arbitrarily reasonable values of bond distance (r) and angle (ψ) between the molecular axis and the average ligand axis. The calculation was then repeated for several values of r, while varying ψ from 0 to 90°. For fixed values of r and ψ, both θ and the geometric factor were evaluated for the protons on the ligand molecule. Each ligand molecule was assumed to be freely rotating, and values of θ and the geometric factor were obtained at 5° rotamer configurations. For each system, the geometric factors were then averaged over all rotations. Calculations were repeated for 10° intervals of ψ and 0.5-Å intervals of r over the range 2.5–3.5 Å. Typical C-C and C-H bond lengths were used, together with molecular models to ascertain the proper geometric relationships among the protons of the ligand molecules. Where necessary, the geometric factor was calculated for more than one proton of a methyl group, and the results were averaged.[18]

The variation in the ratios of the geometric factors with ψ was less than 10% at the α proton and less than 1% at the β proton with 4-ethylpyridine as a ligand. Variation of the geometric factors with the distance vector r was somewhat larger, but was still less than 10% at the α proton and 1% at the β proton for this ligand. Similar results were obtained for all of the other substituted pyridine ligands.

For purposes of separating the contact and pseudocontact shifts, the ratios at $\psi = 0°$ and $r = 3.0$ Å were used. This value of r is close to that reported or the Ln-O bond distance for Ln^{3+}-H_2O coordination as obtained by X-ray crystallography.[19] No bond distances are yet available for an Ln^{3+}-neutral ligand species.

General. A comparison of some of the ratios of the observed isotropic shifts with those of the calculated geometric factors is shown in Table III. The poor agreement in a significant number of cases is indicative of the inability of a purely pseudocontact interaction to explain the observed shifts. The absence of an isotropic shift at the β proton of a *para*-substituted pyridine ligand molecule complexed with an Nd^{3+} ion in a nitrate medium is wholly unexpected in terms of a purely pseudocontact interaction. Only the presence of both

Table III. Comparison of Ratios of $\Delta\nu$ Values with Calculated Ratios of Geometric Factors

Ligand	Ratios of $\Delta\nu$ $\alpha:\beta:\gamma:\gamma'$	Ratios of geometric factors $\alpha:\beta:\gamma:\gamma'$
$Nd(ClO_4)_3$		
γ-Picoline	13.9:10.5:1.0	4.4:1.8:1.0
3,5-Lutidine	4.5:1.0:2.4	4.15:1.0:1.4
4-Ethylpyridine	6.8:5.0:0.8:1.0	5.2:2.1:1.2:1.0
4-*t*-Butylpyridine	6.4:4.7:1.0	5.2:2.1:1.0
$Nd(NO_3)_3$[a]		
3,5-Lutidine	3.7:1.0:0.8	4.15:1.0:1.4
4-Ethylpyridine	3.0:0:1.8:1.0	5.2:2.1:1.2:1.0
4-*t*-Butylpyridine	3.2:0:1.0	5.2:2.1:1.0

[a] Values for γ-picoline not included because of their reduced accuracy.

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

(18) Details are to be found in E. R. Birnbaum, Doctoral Dissertation, University of Illinois, 1968.

(19) J. L. Hoard, B. Lee, and M. D. Lind, *J. Amer. Chem. Soc.*, 87, 1612 (1965).

Table IV. Calculated Pseudocontact Shifts by Subtraction and by Ratios of Geometric Factors for Complexes of γ-Picoline[a]

	Shift, cps		
Type of shift	α	β	γ
$Pr(NO_3)_3$			
Contact shift, initial choice	−937	−423	−200
δ_{comp}, calculated	+403	+117	+105
Pseudocontact shift, geometric ratio	+1340	+540	+305
$Pr(ClO_4)_3$			
Contact shift, as for $Pr(NO_3)_3$	−937	−423	−200
δ_{comp}, calculated	−317	−224	−84
Pseudocontact shift, subtraction	+620	+199	+116
Pseudocontact shift, geometric ratio	+511	+205	+116
$Nd(ClO_4)_3$			
Contact shift, above × 1.18	−1107	−500	−236
δ_{comp}, calculated	−153	−116	−11
Pseudocontact shift, subtraction	+954	+384	+225
Pseudocontact shift, geometric ratio	+990	+398	+225
$Nd(NO_3)_3$[b]			
Contact shift, as for $Nd(ClO_4)_3$	−1107	−500	−236
δ_{comp}, calculated	+106	+4	+72
Pseudocontact shift, subtraction	+1213	+504	+308
Pseudocontact shift, geometric ratio	+1354	+545	+308

[a] Ratio of geometric factors, 4.4:1.77:1.0. [b] Values for δ_{comp} less accurate and not used to calculate initial contact shift.

Table V. Calculated Pseudocontact Shifts by Subtraction and by Ratios of Geometric Factors for Complexes of 3,5-Lutidine[a]

	Shift, cps		
Type of shift	α	β	γ
$Nd(NO_3)_3$			
Contact shift, initial choice	−800	−189	−286
δ_{comp}, calculated	+118	+32	+24
Pseudocontact shift, geometric ratio	+918	+221	+310
$Nd(ClO_4)_3$			
Contact shift, as for $Nd(NO_3)_3$	−800	−189	−286
δ_{comp}, calculated	−148	−33	−79
Pseudocontact shift, subtraction	+652	+156	+207
Pseudocontact shift, geometric ratio	+648	+156	+218
$Pr(NO_3)_3$			
Contact shift, above ÷ 1.18	−678	−160	−242
δ_{comp}, calculated	+466	+101	+115
Pseudocontact shift, subtraction	+1144	+261	+357
Pseudocontact shift, geometric ratio	+1082	+261	+366
$Pr(ClO_4)_3$			
Contact shift, as for $Pr(NO_3)_3$	−678	−160	−242
δ_{comp}, calculated	−255	−77	−152
Pseudocontact shift, subtraction	+423	+83	+90
Pseudocontact shift, geometric ratio	+345	+83	+116

[a] Ratio of geometric factors, 4:15:1.0:1:4.

Table VI. Calculated Pseudocontact Shifts by Subtraction and by Ratios of Geometric Factors for Complexes of 4-Ethylpyridine[a]

	Shift, cps			
Type of shift	α	β	γ	γ'
$Nd(NO_3)_3$				
Contact shift, initial choice	−1115	−492	−221	−200
δ_{comp}, calculated	+101	0	+60	+34
Pseudocontact shift, geometric ratio	+1216	+492	+281	+234
$Nd(ClO_4)_3$				
Contact shift, as for $Nd(NO_3)_3$	−1115	−492	−221	−200
δ_{comp}, calculated	+150	−111	−18	−22
Pseudocontact shift, subtraction	+965	+381	+203	+178
Pseudocontact shift, geometric ratio	+925	+374	+214	+178
$Pr(NO_3)_3$				
Contact shift, above ÷ 1.18	−945	−417	−187	−170
δ_{comp}, calculated	+448	+126	+117	+78
Pseudocontact shift, subtraction	+1393	+543	+304	+248
Pseudocontact shift, geometric ratio	+1290	+522	+298	+248
$Pr(ClO_4)_3$				
Contact shift, as for $Pr(NO_3)_3$	−945	−417	−187	−170
δ_{comp}, calculated	−301	−208	−85	−66
Pseudocontact shift, subtraction	+644	+209	+102	+104
Pseudocontact shift, geometric ratio	+542	+218	+125	+104

[a] Ratio of geometric factors, 5.2:2.1:1.2:1.0.

a contact shift and a pseudocontact shift that are opposed to each other can account for the cancellation of the isotropic shift at the *meta* proton position.

The separation of the isotropic shift into a contact and a pseudocontact term was accomplished in a manner similar to that outlined by Happe and Ward.[9] The size of the contact shift for the proton farthest removed from the paramagnetic center was first estimated, and then the pseudocontact shift necessary to account for the observed shift was calculated for this proton. The pseudocontact contributions at the remainder of the ligand protons were then calculated, using the ratios of the geometric factors. The contact shifts at these remaining protons were obtained by a comparison of these pseudocontact shifts with the observed shifts at the respective positions around the pyridine ligand ring. This procedure permitted the evaluation of the contact and pseudocontact shifts needed to explain the observed spectra for the interaction of one of the ligands with one lanthanide ion, starting with a specific guess as to the contact shift at one of the protons in the ligand molecule.

Once the distribution of contact shifts was known for a particular ligand, it was used to calculate a set of pseudocontact shifts for that ligand when coordinated to a different lanthanide ion in the same or different anion environment with a different observed spectrum. This was done by a comparison of the contact shift distribution as obtained above with the observed shifts for the new system. The set of values for the pseudocontact shifts for a particular ligand ring system as obtained in this way was then compared with the set calculated from geometric ratios. The values of $\Delta\nu$ of the ligand, when complexed with neodymium(III) nitrate, were used to calculate the initial set of contact shifts, with the exception of the γ-picoline system where praseodymium(III) nitrate was used, since these observed shifts were in the poorest agreement with the calculated geometric ratios. The choice of any other salt as a starting point for these calculations led to essentially the same result, and with only small deviations.

In comparing the complexes of the Pr^{3+} ion with those of the Nd^{3+} ion, the contact shifts were reduced by 1.18 in order to take into account the difference in average g value and ground-state J value between these ions.

The best agreement between the calculated pseudocontact shift ratios and the geometric ratios is shown in Tables IV–VII. The initial estimate of −200 cps for the contact shift at the proton farthest removed from the paramagentic center proved to be a minimum value. It was found that a choice of a contact shift significantly less than 200 cps, positive or negative, led to pseudocontact shifts of the ring protons that differed in sign and could not be explained by the geometric ratios calculated earlier.

In view of the smaller enthalpy value recorded for the interaction of 3,5-lutidine with an Ln^{3+} ion as compared

Table VII. Calculated Pseudocontact Shifts by Subtraction and by Ratios of Geometric Factors for Complexes of 4-*t*-Butylpyridine[a]

	Shift, cps		
Type of shift	α	β	γ
$Nd(NO_3)_3$			
Contact shift, initial choice	−1106	−487	−200
δ_{comp}, calculated	+101	0	+32
Pseudocontact shift, geometric ratio	+1207	+487	+232
$Nd(ClO_4)_3$			
Contact shift, as for $Nd(NO_3)_3$	−1106	−487	−200
δ_{comp}, calculated	−159	−118	−25
Pseudocontact shift, subtraction	+947	+369	+175
Pseudocontact shift, geometric ratio	+910	+368	+175
$Pr(ClO_4)_3$			
Contact shift, above ÷ 1.18	−936	−413	−170
δ_{comp}, calculated	−290	−203	−78
Pseudocontact shift, subtraction	+646	+210	+92
Pseudocontact shift, geometric ratio	+478	+193	+92

[a] Ratio of geometric factors, 5.2:2.1:1.0.

to γ-picoline, a reduced contact shift was used in calculations for the former ligand.

The choice of a contact shift of −200 cps for the farthest removed proton of the ligand gave the best agreement between calculated pseudocontact shifts and geometric ratios. However, the agreement between these values remains good as the size of the contact shift is increased. This circumstance is not surprising since, as both the contact and pseudocontact shifts increase, the observed shifts become only small perturbations to these much larger shifts. A choice smaller than −200 cps, however, leads to poor agreement between the calculated values for the pseudocontact shifts and the geometric ratios. Thus the contact shifts calculated here can be regarded only as qualitative lower limits to the sizes of the actual shifts.

The magnitude of the contact shift found for each of these complexes is large in terms of the small amount of covalent bonding usually attributed to a lanthanide complex. However, the size of the contact shift is dependent upon the average g and J values of the lanthanide ions, as well as upon covalency (eq 1). The products $gJ(J+1)$ for the ions Pr^{3+}, Nd^{3+}, and Sm^{3+} are, respectively, 16, 18.9, and 2.54,[20] whereas the equivalent $gJ(J+1)$ value for Ni^{2+} complexes is approximately 4.0. Thus 25% or less of the covalency in the d-transition metal complex will produce a contact shift of the same size.

A comparison of the $gJ(J+1)$ value of the Sm^{3+} ion with those of the Pr^{3+} and Nd^{3+} ions accounts for the fact that only small isotropic shifts were observed for the α and β protons and none for the γ protons of ligands bonded to the Sm^{3+} ion. This fact precluded extension of this study to samarium complexes.

The negative direction of the calculated contact shifts is a consequence of unpaired spin density aligned with the magnetic field on the protons of the ligand. This can be explained in terms of either a direct covalent interaction involving a 6s orbital of the lanthanide ion[21] or a spin polarization of the $5s^25p^6$ octet.[22] The data obtained in this investigation do not permit distinguishing between these mechanisms of transferring unpaired electron spin density.

The general distribution of the isotropic shifts observed in most lanthanide systems amounts to a gradual decrease in the size of the shift with an increase in the distance of the proton from the metal ion. This trend can be explained either by a pseudocontact shift mechanism which is proportional to r^{-3} or by a σ delocalization mechanism, where the contact shift decreases with the number of bonds separating the metal ion from the proton in question. In both cases, the gross features of the distribution of the shifts will be the same. It is only when there is a substantial difference between the ratio of the shifts expected for a pseudocontact mechanism and the ratio of the observed shifts that a contact mechanism, resulting from covalent interactions, can be postulated. This situation is apparent for the neodymium nitrate system where resonances for protons in the *meta* position are not shifted whereas those for all other protons are shifted in a positive direction, indicative of the presence of contact and pseudocontact shifts of opposite sign.

Where the ratios of the pseudocontact shifts for protons in the ligand can be calculated, such as for the rigid ligand systems used in this study, the presence of a contact shift can be detected readily. However, in systems where the geometry of the ligand is not known with accuracy and the contact shift is operating in the same direction as the pseudocontact shift, the contact shift is frequently discounted in view of the small covalent interaction expected in a lanthanide system.

The necessity for involving contact and pseudocontact shifts of similar magnitude but opposite direction in order to account for the observed isotropic shifts characteristic of these systems suggests that sizable contact shifts may occur in other systems but pass unnoticed as a consequence of either the similarity between the effect of a contact shift and a pseudocontact shift or the presence of a pseudocontact shift operating in the same rather than the opposed direction.

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