(17–18°) corresponding to the major component of higher chloride content which assumes the green form at room temperature, as well as a small peak at a higher temperature (26°) corresponding to the minor component of lower chloride content which assumes the purple form at room temperature. Thus, under the condition of the crystallization of the sample with this *average* Cl content, the free energy of crystallization should be very nearly equal, and both forms (with different Cl content) can be in equilibrium with the mother liquor.

From the vibrational frequencies of NO_2 in the ir spectra and the peak positions in the electronic spectra of the parent compound, Tomlinson and Hathaway[2] inferred that in the violet form NO_2 is coordinated to the copper atom through the nitrogen atom and in the green form through the oxygen atom. Thus the green form having the O-coordinated NO_2 has the absorption peak at a lower wave number than the violet form having the N-coordinated NO_2, in conformity with the order in the spectrochemical series. The essential situation is unchanged in the green form in which NO_2 is partially replaced by halogens. The above point of view has been more clearly proved by the present two series of isotopic substitution experiments in the ir study in the region of the metal–ligand vibrations mentioned previously. Thus neither the Cu–N vibration frequency of the Cu–NO_2 moiety nor the $\nu_s(NO_2)$ of the N-coordinated NO_2 group appears in the ir spectrum of the green form.

However, in the violet form there is observed a very weak band at the frequency of 1180 cm^{-1} which was assigned as $\nu_s(NO_2)$ of the O-coordinated NO_2 group in the case of the green form. This may be an indication that a small amount of O-coordinated NO_2 remains in the violet form possibly as a lattice imperfection. In fact, nitro complexes are known to be liable to lattice defects, for various reasons such as easy change of the bond angles and of coordinating atoms, and this may be related to the easy replacement of the nitrite group by indeterminate amounts of such ions of different shape and size as the chloride or bromide ions.

Such behavior of the NO_2 group often makes the exact determination of the crystal structure a difficult task as in the present example. The fact that the temperature factor of one of the nitrite groups in the green form is comparatively small even in the Cl-containing mixed crystal seems to indicate that it is the other nitrite group that is replaced by halogen atoms. In this possibility the resulting complex would be a pentacoordinate one, which is not very unusual among halide complexes.

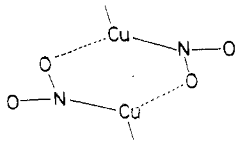

Figure 4. A sketch suggesting the possible path of the superexchange interaction in the purple form.

In the case of N coordination of NO_2, the stereochemistry would be that of an elongated octahedron, the more distant coordination positions probably being occupied by O atoms of NO_2 of other complex units as suggested by the sketch in Figure 4. This is in conformity with the greater value of the Curie–Weiss constant shown by the low-temperature form, since exchange paths between paramagnetic ions should be more easily formed in this case. This kind of network as such would be more difficult to be formed when NO_2 is replaced by Cl, although a complete rearrangement would make possible another way of elongated octahedral coordination as realized in pure $[CuCl_2(NH_3)_2]$. This accounts for the fact that replacement of NO_2 by halogens reduces the transition energies (*i.e.*, energy differences between the two forms), making the purple form relatively unstable.

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Registry No. Purple-$[Cu(NO_2)_2(NH_3)_2]$, 21710-46-3; green-$[Cu(NO_2)_2(NH_3)_2]$, 21710-47-4; Cl_2, 7782-50-5; Br_2, 7726-95-6.

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Calculations of Lanthanide-Induced Shifts from Molecular Structure. II[1]

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The nmr spectra of adducts of various pyridine derivatives with $Eu(thd)_3$ were observed at both high and low temperatures, and lanthanide-induced shifts for all protons, including those of the chelates, were calculated using the complete dipolar shift equation. In all cases integration of the low-temperature spectra showed that the 1:2 adduct was present in solution.

In a recent article Springer, *et al.*,[2] stated that "no direct evidence has been noted of solution 1:2 adducts" of $Ln(thd)_3$ complexes. We have[3,4] reported direct evidence for the existence of such a 1:2 adducts in solution and we have demonstrated that the lanthanide-induced shifts (LIS) could be explained with the general dipolar shift equation[5–9]

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

by assuming that the molecular structure obtained crystallographically for the diadducts of $Ln(thd)_3$[10–12] is maintained in solution. We have now extended these studies to include several other pyridine derivatives coordinated to $Eu(thd)_3$ in both the fast-exchange region (∼30°) and the nonexchange region (≤−100°) in order to determine their limiting lanthanide-induced shifts and to correlate them with molecular structure. Furthermore integration of the substrate *vs.* chelate resonances at low temperature allows easy determination of the number of coordinated substrates.

Experimental Section

Sample Preparation. The $Eu(thd)_3$ chelates were obtained from Alfa Inorganics and handled at all times in an inert-atmosphere box

Table I. Relative Peak Areas of Low-Temperature Nmr Spectra of $Eu(thd)_3(sub)_2$ in Freon 12

	[sub]:[SR]		
	Calcd ratios		
Substrates	1:1 adduct	1:2 adduct	Obsd ratios
Pyridine[a]	1:18	1:9	1:8.5
β-Picoline[b]	1:1	2:1	2.2:1
γ-Picoline[c]	1:18	1:9	1:8.5
3,5-Lutidine[d]	1:9	1:4.5	1:4.3
Quinoline[e]	1:18	1:9	1:9.1

[a] Meta and para protons *vs.* chelate *tert*-butyl protons. [b] Previously reported; see ref 4. [c] γ-Methyl protons *vs.* chelate *tert*-butyl protons. [d] 3,5-Methyl protons *vs.* chelate *tert*-butyl protons. [e] H(6) on quinoline *vs.* one type of chelate *tert*-butyl proton.

filled with dry N_2. The pyridine substrates (pyridine, γ-picoline, 3,5-lutidine, and quinoline) were purchased from Aldrich Chemical Co., distilled, and then stored over Molecular Sieve 4A under dry N_2. Samples for the high-temperature experiments were prepared in anhydrous CS_2 and their spectra analyzed using the techniques previously reported.[4]

Samples for the low-temperature experiments were prepared on a vacuum line such that each pyridine substrate was redistilled prior to use. Freon 12 (CCl_2F_2) was purchased from Matheson Gas Products and used as the solvent for most low-temperature experiments. Tetramethylsilane (TMS) was used as the internal reference for all experiments. In each case the substrate:shift reagent ratio was approximately 10:1.

Chemical shifts for the diamagnetic reference were obtained from the appropriate $La(thd)_3$ or $Lu(thd)_3$ adduct.

Nmr Spectroscopy. Measurements were made either on the Varian HA-100 (high temperature, HA mode) or, for the low temperature experiments, on a Varian XL-100 spectrometer, interfaced with a Digilab Nova 1200 computer operating in Fourier transform mode. External ^{19}F lock was used for all low-temperature experiments. Temperatures were measured *via* the Varian temperature controller which had been calibrated with a Digitec 590 thermocouple and all temperatures are reported to ±3°. Integrals either were obtained graphically or were obtained whenever possible electronically through the use of the Digilab Nova 1200 computer.

The geometric factors were calculated from X-ray crystallographic results for $Eu(thd)_3(py)_2$[11,12] with the methyl groups treated as previously described.[4] Since each of the symmetrical substrates examined exhibited only one resonance for each unique proton, even at the lowest temperatures attainable, the geometric factors for the two ortho and two meta positions were averaged. The location of the magnetic axes and the values of D_1 and D_2 were determined using the previously reported techniques.[4]

Results and Discussion

Each sample was lowered in temperature to about −125° at which point the fast exchange between the free pyridine derivative and the eight-coordinate $Eu(thd)_3(sub)_2$ complex was sufficiently slow to see both the resonances due to the paramagnetic rare earth complex and the excess substrate. The results of integration of the resonances due to the complexed substrate *vs.* the "thd" chelate resonances are summarized in Table I. *In all cases the 1:2 adduct is found to be present in solution.*

While it is thus apparent that these compounds exist as 1:2 adducts below −100°, one could argue that at higher temperatures the 1:1 adduct could become important. One can test this hypothesis by comparison of the temperature dependencies of the shifts of the chelate protons and the protons of the pyridines. For both types of protons, the high-temperature shifts are about 25% as large as those at low temperature. If we assume that the shifts of the 1:1 adduct and the 1:2 adduct are similar, for which there is some evidence,[13] then the change in shift of the chelate protons can be assumed to reflect approximately the changes in the magnetism of the complex. However, for the substrate protons, if there is a shift from 1:2 to 1:1 adducts as the temperature is increased, then we will have a smaller fraction of substrate bound at high temperature which will lead to a smaller observed shift. The shift of the substrate protons would then show a decrease with increasing temperature of more than 25%. The average decrease in shift for $Eu(thd)_3(3,5\text{-lut})_2$ from −115° to +30° (see Tables II and III) is 25.4% for the chelate protons and 23.4% for the substrate, which indicates that little if any 1:1 adduct is present at the higher temperature.

It had been noted from an examination of the structures of $Eu(thd)_3(py)_2$ and $Ho(thd)_3(\gamma\text{-pic})_2$ that a substantial barrier to rotation about the Ln–N bond was expected for steric reasons.[12,14,15] We have interpreted results[3,16] for $Eu(thd)_3(\beta\text{-pic})_2$ as confirming the barrier to rotation and we had set a lower limit on the height of the barrier.[3] In the systems reported here we find no doubling of any of the substrate peaks and no splitting of the chelate peaks even at temperatures as low as −150°. These systems, therefore, do not provide any evidence for a barrier to rotation and indicate that there is some fluxional process which is averaging both chelate and substrate positions even at −150°. However, in the case of quinoline below −120°, both the *tert*-butyl and methine chelate peaks split into three and two peaks, respectively,[17] which is in agreement with the X-ray structures of $Eu(thd)_3(py)_2$ and $Ho(thd)_3(\gamma\text{-pic})_2$. This indicates that the added steric bulk of quinoline raises the barrier for the rearrangement process sufficiently that separate resonances can be observed.

Tables II and III list the geometric factors, chemical shifts, and the calculated and observed dipolar shifts for the Eu-

Table II. Chemical Shifts, Geometric Factors, and Isotropic Shifts for $Eu(thd)_3(3,5\text{-lut})_2$ at 30° in CS_2

Assignment	$(3\cos^2\theta - 1)/r^3$	$(\sin^2\theta\cos 2\Omega)/r^3$	Chem shift, ppm	$(\Delta\nu/\nu_0)_{\text{obsd}}$[a]	$(\Delta\nu/\nu_0)_{\text{calcd}}$[b]
Methine	0.0090	−0.0028	2.86	8.37	8.33
tert-Butyl	0.0030	−0.0005	1.77	2.77	2.19
Methyl	−0.0022	0.0015	−5.73	−3.48	−3.21
Para	−0.0019	0.0029	−12.2	−5.08	−5.08
Ortho	−0.0167	0.0051	−23.4	−15.3	−15.4
					$R = 0.035$

[a] Experimental LIS obtained using $La(thd)_3(3,5\text{-lut})_2$ as the diamagnetic reference. [b] Calculated using eq 1.

Table III. Chemical Shifts, Geometric Factors, and Isotropic Shifts for $Eu(thd)_3(3,5\text{-lut})_2$ at −115° in CS_2

Assignment	$(3\cos^2\theta - 1)/r^3$	$(\sin^2\theta\cos 2\Omega)/r^3$	Chem shift, ppm	$(\Delta\nu/\nu_0)_{\text{obsd}}$[a]	$(\Delta\nu/\nu_0)_{\text{calcd}}$[b]
Methine	0.0090	−0.0027	28.5	34.3	33.9
tert-Butyl	0.0030	−0.0007	9.50	10.7	9.89
Methyl	−0.0022	0.0016	−16.7	−14.4	−14.2
Para	−0.0019	0.0030	−29.0	−21.8	−21.7
Ortho	−0.0167	0.0060	−76.5	−68.5	−68.9
					$R = 0.012$

[a] Experimental LIS obtained using $Lu(thd)_3(3,5\text{-lut})_2$ as the diamagnetic reference. [b] Calculated using eq 1.

Table IV. Summary of Magnetic Axis Orientations, Agreement Factors, and Calculated Magnetic Anisotropies

Substrate	Solvent	Temp, °C	$D_1 \pm \sigma_1$[a]	$D_2 \pm \sigma_2$[a]	R[b]	η,[c] deg
Pyridine[d]	CS_2	30	555 ± 49	−1330 ± 190	0.047	24
Pyridine	CCl_2F_2	−122	1620 ± 120	−6520 ± 340	0.017	40
γ-Picoline	CS_2	30	529 ± 68	−1520 ± 270	0.061	22
γ-Picoline	CCl_2F_2	−134	1550 ± 290	−6490 ± 820	0.036	40
3,5-Lutidine	CS_2	30	473 ± 45	−1460 ± 160	0.035	26
3,5-Lutidine	CS_2	−115	2010 ± 84	−5900 ± 260	0.012	32
3,5-Lutidine	CCl_2F_2	−140	1760 ± 130	−6300 ± 380	0.016	36

[a] Units of D_1 and D_2 are VVK/mol (1 VVK = 10^{-6} cgsu). [b] Error function as defined by M. R. Willcott, R. E. Lenkinski, and R. E. David, *J. Amer. Chem. Soc.*, 94, 1744 (1972). [c] η is the angle between the crystallographic axis and the x magnetic axis. The c crystallographic axis is located 34° from the N–N vector in $Eu(thd)_3(py)_2$. [d] Previously reported; see ref 4.

$(thd)_3(3,5\text{-lut})_2$ system at ambient temperatures and in the nonexchanging region in CS_2. Table IV summarizes the results obtained in both the high- and low-temperature regions for pyridine, γ-picoline, and 3,5-lutidine in both CS_2 and Freon 12. Listings of geometric factors, chemical shifts, and the calculated and observed dipolar shifts for the remaining systems listed in Table IV are available (supplementary material).

Examination of Tables II and III indicates that eq 1 satisfactorily accounts for the observed lanthanide-induced shifts of both chelate and substrate protons. Presumably the greater error observed in the high-temperature (R = 3.5% at 30° and 1.2% at −115°) experiment is due to the experimental error incurred during the least-squares extrapolation[4] used in determining the limiting lanthanide-induced shifts. Furthermore in each case the largest individual error occurs in the calculation of the *tert*-butyl protons, presumably due to the fact that the *tert*-butyl protons were assumed to be static in space and their geometric factors were calculated assuming the geometry found in the solid state.

Examination of Table IV reveals that the x magnetic axis has shifted from an average value of 24° at 30° temperature to 37° at temperatures below −115°. Since the high-temperature experiments were all done in CS_2 and the low-temperature experiments in CCl_2F_2, the shift in magnetic axis could be due to either temperature or solvent. However comparison of the low-temperature results of 3,5-lutidine in both CS_2 and Freon 12 indicates that the shift in magnetic axis is a temperature effect.

Comparison of the values of D_1 and D_2 which we obtained from our least-squares fits in solution, shows that there is no significant trend in these values among the various pyridine derivatives reported here.

We have attempted to compare our values for D_1 and D_2, which are obtained in solution, with those which Horrocks has measured in the solid state.[14] Upon shifting the coordinate system from that used by Horrocks into that adopted by us (*i.e.*, we have the z axis along the molecular twofold axis while Horrocks placed the y axis there), we obtain a value for D_1 of 541 VVK from the solid-state results. This value agrees well with those reported in Table IV for room-temperature measurements. In order to compare values for D_2 we must know where the magnetic x axis is within the molecule. While Horrocks has published η, which relates the magnetic x axis to the crystallographic a axis, he has not published complete crystal data which would allow us to locate the position of the axis within the molecule. Earlier,[4] we had assumed that the a crystal axis of $Ho(thd)_3(\gamma\text{-pic})_2$ was coincident with the c crystal axis of $Eu(thd)_3(py)_2$ due to their similar axis lengths. This assumption can now be checked in the following way. Horrocks[18] has recently published the shifts predicted by his susceptibility data[14] for $Eu(thd)_3(\gamma\text{-pic})_2$. Using these numbers and our geometric factors for an x magnetic axis 18° from the c crystal axis of $Eu(thd)_3(py)_2$ we can calculate values of D_1 and D_2 which can then be compared with values calculated from the solid-state susceptibilities. We find that the values do not agree. Therefore our geometric factors must have been calculated with respect to a different x magnetic axis and we conclude that the a and c crystal axes of the two crystal systems are not collinear. We cannot, therefore, make any comparisons between our D_2 and that of Horrocks, although we note that an η value of ~36° gives a value of D_2 in close agreement with those in Table IV.

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Registry No. $Eu(thd)_3(py)_2$, 24189-43-3; $Eu(thd)_3(\gamma\text{-pic})_2$, 38685-78-8; $Eu(thd)_3(3,5\text{-lut})_2$, 54120-15-9; $Eu(thd)_3(quin)_2$, 54120-16-0; pyridine, 110-86-1; γ-picoline, 108-89-4; 3,5-lutidine, 591-22-0.

Supplementary Material Available. Table IVa–d, showing additional chemical shifts, isotropic shifts, and geometric factors for $Eu(thd)_3(py)_2$, $Eu(thd)_3(\gamma\text{-pic})_2$, and $Eu(thd)_3(3,5\text{-lut})_2$, will appear following these pages in the microfilm edition of this volume of the journal. Photocopies of the supplementary material from this paper only or microfiche (105 × 148 mm, 24× reduction, negatives) containing all of the supplementary material for the papers in this issue may be obtained from the Journals Department, American Chemical Society, 1155 16th St., N.W., Washington, D.C. 20036. Remit check or money order for $4.00 for photocopy or $2.50 for microfiche, referring to code number AIC40509H.

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