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The Analysis of Lanthanoid-induced ^{13}C Shifts for Naphthylamines. Contact Shifts Induced by Gd-chelates and the Spin-delocalization Mechanism

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The ^{13}C shifts of 1- and 2-naphthylamines induced by Gd(fod)$_3$ and Gd(dpm)$_3$ were shown to consist predominantly of a contact contribution, based on the fact that these shifts excellently correlate with the hyperfine coupling constants obtained from the graphical analysis of ^{13}C shifts induced by other Ln(fod)$_3$, where Ln is La, Pr, Nd, Sm, Eu, Dy, Ho, Er, or Yb. It was found from the INDO MO calculations of the spin densities of ligand moieties that these Gd-induced shifts parallel the spin-density distribution of the naphthylmethyl radical better than that of the naphthylamine cation radical and that these shifts are best interpreted in terms of the superposition of the β-spin of the naphthylmethyl radical and the α-spin of the naphthyl radical. This may suggest that a direct spin transfer occurs through space from Gd^{3+} to the amine molecule, in addition to the normal through-bond delocalization *via* the N-lone pair.

In order to employ lanthanoid-induced shifts(LIS) for the elucidation of molecular structures, particularly of the sterically detailed geometries of molecules, one must separate a purely dipolar contribution from LIS. It has been well recognized that LIS consists of three contributions: contact(cs), pseudo contact(pcs), and complex formation shifts(cfs).[1] The third term can be easily determined from the shifts induced by a La- or Lu-complex on the plausible assumption that the diamagnetic shift due to the adduct formation with a Ln-complex is equal in magnitude along the lanthanoid series. Among several methods proposed for the separation of a pcs term, there is one which can be carried out by a relatively simple procedure using the experimental shifts induced by a Gd-complex.[2] This is based on the theoretical prediction that Gd^{3+} has an isotropic g-tensor[3] and on the expectation that all the other analogous Ln-complexes cause a ligand cs-pattern identical with that due to the Gd-complex. Indeed, this method has successfully been applied to the ^{13}C shifts of several kinds of organic molecules by Ajisaka *et al.*[2] However, no more such studies have been found, probably because of the severe broadening of resonance lines caused by this ion.

The object of this report is to confirm that Gd-induced shifts are only contact in origin in actual complexes and to investigate a spin-delocalization mechanism for such complexes by means of a "relative method." Some of the results have been reported in a preliminary paper.[4] Naphthylamines were chosen because many kinds of carbons assignable to each position are included, their molecular structures are rigid, which are convenient for pcs calculations, and their chemical equilibria are well known.[5]

Experimental

1- and 2-Naphthylamines were of commercial origin (Nakarai Chemicals, Ltd). CDCl$_3$(Merck Sharp & Dohme Canada, Ltd.) was used as a solvent after having been dried over molecular sieves for 24 h. The lanthanoid shift reagents(LSR) were synthesized by the methods in the literatures[6] and were used after having been dried over P$_2$O$_5$ in a vacuum desiccator. The LSR employed in the present study are Ln(fod)$_3$,[7] where Ln is La, Pr, Nd, Sm, Eu, Gd, Dy, Ho, Er, or Yb, and Ln(dpm)$_3$,[7] where Ln is La or Gd.

The ratio of LSR(L) to the substrate (S) (ρ) was varied by the addition of well-defined amounts of LSR to a 1 M solution of 1-naphthylamine in CDCl$_3$(0.8 M in 2-naphthylamine). For each LSR, five or six ^{13}C spectra were recorded with ρ values ranging from 0 to 0.2 (0 to 0.03 for Gd(fod)$_3$ and Gd(dpm)$_3$), using TMS as the internal standard at 24 °C, on a Varian CFT-20 spectrometer. The assignments of ^{13}C lines were made by the methods in the literature.[8]

The INDO MO calculations of spin densities were carried out on HITAC 8800/8700 computers at The Computer Center of the University of Tokyo. The program used was Y4CB04[9] of the library programs collected in this center. The LISA2 program prepared by Shapiro *et al.*[10] was used for the nonlinear least-squares analysis of LIS *vs.* ρ plots.

Results and Discussion

The nonlinear least-squares analyses of ^{1}H-LIS *vs.* ρ plots ($0<\rho<2.5$, the number of data points is 27), carried out for 1-naphthylamine with Eu(fod)$_3$ in CDCl$_3$, indicated that this system is best interpreted in terms of two-step equilibria:

$$\mathrm{L + S \rightleftharpoons LS} \quad K_1,\ \delta_{\mathrm{LS}}, \tag{1}$$

$$\mathrm{LS + S \rightleftharpoons LS_2} \quad K_2,\ \delta_{\mathrm{LS_2}}, \tag{2}$$

with no self-association of Eu(fod)$_3$ in solution, $\mathrm{L+L \rightleftharpoons L_2}$, where K's, δ_{LS}, and $\delta_{\mathrm{LS_2}}$ are the equilibrium constants and intrinsic shifts of the 1:1 and 1:2 adducts respectively. The equilibrium constants determined are $K_1=75$—95 and $K_2=1$—5,[11] implying that the second equilibrium is negligible compared with the first. Then, considering the one-step equilibrium, the observed shift, δ_{obsd}, is given by:

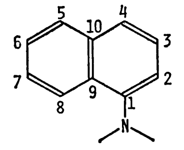
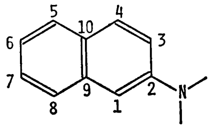
$$\delta_{\mathrm{obsd}} = \frac{[\mathrm{LS}]}{[\mathrm{S_0}]}\delta_{\mathrm{LS}}, \tag{3}$$

in the fast-exchange limit, where $[\mathrm{S_0}]$ is the total concentration of the substrate. When $\rho \ll 1$ and $K_1 \cdot [\mathrm{S_0}] \gg 2(1+\rho)$, one has $[\mathrm{LS}]/[\mathrm{S_0}] \approx \rho$ and Eq. 3 simplifies to:

$$\delta_{\mathrm{obsd}} = \rho \cdot \delta_{\mathrm{LS}}\,.^{12)} \tag{4}$$

Actually, a good linear relation has been obtained for these ^{1}H-LIS *vs.* ρ plots in the range of $\rho \ll 1$.

Table 1. Observed ^{13}C paramagnetic shifts of naphthylamines induced by $Gd(fod)_3$ and $Gd(dpm)_3$[a]

	Position	fod			dpm		
		$\delta_{LS}(Gd)$	$\delta_{LS}(La)$	$\delta'_{LS}(Gd)$[b]	$\delta_{LS}(Gd)$	$\delta_{LS}(La)$	$\delta'_{LS}(Gd)$[c]
1-Naphthylamine	1	88±5	−5.4	93±5	40±4	−2.5	43±4
	2	−41±2	8.9	−50±2	−28±3	5.7	−34±3
	3	30.5	−0.3	30.8	15.8	−0.7	16.5
	4	−22.5	7.8	−30.3	−13.5	4.0	−17.5
	5	−6.0	0.5	−6.5	−6.6	−0.8	−5.8
	6	11.5	1.3	10.2	5.3	0	5.3
	7	−5.0	2.8	−7.8	−4.2	1.1	−5.3
	8	18.0	5.6	12.4	13.4	1.3	12.1
	9	−30.5	3.2	−33.7	−17.0	2.5	−19.5
	10	24.0	0.6	23.4	13.2	0	13.2
2-Naphthylamine	1	−36±4	10.3	−46±4	−19±6	5.6	−25±6
	2	71±10	−5.8	77±10	48±10	−2.7	51±10
	3	−20±2	2.3	−22±2	−7±1	1.8	−9±1
	4	16.0	0.9	15.1	9.2	−0.6	9.8
	5	8.8	0.4	8.4	6.6	−0.7	7.3
	6	−8.0	3.8	−11.8	−4.0	0.6	−4.6
	7	9.6	1.3	8.3	4.7	0	4.7
	8	−9.2	1.8	−11.0	−4.0	0.6	−4.6
	9	19.2	−0.8	20.0	10.6	−1.4	12.0
	10	−12.4	4.0	−16.4	−6.6	1.3	−7.9

a) Values in ppm relative to that of the free naphthylamine. Negative signs denote highfield shifts.
b) $\delta_{LS}(Gd(fod)_3)-\delta_{LS}(La(fod)_3)$. c) $\delta_{LS}(Gd(dpm)_3)-\delta_{LS}(La(dpm)_3)$.

Also, in the present ^{13}C experiments, an excellent linear relation between δ_{obsd} and ρ was obtained within the examined range of $\rho(\rho \ll 1)$. Thus, Eq. 4 can be applied to the analyses of the present ^{13}C data. The correlation coefficients(R) in this linear relation with $Gd(fod)_3$ and $Gd(dpm)_3$ were >0.998 for all the carbons except for the C_1 of 1- and the C_2 of 2-naphthylamine, for which the accuracies of measured shifts are poor because of the severe broadening of the resonance lines (>0.9). Thus, in the present system, δ_{LS} can be found from the slope of the δ_{obsd} *vs.* ρ plot. As is generally accepted, the correction of δ_{LS} for a diamagnetic shift can be made by using the $La(fod)_3$- or $La(dpm)_3$-induced δ_{LS} value, the corrected δ_{LS} being denoted as δ'_{LS} in the present paper. The δ'_{LS} values observed for 1- and 2-naphthylamines with $Gd(fod)_3$ and $Gd(dpm)_3$, $\delta'_{LS}(Gd)$, are summarized in Table 1.

In order to examine whether or not $\delta'_{LS}(Gd)$ consists solely of a cs contribution, δ_{LS} values with a series of $Ln(fod)_3$ for 1-naphthylamine were first observed; the δ'_{LS} values were obtained using the $La(fod)_3$-induced δ_{LS} value. For all the carbons with each $Ln(fod)_3$, the R-values in the δ_{obsd} *vs.* ρ plots were >0.999. These were then separated into cs and pcs contributions by the graphical method,[12,13] which has successfully been utilized in recent years: the δ'_{LS} for a given nucleus, i, $\delta'_{LS,i}$ in a lanthanoid adduct can conveniently be expressed as a sum of two terms:

$$\delta'_{LS,i} = A_i \cdot \langle S_z \rangle + G_i \cdot D, \tag{5}$$

where A_i is the hyperfine coupling constant between the nucleus and the unpaired electron, $\langle S_z \rangle$ is the projection of the lanthanoid total electron-spin magnetization in the direction of the external field, G_i is the geometric factor $(3\cos^2\theta - 1)r^{-3}$, and D is a constant for a given lanthanoid and temperature. If, for this adduct, the constancy of A_i and G_i can be assumed along the series, the contributions of the two terms can readily be separated. By a rearrangement of Eq. 5, one obtains:

$$\delta'_{LS,i}/\langle S_z \rangle = A_i + G_i \cdot D/\langle S_z \rangle. \tag{6}$$

Using the tabulated values of $\langle S_z \rangle$[14] and of D,[3a] a plot of $\delta'_{LS,i}/\langle S_z \rangle$ against $D/\langle S_z \rangle$ can be constructed; the plot should be linear, with a slope of G_i and an intercept on the ordinate of A_i. However, some scattering of points may be anticipated in view of the fact that the values of D were calculated with an arbitrary set of crystal-field parameters.[3] The present data are plotted in this way in Fig. 1. It may be seen that, apart from some scattering of points, all sets of the data closely obey the linear relationship. The R-values are shown in the footnotes of Fig. 1. The data points from Sm-adducts were excluded, since these deviate considerably from the linear relation because of the great sensitivity of $\delta'_{LS}/\langle S_z \rangle$ to a small experimental error in δ'_{LS} because of the extremely small value of $\langle S_z \rangle$. Thus, it may be said that an effective axial symmetry holds in this system and that G_i and A_i are constant through out the series.

The relative A_i-values determined from Fig. 1 are compared with the relative values of $\delta'_{LS}(Gd)$ in Table 2. These two quantities correspond well with each other (R=0.985), considering the A_i-values determined from such plots containing theoretical quantities. Next, the addition of the relative G_i as a pcs pattern to the relative A_i was made tentatively in order to

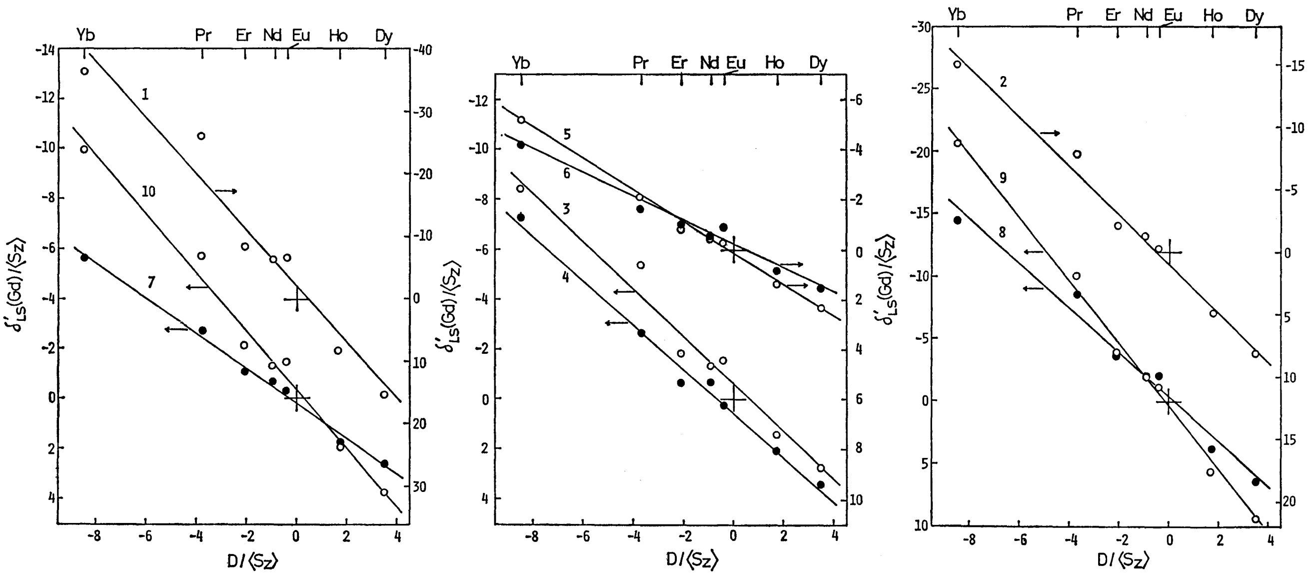


Fig. 1. $\delta'_{LS}(Gd)/\langle S_z\rangle$ *vs.* $D/\langle S_z\rangle$ plots for 1-naphthylamine-Ln(fod)$_3$ system.
Numbers denote positions of carbons. Correlation Coefficients: 0.9714 (C_1), 0.9934 (C_2), 0.9834 (C_3), 0.9945 (C_4), 0.9955 (C_5), 0.9895 (C_6), 0.9947 (C_7), 0.9891 (C_8), 0.9971 (C_9), 0.9908 (C_{10}).

Table 2. Comparisons of Gd(fod)$_3$-induced ^{13}C shifts and hyperfine coupling constants for 1-naphthylamine[a)]

Position	Relative		
	$\delta'_{LS}(Gd)$[b)]	A_i[c)]	$\delta_{calcd}(A_i+G_i)$[d)]
1	3.08	3.56	3.07
2	−1.65	−1.78	−1.80
3	1.02	1.14	1.02
4	−1.00	−0.95	−0.95
5	−0.21	−0.26	−0.29
6	0.34	0.39	0.33
7	−0.26	−0.31	−0.34
8	0.41	0.68	0.45
9	−1.11	−0.86	−0.96
10	0.77	0.71 (0.985)	0.60 (0.997)

a) The numbers in parentheses are the correlation coefficients of A_i or $\delta_{calcd}(A_i+G_i)$ to $\delta'_{LS}(Gd)$. b) With Gd(fod)$_3$. c) Relative hyperfine coupling constant estimated graphically from Fig. 1. d) The relative shift values estimated from the least squares fits of the superposition of A_i- and G_i-patterns on $\delta'_{LS}(Gd)$.

Table 3. Observed and calculated relative geometric factors for 1-naphthylamine

Position	G_i[a)]	GF_{calcd}[b)]
1	5.07	5.02
2	2.20	2.47
3	1.08	1.10
4	1.00	0.92
5	0.72	0.69
6	0.54	0.58
7	0.79	0.78
8	2.00	1.87
9	2.84	2.45
10	1.31	1.21 (0.996)

a) Determined graphically from Fig. 1. b) Calculated geometric factors. The geometric parameters used are shown in Ref. 15. The number in parenthesis is the correlation coefficient between G_i and GF_{calcd}.

interprete $\delta'_{LS}(Gd)$; this resulted in a further, better correlation (R=0.997), as is shown in Table 2. This effectiveness of G_i on the improvement of R may not be completely reliable, considering the effect of the use of theoretical values of D and $\langle S_z\rangle$ on the accuracies of A_i and G_i. However, as long as a relative method is used for the discussion, the possibility of the inclusion of a small amount of a dipolar contribution can not be completely excluded. On the other hand, the G_i-values have fairly well been explained in terms of the geometric factors, calculated using plausible geometric parameters,[15)] as is shown in Table 3.

If the observed ^{13}C shifts are purely contact in origin, their intramolecular ratio should correspond to the spin-density distribution of the carbon 2s-orbitals of the ligand (ρ_{2s}). Therefore, the INDO MO calculations of ρ_{2s} were carried out for the cation radicals of naphthylamines, which can be expected to be a real model for the ligand moiety of lanthanoid adducts. The following standard geometries were used with 120° or tetrahedral bond angles: C–H (aromatic), 1.08 Å; C–C (aromatic), 1.40 Å; C–N, 1.37 Å. Considering the pyramidal structure of nitrogen, the angle between the N–C bond and the NH$_2$ plane (χ) was taken as 50°.[17)] The calculated results imply that the highest occupied MO containing an electron spin is of the π-type, as anticipated. In Table 4, the calculated ρ_{2s} values of cation radicals, $\rho_{2s}(Naam^+)$, are compared with the $\delta'_{LS}(Gd)$ values observed with Gd(fod)$_3$. The feature of sign alternation is almost identical in both; however, only a poor agreement

TABLE 4. COMPARISONS OF Gd-INDUCED ^{13}C SHIFTS AND SPIN DENSITIES ON CARBON 2s ORBITALS[a]

	Position	δ'_{LS}(Gd)[b]	$-\rho_{2s}$(Naam$^+$)	$-\rho_{2s}$(Name)	ρ_{2s}(Naph)	δ_{calcd}[c]
1-Naphthylamine	1	3.1±0.2	0.015	1.262	51.550	2.71
	2	−1.7±0.1	−0.742	−1.377	−2.000	−1.67
	3	1.02	0.576	0.869	4.220	1.13
	4	−1.00	−1.000	−1.000	−1.000	−1.20
	5	−0.21	−0.477	−0.410	0.083	−0.48
	6	0.34	0.295	0.385	0.012	0.46
	7	−0.26	−0.318	−0.418	−0.016	−0.43
	8	0.41	0.008	0.451	0.087	0.47
	9	−1.11	−0.121	−0.689	−0.040	−0.72
	10	0.77	0.538	0.598	0.138	0.62
			(0.611)	(0.937)		(0.987)
2-Naphthylamine	1	−3.1±0.3	−8.101	−2.111	−0.822	−2.80
	2	5.1±0.7	0.748	1.840	16.561	4.38
	3	−1.5±0.1	0.896	−1.173	−0.449	−1.55
	4	1.00	−1.000	1.000	1.000	1.40
	5	0.56	1.303	0.728	0.178	0.95
	6	−0.78	−3.950	−0.778	−0.093	−1.01
	7	0.55	3.452	0.667	0.159	0.73
	8	−0.73	−5.450	−0.765	0.037	−0.84
	9	1.32	3.599	1.049	1.318	1.15
	10	−1.09	−1.602	−1.012	−0.224	−1.11
			(0.583)	(0.925)		(0.990)

a) Relative values. The numbers in parentheses are the correlation coefficients between δ'_{LS}(Gd) and ρ_{2s} or δ_{calcd}. b) With Gd(fod)$_3$. The negative signs denote highfield shifts and thus correspond to the negative signs of ρ_{2s}. c) Relative shifts calculated using Eq. 7 from the least-squares fits of the superposition of ρ_{2s}(Name) and ρ_{2s}(Naph) to δ'_{LS}(Gd).

is obtained.

Horrocks *et al.*[19] and Morishima *et al.*[20] have shown that, for a variety of pyridine-type bases, the Ni(acac)$_2$-induced contact shifts parallel the spin-density distribution in the analogous hydrocarbon radical better than that for the pyridine-like cation radical. Therefore, taking into account this effect for the present system, the spin-density distributions of naphthylmethyl radicals, ρ_{2s}(Name), were calculated. The distance between the ring and the CH$_2$ group was taken as 1.40 Å. Table 4 implies that, on going from ρ_{2s}(Naam$^+$) to ρ_{2s}(Name), the agreement with δ'_{LS}(Gd) becomes considerably better in both 1- and 2-naphthylamines. The difference between these two INDO spin-density distributions may be ascribed mainly to the changes in the σ-π interaction caused by the energy variation in each MO due to the lowering of the nuclear charge of the hetero atom. From this result, one may consider that, in the present system, the interaction between an Ln 4f-orbital and the ligand affects the valence orbital of the ligand fairly much. Thus, the cation radical perturbed in a manner analogous to the effect of lowering the nuclear charge of the hetero atom appears to be a better model for the spin-density distribution of this type of ligand in Ln(fod)$_3$- or Ln(dpm)$_3$-adducts.[21] Comparisons of δ'_{LS}(Gd) and ρ_{2s}(Name) indicate that a β-spin is delocalized into the ligand π-orbital from Gd^{3+}; this seems to be consistent with the minus sign of $\langle S_z \rangle$ calculated for this ion by Golding *et al.*[14]

Although the feature of sign alternation is completely identical in δ'_{LS}(Gd) and ρ_{2s}(Name), it is found that an anomalous component of shifts is included in the shifts of carbons bound to the NH$_2$ group and of its neighbours: considerably large lowfield shifts at C$_1$ and small highfield shifts at C$_2$ and C$_9$ for 1-naphthylamine, and considerably large lowfield shifts at C$_2$ and small highfield shifts at C$_1$ and C$_3$ for 2-naphthylamine. Although an attempt was made to reproduce δ'_{LS}(Gd) by the superposition of a relative pcs on ρ_{2s}(Name), this was unsuccessful. It is then considered that a second contribution to δ'_{LS}(Gd) may be required as a cs occurring through another pathway of an electron spin. Taking into account the mixed delocalization, the addition of the spin-density distribution of the lowest vacant MO (ρ_{2s} of the naphthylamine anion radicals) to ρ_{2s}(Name) was tentatively made; however, this was also unsuccessful. From the comparison of δ'_{LS}(Gd) and ρ_{2s}(Name) in Table 4, one may consider that the distribution of such an anomalous component of shifts is very similar to that expected from a σ-type delocalization of the positive spin placed on C$_1$ for 1- and on C$_2$ for 2-naphthylamine into the ring. Naphthyl radicals may thus be expected to have a required spin-density distribution. Then, the relative spin-density distribution of this radical(ρ_{2s}(Naph)) was added to ρ_{2s}(Name) to obtain the least-squared values in Eq. 7:

$$\delta_{\mathrm{calcd}} = X \cdot \rho_{2s}(\mathrm{Name}) + Y \cdot \rho_{2s}(\mathrm{Naph}), \qquad (7)$$

where X and Y are constants. This examination led to a further, better agreement with the δ'_{LS}(Gd)-pattern in both 1- and 2-naphthylamines, as may be

Table 5. Correlation coefficients between δ'_{LS}(Gd) and the relative shifts predicted tentatively

	1-Naphthylamine		2-Naphthylamine	
	fod	dpm	fod	dpm
A_1 only	0.985	0.982	—	—
A_1+G_1	0.997	0.992	—	—
ρ_{2s}(Naam$^+$) only	0.611	0.673	0.583	0.553
ρ_{2s}(Naam$^+$)+ ρ_{2s}(Naph)	0.913	0.898	0.920	0.926
ρ_{2s}(Name) only	0.937	0.970	0.925	0.893
ρ_{2s}(Name)+ ρ_{2s}(Naph)	0.987	0.982	0.990	0.984
ρ_{2s}(Naam$^+$)+G_1	0.690	0.711	0.636	0.465
ρ_{2s}(Name)+G_1	0.972	0.985	0.940	0.917

seen from Table 4. The correlation coefficients are summarized in Table 5, together with those for the other cases with Gd(fod)$_3$ and Gd(dpm)$_3$. This result may correspond to the delocalization of a significant amount of α-spin into the ligand, in contrast to a β-spin of ρ_{2s}(Name); thus, it may suggest that a through-space transfer of spin occurs from Gd^{3+} to the ligand.

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15) The following geometric parameters for the aniline–Eu(fod)$_3$ system$^{16)}$ are also employed for the present system: the distances of Ln–N and N–C are taken as 2.65 and 1.40 Å respectively, and the ∠C–N–Ln angle as 150°. When the rotational angle of the Ln–N vector about the N–C bond is taken as 30°, the best agreement is obtained.

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17) Although ρ_{2s} was calculated with χ values ranging from 20° to 60°, taking into account several works on the conformation of the NH$_2$ group of aniline,$^{16,18)}$ this variation had no significant effect on the comparison of ρ_{2s} with δ'_{LS}(Gd). Thus, 50° was adopted.

18) T. Yonezawa, I. Morishima, Y. Akana, and K. Fukuta, *Bull. Chem. Soc., Jpn.*, **43**, 379 (1970).

19) W. DeW. Horrocks, Jr., and D. L. Johnston, *Inorg. Chem.*, **10**, 1835 (1971).

20) I. Morishima, K. Okada, and T. Yonezawa, *J. Am. Chem. Soc.*, **94**, 1425 (1972).

21) The situation is the opposite of that for pyridine-type bases. For a detailed study, the effect of an LSR-ligand interaction must be incorporated into the MO calculation of a model radical, except for the attempt at varying the charge of the hetero atom.