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# A Co-59 Nuclear Magnetic Resonance Study of the Interaction of Lanthanoid Shift Reagents with Tris(β-diketonato)-cobalt(III) Complexes

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$Ln(fod)_3$ (Ln=La, Pr, Nd, Sm, and Eu)-induced $^{59}Co$ shifts ($\delta_{Co}$) for a series of tris(β-diketonato)Co(III) complexes were determined directly from separate observations of the free complexes and 1 : 1 adducts with $Ln(fod)_3$ at room temperature (25 °C) in $CHCl_3$; $Ln(dpm)_3$-induced shifts were also observed in $CCl_4$. Values of $\delta_{Co}$ corrected for the adduct-formation shifts ($\delta'_{Co}$) are separated into contact and pseudo-contact contributions by using the intercept and slope in a linear plot of $\delta'_{Co}/\langle S_z\rangle$ *vs.* $D/\langle S_z\rangle$. It is suggested from the estimated hfs constant of $^{59}Co$ ($\approx -0.2$ G, $10^{-4}$ T) that the spin polarization mechanism may be predominant for the electron spin transfer from Ln ion into Co ion.

The lanthanoid shift reagents (LSR) have been extensively used for structural studies of organic substrates, but on their application to inorganic coordination complexes only a few investigations have so far been reported.1—4) It has been found from $^1H$ or $^{13}C$ NMR studies by Lindoy *et al.*2—4) that Ni(II) complexes of $O_2N_2$-donor quadridentate ligands coordinate to $Eu(fod)_3$5) *via* two bridging donor oxygens and rapidly exchange between their free forms and 1 : 1 adducts with $Eu(fod)_3$ in $CDCl_3$ solution at room temperature,2) while tris(β-diketonato)Co(III) complexes are bound to $Eu(fod)_3$ *via* three bridging oxygens and their exchange rates are very slow.3,4)

These investigations prompted us to examine whether or not lanthanoid-induced shifts (LIS) can be detected at the nucleus of central metal ion of such complexes. This paper reports on LIS's of $^{59}Co$ measured for adducts of a series of tris(β-diketonato)Co(III) complexes with $Ln(fod)_3$ and $Ln(dpm)_3$.5) Some of the results have been reported in a preliminary paper.6)

## Experimental

$Co(acac)_3$5) was obtained from Tokyo Kasei Kogyo Co., Ltd. and used without further purification. Benzoylacetone was obtained commercially and *p*-methoxybenzoylacetone synthesized from *p*-methoxyacetophenone and acetic anhydride under boron trifluoride. $Co(bzac)_3$5) and $Co(mbzac)_3$5) were prepared according to the published method.7) $CHCl_3$ and $CCl_4$ as a solvent were dried with molecular sieves before use. Eu- and $Pr(fod)_3$ were obtained from Merck Sharp and Dohme Canada Ltd. La-, Nd-, and $Sm(fod)_3$ and $Ln(dpm)_3$ (Ln=La, Pr, Nd, Sm, and Eu) were synthesized according to the literatures.8) All the LSR's were used after being dried over $P_2O_5$ in a vacuum desiccator.

$^{59}Co$ NMR spectra were recorded on a Varian CFT-20 spectrometer, equipped with a broad band accessory, at 19.104 MHz at room temperature (25 °C) using an external deuterium field-lock system. The aquisition time was taken as 0.05 s for the spectral width of 8065 Hz, the number of data points being 807. The number of transients was 100—500.

## Results and Discussion

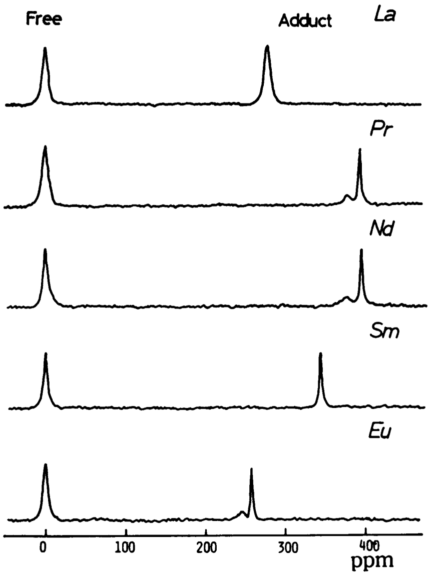


Fig. 1. The $^{59}Co$ NMR of free $Co(acac)_3$ and its adducts with $Ln(fod)_3$ in $CHCl_3$ at 25 °C. $\rho\approx0.5$. High-field shifts are given as positive.

*$^{59}Co$ NMR of the Adducts of $Co(acac)_3$ with $Ln(fod)_3$.* Figure 1 shows the $^{59}Co$ NMR spectra observed with a 0.085 mol $dm^{-3}$ $Co(acac)_3$ solution in $CHCl_3$ at room temperature (25 °C) at a molar ratio ($\rho$) of $Ln(fod)_3$ (Ln=La, Pr, Nd, Sm, and Eu) to $Co(acac)_3$ of about 0.5. These spectra can be interpreted by analogy with the $^1H$ spectra of the $Co(acac)_3$–$Eu(fod)_3$ system measured by Lindoy *et al.* 3,4) as follows: The lower- and higher-field resonances in each spectrum can be determined to arise from the free form of $Co(acac)_3$ and its 1 : 1 adduct with $Ln(fod)_3$, respectively, by observing the change in intensity ratios of these with changing $\rho$. Such a separate observation of $^{59}Co$ shifts indicates that the chemical exchange of $Co(acac)_3$ between its free form and its 1 : 1 adduct with $Ln(fod)_3$ under these experimental conditions is very slow on the NMR time scale. No $^{59}Co$ resonance lines of the adducts with the later members of lanthanoid series (Gd—Yb) could be detected owing to the long $T_1$ of electron spin in addition to the slow exchange rate.

A considerable amount of large high-field shift was observed with diamagnetic $La(fod)_3$. This may not be surprising considering that the paramagnetic term of $^{59}Co$ shift ($\sigma_{para}$) is greatly sensitive to variation in ligand

and ligand field symmetry.[9] Thus, this high-field shift can be ascribed to a slight distortion of ligand field symmetry arising from the geometric distortion of oxygen donor atoms[3] and small changes in electron densities on these oxygens by the adduct formation. On the other hand, one may consider that this diamagnetic high-field shift corresponds to an increase in $\Delta E$, the energy separation between the ground state and the excited $^1T_{1g}$ level of Co$^{3+}$,[9] on going from free Co(acac)$_3$ to the adduct.

Each of the adducts with Pr-, Nd-, and Eu(fod)$_3$ gave rise to a peak of weak intensity at a slightly lower field ($\approx$20 ppm) than the main peak. The ratios of this satellite to the main peak were unchanged with changing $\rho$. These satellites may not be considered to arise from any impurities in Co(acac)$_3$, from the experimental result that the remaining Sm- and La-adducts studied here do not exhibit such a satellite. It has been confirmed by Lindoy *et al.* that symmetrical adducts are formed in these systems, that is, coordination of Ln(fod)$_3$ occurs *via* three $\beta$-diketone oxygen atoms at one available octahedral-face of Co(acac)$_3$ along the $C_3$ axis to form a 1 : 1 adduct. Thus, the possibility of coordination *via* one or two donor oxygens may be excluded and these satellites can, therefore, be presumed to be due to a small amount of geometrical isomer appearing on the adduct formation. It is generally presumed that the intramolecular rapid exchange between the *fac*- and *mer*-isomers of Ln(fod)$_3$ occurs at room temperature in CDCl$_3$ solution.[10] With the adduct formation, however, this exchange rate may be anticipated to become so slow that different effects of these isomers of Ln(fod)$_3$ on $^{59}$Co shifts may separately be observed. Since the *fac*-isomer is more stable from the view of steric hindrance than the *mer*-isomer, the larger main peak may correspond to the adduct containing *fac*-Ln(fod)$_3$. The $^{59}$Co shifts of these peaks relative to that of its free form ($\delta_{Co}$) are shown in Table 1 together with its line widths ($\Delta\omega$). It is very interesting that the line widths of adducts are fairly smaller than those of free complexes for all the adducts except for the La(fod)$_3$-adduct.[11]

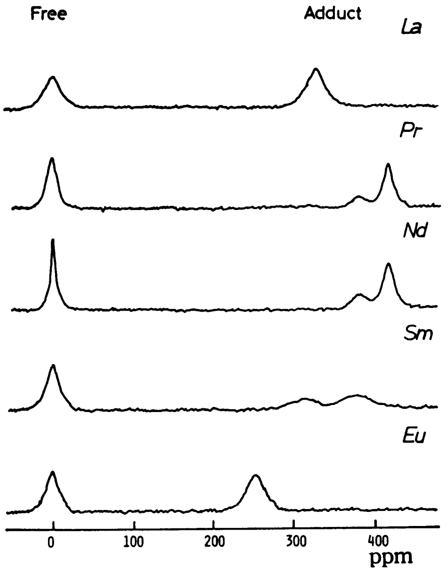


Fig. 2. The $^{59}$Co NMR of free Co(acac)$_3$ and its adducts with Ln(dpm)$_3$ in CCl$_4$ at 25 °C. $\rho\approx0.5$. High-field shifts are given as positive.

*$^{59}$Co NMR of the Adducts of Co(acac)$_3$ with Ln(dpm)$_3$.* It was found that in CHCl$_3$ Co(acac)$_3$ is not bound to Ln(dpm)$_3$ at 25 °C, but that in CCl$_4$ the adducts with Ln(dpm)$_3$ are formed. This may be ascribed to the larger dielectric constant of CHCl$_3$ than that of CCl$_4$. The $^{59}$Co spectra and LIS's of the adducts are shown in Fig. 2 and Table 1, respectively. The chemical exchange of Co(acac)$_3$ between its free form and its 1 : 1 Ln(dpm)$_3$-adduct in CCl$_4$ is considerably slow, as with the Co(acac)$_3$–Ln(fod)$_3$ adduct in CHCl$_3$. In contrast to the Ln(fod)$_3$-adducts, the line widths are comparable in magnitude with those of corresponding free complexes, except for that of the Sm(dpm)$_3$-adduct which is about twice as broad as that of the free form. Furthermore, the high-field shift induced by La(dpm)$_3$ is larger by $\approx$50 ppm than that by La(fod)$_3$. This may be due to the difference in distortion of the octahedral ligand-field of Co$^{3+}$ between these two La-adducts, which may arise from the difference in Lewis acidities and geometries of adducts.[12]

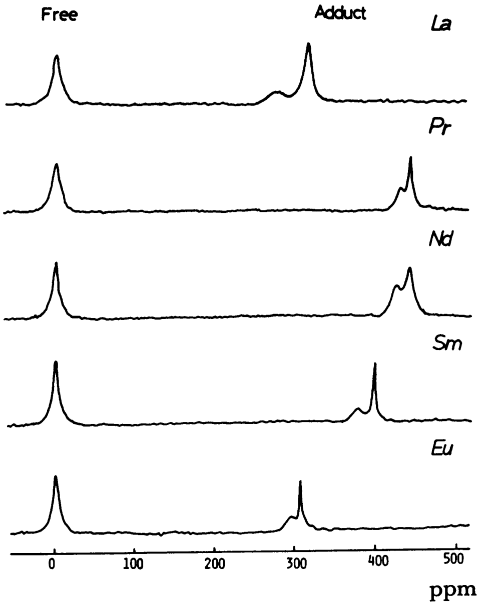


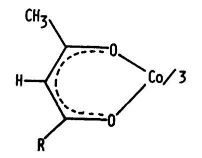
Fig. 3. The $^{59}$Co NMR of free Co(bzac)$_3$ and its adducts with Ln(fod)$_3$ in CHCl$_3$ at 25 °C. $\rho\approx0.5$. High-field shifts are given as positive.

*$^{59}$Co NMR of the Adducts of Co(bzac)$_3$ and Co(mbzac)$_3$ with Ln(fod)$_3$.* Also from Co(bzac)$_3$ and Co(mbzac)$_3$ with Ln(fod)$_3$ in CHCl$_3$ at 25 °C, $^{59}$Co signals assignable to the free complex and the corresponding 1 : 1 adduct with Ln(fod)$_3$ were separately observed. The spectra obtained from Co(bzac)$_3$ are shown in Fig. 3. Both of the free complexes exhibited only one line, though slightly broarder than that of Co(acac)$_3$ in CHCl$_3$, and this suggests that the shift differences between the *fac*- and *mer*-isomers of these complexes are essentially small within the line widths observed or that only the isomer of *fac*-type may exist.[13] The adduct resonances have patterns similar to those from

Table 1. $^{59}$Co LIS of tris($\beta$-diketonato)Co(III)–Ln(fod)$_3$ and –Ln(dpm)$_3$ adducts and its separation into cs and pcs[a)]

| Complex | | | | | | Calculated | | |
|---|---|---|---|---|---|---|---|---|
| | | $\delta_{Co}$[b)] | $\Delta\omega$[c)] | AFS[d)] | $\delta_{Co}$[e)] | pcs | cs | Total |
| Co(acac)$_3$ | La(fod)$_3$ | 281 | 202 | 281 | 0 | | | |
| | Pr(fod)$_3$ | 394(376) | 126 | 305 | 89 | 62.8 | 27.7 | 90.5 |
| | Nd(fod)$_3$ | 396(375) | 76 | 317 | 79 | 24.0 | 41.8 | 65.8 |
| | Sm(fod)$_3$ | 344 | 50 | 341 | 3 | 3.6 | −0.6 | 3.0 |
| | Eu(fod)$_3$ | 257(247) | 50 | 353 | −96 | −22.8 | −99.6 | −122.4 |
| Co(acac)$_3$ | La(dpm)$_3$ | 332 | 680 | 332 | 0 | | | |
| | Pr(dpm)$_3$ | 416(383) | 450 | 350 | 66 | 34.2 | 31.9 | 66.1 |
| | Nd(dpm)$_3$ | 417(381) | 400 | 359 | 58 | 13.1 | 48.1 | 61.2 |
| | Sm(dpm)$_3$ | 378(317) | 875 | 376 | 2 | 2.2 | −0.7 | 1.5 |
| | Eu(dpm)$_3$ | 252 | 600 | 385 | −133 | −12.4 | −114.6 | −127.0 |
| Co(bzac)$_3$ | La(fod)$_3$ | 326(287) | 180 | 326 | 0 | | | |
| | Pr(fod)$_3$ | 446(435) | 173 | 354 | 92 | 74.0 | 21.7 | 95.7 |
| | Nd(fod)$_3$ | 445(430) | 250 | 368 | 77 | 28.3 | 32.7 | 61.0 |
| | Sm(fod)$_3$ | 400(378) | 130 | 396 | 4 | 4.7 | −0.5 | 4.2 |
| | Eu(fod)$_3$ | 308(299) | 90 | 410 | −102 | −26.9 | −77.9 | −104.8 |
| Co(mbzac)$_3$ | La(fod)$_3$ | 332 | 160 | 332 | 0 | | | |
| | Pr(fod)$_3$ | 460(445) | 220 | 361 | 99 | 81.0 | 22.5 | 103.5 |
| | Nd(fod)$_3$ | 462(442) | 160 | 376 | 86 | 30.9 | 33.9 | 64.8 |
| | Sm(fod)$_3$ | 409(395) | 80 | 405 | 4 | 5.2 | −0.5 | 4.7 |
| | Eu(fod)$_3$ | 318(301) | 100 | 419 | −101 | −29.4 | −80.0 | −109.4 |

a) In ppm. Down-field shifts are given as negative. The accuracy of the observed shifts is ±1 ppm for all the adducts except for that of Co(acac)$_3$ with Ln(dpm)$_3$ (±2 ppm). b) Relative to free complex. Values in parentheses are for the small peaks (see text). c) The line widths of adduct peaks in Hz. d) $\delta_{Co}(La)+\alpha\cdot N$, where $\alpha$ is 12 ppm (Co(acac)$_3$ with Ln(fod)$_3$), 8.9 ppm (Co(acac)$_3$ with Ln(dpm)$_3$), 14.0 ppm (Co(bzac)$_3$ with Ln(fod)$_3$), and 14.5 ppm (Co(mbzac)$_3$ with Ln(fod)$_3$).



$R=CH_3$ Co(acac)$_3$
$R=C_6H_5$ Co(bzac)$_3$
$R=p\text{-}CH_3O\text{-}C_6H_5$ Co(mbzac)$_3$

Co(acac)$_3$, except for the adduct of Co(mbzac)$_3$ with La(fod)$_3$ which has only one line; that is, a satellite appears at a lower-field (15—20 ppm) than the main peak, though its intensity relative to the main peak is larger than that for Co(acac)$_3$. This two-line pattern can, therefore, be interpreted as arising from the *fac*- and *mer*-isomers of Ln(fod)$_3$-part in the adduct exchanging each other very slowly on the NMR time scale.[14)] For comparison with the adduct of Co(acac)$_3$ with Ln(fod)$_3$, the larger peaks at higher-field are taken as $\delta_{Co}$, which are listed in Table 1.

*Separation of $^{59}$Co LIS's into Contact (cs), Pseudo-contact (pcs), and Adduct-formation Shifts (AFS).* Since it was found from an X-ray analysis of the Co(acac)$_3$–Eu(fod)$_3$ crystal[3)] that this adduct has a $C_3$ axis, the approximation of magnetic axial symmetry can be applied to the analyses of the $\delta_{Co}$ observed above. Furthermore, the hyperfine splitting constant ($A$) and the geometric factor, $(3\cos^2\theta-1)r^{-3}$, ($G$) of $^{59}$Co nucleus in the adduct are assumed to be constant along the lanthanoid series, on the basis of the reasonable expectation that the bonding nature and geometries of these adducts are almost independent of the lanthanoid metal. Thus, $\delta_{Co}$ can be expressed as

$$\delta_{Co} = A\cdot\langle S_z\rangle + G\cdot D'\cdot D + \text{AFS}, \qquad (1)$$

where AFS is a diamagnetic adduct-formation shift, $\langle S_z\rangle$[15)] is the projection of the total electron spin magnetization of lanthanoid ion in the direction of the external magnetic field, $D'$[16)] is the product of the first and the third term in Bleaney's equation

$$\Delta\nu/\nu_0 = \beta^2/(60(kT)^2)\cdot(3\cos^2\theta-1)/r^3\cdot 2A_2^0\langle r^2\rangle$$
$$\times g^2J(J+1)(2J-1)(2J+3)\langle J\|\alpha\|J\rangle \qquad (2)$$

(a constant for a given temperature and ligand field), and $D$[16)] is the fourth term in the above equation (a constant for a given lanthanoid). When $\delta_{Co}$ corrected for AFS is denoted as $\delta'_{Co}$,

$$\delta'_{Co} = A\cdot\langle S_z\rangle + G\cdot D'\cdot D \qquad (3)$$

is obtained. By rearrangement of Eq. 3, one obtains

$$\delta'_{Co}/\langle S_z\rangle = A + G\cdot D'\cdot(D/\langle S_z\rangle). \qquad (4)$$

If the assumption of constant $A$ and $G$ is reasonable, the $\delta'_{Co}/\langle S_z\rangle$ *vs.* $D/\langle S_z\rangle$ plot should be linear. For several systems consisting of an organic substrate and Ln(fod)$_3$, good linear relations have been obtained by several workers.[17)]

An use as AFS of the La(fod)$_3$-induced shift, $\delta_{Co}$(La), gave no linear relation in Eq. 4 for Co(acac)$_3$ with Ln(fod)$_3$. On the other hand, for the Al(acac)$_3$–Ln(fod)$_3$ system similar in structure to the present adduct,

$\delta'_{Al}/\langle S_z\rangle$ *vs.* $D/\langle S_z\rangle$ plot has given a good linearity on the use of La(fod)$_3$-induced $^{27}$Al shifts as AFS.[18] This result leads us to anticipate that, in contrast to $^{27}$Al shifts, $^{59}$Co shifts (mainly $\sigma_{para}$) are very sensitive to even a slight change in diamagnetic electron-densities on the bridging oxygen atoms. Then, by taking $\delta_{Co}$(La) $+a\cdot N$ as AFS where $N$ is the number of 4f-electrons and $a$ the contribution of a 4f-electron to AFS, $a$ was decided so that the best linearity may be obtained. Consequently, satisfactory values for correlation coefficients were obtained by using the tabulated values for $\langle S_z\rangle$[15] and $D$.[16] The plot obtained is shown in Fig. 4, together with correlation coefficients ($R$). Also for $\delta_{Co}$ of Co(acac)$_3$ with Ln(dpm)$_3$ and Co(bzac)$_3$ and Co(mbzac)$_3$ with Ln(fod)$_3$, the same process gave good results (Figs. 4 and 5). Thus, by using the slope and intercept of the linear relation, $\delta'_{Co}$ was successfully separated into cs and pcs terms. The results are listed in Table 1.

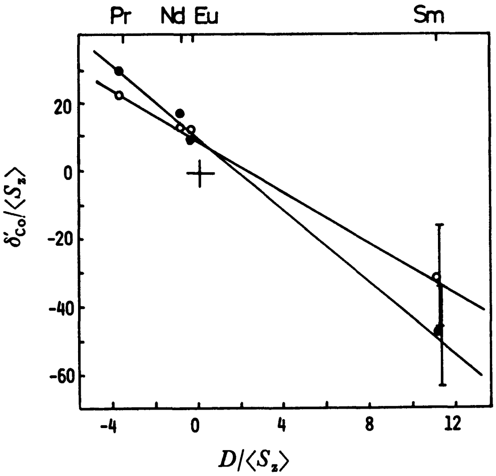


Fig. 4. The $\delta'_{Co}/\langle S_z\rangle$ *vs.* $D/\langle S_z\rangle$ plots. Co(acac)$_3$-Ln(fod)$_3$ and -Ln(dpm)$_3$ adducts are denoted by filled and open symbols, respectively.
●: $R$=0.980, ○: $R$=0.998.

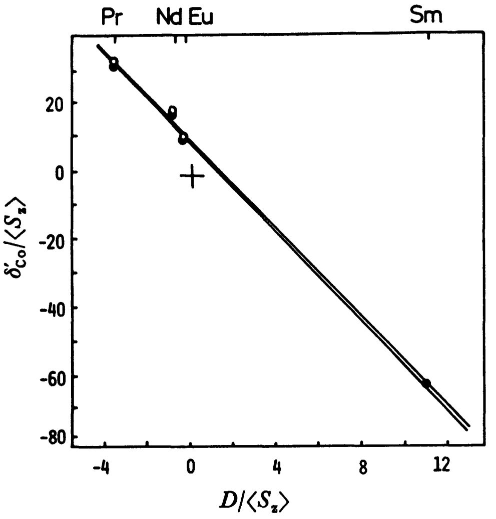


Fig. 5. The $\delta'_{Co}/\langle S_z\rangle$ *vs.* $D/\langle S_z\rangle$ plots. Co(bazc)$_3$- and Co(mbzac)$_3$-Ln(fod)$_3$ adducts are denoted by filled and open symbols, respectively.
●: $R$=0.987, ○: $R$=0.991.

Considering the use of theoretical values of $\langle S_z\rangle$ and $D$ for the above treatment of experimental data, one cannot discuss the details of adduct geometries by comparing the slight differences between the slopes estimated for several complexes. However, it may roughly be said that the slope for the adduct of Co(acac)$_3$ with Ln(fod)$_3$ is larger than that with Ln(dpm)$_3$. The magnitude of slope estimated from Fig. 4 contains the crystal field parameter $A_2^0\langle r^2\rangle$. Since values of $A_2^0\langle r^2\rangle$ for the present systems are unknown, $G$ cannot be estimated directly from the slope. However, if $A_2^0\langle r^2\rangle$ for Ln(fod)$_3$- and Ln(dpm)$_3$-adducts of Co(acac)$_3$ were similar in magnitude, $G$ for the former would be larger than that for the latter. On the other hand, in the former, the coordination interaction *via* three bridging oxygens may be more pronounced because of the strong Lewis-acidity of Ln(fod)$_3$ and the Co–Ln distance can thus be expected to be shorter than the latter. The $G$ value was calculated to be 0.0543 Å$^{-3}$ (the distance of Co to Ln is 3.33 Å) from the X-ray crystal data,[3] on the assumption that the Co atom is located on the principal magnetic axis, as deduced on the basis of the approximation of magnetic axial-symmetry. From this value of $G$ and the slope for the Ln(fod)$_3$-adduct given in Fig. 4, $A_2^0\langle r^2\rangle$ is calculated to be 175 cm$^{-1}$. This value is comparable in magnitude to those estimated for several other adducts, *e.g.*, 200—500 cm$^{-1}$ for the $\gamma$-picoline–Ln(fod)$_3$ system in CDCl$_3$[19] and 100—150 cm$^{-1}$ for the aniline–Ln(fod)$_3$ system in CCl$_4$.[20] If 175 cm$^{-1}$ is taken also for the Co(acac)$_3$–Ln(dpm)$_3$ adduct, the Co–Ln distance for this adduct would be about 1.1 times as long as that of Ln(fod)$_3$-adduct.

$A_{Co}$ for the Co(acac)$_3$–Ln(fod)$_3$ adduct was estimated to be about $-0.2$ G from Fig. 4. The amount of electron spin transferred from Ln ion into Co ion is estimated to be $\approx 2\times10^{-4}$. The minus sign of $A_{Co}$ and the very small amount of spin detected at the Co nucleus may imply that the spin polarization mechanism is predominant for electron spin transfer.

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10) The observation of only one $^{1}$H line arising from *t*-butyl protons was confirmed by a simultaneous $^{1}$H NMR experiment. This is consistent with a rapid exchange between the isomers. Although it is also possible that only one of the two isomers exists, this model may be ineffective for interpretation of these satellites.

11) Two relaxation mechanisms of $^{59}$Co nucleus due to quadrapole interaction and electron spins seem to be influenced each other. A discussion on this problem is in progress.

12) It may be reasonable to consider that when $CHCl_3$ or $CCl_4$ is used as a solvent, the difference of these solvent effects on the $^{59}$Co shifts of a free complex and a corresponding adduct is similar in magnitude. Thus, for interpreting this shift difference, the solvent effect need not be taken into account.

13) Since the rate of isomerization for tris($\beta$-diketonato)Co(III) is generally said to be slow, it may not be considered that the observed one line corresponds to averaging *fac*- and *mer*-isomers.

14) It may not be considered that these satellites arise from the *mer*-isomer of Co-complex-part of the adduct, because of steric hindrance on the adduct formation.

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