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LANTHANOID-INDUCED ^{59}Co NMR SHIFTS OF THE ADDUCTS OF TRIS(ACETYLACETONATO)Co(III) WITH LN(FOD)$_3$ AND LN(DPM)$_3$ IN SOLUTIONS

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The ^{59}Co shifts of tris(acetylacetonato)Co(III) induced by Ln(fod)$_3$ and Ln(dpm)$_3$(Ln=La, Pr, Nd, Sm, Eu) were determined by observing separately the resonances of free and complexed Co(acac)$_3$. An attempt to separate a contact contribution using theoretical D and $\langle S_z \rangle$ values was successfully made by assuming the increase in an adduct formation shift with increasing number of 4f electrons.

It has been found by Lindoy et al.$^{1)}$ that the exchange of Co(acac)$_3$ between its free form and its 1:1 adduct with Eu(fod)$_3$-d$_{27}$$^{2)}$ in CDCl$_3$ near room temperature is slow on the NMR time scale in contrast to the other several transition metal complexes$^{3)}$ binding to a lanthanoid shift reagent(LSR) and that this adduct is formed by the strong binding through three bridging oxygen atoms.

We now report on the ^{59}Co shifts of Co(acac)$_3$ induced by Ln(fod)$_3$ and Ln(dpm)$_3$$^{2)}$ (Ln=La, Pr, Nd, Sm, Eu) in CHCl$_3$ and CCl$_4$, respectively, at room temperature(25 °C). Spectra were measured on a Varian CFT-20 spectrometer equipped with a broad band accessory. 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. With all the LSR's used here, the resonances of free and complexed Co(acac)$_3$ were separately observed in the 0.05 M Co(acac)$_3$ solution at the ratio of LSR to Co(acac)$_3$ of 0.5. This result is consistent with the observation of ^{1}H spectra,$^{1)}$ and may suggest that 1:1 adducts of the similar type are formed also with Ln(dpm)$_3$ in solution. Some of the adduct resonances accompanied a peak of very small intensity at slightly lower field than the main peak, with the exception for the Sm(dpm)$_3$-adduct, where the intensity of this peak was about half that of the main peak, though could not be precisely determined due to its considerable broadening and partial overlapping with the main peak. Table 1 lists the shift values relative to the free Co(acac)$_3$(δ_{Co}) and the line widths($\Delta\omega$) for the adducts.

Fairly large high-field shifts observed with diamagnetic La(fod)$_3$ and La(dpm)$_3$$^{4)}$ are not surprising by considering that ^{59}Co paramagnetic shifts(σ_{para}) are greatly sensitive to a variation of ligand and ligand field symmetry.$^{5)}$ Thus, these may suggest a small increase in the energy separation(ΔE) between the ground state and the excited $^1T_{1g}$ level of Co^{3+} on going from free Co(acac)$_3$ to the adduct. Unfortunately, NMR signals for adducts with the later members of lanthanoid series(from Gd to Yb) were undetectable due to its relatively large electronic T_1. Assuming that

Table 1. Lanthanoid-induced ^{59}Co shifts of the Ln(fod)$_3$- and Ln(dpm)$_3$-adducts of Co(acac)$_3$ and its separation into cs and pcs$^{a)}$

	$\delta_{Co}$$^{b)}$	$\Delta\omega$$^{c)}$	AFS$^{d)}$	$\delta'_{Co}$$^{e)}$	Calculated pcs	Calculated cs	Calculated total
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
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

a) In ppm. Downfield shifts are given as negative. The accuracy of all the observed shifts is ± 1 ppm.

b) Relative to free Co(acac)$_3$. Values in parentheses are of the small peaks (See Text).

c) The line widths of adduct peaks in Hz.

d) δ_{Co}(La) + $\alpha \cdot N$, where α is 12.0 ppm for Ln(fod)$_3$ and 8.9 ppm for Ln(dpm)$_3$, and N is the number of 4f electrons.

e) δ_{Co} - AFS

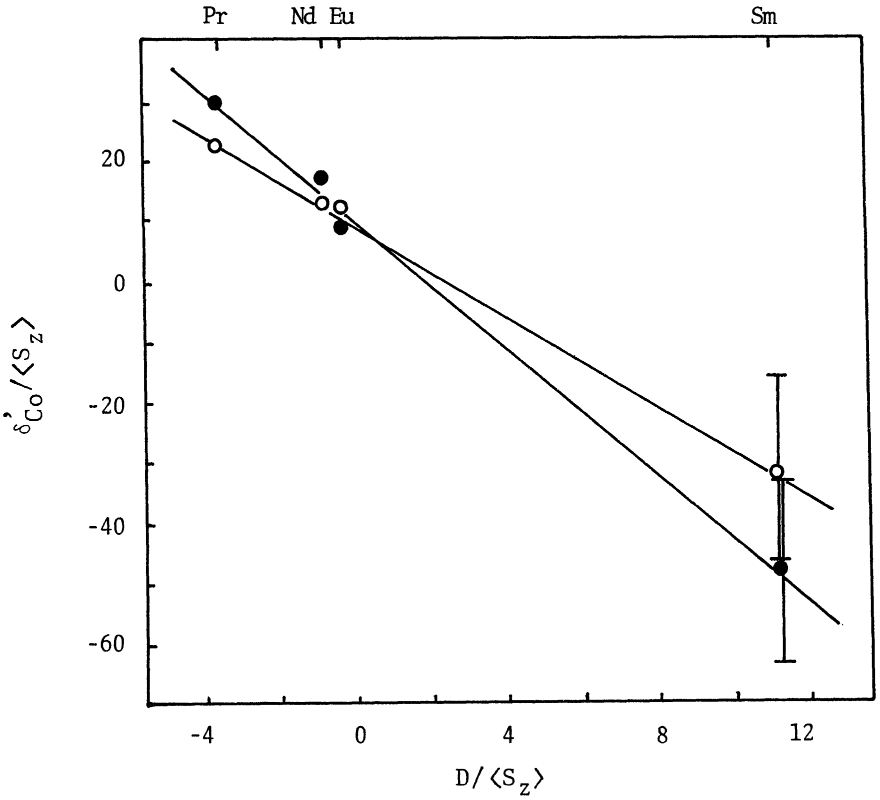

Fig. 1. The ratios of δ'_{Co} to $\langle S_z\rangle$ plotted vs. $D/\langle S_z\rangle$. $Ln(fod)_3$- and $Ln(dpm)_3$-adducts are denoted by filled and open symbols, respectively.

the magnitude of AFS of the adduct is constant along the lanthanoid series, as in many organic substrates complexed with shift reagents, the δ_{Co} values corrected for the $Ln(fod)_3$- or $Ln(dpm)_3$-induced shift, δ'_{Co}, were taken as a sum of contact(cs) and pseudocontact shifts(pcs). Further assuming that the hyperfine splitting constant, A, between Co nucleus and electron spin is constant along the lanthanoid series, an attempt was made for the graphical separation of cs and pcs by using the relation for the system of an axial symmetry

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

where G is the geometric factor $(3\cos^2\theta - 1)/r^3$, $\langle S_z\rangle$[6] is projection of the total electron spin magnetization of lanthanoid ion in the direction of the external magnetic field, and D[7] is a constant for a given lanthanoid and temperature. However, a good linear relation was not obtained.

On the other hand, $Al(acac)_3$-$Ln(fod)_3$ adducts,[8] which may be expected to be similar in geometry to the present adducts, show only a small amount of AFS(~ -2 ppm). The linear relationship obtained over all the data points has been found good with the same set of LSR as in the present study. This allows us to expect that the poor result from the $Co(acac)_3$-adducts may be ascribed to the considerable variation in the AFS along the lanthanoid series. This is also anticipated from the observation of the relatively large difference between the diamagnetic shifts with La(fod)$_3$ and La(dpm)$_3$.

Assuming that ΔE of the Co ion increases with an increase in the number of 4f electrons(N), AFS was taken as δ_{Co}(La) + $\alpha \cdot N$, and α was determined so as to give a best fit for the linear relation between $\delta'_{Co}/\langle S_z \rangle$ and $D/\langle S_z \rangle$. The shift values corrected for AFS, δ'_{Co}, are listed in Table 1. The linear relation is uniquely determined, as shown in Fig. 1. G corresponding to the slope can not be immediately estimated from Fig. 1, because the crystal field parameter $A_2^0\langle r^2 \rangle$ in the Bleaney's equation[7)]

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

is unknown for the present adducts. The value of 0.0543 $\mathring{A}^{-3}$ is obtained for G of the Co(acac)$_3$-Eu(fod)$_3$ adduct from the crystal structure[1)] (the distance between Co and Eu atoms is 3.33 Å), on the plausible assumption that the Co atom is located on the principal magnetic axis on the basis of the approximation of axial symmetry. In order that the value of slope for the Ln(fod)$_3$-adducts in Fig. 1 becomes equal to 0.0543, $A_2^0\langle r^2 \rangle$ must be taken as 175 cm^{-1}. This value is comparable in magnitude to those estimated for the other several adducts; e.g. 200-500 cm^{-1} for the γ-picoline-Ln(fod)$_3$ in CDCl$_3$[9)] and 100-150 cm^{-1} for the aniline-Ln(fod)$_3$ in CCl$_4$.[10)] Although X-ray data of the Ln(dpm)$_3$-Co(acac)$_3$ adduct is not available so far, if the Co-Ln distance could be taken as the value equal to that for the adduct with Ln(fod)$_3$, $A_2^0\langle r^2 \rangle$ for the adduct with Ln(dpm)$_3$ would be 95 cm^{-1} from the value of slope in Fig. 1. A is negative from Fig. 1 for both Ln(fod)$_3$- and Ln(dpm)$_3$-adducts. (The positive sign in δ'_{Co} implies the negative spin at the Co nucleus) The separated cs and pcs contributions by using the A and G values obtained above are shown in Table 1. These results will become reliable if the process described above for estimating the amounts of AFS is accepted to be valid.

References and Notes

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