Observation of ^{27}Al N.M.R. Paramagnetic Shifts (Large Contact Shift Contributions) Induced by Lanthanoid Shift-Reagents in Tris(acetylacetonato)aluminium(III)

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Summary. On the addition of tris(1,1,1,2,2,3,3-heptafluoro-7,7-dimethyloctane-4,6-dionato)Ln^{III} [Ln(fod)$_3$] (Ln = La, Pr, Nd, Sm, and Eu) to a benzene solution of tris(acetylacetonato)Al^{III} [Al(acac)$_3$] the ^{27}Al resonance lines due to the free and the complexed Al(acac)$_3$ have separately been observed at 25 °C, the chemical exchange is slow on the n.m.r. time scale and the separation of paramagnetic shifts into contact(cs) and pseudocontact-(pcs) contributions implies a fairly large cs contribution and that the hyperfine splitting constant of the Al nucleus is positive.

It has been found that some transition-metal complexes incorporating oxygen-donor atoms are co-ordinated to shift reagents and that this results in paramagnetic ^{1}H shifts for the complexes[1] as reported in the literature for many organic substrates. This prompted us to examine whether or not a lanthanoid-induced paramagnetic shift occurs in a central metal ion in such complexes.

We report here that on addition of Ln(fod)$_3$(Ln = La, Pr, Nd, Sm, and Eu) to a 0.05 M benzene solution of Al(acac)$_3$ at ambient probe temperature (25 °C), a new ^{27}Al resonance line, probably due to a 1:1 adduct, appears in addition to that of the free complex. The Table shows the shift values

Table. Lanthanoid-induced ^{27}Al shifts of Al(acac)$_3$ and its separation into cs and pcs.[a]

				Theoretical		
	δ_{Al}[b]	$\Delta\nu$[c]	δ_{Al}[d]	cs	pcs	Total
La(fod)$_3$	-2 ± 1	165[e]	0			
Pr(fod)$_3$	70.2 ± 1	229	72.2 ± 2	16.0	55.0	71.0
Nd(fod)$_3$	44.5 ± 1	178	46.5 ± 2	24.2	21.0	45.2
Sm(fod)$_3$	2 ± 1	216[e]	4 ± 2	-0.3	3.5	3.2
Eu(fod)$_3$	-81.7 ± 1	191	-79.7 ± 2	-57.7	-20.0	-77.7

[a] In p.p.m. High field shifts are denoted as positive. The ^{27}Al n.m.r. spectra were measured on a Varian CFT-20 with a broad band accessory at 20.727 Mz for 8065 Hz spectral width. 807 data points were available taking the aquisition time as 0.05 s. [b,c,d] See text ($\Delta\nu$ in Hz). [e] Values for the superposition of free and complexed species.

of the new peaks relative to those of the corresponding free complexes as an internal reference ($\delta_{\rm Al}$), together with their line widths ($\Delta\nu$), measured at a molar ratio (ρ) of $\rm Ln(fod)_3$ to $\rm Al(acac)_3$ of 0·5 The error range was determined by taking into account the data points and line widths With increasing ρ, the intensity of the new peak gradually increased with the line width remaining almost unchanged, while the intensity of the free complex decreased, then, when $\rho = ca$ 1, the latter almost disappeared These results suggest that a **1 : 1** adduct of $\rm Al(acac)_3$ and $\rm Ln(fod)_3$ is formed and that the chemical exchange is slow on the n m r time scale, analogous to the $\rm Co(acac)_3$–$\rm Eu([^2H_{27}]fod)_3$ system in $\rm CDCl_3$ at 32 °C studied by Lindoy *et al* [1a] Since $\rm Gd(fod)_3$ through to $\rm Yb(fod)_3$ have a relatively long electron spin T_1, the resonances from the adducts could not be detected because of the slow exchange rate

On the reasonable assumption that the geometries of adducts are unchanged along the lanthanoid series, successfully used for many organic substrates complexed with shift reagents, the shift values obtained by subtracting $\delta_{\rm Al}(\rm La)$ from $\delta_{\rm Al}$ (denoted as $\delta'_{\rm Al}$) are composed of the contact shift (cs) and pseudocontact shift (pcs) contributions Thus, using the approximation of axial symmetry, $\sigma_{\rm Al}$ can be expressed as in equation (1), where A is the hyperfine

$$\sigma_{\rm Al} = A\,\langle S_{\rm z}\rangle + G{\cdot}D \qquad (1)$$

coupling constant berween the Al nucleus and the unpaired electron-spin $\langle S_{\rm z}\rangle$ is the projection of the lanthanoid total electron-spin magnetization in the directon of the external magnetic field,[2] G is the geometric factor $(3\cos^2\theta - 1)/r^3$, and D is a constant for a given lanthanoid and temperature [3] If the constancy of A and G can be assumed, a linear relation may be expected between $\sigma'_{\rm Al}/\langle S_{\rm z}\rangle$ and $D/\langle S_{\rm z}\rangle$,[4] and so the two contributions can be graphically separated In practice, the plot using tabulated values of $\langle S_{\rm z}\rangle$ [2] and D [3] gave an excellent linearity Separation into cs and pcs contributions is satisfactory, as seen from the Table It was found that a large proportion of 4f electron spin is transferred to the ^{27}Al nucleus and that the hyperfine splitting constant of Al is positive On the other hand, it was also found that the slope of the linear relation of $\delta_{\rm Al}/\langle S_{\rm z}\rangle$ to $D/\langle S_{\rm z}\rangle$ is almost equal in magnitude to that obtained for the analogous $\rm Co(acac)_3$-adducts [1a] This appears to imply that the structures of the present $\rm Al(acac)_3$-adducts are similar to those of the $\rm Co(acac)_3$-adducts, which are formed through the strong coupling due to the three bridging oxygens

It is well known that negative spin is introduced on the oxygen or nitrogen nucleus directly bound to a lanthanoid ion and that the spin is transferred to the ligand molecule by spin polarization [2,5] Hence, it may be reasonable to consider that the positive spin is introduced on the Al nucleus *via* the pathway Ln - - O - - Al, predominantly by a spin-polarization mechanism

Thus one may consider the possibility that the bonding nature of metal–ligand bonds in metal complexes can be studied using the hyperfine interaction of central metals induced by shift reagents

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