

Pseudo-contact Contributions to Lanthanide-induced Nuclear Magnetic Resonance Shifts

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Summary For a magnetically anisotropic lanthanide complex the pseudo-contact contributions to the induced shift may, under certain definable conditions for internal rotations, still be proportional to an expression of the type $(3 \cos^2 \theta - 1)r^{-3}$ even when the susceptibility tensor is not axially symmetric.

CONSIDERABLE controversy surrounds the discussion of the shifts produced by lanthanide and transition metal shift reagents. We have, therefore, re-examined analytically the basic equations and their underlying assumptions.

One difficulty in this field has been to justify the use, or rationalize the success, of a simplified formula for the

geometrical dependence of the pseudo-contact contribution to the observed shift. This success has been rationalized by many research groups, including our own, in published work, in terms of an axially symmetric susceptibility tensor, generally with $\chi_{||}$ along the bond axis. We present here an alternative rationalization.

The pseudo-contact contribution to the isotropic n.m.r. shift of a given nucleus in a paramagnetic complex is usually expressed by equation (1). r , χ , and ψ are the

$$\Delta H/H_0 = K_1(3 \cos^2 \chi - 1)/r^3 + K_2 \sin^2 \chi \cos 2\psi/r^3 \quad (1)$$

spherical polar co-ordinates of the nucleus if the paramagnetic centre is at the co-ordinate origin and the polar axis is taken to be any one of the principal magnetic susceptibility axes. K_1 and K_2 are constants for a given complex, involving either the principal g -tensor components¹ (g_1, g_2, g_3) or, more correctly, the principal magnetic susceptibility components (χ_1, χ_2, χ_3).²

For axial symmetry in the susceptibility tensor $K_2 = 0$, and only the first term of (1) need be considered.

The results of many experimental studies of induced lanthanide shifts have however been analysed in terms of equation (2), where θ and r relate the co-ordinates of the

$$\Delta H/H_0 = K(3 \cos^2 \theta - 1)/r^3 \quad (2)$$

nucleus being considered to the lanthanide-ligand bond axis,^{3,4} or an axis defined by the ligand,⁵ rather than to a principal susceptibility axis. This simplification is valid, as the theory has been presented so far, only if the susceptibility tensor has axial symmetry and $\chi_{||}$ lies along the bond axis.

Several authors⁶ have suggested that the assumption of magnetic axiality is not valid. This objection seems reasonable in the light of X-ray structural determinations which have shown low symmetry in the complexes studied.⁷ It seems irrefutable from single crystal susceptibility data for a complete lanthanide range of complexes of the type $\text{Ln}(\text{dpm})_3$ (4-pic)₂ (where dpm = dipivaloylmethane; and 4-pic = 4-picoline) which clearly indicate axial magnetic symmetry cannot be assumed in these systems.⁸

We now show that the condition of axial symmetry may be transferred from the susceptibility tensor to the ligand motion relative to the lanthanide. We simply transform equation (1) to a new set of axes, in which (initially at least) the lanthanide-ligand bond axis is the z -axis, related to the old axis by the Euler angles $(\beta, \alpha, 0)$. If the polar co-ordinates of the nucleus in the new frame are (r, θ, ϕ) then we assume that the ligand can rotate around the z -axis and can adopt positions such that $\phi = \phi_1$, $\phi = \phi_1 + 2\pi/n$, $\phi = \phi_1 + 4\pi/n$, etc., where ϕ_1 is an arbitrary angle and n is a positive integer. In this treatment other internal motions affecting the set of nuclei being investigated are not (so far) allowed (*i.e.* θ and r must be constant for any one nucleus) and the populations of the rotamers defined by the values of ϕ above must be equal. For each position we assume that the ligand can move within $\pm\gamma$ of the mean angle. Then the observed shift can be described by equation (3), with $\Delta H/H_0$ given by equation (1).

$$\langle \Delta H/H_0 \rangle = \sum_{i=0}^{n-1} \int \frac{\phi_1 + 2i\pi/n + \gamma}{\phi_1 + 2i\pi/n - \gamma}$$

$$(\Delta H/H_0) d\phi \left/ \sum_{i=0}^{n-1} \int \frac{\phi_1 + 2i\pi/n + \gamma}{\phi_1 + 2i\pi/n - \gamma} d\phi \right. \quad (3)$$

If $n \geq 3$, we can easily derive equation (4). If $n = 1$ or

$$\begin{aligned} \langle \Delta H/H_0 \rangle &= \left[\frac{1}{2} K_1 (3 \cos^2 \alpha - 1) + \frac{1}{2} K_2 \sin^2 \alpha \cos 2\beta \right] \times \\ &= K_3 (3 \cos^2 \theta - 1)/r^3 \end{aligned} \quad (4)$$

2 the equation is much more complicated than (4).

We can make the following statements. Firstly for $\gamma = \pi/n$ we have the case of a freely rotating ligand and equation (4) is valid. Secondly if γ is very small we have the situation which we may describe as hindered rotation or, perhaps more likely, as a case where the ligand is labile and can be attached in any one of n different conformers; equation (4) then holds provided $n \geq 3$. In other words effective axial symmetry in the rotation gives equation (4) in which K_3 is a constant for a given complex. The values of $\langle \Delta H/H_0 \rangle$ then for different nuclei in that complex should be in the ratios of the second term in equation (4); and the success in the use of equation (2) for borneol⁴ can be rationalised. It is clear also that in principle K_3 varies with a change either in the ligand or the lanthanide and not necessarily in a simple way, since K_3 is a function of K_1, K_2 and α and β .

Our result may be generalised to any rotational axis provided the axis passes through the paramagnetic centre, and provided the above conditions for r , θ and the rotational populations are met.

Furthermore for the case of two identical ligands attached to a metal (at sites A and B) we can deduce the following statements provided the rotational conditions are met for each site.

- (1) For non-labile ligands two sets of shifted resonances would be observed each fitting an equation of type (4).
- (2) For labile ligands provided $\theta_A = \theta_B$ and $r_A = r_B$ then one set of resonances, again fitting the simplified equation, should be obtained. In this case the constant K_3 will be given by $\frac{1}{2}(K_{A3} + K_{B3})$.
- (3) Case 2 does not hold rigorously if $\theta_A \neq \theta_B$ or $r_A \neq r_B$.

We have considered other cases which we think are outside the scope of this communication.

We emphasize that equation (4) is valid irrespective of the symmetry of the magnetic susceptibility tensor, provided our rotational conditions are met. Whether these conditions are to be preferred to, *i.e.* are more realistic than, the usual assumptions involving an axially symmetric susceptibility tensor is as yet an open question, which should provoke some interesting discussion. What is true is that if an unwarranted assumption of axial symmetry is made for the susceptibility tensor then computer fitting

of the data based on the first term of equation (1) alone will converge on any rotation axis which effectively satisfies the conditions described here.† On the other hand computer fitting for a complex with both an axial susceptibility and a rotation axis, which are different, could give two solutions.

(Received, 23rd May 1972; Com. 885.)

† Professor J. D. Roberts and his group find, for the published³ data and for their own new data on borneol, only a difference of a few degrees between the lanthanide-oxygen direction and the assumed axis of magnetic symmetry; personal communication.

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