LANTHANIDE-INDUCED CONTACT SHIFTS IN POLYGLYCOLDIMETHYLETHERS

VI. CALCULATION OF FERMI CONTACT AND DIPOLAR CONTRIBUTIONS

FROM THE TEMPERATURE DEPENDENCE OF THE SHIFTS[*]

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In studies of lanthanide (Ln) induced shifts it is usually assumed that the shifts are of dipolar origin, possible contributions from a Fermi contact (Fc) interaction are difficult to establish. If the former mechanism predominates one expects (1) that the shifts induced by one Ln complex can be converted into those of another by multiplying them with a constant factor. Deviations from this proportionality factor are taken as evidence for the presence of Fc contributions to the observed shift. For Pr and Eu compounds Sanders and Williams (2) found a ratio of approximately 3 for the proton shifts of a few phosphates and phosphonates. However, for the ^{31}P shifts a ratio as low as 0.5 was observed, taken as evidence by them for the occurrence of Fc interactions.

OME:

$CH_3-O-CH_2-CH_2-O-CH_3$
3.3   1.6 1.6   3.3

GLYME-3:

$CH_3-O-CH_2-CH_2-O-CH_2-CH_2-O-CH_3$
3.4   2.1 2.3   2.3 2.1   3.4

GLYME-4:

$CH_3-O-CH_2-CH_2-O-CH_2-CH_2-O-CH_2-CH_2-O-CH_3$
2.9   1.8 1.9   3.0 3.0   1.9 1.8   2.9

GLYME-5:

$CH_3-O-CH_2-CH_2-O-CH_2-CH_2-O-CH_2-CH_2-O-CH_2-CH_2-O-CH_3$
2.8   1.7 1.8   2.6 2.8   2.8 2.6   1.8 1.7   2.8

GLYME-6:

$CH_3-O-CH_2-CH_2-O-CH_2-CH_2-O-CH_2-CH_2-O-CH_2-CH_2-O-CH_2-CH_2-O-CH_3$
2.9   1.7 1.8   2.6 2.7   2.6 2.6   2.7 2.6   1.8 1.7   2.9

In the figure the Pr/Eu shift ratios for a number of 1 : 1 $Ln(DPM)_3$, glyme complexes are listed. Though most ratios are approximately 3, the external and penultimate CH_2 groups in each glyme show lower values of about 2. In part V we have shown that the oxygen atoms that surround these groups are just the sites to which the lanthanide complex coordinates preferentially, bringing the external and penultimate CH_2 groups in close proximity to the lanthanide ion. Apparently there are small Fc contributions to the proton shifts for these groups, that may explain the lower shift ratios. A necessary condition for this is that the Eu^{3+}-induced Fc shifts are of opposite sign to and of greater magnitude than those induced by Pr^{3+}, actually observed (3), and that for both ions the Fc shift reinforces the dipolar shift.

Both the Fc and the dipolar shift are in first order proportional to $1/T$. Recently Bleaney [4] has shown that for the Pr complexes the first order contribution of the dipolar shift is equal to zero, and the second order contribution proportional to $1/T^2$. Hence the Pr^{3+}-induced shift, δ_{Pr}, can generally be expressed as $\delta_{Pr} = a/T + b/T^2$ (I), the first term representing the Fermi contact (δ_{Fc}) and the second term the dipolar contribution (δ_{Dp}). An ideal system for studying this relation is the $Pr(FOD)_3$, DME complex, because the binding constant is high (10^5 l mol^{-1}) and no conformational changes are observed. In figure 1 of part III we plotted δ_{Pr} as a function of $1/T^2$, neglecting the $1/T$ Fermi contact term. Good straight lines were obtained with almost zero intercept for the CH_3 protons, but with a significantly non-zero intercept for the CH_2 protons (-2.7 $\pm$ 0.4 ppm). Since for Pr the temperature independent paramagnetism is small the non-zero intercept for the CH_2 protons points to Fc contributions to the shift. If the data are fitted to the relation I, by a quadratic least squares analysis, δ_{Fc} and δ_{Dp} can be determined. At 31.5°C it was found for the CH_3 protons δ_{Fc} = 0.8 $\pm$ 0.4 ppm, δ_{Dp} = -26.0 $\pm$ 0.5 ppm, and for the CH_2 protons δ_{Fc} = -5.0 $\pm$ 0.5 ppm, δ_{Dp} = -25.2 $\pm$ 0.6 ppm. Clearly, for the CH_3 proton shifts the Fc contribution can be neglected, while about 17% of the CH_2 proton shift originates from this interaction. Finally it should be noticed that the Fc contribution indeed reinforces the dipolar contribution for the CH_2 proton shift, as we were forced to assume to explain the low Pr/Eu shift ratios found for these protons.

References

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