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SINGLET-TRIPLET EQUILIBRIUM IN TRIS(DIPIVALOYLMETHANATO)EUROPIUM(III) AS EVIDENCED BY PROTON MAGNETIC RESONANCE

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Temperature dependence was measured of the proton chemical shift of the shift reagent Eu(DPM)$_3$. The shift deviates from the McConnell-Robertson equation below 200°K. This behavior was explained in terms of the low-lying first excited triplet $^7F_1$ state.

We have measured the proton chemical shift of the shift reagent tris(dipivaloylmethanato)europium(III), Eu(DPM)$_3$, as a function of temperature. Measurements were made of a carbon disulfide solution of Eu(DPM)$_3$ (about 0.1 g/ml) which contained a small quantity of ethanol added to enhance the solubility. Spectra were obtained on a JEOL-PS-100 spectrometer operating at 100 MHz. The results are given in Fig. 1, in which we can see that the shift does not follow the ordinary McConnell-Robertson equation (1) in the low temperature region. This behavior can be interpreted in the following way.

Tris-chelated europium(III) complexes have been reported to have the ground singlet $^7F_0$, the first excited state $^7F_1$ lying about 150 cm^{-1} above the ground state, and the second excited state being 1000 cm^{-1} above the $^7F_1$ state (2). Thus the well-populated level at room temperature is only the thermally accessible triplet $^7F_1$. The magnetic susceptibility is given by the equation

$$\chi = \frac{\alpha_0 + (g_J^2\beta^2 J(J+1)/3kT + \alpha_1)\,3\exp(-\Delta/kT)}{1 + 3\exp(-\Delta/kT)} \quad \cdots\cdots\cdots\cdots (1)$$

and the chemical shift (both contact and pseudocontact) of the ligand nuclei in Eu(DPM)$_3$ follows the equation

$$\frac{\delta H}{H_0} = \frac{a + (b/T + c)\exp(-\Delta/kT)}{1 + 3\exp(-\Delta/kT)} \quad \cdots\cdots\cdots\cdots (2)$$

where a, b, and c are constants independent of temperature, and Δ is the separation between $^7F_0$ and $^7F_1$ states. In the region where $kT \gg \Delta$, eq.(2) can be reduced to

$$\frac{\delta H}{H_0} \rightarrow A + B/T \quad \cdots\cdots\cdots\cdots (3)$$

In the region $\Delta \gg kT > 0$, eq.(2) gives

$$\frac{\delta H}{H_0} \rightarrow \mathrm{const.} \quad \cdots\cdots\cdots\cdots (4)$$

which is temperature-independent. By comparing eq.(2) with the results given in Fig. 1, we estimated the singlet-triplet separation at about 200 cm^{-1}, which is in good agreement with the value described in reference (2).

Further study is in progress.

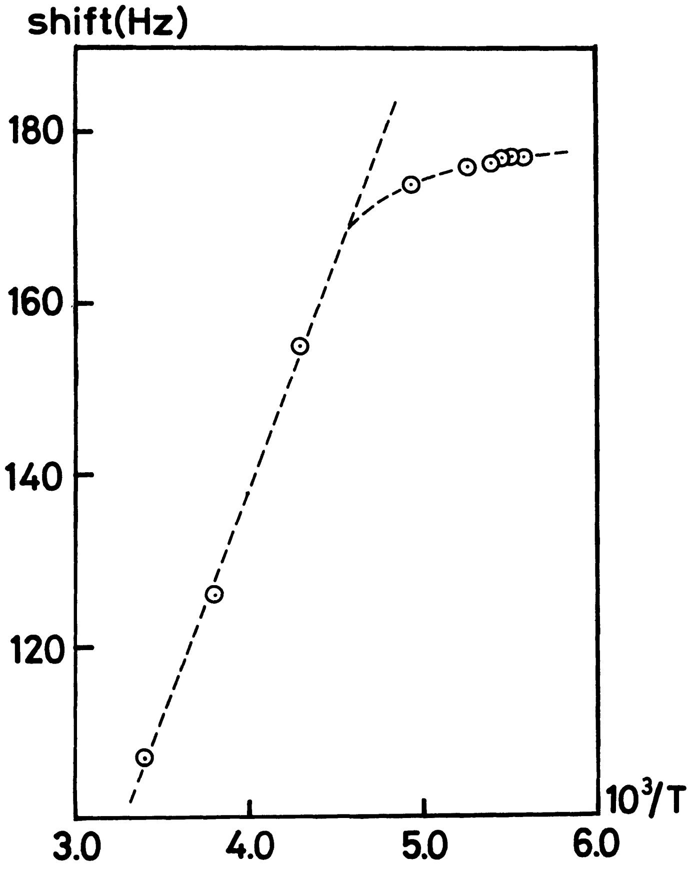
References

(1). H.M.McConnell and R.Robertson, J. Chem. Phys., 29, 1361 (1958).

(2). C.Brecher, H.Samelson, and A.Lempicki, J. Chem. Phys., 42, 1081 (1965), and references cited therein.

Fig. 1

Temperature dependence of the proton chemical shift of tert-butyl groups in tris-(dipivaloylmethanato)europium(III). Chemical shifts are plotted in Hz from TMS internal standard and the high field shifts are taken as positive.



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