Barrier to Rotation About the Eu–N Bond in the 3-Picoline Diadduct of Tris-(2,2,6,6-tetramethylheptane-3,5-dionato)europium(III), $Eu(dpm)_3(3\text{-pic})_2$

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Summary The rotational barrier about the Eu–N bond in $Eu(dpm)_3(3\text{-pic})_2$ is found to be at least 7·0 kcal/mol.

A CONTROVERSY surrounds the method of calculating the shifts produced by lanthanide shift reagents. Many authors[1,2] have assumed that these complexes have axial symmetry and thus the dipolar shifts can be calculated by

$$\Delta\nu/\nu_0 = D_0 < (3\cos^2\theta - 1)/r^3 > \qquad (1)$$

equation (1). Others[3,4] have suggested that this equation is too simple in light of recent *X*-ray crystallographic[5–7] structure determinations which have shown low symmetry for the complexes studied. Furthermore, Horrocks and Sipe[4] have measured the magnetic susceptibility anisotropies for the series of complexes $Ln(dpm)_3(4\text{-pic})_2$, and have found large non-axial anisotropies. In view of these developments the full dipolar shift equation (2) should be necessary to

$$\Delta\nu/\nu_0 = D_1 < (3\cos^2\theta - 1)/r^3 > + D_2 < \sin^2\theta\cos 2\Omega /r^3 > \qquad (2)$$

correlate lanthanide-induced shifts with molecular structure. To complicate the issue further a recent publication by Moss *et al.*,[2] has shown that even for a magnetically non-axial complex the dipolar contribution to the induced shift may, under certain definable conditions for internal rotation, still be proportional to a simple expression of the type $(3\cos^2\theta - 1)/r^3$. In order for this to occur the substrate must either be freely rotating, or the barrier to rotation must be 3-fold or higher.[2] *X*-Ray crystallographic studies of $Eu(dpm)_3(py)_2$[6] and $Ho(dpm)_3(4\text{-pic})_2$[5] show a large number of close contacts between the pyridine rings and the chelate rings, and it has been postulated that the rings are not free to rotate.[4,6] Armitage *et al.* have also reported a model for the shifts induced in aniline in which the aniline is not free to rotate.[8] We report here evidence which shows that free rotation about the Eu–picoline bond does not occur and we report the lower limit of the free energy barrier to rotation.

Upon lowering the temperature of a sample which is 0·024M in $Eu(dpm)_3$ and 0·1120M in 3-picoline in CS_2, the n.m.r. signals begin broadening and finally resolve into peaks due to free and complexed substrate at −110 ± 2·00 °C. At this point two equally intense *ortho*-signals at − 69·5 and − 87·2 are observed, while only a single methyl peak for the co-ordinated 3-pic is found. Further temperature decrease results in the appearance of two methyl resonances at −15·7 and −18·5 p.p.m. at −120 ± 2 °C. The coalescence temperature was found to be −115 ± 2·0 °C. Multiple *ortho*-peaks have also been observed for pyridine and 4-methylpyridine at low temperature, but never for the *para*-peaks. The chemical shifts were measured with respect to internal Me_4Si on a Varian HA-100 spectrometer equipped with a V6040 temperature controller and operating in HR mode during the low-temperature experiments. Temperature was measured by means of a Digitec Series 590 thermocouple mounted in the probe.

These observations can be explained by two models. The two sets of peaks could be due to restricted rotation about the Eu–N bond or due to the presence of $Eu(dpm)_3(3\text{-pic})$ and $Eu(dpm)_3(3\text{-pic})_2$. Comparison of the integrated intensity of the various co-ordinated 3-pic peaks against the dpm methine peaks gives an average 3-pic co-ordination number of 2·2 ± 0·2. Thus there is no detectable amount of $Eu(dpm)_3(3\text{-pic})$ present. The multiple peaks must then result from restricted rotation about the Eu–N bond.

Exchange between the two sites which result from restricted rotation can occur by two processes each of which has a characteristic free-energy barrier. Thus either rotation of the picoline ring about the Eu–N bond, or exchange of free and bound picoline can accomplish the exchange between the two *ortho* or two methyl sites. While the *ortho*-peaks have always been observed to be resolved as soon as the exchange of free and complexed ligand is stopped, the coalescence temperature of the methyl peaks is dependent upon both the concentration of shift reagent and substrate. This suggests that we are not at a sufficiently low temperature to eliminate the contribution of exchange with the bulk picoline. We therefore cannot determine the barrier to rotation since we have not observed a coalescence which can unambiguously be attributed to that process. However, since we have observed two nearly resolved methyl peaks separated by 280 Hz at −115 °C we can place a lower limit of at least 7 kcal/mol on the barrier to rotation.

From these results it is clear that the $Eu(dpm)_3(3\text{-pic})_2$ system does not meet the criteria of Moss *et al.*[2] The barrier to rotation is much too high for free rotation, *i.e.*, all conformers populated equally, and the observation of two methyl peaks shows that it is a 2-fold barrier. It is not clear whether this result can be extended to other substrates co-ordinated to shift reagents. However, it is important to note that 3-picoline is not a very bulky molecule, and that the interactions which produce the barrier are largely with the chelate rings and not the t-butyl groups.[6] Thus we would expect similar barriers in other complexes, and in general we expect that the steric meshing of the shift reagent and the substrate will be important.

Acknowledgement is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this research.

(*Received*, 30*th May* 1973; *Com.* 765.)

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[1] W. DeW. Horrocks, jun., and J. P. Sipe, tert., *J. Amer. Chem. Soc.*, 1971, **93**, 6800; O. A. Gansow, M. R. Willcott, and R. E. Lenkinski, *ibid.*, p. 4296; B. L. Shapiro, J. R. Hlubucek, G. R. Sullivan, and L. F. Johnson, *ibid.*, p. 3282; J. Reuben and J. S. Leigh, jun., *ibid.*, 1972, **94**, 2788.

[2] J. M. Briggs, G. P. Moss, E. W. Randall, and K. D. Sales, *J.C.S. Chem. Comm.*, 1972, 1180.

[3] R. E. Cramer and R. Dubois, *J. Amer. Chem. Soc.*, 1973, **95**, 3801.

[4] W. DeW. Horrocks, jun., and J. P. Sipe, tert., *Science*, 1972, **177**, 994.

[5] W. DeW. Horrocks, jun., J. P. Sipe, tert., and J. R. Luber, *J. Amer. Chem. Soc.*, 1971, **93**, 5258.

[6] R. E. Cramer and K. Seff, *Acta Cryst.*, 1972, **B28**, 3281.

[7] S. J. S. Wasson, D. E. Sands, and W. F. Wagner, *Inorg. Chem.*, 1973, **12**, 187; J. J. Uebel and R. M. Wing, *J. Amer. Chem. Soc.*, 1972, **94**, 8910.

[8] I. Armitage, L. D. Hall, A. G. Marshall, and L. G. Werbelow, *J. Amer. Chem. Soc.*, 1973, **95**, 1437.