# Evidence for Octa-co-ordination in Alcohol–Lanthanide-shift-reagent Complexes and its Implications in the Search for the Geometric Factor Governing Observed Shifts

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*Summary* The c.d. spectral changes induced in the europium $^5F_0 \rightarrow {}^5D_1$ band (524 nm) of the shift reagent, Eu(fod)$_3$, on complexing optically active alcohols indicate that the major species present at standard n.m.r. concentrations and ratios is octa-co-ordinated, Eu(fod)$_3$(ROH)$_2$.

The use of lanthanide-induced shift (LIS) reagents has now become routine; however there is still a controversy concerning the 'geometric factor' governing observed shifts,[1] with $k(3\cos^2\chi - 1)r^{-3}$ and $kr^{-n}$ ($n = 2$ or 3) being advocated. For axially symmetric complexes the formula $(3\cos^2\chi - 1) \times c/r^3$ should give the shift of a given proton by a lanthanide-shift reagent. For complexes of low symmetry or if thermal equilibria average the structures over a number of values of $r$ and $\chi$ a more empirical approach may be valuable. We therefore plot shift against $1/r^n$ (see Figure 1). A satisfactory fit ($R = 0{\cdot}056$, $n = 2{\cdot}4$) is obtained using as the origin a point 1·95 Å from the carbon atom bearing the hydroxy-group.† LIS data for an additional set of twenty polycyclic alcohols yield acceptable correlations ($R = 0{\cdot}04$—$0{\cdot}11$) with no adjustment of the parameters. The agreement factor, $R = [\Sigma(\mathrm{LIS_{obs}} - \mathrm{LIS_{graph}})^2/\Sigma(\mathrm{LIS_{obs}})^2]^{\frac{1}{2}}$, employed is that suggested by Willcott and his co-workers[2] in order to facilitate a comparison with their results ($R = 0{\cdot}032$—$0{\cdot}092$, 10 compounds), obtained by a computer fit to the $(3\cos^2\chi - 1)r^{-3}$ structure factor using three adjustable parameters. Their elegant approach would be expected to yield significantly better $R$-values if the angular dependence model were correct.

The $(3\cos^2\chi - 1)r^{-3}$ geometric factor could be rejected on theoretical grounds as well, if the now established square antiprism structures of Ho(dpm)$_3$(4-pic)$_2$[3] and Eu(dpm)$_3$(py)$_2$[4] hold for Eu(fod)$_3$(ROH)$_2$ in solution since octa-co-ordinate complexes‡ do not possess axial symmetry.[5,6] There are, however, conflicting reports concerning the solution stoicheiometry of complexes produced in the typical n.m.r. experiment. Armitage *et al.*[7] and Kelsey[8] report, for Eu(dpm)$_3$ and Eu(fod)$_3$ respectively, that binding constants ($K_B$[7]) can be calculated from the linear plots of $1/\Delta\delta$ *vs.* total added donor ($S_T$) at constant shift reagent concentration ($L_T$) in the range $S_T >> L_T$. Linear plots are expected for 1 : 1 complexing; however the apparent linearity does not establish 1 : 1 complexing since a similar derivation, based on 2 : 1 complexing, yields an equation which is linear within typical experimental error in the region plotted for appropriately large binding constants ($K_B$[8]). An unrelated graphical method supporting the 1 : 1 complex has been presented by Roth, Grosse,

† Those authors using $kr^{-n}$ have generally measured from near the oxygen nucleus and the value of $n$ reported has been 1·8—2·4. Our use of this simpler method of data-structure correlation does not imply a physical model with the location of the Eu atom at unrealistically small Eu–O distances.

‡ The angular term appropriate for non-axial systems is more complicated, $\mathrm{LIS} = k_\theta\,(3\cos^2\theta - 1)\,r^{-3} + k_\Omega\,(\sin^2\theta\cos 2)\Omega\,r^{-3}$, where $\theta$ and $\Omega$ are measured from the magnetic axes of the complex, not the presumed O–Eu bond vector.[6] The full expression has been used by Cramer and Seff (paper 116, 27th Regional Meeting A.C.S., June 1972) but it requires detailed knowledge, of the exact geometry of the complex in solution.

and Rewicki.[9] However all calculations based on n.m.r. methods in which environment averaging occurs suffer from assuming that the chemical shifts of 'free' substrate in the presence of shift reagent are the same as those observed in its absence.§

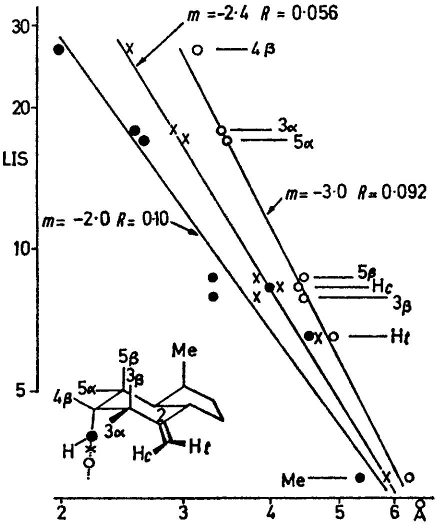

FIGURE 1. *Variation in agreement-factor* (R) *and slope* (-n) *with origin choice in a model hydrindanol. Lanthanide-induced shifts* (*LIS*) *are extrapolated to the expectation value at equimolar ratios of alcohol to* Eu(fod)$_3$ *in* CCl$_4$. *The lines represent the function* LIS = kr$^{-n}$ *fit by least squares. The three origins used to measure* r *were:* ●, *the oxygen nucleus;* ×, *a point* 1·95 Å *from* C-4 *along the* C-4–*oxygen bond axis, and* ○, *a point* 2·6 Å *from* C-4 *on the same axis. All measurements were done on new Dreiding models.*

In contrast the c.d. induced in the electronic transitions of Eu(fod)$_3$ on addition of non-chromophoric, optically active, substrates[11] offers a direct measure of the concentration of the resulting complexes. The addition of (−)-menthol to Eu(fod)$_3$ in CCl$_4$ produces c.d. activity at a number of transitions associated with europium, the negative band at 524 nm ($\Gamma$ 3 nm) being most useful owing to its relatively high $\Delta\epsilon/\epsilon$-ratio.[12] Figure 2 shows the development of this band on addition of (−)-menthol and subsequent quenching by the addition of achiral donors. It is inconsistent with a major contribution by hepta-co-ordinate species once substrate is in excess. In particular: (i) the curvature from $\Sigma S_{\mathrm{T}}/L_{\mathrm{T}}$ 0·8—2·5 is that predicted from the equilibrium expression for the 2:1 complex; (ii) the percentage diminution obtained with equal molar ratios of different achiral donors reflects their known relative binding to Eu(fod)$_3$; and (iii) the addition of ethanol initiated at $\Sigma S_{\mathrm{T}}/L_{\mathrm{T}} = 0{\cdot}85$ is equivalent to a titration of co-ordination sites with no diminution of $\psi_{\mathrm{obs}}$ until a total of two equivalents of alcohols are present.¶ Clearly there can be no significant amounts of the 1:1 complex in the typical n.m.r. shift experiment where $\Sigma S_{\mathrm{T}}/L_{\mathrm{T}} > 2$. We did, however, find some deviation from predicted behaviour assuming only octa-co-ordination when $\Sigma S_{\mathrm{T}}/L_{\mathrm{T}} < 0{\cdot}75$. The excessive curvature in this region is likely the result of contribution of the seven-co-ordinate species.

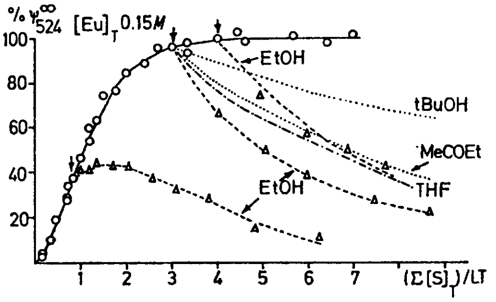

FIGURE 2. *C.d. data for nine runs in which* (−) *menthol was added to* Eu(fod)$_3$/CCl$_4$ *in portions* (—○—○—). *Some of these runs were quenched by the addition of ethanol* (--△--△--) *or other achiral ligands. All data were measured at* 524 nm *and are expressed as* % *of* $\Psi_{524}$ *observed on addition of excess*(−)-*menthol.*

The induction of c.d. activity in the *ca.* 524 nm band of Eu(fod)$_3$ has been observed with the majority of those secondary and tertiary alcohols examined (16). Some of these, particularly tertiary alcohols, give clear evidence of 1:1 complexes showing different c.d. properties; however, in all cases quenching studies demonstrate the predominance of octa-co-ordinate species when $\Sigma S_{\mathrm{T}}/L_{\mathrm{T}} > 2$. The relationship between the absolute configuration of the hydroxy-bearing carbon and the sign of $\Delta\epsilon_{524}$ is under investigation.

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§ The only study for which this is not true has just appeared. Evans and Wyatt have succeeded in freezing-out exchange in the system Eu([$^2$H$_9$]-fod)$_3$ + Me$_2$SO and demonstrated that the resulting complex is octa-co-ordinate.[10]

¶ If the hepta-co-ordinate species of 1:1 stoicheiometry predominated in the entire range $\Sigma S_{\mathrm{T}}/L_{\mathrm{T}} = 0{\cdot}8$—$3{\cdot}0$, as implied in the work of ref. 7—9, then the changes in $\psi_{\mathrm{obs}}$ on quenching should be given by $\psi_{\mathrm{obs}} = \psi_{\mathrm{obs}}(\mathrm{initial})([\mathrm{menthol}]K^{7}_{\mathrm{EtOH}}/[\mathrm{EtOH}]K^{7}_{\mathrm{menthol}})$ throughout the entire ratio range.

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[5] W. DeW. Horrocks, jun., and J. P. Sipe, tert., *J. Amer. Chem. Soc.*, 1971, **93**, 6800; and references therein.

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[8] D. R. Kelsey, *J. Amer. Chem. Soc.*, 1972, **94**, 1764.

[9] K. Roth, M. Grosse, and D. Rewicki, *Tetrahedron Letters*, 1972, 435.

[10] D. F. Evans and M. Wyatt, *J.C.S. Chem. Comm.*, 1972, 312.

[11] Nakanishi has reported strong c.d. effects for 1:1 mixtures of Pr(dpm)$_3$ and vic-glycol in the u.v. region; however, the time-dependent nature of $\Delta\epsilon$ suggests the breaking of the dionato-chelate rings is required to attain the complexing geometry in which the *vic*-hydroxy-groups occupy adjacent co-ordination sites, see K. Nakanishi and J. Dillon, *J. Amer. Chem. Soc.*, 1971, **93**, 4058. Monohydroxylic substances also give c.d. curves in these regions (*ca.* 300 nm for Eu); however, the $\Delta\epsilon/\epsilon$-ratios are too small to be usable for quantitative studies.

[12] The 524 nm band is tentatively assigned to the $^5F_0 \rightarrow {}^5D_1$ transition from the work of L. I. Katzin, *Inorg. Chem.*, 1969, **3**, 1649, and references cited therein.