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Chiral Lanthanide Nuclear Magnetic Resonance Shift Reagents

By Robert G. Denning, Francis J. C. Rossotti,* and Philip J. Sellars
(*Inorganic Chemistry Laboratory, University of Oxford, Oxford* OX1 3QR)

Summary The chiral tris-[3-t-butylhydroxymethylene-(+)-camphorato]lanthanide(III) reagents LnT_3 are dimeric in dry CCl_4 solution, for Ln = Pr, Nd, and Sm, at concentrations commonly used in n.m.r. shift work, unlike the later members of the series and unlike the more widely used dipivaloylmethanato (dpm) and hexafluoro-octanedionato (fod) shift reagents.

Although the chiral lanthanide shift reagent 'LnT_3' have been used to distinguish diastereoisomeric substrates,[1] neither the structures in solution of the reagents themselves, nor those of their adducts have been established. Our interest in these reagents stems from the need to provide a satisfactory model for the natural optical activity of these complexes. It therefore becomes important to know the structures of the reagents and their adducts. The related dpm and fod reagents appear to be monomeric in many organic solvents,[2–4] although monomers,[5] dimers,[6] and even basic oligomers[7] have been found in the solid state. Reagent:substrate adducts (1:1, 1:2, or 2:2) with oxygen and nitrogen donors have been found for the dpm and the fod reagents, both in solution[4,8,9] and in the solid state.[10,12] In the inert related complexes of Cr^{III}, Co^{III}, and Ru^{III} [13] with the (+)-3-acetylcamphorate anion, four isomers, *cis*-Λ, *cis*-Δ, *trans*-Λ, and *trans*-Δ have been isolated, and equilibrium studies show that the Λ-isomers predominate on account of the ligand stereospecificity. The c.d. spectrum of mixtures of the four CoT_3 isomers shows that these complexes also demonstrate the same stereospecificity in favour of the Λ-isomers. We now observe that the analogous LnT_3 complexes undergo rapid ligand exchange on the n.m.r. time scale as indicated by the mean ligand proton resonances in mixtures of ErT_3 and PrT_3. It follows that in the labile equilibrium between monomeric LnT_3 isomers, those with the Λ-configuration will predominate.

Table. *Relative molecular masses in* CCl_4 *determined ebulliometrically*

Metal	Found/calculated for monomer
Eu	1·00 ± 0·05
Gd	1·00 ± 0·05
Tb	0·99 ± 0·05
Er	1·04 ± 0·05
Ho	1·00 ± 0·05
Tm	1·01 ± 0·05

All the LnT_3 complexes (except Ln = Ce and Pm) have now been prepared, using a modification of Whitesides and Lewis's method[14] and the number-average degrees of association determined ebulliometrically[15] in CCl_4 at 76·5 °C. The Eu, Gd, Tb, Er, Ho, and Tm chelates are all monomeric over the range 0—0·02M (Table), but for Pr, Nd, and Sm, the degree of oligomerisation rises sharply from 1 to 2 as the concentration increases to *ca.* 0·02M. For the Nd chelate the ratio of the molecular mass found to that calculated for the monomer is 1·14 at 0·0033M, but 1·71 at 0·0165M, these values being typical of those obtained for the Pr and Sm chelates. For all the compounds, degrees of association appear to be insensitive to a change in the dielectric constant of the solvent. Thus for approximately 0·01M-Pr solutions, the found:calculated molecular mass is 1·48 in CCl_4, CH_2Cl_2, and cyclohexane. No detectable oligomerisation is found for the complexes listed in the Table when the relative molecular mass is determined at lower temperatures (cryometry in benzene at 5·5 °C). Moreover, all the complexes are monomeric in the vapour phase at low pressures (mass spectrometry).

Changes in the degree of association are also apparent in the ^1H n.m.r. spectra. Assignments of 270 MHz spectra were made by integration and comparison with the published spectra for camphor and 3-benzoylcamphor. Shifts of several proton resonances of predominantly monomeric solutions (*ca.* 3×10^{-3}M in C_6D_6) of all the lanthanide series follow Bleaney's pseudo-contact shift equation.[16] At the higher concentrations in which dimers predominate for the earlier members, the resonances are at higher field. Thus the methyl group signals for NdT_3 at τ 9·03 and 9·28 shift to τ 10·35 and 10·70 for Nd_2T_6, and the dimer has a resonance at τ 13·85 which is absent in NdT_3, possibly arising from methyl groups on bridging ligands. However, the position of the t-butyl signal shifts only from τ 8·94 to 8·91 over the same concentration range, presumably indicative of only a minor change in the pseudo-contact shift angular-distance function.[17]

Adduct formation in CCl_4 solution has been studied by plotting the variation of the b.p. against added substrate concentration, and locating the sharp point of inflection corresponding to the complete formation of the adduct. In this way, thermodynamically stable 1:1 adducts of GdT_3 and HoT_3 with butan-1-ol and EuT_3 and HoT_3 with (+)-α-methylbenzylamine have been detected.

Sharp transitions at longer wavelengths than the u.v. cut-off (*ca.* 360 nm, $n \rightarrow \pi^*$ in $>C=O$) in both absorption and also in c.d. have been observed for ErT_3, HoT_3, and TmT_3. Bands hypersensitive to adduct formation were found: at 518·8, 521·0, 522·7 ($^4I_{15/2} \rightarrow {}^2H_{11/2}$), and 382·7 nm ($^4I_{15/2} \rightarrow {}^4G_{11/2}$) for ErT_3; and at 449·5—461·0 ($^5I_8 \rightarrow {}^5G_6$) and 361·5 nm ($^5I_8 \rightarrow {}^3H_6$, $^3H_5$, $^5G_3$) for HoT_3. However, a much larger change is found in the natural c.d. of these complexes. The addition of either chiral or achiral amines and alcohols results in the virtual disappearance of the c.d. of all bands, presumably owing to a total change from the chiral trigonal site symmetry of the LnT_3 chelate on adduct formation.

For the remaining lanthanide complexes with visible absorption spectra, the *f–f* transitions below *ca.* 500 nm are obscured by a broad band of approximately equal intensity, stretching into the diketonate absorption region and, moreover, with intense negative c.d. As this broad band is observable only for those lanthanides with either accessible higher (Pr, Nd, Tb) or lower (Eu, Sm) formal oxidation states, it is probably a charge-transfer band.[18]

Single crystal *X*-ray and powder diffraction studies are in progress.

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