The Stoicheiometry and Stability Constants of Adducts of Lanthanide Shift Reagents

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Application of Job's method to the visible spectra of adducts of tris(2,2,6,6-tetramethylheptane-3,5-dionato)-holmium in carbon tetrachloride shows that 1 : 1 adducts are formed with stability constants which vary considerably with the nature of the added ligand.

THE action of lanthanide shift reagents depends on the reversible formation of adducts between a lanthanide complex A, typically a β-diketonate, and a Lewis base B, typically an alcohol, ketone, or amine. The values of the stability constants K_1 and K_2 will determine the composition of any specified mixture of A with B:

$$[AB] = K_1[A][B] \qquad (1)$$

$$[AB_2] = K_2[AB][B] = K_1K_2[A][B]^2 \qquad (2)$$

where [A], [B], [AB], $[AB_2]$ are equilibrium concentrations or strictly, activities.

Analysis of the variation of induced n.m.r. shift with initial concentration of A or B has been used to determine whether equation (1) alone is sufficient to fit the data, or whether equation (2) is also necessary, and to obtain values of K_1 and K_2.[1,2] These data have been the subject of controversy [1] and it should particularly be noted that rigorous exclusion of water [3] is necessary.

We now report an investigation of adduct formation using a method independent of n.m.r., namely Job's method of continuous variations applied to the visible spectra of $[Ho(tmhd)_3]$ † : CCl_4 : B systems, where B = borneol, cedrol, triphenylphosphine oxide, 2-methoxynaphthalene, or camphor. The $^5I_8 \longrightarrow {}^5G_6$ *f–f* absorption band system of Ho^{3+} near 22 000 cm^{-1} is sensitive to ligand co-ordination and is thus suitable for use in this procedure.[4] The ions Pr^{3+}, Eu^{3+}, and Yb^{3+}, more commonly used in shift reagents, have less suitable spectra, as does Nd^{3+}, whose aqueous complexes have been studied in a similar manner.[5] However, the ionic radius of Ho^{3+} (0.89 Å) is sufficiently close to those of Eu^{3+} (0.95 Å) and Yb^{3+} (0.86 Å) for adduct-forming properties of $[Ho(tmhd)_3]$ to be expected to be comparable with those of $[Eu(tmhd)_3]$ or $[Yb(tmhd)_3]$.

EXPERIMENTAL

Samples of $[Ho(tmhd)_3]$, borneol, cedrol, 2-methoxynaphthalene, camphor, and triphenylphosphine oxide were purified by sublimation and transferred to a nitrogen-filled glove-box. Solutions of all six reagents in carbon tetrachloride dried over calcium hydride were then prepared at 0.05 ± 0.0001M-concentration without exposure to air at any stage. Appropriate proportions of $[Ho(tmhd)_3]$ and ligand solution were next mixed in 1-cm u.v. cells using micro-burettes. The filled cells were removed from the glove-box in an airtight container and their absorbances determined within 30 min using a Perkin-Elmer 402 spectrophotometer (photometric accuracy ±1%). The stoppers of the cells had previously been ground to a close fit and under these conditions no detectable water is absorbed. However, on leaving a dry solution of $[Ho(tmhd)_3]$ tightly Polythene-capped on the bench for 1 week, the resulting spectrum was characteristic of a 1 : 1 adduct, presumably a monohydrate.

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† tmhd = $Bu^tCO{\cdot}CH{\cdot}COBu^t$.

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RESULTS AND DISCUSSION

If the only species present are [Ho(tmhd)$_3$], [Ho(tmhd)$_3$B], and B, then since none of the added ligands B were found to absorb near 22 000 cm^{-1} it follows that:

$$\Delta A = (\varepsilon_{AB} - \varepsilon_{A})\{(1 + K_1c) - \{1 + 2K_1c + K_1^2c^2[1 - 4f(1 - f)]\}^{\frac{1}{2}}\}/2K_1 \quad (3)$$

where ε_{AB}, ε_{A} are the molar extinction coefficients of AB A; *c* is the total molarity; *f* is the mol fraction of B; and ΔA is $A - (1 - f)A_0$, A being the observed absorbance and A_0 the absorbance of 1 cm of 0.05M-[Ho(tmhd)$_3$]. Hence a plot of ΔA *versus* f is symmetrical about $f = \frac{1}{2}$, where it maximises, if K_2 is negligible. Further, the value of K_1 can be obtained from the curvature of the plot even if ε_{AB} is, as in the present case, initially unknown.

The experimental values of ΔA were matched by computer with curves obeying equation (3), varying ε_{AB} and K_1 until a least-squares fit was obtained (Figure 1).

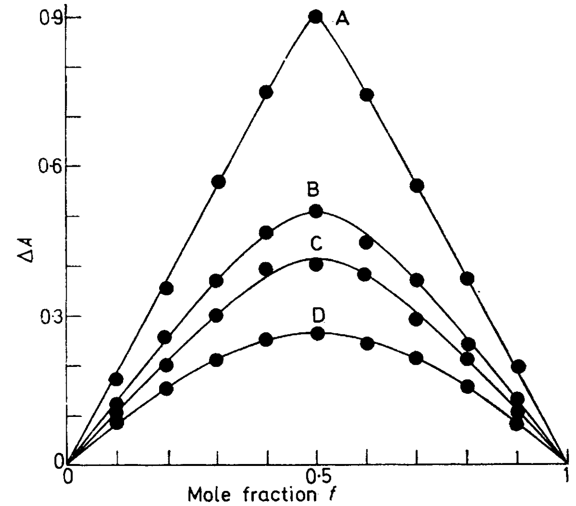

FIGURE 1 Plots of increase in absorbance due to complexation (ΔA) against mol fraction of added ligand (f). Total concentration 0.05M. In CCl$_4$ at 22 °C. Values of ε_{AB}, the molar extinction coefficients at 22 270 cm^{-1} of the adducts, and of log K_1 are: A, triphenylphosphine oxide, $\varepsilon = 66.0$, log $K_1 = 4.48 \pm 0.3$; B, borneol, $\varepsilon = 55.8$, log $K_1 = 2.66 \pm 0.1$; C, cedrol, $\varepsilon = 50.8$, log $K_1 = 2.66 \pm 0.1$; D, camphor, $\varepsilon = 52.7$, log $K_1 = 1.75 \pm 0.1$

Resulting values of ε_{AB} and log K_1 are given in Figure 1. The 2-methoxynaphthalene gave no evidence of any association, ΔA being zero for all f values, within experimental error.

The general trend of the values of K_1 is in accord with qualitative solid-state data, *e.g.* triphenylphosphine oxide is known to form stable, isolable, complexes with lanthanide cations,[6] while isolable ether adducts are restricted to cyclic polyethers.[7] A value of $K_1 \simeq 450$ as found for borneol or cedrol would mean in practical terms of shift-reagent use that a solution 0.01M in shift reagent and 0.1M in substrate would have 98% of the shift reagent in a complexed state and would lead to almost linear plots of induced n.m.r. shift against concentration of added reagent at these concentration levels, but in the corresponding situation for camphor, only 84% of the shift reagent would be complexed.

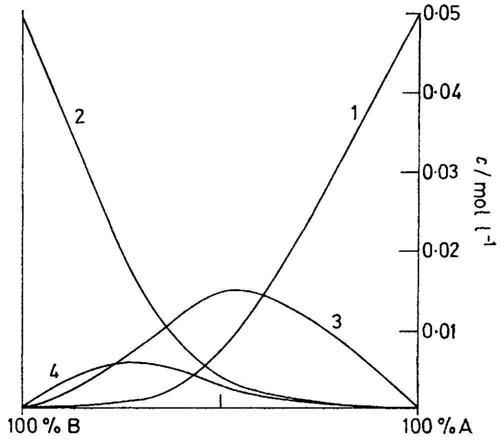

FIGURE 2 Concentrations of complex A (curve 1), base B (curve 2), adduct AB (3), and adduct AB$_2$ (4) which result from mixtures of A with B of total molarity 0.05, if $K_1 = 500$ and $K_2 = 50$

The question arises as to how large a value of K_2 would remain undetected by our procedure. Figure 2 shows concentrations of all four species A, B, AB, and AB$_2$ for the arbitrary values $K_1 = 500$, $K_2 = 50$ when $c = 0.05$M. It can be seen that the clearly evident asymmetry in the curve of [AB] would be masked if ε_{AB_2} were coincidentally nearly equal to ε_{AB}, because ΔA measures [AB]($\varepsilon_{AB} - \varepsilon_{A}$) + [AB$_2$]($\varepsilon_{AB_2} - \varepsilon_{A}$). The plots (Figure 1) at 22 280 cm^{-1} (chosen as giving greatest values of ΔA) show no evidence of asymmetry. A solution of [Ho(tmhd)$_3$] in pyridine ($\varepsilon = 56$) which undoubtedly contains the 2 : 1 adduct[8] has a new maximum at 22 170

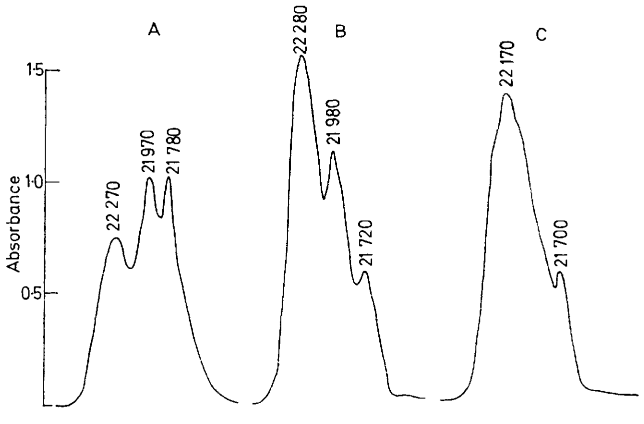

FIGURE 3 Absorbance of 0.025M-solutions (1-cm cells, wavelengths in nm): A, [Ho(tmhd)$_3$] in CCl$_4$; B, [Ho(tmhd)$_3$(OPPh$_3$)] in CCl$_4$; C, [Ho(tmhd)$_3$] in pyridine

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cm^{-1}. Plots at 22 170 cm^{-1} similarly show no evidence of the presence of 2 : 1 adducts in our systems. Assuming $\varepsilon_{AB_2} \simeq 56$ at 22 170 cm^{-1}, such evidence would show itself unless K_2 were smaller than *ca.* 10. As a further indication, Figure 3 shows the solution spectra of (a) [Ho(tmhd)$_3$], (b) [Ho(tmhd)$_3$(OPPh$_3$)], and (c) [Ho(tmhd)$_3$(py)$_2$]. All our systems appear identical with (b) as f approaches unity, while no component of spectral type (c) (which closely resembles the spectrum of [Ho(tmhd)$_3$] in CCl$_4$ saturated with water) appears to be present. Furthermore, this is also true of a more concentrated solution 0.025M in [Ho(tmhd)$_3$] and 0.5M in borneol. All these results lead to the conclusion that K_2 is probably less than 0.3.

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