Nature of the Species Present in Solutions of Lanthanide Nuclear Magnetic Resonance Shift Reagents

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Summary It is shown by electronic spectra, and molecular weight and n.m.r. studies that the lanthanide shift reagents Ln(dpm)$_3$ are essentially monomeric in dry CCl$_4$ solution and form 1:1 adducts with typical substrates.

There is considerable uncertainty regarding the nature of the species present in solutions of lanthanide shift reagents and in solutions where these compounds are mixed with organic substrates. Thus the *X*-ray crystal structures of [Er(dpm)$_3$][1] and [Pr$_2$(dpm)$_6$][2] (dpm = Me$_3$CCOCHCOCMe$_3$) are known, as is that of a hydrated hydrogen-bonded dimer [Dy$_2$(dpm)$_6$(H$_2$O)$_2$][3] whose possible presence in imperfectly dried solutions must be considered. In CCl$_4$ solution, n.m.r. data have been interpreted[4,5] as showing the presence of a majority[4] or minority[5] of the dimeric species [Ln$_2$(dpm)$_6$] (Ln = Pr, Eu) in addition to the monomer. Solution molecular weight measurements[6,7] indicate monomeric species.

In the presence of an organic substrate, there is evidence both for 1:1 and for 1:2 adducts. Thus the *X*-ray crystal structure of a 1:2 adduct [Eu(dpm)$_3$(py)$_2$] has been reported,[8] and low-temperature n.m.r. data strongly indicate a 1:2 adduct between Eu(fod)$_3$ and Me$_2$SO[9] (fod = C$_3$F$_7$-COCHCOCMe$_3$) in CD$_2$Cl$_2$ solution. Measurements of circular dichroism also indicate a 1:2 adduct in the system Eu(fod)$_3$–CCl$_4$–menthol.[10] However, n.m.r. data indicate a predominating 1:1 adduct in the systems Eu(dpm)$_3$–CCl$_4$–2-methyladamantan-2-ol,[4] Eu(dpm)$_3$–CDCl$_3$–n-propylamine or neopentanol,[11] and Eu(dpm)$_3$–CDCl$_3$–pyridine.[12]

The n.m.r. spectra of *ca.* 0·05M-Ln(dpm)$_3$ (Ln = Pr, Eu) have been obtained at 60 MHz in CCl$_4$ solution at 34 °C. To exclude all traces of water, the n.m.r. tubes were filled by means of a vacuum line system, using CCl$_4$ dried with CaH$_2$ and freshly sublimed M(dpm)$_3$, and then sealed off. Under these conditions we obtain a spectrum simpler than those previously reported.[4,5] There is now only one higher-field peak (Pr, τ 9·87; Eu τ 9·53) and one much less intense lower-field peak (Pr, τ 0·74; Eu, broad, τ *ca.* 6·8). In the case of Pr(dpm)$_3$, evidence that the low-field peak arises from the C-4 proton is provided by integration and by deuteriation at C-4, which causes its disappearance. Spectra obtained using less, but even so very considerable, care to exclude moisture show an additional peak at τ 11·97 (Pr) or 6·93 (Eu) which is typically about 10% of the main peak intensity. In such a Pr(dpm)$_3$ solution exposed to ordinary air (but dried air had no effect) in a capped n.m.r. tube for 24 h, this peak became 45% of the main peak intensity. The additional peaks also appeared on unsealing tubes containing very dry solution (where these peaks were absent) and exposing the solutions to air.

Combined with the following molecular weight evidence, these results show that the monomer predominates in dry CCl_4 *solution*. The peak at τ 11·97 (Pr) or 6·93 (Eu) must be due to the methyl groups of a hydrated species, and not to the bridging ligands in a dimer as previously suggested.[4]

We have obtained nearly monomeric values for the molecular weights of $Ln(dpm)_3$ (Ln = La, Pr, Eu, Lu) in CCl_4 solutions in the range 0·01—0·05 M at 37 °C using a Mechrolab Osmometer under anhydrous conditions. This confirms previous results.[6,7] Our values are 12—17% lower than theoretical for monomers, probably because the very small volumes of solutions used in this method are difficult to keep entirely dry. Without precautions to exclude moisture, values are much lower.

Ebullioscopic mol. wt. determinations in CCl_4 with exclusion of moisture gave monomeric values for $Eu(dpm)_3$. Furthermore, upon subsequent additions of borneol or β-naphthoquinoline to the boiling solution, the consequent temperature rise was delayed and reverse extrapolation of the eventual linear rise showed that *ca.* 0·85 and 0·82 molar proportions, respectively, relative to the $Eu(dpm)_3$ present, remained inactive in this respect, presumably because a 1 : 1 adduct had been formed.

To obtain more definite evidence concerning the stoicheiometry of the $Ln(dpm)_3$–substrate adduct in solution, we have used Job's method to investigate equilibria in CCl_4 by a study of the effect of added substrate on the intensity of the *f–f* absorption bands. The 17,000 cm^{-1} Nd^{3+} ($^4I_{9/2} \rightarrow {}^4G_{5/2}$), 22,100 cm^{-1} Ho^{3+} ($^5I_8 \rightarrow {}^5G_6$) and 26,300 cm^{-1} Er^{3+} ($^4I_{15/12} \rightarrow {}^4G_{11/12}$) transitions were used, their extinction coefficient being approximately doubled by addition of *e.g.* pyridine or borneol. Series of CCl_4 solutions of the mixtures (a) $Er(dpm)_3$–pyridine (b) $Ho(dpm)_3$–borneol, and (c) $Ho(dpm)_3$–neopentanol of constant total molarity 0·06—0·07 (*i.e.* about the same as commonly used in shift reagent n.m.r. measurements) were examined. The maxima of the $\Delta A/f$ plots [ΔA = increase in absorbance over that caused by $M(dpm)_3$; f = mole fraction of added ligand] were well-defined and occurred close to $f = 0{\cdot}5$ showing that the principal adduct species present has a 1 : 1 stoicheiometry. The absorption spectra of Eu and Pr are less suitable for this method, but a 1 : 1 adduct was similarly demonstrated in the $Nd(dpm)_3$–pyridine system. The addition of pyridine in very high concentration to $Ho(dpm)_3$ in CCl_4 produced further changes in the absorption spectrum, presumably characteristic of the 1 : 2 adduct which is known to be obtained from strong pyridine solutions. Exposure of $Ho(dpm)_3$ in CCl_4 to moist air produced a spectrum similar to that given by addition of 1 mole of pyridine. These results in no way invalidate evidence[9,10] for 1 : 2 adducts of $Ln(fod)_3$.

We thank the S.R.C. for maintenance grants to J.S.G. and M.L.S.

(*Received, 7th December* 1972; *Com.* 2041.)

[1] J. P. R. de Villiers and J. C. A. Boeyens, *Acta Cryst.*, 1971, **B27**, 2335.
[2] C. S. Erasmus and J. C. A. Boeyens, *Acta Cryst.*, 1970, **B26**, 1843.
[3] C. S. Erasmus and J. C. A. Boeyens, *J. Cryst. Mol. Struct.*, 1971, **1**, 83.
[4] J. K. M. Sanders, S. W. Hanson, and D. H. Williams, *J. Amer. Chem. Soc.*, 1972, **94**, 5325.
[5] M. K. Archer, D. S. Fell, and R. W. Jotham, *Inorg. Nuclear Chem. Letters*, 1971, **7**, 1135.
[6] V. A. Mode and G. S. Smith, *J. Inorg. Nuclear Chem.*, 1969, **31**, 1857.
[7] J. E. Sicre, J. T. Dubois, K. J. Eisentraut, and R. E. Sievers, *J. Amer. Chem. Soc.*, 1969, **91**, 3476.
[8] R. E. Cramer and K. Seff, *J.C.S. Chem. Comm.*, 1972, 400.
[9] D. F. Evans and M. Wyatt, *J.C.S. Chem. Comm.*, 1972, 312.
[10] N. H. Andersen, B. J. Bottino, and S. E. Smith, *J.C.S. Chem. Comm.*, 1972, 1193.
[11] I. Armitage, G. Dunsmore, L. D. Hall, and A. G. Marshall, *Chem. and Ind.*, 1972, 79.
[12] H. Huber and J. Seelig, *Helv. Chim. Acta*, 1972, **55**, 135.