Emission-titration Studies of the Formation of Adducts of Tris(6,6,7,7,8,8,8-heptafluoro-2,2-dimethyloctane-3,5-dionato)europium(III) with Substrates in Solution

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Emission-titration spectroscopy has been used to study the formation of adducts of the title complex, [Eu(fmod)$_3$], with substrates in CCl$_4$ solution. The emission intensity of the $^5D_0 \longrightarrow {}^7F_2$ Eu^{3+} transition in [Eu(fmod)$_3$] is very sensitive to interactions between the complex and substrate molecules containing a nucleophilic functional group. Adduct formation between the complex system and a substrate molecule is generally accompanied by a sharp increase in complex emission intensity. Stepwise addition (titration) of substrate to a [Eu(fmod)$_3$]–CCl$_4$ solution leads to an emission-titration curve (complex emission intensity plotted as a function of the amount of substrate added) whose shape and limiting values are diagnostic of adduct structure and adduct-formation mechanisms.

LANTHANOID β-diketonate complexes have found wide application as paramagnetic shift reagents in n.m.r. spectroscopy.[1-3] Lanthanide shift reagents (l.s.r.s) are now used routinely to enhance spectral resolution and clarification of n.m.r. spectra obtained for functional organic substrate molecules. Additionally, some success has been achieved in using observed lanthanoid-induced shifts (l.i.s.s) to deduce quantitative or semi-quantitative structural information about substrate molecules in solution. This latter application of l.s.r. studies is of great interest and importance. However, crucial to its eventual widespread acceptance and utility is an understanding or knowledge of: (*a*) l.s.r. structure in solution in a variety of solvent systems (neat and mixed); (*b*) the stoicheiometric and stereochemical characteristics of l.s.r.–substrate binding as a function of various solution conditions (such as solvent, concentration ratios, temperature, *etc.*); and (*c*) the detailed nature of the magnetic interactions between the paramagnetic l.s.r. and diamagnetic substrate molecules.

The stoicheiometric and formation properties of l.s.r.–

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[1] J. Reuben, *Progr. N.M.R. Spectroscopy*, 1973, **9**, 1.

[2] A. F. Cockerill, G. L. O. Davies, R. C. Harden, and D. M. Rackham, *Chem. Rev.*, 1973, **73**, 553.

[3] 'Nuclear Magnetic Resonance Shift Reagents,' ed. R. E. Sievers, Academic Press, New York, 1973.

substrate adducts in solution have been studied extensively and considerable information has been obtained on the equilibrium constants and co-ordination characteristics of many of these systems.[4,5] However, as pointed out by Reuben,[1] the problems associated with determining the dissociation constants and stoicheiometries of l.s.r.–substrate adducts in solution remain controversial. In most of the studies conducted to date, n.m.r. spectroscopy has been used to probe the nature of these adducts. For example, Evans and Wyatt [6] reported the first direct determination in solution of the number of coordinated substrate molecules on a l.s.r. They found that 1 mol of deuteriated tris(6,6,7,7,8,8,8-heptafluoro-2,2-dimethyloctane-3,5-dionato)europium(III), [Eu(fmod)$_3$], in CD_2Cl_2 binds 2.0 ± 0.2 mol of dimethyl sulphoxide (dmso). Reuben [1] found the same coordination number for dmso with normal (non-deuteriated) [Eu(fmod)$_3$] in CD_2Cl_2. In CCl_4, it has been shown that [Eu(fmod)$_3$] binds one molecule of t-butyl alcohol but that the 'apparent' co-ordination number for t-butylamine is 1.27,[7] indicating the existence of an equilibrium of more than one complex–substrate species. In a parallel study,[8] both [Eu(fmod)$_3$] and [Eu(tmhd)$_3$] (tmhd = 2,2,6,6-tetramethylheptane-3,5-dionate) were shown to bind one molecule of n-propylamine in $CDCl_3$ while the 'apparent' co-ordination number of neopentyl alcohol was found to be 0.94 (that is, 0.94 mol of substrate bound per mol of chelate) in the same solvent. A number of additional studies have been reported in the recent literature regarding the co-ordination numbers and dissociation constants of various l.s.r.–substrate adducts in solution.[9]

Various products of l.s.r.–substrate interactions have been isolated and analyzed in the solid state. Hinckley,[10] in the first reported use of a lanthanoid chelate system as a shift reagent, isolated the dipyridine adduct of [Eu(tmhd)$_3$]. Subsequently, a series of 1 : 1 adducts of [M(tmhd)$_3$] (M = lanthanoid) and pyridine were synthesized and isolated by Selbin *et al.*[11] 1 : 1 Adducts of [M(tmhd)$_3$] with *NN*-dimethylformamide (dmf) have also been prepared.[12,13] In the case of the chiral l.s.r. [Pr(facam)$_3$] (facam = trifluoroacetyl-D-camphorate), dmf has been found to form 2 : 3 adducts (as isolated in the solid state and determined by *X*-ray diffraction studies).[14] A 1 : 2 adduct of [Ho(tmhd)$_3$] with 4-methylpyridine has also been isolated and its structure has been determined by *X*-ray diffraction.[15]

Very recently the stoicheiometry and stability constants of adducts of [Ho(tmhd)$_3$] in CCl_4 have been studied by the application of Job's method to the visible absorption spectra of these complex–substrate systems.[16] 1 : 1 Adducts of [Ho(tmhd))$_3$] with borneol, cedrol, 2-methoxynaphthalene, camphor, and triphenylphosphine oxide were reported and the stability constants were found to vary considerably with the nature of the substrate. The authors of this study pointed out that, unfortunately, the absorption bands for the more commonly used shift reagents (Pr^{3+}, Eu^{3+}, and Yb^{3+}) are not sufficiently sensitive to the ligand environment to permit application of Job's method in the study of their complexation phenomena.

In the present work we use emission spectroscopy to study the formation of l.s.r.–substrate adducts in solution. Previous studies in our laboratory and in others have demonstrated the sensitivity of Eu^{3+} emission intensity to the detailed nature of the ligand and solvent environment.[17,18] Furthermore, total emission (t.e.) and circularly polarized emission (c.p.e.) studies on the chiral l.s.r. [Eu(facam)$_3$] in both 'neat' and 'mixed' solvents have shown emission spectroscopy to be an especially sensitive probe of both the structural characteristics of the chelate complex system and the nature of complex–substrate (solvent) interactions.[18] In the present study we report results of emission-titration measurements on [Eu(fmod)$_3$] in a number of 'mixed' CCl_4–solvent systems in which its solvent contains a potential donor molecule (that is, one which can coordinate to the complex to form a stable adduct in solution). Conclusions regarding adduct formation are then drawn from the shapes of the resulting emission-titration curves.

EXPERIMENTAL

The complex [Eu(fmod)$_3$] was purchased form Willow Brook Laboratories and was used without further purification. The emission titrations were carried out by dissolving a weighed amount of the complex in CCl_4 (2 cm^3) directly in the emission cuvette and then adding increments (0.01 cm^3) of a substrate stock solution. Complex concentrations ranged from 0.005 to 0.009 mol dm^{-3} in the experiments reported here, and the substrate stock solutions were 0.3—0.5 mol dm^{-3} in substrate. The substrate systems examined in this study were: dimethyl sulphoxide (dmso), *NN*-dimethylformamide (dmf), pyridine, methanol, ethanol, n-propanol, isopropyl alcohol, n-butanol, s-butyl alcohol, t-butyl alcohol, benzyl alcohol, and norborn-2-ene-6-methanol. All the solvents (CCl_4 and substrate) were

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[4] B. C. Mayo, *Chem. Soc. Rev.*, 1973, **2**, 53.

[5] D. H. Williams, *Pure Appl. Chem.*, 1974, **40**, 25.

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

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[9] See, for example, J. K. M. Sanders, S. W. Hanson, and D. H. Williams, *J. Amer. Chem. Soc.*, 1972, **94**, 5325; W. Wenkert, D. W. Cochran, E. W. Hagaman, R. B. Lewis, and F. M. Schell, *ibid.*, 1971, **93**, 6271; H. Huber and J. Seelig, *Helv. Chim. Acta*, 1972, **55**, 135; D. G. Buckley, G. H. Green, E. Ritchie, and W. C. Taylor, *Chem. and Ind.*, 1971, 298.

[10] C. C. Hinckley, *J. Amer. Chem. Soc.*, 1969, **91**, 5160.

[11] J. Selbin, N. Ahmad, and N. Bhacca, *Inorg. Chem.*, 1971, **10**, 1383.

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[13] V. A. Mode and D. H. Sisson, *Inorg. Nuclear Chem. Letters*, 1972, **8**, 357.

[14] J. A. Cunningham and R. E. Sievers, *J. Amer. Chem. Soc.*, 1975, **97**, 1586.

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

[16] G. A. Cotton, F. A. Hart, and G. P. Moss, *J.C.S. Dalton*, 1976, 208.

[17] H. G. Brittain and F. S. Richardson, *Inorg. Chem.*, 1976, **15**, 1507.

[18] H. G. Brittain and F. S. Richardson, *J. Amer. Chem. Soc.*, in the press.

spectroquality grade and water was rigorously excluded from all the samples.

All the emission experiments were made by use of a high-sensitivity high-resolution emission spectrophotometer constructed in this laboratory.[19] Europium(III) excitation was accomplished using the 367-nm output of a 1 000-W mercury–xenon-arc lamp, selected by a Spex ' minimate ' monochromator and appropriate filters. The spectral bandwidth of the exciting light was *ca.* 10 nm and that of the emission was 2 nm. The emission was detected ' head-on ' (180° to excitation) and the emission monochromator was a 3/4 meter single-grating Spex model 1 800 instrument. The emission-titration experiments were conducted by monitoring the intensity of the ${}^5D_0 \rightarrow {}^7F_2$ Eu^{3+} emission band at 613 nm as a function of substrate added to the [Eu(fmod)$_3$]–CCl$_4$ solution. The sample temperature was maintained at 295 K.

RESULTS AND DISCUSSION

Emission-titration curves for [Eu(fmod)$_3$]–CCl$_4$ with 12 different substrates are shown in Figures 1—4. The emission intensities (I) plotted are given in relative intensity units (absolute quantum yields were not determined). The enhancement of Eu^{3+} emission intensity on addition of substrate to [Eu(fmod)$_3$]–CCl$_4$ is diagnostic of complex–substrate interaction and the formation of complex–substrate adducts. The absorption bands of each of the substrates examined in the present study lie substantially to the blue of the excitation wavelength used (λ_{ex} 367 nm, $\Delta\lambda_{ex}$ *ca.* 10 nm) and the observed emission enhancement cannot be attributed, therefore, to substrate (donor) $\longrightarrow$ [Eu(fmod)$_3$] (acceptor) energy-transfer processes. The detailed mechanism of emission-intensity enhancement is not known but is presumed to arise either from structural modifications within the complex system (induced by adduct formation) or from the blocking of complex $\longrightarrow$ solvent (CCl$_4$) radiationless deactivation channels on the formation of complex–substrate adducts. In either case,

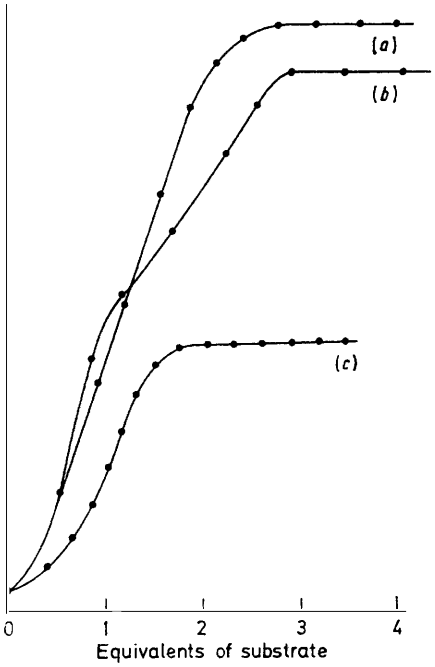

FIGURE 1 Emission-titration curves for [Eu(fmod)$_3$] with (*a*) *NN*-dimethylformamide, (*b*) dimethyl sulphoxide, and (*c*) pyridine. Complex emission intensity (at 613 nm) is plotted against equivalents of substrate added

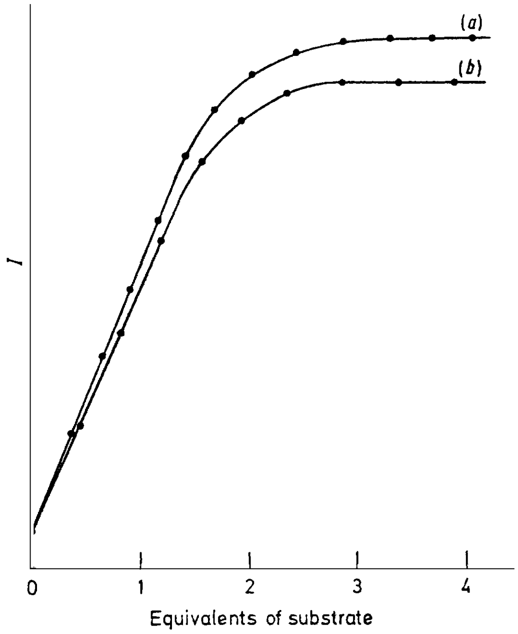

FIGURE 2 Emission-titration curves for [Eu(fmod)$_3$] with (*a*) benzyl alcohol and (*b*) norborn-2-ene-6-methanol plotted as in Figure 1

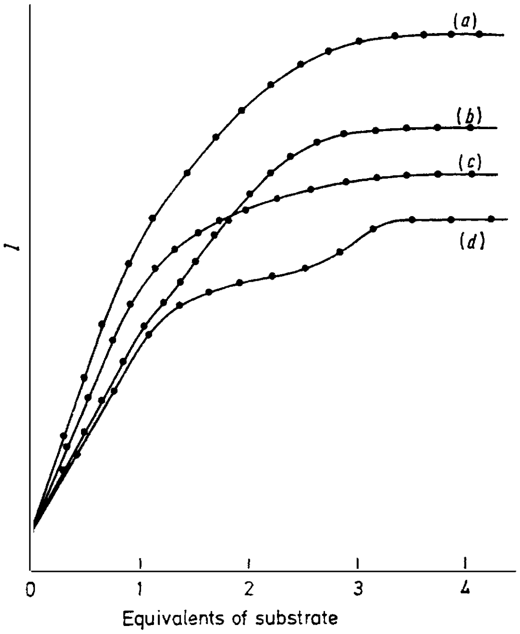

FIGURE 3 Emission-titration curves for [Eu(fmod)$_3$] with (*a*) methanol, (*b*) ethanol, (*c*) n-propanol, and (*d*) isopropyl alcohol plotted as in Figure 1

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[19] C. K. Luk and F. S. Richardson, *J. Amer. Chem. Soc.*, 1975, **97**, 6666.

the enhancement of emission intensity may be related directly to complex–substrate binding.

It is clear from the titration curves presented in Figures 1—4 that the number of mols of substrate bound per mol of [Eu(fmod)$_3$] varies somewhat among the 12 substrates examined. This number appears to depend quite strongly on the size or steric nature of the substrate. The bulkier the substrate molecule or the more sterically crowded the donor moiety of the substrate molecule the smaller is the ' apparent ' or ' effective ' co-ordination number of the complex–substrate adduct. The shapes of the titration curves shown in the Figures also indicate differences in the adduct-formation processes for the various substrate systems studied. With the exception of dmso, dmf, and pyridine, the emission-titration curves rose very rapidly (and nearly linearly) between 0 and 1 equivalent of substrate added and each exhibited a break at, or near, 1 equivalent. These data indicate that, while the first substrate molecule is added to the complex rather easily, the second is added with somewhat more difficulty. The emission-titration curves for dmso, dmf, and pyridine (see Figure 1) suggest possible co-operative behaviour in complex–substrate adduct formation. In these cases, the emission intensity increased rather slowly in the region of 0—0.5 equivalent of substrate added and then underwent a sharp and nearly linear increase over the *ca.* 0.5—1.0 equivalent region of substrate added. Stepwise formation processes are indicated in the cases of dmso (Figure 1), isopropyl alcohol (Figure 3), and, possibly, ethanol (Figure 3).

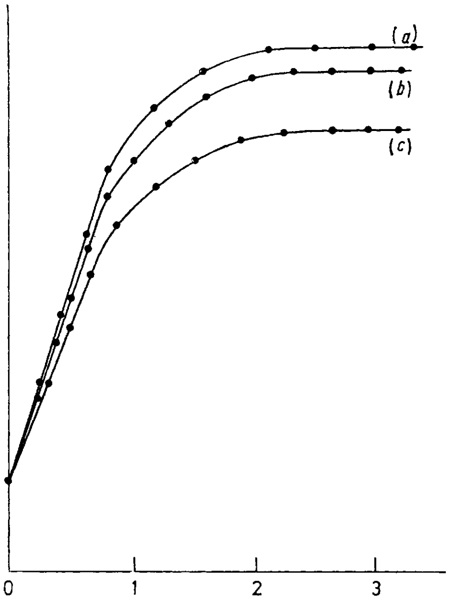

FIGURE 4 Emission-titration curves for [Eu(fmod)$_3$] with (*a*) n-butanol, (*b*) s-butyl alcohol, and (*c*) t-butyl alcohol plotted as in Figure 1

We used a graphical method, similar to that used previously in n.m.r. studies of complex–substrate adduct stoicheiometries,[20] * to determine ' apparent ' or ' effective ' co-ordination numbers (c.n.s) in those cases where the emission-titration curves are clearly monotonic (no breaks) over the range 0—4 equivalents of substrate added. The emission-titration curves of n-butanol, s-butyl alcohol, and t-butyl alcohol (see Figure 4) and of benzyl alcohol and norborn-2-ene-6-methanol (see Figure 2) were monotonic over this range. In an emission titration with one of these systems, initially every substrate molecule added to the [Eu(fmod)$_3$]–CCl$_4$ solution is immediately bound by a complex molecule and one observes a sharp rise in emission intensity which is (approximately) linearly proportional to substrate concentration. At large excesses of added substrate (relative to the amount of complex in solution), further addition of substrate does not yield an increase in emission intensity. Straight lines may be constructed from the titration curves at both low substrate concentrations and ' excess ' of substrate (where the titration curve levels off), and the intersection of these two straight lines may be related to an ' apparent ' or ' effective ' c.n. for the complex–substrate adducts.* ' Apparent ' c.n.s. obtained in this fashion are listed in Table 1.

TABLE 1

' Apparent ' co-ordination numbers of [Eu(fmod)$_3$]–substrate adducts in CCl$_4$ solution

Substrate	Co-ordination number
Benzyl alcohol	1.93
Norborn-2-ene-6-methanol	1.42
n-Butanol	1.11
s-Butyl alcohol	1.13
t-Butyl alcohol	1.10

Non-integer values of the ' apparent ' c.n. presumably reflect the existence of equilibrium mixtures of complex–n(substrate) adducts (n = 1, 2, 3, *etc.*).

The ' breaks ' in the emission-titration curves of dmf and pyridine (see Figure 1) are particularly sharp. In the case of pyridine, it appears that one pyridine molecule will add to [Eu(fmod)$_3$] relatively easily to form a 1 : 1 adduct, but the second molecule is added with somewhat more difficulty. These data further suggest that at ' excess ' of pyridine a nearly equimolar equilibrium mixture of 1 : 1 and 1 : 2 [Eu(fmod)$_3$]–pyridine adducts exist in CCl$_4$ solution. In the case of dmf, the data suggest that at ' excess ' dmf 1 : 2 [Eu(fmod)$_3$]–dmf adducts are preferred.

The data presented in Table 1 and shown in Figure 4 suggest 1 : 1 complexes for the substrates n-butanol, s-butyl alcohol, and t-butyl alcohol. Given the monotonic shapes of the emission-titration curves for these systems and the assumption of predominantly 1 : 1 adduct formation, it is possible to calculate binding

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* The actual state of affairs in solution is probably best thought of as a dynamic equilibrium between chelate molecules, substrate molecules, and chelate-n(substrate) adducts (n is an integer) in which case what we refer to as ' apparent ' co-ordination numbers might better be called ' average ' co-ordination numbers.

[20] See, for example, K. K. Anderson and J. J. Ubell, *Tetrahedron Letters*, 1970, 5253; A. F. Cockerill and D. M. Rackham, *ibid.*, p. 5149.

constants from the emission data obtained in this study. For the reaction, $L + S \rightleftharpoons LS$, where L = [Eu(fmod)$_3$] and S = substrate molecule, it is easily shown that equation (1) is applicable where I_0 is the initial emissive intensity of the chelate–CCl_4 system (before addition of substrate), I_e is the emissive intensity of the complex after the addition of ' excess ' of substrate (where emission intensity levels off), and I is the measured emission intensity of the [Eu(fmod)$_3$] complex followed as a function of substrate added to the solution. Knowledge of $(I - I_0)/(I_e - I)$ and of the amount of starting material enables the calculation of the equilibrium constant for the 1 : 1 LS adduct, $K_1 = [LS]/[L][S]$. Values of K_1 calculated for the [Eu(fmod)$_3$]–n-butanol,–s-butyl alcohol, and –t-butyl alcohol systems are listed in Table 2.

$$\frac{[LS]}{[L]} = \frac{I - I_0}{I_e - I} \qquad (1)$$

TABLE 2

Equilibrium constants calculated for 1 : 1 [Eu(fmod)$_3$]–substrate complexes

Substrate	$10^{-2}K/dm^3\ mol^{-1}$
Bu^nOH	4.4
Bu^sOH	3.4
Bu^tOH	0.46

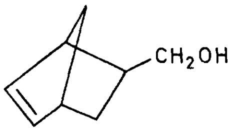
It was found that, in general, the strength of the complex–substrate interaction is reflected in the final emission intensity (I_e) achieved on addition of ' excess ' of substrate. Absolute emission intensities and quantum yields were not determined in the study reported here; however, relative emission intensities (I_e) for the various complex–substrate (excess) systems may be readily compared. These data are collected in Table 3. As was found in our previous emission studies [18] on the chiral l.s.r. [Eu(facam)$_3$], in various ' neat ' and ' mixed ' solvent systems, the emission intensities observed for the [Eu(fmod)$_3$]–dmf and –dmso adducts are considerably stronger than those observed for the [Eu(fmod)$_3$] adducts formed with pyridine and with the various alcohols. Both dmf and dmso are known to co-ordinate strongly to lanthanoid chelate complexes, each being relatively small in size and each having a highly nucleophilic donor moiety. Trends in the relative emission intensities (measured in the presence of excess of substrate) of the various [Eu(fmod)$_3$]–alcohol systems may be related in a qualitative way to the relative co-ordinative strengths and steric features of the alcohol molecules. In general, the bulkier the substrate molecule around its donor moiety the lower is the observed emission intensity.

TABLE 3

Relative emission intensities of various [Eu(fmod)$_3$]–substrate (excess)–CCl_4 systems

Solvent	I_e
CCl_4 (pure)	1.0
dmso–CCl_4	34.8
dmf–CCl_4	37.7
py–CCl_4	17.4
MeOH–CCl_4	5.7
EtOH–CCl_4	4.7
Pr^nOH–CCl_4	4.2
Pr^iOH–CCl_4	3.7
Bu^nOH–CCl_4	3.8
Bu^sOH–CCl_4	3.6
Bu^tOH–CCl_4	3.1
$PhCH_2OH$	3.6
Norborn-2-ene-6-methanol	3.3

It is, perhaps, somewhat surprising that the rather bulky substrate molecule, norborn-2-ene-6-methanol, should bind so well to [Eu(fmod)$_3$]. The emission-titration curve for norborn-2-ene-6-methanol (see Figure 2) did not reach a maximum and level off until almost **3** equivalents had been added to the [Eu(fmod)$_3$]–CCl_4 solution. However, as was found in our previous studies,[18] it appears that complex–substrate adduct formation is inhibited significantly only when ' steric bulk ' is located at the α-carbon site of the substrate (that is, very close to the donor moiety).



Summary.—Detailed structural and stoicheiometric information on lanthanoid complex–substrate adducts in solution media is extremely difficult to obtain. The sensitivity of the emission intensity of the complex to small perturbations on its structural variables (electronic and stereochemical) suggests that this property may be a valuable probe for studying the structural features and formation characteristics of complex–substrate adducts in solution. Emission-intensity data may be obtained on samples of very modest complex concentrations (significantly smaller than those required for analogous n.m.r. studies) and changes in emission intensity by complex–substrate interactions are substantial and are easily measured. Quantitative structural and stoicheiometric information on the lanthanoid complex–substrate adducts in solution remains somewhat elusive. The data we present here are useful only for deducing qualitative and semiquantitative structural information. However, additional work is in progress in our laboratory which should lead to more quantitative spectra–structure correlations for these complex systems.

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