Emission-titration Studies of the Adduct Formation Between Achiral Europium(III) β-Diketonates and Substrates

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Emission-titration spectroscopy has been used to study the formation of five europium(III) β-diketonate complexes with NRH_2 (R = Pr^n, Pr^i, Bu^n, Bu^s, or Bu^t) and R'OH (R' = Me, Et, Pr^n, Pr^i, Bu^n, Bu^s, or Bu^t). The emission intensity of the $^5D_0 \rightarrow {}^7F_2$ Eu^{3+} transition is found to be quite sensitive to the interaction between the chelate complex and a substrate molecule. Emission titrations and also Job's method of continuous variations have been used to find both the formation constant and stoicheiometry of all adducts studied. Depending on the chelate complex and substrate, either a 1 : 1 or a 1 : 2 chelate complex–substrate adduct is formed. Steric factors usually play only a minor role in this interaction, although in a few cases they influence the extent of the interaction.

LANTHANOID complexes of β-diketones have found widespread use in n.m.r. spectroscopy as shift reagents,[1-4] and new applications are constantly being found. The theoretical analysis of these paramagnetic shifts has been hampered somewhat by a lack of knowledge regarding the stoicheiometry and conformation of the adducts formed in solution. Information has been gathered, however, using the techniques of n.m.r.,[5-8] absorption,[9] and fluorescence spectroscopies.[10] The equilibrium constants obtained in some of these studies have been tabulated by Mayo.[4]

It is well known that sharp-line emission observed when certain lanthanoid β-diketonates are excited by u.v. light is dependent both on the geometry of the complex [11] and on the presence of adducts.[12-14] In general, emission in weakly co-ordinating solvents is feeble, while adduct formation results in an enhanced luminescence quantum yield. It thus becomes possible to dissolve the chelate complex in a solvent with which adduct formation is not possible, and to titrate with a dilute solution of a material that is capable of adding to the lanthanoid chelate complex. The changes in metal-ion emission as a function of added substrate will then contain information regarding the nature of the adduct, and it also becomes possible to calculate equilibrium constants.

Emission-titration studies of this sort have been carried out for some alcohol adducts of [Eu(fmod)$_3$] (fmod = 6,6,7,7,8,8,8-heptafluoro-2,2-dimethyloctane-3,5-dionate).[15] In the present study, emission titrations have been used to study the interaction of simple amines and alcohols with [Eu(fmod)$_3$], [Eu(tmhd)$_3$] (tmhd = 2,2,6,6-tetramethylheptane-3,5-dionate), [Eu(dppd)$_3$] (dppd = 1,3-diphenylpropane-1,3-dionate), and [Eu(tftbd)$_3$] (tftbd = 4,4,4-trifluoro-1-(2-thienyl)butane-1,3-dionate). Emission titrations were attempted with [Eu(pbd)$_3$] (pbd = 1-phenylbutane-1,3-dionate), but no emission enhancements were observed with any of the substrates used in this study.

EXPERIMENTAL

The complexes [Eu(fmod)$_3$] and [Eu(tmhd)$_3$] were purchased from Aldrich, while [Eu(dppd)$_3$],[16] [Eu(tftbd)$_3$],[17] and [Eu(pbd)$_3$] [18] were prepared according to the literature. Each complex was sublimed before use, and then dried over P_4O_{10} in a vacuum desiccator. Spectroquality CCl_4 solvent was dried over molecular sieves, as were all spectrograde substrates used in the study. All manipulations were carried out in a glove-bag under a dry nitrogen atmosphere to insure the rigorous exclusion of water from all samples (failure to do so resulted in irreproducible data). Lanthanoid complex concentrations ranged from 5×10^{-4} to 3×10^{-3} mol dm^{-3}, and substrates were added to 3 cm^3 of the chelate complex solution (CCl_4 solvent) in 5 μl amounts from stock solutions (CCl_4 solvent) whose concentrations ranged from 0.1 to 0.25 mol dm^{-3}.

All emission measurements were made on a medium-resolution emission spectrometer constructed in this laboratory and previously described.[19] Samples were excited by the 365-nm output of a 200-W Hg–Xe arc lamp, the emission collected at 90° to the exciting beam and subsequently analysed by a double-prism monochromator, and finally detected by an E.M.I. 9798B photomultiplier tube (S-20 response). The emission titrations were conducted by monitoring the integrated intensity of the $^5D_0 \rightarrow {}^7F_2$ Eu^{3+} emission band at 615 nm as increasing quantities of substrate were added to the solution of the chelate complex. Inner-filter effects involving the chelate emission cannot be expected to influence the results since none of the chelate complexes is capable of absorbing the europium(III) emission at 615 nm. All emission intensities were referenced to the emission of a 1×10^{-3} mol dm^{-3} solution of quinine sulphate in 0.1N H_2SO_4; with this correction, all intensity data were reproducible to within 1%.

RESULTS AND DISCUSSION

Addition of substrate dissolved in CCl_4 to a solution containing one of the europium chelate complexes usually resulted in an increase in Eu^{3+} emission. The shapes of the titration curves ordinarily displayed little detail, but simply showed a rise to a limiting intensity value. This limiting intensity was found to be a function of both the nature of the β-diketone ligand and the substrate used. A summary of the emission intensities with and without substrate present is given in Table 1 for the [Eu(tmhd)$_3$], [Eu(fmod)$_3$], [Eu(dppd)$_3$], and [Eu(tftbd)$_3$] complexes. Data for [Eu(pbd)$_3$] are not shown since no intensity enhancement was observed when any of the amine or alcohol substrates was added.

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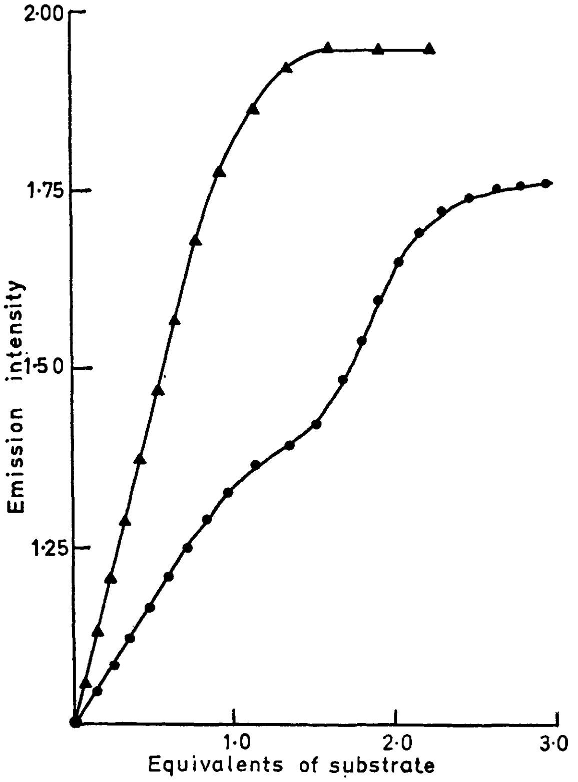
The $[Eu(pbd)_3]$ emission intensity observed in the absence of substrate was found to be 8.72.

(*a*) $[Eu(tmhd)_3]$.—Addition of alcohol or amine substrates to a CCl_4 solution of $[Eu(tmhd)_3]$ resulted in a modest increase in emission intensity. The intensity reaches a maximum after approximately 1 equivalent of alcohol substrate is added, but does not level off until at least 2 equivalents of amine are added. Representative examples of the two types of titration behaviour are shown in the Figure, in which the titrations of $[Eu(tmhd)_3]$ with NPr^nH_2 and Pr^nOH are illustrated. Job's method of continuous variations was used to identify the stoicheiometry of the adducts, and it was found that only 1 : 1 $[Eu(tmhd)_3]$–alcohol complexes were formed. On the other hand, 1 : 1 complexes were formed in the interaction of $[Eu(tmhd)_3]$ with amines at low concentrations of substrate, but 1 : 2 complexes were found to predominate at higher mol fractions of substrate.



Emission-titration curve for $[Eu(tmhd)_3]$ with n-propylamine (●) and n-propanol (▲). Complex emission intensity at 615 nm is plotted against equivalents of substrate added

TABLE 1

Limiting intensities reached in the titration of europium(III) complexes with substrates *

	Complex			
Substrate	$[Eu(tmhd)_3]$	$[Eu(fmod)_3]$	$[Eu(dppd)_3]$	$[Eu(tftbd)_3]$
None	1.00	4.55	1.30	353
NPr^nH_2	1.75	32.0	18.7	1 562
NPr^iH_2	1.57	34.1	9.81	1 416
NBu^nH_2	1.77	32.1	20.5	1 569
NBu^sH_2	1.40	33.5	8.99	1 447
NBu^tH_2	1.35	35.4	2.67	1 317
MeOH	1.79	33.2	3.46	360
EtOH	1.80	31.0	3.23	359
Pr^nOH	1.95	31.4	2.23	357
Pr^iOH	1.64	25.0	2.47	355
Bu^nOH	1.79	29.5	2.14	356
Bu^sOH	1.61	16.8	2.30	355
Bu^tOH	1.36	12.1	2.25	354

* All intensities are relative to the intensity of $[Eu(tmhd)_3]$ in CCl_4.

Knowledge of the stoicheiometries enabled the determination of formation constants, and the methods used for finding these have been previously outlined.[15] Values for all formation constants are found in Table 2.

TABLE 2

Formation constants of the $[Eu(tmhd)_3]$–substrate adducts *

Substrate	log K_1	log K_{12}
NPr^nH_2	2.34	5.00
NPr^iH_2	2.35	4.90
NBu^nH_2	2.33	4.96
NBu^sH_2	2.38	4.89
NBu^tH_2	2.37	4.66
MeOH	2.86	
EtOH	2.90	
Pr^nOH	2.93	
Pr^iOH	2.86	
Bu^nOH	2.97	
Bu^sOH	2.94	
Bu^tOH	2.88	

* The K_1 formation constants have units of $dm^3 mol^{-1}$ while the K_{12} cumulative formation constants have units of $dm^6 mol^{-2}$. Both carry an error of ± 0.02.

It may be seen that little variation is found in the K_1 constants, except that the first molecule of amine substrate is less tightly bound than the molecule of alcohol substrate. Within a particular class of substrate, steric effects are found to play only a minor role in the binding of the first molecule. Greater variations are seen in the log K_{12} values found for the amine adducts, and it seems clear that steric effects are important in the binding of the second molecule of substrate. A break observed in the titration curves of $[Eu(tmhd)_3]$ with all amines enabled the separate determination of both K_1 and K_{12}.

The formation constant of the $[Eu(tmhd)_3]$–NPr^nH_2 adduct has been measured by n.m.r. techniques, and a value of 12.3 was found for the 1 : 1 complex.[5] This value is *ca.* 20 times less than the magnitude found for K_1 using the emission techniques of this study. However, formation constants of $[Eu(tmhd)_3]$ 1 : 1 adducts with borneol and cedrol (as determined by spectrophotometric analysis) are of the same order of magnitude as the alcohol adducts in the present work.[9] Since the calculation of formation constants using n.m.r. methods contains approximations that may or may not be valid for the $[Eu(tmhd)_3]$ adducts, the agreement of spectrophotometric and fluorimetric results lends credence to the formation constants reported here. In the case of $[Eu(tmhd)_3]$–amine complexes, the neglect of 1 : 2 adducts will certainly invalidate any quantitative interpretation of n.m.r. results.

(*b*) $[Eu(fmod)_3]$.—Emission enhancements found with this fluorinated shift reagent are much greater than observed for the previous non-fluorinated chelate.

Application of Job's method indicated that 1 : 2 adducts were formed with all substrates in this study, and this observation is found to agree with other studies.[20,21] No break in the titration curves was observed after the addition of 1 equivalent of any substrate, so it was not possible to compute values of K_1. Values for K_{12} have been calculated, however, and these are found in Table 3.

TABLE 3

Formation constants of the $[Eu(fmod)_3]$–substrate adducts

Substrate	log K_{12} *
NPr^nH_2	5.66
NPr^iH_2	5.64
NBu^nH_2	5.64
NBu^sH_2	5.62
NBu^tH_2	5.60
MeOH	5.17
EtOH	5.08
Pr^nOH	5.01
Pr^iOH	5.34
Bu^nOH	5.25
Bu^sOH	5.36
Bu^tOH	5.49

* All formation constants have units of $dm^6\ mol^{-2}$ and are associated with an error of ± 0.02. log K_1 could not be determined.

Steric effects are found to be somewhat more important for the fmod chelate than for the tmhd chelate, but they do not seem to play a major role in the adduct formation. The formation constants and limiting emission intensities observed for all $[Eu(fmod)_3]$–amine complexes are all roughly the same and quite large. However, the alcohol adducts have formation constants which tend to increase as the steric hindrance about the functional group of the substrate increases; this trend is best illustrated in the n-, s-, and t-butyl alcohol sequence. The limiting emission intensity decreases as the substrate becomes more sterically hindered, but this decrease is not easily related to the strength of the chelate-complex–substrate binding. Exactly why a more bulky substrate should bind more tightly than a less bulky one is unclear at the moment, but suggests that there is a ' pocket ' of some sort on the surface of the co-ordination sphere of the chelate complex that is best filled by substrates having a particular geometry and size.

Formation constants for $[Eu(fmod)_3]$ adducts with a few of the substrates used here have been reported, and these n.m.r. results (which all assumed 1 : 1 stoicheiometry) are all seen to be much smaller than the results reported here. A value of 280 $dm^3\ mol^{-1}$ was reported for K_1 of the Bu^tOH adduct,[22] a value of 97 $dm^3\ mol^{-1}$ was found for K_1 of the Pr^iOH adduct,[23] and it was estimated that K_1 for the NPr^nH_2 adduct exceeded 100 $dm^3\ mol^{-1}$.[6] The neglect of 1 : 2 stoicheiometries certainly casts doubt on the accuracy of these formation constants.

Emission titrations of $[Eu(fmod)_3]$ with the same alcohol substrates used in this study have been reported previously,[15] and somewhat different results were obtained. It is now believed that the earlier work did not deal with the anhydrous chelate complex, but actually titrated the $[Eu(fmod)_3]{\cdot}H_2O$ complex. In some cases, non-integral co-ordination numbers had been reported and a few 1 : 1 complexes were even found. These results represent the effect of water on the substrate binding properties of the $[Eu(fmod)_3]$ complex, and have been reproduced in this study by adding 1 equivalent of water to the stock solution of the chelate complex. It has been noted[24] that anhydrous $[Eu(fmod)_3]$ is a better shift reagent than the hydrated complex; the present results suggest that adduct stoicheiometry also depends upon the state of hydration. Quantitative interpretation of any n.m.r. results therefore cannot be made unless the hydration of $[Eu(fmod)_3]$ is known with certainty.

It is also known that $[Eu(fmod)_3]$ chelate complexes are associated in CCl_4 solution, while those of $[Eu(tmhd)_3]$ are not.[7] It may be concluded that the driving force behind adduct formation is stronger than the force leading to oligomerization since no induction period is noted in the titration curves of $[Eu(fmod)_3]$ with any of the substrates used in this study. If the two processes were competitive, one would have expected a less rapid rise in emission intensity at low substrate concentrations than at higher concentrations. This conclusion implies that self association of $[Eu(fmod)_3]$ chelate molecules does not complicate the binding of chelate complex and substrate, at least as evidenced by the emission data.

(*c*) $[Eu(dppd)_3]$.—The addition of amine substrates to a solution of $[Eu(dppd)_3]$ results in emission-intensity enhancements which strongly depend on the steric hindrance about the functional group of the ligand. Unbranched amines yield an intensity nearly twice that of secondary amines, and almost ten times that of the tertiary amine. Job's method revealed that 1 : 2 adducts were formed for all the amines used. It was somewhat surprising to find that the values of K_{12} did not depend strongly on the steric nature of the substrate, but since values for K_1 could not be determined an explanation cannot be advanced at this time. Formation constants are given in Table 4.

When alcohol substrates were added to $[Eu(dppd)_3]$

TABLE 4

Formation constants of the $[Eu(dppd)_3]$–substrate adducts [a]

Substrate	log K_1	log K_{12}
NPr^nH_2	*b*	4.40
NPr^iH_2	*b*	4.42
NBu^nH_2	*b*	4.42
NBu^sH_2	*b*	4.41
NBu^tH_2	*b*	4.38
MeOH	2.98	
EtOH	2.98	
Pr^nOH	2.97	
Pr^iOH	2.89	
Bu^nOH	2.97	
Bu^sOH	2.78	
Bu^tOH	2.70	

[a] The K_1 formation constants have units of $dm^3\ mol^{-1}$ while the K_{12} have units of $dm^6\ mol^{-2}$. Both carry an error of ± 0.02. [b] Could not be determined.

only 1 : 1 complexes could be detected. The values of K_1 are all roughly the same, as are the limiting intensities observed in the titrations. It is concluded from these studies that steric effects are not very important in the binding of alcohol substrates to [Eu(dppd)$_3$]. It is interesting to note that the formation constants found for the adducts of this complex with alcohols are of the same order of magnitude as found for [Eu(tmhd)$_3$]. If it were not for the poor solubility of [Eu(dppd)$_3$] one would conclude that this complex would function just as well as a shift reagent as does [Eu(tmhd)$_3$].

The complex [Eu(dppd)$_3$] has been investigated as a shift reagent,[25-27] but has not been used due to its low induced shifts and poor solubility. Since the magnitude of the chemical shift is related to the strength of the chelate–substrate complex, it is surprising to find that the values of K_1 and K_{12} for [Eu(tmhd)$_3$] and [Eu(dppd)$_3$] are so similar. This observation suggests that the Lewis acidity of [Eu(dppd)$_3$] is different in the excited state (as obtained from emission spectroscopy) than in the ground state (as obtained from n.m.r. shift data). The similarity in formation constants determined for [Eu(tmhd)$_3$] by emission and absorption spectroscopy suggests that the ground and excited states of this complex possess similar properties.

(*d*) [Eu(pbd)$_3$].—No emission enhancement was seen in the titration of this chelate complex with any of the substrates used in this study. This does not necessarily imply that no adduct formation is taking place, but merely that any adduct formed is no more emissive than the pure chelate complex. However, since n.m.r. evidence [26-28] indicates that little interaction of complex and substrate takes place, it is concluded that adduct formation with [Eu(pbd)$_3$] is feeble indeed.

(*e*) [Eu(tftbd)$_3$].—Examination of the emission intensities summarized for this chelate complex and its adducts in Table 1 shows that the complex is extremely emissive and that large emission enhancements are seen when adduct formation takes place. It is also interesting to note that while amines co-ordinate very strongly to [Eu(tftbd)$_3$], alcohol substrates appear not to be able to co-ordinate at all. In all cases, Job's method revealed that only 1 : 1 complexes were formed. The formation constants of these are in Table 5.

TABLE 5

Formation constants of the [Eu(tftbd)$_3$]–substrate adducts *

Substrate	log K_1
NPr^nH_2	4.08
NPr^iH_2	4.35
NBu^nH_2	4.01
NBu^sH_2	4.34
NBu^tH_2	4.39

* All formation constants have units of dm^3 mol^{-1} and are associated with an error of ±0.02.

The adducts formed between [Eu(tftbd)$_3$] and amines are seen to be extremely stable, and are much stronger than any of the other complexes examined in this study. No ground-state formation constants exist to indicate whether this high stability is merely an excited-state phenomenon, but the data presented here indicate that [Eu(tftbd)$_3$] ought to be a very effective shift reagent for amines. Unfortunately, its very low solubility will probably preclude its effective use.

Conclusions.—Detailed structural and stoicheiometric data on the adducts formed between lanthanoid β-diketonates and substrates are difficult to obtain, but the emission titrations presented in this paper have provided some information. The sensitivity of emission spectroscopy to changes in co-ordination geometry makes it an ideal probe of these systems, and since it is possible to identify the excited-state results of emission spectroscopy with ground-state properties that are of interest to the n.m.r. spectroscopist (since only non-bonding *f* electrons are promoted in the excitation process, the excited-state geometry cannot differ by any great extent from the ground-state geometry), then new and valuable information may be obtained. The possibility that energy transfer from a substrate donor to the lanthanoid chelate acceptor resulted in the enhanced emission observed was discounted since the substrates used in this study were incapable of absorbing the exciting radiation. The present work has shown that the existence of 1 : 2 chelate complex–substrate adducts may be more prevalent than is thought, and that any theoretical analysis of n.m.r. data that neglects the presence of adducts other than 1 : 1 should be viewed with some scepticism unless this stoicheiometry can be verified.

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