Factors affecting the Quantum Efficiencies of Fluorescent Terbium(III) Chelates in the Solid State

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Investigations of tris- and tetrakis-hexafluoroacetylacetonato- and trifluoroacetylacetonato-terbium(III) complexes have established that the temperature-dependence of the $^5D_4$ lifetime is caused by thermal depopulation of the ion level to a ligand triplet state. Ligand triplet to ground state deactivation rates, A, have been determined and range from 10^4 to 10^7 s^{-1}. Neither variation in thermal depopulation rates nor A is sufficient to explain the observed differences in quantum efficiencies and it is suggested that significant losses may occur before the triplet state in the energy transfer process.

LANTHANIDE ions form two general types of complex with β-diketoenolate anions (*a*) neutral tris complexes, LnL_3, which may be solvated, and (*b*) anionic tetrakis complexes, $[LnL_4]^-$, which are associated with a cationic species.[1] Many of these complexes, especially those of Eu^{3+}, Tb^{3+}, and Sm^{3+}, emit narrow line fluorescence owing to radiative transitions within the 4*f* electron shell of the lanthanide ion when they are irradiated in the first excited singlet absorption band of the ligand. The energy-transfer mechanism leading to this emission involves intersystem crossing from the ligand singlet, S_1, to a ligand triplet state, T_1, which may then transfer energy to excited states of the lanthanide ion.[2-4] The overall quantum efficiency of this process depends on the efficiencies of (*a*) the intersystem crossing to the donor triplet within the ligand, (*b*) the transfer from the donor triplet to an excited Ln^{3+} level, and (*c*) the radiative deactivation of the excited lanthanide level.

It has been noted in this laboratory that tetrakis compounds of a given ligand and lanthanide ion often exhibit considerable differences in fluorescent efficiency

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[1] S. P. Sinha, 'Complexes of the Rare Earths,' Pergamon, London, 1966.

[2] S. I. Weissman, *J. Chem. Phys.*, 1942, **10**, 214.

[3] G. A. Crosby, R. E. Whan, and R. M. Alire, *J. Chem. Phys.*, 1961, **34**, 743.

[4] R. E. Whan and G. A. Crosby, *J. Mol. Spectroscopy*, 1962, **8**, 315.

depending on the nature of the associated cation. In order to investigate the relative importance of the various loss mechanisms which may cause this behaviour we have examined two series of terbium(III) complexes in the solid state, namely those of hexafluoroacetylacetone and trifluoroacetylacetone.

EXPERIMENTAL

General Preparative Methods.—99·9% Gd$_2$O$_3$ and 99·9% Tb$_4$O$_7$ (Koch–Light Laboratories Ltd.) were converted into the chloride and nitrate respectively before use. A variety of synthetic methods for the preparation of lanthanide β-diketoenolates have been reported [5] and it has been necessary to use specific procedures to obtain the complexes in Table 1. These general procedures are briefly described below.

TABLE 1

Analytical data for terbium and gadolinium complexes

Compound	M.p.[a]/°C	Found (%)			Calc. (%)			Preparative method [b]
		C	H	N	C	H	N	
Tb(hfaa)$_3$,2H$_2$O	120—121	21·9	0·8		22·1	0·9		(*b*)
Tb(hfaa)$_4$(pipH) [d]	110—111	28·2	1·6	1·1	28·0	1·5	1·3	(*d*)
Tb(hfaa)$_4$NH$_4$	207—208	23·9	0·7	1·4	23·9	0·8	1·4	(*d*)
Tb(hfaa)$_4$Ph$_4$As	136—137	38·4	1·7		38·5	1·8		(*f*)
Tb(hfaa)$_4$Me$_4$N	244—245	27·0	1·5	1·4	27·1	1·5	1·3	(*f*)
Tb(hfaa)$_4$Me$_3$NH	136—137	28·4	1·9	1·2	28·7	1·8	1·3	(*d*)
Tb(hfaa)$_4$Bu^{t}NH$_3$	93—94	26·7	1·6	1·3	27·1	1·5	1·3	(*d*)
Tb(hfaa)$_4$(picH)(pic) [d]	97—98	32·2	1·6	2·2	32·7	1·6	2·4	(*d*)
Tb(tfaa)$_3$,2H$_2$O	139—140	27·4	2·5		27·5	2·5		(*a*)
Tb(tfaa)$_4$(pipH)	100—101	34·9	3·3	1·7	35·0	3·3	1·6	(*e*)
Tb(tfaa)$_4$NH$_4$	174—175	30·2	2·7	2·1	30·4	2·5	1·8	(*e*)
Tb(tfaa)$_4$Ph$_4$As	162—163	45·7	3·2		45·8	3·1		(*f*)
Tb(tfaa)$_4$Na	>250 [c]	30·4	2·0		30·2	2·0		(*c*)
Tb(tfaa)$_4$K	>250 [c]	29·6	2·0		29·6	2·0		(*c*)
Tb(tfaa)$_4$Cs	214—215	26·6	1·8		26·6	1·8		(*c*)
Gd(hfaa)$_3$,2H$_2$O	124—125	22·3	0·8		22·1	0·9		(*b*)
Gd(hfaa)$_4$(pipH) [d]	128—129	28·2	2·0	1·6	28·0	1·5	1·3	(*d*)
Gd(hfaa)$_4$NH$_4$	205—206	24·0	0·8	1·4	24·0	0·8	1·4	(*d*)
Gd(hfaa)$_4$Ph$_4$As	136—137	38·3	1·7		38·6	1·8		(*f*)
Gd(hfaa)$_4$Me$_4$N	235—236	27·1	1·5	1·5	27·2	1·5	1·3	(*f*)
Gd(hfaa)$_4$Me$_3$NH	134—135	28·7	2·0	1·2	28·7	1·8	1·3	(*d*)
Gd(hfaa)$_4$Bu^{t}NH$_3$	95—96	27·5	1·9	1·6	27·2	1·5	1·3	(*d*)
Gd(hfaa)$_3$(picH)(pic)	97—98	32·6	1·6	2·5	32·8	1·6	2·4	(*d*)
Gd(tfaa)$_3$,2H$_2$O	142—143	28·7	2·4		28·4	2·2		(*a*)
Gd(tfaa)$_4$(pipH) [d]	90—92	35·2	3·5	1·6	35·1	3·3	1·6	(*e*)
Gd(tfaa)$_4$NH$_4$	170—171	30·6	2·6	1·9	30·5	2·5	1·8	(*e*)
Gd(tfaa)$_4$Ph$_4$As	158—159	45·8	3·1		45·8	3·1		(*f*)
Gd(tfaa)$_4$Na	>250 [c]	30·3	2·1		30·3	2·0		(*c*)
Gd(tfaa)$_4$K	>250 [c]	30·0	2·0		29·7	2·0		(*c*)
Gd(tfaa)$_4$Cs	214—215	26·9	2·1		26·6	1·8		(*c*)

[a] Uncorrected thermometer. [b] See text. [c] Compounds char before melting. [d] pipH = Piperidinium cation, picH = 4-methylpyridinium cation. pic = 4-methylpyridine.

Method (*a*). Ammonia solution (0·5M) was added dropwise to a rapidly stirred 1 : 1 ethanol–water solution of the ligand (3 mol) and the lanthanide salt (1 mol) until the pH reached 6·3. The product began to precipitate in the pH range 5·8—6·0.

Method (*b*). NaOH solution (0·5M) was added dropwise to a rapidly stirred 1 : 1 ethanol–water solution of the ligand (3 mol) and the lanthanide salt (1 mol) until the pH reached 6·3. The solution was then reduced in volume and addition of water precipitated the product.

Method (*c*). An aqueous solution of the lanthanide salt (1 mol) was added dropwise to a rapidly stirred 95% ethanol solution of ligand (4·5 mol) and alkali-metal hydroxide (4·5 mol). The solution was warmed to redissolve any precipitated product and allowed to cool.

Method (*d*). A 95% ethanol solution of ligand (4 mol), base (8 mol), and lanthanide salt (1 mol) was boiled before addition of water to precipitate the product.

Method (*e*). An aqueous solution of the lanthanide salt (1 mol) was added dropwise to a 95% ethanol solution of the ligand (4·5 mol) and the base (4·5 mol). The product crystallised from the solution.

Method (*f*). Aqueous solutions of the lanthanide salt (1 mol) and the quaternary salt (2·5 mol) were added to a 95% ethanol solution of the ligand (4·0 mol) and sodium hydroxide (4·0 mol). The volume was reduced by boiling until crystallisation began and sufficient ethanol to redissolve the product was added and the solution allowed to cool.

The hexafluoroacetylacetonato-complexes (hfaa) were dried before recrystallisation from CHCl$_3$ and the trifluoroacetylacetonato-complexes (tfaa) were recrystallised from aqueous ethanol solutions. Analytical figures are in Table 1.

Fluorescence Lifetime Measurements.—These were done by a previously described method [4] with the inclusion of a

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[5] H. Samelson and A. Lempicki, *J. Chem. Phys.*, 1963, **39**, 110; H. Winston, O. J. Marsh, C. Z. Suzuki, and C. L. Telk, *ibid.*, p. 267; L. G. Nugent, M. L. Bhaumik, S. George, and S. M. Lee, *ibid.*, 1964, **41**, 1305; C. Brecher, H. Samelson, and A. Lempicki, *ibid.*, 1965, **42**, 1081; T. Moeller and W. F. Ulrich, *J. Inorg. Nuclear Chem.*, 1956, **2**, 164; G. W. Pope, J. F. Steinbach, and W. F. Wagner, *ibid.*, 1961, **20**, 304; R. G. Charles and E. P. Riedel, *ibid.*, 1967, **29**, 715; J. G. Stiles, C. N. McCarthy, and L. L. Quill, *J. Amer. Chem. Soc.*, 1948, **70**, 3142; H. Bauer, J. Blanc, and D. L. Ross, *ibid.*, 1964, **86**, 5125; L. R. Melby, N. J. Rose, E. Abramson, and J. C. Caris, *ibid.*, p. 5117; K. J. Eisentraut and R. E. Sievers, *ibid.*, 1965, **87**, 5254; Y. Matsuda, S. Makishima, and S. Shionoya, *Bull. Chem. Soc. Japan*, 1969, **42**, 356.

Solartron 3230 data transfer unit and Facit 4070 paper tape punch which replaces the X–Y recorder and allows the data to be directly computer-processed. Exponential lifetimes are quoted and are reproducible within ±3%.

Emission Spectra.—The emission spectra of the gadolinium complexes at 77 K were obtained with a Perkin-Elmer–Hitachi MPF-2A spectrofluorimeter. The high-resolution spectra shown in Figures 4 and 5 were determined with a locally designed spectrofluorimeter. The excitation source was a medium-pressure Hg lamp filtered to pass only the 365·5 nm radiation. The emission monochromator was a Hilger and Watts Monospek 1000 with 1200 line nm^{-1} grating, and phase-sensitive detection of the output from EMI 9526 photomultiplier was employed.

RESULTS AND DISCUSSION

Several tetrakistrifluoroacetylacetonate (tfaa) and hexafluoroacetylacetonate (hfaa) complexes of terbium and the corresponding hydrated tris compounds have been prepared. When subjected to u.v. irradiation at room temperature these compounds emit the characteristic green fluorescence of the terbium ion caused largely by the radiative transitions $^5D_4 \longrightarrow {}^7F_{5,6}$.[6] The observed fluorescent intensities of individual members of both series of compounds show considerable variations despite the fact that the β-diketoenolate ligand remains unchanged. This observation suggests that one or more of the energy-transfer rates within the complex is dependent on the nature of the complex.

The emitting $^5D_4$ level of Tb^{3+} lies *ca.* 20,000 cm^{-1} above the $^7F_6$ ground state and it has been established that thermal depopulation of this level may occur in terbium chelates in solution[7] and in the solid state.[8] Back-donation of energy occurs to a triplet state of the ligand and the rate of this temperature-dependent depopulation, $k(T)$, may be expressed [equation (1)] in terms of τ_T, the observed lifetime at temperature T and τ_0, the lifetime in the absence of any back-donation. If the energy is

$$k(T) = 1/\tau_T - 1/\tau_0 \qquad (1)$$

back-donated to a single acceptor level of the ligand at energy E above the $^5D_4$ then we obtain equation (2)

$$k(T) = A \exp\,(-E/RT) \qquad (2)$$

where A is the deactivation rate of the acceptor level to the ground state. Figure 1 shows an energy-level diagram representing this situation. Intersystem crossing within the ligand and the multiplet structure of the ^7F level are omitted. k_4 Is the temperature-dependent back-donation rate constant and the rate of depopulation of the $^5D_4$ level $k(T)$, can be shown to be as in equation (3)

$$k(T) = k_4(k_1 + k_2)/(k_1 + k_2 + k_3) \qquad (3)$$

and the lifetime, τ_T, can be expressed as (4). It is there-

$$\tau_T = 1/[k_5 + k_6 + k(T)] \qquad (4)$$

fore possible if back-donation occurs to determine the energy E and A, *i.e.*, $k_1 + k_2$, in the absence of further deactivation routes of the triplet, from data relating to the $^5D_4$ lifetimes and temperature. Back-donation from the $^5D_0$ level of the Eu^{3+} ion to the $^5D_1$ ion level has also been observed.[9]

The energies of the ligand triplet state can be determined from the emission spectra of the corresponding gadolinium(III) complexes in which, because of the absence of low-lying excited states of Gd^{3+}, no ligand–lanthanide transfer can occur.[10] The analogous gadolinium complexes have been prepared and from their emission spectra at 77 K the triplet-state energies given in Table 2 have been obtained. The triplet levels in the (hfaa) complexes vary over *ca.* 800 cm^{-1} with a mean value of 21,900 cm^{-1} which is close to the previously reported value[7] of 22,000 cm^{-1}. The range of the (tfaa) complexes is slightly larger but all are considerably lower than 23,000 cm^{-1}, the value obtained in solid solution.[7] It is evident that the triplet-level energy can be critically dependent on the environment of the ligand.

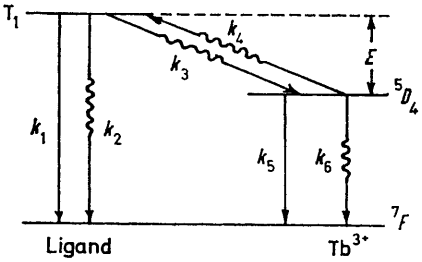

FIGURE 1 Energy-level diagram showing possible transfer steps from the ligand triplet, T$_1$, in Tb^{3+} complexes

TABLE 2

Ligand triplet energies, ν_T, of solid gadolinium complexes[a]

Compound	ν_T/cm^{-1}	Compound	ν_T/cm^{-1}
Gd(hfaa)$_3$,2H$_2$O	21,280	Gd(tfaa)$_3$,2H$_2$O	22,080
Gd(hfaa)$_4$(pipH)	21,410	Gd(tfaa)$_4$(pipH)	21,280
Gd(tfaa)$_4$NH$_4$	21,740	Gd(tfaa)$_4$NH$_4$	21,830
Gd(hfaa)$_4$Ph$_4$As	22,080	Gd(tfaa)$_4$Ph$_4$As	22,220
Gd(hfaa)$_4$Me$_4$N	21,280	Gd(tfaa)$_4$Na	21,790
Gd(hfaa)$_4$Me$_3$NH	21,280	Gd(tfaa)$_4$K	21,790
Gd(hfaa)$_4$Bu^{t}NH$_3$	21,790	Gd(tfaa)$_4$Cs	21,790
Gd(hfaa)$_4$(picH)(pic)	21,280		

[a] Obtained from emission spectrum at 77 K.

Lifetimes of the terbium (hfaa) and (tfaa) complexes in the solid state have been determined at 77 K and where possible at various temperatures up to 323 K. All the complexes investigated showed decreases in lifetime at higher temperatures but the profiles of the temperature-dependence differed considerably from chelate to chelate. Figure 2 illustrates the diversity of behaviour. Some decrease in τ on going from 77 to 195 K occurred in all cases but this was only marked in Tb(hfaa)$_4$Et$_3$NH and Tb(hfaa)$_4$Me$_4$N. The assumption is therefore made that no significant thermal depopulation is likely to occur

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[6] K. S. Thomas, S. Singh, and G. H. Dieke, *J. Chem. Phys.*, 1963, **38**, 2180.

[7] W. R. Dawson, J. L. Kropp, and M. W. Windsor, *J. Chem. Phys.*, 1966, **45**, 2410.

[8] T. D. Brown and T. M. Shepherd, *J.C.S. Dalton*, 1972, 1616.

[9] Y. Haas and G. Stein, *J. Phys. Chem.*, 1972, **76**, 1093.

[10] S. P. Cook and G. H. Dieke, *J. Chem. Phys.*, 1957, **27**, 1213; G. H. Dieke and L. Leopold, *J. Opt. Soc. Amer.*, 1957, **47**, 944.

at 77 K, *i.e.*, that $\tau_{77} = \tau_0$ [equation (1)]. The τ_{77} values are in Table 3.

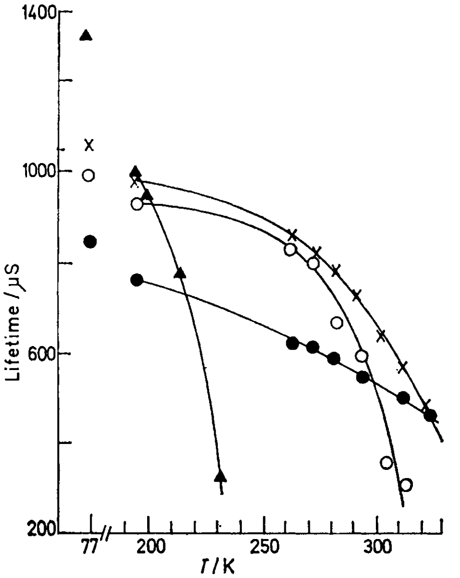

FIGURE 2 Dependence of $^5D_4$ lifetime on temperature in some Tb^{3+} complexes. ▲, $Tb(hfaa)_4Et_3NH$; ●, $Tb(hfaa)_3,2H_2O$; ○, $Tb(hfaa)_4(pipH)$; ×, $Tb(hfaa)_4Bu^tNH_3$

TABLE 3

Spectroscopic parameters for solid terbium complexes

Compound	τ_{77} [a] µs	E [b] cm^{-1}	E_{spec} [c] cm^{-1}	$^5D_4$ [d] cm^{-1}	$10^{-4}A$ [e]/ s^{-1}
$Tb(hfaa)_3,2H_2O$	849	880	950	20,330	4·6
$Tb(hfaa)_4(pipH)$	991	1220	1130	20,280	16
$Tb(hfaa)_4NH_4$	1166	1770	1460	20,280	3100
$Tb(hfaa)_4Ph_4As$ [f]	626	1440	1710	20,370	960
$Tb(hfaa)_4Me_4N$ [f]	1347	1050	1000	20,280	250
$Tb(hfaa)_4Me_3NH$ [f]	1305	980	1040	20,240	33
$Tb(hfaa)_4Bu^tNH_3$	1066	1150	1310	20,480	12
$Tb(hfaa)_4(picH)(pic)$	843	1020	1000	20,280	33
$Tb(tfaa)_3,2H_2O$	891	2100	1750	20,330	3200
$Tb(tfaa)_4(pipH)$	1407	840	910	20,370	5·8
$Tb(tfaa)_4NH_4$	1110	1810	1460	20,370	890
$Tb(tfaa)_4Ph_4As$	1250	1940	1940	20,280	680
$Tb(tfaa)_4Na$	1081	1570	1380	20,410	170
$Tb(tfaa)_4K$	1276	1740	1380	20,410	700
$Tb(tfaa)_4Cs$	1080	1880	1380	20,410	830

[a] $^5D_4$ lifetime at 77 K. [b] $^5D_4$–ligand acceptor level energy difference calculated from lifetime data. [c] $^5D_4$–ligand triplet energy difference using triplet energies derived from corresponding Gd complexes. [d] See text. [e] Deactivation rate constant of ligand triplet. [f] E determined from data at temperatures below 263 K.

Linear plots, within experimental error, of log $(1/\tau_T - 1/\tau_0)$ against $1/T$ were obtained within the temperature range 263—323 K for those complexes giving measurable fluorescence output at these temperatures. These results indicate that thermal depopulation is essentially occurring to a single energy level of the ligand although in some cases slight deviations at higher temperatures suggested that higher ligand levels might also be involved. The values of E and A in Table 3 were obtained by use of a least-squares treatment to obtain the best straight line. The linearity of the plots also shows that no major change in the triplet deactivation rate occurs within the studied temperature ranges.

In order to obtain the energies of the ligand levels predicted by the E values obtained from the lifetime data it is necessary to use a value for the $^5D_4$—$^7F_6$ energy difference. This requires some form of approximation since the Tb^{3+} levels are split by the crystal field to an extent of several hundred cm^{-1}. The centres of gravity of the $^5D_4 \longrightarrow {}^7F_6$ emission lines have therefore been used to obtain the $^5D_4$ energies, ν_{Tb}, in Table 3. Values of E_{spec}, where $E_{spec} = \nu_T - \nu_{Tb}$, are also given.

The agreement found between E and E_{spec} is within experimental error in both the (hfaa) and (tfaa) series and it is concluded that the observed decreases in $^5D_4$ lifetime are consistent with a thermal depopulation mechanism involving the triplet states spectroscopically observed in the corresponding gadolinium complexes.

The calculated deactivation rates, A, vary over the approximate range 10^4—10^7 s^{-1} with, in general, higher deactivation rates for the (tfaa) complexes. Dawson *et al.*[7] have reported A values of $1{\cdot}4 \times 10^8$ and $2{\cdot}5 \times 10^{10}$ s^{-1} for a terbium (hfaa) complex of uncertain composition and $Tb(tfaa)_4NH_4$ respectively, in solution. The lower rates found in the solid state reflect the expected decrease in non-radiative quenching rates, k_2. In addition, the lanthanide fluorescence in these solutions indicates that the transfer rate, k_3, is at least comparable with the triplet deactivation rate, *i.e.*, of the order of 10^{10} s^{-1} or greater. Therefore in the solid complexes the variations in A are only likely significantly to affect the overall quantum efficiencies insofar as they control the rate of thermal depopulation of the $^5D_4$.

In view of the marked differences in the rates of thermal depopulation at room temperature it is worth considering whether this effect alone may be responsible for the differing quantum efficiencies of the solids. Thus if the assumption is made that the radiative rate constant k_5 is constant within each series of complexes the quantum efficiencies of the $^5D_4$ levels, $\Phi_{^5D_4}$, should be proportional to the lifetimes, as in equation (5).

$$\Phi_{^5D_4} = k_5\tau_T \qquad (5)$$

Table 4 lists τ_{293} values along with qualitative visual estimations of the relative fluorescence yields of the complexes at room temperature. In cases where low fluorescence output precluded direct measurements of τ at 293 K the values have been extrapolated from data at lower temperatures. It is evident that no direct correlation between the overall quantum efficiency and the $^5D_4$ lifetime exists. For example, in the (hfaa) series $Tb(hfaa)_4Me_3NH$ and $Tb(hfaa)_4(picH)(pic)$ have the same lifetime within experimental error but quite different overall efficiencies. In the (tfaa) series $Tb(tfaa)_4(pipH)$ has a very low quantum efficiency but a lifetime similar to complexes with relatively high quantum efficiencies. We conclude therefore that although thermal depopulation causes decreases in the quantum efficiencies of these compounds between 77 and 293 K it is not sufficient to explain the observed ordering of quantum efficiencies at 293 K and that other loss mechanisms must be operative to varying extents.

TABLE 4

Room-temperature lifetimes and relative fluorescence outputs

Compound	τ_{293} [a] µs	Relative [b] fluorescence	Compound	τ_{293} [a] µs	Relative [b] fluorescence
$Tb(hfaa)_3,2H_2O$	559	****	$Tb(tfaa)_3,2H_2O$	473	***
$Tb(hfaa)_4(pipH)$	715	*****	$Tb(tfaa)_4(pipH)$	603	*
$Tb(hfaa)_4NH_4$	170	***	$Tb(tfaa)_4NH_4$	481	****
$Tb(hfaa)_4Ph_4As$	106	****	$Tb(tfaa)_4Ph_4As$	789	*****
$Tb(hfaa)_4Me_4N$	68	*	$Tb(tfaa)_4Na$	610	***
$Tb(hfaa)_4Me_3NH$	296	**	$Tb(tfaa)_4K$	474	***
$Tb(hfaa)_4Bu^tNH_3$	730	*****	$Tb(tfaa)_4Cs$	503	*****
$Tb(hfaa)_4(picH)(pic)$	293	*****			

[a] Derived from least-squares treatment of lifetime data. [b] Visual estimate of fluorescence output at 293 K when irradiated in 300—400 nm region; ***** very strong to * very weak.

Since the triplet states lie well below the Tb^{3+} $^5D_3$ state (*ca.* 26,000 cm^{-1}) transfer to this lanthanide level may be neglected and it therefore appears that significant losses occur in at least some cases before the ligand triplet T_1 (Figure 1). Figure 3 illustrates some of the possible energy-transfer routes with the ligand. The first excited singlet state may lose energy (*a*) by internal conversion into the ground state, k_7, (*b*) by fluorescence, k_8, (*c*) by intersystem crossing to T_1, k_9, and (*d*) by intersystem crossing to a lanthanide level such as the $^5D_3$, k_{10}. Intersystem crossing is expected to be a very efficient process in these complexes and it is improbable that singlet deactivation *via* k_7 and/or k_8 is a major process. No singlet fluorescence has been observed. Intersystem crossing from the singlet S_1 to the Tb^{3+} ion directly is a possible loss mechanism which may account for some of the anomalies. An alternative explanation is that the previous assumption, $k_3 \gg k_1 + k_2$ (Figure 1), is not justified for these complexes in the crystalline state.

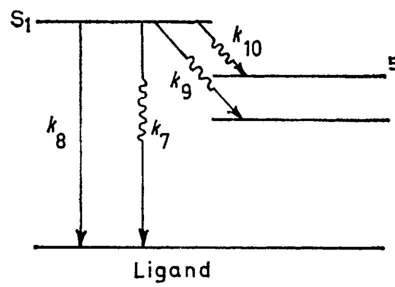

FIGURE 3 Possible routes of deactivation of the ligand singlet, S_1

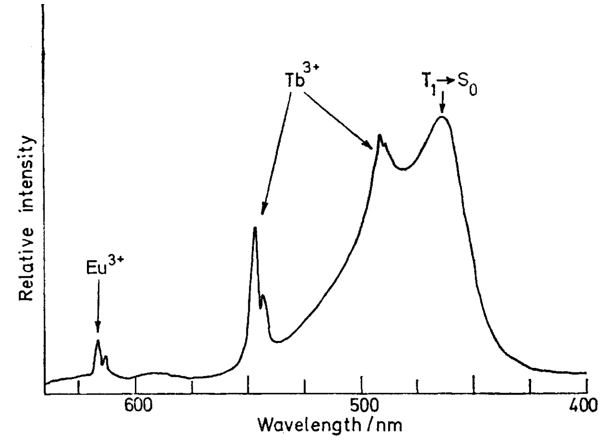

FIGURE 4 Room-temperature uncorrected emission spectra of $Gd(hfaa)_4Bu^tNH_3$

The relatively low triplet deactivation rates derived for the solid terbium complexes suggested that in at least some of the gadolinium complexes ligand phosphorescence should be detectable at room temperature. The room-temperature emission spectra of the gadolinium complexes were determined by use of a high resolution spectrofluorimeter and in all cases ligand triplet phosphorescence was observed. The intensity of this phosphorescence could not be directly related to the *A* values indicating that the radiative rate constant k_1 varies from complex to complex. Two examples of these spectra are given in Figures 4 and 5. The most notable feature of all these spectra is the terbium and europium emission which is due to impurities in the original Gd_2O_3 starting material at less than the 0·1% level. The intensities of the Eu^{3+} and Tb^{3+} are disproportionately high in terms of their relative concentrations. Current work in this laboratory[11] has shown that efficient migration of energy may occur in lanthanide chelate crystals *via* singlet and triplet exciton mechanisms and we consider the high lanthanide ion emissions observed above are

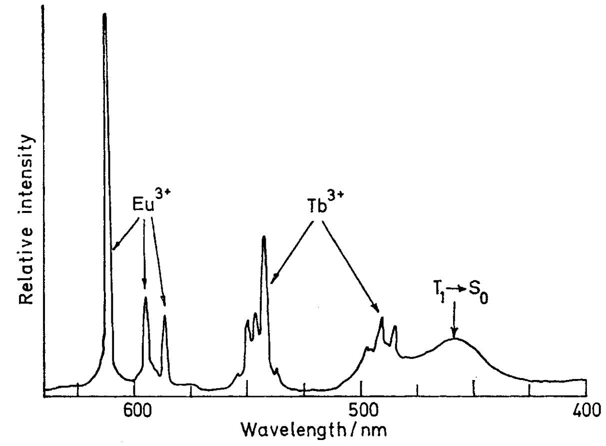

FIGURE 5 Room-temperature uncorrected emission spectra of $Gd(hfaa)_4Me_4N$

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[11] I. S. Curran and T. M. Shepherd, *J.C.S. Faraday II*, 1973, **69**, 126.

also due to varying degrees of exciton migration. The possibility of triplet exciton transfer introduces a further non-radiative deactivation route for individual triplet states and may make some contribution in the reported A values. This type of transfer should not however affect the overall efficiencies of the terbium chelates since the triplet energy is being redistributed but not lost.

[2/1574 *Received, 4th July,* 1972]