Anomalous Triplet-state Behaviour in Solid Tris(Dipivaloylmethanato)-terbium(III)

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Fluorescent decay times of solid Tb(dpm)$_3$ and its monoadducts with EtOH, EtOD, and pyridine have been determined over the temperature range 77—323 K. The decay time of Tb(dpm)$_3$, in contrast to the adducts, is markedly temperature-dependent. This anomalous behaviour is interpreted as a result of thermal population of a low-lying triplet state in Tb(dpm)$_3$ that does not occur in the adducts. This is supported by examination of analogous gadolinium complexes and the occurrence of this triplet is correlated with the known dimeric structure of Tb(dpm)$_3$.

MANY lanthanide β-diketoenolate complexes, especially those of terbium, europium, and samarium, when irradiated in the absorption band of the ligand, emit narrow line fluorescence † characteristic of the lanthanide ion. The general mechanism of this energy-transfer process has been established [1-3] and involves excitation of the ligand to its first excited singlet state, S_1, followed by intersystem crossing in the ligand to the lowest triplet level, T_1. Non-radiative transfer may then occur from T_1 to energetically suitable excited levels of the lanthanide ion and radiative decay of one or more of these levels gives rise to the observed fluorescence. The overall quantum efficiency of this process depends on the relative magnitude of the non-radiative decay rate constants between the ligand and lanthanide ion excited states and the ground state.

In the case of some terbium β-diketoenolate complexes it has been shown [4] that the energy difference between the emitting $^5D_4$ level of the Tb^{3+} ion and T_1 is small enough to allow significant thermal population of the ligand triplet from the $^5D_4$ with a consequent decrease in overall efficiency.[3] Thermal population of the triplet will be negligible if the T_1–$^5D_4$ energy separation is sufficiently large. For example, the fluorescent efficiency of Tb(aa)$_3$H$_2$O (aa = acetylacetonate), where the triplet T_1 lies *ca.* 5000 cm^{-1} above the $^5D_4$,[5] does not show any marked temperature-dependence below 50 °C.

We report in this paper spectroscopic measurements

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† Strictly the term phosphorescence should be used as the radiative transitions involve a change in spin multiplicity.

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of solid Tb(dpm)$_3$ (dpm = dipivaloylmethane anion) and some of its adducts. The complex Tb(dpm)$_3$ is shown to have considerably different spectroscopic properties from those of its adducts and these results are interpreted in terms of differences in the ligand triplet energy levels.

EXPERIMENTAL

Preparation of Tb(dpm)$_3$ *and* Gd(dpm)$_3$.—These compounds were prepared by the method of Eisentraut and Sievers [6] from 99·9% terbium and gadolinium oxides (Koch–Light) and purified by recrystallisation from dried AnalaR n-hexane or by sublimation at 180 °C, 0·01 mmHg. All samples gave satisfactory microanalytical results for C and H and were stored under anhydrous conditions.

Preparation of Adducts.—Solid monopyridine *adducts* of both Tb(dpm)$_3$ and Gd(dpm)$_3$ were obtained by recrystallisation of the anhydrous complexes from dried AnalaR pyridine. Tb(dpm)$_3$,py had m.p. 132—133 °C (Found: C, 58·2; H, 7·8; N, 1·9. $C_{38}H_{65}NO_6Tb$ requires C, 57·9; H, 7·9; N, 1·8%) and Gd(dpm)$_3$,py had m.p. 133—134 °C (Found: C, 57·8; H, 8·2; N, 1·6. $C_{38}H_{65}GdNO_6$ requires C, 58·1; H, 7·9; N, 1·8%). Adducts of Tb(dpm)$_3$ were prepared by recrystallisation from dried EtOH and EtOD and had m.p.s 156—157 and 155—156 °C respectively [Tb(dpm)$_3$ has m.p. 176—177 °C]. Theoretical %C and %H do not differ significantly from Tb(dpm)$_3$ and their stoicheiometry has not been established. However in view of the occurrence of a pyridine monoadduct these are probably monoadducts and are referred to as such in the text.

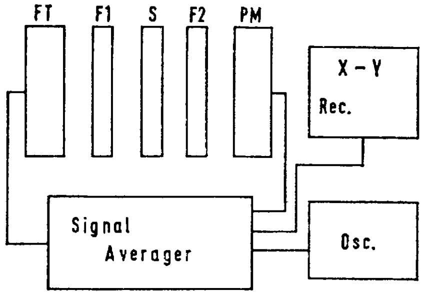

FIGURE 1 Schematic of lifetime apparatus. FT, flash tube with energy variable within the range 0·1—10 J and flash duration of <50 μs; F1, u.v. pass filter with passband *ca.* 300—400 nm; F2, u.v. absorbing filter with passband above 450 nm; S, thermostatted sample cell; PM, RCA IP28 photomultiplier, with cathode voltage −1000 V; Signal Averager, Data Laboratories Ltd., 200 point averager DL 102

Emission Spectra.—These were measured with a Perkin-Elmer–Hitachi MPF-2A spectrofluorimeter with a standard R106 photomultiplier. Emission slit widths corresponding to a resolution of 1 nm were used in all measurements. The spectra in Figures 3 and 6 are not corrected for variations in spectrofluorimeter response with wavelength. A correction curve has been obtained by measuring the emission spectra of solutions of 2-aminopyridine, quinine sulphate, 3-aminophthalimide, and *m*-nitrodimethylaniline and comparison of these spectra with absolute spectra.[7] The relative sensitivity of the spectrofluorimeter over the wavelength region of interest is shown in Figure 2.

Fluorescent Lifetime Measurements.—Exponential decay times of ⩾100 μs were determined with the apparatus depicted in Figure 1. A conventional lens arrangement was used and is omitted from the diagram. The fluorescence was detected normal to the excitation beam.

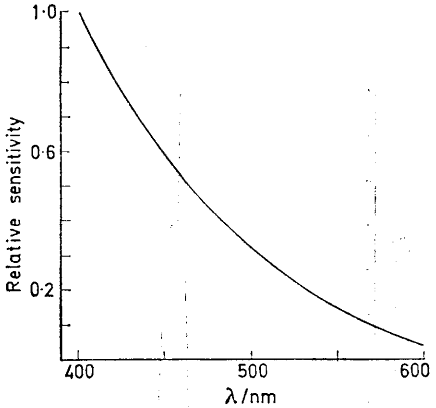

FIGURE 2 Spectral response curve of spectrofluorimeter

A trigger pulse from the signal averager initiated the flash and after a delay of 1—2 ms the photomultiplier output was sampled during, in most cases, 1 ms and the decay curve stored. The cycle was repeated to give a satisfactory signal-to-noise ratio. In general at least 64 cycles were obtained and the averaged decay curve transferred to the *X–Y* recorder. The averaging procedure was monitored on the oscilloscope.

The best straight-line relationship between the logarithm of the fluorescent intensity and time was computed by use of a least-squares method on an IBM 360/44 computer and the exponential decay time evaluated. The lifetimes obtained by this method were reproducible to better than ±3%.

RESULTS AND DISCUSSION

The crystal structure of Pr(dpm)$_3$ has been shown by Erasmus and Boeyens [8] to consist of dimeric units, Pr$_2$(dpm)$_6$, in which two of the β-diketoenolate oxygen atoms are shared by both praseodymium ions. The compound Tb(dpm)$_3$ is isomorphous with Pr(dpm)$_3$ and a similar dimeric molecular unit with seven-co-ordinate Tb^{3+} ions is indicated. It was also noted [9] that sublimed crystals of Tb(dpm)$_3$ contained some orthorhombic crystals in addition to the predominant monoclinic form. We have therefore made all spectroscopic measurements with both sublimed samples of Tb(dpm)$_3$ and with samples recrystallised from n-hexane but have obtained identical results within experimental error.

The emission spectrum of solid Tb(dpm)$_3$ is shown in Figure 3. The emission bands correspond to the Tb^{3+} transitions, $^5D_4 \longrightarrow {}^7F_6$ (*ca.* 490 nm), $^5D_4 \longrightarrow {}^7F_5$ (*ca.* 550 nm), and $^5D_4 \longrightarrow {}^7F_4$ (*ca.* 590 nm). The

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transitions ${}^5D_4 \longrightarrow {}^7F_3$, ${}^7F_2$, ${}^7F_1$, and ${}^7F_0$ were not observed owing to the low photomultiplier sensitivity in the region above 600 nm. Since all the observed transitions originate on the terbium ${}^5D_4$ level the fluorescent decay times reported below refer to the deactivation of this level.

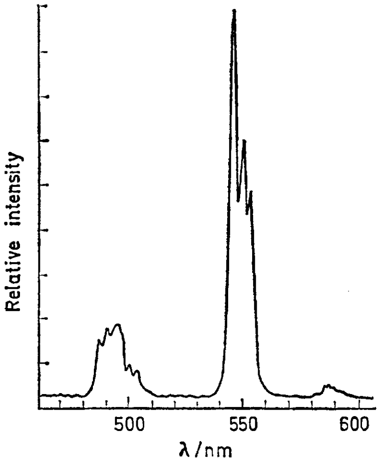

FIGURE 3 Emission spectrum of solid Tb(dpm)$_3$ at 20 °C. Excitation wavelength 320 nm

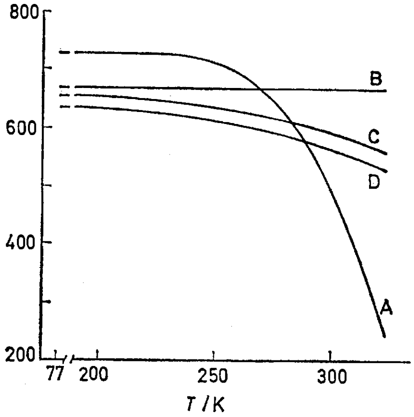

FIGURE 4 Temperature-dependence of the exponential decay time of A, Tb(dpm)$_3$; B, Tb(dpm)$_3$,py; C, Tb(dpm)$_3$,EtOD; and D, Tb(dpm)$_3$,EtOH

The relationship between the exponential decay time, τ, and sample temperature for solid Tb(dpm)$_3$ over the range 77—323 K is shown in Figure 4. τ remains constant between 77 and *ca.* 250 K and thereafter decreases rapidly with increasing temperature. This behaviour is in marked contrast to that shown by the solid monoadducts, Tb(dpm)$_3$A where A = pyridine, EtOH, and EtOD. The τ value of the pyridine adduct remains constant, within experimental error, over the entire temperature range studied and the ethanol adducts show only a relatively small decrease in τ at the higher temperatures (Figure 4). It was found that the relative quantum efficiency of Tb(dpm)$_3$ decreased at higher temperatures approximately in proportion to the observed τ; the efficiencies of the ethanol adducts showed a slight decrease with increasing temperature and that of the pyridine adduct remained almost constant over the temperature range. These results suggest that the efficiency of the non-radiative energy transfer from the ligand triplet state(s) to the ${}^5D_4$ is not significantly temperature-dependent, the decreasing quantum efficiencies where present being due to an increasing rate of deactivation of the ${}^5D_4$ level. The deuteriated adduct, Tb(dpm)$_3$,EtOD, has τ values *ca.* 5% higher than those of the corresponding EtOH adduct indicating that deactivation of the ${}^5D_4$ level involving OH vibrational modes only occurs to a very limited extent.

The anomalous behaviour shown by Tb(dpm)$_3$ may be attributed to the presence of one or more temperature-dependent deactivation processes in the solid which operate much less strongly, if at all, in the adducts. Such a process or processes, which may be represented by an overall deactivation rate constant, $k(T)$, would be accompanied by temperature-independent deactivation with rate constant k', as in equation (1), or if τ'

$$1/\tau = k(T) + k' \qquad (1)$$

is the decay time in the absence of any temperature-dependent deactivation then as in equation (2). It

$$k(T) = (1/\tau - 1/\tau') \qquad (2)$$

has been reported that in methanol and toluene solutions of $[\mathrm{Tb(tfaa)_4}]^-\mathrm{NH_4}^+$ (tfaa = trifluoroacetylacetonate) the ligand triplet state T_1, which lies 2500 cm^{-1} above the ${}^5D_4$ level, may be thermally populated by back-donation of energy, ${}^5D_4 \rightsquigarrow T_1$. The observed variation of lifetimes with temperature in these cases was successfully correlated with the established energy separation between the two energy levels.

If a single process occurs in solid Tb(dpm)$_3$ whereby the ${}^5D_4$ is thermally depopulated to a ligand level at energy E above the lanthanide level then expression (3)

$$(1/\tau - 1/\tau') = A\,\exp(-E/RT) \qquad (3)$$

should be obeyed, where A represents the deactivation rate constant of the ligand level. The value of τ for Tb(dpm)$_3$ at 77 K (*i.e.*, 730 μs) may be reasonably taken as τ' since no significant decrease in τ occurs between 77 and 250 K. The resulting straight-line plot (Figure 5) supports the presence of a single temperature-controlled mechanism and gives values of $E = 3050$ cm^{-1} and $A = 1{\cdot}6 \times 10^{10}$ s^{-1}. It further indicates that the transfer rate for the ligand level $\rightsquigarrow {}^5D_4$ is greater than A. Treatments of the slight temperature-dependence shown by the ethanol adducts were attempted but did not give straight-line plots. The above results suggest that Tb(dpm)$_3$ has a ligand acceptor level some 3050 cm^{-1} above the Tb^{3+} ${}^5D_4$ level ($\bar{\nu} = 20{,}500$ cm^{-1}), *i.e.*, at *ca.* 23,550 cm^{-1} above the ground state, and that this level is absent from the adducts.

To investigate this possibility the corresponding gadolinium complex Gd(dpm)$_3$ and its monopyridine adduct were prepared. $Gd(dpm)_3$ is isomorphous with $Tb(dpm)_3$.[8] The first excited state of Gd^{3+}, the $^6P_{7/2}$, lies 33,000 cm^{-1} above the ^8S ground state so that deactivation of the lowest triplet of β-diketoenolate ligands cannot occur *via* the lanthanide ion. The enforced phosphoresence of gadolinium complexes at low temperature thus allows the triplet energy of the ligand to be determined. Figure 6 shows the emission spectra of solid $Gd(dpm)_3$ and $Gd(dpm)_3$,py at 77 K.

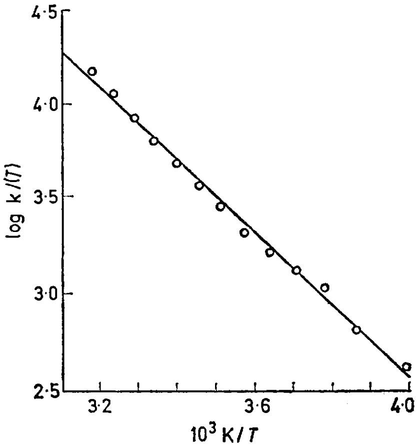

FIGURE 5 Plot of $\log_{10}(1/\tau - 1/\tau')$ against $1/T$ for solid $Tb(dpm)_3$

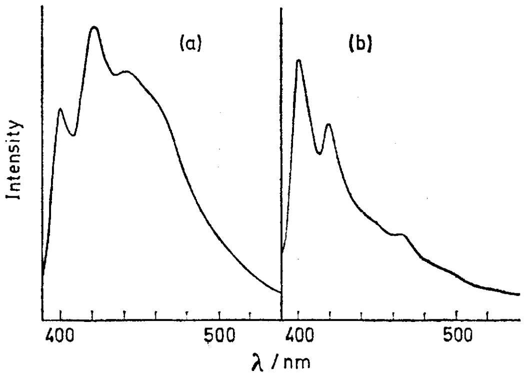

FIGURE 6 Emission spectra of solid (a) $Gd(dpm)_3$ and (b) $Gd(dpm)_3$,py at 77 K. Excitation wavelength 320 nm

The emission spectrum of $Gd(dpm)_3$,py is almost identical in profile to that of a 10^{-2}M solution of $Gd(dpm)_3$ in ethanol and indicates that the ligand triplet level T_1 lies *ca.* 25,000 cm^{-1} above the ground state. The emission spectrum of $Gd(aa)_3,2H_2O$ (aa = acetylacetonate) in 10^{-2}M ethanol solution also indicates a triplet level at *ca.* 25,000 cm^{-1}, in agreement with previous measurements.[5,9] The spectrum of solid $Gd(dpm)_3$ differs in profile from that of the pyridine adduct in having, in addition to a peak at 400 nm, a stronger peak at 424 nm. Although the stronger peak may be attributed to a transition from the triplet at 25,000 cm^{-1} to a vibrationally excited ground state level we suggest that it is caused by the presence of a second triplet level at *ca.* 23,600 cm^{-1}, in good agreement with the predicted value of 23,550 cm^{-1} obtained from the lifetime dependence of τ in $Tb(dpm)_3$.

The presence of two triplet states in this region may be correlated with the known dimeric structures of $Tb(dpm)_3$ and $Gd(dpm)_3$. We suggest that the higher triplet state at 25,000 cm^{-1} is characteristic of the (dpm) ligand with both oxygen atoms bonded to a single lanthanide, *i.e.*, the situation in the solid monomeric adducts and in four of the ligands of the dimeric unit $Ln_2(dpm)_6$, whereas the lower triplet is characteristic of the bridging (dpm) ligands in the dimer. The increased electron-withdrawing effect on the ligand caused by the proximity of the bridging oxygen atom to two lanthanide ions is qualitatively consistent with the triplet state occurring at lower energy. Further the structure[8] of the dimer indicates that relatively large deviations from planarity occur in the chelate rings involved in bridging and this is likely to affect the ligand electronic energy levels. Similar deviations from planarity have been reported for polymeric acetylacetonato-complexes.[9-11]

Our results indicate that the triplet energies of the ligand and hence the overall quantum efficiency of lanthanide chelates in the solid state depend on the environment of the ligand. We are investigating the effects of the nature of the cation in solid tetrakislanthanide complexes on the position of the ligand triplet.

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[2/480 *Received*, 1*st March*, 1972]

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