Use of the Fluorescence of Lanthanide Complexes to Study the Kinetics of a Ligand-transfer Reaction

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Summary The kinetics of the transfer of a 2,2′6′,2″-terpyridyl (terpy) molecule from [Eu terpy$_3$]$^{3+}$ to Tb^{3+} in nitromethane solution have been determined by a study of the fluorescence of the europium complex; the reaction is first order in [Eu terpy$_3$]$^{3+}$, independent of the Tb^{3+} concentration, and has $t_{\frac{1}{2}}$ = 6·1 min. at 2·8°.

THE limited evidence at present available indicates that lanthanide complexes are extremely labile.[1] However, we report a fairly slow ligand-exchange reaction. The kinetics of the reaction have been deduced from the fluorescence intensity of the species present, the absorption spectra of lanthanides being unsuitable for this type of study.

TABLE 1. *Intensity of emission of nitromethane solutions of mixed* [Eu terpy$_3$](ClO$_4$)$_3$ *and* [Tb terpy$_3$](ClO$_4$)$_3$ (*intensities given as peak heights in arbitrary units using the Beckmann DK2A with irradiation at* ca. 360 *nm*).

[Eu terpy$_3$]$^{3+}$ Molarity × 10^3	[Tb terpy$_3$]$^{3+}$ Molarity × 10^3	Intensity 595 nm (Eu)	Intensity 539 nm (Tb)
2·36	0	100	0
1·89	0·50	77	5·7
1·42	0·99	57	10·7
0·94	1·49	37	18·6
0·47	1·98	21	25·7
0	2·48	0	34·3

Many lanthanide complexes fluoresce strongly in the solid state by an intramolecular energy-transfer process;[2,3] less usually, this occurs in solution also.[4] Thus a nitromethane solution of [Eu terpy$_3$](ClO$_4$)$_3$,[3] fluoresces at 595 nm ($^5D_0 \rightarrow {}^7F_J$) when irradiated at *ca.* 360 nm. Upon addition of terbium perchlorate, the red fluorescence is slowly replaced by a green fluorescence from the terbium transitions $^5D_4 \rightarrow {}^7F_J$. We interpret this change as being caused by the reaction,

$$[\text{Eu terpy}_3]^{3+} + \text{Tb}^{3+} \rightarrow [\text{Eu terpy}_2]^{3+} + [\text{Tb terpy}]^{3+}.\dagger$$

The intensity of the 595 nm fluorescence is interpreted as directly proportional to the concentration of [Eu terpy$_3$]$^{3+}$. The evidence for these conclusions is as follows. Firstly, mixtures of [Eu terpy$_3$](ClO$_4$)$_3$ and [Tb terpy$_3$](ClO$_4$)$_3$ fluoresce at 595 nm with an intensity proportional to the [Eu terpy$_3$]$^{3+}$ concentration (Table 1). Secondly, equilibrated mixtures of europium perchlorate and terpyridyl show intense fluorescence only near a 1 : 3 mole ratio (Table 2); evidently the species [Eu terpy]$^{3+}$ and [Eu terpy$_2$]$^{3+}$ do not fluoresce appreciably.

The rate of decay of the 595 nm fluorescence (Table 3) is unaffected by a tenfold decrease in the initial concentration of terbium perchlorate; this preliminary indication that the mechanism may be:

$$[\text{Eu terpy}_3]^{3+} \xrightarrow{\text{R.D.}} [\text{Eu terpy}_2]^{3+} + \text{terpy}$$

$$\text{terpy} + \text{Tb}^{3+} \xrightarrow{\text{fast}} [\text{Tb terpy}]^{3+}$$

is confirmed by (a) the first-order plot of fluorescence intensity *v* time (b) the observation that addition of terpyridyl (1 mol.) to an 0·01M-solution of terbium perchlorate gives an 'instant' green fluorescence in the region 490—550 nm due to the formation of [Tb terpy]$^{3+}$.‡

TABLE 2. *Intensity of emission of nitromethane solutions of mixed europium perchlorate* (0·0200 M) *and terpyridyl. Other details as for Table* 1

Mole ratio, Eu/terpy	0	0·78	1·62	2·29	2·85	3·10	3·46	3·73
Intensity at 595 nm	0	0	4·7	58·4	91·8	100	27.3	7·8

TABLE 3. *Variation of intensity of fluorescence* (F) *with elapsed time.* F$_0$ *is initial intensity. Solution in nitromethane of* [Eu terpy$_3$]-(ClO$_4$)$_3$ (0·00217M) *and terbium perchlorate* (0·0184M). *Other details as in Table* 1. *From* 7 *runs at* 2·8°, k = 0·0019 *sec*$^{-1}$.

Time (sec.)	0	100	200	300	400	500	600	700	800	900	1000
F	80	67	56	46·5	38	31·5	25·5	21	17	14	12
ln (F_0/F)	0	0·076	0·155	0·235	0·33	0·405	0·50	0·58	0·67	0·76	0·82

At 2·8° the first-order rate constant is 0·0019 sec^{-1}. Evidently the entropy effect of a terdentate ligand is sufficient to place the rate constant in this conveniently studied region. The implications of the mechanism suggested are more appropriately discussed elsewhere.

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† The latter three species are presumably solvated by nitromethane.

‡ The ligand transfer reaction could in principle also be followed by a study of the terbium fluorescence; the latter is however, in this as in other cases, much less characteristic of individual complex species than is the Eu fluorescence. We emphasise that the reaction is not photochemical, as the rate is unaffected by prolonged extinction of the fluorescence-inducing irradiation.

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