Studies of the Conformations of the N.m.r. Shift Reagent Tris(2,2,6,6-tetramethylheptane-3,5-dionato)europium(III) and its Adducts by means of Fluorescence Spectra

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Fluorescence spectra of the n.m.r. shift reagent tris(2,2,6,6-tetramethylheptane-3,5-dionato)europium(III) and some of its adducts are reported and deductions made regarding equilibria and conformations in solution.

IN order to understand quantitatively the n.m.r. shifts induced in a substrate by a lanthanoid-shift reagent, the exact conformation of the adduct must be known. We may then, assuming that pseudo-contact effects only are present, use the relation:[1] $\Delta H/H_0 = [(\chi_z - \bar{\chi})(3\cos^2\theta - 1) + (\chi_x - \chi_y)\sin^2\theta\cos 2\phi]/2Nr^3$. The important question, however, arises as to whether a single conformation obtains in solution, or whether more than one is involved whose averaged n.m.r. shifts are observed. This question cannot in all cases be answered by means of n.m.r. measurements alone. Moreover, it would be of considerable interest if adduct conformation in solution could be established by methods other than n.m.r., as such data would constitute an independent test of the validity of the current usage of the pseudo-contact equation for conformation determination.

Although axial symmetry is usually assumed in practical calculations and appears to be justified by results,[2,3] a static axis of symmetry would in most cases not be expected. Thus *X*-ray determinations show two main types of structure adopted by adducts of lanthanoid tris(β-diketonates). Only two examples have a C_3 axis in the crystalline state [structure (I), a distorted capped octahedron], namely [$\text{Ho(PhCO{\cdot}CH{\cdot}COPh)}_3\text{H}_2\text{O}$] [4] and, imperfectly, [$\text{Y(PhCO{\cdot}CH{\cdot}COMe)}_3\text{H}_2\text{O}$].[5] There are many examples which have no such axis,[6,7] adopting structures approximating to

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[1] B. Bleaney, *J. Magnetic Resonance*, 1972, **8**, 91.

[2] J. Briggs, F. A. Hart, and G. P. Moss, *Chem. Comm.*, 1970, 1506.

[3] M. R. Willcott, tert., R. Lankinski, and R. E. Davis, *J. Amer. Chem. Soc.*, 1972, **94**, 1742.

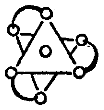
[4] A. Zalkin, D. H. Templeton, and D. G. Karraker, *Inorg. Chem.*, 1969, **8**, 2680.

[5] F. A. Cotton and P. Legzdins, *Inorg. Chem.*, 1968, **7**, 1777.

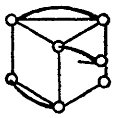
[6] R. M. Wing, J. J. Uebel, and K. K. Andersen, *J. Amer. Chem. Soc.*, 1973, **95**, 6046.

[7] D. L. Kepert, *J.C.S. Dalton*, 1974, 617 and refs. therein.

(II), a distorted face-centred trigonal prism. Calculations [7] of the oxygen–oxygen repulsions on an electrostatic model have provided a theoretical basis for the particular stability of structures (I) and (II) relative to other possible structures.



(I)



(II)

Very few substrate ligands have a C_3 axis themselves, and even if a configuration similar to (I) [rather than (II)] were adopted, strict three-fold symmetry of the seven ligand atoms might well be prevented by steric interaction in the periphery of the adduct. Rotation of the substrate about any axis which passes through the lanthanoid ion will, however, give the effect of a uniaxial susceptibility tensor [8] and hence agreement with experimental results will be obtained. It would be surprising, however, if such rotation did not involve a preferred orientation or orientations which, if the complex did not itself possess a three-fold axis, would lead to partial loss of the averaging effect.

RESULTS AND DISCUSSION

Fluorescence Spectra.—(a) *Introduction*. Studies of fluorescence and absorption spectra of lanthanoid compounds, especially the fluorescence spectra of europium(III), have achieved some success in determining molecular symmetry. An early result was the correct assignment [9] of near-icosahedral symmetry (I_h slightly distorted to C_3) to the series of lanthanoid double nitrates $[Mg(H_2O)_6]_3[M(NO_3)_6]_2,6H_2O$. Later assignments [10,11] have included $[Et_4N][Eu(PhCO{\cdot}CH{\cdot}COPh)_4]$ (D_2) and $[Eu(terpy)_3][ClO_4]_3$ (terpy = 2,2′:6′,2″-terpyridyl; D_3 slightly distorted to C_2).

Although fluorescent spectra give useful information concerning solids at low temperatures, considerable problems arise at higher temperatures and in solution, as discussed below. However, in view of the fact that direct investigation of the co-ordination geometry in solution at an instantaneous time (*i.e.* not time averaged) is in principle possible by this method and by no other, it seemed highly desirable to investigate the fluorescence spectra of europium-shift reagents. Fluorescence spectra have been reported [12-15] of a number of lanthanoid β-diketonates from the groups $[M(RCO{\cdot}CH{\cdot}COR')_3]$, $[M(RCO{\cdot}CH{\cdot}COR')_4]^-$, and $[M(RCO{\cdot}CH{\cdot}COR')_3L]$ [M = Eu or Tb; R, R′ = Me, CF_3, CMe_3, Ph, or 2-C_4H_3S; L = 1,10-phenanthroline, $P(O)Ph_3$ or $P(O)(n\text{-}C_8H_{17})_3$]. The solution studies, performed in connection with possible laser systems, employed chilled alcohol glasses without exclusion of moisture. The constitution of the lanthanoid species involved must remain uncertain.

Complexes of europium(III) having conjugated ligands will absorb radiation at *ca.* 300 nm, a ligand molecule being excited. The excitation energy, by an intramolecular process,[16] is transferred to the *f*-electron system of the europium ion, which will then occupy a component of the excited $^5D_0$–$^5D_4$ multiplet. The relaxation time among these components is very short (*ca.* 10^{-12} s) so that a Boltzmann distribution is obtained, *i.e.* the lowest component, $^5D_0$, is predominantly populated. This has a lifetime of 10^{-4}—10^{-3} s after which a transition occurs to a component of the ground-state multiplet, $^7F_0$–$^7F_6$. This last transition may or may not involve a simultaneous vibrational transition also, and results in emission of a quantum of light. The overall process has a quantum efficiency which can approach unity.

Information regarding point-group symmetry can be obtained because the ligand field may split the degenerate electronic levels, *e.g.* the $^7F_1$ level remains degenerate (T_{1g}) in a cubic field, but splits into two levels (A_{2g} and E_g) in a ligand field of D_{3d} symmetry, or into three ($A_g + 2B_g$) under C_{2h}. A fluorescence transition between two levels is allowed if their direct products transform as x,y,z (for an electric-dipole transition) or as R_x,R_y,R_z (for a magnetic-dipole transition). Thus in D_{3d} symmetry, two transitions will be observed from $^5D_0$ (A_{1g}) to $^7F_1$ (A_{2g}, magnetic dipole; E_g, magnetic dipole), but none to $^7F_0$ (A_{1g}, inactive). Hence an analysis of the number of $^5D_0 \rightarrow {}^7F_J$ transitions observed for each value of J will considerably restrict the choice of molecular point group, and together with a consideration of the molecular stoicheiometry may sometimes indicate it uniquely.

(b) *Experimental results*. Fluorescence spectra of the following were obtained from Nujol mulls or from solutions in CH_2Cl_2–$CHCl_3$–CCl_4 (5 : 5 : 1): $Eu(tmhd)_3$ at −196 (mull) and 25, −78, and −196 °C (solution); $Eu(tmhd)_3$ doped into $[Er(tmhd)_3]$ host at −196 °C (mull); $[Eu(tmhd)_3\{P(O)Ph_3\}]$ at 25 and −196 °C (mull or solution); $[Eu(tmhd)_3(py)_2]$ at −196 °C (mull or solution); and $[Eu(tmhd)_3(bn)]$ at 25, −78, and −196 °C (solution) (tmhd = 2,2,6,6-tetramethylheptane-3,5-dionato, py = pyridine, and bn = borneol). $[Eu(tmhd)_3\{P(O)Ph_3\}]$ is apparently a new compound; the Sm and Tb analogues were also prepared.

(c) *Interpretation*. Fluorescence spectra of lanthanoid compounds, when obtained from the solids at low temperatures, may contain groups of lines on the long-wavelength side of the pure electronic transitions. These groups correspond to simultaneous excitation of a

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[10] S. Borklund, N. Filipescu, N. McAvoy, and J. Degnan, *J. Phys. Chem.*, 1968, **72**, 970.

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[15] C. Brecher, H. Samelson, and A. Lempicki, *J. Chem. Phys.*, 1965, **42**, 1081.

[16] G. A. Crosby and R. E. Whan, *J. Chem. Phys.*, 1962, **36**, 863.

vibrational mode of the complex, very probably a metal–ligand stretching mode which would have a wavenumber of the order of 400 cm^{-1}. When obtained from solution at higher temperatures, as is necessary if it is desired to investigate shift-reagent adducts under the conditions in which they are commonly used, further difficulties are manifest. First, additional lines may appear owing to thermal population of vibrationally excited states of the $^5D_0$ term. Secondly, considerable broadening occurs probably due to the instantaneous effect on the ligand-field symmetry of metal–ligand vibrations of increased amplitude and of small ligand displacements caused by random ligand–solvent intermolecular forces.

[Eu(tmhd)$_3${P(O)Ph$_3$}]. Figure 1 shows that the $^5D_0 \to {}^7F_2$ transition was much the most intense, being a triplet with the short-wavelength component showing a further splitting of *ca.* 2 Å. The $^5D_0 \to {}^7F_0$ was a singlet and $^5D_0 \to {}^7F_1$ a doublet. In the ranges 5 930—6 010 and 6 220—6 280 Å, less intense and broader bands were found which we assign as vibronic transitions. Thus the two emissions on the low-energy side of $^5D_0 \to {}^7F_1$ were 210—470 cm^{-1} distant from the pure electronic transition, an energy difference which can very reasonably be associated with simultaneous excitation of a Eu–O vibrational mode. Confirmation that the low-energy lines were not caused by traces of other lanthanoids was provided by obtaining the corresponding spectra of the analogous Tb and Sm compounds, in which these lines proved to be absent (Tb and Sm are the only lanthanoid impurities expected to be detectable if present).

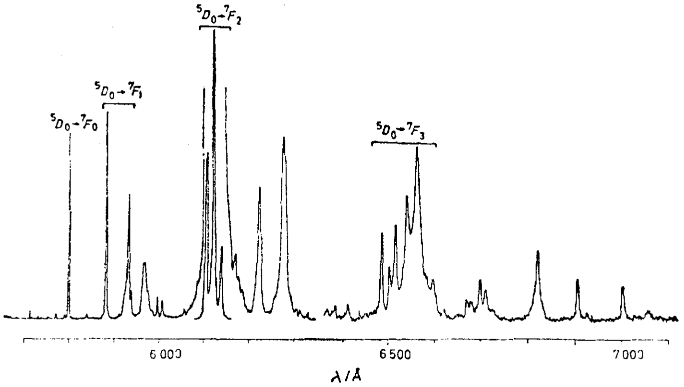
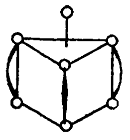
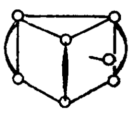


FIGURE 1 Fluorescence spectrum of [Eu(tmhd)$_3${P(O)Ph$_3$}] from a Nujol mull at −196 °C



(III)



(IV)

The two highest-symmetry point groups possible for this compound are C_3 and C_{3v} corresponding to the geometries (I) and (III) respectively. Allowed transitions would be:

	$^5D_0 \to {}^7F_0$	$^7F_1$	$^7F_2$	$^7F_3$
C_{3v}	A_1	$A_2 + E$	$A_1 + 2E$	$A_1 + 2A_2 + 2E$
C_3	A	$A + E$	$A + 2E$	$3A + 2E$

Configurations based on a face-centred prism have either C_1 or C_{2v} symmetry, corresponding with the geometries (II) and (IV). For both these, splitting is into $2J + 1$ levels, and all transitions are active, so 1, 3, 5, and 7 lines are expected for $^5D_0 \to {}^7F_0$, $^7F_1$, $^7F_2$, and $^7F_3$ respectively. The observed splitting was 1, 2, and 3 for $^5D_0 \to {}^7F_0$, $^7F_1$, and $^7F_2$. In the case of the $^5D_0 \to {}^7F_3$ transition we cannot clearly distinguish the pure electronic from the vibronic bands, but the observed multiplet is not inconsistent with a five-line electronic spectrum. We therefore suggest that, in the solid state, [Eu(tmhd)$_3${P(O)PPh$_3$}] has one of the configurations (I) or (III), very probably (III) which is a previously observed configuration [7] and appears to have less interligand repulsion than (I). The crystallographic symmetry must, however, be slightly lower than three-fold as indicated by the minimal splitting of the 6 105 Å peak. Other instances where ideal symmetry is reduced by crystal-packing forces are [Er(tmhd)$_3$] [17] and [Eu(terpy)$_3$][ClO$_4$]$_3$.[18] In glass solution at −196 °C the spectrum was broadened for the reasons given above and could not by itself be used for direct assignment of configuration. However, it is clear that this spectrum (Figure 2) is derived from the solid-state spectrum merely by broadening and does not differ from it in any essential feature; hence the structure in solution is the same as in the solid state. At 25 °C the broadening process was continued, both in the solution and solid spectra.

To obtain a more complete understanding of the fluorescence process and of the energy levels of the ^5D_J states, the absorption and excitation spectra of [Eu(tmhd)$_3${P(O)Ph$_3$}] were obtained. In the absorption spectrum in CH_2Cl_2 solution, the complex showed a broad intense (ε 39 900 l mol^{-1} cm^{-1}) band with $\lambda_{max.}$ at 289 nm associated with the β-diketonate system. A weak sharp band (ε 25 l mol^{-1} cm^{-1}) at 464 nm is assigned as $^7F_0 \to {}^5D_2$ and a weaker band (ε 4 l mol^{-1} cm^{-1}) at 535 nm showing splitting as $^7F_0 \to {}^5D_1$; $^7F_0 \to {}^5D_0$ was detectable (ε *ca.* 1 l mol^{-1} cm^{-1}) at 579 nm. The excitation spectrum, obtained by measuring the $^5D_0 \to {}^7F_2$ emission at 612 nm, showed that all three $^7F_0 \to {}^5D_J$ ($J = 0$—2) absorption bands produce efficient emission by simple direct excitation of the Eu^{3+} ion. That indirect energy transfer through preliminary ligand excitation is also effective was shown by broad excitation bands at 314 and 330 nm. Presumably these are associated with the broad 289 nm β-diketonate absorption which is, however, ineffective at its position of maximum absorption. This last result could be caused by saturation of the surface layers at the

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[17] J. P. R. de Villiers and J. C. A. Boeyens, *Acta Cryst.*, 1971, **B27**, 2335.

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relatively large absorption coefficients near the band centre.

These results enable the energy levels of the baricentres of the following states of $[Eu(tmhd)_3\{P(O)Ph_3\}]$ to be listed: $^7F_0$, 0; $^7F_1$, 346; $^7F_2$, 890; $^7F_3$, 2 010; $^5D_0$, 17 250; $^5D_1$, 18 730; and $^5D_2$, 21 550 cm^{-1}.

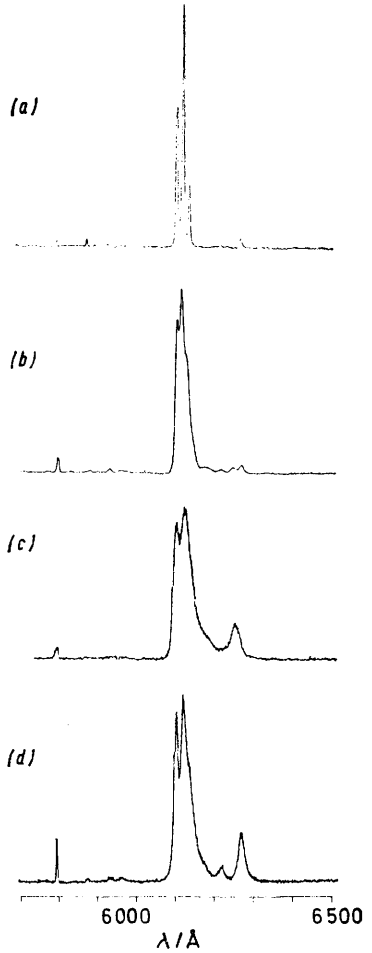

FIGURE 2 Fluorescence spectra of $[Eu(tmhd)_3\{P(O)Ph_3\}]$: (*a*), Nujol mull at −196 °C; (*b*), solution in CH_2Cl_2–$CHCl_3$–CCl_4 (5 : 5 : 1) at −196 °C; (*c*), solution at 25 °C; (*d*), Nujol mull at 25 °C

$Eu(tmhd)_3$. The shift reagent $Eu(tmhd)_3$ was studied in the absence of any substrate. In the solid state $Eu(tmhd)_3$ is dimeric with C_1 symmetry as are all $M(tmhd)_3$ (M = La to Gd);[19] it is predominantly monomeric in carbon tetrachloride solution above 37 °C.[20] The compounds $M(tmhd)_3$ (M = Ho to Lu) are reported as monomeric with near-D_{3h} symmetry in the solid state,[17] while the Tb and Dy compounds have been isolated in both forms.[19] We find that the holmium compound can also be obtained in both forms as $[Ho(tmhd)_3]$ and $[Ho_2(tmhd)_6]$. The monomer was obtained by crystallisation from light petroleum (b.p. 60—80 °C) or by sublimation at 0·1 mmHg along a glass tube maintained at ambient temperature. Crystallisation from aqueous alcohol followed by drying over P_4O_{10} gave a mixture of monomer with dimer. Sublimation on to a probe at −196 °C at 0·1 mmHg can give the pure dimer, but usually gave a mixture of dimer and monomer in proportions which were not reproducible in successive experiments and may depend on seeding. This type of isomerism, where a monomer and its directly associated dimer both exist in the solid state, is quite unusual. Besides distinguishing between the dimer and monomer by *X*-ray determination of the space group, we find that distinction by i.r. spectrum is possible (details of band positions are given below).

The fluorescence spectrum of $Eu(tmhd)_3$ (Figure 3) at −196 °C showed $^5D_0 \rightarrow {}^7F_2$ as much the most-intense transition with splitting into all $2J + 1$ peaks, consistent with the C_1 symmetry at the europium ion. Surprisingly, in glass solution at −196 °C and in mobile solution at −78 °C, this spectrum though somewhat broadened was still perfectly characteristic of the dimeric structure. There is therefore temperature dependent dissociation of the dimer in solution. To obtain the spectrum of the solid monomer, $[Er(tmhd)_3]$ was crystallised from pentane in the presence of 3% $Eu(tmhd)_3$. The spectrum of the doped specimen at

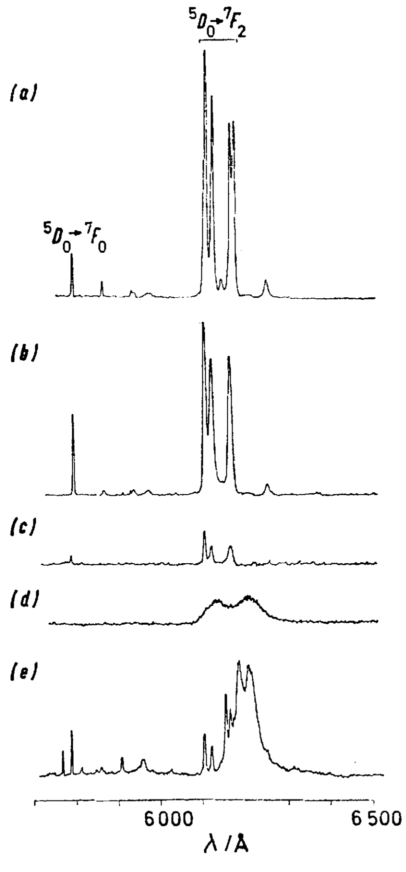

FIGURE 3 Fluorescence spectra of $Eu(tmhd)_3$: (*a*), Nujol mull at −196 °C; (*b*), solution at −196; (*c*), at −78; (*d*), at 25 °C; (*e*), in $[Er(tmhd)_3]$ host in Nujol mull at −196 °C

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[19] C. S. Erasmus and J. C. A. Boeyens, *Acta Cryst.*, 1970, **B26**, 1843.

[20] J. S. Ghotra, F. A. Hart, G. P. Moss, and M. L. Staniforth, *J.C.S. Chem. Comm.*, 1973, 113.

—196 °C {pure [Er(tmhd)$_3$] did not fluoresce} showed only traces of the dimer, and was a rather broad multiplet at *ca.* 6 200 Å. The broadening is presumably due to packing variations in lattice site symmetry in the doped sample. Comparison of the spectra of the monomer and dimer with the very broadened solution spectrum at 25 °C is not inconsistent with occurrence of a monomer–dimer exchange process at 25 °C in solution. The compound was too insoluble to permit determination of its molecular weight by depression of freezing point, even in ethylene dibromide.

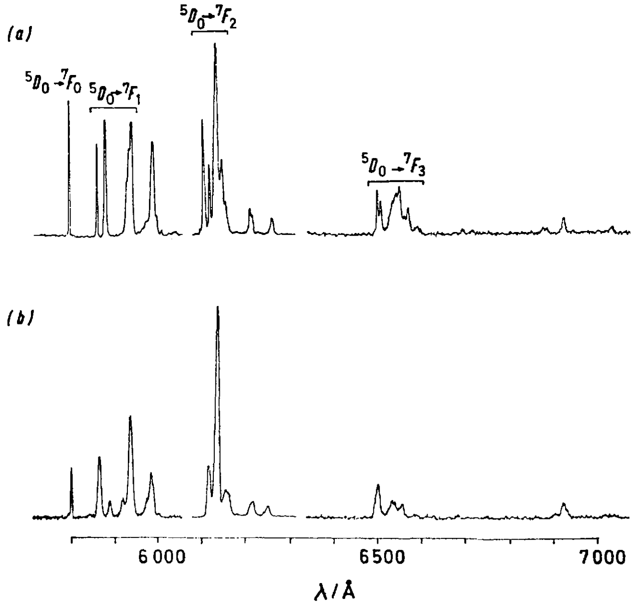

FIGURE 4 Fluorescence spectra of [Eu(tmhd)$_3$(py)$_2$] at —196 °C in Nujol mull (*a*) and solution (*b*)

When a spectrum was obtained from a solution of Eu(tmhd)$_3$ which had been prepared normally, instead of under the strictly anhydrous conditions which were used throughout all other experiments, a quite different spectrum was observed with a dominant $^5D_0 \to {}^7F_2$ triplet at 6 113, 6 124, and 6 130 Å. This clearly shows the necessity of anhydrous conditions in order to obtain comparability of experimental results in investigations of shift reagents.

[Eu(tmhd)$_3$(py)$_2$]. This compound, which has near-C_2 symmetry in the solid state [21] and being eight-co-ordinate is likely to be configurationally fairly rigid in solution, showed (Figure 4) a 1,3,5-line spectrum characteristic of low symmetry in a mull at —196 °C. As a glass solution at —196 °C there was broadening and some alterations in band intensities but the spectrum as a whole was relatively little changed. Hence the solid-state configuration of the complex remains unaltered in solution, a result which agrees with the reported correspondence between the observed solution n.m.r. shifts of the similar [22] compounds [M(tmhd)$_3$(4-Mepy)$_2$] (M = Pr to Yb) and those calculated using a susceptibility tensor whose magnitudes were experimentally obtained from measurements on single crystals.[23]

Adduct between Eu(tmhd)$_3$ *and borneol.* In this case there is evidence for 1 : 1 adduct formation in solution,[20] but we obtained only a poorly crystalline solid adduct on evaporation of a 1 : 1 mixture in solution. Even at —196 °C, a glass solution of the adduct showed a spectrum (Figure 5) which was very much broader than those of [Eu$_2$(tmhd)$_6$], [Eu(tmhd)$_3$(py)$_2$], or [Eu(tmhd)$_3${P(O)Ph$_3$}] and broadened still further at higher temperatures. The vibronic transitions at *ca.* 6.280 Å were of considerable relative intensity and were at *ca.* 420 cm^{-1} to low energy of the main $^5D_0 \to {}^7F_2$ peak, again a reasonable value for Eu–O stretching modes. The broadened spectra strongly suggest that the borneol adduct is configurationally labile and has no single preferred co-ordination geometry in solution, in contrast to [Eu(tmhd)$_3$(py)$_2$] which is more crowded being eight-co-ordinate or [Eu(tmhd)$_3${P(O)Ph$_3$}] where the phosphine oxide ligand has itself three-fold symmetry and would conform well to the steric requirements of the β-diketone ligands in a symmetrical structure such as (I).

A space-filling molecular model of the borneol adduct which takes account of interhydrogen repulsions shows that very little reorganisation of the ligands is needed to interconvert the symmetrical capped octahedral (c.o.) structure (I) with the face-centred prismatic (f.p.) arrangement (II). The main motion required to convert c.o. into f.p. is for only one of the three β-diketonate ligands to twist into a position more parallel with the C_3 vertical axis and with its central CH group at a rather greater angular distance from the substrate molecule. The other two ligands need only minor

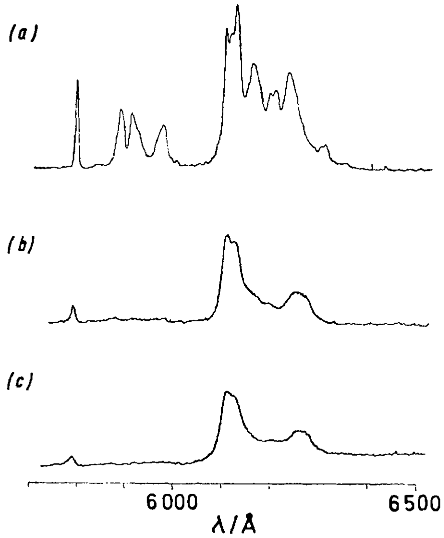

FIGURE 5 Fluorescence spectra of Eu(tmhd)$_3$ in solution together with borneol (1 mol) at —196 (*a*), —78 (*b*), and 25 °C (*c*)

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[21] R. E. Cramer and K. Seff, *Acta Cryst.*, 1972, **B28**, 3281.

[22] W. De W. Horrocks, jun., J. P. Sipe, tert., and J. R. Luber, *J. Amer. Chem. Soc.*, 1971, **93**, 5258.

[23] W. de W. Horrocks, jun., and J. P. Sipe, tert., *Science*, 1972, **177**, 994.

adjustment. With a substrate such as borneol, whose own low symmetry imposes no preference for three-fold symmetry on the adduct, this interconversion is expected to be of very low activation energy. Further, the correlation times for c.o.–f.p. interconversion and for borneol rotation are unlikely to be the same. This might provide a means of decoupling the steric interaction between the substrate and the three β-diketone ligands which could otherwise lead to a preferred rotational orientation of the substrate. Such a preferred orientation would in turn lead to loss of the time-averaged uniaxial tensor which is in fact experimentally observed [2,3] to be present.

EXPERIMENTAL

Lanthanoid oxides of 99·9% purity were obtained from Rare Earth Products Ltd.

Tris(2,2,6,6-*tetramethylheptane*-3,5-*dionato*)(*triphenylphosphine oxide*)*europium*(III) *and Analogues*.—The compound Eu(tmhd)$_3$ (0·126 g) and P(O)Ph$_3$ (0·050 g, 1 mol) were stirred under reflux in the minimum of dry light petroleum (b.p. 60—80 °C) (*ca.* 2 cm^3) until dissolved. The ***product*** crystallised on cooling (85% yield), m.p. 266—274 °C ***in vacuo*** (Found: C, 62·6; H, 7·4; Eu, 15·6. Calc. for $C_{51}H_{72}EuO_7P$: C, 62·5; H, 7·4; Eu, 15·5%). The crystals were colourless but with a pink fluorescence. The space group was $P2_1/a$, with $Z = 4$. In the i.r. spectrum (Nujol mull), ν(PO) occurred at 1 179 cm^{-1}. Similarly prepared were the analogous cream ***samarium*** compound (Found: C, 62·6; H, 7·4. Calc. for $C_{51}H_{72}O_7PSm$: C, 62·6; H, 7·4%), m.p. 261—269 °C ***in vacuo***, and the very pale green terbium compound (Found: C, 62·0; H, 7·4. Calc. for $C_{51}H_{72}O_7PTb$: C, 62·1; H, 7·4%), m.p. 255—270 °C ***in vacuo***.

Monomeric and Dimeric Forms of Tris(2,2,6,6-*tetramethylheptane*-3,5-*dionato*)*holmium*(III).—The i.r. spectra of the two forms (Nujol or hexachlorobutadiene mulls) follow, with diagnostic features italicised. Monomer: 2 961vs; 2 933w; 2 905m; 2 864m; *1 596m*; 1 571p; 1 551s; 1 546 (sh); 1 525w; 1 506s; 1 479w; 1 461 (sh); 1 451m; 1 401s; 1 384m; 1 360 (sh); 1 357s; 1 289w; 1 248w; 1 230s; 1 198w; 1 176m; *1 146s*; 1 026w; *966m*; *937w*; *933* (*sh*); 875s; 823w, *799s*; 767m; 737w; 726 (sh); 613s; 577w; *490m*; and *476w*. Dimer: 2 964 (sh); 2 954s; 2 906w; 2 870m; *1611* (*sh*); *1 594* (*sh*); *1 587* (*sh*); *1 581s*; 1 572s; 1 552m; 1 538m; 1 508 (sh); 1 502s; 1 481w; 1 463w; 1 451m; 1 404s; 1 384s; 1 372w; 1 305s; 1 281m; 1 246w; 1 229s; 1 200w; 1 182m; *1 148w*; *1 133s*; 1 025w; *963* (*sh*); *953w*; *938w*; *932w*; 872s; 823w; *806m*; *795m*; 763m; 740m; 723 (sh); 602m; and *478s* cm^{-1}. The first spectrum is very closely matched by monomeric compounds of the heavier lanthanoids, as is the second spectrum by dimeric compounds of the lighter lanthanoids.

Fluorescence Spectra.—Shift reagents and borneol were sublimed before use, while the 5 : 5 : 1 CH_2Cl_2–$CHCl_3$–CCl_4 solvent was dried over CaH_2 and distilled from it in a closed apparatus. Without exposure to air at any stage, using a nitrogen-filled glove-box where necessary, solutions (*ca.* 5 mg cm^{-3} concentration) or mulls were made up and transferred to an annular cavity in a specially constructed quartz cell. The cavity was cooled by refrigerant on the inside if required and was vacuum jacketed on its outer surface. The cell was irradiated by a low-pressure Hg vapour lamp (Allen, type A409). The radiation emitted from the sample traversed a Bass Kessler grating monochromator and was recorded by means of a 35 mm camera, giving a dispersion of *ca.* 40 Å mm^{-1}. A xenon discharge lamp provided calibration. The resulting films were traversed with a microdensitometer to yield the Figures, resolution being *ca.* 2 Å.

Excitation Spectra.—These were obtained, using an Aminco–Bowman spectrophotofluorometer, from CH_2Cl_2 solutions at *ca.* 1 mg cm^{-3} concentration.

Absorption Spectra.—These were obtained, using a Perkin-Elmer 402 spectrophotometer, from CH_2Cl_2 solutions at *ca.* 0·2 or 10 mg cm^{-3} concentration in 1 cm cells.

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