Solvent Dependence of the Optical Activity associated with Tris(DD-dicampholylmethanato)europium(III) *

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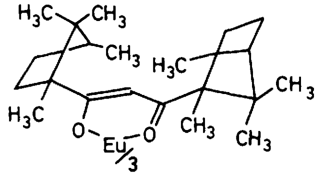
Circularly polarized luminescence (c.p.l.) spectroscopy has been used to study the optical activity of the title complex dissolved in 40 different solvents. The solvents ranged from being non-co-ordinating in nature ($CHCl_3$ or CCl_4) to being strongly co-ordinative toward the Eu^{III} ion (phosphate esters, amines, *N*-substituted amines, formamide and acetamide derivatives, alcohols, and ketones). Strong optical activity could be observed within the $^5D_0 \rightarrow {}^7F_1$ and $^5D_0 \rightarrow {}^7F_2$ Eu^{III} transitions in almost every case. Two basic c.p.l. lineshapes were found to exist, and many solvents were found in which both patterns were observed to superimpose. The plausible stereochemistries of the $[Eu(dcm)_3(S)_2]$ (dcm = DD-dicampholylmethanate, S = substrate) adduct complex were examined in order to understand the nature of the observed chiroptical spectra. A variety of geometrical and enantiomeric isomerism accounted for the observed trends.

The advantages and utility associated with chiral shift reagents in the n.m.r. determination of enantiomeric purities has been detailed,[1] and the n.m.r. method shown to be applicable to a much broader range of compounds than are the more classical methods. Most of the studies which have been carried out to date have employed the Eu^{III}, Pr^{III}, or Yb^{III} derivatives of chiral β-diketones derived from D-camphor.[2,3]

It has been noted [2] that tris(DD-dicampholoylmethanato)europium(III) {abbreviated as $[Eu(dcm)_3]$, for structure see below} yields the largest degree of enantiomeric discrimination of all the chiral shift reagents reported to date, although its difficulty of preparation has prevented wider application of this material. Nevertheless, the utility of $[Eu(dcm)_3]$ as a shift reagent has been amply demonstrated.[4-8]



The ability of the Eu^{III} ion to expand its co-ordination number beyond six allows this ion to induce paramagnetic shifts in the n.m.r. spectra of a bound substrate, but it also presents a situation in which the stereochemistry of seven- or eight-co-ordinate metal ions may be examined. A great deal of research activity has been expended in the study of transition-metal chelates of optically active β-diketone ligands, and in our laboratory we have concentrated on analogous studies of lanthanide chelates of chiral β-diketone ligands. With β-diketone ligands derived from D-camphor (bornan-2-one), it has generally been found that in non-co-ordinating solvents (such as CCl_4 or $CHCl_3$), no optical activity can be observed in the *f–f* transition bands. Dissolution of the chelates into strongly co-ordinating solvents (such as dimethyl sulphoxide or *NN*-dimethylformamide) can result in the generation of extremely strong optical activity. We have interpreted these results as to imply that little steric interaction between the bulky ligands takes place as long as the Eu^{III} ion remains six-co-ordinate, but formation of the adducts (with a subsequent increase in co-ordination number) causes crowding of the ligands and the complex adopts the configuration of lowest energy. Since the ligands are chiral, this process results in a net resolution of the complex, and any perturbation on the ratio of Δ/Λ isomers is manifested by the appearance of optical activity.[9,10] In the absence of steric interactions, the relative amounts of Δ and Λ isomers remain equal.

In the present report, we extend the chiroptical investigations to include studies on $[Eu(dcm)_3]$ and its adduct complexes. While the Eu^{III} compounds derived from D-camphor are unsymmetrical (and hence, the metal tris-complexes can have *cis* and *trans* stereochemistries in addition to the Δ and Λ isomerism), the dcm ligand is symmetrical in that the two groups bound at the perimeter of the β-diketone ring are identical. As before, we have measured the optical activity of the complex by means of circularly polarized luminescence (c.p.l.) spectroscopy rather than by the more conventional method of circular dichroism, and this choice of chiroptical method was dictated by the low absorptivity of the *f–f* absorption bands and the relatively intense *f–f* luminescence bands.

Experimental

The complex $[Eu(dcm)_3]$ was obtained from Alfa/Ventron, and was used as received. For each spectral measurement, approximately 6 mg of material was dissolved directly in 3.0 cm^3 of the desired solvent. The $[Eu(dcm)_3]$ concentration thus used for each determination was approximately 1.8 mmol dm^{-3}. The chelate was dissolved in a total of 40 different solvents (all of which were commercially obtained and of the highest available quality), ranging from formamide and acetamide derivatives, primary-, secondary-, and tertiary-amines and alcohols, ketones, nitriles, and trialkyl phosphates. Our previous work employing dimethyl sulphoxide (dmso) [9] indicated that sulphoxides would be very important to study, but $[Eu(dcm)_3]$ was not found to dissolve in dmso.

All luminescence spectra were obtained on a medium-resolution c.p.l. spectrometer constructed in our laboratory.[11] The $[Eu(dcm)_3]$ samples were excited by the 365 nm output of a 200-W mercury–xenon arc lamp, with this u.v. excitation being selected by a combination of a 0.1-m grating monochromator and suitable u.v.-transmitting glass filters. Due to the low emission quantum yield of $[Eu(dcm)_3]$ in the various solvents, a wide excitation bandpass of 16 nm was employed

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* Tris[1,3-bis(1′,2′,2′,3′-tetramethylcyclopentyl)propane-1,3-dionato]europium(III).

to obtain a suitable signal-to-noise ratio. The emission was analysed by a 0.5-m grating monochromator at 1-nm resolution, and this resolution was found to be sufficient fully to resolve (as far as possible under the conditions) all observed spectral features. All measurements were carried out at room temperature in fluid solution.

Results

Irradiation of a Eu^{III} complex by ultraviolet light can result in efficient population of the luminescent $^5D_0$ excited state, and at room temperature all luminescence will originate from this level. The sharp line emission associated with the Eu^{III} ion tends to be found at transition energies close to those predicted from considerations of the free ion,[12] as little co-valency exists in the lanthanide–oxygen bonds of the chelate systems. Numerous studies have shown that the fine structure within the luminescence spectra of Eu^{III} β-diketone complexes is dependent on the geometry of the complex [13] and on the presence of additional substrates bound in the inner-sphere co-ordination shell of the metal ion.[14–16] The luminescence spectrum of the Eu^{III} ion consists of transitions from the $^5D_0$ level to the various J components of the ^7F_J ground state. If we denote the transitions by the corresponding J quantum numbers, then the bands commonly observed are the 0–0 (580), 0–1 (595), 0–2 (615), 0–3 (645), and 0–4 (690 nm).

The c.p.l. measurement results in the generation of two quantities, the total luminescence (t.l.) intensity, I [equation (1)] and the c.p.l. intensity, ΔI [equation (2)].[17] Any unit

$$I = \tfrac{1}{2}(I_L + I_R) \qquad (1)$$

$$\Delta I = (I_L - I_R) \qquad (2)$$

dependence of these quantities is eliminated by taking the ratio of these, equation (3), which is termed the luminescence dissymmetry factor.[17]

$$g_{\mathrm{lum}} = \Delta I/I \qquad (3)$$

Richardson [18] provided a series of selection rules based on considerations of the S, L, and J quantum numbers of f–f transitions, which may be used to predict the relative magnitude of optical activity within a given band. The dissymmetry factors associated with the 0–1 band are the largest, those of the 0–2 band are significantly smaller, and the 0–0 band is required not to exhibit any optical activity. Regardless of the magnitude of the dissymmetry factors associated with the 0–3 and 0–4 bands, the low overall intensity of these precludes their use in chiroptical studies.

Dissolution of [Eu(dcm)$_3$] into non-co-ordinating solvents (such as CHCl$_3$ or CCl$_4$) insures that the Eu^{III} ion remains six-co-ordinate, but when the chelate is dissolved in a co-ordinating solvent, adduct formation takes place. In the course of the present work, the c.p.l. could be measured in almost all 39 solvents in which [Eu(dcm)$_3$] could be dissolved in, and this behaviour may be contrasted to our earlier observations with the Eu^{III} derivative of 3-trifluoroacetyl-D-camphor in which optical activity could be observed in only a limited range of solvents.[9,10,19]

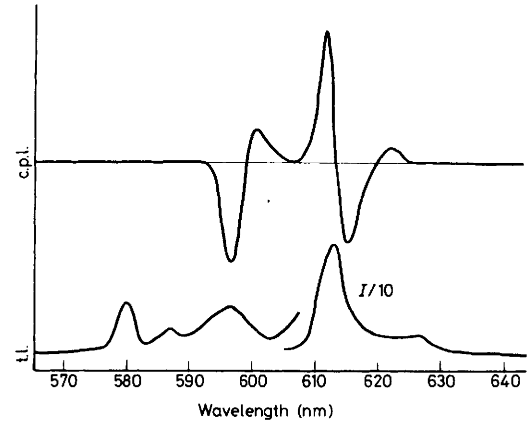

Figure 1. C.p.l. (upper) and t.l. (lower) spectra obtained within the $^5D_0 \longrightarrow {}^7F_J$ (J = 0—2) transitions of [Eu(dcm)$_3$] dissolved in CHCl$_3$. The intensity scales are shown in arbitrary units, and all quantitative data should be obtained from the Table

Chloroform and Carbon Tetrachloride.—It is generally recognized that both CHCl$_3$ and CCl$_4$ can be regarded as non-co-ordinating solvents as far as Eu^{III} β-diketone chelates are concerned, since these solvents do not contain any functional groups suitable for strong and specific interaction with a lanthanide ion. In non-co-ordinating solvents, Eu^{III} chelates derived from D-camphor do not exhibit measurable c.p.l.,[9,10,19] but it was found that [Eu(dcm)$_3$] did exhibit fairly strong optical activity when dissolved in CHCl$_3$ and CCl$_4$. The c.p.l. and t.l. spectra obtained within the 0–0, 0–1, and 0–2 band systems are shown in Figure 1. Luminescence dissymmetry factors were calculated at each of the c.p.l. maxima which are given in the Table together with the wavelength at which the c.p.l. was found.

The c.p.l. spectra presented in Figure 1 represent a significant departure from the spectra ordinarily obtained from studies on chiral Eu^{III} compounds containing β-diketone ligands. The observation that the 0–1 band contains both positive and negative natural c.p.l. (as opposed to magnetically induced c.p.l.) provides evidence that some unusual phenomenon exists for [Eu(dcm)$_3$] in the non-co-ordinating solvents. The c.p.l. associated with the 0–1 band is invariably totally positive or totally negative, and this general trend has been noted in Eu^{III} complexes containing inherently chiral β-diketone ligands [9,10,19–21] and in Eu^{III} β-diketone chelates where chirality was induced upon complexation with an optically active substrate.[22–25] The sole exception to this general trend was observed when addition of chiral amino-alcohols to achiral Eu^{III} β-diketonate complexes was found to generate Schiff-base complexes, and double-signed c.p.l. could be observed in the 0–1 band system at intermediate stages during the reactions.[26]

Phosphate Esters.—The c.p.l. spectra of [Eu(dcm)$_3$] dissolved in phosphate ester solvents are completely different from those obtained in CHCl$_3$ or CCl$_4$ solvent, as is shown in Figure 2. In addition, the c.p.l. observed with trimethyl phosphate was inverted relative to that observed in either triethyl- or tributyl-phosphate. However, the c.p.l. within the 0–1 band is always of the same sign, and the lineshape pattern is essentially identical to that observed for Eu^{III} chelates of acetyl-D-camphor and its derivatives when these are dissolved in co-ordinating solvents.[9,10,19,20]

A close examination of the two sets of c.p.l. spectra within Figure 2 reveals that they are not exactly mirror images, as would be required if the spectra represented different enantiomers of the same compound. This observation is best illustrated by examining the wavelengths of c.p.l. maxima and dissymmetry factors which are found in the Table. Trimethyl phosphate is seen to permit the observation of considerably more chirality than either of the other two substrates, and it should be noted that the wavelengths of one of the 0–1

Table. Luminescence dissymmetry factors associated with the emission of [Eu(dcm)$_3$] dissolved in various solvents

Solvent	Wavelength (0—1 band)/nm	g_{lum}	Wavelength (0—2 band)/nm	g_{lum}
$CHCl_3$	596	−0.254	610.5	+0.0352
	600	+0.106	613.5	−0.0194
CCl_4	596	−0.276	610.5	+0.0658
	600	+0.115	613.5	−0.0444
Trimethyl phosphate	587	−0.310	610.5	+0.0740
	596	−0.712		
Triethyl phosphate	587	+0.169	614	−0.0316
	598.5	+0.388		
Tributyl phosphate	587	+0.109	614	−0.0248
	598.5	+0.250		
n-Propylamine	593.5	+1.192	613.5	−0.0606
Isopropylamine	593.5	+1.762	613.5	−0.102
n-Butylamine	593.5	+0.910	613.5	−0.0474
Isobutylamine	593.5	+1.086	613.5	−0.0556
s-Butylamine	593.5	+1.510	613.5	−0.0872
n-Pentylamine	593.5	+0.946	613.5	−0.0464
3-Aminopentane	593.5	+0.870	613.5	−0.0768
Benzylamine	593.5	+0.880	613.5	−0.0506
β-Phenethylamine	593.5	+0.964	613.5	−0.0468
t-Butylamine	586.5	+0.360	614.5	−0.0758
	595.5	+0.820		
	598	+1.070		
t-Pentylamine	586.5	+0.424	614.5	−0.0702
	595.5	+1.062		
	598	+1.316		
Pyridine	586.5	+0.0501	614	−0.0618
	593	+0.500		
	598	+0.332		
Diethylamine	586.5	+0.306	614	−0.0488
	595	+0.430		
	598	+0.758		
NN-Dimethylformamide	587	+0.152	613	−0.0222
	593.5	+0.344		
	598.5	+0.292		
NN-Diethylacetamide	587	+0.145	613	−0.0191
	593.5	+0.354		
	598.5	+0.268		
Methanol	596	−0.296	610.5	+0.0964
	600	+0.123	613.5	−0.0696
Ethanol	585	+0.0796	614.5	−0.0464
	593	+0.127		
	599	+0.310		
n-Propyl alcohol	585	+0.0876	614.5	−0.0384
	593	+0.144		
	599	+0.330		
Isopropyl alcohol	585	+0.146	614.5	−0.0526
	593	+0.242		
	599	+0.478		
n-Butyl alcohol	585	+0.0578	614.5	−0.0394
	593	+0.113		
	599	+0.226		
Isobutyl alcohol	585	+0.105	614.5	−0.0600
	593	+0.137		
	599	+0.306		
s-Butyl alcohol	585	+0.0964	614.5	−0.0540
	593	+0.189		
	599	+0.328		
t-Butyl alcohol	585	+0.360	614.5	−0.0988
	593	+0.650		
	599	+1.022		

components differ by a significant amount (as do the maxima of the 0–2 c.p.l.).

It has been determined for six-co-ordinate trigonal Eu^{III} complexes that if the sign of the 0–1 c.p.l. is totally negative then the absolute configuration of the Eu^{III} ion is Δ.[27] In co-ordinating solvents, the Eu^{III} ion in [Eu(dcm)$_3$] is certainly not six-co-ordinate (and hence the Δ or Λ system for describing absolute configuration is not strictly applicable), but the c.p.l. results indicate that the Eu^{III} ion adopts the opposite absolute configuration in trimethyl phosphate relative to that existing in triethyl- or tributyl-phosphate. However, it may be suggested that the parent trigonal isomer existing in trimethyl phosphate possesses the Δ configuration, while the Λ configuration predominates in triethyl- and

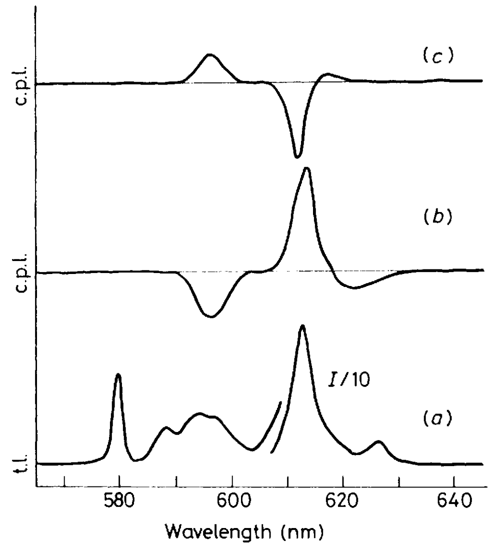

Figure 2. T.l. and c.p.l. spectra obtained within the $^5D_0 \longrightarrow {}^7F_J$ (J = 0—2) bands of [Eu(dcm)$_3$] dissolved in phosphate ester solvents. The t.l. spectra (*a*) were identical in lineshape for both solvents, but the c.p.l. spectrum obtained in triethyl phosphate (*c*) differed from that obtained in trimethyl phosphate (*b*)

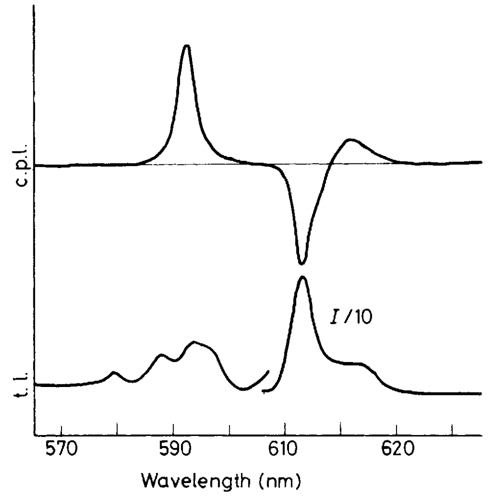

Figure 3. C.p.l. (upper) and t.l. (lower) spectra obtained within the $^5D_0 \longrightarrow {}^7F_J$ (J = 0—2) transitions of [Eu(dcm)$_3$] dissolved in n-propylamine

tributyl-phosphate. The existence of diastereomers (*e.g. cis*-Δ and *trans*-Δ) would require the presence of a non-symmetric β-diketone ligand, and such a possibility could be realized if the substituents on the β-diketone ring of dcm exhibited a definite spatial preference. This preference would arise from steric interactions between the rings causing the β-diketone ligands to adopt the configuration of lowest energy.

Amines.—Dissolution of [Eu(dcm)$_3$] into amine solvents led to the observation of strong optical activity, but the c.p.l. spectra were unlike any obtained before with a Eu^{III} chelate containing only chiral β-diketone ligands. The lineshapes observed in n-propylamine, isopropylamine, n-butylamine, isobutylamine, s-butylamine, n-pentylamine, 3-aminopentane, benzylamine, and β-phenethylamine were all found to be identical, and a representative example is shown in Figure 3.

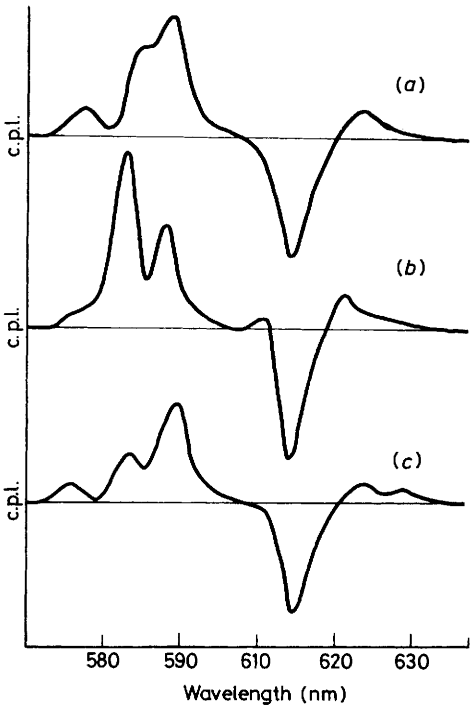

Figure 4. C.p.l. spectra obtained within the $^5D_0 \longrightarrow {}^7F_J$ (J = 0—2) transitions of [Eu(dcm)$_3$] dissolved in t-butylamine (*a*), pyridine (*b*), and t-butyl alcohol (*c*)

The dissymmetry factors associated with the [Eu(dcm)$_3$]–amine adducts have been presented as part of the Table. Thus, the results obtained in the amine solvents indicate that isomerism can exist in the [Eu(dcm)$_3$] chelates which has not been noted in lanthanide chelates containing only chiral β-diketone ligands, with a new stereochemistry being observed in the case of sterically hindered amines. However, with highly substituted amines the c.p.l. spectra clearly revealed the existence of a mixture of isomers. In Figure 4, the c.p.l. spectra obtained when [Eu(dcm)$_3$] was dissolved in t-butylamine is shown, and it is apparent that the observed spectrum appears to be a superimposition of the lineshapes presented in Figures 2 and 3. It is not likely that the lineshapes shown in Figure 4 are due to a single emitting species, as natural c.p.l. associated with the 0–1 emission band of a chiral Eu^{III} compound will not exhibit more than two c.p.l. peaks.[17,18] The c.p.l. spectrum in t-pentylamine was essentially identical with that of t-butylamine, indicating that the solution phase isomerism is a consequence of steric crowding at the amine functionality. Dissymmetry factors associated with the [Eu(dcm)$_3$] optical activity in tertiary amine solvents are given in the Table.

Substituted Amines.—Further study of the interactions existing between the amine functionality and [Eu(dcm)$_3$] was possible by examining the c.p.l. behaviour of the chelate dissolved in substituted amines. Dissolution of [Eu(dcm)$_3$] into diethylamine yielded t.l. and c.p.l. spectra which were identical in lineshape to those presented in Figure 4 for tertiary amine solvents. The luminescence dissymmetry factors (found in the Table) are also of comparable magnitude to those presented for t-butylamine and t-pentylamine solvents, and therefore it can be concluded that with diethylamine, the substrate presents a steric requirement to [Eu(dcm)$_3$] which is comparable to that of the tertiary amines.

[Eu(dcm)$_3$] was found to dissolve easily in triethyl- and tripropyl-amine solvents, but the resulting solution was found to be cloudy and no Eu^{III} emission could be obtained from such a solution. It would appear that the metal complex is decomposed upon co-ordination with the dialkylamine solvents.

Dissolution of [Eu(dcm)$_3$] into pyridine did not result in decomposition of the complex, and analysis of the emission spectra revealed a c.p.l. pattern in which the presence of multiple isomers was demonstrated most clearly. In Figure 4, the c.p.l. spectrum of [Eu(dcm)$_3$] in pyridine is shown, and a c.p.l. lineshape is seen which results from an overlapping of the patterns shown in Figures 2 and 3. Unlike the spectra obtained in the tertiary amine solvents, in pyridine the ' primary amine '-like peak at 593 nm is fully developed. The dissymmetry factors obtained in this solvent are also found in the Table, and it may be noted from the values that in its interaction with [Eu(dcm)$_3$], pyridine acts more as a primary amine than as a substituted amine.

Formamide and Acetamide Derivatives.—[Eu(dcm)$_3$] was found to be soluble in *NN*-dimethylformamide (dmf), *NN*-diethylformamide, *NN*-dibutylformamide, *NN*-dimethylacetamide, and *NN*-diethylacetamide (dea), but Eu^{III} emission was only found to be observable in the dmf and dea solvents. The c.p.l. lineshapes observed in these solvents were found to resemble strongly those found in the tertiary amine solvents, illustrated in Figure 4(*a*). The dissymmetry factors associated with the c.p.l. are found in the Table.

Examination of the dissymmetry factors reveals that the two basic lineshapes observed in Figures 2 and 3 (and whose superimposition is illustrated in Figure 4) are present in roughly equal amounts. We conclude that the dmf and dea substrates do not provide the strong stereochemical direction associated with the primary and secondary amines, and this behaviour is consistent with the fact that the formamide and acetamide substrates are *NN*-substituted.

Alcohols.—[Eu(dcm)$_3$] was found to dissolve quite readily into a wide variety of alcohol solvents, and strong c.p.l. was observed in each case. Interestingly, methanol yielded c.p.l. spectra which were identical in lineshape to those obtained with $CHCl_3$ or CCl_4 (see Figure 1 for the spectra, the Table for the dissymmetry factors). Presumably, in methanol [Eu(dcm)$_3$] does not form a well defined adduct (or the rate of substrate exchange is very fast) so that the resulting complex experiences a chiral environment characteristic of a non-co-ordinated chelate.

However, in ethanol, n-propyl-, isopropyl-, n-butyl, isobutyl-, s-butyl-, and t-butyl-alcohol a particular c.p.l. lineshape was observed which remained invariant throughout the series. As may be seen in Figure 4, the presence of different isomers is indicated by multitude of c.p.l. peaks observed within the 0–1 band system. However, the isomer existing in the phosphate ester solvents (illustrated in Figure 2) is found to be present in the largest quantity, unlike the situation existing in pyridine solvent. The dissymmetry factors calculated at each of the c.p.l. maxima are found in the Table.

Ketones.—[Eu(dcm)$_3$] was found to dissolve in acetone, ethyl methyl ketone, 4-methylpentan-2-one, and acetophenone, but Eu^{III} emission only occurred in acetone. C.p.l. was observed in this solvent, and the lineshape was found to be identical to that shown in Figure 4 with Bu^{t}OH as the solvent. The dissymmetry factors obtained in acetone were of comparable magnitude to those found in the alcohol solvents, and this indicates that similar interactions probably exist. These values were found to be +0.238 (585), +0.258 (593), +0.434 (599), and −0.0340 (614.5 nm).

Nitriles.—[Eu(dcm)$_3$] was found to dissolve in acetonitrile and benzonitrile, but no Eu^{III} emission could be observed in these solvent systems. As a result, no chiroptical information could be obtained.

Discussion

The dissolution of [Eu(dcm)$_3$] into a solvent capable of co-ordinating to the Eu^{III} ion certainly results in the formation of the 1 : 1 chelate–substrate (S) adduct [equation (4)] and

$$[\mathrm{Eu(dcm)_3}] + \mathrm{S} \rightleftharpoons [\mathrm{Eu(dcm)_3S}] \qquad (4)$$

probably in the formation of the 1 : 2 adduct as well [equation (5)].[3] The existence of 1 : 2 chelate–substrate adducts has

$$[\mathrm{Eu(dcm)_3S}] + \mathrm{S} \rightleftharpoons [\mathrm{Eu(dcm)_3(S)_2}] \qquad (5)$$

also been implicated in our studies of the solution-phase stereochemistries associated with the Eu^{III} complexes of 3-trifluoroacetyl-D-camphor and 3-heptafluorobutyryl-D-camphor.[9,10]

Since the substrates considered during the course of the present studies are all expected to co-ordinate to the Eu^{III} ion in a unidentate fashion, it is reasonable to expect that the metal would be eight-co-ordinate in the adduct complexes. A consideration of the polyhedra suitable for eight-co-ordination reveals that the basic structure would either be that of a dodecahedron (D_{2d} symmetry) or that of a square antiprism (D_{4d} symmetry). While dodecahedral geometry can be important for lanthanide oxyhalides or carboxylates, the square antiprismatic geometry appears to dominate in the β-diketone complexes.[28] Of course it must be recognized that the actual complexes do not possess the idealized square antiprism structure, but will exist as a distorted version thereof.

In a [Eu(dcm)$_3$(S)$_2$] adduct complex, a number of possibilities exist for placement of the unidentate ligands, and the important structures are summarized in Figure 5. Structure (I) has been observed for tris(acetylacetonato)diaqualanthanum(III),[29] (II) was identified with diaquatris[4,4,4-trifluoro-1-(2-thienyl)butane-1,3-dionato]europium(III),[30] and (III) was found to exist for bis(4-methylpyridine)tris(2,2,6,6-tetramethylheptane-3,5-dionato)holmium(III).[31] It has been pointed out that bulky substrates should lead to a dominance of structure (III), as this arrangement allows for maximum separation of the substrate molecules.[31] It may also be noted that while structures (I) and (II) contain the substrate molecules on the same square face of the antiprism, structure (III) contains these substituents on the apices of opposite square faces. The basic stereochemistry of eight-co-ordination has been discussed by Hoard and Silverton.[32]

The evidence presented in the preceding section strongly indicates the existence of two basic c.p.l. lineshapes, and all the observed results can be interpreted as being due to one pattern (or the other) or as a superimposition of the two patterns. This conclusion includes the earlier work involving the Eu^{III} complexes of 3-trifluoroacetyl-D-camphor and 3-heptafluorobutyryl-D-camphor, as the c.p.l. spectra obtained with these compounds are essentially identical to those shown in Figure 2 of the present work.[9,10,19,20] It is useful to label the c.p.l. patterns at this time, and we shall refer to the c.p.l. lineshapes of Figure 2 as pattern ' A ' and to those of Figure 3 as pattern ' B '.

A significant difference is also observable in the t.l. spectra

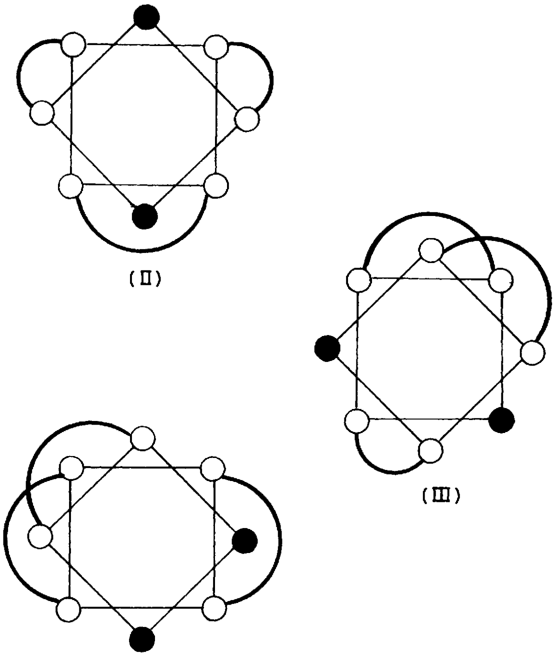

Figure 5. Known structures observed for [Ln(diketone)$_3$(substrate)$_2$] complexes. The unidentate substrates are shown as filled circles

of the A and B patterns. The 0–0 transition (which becomes more allowed as the molecular symmetry is lowered) is considerably weaker relative to the 0–1 band in pattern B, while in pattern A the 0–0 band is actually more intense than the 0–1 band. This observation strongly suggests that the symmetry of the Eu^{III} complex leading to pattern B is significantly higher than the complex symmtry leading to pattern A. Examination of structure (III) reveals that this compound contains a C_2 axis of symmetry, while structures (I) and (II) do not contain any symmetry elements. We would like to suggest, therefore, that pattern B is due to a Eu^{III} complex symmetry similar to structure (III), and that pattern A arises from either structure (I) or (II).

It was noted that the c.p.l. of [Eu(dcm)$_3$] in trimethyl phosphate was not an exact mirror image of the c.p.l. found in either triethyl- or tributyl-phosphate, and we suggest now that one A-type c.p.l. pattern arises as a result of the adduct having structure (I), and the other A-type pattern is a consequence of structure (II).

In structure (III), greatest separation of substrates is possible, while in structures (I) and (II) greatest separation of the β-diketone ligands is achieved. We conclude that the steric requirements of the substrates dictate what complex structure ultimately results, as each substrate must fit into a ' pocket ' in the Eu^{III} co-ordination sphere. The complex will adopt the configuration of lowest energy, and as we have seen there may be more than one manner in which to minimize ligand repulsions. It must be noted that the lanthanide β-diketone complexes are quite labile, and interconversion between structures may actually be quite facile if there is no strong preference for a particular structure. Such facile interconversions would account for the simultaneous observation of patterns A and B in the c.p.l. spectra of [Eu(dcm)$_3$] dissolved in the tertiary amine, *N*-substituted amine, formamide and acetamide derivatives, and alcohol solvents.

The optical activity observed during the course of the present work is certainly configurational in nature, as we have shown that vicinal effects in Eu^{III} chelates of β-diketones induce chirality at the Eu^{III} ion which is at least two orders of magnitude smaller than the degree of optical activity observed in the present work.[2] No conformational effect is possible, since the β-diketone rings will be planar in the solution phase (although not necessarily so in the solid state [28]). It is significant to note that although all ligands are derived from natural products of the same absolute configuration, the Eu^{III} ion can exist in either a Δ or R configuration over a range of stereochemical forms, depending on the nature of the chelate-substrate interactions.

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