Circularly Polarized Luminescence Studies of the Optical Activity induced in the Europium(III) Chelate of 4,4,4-Trifluoro-1-(2-thienyl)butane-1,3-dionate Through Adduct Formation with Cinchona Alkaloids

By **Harry G. Brittain**, Department of Chemistry, Seton Hall University, South Orange, New Jersey 07079, U.S.A.

The optical activity induced in the title compound by association with cinchonine, cinchonidine, quinine, and quinidine has been studied by means of circularly polarized luminescence (c.p.l.) spectroscopy. Optical activity was induced in each case, and generally the sign of the induced c.p.l. could be correlated with the absolute configuration of the alkaloid. The intensities of the c.p.l. and total emission spectra indicated that adduct formation was characterized by stereoselectivity; stronger induced chirality was noted when the alkaloid had the *S* configuration at the hydroxy-carbon. Other spectral features indicated that the presence of the methoxy-group (quinine and quinidine) exerted a secondary influence on adduct formation, presumably through an electronic effect.

THE use of lanthanide β-diketonate complexes as shift reagents for the clarification of overlapping n.m.r. resonances is a well refined technique, and the uses of these complexes have been reviewed several times.[1-4] The great sensitivity of chiro-optical techniques to intermolecular interactions allows for detailed interpretations of these interactions, and is therefore eminently suited to the study of shift-reagent–substrate adducts. Nakanishi and co-workers [5,6] have studied the circular dichroism (c.d.) induced in praseodymium(III) chelates of 2,2,6,6-tetramethylheptane-3,5-dionate by a variety of chiral alcohols, and have developed a series of techniques useful in the prediction of absolute configurations based on c.d. results.

Another chiro-optical technique that is of great value in the study of lanthanide β-diketonate complexes and their adducts is circularly polarized luminescence (c.p.l.) spectroscopy. This method measures the differential emission of left- and right-circularly polarized light by a chiral emissive molecule, and thus combines the structural selectivity of chiro-optical spectroscopy with the instrumental sensitivity of emission spectroscopy Clearly, the measurement of c.p.l. induced in a β-diketonate complex upon complexation with a chiral substrate is an excellent way to examine the nature of the intermolecular interactions. The c.p.l. technique is to be preferred over the c.d. method in the study of *f-f* lanthanide optical activity since the very low absorption coefficients of the lanthanide ions preclude the effective use of c.d. as a probe of molecular geometry.

In the present study, we report the c.p.l. induced in a europium(III) β-diketonate chelate when this material is complexed to several alkaloids. In previous works, we had examined the c.p.l. induced in europium(III) β-diketonates when these were complexed to resolved α-phenethylamine,[7] and when a terbium(III) chelate was complexed to chiral amines.[8] In both of these earlier works, the c.p.l. line shapes observed correlated nicely with the absolute configuration of the substrate inducing the optical activity. We have therefore expanded our efforts to examine natural product adducts containing chiral systems of known configuration in an attempt to further understand the nature of the induced optical activity. Since earlier work indicated that the europium(III) chelate of 4,4,4-trifluoro-1-(2-thienyl)-butane-1,3-dionate (tftbd) formed the strongest adducts with amine substrates,[9] we have chosen to work exclusively with this in our present study.

EXPERIMENTAL

The $[Eu(tftbd)_3]$ chelate was prepared and purified according to the literature.[10] Quinine, quinidine, cinchonine, and cinchonidine were all obtained from a variety of commercial sources, and were all used without subsequent purification. Stock solutions of europium(III) chelates were made up in dried $CHCl_3$, and the initial $[Eu(tftbd)_3]$ concentration was 0.000 5 mol dm^{-3}. Stock solutions of alkaloids were made up in $CHCl_3$ and added to the β-diketonate solutions in each c.p.l. determination. It was found that excess of alkaloid was required in each case, and no difference in spectral results was obtained if the excess of alkaloid was added as a solution or in solid form to the $[Eu(\beta\text{-diketonate})_3]$ complex solution.

All c.p.l. and luminescence spectra were obtained on an instrument constructed in this laboratory, and which has recently been described.[11] An excitation wavelength of 290 nm was used for all studies, and this excitation was selected by passing the output of a 200-W Hg–Xe arc lamp through a 0.1-m grating monochromator (model H-10-UV-V, Instruments SA). The emission was collected at 180° to the exciting light to eliminate the possible presence of any linear polarization in the emission; this beam was passed through a long-pass filter (consisting of a concentrated solution of $Na[NO_2]$) to remove any exciting light not absorbed by the sample. The emission was analyzed by a 0.5-m grating monochromator (model 1870, Spex Industries) whose resolution was equal to a 15 Å band-pass. Further increases in resolving power did not reveal any new spectral features. The emission was finally detected by an E.M.I. 9798B photomultiplier tube (S-20 response), whose output was converted to a voltage and split. One signal was fed directly to one channel of a dual-channel recorder, and the other underwent phase-sensitive detection to obtain the c.p.l. component (which was then displayed on the other recorder channel).

RESULTS AND DISCUSSION

The irradiation of $[Eu(\beta\text{-diketonate})_3]$ complexes by near-u.v. light results in the observation of fairly intense emission in the red region of the spectrum. This emission consists of transitions from the excited $^5D_0$ Eu^{III} level to the $^7F_0$ (*ca.* 580 nm), $^7F_1$ (*ca.* 595 nm), and $^7F_2$ (*ca.* 615 nm) ground-state levels. In most of these β-diketonate complexes, the 0—0 and 0—1 transitions are of approximately equal intensity, and the 0—2 transition is typically an order of magnitude more intense (we shall label the emissions according to their J quantum numbers). In all chiral europium(III) β-diketonate complexes whose c.p.l. has been reported so far,[7,12] no c.p.l. has ever been found in the 0—0 transition. The c.p.l. of the 0—1 and 0—2 transitions has roughly the same intensity.

The c.p.l. measurement actually results in the detection of two quantities. One is the total luminescence (t.l.) intensity, usually given by equation (1) and the

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

other is the circularly polarized luminescence (c.p.l.) intensity [equation (2)]. In equations (1) and (2), I_L and I_R

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

represent the emitted intensities of left- and right-circularly polarized light respectively. Since I and ΔI are measured in arbitrary quantal units, it is common practice to calculate the luminescence disymmetry factor, $g_{lum.}$, by taking the ratio of these quantities, and thus eliminating any unit dependence[13] [equation (3)].

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

The $g_{lum.}$ factor has theoretical as well as experimental significance as it may be related to the rotational strength of the transition[13] [equation (4)] where R_{ab} is the

$$g_{lum.} = 4\,(R_{ab})/D_{ab} \qquad (4)$$

rotatory strength given by equation (5) and D_{ab} is the dipole strength given by equation (6).

$$R_{ab} = Im <\psi_a|\hat{u}|\psi_b> <\psi_b|\hat{m}|\psi_a> \qquad (5)$$

$$D_{ab} = <\psi_a|\mu|\psi_b>^2 \qquad (6)$$

Equations (4)—(6) are valid for randomly oriented emitting systems in which the luminescent excited state is thermally equilibrated prior to emission. It should be noted that while the value of $g_{lum.}$ has little theoretical significance without a detailed analysis of the c.p.l. line shape, values of $g_{lum.}$ may be compared to each other to evaluate trends in the data that may be correlated with changes in complex structure.[13]

When [Eu(tftbd)$_3$] was complexed with quinine, quinidine, cinchonine, or cinchonidine, the t.l. intensity increased somewhat relative to that of [Eu(tftbd)$_3$] in CHCl$_3$. This increase in intensity is a common feature of adduct formation for these complexes, and is thought to result from a protection of the central lanthanide ion from solvent quenching.[14] This protection can be thought of as the formation of an insulation layer, and the adduct then provides additional protection when compared to the uncomplexed chelate since more ligands are packed around the metal in the adduct. We have used this behaviour previously to calculate association constants of β-diketonate complexes and a wide variety of substrates.[9,15] Formation constants were not calculated during the course of the present study since the actual emission enhancements were not sufficiently large to allow for accurate calculation.

The line shapes associated with the various emissions showed interesting behaviour, and significant trends were noted in the maxima of these lines. A complete summary of relative peak intensities and band maxima is shown for all alkaloid adducts of [Eu(tftbd)$_3$] in the Table. In all cases, the intensity and wavelength maximum of the 0—0 emission band remained unchanged in any of the adducts, and did not differ to an appreciable extent from the uncomplexed chelate. This behaviour is in keeping with the highly forbidden nature of a transition from $J = 0$ to $J' = 0$, and since its intensity is not greatly affected by adduct formation we can infer that the geometry of the adduct is not greatly different from that of the free chelate. The holohedrized symmetry about the Eu^{III} ion must be considerably lower than cubic, since the 0—0 band is not observed in octahedral environments.[16]

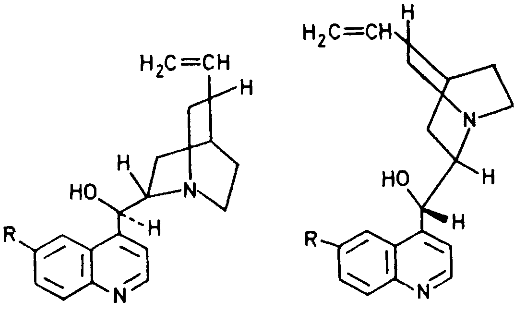
Total luminescence features of the $^5D_0\rightarrow{}^7F_{0,1,2}$ emission bands of [Eu(tftbd)$_3$]

Substrate	Transition	Wavelength maximum (nm)	Relative intensity	$g_{lum.}$
None	0—0	579.3	45	
	0—1	590 (sh)	34	
	0—1	591.8	40	
	0—1	595.7	42	
	0—2	613.1	750	
Quinine	0—0	579.5	52	
	0—1	592.6	57	0.066
	0—2	611.2	1 355	−0.004 6
Quinidine	0—0	579.5	50	
	0—1	592.5	39	−0.041
	0—2	611.3	1 100	0.004 5
Cinchonine	0—0	579.4	51	
	0—1	590 (sh)	47	*
	0—1	592.0	58	−0.018
	0—1	594.9	54	*
	0—2	611.9	1 275	0.001 5
Cinchonidine	0—0	579.4	53	
	0—1	590 (sh)	54	*
	0—1	591.9	72	0.036
	0—1	594.6	62	*
	0—2	611.9	1 550	−0.003 3

* Values for $g_{lum.}$ were not calculated at these wavelengths due to the poorer resolution of the t.l. features.

The t.l. behaviour of the 0—1 band system was found to contain the most information. As may be seen in the Table, two classes of binding behaviour are apparent: poor resolution of the three possible crystal-field transitions permissible within the 0—1 system is found for the quinine and quinidine adducts, while good resolution of these components is observed for the cinchonine and cinchonidine adducts. The structures of these alkaloids are all related. The poorer resolution observed for the quinine alkaloids *versus* the cinchonine alkaloids may thus be a consequence of the existence of somewhat different complex geometries between the two, and this difference must be caused by the methoxy-groups that are present for the quinine alkaloids and absent on the cinchonine materials.

The 0—2 emission bands all appear basically similar, and no great differences in band shape are noted. No resolution of the possible five crystal-field components was obtained, and the spectra consisted of a single intense band with several apparent shoulders. A most interesting trend was noted in the wavelength maxima of the most intense 0—2 component: while the transition energy of uncomplexed [Eu(tftbd)$_3$] is essentially the same as is observed in cubic[17] or hexagonal[18] environments, upon complex formation with the alkaloids of our study this transition displays a definite shift toward higher energy. A 10 Å shift is found for the cinchonine adducts, and a 20 Å shift is found for the quinine adducts. Since the 0—2 emission can be classified as one of the ' hypersensitive ' transitions ($\Delta J = 2$), it is to be expected that the intensity and position of this peak should be a sensitive measure of the local environment about the Eu^{III} ion.[19] It is very tempting to assign this wavelength shift to an increased degree of covalency in the complex, but it is probably more likely that the shift merely represents the intensification of a higher-energy crystal-field component as a result of bonding changes.



R = H, cinchonidine
R = OCH$_3$, quinine

The t.l. intensities in the Table reveal an interesting feature that appears to indicate the existence of some sort of stereoselective interaction. If one compares the t.l. intensities of corresponding bands for quinine and quinidine, it is found that both the 0—1 and 0—2 t.l. intensities are significantly smaller for the quinidine adduct. On the other hand, the corresponding intensities for cinchonine are less than those of cinchonidine. It is well known that the two pairs of alkaloids only differ by the presence of a methoxy-group on the aromatic ring and by the chirality of the 9-carbon which contains the hydroxy-group. It is highly significant to note that this carbon has the *R* configuration in quinine and cinchonidine, and the *S* configuration in quinidine and cinchonine.[20] It would therefore appear that the lowered t.l. intensity in the quinidine–cinchonine pair indicates that the chelate-substrate adduct has a lower formation constant when the configuration of the 9-carbon is *S*.

Circularly polarized luminescence was observed in the 0—1 and 0—2 emission bands of [Eu(tftbd)$_3$] when this chelate was complexed with all four alkaloids, but none was ever seen in the 0—0 band. The c.p.l. spectra associated with the 0—1 band differed in each of the alkaloid adducts, as may be seen in Figure 1. In general, the c.p.l. consists of one major peak and a few, much weaker, features. The sign of the most intense band correlates nicely with the configuration of the added alkaloid; quinine and cinchonidine (*R* configuration at the 9-carbon) both exhibit positive c.p.l., while quinidine and cinchonine (*S* configuration) exhibit negative c.p.l. This type of correlation was noted before in the c.p.l. of a terbium(III) β-diketonate complexed to chiral amines,[8] and may be a general feature of lanthanide ion-induced c.p.l.

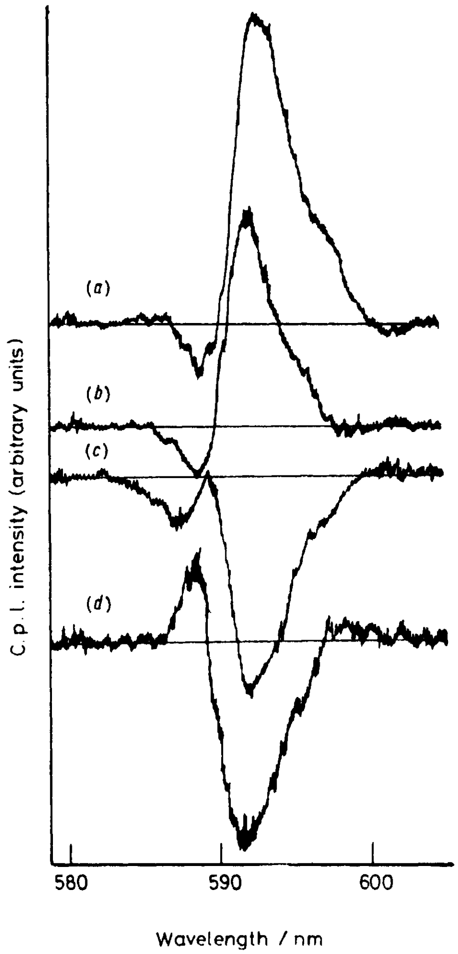


FIGURE 1 C.p.l. spectra associated with the $^5D_0 \rightarrow {}^7F_1$ transition of the [Eu(tftbd)$_3$] adducts with: (*a*) quinine, (*b*) cinchonidine, (*c*) quinidine, and (*d*) cinchonine. The intensity scales are completely arbitrary, and all quantitative data should be obtained from the Table

The signs of the lower intensity c.p.l. peaks present interesting features. Except for the better resolution of t.l. features, the 0—1 emission bands of the quinine and cinchonidine adducts of [Eu(tftbd)$_3$] are essentially identical, and even the t.l. intensities are markedly similar. On the other hand, the t.l. intensities of the cinchonine and quinidine adducts are quite different, and the c.p.l. spectra also differ in that the peak at highest energy is negative for the quinidine compound but positive for the cinchonine complex. In this respect, the c.p.l. spectrum of the cinchonine adduct resembles that of two europium(III) β-diketonate complexes dissolved in *R*-α-phenethylamine,[7] while the c.p.l. of the quinidine adduct resembles that of an inherently chiral europium(III) β-diketonate dissolved in dimethyl sulphoxide.[12] This behaviour clearly indicates that the structures of the two adducts must be slightly different, although it is impossible at the present time to elaborate further.

The c.p.l. spectra of [Eu(tftbd)$_3$] adducts with the four alkaloids are shown in Figure 2, and two general trends may be noted. The t.l. spectra of the quinine and quinidine adducts are much sharper and better resolved than the analogous spectra for the cinchonine and cinchonidine complexes. This behaviour is exactly opposite to that seen in the 0—1 bands, where better resolution was found for the cinchonine adducts. This trend clearly indicates that the methoxy-group present in the quinine alkaloids can influence the bonding, even though it lies far from any plausible co-ordination site.

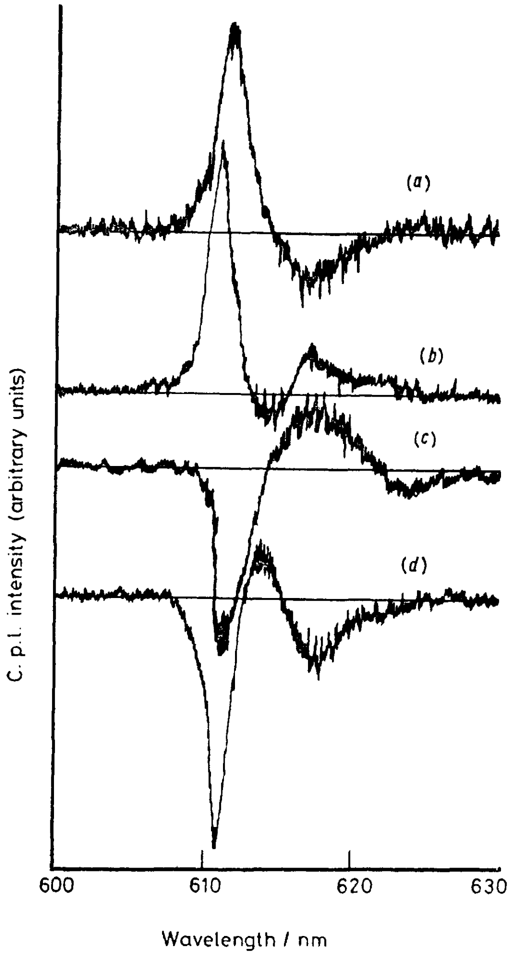


FIGURE 2 C.p.l. spectra associated with the $^5D_0 \rightarrow {}^7F_2$ transition of the [Eu(tftbd)$_3$] adducts with: (*a*) cinchonine, (*b*) quinidine, (*c*) cinchonidine, and (*d*) quinine

Slight differences are noted in the c.p.l. of the various adduct systems, but in general the c.p.l. spectra all bear a strong resemblance to each other (aside from mirror-image relationships). The alkaloid pairs of related configuration exhibit c.p.l. spectra in which the sign of the major component correlates with absolute configuration at the 9-carbon. The data presented indicate that the sign of the 0—2 c.p.l. is also a reliable method of absolute configuration correlation, and in general we can state that a substrate having the *R* configuration will induce negative c.p.l. in the 0—2 emission of a europium(III) β-diketonate complex. This conclusion is in agreement with the earlier work involving *R*-α-phenethylamine and a variety of achiral europium(III) β-diketonate complexes.

Values for the luminescence disymmetry factor, $g_{\text{lum.}}$, have been calculated for all of the adduct systems, and these are also summarized in the Table. The data for all bands indicate that alkaloids containing the methoxy-group (the quinine class) have a greater degree of optical activity than do those without the methoxy-group. One is able to conclude from this observation, and from the earlier results, that the methoxy-group must be playing an important role in complex formation. Presumably this electron-donating group is able to perturb the electronic states of the alkaloids in such a way as to increase the degree of optical activity.

When one compares the $g_{\text{lum.}}$ values of quinine and quinidine, and then separately cinchonine and cinchonidine, a second trend may be noted. The alkaloids having the *S* configuration at the 9-carbon (quinine and cinchonidine) exhibit larger values of $g_{\text{lum.}}$ than the alkaloids having the *R* configuration. Since the $g_{\text{lum.}}$ value is the indicator of the magnitude of the induced optical activity, we can conclude that the binding of the chiral alkaloid by the achiral chelate is clearly a stereoselective matter.

Conclusions.—The results presented in this paper clearly demonstrate the utility of c.p.l. and t.l. spectroscopy to the study of lanthanide complex interactions with substrates. A wide variety of information and conclusions may be obtained from consideration of the data trends, and this information may be directly related to the nature of the bonding in the adduct. Since the *f–f* excited states probed with the c.p.l. technique are completely non-bonding in nature, we are confident that measurements of excited-state optical activity can be applied to discussions of ground-state properties. Much work is still required to probe the relationships between c.p.l. spectral features and molecular stereochemistries, and studies of this type are being actively pursued in this laboratory.

This work was supported by the Research Corporation through their Cottrell Research Program.

[0/377 *Received, 7th March,* 1980]

REFERENCES

[1] 'Nuclear Magnetic Resonance Shift Reagents,' ed. R. E. Sievers, Academic Press, 1973.

[2] A. F. Cockerill, G. L. O. Davies, R. C. Harden, and D. M. Rackham, *Chem. Rev.*, 1973, **73**, 553.

[3] B. C. Mayo, *Chem. Soc. Rev.*, 1973, **2**, 49.

[4] J. Reuben, *Progr. N.M.R. Spectroscopy*, 1973, **9**, 1.

[5] K. Nakanishi, D. A. Schooley, M. Koreeda, and J. Dillon, *Chem. Comm.*, 1971, 1235.

[6] J. Dillon and K. Nakanishi, *J. Amer. Chem. Soc.*, 1974, **96**, 4057, 4059; *ibid.*, 1975, **97**, 5417.

[7] H. G. Brittain and F. S. Richardson, *J. Amer. Chem. Soc.*, 1977, **99**, 65.

[8] H. G. Brittain, *J. Amer. Chem. Soc.*, 1980, **102**, 1207.

[9] H. G. Brittain, *J.C.S. Dalton*, 1979, 1187.

[10] L. R. Melby, N. J. Rose, E. Abramson, and J. C. Caris, *J. Amer. Chem. Soc.*, 1964, **86**, 5117.

[11] H. G. Brittain, *J. Amer. Chem. Soc.*, 1980, **102**, 3693.

[12] H. G. Brittain and F. S. Richardson, *J. Amer. Chem. Soc.*, 1976, **98**, 5858.

[13] F. S. Richardson and J. P. Riehl, *Chem. Rev.*, 1977, **77**, 773.

[14] F. Halverson, J. S. Brinen, and J. R. Leto, *J. Chem. Phys.*, 1964, **41**, 157.

[15] H. G. Brittain and F. S. Richardson, *J.C.S. Dalton*, 1976, 2253; H. G. Brittain, *J. Amer. Chem. Soc.*, 1979, **101**, 1733.

[16] O. A. Serra and L. C. Thompson, *Inorg. Chem.*, 1976, **15**, 504.

[17] L. G. DeShazer and G. H. Dieke, *J. Chem. Phys.*, 1963, **38**, 2190.

[18] A. A. F. Lagerwey and G. Blasse, *Chem. Phys. Letters*, 1975, **31**, 27.

[19] D. E. Henrie, R. L. Fellows, and G. R. Choppin, *Co-ordination Chem. Rev.*, 1976, **18**, 199.

[20] W. Klyne and J. Buckingham, 'Atlas of Stereochemistry,' Oxford University Press, 1974.