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Vicinal Effects Observed in the Circularly Polarized Luminescence Spectra of Mixed-Ligand Tb(III) Complexes

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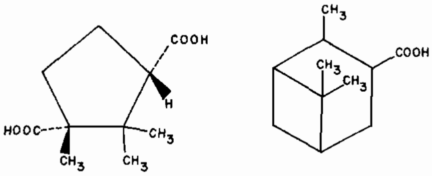

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Fig. 1. Structures of camphoric acid (1) and pinanecarboxylic acid (2).

While the chirality of a metal complex is a fundamental property relating to the structure of that complex, it is convenient to evaluate the overall chirality in terms of three distinct contributions: (a) a configurational effect (due to a chiral arrangement of chelate rings), (b) a conformational effect (due to the optical activity of a single ring), and (c) a vicinal effect (due to the presence of an asymmetric-atom somewhere near the metal center) [1]. The vicinal effect is the weakest of the three effects, and usually is measured in situations where the other two effects are lacking. One such case involved monodentate attachment of a chiral amino acid to pentaamine cobalt(III) [2].

Studies of f-f optical activity associated with lanthanide complexes have lagged far behind the corresponding studies involving transition metal complexes, primarily since the circular dichroism (CD) spectra of the rare earth complexes is weak and not easily measured (the f-f absorptions are extremely weak([3]. At the same time, the lanthanide complexes have been shown to associate at the concentrations necessary for the observation of CD [4, 5]. A far better approach to the study of chiral lanthanide complexes has used circularly polarized luminescence (CPL) spectroscopy, since a few of the lanthanide ions emit strongly in fluid solution at room temperature [6], and the sensitivity of emission spectroscopy permits work at much lower concentrations. Almost all of the studies reported to date have involved chirality due either to configurational or conformational effects, but we have recently reported the CPL of several mixed-ligand complexes where a sole vicinal effect was detected [7].

In the present report, the experimental lineshapes and magnitudes of CPL associated with vicinal effects in some mixed-ligand Tb(III) complexes are reported. While detailed theoretical analyses are not possible at the present time, the lineshapes arising from sole vicinal effects are sufficiently different from those due to conformational and configurational effect to warrent investigation.

Lanthanide complexes of pyridine-2,6-dicarboxylic acid (dipicolinic acid, or DPA) are of unusual interest in that they are monomeric at all concentrations and pH values, and that a fairly high degree of symmetry is preserved in solution [8, 9]. Mixed-ligand complexes of Tb(III), DPA, and another chiral ligand have proved most useful in the investigation of metal–ligand interactions; the DPA ligand serves to fill out the coordination sphere and also provides a means to photo-excite the Tb(III) ion via transfer of electronic energy [7, 10]. In these studies, it proved possible to observe all three contributions to overall chirality: the conformational and configurational effects were roughly of the same order of magnitude (but with the configurational being the strongest), while the vicinal effect was an order of magnitude smaller than either of the other two.

To extend these observatiohs further, we have obtained the CPL spectra within the $^5D_4 \rightarrow {}^7F_5$ Tb(III) transition of new mixed-ligand complexes of Tb(III), DPA, and chiral carboxylic acids capable of binding only in a monodentate fashion. We shall define monodentate as attachment *via* the carboxylic acid group only (and therefore exclude the formation of a chelate ring), and shall not address the question whether this group binds through one or two oxygen atoms. Solutions were prepared in which a 1:1 and 1:2 ratio of Tb(III) to DPA was fixed, and then an excess of chiral third ligand was added (structures of the less-familiar ligands are shown in Fig. 1). The extremely high formation constants of the Tb(III)/DPA complexes insures that the Tb(DPA) or Tb(DPA)$_2$ complexes form completely, and the formation of these complexes leaves only a restricted number of coordination positions open on the metal for further complexation. The chiral ligand was always added in a sufficiently large amount that led to miximization of the CPL signal, this practice being necessary to fully saturate the Tb(III)/DPA complexes with the chiral ligand. At very low pH, no CPL was observed in the Tb(III) emission spectrum. Once the solution pH exceeded the value necessary to allow deprotonation of the carboxylic acid group on the chiral ligand, weak CPL was then observed. A typical example of the CPL lineshape is shown in Fig. 2 along with the total luminescence (TL)

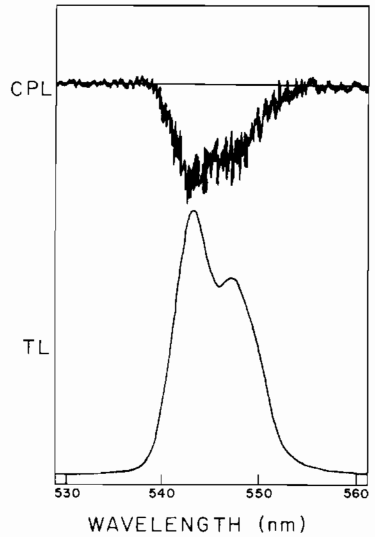

Fig. 2. Total luminescence (lower) and circularly polarized luminescence (upper) spectra obtained for the $Tb(DPA)_2$ (1) compound at pH 8.5. The data are for the $^5D_4 \rightarrow {}^7F_5$ Tb(III) emission band.

spectrum. Once the CPL appeared, its sign and magnitude were invariant to further increases in pH.

Since the TL and CPL spectra are recorded in arbitrary units, it is common practice to relate the ratio of these quantities [6]:

$$g_{lum} = \frac{(I_L - I_R)}{\frac{1}{2}(I_L + I_R)} = \frac{2\Delta I}{I}$$

where g_{lum} is the luminescence disymmetry factor, and I_L and I_R represent the emitted intensities of left- and right-circularly polarized light, respectively. It should be noted that g_{lum} may be related to the rotational and dipole strengths of the transition [6]. Values for the luminescence disymmetry factor have been calculated at the emission maxima, and these are collected in Table I. For the sake of completeness, the g_{lum} values found during the earlier study of $Tb(DPA)_2(AA)$ (AA is a series of chiral amino acids) are included as well.

All of the g_{lum} values in the Table are roughly of the same order of magnitude, only differ in the sign of the CPL, and are essentially independent of pH. A most interesting observation was that the value of g_{lum} remained constant throughout the emission band. This latter result is somewhat surprising when one considers the number of crystal-field transitions permitted within the $^5D_4 \rightarrow {}^7F_5$ Tb(III) transition that was studied. It may be noted that the absolute configuration of all the amino acids is S, while the absolute configuration of the pinanecarboxylic acid is R [11]. It is then not surprising that the CPL spectra of the two classes of compounds should be of opposite sign. Camphoric acid possesses two asymmetric carbon atoms, and these are of opposite configuration [11]. In addition, examination of molecular models reveals that while camphoric acid possesses two carboxylic acid groups, steric effects prevent these from both binding to the same metal and forming a chelate ring. However, the carbon bearing the R configuration is less sterically hindered than the S-carbon, and one might anticipate that a higher degree of bonding would take place between the Tb(III) ion and the R-carbon. This prediction is borne out by the data, since the CPL is found to be negative. The stereospecificity of the induced CPL is further demonstrated in that both (+)-3-methyladipic acid and L-menthoxyacetic acid are both of the R configuration, and the sign of their CPL is

TABLE I. Luminescence Dissymmetry Factors for the Mixed–Ligand Tb(III) Complexes.[a]

Ligand	$g_{lum} \times 10^4$ $Tb(DPA)_2(L)$	$g_{lum} \times 10^4$ Tb(DPA)(L)	Reference
L-camphoric acid	−9.71	−10.50	this work
(+)-pinanecarboxylic acid	−6.27	−8.12	this work
(+)-3-methyladipic acid	−8.63	−9.44	this work
L-menthoxyacetic acid	−6.11	−7.99	this work
D-α-phenylglycine	−9.01	−10.33	this work
L-alanine	+8.80	–	7
L-valine	+9.38	–	7
L-leucine	+9.86	–	7
L-isoleucine	+9.30	–	7
L-norvaline	+9.26	+10.32	this work
L-norleucine	+9.51	+10.67	this work
L-proline	+8.97	+10.01	this work
L-azetidinecarboxylic acid	+9.71	+10.84	this work

[a] All dissymmetry factors were calculated at the maximum of the emission (544 nm), and have an associated error of ±0.05.

opposite to that obtained for the S-amino acids. The lack of double-signed CPL for the 3-methyl-adipic acid indicated the inability of this ligand to bind to the Tb(III) ion in a bidentate fashion, but this is not surprising in view of the size of the chelate ring that would have to be formed in such a case.

If one only provides one DPA ligand per Tb(III) ion, a modest increase in CPL intensity is noted. While the formation constants for the Tb(III) complexes of camphoric and pinanecarboxylic acids are not known, the data obtained here indicate that these must be fairly small. In the Tb (DPA) (Ligand) complexes, we propose that only one molecule of chiral carboxylic acid binds per Tb(III) ion and that the increase in CPL intensity observed is due to a more complete formation of the Tb–ligand complex. Of course, the formation of a small amount of Tb(DPA)(ligand)$_2$ complex cannot be excluded, but if the formation constants of the Tb–ligand complexes are as small as those of the amino acid complexes [12] (not an unlikely situation for monodentate carboxylic acids) then this latter possibility is not favorable.

On the basis of the experimental work presented thus far, we can conclude that a vicinal effect experienced by a Tb(III) ion is manifested by a purely positive or negative CPL lineshape, and the sign of the CPL is governed by the absolute configuration of the ligand. The observation of double-signed CPL in the luminescence spectrum of a Tb(III) complex may then be taken to imply the presence of either a conformational or a configurational effect. We conclude that the addition of a conformational or configurational effect to an existing vicinal effect simply contributes a much higher degree of chirality (manifested by double-signed CPL) to that experienced by the metal ion. Further work is clearly necessary to probe these trends further, and is currently under way in our laboratory.

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