a reduction of the anisotropy, and also the principal directions of g are rotated by large angles from the positions experimentally observed. Therefore, it is possible that $e_{\pi c} \neq e_{\pi s}$ also in the present case, but the anisotropy must be smaller than that suggested for sp^2 oxygen.

Our feeling is that anisotropic e_λ values are actually required for the interpretation of the spectral and magnetic properties of pyridine *N*-oxide complexes but that large significance cannot be given to prediction based on orbital hybridizations.

The g_z value observed in the present case is smaller than those observed for tetrahedral complexes,[4,5] and also the hyperfine splitting is larger in the present case than usually observed for tetrahedral complexes, but more experimental data are required before any significant trend is obtained.

Registry No. Co(picoline *N*-oxide)$_5$(ClO$_4$)$_2$, 21460-56-0; Zn(picoline *N*-oxide)$_5$(ClO$_4$)$_2$, 74763-42-1.

Contribution from the Department of Chemistry,
Seton Hall University, South Orange, New Jersey 07079

Induced Optical Activity in the Terbium(III) Complex of Pyridine-2,6-dicarboxylic Acid through Association with Resolved Tris(ethylenediamine)chromium(III)

John S. Madaras and Harry G. Brittain*

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The observation of optical activity in a racemic mixture of a labile complex upon addition of a chiral compound is termed the Pfeiffer effect and serves as a useful means to study the chiroptical spectra of compounds that are too labile to be resolved into enantiomers.[1,2] Almost all of the Pfeiffer-active systems have involved a racemic metal complex and some chiral organic molecule, but two studies have been reported in which the added chiral agent was a dissymmetric metal complex.[3] In our present study, we wish to report the third Pfeiffer-active system, in which a chiral metal complex induces optical activity in another metal complex, and the first Pfeiffer-active system involving a lanthanide complex. The induced optical activity has been studied by means of circularly polarized luminescence (CPL) spectroscopy rather than circular dichroism (CD) spectroscopy, since the low absorptivity of Tb(III) complexes in the visible region makes any CD measurement of f–f optical activity difficult. On the other hand, the Tb(III) complexes tend to be strongly luminescent, and therefore the CPL technique is the preferrable method to study lanthanide optical activity. The work presented here also represents the first measurement of a classical Pfeiffer effect by means of CPL spectroscopy.

Experimental Section

Tb(III) stock solutions were obtained by dissolving Tb$_4$O$_7$ (obtained as 99.9% pure, Kerr-McGee) in the minimum amount of 70% HClO$_4$, neutralizing to pH 3 with NaOH, and then diluting to the desired volume. Pyridine-2,6-dicarboxylic acid (which shall be abbreviated as DPA) was obtained from Aldrich and used as received. The Tb(DPA)$_3^{3-}$ complex was prepared by mixing the Tb(III) and DPA stock solutions in a 1:3 mole ratio; this procedure yielded material which analyzed properly for Tb(DPA)$_3^{3-}$. The tris(ethylenediamine)chromium(III) complex was prepared[4] and resolved[5] according to literature methods.

The CPL spectra were all taken at pH 8 and were recorded on a high-resolution spectrometer constructed in this laboratory. This apparatus has been described in detail.[6] The Tb(DPA)$_3^{3-}$ complex was excited at 290 nm, and the emitted light was analyzed by a grating monochromator whose resolution was set to a 10-Å band-pass. Further increases in resolution did not lead to any improvement of the spectral features. The induced optical activity was found to increase when excess Cr(en)$_3^{3+}$ was added in solid form to an aqueous solution of Tb(DPA)$_3^{3-}$ at pH 8.

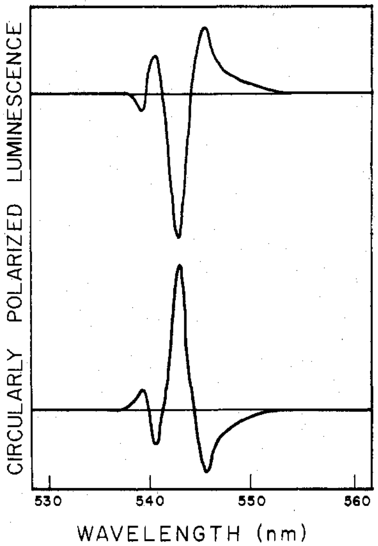

Figure 1. CPL spectra of Tb(DPA)$_3^{3-}$/Λ-Cr(en)$_3^{3-}$ (upper) and Tb(DPA)$_3^{3-}$/Δ-Cr(en)$_3^{3+}$ (lower). Both intensity scales are arbitrary.

Results and Discussion

The CPL spectra presented in Figure 1 clearly indicate that the racemic Tb(DPA)$_3^{3-}$ complex can be partially resolved upon addition of either enantiomer of Cr(en)$_3^{3+}$. The Tb(DPA)$_3^{3-}$ complex is quite unique aong lanthanide complexes in that the metal is observed to be 9-coordinate, and yet the complex possesses a C_3 axis and an approximate D_3 symmetry in solution.[7] This molecular symmetry implies that the complex theoretically is resolvable into enantiomers, but the high degree of lability associated with Tb(III) ensures that only racemic mixtures of rapidly interconverting Δ and Λ enantiomers can be prepared.

The mirror-image relationship of the CPL spectra induced by the Δ and Λ forms of Cr(en)$_3^{3+}$ strongly suggests that a definite isomer of the Tb(DPA)$_3^{3-}$ is enriched in each case and that opposite enantiomers of the Tb(III) complex are enriched by opposite enantiomers of the Cr(III) complex.

During the course of CPL measurement, two observables are recorded. One is the mean total luminescence (TL) intensity, given by

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

and the other is the differential luminescent intensity (CPL), given by

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

where I_L and I_R refer to the emitted intensities of left and right circularly polarized light, respectively. Since I and ΔI are normally measured in relative units, it is of value to calculate the luminescence dissymmetry factor:

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

The g_{lum} factor is also of theoretical interest, since it is related to the dipole and rotational strength of the transition.[8] We have calculated the values of g_{lum} for the major CPL component (found at 543 nm) in the Tb(DPA)$_3^{3-}$ spectra and have

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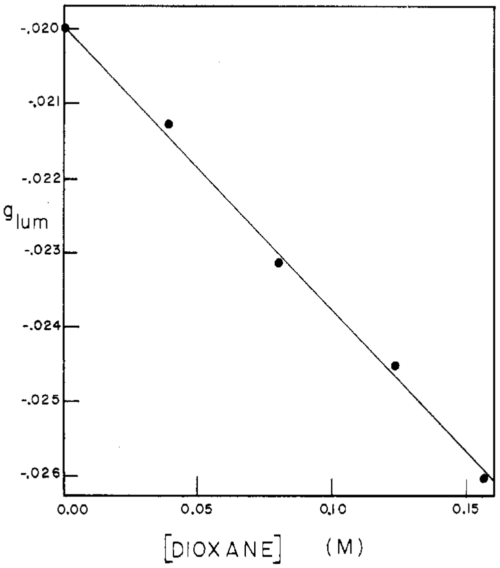

Figure 2. Enhancement of the luminescence dissymmetry factor in the $Tb(DPA)_3{}^{3-}/\Lambda\text{-}Cr(en)_3{}^{3+}$ system by the addition of dioxane.

found that g_{lum} = 0.020 when the CPL was induced by Λ-$Cr(en)_3{}^{3+}$ and g_{lum} = +0.022 when the CPL was induced by Δ-$Cr(en)_3{}^{3+}$.

For an understanding of the mechanism by which the optical activity was induced in the $Tb(DPA)_3{}^{3-}$ complex, a study was carried out in which the CPL of a $Tb(DPA)_3{}^{3-}/\Lambda\text{-}Cr(en)_3{}^{3-}$ solution was monitored during the addition of microliter amounts of neat dioxane. As may be seen in Figure 2 , the g_{lum} factor increases with added dioxane. This behavior with decreasing dielectric constant of the solvent is consistent with the existence of $Tb(DPA)_3{}^{3-}/Cr(en)_3{}^{3+}$ ion pairs. The decreased dielectric constant of the mixed solvent will lead to enhanced electrostatic attraction between the two complex ions. We therefore conclude that the Pfeiffer mechanism operational in the present system is one where optical activity is induced through the formation of an adduct species. Our work thus provides evidence that the associative mechanism[2] is operational in this Pfeiffer-active system.

It is of great interest to determine which isomer of the $Tb(DPA)_3{}^{3-}$ is favored by complexation with a particular enantiomer of $Cr(en)_3{}^{3+}$, since this would then permit one (hopefully) to assign absolute configurations of other Tb(III) complexes on the basis of CPL sign patterns. Such a possibility would be of great utility in the study of Tb(III)-substituted Ca-binding proteins, since the CPL associated with the Tb(III) emission in these proteins usually consists of one particular mirror image of a certain line shape.[9] Unfortunately, no CPL spectra of Tb(III) complexes having known absolute configurations have yet been reported, but it is possible to make certain predictions on the basis of existing information. In a recent study,[10] we have found that CPL can be induced in the emission spectrum of $Tb(DPA)_3{}^{3-}$ through outer-sphere coordination with L-ascorbic acid. TL and CPL spectra were obtained that were identical with those obtained in the present study when Λ-$Cr(en)_3{}^{3+}$ was used to induce the optical activity. One cannot assume that the L isomer of an added chiral agent will always enrich the L isomer of a racemic mixture in the course of a Pfeiffer-effect measurement.[3] Since our work represents the first investigation into Pfeiffer effects involving 9-coordinate complexes, we have no evidence to predict which enantiomer of $Tb(DPA)_3{}^{3-}$ ought to be enriched by a particular enantiomer of $Cr(en)_3{}^{3+}$. However, if one were to assume that the Λ isomer of $Cr(en)_3{}^{3+}$ enriches the system in the Λ isomer of $Tb(DPA)_3{}^{3-}$, the Tb(III) CPL spectrum having the major negative component at 543 nm would be due to the presence of the Λ isomer of $Tb(DPA)_3{}^{3-}$.

No evidence was obtained during the course of the present study to indicate that the added $Cr(en)_3{}^{3+}$ did anything to the $Tb(DPA)_3{}^{3-}$ complex except to coordinate in an outer-sphere fashion. The TL spectra of the Tb(III) ion were identical in $Tb(DPA)_3{}^{3-}$ and $Tb(DPA)_3{}^{3-}/Cr(en)_3{}^{3+}$, and we have reported this TL line shape before.[6,11] Some quenching of the Tb(III) TL intensity was noted after addition of the Cr(III) complex, but this quenching appears to be due to a combination of Tb(III)–Cr(III) energy transfer and an "inner-filter" effect of the Cr(III) complex absorbing some of the exciting light.

Comparison of the g_{lum} values obtained during the course of the present study with earlier data (obtained in a study of mixed-ligand complexes formed between Tb(III), DPA, and L-malic acid[11]) provides strong evidence that we are dealing with configurational optical activity in the $Tb(DPA)_3{}^{3-}/Cr(en)_3{}^{3+}$ system. We believe that while lanthanide complexes may not be resolved through conventional techniques, the CD of these complexes may be studied via the Pfeiffer effect. Many studies have shown that the Pfeiffer CD of a particular complex is identical with that of resolved complex CD.[1] While it is difficult to place the data on an absolutely quantitative basis (one is never sure of the degree of resolution permitted by a Pfeiffer effect), it seems clear that line shapes and trends within the CPL data can be used to deduce stereochemical information for lanthanide complexes in the same manner that CD results have been used for transition metal complexes.

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Registry No. $Tb(DPA)_3{}^{3-}$, 38682-37-0; Λ-$Cr(en)_3{}^{3+}$, 41509-53-9; Δ-$Cr(en)_3{}^{3+}$, 51002-41-6.

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Contribution from the Department of Chemistry,
The Pennsylvania State University,
University Park, Pennsylvania 16802

Crystal and Molecular Structure of Hexa(imidazolyl)cyclotriphosphazene

R. J. Ritchie, T. J. Fuller, and H. R. Allcock*

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A knowledge of the structure and hydrolytic stability of cyclic and high polymeric aminophosphazenes is important for both fundamental mechanistic and biomedical reasons.[1-7] Imidazolyl-substituted phosphazenes are of particular interest because of their potential use as coordinative ligands for

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