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Induced Optical Activity in the Tb(III) Complex of Pyridine-2,6-Dicarboxylic Acid through Outer-Sphere Coordination With L-Ascorbic Acid

JOHN S. MADARAS and HARRY G. BRITTAIN*

Department of Chemistry, , Seton Hall University, South Orange, N.J. 07079, U.S.A.

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Pfeiffer effect optical activity has been induced in $Tb(DPA)_3^{3-}$ (DPA = pyridine-2,6-dicarboxylate) through an outer-sphere complexation with L-ascorbic acid. The optical activity was found to be essentially pH independent, and is thought to be a consequence of a perturbation upon diasteromer interconversion of the D- and L-forms of the $Tb(DPA)_3^{3-}$ complex that had been induced by the L-ascorbic acid. It was found that the Tb(III) emission could be quenched by the oxidized form of the ascorbic acid, and that this quenching became more efficient as the solution pH was raised. This work represents the first measurement of a Pfeiffer effect for a lanthanide complex where the optical activity was induced by an outer-sphere coordination with a chiral resolving agent.

Introduction

The observation of optical activity associated with a racemic mixture of a chiral substance upon addition of some other chiral substance is termed the Pfeiffer effect [1, 2]. This effect has been extensively studied in a wide variety of systems containing transition metal complexes [3, 4] and has been found to be most pronounced in potentially chiral complexes that happen to be too labile for the successful resolution of enantiomers. Some disagreement has existed regarding the mechanism of the effect, but it seems most reasonable that through complexation, the added chiral agent perturbs the enantiomer interconversion of the labile complex and enriches the system in one of the optical antipodes.

We have been interested in the optical activity of lanthanide complexes for some time, and have used the comparatively new technique of circularly polarized luminescence (CPL) spectroscopy to study the optical activity of these complexes. Through this method, complexes of lanthanide ions with carboxylic and amino acids have been examined [5], and the stereochemistry of β-diketone complexes has been probed with CPL [6]. Enantiomeric separation was never carried out in any of these studies due to the high degree of lability of the complexes, but various methods were used to favor the presence of one diasteromer over another, and thus enabled the detection of CPL. CPL is clearly the most useful method for the study of lanthanide complex chirality since it combines the instrumental selectivity of circular dichroism spectroscopy with the sensitivity of luminescence spectroscopy; the very low extinction coefficients of lanthanide ions in solution preclude the effective use of circular dichroism as a probe of lanthanide chirality.

Studies involving transition metal complexes have shown that when optical activity is introduced into a potentially optically active molecule by means of the Pfeiffer effect, the chiroptical spectra that result are identical with spectra obtained through complex resolution [3, 4]. For this reason, we have undertaken to obtain the chiroptical spectra of lanthanide complexes that are too labile to be resolved by conventional means. For the first studies, we have examined the effect of chiral agents on the Tb(III) complex of pyridine-2,6-dicarboxylic acid (DPA). It is well known that lanthanide complexes of DPA have a clearly defined 3:1 ligand-to-metal ratio, and that they possess and approximate D_3 geometry in solution when the tris complex is formed [7, 8]. Complexes having this symmetry are capable of being resolved into optical enantiomers, but since the Tb(III) complexes are so labile all attempts at resolution must fail. We have found that optical activity may be introduced in solutions of $Tb(DPA)_3^{3-}$ by the formation of an outer-sphere complex with L-ascorbic acid, and that this optical activity can be measured by means of CPL spectroscopy.

Experimental

Solutions of Tb(III) were prepared by dissolving Tb_4O_7 (99.9% pure) in the minimum amount of

*Author to whom correspondence should be addressed.

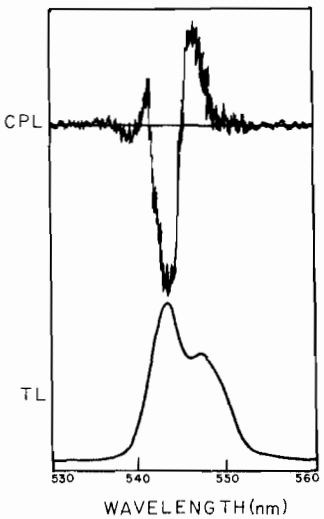


Fig. 1. Circularly polarized luminescence (upper) and total luminescence (lower) spectra for $Tb(DPA)_3^{3-}$/L-ascorbic acid at pH 5.0. Both intensity scales are arbitrary.

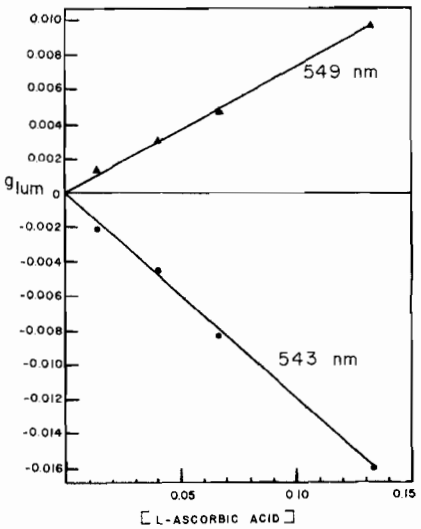


Fig. 2. Dependence of the luminescence disymmetry factor, g_{lum}, associated with $Tb(DPA)_3^{3-}$ CPL on the concentration of L-ascorbic acid.

70% $HClO_4$; after dissolution was complete, the solution was neutralized to pH 3 with NaOH and then diluted to the desired volume. DPA and all other chiral ligands were obtained from commercial sources and used without any subsequent purification. Stock solutions of all materials were prepared, and the sample used in the CPL study was obtained from these. In all cases, the Tb(III) concentration was 1.4×10^{-2} *M* and the DPA concentration was fixed at 4.25×10^{-2} *M*. Of all the chiral agents examined, only L-ascorbic acid was found to induce CPL in the $Tb(DPA)_3^{3-}$ emission. The CPL of this system was examined using Tb(III)/L-Ascorbic acid ratios of 1:1, 1:3, 1:5, and 1:10. The ionic strength was held fixed during all studies at 0.1 *M* using $NaClO_4$.

All CPL and luminescence spectra were obtained on an instrument constructed in this laboratory, and which has recently been described [9]. An excitation wavelength of 295 nm was used for all studies, and this excitation was selected by passing the output of a 200 watt Hg-Xe arc lamp through a 0.1 meter 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 $NaNO_2$) to remove any exciting light not absorbed by the sample. The emission was analyzed by a 0.5 meter grating monochromator (model 1870, Spex Industries) whose resolution was equal to a 15 Å bandpass. Further increase in resolving power did not reveal any new spectral features. The emission was finally detected by an EMI 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 CPL component (which was then displayed on the other recorder channel).

The pH of all solutions was obtained using an Orion 701A pH meter, and used a glass micro-combination electrode which could be directly inserted into the spectral cuvette. The system was calibrated daily using phosphate buffers.

Results

Irradiation of the $Tb(DPA)_3$ complex at 295 nm results in the observation of strong Tb(III) luminescence, corresponding primarily to the $^5D_4 \rightarrow {}^7F_5$ transition. Here, the DPA ligand absorbs the exciting light and transfers it in a non-radiative fashion to the lanthanide ion. This sensitized emission can be as much as 200 times as intense as the emission of Tb(III) alone in H_2O [10]. Addition of L-ascorbic acid to solutions of $Tb(DPA)_3$ at neutral pH leads to the immediate observation of CPL in the Tb(III) emission. The CPL consists of a negative signed peak at 543 nm, and a positive peak at 549 nm, and the maxima of these correspond to features present in the total luminescence (TL) spectrum. The band shape was found to be pH invariant, and a representative example of TL and CPL is shown in Fig. 1.

In the CPL experiment, two observables are produced: (a) the total luminescence (TL), given by $I = \frac{1}{2}(I_L + I_R)$ and (b) the circularly polarized luminescence (CPL), given by $\Delta I - (I_L - I_R)$. I_L and I_R represent the intensities of left- and right-circularly

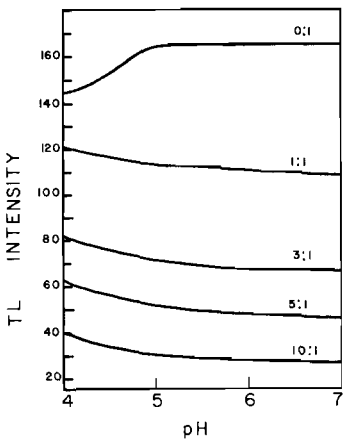


Fig. 3. pH Dependence of total luminescence intensity associated with the Tb(III) emission in $Tb(DPA)_3^{3-}$ as a function of pH and added L-ascorbic acid. The intensity scale is arbitrary, and each curve is labeled with the corresponding ratio of ascorbic acid: $Tb(DPA)_3^{3-}$.

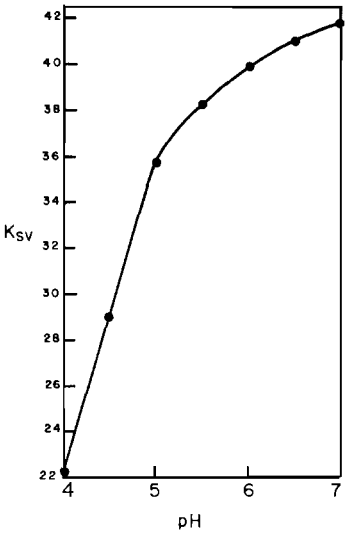


Fig. 4. pH Dependence of the Stern–Volmer quenching constants obtained from the quenching of Tb(III) emission by L-ascorbic acid.

polarized light, respectively, and are measured in totally arbitrary units. This unit dependence may be eliminated by calculating the luminescence disymmetry factor [11]:

$$g_{lum} = \Delta I/I \quad (1)$$

Values for g_{lum} were calculated at each CPL maximum. It was found that these values depended only on the concentration of L-ascorbic acid, and that at a particular ratio of $Tb(DPA)_3^{3-}$ and L-ascorbic acid the value of g_{lum} remained relatively constant over the entire pH range. g_{lum} was found to increase in a linear fashion with ascorbic acid concentration, and this behavior is shown in Fig. 2.

Addition of ascorbic acid to the $Tb(DPA)_3^{3-}$ solution also resulted in a partial quenching of the Tb(III) emission. All luminescence disappeared once the pH was raised above 8, but it could be regenerated by immediately lowering the pH to within the 4 to 7 region. The pH behavior of the Tb(III) luminescence is shown in Fig. 2 as a function of pH and of ascorbic acid concentration. The quenching followed the Stern-Volmer equation for intensity quenching very well [12]:

$$\frac{I_o - I}{I} = K_{sv}\,[\text{L-ascb}] \quad (2)$$

where I_o is the Tb(III) emission intensity in the absence of ascorbic acid quencher, I is the intensity with acid present, and K_{sv} is the Stern-Volmer quenching constant. Values for K_{sv} were found to be pH dependent, and this pH dependence is found in Fig. 4.

It was found that the luminescence intensity changes were all reversible as long as the solution pH did not exceed 7, but above this pH value the observed TL and CPL magnitudes exhibited interesting behavior. If the pH was raised above 8 and then lowered again, the magnitude of the CPL was found to depend on the length of time that the solution remained at the elevated pH. Full restoration of CPL intensity could be obtained with a rapid (within 5 minutes) pH reversal, but longer time periods led to an irreversible degradation of the CPL signal.

Discussion

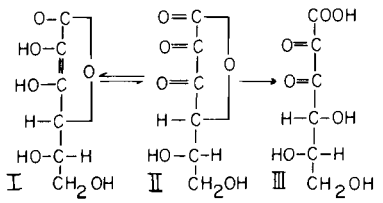
The observation that q_{lum} increases in a linear fashion with increasing L-ascorbic acid concentration (even up to ratios of 10:1) is a good indication that the interaction between the Tb(III) complex and the acid must be fairly weak. Such a weak interaction is consistent with the accepted mechanisms of the Pfeiffer effect [4]. We propose here that the L-ascorbic acid ligand is able to coordinate to the outer-sphere of $Tb(DPA)_3^{3-}$, and this complexation perturbs the interconversion of the optical enantiomers of the $Tb(DPA)_3^{3-}$ complex. An enrichment of the solution in one isomer or the other would lead to the observance of CPL. We believe that some sort of complexation is taking place since addition of L-tartaric, L-malic, or L-aspartic acids to a solution of $Tb(DPA)_3^{3-}$ does not lead to the observation of CPL.

We believe that the complexation of the ascorbic acid is outer-sphere rather than inner-sphere since the

acid is a much poorer ligand toward lanthanide ions than is the DPA ligand. While formation constants for lanthanide ion/L-ascorbic acid complexes have not been reported, it is known that the formation constants of the Ca(II) complexes are approximately 2–3 orders of magnitude smaller than the corresponding constants of the DPA ligands [12]. It is therefore unlikely that an ascorbic acid molecule could displace a DPA ligand from the metal ion coordination sphere.

It is difficult to state whether the D- or L-isomer of the $Tb(DPA)_3^{3-}$ complex has been enriched by coordination to the L-ascorbic acid. Usually, the addition of a chiral resolving agent to a racemic mixture of a metal complex will enrich the metal isomer having the same configuration as the resolving agent [3], but exceptions to this general rule are known [13]. Nevertheless, we feel that the bulk of the experimental evidence points toward an assignment in our present study of a L-configuration to the $Tb(DPA)_3^{3-}$ isomer whose CPL was illustrated in Fig. 1. Since the DPA chelate rings are rigid and planar [8], the source of the optical activity in the Tb(III) complex must be purely configurational in origin and cannot contain any effects due to either vicinal or ligand conformational effects.

It is well known that L-ascorbic acid (*I*) undergoes a reversible conversion to L-dehydroascorbic acid (*II*) in basic solution, and that the dehydroascorbic acid can undergo an irreversible hydrolysis to yield L-diketogulonic acid (*III*):



We believe that the irreversibility noted in the CPL magnitudes that was found after the solution pH was raised beyond 8 is a reflection of the degree of formation of compound *III*. If a solution of $Tb(DPA)_3^{3-}$ and L-ascorbic acid is left at pH overnight and acidified the next day, no CPL can be obtained. We may therefore conclude from this experiment that L-diketogulonic acid is incapable of inducing optical activity, and is therefore in the same class as the other chiral acids mentioned earlier. Since the basic difference between *I* and *III* is the presence of the lactone ring in *I*, we conclude that the probably site on ascorbic acid for coordination to the $Tb(DPA)_3^{3-}$ complex is at the oxygen atom of the lactone ring.

An examination of Fig. 3 reveals a very important difference in TL behavior for $Tb(DPA)_3^{3-}$ when ascorbic acid is present. In the absence of this material, the Tb(III) emission intensity rises as the pH is raised from pH 4 to pH 5, and remains at a constant value up to pH 7. In contrast, when ascorbic acid is present, the emission intensity decreases as the pH is raised. Figure 4 indicates that the quenching increases rapidly as the pH is raised from 4 to 5, and less rapidly after that. In an attempt to identify the source of the luminescence quenching, we prepared the dehydroascorbic acid(II) by a reaction with ceric ion:

$$I + 2\ Ce^{4+} \rightarrow II + 2Ce^{3+} \qquad (3)$$

Addition of *II* to a solution of $Tb(DPA)_3^{3-}$ led to a complete quenching of the Tb (III) luminescence, even in acidic solution (it should be noted that the addition of Ce(III) ion to a $Tb(DPA)_3^{3-}$ solution does not lead to emission quenching). We can therefore conclude that the compound *II* is responsible for the luminescence quenching at moderate pH values, and the K_{sv} constants are representative of how much dehydroascorbic acid exists at a particular pH value.

These studies have illustrated the value of induced optical activity as a probe of the solution chemistry of these lanthanide complexes. Since the extreme lability of these complexes precludes their resolution, studies involving the Pfeiffer will be of immeasurable effect in studying their solution chemistry. The studies reported here represent the first measure of a Pfeiffer effect involving lanthanide complexes that does not involve direct coordination of the chiral resolving agent to the metal ion. Further studies are now underway to probe the effect in more detail, and to further evaluate its applicability to the study of lanthanide ion stereochemistry.

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