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Circularly Polarized Luminescence Studies of the Ternary Complexes formed by Tb(III) Aminopolycarboxylates and (R,R)-Tartaric Acid

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The nature of the bonding between Tb(III) and (R,R)-tartaric acid in ternary aminopolycarboxylate complexes has been investigated by means of circularly polarized luminescence spectroscopy. Additional evidence regarding the inner coordination sphere of the Tb(III) ion was deduced from studies of emission lifetimes in H_2O *and* D_2O *solvents. It was found that in one system, the tartrate ligand bound the Tb(III) ion in a terdentate manner (two carboxylates and a hydroxyl group). In another system, the tartrate was found to bind in a tetradentate fashion employing all functional groups of the ligand. Finally, in two other systems, evidence was obtained which indicated that the tartrate bound the Tb(III) ion through a mixture of bonding types. No evidence was found to indicate that tartrate could bind in the purely bidentate manner of aspartic acid.*

Introduction

The family of α-hydroxycarboxylic acids consists of an extensive series of potentially chiral ligands, the members of which present a variety of complexation possibilities for a metal ion. Studies of the optical activity induced in lanthanide complexes would be a useful source of information regarding the nature of these complexes [1]. Through a systematic variation of the ligand functionalities, one should be able to deduce the nature of bonding existing between a lanthanide ion and the ligand under study. The simplest members of the series contain only the α-hydroxycarboxyl group (*e.g.*, lactic or mandelic acids) and a variable alkyl sidechain, and hence can function only as bidentate ligands. More complicated ligands (*e.g.*, malic or tartaric acids) possess different ligational properties, but studies of the simple ligands can be used to deduce the conditions under which more complicated bonding takes place.

These spectra-structure correlations require that the solution phase species be well defined, a situation not always possible in lanthanide chemistry. We have achieved this desirable situation by working with mixed-ligand lanthanide compounds. In these ternary complexes, the majority of the metal ion coordination sites are occupied by a multidentate ligand (such as an aminopolycarboxylate), and therefore only a single chiral α-hydroxycarboxylic acid ligand may be bound by the lanthanide ion. This approach simplifies all interactions to that of one metal and one chiral ligand, and also eliminates any formation of bridged polynuclear species. We have been successful in correlating chiroptical spectra with plausible solution phase bonding modes when studying the mixed-ligand complexes formed with the simple α-hydroxycarboxylic acids [2–5], and with malic acid [3–6]. Interpretation of the malic acid data required studies of the chirality associated with the mixed-ligand complexes of aspartic acid [7]. In the aspartic acid work, it was noted that the conformation of the chelated aspartate could be affected by the identity of the achiral ligand used to prepare the complex [7], and analogous effects were subsequently found in the malic acid complexes [8].

In the present work, we continue these investigations by studying the mixed-ligand complexes formed with (R,R)-tartaric acid. Richardson and Das Gupta have presented some data regarding mixed-ligand tartrate complexes [9], but have not attempted to correlate their tartrate spectra with plausible modes of metal–ligand bonding. The present work will focus primarily on the Tb(APC) (APC = an aminopolycarboxylate ligand) derivatives of tartaric acid, but will consider the relation to the systems examined by Richardson. All chiroptical studies have been carried out using circularly polarized luminescence (CPL) spectroscopy, as it has been amply demonstrated that this technique is the method of choice when examining chiral lanthanide compounds [1, 10].

Experimental

All ligands were obtained from either Aldrich or Eastman, and were used as received. Stock solutions of Tb(III) were prepared by dissolving the 99.9%

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oxides (Research Chemicals) in a stoichiometric amount of 70% $HClO_4$, neutralizing to pH 3.5 with NaOH, and then diluting to the desired volume. The aminopolycarboxylate ligands used to prepare the Tb(APC) parent compounds were ethylenediaminetetraacetic acid (EDTA), 1,2-propylenediaminetetraacetic acid (PDTA), *trans*-1,2-cyclohexanediaminetetraacetic acid (CDTA), and (2-hydroxyethyl)ethylenediaminetriacetic acid (HEDTA). A Tb:APC ratio of 1:1 was used for all studies. Concentrated stock solutions of d-tartaric acid were prepared (ranging from 0.1 to 0.4 *M*) so that variation in the Tb(APC)/TART ratios could be effected in a systematic manner. In solutions used for the CPL studies, the Tb(APC) concentration was 15 m*M* and the Tb(APC)/TART ratios varied between 1:1 and 1:20. The pH of these solutions was varied between 3.0 and 12.0.

All CPL measurements were obtained on apparatus constructed in our laboratory. In all cases, an excitation wavelength of 365 nm (selected by a 0.1 m grating monochromator) was employed, and all CPL measurements were obtained within the $^5D_4 \rightarrow {}^7F_5$ Tb(III) band system. It has been established that of all the Tb(III) emission bands, this particular transition exhibits the highest degree of both total and circularly polarized emission [11]. The emission was analyzed by a 0.5 m grating monochromator at 1 nm resolution, and it was determined that further increases in resolving power did not yield a significant improvement in the spectral features.

Variation of the solution pH within the solutions was effected by the addition of microliter amounts of standard $HClO_4$ or NaOH directly to the fluorescence cuvette. The pH was obtained using a glass microcombination electrode which could be inserted directly into the cuvette, and read on an Orion 701A pH meter. The system was calibrated daily with phosphate buffers.

Emission lifetimes were obtained on the same basic system as described above, but with the replacement of the arc lamp by a nitrogen laser (PRA Associates, model LN-100). The transient currents developed upon pulsed excitation of the sample were converted into voltages using a 220 K load resistor, and these voltage pulses were captured on a storage oscilloscope. The emission lifetimes were obtained from the decay curves using a linear regression analysis of the ln(I) *vs.* time data points. Plots of ln(I) *vs.* time were invariably found to be linear, and thus indicate the presence of only one emitting species.

The number of water molecules remaining attached to the lanthanide ions after formation of the Ln/APC complexes was determined by the method described by Horrocks and Sudnick [12]. Tb/APC solutions were brought to dryness by heating at 110 °C in a vacuum desiccator, and then redissolved in either H_2O or D_2O. The emission lifetime of the Tb(III) ion was then measured in each solvent, and the reciprocal lifetime was then used to estimate the number of coordinated water molecules.

Results and Discussion

Addition of one equivalent of any aminopolycarboxylate ligand to a solution containing lanthanide ions results in total formation of the 1:1 complex:

$$Ln^{3+} + APC^{4-} \rightleftharpoons Ln(APC)^-$$

The formation constants corresponding to the Tb(III) complexes have been determined, and it has been found that log K_1 = 17.92 for EDTA, log K_1 = 18.64 for PDTA, log K_1 = 20.20 for CDTA, and log K_1 = 15.42 for HEDTA [13]. Unlike transition metal complexes, the Ln(APC) compounds are known not to be coordinatively saturated. Horrocks and coworkers have used crystallographic techniques to determine the number of water molecules remaining bound by the lanthanide ion [14].

In the Ln(APC) compounds the coordinated solvent is labile and may easily be replaced by more strongly binding ligands: for instance, the Ln(APC) compounds are capable of functioning as aqueous shift reagents [15]. The formation of the ternary tartrate complexes may be represented by:

$$Ln(APC)^- + TART^{2-} \rightleftharpoons Ln(APC)(TART)^{3-}$$

It is clear that formation of the tartrate compounds must be accompanied by the loss of one or more of the coordinated water molecules, but it cannot be assumed beforehand that all solvent will be expelled from the Ln(III) coordination sphere.

Fortunately, it is possible to count the average number of water molecules present in the inner coordination sphere of Ln(III) ions in complexes through the technique developed by Horrocks and Sudnick [12]. It is well known that the luminescence intensity and and lifetime of emissive lanthanide compounds will increase significantly upon passing from H_2O to D_2O solvent, as long as one or more water molecules are present in the inner coordination sphere of the metal ion. Horrocks and Sudnick have determined that the difference in radiative rate constants (calculable from the emission lifetime) measured in H_2O and D_2O solutions is proportional to the number of coordinated solvent molecules [12]. Using this method, these workers found that 2.8 water molecules were coordinated in the first coordination sphere of Tb(III) in Tb(EDTA).

We have measured the emission lifetimes within the $^5D_4 \rightarrow {}^7F_5$ Tb(III) transition (545 nm) in H_2O

TABLE I. Luminescence Decay Constants and Characterization of the Tb(APC) and Tb(APC)(TART) Complexes.

	H_2O (μsec)	k_{obs} ($msec^{-1}$)	D_2O (μsec)	k_{obs} ($msec^{-1}$)	# H_2O
Tb(EDTA)	1053	0.95	3571	0.28	3.0
Tb(PDTA)	876	1.14	2455	0.41	3.3
Tb(CDTA)	983	1.02	2781	0.36	3.0
Tb(HEDTA)	777	1.29	2564	0.39	4.1
Tb(EDTA)(TART)	1544	0.65	1923	0.52	0.6
Tb(PDTA)(TART)	1322	0.76	1538	0.65	0.5
Tb(CDTA)(TART)	1375	0.73	2041	0.49	1.1
Tb(HEDTA)(TART)	1863	0.54	1923	0.52	0.1

and D_2O solvent for all the Tb(APC) and Tb(APC)(TART) complexes, and have used the Horrocks method to evaluate the number of coordinated solvent molecules. The results of this investigation are summarized in Table I. It may be noted that the results we have obtained for Tb(EDTA) agree excellently with those found by Horrocks and Sudnick for the same compound [12]. All the Tb(APC) data were obtained at pH 9.0 employing a 1:1 Tb(III)/APC molar ratio. The data obtained for Tb(EDTA), Tb(PDTA), and Tb(CDTA) indicate that 3 water molecules remain coordinated to the Tb(III) ion in each instance. For the Ln(APC) compounds, it is known that at pH 9 each APC ligand binds in a hexadentate manner [16] and that the complexes are all monomeric at this pH value [17]. One may then conclude that the Tb(III) ion is 9-coordinate in each compound. The HEDTA ligand was found to bind 4 water molecules, an observation consistent with a pentadentate bonding mode for this ligand.

The Tb(APC)(TART) data were obtained at pH 11 on solutions having a 1:2.5 molar ratio of Tb(APC)/TART, since the CPL studies (which will be discussed in the next section) provided evidence that full formation of the ternary complexes took place under this particular set of experimental conditions. The lifetimes of each Tb(APC)(TART) complex were invariably longer than those of the analogous Tb(APC) compounds, but the lifetime difference between H_2O and D_2O solvents was substantially less for the TART ternary compounds. One surprising result was that there appears to be no solvent bound at the inner coordination sphere of Tb(HEDTA)(TART). Tb(CDTA)(TART) appears to contain a single water molecule, while Tb(EDTA)(TART) and Tb(PDTA)(TART) appear to bind (on the average) half a water molecule. This last result suggests that solutions of Tb(EDTA)(TART) and Tb(PDTA)(TART) might actually consist of equimolar mixtures of species binding one or zero solvent molecules.

Four possible bonding modes may be proposed for the interaction of tartaric acid with a lanthanide ion. The first of these is bidentate binding at one of the α-hydroxycarboxylic groups, as is observed for mandelic or lactic acids [2, 3]. The second bidentate coordination mode might involve only the two carboxylate groups, as is known for aspartic acid [7]. Another possibility would be the terdentate mode, in which bonding involves one hydroxyl group and both carboxylates. Such bonding has been observed for malic acid complexes above neutral pH [6, 8]. Finally, the TART ligand might bind a Tb(III) ion in a tetradentate manner, using all possible functional groups. The chiroptical spectra obtained for the various Ln(APC)(TART) complexes should be reliable indicators of the mode of ligand bonding in each system.

Formation of the ternary tartrate complexes led to the observation of strong optical activity within all Tb(III) luminescence bands. However, only very weak CPL was observed below pH 10, but between pH 10.5 and 12.0 extremely strong CPL could be recorded. Any one of the $^5D_4 \rightarrow {}^7F_J$ transitions (J = 3–6) could have been used to establish the general trends, but in the present work we have elected to work exclusively with the $^5D_4 \rightarrow {}^7F_5$ transition. This choice was made since the $^5D_4 \rightarrow {}^7F_5$ band is the most intense of all the Tb(III) bands, and is also known to exhibit the largest degree of optical activity [11]. Representative examples of the observed spectra may be found in Figs. 1–3.

Should the TART ligand choose to bind in a purely bidentate manner between its two carboxylate groups, then one would anticipate that the induced chirality would closely match that of the aspartic acid derivative of Tb(APC). The Tb(APC)(S-ASP) complexes have been studied [7], and it has been found that all APC ligands yielded identical CPL lineshapes. These spectra are difficult to compare to those of Tb(APC)(R,R-TART) due to the difference in absolute configuration of the chiral

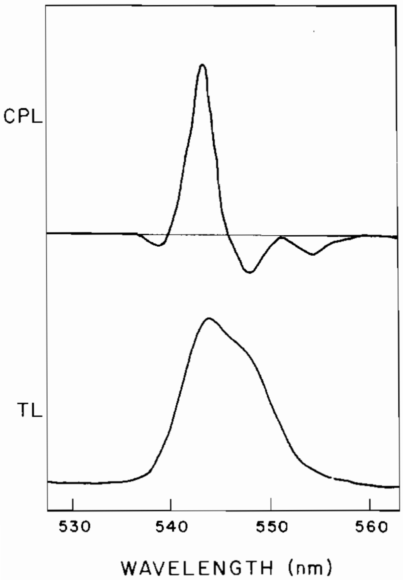

Fig. 1. Total luminescence (lower) and circularly polarized luminescence (upper) spectra obtained within the $^5D_4 \rightarrow {}^7F_5$ transition of Tb(HEDTA)(TART) at pH 11. The intensity scales for both spectra are purely arbitrary.

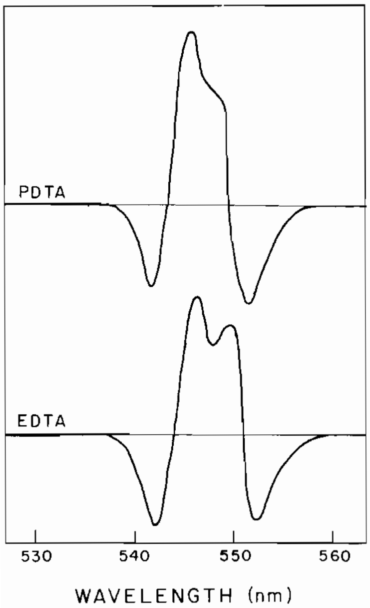

Fig. 2. Circularly polarized luminescence spectra obtained within the $^5D_4 \rightarrow {}^7F_5$ transition of Tb(PDTA)(TART) (upper spectrum) and Tb(EDTA)(TART) (lower spectrum), both measured at pH 11.

ligands, so the CPL spectra of the Tb(APC)(R-ASP) compounds were recorded as part of the present work. The resulting spectra were again not found to vary with the identity of the APC ligand. An example Tb(APC)(R-ASP) CPL within the $^5D_4 \rightarrow {}^7F_5$ transition is found in Fig. 4. Comparison of the CPL spectrum of Fig. 4 with those of Figs. 1–3 demonstrates clearly that sole bidentate attachment of the TART ligand in the Tb(APC) complexes is not a viable bonding mode.

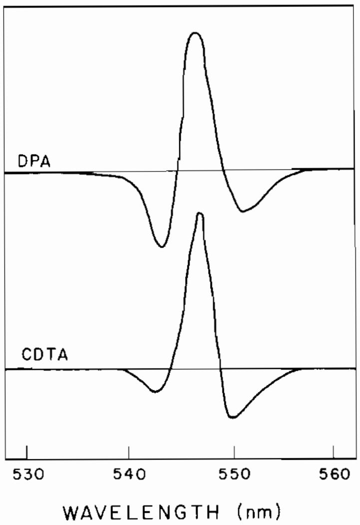

Fig. 3. Circularly polarized luminescence spectra obtained within the $^5D_4 \rightarrow {}^7F_5$ transition of Tb(CDTA)(TART) (lower trace, pH 11) and Tb(DPA)(R-Malate) (upper trace. pH 10).

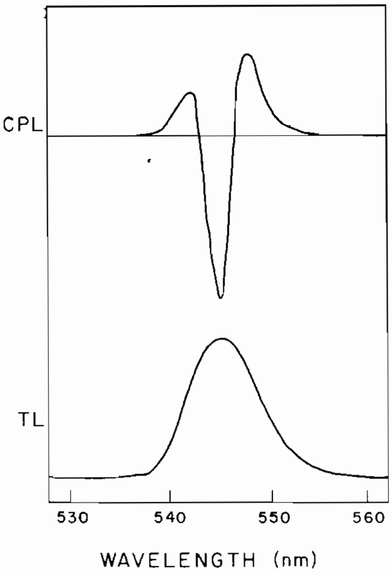

Fig. 4. Total luminescence (lower trace) and circularly polarized luminescence (upper trace) spectra obtained within the $^5D_4 \rightarrow {}^7F_5$ transition of Tb(EDTA)(R-aspartate) at pH 11.

On the other hand, the CPL spectrum obtained for Tb(CDTA)(TART) matches quite closely a previously reported example. Above neutral pH values, the CPL spectra of malic acid complexes are found to undergo lineshape alterations indicative that the ligand is binding in a terdentate mode [3–6]. The spectra obtained for $Tb(DPA)_2$-(R-MAL) [DPA = pyridine-2,6-dicarboxylate] at high pH values (see Fig. 3) are not exactly superimposable with those of Tb(CDTA)(TART), but the correspondence is extremely close. The steric bulk of the CDTA ligand is much larger than any of the other APC ligands, and consequently one might expect that the TART ligand could be prevented from binding as a tetradentate ligand. At the same time, the water counting experiments have established that a single water molecule remains bound by the Tb(III) ion. It would thus appear that while a coordination position exists at the Tb(III) ion, the steric bulk of the CDTA ligand prevents the formation of the last TART chelate ring.

The Tb(HEDTA)(TART) spectrum is of a type not found in any of the earlier studies involving α-hydroxycarboxylic acids [2–6, 8], and is therefore identified as being indicative of the tetradentate bonding mode of tartaric acid. The CPL lineshape is very similar to that of $Tb(DPA)_2$(R,R-TART) at pH 5 [9]. In this system, the CPL spectra undero drastic changes as the pH is raised to 9.0, but energy transfer experiments indicate that self-association of the ternary complexes into unknown species is taking place [18]. The water counting experiments indicated that no solvent remained in the Tb(III) inner coordination sphere, which would indicate that the process not possible for Tb(CDTA)(TART) can take place with Tb(HEDTA)(TART). In the Tb(HEDTA) parent compound, an extra coordination position appears to exist, and the CPL data indicate that this extra space on the Tb(III) ion promotes full tetradentate bonding on the part of the TART ligand.

The water counting experiments indicated that the solutions of Tb(EDTA)(TART) and Tb-(PDTA)(TART) contained mixtures of complex species. The CPL spectra shown in Fig. 2 support this hypothesis, as the major positive CPL peaks clearly consist of at least two components. It may be noted that the wavelengths of these lie intermediate between the wavelengths characteristic of the terdentate (CDTA) and tetradentate (HEDTA) tartrate bonding modes. It is plausible to assume that in the Tb(EDTA)(TART) and Tb(PDTA)-(TART) complexes, the steric bulk of the APC ligands cannot play the defining role in determining the bonding mode of the TART ligand. The spectra appear to contain almost equal contributions from each bonding mode, and one may note that an average of 0.5 water molecules remain in the inner Tb(III) coordination sphere. Such a situation would prevail if the solution contained equal amounts of Tb(III) compounds which bound zero and one water molecule, respectively.

Conclusions

A combination of luminescence spectral techniques has been shown to be extremely useful in the characterization of the ternary compounds formed between Tb(APC) and tartaric acid. As in previous works, the chiroptical spectra have been extremely useful in evaluating modes of metal–ligand bonding . From the results of the present and earlier works [2–8], it is becoming increasingly clear that differing steric natures of the ligands in these ternary complexes can profoundly affect the nature of the bonding. When dealing with simple ligands only capable of interacting with a metal ion in one or two manners, the CPL spectra alone could be used to deduce the desired structural information. As the ligand becomes more complex and contains a variety of ligating possibilities, supporting evidence from other methods becomes invaluable in the data interpretation.

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