OPTICAL ACTIVITY OF MIXED-LIGAND COMPLEXES OF Tb(III) WITH PYRIDINE-2,6-DICARBOXYLIC ACID AND HYDROXYCARBOXYLIC ACIDS

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ABSTRACT

The interaction between Tb(III) and several α-hydroxy­carboxylic acids has been studied by means of circularly polarized luminescence (CPL) spectroscopy. Complexes having the general formula Tb(DPA)(L) in ratios of 1:2:1 and 1:1:1 were studied (where DPA signifies pyridine-2,6-dicarboxylate) were studied in an attempt to use CPL spectroscopy as a probe of the solution chemistry existing between the Tb/DPA complexes and the chiral hydroxycarboxylic acids. The chiral L ligands used were L-hydroxy­isocaproic acid, L-argininic acid, L-hydroxyglutaric acid, and D­isocitric acid. All of the ligands were found to bind Tb(III) in a bidentate fashion, except for isocitrate which appeared to be terdentate. Equilibrium quotients for the interaction of the Tb/DPA complexes were calculated from the CPL data.

INTRODUCTION

The lanthanide complexes of hydroxycarboxylic acids have been of interest since the early observation that these ligands could be used in the ion exchange separation of the rare-earth cations, and many workers have studied the solution phase equilibria of these complexes (1). On the other hand, little attention has been paid to chiroptical studies of the lanthanide complexes, in spite of the degree of information that can be gleaned from such studies and the commercial availability of the resolved ligands. In our laboratory, we have shown that CPL spectroscopy is the best

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chiroptical method for the study of chiral lanthanide complexes, since the emission bands do not overlap and the technique is very sensitive. In earlier studies, we have examined the solution phase chemistry of Tb/DPA mixed-ligand complexes which contained L-malic acid (2) and L-lactic, L-mandelic, and L-phenyllactic acids (3), and have been able to deduce information regarding the mode of metal/ligand bonding in these complexes. In the present report, we extend our studies to include four new hydroxycarboxylic acid ligands and as a result have been able to develop new details of the solution phase bonding.

EXPERIMENTAL

The procedures required to obtain the Tb(DPA)(L) and Tb(DPA)₂(L) mixed-ligand complexes have been described previously in great detail (2,3), as has been the CPL spectrometer (4). L-α-hydroxyisocaproic (HIC), L-argininic (ARG), L-hydroxyglutaric (HGT), and D-isocitric (ICT) acids were used as received from Sigma, with

HIC, \( R = \text{CH}_2\text{CH(CH}_3)_2\text{CH}_3 \)

ARG, \( R = \text{CH}_2\text{CH}_2\text{CH}_2\text{C(NH)}\text{-NH}_2 \)

HGT, \( R = \text{CH}_2\text{CH}_2\text{COOH} \)

ICT, \( R = \text{CH(COOH)}\text{-CH}_2\text{COOH} \)

RESULTS AND DISCUSSION

The binding of a chiral hydroxycarboxylic acid ligand by either Tb(DPA) or Tb(DPA)₂ results in the generation of strong CPL in the Tb(III) emission bands. This CPL is a reliable indicator of the absolute configuration of the chiral ligand, and we have found that the \(^{5}D_4 \rightarrow ^{7}F_5\) Tb(III) emission band (4-5) yields the maximum amount of information (2-4). In one previous study (5), we showed that the CPL associated with Tb/DPA complexes containing monodentate chiral ligands was considerably weaker than the CPL of complexes known to bind in a bidentate manner, and the CPL lineshape was also quite different (3). We then concluded that the hydroxycarboxylic acids bind to the Tb(III) ion in a bidentate fashion, even in acid solution where the hydroxyl group cannot be ionized (3).

In the present work, we find that the CPL of mixed-ligand complexes which contain HIC, ARG, or HGT is identical to the lineshapes reported before (3), and that this CPL is invariant from pH 3.0 to 7.0. It is therefore possible to conclude that these ligands also bind in the same bidentate manner. Such a conclusion is not surprising for the HIC and ARG ligands, but HGT contains an additional carboxylic acid group which might become involved in bonding.