Luminescence Spectra of the Tetrahydrofuran Adducts of $TbCl_3$

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The measurement of Tb(III) luminescence spectra under conditions of high resolution has proved to be extremely valuable in the past as a means to detail the energy levels of this ion in a variety of host environments [1, 2]. While the data obtained from cubic or octahedral Tb(III) site symmetries may be fully interpreted by the existing theory, the extremely complicated nature of the Tb(III) emission bands makes it impossible to apply the same procedures to systems with the Tb(III) ions at centers of low symmetry. Nevertheless, such systems are extremely important to study, since low symmetry characterizes essentially all inorganic, organometallic, and bioinorganic solution phase chemistry. In addition, luminescence spectroscopy provides a means by which structural data may be obtained on both solution and solid phase systems involving the same Tb(III) species. Currently, nmr techniques are usually restricted to solution phase work, and in the solid state one normally works exclusively with X-ray diffraction methods.

Recently, the high resolution luminescence spectra of tris(cyclopentadienyl)Tb(III) and tris(methylcyclopentadienyl)Tb(III) in frozen tetrahydrofuran (THF) solutions were reported [3]. While the observed spectra were found to be quite complicated, significant chemical information was still available in the data. A precursor of the organometallic Tb(III) compounds is the THF adduct of $TbCl_3$, and we report here studies in which the luminescence spectra (obtained at cryogenic temperatures under conditions of high resolution) of anhydrous $TbCl_3$ have been contrasted with spectra obtained from THF adducts of the same Tb(III) salt.

Experimental

The complexes described herein were moisture sensitive. Therefore, the synthesis and manipulations of these materials were conducted with rigorous exclusion of water using Schlenk, vacuum line, and dry box (Vacuum/Atmospheres HE-43 Dri-Lab, recirculated argon atmosphere) techniques.

Hydrated $TbCl_3 \cdot 6H_2O$ was obtained from Research Chemicals, and was dehydrated by the method of Taylor and Carter [4]. Tetrahydrofuran was dried and degassed by distillation from sodium benzophenone ketyl under argon. Infrared spectra of these sensitive materials were recorded on a Nicolet 5DX FT-IR spectrometer, and were obtained as Nujol mulls held in an O-ring sealed Barnes Presslok holder. Complexometric metal analyses were conducted using procedures which have been described previously [5].

The THF solvates of $TbCl_3$ were prepared following a minor modification of the method of Rossmanith and Auer-Welsbach [6]. Typically, about 2 g of anhydrous $TbCl_3$ was introduced into a Schlenkware Soxhlet extractor. The solid was then extracted with 70 mL of THF until no solid material remained on the frit of the extractor. Cooling the receiver solution to room temperature was followed by a vacuum filtration of the resulting slurry, and in this manner the microcrystalline THF solvate of $TbCl_3$ was isolated. The white needles obtained were then allowed to stand open in the dry box until constant weight was achieved. The clear, colorless filtrate obtained after the separation step was reserved for additional luminescence studies.

For the luminescence work, samples of the initial anhydrous $TbCl_3$, solid $TbCl_3$ solvate, and $TbCl_3$/THF solution were sealed in 25 cm quartz tubes. All spectra were obtained on a high-resolution emission spectrometer constructed at Seton Hall University. Samples were excited by the 350 nm output (50 mW) of an Ar-ion laser, and the emission was analyzed at 1 Å resolution by a 1-meter grating monochromator (Spex model 1704), detected by a cooled photomultiplier tube (S-20 response), and processed through the Spex digital photometer. All luminescence was obtained at a sample temperature of 77 K, with the quartz sample tubes immersed in liquid nitrogen. The THF solution formed an acceptable glass.

Results and Discussion

Complexometric metal analysis performed on the weight-stable crystalline $TbCl_3$/THF adduct indicated that this material could be formulated as $TbCl_3 \cdot 3.5THF$, and this value is within the range found by Rossmanith and Auer-Welsbach [6]. The infrared spectrum of this material is shown in Fig. 1, and there one may clearly observe the presence of coordinated THF. The strong IR bands observed at 859 and 1011

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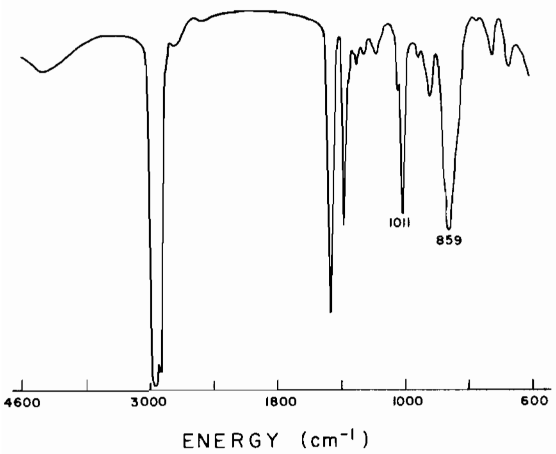

Fig. 1. Infrared spectrum of $TbCl_3 \cdot 3.5THF$. The bands corresponding to coordinated THF at 859 and 1011 cm^{-1} are marked.

cm^{-1} are consistent with the coordination of THF to a neutral lanthanide complex.

Excitation of the Tb(III) compounds at 350 nm resulted in strong luminescence, and at 77 K a considerable amount of fine structure was noted in each Tb(III) band. Emission normally originates from the $^5D_4$ excited state, and transitions to each of the ^7F_J ($J = 1$ to 6) ground state levels can be observed. Probably the most successful interpretations of Tb(III) spectra have been made when this ion was substituted into host lattices in which the Tb(III) site symmetry was known to be cubic or higher. Spectra obtained for the $LaCl_3$:Tb [2, 7] or $CsNaYCl_6$:Tb [8–10] have been compared to those calculated for the free ion [11], and it has become possible to compute magnetic and electric dipole intensities for the $CsNaTbCl_6$ system [12].

Since the exact metal ion site symmetry is not known for any of the Tb(III) species discussed here, detailed analyses of the spectra are not possible. Nevertheless, a number of trends are apparent in the data, and these can be shown to have significant importance for the use of luminescence spectroscopy in the study of organometallic Tb(III) compounds. These trends may be discussed through examination of the representative spectra shown in Figs. 2 and 3. Spectra have been obtained for all $^5D_4 \rightarrow {}^7F_J$Tb(III) transitions, and those not illustrated are in the supplemental section of this journal.

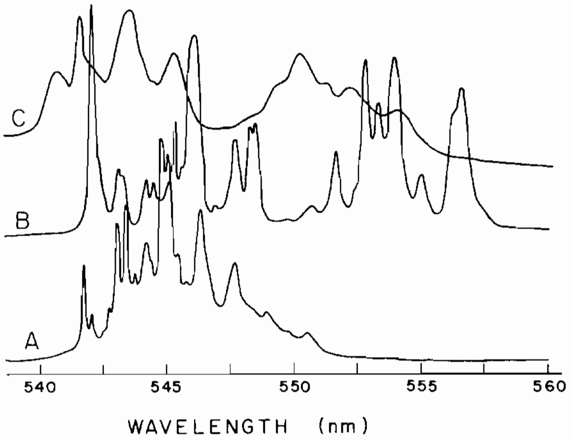

Fig. 2. Luminescence spectra of anhydrous $TbCl_3$ (A), crystalline $TbCl_3 \cdot 3.5THF$ (B), and THF saturated with $TbCl_3$ (C), obtained at 77 K. The spectra correspond to the $^5D_4 \rightarrow {}^7F_5$ transition, and the intensity scale is purely arbitrary.

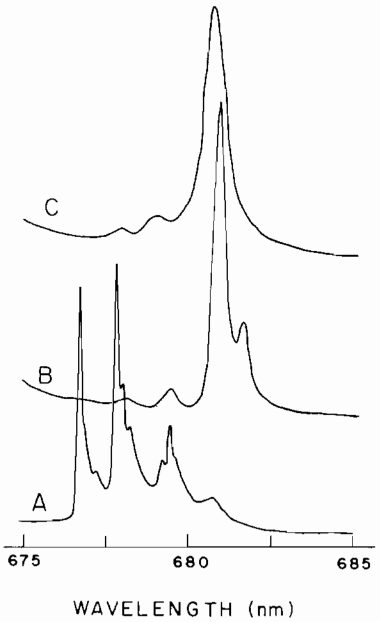

Fig. 3. Luminescence spectra of anhydrous $TbCl_3$ (A), crystalline $TbCl_3 \cdot 3.5THF$ (B), and THF saturated with $TbCl_3$ (C), obtained at 77 K. The spectra correspond to the $^5D_4 \rightarrow {}^7F_0$ transition.

It is generally assumed that crystal field effects are of minor importance in Tb(III) luminescence spectroscopy, but a comparison of the spectra obtained for anhydrous $TbCl_3$ and $TbCl_3 \cdot 3.5THF$ clearly illustrates that the coordinated THF molecules strongly perturb the energy levels of the Tb(III) ion. Most of the emission peaks observed in solid $TbCl_3 \cdot 3.5THF$ are present in the $TbCl_3(THF)_x$ solution (broadened, of course), but in many instances sharp lines observed in the solid disappear upon dissolution in THF. This observation suggests that the solid $TbCl_3$ solvate actually contains more than one Tb(III) species. The sharp line emission would correspond to well-defined Tb(III) sites in the microcrystalline solid, and the loss of these lines in solution implies a corresponding loss of these sites. The existence of multiple Tb(III) complexes would account for the observation that a non-integral number of THF molecules are bound by the $TbCl_3$.

The most significant trends observed in the luminescence spectra concern the energies observed for each band system. It is generally assumed that Tb(III) emission bands in complexes are found at essentially the same energies as calculated for the free ion. However, in the present work, we have noted a consistent (though small) shifting of the barycenters of all Tb(III) emission bands upon passing from anhydrous $TbCl_3$ to the THF solvates. For the $^5D_4 \rightarrow {}^7F_6, {}^7F_5, {}^7F_4, {}^7F_3$ bands this shift is manifested by the appearance of many new bands at lower energies (see Fig. 2 for an example of this behavior). In other band systems ($^5D_4 \rightarrow {}^7F_2, {}^7F_1, {}^7F_0$), the entire band system shifts toward lower energies. This latter observation is best illustrated in Fig. 3, where the movement of the $^5D_4 \rightarrow {}^7F_0$ band system to longer wavelengths is quite clear. The shifting of these emission bands to lower energies strongly suggests the presence of nephelauxetic effects, and evidence for possible covalence in lanthanide bonding may lie in these weak Tb(III) bands. For instance, in anhydrous $TbCl_3$ the highest energy $^5D_4 \rightarrow {}^7F_0$ band is found at 14,778 cm^{-1} (6767 Å). The corresponding peak in $TbCl_3 \cdot 3.5THF$ is located at 14,747 cm^{-1} (6781 Å), and in the THF adduct of tris(cyclopentadienyl)Tb(III) the highest energy peak is found at 14,589 cm^{-1} (6854 Å).

The nephelauxetic effects are much more apparent when one considers the barycenters of the emission bands, as these are the quantities which may be compared to the free ion values. These values enable one to estimate the position of each f-state derived from the f^8 configuration, and the energy levels corresponding to the ^7F_J and $^5D_4$ states have been collected in Table I. It is clear that the complexation of THF by $TbCl_3$ results generally in a lowering of the energy levels of all the states considered, and this effect represents a classic nephelauxetic effect. For comparison, data obtained from the THF adduct of tris(cyclopentadienyl)Tb(III) [3] are also included, and one may note that the trend toward lower energy levels is continued even further in this compound.

TABLE I. Energy Levels of Tb(III) as Determined from the Luminescence Spectra.

	Anhydrous $TbCl_3$	$TbCl_3 \cdot$ 3.5THF	Saturated $TbCl_3$ in THF	$Tb(Cp)_3$ in THF
$^7F_6$	0	0	0	0
$^7F_5$	2106	2051	2058	1930
$^7F_4$	3553	3286	3287	3230
$^7F_3$	4308	4241	4225	3911
$^7F_2$	5014	4978	4951	4849
$^7F_1$	5449	5410	5404	5266
$^7F_0$	5680	5611	5594	5593
$^5D_4$	20,408	20,313	20,300	20,105

All energies are given in cm^{-1}, and the data for tris(cyclopentadienyl)Tb(III) were taken from reference [3].

Given that all Tb(III) compounds in the present work are neutral and similar in nature indicates that the shift in energy levels (the nephelauxetic effect) may be related to small degrees of covalency in the bonding.

The bonding discussion may be placed on a more quantitative level through a calculation of the nephelauxetic ratio:

$$\beta = E_S/E_A$$

and the bonding parameter:

$$\delta = \left[\frac{1-\beta}{B}\right](100).$$

E_S and E_A refer to the energies of the corresponding transitions in the THF solvates and in anhydrous $TbCl_3$, respectively. It has been suggested [13–15] that the sign of the bonding parameter may provide information regarding the nature of the bonding: a negative value for δ would imply the presence of predominately ionic bonding. Values for β were calculated from all 7 emission band systems observed for the $TbCl_3THF$ solvates and for $Tb(Cp)_3$, and then these were averaged so as to provide a β value for each complex system. δ values were then calculated from these average values. It was found that for the solid $TbCl_3 \cdot 3.5THF$ solvate $\beta = 0.9968$ and $\delta = 0.321$, while for $TbCl_3$ dissolved in THF $\beta = 0.9964$ and $\delta = 0.361$. These values are essentially equal, but for $Tb(Cp)_3(THF)$ it was determined that $\beta = 0.9880$ and $\delta = 1.215$ [3]. These results may be contrasted to those obtained from absorption measurements on $PrCl_3$ complexes in aqueous solution, where it was found that the δ parameter was uniformly negative in sign and hence the bonding could be taken as being totally ionic in nature [16].

From this spectroscopic information, one may conclude that there appears to be a slight degree of covalency in the bonding between $TbCl_3$ and coordinated THF. The covalency appears to be considerably greater in the cyclopentadienyl compound compared to the THF adducts of $TbCl_3$. Of course, on an absolute scale, the data indicate that the bonding in the Tb(III) compounds is still predominately ionic in nature. Nevertheless, it is clear that careful studies of the luminescence spectra of Tb(III) organometallic compounds may yield valuable bonding information, and therefore such work is in progress.

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Supplementary Material Available

Luminescence spectra corresponding to the $^5D_4 \rightarrow {}^7F_6$, $^7F_4$, $^7F_3$, $^7F_2$, $^7F_1$ transitions for anydrous $TbCl_3$, crystalline $TbCl_3 \cdot 3.5THF$, and THF saturated with $TbCl_3$. Ordering information is given on any current masthead page.

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