tration, and the filtrate was washed with water and then dried. The mixture was concentrated and subjected to Kugelrohr distillation (80–90 °C (0.75 mmHg)) to give 40 mg of a colorless liquid (29%): ^{1}H NMR (360 MHz, $CDCl_3$, Me_4Si) δ 5.22 (d, 2 H, J = 0.8 Hz, $=CH_2$), 4.79 (d, 2 H, J = 1.2 Hz, $=CH_2$), 3.41 (br, 4 H, $=CCH_2N$), 2.45 (s, 6 H, CH_3N); IR (neat) 3078 (m), 1635 (m), 1450 (m), 1239 (m), 1103 (m), 887 (s), 753 (m) cm^{-1}. mass spectrum, *m/e* (relative intensity) 138 (M^+, 94), 123 (100), 108 (17). Anal. Calcd for $C_8H_{14}N_2$: C, 69.52; H, 10.21; N, 20.27. Found: C, 69.48; H, 10.06; N, 20.37.

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Registry No. 1, 12090-04-9; 2, 87185-05-5; 3, 87185-06-6; 4, 87185-07-7; 7, 87185-08-8; 8, 87185-09-9; $NaCH(CO_2Me)_2$, 18424-76-5; PPh_3, 603-35-0; Na_2PhSO_2CCN, 87185-10-2; dimethyl malonate, 108-59-8; phenyl cyanomethyl sulfone, 7605-28-9; dimethyl succinate, 106-65-0; dimethyl succinate (dianion), 87185-11-3; 1,4-bis(diisopropylamino)-2,3-dimethylenebutane, 87185-12-4; *n*-butylamine, 109-73-9; dimethylhydrazine, 30260-66-3.

Luminescence of Organometallic Lanthanide Compounds. Tetrahydrofuran Adducts of Tricyclopentadienylterbium(III) and Tris(methylcyclopentadienyl)terbium(III)

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The photoluminescence of the title compounds has been studied at room and cyrogenic temperatures. Transitions from the luminescent $^5D_4$ level to every member of the ground ^7F_J manifold (J = 0–6) were observed. When examined at 2-Å resolution, each J–J transition was found to contain a very large number of components and the resolution of these improved noticeably at 77 K. Group theoretical analysis of the various J levels was carried out for C_{3v} symmetry, and the results used to predict the number of allowed transitions permissible for each transition. Almost without exception fewer peaks were observed than were predicted, and this observation prevented a complete theoretical analysis of the data. However, in the $^5D_4 \rightarrow {}^7F_0$ transition of $Tb(Cp)_3(THF)$ a full determination of the origin of all bands could be made, and it was established that emission took place out of all crystal field components of the $^5D_4$ excited state. At room temperature, the cyclopentadienyl compound appeared to be spectroscopically identical with the methylcyclopentadienyl compound, but at cryogenic temperatures significant differences exist between the two.

Introduction

Investigation of the organometallic chemistry of lanthanide ions has become an area of intense research activity, with the complexes containing cyclopentadienyl (Cp) ligands being the best understood.[1-5] Much research has centered on identifying the differences between organolanthanide and organotransition-metal complexes in order to exploit the special features of lanthanides to provide materials with new types of physical, chemical, and catalytic properties. One main area of difference is the role of covalency in the metal–ligand bonding. It is generally agreed that the bonding in lanthanide organometallic compounds is essentially totally ionic in nature.[5,6]

To characterize organometallic lanthanide complexes, most workers have employed techniques suited for structural determination, such as X-ray crystallography and NMR spectroscopy. The use of optical spectroscopy as a means of characterization has not been extensively exploited, and only a few studies are in the literature. The f–f absorption bands of $Yb(Cp)_3$, $Er(Cp)_3$, and several Lewis base adducts of these have been studied down to liquid-helium temperatures,[7-9] and it became established that little perturbation of the free ion energy levels resulted after complexation. However, the appearance of a new charge-transfer band was noted in the organometallic compounds,[7-9] and the existence of such transitions was deduced in other studies involving different compounds.[10]

Even less work has been carried out by using luminescence methods, in spite of the situation where it is known that the emission spectra associated with f–f transitions generally consists of only a few well-separated band systems. It has been determined that $Gd(Cp)_3$ and $La(Cp)_3$ exhibit strong emission at both room and cryogenic temperatures,[8] although this luminescence is certainly localized on the Cp ligands. The f–f luminescence bands of $Yb(Cp)_3$ and several adducts of this compound have also been re-

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ported.[9] In the present work, we wish to detail studies of the luminescence spectra obtained for the Tb(III) derivatives of cyclopentadiene (Cp) and methylcyclopentadiene (MeCp) in tetrahydrofuran. The emission obtained upon UV irradiation of these complexes originates within the f–f transitions of the Tb(III) ion and contains information pertinent to the solution-phase structures.

Experimental Section

The organoterbium complexes described in this paper are extremely air and moisture sensitive. Syntheses were conducted with rigorous exclusion of air and water by using Schlenk, vacuum line, and glovebox (Vacuum/Atmospheres HE-43 Dri-Lab) techniques.

Anhydrous terbium chloride was prepared from the hydrate (Research Chemicals) by the method of Taylor and Carter,[12] and NaC_5H_4R (R = H, CH_3) was prepared as previously described.[13] Both Tb(Cp)$_3$(THF) and Tb(MeCp)$_3$(THF) were prepared from $TbCl_3$ and NaC_5H_4R following the method of Wilkinson.[14] For these syntheses, the THF used was distilled from potassium benzophenone ketyl. For the luminescence studies, a solution of known concentration was prepared from freshly recrystallized material in the glovebox, and a portion was transferred to a quartz tube (3-mm o.d.) attached to a ground glass joint and a stopcock adapter. This assembly was removed from the glovebox and attached to a high vacuum line. The bottom part of the tube was cooled to 77 K, and the tube was evauucated and then sealed with a torch.

All spectra were obtained on a high-resolution emission spectrometer constructed in our laboratory. Samples were excited by the 325-nm output (10 mW) of a He–Cd laser, and the emission was analyzed at 2-Å resolution by a 1-m grating monochromator (Spex Model 1704). The emission was then detected by a cooled photomultiplier tube (S-20 response) and processed through the Spex digital photometer. The luminescence was obtained at sample temperatures of 295 and 77 K. For the low-temperature work, the samples were contained in a quartz tube, which could in turn be immersed in liquid nitrogen. The THF solutions were found to form acceptable glasses at the cryogenic temperature.

Emission lifetimes were obtained by exciting the samples with a nitrogen laser having a 300-ps pulse width. The luminescence decay curves were obtained by photographing the decay curves as displayed on a storage oscilloscope, and these were analyzed by a least-squares method. In these experiments, the current output of the photomultiplier tube was converted to a voltage signal after passage of the output current through a 220 K load resistor. Given the 47 pf input capacitance of the oscilloscope, the system was calculated to exhibit an inherent 10-μs RC time constant. However, all the measured lifetimes were at least 10 times longer than that of the system time constant, and thus no correction had to be made for system over a time span exceeding 3 times the calculated lifetime, and all decay curves appeared to consist of only single exponentials. Plots of ln I vs. time were constructed to verify the simplicity of the decay curves.

Results and Discussion

1. Effect of the Crystal Field on the Tb(III) Luminescence Bands. Irradiation of a Tb(III) ion through UV excitation generally results in an efficient population of the $^5D_4$ state, which in turn may relax to one of the ^7F_J manifold of lower lying states. The large degree of spin–orbit coupling associated with the Tb(III) ion leads to considerable splitting of the J levels within the ^7F_J manifold, as has been illustrated in Figure 1. It we label the levels solely by their J quantum numbers, the 4–6 and 4–5 transitions exhibit the largest emission quantum yields, the 4–4 and 4–3 bands generally are lower in intensity by an order of magnitude, and the 4–2, 4–1, and 4–0 band systems are typically 3 orders of magnitude less intense than the 4–6 and 4–5.

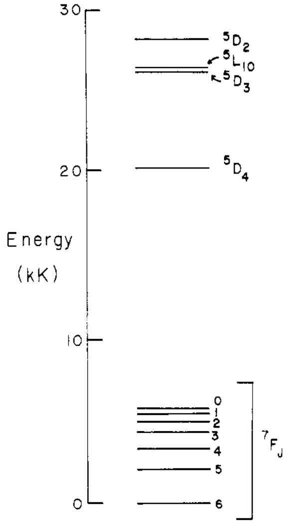

Figure 1. Free ion energy levels of the Tb(III) ion.

In the Ln(Cp)$_3$(THF) series of complexes, the lanthanide ion binds each Cp ligand in a η^5 manner, and thus the metal can be considered to have an effective coordination number of 4.[1-5] The four ligands would of course be located in essentially a tetrahedral arrangement, and this prediction has been observed.[1-5] The actual site symmetry of the metal in the Tb(Cp)$_3$(THF) complex would therefore be C_{3v}. The metal ion of Tb(MeCp)$_3$(THF) would be expected to experience the same symmetry as long as the MeCp rings were free to rotate.

As mentioned earlier, in most Tb(III) compounds all emission originates from the $^5D_4$ excited state. In T_d symmetry, this 9-fold dengenerate level characterized by J = 4 would be expected to split into four levels (A_1 + E + T_1 + T_2) by the crystal field. Further splitting of the $^5D_4$ state is expected when the point group of the molecule is lowered to C_{3v}, and it is found that the J = 4 level now splits into six components (2 A_1 + A_2 + 3 E). At room temperature luminescence out of all six crystal field components would be expected, although at cryogenic temperatures one must consider the possibility that emission might occur only out of the lowest lying levels.

In a similar manner, one may obtain the splitting in the ^7F_J levels as caused by a C_{3v} crystal field. For J = 0, no splitting can occur (the state is of A_1 symmetry). With J = 1 splitting into two states occurs (symmetry being A_2 + E), and with J = 2 a total of three states are produced (A_1 + 2 E). For J = 3, five states result from the crystal field splitting (A_1 + 2 A_2 + 2 E), and for J = 4 one obtains six states (2 A_1 + A_2 + 3 E). In the case of J = 5 a total of seven states result (A_1 + 2 A_2 + 4 E), and finally with J = 6 a splitting into nine states also is predicted (3 A_1 + 2 A_2 + 4 E).

Knowing the symmetries of the initial (J = 4 from the $^5D_4$) and final (^7F_J in origin) states permits a determination of the electric dipole selection rules for molecules of C_{3v} symmetry from standard group theoretical procedures. These are the following: $A_1 \rightarrow A_1$, allowed, Z polarization; $A_1 \rightarrow A_2$, forbidden; $A_1 \rightarrow E$, allowed, XY polarization; $A_2 \rightarrow A_1$, forbidden; $A_2 \rightarrow A_2$, allowed, Z polarization; $A_2 \rightarrow E$, allowed, XY polarization; $E \rightarrow A_1$, allowed, XY polarization; $E \rightarrow A_2$, allowed, XY polarization; $E \rightarrow E$, allowed, XYZ polarization (unpolarized). One may then combine the conclusions just reached regarding the behavior of the various J levels in a C_{3v} crystal field with the group theoretical selection rules to determine the number of allowed

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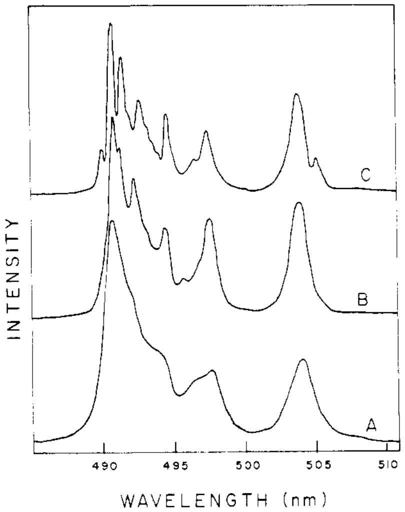

Figure 2. Photoluminescence spectra within the $^5D_4 \rightarrow {}^7F_6$ Tb(III) emission of Tb(Cp)$_3$(THF) at room temperature (A) and 77 K (B). The room temperature spectrum of Tb(MeCp)$_3$(THF) is identical with that of Tb(Cp)$_3$(THF); and the 77 K spectrum of Tb(MeCp)$_3$(THF) is shown as spectrum C.

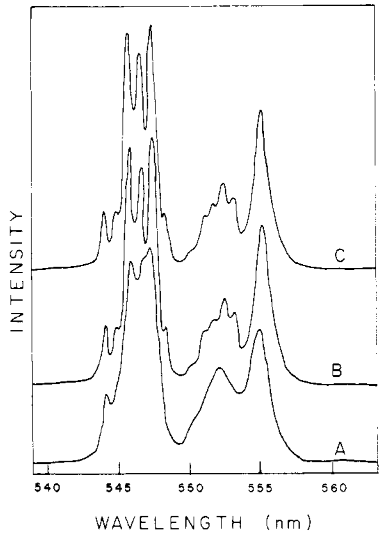

Figure 3. Photoluminescence spectra within the $^5D_4 \rightarrow {}^7F_5$ Tb(III) emission of Tb(Cp)$_3$(THF) at room temperature (A) and 77 K (B). The 77 K spectrum of Tb(MeCp)$_3$(THF) is shown as spectrum C.

Table I. Allowed Transitions and Polarizations for the Luminescence Bands of Tb(III) in C_{3v} Symmetry

		ES = 2 A$_1$	ES = A$_2$	ES = 3 E
$^5D_4 \rightarrow {}^7F_0$:	A$_1$	2 *Z*	*a*	3 *XY*
$^5D_4 \rightarrow {}^7F_1$:	A$_2$	*a*	*Z*	3 *XY*
	E	2 *XY*	*XY*	3 *XYZ*
$^5D_4 \rightarrow {}^7F_2$:	A$_1$	2 *Z*	*a*	3 *XY*
	2 E	4 *XY*	2 *XY*	6 *XYZ*
$^5D_4 \rightarrow {}^7F_3$:	A$_1$	2 *Z*	*a*	3 *XY*
	2 A$_2$	*a*	2 *Z*	6 *XY*
	2 E	4 *XY*	2 *XY*	6 *XYZ*
$^5D_4 \rightarrow {}^7F_4$:	2 A$_1$	4 *Z*	*a*	6 *XY*
	A$_2$	*a*	*Z*	3 *XY*
	3 E	6 *XY*	3 *XY*	9 *XYZ*
$^5D_4 \rightarrow {}^7F_5$:	A$_1$	2 *Z*	*a*	3 *XY*
	2 A$_2$	*a*	2 *Z*	6 *XY*
	4 E	8 *XY*	4 *XY*	12 *XYZ*
$^5D_4 \rightarrow {}^7F_6$:	3 A$_1$	6 *Z*	*a*	9 *XY*
	2 A$_2$	*a*	2 *Z*	6 *XY*
	4 E	8 *XY*	4 *XY*	12 *XYZ*

[a] Transition forbidden by group theory.

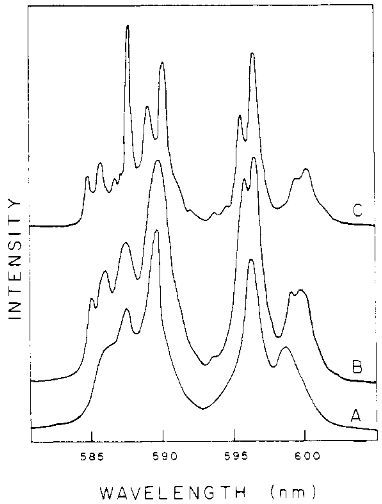

Figure 4. Photoluminescence spectra within the $^5D_4 \rightarrow {}^7F_4$ Tb(III) emission of Tb(Cp)$_3$(THF) at room temperature (A) and 77 K (B). The 77 K spectrum of Tb(MeCp)$_3$(THF) is shown as spectrum C.

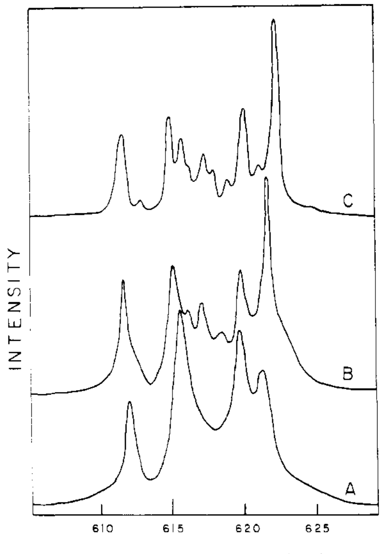

Figure 5. Photoluminescence spectra within the $^5D_4 \rightarrow {}^7F_3$ Tb(III) emission of Tb(Cp)$_3$(THF) at room temperature (A) and 77 K (B). The 77 K spectrum of Tb(MeCp)$_3$(THF) is shown as spectrum C.

transitions that might be observed. These have been summarized in Table I. If one totals up all the allowed transitions for each Tb(III) band system, one finds the following results: 4–0, 5 allowed transitions; 4–1, 10 allowed transitions; 4–2, 17 allowed transitions; 4–3, 25 allowed transitions; 4–4, 32 allowed transitions; 4–5, 44 allowed transitions; 4–6, 47 allowed transitions. It is quite clear that the most intense Tb(III) emission bands (4–6 and 4–5) contain the most complex spectra and that any detailed theoretical interpretation of the results must center around the bands which correspond to transitions to states characterized by low *J* quantum numbers.

2. Luminescence of Tb(Cp)$_3$(THF) and Tb(MeCp)$_3$(THF). Luminescence spectra obtained within the various Tb(III) emission band systems are shown in Figures 2–7, and a few features are immediately apparent. While the spectra obtained for Tb(Cp)$_3$(THF) and Tb(MeCp)$_3$(THF) are absolutely identical in every 4–*J* transition when the data are obtained at room temperature, the spectra for the two compounds display slight differences at 77 K. It is hardly surprising to note that

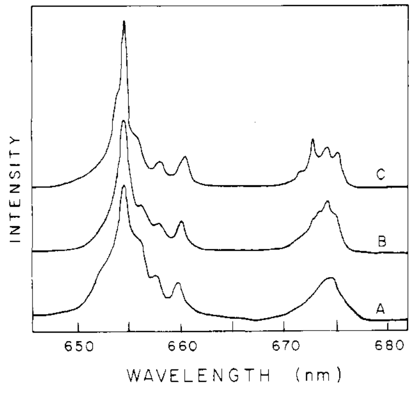

Figure 6. Photoluminescence spectra within the $^5D_4 \rightarrow {}^7F_2$ and $^5D_4 \rightarrow {}^7F_1$ Tb(III) emissions of Tb(Cp)$_3$(THF) at room temperature (A) and 77 K (B). The 77 K spectrum of Tb(MeCp)$_3$(THF) is shown as spectrum C.

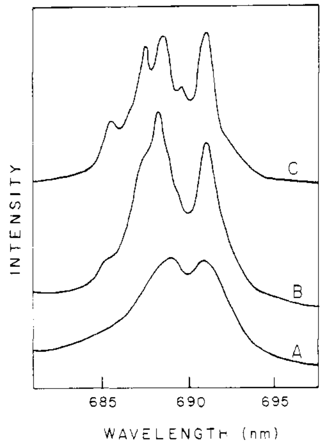

Figure 7. Photoluminescence spectra within the $^5D_4 \rightarrow {}^7F_0$ Tb(III) emission of Tb(Cp)$_3$(THF) at room temperature (A) and 77 K (B). The 77 K spectrum of Tb(MeCp)$_3$(THF) is shown as spectrum C.

a considerable degree of peak resolution is noted upon cooling to cryogenic temperatures. It is also noted that while all the peaks within the Tb(Cp)$_3$(THF) bands appear to have correspondences within the Tb(MeCp)$_3$(THF) spectra, the degree of peak resolution in the MeCp spectra is significantly worse when compared to the Cp spectra.

Other differences between the Cp and MeCp compounds are apparent in the luminescent lifetimes. At room temperature, both Tb(Cp)$_3$(THF) and Tb(MeCp)$_3$(THF) exhibit an emission lifetime of 300 μs. Upon cooling to 77 K, the lifetime of the Cp compound increases to 320 μs, while that of the MeCp compound actually decreases to 260 μs. These results clearly show (as do the luminescence spectra) that while Tb(Cp)$_3$(THF) and Tb(MeCp)$_3$(THF) are equivalent compounds at room temperature, differences exist at cryogenic temperatures. We shall attempt to provide an explanation for these processes in due course.

A very crucial question to be answered concerns how many of the five crystal field components of the $^5D_4$ state actually participate in the luminescence process. This question may be answered through an examination of the 4–0 band system of Figure 7. For this transition the terminating level ($^7F_0$) cannot be split by the crystal field, and thus the number of observed peaks must equal the number of emitting levels in the $^5D_4$ state. The resolution is best for the Tb(Cp)$_3$(THF) compound, and it is clear that all five transitions indicated in Table I are observed in the luminescence spectrum. The intensity of the transitions from the E components ought to be twice as intense as the transitions from the A_1 components, and hence we arrive at the mapping of the 4–0 transitions, which are shown in Table II. From these considerations, one obtains the relative energy level diagram of the $^5D_4$ excited state, which is shown in Figure 8.

Table II. Wavelengths and Energies of the Luminescence Bands Obtained within the $^5D_4 \rightarrow {}^7F_0$ Tb(III) Luminescence Band System at 77 K[a]

		Tb(CP)$_3$(THF)	Tb(MECP)$_3$(THF)
$A_1(2) \rightarrow A_1$:	λ	6854	~6853
	ε	14 589	~14 595
$E(3) \rightarrow A_1$:	λ	6875	~6874
	ε	14 546	~14 550
$E(2) \rightarrow A_1$:	λ	6885	6882
	ε	14 524	14 531
$A_1(1) \rightarrow A_1$:	λ	6895	~6893
	ε	14 503	~14 505
$E(1) \rightarrow A_1$:	λ	6910	6910
	ε	14 471	14 471

[a] The wavelength (λ) values are given in angstroms, while the energy (ε) values are in cm^{-1}. In the Tb(MECP)$_3$(THF) compound, several peaks were observed as shoulders and could not be resolved.

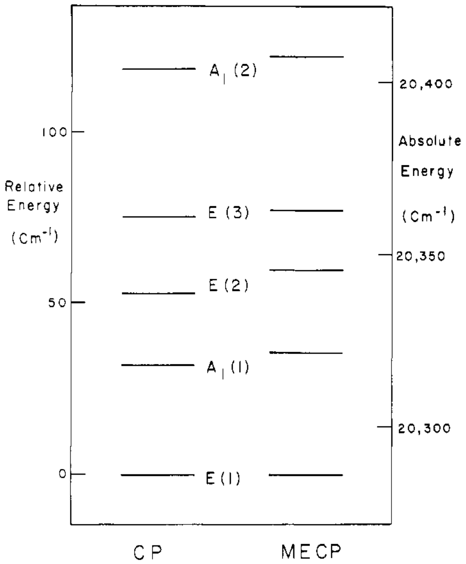

Figure 8. Relative and absolute energies for the crystal field components of the $^5D_4$ excited state in Tb(Cp)$_3$(THF).

The absolute energies (relative to the $^7F_6$ ground state) of the $^5D_4$ crystal field components are also available from the data. The 4–6 peak of highest energy (4901 Å or 20.403 × 10^3 cm^{-1} for Tb(Cp)$_3$(THF)) would clearly correspond to the emission from the $A_1(2)$ component of $^5D_4$ to the lowest crystal field component of the $^7F_6$ ground state. According to the selection rules, the transition would be either $A_1 \rightarrow A_1$ or $A_1 \rightarrow E$ in nature. From a comparison of the transition energies, one finds that the $^7F_0$ level lies 5815 cm^{-1} higher in energy than the lowest crystal field component of the $^7F_6$ ground manifold, and thus absolute energies of the components of the $^5D_4$ state are calculable.

Unfortunately, it is only within the 4–0 band system that the predicted number of transitions is actually observed. As is clearly visible in Figures 2–6, one finds that in every other 4–J transition fewer bands are observed than would be expected from Table I. These observations imply that considerable overlapping of emissive transitions occurs, and this situation prevents the full resolution of the data into energy level diagrams. For instance, in the still relatively simple 4–1 band system one only observes four out of nine possible transitions.

In every case, however, it is possible to identify the highest energy transition for a given 4–J band system. The energy of this peak would then correspond to the energy difference between the highest energy crystal field component of the $^5D_4$ level and the lowest energy crystal field component of the ^7F_J ground state. If one then sets the energy of the lowest crystal field component of the $^7F_6$ level equal to zero, when it becomes possible to determine the energies of the lowest energy crystal field component of each of the ^7F_J manifolds. For the Tb(Cp)$_3$(THF) compound, these are as follows: $J = 6$, 0 cm^{-1}; $J = 5$, 2021 cm^{-1}; $J = 4$, 3304 cm^{-1}; $J = 3$, 4314 cm^{-1}; $J = 2$, 5076 cm^{-1}; $J = 1$, 5510 cm^{-1}; $J = 0$, 5815 cm^{-1}. These values are in good agreement with analogous values obtained for Tb(III) substituted into LaCl$_3$.[15] Nevertheless, invariably the positions of the various bands are located at slightly longer wavelengths than are the corresponding bands of the free ion. Such differences may be attributed to small amounts of covalency in the bonding between the Tb(III) ion and the Cp ligands.

Conclusions

It is difficult to be more definitive about the luminescence results owing to the complexity of the Tb(III) emission bands. The high multiplicity of the states leads to the prediction of large numbers of crystal field components for each band system, and such a situation was actually realized in the experiment. Unfortunately, since full resolution of all crystal field components could not be achieved, a full theoretical analysis of the data is not possible. However, it has been determined that luminescence occurs out of all crystal field components of the emissive excited state. The luminescence of the 4–0 band can be described by assuming a C_{3v} point group for the Tb(III) ion, thus indicating that in THF solution this effective symmetry is suitable for a spectroscopic description of the Tb(III) energy levels.

Measurements of emission lifetimes and spectral features have indicated that as far as spectroscopy can determine, Tb(Cp)$_3$(THF) and Tb(MeCp)$_3$(THF) are completely equivalent at room temperature in THF solution. On the other hand, cooling the compounds to 77 K leads to the observation of nonequivalent emission lifetimes. While the spectra of Tb(Cp)$_3$(THF) and Tb(MeCp)$_3$(THF) are very similar at cryogenic temperatures, the crystal field components within each individual Tb(III) emission band are not as well resolved with the MeCp compound as with the Cp compound. Should the rotation of the cyclopentadienyl rings be free and unhindered, it would follow that analogous complexes derived from Cp and MeCp should be totally equivalent. This situation clearly exists in solutions studied at ambient temperatures. Should the ring rotation becomed hindered (certainly possible at low temperatures), then the MeCp compound would exist in a large number of geometrical isomers that would only differ in the orientation of the methyl group on the MeCp ring. A multitude of isomers would certainly yield some degree of broadening in the luminescence spectra, and thus a loss of resolution would occur.

The results obtained thus far are quite encouraging in that they provide an impetus for further work. While analysis of the Tb(III) emission bands is a difficult matter, conclusions regarding molecular symmetries in solution may still be drawn through a careful analysis of the fine structure within the Tb(III) emission bands.

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Registry No. Tb(Cp)$_3$(THF), 87184-38-1; Tb(MeCp)$_3$(THF), 87184-39-2.

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