

Articles

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Luminescence Studies of Tris(bis(trimethylsilyl)amido)terbium(III) and of Its Adduct Complexes

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Luminescence spectra obtained at high-resolution and cryogenic temperatures have been used to study the Tb(III) energy levels of tris(bis(trimethylsilyl)amido)terbium(III) [Tb(TMSA)₃]. Tb(TMSA)₃ was shown to have essentially the same trigonal structure in the solid state as it has when dissolved in noncoordinating solvents, such as pentane. Analysis of the solid-state spectra revealed that the effective symmetry of the Tb(III) ion was determined primarily by the ligand arrangement of the inner coordination sphere and that the remaining portion of the ligands played only a secondary role in symmetry considerations. An effective point group of *D*_{3h} was obtained for the Tb(III) ion in Tb(TMSA)₃, indicating that the major crystal field interaction was that of Tb(III) and a trigonal-planar arrangement of nitrogen atoms. Dissolution of Tb(TMSA)₃ in tetrahydrofuran led to large changes in the luminescence spectra and thus implied the formation of a THF adduct species. This observation precipitated a general investigation of the formation of adduct complexes between Tb(TMSA)₃ and various substrates, using emission spectra and luminescence lifetime data as spectroscopic probes. In the solid, or in noncoordinating solvents such as pentane or heptane, the emission spectrum of the complex is sharp and unperturbed and the luminescence lifetime short. When Lewis bases capable of coordinating strongly to the metal center are introduced, the resulting emission spectra are severely perturbed (by shifting and broadening) and the luminescence lifetimes are substantially lengthened (574 μs (pentane) vs. 1396 μs (triphenylphosphine oxide (Ph₃P=O))). Intermediate on this continuum are olefins, alkynes, and ethers, which are weak but observable adducts. Correlation of the emission spectra and luminescence lifetimes permits construction of a quantitative scale upon which to assess the strength of a variety of adducts of trivalent organolanthanoid complexes.

Introduction

Modern organolanthanoid chemistry relies almost entirely upon X-ray crystallography for the study of complex structure.^{1,2} Unfortunately, solid-state and solution-phase structures of a given compound are not necessarily related. Since many organolanthanoid compounds have been proposed as homogeneous catalytic reagents,³ the evaluation of their solution-phase structures represents an important problem. In particular, information on the perturbations of complex structure caused by solvation phenomena and adduct formation are of vital importance in understanding the chemistry of these materials, but this information is obviously not available from solid-state structural studies. NMR spectroscopy has proved to be useful for such work, but often the deduction of structural parameters requires the use of difficult-to-justify assumptions.

We have sought to study the solution-phase structures of organolanthanoid compounds through measurements of the intrinsic luminescence associated with Tb(III) derivatives. The measurement of Tb(III) luminescence spectra under conditions of high resolution has proven to be of great utility in detailing the energy levels of this ion in a variety of host environments.^{4,5} Although the low symmetry of most Tb(III) solution-phase species precludes full application of existing theory, the study of such systems is relevant 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.

Recently, the high-resolution luminescence spectra of tris(cyclopentadienyl)terbium(III) and tris(methylcyclopentadienyl)terbium(III) in frozen tetrahydrofuran (THF) solutions were reported.⁶ These same compounds exist as dimers in certain noncoordinating solvents. The Tb(III) luminescence spectra of these dimers were found to be greatly perturbed from the spectra

recorded for analogous monomeric compounds.⁷ In a different study, the tetrahydrofuran adducts of anhydrous terbium chloride (the starting material employed in virtually all syntheses of Tb(III) organometallic compounds) were investigated⁸ and evidence was documented for the existence of several such species in the solid state.

In all of these studies, we have sought to relate solid-state and solution-phase structures. This line of investigation has been continued, and in the present report we wish to detail luminescence studies of tris(bis(trimethylsilyl)amido)terbium(III) [abbreviated henceforth as Tb(TMSA)₃]. Spectra obtained in the solid state and in various solvents have been used to evaluate the coordinative behavior of these solvents, and luminescence lifetime data were used to further study the formation of adduct complexes with a variety of chemically relevant organic compounds.

Experimental Section

Tb(TMSA)₃ is both air and moisture sensitive. Therefore, the synthesis and manipulation of this material was conducted with rigorous exclusion of air and water by using Schlenk, vacuum-line, and drybox (Vacuum/Atmospheres HE-43 Dri-Lab, recirculated argon atmosphere) techniques.

Hydrated TbCl₃·6H₂O was obtained from Research Chemicals and was dehydrated by the method of Taylor and Carter.⁹ THF was dried and degassed by distillation from sodium benzophenone ketyl under argon. Pentane was distilled from sodium benzophenone ketyl (stabilized with tetraglyme) under argon. Triphenylphosphine oxide was obtained from Aldrich and was used without further purification. All other organic solvents and substrates were dried over 4-Å molecular sieves and

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degassed by vacuum transfer and several freeze-pump-thaw cycles. The infrared spectrum of $\text{Tb}(\text{TMSA})_3$ was recorded on a Nicolet 5DX FTIR spectrometer and was obtained in a Nujol mull on 25×4 mm NaCl plates held in an O-ring sealed Barnes Presslok holder. Complexometric metal analysis was conducted by using procedures which have been described previously.¹⁰

$\text{Tb}(\text{TMSA})_3$ was synthesized by minor modification of the method of Bradley et al.¹¹ In our hands, use of $\text{LiN}(\text{SiMe}_3)_2$ in the metathetical synthesis of $\text{Tb}(\text{TMSA})_3$ from TbCl_3 resulted in a final product that could not be freed of contaminating chloride (as determined by X-ray fluorescence). However, substitution of the sodium salt, $\text{NaN}(\text{SiMe}_3)_2$, for the lithium reagent permitted the isolation of pure, chloride-free $\text{Tb}(\text{TMSA})_3$ after several cycles of pentane extraction, filtration, and solvent removal (as determined by X-ray fluorescence, complexometric metal analysis, and infrared spectroscopy).

For the luminescence work, samples of microcrystalline solid $\text{Tb}(\text{TMSA})_3$ and $\text{Tb}(\text{TMSA})_3$ solutions were sealed in 25-cm quartz tubes. The $\text{Tb}(\text{TMSA})_3$ concentration used for all work was 0.01 M, with noncoordinating pentane usually employed as a solvent. Adduct complexes were obtained by the codissolution of an equimolar amount of substrate in the pentane solvent (except in those cases where competitive binding studies were investigated). Acceptable glasses were obtained by immersing the quartz tubes containing the liquid samples in liquid nitrogen; all luminescence data were collected at 77 K. The luminescence of the crystalline solid was also obtained at 9 K, with the sample mounted on the cold stage of a closed-cycle cryogenic refrigerator system. All spectra were obtained on a high-resolution emission spectrometer constructed in our laboratory. Samples were excited by the 350-nm output (50 mW) of an Ar ion laser, and the emission was analyzed at 3-cm⁻¹ 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.

Emission lifetimes were obtained on the same high-resolution fluorometer, but with the replacement of the Ar ion laser by a pulsed nitrogen laser (PRA Associates, Model LN-1000). The transient currents developed upon pulsed excitation of the sample were converted into voltages by using a 100 K load resistor, and these voltage pulses were then captured for viewing on a storage oscilloscope. At the same time, the data were digitized at 4- μs intervals with a homebuilt analog/digital converter, and the digitized data were fed directly into a Commodore PET 4032 microcomputer. The base line corrected decay curves were then analyzed by using 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.

Results and Discussion

The bis(trimethylsilyl)amido derivatives of the lanthanoids are unusual in that a coordination number of 3 for the metal ions is a relatively rare occurrence.¹³ This situation undoubtedly arises from the extreme steric bulk associated with each TMSA ligand. Crystal structures for $\text{Sc}(\text{TMSA})_3$ and $\text{Eu}(\text{TMSA})_3$ have been reported,¹⁴ as well as the structure of the $\text{Nd}(\text{TMSA})_3$ derivative.¹⁵ While the structures of the $(\text{TMSA})_3$ derivatives of transition metals contain a planar $\text{M}(\text{N})_3$ polyhedron, the lanthanoid compounds all feature a slightly pyramidal $\text{Ln}(\text{N})_3$ unit. However, dissolution of the lanthanoid compounds apparently results in a planar $\text{Ln}(\text{N})_3$ moiety and in the generation of D_3 symmetry for the $\text{Ln}(\text{III})$ ion.⁹ The information gathered to date indicates that all members of the lanthanoid series form isomorphous compounds.

Excitation of $\text{Tb}(\text{TMSA})_3$ at 350 nm resulted in strong luminescence, and at 77 K a considerable amount of fine structure was noted in each $\text{Tb}(\text{III})$ band. In $\text{Tb}(\text{III})$ compounds, emission originates from the $^5\text{D}_4$ excited state, and transitions to each of the $^7\text{F}_j$ ($J = 1-6$) ground-state levels can be observed. For the sake of simplicity, we shall henceforth label these spectroscopic transitions by their defining J quantum numbers. The luminescence spectra obtained for the 4-6, 4-5, 4-4, and 4-3 band systems

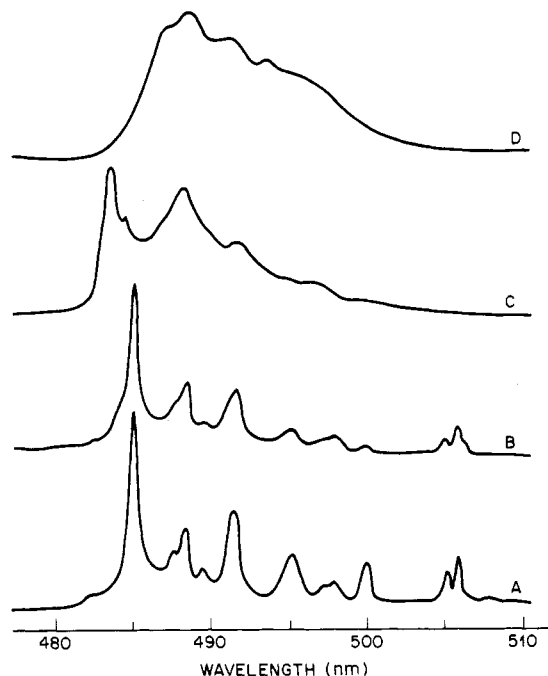


Figure 1. Luminescence spectra of microcrystalline $\text{Tb}(\text{TMSA})_3$ (trace A) and of the pentane (trace B), tetrahydrofuran (trace C), and triphenylphosphine oxide/pentane solutions (trace D). The data were all obtained at 77 K and correspond to the $^5\text{D}_4 \rightarrow ^7\text{F}_6$ transition. The intensity scale is purely arbitrary.

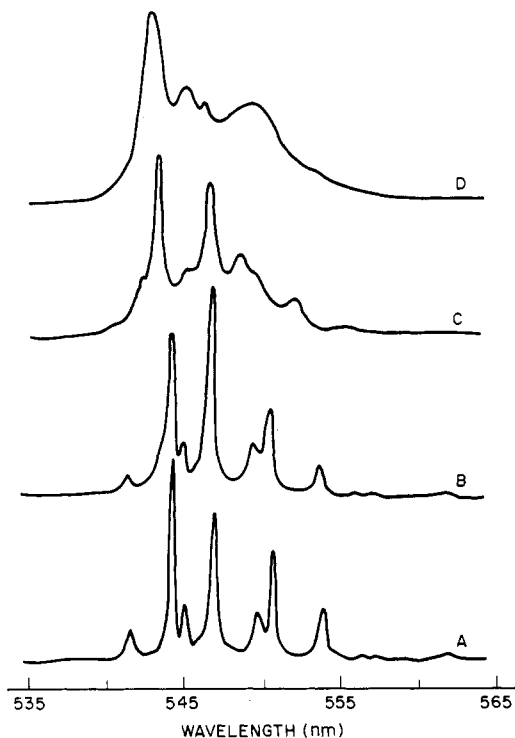


Figure 2. Luminescence spectra of microcrystalline $\text{Tb}(\text{TMSA})_3$ (trace A) and of the pentane (trace B), tetrahydrofuran (trace C), and triphenylphosphine oxide/pentane solutions (trace D). The data were all obtained at 77 K and correspond to the $^5\text{D}_4 \rightarrow ^7\text{F}_5$ transition.

of solid $\text{Tb}(\text{TMSA})_3$, $\text{Tb}(\text{TMSA})_3$ /pentane, $\text{Tb}(\text{TMSA})_3$ /THF, and $\text{Tb}(\text{TMSA})_3$ /triphenylphosphine oxide are shown in Figures 1-4.

It is immediately apparent from an examination of the results that the spectra obtained in pentane solvent are almost identical with those observed for the microcrystalline solid. This observation provides strong evidence that the structure of the $\text{Tb}(\text{TMSA})_3$ compound is essentially unchanged in pentane solution relative to that of the solid. It is known that the $\text{Ln}(\text{TMSA})_3$ compounds

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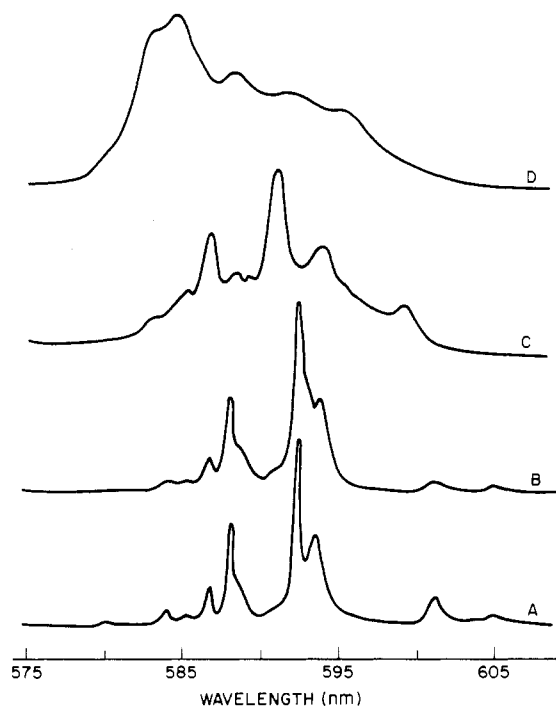


Figure 3. Luminescence spectra of microcrystalline $\text{Tb}(\text{TMSA})_3$ (trace A) and of the pentane (trace B), tetrahydrofuran (trace C), and triphenylphosphine oxide/pentane solutions (trace D). The data were all obtained at 77 K and correspond to the ${}^5\text{D}_4 \rightarrow {}^7\text{F}_4$ transition.

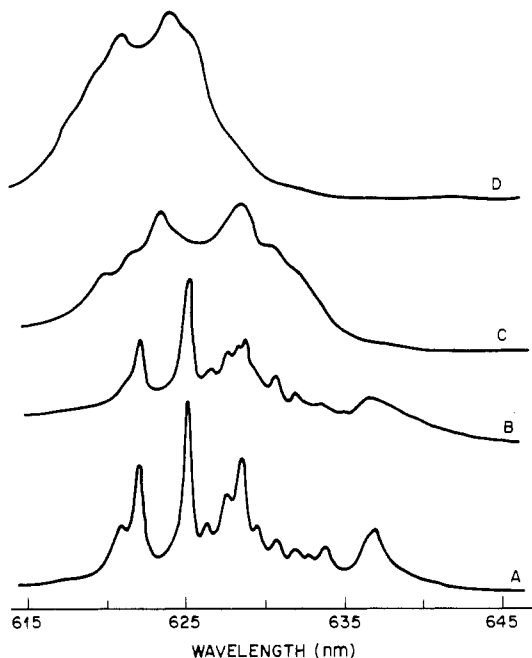


Figure 4. Luminescence spectra of microcrystalline $\text{Tb}(\text{TMSA})_3$ (trace A) and of the pentane (trace B), tetrahydrofuran (trace C), and triphenylphosphine oxide/pentane solutions (trace D). The data were all obtained at 77 K and correspond to the ${}^5\text{D}_4 \rightarrow {}^7\text{F}_3$ transition.

are monomers in solution under these conditions, since molecular weight determinations in benzene and alkane solvents indicate that no association or adduct formation takes place.¹¹ On the basis of this information, it may be concluded that the spectra shown in Figures 1-4 for $\text{Tb}(\text{TMSA})_3$ (solid and pentane solvent) are indicative of trigonal complexes of D_3 symmetry.

A significant point regarding the $\text{Tb}(\text{TMSA})_3$ solutions concerns the effective point group for the $\text{Tb}(\text{III})$ ion. It is known that the solid-state structure implies D_3 symmetry, and we have now shown that such symmetry is effectively maintained in the solution phase. However, often lanthanoid ions only sense the ligating atoms in their immediate coordination environment. In the case

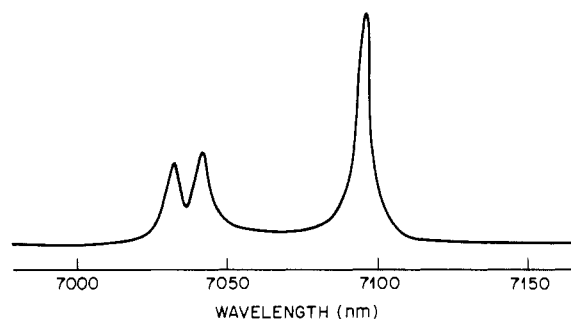


Figure 5. Luminescence spectra of microcrystalline $\text{Tb}(\text{TMSA})_3$ at 9 K, corresponding to the ${}^5\text{D}_4 \rightarrow {}^7\text{F}_0$ transition.

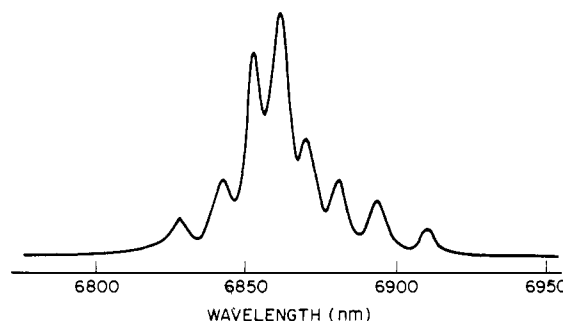


Figure 6. Luminescence spectra of microcrystalline $\text{Tb}(\text{TMSA})_3$ at 9 K, corresponding to the ${}^5\text{D}_4 \rightarrow {}^7\text{F}_1$ transition.

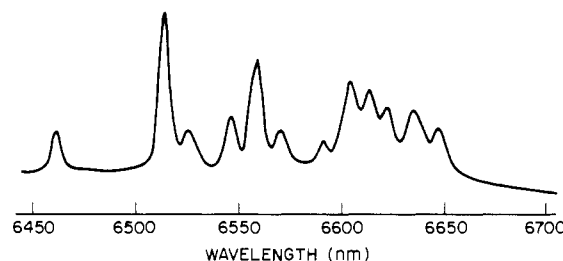


Figure 7. Luminescence spectra of microcrystalline $\text{Tb}(\text{TMSA})_3$ at 9 K, corresponding to the ${}^5\text{D}_4 \rightarrow {}^7\text{F}_2$ transition.

of $\text{Tb}(\text{TMSA})_3$, this would imply a planar $\text{Tb}(\text{N})_3$ unit having an approximate D_{3h} symmetry. Since the electric dipole selection rules for the two point groups are so different, an analysis of the fine structure within the various $\text{Tb}(\text{III})$ emission bands should permit a discriminating choice to be made between the two geometries.

Since data obtained at 77 K were found to be insufficient for this purpose, luminescence spectra of solid $\text{Tb}(\text{TMSA})_3$ were obtained at 9 K. The 9 K spectra corresponding to the 4-6, 4-5, 4-4, and 4-3 transitions were found to be significantly sharper than those obtained at 77 K, but fewer lines than predicted for either D_3 or D_{3h} symmetry were observed. However, a better fit was observed for the 4-2, 4-1, and 4-0 band systems. For the 4-0 band system, three peaks were found (Figure 5). Eight peaks were obtained within the 4-1 band system (Figure 6), and twelve peaks were found for the 4-2 band system (Figure 7). Comparison with the selection rules of Tables I and II reveals that this pattern is exactly what would be predicted on the basis of D_{3h} symmetry.

This result may be rationalized in the following manner. In the $\text{Tb}(\text{TMSA})_3$ complexes, the $\text{Tb}(\text{III})$ ion only senses the symmetry of its immediate coordination environment. The symmetry of the second coordination sphere appears to be of little consequence. The experimental results imply that the $\text{Tb}(\text{III})$ ion sees itself in a trigonal-planar site, even though the remainder of the ligands lower the overall symmetry to D_3 . Thus, we conclude that the $\text{Tb}(\text{III})$ luminescence may be used to probe details of the immediate coordination sphere of the metal ion in $\text{Tb}(\text{TMSA})_3/\text{solvent}$ and $\text{Tb}(\text{TMSA})_3/\text{solvent}/\text{substrate}$ studies.

Solvation studies of $\text{Tb}(\text{TMSA})_3$ were conducted by preparing a series of solutions in which potentially coordinating substrates

Table I. Selection Rules Governing the $^5D_4 \rightarrow ^7F_J$ Tb(III) Luminescent Transitions in D_3 Symmetry^a

transition	GS	ES = 2 A1	ES = A2	ES = 3 E	total no. of bands
4-0	A1	--	+	+++	4
4-1	A2	++	-	+++	11
	E	++	+	+++	
4-2	A1	--	+	+++	16
	2 E	++++	++	+++++	
4-3	A1	--	+	+++	26
	2 A2	++++	--	+++++	
	2 E	++++	++	+++++	
4-4	2 A1	----	++	+++++	31
	A2	++	-	+++	
	3 E	+++++	+++	+++++	
4-5	A1	--	+	+++	38
	2 A2	++++	--	+++++	
	4 E	+++++	++++	+++++	
4-6	3 A1	-----	+++	+++++	46
	2 A2	++++	--	+++++	
	4 E	+++++	++++	+++++	

^a A plus sign implies an electric dipole transition, and a minus sign signifies that the transition is electric dipole forbidden. The total number of allowed transitions is provided for each band system as the final column.

Table II. Selection Rules Governing the $^5D_4 \rightarrow ^7F_J$ Tb(III) Luminescent Transitions in D_{3h} Symmetry^a

transition	GS	ES = A1'	ES = 2E'	ES = A1''	ES = A2''	ES = E''	total no. of bands
4-0	A1'	-	++	-	+	-	3
4-1	A2'	-	++	+	-	-	8
	E''	-	++	+	+	+	
4-2	A1'	-	++	-	+	-	12
	E'	+	++	-	-	+	
	E''	-	++	+	+	+	
4-3	A2'	-	++	+	-	-	15
	E'	+	++	-	-	+	
	A1''	-	--	-	-	+	
	A2''	+	--	-	-	+	
	E''	-	++	+	+	+	
4-4	A1'	-	++	-	+	-	19
	2 E'	++	++++	--	--	++	
	A1''	-	--	-	-	+	
	A2''	+	--	-	-	+	
	E'	-	++	+	+	+	
4-5	A2'	-	++	+	-	-	24
	2 E'	++	++++	--	--	++	
	A1'	-	--	-	-	+	
	A2''	+	--	-	-	+	
	2 E''	--	++++	++	++	++	
4-6	2 A1'	--	++++	--	++	--	30
	A2'	-	++	+	-	-	
	2 E'	++	++++	--	--	++	
	A1''	-	--	-	-	+	
	A2''	+	--	-	-	+	
	2 E''	--	++++	++	++	++	

^a Note: A plus sign implies an electric dipole transition, and a minus sign signifies that the transition is electric dipole forbidden. The total number of allowed transitions is provided for each band system as the final column.

were codissolved in pentane with the Tb(III) complex and by recording the resultant emission spectra. In several instances, the addition of a given substrate (for example, cyclohexane or heptane) did not yield any perturbation of the basic luminescence line shapes. This behavior may be interpreted as implying a lack of interaction between the Tb(TMSA)₃ compound and the substrate. The addition of certain other substrates (for example, hexamethylbenzene or *trans*-4-octene) led to spectra that were significantly broadened relative to the pentane spectrum, but correspondence could still be made with all major luminescence peaks. This effect is consistent with a relatively small degree of complex-substrate interaction.

Addition of substrates that were previously known to coordinate lanthanoid TMSA complexes led to the observation of dramatic perturbations of the Tb(III) luminescence spectrum. It had been noted that triphenylphosphine oxide (Ph₃PO) forms 1:1 complexes with Ln(TMSA)₃ (Ln = La, Eu, and Lu) resulting in the generation of a four-coordinate lanthanoid species.¹³ The spectra observed upon addition of 1 equiv of Ph₃PO to a Tb(TMSA)₃/pentane solution are shown as part of Figures 1-4, where one may note the significant luminescence changes that accompany the formation of the adduct complex. The addition of cyclohexene oxide was also found to yield spectra that were absolutely superimposable on those of the Ph₃PO adduct.

Table III. Luminescence Lifetimes of Tb(TMSA)₃ and of the Adduct Complexes^a

system	lifetime, μ s
crystalline solid	548
pentane	574
cyclohexane	598
cyclohexane- <i>d</i> ₁₂	1164
hexamethylbenzene/pentane	603
tetrahydrofuran (neat)	686
2-methyltetrahydrofuran/pentane	642
2,5-dimethyltetrahydrofuran/pentane	624
heptane/pentane	590
1-heptene/pentane	615
<i>trans</i> -4-octene/pentane	607
4-octyne/pentane	596
cyclohexene oxide/pentane	1387
cyclohexene oxide/diethyl ether	774
diethyl ether (neat)	698
triphenylphosphine oxide/pentane	1396
triphenylphosphine oxide/THF	945

^aThe Tb(TMSA)₃ concentration was maintained at 0.01 M in all solution-phase studies; in the mixed systems the concentration of substrate was also set at 0.01 M. Each lifetime value carries a standard deviation of $\pm 5 \mu$ s.

Several substrates were found to yield spectra that, although shifted and broadened, did not exhibit the profound perturbations noted in the previous two examples. This behavior is indicative of the formation of adduct complexes of intermediate stability. The dissolution of Tb(TMSA)₃ in neat THF is an example of this phenomenon, and representative spectra are also contained in Figures 1–4. Although isolable adduct formation between Tb(TMSA)₃ has been discounted,¹³ the changes in the Tb(III) luminescence spectrum provide strong evidence that complexation is possible. A dissolution of Tb(TMSA)₃ in neat diethyl ether was found to yield Tb(III) luminescence spectra similar to those observed in THF solvent.

These qualitative observations were placed on a quantitative scale through measurement of the Tb(III) luminescence lifetimes (Table III). The trend that emerges upon examination of the data is that the magnitude of the lifetime is directly related to the degree of perturbation observed in the Tb(III) luminescence spectra. The lifetimes observed for the Tb(TMSA)₃ adducts with the strongly coordinating Lewis bases cyclohexene oxide and Ph₃PO were essentially the same, as were the emission spectra. The same correlation holds for the lifetimes of adducts of intermediate stability and for those of weakly coordinating substrates. Thus, one may use the Tb(III) luminescence lifetimes as parameters that directly reflect the stability of the adduct complexes.

The luminescence lifetimes can also be used to examine competitive binding phenomena. The Tb(TMSA)₃/Ph₃PO/THF system was found to yield Tb(III) luminescence spectra that were broad and featureless (and hence useless for characterization of the chemistry). However, the Tb(III) luminescence lifetime was found to exhibit a value intermediate between the values obtained for the pure adduct complexes. A similar situation was noted with the Tb(TMSA)₃/cyclohexene oxide/diethyl ether system. The fact that the luminescence decay curves invariably consisted of single exponentials indicates that only one species was present over the millisecond emission lifetimes. These observations indicate that the rate of substrate exchange in the adduct complexes must be much faster than the radiative decay rates. If the exchange rates were comparable to the radiative decay rates, one would observe multicomponent decay curves.

The predominant luminescence quenching mode for lanthanoid complexes is normally associated with solvent interactions.¹⁶ It is well-known that deuterium substitution in the bulk solvent will yield enhanced luminescence intensities and lifetimes. This behavior is observed since the molecular C–D vibrations in deuterated compounds provide less efficient nonradiative deactivation mechanisms than do the higher frequency C–H vibrations in the corresponding hydrogenated solvents.¹⁷ A large difference in emission lifetimes in ordinary and deuterated solvents may thus be taken as proof of direct interaction of the solvent with the lanthanoid ion. Where solvent access to the lanthanoid ion is prevented, the lifetimes in ordinary and deuterated solvents are found to be identical.¹⁸

The luminescence lifetime of Tb(TMSA)₃ dissolved in cyclohexane-*d*₁₂ was found to be almost double the value obtained in cyclohexane (1164 vs. 598 μ s). This observation provides direct evidence that, even for the noncoordinating substrates, the lanthanoid ion will interact with substrate molecules. All evidence indicates that the adducts formed by Tb(TMSA)₃ are in states of dynamic equilibrium with the substrate and solvent in a condition of fast exchange.

Conclusions

Tb(III) luminescence has been shown to be an effective method for the study of lanthanoid complex structure in both solution and solid phases. Tb(TMSA)₃ was shown to have essentially the same trigonal structure in the solid state as it has when dissolved in noncoordinating solvents, such as pentane. Analysis of the solid-state spectra revealed that the site symmetry of the Tb(III) ion was determined primarily by the ligand arrangement of the inner coordination sphere. An effective point group of *D*_{3h} was obtained for Tb(III) in Tb(TMSA)₃, indicating that the major crystal field interaction is that of Tb(III) and a trigonal-planar arrangement of nitrogen atoms.

Complexation of Tb(TMSA)₃ with substrates led to changes in the luminescence spectra that could be related to the strength of the adduct species. The Tb(III) luminescence lifetimes were found to be useful in placing substrate interactions on a quantitative scale: the more stable the adduct, the longer the luminescence lifetime. As expected, sterically open oxygen-containing Lewis base donors produced the strongest adducts, and noncoordinating substrates the weakest. Lewis bases capable of donating unsaturated electron density from double and triple bonds gave weak but observable adducts, when these methods were used. Evidence for such interactions is of importance in understanding reaction pathways accessible to organolanthanoid species since such interactions have been routinely postulated as the necessary first step in organolanthanoid reaction systems involving these organic substrates.¹⁹ However, methods capable of reliably measuring the presence of such adducts have been lacking until now.

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Registry No. Tb(TMSA)₃, 109433-86-5; pentane, 109-66-0; tetrahydrofuran, 109-99-9; triphenylphosphine, 603-35-0.

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