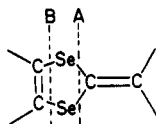


2.6 and 2.2 for the methylene protons adjacent to the  $sp^2$  C atoms and between  $\delta$  1.5 and 1.8 for the remaining methylene protons.

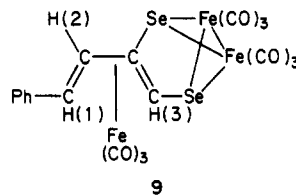
**Diselenafulvenes.** The reactions of the various diselenafulvenes lead to a related asymmetric cleavage of the organoselenium compound to form (diselenato)diiron complexes of the same general type as obtained with the diselenacyclohexadienes 1. In each case small amounts of  $Se_2Fe_2(CO)_9$  (8) are also obtained. The spectral and analytical properties of the new (diselenato)diiron complexes are recorded in Tables I and II.

It is of interest that cleavage of the Se-C bonds occurs only in the direction A outlined below, and no evidence was obtained for cleavage as in mode B. It is conceivable that cleavage occurs via route B followed by a rapid isomerization involving Se-C and C-C migrations. The absence of any acetylenic derived products as noted for the diselenacyclohexadiene effectively rules out this rather improbable process.



Given the yields of the diselenato complexes it is also surprising, and disappointing, that we observe no iron complexes derived from the vinylcarbene fragment, nor its isomers and oligomers. The fate of this portion of the molecules is therefore unknown at this time.

The reaction of  $Fe_2(CO)_9$  with the 2, $\omega$ -distyryl-diselenafulvene leads to both of the above-mentioned complexes and also a third complex, 9. In this complex the conjugated diene system is able to form a bonding interaction with another  $Fe(CO)_3$  fragment. The  $^1H$  NMR data for this complex and for the styryl(diselenato)diiron



hexacarbonyl are useful for structure corroboration. For the hexacarbonyl complex, the olefinic protons 1, 2, and 3 have resonances at  $\delta$  7.26, 6.71, and 6.44, respectively, with  $J_{12}$  of 9.6 Hz. Proton 3 is a singlet. Upon coordination of the third  $Fe(CO)_3$  unit the expected shifts are observed due to the complexation of the diene unit, resulting in the resonances for protons 1, 2, and 3 being at  $\delta$  6.16, 2.10, and 5.52, respectively ( $J_{12} = 9.6$  Hz).

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**Registry No.** 1a, 97353-00-9; 1b, 97353-01-0; 1c, 97374-09-9; 1d, 97353-02-1; 1e, 97353-03-2; 1f, 97353-04-3; 1g, 97374-10-2; 1h, 97353-05-4; 2d, 97374-11-3; 3d, 97390-81-3; 5b, 1610-39-5; 5c, 737-48-4; 5d, 7099-19-6; 6b, 97353-06-5; 6c, 97353-07-6; 7c, 97353-08-7; 9, 97374-12-4;  $Fe_2(CO)_9$ , 15321-51-4; biscyclopenta-1,4-diselena-2,5-cyclohexadiene, 35676-33-6; biscyclohexa-1,4-diselena-2,5-cyclohexadiene, 35831-82-4; biscyclohepta-1,4-diselena-2,5-cyclohexadiene, 35831-83-5; biscycloocta-1,4-diselena-2,5-cyclohexadiene, 34631-75-9; 2, $\omega$ -dimethyl-1,4-diselenafulvene, 69773-65-5; 2, $\omega$ -di-*tert*-butyl-1,4-diselenafulvene, 97353-09-8; 2, $\omega$ -diphenyl-1,4-diselenafulvene, 15995-14-9; 2, $\omega$ -distyryl-1,4-diselenafulvene, 73214-45-6.

**Supplementary Material Available:** Tables of observed and calculated structure factors, atomic coordinates temperature factor expressions, and bond lengths and angles for the metallapropellane structure (51 pages). Ordering information is given on any current masthead.

## Solvent Effects in the Luminescence Spectra of Terbium(III) Methylcyclopentadienyl Compounds

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The photoluminescence of monomeric and dimeric Tb(III) methylcyclopentadienyl (MeCp) derivatives has been obtained at cryogenic temperatures under conditions of high resolution. The spectra obtained for monomeric  $Tb(MeCp)_3(THF)$ ,  $Tb(MeCp)_2(Cl)(THF)$ , and  $Tb(MeCp)_2(CH_3)(THF)$  compounds were all found to be extremely similar, as were the Tb(III) luminescence lifetimes. The spectra of the analogous dimeric compounds  $[Tb(MeCp)_2Cl]_2$  and  $[Tb(MeCp)_2CH_3]_2$  were noted to differ significantly from those of the corresponding monomers, and the lifetime trends also were quite different. Since the monomer/dimer structure is largely an effect caused by solvent coordination, the Tb(III) luminescence is therefore a useful property for studies of complex solvation.

### Introduction

Modern organolanthanide chemistry relies almost entirely upon X-ray crystallography for studies of solid-state chemistry and upon nuclear magnetic resonance for the examination of compounds in the solution phase. Far less work has concentrated on the use of optical spectroscopic techniques for the study of solution phase structures.

Recently, luminescence within f-f transitions has been used to study cyclopentadienyl derivatives of Tb(III)<sup>1</sup> and Yb(III).<sup>2,3</sup>

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The luminescence associated with Tb(III) compounds may be used to study possible solvation effects. Coordination of tetrahydrofuran by  $\text{TbCl}_3$  results in spectral alterations suggestive of slight covalency effects.<sup>4</sup> It has also been shown that solvation greatly affects the luminescence spectrum of tris(bis(trimethylsilyl)amido)terbium(III).<sup>5</sup> Comparison of solid-state and solution-phase spectra can also be used to demonstrate a correspondence between complex structures under both sets of conditions.

In the present work, we have taken these studies one step further. It is known that mixed-ligand lanthanide complexes can exist as either monomers or dimers, depending on the choice of solvent.<sup>6</sup> It is quite clear that the Tb(III) ion must experience a vastly different crystal field in a dimeric compound when compared to that of a monomeric compound and that this difference should be visible in the Tb(III) luminescence spectrum. Accordingly, the luminescence spectra of  $\text{Tb}(\text{MeCp})_2\text{Cl}$  and  $\text{Tb}(\text{MeCp})_2\text{CH}_3$  [MeCp = methylcyclopentadienide] have been obtained in coordinating and noncoordinating solvents to study this relation between complex structure and spectra.

### Experimental Section

The organoterbium complexes described in this paper are extremely air and moisture sensitive. Therefore, the synthesis and manipulations of these materials were conducted with rigorous exclusion of air and water using Schlenk, vacuum line, and glovebox (Vacuum/Atmospheres HE-43 Dri-Lab, recirculated nitrogen atmosphere) techniques.

Anhydrous terbium chloride was prepared from the hydrate by the method of Taylor and Carter.<sup>7</sup> (Methylcyclopentadienyl)sodium,  $\text{Na}(\text{MeCp})$ , was prepared as previously described.<sup>8</sup>  $\text{Tb}(\text{MeCp})_3(\text{THF})$  was prepared following the method of Wilkinson for preparing  $\text{LnCp}_3$  complexes,<sup>9</sup> except that the product was isolated as the THF solvate by extracting the product mixture with toluene.  $[\text{Tb}(\text{MeCp})_2\text{Cl}]_2$  and  $[\text{Tb}(\text{MeCp})_2\text{CH}_3]_2$  were prepared following the literature preparations for the analogous yttrium complexes<sup>8,10</sup> as described below.

$[\text{Tb}(\text{MeCp})_2\text{Cl}]_2$ ,  $\text{Na}(\text{MeCp})$  (1.01 g, 9.90 mmol) and  $\text{TbCl}_3$  (1.375 g, 5.18 mmol, MeCp/Tb = 1.9) were placed in a round-bottom flask in a glovebox. THF (30 mL) was added, and the suspension was stirred overnight. The solvent was removed by rotary evaporation, and toluene (50 mL) was added. After being stirred 1 h, the suspension was filtered and the filtrate was evaporated to leave a white flaky powder (1.57 g). Complexometric metal analysis and IR spectroscopy indicated that the product was impure. The data were consistent with the presence of approximately 10%  $\text{Tb}(\text{MeCp})_3(\text{THF})$  or the equivalent. Cooling a saturated THF/hexane solution of the white powder to 0 °C generated colorless needles. These crystals were dissolved in toluene, and the solution was rotary evaporated to give a white microcrystalline THF-free product: IR (Nujol,  $\text{cm}^{-1}$ ) 1535 (w, br), 1300 (w, br), 1260 (w), 1235 (w), 1060 (m), 1045 (m), 1030 (s), 1010 (w), 930 (m), 880 (w), 835 (s), 770 (s). Anal. Calcd for  $[\text{Tb}(\text{MeCp})_2\text{Cl}]_2$ : Tb, 45.10. Found: Tb, 44.6. Alternatively  $[\text{Tb}(\text{MeCp})_2\text{Cl}]_2$  can be obtained by sublimation.

$\text{Tb}(\text{MeCp})_2(\text{Cl})(\text{THF})$  was obtained by dissolving  $[\text{Tb}(\text{MeCp})_2\text{Cl}]_2$  in THF.

$[\text{Tb}(\text{MeCp})_2\text{CH}_3]_2$ . Freshly prepared  $[\text{Tb}(\text{MeCp})_2\text{Cl}]_2$  (811 mg, 1.1 mmol) was placed in a Schlenk flask containing diethyl ether (30 mL). Methylolithium (1.2 mL of a 1.6 M solution in

diethyl ether, 1.92 mmol) was added via syringe to the suspension at 0 °C. A colorless solution resulted, which turned cloudy after about 1 h. After the solution was stirred overnight, the flask contained a light yellow solution and a white precipitate. The solvent was removed, and the resulting solids were extracted twice with pentane. The pentane solution was rotary evaporated to a slightly sticky yellow powder (562 mg). Recrystallization of this material from hexane at -50 °C gave a light yellow powder which was used for the luminescence work. The IR spectrum of this complex contained the strong, sharp methyl bond deformation mode at  $1170 \text{ cm}^{-1}$  characteristic of  $[\text{Ln}(\text{MeCp})_2\text{CH}_3]_2$  complexes and was THF free: IR (KBr,  $\text{cm}^{-1}$ ) 1455 (m), 1380 (m), 1250 (m), 1235 (m), 1170 (s), 1090 (w), 1045 (m), 1030 (s), 930 (m), 865 (w), 832 (s), 760 (s).

$\text{Tb}(\text{MeCp})_2(\text{CH}_3)(\text{THF})$  was formed by dissolving the above product in THF.

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 stockcock 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 evacuated and then sealed with a torch.

To obtain cryogenic luminescence spectra, the tubes were immersed in liquid nitrogen and mounted in a optical Dewar. Acceptable glasses for the luminescence work were formed by both THF and pentane, and hence all luminescence data was collected at 77 K. The 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  $5 \text{ cm}^{-1}$  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 fluorimeter, 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 using a 100K load resistor, and these voltage pulses were captured for viewing on a storage oscilloscope. At the same time, the data were digitized at  $4 \mu\text{s}$  intervals via a homebuilt analog/digital converter, and the digitized data 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

It is known that the mixed-ligand Tb(III) organometallic compounds studied as part of the current work form adducts with THF. The THF solvates of  $\text{Ln}(\text{MeCp})_2\text{Cl}$  are known to be monomeric, while the same compounds form dimers when dissolved in noncoordinating solvents.<sup>11,12</sup> In the same fashion, dissolution of  $\text{Ln}(\text{MeCp})_2\text{CH}_3$  into THF yields monomeric complexes,<sup>13,14</sup> while dimers are observed in non-coordinating solutions.<sup>15</sup> The crystal field experienced by a Tb(III) ion in a monomeric complex must be very different than that experienced in a dimeric complex, and consequently such differences ought to be manifest in the luminescence spectra.

Excitation of the Tb(III) compounds at 350 nm resulted in the observation of strong luminescence, and at 77 K a considerable amount of fine structure was noted in each

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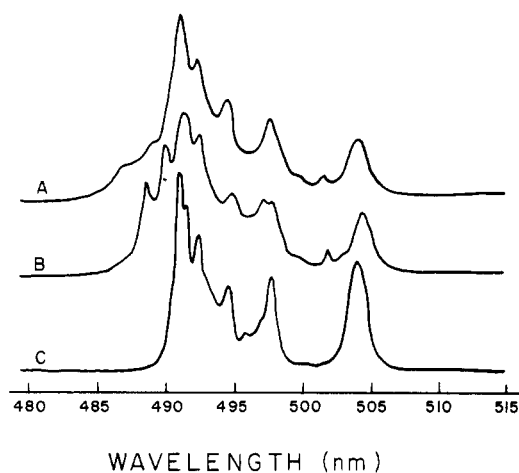
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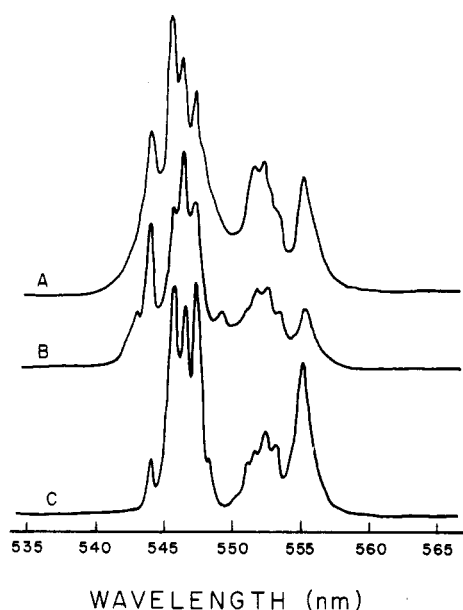
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**Figure 1.** Luminescence spectra obtained at 77 K for the  ${}^5D_4 \rightarrow {}^7F_6$  Tb(III) transition of (A)  $Tb(MeCp)_2CH_3$ , (B)  $Tb(MeCp)_2Cl$ , and (C)  $Tb(MeCp)_3$  dissolved in tetrahydrofuran.

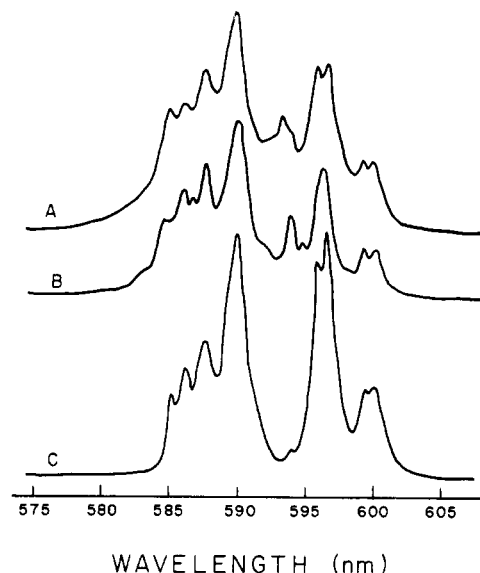


**Figure 2.** Luminescence spectra obtained at 77 K for the  ${}^5D_4 \rightarrow {}^7F_5$  Tb(III) transition of (A)  $Tb(MeCp)_2CH_3$ , (B)  $Tb(MeCp)_2Cl$ , and (C)  $Tb(MeCp)_3$  dissolved in tetrahydrofuran.

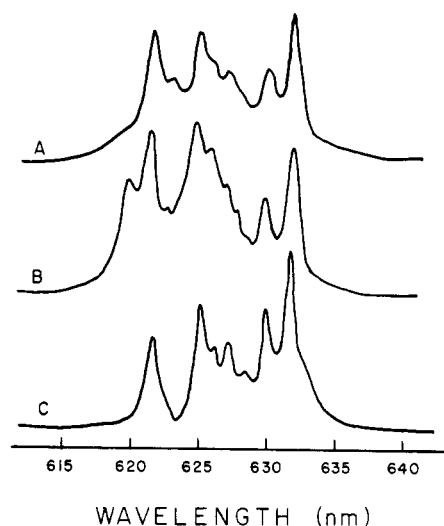
Tb(III) band. In Tb(III) compounds emission originates from the  ${}^5D_4$  excited state, and transitions to each of the  ${}^7F_J$  ( $J = 0-6$ ) groundstate levels can be observed. Since it is only the  $J$  quantum number which is needed to specify a particular spectroscopic state, we shall henceforth label these spectroscopic transitions by their defining  $J$  quantum numbers.

In the earlier work involving  $Tb(Cp)_3$  and  $Tb(MeCp)_3$  dissolved in coordinating THF solutions, it was noted that full resolution of all crystal field components was not possible in each band system.<sup>1</sup> In fact, only the 4-0 band could actually be resolved, but analysis of this band system permitted a conclusion that the Tb(III) site symmetry could be described approximately as  $C_{2v}$ . With the ternary complexes studied as part of the present investigation, none of the Tb(III) bands (including the 4-0 band) could be fully resolved into all possible components. Consequently, full application of group theoretical analysis could not be made.

While a detailed theoretical analysis is not therefore possible, the data can still be used to study the monomer/dimer bonding situations for the various  $Tb(MeCp)_2$  complexes. It was observed that the actual line-shape



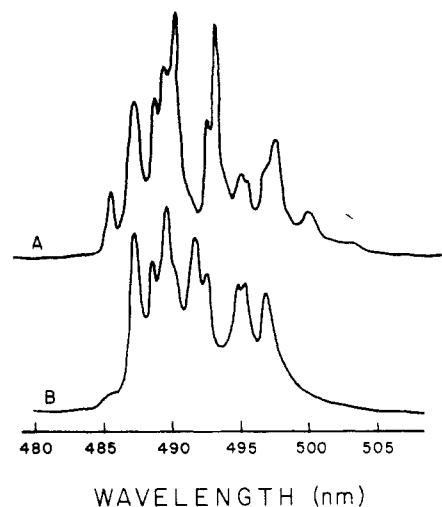
**Figure 3.** Luminescence spectra obtained at 77 K for the  ${}^5D_4 \rightarrow {}^7F_4$  Tb(III) transition of (A)  $Tb(MeCp)_2CH_3$ , (B)  $Tb(MeCp)_2Cl$ , and (C)  $Tb(MeCp)_3$  dissolved in tetrahydrofuran.



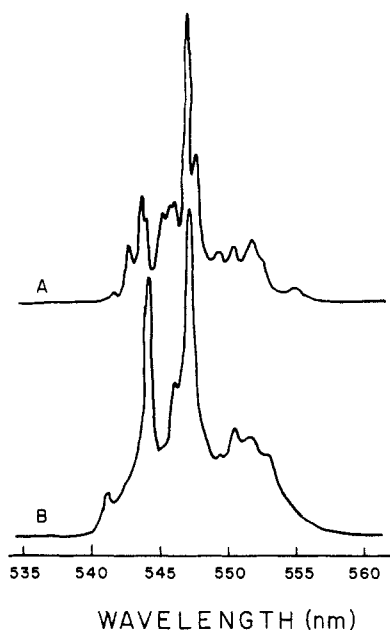
**Figure 4.** Luminescence spectra obtained at 77 K for the  ${}^5D_4 \rightarrow {}^7F_3$  Tb(III) transition of (A)  $Tb(MeCp)_2CH_3$ , (B)  $Tb(MeCp)_2Cl$ , and (C)  $Tb(MeCp)_3$  dissolved in tetrahydrofuran.

patterns observed for a given Tb(III) compound were extremely sensitive to the existence of monomeric or dimeric compounds. The spectral differences associated with the different complexation modes were found to show up dramatically in the 4-6, 4-5, 4-4, and 4-3 Tb(III) band systems, with the 4-5 band exhibiting a most useful multiplet. Examples of the spectra obtained within these bands are shown in Figures 1 through 4 for compounds dissolved in THF, and the corresponding data obtained toluene solution are located in Figures 5 through 8.

The 4-5 Tb(III) emission bands observed with the monomeric  $Tb(Cp)_3$  and  $Tb(MeCp)_3$  compounds contain a particular pattern of crystal field components which are visible to some degree in all the monomeric compounds. For instance, the triplet of intense peaks located at 5457, 5465, and 5473 Å for  $Tb(MeCp)_3$  are still observable in the spectra of  $Tb(MeCp)_2Cl$  and  $Tb(MeCp)_2CH_3$  as long as these are dissolved in the coordinating THF solvent.<sup>1</sup> It is very interesting to note that the spectra of all three monomeric compounds are fairly similar. One might have anticipated that the spectra of the ternary compounds would differ greatly from the spectra of the analogous



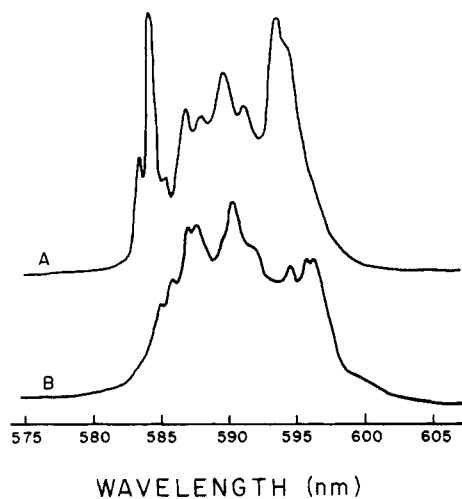
**Figure 5.** Luminescence spectra obtained at 77 K for the  $^5D_4 \rightarrow ^7F_6$  Tb(III) transition of (A)  $[\text{Tb}(\text{MeCp})_2\text{CH}_3]_2$  and (B)  $[\text{Tb}(\text{MeCp})_2\text{Cl}]_2$  dissolved in toluene.



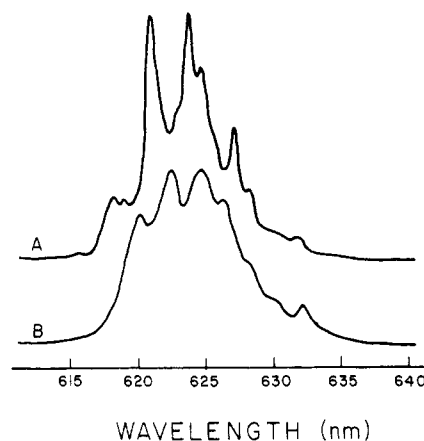
**Figure 6.** Luminescence spectra obtained at 77 K for the  $^5D_4 \rightarrow ^7F_5$  Tb(III) transition of (A)  $[\text{Tb}(\text{MeCp})_2\text{CH}_3]_2$  and (B)  $[\text{Tb}(\text{MeCp})_2\text{Cl}]_2$  dissolved in toluene.

$\text{Tb}(\text{MeCp})_3$  compound. If we consider the MeCp ligands as monodentate ligands, then the point group of  $\text{Tb}(\text{MeCp})_3(\text{THF})$  would be  $C_{3v}$ .<sup>1</sup> The point group of the  $\text{Tb}(\text{MeCp})_2(\text{Cl})(\text{THF})$  or  $\text{Tb}(\text{MeCp})_2(\text{CH}_3)(\text{THF})$  compounds would be  $C_2$  at the highest. In spite of the large reduction in symmetry the spectra remain quite similar in terms of spectral distribution. Hence, one may conclude that the crystal field experienced by the Tb(III) ion is primarily that of a low-symmetry, approximate tetrahedral ligand arrangement. The actual identity of the ligands appears not to play a dominant role in determining the observed spectral features.

The characteristic luminescence patterns associated with the spectra of the monomeric compounds are lost, however, upon dissolution into the noncoordinating toluene solvent. Since it is already known that dimerization of the organometallic compounds takes place in such solvents, one must conclude that the spectral changes observed in toluene solvent reflect this new bonding situation. The dimer spectra do resemble each other to some extent, but significant differences are quite apparent. This situation



**Figure 7.** Luminescence spectra obtained at 77 K for the  $^5D_4 \rightarrow ^7F_4$  Tb(III) transition of (A)  $[\text{Tb}(\text{MeCp})_2\text{CH}_3]_2$  and (B)  $[\text{Tb}(\text{MeCp})_2\text{Cl}]_2$  dissolved in toluene.



**Figure 8.** Luminescence spectra obtained at 77 K for the  $^5D_4 \rightarrow ^7F_3$  Tb(III) transition of (A)  $[\text{Tb}(\text{MeCp})_2\text{CH}_3]_2$  and (B)  $[\text{Tb}(\text{MeCp})_2\text{Cl}]_2$  dissolved in toluene.

indicates that the Tb(III) crystal field must be somewhat different for the two dimer compounds and is certainly different than that of the monomeric compounds. Since the dimers are bridged by different species in the two compounds, such a variation is not surprising.

Another significant difference was noted when comparing the spectra of analogous monomer and dimer compounds. Invariably, it was observed that the band envelope for a particular  $4-J$  system was wider for the monomer compounds than for the dimer compounds. In addition, the onset of luminescence was normally found at slightly higher energies for the dimeric compounds than was observed for the corresponding monomers. The shifting of Tb(III) levels to energies lower than those of the free ion is due to the small degrees of covalency in the bonding.<sup>4</sup> These observations all imply systematic shifting of Tb(III) energy levels, which may be taken as the barycenters of the band systems. Tb(III) energy levels were calculated for each of the complexes, and these may be found in Table I.

The largest degree of Tb(III) energy level shifting (relative to free ion values) was observed for the  $\text{Tb}(\text{Cp})_3(\text{THF})$  and  $\text{Tb}(\text{MeCp})_3(\text{THF})$ , and these compounds were not found to differ greatly from each other. The monomeric, mixed-ligand complexes  $\text{Tb}(\text{MeCp})_2\text{CH}_3$  and  $\text{Tb}(\text{MeCp})_2\text{Cl}$  each exhibited lower amounts of energy level shifting relative to the Tb(III) free ion values. Finally, the dimeric  $[\text{Tb}(\text{MeCp})_2\text{CH}_3]_2$  and  $[\text{Tb}(\text{MeCp})_2\text{Cl}]_2$  com-

**Table I. Energy Levels Obtained for the Terbium(III) Methylcyclopentadienyl Derivatives<sup>a</sup>**

	<sup>7</sup> F <sub>6</sub>	<sup>7</sup> F <sub>4</sub>	<sup>7</sup> F <sub>3</sub>	<sup>5</sup> D <sub>4</sub>
Tb(Cp) <sub>3</sub> (THF)	1930	3230	3911	20 105
Tb(MeCp) <sub>3</sub> (THF)	1947	3240	4068	20 107
Tb(MeCp) <sub>2</sub> (Cl)(THF)	1976	3266	4187	20 170
Tb(MeCp) <sub>2</sub> (CH <sub>3</sub> )(THF)	1980	3287	4208	20 191
[Tb(MeCp) <sub>2</sub> (Cl)] <sub>2</sub>	2083	3428	4316	20 330
[Tb(MeCp) <sub>2</sub> (CH <sub>3</sub> )] <sub>2</sub>	2061	3362	4288	20 300

<sup>a</sup>The monomer data were obtained in tetrahydrofuran solutions, while the dimer data were obtained in toluene solutions. The energy levels of Tb(Cp)<sub>3</sub>(THF) were taken from ref 1. The energy of the ground <sup>7</sup>F<sub>6</sub> level has been set equal to zero.

**Table II. Luminescence Lifetimes Obtained for the Terbium(III) Methylcyclopentadienyl Derivatives<sup>a</sup>**

	luminescence lifetime, μs	
	298 K	77 K
Tb(MeCp) <sub>3</sub> (THF)	285	386
Tb(MeCp) <sub>2</sub> (Cl)(THF)	300	405
Tb(MeCp) <sub>2</sub> (CH <sub>3</sub> )(THF)	307	401
[Tb(MeCp) <sub>2</sub> (Cl)] <sub>2</sub>	252	546
[Tb(MeCp) <sub>2</sub> (CH <sub>3</sub> )] <sub>2</sub>	267	581

<sup>a</sup>The monomer data were obtained in tetrahydrofuran solutions, while the dimer data were obtained in toluene solutions.

pounds exhibited the least amount of shifting. In fact, the energy levels for the dimers were almost equal to those obtained for anhydrous TbCl<sub>3</sub>.<sup>4</sup>

Several conclusions may be drawn from the observed trends. First, the simple monomeric compounds all contain essentially the same degree of covalency, since there is little shifting of energy levels in the various spectra. Second, the degree of covalency is reduced by a small extent upon formation of the monomeric mixed-ligand complexes. Third, the degree of covalency in the bridged dimers is reduced further relative to that of the corresponding solvated monomers and is indicative of essentially no covalency at all. This observation sets aside the prediction made by Tsutsui,<sup>16</sup> who thought that the σ-bonded organic derivatives of lanthanides would exhibit larger amounts of covalency in their bonding.

Further probing of the effect of complex structure on the Tb(III) spectral properties was available from studies of the luminescence lifetimes. These were all obtained both at room and cryogenic temperatures, and a complete summary is found in Table II.

At room temperature, one finds that the Tb(III) emission lifetimes associated with compounds dissolved in THF are almost the same. The Tb(III) luminescence lifetimes of the same compounds in toluene solutions were found to be somewhat shorter. Upon cooling to cryogenic temperatures, one finds that all luminescence lifetimes increase but that the rate of increase differs with the nature of the compound. The THF-solvated compounds exhibit a lifetime enhancement of approximately 35%, while in toluene solution the same compounds exhibit an enhancement of almost 120%. The lifetime values were obtained using at least 95% of the decay curve, and consequently the linearity of the ln(I) vs. time plots indicates no significant impurity problem.

This difference in decay times may be rationalized through consideration of intermolecular energy-transfer properties. It is well-known that electronic energy may be transferred among lanthanide complexes, and such processes are known to limit the emission intensities of

lanthanide activated phosphor systems.<sup>17</sup> An efficient transfer of energy among Tb(III) organometallic complexes would certainly perturb the emission lifetimes, and most of the values in Table II are smaller than those normally obtained for the Tb(III) aquo ion (a very heavily quenched system).<sup>18</sup>

Little difference in emission lifetimes are noted for the monomeric complexes, since these would only undergo energy-transfer processes through collisional interactions. Apparently, the nature of the coordinated ligands does not exert a significant influence upon the intermolecular energy transfer process. The efficiency associated with pure collisional processes (dynamic quenching) is normally low.<sup>19</sup> Cooling the materials to cryogenic temperatures effectively eliminates the dynamic quenching, and the resulting lifetime is determined primarily by vibrational modes associated with the ligand systems. Since the Tb(III) emission lifetimes of the organometallic systems are greatly reduced relative to those of Tb(III) in highly coordinated carboxylate systems,<sup>18</sup> quenching by the cyclopentadienyl ligands is indicated.

The room-temperature lifetimes of the dimers were found to be reduced relative to those of the corresponding monomers. While the Tb(III) ions may still collide and transfer energy through intermolecular processes, with the dimers an intramolecular exchange pathway also exists. An additional amount of quenching will result from transfer of Tb(III) centers bound in the same complex. Cooling the materials to cryogenic temperatures will eliminate the collisional processes. It is significant to note that reduction in the number of coordinated MeCp ligands yields Tb(III) emission lifetimes which are longer. This observation supports ligand quenching of Tb(III) emission and indicates that the triplet levels of the Cp and MeCp ligands cannot be much higher in energy than the <sup>5</sup>D<sub>4</sub> Tb(III) level.

## Conclusions

The data presented in the preceding section indicate that the intrinsic luminescence of Tb(III) organometallic compounds may be used as a method for the study of solvation phenomena. The differences between the monomer and dimer spectra are sufficiently large so that the Tb(III) luminescence could actually be used as a qualitative indicator for the type of bonding existing for a given Tb(III) compound in solution.

The spectra obtained for monomer species were found to resemble each other to a remarkable extent, and this observation indicates that the spectroscopic properties of the Tb(III) ion are determined primarily by the ligand arrangements. The actual identity of the ligands plays only a secondary role in determining the spectral properties. The luminescence trends may also be used to determine qualitative differences in bond covalency associated with the various bonding situations. In the present work, it was noted that the bridged dimers exhibited less covalency in their bonding than did the solvated monomers.

The advantage associated with the luminescence method is that one may directly observe features attributable to complex structure and bonding. Thus, it may be concluded that studies of Tb(III) luminescence can provide important information regarding solvation phenomena. Whenever

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full resolution of all Tb(III) crystal field components is possible, the luminescence data can be used to deduce the actual solution-phase structure of the complex. In the absence of such resolution (which is probably the most likely situation workers will encounter), one can draw distinctions between monomer and dimer complexation modes. This information would be of great use in beginning a quantitative interpretation of NMR data, and correlation of luminescence and NMR investigations could provide the most powerful approach to the study of compound structures in fluid solutions.

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**Registry No.** Tb(MeCp)<sub>3</sub>(THF), 87184-39-2; Tb(MeCp)<sub>2</sub>(Cl)(THF), 97210-70-3; Tb(MeCp)<sub>2</sub>(CH<sub>3</sub>)(THF), 97210-71-4; [Tb(MeCp)<sub>2</sub>(Cl)]<sub>2</sub>, 97210-72-5; [Tb(MeCp)<sub>2</sub>(CH<sub>3</sub>)<sub>2</sub>]<sub>2</sub>, 97234-21-4; Na(MeCp), 55562-83-9; TbCl<sub>3</sub>, 10042-88-3; THF, 109-99-9; PhMe, 108-88-3.

## A Neutron Diffraction Study of [Ph<sub>4</sub>P]<sup>+</sup>[HW<sub>2</sub>(CO)<sub>10</sub>]<sup>-</sup>

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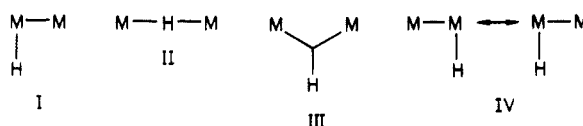
The structure of [Ph<sub>4</sub>P]<sup>+</sup>[HW<sub>2</sub>(CO)<sub>10</sub>]<sup>-</sup> has been analyzed at low temperature with single-crystal neutron diffraction techniques. The W-H-W linkage in the [HW<sub>2</sub>(CO)<sub>10</sub>]<sup>-</sup> anion is bent and symmetric, with W-H and W-W distances of 1.897 (5) Å and 3.340 (5) Å, respectively, and a W-H-W angle of 123.4 (5)°. The anion has a structure almost identical with that of the isoelectronic HW<sub>2</sub>(CO)<sub>9</sub>(NO), including a non-hydrogen skeleton which is bent and staggered. These results support our earlier conclusion that the M-H-M bond is inherently bent. Crystallographic details: crystals of [Ph<sub>4</sub>P]<sup>+</sup>[HW<sub>2</sub>(CO)<sub>10</sub>]<sup>-</sup> are tetragonal, space group P<sub>4</sub>, *a* = *b* = 15.529 (2) Å, *c* = 6.680 (1) Å, *V* = 1611 Å<sup>3</sup>, *Z* = 4. The final *R* value is 0.050 for 2279 neutron reflections measured at 40 K.

### Introduction

Few metal carbonyl complexes have attracted as much interest during the past two decades as the hydridometal carbonyl anions [HM<sub>2</sub>(CO)<sub>10</sub>]<sup>-</sup> (M = Cr, Mo, W). First prepared by Behrens and co-workers in 1957,<sup>2</sup> the anions have been extensively studied because of speculation that they might contain a single unsupported M-H-M three-center/two-electron (3c-2e) bond, a suspicion which was later essentially confirmed by an X-ray analysis of [Et<sub>4</sub>N]<sup>+</sup>[HCr<sub>2</sub>(CO)<sub>10</sub>]<sup>-</sup>.<sup>3</sup> Unsupported<sup>4</sup> 3c-2e bonds are extremely rare: The [HM<sub>2</sub>(CO)<sub>10</sub>]<sup>-</sup> family, and close analogues such as HW<sub>2</sub>(CO)<sub>9</sub>(NO), are among the very few transition-metal complexes known to contain such bonds. For compounds of the main-group elements, unsupported 3c-2e bonds are known to exist in [B<sub>2</sub>H<sub>7</sub>]<sup>-</sup> and related species.<sup>5</sup> In addition, the hybrid M-H-B system, as found in (Ph<sub>2</sub>MeP)<sub>3</sub>Cu(BH<sub>4</sub>), recently has also been accurately characterized.<sup>6</sup>

In 1966, Hayter reported an improved preparation of [HM<sub>2</sub>(CO)<sub>10</sub>]<sup>-</sup> and the mixed derivatives [HMM'(CO)<sub>10</sub>]<sup>-</sup>

(M, M' = Cr, Mo, W) involving the NaBH<sub>4</sub> reduction of the parent hexacarbonyls M(CO)<sub>6</sub> in refluxing THF.<sup>7</sup> At that time, Hayter also described the IR and NMR spectra of the anions, the latter of which were analyzed further by Whitesides and Maglio.<sup>8</sup> Both groups of investigators concluded that the <sup>1</sup>H NMR spectrum of [HW<sub>2</sub>(CO)<sub>10</sub>]<sup>-</sup> is inconsistent with a static terminal structure (I), but were unable to distinguish between a linear bridged (II), a bent bridged (III), or a rapidly equilibrating pair of terminal structures (IV).



Meanwhile, we and other groups have investigated<sup>9-18</sup>

(1) (a) University of Southern California. (b) Present address: Shell Development Co., P.O. Box 481, Houston, TX 77001. (c) Brookhaven National Laboratory.

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(4) We define a molecule having an unsupported 3c-2e bond as one in which the two halves of the molecule are held together solely by one 3c-2e bond, without other bridging groups. Thus, molecules such as B<sub>2</sub>H<sub>6</sub> or H<sub>2</sub>Re<sub>2</sub>(CO)<sub>8</sub>, which have two X-H-X bridges, are not included by this definition.

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(14) For an illustration of the [HW<sub>2</sub>(CO)<sub>10</sub>]<sup>-</sup> anion in [Et<sub>4</sub>N]<sup>+</sup>[HW<sub>2</sub>(CO)<sub>10</sub>]<sup>-</sup>, see Figure 4 in: Bau, R.; Teller, R. G.; Kirtley, S. W.; Koetzle, T. F. *Acc. Chem. Res.* 1979, 12, 176. The anion in this salt has a non-hydrogen framework which is eclipsed and almost linear (or very slightly bent). However, the W-H-W bond is found to be markedly bent and surprisingly asymmetric, with W-H distances of 1.718 (12) and 2.070 (12) Å, a W-W distance of 3.528 (2) Å, and a W-H-W angle of 137.1 (10)°. The H atom is disordered and is displaced by 0.71 (1) Å from the center of the W-W bond. Disorder is also found in the W<sub>2</sub>(CO)<sub>10</sub> framework, where it is minor, and in the [Et<sub>4</sub>N]<sup>+</sup> cation, where it is extensive.

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