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Neodymium, Gadolinium, and Terbium Complexes Containing Hexafluoroacetylacetonate and 2,2′-Bipyrimidine: Structural and Spectroscopic Characterization

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Lanthanide complexes of the form Ln(hfa)$_3$bpm (where Ln = Nd(III), Gd(III), or Tb(III); hfa = 1,1,1,5,5,5-hexafluoroacetylacetone and bpm = 2,2′-bipyrimidine) have been structurally characterized. The Nd and Gd complexes form one-dimensional arrays when X-ray-quality crystals are grown by the slow evaporation of concentrated solutions of the complexes. Each metal is 10-coordinate with repeating Ln–bpm units. The Tb complex does not form a one-dimensional array under these conditions. Its structure is 9-coordinate with the ninth position occupied by a covalently bonded water molecule that is hydrogen-bonded to the bpm group from another complex in solution. Luminescent studies show that the Nd complex undergoes nonradiative relaxation through solvent vibrational deactivation, while the lowest excited state of the Gd complex, $^6P_{7/2}$, is higher in energy than the T$_1$ state of the hfa ligand, making luminescence improbable for both of these complexes. In contrast, the Tb complex emits in the visible region of the spectrum when solutions of the complex are excited at 304 nm associated with the π–π* transition of the hfa ligand. Emission lines corresponding to transitions from the $^5D_4$ state to the ^7F_J manifold of the Tb(III) are observed. The intensity of these emissions decreases as temperature is increased. Lifetime measurements of the Tb monometallic complex fit to a monoexponential with the lifetime decreasing as the temperature is increased.

Introduction

Lanthanide complexes have been utilized in the fabrication of materials for diode lasers and optical fibers.[1−6] Other applications include biomedical assays,[7−9] immunoassays,[10−15] early detection of cancer,[16,17] and time-resolved luminescence measurements.[18,19] Their unusual spectroscopic properties include sharp long-lived emissions in the visible and near-infrared regions of the spectrum. The interest in these spectroscopic properties is surprising in light of the parity-forbidden 4f−4f transitions associated with the lanthanide ions. Excitation of 4f electrons and their subsequent relaxation generates the spectroscopic properties which have made lanthanide complexes attractive for such a wide variety of applications. To overcome the forbidden nature of the 4f−4f transitions, researchers found that by coordinating “antenna” ligands to the lanthanide metals they could stimulate through energy transfer the metal-centered luminescence.[20]

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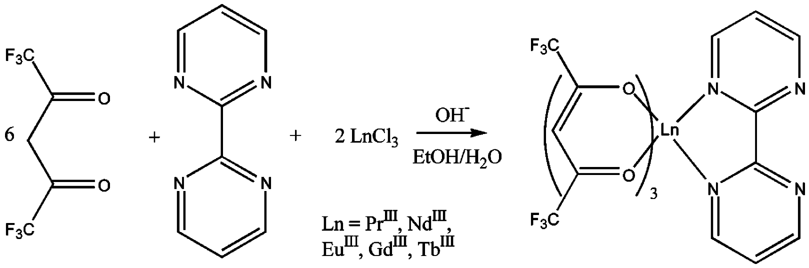
Scheme 1. Formation of Monometallic Lanthanide Complexes with hfa and bpm Ligands



β-Diketones, for example 4,4,4-trifluoro-1-(2-thienyl)-1,3-butanedione, have proven to be exceptional "antenna" ligands forming facile coordination complexes with Ln(III) ions.[21−23] Absorption of light by the "antenna" ligand in the UV region of the spectrum leads to energy transfer and population of the metal-centered excited states. The result is emission of light upon relaxation of the excited metal to its ground state. The emission wavelength associated with the lanthanide complex is related to the energy gap of the 4f orbitals, which is of course related to the lanthanide metal. This allows the emission wavelength to be tuned by choice of the lanthanide metal.

Terbium(III) complexes, like europium(III) complexes, display long-lived visible emissions which have been exploited for luminescent-based devices.[24−26] Despite the very weak luminescence of Gd(III) complexes in solution, researchers have found that incorporation of Gd(III) ions into a rigid matrix enhances its luminescence.[27] This has led to the use of Gd(III) in cell targeting and labeling.[28] To observe luminescence of Nd(III) complexes coordinated to hexafluoroacetylacetonate (hfa) ligands, deuterated systems must be employed to eliminate quenching of the Nd(III) excited states through vibrational energy transfer.[29−31]

Lanthanide complexes of β-diketonates and the polyazine bridging ligand 2,2′-bipyrimidine (bpm) are of particular interest due to their ability to form facile supramolecular complexes. Bpm is a planar heterocycle capable of coordinating to two metal centers through four equivalent nitrogens. Examples of homodinuclear lanthanide complexes of the bonding motif [Ln(β-dik)$_3$]$_2$bpm have been reported.[32−36] In a recent communication it was noted that when LnCl$_3$, bpm, and hfa are combined in a ratio of 2:1:6, respectively, Scheme 1, only monometallic complexes were obtained as indicated by elemental analysis and high-resolution mass spectroscopy.[37] Structural analysis of the Eu(III) complex indicated self-assembly of a linear array with alternating Eu−bpm units.[38] Many examples of coordination polymers and arrays of lanthanides with a variety of bridging ligands have been reported.[39−45] However to our knowledge there are very few reports of linear arrays of lanthanides using bpm as the linking unit.

In this report the unusual structural properties of Nd(III), Gd(III), and Tb(III) complexes formed by reaction of hfa and bpm, Scheme 1, are described. Temperature-dependent luminescence and lifetime data of the Tb(III) complex in solution are also presented.

Experimental Section

Materials and Instruments. All reagents were analytical grade and used without further purification. Neodymium(III) chloride, terbium(III) chloride, and 1,1,1,5,5,5-hexafluoroacetylacetone (hfa) (ACROS), gadolinium(III) chloride (STREM), 2,2′-bipyrimidine-(bpm) (Alfa Aesar), toluene, ethyl acetate, hexanes, methanol, and ethanol (Fisher) were used as received. Diffraction-quality crystals of the three complexes were grown from ethyl acetate. Electronic absorption spectroscopy of the complexes was run in methanol solutions with a Shimadzu Multispec-1501 diode array spectrophotometer. Luminescence spectra of the complexes in a 1 cm quartz spectrophotometer fluorescence cell (Starna) in methanol were run on a Cary Eclipse fluorescence spectrophotometer. Temperature-dependent luminescence of the Tb(III) complex in methanol from 5 to 40 °C was obtained using a Cary single cell

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Table 1. Crystal Data and Structure Refinement Parameters for Complexes with Nd(III), Gd(III), and Tb(III)

params	Nd	Gd	Tb
empirical formula	$C_{23}H_9N_4O_6F_{18}Nd$	$C_{23}H_9N_4O_6F_{18}Gd$	$C_{27}H_{11}N_6O_7F_{18}Tb{\cdot}H_2O$
fw	923.58	936.59	1038.86
cryst system	triclinic	triclinic	monoclinic
space group	$P\bar{1}$	$P\bar{1}$	$C2/c$
cryst size (mm^3)	0.062 × 0.055 × 0.52	0.038 × 0.048 × 0.322	0.18 × 0.34 × 0.38
temp (K)	140	140	140
a (Å)	10.8373(8)	10.8679(8)	30.0019(20)
b (Å)	12.3695(11)	12.3310(11)	17.3996(9)
c (Å)	14.2200(8)	14.1256(6)	21.2343(13)
α (deg)	109.612(8)	109.200(7)	90.00
β (deg)	93.083(5)	93.222(5)	133.588(10)
γ (deg)	114.953(7)	115.428(7)	90.00
V (Å^3)	1584.8(2)	1570.68(19)	8028.9(8)
Z	2	2	8
ρ_{calc} (g cm^{-3})	1.935	1.980	1.719
μ (mm^{-1})	1.788	2.263	1.893
R1 [$I > 2\sigma(I)$]	0.0609	0.0735	0.0901
wR2 [$I > 2\sigma(I)$]	0.1136	0.1469	0.2338
R1 (all data)	0.0610	0.0739	0.0901
wR2 (all data)	0.1136	0.1470	0.2338
GOF	1.746	1.355	1.127
reflcns measd/indpndt reflcns	31 856/5420	35 308/5209	66 791/6593
max θ (deg)	25.03	26.37	23.25

Peltier temperature controller. Elemental analysis was performed by Atlantic Microlabs, Norcross, GA.

Thermal Stability. Thermal stability of the crystalline complexes was measured on a TA instruments Q1000 DSC in hermetically sealed aluminum pans at a heating rate of 10 °C/min. Thermal analysis of the Tb(III) complex shows a melting point at 251.62 °C followed by decomposition most likely of the antenna ligands. The Gd(III) complex melts at 233.44 °C while the Nd(III) complex is more thermally stable melting at 316.06 °C followed in all cases by decomposition.

Nd(hfa)$_3$bpm.[37] A solution of bpm (0.055 g, 0.35 mmol) in absolute ethanol (3.0 mL) was added to a basic (2.1 mL of 1.0 M NaOH) solution of hfa (0.436 g, 2.10 mmol) in absolute ethanol (3.0 mL). The mixture was stirred at room temperature for 30 min. To this solution was added an aqueous (3.5 mL) solution of $NdCl_3{\cdot}6H_2O$ (0.25 g, 0.70 mmol) over a 5 min period. The light blue colored precipitate was vacuum filtered, washed 3 × 10 mL with cold absolute ethanol, and allowed to air-dry. The resulting powder was recrystallized from an ethyl acetate/hexanes mixture to give a light blue powder (0.17 g, 53%). Anal. Calcd for $NdC_{23}H_9N_4O_6F_{18}$: C, 29.91; H, 0.98; N, 6.07. Found: C, 29.52; H, 0.99; N, 5.87.

Gd(hfa)$_3$bpm.[37] A solution of bpm (0.055 g, 0.35 mmol) in absolute ethanol (3.0 mL) was added to a basic (2.1 mL of 1.0 M NaOH) solution of hfa (0.44 g, 2.1 mmol) in absolute ethanol (3.0 mL). The mixture was stirred at room temperature for 30 min. To this solution was added an aqueous (3.5 mL) solution of $GdCl_3$ (0.18 g, 0.70 mmol) over a 5 min period. The light blue colored precipitate was vacuum filtered, washed 3 × 10 mL with cold absolute ethanol, and allowed to air-dry. The resulting powder was recrystallized from an ethyl acetate/hexanes mixture to give a pale yellow powder (0.14 g, 43%). Anal. Calcd for $GdC_{23}H_9N_4O_6F_{18}$: C, 29.50; H, 0.97; N, 5.98. Found: C, 29.61; H, 0.94; N, 6.04.

Tb(hfa)$_3$bpm.[37] A solution of bpm (0.055 g, 0.35 mmol) in absolute ethanol (3.0 mL) was added to a basic (2.1 mL of 1.0 M NaOH) solution of hfa (0.44 g, 2.1 mmol) in absolute ethanol (3.0 mL). The mixture was stirred at room temperature for 30 min. To this solution was added an aqueous (3.5 mL) solution of $TbCl_3{\cdot}6H_2O$ (0.26 g, 0.70 mmol) over a 5 min period. The light blue colored precipitate was vacuum filtered, washed 3 × 10 mL with cold absolute ethanol, and allowed to air-dry. The resulting powder was recrystallized from an ethyl acetate/hexanes mixture to give a pale yellow powder (0.17 g, 52%). Anal. Calcd for $GdC_{23}H_9N_4O_6F_{18}{\cdot}H_2O$: C, 28.89; H, 1.16; N, 5.86. Found: C, 28.36; H, 0.85; N, 5.61.

Table 2. Selected Bond Lengths (Å) for Complexes with Nd(III), Gd(III), and Tb(III)

Nd		Gd		Tb	
Nd–O1	2.431(5)	Gd–O1	2.383(7)	Tb–O7	2.332(8)
Nd–O5	2.448(5)	Gd–O2	2.396(7)	Tb–O5	2.354(7)
Nd–O2	2.444(5)	Gd–O5	2.406(7)	Tb–O3	2.364(8)
Nd–O3	2.465(5)	Gd–O4	2.413(7)	Tb–O4	2.375(7)
Nd–O4	2.464(5)	Gd–O6	2.415(7)	Tb–O1	2.383(8)
Nd–O6	2.466(5)	Gd–O3	2.410(7)	Tb–O2	2.399(7)
Nd–N1	2.747(5)	Gd–N1	2.714(8)	Tb–O6	2.446(8)
Nd–N3	2.760(6)	Gd–N3	2.737(8)	Tb–N1	2.610(9)
Nd–N2	2.759(6)	Gd–N2	2.737(9)	Tb–N3	2.645(9)
Nd–N4	2.777(6)	Gd–N4	2.760(8)		

X-ray Crystallography. The X-ray intensity data were collected at 140 K on an Oxford Diffraction Xcalibur3 system equipped with a graphite monochromator and an Enhance (Mo) X-ray source (λ = 0.710 73 Å) operated at 2 kW power (50 kV and 40 mA). The detector was placed at a distance of 50 mm from the crystal. Final cell constants were obtained through a global refinement of all reflections. Intensity data were collected employing the CrysAlis CCD software program.[46] Data frames using φ and ω scans were integrated with CrysAlis RED.[46] The ω scan width was 1.0°. The structures were solved and refined using Bruker SHELXTL (v6.10).[47]

The refinements converged with crystallographic agreement factors are summarized in Table 1. The selected bond lengths for the complexes are listed in Table 2.

Results and Discussion

Structural Analysis of the Nd(III) and Gd(III) Complexes. The synthesis of Nd(hfa)$_3$bpm and Gd(hfa)$_3$bpm with yields of greater than 40% is illustrated in Scheme 1.[37] As

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(46) *Oxford Diffraction CrysAlis CCD and CrysAlis RED*, versions 171.27p5; Oxford Diffraction Ltd.: Abingdon, Oxfordshire, U.K., 2005.

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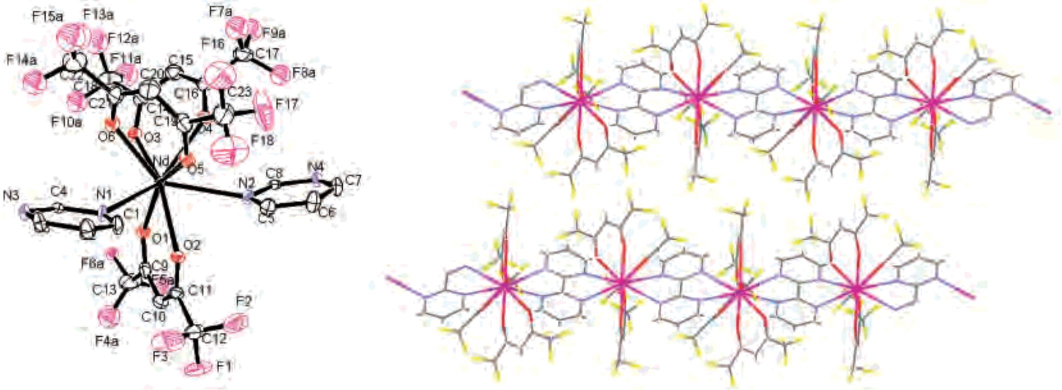

Figure 1. Molecular structure of the asymmetric unit of Nd(III) complex and the one-dimensional array formed by addition of symmetry-related atoms. The atom numbering scheme corresponds to a single component of the disordered structure. Displacement ellipsoids are drawn at the 40% probability level. H atoms have been omitted for clarity in the ORTEP drawing.

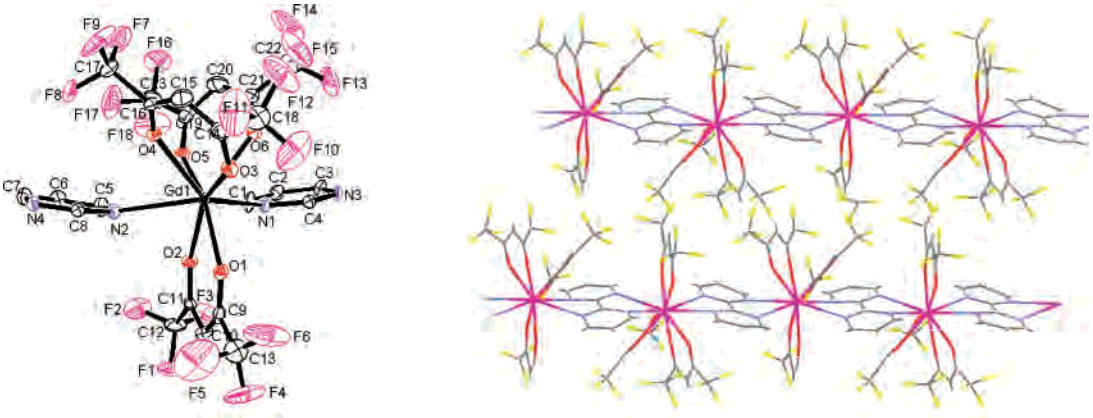

Figure 2. Molecular structure of the asymmetric unit of Gd(III) complex, along with atom numbering scheme, and the one-dimensional array formed by addition of symmetry-related atoms. Displacement ellipsoids are drawn at the 40% probability level. H atoms have been omitted for clarity in the ORTEP drawing.

noted, the initial goal was the synthesis of homodinuclear lanthanides bridged by the polyazine bpm ligand; therefore, the ratio of β-diketone to bpm to $LnCl_3$ was 6 to 1 to 2, respectively. In the case of hfa as the β-diketone only monometallic complexes were isolated. Attempts to synthesize the monometallic complexes directly using a 3 to 1 to 1 stoichiometric reaction mixture of hfa to bpm to $LnCl_3$ respectively resulted in less than 5% yield of the complex, and in some cases a tractable product could not be recovered. Concentrated solutions of the Nd(III) and Gd(III) monometallic complexes in ethyl acetate were allowed to evaporate slowly over a 1−2 month period to obtain diffraction-quality crystals. Slow crystallization of the monometallic complex results in the self-assembly of a one-dimensional array with repeating Nd−bpm units, Figure 1.

Figure 1 illustrates the structure of the asymmetric unit and one-dimensional array. The coordination sphere around each Nd(III) ion consists of six O atoms from three hfa ligands and four N atoms from two bpm ligands (average distances: Nd−O = 2.453(6) Å, Nd−N = 2.761(6) Å). Refinement of the structure was complicated by the fact that four of the six $-CF_3$ groups are disordered. The closest Nd···Nd distance is 7.121 Å. The planar bpm moiety sits on an inversion center.

Structural analysis of Gd(hfa)$_3$bpm also indicates the formation in the triclinic space group $P\bar{1}$ forming a one-dimensional array of Gd−bpm repeat units. Figure 2 illustrates the structure of the asymmetric unit and one-dimensional array. The coordination sphere is identical with those of the Nd(III) complex, Figure 1, and the Eu(III) complex reported previously[38] with six O atoms from three hfa ligands and four N atoms from two bpm ligands (average distances: Gd−O = 2.404(5) Å, Gd−N = 2.737(9) Å). The Gd···Gd distance is 7.070 Å. The planar bpm moiety is located on an inversion center.

Structural Analysis of the Tb(III) Complex. Synthesis, isolation, and purification of the Tb(III) complex was carried out in the same fashion as the Nd(III) and Gd(III) complexes; however, elemental analysis of the Tb(III) complex revealed an associated water molecule with each complex. Drying under elevated temperatures and vacuum did not drive off the associated water molecule. X-ray-quality crystals were grown in the same fashion through slow evaporation of concentrated ethyl acetate solutions of the complex. Structural analysis of the Tb(III) complex indicates that the coordination sphere around the Tb(III) ion is 9 coordinate with six O atoms coming from the hfa ligands, two N atoms coming from the bpm ligand, and one covalently bonded water molecule in agreement with the elemental analysis (average distances: Tb−O = 2.379(14) Å, Tb−N = 2.628(18) Å), Figure 3. In addition to coordination of the water molecule, which could very well prevent self-assembly of

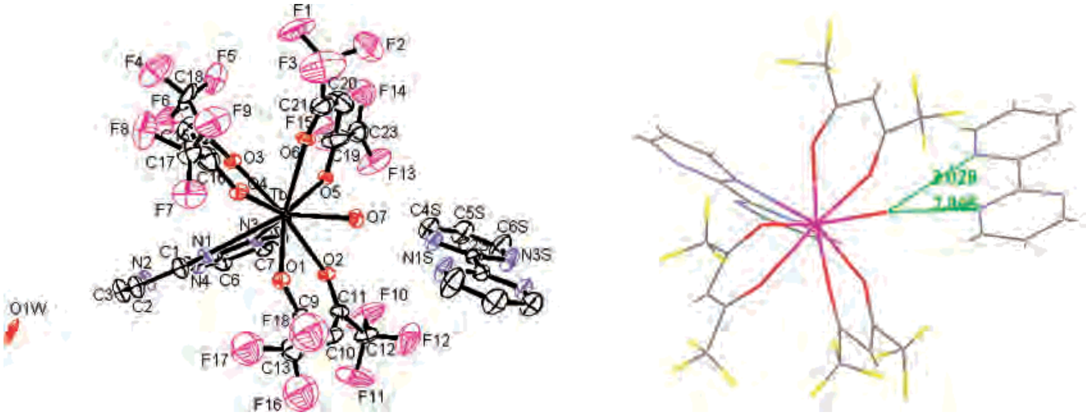

Figure 3. Molecular structure of the asymmetric unit of Tb(III) complex, along with atom numbering scheme, and hydrogen bonding of coordinated water to bpm. Displacement ellipsoids are drawn at the 30% probability level. H atoms have been omitted for clarity in the ORTEP drawing.

Table 3. Average Ln−O, Ln−N, and Ln···Ln Metal Distances (Å) for Nd(III), Gd(III), Tb(III), and Eu(III) Complexes

complex	Ln−O	Ln−N	Ln···Ln
Nd(III)	2.453(6)	2.761(6)	7.121
Eu(III)[a]	2.418(3)	2.746(3)	7.085
Gd(III)	2.404(5)	2.737(9)	7.070
Tb(III)	2.379(14)	2.628(18)	b

[a] Taken from ref 38. [b] Metal−metal distances do not apply to the monometallic Tb(III) complex.

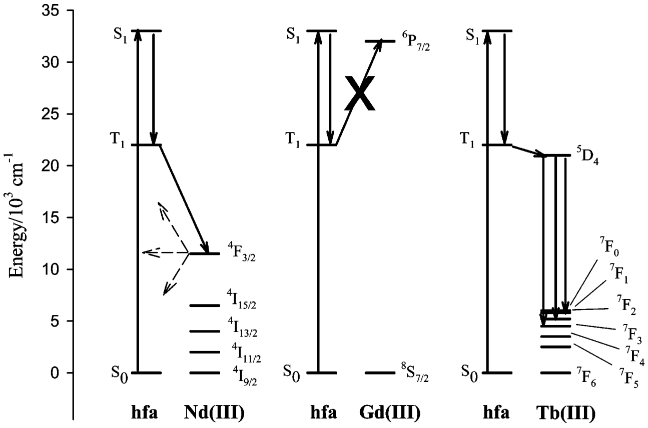

Figure 4. Schematic energy level diagram and energy transfer processes for Nd(III), Gd(III), and Tb(III) complexes. For clarity, the S_1 and T_1 states of the bpm ligand are omitted; their energies measured at 42 000 and 36 000 cm^{-1}, respectively, suggest they play no role in the luminescence of the complexes.

the one-dimensional array, hydrogen bonding through the coordinated water molecule with nitrogen atoms of another bpm ligand is observed. These hydrogen bond distances, O7-H···N1S and O7-H···N3S, are 2.896 and 3.028 Å, Figure 3, respectively. The source of the free bpm ligand is puzzling in light of the fact that only the monometallic Tb(III) complex was used in crystal formation, suggesting that the free bpm ligand comes from another Tb(III) complex in solution. Whether this is a glimpse at how self-assembly of the linear arrays are formed from monometallic complexes is yet to be determined. The lattice also contains a disordered water solvate molecule. The Tb···Tb distance is 8.756 Å.

Similarities in bonding motif for the Nd, Gd, Tb, and previously studied Eu complex[38] allows for comparison of the metal−ligand distances. Table 3 compares the average bond distances for the Ln−O and Ln−N bond distances. However, metal−metal distances could only be compared for the complexes that formed one-dimensional arrays (i.e., Nd, Gd, and Eu). As the ionic radius of the metal becomes smaller in the order Nd(III) > Eu(III) > Gd(III) > Tb(III), their corresponding bond lengths decrease, consistent with the lanthanide contraction, Table 3.

Photoluminescence Studies. The electronic spectra of all three complexes are dominated by the $\pi-\pi^*$ transitions of the hfa "antenna" ligand at ca. 304 nm. Bpm $\pi-\pi^*$ transitions play a minor role in the electronic spectra of the complexes occurring as a high-energy shoulder of the broad hfa transition whose S_1 and T_1 states are too high in energy (42 000 and 36 000 cm^{-1}, respectively) for thermal population of the excited antenna ligands. The mechanism of photoluminescence is described by photoexcitation of the "antenna" ligand to the S_1 state followed by intersystem crossing to the T_1 state which then transfers energy to an excited-state associated with the Ln(III) center as illustrated in Figure 4. Methanol solutions of the Gd(III) complex showed no emission spectrum in the region from 400 to 1100 nm when irradiated at 304 nm. This is due to the lowest lying excited state of the Gd(III) center ($^6P_{7/2}$), which is higher in energy than the T_1 state of the hfa ligand, Figure 4. This prevents efficient energy transfer from hfa to Gd(III). No emission was detected for a methanol solution of the Nd(III) complex in the range 350−1100 nm when irradiated at 304 nm. The low-energy excited states of Nd(III) complexes have been noted to undergo rapid vibrational deactivation through solvent interactions,[31] Figure 4.

Figure 5 illustrates the absorption and emission spectrum of a methanol solution of the Tb(III) complex. When samples are irradiated at 304 nm, emission lines originating from the $^5D_4$ state to the ^7F_J manifold of Tb(III) are observed. The most intense emission at 541 nm corresponds to the $^5D_4 \rightarrow {}^7F_4$ transition. The $^5D_4 \rightarrow {}^7F_0$ transition should appear at ca. 670 nm but is too weak to be observed under our conditions.

Emission studies of the monometallic Tb(III) complex in a methanol solution indicate a decrease in emission intensity with increasing temperature from 5 to 40 °C, Figure 6. This

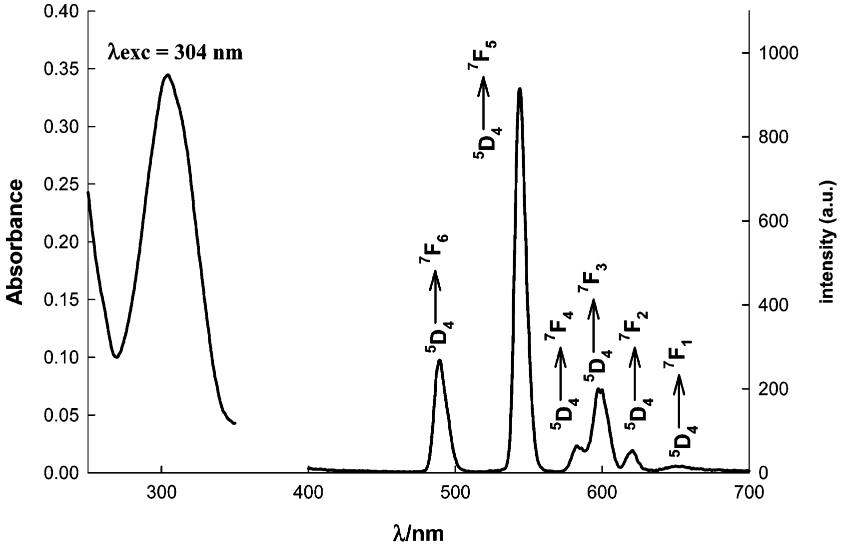

Figure 5. Excitation and emission spectra of a methanol solution of the Tb(III) complex ($\lambda_{exc} = 304$ nm).

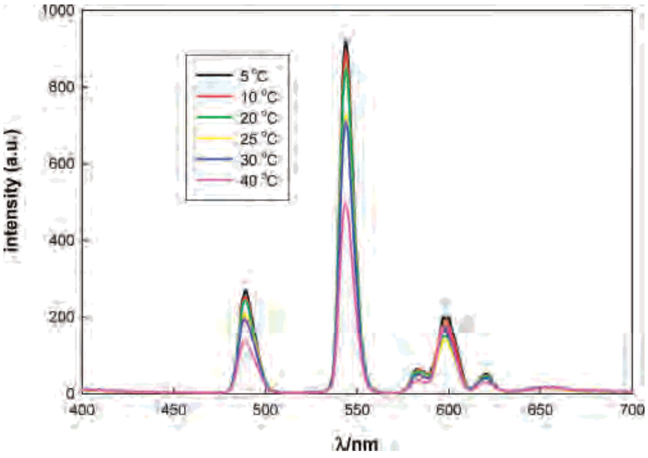

Figure 6. Temperature-dependent emission spectra of a methanol solution of Tb(III) complex in the temperature range of 5 to 40 °C ($\lambda_{exc} = 304$ nm).

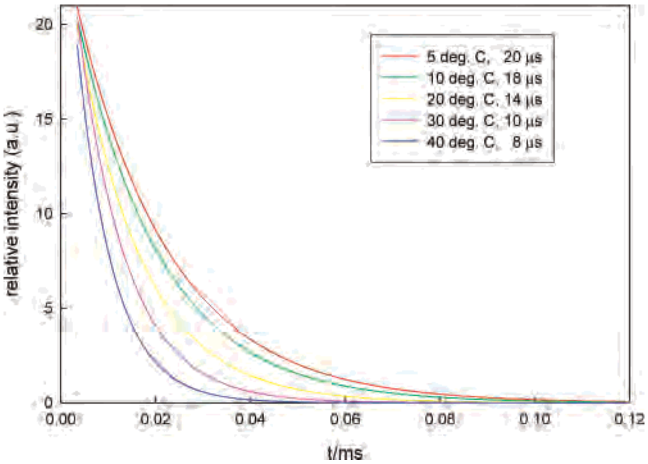

Figure 7. Lifetime measurements of a methanol solution of Tb(III) complex from 5 to 40 °C measured at 541 nm corresponding to the $^5D_4 \rightarrow {}^7F_4$ transition ($\lambda_{exc} = 304$ nm).

is most likely due to quenching through thermal population of the triplet state of the hfa ligand by the emitting $^5D_4$ state of the Tb(III) ion.[48] Lifetimes of the excited Tb(III) complex in methanol as a function of temperature were monitored at the 541 nm line corresponding to the most intense transition, $^5D_4 \rightarrow {}^7F_4$. Decay curves fit to a monoexponential indicating only one species exists in the excited state.[49] Excited-state lifetimes of solutions of the Tb(III) complex ranged from 20 μs at 5 °C to 8 μs (near the limit of our instrument) at 40 °C, inset Figure 7. Lifetimes of the excited Tb(III) complex are orders of magnitude lower than their Eu(III) analog[38] complex but differ very little from the values found for solutions of Tb(hfa)$_3$.[52] The temperature-dependent decay curves, Figure 7, fit to an Arrhenius equation with a correlation coefficient $r^2 > 0.999$:[50−52]

$$k(T) = A \exp(-E/RT) \tag{1}$$

The rate constant $k(T)$ in eq 1 represents the rate of quenching associated with the excited-state of the Tb(III) ion. The preexponential factor A represents the rate of deactivation from the triplet state of hfa to the ground state.[52] A plot of ln $k(T)$ versus T^{-1} gives an intercept equal to ln A and a slope of $-E/R$, where R is the gas constant (8.314 J/(K mol)) and E the activation energy between the hfa triplet state and the Tb(III) emitting state. From this graph the preexponential factor is 1.9×10^8 s^{-1}, which is slightly greater than that observed for Tb(hfa)$_3$.[37] The slope gives a value of ca. 1600 cm^{-1} for the activation energy, consistent with thermal population of the triplet hfa state from the emitting $^5D_4$ state of the Tb(III) center with an energy difference of approximately 1500 cm^{-1}, Figure 4. A value of 2100 cm^{-1} for the activation energy has been reported for methanol solutions of the Tb(hfa)$_3$ complex.[52] The

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emission quantum efficiency of the Tb(III) complex in solution is obtained using eq 2,

$$\phi_{\mathrm{Tb}} = \tau_{\mathrm{obs}}/\tau_{\mathrm{R}} \tag{2}$$

where the observed lifetime, τ_{obs}, is compared to the "natural" lifetime of the ion in the absence of nonradiative processes.[53] For Tb(III), τ_{R} is 300 μs[54] giving a quantum efficiency, ϕ_{Tb}, of 0.047 at 20 °C which is similar to values reported for other Tb(III) β-diketonate complexes.[55]

Conclusions

Slow crystallization of the Nd(III) and Gd(III) monometallic complexes leads to the self-assembly of a one-dimensional array with each metal having a coordination sphere of 10 and a repeat unit consisting of Ln−bpm. The terbium monometallic complex, on the other hand, is nine coordinate with the ninth position taken up by a water molecule. This complex does not form a polymeric array presumably because the coordinated water molecule blocks self-assembly. Only methanol solutions of the Tb(III) complex gave an emission spectrum when irradiated at a wavelength associated with excitation of the hfa ligand. The intensity of these emission lines is inversely related to the temperature of the solution. Temperature-dependent decay curves of the excited Tb(III) complex suggest that thermal population of the hfa ligand triplet state by the Tb(III) emitting level leads to luminescent quenching.

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Supporting Information Available: Structural data as CIF files. This material is available free of charge via Internet at http://pubs.acs.org.

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