# Spectroscopically Distinct Geometrical Isomers in a Single Crystal. Characterization of the Eight-Coordinate Adducts of Tris(dipivaloylmethanato)lanthanide(III) with 2,9-Dimethyl-1,10-phenanthroline

**Richard C. Holz**[†] **and Larry C. Thompson***

Department of Chemistry, The University of Minnesota—Duluth, Duluth, Minnesota 55812

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Tris(dipivaloylmethanato)(2,9-dimethyl-1,10-phenanthroline)lanthanide(III), [Ln(DPM)$_3$·DMOP], complexes (Ln = La, Eu, Tb, Ho) were synthesized from [Ln(DPM)$_3$] and 2,9-dimethyl-1,10-phenanthroline in carbon tetrachloride. The Eu$^{3+}$ and Tb$^{3+}$ complexes were characterized spectroscopically by infrared and luminescence techniques. The luminescence spectra of the Eu$^{3+}$ and Tb$^{3+}$ adducts were recorded at 77 K. For Eu$^{3+}$, two transitions in the $^5D_0 \rightarrow {}^7F_0$ region are observed which are separated by an unprecedented 35 cm$^{-1}$. The $^5D_0 \rightarrow {}^7F_1$ and $^5D_0 \rightarrow {}^7F_2$ spectral regions contain six and eight bands, respectively, indicating two distinct Eu$^{3+}$ environments. The Eu$^{3+}$ luminescence spectrum indicates that both Eu$^{3+}$ environments have local site symmetry $C_1$. The crystal structure of [Eu(DPM)$_3$·DMOP] was solved by single-crystal X-ray diffraction methods. The complex was found to crystallize in the monoclinic space group $P2_1/n$ with $a$ = 13.941(7) Å, $b$ = 16.512(7) Å, $c$ = 21.626(9) Å, $\beta$ = 105.13(4)°, and $V$ = 4805.6 Å$^3$. Two geometrical isomers were found to exist in the unit cell with the ligating atoms forming an eight-coordinate distorted square antiprism. The two isomers differ only in the way the chelate rings span the lateral (l) and square (s) edges of a square antiprism with occupancy factors of 59 and 41%. The average Eu–O and Eu–N bond distances are 2.363 and 2.678 Å. X-ray crystallographic occupancy factors were determined for [La(DPM)$_3$·DMOP], [Tb(DPM)$_3$·DMOP], and [Ho(DPM)$_3$·DMOP], and each complex was found to crystallize in the monoclinic space group $P2_1/n$. For [La(DPM)$_3$·DMOP], $a$ = 14.083(4) Å, $b$ = 16.499(3) Å, $c$ = 21.746(9) Å, $\beta$ = 106.14(3)°, and $V$ = 4853.7 Å$^3$, for [Tb(DPM)$_3$·DMOP], $a$ = 13.897(7) Å, $b$ = 16.508(6) Å, $c$ = 21.621(5) Å, $\beta$ = 104.97(4)°, and $V$ = 4792.1 Å$^3$, and for [Ho(DPM)$_3$·DMOP], $a$ = 13.859(9) Å, $b$ = 16.539(5) Å, $c$ = 21.538(12) Å, $\beta$ = 104.78(5)°, and $V$ = 4773.5 Å$^3$. Each of these adducts contain isomers which exist in 57 to 43%, 58 to 42%, and 55 to 45% ratios for La$^{3+}$, Tb$^{3+}$, and Ho$^{3+}$, respectively. The isomer found more often in each case has all four chelate rings spanning the l edges of a square antiprism while the remaining isomer has two $\beta$-diketonate rings spanning s edges and a $\beta$-diketonate and a DMOP chelate ring spanning l edges.

## Introduction

Lanthanide shift reagents have been of considerable interest since the discovery by Hinckely,[1] in 1969, that an adduct of tris(dipivaloylmethanato)europium(III) ([Eu(DPM)$_3$]) caused large isotropic shifts in the proton NMR spectrum of cholesterol. Since that time, lanthanide shift reagents (particularly [Eu(DPM)$_3$] and [Eu(FOD)$_3$]) have been routinely used in NMR spectral characterizations.[2] It was postulated that steric constraints imposed by the bulky [Eu(DPM)$_3$] shift reagent limited the number of isomeric forms present in solution, thus allowing only a single set of dipolar-shifted resonances to be observed. However, several geometrical isomers are possible for complexes of this type, and if these isomeric forms rapidly interconvert in solution, their dipolar-shifted resonances would signal-average toward zero. In order to fully understand the properties of these geometrical isomers, their solid-state structures determined from both luminescence spectroscopy and X-ray crystallography are vitally important.

Europium(III) complexes of this type are typically quite luminescent, allowing the geometrical nature of the ligands about the metal ion to be obtained in both solution and solid states by luminescence spectroscopy.[3] Specifically, the $^5D_0 \rightarrow {}^7F_0$ emission band of Eu$^{3+}$ ($\lambda_{em} \sim 580$ nm) is of particular importance since neither level ($J = 0$) can be split by the ligand field. This demands that the resulting transition be a single band. Multiple environments for the Eu$^{3+}$ ion may cause more than one electronic transition to appear in the $^5D_0 \rightarrow {}^7F_0$ transition region. Since the remaining energy levels of Eu$^{3+}$ are degenerate, they will be split by the ligand field, depending on the metal ion environment. Consequently, the number of observed components in each luminescent region yields information about the symmetry and thus structure of the Eu$^{3+}$ site. However, the symmetry of many such compounds with large coordination numbers is low, resulting in complete removal of the degeneracy of specific energy levels.

The isolation of solid-state adducts of [Eu(DPM)$_3$] is considerably more straightforward than for those of [Eu(FOD)$_3$]; therefore, very few adducts of the latter have been structurally characterized.[4,5] For this reason, we recently undertook a study of the adducts of [Eu(DPM)$_3$] in which substantial steric requirements are imposed by additional chelate ligands in order to stabilize these isomeric forms. The majority of [Ln(DPM)$_3$] adducts which have been structurally characterized contain neutral oxygen or nitrogen donor ligands and have coordination numbers of 7 or 8.[3–6] However, at least one adduct (that with 2,2′,2″-terpyridine) is nine-coordinate.[7] In several complexes of this type more than one metal ion environment exists due to slightly different bond angles and distances. These differences are typically thought to be due to crystal packing forces and are generally small enough that the overall description of the coordination geometry is unaffected. In some cases, these multiple

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[†] Present address: Department of Chemistry, Utah State University, Logan, Utah.

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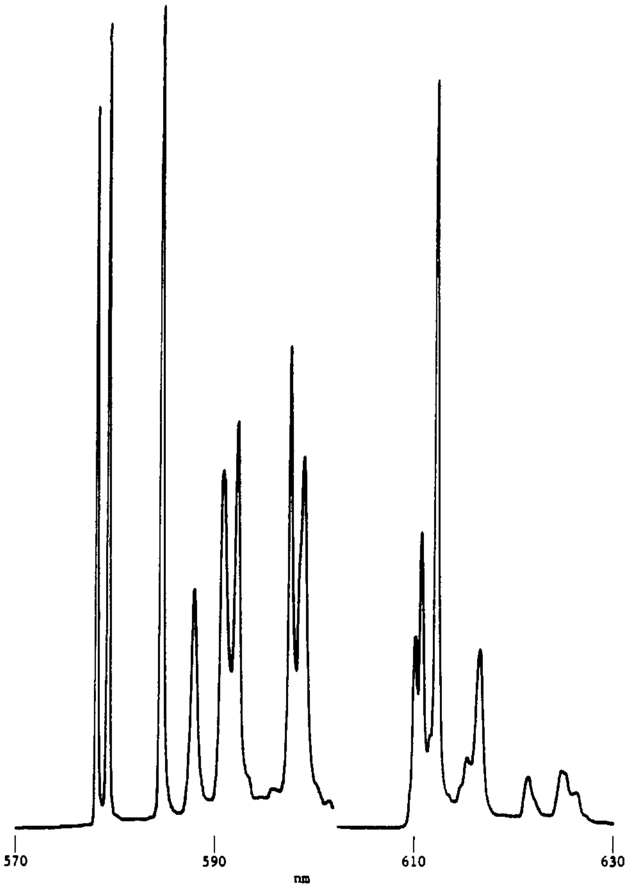

**Figure 1.** $Eu^{3+}$ luminescence spectrum of [Eu(DPM)$_3$·DMOP] for the $^5D_0 \rightarrow {}^7F_J$ ($J$ = 0–2) transition regions at 77 K.

$Eu^{3+}$ environments may be detected in their luminescence spectrum. Reported herein are the synthesis and spectroscopic and X-ray crystallographic characterization of several adducts of [Ln(DPM)$_3$] with 2,9-dimethyl-1,10-phenanthroline (Ln = La, Eu, Tb, Ho) in which two geometrical isomers exist in a single crystal.

## Experimental Section

**Materials.** Hydrated $Eu^{3+}$ and $Tb^{3+}$ nitrates (99.9%) were purchased from Research Chemicals Co. Dipivaloylmethane (98%) was purchased from Willow Brook Laboratories, Inc., while 2,9-dimethyl-1,10-phenanthroline (99%) and [La(DPM)$_3$] and [Ho(DPM)$_3$] were purchased from Aldrich Chemical Co. All other chemicals were either reagent grade or the purest commercially available.

**Preparation of [Ln(DPM)$_3$·DMOP].** The $Eu^{3+}$ and $Tb^{3+}$ (DPM)$_3$ complexes were prepared by the method of Eisentraut and Sievers, and the desired product was purified before use by sublimation under vacuum.[8] The title compounds were prepared analogously to the [Ln(DPM)$_3$·bipy] complexes reported by Selbin et al.[9] One millimole of [Ln(DPM)$_3$] and 1 mmol of 2,9-dimethyl-1,10-phenanthroline were mixed in the solvent carbon tetrachloride. Evaporation of the solvent and subsequent recrystallization of the solid from hexane gave the desired product. Suitable single crystals of each [Ln(DPM)$_3$·DMOP] complex were grown by slow evaporation of a concentrated hexane solution. The analytical purity of each complex was checked by elemental analysis (Galbraith Laboratories, Inc.). Anal. Calcd for $C_{47}H_{69}N_2O_6Eu$: C, 62.03; H, 7.58; N, 3.08. Found: C, 61.86; H, 7.65; N, 3.13 (mp 221–223 °C). Calcd for $C_{47}H_{69}N_2O_6Tb$: C, 61.56; H, 7.53; N, 3.05. Found: C, 61.70; H, 7.46; N, 3.11 (mp 209–210 °C). Calcd for $C_{47}H_{69}N_2O_6La$: C, 62.94; H, 7.69; N, 3.12. Found: C, 62.86; H, 7.68; N, 3.22 (mp 219–221 °C). (For $C_{47}H_{69}N_2O_6Ho$, mp = 188.5–190.5 °C.)

**Spectral Measurements.** Infrared spectra were obtained from KBr pellets with an IBM 32 series FT-IR spectrophotometer. Luminescence and excitation spectra were recorded using the apparatus previously described.[7] The McPherson RS-10 spectrophotometer was calibrated before use against the 435.84-nm emission line of a mercury lamp. The entrance and exit slits of the emission monochromator were routinely set at 100 μm, giving an instrumental resolution of 0.1 nm. The light source used in excitation measurements was a high-pressure 150-W xenon lamp connected to a Farrand high-voltage power supply and coupled to a Farrand Model 137880 monochromator with stepping motor. The Ferrand excitation source, when used, had entrance and exit slits typically set to give a band-pass of 1.0 nm.

**Table I.** Observed Transitions for Selected Regions of the Luminescence Spcetra of [Eu(DPM)$_3$·DMOP] and [Tb(DPM)$_3$·DMOP] at 77 K

| [Eu(DPM)$_3$DMOP] | | | [Tb(DPM)$_3$·DMOP] | | |
|---|---|---|---|---|---|
| | $\lambda_{max}$ (Å) | energy (cm$^{-1}$) | | $\lambda_{max}$ (Å) | energy (cm$^{-1}$) |
| $^5D_0 \rightarrow {}^7F_0$ | 5781.3 | 17 297 (A) | $^5D_4 \rightarrow {}^7F_5$ | 5397.5 | 18 527 |
| | 5793.0 | 17 262 (B) | | 5401.0 | 18 515 |
| | | | | 5407.4 | 18 493 |
| $^5D_0 \rightarrow {}^7F_1$ | 5846.0 | 17 106 (A) | | 5413.8 | 18 471 |
| | 5878.0 | 17 013 (B) | | 5416.1 | 18 464 |
| | 5907.3 | 16 928 (B) | | 5423 sh | 18 440 |
| | 5923.0 | 16 883 (A) | | 5425.5 | 18 432 |
| | 5975.4 | 16 735 (A) | | 5432.0 | 18 409 |
| | 5988.2 | 16 699 (B) | | 5438.6 | 18 387 |
| | | | | 5443.9 | 18 369 |
| $^5D_0 \rightarrow {}^7F_2$ | 6100.0 | 16 393 (B) | | 5460.9 | 18 312 |
| | 6107.0 | 16 375 (A) | | 5482.9 | 18 239 |
| | 6115 sh | 16 353 | | | |
| | 6122.4 | 16 333 (B) | $^5D_4 \rightarrow {}^7F_4$ | 5771.2 | 17 327 |
| | 6134 sh | 16 303 | | 5773.0 | 17 322 |
| | 6145 weak | 16 273 | | 5788.1 sh | 17 277 |
| | 6152.0 | 16 255 (A?) | | 5790.3 | 17 270 |
| | 6165.5 | 16 219 (B) | | 5801.2 | 17 238 |
| | | | | 5809.1 | 17 214 |
| | | | | 5813.5 | 17 201 |
| | | | | 5822.5 | 17 175 |
| | | | | 5828.5 | 17 157 |
| | | | | 5833.2 | 17 143 |
| | | | | 5838.6 | 17 127 |
| | | | | 5846.8 | 17 103 |
| | | | | 5859.7 | 17 066 |
| | | | | 5875.0 | 17 021 |
| | | | | 5887 sh | 16 987 |
| | | | | 5894.5 | 16 965 |
| | | | | 5900.2 sh | 16 949 |
| | | | | 5916.0 | 16 903 |
| | | | | 5933 sh | 16 855 |
| | | | | 5941 sh | 16 832 |
| | | | | 5956.5 | 16 788 |

Luminescence and excitation spectra were obtained from a single crystal or a polycrystalline sample placed in 3-mm quartz tubes immersed in a liquid-nitrogen dewar with a quartz tail. The exciting light was focused onto the sample, and the emitted light was collected at a 45° angle by a mirror which subsequently focused the light onto the entrance slit of the monochromator.

The excited-state lifetime studies and time-delay emission spectra were recorded by exciting the sample at 337 nm with a Photochemical Research Associates (PRA) pulsed nitrogen laser, Model LN1000. The signal was detected by an EMI 9558QB photomultiplier tube powered by a McPherson Model 751 dc power supply. The signal was amplified by an EMI model A1 amplifier and processed by a Stanford Research Systems, Inc., gated integrator boxcar averager. This electronics system consisted of two SR250 gated integrator and boxcar averagers, an SR280 mainframe power supply display module, an SR200 gate scanner, and an SR235 analog processor. A Hitachi oscilloscope, model V-355, was used to position the signal detection window (gate) over the portion of the signal after laser excitation had occurred.

**X-ray Data Collection.** Single crystals of the $La^{3+}$, $Eu^{3+}$, $Tb^{3+}$, and $Ho^{3+}$ adducts were each mounted in a capillary and placed on an Enraf-Nonius CAD4 diffractometer. The structure determinations were carried out in the X-ray diffraction laboratory of the Department of Chemistry at the University of Minnesota, Twin Cities, and the structures were solved by standard Patterson and Fourier techniques in a manner analogous

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**Table II.** Crystal Structure Parameters for [Ln(DPM)$_3$·DMOP] Complexes

| | Ln | | | |
|---|---|---|---|---|
| | La | Eu | Tb | Ho |
| empirical formula | $LaC_{47}H_{69}N_2O_6$ | $EuC_{47}H_{69}N_2O_6$ | $TbC_{47}H_{69}N_2O_6$ | $HoC_{47}H_{69}N_2O_6$ |
| fw | 896.98 | 910.04 | 917.01 | 923.02 |
| $a$ (Å) | 14.083(4) | 13.941(7) | 13.897(7) | 13.859(9) |
| $b$ (Å) | 16.499(3) | 16.512(7) | 16.508(6) | 16.539(5) |
| $c$ (Å) | 21.746(9) | 21.626(9) | 21.621(5) | 21.538(12) |
| $\alpha$ (deg) | 90 | 90 | 90 | 90 |
| $\beta$ (deg) | 106.14(3) | 105.13(4) | 104.97(6) | 104.78(5) |
| $\gamma$ (deg) | 90 | 90 | 90 | 90 |
| $V$ (Å$^3$) | 4853.7 | 4805.6 | 4792.1 | 4773.5 |
| space group | $P2_1/n$ (No. 14) | $P2_1/n$ (No. 14) | $P2_1/n$ (No. 14) | $P2_1/n$ (No. 14) |
| $Z$ | 4 | 4 | 4 | 4 |
| $D_{calc}$ (g cm$^{-3}$) | 1.227 | 1.258 | 1.271 | 1.284 |
| $\mu$ (cm$^{-1}$) | 9.2 | 13.5 | 15.3 | 17.194 |
| $\lambda_{Mo\ K\alpha}$ (Å) | 0.710 69 | 0.710 69 | 0.710 69 | 0.710 69 |
| temp (°C) | 25 | 25 | 25 | 24 |
| residuals:[a] $R$, $R_w$ | 0.053, 0.069 | 0.061, 0.063 | 0.085, 0.077 | 0.082, 0.090 |

[a] $R = \sum||F_o| - |F_c||/\sum|F_o|$; $R_w = [(\sum w(|F_o| - |F_c|)^2/\sum wF_o^2)]^{1/2}$.

**Table III.** Relevant Distances and Angles for [Eu(DPM)$_3$·DMOP][a]

| | | | |
|---|---|---|---|
| Eu···N1A | 2.682(7) | Eu···O1CE | 2.333(5) |
| Eu···N2A | 2.673(6) | Eu···O2CF | 2.363(6) |
| Eu···O1B | 2.354(6) | Eu···O1DF | 2.354(6) |
| Eu···O2B | 2.408(5) | Eu···O2DE | 2.367(6) |
| N1A–Eu–N2A | 62.2(2) | N2A–Eu–O1B | 122.8(2) |
| N1A–Eu–O1B | 81.8(2) | N2A–Eu–O2B | 65.7(2) |
| N1A–Eu–O2B | 86.9(2) | N2A–Eu–O1CE | 155.9(2) |
| N1A–Eu–O1CE | 112.5(2) | N2A–Eu–O2CF | 118.0(2) |
| N1A–Eu–O2CF | 159.0(2) | N2A–Eu–O1D | 83.3(2) |
| N1A–Eu–O1DF | 126.2(2) | N2A–Eu–O2D | 84.0(2) |
| N1A–Eu–O2DE | 64.8(2) | O2B–Eu–O1DF | 116.4(2) |
| O1B–Eu–O2B | 69.6(2) | O2B–Eu–O2DE | 146.1(2) |
| O1B–Eu–O1CE | 76.9(2) | O1CE–Eu–O2CF | 75.7(2) |
| O1B–Eu–O2CF | 81.5(2) | O1CE–Eu–O1DF | 82.4(2) |
| O1B–Eu–O1DF | 150.3(2) | O1CE–Eu–O2DE | 73.2(2) |
| O1B–Eu–O2DE | 120.5(2) | O2CF–Eu–O2DF | 72.8(2) |
| O2B–Eu–O1CE | 138.4(2) | O2CF–Eu–O2DE | 135.4(2) |
| O2B–Eu–O2CF | 75.4(2) | O1DF–Eu–O2DE | 72.1(2) |

[a] All distances are in angstroms, and all angles are in degrees. For labels, see ORTEP drawings.

to that previously reported by Britton and Chow and references therein.[10] The crystallographic parameters of each compound are listed in Table II.

## Results and Discussion

**Infrared Spectra.** The infrared spectrum of each adduct was recorded to determine if both nitrogen atoms of the nitrogen donor ligand were bound, thus forming eight-coordinate complexes. Because of the steric constraints imposed by the *tert*-butyl groups of the $\beta$-diketonate ligands and the methyl groups in the 2- and 9-positions of the donor ligand, it was speculated that the DMOP ligand might not coordinate to the metal ion. The infrared spectra of all of these complexes contained the characteristic "breathing" vibrations at approximately 1025 cm$^{-1}$.[11,12] These data indicate that DMOP does indeed coordinate to the metal ion directly, forming eight-coordinate complexes.

**Luminescence Spectra.** The luminescence spectrum of [Eu(DPM)$_3$·DMOP] was recorded at 77 K for both a polycrystaline sample and a single crystal. Both samples provided identical spectra. The Eu$^{3+}$ luminescence spectrum of the $^5D_0 \rightarrow {}^7F_J$ ($J$ = 0–2) transitions is shown in Figure 1 with the observed transition frequencies for each spectral region being given in Table I. The luminescence spectrum contains strong emission from the $^5D_0$ level, but emission bands originating from the $^5D_1$ level are absent.

Excitation of Eu$^{3+}$ complexes at 337 nm typically occurs by an intramolecular energy-transfer process from a ligand triplet state to an upper level of the Eu$^{3+}$ energy manifold.[13] Since Eu$^{3+}$ emission is observed only from the $^5D_0$ state, the $^5D_1$ level must be higher in energy than the ligand triplet level, allowing only emission from the $^5D_0$ level to occur. Furthermore, the $^5D_0 \rightarrow {}^7F_2$ electric dipole transitions are substantially more intense than the $^5D_0 \rightarrow {}^7F_1$ magnetic dipole transitions, indicating Eu$^{3+}$ ions in environments with lowered symmetry. The remaining transitions, which terminate on the higher components of the ground ($^7F_J$) manifold, are still weaker.

The maximum number of electronic transitions that can be observed in the $^5D_0 \rightarrow {}^7F_0$, $^5D_0 \rightarrow {}^7F_1$, and $^5D_0 \rightarrow {}^7F_2$ spectral regions of Eu$^{3+}$ are 1, 3, and 5, respectively. Since more bands are observed in the Eu$^{3+}$ luminescence spectrum than are theoretically allowed, we prepared the [Tb(DPM)$_3$·DMOP] adduct and measured its luminescence spectrum at 77 K from 450 to 750 nm. Samples of Eu$^{3+}$ of even 99.9% purity (based on rare earth content) occasionally contain small amounts of Tb$^{3+}$ impurities, which luminesce in some of the same regions as Eu$^{3+}$. The observed transition frequencies in the [Tb(DPM)$_3$·DMOP] luminescence spectrum at 77 K in the $^5D_4 \rightarrow {}^7F_J$ ($J$ = 5, 4) regions are listed in Table I. None of the observed transitions in the Tb$^{3+}$ spectrum corresponded to any transitions in the Eu$^{3+}$ luminescence spectrum. Therefore, the extra bands observed in the Eu$^{3+}$ luminescence spectrum are not due to a Tb$^{3+}$ impurity.

The $^5D_0 \rightarrow {}^7F_0$ spectral region of the Eu$^{3+}$ luminescence spectrum contains two bands at 17 297 (A) and 17 262 (B) cm$^{-1}$ which are separated by an unprecedented 35 cm$^{-1}$ at 77 K. Although the peaks are broadened somewhat at room temperature and their relative intensities change, they are still easily resolved with a separation of 36 cm$^{-1}$. Examination of the [Eu(DPM)$_3$·DMOP] spectrum reveals that in each region the number of observed transitions is twice that theoretically allowed. The existence of two bands in the $^5D_0 \rightarrow {}^7F_0$ region, coupled with the elemental analyses and the Tb$^{3+}$ luminescence spectrum of this adduct, suggests that the Eu$^{3+}$ ions exist in two distinct environments.

The excited-state lifetime of each observed band in the $^5D_0 \rightarrow {}^7F_{0,1,2}$ spectral regions of Eu$^{3+}$ was recorded at 77 K in order to establish the emitting species from which it originates. Two different lifetimes were found which had average values of 880 ± 20 and 480 ± 20 μs for chelates A and B, respectively. The excited-state lifetime of the $^5D_4$ state of [Tb(DPM)$_3$·DMOP] was determined to be 780 ± 20 μs from two components of the $^5D_4 \rightarrow {}^7F_5$ transition. These data are further conformation that

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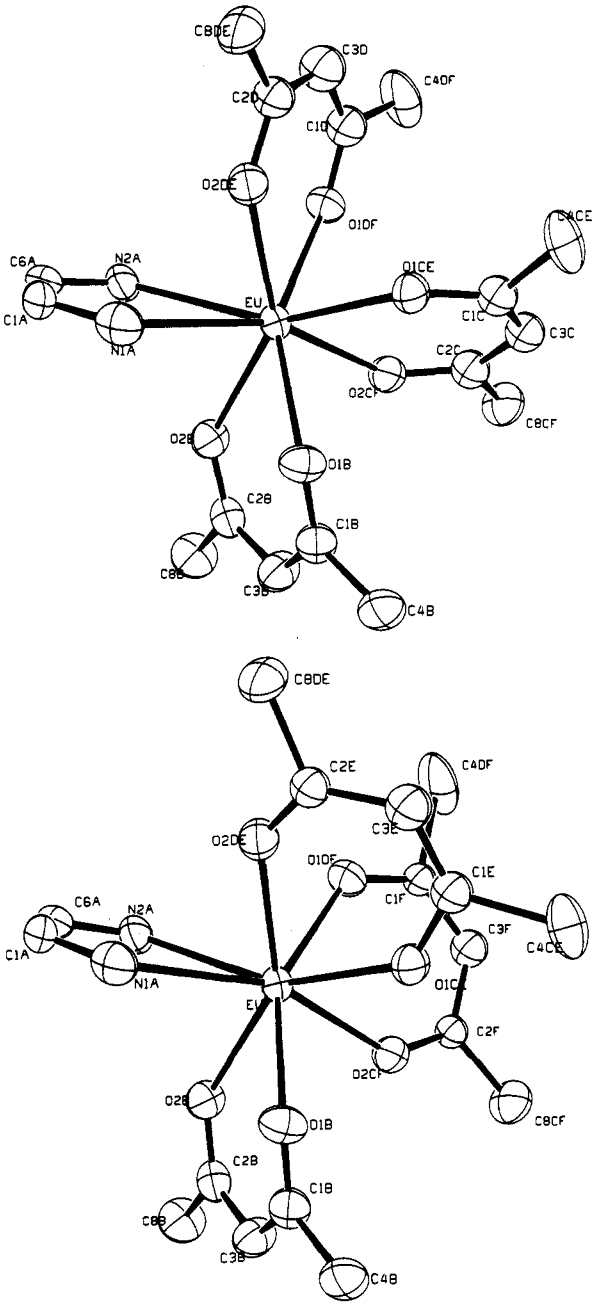

**Figure 2.** ORTEP drawings of both geometrical isomers of $[Eu(DPM)_3\cdot DMOP]$: (top) the more abundant isomer (59%); (bottom) the less abundant isomer (41%). The hydrogen atoms and DPM methyl groups as well as most of the carbons of the DMOP ligand have been omitted for clarity.

none of the bands observed in the $Eu^{3+}$ spectrum originated from a $Tb^{3+}$ impurity. (The possibility of transitions originating from the $^5D_1$ state of $Eu^{3+}$ is further eliminated since the lifetime of the $^5D_1$ state would be much shorter than either observed value.) A $Eu^{3+}$ luminescence spectrum was also run with the gated luminescence delay time set at 2 ms. Such a gated experiment causes the bands in the luminescence spectrum with the shorter excited-state lifetimes to decrease in intensity or to disappear from the spectrum altogether relative to bands which originate from levels possessing longer excited-state lifetimes. The gated $Eu^{3+}$ luminescence spectrum of $[Eu(DPM)_3\cdot DMOP]$ exhibited this type of behavior, allowing accurate assignments of each band to its respective isomeric emitter.

The number of bands observed in each spectral region provides a measure of the local symmetry about the $Eu^{3+}$ ion. The idealized symmetry of a square antiprism is $D_{4d}$ and of a dodecahedron is $D_{2d}$. Since all the ligating atoms of $[Eu(DPM)_3\cdot DMOP]$ are not identical, the highest possible symmetry about the metal center of either geometry would be $C_2$. When the chelate rings and the possible sterically-induced geometrical distortions are included, the symmetry about the $Eu^{3+}$ ion would be reduced to $C_1$ for each isomer. The luminescence spectrum is consistent with this assignment, suggesting the presence of two distinct emitting metal centers which reside in low-symmetry environments.

Energy changes of the $^7F_0 \rightarrow {}^5D_0$ excitation band (or the $^7F_0 \rightarrow {}^5D_0$ emission band) observed for various complexes have been studied extensively.[14] For many of the complexes studied there is more than one band which usually can be attributed to two different emitting species. These species can typically be distinguished by different coordination numbers and/or types of ligating atoms. These differences in the $^7F_0 \rightarrow {}^5D_0$ transition frequencies were reported by Albin and Horrocks to be a function of the interelectronic repulsion parameters of the ion, and any change in its energy was regarded as a nephelauxetic effect.[14] It was suggested that as the total negative charge of the ligands increases, the interelectronic repulsion parameters decrease, thus decreasing the separation of the two terms, assuming a relatively minor covalency contribution to the overall bonding. Transition frequencies taken at room temperature for 36 different compounds in both the solid and solution states were used to derive this correlation. The transition frequencies ranged from 17 275 to 17 226 $cm^{-1}$ (49 $cm^{-1}$), covering total ligand charges from 0 to −6, respectively.

In agreement with the emission spectrum, the excitation spectrum of a polycrystalline sample of $[Eu(DPM)_3\cdot DMOP]$ has two bands in the $^7F_0 \rightarrow {}^5D_0$ region which are located at 17 313 $cm^{-1}$ (chelate A) and 17 277 $cm^{-1}$ (chelate B), a difference of 36 $cm^{-1}$ at room temperature. Since neither transition falls within the range reported by Albin and Horrocks, a total charge for the bound ligands cannot be predicted by this correlation. However, the known value of the total change of the bound ligands is −3. Several other parameters besides the nephelauxetic effect may contribute to the observed shift of this transition. These parameters may well be related to those features reflected in the Racah parameters, such as the length of the metal–ligand bond, ligating atom type, coordination number, and/or geometry. That this difference is not simply due to some unique feature of the DPM ligand is shown by the fact that the $^5D_0 \rightarrow {}^7F_0$ transition of $[Eu(DPM)_3\cdot terpy]$ satisfactorily fits the correlation.[7]

The two distinct emission bands in the $^5D_0 \rightarrow {}^7F_0$ spectral region of $[Eu(DPM)_3\cdot DMOP]$ are separated by an unprecedented 35 $cm^{-1}$ at 77 K. No other $Eu^{3+}$ complex in the solid or solution state exhibits such a separation. These two species are attributed to two distinct isomeric forms in the crystal lattice. (Similarly large differences of 30–40 $cm^{-1}$ have been found for some marocyclic complexes with europium nitrate.[15] However, in these cases it is clear that one of the $Eu^{3+}$ ions is complexed to the macrocycle and another is bound to nitrate ion as either $Eu(NO_3)_6^{3-}$ or $Eu(NO_3)_5^{2-}$. This situation is quite different from that in $[Eu(DPM)_3\cdot DMOP]$, for which there is no reason to suspect that the two $Eu^{3+}$ ions have different chemical environments). To the best of our knowledge, only in the case of the solid-state tris(2,2′,2″-terpyridyl)europium(III) perchlorate, has such a large separation in the $^5D_0 \rightarrow {}^7F_0$ transition frequencies been observed.[16] In that study, two bands were observed at 17 240 and 17 218 $cm^{-1}$ (a separation of 22 $cm^{-1}$); however, these transitions were attributed to an eight- and a nine-coordinate species, respectively. Several aqueous systems are known to exhibit more than one $^7F_0 \rightarrow {}^5D_0$ transition, but in each case the energy difference is less than 35 $cm^{-1}$ and they are usually attributable to different stoichiometric ratios of metal and ligand,

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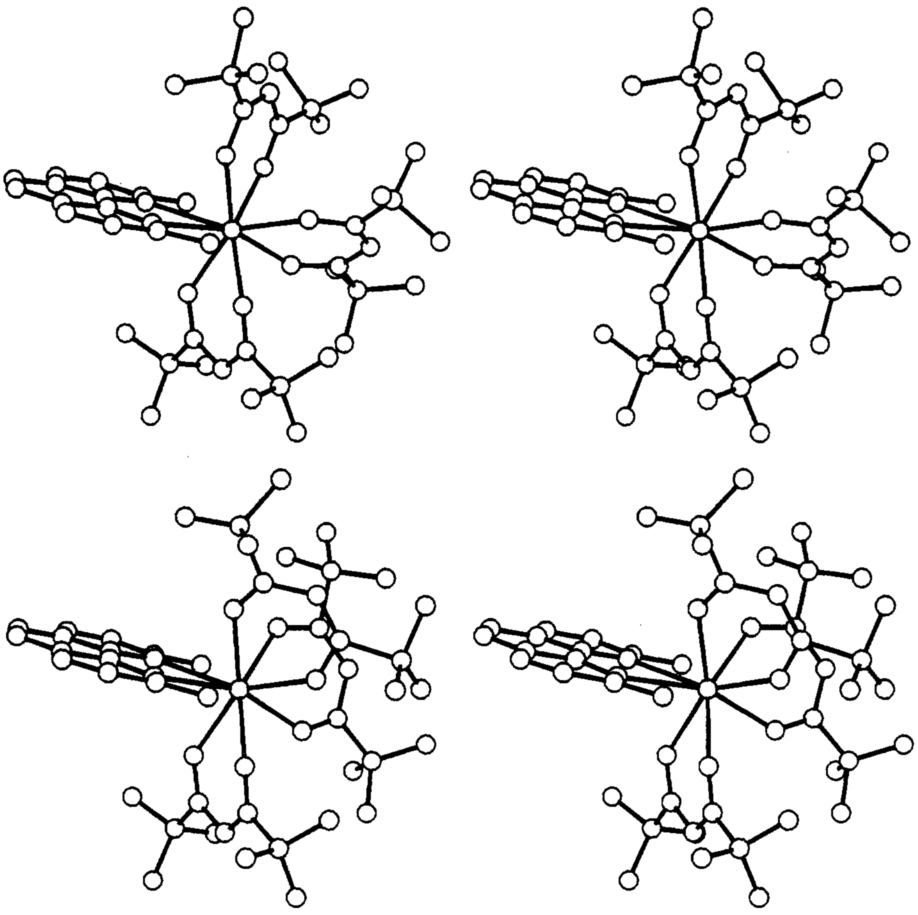

**Figure 3.** Stereoviews of the molecular structure of both geometrical isomers of [Eu(DPM)$_3$·DMOP]: (top) the more abundant isomer (59%); (bottom) the less abundant isomer (41%). The hydrogen atoms have been omitted for clarity.

or different coordination, numbers of a single ligand. For example, three ${}^7F_0 \to {}^5D_0$ bands are observed when Eu$^{3+}$ is mixed in aqueous solution with varying concentrations of dipicolinic acid.[17] In this case, the 1:1 and 1:3 metal–ligand complexes exhibit transition frequencies which differ by 32 cm$^{-1}$. Two bands have also been observed for [EuEDTA]$^-$ which differ by 15 cm$^{-1}$ and have been reported to be due to an equilibrium between an eight- and a nine-coordinate species or a 1:1 and 1:2 metal–ligand complex.[18–20]

**X-ray Crystallographic Studies.** In order to confirm that two isomeric, low-symmetry, eight-coordinate metal centers exist in the crystal lattice of [Eu(DPM)$_3$·DMOP] and to determine to what extent they differ to cause such a large difference in the ${}^5D_0 \to {}^7F_0$ transition frequencies, the solid-state structure was determined. The crystallographic parameters for [Eu(DPM)$_3$·DMOP] are listed in Table II, and selected bond distances and angles are presented in Table III, with the ORTEP drawings and stereoviews of the molecular structure of each isomer given in Figures 2 and 3, respectively.[21] The results indicate that both the Eu$^{3+}$ ions are eight-coordinate with the positions of the bonded atoms approximating a square antiprism. The unit cell does indeed contain two isomers which differ *only in the way in which the chelate rings span the lateral* (*l*) *and square* (*s*) *edges of the antiprism*. These two isomers exist in a 59 to 41% ratio. The isomer found to occupy 59% of the lattice sites has all four chelating rings spanning the l edges of the antiprism while the isomer filling the remaining 41% of the lattice sites has two $\beta$–diketonate rings spanning s edges and a $\beta$-diketonate and a DMOP chelate ring spanning l edges (Figures 2 and 3).

The average Eu–O and Eu–N distances for the Eu$^{3+}$ ions are 2.363 and 2.678 Å, respectively. The average Eu–N bond distances of [Eu(DPM)$_3$·DMOP] are significantly longer than any previously reported Eu–N distances for eight-coordinate complexes. For example, compare the following average Eu–N bond distances: for [Eu(DBM)$_3$·*o*-phen] (DBM = dibenzoylmethanate), 2.642 Å;[22] for [Eu(AcAc)$_3$·*o*-phen] (AcAc = acetylacetonate), 2.643 Å;[23] for [Eu(DPM)$_3$·*o*-phen], 2.616 Å;[24] and for [Eu(DPM)$_3$(Py)$_2$] (Py = pyridine), 2.649 Å.[25] These data suggest that the tert-butyl groups on the DPM ligands interact in a steric fashion with the methyl groups on the *o*-phenanthroline ligand, causing the Eu–N bond distances to be elongated. If crystal packing forces were a major contributor to the formation of these isomeric forms, notable differences in bond distances and angles should be observed similar to those reported by Cunningham and Sievers for the two isomers of [Eu(DPM)$_3$(DMF)$_2$].[26,27]

In order to determine whether this structural motif exists across the lanthanide series, the occupancy factors were determined by X-ray crystallography for the La$^{3+}$, Tb$^{3+}$, and Ho$^{3+}$ adducts. The crystallographic parameters for [La(DPM)$_3$·DMOP], [Tb(DPM)$_3$·DMOP], and [Ho(DPM)$_3$·DMPO] are listed in Table

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II. All of these adducts exhibit structures similar to that of the $Eu^{3+}$ complex, in that two isomers are present in the crystal lattice. The two isomers of the $La^{3+}$, $Tb^{3+}$, and $Ho^{3+}$ adducts exist in 57 to 43%, 58 to 42%, and 55 to 45% ratios, respectively. The isomerfound most often exhibits the same structure as the more prevalent isomer of the $Eu^{3+}$ adduct. These data indicate that the isomeric nature of complexes of this type exists across the lanthanide series.

Only one other instance of isomeric lanthanide complexes coexisting in a single crystal has been reported.[28] Two geometrical isomers of $[Nd(TFA)_3(H_2O)_2]$ (TFA = ((trifluoromethyl)acetyl)-acetonate) were reported to coexist in the crystal lattice in a 74 to 26% ratio. The chelate rings in this case, similarly to those of the $[Ln(DPM)_3{\cdot}DMOP]$ complexes, span the m and g edges of a slightly deformed dodecahedron in different ways. The bond angles and distances of both of these isomers were also indistinguishable. Interestingly, the isomeric forms of $[La(TFA)_3(H_2O)_2]$ were not observed in solution by NMR. A similar NMR experiment for a toluene solution of $[La(DPM)_3{\cdot}DMOP]$ resulted in sample bleaching and decomposition. Decomposition also occurred when we attempted to record a luminescence spectrum of a toluene solution of $[Eu(DPM)_3{\cdot}DMOP]$. These data are not surprising when one considers the strong steric interactions between the methyl groups of the DMOP ligand and the *tert*-butyl groups of the DPM ligands. These results further support the idea that steric effects are the principal contributor to isomeric formation with lesser contributions from crystal packing forces.

## Conclusion

Two of the four possible geometrical isomers for the adducts of $[Ln(DPM)_3]$ with an additional bidentate ligand were found in a single crystal.[2] These isomers were spectroscopically and crystallographically characterized. The isomerization was attributed to steric interactions between the *tert*-butyl groups of DPM and the methyl groups of DMOP. The luminescence spectrum of the $Eu^{3+}$ adduct contained two bands in the nondegenerate $^5D_0 \rightarrow {}^7F_0$ spectral region which were separated by an unprecedented 35 $cm^{-1}$. These data indicated that markedly different electronic environments exist for two of the possible four geometrical isomers which must be considered when such isomeric forms are possible with lanthanide shift reagents.

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**Supplementary Material Available:** Listings of thermal parameters, positional parameters, bond distances, bond angles, least-squares planes, and data pertaining to the trial structure analysis (16 pages). Ordering information is given on any current masthead page.

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