suggests that packing forces may have a significant influence on the Sn–E–Sn angle and also indicates how easily this angle is deformed. There are no intermolecular contacts, involving either Sn or the chalcogen atoms, within van der Waals distances.

Acknowledgment. F.W.B.E. and C.H.W.J wish to acknowledge that this work was supported by grants from the Natural Sciences and Engineering Research Council of Canada.

Registry No. $(((CH_3)_3C)_3Sn)_2Te$, 117680-22-5; $(((CH_3)_3C)_3Sn)_2Se$, 117680-23-6; $(((CH_3)_3C)_3Sn)_2S$, 112164-30-4.

Supplementary Material Available: Tables of crystallographic experimental and structure refinement data, hydrogen atom coordinates and temperature factors, anisotropic temperature factors for the non-hydrogen atoms, C–C bond distances, and Sn–C–C and C–C–C bond angles (11 pages); tables of observed and calculated structure factors (64 pages). Ordering information is given on any current masthead page.

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Spectroscopic and Structural Characterization of the Nine-Coordinate Adduct of Tris(dipivaloylmethanato)europium(III) with 2,2′:6′,2″-Terpyridine

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Received April 21, 1988

Tris(dipivaloylmethanato)(2,2′:6′,2″-terpyridine)europium(III), $[Eu(DPM)_3terpy]$, was synthesized from $[Eu(DPM)_3]$ and 2,2′:6′,2″-terpyridine in carbon tetrachloride. The complex was characterized by infrared and luminescence spectroscopy. The infrared spectrum indicated all three nitrogen atoms of the terpyridine ligand were bound to the metal ion. The luminescence spectrum was recorded at 77 K and revealed a broad (15 cm^{-1}) unresolvable single transition in the $^5D_0 \rightarrow {}^7F_0$ region. The $^5D_0 \rightarrow {}^7F_1$ region contained six bands and the $^5D_0 \rightarrow {}^7F_2$ region contained nine bands, indicating two distinct emitting metal centers. The luminescence spectrum suggested that the site symmetry of both metal centers is C_1. The structure of $[Eu(DPM)_3terpy]$ was solved by single-crystal X-ray diffraction methods. The complex was found to crystallize in the monoclinic space group $P2_1/a$ with $a = 18.487$ (6) Å, $b = 28.175$ (7) Å, $c = 19.434$ (10) Å, $\beta = 91.57$ (3)°, and $V = 10118.8$ Å^3. Two isomers were found to exist in the unit cell with the ligating atoms forming a nine-coordinate distorted tricapped trigonal prism with each metal center. The two isomers differ by only small variations in bond angles and distances due to steric effects. The average Eu–O and Eu–N bond distances are 2.380 and 2.645 Å for the first Eu(III) ion and 2.385 and 2.663 Å for the second Eu(III) ion. The site symmetry of both metal centers is C_1, which is consistent with the luminescence spectrum.

Introduction

Many lanthanide(III) complexes have been studied extensively because of their highly efficient luminescence and lasing ability.[1] The great majority of these contain oxygen or nitrogen donor ligands, and spectroscopic measurements have been used to determine the symmetry, coordination number, dissociation constants, number of bound water molecules, excited-state lifetimes, metal-metal distances (from energy transfer), number of distinct metal environments, and bonding nature of the ligands.[2]

The lanthanide(III) ion most suited for this type of study is the Eu(III) ion because of its nondegenerate ground ($^7F_0$) and first excited ($^5D_0$) states. Since $J = 0$ for both states, neither level can be split by the crystal field, so any subsequent emission from the excited state to the ground state would result in a single electronic transition for each distinct Eu(III) environment. The other energy levels are degenerate and will be split into the various Stark components depending on the symmetry of the crystal field about the metal center. The electronic transitions that occur among these levels are determined by the selection rules appropriate to the crystal field that is present, and as a result, the symmetry about the metal ion can be deduced.[3]

Since the discovery by Hinckley[4] in 1969 that the lanthanide chelate complex tris(dipivaloylmethanato)europium(III) ($[Eu(DPM)_3]$) acted as an NMR shift reagent, the structural features of adducts of this complex have been of great interest. Several adducts of $[Eu(DPM)_3]$ have been synthesized and their properties in the solid and solution states studied.[5,6] Many of these complexes contain neutral nitrogen donor ligands with coordination numbers of 7 or 8. Since the β-diketone ligand DPM contains large, bulky *tert*-butyl groups, adducts of $[Eu(DPM)_3]$ with coordination numbers greater than 8 have never been reported even though other nine-coordinate complexes with β-diketone ligands have been synthesized, specifically $[(facam)_3Pr(DMF)_3Pr(facam)_3]$[7] (facam = 3-(trifluoroacetyl)-*d*-camphorato), $[Eu(TTFA)_3terpy]$[8] (TTFA = thenoyltrifluoroacetonato), and $[Eu(DBM)_3terpy]$[8] (DBM = dibenzoylmethanato). The last two complexes contain the neutral nitrogen donor ligand 2,2′:6′,2″-terpyridine. Because terpyridine is a planar ligand with some flexibility, the steric effects between terpyridine and DPM were expected to be small enough to permit complexation. The synthesis of the first nine-coordinate adduct of $[Eu(DPM)_3]$ with terpyridine and its characterization by spectroscopic methods and X-ray crystallography are reported here.

Experimental Section

Materials. All the reagents required for this work were used without further purification. Hydrated europium nitrate (99.9%) was purchased from the Research Chemicals Co. Dipivaloylmethane (98%) was purchased from Willow Brook Laboratories, Inc., and 2,2′:6′,2″-terpyridine (98%) was purchased from the Aldrich Chemical Co.

Preparation of $[Eu(DPM)_3terpy]$. $[Eu(DPM)_3]$ was prepared by the method of Eisentraut and Sievers, and the desired product was purified before use by sublimation under vacuum.[9] The title compound was

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Table I. Crystallographic Data for [Eu(DPM)$_3$terpy]

chem formula:	space group: $P2_1/a$ (No. 14)
$EuC_{48}H_{68}N_3O_6$	$T = 23$ °C
fw: 935.03	$\lambda = 0.71069$ Å
$a = 18.487$ (6) Å	$\rho_{calcd} = 1.229$ g cm^{-3}
$b = 28.175$ (7) Å	$\mu = 12.83$ cm^{-1}
$c = 19.434$ (10) Å	transmission coeff (rel) =
$\beta = 91.57$ (3)°	0.928–0.955
$V = 10118.8$ Å^3	$R(F_o) = 0.047$
$Z = 8$	$R_w(F_o) = 0.063$

prepared in a manner analogous to that for the [Eu(DPM)$_3$bpy] complex reported by Selbin et al.[10] One millimole of [Eu(DPM)$_3$] and 1 mmol of 2,2′:6′,2″-terpyridine 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 were grown by slow evaporation of a concentrated hexane solution. The purity was checked analytically by elemental analysis by Galbraith Laboratories, Inc. Anal. Calcd for $C_{48}H_{68}N_3O_6Eu$: C, 61.65; H, 7.33; N, 4.49. Found: C, 61.43; H, 7.64; N, 4.44.

Spectral Measurements. An infrared spectrum was obtained from a Nujol mull with a Perkin-Elmer 781 infrared spectrophotometer. Luminescence and excitation spectra were recorded on a McPherson RS-10 spectrophotometer, which consists of a Model 2051 1-m scanning monochromator, a Model 608 prism predisperser attachment, a Model 713 xenon lamp power supply, a Model 606 fluorescence attachment containing a 100-W high-pressure mercury lamp, and a Hewlett-Packard Model 7127A strip chart recorder. The photon-counting detection system consisted of a Products for Research Inc. thermoelectrically cooled detector housing with an RCA-C31034 photomultiplier tube and a SPEX DPC-2 digital photometer. 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 137880 monochromator with stepping motor.

The RS-10 spectrophotometer was calibrated before use against the 4358.35-Å 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 1 Å. The Farrand excitation source, when used, had entrance and exit slits typically set to give a band-pass of 10 Å.

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

The lifetime of the $^5D_0$ state was determined by exciting the sample with a pulsed PRA LN1000 nitrogen laser (337 nm) while the emission from each band in the $^5D_0 \rightarrow {}^7F_1$ spectral region was monitored. The signal was detected by an EMI 9558QB photomultiplier tube and processed with a Stanford Research Systems, Inc., gated integrator boxcar averager.

X-ray Data Collection. A single crystal was mounted in a capillary and placed on an Enraf-Nonius CAD4 diffractometer. The structure determination was carried out in the X-ray diffraction laboratory of the Department of Chemistry at the University of Minnesota, and the structure was solved by standard Patterson and Fourier techniques in an manner analogous to that previously reported by Britton and Chow and references therein.[11] The crystallographic parameters for the title compound are listed in Table I.

Results and Discussion

The infrared spectrum of the [Eu(DPM)$_3$terpy] complex was recorded initially to determine if all three nitrogen atoms of the terpyridine ligand were bound, thus making the complex nine-coordinate. The possibility exists for only two nitrogen atoms to be bound to the metal ion due to the steric hindrance of the *tert*-butyl groups on each end of the β-diketone ligands. The infrared spectrum contained the characteristic "breathing" vibration at approximately 1020 cm^{-1}, indicating a coordinated terpyridine, whereas the band at 988 cm^{-1} for an uncomplexed ligand was absent.[12,13] These results suggest that all three nitrogen atoms of the terpyridine ligand are indeed bound to the metal ion, indicating that the complex is nine-coordinate.

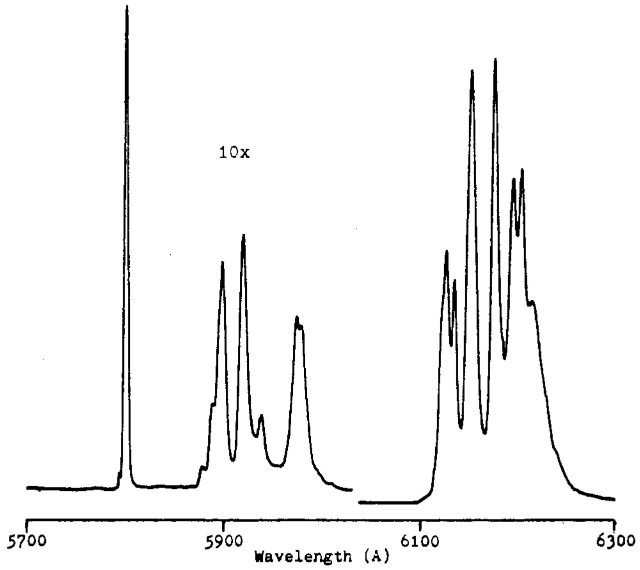

Figure 1. Luminescence spectrum of [Eu(DPM)$_3$terpy].

Table II. Observed Transitions in the Luminescence Spectrum of [Eu(DPM)$_3$terpy]

	λ, Å	E, cm^{-1}		λ, Å	E, cm^{-1}
$^5D_0 \rightarrow {}^7F_0$	5800.8	17239	$^5D_0 \rightarrow {}^7F_2$	6124.2	16329
$^5D_0 \rightarrow {}^7F_1$	5887.9	16984		6127.6	16320
	5897.4	16957		6136.1	16297
	5919.0	16895		6152.9	16252
	5937.6	16842		6176.9	16189
	5974.0	16739		6195.7	16140
	5978.9	16725		6204.6	16117
				6214.5	16091
				6241.1	16023

The luminescence spectrum (Figure 1), obtained from a single crystal of [Eu(DPM)$_3$terpy] at 77 K, is consistent with a low-symmetry environment around the metal ion. The luminescence spectrum contains strong emission from the $^5D_0$ level but only weak emission from the $^5D_1$ level. The electric dipole transition $^5D_0 \rightarrow {}^7F_2$ is also much more intense than the magnetic dipole transition $^5D_0 \rightarrow {}^7F_1$, while the remaining transitions, which terminate on the higher components of the ground state (^7F_J), are still weaker. The energies of the $^5D_0 \rightarrow {}^7F_J$ (J = 0, 1, 2) transitions are given in Table II.

The $^5D_0 \rightarrow {}^7F_0$ transition at 77 K is a single line at 17239 cm^{-1}, but its width at half-height is somewhat broader (15 cm^{-1}) than is often found in similar compounds, which have typical widths of 5 cm^{-1}. The observed broadening of this band may well be indicative of two closely spaced lines, suggesting more than one distinct emitting metal center in the crystal lattice. The excitation spectrum obtained at 77 K from a polycrystalline sample also contains a single broad line in the $^7F_0 \rightarrow {}^5D_0$ region consistent with the luminescence spectrum. A recently reported correlation by Albin and Horrocks[14] suggests that the position of the $^7F_0 \rightarrow {}^5D_0$ transition at room temperature shifts to longer wavelengths as the total negative charge on the ligands increases. The $^5D_0 \rightarrow {}^7F_0$ transition of [Eu(DPM)$_3$terpy] at room temperature is 17254 cm^{-1}, which would predict, from the Albin and Horrocks correlation, a total charge for the bound ligands of −3.7 ± 1.0. The actual total charge of the bound ligands is −3.

The $^5D_0 \rightarrow {}^7F_1$ spectral region contained six bands, indicating that two distinct emitting metal centers do indeed exist. The excited-state lifetimes for the $^5D_0$ state of both metal centers were

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Table III. Positional Parameters and Their Estimated Standard Deviations for [Eu(DPM)$_3$terpy] (Isomer 1)

atom	*x*	*y*	*z*	*B*, Å^2	atom	*x*	*y*	*z*	*B*, Å^2
Eu1	−0.00973 (2)	0.68843 (1)	0.29115 (2)	4.323 (8)	C9B	0.112 (2)	0.4398 (6)	0.247 (1)	21.0 (9)
O1A	−0.0085 (3)	0.6902 (2)	0.2655 (3)	6.1 (1)	C10B	0.1439 (9)	0.4651 (5)	0.1259 (8)	20.1 (5)
O2A	0.0040 (3)	0.6203 (2)	0.1700 (3)	6.2 (1)	C11B	0.0190 (8)	0.4576 (5)	0.163 (1)	20.5 (5)
O1B	0.1159 (3)	0.6147 (2)	0.2812 (3)	5.9 (1)	C1C	−0.1153 (5)	0.6594 (3)	0.4115 (5)	6.2 (2)
O2B	0.0315 (3)	0.5363 (2)	0.2384 (3)	5.4 (1)	C2C	−0.0578 (5)	0.6808 (4)	0.4525 (5)	7.0 (2)
O1C	−0.1056 (3)	0.6309 (2)	0.3632 (3)	5.9 (1)	C3C	0.0141 (5)	0.6720 (3)	0.4408 (4)	5.5 (2)
O2C	0.0372 (3)	0.6456 (2)	0.3943 (3)	5.7 (1)	C4C	−0.1950 (5)	0.6703 (4)	0.4271 (6)	9.5 (3)
N1D	−0.1362 (4)	0.6112 (3)	0.2244 (4)	5.8 (2)	C5C	−0.2048 (7)	0.6974 (5)	0.4958 (7)	11.8 (4)
N2D	−0.1030 (3)	0.5369 (2)	0.3087 (3)	5.2 (2)	C6C	−0.2316 (8)	0.6215 (7)	0.437 (1)	18.2 (6)
N3D	0.0247 (4)	0.5421 (2)	0.3800 (3)	5.6 (2)	C7C	−0.2275 (8)	0.6923 (7)	0.3631 (8)	17.7 (6)
C1A	0.0112 (5)	0.7169 (3)	0.2173 (6)	7.4 (3)	C8C	0.0719 (5)	0.6952 (3)	0.4900 (5)	7.0 (2)
C2A	0.0258 (6)	0.7031 (4)	0.1486 (6)	8.1 (3)	C9C	0.0804 (8)	0.6619 (5)	0.5510 (7)	11.8 (4)
C3A	0.0200 (5)	0.6540 (4)	0.1300 (5)	8.0 (3)	C10C	0.0515 (8)	0.7454 (4)	0.5089 (7)	11.6 (4)
C4A	0.0191 (7)	0.7703 (3)	0.2370 (6)	8.6 (3)	C11C	0.1456 (6)	0.6983 (4)	0.4536 (6)	9.2 (3)
C5A	−0.052 (1)	0.7851 (6)	0.250 (2)	23 (1)	C1D	−0.1503 (6)	0.6504 (4)	0.1873 (6)	8.2 (3)
C6A	0.060 (1)	0.7757 (6)	0.3018 (9)	22.8 (6)	C2D	−0.2200 (7)	0.6565 (5)	0.1538 (7)	10.3 (4)
C7A	0.040 (1)	0.8028 (5)	0.181 (1)	17.7 (7)	C3D	−0.2719 (7)	0.6207 (5)	0.1605 (8)	12.0 (4)
C8A	0.0289 (7)	0.6383 (5)	0.0526 (5)	10.2 (4)	C4D	−0.2557 (6)	0.5795 (4)	0.1994 (7)	9.6 (3)
C9A	0.077 (1)	0.5958 (6)	0.0507 (8)	19.2 (5)	C5D	−0.1867 (5)	0.5781 (3)	0.2311 (5)	6.3 (2)
C10A	0.058 (1)	0.6803 (7)	0.0068 (9)	17.6 (7)	C6D	−0.1682 (5)	0.5375 (3)	0.2773 (4)	6.0 (2)
C11A	−0.051 (1)	0.6247 (8)	0.0281 (7)	17.6 (7)	C7D	−0.2211 (6)	0.5022 (4)	0.2873 (6)	7.9 (3)
C1B	0.1671 (5)	0.5917 (4)	0.2517 (5)	6.7 (2)	C8D	−0.2038 (6)	0.4665 (4)	0.3320 (6)	8.6 (3)
C2B	0.1581 (6)	0.5462 (4)	0.2196 (5)	7.7 (3)	C9D	−0.1349 (6)	0.4640 (4)	0.3653 (5)	7.8 (3)
C3B	0.0861 (6)	0.5216 (3)	0.2147 (5)	7.4 (3)	C10D	−0.0857 (5)	0.5016 (3)	0.3516 (5)	6.0 (2)
C4B	0.2385 (5)	0.6176 (5)	0.2511 (6)	8.7 (3)	C11D	−0.0139 (5)	0.5019 (3)	0.3851 (5)	6.4 (2)
C5B	0.2967 (8)	0.5948 (6)	0.2069 (8)	13.8 (5)	C12D	0.0129 (7)	0.4627 (4)	0.4217 (7)	9.5 (3)
C6B	0.2646 (8)	0.6226 (8)	0.3268 (7)	16.3 (6)	C13D	0.0807 (8)	0.4656 (5)	0.4564 (7)	11.3 (4)
C7B	0.2262 (7)	0.6668 (5)	0.224 (1)	13.9 (6)	C14D	0.1233 (6)	0.5081 (5)	0.4492 (6)	9.2 (3)
C8B	0.0896 (7)	0.4714 (4)	0.1855 (7)	9.8 (3)	C15D	0.0919 (5)	0.5443 (4)	0.4101 (5)	7.0 (2)

Table IV. Positional Parameters and Their Estimated Standard Deviations for [Eu(DPM)$_3$terpy] (Isomer 2)

atom	*x*	*y*	*z*	*B*, Å^2	atom	*x*	*y*	*z*	*B*, Å^2
Eu2	0.07858 (2)	0.10061 (1)	0.20844 (2)	4.414 (8)	C9F	0.151 (1)	0.2346 (5)	−0.0144 (9)	21.4 (7)
O1E	−0.0267 (3)	0.1007 (2)	0.2737 (3)	7.1 (2)	C10F	0.121 (2)	0.1590 (7)	−0.0371 (9)	24.6 (9)
O2E	−0.0219 (3)	0.1313 (2)	0.1390 (3)	6.6 (1)	C11F	0.233 (1)	0.1690 (9)	0.025 (1)	31.6 (7)
O1F	0.0827 (3)	0.1814 (2)	0.2295 (3)	5.6 (1)	C1G	0.0805 (5)	0.0128 (3)	0.3284 (5)	6.5 (2)
O2F	0.1201 (3)	0.1366 (2)	0.1054 (3)	5.5 (1)	C2G	0.0956 (6)	0.0418 (4)	0.3849 (5)	7.1 (2)
O1G	0.0865 (3)	0.0254 (2)	0.2659 (3)	5.7 (1)	C3G	0.1184 (5)	0.0880 (4)	0.3803 (4)	6.4 (2)
O2G	0.1233 (3)	0.1109 (2)	0.3262 (3)	6.5 (1)	C4G	0.0518 (6)	−0.0385 (4)	0.3384 (6)	8.6 (3)
N1H	0.0194 (4)	0.0325 (2)	0.1339 (4)	6.7 (2)	C5G	0.082 (1)	−0.0590 (5)	0.403 (1)	26.4 (7)
N2H	0.1646 (4)	0.0421 (2)	0.1352 (3)	6.1 (2)	C6G	0.074 (1)	−0.0678 (5)	0.277 (1)	23.0 (9)
N3H	0.2202 (3)	0.1135 (2)	0.2120 (4)	5.6 (2)	C7G	−0.0237 (9)	−0.0363 (6)	0.341 (2)	25 (1)
C1E	−0.0908 (8)	0.1168 (5)	0.2737 (6)	10.9 (4)	C8G	0.1401 (7)	0.1172 (5)	0.4466 (5)	9.7 (3)
C2E	−0.1255 (7)	0.1382 (6)	0.2157 (7)	11.6 (4)	C9G	0.199 (1)	0.0898 (8)	0.4851 (7)	21.3 (7)
C3E	−0.0865 (7)	0.1458 (4)	0.1526 (7)	9.9 (3)	C10G	0.174 (1)	0.1612 (7)	0.430 (1)	26.6 (7)
C4E	−0.1343 (7)	0.1169 (7)	0.3358 (7)	14.7 (5)	C11G	0.079 (1)	0.1249 (7)	0.4881 (8)	23.5 (6)
C5E	−0.094 (1)	0.117 (1)	0.3979 (7)	25 (1)	C1H	−0.0531 (6)	0.0278 (4)	0.1432 (6)	9.3 (3)
C6E	−0.176 (2)	0.078 (1)	0.334 (1)	41 (1)	C2H	−0.0903 (8)	−0.0123 (5)	0.1116 (8)	12.8 (4)
C7E	−0.183 (1)	0.160 (1)	0.343 (1)	35.6 (9)	C3H	−0.054 (1)	−0.0450 (5)	0.083 (1)	17.7 (6)
C8E	−0.1220 (6)	0.1708 (4)	0.0843 (6)	9.8 (3)	C4H	0.026 (1)	−0.0407 (5)	0.0718 (8)	14.5 (5)
C9E	−0.121 (1)	0.2205 (5)	0.1024 (8)	14.3 (5)	C5H	0.0562 (7)	0.0003 (4)	0.1012 (5)	8.6 (3)
C10E	−0.197 (1)	0.1482 (9)	0.0766 (9)	22.1 (8)	C6H	0.1334 (7)	0.0085 (4)	0.0963 (5)	8.0 (3)
C11E	−0.086 (1)	0.1663 (9)	0.024 (1)	27.0 (9)	C7H	0.179 (1)	−0.0192 (5)	0.0496 (6)	13.2 (5)
C1F	0.0918 (7)	0.2187 (4)	0.2000 (6)	9.2 (3)	C8H	0.2530 (9)	−0.0074 (6)	0.0497 (7)	14.4 (5)
C2F	0.1175 (7)	0.2217 (4)	0.1280 (7)	9.6 (3)	C9H	0.2792 (7)	0.0253 (5)	0.0856 (6)	10.8 (4)
C3F	0.1271 (6)	0.1767 (4)	0.0846 (6)	9.0 (3)	C10H	0.2365 (5)	0.0516 (4)	0.1300 (5)	7.5 (2)
C4F	0.0771 (8)	0.2649 (3)	0.2391 (7)	11.1 (4)	C11H	0.2645 (5)	0.0902 (3)	0.1728 (5)	7.1 (2)
C5F	0.007 (1)	0.2607 (8)	0.274 (1)	19.8 (7)	C12H	0.3397 (7)	0.1020 (5)	0.1693 (9)	11.9 (5)
C6F	0.137 (1)	0.2711 (5)	0.288 (1)	22.8 (6)	C13H	0.3646 (8)	0.1382 (6)	0.207 (1)	14.0 (6)
C7F	0.069 (1)	0.3047 (6)	0.188 (1)	18.8 (7)	C14H	0.3171 (6)	0.1639 (4)	0.2473 (8)	10.9 (4)
C8F	0.1590 (6)	0.1852 (4)	0.0138 (5)	7.7 (3)	C15H	0.2445 (5)	0.1503 (3)	0.2498 (6)	7.5 (3)

obtained from these six bands in the $^5D_0 \rightarrow {}^7F_1$ region. The two separate lifetimes had average values of 500 ± 20 μs at 16957, 16895, and 16725 cm^{-1} and 550 ± 20 μs at 16984, 16842, and 16739 cm^{-1}. The $^5D_0 \rightarrow {}^7F_2$ spectral region contained nine bands, which also indicates that there is more than one emitting metal center. The fact that only nine bands are observed in the $^5D_0 \rightarrow {}^7F_2$ region instead of the expected ten for two complexes of low symmetry (C_2 or less) suggests that the unseen band is less intense and could be buried under other transitions or that two bands are too close together to be resolved.

In order to confirm that two distinct, low-symmetry, nine-coordinate metal centers existed for this adduct, crystallographic results were obtained. The X-ray diffraction study performed on a single crystal of [Eu(DPM)$_3$terpy] revealed two distinct isomers in the unit cell. The crystallographic parameters are listed in Table I, and the final atomic positional coordinates are given in Tables III and IV for isomers 1 and 2, respectively. Selected bond distances and angles for isomers 1 and 2 are presented in Tables V and VI, respectively, with ORTEP drawings of the molecular structure of each complex being given in Figures 2 and 3, respectively.

The results indicate that both of the Eu(III) ions are nine-coordinate, with the positions of the bonded atoms approximating a tricapped trigonal prism. The first isomer differs from the second by only small variations in bond angles and distances. The average Eu–O and Eu–N distances for the first Eu(III) ion are 2.380 and

Table V. Selected Bond Distances and Angles for [Eu(DPM)$_3$terpy] (Isomer 1)

bond angles, deg				bond distances, Å	
O1A–Eu1–O2A	69.8 (2)	O2B–Eu1–O2C	127.7 (2)	Eu1–O1A	2.357 (4)
O1A–Eu1–O1B	83.9 (2)	O2B–Eu1–N1D	95.9 (2)	Eu1–O2A	2.397 (5)
O1A–Eu1–O2B	136.8 (2)	O2B–Eu1–N2D	68.4 (1)	Eu1–O1B	2.342 (4)
O1A–Eu1–O1C	82.8 (2)	O2B–Eu1–N3D	66.6 (2)	Eu1–O2B	2.409 (4)
O1A–Eu1–O2C	75.3 (2)	O1C–Eu1–O2C	69.5 (1)	Eu1–O1C	2.374 (4)
O1A–Eu1–N1D	83.1 (2)	O1C–Eu1–N1D	67.4 (2)	Eu1–O2C	2.403 (4)
O1A–Eu1–N2D	140.5 (2)	O1C–Eu1–N2D	68.4 (2)	Eu1–N1D	2.644 (5)
O1A–Eu1–N3D	146.7 (2)	O1C–Eu1–N3D	88.5 (2)	Eu1–N2D	2.680 (5)
O2A–Eu1–O1B	77.1 (2)	O2C–Eu1–N1D	133.7 (2)	Eu1–N3D	2.612 (5)
O2A–Eu1–O2B	69.9 (2)	O2C–Eu1–N2D	116.1 (2)	O1A–C1A	1.264 (9)
O2A–Eu1–O1C	130.0 (2)	O2C–Eu1–N3D	71.6 (2)	O2A–C3A	1.268 (10)
O2A–Eu1–O2C	135.5 (2)	N1D–Eu1–N2D	61.4 (2)	O1B–C1B	1.295 (8)
O2A–Eu1–N1D	68.3 (2)	N1D–Eu1–N3D	122.8 (2)	O2B–C3B	1.194 (9)
O2A–Eu1–N2D	108.4 (2)	N2D–Eu1–N3D	61.5 (2)	O1C–C1C	1.253 (7)
O2A–Eu1–N3D	135.9 (2)	Eu1–O1A–C1A	138.1 (5)	O2C–C3C	1.255 (7)
O1B–Eu1–O2B	72.7 (1)	Eu1–O2A–C3A	137.7 (5)	N1D–C1D	1.339 (9)
O1B–Eu1–O1C	141.9 (2)	Eu1–O1B–C1B	137.5 (4)	N1D–C5D	1.328 (9)
O1B–Eu1–O2C	72.5 (1)	Eu1–O2B–C3B	137.5 (5)	N2D–C6D	1.338 (8)
O1B–Eu1–N1D	145.4 (2)	Eu1–O1C–C1C	137.5 (4)	N2D–C10D	1.330 (8)
O1B–Eu1–N2D	135.2 (2)	Eu1–O2C–C3C	137.4 (4)	N3D–C11D	1.345 (8)
O1B–Eu1–N3D	83.3 (2)	Eu1–N1D–C1D	116.4 (5)	N3D–C15D	1.360 (9)
O2B–Eu1–O1C	136.5 (1)	Eu1–N1D–C5D	123.1 (5)	C1A–C2A	1.424 (11)

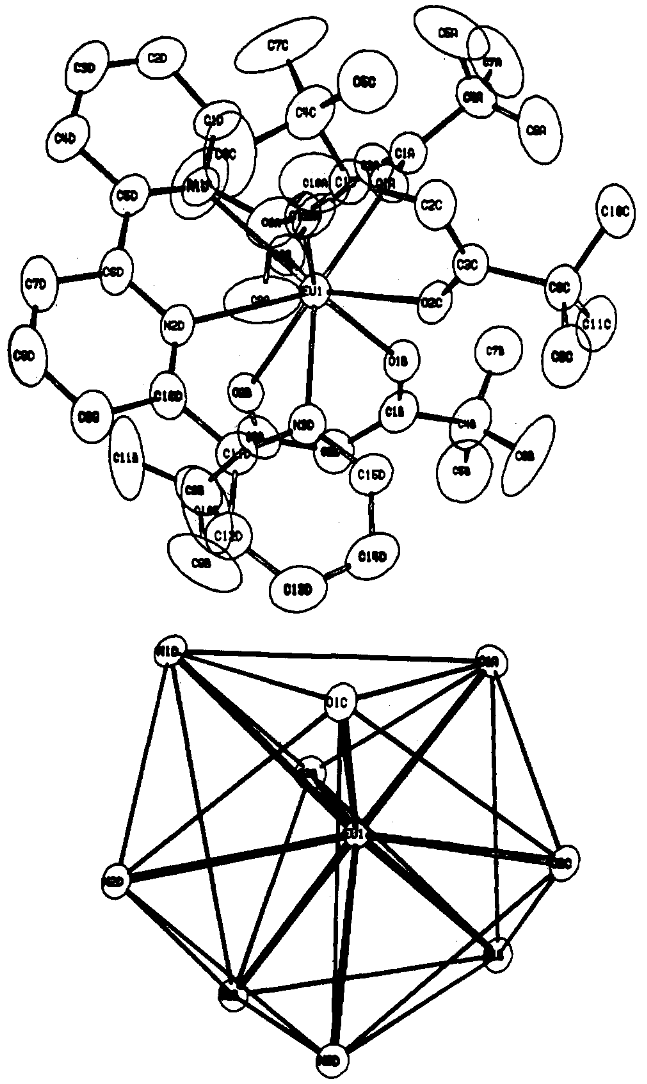

Figure 2. ORTEP drawing of the molecular structure and coordination geometry of [Eu(DPM)$_3$terpy] (isomer 1).

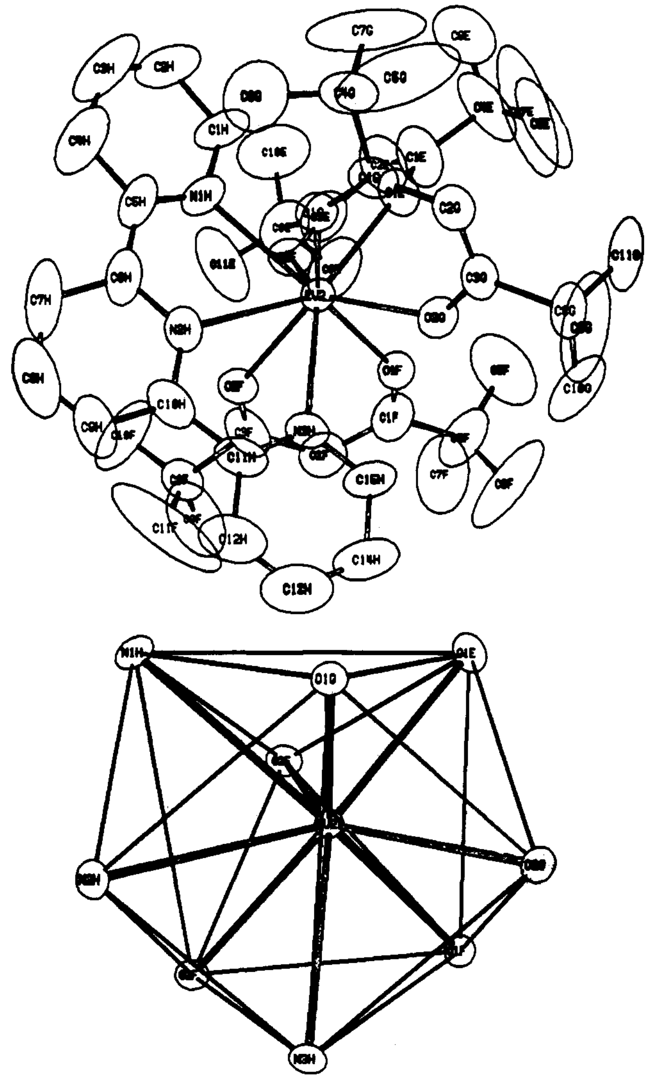

Figure 3. ORTEP drawing of the molecular structure and coordination geometry of [Eu(DPM)$_3$terpy] (isomer 2).

2.645 Å, while the average Eu–O and Eu–N distances for the second Eu(III) ion are 2.385 and 2.663 Å, respectively. The average Eu–N bond distances are equal to or longer than the reported Eu–N distances for the tris(2,2′:6′,2″-terpyridyl)europium(III) perchlorate complex, which lie in the range 2.57–2.62 Å.[15]

The average Eu–O and Eu–N bond distances of [Eu(DPM)$_3$terpy] are also equal to or longer than the reported values

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Table VI. Selected Bond Distances and Angles for [Eu(DPM)$_3$terpy] (Isomer 2)

bond angles, deg				bond distances, Å	
O1E–Eu2–O2E	70.6 (2)	O2F–Eu2–O2G	129.0 (2)	Eu2–O1E	2.352 (5)
O1E–Eu2–O1F	85.9 (2)	O2F–Eu2–N1H	89.2 (2)	Eu2–O2E	2.425 (5)
O1E–Eu2–O2F	137.8 (2)	O2F–Eu2–N2H	67.2 (2)	Eu2–O1F	2.314 (4)
O1E–Eu2–O1G	77.9 (2)	O2F–Eu2–N3H	67.8 (2)	Eu2–O2F	2.391 (4)
O1E–Eu2–O2G	76.0 (2)	O1G–Eu2–O2G	69.6 (2)	Eu2–O1G	2.398 (4)
O1E–Eu2–N1H	87.7 (2)	O1G–Eu2–N1H	68.3 (2)	Eu2–O2G	2.429 (5)
O1E–Eu2–N2H	141.9 (2)	O1G–Eu2–N2H	71.3 (2)	Eu2–N1H	2.626 (6)
O1E–Eu2–N3H	145.0 (2)	O1G–Eu2–N3H	93.5 (2)	Eu2–N2H	2.719 (6)
O2E–Eu2–O1F	76.6 (2)	O2G–Eu2–N1H	137.1 (2)	Eu2–N3H	2.643 (5)
O2E–Eu2–O2F	69.0 (2)	O2G–Eu2–N2H	112.1 (2)	O1E–C1E	1.270 (11)
O2E–Eu2–O1G	127.6 (2)	O2G–Eu2–N3H	69.3 (2)	O2E–C3E	1.297 (11)
O2E–Eu2–O2G	135.8 (2)	N1H–Eu2–N2H	60.6 (2)	O1F–C1F	1.210 (11)
O2E–Eu2–N1H	69.7 (2)	N1H–Eu2–N3H	120.9 (2)	O2F–C3F	1.207 (9)
O2E–Eu2–N2H	112.0 (2)	N2H–Eu2–N3H	60.3 (2)	O1G–C1G	1.273 (8)
O2E–Eu2–N3H	135.1 (2)	Eu2–O1E–C1E	141.8 (6)	O2G–C3G	1.240 (8)
O1F–Eu2–O2F	73.8 (2)	Eu2–O2E–C3E	134.1 (6)	N1H–C1H	1.362 (11)
O1F–Eu2–O1G	141.8 (2)	Eu2–O1F–C1F	140.8 (6)	N1H–C5H	1.309 (11)
O1F–Eu2–O2G	73.0 (2)	Eu2–O2F–C3F	135.7 (5)	N2H–C6H	1.334 (10)
O1F–Eu2–N1H	145.9 (2)	Eu2–O1G–C1G	133.2 (5)	N2H–C10H	1.363 (10)
O1F–Eu2–N2H	132.2 (2)	Eu2–O2G–C3G	134.9 (5)	N3H–C11H	1.311 (9)
O1F–Eu2–N3H	80.3 (2)	Eu2–N1H–C1H	113.2 (6)	N3H–C15H	1.339 (9)
O2F–Eu2–O1G	138.5 (2)	Eu2–N1H–C5H	124.1 (6)	C1E–C2E	1.417 (13)

for several other [Eu(DPM)$_3$] adducts. These complexes are [Eu(DPM)$_3$(py)$_2$][16] (py = pyridine), which has average Eu–O and Eu–N distances of 2.347 and 2.649 Å, respectively, [Eu(DPM)$_3$(DMF)$_2$][18] (DMF = dimethylformamide), which contains two distinct isomers in the unit cell and has average Eu–O(β-diketonate) bond distances for isomers 1 and 2 of 2.376 and 2.349 Å, respectively, and [Eu(DPM)$_3$DMSO][19] (DMSO = dimethyl sulfoxide), which also contains two distinct isomers in the unit cell and has an average Eu–O(β-diketonate) bond length of 2.35 Å for both isomers. This suggests that the *tert*-butyl groups on the DPM ligands do in fact induce some steric effects, causing longer than average Eu–O and Eu–N bond distances. It should be noted that as the coordination number increases, the Eu(III) radii also increase slightly, causing the metal–ligand bond distances to be slightly longer. However, the metal–ligand bond distances not only are a function of the metal ion radius but also are quite dependent on the adopted stereochemistry of a particular complex.[20] This stereochemical influence appears to be the dominant factor for the slight bond lengthening observed in the [Eu(DPM)$_3$terpy] complex.

For the first isomer the three bond angles subtended at the central europium(III) ion by the capped atoms forming the horizontal plane are 135.5, 108.4, and 116.1° for the O2A–Eu1–O2C, O2A–Eu1–N2D, and O2C–Eu1–N2D angles, respectively, while for the second isomer they are 135.8, 112.1, and 112.1° for the O2E–Eu2–O2G, O2E–Eu2–N2H, and O2G–Eu2–N2H angles, respectively. The large deviations from 120.0° for the O–Eu–O bond angles in the horizontal plane of each isomer appear to be due primarily to steric repulsions between the *tert*-butyl groups of adjacent β-diketone ligands with only minor contributions from crystal packing forces, which is in contrast to what was suggested by Cunningham and Sievers[19] for the two geometrical isomers of [Eu(DPM)$_3$(DMF)$_2$]. This steric effect forces the O–Eu–N bond angles in each isomer to be less than 120.0°, thus causing a severe distortion of the capped atoms from the idealized tricapped-trigonal-prism geometry.

The sum of the three angles in the horizontal plane for each isomer is 360.0°, implying a planar arrangement for the three capped atoms and the Eu(III) ion. All four atoms do indeed lie nearly in the same plane except for a small deviation by the Eu(III) ion, which lies 0.016 and 0.024 Å below the horizontal plane for isomers 1 and 2, respectively. The Eu(III) ion also lies slightly out of the plane including a capped atom and the two atoms of an opposite edge in each isomer.

The idealized symmetry of a tricapped trigonal prism is D_{3h}, but since all the ligating atoms of [Eu(DPM)$_3$terpy] are not identical, the highest possible symmetry about the metal center would be C_2. Further, when the chelate rings and the sterically induced geometrical distortions are included, the symmetry about both Eu(III) metal ions would be reduced to C_1. The luminescence spectrum is consistent with the crystallographic results, indicating the presence of two distinct emitting metal centers that reside in a low-symmetry environment.

Acknowledgment. This work was supported by funds provided by the Research Corp. and the Graduate School of the University of Minnesota. We are grateful to Professor Britton for the crystal structure determination.

Registry No. [Eu(DPM)$_3$terpy], 117340-02-0; [Eu(DPM)$_3$], 15522-71-1.

Supplementary Material Available: Listings of thermal parameters, bond distances, bond angles, least-squares planes, intermolecular contacts, and crystallographic parameters (22 pages); tables of structure factors (36 pages). Ordering information is given on any current masthead page.

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