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Structures of Europium Complexes and Implications in Lanthanide Nuclear Magnetic Resonance Shift Reagent Chemistry

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The crystal and molecular structures of a bis(dimethylformamide) adduct of the tris(2,2,6,6-tetramethyl-3,5-heptanedionato)europium(III) complex sometimes used as an NMR shift reagent are described and discussed. Four discrete molecules of the adduct crystallize in a triclinic unit cell of $P\bar{1}$ symmetry. Each asymmetric unit within the unit cell consists of two discrete non-symmetry-related molecules of the complex; the coordination polyhedra are best described as distorted square antiprisms. The variability of the geometries of lanthanide complexes and possible reasons for observed differences are considered with particular reference to implications in NMR shift reagent chemistry.

Introduction[1]

The demonstration by Hinckley[2] that $Eu(thd)_3(py)_2$ induces large paramagnetic shifts in the proton magnetic resonances of cholesterol has been followed by a large number of studies using other shift reagents as powerful probes to elucidate the solution conformations of complex nucleophiles.[3] A major segment of the NMR shift reagent literature is concerned with the use of shift reagents for spectral clarification, but a large number of studies have been undertaken to more fully explain the physical basis for the lanthanide–chelate induced shift phenomenon (the LIS phenomenon). These efforts have provided information in areas ranging from solution configuration determinations[4] to criteria for the selection of the most effective shift reagent for a given experiment.[5]

Quantitative interpretations of the LIS phenomenon have generally been attempts to relate the magnitude and direction of the observed shifts to the solution-state geometry of the substrate/shift reagent complex. Extensive use has been made of the physical–mathematical model wherein the a priori assumption is made that the molecule has either axial or effective axial symmetry and that the observed shifts are caused by interactions that are pseudocontact (dipolar) in nature.[3] Application of the modified McConnell–Robertson[6] relationship (eq 1) requires a detailed knowledge of the molecular

$$\Delta H_i/H = K(1 - 3\cos^2\theta_i)/r_i^3 \qquad (1)$$

stereochemistry of the complex in solution. In particular, the required parameters are the distance, r_i, from the ith resonating nucleus to the paramagnetic ion, and the angle θ_i, which this vector makes with the principal magnetic axis of the molecule. For this simplified relationship to be valid, the complex must possess a C_3 or higher axis of symmetry or be effectively axially symmetrical.[6]

Results of crystal structure determinations of several lanthanide shift reagents and related complexes reveal wide variations in the conformations assumed by these molecules in the crystalline state. For example the unsolvated $Ln(thd)_3$ complexes exist in two modifications.[7,8] The lighter lanthanides (La to Dy) crystallize in the monoclinic system and the molecular structure is characterized by the occurrence of dimeric units. Erasmus and Boeyens[9] have shown that dimerization occurs through the sharing of two oxygen atoms by the metal ions. In contrast, the heavier lanthanide compounds (Ho to Lu) form orthorhombic crystals and the molecules exist as discrete, six-coordinate monomers. Almost ideal trigonal prismatic coordination geometry has been observed in the crystal structure of $Er(thd)_3$.[10]

Single-crystal structures of several solvated shift reagents have recently been determined by X-ray diffraction techniques. $Dy(thd)_3(H_2O)$ exists in the solid state as a seven-coordinate monomer; the coordination polyhedron resembles a monocapped trigonal prism in which the water molecule occupies one of the prism vertices.[11] A similar coordination geometry was observed in the complex $Lu(thd)_3$(3-pic),[12] while the coordination geometry observed in the complex $Eu(thd)_3$(3,3-dimethylthietane 1-oxide)[13] has been described as a wedged octahedron. Several octacoordinate complexes have also been subjected to X-ray diffraction studies, and the structures of $Ho(thd)_3(4\text{-pic})_2$[14] and $Eu(thd)_2(py)_2)$[15] have been reported. Both of these complexes have the same gross stereochemistry based on a distorted square-antiprismatic geometry. The holmium complex is crystallographically required to possess a C_2 axis and the europium compound closely approximates C_2 symmetry. In both structures the adduct ligands occupy coordination sites on opposite square faces and trans to each other.

In none of the above cases does the complex rigorously have axial symmetry. Only two complexes of lanthanide shift reagents and related compounds have been shown to possess or approximate quite closely highly symmetric coordination polyhedra: the monocapped octahedron of $Ho(dbm)_3(H_2O)$[16] is crystallographically required to have threefold symmetry in the solid state and the geometry of the previously mentioned $Er(thd)_3$ complex is almost ideally trigonal prismatic.[10]

We have undertaken a systematic study of the structures of several mono and bis adducts of the lanthanide NMR shift

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(1) Abbreviations used throughout this work are as follows: thd, the anion of 2,2,6,6-tetramethyl-3,5-heptanedione; Ln, a trivalent lanthanide ion; dbm, the anion of 1,3-diphenylpropanedione; DMF, *N*,*N*-dimethylformamide; acac, the anion of 2,4-pentanedione; py, pyridine; pic, picoline.

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reagents. In addition to the parameters required for calculating induced shifts, basic underlying structural principles may also be deduced from the crystal structures. Crystals of Eu(thd)$_3$(DMF)$_2$ suitable for X-ray diffraction studies are easily obtainable, and preliminary studies indicated that four molecules grouped in two nonequivalent pairs occupy a triclinic unit cell. Thus the structure offers the opportunity to obtain direct evidence for steric deformation, which easily occurs in large lanthanide complexes, and to obtain pertinent bonding parameters for lanthanide NMR shift reagents. Despite the magnitude of the problem (the asymmetric unit is comprised of 100 carbon and heavier atoms) the structure has been solved, and we report it herein.[17]

Experimental Section

Eu(thd)$_3$, which had been prepared by the standard method,[18] was sublimed just prior to the crystallization experiments. Spectroscopic grade dimethylformamide was saturated with this Eu(thd)$_3$ and allowed to slowly evaporate at ambient laboratory temperatures. After approximately 1 week, large colorless crystals formed which rapidly decomposed (as evidenced by the crystals turning opaque and crumbling) if they were not kept in intimate contact with the mother liquor.

Elemental analysis of these crystals was virtually prohibited by their extreme instability, and an indirect route was required to establish the composition. Several large crystals were quickly dried, placed in a beaker, exposed to the atmosphere, and weighed. Periodic weighings were made until no further change in the weight was noted. The observed percent decrease in mass, ~8.8%, corresponded to the loss of 1 mol of DMF from a complex of initial composition Eu(thd)$_3$(DMF)$_2$; the calculated weight loss is 8.62%. Elemental analysis[19] of the remaining solid corresponded to the monoadduct, Eu(thd)$_3$DMF. Anal. Calcd for EuC$_{36}$H$_{64}$NO$_7$: Eu, 19.62; C, 55.78; N, 1.81; H, 8.33. Found: Eu, 20.10; C, 55.62; N, 1.78, H, 8.41.

Crystals of size suitable for X-ray diffraction studies were mechanically cleaved from several of the larger specimens and sealed in thin-wall glass capillaries. Excess mother liquor was also sealed in the capillaries to retard decomposition, but despite this precaution, five crystals were required (vide infra) to collect the data necessary for structure analysis. Preliminary precession photographs taken with zirconium-filtered Mo Kα (λ = 0.7107 Å) radiation, established the probable space groups, orientations, and trial unit cell parameters. Accurate cell constants were obtained from the least-squares refinement[20] of the setting angles of 72 automatically centered reflections equally distributed in pairs between the positive and negative regions of 2θ. The Kα_1–α_2 doublet was sufficiently resolved to allow centering on the α_1 component (λ = 0.709 26 Å); the reflections centered were in the range $40 < |2\theta| < 45°$: a = 14.527 (2) Å, b = 18.565 (3) Å, c = 17.583 (2) Å; cos α = 0.0069 (2), cos β = 0.0168 (1), cos γ = 0.0524 (2) or α = 89.60°, β = 89.03°, γ = 87.01°. A Delaunay reduction confirmed a triclinic description.[21] Density measurements, by flotation, were made on several crystals at 22 ± 1 °C. The average of five determinations is 1.187 (7) g/cm^3 and agrees with a calculated density of 1.198 g/cm^3 for four molecules of Eu(thd)$_3$(DMF)$_2$ in the aforementioned triclinic unit cell.

Intensity data were collected with a computer-controlled Picker FACS-1 diffractometer equipped with a highly oriented graphite-crystal monochromator and molybdenum radiation (λ(Kα_1) = 0.709 26 Å). All independent diffraction maxima in the range $0.030 \leq (\sin \theta)/\lambda \leq 0.603$ were measured by the θ–2θ scan technique with a scan rate of 1°/min. The basic scan width of 1.50° at 2θ = 0° was incremented[22] for each reflection by $\Delta(2\theta) = 0.692(\tan \theta)°$ to allow for spectral dispersion; background was measured for 20 s at each extreme of the scan. Three reflections, well distributed in reciprocal space, were monitored at intervals of every 100 data points and showed no large fluctuations. However, a uniform decrease of intensity was observed during the course of data collection. When the intensity value recorded for any standard had fallen to less than 95% of the original value and automatic realignment of the crystal did not restore the intensity, a new crystal was mounted on the diffractometer and data collection was resumed. It was necessary to use five crystals for data collection. No attempt was made to correct the data for the gradual decrease in intensity of the standards due to decomposition, nor were the five portions of data, each collected from a different crystal, scaled to a common level; rather five separate scale constants were assigned for the solution and refinement procedures.

After corrections were made for background effects, 17 360 independent diffraction intensities were directly reduced to relative squared structure amplitudes, $|F_o|^2$, by means of standard Lorentz and polarization corrections; allowance was made for the partial polarization of the incident beam. The irregular shapes[23] of the five crystals used during data collection and the presence of mother liquor on the surface of each crystal precluded accurate allowances for absorption effects, so none were applied. The linear absorption coefficient of the crystalline complex is estimated to be 1.38 mm^{-1} for Mo Kα radiation, and we estimate the average error in any structure factor caused by the neglect of absorption to be ~5%. The 12 780 reflections satisfying the criterion $|F_o| \geq 3.0\sigma(|F_o|)$ were retained as being objectively observed, wherein $\sigma(|F_o|)$ is the standard deviation computed from

$$\sigma^2(|F_o|) = (C_t + k^2B)/4|F_o|^2(Lp)^2$$

C_t being the total count from the scan, k the ratio of scanning time to total background counting time, B the total background count, and Lp the Lorentz–polarization correction.

The straightforward interpretation of the Patterson synthesis[24] of the $|F_o|^2$ data having $(\sin \theta)/\lambda < 0.52$ placed two independent europium atoms in general positions of the assumed triclinic space group $P\bar{1}$.[25] The coordinates of the remaining carbon and heavier atoms were determined through a combination of the heavy-atom technique, difference Fourier syntheses, and least-squares refinements. Five difference syntheses were required to develop the entire structure, except for hydrogen atoms. Large thermal motions and/or partial disordering of all methyl groups were obvious from the outset, and several appeared as diffuse regions of electron density.

For initial refinement[26] of the five scale factors, the coordinates, and the individual isotropic thermal parameters of the 100 atoms, a block-diagonal, least-squares minimization of the function $\sum w(|F_o| - |F_c|)^2$ was utilized. Refinement proceeded smoothly although slowly with the initial choice of unit weights. When refinement of this model had converged (R = 15.3%), the fully anisotropic description was then assumed and empirical weights ($w = 1/\sigma^2$) were calculated from

$$\sigma = \sum_0^3 a_n|F_o|^n$$

the a_n being coefficients from the least-squares fitting of the curve

$$||F_o| - |F_c|| = \sum_0^3 a_n|F_o|^n$$

The values of $|F_c|$ in the above equation came from a final description of the structure (R = 9.6%). The values of $a_{0,1,2,3}$ were 2.76, -4.39×10^{-2}, 5.20×10^{-4}, and -6.80×10^{-7}, respectively.

Refinement continued until no parameter was shifted by more than 5% of its associated standard deviation. The final agreement factors are 0.0621 for the conventional $R = \sum||F_o| - |F_c||/\sum|F_o|$ and 0.0751 for the weighted R; the standard deviation of an observation of unit

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(19) Analytical determination made by Galbraith Laboratories, Knoxville, TN 37921.

(20) Use was made of the PICK II computer program, a revision in this laboratory of W. C. Hamilton's MODE I program.

(21) We have chosen to report the unit cell parameters, fractional coordinates of the atoms, and associated thermal parameters in this nonreduced unit cell because of the nearly mutual orthogonal axis. The transformation to the reduced cell is $a^1 = c$, $b^1 = a - c$, and $c^1 = a + b$.

(22) T. C. Furnas, "Single Crystal Orienter Instruction Manual", The General Electric Co., Milwaukee, WI, 1966, p 79.

(23) The five crystals, all irregularly shaped parallelipipeds, were dimensioned approximately 0.3 × 0.3 × 0.3 mm.

(24) Programs used for the solution and refinement of the structure included local revisions of Zalkin's Fourier program, FORDAP, and J. J. Park's block-diagonal least-squares program REFINE.

(25) "International Tables for X-ray Crystallography, Vol. I. Symmetry Groups", The Kynoch Press, Birmingham, England, 1965 p 75.

(26) Atomic form factors for the neutral atoms were from D. T. Cromer and J. B. Mann, *Acta Crystallogr., Sect. A*, **24**, 321 (1968), with corrections real and imaginary for anomalous dispersion in the europium form factor from D. T. Cromer, *ibid.*, **18**, 17 (1965).

Table I. Atomic Coordinates in Crystalline $\mathrm{Eu(thd)_2(DMF)_2}$[a]

	coordinates				coordinates		
atom type[b]	10^4x	10^4y	10^4z	atom type[b]	10^4x	10^4y	10^4z
Eu_{α}	9415.8 (3)	8182.1 (2)	1329.6 (2)	Eu_{β}	4038.8 (3)	3260.3 (2)	3707.3 (2)
$\mathrm{O}_{\alpha\mathrm{A}1}$	10703 (4)	7537 (3)	779 (4)	$\mathrm{O}_{\beta\mathrm{A}1}$	4735 (4)	2456 (3)	4602 (3)
$\mathrm{O}_{\alpha\mathrm{A}2}$	10760 (3)	8888 (3)	1390 (4)	$\mathrm{O}_{\beta\mathrm{A}2}$	5654 (4)	3384 (3)	3718 (4)
$\mathrm{O}_{\alpha\mathrm{B}1}$	10040 (4)	7730 (3)	2463 (3)	$\mathrm{O}_{\beta\mathrm{B}1}$	4546 (4)	2324 (3)	2908 (3)
$\mathrm{O}_{\alpha\mathrm{B}2}$	8975 (4)	8991 (3)	2318 (3)	$\mathrm{O}_{\beta\mathrm{B}2}$	4246 (4)	3734 (3)	2475 (3)
$\mathrm{O}_{\alpha\mathrm{C}1}$	7789 (3)	8197 (3)	1379 (3)	$\mathrm{O}_{\beta\mathrm{C}1}$	2629 (4)	3889 (3)	3425 (4)
$\mathrm{O}_{\alpha\mathrm{C}2}$	8932 (4)	6996 (3)	1366 (4)	$\mathrm{O}_{\beta\mathrm{C}2}$	2846 (4)	2436 (3)	3730 (4)
$\mathrm{O}_{\alpha\mathrm{DMF}1}{}^{c}$	9035 (6)	7929 (4)	−17 (4)	$\mathrm{O}_{\beta\mathrm{DMF}1}{}^{c}$	4282 (5)	4520 (3)	4020 (4)
$\mathrm{O}_{\alpha\mathrm{DMF}2}{}^{c}$	9013 (5)	9323 (4)	686 (4)	$\mathrm{O}_{\beta\mathrm{DMF}2}{}^{c}$	3285 (5)	3502 (3)	4973 (4)
$\mathrm{C}_{\alpha\mathrm{A}1}$	12093 (7)	6845 (5)	556 (6)	$\mathrm{C}_{\beta\mathrm{A}1}$	5559 (7)	1482 (5)	5206 (6)
$\mathrm{C}_{\alpha\mathrm{A}2}$	11547 (6)	7547 (4)	846 (5)	$\mathrm{C}_{\beta\mathrm{A}2}$	5531 (6)	2150 (4)	4668 (5)
$\mathrm{C}_{\alpha\mathrm{A}3}$	12014 (5)	8109 (4)	1152 (5)	$\mathrm{C}_{\beta\mathrm{A}3}$	6334 (6)	2378 (5)	4317 (6)
$\mathrm{C}_{\alpha\mathrm{A}4}$	11616 (5)	8739 (4)	1379 (5)	$\mathrm{C}_{\beta\mathrm{A}4}$	6341 (5)	2999 (4)	3844 (5)
$\mathrm{C}_{\alpha\mathrm{A}5}$	12210 (6)	9338 (6)	1716 (8)	$\mathrm{C}_{\beta\mathrm{A}5}$	7279 (8)	3237 (7)	3501 (7)
$\mathrm{C}_{\alpha\mathrm{AM}1}$	13102 (9)	6773 (8)	826 (12)	$\mathrm{C}_{\beta\mathrm{AM}1}$	6411 (10)	964 (7)	5048 (9)
$\mathrm{C}_{\alpha\mathrm{AM}2}$	11630 (11)	6178 (6)	913 (11)	$\mathrm{C}_{\beta\mathrm{AM}2}$	5653 (13)	1787 (7)	6026 (7)
$\mathrm{C}_{\alpha\mathrm{AM}3}$	12014 (16)	6840 (10)	−292 (9)	$\mathrm{C}_{\beta\mathrm{AM}3}$	4678 (10)	1076 (7)	5115 (11)
$\mathrm{C}_{\alpha\mathrm{AM}4}$	12134 (14)	9300 (9)	2561 (9)	$\mathrm{C}_{\beta\mathrm{AM}4}$	7105 (11)	3503 (15)	2746 (11)
$\mathrm{C}_{\alpha\mathrm{AM}5}$	11782 (11)	10098 (6)	1444 (10)	$\mathrm{C}_{\beta\mathrm{AM}5}$	8097 (10)	2685 (10)	3599 (11)
$\mathrm{C}_{\alpha\mathrm{AM}6}$	13234 (10)	9248 (9)	1454 (16)	$\mathrm{C}_{\beta\mathrm{AM}6}$	7498 (14)	3870 (13)	3964 (18)
$\mathrm{C}_{\alpha\mathrm{B}1}$	10874 (8)	7508 (6)	3603 (5)	$\mathrm{C}_{\beta\mathrm{B}1}$	5150 (7)	1454 (6)	2022 (6)
$\mathrm{C}_{\alpha\mathrm{B}2}$	10205 (6)	7992 (5)	3098 (4)	$\mathrm{C}_{\beta\mathrm{B}2}$	4802 (6)	2242 (5)	2228 (5)
$\mathrm{C}_{\alpha\mathrm{B}3}$	9831 (6)	8635 (4)	3395 (5)	$\mathrm{C}_{\beta\mathrm{B}3}$	4818 (6)	2788 (5)	1676 (5)
$\mathrm{C}_{\alpha\mathrm{B}4}$	9215 (6)	9094 (5)	3000 (5)	$\mathrm{C}_{\beta\mathrm{B}4}$	4536 (5)	3495 (5)	1836 (5)
$\mathrm{C}_{\alpha\mathrm{B}5}$	8764 (8)	9767 (5)	3359 (6)	$\mathrm{C}_{\beta\mathrm{B}5}$	4571 (7)	4087 (6)	1189 (6)
$\mathrm{C}_{\alpha\mathrm{BM}1}$	10252 (10)	6926 (7)	3989 (8)	$\mathrm{C}_{\beta\mathrm{BM}1}$	5315 (16)	1330 (10)	1191 (8)
$\mathrm{C}_{\alpha\mathrm{BM}2}$	11354 (10)	7946 (7)	4219 (8)	$\mathrm{C}_{\beta\mathrm{BM}2}$	6010 (13)	1289 (9)	2443 (10)
$\mathrm{C}_{\alpha\mathrm{BM}3}$	11621 (9)	7135 (8)	3049 (8)	$\mathrm{C}_{\beta\mathrm{BM}3}$	4465 (16)	960 (9)	2356 (18)
$\mathrm{C}_{\alpha\mathrm{BM}4}$	7737 (9)	9608 (9)	3501 (10)	$\mathrm{C}_{\beta\mathrm{BM}4}$	4612 (13)	3722 (9)	374 (7)
$\mathrm{C}_{\alpha\mathrm{BM}5}$	9213 (10)	9978 (6)	4122 (7)	$\mathrm{C}_{\beta\mathrm{BM}5}$	5378 (14)	4491 (12)	1302 (13)
$\mathrm{C}_{\alpha\mathrm{BM}6}$	8878 (13)	10412 (6)	2801 (7)	$\mathrm{C}_{\beta\mathrm{BM}6}$	3662 (10)	4526 (9)	1178 (9)
$\mathrm{C}_{\alpha\mathrm{C}1}$	6175 (6)	8087 (7)	1413 (6)	$\mathrm{C}_{\beta\mathrm{C}1}$	1146 (8)	4469 (7)	3534 (8)
$\mathrm{C}_{\alpha\mathrm{C}2}$	7167 (5)	7763 (5)	1351 (4)	$\mathrm{C}_{\beta\mathrm{C}2}$	1798 (5)	3740 (5)	3542 (5)
$\mathrm{C}_{\alpha\mathrm{C}3}$	7302 (6)	7023 (5)	1280 (5)	$\mathrm{C}_{\beta\mathrm{C}3}$	1422 (6)	3109 (5)	3682 (6)
$\mathrm{C}_{\alpha\mathrm{C}4}$	8201 (6)	6678 (5)	1282 (5)	$\mathrm{C}_{\beta\mathrm{C}4}$	1969 (6)	2475 (5)	3738 (5)
$\mathrm{C}_{\alpha\mathrm{C}5}$	8344 (7)	5854 (5)	1177 (6)	$\mathrm{C}_{\beta\mathrm{C}5}$	1538 (7)	1736 (5)	3814 (7)
$\mathrm{C}_{\alpha\mathrm{CM}1}$	6080 (10)	8616 (10)	2026 (10)	$\mathrm{C}_{\beta\mathrm{CM}1}$	1363 (13)	4888 (9)	4269 (10)
$\mathrm{C}_{\alpha\mathrm{CM}2}$	5990 (11)	8433 (14)	661 (10)	$\mathrm{C}_{\beta\mathrm{CM}2}$	1371 (10)	4922 (8)	2806 (10)
$\mathrm{C}_{\alpha\mathrm{CM}3}$	5456 (9)	7564 (10)	1537 (18)	$\mathrm{C}_{\beta\mathrm{CM}3}$	122 (9)	4277 (9)	3514 (13)
$\mathrm{C}_{\alpha\mathrm{CM}4}$	7442 (9)	5439 (7)	1243 (9)	$\mathrm{C}_{\beta\mathrm{CM}4}$	2188 (12)	1194 (8)	4127 (16)
$\mathrm{C}_{\alpha\mathrm{CM}5}$	8732 (11)	5745 (7)	362 (7)	$\mathrm{C}_{\beta\mathrm{CM}5}$	1290 (19)	1515 (10)	3020 (10)
$\mathrm{C}_{\alpha\mathrm{CM}6}$	9041 (9)	5550 (7)	1763 (8)	$\mathrm{C}_{\beta\mathrm{CM}6}$	708 (12)	1775 (8)	4317 (13)
$\mathrm{C}_{\alpha\mathrm{DMF}1}{}^{c}$	8620 (16)	7728 (10)	−415 (7)	$\mathrm{C}_{\beta\mathrm{DMF}1}{}^{c}$	3015 (7)	3048 (6)	5415 (5)
$\mathrm{N}_{\alpha\mathrm{DMF}1}{}^{c}$	8488 (8)	7404 (7)	−1039 (4)	$\mathrm{N}_{\beta\mathrm{DMF}1}{}^{c}$	2580 (6)	3198 (5)	6067 (4)
$\mathrm{C}_{\alpha\mathrm{DMFM}1}{}^{d}$	7627 (12)	7419 (15)	−1440 (12)	$\mathrm{C}_{\beta\mathrm{DMFM}2}{}^{d}$	2254 (10)	2615 (9)	6592 (7)
$\mathrm{C'}_{\alpha\mathrm{DMFM}1}{}^{d}$	9257 (18)	6991 (15)	−1388 (10)	$\mathrm{C'}_{\beta\mathrm{DMFM}1}{}^{d}$	2364 (15)	3949 (9)	6259 (10)
$\mathrm{C}_{\alpha\mathrm{DMF}2}{}^{c}$	9252 (11)	9904 (7)	769 (7)	$\mathrm{C}_{\beta\mathrm{DMF}2}{}^{c}$	4326 (13)	4995 (7)	3608 (10)
$\mathrm{N}_{\alpha\mathrm{DMF}2}{}^{c}$	8736 (8)	10528 (5)	775 (6)	$\mathrm{N}_{\beta\mathrm{DMF}2}{}^{c}$	4390 (8)	5687 (4)	3744 (6)
$\mathrm{C}_{\alpha\mathrm{DMFM}2}{}^{d}$	9231 (16)	11198 (8)	824 (11)	$\mathrm{C}_{\beta\mathrm{DMFM}2}{}^{d}$	4415 (24)	5984 (11)	4404 (11)
$\mathrm{C'}_{\alpha\mathrm{DMFM}2}{}^{d}$	7791 (12)	10583 (14)	756 (12)	$\mathrm{C'}_{\beta\mathrm{DMFM}2}{}^{d}$	4424 (29)	6271 (11)	3142 (14)

[a] Figures in parentheses are the estimated standard deviations. [b] In addition to the numerical subscript each atom has several literal designators. The α and β subscript refers to the isomer and the subscript A, B, or C refers to a particular chelate ring. See Figure 2. [c] The subscript DMF indicates the atom is in a unidentate dimethylformamide ligand. [d] The descriptor DMFM is used for the methyl group carbon atoms of the dimethylformamide molecules.

weight was 1.487. A difference synthesis based on the final atomic parameters displayed in Tables I and II showed no significant features; the value of the maximum electron density was 0.78 e/Å^3 and was in the region of Eu_{α}. The choice of the centrosymmetric triclinic space group, $P\bar{1}$, is fully supported by the successful refinement and all details of the determined structure.

Results and Discussion

Four discrete molecules of $\mathrm{Eu(thd)_3(DMF)_2}$ crystallize in a triclinic unit cell of $P\bar{1}$ symmetry. Each asymmetric unit within the unit cell consists of two discrete non-symmetry-related molecules of the complex. The two crystallographically independent molecules have the same overall composition and gross stereochemistry but differ significantly in detail (vide infra). For clarity, the two symmetry-independent molecules will be labeled isomers α and β. Figure 1 is a computer-drawn model[27] of the two isomers as they exist in the triclinic crystal. Each atom is represented by an ellipsoid with the relative size and orientation consistent with the thermal parameters in Table II. In both isomers the europium ion is bonded to eight oxygen atoms donated by three bidentate β-diketonate ions and two monodentate dimethylformamide molecules. Figure 2 is a schematic representation of a square antiprism, showing the ligand connectivity displayed in crystalline $\mathrm{Eu(thd)_3(DMF)_2}$ and a diagram of a thd ion on which are indicated the numbering schemes employed for the atoms. Additional literal subscripts (α or β) and (A, B, or C) are used to identify the particular isomer and thd ligand, respectively.

Discussions of the coordination geometries exhibited by discrete, octacoordinate complexes are generally attempts to

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(27) C. K. Johnson "ORTEP: A Fortran Thermal-Ellipsoid Plot Program for Crystal Structure Illustrations", ORNL-3794, Oak Ridge National Laboratory, Oak Ridge, TN, 1965.

Table II. Anisotropic Thermal Parameters in Crystalline $Eu(thd)_3(DMF)_2$[a]

atom designator[b]	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}	B, Å^2[e]
Eu_{α}	0.00443 (2)	0.00345 (1)	0.00419 (2)	0.00000 (1)	−0.00053 (1)	−0.00066 (1)	4.44
$O_{\alpha A1}$	0.0052 (3)	0.0042 (2)	0.0068 (3)	0.0008 (2)	0.0004 (2)	0.0017 (2)	5.71
$O_{\alpha A2}$	0.0045 (3)	0.0030 (2)	0.0081 (3)	0.0001 (2)	0.0001 (2)	−0.0012 (2)	5.28
$O_{\alpha B1}$	0.0083 (4)	0.0035 (2)	0.0051 (2)	0.0004 (2)	−0.0016 (2)	−0.0006 (2)	5.80
$O_{\alpha B2}$	0.0067 (3)	0.0042 (2)	0.0042 (2)	0.0007 (2)	−0.0008 (2)	−0.0007 (2)	5.40
$O_{\alpha C1}$	0.0034 (2)	0.0039 (2)	0.0064 (3)	0.0005 (2)	−0.0003 (2)	−0.0009 (2)	4.86
$O_{\alpha C2}$	0.0049 (3)	0.0037 (2)	0.0075 (3)	−0.0008 (2)	−0.0011 (2)	−0.0009 (2)	5.57
$O_{\alpha DMF1}$[c]	0.01233 (6)	0.0080 (4)	0.0045 (3)	−0.0008 (4)	−0.0016 (3)	−0.0015 (3)	8.22
$O_{\alpha DMF2}$[c]	0.01035 (5)	0.0051 (3)	0.0059 (3)	0.0009 (3)	−0.0003 (3)	0.0010 (2)	7.54
$C_{\alpha A1}$	0.0071 (6)	0.0042 (3)	0.0080 (6)	0.0002 (4)	0.0016 (4)	−0.0017 (3)	5.84
$C_{\alpha A2}$	0.0054 (4)	0.0033 (3)	0.0056 (4)	0.0003 (3)	0.0003 (3)	−0.0004 (2)	5.22
$C_{\alpha A3}$	0.0047 (4)	0.0030 (2)	0.0070 (4)	−0.0014 (3)	−0.0009 (3)	−0.0013 (3)	4.82
$C_{\alpha A4}$	0.0039 (4)	0.0031 (2)	0.0070 (4)	−0.0001 (2)	−0.0002 (3)	−0.0006 (3)	4.95
$C_{\alpha A5}$	0.0054 (5)	0.0050 (4)	0.0113 (7)	−0.0018 (4)	0.0001 (5)	−0.0023 (4)	7.05
$C_{\alpha AM1}$	0.0088 (9)	0.0068 (6)	0.0207 (15)	0.0015 (6)	−0.0021 (9)	−0.0053 (8)	11.11
$C_{\alpha AM2}$	0.0154 (13)	0.0037 (4)	0.0174 (3)	−0.0010 (6)	0.0049 (10)	−0.0017 (6)	10.72
$C_{\alpha AM3}$	0.0335 (26)	0.0099 (9)	0.0071 (7)	0.0104 (13)	0.0019 (11)	−0.0023 (6)	12.26
$C_{\alpha AM4}$	0.0234 (19)	0.0085 (7)	0.0094 (8)	−0.0062 (10)	−0.0065 (10)	−0.0011 (6)	11.37
$C_{\alpha AM5}$	0.0154 (12)	0.0034 (4)	0.0137 (10)	−0.0027 (5)	−0.0022 (9)	−0.0004 (5)	9.48
$C_{\alpha AM6}$	0.0077 (9)	0.0094 (8)	0.0331 (24)	−0.0049 (7)	0.0034 (12)	−0.0109 (12)	11.07
$C_{\alpha B1}$	0.0097 (8)	0.0058 (4)	0.0058 (4)	0.0014 (4)	−0.0021 (5)	0.0011 (4)	7.27
$C_{\alpha B2}$	0.0075 (6)	0.0041 (3)	0.0046 (4)	−0.0003 (3)	−0.0008 (4)	0.0007 (3)	5.78
$C_{\alpha B3}$	0.0078 (6)	0.0040 (3)	0.0044 (3)	−0.0003 (3)	−0.0011 (3)	−0.0002 (2)	5.49
$C_{\alpha B4}$	0.0062 (5)	0.0036 (3)	0.0040 (3)	−0.0005 (3)	−0.0001 (3)	−0.0004 (2)	5.00
$C_{\alpha B5}$	0.0110 (8)	0.0043 (3)	0.0049 (4)	0.0001 (4)	0.0000 (4)	−0.0016 (3)	6.64
$C_{\alpha BM1}$	0.0134 (11)	0.0060 (5)	0.0087 (7)	0.0008 (6)	−0.0001 (7)	0.0027 (5)	9.48
$C_{\alpha BM2}$	0.0139 (11)	0.0088 (7)	0.0077 (6)	0.0002 (7)	−0.0066 (7)	0.0004 (5)	9.23
$C_{\alpha BM3}$	0.0109 (9)	0.0098 (8)	0.0080 (7)	0.0048 (7)	−0.0007 (6)	0.0011 (6)	9.74
$C_{\alpha BM4}$	0.0080 (8)	0.0103 (8)	0.0150 (1)	0.0018 (6)	0.0019 (8)	−0.0064 (8)	10.37
$C_{\alpha BM5}$	0.0154 (11)	0.0057 (5)	0.0058 (5)	0.0002 (6)	−0.0015 (6)	−0.0021 (4)	8.54
$C_{\alpha BM6}$	0.0268 (19)	0.0041 (4)	0.0065 (6)	0.0022 (7)	−0.0014 (8)	−0.0004 (4)	9.91
$C_{\alpha C1}$	0.0047 (5)	0.0090 (6)	0.0055 (4)	−0.0015 (4)	−0.0012 (4)	−0.0004 (4)	6.83
$C_{\alpha C2}$	0.0038 (4)	0.0061 (4)	0.0039 (3)	−0.0007 (3)	−0.0006 (3)	−0.0010 (3)	4.85
$C_{\alpha C3}$	0.0058 (5)	0.0053 (4)	0.0050 (4)	−0.0011 (3)	−0.0007 (3)	−0.0008 (3)	5.86
$C_{\alpha C4}$	0.0070 (5)	0.0045 (3)	0.0041 (3)	−0.0016 (3)	−0.0005 (3)	−0.0005 (3)	5.38
$C_{\alpha C5}$	0.0084 (6)	0.0049 (4)	0.0056 (4)	−0.0024 (4)	−0.0001 (4)	−0.00101 (3)	6.48
$C_{\alpha CM1}$	0.0103 (10)	0.0149 (12)	0.0122 (10)	0.0058 (9)	−0.0025 (8)	−0.0073 (9)	11.37
$C_{\alpha CM2}$	0.0124 (12)	0.0252 (19)	0.0103 (10)	0.0135 (13)	0.0002 (8)	0.0035 (11)	11.89
$C_{\alpha CM3}$	0.0048 (8)	0.0101 (10)	0.0386 (29)	0.0024 (7)	0.0033 (11)	−0.0042 (14)	12.70
$C_{\alpha CM4}$	0.0093 (8)	0.0066 (6)	0.0135 (10)	−0.0046 (6)	−0.0001 (7)	−0.0007 (6)	9.26
$C_{\alpha CM5}$	0.176 (14)	0.0062 (5)	0.0072 (6)	−0.0020 (7)	0.0023 (7)	−0.0023 (5)	9.76
$C_{\alpha CM6}$	0.0109 (9)	0.0048 (4)	0.0098 (7)	0.0010 (5)	−0.0028 (6)	−0.0001 (4)	8.75
$C_{\alpha DMF1}$[c]	0.0364 (28)	0.0124 (10)	0.0044 (5)	−0.0142 (14)	−0.0015 (9)	0.0013 (6)	11.51
$N_{\alpha DMF1}$[c]	0.0147 (9)	0.0111 (6)	0.0033 (3)	−0.0057 (6)	−0.0007 (4)	−0.0003 (3)	8.46
$C_{\alpha DMFM1}$[d]	0.0127 (14)	0.0248 (22)	0.0126 (12)	−0.0080 (14)	−0.0034 (11)	0.0066 (13)	15.67
$C'_{\alpha DMFM1}$[d]	0.0292 (27)	0.0210 (19)	0.0077 (9)	0.0109 (18)	0.0059 (12)	0.0009 (10)	16.55
$C_{\alpha DMF2}$[c]	0.0192 (14)	0.0054 (5)	0.0069 (6)	0.0026 (7)	0.0008 (7)	0.0014 (4)	9.67
$N_{\alpha DMF2}$[c]	0.0186 (11)	0.0059 (4)	0.0062 (3)	0.0044 (5)	0.0030 (5)	0.0019 (3)	8.89
$C_{\alpha DMFM2}$[d]	0.0277 (23)	0.0057 (6)	0.0131 (12)	0.0001 (9)	0.0050 (13)	0.0036 (7)	13.20
$C'_{\alpha DMFM2}$[d]	0.0121 (13)	0.0221 (9)	0.0130 (13)	0.0080 (13)	0.0019 (10)	0.0041 (12)	15.24
Eu_{β}	0.00616 (2)	0.00272 (1)	0.00414 (2)	−0.0004 (1)	0.00032 (1)	−0.00001 (1)	4.59
$O_{\beta A1}$	0.0081 (4)	0.0038 (2)	0.0051 (2)	−0.0003 (2)	0.0001 (2)	0.0004 (2)	6.02
$O_{\beta A2}$	0.0060 (3)	0.0037 (2)	0.0062 (3)	−0.0003 (2)	−0.0004 (2)	0.0006 (2)	5.80
$O_{\beta B1}$	0.0086 (4)	0.0035 (2)	0.0052 (2)	0.0000 (2)	0.0014 (2)	−0.0005 (2)	5.94
$O_{\beta B2}$	0.0079 (4)	0.0039 (2)	0.0041 (2)	−0.0005 (2)	0.0006 (2)	0.0005 (2)	5.61
$O_{\beta C1}$	0.0072 (4)	0.0038 (2)	0.0066 (3)	−0.0010 (2)	0.0002 (3)	0.0012 (2)	6.21
$O_{\beta C2}$	0.0062 (3)	0.0027 (2)	0.0075 (3)	−0.0008 (2)	0.0013 (3)	−0.0003 (2)	5.53
$O_{\beta DMF1}$[c]	0.0121 (6)	0.0031 (2)	0.0065 (3)	−0.0020 (3)	−0.0004 (3)	0.0000 (2)	6.82
$O_{\beta DMF2}$[c]	0.0115 (5)	0.0042 (2)	0.0042 (2)	−0.0003 (3)	0.0019 (3)	−0.0003 (2)	6.68
$C_{\beta A1}$	0.0089 (7)	0.0035 (3)	0.0063 (4)	0.0001 (4)	−0.0006 (4)	0.0009 (3)	6.45
$C_{\beta A2}$	0.0080 (6)	0.0036 (3)	0.0046 (4)	−0.0006 (3)	−0.0015 (4)	0.0000 (2)	5.59
$C_{\beta A3}$	0.0068 (6)	0.0047 (3)	0.0061 (4)	−0.0011 (4)	−0.0011 (4)	0.0010 (3)	6.33
$C_{\beta A4}$	0.0038 (4)	0.0036 (3)	0.0058 (4)	−0.0005 (2)	−0.0009 (3)	0.0000 (2)	4.72
$C_{\beta A5}$	0.0078 (7)	0.0087 (6)	0.0076 (6)	−0.0040 (6)	−0.0019 (5)	0.0036 (5)	7.72
$C_{\beta AM1}$	0.0133 (11)	0.0059 (5)	0.0114 (10)	0.0022 (6)	0.0015 (8)	0.0030 (6)	10.15
$C_{\beta AM2}$	0.0281 (20)	0.0056 (5)	0.0048 (5)	0.0002 (8)	0.0004 (8)	0.0010 (4)	10.12
$C_{\beta AM3}$	0.0121 (11)	0.0060 (6)	0.0170 (12)	−0.0035 (6)	−0.0044 (9)	0.0044 (7)	10.54
$C_{\beta AM4}$	0.0093 (10)	0.0276 (21)	0.0130 (12)	−0.0053 (12)	−0.0013 (9)	0.0129 (13)	13.08
$C_{\beta AM5}$	0.0092 (9)	0.0114 (10)	0.0164 (13)	0.0055 (8)	0.0056 (9)	0.0059 (9)	10.97
$C_{\beta AM6}$	0.0158 (17)	0.0142 (14)	0.0322 (27)	−0.0107 (13)	0.0100 (18)	−0.0090 (16)	15.83
$C_{\beta B1}$	0.0086 (7)	0.0053 (4)	0.0073 (5)	0.0004 (4)	0.0003 (5)	−0.0025 (4)	7.36
$C_{\beta B2}$	0.0049 (4)	0.0046 (3)	0.0055 (4)	−0.0001 (3)	−0.0006 (3)	−0.0012 (3)	5.48
$C_{\beta B3}$	0.0075 (6)	0.0050 (4)	0.0044 (4)	0.0009 (4)	−0.0005 (4)	−0.0002 (3)	6.16
$C_{\beta B4}$	0.0045 (4)	0.0059 (4)	0.0045 (3)	−0.0006 (3)	−0.0005 (3)	0.0007 (3)	5.44
$C_{\beta B5}$	0.0081 (6)	0.0070 (5)	0.0049 (4)	−0.0001 (4)	0.0006 (4)	0.0024 (4)	6.92
$C_{\beta BM1}$	0.0340 (26)	0.0104 (9)	0.0065 (7)	−0.0001 (13)	−0.0039 (10)	−0.0043 (6)	11.80
$C_{\beta BM2}$	0.0210 (17)	0.0092 (8)	0.0118 (10)	0.0105 (10)	−0.0079 (10)	−0.0042 (7)	11.42

Table II (*Continued*)

atom designator[b]	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}	B, Å^2 [e]
$C_{\beta BM_3}$	0.0241 (23)	0.0058 (7)	0.0360 (29)	0.0086 (10)	0.0168 (21)	−0.0083 (12)	14.72
$C_{\beta BM_4}$	0.0232 (18)	0.0097 (8)	0.0047 (5)	−0.0042 (10)	0.0021 (8)	0.0004 (5)	11.26
$C_{\beta BM_5}$	0.0219 (19)	0.0180 (15)	0.0205 (17)	0.0026 (15)	−0.0118 (15)	0.0146 (14)	12.31
$C_{\beta BM_6}$	0.0117 (10)	0.0103 (8)	0.0104 (8)	−0.0155 (8)	−0.0002 (7)	0.0052 (7)	10.46
$C_{\beta C_1}$	0.0072 (6)	0.0066 (5)	0.0092 (7)	−0.0006 (5)	−0.0003 (5)	0.0015 (5)	8.46
$C_{\beta C_2}$	0.0047 (4)	0.0046 (3)	0.0052 (4)	0.0011 (3)	0.0001 (3)	−0.0008 (3)	5.30
$C_{\beta C_3}$	0.0061 (5)	0.0037 (3)	0.0065 (5)	0.0002 (3)	0.0006 (4)	−0.0002 (3)	5.93
$C_{\beta C_4}$	0.0067 (5)	0.0055 (4)	0.0044 (4)	−0.0025 (4)	0.0013 (3)	−0.0006 (3)	5.66
$C_{\beta C_5}$	0.0088 (7)	0.0044 (4)	0.0083 (6)	−0.0031 (4)	0.0021 (5)	−0.0011 (4)	6.90
$C_{\beta CM_1}$	0.0199 (17)	0.0080 (7)	0.0114 (10)	0.0047 (9)	−0.0018 (10)	0.0042 (7)	12.20
$C_{\beta CM_2}$	0.0128 (11)	0.0080 (7)	0.0116 (9)	0.0017 (7)	0.0017 (7)	−0.0040 (6)	11.11
$C_{\beta CM_3}$	0.0060 (7)	0.0084 (8)	0.0229 (17)	0.0010 (6)	0.0021 (9)	0.0028 (9)	11.49
$C_{\beta CM_4}$	0.0128 (13)	0.0054 (6)	0.0334 (26)	−0.0034 (7)	−0.0016 (15)	0.0058 (10)	12.98
$C_{\beta CM_5}$	0.0425 (34)	0.0097 (9)	0.0082 (8)	−0.0134 (15)	0.0004 (13)	−0.0022 (7)	13.61
$C_{\beta CM_6}$	0.0177 (15)	0.0067 (6)	0.0222 (17)	−0.0060 (8)	0.0135 (14)	−0.0033 (8)	11.12
$C_{\beta DMF_1}$[c]	0.0096 (7)	0.0059 (4)	0.0037 (3)	−0.0002 (4)	0.0004 (4)	−0.0003 (3)	6.66
$N_{\beta DMF_1}$[c]	0.0098 (6)	0.0069 (4)	0.0047 (3)	0.0000 (4)	0.0004 (4)	−0.0001 (3)	7.67
$C_{\beta DMFM_1}$[d]	0.0135 (11)	0.0108 (8)	0.0060 (6)	−0.0018 (8)	0.0006 (6)	0.0031 (5)	10.06
$C_{\beta DMFM_1}$	0.0260 (22)	0.0083 (8)	0.0099 (9)	0.0006 (10)	0.0073 (11)	−0.0026 (7)	12.91
$C_{\beta DMF_2}$[c]	0.0229 (18)	0.0040 (4)	0.0129 (10)	−0.0033 (7)	0.0017 (11)	−0.0010 (5)	11.35
$N_{\beta DMF_2}$[c]	0.0143 (8)	0.0032 (3)	0.0089 (5)	−0.0013 (4)	0.0004 (5)	−0.0003 (3)	8.28
$C_{\beta DMFM_2}$[c]	0.0565 (48)	0.0088 (9)	0.0086 (10)	−0.0061 (17)	0.0086 (17)	−0.0013 (8)	16.41
$C'_{\beta DMFM_2}$[d]	0.0727 (68)	0.0060 (8)	0.0136 (15)	−0.0050 (19)	0.0049 (25)	0.0008 (9)	19.77

[a] Numbers in parentheses are the estimated standard deviations. [b] In addition to the numerical subscript each atom has several literal designators. The α and β subscript refers to the isomer and the subscript A, B, or C refers to a particular chelate ring. See Figure 2. [c] The subscript DMF indicates the atoms in a unidentate dimethylformamide ligand. [d] The descriptor DMFM is used for the methyl group carbon atoms of the dimethylformamide molecules. [e] Isotropic thermal parameter calculated from $B = 4V^2 \det|\beta_{ij}|^{1/3}$, wherein V is the volume of the unit cell. The estimated standard deviation for the isotropic thermal parameter is 0.05.

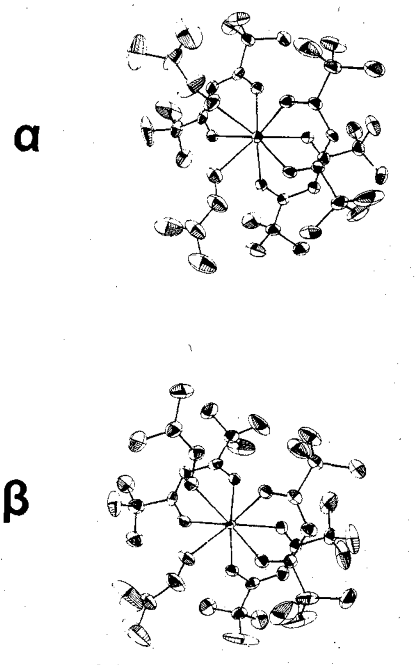

Figure 1. Structures of the two isomers of Eu(thd)$_3$(DMF)$_2$.

describe the observed polyhedron in terms of either the square antiprism (point symmetry $\bar{8}2m$) or the triangular dodecahedron (point symmetry $\bar{4}2m$). Often the choice is not obvious, particularly in mixed-ligand chelates, and must be based on the degree of overall approximation to the ideal. In their classic paper on eight-coordinate stereochemistry, Hoard and Silverton[28] present shape parameters which are useful in describing the two prominent ideal octacoordinate polyhedra. Parameters of "most favorable" coordination polyhedra for both the hard sphere approximation and the model incorporating the minimization of ligand repulsive energy were calculated by Hoard and Silverton for the two ideal MX$_8$ configurations. Although derived principally for MO$_8$ groups in which the central ion has a d^0 electron configuration, these parameters have been used in describing the shapes of other octacoordinate complexes.

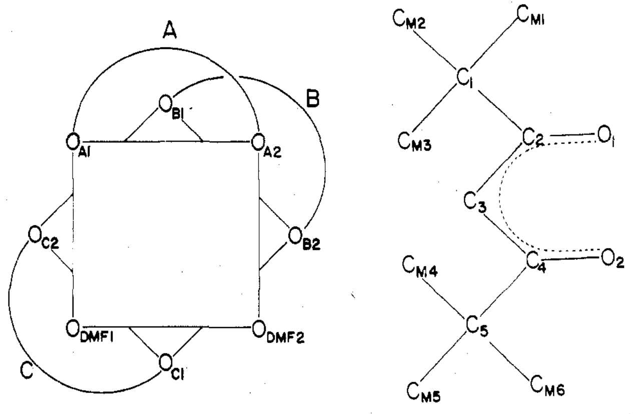

Figure 2. Schematic representation of a square antiprism, showing the ligand connectivity exhibited in crystalline Eu(thd)$_3$(DMF)$_2$, and a diagram of a thd anion, showing numbering schemes employed for the atoms.

Lippard and Russ[29] have presented other criteria which are also useful aids for determining which ideal polyhedron is more closely approximated by an observed configuration. This method is based on visualizing a dodecahedron as consisting of two mutually perpendicular trapezoids; the line of intersection coincides with the $\bar{4}$ axis and contains the central metal atom.[28] Conceptually, the square antiprism is derivable from the dodecahedron by small displacements of the vertices. The atoms constituting the original trapezoids form nonplanar arrays in the square antiprism, and the best planes through these arrays are not perpendicular but intersect at an angle of 77.4°.

Tables III and IV contain the calculated values of the various shape parameters for the two isomers observed in

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(28) J. L. Hoard and J. V. Silverton, *Inorg. Chem.*, 2, 235 (1963).

(29) S. J. Lippard and B. J. Russ, *Inorg. Chem.*, 7, 1686 (1968).

Table III. Shape Parameters for the Independent EuO_8 Coordination Polyhedra[a]

Antiprism[b]

CP	l	s	l/s	θ, deg
EuO_8(α isomer)	1.266 (0.020)	1.186 (0.031)	1.068	56.9 (2.4)
EuO_8(β isomer)	1.275 (0.025)	1.182 (0.032)	1.079	56.6 (2.0)
MFP	1.258	1.190	1.057	57.3
HSM	1.215	1.215	1.000	59.25

Dodecahedron[c,d]

CP	a	m	g	b	θ_A, deg	θ_B, deg	M-A/M-B
EuO_8(α isomer)	1.280 (0.002)	1.212 (0.009)	1.217 (0.058)	1.466 (0.230)	39.6 (0.7)	70.4 (1.7)	1.009
EuO_8(β isomer)	1.284 (0.001)	1.191 (0.028)	1.230 (0.053)	1.454 (0.216)	39.6 (0.8)	71.4 (1.4)	1.009
MFP	1.17	1.17	1.24	1.49	35.2	73.5	1.03
HSM	1.199	1.199	1.199	1.499	36.9	69.5	1.00

[a] Nomenclature, definitions, and the values of the parameters for the coordination polyhedra (CP) of $\bar{8}2m$ and $\bar{4}2m$ symmetry and for both hard sphere models (HSM) are those found in ref 28. The normalizing factor for each EuO_8 grouping is the average of the eight Eu–O bond lengths. Numbers in parentheses are the mean deviations from the averages. [b] For each EuO_8 group the principal quasi-symmetry axis was taken to be coincident with the vector joining the europium atom and the midpoint of the quadrilateral formed by the four β-diketonate oxygen atoms of ligands B and C (see Figure 2). [c] The principal quasi-symmetry axis in each isomer was taken to be coincident with the vector joining the europium atom and the midpoint of the line joining $O_{\alpha A_2}$–$O_{\alpha B_1}$ and $O_{\beta A_2}$–$O_{\beta B_1}$ (see Figure 2). [d] Presented are only the calculations for the polyhedra which most closely approximated the ideal symmetries for the square antiprism and the dodecahedron.

Table IV.[a] Coefficients for Various Mean Planes in the Coordination Polyhedra of $Eu(thd)_3(DMF)_2$

atoms used for determination of mean plane	A	B	C	D	mean dev, Å
		α-Isomer			
$O_{\alpha A_1}$, $O_{\alpha A_2}$, $O_{\alpha DMF_1}$, $O_{\alpha DMF_2}$	0.504	0.348	−0.790	−11.956	0.04
$O_{\alpha B_1}$, $O_{\alpha B_2}$, $O_{\alpha C_1}$, $O_{\alpha C_2}$	0.521	0.338	−0.784	−9.442	0.08
$O_{\alpha B_1}$, $O_{\alpha B_2}$, $O_{\alpha DMF_1}$, $O_{\alpha DMF_2}$	0.896	0.294	−0.333	−16.136	0.32
$O_{\alpha A_1}$, $O_{\alpha A_2}$, $O_{\alpha_2 C_1}$, $O_{\alpha C_2}$	−0.161	0.160	−0.974	1.866	0.31
		β-Isomer			
$O_{\beta A_1}$, $O_{\beta A_2}$, $O_{\beta DMF_1}$, $O_{\beta DMF_2}$	−0.521	−0.308	−0.796	11.620	0.01
$O_{\beta B_1}$, $O_{\beta B_2}$, $O_{\beta C_1}$, $O_{\beta C_2}$	−0.536	−0.274	−0.798	8.884	0.07
$O_{\beta B_1}$, $O_{\beta B_2}$, $O_{\beta DMF_1}$, $O_{\beta DMF_2}$	−0.886	−0.092	−0.454	7.579	0.38
$O_{\beta A_1}$, $O_{\beta A_2}$, $O_{\beta C_1}$, $O_{\beta C_2}$	0.174	−0.400	−0.900	7.502	0.39

[a] The coefficients refer to the equation of a plane in an orthonormal coordinate system derived from the crystal system. The equation of a general plane is $AX + BY + CZ + D = 0$.

crystalline $Eu(thd)_3(DMF)_2$. For each isomer the value (presented in Table III) of a parameter describing an edge length is an average of at least two independent distances and is normalized to the mean of the eight Eu–O bond lengths; the θ parameters are averages of at least four individual angles. Since this procedure obscures wide variations in the individual values being averaged, the mean deviation from the average is presented for each parameter to emphasize the nonequivalence. The widest variation, in each isomer, appears in the b edge of the dodecahedral description; the nonnormalized distances used to calculate the average values are 2.976, 2.930, 4.025, and 4.077 Å for the α isomer and 2.938, 3.010, 3.984, and 4.017 Å for the β isomer. With reference to Table III, the observed parameters for each isomer are in overall better agreement with the values calculated for the coordination polyhedron of $\bar{8}2m$ symmetry than for any of the three other ideal polyhedra. The maximum difference between an observed and corresponding ideal shape parameter in this case is only 2.1% (for the ratio l/s), while for the dodecahedral shape parameters the maximum difference is 12.5%, between the angle θ_A of both isomers and the configuration of point symmetry $\bar{4}2m$.

Table IV contains the coefficients of the best planes for various sets of four atoms in the two polyhedra. The first two sets listed for each isomer are the atoms forming the quadrilateral faces of the distorted square antiprisms; the second two sets constitute the intersecting trapezoids in the approximate dodecahedron description. In addition to the coefficients of the best planes defined by each set, the mean deviation of an atom from this plane is also given. The dihedral angle between the planes of the trapezoids in the α isomer is 76.9°, and in the β isomer this angle is calculated to be 77.5°. These values are nearer to the dihedral angle of 77.4° calculated by Lippard and Russ than to the 90° angle required in the ideal dodecahedral configuration.

Further support for this choice of description can be gained from other data presented in Table IV. In both isomers the mean deviations of an atom from the best planes calculated for the sets of atoms defining the trapezoids are significantly larger than the average displacement of an atom from the planes of the quadrilateral faces. These deviations are in the direction expected for a square antiprism mistakenly identified as a dodecahedron.[29] Additionally, the square faces of an ideal square antiprism are parallel; in the α and β isomers the angles of inclination are calculated to be 1.2 and 2.1°, respectively. Although no crystallographically required symmetry is imposed on either isomer and neither coordination polyhedron has greater than the trivial C_1 rotation symmetry, the overall degree of approximation between observed and calculated shape parameters of both the α and β isomer polyhedra is best when comparison is made with respect to the ideal geometry of $\bar{8}2m$ symmetry. Further discussions of the observed coordination geometries will, therefore, be in terms of distorted square antiprisms.

In contrast to the ligand and bonding patterns displayed in the bis adducts $Ho(thd)_3(4\text{-pic})_2$[14] and $Eu(thd)_3(py)_2$,[15] the DMF ligands are cis on the same square face. The orientations of the bidentate thd ligands are such that no edge joining the square faces of the coordination polyhedron is spanned. A similar molecular stereochemistry is exhibited by both crystalline $La(acac)_3(H_2O)_2$[30] and $Y(acac)_3(H_2O)_2 \cdot H_2O$[31] and is

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(30) T. Phillips, II, D. E. Sands, and W. F. Wagner, *Inorg. Chem.*, **7**, 2295 (1968).

Table V. Distances and Angles in the Coordination Polyhedra[a]

type	α isomer	β isomer	type	α isomer	β isomer
		Distances,[b] Å			
$O_{DMF1}-O_{DMF2}$	2.874 (9)	2.939 (7)	$O_{A1}-O_{C2}$	2.976 (6)	3.168 (7)
$O_{DMF1}-O_{A1}$	2.877 (8)	2.860 (7)	$O_{A1}-O_{B1}$	3.115 (7)	3.000 (9)
$O_{DMF1}-O_{C1}$	3.054 (8)	2.969 (8)	$O_{A2}-O_{B1}$	3.064 (7)	2.992 (7)
$O_{DMF1}-O_{C2}$	2.982 (8)	3.056 (7)	$O_{A2}-O_{B2}$	3.038 (7)	3.061 (7)
$O_{DMF2}-O_{A2}$	2.915 (7)	2.870 (8)	$O_{B1}-O_{B2}$[c]	2.750 (6)	2.736 (6)
$O_{DMF2}-O_{B2}$	2.930 (7)	3.094 (7)	$O_{B1}-O_{C2}$	2.921 (6)	2.839 (6)
$O_{DMF2}-O_{C1}$	3.049 (7)	2.938 (8)	$O_{B2}-O_{C1}$	2.874 (6)	2.863 (7)
$O_{A1}-O_{A2}$[c]	2.741 (6)	2.703 (7)	$O_{C1}-O_{C2}$[c]	2.708 (6)	2.748 (6)
		Angles,[d] deg			
$O_{DMF1}-O_{DMF2}-O_{A2}$	88.5	88.5	$O_{A1}-O_{DMF1}-O_{C2}$	61.0	64.6
$O_{DMF2}-O_{DMF1}-O_{A1}$	88.8	86.8	$O_{DMF1}-O_{C2}-O_{A1}$	57.8	54.7
$O_{DMF2}-O_{A2}-O_{A1}$	90.7	91.2	$O_{C2}-O_{DMF1}-O_{A1}$	61.2	60.6
$O_{A2}-O_{A1}-O_{DMF1}$	91.9	93.5	$O_{C1}-O_{B2}-O_{DMF2}$	63.4	58.9
$O_{C2}-O_{B1}-O_{B2}$	91.9	88.3	$O_{B2}-O_{DMF2}-O_{C1}$	57.4	56.6
$O_{B1}-O_{B2}-O_{C1}$	86.9	91.6	$O_{DMF2}-O_{C1}-O_{B2}$	59.2	64.4
$O_{B2}-O_{C1}-O_{C2}$	93.8	87.6	$O_{B1}-O_{B2}-O_{A2}$	63.7	61.8
$O_{C1}-O_{C2}-O_{B1}$	86.7	91.9	$O_{B2}-O_{A2}-O_{B1}$	53.6	53.7
$O_{DMF1}-O_{C1}-O_{DMF2}$	56.2	59.7	$O_{A2}-O_{B1}-O_{B2}$	62.7	64.4
$O_{C1}-O_{DMF2}-O_{DMF1}$	62.0	60.7	$O_{B1}-O_{C2}-O_{A1}$	63.8	59.8
$O_{DMF1}-O_{DMF2}-O_{C1}$	61.8	59.6	$O_{C2}-O_{A1}-O_{B1}$	57.2	54.6
$O_{DMF2}-O_{A2}-O_{B2}$	58.9	62.8	$O_{A1}-O_{B1}-O_{C2}$	59.0	65.5
$O_{A2}-O_{B2}-O_{DMF2}$	58.4	55.6	$O_{C2}-O_{C1}-O_{DMF1}$	62.0	64.5
$O_{B2}-O_{DMF2}-O_{A2}$	62.6	61.6	$O_{C1}-O_{DMF1}-O_{C2}$	53.3	54.2
$O_{A2}-O_{A1}-O_{B1}$	62.7	62.9	$O_{DMF1}-O_{C2}-O_{C1}$	64.7	61.3
$O_{A1}-O_{B1}-O_{A2}$	52.7	53.5			
$O_{B1}-O_{A2}-O_{A1}$	64.6	63.6			

[a] See Figure 2 for numbering scheme. [b] Numbers in parentheses are the estimated standard deviation in the least significant digit. [c] The bite of the ligand. [d] The estimated standard deviation of all angles cited in this table is 0.2°.

schematically presented in Figure 2. Of the eight geometric isomers[32] possible for complexes of the stoichiometry $M(O-O)_3X_2$ based on square-antiprismatic coordination, examples of two have now been found by single-crystal structure determinations. It is now clear the the bulkiness of *tert*-butyl groups is not as great as was originally thought; there appears to be sufficient room for many different orientations of ligands. Consequently, one might expect a great variety of geometrical isomers to exist. Indeed, almost every structure of lanthanide–thd chelates that has been determined has shown appreciable differences in coordination geometry. Scale models indicate that the molecular configurations observed for crystalline $Eu(thd)_3(py)_2$ and $Ho(thd)_3(4\text{-pic})_2$ can also be assumed by the complex $Eu(thd)_3(DMF)_2$ with no abnormally short interligand contacts. Further, it is also possible, with minor distortions of the coordination polyhedra, to arrange the three thd and two DMF ligands around the Eu(III) ion in any of the patterns consistent with the eight possible configurations. The apparent wide range of ring folding possible for lanthanide–β-diketonato complexes, as evidenced by the values given in Table VIII and results from other structural studies, and virtually unhindered rotation around the C_1-C_2 and C_4-C_5 bonds (vide infra) may be used to arrange the ligands so as to minimize ligand–ligand interactions in any of the eight motifs. Constraints imposed by the "bite" of the bidentate ligand cause several of the configurations to undergo distortions toward a dodecahedral arrangement. In particular, the polyhedra shifted most toward dodecahedral configurations are those in which at least two of the bidentate ligands span an *l* edge in the square-antiprism notation. In connection with this, it is of interest to note that the ratio of the average "bite" of the thd ligand to the average $Eu-O_{thd}$ bond length closely approximates the values of the shape parameters *a* and *m* in the dodecahedron of $\bar{4}2m$ symmetry (1.16 vs. 1.17 Å), and thus dodecahedral coordination geometry may be preferred in these cases.

Table V contains distances and angles[33] observed in the coordination polyhedra of the two isomers present in crystalline $Eu(thd)_3(DMF)_2$. Inspection of the values displayed in this table reveals that significant differences exist between the polyhedra of the α and β isomers. The largest difference, 0.19 Å, is between the two similar edges defined by the lines joining O_{A1} and O_{C2}. Differences of 0.16, 0.11, and 0.11 Å exist between the pairs of similar edges defined by $O_{DMF_2}-O_{B2}$, $O_{DMF2}-O_{C1}$, and $O_{A1}-O_{B1}$, respectively. Differences in the angles of various facial vertices are also present and significant. The largest inequality of 6.5° is between the two linkages defined by $O_{A1}-O_{B1}-O_{C2}$. Other large differences between pairs of similar vertices are 6.2 and 5.2° for the angles defined by the groups $O_{B2}-O_{C1}-O_{C2}$ and $O_{C1}-O_{C2}-O_{B1}$, respectively. We attribute these differences, both angular and distance, to result from crystal packing forces acting upon the molecules and conclude that the large lanthanide complexes are not stereochemically rigid. Consequently, the lack of rigorous axial symmetry in the solid-state structures does not necessarily mean that a configuration of higher symmetry is unattainable in solution.

Releasing the molecules from the constraints imposed by the crystal lattice presumably allows the geometrically nonequivalent polyhedra to assume a single, time-averaged configuration not necessarily related in all detail to either of the two solid-state configurations. Facile ligand exchange (both the DMF and β-diketonate undergo fast exchange on the NMR time scale) and intramolecular reorganizations further complicate the correlation of the solution conformation with the crystal structures. Because rearrangements of seven- and

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(31) J. A. Cunningham, D. E. Sands, and W. F. Wagner, *Inorg. Chem.*, **6**, 499 (1967).

(32) The eight possible geometric isomers have been depicted by W. DeW. Horrocks, Jr., et al., in chapter 3 of ref 3, p 77.

(33) Estimated standard deviations in bond length and angles were calculated following W. R. Busing, K. O. Martin, and H. A. Levy, "ORFFFE, a Fortran Crystallographic Function and Error Program", ORNL-TM-306, Oak Ridge National Laboratory, Oak Ridge, TN, 1964.

Table VI. Bond Lengths (A) in the Metal Chelate Rings[a]

	α isomer			β isomer			
type[b]	ring A	ring B	ring C	ring A	ring B	ring C	av[c]
Eu-O$_1$	2.364 (4)	2.336 (5)	2.362 (4)	2.364 (5)	2.326 (4)	2.362 (5)	2.361 (26)
Eu-O$_2$	2.413 (4)	2.362 (4)	2.345 (4)	2.371 (5)	2.353 (4)	2.370 (4)	
O$_1$-O$_2$	1.234 (8)	1.254 (9)	1.243 (8)	1.267 (9)	1.253 (9)	1.265 (8)	1.255 (13)
O$_2$-C$_4$	1.259 (7)	1.273 (8)	1.254 (8)	1.219 (8)	1.268 (9)	1.272 (9)	
C$_2$-C$_3$	1.391 (10)	1.387 (10)	1.384 (8)	1.395 (11)	1.400 (11)	1.337 (11)	1.387 (13)
C$_3$-C$_4$	1.338 (8)	1.393 (10)	1.425 (11)	1.417 (10)	1.383 (11)	1.390 (11)	
C$_1$-C$_2$	1.573 (10)	1.571 (10)	1.534 (10)	1.555 (10)	1.565 (11)	1.611 (12)	1.560 (18)
C$_4$-C$_5$	1.568 (10)	1.517 (10)	1.545 (11)	1.564 (11)	1.578 (10)	1.540 (10)	
C$_1$-C$_{m1}$	1.548 (14)	1.586 (10)	1.464 (15)	1.548 (13)	1.494 (15)	1.559 (17)	1.526 (39)
C$_1$-C$_{m2}$	1.564 (14)	1.555 (10)	1.489 (16)	1.564 (14)	1.480 (15)	1.566 (15)	
C$_1$-C$_{m3}$	1.496 (16)	1.582 (10)	1.474 (18)	1.530 (13)	1.499 (18)	1.549 (14)	
C$_5$-C$_{m4}$	1.490 (14)	1.553 (14)	1.556 (12)	1.436 (16)	1.589 (15)	1.455 (18)	
C$_5$-C$_{m5}$	1.585 (14)	1.563 (12)	1.540 (13)	1.538 (15)	1.442 (15)	1.513 (16)	
C$_5$-C$_{m6}$	1.552 (14)	1.557 (14)	1.541 (13)	1.485 (20)	1.516 (14)	1.488 (14)	
O$_1$-O$_2$[d]	2.741 (6)	2.750 (6)	2.708 (6)	2.703 (7)	2.736 (6)	2.748 (6)	2.731 (17)

[a] The numbers in parentheses are the estimated standard deviation in the last significant figures. [b] For number scheme see Figure 2. [c] Numbers in parentheses are the mean deviation from the average. [d] The "bite" of the β-diketonate ligand.

Table VII. Bond Angles (Deg) in the Metal-Chelate Rings[a]

	α isomer			β isomer			
type[b]	ring A	ring B	ring C	ring A	ring B	ring C	av[c]
O$_1$-Eu-O$_2$	70.0 (1)	71.7 (2)	70.2 (2)	69.6 (2)	71.6 (2)	71.0 (2)	70.7 (8)
Eu-O$_1$-C$_2$	135.0 (4)	135.0 (4)	138.8 (5)	137.0 (4)	138.1 (5)	132.2 (4)	136.0 (1.5)
Eu-O$_2$-C$_4$	134.3 (4)	136.4 (4)	138.0 (4)	134.6 (5)	136.4 (5)	136.7 (4)	
O$_1$-C$_2$-C$_3$	125.4 (6)	126.7 (6)	125.3 (6)	123.2 (6)	125.6 (6)	130.8 (6)	125.6 (1)
O$_2$-C$_4$-C$_3$	124.7 (6)	124.0 (6)	124.7 (6)	125.3 (6)	126.2 (7)	125.0 (6)	
C$_2$-C$_3$-C$_4$	124.7 (6)	123.1 (6)	121.6 (6)	122.4 (7)	122.0 (7)	120.9 (6)	122.4 (1.0)
O$_1$-C$_2$-C$_1$	114.6 (6)	114.6 (6)	116.3 (7)	117.5 (6)	114.4 (7)	109.9 (6)	114.3 (1.0)
O$_2$-C$_4$-C$_5$	114.2 (6)	114.0 (6)	114.2 (6)	113.9 (6)	114.2 (7)	113.7 (7)	
C$_1$-C$_2$-C$_3$	120.6 (6)	118.7 (7)	118.4 (6)	119.2 (6)	120.0 (7)	119.2 (6)	120.1 (8)
C$_5$-C$_4$-C$_3$	120.3 (6)	122.0 (6)	121.1 (6)	120.8 (6)	119.6 (7)	121.3 (7)	
C$_2$-C$_1$-C$_{M1}$	113.8 (7)	105.6 (7)	111.1 (7)	107.4 (9)	114.4 (9)	106.5 (8)	
C$_2$-C$_1$-C$_{M2}$	108.1 (7)	112.7 (7)	105.2 (7)	114.9 (8)	107.6 (7)	109.4 (8)	
C$_2$-C$_1$-C$_{M3}$	106.8 (8)	107.0 (7)	115.6 (9)	104.1 (1.0)	107.0 (8)	109.7 (8)	
C$_{M1}$-C$_1$-C$_{M2}$	104.5 (1.0)	110.5 (8)	111.0 (1.2)	117.2 (1.3)	110.0 (1.0)	110.8 (1.0)	
C$_{M1}$-C$_1$-C$_{M3}$	113.2 (1.1)	110.8 (8)	107.4 (1.2)	106.5 (1.6)	112.2 (1.3)	111.8 (1.0)	
C$_{M2}$-C$_1$-C$_{M3}$	110.3 (1.1)	110.1 (9)	106.4 (1.4)	105.7 (1.3)	105.1 (1.4)	108.7 (1.0)	
C$_4$-C$_5$-C$_{M4}$	108.1 (8)	106.3 (7)	114.2 (8)	112.3 (7)	110.7 (8)	111.4 (8)	
C$_4$-C$_5$-C$_{M5}$	108.0 (7)	113.5 (7)	105.9 (7)	105.6 (6)	108.0 (7)	106.6 (8)	
C$_4$-C$_5$-C$_{M6}$	111.9 (7)	108.5 (7)	109.2 (6)	109.3 (7)	109.4 (7)	111.6 (7)	109.5 (2.4)
C$_{M4}$-C$_5$-C$_{M5}$	108.5 (9)	109.9 (8)	107.5 (8)	104.5 (9)	110.4 (1.2)	108.9 (1.4)	
C$_{M4}$-C$_5$-C$_{M6}$	110.3 (1.2)	112.2 (1.0)	109.5 (8)	109.6 (8)	108.6 (9)	107.8 (1.2)	
C$_{M5}$-C$_5$-C$_{M6}$	109.9 (1.0)	106.5 (7)	110.5 (8)	112.5 (1.0)	115.6 (1.2)	110.4 (1.2)	

[a] Numbers in parentheses are estimated standard deviations in the least significant digits. [b] For number scheme see Figure 2. [c] Numbers in parentheses are the mean deviation from the average.

Table VIII.[a] Deviations from Planarity and Foldings of Chelate Rings

ring[b]	mean dev of an atom from the mean plane, A	Eu, A	folding,[c] deg
	α Isomer		
A	0.011 (7)	0.59	17.5
B	0.019 (6)	0.40	12.0
C	0.022 (9)	0.24	20.2
	β Isomer		
A	0.007 (2)	0.64	19.2
B	0.002 (9)	0.08	2.5
C	0.028 (8)	0.41	11.7

[a] Figures in parentheses are the estimated standard deviations. [b] See Figure 2 for ring labeling scheme. [c] Folding is along the line joining the two oxygen atoms of the chelate ring.

eight-coordinate lanthanide complexes are so facile, the complex may actually have a higher effective symmetry in solution than in the solid state, allowing the simplified McConnell-Robertson equation (eq 1) to reproduce shifts observed in NMR spectra. Low potential energy barriers[28,34-36] between the idealized higher coordinate polyhedra might also permit the time-averaged solution configuration to be significantly different from that displayed in the solid state.

Table IX. Coefficients of the Least-Squares Planes of the *N,N*-Dimethylformamide Ligands[a,b]

ligand	*A*	*B*	*C*	*D*	mean dev, A
α isomer	0.24	0.80	−0.54	−15.55	0.03
α isomer	0.03	0.06	−0.99	−0.28	0.02
β isomer	−0.88	−0.66	−0.48	8.89	0.01
β isomer	0.99	−0.07	−0.07	−5.54	0.01

[a] The coefficients refer to the equation of a plane in an orthonormal coordinate system derived from the crystal system. The equation of a general plane is $AX + BY + CZ + D = 0$. [b] All atoms, of the DMF ligand were included in the calculation.

Important bond lengths and angles within the metal-β-diketonato rings are listed in Tables VI and VII along with

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(34) E. L. Muetterties and C. M. Wright, *Q. Rev., Chem. Soc.*, **21**, 109 (1967).

(35) S. J. Lippard, *Prog. Inorg. Chem.*, **8**, 109 (1967).

(36) E. L. Muetterties, *Inorg. Chem*, **12**, 1963 (1973), and appropriate references contained therein.

Table X. Bond Distances and Angles of the *N,N*-Dimethylformamide Ligands in $Eu(thd)_3(DMF)_2$[a]

	α isomer	β isomer	av[b]
	Distances, A		
$Eu-O_{DMF1}$	2.494 (5)	2.496 (5)	2.471 (24)
$Eu-O_{DMF2}$	2.442 (5)	2.451 (5)	
$O_{DMF1}-C_{DMF1}$	1.02 (1)	1.22 (1)	1.14 (6)
$O_{DMF2}-C_{DMF2}$	1.16 (1)	1.14 (1)	
$C_{DMF1}-N_{DMF1}$	1.28 (1)	1.32 (1)	1.32 (2)
$C_{DMF2}-N_{DMF2}$	1.35 (1)	1.32 (1)	
$N_{DMF1}-C_{DMFM1}$	1.45 (2)	1.51 (2)	1.45 (4)
$N_{DMF2}-C_{DMFM2}$	1.48 (2)	1.38 (2)	
$N_{DMF1}-C'_{DMFM1}$	1.45 (2)	1.45 (2)	
$N_{DMF1}-C'_{DMFM2}$	1.37 (2)	1.51 (2)	
	Angles, deg		
$Eu-O_{DMF1}-C_{DMF1}$	151.5 (9)	129.8 (5)	135.2 (60)
$Eu-O_{DMF2}-C_{DMF2}$	132.3 (7)	127.4 (7)	
$O_{DMF1}-C_{DMF1}-N_{DMF1}$	135.5 (1.3)	124.1 (1.0)	129.5 (3.3)
$O_{DMF2}-C_{DMF2}-N_{DMF2}$	128.3 (1.3)	130.2 (1.3)	
$C_{DMF1}-N_{DMF1}-C_{DMFM1}$	125.2 (1.5)	122.0 (1.0)	122.2 (3.2)
$C_{DMF2}-N_{DMF2}-C_{DMFM2}$	116.9 (1.2)	126.4 (1.2)	
$C_{DMF1}-N_{DMF1}-C'_{DMFM1}$	118.4 (1.4)	118.8 (1.0)	
$C_{DMF2}-N_{DMF2}-C'_{DMFM2}$	125.1 (1.3)	125.1 (1.2)	
$C_{DMFM1}-N_{DMF1}-C'_{DMFM1}$	116.3 (1.3)	119.1 (1.0)	115.5 (3.5)
$C_{DMFM2}-N_{DMF2}-C'_{DMFM2}$	118.0 (1.2)	108.5 (1.1)	

[a] Figures in parentheses are the estimated standard deviations. [b] Figures in parentheses are mean deviation from the average.

the average for each chemically analogous type. Average bond distances and angles calculated for the β-diketonate backbone are in agreement with those found in similar complexes.[9-16,30,31,37] Averaged values for the O═C and C═C bonds of 1.255 (13) and 1.387 (13) Å, respectively, reflect the delocalization of the π-electron system in the β-diketonate skeleton. The mean Eu–O bond distance of 2.361 Å is 0.06 Å shorter than the sum of the empirical crystal radii[38] and may be indicative of some covalent character in these bonds.

A characteristic common to most metal β-diketonato complexes is the planarity of the ring backbone; usually the metal ion is significantly displaced from this plane. Table VIII contains the mean deviation of an atom from the least-squares plane determined for the six groups: O_1–C_2–C_3–C_4–O_2. Also displayed in this table are the displacements of the europium ion from each plane. An alternative description is to regard the nonplanarity of the metal–chelate ring as a folding along the vector joining the two oxygen atoms; Table VIII also contains the calculated angle of folding for each ring. All six rings (three in each isomer) are essentially planar and in only the B ring of the β isomer does the metal ion nearly reside in the plane of the backbone. The degree of folding for the rings within each isomer is not the same, nor is the folding equal for rings occupying similar positions in the coordination polyhedra of the two isomers. Since the isomers contain the same type ligands in the same ratios and have the same gross stereochemistry, the observed differences in foldings of approximately stereochemically equivalent rings is apparently due primarily to crystal packing effects and underscores the stereochemical nonrigidness of these molecules. Inclusion of the carbon atoms C_1 and C_5 in the least-squares plane calculations for each ring consistently resulted in a larger average deviation of an atom from that plane but did not, in any case, significantly alter the calculated angle of folding.

All methyl groups of the 12 *tert*-butyl ring substituents display large anisotropic thermal motions resulting in a wide range of apparent bond lengths within these groups. The use of five crystals during data collection and the lack of corrections for absorption effects preclude an accurate allowance for librational motion, and none were applied. A difference Fourier synthesis, based on $F_o - F_c$ and phased by the contributions of all atoms save the C_M carbon atoms, was calculated on a fine grid over the region of each *tert*-butyl group. It gave no evidence to justify an attempted refinement of a disordered model for any of these groups but rather lent further support to the description of the large ellipsoids as arising from thermal motions. The possibility of static disorderings on a scale too small to be observed with the resolution afforded by the range of recorded $|F_o|$'s can neither be discounted nor confirmed by the present study.

In Figure 1, it is apparent that the major motion of each *tert*-butyl group is oscillation about the C–C σ bond linking the group to the ring backbone. Several orientations of these groups with respect to the planes of the backbones are also present in the structure and we conclude that in a molecule released from any constraints imposed by the crystalline arrangement there is virtually free rotation about this σ bond.

All four unidentate dimethylformamide ligands are bonded to the europium ions through the carbonyl oxygen atoms; the average $Eu-O_{DMF}$ bond length of 2.471 (24) Å is significantly longer than the average bond between an europium ion and an oxygen atom in the thd ligands. This difference may be due in part to the negative charge residing on the β-diketonate oxygen atoms, imposing a greater degree of nucleophilic character on these atoms. The bonding of the DMF molecules via the carbonyl oxygen atom to the central metal ion had previously been deduced from spectral considerations[39] for the seven-coordinate complexes: $Ln(thd)_3(DMF)$.

As expected, each DMF molecule has an essentially planar configuration; the mean deviations of an atom from the least-squares plane for each DMF moiety are 0.03 (1) and 0.02 (1) Å for DMF1 and DMF2 in the α isomer and 0.01 (1) and 0.01 (1) Å for the DMF ligands 1 and 2 in the β isomer, respectively. Table IX contains the coefficients of the mean planes for each of the independent DMF ligands. Within each isomer the planes of these two ligands are not parallel but are inclined at angles of 53.3 and 31.0° in the α and β isomers, respectively. Apparently this difference results from packing effects and allows more efficient packing of these large molecules. The orientations of the DMF ligands in the two isomers are such that steric interactions between the formyl

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hydrogen atoms are minimized. Table X contains the bonding parameters of the four independent DMF ligands. Large thermal parameters, associated with the atoms of these ligands, possibly in part due to the partial decomposition of the sample crystals observed during data collection, have seriously affected the determination of accurate bonding parameters. A Fourier synthesis reveals regions of diffuse electron density for all atoms except the carbonyl oxygen atom in the DMF ligands.

Intermolecular contact distances are normal, with only two methyl–methyl group distances less than 4.0 Å. The distance from $C_{\alpha AM5}$ to $C_{\beta CM5}$ in an adjacent unit cell is 3.87 (2) Å, and the distance from $C_{\beta BM1}$ to $C_{\beta DMFM1}$ of a centrosymmetrically related molecule is 3.85 (2) Å.

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Formation and Reactions of the (Trifluoromethyl)tin Bromides CF_3SnBr_3 and $(CF_3)_2SnBr_2$

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The formation of CF_3SnBr_3 and $(CF_3)_2SnBr_2$ from the reaction of $(CF_3)_2Hg$ and $SnBr_4$ at temperatures of 112, 121, and 130 °C has been followed in a semikinetic manner. The data indicate that the (trifluoromethyl)tin bromides are easily formed in reactions that proceed to equilibria, but the decomposition of more fully substituted species, e.g., $(CF_3)_3SnBr$, is almost immediate and severely limits the temperature range that can be utilized. The methylated compounds $CF_3Sn(CH_3)_3$ and $(CF_3)_2Sn(CH_3)_2$ are easily formed in high yield. The latter reacts with excess $Cd(CH_3)_2$ to yield $CF_3Sn(CH_3)_3$ while the former reacts with CH_3Li to yield $Sn(CH_3)_4$. The formation of an unstable hydride, CF_3SnH_3, is also demonstrated.

Introduction

Since the preparation of the first perfluorinated analogue of an organometallic compound, $(CF_3)_2Hg$,[1] the properties and stabilities of compounds that contain trifluoromethyl–metal or –metalloid linkages have been the subject of many investigations. The most stable of the perfluoromethyl compounds appear to be formed by the smaller, relatively electronegative group 5- and 6A elements. They react with CF_3I at temperatures between 165 and 250 °C to form mononuclear compounds either by direct means or upon UV irradiation.[2] Much less is known about the trifluoromethyl-containing derivatives of the remaining elements, however. In group 3A, for example, although the compound CF_3BF_2 has been prepared and described as "enduringly metastable",[3] trifluoromethyl derivatives of the other elements are unknown, as are boranes containing more than one CF_3 group.

As might be expected the group 4A elements are very representative of the trends observed throughout the periodic table. The fully substituted compounds of the most electronegative elements of this group, $(CF_3)_4C$ and $(CF_3)_4Ge$, have been easily synthesized by a number of methods,[4,5] while the fully substituted derivative of tin has, as yet, been prepared only by means of discharge reactions.[6] The corresponding compound of the more electropositive[7] element silicon is currently unknown.

While mercuric halides, pseudohalides, and alkyls have all been used extensively in ligand-exchange reactions directed toward the preparation of new inorganic or organometallic species, bis(trifluoromethyl)mercury had been thought to be a very poor ligand-exchange reagent.[8] In a recent study, however, the reactions of $GeBr_4$ and $SnBr_4$ with $(CF_3)_2Hg$ were shown to produce the trifluoromethyl-substituted derivatives $(CF_3)_nMBr_{4-n}$, where $n = 1$ or 2 for M = Sn and $n = 1$–4 for M = Ge.[9] The chemistry of the germanium-containing trifluoromethyl compounds was later examined, and the CF_3–Ge linkage was shown to be very stable chemically when the (trifluoromethyl)germanium halides were shown to react with a variety of reagents to form, e.g., $(CF_3)_3GeH$, $[(CF_3)_3Ge]_2O$, and $(CF_3)_3GeCH_3$ nearly quantitatively.[10]

The present study is directed toward an assessement of the trifluoromethyl–tin linkage. In this study three main areas of interest were investigated: First, since no information about the rates of reaction between $(CF_3)_2Hg$ and a group 4A tetrahalide or any perhalide is available, we have followed the reaction of $SnBr_4$ with $(CF_3)_2Hg$ in a semikinetic manner to determine approximately how quickly the (trifluoromethyl)tin bromides are formed. Second, we have studied the reaction of these bromides with two methylating agents, $(CH_3)_2Cd$ and CH_3Li, to determine the stability of the CF_3–Sn bond toward representative alkylating agents. Finally, because the (trifluoromethyl)germanium hydrides had been synthesized in high (95%) yield, several attempts were made to isolate the currently unknown (trifluoromethyl)tin hydrides.

Experimental Section

General. Except where noted all manipulations were carried out by using a standard vacuum line to ensure the absence of air and water. Proton NMR spectra were obtained from a Varian A-60A spectrometer operating at 60 MHz; positive chemical shifts are deshielded

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