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Template Synthesis and Crystal and Molecular Structure of Bis[1,1,1,12,12,12-hexafluoro-2,11-bis(trifluoromethyl)-4,9-dimethyl-2,11-diolato-5,8-diazadodeca-4,8-diene(2-)]cerium(IV), $CeC_{28}H_{28}F_{24}O_4N_4$. A Fluorinated Schiff Base Complex of Eight-Coordinate Cerium(IV)

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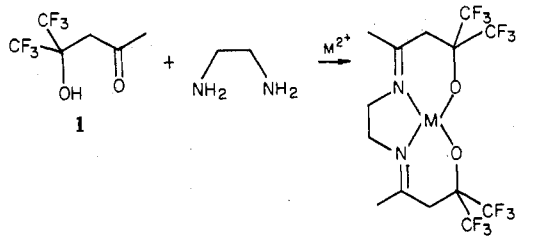
The synthesis and crystal and molecular structure of bis[1,1,1,12,12,12-hexafluoro-2,11-bis(trifluoromethyl)-4,9-dimethyl-2,11-diolate-5,8-diazadodeca-4,8-diene(2-)]cerium(IV), $CeC_{28}H_{28}F_{24}O_4N_4$, is described. The compound was prepared by template condensation of ethylenediamine and 5,5,5-trifluoro-4-hydroxy-4-trifluoromethyl-2-pentanone at an eight-coordinate center. The initial reaction mixture contains Ce(III), and the reaction involves both the template condensation and the oxidation of Ce(III) to Ce(IV); the order of these steps is uncertain. The pale yellow crystalline product is monoclinic and conforms to the space group $P2_1/c$. Cell constants are a = 19.881 (1) Å, b = 10.970 (1) Å, c = 17.605 (2) Å, β = 91.49 (2)°, V = 3838 (1) Å^3, and Z = 4. Final refinement of the structure gave R_F = 0.036, R_{wF} = 0.057, and the error in an observation of unit weight is 1.760. The coordination sphere forms a distorted square antiprism, and the two ligands assume meridional configurations at ~90° to one another. The Ce–O distances range from 2.196 (2) to 2.230 (2) Å, and the Ce–N distances range from 2.609 (3) to 2.641 (3) Å (average 2.623 (6) Å). This is a novel cerium Schiff base complex and also the first report of Ce–N bonding.

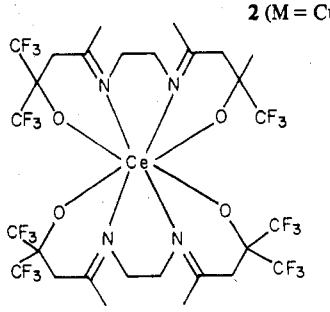
Introduction

The stereochemistry of eight-coordination has become better understood as additional structural examples are characterized, following the early discussions of possible coordination polyhedra.[1-3] In the case of cerium(IV), the geometry in the tetrakis(acetylacetone) complex, $Ce(acac)_4$, has been investigated by several workers.[4,5] The structures found for the two crystalline modifications have been related to those of other $M(acac)_4$ complexes by Steffen and Fay,[6] who recognize two coordination geometries about the metal ion, the bicapped trigonal prism and the square antiprism; these are referred to as α- and β-$Ce(acac)_4$, respectively. The difference in stability between the two forms is slight, and the structure found appears to depend on the polarity of the recrystallization solvent.

There is little structural work reported on cerium(IV) complexes of multidentate ligands, where the steric requirements of polycyclic chelate systems would be expected to outweigh the small differences in stability of different geometries at the metal ion. In view of the ease with which the tetradentate, dinegative, ligand system in **2** is formed by template condensation on metal ions (Cu^{2+}, Ni^{2+})[7,8] it was decided to investigate the analogous reaction in the presence of Ce^{3+} or Ce^{4+}, in the hope that the neutral, eight-coordinate complex **3** would be formed.

An additional novel feature in the latter reaction is the template condensation at an eight-coordinate center, which has not previously been reported. The synthesis and structure of an eight-coordinate Schiff base complex of zirconium(IV) has recently been reported,[9] and this compound may be made





by the condensation of *o*-phenylenediamine with tetrakis(salicylaldehydato)zirconium(IV). However, this is not nec-

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Table I. Positional and Thermal Parameters and Their Estimated Standard Deviations[a]

atom	x	y	z	$B_{1,1}$	$B_{2,2}$	$B_{3,3}$	$B_{1,2}$	$B_{1,3}$	$B_{2,3}$
Ce	0.25496 (1)	0.06209 (2)	0.12747 (1)	0.00155 (1)	0.00612 (2)	0.00204 (1)	−0.00014 (2)	−0.00000 (1)	−0.00082 (2)
F(1)	0.0548 (2)	0.3282 (4)	−0.0089 (2)	0.00317 (9)	0.0224 (5)	0.0065 (2)	0.0060 (4)	−0.0089 (2)	−0.0028 (5)
F(2)	0.1387 (2)	0.2782 (3)	−0.0754 (2)	0.00472 (11)	0.0178 (4)	0.0034 (1)	0.0002 (4)	−0.0014 (2)	0.0008 (4)
F(3)	0.0947 (2)	0.1472 (3)	−0.0061 (2)	0.00477 (11)	0.0142 (4)	0.0058 (1)	0.0048 (3)	−0.0045 (2)	0.0001 (4)
F(4)	0.1366 (2)	0.5055 (3)	0.0351 (3)	0.00473 (12)	0.0102 (3)	0.0132 (3)	0.0052 (3)	−0.0013 (3)	0.0061 (5)
F(5)	0.2252 (2)	0.4377 (3)	−0.0128 (2)	0.00679 (14)	0.0120 (8)	0.0043 (1)	−0.0055 (3)	0.0038 (2)	0.0005 (3)
F(6)	0.2203 (2)	0.4669 (3)	0.1049 (2)	0.00574 (13)	0.0112 (3)	0.0043 (1)	−0.0052 (3)	−0.0011 (2)	−0.0013 (3)
F(7)	0.4111 (2)	−0.1489 (3)	0.0739 (2)	0.00445 (10)	0.0116 (3)	0.0055 (1)	−0.0018 (3)	0.0032 (2)	−0.0001 (4)
F(8)	0.4513 (2)	−0.2823 (3)	0.1504 (2)	0.00334 (9)	0.0158 (4)	0.0066 (2)	−0.0064 (3)	−0.0002 (2)	0.0010 (4)
F(9)	0.3623 (2)	−0.3199 (3)	0.0816 (2)	0.00521 (12)	0.0109 (3)	0.0057 (1)	0.0016 (3)	0.0000 (2)	−0.0067 (3)
F(10)	0.3696 (2)	−0.3674 (3)	0.2526 (2)	0.00431 (11)	0.0108 (3)	0.0075 (2)	0.0026 (3)	−0.0017 (2)	0.0066 (4)
F(11)	0.2739 (2)	−0.3525 (3)	0.1967 (2)	0.00443 (10)	0.0094 (3)	0.0064 (1)	−0.0046 (3)	−0.0023 (2)	0.0023 (4)
F(12)	0.2948 (2)	−0.2496 (3)	0.2964 (2)	0.00526 (11)	0.0124 (3)	0.0045 (1)	−0.0016 (4)	0.0015 (2)	0.0031 (4)
F(13)	0.0371 (2)	−0.0231 (4)	0.0728 (2)	0.00266 (9)	0.0231 (5)	0.0064 (2)	−0.0017 (4)	−0.0014 (2)	−0.0062 (5)
F(14)	0.0202 (2)	0.0489 (3)	0.1847 (3)	0.00277 (9)	0.0167 (4)	0.0097 (2)	−0.0014 (3)	0.0017 (3)	0.0038 (5)
F(15)	−0.0037 (2)	−0.1399 (4)	0.1560 (3)	0.00236 (8)	0.0186 (4)	0.0092 (2)	0.0053 (3)	0.0001 (2)	−0.0028 (6)
F(16)	0.1736 (2)	−0.1605 (4)	0.2782 (2)	0.00427 (11)	0.0263 (6)	0.0041 (1)	0.0003 (4)	−0.0007 (2)	−0.0072 (4)
F(17)	0.0844 (3)	−0.0657 (4)	0.2983 (2)	0.00693 (17)	0.0271 (7)	0.0046 (2)	−0.0007 (6)	0.0043 (3)	−0.0003 (5)
F(18)	0.0806 (2)	−0.2480 (4)	0.2571 (2)	0.00754 (15)	0.0223 (4)	0.0064 (2)	−0.0136 (4)	0.0002 (3)	0.0087 (5)
F(19)	0.4694 (1)	0.0658 (2)	0.0620 (2)	0.00277 (8)	0.0103 (3)	0.0057 (1)	−0.0035 (2)	−0.0009 (2)	0.0044 (3)
F(20)	0.4895 (2)	0.1375 (4)	0.1716 (2)	0.00275 (8)	0.0207 (5)	0.0047 (1)	−0.0014 (4)	−0.0022 (2)	0.0007 (4)
F(21)	0.5149 (1)	0.2414 (3)	0.0735 (2)	0.00206 (7)	0.0132 (3)	0.0097 (2)	0.0022 (3)	0.0027 (2)	−0.0012 (5)
F(22)	0.3411 (2)	0.3961 (3)	0.1482 (2)	0.00358 (10)	0.0112 (3)	0.0091 (2)	0.0019 (3)	0.0016 (2)	−0.0082 (4)
F(23)	0.4288 (2)	0.3412 (3)	0.2123 (2)	0.00490 (12)	0.0149 (4)	0.0057 (1)	−0.0029 (4)	−0.0009 (2)	−0.0079 (4)
F(24)	0.4391 (2)	0.4303 (3)	0.1062 (3)	0.00480 (12)	0.0089 (3)	0.0096 (2)	−0.0055 (3)	0.0049 (3)	−0.0080 (4)
O(1)	0.2122 (1)	0.2148 (3)	0.0579 (2)	0.00198 (7)	0.0071 (3)	0.0020 (1)	−0.0006 (2)	−0.0001 (1)	0.0033 (3)
O(2)	0.2953 (1)	0.1220 (3)	0.1468 (2)	0.00209 (8)	0.0061 (2)	0.0033 (1)	−0.0002 (2)	−0.0005 (2)	0.0007 (3)
O(3)	0.1560 (1)	0.0048 (3)	0.1682 (2)	0.00196 (8)	0.0098 (3)	0.0034 (1)	0.0015 (3)	0.0007 (2)	0.0006 (3)
O(4)	0.3547 (1)	0.1519 (3)	0.1389 (2)	0.00186 (7)	0.0073 (3)	0.0030 (1)	−0.0012 (2)	0.0004 (2)	−0.0005 (3)
N(1)	0.2142 (2)	0.2359 (3)	0.2165 (2)	0.00204 (9)	0.0080 (3)	0.0024 (1)	0.0008 (3)	0.0001 (2)	−0.0014 (3)
N(2)	0.0408 (3)	0.0408 (3)	0.2681 (2)	0.00242 (10)	0.0085 (4)	0.0023 (1)	−0.0002 (3)	−0.0003 (2)	0.0010 (4)
N(3)	0.1958 (2)	−0.0783 (3)	0.0250 (2)	0.00236 (10)	0.0082 (4)	0.0027 (1)	0.0009 (3)	−0.0009 (2)	0.0005 (4)
N(4)	0.3154 (2)	0.0580 (3)	−0.0043 (2)	0.00227 (10)	0.0087 (4)	0.0025 (1)	−0.0003 (3)	0.0002 (2)	0.0010 (4)
C(1)	0.1116 (2)	0.2626 (5)	−0.0089 (3)	0.0027 (1)	0.0109 (5)	0.0038 (2)	−0.0017 (5)	−0.0010 (3)	−0.0008 (6)
C(2)	0.1855 (3)	0.4273 (4)	0.0469 (3)	0.0029 (1)	0.0082 (5)	0.0042 (2)	0.0014 (4)	0.0001 (3)	−0.0006 (5)
C(3)	0.1606 (2)	0.2950 (4)	0.0588 (3)	0.0021 (1)	0.0077 (4)	0.0029 (1)	0.0007 (4)	−0.0006 (2)	0.0004 (4)
C(4)	0.1212 (2)	0.2904 (5)	0.1337 (3)	0.0019 (1)	0.0106 (5)	0.0035 (2)	0.0013 (4)	0.0003 (2)	−0.0005 (5)
C(5)	0.1656 (2)	0.3094 (4)	0.2035 (3)	0.0025 (1)	0.0089 (4)	0.0025 (1)	0.0003 (4)	0.0010 (2)	−0.0009 (5)
C(6)	0.1471 (3)	0.4172 (5)	0.2543 (3)	0.0047 (2)	0.0112 (5)	0.0041 (2)	0.0057 (5)	0.0010 (3)	−0.0046 (6)
C(7)	0.2546 (2)	0.2459 (5)	0.2875 (3)	0.0027 (1)	0.0108 (5)	0.0025 (1)	0.0015 (5)	−0.0006 (2)	−0.0025 (5)
C(8)	0.2627 (3)	0.1193 (5)	0.3213 (3)	0.0031 (1)	0.0102 (5)	0.0025 (1)	−0.0025 (5)	0.0001 (3)	0.0012 (5)
C(9)	0.3503 (2)	−0.0226 (5)	0.2915 (3)	0.0028 (1)	0.0082 (4)	0.0080 (2)	−0.0012 (4)	−0.0017 (3)	0.0013 (5)
C(10)	0.3762 (4)	−0.0806 (6)	0.3733 (4)	0.0063 (2)	0.0154 (7)	0.0047 (2)	−0.0078 (6)	−0.0062 (4)	0.0038 (7)
C(11)	0.3908 (2)	−0.0940 (4)	0.2355 (3)	0.0028 (1)	0.0079 (4)	0.0038 (2)	−0.0011 (4)	−0.0011 (3)	0.0020 (5)
C(12)	0.3471 (2)	−0.1830 (4)	0.1847 (3)	0.0023 (1)	0.0066 (4)	0.0033 (2)	−0.0003 (4)	−0.0005 (2)	−0.0001 (4)
C(13)	0.3927 (3)	−0.2347 (5)	0.1231 (3)	0.0033 (1)	0.0074 (4)	0.0050 (2)	−0.0020 (5)	−0.0000 (3)	0.0011 (6)
C(14)	0.3209 (3)	−0.2878 (4)	0.2314 (3)	0.0032 (1)	0.0075 (5)	0.0048 (2)	−0.0006 (4)	−0.0011 (3)	−0.0018 (5)
C(15)	0.0414 (3)	−0.0513 (5)	0.1469 (4)	0.0022 (1)	0.0142 (6)	0.0055 (3)	0.0022 (5)	0.0007 (3)	−0.0013 (7)
C(16)	0.1133 (3)	−0.1413 (6)	0.2510 (3)	0.0036 (2)	0.0149 (7)	0.0042 (2)	0.0032 (6)	0.0012 (3)	−0.0030 (7)
C(17)	0.1138 (2)	−0.0933 (5)	0.1688 (3)	0.0022 (1)	0.0102 (5)	0.0037 (2)	0.0026 (4)	0.0002 (3)	−0.0012 (5)
C(18)	0.1358 (2)	−0.1951 (5)	0.1166 (3)	0.0027 (1)	0.0090 (5)	0.0042 (2)	0.0017 (4)	0.0006 (3)	−0.0011 (5)
C(19)	0.1500 (2)	−0.1554 (4)	0.0360 (3)	0.0024 (1)	0.0067 (4)	0.0038 (2)	0.0006 (4)	−0.0015 (3)	0.0007 (5)
C(20)	0.1083 (3)	−0.2182 (5)	−0.0262 (3)	0.0046 (2)	0.0121 (6)	0.0047 (2)	−0.0035 (5)	−0.0033 (3)	−0.0037 (6)
C(21)	0.2171 (3)	−0.0511 (5)	−0.0537 (3)	0.0030 (1)	0.0123 (6)	0.0026 (2)	0.0029 (5)	0.0000 (3)	0.0009 (5)
C(22)	0.2938 (3)	−0.0466 (5)	−0.0526 (3)	0.0036 (2)	0.0097 (5)	0.0033 (2)	0.0013 (5)	0.0011 (3)	0.0042 (5)
C(23)	0.3593 (2)	0.1327 (5)	−0.0275 (3)	0.0017 (1)	0.0101 (5)	0.0027 (1)	−0.0008 (4)	0.0003 (2)	−0.0020 (5)
C(24)	0.3982 (3)	0.1222 (6)	−0.0999 (3)	0.0028 (1)	0.0160 (7)	0.0028 (2)	−0.0005 (6)	0.0015 (3)	−0.0001 (6)
C(25)	0.3731 (2)	0.2485 (5)	0.0181 (3)	0.0025 (1)	0.0085 (4)	0.0081 (2)	−0.0001 (4)	0.0007 (2)	0.0015 (5)
C(26)	0.3974 (2)	0.2238 (4)	0.1013 (3)	0.0020 (1)	0.0066 (4)	0.0039 (3)	−0.0006 (4)	0.0007 (2)	−0.0009 (5)
C(27)	0.4678 (2)	0.1670 (5)	0.1038 (3)	0.0019 (1)	0.0100 (5)	0.0044 (2)	0.0007 (4)	−0.0001 (3)	0.0001 (5)
C(28)	0.4036 (3)	0.3505 (5)	0.1422 (4)	0.0027 (1)	0.0088 (5)	0.0068 (3)	−0.0017 (4)	0.0015 (3)	−0.0086 (6)

[a] The form of the anisotropic thermal parameter is $\exp[-(B_{1,1}h^2 + B_{2,2}k^2 + B_{3,3}l^2 + B_{1,2}hk + B_{1,3}hl + B_{2,3}kl)]$.

essarily a template process, since the diamine and aldehyde are known to react in the absence of a metal ion.[10]

In the case of the fluorinated keto alcohol **1**, we have previously noted[8] that since condensation with diamines does not occur in the absence of a metal ion, the production of an imino–alkoxy complex such as **3** would be evidence of a template reaction on cerium.

In this paper, we describe the synthesis and structure of the cerium(IV) complex **3**, the first reported example of a structure containing a Schiff base complex of this metal and the first measurement of a cerium–nitrogen bond length.

Experimental Section

Reagents. Reagent grade or equivalent chemicals and solvents were used. 5,5,5-Trifluoro-4-hydroxy-4-trifluoromethyl-2-pentanone (**1**) was prepared as described previously.[8] Microanalysis was performed

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by Malissa-Reuter Laboratories, West Germany.

Reaction of 1 with Ce^{3+} and Diaminoethane. Cerium(III) nitrate hexahydrate (0.87 g, 2.0 mmol) was dissolved in ethanol with **1** (1.80 g, 8.0 mmol) and excess 1,2-diaminoethane (0.36 g, 6.0 mmol) added. The solution was kept at 25 °C in contact with air. The initially clear solution became red-orange upon standing. A brown precipitate separated but redissolved as the reaction proceeded. When the reaction appeared to be complete (16 h), the solution was filtered, and pale yellow crystals appeared on standing for several days at 25 °C. Recrystallization from chloroform gave the desired product, **3** mp 225 °C dec. Anal. Calcd for $C_{28}H_{28}CeF_{24}N_4O_4$: C, 31.1; H, 2.61; N, 5.18. Found: C, 31.2; H, 2.55; N, 5.31.

The infrared spectrum (Nujol mull) showed strong C=N absorption at 1650 cm^{-1}; no N–H or O–H absorption was present. The mass spectrum did not show a peak corresponding to the parent ion (m/e 1080), but strong peaks were present at m/e 914 [loss of $(CF_3)_2CO$], 845 [loss of $(CF_3)_2CO$ and CF_3], 748 [loss of two $(CF_3)_2$], 610 (loss of one ligand), and 470 (ligand). The complex was diamagnetic, confirming cerium(IV).

Reaction of 1 with Ce^{3+} and Ce^{4+}. In a series of experiments, the keto alcohol **1** was kept with cerium(III) nitrate in varying proportions in ethanolic solution, the pH also being varied by the addition of KOH. From the gradual color change of such solutions, it was evident that oxidation to a Ce^{4+} complex was occurring, but no solid product could be characterized. Attemps to prepare a complex by direct reaction of **1** with Ce^{4+} salts in solution were also unsuccessful.

X-ray Data Collection. A crystal ~0.23 mm × 0.30 mm × 0.33 mm, grown slowly from chloroform solution, was mounted on a CAD-4 automated diffractometer, and 25 medium- and high-angle reflections were collected by using graphite-monochromated Mo $K\alpha_1$ (λ = 0.709 30 Å) radiation. A least-squares treatment[11] of these reflections gave monoclinic unit cell parameters: a = 19.881 (1) Å, b = 10.970 (2) Å, c = 17.605 (2) Å, β = 91.49 (2)°, V = 3838 (1) Å^3, and Z = 4. Intensity data were collected by the θ–2θ method. Scanning speeds ranged from approximately 20°/min for the most intense reflections to approximately 2°/min for the weakest reflections. The angular scan width was A + 0.347(tan $\theta_{\lambda\alpha_2}$), where $\theta_{\lambda\alpha_2}$ is determined from the formula

$$\theta_{\lambda\alpha_2} = \theta_{\lambda\alpha_1} + \left(\frac{\lambda\alpha_2 - \lambda\alpha_1}{\lambda\alpha}\right)\left(\frac{360}{2\pi}\right)(\tan\theta_{\lambda\alpha_1})$$

and A depends on the crystal mosaic spread and on the divergence of the primary beam. A for this structure was 0.60. The scan was extended on each side of the peaks by 25% for background determination. Reflections were collected up to 2θ = 50°. Three standard reflections scanned approximately every 150 reflections were used to place the intensity data on a common scale; systematic variation in these standards was not observed.

Reflection intensities were calculated from peak and background measurements as $I = S(C - RB)$ where S = scan rate, C = total integrated peak count, B = total background count, and R = the ratio of the scan time for the peak to the scan time for the background. The estimated error was calculated as $\sigma(I) = [S^2(C + R^2B) + (pI)^2]^{1/2}$. The value of p was 0.05. Of 7330 reflections originally scanned 5729 unique ones with $I > 3\sigma(I)$ were used in the solution and refinement of the structure. Intensities and $\sigma(I)$ values were corrected for Lorentz and polarization effects.[11] Neutral-atom scattering factors were used.[12] The metal atom was corrected for anomalous dispersion (both real and imaginary). An absorption correction was not required (μ = 13.7 cm^{-1}). The space group was determined to be $P2_1/c$ on the basis of systematic absences: $h0l$, $l = 2n + 1$; $0k0$, $k = 2n + 1$.

Structure Solution and Refinement. The cerium atom position was located by Patterson methods. Remaining nonhydrogen positions were determined by difference Fourier methods.[11] These atoms were refined anisotropically. Hydrogen atom positions were not included. R values were calculated as $R_F = [\sum||F_o| - |F_c||]/\sum|F_o|$ and $R_{wF} = [\sum w(|F_o| - |F_c|)^2/\sum wF_o^2]^{1/2}$. Reflections were weighted as $w = 1/\sigma^2(F_o) = 4F_o^2/[\sigma(F_o)^2]^2$, where $\sigma(F_o)^2 = [\sigma^2(I) + (pI)^2]^{1/2}/Lp$. The function minimized was $\sum w(|F_o| - |F_c|)^2$.[11] Final R values were R_F = 0.036 and R_{wF} = 0.057. The error in an observation of unit weight was 1.760. Calculated and measured densities (measured by flotation in 1,2-dibromopropane and 2-chloroethanol) were 1.87 g cm^{-3} and 1.86 (1) g cm^{-3}, respectively.

Table II. Least-Squares Planes through Selected Atoms and Deviations of the Atoms from the Planes for $CeC_{28}H_{28}F_{24}O_4N_4$

(a) Deviations from the Planes[a]

plane 1: *O(1)* (0.000), *C(3)* (0.000), *C(5)* (0.000), *N(1)* (0.000), Ce (−0.806), C(4) (−0.643)
plane 2: *O(2)* (0.025), *C(12)* (−0.027), *C(9)* (0.029), *N(2)* (−0.027), Ce (0.918), C(11) (0.627)
plane 3: *O(3)* (0.026), *C(17)* (−0.029), *C(19)* (0.032), *N(3)* (−0.029), Ce (−0.689), C(18) (−0.605)
plane 4: *O(4)* (−0.003), *C(23)* (−0.004), *C(26)* (0.003), *N(4)* (0.003), Ce (0.713), C(25) (0.641)
plane 5:[b] *O(1)* (0.157), *N(1)* (−0.239), *N(2)* (0.239), *O(2)* (−0.157), Ce (0.009)
plane 6:[b] *O(3)* (0.121), *N(3)* (−0.182), *N(4)* (0.182), *O(4)* (−0.121), Ce (−0.002)
plane 7:[b] *N(2)* (0.285), *O(2)* (−0.339), *N(3)* (0.308), *O(3)* (−0.254)
plane 8:[b] *N(1)* (−0.251), *O(1)* (0.290), *N(4)* (−0.271), *O(4)* (0.232)

(b) Equations of the Planes[c]

plane	*A*	*B*	*C*	*D*	X^2
1	0.6497	0.7581	−0.0554	4.4534	Q
2	0.6541	0.5642	−0.5039	1.7146	193
3	−0.6935	0.5803	−0.4270	−3.3483	212
4	−0.7037	0.7047	−0.0906	−3.9625	3
5[b]	0.8985	0.4067	−0.1655	4.3990	15037
6[b]	−0.4403	0.8329	−0.3354	−2.3891	7927
7[b]	0.3389	0.8433	−0.4172	0.0998	31889
8[b]	0.3373	0.9033	−0.2650	2.9819	26837

(c) Dihedral Angles (Deg) between Planes

planes	angle	planes	angle
1–2	104.4	2–4	91.0
1–3	180.0	3–4	20.7
1–4	180.0	5–6	90.1
2–3	84.9	7–8	9.4

[a] Planes were calculated by using the italicized atoms. All atoms were weighted equally. The number in parentheses is the distance (Å) of the atom from the plane. Esd's of these distances range from 0.000 to 0.005 Å and average 0.003 Å. [b] These groupings are nonplanar. They are discussed under Description of the Structures. The equations of the planes are of the form $Ax + By + Cz + D = 0$.

Description of the Structure

Figure 1 is an ORTEP[13] drawing of the structure determined for complex **3**. The fluorine atoms are removed for clarity. The structure approximates a square antiprism, although it is obvious from the data in Table II (planes 7 and 8) that the bases of the prism are not truly planar. Furthermore, the bases are diamond shaped rather than square due to the large difference between the Ce–O and Ce–N bond distances. The two ligands have assumed a meridional configuration such that the mean donor planes of the ligands (planes 5 and 6, Table II) intersect at 90° angles. It is obvious both from these planes and from the bond angles given in Table III that the ligand is far from planar; this was expected since there is no delocalization to enforce planarity. In Figure 2 each ligand is shown separately as it binds to cerium(IV). Atomic positions and thermal parameters are given in Table I. A variety of least-squares planes are given in Table II. Table III is a list of important bond distances and bond angles. Torsion angles

(11) All calculations were performed on a PDP11 computer with use of programs from the Enraf-Nonius structure determination package (SDP), Enraf-Nonius, Delft, Holland, 1975; revised 1977.
(12) Cromer, D. T.; Waber, J. T. "International Tables for X-ray Crystallography"; Kynoch Press: Birmingham, England, 1974; Vol. IV; Table 2.2B.
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Table III. Selected Bond Distances (Å) and Bond Angles (Deg) for $CeC_{28}H_{28}F_{24}O_4N_4$

A. Bond Distances

Ce-O(1)	2.230 (2)	Ce-N(1)	2.609 (3)
Ce-O(2)	2.196 (2)	Ce-N(2)	2.617 (3)
Ce-O(3)	2.200 (2)	Ce-N(3)	2.627 (3)
Ce-O(4)	2.219 (2)	Ce-N(4)	2.641 (3)
av Ce-O	2.211 (4)[a]	av Ce-N	2.623 (6)[a]
O(1)-C(3)	1.352 (4)	O(3)-C(17)	1.375 (4)
C(1)-C(3)	1.561 (5)	C(15)-C(17)	1.549 (6)
C(2)-C(3)	1.549 (5)	C(16)-C(17)	1.540 (6)
C(3)-C(4)	1.553 (5)	C(17)-C(18)	1.519 (6)
C(4)-C(5)	1.508 (5)	C(18)-C(19)	1.516 (6)
C(5)-C(6)	1.532 (5)	C(19)-C(20)	1.520 (5)
C(5)-N(1)	1.276 (4)	C(19)-N(3)	1.262 (5)
N(1)-C(7)	1.473 (4)	N(3)-C(21)	1.490 (5)
C(7)-C(8)	1.518 (6)	C(21)-C(22)	1.527 (6)
C(8)-N(2)	1.479 (5)	C(22)-N(4)	1.484 (5)
N(2)-C(9)	1.288 (5)	N(4)-C(23)	1.273 (5)
C(9)-C(10)	1.519 (6)	C(23)-C(24)	1.513 (5)
C(9)-C(11)	1.509 (5)	C(23)-C(25)	1.523 (5)
C(11)-C(12)	1.570 (5)	C(25)-C(26)	1.555 (5)
C(12)-O(2)	1.385 (4)	C(26)-O(4)	1.346 (4)
C(12)-C(13)	1.540 (6)	C(26)-C(27)	1.530 (5)
C(12)-C(14)	1.513 (5)	C(26)-C(38)	1.569 (6)
av O-C	1.365 (8)[a]	av N=C	1.275 (10)[a]
av N-C	1.482 (10)[a]	av C-C	1.533
C(1)-F(1)	1.339 (5)	C(15)-F(13)	1.342 (6)
C(1)-F(2)	1.312 (5)	C(15)-F(14)	1.313 (6)
C(1)-F(3)	1.311 (5)	C(15)-F(15)	1.335 (5)
C(2)-F(4)	1.309 (5)	C(16)-F(16)	1.298 (5)
C(2)-F(5)	1.337 (5)	C(16)-F(17)	1.317 (6)
C(2)-F(6)	1.293 (5)	C(16)-F(18)	1.344 (6)
C(13)-F(7)	1.336 (5)	C(27)-F(19)	1.332 (5)
C(13)-F(8)	1.354 (5)	C(27)-F(20)	1.300 (5)
C(13)-F(9)	1.324 (5)	C(27)-F(21)	1.362 (5)
C(14)-F(10)	1.350 (4)	C(28)-F(22)	1.346 (5)
C(14)-F(11)	1.312 (5)	C(28)-F(23)	1.324 (6)
C(14)-F(12)	1.335 (5)	C(28)-F(24)	1.300 (5)
		av C-F	1.326

B. Bond Angles

O(1)-Ce-O(2)	155.23 (9)	O(3)-Ce-N(1)	73.40 (9)
O(1)-Ce-O(3)	93.27 (9)	O(3)-Ce-N(2)	87.10 (9)
O(1)-Ce-O(4)	92.52 (8)	O(3)-Ce-N(3)	70.82 (9)
O(1)-Ce-N(1)	70.19 (8)	O(3)-Ce-N(4)	135.48 (9)
O(1)-Ce-N(2)	134.49 (9)	O(4)-Ce-N(1)	84.93 (8)
O(1)-Ce-N(3)	84.58 (9)	O(4)-Ce-N(2)	71.02 (9)
O(1)-Ce-N(4)	72.92 (9)	O(4)-Ce-N(3)	134.92 (9)
O(2)-Ce-O(3)	91.07 (9)	O(4)-Ce-N(4)	70.21 (9)
O(2)-Ce-O(4)	94.15 (9)	N(1)-Ce-N(2)	66.39 (9)
O(2)-Ce-N(1)	134.17 (9)	N(1)-Ce-N(3)	134.44 (9)
O(2)-Ce-N(2)	70.06 (9)	N(1)-Ce-N(4)	134.05 (9)
O(2)-Ce-N(3)	73.87 (9)	N(2)-Ce-N(3)	137.01 (9)
O(2)-Ce-N(4)	86.99 (9)	N(2)-Ce-N(4)	132.81 (10)
O(3)-Ce-O(4)	154.10 (9)	N(3)-Ce-N(4)	65.95 (10)
O(1)-C(3)-C(1)	107.6 (3)	O(3)-C(17)-C(15)	109.0 (4)
O(1)-C(3)-C(2)	111.3 (3)	O(3)-C(17)-C(16)	107.3 (3)
O(1)-C(3)-C(4)	112.8 (3)	O(3)-C(17)-C(18)	113.1 (3)
C(1)-C(3)-C(2)	107.8 (3)	C(15)-C(17)-C(16)	107.9 (4)
C(1)-C(3)-C(4)	108.8 (3)	C(15)-C(17)-C(18)	110.4 (4)
C(2)-C(3)-C(4)	108.3 (3)	C(16)-C(17)-C(18)	109.0 (4)
C(3)-C(4)-C(5)	113.0 (3)	C(17)-C(18)-C(19)	114.7 (3)
C(4)-C(5)-N(1)	118.9 (3)	C(18)-C(19)-N(3)	119.3 (3)
C(6)-C(5)-N(1)	125.2 (4)	C(20)-C(19)-N(3)	125.0 (4)
C(4)-C(5)-C(6)	116.0 (3)	C(18)-C(19)-C(20)	115.6 (4)
C(5)-N(1)-C(7)	119.9 (3)	C(19)-N(3)-C(21)	120.1 (3)
N(1)-C(7)-C(8)	108.3 (3)	N(3)-C(21)-C(22)	107.6 (3)
C(7)-C(8)-N(2)	109.5 (3)	C(21)-C(22)-N(4)	107.9 (3)
C(8)-N(2)-C(9)	120.6 (3)	C(22)-N(4)-C(23)	120.3 (3)
N(2)-C(9)-C(10)	125.3 (4)	N(4)-C(23)-C(24)	126.2 (4)
N(2)-C(9)-C(11)	120.0 (3)	N(4)-C(23)-C(25)	118.9 (3)
C(10)-C(9)-C(11)	114.7 (4)	C(24)-C(23)-C(25)	114.8 (3)
C(9)-C(11)-C(12)	113.4 (3)	C(23)-C(25)-C(26)	113.5 (3)
C(11)-C(12)-C(13)	107.6 (3)	C(25)-C(26)-C(27)	107.3 (3)
C(11)-C(12)-C(14)	110.9 (3)	C(25)-C(26)-C(28)	111.0 (3)
C(11)-C(12)-O(2)	111.6 (3)	C(25)-C(26)-O(4)	112.4 (3)
C(13)-C(12)-C(14)	108.7 (3)	C(27)-C(26)-C(28)	106.7 (3)
C(13)-C(12)-O(2)	106.4 (3)	C(27)-C(26)-O(4)	109.7 (3)
C(14)-C(12)-O(2)	111.5 (3)	C(28)-C(26)-O(4)	109.6 (3)

[a] The deviations of the averages are calculated as the square root of the sum of the squares of the deviations for the individual bond lengths.

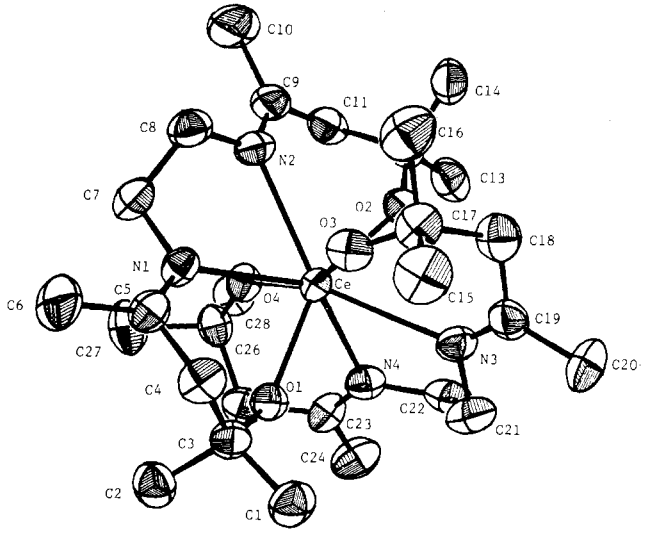
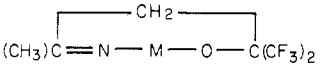


Figure 1. ORTEP[13] drawing of $CeC_{28}H_{28}F_{24}O_4N_4$ with 50% probability ellipsoids. The structure approximates a square antiprism. The bases of the antiprism are formed by N2, O2, N3, O3 and N1, O1, N4, O4. Fluorine atoms were not included.

about the bonds have not been included, but they are available as supplementary material.

The two five-membered chelate rings, N(1)C(7)C(8)N(2)Ce and N(3)C(19)C(18)N(4)Ce, have gauche configurations. Each ligand coordinates the cerium(IV) in a tetradentate fashion with the central five-membered chelate ring flanked by six-membered rings in "boat" and "twist boat" configurations, respectively. The two "boat" rings CeN(1)C(5)C(4)C(3)O(1) and CeN(4)C(23)C(25)C(26)O(4) both have well-defined basal planes (planes 1 and 4 in Table II). Similar "boat" or "twist boat" configurations have been observed in all previous rings of the type



where M = Ni^{2+}[7] or Cu^{2+}.[14,15]

To our knowledge, this is the first report of cerium to nitrogen bond distances. These range from 2.609 (3) to 2.641 (3) Å; the average value is 2.623 (6) Å. The range of M–N distances in complexes of lanthanum and lanthanides are given in Table IV for purposes of comparison. The values for the present structure fall within the expected range.

Discussion

The formation of the cerium(IV) complex **3** involves two processes: oxidation of Ce^{3+} to Ce^{4+} and condensation of the

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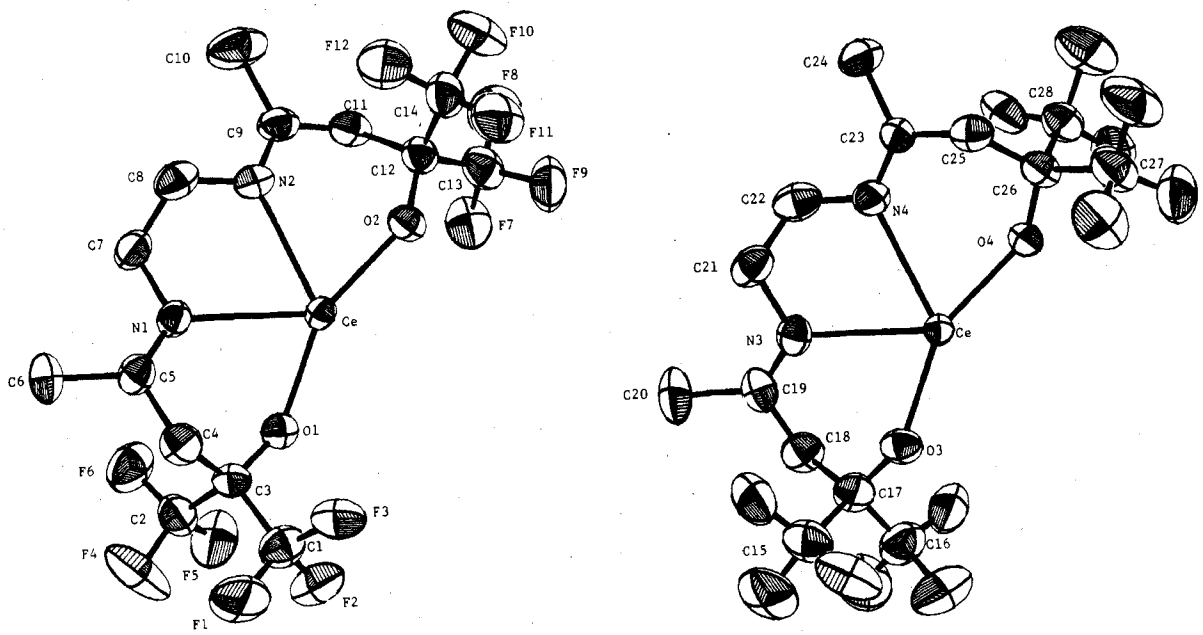
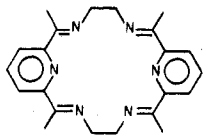


Figure 2. ORTEP[13] drawings (50% probability) of the halves of the molecule, which are almost identical.

Table IV. M–N Distances for Some Complexes of Lanthanum and Lanthanides

compd	bond types	M–N dist, Å	ref
$[La(N(SiMe_3)_2)_3(PPh_3O)]$	La–N (tertiary amine)	2.38 (2)–2.41 (2)	16
$[La(N(SiMe_3)_2)_4O_2(PPh_3O)_2]$	La–N (tertiary amine)	2.37 (2), 2.49 (2)	16
$[La(NO_3)_3L]$[a]	La–N (py)	2.746, 2.764[e]	17
	La–N (imine)	2.672–2.729[e]	
complex **3**	Ce–N (imine)	2.609–2.641	this work
$[Eu(ClO_4\langle 222\rangle)](ClO_4)_2McNC$[b]	Eu–N (tertiary amine)	2.70 (5), 2.64 (3)	18
$[Gd(NO_3)_3(dpae)]$[c]	Gd–N	2.50–2.60	19
$[Yb(paphy)(H_2O)_3(OH)]_2Cl_4\cdot 4H_2O$[d]	Yb–N (py)	2.49 (1), 2.52 (1)	20
	Yb–N (imine)	2.54 (1)	

[a] L = macrocyclic ligand **5**.



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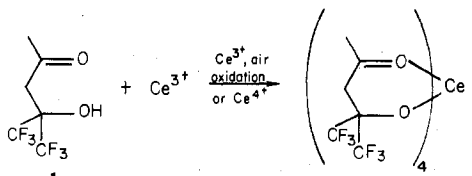
[b] $\langle 222\rangle$ = 4,7,13,16,21,24-hexaoxa-1,10-diazabicyclo[8.8.8]hexacosane. [c] dpae = 1,2-bis(pyridine-2-carboxaldimino)ethane. [d] paphy = pyridine-2-carboxaldehyde 2′-pyridylhydrazone. [e] Esd's were not given in reference.

diamine with the keto alcohol. But present evidence does not permit a decision on the order in which these reactions occur. It is well established that Ce^{4+} is stabilized relative to Ce^{3+} by chelation though oxygen, as in $Ce(acac)_4$, and we find that air oxidation in the presence of **1** proceeds readily. However, a complex such as **4** has not yet been isolated in the solid state from reactions starting with either Ce^{3+} or Ce^{4+}.



1 **4**

This result is not surprising, in view of our previous observation[8] that **1** is a considerably weaker ligand than acac, because of the lack of delocalization. However, the presence of a small concentration of a complex similar to **4** provides a reasonable intermediate for the condensation with diaminoethane to give the final product **3**.

The alternative route to the observed product involves template condensation on Ce^{3+} as the first step, followed by oxidation. Here again, we were unable to characterize any intermediate product by attempting to stop the reaction at the first stage by carrying out the condensation in the absence of air. Clearly, the failure to isolate possible intermediates cannot be taken as evidence in support of either sequence of reaction.

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Registry No. 1, 10487-10-2; **3**, 75045-80-6; 1,2-diaminoethane, 107-15-3.

Supplementary Material Available: A table of calculated and observed structure factors and a table of torsion angles (26 pages). Ordering information is given on any current masthead page.