producing red crystals of **1**, which were collected and dried under vacuum. The supernatant was further concentrated and cooled to yield additional amounts of **1**: yield 0.47 g (44% based on Pd); mp 171–175 °C dec. IR: (Nujol mull, NaCl plates) 1462 s, 1415 m, 1372 m, 1349 s, 1290 w, 1274 m, 1168 br, m, 1013 m, 931 br, s 840 w, 807 m, 713 m, 665 m cm^{-1}. ^{1}H NMR (361.084 MHz): δ 1.427 (t, 36 H, μ-P(*t-Bu*)$_2$), 1.410 (t, 18 H, P*Me*$_3$). ^{31}P{^{1}H} NMR (32.384 MHz): δ 289.0 (t, $^2J_{P-P}$ = 41 Hz, μ-*P*(t-Bu)$_2$), −26.6 (t, $^2J_{P-P}$ = 41 Hz, *P*Me$_3$). For 2: yield 0.11 g (12% based on Pd); mp 170–173 °C dec. IR: (hexane solution, KBr cells) 2035 s, sh, 2030 s cm^{-1}; (Nujol mull, NaCl plates) 2040 s, sh, 2035 s, 1359 m, 1168 m, 1016 m, 809 m cm^{-1}. ^{1}H NMR (361.089 MHz): δ 1.455 (t, 36 H, μ-P(*t-Bu*)$_2$), 1.110 (d, 18 H, $^3J_{P-H}$ = 15 Hz, μ-P(*t-Bu*)$_2$). ^{31}P{^{1}H} NMR (32.384 MHz): δ 280.1 (d, $^2J_{P-P}$ = 119 Hz, μ-*P*(t-Bu)$_2$), 207.5 (t, $^2J_{P-P}$ = 119 Hz, μ-*P*(t-Bu)$_2$). Anal. Calcd for $C_{26}H_{54}ClO_2P_3Pd_3$: C, 36.90; H, 6.43; P, 10.98. Found: C, 37.02; H, 6.58; P, 10.79.

X-ray Experimental Data. Data were collected on an Enraf-Nonius CAD-4 diffractometer at 23 ± 2 °C using graphite-monochromated Mo Kα radiation. All calculations were performed on a PDP 11/44 computer using the Enraf-Nonius software package SDP-PLUS.[12] For each structure, the data were corrected for Lorentz and polarization effects. The structures were solved by direct methods (MULTAN)[13] and successive cycles of difference Fourier maps followed by least-squares refinement.

1. Crystals were grown from hexane solutions (−40 °C) and mounted in thin-walled glass capillaries under nitrogen. Unit cell parameters were obtained by carefully centering 25 reflections having 2θ values between 22 and 32°. Examination of the diffraction symmetry and the systematic absence 00l, l = 2n + 1, indicated a choice of the tetragonal space groups $P4_2$ and $P4_2/m$. The space group $P4_2/m$ was chosen to be the correct one on the basis of successful refinement of the structure. Data were collected in the $+h,+k,+l$ octant between 2θ values of 3 and 48°. The check reflections indicated a 12.0% decrease in intensity over the course of data collection, and hence an anisotropic correction was applied. A Ψ scan of four reflections having χ values between 80 and 90° showed that no absorption correction was necessary, and none was applied. The observed structure factors of equivalent reflections were averaged with agreement factors of 0.025 for intensity and 0.024 on F_o. All non-hydrogen atoms except for C5 and C6 were refined anisotropically. Hydrogen atoms were not located, but their contributions were included in the refinements. Data with intensities less than $3\sigma(I)$ and $(\sin\theta)/\lambda$ less than 0.10 were excluded, and a non-Poisson contribution weighting scheme with an experimental instability factor of $P = 0.05$ was used in the final stages of refinement.[14] The atoms were refined to final values of 0.0465 and 0.0613 for R and R_w, respectively. The maximum peak in the final difference Fourier map had a height of 0.503 e/Å^3 and was located 0.963 Å from Pd.

2. Crystals were grown from hexane solutions (−40 °C) and mounted in thin-walled glass capillaries under nitrogen. Unit cell parameters were obtained by carefully centering 25 reflections having 2θ values between 24 and 28°. Examination of the diffraction symmetry and the systematic absences $0kl$, $k + l = 2n + 1$; $hk0$, $h = 2n + 1$; $h00$, $h = 2n + 1$; $0k0$, $k = 2n + 1$; $00l$, $l = 2n + 1$, indicated a choice of the orthorhombic space groups *Pnma* and $Pn2_1a$. The space group *Pnma* (No. 62) was chosen to be the correct one on the bases of successful refinement of the structure. Data were collected in the $+h,+k,+l$ octant between 2θ values of 3 and 46°. The check reflections indicated <1% decrease in intensity over the course of data collection; hence, no correction was applied. A Ψ scan of four reflections having χ values between 80 and 90° showed a minimum transmission of 77.9% and a maximum transmission of 99.1%. An empirical absorption correction was applied. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were not located but their contribution was included in the refinements. Data with intensities less than $3\sigma(I)$ and $(\sin\theta)/\lambda$ less than 0.10 were excluded, and a non-Poisson contribution weighting scheme with an experimental instability factor of $P = 0.06$ was used in the final stages of refinement.[14] The atoms were refined to final values of 0.0439 and 0.0532 for R and R_w respectively. The maximum peak in the final difference Fourier map had a height of 0.965 e/Å^3 and was located 1.215 Å from Pd1. Supplementary material for **1** and **2** is available.[15] Scattering factors were taken from ref 16.

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Registry No. **1**, 111025-75-3; **2**, 111025-74-2; [Pd(CO)Cl]$_n$, 28551-87-3; Pd, 7440-05-3.

Supplementary Material Available: Tables of thermal parameters for **1** and **2** (2 pages); tables of structure factors for **1** and **2** (13 pages). Ordering information is given on any current masthead page.

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(14) P is used in the calculation of $\sigma(I)$ to downweight intense reflections in the least-square refinement. The function minimized was $\sum w(|F_o| - |F_c|)^2$, where $w = 4(|F_o|)^2/[\sum(|F_o|)^2]^2$, where $[\sum(|F_o|)^2]^2 = [S^2(C + R^2B) + (P(|F_o|)^2)^2]/L_p{}^2$, where S^2 is the scan rate squared, C is the total background count, R^2 is the ratio of scan time to background count squared, and L_p is the Lorentz–polarization factor.

(15) See paragraph at end of paper regrading supplementary material.

(16) *International Tables for X-Ray Crystallography*; Kynoch: Birmingham, England, 1974; Vol. IV.

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Bimetallic Lanthanide Complexes of the Calixarenes: Europium(III) and *tert*-Butylcalix[8]arene

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Addition of a 2 M quantity of $Eu(DMF)_8(ClO_4)_3$ to a solution of the macrocyclic octaphenol *tert*-butylcalix[8]arene in dimethylformamide (DMF) containing triethylamine results in the deposition of yellow crystals of the neutral complex $[Eu_2(LH_2)(DMF)_5]\cdot 4DMF$ (L = $C_{88}H_{104}O_8{}^{8-}$, the octaanion of *tert*-butylcalix[8]arene). The crystals are triclinic, space group $P\bar{1}$, with a = 21.954 (6) Å, b = 17.511 (11) Å, c = 17.315 (10) Å, α = 76.91 (5)°, β = 72.86 (4)°, and γ = 84.14 (4)°. A single-crystal X-ray structure determination has shown the ligand to adopt a "pinched" conformation with near-twofold rotational symmetry, both europium atoms being encompassed by the ligand in essentially identical environments. The europium atoms are bridged by two phenoxide donor atoms of the macrocyclic ligand and by a solvent (DMF) molecule. Each is also independently bound to two solvent molecules and three phenolic groups, giving eight-coordination in a geometry best described as bicapped trigonal prismatic. One of the capping groups on each europium is believed to be a neutral (protonated) phenolic donor of the calixarene. R was 0.056 for 15 137 "observed" reflections.

The calixarenes[1] are a class of macrocyclic molecules obviously well-suited to act as receptors for both neutral and cationic species.[2] The ready availability of larger species such as calix[6]arene and calix[8]arene (Figure 1) suggests that it should be of particular

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Table I. Non-Hydrogen Atom Coordinates[a]

atom	*x*	*y*	*z*	atom	*x*	*y*	*z*
Europium							
Eu(1)	0.18430 (2)	0.33122 (2)	0.35687 (2)	Eu(2)	0.29201 (2)	0.34618 (2)	0.48076 (2)
Ring 1							
O(1)	0.2365 (2)	0.2536 (2)	0.4498 (3)	C(142)	0.2905 (7)	−0.1198 (6)	0.540 (1)
C(11)	0.2346 (3)	0.1750 (4)	0.4742 (4)	C(143)	0.200 (1)	−0.1102 (7)	0.492 (1)
C(12)	0.2709 (3)	0.1262 (4)	0.4211 (4)	C(144)	0.191 (1)	−0.1067 (7)	0.632 (1)
C(13)	0.2687 (4)	0.0461 (4)	0.4461 (4)	C(15)	0.1983 (4)	0.0576 (4)	0.5749 (4)
C(14)	0.2317 (4)	0.0101 (4)	0.5219 (5)	C(16)	0.1997 (4)	0.1400 (4)	0.5531 (4)
C(141)	0.2276 (5)	−0.0796 (5)	0.5479 (6)	C(1)	0.3149 (4)	0.1636 (4)	0.3402 (4)
Ring 2							
O(2)	0.1927 (2)	0.2101 (3)	0.3120 (3)	C(242)	0.3841 (6)	0.1734 (8)	−0.0319 (6)
C(21)	0.2383 (4)	0.1820 (4)	0.2527 (4)	C(243)	0.4544 (6)	0.132 (1)	0.0525 (8)
C(22)	0.2249 (4)	0.1727 (4)	0.1799 (4)	C(244)	0.3883 (8)	0.0370 (8)	0.0386 (9)
C(23)	0.2746 (4)	0.1521 (4)	0.1159 (4)	C(25)	0.3465 (4)	0.1381 (4)	0.1961 (4)
C(24)	0.3368 (4)	0.1369 (4)	0.1204 (4)	C(26)	0.2989 (3)	0.1589 (4)	0.2619 (4)
C(241)	0.3902 (4)	0.1195 (5)	0.0465 (5)	C(2)	0.1572 (4)	0.1861 (4)	0.1716 (4)
Ring 3							
O(3)	0.1049 (2)	0.2955 (3)	0.2753 (3)	C(342)	0.1919 (9)	0.400 (2)	−0.1170 (8)
C(31)	0.1114 (4)	0.3194 (4)	0.1937 (4)	C(343)	0.104 (1)	0.475 (1)	−0.0924 (8)
C(32)	0.0898 (4)	0.3967 (4)	0.1629 (4)	C(344)	0.091 (2)	0.355 (2)	−0.090 (1)
C(33)	0.0964 (4)	0.4199 (5)	0.0789 (4)	C(35)	0.1444 (4)	0.2972 (5)	0.0557 (5)
C(34)	0.1237 (4)	0.3721 (5)	0.0226 (5)	C(36)	0.1384 (4)	0.2699 (4)	0.1389 (4)
C(341)	0.1305 (5)	0.3984 (6)	−0.0688 (5)	C(3)	0.0560 (4)	0.4498 (4)	0.2216 (4)
Ring 4							
O(4)	0.1305 (2)	0.4420 (3)	0.3326 (3)	C(442)	0.161 (1)	0.7873 (8)	0.109 (1)
C(41)	0.1320 (4)	0.5081 (4)	0.2765 (4)	C(443)	0.168 (2)	0.713 (1)	0.015 (1)
C(42)	0.1692 (4)	0.5696 (4)	0.2708 (4)	C(444)	0.072 (1)	0.751 (1)	0.085 (2)
C(43)	0.1686 (4)	0.6384 (4)	0.2135 (5)	C(45)	0.0958 (4)	0.5875 (5)	0.1635 (5)
C(44)	0.1318 (5)	0.6489 (5)	0.1589 (5)	C(46)	0.0945 (4)	0.5174 (4)	0.2204 (4)
C(441)	0.1321 (6)	0.7255 (6)	0.0954 (7)	C(4)	0.2145 (4)	0.5599 (4)	0.3251 (4)
Ring 5							
O(5)	0.2714 (2)	0.4007 (2)	0.3517 (3)	C(542)	0.3902 (7)	0.7140 (7)	0.094 (1)
C(51)	0.3057 (3)	0.4579 (4)	0.2949 (4)	C(543)	0.4525 (8)	0.6125 (8)	0.0322 (8)
C(52)	0.3673 (4)	0.4386 (4)	0.2474 (4)	C(544)	0.4818 (8)	0.645 (1)	0.143 (1)
C(53)	0.4043 (4)	0.4959 (5)	0.1890 (4)	C(55)	0.3213 (4)	0.5909 (4)	0.2212 (5)
C(54)	0.3827 (4)	0.5745 (5)	0.1755 (5)	C(56)	0.2826 (4)	0.5348 (4)	0.2791 (4)
C(541)	0.4249 (5)	0.6371 (5)	0.1129 (6)	C(5)	0.3914 (4)	0.3548 (4)	0.2575 (4)
Ring 6							
O(6)	0.3986 (2)	0.3862 (3)	0.4091 (3)	C(642)	0.611 (1)	0.144 (1)	0.272 (1)
C(61)	0.4498 (4)	0.3517 (4)	0.3629 (4)	C(643)	0.6716 (8)	0.245 (2)	0.227 (2)
C(62)	0.5044 (4)	0.3288 (5)	0.3920 (5)	C(644)	0.611 (1)	0.225 (2)	0.145 (1)
C(63)	0.5555 (4)	0.2874 (5)	0.3452 (5)	C(65)	0.5020 (4)	0.2947 (5)	0.2451 (5)
C(64)	0.5555 (4)	0.2691 (5)	0.2714 (5)	C(66)	0.4500 (4)	0.3341 (4)	0.2884 (4)
C(641)	0.6095 (5)	0.2215 (7)	0.2241 (6)	C(6)	0.5095 (4)	0.3491 (5)	0.4710 (5)
Ring 7							
O(7)	0.3794 (3)	0.3739 (3)	0.5601 (3)	C(742)	0.4742 (6)	0.0556 (7)	0.7668 (8)
C(71)	0.4136 (4)	0.3129 (4)	0.5947 (4)	C(743)	0.5550 (9)	0.1469 (9)	0.750 (1)
C(72)	0.3853 (4)	0.2690 (4)	0.6735 (4)	C(744)	0.559 (1)	0.072 (1)	0.6439 (9)
C(73)	0.4195 (4)	0.2060 (5)	0.7061 (4)	C(75)	0.5078 (4)	0.2306 (5)	0.5880 (5)
C(74)	0.4812 (4)	0.1851 (5)	0.6646 (4)	C(76)	0.4763 (4)	0.2952 (5)	0.5514 (4)
C(741)	0.5181 (5)	0.1159 (5)	0.7045 (5)	C(7)	0.3180 (4)	0.2911 (5)	0.7241 (4)
Ring 8							
O(8)	0.2517 (3)	0.2952 (3)	0.6089 (3)	C(842)	0.2705 (9)	−0.0005 (9)	0.884 (1)
C(81)	0.2380 (4)	0.2389 (4)	0.6753 (4)	C(843)	0.1870 (9)	0.0706 (9)	0.9663 (6)
C(82)	0.1946 (4)	0.1825 (4)	0.6853 (4)	C(844)	0.158 (1)	−0.0126 (9)	0.887 (1)
C(83)	0.1830 (4)	0.1208 (5)	0.7533 (4)	C(85)	0.2580 (4)	0.1696 (5)	0.8030 (4)
C(84)	0.2152 (4)	0.1119 (5)	0.8138 (4)	C(86)	0.2702 (4)	0.2318 (4)	0.7367 (4)
C(841)	0.2053 (6)	0.0427 (6)	0.8876 (5)	C(8)	0.1618 (4)	0.1874 (4)	0.6171 (4)
DMF A							
O(A01)	0.1714 (2)	0.3873 (3)	0.4931 (3)	C(A02)	0.0427 (6)	0.4949 (8)	0.6085 (8)
C(A01)	0.1233 (4)	0.4277 (5)	0.5157 (5)	C(A03)	0.1329 (7)	0.4215 (7)	0.6513 (6)
N(A01)	0.1020 (4)	0.4477 (4)	0.5876 (4)				
DMF B							
O(B01)	0.0875 (3)	0.2858 (3)	0.4577 (3)	C(B02)	−0.0044 (6)	0.2824 (8)	0.6153 (6)
C(B01)	0.0308 (5)	0.3005 (5)	0.4646 (5)	C(B03)	−0.0840 (6)	0.321 (1)	0.5370 (9)
N(B01)	−0.0169 (4)	0.3032 (5)	0.5344 (5)				
DMF C							
O(C01)	0.2388 (3)	0.3630 (3)	0.2144 (3)	C(C02)	0.331 (1)	0.372 (1)	0.044 (1)
C(C01)	0.2563 (8)	0.404 (1)	0.1587 (7)	C(C03)	0.284 (1)	0.4997 (9)	0.039 (1)
N(C01)	0.2891 (4)	0.4217 (4)	0.0842 (4)				

Table I (Continued)

atom	x	y	z	atom	x	y	z
			DMF D				
O(D01)	0.2830 (3)	0.4791 (3)	0.4926 (3)	C(D02)	0.342 (1)	0.670 (1)	0.401 (1)
C(D01)	0.309 (1)	0.5389 (7)	0.457 (1)	C(D03)	0.253 (1)	0.642 (1)	0.502 (1)
N(D01)	0.3083 (4)	0.6069 (4)	0.4517 (5)				
			DMF E				
O(E01)	0.3604 (2)	0.2317 (3)	0.4832 (3)	C(E02)	0.3910 (6)	0.0364 (6)	0.5799 (8)
C(E01)	0.3572 (4)	0.1697 (5)	0.5318 (5)	C(E03)	0.4535 (5)	0.1156 (6)	0.4532 (7)
N(E01)	0.3991 (3)	0.1098 (3)	0.5232 (4)				
			DMF F				
O(F01)	0.2274 (8)	0.7748 (6)	0.3095 (9)	C(F02)	0.176 (1)	0.969 (1)	0.250 (2)
C(F01)	0.1951 (9)	0.8353 (7)	0.3026 (9)	C(F03)	0.278 (1)	0.912 (2)	0.215 (2)
N(F01)	0.2177 (5)	0.9010 (5)	0.2552 (7)				
			DMF G				
O(G01)	0.2977 (8)	0.571 (1)	0.687 (1)	C(G02)	0.4444 (8)	0.4652 (8)	0.6791 (9)
C(G01)	0.3443 (9)	0.5314 (9)	0.6642 (9)	C(G03)	0.378 (1)	0.522 (1)	0.7893 (9)
N(G01)	0.3874 (6)	0.5047 (6)	0.7105 (6)				
			DMF H				
O(H01)*	0.1127 (9)	0.648 (1)	0.645 (1)	C(H02a)*	0.061 (2)	0.693 (2)	0.848 (2)
C(H01a)*	0.069 (2)	0.699 (2)	0.689 (2)	C(H02b)*	0.160 (2)	0.696 (2)	0.808 (2)
C(H01b)*	0.158 (2)	0.653 (2)	0.696 (2)	C(H03a)*	0.179 (2)	0.663 (3)	0.767 (3)
N(H01)	0.1160 (6)	0.6809 (7)	0.7582 (7)	C(H03b)*	0.062 (1)	0.699 (2)	0.770 (2)
			DMF I				
O(I01)	−0.0308 (8)	0.1016 (9)	0.601 (1)	C(I02)*	0.089 (1)	0.082 (1)	0.439 (1)
C(I01)*	0.019 (1)	0.091 (1)	0.544 (1)	C(I03)*	−0.004 (1)	0.128 (1)	0.428 (1)
N(I01)*	0.0292 (6)	0.1004 (7)	0.4765 (7)				
			DMF J				
O(J01)*	0.01820 (–)	−0.02380 (–)	0.08070 (–)	C(J02)*	−0.01827 (–)	0.05327 (–)	0.23081 (–)
C(J01)*	0.01081 (–)	−0.02164 (–)	0.15979 (–)	C(J03)*	0.00155 (–)	0.09816 (–)	0.10850 (–)
N(J01)*	0.00336 (–)	0.04031 (–)	0.16311 (–)				

[a] Atoms marked with an asterisk have site occupancy 0.5.

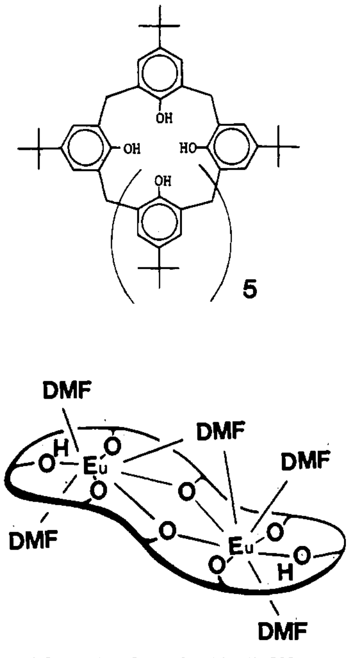
5

Figure 1. Structural formula of *tert*-butylcalix[8]arene and a schematic representation of its dieuropium(III) complex.

interest to explore their coordination chemistry with large metal ions such as the lanthanides and actinides. The possibilities that the calixarenes may function as both neutral and anionic ligands and that ring substituents may be varied considerably further heighten this interest. Although there is a considerable body of information concerning macrocyclic ligand complexes of the lanthanides and actinides,[3] the range of ligand systems is not great, with none showing the exclusively phenolate donors of the calixarenes or being so readily synthesised.

The coordination chemistry of the calixarenes has not, as yet, been sufficiently developed for general conclusions to be apparent,[4] though structural studies[5-8] of several metal complexes of calix[4]arene and calix[6]arene derivatives all show that the metal ions are not included within a cavity defined by the ligand and, in fact, are forced into somewhat unusual environments. These results suggested that structural studies would also be necessary to assist

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Table II. Europium Environments[a]

Eu(1)

	r	O(2)	O(3)	O(4)	O(5)	O(A01)	O(B01)	O(C01)
O(1)	2.351 (5)	81.2 (2)	132.5 (1)	143.6 (2)	72.9 (2)	65.8 (1)	85.8 (2)	119.7 (2)
O(2)	2.393 (5)		56.8 (2)	133.5 (2)	124.5 (2)	141.2 (1)	87.3 (2)	75.8 (2)
O(3)	2.740 (6)			77.3 (2)	148.0 (1)	136.7 (1)	72.1 (2)	73.8 (2)
O(4)	2.189 (5)				89.9 (2)	78.0 (2)	85.6 (2)	85.0 (2)
O(5)	2.338 (5)					65.9 (1)	136.7 (2)	76.1 (2)
O(A01)	2.684 (5)						71.0 (2)	138.0 (2)
O(B01)	2.393 (5)							145.8 (2)
O(C01)	2.366 (4)							

Eu(2)

	r	O(5)	O(6)	O(7)	O(8)	O(A01)	O(D01)	O(E01)
O(1)	2.363 (5)	72.0 (2)	126.3 (2)	147.8 (1)	87.4 (2)	66.6 (2)	140.3 (2)	75.9 (2)
O(5)	2.378 (5)		84.2 (2)	135.0 (2)	146.1 (2)	66.3 (2)	82.9 (2)	115.4 (2)
O(6)	2.395 (5)			56.5 (2)	129.5 (2)	142.9 (1)	79.3 (2)	72.3 (2)
O(7)	2.801 (7)				75.0 (2)	134.1 (2)	70.0 (2)	75.6 (2)
O(8)	2.147 (4)					81.0 (2)	97.8 (2)	83.8 (2)
O(A01)	2.630 (5)						75.4 (2)	139.9 (2)
O(D01)	2.365 (5)							143.7 (2)
O(E01)	2.379 (5)							

[a] *r* is the Eu–O distance (Å). Other entries in the matrix are the angles (deg) subtended at the europium by the relevant atoms at the head of the row and column. Eu(1)···Eu(2) is 3.692 (1) Å.

Table III. Coordinated Oxygen Geometries

O atom	$r_{\text{O-Eu(1)}}$, Å	$r_{\text{O-Eu(2)}}$, Å	Eu(1)–O–Eu(2), deg	Eu(1)–O–C, deg	Eu(2)–O–C, deg	$r_{\text{O-C}}$, Å
O(1)	2.351 (5)	2.363 (5)	103.1 (2)	125.5 (3)	131.4 (5)	1.346 (8)
O(2)	2.393 (5)			130.5 (4)		1.349 (8)
O(3)	2.740 (6)			125.2 (4)		1.347 (8)
O(4)	2.189 (5)			141.6 (4)		1.328 (7)
O(5)	2.338 (5)	2.378 (5)	103.0 (1)	133.7 (5)	123.3 (5)	1.344 (7)
O(6)		2.395 (5)			133.3 (4)	1.349 (8)
O(7)		2.801 (7)			120.6 (5)	1.369 (9)
O(8)		2.147 (4)			156.5 (4)	1.315 (7)
O(A01)	2.684 (5)	2.630 (5)	88.0 (1)	117.0 (6)	152.1 (6)	1.22 (1)
O(B01)	2.393 (5)			134.8 (5)		1.22 (1)
O(C01)	2.366 (4)			152.1 (12)		1.06 (2)
O(D01)		2.365 (5)			138.0 (9)	1.20 (2)
O(E01)		2.379 (5)			132.3 (5)	1.208 (8)

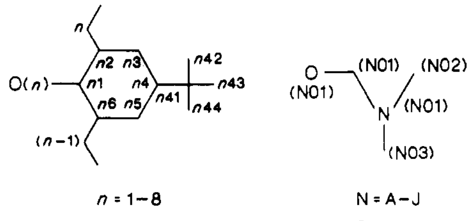
in interpreting the properties of calixarene complexes of the lanthanides, and this has proved to be the case. The largest readily available calixarene, *tert*-butylcalix[8]arene, forms a series of homo- and heterobimetallic complexes with the lanthanide ions,[9] and to establish parameters such as the metal ion separation, the considerable task of solving the crystal structure of these very large molecules was confronted. The dimethylformamide solvate of the dieuropium complex of six-times-deprotonated *tert*-butylcalix[8]arene is one species that crystallizes readily, and its crystal and molecular structure is reported herein.

Experimental Section

Synthesis. [Eu$_2${*tert*-butylcalix[8]arene-6H}(DMF)$_5$·4DMF. As a routine procedure, preparations of lanthanide derivatives of the calixarenes were conducted under an inert atmosphere,[9] though in the case of the europium(III) complex this does not appear to be necessary.

A slurry of *tert*-butylcalix[8]arene[1,2] (1.3 g) in dimethylformamide (DMF, 20 mL) was heated to 80 °C and triethylamine (0.6 g) added drop by drop until a clear, colorless solution formed. $Eu(ClO_4)_3(DMF)_8$ (2.08 g) was quickly dissolved in this mixture, to give a clear, orange solution that, on slow cooling to room temperature, deposited yellow-orange crystals (1.6 g). For X-ray diffraction studies, crystals were sealed to capillaries wet with supernatant DMF solution. Crystals collected, washed with DMF, and dried by vacuum desiccation showed weak efflorescence and became opaque. Microanalyses were consistent with some loss of DMF relative to the amount in the crystals used for structure determination. Anal. Calcd for $C_{115}H_{169}N_9O_{17}Eu_2$: Eu, 13.49. Found: Eu, 14.5 ([$Eu_2(LH_2)(DMF)_5$]·2DMF requires 14.42).

Structure Determination. A unique data set was measured at ~295 K within the limit $2\theta_{\max}$ = 50° by using an Enraf-Nonius four-circle diffractometer in conventional $2\theta/\theta$ scan mode. A total of 21 074 independent reflections were obtained, 15 137 with $I > 3\sigma(I)$ being considered "observed" and used in the 9 × 9 block-diagonal least-squares refinement after absorption correction (Gaussian) and solution of the structure by vector methods. Anisotropic thermal parameters were refined for all non-hydrogen atoms except those in the disordered DMF (H–J) components; *x*, *y*, *z*, and U_{iso} values for the DMF designated H were included at estimated values. Conventional *R* and *R′* values on $|F|$ were 0.056 and 0.069 (statistical weights, derived from $\sigma^2(I) = \sigma^2(I_{\text{diff}}) + 0.0008\sigma^4(I_{\text{diff}})$), the function minimized being $\sum w(\Delta F^2)$. Neutral atom complex scattering factors were used;[10] computation used the XTAL program system[11] implemented by S. R. Hall on a Perkin-Elmer 3241 computer. Results are presented in Figures 1 and 2 and Tables I–III; atom numbering within the phenoxide and DMF groupings is



Crystal Data: [$Eu_2(LH_2)(DMF)_5$]·4DMF ≡ $C_{115}H_{169}Eu_2N_9O_{17}$, M_r = 2253.5, triclinic, space group $P\bar{1}$ (C_i^1, No. 2), *a* = 21.954 (6) Å, *b* = 17.511 (11) Å, *c* = 17.315 (10) Å, α = 76.91 (5)°, β = 72.86 (4)°, γ = 84.14 (4)°, *U* = 6191 Å^3, $D_{\text{calcd}}(Z = 2)$ = 1.21 g cm^{-3}, *F*(000) = 2368, graphite-monochromated Mo Kα radiation, λ = 0.7106$_9$ Å, μ = 10.2 cm^{-1}, specimen 0.40 × 0.28 × 0.70 mm (prism) (capillary), $A^*_{\min}$, $A^*_{\max}$ = 1.27, 1.56.

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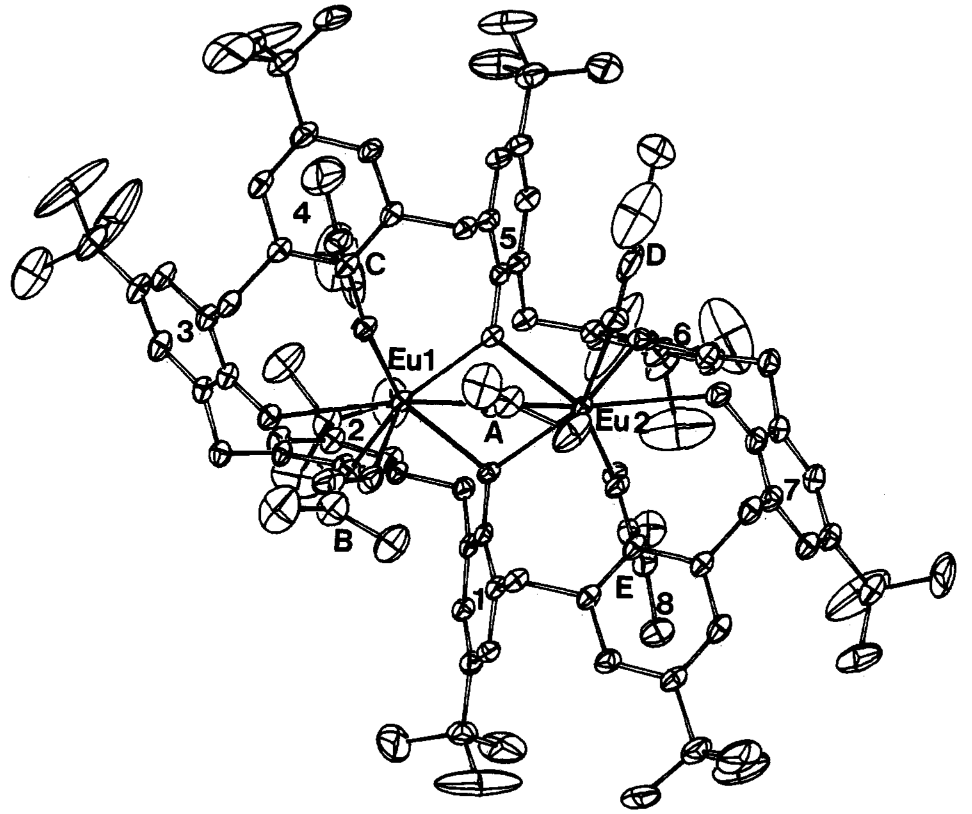

Figure 2. The complex molecule, projected so as to display its pseudo-*2* symmetry. Thermal ellipsoids of 20% probability are shown for the non-hydrogen atoms, with the macroscopic labeling scheme.

Results and Discussion

Results of the single-crystal X-ray structure determination are consistent with the presence of a bimetallic species formulated unambiguously as $[Eu_2(LH_2)(DMF)_5]$ (DMF = dimethylformamide; L = the octaanion derived by complete deprotonation of *tert*-butylcalix[8]arene). Surprisingly for a molecule so large, all atoms are completely ordered, albeit, in the case of the *tert*-butyl groups, encompassed by large thermal ellipsoids. Lattice solvent DMF molecules are disordered in three cases out of four, although this allows reasonable assignment of component fragments. Modeling of these has been made in terms of a total solvation of four molecules. Partial loss of these molecules is rather facile, as indicated by the efflorescence of the crystals when freed of supernatant solvent and analytical results for dried samples.

The complex molecule has incipient *2* symmetry, although divergent in detail (Figure 2). The two europium atoms are encompassed by the macrocycle, eight-coordination of both involving O donor atoms of phenolic and DMF moieties. O(1) and O(5) of the macrocycle bridge the europium atoms, with the planes of their associated phenyl rings lying approximately normal to the Eu(1)···Eu(2) line. A third bridge is provided by a DMF molecule, and two unidentate DMF ligands are found on each europium. Three phenolic oxygens are also bound to each, thus leading to coordination of all donor groups of the macrocycle. Eu–O bond lengths are, however, very irregular, due not only to differences between bridging and nonbridging atoms but also to the fact that two protons remain attached to the macrocycle. The distances Eu(1)–O(3) (2.740 (6) Å) and Eu(2)–O(7) (2.801 (7) Å) are much longer than the other Eu–O separations in the complex, and in view of the close similarity of the associated C–O distances with those of the rest of the macrocycle, it is reasonable to suppose that O(3) and O(7) carry these two protons. The separations Eu(1)–O(2) and Eu(2)–O(6), 2.393 (5) and 2.395 (5) Å, respectively, are similar to those observed for lanthanide(III)-phenoxide bonds in catecholate species,[12] though they differ little from the bond lengths for Eu–bridging O interactions (Eu(1)–O(1), 2.351 (5) Å; Eu(1)–O(5), 2.338 (5) Å; Eu(2)–O(1), 2.363 (5) Å; Eu(2)–O(5), 2.378 (5) Å). This suggests that these bonds may be influenced by the ligand constraints, since marked differences are observed in the bond distances to terminal and bridging DMF molecules (Eu–O(bridging DMF), 2.630–2.684 Å; Eu–O(terminal DMF), 2.365–2.397 Å). It is also noteworthy that the bonds Eu(1)–O(4) and Eu(2)–O(8), lying in relatively uncrowded environments, are short (2.189 (5) and 2.147 (4) Å, respectively). The Eu–O–C bond angles are correspondingly enlarged and the C–O bonds the shortest observed, albeit at a low level of significance. A feature common to all macrocyclic ligand–metal interactions is that the Eu atom lies well out of the plane of associated phenoxide groups (δ(Eu(1)) for phenoxides 1–5 1.89, 2.02, 2.20, 1.27, 1.57 Å; δEu(2)) for phenoxides 5–8 1.97, 1.79, 2.49, 1.02, 1.69 Å). Eu(1)···Eu(2) is 3.692 (1) Å.

Considering only the immediate coordination environment of each europium atom, the geometry of the EuO_8 moieties may be reasonably described in terms of a bicapped trigonal prism. The capping atoms are derived from the protonated-phenoxide and bridging-DMF units, those being the donors most remote from the europium centers. Eight-coordination is not uncommon for europium(III), though the bicapped-trigonal-prismatic geometry is unusual[13,14] and again may result from restrictions enforced by the macrocyclic ligand.

The nearly twofold symmetric conformation observed for the *tert*-butylcalix[8]arene ligand in its Eu(III) complex is essentially the "pinched" form proposed, on the basis of NMR measurements,[2] for the free ligand. A similar conformation has been observed for the ligand in the $TiCl_4$ derivative of hexamethoxycalix[6]arene,[6] suggesting that, even in free calixarene species, intramolecular repulsions may be more important relative to H-bonding attractions than previously considered. Of course, the flexibility of the ligands is still too great for them to be considered "preorganized" metal ion receptors.[15,16] The fact that the pinched

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calixarene conformation has been postulated to involve two circular H-bonding networks is, however, consistent with the behavior, so far as it is presently characterized, of both calix[6]arene and calix[8]arene as ditopic receptors.[17] Bimetallic systems are of interest for many reasons,[17-19] the nature of energy- and electron-transfer processes being especially important in lanthanide compounds.[20-22]

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Registry No. $[Eu_2(LH_2)(DMF)_5]\cdot 4DMF$, 111004-80-9.

Supplementary Material Available: Thermal parameters (Table SUP-1), hydrogen parameters (Table SUP-2), ligand non-hydrogen geometries (Table SUP-3), and DMF geometries (Table SUP-4) (18 pages); a listing of structure factor amplitudes (62 pages). Ordering information is given on any current masthead page.

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Phosphorus Versus Nitrogen Donor Ligands in Edge-Sharing Bioctahedra of Niobium and Tantalum $M_2Cl_6(L\text{-}L)_2$ Complexes

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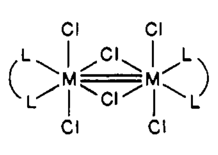
Received June 10, 1987

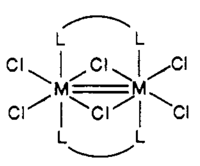
Three new edge-sharing bioctahedra, $Nb_2Cl_6(Et_2NCH_2CH_2NEt_2)_2$ (**1**), $Ta_2Cl_6(Et_2NCH_2CH_2NEt_2)_2$ (**2**), and $Nb_2Cl_6(Et_2PCH_2CH_2PEt_2)_2$ (**3**), have been prepared by a ligand displacement reaction on $M_2Cl_6(SMe_2)_3$ with $Et_2NCH_2CH_2NEt_2$ or $Et_2PCH_2CH_2PEt_2$. All three compounds have been structurally characterized in order to investigate the effect of different donor atoms on the metal–metal bond length. The following crystallographic parameters were found for the three compounds: $Nb_2Cl_6(Et_2NCH_2CH_2NEt_2)_2\cdot C_7H_8$, space group $P\bar{1}$, a = 10.335 (5) Å, b = 10.464 (3) Å, c = 9.482 (2) Å, α = 115.35 (2)°, β = 95.67 (3)°, γ = 94.07 (4)°, Z = 1, Nb=Nb = 2.764 (1) Å; $Ta_2Cl_6(Et_2NCH_2CH_2NEt_2)_2\cdot C_7H_8$, space group $P2_1/a$, a = 10.433 (1) Å, b = 16.680 (3) Å, c = 10.647 (3) Å, β = 99.72 (2)°, Z = 4, Ta=Ta = 2.7776 (6) Å; $Nb_2Cl_6(Et_2PCH_2CH_2PEt_2)_2$, space group $Pca2_1$, a = 14.857 (2) Å, b = 16.642 (3) Å, c = 13.605 (2) Å, Z = 4, Nb=Nb = 2.741 (3) Å.

Introduction

Ligand displacement reactions on niobium or tantalum $M_2Cl_6(SMe_2)_3$ or $M_2Cl_6(tht)_3$ (tht = tetrahydrothiophene) have been shown to give a variety of monomeric and dimeric products of differing geometries. Of particular interest to us is the formation of the edge-sharing bioctahedral dimers typically formed by use of bidentate ligands. These ligands may be arranged about the metal centers in one of two ways, chelating (α) or bridging (β):



α



β

The α-form is typically observed for ligands that form five-membered rings with the metal (e.g. 1,2-bis(diphenylphosphino)ethane (dppe),[1] 1,2-bis(dimethylphosphino)ethane (dmpe),[2] and 3,6-dithiaoctane (dto)[3]), while ligands with a smaller bite size have been found in both chelating [e.g. bis(diphenylphosphino)methane (dppm)[4]] and bridging [e.g. bis(dimethylphosphino)methane (dmpm)[5]] modes.

The preparation of molecules of this type affords us the opportunity to study metal–metal interactions through a variety of ligand sets with different electronic and steric requirements.[6] To date, however, the majority of structurally characterized edge-sharing bioctahedra of niobium and tantalum of the types $M_2Cl_6L_4$ and $M_2Cl_6(L\text{-}L)_2$ contain phosphine donor ligands. We now report the synthesis and structural characterization of three new compounds, two of which contain nitrogen donor ligands. These compounds are $Nb_2Cl_6(dene)_2$ (**1**), $Ta_2Cl_6(dene)_2$ (**2**), and $Nb_2Cl_6(depe)_2$ (**3**) where dene is *N,N,N′,N′*-tetraethylethylenediamine and depe is 1,2-bis(diethylphosphino)ethane. This work was undertaken to see if the metal–metal bond length would be significantly affected by using a very basic, pure σ-donor ligand (dene) in place of a phosphine ligand (depe), which is less basic and can also participate in $M \rightarrow L$ π back-bonding.

Experimental Section

The air sensitivity of the reactants and products necessitated the use of standard Schlenk and vacuum-line techniques. The reaction products were prepared, filtered off, and washed under an atmosphere of argon with subsequent handling in an inert (N_2) atmosphere box. Solvents were freshly distilled from benzophenone ketyl and transferred to and from reaction vessels via stainless steel cannulae and/or syringes. The ligands, 1,2-bis(diethylphosphino)ethane (depe) and *N,N,N′,N′*-tetraethylethylenediamine (dene), were purchased from Organometallics, Inc., and Aldrich Chemical Co., respectively. Both compounds were deaerated prior to use. Infrared spectra were recorded on a Perkin-Elmer 783 spectrophotometer. Peaks coincident with those of Nujol are not reported.

Preparation and Crystallization of $Nb_2Cl_6(dene)_2$ (1). Into a Schlenk tube was filtered a solution of 0.12 g (0.21 mmol) of $Nb_2Cl_6(SMe_2)_3$ in

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