Articles

Calixarenes as Scaffolds: Introduction of Tridentate Rare Earth Metal Binding Units into Calix[4]arene

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The reactions of various derivatives of chelidamic acid (4-hydroxypyridine-2,6-dicarboxylic acid) with *p-tert*-butylcalix[4]arene have produced several new mono- and difunctionalized derivatives of the calixarene in which tridentate functional groups suitable for the binding of rare earth metal cations have been incorporated. Single-crystal X-ray structure determinations have been performed on two difunctionalized calixarenes found to adopt different "cone" and "1,2-alternate" conformations, as well as on a complex of europium(III) with the phenoxide form of a monofunctionalized ligand, this structure confirming that charge factors are dominant in determining the site of lanthanide metal binding in these ligands.

Introduction

The calixarenes have been widely exploited as metal-binding agents.[1−6] The phenolic oxygen atoms of the parent calixarenes often retain a role in metal coordination even in the presence of strong ligating groups added as substituents. In other cases, however, the calixarene serves simply as a three-dimensional scaffold for an array of ligating groups.[1−8] For this purpose, calix[4]arenes are particularly useful because of the conformational control they allow.[7] Total curtailment of conformational mobility may not be necessary, however, when the metal-binding sites are only found in substituents too large to pass through the annulus. Thus, useful orientational control of binding sites should result even in 1,2- or 1,3-disubstituted calix[4]arene derivatives.

We have explored this hypothesis through the synthesis of calix[4]arene derivatives in which the functional group contains a tridentate binding site suitable for the coordination of rare earth metal cations. The mode of functionalization was chosen to differ significantly from that widely explored elsewhere,[8] in the hope that novel relative orientations of rare earth metal and calixarene cavity moieties might be obtained in the product complexes. The construction of complexing agents for the rare earth metals is of interest not only for the treatment of nuclear wastes[8b] but also for the construction of sensing devices that take advantage of the electronic and magnetic properties of compounds of these elements.[9−13] Eu(III) and Tb(III) complexes, for example, are of particular interest for use in light-conversion devices in which it is necessary that they be bound to ligands that absorb light strongly, transfer the excitation efficiently to the rare earth metal, and protect the ion from interactions that provide a quenching pathway.[9,12] It has long been known[14−16] that rigid, tridentate ligands such as the dipicolinate (pyridine-

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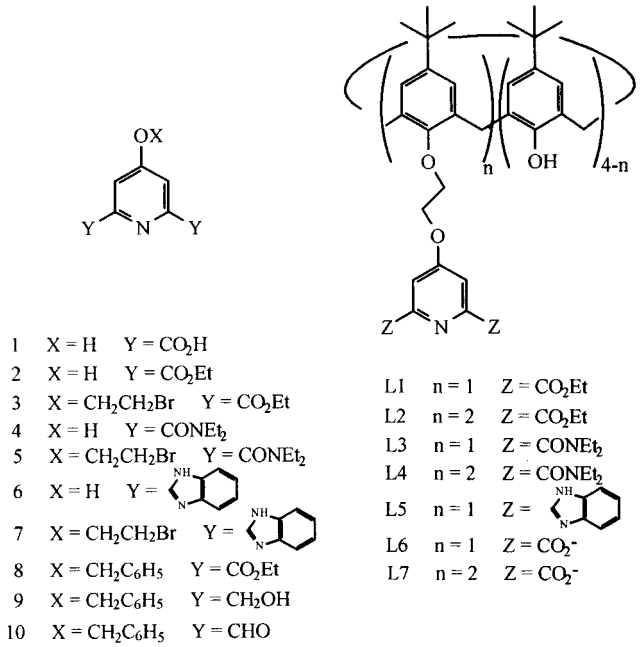

Figure 1. Molecules synthesized in the present work.

2,6-dicarboxylate) dianion provide highly luminescent Eu(III) and Tb(III) complexes, as do newer derivatives of tridentate 2,6-bis(benzimidazol-2-yl)pyridine.[9,17] Thus, our specific investigations have concerned the introduction of such units as substituents on the calix[4]arene skeleton. Since it is known that that the calixarene chromophore can act as an absorption unit for transferring energy to both Eu(III) and Tb(III),[18−20] it was our hope that inclusion of various guests within the cone of a calixarene bound to a rare earth metal by ligation of substituent chelate units might provide a subtle mechanism for luminesence control.

The structures of the ligands used in the present study are shown in Figure 1. Their syntheses from a conveniently available functionalized form of dipicolinate, 4-hydroxypyridine-2,6-dicarboxylate ("chelidamate")[21] are shown in Figure 2. The luminescence properties of their Eu(III) complexes have been studied, and two difunctionalized calixarene ligands and the Eu(III) complex of the deprotonated form of a monofunctionalized ligand have been characterized by X-ray crystallography.

Results and Discussion

1. Ligand Syntheses. Using chelidamic acid and its derivatives and a simple double Williamson synthesis of ethers with 1,2-dibromoethane, *p-tert*-butylcalix[4]arene has been substituted as displayed in Figures 1−4.

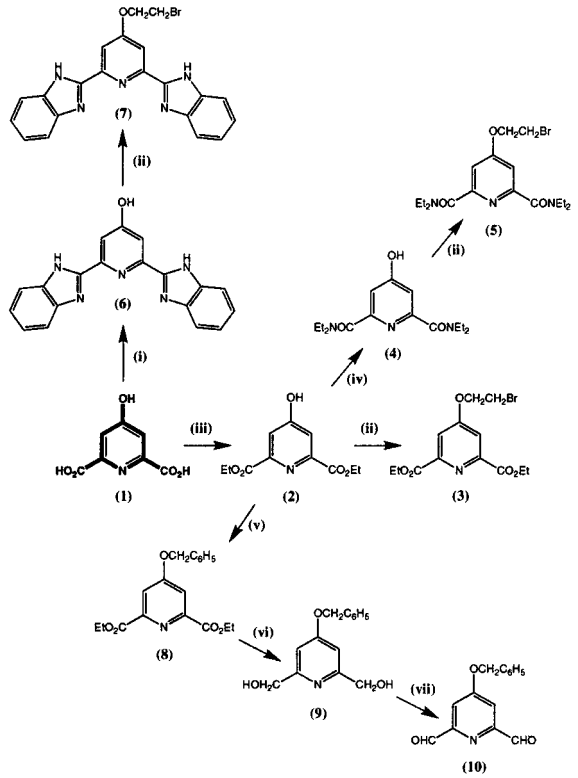

Figure 2. Chemical transformations of the chelidamate unit used in this work: (i) $C_6H_4(NH_2)_2$, H_3PO_4, 210 °C; (ii) $BrCH_2CH_2Br$ (excess), K_2CO_3; (iii) H_2SO_4, ethanol; (iv) $Et_2NH/AlCl_3$, toluene; (v) $C_6H_5CH_2$-Br, K_2CO_3, CH_3CN; (vi) $NaBH_4/AlCl_3$, diglyme; (vii) MnO_2, $CHCl_3$.

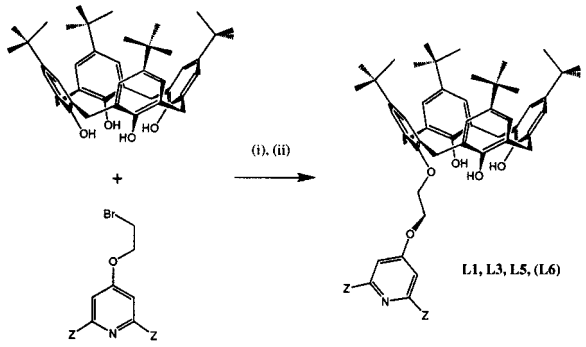

Figure 3. Monoalkylation of *p-tert*-butylcalix[4]arene with chelidamate derivatives: (i) For **L1** (Z = CO_2Et): K_2CO_3/CH_3CN, reflux, 3 d (**L6** obtained by base hydrolysis of **L1**). (ii) For **L3** (Z = $CONEt_2$), **L5** (Z = benzimidazol-2yl): $BaO/Ba(OH)_2$/dmf, RT, 3 d.

(a) Preparation of the Bromo Derivatives of the Tridentate Coordination Units. The formation of calixarene ethers is a well-studied reaction, and the bromoalkyl group, in particular, has been established as a useful alkylating agent for the phenoxide oxygen atoms of calixarenes.[7] Thus, alkylation by the use of a bromoethyl derivative of chelidamic acid (**1**) was envisaged for the syntheses of heterotopic ligands containing as binding units both the hydrophilic cavity of *p-tert*-butylcalix-[4]arene and a tridentate coordination site suited to rare earth metals. The fact that chelidamic acid might be readily converted to ester, amide, and cyclic amidine (imidazole) derivatives also offered the prospect of pathways to tridentate units of different coordinating strengths. The diethyl ester of chelidamic acid (**2**) was easily converted to its 2-bromoethyl ether (**3**) by reaction with 1,2-dibromoethane under base catalysis. If the ester was first reacted with diethylamine to obtain the bis(diethylamide) (**4**), this, too, was easily converted to its 2-bromoethyl ether

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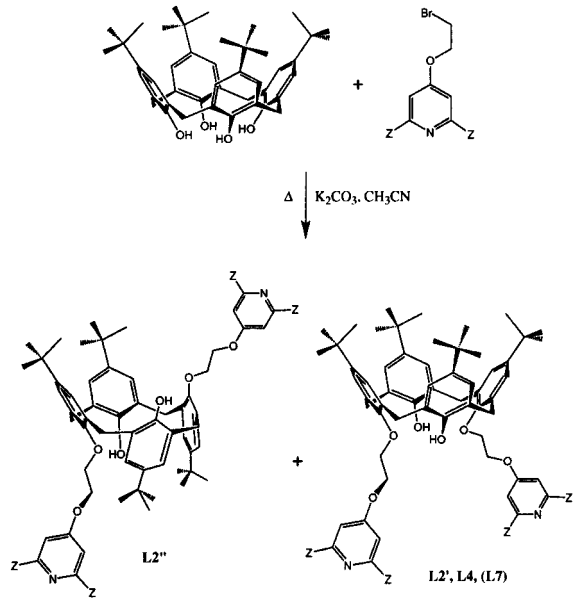

Figure 4. Dialkylation of *p-tert*-butylcalix[4]arene with chelidamate derivatives: **L2′**, **L2″** (Z = CO_2Et) (**L7** obtained by base hydrolysis of **L2**); **L4** (Z = $CONEt_2$).

(**5**), though the preparations of both **3** and **5** require the use of a large excess of 1,2-dibromoethane to avoid the formation of diethers. The functionalized diamide (**5**) proved advantageous over the corresponding ester (**3**) for use in alkylation reactions of calixarenes where strongly basic reagents were present and caused hydrolysis of the ester units. Phillips condensation[22,23] of **1** with 1,2-benzenediamine in 100% H_3PO_4 at 210 °C gave the robust bis(benzimidazole) derivative **6**, care being necessary in the dephosphorylation/neutralization steps of this synthesis to avoid isolation of either the phenoxide (sodium) salt or the N-protonated form. The conversion of **6** to its 2-bromoethyl ether, **7**, was complicated by the very low solubility of **6** in all solvents tested, so that **7** was initially obtained in relatively poor yield (~50%) through reaction conducted under heterogeneous conditions. However, the subsequent discovery that **6** was readily soluble in ethanol in the presence of K_2CO_3 permitted the yield of **7** to be increased to 70%, with no apparent competition for the electrophile by the ethanol solvent.

(b) Functionalization of the Lower Rim of *p-tert*-Butylcalix-[4]arene. Presuming that three tridentate units derived from chelidamate would bind to a single rare earth metal(III) cation, we considered that both monosubstitution and (the easily obtained) 1,3-disubstitution of the lower rim of *p-tert*-butylcalix-[4]arene in a "cone conformation" should provide ligands well suited for the assembly of several *p-tert*-butylcalix[4]arene units around such a cation. The formation of monoethers of calixarenes is well-known to be a rather inefficient process,[24] diethers commonly predominating even for alkylating agent:calixarene ratios <1.[7] Although the easily isolated calixarene monoanion derivative [NBu_4][*p-tert*-butylcalix[4]arene − H][25] reacted readily with benzyl bromide to give an excellent yield of the monobenzyl ether, its reactions with the bromoethyl ethers **3**, **5**, and **7** proved to be negligibly slow. Fortunately, for the alkylating agents **5** and **7**, where the functional group is not base sensitive, the established method for calix[4]arene monoalkylation, based on the use of the mixed $BaO/Ba(OH)_2$ catalyst in dimethylformamide solvent,[26] proved successful for the preparation of the monoalkylated *p-tert*-butylcalix[4]arene-based ligands **L3** and **L5** in acceptable (>65%) yields. For monoalkylation of *p-tert*-butylcalix[4]arene with **3**, the use of K_2CO_3, **3**, and the calixarene in a 0.6:1:1 ratio in CH_3CN gave good results, with a single recrystallization of the product usually being sufficient to separate the ligand **L1** from the small amount of diether also formed.

Reactions of *p-tert*-butylcalix[4]arene with 2-fold molar quantities of the bromo compounds **3** and **5** under conventional conditions for distal (1,3) dialkylation (K_2CO_3 as base in acetonitrile solvent)[7] resulted in the expected 1,3-dialkyl derivatives (**L2** and **L4**), though fractional crystallization or column chromatography were necessary to separate isomers and remove trace amounts of monoethers. Both **L1** and **L2** were readily converted by hydrolysis to the anionic ligands **L6** and **L7**. Although yet to be investigated for their calixarene analogues, reactions of a "model" (benzyloxy)pyridine compound (**8**) in which ethoxycarbonyl substituents have been converted to hydroxymethyl and then to aldehyde groups (compounds **9** and **10**, respectively) show that it should be possible to form a wide range of macrocycles bearing calixarene substituents.

2. Ligand Characterizations. (a) Nuclear Magnetic Resonance Spectroscopy. It is well-known[7] that the ^1H nuclear magnetic resonance spectrum of *p-tert*-butylcalix[4]arene in solution reflects an apparently[27] 4-fold-symmetric cone conformation for the molecule, specifically shown by the doublets observed for the axial and equatorial protons of the bridging methylene groups. This signature for the cone conformation is usually retained even when functionalization of the calixarene, as in the case of monoether formation, removes the 4-fold rotational symmetry.[7,26] Thus, the observation of methylene proton doublets at δ 4.3 and 3.6 for **L1** is taken as evidence that this ligand adopts a cone conformation in chloroform solution. For the ligands **L3** and **L5**, spectra are more complicated, in particular because they exhibit two sets of methylene proton doublet pairs. Strictly, this is compatible with both ligands also having the cone conformation, but on an empirical basis of the magnitude of the proton anisochrony,[7,26,28] we infer that this is evidence that **L3** and **L5** preferentially adopt partial cone conformations where the functionalized phenolic unit is inverted relative to the other three. Given the presence of three unfunctionalized phenolic units, we presume that **L1**, **L3**, and **L5** undergo interconversions of all possible conformers in solution at ambient temperatures which are too rapid for the physical separation of the different forms.[7,28]

Since the substituents introduced onto the calixarene skeleton in all the present instances were expected to be too large to pass through the macrocyclic ring and hence to inhibit inversion of the phenyl ring to which they were attached, it was anticipated that, for the dialkylated ligands **L2** and **L4**, isomers might be detected where the substituents had different relative orientations. In fact, the major product (56% yield) of the reaction of 2 equiv of **3** with *p-tert*-butylcalix[4]arene appeared to be a species that exhibited just one pair of (calixarene) methylene

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(26) See, for example: Iwamoto, K.; Araki, K.; Shinkai, S. *Tetrahedron* **1991**, *47*, 4325−4342.
(27) Conner, M.; Janout, V.; Regen, S. L. *J. Am. Chem. Soc.* **1991**, *113*, 9670−9671.
(28) Iwamoto, K.; Araki, K.; Shinkai, S. *J. Org. Chem.* **1991**, *56*, 4955−4962.

proton doublets and which was therefore assumed to be the 1,3-dialkylated material in the cone conformation (**L2′**). A small amount (2.7% yield) of isomeric material (**L2″**) chromatographically separated from the product mixture exhibited an ^{1}H NMR spectrum in which four well-separated singlets could be assigned as such methylene proton resonances. This pattern is consistent with the 1,2-alternate conformation[7,29] of the 1,3-dialkylated calixarene established in the solid state by X-ray crystallography (see below). Although there appeared to be only one component in the product **L4**, overlap of signals for the amide ethyl groups and the calixarene methylene protons prevented a clear assignment of conformation based on the NMR spectrum, and the (solid state) cone conformation and 1,3-dialkylated configuration of this material were again established by X-ray crystallography.

(b) Electronic Spectra of Li (and Their Eu(III) Complexes). The spectra of the ligand precursors (**1**) − (**7**) in CH_3CN solutions showed that the chelidamate moiety gave absorptions only at rather high energy, except in the case of the bis(benzimidazolyl) derivative (**7**), for which a broad and structured band was observed at about 31 700 cm^{-1}. The electronic spectrum of **3**, for example, displays a $\pi-\pi^*$ transition at 46 500 cm^{-1} and a shoulder at 41 600 cm^{-1}, assigned to the pyridine n$-\pi^*$ transition. For the *p-tert*-butylcalix[4]arene-containing ligands, these absorptions are overlapped by the $\pi-\pi^*$ transition of the four phenolic groups of the macrocycle. A weak absorption at 37 000 cm^{-1} is attributed to the phenol n$-\pi^*$ transition. During complexation, the spectra of **3** as a function of the metal concentration show a shift to lower energy and, for an Eu:L ratio of 1.8, the absorption maximum moves to 43 500 cm^{-1}. Unfortunately, with **L1**−**L4**, this move is only evidenced by the appearance of a shoulder on the low-energy side of the phenol $\pi-\pi^*$ absorption band, resulting in only slight differences between absorptions of the free ligands and the complexes. The absorption band of the bis(benzimidazolyl)pyridine unit is not overlapped by the macrocycle absorption, and the electronic spectral changes in the titration of **L5** by Eu(III) reveal that the phenol absorption is unaffected, while the bis(benzimidazolyl)pyridine absorption band undergoes large changes. This indicates that the phenolic donors of the *p-tert*-butylcalix[4]arene are not involved in complexation under such conditions.

(c) Luminescence Spectroscopy of L1 and L5 and of 1:1 Eu/L1 and Eu/L5 Mixtures in CH_3CN. The emission spectra of **L1** and **L5** in solution show a broad band with a maximum at 27000 cm^{-1} for **L5** (λ_{ex} = 270 nm) and at 32800 cm^{-1} for **L1** (λ_{ex} = 270 nm). These bands are assigned as arising from a $^1\pi\pi^*$ state. No lower $^3\pi\pi^*$ state is detected. For **L1**, the excitation spectrum consists of a broad band centered at 37 700 cm^{-1}, while the excitation spectrum of **L5** diplays two bands, a broad one at 38 500 cm^{-1} and a sharper one at 29 400 cm^{-1}, which is responsible for the visible blue emission of the bis(benzimidazolyl)pyridine unit. Both the phenol and the 4-substituted-pyridine-2,6-dicarboxylate chromophores in the present compounds appear to give almost indistinguishable absorption, excitation, and emission spectra. Therefore, for **L5**, the emission spectrum obviously arises only from the bis(benzimidazolyl)-pyridine $^1\pi\pi^*$ state at low energy, while the excitation spectrum (monitored on bis(benzimidazolyl)pyridine emission) shows both the phenol and the bis(benzimidazolyl)pyridine $^1\pi\pi^*$ states. This result indicates that the energy absorbed by the macrocycle is transmitted to the bis(benzimidazolyl)pyridine unit. When Eu-$(ClO_4)_3.nH_2O$ is added to both ligand solutions, the ligand emissions are quenched because of efficient energy transfers from the ligands to the Eu(III) cation and the Eu(III) emissions are observed ($^5D_0 \rightarrow {}^7F_j$, $j = 0-4$). This has been exploited in a luminescence titration of a ligand by the Eu(III) cation (see below). However, for the solutions of **L5** with Eu(III), the lanthanide luminescence is weak even though the ligand emission is totally quenched. The weak emission of these solutions is attributed to the presence of water molecules in the first coordination sphere of Eu(III), originating from the hydrated perchlorate. When one drop of triethyl orthoformate is added as a desiccant to the measurement cell, the lanthanide cation emission becomes much more intense. The coordinating ability of water molecules is apparently as strong as that of the tridentate unit and reveals the weakness of the wrapping of this unit around Eu(III) when it bears a bulky substituent such as *p-tert*-butylcalix[4]arene.

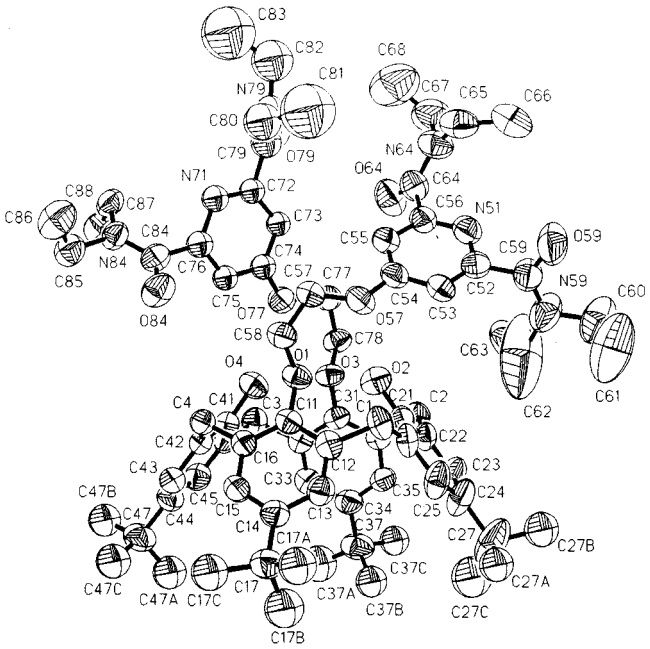

Figure 5. View of **L4**, without solvent molecules and disordered components of *tert*-butyl groups, showing conventional atom numbering. 50% displacement ellipsoids are shown in this and all other crystallographic figures.

(d) Ligand Structures. Given the expectation of greater conformational restrictions within the disubstituted calixarenes, it was of particular interest to establish their detailed solid-state structures. This was therefore done through single-crystal X-ray diffraction studies for the ligands **L4** and **L2″**, the latter being chosen in addition because of spectroscopic indications that it did not adopt the cone conformation.

The expectations based on the synthetic procedures and spectroscopic measurements that **L4** would be a 1,3-dialkylated calix[4]arene in the cone conformation were confirmed by the structure determination (Figure 5). Numerous more subtle chemical features of the ligand are revealed in the details of the solid-state structure, however. As might be expected given the pattern of substitution, the molecular cone is not exactly regular, with the phenyl rings bearing the substituted pyridyl substituents being slightly more steeply inclined (∼72°) to the mean plane of the methylene bridge carbon atoms than are the phenyl rings with the remaining hydroxyl substituents (∼52°). The pendent diethyl chelidamyl groups are in essentially divergent orientations from the calixarene core, so that the ligand

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could certainly not be described as preorganized for chelation of both to a single metal ion. Assuming each pendent unit would function as a tridentate ONO donor, even the donors (pyridine N, amide O) are not oriented so as to facilitate their joint binding. Both residual phenolic groups seem to be involved in intramolecular hydrogen-bonding: O(2)H(2)···O(1), with distances O(2)−H(2) 0.82(3), H(2)···O(1) 1.92(2), and O(2)···O(1) 2.723(5) Å and angle O(2)H(2)O(1) 166(7)°; O(4)H(4)···O(3), with distances O(4)−H(4) 0.82(3), H(4)···O(3) 2.00(2), and O(4)···O(3) 2.785(5) Å and angle O(4)H(4)O(3) 159(5)°. There is also evidence of weaker interactions involving O(2) and O(4) and the chelidamyl 4-oxygen atoms, O(57) and O(77), respectively: O(2)···O(57) 3.204(6) and O(4)···O(77) 3.059(5) Å.

Solvation of the molecule is complicated, with a water molecule being involved in intermolecular associations while ethanol and dichloromethane share occupation of the calixarene cavity. The water is disordered over two sites, with population parameters of $^2/_3$ and $^1/_3$ for O(1W) and O(2W), respectively. Close approaches to calixarene oxygen atoms (O(1W)···O(84) 2.82(1), O(2W)···O(59) 2.88(2) Å; O(1W)···O(59′) 2.90(1), O(2W)···O(84′) 2.88(2) Å), presumably indicative of hydrogen-bonding, can be seen as linking pairs of calixarenes as centrosymmetric dimers. Each calixarene unit is chiral. The included solvent molecules are also disordered, rendering precise modeling of their nature difficult, and at present no more can be said than that ethanol and dichloromethane alternate in their occupancy of the cavities of otherwise equivalent calixarenes. Inadequacies in this model may be associated with apparent disorder in the orientation of one of the pyridyl units (and possibly of the *tert*-butyl substituents, though such disorder is very commonly encountered in structures of *tert*-butylcalixarenes).

The calixarene present in **L2″** is a 1,3-disubstituted species such as **L4** but is unlike it in adopting the relatively rare 1,2-alternate conformation,[7,29] causing the tridentate substituent units to be oriented as divergently as possible (Figure 6). The molecule is sited at a symmetry center of the monoclinic unit cell. There is a close approach between oxygen atoms O(21) and O(11) (2.943(5) Å), and the hydrogen bond therefore presumed to exist must be a factor favoring the 1,2-alternate conformation. Viewed along the *c* axis, the calixarene has an ellipsoidal cross section, with a short axis radius of ∼1.7 Å, approximately half that of the long axis. The lattice consists of stacks of calixarenes defining empty tunnels (Figure 7). Favorable intermolecular interactions between carbonyl group dipoles may be the factor responsible for the stacking array. Were the array to be maintained in the presence of a metal ion, it is conceivable that these tunnels might function as ion channels, but in this regard it may be significant that the polar guest in the present crystal, water, although seemingly involved in hydrogen-bonding to a carbonyl oxygen (O(W)···O(44) 2.681(3) Å), lies outside the tunnels. The dihedral angle between adjacent calixarene phenyl rings is 106.0(2)°, and the plane of the pyridine ring is tilted by 31.0(2)° with respect to that of the phenyl ring on which it is a substituent. The pyridine rings are nearly parallel to the *ac* plane. Some disorder in the structure is associated with both the *tert*-butyl groups and the lattice water.

3. Ligand Coordinations. (a) Solution Complexation Studies. The ligands **Li** (i = **1**−**5**) and the bromoalkyl derivative (**3**) were titrated with $Eu(ClO_4)_3.nH_2O$ in acetonitrile (metal:L ratio in the range 0.1−1.8). Small but significant changes in absorbance were observed along with isosbestic points (for **L1**, **L2**, **L5**, and **3**), but a satisfactory fit of the data to any anticipated

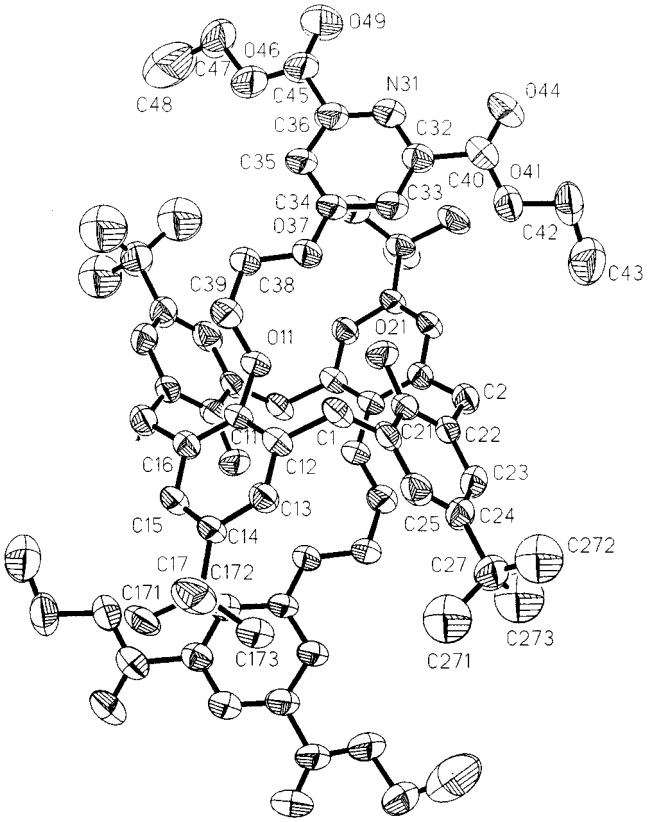

Figure 6. View of **L2″**, without solvent molecules and disordered components of *tert*-butyl groups, showing conventional atom numbering.

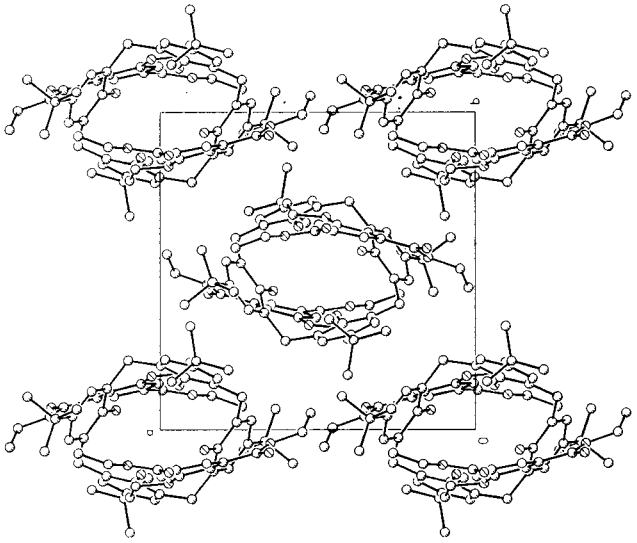

Figure 7. Packing diagram for **L2″**; [110] projection.

model (involving combinations of ML, ML_2, and ML_3 species) could not be obtained. The cessation of significant change in absorbance beyond M:L = 0.5 for the three monosubstituted *p-tert*-butylcalix[4]arenes **L1**, **L3**, and **L5** was perhaps indicative of relatively high stability for an ML_2 species but, at least in the case of **L5**, was inconsistent with luminescence titration data which indicated formation of an ML_3 complex. Electrospray mass spectrometry for the Eu/**L3** system also provided evidence for such a species. As noted above, however, overall indications were that the interactions between the new ligands (at least in their neutral forms—see below) and Eu(III) were disappointingly weak.

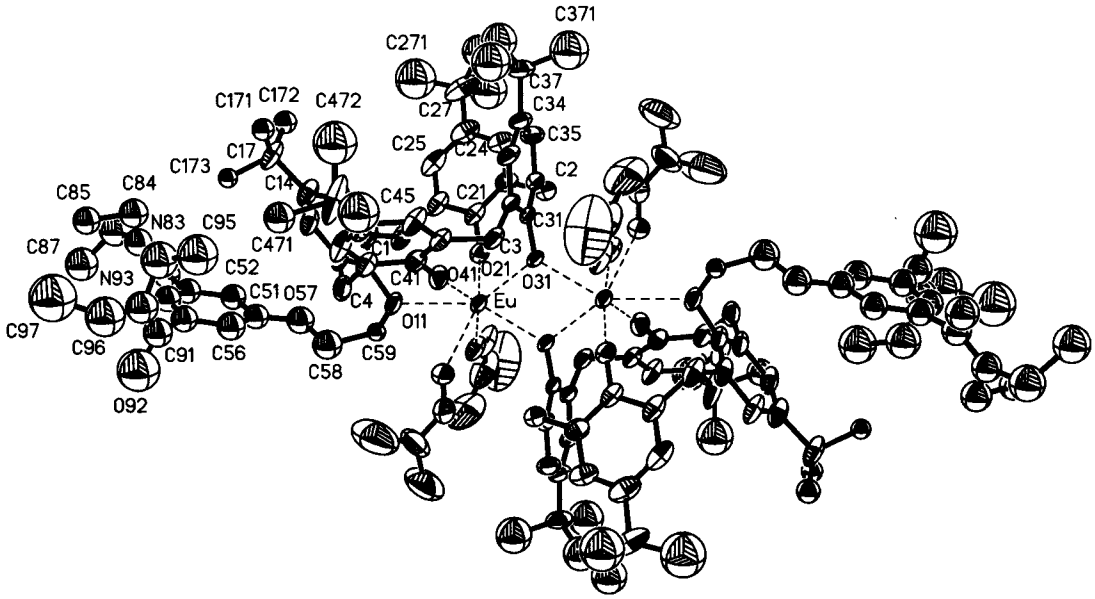

Figure 8. View of the centrosymmetric dimer present in the crystal of the complex $[Eu_2(\mathbf{L3} - 3H)_2(dmf)_4]\cdot 4dmf$, showing conventional atom numbering. Disordered components are not shown (but see the Supporting Information).

Aside from the possible complicating role of traces of water in the solution equilibria, the ambidentate nature of the functionalized calixarenes is a factor requiring consideration. In relatively concentrated ($\sim 10^{-2}$ mol L^{-1}) solutions of Eu(III) and the various ligands, a perceptible yellow color, indicative of the presence of Eu(III) phenoxide species,[19,30] was apparent. Addition of base (triethylamine) to these solutions resulted in a deep yellow coloration and, from dimethylformamide solvent, ready precipitation of yellow, crystalline complexes. The only exception to these observations was provided by the case of the diacid derived from **L1**, where a strongly luminescent and colorless complex did form under basic conditions. Unfortunately, the unusual solubility properties of this complex, which was very soluble in all organic solvents tested but was of extremely low solubility in water, frustrated all efforts to obtain crystals suitable for characterization through X-ray diffraction. It is presumed from its strong luminescence that it is a species in which coordination occurs exclusively through the pyridyl dicarboxylate moieties.[16]

(b) Solid-State Structures. Significantly, the structure (Figure 8) determined by single crystal X-ray diffraction measurements on the complex formed between Eu(III) and **L3** under basic conditions shows that the pendent tridentate groups are rejected by the metal ion in favor of calixarene phenoxide O and solvent O donors. The centrosymmetric, binuclear structure involving seven-coordinate Eu atoms, each bound to two unidentate phenoxide oxygen atoms, two bridging phenoxide oxygen atoms, one unidentate phenol ether oxygen atom, and two oxygen atoms of unidentate dmf ligands, is very similar to that found for the complex of unsubstituted *p-tert*-butylcalix[4]arene with Eu(III),[31] a comparison of pertinent bonding distances being given in Table 1. The calixarene entities have cone conformations very similar to that of **L4**, again with some disorder in the *tert*-butyl groups. Some disorder is also apparent in the orientation of the pendent, uncoordinated chelidamyl amide substituents. Of the four molecules of uncoordinated dmf in the stoichiometric unit $[Eu_2(\mathbf{L3} - 3H)_2(dmf)_4]\cdot 4dmf$, two are found disordered in the lattice between the complex molecules and two are included within the calixarene units (one in each) in each dimer. Inclusion of the dmf molecules is in a "methyl-in, carbonyl-out" manner, with the carbon atom of the more deeply penetrating methyl group being positioned ~0.4 Å below the center of the mean plane of the four *p*-carbon atoms of the calixarene phenyl rings. Obviously, the complex itself can be regarded as a ligand with divergently oriented tridentate chelidamyl amide chelating units, though we have not explored this possible further aspect of its coordination chemistry.

Table 1. Eu Environments in $Eu_2(L - 3H)_2(dmf)_4$ (L = Calixarene) Complexes

L	bond	bond dist/Å
L3	Eu−O(phenoxide)	2.146(4), 2.169(4)
	Eu−O(phenoxide bridge)	2.362(4), 2.392(4)
	Eu−O(dmf)	2.435(5), 2.452(5)
	Eu−OR(phenol ether)	2.693(4)
	Eu···Eu	3.9484(9)
p-tert-butylcalix[4]arene[31]	Eu−O(phenoxide)	2.143(6), 2.150(7)
	Eu−O(phenoxide bridge)	2.332(5), 2.395(6)
	Eu−O(dmf)	2.466(7), 2.465(7)
	Eu−O(phenol)	2.558(6)
	Eu···Eu	3.9067(7)

Conclusions

The syntheses of **L1**−**L5** have been achieved through simple modifications of the chelidamic acid precursor. The syntheses provide the opportunity to build supramolecular assemblies containing *p-tert*-butylcalix[4]arene as a building block via the formation of metal ion complexes. Monosubstitution and 1,3-disubstitution of *p-tert*-butylcalix[4]arene have been successfully achieved with standard methods, and in two cases (**L2″** and **L4**), the detailed solid-state structures have been established by X-ray crystallography. Thus, **L2″** has been shown to be a 1,3-disubstituted calix[4]arene with a 1,2-alternate conformation, while **L4** is also 1,3-disubstituted but has the cone conformation. On the basis of spectroscopic measurements, disubstituted **L2′** and monosubstituted **L1** are assigned the cone conformation, while **L3** and **L5** are assigned partial-cone conformations.

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Preliminary studies on **L5** have shown that the phenolic macrocycle can act as an antenna for the sensitization of the bis(benzimidazolyl)pyridine unit luminescence. The overall antenna effect of both parts of the ligand is considered to be the source of the relatively strong luminescence of the Eu complexes of these ligands. However, for solutions in CH_3CN, water is a competing ligand, which causes strong quenching of the lanthanide emission. This and other results indicate that the new substituted-calix[4]arene ligands are relatively poor rare earth metal binding agents at their chelidamate-derived binding sites unless these pendent arms are in an anionic form. Neutral arms do possess some complexing ability, but this is overwhelmed under basic conditions by the affinity of the rare earth metal cation for phenoxide sites derived from residual phenolic units in partially substituted calix[4]arenes. Presumably, this could be avoided by simple alkylation of the residual phenol units, though our inability to achieve any more than dialkylation of *p-tert*-butylcalix[4]arene with chelidamate derivatives indicates that such reactions may not be observable.

Experimental Section

All solvents were distilled immediately before use. THF and toluene were dried over Na, using benzophenone as an indicator of dryness and freedom from peroxides. C*H*$_3$CN was dried over CaH_2, dmf by distillation under reduced pressure over P_2O_5, and diglyme by distillation under reduced pressure over $LiAlH_4$. Chelidamic acid (**1**) was prepared according to literature methods.[21,32] *p-tert*-Butylcalix[4]arene was prepared according to a literature method[33] and was crystallized from toluene as the monosolvate. TLC was conducted on silica plates (Whatman, 250 μm layer) and flash chromatography on silica (BDH, 40−63 μm) columns. Melting points were determined on a Büchi melting point apparatus, and elemental analyses were performed on a LECO CHNS932 analyzer at the Chemistry Centre of Western Australia.

Crystal Structure Determinations. Crystals (colorless prisms) of both ligands were prepared by diffusion of hexane into 8:2 hexane/C*H*$_2$Cl$_2$ solutions. Preparations of complex compound crystals are described below. All crystals were mounted in capillaries to avoid efflorescence due to loss of solvent. For data collection on a crystal of **L4**, a Siemens P3/P4-PC diffractometer (Mo*K*α, λ 0.707$_3$ Å, graphite monochromator) at the Crystallography Centre of Western Australia was used, while data for **L2″** were collected on a locally (Department of Chemistry) assembled diffractometer with a Huber 512 type goniometer (Mo*K*α, β filter). Both of these data sets were obtained at 293(2) K. Data for the [Eu$_2$(**L3** − 3H)$_2$(dmf)$_4$]·4dmf complex were collected at 153(2) K on a Bruker AXS CCD diffractometer (Mo*K*α, λ 0.7073 Å, graphite monochromator) at the Crystallography Centre of Western Australia. Data analysis (**L4** and **L2″**) was performed with the profile-fitting program PROFIT[34] (without absorption correction). Structure solutions were obtained by using SHELXS-86[35] and refined with SHELXL-93.[36] Atomic scattering factors and anomalous dispersion corrections were taken from ref 37.[37] The models were refined by using the data for which $F^2 > 2\sigma(F^2)$, anisotropic displacement parameters for the ordered non-hydrogen atoms, and corrections for absorption and extinction. We used a full-matrix least-squares procedure minimizing the quantity $w(F_o^2 - F_c^2)$, with $w = [\sigma^2(F_o^2) + (AP)^2 + BP]^{-1}$, where $P = (F_o^2 + 2F_c^2)/3$. Agreement factors were $R1 = \sum||F_o| - |F_c||/\sum|F_o|$, $wR2 = \{\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]\}^{1/2}$, and GOF = $\{\sum[w(F_o^2 - F_c^2)^2]/(n - p)\}^{1/2}$ (where n is the number of reflections and p is the total number of parameters refined). The positions of hydrogen atoms on carbon were calculated from geometrical considerations and were refined in constraint with the bonded carbon atoms for a fixed C−H bond length of 0.96 Å. Phenolic hydrogen atoms were located by difference Fourier syntheses and were refined in constraint with their bonded oxygen atoms. Other crystallographic data, coefficients, refinement parameters, and experimental conditions are summarized in Table 2. Complete crystallographic details and results are given in the Supporting Information.

Spectroscopic Measurements. ^{1}H NMR spectra were measured at 200 MHz using a Varian Gemini 200 spectrometer. Absorption and luminescence spectra in the range 200−800 nm were recorded at 20 °C for acetonitrile solutions using Hewlett-Packard 8452A diode array and Perkin-Elmer 650-40 instruments, respectively.

Spectrophotometric titrations were performed using the HP 8452A diode array spectrophotometer connected to an external computer where data were analyzed with the program SPECFIT.[38] In a typical experiment, 100 mL of ligand (L) in acetonitrile (10^{-4} mol L^{-1}) was titrated with a 1.6×10^{-3} mol L^{-1} solution of Eu(ClO$_4$)$_3$·7H$_2$O in acetonitrile. After each addition of 0.3 mL, a spectrum was recorded using a 0.1 cm quartz cell and transferred to the computer. Plots of absorbance as a function of the metal concentration gave a first indication of the number and stoichiometry of the complexes formed; factor analysis was then applied to the data to confirm the number of absorbing species.

Syntheses. (a) Diethyl 4-Hydroxypyridine-2,6-dicarboxylate (2). Chelidamic acid (7.0 g) was dissolved in ethanol (200 mL), and 15 mL of concentrated sulfuric acid was added. The solution was heated at reflux for 4 h and then neutralized with a saturated aqueous solution of $NaHCO_3$. The bulk of the ethanol was evaporated, and the residual aqueous solution was extracted with C*H*$_2$Cl$_2$ (3×100 mL). The combined organic phases were dried over $MgSO_4$, filtered, and evaporated to dryness. The residue was crystallized from hot hexane/ethanol, 9:1, to provide **2** (7.21 g, 79%) as white prisms. TLC (SiO_2, CH_2Cl_2/MeOH, 93:7): $R_f = 0.45$. Mp: 122−124 °C. ^{1}H NMR (CDCl$_3$), δ: 1.41 (t, CH$_2$C*H*$_3$, 6H); 4.45 (q, C*H*$_2$CH$_3$, 4H); 7.45 (s, py *H*, 2H); 9.4 (br, O*H*, 1H). Anal. Calcd for $C_{11}H_{13}NO_5$: C, 55.2; H, 5.48; N, 5.85. Found: C, 55.1; H, 5.5; N, 6.0.

(b) Diethyl 4-(2-Bromoethoxy)pyridine-2,6-dicarboxylate (3). 2 (5 g, 21 mmol) was dissolved in CH_3CN (150 mL), and this solution was added dropwise to a dispersion of K_2CO_3 (4.15 g, 30 mmol) in dibromoethane (40 g, 210 mmol) at 80 °C over 4 h. The mixture was heated for a further 2 h, and the solvent was then evaporated. The residue was partitioned between H_2O (200 mL) and CH_2Cl_2 (200 mL), the aqueous phase was further extracted with CH_2Cl_2 (2×100 mL), and the combined organic phases dried over $MgSO_4$, filtered, and evaporated to dryness. The residue was crystallized from hexane/EtOH, 9:1, to provide **3** (6.2 g, 83%) as white prisms. TLC (SiO_2, CH_2Cl_2/MeOH, 99:1) $R_f = 0.52$. Mp: 85−87 °C. ^{1}H NMR (CDCl$_3$), δ: 1.44 (t, CH$_2$C*H*$_3$, 6H); 3.69 (t, OC*H*$_2$, 2H); 4.4−4.6 (m, C*H*$_2$Br + C*H*$_2$CH$_3$), 6H); 7.79 (s, py *H*, 2H). Anal. Calcd for $C_{13}H_{16}BrNO_5$: C, 45.10; H, 4.66; N, 4.05. Found: C, 46.5; H, 4.8; N, 4.1.

(c) *N*,*N*-Diethyl-4-hydroxypyridine-2,6-dicarboxamide (4). $AlCl_3$ (14 g, 100 mmol) was suspended in dry toluene (200 mL), and the suspension was cooled in an ice bath. Diethylamine (18.3 g, 250.3 mmol) was added dropwise while the temperature was maintained below 25°C. The mixture was stirred for 1 h; under strong mechanical stirring, **3** (4 g, 16.7 mmol) was added, and the resulting mixture was heated at 40 °C overnight. The red-brown solution was poured into water (400 mL), the organic layer was separated from the mixture and the aqueous phase was extracted with CH_2Cl_2 (2×100 mL). The combined organic phases were treated with activated charcoal, dried over $MgSO_4$, and evaporated to dryness. The residue was crystallized from hot hexane/EtOH, 9:1, to provide **4** (3.51 g, 72%) as white prisms. TLC (SiO_2, CH_2Cl_2/MeOH, 93:7): $R_f = 0.33$. ^{1}H NMR (CDCl$_3$), δ: 6.97 (s, py *H*, 2H); 3.51 (q, C*H*$_2$CH$_3$, 4H); 3.29 (q, C*H*$_2$CH$_3$, 4H); 1.21 (t, CH$_2$C*H*$_3$, 6H); 1.13 (t, CH$_2$C*H*$_3$, 6H).

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Table 2. Crystal Data and Structure Refinement Parameters for **L4**, **L2″** and the Eu(III) Complex of **L3**

	ligand; compound		
	L4; $C_{78}H_{106}N_6O_{10}\cdot H_2O\cdot 0.5C_2H_5OH\cdot 0.5CH_2Cl_2$	**L2″**; $C_{70}H_{86}N_2O_{14}\cdot H_2O$	**L3**; $[Eu_2(C_{61}H_{78}N_3O_7)_2(C_3H_7NO)_4]\cdot 4C_3H_7NO$
temp/K	293(2)	293(2)	153(2)
crystal size/mm	0.80 × 0.50 × 0.30	0.50 × 0.50 × 0.27	0.35 × 0.16 × 0.04
empirical formula	$C_{79.5}H_{112}ClN_6O_{11.5}$	$C_{70}H_{88}N_2O_{15}$	$C_{146}H_{212}Eu_2N_{14}O_{22}$
fw	1371.20	1197.42	2819.22
F(000)/e	1480	1284	1488
crystal system	triclinic	monoclinic	triclinic
space group	$P\bar{1}$	$P2_1/n$	$P\bar{1}$
Z	2	2	1
D_c/g cm^{-3}	1.146	1.204	1.197
μ/mm^{-1}	0.108	0.084	0.859
a/Å	12.395(2)	14.190(3)	12.483(1)
b/Å	18.021(4)	13.444(3)	19.099(1)
c/Å	18.763(4)	18.258(4)	19.176(1)
α/deg	86.45(3)	90	100.93(1)
β/deg	79.09(3)	108.57(3)	108.14(1)
γ/deg	74.87(3)	90	108.28(1)
V/Å^3	3972.3(1)	3301.7(1)	3910.7(4)
θ range/deg	1.6 → 22.5	1.6 → 22.5	2.28 → 25.0
h range	−13 → 13	−15 → 15	−14 → 13
k range	−19 → 19	0 → 14	−22 → 22
l range	0 → 20	−19 → 19	0 → 22
no. of reflns collected	10 864	8397	13 772
no. of indep reflns	10 476	4352	13 772
R(int)	0.0220	0.0519	0.0
data/restraints/params	10 476/92/849	4323/30/408	13 772/176/778
no. of reflns with $I > 2\sigma(I)$	6780	2892	10 197
GOF on F^2	1.004	1.247	1.034
R1 [$I > 2\sigma(I)$]	0.1098	0.0811	0.0696
wR2	0.2982	0.1953	0.1873
R1 (all data)	0.1411	0.1238	0.0947
wR2	0.3314	0.2389	0.2014
weighting coeff A	0.180	0.074	0.132
weighting coeff B	7.294	3.044	0.0
extinction coeff	0.0055(14)	0.0027(8)	0.000(2)
$\Delta\rho$(max)/e Å^{-3}	0.839	0.362	2.052
$\Delta\rho$(min)/e Å^{-3}	−0.631	−0.295	−0.694

(d) *N*,*N*-Diethyl-4-(2-bromoethoxy)pyridine-2,6-dicarboxamide (5). 4 (2 g, 6.8 mmol) was dissolved in CH_3CN (100 mL), and this solution was added dropwise over 4 h to a suspension of K_2CO_3 (1.5 g, 10.8 mmol) in 1,2-dibromoethane (15 g, 80 mmol) at 80°C, The solvent was evaporated to dryness, the residue partitioned between H_2O (200 mL) and CH_2Cl_2 (200 mL), the organic layer separated from the mixture, and the aqueous phase further extracted with CH_2Cl_2 (2 × 100 mL). The combined organic extracts were dried over $MgSO_4$, filtered, and evaporated to dryness. The residue was crystallized from hot hexane/EtOH, 9:1, to provide **5** (2.23 g, 81%) as white needles. TLC (SiO_2, CH_2Cl_2/MeOH, 93:7): R_f = 0.71. Mp: 82−83°C. ^{1}H NMR ($CDCl_3$), δ: 1.18 (t, CH_2CH_3, 6H); 1.21 (t, CH_2CH_3, 6H); 3.34 (q, CH_2CH_3, 4H); 3.54 (q, CH_2CH_3, 4H); 3.65 (t, CH_2O, 2H); 4.39 (t, CH_2-Br, 2H); 7.15 (s, py *H*, 2H). Anal. Calcd for $C_{17}H_{26}BrN_3O_3$: C, 51.01; H, 6.55; N, 10.50. Found: C, 51.5; H, 6.5, N, 10.5.

(e) 2,6-Bis(1*H*-benzimidazolyl)-4-hydroxypyridine (6). Chelidamic acid (8.4 g, 45.6 mmol) and 1,2-diaminobenzene (9.91 g, 91.2 mmol) were dispersed in H_3PO_4 (100%, 20 mL). The mixture was heated at 220°C for 4 h then poured with vigorous stirring into 1 L of cold water. The blue precipitate that formed was collected by filtration, dispersed in 1 L of hot 10% Na_2CO_3, then filtered off again. The solid was suspended in 800 mL of water and the pH adjusted to 4 before the insoluble material was collected again. It was then crystallized from the minimum amount of hot dmso by adding water until a slightly cloudy solution formed. On cooling, **6** (10.9 g, 73%) deposited as white, feathery needles. TLC (SiO_2, CH_2Cl_2/MeOH, 93:7): R_f = 0.24. 1 ^{1}H NMR (dmso-d_6), δ: 7.35 (m, Ar *H*, 4H); 7.78 (m,Ar *H* + py *H*, 4H + 2H); 11.5 (br, O*H*, 1H); imino H not detected.

(f) 2,6-Bis(1*H*-benzimidazolyl)-4-(2-bromoethoxy)pyridine (7). 6 (1.0 g, 3.0 mmol) and K_2CO_3 (0.21 g, 1.5 mmol) were stirred together under boiling ethanol (50 mL) until a red solution formed. This was gradually added over 8 h to a mixture of 1,2-dibromoethane (50 g, 270 mmol) and ethanol (50 mL) maintained at 80 °C. The resulting solution was heated for 24 h at 80 °C before being evaporated to dryness under vacuum. The residue was crystallized from the minimum volume of boiling methanol to provide **7** (0.93 g, 70%) as white, feathery needles.TLC (SiO_2, CH_2Cl_2/MeOH, 93:7): R_f = 0.4. Mp: 272−274 °C. ^{1}H NMR (dmso-d_6), δ: 3.93 (t, CH_2Br, 2H); 4.71 (t, CH_2Opy, 2H); 7.34 (m, Ar *H*, 4H); 7.76 (m, Ar *H*, 4H); 7.85 (s, py *H*, 2H); imino H not detected.

(g) Diethyl 4-(Benzyloxy)pyridine-2,6-dicarboxylate (8). 2 (3.43 g, 14.3 mmol) was dissolved in CH_3CN (100 mL), and K_2CO_3 (3.15 g, 22.8 mmol) and benzyl bromide (2.44 g, 14.3 mmol) were added. The mixture was heated at reflux for 2 h, cooled to room temperature, and filtered.The solvent was evaporated to dryness and the residue crystallized from hot hexane to give **8** (4.2 g, 89%) as white prisms. TLC (SiO_2, CH_2Cl_2/MeOH, 99:1): R_f = 0.49. ^{1}H NMR ($CDCl_3$), δ: 1.44 (t, CH_2CH_3, 6H); 4.45 (q, CH_2CH_3, 4H); 5.21 (s, CH_2Bz, 2H); 7.41 (m, Ar *H*, 5H); 7.85 (s, py *H*, 2H). Anal. Calcd for $C_{18}H_{19}NO_5$: C, 65.64; H, 5.81; N, 4.25. Found: C, 65.6; H, 5.8; N, 4.5.

(h) 4-(Benzyloxy)-2,6-bis(hydroxymethyl)pyridine (9). 8 (3.9 g, 11.8 mmol) and $NaBH_4$ (0.557 g, 14.74 mmol) were dissolved in dry diglyme (20 mL), and the solution was cooled in an ice bath while a solution of $AlCl_3$ (0.654 g, 4.9 mmol) in dry diglyme (3 mL) was added dropwise. The mixture was stirred for 2 h at room temperature and then for 1 h at 70 °C before being poured carefully into cold water (50 mL). The mixture was acidified to pH 6 with 3 M HCl and the solvent evaporated under reduced pressure. The residue was extracted with CH_2Cl_2 (3 × 100 mL), and the combined extracts were taken to dryness. The residue was crystallized from hot hexane/EtOH, 9:1, to give **9** (2.21 g, 73%) as white needles. TLC (SiO_2, CH_2Cl_2/MeOH, 93:7): R_f = 0.31. Mp: 102−104°C. ^{1}H NMR ($CDCl_3$), δ: 4.70 (s, CH_2OH, 4H); 5.13 (s,

CH_2Bz, 2H); 6.79 (s, py *H*, 2H); 7.39 (m, Ar *H*, 5H). Anal. Calcd for $C_{14}H_{15}NO_3$: C, 68.56; H, 6.16; N, 5.71. Found: C, 68.7, H, 6.1, N, 5.8.

(i) 4-(Benzyloxy)pyridine-2,6-dicarboxaldehyde (10). Freshly prepared MnO_2 (10 g, 115 mmol) was added to a solution of **9** (1 g, 3.88 mmol) in $CHCl_3$ (80 mL; filtered through Alox I). The suspension was heated at reflux for 1 h, and the MnO_2 was then filtered off from the hot solution. The MnO_2 cake was washed several times with hot $CHCl_3$, and the combined solution and washings were evaporated to dryness. The residue was crystallized from hot hexane to give **10** (0.73 g, 75%) as white needles. TLC (SiO_2, CH_2Cl_2/MeOH, 93:7): $R_f = 0.54$. Mp: 102−104 °C. ^{1}H NMR ($CDCl_3$), δ: 5.25 (s, CH_2Bz, 2H); 7.43 (m, Ar *H*, 5H); 7.72 (s, py *H*, 2H); 10.11 (s, C*H*═O, 2H). Anal. Calcd for $C_{14}H_{11}NO_3$: C, 69.70; H, 4.60; N, 5.81. Found: C, 69.6; H, 5.9; N, 5.8.

(j) The Monoether from 4-(2-Bromoethoxy)-2,6-bis(ethoxycarbonyl)pyridine and *p-tert*-Butylcalix[4]arene: L1. *p-tert*-Butylcalix[4]arene (3.89 g, 5.24 mmol) and K_2CO_3 (0.44 g, 3.17 mmol) were suspended in dry CH_3CN (200 mL). The suspension was stirred at room temperature for 3 h, and **3** (2 g, 5.77 mmol) was then added. The mixture was heated at reflux under N_2 for 3 days, followed by evaporation of solvent. The residue was partitioned between equal volumes (100 mL) of water and CH_2Cl_2, with dilute HCl being used to adjust the pH of the aqueous layer to ∼6. The aqueous phase was further extracted with CH_2Cl_2 (2 × 100 mL), and the combined organic phases were dried over $MgSO_4$, filtered, and evaporated to dryness. The residue was crystallized from hot CH_3CN to give **L1** (3.21 g, 67%) as white prisms. TLC (SiO_2, CH_2Cl_2/MeOH, 99:1): $R_f = 0.54$. Mp: 226−228 °C. ^{1}H NMR ($CDCl_3$), δ: 1.17−1.22 (s, br, C(CH_3)$_3$, 36H); 1.45 (t, CH_2CH_3, 6H); 3.60 (d, $J = 16$, ArCH_2Ar, 4H); 4.35−4.51 (m, CH_2CH_3 + ArCH_2Ar, 8H); 4.57 (br s, CH_2Opy, 2H); 4.82 (br s, CH_2OPh, 2H); 6.82 (d, Ar *H*, 2H); 7.02 (s, Ar *H*, 2H); 7.07 (d, Ar *H*, 2H); 7.13 (s, Ar *H*, 2H); 7.99 (s, py *H*, 2H); 9.31 (br, ArO*H*, 2H); 9.95 (br, ArO*H*, 1H). Anal. Calcd for $C_{57}H_{71}NO_9$: C, 74.89; H, 7.83; N, 1.53. Found: C, 74.8; H, 7.8; N, 1.8.

(k) The Diether from 4-(2-Bromoethoxy)-2,6-bis(ethoxycarbonyl)pyridine and *p-tert*-Butylcalix[4]arene, Cone Conformation: L2′. *p-tert*-Butylcalix[4]arene (4.85 g, 6.55 mmol) and K_2CO_3 (4.99 g, 36 mmol) were suspended in dry CH_3CN (250 mL). The suspension was stirred for 1 h before **3** (5 g, 14.42 mmol) was added. The mixture was then heated at reflux under N_2 for 2 days, the solvent was evaporated to dryness, and the residue was partitioned between equal volumes (100 mL) of water and CH_2Cl_2, with dilute HCl being used to adjust the pH of the aqueous layer to ∼6. The aqueous phase was further extracted with CH_2Cl_2 (2 × 100 mL), and the combined organic phases were dried over $MgSO_4$, filtered, and the solvent evaporated to dryness. The crude product was crystallized from hot hexane/EtOH, 9.5:0.5, by cooling at −20 °C to give **L2′** (4.37 g, 56%) as white prisms. TLC (SiO_2, CH_2Cl_2/MeOH, 99:1): $R_f = 0.12$. ^{1}H NMR ($CDCl_3$), δ: 0.97 (s, C(CH_3)$_3$, 18H); 1.28 (s, C(CH_3)$_3$, 18H); 1.43 (t, CH_2CH_3, 12H); 3.31 (d, J 18, ArCH_2Ar, 4H); 4.32 (d, $J = 18$, ArCH_2Ar, 4H); 4.39−4.59 (m, CH_2O + CH_2CH$_3$, 16H); 6.81 (s, Ar *H*, 4H); 7.04 (s, Ar *H*, 4H); 7.83 (s, py *H*, 4H); 7.85 (s, ArO*H*, 2H). Anal. Calcd for $C_{70}H_{86}N_2O_{14}$·H_2O: C, 70.21; H, 7.41; N, 2.34. Found: C, 69.9; H, 7.2; N, 2.7.

(l) The Diether from 4-(2-Bromoethoxy)-2,6-bis(ethoxycarbonyl)-pyridine and *p-tert*-Butylcalix[4]arene, 1,2-Alternate Conformation: L2″. The mother liquors of **L2′** were gently evaporated to deposit **L2″** (210 mg, 2.7%) as white prisms after 2 days. TLC (SiO_2, CH_2Cl_2/MeOH, 99:1): $R_f = 0.36$. ^{1}H NMR ($CDCl_3$), δ: 1.07 (s, C(CH_3)$_3$, 18H); 1.33 (s, C(CH_3)$_3$, 18H); 1.44 (t, CH_2CH_3, 12H); 3.44 (br, CH_2Opy, 4H); 3.72 (s, ArCH_2Ar, 2H); 3.79 (br, CH_2OPh, 4H); 3.97 (d, ArCH_2-Ar, 4H); 4.35 (s, ArCH_2Ar, 2H); 7.08 (d, Ar*H*, 8H); 7.56 (s, py *H*, 4H); 7.58 (s, ArO*H*, 1H); 7.60 (s, ArO*H*, 1H). Recrystallization for the purposes of crystallography (see above) gave material for which the structure solution required the composition **L2″**·H_2O.0.5C_2H_5OH·0.5CH_2Cl_2. The crystals effloresced too rapidly for this to be confirmed by elemental analysis.

(m) The Monoether from 4-(2-Bromoethoxy)-2,6-bis((diethylamino)carbonyl)pyridine and *p-tert*-Butylcalix[4]arene: L3. *p-tert*-Butylcalix[4]arene (0.554 g, 0.75 mmol), BaO (0.131 g, 0.853 mmol), and $Ba(OH)_2$·$8H_2O$ (0.269 g, 0.853 mmol) were suspended in dry dmf (20 mL), the suspension was stirred for 1 h, then **5** (0.3 g, 0.748 mmol) was added, and the resulting suspension was stirred under N_2 for 3 days. The final reaction mixture was poured into water (100 mL), and CH_2Cl_2 (100 mL), was added. The aqueous layer was acidified to pH 6 with 1 M HCl, and the organic phase was separated from the mixture. The aqueous layer was extracted twice more with CH_2Cl_2, and the combined organic phases were dried over $MgSO_4$, filtered, and evaporated to dryness. The crude product was purified by column chromatography (silica gel, CH_2Cl_2/MeOH, 99:1−95:5) and then recrystallized from hot hexane/CH_2Cl_2, 9:1, to give **L3** as white prisms (0.530 g, 73%). TLC (SiO_2, CH_2Cl_2/MeOH, 93:7): $R_f = 0.70$. ^{1}H NMR ($CDCl_3$), δ: 1.11 (t, CH_2CH_3, 6H); 1.19 (s, C(CH_3)$_3$, 36H); 1.25 (t, CH_2CH_3, 6H); 3.25−3.6 (m, CH_2CH_3 + ArCH_2Ar, 8H); 4.18 (d, ArCH_2-Ar, 2H); 4.41 (d, ArCH_2Ar, 2H); 4.57 (br, CH_2Opy, 2H); 4.73 (br, CH_2OPh, 2H); 6.95 (d, Ar *H*, 2H); 7.01 (s, Ar *H*, 2H); 7.05 (d, Ar *H*, 2H); 7.10 (s, Ar *H*, 2H); 7.32 (s, py *H*, 2H). Anal. Calcd for $C_{61}H_{81}N_3O_7$·0.25CH_2Cl_2: C, 74.35; H, 8.31; N, 4.25. Found: C, 74.7; H, 8.4; N, 4.5.

(n) The Diether from 4-(2-Bromoethoxy)-2,6-bis((diethylamino)-carbonyl)pyridine and *p-tert*-Butylcalix[4]arene: L4. *p-tert*-Butylcalix[4]arene (0.647 g, 0.873 mmol) and K_2CO_3 (0.507 g, 3.675 mmol) were suspended in dry CH_3CN (150 mL), and the suspension was stirred for 1 h at room temperature. **3** (0.7 g, 1.75 mmol) was added, and the suspension was heated at reflux under N_2 for 5 days. The solvent was removed, the residue partitioned between H_2O (100 mL) and CH_2Cl_2 (100 mL), and the aqueous layer acidified to pH 6. The organic phase was separated from the mixture, and the aqueous phase was further extracted with CH_2Cl_2 (2 × 100 mL). The combined organic phases were dried over $MgSO_4$, filtered, and evaporated to dryness. The crude product was purified by column chromatography (silica gel, CH_2Cl_2/MeOH, 99:1−95:5) and then crystallized from hot hexane/CH_2Cl_2, 9.5:0.5, to give **L4** (0.419 g, 44%) as white prisms. TLC (SiO_2, CH_2Cl_2/MeOH, 93:7): $R_f = 0.51$. Mp: 180−182 °C. ^{1}H NMR ($CDCl_3$), δ: 0.97 (s, C(CH_3)$_3$, 18H); 1.10 (t, CH_2CH_3, 12H); 1.19 (t, CH_2CH_3, 12H); 1.25 (s, C(CH_3)$_3$, 18H); 3.20−3.35 (m, CH_2CH_3 + ArCH_2Ar, 10H); 3.38−3.6 (m, CH_2CH_3 + ArCH_2Ar, 10H); 4.25−4.5 (m, CH_2py, Ar *H*, 12H); 6.79 (s, Ar *H*, 4H); 7.01 (s, Ar *H*, 4H); 7.15 (s, ArO*H*, 2H); 7.18 (s, py *H*, 4H). Anal. Calcd for $C_{78}H_{106}N_6O_{10}$·0.25CH_2Cl_2: C, 71.81; H, 8.19; N, 6.43. Found: C, 71.3; H, 8.2; N, 6.5.

(o) The Monoether from 4-(2-Bromoethoxy)-2,6-bis(benzimidazolyl)pyridine and *p-tert*-Butylcalix[4]arene: L5. *p-tert*-Butylcalix[4]arene (0.339 g, 0.458 mmol), BaO (0.080 g, 0.522 mmol), and $Ba(OH)_2$·$8H_2O$ (0.165 g (0.522 mmol) were suspended in dry dmf (10 mL). **7** (0.200 g, 0.458 mmol) was added, and the mixture was stirred at room temperature for 2 days. The final solution was poured into a water (100 mL)/CH_2Cl_2 (100 mL) mixture, and the aqueous layer was acidified with dilute HCl to pH 6. The organic phase was separated from the mixture and the aqueous phase was further extracted with CH_2Cl_2 (2 × 100 mL). The combined organic phases were dried over $MgSO_4$, filtered, and evaporated to dryness. The crude product was purified by column chromatography (silica gel, CH_2Cl_2/MeOH, 99:1−95:5) and then crystallized by slow evaporation of a CH_2Cl_2/hexane solution to give **L5** (0.11 g, 24%) as white, feathery needles. TLC (SiO_2, CH_2Cl_2/MeOH, 93:7): $R_f = 0.46$. ^{1}H NMR (DMSO-d_6), δ: 1.10 (s, C(CH_3)$_3$, 9H); 1.15 (s, 2 × C(CH_3)$_3$, 18H); 1.17 (s, C(CH_3)$_3$, 9H); 3.31 (s, CH_3, overlaps one component of an adjacent AB doublet); 3.35, 3.57, 3.95, 4.36 (all d, $J = 18$, calixarene CH_2, 8H); 4.60, 4.97 (br m, ethylene link CH_2 units, 4H); 7.03, 7.23−7.38, 7.77, 8.11 (all m, Ar *H* possibly overlapping N*H*); 9.19 (br, O*H*, 2H); 9.69 (br, O*H*, 1H). Anal. Calcd for $C_{65}H_{71}O_5N_5$·3CH_3OH: C, 74.36; H, 7.62; N, 6.38. Found: C, 74.7; H, 7.2; N, 7.1.

(p) Europium(III) Complexes for Crystal Structure Determinations. The three monoethers **L1**, **L3**, and **L5** were used in attempts to form Eu(III) complexes under 3:1 and 1:1 (L:M) conditions of stoichiometry. Thus, solutions of 28 mg of **L1** in 0.3 mL of dmf and 9.3 mg in 0.1 mL were mixed separately with solutions of $Eu(ClO_4)_3$·8dmso (11 mg) in dmf (0.1 mL). Both product mixtures were clear and colorless, but on addition of one drop (10 mg) of triethylamine to each, both became clear yellow. Using 28 and 9.4 mg quantities of **L3** and 30 and 10 mg quantities of **L5** in place of **L1**, the experiments

were repeated with visually similar results. (With **L3**, the yellow color developed much more slowly (over 5−10 min) than with **L5**, though eventually it became much deeper, being almost orange, while the **L5** solution was a clear, almost greenish yellow.) All solutions slowly deposited yellow crystals over periods ranging from hours to days in yields which appeared close to quantitative in that little color could be detected in the supernatant solutions. The first crystal found to be suitable for X-ray diffraction was drawn from a solution containing ligand **L3**.

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Supporting Information Available: A tabulation of electronic spectral data, a figure displaying disorder within the structure of the europium complex, tables of atomic coordinates, thermal parameters, bond distances, bond angles, and torsion angles, and X-ray crystallographic files, in CIF format, for the structures of **L4**, **L2″**, and the Eu(III) complex of **L3**. This material is available free of charge via the Internet at http://pubs.acs.org.

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