Related compounds of both toluene and benzene,[20b,c] however, contain aromatic guest molecules situated parallel to the plane of the phenolic oxygen atoms. In this case the orientation of the guest maximizes interaction of the oxygen atom with the aqueous layer of the structure in which the py-*N*-O guest functions chiefly as a bridging ligand between two sodium ions, O(1P)−Na(1) 2.53 Å, −Na(5) 2.50 Å, and is not further associated with either the gadolinium ion or calixarene. The sodium ion Na(1) is particularly well defined and exists in an octahedral environment consisting of three water molecules and two calixarene sulfonato groups (from different molecules) as well as the py-*N*-O ligand. The sulfonato groups in turn are bound to a symmetry equivalent of Na(1) to generate an eight-membered $Na_2O_4S_2$ ring. This situation contrasts sharply with the role of the py-*N*-O ligands in the structure of $Na[Eu_3(p\text{-sulfonatocalix[4]arene})_2(H_2O)_{18}(py\text{-}N\text{-}O)_3]\cdot 14H_2O$ (**11**)[21] in which the three crystallographically independent py-*N*-O ligands act variously as first- and second-sphere ligands for the Eu^{3+} ions as well as being situated both within and without the calixarene cavities.

Examination of the solid state structure of **5** reveals the same packing mode as in **4** with the sole modification being an expansion of the aqueous layer along the longest axis from 9.1 to 9.9 Å, Figure 3. The fact that the lanthanide ion is not coordinated to the calixarene units forces them somewhat apart to allow the incorporation of the metal ion coordination sphere. The sole relevant differences between the chemistry of La^{3+} and Gd^{3+} are the larger size and coordination number of lanthanum. It seems likely therefore that coordination of lanthanum to the calixarene in the same way as gadolinium would lead to an excessively large interlayer separation and as a result the structure collapses to a more stable form in which the metal ion is not coordinated. This hypothesis implies the interesting possibility that crystal packing forces actually override the electrostatic attraction between the sulfonate groups and the La^{3+} ion. This suggestion is further supported by the structure of $(H_3O)[La(py\text{-}N\text{-}O)_2(H_2O)_6(p\text{-sulfonatocalix[4]arene})]\cdot 6.5H_2O$ (**12**) in which the nine coordinate La(III) ion is bound both to two py-*N*-O ligands and one of the calixarene sulfonate functionalities as well as six water molecules[18] suggesting that $La-O_3S$ binding is possible, and even favorable, within a different crystal environment.

$Na[Eu(H_2O)_9]_2[Eu(py\text{-}N\text{-}O)(H_2O)_5(\text{calix[5]arene-}p\text{-sulfonato})_2]\cdot py\text{-}N\text{-}O\cdot 17.5H_2O$. The similarity of the ionic radii of europium and gadolinium suggests that reaction of **2** with $Eu(NO_3)_3\cdot H_2O$ as for **4** and **5** might lead to a product isostructural with **5**, and indeed the species $Na[Eu(H_2O)_9]_2[Eu(py\text{-}N\text{-}O)(H_2O)_5(p\text{-sulfonatocalix[5]arene})_2]\cdot py\text{-}N\text{-}O\cdot 17.5H_2O$ (**6**) obtained as the sole product from three independent crystallizations does incorporate an eight coordinate Eu^{3+} center bridging two independent *p*-sulfonatocalix[5]arene anions (Figure 5), Eu(1)−H_2O 2.420(9) Å (av), Eu(1)−$O_{sulfonate}$ 2.351(9) Å (av). In this case, however, one of the two crystallographically independent py-*N*-O molecules which occupy the calixarene cavities also forms part of the primary coordination sphere of the bridging Eu(III) ion, Eu(1)−O(1P) 2.33(1) Å. The second py-*N*-O molecule coordinates to one of the sodium ions, O(11P)···Na(5) 2.50(1) Å. In addition, two further $[Eu(H_2O)_9]^{3+}$ counterions occupy the hydrophilic layer of the structure in a similar way to the lanthanum aqua ion in **4** [Eu−OH_2 2.42(1) Å (av), typical of Eu−OH_2 distances[19]]. The structure is related to that observed for the *p*-sulfonatocalix[4]arene complex $Na[Eu_3(p\text{-sulfonatocalix[4]arene})_2(H_2O)_{18}(py\text{-}N\text{-}O)_3]\cdot 14H_2O$ (**11**).[21] In the case of **11**, however, simultaneous first-, second-, and third-sphere coordination occur because of hydrogen bonding of the uncoordinated py-*N*-O ligand to the primary coordination sphere of one of the nine coordinate metal centers. Also in **11**, all three crystallographically independent Eu^{3+} ions are coordinated to the calixarenes, one of them *via* one phenolic oxygen atom at the lower rim of the macrocycle as well as the upper rim sulfonate groups on adjacent molecules.

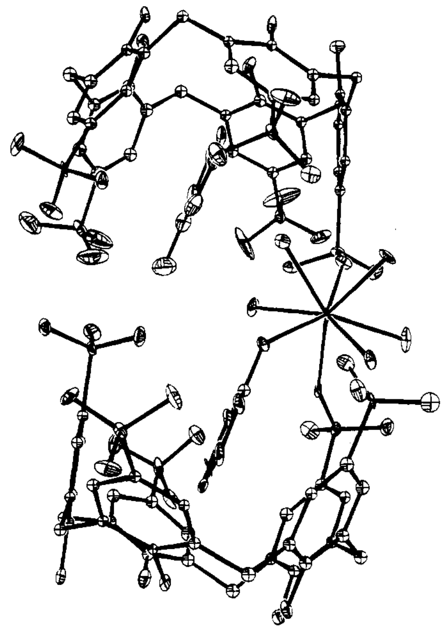


Figure 5. ORTEP diagram of the europium-bridged bis(calixarene) core unit in **6** in various orientations, along with the py-*N*-O guest molecules.

In the solid state, the crystal packing in **6** is remarkably similar to that observed for **4** and **5** and is reflected in the similarity of the unit cell parameters of the three complexes (doubling the length of the *a* axis in **6** results in virtually identical unit cell lengths to **4** in spite of the lower symmetry in the latter case), highlighting the generality of the bilayer structure. In the case of **6** the $[Eu(H_2O)_9]^{3+}$ ions are threaded throughout the 9.3 Å thick hydrophilic layer and simply replace sodium ions and water found in equivalent positions in **4** and **5**. The principal difference between **5** and **6**, coordination of one of the py-*N*-O ligands to the bridging lanthanide ion, probably results from the dominance of crystal packing forces rather than a steric crowding effect, since the slightly smaller[22a] Tb(III) ion in **7** is able to coordinate two py-*N*-O ligands (*vide infra*), as are the Eu(III) ions in **11**.[21]

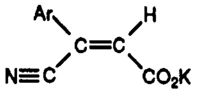
$Na_8[Tb_4(py\text{-}N\text{-}O)_4(H_2O)_{18}(p\text{-sulfonatocalix[5]arene})_4]\cdot 52H_2O$. Reaction of $Tb(NO_3)_3\cdot H_2O$ with **1b** and py-*N*-O as for **4**−**6** resulted in the isolation of colorless crystals of the fascinating "supercomplex" $Na_8[Tb_4(py\text{-}N\text{-}O)_4(H_2O)_{18}(p\text{-sulfonatocalix[5]arene})_4]\cdot 2H_2O$ (**7**). Extreme crystallographic difficulties were encountered in obtaining meaningful data for this compound. While multiple samples were found to be strongly diffracting, none of the crystals examined were single. Furthermore, the crystals exhibited extreme sensitivity with respect to loss of solvent while refinement revealed a great deal of disordered enclathrated water. All these factors contribute to an rather high *R* factor for this determination (Table 1). However, the structure of **7** is perhaps one of the most interesting encountered in this work and, while the quantitative parameters are not determined to a high degree of precision, the gross

---

[21] Atwood, J. L.; Orr, G. W.; Robinson, K. D. *Supramol. Chem.* **1994**, *3*, 89.

[22] (a) Cotton, S. *Lanthanides and Actinides*, Oxford University Press: New York, 1991. (b) Atwood, J. L.; Orr, G. W.; Juneja, R. K.; Bott, S. G.; Hamada, F. *Pure. Appl. Chem.* **1993**, *65*, 1471.

Table I

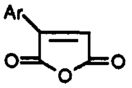


2

Ar	yield (%)	mp (°C)	Anal. C calcd	C found	H calcd	H found	N calcd	N found	NMR (ppm) DMSO-d_6
(a) C_6H_5	86	245	56.72	56.94	2.86	3.08	6.61	6.66	7.75 (m, 5H), 7.28 (br s, 1H)
(b) 4-BrC_6H_4	94	252–253	41.40	41.14	1.74	1.49	4.83	4.81	7.55 (d, 2H, J = 8.0 Hz), 7.63 (d, 2H), 7.25 (s, 1H)
(c) 4-ClC_6H_4	92	252–253	48.88	48.58	2.05	1.86	5.70	5.69	7.5 (d, 2H, J = 8.7 Hz), 7.65 (d, 2H), 7.2 (s, 1H)
(d) 3,4-$Cl_2C_6H_3$	92	252	42.87	42.83	1.44	1.34	5.00	4.81	7.9 (s, 1H), 7.70 (m, 2H), 7.3 (s, 1H)
(e) 4-MeC_6H_4	63	242	58.64	58.31	3.58	3.39	6.22	6.10	7.5 (d, 2H, J = 8.3 Hz), 7.25 (d, 2H), 7.04 (s, 1H), 2.4 (s, 3H)
(f) 3-MeC_6H_4	93	230 (dec)	58.64	58.33	3.58	3.56	6.22	6.19	7.3–7.6 (m, 4H), 7.15 (s, 1H), 2.4 (s, 3H)
(g) 3,4,5-$(MeO)_3C_6H_2$	26	199–200	38.81[a]	39.03	3.01	2.79	3.48	3.41	6.99 (s, H), 6.65 (s, 2H), 3.85 (s, 6H), 3.80 (s, 3H)
(h) 4-PhC_6H_5	73	257 (dec)	66.87	66.45	3.51	3.83	4.87	4.87	8.20–7.45 (m, 9H), 7.05 (s, 1H)

[a] Microanalysis of cesium salt.

Table II

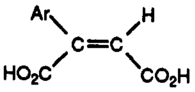


4

Ar	yield (%)	mp (°C)	lit, mp (°C)	NMR (ppm) $CDCl_3$
(a) C_6H_5	48	120–121	119[c]	8.1–7.95 (m, 2H), 7.6 (m, 3H), 7.10 (m, 1H)
(b) 4-BrC_6H_4	81	156–157	156[d]	7.88 (d, 2H, J = 8.7 Hz), 7.68 (d, 2H), 7.05 (s, 1H)
(c) 4-ClC_6H_4	77	146–148	146[e]	7.95 (d, 2H, J = 8.8 Hz), 7.5 (d, 2H), 7.08 (s, 1H)
(d) 3,4-$Cl_2C_6H_3$	71	114.5–116	115–116[f]	8.25–7.75 (m, 3H), 7.01 (s, 1H)
(e) 4-MeC_6H_4	31	109–110	108–111[e]	7.9 (d, 2H, J = 8 Hz), 7.3 (s, 2H), 6.95 (s, 1H)
(f) 3-MeC_6H_4	31	89–90	88–90[g]	7.8–7.3 (m, 4H), 7.05 (s, 1H), 2.95 (s, 3H)
(g) 3,4,5-$(MeO)_3C_6H_2$[a]	21	150–151 (toluene)		7.20 (s, 2H), 6.90 (s, 1H), 3.95 (s, 9H)
(h) 4-PhC_6H_4[b]	76	194.5–196 (chloroform)		8.15 (d, 2H), 7.90 (d, 2H), 7.79 (s, 2H), 7.75 (s, 1H), 7.6–7.4 (m, 3H)

[a] Anal. Calcd: C, 59.09; H, 4.58. Found: C, 58.84; H, 4.41. [b] Anal. Calcd: C, 76.79; H, 4.03. Found: C, 76.47; H, 4.15. [c] Reference 2. [d] Reference 8. [e] Reference 1. [f] Reference 9. [g] Reference 10.

Table III



3

Ar	yield (%)	mp (°C)	Anal. C calcd	C found	H calcd	H found	halogen calcd	halogen found	NMR (ppm) DMSO-d_6
4-BrC_6H_4	91	152–154	44.31	44.13	2.60	2.34	29.48	29.56	11.4 (br s, 2H), 7.68 (d, 2H, J = 8 Hz), 7.53 (d, 2H), 6.23 (s, 1H)
4-ClC_6H_4	85	145–147	53.00	52.73	3.11	3.09	15.64	15.56	13.2 (br s, 2H), 7.63 (d, 2H, J = 8.5 Hz), 7.55 (d, 2H), 6.4 (s, 1H)
3-MeC_6H_4	59	108–110	64.07	64.09	4.89	4.93			7.2–7.4 (m, 4H), 6.3 (s, 1H), 2.38 (s, 3H)
4-MeC_6H_4	61	118–120	64.07	64.15	4.89	4.64			11.2 (s, 2H), 7.48 (d, 2H, J = 8.3 Hz), 7.28 (d, 2H), 6.2 (s, 1H), 2.33 (s, 3H)

were recorded on a Nicolet 205 X B FTIR spectrophotometer as KBr pellets. Combustion analyses of all new compounds were performed by the Analytical Department, American Cyanamid Company, Pearl River, NY.

General Procedure for the Condensation of Arylacetonitriles (1b–d) with Glyoxylic Acid. A mixture of 0.05 mol of the appropriate arylacetonitrile 1 (**b–d**), 0.075 mol of glyoxylic acid hydrate, and 0.127 mol of potassium carbonate in 100 mL of methanol was stirred at room temperature for 3–5 h. The resulting thick solid precipitate was filtered and washed with dichloromethane. This solid was suspended in 500 mL of cold water, stirred overnight, and then filtered and air dried to provide the corresponding potassium (Z)-3-aryl-3-cyanopropenoates 2 (**b–d**). Normally these materials were sufficiently pure for further transformations; however, analytically pure 2 could be obtained by recrystallization from water.

Condensation of Arylacetonitriles (1a,e–h) with Glyoxylic Acid. These reactions were performed as described above except these mixtures were heated at reflux 2–24 h. The products **2a,e–h** were isolated by filtration upon cooling of the reaction mixture.

Cyclization of Potassium (Z)-3-Aryl-3-cyanopropenoates 2 to Arylmaleic Anhydrides 4. The potassium (Z)-3-aryl-3-cyanopropenoates 2 (0.094 mol) were dissolved in ca. 200 mL of 88% formic acid containing 15 mL of concentrated sulfuric acid. These mixtures were heated at reflux for 2–3 h and then cooled and poured into ice water. The resulting solids were filtered, washed with water, and air dried to provide the arylmaleic anhydrides 4. These products were normally of sufficient purity for use in subsequent transformations.

Preparation of Arylmaleic Acids 3. The potassium (Z)-3-aryl-3-cyanopropenoates (0.012 mol) were suspended in 100 mL of 3 N HCl and stirred at room temperature overnight. The solids were collected by filtration, washed with water, and air dried to give the arylmaleic acids, in most cases analytically pure.