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Bilayers, Corrugated Bilayers, and Coordination Polymers of *p*-Sulfonatocalix[6]arene

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Exploration into the host–guest supramolecular chemistry of *p*-sulfonatocalix[6]arene with pyridine *N*-oxide and 4,4′-dipyridine *N*,*N*′-dioxide has resulted in the characterization of three new structural motifs with the calixarene in the "up–down" double partial cone conformation. Two are hydrogen-bonded network structures formed with pyridine *N*-oxide and either nickel or lanthanide metal counterions (**1** and **2**, respectively). Complex **1** displays host–guest interactions between pyridine *N*-oxide and the calixarene in the presence of hexaaquanickel(II) counterions. Complex **2** demonstrates selective coordination modes for different lanthanides involving the calixarene and pyridine *N*-oxide. The third structure, **3**, is a coordination polymer which is formed with 4,4′-dipyridine *N*,*N*′-dioxide molecules which span a hydrophilic layer and join lanthanide/*p*-sulfonatocalix[6]arene fragments. Although complexes **1**–**3** all have the calixarene in the "up–down" double partial cone conformation, **1** and **3** form bilayer arrangements within the extended structures while **2** forms a previously unseen corrugated bilayer arrangement.

Introduction

Crystal engineering, coordination polymer formation, and the enclosure of chemical space are areas of current interest given the ability of the chemist to construct desirable network structures with a view to satisfying particular application requirements.[1] Water-soluble calixarenes are and have been of interest for some time in building up systems which mimic natural biological processes through the presence of hydrophobic pockets which can bind apolar guests.[2] Such molecules can have varying levels of solubility depending on the functionalization at either the "upper" or "lower" rims which thereby alters the overall polarity of the macrocycles.[3]

The *p*-sulfonatocalix[*n*]arenes (where $n = 4, 5, 6, 8$) are some of the most highly water-soluble and versatile container molecules capable of forming a range of complexes with various guest molecules and or counterions in both solution and the solid state.[4,5] The smallest and most conformationally constrained analogue, *p*-sulfonatocalix[4]arene (SO_3[4]) is particularly well suited to forming supramolecular architectures of varying complexity in the solid state.[6] These range from the inclusion of small charged organic species through to the formation of "molecular capsules" which can bear host to a range of charged or uncharged guests in the presence of metal ions.[5,7] This versatility in complex formation is likely

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(1) For example see the following: (a) Robson, R. *J. Chem. Soc., Dalton. Trans.* **2000**, 3735−3744. Eddaoudi, M.; Moler, D. B.; Li, H.; Chen, B.; Reineke, T. M.; O'Keefe, M.; Yaghi, O. M. *Acc. Chem. Res.* **2001**, *34*, 319−330. James, S. L. *Chem. Soc. Rev.* **2003**, *32*, 276−288. Barnett, S. A.; Champness, N. R. *Coord. Chem. Rev.* **2003**, *246*, 145−168. Hamilton, T. D.; MacGillivray, L. R. *Cryst. Growth Des.* **2004**, *3*, 419−430.

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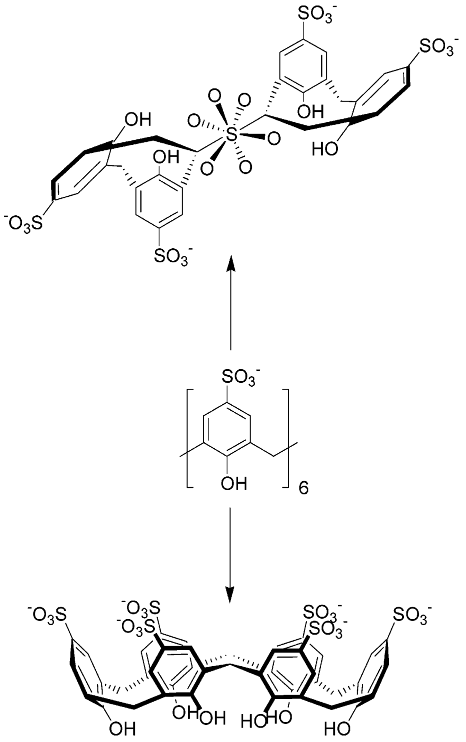
attributable to the affinity of the molecule to form extended hydrophobic–hydrophilic bilayer arrangements in the solid state with infinite layers of hydrophobic cavities which are suitable for hosting appropriate guests.[8] When the affinity to form such bilayer arrangements is overcome, the results are spectacular with the concomitant formation of nanometer scale spheres and tubules of varied geometry depending on the guest and counterion employed.[9,10] Although the supramolecular/host–guest chemistry for $SO_3[4]$ is well documented, new and unusual architectures, molecular capsules, and coordination polymers continue to be discovered on a regular basis which suggests that, as for p-^{t}Bu-calix[4]arene, much of the potential of this calixarene is yet to be discovered.[11] Notably, the formation of several of the aforementioned nanometer scale architectures occurs in the presence of pyridine *N*-oxide (PyNO) and lanthanide(III) nitrates. Thus, PyNO has been shown to be a suitable guest/ligand for the formation of spheres and also as an interstitial spacer unit for the formation of helical tubules given the affinity of lanthanide metals to bind to the hard donor oxygen atom. The related 4,4′-dipyridine *N*,*N*′-dioxide (DiPyNO) is excellent in forming coordination polymers with lanthanide metals with some results displaying unusually high connectivities between the ligand and metal centers.[12] As DiPyNO also possesses hard donor atoms, the bifunctionality associated with the molecule offers the possibility of assembling several new structural motifs with *p*-sulfonatocalix[*n*]arenes.

In contrast to $SO_3[4]$, *p*-sulfonatocalix[6]arene ($SO_3[6]$) is a more highly charged and conformationally flexible molecule, a fact which renders solid-state complex formation and structural characterization a more formidable challenge. This is reflected in the small number of solid-state supramolecular structures that incorporate $SO_3[6]$ and that have been reported in recent times.[13–16] In this respect, we are endeavoring to "map out" the possible supramolecular motifs with a view to forming alternative structures that deviate from the typical bilayer arrangements formed with $SO_3[6]$. *p*-Sulfonatocalix[6]arene has been shown to typically adopt an "up–down" double partial cone conformation when in the form of alkali metal salts and when acting as polyhaptoaromatic ligands for such metal ions (Scheme 1).[13,14] A handful of the solid-state structural examples show the calixarene to be in an "up–up" double cone conformation, the most noteworthy of which displays multiguest inclusion in a "bis-molecular capsule" arrangement.[15] When in the up–down double partial cone conformation, the calixarene can also be shown to act as a ditopic receptor to selected guests in the presence of lanthanide metal counterions. Given this structural versatility, it is reasonable to expect such a flexible molecule to assemble into alternative supramolecular architectures of far greater complexity than a simple bilayer although this has, to date, been unachievable.

Scheme 1. Diagram Showing the Two Possible Conformational Orientations of *p*-Sulfonatocalix[6]arene



Herein we report aqueous transition-metal supramolecular chemistry for $SO_3[6]$ which gives rise to a hydrogen-bonded network in the complex $[(Ni(H_2O)_6)_3]^{6+}$\{(pyridine *N*-oxide)$_2\subset$(*p*-sulfonatocalix[6]arene)\}$^{6-}\cdot 7H_2O$, **1**. The calixarene acts as a ditopic receptor to two PyNO molecules with hexaaquanickel(II) cations residing in the hydrophilic regions within the bilayer.

As mentioned above, $SO_3[4]$/PyNO/Ln(III) systems reported by Atwood et al. had remarkable results in the formation of spheroids and tubules.[9] Examination of similar chemistry for $SO_3[6]$ resulted in the formation of an unusual $SO_3[6]$/PyNO/Yb(III) complex which has varied coordination

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modes of lanthanide metals within the extended structure associated with varied host−guest interactions between tectons.[16] The lanthanide/PyNO coordination mode can be altered through use of La(III) in place of Yb(III) resulting in the formation of the complex $[(La(H_2O)_7(pyridine\text{-}N\text{-}oxide))_2(p\text{-}sulfonatocalix[6]arene)]\cdot 6H_2O$, **2**, where there is only one PyNO molecule bound to any one metal center. Both structures are formed in the presence of excess PyNO with respect to both calixarene and lanthanide(III) nitrate. Although a bilayer is present within the extended structure, it is markedly different from that observed for the Yb(III) complex mentioned above and is described herein as a "corrugated bilayer".

Extension of this chemistry to encompass the use of DiPyNO as a guest molecule in place of PyNO and in the presence of both $SO_3[6]$ and europium(III) nitrate results in the formation of a zigzag coordination polymer $[(Eu(H_2O)_6)_2\text{-}(4,4'\text{-dipyridine } N,N'\text{-dioxide})(p\text{-sulfonatocalix[6]arene})]\cdot 8H_2O$, **3**, with water molecules residing in the partial cones of the calixarene while also displaying OH···aromatic-π interactions similar to those reported for inclusion of water molecules in the hydrophobic cavity of $SO_3[4]$.[17]

Results and Discussion

Crystals of complex **1**, $[(Ni(H_2O)_6)_3]^{6+}\{(pyridine\ N\text{-}oxide)_2\subset(p\text{-}sulfonatocalix[6]arene)\}^{6-}\cdot 7H_2O$, grew from an aqueous solution containing hexaaquanickel(II) chloride, octasodium *p*-sulfonatocalix[6]arene hydrate ($Na_8SO_3[6]$), and excess PyNO. The crystals are in a triclinic cell, and the structure was solved in space group $P\bar{1}$. The asymmetric unit consists of two-half calixarenes, two PyNO molecules, three hexaaquanickel(II) counterions, and seven solvent water molecules. Within the extended structure, the centrosymmetric macrocycles form a bilayer arrangement with sulfonate groups pointing into the hydrophilic layers. This arrangement is similar to that seen for the calixarene in both the corresponding octasodium salt and sulfonic acid and assembles with similar π-stacking distances (centroid···centroid ring distances of 3.806 and 3.850 Å).[13] Within this bilayer arrangement, PyNO molecules reside in the partial cones of the calixarenes with the polar functional group pointing into the hydrophilic region, Figure 1.

Each PyNO has one ArH···π interaction with a phenyl group on each half-calixarene (distances to ring centroids 2.724 and 2.840 Å). In addition, the polar *N*-oxide group is directed into the hydrophilic layer and forms an intricate hydrogen-bonding network with aquo ligands of the nickel(II) ions, Figure 2. Each oxygen of the PyNO molecule has three hydrogen bonds from nickel aquo ligands with NO···ONi distances ranging from 2.664 to 3.031 Å. All three crystallographically independent hexaaquanickel(II) ions are of octahedral geometry as expected and lie entirely within the hydrophilic layer. All have NiO···OS, NiO···O, and NiO···ONi distances consistent with typical H-bonding distances for such interactions.[18] The included solvent water molecules also hydrogen bond to both sulfonate groups and aqua ligands on the Ni(II) centers and are partaking in a complex hydrogen-bonding network within the bilayer.

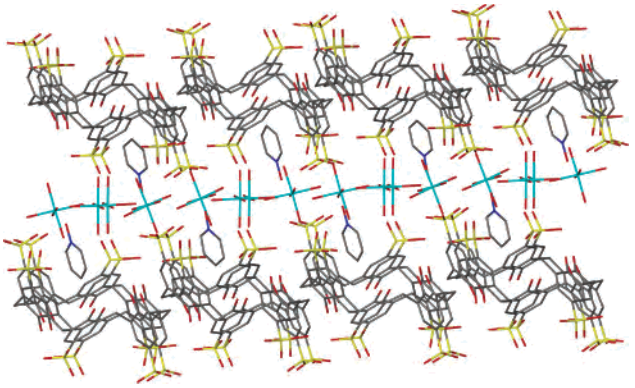

Figure 1. Extended structure of **1**, showing the bilayer arrangement of calixarenes, the PyNO molecules residing in the cavities of the calixarenes, and the nickel(II) counterions included in the hydrophilic layer. (Hydrogen atoms and solvent water molecules are omitted for clarity.)

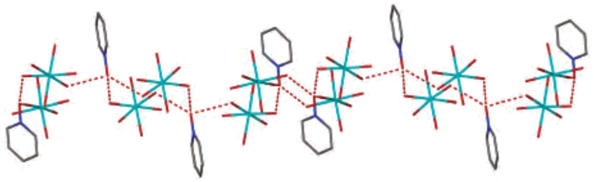

Figure 2. Partial hydrogen-bonding network in **1** showing hydrogen bonds between the PyNO molecules and the aqua ligands bound to the nickel(II) ions. (Calixarenes, hydrogen atoms, and solvent water molecules are omitted for clarity.)

Several other transition metal salts were also examined, but none formed suitable crystals for single-crystal X-ray diffraction studies. Similar work with the smaller and rather synthetically inaccessible *p*-sulfonatocalix[5]arene ($SO_3[5]$) was reported by one of us in 1996 and used pyridine as a potential guest with various transition metal salts.[19] The formation of a complex containing two $SO_3[5]$ molecules hinged via a nickel center with free pyridine guest molecules residing in the calixarene cavities was suggested; however, single crystals of suitable quality for X-ray diffraction studies could not be grown. Notably, it was not possible to crystallize the corresponding transition metal/calix[5]arene/PyNO complex. It would appear that the partial cone of $SO_3[6]$ in **1**, while smaller than that of $SO_3[5]$, is favorably sized for PyNO uptake. It also appears that the aquated nickel(II) in **1** prefers to be noncoordinating rather than forming any Ni−OS coordination with calixarene. This is in contrast to the predicted calix[5]arene structure described above.

Replacement of nickel(II) chloride from the above system with ytterbium(III) nitrate affords a hydrogen-bonded array of a ytterbium/$SO_3[6]$/PyNO complex which has varied coordination modes within the extended structure.[16] There

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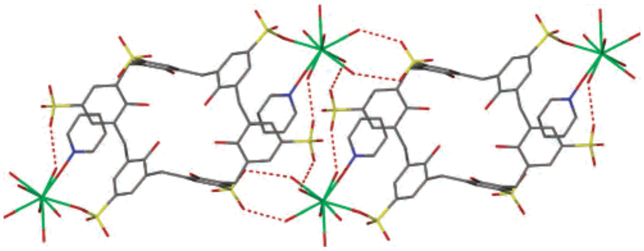

Figure 3. View of hydrogen-bonded chains in **2** along the *a* axis showing intra- and intermolecular H-bonds from aquo ligands of the lanthanum center to sulfonate groups of the calixarene. (Hydrogen atoms and solvent water molecules are omitted for clarity.)

are two independent supramolecular tectons, one of which has two octacoordinate lanthanide(III) ions bound to one calixarene through sulfonate groups with one PyNO molecule also bound to the metal center while residing in the partial cone of the calixarene. The other has identical lanthanide/calixarene binding, but there are two PyNO molecules bound to each lanthanide center. Examination of other early lanthanide metals (La^{3+}) affords complex **2**, $[(La(H_2O)_7$-(pyridine-*N*-oxide$))_2$(*p*-sulfonatocalix[6]arene)$]\cdot 6H_2O$, crystals of which grew from solutions under conditions identical with the aforementioned but which form a structure markedly different from a previously reported ytterbium complex. The crystals are in a monoclinic cell, space group $P2_1/c$, with the asymmetric unit consisting of a half-calixarene, one lanthanum center with seven aquo ligands, one PyNO molecule, and three solvent water molecules. The lanthanum centers are nine-coordinate with tricapped trigonal prismatic geometry in the primary coordination sphere. In addition to being bound to a sulfonate group of the calixarene, the lanthanum has one PyNO ligand which resides in the partial cone of the calixarene but is positioned closer to the hydrophilic layer than free or bound PyNO molecules in either the nickel (**1**) or ytterbium complexes, respectively.[16] Complex **2** forms hydrogen-bonded chains along the *a* axis through H-bonds from four aquo ligands of the lanthanum center to sulfonate groups of the calixarene. These occur as one intramolecular (distance of 2.967 Å) and three intermolecular LaO···OS (distances ranging from 2.657 to 2.917 Å) H-bonds as shown in Figure 3 (dashed lines).

In addition to the formation of the H-bonded chains along the *a* axis, one of the aquo ligands used in the formation of the chain along *a* also hydrogen bonds to the closest sulfonate groups of the nearest-neighboring calixarene moiety in the *bc* plane with the LaO···OS distance of 2.682 Å. Also present is H-bonding from another aquo ligand to another oxygen of the same sulfonate group (LaO···OS distance 2.758 Å) and H-bonding from one other aquo ligand to the oxygen of the nearest PyNO molecule in the *bc* plane (LaO···ON distance of 3.022 Å). When solvent water molecules in the extended structure are taken into account, complex hydrogen-bonding regimes are evident. The result of these intermolecular interactions coupled with one unique π-stacking interaction (aryl centroid···centroid separation of 3.719 Å) between neighboring calixarenes is that the molecules pack in the extended structure into a previously unseen corrugated bilayer type arrangement, Figure 4.

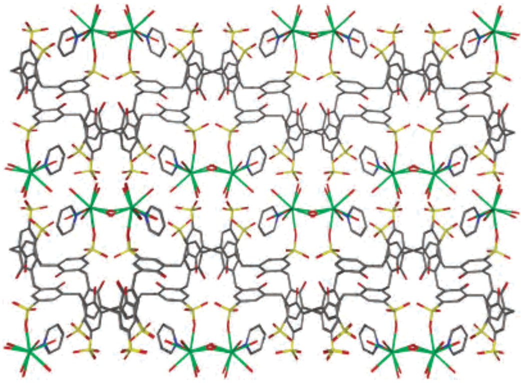

Figure 4. Packing diagram for complex **2** showing the corrugated bilayer arrangement. (Hydrogen atoms and solvent water molecules are omitted for clarity.)

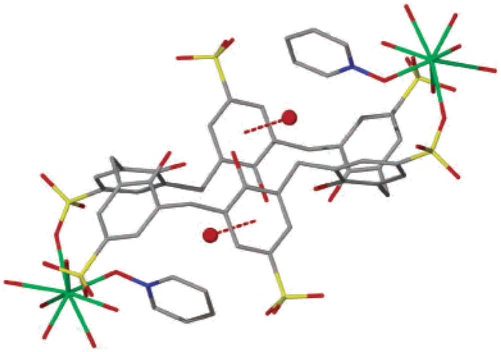

Figure 5. Part of the extended structure in **3** showing the OH···aromatic-π interaction in the cavity of the partial cone. (Hydrogen atoms and solvent water molecules are omitted for clarity).

The structural network chemistry based on DiPyNO and lanthanide(III) metals is currently under investigation by others and shows that the molecule acts as a remarkably versatile linker capable of forming several networks of varied coordination mode and topology.[12] This, coupled with the interesting and often complex structures generated when PyNO is used as a guest with lanthanide(III) ions and *p*-sulfonatocalix[*n*]arenes ($n = 4, 5$), suggests a wealth of supramolecular chemistry yet to be uncovered with such guests and the larger, more flexible calixarene analogues. An entrance into such chemistry is evident in the formation of complex **3**, $[(Eu(H_2O)_6)_2$(4,4′-dipyridine-*N*,*N*′-dioxide)(*p*-sulfonatocalix[6]arene)$]\cdot 8H_2O$, crystals of which grew from an aqueous solution containing Na_8SO_3[6], europium(III) nitrate, and DiPyNO. The crystal structure was solved in the monoclinic space group $P2_1/c$ with the asymmetric unit consisting of a half-calixarene to which an octacoordinate lanthanide metal with six aquo ligands is tethered with also half of a bound DiPyNO molecule (Figure 5). In addition, there are a total of four solvent water molecules, one of which resides in the partial cone at a distance consistent with OH···aromatic-π interactions with one of the aromatic rings of the calixarene fragment although hydrogen atoms could not be located in the Fourier difference map (distance to ring centroid 3.622 Å). This is consistent with those seen for this calixarene as the octasodium salt and for the smaller calix[4]arene analogue when the water molecule is trapped deep in the hydrophobic pocket of the macrocycle.[13,17]

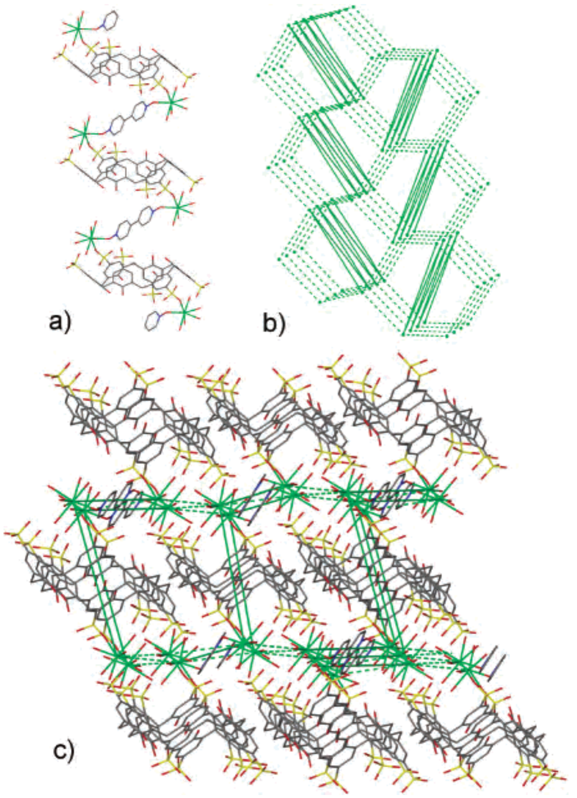

Figure 6. Diagram showing (a) the zigzag coordination polymer in **3**, (b) the coordination and H-bonding network (H-bonding links, dashed lines; coordination links through DiPyNO, solid lines), and (c) the overall bilayer arrangement and organization of the networks within the extended structure.

The extended structure reveals a bilayer arrangement as in **1** (Figure 6c) with the calixarenes packing through one unique π-stacking interaction with an aromatic centroid$\cdots$centroid distance of 3.719 Å. The extended structure also reveals the calixarene/Eu/DiPyNO fragment (devoid of solvent molecules) to form a zigzag coordination polymer chain along the *a* axis with the DiPyNO molecules spanning the hydrophilic layer between two europium centers, Figure 6a,b. These chains are linked via EuO$\cdots$OS/SO$\cdots$Eu hydrogen-bonding interactions through sulfonate groups such that each europium “sees” the three nearest europium centers in a near trigonal planar fashion (H-bonding distances range from 2.746 to 2.943 Å). If each of these europium centers is linked by a dashed line, graphitic sheets of hydrogen bonds are formed in the *bc* plane with adjacent sheets linked via coordination polymer chains as described above (Figure 6b,c).

These hydrogen-bonding sheets are formed entirely within the hydrophilic layer of the bilayer arrangement, and the overall structure, to our knowledge, is the only example of a multicomponent coordination polymer for *p*-sulfonatocalix[6]arene. Similar chemistry has been examined with other lanthanide metals but has to date been unproductive with regard to single crystal formation. Clearly, however, molecules such as PyNO and DiPyNO are excellent in forming hydrogen-bonded network or coordination network supramolecular structures and similar chemistry of other similarly sized and related molecules should be examined in the hope of forming larger and more complex arrangements in the solid state.

Conclusion

Earlier studies revealed that SO$_3$[5] is capable of assembling into capsulelike arrangements with PyNO guests in the presence of various lanthanide metals but is yet to form more complex superstructures similar to those of SO$_3$-[4].[9,10,20] We have previously shown that the conformation of SO$_3$[6] can be controlled through the formation of lanthanide crown ether complexes.[15] Here we have shown that SO$_3$[6] is capable of forming various well-ordered supramolecular architectures of varied complexity while in the “up−down” double partial cone conformation but, at this stage, none as spectacular as those for the SO$_3$[4]. Despite this, it is feasible, when considering the conformational flexibility associated with previously reported supramolecular assemblies coupled with those reported here, that *p*-sulfonatocalix-[5,6]arenes will form larger supramolecular assemblies in the presence of particular guests under specific conditions.

Experimental Section

Octasodium *p*-sulfonatocalix[6]arene hydrate was synthesized by literature methods,[21] while PyNO, DiPyNO, and lanthanide salts were purchased from Aldrich and used as supplied. Bulk samples were analyzed by IR spectroscopy and microanalysis (two of which were adjusted for solvent loss).

Synthesis of $[(Ni(H_2O)_6)_3]^{6+}\{$(pyridine *N*-oxide)$_2\subset$(*p*-sulfonatocalix[6]arene)$\}^{6-}\cdot 7H_2O$, 1. Octasodium *p*-sulfonatocalix[6]arene hydrate (15 mg, 11.5 μmol), pyridine *N*-oxide (2.5 mg, 26.5 μmol), and nickel(II) chloride hexahydrate (14 mg, 60 μmol) were dissolved in distilled water (1.5 cm^3). Over several days, pale green plates formed which were suitable for X-ray diffraction studies. Yield: 10 mg, 45%. IR (KBr disk, ν, cm^{-1}): 3276 s, 2965 m, 1636 m, 1473 s, 1362 m, 1211 s, 1148 s, 1045 s. Anal. Calcd (adjusted for the loss of five water molecules) for $C_{52}H_{80}N_2O_{46}S_6$-Ni$_3$: C, 34.0; H, 4.39; N, 1.52. Found: C, 33.9; H, 4.55; N, 1.50.

Synthesis of $[(La(H_2O)_7$(pyridine-*N*-oxide))$_2$(*p*-sulfonatocalix[6]arene)]$\cdot 6H_2O$, 2. Octasodium *p*-sulfonatocalix[6]arene hydrate (30 mg, 23 μmol), pyridine *N*-oxide (5 mg, 53 μmol), and lanthanum(III) nitrate hexahydrate (20 mg, 46 μmol) were dissolved in distilled water (1.5 cm^3). Over 2 days, colorless plates formed which were suitable for X-ray diffraction studies. Yield: 8 mg, 36%. IR (KBr disk, ν, cm^{-1}): 3250 s, 2949 m, 1642 m, 1472 s, 1364 m, 1240 s, 1149 s, 1044 s. Anal. Calcd (adjusted for the loss of three water molecules) for $C_{26}H_{33}NO_{20}S_3La$: C, 34.14; H, 3.64; N, 1.53. Found: C, 34.1; H, 3.50; N, 1.60.

Synthesis of $[(Eu(H_2O)_6)_2$(4,4′-dipyridine-*N,N*′-dioxide)(*p*-sulfonatocalix[6]arene)]$\cdot 8H_2O$, 3. Octasodium *p*-sulfonatocalix[6]arene hydrate (15 mg, 11.5 μmol), 4,4′-dipyridine-*N,N*′-dioxide (5 mg, 25 μmol), and europium(III) nitrate hydrate (12 mg, 35 μmol) were dissolved in distilled water (2 cm^3). Over several days, small colorless plates formed which were suitable for X-ray diffraction studies. Yield: 5 mg, 44%. IR (KBr disk, ν, cm^{-1}): 3333 s, 2941 m, 1665 s, 1478 s, 1372 m, 1215 s, 1161 s, 1039 s. Anal. Calcd for $C_{26}H_{39}NO_{23}S_3Eu$: C, 31.81; H, 4.00; N, 1.43. Found: C, 31.35; H, 4.05; N, 1.55.

X-ray Crystallography. X-ray data for compounds **1**−**3** were collected on an Enraf-Nonius KappaCCD with Mo Kα radiation

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Table 1. X-ray Crystallographic Data for Compounds **1**−**3**

param	1	2	3
empirical formula	$C_{52}H_{90}N_2O_{51}S_6Ni_3$	$C_{26}H_{39}NO_{23}S_3La$	$C_{26}H_{39}NO_{23}S_3Eu$
M_r	1927.75	968.67	981.72
cryst size (mm)	0.10 × 0.19 × 0.26	0.08 × 0.14 × 0.16	0.03 × 0.13 × 0.14
cryst system	triclinic	monoclinic	monoclinic
space group	$P\bar{1}$	$P2_1/c$	$P2_1/c$
T (K)	150(2)	150(2)	150(2)
a (Å)	12.3959(3)	17.2709(2)	13.8169(2)
b (Å)	17.6908(3)	18.4511(3)	12.2289(2)
c (Å)	20.1012(4)	11.9992(3)	22.3563(4)
α (deg)	66.2390(1)		
β (deg)	72.2680(1)	108.7160(1)	107.8600(1)
γ (deg)	71.2420(1)		
V (Å^3)	3741.43(13)	3621.55(12)	3595.40(10)
Z	2	4	4
ρ_{calcd} (Mg·m^{-3})	1.711	1.777	1.814
θ range (deg)	2.19−27.47	2.49−26.00	2.54−27.50
reflcns collcd	65 851	65 215	29 028
indpndt reflcns (R_{int})	16 881 (0.1087)	7107 (0.1185)	8187 (0.0885)
no. of params	1027	487	487
final R_1 [$I > 2\sigma(I)$]	0.0651	0.0646	0.0362
S	1.024	1.140	1.017
ωR_2 (all data)	0.1956	0.1618	0.0882
min, max resid electron density (e·Å^3)	1.47, −1.36	3.13, −1.00	0.80, −0.97

($\lambda = 0.710\ 73$ Å). Structures were solved by direct methods using SHELXS-97 and refined by full-matrix least squares on F^2 using SHELXL-97. All non-hydrogen atoms were refined anisotropically with the exception of one water molecule in **2**. C−H and alcohol OH hydrogen atoms were included at geometrically estimated positions with a riding refinement. Details of data collection and structure refinement are given in Table 1. Residual electron density in compounds **1** and **2** is located around 1 Å from nickel or lanthanide metal centers, respectively. CCDC-233058, -233055, and -233056 contain the supplementary crystallographic data for this paper as complexes **1**−**3**, respectively. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, U.K.; fax (internat.) +44-1223/336-033; E-mail deposit@ccdc.cam.ac.uk].

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Supporting Information Available: X-ray crystallographic data in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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