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tomer of the hydrazone form (B).

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Supplementary Material Available: Tables SI–SVII, listing bond lengths, bond angles, thermal parameters, and crystallographic data for $C_{22}H_{16}F_2N_2O_2$ (I) and $C_{22}H_{17}F_2N_3O_2Ni$ (II) (13 pages); tables of observed and calculated structure factors for I and II, respectively (43 pages). Ordering information is given on any current masthead page.

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Metal Ion Complexes of Water-Soluble Calix[4]arenes

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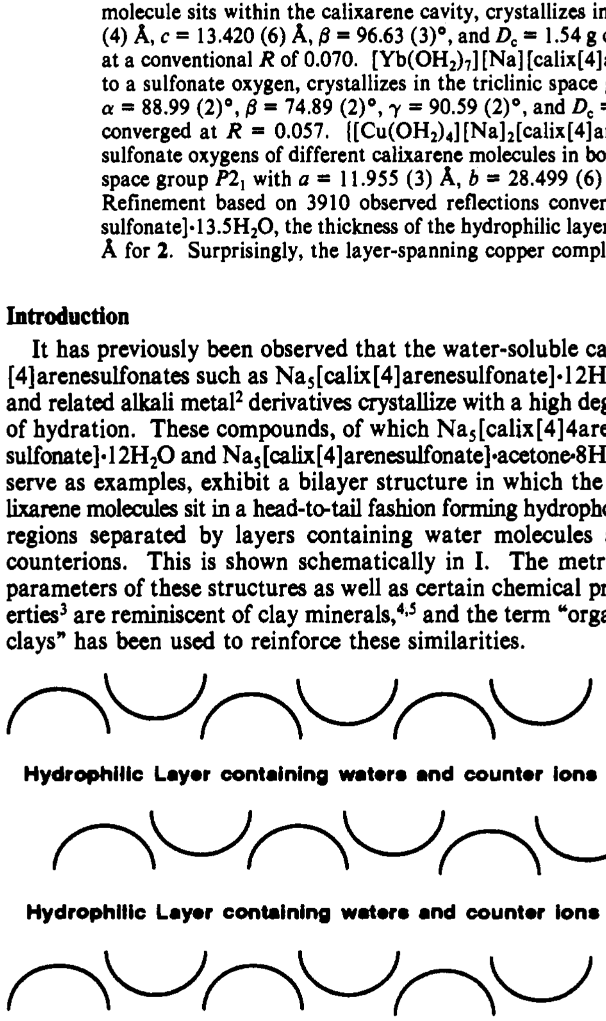
Three transition metal complexes of water-soluble calixarenes have been prepared and structurally characterized, demonstrating the three possible modes of incorporation of metals into the solid-state layered structure. $[Cr(OH_2)_6][Na][calix[4]arenesulfonate](acetone)\cdot 10.5H_2O$ (**1**), in which the $Cr(OH_2)_6^{3+}$ species is intercalated within the hydrophilic layer and an acetone molecule sits within the calixarene cavity, crystallizes in the monoclinic space group $P2_1/n$ with $a = 12.206$ (6) Å, $b = 31.251$ (4) Å, $c = 13.420$ (6) Å, $\beta = 96.63$ (3)°, and $D_c = 1.54$ g cm^{-3} for $Z = 4$. Refinement based on 3518 observed reflections converged at a conventional R of 0.070. $[Yb(OH_2)_7][Na][calix[4]arenesulfonate]\cdot 9H_2O$ (**2**), in which a $Yb(OH_2)_7^{3+}$ moiety binds directly to a sulfonate oxygen, crystallizes in the triclinic space group $P\bar{1}$ with $a = 12.362$ (3) Å, $b = 13.656$ (3) Å, $c = 13.964$ (3) Å, $\alpha = 88.99$ (2)°, $\beta = 74.89$ (2)°, $\gamma = 90.59$ (2)°, and $D_c = 1.80$ g cm^{-3} for $Z = 2$. Refinement based on 4210 observed reflections converged at $R = 0.057$. $\{[Cu(OH_2)_4][Na]_2[calix[4]arenesulfonate]\cdot 7.5H_2O\}_2$ (**3**), in which $Cu(OH_2)_4^{2+}$ units interact with sulfonate oxygens of different calixarene molecules in both an intralayer and an interlayer fashion, crystallizes in the monoclinic space group $P2_1$ with $a = 11.955$ (3) Å, $b = 28.499$ (6) Å, $c = 12.442$ (3) Å, $\beta = 91.49$ (2)°, and $D_c = 1.66$ g cm^{-3} for $Z = 4$. Refinement based on 3910 observed reflections converged at a conventional R of 0.054. In the parent $Na_4[calix[4]arenesulfonate]\cdot 13.5H_2O$, the thickness of the hydrophilic layer is 8.41 Å. The corresponding thickness in **1** is 9.98 Å compared to 7.51 Å for **2**. Surprisingly, the layer-spanning copper complex in **3** reduces this distance only slightly to 8.02 Å.

Introduction

It has previously been observed that the water-soluble calix[4]arenesulfonates such as $Na_5[calix[4]arenesulfonate]\cdot 12H_2O$[1] and related alkali metal[2] derivatives crystallize with a high degree of hydration. These compounds, of which $Na_5[calix[4]4arenesulfonate]\cdot 12H_2O$ and $Na_5[calix[4]arenesulfonate]\cdot acetone\cdot 8H_2O$[1] serve as examples, exhibit a bilayer structure in which the calixarene molecules sit in a head-to-tail fashion forming hydrophobic regions separated by layers containing water molecules and counterions. This is shown schematically in I. The metrical parameters of these structures as well as certain chemical properties[3] are reminiscent of clay minerals,[4,5] and the term "organic clays" has been used to reinforce these similarities.



I

There have been several reports of the interaction of metal ions with calixarenes.[6-15] These have invariably been based on either complexation of the metal by the phenolic oxygen atom or reaction of metal complexes with the phenolic protons of *p-tert*-butylcalixarene. Introduction of a group capable of binding metals such as sulfonate in the position para to the phenolic group opens new possible metal ion coordination modes, and the involvement of these groups with the water molecules of the hydrophilic layer presents an interesting opportunity to study the coordination chemistry of the sulfonate groups with hydrated metal ions.

One can envision three possible modes of interaction between the calix[4]arenesulfonate and a transition metal ion within a layered structure: (1) intercalation of the metal-containing species into the inter-calix layer with no direct metal-sulfonate oxygen bond; (2) interaction between the metal ion and the sulfonate groups of one calixarene unit; (3) interaction between the metal ion and the sulfonate groups of more than one calixarene. The three complexes reported here serve as examples of each of these possibilities.

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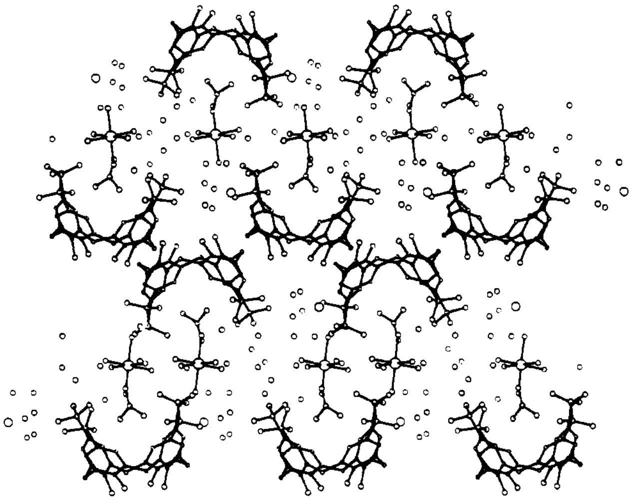

Figure 1. Bilayer of $[Cr(OH_2)_6][Na][calix[4]arenesulfonate](acetone)\cdot 10.5H_2O$ (**1**), illustrating the intercalation of the hexaaquachromium(III) ions into the hydrophilic layers. The acetone molecule resides in the mouth of the calixarene cavity.

Table I. Bond Lengths and Angles for **2**

	Distances, Å		
Yb–O(13)S	2.331 (9)	Yb–W(1)	2.345 (9)
Yb–W(2)	2.328 (9)	Yb–W(3)	2.356 (9)
Yb–W(4)	2.330 (9)	Yb–W(5)	2.325 (9)
Yb–W(6)	2.320 (9)	Yb–W(7)	2.344 (9)
Na–O(31)S′	2.33 (4)	Na–O(41)S	2.40 (1)
Na–W(9)	2.60 (2)	Na–W(10)	2.48 (2)
Na–W(14)	2.55 (2)	Na–W(15)	2.43 (3)
Na–W(19)	2.43 (4)		
	Angles, deg		
O(13)S–Yb–W(1)	144.5 (3)	O(13)S–Yb–W(2)	75.4 (4)
W(1)–Yb–W(2)	71.3 (3)	O(13)S–Yb–W(3)	136.3 (3)
W(1)–Yb–W(3)	73.3 (3)	W(2)–Yb–W(3)	119.9 (4)
O(13)S–Yb–W(4)	75.9 (3)	W(1)–Yb–W(4)	105.3 (4)
W(2)–Yb–W(4)	73.5 (3)	W(3)–Yb–W(4)	71.2 (3)
O(13)S–Yb–W(5)	77.0 (3)	W(1)–Yb–W(5)	84.1 (3)
W(2)–Yb–W(5)	77.4 (4)	W(3)–Yb–W(5)	143.3 (3)
W(4)–Yb–W(5)	144.2 (3)	O(13)S–Yb–W(6)	72.5 (3)
W(1)–Yb–W(6)	142.8 (3)	W(2)–Yb–W(6)	144.2 (3)
W(3)–Yb–W(6)	75.9 (3)	W(4)–Yb–W(6)	83.5 (3)
W(5)–Yb–W(6)	109.9 (4)	O(13)S–Yb–W(7)	123.3 (4)
W(1)–Yb–W(7)	76.8 (3)	W(2)–Yb–W(7)	137.0 (3)
W(3)–Yb–W(7)	75.5 (4)	W(4)–Yb–W(7)	144.1 (3)
W(5)–Yb–W(7)	71.3 (3)	W(6)–Yb–W(7)	75.8 (3)
S(1)–O(13)S–Yb	150.8 (6)		

Results and Discussion

The addition of chromium(III) nitrate to a solution of the $[calix[4]arenesulfonate]^{4-}$ anion produces crystals of the complex $[Cr(OH_2)_6][Na][calix[4]arenesulfonate](acetone)\cdot 10.5H_2O$ (**1**), the layered structure of which is shown in Figure 1. The mode of interaction is that of (1) above, as the primary coordination sphere of the chromium ion is filled by six water molecules in an octahedral arrangement. The hexaaquo complex interacts via hydrogen bonding with other water molecules in the hydrophilic layer and with the sulfonate groups of calixarenes in different layers. The acetone molecule resides in the calixarene cavity and interacts via through-water hydrogen bonding with the sulfonate groups of calixarenes in the opposite layer. As was observed for $Na_5[calix[4]arenesulfonate](acetone)\cdot 8H_2O$,[1] the calixarene conformation changes from one of approximate C_{4v} symmetry to one of C_{2v} symmetry as the phenolic residues that lie perpendicular to the plane of the guest "bend away" and the remaining aromatic moieties close on the planar acetone molecule.

Addition of $YbCl_3$ to a solution of $[calix[4]arenesulfonate]^{4-}$ leads to crystallization of the complex $[Yb(OH_2)_7][Na][calix[4]arenesulfonate]\cdot 9H_2O$ (**2**); the coordination environment of the ytterbium ion and the layered structure are shown in Figure 2, and important distances and angles are given in Table I. This species is an example of (2) above, as the ytterbium atom binds directly to a sulfonate oxygen at 2.331 (9) Å in addition to seven water molecules at an average distance of 2.335 (13) Å arranged in a square antiprismatic geometry. These distances can be compared to those found in the seven-coordinate $YbCl_2\cdot(15\text{-crown-}5)^+$ complex, which range from 2.23 (2) to 2.32 (2) Å,[16] and those in the bicapped trigonal prismatic $Dy(H_2O)_7(CH_3OH)^{3+}$, 2.359 (6)–2.42 (1) Å,[17] with a correction of 0.04 Å for the difference in ionic radii.

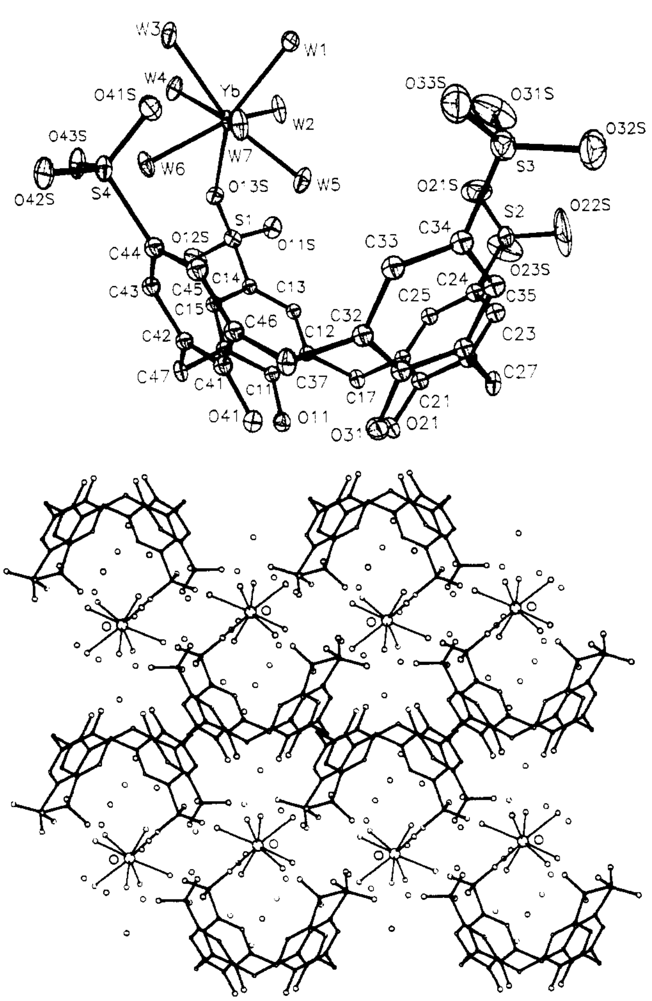

Figure 2. (a, Top) Coordination environment of the ytterbium(III) ion and (b, bottom) bilayer structure of $[Yb(OH_2)_7][Na][calix[4]arenesulfonate]\cdot 9H_2O$ (**2**).

In the case of the ytterbium complex structure, a water molecule is located in the calixarene cavity. In a previously reported example, the water molecule in the calixarene cavity of $Na_4[calix[4]arenesulfonate]\cdot 13.5H_2O$ represents the first X-ray diffraction evidence for aromatic π hydrogen bonding to water.[18] The π hydrogen bond is characterized by aromatic centroid···O(water) distances of 3.16 and 3.14 Å, values is good agreement with 3.11 Å predicted by Monte Carlo methods for the centroid(benzene)···O(water) distance.[19] For $[Yb(OH_2)_7][Na][calix[4]arenesulfonate]\cdot 9H_2O$, the water molecule in the cavity resides 3.48, 3.70, 3.70, and 3.80 Å from the aromatic centroids. This water molecule is also hydrogen bonded to W(5) (2.76 Å) of the ytterbium coordination sphere and to another water molecule (2.63 Å) in the hydrophilic layer. It is likely that the constraints of normal hydrogen bonding to the ytterbium-coordinated water molecule have dictated weaker aromatic π hydrogen bonds.

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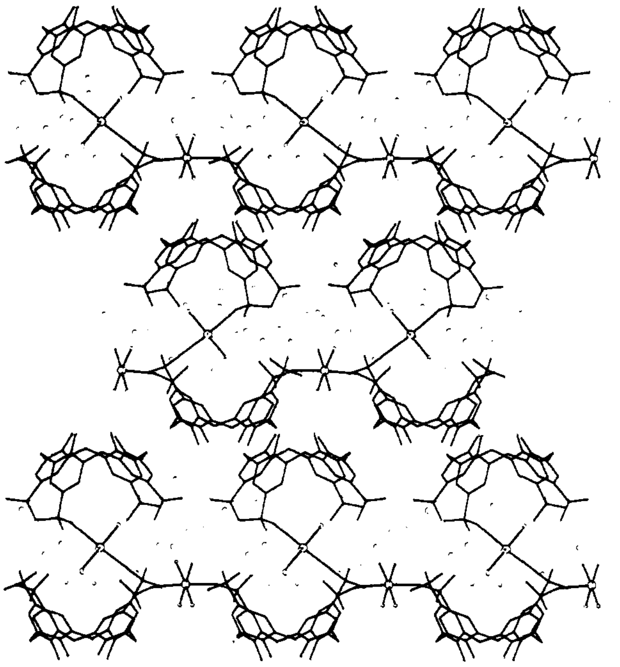

Figure 3. Bilayer structure of $\{[Cu(OH_2)_4][Na]_2[calix[4]arenesulfonate]\cdot 7.5H_2O\}_2$ (**3**), showing the copper(II) ions which span the hydrophilic layers and those which bridge calixarenes within a bilayer.

Table II. Crystallographic Data

	1	**2**	**3**
chem formula	$C_{31}H_{59}CrNaO_{33.5}S_4$	$C_{28}H_{52}YbNaO_{32}S_4$	$C_{28}H_{43}CuNa_2O_{27.5}S_4$
fw	1171	1225	1057
space group	$P2_1/n$	$P\bar{1}$	$P2_1$
a, Å	12.206 (6)	12.362 (3)	11.955 (3)
b, Å	31.251 (4)	13.656 (4)	28.499 (6)
c, Å	13.420 (6)	13.964 (4)	12.442 (3)
α, deg	90	88.99 (2)	90
β, deg	96.63 (3)	74.89 (2)	91.49 (2)
γ, deg	90	90.59 (2)	90
V, Å^3	5085	2275	4238
Z	4	2	4
T, °C	22	22	22
λ, Å	1.5418	0.7107	0.7107
D_c, g cm^{-3}	1.54	1.79	1.66
m_c cm^{-1}	43.5	23.9	8.5
R	0.069	0.057	0.054
R_w	0.080	0.069	0.062

Table III. Fractional Coordinates for **2**

atom[a]	x/a	y/b	z/c	U(eqv), Å^2
Yb	−0.02279 (5)	0.75663 (4)	0.65686 (4)	0.027 (10)
Na	0.0279 (6)	0.3037 (5)	0.8168 (5)	0.069 (13)
S(1)	0.1630 (3)	0.9490 (3)	0.5160 (3)	0.038 (6)
S(2)	0.2083 (3)	1.0368 (3)	1.0265 (3)	0.045 (7)
S(3)	0.2059 (3)	0.5306 (3)	1.1131 (3)	0.041 (8)
S(4)	0.1798 (3)	0.4255 (2)	0.5963 (2)	0.031 (8)
O(11)	0.5942 (8)	0.8257 (7)	0.5806 (7)	0.040 (2)
O(11)S	0.1226 (9)	1.0352 (7)	0.5731 (8)	0.057 (16)
O(12)S	0.193 (1)	0.9700 (9)	0.4083 (8)	0.065 (20)
O(13)S	0.0861 (8)	0.8666 (6)	0.5407 (7)	0.039 (7)
O(21)	0.6097 (8)	0.8598 (7)	0.7672 (7)	0.041 (6)
O(21)S	0.117 (1)	0.989 (1)	1.005 (1)	0.102 (30)
O(22)S	0.217 (2)	1.022 (2)	1.125 (1)	0.216 (160)
O(23)S	0.208 (1)	1.1381 (9)	1.007 (1)	0.100 (40)
O(31}	0.6086 (8)	0.6660 (7)	0.8080 (7)	0.039 ( )
O(31)S	0.125 (1)	0.601 (1)	1.109 (1)	0.083 (20)
O(32)S	0.233 (1)	0.5260 (8)	1.2098 (7)	0.062 (19)
O(33)S	0.177 (1)	0.4333 (9)	1.0851 (8)	0.074 (26)
O(41)	0.5920 (8)	0.6293 (7)	0.6246 (7)	0.042 (5)
O(41)S	0.0956 (8)	0.4291 (7)	0.6920 (7)	0.039 (2)
O(42)S	0.2155 (8)	0.3254 (6)	0.5699 (7)	0.040 (16)
O(43)S	0.1390 (8)	0.4752 (6)	0.5187 (7)	0.041 (18)
C(11)	0.492 (1)	0.8547 (9)	0.5713 (9)	0.029 (3)
C(12)	0.442 (1)	0.9408 (9)	0.615 (1)	0.030 (3)
C(13)	0.342 (1)	0.969 (1)	0.599 (1)	0.032 (3)
C(14)	0.287 (1)	0.913 (1)	0.543 (1)	0.032 (3)
C(15)	0.337 (1)	0.826 (1)	0.502 (1)	0.032 (3)
C(16)	0.438 (1)	0.7968 (9)	0.5159 (9)	0.029 (3)
C(17)	0.500 (1)	1.004 (1)	0.679 (1)	0.036 (11)
C(21)	0.516 (1)	0.901 (1)	0.829 (1)	0.032 (3)
C(22)	0.478 (1)	0.870 (1)	0.928 (1)	0.031 (3)
C(23)	0.387 (1)	0.914 (1)	0.988 (1)	0.037 (3)
C(24)	0.330 (1)	0.988 (1)	0.951 (1)	0.036 (3)
C(25)	0.369 (1)	1.018 (1)	0.850 (1)	0.037 (3)
C(26)	0.461 (1)	0.974 (1)	0.789 (1)	0.032 (3)
C(27)	0.532 (1)	0.7855 (9)	0.973 (1)	0.035 (12)
C(31)	0.514 (1)	0.6318 (9)	0.878 (1)	0.030 (3)
C(32)	0.462 (1)	0.5442 (9)	0.8644 (9)	0.029 (3)
C(33)	0.369 (1)	0.513 (1)	0.939 (1)	0.032 (3)
C(34)	0.328 (1)	0.567 (1)	1.024 (1)	0.032 (3)
C(35)	0.383 (1)	0.655 (1)	1.035 (1)	0.033 (3)
C(36)	0.476 (1)	0.6882 (9)	0.9630 (9)	0.028 (3)
C(37)	0.503 (1)	0.4836 (9)	0.771 (1)	0.032 (9)
C(41)	0.493 (1)	0.5871 (9)	0.619 (1)	0.030 (3)
C(42)	0.441 (1)	0.6160 (9)	0.5451 (9)	0.028 (3)
C(43)	0.345 (1)	0.5662 (9)	0.539 (1)	0.030 (3)
C(44)	0.298 (1)	0.4916 (9)	0.6068 (9)	0.029 (3)
C(45)	0.350 (1)	0.466 (1)	0.682 (1)	0.032 (3)
C(46)	0.446 (1)	0.5128 (9)	0.6899 (9)	0.028 (3)
C(47)	0.489 (1)	0.7006 (9)	0.4727 (9)	0.031 (10)
W(1)	−0.1468 (8)	0.7414 (7)	0.8153 (7)	0.041 (6)
W(2)	−0.100 (1)	0.9090 (7)	0.7027 (7)	0.053 (30)
W(3)	−0.1408 (9)	0.6208 (7)	0.6535 (7)	0.046 (22)
W(4)	−0.1347 (9)	0.7934 (6)	0.5505 (8)	0.049 (18)
W(5)	0.0990 (9)	0.8228 (7)	0.7412 (7)	0.053 (13)
W(6)	0.0768 (9)	0.6664 (6)	0.5243 (7)	0.041 (19)
W(7)	0.0529 (9)	0.6284 (7)	0.7312 (7)	0.047 (21)
W(8)	0.087 (1)	1.0097 (9)	0.8055 (9)	0.077 (16)
W(9)	0.199 (1)	0.197 (1)	0.735 (1)	0.101 (43)
W(10)	−0.014 (1)	0.1963 (9)	0.967 (1)	0.098 (45)
W(11)	0.206 (2)	0.691 (1)	1.3351 (9)	0.116 (74)
W(12)	0.121 (2)	0.654 (2)	0.899 (1)	0.173 (62)
W(13)	0.291 (2)	0.747 (2)	0.778 (2)	0.169 (22)
W(14)	−0.051 (2)	0.168 (2)	0.731 (2)	0.082 (34)
W(15)	0.106 (4)	0.419 (3)	0.912 (3)	0.124 (36)
W(16)	0.345 (3)	1.262 (2)	0.839 (3)	0.142 (66)
W(17)	0.268 (5)	0.870 (3)	0.245 (2)	0.147 (85)
W(18)	0.400 (6)	0.797 (4)	0.240 (3)	0.216 (120)
W(19)	0.169 (5)	0.337 (4)	0.906 (3)	0.177 (63)

[a] W(14)–W(19) have 0.50 occupancy.

The final mode of incorporation of a transition metal species into the calix[4]arenesulfonate layers was obtained by the addition of $CuCl_2$ to a $[calix[4]arenesulfonate]^{4-}$ solution. The resulting complex, $\{[Cu(OH_2)_4][Na]_2[calix[4]arenesulfonate]\cdot 7.5H_2O\}_2$ (**3**), is shown in Figure 3. There are two independent formula units of this complex in the asymmetric unit, due to the two different copper environments. In one, the metal binds to sulfonate oxygen atoms of calixarenes in the *same* layer, and in the other, the copper interacts with sulfonate oxygen atoms across the hydrophilic layer. In both instances the metal atom adopts an octahedral geometry with the sulfonate groups lying mutually trans and the equatorial plane being occupied by four water molecules. There is a notable Jahn–Teller distortion so that the $Cu–O_{(sulfonate)}$ distances average 2.44 (3) Å compared to the $Cu–O_{(water)}$ distance of 1.97 (2) Å. In a fashion similar to that seen for **2**, the calixarene cavity is occupied by a water molecule (centroid(aromatic)···O > 3.5 Å).

It is of interest to compare the thicknesses[20] of the hydrophilic layers in each compound: 9.98 Å for **1**, 7.51 Å for **2**, and 8.09 Å for **3**. These values can be compared to that of 8.41 Å in the parent complex[21] and 6.91–8.68 Å found for the $M_5[calix[4]arenesulfonate]\cdot nH_2O$ complexes.[1,2] It should be expected that the intercalation mode of interaction would produce the widest layer, but it is surprising that the bridging of trans-layer calixarenes by the copper complex does not produce a narrower gap than in the case of the ytterbium complex. This anomaly can be explained

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(20) The thickness of the hydrophilic layer is defined as the perpendicular distance between the planes comprising the sulfur-bonded aromatic carbon atoms.

(21) Atwood, J. L.; Bott, S. G.; Orr, G. W.; Hamada, F. Unpublished results.

by an examination of the calixarene layer itself. This is composed of an alternating up–down arrangement of calixarene molecules, held together by some form of interaction between the sulfonate groups of the "down" calix and the phenolic groups of the "up". In $[Na]_5[calix[4]arene]\cdot 12H_2O$, this interaction is via a sodium ion, so that the closest $O_{(phenol)}\cdots O_{(sulfonate)}$ approach is 3.67 Å, and the 4-parent calixarene substitutes a water molecule for the sodium ($O_{(phenol)}\cdots O_{(sulfonate)} = 3.82$ Å). In contrast, the expansion of the hydrophilic layer in the intercalated chromium complex **1** forces the calixarene layer to contract and utilize two water molecules from the hydrophilic layer for the intra-calix layer adhesion. Thus, not only is the hydrophilic layer sensitive to its contents and adaptable by them, but also the calixarene layer is not constrained to having certain specific dimensions. In the copper complex **3**, the intra-calix sodium ion is replaced by a $Cu(H_2O)_4^{2+}$ moiety, which does constrain one dimension of the calixarene layer, the result of which is that this layer is virtually "two calixarene molecules thick" and the "down" calixarene is "squeezed out" by the proximity of the two "up" molecules. In contrast, the ytterbium complex has no such constraint, and the calixarene layer narrows so that its width is barely more than that of one calixarene, such that the phenolic oxygens hydrogen bond directly to sulfonate groups. This enables the ytterbium-attached water molecules to interact with four calixarenes—i.e. up and down species on each side of the water layer.

Experimental Section

Preparation of Calix[4]arene. A 25-g sample of *p-tert*-butylcalix[4]arene (prepared following the method of Gutsche[22] and recrystallized from toluene) was suspended in 1 L of benzene, and 25 g of anhydrous $AlCl_3$ was added under an N_2 atmosphere. The slurry was stirred for 18 h, and then 650 mL of 1 N HCl solution was poured into the reaction flask. After 0.5 h of stirring, the organic layer was separated from the mixture, washed with distilled H_2O, and concentrated in vacuo. Addition of MeOH produced a white powder, which was subsequently recrystallized from $CHCl_3$/MeOH to give 14 g (78%) of colorless crystals of calix[4]arene (mp 320 °C).

Preparation of Na_4[calix[4]arenesulfonate]. A 1.0-g sample of calix[4]arene and 10 mL of concentrated H_2SO_4 were heated at 60 °C for 4 h. At this point, no insoluble material remained. The reaction mixture was then added to 20 mL of saturated NaCl solution, and the mixture was heated to boiling and allowed to cool to room temperature. The crystals which formed upon standing were collected and recrystallized from hot distilled H_2O to give colorless crystals (70%).

Preparation of $[Cr(OH_2)_6][Na][calix[4]arenesulfonate](acetone)\cdot 10.5H_2O_2$ (1). A 0.10-g sample of $Na_4[calix[4]arenesulfonate]\cdot 13.5H_2O$ was dissolved in 5 mL of distilled H_2O, and 0.02 g of $Cr(NO_3)_3$ was added. The solution was slowly evaporated in a vacuum desiccator. The acetone apparently was trapped from the evaporation of another acetone-containing vessel in the desiccator. Pale blue needles of **1** were mounted in thin-walled capillaries with a drop of mother liquor to prevent crystal decomposition through loss of water.

Preparation of $[Yb(OH_2)_7][Na][calix[4]arenesulfonate]\cdot 9H_2O$ (2). A 0.10-g sample of $Na_4[calix[4]arenesulfonate]\cdot 13.5H_2O$ was dissolved in 5 mL of distilled H_2O, and 0.04 g of $YbCl_3\cdot 6H_2O$ was added. Colorless plates of **2** obtained as for **1** were mounted in thin-walled capillaries.

Preparation of $\{[Cu(OH_2)_4][Na]_2[calix[4]arenesulfonate]\cdot 7.5H_2O\}_2$ (3). A 0.10-g sample of $Na_4[calix[4]arenesulfonate]\cdot 13.5H_2O$ was dissolved in 5 mL of distilled H_2O, and 0.04 g of $CuCl_2$ was added. Very pale blue crystals of **3** obtained as for **1** were mounted in thin-walled capillaries.

Crystal Structure Solution and Refinement. Suitable crystals of **1**–**3** were mounted on the goniometer head of an Enraf-Nonius CAD-4 diffractometer equipped with Mo Kα (**2** and **3**) or Cu Kα (**1**) radiation. Final cell parameters as determined from least-squares refinement of the setting angles of 25 accurately centered reflections ($2\theta > 30°$ for **2** and **3**, $2\theta > 70°$ for **1**) are given in Table II. Data collection procedures followed the procedure in our laboratory detailed previously.[23] Data for all compounds were corrected for Lorentz and polarization effects and for absorption (based on 360° ψ scans of three to five reflections with high χ values).

Initial structure solution was accomplished using the direct methods option of SHELX-86[24] for **1** and **3** and the Patterson option for **2**. In each case, the metal and calixarene atoms were readily located. Fourier difference maps generated using SHELX[25] enabled the location of all other non-hydrogen atoms, including a number of partially occupied water positions (four for **1**, six for **2**, and two for **3**). The site occupancy for these was determined by refinement in which the thermal parameters at each position were constrained to equal the average parameter of the full-occupancy water positions. Refinement was completed by treatment of all atoms heavier than carbon with anisotropic thermal parameters (except for **1**, where the calixarene carbon atoms were treated with isotropic thermal parameters) and inclusion of calixarene hydrogens at calculated positions ($d_{C-H} = 1.00$ Å). The sodium atom in **1** was disordered over two nearby positions. Final atomic coordinates for **2** are given in Table III.

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Supplementary Material Available: Tables of crystal data, data collection parameters, final fractional coordinates, final bond distances and angles, hydrogen atom coordinates, and anisotropic thermal parameters and figures showing the calixarenes and labeled asymmetric units of **1** and **3** (30 pages); listings of observed and calculated structure factors (69 pages). Ordering information is given on any current masthead page.

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