Transition Metal Complexes of *p*-Sulfonatocalix[5]arene

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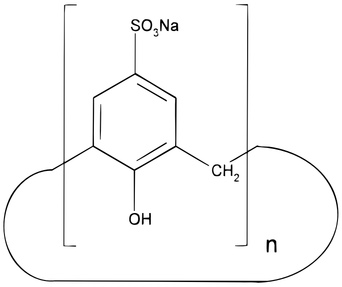
The X-ray crystal structure of the *p*-sulfonatocalix[5]arene^{5-} anion (**1b**) in the form of the dimeric hydrate Na_{10}-[*p*-sulfonatocalix[5]arene]$_2$·33.5H_2O (**2**) is reported. The reactions of **1b** with a number of transition metal salts to form transition metal bridged bis(calixarene) inclusion complexes have also been investigated. The X-ray crystal structure of the "$Co(H_2O)_4^{2+}$" bridged species $Na_8[Co(H_2O)_4$(*p*-sulfonatocalix[5]arene)$_2]$·2$CH_3C(O)N(CH_3)_2$·37H_2O (**3**) which incorporates a "supercavity" large enough to encompass 2 *N*,*N*-dimethylacetamide (dma) guest molecules as well as *ca.* 15 water molecules and Na^+ ions is reported. Crystal data are as follows: for **2**, monoclinic space group $P2_1/c$, $Z = 4$, $a = 22.0644(4)$, $b = 19.1180(3)$, $c = 27.7834(4)$ Å, $\beta = 91.780(1)$, $V = 11714.1(5)$ Å^3; complex **3**, orthorhombic space group *Pnma*, $Z = 4$, $a = 22.2271(5)$, $b = 30.1693(6)$, $c = 18.8503(4)$ Å, $V = 12640.6(5)$ Å^3.

Introduction

The water soluble *p*-sulfonatocalix[*n*]arenes ($n = 4$, **1a**; 5, **1b**; 6, **1c**) have received considerable attention in recent years as a consequence of their ability to bind metal ions in aqueous solution,[1] their formation of interesting clay-like bilayer structures in the solid state,[2] and their remarkable range of inclusion properties.[3] Noteworthy is the inclusion of water within the ostensibly hydrophobic cavities of **1a** (as both the 4− and 5− anions) and **1b** (as the 7− species). In the case of *p*-sulfonatocalix[4]arene^{4-} the included water is stabilized by OH···π-aromatic hydrogen-bonding interactions within the calixarene cavity,[3a] while for *p*-sulfonatocalix[5]arene^{7-} the larger macrocycle size results in long-range hydrogen-bonding interactions with the phenolic oxygen atoms at the lower rim of the host.[4]



n = 4, **1a**

5, **1b**

6, **1c**

Table 1. Crystallographic Data for Complexes **2** and **3**. Unit Cell Parameters for **4**

compound	**2**^{a}	**3**^{a}	**4**
formula	$C_{70}H_{117}Na_{10}O_{73.5}S_{10}$	$C_{78}H_{150}CoN_2Na_8O_{83}S_{10}$	
fw (g mol^{-1})	2685.31	2999.38	
space group	$P2_1/c$	*Pnma*	
a (Å)	22.0644(4)	22.2271(5)	11.104(6)
b (Å)	19.1180(3)	30.1693(6)	19.033(8)
c (Å)	27.7834(4)	18.8503(4)	29.438(8)
α (deg)	90	90	90
β (deg)	91.780(1)	90	97.55(4)
γ (deg)	90	90	90
V (Å^3)	11714.1(5)	12640.6(5)	6168(2)
Z	4	4	
ρ_{calc} (g cm^{-3})	1.52	1.58	
μ (cm^{-1})	3.33	4.42	
λ (Mo Kα)	0.71069	0.71069	
T (K)	123	173	
R, $R_w I > 2\sigma(I)^b$	0.143, 0.391	0.077, 0.233	
R, R_w all data^b	0.205, 0.454	0.097, 0.265	

[a] Data collected using a SMART CCD instrument. [b] $R_1(F) = \sum(|F_o| - |F_c|)/\sum|F_o|$, $R_w(F^2) = \{\sum(wF_o^2 - F_c^2)^2/\sum wF_o^4\}^{1/2}$.

Work by Shinkai *et al.* has demonstrated that **1b** and **1c**, in particular, possess a high affinity for the uranyl ion (UO_2^{2+}) and may form the basis of a method for its extraction from sea

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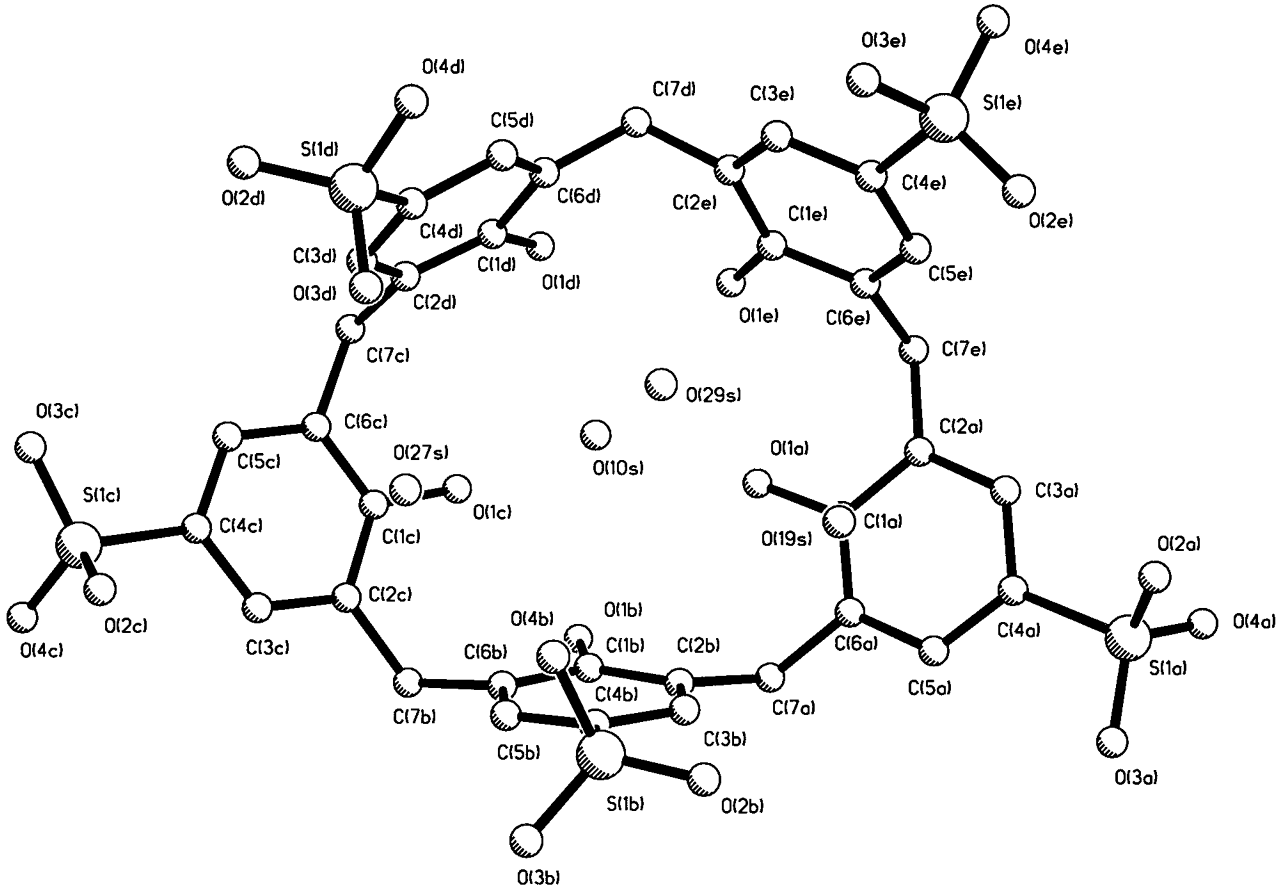

Figure 1. One of the crystallographically independent *p*-sulfonatocalix[5]arene^{5-} anions in **2** (**2a**) showing included water molecules and the atom numbering scheme adopted in the structures of both **2** and **3**.

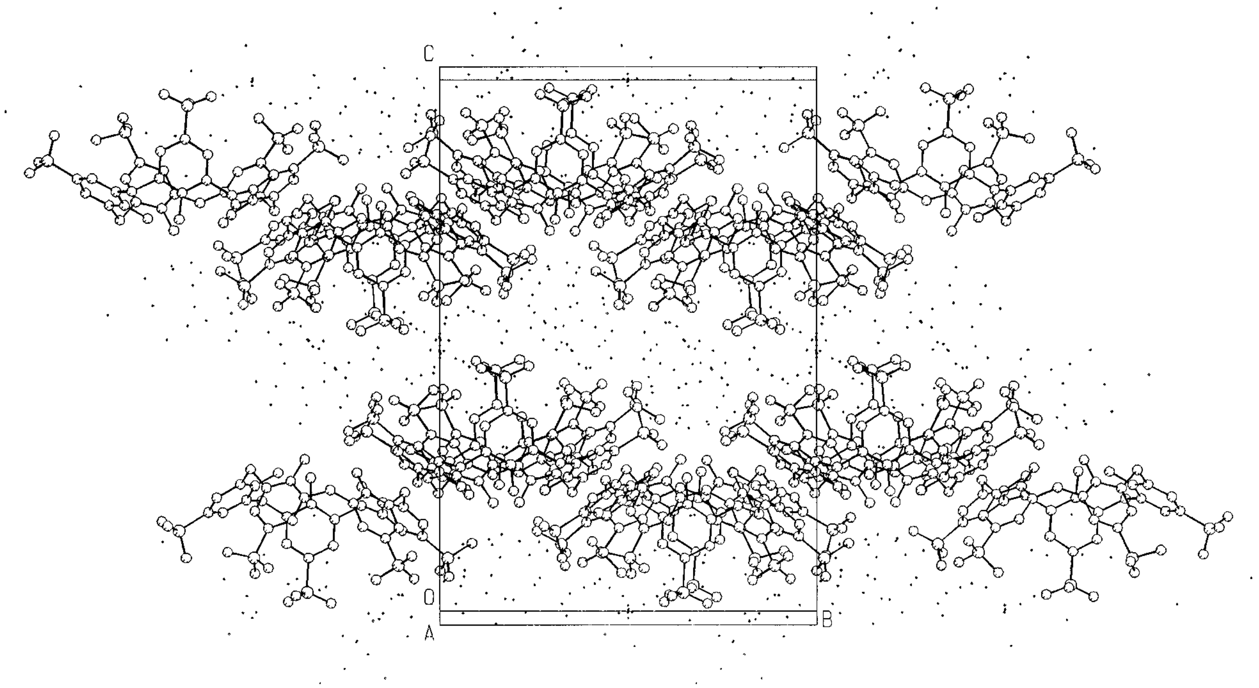

Figure 2. Alternating hydrophilic and hydrophobic layers in **2** viewed along the crystallographic *a* axis.

water.[1j,5] The selectivity of calixarenes **1b** and **1c** for UO_2^{2+} over metal ions such as Ni^{2+}, Zn^{2+}, and Cu^{2+} (factor of 10^{12-17}) was attributed to a proposed "preorganized, pseudoplanar" arrangement of the phenolic oxygen atoms at the lower rim of the macrocycle, forming a cyclic donor array capable of chelating a large metal ion with a preference for a high coordination number. Support for this proposal is provided by the work of Harrowfield *et al.* who have demonstrated the possibility of this type of coordination mode in the uranyl complex $[NHEt_3][UO_2(L)]\cdot 2H_2O$ (H_4L = bis(homo-oxa)-*p*-*tert*-butylcalix[4]arene) which incorporates the chelation of the uranium center by four of the phenolic oxygen atoms.[6] Indeed, coordination of a number of actinide, lanthanide, and transition metals to the phenolic oxygen atoms of *p*-alkylcalixarenes has been reported to occur in the presence of base.[7] In contrast, recent work by ourselves indicates that, while the sodium salt

Table 2. Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters (Å^2 × 10^3) for Complex **2**[a]

	x	*y*	*z*	*U*(eq)		*x*	*y*	*z*	*U*(eq)
O(1A)	4314(3)	2919(3)	2581(2)	42(2)	O(4F)	308(5)	10901(4)	1718(3)	90(3)
C(1A)	4462(4)	3478(4)	2878(3)	36(2)	O(1G)	2128(3)	7092(3)	2818(3)	59(2)
C(2A)	4040(4)	4026(4)	2950(3)	38(2)	C(1G)	2357(4)	7407(4)	2417(4)	45(2)
C(3A)	4222(4)	4553(4)	3268(3)	40(2)	C(2G)	2148(4)	8092(5)	2298(4)	42(2)
C(4A)	4783(4)	4535(4)	3499(3)	37(2)	C(3G)	2346(4)	8356(5)	1868(4)	49(3)
C(5A)	5182(4)	3999(4)	3407(3)	34(2)	C(4G)	2719(4)	7998(5)	1578(4)	52(3)
C(6A)	5021(4)	3477(4)	3100(3)	32(2)	C(5G)	2945(5)	7354(5)	1734(4)	54(3)
C(7A)	5482(4)	2917(4)	2962(4)	39(2)	C(6G)	2762(4)	7073(4)	2158(4)	41(2)
S(1A)	4965(1)	5205(1)	3910(1)	43(1)	C(7G)	3048(4)	6387(5)	2336(4)	50(3)
O(2A)	4471(4)	5241(4)	4237(3)	69(2)	S(1G)	2928(2)	8368(2)	1030(1)	74(1)
O(3A)	5510(4)	5013(4)	4147(4)	89(3)	*O(2G)	2415(8)	8434(13)	759(7)	93(7)
O(4A)	5010(4)	5849(3)	3637(3)	66(2)	*O(3G)	3522(9)	8389(11)	994(6)	90(7)
O(1B)	5350(3)	1565(3)	2445(2)	38(2)	*O(4G)	3112(13)	9123(11)	1197(9)	127(10)
C(1B)	5360(4)	1583(4)	2930(3)	39(2)	*O(2GA)	2656(15)	7881(18)	631(8)	164(14)
C(2B)	5382(4)	2205(4)	3211(3)	36(2)	*O(3GA)	3430(8)	7955(11)	858(7)	89(7)
C(3B)	5353(4)	2159(5)	3692(4)	48(3)	*O(4GA)	2616(15)	9040(12)	994(9)	137(11)
C(4B)	5320(5)	1507(5)	3912(4)	53(3)	O(1H)	1944(3)	5767(3)	2671(2)	45(2)
C(5B)	5337(4)	920(5)	3654(4)	44(2)	C(1H)	2244(4)	5442(4)	2335(3)	38(2)
C(6B)	5354(4)	931(4)	3161(3)	35(2)	C(2H)	2756(4)	5733(5)	2130(3)	42(2)
C(7B)	5414(4)	261(4)	2872(4)	39(2)	C(3H)	3037(5)	5386(5)	1752(4)	48(3)
S(1B)	5228(2)	1470(2)	4543(1)	90(1)	C(4H)	2822(4)	4756(5)	1588(3)	45(2)
*O(2B)	5319(10)	2108(8)	4742(5)	79(6)	C(5H)	2334(5)	4433(5)	1808(4)	49(3)
*O(3B)	5617(16)	954(9)	4738(7)	155(15)	C(6H)	2048(4)	4785(5)	2185(4)	44(2)
*O(4B)	4610(12)	1176(14)	4603(7)	134(11)	C(7H)	1539(4)	4396(5)	2437(4)	48(3)
*O(2BA)	5753(16)	1632(20)	4715(8)	174(14)	S(1H)	3206(1)	4305(2)	1146(1)	64(1)
*O(3BA)	4758(15)	1946(15)	4663(8)	151(12)	O(2H)	2822(5)	3790(6)	951(4)	115(4)
*O(4BA)	5270(17)	734(8)	4671(7)	140(13)	O(3H)	3324(8)	4813(6)	783(5)	159(6)
O(1C)	4327(3)	699(3)	2331(2)	37(2)	O(4H)	3751(4)	4063(6)	1345(4)	111(4)
C(1C)	4329(4)	74(4)	2566(3)	35(2)	O(1I)	716(3)	5558(3)	2486(3)	51(2)
C(2C)	4839(4)	−157(4)	2845(3)	37(2)	C(1I)	549(4)	4980(4)	2214(3)	42(2)
C(3C)	4791(4)	−781(4)	3075(4)	44(2)	C(2I)	945(4)	4418(4)	2154(3)	40(2)
C(4C)	4267(4)	−1176(4)	3054(3)	37(2)	C(3I)	766(5)	3888(5)	1849(4)	50(3)
C(5C)	3777(4)	−939(4)	2775(4)	40(2)	C(4I)	201(4)	3889(5)	1628(4)	46(2)
C(6C)	3810(4)	−318(4)	2526(3)	33(2)	C(5I)	−207(4)	4424(4)	1719(3)	44(2)
C(7C)	3250(4)	−37(4)	2246(3)	39(2)	C(6I)	−36(4)	4976(4)	2019(3)	42(2)
S(1C)	4222(1)	−1948(1)	3393(1)	48(1)	C(7I)	−476(4)	5548(4)	2108(4)	44(2)
O(2C)	4332(4)	−1753(4)	3886(3)	73(2)	S(1I)	13(2)	3224(1)	1222(1)	72(1)
O(3C)	3636(4)	−2242(4)	3292(4)	86(3)	O(2I)	446(6)	3320(5)	840(4)	113(4)
O(4C)	4712(3)	−2403(3)	3232(3)	61(2)	O(3I)	76(5)	2572(4)	1466(4)	97(3)
O(1D)	2804(3)	1408(3)	2048(2)	42(2)	O(4I)	−592(5)	3347(4)	1042(4)	114(4)
C(1D)	2634(4)	1029(5)	2442(3)	39(2)	O(1J)	−410(3)	6944(3)	2543(2)	42(2)
C(2D)	2854(3)	382(4)	2568(3)	33(2)	C(1J)	−370(3)	6864(4)	2060(3)	31(2)
C(3D)	2659(4)	77(5)	2996(3)	41(2)	C(2J)	−374(4)	6226(4)	1830(3)	38(2)
C(4D)	2268(4)	433(5)	3296(4)	41(2)	C(3J)	−303(4)	6189(4)	1359(3)	41(2)
C(5D)	2028(4)	1070(5)	3149(4)	43(2)	C(4J)	−242(5)	6796(5)	1079(4)	49(3)
C(6D)	2209(4)	1394(4)	2735(4)	41(2)	C(5J)	−279(4)	7434(5)	1301(4)	47(2)
C(7D)	1942(4)	2078(4)	2591(4)	43(2)	C(6J)	−341(4)	7474(5)	1796(4)	43(2)
S(1D)	2072(1)	50(2)	3836(1)	61(1)	C(7J)	−427(4)	8188(4)	2035(4)	43(2)
O(2D)	1918(7)	−648(6)	3736(4)	151(6)	S(1J)	−96(2)	6733(1)	462(1)	68(1)
O(3D)	2576(5)	98(9)	4140(4)	170(7)	O(2J)	−355(4)	6095(4)	288(3)	79(3)
O(4D)	1577(6)	444(7)	4009(4)	156(6)	O(3J)	586(4)	6681(6)	437(4)	105(3)
O(1E)	3047(3)	2799(3)	2296(2)	42(2)	O(4J)	−313(6)	7351(4)	244(3)	103(4)
C(1E)	2739(4)	3031(4)	2669(3)	40(2)	Na(1)	4738(2)	3097(2)	4918(2)	76(1)
C(2E)	2223(4)	2699(5)	2837(4)	43(2)	Na(2)	3885(2)	6232(2)	4520(2)	69(1)
C(3E)	1963(5)	2947(5)	3261(4)	48(3)	Na(3)	−4(43)	4993(42)	−18(20)	175(3)
C(4E)	2185(5)	3539(5)	3484(4)	54(3)	*Na(4)	5000	0	5000	325(16)
C(5E)	2668(5)	3897(5)	3292(3)	47(3)	Na(6)	3671(3)	1292(4)	1402(3)	117(2)
C(6E)	2959(4)	3653(4)	2885(3)	39(2)	Na(7)	3002(5)	1346(5)	728(3)	180(4)
C(7E)	3453(4)	4066(4)	2670(4)	42(2)	Na(8)	1352(4)	5779(6)	305(3)	174(4)
S(1E)	1789(2)	3888(2)	3966(1)	80(1)	*Na(9)	−822(13)	4181(19)	5210(8)	272(14)
O(2E)	2176(4)	4297(7)	4220(4)	120(4)	*Na(10)	−1645(14)	1713(16)	6059(10)	246(12)
O(3E)	1527(9)	3297(6)	4215(5)	179(7)	*Na(11)	3540(8)	976(12)	4358(10)	195(9)
O(4E)	1280(5)	4269(7)	3774(4)	125(4)	*Na(12)	2940(19)	7641(10)	4231(10)	339(24)
O(1F)	672(3)	7777(3)	2562(2)	44(2)	*Na(13)	967(6)	2511(8)	501(4)	115(5)
C(1F)	673(4)	8396(5)	2315(4)	45(2)	*Na(14)	1112(7)	3226(8)	159(5)	133(5)
C(2F)	153(4)	8617(4)	2052(3)	37(2)	*Na(15)	662(7)	3482(7)	4813(5)	126(5)
C(3F)	188(4)	9254(5)	1823(3)	43(2)	O(1S)	5258(3)	3079(3)	5675(3)	57(2)
C(4F)	707(4)	9642(4)	1837(3)	42(2)	O(2S)	1353(4)	12142(4)	1370(3)	83(3)
C(5F)	1209(4)	9426(5)	2112(4)	46(2)	O(3S)	5879(4)	−2379(4)	3640(3)	83(3)
C(6F)	1177(4)	8792(5)	2341(4)	45(2)	O(4S)	3639(7)	6370(6)	3638(5)	139(5)
C(7F)	1736(4)	8519(4)	2621(4)	43(2)	O(5S)	1195(4)	6772(6)	1782(5)	120(4)
S(1F)	739(1)	10428(1)	1506(1)	59(1)	O(6S)	5652(4)	3708(4)	4671(3)	77(2)
O(2F)	598(6)	10256(5)	1042(4)	115(4)	O(7S)	−724(5)	5168(5)	−653(4)	109(3)
O(3F)	1351(4)	10675(4)	1548(4)	101(3)	O(8S)	−814(4)	4494(4)	403(3)	79(2)

Table 2. (Continued)

	x	*y*	*z*	*U*(eq)
O(9S)	3105(6)	5422(6)	4695(5)	133(4)
O(10S)	3788(5)	1662(7)	3102(6)	163(6)
O(11S)	4332(6)	4236(6)	4971(5)	136(4)
O(12S)	144(7)	11551(6)	585(4)	140(5)
O(13S)	2556(6)	2374(7)	1090(7)	165(6)
O(14S)	5229(7)	−752(8)	4298(5)	164(6)
*O(15S)	1486(16)	1931(28)	257(10)	259(23)
*O(16S)	3216(12)	6600(13)	3856(12)	142(11)
*O(17S)	3370(19)	8850(18)	4431(10)	200(15)
*O(18S)	2219(7)	5566(7)	4360(5)	64(4)
*O(19S)	4059(9)	3133(8)	4180(6)	79(5)
*O(20S)	2234(8)	5795(8)	3609(6)	75(5)
*O(21S)	3417(8)	7262(8)	4853(7)	90(6)
*O(22S)	1695(11)	1783(12)	4406(9)	122(9)
*O(23S)	3854(9)	2739(12)	5405(9)	106(7)
*O(24S)	2131(9)	5005(15)	150(7)	130(10)
*O(25S)	3227(9)	116(9)	635(7)	97(6)
*O(26S)	1468(12)	5701(11)	1149(9)	123(8)
*O(27S)	3853(10)	294(18)	3820(8)	159(12)
*O(28S)	−1289(9)	5440(10)	98(6)	93(6)
*O(29S)	3269(10)	2012(12)	3923(9)	121(8)
*O(30S)	1113(13)	5627(11)	4030(9)	137(9)
*O(31S)	1218(11)	7814(19)	976(10)	158(11)
*O(32S)	−482(22)	3920(15)	4447(10)	213(18)
*O(33S)	−1515(9)	3527(10)	5953(8)	107(7)
*O(34S)	−992(10)	2783(11)	5264(10)	126(8)
*O(35S)	6921(10)	1222(13)	4333(8)	119(8)
*O(36S)	1227(13)	7080(13)	3510(8)	144(12)
*O(37S)	3073(18)	3364(21)	0(14)	208(15)
*O(38S)	1960(12)	6598(14)	−137(10)	141(9)
*O(39S)	2592(14)	3233(16)	5015(11)	155(10)
*O(40S)	1798(15)	9580(18)	175(12)	180(12)
*O(41S)	2370(12)	489(14)	1019(10)	136(8)
*O(42S)	2231(13)	6681(15)	4609(10)	150(10)
*O(43S)	2297(13)	7748(15)	3687(11)	149(9)
*O(44S)	4429(12)	−126(13)	4604(10)	132(8)
*O(45S)	1268(21)	7024(26)	1087(17)	249(19)
*O(46S)	1818(13)	6078(16)	1053(11)	146(10)
*O(47S)	314(14)	4009(16)	4460(11)	158(10)
*O(48S)	−409(11)	3385(13)	4876(9)	134(8)
*O(49S)	2232(13)	1970(13)	4352(9)	133(9)
*O(50S)	2611(10)	5604(11)	3583(7)	95(6)
*O(51S)	860(13)	6565(16)	3359(10)	147(10)
*O(52S)	1908(16)	592(18)	685(13)	183(12)
*O(53S)	1716(18)	3406(20)	357(14)	189(13)
*O(54S)	3636(26)	309(33)	4830(22)	289(22)
*O(55S)	3396(13)	−577(15)	5267(10)	149(9)
*O(56S)	6067(27)	−137(34)	4966(23)	283(24)
*O(57S)	3104(28)	1458(31)	−157(21)	300(24)
*O(58S)	4009(12)	2392(13)	5328(10)	126(9)
*O(59S)	−545(18)	5546(21)	4803(15)	221(16)
*O(60S)	−1519(24)	2418(31)	5824(20)	299(24)
*O(61S)	1723(26)	3984(32)	508(22)	298(24)

[a] *U*(eq) is defined as one-third of the trace of the orthogonalized U_{ij} tensor. Atoms marked with an asterisk are of 50% site occupancy.

of **1b** does adopt a cone conformation with all the phenolic oxygen atoms in a plane,[4] calixarene **1c** and its parent sulfonic acid both exhibit a double partial cone conformation which can in no way be deemed preorganized for UO_2^{2+} binding.[8] Furthermore, we have recently shown that the mode of interaction of a number of lanthanide ions (Eu, Tb, Gd, and Yb) with **1b** is exclusively *via* the sulfonato oxygen atoms.[4] Similar results are found for a range of lanthanide and transition metal complexes of **1a**.[2d,9] In an extension to these studies we now describe our results on the interactions of *p*-sulfonatocalix[5]arene (**1b**) with transition metal ions. The X-ray crystal structure of the parent salt Na_{10}[*p*-sulfonatocalix[5]arene]$_2$·33.5H_2O is also reported.

Experimental Section

Materials. Na_5[*p*-sulfonatocalix[5]arene] was synthesized according to the method described previously.[4,10] All other reagents and materials were obtained from the usual commercial sources.

Na_{10}[*p*-sulfonatocalix[5]arene]$_2$·33.5H_2O (2). Pentasodium *p*-sulfonatocalix[5]arene **1b** (0.15 g, 0.13 mmol) was dissolved in water (1.5 cm^3) and the solution allowed to slowly evaporate over a period of *ca.* 2 weeks to give the inclusion complex **2** as colorless needles, which were characterized by X-ray crystallography (Table 1). Measurement of the pH of the mother liquor showed it to be *ca.* 2 suggesting the presence of trace amounts of H_2SO_4 remaining from the synthesis of **1b**. Anal. Calcd for $C_{35}H_{58.5}O_{36.75}Na_5S_5$: C, 31.31; H, 4.39. Found: C, 31.55; H, 4.30.

Na_8[Co(H_2O)$_4$(*p*-sulfonatocalix[5]arene)$_2$]·2$CH_3C(O)N(CH_3)_2$·37H_2O (3). To a mixture of Na_5[*p*-sulfonatocalix[5]arene] **1b** (0.15 g, 0.13 mmol) in water (1.5 cm^3) was added *N*,*N*-dimethylacetamide (39 μL, 0.42 mmol) and $Co(NO_3)_2·6H_2O$ (0.046 g, 0.16 mmol), and the mixture was allowed to stand in air for 1 week, resulting in the deposition of the crystalline inclusion compound as large pale pink plates. Yield: 0.08 g, 0.026 mmol, 40%. Anal. Calcd for $C_{78}H_{150}O_{83}CoN_2Na_8S_{10}$: C, 31.15; H, 4.99; N, 0.93. Found: C, 30.75; H, 4.75; N, 1.00. ^{1}H NMR (20 °C, 250 MHz, D_2O, δ/ppm): 7.55 (s, 20H, Ar−H), 3.87 (s, 20H, CH_2), 3.02 (s, 6H, dma), 2.87 (s, 6H, dma), 2.05 (s, 6H, dma).

Na_8[Ni(H_2O)$_4$(*p*-sulfonatocalix[5]arene)$_2$]·2NC_5H_5·38H_2O (4). To a mixture of Na_5[*p*-sulfonatocalix[5]arene] **1b** (0.15 g, 0.13 mmol) in water (1.5 cm^3) was added pyridine (13 μL, 0.16 mmol) and $Ni(NO_3)_2·6H_2O$ (0.046 g, 0.16 mmol), and the mixture was allowed to stand in air for 2 weeks, resulting in the deposition of the crystalline inclusion compound as large green plates. Yield: 0.14 g, 0.046 mmol, 71%. Anal. Calcd for $C_{80}H_{134}O_{82}N_2Na_8NiS_{10}$: C, 32.03; H, 4.50; N, 0.93. Found: C, 31.75; H, 4.05; N, 1.25. ^{1}H NMR (20 °C, 250 MHz, D_2O, δ/ppm, signals broad): 7.45 (s, 20H, Ar−H), 7.13 (s, 4H, py), 6.22 (s, 2H, py), 6.04 (s, 4H, py), 3.81 (s, 20H, CH_2).

X-ray Crystallography. All crystallographic measurements were carried out at low temperature (−150 °C for **2**, −100 °C for **3**) with a Siemens SMART diffractometer equipped with graphite monochromated Mo Kα radiation. Data sets were corrected for Lorentz and polarization effects and absorption using a pseudo-ψ-scan method based upon redundant data. Details of individual structure determinations are given in Table 1. Structures were solved using the direct methods option of SHELXS-86[11] and developed using conventional alternating cycles of least squares refinement and difference Fourier synthesis

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Table 3. Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($Å^2 \times 10^3$) for **3**

	x	*y*	*z*	*U*(eq)		*x*	*y*	*z*	*U*(eq)
*Co(1)	2062(1)	7500	6222(1)	36(1)	C(5E)	2324(2)	5796(2)	5178(3)	21(1)
*O(1)	1114(3)	7500	6408(4)	49(2)	C(6E)	2462(2)	5496(2)	5694(2)	19(1)
*O(2)	2995(3)	7500	6003(3)	49(2)	C(7E)	2012(2)	5368(2)	6249(3)	22(1)
O(3)	1918(2)	7001(1)	5473(2)	47(1)	S(1E)	2552(1)	6316(1)	4026(1)	32(1)
O(1A)	2200(2)	4906(1)	7622(2)	24(1)	O(2E)	2664(2)	6747(1)	4362(2)	41(1)
C(1A)	2150(2)	5355(2)	7587(3)	19(1)	O(3E)	2923(2)	6246(2)	3416(2)	64(2)
C(2A)	2100(2)	5588(2)	6950(3)	19(1)	O(4E)	1913(2)	6262(2)	3879(2)	51(1)
C(3A)	2079(2)	6055(2)	6990(3)	20(1)	*Na(1)	2308(1)	7500	9257(2)	31(1)
C(4A)	2103(2)	6269(2)	7621(3)	22(1)	*Na(2)	4535(1)	7500	6947(2)	36(1)
C(5A)	2127(2)	6035(2)	8258(3)	21(1)	*Na(3)	3222(2)	7500	7867(2)	47(1)
C(6A)	2144(2)	5577(2)	8246(3)	20(1)	*Na(4)	1447(3)	7500	2958(3)	87(2)
C(7A)	2127(2)	5320(2)	8930(3)	22(1)	*Na(5)	3440(3)	7500	2649(3)	107(2)
S(1A)	2024(1)	6849(1)	7660(1)	27(1)	*Na(6)	5582(2)	7500	5042(3)	87(2)
O(2A)	2236(2)	7010(1)	6970(2)	50(1)	Na(7)	494(1)	6620(1)	2926(2)	75(1)
O(3A)	1383(2)	6941(2)	7762(3)	53(1)	O(1G)	3697(2)	7002(2)	7121(3)	59(1)
O(4A)	2384(2)	7001(1)	8241(2)	42(1)	N(1G)	3731(2)	6293(2)	7503(3)	41(1)
O(1B)	3234(2)	4867(1)	8512(2)	26(1)	C(1G)	3718(3)	6591(2)	6991(4)	48(2)
C(1B)	3215(2)	5105(2)	9126(2)	21(1)	C(2G)	3709(4)	6437(3)	6244(4)	66(2)
C(2B)	2705(2)	5338(2)	9348(2)	20(1)	C(3G)	3726(3)	5818(2)	7375(4)	51(2)
C(3B)	2741(2)	5585(2)	9965(2)	22(1)	C(4G)	3748(3)	6432(2)	8248(4)	51(2)
C(4B)	3261(2)	5596(2)	10358(2)	21(1)	*O(1S)	3358(2)	7500	9134(3)	34(1)
C(5B)	3763(2)	5354(2)	10148(3)	23(1)	O(2S)	1063(2)	5945(1)	2924(2)	43(1)
C(6B)	3747(2)	5110(2)	9523(3)	21(1)	O(3S)	3995(2)	5862(2)	2925(2)	53(1)
C(7B)	4303(2)	4874(2)	9259(3)	24(1)	O(4S)	3900(2)	6805(2)	9886(3)	55(1)
S(1B)	3289(1)	5915(1)	11137(1)	25(1)	O(5S)	2270(2)	6891(1)	10093(2)	47(1)
O(2B)	3181(2)	6374(1)	10924(2)	34(1)	*O(6S)	4633(3)	7500	8209(4)	62(2)
O(3B)	2811(2)	5758(1)	11604(2)	30(1)	*O(7S)	2468(3)	7500	3461(4)	60(2)
O(4B)	3885(2)	5852(1)	11436(2)	34(1)	O(8S)	1607(2)	6038(2)	11630(3)	87(2)
O(1C)	4765(2)	4691(1)	7791(2)	28(1)	O(9S)	4901(3)	6451(3)	3092(3)	104(2)
C(1C)	4914(2)	5071(2)	8143(3)	24(1)	O(10S)	1100(2)	6952(2)	3803(3)	73(2)
C(2C)	4699(2)	5182(2)	8822(3)	21(1)	*O(11S)	1267(3)	7500	9070(5)	70(2)
C(3C)	4871(2)	5588(2)	9096(3)	23(1)	*O(12S)	4451(4)	7500	10527(6)	99(3)
C(4C)	5238(2)	5880(2)	8736(3)	25(1)	*O(13S)	647(4)	7500	4865(5)	86(3)
C(5C)	5469(2)	5757(2)	8071(3)	28(1)	*O(14S)	2998(7)	6868(4)	2212(7)	67(4)
C(6C)	5310(2)	5354(2)	7782(3)	21(1)	O(15S)	5122(3)	6859(2)	6872(4)	94(2)
C(7C)	5578(2)	5212(2)	7075(2)	25(1)	*O(16S)	1346(9)	6933(7)	2268(12)	110(8)
S(1C)	5428(1)	6396(1)	9110(1)	30(1)	O(17S)	−175(4)	6473(4)	3708(5)	135(3)
O(2C)	5026(2)	6456(1)	9700(2)	45(1)	†O(18S)	1394(6)	7500	874(7)	55(4)
O(3C)	6052(2)	6369(1)	9324(2)	41(1)	†O(19S)	1329(6)	2500	9768(7)	97(7)
O(4C)	5330(2)	6723(1)	8551(2)	50(1)	†O(20S)	380(40)	7500	2517(37)	343(56)
O(1D)	4457(2)	4893(1)	6420(2)	28(1)	*O(21S)	1113(4)	3020(4)	8449(8)	96(5)
C(1D)	4774(2)	5231(2)	6108(3)	22(1)	†O(22S)	2683(14)	7500	2310(7)	101(8)
C(2D)	5285(2)	5418(2)	6423(3)	23(1)	†O(23S)	2078(14)	7500	1170(9)	134(11)
C(3D)	5565(2)	5769(2)	6078(3)	24(1)	*O(24S)	57(7)	7278(5)	1005(7)	115(5)
C(4D)	5357(2)	5920(2)	5432(3)	24(1)	†O(25S)	4318(11)	7319(11)	1874(11)	116(17)
C(5D)	4865(2)	5719(2)	5114(3)	25(1)	†O(26S)	−7(11)	6142(9)	3907(11)	67(7)
C(6D)	4569(2)	5375(2)	5451(3)	23(1)	†O(27S)	2634(16)	6745(9)	2228(12)	82(9)
C(7D)	4042(2)	5149(2)	5088(3)	23(1)	†O(28S)	952(15)	7500	8106(15)	165(11)
S(1D)	5743(1)	6348(1)	5000(1)	33(1)	*O(29S)	1662(11)	6962(6)	2046(8)	123(9)
O(2D)	6363(2)	6258(2)	5067(4)	112(3)	*O(30S)	4628(6)	7365(4)	5697(6)	93(5)
O(3D)	5586(3)	6742(2)	5351(4)	113(3)	‡O(31S)	5860(42)	7500	3959(27)	175(33)
O(4D)	5564(4)	6351(3)	4289(3)	133(4)	†O(32S)	2139(13)	7500	2411(20)	160(13)
O(1E)	3152(2)	5016(1)	6230(2)	26(1)	†O(33S)	405(7)	7371(7)	2492(10)	36(6)
C(1E)	3037(2)	5301(2)	5692(2)	20(1)	†O(34S)	4230(31)	7229(18)	3012(39)	329(45)
C(2E)	3454(2)	5396(2)	5152(2)	19(1)	‡O(35S)	−82(43)	2500	1464(54)	285(44)
C(3E)	3297(2)	5709(2)	4649(3)	23(1)	‡O(36S)	3986(22)	6954(17)	4530(18)	95(19)
C(4E)	2737(2)	5913(2)	4662(3)	23(1)	‡O(37S)	137(34)	7500	3024(36)	172(30)

[a] *U*(eq) is defined as one-third of the trace of the orthogonalized U_{ij} tensor. * = 50% occupancy, † = 25%, ‡ = 12.5%

(SHELXL-93[12]). In all cases, non-hydrogen atoms were refined anisotropically except some disordered lattice water, while hydrogen atoms were placed in idealized positions, assigned an isotropic displacement factor based upon that of the atom to which they were attached, and refined using a riding model. All calculations were carried out on an IBM-PC compatible personal computer. Positional parameters are given in Tables 2 and 3, while selected bond lengths and angles are given in Tables 4 and 5.

Results and Discussion

Structure and Properties of Na_{10}[*p*-sulfonatocalix[5]arene]$_2 \cdot 33.5H_2O$. The previously reported X-ray crystal structure of the salt Na_7[*p*-sulfonatocalix[5]arene-2*H*]$\cdot 18H_2O$ (**5**)[4] demonstrates the deep inclusion of a single molecule of water within the large calix[5]arene cavity, engaging in weak hydrogen-bonding interactions with the phenolic oxygen atoms ($O_{solv} \cdots O_{phen}$ 3.27 and 3.32 Å), as well as forming stronger hydrogen bonds to two additional molecules of water situated at the upper rim of the cavity ($O_{solv} \cdots O_{solv}$ 2.89 and 2.95 Å). Potentiometric determination of the pK_a values for the phenolic functionalities indicate that *p*-sulfonatocalix[5]arene possesses three ionizable phenolic protons (pK_a values 10.96(8), 7.63(5), and 4.31(1); log β_{11} 4.31, log β_{12} 11.94, log β_{13} 22.90).[4] Hence, crystallization of **1b** by slow evaporation of an aqueous solution of the compound at a pH of *ca.* 2 gave the solvate Na_{10}[*p*-sulfonatocalix-

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Table 4. Selected Bond Lengths and Angles for Complex **2**

O(1A)−C(1A)	1.383(12)	C(2B)−C(3B)	1.34(2)	C(4C)−S(1C)	1.755(11)	C(7D)−C(2E)	1.49(2)
C(1A)−C(6A)	1.360(14)	C(3B)−C(4B)	1.39(2)	C(5C)−C(6C)	1.38(2)	S(1D)−O(3D)	1.379(14)
C(1A)−C(2A)	1.42(2)	C(4B)−C(5B)	1.33(2)	C(6C)−C(7C)	1.537(14)	S(1D)−O(2D)	1.40(2)
C(2A)−C(3A)	1.39(2)	C(4B)−S(1B)	1.771(13)	C(7C)−C(2D)	1.50(2)	S(1D)−O(4D)	1.423(13)
C(2A)−C(7E)	1.49(2)	C(5B)−C(6B)	1.37(2)	S(1C)−O(3C)	1.431(11)	O(1E)−C(1E)	1.333(13)
C(3A)−C(4A)	1.38(2)	C(6B)−C(7B)	1.521(14)	S(1C)−O(2C)	1.432(11)	C(1E)−C(2E)	1.40(2)
C(4A)−C(5A)	1.38(2)	C(7B)−C(2C)	1.499(14)	S(1C)−O(4C)	1.467(10)	C(1E)−C(6E)	1.41(2)
C(4A)−S(1A)	1.753(10)	S(1B)−O(2B)	1.35(2)	O(1D)−C(1D)	1.374(14)	C(2E)−C(3E)	1.41(2)
C(5A)−C(6A)	1.353(14)	S(1B)−O(3B)	1.41(3)	C(1D)−C(2D)	1.370(14)	C(3E)−C(4E)	1.37(2)
C(6A)−C(7A)	1.534(14)	S(1B)−O(4B)	1.49(3)	C(1D)−C(6D)	1.44(2)	C(4E)−C(5E)	1.39(2)
C(7A)−C(2B)	1.54(2)	O(1C)−C(1C)	1.361(12)	C(2D)−C(3D)	1.40(2)	C(4E)−S(1E)	1.754(14)
S(1A)−O(3A)	1.402(11)	C(1C)−C(6C)	1.369(14)	C(3D)−C(4D)	1.40(2)	C(5E)−C(6E)	1.40(2)
S(1A)−O(2A)	1.442(9)	C(1C)−C(2C)	1.42(2)	C(4D)−C(5D)	1.38(2)	C(6E)−C(7E)	1.49(2)
S(1A)−O(4A)	1.450(9)	C(2C)−C(3C)	1.36(2)	C(4D)−S(1D)	1.736(12)	S(1E)−O(2E)	1.343(13)
O(1B)−C(1B)	1.346(13)	C(3C)−C(4C)	1.38(2)	C(5D)−C(6D)	1.38(2)	S(1E)−O(4E)	1.43(2)
C(1B)−C(6B)	1.40(2)	C(4C)−C(5C)	1.39(2)	C(6D)−C(7D)	1.482(14)	S(1E)−O(3E)	1.45(2)
C(1B)−C(2B)	1.42(2)						

C(6A)−C(1A)−O(1A)	117.7(9)	C(2B)−C(3B)−C(4B)	120.0(10)	C(1C)−C(6C)−C(5C)	119.2(10)	O(3D)−S(1D)−O(4D)	111.7(14)
C(6A)−C(1A)−C(2A)	121.6(9)	C(5B)−C(4B)−C(3B)	121.0(11)	C(1C)−C(6C)−C(7C)	120.5(9)	O(2D)−S(1D)−O(4D)	112.7(13)
O(1A)−C(1A)−C(2A)	120.7(9)	C(5B)−C(4B)−S(1B)	120.3(10)	C(5C)−C(6C)−C(7C)	120.0(9)	O(3D)−S(1D)−C(4D)	106.4(7)
C(3A)−C(2A)−C(1A)	116.5(10)	C(3B)−C(4B)−S(1B)	118.6(9)	C(2D)−C(7C)−C(6C)	111.0(9)	O(2D)−S(1D)−C(4D)	107.3(7)
C(3A)−C(2A)−C(7E)	121.6(9)	C(4B)−C(5B)−C(6B)	121.7(11)	O(3C)−S(1C)−O(2C)	114.5(7)	O(4D)−S(1D)−C(4D)	106.5(7)
C(1A)−C(2A)−C(7E)	121.7(9)	C(5B)−C(6B)−C(1B)	118.2(9)	O(3C)−S(1C)−O(4C)	112.2(7)	O(1E)−C(1E)−C(2E)	123.3(10)
C(4A)−C(3A)−C(2A)	121.1(10)	C(5B)−C(6B)−C(7B)	121.2(9)	O(2C)−S(1C)−O(4C)	109.9(6)	O(1E)−C(1E)−C(6E)	115.7(10)
C(3A)−C(4A)−C(5A)	120.1(9)	C(1B)−C(6B)−C(7B)	120.4(10)	O(3C)−S(1C)−C(4C)	106.9(5)	C(2E)−C(1E)−C(6E)	121.0(11)
C(3A)−C(4A)−S(1A)	118.1(8)	C(2C)−C(7B)−C(6B)	112.8(9)	O(2C)−S(1C)−C(4C)	106.5(5)	C(1E)−C(2E)−C(3E)	119.0(11)
C(5A)−C(4A)−S(1A)	121.9(9)	O(2B)−S(1B)−O(3B)	113(2)	O(4C)−S(1C)−C(4C)	106.3(5)	C(1E)−C(2E)−C(7D)	122.7(11)
C(6A)−C(5A)−C(4A)	120.5(10)	O(2B)−S(1B)−O(4B)	115(2)	O(1D)−C(1D)−C(2D)	125.3(10)	C(3E)−C(2E)−C(7D)	118.3(10)
C(5A)−C(6A)−C(1A)	120.2(9)	O(3B)−S(1B)−O(4B)	104(3)	O(1D)−C(1D)−C(6D)	113.1(9)	C(4E)−C(3E)−C(2E)	120.3(12)
C(5A)−C(6A)−C(7A)	120.5(9)	O(2B)−S(1B)−C(4B)	110.5(10)	C(2D)−C(1D)−C(6D)	121.6(11)	C(3E)−C(4E)−C(5E)	120.1(12)
C(1A)−C(6A)−C(7A)	119.0(9)	O(3B)−S(1B)−C(4B)	109(2)	C(1D)−C(2D)−C(3D)	118.5(10)	C(3E)−C(4E)−S(1E)	118.6(11)
C(6A)−C(7A)−C(2B)	113.4(8)	O(4B)−S(1B)−C(4B)	105.1(11)	C(1D)−C(2D)−C(7C)	122.4(10)	C(5E)−C(4E)−S(1E)	120.8(9)
O(3A)−S(1A)−O(2A)	111.7(8)	O(1C)−C(1C)−C(6C)	116.7(9)	C(3D)−C(2D)−C(7C)	118.9(9)	C(4E)−C(5E)−C(6E)	121.6(11)
O(3A)−S(1A)−O(4A)	113.4(7)	O(1C)−C(1C)−C(2C)	121.8(9)	C(4D)−C(3D)−C(2D)	121.0(10)	C(5E)−C(6E)−C(1E)	117.6(11)
O(2A)−S(1A)−O(4A)	110.7(6)	C(6C)−C(1C)−C(2C)	121.5(9)	C(5D)−C(4D)−C(3D)	119.4(11)	C(5E)−C(6E)−C(7E)	120.6(10)
O(3A)−S(1A)−C(4A)	106.9(5)	C(3C)−C(2C)−C(1C)	117.3(9)	C(5D)−C(4D)−S(1D)	121.6(9)	C(1E)−C(6E)−C(7E)	121.6(10)
O(2A)−S(1A)−C(4A)	106.3(5)	C(3C)−C(2C)−C(7B)	121.5(10)	C(3D)−C(4D)−S(1D)	119.0(9)	C(6E)−C(7E)−C(2A)	113.5(9)
O(4A)−S(1A)−C(4A)	107.3(5)	C(1C)−C(2C)−C(7B)	121.2(9)	C(6D)−C(5D)−C(4D)	121.7(10)	O(2E)−S(1E)−O(4E)	112.3(10)
O(1B)−C(1B)−C(6B)	115.8(9)	C(2C)−C(3C)−C(4C)	122.6(11)	C(5D)−C(6D)−C(1D)	117.7(10)	O(2E)−S(1E)−O(3E)	117.3(12)
O(1B)−C(1B)−C(2B)	124.7(10)	C(3C)−C(4C)−C(5C)	118.7(10)	C(5D)−C(6D)−C(7D)	119.9(10)	O(4E)−S(1E)−O(3E)	104.8(13)
C(6B)−C(1B)−C(2B)	119.5(10)	C(3C)−C(4C)−S(1C)	120.0(9)	C(1D)−C(6D)−C(7D)	122.3(11)	O(2E)−S(1E)−C(4E)	107.4(7)
C(3B)−C(2B)−C(1B)	119.3(10)	C(5C)−C(4C)−S(1C)	121.3(8)	C(6D)−C(7D)−C(2E)	114.9(9)	O(4E)−S(1E)−C(4E)	108.3(7)
C(3B)−C(2B)−C(7A)	121.0(9)	C(6C)−C(5C)−C(4C)	120.7(9)	O(3D)−S(1D)−O(2D)	111.8(14)	O(3E)−S(1E)−C(4E)	106.4(7)
C(1B)−C(2B)−C(7A)	119.6(10)						

Table 5. Selected Bond Lengths and Angles for Complex **3**

Co(1)−O(2A)#1	2.079(4)	Co(1)−O(1)	2.136(6)
Co(1)−O(2A)	2.079(4)	O(1G)−C(1G)	1.264(8)
Co(1)−O(3)	2.089(4)	N(1G)−C(1G)	1.320(9)
Co(1)−O(3)#1	2.089(4)	N(1G)−C(3G)	1.452(8)
Co(1)−O(2)	2.114(6)	N(1G)−C(4G)	1.466(8)
		C(1G)−C(2G)	1.483(10)

O(2A)#1−Co(1)−O(2A)	90.6(3)	O(2A)−Co(1)−O(1)	94.1(2)
O(2A)#1−Co(1)−O(3)	178.0(2)	O(3)−Co(1)−O(1)	87.7(2)
O(2A)−Co(1)−O(3)	88.5(2)	O(3)#1−Co(1)−O(1)	87.7(2)
O(2A)#1−Co(1)−O(3)#1	88.5(2)	O(2)−Co(1)−O(1)	178.2(3)
O(2A)−Co(1)−O(3)#1	178.0(2)	C(1G)−N(1G)−C(3G)	123.4(6)
O(3)−Co(1)−O(3)#1	92.2(3)	C(1G)−N(1G)−C(4G)	120.3(5)
O(2A)#1−Co(1)−O(2)	87.1(2)	C(3G)−N(1G)−C(4G)	116.3(6)
O(2A)−Co(1)−O(2)	87.1(2)	O(1G)−C(1G)−N(1G)	121.8(6)
O(3)−Co(1)−O(2)	91.1(2)	O(1G)−C(1G)−C(2G)	119.3(7)
O(3)#1−Co(1)−O(2)	91.1(2)	N(1G)−C(1G)−C(2G)	118.8(6)
O(2A)#1−Co(1)−O(1)	94.1(2)		

[a] Symmetry transformations used to generate equivalent atoms: #1 $x,-y+3/2,z$.

[5]arene]$_2$·33.5H_2O (**2**) in which all the phenolic protons are retained. The X-ray crystal structure of complex **2** (Figure 1) incorporates two independent *p*-sulfonatocalix[5]arene^{5-} anions within the crystallographic asymmetric unit. Unfortunately the crystallographic *R* factor is rather high for this determination, as a consequence of significant disorder of the lattice water molecules and sodium ions and the extreme propensity of the crystals to desolvate. The gross structural features are well defined, however, and structural comparisons are both possible and useful. As with **5**, in both of the *p*-sulfonatocalix[5]arene anions in **2** (**2a**, calixarene aromatic rings A−E; **2b**, rings F−J), the plane of two of the calixarene aromatic rings (A and C in **2a**; F and I in **2b**) are significantly "flattened" with respect to the plane containing the phenolic oxygen atoms; interplanar angles 33.3(4)° (average for **2a**) and 32.8(4)° (average for **2b**). This compares to the analogous value for **5** of 27.8(3)° implying a more upright conformation for the 5− anions in **2** (for comparison, the remaining rings of **2a** and **2b** are inclined at average angles of 71.8(4)° and 70.7(4)°, respectively, with respect to the planes containing O(1A)−O(1E) and O(1F)−O(1J), *cf.* 69.8(4)° for **5**). The reason for this conformational difference may be traced to the nature of the inter-oxygen hydrogen bonding at the lower rim of the calixarenes in **2** and **5**. In the case of **5**, three short hydrogen bonds are formed (2.49−2.64 Å) along with interactions to two sodium ions and two extracavity water molecules (O···Na 2.37(2) Å average, O···O$_{solv}$ 2.65(3), 2.90(3) Å). In contrast, in both **2a** and **2b**, the hydrogen bonding at the lower rim of the calixarene is apparently *weaker* with three relatively short inter-oxygen separations of 2.83(2) Å (average) for **2a** and 2.75(2) Å (average) for **2b**, and two longer ones (*ca.* 3.5 Å). The reason for this is apparent in the formation of a number of *intermolecular* hydrogen bonds to the sulfonato oxygen atoms of neighboring calixarenes. Also, as with **5**, the molecular cavity is primarily occupied by a single molecule of water which, unlike Na_4[*p*-sulfonatocalix[4]arene]·13.5H_2O (**6**),[3a] does not engage in OH···π-aromatic hydrogen bonding but forms long

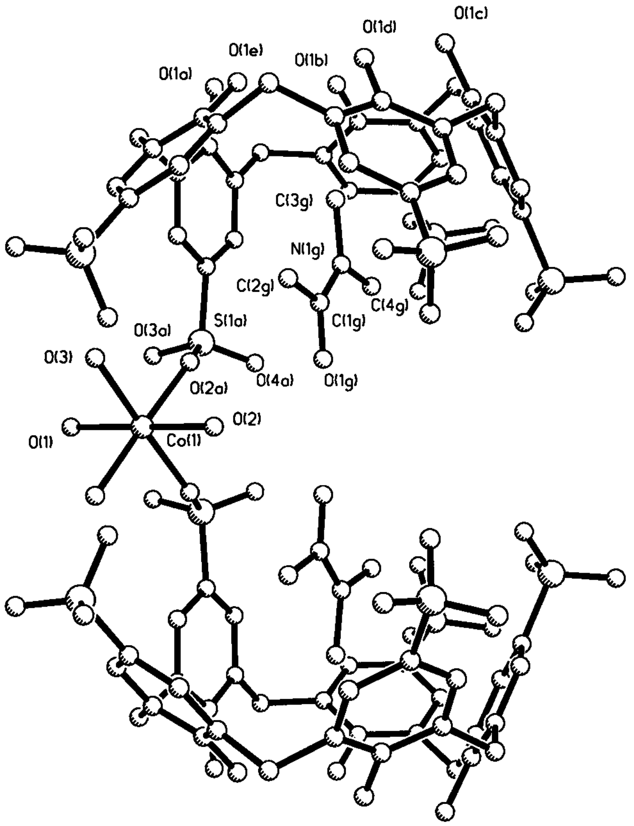

Figure 3. The cobalt-bridged bis(calixarene) moiety in **3** showing the dma guest molecules.

hydrogen bonds to the phenolic oxygen atoms of the flattened rings. Interestingly, because of the more upright conformation in **2a** and **2b**, the guest water molecules penetrate more deeply into the cavity than in **5** with O(10S)···O(1A) and O(1C) distances of 3.05(2) and 3.09(2) Å for **2a** and O(5S)···O(1F), O(1I) 3.14(2) and 3.23(2) Å (**2b**), *cf.* 3.27(2) and 3.32(2) Å for **5**. The upper rim of the cavity in the case of **2a** and **2b** is occupied by a total of three additional waters which link the guest solvent molecules to the hydrophilic portion of the structure *via* an extensive hydrogen-bonded network of molecules (*cf.* two additional water guest molecules for **5** as a consequence of the shallower penetration of the most deeply included water).

As with **5** and most other *p*-sulfonatocalix[n]arene salts structurally characterized to date,[2,4] the crystal packing in **2** is organized into alternating hydrophilic and hydrophobic layers along the crystallographic *c* axis (Figure 2) in a fashion resembling that of clay minerals.[2a] The interlayer separation is on the order of 13.9 Å, with hydrophilic and hydrophobic layers 8.7 and 5.2 Å wide, respectively. Interestingly, the hydrophilic layer in **5** is almost identical in width to that in **2** (8.6 Å) but the hydrophobic layer is more narrow (4.4 Å). This arises as a consequence of the different orientations of calixarenes **2a** and **2b** (**2b** is inclined by 6.8° with respect to **2a**), resulting in an enlarged hydrophobic layer.

Reactions with Transition Metal Salts

A number of attempts were made to react calixarene **1b** with transition metal salts of Cr(III), Cu(II), Zn(II), Co(II), and Ni(II) in aqueous solution in the presence of coligands such as pyridine (py), pyridine-*N*-oxide (py-*N*-O), and *N*,*N*-dimethylacetamide (dma) which might match the dimensions of the calix[5]arene hydrophobic cavity. In many cases products were found to precipitate as amorphous powders of varying composition or, in the case of Zn(II), as separate crystals of metal salt

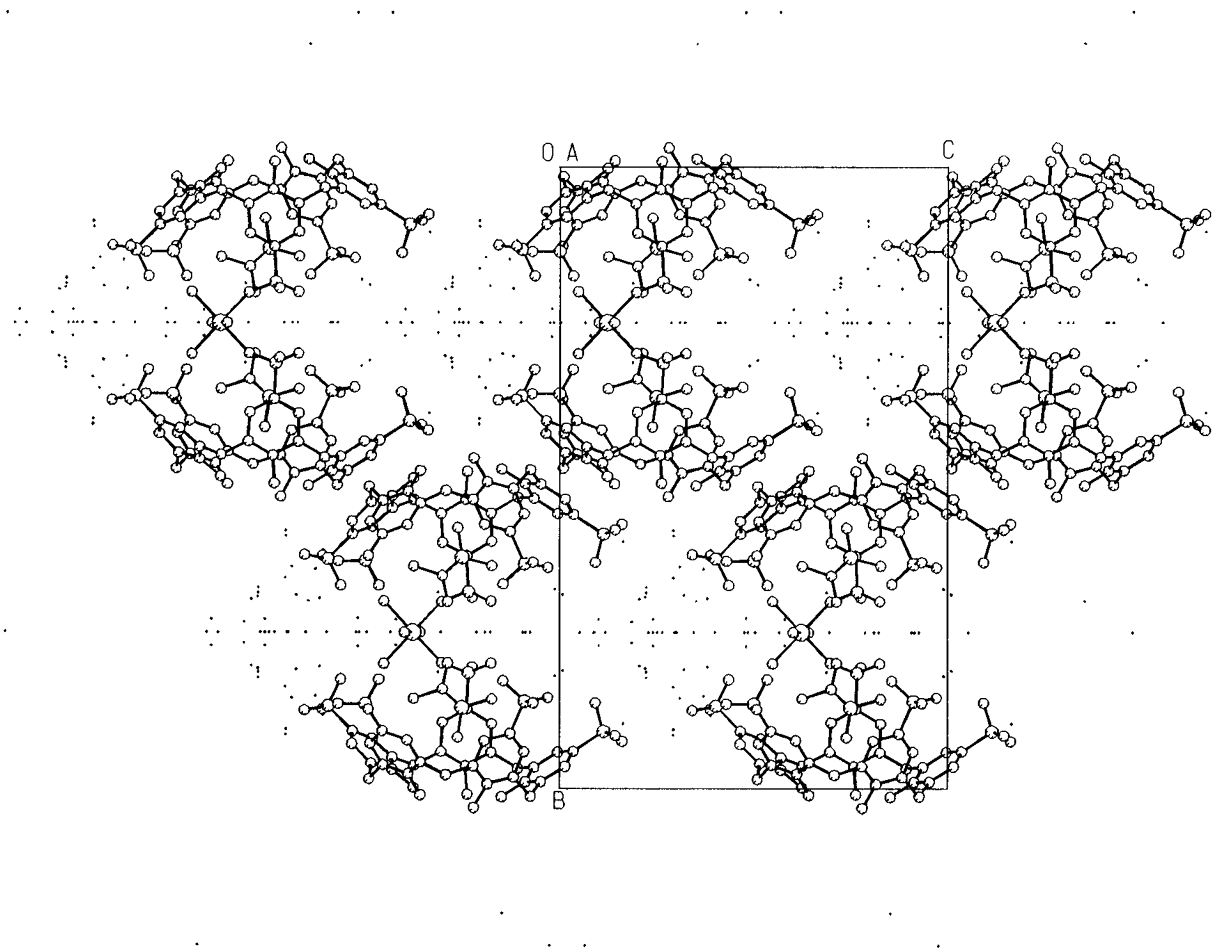

Figure 4. Crystal packing in **3** viewed along the *a* axis, showing the bilayer packing arrangement.

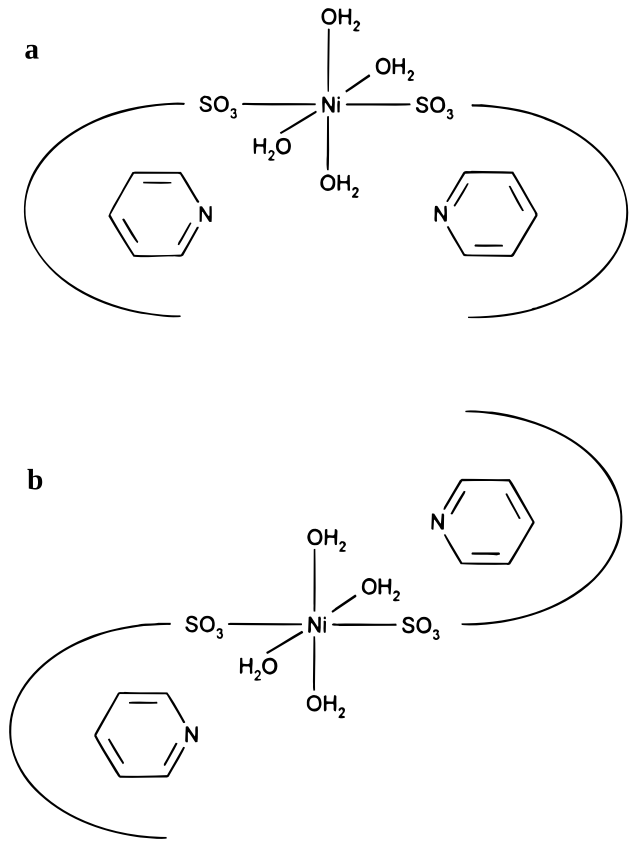

Figure 5. Schematic representations of possible structures for the Ni(II) complex $Na_8[Ni(H_2O)_4$(*p*-sulfonatocalix[5]arene$)_2]\cdot 2NC_5H_5\cdot 38H_2O$ (**4**).

and a calixarene/py-*N*-O 1:1 inclusion complex.[4] However, reproducible results were obtained for Co(II) and Ni(II) in the presence of dma and py, respectively.

Reaction of $Co(NO_3)_2\cdot 6H_2O$ with **1b** in the presence of dma resulted in the deposition of pale pink plates of the cobalt-bridged bis(calixarene) complex $Na_8[Co(H_2O)_4$(*p*-sulfonatocalix[5]arene$)_2]\cdot 2CH_3C(O)N(CH_3)_2\cdot 37H_2O$ (**3**) which was characterized by X-ray crystallography. The structure determination reveals a face-to-face orientation of pairs of calixarene ligands, resulting in the formation of a large “supercavity”, hinged on one side by a “$Co(H_2O)_4{}^{2+}$” moiety incorporating an octahedral Co(II) center situated on a crystallographic mirror plane, Figure 3. The Co−O distances of 2.079(4)−2.136(4) Å are typical.[13] Each calixarene is occupied by a dma guest molecule with the *N*-methyl group C(3G) penetrating most deeply into the cavity (the distance from C(3G) to the O(1A)−O(1E) plane is 2.86 Å, *cf.* 2.20 and 2.38 Å for O(10S) and O(5S) in **2a** and **2b**, respectively). The dma guest does not act as a ligand to the Co(II) center but bridges between two Na^+ ions; O(1G)···Na(2) 2.416(5), Na(3) 2.314(5) Å. The sodium and cobalt ions, as well as a large amount of enclathrated water, form part of an extensive hydrophilic layer which runs between the calixarenes, which adopt a similar bilayer arrangement as that seen for **2**, Figure 4. The total interlayer separation is larger than that for **2** (15.1 Å) as a consequence of the presence of the bridging metal ion (*cf.* 15.2−15.5 Å for related lanthanide element bridged complexes[4]), with hydrophilic and hydrophobic layers 9.5 and 5.6 Å wide, respectively.

The calixarene conformation in **3** is somewhat different to that observed in **2** and **5**, with a markedly more upright arrangement as a consequence of the presence of the bulky dma guest and intermolecular hydrogen-bonding interactions from the phenolic oxygen atoms of the calixarene to solvent water molecules (interplane angles: O(1A)−O(1E)···C(1B)−C(6B) 41.5°, C(1E)−C(6E) 33.2°, remaining carbocyclic rings 68.6° on average). Similar conformational changes were noted upon the introduction of a py-*N*-O guest in Na_5[*p*-sulfonatocalix[5]arene]·py-*N*-O·$8.5H_2O$ (**7**).[4]

Complex **3** was also examined by ^1H NMR spectroscopy which confirmed the presence of a 1:1 ratio of calixarene:dma. The three singlet dma resonances occur at the same chemical shift values found for the free ligand, suggesting that the dma is not strongly associated with either the calixarene or the metal center in solution. Only two resonances are observed for the protons of the calixarene suggesting decomplexation of the metal center in solution.

Reaction of **1b** with $Ni(NO_3)_2\cdot 6H_2O$ in a similar way as for **3** resulted in the formation of the closely related, pale green Ni(II) complex $Na_8[Ni(H_2O)_4$(*p*-sulfonatocalix[5]arene$)_2]\cdot 2NC_5H_5\cdot 38H_2O$ (**4**). While we were unable to obtain a strongly diffracting crystalline sample of this compound, measurement of the unit cell parameters (Table 1) along with the similarity of its composition (analytical and NMR data) strongly suggests that it is identical in structure to **3** with an octahedral Ni(II) ion bridging between two calixarene ligands *via* the sulfonato oxygen atoms, with an uncoordinated pyridine molecule in the cavity of each calixarene. The available data are insufficient to distinguish between the two possible calixarene orientations (a and b) shown in Figure 5, however, and it is noteworthy that the Gd complex $Na_7[Gd(H_2O)_6$(*p*-sulfonatocalix[5]arene)]·2py-*N*-O·$34H_2O$ adopts a structure of type b.[4] The 1:1 calixarene:py ratio in complex **4** was confirmed by ^1H NMR spectroscopy, although the broadness of the lines, coupled with the fact that only two resonances assigned to the calixarene ligands are observed (δ 7.45 and 3.81 ppm), suggests that the complex is undergoing a fluxional process in solution at room temperature involving decomplexation of the metal center. Interestingly, the resonances assigned to the pyridine guest molecules in **4** occur at significantly higher field than the free ligand in D_2O solution (7.13, 6.22, and 6.04 ppm *vs* 8.45, 7.80, and 7.37 ppm) suggesting that the pyridine guest is much more strongly held within the calixarene than the dma ligand in **3**, possibly as a result of a better size match between pyridine and the large calix[5]arene cavity. The low solubility of complex **4** in solvents other than water meant that no low-temperature NMR experiments could be undertaken.

Conclusions

This study has established a very similar binding mode for transition metal ion complexes of **1b** to that observed in related lanthanide species.[4] Binding does not occur *via* the phenolic oxygen atoms, and the low affinity noted by Shinkai *et al.* of **1b** for metal ions such as Ni(II) may readily be explained by the unidentate nature of the coordination and the relatively poor donor ability of the sulfonate functionalities.[1j,5] The fact that better donors such as dma and pyridine do not coordinate to the metal center in complexes such as **3** may well be a consequence of the dominance of crystal packing forces in molecular self-assembly, as noted in the case of the related lanthanide complexes.[4] Noteworthy is the ligation of Ni(II) by pyridine, although not by the calixarene, in the related *p*-sulfonatocalix[4]arene complex Na[*p*-sulfonatocalix[4]arene]·$[Ni(H_2O)_5(NC_5H_5)]_2\cdot 3.5H_2O$,[1g] highlighting the ability of the metal center to adjust its ligand sphere in the presence of closely related calixarenes, to maximize crystal packing interactions in the solid state. In comparison, the Cu(II) center in $Na_3[Cu(H_2O)_3(NC_5H_5)_2$(*p*-sulfonatocalix[4]arene)]·$13H_2O$[1i] is ligated both by pyridine and the calixarene.

In the case of **1b** the calixarene conformation is also highly

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[13] Orpen, A. G.; Brammer, L.; Allen, F. H.; Kennard, O.; Watson D. G.; Taylor, R. *J. Chem. Soc., Dalton Trans.* **1989**, S1.

mobile and varies according to the steric and electronic needs of the guest. In no case, however, is any evidence for OH$\cdots\pi$-aromatic hydrogen bonding by included water observed. This contrasts to the calix[4]arene complex **6** and presumably arises as a consequence of the large size of the calix[5]arene cavity.

Acknowledgment. We are grateful for sponsorship by the National Science Foundation.

Supporting Information Available: Crystallographic summary for **2** and **3** including tables of crystal data and structure refinement, atomic coordinates and equivalent isotropic displacement parameters, bond lengths and angles, anisotropic displacement parameters, and hydrogen atom coordinates and isotropic displacement parameters (31 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, can be ordered from the ACS, and can be downloaded from the Internet; see any current masthead page for ordering information and Internet access instructions.

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