

Calixarenes as Second-Sphere Ligands for Transition Metal Ions. Synthesis and Crystal Structure of $[(\text{H}_2\text{O})_5\text{Ni}(\text{NC}_5\text{H}_5)_2](\text{Na})[\text{calix}[4]\text{arene sulfonate}] \cdot 3.5 \text{H}_2\text{O}$ and $[(\text{H}_2\text{O})_4\text{Cu}(\text{NC}_5\text{H}_5)_2](\text{H}_3\text{O})_3[\text{calix}[4]\text{arene sulfonate}] \cdot 10 \text{H}_2\text{O}$

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(Received: 13 January 1992; in final form: 20 March 1992).

Abstract. The title compounds crystallize such that bilayers of calixarenes are separated by hydrophilic layers. In each case the transition metal has, in addition to a primary sphere of ligands, a second-sphere coordination by a calixarene. $[(\text{H}_2\text{O})_5\text{Ni}(\text{NC}_5\text{H}_5)_2](\text{Na})[\text{calix}[4]\text{arene sulfonate}] \cdot 3.5 \text{H}_2\text{O}$, **1**, crystallizes in the triclinic space group $P\bar{1}$ with $a = 12.487(4)$, $b = 14.281(2)$, $c = 15.055(5)$ Å, $\alpha = 85.66(2)$, $\beta = 80.07(2)$, $\gamma = 80.48(2)^\circ$, and $D_c = 1.64 \text{ g cm}^{-3}$ for $Z = 2$. Refinement based on 2441 observed reflections led to a final R value of 0.066. There are two different environments for the nickel-containing cations: one is positioned within the hydrophilic layer with the pyridine ligand intercalated into the hydrophobic calixarene bilayer and the other is also positioned within the hydrophilic layer, but the pyridine ligand is inserted into the hydrophobic cavity of the calix[4]arene. $[(\text{H}_2\text{O})_4\text{Cu}(\text{NC}_5\text{H}_5)_2](\text{H}_3\text{O})_3[\text{calix}[4]\text{arene sulfonate}] \cdot 10 \text{H}_2\text{O}$, **2**, crystallizes in the triclinic space group $P\bar{1}$ with $a = 15.438(4)$, $b = 15.727(6)$, $c = 12.121(9)$ Å, $\alpha = 112.74(4)$, $\beta = 102.02(4)$, $\gamma = 85.34(4)^\circ$, and $D_c = 1.57 \text{ g cm}^{-3}$ for $Z = 2$. Refinement based on 3925 observed reflections led to a final R value of 0.107. The structure is similar to that of **1** except that the one copper-containing cation spans the hydrophilic layer and is intercalated into the bilayer of calixarenes on one side and positioned into the calixarene cavity on the other.

Key words. Calix[4]arene, crystal structure, second-sphere coordination, nickel(II), copper(II), pyridine.

1. Introduction

Second-sphere coordination, according to Stoddart [1], is the 'non-covalent bonding of chemical entities to the first coordination sphere of a transition metal complex'. Crown ethers [2, 3] and cyclodextrins [1, 4–10] have been used as second sphere ligands, but thus far only one report of the use of calixarenes has appeared [11]. In this contribution, the synthesis and structural characterization of $[(\text{H}_2\text{O})_5\text{Ni}(\text{NC}_5\text{H}_5)_2](\text{Na})[\text{calix}[4]\text{arene sulfonate}] \cdot 3.5 \text{H}_2\text{O}$, **1**, and $[(\text{H}_2\text{O})_4\text{Cu}(\text{NC}_5\text{H}_5)_2](\text{H}_3\text{O})_3[\text{calix}[4]\text{arene sulfonate}] \cdot 10 \text{H}_2\text{O}$, **2**, are described.

2. Experimental

$\text{Na}_5[\text{calix}[4]\text{arene sulfonate}]$ was prepared using a modification of the method of Shinkai [12].

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The nickel complex, **1**, was prepared by dissolving three equivalents of $\text{Ni}(\text{NC}_5\text{H}_5)_3(\text{NO}_3)_2$ [13, 14] in deionized water to which one equivalent of $\text{Na}_5[\text{calix}[4]\text{arene sulfonate}]$ [15] had been added. The $\text{Ni}(\text{NC}_5\text{H}_5)_3(\text{NO}_3)_2$ complex yielded $[(\text{H}_2\text{O})_5\text{Ni}(\text{NC}_5\text{H}_5)]^{2+}$ upon hydrolysis, and the pale blue solution afforded pale blue crystals of **1** upon slow evaporation in a vacuum desiccator.

Crystals of **1** grow as long, flat needles from solution. The light blue compound quickly decomposes via loss of H_2O , so the crystals were mounted in thin-walled capillaries with a drop of mother liquor. Details of usual procedures in our laboratory have been given previously [16]. A summary of data collection parameters and crystal data is presented in Table I. The structure was solved using SHELX-86. The Ni, S, N, and O atoms were treated with anisotropic thermal parameters, while all C atoms and the Na atoms were refined with isotropic thermal parameters. The crystal did not diffract well: only 2441 observed reflections were obtained out of 4955 measured, and there was no observed data beyond 2θ of 40° (Mo $K\alpha$ radiation). Hydrogen atoms on the pyridine ligands and on the calixarene were placed in calculated positions and were not refined. One of the water molecules bonded to a Ni atom was disordered (80:20). Of the non-coordinated water molecules, W(11) was 100% occupied, but W(12), 25%, and W(13)–(16), 75%, were disordered. Occupancy factors were initially assigned by observation of the thermal parameters and finally by refinement. The Na atom was disordered over two sites (50:50). Final fractional coordinates are presented in Table II.

Table I. Crystal data and summary of data collection and refinement

Compound	1	2
Mol. Wt.	1281.6	1253.8
Space Group	$P\bar{1}$	$P\bar{1}$
a (Å)	12.487(4)	15.438(4)
b (Å)	14.281(2)	15.727(6)
c (Å)	15.055(5)	12.121(9)
α (°)	85.66(2)	112.74(4)
β (°)	80.07(2)	102.02(4)
γ (°)	80.48(2)	85.35(4)
Cell Vol. (Å ³)	2605	2655
Mol./unit cell	2	2
D_c (g/cm ³)	1.64	1.57
μ (cm ⁻¹)	10.1	28.6
Radiation	Mo K_α	Cu K_α
Cryst. size (mm)	0.07 × 0.21 × 0.53	0.03 × 0.40 × 0.50
Scan Width (°)	0.80 + 0.35 tan(θ)	0.80 + 0.2 tan(θ)
Std. reflections	700, 080, 007	600, 042, 002
Decay	<1%	<1%
2θ range (°)	2–40	1–100
Reflections measured	4796	5412
Reflections observed	2441	3925
No. Parameters varied	496	707
R	0.065	0.107
R_w	0.066	0.115

Table II. Final fractional coordinates for **1**

Atom	<i>x/a</i>	<i>y/b</i>	<i>z/c</i>	Atom	<i>x/a</i>	<i>y/h</i>	<i>z/c</i>
Ni(1)	0.1993(2)	-0.0315(2)	0.7124(2)	C(33)	-0.013(1)	0.387(1)	0.945(1)
Ni(2)	-0.2805(2)	-0.0247(2)	0.8465(2)	C(34)	0.083(1)	0.353(1)	0.891(1)
Na(1)	-0.717(1)	0.277(1)	0.404(1)	C(35)	0.104(1)	0.382(1)	0.796(1)
Na(2)	-0.188(2)	0.026(2)	0.566(2)	C(36)	0.031(1)	0.456(1)	0.767(1)
S(1)	-0.5809(4)	0.2588(3)	0.5905(3)	C(37)	0.043(1)	0.482(1)	0.666(1)
S(2)	-0.4108(4)	0.2131(4)	1.0569(4)	C(41)	-0.128(1)	0.4834(9)	0.5871(8)
S(3)	0.1725(3)	0.2559(3)	0.9278(3)	C(42)	-0.019(1)	0.4421(9)	0.6109(9)
S(4)	-0.0031(7)	0.1867(4)	0.5078(5)	C(44)	-0.042(1)	0.3082(9)	0.5392(9)
O(11)	-0.3801(8)	0.5695(7)	0.6902(7)	C(43)	0.010(1)	0.349(1)	0.583(1)
O(12)	-0.5792(9)	0.2649(7)	0.4904(7)	C(45)	-0.147(1)	0.351(1)	0.518(1)
O(13)	-0.699(1)	0.2664(9)	0.6341(8)	C(46)	-0.182(1)	0.4470(9)	0.5425(8)
O(14)	-0.517(1)	0.1722(8)	0.6193(8)	C(47)	-0.294(1)	0.493(1)	0.519(1)
O(21)	-0.3462(9)	0.5775(7)	0.8619(8)	W(1)	0.1830(9)	0.1231(8)	0.7106(8)
O(22)	-0.4871(9)	0.1759(8)	1.0177(8)	W(2)	0.109(1)	-0.007(1)	0.8426(9)
O(23)	-0.297(1)	0.159(1)	1.050(1)	W(3)	0.339(1)	-0.0416(8)	0.7679(8)
O(24)	-0.441(1)	0.243(1)	1.1506(9)	W(4)	0.283(1)	-0.033(1)	0.581(1)
O(31)	-0.1403(8)	0.5635(6)	0.7894(6)	W(4)A	-0.343(4)	0.099(3)	1.336(3)
O(32)	0.1681(8)	0.2651(7)	1.0249(7)	W(5)	0.052(1)	-0.0248(7)	0.6614(7)
O(33)	0.145(1)	0.1691(7)	0.9074(8)	W(6)	-0.2341(9)	-0.0169(7)	0.9706(8)
O(34)	0.2861(9)	0.2674(8)	0.8872(7)	W(7)	-0.3413(8)	-0.0302(6)	0.7295(7)
O(41)	-0.1594(8)	0.5789(6)	0.6149(6)	W(8)	-0.3102(9)	-0.1632(8)	0.8766(8)
O(42)	-0.034(2)	0.181(1)	0.427(1)	W(9)	-0.1250(9)	-0.0927(8)	0.7956(9)
O(43)	-0.054(2)	0.127(1)	0.579(1)	W(10)	-0.4396(8)	0.0269(7)	0.9008(7)
O(44)	0.113(2)	0.176(1)	0.507(1)	W(11)	0.4139(8)	0.1156(7)	0.7972(7)
C(11)	-0.422(1)	0.496(1)	0.670(1)	W(12)	0.936(1)	0.141(1)	0.030(1)
C(12)	-0.395(1)	0.4609(9)	0.5833(9)	W(13)	-0.285(2)	0.087(2)	0.578(2)
C(13)	-0.440(1)	0.3894(9)	0.5611(9)	W(15)	-0.156(2)	-0.244(1)	0.699(1)
C(14)	-0.526(1)	0.351(1)	0.620(1)	W(16)	0.385(2)	0.210(1)	0.296(1)
C(15)	-0.550(1)	0.389(1)	0.708(1)	N(2)P	-0.237(1)	0.1092(8)	0.8106(9)
C(16)	-0.506(1)	0.458(1)	0.734(1)	C(21)P	-0.306(1)	0.172(1)	0.765(1)
C(17)	-0.530(1)	0.489(1)	0.8287(9)	C(23)P	-0.184(1)	0.287(1)	0.763(1)
C(21)	-0.367(1)	0.4861(9)	0.9010(9)	C(24)P	-0.116(1)	0.225(1)	0.803(1)
C(22)	-0.447(1)	0.4507(9)	0.8915(9)	C(22)P	-0.280(1)	0.267(1)	0.750(1)
C(23)	-0.463(1)	0.358(1)	0.934(1)	C(25)P	-0.143(1)	0.130(1)	0.821(1)
C(24)	-0.388(1)	0.3254(9)	0.9972(9)	N(1)P	0.211(1)	-0.179(1)	0.7236(9)
C(25)	-0.305(1)	0.3634(9)	1.0077(9)	C(11)P	0.304(2)	-0.230(1)	0.693(1)
C(26)	-0.286(1)	0.4549(9)	0.9652(9)	C(12)P	0.309(2)	-0.329(1)	0.695(1)
C(27)	-0.197(1)	0.4978(9)	0.9744(9)	C(13)P	0.230(2)	-0.378(1)	0.734(1)
C(31)	-0.066(1)	0.494(1)	0.823(1)	C(14)P	0.136(2)	-0.325(1)	0.773(1)
C(32)	-0.089(1)	0.459(1)	0.915(1)	C(15)P	0.129(2)	-0.223(1)	0.769(1)

The copper complex, **2**, was prepared by dissolving one equivalent of $\text{Cu}(\text{NO}_3)_2$ in deionized water to which two equivalents of pyridine had been added. The solution was mixed with a second solution containing one equivalent of $\text{Na}_5[\text{calix}[4]\text{arene sulfonate}]$ in deionized water. The blue-green solution yielded pale blue-green crystals of **2** upon slow evaporation in a vacuum desiccator.

Crystals of **2** grow as thin, flat plates from solution. The pale blue-green compound very quickly decomposes via loss of H_2O , so the crystals were treated as

above. The structure was solved using SHELX-86. All non-hydrogen atoms were treated with anisotropic thermal parameters, but those associated with C(16) were non-positive definite. In the final cycles of refinement C(16) was refined with isotropic thermal parameters. All water molecules were refined with anisotropic thermal parameters, and all were assigned occupancy factors of 1.0, except for W(17) and W(18), which were assigned values of 0.5. The hydrogen atoms on the calixarene were placed in calculated positions and were not refined. The hydrogen atoms on the water molecules and the oxonium ions could not be located. The three oxonium ions are assigned for charge balance. The rather high *R* factor is probably caused by absorption problems. The very thin crystal was subjected to an empirical absorption correction based on ψ scans, but this correction was apparently not sufficient. The problem with the location of water molecules is due to the existence of large channels running through the crystal which contain only water molecules. However, the structure is sufficiently accurate to show the second-sphere coordination of the copper complex by the calixarene. Final fractional coordinates are given in Table III.

3. Results and Discussion

As can be seen in Figure 1, there are two environments for $[(\text{H}_2\text{O})_5\text{Ni}(\text{NC}_5\text{H}_5)]^{2+}$ in the crystal structure. The bilayer structure characteristic of [calix[4]arene sulfonate]⁵⁻ [15] and [calix[4]arene sulfonate]⁴⁻ [17] is maintained, and one nickel-containing cation is positioned within the hydrophilic layer with the pyridine ligand intercalated into the hydrophilic layer. The second cation is also positioned within the hydrophilic layer, but the pyridine ligand is inserted into the hydrophobic cavity of the calixarene. The calixarene thus functions as a second-sphere ligand for the nickel atom. The relative position of the pyridine ligands with respect to the bilayer is shown in Figure 2.

The depth of penetration of the pyridine ligand into the calixarene cavity may be defined by the distance of the centroid of the pyridine ring from the plane of the calixarene $-\text{CH}_2-$ carbon atoms. This value is 4.3 Å. The plane of the pyridine ring makes an angle of 74° with this plane. The $\text{S} \cdots \text{S}(\text{trans})$ approaches are 8.9 and 11.4 Å, indicating a substantial deviation of the cavity from idealized C_{4v} symmetry. This is also shown in the view of the calixarene from the annulus, Figure 3.

It is worthwhile to comment at this point on the forces that organize and hold the bilayer of calixarenes together. $\pi-\pi$ Stacking interactions are important, and there are intermolecular $\text{C} \cdots \text{C}$ approaches as close as 3.41 Å between carbon atoms of the aromatic rings. However, another important factor in stabilizing the bilayer is the interaction shown in Figure 4. W(15)'' from the hydrophilic layer is located 2.92 Å from O(41), 2.96 Å from O(31), and 2.99 Å from O(42)'. While these are not strong hydrogen bonds, added to the $\pi-\pi$ stacking forces, they are apparently sufficient to effect the formation of the bilayer.

At the base of the calix[4]arene the $\text{O} \cdots \text{O}$ intramolecular hydrogen bond distances are $\text{O}(11) \cdots \text{O}(21)$, 2.70 Å, $\text{O}(21) \cdots \text{O}(31)$, 2.60 Å, $\text{O}(31) \cdots \text{O}(41)$, 2.67 Å, and $\text{O}(41) \cdots \text{O}(11)$, 2.82 Å. This pattern of three shorter and one longer $\text{O} \cdots \text{O}$ separation is consistent with the fact that only three hydrogen atoms are available for hydrogen bonding (one phenolic proton is ionized at neutral pH [18]).

Table III. Final fractional coordinates for **2**

Atom	<i>x/a</i>	<i>y/b</i>	<i>z/c</i>	Atom	<i>x/a</i>	<i>y/b</i>	<i>z/c</i>
Cu	0.2499(1)	0.9668(1)	0.4835(2)	O(43)	-0.0135(7)	0.254(1)	0.968(1)
S(1)	-0.0140(2)	0.2018(3)	0.4081(4)	O(44)	0.1157(8)	0.2700(9)	1.124(1)
O(11)	0.1287(6)	0.5780(7)	0.667(1)	C(41)	0.1758(9)	0.4954(9)	0.927(1)
O(12)	0.0415(9)	0.1455(8)	0.467(1)	C(42)	0.2372(9)	0.4516(9)	1.002(1)
O(13)	-0.1035(7)	0.2014(9)	0.423(1)	C(43)	0.2036(9)	0.386(1)	1.021(1)
O(14)	-0.009(1)	0.172(1)	0.280(1)	C(44)	0.1180(9)	0.3522(9)	0.980(1)
C(11)	0.0945(8)	0.490(1)	0.612(1)	C(45)	0.0598(9)	0.395(1)	0.907(1)
C(12)	0.0456(8)	0.454(1)	0.664(1)	C(46)	0.0900(8)	0.4629(9)	0.885(1)
C(13)	0.0115(9)	0.364(1)	0.599(2)	C(47)	0.0294(9)	0.503(1)	0.795(1)
C(14)	0.0272(8)	0.314(1)	0.481(1)	N(1)	0.2491(9)	0.8285(9)	0.412(2)
C(15)	0.0767(8)	0.352(1)	0.433(1)	C(1)	0.211(1)	0.782(1)	0.299(2)
C(16)	0.1124(9)	0.440(1)	0.494(1)	C(2)	0.209(1)	0.686(1)	0.249(2)
C(17)	0.1661(8)	0.482(1)	0.438(1)	C(3)	0.249(1)	0.636(1)	0.319(2)
S(2)	0.4183(3)	0.2580(3)	0.2602(4)	C(4)	0.289(1)	0.684(1)	0.434(2)
O(21)	0.2985(6)	0.5639(7)	0.663(1)	C(5)	0.290(1)	0.783(1)	0.486(2)
O(22)	0.5148(7)	0.2638(9)	0.290(1)	N(2)	0.2501(7)	1.1036(8)	0.553(1)
O(23)	0.3806(8)	0.1718(8)	0.262(1)	C(6)	0.257(1)	1.151(1)	0.484(2)
O(24)	0.3831(8)	0.2687(9)	0.145(1)	C(7)	0.259(1)	1.247(1)	0.530(2)
C(21)	0.3225(9)	0.493(1)	0.563(1)	C(8)	0.250(1)	1.295(1)	0.649(2)
C(22)	0.2655(8)	0.455(1)	0.457(1)	C(9)	0.241(1)	1.247(1)	0.718(2)
C(23)	0.2944(9)	0.384(1)	0.361(2)	C(10)	0.2422(9)	1.151(1)	0.668(2)
C(24)	0.3832(9)	0.353(1)	0.377(1)	W(1)	0.1685(7)	0.9600(8)	0.599(1)
C(25)	0.4390(9)	0.395(1)	0.486(1)	W(2)	0.3316(8)	0.9612(8)	0.361(1)
C(26)	0.4115(8)	0.463(1)	0.581(1)	W(3)	0.3782(8)	0.9789(8)	0.631(1)
C(27)	0.4715(8)	0.503(1)	0.707(1)	W(4)	0.1213(8)	0.9772(8)	0.346(1)
S(3)	0.5141(3)	0.2006(3)	0.7930(4)	W(5)	0.4617(8)	1.0990(8)	0.436(1)
O(31)	0.3723(6)	0.5798(6)	0.9120(9)	W(6)	0.8967(8)	0.2705(9)	0.143(1)
O(32)	0.6039(8)	0.2098(8)	0.781(1)	W(7)	1.0383(8)	0.0987(8)	0.665(1)
O(33)	0.509(1)	0.1726(9)	0.891(1)	W(8)	0.6023(8)	0.2702(9)	0.127(1)
O(34)	0.4587(8)	0.1451(8)	0.686(1)	W(9)	0.187(2)	0.123(1)	0.191(2)
C(31)	0.4053(9)	0.491(1)	0.879(1)	W(10)	0.313(2)	0.120(1)	0.934(2)
C(32)	0.4548(9)	0.454(1)	0.786(1)	W(11)	0.742(1)	0.185(2)	0.234(2)
C(33)	0.4878(8)	0.364(1)	0.764(1)	W(12)	0.803(2)	0.032(1)	0.904(2)
C(34)	0.4712(9)	0.316(1)	0.832(1)	W(13)	0.761(1)	0.183(2)	-0.047(2)
C(35)	0.4230(9)	0.352(1)	0.922(1)	W(14)	0.696(2)	0.033(1)	0.129(2)
C(36)	0.3885(8)	0.441(1)	0.946(1)	W(15)	0.854(2)	0.016(2)	0.106(2)
C(37)	0.3326(8)	0.483(1)	1.046(1)	W(16)	0.644(2)	0.016(1)	-0.090(2)
S(4)	0.0818(3)	0.2588(3)	0.9985(4)	W(17)	0.934(3)	0.066(2)	0.915(3)
O(41)	0.2017(6)	0.5628(7)	0.903(1)	W(18)	0.561(3)	0.062(3)	0.145(4)
O(42)	0.1170(9)	0.1770(8)	0.912(1)				

The crystal structure of $[(\text{H}_2\text{O})_4\text{Cu}(\text{NC}_5\text{H}_5)_2](\text{H}_3\text{O})_3[\text{calix}[4]\text{arene sulfonate}] \cdot 10 \text{H}_2\text{O}$, **2**, shown in Figure 5, is similar to that found for **1**, except that there is only one copper-containing cation per calixarene unit. One pyridine ring is imbedded in the calixarene cavity, while the other is intercalated into the bilayer. The copper complex thus spans the hydrophilic layer. As can be seen in Figure 5, the calixarene-bound pyridine ring makes an angle of 90° with the plane of the $-\text{CH}_2-$ carbon atoms. The $\text{S} \cdots \text{S}(\text{trans})$ separations are 8.5 and 11.2 Å.

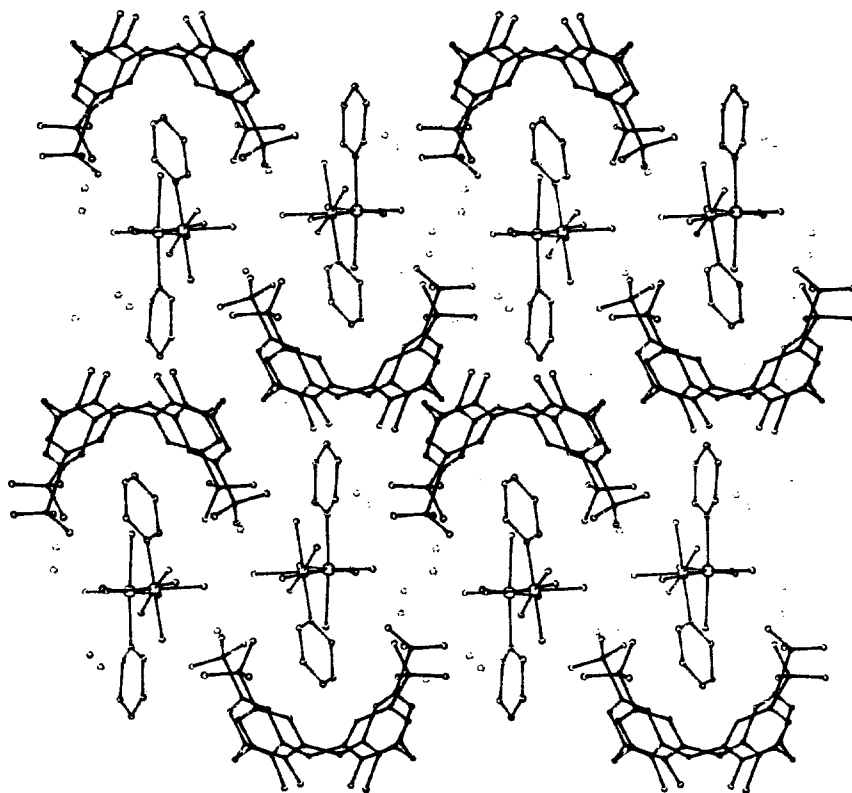


Fig. 1. Layered structure of $[(\text{H}_2\text{O})_5\text{Ni}(\text{NC}_5\text{H}_5)_2]_2(\text{Na})[\text{calix[4]arene sulfonate}] \cdot 3.5 \text{H}_2\text{O}$, **1**.

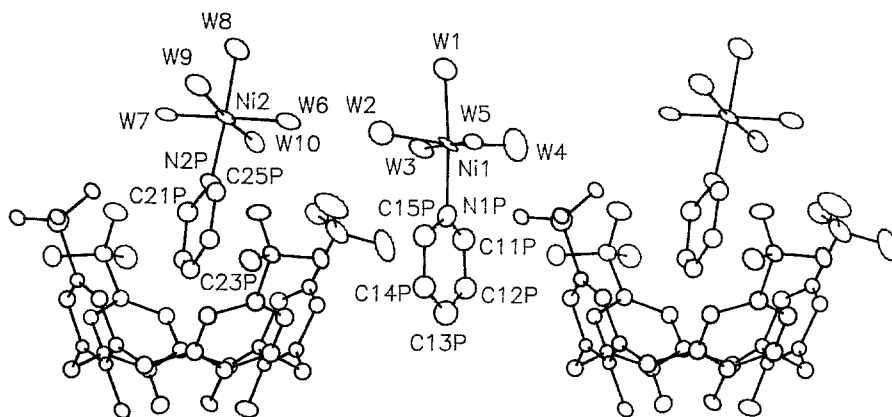


Fig. 2. Atom labelling scheme for **1**. There are two different nickel-containing cations, one exhibiting second-sphere coordination by the calixarene and the other displaying intercalation of the pyridine ring into the calixarene bilayer.

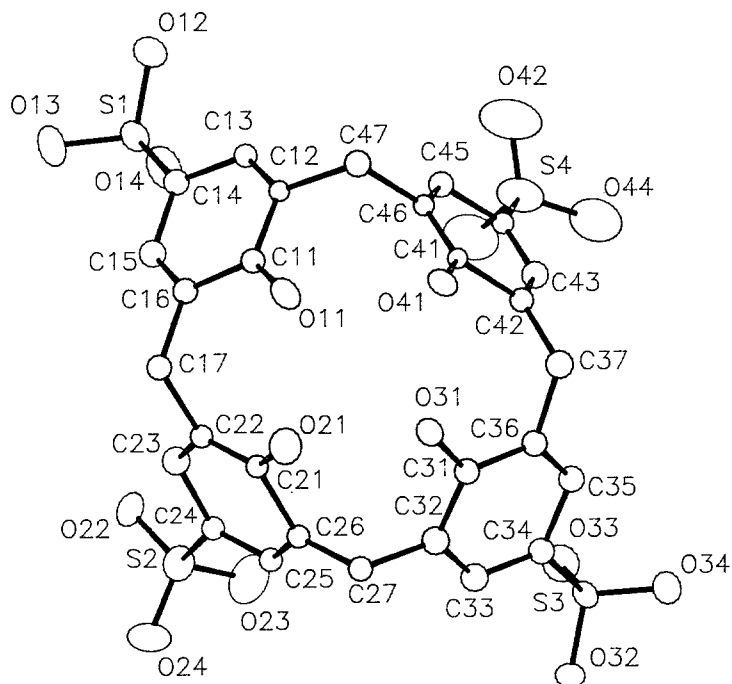


Fig. 3. Atom labelling scheme for the calixarene of **1**, illustrating the ellipsoidal nature of the calixarene cavity.

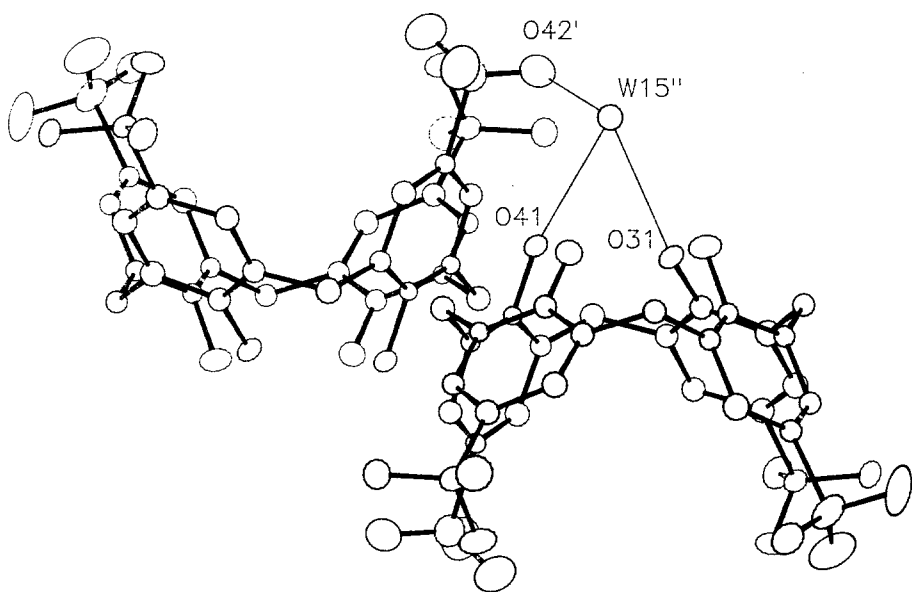


Fig. 4. The interaction of water molecule W15'' with the calixarenes of the bilayer of **1**.

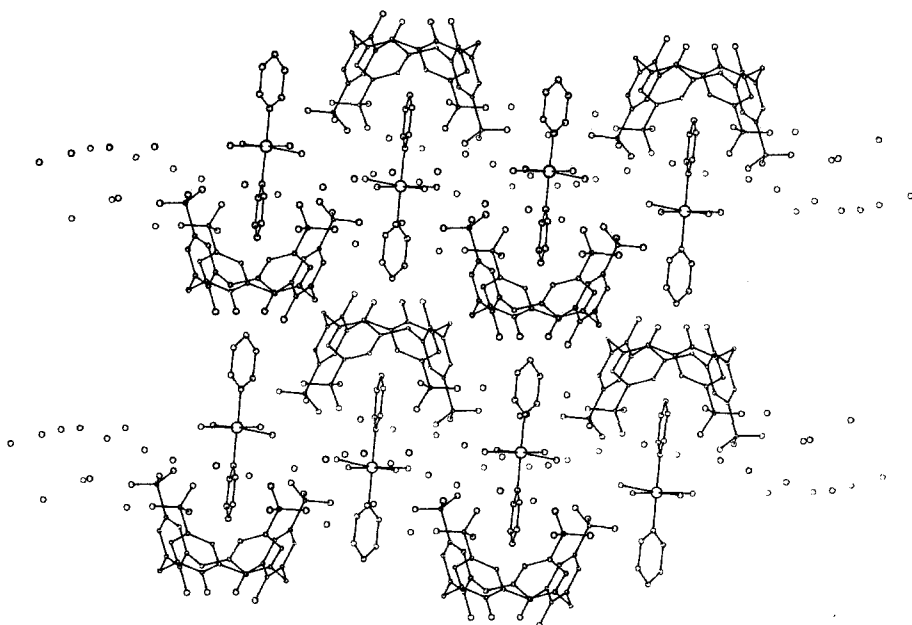


Fig. 5. Layered structure of $[(\text{H}_2\text{O})_4\text{Cu}(\text{NC}_5\text{H}_5)_2](\text{H}_3\text{O})_3[\text{calix}[4]\text{arene sulfonate}]\cdot 10\text{H}_2\text{O}$, **2**.

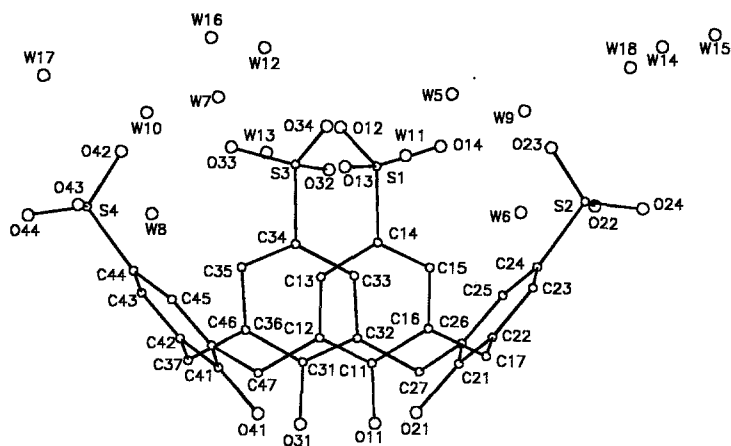


Fig. 6. Atom labelling scheme for the calixarene and water molecules of **2**.

At the base of the calix[4]arene, Figure 6, the intramolecular $\text{O} \cdots \text{O}$ approaches are $\text{O}(11) \cdots \text{O}(21)$, 2.63 Å, $\text{O}(21) \cdots \text{O}(31)$, 2.92 Å, $\text{O}(31) \cdots \text{O}(41)$, 2.64 Å, and $\text{O}(41) \cdots \text{O}(11)$, 2.93 Å. The reason for this symmetrical distribution for the 5-anion is unclear.

The Cu^{2+} ion is found strongly coordinated to the two pyridine nitrogen atoms at 1.99(1) and 2.00(1) Å and two water oxygen atoms at 2.10(2) and 2.11(2) Å. In

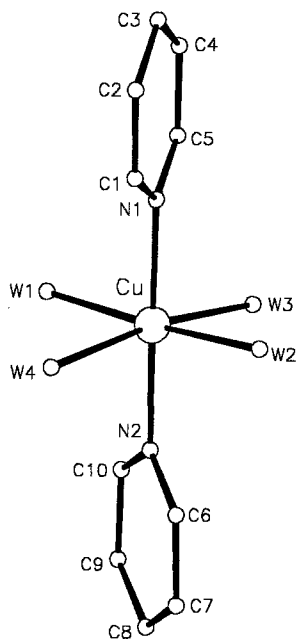


Fig. 7. Atom labelling scheme for the copper-containing cation of **2**.

the Jahn–Teller distorted octahedral field [19], the two axial coordination sites are occupied by water oxygen atoms at 2.34(2) and 2.35(2) Å (see Figure 7).

The crystal structure of **2** reveals more water molecules than does that of **1**. These are located mainly in channels which traverse the crystal parallel to the stacking of the copper(II) coordination complexes. Indeed, the latter may be viewed as pillars which hold apart the calixarene bilayers.

The use of second-sphere coordination to assemble large aggregates and to mimic biological interactions is under investigation.

Acknowledgements

We are grateful to the National Science Foundation for support of this research.

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