

Organic Clays. Synthesis and Structure of $\text{Na}_5[\text{calix}[4]\text{arene sulfonate}] \cdot 12 \text{H}_2\text{O}$, $\text{K}_5[\text{calix}[4]\text{arene sulfonate}] \cdot 8 \text{H}_2\text{O}$, $\text{Rb}_5[\text{calix}[4]\text{arene sulfonate}] \cdot 5 \text{H}_2\text{O}$, and $\text{Cs}_5[\text{calix}[4]\text{arene sulfonate}] \cdot 4 \text{H}_2\text{O}$

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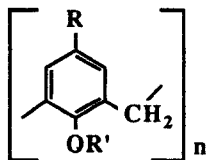
Abstract. The title calixarenes all exist in the solid state as bilayers of anionic calixarenes in the cone configuration. These layers alternate with inorganic regions which contain the cations and the water molecules. The overall structures bear a close resemblance to those found for clay minerals. The sodium salt crystallizes in the triclinic space group $P\bar{1}$ with $a = 10.998(6)$, $b = 13.582(5)$, $c = 14.472(5)$ Å, $\alpha = 74.01(3)$, $\beta = 89.09(4)$, $\gamma = 86.50(4)^\circ$, and $Z = 2$ for $D_{\text{calc}} = 1.72 \text{ g cm}^{-3}$. Refinement based on 4727 observed reflections led to a conventional $R = 0.050$. The potassium salt crystallizes in the triclinic space group $P\bar{1}$ with $a = 11.815(9)$, $b = 13.636(6)$, $c = 14.040(9)$ Å, $\alpha = 100.24(5)$, $\beta = 111.86(9)$, $\gamma = 95.14(9)^\circ$, and $Z = 2$ for $D_{\text{calc}} = 1.77 \text{ g cm}^{-3}$. Refinement based on 2977 observed reflections led to $R = 0.15$. The rubidium and cesium salts are isostructural and crystallize in the monoclinic space group $P2_1/n$ with parameters for $\text{Rb}[\text{Cs}]$ $a = 11.603(5)$ [11.704(3)], $b = 28.607(8)$ [29.747(9)], $c = 12.512(5)$ [12.604(4)] Å, $\beta = 91.70(4)$ [91.63(2)°], and $Z = 4$ for $D_{\text{calc}} = 2.01$ [2.24] g cm^{-3} . Refinement based on 1750 [4257] observed reflections led to $R = 0.108$ [0.075]. Disorder of the cations was observed for the rubidium and cesium salts.

Key words. Calix[4]arene, crystal structure, clay mineral, alkali metal ion, layered structure, water soluble, sulfonate.

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1. Introduction

There is currently significant interest in the chemistry of calixarenes, **1**. Synthesis of modified calixarenes and the formation of alkali metal, as well as main group,



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transition, and inner transition metal complexes was reported during 1987 [1–18]. In the course of the preparation and investigation of water soluble derivatives, $R = -SO_3H$, $-NO_2$, we isolated crystals of $Na_5[calixarene\ sulfonate] \cdot 12 H_2O$ and $Na_5[calixarene\ sulfonate] \cdot 8 H_2O \cdot acetone$ [19]. The bilayer structure found in both cases bore a striking resemblance to that of a clay of 2:1 layer type. If one considers the $-SO_3^-$ groups as part of the hydrated layer, even the thickness of the layers of the calixarene sulfonates is similar to the related ones in clays. The similarities go further than metrical parameters: preparation of the ammonium salt led to a compound with much less water than for the sodium salt, and the bilayer structure was maintained [20]. We report herein the synthesis and structures of the sodium, potassium, rubidium, and cesium salts which further demonstrate the similarity of the $[calixarene\ sulfonate]^{5-}$ complexes to clay minerals.

2. Experimental

The starting compounds for the calixarene syntheses were purchased from Aldrich Chemicals and were used without further purification.

2.1. PREPARATION OF $Na_5[CALIX[4]ARENE\ SULFONATE] \cdot 12 H_2O$

In a typical synthesis, 10.0 g (0.024 mol) of the $[calix[4]arene, R = -H$ and $R' = -H$, were reacted with an excess of H_2SO_4 at $60^\circ C$ for 3 h. This was followed by neutralization with $BaCO_3$ and the addition of Na_2CO_3 to pH 9. The solvent is removed and the compound is recrystallized from water. The overall yield is 15.2 g $Na_5[calix[4]arene\ sulfonate] \cdot 12 H_2O$, 60%. Large, colorless crystals of the compound may be obtained by slow evaporation.

2.2. PREPARATION OF $K_5[CALIX[4]ARENE\ SULFONATE] \cdot 8 H_2O$, $Rb_5[CALIX[4]ARENE\ SULFONATE] \cdot 5 H_2O$, AND $Cs_5[CALIX[4]ARENE\ SULFONATE] \cdot 4 H_2O$

The compounds were prepared as for the sodium analogue, except that K_2CO_3 (or Rb_2CO_3 , Cs_2CO_3) was added to pH 9.

2.3. X-RAY DATA COLLECTION AND STRUCTURE DETERMINATION FOR $Na_5[CALIX[4]ARENE\ SULFONATE] \cdot 12 H_2O$

The crystals are stable for several hours in the absence of an atmosphere of water vapor, but were sealed in thin-walled capillaries to avoid decomposition during the X-ray experiment. Final lattice parameters as determined from 25 high-angle reflections ($2\theta > 40^\circ$) carefully centered on a Enraf Nonius CAD-4 diffractometer are as follows: space group = $P\bar{1}$, $a = 10.998(6)$, $b = 12.582(5)$, $c = 14.472(5)$ Å, $\alpha = 74.01(3)$, $\beta = 89.09(4)$, $\gamma = 86.50(4)^\circ$, and $Z = 2$ for $D_{calc} = 1.72\text{ g cm}^{-3}$. Parameters of data collection are as given in Reference [4]. Structure solution was accomplished by means of direct methods and the subsequent calculation of difference Fourier maps followed by partial cycles of least-squares refinement allowed location of all non-hydrogen atoms. The hydrogen bonding is so extensive that all the hydrogen atoms could be located on a final difference Fourier map.

Table I. Final fractional coordinates for Na₅[calix[4]arene sulfonate]·12 H₂O

Atom	<i>x/a</i>	<i>y/b</i>	<i>z/c</i>	<i>U</i> (eqv)
S(1)	0.3871(1)	0.4671(1)	0.78667(9)	0.020
S(2)	0.9722(1)	0.3171(1)	0.76466(9)	0.023
S(3)	1.0847(1)	0.8013(1)	0.87652(9)	0.022
S(4)	0.4860(1)	1.0304(1)	0.82685(9)	0.021
Na(1)	0.5279(2)	0.2510(2)	0.8385(2)	0.033
Na(2)	0.7464(2)	0.0590(2)	0.9948(1)	0.030
Na(3)	0.1572(2)	0.5311(2)	0.9497(2)	0.035
Na(4)	0.3782(2)	0.3344(2)	0.0288(2)	0.039
Na(5)	0.2664(2)	1.2472(2)	0.6940(1)	0.030
O(1)	0.5929(3)	0.7464(3)	0.4415(2)	0.025
O(2)	0.8593(3)	0.6892(3)	0.4501(2)	0.024
O(3)	0.9067(3)	0.8570(3)	0.4852(2)	0.023
O(4)	0.6810(3)	0.8914(3)	0.4996(2)	0.026
O(5)	0.2816(4)	0.5244(3)	0.8099(3)	0.046
O(6)	0.4723(3)	0.4325(3)	0.8662(3)	0.036
O(7)	0.3596(3)	0.3798(3)	0.7534(3)	0.035
O(8)	0.9147(3)	0.3391(3)	0.8486(3)	0.036
O(9)	0.9158(3)	0.2351(3)	0.7376(3)	0.037
O(10)	1.1042(3)	0.2981(3)	0.7795(3)	0.031
O(11)	0.9677(3)	0.7867(3)	0.9273(3)	0.038
O(12)	1.1663(3)	0.7103(3)	0.9046(3)	0.034
O(13)	1.1369(3)	0.8934(3)	0.8853(3)	0.036
O(14)	0.4172(3)	1.1266(3)	0.7853(3)	0.030
O(15)	0.4117(3)	0.9505(3)	0.8833(3)	0.036
O.16	0.5905(3)	0.0457(3)	0.8808(3)	0.038
C(1)A	0.5548(4)	0.6831(4)	0.5264(3)	0.018
C(2)A	0.4754(4)	0.7239(4)	0.5858(3)	0.019
C(3)A	0.4284(4)	0.6568(4)	0.6671(3)	0.020
C(4)A	0.4585(4)	0.5531(4)	0.6890(3)	0.019
C(5)A	0.5410(4)	0.5148(4)	0.6321(3)	0.018
C(6)A	0.5907(4)	0.5792(4)	0.5514(3)	0.017
C(7)A	0.6875(4)	0.5350(4)	0.4945(3)	0.018
C(1)B	0.8884(4)	0.6060(4)	0.5239(3)	0.017
C(2)B	0.8093(4)	0.5254(4)	0.5451(3)	0.016
C(3)B	0.8402(4)	0.4381(4)	0.6168(3)	0.019
C(4)B	0.9467(4)	0.4281(4)	0.6693(3)	0.020
C(5)B	1.0241(4)	0.5087(4)	0.6498(3)	0.021
C(6)B	0.9966(4)	0.5975(4)	0.5778(3)	0.019
C(7)B	1.0794(4)	0.6863(4)	0.5573(3)	0.021
C(1)C	0.9579(4)	0.8471(4)	0.5711(3)	0.018
C(2)C	1.0422(4)	0.7646(4)	0.6112(3)	0.019
C(3)C	1.0847(4)	0.7524(4)	0.7306(3)	0.020
C(4)C	1.0489(4)	0.8214(4)	0.7542(3)	0.021
C(5)C	0.9706(4)	0.9055(4)	0.7124(3)	0.021
C(6)C	0.9266(4)	0.9197(4)	0.6217(3)	0.019
C(7)C	0.8338(4)	1.0081(4)	0.5806(3)	0.019
C(1)D	0.6377(4)	0.9220(4)	0.5748(3)	0.019
C(2)D	0.7070(4)	0.9801(4)	0.6184(3)	0.019
C(3)D	0.6618(4)	1.0093(4)	0.6966(3)	0.020
C(4)D	0.5450(4)	0.9856(4)	0.7305(3)	0.020
C(5)D	0.4734(5)	0.9311(4)	0.6855(3)	0.021
C(6)D	0.5181(4)	0.8976(4)	0.6089(3)	0.020

Table I. *Continued.*

Atom	x/a	y/b	z/c	$U(\text{eqv})$
C(7)D	0.4403(4)	0.8379(4)	0.5610(3)	0.020
W(1)	0.4114(3)	0.1869(3)	0.9786(3)	0.035
W(2)	0.1793(3)	0.3551(3)	0.9549(3)	0.032
W(3)	0.8215(3)	-0.1153(3)	1.0555(3)	0.038
W(4)	0.0420(3)	0.4786(3)	1.1073(3)	0.048
W(5)	0.2675(4)	0.2255(4)	1.1651(3)	0.057
W(6)	0.3233(4)	0.4880(3)	1.0721(3)	0.051
W(7)	0.1695(4)	0.0908(4)	0.7186(4)	0.060
W(8)	0.2206(5)	0.3806(5)	1.2514(4)	0.082
W(9)	0.7054(3)	0.2421(3)	0.9253(3)	0.035
W(10)	0.9049(4)	0.0504(3)	0.8838(3)	0.043
W(11)	0.6310(4)	0.2600(3)	0.6905(3)	0.057
W(12)	0.5702(4)	0.2770(5)	1.1037(4)	0.074

Final refinement with the non-hydrogen atoms treated with anisotropic thermal parameters gave $R = 0.050$ ($R_w = 0.050$). The final values of the positional parameters are given in Table I. Tables of bond lengths and angles, anisotropic thermal parameters, and structure factors are available as supplementary material.

2.4. X-RAY DATA COLLECTION AND STRUCTURE DETERMINATION FOR $\text{K}_5[\text{CALIX[4]ARENE SULFONATE}] \cdot 8 \text{H}_2\text{O}$

Data were collected and manipulated in the same manner as for the sodium salt. The final lattice parameters are as follows: space group = $P\bar{1}$, $a = 11.815(9)$, $b = 13.636(6)$, $c = 14.040(9)$ Å, $\alpha = 100.24(5)$, $\beta = 111.86(9)$, $\gamma = 95.14(9)^\circ$, and $Z = 2$ for $D_{\text{calc}} = 1.77 \text{ g cm}^{-3}$. The water molecules were clearly resolved and no disorder was apparent. However, the hydrogen atoms could not be located and the final R value was high (0.15). This was presumably caused by an absorption problem and a crystal which scattered poorly (only 2977 observed reflections were obtained out of 5529 measured out to $2\theta = 44^\circ$). The final values of the positional parameters are given in Table II. Tables of bond lengths and angles and structure factors are available as supplementary material.

2.5. X-RAY DATA COLLECTION AND STRUCTURE DETERMINATION FOR $\text{Rb}_5[\text{CALIX[4]ARENE SULFONATE}] \cdot 5 \text{H}_2\text{O}$

Data were collected and manipulated as for the sodium salt. The space group is $P2_1/n$ and the final lattice parameters are as follows: $a = 11.603(5)$, $b = 28.607(8)$, $c = 12.512(5)$ Å, $\beta = 91.70(4)^\circ$, and $Z = 4$ for $D_{\text{calc}} = 2.01 \text{ g cm}^{-3}$. Refinement based on 1750 observed reflections led to $R = 0.108$. The paucity of data together with the disorder of one of the rubidium atoms over three sites led to the high R value. The value of five water molecules should be viewed in the light of the overall structure. The final positional parameters and the observed and calculated structure factors are available as supplementary material.

Table II. Final fractional coordinates for $K_5[\text{calix}[4]\text{arene sulfonate}] \cdot 8 \text{H}_2\text{O}$.

Atom	x/a	y/b	z/c	$U(\text{eqv})$
K(1)	0.2698(5)	0.0707(5)	0.5848(6)	0.056(19)
K(2)	0.5639(5)	0.4425(5)	0.3876(5)	0.052(28)
K(3)	0.8573(5)	0.4124(6)	0.2550(6)	0.062(28)
K(4)	0.7556(9)	0.7357(7)	0.5860(7)	0.087(16)
K(5)	0.9463(6)	0.2141(7)	0.4907(8)	0.088(42)
S(1)	0.2304(6)	0.3558(5)	0.6820(5)	0.027(1)
S(2)	0.3864(6)	-0.1819(5)	0.6523(5)	0.033(1)
S(3)	0.7766(6)	0.4959(5)	0.6518(5)	0.034(1)
S(4)	0.9945(6)	1.0075(5)	0.6580(5)	0.030(1)
O(1)	0.634(1)	0.308(1)	1.066(1)	0.035(4)
O(2)	0.701(1)	0.134(1)	1.029(1)	0.030(3)
O(3)	0.912(1)	0.194(1)	1.035(1)	0.029(3)
O(4)	0.878(1)	0.382(1)	1.057(1)	0.034(4)
O(5)	0.269(2)	0.449(1)	0.661(1)	0.041(4)
O(6)	0.207(2)	0.268(1)	0.597(1)	0.044(4)
O(7)	0.124(2)	0.363(1)	0.716(1)	0.043(4)
O(8)	0.307(2)	-0.133(2)	0.577(2)	0.065(5)
O(9)	0.321(2)	-0.256(2)	0.684(2)	0.069(6)
O(10)	0.471(1)	-0.230(1)	0.613(1)	0.037(4)
O(11)	0.739(2)	0.405(2)	0.570(2)	0.072(6)
O(12)	0.889(2)	0.559(1)	0.664(1)	0.052(5)
O(13)	0.678(2)	0.555(1)	0.634(1)	0.051(5)
O(14)	1.130(2)	1.014(2)	0.693(2)	0.058(5)
O(15)	0.931(2)	0.906(2)	0.621(2)	0.058(5)
O(16)	0.940(2)	1.064(2)	0.584(2)	0.071(6)
C(1)A	0.545(2)	0.314(2)	0.972(2)	0.028(5)
C(2)A	0.554(2)	0.402(2)	0.937(2)	0.028(5)
C(3)A	0.456(2)	0.416(2)	0.845(2)	0.035(6)
C(4)A	0.355(2)	0.337(2)	0.795(2)	0.026(5)
C(5)A	0.348(2)	0.247(2)	0.827(2)	0.025(5)
C(6)A	0.446(2)	0.234(2)	0.919(2)	0.025(5)
C(7)A	0.438(2)	0.136(2)	0.951(2)	0.029(5)
C(1)B	0.629(2)	0.061(2)	0.945(2)	0.022(5)
C(2)B	0.497(2)	0.057(2)	0.899(2)	0.021(5)
C(3)B	0.426(2)	-0.019(2)	0.813(2)	0.026(5)
C(4)B	0.474(2)	-0.087(2)	0.763(2)	0.023(5)
C(5)B	0.606(2)	-0.085(2)	0.812(2)	0.027(5)
C(6)B	0.679(2)	-0.013(2)	0.899(2)	0.022(5)
C(7)B	0.820(2)	-0.016(2)	0.952(2)	0.029(5)
C(1)C	0.931(2)	0.152(2)	0.947(2)	0.024(5)
C(2)C	0.890(2)	0.048(2)	0.905(2)	0.023(5)
C(3)C	0.910(2)	0.004(2)	0.815(2)	0.027(5)
C(4)C	0.972(2)	0.061(2)	0.774(2)	0.029(5)
C(5)C	1.015(2)	0.164(2)	0.816(2)	0.025(5)
C(6)C	0.995(2)	0.211(2)	0.905(2)	0.021(5)
C(7)C	1.035(2)	0.325(2)	0.948(2)	0.029(5)
C(1)D	0.853(2)	0.407(2)	0.963(2)	0.019(5)
C(2)D	0.926(2)	0.380(2)	0.904(2)	0.023(5)
C(3)D	0.901(2)	0.408(2)	0.812(2)	0.026(5)
C(4)D	0.802(2)	0.459(2)	0.769(2)	0.028(5)
C(5)D	0.733(2)	0.487(2)	0.832(2)	0.029(5)
C(6)D	0.756(2)	0.457(2)	0.925(2)	0.023(5)

Table II. *Continued.*

Atom	<i>x/a</i>	<i>y/b</i>	<i>z/c</i>	<i>U</i> (eqv)
C(7)D	0.672(2)	0.483(2)	0.987(2)	0.024(5)
W(1)	0.845(2)	0.748(2)	0.803(2)	0.090(7)
W(2)	0.523(2)	0.655(2)	0.422(2)	0.064(5)
W(3)	0.484(2)	0.814(2)	0.303(2)	0.074(6)
W(4)	0.450(2)	0.337(2)	0.174(2)	0.077(6)
W(5)	0.633(2)	0.912(2)	0.564(2)	0.084(7)
W(6)	0.703(2)	0.133(2)	0.634(2)	0.086(7)
W(7)	1.105(2)	0.782(2)	0.743(2)	0.088(7)
W(8)	1.072(3)	0.591(2)	0.523(2)	0.107(9)

2.6. X-RAY DATA COLLECTION AND STRUCTURE DETERMINATION FOR Cs₃[CALIX[4]ARENE SULFONATE]·4 H₂O

Data were collected and manipulated as for the sodium salt. The compound is isostructural with the rubidium analogue: $a = 11.704(3)$, $b = 29.747(9)$, $c = 12.604(4)$ Å, $\beta = 91.63(2)^\circ$, and $Z = 4$ for $D_{\text{calc}} = 2.24 \text{ g cm}^{-3}$. Refinement based on 4257 observed reflections led to a final $R = 0.075$. One of the cesium atoms is disordered over two sites and the four water molecules are disordered over seven sites. The final positional parameters, bond lengths and angles, and structure factors are available as supplementary material.

3. Results and Discussion

The calix[4]arene sulfonates of the alkali metals all exist as 5⁻ anions at neutral pH. The four protons of the sulfonate groups have been removed, as has one from the hydroxyls [21]. The resulting 5⁻ anion exists in the cone configuration which is stabilized by the hydrogen bonding shown in Figure 1.

The cavity of the sodium salt of the calixarene contains two water molecules. In this respect a similarity with α -cyclodextrin is noted [22]. Indeed, upon exposure to an organic molecule with an appropriately sized hydrophobic region, the water molecules are ejected in favor of the organic guest [19]. This was demonstrated by the structure of Na₅[calix[4]arene sulfonate]·acetone·8 H₂O, in which the acetone molecule is located in the cavity. One methyl group is embedded in the bottom of the cone, the other is directed toward an —SO₃⁻ group, and the carbonyl oxygen is oriented into the inorganic layer.

Figure 2 shows not only the cone configuration with the two guest water molecules, but also the bilayer arrangement of the calix[4]arene anions. The structure is divided into organic and inorganic layers. The former consists of the bilayer of calixarene units, while the latter is comprised of the water molecules, the sodium ions, and the —SO₃⁻ groups. This general structure is maintained throughout the series, as the representation of the rubidium analogue, Figure 3, illustrates.

The bilayer is stabilized in part by the electrostatic interaction of a sodium ion from the inorganic region with a phenoxide oxygen atom and in part by hydrogen bonding of one of the hydroxyl groups with a water molecule of the inorganic layer.

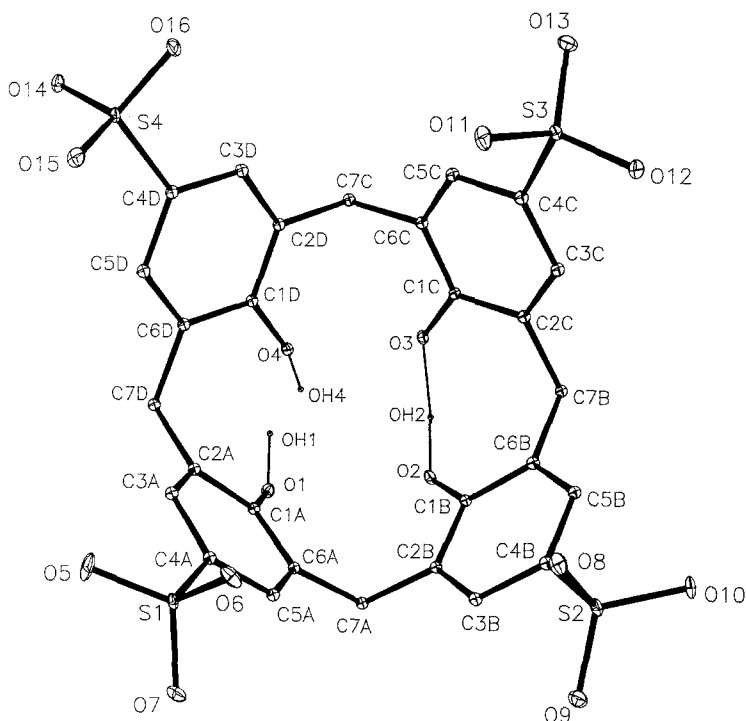


Fig. 1. Structure of the calixarene 5⁻ anion viewed from the top of the cavity. Hydrogen atoms OH1 and OH2 stabilize the cone, while OH4 is used in hydrogen bonding to a water molecule of the inorganic layer.

It is also possible that the packing of the calixarenes such that the aromatic regions of one are positioned near those of its neighbors results in a favorable interaction.

While the structure bears a resemblance to bioorganic bilayer membranes, the overall similarity to the structures of clay minerals is striking. First, consider the repeat distance in the sodium salt of the calixarene, 13.7 Å, compared to

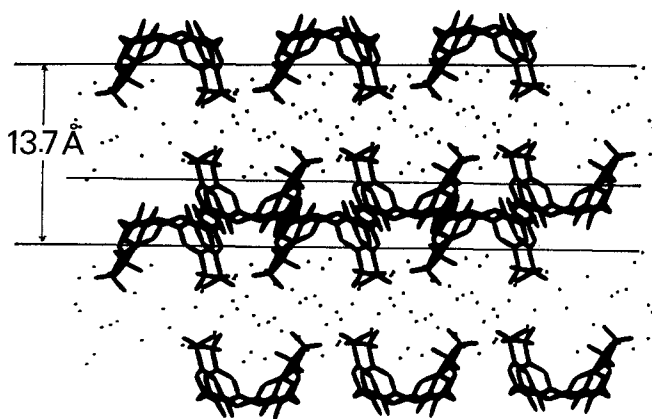


Fig. 2. The bilayer structure of $\text{Na}_2[\text{calix[4]arene sulfonate}] \cdot 12 \text{H}_2\text{O}$. The lines are least-squares best planes of the aromatic carbon atoms bonded to the $-\text{SO}_3^-$ groups.

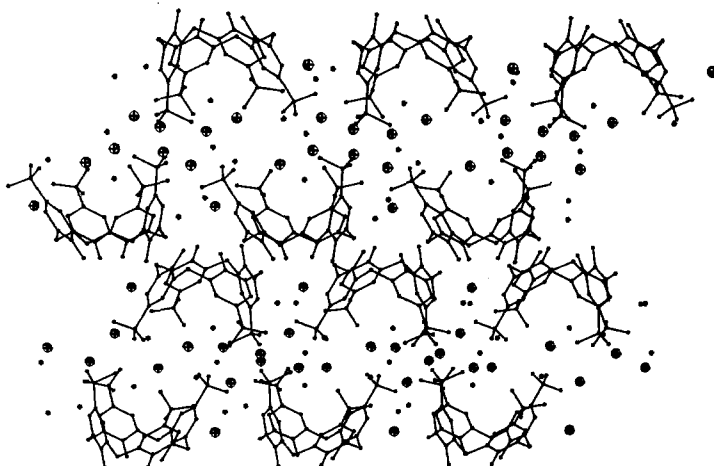


Fig. 3. The bilayer structure for $\text{Rb}_5[\text{calix}[4]\text{arene sulfonate}] \cdot 5\text{H}_2\text{O}$. The cross-hatched spheres are rubidium ions.

14.4–15.6 Å in smectite [23] and 15.0 Å in hydrated sodium vermiculite [24]. Second, the hydrated layer in sodium vermiculite is 9.4 Å, while the inorganic layer in $\text{Na}_5[\text{calix}[4]\text{arene sulfonate}] \cdot 12\text{H}_2\text{O}$ is 8.3 Å. A more complete comparison has been presented [19].

The chemical behavior of clays is also mimicked by the title complexes in two respects: the presence of cation-exchange capabilities and the reduced water content in the ammonium salt [20]. Currently, other similarities between clays and the water-soluble calixarenes are being probed. In particular, the size- and polarity-selective cavity of the calix[4]arene sulfonates is finding utility in the separation of organic substances, cations, anions, and neutral molecules, from aqueous feed streams.

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