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Supramolecular Chemistry

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title~content=t713649759>

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To cite this Article Atwood, Jerry L. , Barbour, Leonard J. , Dawson, Eric S. , Junk, Peter C. and Kienzle, Joanne(1996) 'X-ray Structure of the Water Soluble [Adeninium]-[*p*-Sulfonatocalix[4]arene] which Displays Cationic and Anionic Bilayers', *Supramolecular Chemistry*, 7: 4, 271 – 274

To link to this Article: DOI: 10.1080/10610279608035197

URL: <http://dx.doi.org/10.1080/10610279608035197>

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X-ray Structure of the Water Soluble [Adeninium]- [*p*-Sulfonatocalix[4]arene] which Displays Cationic and Anionic Bilayers

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(Received 7 February 1996)

Treatment of Na₄[*p*-sulfonatocalix[4]arene]·nH₂O with adenine in an acidic medium generates the water soluble [C₅H₆N₅⁺]₄[*p*-sulfonatocalix[4]arene]·14H₂O. The compound crystallizes from solution in the space group P1 with *a* = 12.824(2), *b* = 13.778(1), *c* = 19.536(2) Å, α = 77.85(1), β = 78.78(1), γ = 80.25(1)°, and D_c = 1.557 gcm⁻³ for Z = 2 (C₄₈H₇₂O₃₀N₂₀S₄). Refinement based on 9639 observed reflections led to R = 0.065. The complex crystallizes with a water molecule exhibiting aromatic π hydrogen bonding imbedded within the hydrophobic calixarene cavity. The four adeninium ions form a hydrogen bonded array in a layer external to the cavity. The overall structure exists as bilayers of anionic calix[4]arenes in the cone conformation. These layers are intercalated with bilayers of cationic adeninium ions and are separated by a bed of water molecules. The bilayer structure has been observed in other calix[4]arene complexes, and the intercalation of a cationic bilayer further enhances the similarity in structure of the water-soluble calix[4]arenes to that of clays.

Structural studies of the calixarenes,¹ and in particular, the water soluble *p*-sulfonatocalix[4]arenes, have revealed important information with respect to similarities with biological function² and enzyme mimicry.³ In the *p*-sulfonatocalix[4]arene system, biologically important

interactions, such as the mode of interaction of water and amino residues with aromatic moieties has been observed.^{2a,4} Owing to the separation of the hydrophilic and hydrophobic regions inherent in this system, the complexes also typically crystallize in bilayers with the calixarene sulfonato residues directed toward the hydrophilic layers. The cations are typically found in a "sea" of hydrogen bonded water molecules within the hydrophilic layer. The similarity of these structures to those of the clays has been noted.⁵

It is of some interest to determine the interactions of calixarenes with biologically important molecules, such as the purines and pyrimidines, which are the major bases found in the nucleic acids.⁶ Thus, in this contribution, we report the synthesis and X-ray crystal structure of [C₅H₆N₅⁺]₄[*p*-sulfonatocalix[4]arene]·14H₂O, the product obtained from the interaction of adenine with Na₄[*p*-sulfonatocalix[4]arene] in acidic media. This complex crystallizes as double bilayers of anionic calix[4]arenes and cationic adeninium

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ions separated by a layer of water. Imbedded within the calix[4]arene cavity is a water molecule exhibiting aromatic π -hydrogen bonding to two distal aromatic rings.

Treatment of $\text{Na}_4[p\text{-sulfonatocalix[4]arene}]$ with adenine in acidic medium generates the water soluble $[\text{C}_5\text{H}_6\text{N}_5^+]_4[p\text{-sulfonatocalix[4]arene}]\cdot 14\text{H}_2\text{O}$.⁷ The protonation of adenine at the N1 position (the N center adjacent to the aminated C center) in acidic solution is well established.^{8–12}

The cone conformation of the calix[4]arene is shown in Figure 1.¹³ The calixarene contains one water molecule deeply embedded within the cavity; centroid ... O distances of 3.84, 3.24, 4.45 and 3.29 Å are formed for rings A, B, C and D, respectively. The interaction of the water molecule with rings B and D is established by the O - H ... π aromatic bonding distances, compared to 3.15–3.20 Å from X-ray structure data² and 3.11 Å from Monte Carlo calculations.¹⁴ Two water molecules, W2 and W3, are hydrogen bonded at 2.84 and 3.03 Å to the included water molecule W8, completing the roughly tetrahedral geometry. W2 and W3 reside in the hydrophilic region at the opening of the bowl-like calix[4]arene anion (see Figure 1). While the protons of the water

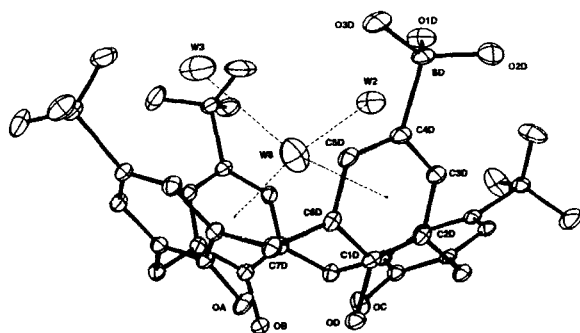


FIGURE 1 The environment of the water molecule W8, which exhibits π hydrogen bonding to two aromatic rings of the *p*-sulfonatocalix[4]arene. Water molecules W2 and W3 complete the near tetrahedral geometry around W8. Bond distances and angles are as follows: W8-centroid A, 3.84 Å, W8-centroid B, 3.24 Å, W8-centroid C, 4.45 Å, W8-centroid D, 3.29 Å, W8-W2, 2.84 Å, W8-W3, 3.03 Å, centroid B-W8-centroid B, 133.6°, W2-W8-W3, 103.8°, W2-W8-centroid B, 95.0°, W2-W8-centroid D, 101.5°, W3-W8-centroid B, 94.0°, W3-W8-centroid D, 122.8°.

molecules were not located, the geometry about the O-centers unequivocally establishes the hydrogen bonding patterns. The B and D rings, which are π aromatic ... H - O bonded to W8 are drawn up, while rings A and C are splayed out: the dihedral angles between rings B and D and A and C are 34 and 105°, respectively. The calix[4]arene portion of the structure is clearly reminiscent of the structure of the sodium salt of *p*-sulfonatocalix[4]arene used in the preparation of the title complex, and demonstrates that π aromatic...H-O bonding is common in such complexes.^{2a}

Two bilayers exist in the overall structure of $[\text{C}_5\text{H}_6\text{N}_5^+]_4[p\text{-sulfonatocalix[4]arene}]\cdot 14\text{H}_2\text{O}$; one of calixarene anions, where the sulfonate groups are directed into the hydrophilic layer, and the other of adeninium cations, where the protonated N1 is directed into the hydrophilic layer (see Figure 2). These two bilayers are separated in part, by thin layers of water molecules. This affords the general pattern of water layer-cation bilayer-water layer-anion bilayer and so forth. The four adeninium ions in the cationic bilayer form two pairs of hydrogen bonded dimers, connected *via* two N5-H...N4 hydrogen bonds (see Figure 3). This type of adeninium dimer has been observed in other mono-protonated adenine structures.¹⁰ In addition to the interaction of adenine bases with one another through hydrogen bonding, an interaction perpendicular to the layers of bases is evident,¹⁵ which is probably of the dipole-induced dipole type.¹⁶ The perpendicular distance between the planes of the base pairs is 3.4 Å, similar to that in $[\text{C}_5\text{H}_5\text{N}_5\cdot\text{HBr}\cdot 0.5\text{H}_2\text{O}]$.¹⁰ In the cationic bilayer, all the protonated nitrogen centers of the adeninium ions form hydrogen bonds with either water molecules, nitrogen centers of adjacent adeninium ions, or oxygen atoms on the sulfonate groups of the calix[4]arene anions (see Figure 3). Thus, while all the protons were not located in the structure, the hydrogen bonding pattern is clearly inferred from short donor...acceptor contacts.

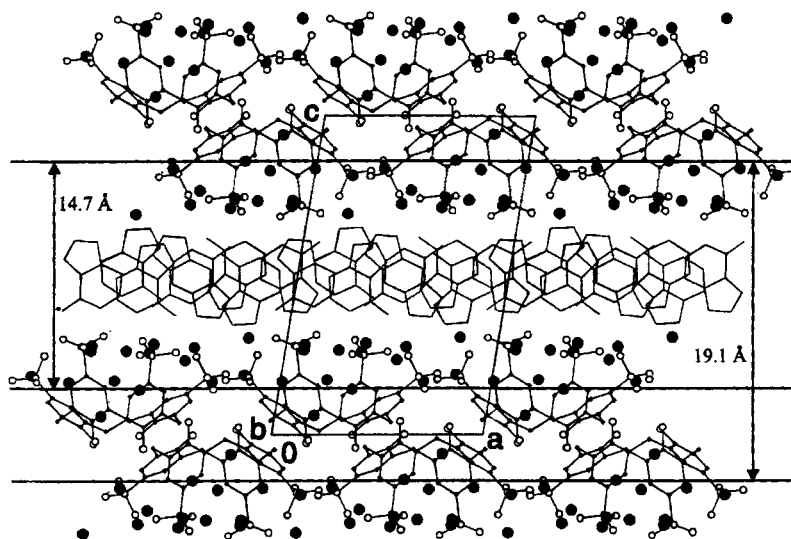


FIGURE 2 Bilayer packing arrangement of $[C_5H_6N_5^+]_4[p\text{-sulfonatocalix[4]arene}] \cdot 14H_2O$. The lines are least-squares best planes of the aromatic carbon atoms attached to the $-SO_3^-$ groups. These separations are much larger than the 8.3 Å and 13.7 Å in the sodium salt of $p\text{-sulfonatocalix[4]arene}$.

Previously we demonstrated the similarity between the layered structures of sulfonated calixarenes and those of clay minerals.⁵ The present structure reinforces these similarities where the cationic layer has been intercalated between the anionic layers in the water layer. The repeat distance in the adeninium salt, 19.1 Å, (see Figure 2) is markedly longer than that in the sodium salt, 13.7 Å,^{5b} (cf 14.4–15.6 Å in smectite¹⁷ and

15.0 Å in hydrated sodium vermiculite¹⁸). The inorganic layer in $Na_4[calix[4]arenesulfonate] \cdot 12H_2O$ is 8.3 Å thick^{5b} (cf 9.4 Å in the hydrated layer of sodium vermiculite¹⁸), while in the adeninium structure, the hydrophilic layer is 14.7 Å wide. The present structure can therefore be viewed as a cationically exchanged clay-like structure of the sodium salt where the adeninium cations have been intercalated between the anionic bilayers.

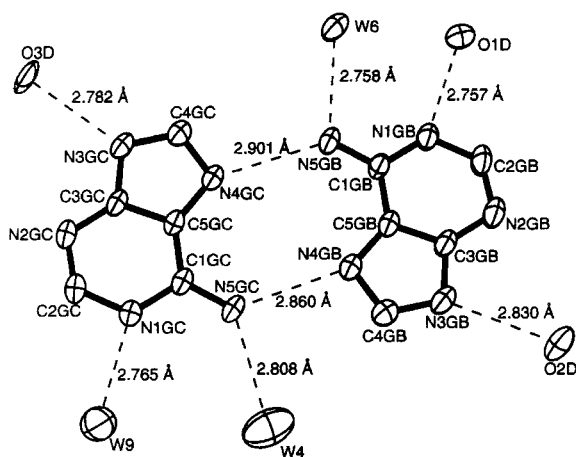


FIGURE 3 Structure of one of the adeninium dimer pairs showing the hydrogen bonding of water molecules and sulfonate oxygen atoms to protons on the N-centers.

Acknowledgments

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

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