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Inclusion of organic cations by *p*-sulfonatocalix[4]arene. Crystal and molecular structure of the supramolecular complexes Na_2(pyridinium)$_2$[$Cu(H_2O)_4(NC_5H_5)_2$][$Cu(H_2O)_4$(*p*-sulfonatocalix[4]arene)$_2$]·$10H_2O$ and Na_4(morpholinium) (*p*-sulfonatocalix[4]arene)·$8H_2O$

Leonard J. Barbour[a]; Andrew K. Damon[a]; G. William Orr[a]; Jerry L. Atwood[a]
[a] Department of Chemistry, University of Missouri-Columbia, Columbia, MO, USA

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Inclusion of organic cations by *p*-sulfonatocalix[4]arene. Crystal and molecular structure of the supramolecular complexes Na_2(pyridinium)$_2$ $[Cu(H_2O)_4(NC_5H_5)_2][Cu(H_2O)_4$ (*p*-sulfonatocalix[4]arene)$_2$]$\cdot 10H_2O$ and Na_4(morpholinium) (*p*-sulfonatocalix[4]arene)$\cdot 8H_2O$

LEONARD J. BARBOUR, ANDREW K. DAMON, G. WILLIAM ORR and JERRY L. ATWOOD*

Department of Chemistry, University of Missouri-Columbia, Columbia, MO, 65211, USA

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The title compounds crystallize with the *p*-sulfonatocalix[4]arene hosts packed in the well-known bilayer mode. In each case a cationic organic guest is situated in the cavity and both structures are stabilized by extensive hydrogen bonded networks. Na_2(pyridinium)$_2[Cu(H_2O)_4(NC_5H_5)_2][Cu(H_2O)_4$(*p*-sulfonatocalix[4]arene)$_2]\cdot 10H_2O$, 1, crystallizes in the space group $P\bar{1}$ with a = 12.3022(6), b = 14.7452(6), c = 14.9026(9) Å, α = 68.672(4), β = 98.821(4), γ = 76.457(4)°, and D_c = 1.62 gcm^{-3} for Z = 1. Full-matrix least-squares refinement on F^2 based on 4941 observed reflections yielded a final R_1 value of 0.064. Two unique octahedral copper environments are encountered, each with the metal coordinated to four water molecules in the equatorial positions. In the axial positions, one copper cation is coordinated to two pyridine ligands, while the other is coordinated to calixarene sulfonate oxygen atoms across the hydrophilic layer. The metal cations are situated centrally in the hydrophilic layer which is also populated by water molecules and sodium cations, while the pyridinium cation is located within the calixarene cavity. Na_4(morpholinium)(*p*-sulfonatocalix[4]arene)$\cdot 8H_2O$, 2, crystallizes in the space group $P\bar{1}$ with a = 11.824(3), b = 13.005(3), c = 15.012(4) Å, α = 110.13(4), β = 98.55(4), γ = 93.68(3)°, and D_c = 1.66 gcm^{-3} for Z = 2. Full-matrix least-squares refinement on F based on 4376 observed reflections yielded a final R value of 0.048. The morpholinium cation is situated in the calixarene cavity and forms two N-H...O hydrogen bonds, one with a sulfonate oxygen atom of its calixarene host and the other with a sulfonate oxygen atom across the hydrophilic layer.

INTRODUCTION

Calixarenes[1,2] can be derivatized at the *para* position with sulfonate groups to render them water soluble,[3–5] and X-ray diffraction studies have shown that cationic,[6] anionic,[7–9] and neutral[10,11] species may be complexed within the hydrophobic cavity. Indeed, the study of this versatile host compound has generated interest in the contexts of catalysis,[5] enzyme[12] and clay[10] mimicry and biological function.[8,11] In addition, second-[13,14] and third-sphere[15] coordination of transition metal complexes by calix[4]arenes have also been noted. Calix[4]arene sulfonates usually crystallize with a high degree of hydration and the bilayer packing arrangement of alternating hydrophilic and hydrophobic layers has been well documented.[7,9,10,16,17,18] In this contribution we report the preparation and X-ray crystal structures of two *p*-sulfonatocalix[4]arene host-guest systems, both of which contain cavity-bound organic cations.

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*To whom correspondence should be addressed.

EXPERIMENTAL

Preparation of crystals

(1) $Na_2(pyridinium)_2[Cu(H_2O)_4(NC_5H_5)_2][Cu(H_2O)_4(p\text{-}sulfonatocalix[4]arene)_2]\cdot 10H_2O$. Dehydrated $Na_4[p$-sulfonatocalix[4]arene] (0.075g, 0.098 mmol), $CuCl_2\cdot 2H_2O$ (0.011g, 6.276 mmol) and pyridine (57 µl, 0.708 mmol) were added to 1.5 mL water and the mixture heated until the solid residue dissolved to yield a dark blue-green solution. This solution was left at room temperature and atmospheric pressure and after a period of several days light green crystals were formed.

(2) $Na_4(morpholinium)(p\text{-}sulfonatocalix[4]arene)\cdot 8H_2O$. Dehydrated $Na_5[p$-sulfonatocalix[4]arene] (0.113 g, 0.136 mmol) was dissolved together with morpholine (0.781 g, 9.08 mmol) in 5.0 mL water at neutral pH. Colorless crystals were formed over a period of ten days.

Crystal structure determination. In each case, a crystal suitable for single crystal X-ray diffraction analysis was sealed with mother liquor into a Lindemann glass capillary and mounted on an Enraf-Nonius CAD4 diffractometer. Intensity data were collected at 293 K using graphite monochromated radiation (Mo-K_α, λ = 0.7107Å). Accurate cell parameters were obtained by least-squares analysis of the setting angles of 25 reflections and the ω-2θ scan mode was used. An empirical absorption correction was applied to the data set for **1**.

The structures were solved by direct methods using SHELXS-86[19] and **1** was refined by the full-matrix least-squares method on F^2 using SHELXL-93[20] while **2** was refined on F using SHELX-76.[21] All non-hydrogen atoms were refined anisotropically with the exception of two water molecules in **2**. The latter were modeled as being disordered over four sites. The site-occupancy factors were deduced from the thermal parameters at full occupancy. Two were fixed at 0.8, one at 0.25 and one at 0.15. Aromatic and methylenic hydrogen atoms were placed in calculated positions and their thermal parameters constrained to 1.2 times that of their parent atoms. Hydroxy hydrogen atoms were placed by modeling the moieties as rigid groups with idealized geometry, maximizing the electron density at the calculated hydrogen positions. No attempt was made to locate water hydrogen atoms. Crystal data, data collection and final refinement parameters are listed in Table 1 and final fractional atomic coordinates, anisotropic thermal parameters, bond lengths and angles and tables of observed and calculated structure factors have been deposited.

Spectral characterization. Several crystals (ca. 10 mg) of **1** were added to 100 mg KBr and the mixture was ground and pressed to form a pellet. Infrared spectra were recorded using a Nicolet Magna IR Spectrometer 550.

Table 1 Crystal data, data collection and final refinement parameters

CRYSTAL DATA		
Compound	**1**	2
Empirical formula	$C_{76}H_{98}O_{50}N_4S_8Na_2Cu_2$	$C_{32}H_{45}O_{25}NS_4Na_4$
Formula weight	2297.12	1063.89
λ (Å)	0.70930	0.70930
Space group	$P\bar{1}$	$P\bar{1}$
Z	1	2
a (Å)	12.3022(6)	11.824(3)
b (Å)	14.7452(6)	13.005(3)
c (Å)	14.9026(9)	15.012(4)
α (°)	68.672(4)	110.13(4)
β (°)	98.821(4)	98.55(4)
γ (°)	76.457(4)	93.68(3)
Volume (Å^3)	2361.7(2)	2127(1)
D_c (gcm^{-3})	1.62	1.66
μ (mm^{-1})	0.74	0.36
F(000)	1190	1104
DATA COLLECTION PARAMETERS		
Crystal dimensions (mm)	0.35 × 0.3 × 0.25	0.20 × 0.25 × 0.30
θ range scanned (°)	1–25	1–22
Range of indices *h,k,l*	±14, 17, ±17	±11, ±13, 15
Overall intensity variation (%)	−12.5	−2.2
No. of unique reflections	8294	5476
No. of observed reflections*	4941	4376
FINAL REFINEMENT PARAMETERS		
Number of variables	647	473
R_1, wR_2† (all data)	0.124, 0.227	0.051, –
R_1*, wR_2*,†	0.064, 0.189	0.048, –
Goodness of fit‡	0.90	1.19

*with $I_{rel} > 2\sigma I_{rel}$ for **1** and $I_{rel} > 3\sigma\ I_{rel}$ for **2**

†$wR_2 = [\sigma(wF_0^2 - F_c^2)^2)/\sigma(w(F_0^2)^2)]^{0.5}$ (reference 20)

‡based on F^2 for **1** and on F for **2**

RESULTS AND DISCUSSION

The atomic labeling scheme adopted for the calixarene anion in both **1** and **2** is shown in Figure 1. The molecular structure of **1** is shown in Figure 2. Two crystallographically unique, octahedrally coordinated copper cations can be distinguished, each occupying a position of $\bar{1}$ site symmetry. Cu(1) is coordinated to four water molecules in the equatorial plane and to O(2B) of two separate *p*-sulfonatocalix[4]arene anions in the axial positions. The latter bond is 2.407(5) Å in length as a result of Jahn-Teller distortion. Cu(2) is coordinated to four water molecules in the equatorial plane and to two pyridine molecules in the axial positions. Jahn-Teller distortion is once again observed, but in this case bond lengthening occurs along Cu(2)-W(4). The calixarene cavity is occupied by a pyridinium cation, the presence of which is confirmed by a band in the infrared spectrum at 1544 cm^{-1} which is assigned to the N_{Ar}-H^+ deformation.[21] Furthermore, five unique water molecules were located during the structure refinement process, in addition to a sodium cation, the latter completing the overall charge balance.

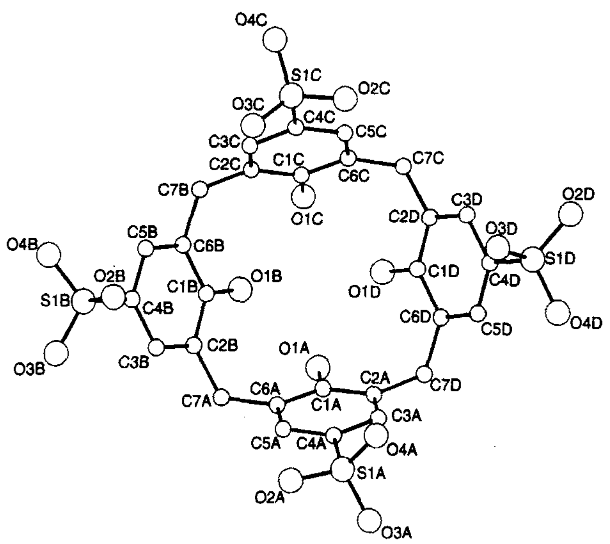

Figure 1 Atomic labeling scheme used for the *p*-sulfonatocalix[4] arene anions.

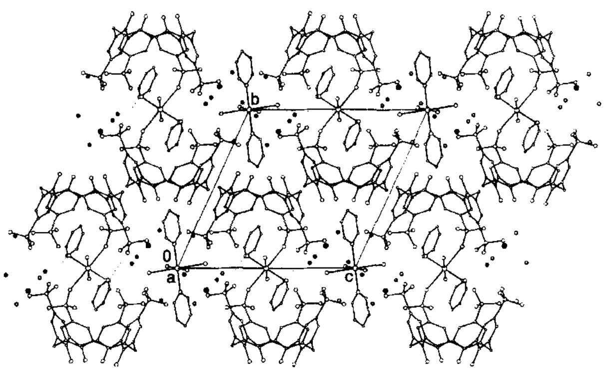

Figure 3 Packing diagram of **1** viewed along [100]. Sodium ions are represented as black circles and water oxygen atoms as grey circles. N-H...O hydrogen bonds are shown as dotted lines.

As seen in Figure 3, the *p*-sulfonatocalix[4]arene anions pack in the familiar bilayer mode. That the structure is stabilized by an extensive hydrogen bonded network is inferred from the many relatively short O...O and O...N contacts listed in Table 2. The two unique copper cations are situated centrally in the hydrophilic layer which also contains the sodium cations and both the coordinated and the free water molecules. The sodium cation is 5-coordinate with Na-O distances ranging from 2.250(6) to 2.55(1) Å. Cu(1) is relatively weakly *trans*-coordinated to two symmetry-related sulfonate oxygen atoms across the hydrophilic layer. The second copper complex, $[Cu(H_2O)_4(NC_5H_5)_2]$, is situated such that the *trans* pyridine moieties are inserted into adjacent hydrophobic layers. The pyridinium cation is positioned in the calixarene cavity with its protonated nitrogen atom protruding into the hydrophilic region. This nitrogen atom, N(1P2), is situated at a distance of 2.84(1)Å from a sulfonate oxygen atom of a calixarene in an adjacent layer, thus forming a hydrogen bond across the hydrophilic layer (see Figure 3).

The structure of **1** has several features in common with previously published structures consisting of a coordinated or protonated pyridine moiety included in the cavity of the *p*-sulfonatocalix[4]arene anion. In order to make comparisons between structures, it is necessary to define the following parameters: (a) ***D***, the distance of

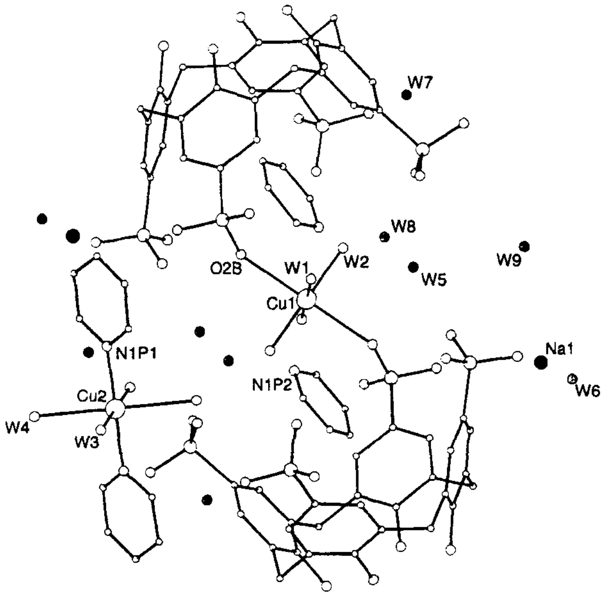

Figure 2 Molecular structure of $Na_2(pyridinium)_2[Cu(H_2O)_4(NC_5H_5)_2][Cu(H_2O)_4(p\text{-sulfonatocalix[4]arene})_2]\cdot 10H_2O$.

Table 2 O ... O and N ... O contacts shorter than 3.3 Å in **1** (values given in Å)

W(1) ... W(2)	2.754(4)	W(1) ... O(2B)	3.182(6)
W(2) ... O(2B)	3.136(7)	W(3) ... N(1P1)	2.814(6)
W(3) ... O(4A)	2.70(1)	W(4) ... N(1P1)	3.216(7)
W(6) ... O(4C)	2.950(9)	W(7) ... O(4D)	2.70(1)
O(1A) ... O(1B)	2.729(7)	O(1A) ... O(1D)	2.817(7)
O(1B) ... O(1C)	2.758(7)	O(1C) ... O(1D)	2.715(7)
W(1) ... W(2)^{a}	2.862(6)	W(1) ... O(2B)^{a}	3.082(7)
W(1) ... O(3B)^{a}	2.704(7)	W(1) ... O(3D)^{b}	2.727(6)
W(2) ... W(5)^{c}	2.722(8)	W(2) ... O(2B)^{a}	3.078(6)
W(2) ... O(2D)^{d}	2.741(5)	W(3) ... W(4)^{e}	3.070(9)
W(3) ... N(1P1)^{e}	2.848(7)	W(3) ... O(4C)^{f}	2.744(6)
W(4) ... W(8)^{g}	3.01(1)	W(4) ... N(1P1)^{e}	3.161(9)
W(4) ... O(3C)^{h}	2.908(8)	W(4) ... O(3D)^{e}	3.246(9)
W(4) ... O(4D)^{e}	3.203(9)	W(5) ... O(2A)^{i}	2.697(6)
W(5) ... O(4B)^{j}	3.272(7)	W(5) ... O(2C)^{k}	2.796(6)
W(6) ... W(7)^{l}	2.77(1)	W(6) ... O(1C)^{k}	2.992(6)
W(6) ... O(1D)^{k}	3.215(8)	W(7) ... W(9)^{f}	3.20(2)
W(7) ... O(1A)^{g}	3.10(2)	W(7) ... O(2A)^{m}	2.76(1)
W(8) ... W(9)^{k}	3.21(2)	W(8) ... O(2B)^{k}	2.89(1)
W(8) ... O(4B)^{k}	3.041(9)	W(9) ... W(9)^{n}	2.87(1)
W(9) ... O(3A)^{l}	3.02(2)	N(1P2) ... O(2C)^{f}	2.84(1)
N(1P2) ... O(3C)^{f}	3.22(1)	O(1A) ... O(3A)^{o}	3.153(9)

Symmetry transformations: $^{a}-x,-y,1-z$; $^{b}1-x,-y,1-z$; $^{c}x,1-y,z$; $^{d}x-1,y,z$; $^{e}1-x,-y,-z$; $^{f}1-x,-y,1-z$; $^{g}1-x,1-y,-z$; $^{h}x,y,z-1$; $^{i}x,y+1,z$; $^{j}-x,1-y,1-z$; $^{k}1-x,1-y,1-z$; $^{l}x,y,z+1$; $^{m}x+1,y,z$; $^{n}-x,-y,2-z$; $^{o}-x,1-y,-z$.

the centroid of the aromatic guest from the plane of the calixarene methylenic carbon atoms, (b) ϕ, the dihedral angle made between the least-squares plane of the aromatic guest and that defined by the methylenic carbon atoms of the calixarene, (c) S_1 and S_2, the S...S *trans* approaches of the sulfonate moieties and (d) O_1, O_2, O_3 and O_4, the O...O distances between adjacent hydroxyl moieties of the host. Inspection of Table 3 reveals that in spite of the variation of the insertion angle of the guest species into the cavity, the depth of penetration remains remarkably constant.

The values of S_1 and S_2 are a measure of the degree of deviation from idealized C_{4v} symmetry of the calixarene (in all cases but one this deviation is marked as the symmetry approaches that of C_{2v}). In each of the previously reported structures described in Table 3, one of the phenolic protons has been removed and the calixarene exists as a 5- anion.[7,13,14] This is consistent with the general pattern of one long and three relatively short distances for O_1 to O_4. In **1** the calixarene is present as a 4- anion and a more symmetrical distribution of these values is observed.

The molecular structure of **2** is shown in Figure 4. In addition to four sodium cations and eight water molecules, the asymmetric unit consists of a [*p*-sulfonatocalix[4]arene]$^{5-}$ anion with a morpholinium cation situated in its cavity. Two of the water molecules are disordered over a total of four sites. The sodium cations are either 5- or 6-coordinate with Na-O bond lengths ranging from 2.017(3) to 2.872(4) Å. Once again the overall structure is stabilized by an extensive network of hydrogen bonds (see Table 4). The morpholinium cation assumes the chair conformation with a CH_2 deepest in the cavity and the NH_2^+ hydrogen bonding to two sulfonate oxygen atoms at N...O separations of 2.767(5) and 2.991(6) Å (this hydrogen bonding mode is facilitated by an O...N...O angle of 117°). As generally observed in previous structures, the cone conformation of the calixarene host is distorted from one of near C_{4v} symmetry to one closer to C_{2v}, and this is evidenced by the parameters S_1 and S_2 listed in Table 3. The bilayer packing arrangement of the structure is shown in Figure 5. Clearly the water molecules are not exclusively confined to the hydrophilic region between the opposing sulfonate head groups which form planes parallel to (001). Instead, interstices are formed between calixarene anions as they pack less efficiently relative to one another and, in order to satisfy space-filling considerations, water molecules and sodium ions occupy these lattice vacancies. There is no significant evidence for the existence of O-H...π hydrogen bonds[11] between any of the water molecules and the outer faces of the aromatic rings of the macrocycle.

Table 3 Geometric parameters in structures of *p*-sulfonatocalix[4]-arene anions with protonated or coordinated pyridine moieties in the cavity (distances are given in Å and angles in °)

D	ϕ	S_1	S_2	O_1	O_2	O_3	O_4	Reference
4.2	69	9.2	11.3	2.73	2.76	2.72	2.82	structure **1**
—	—	9.8	11.2	2.66	2.53	2.53	2.89	structure **2**
4.3	74	8.9	11.4	2.70	2.60	2.67	2.82	13, 14[a]
4.2	91	8.5	11.2	2.63	2.92	2.64	2.93	13, 14[b]
4.0	54	10.0	10.9	2.67	2.55	2.51	2.85	7[c]
4.3	91	8.5	11.3	2.74	2.47	2.56	2.96	7[d]

[a] $Na[(H_2O)_5Ni(NC_5H_5)]_2(C4S)\cdot 3.5H_2O$ (C4S = *p*-sulfonatocalix[4]-arene) [b] $(H_3O)_3[(H_2O)_4Cu(NC_5H_5)_2](C4S)\cdot 10H_2O$ [c] Na_4(pyridinium)(C4S)$\cdot 8H_2O$ [d] $Na_3(H_2O)_3[Cu(NC_5H_5)_2](C4S)\cdot 13H_2O$

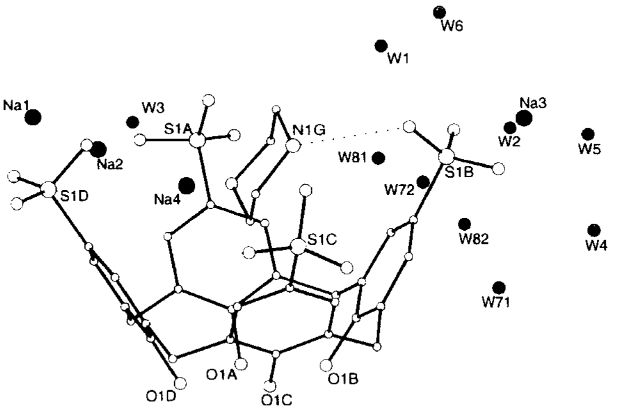

Figure 4 Molecular structure of Na_4(morpholinium)(*p*-sulfonatocalix[4]arene)$\cdot 8H_2O$.

Table 4 O ... O and N ... O contacts shorter than 3.3 Å in **2** (values given in Å).

O(1A) ... O(1B)	2.657(5)	O(1A) ... O(1D)	2.893(5)
O(2A) ... O(3A)	2.411(5)	O(2A) ... O(4A)	2.387(5)
O(3A) ... O(4A)	2.398(5)	O(1B) ... O(1C)	2.527(4)
O(2B) ... O(3B)	2.417(4)	O(2B) ... O(4B)	2.420(5)
O(3B) ... O(4B)	2.410(5)	O(4B) ... W(1)	2.850(4)
O(1C) ... O(1D)	2.531(5)	O(2C) ... O(3C)	2.396(6)
O(2C) ... O(4C)	2.392(5)	O(3C) ... O(4C)	2.410(4)
O(2D) ... O(3D)	2.420(5)	O(2D) ... O(4D)	2.415(5)
O(2D) ... W(3)	3.357(5)	O(2D) ... W(4)	3.477(6)
O(3D) ... O(4D)	2.392(5)	O(3D) ... N(1G)	3.287(6)
O(4D) ... N(1G)	2.767(5)	O(4D) ... W(3)	2.810(5)
W(2) ... W(4)	3.317(5)	W(81) ... W(82)	2.65(4)
O(3A) ... W(1)[a]	2.858(5)	O(4A) ... O(4A)[a]	2.889(4)
O(4A) ... W(1)[a]	3.261(4)	O(2B) ... W(2)[b]	2.892(5)
O(2B) ... W(5)[b]	2.867(5)	O(3B) ... W(5)[a]	2.860(6)
O(3B) ... W(81)[c]	3.21(2)	O(4B) ... O(4C)[d]	3.157(5)
O(4B) ... W(5)[b]	3.291(5)	O(1C) ... W(6)[e]	2.751(5)
O(2C) ... W(72)[c]	3.010(9)	O(2C) ... W(81)[c]	2.58(2)
O(3C) ... W(1)[f]	3.051(6)	O(2D) ... W(81)[g]	3.19(2)
N(1G) ... W(81)[g]	3.00(3)	W(1) ... W(3)[a]	3.175(5)
W(2) ... W(72)[f]	2.83(1)	W(2) ... W(82)[f]	2.74(4)
W(4) ... W(71)[f]	2.84(1)	W(6) ... W(71)[g]	3.244(9)
W(6) ... W(72)[g]	2.89(1)	W(6) ... W(82)[g]	2.54(4)
O(3B) ... N(1G)[h]	2.991(6)	O(2C) ... W(3)[h]	3.190(5)
O(4C) ... W(6)[h]	3.082(6)	O(1D) ... O(3D)[i]	3.227(5)
O(4G) ... W(3)[h]	2.862(4)	W(6) ... O(2D)[j]	2.919(6)

Symmetry transformations: [a] 2 − x,1 − y,−z; [b] x,y,1 − z; [c] x + 1,y,z − 1; [d] x − 1,y,z; [e] x,y − 1,z − 1; [f] x + 1,y,z; [g] 2 − x,1 − y,1 − z; [h] 3 − x,1 − y,−z; [i] 3 − x,−y,−z; [j] 3 − x,1 − y,1 − z.

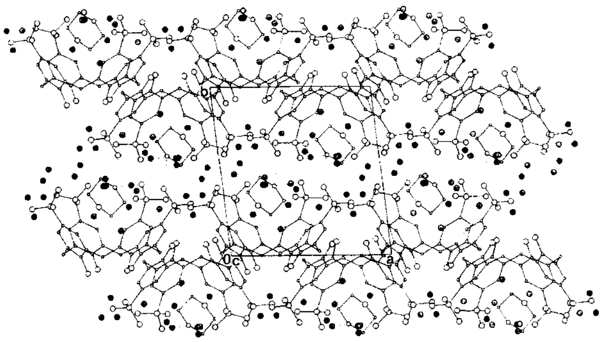

Figure 5 Packing diagram of **2** viewed along [001]. Sodium ions are represented as black circles and water oxygen atoms as grey circles. N-H...O hydrogen bonds are shown as dotted lines.

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