

Structural Variations in Layered Alkali Metal Naphthalenesulfonates

Brian J. Gunderman¹ and Philip J. Squattrito*

Department of Chemistry, Central Michigan University, Mt. Pleasant, Michigan 48859

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A series of alkali metal and ammonium salts of 6-aminonaphthalene-2-sulfonic acid have been prepared by reaction of the metal hydroxide (or ammonia) and the substituted naphthalenesulfonic acid in water or aqueous ethanol. The structures were determined by single-crystal X-ray diffraction techniques. Crystal data: $\text{K}(\text{H}_2\text{NC}_{10}\text{H}_6\text{SO}_3)\cdot\text{H}_2\text{O}$, orthorhombic, *Pca*2₁, $a = 27.139(3)$ Å, $b = 6.172(3)$ Å, $c = 7.135(3)$ Å, $V = 1195(1)$ Å³, $Z = 4$, $R(F_o) = 0.039$ for 659 observations ($I > 3\sigma(I)$), 154 variables; $\text{Na}(\text{H}_2\text{NC}_{10}\text{H}_6\text{SO}_3)\cdot 2\text{H}_2\text{O}$, orthorhombic, *Pna*2₁, $a = 11.200(4)$ Å, $b = 7.916(4)$ Å, $c = 26.752(3)$ Å, $V = 2372(2)$ Å³, $Z = 8$, $R(F_o) = 0.045$ for 1813 observations ($I > 3\sigma(I)$), 325 variables; $\text{NH}_4(\text{H}_2\text{NC}_{10}\text{H}_6\text{SO}_3)\cdot\text{H}_2\text{O}$, orthorhombic, *Pbca*, $a = 12.231(5)$ Å, $b = 26.994(4)$ Å, $c = 7.208(5)$ Å, $V = 2380(2)$ Å³, $Z = 8$, $R(F_o) = 0.056$ for 1145 observations ($I > 3\sigma(I)$), 190 variables. All of the structures contain layers of sulfonate anions in which the long axes of the naphthalene groups are approximately parallel to the stacking direction of the layers. The cations lie between the organic layers bonded to the sulfonate oxygen atoms and one or more water molecules. The structures differ in the detailed packing patterns due to the different sizes and coordination behaviors of the cations. The structure of the monosodium salt of 3-ammonionaphthalene-1,5-disulfonic acid has also been determined: $\text{Na}(\text{H}_3\text{NC}_{10}\text{H}_5(\text{SO}_3)_2)\cdot\text{H}_2\text{O}$, triclinic, *P* $\bar{1}$, $a = 10.823(3)$ Å, $b = 12.885(5)$ Å, $c = 5.127(1)$ Å, $\alpha = 100.33(3)^\circ$, $\beta = 101.65(2)^\circ$, $\gamma = 66.19(2)^\circ$, $V = 636.9(4)$ Å³, $Z = 2$, $R(F_o) = 0.042$ for 1311 observations ($I > 3\sigma(I)$), 223 variables. The sulfonate anions stack face-to-face in infinite columns which are linked into layers by the sodium ions. These layers are held together by hydrogen bonds between the ammonium and sulfonate groups and between water molecules coordinated to the sodium ions. The structures of these compounds are compared with those of previously studied metal sulfonates.

Materials with structures composed of alternating organic and inorganic layers have been of interest during the past few years due to their potential to act as host structures for various chemical processes.² Classes of compounds that have been particularly heavily studied include metal phosphonates^{3–10} and aluminosilicates and other clays.^{11–14} These compounds have two-dimensional metal–oxygen–nonmetal or metal–oxygen–metal frameworks with the organic groups positioned between the layers. The rigid covalent inorganic sheets are thus pillared, or propped apart, by the more weakly interacting organic domains. The size and polarity of the interlayer region can be varied through the use of different organic groups, thus altering the properties of the material.

Our recent studies of metal arenesulfonates^{15–17} showed that the layered structures formed by these compounds differ from

those of analogous phosphonates. In general, the transition metal sulfonates show a much lower tendency to form the sort of rigid covalent network found in the phosphonates and, as a result, the sulfonate structures tend to incorporate much more water bound to the metal ions.^{15,16,18} As might be expected on the basis of size and charge compatibility, alkali metal ions interact well with the sulfonates to form compact layered structures that contain little or no water.¹⁷ Organosulfonates themselves have longstanding industrial applications as surfactants and dyes and have been studied as potential liquid-crystalline¹⁹ and nonlinear optical^{20,21} materials. Prompted by these studies and our own results on arenesulfonates, we have synthesized and structurally characterized a series of alkali metal and ammonium naphthalenesulfonates in order to further probe the structural trends in these materials. The compounds were prepared by reactions of the metal or ammonium hydroxide and 6-aminonaphthalene-2-sulfonic acid or disodium 3-aminonaphthalene-1,5-disulfonate in water. We report here the syntheses and structures of these compounds and discuss their relationships to each other and to previously reported sulfonates.

Experimental Section

Synthesis. $\text{K}(\text{H}_2\text{NC}_{10}\text{H}_6\text{SO}_3)\cdot\text{H}_2\text{O}$. A 0.183 g (2.8 mmol) sample of potassium hydroxide (Mallinckrodt, 85%) was dissolved in 100 mL of distilled water, giving a clear solution. A 0.218 g (0.98 mmol) sample of 6-aminonaphthalene-2-sulfonic acid (Eastman, technical grade) was combined with 50 mL of the potassium hydroxide solution, and the mixture was gently heated and stirred. The solid dissolved

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- (1) American Chemical Society Project SEED II Participant (Clare High School, Clare, MI).
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completely to form a light brown solution. The solution was removed from the heat source and allowed to stand at room temperature in an evaporating dish. After approximately 6 days, the water had evaporated completely, leaving tan, platelike crystals on the bottom and a brown polycrystalline crust on the sides of the evaporating dish. A total of 0.102 g of crystals was isolated, a 37.1% yield based on the reaction $\text{KOH} + \text{H}_3\text{NC}_{10}\text{H}_6\text{SO}_3 \rightarrow \text{K}(\text{H}_2\text{NC}_{10}\text{H}_6\text{SO}_3)\cdot\text{H}_2\text{O}$. Anal. (National Chemical Consulting, Tenafly, NJ). Calcd for $\text{K}(\text{H}_2\text{NC}_{10}\text{H}_6\text{SO}_3)\cdot\text{H}_2\text{O}$: C, 43.00; H, 3.61; N, 5.01. Found: C, 41.08; H, 3.59; N, 4.30. When the reaction was repeated on a larger scale using 0.502 g (9.0 mmol) of KOH and 2.002 g (9.0 mmol) of the sulfonic acid in 50 mL of water, 2.380 g of essentially homogeneous product was recovered (95% yield).

Powder X-ray diffraction patterns of bulk samples (both single crystals and polycrystalline material) of this and subsequent products were recorded on a Rigaku Miniflex diffractometer with Cu K α radiation. In each case, the powder pattern was in good agreement with that calculated from the single-crystal structure and no other phases were evident, indicating that clean acid-base metathesis reactions occurred.

Proton NMR spectra of the sulfonate reagents and products recorded on a General Electric QE-300 spectrometer (D_2O , DSS internal standard) were as expected and showed no alteration of the organic groups in the reactions. Chemical shifts for the naphthalene protons on the 6-aminonaphthalene-2-sulfonate anions were essentially the same for each product: δ (ppm) 7.20 (multiplet, 2 H), 7.73 (d, 1 H, $J(\text{H}-\text{H}) = 6$ Hz), 7.77 (d, 1 H, $J(\text{H}-\text{H}) = 6$ Hz), 7.88 (d, 1 H, $J(\text{H}-\text{H}) = 9$ Hz), 8.21 (s, 1 H).

$\text{Rb}(\text{H}_2\text{NC}_{10}\text{H}_6\text{SO}_3)\cdot\text{H}_2\text{O}$. A 1.212 g (5.9 mmol) sample of a 50 wt % aqueous solution of rubidium hydroxide (Aldrich, 99%) was combined with 25 mL of distilled water, to which was added 1.327 g (5.9 mmol) of 6-aminonaphthalene-2-sulfonic acid. This mixture was heated and stirred while 35 mL of distilled water was added. The solid dissolved slowly to form a dark brown solution. The solution was removed from the heat source and allowed to stand in an open evaporating dish. The water completely evaporated without leaving any suitable crystals. Several different ethanol-water solvent combinations were tried without success. Finally, the solid was redissolved in 40 mL of distilled water and 30 mL of ethanol and transferred to a 100 mL beaker. After approximately 1 week, many large, mauve needlelike crystals had grown in the solution. The crystals (0.253 g) were isolated on a Buchner funnel. Elemental analysis of the crystals is consistent with the formula $\text{Rb}(\text{H}_2\text{NC}_{10}\text{H}_6\text{SO}_3)\cdot\text{H}_2\text{O}$. Anal. Calcd: C, 36.88; H, 3.09; N, 4.30. Found: C, 36.68; H, 3.12; N, 3.83. The filtrate evaporated to leave a polycrystalline brown crust (1.684 g). The powder X-ray pattern of this material is very similar to that of the potassium compound and appears to be single-phase. Thus, the reaction $\text{RbOH} + \text{H}_3\text{NC}_{10}\text{H}_6\text{SO}_3 \rightarrow \text{Rb}(\text{H}_2\text{NC}_{10}\text{H}_6\text{SO}_3)\cdot\text{H}_2\text{O}$ is essentially quantitative.

$\text{Na}(\text{H}_2\text{NC}_{10}\text{H}_6\text{SO}_3)\cdot 2\text{H}_2\text{O}$. A 5 mL sample (30 mmol) of 6 M sodium hydroxide solution was combined with 50 mL of distilled water, to which was added 6.697 g (30 mmol) of 6-aminonaphthalene-2-sulfonic acid. This cloudy mixture was gently heated and stirred, but the solid would not dissolve. A total of 220 mL of distilled water was added to the original solution causing little change. Finally, another 3 mL (18 mmol) of the 6 M NaOH solution was added, and the solid dissolved quickly to form a dark brown solution. The solution was removed from the heat source and allowed to stand at room temperature in an open evaporating dish. After 10 days, several clusters of large, tan, platelike crystals had grown in the solution. The crystals were removed with a spatula and transferred to a Buchner funnel. When the water had completely evaporated a few days later, several more clusters of crystals were isolated, bringing the total yield of crystals to 4.100 g, 48.5% based on the reaction $\text{NaOH} + \text{H}_3\text{NC}_{10}\text{H}_6\text{SO}_3 + \text{H}_2\text{O} \rightarrow \text{Na}(\text{H}_2\text{NC}_{10}\text{H}_6\text{SO}_3)\cdot 2\text{H}_2\text{O}$. Elemental analysis is consistent with the formula obtained from the single-crystal X-ray study. Anal. Calcd: C, 42.70; H, 4.30; N, 4.98. Found: C, 41.25; H, 4.44; N, 4.46. When this reaction was repeated using the same amounts of reagents, 8.664 g of mauve powder was recovered. Presumably, there is some residual NaOH in the product; however the X-ray pattern showed only peaks attributable to the sodium sulfonate salt.

$\text{NH}_4(\text{H}_2\text{NC}_{10}\text{H}_6\text{SO}_3)\cdot\text{H}_2\text{O}$. A 2.006 g (9.0 mmol) sample of 6-aminonaphthalene-2-sulfonic acid was combined with 2 mL (18 mmol) of

Table 1. Crystallographic Data for Alkali Metal and Ammonium Naphthalenesulfonates

$\text{K}(\text{H}_2\text{NC}_{10}\text{H}_6\text{SO}_3)\cdot\text{H}_2\text{O}$	space group: <i>Pca</i> 2 ₁ (No. 29)
$a = 27.139(3)$ Å	$T = 23$ °C
$b = 6.172(3)$ Å	$\lambda = 0.71069$ Å
$c = 7.135(3)$ Å	$\rho_{\text{calcd}} = 1.55$ g cm ⁻³
$V = 1195(1)$ Å ³	$\mu = 6.08$ cm ⁻¹
$Z = 4$	$R(F_o)^a = 0.039$
$fw = 279.35$	$R_w(F_o)^b = 0.032$
$\text{Na}(\text{H}_2\text{NC}_{10}\text{H}_6\text{SO}_3)\cdot 2\text{H}_2\text{O}$	space group: <i>Pna</i> 2 ₁ (No. 33)
$a = 11.200(4)$ Å	$T = 23$ °C
$b = 7.916(4)$ Å	$\lambda = 0.71069$ Å
$c = 26.752(3)$ Å	$\rho_{\text{calcd}} = 1.58$ g cm ⁻³
$V = 2372(2)$ Å ³	$\mu = 3.07$ cm ⁻¹
$Z = 8$	$R(F_o) = 0.045$
$fw = 281.26$	$R_w(F_o) = 0.047$
$\text{NH}_4(\text{H}_2\text{NC}_{10}\text{H}_6\text{SO}_3)\cdot\text{H}_2\text{O}$	space group: <i>Pbca</i> (No. 61)
$a = 12.231(5)$ Å	$T = 23$ °C
$b = 26.994(4)$ Å	$\lambda = 0.71069$ Å
$c = 7.208(5)$ Å	$\rho_{\text{calcd}} = 1.44$ g cm ⁻³
$V = 2380(2)$ Å ³	$\mu = 2.64$ cm ⁻¹
$Z = 8$	$R(F_o) = 0.056$
$fw = 258.29$	$R_w(F_o) = 0.051$
$\text{Na}(\text{H}_3\text{NC}_{10}\text{H}_5(\text{SO}_3)_2)\cdot\text{H}_2\text{O}$	space group: <i>P</i> $\bar{1}$ (No. 2)
$a = 10.823(3)$ Å	$T = 23$ °C
$b = 12.885(5)$ Å	$\lambda = 0.71069$ Å
$c = 5.127(1)$ Å	$\rho_{\text{calcd}} = 1.79$ g cm ⁻³
$\alpha = 100.33(3)^\circ$	$\mu = 4.65$ cm ⁻¹
$\beta = 101.65(2)^\circ$	$R(F_o) = 0.042$
$\gamma = 66.19(2)^\circ$	$R_w(F_o) = 0.045$
$V = 636.9(4)$ Å ³	
$Z = 2$	
$fw = 343.30$	

$$^a R(F_o) = \sum(F_o - F_c) / \sum(F_o)$$

$$^b R_w(F_o) = [\sum w(F_o - F_c)^2 / \sum w(F_o)^2]^{1/2}$$

9 M NH_3 and 50 mL of water. The mixture was gently heated and stirred for approximately 10 min, during which time the sulfonic acid dissolved to give a clear brown solution. This solution was allowed to stand in an open beaker at room temperature until the solvent had completely evaporated (about 1 week). Many tan, platelike crystals formed on the bottom of the beaker, and a polycrystalline crust covered the sides. A total of 2.128 g of solid material was recovered. The powder X-ray diffraction pattern and elemental analysis results on the bulk material are consistent with the formula and structure obtained from the single-crystal X-ray study, indicating that the acid-base reaction $\text{H}_3\text{NC}_{10}\text{H}_6\text{SO}_3 + \text{NH}_3 \rightarrow \text{NH}_4(\text{H}_2\text{NC}_{10}\text{H}_6\text{SO}_3)\cdot\text{H}_2\text{O}$ occurred quantitatively. Anal. Calcd: C, 46.50; H, 5.46; N, 10.85. Found: C, 48.16; H, 5.42; N, 10.33.

$\text{Na}(\text{H}_3\text{NC}_{10}\text{H}_6(\text{SO}_3)_2)\cdot\text{H}_2\text{O}$. A 3.000 g (8.6 mmol) sample of disodium 3-aminonaphthalene-1,5-disulfonate (Eastman Kodak, technical grade) was dissolved in 100 mL of distilled water to form a dark brown solution. A 0.266 g (2.6 mmol) sample of potassium nitrate (Mallinckrodt) was added to the solution. The solid dissolved quickly, causing no change in the color of the solution. The solution was then transferred to a glass evaporating dish and allowed to stand at room temperature. After 13 days, the water evaporated completely leaving clumps of tiny, brown, needlelike crystals on the bottom of the evaporating dish and a lighter tan crust on the sides. The crystals were redissolved in 100 mL of a 50/50 water/ethanol mixture which evaporated after approximately 5 days, leaving dark brown clumps of larger needlelike crystals. A total of 1.902 g of crystals was isolated. It became apparent from the crystal structure analysis that the potassium had not been incorporated into the crystals. The net reaction in this case is the replacement of one sodium ion in the starting salt by a hydrogen ion which protonates the amine group: $\text{Na}_2(\text{H}_2\text{NC}_{10}\text{H}_6(\text{SO}_3)_2) + \text{H}_3\text{O}^+ \rightarrow \text{Na}(\text{H}_3\text{NC}_{10}\text{H}_6(\text{SO}_3)_2)\cdot\text{H}_2\text{O} + \text{Na}^+$. Elemental analysis of the crystals is consistent with the formula derived from the X-ray structure. Anal. Calcd: C, 34.99; H, 2.64; N, 4.08. Found: C, 34.25; H, 2.95; N, 4.39. The ¹H NMR spectrum is consistent with that of the starting material: δ (ppm) 7.80 (t, 1 H, $J(\text{H}-\text{H}) = 7$ Hz), 8.17 (s, 1 H), 8.30 (d, 1 H, $J(\text{H}-\text{H}) = 7$ Hz), 8.82 (s, 1 H), 8.87 (d, 1 H, $J(\text{H}-\text{H}) = 9$ Hz).

Table 2. Positional and Equivalent Isotropic Thermal Parameters

atom	x	y	z	$B_{eq},^a \text{Å}^2$	atom	x	y	z	$B_{eq},^a \text{Å}^2$
K(H₂NC₁₀H₆SO₃)·H₂O									
K(1)	0.28375(6)	0.4541(3)	0.126	3.25(9)	C(3)	0.0972(3)	0.461(1)	0.252(1)	2.9(5)
S(1)	0.17149(7)	0.1873(4)	0.1339(9)	2.6(1)	C(4)	0.0498(3)	0.516(1)	0.287(1)	2.2(4)
O(1)	0.1741(2)	-0.041(1)	0.096(2)	5.2(4)	C(5)	-0.0391(3)	0.423(1)	0.282(1)	2.3(4)
O(2)	0.1998(2)	0.240(1)	0.303(1)	4.5(4)	C(6)	-0.0763(3)	0.276(1)	0.246(1)	2.5(5)
O(3)	0.1866(2)	0.318(1)	-0.024(1)	4.8(4)	C(7)	-0.0642(3)	0.071(1)	0.167(2)	2.7(5)
O(4)	0.2538(4)	0.7692(8)	-0.120(1)	4.3(3)	C(8)	-0.0167(2)	0.014(1)	0.131(2)	2.3(3)
N(1)	-0.1261(2)	0.326(1)	0.281(1)	3.4(4)	C(9)	0.0223(3)	0.161(1)	0.167(2)	2.2(4)
C(1)	0.0721(2)	0.106(1)	0.143(2)	1.9(4)	C(10)	0.0104(3)	0.370(1)	0.246(1)	1.9(4)
C(2)	0.1082(3)	0.251(1)	0.182(1)	2.1(4)					
Na(H₂NC₁₀H₆SO₃)·2H₂O									
S(1)	1.3463(2)	0.2907(3)	0.827	2.07(8)	C(3)	1.4615(7)	0.433(1)	0.7480(3)	2.4(3)
S(2)	0.8547(2)	0.2011(3)	0.98597(8)	2.15(9)	C(4)	1.4770(7)	0.472(1)	0.6988(3)	2.4(3)
Na(1)	1.1055(2)	0.1646(3)	0.9012(1)	2.9(1)	C(5)	1.4185(7)	0.439(1)	0.6097(3)	2.4(3)
Na(2)	0.9107(3)	0.5208(3)	0.9082(2)	3.3(1)	C(6)	1.3453(7)	0.368(1)	0.5743(3)	2.5(3)
O(1)	1.2432(5)	0.1794(7)	0.8328(2)	3.2(3)	C(7)	1.2539(8)	0.257(1)	0.5898(3)	2.6(4)
O(2)	1.3237(5)	0.4583(7)	0.8487(2)	3.5(3)	C(8)	1.2378(7)	0.220(1)	0.6384(3)	2.5(4)
O(3)	1.4552(5)	0.2147(7)	0.8464(2)	3.0(3)	C(9)	1.3126(7)	0.289(1)	0.6758(3)	2.0(3)
O(4)	0.9742(5)	0.1680(8)	0.9669(2)	3.9(3)	C(10)	1.4040(6)	0.4002(9)	0.6615(3)	1.9(3)
O(5)	0.7914(5)	0.3298(7)	0.9565(2)	2.8(2)	C(11)	0.8038(7)	0.228(1)	1.0855(3)	1.9(3)
O(6)	0.7837(4)	0.0473(6)	0.9914(2)	2.7(2)	C(12)	0.8759(6)	0.2812(9)	1.0473(3)	1.9(3)
O(7)	1.1259(4)	0.5017(7)	0.9130(3)	3.9(3)	C(13)	0.9679(7)	0.398(1)	1.0550(3)	2.2(3)
O(8)	0.8970(5)	0.7044(7)	0.8392(3)	3.9(3)	C(14)	0.9887(6)	0.459(1)	1.1026(3)	2.4(3)
O(9)	0.9272(7)	0.7380(8)	0.9684(3)	4.9(3)	C(15)	0.9442(7)	0.456(1)	1.1932(3)	2.5(4)
O(10)	1.1614(5)	-0.1203(7)	0.8890(2)	5.1(4)	C(16)	0.8792(7)	0.396(1)	1.2328(3)	2.4(3)
N(1)	1.3618(7)	0.399(1)	0.5227(2)	3.5(3)	C(17)	0.7844(8)	0.284(1)	1.2240(3)	2.5(4)
N(2)	0.9056(6)	0.441(1)	1.2825(2)	3.4(3)	C(18)	0.7561(7)	0.229(1)	1.1761(3)	2.5(4)
C(1)	1.2959(7)	0.252(1)	0.7274(3)	2.1(4)	C(19)	0.8257(7)	0.286(1)	1.1349(3)	2.0(3)
C(2)	1.3703(6)	0.3240(9)	0.7622(3)	1.9(3)	C(20)	0.9206(6)	0.4010(9)	1.1436(3)	1.9(3)
NH₄(H₂NC₁₀H₆SO₃)·H₂O									
S(1)	0.4324(1)	0.33510(5)	0.2506(2)	3.08(6)	C(3)	0.2962(4)	0.4057(2)	0.4002(8)	2.6(3)
O(1)	0.4441(3)	0.3093(1)	0.4260(6)	4.7(2)	C(4)	0.2671(4)	0.4524(2)	0.4446(8)	2.4(3)
O(2)	0.5363(4)	0.3372(1)	0.1522(7)	5.9(3)	C(5)	0.3041(5)	0.5428(2)	0.4387(8)	2.4(3)
O(3)	0.3459(4)	0.3140(1)	0.1398(6)	5.8(3)	C(6)	0.3686(4)	0.5819(2)	0.3855(7)	2.4(3)
O(4)	0.6216(4)	0.2622(2)	-0.050(1)	12.0(5)	C(7)	0.4645(5)	0.5729(2)	0.2818(8)	2.6(3)
N(1)	0.3392(4)	0.6310(2)	0.4225(8)	3.8(3)	C(8)	0.4952(4)	0.5257(2)	0.2389(8)	2.4(2)
N(2)	0.3087(5)	0.2106(2)	0.251(1)	4.7(3)	C(9)	0.4309(4)	0.4844(2)	0.2924(6)	1.9(2)
C(1)	0.4596(4)	0.4354(2)	0.2500(8)	2.3(2)	C(10)	0.3322(4)	0.4938(2)	0.3946(7)	2.0(2)
C(2)	0.3946(4)	0.3967(2)	0.3023(7)	2.3(3)					
Na(H₃NC₁₀H₅(SO₃)₂)·H₂O									
S(1)	0.8146(2)	0.1999(1)	0.6125(3)	1.85(9)	N(1)	1.3164(5)	-0.0170(4)	1.014(1)	1.6(3)
S(2)	1.4148(1)	0.2336(1)	0.4393(3)	1.66(8)	C(1)	0.9923(6)	0.1753(5)	0.650(1)	1.6(3)
Na	0.5888(2)	0.3273(2)	0.0489(5)	2.6(1)	C(2)	1.0816(6)	0.0934(5)	0.808(1)	1.7(3)
O(1)	0.7653(4)	0.1961(4)	0.3254(8)	2.3(2)	C(3)	1.2207(6)	0.0695(5)	0.840(1)	1.4(3)
O(2)	0.7498(4)	0.3112(4)	0.7566(8)	2.8(3)	C(4)	1.2728(6)	0.1239(5)	0.716(1)	1.5(3)
O(3)	0.8117(4)	0.1060(4)	0.7310(8)	2.8(3)	C(5)	1.2361(6)	0.2702(5)	0.420(1)	1.5(3)
O(4)	1.4717(4)	0.2362(4)	0.7220(8)	2.6(3)	C(6)	1.1477(7)	0.3541(6)	0.267(1)	2.4(4)
O(5)	1.4674(4)	0.1178(3)	0.2986(8)	2.1(2)	C(7)	1.0071(7)	0.3824(6)	0.237(1)	2.9(4)
O(6)	1.4282(4)	0.3183(3)	0.3061(8)	2.5(3)	C(8)	0.9544(7)	0.3266(6)	0.360(1)	2.4(4)
O(7) ^b	0.610(1)	0.472(1)	0.389(2)	4.9(8)	C(9)	1.0415(6)	0.2378(5)	0.519(1)	1.6(3)
O(8) ^b	0.581(2)	0.509(1)	0.219(3)	7(1)	C(10)	1.1851(6)	0.2095(5)	0.552(1)	1.4(3)

^a $B_{eq} = \frac{1}{3}[a^2\beta_{11} + b^2\beta_{22} + c^2\beta_{33} + (2ab \cos \gamma)\beta_{12} + (2ac \cos \beta)\beta_{13} + (2bc \cos \alpha)\beta_{23}]$. ^b Occupancies = 0.5.

Crystallographic Studies. All of the single-crystal X-ray diffraction work was done at room temperature on a Rigaku AFC6S four-circle diffractometer (2.0 kW Mo K α X-ray source; graphite monochromator) operated by the MSC-AFC Diffractometer Control software.²² All crystals were cut from larger fragments and were mounted on glass fibers with silicone cement. Unit cell parameters were obtained from least-squares analyses of the setting angles of 19–25 reflections ($12^\circ < 2\theta(\text{Mo K}\alpha) < 41^\circ$) in which the appropriate cell angles were constrained to their ideal values. Intensity data in the range $3^\circ < 2\theta < 50^\circ$ were collected with ω scans (4°min^{-1}) for the 6-aminonaphthalene-2-sulfonate salts and $\omega-2\theta$ scans (8°min^{-1} in ω) for the 3-aminonaphthalene-1,5-disulfonate salt. Weaker reflections (i.e., those with $I < 10\sigma(I)$) were scanned up to a maximum of four times. The intensities of three standards measured after every 150 data showed no significant decay in any of the experiments. All computations were done on a VAXStation 3100/76 computer with the TEXSAN²³ series

of crystallographic programs. Atomic scattering factors²⁴ and anomalous dispersion terms²⁵ were taken from standard sources. Data were corrected for Lorentz and polarization effects. Absorption (empirical based on ψ scans of three reflections) and secondary extinction²⁶ corrections were applied where warranted. Space groups were determined either uniquely on the basis of systematic absences (*Pbca*, *Okl*, $k \neq 2n$, $h0l$, $l \neq 2n$, $hk0$, $h \neq 2n$) or by a combination of systematic absences and intensity statistics (*Pca2*₁, *Okl*, $l \neq 2n$, $h0l$, $h \neq 2n$; *Pna2*₁, *Okl*, $k + l \neq 2n$, $h0l$, $h \neq 2n$). The assigned space groups were confirmed by successful solutions and refinements. For the noncentrosymmetric structures, refinements of the enantiomers gave essentially the same agreement indices for the unique data sets that were collected.

(23) TEXSAN: Texray Structural Analysis Package; Molecular Structure Corp.: The Woodlands, TX, 1991 (revised).

(24) Cromer, D.; Waber, J. *International Tables for X-ray Crystallography*; The Kynoch Press: Birmingham, England, 1974; Vol. IV, Table 2.2A.

(25) Cromer, D. *International Tables for X-ray Crystallography*; The Kynoch Press: Birmingham, England, 1974; Vol. IV, Table 2.3.1.

(26) Zachariasen, W. *Acta Crystallogr., Sect. A* **1968**, *24*, 212.

(22) MSC/AFC Diffractometer Control Software; Molecular Structure Corp.: The Woodlands, TX, 1988 (revised).

Table 3. Selected Interatomic Distances (Å) and Angles (deg)

$K(H_2NC_{10}H_6SO_3) \cdot H_2O$							
K(1)—O(2)	2.921(8)	K(1)—O(3)	2.76(1)	K(1)—N(1)	3.009(7)	S(1)—O(3)	1.443(9)
K(1)—O(2)	2.691(9)	K(1)—O(4)	2.743(9)	S(1)—O(1)	1.438(6)	S(1)—C(2)	1.795(7)
K(1)—O(3)	2.966(8)	K(1)—O(4)	2.847(9)	S(1)—O(2)	1.469(9)		
O(2)—K(1)—O(2)	106.2(3)	O(2)—K(1)—O(4)	75.8(3)	O(3)—K(1)—O(4)	96.0(3)	O(1)—S(1)—C(2)	107.4(4)
O(2)—K(1)—O(3)	48.3(2)	O(2)—K(1)—N(1)	132.8(3)	O(3)—K(1)—N(1)	169.4(2)	O(2)—S(1)—O(3)	111.6(4)
O(2)—K(1)—O(3)	72.4(2)	O(3)—K(1)—O(3)	120.0(3)	O(1)—S(1)—O(2)	110.4(6)	O(2)—S(1)—C(2)	107.2(5)
O(2)—K(1)—O(4)	111.5(3)	O(3)—K(1)—O(4)	73.0(3)	O(1)—S(1)—O(3)	112.8(7)		
$Na(H_2NC_{10}H_6SO_3) \cdot 2H_2O$							
S(1)—O(1)	1.459(5)	S(2)—O(5)	1.470(5)	Na(1)—O(4)	2.293(6)	Na(2)—O(5)	2.396(6)
S(1)—O(2)	1.466(5)	S(2)—O(6)	1.461(5)	Na(1)—O(5)	2.555(6)	Na(2)—O(7)	2.419(6)
S(1)—O(3)	1.452(5)	S(2)—C(12)	1.774(7)	Na(1)—O(7)	2.696(6)	Na(2)—O(8)	2.356(7)
S(1)—C(2)	1.785(7)	Na(1)—O(1)	2.395(6)	Na(1)—O(10)	2.363(6)	Na(2)—O(9)	2.362(7)
S(2)—O(4)	1.456(6)	Na(1)—O(3)	2.427(6)	Na(2)—O(3)	2.542(6)		
O(1)—S(1)—O(2)	111.8(3)	O(4)—S(2)—C(12)	105.3(3)	O(1)—Na(1)—O(10)	76.8(2)	O(3)—Na(2)—O(8)	87.4(2)
O(1)—S(1)—O(3)	112.3(3)	O(5)—S(2)—O(6)	111.6(3)	O(3)—Na(1)—O(4)	90.8(2)	O(3)—Na(2)—O(9)	164.1(3)
O(1)—S(1)—C(2)	107.8(3)	O(5)—S(2)—C(12)	108.2(3)	O(3)—Na(1)—O(5)	155.2(2)	O(5)—Na(2)—O(7)	119.2(2)
O(2)—S(1)—O(3)	112.6(4)	O(6)—S(2)—C(12)	106.2(3)	O(3)—Na(1)—O(7)	74.9(2)	O(5)—Na(2)—O(8)	140.9(2)
O(2)—S(1)—C(2)	105.8(3)	O(1)—Na(1)—O(3)	88.1(2)	O(3)—Na(1)—O(10)	118.4(2)	O(5)—Na(2)—O(9)	97.8(3)
O(3)—S(1)—C(2)	106.0(3)	O(1)—Na(1)—O(4)	176.5(3)	O(4)—Na(1)—O(5)	94.5(2)	O(7)—Na(2)—O(8)	98.3(2)
O(4)—S(2)—O(5)	112.4(3)	O(1)—Na(1)—O(5)	85.2(2)	O(3)—Na(2)—O(5)	89.9(2)	O(7)—Na(2)—O(9)	86.1(3)
O(4)—S(2)—O(6)	112.6(4)	O(1)—Na(1)—O(7)	89.2(2)	O(3)—Na(2)—O(7)	78.0(2)	O(8)—Na(2)—O(9)	95.2(2)
$NH_4(H_2NC_{10}H_6SO_3) \cdot H_2O$							
S(1)—O(1)	1.451(4)	S(1)—O(3)	1.442(4)	N(2)—O(1)	2.918(9)	N(2)—O(4)	2.804(8)
S(1)—O(2)	1.456(4)	S(1)—C(2)	1.766(5)	N(2)—O(3)	2.941(7)	N(2)—O(3)	2.917(9)
O(1)—S(1)—O(2)	111.0(3)	O(2)—S(1)—O(3)	112.7(3)	O(3)—N(2)—O(1)	129.9(3)	O(4)—N(2)—O(3)	133.0(3)
O(1)—S(1)—O(3)	111.4(3)	O(2)—S(1)—C(2)	107.1(2)	O(3)—N(2)—O(3)	117.0(3)	O(4)—N(2)—O(1)	95.6(3)
O(1)—S(1)—C(2)	107.1(2)	O(3)—S(1)—C(2)	107.2(2)	O(1)—N(2)—O(3)	82.4(2)	O(4)—N(2)—O(3)	74.8(2)
$Na(H_3NC_{10}H_5(SO_3)_2) \cdot H_2O$							
S(1)—O(1)	1.460(4)	S(2)—O(4)	1.456(4)	Na—O(1)	2.383(5)	Na—O(7)	2.37(1)
S(1)—O(2)	1.453(4)	S(2)—O(5)	1.471(4)	Na—O(2)	2.445(5)	Na—O(8)	2.32(1)
S(1)—O(3)	1.462(4)	S(2)—O(6)	1.454(4)	Na—O(4)	2.331(4)	Na—O(8)	2.57(1)
S(1)—C(1)	1.794(6)	S(2)—C(5)	1.782(6)	Na—O(6)	2.433(5)		
O(1)—S(1)—O(2)	112.8(3)	O(4)—S(2)—O(5)	111.7(2)	O(1)—Na—O(2)	91.2(2)	O(2)—Na—O(4)	93.5(2)
O(1)—S(1)—O(3)	112.4(3)	O(4)—S(2)—O(6)	113.0(2)	O(1)—Na—O(4)	111.7(2)	O(2)—Na—O(6)	172.0(2)
O(1)—S(1)—C(1)	106.8(3)	O(4)—S(2)—C(5)	107.3(3)	O(1)—Na—O(6)	87.4(2)	O(2)—Na—O(7)	103.0(3)
O(2)—S(1)—O(3)	113.4(3)	O(5)—S(2)—O(6)	112.9(3)	O(1)—Na—O(7)	86.5(3)	O(2)—Na—O(8)	89.6(4)
O(2)—S(1)—C(1)	106.1(3)	O(5)—S(2)—C(5)	105.4(2)	O(1)—Na—O(8)	107.5(3)	O(2)—Na—O(8)	85.4(4)
O(3)—S(1)—C(1)	104.4(3)	O(6)—S(2)—C(5)	105.9(3)	O(1)—Na—O(8)	170.6(3)	O(4)—Na—O(6)	79.8(2)

All of the structures were solved by direct methods: MITHRIL²⁷ which found the heavy atoms (K, Na, and S) and some of the lighter non-hydrogen atoms (C, N, and O), and DIRDIF²⁸ which found the remaining non-hydrogen atoms. Hydrogen atoms were located on difference electron density maps and were either refined with fixed isotropic thermal parameters or included in fixed positions. Final refinements included anisotropic thermal parameters for all non-hydrogen atoms and were performed on those data with $I > 3\sigma(I)$. For $Na(H_3NC_{10}H_5(SO_3)_2) \cdot H_2O$, two oxygen atoms, representing coordinated water molecules, were found to be only 1 Å apart. The occupancies of these atoms refined to very close to 50%, so they were assigned fixed occupancies of 50% in the final refinement. The final difference electron density maps contained only small random features (maximum and minimum heights 0.58, $-0.63 \text{ e} \cdot \text{Å}^{-3}$). No unusual trends were found in F_o versus F_c as a function of $(\sin \theta)/\lambda$, Miller indices, and F_o . Important crystallographic data for the four compounds are presented in Table 1. Final positional and equivalent isotropic thermal parameters are given in Table 2, while selected interatomic distances and angles appear in Table 3. Full crystallographic details (Table SI), hydrogen atom positions (Table SII), additional bond distances and angles (Table SIII), and anisotropic thermal parameters (Table SIV) are provided as supplementary material.

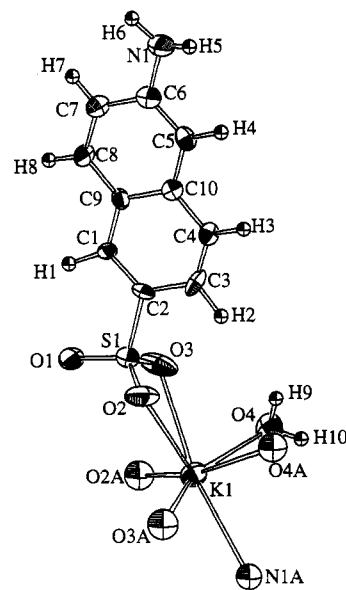


Figure 1. ORTEP diagram of the molecular structure and potassium coordination environment of $K(H_2NC_{10}H_6SO_3) \cdot H_2O$ showing the atom-labeling scheme. In this and subsequent figures, thermal ellipsoids are drawn at the 50% probability level except for those of hydrogen, which are shown as spheres of arbitrary size. Symmetry-equivalent oxygen or nitrogen atoms (designated A, B, or C) attached to the metal atoms are shown as equivalent isotropic spheres.

(27) Gilmore, C. J. *Appl. Crystallogr.* **1984**, *17*, 42.

(28) Beurskens, P. DIRDIF: Direct Methods for Difference Structures. Technical Report 1983/1; Crystallography Laboratory: Toernooiveld, 6525 ED Nijmegen, The Netherlands, 1983.

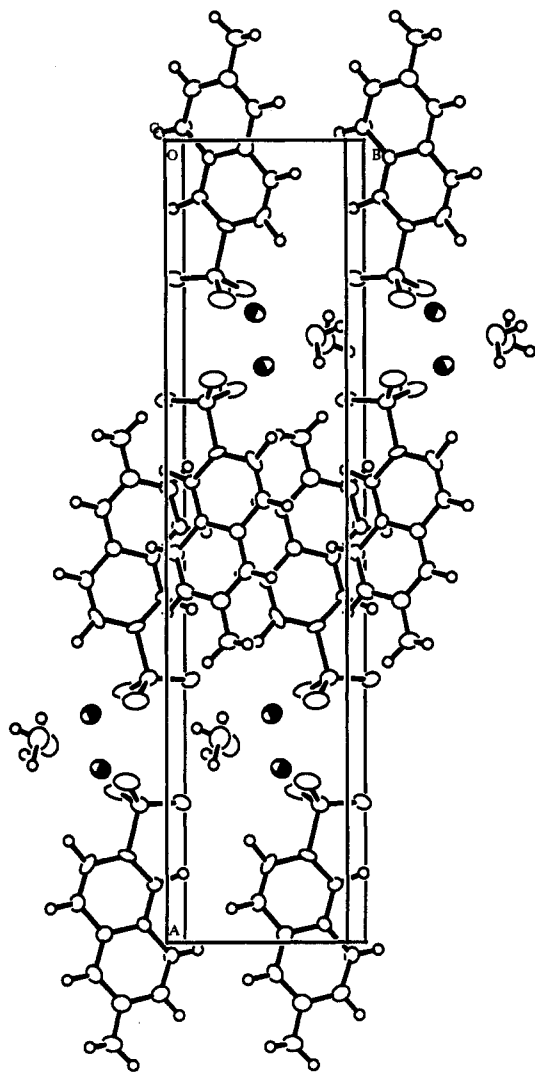


Figure 2. ORTEP packing diagram of $\text{K}(\text{H}_2\text{NC}_{10}\text{H}_6\text{SO}_3)\cdot\text{H}_2\text{O}$ viewed along the c axis. The potassium ions are shown with octant shading, and the bonds to oxygen and nitrogen, omitted.

Results

$\text{K}(\text{H}_2\text{NC}_{10}\text{H}_6\text{SO}_3)\cdot\text{H}_2\text{O}$. The structure (Figures 1 and 2) contains layers of naphthalenesulfonate anions stacked along the a axis with the potassium cations and water molecules between. In this and successive structures, the bond distances and angles for the sulfonate group and the naphthalene rings (provided as supplementary material) are as expected. The anions are arranged vertically within the layer so that the sulfonate groups point into the interlayer region. Half the anions have the sulfonate group "up" and half "down" so that both faces of the layer are ionic and hydrophilic while the interior of the layer is primarily hydrophobic. The interleaving of the anions is such that the amine groups are more toward the interior of the layer than the sulfonate groups. Nevertheless, each amine forms a rather long hydrogen bond to a sulfonate oxygen atom on a neighboring anion within the layer ($\text{N}(1)-\text{H}(5)\cdots\text{O}(3)$, $\text{N}-\text{H}$ distance, $\text{H}\cdots\text{O}$ distance, $\text{N}-\text{H}\cdots\text{O}$ angle: 1.03 Å, 2.24 Å, 137°) and has a bonding interaction (3.009(7) Å) with the potassium ion. The cation sits in a 7-fold coordination sphere containing four sulfonate oxygen atoms and one amine nitrogen atom, from a total of four different anions, and two water molecules. The distances range from 2.691(9) to 3.009(7) Å, and the geometry is irregular. The coordinated water molecule is also hydrogen-bonded to a sulfonate oxygen atom: $\text{O}(4)-\text{H}(9)\cdots\text{O}(1)$ 1.05 Å, 1.91 Å, 156° . As a result of the

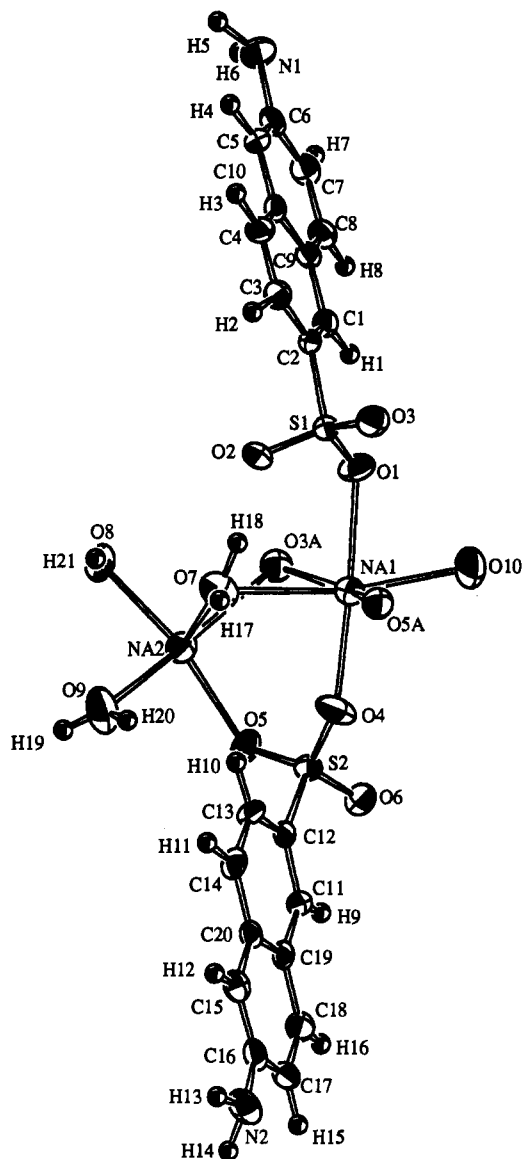


Figure 3. ORTEP diagram of the molecular structure and sodium coordination environments of $\text{Na}(\text{H}_2\text{NC}_{10}\text{H}_6\text{SO}_3)\cdot 2\text{H}_2\text{O}$ showing the atom-labeling scheme.

electrostatic interactions between and within the layers, the small slab-shaped crystals of this material are hard, brittle, and relatively free of stacking defects commonly seen in mixed organic-inorganic layered compounds. It is also of note that this compound crystallizes in the noncentrosymmetric space group $Pca2_1$.

$\text{Rb}(\text{H}_2\text{NC}_{10}\text{H}_6\text{SO}_3)\cdot\text{H}_2\text{O}$. A single-crystal X-ray data set collected in a primitive monoclinic unit cell of dimensions $a = 6.215(5)$ Å, $b = 7.014(3)$ Å, $c = 27.308(3)$ Å, and $\beta = 93.38(3)^\circ$ could be solved in either space group $P2_1$ or $P2_1/n$ and refined down to an R value of about 20%, but no further. In both cases, there were large residual peaks of electron density approximately 1 Å from the Rb atom(s). When larger crystals were examined on the diffractometer, the indexing gave a monoclinic unit cell with the long axis doubled to 54.6 Å, which transformed to a C -centered orthorhombic cell with the long axis doubled again to 109 Å. Weissenberg photographs taken with $\text{Cu K}\alpha$ radiation confirm at least the 54.6 Å length and show the distribution of intense reflections to be consistent with the original monoclinic subcell. The supercell with the 54.6 Å axis would contain 8 formula units. The partial single-crystal structure reveals that the rubidium compound has a layered structure very similar to

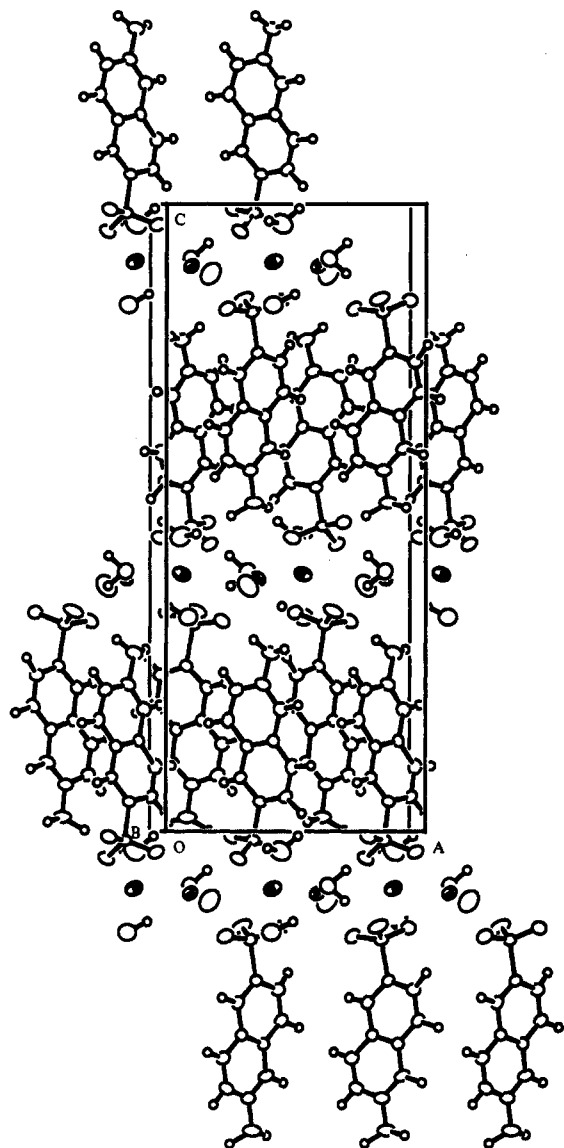


Figure 4. ORTEP packing diagram of $\text{Na}(\text{H}_2\text{NC}_{10}\text{H}_6\text{SO}_3)\cdot 2\text{H}_2\text{O}$ viewed along the b axis. Sodium ions are shown with octant shading, and the bonds to oxygen, omitted.

that of the potassium compound; however apparently the layers stack in a subtly different manner that results in the doubling (or perhaps quadrupling) of the axis in the stacking direction. This difference appears to be reflected in the needle morphology of the crystals, which contrasts with the other salts of the 6-amino-2-naphthalenesulfonate.

$\text{Na}(\text{H}_2\text{NC}_{10}\text{H}_6\text{SO}_3)\cdot 2\text{H}_2\text{O}$. The unit cell and space group of this compound have been reported previously;²⁹ however to our knowledge this is the first complete structure determination. While the structure of this compound (Figures 3 and 4) is similar to that of the potassium salt in that it contains layers of vertically oriented naphthalenesulfonate anions sandwiching cations and water, there are several key differences between the two structures. Perhaps the most obvious is the cation coordination environment. The two symmetry-independent sodium ions adopt distorted octahedral (Na(1)) and trigonal bipyramidal (Na(2)) geometries (Figure 3) in which there are two and three water molecules in the respective coordination spheres. The Na(1) ion bonds to four sulfonate oxygen atoms from different anions and two water molecules (O(7) and O(10)), while Na(2)

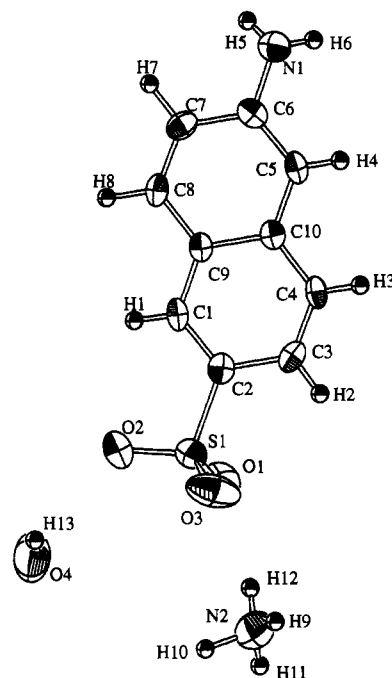


Figure 5. ORTEP diagram of the molecular structure of $\text{NH}_4(\text{H}_2\text{NC}_{10}\text{H}_6\text{SO}_3)\cdot \text{H}_2\text{O}$ showing the atom-labeling scheme.

bonds to sulfonate oxygen atoms from two different anions and three water molecules (O(7), O(8) and O(9)). The sharing of atom O(7) by the cations leads to the ratio of two water molecules per cation. The presence of additional water in the sodium structure follows from the higher hydration energy of the smaller cation. The Na-O distances (Table 3) fall in a very similar range to those observed in other sodium sulfonate salts.^{15,16,30}

The packing diagram (Figure 4) shows that the sodium ions sit almost exactly in the middle of the interlayer space while the potassium ions (Figure 2) are displaced along the stacking direction toward adjacent layers. In addition, the anions adopt a more complicated packing arrangement in the sodium structure. Although half the anions in a given layer have the sulfonate groups up and half down as in the potassium structure, here the nearest pairs of up (or down) anions are related by a glide plane so that the positions of the sulfonate oxygen atoms are inverted. As a result, there are four different orientations of the anions in each layer, which necessitates approximately doubling one of the unit cell axes parallel to the layer. Nevertheless, the 8 formula units in the cell occur as two symmetry-independent variants, maintaining the noncentrosymmetry observed in the potassium structure.

The ionic bonding in the structure is reinforced by hydrogen bonds between the sulfonate groups and hydrogen atoms of the amine ($\text{N}(1)-\text{H}(5)\cdots\text{O}(4)$, 1.19 Å, 2.09 Å, 151°) and water ($\text{O}(7)-\text{H}(17)\cdots\text{O}(6)$, 1.03 Å, 1.85 Å, 147°; $\text{O}(7)-\text{H}(18)\cdots\text{O}(2)$, 1.00 Å, 1.83 Å, 169°). As a result of these interactions, the thin platelike crystals of this material are brittle and do not cleave readily.

$\text{NH}_4(\text{H}_2\text{NC}_{10}\text{H}_6\text{SO}_3)\cdot \text{H}_2\text{O}$. The structure of the ammonium compound (Figures 5 and 6) has features in common with each of the preceding structures. As in the potassium compound, the ammonium cations are displaced toward adjacent layers and there is one water molecule per cation located in a nearby hole. The packing of the anions is more like that found in the sodium compound, with pairs of anions in the up and down positions having the sulfonate oxygen atoms inverted. In this case,

(29) Corbridge, D.; Brown, C.; Wallwork, S. *Acta Crystallogr.* **1966**, *20*, 698.

(30) Brown, C.; Corbridge, D. *Acta Crystallogr.* **1966**, *21*, 485.

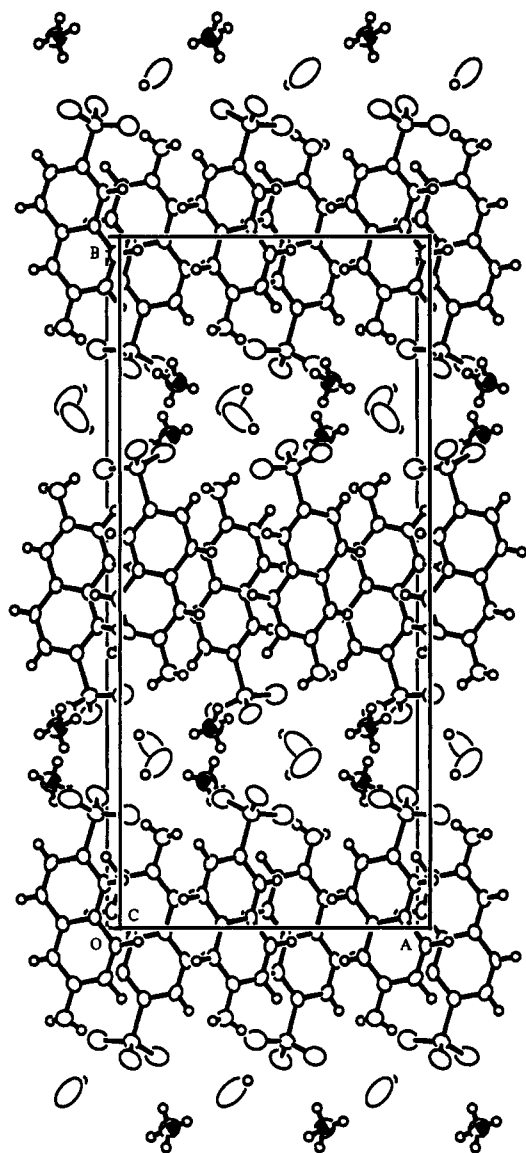


Figure 6. ORTEP packing diagram of $\text{NH}_4(\text{H}_2\text{NC}_{10}\text{H}_6\text{SO}_3)\cdot\text{H}_2\text{O}$ viewed along the c axis. The ammonium nitrogen atoms are shown with octant shading.

however, the four different anion orientations in the layer are related by symmetry and the structure is centrosymmetric.

The ammonium ion is hydrogen-bonded to both the sulfonate group and the water molecule: $\text{N}(2)-\text{H}(10)\cdots\text{O}(1)$, 1.05(6) Å, 1.89(6) Å, 163(5)°; $\text{N}(2)-\text{H}(12)\cdots\text{O}(3)$, 0.88(5) Å, 2.28(6) Å, 132(5)°; $\text{N}(2)-\text{H}(9)\cdots\text{O}(4)$, 0.83(6) Å, 1.99(6) Å, 171(7)°. The closest contact between the amine and sulfonate groups of neighboring anions ($\text{H}(6)\cdots\text{O}(3)$, 2.42(6) Å) is longer than those in the potassium and sodium structures. Though the water molecule is involved in at least one hydrogen bond and is close enough to the sulfonate for another ($\text{O}(4)\cdots\text{O}(2)$, 2.706(7) Å), the large thermal parameter of atom $\text{O}(4)$ indicates that it is not as strongly anchored in this structure as in the others. Nevertheless, the interactions within and between the layers are strong enough that these crystals are similar to those of the potassium and sodium salts in morphology and hardness.

$\text{Na}(\text{H}_3\text{NC}_{10}\text{H}_5(\text{SO}_3)_2)\cdot\text{H}_2\text{O}$. This compound crystallizes as an ammonianaphthalenedisulfonate salt with one sodium ion per anion (Figure 7). There is one water molecule per cation statistically disordered over two positions represented by atoms $\text{O}(7)$ and $\text{O}(8)$. The sodium cation is bonded to four sulfonate oxygen atoms and three half-water molecules at distances from 2.32(1) to 2.57(1) Å. In contrast to the naphthalenemono-

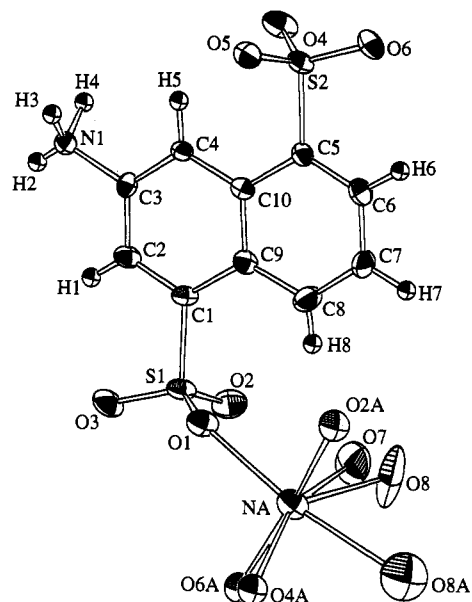


Figure 7. ORTEP diagram of the molecular structure of $\text{Na}(\text{H}_3\text{NC}_{10}\text{H}_5(\text{SO}_3)_2)\cdot\text{H}_2\text{O}$ showing the atom-labeling scheme. Atoms $\text{O}(7)$ and $\text{O}(8)$, representing coordinated water molecules, are present at 50% occupancy.

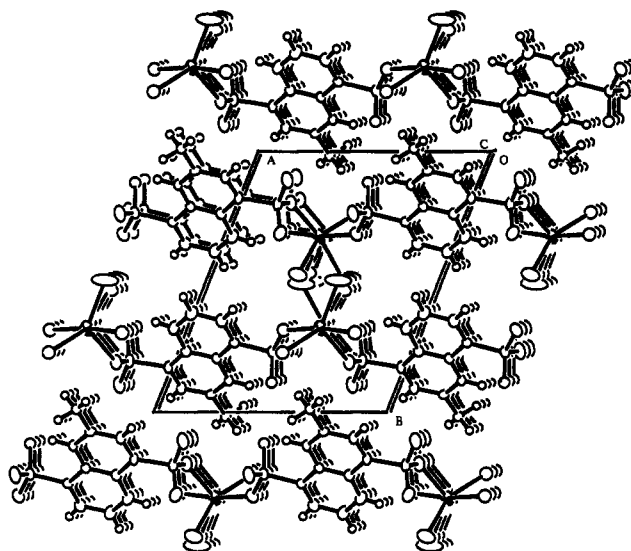


Figure 8. ORTEP packing diagram of $\text{Na}(\text{H}_3\text{NC}_{10}\text{H}_5(\text{SO}_3)_2)\cdot\text{H}_2\text{O}$ viewed along the c axis. The sodium ions are shown with octant shading.

sulfonate structures, the disulfonate anions do not stack vertically in segregated organic layers but rather form infinite columns along the c axis in which they stack face to face (Figure 8). The planes of the naphthalene rings are canted with respect to the stacking axis, so that the closest contacts between adjacent anions, $\text{C}(6)-\text{C}(10)'$ and $\text{C}(7)-\text{C}(9)'$, are shorter (3.8 Å) than the repeat distance along the axis (5.1 Å). These rows of anions are linked in the a direction by the sodium ions and along b by ammonium-sulfonate hydrogen bonds: $\text{N}(1)-\text{H}(2)\cdots\text{O}(3)$, 0.69(6) Å, 2.06(6) Å, 169(7)°; $\text{N}(1)-\text{H}(3)\cdots\text{O}(5)$, 0.96(6) Å, 1.92(6) Å, 158(5)°; $\text{N}(1)-\text{H}(4)\cdots\text{O}(5)$, 1.10(5) Å, 1.83(5) Å, 156(4)°. There may also be hydrogen bonds involving the water molecules, as indicated by a short contact distance (2.78(1) Å) between $\text{O}(6)$ and $\text{O}(7)$, though the hydrogen atoms on the disordered water molecules could not be located. The more one-dimensional nature of this structure is reflected in the needle morphology of the crystals.

Discussion

In a previous study of potassium and rubidium arene-sulfonates,¹⁷ we found that the two alkali metal cations formed isomorphous salts of 4-carboxybenzenesulfonate, while the salts of 4-aminotoluene-2-sulfonate had markedly different structures. In all cases, though, both the relatively symmetric 4-carboxybenzenesulfonate and the unsymmetric 4-aminotoluene-2-sulfonate gave centrosymmetric salts. This work has shown that the sodium, potassium, rubidium and ammonium salts of 6-aminonaphthalene-2-sulfonate all have layered structures that differ subtly in the arrangement of the anions within the layer and in the coordination behavior of the cation. This unsymmetrically substituted sulfonate anion forms both centrosymmetric (NH_4^+) and noncentrosymmetric (Na^+ and K^+) salts. The design of noncentrosymmetric organic salts for nonlinear optical applications is currently an area of active research.^{20,21} One focus in this area concerns the use of organic ions functionalized with hydrogen-bonding groups to try to create noncentrosymmetric ionic packing patterns reinforced by hydrogen bonds. It has been suggested by Marder²⁰ that structures containing alternating layers of organic cations and anions may be more likely to be polar and thus show optical nonlinearities.

Planar, aromatic sulfonate anions show strong tendencies to segregate into layers in salts with both organic^{20,21} and simple inorganic^{15-18,30-34} cations. Among the inorganic sulfonates, noncentrosymmetric structures are found for hexaaquacopper(II) *d*-camphor-10-sulfonate¹⁸ and hexaaquabis(naphthalene-2-sulfonato)praseodymium(III) naphthalene-2-sulfonate tri-

hydrate,³¹ both of which crystallize in the monoclinic space group $P2_1$. In the latter structure, the naphthalene-2-sulfonate anions adopt a packing scheme similar to that of the 6-amino-substituted anions in the structures reported here. By contrast, substantially different packing arrangements are adopted by naphthalenes substituted in the 1-, 4-, 5- or 8-positions. In sodium 1-amino-naphthalene-4-sulfonate tetrahydrate,³⁰ the anions form layers in which the long axis of the naphthalene is parallel to the layer (they are "on their sides", rather than "vertical") with the sulfonate and amine groups directed toward the exterior of the layer. Clearly, the positioning of the sulfonate groups, and to a lesser extent the amine groups, so as to maximize their contacts with the cations and water molecules is the most important driving force in the arrangement of the anions. Indeed, the 3-aminonaphthalene-1,5-sulfonate salt reported here, in which two sulfonate groups are present, has the organic and inorganic ions segregated in one-dimensional columns rather than two-dimensional layers.

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Supplementary Material Available: Table SI (experimental crystallographic details), Table SII (hydrogen atom positions), Table SIII (additional bond distances, angles, and least-squares planes), and Table SIV (anisotropic thermal parameters) (18 pages). Ordering information is given on any current masthead page.

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