

## Synthesis and Structures of Potassium and Rubidium Arenesulfonates

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A series of potassium and rubidium salts of substituted benzenesulfonates have been prepared by reaction of the metal hydroxide and sulfonic acid or sulfonate salt in water or water–ethanol solution. The structures were determined by single-crystal X-ray diffraction techniques. Crystal data:  $K_2(O_2CC_6H_4SO_3)$ , orthorhombic, *Pbca*,  $a = 13.827(2)$  Å,  $b = 7.088(2)$  Å,  $c = 20.536(2)$  Å,  $V = 2013(1)$  Å<sup>3</sup>,  $Z = 8$ ,  $R(F_o) = 0.035$  for 1382 observations ( $I > 3\sigma(I)$ ), 137 variables;  $Rb_{0.81}K_{1.19}(O_2CC_6H_4SO_3)$ , orthorhombic, *Pbca*,  $a = 14.031(3)$  Å,  $b = 7.180(5)$  Å,  $c = 20.656(3)$  Å,  $V = 2081(1)$  Å<sup>3</sup>,  $Z = 8$ ,  $R(F_o) = 0.040$  for 686 observations ( $I > 3\sigma(I)$ ), 138 variables;  $K(HO_2CC_6H_4SO_3) \cdot 2H_2O$ , monoclinic, *P2<sub>1</sub>/a*,  $a = 8.657(5)$  Å,  $b = 9.956(4)$  Å,  $c = 12.912(2)$  Å,  $\beta = 94.94(3)^\circ$ ,  $V = 1108.7(7)$  Å<sup>3</sup>,  $Z = 4$ ,  $R(F_o) = 0.042$  for 1228 observations ( $I > 3\sigma(I)$ ), 146 variables;  $K_3(H_3C(H_2N)C_6H_3SO_3) \cdot 3H_2O$ , monoclinic, *P2<sub>1</sub>/a*,  $a = 11.042(3)$  Å,  $b = 20.930(4)$  Å,  $c = 13.457(2)$  Å,  $\beta = 95.08(2)^\circ$ ,  $V = 3098(1)$  Å<sup>3</sup>,  $Z = 4$ ,  $R(F_o) = 0.043$  for 2752 observations ( $I > 3\sigma(I)$ ), 379 variables;  $Rb(H_3C(H_2N)C_6H_3SO_3)$ , orthorhombic, *Pbca*,  $a = 10.977(4)$  Å,  $b = 7.670(3)$  Å,  $c = 22.591(3)$  Å,  $V = 1902(2)$  Å<sup>3</sup>,  $Z = 8$ ,  $R(F_o) = 0.044$  for 709 observations ( $I > 3\sigma(I)$ ), 118 variables. All of the structures contain alternating layers of metal cations and sulfonate anions. There is direct bonding between the metal ion and the sulfonate oxygen atoms in each structure, with additional coordination to carboxylate, amine or water. The coordination numbers of the cations vary from six to eight and the geometries are irregular. The anhydrous dipotassium and mixed Rb–K 4-carboxybenzenesulfonate salts are isostructural while the monopotassium 4-carboxybenzenesulfonate dihydrate has a distinct structure. In the case of the 4-aminotoluene-2-sulfonate, the potassium and rubidium compounds have very different structures. The structures are compared with those of reported metal sulfonates and phosphonates in terms of the trends in coordination behavior of the metals towards the anions.

### Introduction

Mixed inorganic–organic compounds with layered structures have been of interest due to their potential applications in chemical separations and catalysis.<sup>2,3</sup> Much of the work in this area has involved organically functionalized clays<sup>4–7</sup> and metal phosphonates.<sup>8–18</sup> The latter materials contain infinite two-dimensional M–O<sub>3</sub>P sheets with the organic groups on the phosphorus directed above and below the metal–oxygen–phosphorus framework. The resulting structures have rigid covalent inorganic layers separated by weakly interacting organic domains. The use of different organic groups changes the size and hydrophobic nature of the interlayer region and the physical properties of the material. Recently, we undertook a comparative study of metal organosulfonates with the original goal of producing structural analogs

of the reported phosphonates.<sup>19,20</sup> The initial results showed significant differences between the phosphonates and sulfonates of divalent transition metals, while those of alkali and alkaline earth metals were found to be more similar in terms of the coordination behavior of the metals toward the anions. As a continuation of this work, we have synthesized and structurally characterized several potassium and rubidium arenesulfonates. All of the compounds were prepared by reactions of metal hydroxides with potassium 4-carboxybenzenesulfonate or 4-aminotoluene-2-sulfonic acid in aqueous solution. We report here the syntheses and structures of these compounds and discuss their relationship to the reported phosphonates and sulfonates.

### Experimental Section

**Synthesis.**  $K_2(O_2CC_6H_4SO_3)$ . A 0.503-g sample of potassium hydroxide (Mallinckrodt, 85%) was dissolved in 25 mL of distilled water and 5 mL of absolute ethanol, giving a clear solution. This solution was heated gently while 2.168 g of potassium 4-carboxybenzenesulfonate,  $K(HO_2CC_6H_4SO_3)$  (Aldrich, 98%), was added. The potassium 4-carboxybenzenesulfonate dissolved slowly to form a clear solution. The solution was then removed from the heat source and allowed to stand in an open beaker. After approximately 10 days the solvent had completely evaporated, and numerous small, colorless, platelike crystals had formed on the bottom of the beaker while a white polycrystalline residue coated the sides. A total of 0.923 g of crystals was isolated (the powder was discarded), which represents a 43.5% yield based on the acid-base reaction  $K(HO_2CC_6H_4SO_3) + KOH \rightarrow K_2(O_2CC_6H_4SO_3) + H_2O$ .

Proton NMR spectra of the sulfonate starting materials and products for this and subsequent reactions recorded on a General Electric QE-300 spectrometer (D<sub>2</sub>O, DSS internal standard) were as expected and showed no evidence of any involvement of the organic groups in the reactions. Chemical shifts for the protons on the sulfonate anions are reported for each product. For  $K_2(O_2CC_6H_4SO_3)$ :  $\delta$  (ppm) 7.88 (d, 2 H,  $J(H-H) = 7$  Hz), 8.07 (d, 2 H,  $J(H-H) = 7$  Hz).

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Powder X-ray diffraction patterns of bulk samples of each product were recorded on a Rigaku Miniflex diffractometer with Cu K $\alpha$  radiation. In each case, the powder pattern was consistent with the structure determined in the single crystal analysis. There were no other phases evident, except for small amounts of starting materials in some cases.

**Rb<sub>0.81</sub>K<sub>1.19</sub>(O<sub>2</sub>CC<sub>6</sub>H<sub>4</sub>SO<sub>3</sub>).** A 4.692-g sample of potassium 4-carboxybenzenesulfonate was mixed with 25 mL of distilled water and 5 mL of absolute ethanol with heating and stirring. With the solid acid only partially dissolved, 2.5 mL of a 50 wt. % aqueous solution of rubidium hydroxide (2.18 g RbOH) (Aldrich, 99%) was added to the mixture. Heating and stirring was continued until the potassium 4-carboxybenzenesulfonate was nearly all dissolved. The slightly cloudy solution was then gravity filtered to remove any solids that still remained. The resulting clear, colorless solution was allowed to stand at room temperature in an open container. A week later, most of the solvent had evaporated, and numerous small colorless, blocky crystals had formed in the bottom of the beaker. The crystals (2.248 g) were isolated by filtration. Elemental analysis of a bulk sample of the crystals (Galbraith Laboratories, Knoxville, TN) gave a composition in good agreement with that obtained from the single-crystal X-ray analysis. Anal. Calcd for Rb<sub>0.81</sub>K<sub>1.19</sub>(O<sub>2</sub>CC<sub>6</sub>H<sub>4</sub>SO<sub>3</sub>): Rb, 21.91; K, 14.73. Found: Rb, 21.74; K, 13.86. <sup>1</sup>H NMR:  $\delta$  (ppm) 7.84 (d, 2 H,  $J$ (H-H) = 8 Hz), 7.95 (d, 2 H,  $J$ (H-H) = 8 Hz).

**K(HO<sub>2</sub>CC<sub>6</sub>H<sub>4</sub>SO<sub>3</sub>) $\cdot$ 2H<sub>2</sub>O.** A 1.003-g sample of potassium hydroxide was dissolved in 20 mL of distilled water and 40 mL of absolute ethanol. This clear solution was heated gently and stirred while a 4.332-g sample of potassium 4-carboxybenzenesulfonate was added. When all the solid had dissolved, the solution was removed from the heat source and allowed to stand. The solvent evaporated completely without any crystal growth; only a white, powdery residue remained. The solid was redissolved in 60 mL of distilled water. After 1 week several large, colorless, slab-shaped crystals had grown at the bottom of the solution. These crystals (0.441 g) were isolated from the solvent by filtration. This product is the dihydrate of the starting potassium sulfonate salt. <sup>1</sup>H NMR:  $\delta$  (ppm) 7.90 (d, 2 H,  $J$ (H-H) = 7 Hz), 8.11 (d, 2 H,  $J$ (H-H) = 7 Hz). Efforts to produce salts of the 4-carboxybenzenesulfonate with divalent transition metals (Co<sup>2+</sup> and Ni<sup>2+</sup>) also yielded crystals of K(HO<sub>2</sub>CC<sub>6</sub>H<sub>4</sub>SO<sub>3</sub>) $\cdot$ 2H<sub>2</sub>O, as identified by single-crystal X-ray diffraction. In neither case was the transition metal incorporated into the structure.

**K<sub>3</sub>(H<sub>3</sub>C(H<sub>2</sub>N)C<sub>6</sub>H<sub>3</sub>SO<sub>3</sub>)<sub>3</sub> $\cdot$ 3H<sub>2</sub>O.** A 0.998-g sample of 4-aminotoluene-2-sulfonic acid (Eastman Kodak) was mixed with 50 mL of distilled water to form a tan, cloudy solution. To this mixture was added a clear solution of 0.492 g of KOH in 25 mL of distilled water. The resulting solution remained cloudy and was gravity filtered. The clear tan filtrate was then placed in an open beaker. Approximately 2 weeks later, the solvent had completely evaporated. A thin layer of a dark brown substance covered the bottom of the beaker. No crystals were found in the sample, so it was redissolved in 25 mL of distilled water and 5 mL of ethanol while heating gently. Once the solid was completely dissolved, the solution was removed from the heat source. After approximately 10 days, the solvent had completely evaporated, leaving large, brown, needlelike crystals at the bottom of the beaker. A total of 0.952 g of crystals was recovered, representing a yield of 73.2% based on the reaction 3KOH + 3H<sub>3</sub>C(H<sub>2</sub>N)C<sub>6</sub>H<sub>3</sub>SO<sub>3</sub>  $\rightarrow$  K<sub>3</sub>(H<sub>3</sub>C(H<sub>2</sub>N)C<sub>6</sub>H<sub>3</sub>SO<sub>3</sub>)<sub>3</sub> $\cdot$ 3H<sub>2</sub>O. <sup>1</sup>H NMR:  $\delta$  (ppm) 2.46 (s, 3 H), 4.80 (s, 2 H), 6.88 (d, 1 H,  $J$ (H-H) = 8 Hz), 7.16 (d, 1 H,  $J$ (H-H) = 8 Hz), 7.30 (s, 1 H).

**Rb(H<sub>3</sub>C(H<sub>2</sub>N)C<sub>6</sub>H<sub>3</sub>SO<sub>3</sub>).** A 15.917-g sample of 4-aminotoluene-2-sulfonic acid was dissolved in 35 mL of distilled water and 10 mL of ethanol with heating and stirring. The solution was light brown and cloudy at this time. When 10 mL of 50 wt % aqueous rubidium hydroxide (8.73 g of RbOH) was added, the mixture became dark brown and less cloudy. It was then gravity filtered to remove any undissolved solids. The clear brown filtrate was allowed to stand in an open beaker at room temperature. After 1 week, several large, light brown, irregularly-shaped blocky crystals had grown on the sides and bottom of the beaker. These crystals were isolated by filtration and the filtrate was then allowed to evaporate further. One week later several more crystals had grown in the solution. These crystals were also isolated by filtration. The total mass of the crystals was 8.732 g, a 37.8% yield from the reaction H<sub>3</sub>C(H<sub>2</sub>N)C<sub>6</sub>H<sub>3</sub>SO<sub>3</sub> + RbOH  $\rightarrow$  Rb(H<sub>3</sub>C(H<sub>2</sub>N)C<sub>6</sub>H<sub>3</sub>SO<sub>3</sub>) + H<sub>2</sub>O. <sup>1</sup>H NMR:  $\delta$  (ppm) 2.46 (s, 3 H), 4.80 (s, 2 H), 6.88 (d, 1 H,  $J$ (H-H) = 8 Hz), 7.16 (d, 1 H,  $J$ (H-H) = 8 Hz), 7.30 (s, 1 H).

**Crystallographic Studies.** All of the single crystal X-ray diffraction work was done at room temperature on a Rigaku AFC6S four-circle

**Table 1.** Crystallographic Data for Potassium and Rubidium Arenesulfonates

K <sub>2</sub> (O <sub>2</sub> CC <sub>6</sub> H <sub>4</sub> SO <sub>3</sub> ) $a = 13.827(2)$ Å $b = 7.088(2)$ Å $c = 20.536(2)$ Å $V = 2013(1)$ Å <sup>3</sup> $Z = 8$ fw = 278.36	space group: <i>Pbca</i> (No. 61) $T = 21$ °C $\lambda = 0.71069$ Å $\rho_{\text{calcd}} = 1.84$ g·cm <sup>-3</sup> $\mu = 11.31$ cm <sup>-1</sup> $R(F_o) = 0.035$ $R_w(F_o) = 0.038$
Rb <sub>0.81</sub> K <sub>1.19</sub> (O <sub>2</sub> CC <sub>6</sub> H <sub>4</sub> SO <sub>3</sub> ) $a = 14.031(3)$ Å $b = 7.180(5)$ Å $c = 20.656(3)$ Å $V = 2081(1)$ Å <sup>3</sup> $Z = 8$ fw = 315.93	space group: <i>Pbca</i> (No. 61) $T = 21$ °C $\lambda = 0.71069$ Å $\rho_{\text{calcd}} = 2.02$ g·cm <sup>-3</sup> $\mu = 50.77$ cm <sup>-1</sup> $R(F_o) = 0.040$ $R_w(F_o) = 0.032$
K(HO <sub>2</sub> CC <sub>6</sub> H <sub>4</sub> SO <sub>3</sub> ) $\cdot$ 2H <sub>2</sub> O $a = 8.657(5)$ Å $b = 9.956(4)$ Å $c = 12.912(2)$ Å $\beta = 94.94(3)^\circ$ $V = 1108.7(7)$ Å <sup>3</sup> $Z = 4$ fw = 276.30	space group: <i>P2<sub>1</sub>/a</i> (No. 14) $T = 21$ °C $\lambda = 0.71069$ Å $\rho_{\text{calcd}} = 1.66$ g·cm <sup>-3</sup> $\mu = 6.70$ cm <sup>-1</sup> $R(F_o) = 0.042$ $R_w(F_o) = 0.044$
K <sub>3</sub> (H <sub>3</sub> C(H <sub>2</sub> N)C <sub>6</sub> H <sub>3</sub> SO <sub>3</sub> ) <sub>3</sub> $\cdot$ 3H <sub>2</sub> O $a = 11.042(3)$ Å $b = 20.930(4)$ Å $c = 13.457(2)$ Å $\beta = 95.08(2)^\circ$ $V = 3098(1)$ Å <sup>3</sup> $Z = 4$ fw = 729.96	space group: <i>P2<sub>1</sub>/a</i> (No. 14) $T = 21$ °C $\lambda = 0.71069$ Å $\rho_{\text{calcd}} = 1.57$ g·cm <sup>-3</sup> $\mu = 6.91$ cm <sup>-1</sup> $R(F_o) = 0.043$ $R_w(F_o) = 0.042$
Rb(H <sub>3</sub> C(H <sub>2</sub> N)C <sub>6</sub> H <sub>3</sub> SO <sub>3</sub> ) $a = 10.977(4)$ Å $b = 7.670(3)$ Å $c = 22.591(3)$ Å $V = 1902(2)$ Å <sup>3</sup> $Z = 8$ fw = 271.67	space group: <i>Pbca</i> (No. 61) $T = 21$ °C $\lambda = 0.71069$ Å $\rho_{\text{calcd}} = 1.90$ g·cm <sup>-3</sup> $\mu = 52.49$ cm <sup>-1</sup> $R(F_o) = 0.044$ $R_w(F_o) = 0.039$

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

diffractometer (2.0 kW, Mo K $\alpha$ , graphite monochromator) operated by the MSC-AFC Diffractometer Control software.<sup>21</sup> 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 15–23 high angle reflections ( $20^\circ < 2\theta(\text{Mo K}\alpha) < 50^\circ$ ) in which the  $90^\circ$  cell angles were constrained to their ideal value. Intensity data in the range  $3^\circ < 2\theta < 50^\circ$  were collected with  $\omega$  scans of constant speed (either 4 or 8°·min<sup>-1</sup>) with reflections having  $I < 10\sigma(I)$  scanned up to a maximum of four times. The intensities of three standards measured at 150 reflection intervals remained constant within experimental error in all of the experiments. Crystallographic computations were performed on a VAXStation 3100/76 computer with the TEXSAN<sup>22</sup> series of crystallographic programs. Atomic scattering factors<sup>23</sup> and anomalous dispersion terms<sup>24</sup> were taken from standard sources. Data were corrected for Lorentz and polarization effects. Absorption (empirical based on  $\psi$  scans of three reflections) and secondary extinction corrections were applied where warranted. Space groups were uniquely determined on the basis of systematic absences (*Pbca*,  $0kl$ ,  $k \neq 2n$ ,  $h0l$ ,  $l \neq 2n$ ,  $hk0$ ,  $h \neq 2n$ ; *P2<sub>1</sub>/a*,  $h0l$ ,  $h \neq 2n$ ,  $0k0$ ,  $k \neq 2n$ ) and were confirmed by satisfactory refinements. All of the structures were solved by direct methods. The heavy atoms (Rb, K, and S) were located on *E* maps calculated by the program MITHRIL<sup>25</sup> and most of the lighter non-hydrogen atoms (O, N, and C) were revealed by the direct-methods

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

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Table 2. Positional and Equivalent Isotropic Thermal Parameters

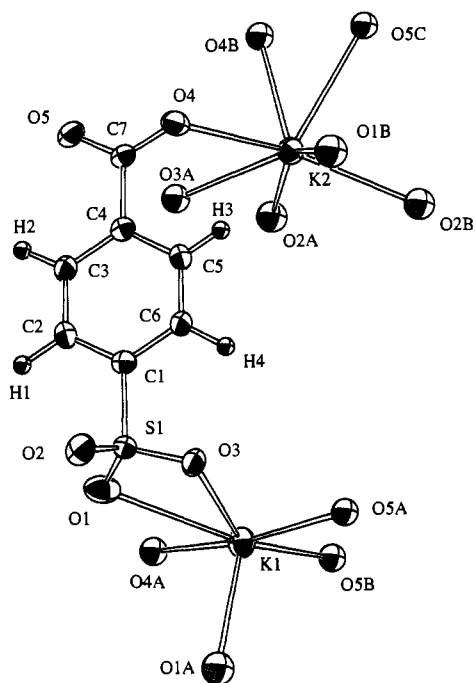
atom	x	y	z	$B_{eq}, \text{\AA}^2$	atom	x	y	z	$B_{eq}, \text{\AA}^2$
<b><math>K_2(O_2CC_6H_4SO_3)</math></b>									
K(1)	0.62826(6)	-0.0119(1)	0.44405(4)	2.52(4)	C(1)	0.3855(2)	0.0592(5)	0.3039(2)	1.8(2)
K(2)	0.61798(6)	0.0507(1)	0.05687(4)	2.25(4)	C(2)	0.3221(3)	-0.0743(5)	0.2784(2)	2.3(2)
S(1)	0.39337(7)	0.0953(1)	0.38943(4)	1.82(4)	C(3)	0.3151(3)	-0.0956(5)	0.2115(2)	2.1(2)
O(1)	0.4131(2)	-0.0869(4)	0.4183(1)	3.4(1)	C(4)	0.3707(3)	0.0142(5)	0.1696(2)	1.7(1)
O(2)	0.3012(2)	0.1755(4)	0.4097(1)	3.0(1)	C(5)	0.4340(3)	0.1455(5)	0.1961(2)	2.2(2)
O(3)	0.4731(2)	0.2248(4)	0.3999(1)	2.5(1)	C(6)	0.4416(3)	0.1696(5)	0.2630(2)	2.1(2)
O(4)	0.4115(2)	0.1074(4)	0.0622(1)	2.4(1)	C(7)	0.3638(2)	-0.0082(5)	0.0961(2)	1.7(2)
O(5)	0.3107(2)	-0.1371(4)	0.0743(1)	2.3(1)					
<b><math>Rb_{0.81}K_{1.19}(O_2CC_6H_4SO_3)</math></b>									
Rb(1) <sup>b</sup>	0.6277(1)	-0.0146(2)	0.44284(7)	2.60(7)	O(5)	0.3133(6)	-0.138(1)	0.0744(4)	2.6(4)
K(1)	0.6277	-0.0146	0.4428	2.6	C(1)	0.3839(9)	0.058(1)	0.3017(4)	1.7(5)
Rb(2) <sup>c</sup>	0.6184(2)	0.0495(3)	0.0588(1)	2.3(1)	C(2)	0.3222(8)	-0.076(2)	0.2773(6)	2.5(6)
K(2)	0.6184	0.0495	0.0588	2.3	C(3)	0.3157(8)	-0.097(2)	0.2097(6)	2.5(6)
S(1)	0.3912(3)	0.0927(4)	0.3879(1)	2.2(1)	C(4)	0.374(1)	0.014(2)	0.1699(5)	1.8(5)
O(1)	0.4129(6)	-0.089(1)	0.4162(4)	4.0(5)	C(5)	0.434(1)	0.143(2)	0.1945(6)	2.5(6)
O(2)	0.2990(5)	0.168(1)	0.4068(3)	3.1(4)	C(6)	0.4409(9)	0.165(2)	0.2626(6)	2.3(6)
O(3)	0.4697(5)	0.223(1)	0.3975(4)	2.7(4)	C(7)	0.367(1)	-0.011(2)	0.0954(5)	2.3(6)
O(4)	0.4160(5)	0.099(1)	0.0622(4)	2.7(4)					
<b><math>K(HO_2CC_6H_4SO_3) \cdot 2H_2O</math></b>									
K(1)	0.3666(1)	0.2334(1)	-0.04038(9)	3.30(6)	O(7)	0.4252(4)	0.4822(4)	-0.1467(3)	3.5(2)
S(1)	0.1466(2)	0.3912(1)	0.1445(1)	2.68(6)	C(1)	0.2129(6)	0.3853(5)	0.2784(3)	2.4(2)
O(1)	0.1473(4)	0.2543(4)	0.1056(2)	3.4(2)	C(2)	0.3296(7)	0.2970(6)	0.3116(4)	3.4(3)
O(2)	0.2565(5)	0.4759(4)	0.0961(3)	4.2(2)	C(3)	0.3877(7)	0.2971(6)	0.4152(4)	3.7(3)
O(3)	-0.0090(4)	0.4480(4)	0.1375(3)	4.1(2)	C(4)	0.3267(6)	0.3845(5)	0.4854(4)	2.8(2)
O(4)	0.4925(5)	0.3029(4)	0.6290(3)	4.9(2)	C(5)	0.2113(7)	0.4719(6)	0.4510(4)	3.7(3)
O(5)	0.3199(5)	0.4628(4)	0.6572(3)	4.6(2)	C(6)	0.1548(7)	0.4737(6)	0.3472(4)	3.6(3)
O(6)	0.1109(4)	0.2863(4)	-0.1716(2)	3.7(2)	C(7)	0.3891(7)	0.3785(6)	0.5971(4)	3.6(3)
<b><math>K_3(H_3C(H_2N)C_6H_3SO_3)_3 \cdot 3H_2O</math></b>									
K(1)	0.0902(1)	0.17750(7)	0.0856(1)	3.25(7)	C(1)	0.2982(5)	0.3221(3)	0.3544(4)	2.3(3)
K(2)	-0.2907(1)	0.13393(7)	-0.0060(1)	3.95(8)	C(2)	0.2215(5)	0.3725(3)	0.3715(4)	2.9(3)
K(3)	0.4470(1)	0.15189(7)	0.1693(1)	3.57(7)	C(3)	0.2277(7)	0.4026(3)	0.4633(5)	3.6(4)
S(1)	0.2854(1)	0.28643(8)	0.2333(1)	2.61(7)	C(4)	0.3135(7)	0.3819(3)	0.5370(5)	4.4(4)
S(2)	-0.1204(1)	0.26989(8)	-0.0718(1)	2.65(7)	C(5)	0.3909(7)	0.3329(3)	0.5184(5)	4.3(4)
S(3)	0.2756(1)	0.02044(8)	0.1982(1)	2.94(8)	C(6)	0.3871(6)	0.3007(3)	0.4279(5)	3.2(3)
O(1)	0.3998(4)	0.2971(2)	0.1907(3)	3.8(2)	C(7)	0.4764(6)	0.2476(4)	0.4130(5)	4.6(4)
O(2)	0.1832(4)	0.3177(2)	0.1771(3)	3.9(2)	C(8)	-0.1414(5)	0.2970(3)	-0.1982(4)	2.3(3)
O(3)	0.2625(4)	0.2185(2)	0.2465(3)	4.0(2)	C(9)	-0.0813(5)	0.3517(3)	-0.2218(4)	2.6(3)
O(4)	-0.0213(4)	0.3075(2)	-0.0226(3)	3.9(2)	C(10)	-0.0919(6)	0.3756(3)	-0.3188(5)	3.5(3)
O(5)	-0.0879(4)	0.2022(2)	-0.0760(3)	3.5(2)	C(11)	-0.1652(6)	0.3426(3)	-0.3914(5)	3.9(4)
O(6)	-0.2355(4)	0.2786(2)	-0.0292(3)	3.8(2)	C(12)	-0.2271(6)	0.2885(3)	-0.3661(5)	3.3(3)
O(7)	0.3642(4)	0.0398(2)	0.2795(3)	4.3(2)	C(13)	-0.2175(5)	0.2644(3)	-0.2705(4)	2.6(3)
O(8)	0.2445(4)	0.0742(2)	0.1310(3)	3.4(2)	C(14)	-0.2931(6)	0.2059(3)	-0.2470(5)	4.2(4)
O(9)	0.3153(4)	-0.0353(2)	0.1450(3)	3.8(2)	C(15)	0.1388(5)	-0.0013(3)	0.2502(4)	2.4(3)
O(10)	-0.2375(5)	-0.0372(2)	0.0707(4)	6.5(3)	C(16)	0.0780(5)	-0.0550(3)	0.2094(4)	2.6(3)
O(11)	-0.4418(5)	0.0397(2)	0.0954(4)	7.2(3)	C(17)	-0.0302(6)	-0.0743(3)	0.2441(5)	3.2(3)
O(12)	-0.0812(5)	0.0701(3)	0.0787(5)	9.1(4)	C(18)	-0.0774(6)	-0.0398(3)	0.3190(5)	3.9(4)
N(1)	0.1477(6)	0.4527(3)	0.4812(4)	5.6(4)	C(19)	-0.0188(6)	0.0134(3)	0.3585(5)	3.9(4)
N(2)	-0.0318(6)	0.4308(3)	-0.3448(4)	5.4(4)	C(20)	0.0917(6)	0.0345(3)	0.3249(5)	3.2(3)
N(3)	-0.0927(5)	-0.1272(3)	0.1972(4)	4.4(3)	C(21)	0.1517(7)	0.0940(3)	0.3718(5)	5.1(4)
<b><math>Rb(H_3C(H_2N)C_6H_3SO_3)</math></b>									
Rb(1)	0.3826(1)	0.1651(2)	0.06228(6)	3.00(6)	C(2)	-0.022(1)	0.251(2)	0.2042(5)	1.9(6)
S(1)	0.0644(3)	0.2180(4)	0.0928(2)	2.2(2)	C(3)	-0.103(1)	0.230(1)	0.2520(6)	2.5(6)
O(1)	0.1031(9)	0.048(1)	0.0731(4)	3.6(5)	C(4)	-0.211(1)	0.133(2)	0.2395(6)	3.0(7)
O(2)	0.1627(6)	0.317(1)	0.1205(3)	2.7(4)	C(5)	-0.231(1)	0.072(2)	0.1839(6)	3.1(8)
O(3)	0.0040(8)	0.316(1)	0.0453(3)	3.2(5)	C(6)	-0.151(1)	0.091(2)	0.1375(5)	2.0(6)
N(1)	-0.085(1)	0.299(1)	0.3071(4)	3.7(6)	C(7)	-0.182(1)	0.014(2)	0.0764(7)	5(1)
C(1)	-0.045(1)	0.186(1)	0.1489(5)	1.5(6)					

<sup>a</sup>  $B_{eq} = \frac{1}{3}[a^2\beta_{11} + b^2\beta_{22} + c^2\beta_{33} + (2ab \cos \gamma)\beta_{12} + (2ac \cos \beta)\beta_{13} + (2bc \cos \alpha)\beta_{23}]$ . <sup>b</sup> Occupancies: Rb(1), 0.667(9); K(1), 0.333. <sup>c</sup> Occupancies: Rb(2), 0.140(7); K(2), 0.860.

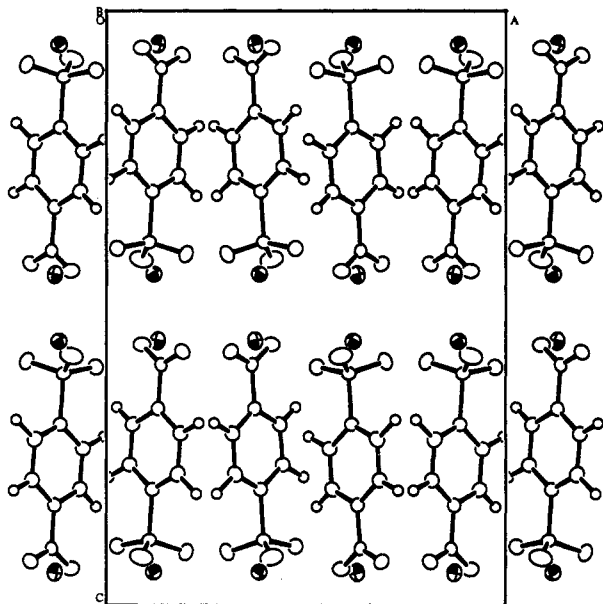
phase-refinement program DIRDIF.<sup>26</sup> The remaining non-hydrogen atoms, as well as most of the H atoms, were located on difference electron density maps calculated following least-squares refinements. The rest of the H atoms were placed in calculated positions and all were included as fixed isotropic scatterers. Final refinements were performed on those data having  $I > 3\sigma(I)$  and included anisotropic thermal parameters for all non-hydrogen atoms. The occupancies of the metal atom sites were also refined for  $Rb_{0.81}K_{1.19}(O_2CC_6H_4SO_3)$ . A Rb and K atom were placed

at each site with the positional and thermal parameters constrained to be equal and the occupancies constrained to sum to 1. The final difference electron density maps showed only very small random features (maximum and minimum heights 0.63, -0.58 e<sup>-</sup>Å<sup>3</sup>). Analyses of  $F_o$  versus  $F_c$  as a function of  $(\sin \theta)/\lambda$ , Miller indices, and  $F_o$  showed no unusual trends. Important crystallographic data for the five compounds are presented in Table 1. Final positional and equivalent isotropic thermal parameters are listed in Table 2, while selected bond 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.

(26) Beurskens, P. DIRDIF: Direct Methods for Difference Structures—An Automatic Procedure for Phase Extension and Refinement of Difference Structure Factors. Technical Report 1984/1; Crystallography Laboratory, Toernooiveld: 6525 Ed Nijmegen, The Netherlands, 1984.



**Figure 1.** ORTEP diagram of the molecular structure and potassium coordination environments of  $K_2(O_2CC_6H_4SO_3)$  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.



**Figure 2.** ORTEP packing diagram of  $K_2(O_2CC_6H_4SO_3)$  viewed along the  $b$  axis. The potassium atoms are shown with octant shading and the bonds to oxygen omitted.

## Results

**$K_2(O_2CC_6H_4SO_3)$ .** The structure, shown in Figures 1 and 2, is built of layers of 4-carboxybenzenesulfonate anions that stack along the  $c$  axis with the potassium cations in between. Each potassium cation is attached to oxygen atoms of both the carboxylate and sulfonate groups on anions in the same layer, as well as in adjacent layers. Atom K(1) is attached to six oxygen atoms in a very distorted octahedral geometry with K–O distances ranging from 2.700(3) to 3.069(3) Å. It is bonded to two oxygen atoms of one sulfonate in a chelating arrangement, one oxygen from another sulfonate group, and three oxygens from three

different carboxylate groups. Atom K(2) is bonded to seven oxygen atoms at 2.654(3)–2.966(3) Å in an irregular geometry. This potassium ion is chelated by both a sulfonate group (O(2A) and O(3A) in Figure 1) and a carboxylate group (O(4B) and O(5C)), with the remainder of the coordination sphere made up of two sulfonate and one carboxylate oxygen atoms from different anions. The term coordination is used throughout this discussion with the understanding that the bonding between the alkali metal cations and sulfonate anions is primarily ionic in nature and does not involve the formation of coordinate covalent bonds in the same way as for metal ions with partially filled valence orbitals. Indeed, the absence of regular coordination geometries for the alkali metal cations suggests that their positioning between the anion layers is governed by electrostatic attraction and packing effects rather than specific orbital interactions.

The anions within a layer are interleaved in a repeat pattern that has the sulfonate groups "up" on two adjacent anions in a layer and the  $CO_2$  groups "up" on the next two anions. The result is the formation of slabs with a nonpolar organic interior and anionic surfaces to which are attached the cations. The strong electrostatic attraction between the potassium cations and the ionic groups serves to link the anions both within and between the layers. This very efficient ionic packing is accomplished without incorporation of any water, which is somewhat atypical of metal sulfonate salts that are crystallized from aqueous solution.<sup>19,20,27–29</sup> Crystals of this compound are hard and brittle, lacking the facile cleavage characteristic of many layered compounds.

The metrical data for the tetrahedral sulfonate group, trigonal planar carboxylate group and aromatic ring (provided as supplementary material) show nearly ideal geometries. The C–O distances are equal within experimental error (1.262(4) and 1.254(4) Å) with the O(4)–C(7)–O(5) angle opened slightly (125.7(3)°) relative to the O–C(7)–C(4) angles which are both about 117°.

**$Rb_{0.81}K_{1.19}(O_2CC_6H_4SO_3)$ .** This compound is isostructural with  $K_2(O_2CC_6H_4SO_3)$ . Refinement of the occupancy factors showed that there is about 67% rubidium and 33% potassium in the K(1) site while the K(2) site (Figure 1) contains roughly 86% potassium and 14% rubidium. Thus the composition of the X-ray data crystal based on the refinement is  $Rb_{0.81}K_{1.19}(O_2CC_6H_4SO_3)$ , which is consistent with the results of elemental analysis of a bulk sample of crystals. Though no other crystals were studied by X-ray diffraction, we attach no special significance to this composition and anticipate that the compound is a solid solution with a range of possible stoichiometries, limited perhaps by the apparent preference of Rb for the K(1) site and K for the K(2) site. Due to the larger ionic radius of rubidium, the metal–oxygen distances (Table 3) in the predominantly rubidium site are all longer than the corresponding K(1)–O distances in the dipotassium compound. The metal–oxygen distances in the seven-coordinate site mainly occupied by potassium show only a slight increase over those in the K(2) site in  $K_2(O_2CC_6H_4SO_3)$ .

**$K(HO_2CC_6H_4SO_3) \cdot 2H_2O$ .** This compound is the potassium salt of the monoacid of 4-carboxybenzenesulfonate. Its structure (Figures 3 and 4) is layered like that of  $K_2(O_2CC_6H_4SO_3)$ , except here the potassium cation bonds only to the sulfonate group on the anion and completes its coordination sphere with water molecules. The acidic hydrogen could not be located in the X-ray study; however, since there is no direct bonding between the potassium and the carboxylate group, it is reasonable to assume that the proton is on one of the carboxylate oxygens. This is also in keeping with the relative acid strengths of benzenesulfonic acid ( $pK_a \approx 0.70$ ) and benzoic acid ( $pK_a \approx 4.2$ ). There is a

(27) Couldwell, C.; Prout, K.; Robey, D.; Taylor, R.; Rossotti, F. *Acta Crystallogr., Sect. B* 1978, 34, 1491.

(28) Ohki, Y.; Suzuki, Y.; Takeuchi, T.; Ouchi, A. *Bull. Chem. Soc. Jpn.* 1988, 61, 393.

(29) Starynowicz, P. *Acta Crystallogr., Sect. C* 1992, 48, 1414.

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

$K_2(O_2CC_6H_4SO_3)$					
K(1)–O(1)	3.069(3)	K(2)–O(2)	2.770(3)	S(1)–O(1)	1.447(3)
K(1)–O(1)	2.968(3)	K(2)–O(2)	2.966(3)	S(1)–O(2)	1.456(3)
K(1)–O(3)	2.870(3)	K(2)–O(3)	2.777(3)	S(1)–O(3)	1.451(3)
K(1)–O(4)	2.757(3)	K(2)–O(4)	2.885(3)	S(1)–C(1)	1.778(4)
K(1)–O(5)	2.700(3)	K(2)–O(4)	2.722(3)	O(4)–C(7)	1.262(4)
K(1)–O(5)	2.813(3)	K(2)–O(5)	2.934(3)	O(5)–C(7)	1.254(4)
K(2)–O(1)	2.654(3)				
O(1)–K(1)–O(1)	91.06(8)	O(1)–K(2)–O(4)	123.18(8)	O(1)–S(1)–O(2)	113.3(2)
O(1)–K(1)–O(3)	47.33(7)	O(1)–K(2)–O(5)	91.66(8)	O(1)–S(1)–O(3)	111.2(2)
O(1)–K(1)–O(4)	68.21(8)	O(1)–K(2)–O(2)	77.95(9)	O(2)–S(1)–O(3)	112.1(2)
O(1)–K(1)–O(5)	145.56(8)	O(1)–K(2)–O(2)	152.19(9)	O(1)–S(1)–C(1)	106.7(2)
O(1)–K(1)–O(5)	115.57(8)	O(2)–K(2)–O(3)	49.52(7)	O(2)–S(1)–C(1)	106.5(2)
O(3)–K(1)–O(4)	114.09(8)	O(2)–K(2)–O(4)	119.28(8)	O(3)–S(1)–C(1)	106.5(2)
O(3)–K(1)–O(5)	147.78(8)	O(3)–K(2)–O(4)	69.81(7)	O(4)–C(7)–O(5)	125.7(3)
O(3)–K(1)–O(5)	68.28(7)	O(3)–K(2)–O(4)	82.92(8)	O(4)–C(7)–C(4)	116.5(3)
O(1)–K(2)–O(3)	132.09(9)	O(3)–K(2)–O(5)	128.30(8)	O(5)–C(7)–C(4)	117.8(3)
O(1)–K(2)–O(4)	72.40(9)				
$Rb_{0.81}K_{1.19}(O_2CC_6H_4SO_3)$					
Rb(1)–O(1)	3.109(9)	Rb(2)–O(1)	2.686(8)	S(1)–O(1)	1.459(8)
Rb(1)–O(1)	3.058(8)	Rb(2)–O(2)	2.764(8)	S(1)–O(2)	1.455(8)
Rb(1)–O(2)	3.452(7)	Rb(2)–O(2)	3.059(8)	S(1)–O(3)	1.457(7)
Rb(1)–O(3)	2.948(8)	Rb(2)–O(3)	2.802(8)	S(1)–C(1)	1.802(9)
Rb(1)–O(4)	2.842(8)	Rb(2)–O(4)	2.864(8)	O(4)–C(7)	1.25(1)
Rb(1)–O(5)	2.775(8)	Rb(2)–O(4)	2.761(8)	O(5)–C(7)	1.26(1)
Rb(1)–O(5)	2.850(8)	Rb(2)–O(5)	2.983(8)		
O(1)–Rb(1)–O(1)	91.7(2)	O(1)–Rb(2)–O(3)	132.5(2)	O(1)–S(1)–O(2)	114.1(5)
O(1)–Rb(1)–O(3)	46.7(2)	O(1)–Rb(2)–O(4)	73.3(2)	O(1)–S(1)–O(3)	111.0(5)
O(1)–Rb(1)–O(4)	67.5(2)	O(1)–Rb(2)–O(4)	121.3(2)	O(1)–S(1)–C(1)	106.4(5)
O(1)–Rb(1)–O(5)	146.4(2)	O(1)–Rb(2)–O(5)	91.4(2)	O(2)–S(1)–O(3)	113.5(5)
O(1)–Rb(1)–O(5)	114.9(2)	O(2)–Rb(2)–O(3)	48.9(2)	O(2)–S(1)–C(1)	105.5(6)
O(3)–Rb(1)–O(4)	113.0(2)	O(2)–Rb(2)–O(4)	118.8(2)	O(3)–S(1)–C(1)	105.5(5)
O(3)–Rb(1)–O(5)	148.1(2)	O(3)–Rb(2)–O(4)	70.0(2)	O(4)–C(7)–O(5)	127(1)
O(3)–Rb(1)–O(5)	68.3(2)	O(3)–Rb(2)–O(4)	83.7(2)	O(4)–C(7)–C(4)	116(1)
O(1)–Rb(2)–O(2)	78.7(3)	O(3)–Rb(2)–O(5)	128.1(2)	O(5)–C(7)–C(4)	117(1)
O(1)–Rb(2)–O(2)	152.2(2)				
$K(HO_2CC_6H_4SO_3) \cdot 2H_2O$					
K(1)–O(1)	2.796(4)	K(1)–O(6)	2.721(4)	S(1)–O(3)	1.456(4)
K(1)–O(1)	2.946(4)	K(1)–O(6)	2.828(4)	S(1)–C(1)	1.776(5)
K(1)–O(2)	3.183(4)	K(1)–O(7)	2.898(4)	O(4)–C(7)	1.214(6)
K(1)–O(2)	2.845(4)	S(1)–O(1)	1.453(4)	O(5)–C(7)	1.321(7)
K(1)–O(3)	3.045(4)	S(1)–O(2)	1.453(4)		
O(1)–K(1)–O(1)	97.8(1)	O(2)–K(1)–O(3)	97.8(1)	O(1)–S(1)–O(3)	112.0(2)
O(1)–K(1)–O(2)	46.9(1)	O(2)–K(1)–O(6)	86.1(1)	O(1)–S(1)–C(1)	107.2(2)
O(1)–K(1)–O(2)	88.6(1)	O(2)–K(1)–O(6)	131.2(1)	O(2)–S(1)–O(3)	112.6(2)
O(1)–K(1)–O(3)	75.7(1)	O(2)–K(1)–O(7)	71.8(1)	O(2)–S(1)–C(1)	105.6(2)
O(1)–K(1)–O(6)	80.9(1)	O(3)–K(1)–O(6)	143.2(1)	O(3)–S(1)–C(1)	107.0(2)
O(1)–K(1)–O(6)	174.4(1)	O(3)–K(1)–O(6)	100.2(1)	O(4)–C(7)–O(5)	123.6(5)
O(1)–K(1)–O(7)	114.4(1)	O(3)–K(1)–O(7)	143.1(1)	O(4)–C(7)–C(4)	123.1(6)
O(2)–K(1)–O(2)	134.43(6)	O(1)–S(1)–O(2)	111.9(2)	O(5)–C(7)–C(4)	113.4(5)
$K_3(H_3C(H_2N)C_6H_3SO_3)_3 \cdot 3H_2O$					
K(1)–O(1)	2.688(4)	K(2)–O(9)	2.783(4)	S(1)–O(2)	1.457(4)
K(1)–O(2)	3.310(5)	K(2)–O(11)	2.989(5)	S(1)–O(3)	1.458(4)
K(1)–O(3)	2.883(5)	K(2)–O(12)	2.822(6)	S(1)–C(1)	1.787(6)
K(1)–O(4)	3.275(5)	K(3)–O(1)	3.101(5)	S(2)–O(4)	1.459(4)
K(1)–O(5)	2.848(4)	K(3)–O(2)	2.678(4)	S(2)–O(5)	1.463(4)
K(1)–O(6)	2.732(4)	K(3)–O(3)	2.748(5)	S(2)–O(6)	1.451(4)
K(1)–O(8)	2.787(4)	K(3)–O(4)	2.770(4)	S(2)–C(8)	1.788(6)
K(1)–O(12)	2.934(6)	K(3)–O(7)	2.963(5)	S(3)–O(7)	1.458(4)
K(2)–O(2)	2.702(5)	K(3)–O(8)	2.776(4)	S(3)–O(8)	1.465(4)
K(2)–O(4)	2.817(4)	K(3)–O(11)	2.868(4)	S(3)–O(9)	1.456(4)
K(2)–O(5)	2.885(5)	S(1)–O(1)	1.450(4)	S(3)–C(15)	1.780(6)
K(2)–O(6)	3.109(5)				
O(1)–K(1)–O(2)	82.0(1)	O(5)–K(2)–O(11)	163.1(1)	O(3)–K(1)–O(12)	129.3(1)
O(1)–K(1)–O(3)	92.4(1)	O(5)–K(2)–O(12)	74.6(1)	O(3)–K(3)–O(7)	86.6(1)
O(1)–K(1)–O(4)	77.8(1)	O(1)–K(3)–O(2)	86.2(1)	O(3)–K(3)–O(8)	75.8(1)
O(1)–K(1)–O(5)	81.2(1)	O(1)–K(3)–O(3)	48.0(1)	O(3)–K(3)–O(11)	154.3(1)
O(1)–K(1)–O(6)	148.6(1)	O(1)–K(3)–O(4)	79.8(1)	O(1)–S(1)–O(2)	112.8(3)
O(1)–K(1)–O(8)	122.0(1)	O(1)–K(3)–O(7)	131.9(1)	O(1)–S(1)–O(3)	111.4(3)
O(1)–K(1)–O(12)	68.7(2)	O(1)–K(3)–O(8)	116.9(1)	O(1)–S(1)–C(1)	107.1(3)
O(2)–K(1)–O(3)	45.1(1)	O(1)–K(3)–O(11)	156.2(1)	O(2)–S(1)–O(3)	111.5(3)
O(2)–K(1)–O(4)	61.4(1)	O(2)–K(3)–O(3)	128.1(1)	O(2)–S(1)–C(1)	106.3(3)
O(2)–K(2)–O(4)	75.0(1)	O(2)–K(3)–O(4)	76.1(1)	O(3)–S(1)–C(1)	107.3(3)
O(2)–K(2)–O(5)	105.1(1)	O(2)–K(3)–O(7)	120.8(1)	O(4)–S(2)–O(5)	111.3(3)

Table 3 (Continued)

$K_3(H_3C(H_2N)C_6H_3SO_3)_3 \cdot 3H_2O$					
O(2)-K(2)-O(6)	76.4(1)	O(2)-K(3)-O(8)	155.9(1)	O(4)-S(2)-O(6)	113.6(3)
O(2)-K(2)-O(9)	151.5(1)	O(2)-K(3)-O(11)	76.3(1)	O(4)-S(2)-C(8)	106.8(3)
O(2)-K(2)-O(11)	73.9(1)	O(3)-K(3)-O(4)	110.8(1)	O(5)-S(2)-O(6)	111.3(3)
O(2)-K(2)-O(12)	87.7(2)	O(2)-K(1)-O(5)	107.1(1)	O(5)-S(2)-C(8)	106.4(3)
O(4)-K(2)-O(5)	118.7(1)	O(2)-K(1)-O(6)	72.6(1)	O(6)-S(2)-C(8)	106.9(3)
O(4)-K(2)-O(6)	75.7(1)	O(2)-K(1)-O(8)	116.2(1)	O(7)-S(3)-O(8)	110.7(3)
O(4)-K(2)-O(9)	103.6(1)	O(2)-K(1)-O(12)	150.3(2)	O(7)-S(3)-O(9)	112.4(3)
O(4)-K(2)-O(11)	77.7(1)	O(3)-K(1)-O(4)	106.5(1)	O(7)-S(3)-C(15)	108.2(3)
O(4)-K(2)-O(12)	160.2(2)	O(3)-K(1)-O(5)	152.2(1)	O(8)-S(3)-O(9)	112.1(3)
O(5)-K(2)-O(6)	47.1(1)	O(3)-K(1)-O(6)	82.7(1)	O(8)-S(3)-C(15)	106.2(3)
O(5)-K(2)-O(9)	100.4(1)	O(3)-K(1)-O(8)	73.5(1)	O(9)-S(3)-C(15)	106.9(3)
$Rb(H_3C(H_2N)C_6H_3SO_3)$					
Rb(1)-O(1)	3.207(9)	Rb(1)-O(3)	2.775(8)	S(1)-O(2)	1.459(8)
Rb(1)-O(1)	2.950(8)	Rb(1)-O(3)	2.980(9)	S(1)-O(3)	1.467(8)
Rb(1)-O(2)	2.985(7)	Rb(1)-N(1)	3.144(9)	S(1)-C(1)	1.76(1)
Rb(1)-O(2)	3.020(9)	S(1)-O(1)	1.442(8)		
O(1)-Rb(1)-O(1)	108.9(2)	O(2)-Rb(1)-O(3)	138.9(2)	O(1)-S(1)-O(2)	112.5(6)
O(1)-Rb(1)-O(2)	45.7(2)	O(2)-Rb(1)-O(3)	138.1(2)	O(1)-S(1)-O(3)	111.7(6)
O(1)-Rb(1)-O(2)	64.0(2)	O(2)-Rb(1)-N(1)	63.4(2)	O(1)-S(1)-C(1)	107.2(6)
O(1)-Rb(1)-O(3)	122.8(3)	O(3)-Rb(1)-O(3)	74.6(3)	O(2)-S(1)-O(3)	112.5(5)
O(1)-Rb(1)-O(3)	99.1(2)	O(3)-Rb(1)-N(1)	138.5(3)	O(2)-S(1)-C(1)	105.4(5)
O(1)-Rb(1)-N(1)	97.4(3)	O(3)-Rb(1)-N(1)	111.5(2)	O(3)-S(1)-C(1)	106.9(5)
O(2)-Rb(1)-O(2)	91.1(2)				

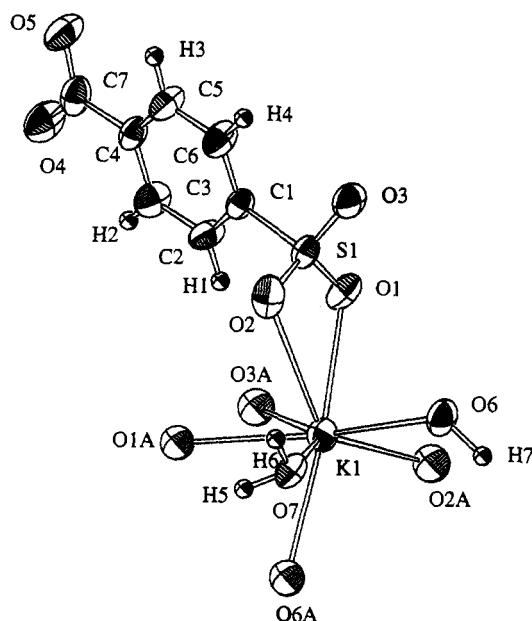


Figure 3. ORTEP diagram of the molecular structure and potassium coordination environment of  $K(HO_2CC_6H_4SO_3) \cdot 2H_2O$  showing the atom-labeling scheme.

noticeable difference in the lengths of the C-O bonds in the carboxylate group ( $C(7)-O(5) = 1.321(7) \text{ \AA}$  and  $C(7)-O(4) = 1.214(6) \text{ \AA}$ ) which suggests that O(5) may be the protonated oxygen atom. These crystals were grown in pure water, whereas those of  $K_2(O_2CC_6H_4SO_3)$  were grown from a 25 mL of water/5 mL of ethanol mixture. Several attempts to prepare 4-carboxybenzenesulfonate salts of divalent transition metals by similar reactions in water-ethanol solutions also produced crystals of  $K(HO_2CC_6H_4SO_3) \cdot 2H_2O$ .

Each potassium cation is coordinated to eight oxygens, five from sulfonate groups and three from water molecules, in a distorted square-antiprism with bond distances ranging from 2.721(4) to 3.183(4) Å. Two pairs of sulfonate oxygens (O(1) and O(2); O(1A) and O(3A)) from different anions in the same layer chelate the potassium, while the fifth sulfonate oxygen is from an anion in another layer. A comparison between the packing diagrams for the dipotassium (Figure 2) and monopotassium (Figure 4) salts shows that, in the absence of the direct bonding between the potassium and carboxylate group, the alternating

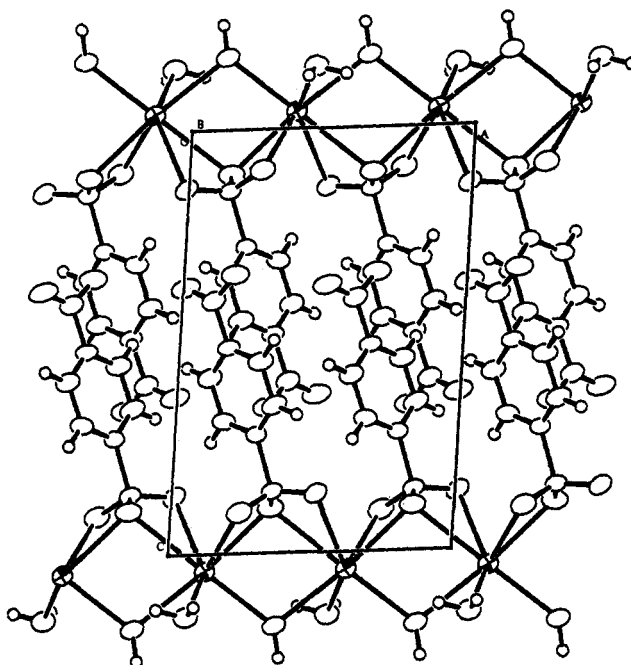


Figure 4. ORTEP packing diagram of  $K(HO_2CC_6H_4SO_3) \cdot 2H_2O$  viewed along the  $b$  axis. Potassium atoms are shown with octant shading.

rows of anions are pulled slightly apart from one another with the sulfonate groups directed toward the intervening cations. Thus the packing within each monoanion layer is not as tight (repeat distance per layer  $\approx 12.9 \text{ \AA}$ ) as in the dianion layers of  $K_2(O_2CC_6H_4SO_3)$  (repeat distance per layer  $\approx 10.3 \text{ \AA}$ ). Owing to the presence of the water, the bonding between the layers is further reinforced by hydrogen bonding between the water molecules and the oxygen atoms of the sulfonate and carboxylate groups. Hydrogen bonding interactions (metrical data given as covalent O-H distance, hydrogen bond distance, O-H...O bond angle) include:  $O(7)-H(6) \cdots O(1)$ , 0.92, 1.93 Å, 168°;  $O(7)-H(5) \cdots O(2)$ , 0.97, 1.85 Å, 170°;  $O(6)-H(7) \cdots O(4)$ , 1.07, 1.80 Å, 161°. There is also an apparent hydrogen bond involving the acidic proton as suggested by the short contact (2.623(5) Å) between O(5) and O(7). As a result of these interactions, the crystals of this compound are also hard, brittle, and relatively free of stacking imperfections.

$K_3(H_3C(H_2N)C_6H_3SO_3)_3 \cdot 3H_2O$ . The 1:1 salt of potassium and

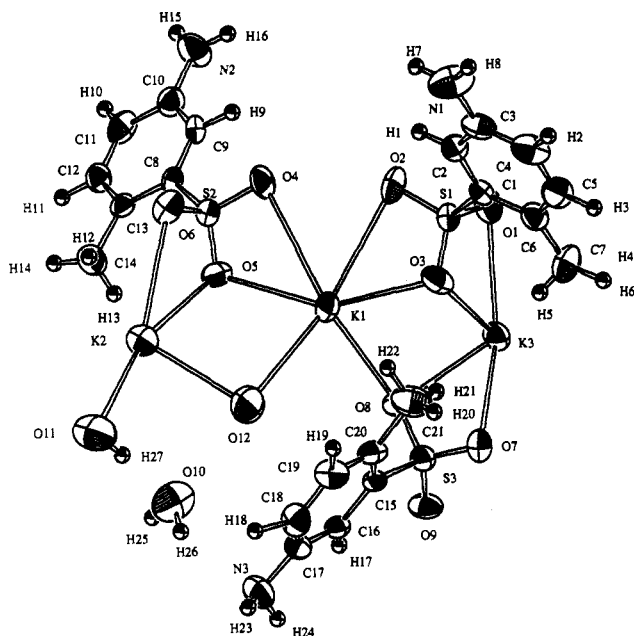


Figure 5. ORTEP diagram of the trimeric asymmetric unit of  $K_3(H_3C(H_2N)C_6H_3SO_3)_3 \cdot 3H_2O$  showing the atom-labeling scheme.

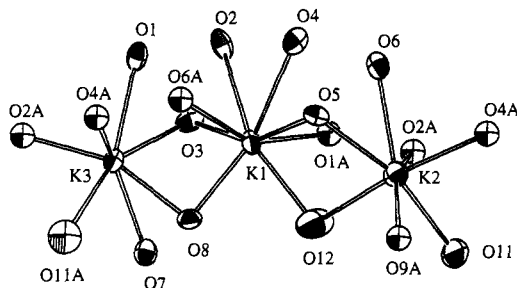


Figure 6. Coordination environments of the potassium atoms in  $K_3(H_3C(H_2N)C_6H_3SO_3)_3 \cdot 3H_2O$ .

4-aminotoluene-2-sulfonate has a complex structure based on an unusual repeat unit (Figure 5) containing three independent cations, anions, and water molecules. The potassium ions are bonded directly to the oxygens of sulfonate groups and to two of the water molecules (O(11) and O(12)). The third water molecule (O(10)) is not coordinated to a potassium cation, but forms hydrogen bonds to a neighboring water molecule and sulfonate group: O(11)–H(27)···O(10), 1.03, 1.80 Å, 169°; O(10)–H(25)···O(8), 1.05, 1.80 Å, 162°. The potassium coordination geometries are shown in Figure 6. The oxygens bonded to K(1) are arranged in a distorted cubic geometry in which two bond distances (K(1)–O(2), 3.310(5) Å, and K(1)–O(4), 3.275(5) Å) are distinctly longer than the others, all of which are less than 3 Å. The other potassium ions are arranged in irregular seven-coordinate geometries with distances ranging from 2.678(4) to 3.109(5) Å. Two of the potassium ions, K(1) and K(3), are chelated by pairs of oxygen atoms from two sulfonate groups, while K(2) is chelated by only one sulfonate group. This difference is probably related to the fact that K(2) has two water molecules in its coordination sphere, while the other two potassium ions have only one each.

The trimeric asymmetric unit is linked in spiraling chains (Figure 7) that run parallel to the *a* axis. This structural feature explains why the crystals grew as flattened needles. The chains pack to form undulating layers that stack along the *c* direction. There are no interatomic distances less than 2 Å between the amine hydrogen atoms and other nitrogen or oxygen atoms, indicating at best only very weak hydrogen bonding between the layers. As a result of the absence of strong nonbonded interactions

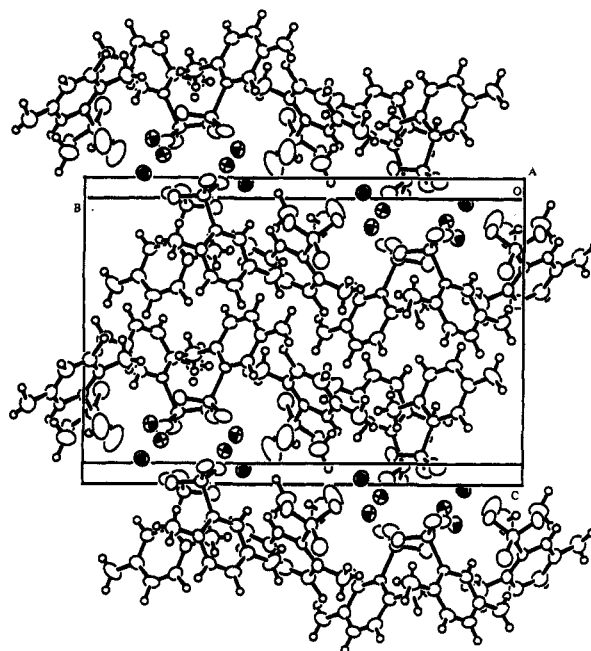


Figure 7. ORTEP packing diagram showing the undulating nature of the layers in  $K_3(H_3C(H_2N)C_6H_3SO_3)_3 \cdot 3H_2O$ . View is along the *a* axis. The potassium atoms are shown with octant shading and the bonds to oxygen omitted.

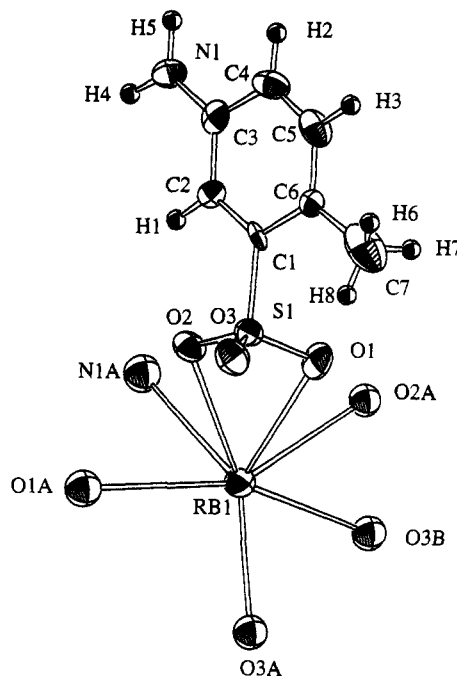


Figure 8. ORTEP diagram of the molecular structure and rubidium coordination sphere in  $Rb(H_3C(H_2N)C_6H_3SO_3)$  showing the atom labeling scheme.

between the organic layers, the crystals of this compound are softer and not as brittle as those of the 4-carboxybenzenesulfonate salts.

$Rb(H_3C(H_2N)C_6H_3SO_3)$ . In contrast to the results for 4-carboxybenzenesulfonate, the potassium and rubidium salts of 4-aminotoluene-2-sulfonate are not isostructural. The rubidium 4-aminotoluene-2-sulfonate crystallizes as an anhydrous salt, with the rubidium ion coordinated to six sulfonate oxygen atoms and one amine nitrogen (Figure 8). Four of the sulfonate oxygen atoms (O(1) and O(2); O(2A) and O(3B)) on two different anions chelate the cation, while the remaining atoms in the coordination sphere come from different anions. As the packing diagram (Figure 9) shows, this compound is also layered but in a very

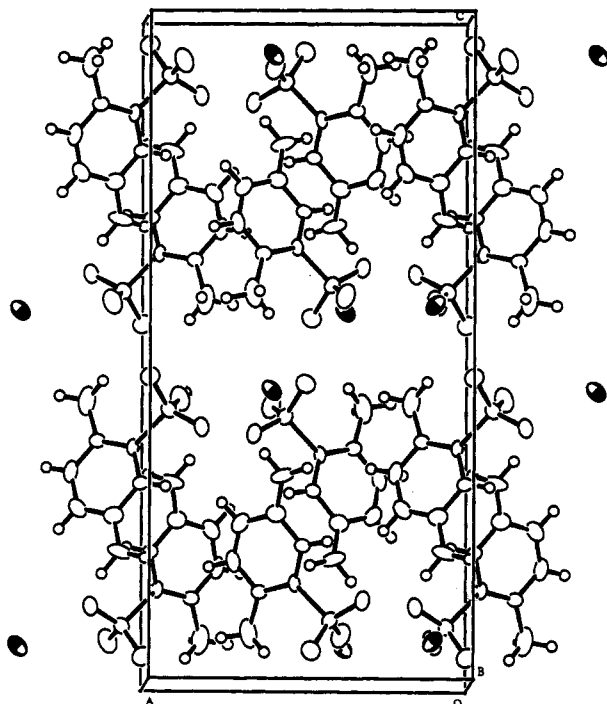


Figure 9. ORTEP packing diagram of  $\text{Rb}(\text{H}_3\text{C}(\text{H}_2\text{N})\text{C}_6\text{H}_3\text{SO}_3)$  viewed along the  $b$  axis. The rubidium atoms are shown with octant shading and bonds to oxygen and nitrogen omitted.

different fashion from the potassium compound. The anions are arranged in each layer in alternating pairs in which the aromatic rings are canted so that the sulfonate groups tilt away from each other. These pairs of anions are only partially interleaved; i.e., they are at different levels along the stacking direction ( $c$  axis). Despite the more complicated packing pattern, the result is flat slabs in which the sulfonate groups are directed to the surfaces, with the rubidium ions in between the layers. Thus, this structure has more in common with the 4-carboxybenzenesulfonate structures than with the potassium 4-aminotoluene-2-sulfonate. As a result of the strong bonding between the rubidium ions and

the organic layers, these crystals are similar to the 4-carboxybenzenesulfonates in appearance and hardness.

### Discussion

Previous work on metal sulfonates<sup>19,20,27</sup> has shown that the divalent first row transition metal ions show no tendency to coordinate to the sulfonate anions in the presence of water. The reported structures contain fully hydrated  $[\text{M}(\text{H}_2\text{O})_6]^{2+}$  cations. This behavior is in marked contrast to that of the phosphonates, which readily coordinate transition metal ions in aqueous solution to give layered structures with at most one or two water molecules per cation.<sup>8,14,18</sup> Alkaline earth<sup>20</sup> and lanthanide<sup>28,29</sup> ions show a somewhat greater affinity for sulfonate ions than do the transition metals. The coordination spheres of these cations in sulfonate salts contain one or two sulfonate oxygen atoms and six or seven water molecules. In the analogous phosphonate salts<sup>9</sup> just the opposite behavior is seen, with the metal coordination sphere formed by a large number of phosphonate oxygen atoms and, at most, one water molecule. When we found that sodium forms structures with still more direct coordination of the sulfonate and less water,<sup>19,20</sup> it followed that the larger alkali metal ions would be even better in this regard because they are less strongly hydrated and are more compatible in size with the large sulfonate ions. In fact, the potassium and rubidium sulfonate salts reported here are either anhydrous or have one or two water molecules per cation. This would appear to be another example of the general trend that more stable ionic structures form between cations and anions of similar charge and size.

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