Synthesis and structures of layered metal sulfonate salts

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Abstract

A series of divalent transition metal benzenesulfonates, $M(C_6H_5SO_3)_2 \cdot 6H_2O$ where M = Mn, Co, Ni and Zn, have been prepared from reactions of metal salts and sodium benzenesulfonate in aqueous solution. The products have been characterized by single crystal X-ray diffraction techniques (monoclinic, space group $P2_1$, $Z = 2$, (M = Co) $a = 7.017(2)$, $b = 6.324(2)$, $c = 22.468(4)$ Å, $\beta = 93.70(3)°$, $V = 995.0(4)$ Å^3, $R(F) = 0.052$ for 1270 observations and 159 variables). These materials are isostructural and contain alternating layers of benzenesulfonate anions and $[M(H_2O)_6]^{2+}$ cations. The reaction of sodium 4-hydroxybenzenesulfonate and nickel(II) chloride in aqueous solution yielded crystals of $Ni(HOC_6H_4SO_3)_2 \cdot 8H_2O$. This compound is also monoclinic, space group $P2_1/c$, $Z = 4$, $a = 11.759(2)$, $b = 7.262(4)$, $c = 25.361(1)$ Å, $\beta = 94.353(8)°$, $V = 2159(1)$ Å^3, $R(F) = 0.043$ for 2090 observations and 284 variables. The structure is similar to that of the unfunctionalized benzenesulfonates in that it contains layers of sulfonate anions and hexaaquanickel cations. There are also two non-coordinated water molecules of hydration associated with the aqua ions. The presence of the hydroxy groups on the phenyl rings allows for enhanced hydrogen bonding between the layers. The crystal structure of the starting sodium 4-hydroxybenzenesulfonate, $Na_2(HOC_6H_4SO_3)_2 \cdot 4H_2O$, has also been determined (monoclinic, space group $P2_1/a$, $Z = 4$, $a = 8.029(4)$, $b = 10.086(3)$, $c = 23.185(2)$ Å, $\beta = 94.07(2)°$, $V = 1873(1)$ Å^3, $R(F) = 0.042$ for 2198 observations and 254 variables) and it, too, has alternating layers of sulfonate ions and hydrated cations. In this structure, the sodium ions do coordinate directly to the sulfonate oxygen atoms. The crystal structures of these materials are discussed in relation to recently reported layered metal phosphonates.

Introduction

Layered inorganic oxoanion compounds have long been of interest for their ion exchange and intercalation behavior [1]. Natural minerals such as the aluminosilicate clays [2] and synthetic compounds such as the α-type M(IV) phosphates (M = Ti, Zr, Hf, Ge, Sn and Pb) [3] have been actively studied. In recent years, particular attention has focused on the potential use of such exchanged materials as hosts for size and shape selective catalysis [4]. Both types of materials contain covalently bonded metal–oxygen–non-metal (Si or P) frameworks that form infinite sheets. These layers carry a net negative charge, so to maintain electrical neutrality there are cations in the interlayer space. These cations are sufficiently weakly bound as to undergo facile exchange with ions in the surrounding solution [1]. Catalytically active species have been placed in the interlayer gap where they react preferentially with those molecules that are small enough and of the correct shape to enter the host structure [2]. In this type of application, the

size of the gap is a critical factor in determining the selectivity of such a system.

In 1978, the synthesis of zirconium phenylphosphonate, $Zr(C_6H_5PO_3)_2$, was reported [5]. From powder X-ray diffraction and other measurements, this material is believed to have a structure containing Zr–O–P layers analogous to those in α-zirconium phosphate with the phosphate oxygen atom that is directed into the interlayer space replaced by the organic group [6]. The presence of the large phenyl rings roughly doubles the size of the gap relative to that in the purely inorganic phase. The use of organic groups to prop open, or pillar, the layers of inorganic solids has been a widely applied technique in clay chemistry [2], as well as in the synthetic phosphate systems [3]. In both cases, it has been shown that the size of the interlayer region, and hence the physical properties of the material, can be controlled by the use of different organic groups.

Much of the recent work in this area has involved the intercalation of cationic organic amines into aluminosilicates [7–9] and the direct synthesis of transition metal phosphonates in which the organic groups are covalently attached to the inorganic layer [6, 10–13]. This study was undertaken to examine the reactions

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of divalent transition metals and organic sulfonates with the goal of preparing compounds with layered structures analogous to the recently reported metal phosphonates. The compounds were prepared by reactions of metal chloride or nitrate salts with sodium benzenesulfonates in water. The products isolated from the syntheses were a series of transition metal benzenesulfonates $M(C_6H_5SO_3)_2 \cdot 6H_2O$ or $M(HOC_6H_4SO_3)_2 \cdot 8H_2O$ where M = the transition metal. The syntheses and structures of these compounds are presented and the results are compared with those of the corresponding phosphonates.

Experimental

Synthesis

$Ni(HOC_6H_4SO_3)_2 \cdot 8H_2O$

A 5.03 g sample of sodium 4-hydroxybenzenesulfonate dihydrate (Aldrich, 98%) was completely dissolved in 50.0 ml of distilled water. A 4.04 g sample of reagent grade nickel chloride ($NiCl_2 \cdot 6H_2O$), was added to the solution. This mixture was heated for about 20 min until it completely dissolved to give a green solution. Upon cooling to room temperature, the mixture stayed in solution and was set out to allow evaporation of the solvent. After five weeks, the solvent had evaporated, leaving behind a mixture of large block-shaped green crystals and plate-like colorless crystals (4.44 g).

$Co(C_6H_5SO_3)_2 \cdot 6H_2O$

A 5.00 g sample of sodium benzenesulfonate (Aldrich, 99%) was completely dissolved in 50.0 mol of distilled water. A 4.01 g sample of reagent grade cobalt nitrate ($Co(NO_3)_2 \cdot 6H_2O$) was added to the solution. The mixture was heated for about 10 min and all the cobalt nitrate went into solution. The solution was then left to cool down to room temperature when concentrated HCl was added until the solution turned purple. A total of 28 ml was added and this was left to crystallize. After one month the plate-like rust-colored crystals that had grown (2.00 g) were collected from the mother liquor. After another two weeks the mother liquor had completely evaporated and more rust-colored crystals were left (5.19 g).

Reactions of cobalt nitrate, manganous nitrate, nickel chloride and zinc chloride with sodium benzenesulfonate in aqueous solution not acidified with HCl also yielded crystals that have been shown by X-ray diffraction to be isomorphous with the product of the above reaction.

$Na_2(HOC_6H_4SO_3)_2 \cdot 4H_2O$

A 4.99 g sample of sodium 4-hydroxybenzenesulfonate (Aldrich, 98%) was completely dissolved in 50.0 ml of distilled water. A 3.99 g sample of reagent grade manganous chloride ($MnCl_2 \cdot 4H_2O$) was added to the

solution. The mixture was heated for 15 min after which time all the manganous chloride had dissolved, giving a clear colorless solution. Once cooled down to room temperature it remained so. After five weeks of standing at room temperature the liquid had evaporated and thick colorless plate-like crystals had grown (3.49 g). Thermogravimetric analysis of the product performed on a DuPont 2100 DTA-TGA unit revealed a 15.3% weight loss between 40 and 170 °C, with no further loss up to 250 °C. This is consistent with loss of four moles of water from the formula $Na_2(HOC_6H_4SO_3)_2 \cdot 4H_2O$ (calculated: 15.5%). A similar reaction with zinc chloride also yielded crystals of the sodium 4-hydroxybenzenesulfonate as determined by X-ray diffraction.

Crystallographic studies

All of the single crystal X-ray diffraction work was done at room temperature on a Rigaku AFC6S diffractometer with a sealed tube Mo X-ray source. Each of the single crystals was mounted on a glass fiber with silicone cement. The general data collection and reduction techniques have been described previously [14]. Reflections were measured at a constant scan rate with a maximum of three identical scans for weak intensities. The intensities of three standards measured after every 150 data showed no significant variations or decay in any of the experiments. Data were corrected for Lorentz and polarization effects. The computations were done on a VAXStation 3100 model 76 computer with the TEXSAN [15] series of crystallographic programs. Space groups were assigned based on the systematic absences and intensity statistics and were confirmed by successful refinements. All the structures were solved by the direct methods program MITHRIL [16] which revealed the locations of the heavy atoms. The light non-hydrogen atoms (oxygen and carbon) were located by direct methods phase refinement techniques (DIRDIF) [17]. Analyses of F_0 versus F_c as a function of F_0, $\sin \theta / \lambda$, and Miller indices showed no unusual trends. Final difference electron density maps contained no significant features. Cell parameters and other crystallographic data are presented in Table 1.

$Ni(HOC_6H_4SO_3)_2 \cdot 8H_2O$

A crystal was cut from a larger green crystal to about the dimensions of $0.30 \times 0.30 \times 0.20$ mm and was mounted on a glass fiber. The unit cell listed in Table 1 was derived from a least-squares refinement of 21 centered reflections in the range of $37.41 < 2\theta < 47.17°$. A total of 4342 reflections was collected (ω–2θ scans, 8° min^{-1}) with 4128 of them being unique ($R(int) = 0.022$). An empirical absorption correction, based on azimuthal scans of three reflections, was applied to the data (transmission factors 0.78–1.00)

TABLE 1. Crystallographic data for layered metal sulfonates

Formula	$NiS_2O_{16}C_{12}H_{26}$	$CoS_2O_{12}C_{12}H_{22}$	$S_2Na_2O_{12}C_{12}H_{18}$
Formula weight	549.15	481.35	464.37
Crystal system	monoclinic	monoclinic	monoclinic
a (Å)	11.759(2)	7.017(2)	8.029(4)
b (Å)	7.262(4)	6.324(2)	10.086(3)
c (Å)	25.361(1)	22.468(4)	23.185(2)
β (°)	94.353(8)	93.70(3)	94.07(2)
V (Å^3)	2159(1)	995.0(4)	1873(1)
Space group	$P2_1/c$	$P2_1$	$P2_1/a$
Z value	4	2	4
D (calc.) (g cm^{-3})	1.69	1.61	1.65
$F(000)$	1144	498	960
μ (Mo Kα) (cm^{-1})	11.60	11.15	3.75
Transmission factors	0.78–1.00	0.82–1.00	none
2θ range for data (°)	3–50	3–50	3–50
No unique observations	4128	1940	3512
No. data $I > 3\sigma(I)$	2090	1270	2198
No. variables	284	159	254
Residuals: R, R_w	0.043, 0.047	0.052, 0.049	0.042, 0.044
Goodness of fit	2.58	2.73	2.20
Largest peaks in final ΔF (e Å^{-3})	0.43, −0.41	0.58, −0.40	0.36, −0.28

as was a correction for secondary extinction (coefficient = 2.88×10^{-6}). With the successful solution and refinement of the structure, the space group was determined to be $P2_1/c$ (No. 14). Hydrogen atoms were located on difference electron density maps and were included as fixed isotropic scatterers. The final refinement of 284 variables (including anisotropic thermal parameters for all non-hydrogen atoms and the secondary extinction coefficient) and 2090 observed reflections with $I > 3\sigma(I)$ converged to final agreement factors $R = 0.043$ and $R_w = 0.047$.

The final empirical formula based on the X-ray structure is $Ni(HOC_6H_4SO_3)_2 \cdot 8H_2O$ ($FW = 549.15$). The final positions and equivalent isotropic thermal parameters of each atom in the unit cell are given in Table 2. The intramolecular distances between the non-hydrogen atoms are listed in Table 3 while the intramolecular bond angles involving the non-hydrogen atoms are provided in Table 4.

$Co(C_6H_5SO_3)_2 \cdot 6H_2O$

A crystal suitable for X-ray diffraction was cut from a larger crystal to approximate dimensions of $0.30 \times 0.10 \times 0.20$ mm and was mounted on a glass fiber. Least-squares refinement of 22 centered reflections in the range of $20.55 < 2\theta < 31.63°$ yielded the monoclinic cell given in Table 1. A total of 2106 reflections was measured (ω scans, 4° min^{-1}) of which 1940 were unique ($R(\text{int}) = 0.021$). An empirical absorption correction, based on azimuthal scans of three reflections, was applied to the data (transmission factors 0.82–1.00). The space group was determined to be $P2_1$ (No. 4) due to the successful solution and refinement of the

structure. The two independent phenyl rings did not refine well initially and were ultimately refined as rigid groups ($d(\text{C–C}) = 1.40$ Å, $d(\text{C–H}) = 0.95$ Å, all bond angles 120°). The hydrogen atoms on the water molecules were located on difference electron density maps and were included as fixed isotropic scatterers. The final refinement of 159 variables (including anisotropic thermal parameters for the Co, S and O atoms) and 1270 data with $I > 3\sigma(I)$ converged to $R = 0.052$ and $R_w = 0.049$.

The empirical formula for this compound is $Co(C_6H_5SO_3)_2 \cdot 6H_2O$ ($FW = 481.35$). The positional and equivalent isotropic thermal parameters for each atom in the unit cell are given in Table 2. The intramolecular bond distances and angles between the non-hydrogen atoms are listed in Tables 3 and 4. The carbon–carbon distances and angles are omitted from the Tables as they were constrained in the group refinement.

$Na_2(HOC_6H_4SO_3)_2 \cdot 4H_2O$

A colorless crystal was cut from a larger crystal to an approximate size of $0.30 \times 0.25 \times 0.15$ mm and was mounted on a glass fiber. The monoclinic unit cell shown in Table 1 was obtained from a least-squares refinement of 25 centered reflections in the range of $36.93 < 2\theta < 43.28°$. A total of 3775 reflections was collected (ω scans, 16° min^{-1}) and averaged ($R(\text{int}) = 0.043$) to yield 3512 unique data. No absorption correction was applied, however, the data were corrected for secondary extinction (coefficient = 4.86×10^{-6}). The structure was successfully solved and refined in space group $P2_1/a$ (No. 14, alternate setting). The hydrogen atoms were located on difference electron density maps and included in the model as fixed isotropic scatterers.

TABLE 2. Final positional and equivalent isotropic thermal parameters

Atom	x	y	z	B_{eq}
Ni(HOC$_6$H$_4$SO$_3$)$_2 \cdot$ 8H$_2$O				
Ni(1)	0	0	0	1.69(6)
Ni(2)	1/2	0	0	1.72(6)
S(1)	0.5942(2)	0.0573(3)	0.36671(7)	2.2(1)
S(2)	0.1041(2)	0.0657(3)	0.36590(7)	2.2(1)
O(1)	0.4770(4)	0.1048(7)	0.3742(2)	2.8(3)
O(2)	0.6165(4)	−0.1396(7)	0.3753(2)	2.8(3)
O(3)	0.6778(4)	0.1701(7)	0.3974(2)	3.0(3)
O(4)	0.6765(4)	0.1645(7)	0.1421(2)	3.1(3)
O(5)	−0.0140(4)	0.1069(7)	0.3735(2)	3.0(3)
O(6)	0.1302(5)	−0.1301(7)	0.3749(2)	3.4(3)
O(7)	0.1838(4)	0.1853(8)	0.3971(2)	3.5(3)
O(8)	0.1816(4)	0.1795(7)	0.1412(2)	3.1(3)
O(9)	0.4119(4)	0.0946(6)	−0.0686(2)	2.6(2)
O(10)	0.4904(4)	0.2564(6)	0.0323(2)	2.5(2)
O(11)	0.6536(4)	0.0547(7)	−0.0294(2)	3.2(2)
O(12)	−0.0590(4)	0.0624(7)	−0.0754(2)	3.1(2)
O(13)	−0.0870(4)	0.2214(7)	0.0262(2)	2.7(2)
O(14)	0.1439(4)	0.1590(6)	−0.0058(2)	2.1(2)
O(15)	0.3359(4)	−0.0021(7)	0.4767(2)	2.9(2)
O(16)	0.8601(4)	−0.0134(7)	0.4567(2)	2.8(2)
C(1)	0.6184(6)	0.101(1)	0.2997(3)	1.9(4)
C(2)	0.7200(6)	0.180(1)	0.2873(3)	2.2(4)
C(3)	0.7404(6)	0.202(1)	0.2337(3)	2.5(4)
C(4)	0.6585(7)	0.145(1)	0.1941(3)	2.2(4)
C(5)	0.5581(6)	0.067(1)	0.2075(3)	2.6(4)
C(6)	0.5354(6)	0.043(1)	0.2598(3)	2.3(4)
C(7)	0.1257(6)	0.110(1)	0.2992(3)	1.8(4)
C(8)	0.2292(6)	0.176(1)	0.2859(3)	2.3(4)
C(9)	0.2507(6)	0.199(1)	0.2330(3)	2.2(4)
C(10)	0.1643(5)	0.157(1)	0.1940(3)	2.0(4)
C(11)	0.0602(6)	0.091(1)	0.2073(3)	2.5(4)
C(12)	0.0401(6)	0.066(1)	0.2595(3)	2.4(4)
H(1)	0.7834	0.2432	0.3180	2.3
H(2)	0.8253	0.2568	0.2191	2.6
H(3)	0.4955	0.0370	0.1814	2.5
H(4)	0.4538	0.0186	0.2751	2.5
H(5)	0.7465	0.2547	0.1504	3.2
H(6)	0.2893	0.2222	0.3203	2.4
H(7)	0.3361	0.2560	0.2226	2.4
H(8)	−0.0089	0.0739	0.1802	2.7
H(9)	−0.0380	0.0202	0.2746	2.3
H(10)	0.2547	0.2469	0.1514	3.2
H(11)	0.3314	0.1065	−0.0487	2.4
H(12)	0.4384	0.1959	−0.0772	2.4
H(13)	0.4743	0.2962	0.0635	2.1
H(14)	0.5316	0.3620	0.0261	2.1
H(15)	0.6663	0.1556	−0.0463	3.2
H(16)	0.7242	−0.0223	−0.0236	3.2
H(17)	−0.0519	0.1756	−0.0906	2.9
H(18)	−0.1152	−0.0314	−0.0976	2.9
H(19)	−0.0912	0.3439	0.0034	2.4
H(20)	−0.0821	0.2386	0.0594	2.4
H(21)	0.1625	0.1731	−0.0346	1.8
H(22)	0.1376	0.2858	0.0044	1.8
H(23)	0.2934	0.0444	0.4463	3.4
H(24)	0.3847	0.1231	0.4652	3.6
H(25)	0.7984	0.0390	0.4480	2.7
H(26)	0.8888	0.0290	0.4249	2.7

(continued)

TABLE 2. *(continued)*

Atom	x	y	z	B_{eq}
Co(C$_6$H$_5$SO$_3$)$_2 \cdot$ 6H$_2$O				
Co(1)	0.2496(6)	0.3909	0.2533(2)	2.34(6)
S(1)	0.7722(7)	0.012(1)	0.3567(2)	2.4(2)
S(2)	0.729(1)	−0.223(1)	0.1462(3)	3.4(3)
O(1)	0.948(2)	−0.084(3)	0.3396(6)	3.5(7)
O(2)	0.771(2)	0.241(3)	0.3497(7)	3.1(7)
O(3)	0.601(2)	−0.085(3)	0.3266(6)	5.0(8)
O(4)	0.725(3)	−0.450(3)	0.1552(8)	5(1)
O(5)	0.896(2)	−0.126(3)	0.1756(6)	2.5(6)
O(6)	0.546(3)	−0.127(2)	0.1614(6)	3.7(7)
O(7)	0.040(3)	0.501(3)	0.3068(7)	4.0(7)
O(8)	0.257(3)	0.108(3)	0.2939(8)	4.5(8)
O(9)	0.479(3)	0.494(3)	0.3057(7)	3.5(8)
O(10)	0.238(3)	0.680(3)	0.2043(8)	3.7(9)
O(11)	0.443(3)	0.278(3)	0.1957(7)	3.8(7)
O(12)	0.026(3)	0.276(3)	0.1934(8)	4.6(8)
H(11)	0.0046	0.6528	0.3185	4.5
H(12)	−0.0888	0.4258	0.3071	4.5
H(13)	0.3750	0.0259	0.2960	5.9
H(14)	0.1257	0.0345	0.3115	5.9
H(15)	0.5377	0.6450	0.3138	4.6
H(16)	0.5853	0.4000	0.3266	4.6
H(17)	0.3619	0.7493	0.1922	3.6
H(18)	0.1396	0.7666	0.2038	3.6
H(19)	0.4995	0.1265	0.1806	4.1
H(20)	0.5771	0.3438	0.1803	4.1
H(21)	0.0359	0.1035	0.1852	4.3
H(22)	−0.1317	0.3124	0.1970	4.3
C(1)	0.757(2)	−0.037(2)	0.4333(4)	3.2(5)
C(2)	0.696(2)	−0.238(2)	0.4489(5)	3.3(4)
C(3)	0.689(2)	−0.293(2)	0.5089(5)	4.1(4)
C(4)	0.743(2)	−0.147(2)	0.5533(4)	3.8(3)
C(5)	0.804(2)	0.055(2)	0.5376(5)	3.1(3)
C(6)	0.811(2)	0.109(2)	0.4777(5)	3.2(4)
H(1)	0.659(3)	−0.338(3)	0.4187(6)	4.0
H(2)	0.648(3)	−0.430(2)	0.5195(7)	4.0
H(3)	0.739(3)	−0.184(2)	0.5941(4)	4.0
H(4)	0.841(3)	0.154(2)	0.5678(6)	4.0
H(5)	0.852(3)	0.247(2)	0.4670(7)	4.0
C(7)	0.743(2)	−0.176(2)	0.0694(4)	3.1(5)
C(8)	0.813(2)	0.012(2)	0.0467(5)	4.0(5)
C(9)	0.826(2)	0.036(2)	−0.0146(6)	5.0(4)
C(10)	0.770(2)	−0.129(2)	−0.0532(4)	4.4(4)
C(11)	0.699(2)	−0.317(2)	−0.0305(5)	5.8(5)
C(12)	0.686(2)	−0.340(2)	0.0308(6)	4.5(5)
H(6)	0.852(3)	0.124(3)	0.0730(7)	5.4
H(7)	0.874(3)	0.163(2)	−0.0301(8)	5.4
H(8)	0.779(3)	−0.113(3)	−0.0950(4)	5.4
H(9)	0.661(3)	−0.428(2)	−0.0568(7)	5.4
H(10)	0.638(3)	−0.468(2)	0.0463(8)	5.4
Na$_2$(HOC$_6$H$_4$SO$_3$)$_2 \cdot$ 4H$_2$O				
S(1)	0.9221(1)	0.0421(1)	0.89845(5)	2.08(5)
S(2)	0.9691(1)	0.5418(1)	0.60231(5)	2.01(5)
Na(1)	1.0918(2)	0.8378(2)	0.52256(7)	2.49(8)
Na(2)	1.0789(2)	0.3368(2)	0.97924(7)	2.55(8)
O(1)	1.0385(4)	0.1276(3)	0.9320(1)	2.6(1)
O(2)	0.7518(4)	0.0502(4)	0.9149(1)	3.6(2)
O(3)	0.9809(4)	−0.0955(3)	0.8979(1)	3.2(2)
O(4)	0.9507(4)	0.1822(3)	0.6522(1)	3.3(2)

(continued)

TABLE 2. (continued)

Atom	x	y	z	B_{eq}
O(5)	1.0768(4)	0.6400(3)	0.5784(1)	2.8(1)
O(6)	0.8044(4)	0.5308(3)	0.5721(1)	3.0(1)
O(7)	1.0524(4)	0.4119(3)	0.6078(1)	2.5(1)
O(8)	0.8782(4)	0.6718(3)	0.8460(1)	3.2(2)
O(9)	1.3228(4)	0.2256(3)	1.0309(1)	2.8(1)
O(10)	0.8717(4)	0.4907(3)	0.9430(1)	2.9(1)
O(11)	1.0988(4)	1.0069(3)	0.4414(1)	2.9(1)
O(12)	0.8131(4)	0.7736(3)	0.4717(1)	2.8(1)
C(1)	0.9228(5)	0.0938(4)	0.8259(2)	1.7(2)
C(2)	0.8430(5)	0.0147(4)	0.7827(2)	1.9(2)
C(3)	0.8536(5)	0.0453(4)	0.7253(2)	2.3(2)
C(4)	0.9422(5)	0.1571(4)	0.7095(2)	2.2(2)
C(5)	1.0189(5)	0.2380(4)	0.7528(2)	2.3(2)
C(6)	1.0091(5)	0.2063(5)	0.8107(2)	2.3(2)
C(7)	0.9380(5)	0.5901(4)	0.6743(2)	1.9(2)
C(8)	0.8328(5)	0.5133(4)	0.7058(2)	2.2(2)
C(9)	0.8145(5)	0.5410(4)	0.7638(2)	2.4(2)
C(10)	0.9013(5)	0.6478(4)	0.7891(2)	2.0(2)
C(11)	1.0061(5)	0.7244(4)	0.7582(2)	2.3(2)
C(12)	1.0246(5)	0.6965(4)	0.7002(2)	2.1(2)
H(1)	0.7628	−0.0608	0.7915	1.8
H(2)	0.7902	−0.0152	0.6889	2.3
H(3)	1.0988	0.3206	0.7467	2.1
H(4)	1.0827	0.2664	0.8340	2.3
H(5)	0.7760	0.4415	0.6849	2.3
H(6)	0.7478	0.4625	0.7902	2.5
H(7)	1.0557	0.8121	0.7805	2.3
H(8)	1.1138	0.7430	0.6747	2.0
H(9)	1.2971	0.1522	1.0521	2.7
H(10)	1.3661	0.2887	1.0558	2.7
H(11)	0.7626	0.4585	0.9446	2.8
H(12)	0.8737	0.5312	0.9081	2.8
H(13)	1.2092	1.0353	0.4284	2.8
H(14)	1.0802	0.9536	0.4149	2.8
H(15)	0.7622	0.8498	0.4593	2.7
H(16)	0.8350	0.7061	0.4429	2.7
H(17)	1.0004	0.2718	0.6484	3.3
H(18)	0.8871	0.7599	0.8601	3.2

The final refinement of 254 variables (including anisotropic thermal parameters for all non-hydrogen atoms and the secondary extinction coefficient) and 2198 data ($I > 3\sigma(I)$) converged to $R = 0.042$ and $R_w = 0.044$.

In this case, it is apparent that the Mn^{2+} ions present in the reaction were not incorporated into the structure as the formula for this crystal is $Na_2(HOC_6H_4SO_3)_2 \cdot 4H_2O$ ($FW = 464.32$). The positional and equivalent isotropic thermal parameters of each atom in the unit cell are given in Table 2. Table 3 lists the intramolecular distances and Table 4 the intramolecular bond angles involving the non-hydrogen atoms.

Results

$Ni(HOC_6H_4SO_3)_2 \cdot 8H_2O$

The structure is shown in Figs. 1 and 2. The nickel atoms are coordinated by six water molecules, with no

TABLE 3. Selected bond distances (Å)

$Ni(HOC_6H_4SO_3)_2 \cdot 8H_2O$

Ni(1)–O(12)	2.036(5)	O(4)–C(4)	1.361(8)
Ni(1)–O(13)	2.043(5)	O(8)–C(10)	1.379(8)
Ni(1)–O(14)	2.064(4)	C(1)–C(2)	1.38(1)
Ni(2)–O(9)	2.073(5)	C(1)–C(6)	1.42(1)
Ni(2)–O(10)	2.041(5)	C(2)–C(3)	1.41(1)
Ni(2)–O(11)	2.045(4)	C(3)–C(4)	1.40(1)
S(1)–O(1)	1.448(5)	C(4)–C(5)	1.38(1)
S(1)–O(2)	1.467(5)	C(5)–C(6)	1.38(1)
S(1)–O(3)	1.459(5)	C(7)–C(8)	1.372(9)
S(1)–C(1)	1.773(7)	C(7)–C(12)	1.41(1)
S(2)–O(5)	1.447(5)	C(8)–C(9)	1.39(1)
S(2)–O(6)	1.469(5)	C(9)–C(10)	1.40(1)
S(2)–O(7)	1.465(5)	C(10)–C(11)	1.38(1)
S(2)–C(7)	1.761(7)	C(11)–C(12)	1.37(1)

$Co(C_6H_5SO_3)_2 \cdot 6H_2O$

Co(1)–O(7)	2.08(2)	S(1)–O(2)	1.46(2)
Co(1)–O(8)	2.01(2)	S(1)–O(3)	1.47(2)
Co(1)–O(9)	2.04(2)	S(1)–C(1)	1.76(1)
Co(1)–O(10)	2.13(2)	S(2)–O(4)	1.45(2)
Co(1)–O(11)	2.06(2)	S(2)–O(5)	1.45(2)
Co(1)–O(12)	2.13(2)	S(2)–O(6)	1.48(2)
S(1)–O(1)	1.45(2)	S(2)–C(7)	1.76(1)

$Na_2(HOC_6H_4SO_3)_2 \cdot 4H_2O$

S(1)–O(1)	1.456(3)	Na(2)–O(9)	2.532(4)
S(1)–O(2)	1.447(3)	Na(2)–O(10)	2.385(4)
S(1)–O(3)	1.467(3)	Na(2)–O(10)	2.517(4)
S(1)–C(1)	1.762(4)	O(4)–C(4)	1.359(5)
S(2)–O(5)	1.450(3)	O(8)–C(10)	1.369(5)
S(2)–O(6)	1.456(3)	C(1)–C(2)	1.400(5)
S(2)–O(7)	1.473(3)	C(1)–C(6)	1.388(6)
S(2)–C(7)	1.774(4)	C(2)–C(3)	1.375(6)
Na(1)–O(5)	2.386(3)	C(3)–C(4)	1.395(6)
Na(1)–O(6)	2.391(4)	C(4)–C(5)	1.401(6)
Na(1)–O(11)	2.544(4)	C(5)–C(6)	1.389(6)
Na(1)–O(11)	2.382(4)	C(7)–C(8)	1.390(6)
Na(1)–O(12)	2.538(4)	C(7)–C(12)	1.392(6)
Na(1)–O(12)	2.472(4)	C(8)–C(9)	1.391(6)
Na(2)–O(1)	2.389(3)	C(9)–C(10)	1.390(6)
Na(2)–O(2)	2.398(4)	C(10)–C(11)	1.379(6)
Na(2)–O(9)	2.489(4)	C(11)–C(12)	1.392(6)

coordination to the sulfonate groups. There are two extra water molecules per formula unit that are not coordinated to either the sulfonates or the nickel atoms. Figure 2 shows that the structure is composed of alternating layers of hexaaquanickel cations and 4-hydroxybenzenesulfonate anions. Within the sulfonate layer, there are rows of anions with the orientations of the 4-hydroxy groups alternating up and down.

The nickel atoms rest on inversion centers and hence have a nearly ideal octahedral geometry. In this arrangement, symmetry equivalent water molecules are present on opposite sides of the Ni atom, exactly 180° apart. The distances from nickel to oxygen range from 2.036(5) to 2.073(5) Å and the angles are all around 90°, ranging from 87.3(2) to 92.7(2)°. The metrical data for the sulfonate groups, given in Tables 3 and 4, are normal. The geometries of the phenyl rings are highly

TABLE 4. Selected intramolecular bond angles (°)

Ni(HOC₆H₄SO₃)₂·8H₂O

Ni(HOC$_6$H$_4$SO$_3$)$_2$·8H$_2$O

O(12)–Ni(1)–O(13)	90.8(2)	S(1)–C(1)–C(6)	118.6(6)
O(12)–Ni(1)–O(14)	91.8(2)	C(2)–C(1)–C(6)	121.4(7)
O(13)–Ni(1)–O(14)	90.9(2)	C(1)–C(2)–C(3)	118.8(7)
O(9)–Ni(2)–O(10)	90.3(2)	C(2)–C(3)–C(4)	120.1(7)
O(9)–Ni(2)–O(11)	91.7(2)	O(4)–C(4)–C(3)	121.1(7)
O(10)–Ni(2)–O(11)	92.7(2)	O(4)–C(4)–C(5)	118.9(7)
O(1)–S(1)–O(2)	112.0(3)	C(3)–C(4)–C(5)	120.1(7)
O(1)–S(1)–O(3)	113.9(3)	C(4)–C(5)–C(6)	121.3(7)
O(1)–S(1)–C(1)	107.8(3)	C(1)–C(6)–C(5)	118.5(7)
O(2)–S(1)–O(3)	111.2(3)	S(2)–C(7)–C(8)	119.7(6)
O(2)–S(1)–C(1)	106.2(3)	S(2)–C(7)–C(12)	120.0(6)
O(3)–S(1)–C(1)	105.1(3)	C(8)–C(7)–C(12)	120.2(7)
O(5)–S(2)–O(6)	111.8(3)	C(7)–C(8)–C(9)	120.5(7)
O(5)–S(2)–O(7)	112.8(3)	C(8)–C(9)–C(10)	118.7(7)
O(5)–S(2)–C(7)	107.4(3)	O(8)–C(10)–C(9)	120.6(6)
O(6)–S(2)–O(7)	111.8(3)	O(8)–C(10)–C(11)	118.6(7)
O(6)–S(2)–C(7)	106.5(3)	C(9)–C(10)–C(11)	120.9(7)
O(7)–S(2)–C(7)	106.1(3)	C(10)–C(11)–C(12)	120.1(7)
S(1)–C(1)–C(2)	119.9(6)	C(7)–C(12)–C(11)	119.6(7)

Co(C₆H₅SO₃)₂·6H₂O

Co(C$_6$H$_5$SO$_3$)$_2$·6H$_2$O

O(7)–Co(1)–O(10)	90.5(7)	O(9)–Co(1)–O(10)	91.5(7)
O(7)–Co(1)–O(11)	176.1(7)	O(9)–Co(1)–O(11)	86.8(7)
O(7)–Co(1)–O(12)	87.6(7)	O(9)–Co(1)–O(12)	175.3(8)
O(8)–Co(1)–O(9)	91.5(7)	O(10)–Co(1)–O(11)	88.8(7)
O(8)–Co(1)–O(10)	176.0(7)	O(10)–Co(1)–O(12)	87.9(7)
O(1)–S(1)–O(2)	113(1)	O(4)–S(2)–O(6)	111(1)
O(1)–S(1)–O(3)	113(1)	O(4)–S(2)–C(7)	108(1)
O(1)–S(1)–C(1)	106.9(8)	O(5)–S(2)–O(6)	114(1)
O(2)–S(1)–O(3)	111(1)	O(5)–S(2)–C(7)	106.2(9)
O(2)–S(1)–C(1)	106.3(8)	O(6)–S(2)–C(7)	105.2(8)
O(3)–S(1)–C(1)	105.9(8)	O(4)–S(2)–O(5)	112(1)

Na₂(HOC₆H₄SO₃)₂·4H₂O

Na$_2$(HOC$_6$H$_4$SO$_3$)$_2$·4H$_2$O

|			
O(1)–S(1)–O(2)	114.1(2)	O(2)–Na(2)–O(9)	159.8(1)
O(1)–S(1)–O(3)	111.7(2)	O(2)–Na(2)–O(10)	83.8(1)
O(1)–S(1)–C(1)	106.9(2)	S(1)–C(1)–C(2)	118.9(3)
O(2)–S(1)–O(3)	111.5(2)	S(1)–C(1)–C(6)	121.3(3)
O(2)–S(1)–C(1)	107.6(2)	C(2)–C(1)–C(6)	119.8(4)
O(3)–S(1)–C(1)	104.4(2)	C(1)–C(2)–C(3)	120.5(4)
O(5)–S(2)–O(6)	114.5(2)	C(2)–C(3)–C(4)	120.2(4)
O(5)–S(2)–O(7)	111.2(2)	O(4)–C(4)–C(3)	117.9(4)
O(5)–S(2)–C(7)	107.4(2)	O(4)–C(4)–C(5)	122.8(4)
O(6)–S(2)–O(7)	111.4(2)	C(3)–C(4)–C(5)	119.4(4)
O(6)–S(2)–C(7)	106.8(2)	C(4)–C(5)–C(6)	120.4(4)
O(7)–S(2)–C(7)	104.8(2)	C(1)–C(6)–C(5)	119.8(4)
O(5)–Na(1)–O(6)	105.3(1)	S(2)–C(7)–C(8)	118.2(3)
O(5)–Na(1)–O(11)	165.2(1)	S(2)–C(7)–C(12)	121.2(3)
O(6)–Na(1)–O(11)	85.5(1)	C(8)–C(7)–C(12)	120.4(4)
O(6)–Na(1)–O(12)	160.2(1)	C(7)–C(8)–C(9)	120.3(4)
O(11)–Na(1)–O(12)	76.3(1)	C(8)–C(9)–C(10)	118.6(4)
O(11)–Na(1)–O(12)	165.4(1)	O(8)–C(10)–C(9)	116.5(4)
O(1)–Na(2)–O(10)	161.5(1)	O(8)–C(10)–C(11)	122.1(4)
O(2)–Na(2)–O(9)	92.5(1)	C(9)–C(10)–C(11)	121.4(4)
O(9)–Na(2)–O(10)	165.6(1)	C(10)–C(11)–C(12)	119.9(4)
O(9)–Na(2)–O(10)	83.6(1)	C(7)–C(12)–C(11)	119.2(4)
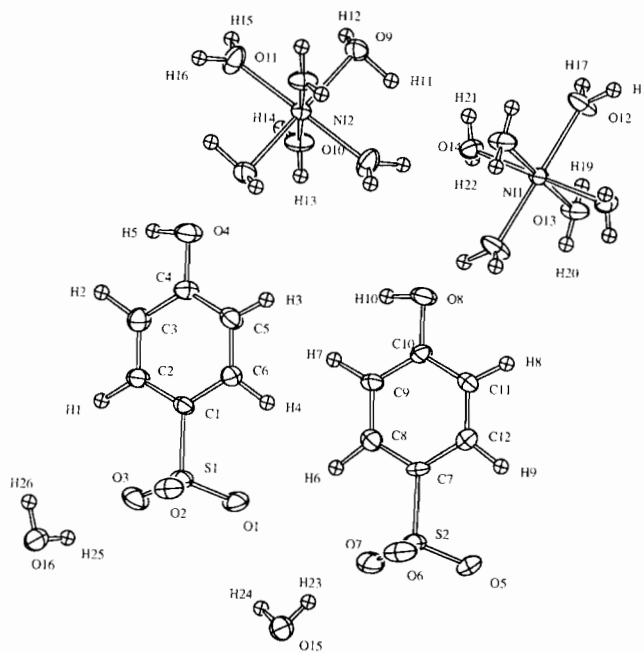
Fig. 1. ORTEP diagram of the asymmetric unit of Ni(HOC$_6$H$_4$SO$_3$)$_2$·8H$_2$O showing atom labelling scheme. In this and subsequent ORTEP diagrams, the thermal ellipsoids are shown at the 50% probability level except for those of the hydrogen atoms, which are drawn as isotropic spheres of arbitrary size.

rical data for hydrogen bonds are given as hydrogen bond distance, covalent O–H distance, O–H–O bond angle). The presence of the hydroxy groups on the phenyl rings results in hydrogen bonding between the OH of one sulfonate anion in the 'up' orientation and a sulfonate oxygen of a neighboring anion in the 'down' orientation: O(6)·····H(5)–O(4), 1.83, 1.06 Å, 146.6°; O(2)·····H(10)–O(8), 1.89, 1.01 Å, 144.1°. There is also hydrogen bonding between the hydroxy groups and the coordinated water molecules: O(8)·····H(18)–O(12), 1.69, 1.08 Å, 168.1°. In addition, there are hydrogen bonds between the non-coordinated water molecules and the sulfonate oxygens and coordinated water molecules: O(5)·····H(26)–O(16), 1.89, 0.95 Å, 163.4°; O(15)·····H(14)–O(10), 1.85, 0.93 Å, 154.2°. As a result of these interactions, the crystals are hard and brittle and lack the distinctive cleavage characteristic of many layered compounds.

Co(C₆H₅SO₃)₂·6H₂O

Co(C$_6$H$_5$SO$_3$)$_2$·6H$_2$O

The structure is shown in Figs. 3 and 4. The cobalt atom is octahedrally coordinated by six water molecules with no direct coordination to the sulfonate groups. As the metrical data in Tables 3 and 4 show, the geometry about the cobalt is fairly regular. This structure is also composed of alternating layers of metal complexes and benzenesulfonate anions. It is apparent from Fig. 4 that the sulfonates, as in the nickel structure, are

regular with carbon–carbon bond distances ranging from 1.37(1) to 1.42(1) Å and angles all within 118.5(7)–121.4(7)°.

This structure is extensively hydrogen bonded. Some important interactions are summarized as follows (met-
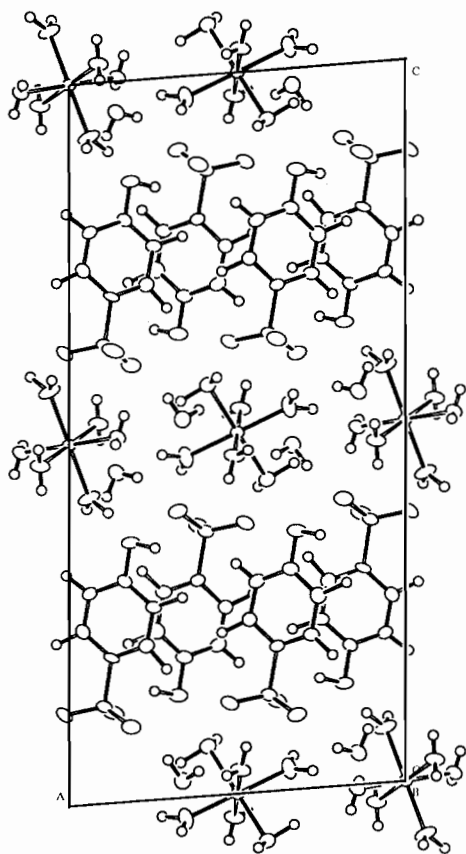
Fig. 2. ORTEP packing diagram of Ni(HOC$_6$H$_4$SO$_3$)$_2$·8H$_2$O showing the outline of the unit cell. View is along the *b* axis.
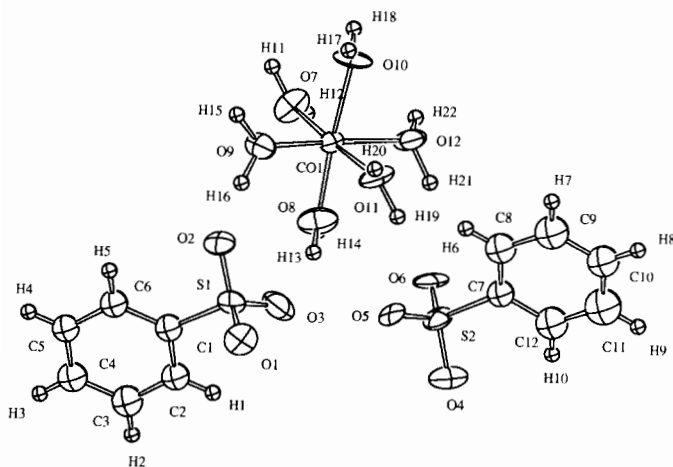
Fig. 3. ORTEP diagram of the asymmetric unit of Co(C$_6$H$_5$SO$_3$)$_2$·6H$_2$O showing the atom labelling scheme.

alternating their orientations within the layer, however, a comparison of Figs. 2 and 4 shows that the topography of the sulfonate layers is different for the 4-hydroxy-substituted and unsubstituted benzenesulfonates. The rows of 4-hydroxybenzenesulfonate anions in the nickel compound are all canted in the same direction and the rings are in register within the layer. This is pre-
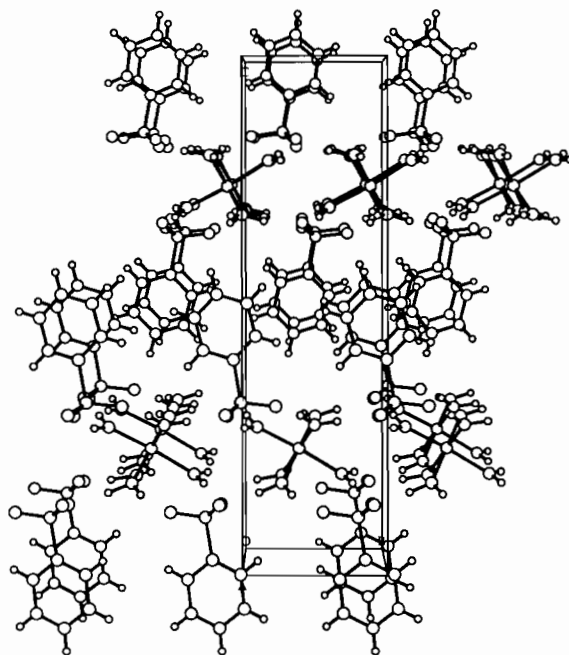
Fig. 4. PLUTO packing diagram of Co(C$_6$H$_5$SO$_3$)$_2$·6H$_2$O showing the outline of the unit cell. View is along the *a* axis.

sumably due to the hydrogen bonding between neighboring anions discussed above. By contrast, the rows of benzenesulfonate anions in the cobalt structure are tilted in opposite directions and the rings are out of register within the layer with the sulfonate groups jutting out towards the cations. In the absence of polar interactions between the anions, the primary interaction is between the sulfonate group and the aqua ion. This is evident in Fig. 4 and from the metrical data which reveal several strong hydrogen bonding interactions between the sulfonate oxygen atoms and coordinated water molecules, including: O(6)·····H(19)–O(11), 1.70, 1.10 Å, 168.9°; O(3)·····H(13)–O(8), 1.82, 0.98 Å, 159.1°; O(2)·····H(16)–O(9), 1.70, 1.04 Å, 170.8°. These strong interactions produce crystals that are hard and brittle, but with a more pronounced cleavage and a somewhat greater tendency toward stacking faults than is observed in the nickel 4-hyroxybenzenesulfonate compound.

Reactions of divalent manganese, nickel and zinc ions with sodium benzenesulfonate in aqueous solution also produced crystals that were examined by X-ray diffraction. On the basis of the unit cell dimensions and symmetry, shown in Table 5, these compounds are isostructural with the cobalt compound. Of note also is the correlation between the unit cell dimensions and the ionic radii of the different metals: Mn^{2+} > Co^{2+} > Ni^{2+} < Zn^{2+}.

Na$_2$(HOC$_6$H$_4$SO$_3$)$_2$·4H$_2$O

The structure with atom labelling scheme is shown in Fig. 5. An extended view with the sodium–oxygen

TABLE 5. Unit cell parameters for $M(C_6H_5SO_3)_2 \cdot 6H_2O$ (M = Mn, Co, Ni and Zn)

	Mn	Co	Ni	Zn
Crystal system		monoclinic		
Space group		$P2_1$ (No. 4)		
Z value		2		
a (Å)	7.050(3)	7.017(2)	6.981(1)	6.996(5)
b (Å)	6.339(3)	6.324(2)	6.308(1)	6.315(2)
c (Å)	22.791(2)	22.468(4)	22.406(6)	22.499(6)
β (°)	93.64(2)	93.70(3)	93.74(2)	93.51(3)
V (Å^3)	1016.6(6)	995.0(4)	984.5(3)	992.0(7)
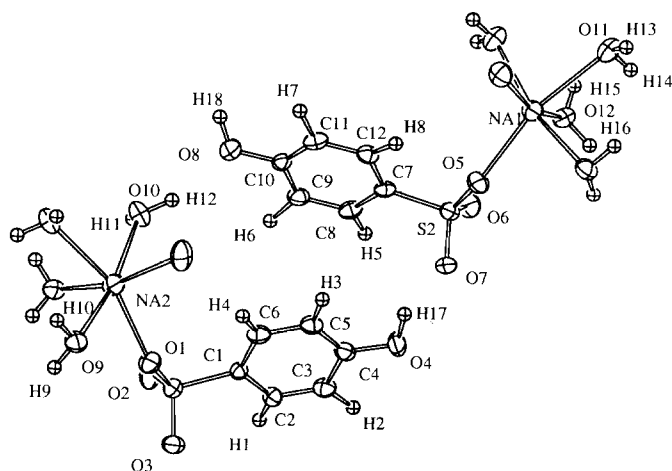
Fig. 5. ORTEP diagram of $Na_2(HOC_6H_4SO_3)_2 \cdot 4H_2O$ showing the atom labelling scheme. Symmetry equivalent oxygen atoms have been included to show the complete coordination environments about the sodium atoms.
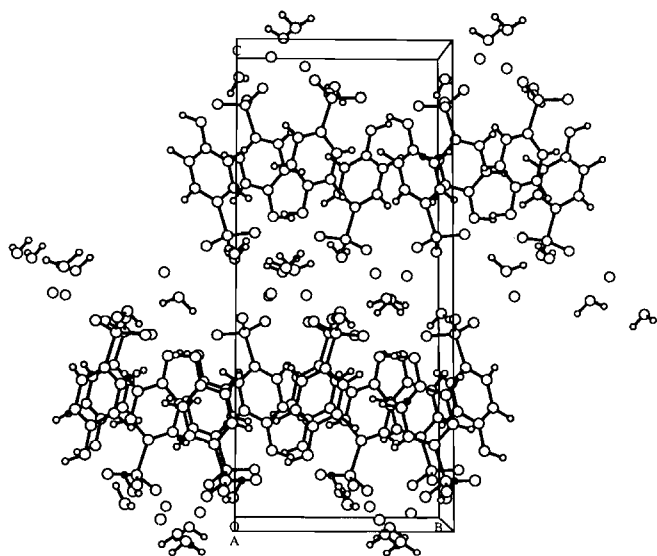
Fig. 6. PLUTO packing diagram of $Na_2(HOC_6H_4SO_3)_2 \cdot 4H_2O$ showing the outline of the unit cell. Bonds to the sodium atoms have been omitted. View is along the a axis.

bonds omitted is provided in Fig. 6. The sodium atom has four water molecules coordinated to it and is also coordinated by two oxygens on two separate sulfonate groups. This is the first direct coordination to the sulfonate groups observed in this study. As shown in Fig. 5 the Na^+ ions are in an approximately octahedral coordination. It is less regular than that seen with the transition metals, with the apical O–Na–O angles ranging from 159.8(1) to 165.4(1)° and the acute angles ranging from 76.3(1)° to 110.2(1)°. These are significantly distorted from the ideal octahedral values of 180° and 90°. The sodium–oxygen distances are long and range from 2.382(4) to 2.544(4) Å. The metrical data for the sulfonate ions, given in Tables 3 and 4, are highly regular. In particular, the ring geometry is nearly ideal with carbon–carbon bonds all falling in the range of 1.379(6) to 1.401(6) Å in length and the angles all between 118.6(4) and 121.4(4)°.

This structure is similar to the others in that it is composed of alternating layers of benzenesulfonate and metal ions. Despite the presence of the 4-hydroxy group, the topography of the organic layer, as shown in Fig. 6, is more like that of the unsubstituted benzenesulfonate in having the alternating rows of anions canted and displaced perpendicular to the plane of the layer. Presumably this is due to the strong bonding interactions between the sulfonate oxygen atoms and the sodium ion. There are also hydrogen bonds between the OH groups and sulfonate oxygen atoms of neighboring anions, $O(7)\cdots\cdots H(17)-O(4)$, 1.77, 0.99 Å, 152.4°; $O(3)\cdots\cdots H(18)-O(8)$, 1.84, 0.95 Å, 158.1°, and between the non-coordinated sulfonate oxygen atoms and coordinated water molecules, $O(3)\cdots\cdots H(10)-O(9)$, 1.96, 0.91 Å, 163.7°; $O(7)\cdots\cdots H(16)-O(12)$, 1.94, 0.98 Å, 162.6°. As a result of these interactions, the crystals of this material, like those of the nickel compound, are quite hard and free of stacking faults.

Discussion

The results of this study show that mixed organic–inorganic materials with layered structures can be prepared from aqueous solutions of metal ions and organic sulfonates. These compounds are quite different in structure and properties from recently reported metal phosphonates of similar composition.

Transition metal phosphonates prepared by similar reactions [6, 10–13] contain covalent metal–oxygen–phosphorus layers with the organic groups directed into the interlayer region. The layers are held together only by the weak non-bonded interactions of the organic groups. As a result, the crystals grow slowly and stacking faults are common. They are soft and easily cleaved.

By contrast, the transition metal sulfonates reported here do not show direct bonding between the metal ions and sulfonate groups. The metal ions are fully hydrated in the solid state and the layers are held together by ionic and hydrogen bonds. As a result, the crystals are more easily grown, harder, and freer of defects than those of the analogous phosphonates. Because they lack the extended covalent network, they are also somewhat water soluble.

The weak coordinating strength of the sulfonates relative to the water molecules prevents the formation of direct metal–oxygen–sulfur bonds in aqueous solution. The ability of the phosphonates to coordinate transition metals under similar conditions may be due to their greater negative charge (-2) relative to that of the sulfonates (-1). Nevertheless, the coordination of the sulfonates by the sodium ion suggests that it may be possible to form structures analogous to the phosphonates under the right conditions. If the reactions are done under non-aqueous conditions it may be possible to force the coordination of the sulfonates and form structures with the desired rigid framework. In addition, thermogravimetric analysis of the sodium material indicates that the water may be removed without destroying the rest of the compound so that dehydration may represent another route to extended covalent structures in these systems. Experiments to test these hypotheses are currently underway.

Supplementary material

Tables of anisotropic thermal parameters, bond distances and angles involving the hydrogen atoms, and observed versus calculated structure amplitudes are available from the authors.

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