

# Structures of layered metal sulfonate salts: trends in coordination behavior of alkali, alkaline earth and transition metals

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## Abstract

Several new metal arylsulfonates have been prepared from reactions of metal salts and sodium arylsulfonate salts in aqueous solution. The products have been characterized by single crystal X-ray diffraction techniques.  $\text{Co}(\text{HO}(\text{O}_2\text{N})\text{C}_6\text{H}_3\text{SO}_3)_2 \cdot 6\text{H}_2\text{O}$ : triclinic, space group  $P\bar{1}$ ,  $Z=1$ ,  $a=6.455(2)$ ,  $b=15.541(5)$ ,  $c=5.687(2)$  Å,  $\alpha=92.55(3)$ ,  $\beta=94.13(2)$ ,  $\gamma=98.76(2)^\circ$ ,  $V=561.4(3)$  Å<sup>3</sup>,  $R(F^2)=0.076$  for 1979 observations ( $I>0$ ) and 160 variables ( $R(F)=0.042$  for 1274 data with  $I>3\sigma(I)$ ). The structure contains layers composed of two sheets of 4-hydroxy-3-nitrobenzenesulfonate anions with  $[\text{Co}(\text{H}_2\text{O})_6]^{2+}$  cations sandwiched in between. There are hydrogen bonds between the coordinated water molecules and sulfonate anions but no direct coordination of the metal by the sulfonate oxygen atoms.  $\text{Na}_4(\text{HO}(\text{O}_2\text{N})\text{C}_6\text{H}_3\text{SO}_3)_4 \cdot 2\text{H}_2\text{O}$ : monoclinic, space group  $Pc$ ,  $Z=2$ ,  $a=8.293(3)$ ,  $b=16.580(2)$ ,  $c=13.465(2)$  Å,  $\beta=90.29(2)^\circ$ ,  $V=1851.5(8)$  Å<sup>3</sup>,  $R(F^2)=0.148$  for 3248 observations ( $I>0$ ) and 229 variables ( $R(F)=0.081$  for 1747 data with  $I>3\sigma(I)$ ). The sodium ions are coordinated directly to the oxygen atoms of the 4-hydroxy-3-nitrobenzenesulfonate ions, forming a double sheet of sulfonate anions with cations in between. There are also two water molecules associated with the sodium ions.  $\text{Ca}(\text{H}_3\text{C}(\text{H}_2\text{N})\text{C}_6\text{H}_3\text{SO}_3)_2 \cdot 7\text{H}_2\text{O}$ : monoclinic, space group  $P2_1/c$ ,  $Z=4$ ,  $a=14.859(3)$ ,  $b=6.227(4)$ ,  $c=25.452(2)$  Å,  $\beta=101.07(1)^\circ$ ,  $V=2311(1)$  Å<sup>3</sup>,  $R(F)=0.059$  for 2186 observations ( $I>3\sigma(I)$ ) and 289 variables. This structure, too, has alternating layers of sulfonate ions and hydrated cations. The calcium ions coordinate directly to one of the sulfonate oxygen atoms and six water molecules in a pentagonal bipyramidal arrangement. The crystal structures of these materials and other recently reported layered metal sulfonates are discussed in relation to apparent trends in the coordination behavior of the metal ions.

**Key words:** Alkali metal complexes; Alkaline earth metal complexes; Transition metal complexes; Sulfonate complexes

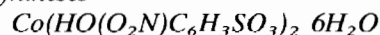
## Introduction

The work reported here is part of an ongoing study of the reactions of various metal ions and organic sulfonates [1], the goal of which is to prepare compounds with layered structures analogous to recently reported metal phosphonates [2, 3]. These mixed inorganic–organic layered compounds contain covalent metal–oxygen–phosphorus frameworks that form infinite sheets with the appended organic groups directed into the interlayer region. They have potential application in such areas as ion exchange and chemical separations [4–7]. Though organic sulfonate anions are widely used industrially as surfactants, relatively little structural data are available on metal sulfonate salts [8–13]. In light of our recent results on transition metal sulfonates [1],

we have begun to examine the structures of alkali and alkaline earth metal sulfonates and have found that these metals show a distinctly greater tendency than the transition metals to bond to the sulfonate groups. The sulfonate compounds reported here were prepared by reactions of metal chloride, nitrate or hydroxide salts with sodium arylsulfonate salts or arylsulfonic acids in water. The syntheses and structures of these compounds are presented and the results are discussed in terms of the coordination behavior of the metal ions in these systems.

## Experimental

### Syntheses



A 5.03 g (0.022 mol) sample of sodium 4-hydroxybenzenesulfonate dihydrate (Aldrich, 98%) was com-

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pletely dissolved in 50 ml of distilled water. A 4.02 g (0.014 mol) sample of reagent grade cobalt(II) nitrate hexahydrate (Mallinckrodt, 99.1%) was added to the solution. The resulting solution was a dusty rose color. A total of 40 ml of concentrated HCl was added to give a purple–blue solution which was allowed to stand at room temperature. The color of the solution changed to a dark brown over several days. After a few weeks, most of the water had evaporated, and a rust-colored crust of small plate-shaped crystals had formed in the bottom of the flask. This solid (5.04 g) was isolated from the remaining liquid by filtration.

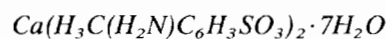
A  $^1\text{H}$  NMR spectrum of the product dissolved in  $\text{D}_2\text{O}$  (DSS internal standard) was recorded on a General Electric QE-300 spectrometer. The major product showed aromatic hydrogen resonances characteristic of a 1,3,4-substituted benzene ring:  $\delta$  7.24 ppm (sharp d, 1 H), 7.95 ppm (sharp d, 1 H), 8.47 ppm (sharp s, 1 H). The spectrum is in good agreement with that reported for 4-hydroxy-3-nitrobenzenearsonic acid [14], which differs only in having an arsonate group in place of the sulfonate group. Also present in the spectrum were two small resonances that are consistent with the reported spectrum for 4-nitrophenol [15]:  $\delta$  6.86 ppm (sharp d) and 8.06 ppm (sharp d). No resonances due to the starting 4-hydroxybenzenesulfonate were observed in the spectrum. Based on the relative intensities of the resonances, the 4-hydroxy-3-nitrobenzenesulfonate appears to be about 95% of the aromatic in the solid product. This is consistent with the elemental analysis (National Chemical Consulting, Tenafly, NJ). *Anal.* Found: C, 22.69; H, 2.92; N, 4.40. Calc. for  $\text{Co}(\text{HO}(\text{O}_2\text{N})\text{C}_6\text{H}_3\text{SO}_3)_2 \cdot 6\text{H}_2\text{O}$ : C, 23.97; H, 3.02; N, 4.66%. Only crystals of the cobalt 4-hydroxy-3-nitrobenzenesulfonate hexahydrate were identified by single crystal X-ray diffraction.



A 0.726 g (4.3 mmol) sample of copper(II) chloride dihydrate (Baker, >99%) and 1.994 g (8.6 mmol) of sodium 4-hydroxybenzenesulfonate dihydrate (Aldrich, 98%) were each dissolved in about 25 ml of distilled water. These solutions were combined and 40 drops (~2 ml) of concentrated nitric acid were added. The resulting solution, which initially had the characteristic aqua blue color of the copper(II) ion, was allowed to stand in an open beaker. As the solvent evaporated slowly, the color gradually changed first to a dark green and then to a dark brownish-orange. Crystals began to grow after about 10 days. Upon complete evaporation of the solvent, a dark reddish-brown crust was left containing platy crystals in a polycrystalline matrix. There were also pale yellow needle-shaped crystals scattered throughout. The total mass of solid product recovered was 2.554 g.

The needle-like crystals were identified as 4-nitrophenol by  $^1\text{H}$  NMR (recorded as described above:  $\delta$  6.96 ppm (sharp d, 2H) and 8.16 ppm (sharp d, 2 H)) and single crystal X-ray diffraction (monoclinic,  $P2_1/n$ ,  $Z=4$ ,  $a=3.772(2)$ ,  $b=11.104(6)$ ,  $c=14.716(9)$  Å,  $\beta=92.68(5)^\circ$ ) [16]. The  $^1\text{H}$  NMR spectrum of the red platy material showed resonances due to 4-hydroxy-3-nitrobenzenesulfonate ( $\delta$  7.29 ppm (d, 1 H), 8.01 ppm (d, 1 H), 8.50 ppm (s, 1 H)) and 4-nitrophenol. Spectra of several different samples of the reddish material showed that the ratio of 4-hydroxy-3-nitrobenzenesulfonate to 4-nitrophenol was lower in this reaction than in the cobalt reaction. Again, none of the 4-hydroxybenzenesulfonate starting material was detected in the product by  $^1\text{H}$  NMR. The only sulfonate product identified by single crystal X-ray diffraction was  $\text{Na}_4(\text{HO}(\text{O}_2\text{N})\text{C}_6\text{H}_3\text{SO}_3)_4 \cdot 2\text{H}_2\text{O}$ . No copper-containing single crystals were found.

The reaction was repeated using only the sodium 4-hydroxybenzenesulfonate (2.000 g dissolved in 25 ml distilled water and 2 ml of concentrated nitric acid). The initially colorless solution turned yellow within the first few hours, gradually darkened to a bright red–orange within 24 h, and then remained the same color. After 15 days in an open beaker, the solution was transferred to a glass evaporating dish. Within 12 h, many large orange flattened rod-shaped crystals had grown and these were isolated from the remaining solution by filtration (0.999 g; 46% yield). The crystals showed the  $^1\text{H}$  NMR pattern of the 4-hydroxy-3-nitrobenzenesulfonate with no signals due to the starting material or 4-nitrophenol. The spectrum of the mother liquor contained resonances due to 4-hydroxy-3-nitrobenzenesulfonate and 4-nitrophenol in approximately equal intensity.



A 0.105 g (1.4 mmol) sample of calcium hydroxide (Fisher, >99%) and 0.527 g (2.8 mmol) of 2-amino-toluene-4-sulfonic acid (Eastman Kodak) were each partially dissolved in about 25 ml of distilled water. The mixtures were combined and heated gently for a short period of time to ensure that all of the reagents went into solution. The now pale yellow solution was then set out to evaporate at room temperature. Upon complete evaporation of the water, a mass of pale brown platy crystals (0.683 g) was left behind. The reaction can be thought of as a simple acid–base neutralization:  $2\text{H}_3\text{C}(\text{H}_2\text{N})\text{C}_6\text{H}_3\text{SO}_3 + \text{Ca}(\text{OH})_2 + 5\text{H}_2\text{O} \rightarrow \text{Ca}(\text{H}_3\text{C}(\text{H}_2\text{N})\text{C}_6\text{H}_3\text{SO}_3)_2 \cdot 7\text{H}_2\text{O}$ .

#### Crystallographic studies

All of the single crystal X-ray diffraction work was done at room temperature on a Rigaku AFC6S diffractometer (Mo  $K\alpha$ ) operated by the MSC-AFC Dif-

fractometer Control software [17]. General data collection and reduction techniques have been described previously [18]. Reflections were measured at a constant scan rate with a maximum of four identical scans for reflections with  $I < 10\sigma(I)$ . Three standards measured after every 150 data showed no significant intensity 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 [19] series of crystallographic programs. Space groups were assigned based on systematic absences and intensity statistics and were confirmed by successful refinements. All the structures were solved by the direct methods program MITHRIL [20] which revealed the locations of the heavy atoms. The oxygen, nitrogen and carbon atoms were located by either direct methods phase refinement techniques (DIRDIF) [21] or difference electron density maps following least-squares refinements. Analyses of  $F_o$  versus  $F_c$  as a function of  $F_o$ ,  $\sin \theta/\lambda$ , 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.

#### $Co(HO(O_2N)C_6H_3SO_3)_2 \cdot 6H_2O$

A crystal fragment (approximate dimensions  $0.30 \times 0.20 \times 0.10$  mm) cut from a larger rust-colored crystal was used. The triclinic unit cell listed in Table 1 was derived from a least-squares refinement of 24

centered reflections in the range  $11.84 < 2\theta < 25.84^\circ$ . A total of 2172 reflections was collected ( $\omega$ - $2\theta$  scans,  $4^\circ \text{ min}^{-1}$  in  $\omega$ ) and merged to yield 1980 unique intensities ( $R(\text{int}) = 0.033$ ). An empirical absorption correction, based on azimuthal scans of three reflections, was applied to the data (transmission factors 0.87–1.00). With the successful solution and refinement of the structure, the space group was determined to be  $P\bar{1}$  (No. 2). Following the location of all the non-hydrogen atoms in the 4-hydroxybenzenesulfonate anion, a difference electron density map revealed the presence of an additional three-atom moiety adjacent to the hydroxy group on the ring. These peaks were included in the model and successfully refined as a nitro group. All the hydrogen atoms, except for the one on the hydroxy group, were located on difference electron density maps and were included as fixed isotropic scatterers. The final refinement, performed on  $F^2$  with 160 variables (including anisotropic thermal parameters for all non-hydrogen atoms) and 1979 observed reflections ( $I > 0$ ), converged to final agreement factors  $R(F^2) = 0.076$  and  $R_w(F^2) = 0.081$ . The conventional  $R(F)$  value for the 1274 data with  $I > 3\sigma(I)$  was 0.042.

The final empirical formula based on the X-ray structure, NMR data and elemental analysis is  $Co(HO(O_2N)C_6H_3SO_3)_2 \cdot 6H_2O$  ( $FW = 601.33$ ). 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 intra-

TABLE 1 Crystallographic data for layered metal sulfonates

Formula	$CoS_2O_{18}N_2C_{12}H_{18}$	$S_4Na_4O_{26}N_4C_{24}H_{20}$	$CaS_2O_{13}N_2C_{14}H_{30}$
Formula weight	601.33	1000.63	538.60
Crystal system	triclinic	monoclinic	monoclinic
$a$ (Å)	6 455(2)	8.293(3)	14.859(3)
$b$ (Å)	15.541(5)	16.580(2)	6.227(4)
$c$ (Å)	5 687(2)	13.465(2)	25.452(2)
$\alpha$ (°)	92.55(3)	90	90
$\beta$ (°)	94.13(2)	90.29(2)	101.07(1)
$\gamma$ (°)	98 76(2)	90	90
$V$ (Å <sup>3</sup> )	561 4(3)	1851.5(8)	2311(1)
Space group	$P\bar{1}$	$Pc$	$P2_1/c$
$Z$ value	1	2	4
$D_{\text{calc}}$ (g cm <sup>-3</sup> )	1.78	1 80	1.55
$F(000)$	307	1016	1136
$\mu$ (Mo $K\alpha$ ) (cm <sup>-1</sup> )	10 26	3.92	5 00
Transmission factors	0 87–1 00	none	none
$2\theta$ Range for data (°)	3–50	3–50	3–50
No. unique observations	1980	3374	4472
No. data $I > 3\sigma(I)$	1274	1747	2186
No. variables	160	229	289
Data/parameter ratio	12.4	14.2	7.6
$R(F)$ ; $R_w(F)$ ( $I > 3\sigma(I)$ )	0.042; 0.040	0.081; 0.078	0.059, 0.058
$R(F^2)$ ; $R_w(F^2)$ ( $I > 0$ )	0.076; 0.081	0.148, 0 157	
Goodness of fit	1.39	2.28	2.69
Largest peaks in final $\Delta F$ (e Å <sup>-3</sup> )	0 64, -0.57	1 44, -1 20	0.66, -0.63

TABLE 2 Final positional and isotropic thermal parameters

Atom	x	y	z	$B_{\text{eq}}^a$ or $B_{\text{iso}}$
<b>Co(HO(O<sub>2</sub>N)C<sub>6</sub>H<sub>3</sub>SO<sub>3</sub>)<sub>2</sub> · 6H<sub>2</sub>O</b>				
Co(1)	1 0000	0	1 0000	2 06(3)
S(1)	0 5186(2)	0.18379(7)	0.4922(2)	2.68(5)
O(1)	0.5712(4)	0.1094(2)	0.3541(5)	3.3(1)
O(2)	0.5397(5)	0.1715(2)	0 7440(5)	3.7(1)
O(3)	0.3159(4)	0.2056(2)	0.4093(6)	3.7(1)
O(4)	1.1720(5)	0 4711(2)	0 2633(6)	5.1(2)
O(5)	1 2550(6)	0.3347(3)	0 8596(7)	5.4(2)
O(6)	1 3896(5)	0 4294(3)	0 6237(7)	6.4(2)
O(7)	0 7153(4)	0.0232(2)	0 8598(5)	3.2(1)
O(8)	0 9507(5)	0.0578(3)	1 3244(5)	6.3(2)
O(9)	1.1353(5)	0.1290(2)	0 9366(8)	6.8(2)
N(1)	1.2437(6)	0.3745(3)	0.6808(8)	4.1(2)
C(1)	0.7114(6)	0 2731(3)	0.4390(7)	2.6(2)
C(2)	0.8941(6)	0 2908(3)	0 5812(7)	2.6(2)
C(3)	1.0510(7)	0 3573(3)	0 5250(8)	3.0(2)
C(4)	1.0256(8)	0 4061(3)	0.3255(9)	3.7(2)
C(5)	0 8368(8)	0 3862(3)	0.1847(8)	3.9(2)
C(6)	0.6825(7)	0 3212(3)	0 2399(8)	3.4(2)
H(1)	0.9274	0 2538	0 7309	3.1
H(2)	0.5530	0.2971	0.1228	4.1
H(3)	0.7977	0.4332	0.0579	4 8
H(4)	0.6844	0 0778	0.8362	3 6
H(5)	0.6113	-0.0185	0.7838	3 6
H(6)	0.8113	0 0605	1.3525	7.0
H(7)	0.9715	0 0235	1.4434	7.0
H(8)	1 0972	0 1042	0 7936	7.9
H(9)	1 2871	0 1509	0.9322	7.9
<b>Na<sub>4</sub>(HO(O<sub>2</sub>N)C<sub>6</sub>H<sub>3</sub>SO<sub>3</sub>)<sub>4</sub> · 2H<sub>2</sub>O</b>				
S(1)	0 5577	0.3877(4)	0 7453	2.1(3)
S(2)	0.030(1)	0.3695(4)	0.4845(6)	2 4(3)
S(3)	0.488(1)	0.6309(4)	0.7792(6)	2.3(3)
S(4)	-0 0370(6)	0.6090(4)	0.5140(4)	2.8(3)
Na(1)	0 261(2)	0 5025(8)	0 630(1)	2.8(2)
Na(2)	0 856(1)	0 5557(6)	0 7493(9)	3.4(5)
Na(3)	0 660(1)	0 4420(6)	0 5162(8)	3.5(5)
Na(4)	0 267(2)	0 4947(3)	0 879(1)	3.7(3)
O(1)	0 439(2)	0.401(1)	0 824(1)	3.8(4)
O(2)	0.465(2)	0.3944(8)	0.653(1)	2.6(3)
O(3)	0.711(2)	0 434(1)	0 762(1)	4.0(4)
O(4)	0.726(2)	0 040(1)	0.763(1)	4.0(4)
O(5)	1.075(2)	0 209(1)	0.729(1)	3.0(3)
O(6)	1 013(2)	0.087(1)	0 730(1)	3.9(3)
O(7)	0.173(2)	0 416(1)	0 496(1)	3 3(3)
O(8)	-0.083(2)	0.380(1)	0 566(1)	2 9(3)
O(9)	-0.048(2)	0.3765(9)	0.386(1)	3 1(3)
O(10)	0.223(2)	0.026(1)	0.498(1)	3 9(4)
O(11)	0.566(2)	0.211(1)	0.526(1)	4 1(4)
O(12)	0.527(2)	0 082(1)	0.510(1)	4.0(3)
O(13)	0.619(2)	0 623(1)	0.708(1)	2.8(3)
O(14)	0.347(2)	0.581(1)	0.752(1)	2.3(3)
O(15)	0.536(2)	0.615(1)	0 880(1)	3.1(3)
O(16)	0 292(2)	0.972(1)	0.735(1)	4.1(4)
O(17)	-0.053(2)	0.794(1)	0 746(1)	3.4(4)
O(18)	0.010(2)	0 923(1)	0.725(1)	4.3(4)
O(19)	0.067(2)	0 599(1)	0 430(1)	3.2(4)
O(20)	0.023(2)	0.5904(9)	0 614(1)	4.0(3)
O(21)	-0.179(2)	0.566(1)	0.515(1)	5.3(5)

(continued)

TABLE 2 (continued)

Atom	x	y	z	$B_{\text{eq}}^a$ or $B_{\text{iso}}$
O(22)	-0 202(2)	0 954(1)	0 514(1)	4.9(5)
O(23)	-0 564(2)	0 779(1)	0.510(1)	4.8(4)
O(24)	-0.506(2)	0 908(1)	0.499(1)	4.5(4)
O(25)	0 449(2)	0 555(1)	0.523(1)	3.1(8)
O(26)	0 047(2)	0 440(1)	0.737(1)	2 8(7)
N(1)	0 995(2)	0 164(1)	0.744(1)	2.7(4)
N(2)	0 472(2)	0 155(1)	0.523(1)	1.6(3)
N(3)	0 042(3)	0.852(2)	0.752(2)	6.3(6)
N(4)	-0.446(2)	0.840(1)	0.516(1)	2.9(4)
C(1)	0 612(2)	0 2864(6)	0.749(1)	2.0(2)
C(2)	0 773(2)	0.2635(8)	0.744(1)	2.0(2)
C(3)	0.815(1)	0 1823(9)	0 751(1)	2.0(2)
C(4)	0.696(2)	0 1240(6)	0.765(1)	2.0(2)
C(5)	0 534(1)	0 1469(7)	0.770(1)	2.0(2)
C(6)	0 492(1)	0 2281(8)	0.763(1)	2.0(2)
C(7)	0 094(2)	0 2668(6)	0.491(1)	2.1(2)
C(8)	0 257(2)	0 2486(8)	0.502(1)	2.1(2)
C(9)	0 308(1)	0 1683(9)	0.504(1)	2 1(2)
C(10)	0 195(2)	0.1063(7)	0.494(1)	2.1(2)
C(11)	0.032(2)	0.1246(7)	0 483(1)	2 1(2)
C(12)	-0 019(1)	0.2048(8)	0 481(1)	2.1(2)
C(13)	0.423(2)	0 7298(7)	0 763(1)	3.0(2)
C(14)	0 541(2)	0 7897(9)	0.763(1)	3.0(2)
C(15)	0 497(2)	0 8705(8)	0.753(1)	3 0(2)
C(16)	0 335(2)	0 8914(7)	0 743(1)	3.0(2)
C(17)	0 217(1)	0 832(1)	0.743(1)	3 0(2)
C(18)	0.261(2)	0 7507(9)	0.754(1)	3 0(2)
C(19)	-0 089(2)	0 7134(7)	0.505(1)	3.0(2)
C(20)	0.033(1)	0 771(1)	0.504(1)	3.0(2)
C(21)	-0 005(2)	0 8530(8)	0.509(1)	3.0(2)
C(22)	-0 166(2)	0 8770(7)	0.515(1)	3.0(2)
C(23)	-0 288(1)	0 819(1)	0.516(1)	3 0(2)
C(24)	-0.250(2)	0 7375(9)	0.511(1)	3 0(2)
H(1)	0 8554	0 3031	0.7365	2.7
H(2)	0 4565	0 1055	0.7778	2.7
H(3)	0 3839	0.2419	0.7663	2.7
H(4)	0 3352	0.2921	0.5100	2.5
H(5)	-0.0401	0.0825	0.4735	2.5
H(6)	-0 1266	0 2171	0.4689	2.5
H(7)	0 6576	0 7742	0.7659	3.4
H(8)	0 5841	0 9102	0 7508	3.4
H(9)	0 1853	0 7097	0 7550	3.4
H(10)	0 1455	0 7533	0 4963	3.4
H(11)	0 0814	0 8908	0 5049	3.4
H(12)	-0 3301	0 6969	0.5142	3.4
H(13)	0 1511	0 9824	0.7717	6.5
H(14)	0 0317	0 3996	0.6737	3 5
<b>Ca(H<sub>3</sub>C(H<sub>2</sub>N)C<sub>6</sub>H<sub>3</sub>SO<sub>3</sub>)<sub>2</sub> · 7H<sub>2</sub>O</b>				
Ca	0.7211(1)	0 3086(3)	0.50806(6)	3 36(7)
S(1)	0.1044(1)	0 0720(4)	0.61097(8)	3 8(1)
S(2)	0.5796(1)	0 0730(3)	0.59462(7)	2.93(8)
O(1)	0 0226(4)	0 167(1)	0.5785(2)	7.5(4)
O(2)	0 1032(4)	-0.158(1)	0.6113(2)	5.3(3)
O(3)	0 1873(3)	0.1542(9)	0.5954(2)	4.8(3)
O(4)	0 4940(3)	0 1686(8)	0.5667(2)	4.0(2)
O(5)	0 6596(3)	0 1566(9)	0 5754(2)	4.2(2)
O(6)	0 5770(3)	-0 1592(8)	0 5935(2)	4.1(3)
O(7)	0 6787(3)	-0.0014(8)	0 4563(2)	3.8(2)

(continued)

TABLE 2 (continued)

Atom	x	y	z	$B_{\text{eq}}^a$ or $B_{\text{iso}}$
O(8)	0.5710(3)	0.4080(9)	0.4612(2)	4.7(3)
O(9)	0.7913(4)	0.4298(9)	0.4377(2)	5.5(3)
O(10)	0.7113(4)	0.6521(8)	0.5437(2)	5.9(3)
O(11)	0.8484(5)	0.037(2)	0.5255(3)	15.4(7)
O(12)	0.8627(5)	0.393(2)	0.5732(3)	13.1(6)
O(13)	0.0638(8)	0.267(3)	0.4683(4)	27(1)
N(1)	0.2012(4)	-0.022(1)	0.8148(2)	5.3(4)
N(2)	0.6857(4)	-0.058(1)	0.7958(2)	5.2(4)
C(1)	0.1078(4)	0.160(1)	0.6775(3)	2.8(3)
C(2)	0.0738(4)	0.360(1)	0.6862(3)	3.2(3)
C(3)	0.0823(4)	0.429(1)	0.7391(3)	3.5(3)
C(4)	0.1228(4)	0.308(1)	0.7820(3)	3.3(3)
C(5)	0.1574(4)	0.105(1)	0.7723(3)	3.2(3)
C(6)	0.1512(4)	0.031(1)	0.7196(3)	3.2(3)
C(7)	0.1296(5)	0.389(1)	0.8387(3)	5.0(4)
C(8)	0.5930(4)	0.156(1)	0.6627(2)	2.6(3)
C(9)	0.5638(5)	0.355(1)	0.6735(3)	3.4(3)
C(10)	0.5752(5)	0.418(1)	0.7268(3)	3.6(3)
C(11)	0.6153(5)	0.285(1)	0.7674(3)	3.2(3)
C(12)	0.6466(4)	0.084(1)	0.7554(3)	3.3(3)
C(13)	0.6352(4)	0.015(1)	0.7020(3)	3.1(3)
C(14)	0.6245(5)	0.355(1)	0.8247(3)	5.3(4)
H(1)	0.0410	0.4566	0.6569	3.6
H(2)	0.0426	0.5678	0.7446	3.8
H(3)	0.1608	-0.1349	0.7113	3.8
H(4)	0.2197	-0.1802	0.8103	6.5
H(5)	0.1781	-0.0165	0.8495	6.5
H(6)	0.0908	0.2987	0.8495	5.5
H(7)	0.0954	0.5422	0.8371	5.5
H(8)	0.2037	0.3614	0.8526	6.3
H(9)	0.5186	0.4515	0.6404	3.8
H(10)	0.5512	0.5629	0.7382	4.3
H(11)	0.6652	-0.1358	0.6959	3.5
H(12)	0.7163	-0.1811	0.7868	6.2
H(13)	0.7110	0.0764	0.8291	6.3
H(14)	0.6166	0.4682	0.8236	5.0
H(15)	0.5994	0.2479	0.8449	5.0
H(16)	0.6970	0.3979	0.8512	6.2
H(17)	0.6222	-0.0563	0.4484	4.3
H(18)	0.7258	-0.0421	0.4356	4.3
H(19)	0.5406	0.5543	0.4526	5.5
H(20)	0.6183	0.4021	0.4359	4.0
H(21)	0.8034	0.5839	0.4207	6.0
H(22)	0.8454	0.3402	0.4243	6.5
H(23)	0.6624	0.7182	0.5639	6.7
H(24)	0.7550	0.8040	0.5460	6.9

$$^a B_{\text{eq}} = 4/3[a^2\beta_{11} + b^2\beta_{22} + c^2\beta_{33} + (2ab \cos \gamma)\beta_{12} + (2ac \cos \beta)\beta_{13} + (2bc \cos \alpha)\beta_{23}]$$

molecular bond angles involving the non-hydrogen atoms are provided in Table 4.

#### $\text{Na}_4(\text{HO}(\text{O}_2\text{N})\text{C}_6\text{H}_3\text{SO}_3)_4 \cdot 2\text{H}_2\text{O}$

A small red–orange irregularly-shaped crystal fragment (approximate dimensions  $0.30 \times 0.25 \times 0.20$  mm) dislodged from a larger mass of crystals was used. Least-squares refinement of 24 centered reflections in the

TABLE 3. Selected bond distances (Å)

$\text{Co}(\text{HO}(\text{O}_2\text{N})\text{C}_6\text{H}_3\text{SO}_3)_2 \cdot 6\text{H}_2\text{O}$			
Co(1)–O(7)	2.039(3)	O(6)–N(1)	1.242(5)
Co(1)–O(8)	2.083(3)	N(1)–C(3)	1.457(5)
Co(1)–O(9)	2.118(3)	C(1)–C(2)	1.365(5)
S(1)–O(1)	1.465(3)	C(1)–C(6)	1.402(6)
S(1)–O(2)	1.453(3)	C(2)–C(3)	1.398(6)
S(1)–O(3)	1.453(3)	C(3)–C(4)	1.406(6)
S(1)–C(1)	1.769(4)	C(4)–C(5)	1.394(6)
O(4)–C(4)	1.352(5)	C(5)–C(6)	1.370(6)
O(5)–N(1)	1.217(5)		
$\text{Na}_4(\text{HO}(\text{O}_2\text{N})\text{C}_6\text{H}_3\text{SO}_3)_4 \cdot 2\text{H}_2\text{O}$			
Na(1)–O(2)	2.48(2)	Na(4)–O(1)	2.23(2)
Na(1)–O(7)	2.41(2)	Na(4)–O(7)	2.31(2)
Na(1)–O(14)	2.22(2)	Na(4)–O(14)	2.33(2)
Na(1)–O(20)	2.46(2)	Na(4)–O(19)	2.37(2)
Na(1)–O(25)	2.29(2)	Na(4)–O(25)	2.59(2)
Na(1)–O(26)	2.53(2)	S(1)–O(1)	1.47(2)
Na(2)–O(3)	2.35(2)	S(1)–O(2)	1.46(1)
Na(2)–O(9)	2.29(2)	S(1)–O(3)	1.50(2)
Na(2)–O(13)	2.32(2)	S(1)–C(1)	1.74(1)
Na(2)–O(20)	2.37(2)	S(2)–O(7)	1.42(2)
Na(2)–O(26)	2.49(2)	S(2)–O(8)	1.46(2)
Na(3)–O(2)	2.59(2)	S(2)–O(9)	1.48(2)
Na(3)–O(8)	2.46(2)	S(2)–C(7)	1.78(1)
Na(3)–O(15)	2.31(2)	S(3)–O(13)	1.45(2)
Na(3)–O(21)	2.45(2)	S(3)–O(14)	1.47(2)
Na(3)–O(25)	2.56(2)	S(3)–O(15)	1.43(2)
S(3)–C(13)	1.74(1)		
S(4)–O(19)	1.44(2)		
S(4)–O(20)	1.46(2)		
S(4)–O(21)	1.37(2)		
S(4)–C(19)	1.79(1)		
$\text{Ca}(\text{H}_3\text{C}(\text{H}_2\text{N})\text{C}_6\text{H}_3\text{SO}_3)_2 \cdot 7\text{H}_2\text{O}$			
Ca–O(5)	2.295(5)	N(2)–C(12)	1.397(9)
Ca–O(7)	2.354(5)	C(1)–C(2)	1.377(9)
Ca–O(8)	2.400(5)	C(1)–C(6)	1.396(9)
Ca–O(9)	2.363(5)	C(2)–C(3)	1.395(9)
Ca–O(10)	2.339(5)	C(3)–C(4)	1.365(9)
Ca–O(11)	2.51(1)	C(4)–C(5)	1.40(1)
Ca–O(12)	2.473(8)	C(4)–C(7)	1.513(9)
S(1)–O(1)	1.456(5)	C(5)–C(6)	1.406(9)
S(1)–O(2)	1.435(6)	C(8)–C(9)	1.362(9)
S(1)–O(3)	1.457(5)	C(8)–C(13)	1.384(9)
S(1)–C(1)	1.772(7)	C(9)–C(10)	1.389(9)
S(2)–O(4)	1.459(5)	C(10)–C(11)	1.37(1)
S(2)–O(5)	1.466(5)	C(11)–C(12)	1.39(1)
S(2)–O(6)	1.447(5)	C(11)–C(14)	1.503(9)
S(2)–C(8)	1.781(6)	C(12)–C(13)	1.405(9)
N(1)–C(5)	1.396(8)		

range  $21.18 < 2\theta < 33.87^\circ$  yielded the monoclinic cell given in Table 1. A statistical comparison of the intensities of symmetry-related reflections satisfactorily confirmed the monoclinic symmetry. A total of 3620 reflections was measured ( $\omega$  scans,  $8^\circ \text{ min}^{-1}$  in  $\omega$ ) of which 3374 were unique ( $R(\text{int}) = 0.035$ ). Azimuthal scans of three reflections indicated no need for an absorption correction ( $\mu(\text{Mo K}\alpha) = 3.9 \text{ cm}^{-1}$ ). The space group was determined to be  $Pc$  (No. 7) based on the

TABLE 4. Selected bond angles (°)

<b>Co(HO(O<sub>2</sub>N)C<sub>6</sub>H<sub>3</sub>SO<sub>3</sub>)<sub>2</sub> · 6H<sub>2</sub>O</b>			
O(7)–Co(1)–O(8)	89 1(1)	C(2)–C(1)–S(1)	120 1(3)
O(7)–Co(1)–O(9)	89 9(1)	C(6)–C(1)–S(1)	119 6(3)
O(8)–Co(1)–O(9)	82 7(2)	C(1)–C(2)–C(3)	119 1(4)
O(2)–S(1)–O(3)	113 7(2)	C(2)–C(3)–C(4)	121 6(4)
O(2)–S(1)–O(1)	111 6(2)	C(2)–C(3)–N(1)	117 6(4)
O(2)–S(1)–C(1)	106 7(2)	C(4)–C(3)–N(1)	120 8(4)
O(3)–S(1)–O(1)	111 8(2)	O(4)–C(4)–C(5)	118 3(5)
O(3)–S(1)–C(1)	107 1(2)	O(4)–C(4)–C(3)	124 1(5)
O(1)–S(1)–C(1)	105 4(2)	C(5)–C(4)–C(3)	117 6(4)
O(5)–N(1)–O(6)	123 1(4)	C(6)–C(5)–C(4)	120 8(4)
O(5)–N(1)–C(3)	118 9(4)	C(5)–C(6)–C(1)	120 6(4)
O(6)–N(1)–C(3)	118 0(5)		
C(2)–C(1)–C(6)	120 2(4)		
<b>Na<sub>4</sub>(HO(O<sub>2</sub>N)C<sub>6</sub>H<sub>3</sub>SO<sub>3</sub>)<sub>4</sub> · 2H<sub>2</sub>O</b>			
O(20)–Na(1)–O(26)	74 0(7)	O(8)–Na(3)–O(15)	115 4(7)
O(25)–Na(1)–O(26)	176 2(9)	O(8)–Na(3)–O(21)	83 2(7)
O(2)–Na(1)–O(14)	96 6(7)	O(8)–Na(3)–O(25)	152 5(7)
O(2)–Na(1)–O(20)	169 4(8)	O(15)–Na(3)–O(21)	125 6(7)
O(7)–Na(1)–O(14)	179 0(9)	O(15)–Na(3)–O(25)	91 5(6)
O(7)–Na(1)–O(20)	92 6(7)	O(21)–Na(3)–O(25)	76 1(7)
O(13)–Na(2)–O(20)	101 5(7)	O(1)–Na(4)–O(7)	152 8(9)
O(13)–Na(2)–O(26)	152 8(7)	O(1)–Na(4)–O(14)	90 0(8)
O(20)–Na(2)–O(26)	76 3(6)	O(1)–Na(4)–O(19)	95 3(7)
O(3)–Na(2)–O(13)	89 8(7)	O(14)–Na(4)–O(25)	125 1(8)
O(3)–Na(2)–O(20)	124 5(7)	O(19)–Na(4)–O(25)	88 9(6)
O(3)–Na(2)–O(26)	70 7(6)	O(7)–Na(4)–O(14)	101 9(6)
O(1)–S(1)–O(2)	104 5(8)	O(13)–S(3)–O(14)	112(1)
O(1)–S(1)–O(3)	112(1)	O(13)–S(3)–O(15)	114(1)
O(1)–S(1)–C(1)	107 4(9)	O(13)–S(3)–C(13)	104 1(9)
O(2)–S(1)–O(3)	122 3(9)	O(14)–S(3)–O(15)	110 3(9)
O(2)–S(1)–C(1)	103 6(8)	O(14)–S(3)–C(13)	104 5(9)
O(3)–S(1)–C(1)	105 7(8)	O(15)–S(3)–C(13)	111 6(9)
O(7)–S(2)–O(8)	113(1)	O(19)–S(4)–O(20)	119 4(9)
O(7)–S(2)–O(9)	115(1)	O(19)–S(4)–O(21)	118(1)
O(7)–S(2)–C(7)	106(1)	O(19)–S(4)–C(19)	102(1)
O(8)–S(2)–O(9)	113(1)	O(20)–S(4)–O(21)	100(1)
O(8)–S(2)–C(7)	105 7(9)	O(20)–S(4)–C(19)	110 2(9)
O(9)–S(2)–C(7)	104 2(9)	O(21)–S(4)–C(19)	107(1)
<b>Ca(H<sub>3</sub>C(H<sub>2</sub>N)C<sub>6</sub>H<sub>3</sub>SO<sub>3</sub>)<sub>2</sub> · 7H<sub>2</sub>O</b>			
O(5)–Ca–O(7)	88 7(2)	O(2)–S(1)–O(3)	111.4(3)
O(5)–Ca–O(8)	90 7(2)	O(2)–S(1)–C(1)	107.6(3)
O(5)–Ca–O(9)	174 0(2)	O(3)–S(1)–C(1)	106.3(3)
O(5)–Ca–O(10)	91 4(2)	O(4)–S(2)–O(5)	112.3(3)
O(5)–Ca–O(11)	89 1(2)	O(4)–S(2)–O(6)	112 4(3)
O(5)–Ca–O(12)	89 8(2)	O(4)–S(2)–C(8)	106.4(3)
O(7)–Ca–O(8)	79 1(2)	O(5)–S(2)–O(6)	111 6(3)
O(7)–Ca–O(9)	87 0(2)	O(5)–S(2)–C(8)	106 0(3)
O(7)–Ca–O(11)	70 0(3)	O(6)–S(2)–C(8)	107 8(3)
O(8)–Ca–O(9)	92 6(2)	S(1)–C(1)–C(2)	119 4(6)
O(8)–Ca–O(10)	80 6(2)	S(1)–C(1)–C(6)	118 5(6)
O(10)–Ca–O(12)	69 8(3)	C(2)–C(1)–C(6)	121 9(6)
O(11)–Ca–O(12)	60 6(3)	C(1)–C(2)–C(3)	117 7(7)
O(1)–S(1)–O(2)	113 4(4)	C(2)–C(3)–C(4)	123 2(7)
O(1)–S(1)–O(3)	111 2(4)	C(3)–C(4)–C(5)	118 4(7)
O(1)–S(1)–C(1)	106 5(3)	C(3)–C(4)–C(7)	121 2(7)
C(5)–C(4)–C(7)	120 4(7)		
N(1)–C(5)–C(4)	120 3(7)		
N(1)–C(5)–C(6)	119 3(7)		
C(4)–C(5)–C(6)	120 3(7)		

TABLE 4. (continued)

C(1)–C(6)–C(5)	118 5(7)
S(2)–C(8)–C(9)	118 7(5)
S(2)–C(8)–C(13)	118 1(6)
C(9)–C(8)–C(13)	123 2(6)
C(8)–C(9)–C(10)	118 0(7)
C(9)–C(10)–C(11)	121.5(7)
C(10)–C(11)–C(12)	119 5(7)
C(10)–C(11)–C(14)	120 4(8)
C(12)–C(11)–C(14)	120 1(7)
N(2)–C(12)–C(11)	121 2(7)
N(2)–C(12)–C(13)	118 3(7)
C(11)–C(12)–C(13)	120 4(7)
C(8)–C(13)–C(12)	117 4(7)

systematic absence of  $h0l$ ,  $l \neq 2n$  and the successful solution and refinement of the structure. Attempts to model the structure in the centrosymmetric space group  $P2_1/c$  (which carries the same absence condition) were unsuccessful. Following location of the S, Na, O and phenyl C atoms, a difference electron density map showed that nitration of the rings had also taken place in this reaction. Due to the limited number of observed data and the large number of atoms in the asymmetric unit, only the S, Na and water O atoms were refined anisotropically and the six carbons of each of the four independent phenyl rings were refined as rigid groups ( $d(\text{C}–\text{C}) = 1.40$ ,  $d(\text{C}–\text{H}) = 0.95$  Å, all bond angles  $120^\circ$ ). In addition, the final cycles of refinement were carried out on  $F^2$  using all data with  $I > 0$  in order to maximize the data to parameter ratio. Only one of the hydrogen atoms on the four hydroxy groups and one on the two water molecules could be located on difference maps. These, as well as the phenyl hydrogens in calculated positions, were included in the model as fixed isotropic scatterers. The final refinement on  $F^2$  of 229 variables (including anisotropic thermal parameters for the S, Na and two water O atoms) and 3248 data ( $I > 0$ ) converged to  $R(F^2) = 0.148$  and  $R_w(F^2) = 0.157$ . There were no chemically meaningful peaks on the final difference electron density map. The conventional  $R(F)$  value calculated on this model for the 1747 data with  $I > 3\sigma(I)$  was 0.081.

The chemical formula for this compound based on the X-ray structure and NMR spectra is  $\text{Na}_4(\text{HO}(\text{O}_2\text{N})\text{C}_6\text{H}_3\text{SO}_3)_4 \cdot 2\text{H}_2\text{O}$  ( $FW = 1000.63$ ). The positional and equivalent isotropic thermal parameters for each atom in the unit cell are given in Table 2. Selected intramolecular bond distances and angles between the non-hydrogen atoms are listed in Tables 3 and 4. The phenyl carbon–carbon distances and angles are omitted from the Tables as they were constrained in the group refinement.

(continued)

$$\text{Ca}(\text{H}_3\text{C}(\text{H}_2\text{N})\text{C}_6\text{H}_3\text{SO}_3)_2 \cdot 7\text{H}_2\text{O}$$

The pale brown columnar crystal used was cut from a larger crystal to an approximate size of  $0.30 \times 0.15 \times 0.10$  mm. The monoclinic unit cell shown in Table 1 was obtained from a least-squares refinement of 23 centered reflections in the range  $23.74 < 2\theta < 39.22^\circ$ . A total of 4655 reflections was collected ( $\omega$ - $2\theta$  scans,  $4^\circ \text{ min}^{-1}$  in  $\omega$ ) and averaged ( $R(\text{int}) = 0.029$ ) to yield 4472 unique data. No absorption correction was applied ( $\mu(\text{Mo K}\alpha) = 5.0 \text{ cm}^{-1}$ ). The structure was successfully solved and refined in space group  $P2_1/c$  (No. 14). The oxygen atoms of six water molecules coordinated to the calcium atom and one non-coordinated water were located on difference maps. The thermal parameter of atom O(13) is large enough to suggest a partial occupancy, however it was not deemed worthwhile to attempt to refine the occupancy factor. (Removal of this atom from the model results in significantly higher residuals.) The hydrogen atoms on the phenyl and methyl carbon atoms, amino nitrogen atoms, and four of the coordinated water molecules were located on difference electron density maps and included in the model as fixed isotropic scatterers. The remaining six water hydrogen atoms could not be located. The final refinement of 289 variables (including anisotropic thermal parameters for all non-hydrogen atoms) and 2186 data ( $I > 3\sigma(I)$ ) converged to  $R(F) = 0.059$  and  $R_w(F) = 0.058$ .

The formula for this compound is  $\text{Ca}(\text{H}_3\text{C}(\text{H}_2\text{N})\text{C}_6\text{H}_3\text{SO}_3)_2 \cdot 7\text{H}_2\text{O}$  ( $FW = 538.60$ ). 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

$$\text{Co}(\text{HO}(\text{O}_2\text{N})\text{C}_6\text{H}_3\text{SO}_3)_2 \cdot 6\text{H}_2\text{O}$$

In an earlier study [1], we found that divalent transition metals such as cobalt crystallize from aqueous solution as hexaaqua cations in the presence of aryl-sulfonate anions. In an attempt to change the aqueous coordination environment around the cobalt to see if it would affect this process, we decided to add concentrated HCl to such a reaction in order to generate tetrachlorocobaltate ions. The product of this reaction, which has a nitro group on the aromatic ring when only 4-hydroxybenzenesulfonate was used in the reaction, was inadvertent. The apparent explanation is that the presence of the nitrate ions (from the cobalt nitrate starting material) and the concentrated HCl created the conditions whereby the nitration reaction could occur in the solution. The nitration of 4-hydroxybenzenesulfonate to produce 4-hydroxy-3-nitro-

benzenesulfonate was reported more than one hundred years ago by Kekule and others [22, 23]. The reaction has also been identified as one step in the production of picric acid from phenol in the presence of nitric and sulfuric acids [24]. Thus, the reaction reported here is known, though not apparently of commercial importance as neither the 4-hydroxy-3-nitrobenzenesulfonic acid nor its salts are available from any of the major chemical companies.

The asymmetric portion of the structure with the atom labelling scheme is shown in Fig. 1. The cobalt atom sits on a center of inversion and the two sulfonate anions in the cell are thus equivalent by symmetry. As in the previously reported sulfonates [1], the cobalt atoms are coordinated by six water molecules, with no direct bonding to the sulfonate groups. The cobalt coordination geometry is that of a fairly regular octahedron. Symmetry equivalent water molecules are present on opposite sides of the Co atom, exactly  $180^\circ$  apart. The acute angles are all close to  $90^\circ$ , ranging from  $82.7(2)$  to  $89.9(1)^\circ$ , and the cobalt-oxygen bond distances show only small variations, from  $2.039(3)$  to  $2.118(3) \text{ \AA}$ .

The metrical data for the sulfonate anion, given in Tables 3 and 4, show nearly ideal geometries about the S atom and the phenyl carbon atoms. The geometry about the N atom has the three appended atoms at the corners of a triangular plane, as expected for an  $sp^2$ -hybridized atom. The bond distances clearly show that the double-bond character is delocalized in the

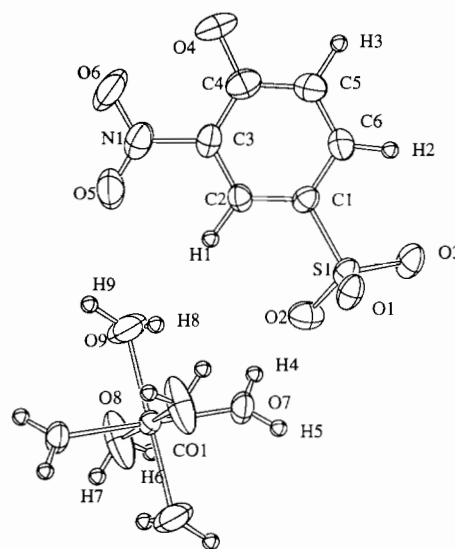


Fig. 1. ORTEP diagram of  $\text{Co}(\text{HO}(\text{O}_2\text{N})\text{C}_6\text{H}_3\text{SO}_3)_2 \cdot 6\text{H}_2\text{O}$  showing atom labelling scheme. Symmetry equivalent oxygen atoms have been included to show the complete coordination environment about the cobalt atom. In Figs. 1 and 2, the 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.



N–O bonds (1.217(5) and 1.242(5) Å), but not in the N–C bond (1.457(5) Å). The slight elongation of the N(1)–O(6) bond may be due to the formation of an intramolecular hydrogen bond to the hydroxyl group (O(6)···H–O(4)), an interaction that is reported to occur in 2-nitrophenol [25], though the X-ray analysis did not reveal the location of the proton.

Figure 2 shows that the structure is composed of layers of hexaaquacobalt(II) cations and 4-hydroxy-3-nitrobenzenesulfonate anions that stack along the crystallographic *b* axis. There are two layers of sulfonate anions for every layer of cations. The sulfonate anions within a given layer all have the same orientation, with the  $\text{SO}_3^-$  groups pointing up or down towards the nearest cation. There is extensive hydrogen bonding between the coordinated water molecules and sulfonate oxygen atoms. Some important interactions are (metrical data for hydrogen bonds are given as hydrogen bond distance, covalent O–H distance, O–H–O bond angle) O(1)···H(5)–O(7), 1.81, 0.93 Å, 173.0°; O(1)···H(6)–O(8), 1.83, 0.93 Å, 155.9°; O(2)···H(4)–O(7), 1.92, 0.92 Å, 162.1°; O(2)···H(9)–O(9), 2.01, 0.99 Å, 148.6°. The overall result of this packing arrangement is the creation of anion–cation–anion sandwiches with only weak non-bonded interactions between the anions of

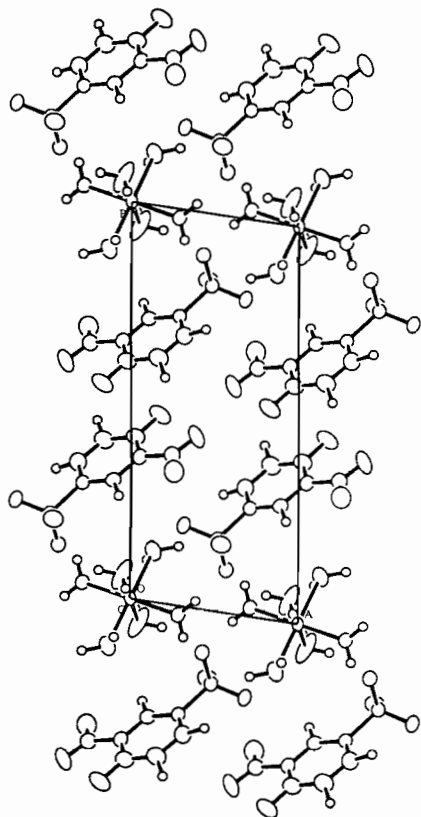


Fig 2. ORTEP packing diagram of  $\text{Co}(\text{HO}(\text{O}_2\text{N})\text{C}_6\text{H}_3\text{SO}_3)_2 \cdot 6\text{H}_2\text{O}$  showing the outline of the unit cell. View is along the *c* axis.

adjacent slabs. This structure is reflected in the plate-like morphology and cleavage of the crystals.

#### $\text{Na}_4(\text{HO}(\text{O}_2\text{N})\text{C}_6\text{H}_3\text{SO}_3)_4 \cdot 2\text{H}_2\text{O}$

The reaction that produced this compound was an attempt to prepare a copper analog of the cobalt 4-hydroxy-3-nitrobenzenesulfonate. In this case, concentrated nitric acid itself was used as the nitrating agent. The X-ray and NMR data showed that the 4-hydroxybenzenesulfonate anion did indeed undergo nitration to form the same 4-hydroxy-3-nitrobenzenesulfonate ion found in the cobalt structure. In this case it crystallized as a sodium salt. This result is consistent with a reported synthesis of sodium 4-hydroxy-3-nitrobenzenesulfonate that involves treating sodium 4-hydroxybenzenesulfonate with concentrated nitric acid at 60 °C [24]. Our reaction was not a clean one, however, as it also produced 4-nitrophenol as a byproduct. The substitution of a nitro group for the sulfonate on a 4-hydroxybenzenesulfonate has also been found to occur in the picric acid reaction mentioned earlier [24].

The asymmetric unit of the structure is shown in Fig. 3 with an extended view in Fig. 4. This structure is also built of anion–cation–anion slabs with all the anions in a given layer oriented so that the sulfonate groups are directed toward the central cation layer. In this case, the cation and anion layers are held together by a substantial network of direct bonds between the

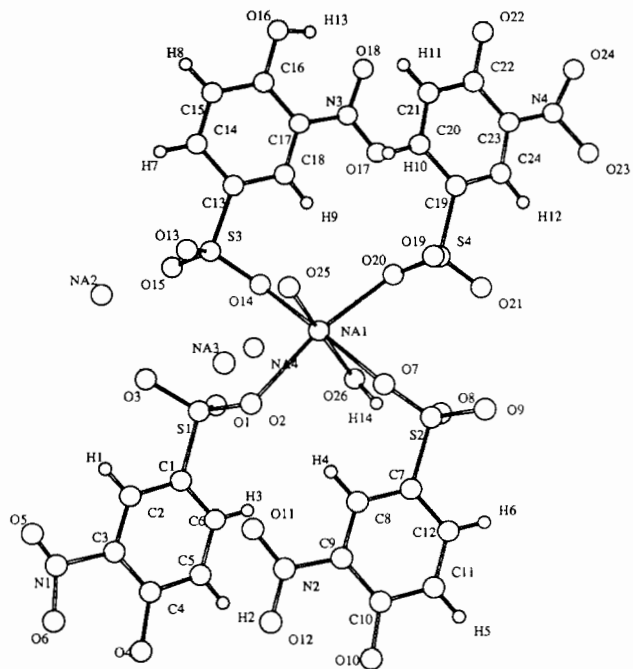


Fig 3. PLUTO diagram of the asymmetric unit of  $\text{Na}_4(\text{HO}(\text{O}_2\text{N})\text{C}_6\text{H}_3\text{SO}_3)_4 \cdot 2\text{H}_2\text{O}$  showing the atom labelling scheme. In this and Fig. 4 bonds to three of the sodium atoms have been omitted.



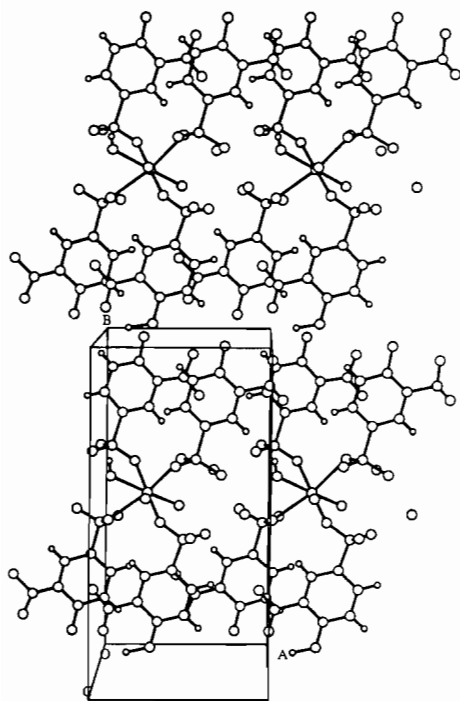


Fig. 4. Extended PLUTO view of  $\text{Na}_4(\text{HO}(\text{O}_2\text{N})\text{C}_6\text{H}_3\text{SO}_3)_4 \cdot 2\text{H}_2\text{O}$  showing the outline of the unit cell. View is along the  $c$  axis.

sodium cations and the sulfonate oxygen atoms, rather than by hydrogen bonds.

Each of the four crystallographically independent sodium ions is bonded to four oxygen atoms from four different sulfonate anions and either one or two water molecules. Metrical data are given in Tables 3 and 4. Atom Na(1), whose bonds to oxygen are shown in Figs. 3 and 4 (the other Na–O bonds have been omitted for clarity), is in a somewhat distorted octahedral environment formed by one oxygen from each of the sulfonate groups and the two water molecules. The Na atom is displaced from the center of the octahedron, being closer to O(14) and O(25) by about 0.2 Å. The three axial O–Na–O bond angles are all within 11° of the ideal 180°, while most of the adjacent angles are close to 90°. The most serious deviation is O(20)–Na(1)–O(26) at 74.0(7)°. Each of the remaining Na atoms is bonded to four sulfonate oxygens and one water molecule in a distorted trigonal bipyramidal environment. The coordination sphere of Na(2), shown in Fig. 5, is representative. The Na–O bond distances vary from 2.29(2) to 2.49(2) Å. The largest deviations of the bond angles from those found in a regular trigonal bipyramid (given in parentheses) are O(13)–Na(2)–O(26), 152.8(7)° (axial–axial, 180°); O(9)–Na(2)–O(20), 107.2(7)° (equatorial–equatorial, 120°); O(3)–Na(2)–O(26), 70.7(6)° (axial–equatorial, 90°). Each sulfonate anion interacts with all four sodium atoms such that one oxygen bonds to both Na(1) and

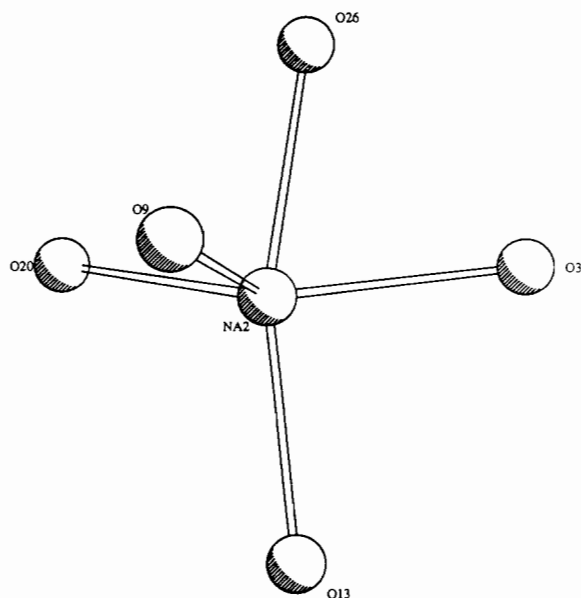


Fig. 5. PLUTO diagram of the coordination environment about atom Na(2) in  $\text{Na}_4(\text{HO}(\text{O}_2\text{N})\text{C}_6\text{H}_3\text{SO}_3)_4 \cdot 2\text{H}_2\text{O}$ .

one of the five-coordinate sodium atoms while the two remaining oxygen atoms each bond to one of the other five-coordinate sodium atoms. One of the water molecules (O(26)) coordinates two sodium atoms and the other (O(25)) coordinates three.

There is an apparent hydrogen bonding interaction between sulfonates in adjacent layers involving the hydroxy group of one sulfonate and the nitro oxygen of another sulfonate: O(6)···H(13)–O(16), 2.16, 1.28 Å, 119.3°. This hydrogen also participates in an intramolecular hydrogen bond with the nitro group on the same ring: O(18)···H(13)–O(16), 1.65, 1.28 Å, 114.9°. Although none of the other hydroxy hydrogen atoms could be located, another such interaction is suggested by the close contact between O(10) and O(24) of 2.99(2) Å.

#### $\text{Ca}(\text{H}_3\text{C}(\text{H}_2\text{N})\text{C}_6\text{H}_3\text{SO}_3)_2 \cdot 7\text{H}_2\text{O}$

The asymmetric unit with atom labelling scheme is shown in Fig. 6. A packing diagram is provided in Fig. 7. The calcium atom has six water molecules coordinated to it and is also coordinated by an oxygen atom on one of the two independent sulfonate groups. The other sulfonate group does not bond directly to the calcium atom. The Ca atom is in a slightly distorted pentagonal bipyramidal coordination with O(5) and O(9) in the apical positions and oxygen atoms 7, 8, 10, 11 and 12 making up the equatorial pentagon. This type of coordination has been observed in calcium methylphosphonate [3]. The Ca–O bond distances are fairly consistent, ranging from 2.295(5) to 2.51(1) Å. The apical O(5)–Ca–O(9) angle, 174.0(2)°, is very close to the

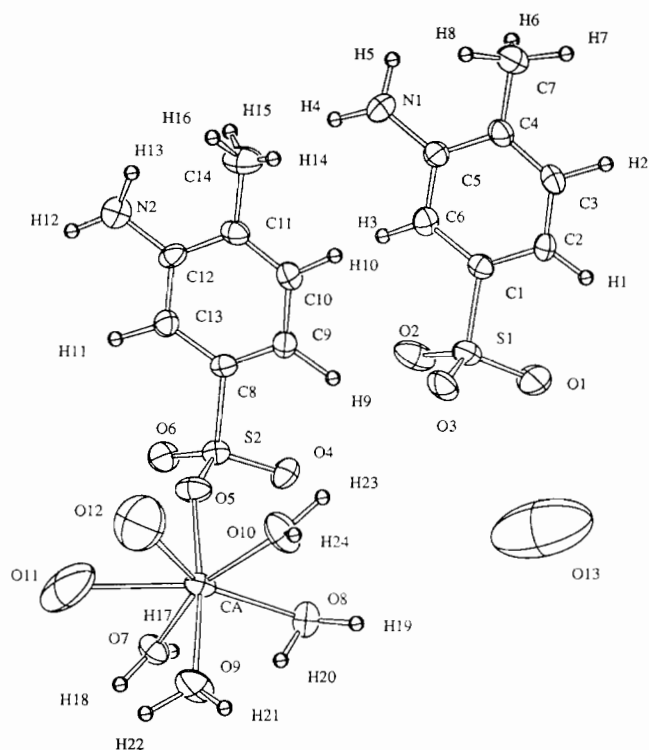


Fig. 6. ORTEP diagram of  $\text{Ca}(\text{H}_3\text{C}(\text{H}_2\text{N})\text{C}_6\text{H}_3\text{SO}_3)_2 \cdot 7\text{H}_2\text{O}$  showing the atom labelling scheme. Ellipsoids in both Figs. 6 and 7 are shown at the 35% probability level, except for the hydrogen atoms which are shown as spheres of arbitrary size.

ideal angle of  $180^\circ$ . The O–Ca–O angles of the adjacent oxygen atoms in the pentagonal plane vary from  $60.6(3)$  to  $80.6(2)^\circ$ . The angles between the apical and equatorial oxygen atoms are all within five degrees of  $90^\circ$ . The metrical data for the sulfonate ions, given in Tables 3 and 4, are highly regular. This structure differs from the others reported here in that it is composed of single layers of sulfonate anions and metal cations that stack along the  $c$  axis. The anions within a given layer alternate along the  $a$  direction between having the sulfonate group up or down. As mentioned above, only one of the two sulfonate ions coordinates the calcium atom and then through just one oxygen atom. In the view shown in Fig. 7, which is in the  $a$ – $c$  plane, the coordinating sulfonates in a given layer are adjacent to each other and bond to cations in different layers. The non-coordinating sulfonates occur on the far left and right in the Figure and they too have adjacent mates in the next unit cells (not shown). Thus the two types of sulfonate ions, coordinating ('A') and non-coordinating ('B'), follow the repeat pattern  $A_{\text{down}}-A^{\text{up}}-B_{\text{down}}-B^{\text{up}}$ .

There is a substantial hydrogen bonding network between the sulfonate oxygen atoms and some of the coordinated water molecules. These interactions, involving both sulfonate groups, are primarily responsible for holding the layers together. The non-coordinated

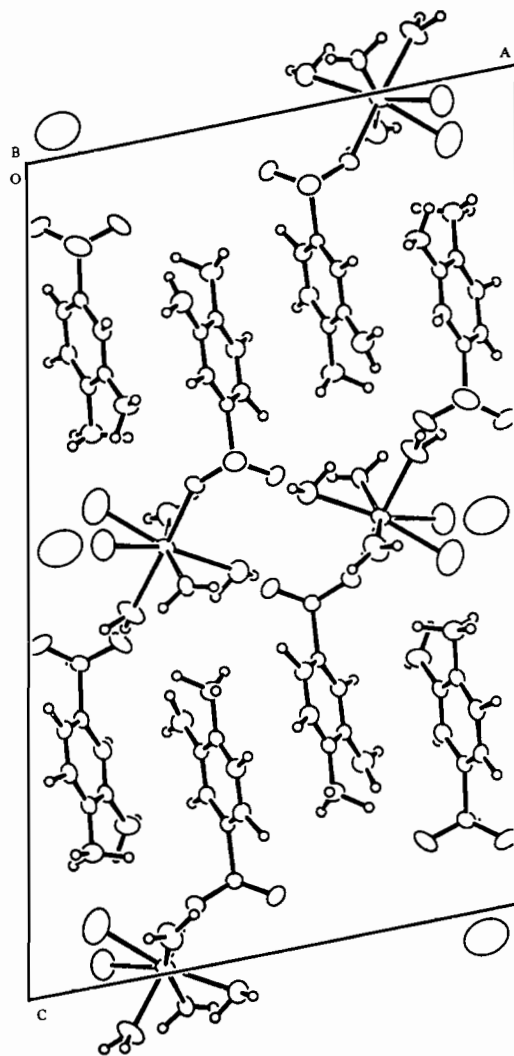


Fig. 7. ORTEP packing diagram of  $\text{Ca}(\text{H}_3\text{C}(\text{H}_2\text{N})\text{C}_6\text{H}_3\text{SO}_3)_2 \cdot 7\text{H}_2\text{O}$  showing the outline of the unit cell. View is along the  $b$  axis.

sulfonate forms three hydrogen bonds:  $\text{O}(2) \cdots \text{H}(22)-\text{O}(9)$ ,  $1.72, 1.09 \text{ \AA}, 159.2^\circ$ ;  $\text{O}(3) \cdots \text{H}(18)-\text{O}(7)$ ,  $1.78, 0.99 \text{ \AA}, 170.7^\circ$ ;  $\text{O}(3) \cdots \text{H}(21)-\text{O}(9)$ ,  $1.69, 1.08 \text{ \AA}, 168.0^\circ$ . The coordinated sulfonate also forms three hydrogen bonds through its two free oxygen atoms:  $\text{O}(4) \cdots \text{H}(17)-\text{O}(7)$ ,  $1.83, 0.89 \text{ \AA}, 179.0^\circ$ ;  $\text{O}(4) \cdots \text{H}(19)-\text{O}(8)$ ,  $1.84, 1.02 \text{ \AA}, 169.3^\circ$ ;  $\text{O}(6) \cdots \text{H}(23)-\text{O}(10)$ ,  $1.77, 1.05 \text{ \AA}, 175.7^\circ$ . Although there are some contacts ( $2.74(1)$  and  $2.80(1) \text{ \AA}$ ) between atoms  $\text{O}(11)$  and  $\text{O}(12)$  and sulfonate oxygen  $\text{O}(1)$  that are close enough for hydrogen bonding, it would appear, based on the large thermal parameters of these atoms, that any such interactions are weaker than those experienced by the other coordinated water molecules. Similarly, the water of hydration represented by atom  $\text{O}(13)$ , is within hydrogen bonding distance of  $\text{O}(2)$ ,  $\text{O}(11)$  and  $\text{O}(12)$ , but does not appear to be strongly attached to any one of these. Indeed, the size and rugby-ball shape of

the ellipsoid suggests that O(13) might actually be disordered over more than one position, however, no such splitting was evident in the X-ray analysis. Inspection of Fig. 7 shows that the primary hydrogen bonding pattern involving water oxygen atoms 7, 8, 9 and 10 occurs in a particular columnar region of the layer and that the pattern apparently breaks down in the region containing the other three water molecules.

## Discussion

The results presented here are part of an ongoing study of the structural chemistry of compounds of metal ions and organic sulfonates. Previously, we reported the structures of a series of divalent transition metal benzenesulfonates and nickel and sodium salts of 4-hydroxybenzenesulfonate [1]. Our work and that of others [8–13] to date shows that the benzenesulfonate salts of a variety of metals all crystallize in layered structures, but that the exact nature of the structure varies with the type of metal used.

The divalent first row transition metal ions show no tendency to coordinate to the sulfonate anions in the presence of water. The reported structures [8], like that of  $\text{Co}(\text{HO}(\text{O}_2\text{N})\text{C}_6\text{H}_3\text{SO}_3)_2 \cdot 6\text{H}_2\text{O}$ , contain fully hydrated  $[\text{M}(\text{H}_2\text{O})_6]^{2+}$  cations that interact with the sulfonate anions through hydrogen bonds. That this occurs is not too surprising as the borderline hard transition metal cations would not be expected to have a strong affinity for arylsulfonates, which are considered good leaving groups and ought to be softer ligands than water, though they are not to be found in any of the common tabulations [26]. Indeed, this mismatch is one reason for the desirability of alkylsulfonates as anionic surfactants in detergents that may be used in hard water. The magnitude of the difference in affinity of these ions for water versus sulfonate is reflected in the fact that  $\text{M}(\text{C}_6\text{H}_5\text{SO}_3)_2 \cdot 6\text{H}_2\text{O}$  ( $\text{M} = \text{Mn}, \text{Co}, \text{Ni}$  or  $\text{Zn}$ ) compounds can be dehydrated under relatively mild conditions to yield crystalline anhydrous metal sulfonates which are extremely hygroscopic and rapidly rehydrate on exposure to air [27]. This behavior is in marked contrast to that of the phosphonate anions which readily coordinate transition metal ions in aqueous solution to give layered structures with at most one or two water molecules per cation [2, 3, 5].

Sodium ion shows a much greater tendency than the transition metal ions to coordinate sulfonate anions. In the  $\text{Na}_4(\text{HO}(\text{O}_2\text{N})\text{C}_6\text{H}_3\text{SO}_3)_4 \cdot 2\text{H}_2\text{O}$  structure, the majority of the coordination sphere of the sodium is made up of the sulfonate oxygen atoms with the balance being water. In the compound  $\text{Na}_2(\text{HOC}_6\text{H}_4\text{SO}_3)_2 \cdot 4\text{H}_2\text{O}$  [1], in which the sulfonate lacks the nitro group, the sodium atoms coordinate two sulfonate oxygens

and four water molecules. Thus, the latter compound is more highly hydrated (two waters per Na) than the former (one water per two Na). The structures also differ in that the present one (Fig. 4) has two layers of sulfonate anions for every layer of cations while the other has only one sulfonate layer per cation layer. The difference is due to whether the sulfonates are interleaved (both up and down orientations in the same layer), which results in the one to one stacking, or segregated into separate layers of all up and all down. It is not clear why two such similar compounds would adopt the different packing patterns, though possible influences may include variations in reaction conditions (concentrations, pH, etc.) or differences in intermolecular interactions caused by the substitutional change on the ring.

The divalent alkaline earth ion  $\text{Ca}^{2+}$  shows an intermediate tendency to bond to the sulfonate. In the  $\text{Ca}(\text{H}_3\text{C}(\text{H}_2\text{N})\text{C}_6\text{H}_3\text{SO}_3)_2 \cdot 7\text{H}_2\text{O}$  structure, the seven-fold coordination sphere of the calcium contains one sulfonate oxygen atom and six water molecules, despite the availability of another sulfonate ion. This pattern is similar to that found in neodymium 4-aminobenzenesulfonate octahydrate, in which the nine-coordinate  $\text{Nd}^{3+}$  ion coordinates two sulfonate oxygens and seven water molecules in a tricapped trigonal prism [12] and in a series of lanthanide toluenesulfonate nonahydrates, in which the metal ions coordinate two sulfonate oxygens and six water molecules in a square antiprism [11]. In both cases, as in the calcium structure, one of the sulfonates is not bonded to the lanthanide ion. Uranyl ion,  $\text{UO}_2^{2+}$ , shows a somewhat greater affinity for sulfonate, forming a series of seven-coordinate pentagonal-bipyramidal complexes with various alkyl- and arylsulfonates [13]. The  $\text{UO}_2^{2+}$  ion coordinates four ethanesulfonate anions and one water molecule, two toluenesulfonate anions and three water molecules, and two 2,4,6-trimethylbenzenesulfonate anions and three water molecules.

Though the number of examples is quite limited, a tentative trend in the coordinating ability of metal ions toward arylsulfonates is emerging: alkali metals  $\gg$  alkaline earth metals  $\approx$  trivalent lanthanides  $\gg$  divalent transition metals. This trend cannot be explained in terms of hardness alone, as  $\text{Na}^+$  and  $\text{Ca}^{2+}$  are both considered to be harder than ions like  $\text{Co}^{2+}$  [26]. The ionic radius and charge (i.e. charge density) are probably both important as they will affect the hydration energy and compatibility of the cation with the large sulfonate anions. The sodium, calcium, neodymium and uranyl ions are all substantially larger than the divalent first row transition metal ions and all show a greater affinity for sulfonate. One would expect a large weakly-hydrated monovalent cation such as  $\text{K}^+$  or  $\text{Rb}^+$  to be the most compatible with the single-charged sulfonate anions.

Our most recent results confirm this hypothesis and will be presented in a forthcoming report [28].

### Supplementary material

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

### Acknowledgements

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