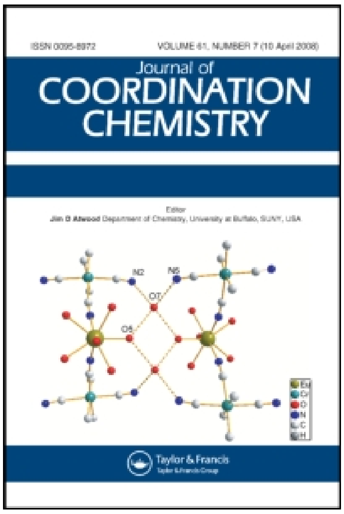

Journal of Coordination Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713455674

Correlated substituent rotation in the 1,2-benzenedisulfonate anion: the structure of the hydrated potassium salt

Glen B. Deacon[a]; Rita Harika[a]; Peter C. Junk[a]; Brian W. Skelton[b]; Allan H. White[b]
[a] School of Chemistry, Monash University, Clayton, VIC 3800, Australia [b] Chemistry M313, School of Biomedical, Biomolecular and Chemical Sciences, The University of Western Australia, Crawley, WA 6009, Australia

To cite this Article Deacon, Glen B. , Harika, Rita , Junk, Peter C. , Skelton, Brian W. and White, Allan H.(2009) 'Correlated substituent rotation in the 1,2-benzenedisulfonate anion: the structure of the hydrated potassium salt', Journal of Coordination Chemistry, 62: 19, 3098 — 3109

To link to this Article: DOI: 10.1080/00958970903033294

URL: http://dx.doi.org/10.1080/00958970903033294

Journal of Coordination Chemistry
Vol. 62, No. 19, 10 October 2009, 3098–3109

Taylor & Francis
Taylor & Francis Group

Correlated substituent rotation in the 1,2-benzenedisulfonate anion: the structure of the hydrated potassium salt

GLEN B. DEACON†, RITA HARIKA†, PETER C. JUNK*†,
BRIAN W. SKELTON‡ and ALLAN H. WHITE‡

†School of Chemistry, Monash University, Clayton, VIC 3800, Australia
‡Chemistry M313, School of Biomedical, Biomolecular and Chemical Sciences,
The University of Western Australia, Crawley, WA 6009, Australia

(*Received 17 March 2009; in final form 4 May 2009*)

Structure determinations have previously been recorded on the dipotassium and potassium tetramethylammonium salts of 1,2-benzenedisulfonic acid (methanol solvate and hydrate, respectively), as a platform for examining the gear-like interactions of adjacent sulfonate substituents on the aromatic ring. The present report records a single crystal X-ray study of the hydrated potassium salt, showing it to be $8K_2[(O_3S)_2C_6H_4] \cdot 11H_2O$, with eight independent anions in the asymmetric unit, enabling a more broadly-based consideration of substituent dispositions.

Keywords: Crystal structure; Benzenedisulfonate; Potassium; Conformation

1. Introduction

Although hydrated potassium 1,2-benzenedisulfonate is the commercial source of the 1,2-benzenedisulfonate ligand, it has not yet been defined structurally by a single crystal X-ray study; surveys of the more crystallographically accessible methanol solvate and the tetramethylammonium double salt have provided a basis for examination of the rotational interaction of the pair of adjacent sulfonate substituents and the associated potential energy surface [1]. In the course of synthesizing complexes of other metal ions, as described in an associated paper [2], crystals of a hydrated potassium salt were obtained adventitiously from hot aqueous solution, a single crystal X-ray study showing them to be of the form $8K_2L \cdot 11H_2O$ ($L = [(O_3S)_2C_6H_4]$). Unusually, eight independent anions, devoid of crystallographic symmetry, are found in the asymmetric unit of the structure, providing an opportunity for a broader survey of substituent dispositions than those provided by previous study, in which the asymmetric units of the two structures each contain only one anion, one of those with a symmetry constraint.

---

*Corresponding author. Email: peter.junk@sci.monash.edu.au

Journal of Coordination Chemistry
ISSN 0095-8972 print/ISSN 1029-0389 online © 2009 Taylor & Francis
DOI: 10.1080/00958970903033294

2. Experimental: structure determination

A full sphere of CCD area-detector diffractometer data was measured (Bruker AXS instrument, ω-scans, $2\theta_{\max} = 75°$; monochromatic Mo-Kα radiation; $\lambda = 0.7107_3$ Å; $T_{ca} = 153$ K) yielding 95,874 reflections, these merging to 48,017 unique (R_{int} 0.043) after "empirical"/multiscan absorption correction (proprietary software), 34,123 with $I > 2\sigma(I)$ being considered "observed". Full matrix least squares refinement on F^2 (all data) refined anisotropic displacement parameters for the nonhydrogen atoms, hydrogen atom parameter treatment following a riding model; reflection weights were $(\sigma^2(F_o^2) + (0.066P)^2 + 0.122P)^{-1}$ $(P = (F_o^2 + 2F_c^2)/3)$, $R_1 = 0.043$, $wR_2 = 0.13$, $S = 1.10$. Neutral atom complex scattering factors were employed within the SHELXL-97 program [3]. Pertinent results are given below and in the tables and figures, the latter showing 50% probability amplitude displacement envelopes for the nonhydrogen atoms with hydrogen atoms (where shown) having arbitrary radii of 0.1 Å.

$8K_2L \cdot 11H_2O$ (1). $C_{48}H_{54}K_{16}O_{59}S_{16}$, $M = 2713.5$. Triclinic, space group $P\bar{1}$ (C_i^1, No. 2), $a = 13.012(2)$, $b = 16.134(3)$, $c = 23.169(5)$ Å, $\alpha = 94.150(5)$, $\beta = 91.720(5)$, $\gamma = 105.801(5)°$, $V = 4662$ Å^3 $\cdot$ D_{Calcd} $(Z = 2) = 1.93_3$ g cm^{-3} $\cdot$ $\mu_{\text{Mo}} = 1.19$ mm^{-1}; specimen: $= 0.35 \times 0.35 \times 0.16$ mm^3; $T_{\min/\max} = 0.73$.

Variata. Sulfonate groups 21 and 71 were modeled as rotationally disordered about the C–S pendant, component occupancies refining to 0.825(3), 0.918(3), and complements, respectively (isotropic displacement parameter forms for the minor components); these groups are involved in "chelation" to the same potassium atom (K(4)), so that there is a possibility that the disorder may be concerted. Site occupancies of K(15, 17, 17′) were set at 0.5 after trial refinement (note that K(16) lies on an inversion center). Water molecule hydrogen atoms were refined in $(x, y, z, U_{\text{iso}})_{\text{H}}$ (exception: those for O(10) (not located), modeled as disordered over a pair of sites O(10,10′), occupancies 0.5).

3. Discussion

(Brief comment on sulfonate complexes of s-block metal ions has recently been made in [4].)

The results of the single crystal X-ray study are consistent with the formulation of the potassium salt as $8K_2L \cdot 11H_2O$, a full formula unit comprising the asymmetric unit of the structure; one potassium (K(16)) lies on a crystallographic inversion center, with another (K(15)), modeled with 50% occupancy, disposed close to an inversion center (the distance between the two fragments being 1.433(2) Å) and yet another (K(17,17′)) also modeled as disordered over a pair of sites 0.698(1) Å apart. Sulfonate groups 21 and 71 were modeled as rotationally disordered about their C–S pendants. The residue modeled as water O(10) was also modeled as disordered over a pair of sites (separated by 1.505(6) Å) in proximity to/concerted with the disordered K(17). Overall, however, these disordered components represent only a minor portion of the gross structure which, despite its complexity, is otherwise well-ordered, so much so that smooth refinement of all other water molecule hydrogens was possible. The potassium environments (table 1) are generally irregular with respect to their associated coordination polyhedra; the centrosymmetric K(16) appears to be genuinely six-coordinate, with the shortest K–O distances (2.647(1), 2.683(1), 2.783(2) Å), together with K(4,5). The other environments are seven-coordinate

Table 1. The potassium atom environments, (*r* (K–O) in Å, O–K–O in degrees); θ (degrees) are the K–O–S angles.

Atom	*r*	O(122)	O(413)	O(422)	O(311^{i})	O(322^{i})	O(323^{i})	θ
K(1)^{a}								
O(111)	2.685(2)	73.68(4)	109.50(4)	136.47(5)	71.62(4)	91.78(5)	133.89(4)	152.33(8)
O(122)	2.669(2)		136.64(5)	76.60(4)	129.36(5)	83.87(5)	117.85(4)	131.68(7)
O(413)	2.727(1)			73.06(4)	89.83(4)	137.48(4)	91.56(4)	156.04(7)
O(422)	2.673(1)				150.40(5)	115.91(4)	88.25(5)	133.83(7)
O(311^{i})	2.689(1)					61.80(4)	67.81(4)	135.05(8)
O(322^{i})	2.947(2)						49.86(4)	95.94(7)
O(323^{i})	2.806(2)							101.76(7)

^{a}K(1) ··· K(2, 7, 10, 11) are 3.8806(7), 4.2967(7), 4.3070(7), 3.8898(8) Å.

Atom	*r*	O(413)	O(421)	O(612)	O(621)	O(312^{i})	O(323^{i})	θ
K(2)^{b}								
O(411)	2.953(2)	49.93(4)	61.62(4)	86.86(5)	78.24(4)	115.10(4)	137.18(4)	95.20(7)
O(413)	2.777(2)		67.34(4)	132.57(4)	113.77(4)	84.82(4)	90.90(4)	102.39(7)
O(421)	2.714(1)			75.69(4)	125.11(4)	145.70(5)	90.13(4)	138.34(8)
O(612)	2.659(2)				65.73(4)	138.16(5)	118.46(4)	146.78(7)
O(621)	2.697(1)					83.61(4)	142.14(4)	153.82(9)
O(312^{i})	2.647(1)						69.92(4)	138.23(7)
O(323^{i})	2.788(1)							158.30(7)

^{b}K(2) ··· K(9, 13) are 4.0341(10), 3.9999(7) Å.

Atom	*r*	O(813)	O(821)	O(313^{i})	O(312^{i})	O(712^{ii})	*O(715^{ii})*	θ
K(3)^{c}								
O(622)	2.719(2)	121.32(5)	81.01(4)	147.52(4)	103.97(4)	103.56(5)	*114.4(3)*	120.25(7)
O(813)	2.662(2)		71.93(5)	81.85(4)	94.45(5)	124.00(5)	*117.4(3)*	116.01(9)
O(821)	2.747(1)			130.48(4)	165.91(5)	85.13(5)	*91.8(2)*	115.93(7)
O(313^{i})	3.106(2)				47.82(3)	75.71(5)	*64.0(3)*	92.70(6)
O(312^{i})	2.775(1)					106.10(5)	*98.0(2)*	107.10(6)
O(712^{ii})	2.730(2)						*11.9(3)*	140.82(10)
O(715^{ii})	*3.067(14)*							*117.9(7)*

^{c}K(3) ··· K(6, 12) are 4.1349(10), 3.8739(7); K ··· O (<4 Å): K(3) ··· O(621, 812, 822, 5^{ii}) 3.518(1), 3.366(2), 3.415(1), 3.650(2) Å.

Atom	*r*	*O(216)*	O(222)	O(423)	O(522^{iii})	O(713^{iv})	*O(716^{iv})*	O(723^{iv})	θ
K(4)^{d}									
O(213)	2.704(2)	23.6(2)	58.39(5)	109.95(5)	78.21(5)	116.53(5)	139.9(3)	151.57(6)	147.0(1)
O(216)	*2.542(9)*		*72.2(2)*	*133.2(2)*	*75.6(2)*	*93.2(2)*	*117.1(3)*	*142.3(2)*	*143.9(4)*
O(222)	3.009(2)			82.77(5)	131.85(5)	136.91(5)	*144.1(3)*	97.48(5)	146.48(9)
O(423)	2.642(1)				94.56(5)	130.27(5)	*106.5(3)*	78.48(5)	155.68(10)
O(522^{iii})	2.958(2)					78.93(5)	*82.9(3)*	129.25(5)	112.53(8)
O(713^{iv})	2.704(2)						*24.1(3)*	69.30(4)	140.67(9)
O(716^{iv})	*3.019(14)*							*52.8(3)*	*127.2(8)*
O(723^{iv})	2.822(2)								153.43(7)

^{d}K(4) ··· K(10, 12^{i}, 5^{iv}) are 3.8862(7), 4.2185(9), 4.0561(10); K ··· O (<4 Å): K(4) ··· O(523^{iii}, 7^{iv}) 3.663(2), 3.700(2) Å.

Atom	*r*	O(711)	O(716)	O(722)	O(723)	O(1)	O(7)	O(823^{ii})	θ
K(5)^{e}									
O(623)	2.725(1)	103.93(4)	*132.2(3)*	70.90(4)	114.21(5)	69.33(4)	139.64(5)	79.17(4)	143.59(9)
O(711)	2.799(2)		*28.7(3)*	56.10(4)	66.41(4)	145.29(5)	91.69(5)	65.96(4)	131.16(8)
O(716)	*2.823(13)*			*71.6(4)*	*55.2(3)*	*138.9(3)*	*72.4(4)*	*81.4(3)*	*137.4(9)*

(*Continued*)

Table 1. Continued.

Atom	*r*	O(711)	*O(716)*	O(722)	O(723)	O(1)	O(7)	O(823^{ii})	θ
O(722)	3.009(2)				49.23(4)	90.60(5)	143.88(4)	102.77(4)	94.47(7)
O(723)	2.795(2)					84.94(4)	106.16(5)	132.34(4)	103.62(7)
O(1)	2.739(2)						115.82(5)	139.49(4)	
O(7)	2.708(2)							73.66(5)	
O(823^{ii})	2.830(1)								128.26(8)

[e] K(5)···K(6, 4^{iv}) are 3.6804(7), 4.0561(10); K···O (<4 Å): K(5)···O(423^{iv}, 713, 714, 822^{ii}) 3.676(2), 3.948(2), 3.950(14), 3.898(2) Å.

Atom	*r*	O(623)	O(711)	*O(714)*	O(722)	O(812)	O(821)	O(5)	O(823^{ii})	θ
K(6)[f]										
O(622)	2.884(1)	46.82(3)	129.67(5)	*149.9(4)*	111.13(4)	81.45(4)	78.24(4)	146.25(5)	71.49(4)	104.88(7)
O(623)	3.166(1)		94.31(4)	*120.8(3)*	65.57(4)	85.57(4)	120.57(4)	164.74(5)	70.57(4)	93.07(6)
O(711)	2.756(2)			*26.5(3)*	56.81(4)	133.89(5)	144.36(4)	70.64(5)	64.78(5)	145.10(9)
O(714)	*2.635(14)*				*72.4(3)*	*128.0(4)*	*118.3(3)*	*44.1(3)*	*78.5(4)*	*138.6(7)*
O(722)	2.983(2)					82.10(5)	141.82(5)	102.61(5)	100.41(4)	146.29(8)
O(812)	2.905(2)						62.21(4)	102.87(5)	151.91(4)	144.22(8)
O(821)	2.741(2)							74.68(5)	117.39(5)	142.06(8)
O(5)	2.814(2)								103.82(5)	
O(823^{ii})	2.956(2)									110.22(7)

[f] K(6)···K(6^{ii}) is 4.3848(9); K···O (<4 Å): K(6)···O(821^{ii}, 5^{ii}) are 3.444(2), 3.783(2) Å.

Atom	*r*	O(113)	O(3)	O(4)	O(311^{i})	O(313^{i})	O(512^{v})	O(513^{v})	θ
K(7)[g]									
O(111)	2.873(1)	47.04(4)	87.09(5)	93.92(4)	67.98(4)	116.80(4)	115.16(4)	151.85(5)	98.89(6)
O(113)	3.116(2)		106.32(5)	97.69(4)	114.02(4)	162.20(4)	70.55(4)	117.84(5)	88.98(8)
O(3)	2.767(2)			147.59(5)	76.71(5)	76.75(5)	96.37(5)	74.46(5)	
O(4)	2.668(2)				73.75(4)	73.93(4)	112.20(5)	113.10(4)	
O(311^{i})	2.748(2)					48.92(4)	172.45(4)	125.66(5)	104.83(6)
O(313^{i})	3.058(2)						127.02(4)	79.95(4)	91.44(6)
O(512^{v})	3.028(2)							48.35(4)	91.21(8)
O(513^{v})	2.845(1)								99.09(8)

[g] K(7)···K(11,12,17,17′) are 3.9499(8), 4.1211(9), 4.2316(12), 4.3641(15); K···O (<4 Å): K(7)···O(112, 8) 3.955(2), 3.396(2) Å.

Atom	*r*	O(811)	O(4)	O(8)	O(613^{vi})	O(721^{vii})	O(2^{vii})	θ
K(8)[h]								
O(412)	2.711(2)	75.58(4)	73.35(4)	138.93(4)	144.87(4)	95.55(4)	70.54(4)	142.72(8)
O(811)	2.768(2)		78.28(5)	128.25(4)	84.69(4)	164.69(4)	87.74(4)	132.58(8)
O(4)	2.716(2)			79.55(5)	130.92(4)	111.54(5)	143.50(4)	
O(8)	2.740(2)				75.83(5)	66.43(5)	133.31(5)	
O(613^{vi})	2.667(1)					96.39(5)	80.04(4)	158.48(9)
O(721^{vii})	2.663(2)						77.45(4)	140.7(1)
O(2^{vii})	3.037(2)							

[h] K(8)···K(16, 13^{vi}, 9^{vii}) are 3.6539(7), 4.0347(7), 4.3202(8); K···O(<4 Å): K(8)···O(813) 3.946(2) Å.

Atom	*r*	O(611)	O(621)	O(623)	O(2)	O(611^{iv})	O(613^{iv})	θ
K(9)[i]								
O(411)	2.636(2)	124.01(4)	81.75(5)	126.83(4)	92.12(4)	104.29(4)	110.24(5)	162.46(8)
O(611)	2.660(2)		72.58(4)	62.82(4)	136.08(4)	69.92(4)	104.76(4)	116.09(7)

(*Continued*)

Table 1. Continued.

Atom	*r*	O(611)	O(621)	O(623)	O(2)	O(611^{iv})	O(613^{iv})	*θ*
O(621)	2.816(2)			47.83(4)	91.31(4)	138.06(4)	165.93(4)	105.68(7)
O(623)	3.122(2)				75.95(4)	123.56(4)	118.38(4)	92.54(6)
O(2)	2.727(1)					129.11(4)	81.17(4)	
O(611^{iv})	2.980(1)						47.94(3)	97.05(5)
O(613^{iv})	2.922(2)							99.44(7)

[i] K(9)···K(16) is 4.3981(8); K···O (<4Å): K(9)···O(612, 1) 3.374(2), 3.840(2) Å.

Atom	*r*	O(213)	*O(215)*	O(222)	O(223)	O(422)	O(11)	O(523^{iii})	*θ*
K(10)[j]									
O(122)	2.844(1)	154.45(5)	*123.0(2)*	115.25(5)	86.39(5)	72.70(4)	91.02(5)	129.63(5)	125.38(8)
O(213)	2.838(2)		*34.1(2)*	56.23(5)	70.36(5)	125.68(5)	86.53(6)	70.78(5)	122.08(10)
O(215)	*2.772(8)*			*72.9(2)*	*56.4(2)*	*156.9(2)*	*66.9(2)*	*86.5(2)*	*130.4(4)*
O(222)	3.084(2)				48.29(5)	85.17(5)	139.47(5)	112.20(5)	93.30(9)
O(223)	2.806(2)					113.31(5)	108.19(6)	140.36(5)	105.7(1)
O(422)	2.741(1)						133.83(5)	95.50(5)	120.59(7)
O(11)	2.795(2)							61.85(5)	
O(523^{iii})	2.905(2)								135.22(10)

[j] K(10)···K(14) is 3.844(1) Å; K···O (<4 Å) are K(10)···O(121, 212, 216, 423) 3.826(2), 3.697(2), 3.865(8), 3.577(2) Å.

Atom	*r*	O(112)	O(123)	O(3)	O(311^{i})	O(322^{i})	O(112^{v})	O(123^{v})	*θ*
K(11)[k]									
O(111)	2.826(2)	46.22(4)	64.28(4)	88.64(5)	62.15(4)	92.73(5)	136.30(5)	107.56(5)	109.95(7)
O(112)	3.264(2)		58.17(4)	82.33(5)	102.62(4)	135.79(4)	100.42(4)	63.16(4)	90.90(7)
O(123)	2.686(2)			140.49(6)	115.34(4)	92.93(4)	74.14(4)	94.06(4)	137.04(8)
O(3)	2.736(2)				69.46(4)	117.86(5)	117.97(5)	65.99(5)	
O(311^{i})	3.229(2)					57.29(4)	156.62(5)	134.52(3)	135.63(8)
O(322^{i})	2.767(2)						102.50(4)	159.61(5)	150.17(7)
O(112^{v})	2.757(2)							61.34(4)	144.66(7)
O(123^{v})	2.986(2)								133.35(9)

[k] K(11)···K(11^{v}) is 3.8725(8) Å.

Atom	*r*	O(6)	O(313^{i})	O(513^{v})	O(522^{v})	O(713^{ii})	*O(715^{ii})*	*O(716^{ii})*	*θ*
K(12)[l]									
O(822)	2.770(1)	168.88(5)	109.76(4)	119.05(5)	95.42(4)	82.73(5)	*80.0(3)*	*61.5(3)*	161.45(9)
O(6)	2.810(2)		81.01(5)	62.27(6)	74.52(5)	91.11(6)	*101.4(3)*	*111.5(3)*	
O(313^{i})	2.660(1)			89.71(5)	153.00(5)	109.59(5)	*71.94(2)*	*118.3(3)*	176.25(9)
O(513^{v})	2.722(2)				68.99(5)	144.78(5)	*157.7(3)*	*150.9(3)*	163.67(8)
O(522^{v})	2.760(2)					82.45(5)	*123.7(2)*	*81.9(3)*	138.58(9)
O(713^{ii})	2.709(2)						*41.3(2)*	*21.6(3)*	108.89(8)
O(715^{ii})	*2.902(2)*							*46.6(3)*	*100.5(7)*
O(716^{ii})	*3.252(16)*								*88.6(7)*

[l] K···O (<4 Å) are K(12)···O(712^{ii}, 813, 7^{ii}) 3.327(2), 3.928(2), 3.770(2) Å.

Atom	*r*	O(612)	O(9)	O(8^{i})	O(721^{iv})	O(723^{iv})	O(1^{iv})	*θ*
K(13)[m]								
O(421)	2.807(2)	73.20(4)	76.83(5)	140.07(4)	155.89(4)	106.42(4)	60.01(4)	115.72(6)
O(612)	2.721(1)		104.92(5)	85.46(5)	124.21(5)	151.01(4)	75.07(5)	115.93(7)
O(9)	2.692(2)			76.68(6)	110.10(5)	103.09(5)	135.21(6)	

(*Continued*)

Table 1. Continued.

Atom	*r*	O(612)	O(9)	O(8$^{\rm i}$)	O(721$^{\rm iv}$)	O(723$^{\rm iv}$)	O(1$^{\rm iv}$)	*θ*
O(8$^{\rm i}$)	2.852(2)				62.98(4)	108.31(4)	145.73(5)	
O(721$^{\rm iv}$)	2.815(2)					49.91(4)	105.47(5)	96.93(7)
O(723$^{\rm iv}$)	2.898(1)						79.87(4)	93.58(6)
O(1$^{\rm iv}$)	2.923(2)							

[m] K(13) ··· O(423, 613) are 3.498(2), 3.377(2) Å.

Atom	*r*	O(212)	*O(215)*	O(511)	O(521)	O(11)	O(211$^{\rm iii}$)	*O(214$^{\rm iii}$)*	*θ*
K(14)[n]									
O(121)	2.578(1)	136.74(6)	*116.0(2)*	86.38(5)	122.78(6)	75.52(5)	79.88(6)	*82.2(2)*	149.48(9)
O(212)	2.607(2)		*20.7(2)*	119.20(7)	100.24(6)	75.38(6)	115.00(7)	*106.5(2)*	154.2(1)
O(215)	*2.839(9)*			*127.5(2)*	*120.9(2)*	*62.6(2)*	*117.5(2)*	*107.6(3)*	*142.5(5)*
O(511)	2.735(2)				64.69(5)	161.89(5)	112.72(6)	*122.9(2)*	142.74(10)
O(521)	2.604(2)					126.23(6)	69.35(7)	*75.7(2)*	165.98(14)
O(11)	3.058(2)						65.20(6)	*55.9(2)*	
O(211$^{\rm iii}$)	3.104(3)							*10.2(2)*	108.3(1)
O(214$^{\rm iii}$)	*2.907(11)*								*121.7(5)*

[n] K(14) ··· O(212$^{\rm iii}$, 215$^{\rm iii}$, 223, 6$^{\rm v}$) are 3.614(3), 3.921(10), 3.337(2), 3.860(2) Å.

Atom	*r*	O(322)	O(10′)	O(221$^{\rm vi}$)	O(221$^{\rm v}$)	O(321$^{\rm viii}$)	O(10$^{\rm viii}$)	*θ*
K(15)[o]								
O(321)	2.647(2)	48.18(4)	130.9(1)	80.44(5)	94.54(6)	149.70(7)	74.52(6)	111.03(8)
O(322)	3.159(2)		82.80(9)	108.48(6)	88.84(5)	154.85(5)	118.15(6)	88.75(7)
O(10′)	2.725(5)			120.0(1)	85.7(1)	77.3(1)	148.6(1)	
O(221$^{\rm vi}$)	2.652(2)				149.87(7)	94.85(5)	77.56(7)	115.8(1)
O(221$^{\rm v}$)	2.834(2)					74.57(5)	72.49(7)	143.0(1)
O(321$^{\rm viii}$)	2.815(2)						75.23(6)	137.04(8)
O(10$^{\rm viii}$)	2.875(3)							

[o] K(15) ··· K(17, 17′, 15$^{\rm viii}$, 17$^{\rm viii}$, 17′$^{\rm viii}$) are 3.763(2), 3.885(2), 1.437(2), 3.105(2), 3.469(2); K(15) ··· O(10, 223$^{\rm vi}$, 10′$^{\rm viii}$) 1.464(3), 3.344(2), 3.946(5) Å.

Atom	*r*	O(811)	O(2)	O(412$^{\rm vii}$)	O(811$^{\rm vii}$)	O(2$^{\rm vii}$)	*θ*
K(16)[p]							
O(412)	2.683(1)	78.10(4)	104.98(5)	180(–)	101.90(4)	75.02(5)	128.42(8)
O(811)	2.647(1)		84.27(4)	101.90(4)	180(–)	95.73(2)	133.42(8)
O(2)	2.783(2)			75.02(4)	95.73(4)	180(–)	

[p] K(16) ··· O(411, 812) are 3.769(2), 3.867(2) Å (×2).

Atom	*r*	O(113)	O(321)	O(221$^{\rm vi}$)	O(9$^{\rm vi}$)	O(512$^{\rm v}$)	O(10$^{\rm viii}$)	*θ*
K(17)[q]								
O(112)	3.023(2)	49.07(4)	157.22(6)	85.58(5)	118.36(5)	109.02(5)	84.44(6)	93.91(7)
O(113)	2.759(2)		145.58(6)	94.37(6)	77.73(5)	80.15(5)	133.46(7)	105.20(8)
O(321)	2.660(2)			76.85(5)	68.10(5)	92.90(5)	77.86(7)	152.56(9)
O(221$^{\rm vi}$)	2.841(2)				67.68(6)	153.30(6)	77.92(8)	147.1(1)
O(9$^{\rm vi}$)	3.127(2)					85.63(6)	135.75(8)	
O(512$^{\rm v}$)	2.754(2)						124.50(8)	116.09(9)
O(10$^{\rm viii}$)	2.669(3)							

[q] K(17) ··· K(17′) is 0.698(2); K(17) ··· O(511$^{\rm v}$, 810$^{\rm viii}$) 3.344(2), 3.977(2, 1.813(5)) Å.

(*Continued*)

Table 1. Continued.

Atom	*r*	O(321)	O(221$^{\mathrm{vi}}$)	O(9$^{\mathrm{vi}}$)	O(512$^{\mathrm{v}}$)	O(10$^{\mathrm{viii}}$)	O(10′$^{\mathrm{viii}}$)	θ
K(17′)$^{\mathrm{r}}$								
O(113)	2.573(2)	174.30(7)	102.54(6)	95.16(7)	83.36(6)	116.99(7)	99.60(10)	117.28(8)
O(321)	2.610(2)		80.38(6)	80.39(6)	93.89(6)	68.54(6)	85.05(10)	139.02(9)
O(221$^{\mathrm{vi}}$)	2.692(2)			80.76(7)	173.80(7)	70.51(7)	93.19(12)	133.4(1)
O(9$^{\mathrm{vi}}$)	2.443(3)				100.54(7)	140.33(9)	164.97(12)	
O(512$^{\mathrm{v}}$)	2.760(2)					105.44(8)	84.09(12)	129.71(10)
O(10$^{\mathrm{viii}}$)	3.260(3)						26.5(1)	
O(10′$^{\mathrm{viii}}$)	2.511(5)							

$^{\mathrm{r}}$K(17′) ··· O(112, 222$^{\mathrm{vi}}$, 313, 511$^{\mathrm{v}}$, 8) are 3.324(2), 3.879(2), 3.992(2), 3.782(2), 2.556(2) Å.
Values associated with minor components of sulfonate disorder (O(214-6, 714-6)) are italicized.
Angles subtended at oxygen atoms by pairs of potassium atoms are presented as (O; K, K′):
(1) Sulfate oxygen atoms: (111; 1, 7): 101.19(5); (111; 1, 11) 89.75(5); (111; 7, 11) 87.73(4); (112; 11, 17) 127.49(5); (112; 11, 11$^{\mathrm{v}}$) 79.58(4); (112; 17, 11$^{\mathrm{v}}$) 118.94(5); (113; 7, 17) 91.95(5); (113; 7, 17′) 99.74(6); (113; 17, 17′) 14.52(4); (122; 1, 10) 102.70(5); (123; 11, 11$^{\mathrm{v}}$) 85.94(4); (213; 4, 10) 89.00(5); (215; 10, 14) 86.5(2); (221; 15$^{\mathrm{i}}$, 17$^{\mathrm{i}}$) 86.41(5); (221; 15$^{\mathrm{i}}$, 17′$^{\mathrm{i}}$) 93.25(6); (221; 15$^{\mathrm{i}}$, 15$^{\mathrm{v}}$) 30.13(4); (221; 17$^{\mathrm{i}}$, 17′$^{\mathrm{i}}$) 14.17(4); (221; 17$^{\mathrm{i}}$, 15$^{\mathrm{v}}$) 66.34(5); (221; 17′$^{\mathrm{i}}$; 15$^{\mathrm{v}}$) 77.73(6); (222; 4, 10) 79.24(5); (311; 1$^{\mathrm{vi}}$, 7$^{\mathrm{vi}}$) 104.40(5); (311; 1$^{\mathrm{vi}}$, 11$^{\mathrm{vi}}$) 81.63(3); (311; 7$^{\mathrm{vi}}$, 11$^{\mathrm{vi}}$) 82.30(4); (312; 2$^{\mathrm{vi}}$, 3$^{\mathrm{vi}}$) 114.18(5); (313; 3$^{\mathrm{vi}}$, 7$^{\mathrm{vi}}$) 125.15(5); (313; 3$^{\mathrm{vi}}$, 12$^{\mathrm{vi}}$) 84.05(4); (313; 7$^{\mathrm{vi}}$, 12$^{\mathrm{vi}}$) 91.96(4); (321; 15, 17) 90.33(5); (321; 15, 17′) 95.30(5); (321; 15, 15$^{\mathrm{viii}}$) 30.30(4); (321; 17, 17′) 15.19(4); (321; 17, 15$^{\mathrm{viii}}$) 69.02(4); (321; 17′, 15$^{\mathrm{viii}}$) 79.41(5); (322; 15, 1$^{\mathrm{vi}}$) 125.68(5); (322; 15, 11$^{\mathrm{vi}}$) 114.41(5); (322; 1$^{\mathrm{vi}}$, 11$^{\mathrm{vi}}$) 85.74(5); (323; 1$^{\mathrm{vi}}$, 2$^{\mathrm{vi}}$) 87.84(4); (411; 2, 9) 92.23(5); (412; 8, 16) 85.29(4); (413; 1, 2) 89.66(4); (421; 2, 13) 92.84(5); (422; 1, 10) 105.41(4); (512; 7$^{\mathrm{v}}$, 17$^{\mathrm{v}}$) 93.97(4); (512; 7$^{\mathrm{v}}$, 17′$^{\mathrm{v}}$) 97.78(5); (512; 17$^{\mathrm{v}}$, 17′$^{\mathrm{v}}$) 14.55(4); (513; 7$^{\mathrm{v}}$, 12$^{\mathrm{v}}$) 95.48(5); (522; 4$^{\mathrm{iii}}$, 12$^{\mathrm{v}}$) 95.02(5); (611; 9, 9$^{\mathrm{iv}}$) 110.08(5); (612; 2, 13) 96.05(5); (613; 8$^{\mathrm{i}}$, 9$^{\mathrm{iv}}$) 101.13(4); (621; 2, 9) 94.05(4); (622; 3, 6) 95.09(4); (623; 5, 6) 76.94(3); (623; 5, 9) 123.02(5); (623; 6, 9) 119.50(5); (711; 5, 6) 82.98(4); (713; 4$^{\mathrm{iv}}$, 12$^{\mathrm{ii}}$) 102.41(6); (715; 3$^{\mathrm{ii}}$, 12$^{\mathrm{ii}}$) 80.9(4); (716; 5, 4$^{\mathrm{iv}}$) 87.9(4); (716; 5, 12$^{\mathrm{ii}}$) 121.7(6); (716; 4$^{\mathrm{iv}}$, 12$^{\mathrm{ii}}$) 84.5(4); (721; 13$^{\mathrm{iv}}$, 8$^{\mathrm{vii}}$) 94.85(4); (722; 5, 6) 75.79(4); (723; 5, 4$^{\mathrm{iv}}$) 92.46(5); (723; 5, 13$^{\mathrm{iv}}$) 97.25(4); (723; 4$^{\mathrm{iv}}$, 13$^{\mathrm{iv}}$) 105.38(4); (811; 8, 16) 84.84(4); (821; 3, 6) 97.79(4); (823; 5$^{\mathrm{ii}}$, 6$^{\mathrm{ii}}$) 78.96(4).
(2) Water molecule oxygen atoms: (1; 5, 13$^{\mathrm{iv}}$) 97.92(5); (2; 9, 16) 105.90(4); (2; 9, 8$^{\mathrm{vii}}$) 96.95(4); (2; 16, 8$^{\mathrm{vii}}$) 77.65(4); (3; 7, 11) 91.74(5); (4; 7, 8) 115.81(6); (8; 8, 13$^{\mathrm{vi}}$) 92.34(4); (9; 13, 17$^{\mathrm{i}}$) 127.61(8); (9; 13, 17′$^{\mathrm{i}}$) 125.11(9); (9; 17$^{\mathrm{i}}$, 17′$^{\mathrm{i}}$) 2.93(3); (10; 15, 15$^{\mathrm{viii}}$) 7.51(7); (10; 15, 17$^{\mathrm{viii}}$) 92.7(1); (10; 15, 17′$^{\mathrm{viii}}$) 85.6(1); (10; 15$^{\mathrm{viii}}$, 17$^{\mathrm{viii}}$) 85.42(9); (10; 15$^{\mathrm{viii}}$, 17′$^{\mathrm{viii}}$) 78.30(8); (10; 17$^{\mathrm{viii}}$, 17′$^{\mathrm{viii}}$) 7.23(4); (10′; 15, 17$^{\mathrm{viii}}$) 83.7(2); (10’; 15, 17′$^{\mathrm{viii}}$) 82.9(2); (10′; 17$^{\mathrm{viii}}$, 17′$^{\mathrm{viii}}$) 0.87(6); (11; 10, 14) 81.98(6).
Coordinate transformations: (i) $x-1, y, z$; (ii) $1-x, 1-y, 1-z$; (iii) $\bar{x}, \bar{y}-1, \bar{z}$; (iv) $\bar{x}, \bar{y}, 1-z$; (v) $1-x, \bar{y}, \bar{z}$; (vi) $x+1, y, z$; (vii) $1-x, \bar{y}, 1-z$; (viii) $2-x, \bar{y}, \bar{z}$.

(K(1, 2, 3, 8, 9, 10, 12, 13, 14, 15, 17(′))) with their associated K–O distances ranging upwards from 2.6 Å and eight-coordinate (K(6, 7, 11)), although the upper limits of what might be considered "bonding" K···O distances become diffuse in the higher coordination number environments. The coordinating oxygens may be diversely from water or sulfonate groups, the latter predominating; the water oxygen coordination modes may be terminal O(1, 5, 6, 7) or bridging (the others), as may the sulfonate oxygens also. The sulfonate groups not infrequently coordinate to the same metal atom through more than one oxygen, and the two sulfonates of the same ligand may coordinate to the same or to different metals. The interactions of the various ligands may be summarized as follows:

(1) μ_7-η^3(O(111, 112, 123))(K(11)) : η^2(O(111, 122))(K(1)) : η^2(O(111, 113))(K(7)) : η^2(O(112, 123))(K(11$^{\mathrm{vi}}$)) : η^1(O(121))(K(14)) : η^1(O(122))(K(10)) : η^1(O(112, 113)) (K(17, 17′)) (vi $= x+1, y, z$ (table 1)).

(2) μ_6-η^3(O(213, 215, 222, 223))(K(10)) : η^2(O(213/216, 222))(K(4)) : η^2(O(211, 214) (K(14$^{\mathrm{iii}}$)) : η^1(O(212/215))(K(14)) : η^1(O(221)(K(15), K(15$^{\mathrm{v}}$)) : η^1(O(221))(K(17, 17′)) (iii $= \bar{x}, \bar{y}-1, \bar{z}$; v $= 1-x, \bar{y}, \bar{z}$).

(3) μ_8-η^3(O(311, 322,323))(K(1$^{\mathrm{vi}}$)) : η^2(O(312, 323))(K(2$^{\mathrm{vi}}$)) : η^2(O(311, 322))(K(11$^{\mathrm{vi}}$)) : η^2(O (312, 313))(K(3$^{\mathrm{vi}}$)) : η^2(O(321, 322))(K(15)/K(15$^{\mathrm{viii}}$)) : η^1(O(313))(K(12$^{\mathrm{vi}}$)) : η^1(O(311, 313))(K(7)) : η^1(O(321))(K(17, 17′)) (viii $= 2-x, \bar{y}, \bar{z}$).

(4) μ_8-η^3(O(411, 413, 421))(K(2)) : η^2(O(413, 422))(K(1)) : η^1(O(411))(K(9)) : η^1(O(412)) (K(8)) : η^1(O(421))(K(13)) : η^1(O(422))(K(10)) : η^1(O(423))(K(4)) : η^1(O(412))(K(16)).

(5) μ_6-η^2(O(511, 521)(K(14)) : η^2(O(513, 522))(K(12^{v})) : η^2(O(512, 513))(K(7^{v})) : η^1(O(512)) (K(17/17′)) : η^1(O(522))(K(4^{iii})) : η^1(O(523))(K(10^{iii})).

(6) μ_8-η^3(O(611, 621, 623))(K(9)) : η^2(O(612, 621))(K(2)) : η^2(O(622, 623))(K(6)) : η^2(O(611, 613))(K(9^{iv})) : η^1(O(612))(K(13)) : η^1(O(613))(K(8^{i})) : η^1(O(622))(K(3)) : η^1(O(623))(K(5)), (i $= x-1, y, z$).

(7) μ_7-η^3(O(711/716, 722, 723))(K(5)) : η^2(O(711/714, 722))(K(6)) : η^2(O(713/716, 723)) (K(4^{iv})) : η^2(O(721, 723))(K(13^{iv})) : η^1(O(712/715))(K(3^{ii})) : η^1(O(713/715/716)(K(12^{ii})) : η^1(O(721))(K(8^{vii})) (ii $= 1-x, 1-y, 1-z$; iv $= \bar{x}, \bar{y}, 1-z$; vii $= 1-x, \bar{y}, 1-z$).

(8) μ_7-η^3(O(812, 821))(K(6)) : η^2(O(813, 821)) (K(3)) : η^1(O(811))(K(8)) : η^1(O(811)) (K(16)) : η^1(O(822))(K(12)) : η^1(O(823))(K(5^{ii})) : η^1(O(823))(K(6^{ii})).

Chelation modes are widespread and involve all ligands:
K(1) : O(111) and O(122); O(413) and O(422); O(311^{i}) and O(322^{i}, 323^{i}); K(2) : O(411, 413) and O(421); O(612) and O(621); O(312^{i}) and O(323^{i}); K(3) : O(813) and O(821); K(4) : O(213/216) and O(222); O(713^{iv}/716^{iv}) and O(723^{iv}); K(5) : O(711/716) and O(722, 723); K(6) : O(711/714) and O(722); O(812) and (821); K(9) : O(611) and O(621, 623); K(10) : O(213/215) and O(222, 223); K(11) : O(111, 112) and O(123); O(311^{i}) and O(322^{i}); O(112^{vi}) and O(123^{vi}); K(12) : O(513^{vi}) and O(522^{vi}); K(14) : O(511) and O(521), (O(lmn, lmn′) referring to pairs of oxygens on the same sulfonate, O(lmn/lmn′) referring to pairs in which the first is a major and the second a minor disordered component). Pairs of sulfonate groups on a given ligand may chelate two (ligands 2, 4–6, 8) or three (1, 3, 7) potassiums bringing the potassiums into close proximity (table 1). Angular geometries about bridging oxygens are summarized at the foot of table 1. Hydrogen bonds (table S1, supplementary material) bridge overwhelmingly to sulfonate oxygens. All water molecule oxygens (and fragments) interact with one or two potassiums; all sulfonate oxygens (and fragments) interact with one, two, or three potassiums. The result is a dense and complex structure [figure 1(a)]. Within the overall array, it may be discerned that two motifs predominate, one a sheet, comprising K(1, 2, 7, 8, 9, 11, 13, 15–17) lying between $y \pm 0.13$ [figure 1(b)] (coordinated oxygen and associated sulfurs of the ligand only are shown) and the other between $y \sim \frac{1}{3}$–$\frac{2}{3}$ a column parallel to [101] [Figure 1(c)], these motifs being bridged to form the gross 3-D array.

Reference [1] provides a study into the relative orientations of pairs of adjacent sulfonates in the potassium salt (methanol solvate) and the tetramethylammonium double salt (hemihydrate). Descriptors $\phi = (\omega_1 + \omega_2 + \omega_3 - 360)/3$ are obtained in terms of the (S)C–C–S–O torsion angles ω for the three oxygens of each group ($0 \leq \omega \leq 360^\circ$), and a semi-empirical PM3 enthalpy surface for the free anion was presented in terms of ϕ_1 and ϕ_2. In the potassium salt (methanol solvate), the one anion, devoid of crystallographic symmetry, lies within the asymmetric unit of the structure; in the tetramethylammonium double salt, two independent anions are disposed with their aromatic rings and sulfurs, and one pendant oxygen on each of the latter in crystallographic mirror planes, so that the anions have C_{2v} symmetry. In each of the latter, the pairs of in-plane S–O components lie directed away from each other, the other oxygens comprising chelating pairs about a potassium. Data for these two compounds are presented along with counterpart values for the eight independent anions of the present structure in table 2. The calculated lowest energy conformation corresponds to ϕ_1 and $\phi_2 = 0^\circ$ and 60° (the C_s form), the highest, at 0° and 0°, (a C_{2v} form) corresponding to the pair of in-plane oxygens directed at each other, with the 60°

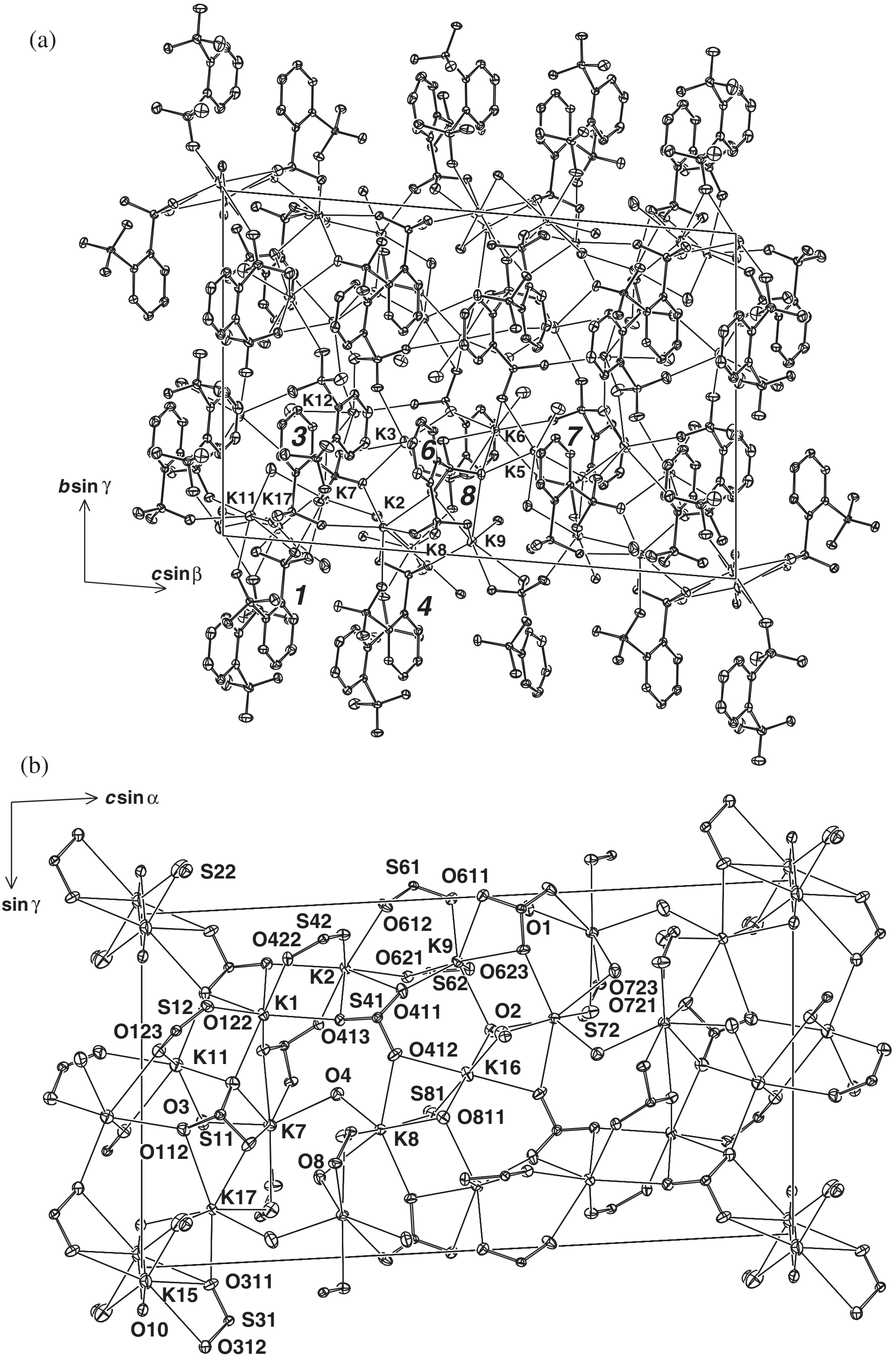

Figure 1. (a) Unit cell contents of $8K_2L \cdot 11H_2O$, projected down *a*, (b) the $K_xO(S)_y$ sheet between $y \pm 0.13$ and (c) the column between $y = 1/3 - 2/3$ (see text).

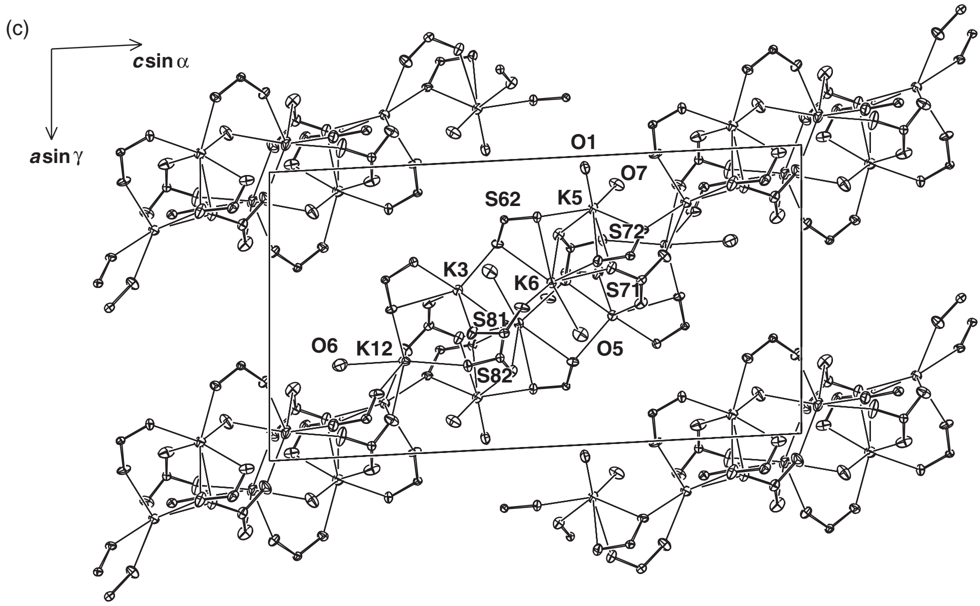

Figure 1. Continued.

Table 2. Sulfonate group torsion angles (degrees).

Anion	Sulfonate $n1$ $\omega(Cn2)–C(n1)–S(n1)–O(n11\text{-}3))$	Sulfonate $n2$ $\omega(C(n1)–C(n2)–S(n2)–O(n21\text{-}3))$
$n = 1$	49.4(2), −72.6(4), 168.2(2)	158.8(2), −82.3(2), 40.3(2)
	$\phi_1 = 48.3$	$\phi_2 = 38.9$, $\delta\phi = 9.4$
$n = 2$	168.7(2), −76.8(2), 44.2(2)	176.1(2), −65.5(2), 55.8(2)
(minor)	(−167.5(4), −34.3(5), 84.4(3))	
	$\phi_1 = 45.4$ ((−)39.1)	$\phi_1 = 55.5$, $\delta\phi = 10.1$ (16.4)
$n = 3$	43.7(3), −77.8(2), 164.4(2)	170.5(2), –70.3(2), 51.1(2)
	$\phi_2 = 43.4$, $\delta\phi = 7.0$	$\phi_1 = 50.4$
$n = 4$	68.4(2), −172.2(2), −53.0(2)	−42.3(2), 78.6(2), −162.2(2)
	$\phi_1 = (-)52.3$	$\phi_2 = (-)42.0$, $\delta\phi = (-)10.3$
$n = 5$	−73.6(2), 169.5(2), 49.4(2)	40.1(2), −80.8(2), 161.6(2)
	$\phi_1 = 48.4$	$\phi_2 = 40.3$, $\delta\phi = 8.1$
$n = 6$	44.0(2), −77.2(2), 162.2(2)	40.0(2), 158.7(1), −81.7(2)
	$\phi_1 = 43.0$	$\phi_2 = 39.0$, $\delta\phi = 4.0$
$n = 7$	−38.1(2), −160.0(2), 82.4(2)	−172.3(2), 68.6(2), −53.3(2)
(minor)	(−85.1(5), 171.6(6), 27.6(7))	
	$\phi_1 = (-)38.6$, 38.0	$\phi_2 = (-)52.3$, $\delta\phi = (-)13.7$, (14.3)
$n = 8$	173.5(1), −67.1(2), 54.2(2)	48.6(2), −71.3(2), 169.9(1)
	$\phi_1 = 53.5$	$\phi_2 = 49.1$, $\delta\phi = 4.4$
	Ranges of ϕ: Upper values	43.0–55.5
	Lower values	38.0–49.1
	Range of $\delta\phi$:	4.0–13.7 (16.4)
	Range of $\omega_{\max}(\lvert\rvert)$:	158.7(1)–176.1(2) ($n = 6, 2$)
	Range of $\omega_{\min}(\lvert\rvert)$	38.1(2)–55.8(2) ($n = 7, 2$)
MeOH	156.8(2), 38.4(2), –83.9(2)	−72.2(2), 47.9(2), 167.5(1)
solvate [1]	$\phi_1 = 37.1$	$\phi_2 = 47.7$, $\delta\phi = 10.6$
Me_4N	180, 60.0(1), –60.0(1)	60.5(1), −60.5(1), 180
double salt [1]	$\phi_1 = 60.0$	$\phi_2 = 60.0$, $\delta\phi = 0.0$

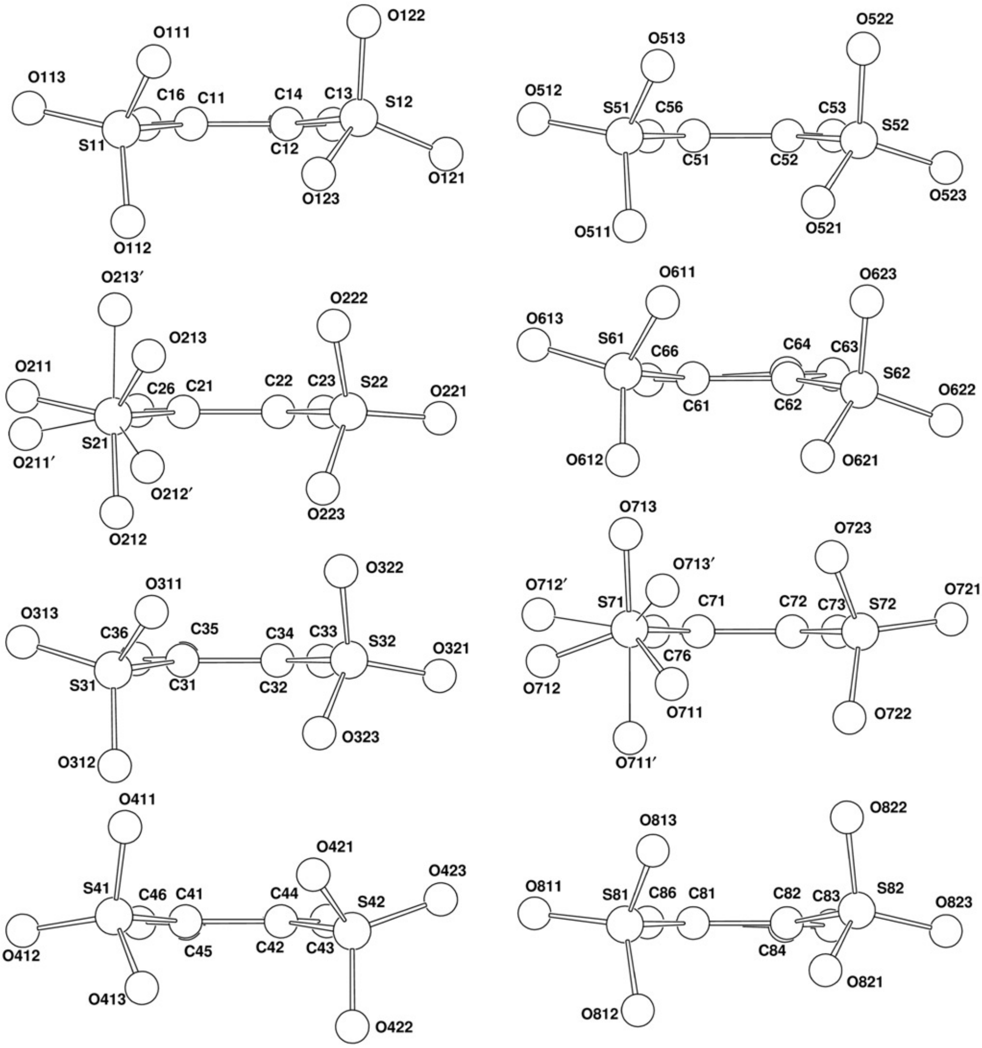

Figure 2. Projections of the anions through the planes of the aromatic rings and between the pairs of sulfonate substituents, showing the dispositions of the oxygen atoms.

and 60° disposition (the in-plane oxygens directed away from each other, as in the tetramethylammonium salt, also C_{2v}) intermediate, but of low energy, and presumably stabilized by interaction with the associated potassium. The data of table 2 (depicted for the present compound also in figure 2) suggest the C_{2v} form of the tetramethylammonium salt to provide a useful starting-point from where all other examples (including the methanol solvated potassium salt) are derived, by conrotation of the pair of sulfonate groups but by somewhat differing amounts ($\delta\phi$ in the table), resulting in an inherently unsymmetrical array, typically ϕ_1 *ca* 50° and ϕ_2 *ca* 40°, distorted from C_{2v} and C_2 symmetry ($\delta\phi$ the measure of the latter). In the anion with greatest ϕ (i.e. with a most nearly in-plane S–O component), anion 2 ($\phi_2 = 55.5$; $\omega_1 = 176.1(2)^\circ$), minor disorder expressing the associated ambiguity is found in the other sulfonate;

minor disorder is also found in sulfonate 1 of anion 7, which also has a rather high ϕ_2 (52.3, $\omega_1 = (-)172.3(2)^\circ$), although there are other groupings with high ϕ (in anions 4, 8) where no disorder is found.

4. Conclusions

A single crystal X-ray study of a hydrated form of dipotassium 1,2-benzenedisulfonate shows it to be $8K_2[(O_3S)_2C_6H_4] \cdot 11H_2O$. The sulfonate group dispositions are displaced from the (lower energy) C_{2v} arrangement by conrotatory twists of *ca* 10°–20°, with differences of *ca* 10° degrading the symmetry further from C_2. Diverse coordination modes are found.

Supplementary material

A full cif deposition (excluding structure factor amplitudes) resides with the Cambridge Crystallographic Data Centre, CCDC 623077.

Acknowledgments

We are grateful to the Australian Research Council for continued support.

References

[1] N. Nagel, P. Eller, H. Bock. *Acta Crystallogr.*, **B52**, 562 (1996).
[2] G.B. Deacon, C.M. Forsyth, R. Harika, P.C. Junk, B.W. Skelton, A.H. White. *Z. Anorg. Allg. Chem.*, **635**, 949 (2009).
[3] G.M. Sheldrick. *SHELXL*-97, *A Program for Crystal Structure Refinement*, University of Göttingen, Germany (1997) (*Acta Crystallogr.*, **A64**, 112 (2008)).
[4] K.M. Fromm. *Coord. Chem. Rev.*, **252**, 856 (2008).