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## Structure Reports

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# Benzene-1,2-di(aminium) naphthalene-1,5-disulfonate methanol monosolvate trihydrate

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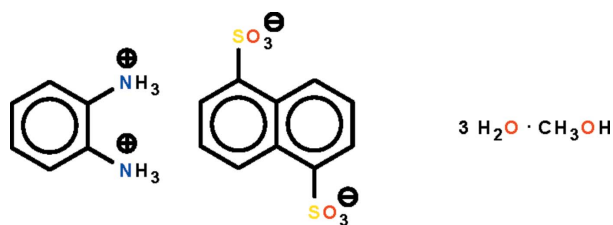
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Key indicators: single-crystal X-ray study;  $T = 293$  K; mean  $\sigma(\text{C}-\text{C}) = 0.005$  Å; disorder in solvent or counterion;  $R$  factor = 0.055;  $wR$  factor = 0.176; data-to-parameter ratio = 14.4.

In the title salt,  $\text{C}_6\text{H}_{10}\text{N}_2^{2+} \cdot \text{C}_{10}\text{H}_6\text{O}_6\text{S}_2^{2-} \cdot \text{CH}_3\text{OH} \cdot 3\text{H}_2\text{O}$ , the cation lies on a mirror plane and the anion on a center of inversion. One lattice water molecule is located on a mirror plane, another is equally disordered over two sites. The methanol solvent molecule is disordered about a mirror plane. In the crystal, the cations, anions, water and methanol molecules are linked by  $\text{O}-\text{H} \cdots \text{O}$  and  $\text{N}-\text{H} \cdots \text{O}$  hydrogen bonds, forming a three-dimensional network.

## Related literature

For other diammonium naphthalene-1,5-disulfonates, see: Wei (2011); Zhu *et al.* (2009).



## Experimental

### Crystal data

 $\text{C}_6\text{H}_{10}\text{N}_2^{2+} \cdot \text{C}_{10}\text{H}_6\text{O}_6\text{S}_2^{2-} \cdot \text{CH}_3\text{O} \cdot 3\text{H}_2\text{O}$ 
 $M_r = 482.52$ Monoclinic,  $P2_1/m$  $a = 8.1727$  (15) Å $b = 13.681$  (2) Å $c = 9.5173$  (15) Å $\beta = 98.390$  (5)° $V = 1052.8$  (3) Å<sup>3</sup> $Z = 2$ Mo  $K\alpha$  radiation  
 $\mu = 0.31$  mm<sup>-1</sup> $T = 293$  K  
 $0.25 \times 0.22 \times 0.19$  mm

### Data collection

Rigaku R-Axis RAPID IP  
diffractometerAbsorption correction: multi-scan  
(*ABSCOR*; Higashi, 1995)  
 $T_{\min} = 0.926$ ,  $T_{\max} = 0.943$ 10378 measured reflections  
2503 independent reflections  
1935 reflections with  $I > 2\sigma(I)$   
 $R_{\text{int}} = 0.044$ 

### Refinement

 $R[F^2 > 2\sigma(F^2)] = 0.055$  $wR(F^2) = 0.176$  $S = 1.13$ 

2503 reflections

174 parameters

H-atom parameters constrained

 $\Delta\rho_{\max} = 0.85$  e Å<sup>-3</sup> $\Delta\rho_{\min} = -0.41$  e Å<sup>-3</sup>

Table 1

Hydrogen-bond geometry (Å, °).

$D-H \cdots A$	$D-H$	$H \cdots A$	$D \cdots A$	$D-H \cdots A$
$\text{O4}-\text{H4} \cdots \text{O3}$	0.84	1.94	2.783 (6)	175
$\text{O1}w-\text{H1}w \cdots \text{O2}w$	0.84	2.32	2.915 (6)	128
$\text{O1}w-\text{H1}w \cdots \text{O2}w'$	0.84	2.19	2.799 (7)	130
$\text{O2}w-\text{H2}w \cdots \text{O3}^i$	0.84	2.35	2.873 (5)	121
$\text{O2}w'-\text{H2}w4 \cdots \text{O3}^i$	0.84	2.25	2.808 (6)	124
$\text{N1}-\text{H12} \cdots \text{O1}^{ii}$	0.88	2.07	2.880 (3)	153
$\text{N1}-\text{H11} \cdots \text{O2}w'$	0.88	2.03	2.816 (5)	149
$\text{N2}-\text{H22} \cdots \text{O1}$	0.88	1.99	2.815 (3)	156
$\text{N2}-\text{H21} \cdots \text{O1}w^{iii}$	0.88	1.88	2.735 (4)	164

Symmetry codes: (i)  $-x + 1, -y + 1, -z + 2$ ; (ii)  $x, -y + \frac{1}{2}, z$ ; (iii)  $x, y, z - 1$ .

Data collection: *RAPID-AUTO* (Rigaku, 1998); cell refinement: *RAPID-AUTO*; data reduction: *CrystalClear* (Rigaku/MSK, 2002); program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *X-SEED* (Barbour, 2001); software used to prepare material for publication: *pubCIF* (Westrip, 2010).

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: XU5520).

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## supporting information

*Acta Cryst.* (2012). E68, o1574 [doi:10.1107/S1600536812018284]

## Benzene-1,2-di(aminium) naphthalene-1,5-disulfonate methanol monosolvate trihydrate

Shan Gao and Seik Weng Ng

### S1. Comment

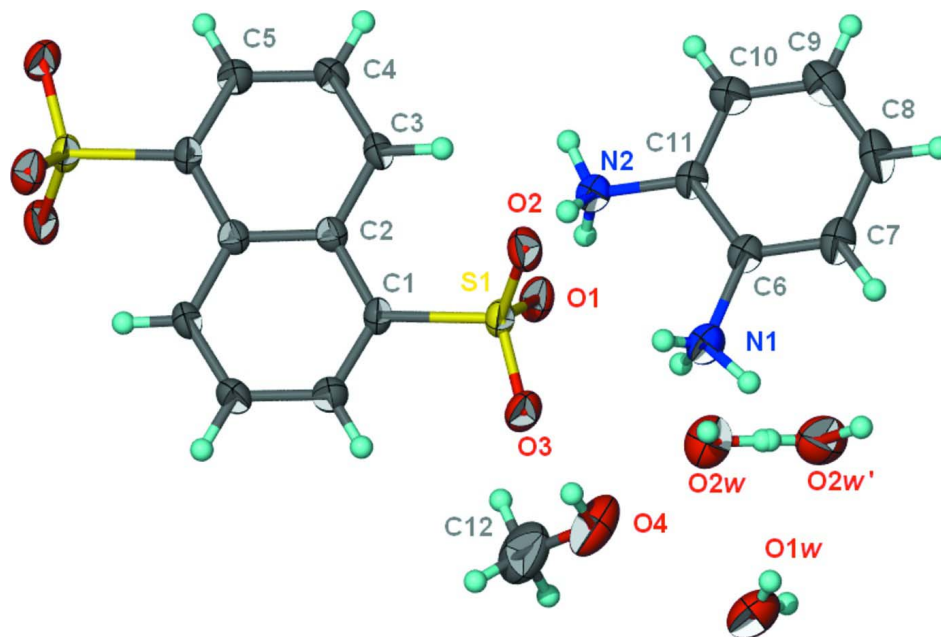
Naphthalene-1,5-disulfonic acid has been characterized as several diammonium salts, *e.g.*, as the ethane-1,2-diammonium (Zhu *et al.*, 2009), the piperazine-1,4-dium (Wei, 2011) derivatives. In the salt,  $C_6H_{10}N_2^{2+}C_{10}H_6O_6S_2^{2-} \cdot 3H_2O \cdot CH_3OH$  (Scheme I, Fig. 1), the cation lies on a mirror plane and the anion on a center-of-inversion. The cation, anion, water and methanol molecules are linked by O–H $\cdots$ O hydrogen bonds to form a three-dimensional network (Table 1).

### S2. Experimental

A methanol solution (5 ml) of 1,2-benzenediamine (1 mmol, 108 mg) was added to an aqueous solution (5 ml) of 1,5-naphthalenedisulfonic acid tetrahydrate (0.5 mmol, 180 mg). The mixture was heated at 343 K until the reactants dissolved completely. The solution was filtered; colorless crystals were isolated after several days. Suitable for X-ray diffraction were isolated from the filtrate after four days.

### S3. Refinement

Carbon- and nitrogen-bound H-atoms were placed in calculated positions (C–H 0.93, N–H 0.88 Å) and were included in the refinement in the riding model approximation, with  $U(H)$  set to  $1.2U(C,N)$ . The water H-atoms were placed in chemically sensible positions on the basis of hydrogen bonding interactions (O–H 0.84 Å) and their temperature factors similar tied. One of the water molecules is disordered over a center-of-inversion.

**Figure 1**

Thermal ellipsoid plot (Barbour, 2001) of  $C_6H_{10}N_2^{2+} \cdot C_{10}H_6O_6S_2^{2-} \cdot 3H_2O \cdot CH_3OH$  at the 50% probability level; hydrogen atoms are drawn as spheres of arbitrary radius. The symmetry-related atoms of the anion are not labeled.

### Benzene-1,2-di(aminium) naphthalene-1,5-disulfonate methanol monosolvate trihydrate

#### Crystal data

$C_6H_{10}N_2^{2+} \cdot C_{10}H_6O_6S_2^{2-} \cdot CH_3O \cdot 3H_2O$

$M_r = 482.52$

Monoclinic,  $P2_1/m$

Hall symbol:  $-P\ 2_1/m$

$a = 8.1727$  (15) Å

$b = 13.681$  (2) Å

$c = 9.5173$  (15) Å

$\beta = 98.390$  (5)°

$V = 1052.8$  (3) Å<sup>3</sup>

$Z = 2$

$F(000) = 508$

$D_x = 1.522$  Mg m<sup>-3</sup>

Mo  $K\alpha$  radiation,  $\lambda = 0.71073$  Å

Cell parameters from 6427 reflections

$\theta = 3.1\text{--}27.5^\circ$

$\mu = 0.31$  mm<sup>-1</sup>

$T = 293$  K

Prism, colorless

$0.25 \times 0.22 \times 0.19$  mm

#### Data collection

Rigaku R-AXIS RAPID IP

diffractometer

Radiation source: fine-focus sealed tube

Graphite monochromator

$\omega$  scan

Absorption correction: multi-scan

(*ABSCOR*; Higashi, 1995)

$T_{\min} = 0.926$ ,  $T_{\max} = 0.943$

10378 measured reflections

2503 independent reflections

1935 reflections with  $I > 2\sigma(I)$

$R_{\text{int}} = 0.044$

$\theta_{\max} = 27.5^\circ$ ,  $\theta_{\min} = 3.1^\circ$

$h = -10 \rightarrow 10$

$k = -16 \rightarrow 17$

$l = -12 \rightarrow 12$

Refinement

Refinement on  $F^2$

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.055$

$wR(F^2) = 0.176$

$S = 1.13$

2503 reflections

174 parameters

0 restraints

Primary atom site location: structure-invariant  
direct methods

Secondary atom site location: difference Fourier  
map

Hydrogen site location: inferred from  
neighbouring sites

H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0909P)^2 + 0.6772P]$

where  $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\max} = 0.001$

$\Delta\rho_{\max} = 0.85 \text{ e } \text{\AA}^{-3}$

$\Delta\rho_{\min} = -0.41 \text{ e } \text{\AA}^{-3}$

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters ( $\text{\AA}^2$ )

	x	y	z	$U_{\text{iso}}^*/U_{\text{eq}}$	Occ. (<1)
S1	0.71163 (7)	0.51770 (5)	0.72850 (6)	0.0322 (2)	
O1	0.6469 (2)	0.61258 (14)	0.6776 (2)	0.0425 (5)	
O2	0.6097 (2)	0.43755 (15)	0.6701 (2)	0.0443 (5)	
O3	0.7450 (3)	0.51585 (15)	0.8836 (2)	0.0433 (5)	
O1w	0.5509 (5)	0.7500	1.2108 (4)	0.0707 (10)	
H1w	0.4934	0.6998	1.1902	0.106*	
N1	0.4198 (5)	0.7500	0.7729 (4)	0.0509 (9)	
H11	0.3788	0.7500	0.8535	0.076*	
H12	0.4809	0.8025	0.7685	0.076*	
N2	0.4862 (4)	0.7500	0.4847 (3)	0.0368 (7)	
H21	0.4867	0.7500	0.3923	0.055*	
H22	0.5374	0.6975	0.5221	0.055*	
C1	0.9077 (3)	0.50513 (18)	0.6689 (3)	0.0300 (5)	
C2	0.9198 (3)	0.50489 (17)	0.5204 (3)	0.0292 (5)	
C3	0.7803 (3)	0.51357 (19)	0.4131 (3)	0.0338 (6)	
H3	0.6752	0.5191	0.4388	0.041*	
C4	0.7984 (3)	0.5140 (2)	0.2731 (3)	0.0387 (6)	
H4A	0.7057	0.5207	0.2045	0.046*	
C5	0.9552 (3)	0.5044 (2)	0.2309 (3)	0.0373 (6)	
H5	0.9659	0.5044	0.1349	0.045*	
C6	0.2850 (5)	0.7500	0.6545 (4)	0.0354 (8)	
C7	0.1240 (5)	0.7500	0.6818 (5)	0.0453 (10)	
H7	0.1025	0.7500	0.7751	0.054*	
C8	-0.0050 (5)	0.7500	0.5712 (6)	0.0527 (11)	
H8	-0.1133	0.7500	0.5904	0.063*	
C9	0.0245 (6)	0.7500	0.4325 (5)	0.0499 (10)	
H9	-0.0631	0.7500	0.3582	0.060*	
C10	0.1866 (5)	0.7500	0.4045 (4)	0.0431 (9)	
H10	0.2077	0.7500	0.3111	0.052*	
C11	0.3153 (4)	0.7500	0.5139 (4)	0.0315 (7)	
O4	0.7361 (8)	0.6961 (4)	1.0177 (6)	0.0782 (17)	0.50
H4	0.7426	0.6406	0.9812	0.117*	0.50
C12	0.8778 (11)	0.751 (2)	1.0006 (8)	0.090 (3)	0.5
H12A	0.8778	0.8110	1.0533	0.135*	0.50

H12B	0.8767	0.7658	0.9018	0.135*	0.50
H12C	0.9753	0.7143	1.0351	0.135*	0.50
O2w	0.4770 (6)	0.6054 (4)	0.9855 (5)	0.0635 (13)	0.50
H2w1	0.3897	0.6342	0.9987	0.095*	0.50
H2w2	0.4637	0.5451	0.9955	0.095*	0.50
O2w'	0.2979 (7)	0.6729 (4)	1.0117 (5)	0.0657 (13)	0.50
H2w3	0.3789	0.6375	1.0001	0.099*	0.50
H2w4	0.2196	0.6366	1.0271	0.099*	0.50

*Atomic displacement parameters (Å<sup>2</sup>)*

	$U^{11}$	$U^{22}$	$U^{33}$	$U^{12}$	$U^{13}$	$U^{23}$
S1	0.0272 (4)	0.0378 (4)	0.0335 (4)	0.0033 (2)	0.0108 (2)	0.0024 (2)
O1	0.0421 (11)	0.0428 (11)	0.0451 (10)	0.0138 (9)	0.0152 (8)	0.0056 (9)
O2	0.0313 (10)	0.0483 (12)	0.0553 (12)	-0.0061 (8)	0.0127 (8)	-0.0051 (10)
O3	0.0434 (11)	0.0557 (12)	0.0333 (10)	0.0051 (9)	0.0143 (8)	0.0054 (9)
O1w	0.086 (3)	0.083 (3)	0.0472 (18)	0.000	0.0224 (18)	0.000
N1	0.044 (2)	0.074 (3)	0.0366 (17)	0.000	0.0125 (15)	0.000
N2	0.0354 (17)	0.0422 (17)	0.0341 (16)	0.000	0.0096 (13)	0.000
C1	0.0241 (12)	0.0339 (12)	0.0335 (13)	0.0028 (9)	0.0096 (9)	0.0008 (10)
C2	0.0265 (13)	0.0297 (12)	0.0314 (12)	0.0016 (9)	0.0045 (9)	0.0021 (10)
C3	0.0219 (12)	0.0428 (14)	0.0367 (13)	0.0009 (10)	0.0050 (10)	0.0003 (11)
C4	0.0281 (13)	0.0520 (17)	0.0343 (14)	0.0034 (11)	-0.0007 (10)	0.0015 (11)
C5	0.0339 (14)	0.0480 (15)	0.0299 (12)	0.0026 (11)	0.0045 (10)	0.0024 (11)
C6	0.038 (2)	0.0342 (18)	0.0360 (18)	0.000	0.0101 (15)	0.000
C7	0.043 (2)	0.044 (2)	0.054 (2)	0.000	0.0200 (19)	0.000
C8	0.032 (2)	0.048 (2)	0.081 (3)	0.000	0.016 (2)	0.000
C9	0.038 (2)	0.045 (2)	0.064 (3)	0.000	-0.0007 (19)	0.000
C10	0.043 (2)	0.045 (2)	0.040 (2)	0.000	0.0021 (17)	0.000
C11	0.0317 (18)	0.0271 (16)	0.0372 (18)	0.000	0.0100 (14)	0.000
O4	0.098 (4)	0.069 (3)	0.079 (4)	-0.002 (3)	0.050 (3)	-0.012 (3)
C12	0.097 (6)	0.093 (6)	0.086 (5)	0.035 (14)	0.031 (4)	-0.009 (16)
O2w	0.067 (3)	0.060 (3)	0.066 (3)	0.004 (2)	0.020 (2)	0.002 (2)
O2w'	0.071 (3)	0.077 (3)	0.051 (3)	-0.010 (3)	0.015 (2)	0.011 (2)

*Geometric parameters (Å, °)*

S1—O2	1.439 (2)	C6—C7	1.377 (5)
S1—O1	1.4578 (19)	C6—C11	1.396 (5)
S1—O3	1.461 (2)	C7—C8	1.377 (7)
S1—C1	1.785 (2)	C7—H7	0.9300
O1w—H1w	0.8391	C8—C9	1.376 (7)
N1—C6	1.456 (5)	C8—H8	0.9300
N1—H11	0.8800	C9—C10	1.389 (6)
N1—H12	0.8800	C9—H9	0.9300
N2—C11	1.463 (4)	C10—C11	1.368 (5)
N2—H21	0.8800	C10—H10	0.9300
N2—H22	0.8800	O4—C12	1.41 (2)

C1—C5 <sup>i</sup>	1.367 (4)	O4—H4	0.8400
C1—C2	1.430 (3)	C12—H12A	0.9600
C2—C3	1.420 (4)	C12—H12B	0.9600
C2—C2 <sup>i</sup>	1.428 (5)	C12—H12C	0.9600
C3—C4	1.362 (4)	O2w—H2w1	0.8401
C3—H3	0.9300	O2w—H2w2	0.8400
C4—C5	1.404 (4)	O2w—H2w3	0.9423
C4—H4A	0.9300	O2w'—H2w1	0.9412
C5—C1 <sup>i</sup>	1.367 (4)	O2w'—H2w3	0.8400
C5—H5	0.9300	O2w'—H2w4	0.8400
O2—S1—O1	112.86 (13)	C1 <sup>i</sup> —C5—H5	120.1
O2—S1—O3	112.92 (12)	C4—C5—H5	120.1
O1—S1—O3	110.88 (12)	C7—C6—C11	119.2 (4)
O2—S1—C1	107.45 (12)	C7—C6—N1	119.3 (3)
O1—S1—C1	106.22 (12)	C11—C6—N1	121.5 (3)
O3—S1—C1	105.98 (12)	C8—C7—C6	120.1 (4)
C6—N1—H11	109.5	C8—C7—H7	119.9
C6—N1—H12	109.5	C6—C7—H7	119.9
H11—N1—H12	109.5	C9—C8—C7	120.8 (4)
C11—N2—H21	109.5	C9—C8—H8	119.6
C11—N2—H22	109.5	C7—C8—H8	119.6
H21—N2—H22	109.5	C8—C9—C10	119.3 (4)
C5 <sup>i</sup> —C1—C2	121.4 (2)	C8—C9—H9	120.3
C5 <sup>i</sup> —C1—S1	118.00 (19)	C10—C9—H9	120.3
C2—C1—S1	120.56 (19)	C11—C10—C9	120.2 (4)
C3—C2—C2 <sup>i</sup>	119.0 (3)	C11—C10—H10	119.9
C3—C2—C1	123.1 (2)	C9—C10—H10	119.9
C2 <sup>i</sup> —C2—C1	117.9 (3)	C10—C11—C6	120.4 (3)
C4—C3—C2	120.9 (2)	C10—C11—N2	120.3 (3)
C4—C3—H3	119.6	C6—C11—N2	119.3 (3)
C2—C3—H3	119.6	H2w1—O2w—H2w2	108.5
C3—C4—C5	120.9 (2)	H2w2—O2w—H2w3	108.3
C3—C4—H4A	119.5	H2w1—O2w'—H2w4	109.5
C5—C4—H4A	119.5	H2w3—O2w'—H2w4	108.5
C1 <sup>i</sup> —C5—C4	119.9 (2)		
O2—S1—C1—C5 <sup>i</sup>	-120.4 (2)	C3—C4—C5—C1 <sup>i</sup>	-0.3 (4)
O1—S1—C1—C5 <sup>i</sup>	118.6 (2)	C11—C6—C7—C8	0.000 (2)
O3—S1—C1—C5 <sup>i</sup>	0.6 (3)	N1—C6—C7—C8	180.000 (1)
O2—S1—C1—C2	59.5 (2)	C6—C7—C8—C9	0.000 (2)
O1—S1—C1—C2	-61.5 (2)	C7—C8—C9—C10	0.000 (2)
O3—S1—C1—C2	-179.51 (19)	C8—C9—C10—C11	0.000 (1)
C5 <sup>i</sup> —C1—C2—C3	179.3 (3)	C9—C10—C11—C6	0.0
S1—C1—C2—C3	-0.5 (3)	C9—C10—C11—N2	180.0
C5 <sup>i</sup> —C1—C2—C2 <sup>i</sup>	-0.5 (4)	C7—C6—C11—C10	0.000 (1)
S1—C1—C2—C2 <sup>i</sup>	179.7 (2)	N1—C6—C11—C10	180.000 (1)
C2 <sup>i</sup> —C2—C3—C4	-0.9 (4)	C7—C6—C11—N2	180.000 (1)

C1—C2—C3—C4	179.3 (2)	N1—C6—C11—N2	0.000 (1)
C2—C3—C4—C5	0.9 (4)		

Symmetry code: (i)  $-x+2, -y+1, -z+1$ .

*Hydrogen-bond geometry (Å, °)*

<i>D—H...A</i>	<i>D—H</i>	<i>H...A</i>	<i>D...A</i>	<i>D—H...A</i>
O4—H4...O3	0.84	1.94	2.783 (6)	175
O1 <sub>w</sub> —H1 <sub>w</sub> ...O2 <sub>w</sub>	0.84	2.32	2.915 (6)	128
O1 <sub>w</sub> —H1 <sub>w</sub> ...O2 <sub>w</sub> '	0.84	2.19	2.799 (7)	130
O2 <sub>w</sub> —H2 <sub>w2</sub> ...O3 <sup>ii</sup>	0.84	2.35	2.873 (5)	121
O2 <sub>w</sub> '—H2 <sub>w4</sub> ...O3 <sup>ii</sup>	0.84	2.25	2.808 (6)	124
N1—H12...O1 <sup>iii</sup>	0.88	2.07	2.880 (3)	153
N1—H11...O2 <sub>w</sub> '	0.88	2.03	2.816 (5)	149
N2—H22...O1	0.88	1.99	2.815 (3)	156
N2—H21...O1 <sub>w</sub> <sup>iv</sup>	0.88	1.88	2.735 (4)	164

Symmetry codes: (ii)  $-x+1, -y+1, -z+2$ ; (iii)  $x, -y+3/2, z$ ; (iv)  $x, y, z-1$ .