

The Crystal and Molecular Structure of Methanesulfinic Acid*

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Methanesulfinic acid, CH_3SOOH , the first low-molecular-weight aliphatic sulfinic acid to yield crystals suitable for structure studies, crystallizes in space group $P2_12_12_1$, with $a_0=7.832$, $b_0=8.234$ and $c_0=5.360$ Å, and four molecules per unit cell. Complete integrated Weissenberg intensity data collected about the c axis with Cu $K\alpha$ radiation were scaled with two layers of similar data collected about [112]. The structure was solved from a three-dimensional Patterson synthesis and ultimately refined by least squares to an R index of 0.082 for observed reflections. The configuration about the sulfur atom is pyramidal, with an S–C distance of 1.786 ± 0.011 Å and S–O distances of 1.502 ± 0.009 and 1.604 ± 0.009 Å. Hydrogen bonds link the molecules together in spirals along the c axis.

Introduction

Methanesulfinic acid, CH_3SOOH , is the first aliphatic sulfinic acid with a molecular weight below 200 to be isolated in single-crystal form (Wudl, Lightner & Cram, 1967). This synthesis afforded an excellent opportunity to establish the geometry of the sulfinic acid group. The space group $P2_12_12_1$, requires that all molecules be of the same chirality. An attempt was made (Wudl, Lightner & Cram, 1967) to determine the chirality of the molecules in a single crystal, but the methods employed involved ionic intermediates, which rendered the oxygens indistinguishable.

Experimental

Crystals of CH_3SOOH are colorless, long prismatic (c), low melting ($40\text{--}42^\circ\text{C}$), and hygroscopic. They decompose in air and in sealed capillaries at room temperature. The space group, $P2_12_12_1$, was assigned on the basis of the systematic absences ($h00$, $h=2n+1$; $0k0$, $k=2n+1$; $00l$, $l=2n+1$). Unit-cell dimensions at about 21°C are: $a_0=7.832 \pm 0.001$, $b_0=8.234 \pm 0.001$, $c_0=5.360 \pm 0.001$ Å; these were determined by a least-squares refinement of eighty 2θ values measured on $hk0$ Weissenberg and $h0l$ and $0kl$ precession photographs calibrated with quartz reflections. The measured density of 1.52 g.cm^{-3} agrees reasonably well with the value of 1.54 g.cm^{-3} calculated for a four-molecule unit cell. The intensities of 448 independent reflections (about 92% of the Cu sphere) were estimated with a densitometer from integrated Weissenberg films of the layers 0 to 5 along c ; the intensities of 387 of these were above the minimum observable limit. Intensity data on layers 0 and 1 about [112] were collected in a similar way and used to scale the c axis data. Cu $K\alpha$ radiation ($\lambda=1.5418$ Å), reasonably monochromatized with a $K\beta$ filter, was used throughout. Spherical ab-

sorption corrections ($\mu=6.2\text{ mm}^{-1}$) were made assuming approximate crystal radii of 0.1 mm for prisms approximately $0.2 \times 0.4 \times 0.8$ mm in size. No accurate absorption corrections could be calculated because the crystal shape varied continuously as a result of slow decomposition to an oil. To decrease absorption errors further, intensities were estimated in more than two octants of reciprocal space and were reduced to a unique set by averaging.

Structure determination

The positions of the sulfur and the two oxygen atoms were found by examination of a sharpened three-dimensional Patterson synthesis, and refined with isotropic temperature factors. When two carbon atoms were placed in the model, one near each of the two available tetrahedral positions about the sulfur atom, and their positions and temperature factors were refined by least squares, only one set of the carbon parameters refined reasonably. Positions were calculated for the methyl hydrogen atoms, assuming a tetrahedral arrangement, *gauche* with respect to the oxygen atoms, around the carbon atom; the acidic hydrogen atom was assumed to be 1.0 Å from the oxygen atom with the longer S–O bond, on a line toward the close non-equivalent oxygen atom of another molecule. These positions proved to be suitable for least-squares refinement. At this point it was clear that the scaling of the layers along c was inadequate. Consequently, the positions of the four heavy atoms, with individual isotropic temperature factors, were refined by least squares [minimizing $\sum w(\Delta|F|)^2$]. The scale factors for individual layers were adjusted to minimize $\sum \Delta|F|$. Effective convergence was reached in eight cycles; structure parameters changed little throughout. The revised scale factors were then incorporated in a full-matrix least-squares refinement, with anisotropic temperature factors for the non-hydrogen atoms and isotropic temperature factors for the hydrogen atoms; it converged quickly to an R index of 0.082 for 385 observed reflections. Two

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intense low-order reflections which appeared to be in error because of absorption were omitted from the final refinement. The methyl hydrogen atom, H(6), nearest to the oxygen atom refined to a position too close (0.4 Å) to the carbon atom; consequently, the z parameter of this hydrogen was fixed so that the C-H bond would be 1.0 Å long and the isotropic temperature factor of H(6) was also held fixed. The program used was that of Gantzel, Sparks & Trueblood (A.C.A. (old) No. 317, modified) which minimizes $\sum w(|\Delta F|)^2$. Hughes (1941) weights were used, modified to account for the number of times a reflection was observed. Of the sixty-one unobserved reflections, only one is calculated to be greater than the minimum observable intensity (F_{min}).

The scattering factors used were: C(valence) and O, Hoerni & Ibers (1954); S, Dawson (1960); and H(bonded), Stewart, Davidson & Simpson (1965). In the last cycle of least-squares refinement, the average shifts were about 0.07 estimated standard deviations of position; no non-hydrogen coordinate shift exceeded 0.0015 Å, or 0.2 σ, and no hydrogen coordinate shift exceeded 0.08 Å, or 0.4 σ. Table 1 gives the observed and calculated structure factors; unobserved reflections are assigned an intensity of 0.5 F_{min} . The final positional and thermal parameters are given in Tables 2 and 3 respectively. The thermal parameters of the non-hydrogen atoms do not conform to those of a rigid body

(Schomaker & Trueblood, 1968). Bond-length corrections were made by the method of Leung & Marsh (1958). The structure is shown in Fig. 1 and geometrical features are given in Table 4. No angles involving hydrogen atoms are shown; they did not deviate significantly from the tetrahedral value.

Table 2. Positional parameters and their standard deviations*

	x, σ(x)	y, σ(y)	z, σ(z)
S(1)	2141,2	1850,2	0730,4
O(2)	3825,6	0768,7	0933,14
O(3)	0716,6	0911,7	1897,14
C(4)	2764,13	3248,9	3096,29
H(5)	396,13	014,15	-058,52
H(6)	245,13	260,17	463†
H(7)	354,10	363,11	300,26
H(8)	208,13	425,13	219,38

* Values given are × 10⁴ for S, O and C and × 10³ for H. See Fig. 1 for the identities of the atoms. The e.s.d., separated by a comma, is in the units of the least significant digit given for the corresponding parameter.

† Held fixed in least squares; see text.

Crystal and molecular structure

The methanesulfonic acid molecules are joined to one another by hydrogen bonds in infinite spiral chains along a 2₁ axis parallel to c; the O-O distance is 2.59 Å.

Table 1. Observed and calculated structure factors

The running index is h; values of k and l for each group immediately precede that group. The second through fourth columns are, respectively, 10F_o, 10|F_c|, and α. Values marked with U were below the observable limit; the F_o listed for these reflections is 5 F_{min}. Those marked with * have been omitted from structure-parameter refinement.

h	k	l	10F _o	10 F _c	α
0	0	0	0	0	0
1	0	0	467	492	180
2	0	0	72	76	180
3	0	0	116	158	180
4	0	0	200	11	180
5	0	0	17	48	0
6	0	0	124	110	270
7	0	0	40	50	60
8	0	0	36	32	132
9	0	0	43	45	270
10	0	0	42	44	288
11	0	0	26	37	87
12	0	0	332	290	270
13	0	0	243	215	275
14	0	0	260	38	0
15	0	0	198	1	161
16	0	0	45	11	161
17	0	0	37	37	108
18	0	0	320	197	124
19	0	0	121	100	286
20	0	0	160	14	0
21	0	0	128	60	286
22	0	0	28	31	180
23	0	0	67	44	48
24	0	0	37	44	48
25	0	0	290	9	64
26	0	0	42	149	2
27	0	0	35	43	18
28	0	0	46	56	270
29	0	0	146	110	270
30	0	0	98	78	270
31	0	0	67	60	0
32	0	0	110	108	291
33	0	0	118	112	80
34	0	0	93	81	50
35	0	0	124	134	232
36	0	0	250	14	286
37	0	0	44	42	105
38	0	0	57	47	95
39	0	0	53	43	18
40	0	0	67	60	0
41	0	0	108	291	6
42	0	0	118	112	80
43	0	0	93	81	50
44	0	0	124	134	232
45	0	0	250	14	286
46	0	0	44	42	105
47	0	0	57	47	95
48	0	0	53	43	261
49	0	0	67	60	0
50	0	0	108	291	6
51	0	0	118	112	80
52	0	0	93	81	50
53	0	0	124	134	232
54	0	0	250	14	286
55	0	0	44	42	105
56	0	0	57	47	95
57	0	0	53	43	261
58	0	0	67	60	0
59	0	0	108	291	6
60	0	0	118	112	80
61	0	0	93	81	50
62	0	0	124	134	232
63	0	0	250	14	286
64	0	0	44	42	105
65	0	0	57	47	95
66	0	0	53	43	261
67	0	0	67	60	0
68	0	0	108	291	6
69	0	0	118	112	80
70	0	0	93	81	50
71	0	0	124	134	232
72	0	0	250	14	286
73	0	0	44	42	105
74	0	0	57	47	95
75	0	0	53	43	261
76	0	0	67	60	0
77	0	0	108	291	6
78	0	0	118	112	80
79	0	0	93	81	50
80	0	0	124	134	232
81	0	0	250	14	286
82	0	0	44	42	105
83	0	0	57	47	95
84	0	0	53	43	261
85	0	0	67	60	0
86	0	0	108	291	6
87	0	0	118	112	80
88	0	0	93	81	50
89	0	0	124	134	232
90	0	0	250	14	286
91	0	0	44	42	105
92	0	0	57	47	95
93	0	0	53	43	261
94	0	0	67	60	0
95	0	0	108	291	6
96	0	0	118	112	80
97	0	0	93	81	50
98	0	0	124	134	232
99	0	0	250	14	286
100	0	0	44	42	105
101	0	0	57	47	95
102	0	0	53	43	261
103	0	0	67	60	0
104	0	0	108	291	6
105	0	0	118	112	80
106	0	0	93	81	50
107	0	0	124	134	232
108	0	0	250	14	286
109	0	0	44	42	105
110	0	0	57	47	95
111	0	0	53	43	261
112	0	0	67	60	0
113	0	0	108	291	6
114	0	0	118	112	80
115	0	0	93	81	50
116	0	0	124	134	232
117	0	0	250	14	286
118	0	0	44	42	105
119	0	0	57	47	95
120	0	0	53	43	261
121	0	0	67	60	0
122	0	0	108	291	6
123	0	0	118	112	80
124	0	0	93	81	50
125	0	0	124	134	232
126	0	0	250	14	286
127	0	0	44	42	105
128	0	0	57	47	95
129	0	0	53	43	261
130	0	0	67	60	0
131	0	0	108	291	6
132	0	0	118	112	80
133	0	0	93	81	50
134	0	0	124	134	232
135	0	0	250	14	286
136	0	0	44	42	105
137	0	0	57	47	95
138	0	0	53	43	261
139	0	0	67	60	0
140	0	0	108	291	6
141	0	0	118	112	80
142	0	0	93	81	50
143	0	0	124	134	232
144	0	0	250	14	286
145	0	0	44	42	105
146	0	0	57	47	95
147	0	0	53	43	261
148	0	0	67	60	0
149	0	0	108	291	6
150	0	0	118	112	80
151	0	0	93	81	50
152	0	0	124	134	232
153	0	0	250	14	286
154	0	0	44	42	105
155	0	0	57	47	95
156	0	0	53	43	261
157	0	0	67	60	0
158	0	0	108	291	6
159	0	0	118	112	80
160	0	0	93	81	50
161	0	0	124	134	232
162	0	0	250	14	286
163	0	0	44	42	105
164	0	0	57	47	95
165	0	0	53	43	261
166	0	0	67	60	0
167	0	0	108	291	6
168	0	0	118	112	80
169	0	0	93	81	50
170	0	0	124	134	232
171	0	0	250	14	286
172	0	0	44	42	105
173	0	0	57	47	95
174	0	0	53	43	261
175	0	0	67	60	0
176	0	0	108	291	6
177	0	0	118	112	80
178	0	0	93	81	50
179	0	0	124	134	232
180	0	0	250	14	286

In crystals of benzeneseleninic acid and one of its derivatives (Bryden & McCullough, 1954, 1956) similar chains along 2_1 axes have been observed. Intermolecular packing distances between chains are normal (Table 5).

The carbon-sulfur bond distance of 1.786 ± 0.011 Å is in agreement with values of 1.79 ± 0.01 in trimethyl-oxosulfonium perchlorate (Coulter, Gantzel & McCullough, 1963), 1.78 ± 0.01 in trimethyl-oxosulfonium fluoborate (Zimmerman, Barlow & McCullough, 1963) 1.780 ± 0.002 in 2-aminoethylsulfonic acid (Okaya, 1966), 1.80 in a phenylsulfinate (Langs & Hare, 1967), and 1.797 ± 0.005 in a sulphonic acid sultone (Bjåmer & Ferguson, 1967). The Schomaker & Stevenson (1941) value for the S-C single bond length is 1.81 Å.

The pyramidal geometry about the sulfur atom is consistent with the Gillispie & Nyholm (1957) rules. The fact that the average bond angle in the present molecule, 102° , is significantly lower than the tetrahedral value of 109.5° is presumably another manifestation of the effect of the unshared pair of electrons on the sulfur atom (Battelle & Trueblood, 1965). Similar effects are observed in sulfoxides, sulfonates, dithionite, and seleninic acids, for which the average angles vary from 100 to 104° .

The difference between the lengths of the S-OH and S-O bonds in the present molecule, 0.10 Å, is comparable to that in sulfuric acid, 0.11 Å (Pascard-Billy,

1965) and to the corresponding difference in carboxylic acids, about 0.12 Å. The shorter of the sulfur-oxygen bond lengths, 1.502 ± 0.009 Å, is not significantly diffe-

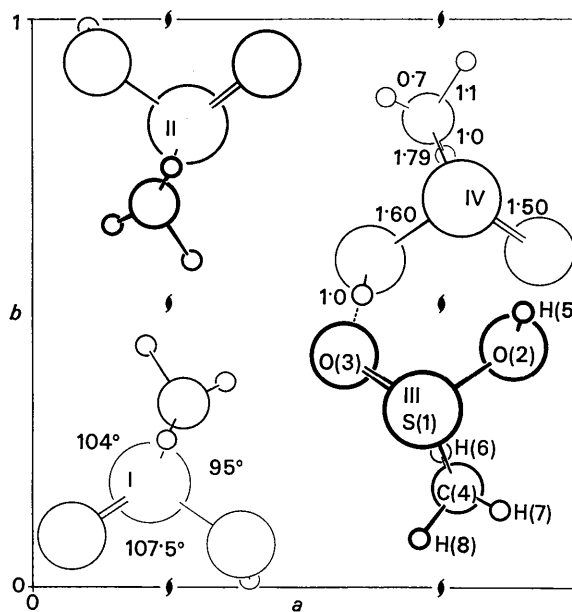


Fig. 1. The crystal and molecular structure of methanesulfinic acid.

Table 3. Thermal vibration parameters* and their standard deviations

I. Sulfur, oxygen, and carbon temperature factors = $\exp \{-(b_{11}h^2 + b_{22}k^2 + b_{33}l^2 + b_{12}hk + b_{13}hl + b_{23}kl)\} (\times 10^4)$.

	b_{11}	b_{22}	$b_{33} \dagger$	b_{12}	b_{13}	b_{23}
S(1)	131,2	121,2	279,5	10,4	-33,8	27,7
O(2)	127,7	160,8	417,21	48,11	-166,26	-50,30
O(3)	160,9	165,8	338,20	-40,14	-41,26	110,25
C(4)	184,15	164,11	584,45	12,24	-32,54	41,50

II. Hydrogen

	B (Å ²)
H(5)	6,3
H(6)	6 [†]
H(7)	2,2
H(8)	6,4

* See Fig. 1 for the identities of the atoms. The e.s.d., separated by a comma, is in the units of the least significant digit given for the corresponding parameter.

† Held fixed in least squares; see text.

‡ The b_{33} values, and especially their e.s.d.'s, are of limited significance because least-squares was used, together with precession photographs, to scale the layers around c (see text).

Table 4. Bond lengths (Å) and angles ($^\circ$) and their standard deviations*

Atoms	Distance		Atoms	Angles
	Uncorrected	Corrected		
S(1)-O(2)	1.595,7	1.604,9	O(2), S(1), O(3)	107.5,7
S(1)-O(3)	1.495,7	1.502,9	O(2), S(1), C(4)	95,1
S(1)-C(4)	1.781,10	1.786,11	O(3), S(1), C(4)	04,1
O(2)-H(5)	0.97,32			
C(4)-H(6)	1.01			
C(4)-H(7)	0.68,10			
C(4)-H(8)	1.10,16			

* See Fig. 1 for the identities of the atoms. The e.s.d., separated by a comma, is in the units of the least significant digit given for the corresponding parameter. The corrections to bond distances are described in the text; an arbitrary uncertainty of 0.005 Å in each such correction has been included.

rent from the distance of 1.51 Å in hydroxymethanesulfinate ion (Truter, 1962), the dithionite ion, $O_2SSO_2^{2-}$ (Dunitz, 1956), and (for the shorter S–O bond) bis-(toluene-*p*-sulfinato)copper(II) tetrahydrate (Langs & Hare, 1967). On the other hand the average distance in the present molecule, 1.55 Å, is significantly greater than that in the comparable species just cited (1.51, 1.51, and 1.53 Å respectively). This discrepancy seems somewhat surprising, since the average sulfur–oxygen bond distance in sulfuric acid (Pascard-Billy, 1965) is essentially the same as that in the sulfate ion (Larson, 1965), 1.48 Å, and the same relation holds for phosphoric acid, phosphate esters, and the phosphate ion and for other tetrahedral X–O species (Cruikshank, 1961), as well as for carboxylic acids and their anions. Perhaps in molecules in which the sulfur atom has an unshared pair and fewer than four bonded neighbors, the sum of the bond orders of the S–O bonds is not constant, unlike the tetrahedral species; rather, the bond order of the shorter bond may remain substantially constant, independent of the character of the other bond(s). No precise studies of sulfite diesters and other species which could be used to test this speculation have been reported. We will not attempt any rationalization of this suggestion; as Truter (1962) has pointed out, many interdependent factors probably contribute to the observed variations in S–O bond lengths, and this does not seem the place to review them.

The S–O distance in sulfoxides, sulfinate anions, and related species is somewhat shorter than in sulfite ion (1.53 Å; Battelle & Trueblood, 1965), in accord with the general observation that successive replacement of the hydroxyl groups or oxygen atoms of sulfuric acid by alkyl groups to form sulfonic acids, sulfones, and trimethylxosulfonium ion results in shortening the

average S–O distance by 0.01 to 0.03 Å (see Brandon & Brown, 1967, and references cited therein). The lengthening of the average S–O bond in sulfites and sulfates relative to S–O bonds in four-coordinated sulfur species is presumably due in significant part to the effect of the unshared pair of electrons on the sulfur atom, as discussed by Cruickshank (1961).

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Table 5. Some non-bonded interatomic distances (Å)*

(a) Intramolecular				
	S(1) ··· H(5)	2.1	O(2) ··· H(6)	2.7
	··· H(6)	2.2	··· H(7)	2.6
	··· H(7)	2.2	O(3) ··· H(5)	2.9
	··· H(8)	2.1	··· H(6)	2.4
	O(2) ··· O(3)	2.49	H(6) ··· H(7)	1.5
	··· C(4)	2.49	··· H(8)	1.9
	O(3) ··· C(4)	2.59	H(7) ··· H(8)	1.3
(b) Intermolecular†				
II. ($\frac{1}{2}-x, -y, \frac{1}{2}+z$)	S(1) ··· H(5)	2.7	O(3) ··· S(1)	3.49
	O(2) ··· S(1)	3.44	··· O(2)	2.59
	··· O(3)	3.50	··· H(5)	1.6
	··· H(5)	3.0	H(6) ··· H(5)	2.5
($\frac{1}{2}-x, 1-y, -\frac{1}{2}+z$)	H(8) ··· C(4)	3.0		
III. ($\frac{1}{2}+x, \frac{1}{2}-y, -z$)	O(2) ··· S(1)	3.38	O(2) ··· H(8)	3.0
	··· O(3)	3.46	H(5) ··· H(8)	2.6
IV. ($-x, \frac{1}{2}+y, \frac{1}{2}-z$)	C(4) ··· O(3)	3.50	H(8) ··· O(3)	2.6
($1-x, -\frac{1}{2}+y, \frac{1}{2}-z$)	O(2) ··· C(4)	3.42	H(5) ··· H(7)	2.7
	··· H(7)	2.8		

* Some intramolecular distances and all intermolecular distances not greater than the following are given: H···H, 2.7 Å; H···C, O, S, 3.0 Å; otherwise, 3.5 Å.

† The first atom of each pair has coordinates as given in Table 2. The second atom is related to the one in Table 2 by the symmetry operation given in the subheading. The Roman numerals help to identify the different equivalent molecules in Fig. 1.

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The Crystal Structures of Nitrates of Divalent Hexaquocations. II. Hexaquomagnesium Nitrate

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The crystals of hexaquomagnesium nitrate are monoclinic, space group $P2_1/c$. The structure, determined from three-dimensional data, consists of hexaquomagnesium cations which are nearly octahedral with Mg-OH_{2av} equal to 2.058 Å and of nitrate groups which are not trigonally symmetric with N-O bond lengths 1.20, 1.25, 1.26 Å. The hexaquocations and the nitrate groups are bound together by hydrogen bonds whose lengths are in the range 2.75–2.90 Å. The differences in the crystal structures of the hexaquozinc nitrate, orthorhombic, and of the hexaquomagnesium nitrate, monoclinic, seem to be related to the different disposition of the hydrogen bonds radiating from the hexaquocations towards the nitrate groups.

Introduction

The hexaquocations of divalent metals are assigned octahedral structures, but small deviations from perfectly cubic symmetry are expected either because of the electronic configuration of the metal cation or because of the strains from the hydrogen bonds in the crystal.

The assessment of the extent of these perturbations is the object of the widely extending structural studies on the compounds of hexaquocations. The hexaquometal (II) nitrates crystallize in several different crystal systems or space groups and it seems to us worth while to endeavour to understand how far this fact is related to the distortions in the octahedral arrangement of the water molecules around the metal. Here are presented the results of the crystal structure determination of the magnesium compound.

Experimental

Preparation

The crystals are obtained by crystallization from aqueous solutions. They are prismatic, highly hygroscopic and, for X-ray work, need to be sealed into capillary tubes.

Crystal data

Hexaquomagnesium nitrate, [Mg(OH₂)₆](NO₃)₂; F.W. 256.432.

For the structure determinations we used the refined crystal data of Mozzi & Bekebrede (1961):

$a = 6.194 \pm 0.002$, $b = 12.707 \pm 0.003$, $c = 6.600 \pm 0.002$ Å
 $\beta = 92.99 \pm 0.02^\circ$, $V = 518.8$ Å³ $Z = 2$

$D_m = 1.636$ g.cm⁻³, $D_x = 1.641$ g.cm⁻³, $\mu = 21.45$ cm⁻¹ (Cu K α)

Space group $P2_1/c$ (C_{2h}^5 , No.14) from systematic absences.

Intensity data

Integrated reflexions $0kl$, $1kl$, $2kl$, $3kl$, $4kl$, $5kl$, photographically recorded on a Weissenberg camera, were

Table 1. Fractional atomic coordinates $\times 10^4$ (with e.s.d.'s).

	x	y	z
Mg	0000	5000	5000
H ₂ O(1)	-0358 (11)	3398 (4)	4764 (13)
H ₂ O(2)	3022 (10)	4805 (5)	4616 (10)
H ₂ O(3)	-1432 (13)	4993 (4)	7750 (10)
N(4)	4668 (12)	2040 (4)	5362 (11)
O(5)	6031 (14)	1301 (4)	5330 (12)
O(6)	2814 (15)	1881 (3)	5685 (17)
O(7)	5339 (14)	2962 (4)	5172 (16)