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Refinement of the Crystal Structure of Sodium Hexahydroxoantimonate(V), $NaSb(OH)_6$

Takeshi ASAI

Institute of Scientific and Industrial Research, Osaka University, Yamada-kami, Suita, 565

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The crystal structure of sodium hexahydroxoantimonate (V), $NaSb(OH)_6$, has been refined. The previous structure given by Schrewelius was confirmed, but the positional parameters of oxygen atoms were shifted significantly. Both antimony and sodium atoms are surrounded by six oxygen atoms octahedrally. The interatomic distances are: Sb-O=1.972—1.999 Å (mean 1.98 Å), O-O=2.758—2.834 Å (2.80 Å) for an SbO_6 octahedron, Na-O=2.375—2.406 Å (2.39 Å) and O-O=3.229—3.526 Å (3.38Å) for an NaO_6 octahedron. Two types of sequences of hydrogen bonds were recognized. They were compared with the sequences of hydrogen bonds in $In(OH)_3$ and $MnSn(OH)_6$.

In the course of our NMR studies on the metal hydroxides, $In(OH)_3$, $MgSn(OH)_6$ and $NaSb(OH)_6$, accurate structural information was needed on these compounds. The crystal structure of $In(OH)_3$,[1] and that of $MnSn(OH)_6$,[2] which is isomorphous with $MgSn(OH)_6$,[3,4] have already been analyzed with single crystal X-ray diffraction data. On the other hand, the crystal structure of $NaSb(OH)_6$ was derived from powder X-ray diffraction intensities[5,6] with accordingly poor accuracy. The analysis resulted in an OH group free from hydrogen bonding and another with a very short OH···O distance (2.55 Å).

Experimental

The compound was obtained by slow evaporation of a dilute aqueous solution containing $KSb(OH)_6$ and NaCl in the molar ratio of 2 : 1. The crystals thus obtained were enclosed with one (001) and eight {111} faces.

The space group and lattice constants[5,6] were confirmed from Weissenberg and precession photographs. Crystallographic data obtained in this study are given in Table 1.

The intensity data were collected using a Rigaku automatic four-circle diffractometer with a scintillation counter and the Mo$K\alpha$ radiation. A total of 821 reflections in two octants, among which 465 reflections were independent, were measured within $\sin\theta/\lambda$ of 0.60 $Å^{-1}$. Ninety-six reflections with $|F_o|$ values less than 2σ, twice the estimated standard deviations based on the counting statistics, were assumed to have zero amplitudes. The whole reflections were corrected for Lorentz and polarization effects, but not for absorption nor extinction effects ($\mu R=0.55$).

TABLE 1. CRYSTALLOGRAPHIC DATA

$NaSb(OH)_6$, F. W. 246.8
Tetragonal
$a=8.029(2)$, $c=7.894(3)$ Å
$U=508.9 Å^3$, $Z=4$
$D_m = 3.20\ g\cdot cm^{-3}$ [5]
$D_x=3.22\ g\cdot cm^{-3}$
Systematic absences: $hk0$ with $h+k=2n+1$
$00l$ with $l=2n+1$
Space group $P4_2/n$ (No. 86)

From a three-dimensional Patterson synthesis, approximate positional parameters for all non-hydrogen atoms were obtained. They were refined by a block-diagonal least-squares method firstly with isotropic thermal factors and then with anisotropic ones. The final residual R was 0.063. A trial to find hydrogen positions in the difference Fourier maps was unsuccessful. The weighting scheme was; $w=1$ for $|F_o|\neq 0$, and $w=0$ for $|F_o|=0$. Reflections of 020 and 002 were omitted in the refinement because they were seriously affected by extinction. The atomic scattering amplitudes for Sb^{5+}, Na^+ and O^- with anomalous dispersion corrections were taken from Ref. 7. All calculations were performed on a NEAC 2200/700 computer at the Computer Center, Osaka University, using UNICS programs RSSFR-5, HBLS-V and RSDA-4 with some modifications. The final parameters are given in Table 2. The final observed and calculated structure factors are listed in Table 3.

Discussion

The crystal structure is projected in Fig. 1. Interatomic distances and angles are shown in Fig. 2. The structure is in general the same as that given by Schrewelius.[6] The oxygen atoms, however, were significantly shifted (0.13—0.69 Å); as a result, his short OH···O distance (2.55 Å) increased to a normal distance of 2.859 Å, while his longer O···O distance (4.51 Å) decreased to 3.149 Å. The antimony atom is surrounded by six oxygen atoms. This coordination polyhedron is a nearly regular octahedron with the mean interatomic distances of 1.98 Å for Sb–O and 2.80 Å for O–O. The sodium ion is surrounded by six oxygen atoms belonging to six different

TABLE 2. FINAL POSITIONAL AND THERMAL PARAMETERS (× 10^4) WITH THEIR e.s.d.'s IN PARENTHESES
Thermal factors are of the form $T=\exp[-(h^2B_{11}+\cdots+klB_{23})]$.

Atom	x	y	z	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Na	7500	7500	7500	45(9)	49(9)	57(8)	−8(14)	18(16)	−10(15)
Sb	2500	2500	2500	22(1)	15(1)	24(1)	−3(2)	4(2)	5(2)
O(1)	1942(8)	274(8)	3482(8)	63(11)	35(10)	26(10)	−14(17)	4(18)	−11(17)
O(2)	292(8)	3320(8)	3228(9)	35(10)	51(10)	39(10)	10(17)	7(18)	54(17)
O(3)	1605(8)	1815(7)	281(8)	48(10)	13(9)	22(9)	6(16)	−22(17)	−9(16)

TABLE 3. FINAL OBSERVED AND CALCULATED STRUCTURE FACTORS, $|F_o|$ and $|F_c|$

K	Fo	Fc
H,L= 0,0		
2	210	225
4	184	182
6	88	89
8	88	89
H,L= 1,0		
1	7	4
3	18	14
5	8	8
7	5	8
9	0	3
H,L= 2,0		
2	149	151
4	193	199
6	114	110
8	117	115
H,L= 3,0		
1	32	26
3	40	36
5	6	4
7	9	12
9	13	16
H,L= 4,0		
2	160	157
4	142	141
6	95	91
8	99	101
H,L= 5,0		
1	17	17
3	21	20
5	8	8
7	0	1
H,L= 6,0		
2	143	146
4	134	139
6	117	119
H,L= 7,0		
1	6	4
3	10	10
5	0	1
H,L= 8,0		
2	107	102
4	82	83
H,L= 9,0		
1	0	2
3	11	11
H,L= 0,1		
1	0	1
2	0	0
3	73	62
4	8	7
5	5	3
6	6	3
7	6	6
8	0	2
9	11	11
H,L= 1,1		
1	159	160
2	7	5
3	156	155
4	7	3
5	127	126
6	5	4
7	72	72
8	6	4
9	75	76
H,L= 2,1		
1	0	1
2	0	1
3	53	49
4	7	5
5	0	2
6	0	5
7	7	5
8	0	1
9	13	14
H,L= 3,1		
1	74	62
2	21	17
3	109	107
4	21	21
5	86	82
6	26	26
7	87	87
8	7	7
9	76	78
H,L= 4,1		
1	12	10
2	18	18
3	4	3
4	6	3
5	12	11
6	0	0
7	0	3
8	8	8
H,L= 5,1		
1	111	107
2	9	10
3	129	132
4	4	3
5	77	76
6	8	7
7	77	78
8	8	1
H,L= 6,1		
1	8	8
2	5	5
3	18	17
4	5	7
5	0	0
6	8	5
7	9	9
H,L= 7,1		
1	67	68
2	0	1
3	84	83
4	7	7
5	72	72
6	0	2
H,L= 8,1		
1	6	4
2	0	3
3	16	16
4	0	1
5	0	0
H,L= 9,1		
1	85	84
2	7	8
3	69	69
H,L= 0,2		
0	178	209
1	19	14
2	158	162
3	40	35
4	182	185
5	20	17
6	135	137
7	7	5
8	106	107
9	6	4
H,L= 1,2		
1	24	20
2	28	24
3	17	16
4	27	25
5	5	2
6	11	8
7	0	0
8	6	2
9	0	0
H,L= 2,2		
1	29	24
2	154	150
3	30	24
4	180	188
5	18	16
6	138	140
7	0	0
8	113	114
9	0	5
H,L= 3,2		
1	28	24
2	24	19
3	22	20
4	15	14
5	13	15
6	5	4
7	0	1
8	7	4
H,L= 4,2		
1	27	23
2	155	156
3	25	25
4	131	131
5	8	6
6	102	101
7	8	5
8	93	94
H,L= 5,2		
1	15	15
2	17	15
3	13	14
4	17	15
5	0	6
6	9	8
7	12	10
H,L= 6,2		
1	22	20
2	137	138
3	6	4
4	107	106
5	7	6
6	91	90
7	9	9
H,L= 7,2		
1	9	10
2	7	2
3	0	0
4	9	9
5	7	3
6	12	12
H,L= 8,2		
1	9	12
2	101	101
3	6	7
4	75	74
H,L= 9,2		
1	13	13
2	0	3
H,L= 0,3		
1	68	57
2	11	13
3	0	2
4	10	7
5	32	30
6	0	1
7	0	1
8	0	1
9	0	4
H,L= 1,3		
1	109	106
2	31	27
3	115	113
4	11	12
5	105	106
6	16	14
7	89	89
8	10	8
9	65	68
H,L= 2,3		
1	47	42
2	18	16
3	11	10
4	5	3
5	22	20
6	6	9
7	25	27
8	0	0
H,L= 3,3		
1	113	113
2	8	8
3	108	106
4	0	2
5	95	97
6	0	2
7	82	82
8	7	3
H,L= 4,3		
1	7	7
2	12	14
3	9	10
4	0	2
5	16	15
6	0	0
7	8	7
8	7	8
H,L= 5,3		
1	103	104
2	7	2
3	90	88
4	23	23
5	77	77
6	18	18
7	67	68
H,L= 6,3		
1	24	24
2	0	0
3	11	10
4	5	5
5	10	10
6	10	3
H,L= 7,3		
1	89	88
2	8	0
3	75	75
4	15	15
5	67	66
H,L= 8,3		
1	17	15
2	8	10
3	0	2
4	8	2
H,L= 9,3		
1	67	70
H,L= 0,4		
0	162	162
1	20	19
2	172	181
3	20	17
4	124	125
5	10	9
6	114	113
7	6	4
8	92	89
H,L= 1,4		
1	6	1
2	17	13
3	0	2
4	0	1
5	0	3
6	6	3
7	7	8
8	14	15
H,L= 2,4		
1	32	29
2	171	181
3	21	20
4	115	113
5	8	4
6	105	103
7	7	5
8	77	76
H,L= 3,4		
1	15	13
2	13	10
3	25	25
4	18	18
5	12	11
6	0	2
7	7	4
8	8	8
H,L= 4,4		
1	0	2
2	136	136
3	20	20
4	122	122
5	10	12
6	113	112
7	0	2
H,L= 5,4		
1	5	3
2	25	25
3	8	9
4	0	2
5	5	4
6	7	8
7	6	6
H,L= 6,4		
1	20	19
2	105	103
3	0	0
4	104	104
5	7	2
6	91	92
H,L= 7,4		
1	0	2
2	10	9
3	9	8
4	8	2
5	0	1
H,L= 8,4		
1	10	11
2	88	88
3	7	3
H,L= 0,5		
1	0	2
2	13	13
3	32	31
4	6	6
5	11	8
6	0	4
7	0	0
8	8	6
H,L= 1,5		
1	111	113
2	0	2
3	87	81
4	4	1
5	61	58
6	9	7
7	73	72
8	0	1
H,L= 2,5		
1	7	7
2	14	12
3	13	12
4	14	15
5	5	2
6	0	4
7	0	6
H,L= 3,5		
1	126	130
2	0	0
3	94	94
4	5	6
5	86	86
6	17	14
7	64	64
H,L= 4,5		
1	7	5
2	7	4
3	8	5
4	12	13
5	0	2
6	8	3
7	0	1
H,L= 5,5		
1	74	76
2	0	1
3	64	63
4	4	6
5	86	88
6	7	6
H,L= 6,5		
1	5	6
2	0	2
3	14	13
4	6	6
5	7	2
H,L= 7,5		
1	81	81
2	0	1
3	72	75
4	0	1
H,L= 8,5		
1	0	3
H,L= 0,6		
0	81	82
1	6	8
2	125	127
3	0	8
4	109	108
5	8	8
6	119	117
7	0	1
H,L= 1,6		
1	0	0
2	13	10
3	0	3
4	14	14
5	10	4
6	0	7
7	10	7
H,L= 2,6		
1	18	21
2	137	139
3	7	6
4	95	91
5	6	2
6	101	101
7	11	7
H,L= 3,6		
1	0	4
2	7	5
3	8	10
4	0	1
5	0	2
6	0	4
H,L= 4,6		
1	11	12
2	110	113
3	0	6
4	103	102
5	7	6
6	100	102
H,L= 5,6		
1	0	4
2	8	10
3	7	7
4	0	0
5	0	6
H,L= 6,6		
1	0	1
2	87	84
3	7	3
4	79	77
H,L= 7,6		
1	7	3
2	15	14
H,L= 0,7		
1	6	8
2	6	8
3	6	5
4	0	3
5	7	9
6	7	3
H,L= 1,7		
1	67	67
2	0	3
3	73	71
4	6	2
5	74	75
6	0	0
H,L= 2,7		
1	0	0
2	9	8
3	14	16
4	10	7
5	0	0
6	0	5
H,L= 3,7		
1	95	97
2	5	7
3	78	78
4	0	6
5	79	80
H,L= 4,7		
1	8	7
2	15	16
3	0	5
4	10	13
5	0	10
H,L= 5,7		
1	77	77
2	7	6
3	55	54
4	0	3
H,L= 6,7		
1	7	4
2	7	4
H,L= 0,8		
0	94	94
1	0	0
2	102	101
3	13	11
4	89	88
5	8	6
H,L= 1,8		
1	5	7
2	15	16
3	0	7
4	14	15
H,L= 2,8		
1	7	2
2	101	99
3	8	6
4	82	79
H,L= 3,8		
1	0	1
2	0	6
3	8	9
4	0	2
H,L= 4,8		
1	13	12
2	87	87
3	9	7
H,L= 5,8		
1	8	12
H,L= 0,9		
1	7	8
2	0	11
H,L= 1,9		
1	78	79
2	8	5
H,L= 2,9		
1	0	7
2	14	12

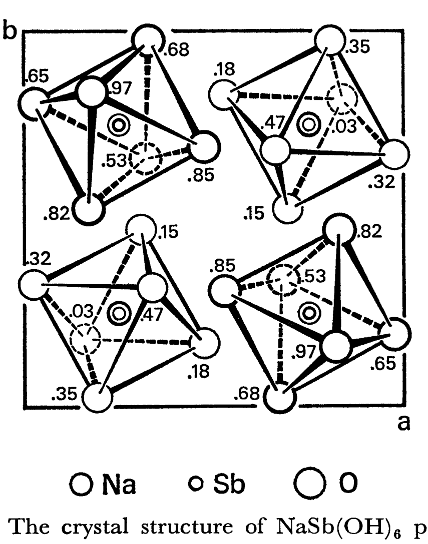
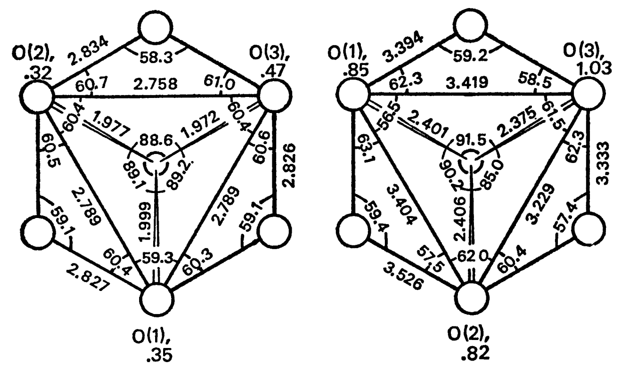


Fig. 1. The crystal structure of $NaSb(OH)_6$ projected along the [001] axis. Numbers attached to the oxygen atoms are their z-parameters.



SbO_6 Octahedron NaO_6 Octahedron

Fig. 2. Interatomic distances (l/Å) and angles (ϕ/°) for SbO_6 and NaO_6 octahedra. The e. s. d.'s are ±0.009 Å and ±0.2°, respectively. The metal atoms are situated on the center of inversion, Sb at (1/4, 1/4, 1/4) and Na at (3/4, 3/4, 3/4). Numbers attached to the oxygen atoms are their z-parameters.

SbO_6 octahedra. The coordination polyhedron is also octahedral, but the distortion is greater than that of the SbO_6 octahedron. The interatomic distances are 2.375—2.406 Å (mean 2.39 Å) for Na–O and 3.229—3.526 Å (mean 3.38 Å) for O–O.

Interatomic distances of O···O which can be associated with hydrogen bonding are given in Table 4. The table shows that all OH groups are hydrogen-bonded[8], and the OH group free from hydrogen bonding in the Schrewelius' analysis is eliminated. These hydrogen bonds extend in the whole crystal. The sequences of hydrogen bonding in $In(OH)_3$, $MnSn(OH)_6$ and $NaSb(OH)_6$ are compared schematically in Fig. 3. Squares of four hydrogen-bonded OH's

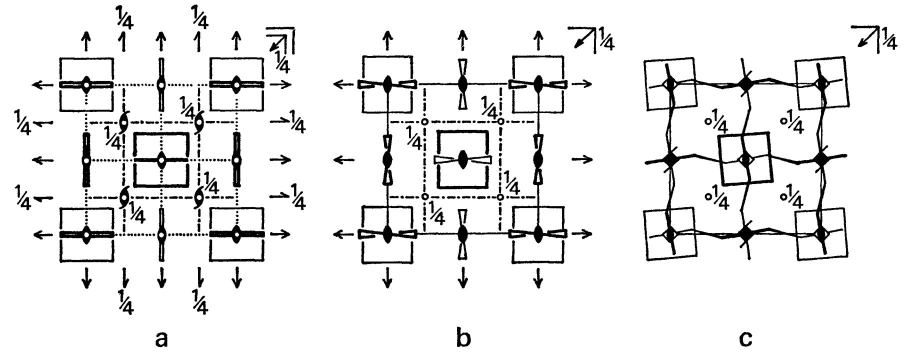


Fig. 3. Schematic sequences of hydrogen bonding viewed along the [001] axis; (a) $In(OH)_3$, (b) $MnSn(OH)_6$ and (c) $NaSb(OH)_6$. The squares at $z\simeq 0$ are shown in thin lines and those at $z\simeq 1/2$ in heavy lines. Vertical mirror planes in $In(OH)_3$ are shown in dotted lines, while the other symmetry elements are shown after the usual fashion.

Table 4. INTERATOMIC DISTANCES ASSOCIATED WITH THE HYDROGEN BONDING

The e.s.d.'s are ±0.009 Å

$O(1)^{i}\cdots O(2)^{iv}$	2.859 Å
$O(1)^{i}\cdots O(1)^{ii}$	3.149
$O(2)^{i}\cdots O(2)^{v}$	2.738
$O(3)^{i}\cdots O(3)^{iii}$	2.787

Superscripts in this table and in the text mean the following symmetry operations to the positional parameters given in Table 2.

i	$1/2-x$,	$1/2-y$,	$1/2-z$
ii	$1/2+x$,	$1/2+y$,	$1/2-z$
iii	$1/2+y$,	$1/2-x$,	$1/2+z$
iv	$1/2-y$,	$1/2+x$,	$-1/2+z$
v	$1/2+x$,	$-1/2+y$,	$1/2-z$
vi	$3/2-y$,	$1/2+x$,	$1/2+z$

are found in $In(OH)_3$ and $MnSn(OH)_6$. Each edge of these squares affords two sites for a hydrogen atom, yielding a statistical structure of hydrogen atoms.[1,2,9] A similar hydrogen-bonded square of O(3)'s is found also in $NaSb(OH)_6$. At the same time, however, hydrogen-bonded chains of the type$\cdots O(2)^{iv}\cdots O(1)^{i}\cdots O(1)^{ii}\cdots O(2)^{iii}\cdots O(2)^{vi}\cdots$are running along the a and b axes. These chains are found only in $NaSb(OH)_6$ among these compounds; therefore the chain structure of the hydrogen bond is a characteristic feature of this compound. Considering the symmetry, hydrogen atoms in $NaSb(OH)_6$ may also take a statistical structure.

Appearance of the chain sequences of hydrogen bonding in $NaSb(OH)_6$ can be explained well if we consider the differences in the bond nature in these $AB(OH)_6$ compounds. In $In(OH)_3$ the lattice is constructed with equivalent $In(OH)_6$ octahedra through sharing their corners, while in $NaSb(OH)_6$ it is constructed with Na^+ and $Sb(OH)_6^-$ ions. The more ionic character in $NaSb(OH)_6$ will allow an anion to take a different orientation from that of $In(OH)_6$ octahedra, yielding a distortion of $Na(OH)_6$ octahedra. The distortion in $NaSb(OH)_6$ is such that the interatomic distances of O(1)'s in the same square become longer and the distance of $O(1)\cdots O(1)^{ii}$ between the adjacent squares becomes shorter; thus a hydrogen-bonded chain is formed. A similar trend is also seen in $MnSn(OH)_6$. However, the difference between the ionic radii of Mn^{2+} and Sn^{4+} cations is much smaller than that between those of Na^+ and Sb^{5+} cations in $NaSb(OH)_6$. This means that $Sb(OH)_6^-$ octahedra must rotate much more than $Sn(OH)_6^{2-}$ octahedra in order for the lattice to accomodate A^{n+} cations in the interstices of $B(OH)_6^{n-}$ anions. Therefore, the hydrogen-bonded squares in $MnSn(OH)_6$ experience only a little distortion, while two thirds of the squares in $NaSb(OH)_6$ are forced to break and to recombine into chains.

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8) This statement does not mean that a hydrogen atom is located just on the line connecting two oxygen atoms. In fact, it must deviate slightly from the line in order to avoid closer contact than the van der Waals one. See, Refs. 1 and 9.

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