An X-Ray Redetermination of the Crystal Structure of Tin(II) Chloride Dihydrate

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(Received December 28, 1972)

The crystal structure of tin(II) chloride dihydrate, $SnCl_2 \cdot 2H_2O$ has been redetermined by a single crystal X-ray diffractometer technique. The crystal is monoclinic, space group $P2_1/c$ with $a=9.313$, $b=7.250$, $c=8.970$ Å, $\beta=114°55'$ and Z=4. The structure was solved by three-dimensional Patterson and electron density syntheses. An anisotropic least-squares refinement, based on 1695 independent reflections gave an R value of 0.04. The tin(II) atom forms a pyramidal complex with two chlorine atoms and one oxygen atom; the bond lengths in the pyramid are Sn–O, 2.33 and Sn–Cl, 2.50 and 2.56 Å and the bond angles are 86.9, 85.0, and 87.9°. These results support a view that the bonding in dichloroaquotin(II) complex is considerably ionic in character. This crystal consists of double layers of the aquocomplex, $SnCl_2 \cdot (OH_2)$, parallel to (100) with intervening layers of the second water molecules. Both kinds of the water molecules are linked together by hydrogen bonds of 2.74, 2.79, and 2.80 Å into two-dimensional networks. The structure reported previously was found to be in error, although its essential feature was quite similar to the present one.

The crystal structure of $SnCl_2 \cdot 2H_2O$ has been analysed by Kamenar and Grdenić (hereinafter abbreviated as K & G) in 1961.[1] According to their description, the crystal consists of dichloroaquotin(II) complexes and the second water molecules, both of which form alternate layers parallel to the (100) plane and are linked through hydrogen bonds alone. Such an arrangement of the water molecules, especially their hydrogen bonding scheme, strongly suggested the presence of dielectric anomaly similar to those found in copper(II) formate tetrahydrate[2] and also in potassium ferrocyanide trihydrate.[3] Recently, Kiriyama and Kiriyama have found a phase transition at −55 °C from dielectric measurements of this compound and have investigated its mechanism from many approaches such as electric conductivities, thermal analyses, X-ray diffractions, proton and deuteron magnetic resonances (PMR and DMR).[4]

On the basis of these results the phase transition could be ascribed to the ordering of hydrogen atoms within the layer of hydrogen bonded water molecules. However, it was noticed that our PMR and DMR data could not provide consistent locations of the hydrogen atom positions, so far as the crystal structure described by K & G was used. It was therefore thought profitable to redetermine the structure by use of a three-dimentional single crystal X-ray diffractometer, because the previous structure had been derived from incomplete data.

Experimental

Single crystals were prepared from about 18% hydrochloric acid saturated with tin(II) chloride, this being the best condition to obtain large transparent single crystals for NMR and dielectric measurements. The crystal used for the present X-ray work was a monoclinic prism of length 0.50 mm (the c-axis direction) and cross-section 0.08×0.10 mm². It was sealed in a Lindeman glass capillary to protect from atmospheric moisture. With the c-axis as the Φ-axis of the instrument, a set of intensity data was collected by use of a Rigaku automatic four-circle diffractometer with Mo$K\alpha$ radiation and the 2θ-ω scan technique. A total of 1695 independent reflections was measured up to a $\sin\theta/\lambda$ limit of 0.72 Å^{-1}. Their intensity data were corrected for polarization and Lorentz effects, but absorption correction was neglected becauce of the small μR value of 0.26.

Unit Cell and Space Group

The systematically absent reflections, ($0k0$) with k odd and ($h0l$) with l odd, confirmed the monoclinic space group of $P2_1/c$ originally derived by K & G. The cell dimensions were:

$a=9.313$, $b=7.250$, $c=8.970$Å, $\beta=114°55'$, $V=549.275$Å³.

The calculated density of 2.707 g cm^{-3}, assuming a unit cell content of four formula units, agreed well with the value of 2.710 g cm^{-3} measured by K & G.

Structure Analysis and Refinement

Fourier syntheses of the three main projections were computed starting from the atomic coordinates given by K & G. The [010] and [001] projections were roughly consistent with their description of structure, while the [100] projection was in quite disagreement. Therefore, three-dimensional Patterson functions were calculated from 1695 reflection data and from this it became evident that all atoms, of course except hydrogens, were located incorrectly. This finding forced us to redetermine the crystal structure of this compound, instead of its refinement.

The tin and chlorine positions could be easily derived from the three-dimensioanl Patterson map, and the oxygen's were located from successive electron density calculations. New parameters thus obtained were used in a block-diagonal least-squares refinement. After four cycles of refinement in which were varied the coordinates, the individual isotropic temperature factors for all non-hydrogen atoms, a scale factor and an over-all temperature factor (a total of 22 parameters), the "discrepancy index" $R=\sum||F_o|-|F_c||/\sum|F_o|$ was

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[1] B. Kamenar and D. Grdenić, *J. Chem. Soc.*, **1961**, 3954.

[2] H. Kiriyama, This Bulletin, **35**, 1199 (1962).

[3] S. Waku, H. Hirabayashi, H. Iwasaki, and R. Kiriyama, *J. Phys. Soc. Jap.*, **14**, 973 (1959).

[4] H. Kiriyama and R. Kiriyama, *ibid.*, **28**, S 114 (1970).

Table 1. Atomic coordinates with their estimated standard deviations

	x/a	y/b	z/c	$B(\text{Å}^2)^{a)}$
Sn	0.37441 (5)	0.26178 (6)	0.53584 (5)	2.34 (1)
Cl (1)	0.28643 (22)	0.49226 (25)	0.68748 (22)	2.85 (4)
Cl (2)	0.30612 (20)	0.49997 (24)	0.30501 (20)	2.45 (4)
O (1)	0.10937 (53)	0.17555 (65)	0.41282 (55)	2.41 (12)
O (2)	−0.06738 (58)	0.20658 (71)	0.59835 (62)	2.83 (13)

a) These are values for an isotropic refinement giving the final R-value of 0.068.
Temperature factors are in the form of $\exp[-B(\sin\theta/\lambda)^2]$.

Table 2. Thermal parameters ($\times 10^4$) and their e.s.d.'s
$T = \exp[-(\beta_{11}h^2+\beta_{22}k^2+\beta_{33}l^2+\beta_{12}hk+\beta_{13}hl+\beta_{23}kl)]$

	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Sn	86 (1)	103 (1)	87 (1)	12 (1)	61 (1)	12 (1)
Cl (1)	121 (3)	123 (3)	100 (2)	−5 (5)	105 (4)	−35 (4)
Cl (2)	91 (2)	115 (3)	87 (2)	−5 (4)	60 (4)	42 (4)
O (1)	81 (6)	110 (9)	81 (6)	−30 (12)	55 (10)	−6 (12)
O (2)	92 (7)	120 (9)	112 (8)	26 (13)	65 (12)	0 (14)

reduced to 0.063 for the observed reflections (0.068 including 47 unobserved reflections). At this stage of the refinement the structure obtained was checked by a three-dimensional (F_o-F_c) synthesis, which showed no ripple of more than $8e/\text{Å}^3$. Further refinements were computed with five cycles of least-squares calculations, which now included anisotropic temperature factors for tin, chlorine, and oxygen. The other parameters varied were the same as before; the total number was 47. During the last cycle, the shifts in coordinate or thermal parameter values were less than one tenth of the standard deviation for the parameter in question. The R value was now 0.040.

The atomic coordinates and the thermal parameters with their standard deviations obtained from the final anisotropic least squares refinement are listed in Tables 1 and 2. The observed and calculated structure factors are compared in Table 3. The atomic scattering factors used in the above calculations were those for neutral Sn, Cl, and O, respectively, given in International Tables Vol. III. All calculations were performed on the NEAC 2200/500 in the Computer Center Osaka University, using UNICS computer programs, HBLS-LV, RSSFR-5 and RSDA-4.

Description and Discussion of the Structure

The crystal structures projected along [100] and [010] are given in Figs. 1 and 2, respectively. It can be seen that tin(II) chloride dihydrate has a predominant layer-structure parallel to the (100) plane; it is built up from double layers of the dichloroaquotin (II) complex and intervening layers of the second water molecules. Apart from van der Waals forces, these layers are held together by hydrogen bonds. Such a description of the structure appears to be the same as the earlier one. However, the projection along the a axis given in Fig. 1 is largely different from that reported by K & G. It is conceivable that the lack of the [100] projection led the previous work to the erroneous conclusion. Both the structures are compared in Fig. 3, where only the aquocomplex double layers are shown for simplicity.

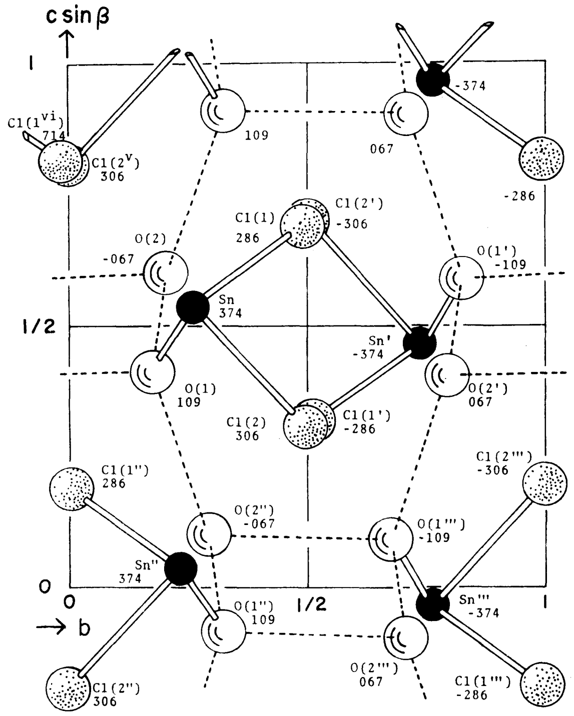

Fig. 1. The crystal structure viewed along the a axis. Hydrogen bonds are indicated by broken lines.

The main interatomic distances and bond angles with the corresponding estimated standard deviations are listed in Table 4, some of them are also shown in Figs. 4 and 5. These values are based on the parameters listed in Table 1. No correction for thermal motions was made.

Structure and Bonding of Dichloroaquotin(II) Complexes

A geometry of the tin(II) coordination is somewhat different from the previous one. The dimensions of the trigonal pyramid, $SnCl_2(OH_2)$ complex, are illus-

TABLE 3. OBSERVED AND CALCULATED STRUCTURE FACTORS FOR $SnCl_2 \cdot 2H_2O$

H	FO	FC
K = 0 L = 0		
1	104	-121
2	74	-72
3	161	177
4	124	-124
5	4	2
6	3	-3
7	33	-33
8	43	43
9	43	-42
10	14	15
11	20	21
12	32	-31
K = 0 L = 2		
-12	13	-14
-11	37	37
-10	41	-41
-9	1	0
-8	94	93
-7	114	-115
-6	33	33
-5	82	81
-4	176	-184
-3	37	42
-2	43	-36
-1	39	-36
0	83	94
1	91	-97
2	145	149
3	40	37
4	102	-103
5	110	111
6	44	-43
7	38	-38
8	52	51
9	39	-39
10	9	9
11	11	12
K = 0 L = 4		
-13	0	0
-12	27	-28
-11	36	36
-10	25	-24
-9	3	2
-8	35	35
-7	53	-53
-6	100	99
-5	31	-29
-4	75	-73
-3	123	128
-2	139	-158
-1	28	-23
0	66	66
1	123	-129
2	98	97
3	4	2
4	46	-45
5	82	84
6	39	-39
7	3	-4
8	25	25
9	25	-26
K = 0 L = 6		
-13	13	-13
-12	5	-3
-11	26	27
-10	46	-46
-9	27	26
-8	6	6
-7	52	-50
-6	96	96
-5	51	-49
-4	3	2
-3	109	115
-2	116	-122
-1	27	27
0	30	32
1	87	-91
2	42	40
3	21	-22
4	3	2
5	27	27
6	35	-37
7	30	32
8	2	1
K = 0 L = 8		
-13	22	-22
-12	15	14
-11	18	18
-10	52	-52
-9	41	40
-8	0	-1
-7	55	-54
-6	50	49
-5	22	-22
-4	20	19
-3	19	18
-2	32	-31
-1	76	77
0	44	-46
1	32	-32
2	63	66
3	54	-56
4	6	-4
5	31	31
6	24	-25
K = 0 L =10		
-12	7	6
-11	0	0
-10	5	-5
-9	27	28
-8	44	-43
-7	9	8
-6	36	37
-5	73	-74
-4	33	32
-3	28	27
-2	42	-44
-1	39	38
0	0	-2
1	4	-3
2	12	13
3	21	-22
K = 0 L =12		
-9	26	26
-8	13	-13
-7	2	2
-6	4	5
-5	22	-22
-4	20	21
-3	18	-19
-2	8	-8
-1	26	27
K = 1 L = 0		
1	132	-138
2	158	166
3	107	-101
4	6	6
5	96	94
6	83	-79
7	63	61
8	5	3
9	39	-38
10	36	35
11	25	-25
12	4	-4
K = 1 L = 1		
-12	2	2
-11	0	0
-10	5	-5
-9	1	0
-8	4	4
-7	8	-8
-6	7	6
-5	9	8
-4	5	4
-3	39	34
-2	23	-21
-1	32	-26
0	42	39
1	50	-42
2	58	-49
3	34	31
4	11	11
5	21	-20
6	5	4
7	24	23
8	8	-7
9	13	-14
10	12	12
11	1	1
K = 1 L = 2		
-12	14	13
-11	13	13
-10	33	-34
-9	62	63
-8	25	-24
-7	23	-22
-6	89	89
-5	123	-122
-4	46	44
-3	39	36
-2	145	-152
-1	147	157
0	82	-77
1	61	-57
2	120	118
3	131	-132
4	43	40
5	34	33
6	65	-64
7	65	66
8	13	-12
9	9	-10
10	30	30
11	23	-24
K = 1 L = 3		
-13	3	-2
-12	0	2
-11	6	6
-10	12	-12
-9	3	3
-8	17	17
-7	34	-33
-6	10	-8
-5	48	46
-4	19	-19
-3	33	-31
-2	76	69
-1	45	38
0	74	-69
1	0	0
2	57	54
3	51	-48
4	33	-32
5	44	43
6	6	-5
7	22	-22
8	17	16
9	6	6
10	10	-10
K = 1 L = 4		
-13	26	-26
-12	20	20
-11	8	-8
-10	27	-27
-9	62	60
-8	48	-47
-7	24	24
-6	67	67
-5	106	-106
-4	98	97
-3	21	-20
-2	94	-89
-1	134	134
0	100	-96
1	13	13
2	65	63
3	99	-100
4	55	54
5	15	-15
6	40	-40
7	46	46
8	26	-26
9	6	6
K = 1 L = 5		
-13	5	6
-12	11	-11
-11	1	0
-10	19	19
-9	8	-7
-8	24	-23
-7	25	25
-6	14	14
-5	64	-63
-4	10	9
-3	63	61
-2	55	-51
-1	12	-11
0	71	68
1	11	-11
2	33	-31
3	21	20
4	8	8
5	22	-22
6	2	-1
7	13	13
8	6	-6
K = 1 L = 6		
-13	20	-20
-12	25	26
-11	26	-25
-10	13	-13
-9	40	40
-8	62	-61
-7	44	43
-6	23	23
-5	65	-66
-4	97	97
-3	55	-53
-2	20	-20
-1	84	82
0	84	-86
1	50	50
2	21	22
3	54	-54
4	52	53
5	29	-28
6	14	-14
7	23	24
8	26	-27
K = 1 L = 7		
-13	8	-8
-12	10	10
-11	4	5
-10	21	-21
-9	13	12
-8	22	22
-7	25	-24
-6	6	-5
-5	24	23
-4	13	-12
-3	29	-27
-2	13	11
-1	16	15
0	18	-18
1	6	4
2	19	19
3	10	-10
4	0	-1
5	5	5
6	5	-6
7	0	0
K = 1 L = 8		
-12	25	25
-11	29	-28
-10	6	6
-9	15	16
-8	53	-53
-7	45	45
-6	15	-15
-5	31	-31
-4	69	68
-3	59	-57
-2	16	15
-1	32	32
0	58	-59
1	48	49
2	8	-7
3	20	-19
4	38	39
5	24	-24
K = 1 L = 9		
-12	5	-5
-11	3	-1
-10	4	4
-9	0	0
-8	6	-6
-7	7	6
-6	8	7
-5	7	-6
-4	1	1
-3	2	-1
-2	7	-5
-1	4	3
0	6	-7
1	1	-1
2	9	10
3	3	-3
4	0	-2
K = 1 L =10		
-11	21	-22
-10	19	20
-9	4	0
-8	30	-30
-7	36	37
-6	31	-30
-5	5	-5
-4	37	36
-3	45	-44
-2	27	26
-1	2	3
0	30	-31
1	31	32
2	19	-19
3	1	-1
K = 1 L =11		
-11	3	-1
-10	2	1
-9	1	0
08	7	-8
-7	8	7
-6	6	7
-5	10	-12
-4	5	5
-3	11	11
-2	9	-10
-1	6	-6
0	7	8
1	0	0
K = 1 L =12		
-9	6	-6
-8	9	-9
-7	22	23
-6	26	-26
-5	10	9
-4	10	10
-3	25	-26
-2	25	26
-1	8	-8
K = 2 L = 0		
0	105	-97
1	55	55
2	104	-91
3	41	-38
4	150	156
5	114	-111
6	16	15
7	88	86
8	77	-75
9	25	24
10	16	15
11	24	-24
K = 2 L = 1		
-12	1	0
-11	2	0
-10	10	-11
-9	4	3
-8	1	-2
-7	5	-5
-6	21	21
-5	2	0
-4	10	10
-3	9	10
-2	27	-24
-1	14	15
0	16	-13
1	7	-7
2	38	34
3	10	-10
4	6	5
5	4	5
6	17	-17
7	0	0
8	7	-7
9	4	-3
10	5	5
11	3	-1
K = 2 L = 2		
-12	33	34
-11	32	-32
-10	0	-1
-9	25	25
-8	38	-39
-7	41	41
-6	49	-48
-5	34	31
-4	114	111
-3	156	-163
-2	146	145
-1	86	79
0	193	-218
1	130	128
2	44	-38
3	91	-86
4	75	73
5	61	-60
6	27	27
7	14	15
8	34	-34
9	37	37
10	14	-15
K = 2 L = 3		
-12	1	3
-11	0	1
-10	7	-7
-9	1	2
-8	12	-13
-7	6	-6
-6	11	11
-5	12	-13
-4	20	19
-3	13	12
-2	14	-13
-1	14	13
0	20	-18
1	1	-1
2	15	13
3	9	-9
4	19	18
5	4	4
6	7	-7
7	6	6
8	8	-7
9	4	-3
10	0	0
K = 2 L = 4		
-13	9	8
-12	8	7
-11	36	-36
-10	49	49
-9	19	-18
-8	57	-57
-7	87	87
-6	76	-75
-5	12	-11
-4	81	79
-3	91	-90
-2	112	107
-1	3	3
0	58	-53
1	113	113
2	83	-79
3	0	0
4	36	35
5	65	-64
6	40	41
7	12	-12
8	21	-21
9	33	34
K = 2 L = 5		
-13	1	-1
-12	6	6
-11	2	2
-10	0	0
-9	5	6
-8	11	-11
-7	2	-1
-6	4	-3
-5	17	-16
-4	17	17
-3	3	-2
-2	4	-4
-1	18	17
0	17	-16
1	1	-2
2	0	0
3	8	-8
4	11	10
5	0	0
6	3	3
7	6	7
8	5	-5
K = 2 L = 6		
-13	13	12
-12	8	7
-11	27	-27
-10	43	43
-9	26	-26
-8	15	-15
-7	58	58
-6	78	-79
-5	22	20
-4	13	13
-3	65	-64
-2	78	73
-1	54	-52
0	19	19
1	75	74
2	87	-86
3	48	49
4	23	24
5	56	-58
6	33	33
7	5	-4
K = 2 L = 7		
-13	4	-2
-12	5	5
-11	0	-1
-10	3	3
-9	10	10
-8	6	-6
-7	3	3
-6	2	-2
-5	9	-9
-4	5	5
-3	8	-8
-2	7	6
-1	7	7
0	12	-11
1	7	8
2	4	-4
3	10	-10
4	5	5
5	2	-3
6	0	1
K = 2 L = 8		
-12	0	0
-11	10	-11
-10	23	23
-9	28	-27
-8	32	31
-7	12	11
-6	65	-65
-5	78	79
-4	30	-28
-3	72	-70
-2	80	78
-1	41	-40
0	16	-16
1	33	33
2	19	-19
3	25	25
4	14	-15
5	2	-2
K = 2 L = 9		
-12	0	0
-11	3	-3
-10	2	3
-9	0	2
-8	2	-2
-7	11	11
-6	4	-4
-5	6	-4
-4	5	6
-3	9	-8
-2	3	2
-1	5	4
0	2	-2
1	4	6
2	3	-3
3	2	-1
4	1	0
K = 2 L =10		
-11	5	-5
-10	34	35
-9	35	-35
-8	9	8
-7	21	22
-6	19	-18
-5	22	22
-4	23	-23
-3	13	13
-2	14	14
-1	52	-52
0	34	35
1	3	0
2	32	-33
K = 2 L =11		
-10	2	1
-9	1	0
-8	2	-1
-7	5	5
-6	0	-2
-5	3	2
-4	2	1
-3	6	-6
-2	3	3
-1	1	-1
0	2	-1
1	5	5
K = 3 L = 0		
1	96	90
2	136	-135
3	85	80
4	8	-8
5	76	-74
6	79	77
7	48	-47
8	3	-3
9	33	33
10	33	-32
11	19	19
K = 3 L = 1		
-12	8	8
-11	5	-6
-10	0	0
-9	12	13
-8	9	-9
-7	9	9
-6	7	-7
-5	30	-30
-4	6	6
-3	30	-30
-2	14	-13
-1	24	21
0	33	27
1	56	49
2	14	-14
3	21	19
4	35	33
5	53	-53
6	0	-1
7	21	21
8	23	-22
9	1	0
10	9	9
11	0	0
K = 3 L = 2		
-12	11	-11
-11	11	-11
-10	31	32
-9	48	-48
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7	54	-54
8	16	16
9	10	11
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7	24	-24
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4	51	-50
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7	39	-40
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9	3	-3
K = 3 L = 5		
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4	22	22
5	25	-25
6	14	14
7	6	7
8	10	-9
K = 3 L = 6		
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4	46	-46
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6	10	10
7	23	-23
K = 3 L = 7		
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2	7	-8
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4	2	-2
5	0	1
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K = 3 L = 8		
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1	41	-40
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3	17	18
4	30	-31
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K = 3 L = 9		
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-1	4	-2
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1	0	0
2	4	-3
3	0	2
4	9	-10
K = 3 L =10		
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-4	27	-26
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1	31	-32
2	15	16
K = 3 L =11		
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0	17	18
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7	21	-21
8	30	29
9	35	-35
10	10	8
11	16	16
K = 4 L = 1		
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2	34	-32
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4	11	-10
5	3	-3
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7	10	-9
8	9	9
9	7	7
10	9	-9

Table 3. Continued

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0	58	54
1	90	-88
2	76	71
3	12	11
4	76	-75
5	86	83
6	25	-24
7	24	-23
8	41	41
9	29	-30
10	5	5
K = 4 L = 3		
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-6	13	-13
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2	28	-27
3	15	15
4	18	-18
5	2	-4
6	9	8
7	8	-9
8	12	12
9	3	2
K = 4 L = 4		
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0	62	59
1	90	-88
2	61	60
3	8	-8
4	43	-43
5	58	58
6	29	-28
7	2	-1
8	21	22
K = 4 L = 5		
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-6	5	-4
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-4	17	-16
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-2	3	3
-1	19	-18
0	28	27
1	11	-10
2	4	-4
3	18	19
4	20	-20
5	2	0
6	0	1
7	10	-10
8	6	5
K = 4 L = 6		
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-5	47	-47
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1	56	-55
2	34	33
3	15	-16
4	1	-1
5	17	16
6	30	-31
7	22	23
K = 4 L = 7		
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1	5	-6
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3	7	7
4	7	-8
5	8	9
6	4	-4
K = 4 L = 8		
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1	21	-20
2	55	56
3	38	-39
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K = 4 L = 9		
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1	12	-13
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K = 4 L =10		
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K = 4 L =11		
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6	57	-56
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8	2	-1
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K = 5 L = 1		
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3	24	23
4	17	-16
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8	7	8
9	16	-17
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K = 5 L = 2		
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3	71	-69
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5	26	26
6	46	-45
7	36	35
8	12	-12
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K = 5 L = 3		
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1	28	-27
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3	33	-32
4	38	-37
5	42	41
6	14	-14
7	14	-15
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K = 5 L = 4		
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K = 5 L = 5		
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7	11	12
K = 5 L = 6		
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3	39	-40
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K = 5 L = 7		
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3	14	-13
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5	9	9
K = 5 L = 8		
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2	7	-6
3	17	-18
4	22	24
K = 5 L = 9		
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2	14	14
K = 5 L =10		
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3	23	-23
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5	69	-68
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8	42	-42
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3	30	-29
4	3	1
5	10	10
6	22	-22
7	10	10
8	6	-6
9	4	-4
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5	33	-33
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7	4	5
8	21	-22
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2	22	21
3	24	-24
4	20	20
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8	10	-9
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4	27	26
5	32	-31
6	23	24
7	7	-8
K = 6 L = 5		
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0	21	-21
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3	12	-11
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5	5	-6
6	2	0
K = 6 L = 6		
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3	26	26
4	17	18
5	30	-31
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3	12	-12
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1	14	15
2	16	-15
3	10	10
K = 6 L = 9		
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0	8	-8
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K = 7 L = 0		
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4	0	-2
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7	18	-18
8	4	-2
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3	1	0
4	34	34
5	33	-32
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7	15	16
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K = 7 L = 2		
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1	24	24
2	46	-46
3	35	34
4	18	-18
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6	27	27
7	23	-23
K = 7 L = 3		
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3	13	-13
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K = 7 L = 4		
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1	4	-4
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3	39	40
4	27	-27
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K = 7 L = 5		
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2	37	-37
3	17	18
4	10	11
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K = 7 L = 6		
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2	5	-4
3	24	25
4	22	-24
K = 7 L = 7		
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0	10	-7
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2	11	-12
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K = 7 L = 8		
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0	23	23
1	18	-18
K = 7 L = 9		
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-4	3	-5
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K = 8 L = 0		
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1	41	-41
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4	25	-25
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6	7	7
7	7	-7
K = 8 L = 1		
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1	14	14
2	20	-19
3	23	23
4	6	-5
5	5	-5
6	18	19
7	14	-15
K = 8 L = 2		
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1	37	-36
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3	1	0
4	33	-33
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6	9	-9
K = 8 L = 3		
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1	0	0
2	21	-22
3	19	19
4	9	-9
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K = 8 L = 4		
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4	22	-23
5	23	23
K = 8 L = 5		
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-5	18	19
-4	11	-12
-3	9	10
-2	7	7
-1	14	-15
0	20	21
1	14	-14
2	9	-9
3	15	16
4	17	-17
K = 8 L = 6		
-8	3	2
-7	17	-17
-6	24	25
-5	22	-23
-4	8	-8
-3	29	30
-2	31	-34
-1	10	11
0	19	20
1	19	-20
2	15	15
K = 8 L = 7		
-7	15	-15
-6	2	1
-5	12	12
-4	21	-22
-3	14	14
-2	5	6
-1	11	-10
0	14	15
1	7	-7
K = 9 L = 0		
1	26	-26
2	30	31
3	19	-17
4	4	-4
5	15	15
6	19	-20
K = 9 L = 1		
-6	5	5
-5	10	9
-4	21	-23
-3	19	20
-2	8	-9
-1	15	-16
0	31	31
1	20	-20
2	1	-1
3	13	15
4	16	-16
5	6	5
K = 9 L = 2		
-6	20	22
-5	19	-21
-4	7	9
-3	9	10
-2	20	-21
-1	25	26
0	14	-15
1	6	-5
2	26	27
3	26	-27
4	9	10
K = 9 L = 3		
-6	9	9
-5	13	14
-4	17	-18
-3	9	9
-2	5	-4
-1	3	3
0	1	1
1	18	-18
2	28	28
3	6	-7
4	18	-19
K = 9 L = 4		
-6	9	9
-5	25	-27
-4	22	23
-3	0	-2
-2	20	-21
-1	26	28
0	15	-16
1	2	0
2	14	14
3	17	-18
K = 9 L = 5		
-6	17	19
-5	16	-17
-4	1	-2
-3	28	31
-2	27	-29
-1	1	0
0	19	19
1	17	-18
K = 9 L = 6		
-5	14	-15
-4	17	18
-3	12	-13
-2	1	-3
-1	16	18
K =10 L = 0		
0	7	-7
1	13	13
2	9	-8
3	4	-5
K =10 L = 1		
-3	8	10
-2	12	-14
-1	20	21
0	5	-6
1	10	-10
2	19	20
K =10 L = 2		
-3	26	-29
-2	15	17
-1	9	10
0	27	-29
1	23	24
2	1	0
K =10 L = 3		
-3	2	2
-2	12	-14
-1	17	19
0	9	-8

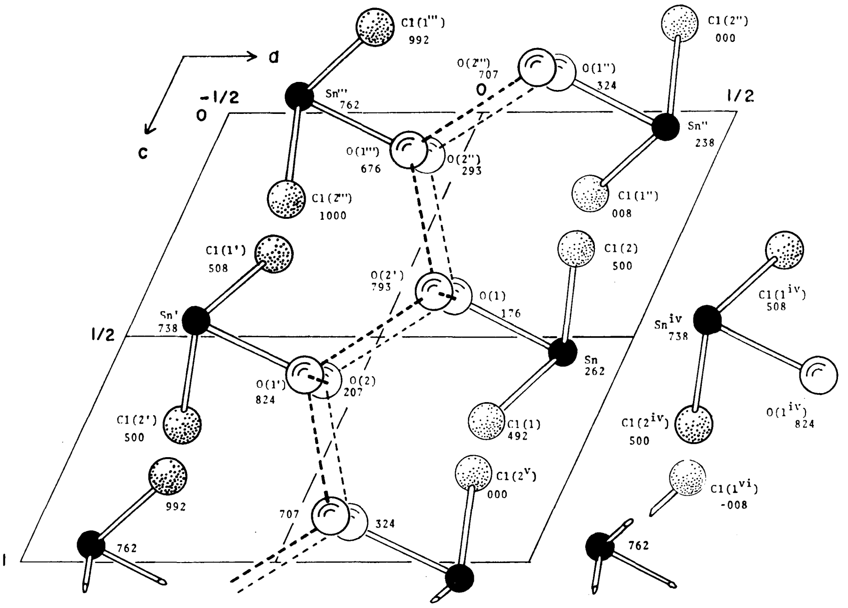

Fig. 2. The crystal structure viewed along the monoclinic *b* axis. Broken lines indicate hydrogen bonds.

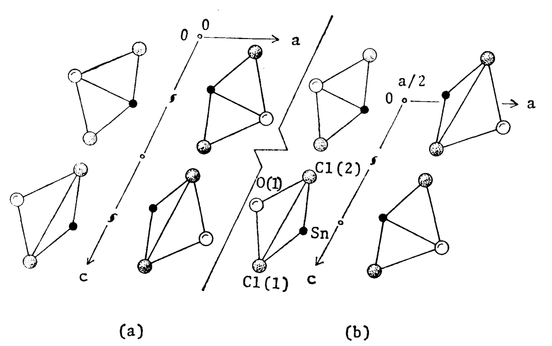

Fig. 3. Comparison of the earlier structure (a) with the present one (b).

trated in Fig. 4. The tin atom is bonded to two chlorine atoms at distances of 2.50 and 2.56 Å and one oxygen atom at a distance of 2.33 Å; its pyramidal angles are 87.9, 86.9, and 85.0°. Four additional chlorine atoms at distances of 3.21, 3.34, 3.42, and 3.64 Å complete an environment of the tin atom (Table 4(b)). The difference between the two Sn–Cl bond lengths in each pyramid, 0.06 Å, is significantly large, this being thirty times the standard deviation. This might be reasonable if the effects of the lone-pair electrons of a tin atom in the adjacent complex and possibly of the hydrogen bonds are different for two chlorine atoms. The average Sn–Cl distance of 2.53 Å

Table 4. Distances (Å) and angles (°) in $SnCl_2 \cdot 2H_2O$ (Standard deviations in parentheses)

(a)	In the aquocomplex $SnCl_2(OH)_2$			
	Sn–Cl (1)	2.500 (2)	Cl (1)–Sn–Cl (2)	87.85 (8)
	Sn–Cl (2)	2.562 (2)	Cl (1)–Sn–O (1)	84.96 (14)
	Sn–O (1)	2.325 (5)	Cl (2)–Sn–O (1)	86.86 (13)
(b)	On other side of the Sn atom			
	Sn–Cl (1″)	3.416 (3)	Sn–Cl (1^{VI})	3.654 (2)
	Sn–Cl (2^{IV})	3.209 (2)		
	Sn–Cl (2^{V})	3.336 (2)		
(c)	Around the water oxygen atoms			
	O (1)–O (2)	2.800 (9)	O (2′)–O (1‴)–O (2‴)	109.80 (23)
	O (1)–O (2″)	2.736 (6)	O (2″)–O (1‴)–O (2′)	104.98 (20)
	O (1‴)–O (2″)	2.794 (7)	O (2″)–O (1‴)–O (2‴)	89.57 (23)
	Sn‴–O (1‴)–O (2′)	117.56 (25)	O (1)–O (2″)–O (1″)	112.89 (23)
	Sn‴–O (1‴)–O (2″)	112.84 (20)	O (1)–O (2″)–O (1‴)	111.17 (22)
	Sn‴–O (1‴)–O (2‴)	117.95 (20)	O (1″)–O (2″)–O (1‴)	90.43 (23)

Symmetry relations

Atom	*x*	*y*	*z*
Atom′	$-x$	$1.0-y$	$1.0-z$
Atom″	x	$0.5-y$	$z-0.5$
Atom‴	$-x$	$0.5+y$	$0.5-z$
Atom$^{\mathrm{IV}}$	$1.0-x$	$1.0-y$	$1.0-z$
Atom$^{\mathrm{V}}$	x	$0.5-y$	$0.5+z$
Atom$^{\mathrm{VI}}$	$1.0-x$	$y-0.5$	$1.5-z$

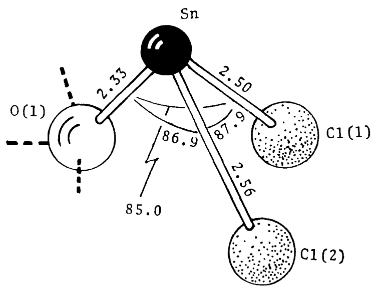

Fig. 4. The geometry of trigonal pyramid, $SnCl_2(OH)_2$ in $SnCl_2\cdot 2H_2O$.

is close to those of 2.54, 2.54, and 2.63 Å for $K_2SnCl_4\cdot H_2O$ and also of 2.50, 2.52, and 2.55 Å for $CsSnCl_3$, both of which contain pyramidal trichlorotin(II) complex ions.[5,6]

Molecules of anhydrous tin(II) chloride, $SnCl_2$, in the vapor phase are bent with a bond angle of 95° and with lengths of 2.42 Å.[7] In contrast with these, the tin atom in the crystalline state forms a pyramid with three chlorine atoms at 2.67, 2.78, and 2.78 Å and with Cl–Sn–Cl bond angles 78.0, 79.6, and 79.6°. It is noted here that three additional chlorine atoms at 3.06, 3.18, and 3.28 Å from the tin atom complete the distorted octahedron.[8] The increase in the Sn–Cl bond length of the molecular form must imply an increase in ionic character of this bond. A comparison of these coordinations of the tin atoms with that of $SnCl_2\cdot 2H_2O$ indicates that an ionicity of the Sn–Cl bond in dichloroaquotin(II) complex molecules is less than that in the anhydrous crystal. This view is supported by ^{119}Sn Mössbauer studies, which have shown that the isomer shifts for the tin(II) atoms in $SnCl_2\cdot 2H_2O$ and $SnCl_2$ are $+(1.30—1.70)$ and $+(2.40—2.50)$ mm/sec respectively (relative to α-Sn), as compared with a calculated value of $+5.6$ mm/sec for the hypothetical Sn^{2+} ion.[9]

On the other hand, the Sn–O bond length in the dichloroaquotin(II) complex was found to be 2.32 Å which was larger than the previous value (2.16 Å) given by K & G and also longer than that (2.21 Å) in tin(II) oxide.[10] A recent X-ray work on $KSn(HCOO)_3$ has shown that $Sn(HCOO)_3^-$ ions have again pyramidal configurations with Sn–O distances of 2.14, 2.17, and 2.18 Å and with bond angles of 78.4, 82.9, 83.2°.[11] A comparison of these values suggests that the Sn–O bond in the $SnCl_2(OH_2)$ complex is not essentially covalent, or at least less covalent than those in $KSn(HCOO)_3$ and SnO. However, it must be pointed out that the tin(II) atom in $SnSO_4$ has also a definite pyramidal three coordination with Sn–O bond distances of 2.27, 2.27, 2.25 Å and O–Sn–O angles of 79.0, 77.1, 77.1.[12]

The pyramidal bond angles of 85.0, 86.9, and 87.9° for $SnCl_2\cdot 2H_2O$ are considerably less than the tetrahedral value required by the sp^3 hybrid configuration, as observed in many tin(II) compounds. Such the pyramidal three coordination of the tin atom can be explained in terms of strong repulsion between lone pair and bond pair from the covalent viewpoint or in terms of an unsymmetrical crystal field distorsion from the electrostatic viewpoint. The experimental values of the bond lengths precisely determined as well as the Mössbauer isomer shift support the idea that the bonding in the dichloroaquotin(II) complex is considerably ionic in character.

Arrangement of the Hydrogen Bonds

Figure 5 shows interatomic distances and bond angles concerning two kinds of the water molecules, one of which, $H_2O(1)$, is coordinated with the tin atom and the other $H_2O(2)$ is not so. Both water oxygen atoms have approximately tetrahedral configurations. These coordinations suggest that one of the lone pairs of oxygen O(1) is specifically directed toward the tin atom and the other is toward a hydrogen bond donor oxygen, namely $H_2O(1)$ is of type H according to the classification by Chidambaram *et al.*[13] Whereas, the water molecule $H_2O(2)$ is probably of type E with the two lone pairs directed toward two hydrogen bond donor oxygens.

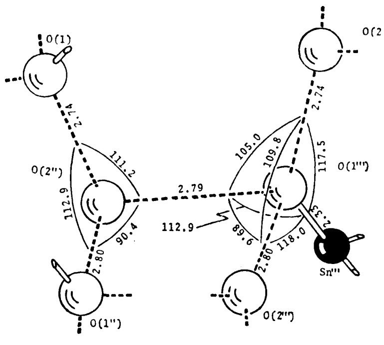

Fig. 5. The coordination of two kinds of water molecules.

The most striking feature of the structure is the arrangement of these water molecules, in particular their hydrogen bonding scheme. Different types of the water molecules are alternately connected by hydrogen bonds and the resulting sheets run parallel to (100) planes throughout the structure (Fig. 2). As mentioned earlier, this compound undergoes the phase transition with sharp peaks of the dielectric constant and the DC conductivity at −55 °C.[4] The remarkable dielectric dispersion observed in the high temperature phase, only when the electric field is applied in the (100) plane, can easily be understood on the basis of the

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present structure. Thus, in combination of the NMR results the phase transition can be interpreted in terms of the order-disorder model of the hydrogen atoms within the two-dimentional network of O–H—O hydrogen bonds.

It is interesting to note that there are only three O–H···O hydrogen bonds with distances of 2.736, 2.794, and 2.800 Å and with O··O··O angles near the tetrahedral angle against four available protons of two non-equivalent water molecules. Direct location of these hydrogen atoms was studied by proton and deuteron magnetic resonance and also neutron diffraction experiments.[14,15] These results confirmed our expectation that the hydrogen atom free from the O–H···O bonds should be directed toward one or two chlorine atoms. The further details will be published soon.

As given in Table 2, thermal parameters for all atoms are noticeably large, indicating large thermal motion. Actually this crystal dissolves in its own water of crystallization at about 40 °C.

In passing through the transition and also on deuterium substitution, no significant change in the non-hydrogen atom positions could be detected from the X-ray and the subsequent neutron diffraction works. At the transition point, however, the layer spacing, $a\sin\beta$, of $SnCl_2 \cdot 2H_2O$ did reduce suddenly by an amount of 0.02 Å and the line profiles of all (h00) reflections in the low temperature phase became broader, their half widths being twice the corresponding ones in the high temperature phase.

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