770. *The Crystal Structure of Stannous Chloride Dihydrate.*

By B. Kamenar and D. Grdenić.

The crystal structure of stannous chloride dihydrate has been determined by methods of *X*-ray analysis. It follows from interatomic distances that the compound is dichloroaquotin(II) hydrate, $Sn(OH_2)Cl_2,H_2O$.

The molecules of aquo-complex and water of crystallization form alternate double layers parallel to the (100) planes and linked by hydrogen bonds. The aquo-complex is pyramidal which shows that the non-bonding pair of electrons of the tin atom is stereochemically active; the bond angles are low, proving a strong " lone-pair–bond-pair repulsion."

The crystal structure of such a common and simple compound as stannous chloride dihydrate has been studied in order to determine the co-ordination of water molecules around the tin atom, a point not only of interest for the structural chemistry of tin(II) compounds, but also having a general significance for the stereochemistry of molecules or complexes with a lone pair of electrons on the central atom.[1]

The molecule of anhydrous stannous chloride is bent, with a bond angle of about 95°, as determined by the electron diffraction of the vapour.[2] This angle is a result of the influence of the lone pair of the tin atom on the bonding pairs, giving a triangular arrangement of pairs of electrons according to Sidgwick and Powell's rule.[3] Thus, there are two possibilities for dihydrated stannous chloride, as pointed out in our preliminary communication [4]—one or both water molecules may be co-ordinated to the tin. In the former case the complex would have to be pyramidal as a result of the tetrahedral arrangement of one non-bonding and three bonding pairs of electrons. In the latter, a distorted pyramidal configuration, as in the SnO or $TeCl_4$ structure, would result into one non-bonding and four bonding pairs of electrons. The complex with one co-ordinated water molecule with $5s^2p^6$-electrons in a tetrahedral hybridization was *a priori* more probable and has been shown to be correct by the present investigation.

Experimental

Crystallographic and X-*Ray Data*.—The crystals of stannous chloride dihydrate, prepared from a saturated aqueous solution, are monoclinic prisms elongated along the *c*-axis direction. The crystals were described and examined crystallographically by Marignac; [5] in the present paper all crystallographic data are referred to the axes chosen by this author. The unit cell as determined from oscillation photographs has the dimensions: $a = 9{\cdot}38$ Å, $b = 7{\cdot}22$ Å, $c = 9{\cdot}02$ Å, $\beta = 114° 58'$. The axial ratios $a:b:c = 1{\cdot}299:1:1{\cdot}249$ agree well with the values $a:b:c = 1{\cdot}2888:1:1{\cdot}2452$ (and $\beta = 114° 58'$) given by Marignac. There are four formula units in the unit cell [calculated density (D_c) 2·707, measured density (D_m) 2·710; $M = 225{\cdot}66$; $U = 553{\cdot}8$ Å^3, $F(000) = 416$]. Nickel-filtered Cu-*K* radiation was used. Systematic extinctions were observed only for $0k0$ reflexions with k odd and for $h0l$ with l odd. The space group is, therefore, $P2_1/c$ (C^5_{2h}, No. 14).

Intensity Measurements.—Specimens cylindrically ground along the *b*- and the *c*-axis with diameters 0·39 and 0·33 mm., respectively, were sealed in Lindemann glass capillaries to protect them from the atmospheric moisture. All possible ($h0l$) and ($hk0$) reflexions were recorded on multiple-film Weissenberg photographs by means of a Nonius integrating camera. The relative intensities of the reflexions were determined from the optical densities which were measured in the centre of each spot by means of a microdensitometer and corrected by means of the characteristic curve of the film. The number of $hk0$ and $h0l$ reflexions observed was 71 and 84 (out of 85 and 98 possible reflexions), respectively. The absorption correction

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[1] Gillespie and Nyholm, *Quart. Rev.*, 1957, **11**, 339.

[2] Lister and Sutton, *Trans. Faraday Soc.*, 1941, **37**, 406.

[3] Sidgwick and Powell, *Proc. Roy. Soc.*, 1940, *A*, **176**, 153.

[4] Grdenić and Kamenar, *Proc. Chem. Soc.*, 1960, 312.

[5] Marignac, *Ann. Mines*, 1856, **9**, 5.

(μ 470 cm.$^{-1}$) was carried out with the help of Tables.[6] The corrections for polarization and Lorentz factor were made in the usual way.

Determination of the Structure.—By using the values of the tin and chlorine co-ordinates, evaluated from the [010] Patterson projection, the signs for observed structure factors $F_0(h0l)$ were calculated, contributions of the oxygen atoms being neglected. The Fourier projection along [010], computed with these signs, is shown in Fig. 1. The peaks of all but oxygen atoms are well resolved. In the next step the Fourier projections along [001] were computed (Fig. 2) with the signs of $F_0(hk0)$ obtained by taking into account the contributions only of tin and chlorine atoms. The x-co-ordinates from the [010] Fourier projection and the y-co-ordinates from the [001] Patterson projection were used. Since the y-co-ordinate for tin atom is almost exactly $\frac{1}{4}$, two and two atoms overlap in [001] projection, giving peaks of double height. Both chlorine atoms of each molecule are also concealed within common peaks in this projection, while the oxygen peaks of water molecules are but slightly resolved. The diffraction effect of the tin atom is apparent and not without influence on the position of the nearest peaks, especially on the oxygen peak. Improved resolution was achieved in the [010] and [001] difference Fourier projections which were computed with (F_0-F_{Sn}) as coefficients. The final values for the x,y-co-ordinates of the oxygen atoms were obtained by graphical resolution of the double peak into two components for which the form of a Gaussian curve had been assumed. The mean values of the standard deviations in the atomic co-ordinates were calculated by Cruickshank's method.[7] They are listed together with the final atomic co-ordinates in Table 1.

TABLE 1. *Atomic co-ordinates and their standard deviations*

	x/a	y/b	z/c	$\sigma(x)$ (Å)	$\sigma(y)$ (Å)	$\sigma(z)$ (Å)
Sn	0·126	0·250	0·217	0·0033	0·0056	0·0041
Cl(1)	0·196	0·005	0·448	0·0111	0·0186	0·0142
Cl(2)	0·213	0·001	0·065	0·0140	0·0186	0·0182
O(1)	0·374	0·320	0·327	0·0294	0·0656	0·0404
O(2)	0·436	0·705	0·358	0·0297	0·0738	0·0317

Numbering: O(1) belongs to $Sn(OH_2)Cl_2$ complex, O(2) to the water of crystallization.

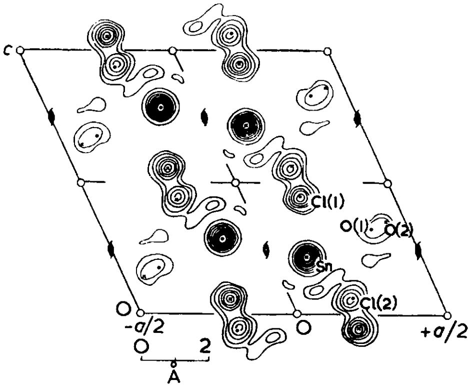

FIG. 1. *Electron-density projection along the b-axis. Contours are at equal intervals of* 10 eÅ^{-2} *for tin and* 5 eÅ^{-2} *for chlorine and oxygen peaks. The zero electron density line is omitted. The crosses denote the final atomic positions derived from difference syntheses.*

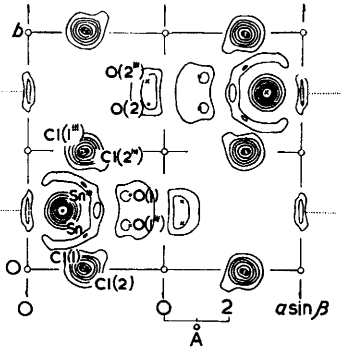

FIG. 2. *Electron-density projection along the c-axis. Contours are at equal intervals of* 30 eÅ^{-2} *for tin,* 10 eÅ^{-2} *for chlorine, and* 5 eÅ^{-2} *for oxygen atom peaks, the zero electron-density line being omitted. The crosses denote the final atomic positions derived from difference syntheses.*

Structure factors were calculated by using values for the atomic scattering factors, given in Tables,[8] multiplied by an average temperature factor exp $(-B \sin^2 \theta/\lambda^2)$ with $B = 2{\cdot}5$ and

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[6] "International Tables for X-Ray Crystallography," Internat. Union of Crystallography, The Kynoch Press, Birmingham, 1959, Vol. II, p. 295.

[7] Cruickshank, *Acta Cryst.*, 1949, **2**, 65.

[8] Sagel, "Tabellen zur Röntgenstrukturanalyse," Springer Verlag, Berlin, 1958, p. 106.

1·8 Å² for $h0l$ and $hk0$ reflexions, respectively. These values of B, as well as the scale factor, were obtained by Wilson's statistical method [9] and subsequently improved by plotting ln (F_o/F_c) against $(\sin\theta/\lambda)$.[2]

TABLE 2. *Observed and calculated structure amplitudes.*

(The minimum observable values are given in parentheses.)

$h0l$	F_o	F_c	$h0l$	F_o	F_c	$h0l$	F_o	F_c	$h0l$	F_o	F_c	$hk0$	F_o	F_c	$hk0$	F_o	F_c
002	92	−101	602	50	32	$80\bar{6}$	0(6)	−9	$7,0,\overline{10}$	0(6)	−1	120	59	−58	350	58	−57
004	61	74	702	43	−39	$90\bar{6}$	30	24	$8,0,\overline{10}$	48	43	220	99	−86	450	0(8)	−5
006	31	−42	802	49	−54	$10,0,\bar{6}$	45	45	$9,0,\overline{10}$	30	34	320	48	41	550	56	54
008	44	−36	902	35	−31	$11,0,\bar{6}$	26	34	$10,0,\overline{10}$	0(6)	8	420	147	164	650	66	68
0,0,10	0(6)	−1	$10\bar{4}$	22	34	106	82	−89	1,0,10	0(6)	−8	520	121	122	750	38	37
100	111	122	$20\bar{4}$	123	−151	206	43	−39				620	0(8)	9	850	0(8)	−1
200	101	−75	$30\bar{4}$	107	−131	306	25	−14	$hk0$			720	98	−100	950	24	−29
300	170	−171	$40\bar{4}$	68	−77	406	0(6)	4	100	115	120	820	84	−91	160	53	−54
400	122	−122	$50\bar{4}$	32	17	506	28	24	200	106	−76	920	31	−25	260	38	−35
500	0(6)	−6	$60\bar{4}$	94	98	606	33	39	300	164	−173	10,2,0	17	27	360	32	30
600	0(6)	3	$70\bar{4}$	58	59	$10\bar{8}$	68	−76	400	132	−127	130	96	97	460	77	83
700	41	24	$80\bar{4}$	39	35	$20\bar{8}$	32	−37	500	0(8)	−5	230	134	139	560	76	83
800	49	43	$90\bar{4}$	0(6)	1	$30\bar{8}$	22	−25	600	0(8)	4	330	87	83	660	0(8)	2
900	46	48	$10,0,\bar{4}$	29	−23	$40\bar{8}$	22	15	700	47	27	430	0(8)	10	760	48	−63
10,0,0	16	13	$11,0,\bar{4}$	34	−39	$50\bar{8}$	26	19	800	55	50	530	85	−82	860	43	−56
$10\bar{2}$	37	−43	$12,0,\bar{4}$	24	−29	$60\bar{8}$	47	47	900	52	58	630	88	−85	170	41	42
$20\bar{2}$	58	40	104	110	125	$70\bar{8}$	50	64	10,0,0	20	17	730	57	−55	270	65	70
$30\bar{2}$	48	45	204	93	87	$80\bar{8}$	0(6)	7	020	131	−105	830	0(8)	4	370	45	46
$40\bar{2}$	175	179	304	0(6)	−5	$90\bar{8}$	40	−40	040	191	196	930	38	44	470	0(8)	0
$50\bar{2}$	88	87	404	50	−53	$10,0,\bar{8}$	55	−59	060	36	−33	10,3,0	39	42	570	34	−35
$60\bar{2}$	40	−35	504	81	−76	$11,0,\bar{8}$	19	−25	080	69	81	140	104	101	670	50	−57
$70\bar{2}$	114	−116	604	43	−40	108	32	40	110	145	−142	240	57	−49	770	17	−27
$80\bar{2}$	94	−94	704	0(6)	6	208	60	71	210	166	−166	340	126	−126	180	46	54
$90\bar{2}$	0(6)	−4	804	28	31	308	58	44	310	103	−99	440	83	−77	280	28	−28
$10,0,\bar{2}$	41	48	$10\bar{6}$	28	19	408	0(6)	−11	410	0(8)	−13	540	0(8)	−16	380	49	−61
$11,0,\bar{2}$	41	37	$20\bar{6}$	101	117	$1,0,\overline{10}$	34	32	510	100	107	640	0(8)	6	480	26	−34
102	94	−101	$30\bar{6}$	100	126	$2,0,\overline{10}$	38	46	610	92	84	740	31	22	580	0(8)	−11
202	142	−140	$40\bar{6}$	10	6	$3,0,\overline{10}$	27	37	710	71	65	840	36	36	190	31	−35
302	45	37	$50\bar{6}$	49	−47	$4,0,\overline{10}$	33	−22	810	0(8)	−2	940	44	47	290	32	−46
402	104	113	$60\bar{6}$	87	−98	$5,0,\overline{10}$	78	−77	910	45	−51	150	80	−73	390	14	−27
502	110	108	$70\bar{6}$	54	−57	$6,0,\overline{10}$	35	−45	10,1,0	38	−44	250	110	−109			

The observed F_o and calculated F_c structure amplitudes are given in Table 2. The reliability indices have values $R(h0l) = 0{\cdot}140$ and $R(hk0) = 0{\cdot}120$. If unobserved reflexions are included with the values given in Table 2 (0·578 × minimum observable value [10]), we have $R(h0l) = 0{\cdot}129$ and $R(hk0) = 0{\cdot}092$. The ratio of the smallest to the largest absorption factor was 1 : 46 and 1 : 42 for $h0l$ and $hk0$ reflexions, respectively.

DISCUSSION

The values of the intramolecular and intermolecular distances in the crystal structure of stannous chloride dihydrate are given in Table 3. Their standard errors were calculated from the standard deviations of the atomic co-ordinates (Table 1) by means of Ahmed and Cruickshank's formula.[11]

TABLE 3. *Interatomic distances* (Å) *and bond angles.*

(a) *Intramolecular.*

Sn–Cl(1)	2·59 ± 0·02	Cl(1) . . . Cl(2)	3·53 ± 0·03	Cl–Sn–Cl	85·2 ± 1°
Sn–Cl(2)		Cl(1) . . . O(1)	3·27 ± 0·06	Cl–Sn–O	86·6 ± 1
Sn–O(1)	2·16 ± 0·04	Cl(2) . . . O(1)	3·19 ± 0·06	O–Sn–Cl	83·4 ± 1

(b) *Intermolecular.*

Sn . . . Cl(2‴)	3·40 ± 0·02	Cl(1) . . . Cl(2‴)	3·70 ± 0·03	O(1) . . . O(2)	2·83 ± 0·09
Sn . . . Cl(1‴)	3·29 ± 0·02	Cl(2) . . . Cl(1‴)	3·70 ± 0·03	O(1) . . . O(2′)	2·65 ± 0·06
Sn . . . Cl(1″)	3·31 ± 0·02	Cl(2) . . . Cl(2′)	3·66 ± 0·03	O(1) . . . O(2″)	3·02 ± 0·05
Sn . . . Cl(2′)	3·62 ± 0·02				

Numbering of atoms: single prime denotes centre of symmetry, double prime screw axis, triple prime glide-plane symmetry relation to the atom defined by the co-ordinates in Table 1.

The main result is to prove the existence of a neutral aquo-complex, the $SnCl_2(OH_2)$ molecule, with a pyramidal configuration with the geometry given in Fig. 3. The Sn–Cl

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[9] Wilson, *Nature*, 1942, **150**, 152.

[10] Hamilton, *Acta Cryst.*, 1955, **8**, 185.

[11] Ahmed and Cruickshank, *Acta Cryst.*, 1953, **6**, 385.

bond length is greater than the values for anhydrous stannous chloride (2·42 Å) and for stannic chloride (2·30 Å) and its methyl derivatives.[12] Until there are more data available, this bond lengthening can be interpreted as a weakening of the tin–chlorine link under the influence of the co-ordinated water.

The length of the Sn–O bond which proves a strong link between tin and oxygen is very significant. It is even less than the Sn–O distance (2·21 Å) in the structure of stannous oxide,[13] which may be explained by the greater polarizability of the water molecule in the sense $\mathrm{Cl_2\bar{S}n\text{–}\overset{+}{O}H_2}$. Moreover, we have here the oxygen atom which belongs only to one tin atom whereas in SnO the charge is spread throughout a polymeric layer of atoms in four co-ordination. Therefore, the Sn–O bond in $\mathrm{Cl_2Sn(OH_2)}$ can be considered as essentially covalent or, at least, similar in nature to the Sn–O bond in stannous oxide.

The values of the bond angles are also significant, since such a considerable departure from the ideal value for tetrahedral hybridization could hardly be expected. The similar decrease in the bond angles for the series of hydrides of the VB and VIB elements has been satisfactorily explained by bond lengthening accompanied by a reduction in the repulsion between hydrogen atoms.[14] In the present case, there is no model for comparison but, nevertheless, the same explanation should be valid. Moreover, in the molecule of $\mathrm{SnCl_2(OH_2)}$, there is attraction between chlorine and positively charged oxygen, producing an additional decrease in the bond angles.

FIG. 3. *Pyramidal dichloroaquotin*(II) *complex with the values of bond lengths and angles.*

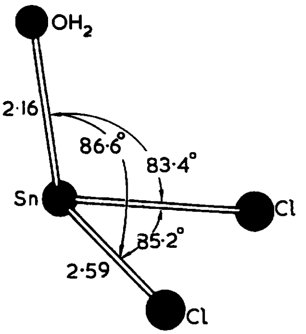
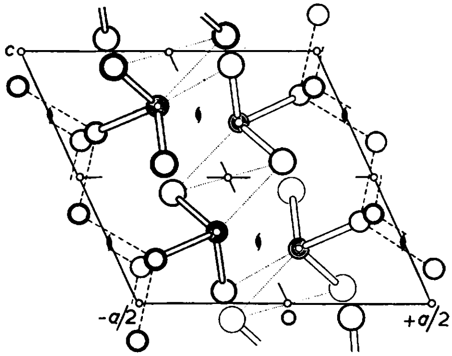


FIG. 4. *The structure of stannous chloride dihydrate viewed down the b-axis. Large circles depict chlorine atoms, small circles water molecules, and shaded circles tin atoms. Covalent bonds are shown by lines, hydrogen bonds by broken lines, and van der Waals contacts by dotted lines.*



The crystal structure of dichloroaquotin(II) hydrate is best described by means of the projection along the *b*-axis, as in Fig. 4. The molecules of aquo-complex form double layers, parallel to the (100) plane and alternating with the layers of water of crystallization. The pyramids of $\mathrm{Cl_2Sn(OH_2)}$ face one another with their apices occupied by tin atoms towards the inside of the layer, while co-ordinated water molecules point outwards from the layer. There is no direct contact between the $\mathrm{Cl_2Sn(OH_2)}$ layers since they are separated by a layer of water of crystallization. Each molecule of water of crystallization acts as a bridge between two co-ordinated waters of adjacent layers at a O–O distance of 2·65 Å and 2·83 Å, respectively, and *vice versa*. These distances, as well as their steric arrangement, undoubtedly indicate hydrogen bonding due to hydrogen atoms from co-ordinated water. The O–O distance of 3·02 Å is also due to a hydrogen bond formed by a hydrogen atom which belongs to water of crystallization.

[12] Wells, " Structural Inorganic Chemistry," 2nd edn., Clarendon Press, Oxford, 1952, p. 368.
[13] Moore and Pauling, *J. Amer. Chem. Soc.*, 1941, **63**, 1392.
[14] Linnett and Mellish, *Trans. Faraday Soc.*, 1954, **50**, 665.

The intermolecular chlorine atom contacts are realized between layers at a distance of 3·66 Å, as well as within the layer between the molecules related by a glide plane at a distance of 3·70 Å. There are four Sn–Cl contacts in the layer: two between the sheets of $Cl_2Sn(OH_2)$ molecules amounting to 3·31 and 3·61 Å; and two in the sheet, amounting to 3·29 and 3·40 Å. The former two contacts are made exactly laterally to the direction along which one expects the lone pair to point. The mean value of these Sn–Cl distances is equal to the sum of atomic radii (1·80 Å for chlorine; 1·51 Å for tin, the intermetallic radius in white tin [15]).

The physical and chemical properties of hydrated stannous chloride are well explained by our results. The crystals show marked cleavage parallel to the (100) plane. The dehydration under controlled conditions (80°, atmospheric pressure) leads to the loss of only one mol. of water, which is obviously the water of crystallization, giving dichloroaquotin(II), which proves the considerable strength of the co-ordinated link of water to tin.

Department of Inorganic and Structural Chemistry,
Rudjer Bošković Institute, Bijenička 54,
Zagreb, Yugoslavia.

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[15] Wells, ref. 12, p. 674.