

The Crystal Structure of Hydrazinium Chlorostannate, $(\text{N}_2\text{H}_5)_2\text{SnCl}_6$

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$(\text{N}_2\text{H}_5)_2\text{SnCl}_6$ is orthorhombic, *Pnca*, with $a = 11.8_4$, $b = 11.8_4$, $c = 8.2_3$ Å, and with four molecular units in the unit cell. The structure may be compared with that of K_2PtCl_6 , but alternate layers of tin atoms (together with their attached chlorine atoms) are shifted by $\frac{1}{4}$ of the cell edge in the direction of the short axis, and the SnCl_6 octahedra are twisted alternately right and left handedly through a small angle. The hydrazinium ion appears to have space for a considerable amplitude of vibration while retaining plausible hydrogen bond lengths and angles with neighbouring chlorine atoms.

1. Introduction

There has been some uncertainty concerning the structure of hydrazinium chlorostannate and related substances (Druce, 1922; Pugh & Stephen, 1952). The investigation of the crystal structure of $(\text{N}_2\text{H}_5)_2\text{SnCl}_6$ was one of several undertaken at the suggestion of the latter authors to throw light on the modes of linking in these compounds.

Most of the X-ray reflexions were consistent with a face-centred tetragonal structure. But there were a few, mainly of low intensity, which did not fit this symmetry, and it was a point of interest in the work to distinguish between a lower symmetry and the possible effects of twinning. The nature of the departure from the simpler and more symmetrical structure was established by the use of these weak reflexions.

2. Preliminary observations

The crystals were white or clear, and usually long with a nearly square cross-section. Faces parallel to the needle axis (c) were found to be perpendicular to each other. A large proportion of the crystals appeared under the microscope to be single with no obvious indications of twinning. They were moderately deliquescent.

3. Experimental data

The symmetry of oscillation photographs taken with $\text{Cu } K\alpha$ radiation showed that the three axes were mutually perpendicular. The cell dimensions are

$$a = 11.8_4, \quad b = 11.8_4, \quad c = 8.2_3 \text{ Å.}$$

The density is 2.40 g.cm.^{-3} , giving four formula units of $(\text{N}_2\text{H}_5)_2\text{SnCl}_6$ per unit cell.

From the oscillation photographs and from zero-layer-line Weissenberg photographs taken with molybdenum radiation it was found that $0kl$ reflexions were absent if $(k+l)$ was odd, $h0l$ reflexions were absent if l was odd and $hk0$ reflexions were absent if h was odd.

These systematic absences imply the space group *Pnca* of the orthorhombic system (No. 60, *International Tables for X-ray Crystallography*, 1952). In addition to these systematic absences there were other properties of the sets of reflexions which helped to suggest the postulated structure. Thus in $hk0$ reflexions k was even except for a few weak reflexions. There were relatively few reflexions of type hkl for which $(k+l)$ was odd. Further, hkl reflexions with $(k+l)$ odd were few and weak when h was 3 or less, and never very intense for high values of h . For these reasons, and because the a and b axes were equal (or nearly equal), it was thought possible that the crystal was tetragonal and that the differences between h and k shown above required closer investigation. Additional photographs were therefore taken using different specimens and it was found that reflexions 530 and 510 occurred with one specimen only and were discarded, but reflexions of type $hk0$ with h even and k odd (410, 810 and a few others) occurred with all the crystals used and with the same relative intensities. The acceptance of these k -odd reflexions as genuine implied that the crystal was orthorhombic instead of tetragonal. As the departure from tetragonal symmetry was shown by only a few reflexions, mostly of low intensity, no further use was made of space-group methods until the main structure had been established by means of Patterson and Fourier summations and found to agree completely with the space group mentioned.

Intensity measurements for the Patterson and Fourier summations were made using Weissenberg photographs taken with molybdenum radiation and a zirconium filter. Two films were placed in the camera at the same time, separated by tin foil 0.07 mm. thick to give different exposures. Molybdenum radiation was used because absorption with copper radiation was excessive. The intensities of the reflexions were measured using a visual scale and were then reduced to absolute values by means of Wilson's method of scaling (Wilson, 1942). The intensities for reflexions $hk0$, $\bar{h}k0$, $h\bar{k}0$, $k\bar{h}0$, $\bar{k}h0$ and $k\bar{h}0$ were found to be

nearly the same (for k even), and mean values were taken. It is thought that these mean intensities are reliable to about 10% for reflexions of moderate strength, the relative accuracy being less for the highest intensities and much less for very low ones. Five films of different exposures were used for the $hk0$ intensity estimations, four for the $0kl$ estimations.

4. The analysis of the structure

(a) Patterson summations

The Patterson projection on (001) (Fig. 1) strongly suggested a structure similar to that of K_2PtCl_6 (Scherrer & Stoll, 1922). The Patterson projection on (010) (Fig. 2), however, showed a marked deviation

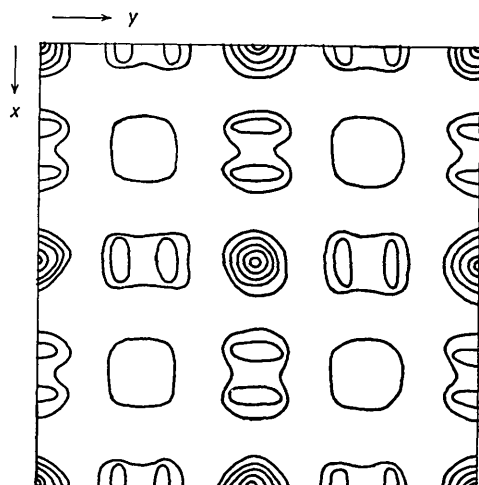


Fig. 1. Patterson function: projection on (001). Contours at 10, 30, 60, 110, 210 (arbitrary scale).

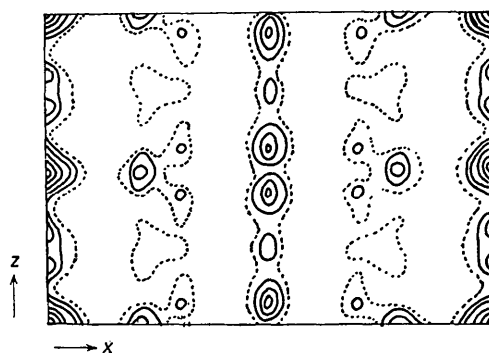


Fig. 2. Patterson function: projection on (010). Contours at 15, 30, 45, 75, 105, 135 (arbitrary scale).

from this structure. It was consistent with a displacement of each alternate plane of tin atoms (together with their attendant chlorine atoms) by about $\frac{1}{15}$ of the cell edge in the z direction. An additional distortion was necessary to account for the k -odd reflexions of type $hk0$, and the nature of this additional distortion was suggested by the elongation of the chlorine contours in the Patterson projection on (001). It was

postulated that each octahedron, consisting of a tin atom together with its six chlorine atoms, was rotated in this projection through a small angle about an axis through its centre and parallel to z . Further, as in

Table 1. Amplitudes of $hk0$ reflexions with k odd

Column (1): Index.
 Column (2): Contribution by rotation of $SnCl_6$ octahedra calculated from Sn-Cl separation of 2.43 Å and rotation of the octahedra of 10° .
 Column (3): Hydrazinium ion contribution calculated from one set of nitrogen atom positions.
 Column (4): Sum of columns (2) and (3).
 Column (5). Estimated amplitude calculated from observed intensities for the stronger reflexions. For other reflexions p indicates that the reflexion was present, a that it was absent or too weak to be observed, u that its presence (or indexing) was uncertain.

(1)	(2)	(3)	(4)	(5)
210	$\bar{9}$	10	1	a
410	$\bar{23}$	5	$\bar{28}$	41
610	$\bar{15}$	2	$\bar{17}$	a
810	$\bar{19}$	4	$\bar{15}$	31
10,1,0	$\bar{11}$	—	—	a
12,1,0	5	—	—	a
230	16	0	16	p
430	2	0	2	a
630	23	0	23	p
830	3	0	3	a
10,3,0	8	—	—	a
12,3,0	8	—	—	a
250	11	6	5	p
450	$\bar{17}$	4	$\bar{13}$	24
650	14	2	16	p
850	$\bar{10}$	4	$\bar{14}$	19
10,5,0	1	—	—	a
12,5,0	6	—	—	a
270	6	4	10	a
470	$\bar{23}$	3	$\bar{26}$	15
670	7	1	6	a
870	$\bar{18}$	3	$\bar{15}$	15
10,7,0	4	—	—	a
12,7,0	3	—	—	a
290	15	—	—	13
490	2	—	—	a
690	27	—	—	23
890	4	—	—	a
10,9,0	11	—	—	a
12,9,0	10	—	—	a
2,11,0	$\bar{1}$	—	—	a
4,11,0	$\bar{20}$	—	—	25
6,11,0	5	—	—	a
8,11,0	$\bar{18}$	—	—	24
10,11,0	9	—	—	a
12,11,0	2	—	—	a
2,13,0	6	—	—	u
4,13,0	4	—	—	a
6,13,0	12	—	—	u

Coordinates of the nitrogen-atoms used in this table were (2.96, 3.16, 2.60) and (4.08, 3.98, 2.80) Å, ($z = 0$ at level of one of the lowered tin atoms). Positions in the other octants are given by the symmetry. Corresponding lengths of hydrogen bonds between N and neighbouring Cl atoms are 3.3, 3.1, 3.2 Å and 3.2, 3.1 Å. N-N bond length = 1.4 Å.

$hk0$ reflexions h was always even while k was sometimes odd, it was supposed that all octahedra along lines parallel to the x axis were turned in the same sense, whereas along lines parallel to the y axis the rotations would be alternately right-handed and left-handed.

(b) *Fourier summations*

The postulated structure discussed in the preceding paragraph was used to calculate the phases of the reflexions for the Fourier projection on (010), the nitrogen contributions to the phases being neglected. The resulting projection is shown in Fig. 3, the agree-

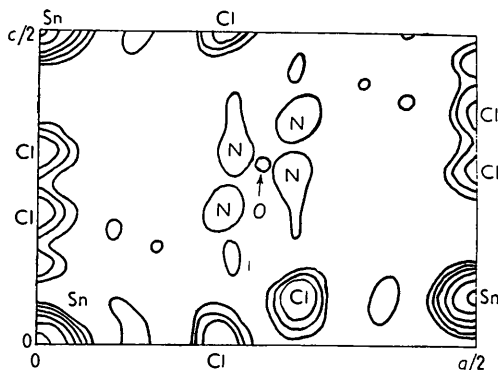


Fig. 3. Electron density: projection on (010). Contours at 25, 50, 100, 200, 400, 600 (arbitrary scale). O : centre of symmetry used as origin in this figure and in Table 3.

ment with the postulated structure being very good. For the Fourier projection on (001) (Fig. 4) the origin was chosen so as to make the projection centrosymmetric and it was assumed that the signs for all even indices would be positive. For this projection the few k -odd reflexions were omitted, these being used separately, as described below. The main structure

was thus determined and it remained to find the sense and amount of rotation of the $SnCl_6$ octahedra (from their positions in the ideal structure, K_2PtCl_6 -type) and the positions of the hydrazinium ions.

(c) *The reflexions with k odd*

The contributions of the $SnCl_6$ octahedra to the k -odd reflexions of type $(hk0)$ were calculated for various angles of rotation and compared with the observed intensities. As the rotation of the octahedra is about axes passing through the tin atoms, the latter do not affect these reflexions. Eventually it was found that a tin-chlorine separation of 2.43 Å and a rotation of 10° gave good agreement (Table 1). The resulting amplitudes of the k -odd reflexions were, however, not very sensitive to small changes either in the tin-chlorine separation or in the angle of rotation, and it is possible that when the hydrazinium ion positions are more accurately known even better agreement may be obtained with rather different distances between tin and chlorine atoms and with a different angle of rotation of the octahedra, though an error of more than 2° seems unlikely.

The nitrogen atoms of the hydrazinium ions were represented on the Patterson and Fourier projections but the peaks were not very definite, as was to be expected from the low scattering power of nitrogen compared with that of tin. In view of the false detail present on the projections it is not possible to determine the nitrogen atom positions with much accuracy. An attempt was made to determine these positions from considerations of packing and of hydrogen bond lengths by making an accurate model of the structure. The tin and chlorine atoms were arranged in the positions described earlier in this paper and the nitrogen atoms of the hydrazinium ions were represented by

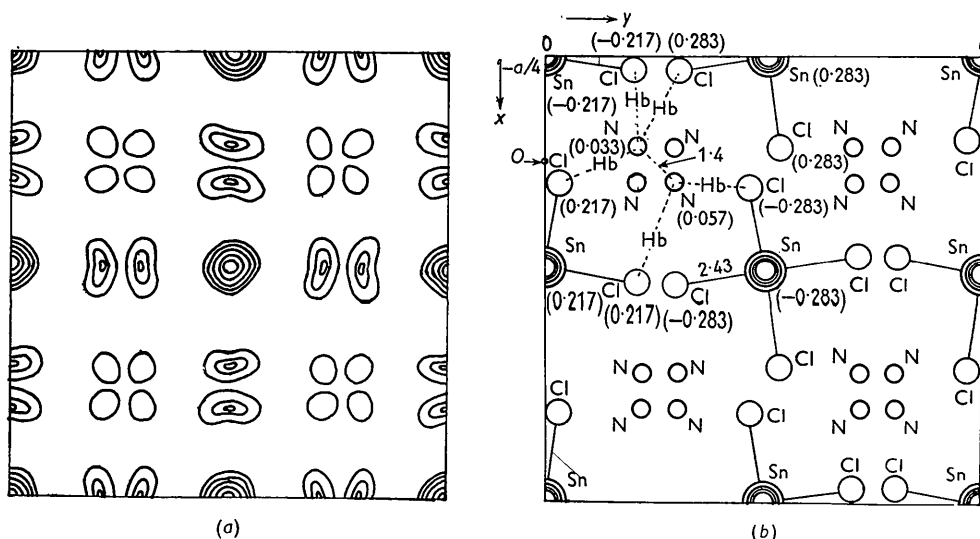


Fig. 4. (a) Electron density: projection on (001). Contours at 15, 40, 65, 115, 215 and 315 (arbitrary scale). (b) Plan of atomic positions. Hb: hydrogen bonds of length between 3.1 and 3.2 Å. O : centre of symmetry used as origin in this figure and in Table 3. Heights of atoms for one octant are marked in fractions of the unit-cell edge c .

Table 2. Comparison of structure amplitudes

Column (1): Index.

Column (2): Modulus of amplitude calculated from postulated structure (nitrogen atoms in positions suggested by Fourier projection 2.4 Å from edge of cell).

Column (3): Amplitude derived from observed intensities.

(1)	(2)	(3)	(1)	(2)	(3)	(1)	(2)	(3)
020	61	68	008	5	<i>a</i>	602	39	36
040	111	112	0,0,10	29	18	604	42	32
060	74	83	0,0,12	25	<i>a</i>	606	14	9
080	36	43	102	23	18	608	4	<i>a</i>
0,10,0	57	69	104	55	63	6,0,10	23	<i>a</i>
0,12,0	12	<i>a</i>	106	48	54	702	8	9
0,14,0	46	35	108	40	33	704	31	22
220	45	58	1,1,10	42	39	706	26	19
240	59	61	1,0,12	14	<i>a</i>	708	22	10
260	54	58	200	84	68	7,0,10	29	15
280	56	35	202	23	41	800	57	52
2,10,0	59	52	204	33	29	802	17	10
2,12,0	47	19	206	10	<i>a</i>	804	27	20
2,14,0	59	51	208	2	<i>a</i>	806	8	<i>a</i>
440	84	80	2,0,10	17	12	808	2	<i>a</i>
460	63	67	302	10	18	8,0,10	16	<i>a</i>
480	48	38	304	37	32	902	15	10
4,10,0	60	55	306	29	37	904	41	35
4,12,0	30	21	308	22	19	906	40	35
4,14,0	50	38	3,0,10	29	24	908	34	23
660	50	61	400	98	98	9,0,10	37	17
680	35	40	402	45	40	10,0,0	75	72
6,10,0	46	37	404	46	47	10,0,2	41	35
6,12,0	31	23	406	15	11	10,0,4	43	30
880	64	34	408	4	<i>a</i>	10,0,6	15	19
8,10,0	43	30	4,0,10	24	12	10,0,8	4	<i>a</i>
8,12,0	60	27	502	24	15	11,0,2	13	<i>a</i>
10,10,0	32	26	504	58	56	11,0,4	39	20
			506	55	57	11,0,6	37	15
002	69	65	508	47	38	12,0,0	45	<i>u</i>
004	60	65	5,0,10	49	44	12,0,2	14	<i>a</i>
006	20	27	600	83	70	14,0,0	53	43

balls at a distance apart corresponding to the length of the nitrogen-nitrogen bond (1.46 Å). The nitrogen atoms were moved about until the lengths and angles of the hydrogen bonds to the chlorine atoms fell within the limits given by Donohue (1952).

Unfortunately several sets of such positions could be found and there seemed no method of calculating the corresponding potential energies so as to decide between these possibilities. The contributions of the nitrogen atoms to the structure amplitudes of the *k*-odd reflexions (for which alone they would be appreciable) were then calculated for each of several sets of possible positions. These contributions by the nitrogen atoms were then added to the contributions due to the rotations of the SnCl₆ octahedra and the sums were compared with the observations. The results were not convincing, in that the agreement was little (if any) better than that obtained without any contribution from the nitrogen atoms. The structure amplitudes for one such set of positions are shown in Table 1.

The good agreement obtained without using the contributions of the nitrogen atoms suggests that these are small, at any rate for reflexions at high and moderate angles. This seems probable, as quite considerable movement of the hydrazinium ion in the model is possible while still keeping to possible hydrogen bond

lengths. It is therefore probable that the forces holding the nitrogen atoms in position are weak in certain planes and that a large amplitude of thermal vibration is to be expected, with a corresponding reduction in scattering power.

A comparison of calculated and observed structure amplitudes for the two projections used is given in Table 2. Atomic coordinates are given in Table 3.

Table 3. Atomic coordinates

The following atomic coordinates (corresponding to Table 1) are given with reference to a centre of symmetry as origin and in fractions of the lengths of the edges of the unit cell. The other atomic positions follow from considerations of symmetry of space group *Pnca*.

Sn	(-0.25, 0, -0.21 ₆)
Cl	(-0.04 ₈ , -0.036, -0.21 ₆)
	(-0.21 ₅ , 0.20 ₂ , -0.21 ₆)
	(-0.25, 0, 0.07 ₉)
	(-0.25, 0, -0.51 ₂)
N	(0.00 ₀ , 0.26 ₇ , 0.03 ₃)
	(0.09 ₃ , 0.33 ₄ , 0.05 ₇)

5. Conclusion

The structure is illustrated in Fig. 4(b). The positions of the nitrogen atoms must be considered as approximate, and it is likely that they have a large amplitude

of thermal movement in particular planes. The accuracy claimed in this work is not enough for the discrepancy between the tin-chlorine separation found and the values quoted in the literature (Pauling, 1939) to be taken as significant. An attempt is being made to find an isomorphous crystal with a lighter atom replacing the tin so that the hydrazinium ion position may be found more accurately.

The work was begun in the Physics Department, University of Cape Town, and completed in the Crystallographic Laboratory, Cavendish Laboratory, Cambridge. I wish to thank Prof. R. W. James (who

introduced me to crystallography) for help and encouragement and Dr W. Cochran for frequent and valuable advice.

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The Crystal Structure of Mg_6MnO_8

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The structure of Mg_6MnO_8 is found to be of a simple new type. It is cubic, with $a_0 = 8.381 \pm 0.002$ Å and space group $Fm\bar{3}m$. The oxygens are slightly distorted from a close-packed arrangement, and there occurs an ordered arrangement of the metal ions and of vacancies among the octahedral interstices.

Introduction

In the course of studying the reaction products from combining magnesium and manganese oxides in different proportions, we have observed that a new cubic phase is formed when the ratio of magnesium to manganese exceeds 6. The composition of this phase has been found to correspond to the formula Mg_6MnO_8 and its structure has been determined to be of a simple new type wherein there occurs an ordering of the respective metal ions *as well as of vacancies* among the octahedral interstices of close-packed oxygen ions. Another example of this structure type has been found independently by Christ, Clark & Fahey (1953) for a mineral of formula Cu_6PbO_8 . A preliminary note on both these compounds appears elsewhere (Kasper & Christ, 1953).

Preparation and analysis

An intimate mixture of magnesium oxide and manganese carbonate in a molar ratio of 8:1 was fired at 1100° C. for 5 hr. in an oxygen atmosphere. Although the mixed oxide phase described in this paper corresponds to a molar ratio of magnesium oxide to manganese dioxide of 6:1, the excess magnesium oxide was found to be necessary in order that all of the manganese be oxidized to the tetravalent state. The X-ray diffraction pattern showed the presence of the excess

magnesium oxide in addition to the new mixed oxide phase. It was found that this excess of magnesium oxide could be removed by boiling the powdered mixture in a 10% ammonium chloride solution for about 15 min. The X-ray diffraction pattern of this treated material no longer contained the lines of magnesium oxide.

A chemical analysis of the mixed oxide phase gave the following results:

	Found (%)	Calculated for Mg_6MnO_8 (%)
Mg	42.9	44.3
Mn (total)	16.9	16.7
Mn (as +4)	16.8	16.7

In view of the difficulties involved in determining magnesium in the presence of large quantities of manganese, the agreement is good.

Measurement of intensities

Preliminary investigations were done by means of Debye-Scherrer photographs. When the new phase was found, however, the attempts to determine the details of structure indicated the desirability of quantitative intensity measurements. That was accomplished readily by using powder in the form of a thick slab and a Geiger counter for the detection of the