

321. Basic Tin(II) Chloride.

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Of the various tin(II) chlorides reported in the literature, the only one preparable as a clearly defined crystalline phase from aqueous solution is found to be tetratin(II) hexahydroxide dichloride, $\text{Sn}_4(\text{OH})_6\text{Cl}_2$. The pure material can be obtained from solutions of pH ranging from 1.14 to 4.5. The dehydration of this phase at 212° is described, and the subsequent decomposition of the product, tetratin(II) trioxide dichloride, discussed.

Precipitates obtained from solutions above pH 4.5 are not true basic chloride phases, but are either mixtures of the basic chloride and hydrous tin(II) oxide, or simply impure hydrous oxide. Their dehydration to red or blue-black tin(II) oxides is discussed.

X-Ray diffraction data given show that the crystals of tetratin(II) hexahydroxide dichloride are orthorhombic with unit-cell dimensions: $a = 10.18 \text{ \AA}$, $b = 17.06 \text{ \AA}$, $c = 14.66 \text{ \AA}$, and eight formula-units per cell.

THE precipitation of basic tin(II) chlorides, by the addition of alkali or alkali carbonate solutions to solutions of tin(II) chloride has been reported by a number of workers. There is, however, little agreement on the formulæ of the materials obtained. Ditte¹ reported the existence of three basic chlorides, $4\text{SnO} \cdot 3\text{SnCl}_2 \cdot 6\text{H}_2\text{O}$, $\text{SnO} \cdot \text{SnCl}_2 \cdot 4\text{H}_2\text{O}$, and $3\text{SnO} \cdot 2\text{SnCl}_2 \cdot 6\text{H}_2\text{O}$, while Carson² stated that two distinct basic salt phases were obtained, *viz.* $7\text{Sn}(\text{OH})_2 \cdot 2\text{SnCl}_2$, and $5\text{SnO} \cdot 3\text{SnCl}_2 \cdot 6\text{H}_2\text{O}$. Britton³ reported that precipitation began at pH 1.9 and that a range of compounds existed, having compositions from $\text{Sn}(\text{OH})_{0.67} \cdot \text{SnCl}_{1.33}$ at pH 1.9 to $\text{Sn}(\text{OH})_{1.86} \cdot \text{SnCl}_{0.14}$ at pH 7. Hayek⁴ formulated the basic chloride which he obtained as $\text{Sn}(\text{OH})_2 \cdot \text{SnCl}_2$, while Randall and Murkami⁵ found the composition to be $\text{Sn}(\text{OH})\text{Cl} \cdot \text{H}_2\text{O}$.

We have prepared and studied precipitates obtained by the addition of alkali or alkali carbonate solutions to solutions of tin(II) chloride over the pH range 1.2—8.2. We were able to identify only one definite crystalline basic chloride phase, tetratin(II) hexahydroxide dichloride. We have studied the thermal decomposition of this phase and listed the X-ray-powder and unit-cell data of the material for reference purposes. Precipitates obtained over the pH range 4.9—6.2 were also examined for possible conversion into red tin(II) oxide.⁶

EXPERIMENTAL

Preparation of the Basic Chloride Phase in a Pure Crystalline Form.—Because of the ease of oxidation of bivalent tin, all stages of the preparation were carried out under oxygen-free nitrogen. Tin(II) chloride dihydrate (25 g.) was dissolved in concentrated hydrochloric acid (20 ml.) and water (10 ml.), and the solution cleared by warming in the presence of tin metal. The solution was cooled and 1 : 1 (v/v) ammonia (d 0.880)—water added until the pH of the solution was about 1. 2N-Ammonia solution was then added until a permanent precipitate was obtained, the solution was boiled to clear this and further alkali added until a slight precipitate reappeared. The solution was filtered by suction into a warm flask and allowed to

¹ Ditte, *Ann. Chim. Phys.*, 1882, **27**, 145.

² Carson, *J. Amer. Chem. Soc.*, 1919, **41**, 1969.

³ Britton, *J.*, 1925, **127**, 2120.

⁴ Hayek, *Z. anorg. Chem.*, 1933, **210**, 241.

⁵ Randall and Murkami, *J. Amer. Chem. Soc.*, 1930, **52**, 3967.

⁶ Donaldson, Moser, and Simpson, *J.*, 1961, 839.

cool slowly. The crystalline product was filtered off, washed with water, alcohol, and ether, and dried by suction and *in vacuo* over potassium hydroxide pellets and paraffin wax.

The basic tin(II) chloride so obtained is a crystalline solid which is insoluble in, and unattacked by, water or organic solvents. It is, however, soluble in dilute mineral acids and alkali. On storage, the crystals are stable for at least 12 months.

Analysis.—Previous workers, in determining the composition of the precipitate have relied on an assay of total tin, generally by ignition to tin(IV) oxide, thus neglecting the possible presence of tin(IV) impurities. We have determined stannous and total tin by Donaldson and Moser's ⁷ method, and chloride by oxidising the tin with concentrated nitric acid, diluting the solution, adding 0.1N-silver nitrate solution and weighing the silver chloride precipitated. Water was determined by heating the sample in a flow of oxygen and weighing the water in an anhydrous absorption tube. The results of triplicate analyses on two typical samples are as follows:

	Sample 1	Sample 2	3SnO, SnCl ₂ , 3H ₂ O requires
Stannous tin (%)	73.2, 73.1, 73.1	73.3, 73.3, 73.1	73.3
Total tin (%)	73.3, 73.1, 73.1	73.3, 73.3, 73.2	
Chloride (%)	10.9, 10.8, 10.8	10.7, 10.9, 10.7	11.0
Water (%)	8.2, 8.4, 8.4	8.5, 8.4, 8.4	8.3

The basic tin(II) cation present in aqueous solution is, according to Tobias,⁸ Sn₃(OH)₄²⁺. This is also the cation found in the crystalline basic nitrate⁹ and basic sulphate¹⁰ reported by us. It is clear that the basic chloride cannot be a simple salt of this ion, but since tin(II) chloride solutions have been stated¹¹ to contain complex ions such as SnCl₄²⁻ and SnCl₃⁻, solutions of the basic chloride were examined by ion-exchange methods.

A clear concentrated aqueous solution of recrystallised tin(II) chloride dihydrate was treated with very little 2N-ammonia to raise the pH almost to the point of precipitation of the basic chloride (approx. pH 1.1). The clear solution was passed through a column of cation-exchange resin (Amberlite IR 120 in H⁺ form). The ratio of tin(II) in the eluate to tin(II) in the original solution was 1 : 3.98 (mean of 3.93, 4.09, 3.93). The ratio of tin(II) to chloride in the eluate was found to be 1 : 8.50 (mean of 8.39, 8.50, 8.39, 8.71). In control experiments, clear solutions as above were passed through anion-exchange resin (Amberlite IRA 400); the ratio of eluted tin(II) to original tin(II) was 3 : 3.99 (mean of 3.94, 4.04). When the solutions were passed through the cation- and anion-resins in succession, only about a thirtieth of the original tin(II) was eluted, showing that tin(II) present as molecular species may be neglected. The other results demand a ratio of cationic to anionic tin(II) 3 : 1, and absence of cationic chloro-complexes. Both of these requirements, as well as the analytical results, are met by a formula Sn₃(OH)₄²⁺, Sn(OH)₂Cl₂²⁻, but this cannot be taken as conclusive evidence of the presence of these units in the solid, or indeed in the solution (see Discussion).

Variation of Composition of Basic Chloride or Hydrrous Oxide Precipitate with pH.—A clear solution of tin(II) chloride dihydrate was prepared as before and the change in composition of the precipitate (hydrrous oxide or basic chloride) with pH was studied by adding varying amounts of 1 : 1 (v/v) ammonia (*d* 0.880)—water and analysing the precipitates obtained. The results are shown in Table 1.

Thermal Stability of Basic Tin(II) Chloride.—The dehydration of tetratin(II) hexahydroxide dichloride was followed on a Stanton thermobalance in an atmosphere of oxygen-free nitrogen. Water is lost in one stage at 212° and the initial decomposition product is a brown solid, analysis of which shows it to be an oxide chloride, 3SnO, SnCl₂. The results of stannous tin, total tin, and chloride analyses on three samples of the dehydrated product gave 79.1, 80.2, 11.8; 79.2, 80.0, 12.0; 79.0, 80.1, 12.0% [Calc. for 3SnO, SnCl₂: Sn(II), 80.1; Cl, 12.0%]. Further heating of this oxide chloride results in the volatilisation of some tin(II) chloride at about 300° and the formation of a residual mixture of blue-black tin(II) oxide, tin(IV) oxide, and β-tin [tin(IV) oxide and β-tin are formed from the disproportionation^{12,13} of the blue-black oxide].

⁷ Donaldson and Moser, *Analyst*, 1959, **84**, 10.

⁸ Tobias, *Acta Chem. Scand.*, 1958, **12**, 198.

⁹ Donaldson and Moser, *J.*, 1961, 1996.

¹⁰ Donaldson, unpublished work.

¹¹ Allison, Hartung, and Heymann, *J. Phys. Chem.*, 1940, **44**, 1033.

¹² Donaldson and Moser, *J.*, 1961, 835.

¹³ Straumanis and Strenk, *Z. anorg. Chem.*, 1933, **213**, 301.

TABLE 1.

Analytical results for basic tin(II) chloride precipitates.

pH	Tin(II) (%)	Total tin (%)	Chloride (%)	Water (%)	X-Ray diffraction
1.24	72.7	73.0	10.95	8.30	} basic chloride
2.38	73.0	73.2	10.91	8.34	
2.87	72.6	73.1	10.88	8.61	
3.55	72.5	73.0	10.79	8.64	
4.13	72.8	73.3	10.60	8.84	
4.50	73.3	73.9	10.35	8.99	} some lines of basic chloride and hydrous oxide
5.08	77.7	78.1	9.05	8.25	
5.61	80.3	80.4	4.04	5.36	
6.12	79.1	80.6	2.85	4.98	} hydrous oxide
6.66	78.2	80.5	2.19	4.75	
7.14	78.5	80.6	1.35	4.30	
8.14	78.3	80.2	0.09	4.17	

Dehydration of Basic Chloride-Hydrous Oxide Mixtures.—Freshly prepared, washed precipitates from the pH range 4.9—6.2, previously shown to be the critical range in the formation of red tin(II) oxide,⁶ were dehydrated under the conditions recommended for the preparation of the red oxide, but without the excess of soluble chlorides normally present in that preparation. Dehydration of the precipitates (i) by heating them in suspension in an acetate buffer with some phosphite, (ii) by uniform drying of a paste made with water only, and (iii) by dry heating in nitrogen above 120° yielded only blue-black tin(II) oxide in all three methods.

Addition of some *N*-hydrochloric acid [in method (i)] or preparation of the paste with ammonium chloride solution [in method (ii)] produced instead good yields of red tin(II) oxide. Admixture of dry alkali or alkaline-earth chlorides in method (iii) was without effect, blue-black tin(II) oxide being formed as before.

Crystallography.—Tetratin(II) hexahydroxide dichloride consists of six-sided crystals, which show parallel extinction and, when freshly prepared, are pleochroic. They have high refractive index (>1.74) and high birefringence. X-Ray diffraction data show that the crystals are orthorhombic with cleavage (010). Crystal data: $\text{Sn}_4(\text{OH})_6\text{Cl}_2$, $M = 647.8$, orthorhombic, $a = 10.18 \pm 0.02$, $b = 17.06 \pm 0.03$, $c = 14.66 \pm 0.02$ Å, $U = 2546$ Å³, $D_m = 3.39 \pm 0.01$

TABLE 2.

X-Ray powder data for basic tin(II) chloride.

d (Å)	Relative intensity	Index of reflection	$d_{\text{calc.}}$	d (Å)	Relative intensity	Index of reflection	$d_{\text{calc.}}$	d (Å)	Relative intensity
8.54	vvw	020	8.54	2.50	vvs	{ 314 2.49 } { 333 2.51 }		1.554	m
7.33	vw	002	7.33	2.40	vw	350 2.41		1.518	w
5.09	w	200	5.09	2.36	vw	026 2.35		1.500	mw
4.89	vw	003	4.89	2.28	w	352 2.28		1.481	m
4.75	w	201	4.78	2.24	w	064 2.23		1.474	w
4.29	vw	040	4.27	2.20	vw	440 2.19		1.448	vvw
4.18	s	{ 202 4.19 } { 221 4.18 }		2.16	w	353 2.16		1.416	w
4.04	mw	212 4.05		2.14	mw	080 2.14		1.387	w
3.93	vvw	123 3.94		2.07	vw	362 2.08		1.375	w
3.75	w	141 3.76		2.05	vvw	082 2.05		1.345	mw
3.64	w	004 3.67		2.02	vw	511 2.02		1.310	w
3.50	w	133 3.48		1.969	vw			1.293	w
3.41	m	114 3.41		1.937	mw			1.274	w
3.37	vw	024 3.39		1.923	w			1.263	w
3.24	w	240 3.25		1.893	w			1.239	vw
3.15	vw	241 3.16		1.828	m			1.208	vvw
3.09	ms	321 3.10		1.778	w			1.194	vw
2.96	vw	214 2.96		1.764	w			1.163	vw
2.90	mw	330 2.91		1.716	vw			1.128	vvw
2.85	s	331 2.86		1.675	w			1.099	vvw
2.82	ms	061 2.81		1.645	mw			1.079	vw
2.70	vw	332 2.68		1.619	vw			1.055	vvw
2.64	} m	{ 252 2.64 } { 062 2.64 }		1.616	vvw			1.043	vvw
2.63				1.606	vw			1.028	vvw
2.55	vs	400 2.55		1.584	w			1.013	vvw

TABLE 3.
X-Ray powder data for tin(II) oxide chloride.

d (Å)	Relative intensity	d (Å)	Relative intensity	d (Å)	Relative intensity	d (Å)	Relative intensity	d (Å)	Relative intensity
12.79	vw	4.53	w	2.71	vvs	1.836	vw	1.343	w
11.68	vw	3.91	ms	2.62	m	1.765	vw	1.320	w
10.15	vw	3.76	s	2.59	mw	1.728	m	1.289	vw
9.83	w	3.71	m	2.53	m	1.685	vw	1.273	vw
9.58	mw	3.42	ms	2.42	vw	1.596	w	1.254	vw
8.66	vw	3.21	vs	2.37	m	1.567	w	1.212	vw
7.51	m	3.18	vw	2.29	w	1.555	vw	1.172	vw
7.41	w	3.09	mw	2.28	w	1.534	vw	1.158	vw
6.85	w	3.04	ms	2.20	mw	1.482	vw	1.119	w
6.65	mw	2.97	s	2.14	vw	1.439	vw	1.113	vw
5.95	w	2.87	s	2.09	vw	1.379	vw	1.066	vw
5.20	m	2.83	vw	1.927	vw	1.364	w	1.002	vw
4.69	ms	2.77	mw						

(by suspension in a mutual solution¹⁴ of thallos malonate and thallos formate in water), $Z = 8$, $D_c = 3.38$. Filtered Cu- K_α radiation, single-crystal rotation and Weissenberg photographs about all three axes.

There were the following systematic absences of reflection: $h00$ absent for h odd, $0k0$ absent for k odd, $hk0$ absent for $h + k$ odd, $0kl$ absent for k odd and $h0l$ absent for h odd. The space group is therefore Pbn (D_{2h}^4 , No. 50).

Table 2 contains the X-ray diffraction powder data for tetratin(II) hexahydroxide and Table 3 the data for tetratin(II) trioxide dichloride obtained by using 11.64 cm. cameras and a Philips X-ray diffractometer with filtered Cu K_α radiation. For the basic chloride the spacings longer than 2.00 Å have been indexed by comparison of single-crystal and powder photographs and by calculation from the unit-cell dimensions.

DISCUSSION

The results show that only one basic tin(II) chloride phase can be obtained by precipitation from aqueous solution. Careful analytical and X-ray diffraction studies show that changes in analytical composition of the precipitates with pH do not correspond to the formation of other basic chloride phases, but merely to increasing admixture of hydrous tin(II) oxide.¹² All precipitates obtained from solutions of pH 1.14—4.5 have the same composition and the characteristic X-ray diffraction powder pattern of pure crystalline basic tin(II) chloride. Above pH 4.5, however, the analytical composition of precipitates varies considerably with pH, and lines due to basic chloride are augmented and ultimately replaced by lines due to hydrous oxide. The various basic-salt compositions reported by previous workers merely represent the composition, as found by analysis, of heterogeneous stages in the replacement of chloride by hydroxide in the anion. Similar results have been obtained in the study of basic tin(II) sulphate.⁹

The ion-exchange results are consistent with, but not conclusive evidence for, the presence of $\text{Sn}_3(\text{OH})_4^{2+}$ and $\text{Sn}(\text{OH})_2\text{Cl}_2^{2-}$ in the saturated solution just before precipitation of the basic chloride. Tobias and Hugus¹⁵ in a recent study found no evidence of mixed chlorohydroxo-complexes of tin(II) in similar solutions, but this would not preclude their existence in a solid phase. In the absence of further evidence, *e.g.*, of a complete structure determination, the solid phase is best represented by $\text{Sn}_3(\text{OH})_4\text{Sn}(\text{OH})_2\text{Cl}_2$. This brings the basic chloride into line with the basic nitrate and basic sulphate. Further evidence of the correctness of the analytical composition, *viz.*, $3\text{SnO}\cdot\text{SnCl}_2\cdot 3\text{H}_2\text{O}$, is that the unit-cell dimensions, the measured density, and the suggested formula-weight of the basic chloride together give the calculated value of Z as 8.01, sufficiently close to the whole number required by lattice considerations.

In the absence of oxygen, tetratin(II) hexahydroxide dichloride is dehydrated in one

¹⁴ Clerici, *Rend. Accad. Lincei*, 1907, **16**, 187; 1922, **31**, 116.

¹⁵ Tobias and Hugus, *J. Phys. Chem.*, 1961, **65**, 2165.

stage at 212° to give a brown material, which has not been previously reported, namely tetratin(II) trioxide dichloride. The brown colour¹² may be attributed to the presence of about 1% of tin(IV) which is produced during the dehydration. The oxide salt has a characteristic X-ray diffraction powder pattern but none of the samples contained crystals large enough for single-crystal X-ray diffraction work. The tetratin(II) trioxide dichloride decomposes on further heating; tin(II) chloride volatilises and the residue, tin(II) oxide, disproportionates.

All attempts to convert the pure basic chloride directly into red tin(II) oxide failed, as did those to prepare it from the washed basic chloride-hydrous oxide mixed precipitates (pH 4.9—6.2). The red oxide was formed only at pH above the limit of stability of the pure basic chloride, and then only when further soluble chloride was added. Our previous report,⁶ that the presence of chloride ion seemed essential for the production of red tin(II) oxide in good yield, is thus confirmed, and the hydrous oxide, rather than the basic chloride, shown to be the precursor of the red oxide. Work is at present in progress to study the mechanism of this dehydration, and especially the effect of phosphite and other additives on the reaction.

One of us (W. B. S.) is grateful to the International Tin Research Council for a maintenance grant.

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[Received, August 23rd, 1961.]
