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Abstract

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TIN CHALCOGENOCHLORIDES

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1. Tin salts with mixed anions have been known for a long time—the mixed halides $SnCl_2Br_2$, $SnCl_2J_2$, as well as the oxychloride $SnOCl_2$, were synthesized as early as the last century ([1-3]), and all these compounds were obtained by the direct action of oxidizing agents on crystalline salts of divalent tin. Owing to the high electronegativity of tin ($\chi = 1.7$ for Sn), the chemical bonds in a molecule, for example $SnCl_2$, have 30% ionicity (see [4], p. 167). In crystalline $SnCl_2$, assuming c.n. = 9 ([5]), the ionicity of the Sn—Cl bond will be equal to 67%; hence the effective coordination charge of tin will be equal to (see [4], pp. 104-106):

$$z = -0.33 \cdot 9 + 2 = -0.97e.$$

This latter circumstance, in accordance with the criterion proposed by us ([6,7]), accounts for the possibility of direct oxidation of the metal without displacement of anions according to the reaction:

$$2SnCl_2 + Y_2 = 2SnCl_2Y,$$

where Y is, for example, oxygen.

It is obvious that analogous reactions can also be carried out with chalcogens, which is the subject of the present work.

2. The addition of sulfur to $SnCl_2$ was carried out by melting mixtures of $SnCl_2$ + S and $SnCl_2$ + 2S in sealed ampoules at a temperature of 140-150° for 8 hr.

As a result of the reaction, a liquid appeared among the contents of the ampoules; it fumed on contact with air (like tin tetrachloride or sulfur); this liquid was removed in a vacuum desiccator. The remaining dark-gray powder did not dissolve either in cold or in hot water, nor in hydrochloric and sulfuric acids or toluene, but dissolved slowly in nitric acid and more rapidly in alkalis. This behavior distinguishes the resulting substance from the initial reagents, as well as from $SnCl_4$ and SnS_2.

The product obtained was analyzed for tin by dissolving a 0.15-0.2 g sample in nitric acid, precipitating tin hydroxide with ammonia, and subsequently igniting

at 900° to SnO_2; it was analyzed for chlorine by precipitation as AgCl from a nitric-acid solution, and for sulfur by precipitation of $BaSO_4$ from a solution of the fusion of the sample with sodium peroxide. The analytical results correspond to the formula $Sn_2Cl_2S_3$.

Found, %: Sn 58.82; Cl 17.59; S 22.11.
Calculated, %: Sn 58.69; Cl 17.53; S 23.78.

Thus, the reaction of sulfur addition to tin dichloride proceeds either according to the scheme:

$$3SnCl_2 + 3S = Sn_2Cl_2S_3 + SnCl_4,$$

or

$$2SnCl_2 + 4S = Sn_2Cl_2S_3 + SCl_2.$$

The formation of a substance of one and the same composition in the interaction of $SnCl_2$, regardless of the amount of sulfur, is sufficient grounds for considering $Sn_2Cl_2S_3$ an individual compound. To confirm this conclusion, we carried out a physicochemical study of tin sulfochloride.

The density of $Sn_2Cl_2S_3$ is 3.48 g/cm^3; moreover, it did not change upon heating the sample at a temperature of 140° for another 12 hr, which indicates completion of the reaction.

The X-ray diffraction pattern of this compound is given in Table 1 together with the X-ray diffraction pattern of $SnCl_2$; they were obtained in a camera of 57 mm diameter, with copper radiation.

Table 1

X-ray constants of tin chloride and chalcogenochlorides

$SnCl_2$		$SnCl_2$		$Sn_2Cl_2S_3$		$Sn_2Cl_2Se_5$		$Sn_2Cl_2Te_7$	
Intensity	$SnCl_2$ d/n	Intensity	$SnCl_2$ d/n	Intensity	$Sn_2Cl_2S_3$ d/n	Intensity	$Sn_2Cl_2Se_5$ d/n	Intensity	$Sn_2Cl_2Te_7$ d/n
v.w.	4.52	v.w.	1.286	med.	5.87	med.	6.20	med.	3.387
med.	3.911	»	1.251	v.w.	3.916	very v.w.	4.28	med.	3.313
»	3.514	very v.w.	1.237	»	3.547	med.	2.914	w.	2.406
v.w.	3.321	v.w.	1.192	»	3.127	w.	2.232	w.	2.288
very v.w.	3.207	very v.w.	1.157	»	2.945	very v.w.	2.040	med.	2.133
med.	2.936	v.w.	1.146	med.	2.759	v.w.	1.897	»	2.057

$SnCl_2$ Intensity	$SnCl_2$ d/n	$SnCl_2$ Intensity	$SnCl_2$ d/n	$Sn_2Cl_2S_3$ Intensity	$Sn_2Cl_2S_3$ d/n	$Sn_2Cl_2Se_5$ Intensity	$Sn_2Cl_2Se_5$ d/n	$Sn_2Cl_2Te_7$ Intensity	$Sn_2Cl_2Te_7$ d/n
w.	2.775	»	1.126	v.w.	2.568	very v.w.	1.812	»	1.956
»	2.525	very v.w.	1.112	»	2.186	w.	1.741	w.	1.858
very v.w.	2.405	»	1.099	»	2.103	v.w.	1.586	v.w.	1.817
»	2.327	»	1.075	very v.w.	1.975	»	1.530	very v.w.	1.686
v.w.	2.243	v.w.	1.047	w.	1.808	»	1.444	w.	1.636
»	2.206	very v.w.	1.016	med.	1.729	»	1.398	very v.w.	1.583
»	2.181	» »	0.9927	very v.w.	1.696	»	1.283	med.	1.477
»	2.166	» »	0.9857	very v.w.	1.629	»	1.218	»	1.441
w.	2.103	» »	0.9789	very v.w.	1.595	med.	1.193	»	1.400
very v.w.	1.979	» »	0.9482	v.w.	1.482	»	1.150	very v.w.	1.296
v.w.	1.916	» »	0.9255	»	1.426	v.w.	1.099	v.w.	1.270
very v.w.	1.757	» »	0.9150	»	1.331	»	1.064	»	1.230
»	1.711	» »	0.9011	very v.w.	1.212	very v.w.	0.9834	med.	1.182
»	1.693	» »	0.8934	v.w.	1.145	v.w.	0.9760	»	1.160
v.w.	1.682	» »	0.8686	»	1.085	very v.w.	0.9517	v.w.	1.083
»	1.654	» »	0.8616	»	1.048	v.w.	0.9039	»	1.034
very v.w.	1.621	» »	0.8527	very v.w.	1.096	»	0.8934	»	1.003
v.w.	1.573	» »	0.8424	»	0.9228	»	0.8759	»	0.9504
very v.w.	1.554	» »	0.8386	»	0.9074	very v.w.	0.8678	»	0.9348
v.w.	1.528	» »	0.8271	»	0.8539	very v.w.	0.8472	»	0.9143
very v.w.	1.469	» »	0.8159	»	0.8142	v.w.	0.8342	med.	0.8634
v.w.	1.442	» »	0.8069			»	0.8179	»	0.8474
»	1.416	» »	0.8029			»	0.8092	v.w.	0.8296
very v.w.	1.377	» »	0.7967			»	0.7959	»	0.8176

$SnCl_2$ Intensity	$SnCl_2$ d/n	$SnCl_2$ Intensity	$SnCl_2$ d/n	$Sn_2Cl_2S_3$ Intensity	$Sn_2Cl_2S_3$ d/n	$Sn_2Cl_2Se_5$ Intensity	$Sn_2Cl_2Se_5$ d/n	$Sn_2Cl_2Te_7$ Intensity	$Sn_2Cl_2Te_7$ d/n
v.w.	1.353	» »	0.7928			»	0.7941	»	0.8049
very v.w.	1.325					very v.w.	0.7911		

Comparison of the X-ray patterns of $Sn_2Cl_2S_3$ with $SnCl_2$, and also with the values of d/n for SnS_2 (8), shows that more than one third of the lines (and, moreover, the most intense ones) of tin sulfochloride are specific; half of the lines, either in magnitude or in magnitude and intensity, are close to the values for $SnCl_2$, while one quarter of the lines resemble the X-ray pattern of SnS_2, including four lines characteristic simultaneously of the X-ray patterns of $SnCl_2$ and SnS_2. There are no sulfur lines in the X-ray pattern. Hence it may be concluded that the newly obtained compound has certain structural features in common with the starting substance and with tin disulfide.

The thermogram of the sulfochloride, recorded on a Kurnakov pyrometer in the temperature range 25–800° at a heating rate of 15°/min, is reproduced in Fig. 1 together with the curve for $SnCl_2$. The figure clearly shows the individuality of the product obtained.

The reactions of interaction of $SnCl_2$ with selenium and tellurium were likewise carried out by fusion (1 : 1 mixtures) in sealed ampoules for 20 hr at temperatures of 240 and 480°, respectively. The reaction products were dried in a vacuum oven and then analyzed (in the same way as the sulfochloride).

The results of the analysis lead to the following formulas:

$Sn_3Cl_2Se_5$	Found %:	Sn 40.35; Cl 8.68; Se 47.54.
	Calculated %:	Sn 43.33; Cl 8.63; Se 48.04.
$Sn_4Cl_2Te_7$	Found %:	Cl 5.37; Te 62.24.
	Calculated %:	Cl 4.93; Te 62.08.

The chemical properties of the seleno- and tellurochlorides are qualitatively similar to the properties of tin sulfochloride, except that $Sn_4Cl_2Te_7$

dissolves in alkalis only on heating and with liberation of tellurium. The density of $Sn_3Cl_2Se_5$ is 5.32; that of $Sn_4Cl_2Te_7$ is 6.15 g/cm^3.

Thermograms of the seleno- and tellurochlorides, reproduced in Fig. 1, show complete specificity. The X-ray patterns of these substances are given in Table 1, from which it is seen that approximately $^2/_5$ of all their lines are specific, while the rest are close in magnitude or in intensity to the lines of $SnCl_2$; there are no Se and Te lines.

Fig. 1

Figure 1: Fig. 1

Fig. 1

The totality of the physical and chemical characteristics of these substances unambiguously indicates their individuality.

In conclusion, it is useful to compare the compositions of the oxy- and chalcogenochlorides of tin, which change in a quite regular manner:

$$SnCl_2O \rightarrow Sn_2Cl_2S_3 \rightarrow Sn_3Cl_2Se_5 \rightarrow$$

$$\rightarrow Sn_4Cl_2Te_7,$$

namely, on going from O to Te, the compositions of the mixed salts successively change by SnY_2.

In other words, the compounds synthesized by us may be represented as derivatives of the SnY_2 structure, in which, for $Y = O$, every second Y is replaced by 2Cl; for $Y = S$, $^1/_4$ of all Y is replaced; for $Y = Se$, $^1/_6$ of all Y is replaced; and for $Y = Te$, $^1/_8$ of all Y is replaced. Naturally, it should be assumed that such a regularity is due to the requirements of the densest packing of atoms in the crystal structures of tin chalcogenochlorides.

To confirm the considerations expressed, we shall give some qualitative results of analysis of the X-ray patterns of tin sulfo-, seleno-, and tellurochlorides. Thus, in the case of $Sn_2Cl_2S_3$, of 14 lines close to the lines of $SnCl_2$, $^2/_3$ are also close in intensity; in the case of $Sn_3Cl_2Se_5$, of 18 lines only $^1/_3$ are close in intensity, while for $Sn_4Cl_2Te_7$, of 17 lines close to the lines of $SnCl_2$, not one is close in intensity. Thus, in going from S to Te, the structure of the chalcogenochlorides increasingly departs from the structure of stannous chloride.

$Sn_2Cl_2S_3$, $Sn_3Cl_2Se_5$, and $Sn_4Cl_2Te_7$ have been synthesized; their physicochemical properties have been studied—their thermograms and X-ray patterns have been taken, their densities measured, and the behavior of the chalcogenochlorides toward various media investigated.

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Note: Figure translations are in progress. See original paper for figures.