789. *Pure Tin*(II) *Sulphate.*

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The preparation and analysis of pure tin(II) sulphate are described. The solubility of the material in various solvents is reported and its stability discussed. The thermal decomposition of tin(II) sulphate has been studied in detail and the decomposition temperature found to be 378° C. The unit-cell dimensions, cell contents, and *X*-ray diffraction powder data are included.

TIN(II) SULPHATE has been found to be a purer and more satisfactory source of bivalent tin than the dihydrated chloride which is normally used. It is usually prepared [1-4] by dissolving tin, or a tin(II) salt, in sulphuric acid and evaporating the solution. Carson [5] prepared a pure solution of tin(II) sulphate by displacement of copper from a copper sulphate solution with metallic tin.

The properties of tin(II) sulphate are not well documented but its solubility in water has been reported [2] as 18·9 g. in 100 g. at 20° and 18·2 g. at 100°. The material is also reported [6] to be thermally stable up to 360°, above which it is said to decompose to sulphur dioxide and tin(IV) oxide. We have extended the data.

EXPERIMENTAL

Preparation and Analysis.—Pure tin(II) sulphate can be obtained from a solution prepared by Carson's method as follows:

Metallic tin (37 g.), of analytical-reagent grade, was added to a solution of copper(II) sulphate (analytical-reagent grade) (37 g.) in water (300 ml.) and sulphuric acid (15 ml.), the solution being kept under oxygen-free nitrogen. The solution was boiled, copper being deposited. Eventually the solution became colourless and the deposit became grey owing to redeposition of tin on the surface of copper. At this point the solution was filtered rapidly and concentrated

[1] Bouquet, *J. Pharm. Chim.*, 1847, **11**, 459.
[2] de Marignac, *Ann. Mines*, 1857, **22**, 1.
[3] Longi, *L'Orosi*, 1885, 253.
[4] Ditte, *Ann. Chim. Phys.*, 1882, **27**, 159; *Compt. rend.*, 1887, **104**, 172.
[5] Carson, *J. Amer. Chem. Soc.*, 1926, **48**, 906.
[6] Durrant, *J.*, 1915, **107**, 622.

to about 50 ml. in a vacuum rotary evaporator. The mother-liquor was filtered off, and the tin(II) sulphate (~25 g.) washed with alcohol and ether and dried at 100°.

Tin(II) sulphate can also be obtained from its solution by precipitation with organic solvents, but the final product is less pure and is often yellowish owing to the presence of quadrivalent tin.

In assessing the purity of tin(II) sulphate, previous workers have relied on assay of total tin, generally by ignition to tin(IV) oxide, and have neglected the possible presence of tin(IV) as impurity. We determined tin by the method of Donaldson and Moser.[7] We determined sulphate by combustion in an oxygen-free atmosphere and weighing of the sulphur dioxide liberated, the apparatus consisting of a silica tube in which a weighed sample was heated above 400°; oxygen-free nitrogen was passed through guard tubes containing anhydrone and soda asbestos and used as a gas to carry the sulphur dioxide from the combustion, through a tube containing anhydrone, into a weighed absorption tube containing soda asbestos. Proof that the thermal decomposition of tin(II) sulphate is quantitative is given below. The percentages of stannous tin, total tin, and sulphate in three typical samples were: 55·4, 55·4, 44·4; 55·6, 55·5, 44·7; 55·5, 55·5, 44·8; respectively. As the second anhydrone tube never increased in weight, all samples were free from water.

Solubility of Tin(II) *Sulphate.*—The solubility in five common solvents (see Table 1), under a non-oxidising atmosphere at various temperatures, was measured by titrating [7] the bivalent tin in solution. Aqueous solutions of tin(II) sulphate must be prepared by addition of water to an excess of the sulphate because an excess of water hydrolyses [1,4] the material to an insoluble basic salt. Clear solutions of tin(II) sulphate can be obtained at 20° provided that the concentration of solute is greater than 18·9 g. per 100 ml.

Stability of Tin(II) *Sulphate.*—Tin(II) sulphate can be kept for several months in contact with air, and much longer in the dark under a vacuum. The first sign of impurity is formation of a small area of yellow material near the walls of the container. This colour gradually spreads throughout the sample and is presumably due to the formation of tin(IV); certainly all yellowish samples of the sulphate, prepared by precipitation methods, contained up to 2% of quadrivalent tin. Pure tin(II) sulphate has been stored out of direct sunlight for 20 months in stoppered colourless Pyrex glass, brown glass, and polythene, and so far shows no signs of yellowing or of analytical presence of tin(IV).

TABLE 1. *Solubility of tin*(II) *sulphate.*

Solvent	Solubility (g./100 ml. of solution) at 20°	30°	50°	60°	100°
Water	35·2	33·4	30·0	28·2	22·0
N-Sulphuric acid	23·2	22·6	20·6	19·0	13·2
Glacial acetic acid	0·0010	0·0011	0·0013	n.d.	n.d.
Methylated spirit	0·0017	0·0017	0·0017	n.d.	—
N-Sodium hydroxide *	2·27	2·29	2·52	2·62	n.d.

* Maximum concn. of stannite expressed as g. of $SnSO_4$. n.d. = not determined.

The thermal decomposition of tin(II) sulphate above 360° in an atmosphere of oxygen-free nitrogen was followed by means of a silica spring balance.[8,9] Complete decomposition into tin(IV) oxide and sulphur dioxide occurred at 378° and there was little decomposition below this temperature.

Further proof of the stoicheiometry of the decomposition was obtained by igniting the solid decomposition product at 700° in the presence of oxygen. Since tin(IV) oxide is the only tin compound which is unchanged on ignition under these conditions, any impurity in the decomposition product would result in an alteration in weight. However, when six samples of the decomposition product (0·1232—0·1443 g.) were ignited the maximum weight difference was 0·33%.

The thermal decomposition of tin(II) sulphate is an example of the internal oxidation–reduction reactions undergone by oxygen-containing tin(II) compounds to give the very stable tin(IV) oxide.

Crystallography.—Tin(II) sulphate consists of snow-white acicular crystals which show

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[7] Donaldson and Moser, *Analyst*, 1959, **84**, 10.
[8] Buttler, Ph.D. Thesis Aberdeen, 1958, p. 30.
[9] Buckle, *J. Phys. Chem.*, 1959, **63**, 1231.

parallel extinction and have $n > 1{\cdot}74$, positive elongation, and high birefringence. *X*-Ray data show that the crystals are orthorhombic with needle axis *c* and cleavage (010).

Crystal data: $SnSO_4$, $M = 214{\cdot}8$. Orthorhombic $a = 8{\cdot}81 \pm 0{\cdot}02$, $b = 7{\cdot}17 \pm 0{\cdot}02$, $c = 5{\cdot}35 \pm 0{\cdot}01$ Å, $U = 337{\cdot}9$ Å^3. $D_m = 4{\cdot}21 \pm 0{\cdot}01$ g./c.c. (by suspension in a mutual solution [10] of thallous formate and thallous malonate in water). $Z = 4$, $D_c = 4{\cdot}22$ g./c.c. Filtered Cu-K_α radiation; single-crystal rotation and Weissenberg photographs about all three axes.

There were the following systematic absences of reflection: *h*00 absent for *h* odd, 0*k*0 absent for *k* odd, 00*l* absent for *l* odd, *h*0*l* absent for *h* odd, and 0*kl* absent for $k + l$ odd. The space group is therefore *Pnma* (D_{2h}^{16}, No. 62) or *Pna*2$_1$ (C_{2v}^{9}, No. 33). No evidence of pyro- or piezoelectricity was found in tin(II) sulphate.

Table 2 contains the *X*-ray diffraction powder data obtained by using 11·64 cm. cameras and a Philips *X*-ray diffractometer with filtered Cu-K_α radiation. The spacings longer than 2·10 Å have been indexed by comparison of single-crystal and powder photographs and by calculation from the unit-cell dimensions. The data agree with, and improve upon those, in the A.S.T.M. index.[11]

TABLE 2. *X-Ray diffraction powder data for tin*(II) *sulphate.*

d (Å)	Rel. intensity	Index of refln.	Calc. *d* spacing	*d* (Å)	Rel. intensity	*d* (Å)	Rel. intensity
5·52	vw	110	5·50	2·06	vw	1·338	vvw
4·40	mw	200	4·41	2·03	vw	1·316	vw
4·27	mw	011	4·27	1·95	mw	1·281	vw
3·94	vvw	111	3·99	1·91	w	1·266	vvw
3·57	m	020	3·59	1·86	vw	1·249	ms
3·45	m	201	3·42	1·78	vvw	1·177	w
3·31	vw	120	3·32	1·75	m	1·155	vw
3·08	vvs	211	3·08	1·73	vvw	1·130	vw
2·82	w	121	2·82	1·72	vw	1·100	vvw
2·77	w	220	2·78	1·63	mw	1·073	w
2·68	mw	002	2·68	1·61	mw	1·040	vvw
2·46	mw	221	2·47	1·475	w	1·021	vw
2·40	vvw	112	2·42	1·440	vw	1·007	vvw
2·27	mw	320	2·27	1·416	vw	0·990	vw
		202	2·24	1·406	vvw	0·974	vvw
2·17	mw	031	2·16	1·382	w	0·965	vvw
		212	2·19	1·360	w		
2·13	vw	022	2·15				
2·10	m	131	2·12				

DISCUSSION

The usual starting material for the preparation of tin compounds is tin(II) chloride dihydrate which is rapidly oxidised, in part, to tin(IV) material on storage. Even new tin(II) chloride dihydrate of analytical-reagent grade was found to contain about 5% of tin(IV), and materials prepared from it tend to be heavily contaminated with tin(IV) and with chloride. Tin(II) sulphate can, on the other hand, be prepared rapidly from pure and readily available materials and stored in a pure state; sulphate does not seem to contaminate the products to the same extent as chloride does. Tin(II) sulphate has also been used successfully in the reduction of many organic and inorganic materials.[12]

The use of tin(II) sulphate as a general reagent is limited by its insolubility in common organic solvents, but its solubility in water is considerably greater than was reported previously.

The unit-cell dimensions, crystal data, and *X*-ray diffraction powder pattern of tin(II) sulphate closely resemble those of the isomorphous sulphates [13] of barium, strontium, and lead. A comparison of the ionic radii and unit-cell volumes of the four sulphates shows,

[10] Clerici, *Rend. Accad. Lincei*, 1907, **16**, 187; 1922, **31**, 116.

[11] Hanawalt, Rinn, and Frevel, *Ind. Eng. Chem. Analyt.*, 1938, **10**, 457; A.S.T.M. index No. 1—0814.

[12] Sinclair and Smith, personal communication.

[13] James and Wood, *Proc. Roy, Soc.*, 1925, **109**, 598.

however, that the unit-cell volume of tin(II) sulphate is much greater than would be expected for a structure identical with that of the other sulphates:

Sulphate	Ba	Pb	Sr	Sn
Unit-cell volume (Å^3)	342·1	315·0	306·5	337·9
Ionic radius (Å)	1·35	1·21	1·13	0·92

Tin(II) sulphate is, therefore, unlikely to be isomorphous with these three sulphates, and, in fact, structure-factor calculations based on the barium sulphate structure[13] confirm the view that tin(II) sulphate does not have the same structure. Work in progress indicates that tin(II) sulphate has the space group $Pna2_1$, and not the alternative $Pnma$.

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