381. *Basic Tin*(II) *Nitrate.*

By J. D. DONALDSON and W. MOSER.

Of the various tin(II) nitrates reported in the literature, the only one preparable in a pure state from aqueous solution is found to be a basic nitrate $Sn_3(OH)_4(NO_3)_2$. The difficulties inherent in work with tin(II) nitrates are discussed, and the preparation and analysis of the basic nitrate described. The substance is a high-explosive; full tests of its explosive characteristics are listed.

The thermal decomposition, at 125°, has been studied in detail. The main products are found to be tin(IV) oxide, nitric oxide, and water, in agreement with the suggested formula. *X*-Ray diffraction data show that the crystals are monoclinic with unit-cell dimensions $a = 16{\cdot}16$ Å, $b = 9{\cdot}07$ Å, $c = 16{\cdot}38$ Å, $\beta = 122°$, and 8 formula units per cell.

AN explosive tin(II) nitrate was investigated by Weber[1] who obtained it by slow addition of sodium carbonate to a freshly prepared solution of tin(II) oxide in nitric acid. The white crystalline product was partly decomposed by water, oxidised slowly in air, and exploded when rubbed, struck, or heated above 100°. Weber considered it to be anhydrous and gave it the formula $Sn_2O(NO_3)_2$. Bury and Partington[2] were unable to prepare a truly explosive solid. The only other mention of a similar material is in a report of the Government Chemist[3] in which an explosion in a flour mill was attributed to the formation of basic tin(II) nitrate.

Dilute solutions of tin(II) nitrate are reasonably stable. They may be prepared either by metathesis from the chloride or sulphate, or by dissolution of tin(II) oxide, hydrous or anhydrous, in dilute nitric acid. Attempts to evaporate to crystallisation result in decomposition, which may occasionally be violent. The decomposition produces tin(IV) oxide and various nitrogen compounds, principally hydroxylamine and nitrous oxide.[4,5] From the equations for the various possible nitrate electrodes, the oxidation potential of the nitrate ion is strongly dependent on pH; the nitrate ion is a more powerful oxidant in strongly acid than in weakly acid or neutral solution. It follows that preparation of a

---

[1] Weber, *J. prakt. Chem.*, 1882, **26**, 121.
[2] Bury and Partington, *J.*, 1922, **121**, 1998.
[3] Report of the Government Chemist, 1922—1923.
[4] Milligan and Gillette, *J. Phys. Chem.*, 1924, **28**, 747.
[5] Montemartini and Vernazza, *Ind. Chim.* (*Italy*), 1931, **6**, 632.

normal nitrate would be even more difficult than that of the basic nitrate, especially as Tobias [6] has shown that tin(II)-hydroxo-cation complexes persist to as low a pH as 1·5.

EXPERIMENTAL

We find that a satisfactory yield of the moderately soluble crystals can be obtained only by starting from fairly concentrated nitric acid and hydrous tin(II) oxide.[7] To avoid decomposition, the first portions of hydrous oxide must be added very slowly to the cooled acid. After saturation, amounting also to partial neutralisation, the temperature can be raised slightly without decomposition, the acid saturated with further hydrous oxide, and the process continued in stages to a boiling saturated solution. This stepwise procedure is essential for the preparation of a pure product in good yield.

Preparation.—Copper(II) sulphate (50 g.) of analytical-reagent grade was dissolved in water (400 ml.) and sulphuric acid (20 ml.), and boiled with metallic tin (50 g.), also of analytical-reagent grade, until the solution became colourless and the deposited copper was covered with a grey coating of tin. The resulting solution of tin(II) sulphate [8] was filtered, kept under an atmosphere of carbon dioxide, and treated with a 1 : 1 v/v ammonia (*d* 0·88)-water solution (280 ml.) to precipitate hydrous tin(II) oxide.[7] The precipitate was washed by centrifuging it with air-free distilled water until quite free from ammonia. It was suspended in a little air-free distilled water, filtered by suction (Whatman no. 5 paper), and partly dried by pressure on the filter. Two batches of this partly dried paste are required for the remaining stages but are best prepared separately because of difficulties with washing and drying of bigger batches.

Nitric acid (26 ml.; *d* 1·42) of analytical-reagent grade and water (39 ml.) were cooled to approx. −20° in ice-salt. Hydrous tin(II) oxide paste was added gradually in very small portions and with stirring until the acid was saturated. The temperature was allowed to rise to 0°, the acid saturated with more hydrous oxide, and the process continued in further stages of about 20° each to a boiling saturated suspension. The suspension was boiled for about 2 min., filtered by suction into a warm flask, and allowed to cool slowly. The crystalline product was filtered off, washed rapidly with acetone (without prior washing with water!), and dried successively by suction and *in vacuo* over silica gel and paraffin wax (yield, 18—25 g.). The pH of the mother-liquor was about 1·5.

A less pure product, in poorer yield, can be obtained by the simpler procedure of treating the double batch of hydrous oxide with the minimum of 2 : 3 v/v nitric acid-water required to dissolve it at −20° and adding solid sodium hydrogen carbonate in small amounts until a permanent precipitate is obtained. The suspension can then be boiled, filtered, and cooled, and the crystalline product treated as in the first method.

General Properties.—Basic tin(II) nitrate is crystalline, slightly soluble in cold, more soluble in hot water, but partly decomposed by either to hydrous tin(II) oxide. Careful control of the hydrolysis results in the production of crystalline hydrous tin(II) oxide.[9] Basic tin(II) nitrate decomposes explosively at 125°. On storage, the crystals are stable for a few months in a glass container, but eventually become yellow and finally decompose spontaneously with slight explosion to give tin(IV) oxide.

When a concentrated solution of basic tin(II) nitrate in 2N-hydrochloric acid, or a similar solution prepared by metathesis from tin(II) chloride and lead nitrate, is kept for a few days, a gelatinous material is deposited. The rather diffuse *X*-ray powder pattern of the dried material, typical of a vitreous solid, is essentially that of tin(IV) oxide. When this material is heated, water and oxides of nitrogen are given off. The material must therefore be regarded as a hydrated tin(IV) oxide with sorbed nitric acid or nitrate inclusions, and previous [10,11] reports of it as a tin(IV) nitrate are, in our opinion, erroneous.

Analysis.—Tin(II) and total tin were determined by the method of Donaldson and Moser,[12] except that in the tin(II) determination the sample was simultaneously dissolved and oxidised by a single injection of iron(III) chloride solution. Nitrate was determined by reduction with

---

[6] Tobias, *Acta Chem. Scand.*, 1958, **12**, 198.

[7] Donaldson and Moser, *J.*, 1961, 835.

[8] Donaldson and Moser, *J.*, 1960, 4000.

[9] Donaldson, *Acta Cryst.*, 1961, **14**, 65.

[10] Ditte, *Ann. Chim. Phys.*, 1882, **27**, 159.

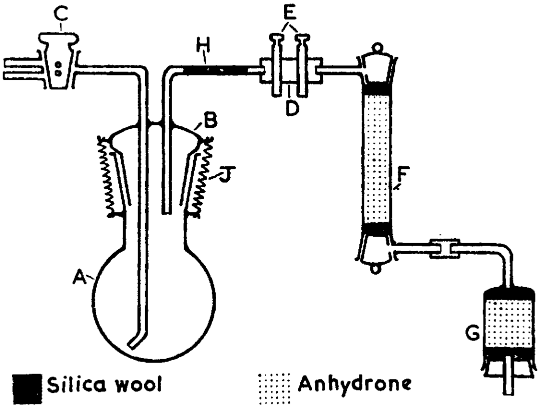
[11] Walker, *J.*, 1893, **63**, 845.

[12] Donaldson and Moser, *Analyst*, 1959, **84**, 10.

Devarda's alloy and estimation as ammonia. The substance was found to contain water (contrary to Weber's finding [1]) and a special apparatus was devised for its determination because of the explosive nature of the material.

The apparatus (see Figure) consisted of a 50 ml. explosion vessel (A) fitted with a cap (B) through which passed two tubes. One led through a two-way tap (C) to a vacuum pump or to a supply of dry oxygen; the other tube was packed with silica wool (H) and terminated in a piece of aged rubber tubing (D), closed during the explosion by two spring clips (E). An absorption tube (F) and a guard-tube (G) were attached for the water determination. A tap at (E) was found unsatisfactory because grease volatilised into the absorption tube. The B 19 ground-glass joint was held in place by two springs (J). In each determination about 0·15 g. of sample was weighed into the explosion vessel, the vessel evacuated, and the sample exploded by heat. The vessel was then swept out with dry oxygen and the water determined.

Apparatus for water analysis.



The results of triplicate analyses on two typical samples were:

	Sample 1	Sample 2	Required for $Sn(NO_3)_2,2SnO,2H_2O$
Tin(II)	64·7, 64·9, 64·5	64·8, 64·8, 64·9	64·9
Tin (total)	65·1, 65·1, 65·1	64·8, 65·1, 65·1	
Nitrate	22·3, 22·3, 22·4	22·1, 22·1, 22·2	22·1
Water	6·3, 6·6, 6·7	6·7, 6·8, 6·8	6·6

Thermal Decomposition.—The thermal stability of basic tin(II) nitrate was tested in an m. p. apparatus. The purest samples exploded at 125°, all others between 120° and 125°.

The decomposition products were studied by exploding samples in a vessel similar to that illustrated, but attached through a tap at (E) to a grid consisting of a liquid-air trap, a manometer, and a gas cell. The solid residue was found, by *X*-ray diffraction powder examination and by constancy of weight on ignition,[7] to be tin(IV) oxide. The gaseous products were water (see analysis above) and oxides of nitrogen. The dried gases were examined by infrared spectroscopy [13] and found to contain 93% or more of nitric oxide, approximately 3% of nitrogen dioxide, and ½% of nitrous oxide. A small amount of gas was not condensed in the liquid-air trap, and can be accounted for as nitrogen.

Explosive Characteristics.—Ignition of samples by friction, impact, spark, and heat was examined by standard tests, as was the explosive power. The results are quoted, in the same order, as length of a pendulum initiating the friction, weight and fall-height of a hammer, energy of a spark from a condenser discharge, temperature of a Wood's metal bath, and expansion of a lead block.

	Friction (cm.)	Impact (oz./inch)	Spark (% ignitions at erg)	Heat (° c)	Power (c.c./g.)
Basic tin(II) nitrate	72—82	45—75	None at $1·25 \times 10^6$	150—152	6
Lead azide	0·6—2·7	120	50% at 400—18,000	315	10
Lead styphnate		140	50% at 500	250—255	15

---

[13] Nightingale, *et al.*, *J. Phys. Chem.*, 1954, **58**, 1047.

The ignition temperatures recorded in the standard test are higher than those found in an m. p. apparatus, because in the former test the sample is heated rapidly and required to ignite in less than 5 sec., whereas in the latter the sample and surroundings are at nearly the same temperature.

Crystallography.—Basic tin(II) nitrate consists of snow-white acicular crystals which show parallel extinction and have $n > 1{\cdot}74$, negative elongation, and high birefringence. *X*-Ray data show that the crystals are monoclinic with long axis *b* and cleavage (100).

Crystal data: $Sn_3(OH)_4(NO_3)_2$, $M = 548{\cdot}1$. Monoclinic $a = 16{\cdot}16 \pm 0{\cdot}02$, $b = 9{\cdot}07 \pm 0{\cdot}02$, $c = 16{\cdot}38 \pm 0{\cdot}02$ Å, $\beta = 122°$, $U = 2036$ Å^3, $D_m = 3{\cdot}61 \pm 0{\cdot}02$ g./c.c. (by suspension in a mutual solution [14] of thallous formate and thallous malonate in water). $Z = 8$. $D_c = 3{\cdot}64$ g./c.c. Filtered Cu-K_α radiation; single-crystal rotation photographs about all three axes, and Weissenberg and oscillation photographs about *b*.

There is strong pseudo-halving of both *a* and *c*, giving a pseudo-unit-cell with dimensions $a = 8{\cdot}08$, $b = 9{\cdot}07$, $c = 8{\cdot}19$ Å, $\beta = 122°$. The weak superlattice reflections were detected in the rotation photographs about *a* and *c*. The Table contains the *X*-ray diffraction powder data obtained by using 11·64 cm. cameras with filtered Cu-K_α radiation. The spacings longer than 2·8 Å have been indexed.

TABLE 1. X-*Ray diffraction powder data for basic tin*(II) *nitrate.*

d (Å)	Rel. intensity	Index of reflection	Calc. *d* spacings	*d* (Å)	Rel. intensity	*d* (Å)	Rel. intensity
7·03	m	002	7·12	2·79	m	1·996	vw
6·78	ms	200	6·85	2·69	w	1·982	vw
5·55	vw	$\bar{2}12$	5·57	2·60	vvw	1·880	w
5·52	vw	012	5·55	2·56	vvw	1·822	vw
4·58	s	020	4·55	2·53	vvw	1·789	vvw
4·33	w	$\bar{2}04$	4·28	2·26	m	1·738	vvw
3·79	s	014	3·78	2·23	vw	1·710	vvw
3·49	w	004	3·47			1·591	vw
3·41	w	400	3·43			1·507	vw
3·30	w	014	3·33			1·397	vvw
3·18	vs	410	3·18				
2·98	vw	222	2·98				
2·89	vvw	$\bar{4}14$	2·89				

DISCUSSION

The analytical results agree with a formula $Sn(NO_3)_2,2SnO,2H_2O$. A basic tin(II) nitrate of this formula would, in a stoicheiometric reaction, be expected to break down to $3SnO_2$, $2H_2O$, and $2NO$, in complete agreement with the results of the thermal decomposition studies. Moreover, the unit-cell dimensions, the measured density, and the suggested formula weight together give the calculated value of *Z* as 8·01. Lattice considerations require *Z* to be an integer, so that the calculated value's proximity to a whole number may be taken as a further indication of the correctness of the formula.

However, since oxide ions cannot co-exist in a solid structure with free water, the water must be present as hydroxyl, and the most satisfactory formula must be tritin(II) tetrahydroxide dinitrate $Sn_3(OH)_4(NO_3)_2$. This formulation would be in agreement with the work of Tobias [6] who has shown that $Sn_3(OH)_4{}^{2+}$ is the main species formed in the hydrolysis of tin(II) solutions.

The co-existence in the substance of tin(II) and nitrate is responsible for the explosive properties and for many difficulties encountered in all stages of the work. Attempts to prepare a normal nitrate are still in progress. At the low pH needed to suppress hydrolysis, only dilute solutions are stable. Freezing of these solutions has so far produced only ice, alone or in admixture with a possible normal nitrate. A eutectic mixture of this kind would account for the dubious $Sn(NO_3)_2,20H_2O$ reported by Weber.[1]

Comparison with the standard initiating explosives lead azide and lead styphnate shows basic tin(II) nitrate to be more sensitive to impact and heat, but less sensitive to friction than either. The only remarkable feature is its very high resistance to spark

---

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

ignition, not a single ignition having been recorded in 50 discharges at maximum spark energy. The power, as measured by the lead-block test, is less than that of the standard explosives, the most likely reason being that only 18% of the solid is converted into gaseous products in the explosion. In the circumstances, basic tin(II) nitrate seems unlikely to have commercial uses, unless its high spark-resistance or low detonation temperature should suit some specialised application.

We are grateful to Imperial Chemical Industries Limited, Nobel Division, for conducting the explosive tests, to Dr. D. C. McKean and Dr. H. F. W. Taylor for helpful discussion, and to D.S.I.R. for a research grant (to J. D. D.).

UNIVERSITY OF ABERDEEN, CHEMISTRY DEPARTMENT,
OLD ABERDEEN, SCOTLAND.

[*Received, November 14th*, 1960.]