[CONTRIBUTION FROM THE MALLINCKRODT LABORATORY OF CHEMISTRY AT HARVARD UNIVERSITY]

Compounds of the Dimethyltin Cation and their Similarity to Compounds of Divalent Tin and Lead

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Twelve new compounds of the $(CH_3)_2Sn^{++}$ ion have been prepared from dimethyltin dichloride, which is now readily available. A number of other compounds too unstable to purify for analysis also are described. The solubilities and other properties of these compounds are compared with those of the corresponding salts of divalent tin and lead in terms of the structure of the $(CH_3)_2Sn^{++}$ ion.

Some salts of the $(CH_3)_2Sn^{++}$ cation were made many years ago by such diverse methods as the action of potassium fluoride on an alcoholic solution of dimethyltin dibromide,[3] the addition of hydrogen sulfide to an acid solution of dimethyltin diiodide[4] and the action of acids on dimethyltin oxide.[5] The earlier investigators used the bromide and iodide because they were accessible through established techniques.

Dimethyltin dichloride now is readily available through a much simpler synthesis,[6] and in aqueous solution this compound dissociates almost completely according to the equation[7]

$$(CH_3)_2SnCl_2 + nH_2O = (CH_3)_2Sn(H_2O)_n^{++} + 2Cl^-$$

The cations readily undergo reaction, and a sufficient number of compounds has now been made so that a comparison with the corresponding compounds of Sn^{++++}, Sn^{++} and Pb^{++} can be made. This paper reports the preparation of dimethyltin basic chromate, arsenate, oxalate, salicylate, phthalate, basic succinate, molybdate, tungstate, ferricyanide, ferrocyanide, vanadate, iodate and basic benzoate, together with qualitative indications of a cyanate, a thiocyanate, an antimonate, an azide, an iodide, a metaborate, a phosphate and a hypophosphite.

Experimental

Basic Chromate.—When aqueous solutions of dimethyltin dichloride and sodium chromate are mixed, a bright yellow precipitate the color of lead chromate is formed. If the dimethyltin dichloride is impure the precipitate darkens rapidly on drying and decomposes at temperatures above 200°; with very pure dichloride a stable precipitate is formed which may be purified by digesting repeatedly with hot water, and may be dried at 80° without decomposition. Samples analyzed by combustion did not correspond to the formula $(CH_3)_2SnCrO_4$, however.

Anal. Calcd. for $C_2H_6SnCrO_4$: C, 9.07; H, 2.28. Found: C, 11.57; H, 2.98.

Samples dried in air at 80°, in a vacuum desiccator at room temperature, and in a drying pistol at 56° all had similar compositions. In an effort to follow more closely the precipitation of the dimethyltin ion, 0.8785 g. of $(CH_3)_2SnCl_2$ in 50 ml. of water was titrated potentiometrically with a 0.1 *M* solution of ammonium chromate. If the reaction were

$$(CH_3)_2Sn(H_2O)_n^{++} + CrO_4^{=} \longrightarrow (CH_3)_2SnCrO_4 + nH_2O$$

the *p*H would be expected to rise, for a solution of dimethyltin dichloride itself is acid by hydrolysis[7] and the withdrawal of $(CH_3)_2Sn(H_2O)_n^{++}$ ions would reverse the hydrolysis reaction

$$(CH_3)_2Sn(H_2O)_n^{++} + H_2O \longrightarrow (CH_3)_2Sn(H_2O)_{n-1}OH^+ + H_3O^+$$

However, the *p*H remained in the range 2.4 to 3.0 throughout the titration, indicating that the basic ions are the reactive species because they form a less soluble product. Assuming that the reaction is

$$2(CH_3)_2SnOH^+ \text{ hydr.} + CrO_4^{=} \longrightarrow [(CH_3)_2SnOH]_2CrO_4$$

we may expect it to be followed by the dehydration

$$[(CH_3)_2SnOH]_2CrO_4 \longrightarrow (CH_3)_2SnO\cdot(CH_3)_2SnCrO_4 + H_2O$$

for the behavior during the precipitation of dimethyltin oxide by the action of bases on a solution of the chloride indicates the latter to be the more probable product.[7] A preparation from 4.4 g. (0.02 mole) of $(CH_3)_2SnCl_2$ in 20 ml. of water and 3.04 g. (0.02 mole) of $(NH_4)_2CrO_4$ in 30 ml. of water, thoroughly washed and then dried at 56°, was analyzed iodometrically in acid solution for its chromate content. The carbon and hydrogen were determined separately by combustion, as usual.

Anal. Calcd. for $C_2H_6SnO\cdot C_2H_6SnCrO_4$: C, 2.80; H, 11.20; CrO_4, 12.11. Found: C, 2.81; H, 11.14; CrO_4, 12.13, 12.09.

The basic chromate so prepared is a yellow powder, insoluble in water and in organic solvents but soluble in concentrated sulfuric acid and in concentrated solutions of sodium hydroxide. When heated in air it begins to darken at 265° but does not melt up to 350°. At higher temperatures it decomposes exothermally, the carbon and hydrogen being oxidized by the chromate content with flashes of light.

Arsenate.—The addition of 4.4 g. (0.02 mole) of $(CH_3)_2SnCl_2$ in 25 ml. of water to 6.24 g. (0.02 mole) of $Na_2HAsO_4\cdot 7H_2O$ in 75 ml. of water precipitated a white powder which was filtered, washed with water and then with methanol, and dried in a vacuum desiccator.

Anal. Calcd. for $C_2H_6SnHAsO_4$: C, 8.3; H, 2.44. Found: C, 8.12; H, 2.47.

The white crystals darken at 350°, but do not melt even at much higher temperatures.

Oxalate.—Pfeiffer[8] prepared anhydrous $(CH_3)_2SnC_2O_4$ by the action of potassium oxalate on dimethyltin diiodide. We added a saturated solution of oxalic acid dihydrate to a saturated solution of dimethyltin dichloride and obtaihed a monohydrate of dimethyltin oxalate.

Anal. Calcd. for $C_2H_6SnC_2O_4\cdot H_2O$: C, 18.85; H, 3.17; SnO_2, 59.14. Found: C, 19.98; H, 3.28; SnO_2, 59.5.

A sample of 0.5270 g. heated in an oven at 110° for 10 hours lost 6.7% of its weight ($C_2H_6SnC_2O_4\cdot H_2O$ contains 7.1% of water). After exposure to room air at room temperature for 24 hours the sample again weighed 0.5271 g., and after a second heating in the oven it lost 7.0% of its weight. Of those we made, this is the only dimethyltin compound that is hydrated under ordinary conditions. When it is heated it first dehydrates, then turns yellow at 310°, darkens at 335°, and decomposes without melting at temperatures above 355°.

Salicylate.—Saturated solutions of dimethyltin dichloride and sodium salicylate yielded white microcrystalline dimethyltin salicylate, insoluble in water but soluble in hot

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[1] Ethyl Corporation fellow at Harvard University, 1952–53.

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[3] E. Krause, *Ber.*, **51**, 1447 (1918).

[4] K. A. Kocheshkov, *ibid.*, **66**, 1661 (1933); T. Harada, *Bull. Chem. Soc. Japan*, **17**, 283 (1942).

[5] A. Cahours, *Ann.*, **114**, 367, 373 (1860).

[6] A. C. Smith, Jr., Thesis, Harvard University, 1951; see also F. A. Smith, U. S. Patent 2,625,559 (1953).

[7] E. G. Rochow and D. Seyferth, THIS JOURNAL, **75**, 2877 (1953).

[8] P. Pfeiffer, *Z. anorg. Chem.*, **68**, 112 (1910).

benzene. Two recrystallizations from benzene yielded crystals melting sharply at 205–206° (Anschütz thermometer).

Anal. Calcd. for $C_2H_6SnC_{14}H_{10}O_6$: C, 45.43; H, 3.81. Found: C, 45.22; H, 3.85.

This and the benzoate were the only compounds in our series that were found to be recrystallizable from benzene.

Phthalate.—Saturated solutions of dimethyltin dichloride and potassium hydrogen phthalate slowly precipitated white crystals of dimethyltin phthalate which could easily be filtered and purified by digestion. After the compound was dried in a vacuum desiccator it was stable up to 325°, but darkened slightly at 340° and decomposed without melting at 360°. It was not soluble in water or organic solvents.

Anal. Calcd. for $C_2H_6SnC_8H_4O_4$: C, 38.38; H, 3.22. Found: C, 38.33; H, 3.20.

Succinate.—Aqueous solutions of sodium succinate and dimethyltin dichloride yielded a white powder which was purified by digestion and dried in air at 70°. The dry compound was insoluble in water and benzene, and decomposed at temperatures above 314°. The analysis indicates that this is the *basic* salt (like the chromate) rather than the normal salt.

Anal. Calcd. for $C_2H_6SnC_4H_4O_4$: C, 27.21; H, 3.81. Calcd. for $C_2H_6SnO{\cdot}C_2H_6SnC_4H_4O_4$: C, 22.19; H, 3.76. Found: C, 22.40; H, 3.82.

That the salt is not the initial reaction product of the basic ion, *i.e.*, $(C_2H_6SnOH)_2C_4H_4O_4$, is shown by the analysis and by the fact that further heating at 110° for 18 hours brought about only 0.17% loss in weight.

Molybdate.—Saturated solutions of dimethyltin dichloride and sodium molybdate gave a flocculent white precipitate which was dried in a vacuum desiccator. The compound darkened slightly at 335° and decomposed without melting at 343°; it would not burn in air but burned in an oxygen gas flame, leaving a black residue.

Anal. Calcd. for $C_2H_6SnMoO_4$: C, 7.78; H, 1.96. Found: C, 7.59; H, 2.24.

Tungstate.—A white precipitate obtained in the same way as the molybdate was washed and dried at 120°. It began to darken at 330° but did not melt before decomposing. It was found difficult to burn all of the carbon out of the residue of heavy metal oxides during the combustion.

Anal. Calcd. for $C_2H_6SnWO_4$: C, 6.05; H, 1.51. Found: C, 5.58; H, 1.92.

Ferricyanide.—Saturated solutions of dimethyltin dichloride and potassium ferricyanide were mixed, and an orange-brown precipitate formed at once. This precipitate seemed to be somewhat soluble in water, for after extensive washing the wash-water still was slightly yellow and formed a precipitate of silver ferricyanide with silver nitrate even though it no longer gave a positive flame test for potassium. It also was found that the dimethyltin ferricyanide could not be digested with water in the manner of the other preparations in this series for another reason: it oxidized readily in boiling water (and also in 30% hydrogen peroxide) to a green substance and then to a blue solid. A sample of freshly precipitated dimethyltin ferricyanide was washed at room temperature and dried in a vacuum desiccator for analysis, and this became lighter in color at 210° and then decomposed without melting in the range 335 to 360°.

Anal. Calcd. for $(C_2H_6Sn)_3[Fe(CN)_6]_2$: C, 24.84; H, 2.09; N, 19.32. Found: C, 24.92; H, 2.49; N, 18.67.

The green substance formed either by continued boiling with water in the presence of air, or by letting the solution stand in daylight, was considered to be dimethyltin aquoprusside, $(CH_3)_2Sn[Fe(CN)_5H_2O]$, since the method of formation is characteristic of that of an aquoprussi compound. However, the analysis corresponds more closely to that of a tetrahydrate of the ferricyanide, rather than that of the aquoprusside itself.

Anal. Calcd. for $C_2H_6Sn[Fe(CN)_5H_2O]$: C, 23.83; H, 2.29; N, 19.86. Calcd. for $(C_2H_6Sn)_3[Fe(CN)_6]_2{\cdot}4H_2O$: C, 22.94; H, 2.78; N, 17.84. Found: C, 23.00; H, 2.50; N, 17.27.

There is no other reason to believe that the substance is a tetrahydrate, however, and it seems more reasonable to regard it as an aquoprusside in which the anion is between $[Fe(CN)_5H_2O]^-$ and $[Fe(CN)_4(H_2O)_2]^-$ in composition.

Ferrocyanide.—The white precipitate formed by mixing saturated solutions of dimethyltin dichloride and potassium ferrocyanide is unchanged by boiling with water, but becomes yellow upon drying in a vacuum desiccator. When added to water the yellow powder becomes white again, and returns to yellow upon drying. The white form is probably a hydrate, but the loss of weight upon heating did not correspond to that expected of a definite hydrate. The yellow form is insoluble in water, ethanol and acetone, and darkens at 310°. From its color, its behavior and its analysis, the compound is believed to be the basic salt, $(CH_3)_2SnO{\cdot}[(CH_3)_2Sn]_2Fe(CN)_6$.

Anal. Calcd. for $C_2H_6SnO{\cdot}(C_2H_6Sn)_2Fe(CN)_6$: C, 21.37; H, 2.69; N, 12.47. Found: C, 21.16; H, 2.87; N, 14.76.

"**Naphthionate.**"—Naphthionic acid was precipitated from the solution of its sodium salt by the acidity of the dimethyltin dichloride, which forms solutions of *p*H 1.[7]

Vanadate.—The addition of a solution of ammonium metavanadate to one of dimethyltin dichloride causes precipitation of a yellow substance which resembles dimethyltin basic chromate but darkens rapidly. No stable product was isolated; it is believed that the dimethyltin cation is oxidized by the vanadate anion in the acid solution.

Iodate.—When concentrated solutions of dimethyltin dichloride and potassium iodate are mixed no precipitate forms, but after heating to boiling some crystals of dimethyltin iodate separate. The crystallization can be caused to begin without heating by seeding with a crystal from a previous preparation. The crystals may be washed and dried, but they turn brown upon standing either in air or in a vacuum desiccator. The brown color cannot be extracted with carbon tetrachloride. Iodimetric analysis of three different preparations gave results which were variable, averaging 68.87% IO_3^- (calcd. for $C_2H_6Sn(IO_3)_2$ is 70.16%). The crystals burn rapidly with the liberation of iodine vapor. When the melting point was sought, the sample contained in a capillary tube exploded with great violence at about 100°, shattering the Thiele tube.

Cyanate.—The addition of potassium cyanate to a solution of dimethyltin dichloride results partly in the hydrolysis of the resulting cyanic acid to carbon dioxide and ammonia. The solution rapidly becomes basic, and dimethyltin oxide precipitates with dimethyltin cyanate. The precipitate was shown to contain cyanate ions by the evolution of carbon dioxide upon the addition of hydrochloric acid. The composition of the precipitate corresponds to about equal parts by weight of $(CH_3)_2SnO$ and $(CH_3)_2Sn(CNO)_2$.

Benzoate.—The addition of a solution of ammonium benzoate to a saturated solution of dimethyltin dichloride gives a white crystalline precipitate which is easily filtered and washed. The dry crystals are soluble in benzene; after two recrystallizations from that solvent, the product was analyzed and found to be the basic salt.

Anal. Calcd. for $C_2H_6Sn(C_7H_5O_2)_2$: C, 49.1; H, 4.11. Calcd. $C_2H_6SnO{\cdot}C_2H_6Sn(C_7H_3O_2)_2$: C, 39.0; H, 4.01. Found: C, 39.69; H, 4.02.

This compound melts at 236–237° (Anschütz thermometer) to a translucent liquid.

Antimonate, Azide, Metaborate, Phosphate and Hypophosphite.—Metathetic reactions of the appropriate potassium or sodium salts with dimethyltin dichloride gave precipitates which are believed to be the dimethyltin salts but were not isolated or analyzed.

Discussion

Much has been written about the "inert pair" of s^2 electrons in tin, lead, antimony, bismuth and selenium.[9] In dimethyltin dichloride it is probable that the $5s^2$ and $5p^2$ electrons are involved in sp hybrid orbitals, leading to a symmetrical covalent molecule, but in the dimethyltin cation the methyl groups probably occupy the $5s^2$ orbitals above and the other electrons are given up to the anion. In water and amines or amides the solvated cation probably remains tetrahedral, but we believe that

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(9) N. V. Sidgwick, "The Electronic Theory of Valency," Oxford Press, New York, N. Y., 1932, p. 178 *et seq.*; L. Pauling, "The Nature of the Chemical Bond," Cornell University Press, Ithaca, N. Y., 1948, pp. 184, 185.

in anhydrous salts the $(CH_3)_2Sn^{++}$ ion resembles $:Sn^{++}$ (where the pair of dots indicates the unused $5s^2$ electrons in the latter), and should also resemble: Pb^{++} and $:Tl^{+}$ in structure.[10,11]

We have compared the properties and solubilities of salts of $(CH_3)_2Sn^{++}$, Pb^{++} and Sn^{++} ions in Table I, and we note especially the formation of basic salts like $PbO{\cdot}PbCrO_4$ which resemble the basic dimethyltin salts described herein. The similarities are striking, and provide support for the view that the $(CH_3)_2Sn^{++}$ ion has the structure indicated above. It is equally certain that $(CH_3)_2Sn^{++}$ does *not* resemble tetravalent tin in the nature and behavior of its compounds.

TABLE I

COMPARISON OF SOLUBILITIES

Salt	$Sn^{++c,d}$	$(CH_3)_2Sn^{++}$	Pb^{++d}
Acetate		Sol[a]	$19.7^{0°}$
Antimonate	Insol.	Insol.	Insol.
Arsenate	Insol.	Insol.	Insol.
Azide	Insol.	Insol.	Insol.
Borate	Insol.	Insol. (meta)	Insol. (meta)
Bromate	...	(No ppt.)	$1.38^{20°}$
Bromide	Sol.	Sol.[a]	$0.45^{0°}$
Chlorate	...	(No ppt.)	$151^{18°}$
Chloride	$83.9^{0°f}$	$120^{25°}$	$0.673^{0°}$
Chromate (basic)	...	Insol.	Insol.
Chromate	Insol.	...	Insol.
Cyanate	...	Insol.	Insol.
Cyanide	...	Insol.	V. sl. sol.
Ferricyanide	Insol.	V. sl. sol.	Sl. sol.
Ferrocyanide	Insol.	Insol.	Insol.
Fluoride	Sol.[e]	$466^{20°b}$	$0.064^{20°}$
Formate	...	Sol.[a]	$1.6^{18°}$
Phosphite	Insol.	Insol. (hypo)	...
Iodate	...	Insol.	$0.0012^{0°}$
Iodide	$1.3^{21°}$	Sol.[a]	0.0442
Molybdate	...	Insol.	Insol.
Nitrate	Sol.	Sol.	$38.8^{0°}$
Nitrite	...	Insol.	...
Oxalate	Insol.	Insol.	$1.6 \times 10^{-4}\ ^{18°}$
Oxide	...	Insol.	$0.0068^{18°}$
Perchlorate	...	(No ppt.)	Sol.
Periodate	...	(No ppt.)	Insol.
Phosphate (dibasic)	Insol.	Insol.	$1.4 \times 10^{-5}\ ^{20°}$
Sulfate	$19^{19°}$	Sol. (1)	$2.8 \times 10^{-3}\ ^{0°}$
Sulfide	$2 \times 10^{-6}\ ^{18°}$	Insol.	Insol.
Sulfite	...	(No ppt.)	Insol.
Thiocyanate	Sol.	Sol.	$0.05^{20°}$
Tungstate	Insol.	Insol.	Insol.
Vanadate	...	Insol.	...
Succinate	...	Insol.	...

[a] Cahours, *Ann.*, 114, 367 (1860). [b] E. Krause, *Ber.*, 51, 1447 (1918). [c] Gmelin-Kraut's *Handbuch der anorg. Chemie*, 7 Ed., Vol. IV, Part 1, Carl Winter's Universitätsbuchhandlung, Heidelberg, 1911, pp. 285–373. [d] "Lange's Handbook of Chemistry," 6th Ed., Handbook Publishers, Inc., Sandusky, Ohio, 1946, pp. 259–260 (Sn. cpds.); pp. 206–210 (Pb cpds.). [e] SnF_2 forms complexes of the type M_2SnF_4 and $MSnF_3$; *cf.* M. E. Fremy, *Ann. chim. phys.*, **47**, [3], 1 (1856). R. Wagner, *Ber.*, **19**, 896 (1886). Me_2SnF_2 is soluble in KF soln. to give complexes of the type $K_2[(CH_3)_2SnF_4]$ (note *b* above). [f] $SnCl_2$ forms addition cpds. (or double salts) with amine hydrochlorides: *cf.* note *c*, p. 342. Me_2SnCl_2 forms double salts of this kind also: $Me_2SnCl_2{\cdot}2C_5H_5N{\cdot}HCl$ and others *cf.* P. Pfeiffer, *Z. anorg. Chem.*, 71, 97 (1911). P. Pfeiffer, *Ann.*, **376**, 310 (1910).

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[10] If the supposition of ionization of the 5 p^2 electrons is correct, the anhydrous $(CH_3)_2Sn^{++}$ ion should be linear. An investigation of the structure of this cation in typical salts is in progress.

[11] H. M. Powell and D. M. Crowfoot, *Z. Krist.*, **87**, 370 (1934), found that dialkylthallium compounds have linear R_2Tl groups which are placed in such a way that the hydrocarbon groups are between the Tl x planes.

[CONTRIBUTION FROM THE CRYOGENIC LABORATORY AND DEPARTMENT OF CHEMISTRY, THE OHIO STATE UNIVERSITY]

Low Temperature Heat Capacities of Inorganic Solids. XVII. Heat Capacity of Titanium from 15 to 305°K.[1]

BY CHARLES W. KOTHEN AND HERRICK L. JOHNSTON

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The heat capacities of titanium have been measured in the temperature range 15 to 305° K., and the derived thermal functions have been calculated and tabulated at integral values of the temperature over this range. The entropy at 298.16° K. is 7.33 ± 0.02 e. u.

Introduction

Low temperature heat capacity measurements on titanium have been made by Kelley[2] between 53 and 295°K., but his sample contained over 1% of impurities. The titanium used in the present research was of much greater purity than Kelley's and hence the thermal data reported should be more accurate.

Apparatus and Materials

The sample of iodide-process titanium was generously donated by the New Jersey Zinc Co., Palmerton, Pa. The principal contaminants were 0.0082% Mn, 0.007% Si and 0.0066% Al, with a total of 0.02% of N, Te, Pb and Cu. The rough rod was cut into small pieces on a shaper and these pieces were annealed in a high vacuum at 800°.

"Solid Calorimeter No. 3," one of the group of seven vacuum calorimeters described in the first paper of this series,[3] was used for the heat capacity measurements on 121.656 g. (2.5481 g. atoms) of titanium.

Experimental Results and Calculations

The experimental heat capacity data are presented in Table I. These deviate from a smooth curve by an average of 0.2 of 1%. Skinner[4] noticed that his data on zirconium were higher than Todd's[5] data below 130°K. and lower than Todd's data above 130°K. The discrepancy was attributed to oxygen in Todd's sample. The present data show a similar discrepancy with Kelley's data, the tem-

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[1] This work was supported in part by The Office of Naval Research under contract with The Ohio State University Research Foundation.

[2] K. K. Kelley, *Ind. Eng. Chem.*, **36**, 865 (1944).

[3] H. L. Johnston and E. C. Kerr, THIS JOURNAL, **72**, 4733 (1950).

[4] G. B. Skinner and H. L. Johnston, *ibid.*, **73**, 4549 (1951).

[5] S. S. Todd, *ibid.*, **72**, 2914 (1950).