Table III. Lattice Parameters and Densities for High-Pressure Phases

	a_0, Å	ρ_{exptl}, g/cm^3	ρ_{calcd}, g/cm^3
$Ni_{0.7}Co_{0.3}Te_2$	6.358 (3)		
$Ni_{0.6}Co_{0.4}Te_2$	6.354 (3)		
$Ni_{0.5}Co_{0.5}Te_2$	6.350 (3)		
$Ni_{0.4}Co_{0.6}Te_2$	6.347 (3)		
$CoTe_2$	6.320 (3)	8.24 (6)	8.28
$Ni_{0.8}Fe_{0.2}Te_2$	6.368 (1)		
$Ni_{0.6}Fe_{0.4}Te_2$	6.365 (3)	8.01 (2)	8.06
$Ni_{0.5}Fe_{0.5}Te_2$	6.354 (2)	8.07 (3)	8.09
$Ni_{0.3}Fe_{0.7}Te_2$	6.331 (2)	8.21 (2)	8.16
$Ni_{0.2}Fe_{0.8}Te_2$	6.314 (3)	8.18 (2)	8.22
$Ni_{0.1}Fe_{0.9}Te_2$	6.301 (1)		

transform even when subjected to 1400 °C and 60 kbars pressure.

Acknowledgment. The assistance of the Army Research Office, Triangle Park, N.C., and the Materials Research Laboratory, Brown University is acknowledged. The authors also wish to thank Dr. Stuart Soled for helpful discussions.

Registry No. $NiTe_2$, 12035-59-5; $CoTe_2$, 12017-14-0; $FeTe_2$, 12023-03-9.

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Tin(II) Hydroxide

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Received February 25, 1976 AIC60151K

Tin(II) hydroxide, $Sn(OH)_2$, long sought via aqueous routes, has been synthesized by an anhydrous, organometallic method involving the exchange of groups between a triorganotin hydroxide and tin(II) chloride: $2R_3SnOH + SnCl_2 \rightarrow Sn(OH)_2 + 2R_3SnCl$. The resulting white, infusible, amorphous solid has been characterized by microanalysis and infrared and tin-119m Mössbauer spectroscopies. Tin(II) hydroxide is soluble in acid and alkali, gives an ambient-temperature Mössbauer spectrum (IS = 2.78, QS = 2.20 mm/s), loses water in two stages at 126 and 195 °C to give an orange residue containing both tin(IV) and tin(II), exhibits an infrared spectrum containing ν(Sn–O) at 575 and 340 cm^{-1} and ν(SnO–H) at 3390 cm^{-1}, and reacts with catechol to give *o*-phenylenedioxytin(II).

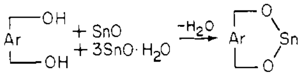
Blue-black tin(II) oxide was first prepared by Berzelius in 1812 by the addition of excess potassium carbonate to an aqueous solution of a tin(II) salt.[1] Gay-Lussac precipitated a hydrous material from aqueous ammonia in 1816,[2] and Frémy obtained a similar solid by evaporating a slurry of precipitated tin(II) oxide in aqueous ammonium chloride in 1844.[3] These materials formed by the interaction of solutions of tin(II) salts and an alkali were formulated as $Sn(OH)_2$, although Proust had found that an excess of potassium carbonate gave a white precipitate containing 5% water,[4] and Schaffner postulated in 1844 that the composition of the solid was $2SnO{\cdot}H_2O$ when dried below 80 °C.[5]

In the modern era Bury and Partington investigated the precipitate prepared in several ways and assigned the formula $3SnO{\cdot}2H_2O$ in 1922,[6] but Weiser and Milligan proposed $2SnO{\cdot}H_2O$ instead on the basis of tin analysis, x-ray powder diffraction, and composition–temperature plots 10 years later.[7] Weber claimed in 1959 to have prepared fine crystals of bright yellow tin(II) hydroxide stabilized by SiO_2 by a hydrothermal method,[8] but Donaldson showed that these materials differ from hydrous tin(II) oxide in their x-ray powder patterns.[9] Donaldson and Moser pointed out in 1961 the impossibility of preparing the compound free of both tin(IV) and anionic impurity by precipitation, but their microanalyses which were designed to distinguish the tin(IV) impurity from the remaining tin gave $5SnO{\cdot}2H_2O$ (requiring 83.7% tin and 5.07% water) as the formula of their solid,[10] by analogy with that proposed for the hydrous lead(II) oxide.[11] Finally, Howie and Moser were able to solve the structure in 1968 using single, tetragonal crystals of the hydrous oxide prepared by the very slow passage of diluted ammonia vapor through a solution of tin(II) perchlorate. The unit cell dimensions and density specified $3SnO{\cdot}H_2O$ as the correct formula of their precipitate, interpreted structurally as $Sn_6O_4(OH)_4$ with all eight oxygen atoms joined by hydrogen bonds in a regular cube superimposed upon an octahedron of tin atoms[12] and related to the cyclic $Sn_3(OH)_4{}^{2+}$ cation proposed by Tobias[13] and derivable from his species by a condensation–deprotonation reaction

$$2Sn_3(OH)_4{}^{2+} \rightarrow Sn_6O_4(OH)_4 + 4H^+ \qquad (1)$$

The lead oxyhydroxide is said to be isostructural.[12]

We had previously carried out esterification reactions on blue-black tin(II) oxide[14,15] and hydrous tin(II) oxide,[15] prepared by raising the pH of a tin(II) salt solution by addition of ammonia,[10] to yield aromatic tin(II)–oxygen heterocycles



(2)

The reactions with hydrous tin(II) oxide proceed under milder conditions,[15] presumably owing to the presence of the Sn–OH groups in the material,[12] and monofunctional phenols which fail to react with blue-black tin(II) oxide[14] give products of the formula $RO(SnO)_nR$ with the hydrous material.[15]

The infrared spectrum of hydrous tin(II) oxide contains a broad band centered at 3350 cm^{-1} which can be assigned to the ν(SnO–H) mode,[15] and the tin-119m Mössbauer spectrum[16] [IS = 2.74 ± 0.06, QS = 2.19 ± 0.12 mm/s] confirms the presence of tin(II)[16] and reflects the change in structure from blue-black tin(II) oxide [IS = 2.64 ± 0.06, QS = 1.33 ± 0.12 mm/s].[17]

Thus the only known stable solid tin(II) hydroxide must be described as a hydrous oxide or oxyhydroxide,[12] $3SnO{\cdot}H_2O$. It seemed obvious that only hydrated materials could be

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precipitated from aqueous solution, and we directed our attention toward a nonaqueous synthetic route. We report in this paper the preparation for the first time of a material of the composition SnO_2H_2 by an organometallic method.[18]

Experimental Section

Infrared spectra were recorded as KBr pellets and Nujol mulls on a Beckman IR-12 instrument. Our cam-drive, constant-acceleration Mössbauer spectrometer and curve-fitting techniques have been previously described.[39] Thermogravimetric analyses were carried out on a Fischer tga apparatus consisting of a Model 360 temperature programmer, a Model 260F furnace, and a Cahn Model RG electrobalance.

Anhydrous tin(II) chloride was prepared by dehydration of tin(II) chloride dihydrate with acetic acid anhydride. THF was distilled under nitrogen from sodium metal.

Tin(II) Hydroxide. Trimethyltin hydroxide (1.90 g, 10.5 mmol)[40,41] was dissolved in dry THF and added to a tin(II) chloride (1.00 g, 5.3 mmol) solution in THF under nitrogen to give the immediate precipitation of the white product in quantitative yield with the evolution of heat. The precipitate was filtered and dried in vacuo. Trimethyltin chloride was recovered and identified by comparison of its physical properties (mp 36–37 °C) with an authentic sample. Anal. Calcd for SnO_2H_2: Sn, 77.73; H, 1.31. Found: Sn, 77.64; H, 1.28. Tin(II) hydroxide is infusible, and even slow precipitation using dilute solutions gives an amorphous product which is soluble in acid and base and insoluble in alcohol.

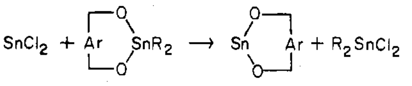
Preparation of *o*-Phenylenedioxytin(II).[42] Tin(II) hydroxide (2.00 g, 13 mmol) was added to catechol (1.45 g, 13 mmol) in xylene, and the mixture refluxed for 12 h during which time water (0.25 ml) was removed by a Dean and Stark trap. The product was filtered and washed with pentane. *o*-Phenylenedioxytin(II) was identified by comparison of its infrared spectrum with that of an authentic sample.

Results and Discussion

Tin(II) chloride participates in an apparently general esterification reaction with triorganotin(IV) oxygen compounds[43]

$$SnCl_2 + 2R_3SnOR \rightarrow Sn(OR)_2 + 2R_3SnCl \qquad (3)$$

or with aromatic, heterocyclic tin(IV)–oxygen compounds[44]



(4)

to exchange groups. Oxides of bis tin compounds also take part[45]

$$SnCl_2 + (R_3Sn)_2O \rightarrow SnO + 2R_3SnCl \qquad (5)$$

These reactions are examples of a general class of organometallic transformation reactions represented by the equation

$$M\text{–}E + Q\text{–}X \rightleftarrows M\text{–}X + Q\text{–}E \qquad (6)$$

elucidated by us a decade ago in which M and Q are metals or metalloids, X is a halogen, and E an organic grouping RO–, R_2N–, etc.[46] In this paper we extend the range of these transformations to an example in which M and Q are the element tin in different oxidation states and E is the hydroxide group, and use the reaction to yield the simple inorganic compound of tin with composition SnO_2H_2 sought by chemists for over 175 years.

Trimethyl-[40] and triphenyltin[41] hydroxides react with tin(II) chloride in a 2:1 ratio to give tin(II) hydroxide and the corresponding triorganotin chloride

$$SnCl_2 + 2R_3SnOH \rightarrow Sn(OH)_2 + 2R_3SnCl \qquad (7)$$

Table I. Comparison of Calculated Analytical Data

Formula	% Sn	% H
$Sn(OH)_2 \equiv SnO_2H_2$	77.73	1.31
$2SnO{\cdot}H_2O^{5,7} \equiv Sn_2O_3H_2$	82.01	0.70
$3SnO{\cdot}H_2O^{12} \equiv Sn_3O_4H_2$	84.36	0.48
$3SnO{\cdot}2H_2O^{6} \equiv Sn_3O_5H_4$	80.91	0.92
$5SnO{\cdot}2H_2O^{10} \equiv Sn_5O_7H_4$	83.59	0.56
SnO^{1}	88.12	

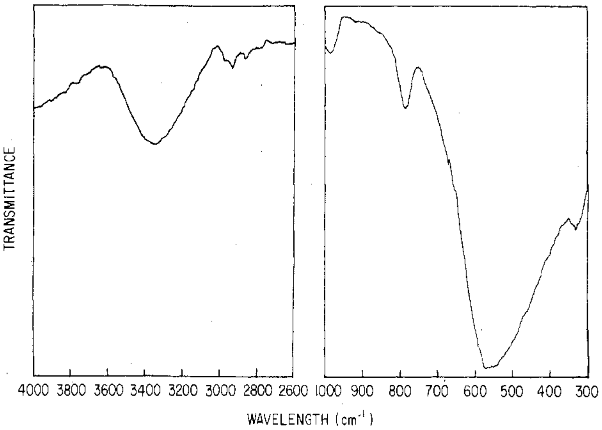


Figure 1. Infrared spectrum of SnO_2H_2.

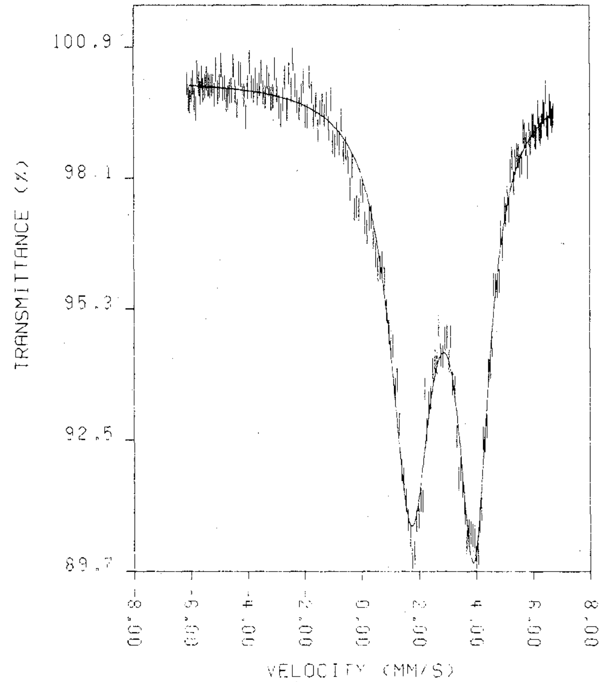
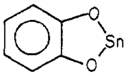
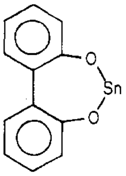


Figure 2. Tin-119m Mössbauer spectrum of SnO_2H_2 at 77 K vs. $Ba^{119m}SnO_3$.

The product is a white solid which can be distinguished from all other claimed forms of tin(II) hydroxide by microanalytical data which are compared in Table I and from some of the claimed forms by its infrared (see Figure 1) and tin-119m Mössbauer spectra (see Figure 2). We find 77.64% Sn and 1.28% H, which rules out all other formulas in Table I except SnO_2H_2. The ^{119m}Sn Mössbauer data listed in Table II do not, on the other hand, serve to distinguish tin(II) hydroxide from the hydrous oxide[36] but do reflect the change from the layer structure of the blue-black tin(II) oxide.[48] The broad bands centered at 3390 cm^{-1} in the infrared spectrum can be assigned to ν(O–H) and interpreted in terms of a hydrogen-bonded hydroxide group. The similarity of the Mössbauer and infrared data to those for the hydrous tin(II) oxide leads to the conclusion that the tin(II) atom in $Sn(OH)_2$ achieves a higher coordination number through bridging oxygen atoms[49] and, from the breadth of the infrared absorptions associated with the –OH group, that the oxygen atoms also participate in hydrogen bonding. Bands at 3380 cm^{-1} in the infrared spectra of the basic salt $Pb(NO_3)_2{\cdot}5PbO{\cdot}xH_2O$[50] and at 3425, 3210, and 3030 cm^{-1} [51] for hydrous germanium(II) oxide

Table II. Tin-119m Mössbauer Data for Tin(II)–Oxygen Derivatives at 77 K (mm/s)

Compd	IS	QS	Γ_1	Γ_2	Ref
$Sn(OH)_2$	2.78 ± 0.06[a]	2.20 ± 0.06[a]	1.64[a]	1.06[a]	*b*
	2.83 ± 0.06	2.20 ± 0.06	1.78	1.33	*b*
$3SnO \cdot H_2O$	2.74 ± 0.06	2.19 ± 0.12			*c*
SnO	2.64 ± 0.06	1.22 ± 0.12			*d*
$Sn(OCH_3)_2$	2.82 ± 0.06	1.99 ± 0.12	1.64	1.34	*e, f*
$Sn(OC_6H_5)_2$	2.68 ± 0.06	2.19 ± 0.12			*f*
	2.95 ± 0.06[a]	1.53 ± 0.12[a]			*g*
	2.95 ± 0.06	1.76 ± 0.12			*g*
	3.13 ± 0.06	1.98 ± 0.12			*g*

[a] Recorded at ambient temperature. [b] This work. [c] Reference 36. [d] Reference 38. [e] Reference 44. [f] Given as IS = 3.02 and QS = 1.97 mm/s in P. G. Harrison and S. R. Stobart, *J. Chem. Soc., Dalton Trans.*, 940 (1973), and as IS = 2.80 and QS = 2.02 mm/s in M. Zeldin and R. Gsell, *J. Inorg. Nucl. Chem.*, 37, 1133 (1975). [g] Reference 57.

precipitated by raising the pH of an acidic solution of germanium(II) oxide[52] are assigned to ν(O–H) modes.[50,51] By contrast, sharp ν(O–H) absorptions which rule out hydrogen bonding are found for the trimethyl-,[41] tricyclohexyl-,[53] and trineophyltin hydroxides at 3620, 3615, and 3620 cm^{-1}, respectively, the last for the melt.[54] In solutions in which trimethyltin hydroxide has been shown to be a dimer,[41] presumably oxygen bridged, ν(O–H) shifts to 3658 cm^{-1}, while ν(O–H) for tricyclohexyltin hydroxide is found at 3638 cm^{-1} in a variety of inert solvents in which the degree of association has not been determined.[53] A strong band at 920 cm^{-1} has been assigned to the Sn–OH deformation in solid trimethyltin hydroxide,[40,41] which is oxygen bridged but not hydrogen bonded.[49] Our tin(II) hydroxide, on the other hand, shows several weak bands in this region as seen in Figure 1, and we are unable to assign the δ(Sn–OH) mode with confidence. Okawara et al. assigned the tin–oxygen stretching frequency to a strong band at 370 cm^{-1} in trimethyltin hydroxide, and we find a strong, sharp band at 340 cm^{-1} in tin(II) hydroxide. Figure 1 also shows, however, a strong, broad band at 575 cm^{-1}, in a region in which trimethyltin hydroxide also absorbs when in dilute solution in CCl_4.[41] This observation would suggest two modes of attachment of tin to oxygen in solid tin(II) hydroxide.

Thermogravimetric analysis reveals loss of water on heating under nitrogen occurring in two stages, the first beginning at 126 °C and proceeding slowly over a temperature range of 126–152 °C and the second occurring more sharply at 195 °C. No further weight loss was observed to above 500 °C (the sample was heated at an average rate of 7.7 °C/min). A sample of 9.60 mg (6.29×10^{-2} mmol) lost 0.76 mg (4.22×10^{-2} mmol) of water to yield an orange solid whose Mössbauer spectrum contained a small resonance in the region associated with tin(IV) oxide. Without knowing the respective Debye temperatures of the products it is impossible to assign their relative amounts. Unlike the metastable red form of tin(II) oxide first prepared by Frémy[3] in 1842 and characterized by Donaldson et al.[56] in 1961, our orange product did not transform into blue-black tin(II) oxide on standing. Heating under vacuum to 150 °C produces a light brown material which is stable on standing as well. The buff-colored residues obtained from hydrous tin(II) oxide on drying have been rationalized by the presence of tin(IV) in the hydrous oxide lattice which arises from the internal reaction[56,57]

$$Sn(OH)_2 \rightarrow SnO_2 + H_2 \qquad (8)$$

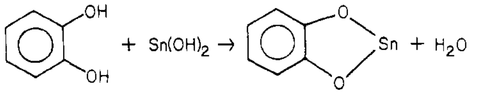
which would accompany the dehydration process

$$Sn(OH)_2 \rightarrow SnO + H_2O \qquad (9)$$

to produce the colored, mixed-valence materials we have observed.

Knowledge of the structure of the SnO_2H_2 material must await the development of a method for the production of single crystals for x-ray analysis. Our product may be a coordination polymer of the form $[SnO \cdot H_2O]_n$ or some other condensed structure containing Sn–OH, Sn–O, and $>Sn \leftarrow OH_2$ moieties which available physical techniques are unable to distinguish.

Like blue-black tin(II) oxide[35,36] and hydrous tin(II) oxide,[36] tin(II) hydroxide reacts with catechol in xylene to release water and form *o*-phenylenedioxytin(II)[41]



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Acknowledgment. Our work is supported by the National Science Foundation under Grant 16 544. We thank M&T Chemicals for generous gifts of trimethyl- and triphenyltin hydroxides and Mr. G. Gould of the General Electric Co. for assisting with the thermogravimetric analyses.

Registry No. $Sn(OH)_2$, 12026-24-3; ^{119}Sn, 14314-35-3; trimethyltin hydroxide, 56-24-6; tin(II) chloride, 7772-99-8.

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Kinetics of Nitrogen Tribromide Decomposition in Aqueous Solution[1]

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Received January 16, 1976   AIC600473

Tribromamine decomposes to give nitrogen gas and hypobromous acid accordng to the overall reaction $2NBr_3 + 3OH^- \rightarrow N_2 + 3Br^- + 3HOBr$. Decomposition rates were measured over the pH range 6.00 ± 0.05 to 8.00 ± 0.05 for initial bromine to ammonia molar ratios between 4.00 and 12.0. The experimental rate law was found to be $-d[NBr_3]/dt = k_a[NBr_3]^2[OH^-]/[HOBr] + k_b[NBr_3]^2$, where $k_a = 1.07 \times 10^4$ and $k_b = 0.34$ l./(mol s) at 20 °C. The first term in the rate equation is consistent with a mechanism in which the rate-determining step is preceded by equilibria among NBr_3, $NHBr_2$, HOBr, NBr_2^-, and OH^-. Hydroxide may attack either NBr_3 or $NHBr_2$ to produce NBr_2^- which subsequently reacts with NBr_3. The second term is a simple second-order alternate pathway, occurring in acid solutions.

Introduction

When bromine or hypobromous acid is added to an aqueous ammonia solution, one or more of the bromamines are rapidly formed with their concentrations being a function of temperature, pH, and the bromine to ammonia ratio. Tribromamine, NBr_3, predominates at neutral pH when the molar ratio of bromine to ammonia is greater than 1.5.[2] The decomposition reactions of this compound and the other bromamines are of considerable importance to the field of disinfection whenever bromine, bromine chloride, or hypobromite are added to water containing ammonia.[3a] In comparison to the bromamines, the chloramines are inferior disinfectants[3b,4] and their persistence and high fish toxicity[5] have initiated a search for alternatives to chlorine. Although bromine has had widespread use as a swimming pool disinfectant[6] and is currently being considered as a waste water and cooling water disinfectant, there has been no thorough study of the decomposition kinetics of the bromamines. For this reason a research program was begun in this laboratory to measure the decomposition rates of tribromamine and dibromamine, the compounds most relevant to disinfection practices.

Tribromamine was first shown to exist in dilute aqueous solution by Galal-Gorchev and Morris,[7] who also measured its rate of decomposition under a variety of conditions. They obtained pure and relatively stable NBr_3 solutions at low pH even when the molar ratio of bromine to ammonia was 2.5. They also noted that the distribution of the bromamines should be predictable from the ammonium ion and hypobromous acid equilibria. Further work by Johnson and Overby[6] showed this to be true, with the relative concentrations of the bromamines being dependent on both ammonia concentration and pH. They observed rapid formation of all of the bromamines in contrast to the slower formation reactions of $NHCl_2$ and NCl_3. Unlike the chloramine reactions, an equilibrium allows interconversion of the bromamines by merely changing pH, ammonia, or bromine concentration.

The rate of NBr_3 disappearance was determined by monitoring the ultraviolet absorbance at 258 nm due to NBr_3 and HOBr and the total reducible bromine as determined by amperometric titration. Reaction orders with respect to different species were determined from initial rate data rather than concentration–time data taken over a long period of time. This was done because bromide and hypobromous acid, products of NBr_3 decomposition, respectively catalyze and inhibit the reaction.

Experimental Section

Materials. The following procedure was used to eliminate or oxidize any impurities in the reagent water that might reduce bromine. Tap water was filtered through a 0.1-μ filter and a bed of activated carbon for the removal of organic compounds and then passed through 4 ft