gave a red-brown precipitate of $[NMe_3(CH_2Ph)]_2[Ni_9(CO)_{18}]$; yield 1.2 g.

3. Synthesis of $[AsPh_4][AgNi_9(CO)_{18}]$. $[AsPh_4]_2[Ni_9(CO)_{18}]$ (1.2 g) was dissolved under nitrogen in THF (20 ml) and cooled to −70 °C. After dropwise addition during stirring of a solution of $AgBF_4$ (0.13 g) in THF (10 ml), the initial dark red solution became colorless and a dark precipitate separated out. This was filtered, washed with THF (10 ml), and dried under vacuum. Extraction with acetonitrile (30 ml) gave a red-orange solution which gave an orange microcrystalline precipitate of $[AsPh_4][AgNi_9(CO)_{18}]$ by addition of diisopropyl ether (30 ml); yield 0.72 g. The compound is soluble in acetone and acetonitrile and sparingly soluble or insoluble in methanol, 2-propanol, and THF. Anal. Calcd for $[AsPh_4][AgNi_9(CO)_{18}]$: $AsPh_4^+$, 25.0; Ag, 7.05; Ni, 34.5. Found: $AsPh_4^+$, 24.4; Ag, 7.3; Ni, 32.3.

Acknowledgment. We acknowledge Professor L. F. Dahl and Dr. L. Lower for their collaboration on the structural aspects of this work and NATO for making available a grant.

Registry No. $[PPh_4]_2[Ni_9(CO)_{18}]$, 60512-63-2; $[NMe_3(CH_2Ph)]_2[Ni_9(CO)_{18}]$, 60512-62-1; $[PPh_3Me]_2[Ni_9(CO)_{18}]$, 60512-61-0; $[AsPh_4]_2[Ni_9(CO)_{18}]$, 60512-60-9; $[PPN]_2[Ni_9(CO)_{18}]$, 60512-59-6; $[AsPh_4][AgNi_9(CO)_{18}]$, 60512-58-5; $K_2[Ni_6(CO)_{12}]$, 60464-08-6; $Ni(CO)_4$, 13463-39-3.

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High-Pressure Phase Transformations of the Systems $Ni_{1-x}Co_xTe_2$ and $Ni_{1-x}Fe_xTe_2$

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The solid solutions $Ni_{1-x}Co_xTe_2$ ($x \leq 0.6$) and $Ni_{1-x}Fe_xTe_2$ ($x \leq 0.1$) were found to crystallize at ambient pressure with the cadmium iodide structure. Transformations to the pyrite structure at 1000–1300 °C and under 60 kbars pressure in a high-pressure belt apparatus were found to be a function of the cobalt or iron substitution.

Introduction

It has been reported[1] that several 3d transition metal ditellurides transform to the pyrite structure under pressure. Bither[1] studied both iron and cobalt ditelluride which crystallize with the marcasite structure and transform to the pyrite structure at 1200 °C and 65 kbars pressure. He also observed the partial transformation of nickel ditelluride from the cadmium iodide to the pyrite structure at 1000 °C and 89 kbars pressure.

Since the disulfides of iron, cobalt, and nickel have been reported[2] to form solid-solution series of the type $Fe_xCo_{1-x}S_2$ and $Ni_xCo_{1-x}S_2$ ($0 \leq x \leq 1$), it would be of interest to determine the extent of solid solution formation of the series $Ni_{1-x}Co_xTe_2$ and $Ni_{1-x}Fe_xTe_2$. In addition, the degree of transformation from the cadmium iodide to the pyrite structure can be investigated in this series as a function of the cobalt or iron substitution.

Experimental Section

1. Preparation. The metals (Gallard–Schlesinger, 99.999%) were reduced prior to use by heating under a 15% hydrogen/85% argon mixture (nickel, 3 h at 600 °C; cobalt, 8 h at 850 °C; iron, 20 h at 950 °C). The tellurium (Gallard–Schlesinger, 99.999%) was sublimed under vacuum from 600 to 400 °C.

Polycrystalline samples of the systems $Ni_{1-x}Co_xTe_2$ and $Ni_{1-x}Fe_xTe_2$ were synthesized by reacting stoichiometric quantities of the elements in sealed, evacuated silica tubes. All samples were reacted for a period of 2–3 weeks with several intermittent grindings in a dry nitrogen atmosphere. At the end of each heat treatment the samples were cooled to room temperature at the rate of 15 °C/h.

The reacted polycrystalline powders were subjected to high pressures and temperatures in a belt apparatus of the type described by Hall.[3] Pyrex capsules served as reaction containers. The experimental conditions are given in Table I. At the end of each experiment the temperature was lowered to 600 °C over a period of several hours and then reduced to room temperature in less than 20 min. Subsequently the pressure was reduced to 1 atm.

Table I. High-Pressure Results

Compn	Exptl conditions	Results
$NiTe_2$	1300 °C, 60 kbars	No transformn
$CoTe_2$	1300 °C, 60 kbars	Complete transformn to pyrite
$FeTe_2$	750 °C, 60 kbars	No transformn
	1000 °C, 60 kbars	No transformn
	1400 °C, 60 kbars	No transformn; decompn
$Ni_{1-x}Co_xTe_2$ ($0.1 \leqslant x \leqslant 0.8$)	1300 °C, 60 kbars	Partial transformn to pyrite plus cadmium iodide
$Ni_{1-x}Fe_xTe_2$ ($0.1 \leqslant x \leqslant 0.3$)	1000 °C, 60 kbars	Partial transformn to pyrite plus marcasite
$Ni_{1-x}Fe_xTe_2$ ($0.4 \leqslant x \leqslant 0.8$)	1000 °C, 60 kbars	Complete transformn to pyrite
$Ni_{0.1}Fe_{0.9}Te_2$	1000 °C, 60 kbars	Partial transformn to pyrite plus marcasite

2. X-Ray Measurements. Powder diffraction patterns were obtained with a Norelco diffractometer using monochromatic high-intensity Cu Kα radiation (λ 1.5405 Å). Fast scans of 1° (2θ) $\min^{-1}$ were taken to determine the phases present in each sample. Lattice parameters were determined from slow scans of $^1/_4$ (2θ) $\min^{-1}$ in the interval $12° \leq 2\theta \leq 130°$. The parameters were refined by a least-squares fit of the data obtained from high-angle reflections ($2\theta > 50°$) corrected relative to an internal MgO standard.

3. Density Measurements. The densities of the single-phase samples were determined using the hydrostatic technique described by Adams.[4] A Mettler H54 analytical balance was employed and the density fluid, perfluoro(1-methyldecalin), was calibrated with a high-purity silicon crystal (ρ = 2.328 g/cm^3 at 22 °C). Prior to any density measurements, the samples were ground and outgassed thoroughly to ensure reproducible results.

Results

1. Ambient Pressure. Compounds crystallizing with the cadmium iodide structure were obtained for $x \leq 0.6$ in the $Ni_{1-x}Co_xTe_2$ system. The lattice parameters and densities of these compounds are listed in Table II. Figure 1 shows the variation in the a_0 and c_0 values as a function of composition. In the $Ni_{1-x}Fe_xTe_2$ system, the cadmium iodide structure was found only for $x \leq 0.1$. Mixtures of both cadmium iodide and

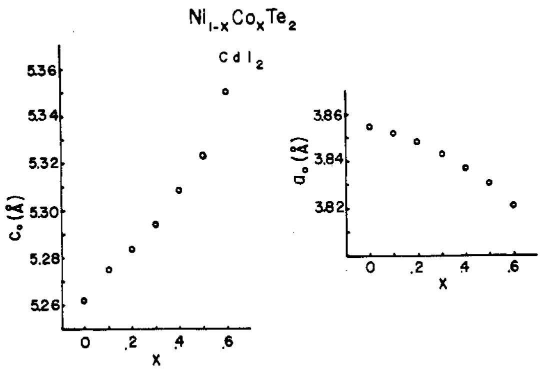

Figure 1. Variation in the a_0 and c_0 parameters with composition for low-pressure $Ni_{1-x}Co_xTe_2$ system.

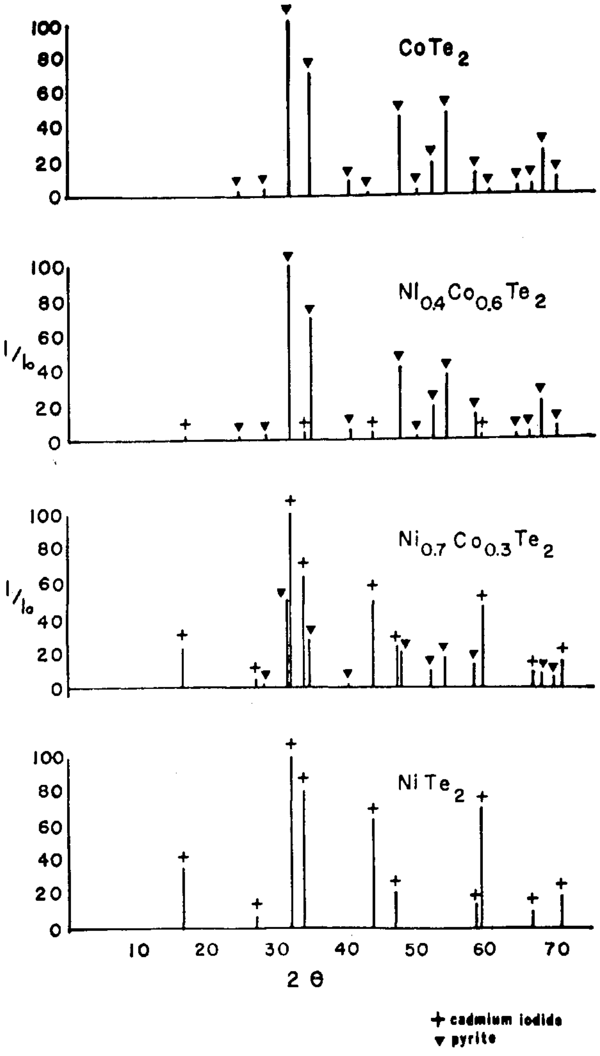

Figure 2. X-ray spectra for some compositions of the $Ni_{1-x}Co_xTe_2$ low-pressure system.

marcasite phases were found in both systems for $x > 0.6$ and $x > 0.1$, respectively.

2. High Pressure. Members of the series $Ni_{1-x}Co_xTe_2$ and $Ni_{1-x}Fe_xTe_2$ $(0 \leq x \leq 1)$ were subjected to the elevated temperature and pressure conditions given in Table I. Single-phase pyrite compounds were not obtained in the $Ni_{1-x}Co_xTe_2$ system. However, from the x-ray spectra of some of the compositions shown in Figure 2, it is seen that the degree of transformation increases with cobalt substitution. Similar results are found in the $Ni_{1-x}Fe_xTe_2$ system, and for $0.4 \leq x \leq 0.8$ only pyrite phases are obtained. The cell edge and densities of the cubic phases are listed in Table III. Figures 3 and 4 show the variation in the cell edge as a function of composition.

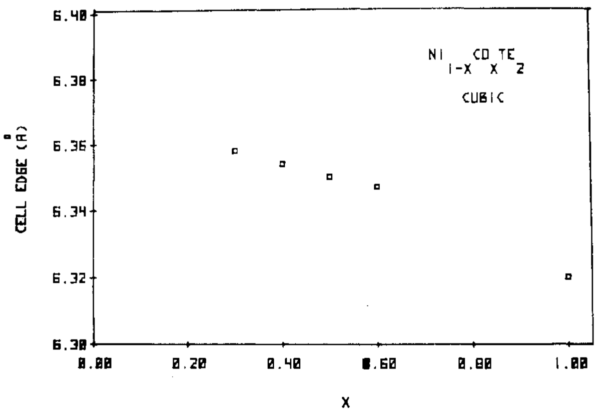

Figure 3. Variation in cell edge with composition for the high-pressure $Ni_{1-x}Co_xTe_2$ cubic system.

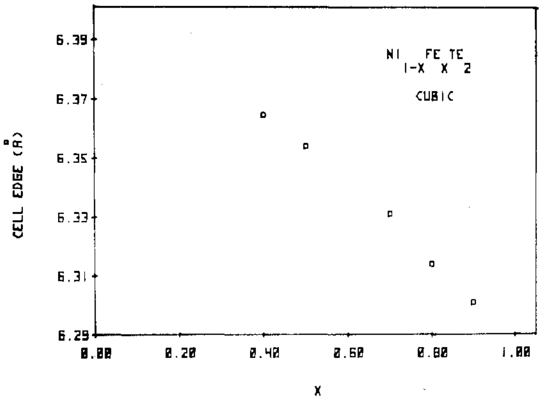

Figure 4. Variation in cell edge with composition for the high-pressure $Ni_{1-x}Fe_xTe_2$ cubic system.

$NiTe_2$ and $FeTe_2$ did not transform even when subjected to 1400 °C and 60 kbars pressure. In contrast, $CoTe_2$ transformed completely to the pyrite structure at 1300 °C and 60 kbars pressure.

Annealing experiments at 300 °C under vacuum indicated that the pyrite compounds are not stable and convert back to the ambient-pressure phases.

Discussion

This study has shown that the solid solutions $Ni_{1-x}Co_xTe_2$ with $x \leq 0.6$ and $Ni_{1-x}Fe_xTe_2$ with $x \leq 0.1$ crystallize at ambient pressure with the cadmium iodide structure. The formation of solid solutions between either $CoTe_2$ or $FeTe_2$ (both marcasites, crystallizing in the space group *Pnn*2) and $NiTe_2$ (cadmium iodide, crystallizing in the space group $P\bar{3}m1$) is consistent with the close relationship of the two structural types. Both the marcasite and cadmium iodide structures consist of distorted hexagonal close-packed layers of anions. In marcasite the octahedral holes between every layer are half-filled, whereas in cadmium iodide the octahedral holes between alternate layers are completely filled (Figure 5). The greater range of substitution of cobalt (60%) than iron (10%) into $NiTe_2$ may be attributed to the larger difference in size between octahedrally coordinated iron and nickel compared to the difference in size between octahedrally coordinated cobalt and nickel.[5]

The pyrite structure, crystallizing with space group *Pa*3, is related to the sodium chloride structure type with the cations occupying the face-centered sodium ion positions and the

Table II. Lattice Parameters and Densities for Low-Pressure Phases

	a_0, Å	b_0, Å	c_0, Å	ρ_{exptl}, g/cm^3	ρ_{calcd}, g/cm^3
$NiTe_2$	3.857 (3)		5.262 (3)	7.68 (3)	7.69
$Ni_{0.9}Co_{0.1}Te_2$	3.852 (3)		5.275 (3)	7.66 (3)	7.69
$Ni_{0.8}Co_{0.2}Te_2$	3.848 (3)		5.284 (3)	7.67 (3)	7.69
$Ni_{0.7}Co_{0.3}Te_2$	3.843 (3)		5.294 (3)	7.69 (3)	7.70
$Ni_{0.6}Co_{0.4}Te_2$	3.837 (3)		5.308 (3)	7.69 (3)	7.70
$Ni_{0.5}Co_{0.5}Te_2$	3.831 (3)		5.323 (3)	7.70 (3)	7.71
$Ni_{0.4}Co_{0.6}Te_2$	3.821 (3)		5.350 (3)	7.69 (3)	7.71
$CoTe_2$	5.312 (3)	6.311 (3)	3.889 (3)	7.96 (6)	8.01
$FeTe_2$	5.274 (3)	6.271 (3)	3.871 (3)	8.05 (2)	8.07

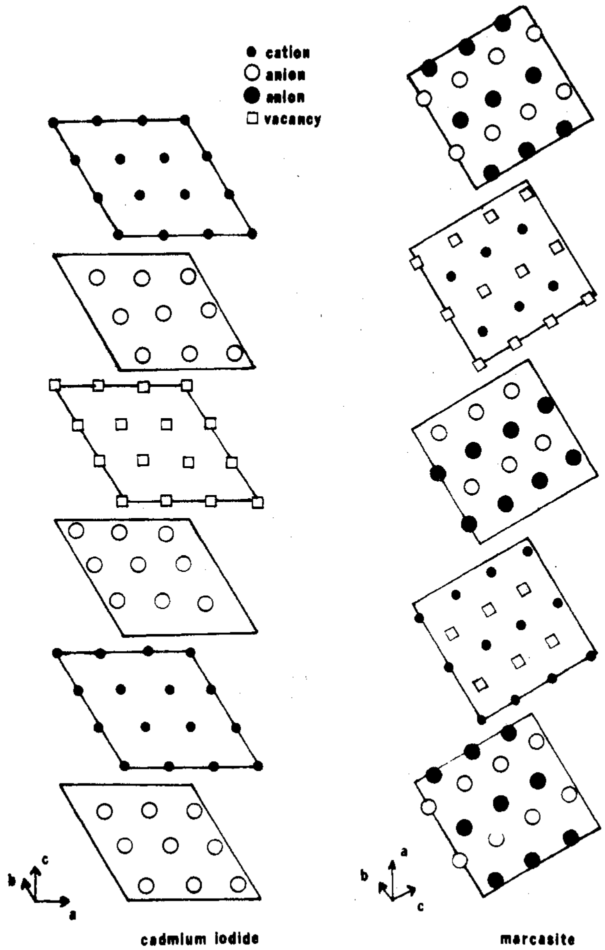

Figure 5. Arrangement of atoms in layers for the cadmium iodide and marcasite structures. In marcasite ○ represents an atom slightly above the plane and ● represents an atom slightly below the plane.

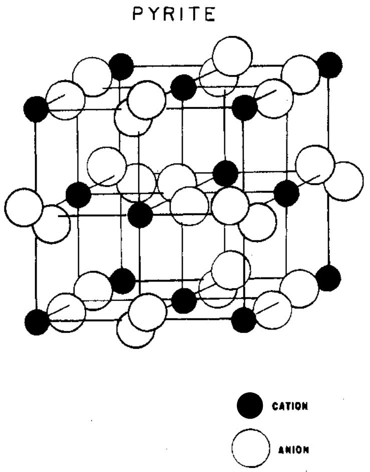

Figure 6. The pyrite structure.

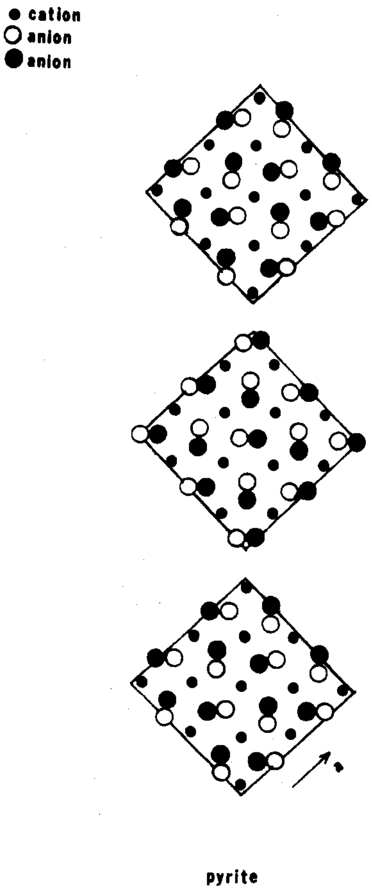

Figure 7. Arrangement of atoms in layers for the pyrite structure: ○, atoms slightly above the plane; ●, atoms slightly below the plane.

center of the anion–anion pairs occupying the chloride ion sites (Figure 6). The arrangement of the atoms in the layers (Figure 7) results in a more efficient packing than occurs in either the marcasite or cadmium iodide structures (compare with Figure 5). Hence, the pyrite structure is favored under the conditions of elevated temperature and pressure given in Table I. For the $Ni_{1-x}Co_xTe_2$ system studied, the extent of the transformation to the pyrite structure increases with cobalt substitution. This is consistent with the observed complete transformation of $CoTe_2$ from the marcasite to the pyrite structure under 1300 °C and 60 kbars pressure. In the $Ni_{1-x}Fe_xTe_2$ system, the formation of the pyrite structure again increases with iron substitution, and for $0.4 \leq x \leq 0.8$, only pyrite phases are obtained under 1000 °C and 60 kbars pressure. However, at $x = 0.9$ only a partial transformation to the pyrite structure was observed, while $FeTe_2$ did not

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.

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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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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).

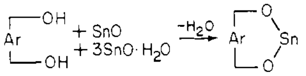
Blue-black tin(II) oxide was first prepared by Berzelius in 1812 by the addition of excess potassium carbonate to an aqueous solution of a tin(II) salt.[1] Gay-Lussac precipitated a hydrous material from aqueous ammonia in 1816,[2] and Frémy obtained a similar solid by evaporating a slurry of precipitated 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

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

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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